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Thomas C. Coombs

I. **Organometallic Enantiomeric Scaffolding: Total Synthesis of (-)-Adaline and (-)-Adalinine Using a Key 5-Oxo-Pyridinyl Molybdenum Scaffold and Featuring a Semipinacol Rearrangment/1,5-"Michael-like" Sequence.**

II. **Exchange Reactions of 1-Alkoxy and 1-Sulfonyloxy η^3-Allyl Molybdenum Complexes**

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An Abstract of
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Department of Chemistry
Graduate School of Arts and Sciences

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Abstract

A short, practical route to a versatile 5-oxo-(η-2,3,4)-allylmolybdenum pyridinyl scaffold has been developed using the aza-Achmatowicz rearrangement. This route features a one-pot rearrangement/metalation protocol, eliminating the need for purification of sensitive intermediates, and enabling the easy synthesis of multi-gram quantities of the scaffold in a timely manner. The protocol has been extended to chiral non-racemic substrates, providing improved access to both enantiomers of this complex in high enantiomeric excesses.

A new variant of the semipinacol rearrangement was investigated utilizing allylic alcohols available in three steps from 5-oxo-(η-2,3,4)-allylmolybdenum pyranyl and pyridinyl organometallic enantiomeric scaffolds. The protic acid-induced semipinacol rearrangement itself occured with complete diastereoselectivity under mild conditions and required a full equivalent of HCl. Off-ring stereocenters were efficiently generated using electrophilic halogen sources to initiate the rearrangement. The major diastereomer in each case resulted from addition to the alkene *syn* to the $TpMo(CO)_2$ fragment, suggesting participation of the metal in this rearrangment. Solvent choice was especially important in these reactions to achieve synthetically-useful diastereoselectivities at the off-ring site.

Asymmetric syntheses of (-)-adaline and (-)-adalinine were carried out using the enantiomerically-enriched 5-oxo-(η-2,3,4)-allylmolybdenum pyridinyl complex. The synthesis of (-)-adalinine highlighted the utility of the semipinacol rearrangement for the stereocontrolled construction of quaternary centers, and also employed an oxidative demetalation protocol previously developed by the Liebeskind group to install the lactam

carbonyl found in the natural product. The synthesis of (-)-adaline showcased the power of coupling the semipinacol rearrangement and 1,5-Michael-like reaction to access quaternary center-bearing bicyclic compounds.

A family of related 1-alkoxy and 1-sulfonyloxy-η^3-allylmolybdenum complexes were shown to undergo a series of exchange reactions with external amines and alcohol nucleophiles. Alkoxy complexes reacted directly with amines, but required the participation of a Lewis acid catalyst to undergo substitution with alcohols. Sulfonyloxy complexes reacted directly with both amines and alcohols in the absence of any catalyst. In all cases, optically-active starting materials racemized when subjected to exchange conditions, suggesting that this family of reactions proceeds *via* carbene intermediates. Additionally, 5-oxo-pyranyl complex **1.6** was found to undergo rapid ring-opening amination reactions with both primary and secondary amines, suffering only small loss in enantiomeric purity.

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Dedicated to Maggie (Tilly) Norconk,

For Everything

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Table 4.22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (1*R*, *R*)-**4.13**……..……..335

Table 4.23. Torsion angles [°] for (1*R*, *R*)-**4.13**……..…336

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Table 4.26. Bond lengths [Å] and angles [°] for **4.15**……...…..341

Table 4.27. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4.15**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$……..344

Table 4.28. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement
parameters ($Å^2 x\ 10^3$) for **4.15**……..….345

Table 4.29. Hydrogen bonds for **4.15** [Å and °]…….…345

List of Abbreviations

[a]	specific rotation
Ac	acetyl
AIBN	azobisisobutyronitrile
anal	analysis
Aq	aqueous
Ar	argon
Bn	benzyl
br	broad
bu	butyl
^{o}C	degree Celsius
calcd	calculated
CAN	ceric ammonium nitrate
Cbz	benzyloxycarbonyl
δ	chemical shift(s)
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMAP	demethylamino pyridine
Decomp	decomposed
DMDO	dimethyl dioxirane
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
DMS	dimethyl sulfide
E	entgegen
ee	enantiomeric excess
ESI	electrospray ionization
Et	ethyl
FT	Fourier transform
g	gram(s)
h	hour(s)
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectroscopy
Hz	hertz
IR	Infrared Spectroscopy
J	coupling constant
LA	Lewis acid
mol	mole
m	multiplet
m-CPBA	meta-chloroperbenzoic acid
Me	methyl
mg	milligram(s)
MHz	megahertz
min	minute(s)
mL	milliliter(s)
μL	microliter(s)
mmol	millimole(s)
mp	melting point

MsCl	methanesulfonyl chloride
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NIS	*N*-iodosuccinimide
NMR	nuclear magnetic resonance
nm	nanometer(s)
ORTEP	Oak Ridge thermal ellipsoid plot
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
PG	protecting group
Ph	phenyl
ppm	parts per million
pr	propyl
py	pyridine
q	quartet
R_f	retention factor
rt	retention time
r.t.	room temperature
s	singlet
SAR	structure activity relationship
t	triplet
t	tertiary
TBAF	tetrabutylammonium fluoride
TBAT	tetrabutylammonium triphenyl(difluoro)silicate
TBS	*tert*-butyl dimethyl silyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
Tp	hydridotris(1-pyrazolyl)borate
Tr	triphenylmethyl
Ts	*p*-toluenesulfonyl
UV	ultraviolet
Z	zusammen

Chapter 1:

Development of an Improved Route to a Key 5-Oxo-Pyridinyl Organometallic Enantiomeric Scaffold

Introduction

The development of structurally-simple scaffolds which may be used in the rapid construction of molecular complexity in an enantiocontrolled manner is one area of modern organic synthesis which has received significant attention. Scaffolding methodologies have found many applications in the total synthesis of natural products and the construction of biologically-active nonnatural compounds. Designing versatile scaffolds has been of particular relevance to the field of medicinal chemistry where the synthesis of structurally-diverse compounds from a common precursor facilitates structure-activity relationship (SAR) studies.

The "chiron" and the "chiron approach" to organic synthesis, an early "chiral template" concept related to scaffolding, was pioneered by Hanessian[1] who noted the value of using carbohydrates, amino acids, hydroxy acids and terpenes as cheap, chiral non-racemic starting materials available in large quantities from the chiral pool. These compounds have been extensively utilized since the earliest day of organic synthesis to access many classes of natural products. However, many of the chirons discussed by Hanessian possess extra unnecessary functionality that must be removed or selectively protected. The focus of modern scaffolding has begun to shift to compounds with minimal functionality possessing maximum tactical versatility. This shift has helped to shorten synthetic routes by removing protection/deprotection and defunctionalization steps.

A practical scaffold is one that may be easily assembled from readily-available, affordable starting materials. It should be attainable in large quantities and high

[1] Hanessian, S. *Total Synthesis of Natural Products: The "Chiron" Approach*; Pergamon Press: Oxford, UK, 1983.

enantiomeric excess, and should participate in a variety of reactions allowing maximum exploration of chemical space and access to desired structural types. That the scaffold undergo regio- and stereocontrolled transformations in a highly predictable fashion for a wide range of substitution patterns is of critical importance. It is in this predictable elaboration of simple, chiral non-racemic compounds that the value of scaffolding lies: *minimal optimization is required to access a multitude of chiral non-racemic structure types.*

Asymmetry is typically introduced to the scaffold in a stoichiometric manner by the incorporation of a chiral, non-racemic auxiliary. In some cases, catalytic asymmetric transformations are employed to impart this asymmetry. The requirement that a practical scaffold undergo stereocontrolled transformations allows an asymmetric route to be developed for a single compound. This compound may then take part in predictable diastereoselective reactions leading to a variety of chiral, non-racemic desired compounds. The scaffolding approach avoids the need to develop individual asymmetric routes to each desired compound, a process that can be expensive and time consuming as it often requires extensive optimization.

A classic example of a versatile scaffold is the Wieland-Miescher ketone,[2] which has found wide application in the synthesis of biologically-active carbocyclic compounds, including diterpenes and steroids (Figure 1.1). The Wieland-Miescher ketone is synthesized by Michael addition and Robinson annulation of 2-methyl-1,3-cyclohexanedione with methyl vinyl ketone. A number of enantioselective routes have been reported.[3,4,5,6] Figure 1.1 highlights just three of the many carbocyclic natural

[2] Wieland, P.; Miescher, K. *Helv. Chim. Acta* **1950**, *33*, 2215.
[3] Akahane, Y.; Inage, N.; Nagamine, T.; Inomata, K.; Endo, Y. *Heterocycles* **2007**, *74*, 637-648.

products synthesized from this scaffold, including the steroid adrenosterone,[7] the neurotrophic diterpenoid (-)-scabronine G,[8] and baccatin III,[9] the natural product harvested for industrial hemi-synthesis of taxol.

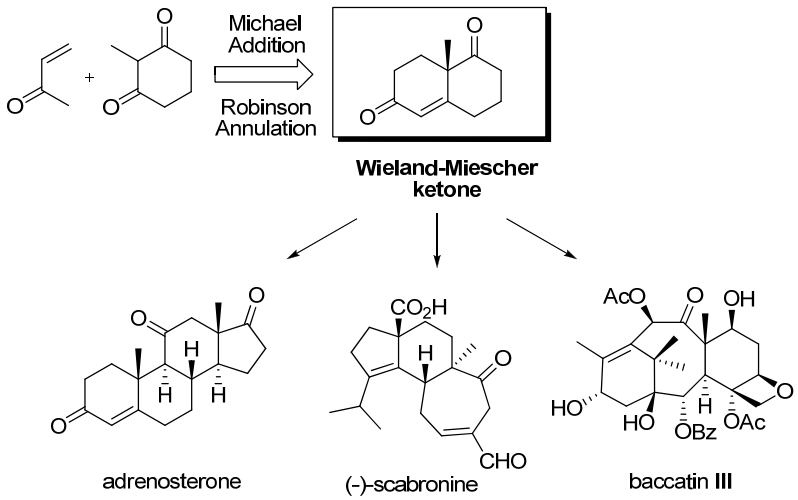


Figure 1.1. Wieland-Miescher Ketone: Synthesis and Applications

In the area of nitrogen-based scaffolds, Comins, Bosch, and Husson/Royer have all developed practical heterocycles and highlighted their respective utilities in the synthesis of a variety of alkaloids (Figures 1.2 and 1.3).

Comins has made excellent use of chiral, nonracemic 1-acyl-4-methoxy-3-(triisopropylsilyl)pyridinium salt **1.1** formed by condensation of the corresponding

---

[4] Kriis, K.; Kanger, T.; Laars, M.; Kailas, T.; Muurisepp, A.-M.; Pehk, T.; Lopp, M. *Synlett* **2006**, *11*, 1699-1702.
[5] Fuhshuku, K.; Funa, N.; Akeboshi, T.; Ohta, H.; Hosomi, H.; Ohba, S.; Sugai, T. *J. Org. Chem.* **2000**, *65*, 129-135.
[6] Harada, N.; Sugioka, T.; Uda, H.; Kuriki, T. *Synthesis* **1990**, *1*, 53-56.
[7] Dzierba, C. D.; Zandi, K. S.; Möllers, T.; Shea, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 4711-4712.
[8] Waters, S. P.; Tian, Y.; Li, Y.-M.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2005**, *127*, 13514-13515.
[9] Masters, J. J.; Link, J. T.; Snyder, L. B.; Young, W. B.; Danishefsky, S. J. *Angew. Chem. Int. Ed.* **1995**, *34*, 1723-1726.

pyridine and (-)-*trans*-2-(α-cumyl)cyclohexyl chloroformate.[10] Diastereo- and regioselective addition of nucleophiles to **1.1**, followed by acid work-up delivers dihydropyridones **1.2**, which the Comins group has used to synthesize a number of piperidine-based alkaloids. Scheme 2 highlights three examples: (-)-lasubine I,[11] (+)-benzomorphan,[12] and (-)-pumiliotoxin C.[13]

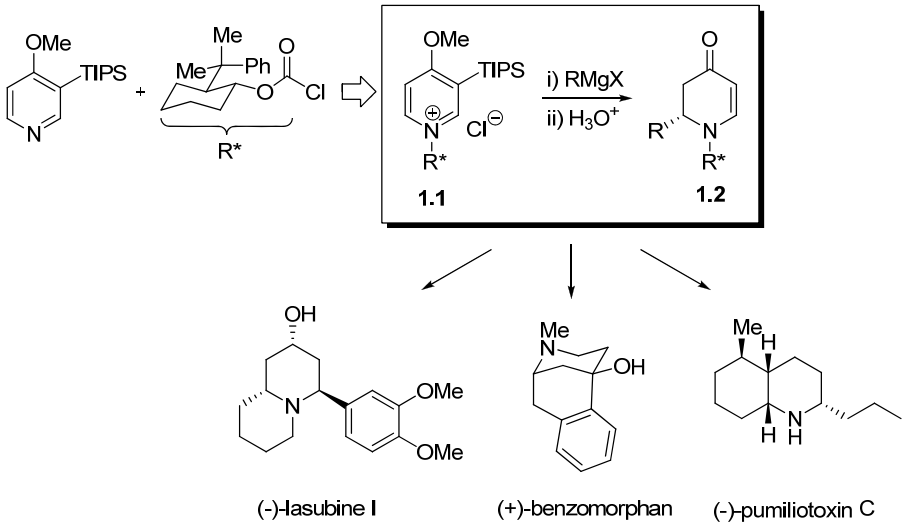


Figure 1.2. Comins Pyridinum Scaffold

Bosch has developed oxazolopiperidone lactams such as **1.3**, derived from cyclocondensation of phenylglycinol and the methyl ester of 5-oxo-pentanoic acid, as scaffolds for enantioselective synthesis.[14] Husson and Royer have utilized a similar cyclocondensation of phenylglycinol and glutaraldehyde to access chiral, non-racemic *N*-cyanomethyloxazolidines **1.4**.[15] Both **1.3** and **1.4** have been used to introduce

[10] Comins, D. L.; Joseph, S. P.; Goehring, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 4719-4728.
[11] Comins, D. L.; LaMunyon, D. H. *J. Org. Chem.* **1992**, *57*, 5807-5809.
[12] Comins, D. L.; Zhang, Y.; Joseph, S. P. *Org. Lett.* **1999**, *1*, 657-659.
[13] Comins, D. L.; Dehghani, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1838-1839.
[14] Escolano, C.; Amat, M.; Bosch, J. *Chem. Eur. J.* **2006**, *12*, 8198-8207.
[15] Husson, H.-P.; Royer, J. *Chem. Soc. Rev.* **1999**, *28*, 383-394.

substituents at desired positions on the piperidine ring in a regio- and stereocontrolled manner. Further elaboration to a wide variety of piperidine-based alkaloids and nonnatural biologically-active compounds has been carried out over the past several years and Figure 1.3 shows just some of the structures that have been synthesized.

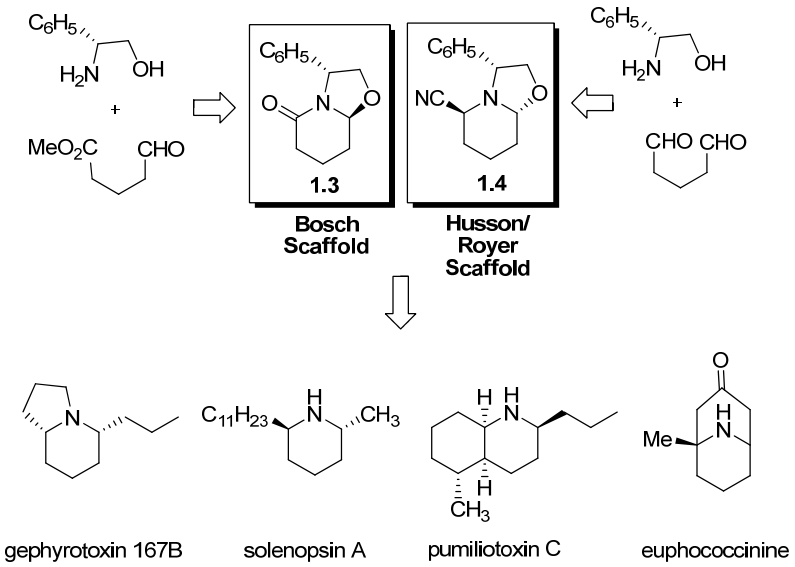


Figure 1.3. Related Bosch and Husson/Royer Nitrogen-based Scaffolds

Development of Organometallic Enantiomeric Scaffolds

The utility and impact of organic scaffolding have rendered it an active area of research over the years. The result has been the development of new scaffolds and improved strategies for their synthesis and use. However, the design of transition-metal-based scaffolds has been much less explored. This is somewhat surprising given the expanded reactivity profiles available to transition-metal-bound heterocycles and not found in their metal-free counterparts. Indeed, metal π-complexes have been extensively

used for stereocontrolled organic synthesis.[16,17,18,19,20,21] Thus, the development of transition-metal-based scaffolds would likely enhance the field of scaffolding by enabling new reactions for diversity synthesis not achievable in the absence of the metal. Furthermore, access to chiral, non-racemic transition-metal-based scaffolds would allow the application of such new reactions to asymmetric synthesis.

In this vein, the Liebeskind laboratory has developed four strategically-functionalized η^3-allyl $TpMo(CO)_2$-based heterocyclic scaffolds (Figure 1.4) and highlighted their value in the synthesis of numerous heterocyclic compounds and natural products.[22,23,24,25,26,27,28,29,30,31,32,33,34,35] As their potential has been increasingly expanded and recognized, these compounds have come to be viewed as *organometallic enantiomeric scaffolds*. Although they are stoichiometric transition-metal-based complexes, scaffolds **1.5-1.8** are both air and moisture stable making their routine

[16] Uemura, M. *Top. Organomet. Chem.* **2004**, *7*, 129-156.
[17] Harman, W. D. *Top. Organomet. Chem.* **2004**, *7*, 95-127.
[18] Paley, R. S. *Chem. Rev.* **2002**, *102*, 1493-1524.
[19] Pape, A. R.; Kaliappan, K. P.; Kündig, E. P. *Chem. Rev.* **2000**, *100*, 2917-2940.
[20] Li, C.-L.; Liu, R.-S. *Chem. Rev.* **2000**, *100*, 3127-3162.
[21] Pearson, A. J. Recent Developments in the Synthetic Applications of Organoiron and Organomolybdenum Chemistry. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed; JAI Press: Greenwich, CT, 1989; Vol. I, p. 1.
[22] Garnier, E. C.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2008**, in press.
[23] Arrayás, R. G.; Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2007**, *129*, 1816-1825.
[24] Zhang, Y.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2006**, *128*, 465-472.
[25] Zhang, Y.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2005**, *127*, 11258-11259.
[26] Shu, C.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 2878-2879.
[27] Arrayás, R. G.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 9026-9027.
[28] Alcudia, A.; Arrayás, R. G.; Liebeskind, L. S. *J. Org. Chem.* **2002**, *67*, 5773-5778.
[29] Shu, C.; Alcudia, A.; Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 12477-12487.
[30] Arrayás, R. G.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 6185-6186.
[31] Yin, J.; Llorente, I.; Villanueva, L. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2000**, *122*, 10458-10459.
[32] Moretto, A. F.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 7445-7455.
[33] Malinakova, H. C. Liebeskind, L. S. *Org. Lett.* **2000**, *2*, 4083-4086.
[34] Malinakova, H. C. Liebeskind, L. S. *Org. Lett.* **2000**, *2*, 3909-3911.
[35] Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1999**, *121*, 5811-5812.

manipulation using normal benchtop techniques possible. Additionally, asymmetric routes to scaffolds **1.5**-**1.8** have been developed and single enantiomers are available.[36,22]

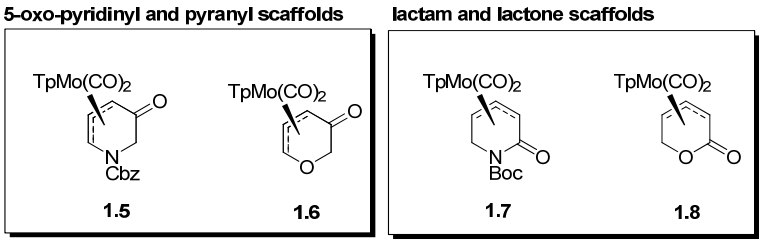


Figure 1.4. Core Organometallic Enantiomeric Scaffolds

The 5-oxo-pyridinyl scaffold **1.5**, and progeny platforms **1.9** derived from it, have been particularly useful in the synthesis of alkaloids possessing a variety of skeletal types (Figure 1.5). Through the development and application of new reactions, scaffold **1.5** and related compounds **1.9** have undergone [5+2] cycloadditions allowing access to tropanes such as Bao Gong Teng A.[24,33,34] Substituted piperidine and indolizidine alkaloids have been made *via* oxidative methanolysis protocols taking advantage of selective ionization/nucleophilic functionalization strategies.[26,29] Most recently, the discovery of 1,5-Michael-like reactivity has enabled the synthesis of 9-azabicyclo[3.3.1]nonanes, including (-)-adaline, and this extension of the scaffolding method will be discussed in Chapter 3.

[36] Coombs, T. C.; Lee, M. D., IV; Wong, H.; Armstrong, M.; Cheng, B.; Chen, W.; Moretto, A. F.; Liebeskind, L. S. *J. Org. Chem.* **2008**, *73*, 882-888.

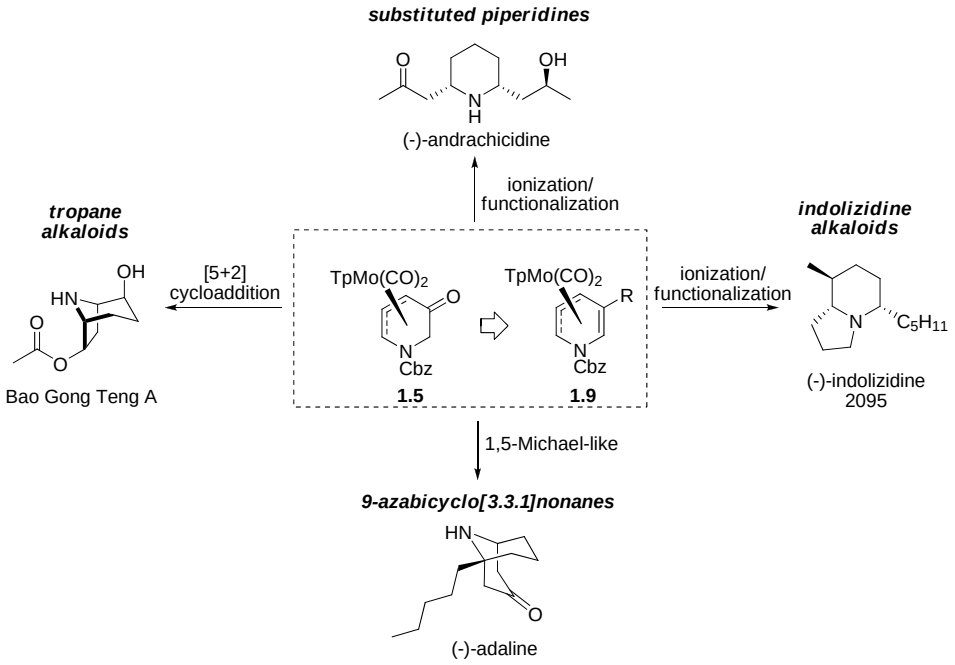


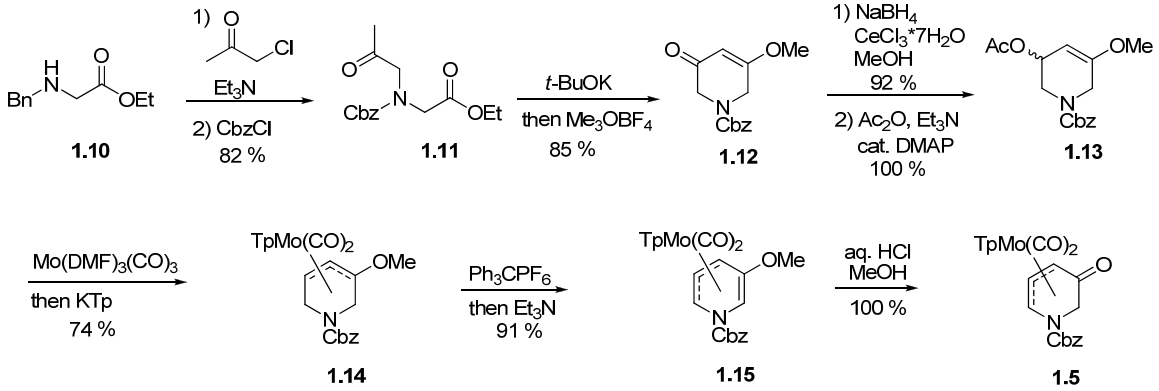
Figure 1.5. Scaffolding Concept Illustrated with 5-Oxo-pyridinyl Complex 1.5

While highly versatile, a significant drawback to the use of 5-oxo-pyridinyl complex **1.5** has remained its lengthy synthesis from commercial materials (Scheme 1.1).[29,32,34] The previously-employed synthesis evolved over several years and a full account has been written.[37] Beginning with commercially-available *N*-benzyl glycine ethyl ester **1.10**, alkylation with chloroacetone and exchange of the benzyl protecting group for Cbz, provided **1.11**. Treating **1.11** with potassium *t*-butoxide induced Dieckmann cyclization and the β-diketone product was trapped with Meerwein's reagent, delivering methoxyenone **1.12**. Luche reduction of the enone and acylation of the resultant allylic alcohol afforded allylic acetate **1.13**, which underwent oxidative addition to $Mo(DMF)_3(CO)_3$. Ligand exchange with KTp provided complex **1.14**. Two-step

[37] Wong, H. Design, Synthesis and Resolution of a Chiral, Non-Racemic Organometallic Chiron: Asymmetric Total Syntheses of Tetrahydropyridine-Based Alkaloids. Ph.D. Dissertation, Emory University, Atlanta, 2006.

migration of the $TpMo(CO)_2$ moiety by hydride abstraction with $TrPF_6$ and deprotonation with Et_3N led to fully-unsaturated complex **1.15**, which underwent acid-mediated hydrolysis of the enol ether to afford the desired 5-oxo-pyridinyl scaffold **1.5**. In total, eight steps were required to synthesize the racemic scaffold.

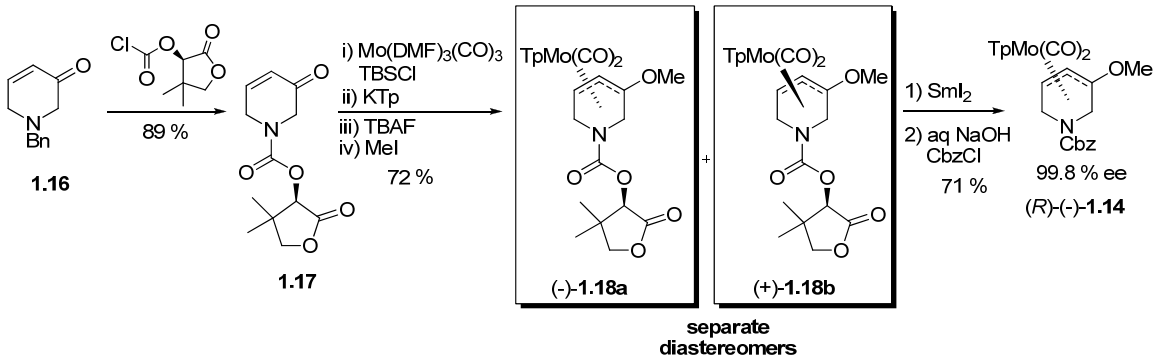
Scheme 1.1. Synthesis of 5-Oxo-Pyridinyl Scaffold 1.5



To access single enantiomers of scaffold **1.5**, additional steps were necessary using one of two different protocols: In the first, benzyl-protected compound **1.16**[38] was subjected to protecting group exchange with (*R*)-(-)-pantolactone chloroformate to give urethane **1.17** (Scheme 1.2). Metalation with $Mo(DMF)_3(CO)_3$, TBSCl, and KTp, followed by treatment with TBAF/MeI provided diastereomeric complexes **1.18a** and **1.18b** (Scheme 1.2). The two diastereomers could be resolved *via* recrystallization to dr's > 99.5 : 0.5. SmI_2-mediated removal of the chiral auxiliary and reprotection of the free amine with CbzCl delivered (*R*)-(-)-**1.14** (99.8 % ee) and its enantiomer.

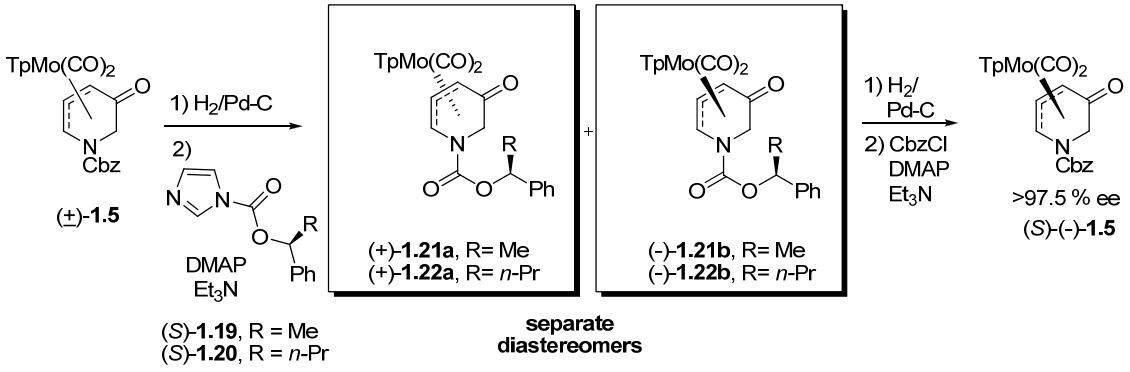
[38] In a prior generation of the route shown in Scheme 1, the Bn group was exchanged *after* metalation, and thus, the Bn-protected analog of compound **1.11** was carried through to **1.16** using a related sequence.

Scheme 1.2. Diastereomeric Scaffold Resolution-First Approach



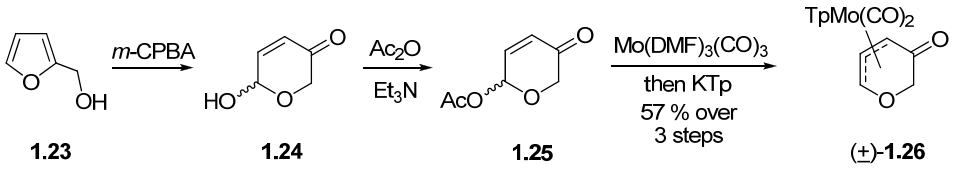
In the second protocol, (±)-**1.5** was subjected to hydrogenolytic removal of the Cbz group and the free amine was reprotected with a chiral auxiliary, delivering diastereomers (+)-**1.21a** and (-)-**1.21b** (Scheme 1.3). Chromatographic resolution of these diastereomers, followed by hydrogenolysis of the auxiliary and reprotection with CbzCl provided (*S*)-(-)-**1.5** in high enantiomeric excess. The identity of the chiral auxiliary was critical for minimizing racemization during its removal: mandelic carbamates led to significant racemization, while phenylbutanol- and phenylethanol-derived carbamates led to only slight racemization.

Scheme 1.3. Diastereomeric Scaffold Resolution-Second Approach



In contrast to 5-oxo-pyridinyl scaffold **1.5**, the corresponding racemic 5-oxo-pyranyl scaffold **1.26** could be easily synthesized in three steps using the Achmatowicz rearrangement of furfuryl alcohol **1.23** (Scheme 1.4). In this protocol, oxidative rearrangement of furfuryl alcohol with *m*-CPBA followed by acylation of the resultant hydroxypyranone provided **1.25**. Metalation with $Mo(DMF)_3(CO)_3$ and ligand exchange with KTp afforded (±)-**1.26**. A fourth step and diastereomer resolution were required to access homochiral scaffolds.[35,36]

Scheme 1.4. Achmatowicz-based Synthesis of 5-Oxo-pyranyl Scaffold 1.26.



1.23 **1.24** **1.25** (±)-**1.26**

The Aza-Achmatowicz Reaction: Background and Application

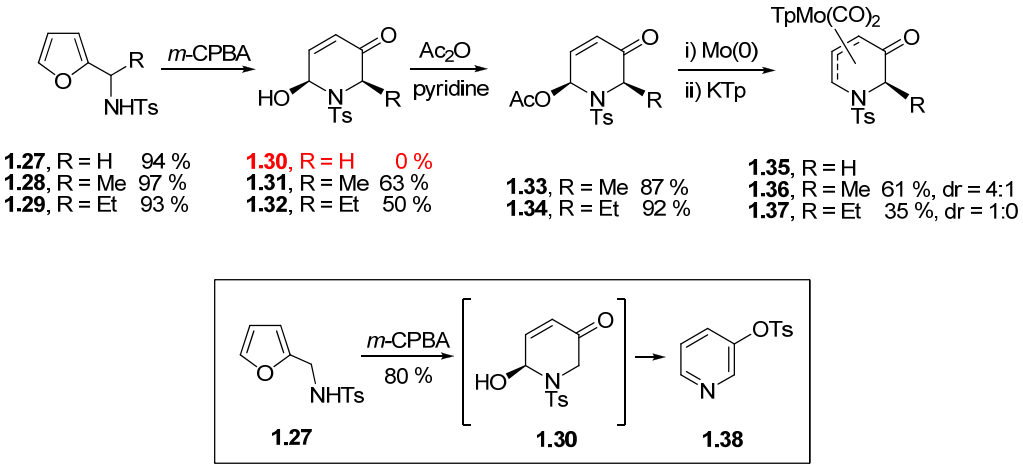
Employing the related aza-Achmatowicz reaction, Dr. Alessandro Moretto, a former graduate student in the Liebeskind laboratory, found that 6-substituted-5-oxo-pyridinyl complexes **1.36** and **1.37** could be made in an analogous manner (Scheme 1.5).[39,40] However, the parent unsubstituted scaffold **1.35** could not be synthesized by this method as the rearrangement did not stop at the desired dihydropyridinone **1.30**. It

[39] Moretto, A. F. The Utilization of Stoichiometric Molybdenum π-Complexes for the Synthesis of Substituted Piperidines. Ph.D. Dissertation, Emory University, Atlanta, 1999.

[40] The relative stereochemistry of compounds **1.31**-**1.37** was not rigorously established. The *cis* stereochemistry of **1.31**-**1.34** was assigned based on literature precedent and X-ray data from unpublished work by D. C. Liotta (refer to reference 39 and references therein). The major diastereomers of **1.36** and **1.37** were assumed to possess a *trans* relationship between the $TpMo(CO)_2$ moiety and the R group. This assumption was based on prior observations in which 2.0 equivalents of a Mo(0) source favored inversion in the oxidative addition of allylic acetates.

underwent further aromatization and protecting group transfer to give **1.38** (Scheme 1.5, inset).

Scheme 1.5. Aza-Achmatowicz Approach to 5-Oxo-pyridinyl Molybdenum Complexes



These results are consistent with other literature reports indicating that 2,6-dihydro-1*H*-pyridin-5-ones usually undergo facile aromatization.[41,42,43,44] This process has even been capitalized upon by some research groups who have deliberately oxidatively rearranged furfural amines to the corresponding 3-oxidopyridinium betaines for use in dipolar cycloadditions.[45,46] However, it has been shown that protecting nitrogen as a sulfonamide, and installing a substituent in the 6-position of the 2,6-dihydro-1*H*-pyridin-5-one inhibit aromatization.[47] These observations were incorporated into the chemistry highlighted in Scheme 1.5. Both iminium formation and enolization of

[41] McKillop, A.; Boulton, A. J. in *Comprehensive Heterocyclic Chemistry*; Katritzsky, A. R.; Rees, C. W., Eds.; Pergamon Press: Oxford, U.K. 1984; V. 2A, P. 90 ff.
[42] Shono, T.; Matsumura, Y.; Tsubata, K.; Inoue, K.; Nishida, R. *Chem. Lett.* **1983**, 21.
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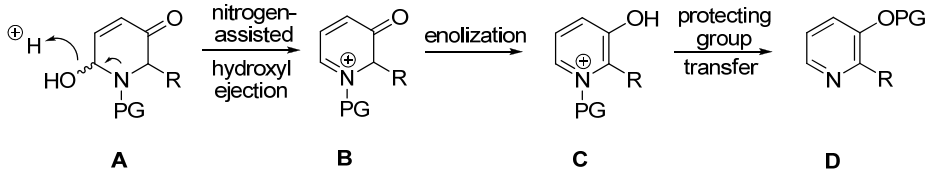
[44] Ciufolini, M. A.; Hermann, C. Y. W.; Dong, Q.; Shimizu, T.; Swaminathan, S.; Xi, N. *Synlett* **1998**, 105-114.
[45] Curtis, N. R.; Ball, R. G.; Kulagowski, J. J. *Tetrahedron Lett.* **2006**, *47*, 2635-2638.
[46] Peese, K. M.; Gin, D. Y. *Org. Lett.* **2005**, *7*, 3323-3325.
[47] Xu, Y. M.; Zhou, W. S. *Tetrahedron Lett.* **1996**, *37*, 1461.

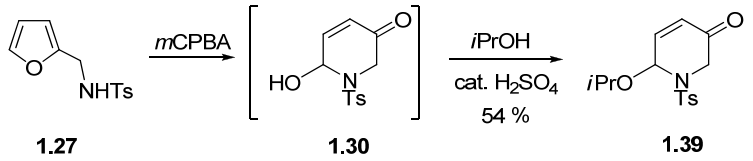
the ketone are necessary for dihydropyridinones **A** to aromatize (Scheme 1.6). Presumably, the electron-withdrawing sulfonyl protecting group inhibits the formation of iminium ion **B**, which would occur *via* nitrogen-assisted ejection of the hydroxyl group. Substituents in the 6-position raise the barrier to enolization of the ketone in **A** and/or **B**.

Scheme 1.6. The Aromatization Process



The only example of an aza-Achmatowicz reaction in which a 2,6-dihydro-1*H*-pyridin-5-one bearing no substitution at the 6-position could be isolated was reported by the Speckamp research group in 1995.[48] In this report, tosyl-protected furfuryl amine **1.27** was oxidatively rearranged with *m*-CPBA to hydroxy-substituted dihydropyridone **1.30** (Scheme 1.7). This intermediate was not isolated, but instead subjected to an acid-catalyzed exchange with isopropanol to give isolable isopropyloxy-substituted dihydropyridone **1.39**. Speckamp noted in this publication that the corresponding ethoxy derivative and alcohol **1.30** were quite sensitive and could only be isolated in low yields.

Scheme 1.7. Isolation of an Unsubstituted 2,6-Dihydro-1*H*-pyridin-5-one



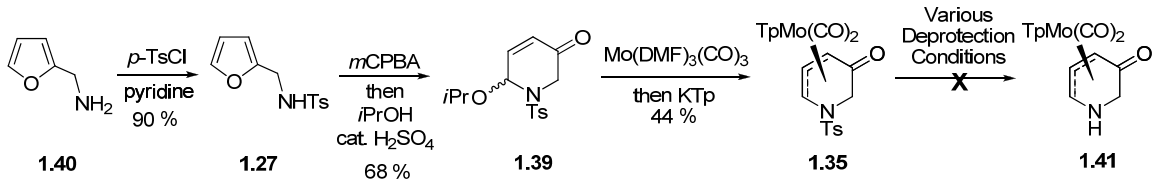
[48] Hopman, J. C. P.; Van den Berg, E.; Ollero, L. O.; Hiemstra, H.; Speckamp, W. N. *Tetrahedron Lett.* **1995**, *36*, 4315-4318.

Additionally, in a lone communication from O'Doherty, *N*-**Cbz**-6-substituted-2,6-dihydro-1*H*-pyridin-5-ones could be *isolated* from the aza-Achmatowicz rearrangement of **Cbz**-protected furfuryl amines.[49] Furthermore, the hydroxyl group could be exchanged for an ethoxy group with triethylorthoformate under acidic conditions.

Results and Discussion

The Speckamp publication led to a revisitation of the aza-Achmatowicz reaction as a route to tosyl-protected 5-oxo-pyridinyl complex **1.35**. Repeating the Speckamp protocol, isopropyloxy-substituted dihydropyridone **1.39** was isolated, purified and subjected to metalation with $Mo(DMF)_3(CO)_3$ and KTp (Scheme 1.8). The yield of this metalation reaction was a modest, but promising 44 %. Compound **1.35** would likely have made a useful scaffold, but the Cbz-protected complex was desired, both for ease of later protecting group removal and consistency with past work using the Cbz-protected complex. However, all efforts to remove the tosyl protecting group for reprotection with Cbz failed, resulting only in decomposition of the scaffold. Using other sulfone protecting groups led to low yields in the metalation step, so the approach was abandoned in favor of a new strategy.

Scheme 1.8. Unsubstituted Scaffold Synthesis *via* aza-Achmatowicz Reaction



1.40 **1.27** **1.39** **1.35** **1.41**

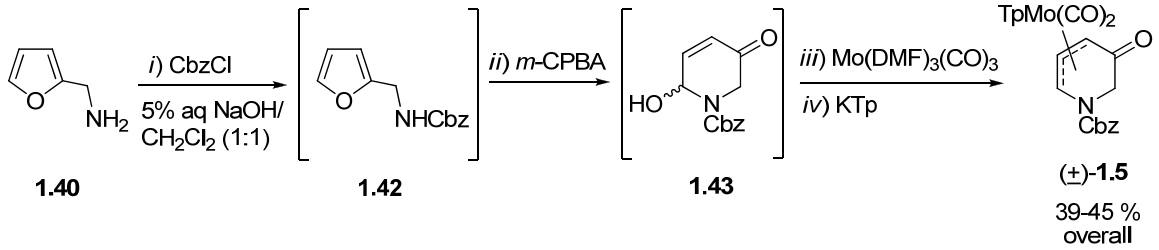
[49] Haukaas, M. H.; O'Doherty, G. A. *Org. Lett.* **2001**, *3*, 401-404.

The exchange from hydroxy to isopropyloxy in the Speckamp protocol suggested that 2-hydroxy-2,6-dihydro-1*H*-pyridin-5-ones lacking a substituent in the 6-position did not undergo immediate aromatization under the oxidative rearrangement conditions, but rather could be manipulated in solution. Furthermore, O'Doherty had shown that in some cases, *N*-Cbz-protected 2,6-dihydro-1*H*-pyridin-5-ones could be isolated. These literature precedents led to the hypothesis that oxidative rearrangement of Cbz-protected furfuryl amine **1.42** might deliver hydroxypyridinone **1.43**, stable in solution, which could undergo direct oxidative addition to $Mo(DMF)_3(CO)_3$ without purification of the hydroxypyridinone intermediate. Gratifyingly, direct formation of scaffold (±)-**1.5** in 39-45 % overall yield did indeed occur. In the optimized sequence, Cbz protection of furfuryl amine was followed by treatment *in one pot* with *m*-CPBA (~77 % purity), followed by $Mo(DMF)_3(CO)_3$, and then KTp additions. Schotten-Bauman conditions (5 % NaOH/CH_2Cl_2 [1:1]) were used to protect furfuryl amine with CbzCl, providing very clean **1.42**, which could be washed with water and directly used without chromatographic purification. However, the presence of base completely inhibited the aza-Achmatowicz rearrangement, necessitating thorough washing of the Schotten-Bauman product **1.42** prior to *m*-CPBA addition. Chromatography was only necessary at the end of the sequence.

Possible reasons for the moderate yield were: 1) slow oxidative addition of the allylic alcohol to $Mo(DMF)_3(CO)_3$; 2) interference of benzoic acid and water in the metalation/ligand exchange steps; and 3) facile aromatization of the hydroxy-pyridinone. Several reaction parameters were modified in an attempt to improve the overall yield of the sequence. Extending the reaction time for oxidative addition after adding

$Mo(DMF)_3(CO)_3$ to the Achmatowicz product **1.43**, and before ligand exchange with KTp, led to decreased overall yields of (±)-**1.5**. Decreased yields were also observed when purified *m*-CPBA was used in the reaction and when KF was added to the crude aza-Achmatowicz rearrangement product to precipitate benzoic acid salts. The addition of *i*PrOH and catalytic acid to exchange the hydroxyl group of **1.43** for an isopropyloxy group, thereby generating a more stable pyridinone for metalation, also led to decreased isolated yields of (±)-**1.5**. In the end, the best conditions were found to involve filtering off any solids that precipitated over the course of the aza-Achmatowicz rearrangement without adding KF, washing the solution with water, and drying over $MgSO_4$. Solid $Mo(DMF)_3(CO)_3$ was added directly to the degassed solution after filtration to remove the $MgSO_4$. It was not necessary to filter precipitated solids or to wash the crude aza-Achmatowicz product to achieve the 39-45 % yields observed for this sequence. However, stirring the reaction and purifying the crude metalation product were notably easier if this was done. Starting with 5.0 mL of furfuryl amine **1.40**, >13 grams of scaffold (±)-**1.5** could be made in the course of a single day.

Scheme 1.9. Aza-Achmatowicz Approach to Cbz-protected Scaffold (±)-1.5

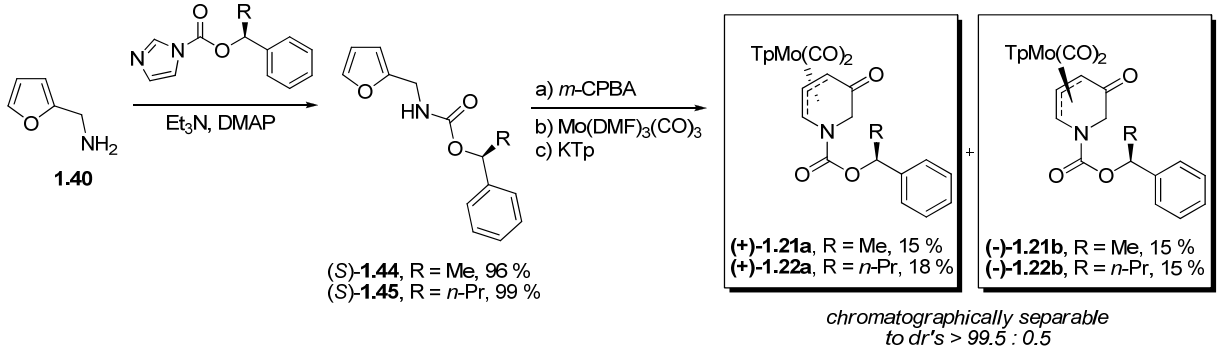


1.40 **1.42** **1.43** (±)-**1.5**

39-45 % overall

This protocol was extended by Matt Armstrong, as part of his master's thesis[50] in the Liebeskind research group, to the use of chiral, non-racemic nitrogen protecting groups (Scheme 1.10). Upon oxidative rearrangement with *m*-CPBA and direct metalation with $Mo(DMF)_3(CO)_3$ and KTp, diastereomeric complexes **1.21a**/**1.21b** and **1.22a**/**1.22b** could be isolated in 30 % and 33 % combined yields, respectively. Each pair of diastereomers could be resolved to dr's > 99.5 : 0.5 *via* silica gel column chromatography, as described in Scheme 3. Removal of the chiral auxiliary with minimal racemization was also described in Scheme 1.3.

Scheme 1.10. Accessing Single Diastereomers

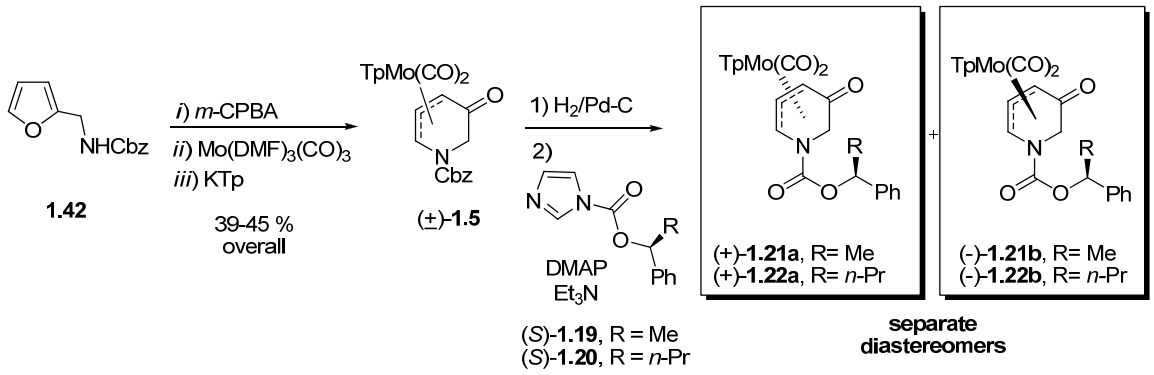


The price of chiral, non-racemic alcohols (*S*)-1-phenylethanol and (*S*)-1-phenylbutanol, used as chiral auxiliaries in the sequences highlighted in Scheme 1.10, has sharply increased in recent years, making their efficient use especially important. The sequences using these auxiliaries provide direct access to **1.21a**/**1.21b** and **1.22a**/**1.22b**, but in relatively low yields. A more cost-effective approach is to synthesize (±)-**1.5** as described in Scheme 1.9 and then use the protocol from Scheme 1.3 to access single

[50] Armstrong, M. A. Synthesis and Resolution of Chiral, Non-Racemic $TpMo(CO)_2(\eta^3$-pyridinyl) Complexes. Master Dissertation, Emory University, Atlanta, 2007

diastereomers (Scheme 1.11). In this way, higher yields are achieved for transformations utilizing the expensive chiral auxiliary.

Scheme 1.11. A More Cost-effective Approach to Single Enantiomers of Scaffold 1.5



Additionally, making the auxiliaries instead of buying them might be worth exploring using Noyori's protocol.[51] This protocol would involve catalytic asymmetric reduction of acetophenone and butyrophenone. If good yields and high ee's could be achieved, the cost of the catalyst would be considerably less than the cost of the auxiliaries. As previously noted, other auxiliaries have been explored for accessing single enantiomers of complex **1.5**, but difficulties encountered in the resolutions or removal of the auxiliaries led to their dismissal.[37,50]

In conclusion, a much shorter and more practical route to parent, unsubstituted 5-oxo-pyridinyl scaffold (±)-**1.5** has been developed using the aza-Achmatowicz rearrangement. To avoid the undesired aromatization that has hitherto prevented the application of this reaction to the synthesis of (±)-**1.5**, a one-pot rearrangement/metalation protocol was employed, eliminating the need for purification of sensitive intermediates. This protocol has been extended by other group members to

[51] Fujii, A.; Hashigucki, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521-2522.

chiral non-racemic substrates, providing improved access to both enantiomers of **1.5** in high enantiomeric excesses.

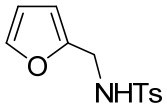
Experimental Section:

General Methods

Unless otherwise indicated, all reactions were carried out under a positive pressure of argon in oven- or flame-dried glassware using solvents dried over 4 Å molecular sieves or dispensed and used directly from a Seca Solvent System purchased from Glass Contour. Analytical thin-layer chromatography (TLC) was performed using commercial Merck KGaA aluminum-supported silica gel plates with fluorescent indicator (F-254). Visualization was accomplished using UV light, 5 % phosphomolybdic acid in ethanol, or aqueous $KMnO_4$. Flash column chromatography was carried out using 32-63 μm silica gel, with compressed air as a source of positive pressure. All reagents were used as received, with the exception of amines, which were distilled and stored over 4 Å molecular sieves prior to use.

^1H and ^{13}C NMR spectra were recorded on Mercury 300 (300 MHz ^1H, 75 MHz ^{13}C), Varian INOVA 400 (400 MHz ^1H, 100 MHz ^{13}C), and Varian INOVA 600 (600 MHz ^1H, 150 MHz ^{13}C) instruments in $CDCl_3$, with $CHCl_3$ as internal reference (7.27 ppm for ^1H and 77.23 ppm for ^{13}C), and C_6D_6, with C_6H_6 as internal reference (7.16 ppm for ^1H and 128.39 ppm for ^{13}C). Infrared spectra were recorded on an ASI ReactIR® 1000 FT-IR spectrometer equipped with a silicon probe. Peaks are reported with the following relative intensities: s (strong, 67-100 %), m (medium, 40-67 %), w (weak, 20-40 %), and br (broad). Melting points (mp) are uncorrected and were taken in open capillary tubes on a Thomas Hoover capillary melting point apparatus. *Since almost all*

of the Tp molybdenum complexes decompose over 180-200 °C, melting points are not significant and are not shown in the experimental section. Optical rotations were measured with Perkin-Elmer 241MC or Perkin-Elmer Model 341 polarimeters. HPLC was performed using an Agilent 1100 Series with UV detector (254 nm or 210 nm) and Daicel® Chiralpak AS-RH, Chiralpak AD-RH, Chiralcel OJ-RH, Chiralcel OD-RH, or Agilent Eclipse XDB-C8 columns. Samples for HPLC analysis were prepared by dissolving 1-2 mg of of the pure material in approximately 0.5 mL of acetonitrile. One microliter (1 μL) of the solution was injected for analysis. The nomenclature for determining the chirality of the molybdenum complexes is straightforward.[52]

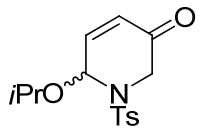


***N*-(furan-2-ylmethyl)-4-methylbenzenesulfonamide, 1.27.** Furfuryl amine (5.0 mL, 56.6 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (40 mL) and the solution was cooled to 0 °C. Pyridine (5.49 mL, 68.0 mmol, 1.2 equiv) and *p*-TsCl (13.0 g, 68.0 mmol, 1.2 equiv) were added and the solution was warmed to room temperature. After 12.5 hours, the solution was concentrated and subjected to flash chromatography over silica gel with hexanes-EtOAc (1:1, then 0:1), affording **1.27** (12.9 g, 51.2 mmol, 90 %) as a white, crystalline solid (mp 117-118 °C).

1.27: TLC: R_f = 0.61, (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3281 (s), 3254 (s), 1598 (m), 1494 (m), 1451 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1 H), 7.69 (s, 1 H), 7.27 (m, 1 H), 7.25 (m, 1 H), 7.22 (m, 1 H), 6.20 (dd, *J* = 3.2 Hz, 2.0 Hz, 1 H), 6.07-6.08

[52] Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1-36.

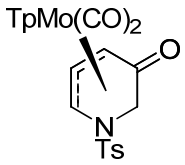
(m, 1 H), 4.99 (t, J = 6.0 Hz, 1 H), 4.15 (d, J = 6.0 Hz, 2 H), 2.41 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 143.6, 142.6, 136.9, 129.8, 127.2, 110.5, 108.3, 40.2, 21.6.



(±)-2-isopropyloxy-1-tosyl-5,6-dihydropyridin-5(2*H*)-one, (±)-1.39. Tosyl-protected furfuryl amine **1.27** (200 mg, 0.80 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (5 mL) and purified *m*-CPBA (276 mg, 1.60 mmol, 2.0 equiv) was added at room temperature. After 2 hours, 10 mL of *i*-PrOH containing a catalytic amount of concentrated H_2SO_4 was added and the solution was stirred two additional hours. The reaction mixture was poured into water and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed several times with water. KF (93 mg, 1.60 mmol, 2.0 equiv) was added to the organic layer and stirred 15 minutes. Solids were removed *via* filtration and the solution was concentrated. The residue was dissolved in Et_2O, water was added, and the solution was treated with 10 % aqueous NaOH until basic. The layers were separated, the organic layer was dried over $MgSO_4$, filtered, and concentrated to afford dihydropyridinone (±)-**1.39** (164 mg, 0.53 mmol, 66 %) as a white solid (mp 97-98 ^{o}C).

(±)-**1.39**: TLC: R_f = 0.51, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2976 (m), 1745 (m), 1695 (s), 1598 (m), 1455 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 2 H), 7.23 (d, J = 7.6 Hz, 2 H), 6.70 (dd, J = 10.4 Hz, 4.4 Hz, 1 H), 5.76 (d, J = 10.4 Hz, 1 H), 5.65 (d, J = 4.8 Hz, 1 H), 4.16 (d, J = 18.4 Hz, 1 H), 4.12 (hep, J = 6.0 Hz, 1 H), 3.98 (d, J = 18.4 Hz, 1 H), 2.36 (s, 3 H), 1.23 (d, J = 6.0 Hz, 3 H), 1.18 (d, J = 6.0 Hz, 3 H). ^{13}C

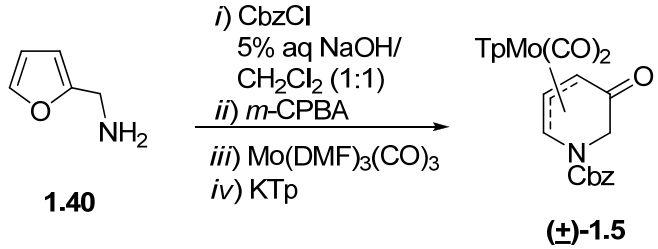
NMR (100 MHz, $CDCl_3$): δ 192.0, 144.3, 143.5, 136.0, 130.1 (2), 128.0, 127.1 (2), 77.2, 70.2, 48.6, 23.1, 21.6, 21.4.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-1-(4-methylbenzenesulfonamide)-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-1.35. Dihydropyridinone (±)-**1.39** (164 mg, 0.53 mmol, 1.0 equiv) in dry, degassed CH_2Cl_2 (5 mL) was added to a solution of $Mo(DMF)_3(CO)_3$ (507 mg, 1.27 mmol, 2.4 equiv) in dry, degassed CH_2Cl_2 (10 mL). The solution turned deep red-brown. TBSCl (191 mg, 1.27 mmol, 2.4 equiv) was added and the solution was stirred 10 hours at room temperature before KTp (320 mg, 1.27 mmol, 2.4 equiv) was added. The reaction mixture was stirred an additional 35 minutes and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1, then 0:1) afforded (±)-**1.35** (145 mg, 0.23 mmol, 44 %) as a red solid.

(±)-**1.35**: TLC: R_f = 0.39, (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3127 (w), 1965 (s), 1880 (s), 1660 (s), 1598 (m), 1505 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 1.6 Hz, 1 H), 8.09 (d, *J* = 2.4 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.72 (d, *J* = 2.4 Hz, 1 H), 7.65 (d, *J* = 2.0 Hz, 1 H), 7.60 (d, *J* = 2.0 Hz, 1 H), 7.51 (d, *J* = 2.0 Hz, 1 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.15 (dd, *J* = 6.4 Hz, 1.6 Hz, 1 H), 6.32 (t, *J* = 2.4 Hz, 1 H), 6.29 (t, *J* = 2.4 Hz, 1 H), 6.19 (t, *J* = 2.4 Hz, 1 H), 4.61 (dd, *J* = 6.0 Hz, 2.0 Hz, 1 H), 3.98 (t, *J* = 6.4 Hz, 1 H), 3.24 (d, *J* = 18.8 Hz, 1 H), 3.10 (d, *J* = 18.8 Hz, 1 H), 2.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.3, 222.3, 191.3, 147.6, 144.4, 143.3, 142.5, 136.9, 136.6, 135.2,

135.0, 130.2, 127.3, 106.6, 106.5, 106.1, 89.4, 66.9, 64.2, 47.5, 21.8. HRMS (ESI) Calcd for $C_{23}H_{23}BMoN_7O_5S$ ($[M+H]^+$): 618.0623. Found: 618.0629.

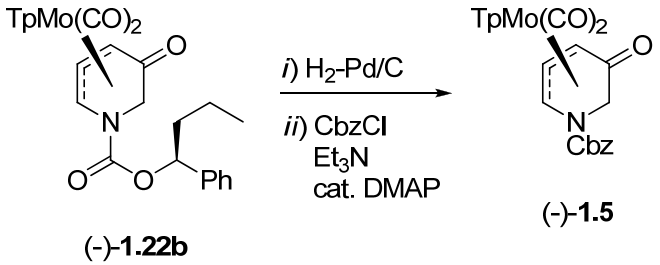


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η^3-2,3,4)-1-benzyloxycarbonyl-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-1.5. To a Schlenk flask was added CH_2Cl_2 (40 mL), furfuryl amine **1.40** (5.00 mL, 56.6 mmol, 1.0 equiv), and 5 % aqueous NaOH (40 mL). The suspension was cooled to 0 ^oC, and benzyl chloroformate (95 % purity, 10.9 mL, 73.6 mmol, 1.3 equiv) was added dropwise while keeping the temperature below 25 ^oC. The reaction was stirred at room temperature for 15 minutes before the organic phase was washed with water (2 x 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (80 mL), cooled to 0 ^oC, and *m*-CPBA (~77 % purity, 19.0 g, 84.9 mmol, 1.50 equiv) was added portionwise. After holding the temperature at 0 ^oC for 1.5 hours, the white solids were removed by vacuum filtration. The filtrate was washed with water (50 mL) and dried over $MgSO_4$. The $MgSO_4$ was removed *via* filtration, and the filtrate was degassed with argon for 10 minutes. To the degassed solution at 0 ^oC was added solid $Mo(DMF)_3(CO)_3$ (22.4 g, 56.2 mmol, 0.99 equiv). After stirring for 5 minutes at 0 ^oC, the reaction was warmed to room temperature and stirred for 1 hour. The reaction mixture was cooled to 0 ^oC and potassium hydridotris(1-pyrazolyl)borate (KTp) (14.3 g, 56.6 mmol, 1.0 equiv) was added. The reaction mixture was stirred at room temperature for 1 hour, filtered

through a pad of Celite, and concentrated under reduced pressure. The crude product was subjected to short filter chromatography (SiO_2, 9.0 cm x 6.0 cm, 10 % EtOAc in hexanes ramping gradually to 33% EtOAc in hexanes). Fractions overlapping with impurities were collected and subjected to a second chromatography (20% EtOAc in hexanes) to afford the product (±)-**1.5** (13.2 g, 22.2 mmol, 39 %) as an orange solid.

(±)-1.5: TLC: R_f = 0.62 (50 % EtOAc in hexanes). IR (cm^{-1}): 1968 (s), 1875 (s), 1696 (s), 1654 (s). ^{1}H NMR (mixture of two rotamers- 400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 1.9 Hz, 0.4 H), 8.42 (d, *J* = 1.9 Hz, 0.6 H), 8.31 (d, *J* = 1.9 Hz, 0.6 H), 7.76 (d, *J* = 1.9 Hz, 0.4 H), 7.74 (d, *J* = 1.9 Hz, 0.6 H), 7.70 (d, *J* = 1.9 Hz, 0.4 H), 7.65 (d, *J* = 1.9 Hz, 0.6 H), 7.62 (d, *J* = 1.9 Hz, 0.6 H), 7.60 (d, *J* = 1.9 Hz, 0.4 H), 7.58 (d, *J* = 1.9 Hz, 0.4 H), 7.47-7.52 (m, 1.6 H), 7.40-7.44 (m, 2 H), 7.27-7.38 (m, 3 H), 7.22 (dd, *J* = 6.4, 1.9 Hz, 0.4 H), 6.28-6.30 (m, 1.6 H), 6.22-6.24 (m, 1 H), 5.97 (t, *J* = 2.2 Hz, 0.4 H), 5.27 (AB quartet, *J* = 11.4 Hz, 0.4 Hz), 5.24 (s, 0.6 H), 4.74-4.77 (m, 1 H), 4.09 (t, *J* = 6.4 Hz, 0.6 H), 3.98 (t, *J* = 6.4 Hz, 0.4 H), 3.41 (AB quartet, *J* = 20.0 Hz, 0.4 H), 3.39 (AB quartet, *J* = 19.7 Hz, 0.6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.9, 224.5, 222.6, 221.9, 193.3, 192.6, 154.4, 153.6, 147.1, 147.0, 144.2, 143.3, 141.3, 141.2, 136.33, 136.31, 136.2, 136.1, 135.4, 135.1, 134.6, 128.7, 128.5, 128.4, 128.3, 128.0, 127.6, 106.0, 105.8, 105.6, 93.7, 92.2, 68.7, 67.9, 64.4, 64.0, 63.7, 63.3, 47.7, 47.6. HRMS (ESI) Calcd. for $C_{24}H_{23}BMoN_7O_5$ $[M + H]^+$: 598.0908. Found: 598.0905. HPLC: Daicel® Chiralcel OD-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1% TFA) 0-20 mins (50% to 75%), 1.5 mL/min., λ = 254 nm, (*S*)-(-)-7: t_S=11.51 min; (*R*)-(+)-7: t_R = 9.25 min.

Representative procedure for the conversion of (-)-**1.22b** to (-)-**1.5**:



(-)-**1.22b** (-)-**1.5**

Complex **(-)-1.22b** (3.26 g, 5.11 mmol, 1.0 equiv, 99.8 % de) was dissolved in THF (50 mL) and Pd/C (10 % w/w, 816 mg, 0.77 mmol, 0.15 equiv) was added. A balloon of H_2 (g) was added to the reaction vessel and the reaction was stirred 4.5 hours during which time the solution turned from bright orange to dark purple. The solution was concentrated and the residue was dissolved in CH_2Cl_2 (100 mL). CbzCl (95 % purity, 0.83 mL, 5.62 mmol, 1.1 equiv), Et_3N (0.78 mL, 5.62 mmol, 1.1 equiv) and several crystals of DMAP were added, and the reaction mixture was stirred for one hour. The solution was concentrated under reduced pressure to a volume of ~20 mL, and then passed through a short pad of silica gel with 100 % EtOAc. Flash chromatography over silica gel with hexanes-EtOAc (4:1, then 2:1, then 1:1) afforded (-)-**1.5** (2.12 g, 3.55 mmol, 70 %, 99.0 % ee) as an orange solid.

Chapter 2:

Semipinacol Rearrangement of $TpMo(CO)_2$-Based Allylic Alcohols

Background

The controlled, asymmetric construction of quaternary stereocenters remains a considerable challenge to contemporary synthetic organic chemists. Overman has recently reviewed the synthesis of all-carbon quaternary stereocenters[53,54] noting that it is the steric congestion resulting from having four carbon substituents attached to the same carbon atom which creates this challenge. Additionally, there are a limited number of reliable methods for forming carbon-carbon bonds in the synthesis of all-carbon quaternary stereocenters.[55] The presence of a heteroatom on the quaternary carbon expands the scope of available strategies for the synthesis of such carbons, with nitrogen being especially enabling.[56] However, the construction of heteroatom-bearing quaternary stereocenters is an area of organic synthesis in need of additional development.

A number of naturally-occuring piperidine-based alkaloids possessing α-amino quaternary stereocenters and interesting biological properties have been isolated over the years (Figure 2.1).[57,58,59,60,61]

[53] Douglas, C. J.; Overman, L. E. *Proc. Natl. Acad. Sci.* **2004**, *101*, 5363-5367.
[54] Peterson, E. A.; Overman, L. E. *Proc. Natl. Acad. Sci.* **2004**, *101*, 11943-11948.
[55] Corey, E. J.; Guzman-Perez, A. *Angew. Chem. Int. Ed.* **1998,** *37*, 388-401.
[56] Ramon, D. J.; Yus, M. *Curr. Org. Chem.* **2004,** *8*, 149-183.
[57] Ma, X.; Gang, D. R. *Nat. Prod. Rep.* **2004**, *21*, 752-772.
[58] Daly, J. W.; Spande, T. F.; Garraffo, H. M. *J. Nat. Prod.* **2005**, *68*, 1556-1575.
[59] King, A. G.; Meinwald, J. *Chem. Rev.* **1996**, *96*, 1105-1122.
[60] Weinreb, S. M. *Chem. Rev.* **2006**, *106*, 2531-2549.
[61] Clive, D. L. J.; Yu, M.; Wang, J.; Yeh, V. S. C.; Kang, S. *Chem. Rev.* **2005**, *105*, 4483-4514.

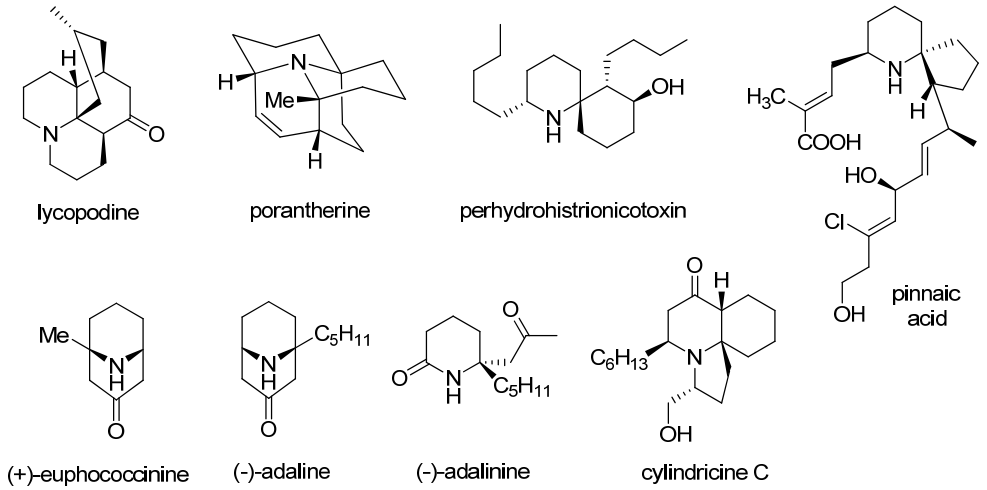


Figure 2.1. Piperidine-based Alkaloids Bearing Quaternary Centers α to Nitrogen

The pursuit of these compounds has led many research groups to develop novel methods and strategies for the synthesis of α-hetero quaternary centers. Most common and widely applied among these are: (a) asymmetric enamine and enolate alkylation/Curtius rearrangement,[62,63] (b) asymmetric nucleophilic addition to a Lewis acid-induced imminium ion,[64,65,66] (c) nitrone-olefin dipolar cycloadditions,[67,68,69,70,71,72] (d) oxidative spirocyclization,[73] (e) tandem Michael additions,[74,75,76,77,78] and (f) semipinacol-induced ring expansions.[79,80]

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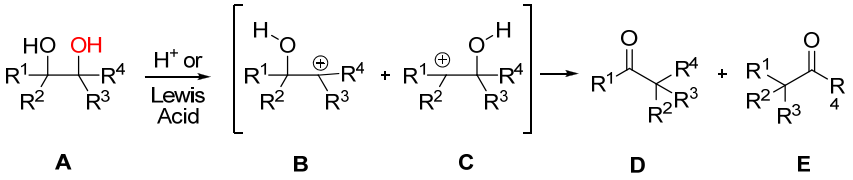
[62] Arimoto, H.; Asano, S.; Uemura, D. *Tetrahedron Lett.* **1999**, *40*, 3583-3586.
[63] Arai, T.; Abe, H.; Aoyagi, S.; Kibayashi, C. *Tetrahedron Lett.* **2004**, *45*, 5921-5924.
[64] Carson, M. W.; Kim, G.; Hentemann, M. F.; Trauner, D.; Danishefsky, S. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4450-4452.
[65] Christie, H. S.; Heathcock, C. H. *Proc. Natl. Acad. Sci.* **2004**, *101*, 12079-12084.
[66] Itoh, T.; Yamazaki, N.; Kibayashi, C. *Org. Lett.* **2002**, *4*, 2469-2472.
[67] White, J. D.; Blakemore, P. R.; Korf, E. A.; Yokochi, A. F. *Org. Lett.* **2001**, *3*, 413-415.
[68] Shindo, M.; Fukuda, Y.; Shishido, K. *Tetrahedron Lett.* **2000**, *41*, 929-932.
[69] Werner, K. M.; Santos, J. M.; Weinreb, S. M. *J. Org. Chem.* **1999**, *64*, 4865-4873.
[70] Oppolzer, W.; Bochet, C. G. *Tetrahedron: Asymmetry* **2000**, *11*, 4761-4770.
[71] Stockman, R. A.; Sinclair, A.; Arini, L. G.; Szeto, P.; Hughes, D. L. *J. Org. Chem.* **2004**, *69*, 1598-1602.
[72] Davison, E. C.; Holmes, A. B.; Forbes, I. F. *Tetrahedron Lett.* **1995**, *36*, 9047-9050.
[73] Canesi, S.; Bouchu, D.; Ciufolini, M. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 4336-4338.
[74] Molander, G. A.; Ronn, M. *J. Org. Chem.* **1999**, *64*, 5183-5187.
[75] Trost, B. M.; Rudd, M. T. *Org. Lett.* **2003**, *5*, 4599-4602.
[76] Snider, B. B.; Liu, T. *J. Org. Chem.* **1997**, *62*, 5630-5633.
[77] Liu, J. F. Heathcock, C. H. *J. Org. Chem.* **1999**, *64*, 8263-8266.

The pinacol[81] and semipinacol[82] reactions have been extensively used in the field of organic synthesis. In the classic pinacol rearrangement, a vicinal diol **A** (Scheme 2.1) is subjected to acid- or Lewis acid-catalyzed ionization of one of the hydroxyl groups, generating an α-hydroxy carbocation intermediate **B**, which undergoes a [1,2]-shift to afford carbonyl compound **D**. Poor regiocontrol in the ionization step often leads to a second carbocation **C**, producing a second carbonyl compound **E**.

Scheme 2.1. Pinacol Rearrangement



The relatively harsh reaction conditions and poor regiocontrol in this transformation have led to the development of the modified semipinacol rearrangement. Substrates for the semipinacol rearrangement have replaced one of the hydroxyl groups of the vicinal diol with a different leaving group X or an olefin, which may be selectively ionized or activated under milder conditions (Scheme 2.2). Thus, harsh reaction conditions and regioselectivity problems are avoided, making the semipinacol rearrangement of great synthetic utility for the stereocontrolled construction of quaternary centers in complex molecules.[83,84,85] The scope of this reaction has been continually

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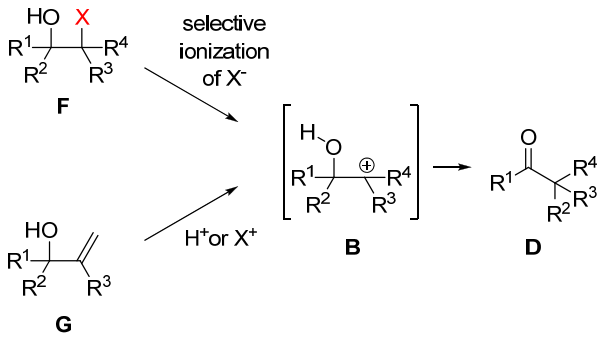
[78] Hill, R. K.; Renbaum, L. A. *Tetrahedron* **1982**, *38*, 1959-1963.
[79] Dake, G. R.; Fenster, M. D.; Hurley, P. B.; Patrick, B. O. *J. Org. Chem.* **2004**, *69*, 5668-5675.
[80] Fenster, M. D.; Dake, G. R. *Chem. Eur. J.* **2005**, *11*, 639-649.
[81] Rickborn, B. The Pinacol Rearrangement. In *Comprehensive Organic Synthesis*; Trost, B, M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp 721-732.
[82] Coveney, D. J. The Semipinacol and Other Rearrangements. In *Comprehensive Organic Synthesis*; Trost, B, M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp 777-801.

[83] Seki, M.; Sakamoto, T.; Suemune, H.; Kanematsu, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1707-1714.

expanded over the years, and many modifications have been reported.[86,87,88,89] A common feature of these rearrangements is the migration of the R group that is best able to stabilize the developing positive charge on the α-carbon. From best to worst migratory aptitude, the following order applies: aryl/H/vinyl > 3° alkyl > 2° alkyl > 1° alkyl.

Scheme 2.2. Semipinacol Rearrangement



Three common variants of the semipinacol rearrangement have been reported in the literature relying on different modes of electrophilic initiation of the reaction: Brønsted-acid-promoted, halogen-cation-promoted, and Lewis-acid-mediated epoxide opening. In all of these cases, the electrophile generates a carbocation or a heterocyclopropane intermediate α to a hydroxyl group, causing a [1,2]-shift and delivering a carbonyl compound with an α quaternary center. Diastereocontrol in these rearrangements is usually very good.

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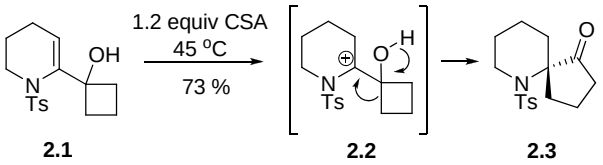
[84] Wendt, J. A.; Gauvreau, P. J.; Bach, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 9921-9926.
[85] Suzuki, K.; Tomooka, K.; Katayama, E.; Matsumoto, T.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1986**, *108*, 5221-5229.
[86] Blanco, F. E.; Harris, F. L. *J. Org. Chem.* **1977**, *42*, 868-871.
[87] Bickley, J. F.; Hauer, B.; Pena, P. C. A.; Roberts, S. M.; Skidmore, J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1253-1255.
[88] Wang, B. M.; Song, Z. L.; Fan, C. A.; Tu, Y. Q.; Chen, W. M. *Synlett* **2003**, 1497-1499.
[89] Hu, X.-D.; Fan, C.-A.; Zhang, F.-M.; Tu, Y. Q. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 1702-1705.

A nice example of the Brønsted acid-promoted semipinacol rearrangement was reported by Dake and co-workers and is highlighted in Scheme 2.3. Stirring allylic cyclobutanol **2.1** in the presence of 1.2 equivalents of camphorsulfonic acid (CSA) at room temperature resulted in almost no reaction after 24 hours. However, heating the reaction at 45 ^{o}C for 13 hours provided spirocyclic ketone **2.3** in 73 % yield.

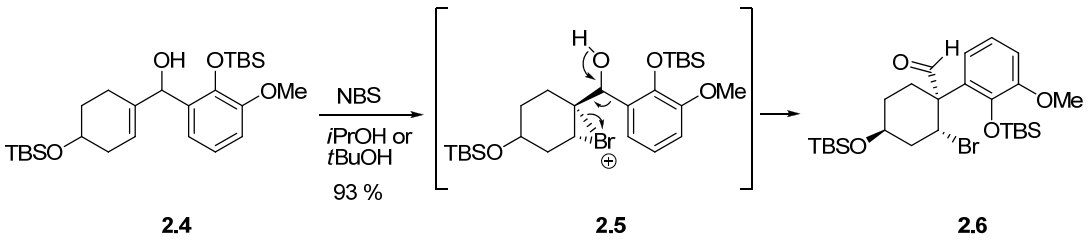
Scheme 2.3. Brønsted Acid-Promoted Semipinacol Rearrangement



An elegant example of the halogen cation-promoted semipinacol rearrangement may be found in the synthesis of lycoramine by Fan and co-workers[90] (Scheme 2.4). The key quaternary center-forming reaction in their synthesis took advantage of an NBS-promoted semipinacol rearrangement of allylic alcohol **2.4**. This reaction proceeded through α-hydroxy heterocyclopropane intermediate **2.5**, delivering β-bromo aldehyde **2.6** after [1,2]-migration of the aromatic moiety.

[90] Fan, C.-A.; Tu, Y.-Q.; Song, Z.-L.; Zhang, E.; Shi, L.; Wang, M.; Wang, B.; Zhang, S.-Y. *Org. Lett.* **2004**, *6*, 4691-4694.

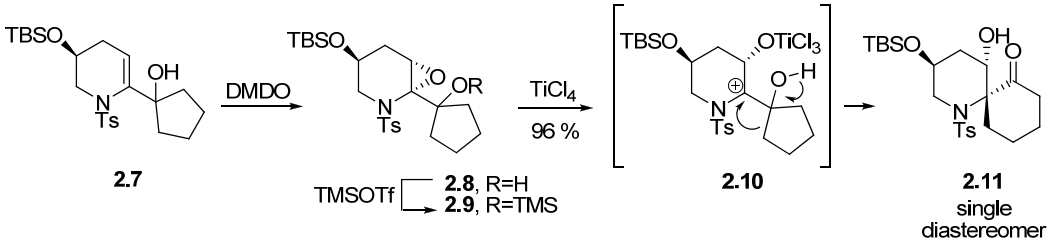
Scheme 2.4. *N*-Halosuccinimide-Promoted Semipinacol Rearrangement



2.4 **2.5** **2.6**

Semipinacol rearrangement of an α-siloxy epoxide was used in an asymmetric synthesis of fasicularin by Fenster and Dake after both Brønsted acids and NBS failed to initiate the rearrangement of allylic cyclopentanol **2.7** (Scheme 2.5). Allylic alcohol **2.7** was first epoxidized with DMDO and the alcohol of **2.8** was then protected as the trimethylsilyl ether. Addition of $TiCl_4$ initiated the ring-expanding semipinacol reaction, affording spirocyclic ketone **2.11** in 96 %. Attempts to directly rearrange **2.8** with $TiCl_4$ led to a messy reaction and low yields of **2.11**.

Scheme 2.5. Alpha Siloxy-Epoxide Semipinacol Rearrangement



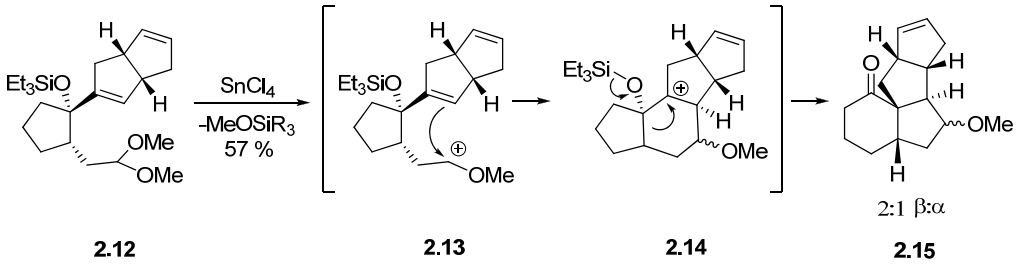
2.7 **2.10** **2.11** single diastereomer

The semipinacol rearrangement has also been incorporated into tandem reaction sequences to excellent effect. Overman has made significant contributions to the scope of this rearrangement by incorporating it into a tandem process with the Prins reaction.[91]

[91] Overman, L. E.; Pennington, L. D. Strategic use of pinacol-terminated Prins cyclizations in target-oriented total synthesis. *J. Org. Chem.* **2003**, *68*, 7143-7157.

Scheme 2.6 highlights one application [92] in which carbocation intermediate **2.13**, generated by Lewis acid-mediated ionization of one of the acetal methoxy groups in **2.12**, underwent intramolecular Prins reaction, delivering α-siloxy carbocation intermediate **2.14**. The sequence was terminated by a semipinacol rearrangement, delivering **2.15** as a 2:1 (β:α) ratio of diastereomers.

Scheme 2.6. Pinacol-Terminated Prins Reaction

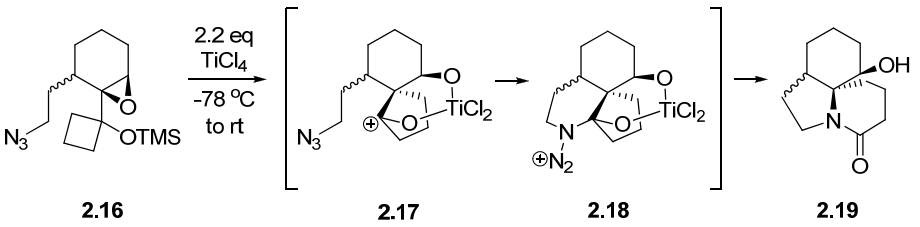


2.12 **2.13** **2.14** **2.15**

Incorporating the semipinacol rearrangement into a tandem sequence with the intramolecular Schmidt reaction allowed Gu and co-workers to efficiently synthesize tricyclic azaquaternary compound **2.19**, a common alkaloid skeleton (Scheme 2.7).[93] In this sequence, treating epoxy-ether **2.16** with excess $TiCl_4$ opened the epoxide initiating the ring-expanding semipinacol rearrangement. Attack of the tethered azide onto the carbocation of **2.17** provided intermediate aminal **2.18**. Collapse of the titanium aminal and the final [1,2]-shift of the Schmidt reaction afforded tricyclic lactam **2.19**.

[92] Hirst, G. C.; Johnson, T. O.; Overman, L. E. *J. Am. Chem. Soc.* **1993**, *115*, 2992-2993.
[93] Gu, P.; Zhao, Y.-M.; Tu, Y. Q.; Ma, Y.; Zhang, F. *Org. Lett.* **2006**, *8*, 5271-5273.

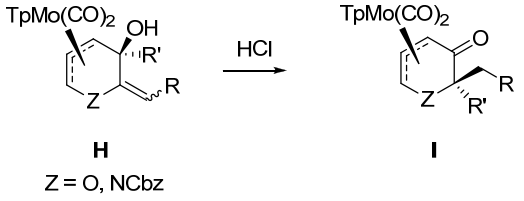
Scheme 2.7. Tandem Pinacol-Schmidt Reaction



Introduction

In the Liebeskind laboratory, Dr. Yongquiang Zhang found that $TpMo(CO)_2$-pyranyl and pyridinyl complexes **H** functionalized with allylic alcohols underwent facile semipinacol rearrangement upon treatment with a full equivalent of HCl to afford α,α'-disubstituted ketones **I** (Scheme 2.8).[94] Dr. Ethel Garnier followed up with studies utilizing enantiomerically-enriched 5-oxo-pyranyl scaffold (-)-**1.6**. The results of Dr. Zhang and Dr. Garnier are presented here.

Scheme 2.8. Semipinacol Rearrangement of Organometallic Enantiomeric Scaffolds

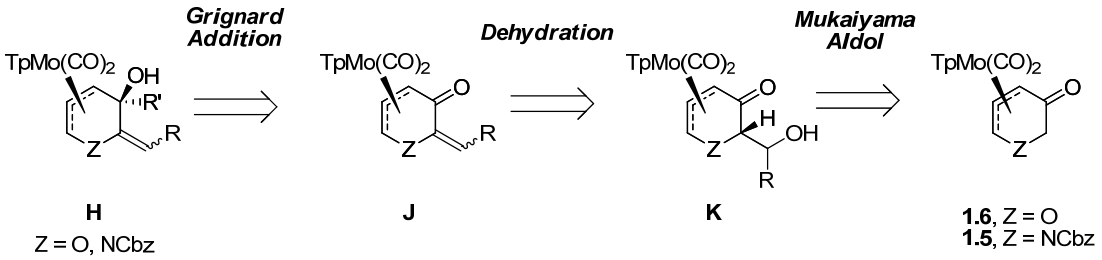


The requisite allylic alcohols **H** were synthesized according to the retrosynthesis shown in Scheme 2.9. Allylic alcohols **H** were accessed by Grignard addition to enones **J**. Enones **J** were in turn made by dehydration of β-hydoxy ketones **K**, which were

[94] Zhang, Y. Preliminary Studies: Stereocontrolled Construction of Oxa- and Aza Heterocycles from the two Common Molybdenum Scaffolds, $TpMo(CO)_2$(5-oxopyranyl) and $TpMo(CO)_2$(5-oxopyridinyl). Unpublished Results, Emory University, Atlanta, 2005.

synthesized by Mukaiyama aldol reaction of 5-oxo-η^3-allylmolybdenum pyranyl and pyridinyl organometallic enantiomeric scaffolds **1.6** and **1.5** with the appropriate aldehydes. The details of each step are discussed below.

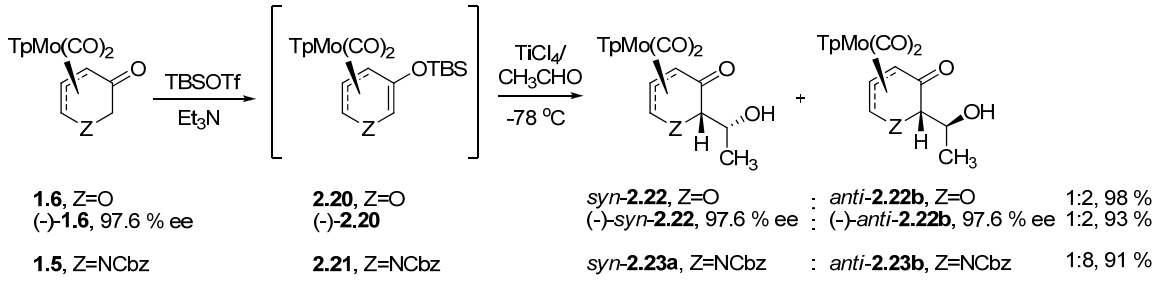
Scheme 2.9. Synthesis of Semipinacol Substrates



Results and Discussion

Conversion of 5-oxo-pyranyl and pyridinyl complexes **1.6** and **1.5** to the corresponding enol silanes **2.20** and **2.21** by treatment with TBSOTf and Et_3N, followed by low-temperature reaction with the $TiCl_4$ complex of acetaldehyde, delivered the desired β-hydroxy ketones **2.22** and **2.23** (Scheme 2.10). While both reactions were *anti*-selective, the selectivity was significantly greater with the pyridinyl complex **1.5** than with pyranyl complex **1.6**. Using enantiomerically-enriched 5-oxo-pyranyl complex (-)-**1.6** (97.6 % ee), the Mukaiyama aldol reaction proceeded with no loss in enantiomeric excess.

Scheme 2.10. Mukaiyama Aldol Reaction of 5-Oxo-pyranyl and Pyridinyl Scaffolds



1.6, Z=O (-)-**1.6**, 97.6 % ee	**2.20**, Z=O (-)-**2.20**	*syn*-**2.22**, Z=O (-)-*syn*-**2.22**, 97.6 % ee	: *anti*-**2.22b**, Z=O : (-)-*anti*-**2.22b**, 97.6 % ee	1:2, 98 % 1:2, 93 %
1.5, Z=NCbz	**2.21**, Z=NCbz	*syn*-**2.23a**, Z=NCbz	: *anti*-**2.23b**, Z=NCbz	1:8, 91 %

Transition state structures leading to both *syn* and *anti* aldol products from enol silanes **2.20** and **2.21** are shown in Figure 2.2. Open transition states are usually invoked to rationalize the stereo-outcome of Mukaiyama aldol reactions due to the bulky nature of the silyl protecting group, which prevents coordination of the Lewis acid.[95] There are three possible transition state structures (**I-III**) leading to *syn* aldol products **L** and three (**IV-VI**) leading to *anti* aldol products **M**. With open models, steric and dipolar effects determine which transition states are favored and which are disfavored. In the present case, transition states **II** and **V** are disfavored for both pyranyl and pyridinyl complexes due to dipolar repulsions between the aligned C-O bonds of both the aldehyde and the silyl enol ether. Transition states **III** and **VI** are also disfavored due to nonbonded interactions between the Lewis acid and the 6-membered ring of the enol silane. Transition state **IV** is favored for both pyranyl and pyridinyl complexes, while transition state **I** is somewhat favored for pyranyl complexes. Steric interactions between the Lewis acid and the Z = Cbz group disfavor transition state **I** in pyridinyl complexes. Thus, the *anti* selectivity observed in both the pyranyl and pyridinyl series may be attributed to the predominance of transition state **IV**. A second transition state (**I**) appears to be somewhat

[95] Mahrwald, R. *Chem. Rev.* **1999**, *99*, 1095-1120.

favored in the pyranyl series, leading to increased quantities of the *syn* compound, and thus, lower *anti*:*syn* selectivity.

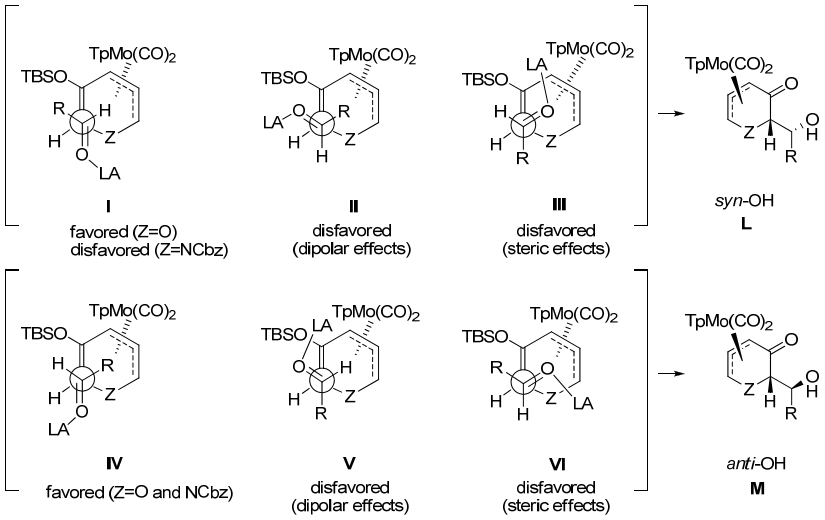


Figure 2.2. Mukaiyama Aldol Transition States

The relative stereochemical assignments of **2.22** and **2.23** were determined by single crystal X-ray diffraction analysis. The structures of *anti*-**2.22** and *anti*-**2.23** are shown in Figures 2.3 and 2.4, respectively.

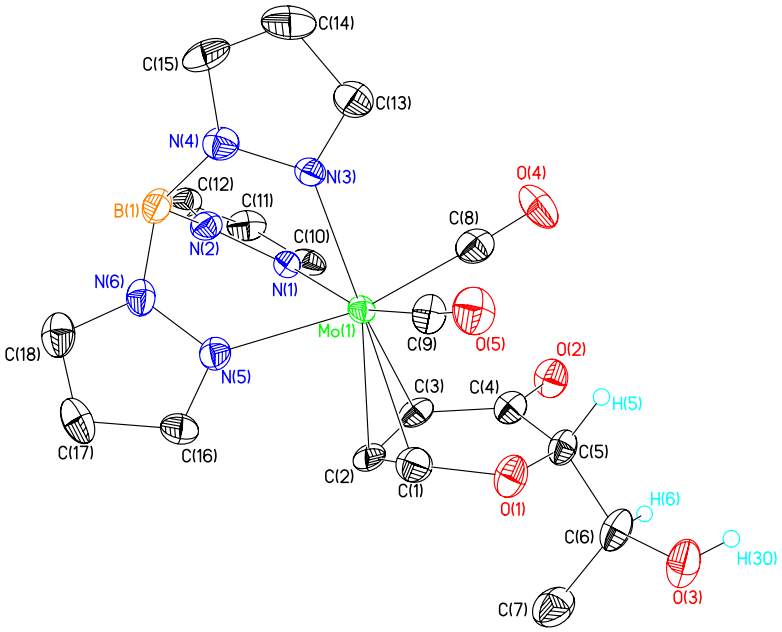


Figure 2.3. ORTEP View of *anti*-2.22

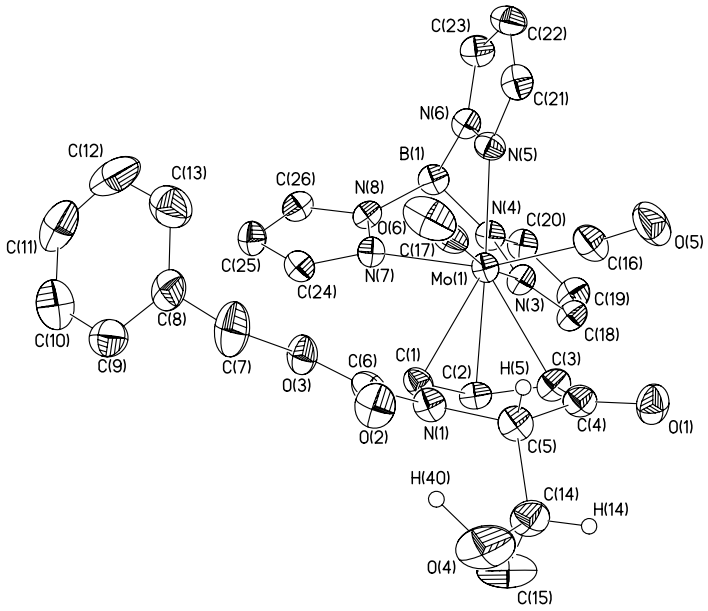
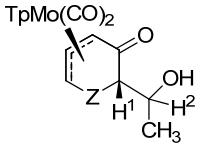


Figure 2.4. ORTEP View of *anti*-2.23

Anti-**2.22** and other pyranyl-derived β-hydroxy ketones exhibit vicinal coupling constants (J_{H1-H2}) in the range of 2.5-3.5 Hz for *syn* isomers and 5.4-6.3 Hz for *anti* isomers (Table 2.1). In contrast, *anti*-**2.23** and other pyridinyl-derived β-hydroxy ketones exhibit larger coupling constants for the *syn* isomers (4.1-5.1 Hz) and smaller coupling constants for the *anti* isomers (2.5-3.3 Hz).

Table 2.1. Vicinal Coupling Constants (J_{H1-H2}, Hz) for *syn* and *anti* Isomers



Z = O, NCbz

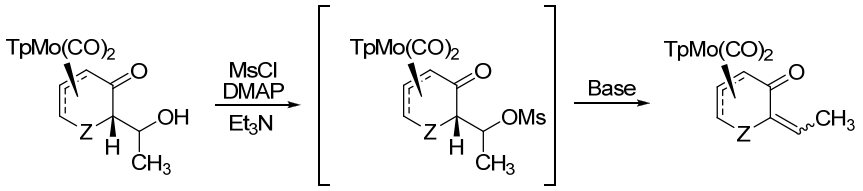
Compound	Z	*Syn* coupling constants *J* (Hz)	*Anti* coupling constants *J* (Hz)
2.22	O	3.2	6.3
2.23	NCbz	5.1, 4.3*	3.3, 2.7*

*The two coupling constants correspond to two different rotamers of **2.23**.

β-Hydroxy ketones **2.22** and **2.23** were converted to the corresponding mesylates **2.24** and **2.25** by treatment with methanesulfonyl chloride, DMAP, and Et_3N. After passing the mesylates through a short pad of silica gel, elimination was effected as shown in Table 2.2. In the pyranyl series, elimination of *syn*-**2.22** could be carried out over 4 days with Et_3N (Entry 1) or in 10 minutes with DBU (Entry 2). The *Z*:*E* ratio in both cases was > 98:2. In the case of *anti*-**2.22**, no elimination was observed after stirring 4 days with Et_3N (Entry 3). However, DBU worked well for this elimination delivering **2.26** in 94 % as a 1:2 (*Z*:*E*) mixture of alkenes after one hour (Entry 4). In the pyridinyl series, *syn*-**2.23** was eliminated with DBU over one hour, delivering **2.27** with a *Z*:*E* ratio of 96:4 (Entry 6). Elimination of *anti*-**2.23** with DBU provided **2.27** as a 10:90 (*Z*:*E*)

mixture of alkenes after 16 hours (Entry 7). Enantioenriched samples of both (-)-*syn*-**2.22** and (-)-*anti*-**2.22** underwent mesylation and elimination with no loss in enantiomeric excess (Entries 2 and 5). However, when an *E*/*Z* mixture of **2.26** (97.6 % ee) was converted to the corresponding silyl enol ether with TBSOTf/Et_3N and then treated with HCl, *Z*-**2.26** was obtained as the sole isomer in a slightly lower 97.1 % ee.

Table 2.2. Dehydration of β-Hydroxy Ketones



2.22, Z=O
2.23, Z=NCbz

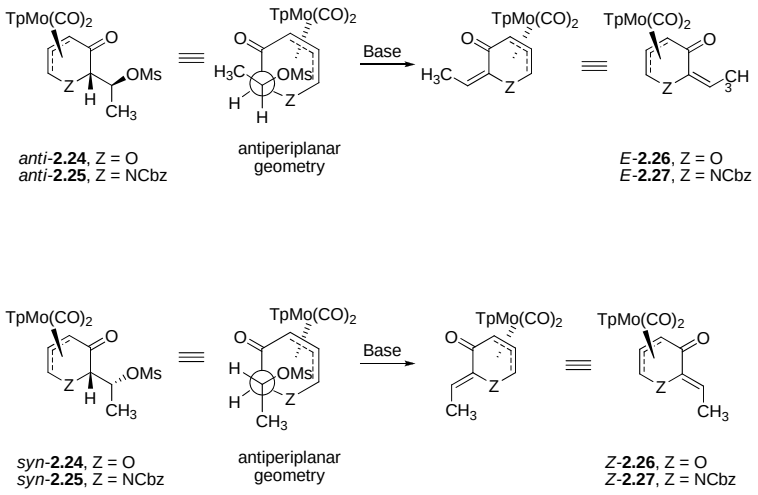
2.24, Z=O
2.25, Z=NCbz

2.26, Z=O
2.27, Z=NCbz

Entry	SM	Z =	Base	Time	Prod	*Z:E*	Yield (%)
1	*syn*-**2.22**	O	Et_3N	4 d	**2.26**	> 98:2	85
2	(-)-*syn*-**2.22** (97.6 % ee)	O	DBU	10 min	(-)-**2.26** (97.6 % ee)	>98:2	80
3	*anti*-**2.22**	O	Et_3N	4 d	**2.26**	NA	--
4	*anti*-**2.22**	O	DBU	1 h	**2.26**	1:2	94
5	(-)-*anti*-**2.22** (97.6 % ee)	O	DBU	1 h	(-)-**2.26** (97.6 % ee)	1:2.2	94
6	*syn*-**2.23**	NCbz	DBU	1 h	**2.27**	96:4	87
7	*anti*-**2.23**	NCbz	DBU	16 h	**2.27**	1:9.6	85

Scheme 2.11 shows the antiperiplanar conformations that must be achieved for E_2 elimations to take place. The higher barrier to elimination of *anti*-**2.22** relative to *syn*-**2.22** is consistent with these conformations: For *anti*-**2.22** to achieve antiperiplanarity to eliminate, the ethyl group must be gauche to the ketone carbonyl, resulting in barrier-raising steric strain. For *syn*-**2.22** to achieve antiperiplanarity, hydrogen is placed gauche to the ketone carbonyl, minimizing non-bonded interactions.

Scheme 2.11. Mesylate Elimination *via* E_2 Pathway



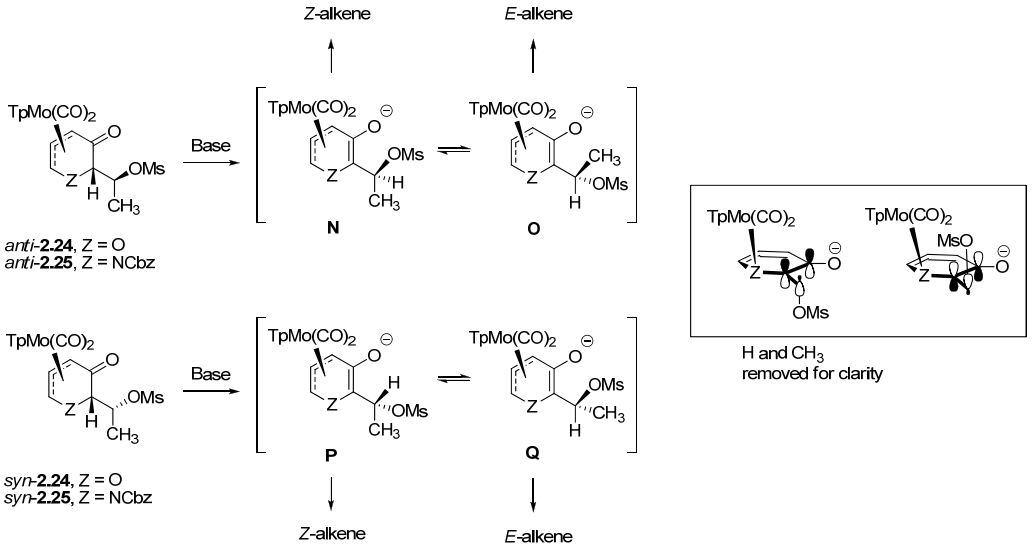
If E_2 elimination was the only reaction leading to product, and if the products didn't equilibrate under the reaction conditions, complete stereospecificity would be expected. *Anti*-mesylates would afford exclusively *E*-alkenes while *syn* mesylates would lead exclusively to *Z*-alkenes. It has been shown that *E*-**2.26** can be converted to *Z*-**2.26** by conversion to the corresponding enol silane and then treatment with acid.[96] However, *E*-**2.26** is stable in solution; even in the presence of DBU, no isomerization to *Z*-**2.26** is observed. Thus, the mixture obtained in the elimination of mesylate **2.24** is not the result of post-elimination isomerization.

A likely explanation is involvement of an E_{1cB} elimination pathway (Scheme 2.12). In this pathway, deprotonation leads to enolate intermediates **N**-**Q**, which then undergo elimination of the mesylate. Product distributions in these reactions would be determined by the conformations of **N**-**Q**. The lowest-energy conformations for

[96] This isomerization was first probed by M. D. Lee, IV: Lee, M. D., IV. Organometallic Scaffolding as a Practical Approach to Diversity-Oriented Synthesis: Stereo- and Regiocontrolled Sequential Functionalization of Pyranylalkylidene Allyl Molybdenum Compleses. Ph.D. Dissertation, Emory University, Atlanta, 2008.

elimination of **2.24** and **2.25** are shown in Scheme 12, in which each has the σ* orbital of the mesylate geometrically aligned with the π-system of the enolate (Scheme 2.12, inset). For each case, two conformations are possible and it is expected that **N** and **P** would be lower-energy conformations than **O** and **Q** as the methyl group is rotated away from the oxygen atom of the enolate in these cases. For *syn* mesylates, this preferred conformer (**P**) leads to the *Z*-alkene, the product that is also expected from E_2 elimination. For *anti* mesylates, the preferred conformer (**N**) again leads to the *Z*-alkene, which is not the product expected from E_2 elimination in this case. Thus, for *anti* mesylates, decreased stereospecificity would be expected as E_2 and E_{1cB} reactions lead to different products.

Scheme 2.12. E_{1cB} Mechanistic Analysis



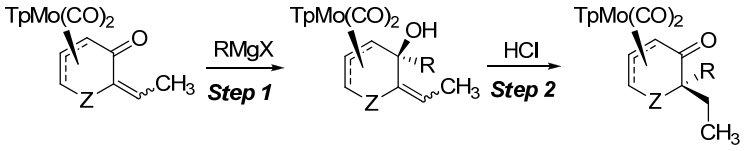
Grignard addition to enones **2.26** and **2.27** occurred in high yields for all substrates investigated (Table 2.3).[97] Semipinacol rearrangement also took place in excellent yields for vinyl, allyl, and phenyl migratory groups at room temperature when a

[97] In the case of vinylMgBr, it was imperative that a new bottle or a freshly-prepared solution be used. Aged solutions of vinylMgBr resulted in messy reactions and almost no desired product. Fresh solutions gave the desired product in a very clean transformation.

full equivalent of HCl (4.0 M in dioxane) was used (entries 1-5). In the pyranyl series, rearrangement occurred in less than 5 minutes, while rearrangement of pyridinyl *E*-**2.29** took place over the course of one hour. Rearrangement of *t*-butyl-substituted complex *Z*-**2.28f** (Entry 8) was sluggish at room temperature, but in refluxing CH_2Cl_2, the reaction occurred in 98 % yield in 10 minutes. Using methyl and isopropyl migratory groups led only to decomposition upon treatment with HCl at room temperature (Entries 6 and 7). Immediate IR analysis of an aliquot of the mixture following HCl addition to *Z*-**2.26** showed a shift of the metal carbonyl stretches to higher wavenumbers. This shift is consistent with formation of a cationic diene and suggests that when semipinacol rearrangement is not facile due to poor substituent migratory ability, ionization of the *syn* hydroxyl group may occur, resulting in cationic diene formation and decomposition.

A representative example using vinylmagnesium bromide showed that both Grignard addition and semipinacol rearrangement occurr with no loss in enantiomeric excess (Entry 2). The relative stereochemistry of **2.30a** was confirmed by single crystal X-ray diffraction (Figure 2.5).

Table 2.3. Grignard Addition and Semipinacol Rearrangement



2.26, Z=O
2.27, Z=NCbz

2.28, Z=O
2.29, Z=NCbz

2.30, Z=O
2.31, Z=NCbz

Entry	Z =	Enone	R =	% Yield (Step 1)	% Yield (Step 2)
1	O	*Z*-**2.26**	$CH{=}CH_2$	98, *Z*-**2.28a**	100, **2.30a**
2	O	*Z*-(-)-**2.26** (97.1 % ee)	$CH{=}CH_2$	81, *Z*-(-)-**2.28a** (97.1 % ee)	99, (-)-**2.30a** (97.1 % ee)
3	O	*Z*-**2.26**	Ph	64, *Z*-**2.28b**	98, **2.30b**
4	O	*Z*-**2.26**	$CH_2CH{=}CH_2$	87, *Z*-**2.28c**	95, **2.30c**
5	O	*E*-**2.26**	$CH_2CH{=}CH_2$	81, *E*-**2.28c**	94, **2.30c**
6	O	*Z*-**2.26**	CH_3	71, *Z*-**2.28d**	Decomp.*
7	O	*Z*-**2.26**	*i*Pr	21, *Z*-**2.28e**	Decomp.
8	O	*Z*-**2.26**	*t*Bu	25, *Z*-**2.28f**	98, **2.30f**
9	NCbz	*Z*-**2.27**	$CH_2CH{=}CH_2$	99, *Z*-**2.29**	Decomp.
10	NCbz	*E*-**2.27**	$CH_2CH{=}CH_2$	99, *E*-**2.29**	96, **2.31**

*Immediate IR analysis of an aliquot of the reaction mixture after HCl addition indicated a shift to higher wavenumbers (cm^{-1}) for the metal carbonyls, consistent with cationic diene formation.

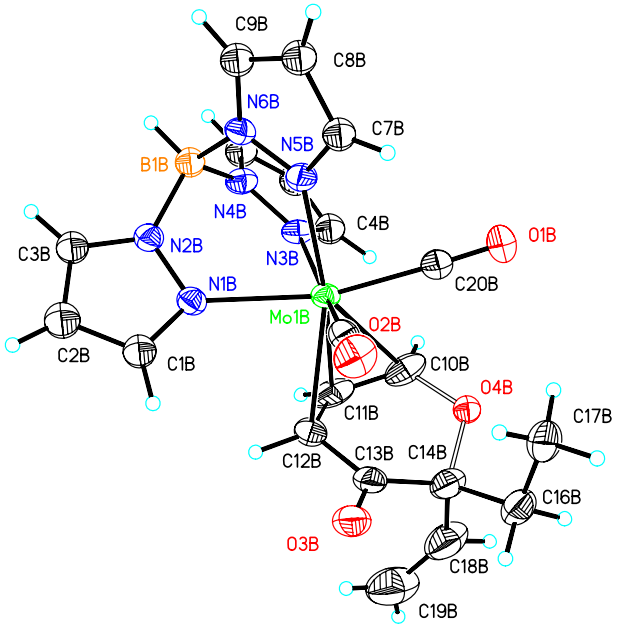
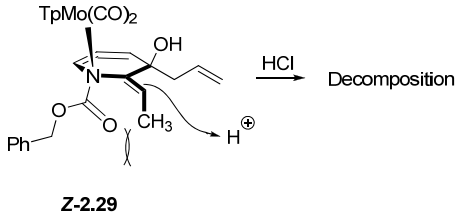


Figure 2.5. ORTEP View of 2.30a

While both *E*- and *Z*-alkenes underwent efficient semipinacol rearrangement in the pyranyl series, only the *E*-alkene rearranged in the pyridinyl series (Table 2.3, Entry 10). The pyridinyl *Z*-alkene *Z*-**2.29** decomposed upon exposure to acid (Table 2.3, Entry 9). Presumably, nonbonded interactions between the Cbz protecting group and the methyl group on the *Z*-alkene during sp^2 to sp^3 rehybridization of the alkene upon protonation with HCl inhibit the semipinacol rearrangement and lead, instead, to decomposition (Figure 2.6).

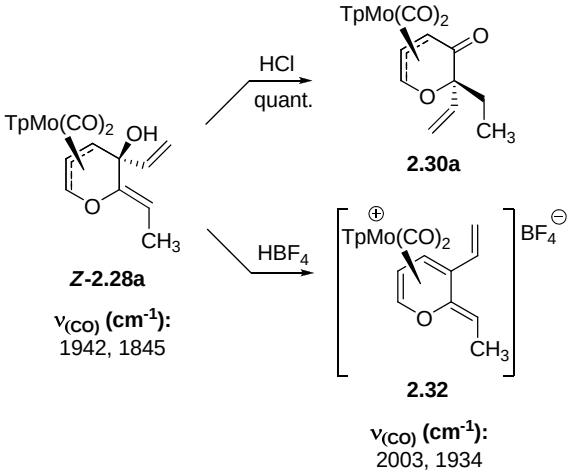


Z-2.29

Figure 2.6. Rearrangement of *Z*-Pyridinyl Allylic Alcohol

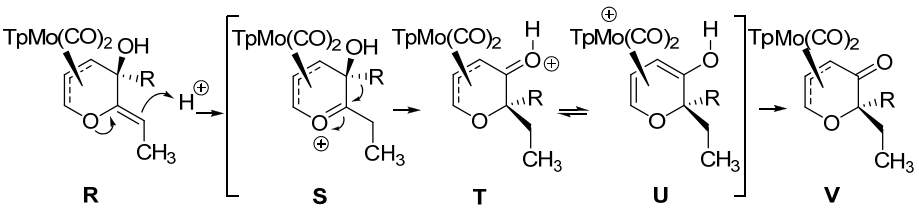
It should be noted that when *Z*-**2.28a** was treated with HBF_4, the corresponding cationic diene **2.32** was formed, resulting from ionization of the *syn* hydroxyl group (Scheme 2.13). This result is in marked contrast to the use of HCl, which delivered α,α'-disubstituted ketone **2.30a** in quantitative yield. Presumably, the non-coordinating BF_4^- counterion stabilized the cationic diene and enabled its formation, while Cl^- could not.

Scheme 2.13. Counterion-Directed Reaction Pathways



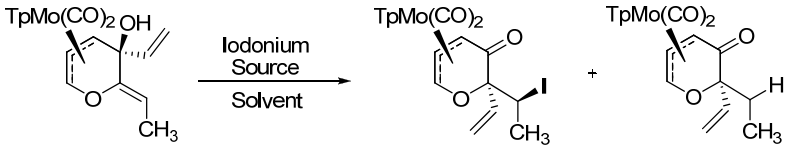
While the semipinacol rearrangement should require only a catalytic quantity of acid to occur, a full equivalent was required to effect this transformation with $TpMo(CO)_2$-based pyranyl and pyridinyl complexes. Therefore, the mechanism of the reaction with these complexes should account for the consumption of a full equivalent of H^+ (Scheme 2.14). Protonation of the exocyclic alkene of **R** generates oxonium intermediate **S**. Migration of the R group delivers **T**, which is in equilibrium with dienyl cation **U**. Thus, one full equivalent of H^+ is trapped. Aqueous work-up affords α,α-disubstituted ketone **V**.

Scheme 2.14. Proposed Mechanism of the Semipinacol Rearrangement



To investigate the diastereoselectivity of incorporating electrophiles other than H^+ to form a new, exocyclic chiral center, halogen cation sources were used to initiate the semipinacol rearrangement. Incorporation of iodine using I_2/$AgOC(O)CF_3$ and NIS gave a single diastereomer **2.33** in each case with good yields if MeCN was used as solvent (Table 2.4; Entries 1,4, and 5). In CH_2Cl_2 and THF, a single diastereomer **2.33** was again formed. However, significant quantities of **2.30a**, the product of H^+-induced semipinacol rearrangement were also isolated using these reaction solvents, even when recrystallized NIS was used in the reaction. Yields were also much lower in these solvents, due to significant decomposition. The relative stereochemistry of the new, exocyclic stereocenter was confirmed by single crystal X-ray diffraction (Figure 2.7), and this outcome is rationalized below (Scheme 2.15).

Table 2.4. Iodonium-induced Semipinacol Rearrangement



***Z*-2.28a** **2.33** **2.30a**

Entry	Electrophile	Solvent	Temp (^{o}C)	Ratio of 2.33 : 2.30a	Yield (%)
1	NIS	MeCN	23	1 : 0	76
2	NIS	CH_2Cl_2	23	1.0 : 1.5	32
3	NIS	THF	23	1.0 : 2.4	31
4	I_2/$AgOC(O)CF_3$	MeCN	23	1 : 0	87
5	I_2/$AgOC(O)CF_3$	MeCN	-40	1 : 0	70
6	I_2/$AgOC(O)CF_3$	CH_2Cl_2	23	1.0 : 3.4	45
7	I_2/$AgOC(O)CF_3$	THF	23	1.8 : 1.0	54

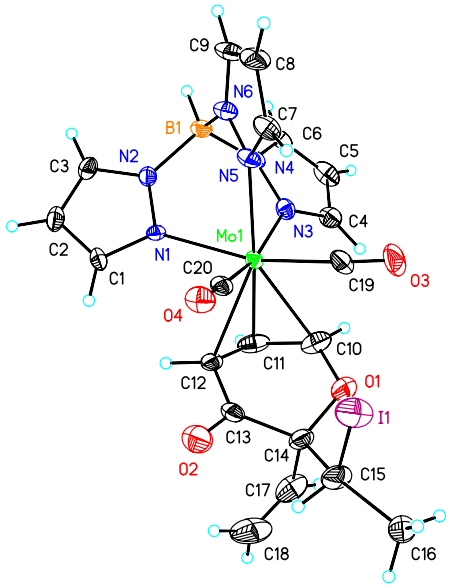
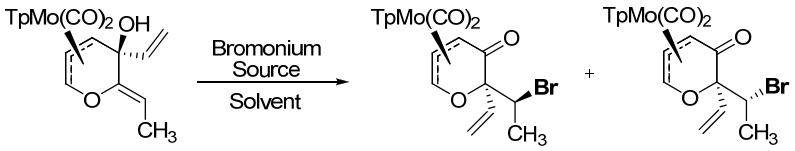


Figure 2.7. ORTEP View of 2.33

Incorporation of bromine using recrystallized NBS and unpurified hydantoin produced a mixture of diastereomers **2.34a** and **2.34b** in all solvents investigated (Table 2.5). At room temperature (23 ^{o}C), the best **2.34a** : **2.34b** ratios were obtained in CH_2Cl_2 (Entry 3) and $CHCl_3$ (Entry 5). In MeCN, a temperature effect was noted as the diastereomeric ratio improved from 1.2 : 1.0 at 23 ^{o}C to 3.4 : 1.0 at -40 ^{o}C (Entries 1 and 2). Surprisingly, however, no enhancement of selectivity was observed in CH_2Cl_2 when the reaction was performed at -78 ^{o}C (Entries 3 and 4). The relative configurations of both the major diastereomer **2.34a** (Figure 2.8) and the minor diastereomer **2.34b** (Figure 2.9) were determined by single crystal X-ray diffraction. The major diastereomer **2.34a** had the same relative configuration as that of the sole diastereomer **2.33** formed in the iodonium-induced semipinacol rearrangements described in Table 2.4, above. Using 1,3-dibromo-5,5-dimethylhydantoin in MeCN gave a 1.2 : 1.0 mixture of diastereomers

(Entry 7). The low yield in this case may be attributed to the observation of significant decomposition.

Table 2.5. Bromonium-induced Semipinacol Rearrangement



Z-**2.28a** **2.34a** **2.34b**

Entry	Electrophile	Solvent	Temp (^{o}C)	Ratio of 2.34a : 2.34b	Yield (%)
1	NBS	MeCN	23	1.2 : 1.0	91
2	NBS	MeCN	-40	3.4 : 1.0	86
3	NBS	CH_2Cl_2	23	5.4 : 1.0	71
4	NBS	CH_2Cl_2	-78	5.3 : 1.0	84
5	NBS	$CHCl_3$	23	4.0 : 1.0	79
6	NBS	THF	23	1.6 : 1.0	76
7	Hydantoin	MeCN	23	1.2 : 1.0	40

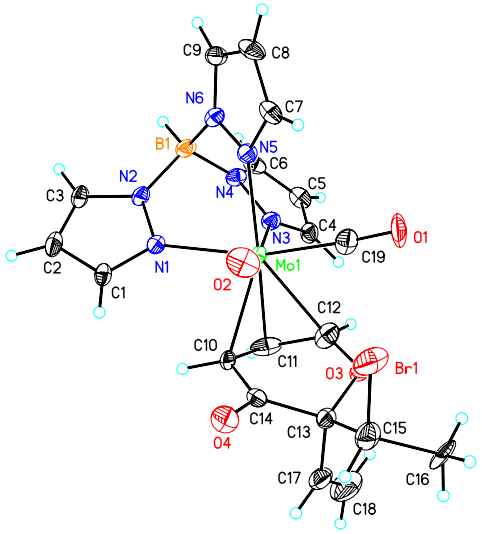


Figure 2.8. ORTEP View of 2.34a

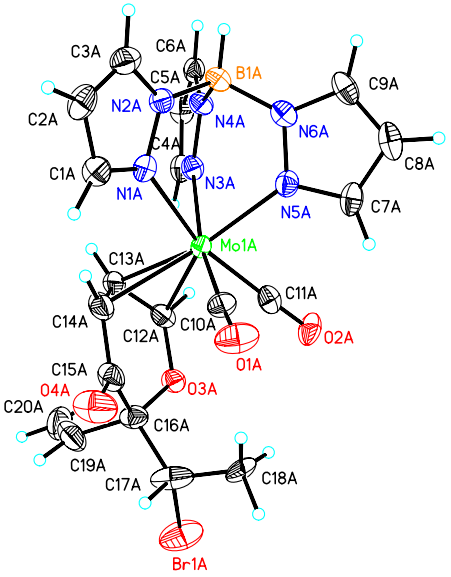
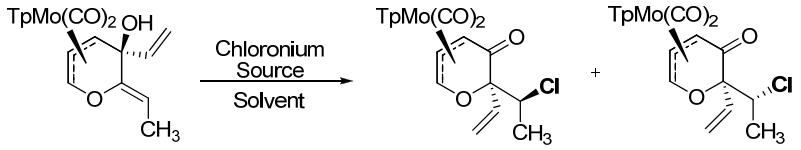


Figure 2.9. ORTEP View of 2.34b

To probe chlorine incorporation, NCS was first investigated as the halogen source. However with NCS in MeCN at room temperature (Table 2.6, Entry 1), the rearrangement proceeded very slowly, affording the desired compound as a single diastereomer in 19 % yield. Prolonged reaction times led to significant decomposition. Performing the reaction in refluxing MeCN (Entry 2) led to a slight, but still unsatisfactory, improvement in yield. Switching to *t*BuOCl, the reaction proceeded in good to excellent yields at room temperature in less than 5 minutes. However, a mixture of two diastereomers was observed in all solvents investigated. The best **2.35a** : **2.35b** ratio was observed in CH_2Cl_2 (Entry 5), in accordance with the results obtained using NBS. A temperature effect was also again observed in MeCN as noted by the improvement in diastereomeric ratio from 1.2 : 1.0 at 23 ^{o}C to 3.4 : 1.0 at -40 ^{o}C. The correspondence of spectral data and polarity between the more-polar major chlorine-containing diastereomer **2.35a** and the more-polar major bromine-containing

diastereomer **2.34a** support the stereochemical assigments shown in Table 6. A similar correspondence exists for the less-polar minor diastereomers **2.35a** and **2.34a**. Thus for all three halogens, despite the identity of the reagent, the major diastereomers result from halogen incorporation *syn* the $TpMo(CO)_2$ fragment.

Table 2.6. Chloronium-induced Semipinacol Rearrangement



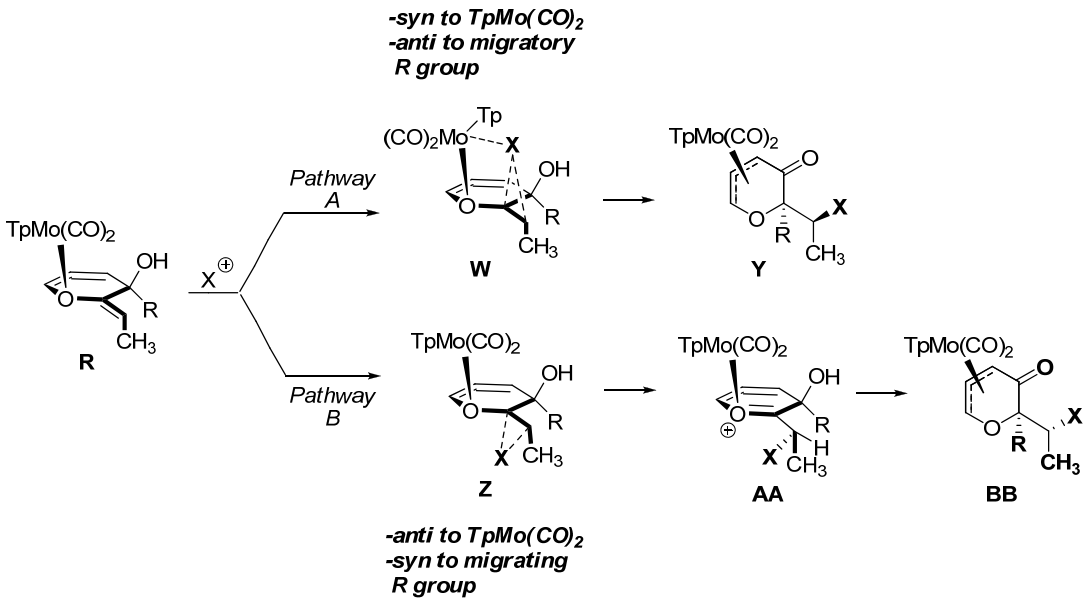
Z-**2.28a** **2.35a** **2.35b**

Entry	Electrophile	Solvent	Temp (^oC)	Ratio of 2.35a : 2.35b	Yield (%)
1	NCS	MeCN	23	1 : 0	19
2	NCS	MeCN	82	1 : 0	33
3	*t*BuOCl	MeCN	23	1.1 : 1.0	80
4	*t*BuOCl	MeCN	-40	2.4 : 1.0	94
5	*t*BuOCl	CH_2Cl_2	23	7.9 : 1.0	72
6	*t*BuOCl	THF	23	1.0 : 1.0	53

Stereoelectronically, initiation of the semipinacol rearrangement from the face of the alkene opposite the migrating R group is favored as it allows the R group to begin migrating while the new bond to the electrophile forms. In the case of $TpMo(CO)_2$ pyranyl complexes, this requires the electrophile to approach the alkene from the face of the pyran *syn* to the $TpMo(CO)_2$ moiety (Scheme 2.15, Pathway A). Alternatively, the electrophile may approach the alkene from the less-hindered face *anti* to the $TpMo(CO)_2$ moiety (Pathway B). However, in this case the reaction is likely step-wise, proceeding through oxonium intermediate **AA** to minimize nonbonded interactions that would build up if the R group began to migrate as the electrophile initiated bond formation with the

alkene. The observation of increased quantities of the **2.34a** and **2.35a**, the diastereomers resulting from Pathway B, in polar solvents (MeCN and THF) is consistent with the ability of such solvents to stabilize charged intermediate **AA**. That a single diastereomer is formed with iodonium ion sources is consistent with the decreased reactivity and increased selectivity associated with this larger, softer, less-electronegative cation relative to bromonium and chloronium sources. The improvements in diastereomeric ratio observed at lower temperatures in MeCN for bromonium and chloronium ion sources are also consistent with a temperature-mediated attenuation of their reactivity, allowing greater selectivity over the course of the reaction.

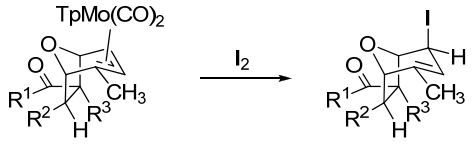
Scheme 2.15. Stereoelectronic Considerations for Semipinacol Rearrangement



Precedent for oxidative addition of a halogen cation to the $TpMo(CO)_2$ moiety, followed by *syn* delivery to a complexed ligand is highlighted in Scheme 2.16: Yin and Liebeskind showed that bicyclic complex **2.36** underwent demetalation with I_2, affording

2.37 in which the iodide had been delivered to the face of the bicycle previously occupied by the metal.[98]

Scheme 2.16. Precedent for *syn* Delivery of Halogens



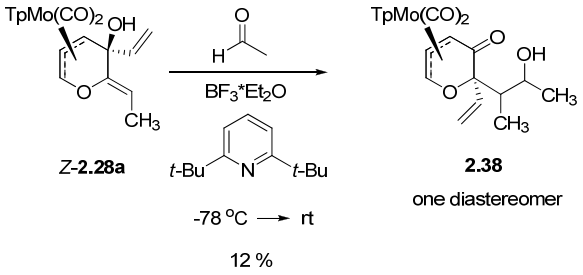
2.36 **2.37**

Attempts to epoxidize the enol ether alkene and induce an epoxide-opening semipinacol rearrangement were unsuccessful with both purified *m*-CPBA and dimethyl dioxirane (DMDO). Stirring allylic alcohol *Z*-**2.28a** with *m*-CPBA in CH_2Cl_2 at room temperature and reflux resulted in no reaction. Only slight decomposition was noted. Reaction with DMDO led only to decomposition at room temperature.

A tandem pinacol-terminated Mukaiyama aldol reaction was also investigated as shown in Scheme 2.17. Addition of complex *Z*-**2.28a** to a low-temperature solution of acetaldehyde and BF_3-OEt_2 in the presence of 2,6-di-*t*-butylpyridine (DTBP) led to 12 % of a single diastereomer **2.38**, whose relative configuration was not determined. The yield of this transformation could not be improved despite extensive optimization efforts in which temperature, order of addition, Lewis acid and aldehyde identity, reagent stoichiometry, and reaction time were explored.

[98] Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1999**, *121*, 5811-5812.

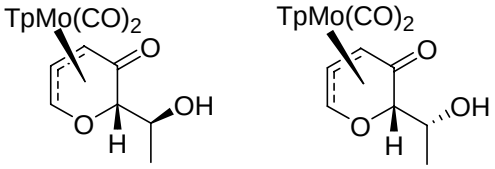
Scheme 2.17. Tandem Pinacol-terminated Mukaiyama Aldol Reaction



In conclusion, a new variant of the semipinacol rearrangement has been developed utilizing allylic alcohols available in three steps from 5-oxo-η^3-allylmolybdenum pyranyl and pyridinyl organometallic enantiomeric scaffolds **1.6** and **1.5**. The protic acid-induced semipinacol rearrangement itself occurs with complete diastereoselectivity under mild conditions and requires a full equivalent of HCl. Off-ring stereocenters were efficiently generated using electrophilic halogen sources to initiate the rearrangement. The major diastereomer in each case resulted from addition to the alkene *syn* to the $TpMo(CO)_2$ fragment, suggesting participation of the metal in this rearrangment. Solvent choice was especially important in these reactions to achieve synthetically-useful diastereoselectivities at the off-ring site. Further work is required to determine if the metal plays any role in delivery of H^+. Studies carried out with enantiomerically-enriched (-)-**1.6** indicated retention of enantiopurity over the entire synthetic sequence through the semipinacol rearrangement.

Experimental Section:

General Methods: Refer to Chapter One.



anti *syn*

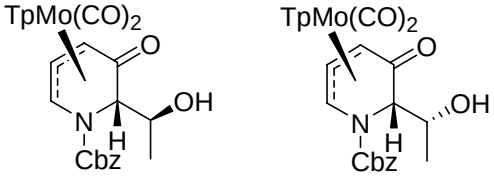
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.22; and (-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)-2.22. To solution of (±)-**1.6** (3.00 g, 6.6 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL) was successively added Et_3N (1.06 mL, 7.6 mmol, 1.15 equiv) and TBSOTf (1.74 mL, 7.6 mmol, 1.15 equiv). The reaction mixture was stirred for 1 h at room temperature, and then cooled –78 ºC. To this mixture was slowly added a low-temperature (–78 ºC) premixed solution of acetaldehyde (378 mg, 8.56 mmol, 1.3 equiv) and $TiCl_4$ (1.0 M in CH_2Cl_2, 8.56 mL, 8.56 mmol, 1.3 equiv) in CH_2Cl_2 (20 mL) *via* syringe. The mixture was stirred for 10 minutes at –78 ºC and then quenched with 5 mL of water. The cold bath was removed, and the reaction mixture was allowed to warm to room temperature before it was transferred to a separatory funnel containing CH_2Cl_2 (60 mL) and water (100 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (40 mL). The combined organic phases were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated. The resultant solid product was washed with CH_2Cl_2 (20 mL × 2) and a 1:1 mixture of CH_2Cl_2 and hexanes (20 mL × 3) to afford pure (±)-*anti*-**2.22** (2.12 g, 4.19 mmol, 65%) as a yellow solid. The filtrates

were combined, concentrated, and subjected to flash chromatography over silica gel with hexanes-EtOAc (1:1) to give pure (±)-*syn*-**2.22** (1.08 g, 2.13 mmol, 33%) as a yellow solid.

Similar treatment of (-)-**1.6** (500 mg, 1.08 mmol, 1.0 equiv, 97.6 %ee) in CH_2Cl_2 (7 mL) with Et_3N (173 μL, 1.24 mmol, 1.15 equiv), and TBSOTf (286 μL, 1.24 mmol, 1.15 equiv), and then with $TiCl_4$ (1.0 M in CH_2Cl_2, 1.41 mL, 1.41 mmol, 1.3 equiv) and acetaldehyde (97 μL, 1.73 mmol, 1.6 equiv) in CH_2Cl_2 (2 mL), afforded (-)-*anti*-**2.22** (345 mg, 0.68 mmol, 63 %, 97.6 %ee) [$[\alpha]_D^{25}$ -490 (*c* 0.22, CH_2Cl_2)], and (-)-*syn*-**2.22** (164 mg, 0.32 mmol, 30 %, 97.6 %ee) [$[\alpha]_D^{25}$ -514 (*c* 0.26, CH_2Cl_2)].

(±)-*Anti*-**2.22**: TLC: R_f = 0.39 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3401 (w), 3127 (w), 2980 (w), 2934 (w), 2899(w), 2486 (w), 1961 (s), 1872 (s), 1640 (m), 1505 (w), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 2.0 Hz, 1 H), 7.89 (d, *J* = 2.0 Hz, 1 H), 7.65 (d, *J* = 2.0 Hz, 1 H), 7.62 (d, *J* = 2.4 Hz, 1 H), 7.60 (d, *J* = 2.0 Hz, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 7.39 (dd, *J* = 4.8 Hz, 2.4 Hz, 1 H), 6.30 (t, *J* = 2.0 Hz, 1 H), 6.26 (t, *J* = 2.4 Hz, 1 H), 6.21 (t, *J* = 2.0 Hz, 1 H), 4.78 (dd, *J* = 6.4 Hz, 2.0 Hz, 1 H), 4.19 (dd, *J* = 6.4 Hz, 4.8 Hz, 1 H), 3.95 (app pent, *J* = 6.4 Hz, 1 H), 3.27 (d, *J* = 6.0 Hz, 1 H), 3.15 (br s, 1 H), 1.22 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 224.5, 223.6, 195.0, 147.6, 143.9, 141.7, 136.6 (2), 134.9, 107.4, 106.6, 106.3, 106.0, 78.9, 69.5, 68.8, 65.0, 18.6. Anal. Calcd for $C_{18}H_{19}BMoN_6O_5$: C, 42.72; H, 3.78; N, 16.60. Found: C, 42.32; H, 3.81; N, 16.17. HPLC: Daicel® Chiralpak AS-RH column, Isocratic solvent system: 65 % CH_3CN in H_2O, 1.0 mL/min, λ = 254 nm, (-)-*anti*-**2.22**: $t_{(-)}$ = 22.29 min; (+)-*anti*-**2.22**: $t_{(+)}$ = 15.30 min.

(±)-*Syn*-**2.22**: TLC: R_f = 0.31 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3405 (w), 3127 (w), 2976 (w), 2934 (w), 2490 (w), 1961 (s), 1872 (s), 1644 (m), 1505 (m), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 1.9 Hz, 1 H), 7.90 (d, *J* = 1.6 Hz, 1 H), 7.66 (d, *J* = 1.6 Hz, 1 H), 7.62 (d, *J* = 2.0 Hz, 1 H), 7.59 (d, *J* = 2.0 Hz, 1 H), 7.51 (d, *J* = 1.6 Hz, 1 H), 7.43 (dd, *J* = 4.8 Hz, 2.0 Hz, 1 H), 6.33 (t, *J* = 2.2 Hz, 1 H), 6.28 (t, *J* = 2.2 Hz, 1 H), 6.23 (t, *J* = 2.2 Hz, 1 H), 4.84 (dd, *J* = 6.4 Hz, 2.0 Hz, 1 H), 4.20 (t, *J* = 6.0 Hz, 1 H), 4.10-4.15 (m, 1 H), 3.29 (d, *J* = 2.8 Hz, 1 H), 2.67 (br s, 1 H), 1.23 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.8, 223.8, 194.9, 147.4, 143.8, 141.7, 136.5(2), 134.9, 108.1, 106.4, 106.2, 105.9, 78.9, 70.3, 68.6, 65.0, 19.1. Anal. Calcd for $C_{18}H_{19}BMoN_6O_5$: C, 42.72; H, 3.78; N, 16.60. Found: C, 43.01; H, 3.94; N, 16.34. HPLC: Daicel® Chiralpak AS-RH column, isocratic solvent system: 60 % CH_3CN in H_2O (without TFA), 1.0 mL/min., λ = 254 nm, (-)-*syn*-**2.22**: $t_{(-)}$ = 15.60 min; (+)-*syn*-**2.22**: $t_{(+)}$ = 11.96 min.



anti *syn*

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-1-(benzyloxycarbonyl)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-2.23. To a Schlenk flask charged with a solution of (±)-**1.5** (1.0 g, 1.68 mmol, 1.0 equiv) in CH_2Cl_2 (16 mL) was successively added Et_3N (269 μL, 1.93 mmol, 1.15 equiv) and TBSOTf (424 μL, 1.85 mmol, 1.1 equiv). The reaction mixture

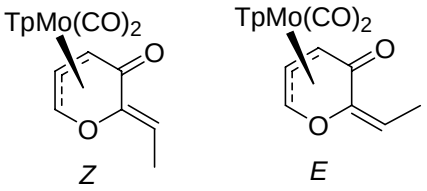
was stirred for 20 minutes at room temperature, and was cooled down to –78 ºC. To this mixture was slowly added a low-temperature (–78 ºC) premixed solution of acetaldehyde (103.6 mg, 2.35 mmol, 1.4 equiv) and $TiCl_4$ (1.0 M in CH_2Cl_2, 2.18 mL, 2.18 mmol, 1.3 equiv) in CH_2Cl_2 (10 mL) *via* syringe. The mixture was stirred for 10 minutes at –78 ºC and then quenched with 1 mL of water. The cold bath was removed, and the reaction mixture was warmed to room temperature. The solution was poured into a separatory funnel containing CH_2Cl_2 (30 mL) and water (30 mL), and the layers were separated. The organic layer was washed with water (2 × 20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (1:1). The first yellow band gave recovered starting material (75 mg, 0.12 mmol, 8 %), and the second yellow band afforded (±)-*syn*-**2.23** (105 mg, 0.16 mmol, 10 %) as a yellow solid after solvent removal. The third yellow band afforded (±)-*anti*-**2.23** (872 mg, 1.36 mmol, 81 %) as a yellow solid after solvent removal.

(±)-*Anti*-**2.23**: TLC: R_f = 0.30 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3443 (w), 3123 (w), 2978 (w), 2490 (w), 1969 (s), 1864 (s), 1702 (m), 1664 (m), 1505 (m), 1409 (m), 1305 (s), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (a mixture of two rotamers) 8.59 (d, *J* = 2.1 Hz, 0.3 H), 8.42 (d, *J* = 3.0 Hz, 0.7 H), 8.38 (d, *J* = 1.8 Hz, 0.4 H), 7.68 (d, *J* = 2.1 Hz, 1 H), 7.65 (d, *J* = 2.1 Hz, 1.0 H), 7.65-7.60 (m, 2 H), 7.58 (d, *J* = 2.4 Hz, 0.8 H), 7.52-7.34 (m, 7.5 H), 7.15 (dd, *J* = 1.8, 6.3 Hz, 0.8 H), 6.27-6.31 (m, 1.5 H), 6.22-6.20 (m, 1.2 H), 5.76 (t, *J* = 2.4 Hz, 0.7 H), 5.27 (AB quartet, *J* = 11.1 Hz, 1.4 H), 5.20 (AB quartet, *J* = 11.8 Hz, 0.6 H), 4.81 (dd, *J* = 5.8 Hz, 1.5 Hz, 0.3 H), 4.76 (dd, *J* = 6.0 Hz, 1.8 Hz, 1 H), 4.30-4.27 (m, 1 H), 4.06 (t, *J* = 6.3 Hz, 0.6 H), 3.92 (t, *J* =

6.3 Hz, 0.8 H), 3.90 (d, *J* = 3.3 Hz, 0.8 H), 3.62 (d, *J* = 2.7 Hz, 0.6 H), 1.30 (t, *J* = 6.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 225.5, 224.9, 222.7, 221.6, 195.4, 195.3 156.2, 147.6, 147.5, 146.2, 144.7, 140.6, 136.7, 136.6, 136.5, 135.1, 134.9, 129.9, 129.1, 129.1, 128.9, 128.7, 128.5, 128.3, 99.6, 96.1, 71.7, 71.2, 70.1, 68.9, 66.1, 64.8, 63.3, 60.6, 60.5, 59.7, 19.7, 18.9, 14.4. Anal. Calcd for $C_{26}H_{26}BMoN_7O_6$: C, 48.85; H, 4.10; N, 15.34. Found: C, 48.21; H, 4.08; N, 15.12. HRMS (ESI) Calcd for $C_{26}H_{26}BMoN_7O_6$ ($[M]^+$): 641.1092. Found: 641.1091.

(±)-*Syn*-**2.23**: TLC: R_f = 0.36 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3459 (w), 3123 (w), 2976 (w), 2486 (w), 1969 (s), 1864 (s), 1706 (m), 1664 (m), 1505 (w), 1409 (m), 1305 (s), 1220 (m), 1123 (m), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$) (a mixture of two rotamers): δ 8.54 (d, *J* = 1.9 Hz, 0.5 H), 8.43 (d, *J* = 2.4 Hz, 0.5 H), 8.38 (d, *J* = 2.4 Hz, 0.5 H), 7.71 (d, *J* = 1.9 Hz, 0.5 H), 7.68 (d, *J* = 1.9 Hz, 0.5 H), 7.64-7.65 (m, 1 H), 7.63 (d, *J* = 2.4 Hz, 0.5 H), 7.59 (d, *J* = 2.4 Hz, 0.5 H), 7.54 (d, *J* = 1.9 Hz, 0.5 H), 7.52 (d, *J* = 2.4 Hz, 0.5 H), 7.49-7.50 (m, 1.5 H), 7.42-7.43 (m, 2 H), 7.32-7.36 (m, 0.5 H), 7.18 (dd, *J* = 6.9 Hz, 1.5 Hz, 0.5 H), 6.29-6.30 (m, 1 H), 6.28 (t, *J* = 2.4 Hz, 0.5 H), 6.24 (t, *J* = 1.9 Hz, 0.5 H), 6.22 (t, *J* = 2.4 Hz, 0.5 H), 5.82 (t, *J* = 1.9 Hz, 0.5 H), 5.26 (AB quartet, *J* = 11.9 Hz, 1 H), 5.25 (AB quartet, *J* = 11.4 Hz, 1 H), 4.82 (dd, *J* = 6.2 Hz, 1.9 Hz, 0.5 H), 4.79 (dd, *J* = 6.2 Hz, 1.9 Hz, 0.5 H), 4.17-4.26 (m, 1 H), 4.07 (t, *J* = 6.2 Hz, 0.5 H), 3.95 (t, *J* = 6.2 Hz, 0.5 H), 3.76 (d, *J* = 4.8 Hz, 0.5 H), 3.68 (d, *J* = 4.3 Hz, 0.5 H), 3.27 (br s, 1 H), 1.26 (d, *J* = 6.6 Hz, 1 H), 1.21 (d, *J* = 6.2 Hz, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 225.5, 224.9, 222.8, 221.6, 198.0, 197.7, 155.2, 154.5, 147.6, 147.5, 146.1, 144.5, 140.9, 140.6, 136.8, 136.7, 136.54, 136.47, 135.5, 135.2, 135.1, 129.8, 129.0, 128.8, 128.6, 128.3, 106.53, 106.50, 106.12, 106.09, 106.06, 99.2, 95.8, 69.7, 69.0, 68.9, 68.6, 65.7,

64.9, 61.8, 61.6, 61.1, 60.2, 19.6, 19.0. HRMS (ESI) Calcd for $C_{26}H_{26}BMoN_7O_6$ ($[M]^+$): 641.1092. Found: 641.1096.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-6-ethylene-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.26; and (-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-6-ethylene-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)-2.26.

There are two different methods to perform mesylation-elimination reactions:

To a solution of (±)-*syn*-**2.22** (55 mg, 0.11 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added DMAP (6.7 mg, 0.055 mmol, 0.5 equiv), Et_3N (100 μL, 0.715 mmol, 6.5 equiv), and methanesulfonyl chloride (11.3 μL, 0.14 mmol, 1.3 equiv). The reaction mixture was stirred 4 days at room temperature and then concentrated under reduced pressure. The crude reaction mixture was subjected to flash chromatography over silica gel with hexanes-EtOAc (7:3), affording the major isomer *Z*-(±)-**2.26** (45 mg, 0.092 mmol, 85%) and the minor isomer *E*-(±)-**2.26** (less than 1 mg) as yellow solids.

To a solution of (±)-*anti*-**2.22** (205 mg, 0.41 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) was added DMAP (24.6 mg, 0.20 mmol, 0.5 equiv), Et_3N (85 μL, 0.61 mmol, 1.5 equiv), and methanesulfonyl chloride (42.6 μL, 0.53 mmol, 1.3 equiv). The reaction mixture was stirred 10 minutes at room temperature and then passed through a short pad of silica gel (50% EtOAc in hexanes). The solvents were completely removed on a rotary evaporator,

and the residue was dissolved in CH_2Cl_2 (15 mL). The solution was cooled to 0 ºC and DBU (91 μL, 0.61 mmol, 1.5 equiv) was slowly added *via* syringe. The reaction mixture was stirred for 1 hour at room temperature and then passed through a short pad of silica gel and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (7:3) afforded the major isomer *E*-(±)-**2.26** (125 mg, 0.26 mmol, 63%) and the minor isomer *Z*-(±)-**2.26** (61 mg, 0.12 mmol, 31%), both as yellow solids.

Similar treatment of (-)-*anti*-**2.22** (600 mg, 1.18 mmol, 1.0 equiv, 97.6 %ee) in CH_2Cl_2 (7.6 mL) and DMAP (0.014 mg, 0.12 mmol, 0.1 equiv), Et_3N (246 μL, 1.77 mmol, 1.5 equiv), and methanesulfonyl chloride (149 μL, 1.53 mmol, 1.3 equiv) and then with DBU (352 μL, 2.35 mmol, 2.0 equiv) in CH_2Cl_2 (7.6 mL) afforded the major isomer *E*-(-)-**2.26** (376 mg, 0.77 mmol, 65%, 97.6 %ee) $[[\alpha]_D^{25}$ -513 (*c* 0.13, $CH_2Cl_2)]$ and the minor isomer *Z*-(-)-**2.26** (168 mg, 0.34 mmol, 29 %, 97.6 %ee) $[[\alpha]_D^{25}$ -267 (*c* 0.19, $CH_2Cl_2)]$.

Similar treatment of (-)-*syn*-**2.22** (200 mg, 0.40 mmol, 1.0 equiv, 97.6 %ee) in CH_2Cl_2 (2.5 mL) and DMAP (4 mg, 0.04 mmol, 0.1 equiv), Et_3N (83 μL, 0.60 mmol, 1.5 equiv), and methanesulfonyl chloride (50 μL, 0.51 mmol, 1.3 equiv) and then with DBU (0.12 mL, 0.79 mmol, 2.0 equiv) in CH_2Cl_2 (2.5 mL) afforded *Z*-(-)-**2.26** (462 mg, 0.94 mmol, 80%, 97.6 %ee). No *E*-(-)-**2.26** was detectable by ^1H NMR.

*Procedure for converting mixtures of E-(-)-**2.26** /Z-(-)-**2.26** to Z-(-)-**2.26**:*

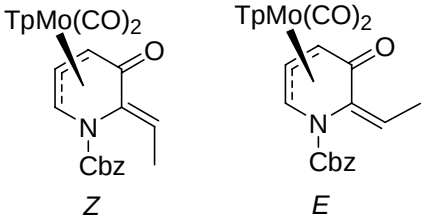
To a 1:1 mixture of *E*-(-)-**2.26** /*Z*-(-)-**2.26** (0.285 g, 0.58 mmol, 1.0 equiv, 97.6 %ee) in dry dichloromethane (5.6 mL) was added Et_3N (94 μL, 0.67 mmol, 1.15 equiv) followed by TBSOTf (154 μL, 0.67 mmol, 1.15 equiv). After 10 minutes at 23 °C, the

reaction mixture was quenched with water (2 mL). After extraction with dichloromethane, the organic layer was cooled to 0 °C and HCl (4.0 M in dioxane, 29 μL, 0.12 mmol, 0.2 equiv) was added. After 5 minutes, volatiles were removed under vacuum. The crude product was purified by silica gel chromatography using hexanes-EtOAc (1:1) to afford *Z*-**(-)-2.26** (0.23 g, 82%, 97.1 %ee) as a yellow solid.

E-(±)-**2.26**: TLC: R_f = 0.57 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3138 (w), 2926 (w), 2494 (w), 1965 (s), 1876 (s), 1660 (m), 1610 (s), 1505 (m), 1409 (m), 1351 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.48 (d, *J* = 1.8 Hz, 1 H), 7.93 (d, *J* = 2.4 Hz, 1 H), 7.65 (d, *J* = 2.4 Hz, 1 H), 7.61 (d, *J* = 2.4 Hz, 1 H), 7.59 (d, *J* = 2.4 Hz, 1 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 7.23 (dd, *J* = 4.8 Hz, 2.4 Hz, 1 H), 6.29 (t, *J* = 2.4 Hz, 1 H), 6.25 (t, *J* = 1.8 Hz, 1 H), 6.21 (t, *J* = 2.4 Hz, 1 H), 5.51 (q, *J* = 7.8 Hz, 1 H), 4.85 (dd, *J* = 6.0 Hz, 2.4 Hz, 1 H), 4.15 (dd, *J* = 6.0 Hz, 4.8 Hz, 1 H), 2.02 (d, *J* = 7.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 224.7, 223.4, 184.0, 147.4, 143.8, 142.8, 141.7, 136.5, 136.4, 134.9, 117.5, 106.5, 106.2, 105.9, 104.9, 73.2, 65.2, 13.2. HRMS (ESI) Calcd for $C_{18}H_{17}BMoN_6O_4$ ($[M]^+$): 490.0458. Found: 490.0475. HPLC: Daicel® Chiralpak AS-RH column, isocratic solvent system: 55 % CH_3CN in H_2O (+ 0.1 % TFA), 1.0 mL/min, λ = 254 nm, *E*-(-)-**2.26**: $t_{(-)}$ = 8.94 min; *E*-(+)-**2.26**: $t_{(+)}$ = 7.43 min.

Z-(±)-**2.26**: TLC: R_f = 0.49 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3127 (w), 2918 (w), 2490 (m), 1965 (s), 1880 (s), 1671 (m), 1617 (s), 1505 (m), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 1.6 Hz, 1 H), 7.90 (d, *J* = 2.0 Hz, 1 H), 7.71 (d, *J* = 2.0 Hz, 1 H), 7.62 (d, *J* = 2.0 Hz, 1 H), 7.59 (d, *J* = 2.4 Hz, 1 H), 7.51 (d, *J* = 2.0 Hz, 1 H), 7.29 (dd, *J* = 4.4 Hz, 2.0 Hz, 1 H), 6.28 (t, *J* = 2.0 Hz, 1 H), 6.26 (t, *J* = 2.0 Hz, 1 H), 6.19 (t, *J* = 2.0 Hz, 1 H), 6.03 (q, *J* = 7.6 Hz, 1 H), 4.90

(dd, J = 6.4 Hz, 2.4 Hz, 1 H), 4.28 (dd, J = 6.4 Hz, 4.8 Hz, 1 H), 1.61 (d, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.2, 223.2, 181.1, 147.3, 144.7, 143.4, 141.7, 136.5, 136.4, 134.9, 111.2, 106.4, 106.2, 105.8, 104.6, 71.3, 65.9, 10.2. HRMS (ESI) Calcd for $C_{18}H_{17}BMoN_6O_4$ ($[M]^+$): 490.0458. Found: 490.0480. HRMS (ESI) Calcd for $C_{16}H_{17}BMoN_6O_2$ ($[M\text{-}2CO]^+$): 434.0560. Found: 434.0565. HPLC: Daicel® Chiralpak AS-RH column, isocratic solvent system: 55 % CH_3CN in H_2O (+ 0.1 % TFA), 1.0 mL/min., λ = 254 nm, *Z*-(-)-**2.26**: $t_{(-)}$ = 8.81 min; *Z*-(+)-**2.26**: $t_{(+)}$ = 6.99 min.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-1-(benzyloxycarbonyl)-6-ethylene-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-2.27. To a solution of (±)-*anti*-**2.23** (64 mg, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added DMAP (6.1 mg, 0.05 mmol, 0.5 equiv), Et_3N (21 μL, 0.15 mmol, 1.5 equiv), and methanesulfonyl chloride (10.5 μL, 0.13 mmol, 1.3 equiv). The reaction mixture was stirred 30 minutes at room temperature and then passed through a short pad of silica gel (50% EtOAc in hexanes). The solvents were completely removed on a rotary evaporator, and the residue was dissolved in CH_2Cl_2 (4 mL). DBU (22.5 μL, 0.15 mmol, 1.5 equiv) was slowly added *via* syringe. The reaction mixture was stirred overnight (16 h) at room temperature and then passed through a short pad of silica gel and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (1:1) afforded the major isomer *E*-

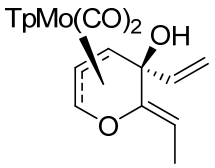
(±)-**X** (48 mg, 0.077 mmol, 77%) and the minor isomer *Z*-(±)-**2.27** (5 mg, 0.008 mmol, 8%).

Similar treatment of (±)-*syn*-**2.23** (162 mg, 0.254 mmol) over 1 h afforded a mixture of two isomers (139 mg, 87%). HPLC analysis of the reaction mixture showed a ratio of *Z*/*E* = 96:4.

E-(±)-**2.27**: TLC: R_f = 0.57 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3123 (w), 2490 (m), 1965 (s), 1880 (s), 1714 (s), 1671 (m), 1617 (s), 1505 (m), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.45 (d, *J* = 2.2 Hz, 1 H), 7.75 (d, *J* = 2.2 Hz, 1 H), 7.59 (d, *J* = 1.9 Hz, 1 H), 7.56 (d, *J* = 2.2 Hz, 1 H), 7.50 (d, *J* = 2.5 Hz, 1 H), 7.39-7.44 (m, 6 H), 7.24 (br s, 1 H), 6.63 (br s, 1 H), 6.29 (t, *J* = 2.2 Hz, 1 H), 6.22 (t, *J* = 2.2 Hz, 1 H), 5.99 (br s, 1 H), 5.26 (AB quartet, *J* = 12.1 Hz, 2 H), 4.82 (dd, *J* = 7.0 Hz, 2.2 Hz, 1 H), 4.00 (br s, 1 H), 2.11 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 225.1, 223.1, 188.0, 154.0, 147.5, 144.1, 141.1, 136.6, 136.4, 135.5, 135.0, 129.7, 129.2, 128.9 (3), 128.8, 106.4, 106.2, 106.1, 106.0, 91.9, 69.1, 66.0, 65.0, 14.9. HRMS (ESI) Calcd for $C_{26}H_{24}BMoN_7O_5$ ($[M]^+$): 623.0986. Found: 623.0980.

Z-(±)-**2.27**: TLC: R_f = 0.51 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3123 (w), 2490 (m), 1969 (s), 1876 (s), 1722 (s), 1702 (m), 1671 (m), 1621 (m), 1505 (m), 1409 (m), 1305 (m), 1262 (m), 1220 (s), 1123 (m), 1050 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.6 Hz, 1 H), 8.02 (br s, 1 H), 7.76 (d, *J* = 1.9 Hz, 1 H), 7.57-7.59 (m, 2 H), 7.49 (dd, *J* = 2.2 Hz, 0.6 Hz, 1 H), 7.35-7.38 (m, 5 H), 7.19-7.21 (m, 1 H), 6.34 (q, *J* = 7.3 Hz, 1 H), 6.28 (t, *J* = 2.2 Hz, 1 H), 6.20 (t, *J* = 2.2 Hz, 1 H), 6.14 (br s, 1 H), 5.22 (s, 2 H), 4.81 (dd, *J* = 6.0 Hz, 2.5 Hz, 1 H), 4.24-4.26 (m, 1 H), 1.54-1.59 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.5, 223.7, 186.8, 147.6, 143.6, 142.1, 136.7, 136.5, 135.5, 135.0, 131.8,

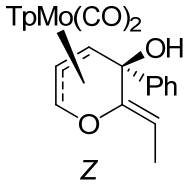
129.0, 129.0 (2), 128.9 (2), 128.7, 127.3, 125.2, 106.5, 106.2, 106.0, 89.3, 69.1, 68.3, 16.0. HRMS (ESI) Calcd for $C_{26}H_{24}BMoN_7O_5$ ($[M]^+$): 623.0986. Found: 623.0988.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-5-hydroxy-6-propylene-5-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(±)-2.28a; and (-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-5-hydroxy-6-propylene-5-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(-)-2.28a. To a solution of *Z*-(±)-**2.26** (488 mg, 1.0 mmol, 1.0 equiv) in THF (6 mL) was added vinylmagnesium bromide (0.87 M in THF, 0.23 mL, 2.0 mmol, 2.0 equiv) at –40 ºC. The mixture was stirred at –40 ºC for 1 hour, warmed to –10 ºC over 30 minutes, and then quenched with 1 mL of H_2O. The mixture was poured into a separatory funnel containing CH_2Cl_2 (10 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers dried over Na_2SO_4, filtered, and concentrated to give a yellow oil. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *Z*-(±)-**2.28a** (506 mg, 0.98 mmol, 98%) as a bright yellow solid.

Similar treatment of *Z*-(-)-**2.26** (25 mg, 0.050 mmol, 1.0 equiv, 97.1 %ee) in THF (2 mL) with vinylmagnesium bromide (1.0 M in THF, 0.21 mL, 0.20 mmol, 4.0 equiv) afforded *Z*-(-)-**2.28a** (21 mg, 0.041 mmol, 81%, 97.1 %ee) $[[\alpha]_D^{25}$ -214 (*c* 2.0, CH_2Cl_2)].

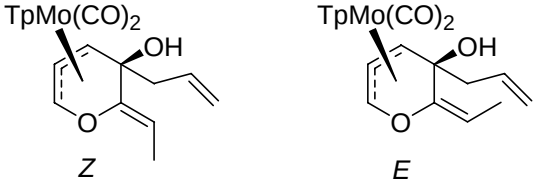
Z-(±)-**2.28a**: TLC: R_f = 0.66 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3474 (br w), 3146 (w), 3127 (w), 2918 (w), 2864 (w), 2482 (m), 1942 (s), 1845 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1197 (s), 1123 (s), 1050 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 2.0 Hz, 1 H), 7.94 (d, *J* = 2.0 Hz, 1 H), 7.69 (d, *J* = 2.0 Hz, 1 H), 7.59 (d, *J* = 2.4 Hz, 1 H), 7.57 (d, *J* = 2.4 Hz, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 7.07 (dd, *J* = 4.4 Hz, 2.4 Hz, 1 H), 6.28 (t, *J* = 2.4 Hz, 1 H), 6.22 (t, *J* = 2.0 Hz, 1 H), 6.19 (t, *J* = 2.0 Hz, 1 H), 6.11 (ddd, *J* = 17.2 Hz, 10.8 Hz, 0.8 Hz, 1 H), 5.46 (dd, *J* = 17.2 Hz, 1.2 Hz, 1 H), 5.08 (dd, *J* = 10.4 Hz, 0.8 Hz, 1 H), 5.04 (q, *J* = 6.8 Hz, 1 H), 4.59 (dd, *J* = 7.6 Hz, 2.4 Hz, 1 H), 3.67 (dd, *J* = 7.6 Hz, 4.4 Hz, 1 H), 3.34 (d, *J* = 0.8 Hz, 1 H), 1.58 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 232.5, 225.1, 150.9, 146.8, 145.0, 142.8, 141.6, 136.3, 136.1, 134.6, 111.4, 107.2, 106.1, 105.8, 105.5, 102.5, 76.4, 76.1, 60.2, 9.7. HRMS (ESI) Calcd for $C_{20}H_{21}BMoN_6O_4$ ($[M]^+$): 518.0771. Found: 518.0775. HPLC: Daicel® Chiralpak AS-RH column, isocratic solvent system: 50 % CH_3CN in H_2O (+ 0.1 % TFA), 0.9 mL/min, λ = 254 nm, *Z*-(-)-**2.28a**: $t_{(-)}$ = 14.39 min; *Z*-(+)-**2.28a**: $t_{(+)}$ = 16.46 min.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(η-2,3,4)-6-ethylene-5-hydroxy-5-phenyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(±)-2.28b. To a solution of *Z*-(±)-**2.26** (300 mg, 0.62 mmol, 1.0 equiv) in THF (2 mL) was added phenylmagnesium bromide (1.0 M in THF, 1.23 mL, 1.23 mmol, 2.0 equiv) at –78 ºC. The mixture was stirred at -78 °C for 2 hours, warmed to –15 ºC over 30 minutes, and

then quenched with 1 mL of H_2O. The mixture was poured into a separatory funnel containing CH_2Cl_2 (10 mL) and H_2O (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *Z*-(±)-**2.28b** (223 mg, 0.39 mmol, 64%) as a bright yellow solid.

Z-(±)-**2.28b**: TLC: R_f = 0.70 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3474 (br w), 3146 (w), 3127 (w), 2918 (w), 2864 (w), 2486 (m), 1942 (s), 1845 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, *J* = 1.8 Hz, 1 H), 7.95 (d, *J* = 2.1 Hz, 1 H), 7.74 (d, *J* = 1.5 Hz, 1 H), 7.72 (d, *J* = 7.2 Hz, 1 H), 7.67 (d, *J* = 1.8 Hz, 1 H), 7.57-7.54 (m, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 7.37 (app t, *J* = 7.5 Hz, 2 H), 7.26 (dd, *J* = 8.2 Hz, 5.1 Hz, 2 H), 7.14 (dd, *J* = 4.3 Hz, 1.8 Hz, 1 H), 6.30 (app t, *J* = 2.1 Hz, 1 H), 6.20 (app t, *J* = 2.1 Hz, 1 H), 6.17 (app t, *J* = 2.1 Hz, 1 H), 5.15 (q, *J* = 6.9 Hz, 2 H), 4.84 (dd, *J* = 7.6 Hz, 2.7 Hz, 1 H), 1.62 (d, *J* = 6.9 Hz, 3 H).^{13}C NMR (100 MHz, $CDCl_3$): δ 233.3, 225.5, 152.0, 149.3, 147.1, 143.2, 141.7, 136.4, 136.2, 134.8, 128.6 (2), 128.6, 127.5, 124.8, 106.6, 106.3, 105.9, 105.6, 103.8, 80.4, 61.1, 9.8. HRMS (ESI) Calcd for $C_{24}H_{23}BMoN_6O_4$ ($[M]^+$): 568.0928. Found: 568.0918.



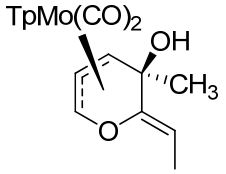
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(η-2,3,4)-5-allyl-6-ethylene-5-hydroxy-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.28c. To a solution of *Z*-

(±)-**2.26** (120 mg, 0.25 mmol, 1.0 equiv) in THF (3 mL) was added allylmagnesium bromide (1.0 M in Et_2O, 0.37 mL, 0.37 mmol, 1.5 equiv) at –78 ºC. The reaction mixture was slowly warmed to –50 ºC over 1 hour, and then quenched with 1 mL of saturated $NaHCO_3$ solution. The mixture was poured into a separatory funnel containing CH_2Cl_2 (10 mL) and H_2O (10 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *Z*-(±)-**2.28c** (114 mg, 0.22 mmol, 87%) as a bright yellow solid.

Similar treatment of *E*-(±)-**2.26** (100 mg, 0.21 mmol, 1.0 equiv) with allylmagnesium bromide (0.31 mL, 0.31 mmol, 1.5 equiv) afforded *E*-(±)-**2.28c** (88 mg, 0.17 mmol, 81%) as a bright yellow solid.

Z-(±)-**2.28c**: TLC: R_f = 0.71 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3478 (br w), 3127 (w), 3146 (w), 3076 (w), 2918 (w), 2864 (w), 2482 (m), 1942 (s), 1845 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 1.9 Hz, 1 H), 7.94 (d, *J* = 1.9 Hz, 1 H), 7.69 (d, *J* = 1.9 Hz, 1 H), 7.58 (d, *J* = 2.2 Hz, 1 H), 7.57 (d, *J* = 2.5 Hz, 1 H), 7.50 (d, *J* = 2.5 Hz, 1 H), 7.04 (dd, *J* = 4.1 Hz, 2.5 Hz, 1 H), 6.28 (t, *J* = 2.2 Hz, 1 H), 6.22 (t, *J* = 2.2 Hz, 1 H), 6.21 (t, *J* = 2.2 Hz, 1 H), 5.93-6.03 (m, 1 H), 5.15-5.19 (m, 2 H), 4.94 (q, *J* = 7.0 Hz, 1 H), 4.64 (dd, *J* = 7.3 Hz, 2.5 Hz, 1 H), 3.60 (dd, *J* = 7.6 Hz, 4.4 Hz, 1 H), 3.18 (s, 1 H), 2.63 (doublets of AB quartet, *J* = 13.0 Hz, 8.3 Hz, 2 H), 1.58 (d, *J* = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 232.1, 225.3, 151.5, 147.0, 142.9, 141.8, 136.3, 136.2, 134.7, 133.9, 118.5, 107.2, 106.3, 105.9, 105.6, 102.6, 77.4, 75.7, 60.0, 52.1, 9.7. HRMS (ESI) Calcd for $C_{21}H_{23}BMoN_6O_4$ ($[M]^+$): 532.0928. Found: 532.0935.

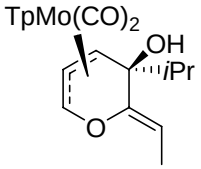
E-(±)-**2.28c**: TLC: R_f = 0.70 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3601 (m), 3474 (br w), 3127 (w), 3146 (w), 2922 (w), 2482 (m), 1938 (s), 1841 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1200 (s), 1123 (s), 1050 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 1.9 Hz, 1 H), 7.98 (d, *J* = 2.2 Hz, 1 H), 7.60 (d, *J* = 1.9 Hz, 1 H), 7.57 (d, *J* = 2.3 Hz, 2 H), 7.50 (d, *J* = 1.9 Hz, 1 H), 6.93 (dd, *J* = 4.4 Hz, 2.9 Hz, 1 H), 6.29 (t, *J* = 2.1 Hz, 1 H), 6.21 (t, *J* = 2.2 Hz, 2 H), 6.02 (dddd, *J* = 16.6 Hz, 10.2 Hz, 6.7 Hz, 3.5 Hz, 1 H), 5.16-5.22 (m, 2 H), 4.94 (q, *J* = 7.6 Hz, 1 H), 4.63 (dd, *J* = 7.6 Hz, 2.5 Hz, 1 H), 3.61 (dd, *J* = 7.3 Hz, 4.5 Hz, 1 H), 3.39 (s, 1 H), 2.68 (doublets of AB quartet, *J* = 13. 7 Hz, 5.6 Hz, 2 H), 1.75 (d, *J* = 7.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 232.1, 225.5, 149.5, 147.1, 143.5, 141.5, 136.3, 136.1, 134.7, 133.9, 118.7, 107.2, 106.2, 105.9, 105.7, 105.6, 81.2, 77.4, 60.8, 51.1, 11.6. HRMS (ESI) Calcd for $C_{21}H_{23}BMoN_6O_4$ ($[M]^+$): 532.0928. Found: 532.0937.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(η-2,3,4)-6-ethylene-5-hydroxy-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(±)-2.28d. To a solution of *Z*-(±)-**2.26** (300 mg, 0.62 mmol, 1.0 equiv) in THF (4 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 0.41 mL, 1.23 mmol, 2.0 equiv) at –78 ºC. The mixture was stirred at the same temperature for 1 hour, and then quenched with 1 mL of H_2O. The mixture was poured into a separatory funnel containing CH_2Cl_2 (10 mL) and H_2O (10 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined

organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1), affording *Z*-(±)-**2.28d** (220 mg, 0.44 mmol, 71%) as a bright yellow solid.

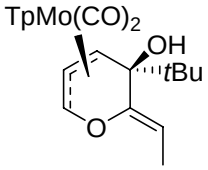
Z-(±)-**2.28d**: TLC: R_f = 0.72 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3462 (br w), 3146 (w), 3127 (w), 2926 (w), 2856 (w), 2482 (m), 1942 (s), 1841 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1200 (s), 1123 (s), 1050 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, *J* = 1.8 Hz, 1 H), 7.94 (d, *J* = 1.8 Hz, 1 H), 7.70 (d, *J* = 1.8 Hz, 1 H), 7.58-7.56 (m, 2 H), 7.49 (d, *J* = 1.8 Hz, 1 H), 7.04 (dd, *J* = 4.0 Hz, 2.7 Hz, 1 H), 6.28 (app t, *J* = 2.1 Hz, 1 H), 6.22-6.19 (m, 2 H), 4.99 (q, *J* = 6.9 Hz, 1 H), 4.66 (dd, *J* = 7.5 Hz, 2.4 Hz, 1 H), 3.54 (dd, *J* = 7.5 Hz, 4.5 Hz, 1 H), 3.26 (br s, 1 H), 1.67 (s, 3 H), 1.55 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 232.8, 225.0, 153.4, 147.0, 142.8, 141.9, 136.4, 136.2, 134.7, 107.6, 106.3, 105.9, 105.6, 101.0, 78.4, 74.1, 59.8, 35.8, 9.7. HRMS (ESI) Calcd for $C_{19}H_{21}BMoN_6O_4$ ($[M]^+$): 506.0771. Found: 506.0779.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(η-2,3,4)-6-ethylidene-5-hydroxy-5-isopropyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(±)-2.28e. To a solution of *Z*-(±)-**2.26** (25 mg, 0.050 mmol, 1.0 equiv) in dry THF (2 mL) at -40 °C was added isopropyl magnesium chloride (1.6 M in ether, 128 μL, 0.20 mmol, 4 equiv). After one hour, the reaction mixture was quenched with water and extracted with dichloromethane (2 x 10 mL). The combined organic layers were washed with brine,

dried over $MgSO_4$, and concentrated under vacuum. The yellow oil was then purified by flash chromatography over silica gel with hexanes-EtOAc (4:1), affording ***Z*-(±)-2.28e** (6.0 mg, 0.011 mmol, 21%) as a yellow solid.

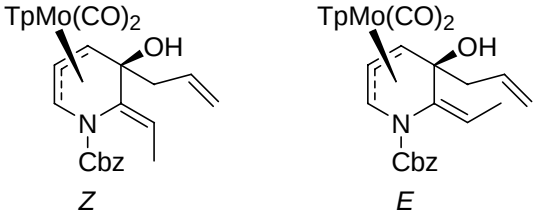
Z-(±)-**2.28e**: TLC: R_f = 0.72 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 2956 (w), 2483 (w), 1956 (s), 1865 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.6 Hz, 1 H), 7.93 (d, *J* = 1.6 Hz, 1 H), 7.65 (d, *J* = 2.4 Hz, 1 H), 7.57-7.56 (m, 2 H), 7.48 (d, *J* = 2.4 Hz, 1 H), 6.98 (dd, *J* = 4.4, 2.4 Hz, 1 H), 6.27 (app t, *J* = 2.0 Hz, 1 H), 6.22-6.20 (m, 2 H), 4.93-4.89 (m, 1 H), 4.73 (dd, *J* = 7.6 Hz, 2.8 Hz, 1 H), 3.70 (dd, *J* = 7.6 Hz, 4.4 Hz, 1 H), 3.06 (br s, 1 H), 1.95-1.90 (m, 1 H), 1.56 (d, *J* = 7.2 Hz, 3 H), 1.19 (d, *J* = 6.4 Hz, 3 H), 1.03 (d, *J* = 6.8 Hz, 3 H).^{13}C NMR (100 MHz, $CDCl_3$): δ 232.8, 225.9, 151.4, 147.0, 143.1, 141.7, 136.4, 136.1, 134.7, 106.4, 106.2, 105.9, 105.7, 103.3, 77.8, 61.7, 42.6, 18.3, 16.9 (2), 9.7. HRMS (ESI) Calcd for $C_{21}H_{25}BMoN_6O_4$ ($[M]^+$): 534.1084. Found: 534.1080.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(η-2,3,4)-6-ethylidene-5-hydroxy-5-*tert*-butyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(±)-2.28f. To a solution of *Z*-(±)-**2.26** (0.100 g, 0.20 mmol, 1.0 equiv) in dry THF (2 mL) was added *tert*-butylmagnesium chloride (2.0 M in ether, 205 μL, 0.41 mmol, 2 equiv). After one hour, the reaction mixture was quenched with water and extracted with dichloromethane (2 x 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The yellow oil was then purified by flash chromatography

over silica gel with hexanes-EtOAc (4:1), affording *Z*-(±)-**2.28f** as a yellow solid (28 mg, 0.051 mmol, 25%).

Z-(±)-**2.28f**: TLC: R_f = 0.68 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 2920 (w), 2469 (m), 1920 (s), 1829 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.8 Hz, 1 H), 7.95 (d, *J* = 1.8 Hz, 1 H), 7.61 (d, *J* = 1.5 Hz, 1 H), 7.58-7.56 (m, 2 H), 7.48 (d, *J* = 2.1 Hz, 1 H), 6.96 (dd, *J* = 4.0 Hz, 2.4 Hz, 1 H), 6.27 (app t, *J* = 2.1 Hz, 1 H), 6.22-6.20 (m, 2 H), 4.92 (q, *J* = 6.6 Hz, 1 H), 4.76 (dd, *J* = 7.6 Hz, 2.1 Hz, 1 H), 3.91 (dd, *J* = 7.6 Hz, 4.3 Hz, 1 H), 3.08 (br s, 1 H), 1.58 (d, *J* = 6.6 Hz, 3 H), 1.14 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 233.4, 226.7, 150.5, 147.0, 143.7, 141.4, 136.4, 136.1, 134.7, 106.2, 105.9, 105.7, 105.4, 104.6, 79.3, 78.8, 64.6, 41.8, 25.8 (3), 9.8. HRMS (ESI) Calcd for $C_{22}H_{27}BMoN_6O_4$ ($[M]^+$): 548.1241. Found: 548.1248.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(η-2,3,4)-5-allyl-1-(benzyloxycarbonyl)-6-ethylene-5-hydroxy-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-2.29. To a solution of *Z*-(±)-**2.27** (460 mg, 0.74 mmol, 1.0 equiv) in THF (12 mL) was added allylmagnesium bromide (1.0 M in Et_2O, 0.89 mL, 0.89 mmol, 1.2 equiv) at –78 ºC. The reaction mixture was stirred at –78 ºC for 5 minutes and then quenched with 1 mL of H_2O. The mixture was poured into a separatory funnel containing CH_2Cl_2 (10 mL) and H_2O (10 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers dried over

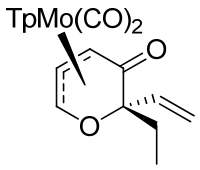
Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *Z*-(±)-**2.29** (484 mg, 0.73 mmol, 99 %) as a bright yellow solid.

Similar treatment of *E*-(±)-**2.27** (600 mg, 0.97 mmol, 1.0 equiv) with allylmagnesium bromide (1.0 M in Et_2O, 1.1 mL, 1.16 mmol, 1.2 equiv) in THF (15 mL) afforded *E*-(±)-**2.29** (640 mg, 0.96 mmol, 99 %) as a bright yellow solid.

Z-(±)-**2.29**: TLC: R_f = 0.41 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3590 (w), 3470 (br w), 2941(w), 2918 (w), 2482 (m), 1949 (s), 1872 (s), 1849 (s), 1687 (s), 1505 (m), 1447 (s), 1409 (s), 1293 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (br s, 1 H), 7.90 (br s, 2 H), 7.60 (br s, 2 H), 7.49 (d, *J* = 1.4 Hz, 1 H), 7.30-7.44 (m, 5 H), 6.93 (br s, 1 H), 6.28 (br s, 1 H), 6.16-6.22 (m, 2 H), 5.82-5.90 (m, 1 H), 5.36-5.48 (m, 1 H), 5.28 (d, *J* = 12.0 Hz, 1 H), 5.05-5.13 (m, 2 H), 4.61-4.62 (m, 1 H), 3.74-3.76 (m, 1 H), 3.59-3.65 (m, 1 H), 3.03 (br s, 1 H), 2.56-2.60 (m, 1 H), 2.45-2.46 (m, 1 H), 1.49 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 231.3, 224.9, 155.6, 147.0, 143.2, 142.1, 136.5, 136.4, 136.2, 136.1, 134.7, 134.0, 128.7(2), 128.32, 128.30, 127.8, 118.5, 115.6, 106.2, 105.9, 105.7, 83.5, 83.1, 76.3, 68.3, 61.1, 49.7, 14.4. HRMS (ESI) Calcd for $C_{29}H_{30}BMoN_7O_5$ ($[M]^+$): 665.1456. Found: 665.1465.

E-(±)-**2.29**: TLC: R_f = 0.43 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3601 (m), 3478 (br w), 3123 (w), 2937 (w), 2482 (m), 1945 (s), 1845 (s), 1691 (s), 1505 (m), 1455 (w), 1409 (s), 1293 (s), 1220 (s), 1123 (s), 1073 (s), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.50 (d, *J* = 1.9 Hz, 1 H), 7.91 (d, *J* = 1.4 Hz, 1 H), 7.85 (br s, 1 H), 7.58 (d, *J* = 1.4 Hz, 2 H), 7.50 (d, *J* = 1.9 Hz, 1 H), 7.34-7.38 (m, 5 H), 7.00 (d, *J* = 4.8 Hz, 1 H), 6.28 (t, *J* = 2.4 Hz, 1 H), 6.20 (t, *J* = 2.4 Hz, 1 H), 6.17 (br s, 1 H), 5.80-5.97 (m, 1 H), 5.48 (br s, 1 H), 5.23-5.30 (m, 2 H), 5.12-5.16 (m, 2 H), 4.65 (dd, *J* = 7.2 Hz, 1.9 Hz, 1 H), 3.57 (br s, 1 H),

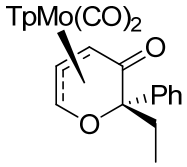
3.28 (br s, 1 H), 2.61 (doublets on the left side of AB quartet, J = 13. 8 Hz, 8.1 Hz, 1 H), 2.53-2.54 (m, 1 H), 1.93 (d, J = 7.1 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): 231.7, 224.6, 147.1, 143.1, 142.1, 136.6, 136.4, 136.2, 134.6, 134.3, 133.9(2), 128.7(3), 128.2, 127.7, 120.7, 118.7, 106.2, 105.8, 105.6, 83.1, 78.4, 68.1, 68.0, 60.3, 50.0, 13.2. HRMS (ESI) Calcd for $C_{29}H_{30}BMoN_7O_5$ ($[M]^+$): 665.1456. Found: 665.1435.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-ethyl-5-oxo-6-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.30a; and (-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-ethyl-5-oxo-6-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)-2.30a. To a solution of *Z*-(±)-**2.28a** (16 mg, 0.031 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added HCl (4.0 M in dioxane, 8.0 μL, 0.031 mmol, 1.0 equiv) at 0 ºC. The reaction mixture was stirred at 0 ºC for 5 minutes and then passed through a short pad of silica gel. The solvents were completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (5:1) to afford (±)-**2.30a** (16 mg, 0.031 mmol, 100%) as an orange solid.

Similar treatment of *Z*-(-)-**2.28a** (23 mg, 0.040 mmol, 1.0 equiv, 97.1 %ee) in CH_2Cl_2 (2.5 mL) with HCl (4.0 M in dioxane, 12 μL, 0.050 mmol, 1.1 equiv) afforded (-)-**2.30a** (23 mg, 0.045 mmol, 99 %, 97.1 %ee) [$[\alpha]_D^{25}$ -225 (*c* 1.8, CH_2Cl_2)].

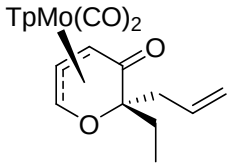
(±)-**2.30a**: TLC: R_f = 0.49 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3146 (m), 3127 (m), 2980 (m), 2941 (m), 2880 (w), 2486 (m), 1961 (s), 1872 (s), 1660 (s), 1505 (s), 1409 (s), 1305 (s), 1262 (s), 1220 (s), 1123 (s), 1050 (s), 1015 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 1.6 Hz, 1 H), 7.94 (d, *J* = 2.4 Hz, 1 H), 7.69 (d, *J* = 2.0 Hz, 1 H), 7.58-7.61 (m, 3 H), 7.51 (d, *J* = 1.6 Hz, 1 H), 6.30 (t, *J* = 2.4 Hz, 1 H), 6.25 (t, *J* = 2.0 Hz, 1 H), 6.20 (t, *J* = 2.4 Hz, 1 H), 5.63 (dd, *J* = 17.2 Hz, 10.8 Hz, 1 H), 5.37 (dd, *J* = 17.2 Hz, *J* = 1.2 Hz, 1 H), 5.23 (dd, *J* = 10.4 Hz, 0.8 Hz, 1 H), 4.72 (dd, *J* = 5.6 Hz, 2.0 Hz, 1 H), 4.11 (dd, *J* = 5.6 Hz, 4.4 Hz, 1 H), 1.76 (doublets of AB quartet, *J* = 14.3 Hz, *J*= 7.3 Hz, 1 H), 1.55 (doublets of AB quartet, *J* = 14.3 Hz, *J* = 7.3 Hz, 1 H), 0.77 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 226.4, 224.0, 198.4, 147.7, 143.3, 141.6, 136.9, 136.5, 134.8, 115.4, 109.0, 106.5, 106.1, 105.8, 84.5, 70.1, 65.2, 64.7, 28.7, 7.2. HRMS (ESI) Calcd for $C_{20}H_{21}BMoN_6O_4$ ($[M]^+$): 518.0771. Found: 518.0778. HPLC: Daicel® Chiralcel OJ-RH column, Isocratic solvent system: 50 % CH_3CN in H_2O (+ 0.1 % TFA), 1.0 mL/min, λ = 254 nm, (-)-**2.30a**: $t_{(-)}$ = 13.62 min; (+)-**2.30a**: $t_{(+)}$ = 17.32 min.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-ethyl-5-oxo-6-phenyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.30b. To a solution of *Z*-(±)-**2.28b** (18 mg, 0.032 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added HCl (4.0 M in dioxane, 8.0 μL, 0.035 mmol, 1.1 equiv) at 0 ºC. The reaction mixture was stirred at 0 ºC for 5 minutes and then passed through a short pad of silica gel. The solvents were

completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (4:1) to afford (±)-**2.30b** (17.7 mg, 0.031 mmol, 98 %) as an orange solid.

(±)-**2.30b**: TLC: R_f = 0.47 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3146 (w), 3127 (w), 2980 (m), 2937 (w), 2490 (m), 1961 (s), 1876 (s), 1660 (m), 1505 (m), 1447 (m), 1409 (s), 1305 (s), 1258 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.59 (d, *J* = 1.9 Hz, 1 H), 7.92 (d, *J* = 1.9 Hz, 1 H), 7.73 (d, *J* = 1.9 Hz, 1 H), 7.69 (dd, *J* = 4.4 Hz, 2.2 Hz, 1 H), 7.61 (d, *J* = 2.3 Hz, 1 H), 7.57 (d, *J* = 2.2 Hz, 1 H), 7.52 (d, *J* = 2.2 Hz, 1 H), 7.47-7.49 (m, 2 H), 7.36-7.40 (m, 2 H), 7.27-7.32 (m, 1 H), 6.33 (t, *J* = 2.2 Hz, 1 H), 6.26 (t, *J* = 2.2 Hz, 1 H), 6.18 (t, *J* = 2.2 Hz, 1 H), 4.70 (dd, *J* = 5.5 Hz, 2.2 Hz, 1 H), 4.04 (dd, *J* = 5.7 Hz, 4.5 Hz, 1 H), 1.88 (doublet of AB quartets, *J* = 14.3 Hz, 7.3 Hz, 2 H), 0.69 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 226.6, 223.9, 198.5, 147.7, 143.1, 141.7, 139.1, 136.54, 136.51, 134.8, 128.6 (2), 127.7, 125.5 (2), 108.5, 106.5, 106.1, 105.8, 85.1, 65.8, 65.1, 31.9, 7.7. HRMS (ESI) Calcd for $C_{24}H_{23}BMoN_6O_4$ ($[M]^+$): 568.0928. Found: 568.0949.

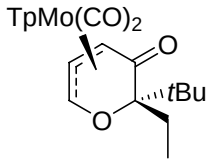


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-allyl-6-ethyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.30c. To a solution of *Z*-(±)-**2.28c** (61 mg, 0.11 mmol, 1.0 equiv) in CH_2Cl_2 (4 mL) was added HCl (4.0 M in dioxane, 32 μL, 0.13 mmol, 1.2 equiv) at 0 ºC. The reaction mixture was stirred at 0 ºC for 5 minutes

and then passed through a short pad of silica gel. The solvents were completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (4:1) to afford (±)-**2.30c** (58 mg, 0.11 mmol, 95 %) as an orange solid.

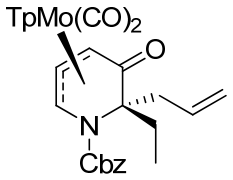
Similar treatment of *E*-(±)-**2.28c** (27 mg, 0.051 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) with HCl (14 μL, 0.056 mmol, 4.0 M in dioxane, 1.1 equiv) at 0 ºC afforded (±)-**2.30c** (25.5 mg, 0.048 mmol, 94 %) as an orange solid.

(±)-**2.30c**: TLC: R_f = 0.49 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3478 (br w), 3127 (w), 3146 (w), 3076 (w), 2918 (w), 2864 (w), 2482 (m), 1942 (s), 1845 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.53 (d, *J* = 1.9 Hz, 1 H), 7.96 (d, *J* = 1.4 Hz, 1 H), 7.68 (d, *J* = 1.4 Hz, 1 H), 7.62 (d, *J* = 2.4 Hz, 1 H), 7.57 (d, *J* = 2.4 Hz, 1 H), 7.53 (dd, *J* = 4.3 Hz, 1.9 Hz, 1 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 6.30 (t, *J* = 1.9 Hz, 1 H), 6.25 (t, *J* = 1.9 Hz, 1 H), 6.21 (t, *J* = 1.9 Hz, 1 H), 5.80-5.87 (m, 1 H), 5.14 (s, 1 H), 5.12 (d, *J* = 5.2 Hz, 1 H), 4.74 (dd, *J* = 5.7 Hz, 1.9 Hz, 1 H), 4.13 (t, *J* = 5.2 Hz, 1 H), 2.47 (doublet of AB quartet, *J* = 15.3 Hz, 7.2 Hz, 2 H), 1.6 (doublet of AB quartet, *J* = 14.3 Hz, 7.2 Hz, 2 H), 0.84 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 219.9, 217.5, 195.3, 144.5, 140.3, 138.7, 133.94, 133.87, 132.3, 130.4, 116.9, 108.3, 105.2, 104.9, 104.6, 82.9, 65.4, 65.2, 43.0, 30.1, 10.5. HRMS (ESI) Calcd for $C_{21}H_{23}BMoN_6O_4$ ($[M]^+$): 532.0928. Found: 532.0948.



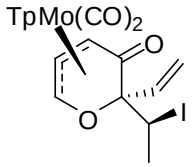
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-ethyl-5-oxo-6-*tert*-butyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.30f. To a solution of Z-(±)-**2.28f** (28 mg, 0.050 mmol, 1.0 equiv) in CH_2Cl_2 (3.1 mL) was added a solution of HCl (4.0 M in dioxane, 14 μL, 0.060 mmol, 1.1 equiv). The reaction mixture was refluxed for 10 minutes and then cooled to room temperature. The crude reaction mixture was purified by flash chromatography over silica gel with hexanes-EtOAc (4:1), affording (±)-**2.30f** (27 mg, 0.049 mmol, 98%) as a yellow solid.

(±)-2.30f: TLC: R_f=0.40 (hexanes-EtOAc = 4:1). IR (cm^{-1}): 3120 (w), 2485 (w), 1954 (s), 1859 (s), 1656 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 1.6 Hz, 1 H), 7.95 (d, *J* = 1.6 Hz, 1 H), 7.70 (d, *J* = 1.6 Hz, 1 H), 7.65 (dd, *J* = 4.3 Hz, 2.6 Hz, 1 H), 7.61 (d, *J* = 2.5 Hz, 1 H), 7.58 (d, *J* = 2.4 Hz, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 6.28 (app t, *J* = 2.4 Hz, 1 H), 6.25 (app t, *J* = 2.0 Hz, 1 H), 6.20 (app t, *J* = 2.4 Hz, 1 H), 4.69 (dd, *J* = 6.2 Hz, 2.2 Hz, 1 H), 4.10 (dd, *J* = 6.2 Hz, 4.6 Hz, 1 H), 1.79-1.61 (m, 2 H), 1.10 (s, 9 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 226.7, 224.4, 201.7, 147.6, 143.1, 141.5, 136.5, 136.5, 134.8, 112.1, 106.5, 106.1, 105.8, 87.5, 65.8, 64.2, 40.0, 27.9 (3), 27.3, 9.3. HRMS (ESI) Calcd for $C_{22}H_{27}BMoN_6O_4$ ($[M]^+$): 548.1241. Found: 548.1236.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-allyl-1-(benzyloxycarbonyl)-6-ethyl-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-2.31. To a solution of *E*-(±)-**2.29** (566 mg, 0.85 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) was added HCl (4.0 M in dioxane, 235 μL, 0.94 mmol, 1.1 equiv) at 0 ºC. The reaction mixture was stirred at room temperature for 1 hour and then passed through a short pad of silica gel. The solvents were completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (4:1) to afford (±)-**2.31** (543 mg, 0.82 mmol, 96 %) as an orange solid.

(±)-**2.31**: TLC: R_f = 0.49 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3127 (w), 2980 (w), 2954 (w), 2486 (m), 1965 (s), 1884 (s), 1710 (s), 1664 (s), 1505 (w), 1459 (w), 1440 (w), 1301 (s), 1251 (m), 1220 (s), 1127 (m), 1054 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (br s, 1 H), 7.80 (br s, 1 H), 7.52-7.58 (m, 3 H), 7.47 (br s, 3 H), 7.38 (br s, 3 H), 7.17 (br s, 1 H), 6.27 (t, *J* = 1.9 Hz, 1 H), 6.19 (br s, 1 H), 5.85 (br s, 1 H), 5.23-5.25 (m, 2 H), 5.15-5.16 (m, 1 H), 5.02-5.10 (m, 2 H), 4.67 (dd, *J* = 5.7 Hz, 1.9 Hz, 1 H), 3.79 (br s, 1 H), 2.75 (br s, 1 H), 2.55 (br s, 1 H), 2.29 (br s, 2 H), 0.93 (br s 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): 224.8, 223.9, 199.7, 153.5, 147.3, 143.2, 141.5, 136.6 (2), 135.8, 134.9, 133.6, 129.3, 128.9 (2), 128.7 (2), 118.5, 106.4, 106.0, 105.8, 91.8, 69.6, 68.8, 62.5, 42.8, 27.2, 9.4. HRMS (ESI) Calcd for $C_{29}H_{30}BMoN_7O_5$ ($[M]^+$): 665.1456. Found: 665.1481.



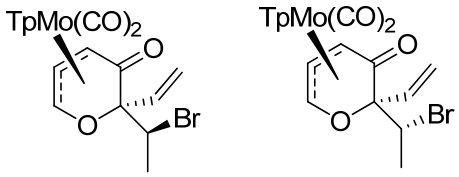
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-6-(1*S*-iodoethyl)-5-oxo-6-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.33.

Two different protocols were used to synthesize (±)-**2.33**:

Complex *Z*-(±)-**2.28a** (25 mg, 0.048 mmol, 1.0 equiv) was dissolved in MeCN (2 mL) and *N*-iodosuccinimide (16.4 mg, 0.073 mmol, 1.5 equiv) was added in one portion at room temperature. After 10 minutes, the solution was poured into a separatory funnel containing water (5 mL) and CH_2Cl_2 (5 mL), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography over silica gel with hexanes-EtOAc (2 :1), affording (±)-**2.33** (23 mg, 0.036 mmol, 76 %) as an orange solid.

Alternatively, $AgOC(O)CF_3$ (17.0 mg, 0.077 mmol, 1.6 equiv) was dissolved in MeCN (2 mL), I_2 (15.9 mg, 0.072 mmol, 1.5 equiv) was added, and the solution was stirred at room temperature. After 5 minutes, *Z*-(±)-**2.28a** (25.0 mg, 0.048 mmol, 1.0 equiv) was added in one portion and the solution was again stirred at room temperature. After 10 minutes, the reaction mixture was poured into a separatory funnel containing water (5 mL) and CH_2Cl_2 (5 mL), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography over silica gel with hexanes-EtOAc (2 :1), affording (±)-**2.33** (26.7 mg, 0.042 mmol, 87 %) as an orange solid.

(±)-**2.33**: TLC: R_f = 0.43 (hexanes-EtOAc = 2 :1). IR (cm^{-1}): 3127 (m), 2930 (m), 1972 (s), 1888 (s), 1668 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 2.0 Hz, 1 H), 7.91 (d, *J* = 1.6 Hz, 1 H), 7.68 (d, *J* = 2.4 Hz, 1 H), 7.60 (d, *J* = 2.0 Hz, 1 H), 7.59 (d, *J* = 2.0 Hz, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 7.47 (dd, *J* = 4.8 Hz, 2.4 Hz, 1 H), 6.31 (t, *J* = 2.4 Hz, 1 H), 6.25 (t, *J* = 2.4 Hz, 1 H), 6.20 (t, *J* = 2.4 Hz, 1 H), 5.75 (dd, *J* = 17.2 Hz, 10.4 Hz, 1 H), 5.51 (d, *J* = 17.2 Hz, 1 H), 5.44 (d, *J* = 10.8 Hz, 1 H), 4.64 (dd, *J* = 5.6 Hz, 2.4 Hz, 1 H), 4.32 (q, *J* = 7.6 Hz, 1 H), 4.14 (dd, *J* = 5.6 Hz, 4.4 Hz, 1 H), 1.93 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.5, 222.9, 196.7, 147.7, 142.8, 141.5, 136.7, 136.6, 134.8, 134.4, 118.5, 107.2, 106.6, 106.2, 105.9, 84.6, 65.0, 63.5, 27.8, 23.9. HRMS (ESI) Calcd for $C_{20}H_{21}BIMoN_6O_4$ ($[M+H]^+$): 644.9810. Found: 644.9812.



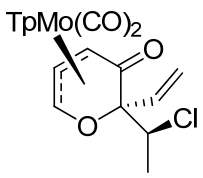
2.34a **2.34b**

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1*S*-bromoethyl)-5-oxo-6-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum [(±)-2.34a] and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1*R*-bromoethyl)-5-oxo-6-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.34b. Complex *Z*-(±)-**2.28a** (25 mg, 0.048 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2 mL) and *N*-bromosuccinimide (12.9 mg, 0.073 mmol, 1.5 equiv) was added in one portion at room temperature. After 10 minutes, the solution was poured into a separatory funnel containing water (5 mL) and CH_2Cl_2 (5 mL), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5 mL). The combined organic layers were dried over

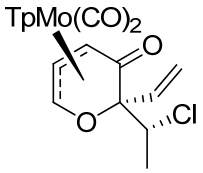
$MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography over silica gel with hexanes-EtOAc (2:1), affording a 5.3 : 1.0 mixture of (±)-**2.34a** and (±)-**2.34b** (24.0 mg, 0.040 mmol, 84 %), as orange solids.

(±)-**2.34a**: TLC: R_f = 0.41 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3127 (m), 2934 (m), 1972 (s), 1888(s), 1668(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 2.0 Hz, 1 H), 7.92 (d, *J* = 2.0 Hz, 1 H), 7.71 (d, *J* = 2.0 Hz, 1 H), 7.61 (d, *J* = 2.4 Hz, 1 H), 7.59 (d, *J* = 2.4 Hz, 1 H), 7.49-7.51 (m, 2 H), 6.31 (t, *J* = 2.4 Hz, 1 H), 6.25 (t, *J* = 2.4 Hz, 1 H), 6.20 (t, *J* = 2.0 Hz, 1 H), 5.67 (dd, *J*= 17.2 Hz, 10.8 Hz, 1 H), 5.54 (d, *J* = 17.2 Hz, 1 H), 5.40 (d, *J* = 10.4 Hz, 1 H), 4.65 (dd, *J* = 5.6 Hz, 2.0 Hz, 1 H), 4.37 (q, *J* = 7.2 Hz, 1 H), 4.11 (t, *J* = 5.2 Hz, 1 H), 1.59 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.0, 222.7, 196.9, 147.7, 142.7, 141.5, 136.7, 136.6, 134.8 (2), 118.4, 107.0, 106.6, 106.1, 105.8, 85.3, 64.2, 62.7, 47.9, 20.2. HRMS (ESI) Calcd for $C_{20}H_{21}BBrMoN_6O_4$ ($[M+H]^+$): 596.9949. Found: 596.9921.

(±)-**2.34b**: TLC: R_f = 0.47 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3127 (w), 1969 (s), 1880 (s), 1664 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 1.6 Hz, 1 H), 7.91 (d, *J* = 2.4 Hz, 1 H), 7.69 (d, *J* = 2.4 Hz, 1 H), 7.59-7.62 (m, 3 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 6.31 (t, *J* = 2.8 Hz, 1 H), 6.26 (t, *J* = 2.4 Hz, 1 H), 6.20 (t, *J* = 2.4 Hz, 1 H), 5.75 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 5.49 (d, *J* = 17.2 Hz, 1 H), 5.38 (d, *J* = 10.8 Hz, 1 H), 4.69 (dd, *J* = 5.6 Hz, 2.0 Hz, 1 H), 4.52 (q, *J* = 7.2 Hz, 1 H), 4.16 (dd, *J* = 5.6 Hz, 4.8 Hz, 1 H), 1.58 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.4, 223.5, 196.8, 147.6, 142.8, 141.5, 137.5, 136.7, 136.6, 134.9, 117.5, 107.8, 106.6, 106.3, 105.9, 85.3, 65.0, 63.8, 53.5, 21.1. HRMS (ESI) Calcd for $C_{20}H_{21}BBrMoN_6O_4$ ($[M+H]^+$): 596.9949. Found: 596.9946.



2.35a



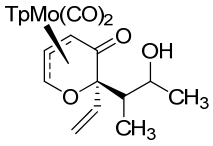
2.35b

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1*S*-chloroethyl)-5-oxo-6-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.35a and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1*R*-chloroethyl)-5-oxo-6-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.35b. Complex *Z*-(±)-**2.28a** (25 mg, 0.048 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2 mL) and *t*-BuOCl (8.7 μL, 0.073 mmol, 1.5 equiv) was added at room temperature. After 10 minutes, the solution was poured into a separatory funnel containing water (5 mL) and CH_2Cl_2 (5 mL), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography over silica gel with hexanes-EtOAc (2:1), affording a 7.9 : 1.0 mixture of (±)-**2.35a** and (±)-**2.35b** (18.9 mg, 0.034 mmol, 72 %), as orange solids.

(±)-**2.35a**: TLC: R_f = 0.36 (hexanes-EtOAc = 2 :1). IR (cm^{-1}): 3130 (w), 1972 (s), 1888 (s), 1668 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 2.0 Hz, 1 H), 7.93 (d, *J* = 1.6 Hz, 1 H), 7.72 (d, *J* = 1.6 Hz, 1 H), 7.62 (d, *J* = 2.0 Hz, 1 H), 7.60 (d, *J* = 2.0 Hz, 1 H), 7.53 (d, *J* = 2.4 Hz, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 6.31 (t, *J* = 2.0 Hz, 1 H), 6.26 (t, *J* = 2.4 Hz, 1 H), 6.21 (t, *J* = 2.0 Hz, 1 H), 5.64 (dd, *J* = 17.6 Hz, 10.4 Hz, 1 H), 5.55 (dd, *J* = 17.2 Hz, 1.2 Hz, 1 H), 5.39 (dd, *J* = 10.0 Hz, 1.6 Hz, 1 H), 4.67 (dd, *J* = 5.6 Hz, 2.0 Hz, 1 H), 4.40 (q, *J* = 6.8 Hz, 1 H), 4.11 (dd, *J* = 5.6 Hz, 4.4 Hz, 1 H), 1.38 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.8, 222.6, 196.7, 147.6, 142.7, 141.4, 136.6, 136.5,

134.8 (2), 118.2, 107.0, 106.5, 106.1, 105.8, 85.6, 63.9, 62.9, 56.3, 18.5. HRMS (ESI) Calcd for $C_{20}H_{21}BClMoN_6O_4$ ($[M+H]^+$): 553.0454. Found: 553.0459.

(±)-**2.35b**: TLC: R_f = 0.45 (hexanes-EtOAc = 2 :1). IR (cm^{-1}): 3146 (m), 1965 (s), 1880 (s), 1664 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J* = 2.4 Hz, 1 H), 7.92 (d, *J* = 2.0 Hz, 1 H), 7.69 (d, *J* = 2.4 Hz, 1 H), 7.60-7.63 (m, 3 H), 7.52 (d, *J* = 2.4 Hz, 1 H), 6.32 (t, *J* = 2.4 Hz, 1 H), 6.27 (t, *J* = 2.4 Hz, 1 H), 6.22 (t, *J* = 2.0 Hz, 1 H), 5.79 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 5.53 (d, *J* = 17.2 Hz, 1 H), 5.41 (d, *J* = 10.8 Hz, 1 H), 4.71 (dd, *J* = 5.6 Hz, 2.4 Hz, 1 H), 4.48 (q, *J* = 6.8 Hz, 1 H), 4.18 (dd, *J* = 6.0 Hz, 4.8 Hz, 1 H), 1.41 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.5, 223.5, 197.3, 147.6, 142.8, 141.5, 136.7, 136.6, 136.3, 134.9, 117.6, 107.6, 106.6, 106.2, 105.9, 85.3, 64.9, 63.8, 60.7, 19.8. HRMS (ESI) Calcd for $C_{20}H_{21}BClMoN_6O_4$ ($[M+H]^+$): 553.0454. Found: 553.0460.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-(η-2,3,4)-6-(2-hydroxybutan-3-yl)-5-oxo-6-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-2.38.

To a solution of acetaldehyde (6.7 μL, 0.12 mmol, 2.5 equiv) and 2,6-di-*tert*-butylpyridine (16 μL, 0.072 mmol, 1.5 equiv) in CH_2Cl_2 (2.5 mL) at -78 ^{o}C was added BF_3-OEt_2 (15 μL, 0.12 mmol, 2.5 equiv). The solution was stirred for 10 minutes before molybdenum complex *Z*-(±)-**2.28a** (25.0 mg, 0.048 mmol, 1.0 equiv) was added in CH_2Cl_2 (0.5 mL). The solution was stirred at -78 ^{o}C for 1 hour and then warmed to -40 ^{o}C. After stirring at -40 ^{o}C for 2 hours, aq $NaHCO_3$ (10 mL) was added, the solution was warmed to room temperature, and then poured into a separatory funnel. The layers were

separated and the aqueous layer was extracted with CH_2Cl_2 (5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography over silica gel with hexanes-EtOAc (2:1), affording (±)-**2.38** (3.2 mg, 0.0057 mmol, 12 %) as an orange solid.

(±)-**2.38**: TLC: R_f = 0.39 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3432 (br), 3127 (w), 2926 (m), 1965 (s), 1880 (s), 1664 (m), 1505 (m), 1409 (s), 1305 (s), 1247 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 1.8 Hz, 1 H), 7.92 (d, *J* = 2.4 Hz, 1 H), 7.69 (d, *J* = 1.8 Hz, 1 H), 7.61 (d, *J* = 1.8 Hz, 1 H), 7.59 (d, *J* = 2.4 Hz, 1 H), 7.52 (dd, *J* = 4.8 Hz, 2.4 Hz, 1 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 6.32 (t, *J* = 2.4 Hz, 1 H), 6.25 (t, *J* = 2.4 Hz, 1 H), 6.20 (t, *J* = 2.4 Hz, 1 H), 5.78 (dd, *J* = 17.4 Hz, 10.8 Hz, 1 H), 5.46 (d, *J* = 17.4 Hz, 1 H), 5.33 (d, *J* = 10.8 Hz, 1 H), 4.66 (dd, *J* = 5.4 Hz, 2.4 Hz, 1 H), 4.15 (dd, *J* = 5.4 Hz, 4.8 Hz, 1 H), 3.86 (app pent, *J* = 6.6 Hz, 1 H), 2.29-2.32 (m, 1 H), 2.07 (br s, 1 H), 1.12 (d, *J* = 6.0 Hz, 3 Hz), 0.79 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 226.1, 223.6, 199.0, 147.7, 142.9, 141.5, 136.9, 136.6, 136.5, 134.8, 116.1, 108.0, 106.6, 106.1, 105.8, 87.0, 67.9, 65.0, 63.3, 44.4, 20.1, 9.2. HRMS (ESI) Calcd for $C_{22}H_{25}BMoN_6O_5$ ($[M+H]^+$): 563.1106. Found: 563.1107.

Crystal Structure Analyses

Suitable crystals of *anti*-**2.22b**, *anti*-**2.23b**, **2.30a**, **2.33**, **2.34a**, and **2.34b** were obtained by diffusion recrystallization from CH_2Cl_2/hexanes. These crystals were coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART 1000 CCD sealed tube diffractometer with graphite monochromated CuK_α (1.54178 Å) radiation. Data were measured using a

series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART [99] software. Frame integration and final cell refinements were done using SAINT [100] software. The final cell parameters were determined from least-squares refinement on 5420 reflections. The SADABS [101] program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V5.10).[102] All the hydrogen atoms were located in a difference Fourier map and were included in the final cycles of least squares with isotropic U_{ij} 's; all non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography* [103] . Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V5.10 software.

[99] SMART Version 5.628, **2003**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[100] SAINT Version 6.02, **1999**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[101] SADABS, **1996**, George Sheldrick, University of Göttingen,
[102] SHELXTL V5.10, **1997**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[103] A. J. C. Wilson (ed), *International Tables for X-ray Crystallography, Volume C.* Kynoch, Academic Publishers, Dordrecht, **1992**, Tables 6.1.1.4 (pp. 500-502) and 4.2.6.8 (pp. 219-222).

Table 2.7. Crystal data and structure refinement for *anti*-2.22b

Identification code	***anti*-2.22b**	
Empirical formula	C19 H20 B Cl3 Mo N6 O5	
Formula weight	625.51	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.4627(2) Å	α= 72.5130(10)°.
	b = 10.5711(2) Å	β= 80.9270(10)°.
	c = 12.7700(2) Å	γ = 84.3610(10)°.
Volume	1201.36(4) $Å^3$	
Z	2	
Density (calculated)	1.729 Mg/m^3	
Absorption coefficient	7.931 mm^{-1}	
F(000)	628	
Crystal size	0.33 x 0.26 x 0.11 mm^3	
Theta range for data collection	3.66 to 66.55°.	
Index ranges	-10<=h<=10, -10<=k<=12, -15<=l<=13	
Reflections collected	5747	
Independent reflections	3544 [R(int) = 0.0174]	
Completeness to theta = 66.55°	83.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4758 and 0.1794	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3544 / 0 / 394	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.1357	
R indices (all data)	R1 = 0.0418, wR2 = 0.1373	
Largest diff. peak and hole	0.787 and -1.034 $e.Å^{-3}$	

Table 2.8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for *anti*-2.22b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
B(1)	4967(7)	2930(6)	8219(5)	25(1)
C(1)	4449(6)	7941(6)	5629(4)	28(1)
C(2)	4298(6)	6895(5)	5211(4)	23(1)
C(3)	2885(6)	6614(5)	5205(4)	23(1)
C(4)	1753(6)	7638(5)	5187(4)	23(1)
C(5)	2126(6)	8971(5)	5229(4)	23(1)
C(6)	1938(6)	10033(5)	4129(5)	30(1)
C(7)	3100(8)	9843(7)	3210(5)	40(2)
C(8)	1489(7)	6456(5)	7384(4)	29(1)
C(9)	3745(6)	7479(5)	7571(4)	23(1)
C(10)	2198(6)	3491(6)	6421(4)	25(1)
C(11)	2335(6)	2120(6)	6674(5)	29(1)
C(12)	3399(6)	1742(5)	7348(5)	28(1)
C(13)	2895(6)	5117(6)	9691(4)	28(1)
C(14)	3217(8)	4114(7)	10604(5)	38(2)
C(15)	4025(7)	3191(7)	10194(5)	33(1)
C(16)	7107(6)	5686(6)	6556(4)	24(1)
C(17)	8242(6)	4764(6)	6840(5)	29(1)
C(18)	7588(6)	3612(6)	7459(5)	29(1)
Mo(1)	3539(1)	5966(1)	7013(1)	17(1)
N(1)	3144(4)	3935(4)	6900(3)	20(1)
N(2)	3884(5)	2829(4)	7469(3)	23(1)
N(3)	3487(4)	4810(4)	8762(3)	20(1)
N(4)	4178(5)	3602(4)	9081(4)	25(1)
N(5)	5851(4)	5130(4)	6979(3)	22(1)
N(6)	6155(5)	3838(4)	7533(4)	24(1)
O(1)	3539(4)	9066(4)	5484(3)	29(1)
O(2)	508(4)	7498(4)	5083(3)	31(1)
O(3)	2041(5)	11324(4)	4227(4)	39(1)
O(4)	296(4)	6724(5)	7652(4)	40(1)
O(5)	3800(4)	8324(4)	7947(3)	33(1)
Cl(1S)	2393(2)	354(2)	311(1)	51(1)
Cl(2S)	431(2)	2574(2)	-494(2)	62(1)
Cl(3S)	-374(2)	522(2)	1569(2)	70(1)
C(1S)	1023(7)	1450(7)	689(6)	44(2)

Table 2.9. Bond lengths [Å] and angles [°] for *anti*-2.22b

B(1)-N(6)	1.533(8)	C(3)-C(4)	1.444(7)
B(1)-N(2)	1.539(7)	C(3)-Mo(1)	2.366(5)
B(1)-N(4)	1.543(7)	C(4)-O(2)	1.234(6)
C(1)-O(1)	1.381(7)	C(4)-C(5)	1.504(7)
C(1)-C(2)	1.392(8)	C(5)-O(1)	1.445(6)
C(1)-Mo(1)	2.425(6)	C(5)-C(6)	1.536(7)
C(2)-C(3)	1.400(8)	C(6)-O(3)	1.422(7)
C(2)-Mo(1)	2.244(5)	C(6)-C(7)	1.522(9)

C(8)-O(4)	1.159(7)	N(5)-C(16)-C(17)	110.6(5)
C(8)-Mo(1)	1.979(6)	C(18)-C(17)-C(16)	104.3(5)
C(9)-O(5)	1.142(6)	N(6)-C(18)-C(17)	109.3(5)
C(9)-Mo(1)	1.974(5)	C(9)-Mo(1)-C(8)	80.7(2)
C(10)-N(1)	1.351(7)	C(9)-Mo(1)-N(3)	83.75(18)
C(10)-C(11)	1.385(8)	C(8)-Mo(1)-N(3)	86.85(19)
C(11)-C(12)	1.379(8)	C(9)-Mo(1)-C(2)	98.9(2)
C(12)-N(2)	1.337(7)	C(8)-Mo(1)-C(2)	111.0(2)
C(13)-N(3)	1.347(7)	N(3)-Mo(1)-C(2)	162.19(18)
C(13)-C(14)	1.371(9)	C(9)-Mo(1)-N(1)	163.44(19)
C(14)-C(15)	1.358(10)	C(8)-Mo(1)-N(1)	94.83(19)
C(15)-N(4)	1.343(7)	N(3)-Mo(1)-N(1)	80.08(15)
C(16)-N(5)	1.339(7)	C(2)-Mo(1)-N(1)	97.62(17)
C(16)-C(17)	1.393(8)	C(9)-Mo(1)-N(5)	98.40(18)
C(17)-C(18)	1.381(9)	C(8)-Mo(1)-N(5)	167.48(19)
C(18)-N(6)	1.347(7)	N(3)-Mo(1)-N(5)	80.64(15)
Mo(1)-N(3)	2.195(4)	C(2)-Mo(1)-N(5)	81.55(17)
Mo(1)-N(1)	2.265(4)	N(1)-Mo(1)-N(5)	82.48(15)
Mo(1)-N(5)	2.277(4)	C(9)-Mo(1)-C(3)	113.5(2)
N(1)-N(2)	1.369(6)	C(8)-Mo(1)-C(3)	81.5(2)
N(3)-N(4)	1.353(6)	N(3)-Mo(1)-C(3)	157.06(18)
N(5)-N(6)	1.362(6)	C(2)-Mo(1)-C(3)	35.24(19)
Cl(1S)-C(1S)	1.761(7)	N(1)-Mo(1)-C(3)	81.32(17)
Cl(2S)-C(1S)	1.751(8)	N(5)-Mo(1)-C(3)	110.06(17)
Cl(3S)-C(1S)	1.760(7)	C(9)-Mo(1)-C(1)	64.5(2)
N(6)-B(1)-N(2)	109.8(4)	C(8)-Mo(1)-C(1)	103.9(2)
N(6)-B(1)-N(4)	106.8(4)	N(3)-Mo(1)-C(1)	143.62(17)
N(2)-B(1)-N(4)	108.0(4)	C(2)-Mo(1)-C(1)	34.41(19)
O(1)-C(1)-C(2)	123.8(5)	N(1)-Mo(1)-C(1)	131.99(17)
O(1)-C(1)-Mo(1)	115.8(4)	N(5)-Mo(1)-C(1)	86.71(17)
C(2)-C(1)-Mo(1)	65.7(3)	C(3)-Mo(1)-C(1)	59.02(19)
C(1)-C(2)-C(3)	115.4(5)	C(10)-N(1)-N(2)	106.0(4)
C(1)-C(2)-Mo(1)	79.9(3)	C(10)-N(1)-Mo(1)	133.6(4)
C(3)-C(2)-Mo(1)	77.1(3)	N(2)-N(1)-Mo(1)	120.2(3)
C(2)-C(3)-C(4)	19.8(5)	C(12)-N(2)-N(1)	109.7(4)
C(2)-C(3)-Mo(1)	67.6(3)	C(12)-N(2)-B(1)	128.8(4)
C(4)-C(3)-Mo(1)	106.3(3)	N(1)-N(2)-B(1)	121.1(4)
O(2)-C(4)-C(3)	123.3(5)	C(13)-N(3)-N(4)	107.1(4)
O(2)-C(4)-C(5)	118.2(5)	C(13)-N(3)-Mo(1)	130.6(4)
C(3)-C(4)-C(5)	118.4(4)	N(4)-N(3)-Mo(1)	122.3(3)
O(1)-C(5)-C(4)	117.1(4)	C(15)-N(4)-N(3)	108.2(5)
O(1)-C(5)-C(6)	107.7(4)	C(15)-N(4)-B(1)	130.7(5)
C(4)-C(5)-C(6)	110.3(4)	N(3)-N(4)-B(1)	121.1(4)
O(3)-C(6)-C(7)	107.6(5)	C(16)-N(5)-N(6)	106.9(4)
O(3)-C(6)-C(5)	110.6(5)	C(16)-N(5)-Mo(1)	132.7(4)
C(7)-C(6)-C(5)	110.8(5)	N(6)-N(5)-Mo(1)	120.2(3)
O(4)-C(8)-Mo(1)	176.9(5)	C(18)-N(6)-N(5)	109.0(5)
O(5)-C(9)-Mo(1)	175.8(5)	C(18)-N(6)-B(1)	129.4(5)
N(1)-C(10)-C(11)	110.4(5)	N(5)-N(6)-B(1)	121.2(4)
C(12)-C(11)-C(10)	105.0(5)	C(1)-O(1)-C(5)	117.3(4)
N(2)-C(12)-C(11)	108.9(5)	Cl(2S)-C(1S)-Cl(3S)	112.1(4)
N(3)-C(13)-C(14)	109.8(5)	Cl(2S)-C(1S)-Cl(1S)	110.3(4)
C(15)-C(14)-C(13)	105.2(5)	Cl(3S)-C(1S)-Cl(1S)	109.1(4)
N(4)-C(15)-C(14)	109.7(6)		

Symmetry transformations used to generate equivalent atoms:

Table 2.10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for *anti*-2.22b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	29(3)	22(3)	23(3)	-5(2)	-7(2)	5(2)
C(1)	23(3)	35(3)	23(3)	-4(2)	-6(2)	0(2)
C(2)	31(3)	25(3)	10(2)	0(2)	-4(2)	3(2)
C(3)	34(3)	23(3)	11(2)	-3(2)	-9(2)	-2(2)
C(4)	27(3)	24(3)	21(3)	-7(2)	-8(2)	-2(2)
C(5)	28(3)	17(3)	24(3)	-8(2)	-7(2)	3(2)
C(6)	39(3)	19(3)	36(3)	-8(2)	-15(3)	2(2)
C(7)	56(4)	35(4)	27(3)	-5(3)	-7(3)	0(3)
C(8)	41(4)	28(3)	20(3)	-9(2)	-7(2)	-2(2)
C(9)	26(3)	23(3)	24(3)	-11(2)	-9(2)	1(2)
C(10)	21(3)	39(3)	16(3)	-9(2)	0(2)	-6(2)
C(11)	39(3)	29(3)	23(3)	-11(2)	-2(2)	-10(2)
C(12)	37(3)	19(3)	26(3)	-6(2)	2(2)	-4(2)
C(13)	36(3)	31(3)	20(3)	-13(2)	-2(2)	0(2)
C(14)	54(4)	51(4)	14(3)	-15(3)	-1(3)	-10(3)
C(15)	44(4)	36(4)	17(3)	1(2)	-12(3)	-9(3)
C(16)	26(3)	27(3)	17(3)	-8(2)	1(2)	-4(2)
C(17)	18(3)	40(3)	36(3)	-21(3)	-5(2)	3(2)
C(18)	29(3)	34(3)	29(3)	-16(3)	-13(2)	7(2)
Mo(1)	18(1)	19(1)	14(1)	-7(1)	-2(1)	1(1)
N(1)	20(2)	20(2)	18(2)	-4(2)	0(2)	2(2)
N(2)	30(2)	19(2)	19(2)	-6(2)	-1(2)	-1(2)
N(3)	22(2)	19(2)	18(2)	-5(2)	2(2)	-1(2)
N(4)	25(2)	31(2)	20(2)	-7(2)	-6(2)	-3(2)
N(5)	23(2)	24(2)	18(2)	-7(2)	-5(2)	2(2)
N(6)	22(2)	25(2)	25(2)	-8(2)	-7(2)	4(2)
O(1)	27(2)	27(2)	33(2)	-7(2)	-15(2)	3(2)
O(2)	26(2)	32(2)	37(2)	-10(2)	-12(2)	-1(2)
O(3)	31(2)	25(2)	61(3)	-10(2)	-14(2)	3(2)
O(4)	23(2)	59(3)	43(3)	-24(2)	2(2)	4(2)
O(5)	40(2)	31(2)	35(2)	-18(2)	-8(2)	0(2)
Cl(1S)	56(1)	50(1)	46(1)	-16(1)	-6(1)	3(1)
Cl(2S)	67(1)	61(1)	57(1)	-15(1)	-21(1)	12(1)
Cl(3S)	61(1)	93(2)	65(1)	-35(1)	16(1)	-39(1)
C(1S)	45(4)	55(4)	41(4)	-24(3)	-4(3)	-13(3)

Table 2.11. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for *anti*-2.22b

	x	y	z	U(eq)
H(1B)	5470(60)	1940(50)	8590(50)	19(13)
H(1)	5290(60)	8210(50)	5710(40)	8(12)
H(2)	5100(60)	6370(60)	5000(50)	19(14)
H(3)	2680(60)	5960(60)	4990(50)	27(16)
H(5)	1490(70)	9120(60)	5860(60)	38(18)
H(6)	990(80)	9930(70)	3870(60)	42(18)
H(7A)	4070(90)	10020(70)	3360(60)	50(20)

H(7B)	2940(80)	10550(80)	2680(70)	50(20)
H(7C)	3110(70)	8910(70)	3080(50)	35(17)
H(10)	1590(70)	4110(70)	5940(60)	41(18)
H(11)	1870(70)	1500(70)	6480(50)	38(18)
H(12)	3750(70)	930(70)	7680(50)	30(16)
H(13)	2450(70)	5910(70)	9620(50)	30
H(14)	3040(60)	4130(60)	11150(50)	16(15)
H(15)	4380(60)	2550(60)	10440(50)	11(15)
H(16)	7140(60)	6550(60)	6110(50)	20(14)
H(17)	9220(80)	5020(60)	6620(50)	36(17)
H(18)	7930(70)	2860(70)	7780(60)	34(18)
H(3O)	1280(80)	11580(70)	4360(50)	30
H(1S)	1420(70)	1960(60)	1160(50)	30(16)

Table 2.12. Torsion angles [°] for *anti*-2.22b

O(1)-C(1)-C(2)-C(3)	-35.4(7)
Mo(1)-C(1)-C(2)-C(3)	70.4(4)
O(1)-C(1)-C(2)-Mo(1)	-105.8(5)
C(1)-C(2)-C(3)-C(4)	24.4(7)
Mo(1)-C(2)-C(3)-C(4)	96.5(4)
C(1)-C(2)-C(3)-Mo(1)	-72.1(4)
C(2)-C(3)-C(4)-O(2)	173.4(5)
Mo(1)-C(3)-C(4)-O(2)	-113.4(5)
C(2)-C(3)-C(4)-C(5)	-2.9(7)
Mo(1)-C(3)-C(4)-C(5)	70.2(5)
O(2)-C(4)-C(5)-O(1)	172.7(4)
C(3)-C(4)-C(5)-O(1)	-10.8(7)
O(2)-C(4)-C(5)-C(6)	-63.7(6)
C(3)-C(4)-C(5)-C(6)	112.8(5)
O(1)-C(5)-C(6)-O(3)	-61.4(6)
C(4)-C(5)-C(6)-O(3)	169.7(5)
O(1)-C(5)-C(6)-C(7)	57.8(6)
C(4)-C(5)-C(6)-C(7)	-71.0(6)
N(1)-C(10)-C(11)-C(12)	0.9(6)
C(10)-C(11)-C(12)-N(2)	-1.1(6)
N(3)-C(13)-C(14)-C(15)	0.1(7)
C(13)-C(14)-C(15)-N(4)	-0.7(7)
N(5)-C(16)-C(17)-C(18)	0.3(6)
C(16)-C(17)-C(18)-N(6)	0.2(6)
O(5)-C(9)-Mo(1)-C(8)	45(6)
O(5)-C(9)-Mo(1)-N(3)	-43(6)
O(5)-C(9)-Mo(1)-C(2)	155(6)
O(5)-C(9)-Mo(1)-N(1)	-31(6)
O(5)-C(9)-Mo(1)-N(5)	-123(6)
O(5)-C(9)-Mo(1)-C(3)	121(6)
O(5)-C(9)-Mo(1)-C(1)	155(6)
O(4)-C(8)-Mo(1)-C(9)	-68(9)
O(4)-C(8)-Mo(1)-N(3)	16(9)
O(4)-C(8)-Mo(1)-C(2)	-164(9)
O(4)-C(8)-Mo(1)-N(1)	96(9)
O(4)-C(8)-Mo(1)-N(5)	19(10)

O(4)-C(8)-Mo(1)-C(3)	176(9)
O(4)-C(8)-Mo(1)-C(1)	-129(9)
C(1)-C(2)-Mo(1)-C(9)	0.7(3)
C(3)-C(2)-Mo(1)-C(9)	-118.5(3)
C(1)-C(2)-Mo(1)-C(8)	84.1(4)
C(3)-C(2)-Mo(1)-C(8)	-35.1(4)
C(1)-C(2)-Mo(1)-N(3)	-96.5(6)
C(3)-C(2)-Mo(1)-N(3)	144.3(5)
C(1)-C(2)-Mo(1)-N(1)	-177.7(3)
C(3)-C(2)-Mo(1)-N(1)	63.1(3)
C(1)-C(2)-Mo(1)-N(5)	-96.6(3)
C(3)-C(2)-Mo(1)-N(5)	144.2(3)
C(1)-C(2)-Mo(1)-C(3)	119.2(5)
C(3)-C(2)-Mo(1)-C(1)	-119.2(5)
C(2)-C(3)-Mo(1)-C(9)	71.2(4)
C(4)-C(3)-Mo(1)-C(9)	-44.9(4)
C(2)-C(3)-Mo(1)-C(8)	147.1(3)
C(4)-C(3)-Mo(1)-C(8)	31.0(4)
C(2)-C(3)-Mo(1)-N(3)	-152.7(4)
C(4)-C(3)-Mo(1)-N(3)	91.2(5)
C(4)-C(3)-Mo(1)-C(2)	-116.1(5)
C(2)-C(3)-Mo(1)-N(1)	-116.6(3)
C(4)-C(3)-Mo(1)-N(1)	127.3(4)
C(2)-C(3)-Mo(1)-N(5)	-38.0(4)
C(4)-C(3)-Mo(1)-N(5)	-154.1(3)
C(2)-C(3)-Mo(1)-C(1)	35.1(3)
C(4)-C(3)-Mo(1)-C(1)	-81.0(4)
O(1)-C(1)-Mo(1)-C(9)	-61.9(4)
C(2)-C(1)-Mo(1)-C(9)	-179.2(4)
O(1)-C(1)-Mo(1)-C(8)	10.5(4)
C(2)-C(1)-Mo(1)-C(8)	-106.9(3)
O(1)-C(1)-Mo(1)-N(3)	-93.5(4)
C(2)-C(1)-Mo(1)-N(3)	149.2(3)
O(1)-C(1)-Mo(1)-C(2)	117.3(5)
O(1)-C(1)-Mo(1)-N(1)	120.4(4)
C(2)-C(1)-Mo(1)-N(1)	3.0(4)
O(1)-C(1)-Mo(1)-N(5)	-162.8(4)
C(2)-C(1)-Mo(1)-N(5)	79.8(3)
O(1)-C(1)-Mo(1)-C(3)	81.4(4)
C(2)-C(1)-Mo(1)-C(3)	-36.0(3)
C(11)-C(10)-N(1)-N(2)	-0.3(6)
C(11)-C(10)-N(1)-Mo(1)	-175.2(4)
C(9)-Mo(1)-N(1)-C(10)	118.7(7)
C(8)-Mo(1)-N(1)-C(10)	45.2(5)
N(3)-Mo(1)-N(1)-C(10)	131.2(5)
C(2)-Mo(1)-N(1)-C(10)	-66.7(5)
N(5)-Mo(1)-N(1)-C(10)	-147.1(5)
C(3)-Mo(1)-N(1)-C(10)	-35.3(5)
C(1)-Mo(1)-N(1)-C(10)	-68.4(5)
C(9)-Mo(1)-N(1)-N(2)	-55.5(8)
C(8)-Mo(1)-N(1)-N(2)	-129.1(4)
N(3)-Mo(1)-N(1)-N(2)	-43.1(3)
C(2)-Mo(1)-N(1)-N(2)	119.0(4)
N(5)-Mo(1)-N(1)-N(2)	38.6(3)
C(3)-Mo(1)-N(1)-N(2)	150.4(4)
C(1)-Mo(1)-N(1)-N(2)	117.3(4)

C(11)-C(12)-N(2)-N(1)	1.0(6)
C(11)-C(12)-N(2)-B(1)	174.0(5)
C(10)-N(1)-N(2)-C(12)	-0.4(5)
Mo(1)-N(1)-N(2)-C(12)	175.3(3)
C(10)-N(1)-N(2)-B(1)	-174.1(4)
Mo(1)-N(1)-N(2)-B(1)	1.6(6)
N(6)-B(1)-N(2)-C(12)	128.0(5)
N(4)-B(1)-N(2)-C(12)	-115.9(6)
N(6)-B(1)-N(2)-N(1)	-59.7(6)
N(4)-B(1)-N(2)-N(1)	56.4(6)
C(14)-C(13)-N(3)-N(4)	0.6(6)
C(14)-C(13)-N(3)-Mo(1)	-176.0(4)
C(9)-Mo(1)-N(3)-C(13)	37.2(5)
C(8)-Mo(1)-N(3)-C(13)	-43.8(5)
C(2)-Mo(1)-N(3)-C(13)	136.7(6)
N(1)-Mo(1)-N(3)-C(13)	-139.3(5)
N(5)-Mo(1)-N(3)-C(13)	136.8(5)
C(3)-Mo(1)-N(3)-C(13)	-103.0(6)
C(1)-Mo(1)-N(3)-C(13)	65.5(6)
C(9)-Mo(1)-N(3)-N(4)	-139.0(4)
C(8)-Mo(1)-N(3)-N(4)	140.0(4)
C(2)-Mo(1)-N(3)-N(4)	-39.4(8)
N(1)-Mo(1)-N(3)-N(4)	44.6(4)
N(5)-Mo(1)-N(3)-N(4)	-39.4(4)
C(3)-Mo(1)-N(3)-N(4)	80.8(6)
C(1)-Mo(1)-N(3)-N(4)	-110.6(4)
C(14)-C(15)-N(4)-N(3)	1.0(7)
C(14)-C(15)-N(4)-B(1)	-179.0(6)
C(13)-N(3)-N(4)-C(15)	-1.0(6)
Mo(1)-N(3)-N(4)-C(15)	176.0(4)
C(13)-N(3)-N(4)-B(1)	179.1(5)
Mo(1)-N(3)-N(4)-B(1)	-4.0(6)
N(6)-B(1)-N(4)-C(15)	-118.0(6)
N(2)-B(1)-N(4)-C(15)	123.9(6)
N(6)-B(1)-N(4)-N(3)	61.9(6)
N(2)-B(1)-N(4)-N(3)	-56.2(6)
C(17)-C(16)-N(5)-N(6)	-0.6(6)
C(17)-C(16)-N(5)-Mo(1)	174.8(3)
C(9)-Mo(1)-N(5)-C(16)	-50.3(5)
C(8)-Mo(1)-N(5)-C(16)	-135.3(8)
N(3)-Mo(1)-N(5)-C(16)	-132.5(5)
C(2)-Mo(1)-N(5)-C(16)	47.5(5)
N(1)-Mo(1)-N(5)-C(16)	146.4(5)
C(3)-Mo(1)-N(5)-C(16)	68.6(5)
C(1)-Mo(1)-N(5)-C(16)	13.3(5)
C(9)-Mo(1)-N(5)-N(6)	124.6(4)
C(8)-Mo(1)-N(5)-N(6)	39.6(10)
N(3)-Mo(1)-N(5)-N(6)	42.5(3)
C(2)-Mo(1)-N(5)-N(6)	-137.6(4)
N(1)-Mo(1)-N(5)-N(6)	-38.7(3)
C(3)-Mo(1)-N(5)-N(6)	-116.5(4)
C(1)-Mo(1)-N(5)-N(6)	-171.8(4)
C(17)-C(18)-N(6)-N(5)	-0.6(6)
C(17)-C(18)-N(6)-B(1)	-173.2(5)
C(16)-N(5)-N(6)-C(18)	0.8(6)
Mo(1)-N(5)-N(6)-C(18)	-175.3(3)

C(16)-N(5)-N(6)-B(1)	174.1(4)
Mo(1)-N(5)-N(6)-B(1)	-2.0(6)
N(2)-B(1)-N(6)-C(18)	-128.3(5)
N(4)-B(1)-N(6)-C(18)	114.8(6)
N(2)-B(1)-N(6)-N(5)	59.8(6)
N(4)-B(1)-N(6)-N(5)	-57.1(6)
C(2)-C(1)-O(1)-C(5)	21.6(7)
Mo(1)-C(1)-O(1)-C(5)	-55.3(5)
C(4)-C(5)-O(1)-C(1)	2.2(6)
C(6)-C(5)-O(1)-C(1)	-122.6(5)

Symmetry transformations used to generate equivalent atoms:

Table 2.13. Hydrogen bonds for *anti*-2.22b [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3O)...O(2)#1	0.76(7)	2.01(7)	2.746(6)	166(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z+1

Table 2.14. Crystal data and structure refinement for *anti*-2.23b

Identification code	*anti*-**2.23b**	
Empirical formula	C29 H33 B Mo N7 O6	
Formula weight	682.37	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4754(2) Å	α= 104.527(1)°.
	b = 12.8534(2) Å	β= 112.404(1)°.
	c = 13.4732(3) Å	γ = 103.191(1)°.
Volume	1513.55(5) $Å^3$	
Z	2	
Density (calculated)	1.497 Mg/m^3	
Absorption coefficient	4.005 mm^{-1}	
F(000)	702	
Crystal size	0.28 x 0.22 x 0.12 mm^3	

Theta range for data collection	3.81 to 66.04°.
Index ranges	-12<=h<=12, -15<=k<=14, -13<=l<=15
Reflections collected	6979
Independent reflections	4400 [R(int) = 0.0169]
Completeness to theta = 66.04°	83.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6451 and 0.4002
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4400 / 0 / 492
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.1112
R indices (all data)	R1 = 0.0385, wR2 = 0.1118
Largest diff. peak and hole	1.403 and -0.719 e.$Å^{-3}$

Table 2.15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for *anti*-2.23b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
B(1)	6844(5)	7750(4)	2832(4)	28(1)
C(1)	6402(4)	3586(3)	963(3)	25(1)
C(2)	6777(4)	4298(3)	400(3)	26(1)
C(3)	8264(5)	4637(3)	607(4)	30(1)
C(4)	9067(4)	3853(3)	837(3)	29(1)
C(5)	8343(4)	2744(3)	956(4)	28(1)
C(6)	6652(4)	2058(3)	1683(4)	31(1)
C(7)	5301(7)	1663(5)	2697(6)	50(1)
C(8)	4251(5)	2083(4)	3026(4)	37(1)
C(9)	2745(6)	1540(4)	2324(4)	40(1)
C(10)	1754(7)	1927(5)	2603(6)	56(1)
C(11)	2253(7)	2854(5)	3587(6)	57(2)
C(12)	3754(9)	3407(5)	4318(5)	62(2)
C(13)	4752(7)	3022(5)	4036(5)	52(1)
C(14)	8033(5)	1725(4)	-108(4)	36(1)
C(15)	6834(9)	1666(6)	-1196(5)	63(2)
C(16)	10161(5)	5908(4)	2692(4)	37(1)
C(17)	8401(4)	4637(3)	3167(3)	30(1)
C(18)	8011(5)	7171(4)	607(4)	30(1)
C(19)	7755(5)	8169(4)	532(4)	36(1)
C(20)	7242(5)	8493(4)	1319(4)	31(1)
C(21)	10088(5)	7444(4)	4838(4)	31(1)
C(22)	10229(5)	8465(4)	5575(4)	36(1)
C(23)	9072(5)	8732(4)	4938(4)	33(1)
C(24)	4814(4)	4796(3)	2285(3)	28(1)
C(25)	3849(5)	5280(4)	2500(4)	33(1)

C(26)	4439(4)	6421(4)	2672(3)	30(1)
C(1S)	1578(8)	8926(6)	3237(6)	78(2)
C(2S)	3026(7)	9201(6)	4388(6)	69(2)
C(3S)	4295(8)	9782(13)	4426(8)	179(7)
Mo(1)	8016(1)	5560(1)	2224(1)	22(1)
N(1)	7001(4)	2718(3)	1108(3)	27(1)
N(3)	7683(4)	6888(3)	1385(3)	26(1)
N(4)	7189(4)	7713(3)	1820(3)	26(1)
N(5)	8901(3)	7083(3)	3810(3)	26(1)
N(6)	8272(4)	7902(3)	3881(3)	26(1)
N(7)	5921(3)	5588(3)	2301(3)	24(1)
N(8)	5674(3)	6599(3)	2542(3)	25(1)
O(1)	10268(3)	4003(3)	859(3)	37(1)
O(2)	7172(3)	1319(2)	1865(3)	37(1)
O(3)	5663(3)	2293(2)	2009(2)	32(1)
O(4)	7706(5)	662(3)	29(3)	61(1)
O(5)	11407(3)	6114(3)	3036(3)	59(1)
O(6)	8662(4)	4090(3)	3724(3)	51(1)

Table 2.16. Bond lengths [Å] and angles [°] for *anti*-2.23b

B(1)-N(4)	1.531(6)	C(18)-C(19)	1.390(6)
B(1)-N(8)	1.536(6)	C(19)-C(20)	1.379(6)
B(1)-N(6)	1.547(6)	C(20)-N(4)	1.345(5)
C(1)-C(2)	1.407(5)	C(21)-N(5)	1.334(5)
C(1)-N(1)	1.417(5)	C(21)-C(22)	1.370(6)
C(1)-Mo(1)	2.424(4)	C(22)-C(23)	1.367(6)
C(2)-C(3)	1.411(6)	C(23)-N(6)	1.337(5)
C(2)-Mo(1)	2.228(4)	C(24)-N(7)	1.346(5)
C(3)-C(4)	1.472(6)	C(24)-C(25)	1.383(6)
C(3)-Mo(1)	2.344(4)	C(25)-C(26)	1.376(6)
C(4)-O(1)	1.216(5)	C(26)-N(8)	1.348(5)
C(4)-C(5)	1.532(5)	C(1S)-C(2S)	1.587(9)
C(5)-N(1)	1.490(5)	C(2S)-C(3S)	1.343(9)
C(5)-C(14)	1.545(6)	C(3S)-C(3S)#1	1.527(15)
C(6)-O(2)	1.228(5)	Mo(1)-N(5)	2.196(3)
C(6)-O(3)	1.334(5)	Mo(1)-N(7)	2.245(3)
C(6)-N(1)	1.364(5)	Mo(1)-N(3)	2.292(3)
C(7)-O(3)	1.470(5)	N(3)-N(4)	1.380(4)
C(7)-C(8)	1.490(7)	N(5)-N(6)	1.366(5)
C(8)-C(9)	1.378(7)	N(7)-N(8)	1.367(4)
C(8)-C(13)	1.387(7)	N(4)-B(1)-N(8)	110.5(3)
C(9)-C(10)	1.381(7)	N(4)-B(1)-N(6)	107.9(3)
C(10)-C(11)	1.358(9)	N(8)-B(1)-N(6)	106.8(3)
C(11)-C(12)	1.380(9)	C(2)-C(1)-N(1)	122.1(3)
C(12)-C(13)	1.389(9)	C(2)-C(1)-Mo(1)	64.9(2)
C(14)-O(4)	1.408(5)	N(1)-C(1)-Mo(1)	116.9(2)
C(14)-C(15)	1.493(8)	C(1)-C(2)-C(3)	115.7(4)
C(16)-O(5)	1.144(5)	C(1)-C(2)-Mo(1)	80.2(2)
C(16)-Mo(1)	1.991(4)	C(3)-C(2)-Mo(1)	76.6(2)
C(17)-O(6)	1.152(5)	C(2)-C(3)-C(4)	118.6(4)
C(17)-Mo(1)	1.942(4)	C(2)-C(3)-Mo(1)	67.6(2)
C(18)-N(3)	1.325(5)	C(4)-C(3)-Mo(1)	111.0(3)

O(1)-C(4)-C(3)	122.5(4)	N(5)-Mo(1)-N(7)	79.32(12)
O(1)-C(4)-C(5)	117.0(4)	C(2)-Mo(1)-N(7)	92.36(13)
C(3)-C(4)-C(5)	120.3(4)	C(17)-Mo(1)-N(3)	170.76(14)
N(1)-C(5)-C(4)	113.3(3)	C(16)-Mo(1)-N(3)	98.37(15)
N(1)-C(5)-C(14)	113.1(3)	N(5)-Mo(1)-N(3)	81.79(12)
C(4)-C(5)-C(14)	107.1(3)	C(2)-Mo(1)-N(3)	83.86(13)
O(2)-C(6)-O(3)	123.9(4)	N(7)-Mo(1)-N(3)	83.29(11)
O(2)-C(6)-N(1)	123.8(4)	C(17)-Mo(1)-C(3)	104.51(15)
O(3)-C(6)-N(1)	112.2(3)	C(16)-Mo(1)-C(3)	71.34(16)
O(3)-C(7)-C(8)	107.3(4)	N(5)-Mo(1)-C(3)	147.47(14)
C(9)-C(8)-C(13)	118.4(5)	C(2)-Mo(1)-C(3)	35.85(14)
C(9)-C(8)-C(7)	120.2(5)	N(7)-Mo(1)-C(3)	127.69(13)
C(13)-C(8)-C(7)	121.4(5)	N(3)-Mo(1)-C(3)	83.89(13)
C(8)-C(9)-C(10)	121.1(5)	C(17)-Mo(1)-C(1)	73.59(15)
C(11)-C(10)-C(9)	120.2(6)	C(16)-Mo(1)-C(1)	115.52(15)
C(10)-C(11)-C(12)	120.1(5)	N(5)-Mo(1)-C(1)	152.04(13)
C(11)-C(12)-C(13)	119.7(5)	C(2)-Mo(1)-C(1)	34.88(14)
C(8)-C(13)-C(12)	120.4(5)	N(7)-Mo(1)-C(1)	80.33(12)
O(4)-C(14)-C(15)	110.5(5)	N(3)-Mo(1)-C(1)	114.57(12)
O(4)-C(14)-C(5)	112.6(4)	C(3)-Mo(1)-C(1)	60.04(14)
C(15)-C(14)-C(5)	111.7(4)	C(6)-N(1)-C(1)	121.1(3)
O(5)-C(16)-Mo(1)	175.3(4)	C(6)-N(1)-C(5)	116.9(3)
O(6)-C(17)-Mo(1)	178.2(4)	C(1)-N(1)-C(5)	119.6(3)
N(3)-C(18)-C(19)	110.9(4)	C(18)-N(3)-N(4)	106.0(3)
C(20)-C(19)-C(18)	105.4(4)	C(18)-N(3)-Mo(1)	134.8(3)
N(4)-C(20)-C(19)	107.8(4)	N(4)-N(3)-Mo(1)	118.7(2)
N(5)-C(21)-C(22)	111.1(4)	C(20)-N(4)-N(3)	109.9(3)
C(23)-C(22)-C(21)	104.7(4)	C(20)-N(4)-B(1)	128.0(3)
N(6)-C(23)-C(22)	109.2(4)	N(3)-N(4)-B(1)	121.7(3)
N(7)-C(24)-C(25)	110.7(4)	C(21)-N(5)-N(6)	106.0(3)
C(26)-C(25)-C(24)	104.8(4)	C(21)-N(5)-Mo(1)	131.3(3)
N(8)-C(26)-C(25)	109.1(4)	N(6)-N(5)-Mo(1)	122.7(2)
C(3S)-C(2S)-C(1S)	114.5(6)	C(23)-N(6)-N(5)	108.9(3)
C(2S)-C(3S)-C(3S)#1	117.0(8)	C(23)-N(6)-B(1)	131.2(3)
C(17)-Mo(1)-C(16)	81.04(18)	N(5)-N(6)-B(1)	119.9(3)
C(17)-Mo(1)-N(5)	89.01(14)	C(24)-N(7)-N(8)	106.3(3)
C(16)-Mo(1)-N(5)	82.05(15)	C(24)-N(7)-Mo(1)	133.0(3)
C(17)-Mo(1)-C(2)	105.18(15)	N(8)-N(7)-Mo(1)	120.2(2)
C(16)-Mo(1)-C(2)	106.78(16)	C(26)-N(8)-N(7)	109.1(3)
N(5)-Mo(1)-C(2)	164.14(14)	C(26)-N(8)-B(1)	128.4(3)
C(17)-Mo(1)-N(7)	94.26(15)	N(7)-N(8)-B(1)	121.5(3)
C(16)-Mo(1)-N(7)	160.87(15)	C(6)-O(3)-C(7)	115.2(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Table 2.17. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for *anti*-2.23b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	35(2)	20(2)	34(2)	14(2)	15(2)	15(2)
C(1)	23(2)	18(2)	31(2)	7(2)	11(2)	7(2)

C(2)	31(2)	24(2)	23(2)	10(2)	12(2)	13(2)
C(3)	41(2)	22(2)	36(2)	15(2)	22(2)	16(2)
C(4)	31(2)	23(2)	32(2)	9(2)	14(2)	12(2)
C(5)	30(2)	23(2)	35(2)	13(2)	14(2)	15(2)
C(6)	32(2)	20(2)	34(2)	10(2)	11(2)	5(2)
C(7)	60(3)	46(3)	75(4)	45(3)	45(3)	25(3)
C(8)	50(3)	31(2)	43(2)	26(2)	27(2)	15(2)
C(9)	51(3)	36(3)	37(2)	19(2)	20(2)	14(2)
C(10)	49(3)	55(3)	72(4)	31(3)	31(3)	17(3)
C(11)	79(4)	60(4)	77(4)	42(3)	60(4)	41(3)
C(12)	111(5)	50(3)	48(3)	21(3)	52(4)	34(4)
C(13)	53(3)	45(3)	45(3)	21(2)	16(3)	7(3)
C(14)	46(3)	24(2)	43(2)	12(2)	25(2)	16(2)
C(15)	82(5)	50(3)	37(3)	4(2)	14(3)	30(4)
C(16)	29(2)	26(2)	46(3)	7(2)	12(2)	11(2)
C(17)	29(2)	22(2)	30(2)	8(2)	7(2)	8(2)
C(18)	40(2)	28(2)	33(2)	16(2)	21(2)	16(2)
C(19)	50(3)	32(2)	40(2)	25(2)	25(2)	18(2)
C(20)	38(2)	26(2)	37(2)	19(2)	18(2)	16(2)
C(21)	33(2)	30(2)	36(2)	21(2)	16(2)	14(2)
C(22)	37(2)	33(2)	28(2)	9(2)	9(2)	7(2)
C(23)	41(2)	21(2)	37(2)	10(2)	18(2)	14(2)
C(24)	28(2)	24(2)	30(2)	13(2)	12(2)	10(2)
C(25)	29(2)	34(2)	41(2)	17(2)	19(2)	13(2)
C(26)	32(2)	34(2)	31(2)	15(2)	16(2)	20(2)
C(3S)	41(4)	391(19)	121(7)	187(11)	24(5)	30(7)
Mo(1)	23(1)	17(1)	28(1)	12(1)	12(1)	9(1)
N(1)	29(2)	20(2)	34(2)	13(1)	14(2)	12(1)
N(3)	33(2)	23(2)	32(2)	16(1)	19(2)	15(2)
N(4)	33(2)	18(2)	34(2)	14(1)	16(2)	14(1)
N(5)	27(2)	25(2)	24(2)	10(1)	8(1)	9(1)
N(6)	32(2)	18(2)	33(2)	13(1)	17(2)	12(1)
N(7)	26(2)	23(2)	30(2)	13(1)	14(1)	13(1)
N(8)	31(2)	25(2)	26(2)	12(1)	15(2)	15(1)
O(1)	36(2)	33(2)	52(2)	16(1)	26(2)	17(1)
O(2)	47(2)	28(2)	51(2)	24(1)	27(2)	21(1)
O(3)	37(2)	27(2)	43(2)	21(1)	24(1)	11(1)
O(4)	108(3)	22(2)	65(2)	19(2)	50(2)	26(2)
O(5)	28(2)	47(2)	76(3)	-5(2)	18(2)	11(2)
O(6)	60(2)	32(2)	45(2)	26(2)	6(2)	11(2)

Table 2.18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for *anti*-2.23b

	x	y	z	U(eq)
H(1S1)	1506	9650	3154	117
H(1S2)	704	8506	3278	117
H(1S3)	1629	8454	2569	117
H(2S1)	2945	9656	5058	83
H(2S2)	3072	8465	4472	83
H(3S1)	4179	10454	4220	215
H(3S2)	4436	9276	3820	215

H(1)	5480(40)	3390(30)	910(30)	17(9)
H(2)	6080(40)	4550(30)	-40(30)	21(10)
H(3)	8570(50)	5090(40)	280(40)	30(11)
H(5)	9020(50)	2700(40)	1650(40)	33(12)
H(9)	2310(70)	890(50)	1620(50)	69(18)
H(10)	780(70)	1540(50)	2160(50)	56(16)
H(11)	1620(60)	3130(40)	3860(40)	47(14)
H(12)	4020(70)	4040(60)	4980(60)	80(20)
H(13)	5780(70)	3330(50)	4500(50)	70(18)
H(14)	8960(50)	1790(40)	-140(40)	29(11)
H(18)	8370(40)	6710(30)	210(30)	20(10)
H(19)	7860(40)	8500(30)	70(40)	20(10)
H(20)	6890(50)	9140(40)	1510(40)	32(11)
H(21)	10590(40)	7020(30)	4960(30)	13(9)
H(22)	10900(50)	8890(40)	6260(40)	33(12)
H(23)	8770(40)	9250(40)	5100(30)	11(9)
H(24)	4760(50)	3990(40)	2180(40)	30(11)
H(25)	2970(50)	4920(40)	2510(40)	30(11)
H(26)	4110(50)	7020(40)	2880(40)	39(13)
H(15A)	7190(80)	2360(70)	-1300(60)	80(20)
H(1B)	6510(50)	8520(40)	3080(40)	44(13)
H(7B)	4810(70)	770(60)	2200(50)	70(18)
H(15B)	6740(60)	1110(50)	-1830(50)	57(16)
H(4O)	7430(100)	780(80)	720(80)	130(30)
H(7A)	5990(100)	1720(80)	3170(80)	110(30)
H(15C)	5980(90)	1620(70)	-1160(70)	90(30)

Table 2.19. Torsion angles [°] for *anti*-2.23b

N(1)-C(1)-C(2)-C(3)	-37.4(5)
Mo(1)-C(1)-C(2)-C(3)	69.8(3)
N(1)-C(1)-C(2)-Mo(1)	-107.2(3)
C(1)-C(2)-C(3)-C(4)	30.5(5)
Mo(1)-C(2)-C(3)-C(4)	102.5(3)
C(1)-C(2)-C(3)-Mo(1)	-72.0(3)
C(2)-C(3)-C(4)-O(1)	169.2(4)
Mo(1)-C(3)-C(4)-O(1)	-115.6(4)
C(2)-C(3)-C(4)-C(5)	-5.4(6)
Mo(1)-C(3)-C(4)-C(5)	69.8(4)
O(1)-C(4)-C(5)-N(1)	170.9(3)
C(3)-C(4)-C(5)-N(1)	-14.2(5)
O(1)-C(4)-C(5)-C(14)	-63.7(5)
C(3)-C(4)-C(5)-C(14)	111.2(4)
O(3)-C(7)-C(8)-C(9)	90.8(5)
O(3)-C(7)-C(8)-C(13)	-89.1(6)
C(13)-C(8)-C(9)-C(10)	1.0(7)
C(7)-C(8)-C(9)-C(10)	-178.9(4)
C(8)-C(9)-C(10)-C(11)	-0.3(8)
C(9)-C(10)-C(11)-C(12)	-0.6(8)
C(10)-C(11)-C(12)-C(13)	0.9(8)
C(9)-C(8)-C(13)-C(12)	-0.7(7)
C(7)-C(8)-C(13)-C(12)	179.2(4)
C(11)-C(12)-C(13)-C(8)	-0.2(8)

N(1)-C(5)-C(14)-O(4)	-69.0(5)
C(4)-C(5)-C(14)-O(4)	165.5(4)
N(1)-C(5)-C(14)-C(15)	56.0(6)
C(4)-C(5)-C(14)-C(15)	-69.5(6)
N(3)-C(18)-C(19)-C(20)	0.0(5)
C(18)-C(19)-C(20)-N(4)	-0.5(5)
N(5)-C(21)-C(22)-C(23)	-1.1(5)
C(21)-C(22)-C(23)-N(6)	0.9(5)
N(7)-C(24)-C(25)-C(26)	-1.1(5)
C(24)-C(25)-C(26)-N(8)	1.2(5)
C(1S)-C(2S)-C(3S)-C(3S)#1	171.8(15)
O(6)-C(17)-Mo(1)-C(16)	-19(11)
O(6)-C(17)-Mo(1)-N(5)	-101(11)
O(6)-C(17)-Mo(1)-C(2)	87(11)
O(6)-C(17)-Mo(1)-N(7)	-180(100)
O(6)-C(17)-Mo(1)-N(3)	-106(11)
O(6)-C(17)-Mo(1)-C(3)	49(11)
O(6)-C(17)-Mo(1)-C(1)	102(11)
O(5)-C(16)-Mo(1)-C(17)	-41(5)
O(5)-C(16)-Mo(1)-N(5)	49(5)
O(5)-C(16)-Mo(1)-C(2)	-144(5)
O(5)-C(16)-Mo(1)-N(7)	36(5)
O(5)-C(16)-Mo(1)-N(3)	130(5)
O(5)-C(16)-Mo(1)-C(3)	-150(5)
O(5)-C(16)-Mo(1)-C(1)	-108(5)
C(1)-C(2)-Mo(1)-C(17)	25.7(3)
C(3)-C(2)-Mo(1)-C(17)	-93.9(3)
C(1)-C(2)-Mo(1)-C(16)	110.8(3)
C(3)-C(2)-Mo(1)-C(16)	-8.9(3)
C(1)-C(2)-Mo(1)-N(5)	-127.1(5)
C(3)-C(2)-Mo(1)-N(5)	113.3(5)
C(1)-C(2)-Mo(1)-N(7)	-69.3(2)
C(3)-C(2)-Mo(1)-N(7)	171.1(2)
C(1)-C(2)-Mo(1)-N(3)	-152.3(2)
C(3)-C(2)-Mo(1)-N(3)	88.1(2)
C(1)-C(2)-Mo(1)-C(3)	119.6(3)
C(3)-C(2)-Mo(1)-C(1)	-119.6(3)
C(2)-C(3)-Mo(1)-C(17)	95.9(3)
C(4)-C(3)-Mo(1)-C(17)	-17.5(3)
C(2)-C(3)-Mo(1)-C(16)	171.0(3)
C(4)-C(3)-Mo(1)-C(16)	57.6(3)
C(2)-C(3)-Mo(1)-N(5)	-152.2(2)
C(4)-C(3)-Mo(1)-N(5)	94.4(3)
C(4)-C(3)-Mo(1)-C(2)	-113.4(4)
C(2)-C(3)-Mo(1)-N(7)	-11.3(3)
C(4)-C(3)-Mo(1)-N(7)	-124.7(3)
C(2)-C(3)-Mo(1)-N(3)	-88.0(2)
C(4)-C(3)-Mo(1)-N(3)	158.6(3)
C(2)-C(3)-Mo(1)-C(1)	35.0(2)
C(4)-C(3)-Mo(1)-C(1)	-78.4(3)
C(2)-C(1)-Mo(1)-C(17)	-154.1(3)
N(1)-C(1)-Mo(1)-C(17)	-39.2(3)
C(2)-C(1)-Mo(1)-C(16)	-82.8(3)
N(1)-C(1)-Mo(1)-C(16)	32.1(3)
C(2)-C(1)-Mo(1)-N(5)	152.3(3)
N(1)-C(1)-Mo(1)-N(5)	-92.8(4)

N(1)-C(1)-Mo(1)-C(2)	114.9(4)
C(2)-C(1)-Mo(1)-N(7)	108.5(2)
N(1)-C(1)-Mo(1)-N(7)	-136.6(3)
C(2)-C(1)-Mo(1)-N(3)	30.5(3)
N(1)-C(1)-Mo(1)-N(3)	145.4(3)
C(2)-C(1)-Mo(1)-C(3)	-36.0(2)
N(1)-C(1)-Mo(1)-C(3)	78.9(3)
O(2)-C(6)-N(1)-C(1)	-177.7(4)
O(3)-C(6)-N(1)-C(1)	3.3(5)
O(2)-C(6)-N(1)-C(5)	-15.5(6)
O(3)-C(6)-N(1)-C(5)	165.5(3)
C(2)-C(1)-N(1)-C(6)	178.3(4)
Mo(1)-C(1)-N(1)-C(6)	102.3(4)
C(2)-C(1)-N(1)-C(5)	16.6(5)
Mo(1)-C(1)-N(1)-C(5)	-59.3(4)
C(4)-C(5)-N(1)-C(6)	-153.4(3)
C(14)-C(5)-N(1)-C(6)	84.5(4)
C(4)-C(5)-N(1)-C(1)	9.0(5)
C(14)-C(5)-N(1)-C(1)	-113.1(4)
C(19)-C(18)-N(3)-N(4)	0.6(5)
C(19)-C(18)-N(3)-Mo(1)	-170.9(3)
C(17)-Mo(1)-N(3)-C(18)	135.4(8)
C(16)-Mo(1)-N(3)-C(18)	49.7(4)
N(5)-Mo(1)-N(3)-C(18)	130.4(4)
C(2)-Mo(1)-N(3)-C(18)	-56.4(4)
N(7)-Mo(1)-N(3)-C(18)	-149.5(4)
C(3)-Mo(1)-N(3)-C(18)	-20.3(4)
C(1)-Mo(1)-N(3)-C(18)	-73.4(4)
C(17)-Mo(1)-N(3)-N(4)	-35.3(10)
C(16)-Mo(1)-N(3)-N(4)	-120.9(3)
N(5)-Mo(1)-N(3)-N(4)	-40.3(3)
C(2)-Mo(1)-N(3)-N(4)	132.9(3)
N(7)-Mo(1)-N(3)-N(4)	39.8(3)
C(3)-Mo(1)-N(3)-N(4)	169.0(3)
C(1)-Mo(1)-N(3)-N(4)	116.0(3)
C(19)-C(20)-N(4)-N(3)	0.9(5)
C(19)-C(20)-N(4)-B(1)	173.4(4)
C(18)-N(3)-N(4)-C(20)	-0.9(4)
Mo(1)-N(3)-N(4)-C(20)	172.2(3)
C(18)-N(3)-N(4)-B(1)	-173.9(4)
Mo(1)-N(3)-N(4)-B(1)	-0.8(4)
N(8)-B(1)-N(4)-C(20)	131.1(4)
N(6)-B(1)-N(4)-C(20)	-112.4(4)
N(8)-B(1)-N(4)-N(3)	-57.2(5)
N(6)-B(1)-N(4)-N(3)	59.3(4)
C(22)-C(21)-N(5)-N(6)	0.9(5)
C(22)-C(21)-N(5)-Mo(1)	178.8(3)
C(17)-Mo(1)-N(5)-C(21)	43.0(4)
C(16)-Mo(1)-N(5)-C(21)	-38.1(4)
C(2)-Mo(1)-N(5)-C(21)	-163.2(4)
N(7)-Mo(1)-N(5)-C(21)	137.5(4)
N(3)-Mo(1)-N(5)-C(21)	-137.8(4)
C(3)-Mo(1)-N(5)-C(21)	-73.0(4)
C(1)-Mo(1)-N(5)-C(21)	93.5(4)
C(17)-Mo(1)-N(5)-N(6)	-139.4(3)
C(16)-Mo(1)-N(5)-N(6)	139.5(3)

C(2)-Mo(1)-N(5)-N(6)	14.4(6)
N(7)-Mo(1)-N(5)-N(6)	-44.9(3)
N(3)-Mo(1)-N(5)-N(6)	39.8(3)
C(3)-Mo(1)-N(5)-N(6)	104.5(3)
C(1)-Mo(1)-N(5)-N(6)	-88.9(4)
C(22)-C(23)-N(6)-N(5)	-0.3(5)
C(22)-C(23)-N(6)-B(1)	178.5(4)
C(21)-N(5)-N(6)-C(23)	-0.4(4)
Mo(1)-N(5)-N(6)-C(23)	-178.5(3)
C(21)-N(5)-N(6)-B(1)	-179.4(3)
Mo(1)-N(5)-N(6)-B(1)	2.5(4)
N(4)-B(1)-N(6)-C(23)	119.9(4)
N(8)-B(1)-N(6)-C(23)	-121.2(4)
N(4)-B(1)-N(6)-N(5)	-61.3(4)
N(8)-B(1)-N(6)-N(5)	57.6(4)
C(25)-C(24)-N(7)-N(8)	0.6(4)
C(25)-C(24)-N(7)-Mo(1)	172.5(3)
C(17)-Mo(1)-N(7)-C(24)	-37.7(4)
C(16)-Mo(1)-N(7)-C(24)	-112.5(5)
N(5)-Mo(1)-N(7)-C(24)	-125.9(4)
C(2)-Mo(1)-N(7)-C(24)	67.7(3)
N(3)-Mo(1)-N(7)-C(24)	151.3(3)
C(3)-Mo(1)-N(7)-C(24)	74.3(4)
C(1)-Mo(1)-N(7)-C(24)	34.9(3)
C(17)-Mo(1)-N(7)-N(8)	133.3(3)
C(16)-Mo(1)-N(7)-N(8)	58.5(5)
N(5)-Mo(1)-N(7)-N(8)	45.1(3)
C(2)-Mo(1)-N(7)-N(8)	-121.3(3)
N(3)-Mo(1)-N(7)-N(8)	-37.8(3)
C(3)-Mo(1)-N(7)-N(8)	-114.7(3)
C(1)-Mo(1)-N(7)-N(8)	-154.2(3)
C(25)-C(26)-N(8)-N(7)	-0.9(4)
C(25)-C(26)-N(8)-B(1)	-169.4(4)
C(24)-N(7)-N(8)-C(26)	0.2(4)
Mo(1)-N(7)-N(8)-C(26)	-173.0(2)
C(24)-N(7)-N(8)-B(1)	169.7(3)
Mo(1)-N(7)-N(8)-B(1)	-3.5(4)
N(4)-B(1)-N(8)-C(26)	-132.1(4)
N(6)-B(1)-N(8)-C(26)	110.7(4)
N(4)-B(1)-N(8)-N(7)	60.6(4)
N(6)-B(1)-N(8)-N(7)	-56.6(4)
O(2)-C(6)-O(3)-C(7)	4.6(6)
N(1)-C(6)-O(3)-C(7)	-176.4(4)
C(8)-C(7)-O(3)-C(6)	177.1(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Table 2.20. Hydrogen bonds for *anti*-2.23b [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4O)...O(2)	1.06(9)	1.68(9)	2.715(5)	166(8)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Table 2.21. Crystal data and structure refinement for 2.30a

Identification code	**2.30a**	
Empirical formula	C20.50 H21 B Cl Mo N6 O4	
Formula weight	557.63	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9755(8) Å	α= 93.080(2)°.
	b = 11.0228(7) Å	β= 93.7400(10)°.
	c = 19.1046(13) Å	γ = 91.279(2)°.
Volume	2302.3(3) $Å^3$	
Z	4	
Density (calculated)	1.609 Mg/m^3	
Absorption coefficient	0.726 mm^{-1}	
F(000)	1128	
Crystal size	0.24 x 0.18 x 0.12 mm^3	
Theta range for data collection	1.85 to 27.10°.	
Index ranges	-14<=h<=14, -14<=k<=14, -24<=l<=24	
Reflections collected	38759	
Independent reflections	10145 [R(int) = 0.0352]	
Completeness to theta = 27.10°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.795778	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10145 / 9 / 553	
Goodness-of-fit on F^2	1.231	

Final R indices [I>2sigma(I)]	R1 = 0.0879, wR2 = 0.2027
R indices (all data)	R1 = 0.0945, wR2 = 0.2065
Largest diff. peak and hole	1.172 and -2.807 e.Å^{-3}

Table 2.22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 2.30a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
B(1)	6911(7)	-9(7)	3387(4)	37(2)
C(1)	3838(7)	-1093(7)	3585(4)	43(2)
C(2)	4317(8)	-2205(8)	3405(4)	49(2)
C(3)	5549(7)	-1954(7)	3356(4)	41(2)
C(4)	7162(6)	2244(8)	4842(4)	42(2)
C(5)	8320(7)	1805(9)	4928(4)	52(2)
C(6)	8377(7)	891(8)	4413(4)	48(2)
C(7)	5612(7)	2154(7)	2218(3)	38(2)
C(8)	6441(7)	1695(7)	1771(4)	44(2)
C(9)	7033(7)	828(7)	2135(4)	43(2)
C(10)	4274(7)	3059(9)	4780(4)	53(2)
C(11)	4012(8)	1854(10)	4827(4)	58(3)
C(12)	2978(9)	1423(8)	4422(5)	60(2)
C(14)	2066(7)	3419(9)	4652(5)	57(2)
C(13C)	3341(4)	3920(4)	4698(2)	30
O(3C)	3628(13)	4942(11)	4818(7)	30
O(4C)	1937(5)	2227(5)	4291(3)	30
C(13)	1937(5)	2227(5)	4291(3)	30
O(3)	1066(5)	1738(5)	4009(3)	30
O(4)	3341(4)	3920(4)	4698(2)	30
C(15)	1249(9)	4368(10)	4321(6)	70(3)
C(16)	1577(10)	4680(11)	3609(6)	75(3)
C(17)	1796(10)	3607(10)	5451(6)	30
C(18)	1447(10)	2661(9)	5795(6)	30
C(17C)	1593(13)	3024(13)	5346(6)	30
C(18C)	1977(12)	3637(12)	5925(6)	30
C(19)	4800(7)	3591(7)	3593(4)	42(2)
C(20)	3210(6)	1928(6)	3107(3)	34(1)
Mo(1)	4648(1)	1851(1)	3757(1)	30(1)
N(1)	4700(5)	-207(5)	3648(3)	35(1)
N(2)	5767(5)	-771(5)	3504(3)	37(1)
N(3)	6523(5)	1649(5)	4303(3)	34(1)
N(4)	7298(5)	807(6)	4042(3)	38(1)
N(5)	5707(5)	1611(5)	2828(3)	33(1)
N(6)	6601(5)	795(5)	2775(3)	35(1)
O(1)	4897(6)	4601(5)	3466(4)	62(2)
O(2)	2402(5)	1981(5)	2699(3)	51(1)
B(1B)	9917(7)	3012(7)	1586(4)	35(2)
C(1B)	11009(7)	6083(7)	1418(4)	42(2)
C(2B)	12123(8)	5606(7)	1612(4)	47(2)
C(3B)	11875(7)	4383(7)	1646(4)	40(2)

C(4B)	7655(7)	2836(7)	122(4)	40(2)
C(5B)	8088(7)	1677(7)	34(4)	47(2)
C(6B)	8995(7)	1607(7)	549(4)	45(2)
C(7B)	7751(7)	4299(6)	2746(4)	38(2)
C(8B)	8231(7)	3472(7)	3200(4)	42(2)
C(9B)	9089(7)	2870(7)	2832(4)	41(2)
C(10B)	6809(9)	5720(7)	194(4)	50(2)
C(11B)	8015(9)	5931(8)	136(4)	55(2)
C(12B)	8509(8)	6953(9)	547(5)	56(2)
C(14B)	6478(8)	7895(7)	307(4)	46(2)
C(13D)	5977(4)	6637(4)	275(2)	30
O(3D)	4974(12)	6377(14)	112(8)	30
O(4D)	7731(5)	8002(5)	674(3)	30
C(13B)	7731(5)	8002(5)	674(3)	30
O(3B)	8136(5)	8887(5)	960(3)	30
O(4B)	5977(4)	6637(4)	275(2)	30
C(15B)	5575(8)	8717(8)	651(5)	52(2)
C(16B)	5230(9)	8339(9)	1368(5)	63(2)
C(17B)	6483(10)	8199(10)	-461(6)	78(3)
C(18B)	7385(12)	8610(10)	-787(7)	91(4)
C(19B)	6312(7)	5143(7)	1361(4)	40(2)
C(20B)	7977(6)	6710(6)	1868(4)	35(1)
Mo(1B)	8061(1)	5300(1)	1215(1)	29(1)
N(1B)	10131(5)	5239(5)	1335(3)	32(1)
N(2B)	10690(5)	4180(5)	1481(3)	35(1)
N(3B)	8268(5)	3448(5)	666(3)	34(1)
N(4B)	9090(5)	2670(5)	929(3)	35(1)
N(5B)	8295(5)	4218(5)	2139(3)	35(1)
N(6B)	9123(5)	3330(5)	2201(3)	35(1)
O(1B)	5309(5)	5059(6)	1486(3)	58(2)
O(2B)	7945(5)	7506(5)	2288(3)	50(1)
C(1S)	483(14)	9445(15)	2480(13)	148(9)
Cl(1S)	1600(20)	9300(20)	1883(12)	101(11)
Cl(2S)	580(20)	8470(20)	3165(12)	99(10)
Cl(3S)	800(20)	9429(15)	1867(12)	123(8)
Cl(4S)	494(14)	9280(20)	3136(10)	105(6)
Cl(5S)	780(20)	7983(17)	3066(12)	78(6)
Cl(6S)	1991(16)	9039(17)	1981(10)	64(4)

Table 2.23. Bond lengths [Å] and angles [°] for 2.30a

B(1)-N(2)	1.529(10)	C(4)-C(5)	1.373(11)
B(1)-N(6)	1.530(10)	C(4)-H(4)	0.9500
B(1)-N(4)	1.532(10)	C(5)-C(6)	1.376(12)
B(1)-H(1)	1.0000	C(5)-H(5)	0.9500
C(1)-N(1)	1.339(9)	C(6)-N(4)	1.339(9)
C(1)-C(2)	1.380(11)	C(6)-H(6)	0.9500
C(1)-H(1)	0.9500	C(7)-N(5)	1.338(8)
C(2)-C(3)	1.385(11)	C(7)-C(8)	1.374(10)
C(2)-H(2)	0.9500	C(7)-H(7)	0.9500
C(3)-N(2)	1.333(9)	C(8)-C(9)	1.363(11)
C(3)-H(3)	0.9500	C(8)-H(8)	0.9500
C(4)-N(3)	1.338(9)	C(9)-N(6)	1.343(8)

C(9)-H(9)	0.9500	C(5B)-H(5B)	0.9500
C(10)-C(11)	1.363(14)	C(6B)-N(4B)	1.343(9)
C(10)-C(13C)	1.418(10)	C(6B)-H(6B)	0.9500
C(10)-Mo(1)	2.368(8)	C(7B)-N(5B)	1.339(9)
C(10)-H(10)	1.0000	C(7B)-C(8B)	1.381(10)
C(11)-C(12)	1.390(14)	C(7B)-H(7B)	0.9500
C(11)-Mo(1)	2.203(7)	C(8B)-C(9B)	1.373(10)
C(11)-H(11)	1.0000	C(8B)-H(8B)	0.9500
C(12)-O(4C)	1.479(11)	C(9B)-N(6B)	1.334(9)
C(12)-Mo(1)	2.351(7)	C(9B)-H(9B)	0.9500
C(12)-H(12)	1.0000	C(10B)-C(11B)	1.352(13)
C(14)-O(4C)	1.450(11)	C(10B)-C(13D)	1.387(9)
C(14)-C(13C)	1.488(9)	C(10B)-Mo(1B)	2.385(8)
C(14)-C(15)	1.529(13)	C(10B)-H(10B)	1.0000
C(14)-C(17C)	1.536(16)	C(11B)-C(12B)	1.414(13)
C(14)-C(17)	1.576(15)	C(11B)-Mo(1B)	2.209(7)
C(13C)-O(3C)	1.169(12)	C(11B)-H(11B)	1.0000
C(15)-C(16)	1.486(15)	C(12B)-O(4D)	1.472(11)
C(15)-H(16A)	0.9900	C(12B)-Mo(1B)	2.341(7)
C(15)-H(15B)	0.9900	C(12B)-H(12B)	1.0000
C(16)-H(18A)	0.9800	C(14B)-C(13D)	1.477(9)
C(16)-H(17B)	0.9800	C(14B)-O(4D)	1.501(10)
C(16)-H(19C)	0.9800	C(14B)-C(15B)	1.516(11)
C(17)-C(18)	1.325(9)	C(14B)-C(17B)	1.521(12)
C(17)-H(20)	0.9500	C(13D)-O(3D)	1.150(13)
C(18)-H(22A)	0.9500	C(15B)-C(16B)	1.522(12)
C(18)-H(21B)	0.9500	C(15B)-H(26B)	0.9900
C(17C)-C(18C)	1.304(9)	C(15B)-H(27B)	0.9900
C(17C)-H(23C)	0.9500	C(16B)-H(29B)	0.9800
C(18C)-H(25C)	0.9500	C(16B)-H(28B)	0.9800
C(18C)-H(24D)	0.9500	C(16B)-H(30B)	0.9800
C(19)-O(1)	1.156(9)	C(17B)-C(18B)	1.290(9)
C(19)-Mo(1)	1.965(8)	C(17B)-H(31B)	0.9500
C(20)-O(2)	1.145(8)	C(18B)-H(33B)	0.9500
C(20)-Mo(1)	1.951(7)	C(18B)-H(32B)	0.9500
Mo(1)-N(5)	2.191(5)	C(19B)-O(1B)	1.145(9)
Mo(1)-N(3)	2.267(5)	C(19B)-Mo(1B)	1.962(7)
Mo(1)-N(1)	2.269(6)	C(20B)-O(2B)	1.159(8)
N(1)-N(2)	1.375(8)	C(20B)-Mo(1B)	1.947(7)
N(3)-N(4)	1.369(8)	Mo(1B)-N(5B)	2.187(5)
N(5)-N(6)	1.350(8)	Mo(1B)-N(3B)	2.268(6)
B(1B)-N(4B)	1.525(10)	Mo(1B)-N(1B)	2.272(6)
B(1B)-N(6B)	1.538(9)	N(1B)-N(2B)	1.364(7)
B(1B)-N(2B)	1.555(9)	N(3B)-N(4B)	1.351(8)
B(1B)-H(1B)	1.0000	N(5B)-N(6B)	1.355(8)
C(1B)-N(1B)	1.320(9)	C(1S)-Cl(3S)	1.24(3)
C(1B)-C(2B)	1.377(11)	C(1S)-Cl(4S)	1.28(3)
C(1B)-H(1B)	0.9500	C(1S)-Cl(1S)	1.736(18)
C(2B)-C(3B)	1.376(11)	C(1S)-Cl(2S)	1.738(18)
C(2B)-H(2B)	0.9500	C(1S)-Cl(6S)	2.01(3)
C(3B)-N(2B)	1.329(9)	C(1S)-Cl(5S)	2.03(3)
C(3B)-H(3B)	0.9500	Cl(1S)-Cl(6S)	0.55(3)
C(4B)-N(3B)	1.342(9)	Cl(1S)-Cl(3S)	0.89(3)
C(4B)-C(5B)	1.379(11)	Cl(2S)-Cl(5S)	0.61(3)
C(4B)-H(4B)	0.9500	Cl(2S)-Cl(4S)	0.90(2)
C(5B)-C(6B)	1.359(11)	Cl(3S)-Cl(6S)	1.39(4)

Cl(4S)-Cl(5S)	1.47(3)	C(13C)-C(14)-C(17C)	115.6(8)
N(2)-B(1)-N(6)	107.8(6)	C(15)-C(14)-C(17C)	111.4(8)
N(2)-B(1)-N(4)	110.9(6)	O(4C)-C(14)-C(17)	120.9(8)
N(6)-B(1)-N(4)	108.8(6)	C(13C)-C(14)-C(17)	98.7(7)
N(2)-B(1)-H(1)	109.8	C(15)-C(14)-C(17)	101.3(8)
N(6)-B(1)-H(1)	109.8	C(17C)-C(14)-C(17)	25.6(5)
N(4)-B(1)-H(1)	109.8	O(3C)-C(13C)-C(10)	116.7(9)
N(1)-C(1)-C(2)	111.7(7)	O(3C)-C(13C)-C(14)	125.5(9)
N(1)-C(1)-H(1)	124.1	C(10)-C(13C)-C(14)	115.8(6)
C(2)-C(1)-H(1)	124.1	C(14)-O(4C)-C(12)	114.8(6)
C(1)-C(2)-C(3)	104.2(7)	C(16)-C(15)-C(14)	113.9(8)
C(1)-C(2)-H(2)	127.9	C(16)-C(15)-H(16A)	108.8
C(3)-C(2)-H(2)	127.9	C(14)-C(15)-H(16A)	108.8
N(2)-C(3)-C(2)	108.8(7)	C(16)-C(15)-H(15B)	108.8
N(2)-C(3)-H(3)	125.6	C(14)-C(15)-H(15B)	108.8
C(2)-C(3)-H(3)	125.6	H(16A)-C(15)-H(15B)	107.7
N(3)-C(4)-C(5)	111.1(7)	C(15)-C(16)-H(18A)	109.5
N(3)-C(4)-H(4)	124.5	C(15)-C(16)-H(17B)	109.5
C(5)-C(4)-H(4)	124.4	H(18A)-C(16)-H(17B)	109.5
C(4)-C(5)-C(6)	105.3(7)	C(15)-C(16)-H(19C)	109.5
C(4)-C(5)-H(5)	127.4	H(18A)-C(16)-H(19C)	109.5
C(6)-C(5)-H(5)	127.4	H(17B)-C(16)-H(19C)	109.5
N(4)-C(6)-C(5)	108.1(7)	C(18)-C(17)-C(14)	119.4(11)
N(4)-C(6)-H(6)	125.9	C(18)-C(17)-H(20)	120.3
C(5)-C(6)-H(6)	125.9	C(14)-C(17)-H(20)	120.3
N(5)-C(7)-C(8)	110.5(7)	C(17)-C(18)-H(22A)	120.0
N(5)-C(7)-H(7)	124.8	C(17)-C(18)-H(21B)	120.0
C(8)-C(7)-H(7)	124.8	H(22A)-C(18)-H(21B)	120.0
C(9)-C(8)-C(7)	104.8(6)	C(18C)-C(17C)-C(14)	118.1(13)
C(9)-C(8)-H(8)	127.6	C(18C)-C(17C)-H(23C)	121.0
C(7)-C(8)-H(8)	127.6	C(14)-C(17C)-H(23C)	121.0
N(6)-C(9)-C(8)	109.1(7)	C(17C)-C(18C)-H(25C)	120.0
N(6)-C(9)-H(9)	125.4	C(17C)-C(18C)-H(24D)	120.0
C(8)-C(9)-H(9)	125.4	H(25C)-C(18C)-H(24D)	120.0
C(11)-C(10)-C(13C)	121.8(7)	O(1)-C(19)-Mo(1)	176.9(7)
C(11)-C(10)-Mo(1)	66.1(4)	O(2)-C(20)-Mo(1)	176.7(6)
C(13C)-C(10)-Mo(1)	115.7(5)	C(20)-Mo(1)-C(19)	83.0(3)
C(11)-C(10)-H(10)	114.5	C(20)-Mo(1)-N(5)	86.8(2)
C(13C)-C(10)-H(10)	115.4	C(19)-Mo(1)-N(5)	84.5(3)
Mo(1)-C(10)-H(10)	114.1	C(20)-Mo(1)-C(11)	107.5(3)
C(10)-C(11)-C(12)	114.6(8)	C(19)-Mo(1)-C(11)	102.9(4)
C(10)-C(11)-Mo(1)	79.4(5)	N(5)-Mo(1)-C(11)	164.5(3)
C(12)-C(11)-Mo(1)	78.1(5)	C(20)-Mo(1)-N(3)	167.8(2)
C(10)-C(11)-H(11)	122.0	C(19)-Mo(1)-N(3)	97.5(3)
C(12)-C(11)-H(11)	122.0	N(5)-Mo(1)-N(3)	81.1(2)
Mo(1)-C(11)-H(11)	122.0	C(11)-Mo(1)-N(3)	84.4(3)
C(11)-C(12)-O(4C)	120.2(8)	C(20)-Mo(1)-N(1)	93.5(2)
C(11)-C(12)-Mo(1)	66.5(4)	C(19)-Mo(1)-N(1)	163.9(3)
O(4C)-C(12)-Mo(1)	113.4(5)	N(5)-Mo(1)-N(1)	79.6(2)
C(11)-C(12)-H(12)	115.8	C(11)-Mo(1)-N(1)	93.2(3)
O(4C)-C(12)-H(12)	115.8	N(3)-Mo(1)-N(1)	82.7(2)
Mo(1)-C(12)-H(12)	115.8	C(20)-Mo(1)-C(12)	74.8(3)
O(4C)-C(14)-C(13C)	113.2(6)	C(19)-Mo(1)-C(12)	111.8(3)
O(4C)-C(14)-C(15)	113.5(8)	N(5)-Mo(1)-C(12)	153.1(3)
C(13C)-C(14)-C(15)	107.3(7)	C(11)-Mo(1)-C(12)	35.4(3)
O(4C)-C(14)-C(17C)	95.6(8)	N(3)-Mo(1)-C(12)	116.0(3)

N(1)-Mo(1)-C(12)	82.1(3)
C(20)-Mo(1)-C(10)	107.2(3)
C(19)-Mo(1)-C(10)	68.8(3)
N(5)-Mo(1)-C(10)	147.4(3)
C(11)-Mo(1)-C(10)	34.4(3)
N(3)-Mo(1)-C(10)	84.1(2)
N(1)-Mo(1)-C(10)	127.0(3)
C(12)-Mo(1)-C(10)	58.8(3)
C(1)-N(1)-N(2)	105.1(6)
C(1)-N(1)-Mo(1)	133.8(5)
N(2)-N(1)-Mo(1)	120.2(4)
C(3)-N(2)-N(1)	110.0(6)
C(3)-N(2)-B(1)	128.7(6)
N(1)-N(2)-B(1)	119.9(6)
C(4)-N(3)-N(4)	105.5(6)
C(4)-N(3)-Mo(1)	134.7(5)
N(4)-N(3)-Mo(1)	119.7(4)
C(6)-N(4)-N(3)	110.0(6)
C(6)-N(4)-B(1)	129.1(6)
N(3)-N(4)-B(1)	120.8(5)
C(7)-N(5)-N(6)	106.6(5)
C(7)-N(5)-Mo(1)	130.2(5)
N(6)-N(5)-Mo(1)	123.2(4)
C(9)-N(6)-N(5)	108.9(6)
C(9)-N(6)-B(1)	131.5(6)
N(5)-N(6)-B(1)	119.5(5)
N(4B)-B(1B)-N(6B)	109.2(6)
N(4B)-B(1B)-N(2B)	110.5(6)
N(6B)-B(1B)-N(2B)	106.1(5)
N(4B)-B(1B)-H(1B)	110.3
N(6B)-B(1B)-H(1B)	110.3
N(2B)-B(1B)-H(1B)	110.3
N(1B)-C(1B)-C(2B)	112.1(7)
N(1B)-C(1B)-H(1B)	124.0
C(2B)-C(1B)-H(1B)	124.0
C(3B)-C(2B)-C(1B)	104.1(7)
C(3B)-C(2B)-H(2B)	127.9
C(1B)-C(2B)-H(2B)	127.9
N(2B)-C(3B)-C(2B)	108.3(7)
N(2B)-C(3B)-H(3B)	125.9
C(2B)-C(3B)-H(3B)	125.9
N(3B)-C(4B)-C(5B)	110.6(7)
N(3B)-C(4B)-H(4B)	124.7
C(5B)-C(4B)-H(4B)	124.7
C(6B)-C(5B)-C(4B)	104.9(7)
C(6B)-C(5B)-H(5B)	127.5
C(4B)-C(5B)-H(5B)	127.5
N(4B)-C(6B)-C(5B)	108.9(7)
N(4B)-C(6B)-H(6B)	125.6
C(5B)-C(6B)-H(6B)	125.6
N(5B)-C(7B)-C(8B)	110.3(6)
N(5B)-C(7B)-H(7B)	124.8
C(8B)-C(7B)-H(7B)	124.8
C(9B)-C(8B)-C(7B)	104.9(7)
C(9B)-C(8B)-H(8B)	127.6
C(7B)-C(8B)-H(8B)	127.6
N(6B)-C(9B)-C(8B)	108.7(7)
N(6B)-C(9B)-H(9B)	125.7
C(8B)-C(9B)-H(9B)	125.7
C(11B)-C(10B)-C(13D)	123.4(8)
C(11B)-C(10B)-Mo(1B)	65.9(4)
C(13D)-C(10B)-Mo(1B)	116.2(5)
C(11B)-C(10B)-H(10B)	114.3
C(13D)-C(10B)-H(10B)	114.4
Mo(1B)-C(10B)-H(10B)	113.8
C(10B)-C(11B)-C(12B)	114.4(7)
C(10B)-C(11B)-Mo(1B)	80.2(5)
C(12B)-C(11B)-Mo(1B)	77.1(4)
C(10B)-C(11B)-H(11B)	122.1
C(12B)-C(11B)-H(11B)	122.1
Mo(1B)-C(11B)-H(11B)	122.1
C(11B)-C(12B)-O(4D)	119.0(7)
C(11B)-C(12B)-Mo(1B)	66.9(4)
O(4D)-C(12B)-Mo(1B)	113.6(5)
C(11B)-C(12B)-H(12B)	116.1
O(4D)-C(12B)-H(12B)	116.1
Mo(1B)-C(12B)-H(12B)	116.1
C(13D)-C(14B)-O(4D)	112.1(5)
C(13D)-C(14B)-C(15B)	108.2(6)
O(4D)-C(14B)-C(15B)	112.5(7)
C(13D)-C(14B)-C(17B)	103.7(7)
O(4D)-C(14B)-C(17B)	112.2(7)
C(15B)-C(14B)-C(17B)	107.5(7)
O(3D)-C(13D)-C(10B)	116.0(9)
O(3D)-C(13D)-C(14B)	123.8(9)
C(10B)-C(13D)-C(14B)	116.3(6)
C(12B)-O(4D)-C(14B)	114.9(6)
C(14B)-C(15B)-C(16B)	114.3(7)
C(14B)-C(15B)-H(26B)	108.7
C(16B)-C(15B)-H(26B)	108.7
C(14B)-C(15B)-H(27B)	108.7
C(16B)-C(15B)-H(27B)	108.7
H(26B)-C(15B)-H(27B)	107.6
C(15B)-C(16B)-H(29B)	109.5
C(15B)-C(16B)-H(28B)	109.5
H(29B)-C(16B)-H(28B)	109.5
C(15B)-C(16B)-H(30B)	109.5
H(29B)-C(16B)-H(30B)	109.5
H(28B)-C(16B)-H(30B)	109.5
C(18B)-C(17B)-C(14B)	127.8(12)
C(18B)-C(17B)-H(31B)	116.1
C(14B)-C(17B)-H(31B)	116.1
C(17B)-C(18B)-H(33B)	120.0
C(17B)-C(18B)-H(32B)	120.0
H(33B)-C(18B)-H(32B)	120.0
O(1B)-C(19B)-Mo(1B)	176.0(7)
O(2B)-C(20B)-Mo(1B)	176.0(6)
C(20B)-Mo(1B)-C(19B)	83.0(3)
C(20B)-Mo(1B)-N(5B)	86.9(2)
C(19B)-Mo(1B)-N(5B)	84.6(2)
C(20B)-Mo(1B)-C(11B)	108.5(3)
C(19B)-Mo(1B)-C(11B)	101.4(3)

N(5B)-Mo(1B)-C(11B)	164.0(3)	N(6B)-N(5B)-Mo(1B)	123.5(4)
C(20B)-Mo(1B)-N(3B)	167.7(2)	C(9B)-N(6B)-N(5B)	109.8(6)
C(19B)-Mo(1B)-N(3B)	97.4(3)	C(9B)-N(6B)-B(1B)	130.8(6)
N(5B)-Mo(1B)-N(3B)	81.0(2)	N(5B)-N(6B)-B(1B)	119.4(5)
C(11B)-Mo(1B)-N(3B)	83.5(3)	Cl(3S)-C(1S)-Cl(4S)	161(2)
C(20B)-Mo(1B)-N(1B)	94.0(2)	Cl(3S)-C(1S)-Cl(1S)	29.3(14)
C(19B)-Mo(1B)-N(1B)	164.2(2)	Cl(4S)-C(1S)-Cl(1S)	132.0(16)
N(5B)-Mo(1B)-N(1B)	79.7(2)	Cl(3S)-C(1S)-Cl(2S)	136.0(16)
C(11B)-Mo(1B)-N(1B)	94.3(3)	Cl(4S)-C(1S)-Cl(2S)	30.1(11)
N(3B)-Mo(1B)-N(1B)	82.3(2)	Cl(1S)-C(1S)-Cl(2S)	115.8(14)
C(20B)-Mo(1B)-C(12B)	75.8(3)	Cl(3S)-C(1S)-Cl(6S)	42.9(15)
C(19B)-Mo(1B)-C(12B)	112.3(3)	Cl(4S)-C(1S)-Cl(6S)	117.9(13)
N(5B)-Mo(1B)-C(12B)	153.6(3)	Cl(1S)-C(1S)-Cl(6S)	14.6(10)
C(11B)-Mo(1B)-C(12B)	36.1(3)	Cl(2S)-C(1S)-Cl(6S)	101.7(12)
N(3B)-Mo(1B)-C(12B)	114.9(3)	Cl(3S)-C(1S)-Cl(5S)	119.8(13)
N(1B)-Mo(1B)-C(12B)	81.7(2)	Cl(4S)-C(1S)-Cl(5S)	46.0(14)
C(20B)-Mo(1B)-C(10B)	106.4(3)	Cl(1S)-C(1S)-Cl(5S)	102.0(12)
C(19B)-Mo(1B)-C(10B)	67.6(3)	Cl(2S)-C(1S)-Cl(5S)	16.3(11)
N(5B)-Mo(1B)-C(10B)	146.8(3)	Cl(6S)-C(1S)-Cl(5S)	88.7(10)
C(11B)-Mo(1B)-C(10B)	34.0(3)	Cl(6S)-Cl(1S)-Cl(3S)	149(5)
N(3B)-Mo(1B)-C(10B)	85.0(2)	Cl(6S)-Cl(1S)-C(1S)	113(4)
N(1B)-Mo(1B)-C(10B)	127.9(3)	Cl(3S)-Cl(1S)-C(1S)	43(2)
C(12B)-Mo(1B)-C(10B)	58.9(3)	Cl(5S)-Cl(2S)-Cl(4S)	152(6)
C(1B)-N(1B)-N(2B)	105.0(6)	Cl(5S)-Cl(2S)-C(1S)	110(4)
C(1B)-N(1B)-Mo(1B)	133.6(5)	Cl(4S)-Cl(2S)-C(1S)	45.3(18)
N(2B)-N(1B)-Mo(1B)	120.3(4)	Cl(1S)-Cl(3S)-C(1S)	108(3)
C(3B)-N(2B)-N(1B)	110.5(6)	Cl(1S)-Cl(3S)-Cl(6S)	12(2)
C(3B)-N(2B)-B(1B)	127.9(6)	C(1S)-Cl(3S)-Cl(6S)	99(2)
N(1B)-N(2B)-B(1B)	120.4(5)	Cl(2S)-Cl(4S)-C(1S)	105(2)
C(4B)-N(3B)-N(4B)	105.9(6)	Cl(2S)-Cl(4S)-Cl(5S)	11(2)
C(4B)-N(3B)-Mo(1B)	133.8(5)	C(1S)-Cl(4S)-Cl(5S)	95(2)
N(4B)-N(3B)-Mo(1B)	120.1(4)	Cl(2S)-Cl(5S)-Cl(4S)	16(3)
C(6B)-N(4B)-N(3B)	109.7(6)	Cl(2S)-Cl(5S)-C(1S)	53(4)
C(6B)-N(4B)-B(1B)	128.6(6)	Cl(4S)-Cl(5S)-C(1S)	38.7(11)
N(3B)-N(4B)-B(1B)	121.6(5)	Cl(1S)-Cl(6S)-Cl(3S)	20(4)
C(7B)-N(5B)-N(6B)	106.3(5)	Cl(1S)-Cl(6S)-C(1S)	53(3)
C(7B)-N(5B)-Mo(1B)	130.1(5)	Cl(3S)-Cl(6S)-C(1S)	37.6(12)

Symmetry transformations used to generate equivalent atoms:

Table 2.24. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for 2.30a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	35(4)	48(4)	47(4)	7(3)	1(3)	-5(3)
C(2)	52(5)	47(4)	49(4)	10(3)	6(4)	-6(4)
C(3)	50(4)	40(4)	35(4)	4(3)	10(3)	6(3)
C(4)	29(3)	64(5)	31(3)	2(3)	4(3)	-2(3)
C(5)	32(4)	86(6)	38(4)	10(4)	4(3)	-1(4)
C(6)	32(4)	70(5)	44(4)	15(4)	10(3)	6(3)
C(7)	40(4)	46(4)	29(3)	8(3)	7(3)	-8(3)
C(8)	44(4)	62(5)	27(3)	7(3)	10(3)	-14(3)

C(9)	38(4)	59(5)	33(3)	1(3)	13(3)	-7(3)
C(10)	35(4)	91(7)	33(4)	-12(4)	3(3)	15(4)
C(11)	53(5)	96(7)	33(4)	25(4)	22(4)	36(5)
C(12)	72(6)	52(5)	61(5)	12(4)	44(5)	-4(4)
C(14)	29(4)	76(6)	67(6)	15(5)	6(4)	7(4)
C(15)	48(5)	81(7)	83(7)	5(6)	10(5)	15(5)
C(16)	55(6)	88(8)	81(7)	9(6)	9(5)	2(5)
C(19)	34(4)	50(4)	44(4)	-3(3)	11(3)	3(3)
C(20)	36(3)	34(3)	33(3)	6(3)	3(3)	2(3)
Mo(1)	25(1)	40(1)	26(1)	7(1)	6(1)	0(1)
N(1)	29(3)	43(3)	34(3)	11(2)	6(2)	2(2)
N(2)	35(3)	44(3)	34(3)	9(2)	7(2)	4(2)
N(3)	26(3)	50(3)	28(3)	5(2)	6(2)	-3(2)
N(4)	22(3)	55(4)	38(3)	8(3)	5(2)	1(2)
N(5)	34(3)	38(3)	29(3)	7(2)	7(2)	-4(2)
N(6)	30(3)	44(3)	33(3)	3(2)	12(2)	-2(2)
O(1)	64(4)	42(3)	84(5)	12(3)	27(3)	3(3)
O(2)	47(3)	61(3)	43(3)	6(3)	-9(2)	5(3)
C(10B)	73(6)	43(4)	33(4)	1(3)	-4(4)	16(4)
C(11B)	87(7)	55(5)	28(4)	20(3)	23(4)	31(5)
C(12B)	42(4)	73(6)	58(5)	38(5)	16(4)	4(4)
C(14B)	53(4)	41(4)	45(4)	9(3)	5(3)	11(3)
C(15B)	53(5)	44(4)	61(5)	6(4)	7(4)	14(4)
C(16B)	57(5)	58(5)	77(6)	7(5)	26(5)	20(4)
C(17B)	95(8)	74(7)	72(7)	37(5)	28(6)	38(6)
C(18B)	128(11)	67(7)	85(8)	19(6)	30(8)	23(7)
C(19B)	39(4)	43(4)	40(4)	11(3)	3(3)	3(3)
C(20B)	33(3)	38(4)	37(3)	5(3)	12(3)	4(3)
Mo(1B)	34(1)	30(1)	26(1)	6(1)	8(1)	2(1)
N(1B)	36(3)	28(3)	33(3)	3(2)	8(2)	0(2)
N(2B)	33(3)	36(3)	37(3)	7(2)	7(2)	2(2)
N(3B)	43(3)	32(3)	28(3)	9(2)	5(2)	1(2)
N(4B)	44(3)	27(3)	35(3)	4(2)	7(2)	3(2)
N(5B)	34(3)	41(3)	30(3)	5(2)	6(2)	1(2)
N(6B)	35(3)	36(3)	33(3)	9(2)	4(2)	-4(2)
O(1B)	34(3)	66(4)	77(4)	22(3)	11(3)	2(3)
O(2B)	61(4)	47(3)	40(3)	-10(2)	11(2)	10(3)
C(1S)	82(11)	95(12)	260(30)	-43(18)	-24(17)	11(9)
Cl(1S)	170(30)	49(9)	81(13)	-17(8)	23(18)	6(14)
Cl(2S)	52(7)	160(30)	85(12)	20(20)	-13(7)	-3(18)
Cl(3S)	230(30)	41(6)	104(10)	10(6)	22(16)	-8(11)
Cl(4S)	40(5)	183(19)	94(9)	6(12)	16(5)	6(9)
Cl(5S)	83(15)	84(9)	61(7)	8(6)	-18(7)	-24(8)
Cl(6S)	81(7)	60(10)	49(5)	-1(5)	6(5)	-10(6)

Table 2.25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2.30a

	x	y	z	U(eq)
H(1)	7592	-555	3269	44
H(1)	3000	-971	3655	52
H(2)	3897	-2969	3332	59

H(3)	6142	-2531	3236	50
H(4)	6855	2885	5126	50
H(5)	8948	2075	5271	62
H(6)	9063	403	4334	57
H(7)	5050	2770	2108	46
H(8)	6573	1930	1311	53
H(9)	7653	326	1963	51
H(10)	5030	3362	5061	64
H(11)	4415	1369	5200	70
H(12)	2764	542	4456	72
H(16A)	392	4058	4291	84
H(15B)	1296	5117	4633	84
H(18A)	2366	5120	3644	112
H(17B)	948	5193	3400	112
H(19C)	1633	3933	3312	112
H(20)	1882	4392	5683	36
H(22A)	1362	1879	5561	36
H(21B)	1282	2766	6277	36
H(23C)	1037	2352	5354	36
H(25C)	2533	4306	5909	36
H(24D)	1700	3414	6362	36
H(1B)	10462	2326	1702	42
H(1B)	10887	6921	1353	50
H(2B)	12887	6027	1701	57
H(3B)	12452	3786	1766	48
H(4B)	7012	3157	-164	48
H(5B)	7813	1061	-311	56
H(6B)	9482	920	627	53
H(7B)	7125	4848	2850	46
H(8B)	8015	3346	3664	50
H(9B)	9578	2232	2998	49
H(10B)	6470	4975	-80	60
H(11B)	8472	5517	-241	66
H(12B)	9395	7143	504	67
H(26B)	4823	8733	336	63
H(27B)	5929	9554	703	63
H(29B)	4925	7494	1329	94
H(28B)	4591	8867	1537	94
H(30B)	5950	8412	1700	94
H(31B)	5730	8071	-732	93
H(33B)	8161	8757	-543	110
H(32B)	7273	8766	-1271	110

Table 2.26. Torsion angles [°] for 2.30a

N(1)-C(1)-C(2)-C(3)	-0.3(9)
C(1)-C(2)-C(3)-N(2)	0.5(8)
N(3)-C(4)-C(5)-C(6)	-0.2(9)
C(4)-C(5)-C(6)-N(4)	0.2(9)
N(5)-C(7)-C(8)-C(9)	1.1(8)
C(7)-C(8)-C(9)-N(6)	-1.6(8)
C(13C)-C(10)-C(11)-C(12)	35.0(10)
Mo(1)-C(10)-C(11)-C(12)	-71.6(6)

C(13C)-C(10)-C(11)-Mo(1)	106.6(6)
C(10)-C(11)-C(12)-O(4C)	-32.0(10)
Mo(1)-C(11)-C(12)-O(4C)	-104.4(6)
C(10)-C(11)-C(12)-Mo(1)	72.4(6)
C(11)-C(10)-C(13C)-O(3C)	163.5(10)
Mo(1)-C(10)-C(13C)-O(3C)	-119.8(9)
C(11)-C(10)-C(13C)-C(14)	-1.4(10)
Mo(1)-C(10)-C(13C)-C(14)	75.3(7)
O(4C)-C(14)-C(13C)-O(3C)	161.9(10)
C(15)-C(14)-C(13C)-O(3C)	35.8(13)
C(17C)-C(14)-C(13C)-O(3C)	-89.2(13)
C(17)-C(14)-C(13C)-O(3C)	-68.9(12)
O(4C)-C(14)-C(13C)-C(10)	-34.7(9)
C(15)-C(14)-C(13C)-C(10)	-160.8(7)
C(17C)-C(14)-C(13C)-C(10)	74.1(10)
C(17)-C(14)-C(13C)-C(10)	94.4(7)
C(13C)-C(14)-O(4C)-C(12)	36.5(9)
C(15)-C(14)-O(4C)-C(12)	159.2(7)
C(17C)-C(14)-O(4C)-C(12)	-84.5(8)
C(17)-C(14)-O(4C)-C(12)	-80.1(9)
C(11)-C(12)-O(4C)-C(14)	-4.1(10)
Mo(1)-C(12)-O(4C)-C(14)	-79.5(7)
O(4C)-C(14)-C(15)-C(16)	-66.7(11)
C(13C)-C(14)-C(15)-C(16)	59.3(11)
C(17C)-C(14)-C(15)-C(16)	-173.3(10)
C(17)-C(14)-C(15)-C(16)	162.2(9)
O(4C)-C(14)-C(17)-C(18)	0.1(14)
C(13C)-C(14)-C(17)-C(18)	-123.7(10)
C(15)-C(14)-C(17)-C(18)	126.5(11)
C(17C)-C(14)-C(17)-C(18)	10.1(14)
O(4C)-C(14)-C(17C)-C(18C)	152.6(12)
C(13C)-C(14)-C(17C)-C(18C)	33.5(16)
C(15)-C(14)-C(17C)-C(18C)	-89.3(14)
C(17)-C(14)-C(17C)-C(18C)	-18.8(12)
O(2)-C(20)-Mo(1)-C(19)	70(11)
O(2)-C(20)-Mo(1)-N(5)	-14(11)
O(2)-C(20)-Mo(1)-C(11)	172(11)
O(2)-C(20)-Mo(1)-N(3)	-22(12)
O(2)-C(20)-Mo(1)-N(1)	-94(11)
O(2)-C(20)-Mo(1)-C(12)	-175(11)
O(2)-C(20)-Mo(1)-C(10)	136(11)
O(1)-C(19)-Mo(1)-C(20)	-64(13)
O(1)-C(19)-Mo(1)-N(5)	24(13)
O(1)-C(19)-Mo(1)-C(11)	-170(13)
O(1)-C(19)-Mo(1)-N(3)	104(13)
O(1)-C(19)-Mo(1)-N(1)	15(13)
O(1)-C(19)-Mo(1)-C(12)	-134(13)
O(1)-C(19)-Mo(1)-C(10)	-175(13)
C(10)-C(11)-Mo(1)-C(20)	-95.2(5)
C(12)-C(11)-Mo(1)-C(20)	23.0(6)
C(10)-C(11)-Mo(1)-C(19)	-8.6(6)
C(12)-C(11)-Mo(1)-C(19)	109.6(6)
C(10)-C(11)-Mo(1)-N(5)	108.5(12)
C(12)-C(11)-Mo(1)-N(5)	-133.3(11)
C(10)-C(11)-Mo(1)-N(3)	87.8(5)
C(12)-C(11)-Mo(1)-N(3)	-154.0(6)

C(10)-C(11)-Mo(1)-N(1)	170.1(5)
C(12)-C(11)-Mo(1)-N(1)	-71.7(6)
C(10)-C(11)-Mo(1)-C(12)	-118.2(7)
C(12)-C(11)-Mo(1)-C(10)	118.2(7)
C(11)-C(12)-Mo(1)-C(20)	-157.2(6)
O(4C)-C(12)-Mo(1)-C(20)	-43.1(6)
C(11)-C(12)-Mo(1)-C(19)	-81.4(6)
O(4C)-C(12)-Mo(1)-C(19)	32.7(7)
C(11)-C(12)-Mo(1)-N(5)	154.5(6)
O(4C)-C(12)-Mo(1)-N(5)	-91.4(8)
O(4C)-C(12)-Mo(1)-C(11)	114.1(9)
C(11)-C(12)-Mo(1)-N(3)	29.1(6)
O(4C)-C(12)-Mo(1)-N(3)	143.2(5)
C(11)-C(12)-Mo(1)-N(1)	106.9(6)
O(4C)-C(12)-Mo(1)-N(1)	-139.0(6)
C(11)-C(12)-Mo(1)-C(10)	-35.6(5)
O(4C)-C(12)-Mo(1)-C(10)	78.5(6)
C(11)-C(10)-Mo(1)-C(20)	96.0(5)
C(13C)-C(10)-Mo(1)-C(20)	-19.2(7)
C(11)-C(10)-Mo(1)-C(19)	171.0(6)
C(13C)-C(10)-Mo(1)-C(19)	55.9(6)
C(11)-C(10)-Mo(1)-N(5)	-151.9(5)
C(13C)-C(10)-Mo(1)-N(5)	92.9(7)
C(13C)-C(10)-Mo(1)-C(11)	-115.2(8)
C(11)-C(10)-Mo(1)-N(3)	-88.6(5)
C(13C)-C(10)-Mo(1)-N(3)	156.2(6)
C(11)-C(10)-Mo(1)-N(1)	-12.4(6)
C(13C)-C(10)-Mo(1)-N(1)	-127.5(6)
C(11)-C(10)-Mo(1)-C(12)	36.6(5)
C(13C)-C(10)-Mo(1)-C(12)	-78.6(6)
C(2)-C(1)-N(1)-N(2)	0.0(8)
C(2)-C(1)-N(1)-Mo(1)	168.9(5)
C(20)-Mo(1)-N(1)-C(1)	-38.0(7)
C(19)-Mo(1)-N(1)-C(1)	-114.8(10)
N(5)-Mo(1)-N(1)-C(1)	-124.1(7)
C(11)-Mo(1)-N(1)-C(1)	69.8(7)
N(3)-Mo(1)-N(1)-C(1)	153.7(7)
C(12)-Mo(1)-N(1)-C(1)	36.1(7)
C(10)-Mo(1)-N(1)-C(1)	76.7(7)
C(20)-Mo(1)-N(1)-N(2)	129.6(5)
C(19)-Mo(1)-N(1)-N(2)	52.8(11)
N(5)-Mo(1)-N(1)-N(2)	43.5(5)
C(11)-Mo(1)-N(1)-N(2)	-122.6(5)
N(3)-Mo(1)-N(1)-N(2)	-38.7(5)
C(12)-Mo(1)-N(1)-N(2)	-156.3(5)
C(10)-Mo(1)-N(1)-N(2)	-115.7(5)
C(2)-C(3)-N(2)-N(1)	-0.5(8)
C(2)-C(3)-N(2)-B(1)	-167.1(7)
C(1)-N(1)-N(2)-C(3)	0.3(7)
Mo(1)-N(1)-N(2)-C(3)	-170.4(4)
C(1)-N(1)-N(2)-B(1)	168.3(6)
Mo(1)-N(1)-N(2)-B(1)	-2.5(8)
N(6)-B(1)-N(2)-C(3)	107.4(8)
N(4)-B(1)-N(2)-C(3)	-133.7(7)
N(6)-B(1)-N(2)-N(1)	-58.1(8)
N(4)-B(1)-N(2)-N(1)	60.9(8)

C(5)-C(4)-N(3)-N(4)	0.1(8)
C(5)-C(4)-N(3)-Mo(1)	-175.0(5)
C(20)-Mo(1)-N(3)-C(4)	142.2(11)
C(19)-Mo(1)-N(3)-C(4)	51.0(7)
N(5)-Mo(1)-N(3)-C(4)	134.1(7)
C(11)-Mo(1)-N(3)-C(4)	-51.3(7)
N(1)-Mo(1)-N(3)-C(4)	-145.3(7)
C(12)-Mo(1)-N(3)-C(4)	-67.8(7)
C(10)-Mo(1)-N(3)-C(4)	-16.7(7)
C(20)-Mo(1)-N(3)-N(4)	-32.4(14)
C(19)-Mo(1)-N(3)-N(4)	-123.6(5)
N(5)-Mo(1)-N(3)-N(4)	-40.5(5)
C(11)-Mo(1)-N(3)-N(4)	134.0(5)
N(1)-Mo(1)-N(3)-N(4)	40.1(5)
C(12)-Mo(1)-N(3)-N(4)	117.6(5)
C(10)-Mo(1)-N(3)-N(4)	168.7(5)
C(5)-C(6)-N(4)-N(3)	-0.1(8)
C(5)-C(6)-N(4)-B(1)	176.0(7)
C(4)-N(3)-N(4)-C(6)	0.0(8)
Mo(1)-N(3)-N(4)-C(6)	176.1(5)
C(4)-N(3)-N(4)-B(1)	-176.5(6)
Mo(1)-N(3)-N(4)-B(1)	-0.5(8)
N(2)-B(1)-N(4)-C(6)	124.9(8)
N(6)-B(1)-N(4)-C(6)	-116.8(8)
N(2)-B(1)-N(4)-N(3)	-59.4(8)
N(6)-B(1)-N(4)-N(3)	59.0(8)
C(8)-C(7)-N(5)-N(6)	-0.1(8)
C(8)-C(7)-N(5)-Mo(1)	-177.9(5)
C(20)-Mo(1)-N(5)-C(7)	40.7(6)
C(19)-Mo(1)-N(5)-C(7)	-42.5(6)
C(11)-Mo(1)-N(5)-C(7)	-161.8(12)
N(3)-Mo(1)-N(5)-C(7)	-141.0(6)
N(1)-Mo(1)-N(5)-C(7)	134.9(6)
C(12)-Mo(1)-N(5)-C(7)	86.9(9)
C(10)-Mo(1)-N(5)-C(7)	-76.9(8)
C(20)-Mo(1)-N(5)-N(6)	-136.8(5)
C(19)-Mo(1)-N(5)-N(6)	140.0(5)
C(11)-Mo(1)-N(5)-N(6)	20.7(15)
N(3)-Mo(1)-N(5)-N(6)	41.5(5)
N(1)-Mo(1)-N(5)-N(6)	-42.6(5)
C(12)-Mo(1)-N(5)-N(6)	-90.6(8)
C(10)-Mo(1)-N(5)-N(6)	105.6(6)
C(8)-C(9)-N(6)-N(5)	1.6(8)
C(8)-C(9)-N(6)-B(1)	178.5(7)
C(7)-N(5)-N(6)-C(9)	-0.9(7)
Mo(1)-N(5)-N(6)-C(9)	177.1(5)
C(7)-N(5)-N(6)-B(1)	-178.3(6)
Mo(1)-N(5)-N(6)-B(1)	-0.3(8)
N(2)-B(1)-N(6)-C(9)	-115.7(8)
N(4)-B(1)-N(6)-C(9)	124.0(8)
N(2)-B(1)-N(6)-N(5)	60.9(8)
N(4)-B(1)-N(6)-N(5)	-59.3(8)
N(1B)-C(1B)-C(2B)-C(3B)	-0.2(9)
C(1B)-C(2B)-C(3B)-N(2B)	0.0(8)
N(3B)-C(4B)-C(5B)-C(6B)	0.0(9)
C(4B)-C(5B)-C(6B)-N(4B)	0.6(9)

N(5B)-C(7B)-C(8B)-C(9B)	-0.7(8)
C(7B)-C(8B)-C(9B)-N(6B)	0.8(8)
C(13D)-C(10B)-C(11B)-C(12B)	35.7(10)
Mo(1B)-C(10B)-C(11B)-C(12B)	-70.8(6)
C(13D)-C(10B)-C(11B)-Mo(1B)	106.5(7)
C(10B)-C(11B)-C(12B)-O(4D)	-32.3(9)
Mo(1B)-C(11B)-C(12B)-O(4D)	-105.1(6)
C(10B)-C(11B)-C(12B)-Mo(1B)	72.7(6)
C(11B)-C(10B)-C(13D)-O(3D)	157.8(11)
Mo(1B)-C(10B)-C(13D)-O(3D)	-125.0(10)
C(11B)-C(10B)-C(13D)-C(14B)	-0.8(10)
Mo(1B)-C(10B)-C(13D)-C(14B)	76.4(7)
O(4D)-C(14B)-C(13D)-O(3D)	168.2(11)
C(15B)-C(14B)-C(13D)-O(3D)	43.5(13)
C(17B)-C(14B)-C(13D)-O(3D)	-70.5(12)
O(4D)-C(14B)-C(13D)-C(10B)	-35.1(8)
C(15B)-C(14B)-C(13D)-C(10B)	-159.7(6)
C(17B)-C(14B)-C(13D)-C(10B)	86.3(7)
C(11B)-C(12B)-O(4D)-C(14B)	-3.3(9)
Mo(1B)-C(12B)-O(4D)-C(14B)	-79.0(7)
C(13D)-C(14B)-O(4D)-C(12B)	36.0(8)
C(15B)-C(14B)-O(4D)-C(12B)	158.2(6)
C(17B)-C(14B)-O(4D)-C(12B)	-80.3(8)
C(13D)-C(14B)-C(15B)-C(16B)	54.7(10)
O(4D)-C(14B)-C(15B)-C(16B)	-69.7(9)
C(17B)-C(14B)-C(15B)-C(16B)	166.2(9)
C(13D)-C(14B)-C(17B)-C(18B)	-127.2(12)
O(4D)-C(14B)-C(17B)-C(18B)	-5.9(14)
C(15B)-C(14B)-C(17B)-C(18B)	118.3(12)
O(2B)-C(20B)-Mo(1B)-C(19B)	92(9)
O(2B)-C(20B)-Mo(1B)-N(5B)	7(9)
O(2B)-C(20B)-Mo(1B)-C(11B)	-169(9)
O(2B)-C(20B)-Mo(1B)-N(3B)	-1(10)
O(2B)-C(20B)-Mo(1B)-N(1B)	-73(9)
O(2B)-C(20B)-Mo(1B)-C(12B)	-153(9)
O(2B)-C(20B)-Mo(1B)-C(10B)	156(9)
O(1B)-C(19B)-Mo(1B)-C(20B)	-48(10)
O(1B)-C(19B)-Mo(1B)-N(5B)	39(10)
O(1B)-C(19B)-Mo(1B)-C(11B)	-156(10)
O(1B)-C(19B)-Mo(1B)-N(3B)	119(10)
O(1B)-C(19B)-Mo(1B)-N(1B)	31(10)
O(1B)-C(19B)-Mo(1B)-C(12B)	-120(10)
O(1B)-C(19B)-Mo(1B)-C(10B)	-159(10)
C(10B)-C(11B)-Mo(1B)-C(20B)	-92.0(5)
C(12B)-C(11B)-Mo(1B)-C(20B)	26.0(6)
C(10B)-C(11B)-Mo(1B)-C(19B)	-5.7(6)
C(12B)-C(11B)-Mo(1B)-C(19B)	112.4(5)
C(10B)-C(11B)-Mo(1B)-N(5B)	105.0(11)
C(12B)-C(11B)-Mo(1B)-N(5B)	-137.0(10)
C(10B)-C(11B)-Mo(1B)-N(3B)	90.6(5)
C(12B)-C(11B)-Mo(1B)-N(3B)	-151.3(5)
C(10B)-C(11B)-Mo(1B)-N(1B)	172.3(5)
C(12B)-C(11B)-Mo(1B)-N(1B)	-69.6(5)
C(10B)-C(11B)-Mo(1B)-C(12B)	-118.1(7)
C(12B)-C(11B)-Mo(1B)-C(10B)	118.1(7)
C(11B)-C(12B)-Mo(1B)-C(20B)	-154.6(6)

O(4D)-C(12B)-Mo(1B)-C(20B)	-41.7(6)
C(11B)-C(12B)-Mo(1B)-C(19B)	-78.4(6)
O(4D)-C(12B)-Mo(1B)-C(19B)	34.5(7)
C(11B)-C(12B)-Mo(1B)-N(5B)	154.9(6)
O(4D)-C(12B)-Mo(1B)-N(5B)	-92.2(7)
O(4D)-C(12B)-Mo(1B)-C(11B)	112.9(8)
C(11B)-C(12B)-Mo(1B)-N(3B)	31.7(6)
O(4D)-C(12B)-Mo(1B)-N(3B)	144.6(5)
C(11B)-C(12B)-Mo(1B)-N(1B)	109.2(5)
O(4D)-C(12B)-Mo(1B)-N(1B)	-138.0(6)
C(11B)-C(12B)-Mo(1B)-C(10B)	-35.1(5)
O(4D)-C(12B)-Mo(1B)-C(10B)	77.7(6)
C(11B)-C(10B)-Mo(1B)-C(20B)	99.0(5)
C(13D)-C(10B)-Mo(1B)-C(20B)	-17.9(7)
C(11B)-C(10B)-Mo(1B)-C(19B)	174.0(6)
C(13D)-C(10B)-Mo(1B)-C(19B)	57.2(6)
C(11B)-C(10B)-Mo(1B)-N(5B)	-150.8(5)
C(13D)-C(10B)-Mo(1B)-N(5B)	92.4(7)
C(13D)-C(10B)-Mo(1B)-C(11B)	-116.8(9)
C(11B)-C(10B)-Mo(1B)-N(3B)	-85.8(5)
C(13D)-C(10B)-Mo(1B)-N(3B)	157.3(6)
C(11B)-C(10B)-Mo(1B)-N(1B)	-9.7(6)
C(13D)-C(10B)-Mo(1B)-N(1B)	-126.5(5)
C(11B)-C(10B)-Mo(1B)-C(12B)	37.3(5)
C(13D)-C(10B)-Mo(1B)-C(12B)	-79.5(6)
C(2B)-C(1B)-N(1B)-N(2B)	0.3(8)
C(2B)-C(1B)-N(1B)-Mo(1B)	167.4(5)
C(20B)-Mo(1B)-N(1B)-C(1B)	-36.4(7)
C(19B)-Mo(1B)-N(1B)-C(1B)	-114.8(11)
N(5B)-Mo(1B)-N(1B)-C(1B)	-122.5(7)
C(11B)-Mo(1B)-N(1B)-C(1B)	72.5(7)
N(3B)-Mo(1B)-N(1B)-C(1B)	155.3(7)
C(12B)-Mo(1B)-N(1B)-C(1B)	38.6(7)
C(10B)-Mo(1B)-N(1B)-C(1B)	77.9(7)
C(20B)-Mo(1B)-N(1B)-N(2B)	129.2(5)
C(19B)-Mo(1B)-N(1B)-N(2B)	50.8(11)
N(5B)-Mo(1B)-N(1B)-N(2B)	43.1(5)
C(11B)-Mo(1B)-N(1B)-N(2B)	-121.9(5)
N(3B)-Mo(1B)-N(1B)-N(2B)	-39.1(4)
C(12B)-Mo(1B)-N(1B)-N(2B)	-155.8(5)
C(10B)-Mo(1B)-N(1B)-N(2B)	-116.5(5)
C(2B)-C(3B)-N(2B)-N(1B)	0.2(8)
C(2B)-C(3B)-N(2B)-B(1B)	-166.7(7)
C(1B)-N(1B)-N(2B)-C(3B)	-0.3(7)
Mo(1B)-N(1B)-N(2B)-C(3B)	-169.5(4)
C(1B)-N(1B)-N(2B)-B(1B)	167.7(6)
Mo(1B)-N(1B)-N(2B)-B(1B)	-1.5(8)
N(4B)-B(1B)-N(2B)-C(3B)	-135.1(7)
N(6B)-B(1B)-N(2B)-C(3B)	106.8(8)
N(4B)-B(1B)-N(2B)-N(1B)	59.2(8)
N(6B)-B(1B)-N(2B)-N(1B)	-58.9(7)
C(5B)-C(4B)-N(3B)-N(4B)	-0.5(8)
C(5B)-C(4B)-N(3B)-Mo(1B)	-174.4(5)
C(20B)-Mo(1B)-N(3B)-C(4B)	141.5(11)
C(19B)-Mo(1B)-N(3B)-C(4B)	50.2(7)
N(5B)-Mo(1B)-N(3B)-C(4B)	133.6(7)

C(11B)-Mo(1B)-N(3B)-C(4B)	-50.4(7)
N(1B)-Mo(1B)-N(3B)-C(4B)	-145.7(6)
C(12B)-Mo(1B)-N(3B)-C(4B)	-68.6(7)
C(10B)-Mo(1B)-N(3B)-C(4B)	-16.3(7)
C(20B)-Mo(1B)-N(3B)-N(4B)	-31.8(14)
C(19B)-Mo(1B)-N(3B)-N(4B)	-123.0(5)
N(5B)-Mo(1B)-N(3B)-N(4B)	-39.7(5)
C(11B)-Mo(1B)-N(3B)-N(4B)	136.3(5)
N(1B)-Mo(1B)-N(3B)-N(4B)	41.0(5)
C(12B)-Mo(1B)-N(3B)-N(4B)	118.2(5)
C(10B)-Mo(1B)-N(3B)-N(4B)	170.4(5)
C(5B)-C(6B)-N(4B)-N(3B)	-0.9(8)
C(5B)-C(6B)-N(4B)-B(1B)	176.1(7)
C(4B)-N(3B)-N(4B)-C(6B)	0.8(7)
Mo(1B)-N(3B)-N(4B)-C(6B)	175.8(5)
C(4B)-N(3B)-N(4B)-B(1B)	-176.4(6)
Mo(1B)-N(3B)-N(4B)-B(1B)	-1.4(8)
N(6B)-B(1B)-N(4B)-C(6B)	-118.0(8)
N(2B)-B(1B)-N(4B)-C(6B)	125.7(7)
N(6B)-B(1B)-N(4B)-N(3B)	58.6(8)
N(2B)-B(1B)-N(4B)-N(3B)	-57.7(8)
C(8B)-C(7B)-N(5B)-N(6B)	0.3(8)
C(8B)-C(7B)-N(5B)-Mo(1B)	-176.5(5)
C(20B)-Mo(1B)-N(5B)-C(7B)	40.1(6)
C(19B)-Mo(1B)-N(5B)-C(7B)	-43.1(6)
C(11B)-Mo(1B)-N(5B)-C(7B)	-156.0(11)
N(3B)-Mo(1B)-N(5B)-C(7B)	-141.6(6)
N(1B)-Mo(1B)-N(5B)-C(7B)	134.7(6)
C(12B)-Mo(1B)-N(5B)-C(7B)	88.7(8)
C(10B)-Mo(1B)-N(5B)-C(7B)	-75.5(8)
C(20B)-Mo(1B)-N(5B)-N(6B)	-136.3(5)
C(19B)-Mo(1B)-N(5B)-N(6B)	140.5(5)
C(11B)-Mo(1B)-N(5B)-N(6B)	27.6(14)
N(3B)-Mo(1B)-N(5B)-N(6B)	42.0(5)
N(1B)-Mo(1B)-N(5B)-N(6B)	-41.7(5)
C(12B)-Mo(1B)-N(5B)-N(6B)	-87.7(8)
C(10B)-Mo(1B)-N(5B)-N(6B)	108.1(6)
C(8B)-C(9B)-N(6B)-N(5B)	-0.6(8)
C(8B)-C(9B)-N(6B)-B(1B)	179.2(7)
C(7B)-N(5B)-N(6B)-C(9B)	0.2(7)
Mo(1B)-N(5B)-N(6B)-C(9B)	177.3(5)
C(7B)-N(5B)-N(6B)-B(1B)	-179.6(6)
Mo(1B)-N(5B)-N(6B)-B(1B)	-2.5(8)
N(4B)-B(1B)-N(6B)-C(9B)	123.5(7)
N(2B)-B(1B)-N(6B)-C(9B)	-117.4(8)
N(4B)-B(1B)-N(6B)-N(5B)	-56.8(8)
N(2B)-B(1B)-N(6B)-N(5B)	62.3(7)
Cl(3S)-C(1S)-Cl(1S)-Cl(6S)	-156(7)
Cl(4S)-C(1S)-Cl(1S)-Cl(6S)	16(6)
Cl(2S)-C(1S)-Cl(1S)-Cl(6S)	-15(6)
Cl(5S)-C(1S)-Cl(1S)-Cl(6S)	-24(5)
Cl(4S)-C(1S)-Cl(1S)-Cl(3S)	172(3)
Cl(2S)-C(1S)-Cl(1S)-Cl(3S)	141(3)
Cl(6S)-C(1S)-Cl(1S)-Cl(3S)	156(7)
Cl(5S)-C(1S)-Cl(1S)-Cl(3S)	131(3)
Cl(3S)-C(1S)-Cl(2S)-Cl(5S)	-7(7)

Cl(4S)-C(1S)-Cl(2S)-Cl(5S)	-164(6)
Cl(1S)-C(1S)-Cl(2S)-Cl(5S)	-34(6)
Cl(6S)-C(1S)-Cl(2S)-Cl(5S)	-38(5)
Cl(3S)-C(1S)-Cl(2S)-Cl(4S)	157(3)
Cl(1S)-C(1S)-Cl(2S)-Cl(4S)	130(2)
Cl(6S)-C(1S)-Cl(2S)-Cl(4S)	127(2)
Cl(5S)-C(1S)-Cl(2S)-Cl(4S)	164(6)
Cl(6S)-Cl(1S)-Cl(3S)-C(1S)	47(12)
C(1S)-Cl(1S)-Cl(3S)-Cl(6S)	-47(12)
Cl(4S)-C(1S)-Cl(3S)-Cl(1S)	-19(7)
Cl(2S)-C(1S)-Cl(3S)-Cl(1S)	-55(4)
Cl(6S)-C(1S)-Cl(3S)-Cl(1S)	-9(2)
Cl(5S)-C(1S)-Cl(3S)-Cl(1S)	-58(3)
Cl(4S)-C(1S)-Cl(3S)-Cl(6S)	-11(7)
Cl(1S)-C(1S)-Cl(3S)-Cl(6S)	9(2)
Cl(2S)-C(1S)-Cl(3S)-Cl(6S)	-47(3)
Cl(5S)-C(1S)-Cl(3S)-Cl(6S)	-49(2)
Cl(5S)-Cl(2S)-Cl(4S)-C(1S)	33(12)
C(1S)-Cl(2S)-Cl(4S)-Cl(5S)	-33(12)
Cl(3S)-C(1S)-Cl(4S)-Cl(2S)	-55(7)
Cl(1S)-C(1S)-Cl(4S)-Cl(2S)	-67(3)
Cl(6S)-C(1S)-Cl(4S)-Cl(2S)	-63(3)
Cl(5S)-C(1S)-Cl(4S)-Cl(2S)	-6(2)
Cl(3S)-C(1S)-Cl(4S)-Cl(5S)	-49(7)
Cl(1S)-C(1S)-Cl(4S)-Cl(5S)	-61(3)
Cl(2S)-C(1S)-Cl(4S)-Cl(5S)	6(2)
Cl(6S)-C(1S)-Cl(4S)-Cl(5S)	-57(2)
C(1S)-Cl(2S)-Cl(5S)-Cl(4S)	24(9)
Cl(4S)-Cl(2S)-Cl(5S)-C(1S)	-24(9)
C(1S)-Cl(4S)-Cl(5S)-Cl(2S)	-148(12)
Cl(2S)-Cl(4S)-Cl(5S)-C(1S)	148(12)
Cl(3S)-C(1S)-Cl(5S)-Cl(2S)	174(5)
Cl(4S)-C(1S)-Cl(5S)-Cl(2S)	11(4)
Cl(1S)-C(1S)-Cl(5S)-Cl(2S)	149(5)
Cl(6S)-C(1S)-Cl(5S)-Cl(2S)	143(5)
Cl(3S)-C(1S)-Cl(5S)-Cl(4S)	163(3)
Cl(1S)-C(1S)-Cl(5S)-Cl(4S)	138(2)
Cl(2S)-C(1S)-Cl(5S)-Cl(4S)	-11(4)
Cl(6S)-C(1S)-Cl(5S)-Cl(4S)	132.3(19)
C(1S)-Cl(1S)-Cl(6S)-Cl(3S)	33(8)
Cl(3S)-Cl(1S)-Cl(6S)-C(1S)	-33(8)
C(1S)-Cl(3S)-Cl(6S)-Cl(1S)	-135(11)
Cl(1S)-Cl(3S)-Cl(6S)-C(1S)	135(11)
Cl(3S)-C(1S)-Cl(6S)-Cl(1S)	17(5)
Cl(4S)-C(1S)-Cl(6S)-Cl(1S)	-167(5)
Cl(2S)-C(1S)-Cl(6S)-Cl(1S)	166(5)
Cl(5S)-C(1S)-Cl(6S)-Cl(1S)	156(5)
Cl(4S)-C(1S)-Cl(6S)-Cl(3S)	176(3)
Cl(1S)-C(1S)-Cl(6S)-Cl(3S)	-17(5)
Cl(2S)-C(1S)-Cl(6S)-Cl(3S)	149(2)
Cl(5S)-C(1S)-Cl(6S)-Cl(3S)	139(2)

Symmetry transformations used to generate equivalent atoms:

Table 2.27. Crystal data and structure refinement for 2.33

Identification code	**2.33**	
Empirical formula	C20.17 H16.50 B Cl0.35 I Mo N6 O4	
Formula weight	653.05	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.3313(11) Å	α= 81.245(2)°.
	b = 14.8446(12) Å	β= 65.266(1)°.
	c = 15.3143(12) Å	γ = 64.853(1)°.
Volume	2490.5(3) $Å^3$	
Z	4	
Density (calculated)	1.742 Mg/m^3	
Absorption coefficient	1.841 mm^{-1}	
F(000)	1270	
Crystal size	0.31 x 0.21 x 0.085 mm^3	
Theta range for data collection	1.46 to 28.39°.	
Index ranges	-17<=h<=17, -19<=k<=19, -20<=l<=20	
Reflections collected	36926	
Independent reflections	12429 [R(int) = 0.0415]	
Completeness to theta = 28.39°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12429 / 2 / 587	
Goodness-of-fit on F^2	1.197	
Final R indices [I>2sigma(I)]	R1 = 0.0876, wR2 = 0.2307	
R indices (all data)	R1 = 0.0994, wR2 = 0.2376	
Largest diff. peak and hole	4.200 and -1.889 $e.Å^{-3}$	

Table 2.28. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2.33. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
B(1)	6437(7)	9284(6)	1861(6)	28(2)
C(1)	4220(7)	11661(5)	1595(5)	27(2)
C(2)	5136(8)	11955(6)	1418(6)	35(2)
C(3)	6075(7)	11127(6)	1446(6)	32(2)
C(4)	5852(8)	7728(6)	685(6)	34(2)
C(5)	7117(8)	7289(6)	266(6)	39(2)
C(6)	7474(7)	7819(6)	616(6)	33(2)
C(7)	4171(8)	9046(7)	4146(6)	37(2)
C(8)	5076(9)	8809(7)	4455(6)	42(2)
C(9)	6048(9)	8842(7)	3664(6)	40(2)
C(10)	2968(8)	9095(8)	1256(7)	45(2)
C(11)	3247(8)	9911(8)	915(6)	41(2)
C(12)	2425(8)	10778(7)	1496(7)	39(2)
C(13)	1143(7)	10947(6)	1969(6)	34(2)
C(14)	854(8)	10140(7)	1735(7)	38(2)
C(15)	-342(9)	10109(9)	2438(8)	53(3)
C(16)	-1334(9)	9643(7)	2606(7)	43(2)
C(17)	762(10)	10396(10)	735(8)	56(3)
C(18)	188(12)	11227(13)	502(9)	76(4)
C(19)	3017(7)	8608(6)	2859(6)	36(2)
C(20)	2240(7)	10519(6)	3266(5)	26(1)
I(1)	-415(1)	9826(1)	3887(1)	60(1)
Mo(1)	3638(1)	9619(1)	2215(1)	21(1)
N(1)	4587(5)	10682(4)	1729(4)	21(1)
N(2)	5740(5)	10363(4)	1634(4)	25(1)
N(3)	5464(6)	8511(5)	1268(4)	27(1)
N(4)	6488(6)	8556(5)	1218(4)	26(1)
N(5)	4563(6)	9221(5)	3198(4)	27(1)
N(6)	5717(6)	9109(5)	2917(5)	29(1)
O(1)	1776(6)	9170(5)	1674(6)	49(2)
O(2)	361(7)	11694(6)	2382(6)	54(2)
O(3)	2689(6)	8009(5)	3261(6)	60(2)
O(4)	1448(5)	11044(5)	3896(4)	39(1)
B(1B)	6757(7)	5632(6)	5141(6)	27(2)
C(1B)	8016(7)	7399(6)	5009(6)	33(2)
C(2B)	7069(8)	7714(6)	5895(6)	35(2)
C(3B)	6539(8)	7073(6)	6077(6)	35(2)
C(4B)	9495(7)	3439(6)	4120(6)	33(2)
C(5B)	8847(8)	2962(6)	4826(7)	37(2)
C(6B)	7766(8)	3734(6)	5317(6)	33(2)
C(7B)	6923(8)	6301(7)	2718(7)	38(2)
C(8B)	5707(9)	6437(8)	3146(8)	49(2)
C(9B)	5505(8)	6188(7)	4075(8)	43(2)
C(10B)	10565(8)	6426(7)	3088(7)	39(2)
C(11B)	10708(7)	5569(7)	3612(7)	39(2)
C(12B)	11194(7)	4687(6)	3057(8)	40(2)
C(13B)	12047(8)	4642(7)	2055(7)	39(2)
C(14B)	12319(9)	5561(7)	1711(7)	43(2)
C(15B)	12640(14)	5707(12)	637(12)	81(4)
C(16B)	13506(18)	4876(15)	-128(14)	100(5)
C(17B)	13590(30)	5140(30)	1730(20)	50

C(18B)	13760(30)	5820(20)	2170(20)	50
C(17C)	13330(16)	5532(14)	2022(13)	50
C(18C)	14241(15)	4959(12)	2059(12)	50
C(19B)	9841(8)	4880(6)	2081(6)	35(2)
C(20B)	9153(7)	6774(6)	2384(6)	30(2)
I(1B)	12605(2)	7053(1)	232(1)	65(1)
I(2B)	11650(2)	5765(1)	-56(1)	61(1)
Mo(1B)	9214(1)	5689(1)	3264(1)	20(1)
N(1B)	8060(5)	6609(4)	4659(4)	24(1)
N(2B)	7123(6)	6411(5)	5335(5)	28(1)
N(3B)	8892(5)	4423(5)	4198(4)	26(1)
N(4B)	7811(5)	4591(5)	4937(4)	25(1)
N(5B)	7406(6)	5996(5)	3376(5)	28(1)
N(6B)	6512(6)	5937(5)	4224(5)	29(1)
O(1B)	11375(6)	6465(5)	2166(5)	45(2)
O(2B)	12616(7)	3876(5)	1550(6)	59(2)
O(3B)	10131(8)	4432(7)	1411(6)	70(2)
O(4B)	9099(6)	7399(5)	1832(5)	48(2)
C(1S)	3088(19)	7361(12)	6143(12)	28(4)
Cl(1)	3016(8)	6123(7)	6801(6)	64(2)
Cl(2)	3237(6)	7884(7)	7021(9)	80(3)

Table 2.29. Bond lengths [Å] and angles [°] for 2.33

B(1)-N(4)	1.533(11)	C(17)-C(18)	1.236(18)
B(1)-N(2)	1.544(10)	C(19)-O(3)	1.139(11)
B(1)-N(6)	1.546(11)	C(19)-Mo(1)	1.959(9)
C(1)-N(1)	1.335(9)	C(20)-O(4)	1.154(9)
C(1)-C(2)	1.377(11)	C(20)-Mo(1)	1.969(7)
C(2)-C(3)	1.342(12)	Mo(1)-N(5)	2.191(6)
C(3)-N(2)	1.339(10)	Mo(1)-N(3)	2.259(6)
C(4)-N(3)	1.353(10)	Mo(1)-N(1)	2.279(6)
C(4)-C(5)	1.403(12)	N(1)-N(2)	1.350(8)
C(5)-C(6)	1.339(13)	N(3)-N(4)	1.365(9)
C(6)-N(4)	1.358(9)	N(5)-N(6)	1.353(9)
C(7)-N(5)	1.347(9)	B(1B)-N(6B)	1.533(11)
C(7)-C(8)	1.367(13)	B(1B)-N(2B)	1.539(11)
C(8)-C(9)	1.368(14)	B(1B)-N(4B)	1.547(10)
C(9)-N(6)	1.340(10)	C(1B)-N(1B)	1.333(10)
C(10)-C(11)	1.380(15)	C(1B)-C(2B)	1.382(12)
C(10)-O(1)	1.402(11)	C(2B)-C(3B)	1.345(13)
C(10)-Mo(1)	2.366(9)	C(3B)-N(2B)	1.347(10)
C(11)-C(12)	1.408(14)	C(4B)-N(3B)	1.329(10)
C(11)-Mo(1)	2.200(8)	C(4B)-C(5B)	1.387(12)
C(12)-C(13)	1.471(12)	C(5B)-C(6B)	1.381(12)
C(12)-Mo(1)	2.310(8)	C(6B)-N(4B)	1.331(10)
C(13)-O(2)	1.181(11)	C(7B)-N(5B)	1.337(10)
C(13)-C(14)	1.533(12)	C(7B)-C(8B)	1.405(14)
C(14)-O(1)	1.427(11)	C(8B)-C(9B)	1.355(14)
C(14)-C(15)	1.522(12)	C(9B)-N(6B)	1.342(10)
C(14)-C(17)	1.563(15)	C(10B)-C(11B)	1.382(14)
C(15)-C(16)	1.652(13)	C(10B)-O(1B)	1.383(11)
C(15)-I(1)	2.164(11)	C(10B)-Mo(1B)	2.386(9)

C(11B)-C(12B)	1.420(13)	C(13)-C(14)-C(17)	106.2(8)
C(11B)-Mo(1B)	2.201(8)	C(14)-C(15)-C(16)	143.8(10)
C(12B)-C(13B)	1.469(13)	C(14)-C(15)-I(1)	112.1(6)
C(12B)-Mo(1B)	2.321(7)	C(16)-C(15)-I(1)	93.7(6)
C(13B)-O(2B)	1.228(11)	C(18)-C(17)-C(14)	125.5(12)
C(13B)-C(14B)	1.521(13)	O(3)-C(19)-Mo(1)	176.6(9)
C(14B)-O(1B)	1.409(11)	O(4)-C(20)-Mo(1)	177.6(7)
C(14B)-C(15B)	1.523(19)	C(19)-Mo(1)-C(20)	84.7(3)
C(14B)-C(17B)	1.55(3)	C(19)-Mo(1)-N(5)	85.6(3)
C(14B)-C(17C)	1.59(2)	C(20)-Mo(1)-N(5)	85.7(3)
C(15B)-C(16B)	1.52(2)	C(19)-Mo(1)-C(11)	103.5(4)
C(15B)-I(2B)	1.979(16)	C(20)-Mo(1)-C(11)	108.7(3)
C(15B)-I(1B)	1.986(16)	N(5)-Mo(1)-C(11)	163.3(3)
C(17B)-C(18B)	1.44(5)	C(19)-Mo(1)-N(3)	94.7(3)
C(17C)-C(18C)	1.17(2)	C(20)-Mo(1)-N(3)	165.8(3)
C(19B)-O(3B)	1.141(11)	N(5)-Mo(1)-N(3)	80.1(2)
C(19B)-Mo(1B)	1.991(9)	C(11)-Mo(1)-N(3)	85.2(3)
C(20B)-O(4B)	1.156(10)	C(19)-Mo(1)-N(1)	165.7(3)
C(20B)-Mo(1B)	1.933(8)	C(20)-Mo(1)-N(1)	94.0(3)
Mo(1B)-N(5B)	2.190(6)	N(5)-Mo(1)-N(1)	80.1(2)
Mo(1B)-N(3B)	2.262(6)	C(11)-Mo(1)-N(1)	90.4(3)
Mo(1B)-N(1B)	2.269(6)	N(3)-Mo(1)-N(1)	83.1(2)
N(1B)-N(2B)	1.362(9)	C(19)-Mo(1)-C(12)	111.8(3)
N(3B)-N(4B)	1.355(8)	C(20)-Mo(1)-C(12)	74.4(3)
N(5B)-N(6B)	1.369(9)	N(5)-Mo(1)-C(12)	151.7(3)
C(1S)-Cl(2)	1.768(15)	C(11)-Mo(1)-C(12)	36.3(4)
C(1S)-Cl(1)	1.976(15)	N(3)-Mo(1)-C(12)	118.7(3)
N(4)-B(1)-N(2)	109.5(6)	N(1)-Mo(1)-C(12)	81.4(2)
N(4)-B(1)-N(6)	107.9(7)	C(19)-Mo(1)-C(10)	69.0(4)
N(2)-B(1)-N(6)	107.5(6)	C(20)-Mo(1)-C(10)	109.7(3)
N(1)-C(1)-C(2)	110.1(7)	N(5)-Mo(1)-C(10)	148.2(3)
C(3)-C(2)-C(1)	105.9(7)	C(11)-Mo(1)-C(10)	34.9(4)
N(2)-C(3)-C(2)	108.1(7)	N(3)-Mo(1)-C(10)	83.1(3)
N(3)-C(4)-C(5)	110.4(8)	N(1)-Mo(1)-C(10)	124.4(3)
C(6)-C(5)-C(4)	105.3(7)	C(12)-Mo(1)-C(10)	59.7(4)
C(5)-C(6)-N(4)	109.2(8)	C(1)-N(1)-N(2)	105.5(6)
N(5)-C(7)-C(8)	109.9(8)	C(1)-N(1)-Mo(1)	133.9(5)
C(7)-C(8)-C(9)	106.0(7)	N(2)-N(1)-Mo(1)	120.1(4)
N(6)-C(9)-C(8)	108.0(8)	C(3)-N(2)-N(1)	110.2(6)
C(11)-C(10)-O(1)	122.3(9)	C(3)-N(2)-B(1)	128.1(7)
C(11)-C(10)-Mo(1)	65.9(5)	N(1)-N(2)-B(1)	121.2(6)
O(1)-C(10)-Mo(1)	117.1(6)	C(4)-N(3)-N(4)	105.2(6)
C(10)-C(11)-C(12)	113.2(8)	C(4)-N(3)-Mo(1)	134.9(6)
C(10)-C(11)-Mo(1)	79.1(5)	N(4)-N(3)-Mo(1)	119.9(4)
C(12)-C(11)-Mo(1)	76.1(5)	C(6)-N(4)-N(3)	109.9(7)
C(11)-C(12)-C(13)	118.8(8)	C(6)-N(4)-B(1)	128.4(7)
C(11)-C(12)-Mo(1)	67.6(5)	N(3)-N(4)-B(1)	121.4(6)
C(13)-C(12)-Mo(1)	114.7(5)	C(7)-N(5)-N(6)	106.2(6)
O(2)-C(13)-C(12)	124.3(9)	C(7)-N(5)-Mo(1)	130.6(6)
O(2)-C(13)-C(14)	120.7(8)	N(6)-N(5)-Mo(1)	123.2(5)
C(12)-C(13)-C(14)	114.1(8)	C(9)-N(6)-N(5)	109.9(7)
O(1)-C(14)-C(15)	107.7(8)	C(9)-N(6)-B(1)	130.3(7)
O(1)-C(14)-C(13)	112.0(7)	N(5)-N(6)-B(1)	119.8(6)
C(15)-C(14)-C(13)	114.7(9)	C(10)-O(1)-C(14)	116.5(7)
O(1)-C(14)-C(17)	109.2(8)	N(6B)-B(1B)-N(2B)	106.6(6)
C(15)-C(14)-C(17)	106.8(7)	N(6B)-B(1B)-N(4B)	107.4(6)

N(2B)-B(1B)-N(4B)	110.7(6)	C(20B)-Mo(1B)-C(11B)	100.4(4)
N(1B)-C(1B)-C(2B)	111.4(8)	C(19B)-Mo(1B)-C(11B)	110.5(3)
C(3B)-C(2B)-C(1B)	104.7(7)	N(5B)-Mo(1B)-C(11B)	162.2(3)
C(2B)-C(3B)-N(2B)	109.2(7)	C(20B)-Mo(1B)-N(3B)	164.8(3)
N(3B)-C(4B)-C(5B)	111.8(7)	C(19B)-Mo(1B)-N(3B)	90.8(3)
C(6B)-C(5B)-C(4B)	103.4(7)	N(5B)-Mo(1B)-N(3B)	80.2(2)
N(4B)-C(6B)-C(5B)	108.9(7)	C(11B)-Mo(1B)-N(3B)	94.7(3)
N(5B)-C(7B)-C(8B)	109.5(8)	C(20B)-Mo(1B)-N(1B)	98.1(3)
C(9B)-C(8B)-C(7B)	105.0(8)	C(19B)-Mo(1B)-N(1B)	165.8(3)
N(6B)-C(9B)-C(8B)	109.7(9)	N(5B)-Mo(1B)-N(1B)	79.4(2)
C(11B)-C(10B)-O(1B)	123.3(8)	C(11B)-Mo(1B)-N(1B)	83.2(3)
C(11B)-C(10B)-Mo(1B)	65.3(5)	N(3B)-Mo(1B)-N(1B)	84.3(2)
O(1B)-C(10B)-Mo(1B)	117.2(6)	C(20B)-Mo(1B)-C(12B)	110.5(3)
C(10B)-C(11B)-C(12B)	114.2(8)	C(19B)-Mo(1B)-C(12B)	76.9(4)
C(10B)-C(11B)-Mo(1B)	79.9(5)	N(5B)-Mo(1B)-C(12B)	155.2(3)
C(12B)-C(11B)-Mo(1B)	76.4(5)	C(11B)-Mo(1B)-C(12B)	36.5(3)
C(11B)-C(12B)-C(13B)	117.8(8)	N(3B)-Mo(1B)-C(12B)	81.5(3)
C(11B)-C(12B)-Mo(1B)	67.1(4)	N(1B)-Mo(1B)-C(12B)	115.3(3)
C(13B)-C(12B)-Mo(1B)	112.4(6)	C(20B)-Mo(1B)-C(10B)	66.0(3)
O(2B)-C(13B)-C(12B)	122.6(9)	C(19B)-Mo(1B)-C(10B)	109.2(3)
O(2B)-C(13B)-C(14B)	120.8(9)	N(5B)-Mo(1B)-C(10B)	144.5(3)
C(12B)-C(13B)-C(14B)	116.1(8)	C(11B)-Mo(1B)-C(10B)	34.8(3)
O(1B)-C(14B)-C(13B)	114.9(8)	N(3B)-Mo(1B)-C(10B)	129.2(3)
O(1B)-C(14B)-C(15B)	105.9(9)	N(1B)-Mo(1B)-C(10B)	84.1(3)
C(13B)-C(14B)-C(15B)	112.7(9)	C(12B)-Mo(1B)-C(10B)	60.0(3)
O(1B)-C(14B)-C(17B)	124.6(15)	C(1B)-N(1B)-N(2B)	105.2(6)
C(13B)-C(14B)-C(17B)	97.7(14)	C(1B)-N(1B)-Mo(1B)	134.8(5)
C(15B)-C(14B)-C(17B)	100.2(15)	N(2B)-N(1B)-Mo(1B)	119.9(4)
O(1B)-C(14B)-C(17C)	100.2(9)	C(3B)-N(2B)-N(1B)	109.4(7)
C(13B)-C(14B)-C(17C)	110.2(10)	C(3B)-N(2B)-B(1B)	128.7(7)
C(15B)-C(14B)-C(17C)	112.3(11)	N(1B)-N(2B)-B(1B)	121.3(6)
C(17B)-C(14B)-C(17C)	24.5(12)	C(4B)-N(3B)-N(4B)	105.5(6)
C(14B)-C(15B)-C(16B)	124.1(14)	C(4B)-N(3B)-Mo(1B)	133.5(5)
C(14B)-C(15B)-I(2B)	125.7(10)	N(4B)-N(3B)-Mo(1B)	120.1(4)
C(16B)-C(15B)-I(2B)	77.3(10)	C(6B)-N(4B)-N(3B)	110.3(6)
C(14B)-C(15B)-I(1B)	113.2(10)	C(6B)-N(4B)-B(1B)	127.5(7)
C(16B)-C(15B)-I(1B)	115.5(12)	N(3B)-N(4B)-B(1B)	121.4(6)
I(2B)-C(15B)-I(1B)	92.9(7)	C(7B)-N(5B)-N(6B)	106.9(7)
C(18B)-C(17B)-C(14B)	113(3)	C(7B)-N(5B)-Mo(1B)	130.7(6)
C(18C)-C(17C)-C(14B)	139.0(18)	N(6B)-N(5B)-Mo(1B)	122.4(5)
O(3B)-C(19B)-Mo(1B)	175.9(8)	C(9B)-N(6B)-N(5B)	108.8(7)
O(4B)-C(20B)-Mo(1B)	176.3(7)	C(9B)-N(6B)-B(1B)	130.8(7)
C(20B)-Mo(1B)-C(19B)	83.4(3)	N(5B)-N(6B)-B(1B)	120.4(6)
C(20B)-Mo(1B)-N(5B)	85.5(3)	C(10B)-O(1B)-C(14B)	117.7(7)
C(19B)-Mo(1B)-N(5B)	86.7(3)	Cl(2)-C(1S)-Cl(1)	98.3(8)

Symmetry transformations used to generate equivalent atoms:

Table 2.30. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for 2.33. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	22(4)	27(4)	32(4)	1(3)	-14(3)	-6(3)
C(1)	35(4)	17(3)	26(3)	2(3)	-11(3)	-9(3)
C(2)	46(4)	29(4)	38(4)	3(3)	-17(4)	-23(3)
C(3)	30(4)	33(4)	37(4)	1(3)	-11(3)	-19(3)
C(4)	39(4)	31(4)	30(4)	-3(3)	-17(3)	-8(3)
C(5)	40(4)	30(4)	23(4)	-6(3)	-5(3)	2(3)
C(6)	31(4)	28(4)	25(3)	5(3)	-8(3)	-2(3)
C(7)	43(4)	39(4)	23(4)	11(3)	-13(3)	-14(4)
C(8)	57(5)	48(5)	26(4)	6(3)	-27(4)	-15(4)
C(9)	44(5)	43(5)	35(4)	7(4)	-28(4)	-8(4)
C(10)	31(4)	59(6)	46(5)	-16(4)	-17(4)	-13(4)
C(11)	30(4)	73(6)	25(4)	6(4)	-14(3)	-21(4)
C(12)	46(4)	43(4)	52(5)	34(4)	-38(4)	-33(4)
C(13)	34(4)	31(4)	41(4)	14(3)	-24(3)	-12(3)
C(14)	34(4)	48(5)	46(5)	14(4)	-23(4)	-25(4)
C(15)	35(4)	72(7)	62(6)	31(5)	-23(4)	-36(5)
C(17)	47(5)	81(8)	50(6)	-1(5)	-15(5)	-37(6)
C(18)	71(7)	129(12)	51(6)	43(7)	-43(6)	-55(8)
C(19)	29(4)	28(4)	41(4)	10(3)	-11(3)	-7(3)
C(20)	30(3)	29(4)	22(3)	8(3)	-15(3)	-13(3)
I(1)	42(1)	82(1)	48(1)	25(1)	-16(1)	-29(1)
Mo(1)	22(1)	20(1)	19(1)	4(1)	-8(1)	-9(1)
N(1)	21(3)	25(3)	21(3)	2(2)	-12(2)	-9(2)
N(2)	23(3)	22(3)	30(3)	1(2)	-10(2)	-10(2)
N(3)	31(3)	23(3)	25(3)	-1(2)	-10(2)	-9(2)
N(4)	25(3)	24(3)	23(3)	2(2)	-9(2)	-3(2)
N(5)	29(3)	28(3)	21(3)	4(2)	-12(2)	-6(2)
N(6)	28(3)	29(3)	26(3)	-2(2)	-15(3)	-3(3)
O(1)	37(3)	45(4)	71(5)	1(3)	-25(3)	-18(3)
O(2)	48(4)	51(4)	62(5)	7(3)	-26(4)	-17(3)
O(3)	45(4)	39(4)	93(6)	31(4)	-24(4)	-26(3)
O(4)	32(3)	42(3)	32(3)	-9(3)	-9(2)	-5(3)
B(1B)	20(3)	26(4)	28(4)	-1(3)	-5(3)	-5(3)
C(1B)	35(4)	31(4)	38(4)	-1(3)	-21(3)	-11(3)
C(2B)	36(4)	34(4)	32(4)	-9(3)	-16(3)	-6(3)
C(3B)	30(4)	35(4)	29(4)	-4(3)	-10(3)	-3(3)
C(4B)	29(4)	24(4)	35(4)	-2(3)	-6(3)	-6(3)
C(5B)	41(4)	25(4)	45(5)	7(3)	-19(4)	-12(3)
C(6B)	41(4)	32(4)	32(4)	7(3)	-15(3)	-21(3)
C(7B)	41(4)	38(4)	41(4)	10(4)	-25(4)	-15(4)
C(8B)	43(5)	53(6)	58(6)	8(5)	-37(5)	-13(4)
C(9B)	28(4)	44(5)	57(6)	4(4)	-24(4)	-10(4)
C(10B)	31(4)	38(4)	46(5)	-8(4)	-8(4)	-17(3)
C(11B)	21(3)	54(5)	44(5)	0(4)	-15(3)	-15(4)
C(12B)	20(3)	26(4)	69(6)	11(4)	-21(4)	-5(3)
I(1B)	92(1)	61(1)	50(1)	8(1)	-14(1)	-53(1)
I(2B)	81(1)	45(1)	36(1)	10(1)	-16(1)	-16(1)
Mo(1B)	18(1)	19(1)	21(1)	2(1)	-9(1)	-5(1)
N(1B)	23(3)	25(3)	25(3)	2(2)	-12(2)	-9(2)
N(2B)	22(3)	27(3)	26(3)	-3(2)	-6(2)	-5(2)
N(3B)	25(3)	25(3)	28(3)	7(2)	-13(2)	-9(2)

N(4B)	23(3)	25(3)	25(3)	3(2)	-10(2)	-8(2)
N(5B)	28(3)	30(3)	27(3)	3(2)	-15(2)	-9(3)
N(6B)	23(3)	33(3)	33(3)	3(3)	-12(3)	-12(3)
O(1B)	40(3)	36(3)	49(4)	-6(3)	0(3)	-22(3)
O(2B)	50(4)	35(4)	74(5)	-10(3)	-24(4)	4(3)
O(3B)	58(5)	89(6)	47(4)	-35(4)	-15(4)	-9(4)
O(4B)	55(4)	33(3)	48(4)	19(3)	-24(3)	-14(3)
Cl(1)	80(5)	70(5)	65(5)	-5(4)	-23(4)	-53(4)
Cl(2)	16(3)	67(5)	158(9)	-51(6)	-28(4)	-5(3)

Table 2.31. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 2.33

	x	y	z	U(eq)
H(1)	7269	9180	1765	33
H(1)	3440	12092	1619	32
H(2)	5109	12611	1299	42
H(3)	6843	11089	1350	38
H(4)	5340	7508	576	41
H(5)	7615	6732	-172	47
H(6)	8288	7700	466	40
H(7)	3384	9081	4541	44
H(8)	5037	8653	5091	51
H(9)	6821	8701	3647	48
H(10)	3568	8464	873	54
H(11)	3863	9919	258	50
H(12)	2593	11387	1271	46
H(15)	-874	10836	2507	63
H(16A)	-1888	10066	2303	64
H(16B)	-1791	9618	3297	64
H(16C)	-910	8969	2318	64
H(17)	1183	9868	267	68
H(18)	205	11340	-184	91
H(19)	-101	11820	913	91
H(1B)	6021	5615	5695	33
H(1B)	8566	7707	4691	39
H(2B)	6843	8262	6288	42
H(3B)	5859	7086	6641	42
H(4B)	10275	3104	3639	40
H(5B)	9088	2270	4943	45
H(6B)	7098	3664	5842	40
H(7B)	7340	6409	2062	46
H(8B)	5147	6656	2849	58
H(9B)	4762	6191	4548	51
H(10B)	10179	7051	3485	47
H(11B)	10639	5555	4290	46
H(12B)	11334	4048	3407	48

Table 2.32. Torsion angles [°] for 2.33

N(1)-C(1)-C(2)-C(3)	0.1(9)
C(1)-C(2)-C(3)-N(2)	0.0(9)
N(3)-C(4)-C(5)-C(6)	0.4(10)
C(4)-C(5)-C(6)-N(4)	-0.3(9)
N(5)-C(7)-C(8)-C(9)	-0.1(11)
C(7)-C(8)-C(9)-N(6)	1.2(11)
O(1)-C(10)-C(11)-C(12)	38.3(12)
Mo(1)-C(10)-C(11)-C(12)	-69.6(6)
O(1)-C(10)-C(11)-Mo(1)	107.9(8)
C(10)-C(11)-C(12)-C(13)	-35.3(11)
Mo(1)-C(11)-C(12)-C(13)	-106.8(7)
C(10)-C(11)-C(12)-Mo(1)	71.5(7)
C(11)-C(12)-C(13)-O(2)	-171.2(9)
Mo(1)-C(12)-C(13)-O(2)	111.9(9)
C(11)-C(12)-C(13)-C(14)	-1.8(11)
Mo(1)-C(12)-C(13)-C(14)	-78.7(8)
O(2)-C(13)-C(14)-O(1)	-152.0(9)
C(12)-C(13)-C(14)-O(1)	38.1(10)
O(2)-C(13)-C(14)-C(15)	-28.8(12)
C(12)-C(13)-C(14)-C(15)	161.3(7)
O(2)-C(13)-C(14)-C(17)	88.8(10)
C(12)-C(13)-C(14)-C(17)	-81.0(9)
O(1)-C(14)-C(15)-C(16)	-67.2(16)
C(13)-C(14)-C(15)-C(16)	167.2(12)
C(17)-C(14)-C(15)-C(16)	50.0(17)
O(1)-C(14)-C(15)-I(1)	65.3(9)
C(13)-C(14)-C(15)-I(1)	-60.2(9)
C(17)-C(14)-C(15)-I(1)	-177.5(7)
O(1)-C(14)-C(17)-C(18)	-168.4(11)
C(15)-C(14)-C(17)-C(18)	75.4(14)
C(13)-C(14)-C(17)-C(18)	-47.4(14)
O(3)-C(19)-Mo(1)-C(20)	-89(14)
O(3)-C(19)-Mo(1)-N(5)	-3(14)
O(3)-C(19)-Mo(1)-C(11)	163(14)
O(3)-C(19)-Mo(1)-N(3)	77(14)
O(3)-C(19)-Mo(1)-N(1)	-4(15)
O(3)-C(19)-Mo(1)-C(12)	-160(14)
O(3)-C(19)-Mo(1)-C(10)	157(14)
O(4)-C(20)-Mo(1)-C(19)	105(17)
O(4)-C(20)-Mo(1)-N(5)	19(17)
O(4)-C(20)-Mo(1)-C(11)	-152(17)
O(4)-C(20)-Mo(1)-N(3)	17(17)
O(4)-C(20)-Mo(1)-N(1)	-60(17)
O(4)-C(20)-Mo(1)-C(12)	-140(17)
O(4)-C(20)-Mo(1)-C(10)	171(17)
C(10)-C(11)-Mo(1)-C(19)	-8.9(6)
C(12)-C(11)-Mo(1)-C(19)	108.5(5)
C(10)-C(11)-Mo(1)-C(20)	-97.9(6)
C(12)-C(11)-Mo(1)-C(20)	19.5(6)
C(10)-C(11)-Mo(1)-N(5)	113.0(11)
C(12)-C(11)-Mo(1)-N(5)	-129.6(10)
C(10)-C(11)-Mo(1)-N(3)	84.8(5)
C(12)-C(11)-Mo(1)-N(3)	-157.8(5)
C(10)-C(11)-Mo(1)-N(1)	167.8(5)

C(12)-C(11)-Mo(1)-N(1)	-74.8(5)
C(10)-C(11)-Mo(1)-C(12)	-117.4(7)
C(12)-C(11)-Mo(1)-C(10)	117.4(7)
C(11)-C(12)-Mo(1)-C(19)	-83.2(6)
C(13)-C(12)-Mo(1)-C(19)	29.4(8)
C(11)-C(12)-Mo(1)-C(20)	-160.8(6)
C(13)-C(12)-Mo(1)-C(20)	-48.3(7)
C(11)-C(12)-Mo(1)-N(5)	152.2(6)
C(13)-C(12)-Mo(1)-N(5)	-95.2(8)
C(13)-C(12)-Mo(1)-C(11)	112.5(9)
C(11)-C(12)-Mo(1)-N(3)	25.4(6)
C(13)-C(12)-Mo(1)-N(3)	137.9(6)
C(11)-C(12)-Mo(1)-N(1)	102.5(5)
C(13)-C(12)-Mo(1)-N(1)	-144.9(7)
C(11)-C(12)-Mo(1)-C(10)	-36.1(5)
C(13)-C(12)-Mo(1)-C(10)	76.5(7)
C(11)-C(10)-Mo(1)-C(19)	170.7(6)
O(1)-C(10)-Mo(1)-C(19)	55.3(7)
C(11)-C(10)-Mo(1)-C(20)	94.7(6)
O(1)-C(10)-Mo(1)-C(20)	-20.7(9)
C(11)-C(10)-Mo(1)-N(5)	-150.0(6)
O(1)-C(10)-Mo(1)-N(5)	94.6(8)
O(1)-C(10)-Mo(1)-C(11)	-115.4(10)
C(11)-C(10)-Mo(1)-N(3)	-91.6(5)
O(1)-C(10)-Mo(1)-N(3)	153.0(8)
C(11)-C(10)-Mo(1)-N(1)	-14.9(6)
O(1)-C(10)-Mo(1)-N(1)	-130.3(7)
C(11)-C(10)-Mo(1)-C(12)	37.5(5)
O(1)-C(10)-Mo(1)-C(12)	-77.9(7)
C(2)-C(1)-N(1)-N(2)	-0.1(8)
C(2)-C(1)-N(1)-Mo(1)	171.9(5)
C(19)-Mo(1)-N(1)-C(1)	-128.1(12)
C(20)-Mo(1)-N(1)-C(1)	-43.7(7)
N(5)-Mo(1)-N(1)-C(1)	-128.7(7)
C(11)-Mo(1)-N(1)-C(1)	65.1(7)
N(3)-Mo(1)-N(1)-C(1)	150.2(7)
C(12)-Mo(1)-N(1)-C(1)	29.8(7)
C(10)-Mo(1)-N(1)-C(1)	73.5(7)
C(19)-Mo(1)-N(1)-N(2)	42.8(14)
C(20)-Mo(1)-N(1)-N(2)	127.2(5)
N(5)-Mo(1)-N(1)-N(2)	42.3(5)
C(11)-Mo(1)-N(1)-N(2)	-123.9(5)
N(3)-Mo(1)-N(1)-N(2)	-38.8(5)
C(12)-Mo(1)-N(1)-N(2)	-159.2(6)
C(10)-Mo(1)-N(1)-N(2)	-115.5(5)
C(2)-C(3)-N(2)-N(1)	0.0(9)
C(2)-C(3)-N(2)-B(1)	-171.8(7)
C(1)-N(1)-N(2)-C(3)	0.0(8)
Mo(1)-N(1)-N(2)-C(3)	-173.2(5)
C(1)-N(1)-N(2)-B(1)	172.5(6)
Mo(1)-N(1)-N(2)-B(1)	-0.7(8)
N(4)-B(1)-N(2)-C(3)	-130.0(8)
N(6)-B(1)-N(2)-C(3)	113.0(8)
N(4)-B(1)-N(2)-N(1)	59.0(9)
N(6)-B(1)-N(2)-N(1)	-58.0(9)
C(5)-C(4)-N(3)-N(4)	-0.5(9)

C(5)-C(4)-N(3)-Mo(1)	-179.5(6)
C(19)-Mo(1)-N(3)-C(4)	49.3(8)
C(20)-Mo(1)-N(3)-C(4)	136.3(11)
N(5)-Mo(1)-N(3)-C(4)	134.0(8)
C(11)-Mo(1)-N(3)-C(4)	-53.9(8)
N(1)-Mo(1)-N(3)-C(4)	-144.8(8)
C(12)-Mo(1)-N(3)-C(4)	-68.6(8)
C(10)-Mo(1)-N(3)-C(4)	-18.8(8)
C(19)-Mo(1)-N(3)-N(4)	-129.7(6)
C(20)-Mo(1)-N(3)-N(4)	-42.7(14)
N(5)-Mo(1)-N(3)-N(4)	-44.9(5)
C(11)-Mo(1)-N(3)-N(4)	127.1(6)
N(1)-Mo(1)-N(3)-N(4)	36.2(5)
C(12)-Mo(1)-N(3)-N(4)	112.4(5)
C(10)-Mo(1)-N(3)-N(4)	162.2(6)
C(5)-C(6)-N(4)-N(3)	0.0(9)
C(5)-C(6)-N(4)-B(1)	173.4(7)
C(4)-N(3)-N(4)-C(6)	0.3(8)
Mo(1)-N(3)-N(4)-C(6)	179.5(5)
C(4)-N(3)-N(4)-B(1)	-173.7(7)
Mo(1)-N(3)-N(4)-B(1)	5.6(9)
N(2)-B(1)-N(4)-C(6)	125.0(8)
N(6)-B(1)-N(4)-C(6)	-118.2(8)
N(2)-B(1)-N(4)-N(3)	-62.2(9)
N(6)-B(1)-N(4)-N(3)	54.6(8)
C(8)-C(7)-N(5)-N(6)	-1.0(10)
C(8)-C(7)-N(5)-Mo(1)	179.3(6)
C(19)-Mo(1)-N(5)-C(7)	-43.0(8)
C(20)-Mo(1)-N(5)-C(7)	42.0(7)
C(11)-Mo(1)-N(5)-C(7)	-167.1(11)
N(3)-Mo(1)-N(5)-C(7)	-138.5(8)
N(1)-Mo(1)-N(5)-C(7)	136.9(7)
C(12)-Mo(1)-N(5)-C(7)	86.9(9)
C(10)-Mo(1)-N(5)-C(7)	-79.4(9)
C(19)-Mo(1)-N(5)-N(6)	137.3(6)
C(20)-Mo(1)-N(5)-N(6)	-137.6(6)
C(11)-Mo(1)-N(5)-N(6)	13.2(15)
N(3)-Mo(1)-N(5)-N(6)	41.8(6)
N(1)-Mo(1)-N(5)-N(6)	-42.8(6)
C(12)-Mo(1)-N(5)-N(6)	-92.7(8)
C(10)-Mo(1)-N(5)-N(6)	101.0(7)
C(8)-C(9)-N(6)-N(5)	-1.9(10)
C(8)-C(9)-N(6)-B(1)	178.5(8)
C(7)-N(5)-N(6)-C(9)	1.8(9)
Mo(1)-N(5)-N(6)-C(9)	-178.5(6)
C(7)-N(5)-N(6)-B(1)	-178.6(7)
Mo(1)-N(5)-N(6)-B(1)	1.2(9)
N(4)-B(1)-N(6)-C(9)	120.2(9)
N(2)-B(1)-N(6)-C(9)	-121.7(9)
N(4)-B(1)-N(6)-N(5)	-59.4(8)
N(2)-B(1)-N(6)-N(5)	58.7(9)
C(11)-C(10)-O(1)-C(14)	-0.3(13)
Mo(1)-C(10)-O(1)-C(14)	77.1(9)
C(15)-C(14)-O(1)-C(10)	-164.7(8)
C(13)-C(14)-O(1)-C(10)	-37.6(11)
C(17)-C(14)-O(1)-C(10)	79.7(9)

N(1B)-C(1B)-C(2B)-C(3B)	0.6(10)
C(1B)-C(2B)-C(3B)-N(2B)	-0.8(9)
N(3B)-C(4B)-C(5B)-C(6B)	2.9(10)
C(4B)-C(5B)-C(6B)-N(4B)	-1.8(10)
N(5B)-C(7B)-C(8B)-C(9B)	-0.7(11)
C(7B)-C(8B)-C(9B)-N(6B)	1.4(12)
O(1B)-C(10B)-C(11B)-C(12B)	-37.4(12)
Mo(1B)-C(10B)-C(11B)-C(12B)	70.0(6)
O(1B)-C(10B)-C(11B)-Mo(1B)	-107.5(8)
C(10B)-C(11B)-C(12B)-C(13B)	32.0(11)
Mo(1B)-C(11B)-C(12B)-C(13B)	104.2(7)
C(10B)-C(11B)-C(12B)-Mo(1B)	-72.2(6)
C(11B)-C(12B)-C(13B)-O(2B)	171.8(9)
Mo(1B)-C(12B)-C(13B)-O(2B)	-113.1(9)
C(11B)-C(12B)-C(13B)-C(14B)	-0.3(12)
Mo(1B)-C(12B)-C(13B)-C(14B)	74.8(9)
O(2B)-C(13B)-C(14B)-O(1B)	158.4(9)
C(12B)-C(13B)-C(14B)-O(1B)	-29.3(12)
O(2B)-C(13B)-C(14B)-C(15B)	37.0(14)
C(12B)-C(13B)-C(14B)-C(15B)	-150.8(10)
O(2B)-C(13B)-C(14B)-C(17B)	-67.5(17)
C(12B)-C(13B)-C(14B)-C(17B)	104.7(15)
O(2B)-C(13B)-C(14B)-C(17C)	-89.3(12)
C(12B)-C(13B)-C(14B)-C(17C)	83.0(11)
O(1B)-C(14B)-C(15B)-C(16B)	-171.7(14)
C(13B)-C(14B)-C(15B)-C(16B)	-45.3(18)
C(17B)-C(14B)-C(15B)-C(16B)	58(2)
C(17C)-C(14B)-C(15B)-C(16B)	79.8(18)
O(1B)-C(14B)-C(15B)-I(2B)	-72.6(13)
C(13B)-C(14B)-C(15B)-I(2B)	53.9(14)
C(17B)-C(14B)-C(15B)-I(2B)	156.8(16)
C(17C)-C(14B)-C(15B)-I(2B)	179.0(11)
O(1B)-C(14B)-C(15B)-I(1B)	39.5(12)
C(13B)-C(14B)-C(15B)-I(1B)	165.9(8)
C(17B)-C(14B)-C(15B)-I(1B)	-91.2(16)
C(17C)-C(14B)-C(15B)-I(1B)	-69.0(13)
O(1B)-C(14B)-C(17B)-C(18B)	-6(3)
C(13B)-C(14B)-C(17B)-C(18B)	-134(2)
C(15B)-C(14B)-C(17B)-C(18B)	111(2)
C(17C)-C(14B)-C(17B)-C(18B)	-11(2)
O(1B)-C(14B)-C(17C)-C(18C)	163(2)
C(13B)-C(14B)-C(17C)-C(18C)	42(3)
C(15B)-C(14B)-C(17C)-C(18C)	-85(3)
C(17B)-C(14B)-C(17C)-C(18C)	-21(3)
O(4B)-C(20B)-Mo(1B)-C(19B)	36(12)
O(4B)-C(20B)-Mo(1B)-N(5B)	-51(12)
O(4B)-C(20B)-Mo(1B)-C(11B)	146(12)
O(4B)-C(20B)-Mo(1B)-N(3B)	-31(12)
O(4B)-C(20B)-Mo(1B)-N(1B)	-129(12)
O(4B)-C(20B)-Mo(1B)-C(12B)	110(12)
O(4B)-C(20B)-Mo(1B)-C(10B)	151(12)
O(3B)-C(19B)-Mo(1B)-C(20B)	-85(13)
O(3B)-C(19B)-Mo(1B)-N(5B)	1(13)
O(3B)-C(19B)-Mo(1B)-C(11B)	177(100)
O(3B)-C(19B)-Mo(1B)-N(3B)	81(13)
O(3B)-C(19B)-Mo(1B)-N(1B)	12(13)

O(3B)-C(19B)-Mo(1B)-C(12B)	163(13)
O(3B)-C(19B)-Mo(1B)-C(10B)	-146(13)
C(10B)-C(11B)-Mo(1B)-C(20B)	7.6(6)
C(12B)-C(11B)-Mo(1B)-C(20B)	-110.6(6)
C(10B)-C(11B)-Mo(1B)-C(19B)	94.3(6)
C(12B)-C(11B)-Mo(1B)-C(19B)	-23.8(7)
C(10B)-C(11B)-Mo(1B)-N(5B)	-100.6(11)
C(12B)-C(11B)-Mo(1B)-N(5B)	141.3(9)
C(10B)-C(11B)-Mo(1B)-N(3B)	-173.1(5)
C(12B)-C(11B)-Mo(1B)-N(3B)	68.8(6)
C(10B)-C(11B)-Mo(1B)-N(1B)	-89.5(5)
C(12B)-C(11B)-Mo(1B)-N(1B)	152.4(6)
C(10B)-C(11B)-Mo(1B)-C(12B)	118.1(8)
C(12B)-C(11B)-Mo(1B)-C(10B)	-118.1(8)
C(11B)-C(12B)-Mo(1B)-C(20B)	79.5(6)
C(13B)-C(12B)-Mo(1B)-C(20B)	-32.4(7)
C(11B)-C(12B)-Mo(1B)-C(19B)	157.2(6)
C(13B)-C(12B)-Mo(1B)-C(19B)	45.3(7)
C(11B)-C(12B)-Mo(1B)-N(5B)	-152.9(7)
C(13B)-C(12B)-Mo(1B)-N(5B)	95.1(8)
C(13B)-C(12B)-Mo(1B)-C(11B)	-111.9(9)
C(11B)-C(12B)-Mo(1B)-N(3B)	-110.0(6)
C(13B)-C(12B)-Mo(1B)-N(3B)	138.0(7)
C(11B)-C(12B)-Mo(1B)-N(1B)	-30.5(6)
C(13B)-C(12B)-Mo(1B)-N(1B)	-142.5(6)
C(11B)-C(12B)-Mo(1B)-C(10B)	35.5(5)
C(13B)-C(12B)-Mo(1B)-C(10B)	-76.4(7)
C(11B)-C(10B)-Mo(1B)-C(20B)	-171.9(6)
O(1B)-C(10B)-Mo(1B)-C(20B)	-55.6(7)
C(11B)-C(10B)-Mo(1B)-C(19B)	-98.6(6)
O(1B)-C(10B)-Mo(1B)-C(19B)	17.6(8)
C(11B)-C(10B)-Mo(1B)-N(5B)	148.8(5)
O(1B)-C(10B)-Mo(1B)-N(5B)	-94.9(7)
O(1B)-C(10B)-Mo(1B)-C(11B)	116.2(9)
C(11B)-C(10B)-Mo(1B)-N(3B)	8.9(7)
O(1B)-C(10B)-Mo(1B)-N(3B)	125.2(6)
C(11B)-C(10B)-Mo(1B)-N(1B)	86.5(5)
O(1B)-C(10B)-Mo(1B)-N(1B)	-157.2(7)
C(11B)-C(10B)-Mo(1B)-C(12B)	-37.3(6)
O(1B)-C(10B)-Mo(1B)-C(12B)	79.0(7)
C(2B)-C(1B)-N(1B)-N(2B)	-0.1(9)
C(2B)-C(1B)-N(1B)-Mo(1B)	176.1(5)
C(20B)-Mo(1B)-N(1B)-C(1B)	-46.1(8)
C(19B)-Mo(1B)-N(1B)-C(1B)	-141.1(12)
N(5B)-Mo(1B)-N(1B)-C(1B)	-129.9(7)
C(11B)-Mo(1B)-N(1B)-C(1B)	53.5(7)
N(3B)-Mo(1B)-N(1B)-C(1B)	149.0(7)
C(12B)-Mo(1B)-N(1B)-C(1B)	71.2(8)
C(10B)-Mo(1B)-N(1B)-C(1B)	18.5(7)
C(20B)-Mo(1B)-N(1B)-N(2B)	129.7(5)
C(19B)-Mo(1B)-N(1B)-N(2B)	34.7(14)
N(5B)-Mo(1B)-N(1B)-N(2B)	45.9(5)
C(11B)-Mo(1B)-N(1B)-N(2B)	-130.7(6)
N(3B)-Mo(1B)-N(1B)-N(2B)	-35.2(5)
C(12B)-Mo(1B)-N(1B)-N(2B)	-113.0(5)
C(10B)-Mo(1B)-N(1B)-N(2B)	-165.7(6)

C(2B)-C(3B)-N(2B)-N(1B)	0.8(9)
C(2B)-C(3B)-N(2B)-B(1B)	-170.6(7)
C(1B)-N(1B)-N(2B)-C(3B)	-0.4(8)
Mo(1B)-N(1B)-N(2B)-C(3B)	-177.3(5)
C(1B)-N(1B)-N(2B)-B(1B)	171.7(7)
Mo(1B)-N(1B)-N(2B)-B(1B)	-5.2(8)
N(6B)-B(1B)-N(2B)-C(3B)	114.7(8)
N(4B)-B(1B)-N(2B)-C(3B)	-128.9(8)
N(6B)-B(1B)-N(2B)-N(1B)	-55.8(8)
N(4B)-B(1B)-N(2B)-N(1B)	60.7(9)
C(5B)-C(4B)-N(3B)-N(4B)	-2.9(10)
C(5B)-C(4B)-N(3B)-Mo(1B)	-172.1(6)
C(20B)-Mo(1B)-N(3B)-C(4B)	104.9(12)
C(19B)-Mo(1B)-N(3B)-C(4B)	38.0(8)
N(5B)-Mo(1B)-N(3B)-C(4B)	124.5(8)
C(11B)-Mo(1B)-N(3B)-C(4B)	-72.7(8)
N(1B)-Mo(1B)-N(3B)-C(4B)	-155.3(8)
C(12B)-Mo(1B)-N(3B)-C(4B)	-38.6(8)
C(10B)-Mo(1B)-N(3B)-C(4B)	-77.8(8)
C(20B)-Mo(1B)-N(3B)-N(4B)	-63.1(13)
C(19B)-Mo(1B)-N(3B)-N(4B)	-130.0(6)
N(5B)-Mo(1B)-N(3B)-N(4B)	-43.4(5)
C(11B)-Mo(1B)-N(3B)-N(4B)	119.4(6)
N(1B)-Mo(1B)-N(3B)-N(4B)	36.7(5)
C(12B)-Mo(1B)-N(3B)-N(4B)	153.4(6)
C(10B)-Mo(1B)-N(3B)-N(4B)	114.3(5)
C(5B)-C(6B)-N(4B)-N(3B)	0.1(9)
C(5B)-C(6B)-N(4B)-B(1B)	169.8(7)
C(4B)-N(3B)-N(4B)-C(6B)	1.7(9)
Mo(1B)-N(3B)-N(4B)-C(6B)	172.6(5)
C(4B)-N(3B)-N(4B)-B(1B)	-168.7(7)
Mo(1B)-N(3B)-N(4B)-B(1B)	2.2(9)
N(6B)-B(1B)-N(4B)-C(6B)	-111.7(8)
N(2B)-B(1B)-N(4B)-C(6B)	132.4(8)
N(6B)-B(1B)-N(4B)-N(3B)	56.9(9)
N(2B)-B(1B)-N(4B)-N(3B)	-59.0(9)
C(8B)-C(7B)-N(5B)-N(6B)	-0.2(10)
C(8B)-C(7B)-N(5B)-Mo(1B)	-177.3(6)
C(20B)-Mo(1B)-N(5B)-C(7B)	34.7(8)
C(19B)-Mo(1B)-N(5B)-C(7B)	-48.9(8)
C(11B)-Mo(1B)-N(5B)-C(7B)	145.1(10)
N(3B)-Mo(1B)-N(5B)-C(7B)	-140.2(8)
N(1B)-Mo(1B)-N(5B)-C(7B)	133.8(8)
C(12B)-Mo(1B)-N(5B)-C(7B)	-97.1(10)
C(10B)-Mo(1B)-N(5B)-C(7B)	70.2(9)
C(20B)-Mo(1B)-N(5B)-N(6B)	-141.9(6)
C(19B)-Mo(1B)-N(5B)-N(6B)	134.5(6)
C(11B)-Mo(1B)-N(5B)-N(6B)	-31.5(13)
N(3B)-Mo(1B)-N(5B)-N(6B)	43.1(6)
N(1B)-Mo(1B)-N(5B)-N(6B)	-42.8(6)
C(12B)-Mo(1B)-N(5B)-N(6B)	86.2(9)
C(10B)-Mo(1B)-N(5B)-N(6B)	-106.5(7)
C(8B)-C(9B)-N(6B)-N(5B)	-1.6(11)
C(8B)-C(9B)-N(6B)-B(1B)	177.9(8)
C(7B)-N(5B)-N(6B)-C(9B)	1.1(9)
Mo(1B)-N(5B)-N(6B)-C(9B)	178.4(6)

C(7B)-N(5B)-N(6B)-B(1B)	-178.4(7)
Mo(1B)-N(5B)-N(6B)-B(1B)	-1.1(9)
N(2B)-B(1B)-N(6B)-C(9B)	-119.0(9)
N(4B)-B(1B)-N(6B)-C(9B)	122.4(9)
N(2B)-B(1B)-N(6B)-N(5B)	60.4(8)
N(4B)-B(1B)-N(6B)-N(5B)	-58.2(9)
C(11B)-C(10B)-O(1B)-C(14B)	6.7(13)
Mo(1B)-C(10B)-O(1B)-C(14B)	-70.3(9)
C(13B)-C(14B)-O(1B)-C(10B)	26.7(12)
C(15B)-C(14B)-O(1B)-C(10B)	151.8(9)
C(17B)-C(14B)-O(1B)-C(10B)	-93.3(18)
C(17C)-C(14B)-O(1B)-C(10B)	-91.3(10)

Symmetry transformations used to generate equivalent atoms:

Table 2.33. Crystal data and structure refinement for 2.34a

Identification code	**2.34a**	
Empirical formula	C20 H20 B Br Mo N6 O4	
Formula weight	595.08	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 20.4669(9) Å	α= 90°.
	b = 16.7217(8) Å	β= 90°.
	c = 13.3120(6) Å	γ = 90°.
Volume	4555.9(4) Å^3	
Z	8	
Density (calculated)	1.735 Mg/m^3	
Absorption coefficient	7.113 mm^{-1}	
F(000)	2368	
Crystal size	0.51 x 0.19 x 0.09 mm^3	
Theta range for data collection	4.32 to 66.79°.	
Index ranges	-23<=h<=22, -18<=k<=18, -14<=l<=15	
Reflections collected	33195	
Independent reflections	3850 [R(int) = 0.0366]	
Completeness to theta = 66.79°	95.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5669 and 0.1222	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3850 / 0 / 310
Goodness-of-fit on F^2	1.283
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1604
R indices (all data)	R1 = 0.0611, wR2 = 0.1615
Extinction coefficient	0.00013(3)
Largest diff. peak and hole	1.198 and -0.759 e.Å^{-3}

Table 2.34. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 2.34a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
B(1)	-449(4)	2580(6)	8529(6)	31(2)
C(1)	-608(3)	1297(4)	6348(6)	26(2)
C(2)	-1263(3)	1542(5)	6426(6)	35(2)
C(3)	-1273(3)	2065(5)	7197(6)	34(2)
C(4)	1070(4)	3520(4)	7819(6)	30(2)
C(5)	765(4)	4204(4)	8205(6)	33(2)
C(6)	161(4)	3945(4)	8482(5)	32(2)
C(7)	466(4)	1029(4)	9809(5)	32(2)
C(8)	40(4)	1181(5)	10582(5)	37(2)
C(9)	-370(4)	1779(5)	10226(5)	34(2)
C(10)	953(3)	1214(6)	5880(5)	38(2)
C(11)	1208(4)	1999(5)	6103(6)	41(2)
C(12)	1770(4)	1986(5)	6668(7)	40(2)
C(13)	2137(3)	835(4)	5757(5)	28(2)
C(14)	1426(3)	563(4)	5710(5)	24(1)
C(15)	2605(4)	140(5)	5978(7)	44(2)
C(16)	3344(3)	380(5)	6090(8)	47(2)
C(17)	2302(4)	1130(6)	4726(6)	43(2)
C(18)	2562(5)	1835(7)	4523(9)	69(3)
C(19)	1628(4)	1452(5)	8318(6)	36(2)
C(20)	864(3)	397(5)	7643(5)	28(2)
Mo(1)	821(1)	1574(1)	7552(1)	21(1)
N(1)	-248(3)	1660(3)	7048(4)	23(1)
N(2)	-663(3)	2145(4)	7583(4)	28(1)
N(3)	679(3)	2884(4)	7882(4)	27(1)
N(4)	111(3)	3157(4)	8296(4)	27(1)
N(5)	336(3)	1492(3)	9012(4)	26(1)
N(6)	-183(3)	1951(3)	9281(4)	26(1)
O(1)	2086(3)	1332(4)	8817(5)	54(2)
O(2)	891(3)	-276(3)	7781(5)	45(1)
O(3)	2260(2)	1425(3)	6518(5)	42(1)
O(4)	1260(3)	-79(4)	5417(4)	48(2)
Br(1)	2376(1)	-431(1)	7197(1)	58(1)
Br(1B)	2473(4)	-814(4)	5961(6)	93(2)

Table 2.35. Bond lengths [Å] and angles [°] for 2.34a

B(1)-N(2)	1.518(11)	C(20)-O(2)	1.142(10)
B(1)-N(4)	1.529(11)	C(20)-Mo(1)	1.974(8)
B(1)-N(6)	1.551(10)	Mo(1)-N(5)	2.186(6)
B(1)-H(1B)	0.9767	Mo(1)-N(3)	2.253(6)
C(1)-N(1)	1.335(9)	Mo(1)-N(1)	2.291(5)
C(1)-C(2)	1.404(10)	N(1)-N(2)	1.373(8)
C(1)-H(1)	0.9500	N(3)-N(4)	1.365(8)
C(2)-C(3)	1.349(11)	N(5)-N(6)	1.358(8)
C(2)-H(2)	0.9500	Br(1)-Br(1B)	1.777(9)
C(3)-N(2)	1.358(9)	Br(1)-H(15B)	1.2398
C(3)-H(3)	0.9500	Br(1B)-H(15)	1.2098
C(4)-N(3)	1.334(9)	Br(1B)-H(15B)	1.7692
C(4)-C(5)	1.400(11)	N(2)-B(1)-N(4)	110.5(6)
C(4)-H(4)	0.9500	N(2)-B(1)-N(6)	108.2(7)
C(5)-C(6)	1.361(11)	N(4)-B(1)-N(6)	107.2(6)
C(5)-H(5)	0.9500	N(2)-B(1)-H(1B)	104.7
C(6)-N(4)	1.346(10)	N(4)-B(1)-H(1B)	111.0
C(6)-H(6)	0.9500	N(6)-B(1)-H(1B)	115.2
C(7)-N(5)	1.340(9)	N(1)-C(1)-C(2)	110.0(7)
C(7)-C(8)	1.373(11)	N(1)-C(1)-H(1)	125.0
C(7)-H(7)	0.9500	C(2)-C(1)-H(1)	125.0
C(8)-C(9)	1.388(12)	C(3)-C(2)-C(1)	105.2(7)
C(8)-H(8)	0.9500	C(3)-C(2)-H(2)	127.4
C(9)-N(6)	1.346(9)	C(1)-C(2)-H(2)	127.4
C(9)-H(9)	0.9500	C(2)-C(3)-N(2)	109.7(6)
C(10)-C(11)	1.444(13)	C(2)-C(3)-H(3)	125.2
C(10)-C(14)	1.473(11)	N(2)-C(3)-H(3)	125.2
C(10)-Mo(1)	2.322(7)	N(3)-C(4)-C(5)	111.2(7)
C(10)-H(10)	1.0000	N(3)-C(4)-H(4)	124.4
C(11)-C(12)	1.374(12)	C(5)-C(4)-H(4)	124.4
C(11)-Mo(1)	2.204(8)	C(6)-C(5)-C(4)	104.1(7)
C(11)-H(11)	1.0000	C(6)-C(5)-H(5)	127.9
C(12)-O(3)	1.389(10)	C(4)-C(5)-H(5)	127.9
C(12)-Mo(1)	2.373(8)	N(4)-C(6)-C(5)	109.3(7)
C(12)-H(12)	1.0000	N(4)-C(6)-H(6)	125.3
C(13)-O(3)	1.436(9)	C(5)-C(6)-H(6)	125.3
C(13)-C(17)	1.497(11)	N(5)-C(7)-C(8)	111.2(7)
C(13)-C(14)	1.526(9)	N(5)-C(7)-H(7)	124.4
C(13)-C(15)	1.533(11)	C(8)-C(7)-H(7)	124.4
C(14)-O(4)	1.192(9)	C(7)-C(8)-C(9)	105.1(7)
C(15)-C(16)	1.572(11)	C(7)-C(8)-H(8)	127.4
C(15)-Br(1B)	1.617(12)	C(9)-C(8)-H(8)	127.4
C(15)-Br(1)	1.940(9)	N(6)-C(9)-C(8)	107.5(7)
C(15)-H(15)	1.0143	N(6)-C(9)-H(9)	126.2
C(15)-H(15B)	0.8698	C(8)-C(9)-H(9)	126.2
C(16)-H(16A)	0.9800	C(11)-C(10)-C(14)	117.8(6)
C(16)-H(16B)	0.9800	C(11)-C(10)-Mo(1)	67.0(4)
C(16)-H(16C)	0.9800	C(14)-C(10)-Mo(1)	114.6(5)
C(17)-C(18)	1.321(14)	C(11)-C(10)-H(10)	116.1
C(17)-H(17)	0.9500	C(14)-C(10)-H(10)	116.1
C(18)-H(18A)	0.9500	Mo(1)-C(10)-H(10)	116.1
C(18)-H(18B)	0.9500	C(12)-C(11)-C(10)	113.6(7)
C(19)-O(1)	1.166(10)	C(12)-C(11)-Mo(1)	79.4(5)
C(19)-Mo(1)	1.952(8)	C(10)-C(11)-Mo(1)	75.9(4)

C(12)-C(11)-H(11)	122.7
C(10)-C(11)-H(11)	122.7
Mo(1)-C(11)-H(11)	122.7
C(11)-C(12)-O(3)	122.5(7)
C(11)-C(12)-Mo(1)	65.9(4)
O(3)-C(12)-Mo(1)	117.8(5)
C(11)-C(12)-H(12)	114.1
O(3)-C(12)-H(12)	114.1
Mo(1)-C(12)-H(12)	114.1
O(3)-C(13)-C(17)	112.4(7)
O(3)-C(13)-C(14)	113.6(6)
C(17)-C(13)-C(14)	106.0(6)
O(3)-C(13)-C(15)	106.0(6)
C(17)-C(13)-C(15)	106.6(6)
C(14)-C(13)-C(15)	112.2(6)
O(4)-C(14)-C(10)	121.9(7)
O(4)-C(14)-C(13)	123.6(7)
C(10)-C(14)-C(13)	113.6(6)
C(13)-C(15)-C(16)	115.2(7)
C(13)-C(15)-Br(1B)	129.8(7)
C(16)-C(15)-Br(1B)	114.4(6)
C(13)-C(15)-Br(1)	112.5(5)
C(16)-C(15)-Br(1)	106.1(6)
Br(1B)-C(15)-Br(1)	59.1(4)
C(13)-C(15)-H(15)	106.8
C(16)-C(15)-H(15)	109.0
Br(1B)-C(15)-H(15)	48.3
Br(1)-C(15)-H(15)	106.9
C(13)-C(15)-H(15B)	88.6
C(16)-C(15)-H(15B)	106.2
Br(1B)-C(15)-H(15B)	85.1
Br(1)-C(15)-H(15B)	27.9
H(15)-C(15)-H(15B)	130.0
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(13)	124.9(9)
C(18)-C(17)-H(17)	117.5
C(13)-C(17)-H(17)	117.5
C(17)-C(18)-H(18A)	120.0
C(17)-C(18)-H(18B)	120.0
H(18A)-C(18)-H(18B)	120.0
O(1)-C(19)-Mo(1)	174.7(8)
O(2)-C(20)-Mo(1)	174.2(6)
C(19)-Mo(1)-C(20)	79.9(3)
C(19)-Mo(1)-N(5)	85.0(3)
C(20)-Mo(1)-N(5)	84.5(3)
C(19)-Mo(1)-C(11)	100.7(3)
C(20)-Mo(1)-C(11)	111.1(3)
N(5)-Mo(1)-C(11)	164.1(3)
C(19)-Mo(1)-N(3)	96.2(3)
C(20)-Mo(1)-N(3)	164.4(3)
N(5)-Mo(1)-N(3)	80.2(2)
C(11)-Mo(1)-N(3)	84.4(3)
C(19)-Mo(1)-N(1)	165.2(3)
C(20)-Mo(1)-N(1)	97.1(2)
N(5)-Mo(1)-N(1)	80.3(2)
C(11)-Mo(1)-N(1)	93.8(3)
N(3)-Mo(1)-N(1)	82.7(2)
C(19)-Mo(1)-C(10)	112.0(3)
C(20)-Mo(1)-C(10)	78.2(3)
N(5)-Mo(1)-C(10)	152.8(3)
C(11)-Mo(1)-C(10)	37.1(3)
N(3)-Mo(1)-C(10)	117.0(3)
N(1)-Mo(1)-C(10)	81.2(2)
C(19)-Mo(1)-C(12)	66.2(3)
C(20)-Mo(1)-C(12)	106.4(3)
N(5)-Mo(1)-C(12)	146.1(3)
C(11)-Mo(1)-C(12)	34.7(3)
N(3)-Mo(1)-C(12)	85.4(2)
N(1)-Mo(1)-C(12)	128.1(3)
C(10)-Mo(1)-C(12)	60.3(3)
C(1)-N(1)-N(2)	106.8(5)
C(1)-N(1)-Mo(1)	134.7(5)
N(2)-N(1)-Mo(1)	118.4(4)
C(3)-N(2)-N(1)	108.4(6)
C(3)-N(2)-B(1)	128.8(6)
N(1)-N(2)-B(1)	122.3(5)
C(4)-N(3)-N(4)	105.7(6)
C(4)-N(3)-Mo(1)	133.3(5)
N(4)-N(3)-Mo(1)	120.9(4)
C(6)-N(4)-N(3)	109.7(6)
C(6)-N(4)-B(1)	129.6(6)
N(3)-N(4)-B(1)	120.6(6)
C(7)-N(5)-N(6)	105.8(6)
C(7)-N(5)-Mo(1)	130.5(5)
N(6)-N(5)-Mo(1)	123.7(4)
C(9)-N(6)-N(5)	110.4(6)
C(9)-N(6)-B(1)	130.4(6)
N(5)-N(6)-B(1)	119.1(5)
C(12)-O(3)-C(13)	116.0(6)
Br(1B)-Br(1)-C(15)	51.4(4)
Br(1B)-Br(1)-H(15B)	69.2
C(15)-Br(1)-H(15B)	19.1
C(15)-Br(1B)-Br(1)	69.6(5)
C(15)-Br(1B)-H(15)	38.8
Br(1)-Br(1B)-H(15)	107.9
C(15)-Br(1B)-H(15B)	29.3
Br(1)-Br(1B)-H(15B)	40.9
H(15)-Br(1B)-H(15B)	67.4

Table 2.36. Anisotropic displacement parameters ($Å^2 x 10^3$) for 2.34a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	23(4)	43(5)	28(4)	1(4)	5(3)	10(4)
C(1)	22(3)	24(4)	33(4)	4(3)	-3(3)	-5(3)
C(2)	19(3)	42(5)	42(4)	9(4)	-5(3)	-3(3)
C(3)	16(3)	47(5)	37(4)	1(4)	-2(3)	6(3)
C(4)	26(4)	29(4)	35(4)	-8(3)	-1(3)	-6(3)
C(5)	45(5)	23(4)	31(4)	0(3)	-6(3)	-1(3)
C(6)	45(4)	27(4)	23(4)	-2(3)	-2(3)	11(3)
C(7)	42(4)	28(4)	25(4)	2(3)	-9(3)	-2(3)
C(8)	57(5)	32(4)	20(4)	6(3)	-3(3)	-10(4)
C(9)	36(4)	40(4)	24(4)	-3(3)	4(3)	-10(3)
C(10)	14(3)	80(6)	21(4)	0(4)	-4(3)	5(4)
C(11)	56(5)	32(4)	34(4)	10(4)	20(4)	17(4)
C(12)	36(4)	26(4)	58(5)	-7(4)	10(4)	-8(3)
C(13)	24(3)	30(4)	30(4)	-4(3)	1(3)	1(3)
C(14)	30(4)	22(4)	19(3)	1(3)	1(3)	-9(3)
C(15)	33(5)	48(5)	51(5)	3(4)	-1(4)	14(4)
C(16)	18(4)	45(5)	78(6)	-8(5)	17(4)	16(3)
C(17)	28(4)	70(6)	32(4)	9(4)	8(3)	3(4)
C(18)	55(6)	83(8)	69(7)	27(6)	21(6)	-1(6)
C(19)	31(4)	28(4)	50(5)	-11(4)	0(4)	4(3)
C(20)	23(4)	36(5)	25(4)	-2(3)	-4(3)	1(3)
Mo(1)	16(1)	21(1)	25(1)	1(1)	-1(1)	1(1)
N(1)	21(3)	25(3)	23(3)	7(2)	0(2)	1(2)
N(2)	16(3)	39(4)	29(3)	-1(3)	2(2)	7(3)
N(3)	26(3)	28(3)	26(3)	-1(3)	2(2)	3(2)
N(4)	27(3)	27(3)	27(3)	2(2)	4(2)	9(2)
N(5)	25(3)	28(3)	24(3)	4(2)	0(2)	2(2)
N(6)	23(3)	26(3)	29(3)	-1(3)	5(2)	1(2)
O(1)	26(3)	72(4)	65(4)	-12(3)	-25(3)	5(3)
O(2)	65(4)	23(3)	46(3)	5(3)	-2(3)	8(3)
O(3)	27(3)	49(3)	50(3)	-18(3)	9(2)	3(2)
O(4)	48(3)	53(4)	42(3)	1(3)	-1(3)	-1(3)
Br(1)	50(1)	80(1)	45(1)	30(1)	13(1)	40(1)
Br(1B)	97(5)	71(4)	110(6)	-3(4)	-26(5)	18(4)

Table 2.37. Hydrogen coordinates ($x 10^4$) and isotropic displacement parameters ($Å^2 x 10^3$) for 2.34a

	x	y	z	U(eq)
H(1B)	-837	2869	8750	38
H(1)	-446	927	5867	32
H(2)	-1621	1375	6023	42
H(3)	-1651	2336	7435	40
H(4)	1499	3510	7548	36
H(5)	940	4728	8260	40
H(6)	-172	4270	8764	38

H(7)	808	646	9835	38
H(8)	29	931	11223	44
H(9)	-719	2021	10584	40
H(10)	547	1196	5464	46
H(11)	1044	2494	5765	49
H(12)	1933	2528	6864	48
H(16A)	3508	578	5445	71
H(16B)	3598	-89	6296	71
H(16C)	3386	800	6599	71
H(17)	2214	784	4177	52
H(18A)	2657	2197	5053	83
H(18B)	2652	1979	3847	83
H(15)	2559	-253	5402	70
H(15B)	2447	120	6584	111

Table 2.38. Torsion angles [°] for 2.34a

N(1)-C(1)-C(2)-C(3)	0.2(9)
C(1)-C(2)-C(3)-N(2)	-0.1(9)
N(3)-C(4)-C(5)-C(6)	-1.4(9)
C(4)-C(5)-C(6)-N(4)	1.2(8)
N(5)-C(7)-C(8)-C(9)	-0.4(9)
C(7)-C(8)-C(9)-N(6)	0.4(8)
C(14)-C(10)-C(11)-C(12)	-35.1(10)
Mo(1)-C(10)-C(11)-C(12)	71.6(6)
C(14)-C(10)-C(11)-Mo(1)	-106.7(6)
C(10)-C(11)-C(12)-O(3)	39.3(11)
Mo(1)-C(11)-C(12)-O(3)	108.7(7)
C(10)-C(11)-C(12)-Mo(1)	-69.4(6)
C(11)-C(10)-C(14)-O(4)	-171.8(7)
Mo(1)-C(10)-C(14)-O(4)	112.4(7)
C(11)-C(10)-C(14)-C(13)	-2.3(9)
Mo(1)-C(10)-C(14)-C(13)	-78.1(7)
O(3)-C(13)-C(14)-O(4)	-152.7(7)
C(17)-C(13)-C(14)-O(4)	83.5(9)
C(15)-C(13)-C(14)-O(4)	-32.4(10)
O(3)-C(13)-C(14)-C(10)	38.1(8)
C(17)-C(13)-C(14)-C(10)	-85.8(7)
C(15)-C(13)-C(14)-C(10)	158.3(6)
O(3)-C(13)-C(15)-C(16)	-52.6(9)
C(17)-C(13)-C(15)-C(16)	67.3(9)
C(14)-C(13)-C(15)-C(16)	-177.2(7)
O(3)-C(13)-C(15)-Br(1B)	136.9(9)
C(17)-C(13)-C(15)-Br(1B)	-103.2(10)
C(14)-C(13)-C(15)-Br(1B)	12.4(12)
O(3)-C(13)-C(15)-Br(1)	69.2(7)
C(17)-C(13)-C(15)-Br(1)	-170.9(6)
C(14)-C(13)-C(15)-Br(1)	-55.4(8)
O(3)-C(13)-C(17)-C(18)	3.1(12)
C(14)-C(13)-C(17)-C(18)	127.8(9)
C(15)-C(13)-C(17)-C(18)	-112.6(10)
O(1)-C(19)-Mo(1)-C(20)	-41(8)
O(1)-C(19)-Mo(1)-N(5)	44(8)

O(1)-C(19)-Mo(1)-C(11)	-151(8)
O(1)-C(19)-Mo(1)-N(3)	124(8)
O(1)-C(19)-Mo(1)-N(1)	39(8)
O(1)-C(19)-Mo(1)-C(10)	-114(8)
O(1)-C(19)-Mo(1)-C(12)	-154(8)
O(2)-C(20)-Mo(1)-C(19)	57(6)
O(2)-C(20)-Mo(1)-N(5)	-29(6)
O(2)-C(20)-Mo(1)-C(11)	154(6)
O(2)-C(20)-Mo(1)-N(3)	-20(7)
O(2)-C(20)-Mo(1)-N(1)	-109(6)
O(2)-C(20)-Mo(1)-C(10)	172(6)
O(2)-C(20)-Mo(1)-C(12)	118(6)
C(12)-C(11)-Mo(1)-C(19)	-5.4(5)
C(10)-C(11)-Mo(1)-C(19)	112.4(5)
C(12)-C(11)-Mo(1)-C(20)	-88.7(5)
C(10)-C(11)-Mo(1)-C(20)	29.1(5)
C(12)-C(11)-Mo(1)-N(5)	104.7(10)
C(10)-C(11)-Mo(1)-N(5)	-137.5(9)
C(12)-C(11)-Mo(1)-N(3)	89.9(5)
C(10)-C(11)-Mo(1)-N(3)	-152.3(5)
C(12)-C(11)-Mo(1)-N(1)	172.2(5)
C(10)-C(11)-Mo(1)-N(1)	-70.0(4)
C(12)-C(11)-Mo(1)-C(10)	-117.8(7)
C(10)-C(11)-Mo(1)-C(12)	117.8(7)
C(11)-C(10)-Mo(1)-C(19)	-78.4(5)
C(14)-C(10)-Mo(1)-C(19)	32.8(7)
C(11)-C(10)-Mo(1)-C(20)	-152.3(5)
C(14)-C(10)-Mo(1)-C(20)	-41.1(6)
C(11)-C(10)-Mo(1)-N(5)	156.1(5)
C(14)-C(10)-Mo(1)-N(5)	-92.6(6)
C(14)-C(10)-Mo(1)-C(11)	111.3(7)
C(11)-C(10)-Mo(1)-N(3)	31.3(5)
C(14)-C(10)-Mo(1)-N(3)	142.6(5)
C(11)-C(10)-Mo(1)-N(1)	108.4(5)
C(14)-C(10)-Mo(1)-N(1)	-140.3(6)
C(11)-C(10)-Mo(1)-C(12)	-35.4(5)
C(14)-C(10)-Mo(1)-C(12)	75.8(5)
C(11)-C(12)-Mo(1)-C(19)	174.2(6)
O(3)-C(12)-Mo(1)-C(19)	58.8(6)
C(11)-C(12)-Mo(1)-C(20)	103.4(5)
O(3)-C(12)-Mo(1)-C(20)	-12.0(7)
C(11)-C(12)-Mo(1)-N(5)	-151.6(5)
O(3)-C(12)-Mo(1)-N(5)	93.0(7)
O(3)-C(12)-Mo(1)-C(11)	-115.4(8)
C(11)-C(12)-Mo(1)-N(3)	-86.9(5)
O(3)-C(12)-Mo(1)-N(3)	157.7(6)
C(11)-C(12)-Mo(1)-N(1)	-9.9(6)
O(3)-C(12)-Mo(1)-N(1)	-125.3(6)
C(11)-C(12)-Mo(1)-C(10)	37.9(5)
O(3)-C(12)-Mo(1)-C(10)	-77.5(6)
C(2)-C(1)-N(1)-N(2)	-0.2(8)
C(2)-C(1)-N(1)-Mo(1)	175.1(5)
C(19)-Mo(1)-N(1)-C(1)	-125.4(11)
C(20)-Mo(1)-N(1)-C(1)	-47.9(7)
N(5)-Mo(1)-N(1)-C(1)	-131.0(6)
C(11)-Mo(1)-N(1)-C(1)	63.9(7)

N(3)-Mo(1)-N(1)-C(1)	147.8(6)
C(10)-Mo(1)-N(1)-C(1)	28.9(7)
C(12)-Mo(1)-N(1)-C(1)	69.5(7)
C(19)-Mo(1)-N(1)-N(2)	49.6(12)
C(20)-Mo(1)-N(1)-N(2)	127.1(5)
N(5)-Mo(1)-N(1)-N(2)	43.9(5)
C(11)-Mo(1)-N(1)-N(2)	-121.2(5)
N(3)-Mo(1)-N(1)-N(2)	-37.3(5)
C(10)-Mo(1)-N(1)-N(2)	-156.2(5)
C(12)-Mo(1)-N(1)-N(2)	-115.5(5)
C(2)-C(3)-N(2)-N(1)	-0.1(9)
C(2)-C(3)-N(2)-B(1)	-171.5(7)
C(1)-N(1)-N(2)-C(3)	0.2(8)
Mo(1)-N(1)-N(2)-C(3)	-176.1(5)
C(1)-N(1)-N(2)-B(1)	172.3(7)
Mo(1)-N(1)-N(2)-B(1)	-4.0(8)
N(4)-B(1)-N(2)-C(3)	-128.6(8)
N(6)-B(1)-N(2)-C(3)	114.3(8)
N(4)-B(1)-N(2)-N(1)	61.1(9)
N(6)-B(1)-N(2)-N(1)	-56.0(8)
C(5)-C(4)-N(3)-N(4)	1.1(8)
C(5)-C(4)-N(3)-Mo(1)	-174.4(5)
C(19)-Mo(1)-N(3)-C(4)	49.9(7)
C(20)-Mo(1)-N(3)-C(4)	124.7(10)
N(5)-Mo(1)-N(3)-C(4)	133.7(7)
C(11)-Mo(1)-N(3)-C(4)	-50.3(7)
N(1)-Mo(1)-N(3)-C(4)	-144.9(7)
C(10)-Mo(1)-N(3)-C(4)	-68.7(7)
C(12)-Mo(1)-N(3)-C(4)	-15.5(7)
C(19)-Mo(1)-N(3)-N(4)	-125.0(5)
C(20)-Mo(1)-N(3)-N(4)	-50.3(11)
N(5)-Mo(1)-N(3)-N(4)	-41.2(5)
C(11)-Mo(1)-N(3)-N(4)	134.7(5)
N(1)-Mo(1)-N(3)-N(4)	40.1(5)
C(10)-Mo(1)-N(3)-N(4)	116.4(5)
C(12)-Mo(1)-N(3)-N(4)	169.6(5)
C(5)-C(6)-N(4)-N(3)	-0.6(8)
C(5)-C(6)-N(4)-B(1)	176.0(7)
C(4)-N(3)-N(4)-C(6)	-0.3(8)
Mo(1)-N(3)-N(4)-C(6)	175.9(5)
C(4)-N(3)-N(4)-B(1)	-177.2(6)
Mo(1)-N(3)-N(4)-B(1)	-1.0(8)
N(2)-B(1)-N(4)-C(6)	125.7(8)
N(6)-B(1)-N(4)-C(6)	-116.6(8)
N(2)-B(1)-N(4)-N(3)	-58.0(8)
N(6)-B(1)-N(4)-N(3)	59.6(8)
C(8)-C(7)-N(5)-N(6)	0.2(8)
C(8)-C(7)-N(5)-Mo(1)	179.1(5)
C(19)-Mo(1)-N(5)-C(7)	-39.3(7)
C(20)-Mo(1)-N(5)-C(7)	41.0(6)
C(11)-Mo(1)-N(5)-C(7)	-151.5(10)
N(3)-Mo(1)-N(5)-C(7)	-136.5(7)
N(1)-Mo(1)-N(5)-C(7)	139.3(7)
C(10)-Mo(1)-N(5)-C(7)	91.4(8)
C(12)-Mo(1)-N(5)-C(7)	-70.4(8)
C(19)-Mo(1)-N(5)-N(6)	139.5(6)

C(20)-Mo(1)-N(5)-N(6)	-140.2(5)
C(11)-Mo(1)-N(5)-N(6)	27.3(13)
N(3)-Mo(1)-N(5)-N(6)	42.3(5)
N(1)-Mo(1)-N(5)-N(6)	-41.9(5)
C(10)-Mo(1)-N(5)-N(6)	-89.8(7)
C(12)-Mo(1)-N(5)-N(6)	108.4(6)
C(8)-C(9)-N(6)-N(5)	-0.4(8)
C(8)-C(9)-N(6)-B(1)	-178.2(7)
C(7)-N(5)-N(6)-C(9)	0.1(8)
Mo(1)-N(5)-N(6)-C(9)	-178.9(5)
C(7)-N(5)-N(6)-B(1)	178.3(6)
Mo(1)-N(5)-N(6)-B(1)	-0.8(8)
N(2)-B(1)-N(6)-C(9)	-122.4(8)
N(4)-B(1)-N(6)-C(9)	118.4(8)
N(2)-B(1)-N(6)-N(5)	59.9(8)
N(4)-B(1)-N(6)-N(5)	-59.3(8)
C(11)-C(12)-O(3)-C(13)	-2.2(11)
Mo(1)-C(12)-O(3)-C(13)	75.6(8)
C(17)-C(13)-O(3)-C(12)	83.4(8)
C(14)-C(13)-O(3)-C(12)	-36.9(9)
C(15)-C(13)-O(3)-C(12)	-160.6(7)
C(13)-C(15)-Br(1)-Br(1B)	124.1(7)
C(16)-C(15)-Br(1)-Br(1B)	-109.1(7)
C(13)-C(15)-Br(1B)-Br(1)	-94.7(9)
C(16)-C(15)-Br(1B)-Br(1)	94.8(7)

Symmetry transformations used to generate equivalent atoms:

Table 2.39. Crystal data and structure refinement for 2.34b

Identification code	**2.34b**	
Empirical formula	C20 H19.50 B Br Mo N6 O4	
Formula weight	594.58	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.8097(4) Å	α= 90°.
	b = 14.8595(3) Å	β= 103.128(1)°.
	c = 17.8518(4) Å	γ = 90°.
Volume	4859.22(18) $Å^3$	
Z	8	
Density (calculated)	1.625 Mg/m^3	
Absorption coefficient	2.222 mm^{-1}	

F(000)	2364
Crystal size	0.36 x 0.24 x 0.21 mm^3
Theta range for data collection	1.76 to 26.37°.
Index ranges	-23<=h<=23, -18<=k<=18, -21<=l<=22
Reflections collected	39764
Independent reflections	9905 [R(int) = 0.0562]
Completeness to theta = 26.37°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6526 and 0.5018
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9905 / 0 / 607
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1386
R indices (all data)	R1 = 0.0638, wR2 = 0.1464
Largest diff. peak and hole	1.466 and -1.748 e.$Å^{-3}$

Table 2.40. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2.34b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
B(1)	3629(3)	6509(4)	-1392(3)	35(1)
B(1A)	-555(3)	1046(3)	8107(3)	28(1)
Br(1)	3388(1)	3867(1)	3412(1)	55(1)
Br(1A)	2423(1)	2487(1)	4550(1)	58(1)
C(1)	3489(3)	4195(3)	-845(3)	36(1)
C(2)	3418(3)	4028(4)	-1623(3)	42(1)
C(3)	3480(2)	4871(4)	-1924(3)	38(1)
C(4)	4986(3)	7222(3)	296(3)	38(1)
C(5)	5236(3)	7708(4)	-254(4)	48(1)
C(6)	4798(3)	7484(3)	-937(3)	44(1)
C(7)	2236(2)	7150(3)	-393(3)	32(1)
C(8)	1933(3)	7568(3)	-1081(3)	36(1)
C(9)	2402(2)	7383(3)	-1538(3)	34(1)
C(10)	2702(2)	5453(3)	675(3)	30(1)
C(11)	3534(2)	6741(3)	1210(3)	30(1)
C(12)	3730(3)	4430(3)	1051(3)	35(1)
C(13)	4377(2)	4788(3)	914(3)	32(1)
C(14)	4648(2)	5530(3)	1361(3)	31(1)
C(15)	4543(2)	5585(3)	2149(3)	32(1)
C(16)	4154(2)	4752(3)	2398(3)	34(1)
C(17)	3804(3)	4988(4)	3063(3)	41(1)
C(18)	3194(3)	5679(4)	2888(3)	49(1)
C(19)	4738(4)	4027(5)	2632(4)	60(2)

C(20)	5315(8)	4065(10)	3008(8)	85(4)
C(20B)	4776(8)	3290(9)	2507(9)	44(3)
C(1A)	-364(2)	3398(3)	7636(3)	30(1)
C(2A)	-816(3)	3515(3)	8157(3)	37(1)
C(3A)	-910(3)	2676(3)	8409(3)	33(1)
C(4A)	1334(2)	444(3)	8222(3)	29(1)
C(5A)	1254(2)	-4(3)	8874(3)	28(1)
C(6A)	545(2)	169(3)	8922(3)	28(1)
C(7A)	-1012(2)	464(3)	6082(3)	30(1)
C(8A)	-1578(3)	7(3)	6283(3)	37(1)
C(9A)	-1494(2)	169(3)	7055(3)	33(1)
C(10A)	-148(2)	2400(3)	5885(3)	28(1)
C(11A)	583(2)	896(3)	6021(3)	26(1)
C(12A)	1647(2)	1690(3)	6745(3)	28(1)
C(13A)	1470(2)	2339(3)	7248(3)	32(1)
C(14A)	1063(3)	3067(3)	6875(3)	36(1)
C(15A)	1172(3)	3360(3)	6131(3)	32(1)
C(16A)	1755(2)	2838(3)	5824(3)	29(1)
C(17A)	1578(3)	2888(4)	4948(3)	41(1)
C(18A)	941(2)	2371(3)	4505(2)	30(1)
C(19A)	2475(3)	3319(3)	6167(4)	45(1)
C(20A)	3062(3)	2948(4)	6578(3)	48(1)
Mo(1)	3603(1)	5871(1)	410(1)	22(1)
Mo(1A)	378(1)	1734(1)	6803(1)	20(1)
N(1)	3577(2)	5066(2)	-676(2)	28(1)
N(2)	3585(2)	5478(3)	-1355(2)	30(1)
N(3)	4423(2)	6700(2)	-48(2)	28(1)
N(4)	4310(2)	6868(3)	-814(2)	32(1)
N(5)	2860(2)	6732(2)	-427(2)	28(1)
N(6)	2957(2)	6885(2)	-1149(2)	29(1)
N(1A)	-202(2)	2529(2)	7582(2)	26(1)
N(2A)	-544(2)	2084(2)	8069(2)	25(1)
N(3A)	726(2)	863(2)	7878(2)	24(1)
N(4A)	231(2)	682(2)	8326(2)	24(1)
N(5A)	-602(2)	894(2)	6688(2)	26(1)
N(6A)	-912(2)	696(2)	7302(2)	29(1)
O(1)	2170(2)	5279(3)	861(2)	49(1)
O(2)	3436(2)	7279(2)	1657(2)	50(1)
O(3)	3587(2)	4419(2)	1781(2)	34(1)
O(4)	4813(2)	6141(3)	2615(2)	45(1)
O(1A)	-486(2)	2766(3)	5359(2)	46(1)
O(2A)	662(2)	419(2)	5546(2)	36(1)
O(3A)	1806(2)	1911(2)	6044(2)	26(1)
O(4A)	890(2)	4028(2)	5793(3)	56(1)

Table 2.41. Bond lengths [Å] and angles [°] for 2.34b

B(1)-N(6)	1.533(7)	C(18)-H(18C)	0.9800
B(1)-N(2)	1.537(7)	C(19)-C(20B)	1.122(14)
B(1)-N(4)	1.545(7)	C(19)-C(20)	1.140(15)
B(1)-H(1)	1.0000	C(20)-H(20A)	0.9500
B(1A)-N(6A)	1.532(7)	C(20)-H(20B)	0.9500
B(1A)-N(4A)	1.539(6)	C(20B)-H(20C)	0.9500
B(1A)-N(2A)	1.545(6)	C(20B)-H(20D)	0.9500
B(1A)-H(1A)	1.0000	C(1A)-N(1A)	1.336(5)
Br(1)-C(17)	2.000(5)	C(1A)-C(2A)	1.406(6)
Br(1A)-C(17A)	1.975(4)	C(1A)-H(1A)	0.9500
C(1)-N(1)	1.331(6)	C(2A)-C(3A)	1.351(7)
C(1)-C(2)	1.386(7)	C(2A)-H(2A)	0.9500
C(1)-H(1)	0.9500	C(3A)-N(2A)	1.344(6)
C(2)-C(3)	1.379(8)	C(3A)-H(3A)	0.9500
C(2)-H(2)	0.9500	C(4A)-N(3A)	1.325(5)
C(3)-N(2)	1.340(6)	C(4A)-C(5A)	1.379(6)
C(3)-H(3)	0.9500	C(4A)-H(4A)	0.9500
C(4)-N(3)	1.344(6)	C(5A)-C(6A)	1.379(6)
C(4)-C(5)	1.385(7)	C(5A)-H(5A)	0.9500
C(4)-H(4)	0.9500	C(6A)-N(4A)	1.333(6)
C(5)-C(6)	1.349(8)	C(6A)-H(6A)	0.9500
C(5)-H(5)	0.9500	C(7A)-N(5A)	1.340(6)
C(6)-N(4)	1.349(6)	C(7A)-C(8A)	1.378(7)
C(6)-H(6)	0.9500	C(7A)-H(7A)	0.9500
C(7)-N(5)	1.341(5)	C(8A)-C(9A)	1.372(7)
C(7)-C(8)	1.379(7)	C(8A)-H(8A)	0.9500
C(7)-H(7)	0.9500	C(9A)-N(6A)	1.337(6)
C(8)-C(9)	1.359(7)	C(9A)-H(9A)	0.9500
C(8)-H(8)	0.9500	C(10A)-O(1A)	1.143(6)
C(9)-N(6)	1.338(6)	C(10A)-Mo(1A)	1.978(5)
C(9)-H(9)	0.9500	C(11A)-O(2A)	1.140(5)
C(10)-O(1)	1.153(5)	C(11A)-Mo(1A)	1.973(5)
C(10)-Mo(1)	1.962(4)	C(12A)-O(3A)	1.391(5)
C(11)-O(2)	1.174(6)	C(12A)-C(13A)	1.408(7)
C(11)-Mo(1)	1.952(5)	C(12A)-Mo(1A)	2.413(4)
C(12)-O(3)	1.389(5)	C(12A)-H(12A)	0.9500
C(12)-C(13)	1.398(7)	C(13A)-C(14A)	1.403(7)
C(12)-Mo(1)	2.414(5)	C(13A)-Mo(1A)	2.218(4)
C(12)-H(12)	0.9500	C(13A)-H(13A)	0.9500
C(13)-C(14)	1.388(7)	C(14A)-C(15A)	1.456(7)
C(13)-Mo(1)	2.219(4)	C(14A)-Mo(1A)	2.350(4)
C(13)-H(13)	0.9500	C(14A)-H(14A)	0.9500
C(14)-C(15)	1.467(6)	C(15A)-O(4A)	1.218(6)
C(14)-Mo(1)	2.341(4)	C(15A)-C(16A)	1.542(6)
C(14)-H(14)	0.9500	C(16A)-O(3A)	1.430(5)
C(15)-O(4)	1.201(6)	C(16A)-C(17A)	1.526(7)
C(15)-C(16)	1.554(7)	C(16A)-C(19A)	1.530(7)
C(16)-O(3)	1.435(6)	C(17A)-C(18A)	1.491(7)
C(16)-C(17)	1.524(6)	C(17A)-H(17A)	1.0000
C(16)-C(19)	1.528(7)	C(18A)-H(18D)	0.9800
C(17)-C(18)	1.517(7)	C(18A)-H(18E)	0.9800
C(17)-H(17)	1.0000	C(18A)-H(18F)	0.9800
C(18)-H(18A)	0.9800	C(19A)-C(20A)	1.301(8)
C(18)-H(18B)	0.9800	C(19A)-H(19A)	0.9500

C(20A)-H(20E)	0.9500	O(3)-C(12)-Mo(1)	115.8(3)
C(20A)-H(20F)	0.9500	C(13)-C(12)-Mo(1)	65.0(2)
Mo(1)-N(5)	2.208(4)	O(3)-C(12)-H(12)	119.0
Mo(1)-N(3)	2.265(4)	C(13)-C(12)-H(12)	119.0
Mo(1)-N(1)	2.271(4)	Mo(1)-C(12)-H(12)	89.3
Mo(1A)-N(5A)	2.197(3)	C(14)-C(13)-C(12)	115.0(4)
Mo(1A)-N(1A)	2.280(3)	C(14)-C(13)-Mo(1)	77.2(3)
Mo(1A)-N(3A)	2.284(4)	C(12)-C(13)-Mo(1)	80.2(3)
N(1)-N(2)	1.360(5)	C(14)-C(13)-H(13)	122.5
N(3)-N(4)	1.359(5)	C(12)-C(13)-H(13)	122.5
N(5)-N(6)	1.361(5)	Mo(1)-C(13)-H(13)	111.4
N(1A)-N(2A)	1.364(5)	C(13)-C(14)-C(15)	118.9(4)
N(3A)-N(4A)	1.383(5)	C(13)-C(14)-Mo(1)	67.5(3)
N(5A)-N(6A)	1.385(5)	C(15)-C(14)-Mo(1)	114.2(3)
N(6)-B(1)-N(2)	107.1(4)	C(13)-C(14)-H(14)	120.6
N(6)-B(1)-N(4)	107.3(4)	C(15)-C(14)-H(14)	120.6
N(2)-B(1)-N(4)	111.1(4)	Mo(1)-C(14)-H(14)	88.5
N(6)-B(1)-H(1)	110.4	O(4)-C(15)-C(14)	125.2(4)
N(2)-B(1)-H(1)	110.4	O(4)-C(15)-C(16)	120.2(4)
N(4)-B(1)-H(1)	110.4	C(14)-C(15)-C(16)	113.9(4)
N(6A)-B(1A)-N(4A)	108.1(4)	O(3)-C(16)-C(17)	107.5(4)
N(6A)-B(1A)-N(2A)	107.8(4)	O(3)-C(16)-C(19)	109.3(5)
N(4A)-B(1A)-N(2A)	109.9(4)	C(17)-C(16)-C(19)	111.1(4)
N(6A)-B(1A)-H(1A)	110.3	O(3)-C(16)-C(15)	111.7(4)
N(4A)-B(1A)-H(1A)	110.3	C(17)-C(16)-C(15)	110.8(4)
N(2A)-B(1A)-H(1A)	110.3	C(19)-C(16)-C(15)	106.5(4)
N(1)-C(1)-C(2)	112.3(5)	C(18)-C(17)-C(16)	115.8(4)
N(1)-C(1)-H(1)	123.9	C(18)-C(17)-Br(1)	107.3(3)
C(2)-C(1)-H(1)	123.9	C(16)-C(17)-Br(1)	108.7(4)
C(3)-C(2)-C(1)	103.4(4)	C(18)-C(17)-H(17)	108.3
C(3)-C(2)-H(2)	128.3	C(16)-C(17)-H(17)	108.3
C(1)-C(2)-H(2)	128.3	Br(1)-C(17)-H(17)	108.3
N(2)-C(3)-C(2)	109.0(4)	C(17)-C(18)-H(18A)	109.5
N(2)-C(3)-H(3)	125.5	C(17)-C(18)-H(18B)	109.5
C(2)-C(3)-H(3)	125.5	H(18A)-C(18)-H(18B)	109.5
N(3)-C(4)-C(5)	109.7(5)	C(17)-C(18)-H(18C)	109.5
N(3)-C(4)-H(4)	125.2	H(18A)-C(18)-H(18C)	109.5
C(5)-C(4)-H(4)	125.2	H(18B)-C(18)-H(18C)	109.5
C(6)-C(5)-C(4)	106.0(5)	C(20B)-C(19)-C(20)	94.1(11)
C(6)-C(5)-H(5)	127.0	C(20B)-C(19)-C(16)	134.9(11)
C(4)-C(5)-H(5)	127.0	C(20)-C(19)-C(16)	131.0(11)
C(5)-C(6)-N(4)	108.6(5)	C(19)-C(20)-H(20A)	120.0
C(5)-C(6)-H(6)	125.7	C(19)-C(20)-H(20B)	120.0
N(4)-C(6)-H(6)	125.7	H(20A)-C(20)-H(20B)	120.0
N(5)-C(7)-C(8)	110.9(4)	C(19)-C(20B)-H(20C)	120.0
N(5)-C(7)-H(7)	124.5	C(19)-C(20B)-H(20D)	120.0
C(8)-C(7)-H(7)	124.5	H(20C)-C(20B)-H(20D)	120.0
C(9)-C(8)-C(7)	104.5(4)	N(1A)-C(1A)-C(2A)	110.5(4)
C(9)-C(8)-H(8)	127.8	N(1A)-C(1A)-H(1A)	124.7
C(7)-C(8)-H(8)	127.8	C(2A)-C(1A)-H(1A)	124.7
N(6)-C(9)-C(8)	109.7(4)	C(3A)-C(2A)-C(1A)	104.5(4)
N(6)-C(9)-H(9)	125.2	C(3A)-C(2A)-H(2A)	127.7
C(8)-C(9)-H(9)	125.2	C(1A)-C(2A)-H(2A)	127.7
O(1)-C(10)-Mo(1)	174.0(4)	N(2A)-C(3A)-C(2A)	109.6(4)
O(2)-C(11)-Mo(1)	174.6(4)	N(2A)-C(3A)-H(3A)	125.2
O(3)-C(12)-C(13)	122.0(5)	C(2A)-C(3A)-H(3A)	125.2

N(3A)-C(4A)-C(5A)	111.6(4)	C(17A)-C(18A)-H(18F)	109.5
N(3A)-C(4A)-H(4A)	124.2	H(18D)-C(18A)-H(18F)	109.5
C(5A)-C(4A)-H(4A)	124.2	H(18E)-C(18A)-H(18F)	109.5
C(4A)-C(5A)-C(6A)	104.8(4)	C(20A)-C(19A)-C(16A)	126.1(5)
C(4A)-C(5A)-H(5A)	127.6	C(20A)-C(19A)-H(19A)	117.0
C(6A)-C(5A)-H(5A)	127.6	C(16A)-C(19A)-H(19A)	117.0
N(4A)-C(6A)-C(5A)	108.4(4)	C(19A)-C(20A)-H(20E)	120.0
N(4A)-C(6A)-H(6A)	125.8	C(19A)-C(20A)-H(20F)	120.0
C(5A)-C(6A)-H(6A)	125.8	H(20E)-C(20A)-H(20F)	120.0
N(5A)-C(7A)-C(8A)	111.2(4)	C(11)-Mo(1)-C(10)	80.11(19)
N(5A)-C(7A)-H(7A)	124.4	C(11)-Mo(1)-N(5)	88.51(16)
C(8A)-C(7A)-H(7A)	124.4	C(10)-Mo(1)-N(5)	84.11(16)
C(9A)-C(8A)-C(7A)	104.8(4)	C(11)-Mo(1)-C(13)	109.31(18)
C(9A)-C(8A)-H(8A)	127.6	C(10)-Mo(1)-C(13)	101.26(18)
C(7A)-C(8A)-H(8A)	127.6	N(5)-Mo(1)-C(13)	161.97(16)
N(6A)-C(9A)-C(8A)	109.4(4)	C(11)-Mo(1)-N(3)	93.94(16)
N(6A)-C(9A)-H(9A)	125.3	C(10)-Mo(1)-N(3)	162.79(16)
C(8A)-C(9A)-H(9A)	125.3	N(5)-Mo(1)-N(3)	79.57(13)
O(1A)-C(10A)-Mo(1A)	176.4(4)	C(13)-Mo(1)-N(3)	95.95(15)
O(2A)-C(11A)-Mo(1A)	176.1(4)	C(11)-Mo(1)-N(1)	169.07(16)
O(3A)-C(12A)-C(13A)	122.8(4)	C(10)-Mo(1)-N(1)	100.74(16)
O(3A)-C(12A)-Mo(1A)	116.7(3)	N(5)-Mo(1)-N(1)	80.76(13)
C(13A)-C(12A)-Mo(1A)	64.9(2)	C(13)-Mo(1)-N(1)	81.32(16)
O(3A)-C(12A)-H(12A)	118.6	N(3)-Mo(1)-N(1)	82.10(13)
C(13A)-C(12A)-H(12A)	118.6	C(11)-Mo(1)-C(14)	78.37(17)
Mo(1A)-C(12A)-H(12A)	88.5	C(10)-Mo(1)-C(14)	112.69(17)
C(14A)-C(13A)-C(12A)	114.1(4)	N(5)-Mo(1)-C(14)	156.10(15)
C(14A)-C(13A)-Mo(1A)	77.3(3)	C(13)-Mo(1)-C(14)	35.30(18)
C(12A)-C(13A)-Mo(1A)	80.1(3)	N(3)-Mo(1)-C(14)	81.47(14)
C(14A)-C(13A)-H(13A)	122.9	N(1)-Mo(1)-C(14)	110.89(15)
C(12A)-C(13A)-H(13A)	122.9	C(11)-Mo(1)-C(12)	104.88(17)
Mo(1A)-C(13A)-H(13A)	111.1	C(10)-Mo(1)-C(12)	66.59(18)
C(13A)-C(14A)-C(15A)	119.2(4)	N(5)-Mo(1)-C(12)	144.47(16)
C(13A)-C(14A)-Mo(1A)	67.0(2)	C(13)-Mo(1)-C(12)	34.80(17)
C(15A)-C(14A)-Mo(1A)	113.0(3)	N(3)-Mo(1)-C(12)	130.61(15)
C(13A)-C(14A)-H(14A)	120.4	N(1)-Mo(1)-C(12)	85.28(15)
C(15A)-C(14A)-H(14A)	120.4	C(14)-Mo(1)-C(12)	59.20(17)
Mo(1A)-C(14A)-H(14A)	90.0	C(11A)-Mo(1A)-C(10A)	82.56(18)
O(4A)-C(15A)-C(14A)	124.0(4)	C(11A)-Mo(1A)-N(5A)	82.53(15)
O(4A)-C(15A)-C(16A)	119.9(4)	C(10A)-Mo(1A)-N(5A)	87.43(16)
C(14A)-C(15A)-C(16A)	115.7(4)	C(11A)-Mo(1A)-C(13A)	101.23(17)
O(3A)-C(16A)-C(17A)	108.3(4)	C(10A)-Mo(1A)-C(13A)	110.04(18)
O(3A)-C(16A)-C(19A)	110.0(4)	N(5A)-Mo(1A)-C(13A)	162.42(16)
C(17A)-C(16A)-C(19A)	110.8(4)	C(11A)-Mo(1A)-N(1A)	162.76(15)
O(3A)-C(16A)-C(15A)	113.3(3)	C(10A)-Mo(1A)-N(1A)	91.60(15)
C(17A)-C(16A)-C(15A)	109.5(4)	N(5A)-Mo(1A)-N(1A)	81.01(13)
C(19A)-C(16A)-C(15A)	105.0(4)	C(13A)-Mo(1A)-N(1A)	96.01(15)
C(18A)-C(17A)-C(16A)	118.7(4)	C(11A)-Mo(1A)-N(3A)	99.90(15)
C(18A)-C(17A)-Br(1A)	105.7(3)	C(10A)-Mo(1A)-N(3A)	166.96(15)
C(16A)-C(17A)-Br(1A)	110.4(3)	N(5A)-Mo(1A)-N(3A)	80.24(13)
C(18A)-C(17A)-H(17A)	107.2	C(13A)-Mo(1A)-N(3A)	82.19(15)
C(16A)-C(17A)-H(17A)	107.2	N(1A)-Mo(1A)-N(3A)	82.34(13)
Br(1A)-C(17A)-H(17A)	107.2	C(11A)-Mo(1A)-C(14A)	112.19(16)
C(17A)-C(18A)-H(18D)	109.5	C(10A)-Mo(1A)-C(14A)	77.80(19)
C(17A)-C(18A)-H(18E)	109.5	N(5A)-Mo(1A)-C(14A)	157.18(15)
H(18D)-C(18A)-H(18E)	109.5	C(13A)-Mo(1A)-C(14A)	35.63(18)

N(1A)-Mo(1A)-C(14A)	82.11(14)	C(9)-N(6)-N(5)	109.1(4)
N(3A)-Mo(1A)-C(14A)	112.53(16)	C(9)-N(6)-B(1)	130.6(4)
C(11A)-Mo(1A)-C(12A)	66.29(16)	N(5)-N(6)-B(1)	120.2(4)
C(10A)-Mo(1A)-C(12A)	106.96(16)	C(1A)-N(1A)-N(2A)	105.9(3)
N(5A)-Mo(1A)-C(12A)	142.88(14)	C(1A)-N(1A)-Mo(1A)	133.9(3)
C(13A)-Mo(1A)-C(12A)	35.08(16)	N(2A)-N(1A)-Mo(1A)	119.9(2)
N(1A)-Mo(1A)-C(12A)	130.92(14)	C(3A)-N(2A)-N(1A)	109.6(3)
N(3A)-Mo(1A)-C(12A)	85.61(14)	C(3A)-N(2A)-B(1A)	128.4(4)
C(14A)-Mo(1A)-C(12A)	59.36(16)	N(1A)-N(2A)-B(1A)	121.6(3)
C(1)-N(1)-N(2)	105.2(4)	C(4A)-N(3A)-N(4A)	105.4(3)
C(1)-N(1)-Mo(1)	133.1(3)	C(4A)-N(3A)-Mo(1A)	135.1(3)
N(2)-N(1)-Mo(1)	121.4(3)	N(4A)-N(3A)-Mo(1A)	119.6(2)
C(3)-N(2)-N(1)	110.0(4)	C(6A)-N(4A)-N(3A)	109.8(3)
C(3)-N(2)-B(1)	129.7(4)	C(6A)-N(4A)-B(1A)	129.0(4)
N(1)-N(2)-B(1)	120.0(4)	N(3A)-N(4A)-B(1A)	121.2(3)
C(4)-N(3)-N(4)	106.3(4)	C(7A)-N(5A)-N(6A)	105.6(3)
C(4)-N(3)-Mo(1)	132.8(3)	C(7A)-N(5A)-Mo(1A)	131.5(3)
N(4)-N(3)-Mo(1)	120.0(3)	N(6A)-N(5A)-Mo(1A)	122.8(3)
C(6)-N(4)-N(3)	109.4(4)	C(9A)-N(6A)-N(5A)	108.9(4)
C(6)-N(4)-B(1)	128.0(4)	C(9A)-N(6A)-B(1A)	131.3(4)
N(3)-N(4)-B(1)	121.7(4)	N(5A)-N(6A)-B(1A)	119.7(3)
C(7)-N(5)-N(6)	105.8(4)	C(12)-O(3)-C(16)	116.6(4)
C(7)-N(5)-Mo(1)	131.6(3)	C(12A)-O(3A)-C(16A)	117.4(3)
N(6)-N(5)-Mo(1)	122.5(3)		

Symmetry transformations used to generate equivalent atoms:

Table 2.42. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2.34b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	33(3)	43(3)	27(3)	7(3)	3(2)	2(2)
B(1A)	31(3)	25(2)	29(3)	2(2)	10(2)	-5(2)
Br(1)	48(1)	72(1)	46(1)	21(1)	13(1)	3(1)
Br(1A)	48(1)	88(1)	44(1)	7(1)	21(1)	21(1)
C(1)	34(3)	35(3)	38(3)	-6(2)	7(2)	-7(2)
C(2)	36(3)	52(3)	35(3)	-19(3)	3(2)	-5(2)
C(3)	26(2)	61(3)	24(2)	-6(2)	0(2)	4(2)
C(4)	30(3)	35(3)	40(3)	6(2)	-8(2)	-5(2)
C(5)	33(3)	44(3)	63(4)	18(3)	1(3)	-8(2)
C(6)	33(3)	46(3)	53(3)	24(3)	8(3)	-4(2)
C(7)	25(2)	26(2)	42(3)	-1(2)	4(2)	-1(2)
C(8)	24(2)	25(2)	54(3)	6(2)	-3(2)	1(2)
C(9)	28(2)	27(2)	39(3)	10(2)	-6(2)	-3(2)
C(10)	26(2)	32(2)	27(2)	1(2)	0(2)	-1(2)
C(11)	29(2)	31(2)	26(2)	3(2)	-3(2)	2(2)
C(12)	50(3)	26(2)	27(2)	2(2)	7(2)	6(2)
C(13)	35(2)	35(3)	28(2)	9(2)	9(2)	20(2)
C(14)	22(2)	40(3)	29(2)	10(2)	3(2)	4(2)
C(15)	17(2)	44(3)	31(3)	5(2)	-4(2)	4(2)
C(16)	30(2)	42(3)	29(2)	7(2)	5(2)	6(2)

C(17)	34(3)	59(3)	29(3)	0(2)	7(2)	0(2)
C(18)	66(4)	39(3)	47(3)	5(3)	23(3)	8(3)
C(19)	50(4)	77(5)	61(4)	35(4)	27(3)	34(3)
C(20)	89(10)	106(11)	62(8)	35(7)	22(8)	47(8)
C(20B)	47(8)	32(7)	52(9)	10(6)	8(7)	10(6)
C(1A)	37(3)	22(2)	31(2)	4(2)	6(2)	6(2)
C(2A)	46(3)	27(2)	39(3)	-9(2)	11(2)	10(2)
C(3A)	32(2)	39(3)	30(2)	-1(2)	10(2)	2(2)
C(4A)	24(2)	28(2)	31(2)	-3(2)	0(2)	-1(2)
C(5A)	32(2)	20(2)	29(2)	7(2)	-1(2)	4(2)
C(6A)	37(2)	21(2)	23(2)	1(2)	2(2)	-5(2)
C(7A)	26(2)	28(2)	32(3)	-7(2)	-4(2)	3(2)
C(8A)	27(2)	27(2)	50(3)	-4(2)	-4(2)	-4(2)
C(9A)	20(2)	28(2)	49(3)	3(2)	2(2)	-2(2)
C(10A)	28(2)	32(2)	26(2)	0(2)	10(2)	4(2)
C(11A)	16(2)	26(2)	32(2)	3(2)	-3(2)	0(2)
C(12A)	26(2)	28(2)	30(2)	6(2)	5(2)	-5(2)
C(13A)	32(2)	42(3)	22(2)	-2(2)	2(2)	-18(2)
C(14A)	41(3)	25(2)	50(3)	-10(2)	25(3)	-8(2)
C(15A)	38(3)	18(2)	44(3)	-2(2)	17(2)	1(2)
C(16A)	35(2)	27(2)	30(2)	3(2)	14(2)	5(2)
C(17A)	50(3)	44(3)	38(3)	21(2)	26(3)	30(2)
C(18A)	17(2)	57(3)	12(2)	2(2)	-3(2)	6(2)
C(19A)	45(3)	33(3)	65(4)	-5(3)	29(3)	-13(2)
C(20A)	39(3)	59(4)	45(3)	-18(3)	7(3)	-15(3)
Mo(1)	19(1)	23(1)	22(1)	0(1)	2(1)	0(1)
Mo(1A)	22(1)	19(1)	18(1)	-1(1)	3(1)	0(1)
N(1)	29(2)	30(2)	23(2)	-4(2)	2(2)	-2(2)
N(2)	25(2)	37(2)	25(2)	3(2)	-2(2)	1(2)
N(3)	23(2)	32(2)	26(2)	6(2)	-2(2)	0(2)
N(4)	29(2)	35(2)	31(2)	10(2)	4(2)	-1(2)
N(5)	19(2)	28(2)	33(2)	1(2)	0(2)	2(2)
N(6)	25(2)	32(2)	26(2)	7(2)	-2(2)	0(2)
N(1A)	28(2)	24(2)	25(2)	-4(2)	4(2)	0(2)
N(2A)	29(2)	22(2)	25(2)	0(2)	8(2)	1(2)
N(3A)	22(2)	22(2)	26(2)	1(2)	3(2)	0(1)
N(4A)	25(2)	21(2)	26(2)	5(2)	6(2)	0(1)
N(5A)	23(2)	29(2)	26(2)	-5(2)	4(2)	-1(2)
N(6A)	25(2)	28(2)	33(2)	2(2)	7(2)	-2(2)
O(1)	31(2)	62(2)	54(2)	9(2)	10(2)	-13(2)
O(2)	76(3)	33(2)	39(2)	-11(2)	9(2)	4(2)
O(3)	42(2)	33(2)	28(2)	2(1)	7(2)	0(2)
O(4)	43(2)	57(2)	31(2)	-9(2)	1(2)	-11(2)
O(1A)	42(2)	61(2)	34(2)	18(2)	8(2)	19(2)
O(2A)	33(2)	36(2)	38(2)	-19(2)	8(2)	2(1)
O(3A)	33(2)	18(1)	28(2)	3(1)	9(1)	1(1)
O(4A)	78(3)	34(2)	69(3)	14(2)	41(2)	20(2)

Table 2.43. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2.34b

	x	y	z	U(eq)
H(1)	3634	6709	-1926	42
H(1A)	-837	841	8488	34
H(1)	3476	3739	-475	43
H(2)	3344	3468	-1885	50
H(3)	3453	5001	-2451	46
H(4)	5182	7253	835	45
H(5)	5635	8116	-168	58
H(6)	4828	7721	-1423	53
H(7)	2030	7156	46	38
H(8)	1494	7910	-1207	43
H(9)	2344	7577	-2055	40
H(12)	3378	4188	632	42
H(13)	4613	4541	544	39
H(14)	4897	5994	1159	37
H(17)	4193	5219	3498	49
H(18A)	3383	6244	2727	74
H(18B)	3007	5783	3349	74
H(18C)	2800	5455	2473	74
H(20A)	5613	3542	3092	102
H(20B)	5498	4621	3237	102
H(20C)	5211	2968	2719	53
H(20D)	4372	2990	2189	53
H(1A)	-198	3871	7361	36
H(2A)	-1012	4062	8299	45
H(3A)	-1191	2527	8771	40
H(4A)	1772	451	8041	34
H(5A)	1609	-353	9216	34
H(6A)	319	-43	9313	33
H(7A)	-923	472	5579	36
H(8A)	-1946	-343	5959	44
H(9A)	-1802	-58	7366	40
H(12A)	1657	1074	6891	34
H(13A)	1615	2289	7792	39
H(14A)	720	3366	7106	44
H(17A)	1491	3535	4803	50
H(18D)	1038	1724	4574	45
H(18E)	860	2523	3958	45
H(18F)	505	2524	4692	45
H(19A)	2494	3946	6072	54
H(20E)	3068	2322	6689	58
H(20F)	3485	3303	6767	58

Table 2.44. Torsion angles [°] for 2.34b.

N(1)-C(1)-C(2)-C(3)	0.9(6)
C(1)-C(2)-C(3)-N(2)	0.4(5)
N(3)-C(4)-C(5)-C(6)	1.6(6)
C(4)-C(5)-C(6)-N(4)	-1.5(6)

N(5)-C(7)-C(8)-C(9)	0.2(5)
C(7)-C(8)-C(9)-N(6)	-0.2(5)
O(3)-C(12)-C(13)-C(14)	-35.2(6)
Mo(1)-C(12)-C(13)-C(14)	70.8(4)
O(3)-C(12)-C(13)-Mo(1)	-105.9(4)
C(12)-C(13)-C(14)-C(15)	33.5(6)
Mo(1)-C(13)-C(14)-C(15)	106.1(4)
C(12)-C(13)-C(14)-Mo(1)	-72.7(4)
C(13)-C(14)-C(15)-O(4)	172.0(5)
Mo(1)-C(14)-C(15)-O(4)	-111.3(5)
C(13)-C(14)-C(15)-C(16)	2.5(6)
Mo(1)-C(14)-C(15)-C(16)	79.1(4)
O(4)-C(15)-C(16)-O(3)	151.6(4)
C(14)-C(15)-C(16)-O(3)	-38.3(5)
O(4)-C(15)-C(16)-C(17)	31.8(6)
C(14)-C(15)-C(16)-C(17)	-158.0(4)
O(4)-C(15)-C(16)-C(19)	-89.1(6)
C(14)-C(15)-C(16)-C(19)	81.0(5)
O(3)-C(16)-C(17)-C(18)	-58.4(6)
C(19)-C(16)-C(17)-C(18)	-177.9(5)
C(15)-C(16)-C(17)-C(18)	64.0(6)
O(3)-C(16)-C(17)-Br(1)	62.4(4)
C(19)-C(16)-C(17)-Br(1)	-57.1(5)
C(15)-C(16)-C(17)-Br(1)	-175.2(3)
O(3)-C(16)-C(19)-C(20B)	-12.4(13)
C(17)-C(16)-C(19)-C(20B)	106.1(12)
C(15)-C(16)-C(19)-C(20B)	-133.3(12)
O(3)-C(16)-C(19)-C(20)	166.7(10)
C(17)-C(16)-C(19)-C(20)	-74.8(11)
C(15)-C(16)-C(19)-C(20)	45.9(11)
N(1A)-C(1A)-C(2A)-C(3A)	0.3(6)
C(1A)-C(2A)-C(3A)-N(2A)	-0.1(6)
N(3A)-C(4A)-C(5A)-C(6A)	-0.4(5)
C(4A)-C(5A)-C(6A)-N(4A)	0.5(5)
N(5A)-C(7A)-C(8A)-C(9A)	-0.7(5)
C(7A)-C(8A)-C(9A)-N(6A)	0.2(5)
O(3A)-C(12A)-C(13A)-C(14A)	35.5(6)
Mo(1A)-C(12A)-C(13A)-C(14A)	-71.2(3)
O(3A)-C(12A)-C(13A)-Mo(1A)	106.7(4)
C(12A)-C(13A)-C(14A)-C(15A)	-31.6(6)
Mo(1A)-C(13A)-C(14A)-C(15A)	-104.5(4)
C(12A)-C(13A)-C(14A)-Mo(1A)	72.9(3)
C(13A)-C(14A)-C(15A)-O(4A)	-173.7(5)
Mo(1A)-C(14A)-C(15A)-O(4A)	110.7(5)
C(13A)-C(14A)-C(15A)-C(16A)	-1.3(6)
Mo(1A)-C(14A)-C(15A)-C(16A)	-76.9(5)
O(4A)-C(15A)-C(16A)-O(3A)	-154.4(5)
C(14A)-C(15A)-C(16A)-O(3A)	32.9(6)
O(4A)-C(15A)-C(16A)-C(17A)	-33.5(6)
C(14A)-C(15A)-C(16A)-C(17A)	153.8(4)
O(4A)-C(15A)-C(16A)-C(19A)	85.5(6)
C(14A)-C(15A)-C(16A)-C(19A)	-87.2(5)
O(3A)-C(16A)-C(17A)-C(18A)	52.5(5)
C(19A)-C(16A)-C(17A)-C(18A)	173.3(4)
C(15A)-C(16A)-C(17A)-C(18A)	-71.4(5)
O(3A)-C(16A)-C(17A)-Br(1A)	-69.6(4)

C(19A)-C(16A)-C(17A)-Br(1A)	51.1(5)
C(15A)-C(16A)-C(17A)-Br(1A)	166.4(3)
O(3A)-C(16A)-C(19A)-C(20A)	2.2(7)
C(17A)-C(16A)-C(19A)-C(20A)	-117.5(6)
C(15A)-C(16A)-C(19A)-C(20A)	124.4(6)
O(2)-C(11)-Mo(1)-C(10)	-54(4)
O(2)-C(11)-Mo(1)-N(5)	30(4)
O(2)-C(11)-Mo(1)-C(13)	-153(4)
O(2)-C(11)-Mo(1)-N(3)	109(4)
O(2)-C(11)-Mo(1)-N(1)	41(5)
O(2)-C(11)-Mo(1)-C(14)	-170(4)
O(2)-C(11)-Mo(1)-C(12)	-117(4)
O(1)-C(10)-Mo(1)-C(11)	16(4)
O(1)-C(10)-Mo(1)-N(5)	-73(4)
O(1)-C(10)-Mo(1)-C(13)	124(4)
O(1)-C(10)-Mo(1)-N(3)	-55(4)
O(1)-C(10)-Mo(1)-N(1)	-153(4)
O(1)-C(10)-Mo(1)-C(14)	89(4)
O(1)-C(10)-Mo(1)-C(12)	127(4)
C(14)-C(13)-Mo(1)-C(11)	-30.2(3)
C(12)-C(13)-Mo(1)-C(11)	88.4(3)
C(14)-C(13)-Mo(1)-C(10)	-113.6(3)
C(12)-C(13)-Mo(1)-C(10)	5.1(3)
C(14)-C(13)-Mo(1)-N(5)	140.6(5)
C(12)-C(13)-Mo(1)-N(5)	-100.8(5)
C(14)-C(13)-Mo(1)-N(3)	66.1(3)
C(12)-C(13)-Mo(1)-N(3)	-175.3(3)
C(14)-C(13)-Mo(1)-N(1)	147.1(3)
C(12)-C(13)-Mo(1)-N(1)	-94.2(3)
C(12)-C(13)-Mo(1)-C(14)	118.6(4)
C(14)-C(13)-Mo(1)-C(12)	-118.6(4)
C(13)-C(14)-Mo(1)-C(11)	151.0(3)
C(15)-C(14)-Mo(1)-C(11)	38.2(4)
C(13)-C(14)-Mo(1)-C(10)	77.0(3)
C(15)-C(14)-Mo(1)-C(10)	-35.8(4)
C(13)-C(14)-Mo(1)-N(5)	-151.0(3)
C(15)-C(14)-Mo(1)-N(5)	96.2(5)
C(15)-C(14)-Mo(1)-C(13)	-112.8(5)
C(13)-C(14)-Mo(1)-N(3)	-113.2(3)
C(15)-C(14)-Mo(1)-N(3)	134.0(4)
C(13)-C(14)-Mo(1)-N(1)	-35.0(3)
C(15)-C(14)-Mo(1)-N(1)	-147.8(3)
C(13)-C(14)-Mo(1)-C(12)	35.7(3)
C(15)-C(14)-Mo(1)-C(12)	-77.1(4)
O(3)-C(12)-Mo(1)-C(11)	12.5(4)
C(13)-C(12)-Mo(1)-C(11)	-102.5(3)
O(3)-C(12)-Mo(1)-C(10)	-59.5(4)
C(13)-C(12)-Mo(1)-C(10)	-174.6(3)
O(3)-C(12)-Mo(1)-N(5)	-96.5(4)
C(13)-C(12)-Mo(1)-N(5)	148.4(3)
O(3)-C(12)-Mo(1)-C(13)	115.0(5)
O(3)-C(12)-Mo(1)-N(3)	121.2(3)
C(13)-C(12)-Mo(1)-N(3)	6.2(4)
O(3)-C(12)-Mo(1)-N(1)	-163.4(4)
C(13)-C(12)-Mo(1)-N(1)	81.6(3)
O(3)-C(12)-Mo(1)-C(14)	78.8(4)

C(13)-C(12)-Mo(1)-C(14)	-36.2(3)
O(2A)-C(11A)-Mo(1A)-C(10A)	-41(6)
O(2A)-C(11A)-Mo(1A)-N(5A)	48(6)
O(2A)-C(11A)-Mo(1A)-C(13A)	-150(6)
O(2A)-C(11A)-Mo(1A)-N(1A)	30(6)
O(2A)-C(11A)-Mo(1A)-N(3A)	126(6)
O(2A)-C(11A)-Mo(1A)-C(14A)	-114(6)
O(2A)-C(11A)-Mo(1A)-C(12A)	-153(6)
O(1A)-C(10A)-Mo(1A)-C(11A)	100(6)
O(1A)-C(10A)-Mo(1A)-N(5A)	17(6)
O(1A)-C(10A)-Mo(1A)-C(13A)	-161(6)
O(1A)-C(10A)-Mo(1A)-N(1A)	-64(6)
O(1A)-C(10A)-Mo(1A)-N(3A)	-2(7)
O(1A)-C(10A)-Mo(1A)-C(14A)	-146(7)
O(1A)-C(10A)-Mo(1A)-C(12A)	162(6)
C(14A)-C(13A)-Mo(1A)-C(11A)	112.6(3)
C(12A)-C(13A)-Mo(1A)-C(11A)	-5.1(3)
C(14A)-C(13A)-Mo(1A)-C(10A)	26.5(3)
C(12A)-C(13A)-Mo(1A)-C(10A)	-91.2(3)
C(14A)-C(13A)-Mo(1A)-N(5A)	-146.6(4)
C(12A)-C(13A)-Mo(1A)-N(5A)	95.7(5)
C(14A)-C(13A)-Mo(1A)-N(1A)	-67.4(3)
C(12A)-C(13A)-Mo(1A)-N(1A)	174.9(3)
C(14A)-C(13A)-Mo(1A)-N(3A)	-148.8(3)
C(12A)-C(13A)-Mo(1A)-N(3A)	93.5(3)
C(12A)-C(13A)-Mo(1A)-C(14A)	-117.7(4)
C(14A)-C(13A)-Mo(1A)-C(12A)	117.7(4)
C(13A)-C(14A)-Mo(1A)-C(11A)	-78.0(3)
C(15A)-C(14A)-Mo(1A)-C(11A)	35.3(4)
C(13A)-C(14A)-Mo(1A)-C(10A)	-154.6(3)
C(15A)-C(14A)-Mo(1A)-C(10A)	-41.3(3)
C(13A)-C(14A)-Mo(1A)-N(5A)	154.6(4)
C(15A)-C(14A)-Mo(1A)-N(5A)	-92.1(5)
C(15A)-C(14A)-Mo(1A)-C(13A)	113.3(4)
C(13A)-C(14A)-Mo(1A)-N(1A)	112.0(3)
C(15A)-C(14A)-Mo(1A)-N(1A)	-134.7(4)
C(13A)-C(14A)-Mo(1A)-N(3A)	33.7(3)
C(15A)-C(14A)-Mo(1A)-N(3A)	147.0(3)
C(13A)-C(14A)-Mo(1A)-C(12A)	-36.3(3)
C(15A)-C(14A)-Mo(1A)-C(12A)	77.0(3)
O(3A)-C(12A)-Mo(1A)-C(11A)	58.8(3)
C(13A)-C(12A)-Mo(1A)-C(11A)	174.5(3)
O(3A)-C(12A)-Mo(1A)-C(10A)	-14.8(4)
C(13A)-C(12A)-Mo(1A)-C(10A)	100.9(3)
O(3A)-C(12A)-Mo(1A)-N(5A)	94.1(4)
C(13A)-C(12A)-Mo(1A)-N(5A)	-150.1(3)
O(3A)-C(12A)-Mo(1A)-C(13A)	-115.7(4)
O(3A)-C(12A)-Mo(1A)-N(1A)	-122.5(3)
C(13A)-C(12A)-Mo(1A)-N(1A)	-6.7(3)
O(3A)-C(12A)-Mo(1A)-N(3A)	161.6(3)
C(13A)-C(12A)-Mo(1A)-N(3A)	-82.6(3)
O(3A)-C(12A)-Mo(1A)-C(14A)	-78.9(3)
C(13A)-C(12A)-Mo(1A)-C(14A)	36.8(3)
C(2)-C(1)-N(1)-N(2)	-1.7(5)
C(2)-C(1)-N(1)-Mo(1)	172.1(3)
C(11)-Mo(1)-N(1)-C(1)	-144.5(8)

C(10)-Mo(1)-N(1)-C(1)	-51.0(5)
N(5)-Mo(1)-N(1)-C(1)	-133.2(4)
C(13)-Mo(1)-N(1)-C(1)	48.9(4)
N(3)-Mo(1)-N(1)-C(1)	146.2(4)
C(14)-Mo(1)-N(1)-C(1)	68.5(5)
C(12)-Mo(1)-N(1)-C(1)	14.1(4)
C(11)-Mo(1)-N(1)-N(2)	28.5(10)
C(10)-Mo(1)-N(1)-N(2)	122.0(3)
N(5)-Mo(1)-N(1)-N(2)	39.9(3)
C(13)-Mo(1)-N(1)-N(2)	-138.1(3)
N(3)-Mo(1)-N(1)-N(2)	-40.8(3)
C(14)-Mo(1)-N(1)-N(2)	-118.5(3)
C(12)-Mo(1)-N(1)-N(2)	-172.9(3)
C(2)-C(3)-N(2)-N(1)	-1.5(5)
C(2)-C(3)-N(2)-B(1)	-174.9(4)
C(1)-N(1)-N(2)-C(3)	1.9(5)
Mo(1)-N(1)-N(2)-C(3)	-172.8(3)
C(1)-N(1)-N(2)-B(1)	176.1(4)
Mo(1)-N(1)-N(2)-B(1)	1.4(5)
N(6)-B(1)-N(2)-C(3)	112.7(5)
N(4)-B(1)-N(2)-C(3)	-130.5(5)
N(6)-B(1)-N(2)-N(1)	-60.2(5)
N(4)-B(1)-N(2)-N(1)	56.6(5)
C(5)-C(4)-N(3)-N(4)	-1.1(5)
C(5)-C(4)-N(3)-Mo(1)	-169.4(3)
C(11)-Mo(1)-N(3)-C(4)	36.8(4)
C(10)-Mo(1)-N(3)-C(4)	105.8(7)
N(5)-Mo(1)-N(3)-C(4)	124.6(4)
C(13)-Mo(1)-N(3)-C(4)	-73.1(4)
N(1)-Mo(1)-N(3)-C(4)	-153.4(4)
C(14)-Mo(1)-N(3)-C(4)	-40.8(4)
C(12)-Mo(1)-N(3)-C(4)	-76.6(5)
C(11)-Mo(1)-N(3)-N(4)	-130.3(3)
C(10)-Mo(1)-N(3)-N(4)	-61.3(7)
N(5)-Mo(1)-N(3)-N(4)	-42.5(3)
C(13)-Mo(1)-N(3)-N(4)	119.8(3)
N(1)-Mo(1)-N(3)-N(4)	39.5(3)
C(14)-Mo(1)-N(3)-N(4)	152.1(3)
C(12)-Mo(1)-N(3)-N(4)	116.3(3)
C(5)-C(6)-N(4)-N(3)	0.9(6)
C(5)-C(6)-N(4)-B(1)	170.3(5)
C(4)-N(3)-N(4)-C(6)	0.1(5)
Mo(1)-N(3)-N(4)-C(6)	170.3(3)
C(4)-N(3)-N(4)-B(1)	-170.0(4)
Mo(1)-N(3)-N(4)-B(1)	0.1(5)
N(6)-B(1)-N(4)-C(6)	-109.6(5)
N(2)-B(1)-N(4)-C(6)	133.6(5)
N(6)-B(1)-N(4)-N(3)	58.6(5)
N(2)-B(1)-N(4)-N(3)	-58.1(5)
C(8)-C(7)-N(5)-N(6)	-0.1(5)
C(8)-C(7)-N(5)-Mo(1)	-175.9(3)
C(11)-Mo(1)-N(5)-C(7)	-45.2(4)
C(10)-Mo(1)-N(5)-C(7)	35.0(4)
C(13)-Mo(1)-N(5)-C(7)	143.5(5)
N(3)-Mo(1)-N(5)-C(7)	-139.5(4)
N(1)-Mo(1)-N(5)-C(7)	136.9(4)

C(14)-Mo(1)-N(5)-C(7)	-101.4(5)
C(12)-Mo(1)-N(5)-C(7)	68.7(5)
C(11)-Mo(1)-N(5)-N(6)	139.6(3)
C(10)-Mo(1)-N(5)-N(6)	-140.2(3)
C(13)-Mo(1)-N(5)-N(6)	-31.7(7)
N(3)-Mo(1)-N(5)-N(6)	45.3(3)
N(1)-Mo(1)-N(5)-N(6)	-38.3(3)
C(14)-Mo(1)-N(5)-N(6)	83.4(5)
C(12)-Mo(1)-N(5)-N(6)	-106.5(3)
C(8)-C(9)-N(6)-N(5)	0.2(5)
C(8)-C(9)-N(6)-B(1)	-179.1(5)
C(7)-N(5)-N(6)-C(9)	0.0(5)
Mo(1)-N(5)-N(6)-C(9)	176.3(3)
C(7)-N(5)-N(6)-B(1)	179.4(4)
Mo(1)-N(5)-N(6)-B(1)	-4.4(5)
N(2)-B(1)-N(6)-C(9)	-117.8(5)
N(4)-B(1)-N(6)-C(9)	122.8(5)
N(2)-B(1)-N(6)-N(5)	62.9(5)
N(4)-B(1)-N(6)-N(5)	-56.4(5)
C(2A)-C(1A)-N(1A)-N(2A)	-0.3(5)
C(2A)-C(1A)-N(1A)-Mo(1A)	172.3(3)
C(11A)-Mo(1A)-N(1A)-C(1A)	-113.2(6)
C(10A)-Mo(1A)-N(1A)-C(1A)	-43.5(4)
N(5A)-Mo(1A)-N(1A)-C(1A)	-130.6(4)
C(13A)-Mo(1A)-N(1A)-C(1A)	66.9(4)
N(3A)-Mo(1A)-N(1A)-C(1A)	148.1(4)
C(14A)-Mo(1A)-N(1A)-C(1A)	34.0(4)
C(12A)-Mo(1A)-N(1A)-C(1A)	70.7(5)
C(11A)-Mo(1A)-N(1A)-N(2A)	58.6(7)
C(10A)-Mo(1A)-N(1A)-N(2A)	128.3(3)
N(5A)-Mo(1A)-N(1A)-N(2A)	41.2(3)
C(13A)-Mo(1A)-N(1A)-N(2A)	-121.4(3)
N(3A)-Mo(1A)-N(1A)-N(2A)	-40.1(3)
C(14A)-Mo(1A)-N(1A)-N(2A)	-154.2(3)
C(12A)-Mo(1A)-N(1A)-N(2A)	-117.5(3)
C(2A)-C(3A)-N(2A)-N(1A)	-0.1(5)
C(2A)-C(3A)-N(2A)-B(1A)	-172.7(5)
C(1A)-N(1A)-N(2A)-C(3A)	0.3(5)
Mo(1A)-N(1A)-N(2A)-C(3A)	-173.6(3)
C(1A)-N(1A)-N(2A)-B(1A)	173.5(4)
Mo(1A)-N(1A)-N(2A)-B(1A)	-0.4(5)
N(6A)-B(1A)-N(2A)-C(3A)	113.3(5)
N(4A)-B(1A)-N(2A)-C(3A)	-129.1(5)
N(6A)-B(1A)-N(2A)-N(1A)	-58.5(5)
N(4A)-B(1A)-N(2A)-N(1A)	59.1(5)
C(5A)-C(4A)-N(3A)-N(4A)	0.1(5)
C(5A)-C(4A)-N(3A)-Mo(1A)	-180.0(3)
C(11A)-Mo(1A)-N(3A)-C(4A)	57.1(4)
C(10A)-Mo(1A)-N(3A)-C(4A)	156.9(6)
N(5A)-Mo(1A)-N(3A)-C(4A)	137.7(4)
C(13A)-Mo(1A)-N(3A)-C(4A)	-43.0(4)
N(1A)-Mo(1A)-N(3A)-C(4A)	-140.2(4)
C(14A)-Mo(1A)-N(3A)-C(4A)	-62.0(4)
C(12A)-Mo(1A)-N(3A)-C(4A)	-7.9(4)
C(11A)-Mo(1A)-N(3A)-N(4A)	-123.0(3)
C(10A)-Mo(1A)-N(3A)-N(4A)	-23.2(8)

N(5A)-Mo(1A)-N(3A)-N(4A)	-42.4(3)
C(13A)-Mo(1A)-N(3A)-N(4A)	136.9(3)
N(1A)-Mo(1A)-N(3A)-N(4A)	39.7(3)
C(14A)-Mo(1A)-N(3A)-N(4A)	117.9(3)
C(12A)-Mo(1A)-N(3A)-N(4A)	172.0(3)
C(5A)-C(6A)-N(4A)-N(3A)	-0.4(5)
C(5A)-C(6A)-N(4A)-B(1A)	178.8(4)
C(4A)-N(3A)-N(4A)-C(6A)	0.2(4)
Mo(1A)-N(3A)-N(4A)-C(6A)	-179.7(3)
C(4A)-N(3A)-N(4A)-B(1A)	-179.1(4)
Mo(1A)-N(3A)-N(4A)-B(1A)	0.9(5)
N(6A)-B(1A)-N(4A)-C(6A)	-120.9(5)
N(2A)-B(1A)-N(4A)-C(6A)	121.7(5)
N(6A)-B(1A)-N(4A)-N(3A)	58.3(5)
N(2A)-B(1A)-N(4A)-N(3A)	-59.1(5)
C(8A)-C(7A)-N(5A)-N(6A)	0.9(5)
C(8A)-C(7A)-N(5A)-Mo(1A)	179.5(3)
C(11A)-Mo(1A)-N(5A)-C(7A)	-33.6(4)
C(10A)-Mo(1A)-N(5A)-C(7A)	49.2(4)
C(13A)-Mo(1A)-N(5A)-C(7A)	-137.3(5)
N(1A)-Mo(1A)-N(5A)-C(7A)	141.2(4)
N(3A)-Mo(1A)-N(5A)-C(7A)	-135.1(4)
C(14A)-Mo(1A)-N(5A)-C(7A)	98.5(5)
C(12A)-Mo(1A)-N(5A)-C(7A)	-65.9(5)
C(11A)-Mo(1A)-N(5A)-N(6A)	144.8(3)
C(10A)-Mo(1A)-N(5A)-N(6A)	-132.4(3)
C(13A)-Mo(1A)-N(5A)-N(6A)	41.2(7)
N(1A)-Mo(1A)-N(5A)-N(6A)	-40.3(3)
N(3A)-Mo(1A)-N(5A)-N(6A)	43.4(3)
C(14A)-Mo(1A)-N(5A)-N(6A)	-83.1(5)
C(12A)-Mo(1A)-N(5A)-N(6A)	112.5(3)
C(8A)-C(9A)-N(6A)-N(5A)	0.3(5)
C(8A)-C(9A)-N(6A)-B(1A)	-177.0(4)
C(7A)-N(5A)-N(6A)-C(9A)	-0.7(4)
Mo(1A)-N(5A)-N(6A)-C(9A)	-179.5(3)
C(7A)-N(5A)-N(6A)-B(1A)	177.0(4)
Mo(1A)-N(5A)-N(6A)-B(1A)	-1.8(5)
N(4A)-B(1A)-N(6A)-C(9A)	118.5(5)
N(2A)-B(1A)-N(6A)-C(9A)	-122.7(5)
N(4A)-B(1A)-N(6A)-N(5A)	-58.5(5)
N(2A)-B(1A)-N(6A)-N(5A)	60.2(5)
C(13)-C(12)-O(3)-C(16)	-3.2(6)
Mo(1)-C(12)-O(3)-C(16)	-78.5(4)
C(17)-C(16)-O(3)-C(12)	160.5(4)
C(19)-C(16)-O(3)-C(12)	-78.8(5)
C(15)-C(16)-O(3)-C(12)	38.8(5)
C(13A)-C(12A)-O(3A)-C(16A)	-2.6(6)
Mo(1A)-C(12A)-O(3A)-C(16A)	73.4(4)
C(17A)-C(16A)-O(3A)-C(12A)	-152.6(4)
C(19A)-C(16A)-O(3A)-C(12A)	86.1(4)
C(15A)-C(16A)-O(3A)-C(12A)	-31.0(5)

Symmetry transformations used to generate equivalent atoms:

Chapter 3:

Total Synthesis of (-)-Adaline and (-)-Adalinine

Background

The 9-azabicyclo[3.3.1]nonane skeleton (Figure 3.1) constitutes the core structure of several insect- and plant-derived alkaloids, including pseudopelletierine, (+)-euphococcinine, (-)-adaline, and porantherine. This structure is a higher homolog of the tropane skeleton found in alkaloids such as cocaine, atropine and tropinone, and therefore, is commonly referred to as the homotropane skeleton.

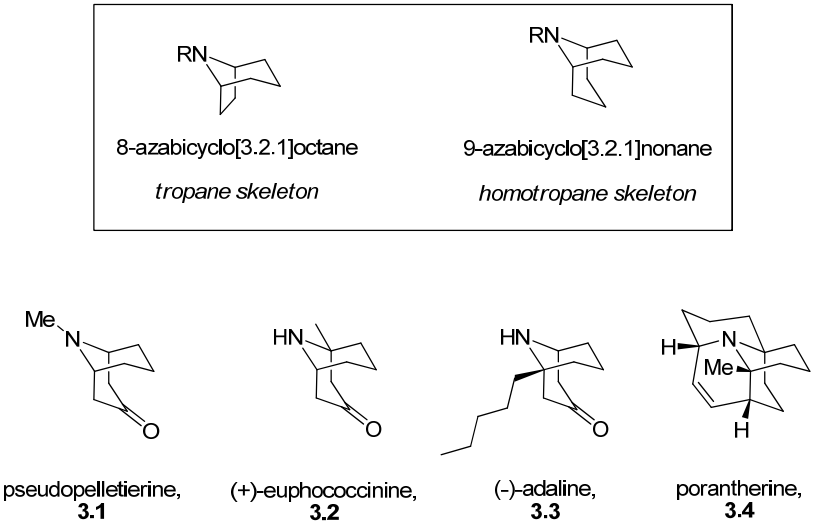


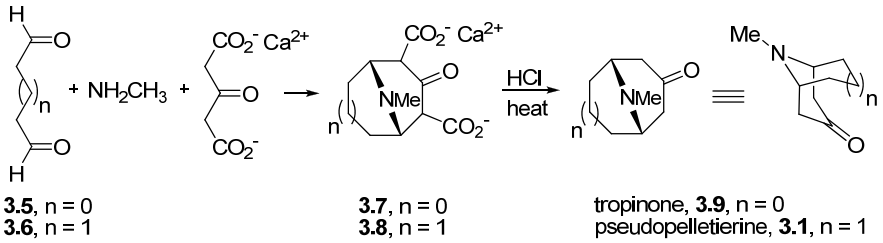
Figure 3.1. Homotropane-based Alkaloids

A comprehensive review of synthetic efforts aimed at total synthesis of pseudopelletierine, (+)-euphococcinine, and (-)-adaline follows. Syntheses of the piperidone-based (-)-adalinine, biosynthetically-related to (-)-adaline, are also included. *This review is meant to provide background and context for reading the work that is the subject of this dissertation rather than a criticism of past efforts.*

Early Work on Homotropanes: Pseudopelletierine

Pseudopelletierine, the simplest homotropane alkaloid, is a meso compound found in the bark of pomegranate trees with a history dating back to its isolation in 1879.[104,105] Pseudopelletierine was first synthesized by Robinson in 1924 using a variant of the classic biomimetic strategy published in 1917 for the synthesis of tropinone (Scheme 3.1).[106,107] In these syntheses, dialdehydes **3.5** and **3.6** were condensed with methyl amine and double Mannich reactions with the calcium salt of acetone dicarboxylate ensued producing **3.7** and **3.8**, respectively. Heating **3.7** and **3.8** in the presence of HCl led to tropinone and pseudopelletierine after double decarboxylation.

Scheme 3.1. Robinson's Syntheses of Tropinone and Pseudopelletierine



3.5, n = 0
3.6, n = 1

3.7, n = 0
3.8, n = 1

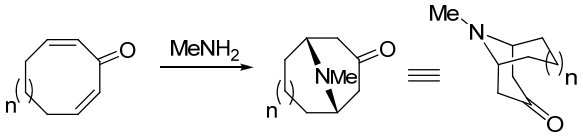
tropinone, **3.9**, n = 0
pseudopelletierine, **3.1**, n = 1

Robinson also noted in the original publication, "The possibility that tropinone might result from…the addition of methylamine to cycloheptadienone." This suggestion was put into practice by Bottini and Gal who reported the syntheses of both tropinone and pseudopelletierine by double Michael addition of methyl amine to cyclic dieneones **3.10** and **3.11** (Scheme 3.2) in 1971.[108] As will be seen, the approaches to pseudopelletierine

[104] Tanret, C. *C. R. Hebd. Seances Acad. Sci.* **1879**, *88*, 716.
[105] Hess, *Eichel Ber.* **1917**, *50*, 380; 1391; 1395.
[106] Robinson, R. *J. Chem. Soc.* **1917**, *111*, 762-768.
[107] Menzies, R. C.; Robinson, R. *J. Chem. Soc.* **1924**, *125*, 2163-2168.
[108] Bottini, A. T.; Gal, J. *J. Org. Chem.* **1971**, *36*, 1718-1719.

described in Schemes 3.1 and 3.2 informed initial syntheses of the more challenging quaternary-center-bearing structures of euphococcinine and adaline.

Scheme 3.2. Double Michael Additions Yielding Tropinone and Pseudopelletierine



3.10, n = 0
3.11, n = 1

tropinone, **3.9**, n = 0
pseudopelletierine, **3.1**, n = 1

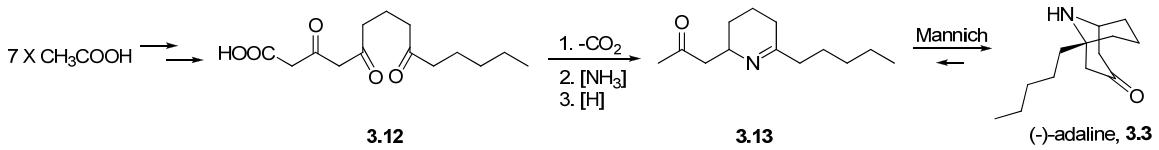
Isolation and Biosynthetic Studies: (+)-Euphococcinine, (-)-Adaline, and (-)-Adalinine

(+)-Euphococcinine was first discovered in *Euphoria atoto*, an Australian coastal plant.[109] It was later isolated from the haemolymph of the Australian mealybug ladybug *Cryptolaenus montrouzieri* and the Mexican bean beatle *Epilachna varivestis*.[110,111] The name euphococcinine is a hybrid indicating its origins in both plants and coccinellid beetles. (-)-Adaline has been isolated from the haemolymph of the European two-spotted ladybird beetles *Adalia bipunctata*[112] and *Adalia decempunctata.*[113] It has also been found in *Cryptolaenus montrouziera*,[114] *Pantherina* L, and *Quadrimaculata* Scopoli. Both (+)-euphococcinine and (-)-adaline are ant and spider feeding deterrents.[115,116]

[109] Hart, N. K.; Johns, S. R.; Lamberton, J. A. *Aust. J. Chem.* **1967**, *20*, 561-563.
[110] Brown, W. V.; Moore, B. P. *Aust. J. Chem.* **1982**, *35*, 1255-1261.
[111] Eisner, T.; Goetz, M.; Aneshansley, D.; Ferstandig-Arnold, G.; Meinwald, J. *Experientia* **1986**, *42*, 204-207.
[112] Tursch, B.; Braekman, J. C.; Daloze, D.; Hootele, C.; Losman, D.; Karlsson, R.; Pasteels, J. M. *Tetrahedron Lett.* **1973**, *3*, 201-202.
[113] Pasteels, J. M.; Deroe, C.; Tursch, B.; Braekman, J. C.; Daloze, D.; Hootele, C. *J. Insect. Physiol.* **1973**, *19*, 1771-1784.
[114] Brown, W. V.; Moore, B. P. *Aust. J. Chem.* **1982**, *35*, 1255.
[115] Marples, N. M.; Brakefield, P. M.; Cowie, R. *J. Ecol. Entomol.* **1989**, *14*, 79-84.
[116] De Jong, P. W.; Holloway, G. J.; Brakefield, P. M.; de Vos, H. *Chemoecology* **1991**, *2*, 15-19.

Biosynthetic studies by Laurent and co-workers[117,118] support the proposal that (-)-adaline is synthesized from seven acetate units, providing a 14-carbon chain **3.12** *via* a fatty acid pathway (Scheme 3.3). Keto-imine **3.13** is believed to then come from **3.12** *via* a decarboxylation/reductive amination/cyclization sequence. Further Mannich reaction of **3.13** would lead to (-)-adaline.

Scheme 3.3. Proposed Biosynthesis of (-)-Adaline

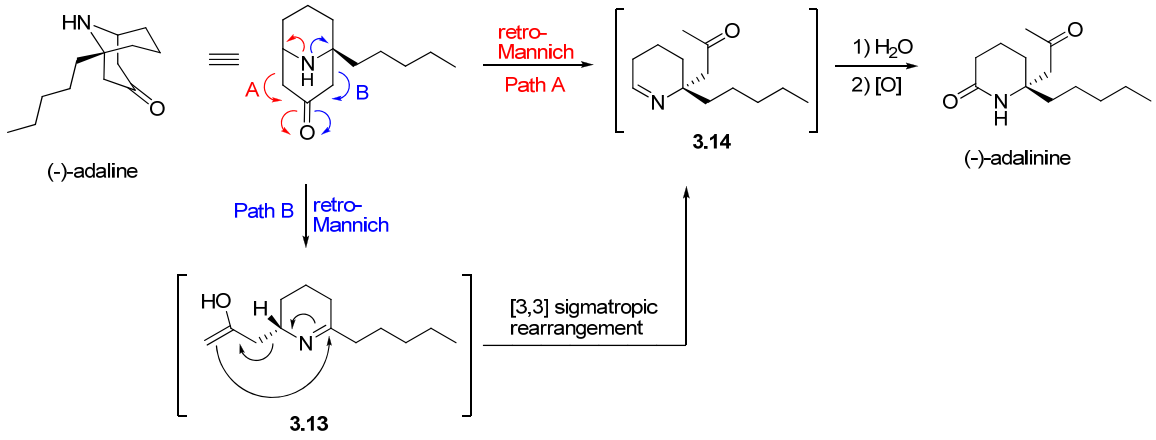


(-)-Adalinine, a quaternary-center-bearing 2-piperidone alkaloid, constitutes a minor component of the *Adalia bipunctata* and *Adalia decempunctata* haemolymph (approximately 10 %).[119] This alkaloid is thought to be biosynthetically related to (-)-adaline, the main component of the haemolymph, *via* a retro-Mannich reaction as shown in Scheme 3.4. In this proposal, reversible retro-Mannich fragmentation of (-)-adaline would lead to piperidinyl imine **3.14** (Path A), which could then be hydrated and oxidized to afford (-)-adalinine. Alternatively, retro-Mannich fragmentation to intermediate **3.13** (Path B) followed by [3,3]-sigmatropic rearrangement would lead to piperidinyl imine **3.14**. Addition of water and oxidation to the lactam would afford (-)-adalinine. It is not clear from the studies of Laurent and co-workers if adalinine is produced by one or both of these pathways. It is also possible that (-)-adalinine could be formed directly from

[117] Laurent, P.; Lebrun, B.; Braekman, J.-C.; Daloze, D.; Pasteels, J. M. *Tetrahedron* **2001**, *57*, 3403-3412.
[118] Laurent, P.; Braekman, J.-C.; Daloze, D.; Pasteels, J. M. *Insect Biochem. Mol. Biol.* **2002**, *32*, 1017-1023.
[119] Lognay, G.; Hemptinne, J. L.; Chan, F. Y.; Gaspar, C. H.; Marlier, M.; Braekman, J. C.; Daloze, D.; Pasteels, J. M. *J. Nat. Prod.* **1996**, *59*, 510-511.

3.13. If true, **3.13** would be an intermediate in the biosynthetic production of both adaline and adalinine.

Scheme 3.4. Biosynthetic Proposal for the Synthesis of (-)-Adalinine from (-)-Adaline

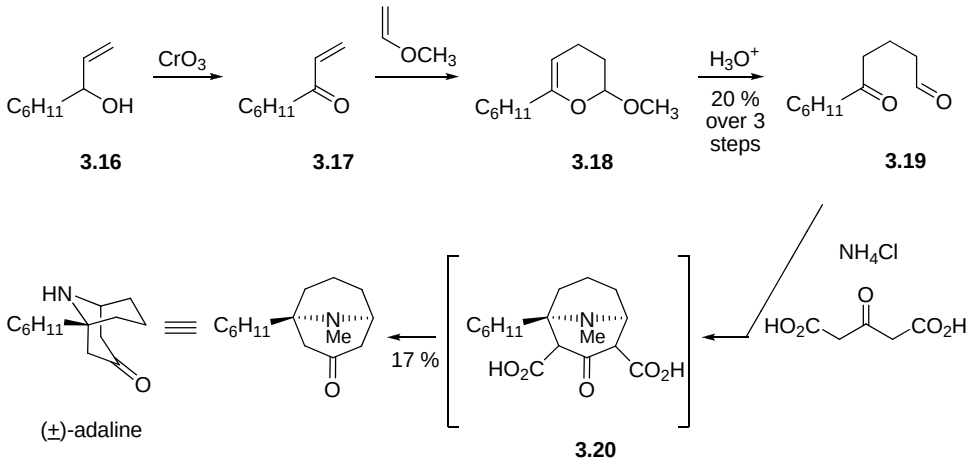


Racemic Approaches to Adaline and Euphococcinine

After Robinson's synthesis of pseudopelletierine in 1924 (Scheme 3.1), Tursch and co-workers[120] employed a similar approach to the first racemic synthesis of adaline (Scheme 3.5) in 1973. Oxidation of 1-octen-3-ol **3.16** to the corresponding enone **3.17** was followed by Diels-Alder reaction with methyl vinyl ether. The product dihydropyran **3.18** underwent acid-mediated hydrolyis of the acetal, affording keto-aldehyde **3.19**. The biomimetic Robinson-Schöpf reaction ensued upon treatment with NH_4Cl and acetone dicarboxylic acid, delivering adaline after double decarboxylation.

[120] Tursch, B.; Chome, C.; Braekman, J. C.; Daloze, D. *Bull. Soc. Chim. Belg.* **1973**, *82*, 699-703.

Scheme 3.5. Robinson-Schöpf-like Approach to (±)-Adaline

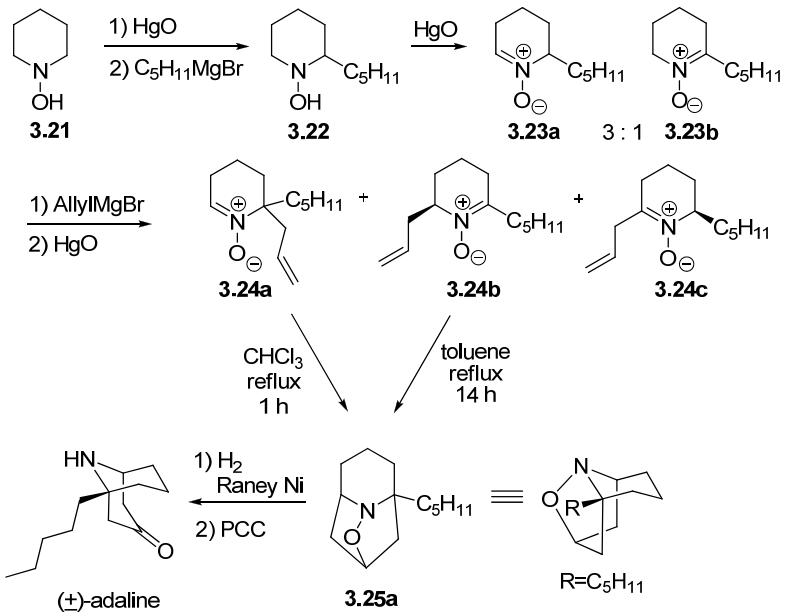


3.16 **3.17** **3.18** **3.19** **3.20**

In 1980, Gossinger and Witkop[121] published the second racemic synthesis of adaline starting from 1-hydroxypiperidine **3.21** (Scheme 3.6). Oxidation to the corresponding nitrone with HgO followed by addition of *n*-pentyl magnesium bromide produced **3.22**, which was again treated with HgO to generate nitrones **3.23a** and **3.23b** as a 3:1 mixture. Addition of allyl Grignard to this mixture, followed by a third oxidation with HgO generated nitrones **3.24a**-**3.24c**. Nitrone **3.24a** underwent intramolecular 1,3-dipolar nitrone-olefin cycloaddition in refluxing chloroform over the course of one hour to provide tricyclic isoxazoline **3.25a**. Nitrone **3.24b** underwent a similar 1,3-dipolar cycloaddition in refluxing tolune to provide the same isoxazoline **3.25a**, but in this case the reaction required 14 hours to go to completion. Reduction of the N-O bond in **3.25a** with Raney nickel followed by chemoselective PCC oxidation of the resultant alcohol provided (±)-adaline.

[121] Gossinger, E.; Witkop, B. *Monatsh. Chem.* **1980**, *111*, 803-811.

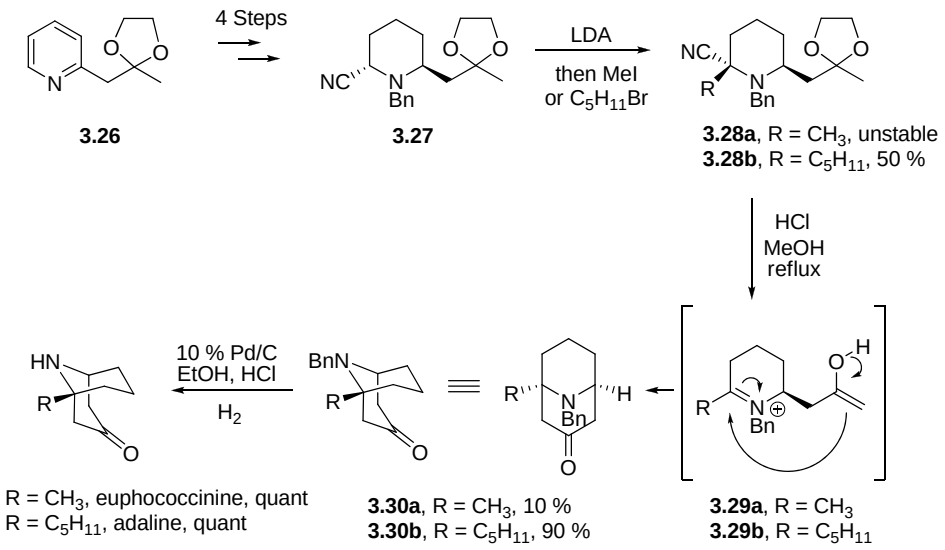
Scheme 3.6. Intramolecular 1,3-Dipolar Cycloaddition Approach to (±)-Adaline



The Husson research group followed in 1983 with syntheses of (±)-adaline and (±)-euphococcinine featuring intramolecular Mannich reactions of iminium-enols derived from 2-cyano piperidines (Scheme 3.7).[122] In this approach, pyridine **3.26** was converted in four steps to 2,6-*trans* disubstituted piperidine **3.27**, setting the stage for alkylation of the cyano-enolate derived from treatment of **3.27** with LDA. Alkylation with either MeI or *n*-pentyl bromide occured on the face of the enolate *syn* to the ketal-protected side chain, producing **3.28a** and **3.28b**, respectively. Treating 2-cyano piperidines **3.28a** and **3.28b** with HCl to ionize the cyano group produced intermediate iminium enols **3.29a** and **3.29b**. The key Mannich reaction ensued, delivering azabicyclo[3.3.1]nonanes **3.30a** and **3.30b**. Hydrogenolytic removal of the benzyl protecting groups provided (±)-euphococcinine and (±)-adaline.

[122] Gnecco Medina, D. H.; Grierson, D. S.; Husson, H.-P. *Tetrahedron Lett.* **1983**, *24*, 2099-2102.

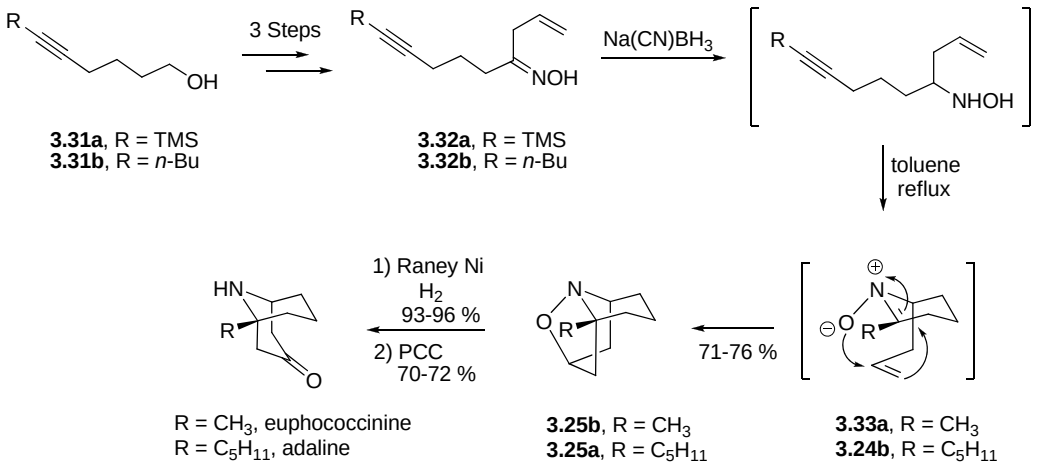
Scheme 3.7. Intramolecular Mannich Approach to Homotropane Alkaloids



An intramolecular hydroxylamine-alkyne cyclization approach to (±)-euphococcinine and (±)-adaline,[123] conceptually related to the synthesis of (±)-adaline by Gossinger and Witkop (Scheme 3.6), was reported by Holmes and co-workers in 1995 (Scheme 3.8). In this approach, oximes **3.32a** and **3.32b**, available in 3 steps from 5-hexyn-1-ols **3.31a** and **3.31b**, were reduced to the corresponding hydroxylamines and then refluxed in toluene. Intramolecular 1,3-dipolar cycloaddition of intermediate nitrones **3.33a** and **3.24b** produced tricyclic isoxazolines **3.25b** and **3.25a**. To finish the syntheses, reduction of the N-O bonds in **3.25b** and **3.25a** with Raney Ni/hydrogen, followed by PCC oxidation of the resulting alcohols provided (±)-euphococcinine and (±)-adaline, respectively.

[123] Davison, E. C.; Holmes, A. B. *Tetrahedron Lett.* **1995**, *36*, 9047-9050.

Scheme 3.8. Nitrone-olefin 1,3-Dipolar Cycloaddition Approach to Homotropanes



3.31a, R = TMS
3.31b, R = *n*-Bu

3.32a, R = TMS
3.32b, R = *n*-Bu

R = CH_3, euphococcinine
R = C_5H_{11}, adaline

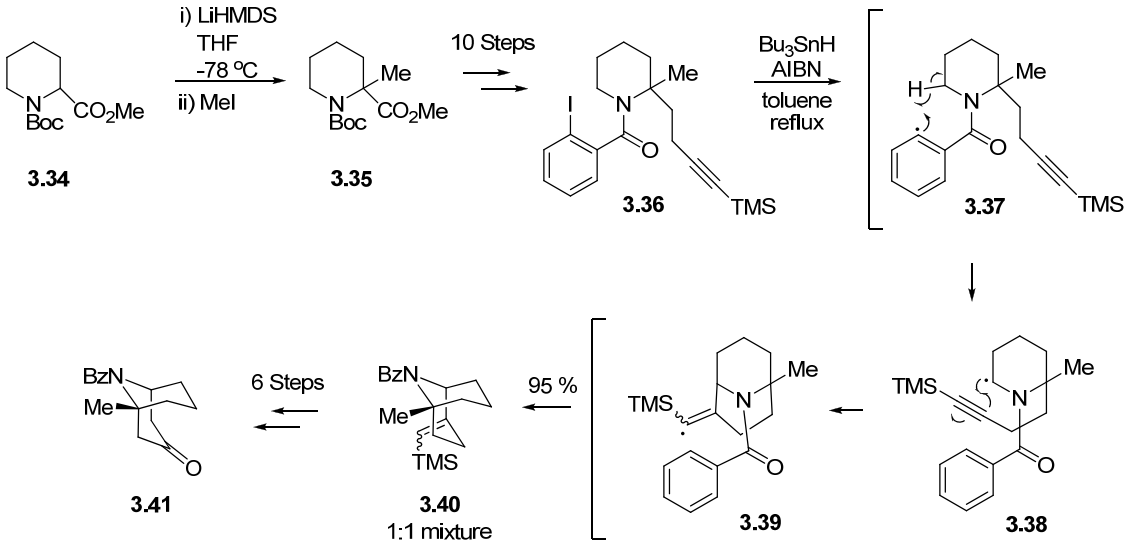
3.25b, R = CH_3
3.25a, R = C_5H_{11}

3.33a, R = CH_3
3.24b, R = C_5H_{11}

Sato and co-workers reported a radical translocation/cyclization approach to 9-azabicyclo[3.3.1]nonanes in 2002 and applied it to the synthesis of a benzyl-protected precursor to (±)-euphococcinine (Scheme 3.9).[124] In this approach, the lithium enolate of *N*-Boc-pipecolinate **3.34** was alkylated with MeI to afford quaternary-center-bearing intermediate **3.35**, which was converted to the desired cyclization precursor **3.36** in 10 steps. Refluxing **3.36** with Bu_3SnH and AIBN in toluene induced the key radical generation/translocation/cyclization sequence, delivering bicycle **3.40**. In this sequence, aryl radical **3.37** is generated and participates in a 1,5-hydrogen transfer, furnishing translocated radical **3.38**. Radical **3.38** then undergoes a 6-*exo*-*dig* cyclization with the tethered alkyne, affording the desired 9-azabicyclo[3.3.1]nonane **3.40**. Bicycle **3.40** was transformed in six steps to benzyl-protected euphococcine precursor **3.41**.

[124] Sato, T.; Yamazaki, T.; Nakanishi, Y.; Uenishi, J.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1438-1443.

Scheme 3.9. Radical Translocation Approach to 9-Azabicyclo[3.3.1]nonanes

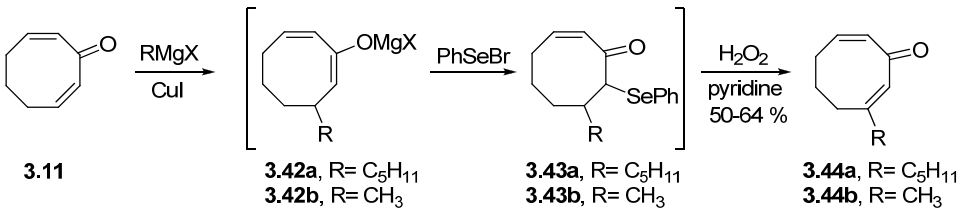


Asymmetric Syntheses of (-)-Adaline and (+)-Euphococcinine

Hill and Renbaum reported the first asymmetric syntheses of (-)-adaline and (+)-euphococcinine in 1981 employing a double Michael addition of *R*-(+)-1-phenylethylamine with substituted cyclooctadienones (Scheme 3.11).[125] This strategy is reminiscent of the earlier tropinone and pseudopelletierine syntheses proposed by Robinson and carried out by Bottini and Gal (Scheme 3.2). In this approach, conjugate addition of either *n*-pentyl magnesium bromide or methyl magnesium iodide to 2,7-cyclooctadienone **3.11**, and trapping of the intermediate enolate with phenylselenium bromide, afforded **3.43a** and **3.43b** (Scheme 3.10). These α-keto selenides were oxidized without isolation to substituted dienones **3.44a** and **3.44b** using H_2O_2/pyridine.

[125] Hill, R. K.; Renbaum, L. A. *Tetrahedron* **1982**, *38*, 1959-1963.

Scheme 3.10. Synthesis of Substituted Cyclooctadienones



3.11

3.42a, R= C_5H_{11}
3.42b, R= CH_3

3.43a, R= C_5H_{11}
3.43b, R= CH_3

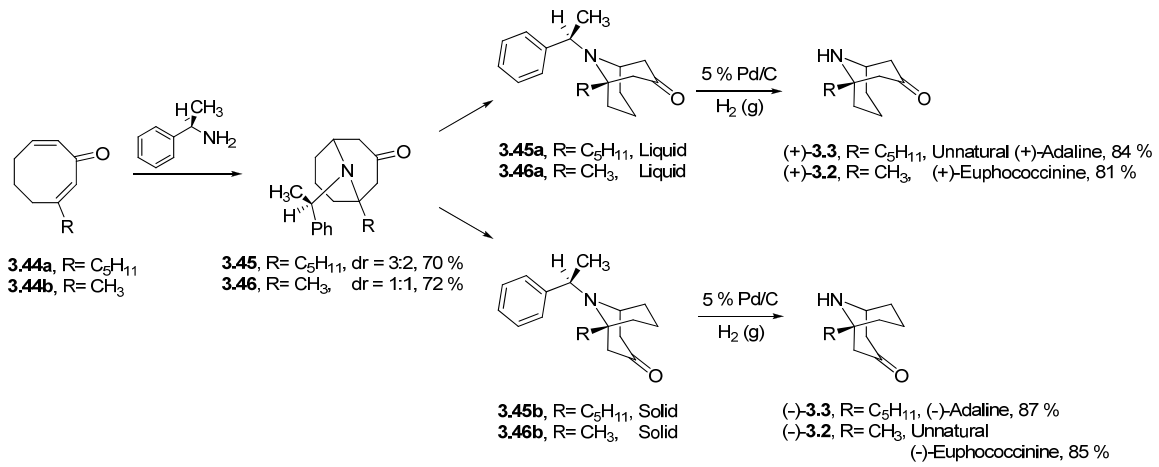
3.44a, R= C_5H_{11}
3.44b, R= CH_3

Addition of (*R*)-(+)-α-methylbenzylamine to pentyl-substituted dienone **3.44a** provided double addition product **3.45** as a 3:2 mixture of diastereomers (Scheme 3.11). The mixture could be separated by a combination of chromatography and low-temperature crystallization, providing a solid diastereomer **3.45b** and a liquid diastereomer **3.45a**. Hydrogenolytic removal of the benzyl group belonging to the solid **3.45b** provided natural (-)-adaline, $[\alpha]_D = -11^o$, while hydrogenolysis of the liquid **3.45a** provided the unnatural enantiomer, $[\alpha]_D = +12^o$.

Repeating this sequence to access euphococcinine, (*R*)-(+)-α-methylbenzylamine was added to dienone **3.44b** providing **3.46** as a 1:1 mixture of diastereomers. The two were separated by chromatography, again providing a solid diastereomer **3.46b** and a liquid diastereomer **3.46a**. Hydrogenolysis of the solid provided (-)-**3.2**, $[\alpha]_D = -6.8^o$, while hydrogenolysis of the liquid provided (+)-**3.2**, $[\alpha]_D = +7.5^o$. The close correspondence of physical properties between the two series of compounds leading to adaline and euphococcinine led the authors to suggest that a correspondence in configurations likely existed. Therefore, natural (+)-euphococcinine was proposed to have the (1*S*, 5*R*) configuration, the opposite configuration of (-)-adaline,[126] which was later confirmed.

[126] Natural (-)-adaline had been previously shown by ORD to have the (1*R*, 5*S*) configuration—see ref. 17.

Scheme 3.11. Double Michael Addition Approach to Homotropanes



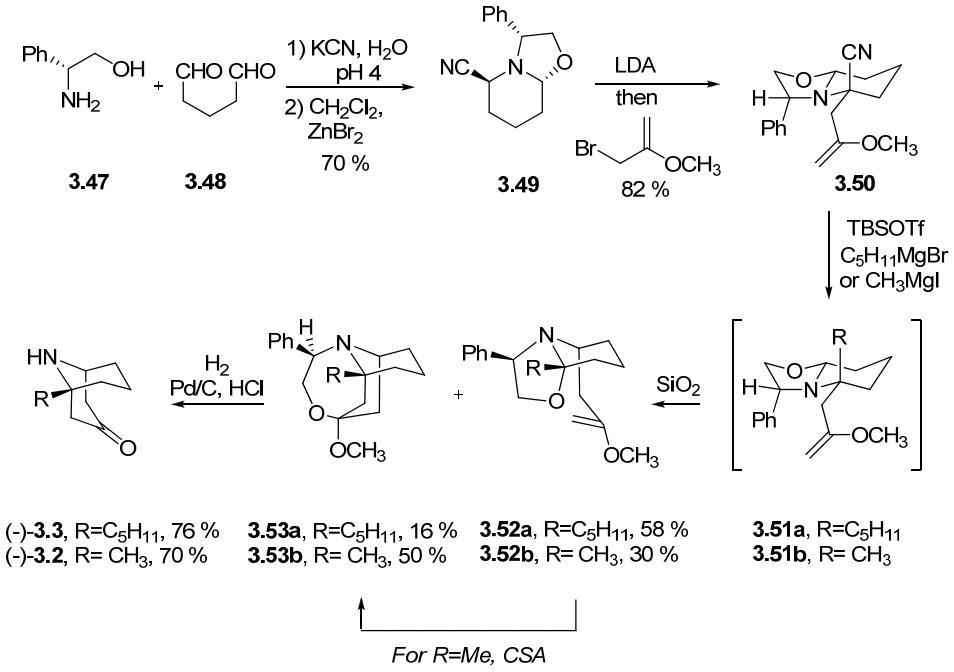
Husson and Royer followed in 1992 with asymmetric syntheses of natural (-)-adaline and unnatural (-)-euphococcinine using the CN(*R*,*S*) method (Scheme 3.12).[127] Their strategy took advantage of synthon **3.49**, available from the condensation of (*R*)-(-)-2-phenylglycinol **3.47** with glutaraldehyde **3.48** in the presence of potassium cyanide at pH 4. Treating **3.49** with LDA and then adding 3-bromo-2-methoxy-1-propene gave alkylation product **3.50** in 82 % yield. Regioselective introduction of the desired alkyl chain was accomplished by selective ionization of the cyano group (oriented antiperiplanar to the nitrogen lone pair for facile elimination) using TBSOTf. The iminium ion intermediate was then intercepted with methylmagnesium iodine to provide a mixture of **3.53b** (50 %) and **3.52b** (30 %) or with pentyl magnesium bromide to provide a mixture of **3.53a** (16 %) and **3.52a** (58 %). Towards (-)-euphococcinine, **3.52b** could be converted to **3.53b** by treatment with catalytic camphor sulfonic acid (CSA), which led to a practical approach in which the crude product of **3.50** and methyl Grignard was treated with CSA to directly form **3.53b** in 70 %. One-pot hydrolysis of the ketal

[127] Yue, C.; Royer, J.; Husson, H.-P. *J. Org. Chem.* **1992**, *57*, 4211-4214.

and hydrogenolysis of the chiral benzyl group on nitrogen provided (-)-euphococcinine in 70 % yield.

Towards (-)-adaline, pentyl-substituted compound **3.52a** could not be converted to **3.53a** *via* Mannich reaction, despite numerous attempts with a variety of acids, Lewis acids, and reaction conditions. Compound **3.53a** was converted to (-)-adaline in 76 % by the same one-pot hydrolysis/hydrogenolysis used to access (-)-euphococcinine from **3.53b**.

Scheme 3.12. Asymmetric Mannich Approach to 9-Azabicyclo[3.3.1]nonanes



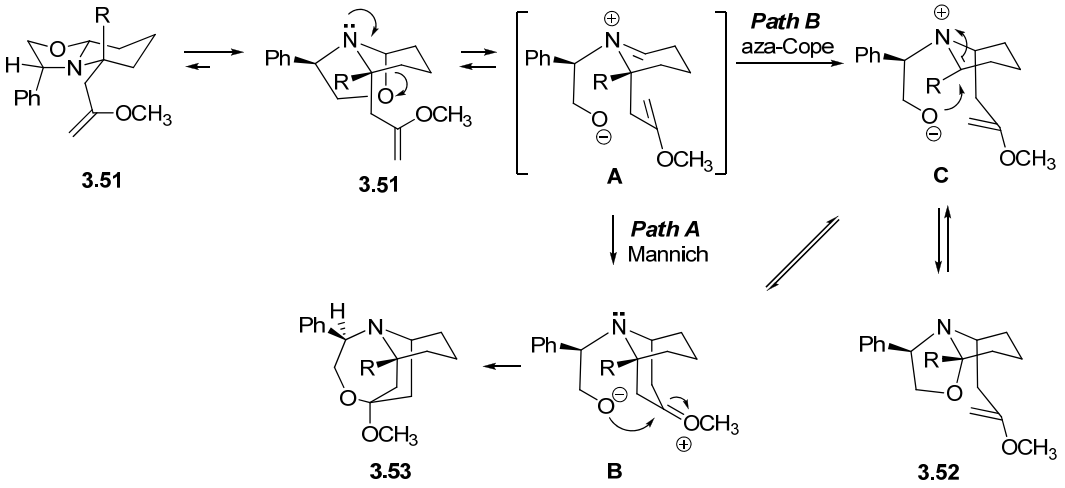
3.47 3.48 3.49 3.50

(-)-**3.3**, R=C_5H_{11}, 76 % **3.53a**, R=C_5H_{11}, 16 % **3.52a**, R=C_5H_{11}, 58 % **3.51a**, R=C_5H_{11}
(-)-**3.2**, R= CH_3, 70 % **3.53b**, R= CH_3, 50 % **3.52b**, R= CH_3, 30 % **3.51b**, R= CH_3

Compounds **3.52** and **3.53** could not form directly, so the mixtures were rationalized as shown in Scheme 3.13. NMR analysis of the crude product revealed that the desired quaternary center-bearing compounds **3.51** had indeed formed, but then rearranged upon purification with silica gel by opening the oxazolidine ring to form

iminium-alkoxide **A**. Mannich reaction of **A**, followed by intramolecular trapping of the oxonium by the alkoxide in **B** would provide **3.53** (Path A). Alternatively, **A** could undergo an aza-Cope rearrangement leading to **C**, followed by intramolecular alkoxide attack onto the iminium (Path B). Intermediates **B** and **C** are related by reversible Mannich/retro-Mannich reactions.

Scheme 3.13. Mechanistic Considerations

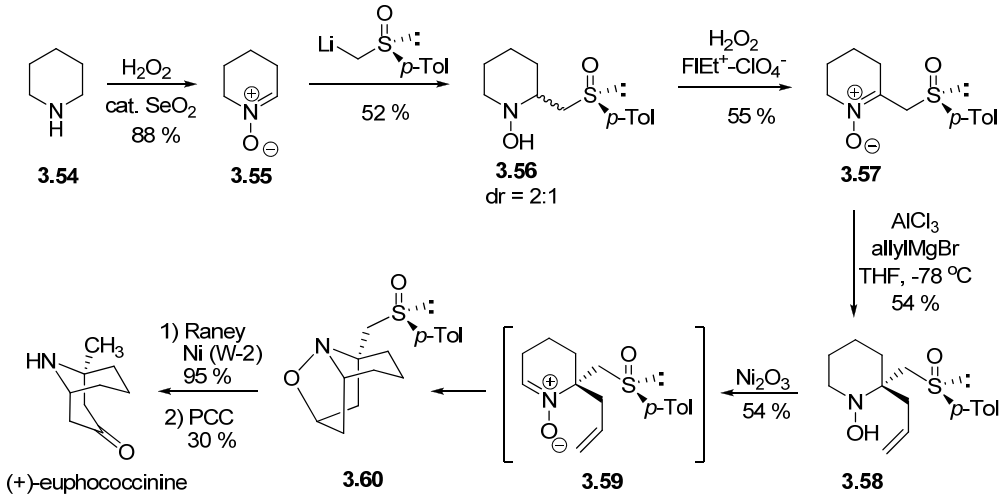


The Murahashi group published an asymmetric synthesis of (+)-euphococcinine in 2000 using chiral, non-racemic β-sulfinyl nitrone **3.57** to carry out a diastereoselective allylation/1,3-dipolar cycloaddition in the key sequence (Scheme 3.14).[128] Oxidation of piperidine with H_2O_2/SeO_2 to nitrone **3.55**, followed by addition of (*R*)-*p*-tolylsulfinylmethyllithium provided sulfinyl hydroxylamine **3.56**. Biomimetic oxidation of **3.56** with 3 mol % of 5-ethyllumiflavinium perchlorate ($FlEt^+$-ClO_4^-) delivered the desired β-sulfinylnitrone **3.57**. Diastereoselective allylation provided the quaternary center-bearing hydroxylamine **3.58** as a chromatographically-separable 83:17 mixture of

[128] Murahashi, S.-I.; Sun, J.; Kurosawa, H.; Imada, Y. *Heterocycles* **2000**, *52*, 557-561.

diastereomers. The major diastereomer was oxidized with Ni_2O_3 to nitrone **3.59**, which underwent intramolecular 1,3-dipolar cycloaddition with the tethered alkene, affording tricyclic isoxazoline **3.60**. Reduction of the N-O bond and the sulfoxide with Raney Ni, followed by PCC oxidation of the resultant secondary alcohol, furnished (+)-euphococcinine.

Scheme 3.14. Asymmetric Allylation/Cycloaddition with Homochiral β-Sulfinyl Nitrones

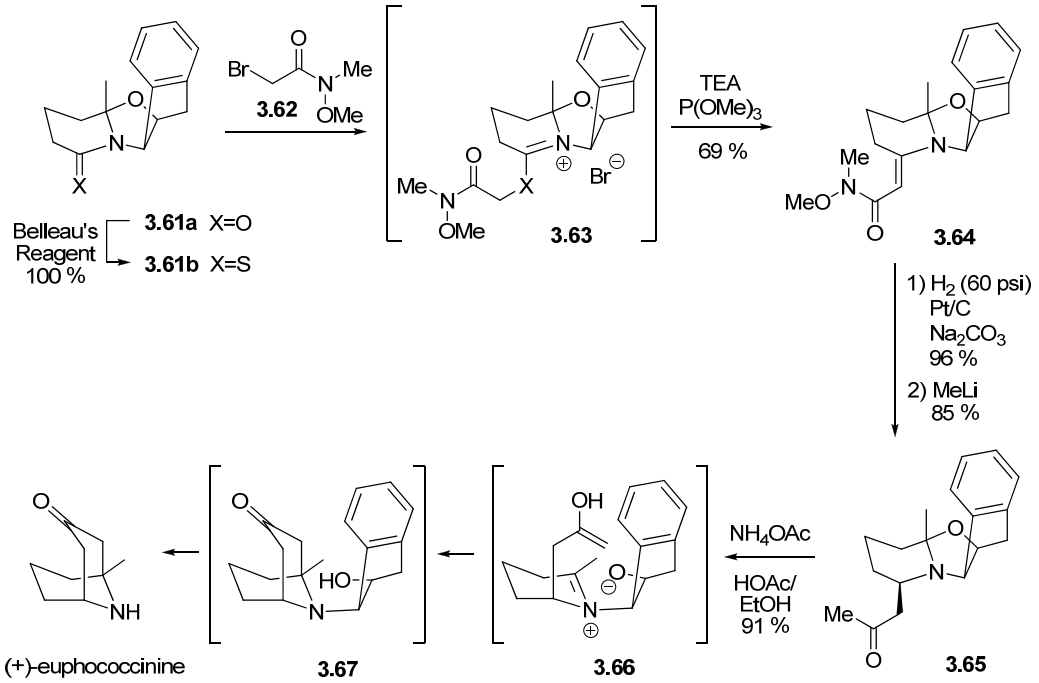


In 2000, Myers published an approach [129] to (+)-euphococcinine similar in strategy to the Husson/Royer CN(*R*,*S*) method employed in their 1992 disclosure of the asymmetric syntheses of (-)-adaline and unnatural (-)-euphococcinine. In the Myers approach (Scheme 3.15), *cis*-1-amino-2-indanol-derived lactam **3.61a** was converted to the corresponding thiolactam **3.61b** and then alkylated with bromoamide **3.62**. The resultant thioiminium salt **3.63** underwent Eschenmosher sulfide contraction upon reflux in triethylamine and trimethylphosphite providing **3.64**. Catalytic hydrogenation followed by reaction of the Weinreb amide with MeLi delivered methyl ketone **3.65**.

[129] Mechelke, M. F.; Meyers, A. I. *Tetrahedron Lett.* **2000**, *41*, 4339-4342.

Treatment with 10 equivalents of NH_4OAc in a 1:1 mixture of acetic acid and ethanol afforded (+)-euphococcinine after stirring overnight at 75 ^oC.

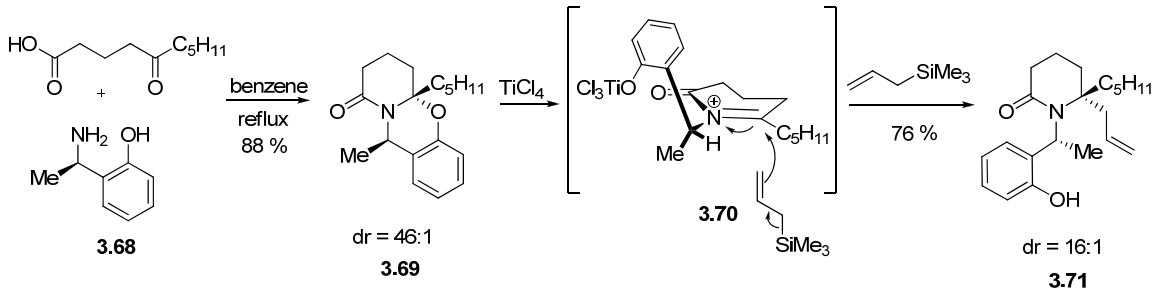
Scheme 3.15. Myers Asymmetric Mannich Approach to (+)-Euphococcinine



Kibayashi's 2002 synthesis of (-)-adaline began with the condensation of enantiomerically-pure 2-(1-aminoethyl)phenol **3.68** and 5-oxodecanoic acid in refluxing benzene, providing **3.69** as a 46:1 mixture of diastereomers (Scheme 3.16).[130] Both diastereomers led to the same iminium intermediate **3.70** when treated with $TiCl_4$, so the mixture was used directly in the reaction with allyltrimethylsilane, providing **3.71** in a 16:1 ratio of diastereomers.

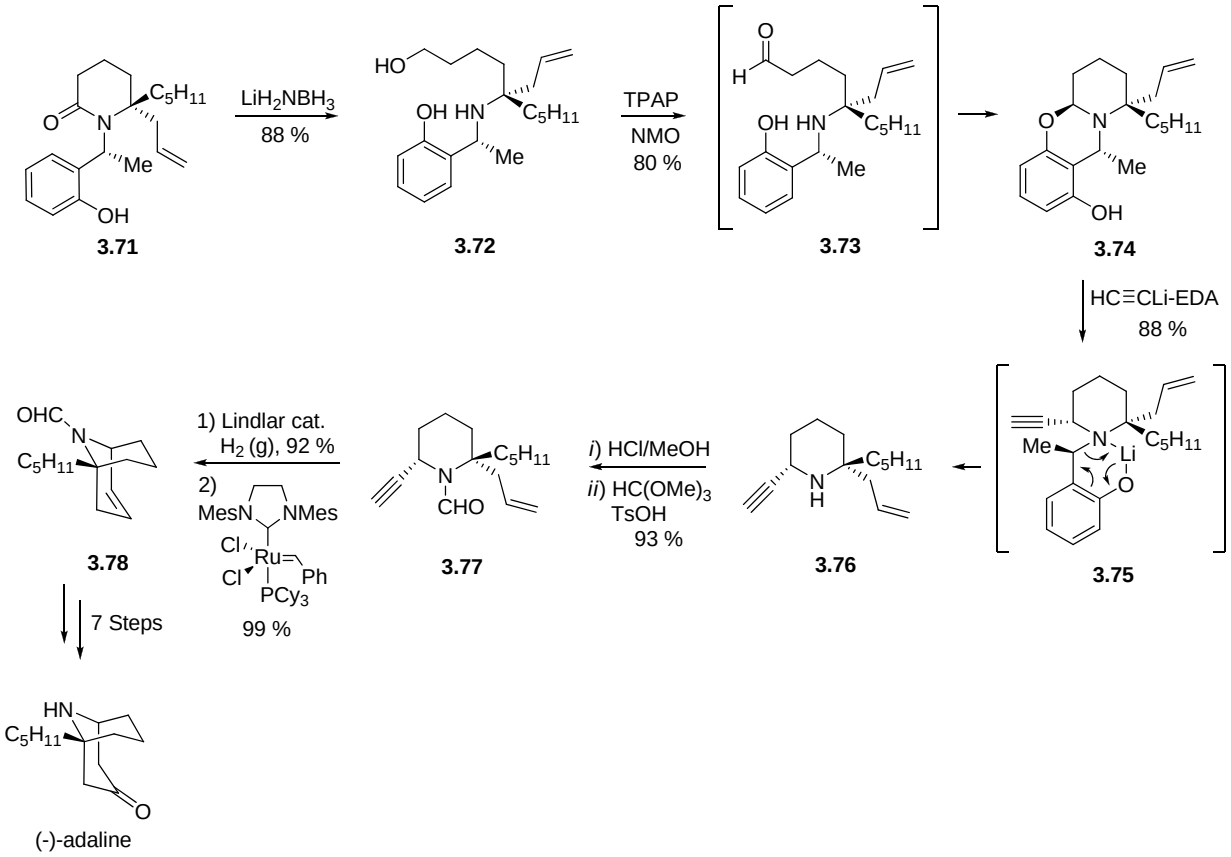
[130] Itoh, T.; Yamazaki, N.; Kibayashi, C. *Org. Lett.* **2002**, *4*, 2469-2472.

Scheme 3.16. Kibayashi's Asymmetric Allylation



Reductive opening of lactam **3.71** with LiH_2NBH_3 provided amino alcohol **3.72** (Scheme 3.17), which was subjected to a one-pot TPAP-NMO oxidation to aldehyde **3.73**/dehydrocondensation sequence, delivering tricyclic *N*,*O*-acetal **3.74** as a single diastereomer. Addition of lithium acetylide ethylenediamine complex provided alkynylation product **3.76**, in which the chiral *N*-protecting group had been removed. The alkyne added with inversion of configuration at the reactive center *via* S_N2-type displacement of the *N*,*O*-acetal. The resultant lithium phenoxide was thought to then form a 6-membered chelate complex **3.75**, resulting in cleavage of the N-C bond. Treating **3.76** with trimethylorthoformate and HCl gave formamide **3.77**, which was subjected to Lindlar-catalyzed hydrogenation of the alkyne to the alkene. Ring-closing metathesis with the second-generation Grubbs catalyst gave homotropane **3.78** in near-quantitative yield. Introduction of the C-7 ketone and removal of the formamide protecting group over 7 steps afforded (-)-adaline.

Scheme 3.17. Kibayashi's Asymmetric Synthesis of (-)-Adaline



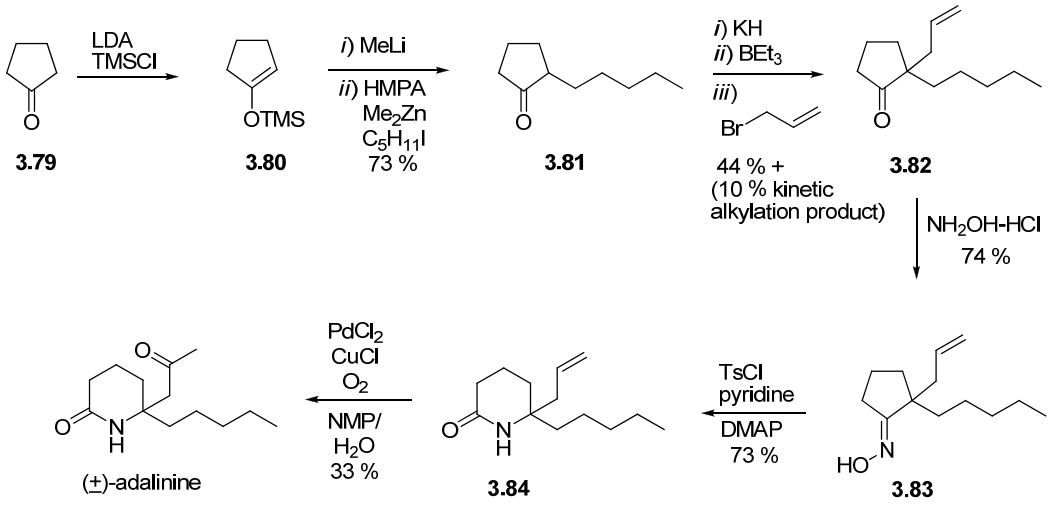
Racemic Approaches to Adalinine

The first racemic synthesis of adalinine was carried out by Broeders and co-workers in 1997, using a Beckmann rearrangement in the key step (Scheme 3.18).[131] To begin the synthesis, cyclopentanone was converted to silyl enol ether **3.80** and stoichiometric MeLi was added to generate the corresponding lithium enolate. Alkylation with 1-iodopentane, HMPA, and Me_2Zn, delivered 2-pentylcyclopentanone **3.81**. To carry out the allylation necessary to form the quaternary carbon center of adalinine, the ketone of **3.81** was transformed to the corresponding potassium enoxyborate under thermodynamic control, and then alkylated with allyl bromide. The

[131] Broeders, F.; Braekman, J. C.; Daloze, D. *Bull. Soc. Chim. Belg.* **1997**, *106*, 377-382.

desired α-quaternary ketone **3.82** was obtained in 44 % yield along with 10 % of the kinetic alkylation product. Stirring **3.82** with hydroxylamine hydrochloride provided a single oxime isomer **3.83**, which was presumed to possess the *anti* configuration. Treating **3.83** with *p*-TsCl and catalytic DMAP in pyridine initiated the key Beckmann rearrangement, affording lactam **3.84**. Wacker oxidation delivered (±)-adalinine in 33 %, confirming the structure they had proposed for the natural product.

Scheme 3.18. Beckmann Rearrangement Approach to (±)-Adalinine

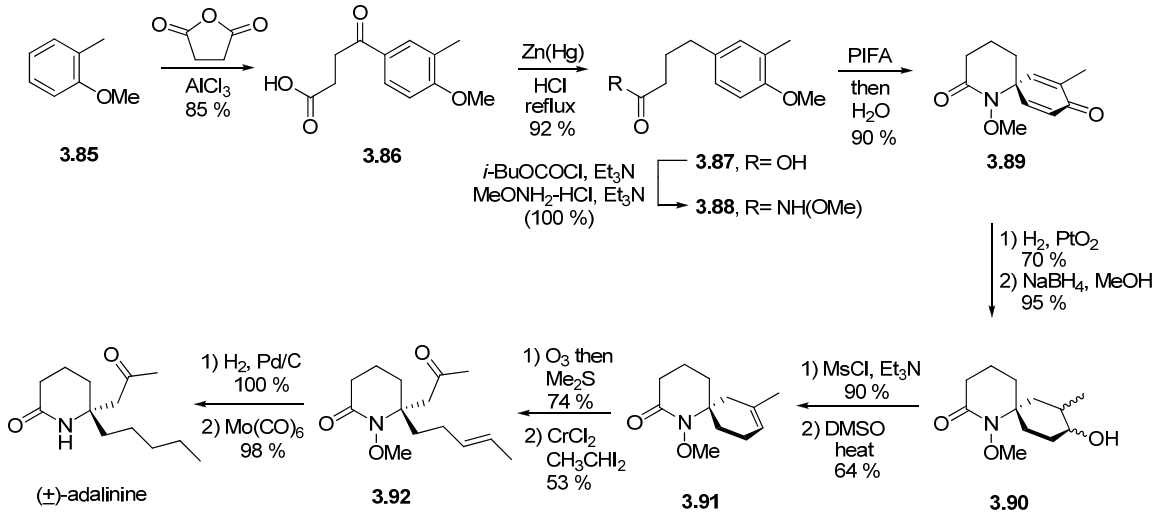


Wardrop and co-workers reported a second racemic synthesis of adalinine in 2003 featuring a nitrenium ion cyclization in the key quaternary-center-forming step (Scheme 3.19).[132] *N*-methoxyamide **3.88**, available from *o*-cresol methyl ether **3.85** *via* a three-step Friedel-Crafts acylation/reduction/*O*-methylhydroxylamine condensation sequence, underwent azaspirocyclization to afford **3.89** upon treatment with one equivalent of phenyliodine(III) bis(trifluoroacetate) (PIFA). Hydrogenation of dienone **3.89**, followed

[132] Wardrop, D. J.; Landrie, C. L.; Ortíz, J. A. *Synlett* **2003**, 1352-1354.

by sodium borohydride reduction, provided **3.90** as a complex mixture of diastereomers. This mixture of alcohols was dehydrated by conversion to the corresponding mesylates and thermolysis, yielding alkene **3.91** and 10 % of the disubstituted regioisomer. Ozonolysis and chemoselective Takai ethylidenation of the resultant aldehyde with $CrCl_2/CH_3CHI_2$ provided alkene **3.92**. Hydrogenation of the alkene and reduction of the N-O bond with $Mo(CO)_6$ provided (±)-adalinine.

Scheme 3.19. Nitrenium Ion Cyclization Approach to (±)-Adalinine



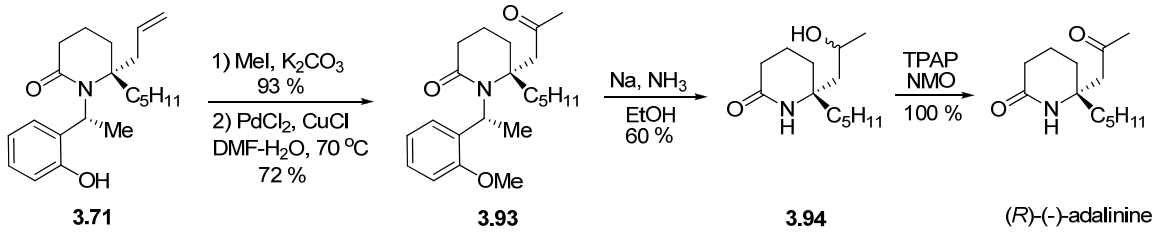
Asymmetric Syntheses of (-)-Adaline

Using the same Lewis acid-mediated allylation of chiral, nonracemic *N*-acyl-*N*,*O*-acetal **3.69** used in their 2002 asymmetric synthesis of (-)-adaline (Scheme 3.16), the Kibayashi group had previously carried out the first asymmetric synthesis of (-)-adalinine, confirming its absolute configuration (Scheme 3.20).[133] Diverting from common intermediate **3.71**, protection of the phenol as the methyl ether using MeI and K_2CO_3 in

[133] Yamazaki, N.; Ito, T.; Kibayashi, C. *Tetrahedron Lett.* **1999**, *40*, 739-742.

acetone provided **3.93**, which was subjected to Wacker oxidation of the terminal alkene. Birch reduction with Na/NH_3 in EtOH cleaved the chiral auxiliary and reduced the ketone of **3.93**, providing a 1:1 mixture of alcohols **3.94**. Oxidation with TPAP/NMO provided (*R*)-(-)-adalinine in quantitative yield, whose optical rotation matched that of the natural product.

Scheme 3.20. Kibayashi's Asymmetric Synthesis of (-)-Adalinine

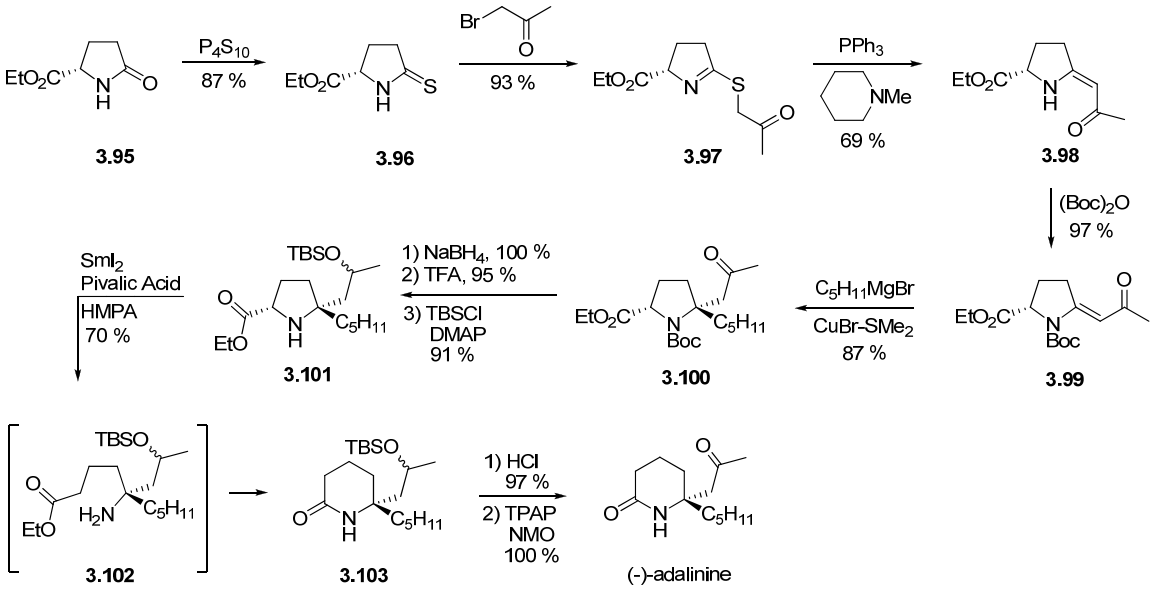


A second asymmetric approach to (-)-adalinine was reported by Honda and co-workers in 2000, and took advantage of a SmI_2-based cleavage protocol for α-amino carbonyl compounds developed by their research group (Scheme 3.21).[134] To begin the synthesis, ethyl (*S*)-(-)-pyroglutamate **3.95** was treated with phosphorous pentasulfide to covert the lactam to a thiolactam, which was then alkylated with bromoacetone. Eschenmoser sulfide contraction ensued upon treatment with PPh_3 to deliver (*Z*)-enaminone **3.98** whose stereochemistry was confirmed by an infrared stretch at 1630 cm^{-1} indicating the presence of an intramolecular hydrogen bond between the NH and carbonyl of the enaminone. Protection of (*Z*)-enaminone **3.98** with Boc_2O provided Boc-protected (*E*)-enaminone **3.99**, in which the geometry of the enaminone had been completely isomerized. At this stage, the α-amino quaternary center was established by

[134] Honda, T.; Kimura, M. *Org. Lett.* **2000**, *2*, 3925-3927.

copper-mediated Michael addition of pentyl magnesium bromide to the enaminone **3.99**, delivering pyrrolidine **3.100**. The key SmI_2-mediated C-N cleavage reaction was sluggish at this point, which was attributed to the presence of the ketone, a competitive site for reduction. Thus, the ketone of **3.100** was reduced to a 1:1 mixture of alcohols with $NaBH_4$. TFA-induced removal of the Boc protecting group and TBS protection of the mixture of alcohols brought the synthesis to the key step. C-N bond cleavage was carried out with 5 equivalents of SmI_2 in THF-HMPA (7:1), and the δ-amino ester **3.102** produced in the fragmentation reaction underwent further cyclization to δ-lactam **3.103** in 70 % overall yield. To finish the synthesis, cleavage of the TBS ethers with HCl and oxidation of the resultant alcohols with TPAP/NMO, following Kibayashi's protocol, provided (-)-adalinine in quantitative yield.

Scheme 3.21. Honda's Asymmetric Synthesis of (-)-Adalinine



In summary, a number of methods have been developed over several decades for the synthesis of both 9-azabicyclo[3.3.1]nonanes and 2-piperidones bearing quaternary

centers α to nitrogen. Euphococcinine, adaline, and adalinine have been shown to be popular targets for highlighting novel methods and strategies developed for the synthesis of amino-substituted quaternary centers. At present, Kibayashi's *N*,*O*-acetal protocol is the only methodology which has been applied to asymmetric syntheses of both (-)-adaline and (-)-adalinine.

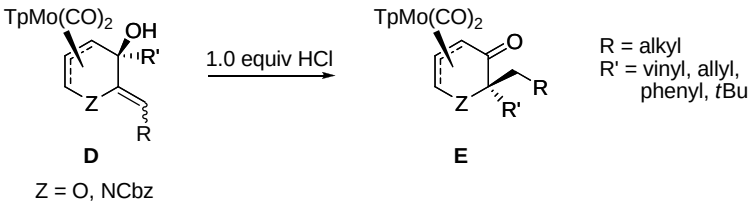
Introduction

Having developed a novel application of the semipinacol rearrangement for the asymmetric synthesis of heteroatom-substituted quaternary centers and recently publishing a conceptually-new 1,5-Michael-like[135] approach to bicyclic heterocycles, the next step for the Liebeskind laboratory was to showcase the utility of these methodologies in total synthesis. Strategically coupled, the semipinacol rearrangement and the 1,5-Michael-like reaction appeared to represent a powerful new approach to quaternary-center-bearing bicyclic natural products.

To review, η^3-allylmolybdenum complexes **D** bearing allylic alcohols in which the R group had a good migratory aptitude were found to undergo facile semipinacol rearrangement to the corresponding α,α'-disubstituted ketones **E** upon treatment with a full equivalent of HCl (Scheme 3.22).

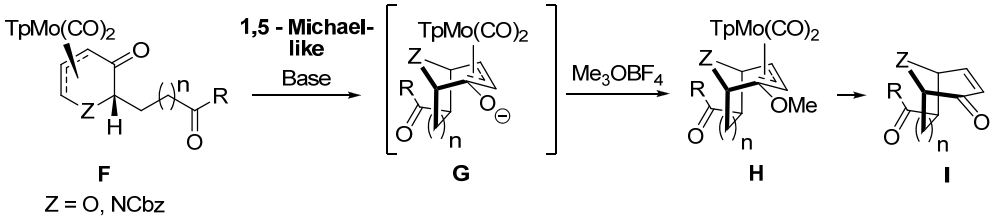
[135] Zhang, Y.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2005**, *127*, 11258-11259.

Scheme 3.22. Semipinacol Rearrangement of 5-oxo-η^3-Allylmolybdenum Complexes



The 1,5-Michael-like reaction, as originally reported, involved intramolecular addition of an enolate to the terminal end of neutral 5-oxo-η^3-allylmolybdenum pyranyl and pyridinyl complexes **F**, generating bicyclic complexes **H** after the addition of Meerwein's reagent (Me_3OBF_4) (Scheme 3.23). These complexes could be further demetalated under oxidative conditions, providing bicyclic enones **I**. In the original disclosure, the bicyclo[3.2.1] ring system could be selectively generated, and under some reaction conditions, the bicyclo[4.3.1] ring system could also be accessed, but as part of a mixture with the bicyclo[3.2.1] skeleton.

Scheme 3.23. Intramolecular l,5-Michael-like Reaction

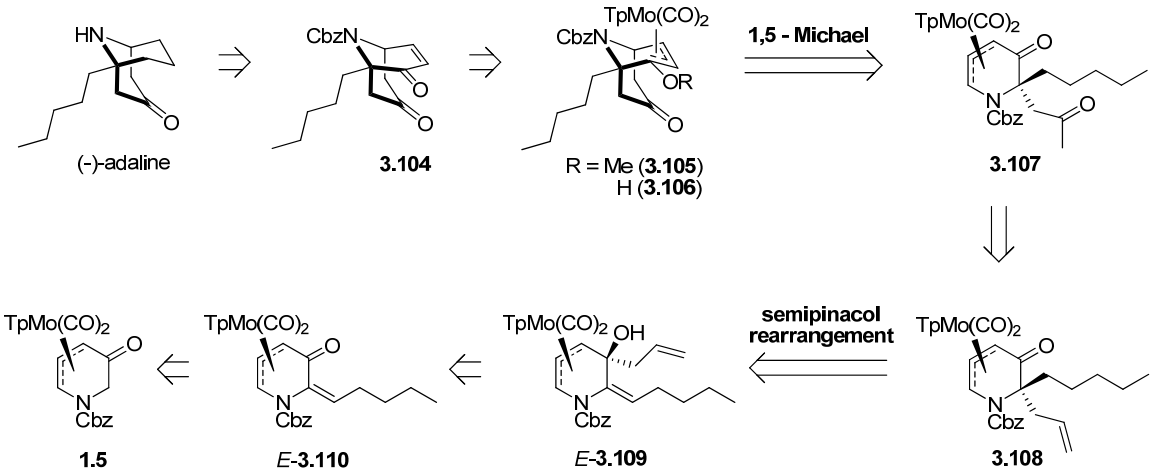


The coccinellid alkaloid (-)-adaline was chosen as the application to highlight these reactions as it possessed both an α-amino quaternary carbon center and the 9-azabicyclo[3.3.1]nonane skeleton represented a new class of structures to which the 1,5-Michael-like reaction had yet to be extended. A retrosynthetic analysis of (-)- adaline is

shown in Scheme 3.24. Adaline was viewed as coming from enone **3.104** after defunctionalization to remove the α,β-unsaturated ketone. Enone **3.104** would come from bicyclic η^3-allylmolybdenum complex **3.105** or **3.106** *via* oxidative demetalation, and these complexes would be available from diketone **3.107** *via* 1,5-Michael-like reaction. Diketone **3.107** should come from Wacker oxidation of the terminal olefin in **3.108**, arising from the key semipinacol rearrangement of allylic alcohol *E*-**3.109**. Allylic alcohol *E*-**3.109** would, in turn, be available from enone *E*-**3.110** *via* 1,2-Grignard addition, and enone *E*-**3.110** would come from scaffold **1.5** after Mukaiyama aldol reaction with valeraldehyde and dehydration of the resultant alcohol.

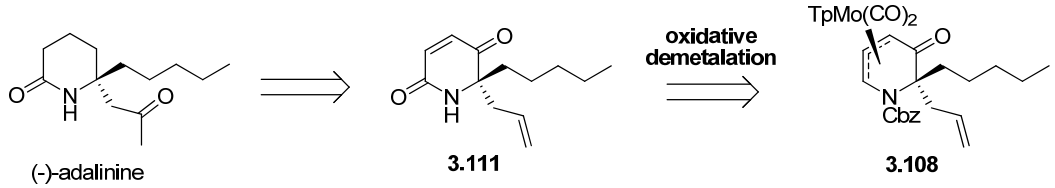
As described in Chapter 2, pyridinyl scaffold **1.5** undergoes *anti*-selective Mukaiyama aldol reactions with aldehydes, and the resultant *anti* alcohols undergo stereospecific elimination to the *E*-alkenes after conversion to the corresponding mesylate intermediates. The selectivities of the aldol/dehydration steps were of particular importance in planning the syntheses of adaline and adalinine as it was known from Zhang's initial studies with acetaldehyde (Chapter 2, Table 2.3) that only *E*-alkenes undergo semipinacol rearrangement in the pyridinyl series.

Scheme 3.24. Retrosynthetic Analysis of (-)-Adaline



Adalinine was also viewed as coming from the common quaternary center-bearing intermediate **3.108** *via* an oxidative demetalation protocol[136] to give unsaturated keto-lactam **3.111** (Scheme 3.25). Oxidation of the terminal alkene to the corresponding methyl ketone and defunctionalization to remove the undesired α,β-unsaturated ketone would lead to adalinine.

Scheme 3.25. Retrosynthetic Analysis of (-)-Adalinine



[136] Alcudia, A.; Arrayás, R. G.; Liebeskind, L. S. *J. Org. Chem.* **2002**, *67*, 5773-5778.

Results and Discussion

Synthesis of Common Intermediate[137]

To begin the synthesis, Mukaiyama aldol reaction of the enol silane derived from ketone **1.5** with the $TiCl_4$ complex of valeraldehyde at -78 ^oC produced *anti*-β-hydroxy ketone **3.112** in 57-70 %, with an *anti*:*syn* ratio of 6:1 (Scheme 3.26). With careful chromatography, the minor (*syn*) diastereomer could be separated from the major (*anti*) diastereomer, as could 10-15 % of recovered **1.5**. *Anti* alcohol **3.112** was then dehydrated by conversion to the corresponding mesylate, and elimination with DBU. A mixture of three isomeric alkenes was isolated in 74 % yield: *E*-**3.110a**; *Z*-**3.110b**; unconjugated **3.110c** = 77:7:16. The *Z*-alkene could be chromatographically separated, but the unconjugated alkene **3.110c** co-eluted with the *E*-alkene during chromatography and could not be removed. *E*-**3.110a** was characterized by collecting the initial fractions of the orange product band during chromatography, which contained smaller quantities of **3.110c**. A pure sample of **3.110c** could not be obtained.

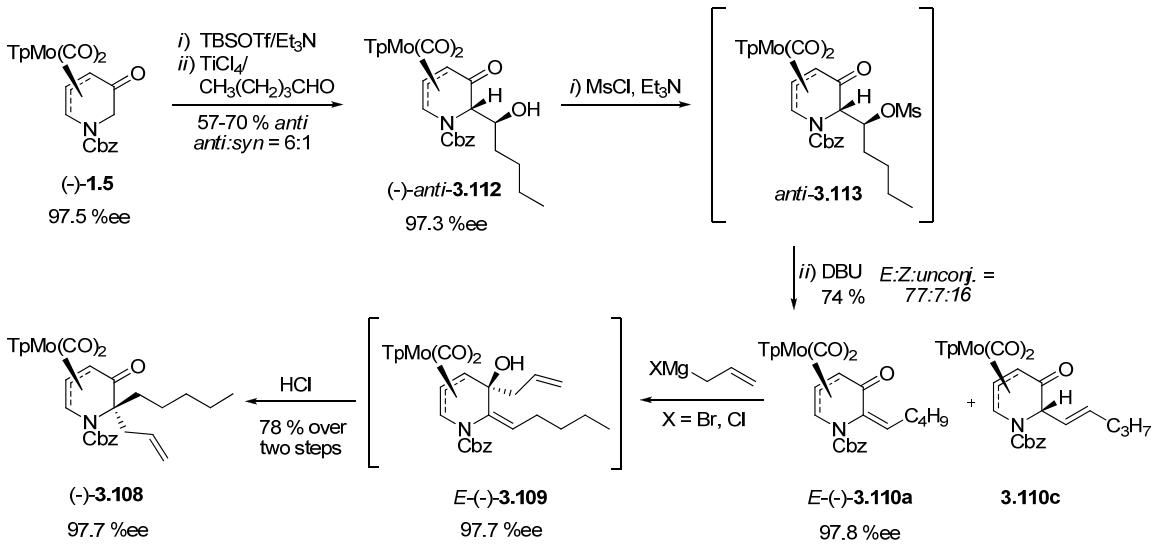
Other bases were explored for this elimination with inferior results: Et_3N, pyridine, and Hunig's base all failed to bring about elimination. DABCO produced a small amount of product after 15 hours by TLC, and DMAP delivered a 52 % yield of product in which *Z*-**3.110b** constituted 35 % and the remaining 17 % was composed of *E*-**3.110a** with some detectable **3.110c**.

[137] Exploratory racemic studies were carried out by Dr. Yongqiang Zhang, up to the Wacker oxidation of compound **3.108**: see Zhang, Y. Preliminary Studies: Stereocontrolled Construction of Oxa- and Aza Heterocycles from the two Common Molybdenum Scaffolds, $TpMo(CO)_2$(5-oxopyranyl) and $TpMo(CO)_2$(5-oxopyridinyl). Unpublished Results, Emory University, Atlanta, 2005.

Addition of allylMgCl to the mixture of *E*-**3.110a** and **3.110c** provided tertiary allylic alcohol *E*-**3.109** containing an uncharacterized impurity. This mixture was typically subjected to aqueous work-up and then directly rearranged with 1.1 equiv of HCl (4.0 M in dioxane), affording pure **3.108**. The overall yield for the 2-step Grignard addition/semipinacol rearrangement sequence was 78 %.

Using (-)-**1.5**[138] (97.5 % ee), the sequence described above was used to obtain (-)-**3.108** (97.7 % ee). Enantiomeric excesses for synthetic intermediates are shown in Scheme 3.26.

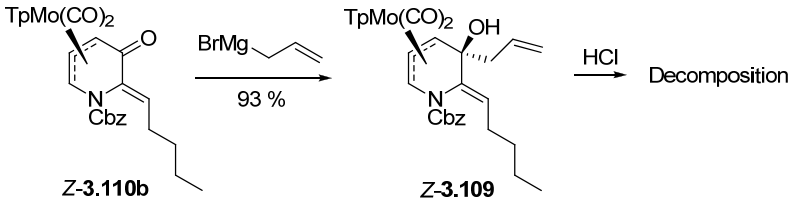
Scheme 3.26. Synthesis of Quaternary Center-Bearing Intermediate



Addition of allylMgBr to *Z*-**3.110b** also occured in excellent yield, but treating allylic alcohol *Z*-**3.109** with HCl led only to slow decomposition. No desired semipinacol rearrangement product **3.108** was observed. A similar result was noted with the ethyl analog ***Z*-2.27** (Chapter 2, Table 2.3, Entry 9).

[138] Coombs, T. C.; Lee, M. D., IV; Wong, H.; Armstrong, M.; Cheng, B.; Chen, W.; Moretto, A. F.; Liebeskind, L. S. *J. Org. Chem.* **2008**, *73*, 882-888.

Scheme 3.27. Elimination of *syn* Diastereomer and Semipinacol Rearrangement

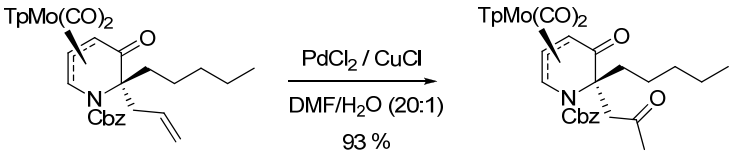


Z-**3.110b** *Z*-**3.109**

Synthesis of (-)-Adaline

Pursuing adaline, the terminal alkene of α-quaternary ketone **3.108** was oxidized to the methyl ketone **3.114** in 93 % using the Wacker oxidation (Scheme 3.28). This transformation was found to work well using 1-2 gram samples of alkene **3.108**, but attempts to scale up the reaction met with a tendancy of the starting material to precipitate from solution over the course of the several-day period required for the transformation.

Scheme 3.28. Wacker Oxidation of Terminal Alkene



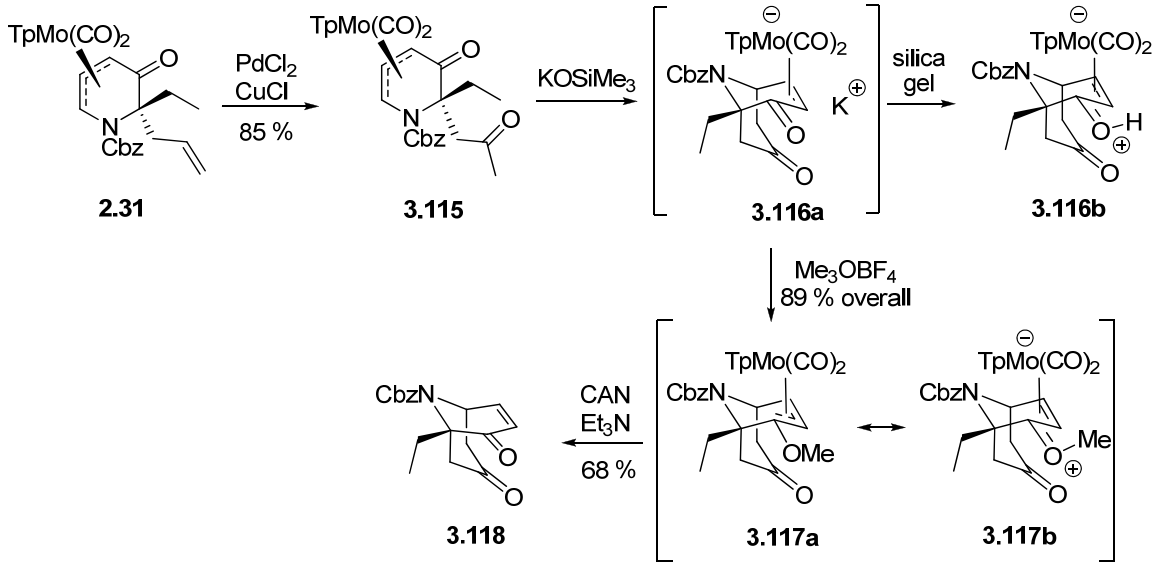
(-)-**3.108**
97.7 %ee

(-)-**3.114**

Model 1,5-Michael Study

Previous studies of the 1,5-Michael-like reaction with ethyl analog **3.115** by Dr. Yongqiang Zhang had been carried out, delivering **3.117** in 89 %. Further demetalation with CAN delivered bicyclic enone **3.118** in 68 %.

Scheme 3.29. Wacker Oxidation/1,5-Michael Sequence



A single crystal of cyclization product **3.116b**, the compound formed from anionic intermediate **3.116a** upon subjection to silica gel chromatography, was grown and submitted to X-ray diffraction analysis. The structure is shown in Figure 3.2. It is interesting to note that **3.116b** possesses significant η^2-alkenyl molybdenum character accompanied by an adjacent C-O bond whose length is suggestive of multiple bond character. While the Mo(1)-C(11) and Mo(1)-C(12) bond lengths are 2.296 Å and 2.261 Å, respectively, the Mo(1)-C(13) bond is nearly a full angstrom longer (3.229 Å). The C(13)-O(1) bond length is 1.211 Å, while a typical C-O single bond is 1.42 Å in length and a typical C=O double bond is 1.22 Å in length.[139] This phenomenon has been previously observed for η^3-allylmolybdenum complexes bearing methoxy substituents at one of the termini.[140]

[139] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, 4th ed. Part A: Structure and Mechanisms*; Kluwer Academic/Plenum Publishers: New York, 2000.
[140] Ward, Y. D.; Villanueva, L. A.; Allred, G. A.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132-4156.

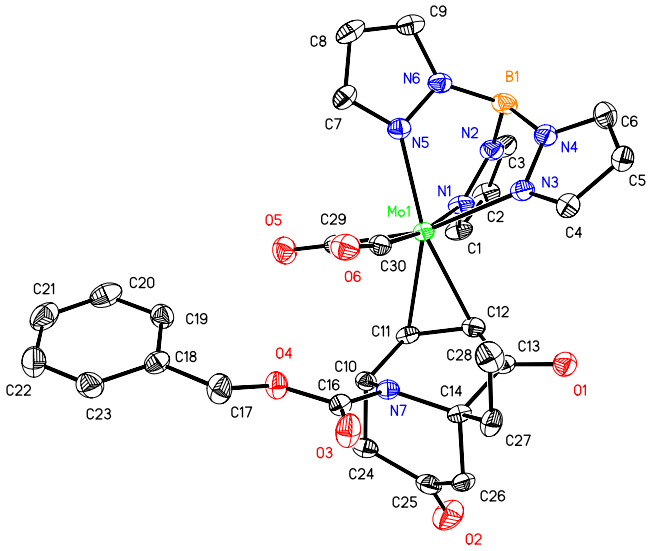


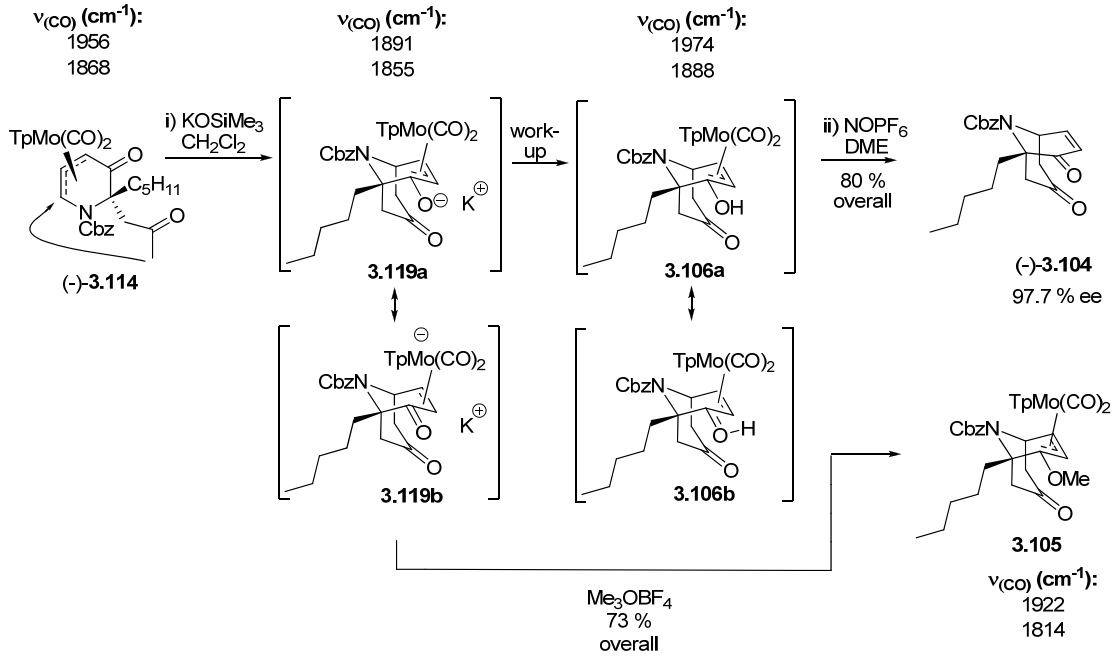
Figure 3.2. ORTEP View of (±)-3.116

Continuing Towards (-)-Adaline

Treating ketone **3.114** with 3.0 equivalents of $KOSiMe_3$ induced the 1,5-Michael-like reaction, delivering anionic intermediate **3.119** possessing the 9-azabicyclo[3.3.1]nonane skeleton (Scheme 3.30). Treating intermediate **3.119** with 3.0 equivalents of Meerwein's reagent (Me_3OBF_4) generated (η-3,4,5)-3-methoxyallylmolybdenum complex **3.105** in 73 % yield. (η-3,4,5)-3-Methoxyallylmolybdenum complexes of this type are known to undergo oxidative decomplexation upon treatment with CAN, delivering enones similar to **3.104**. However, when intermediate **3.106** was treated with 1.0 equivalents of $NOPF_6$ in DME, bicyclic enone **3.104** could be isolated directly in 80 % yield, resulting from oxidative CO→NO exchange and subsequent decomplexation of the metal from the bicyclic ligand. Heating intermediate **3.106** in acetonitrile with 5 equivalents of HCl also delivered enone **3.104**,

though in a lower 44 % yield. Bicyclic enone (-)-**3.104** was obtained in 97.7 %ee, indicating no change in enantiomeric excess from terminal alkene (-)-**3.108** (97.7 %ee).

Scheme 3.30. 1,5-Michael-like Reaction



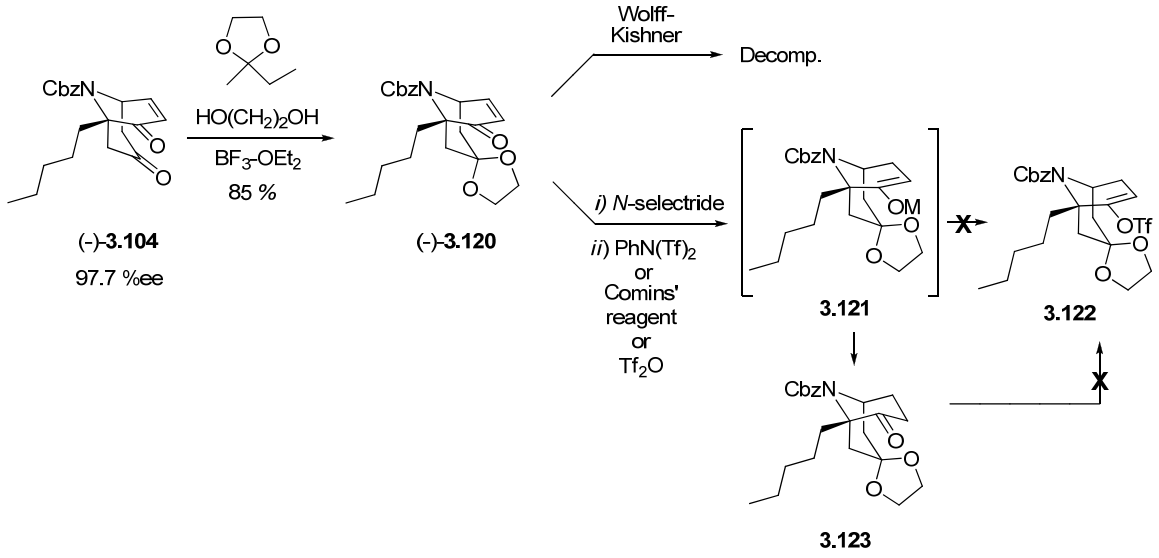
Analysis of the metal carbonyl stretches by IR confirmed that upon treating **3.114** with $KOSiMe_3$, 1,5-Michael cyclization produced an anionic intermediate **3.119** in which the electron density on the metal was significantly increased (Scheme 3.30). This was evidenced by a shift to lower wavenumbers for the metal carbonyls due to increased backbonding from the electron-rich metal. Upon quench with H^+ (**3.106**) or Meerwein's reagent (**3.105**), the metal carbonyls shifted back to higher wavenumbers, indicating that electron density had been removed from the metal, decreasing backbonding.

Two resonance structures are shown for both **3.119** and **3.106** (Scheme 3.30). The crystal structure of **3.116** (Figure 3.2) indicates that intermediates of this type possess significant η^2-alkenyl molybdenum character accompanied by a shortening of the

adjacent C-O bond. These structural features may be accounted for by significant contributions from resonance forms **3.119b** and **3.106b**.

Continuing with the synthesis of adaline, selective protection of the ketone of **3.104** in the presence of the enone was achieved in 85 % yield (Scheme 3.31). Direct deoxygenation of enone **3.120** under Wolff-Kishner reduction conditions resulted only in decomposition, while attempts to trap the intermediate enolate **3.121**, coming from 1,4-hydride addition to the enone could not be achieved with either $PhN(Tf)_2$ or Comins' reagent. Instead, ketone **3.123** was isolated after work-up. Additionally, treating ketone **3.123** with base to generate the enolate **3.121** followed by addition of $PhN(Tf)_2$ or Tf_2O never produced the desired vinyl triflate.

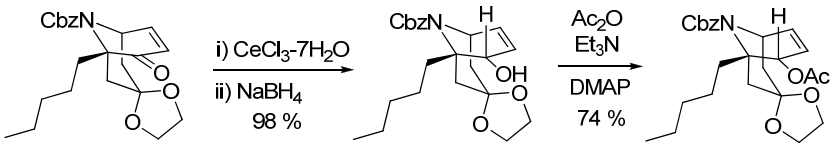
Scheme 3.31. Attempts at Deoxygenation



Alternatively, Luche reduction of enone **3.120** provided a single diastereomer of alcohol **3.124** in 98 % (Scheme 3.32). This alcohol was determined to be equatorial at a later

stage, resulting from 1,2-hydride addition to the carbonyl from the less-hindered, convex face of the bicycle. Acylation delivered allylic acetate **3.125**.

Scheme 3.32. Luche Reduction and Acylation

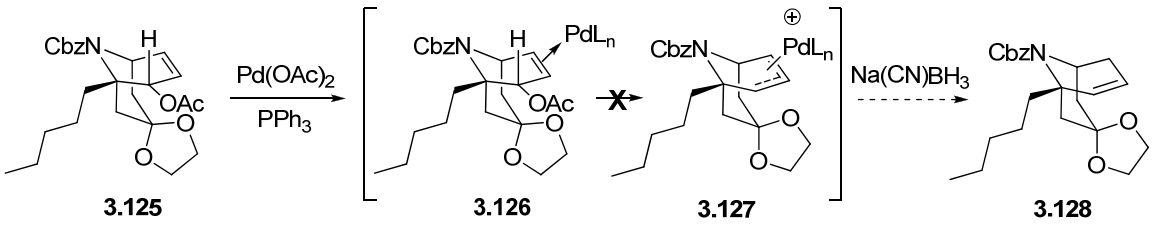


(-)-**3.120** (-)-**3.124** *one diastereomer* **3.125**

Attempts to carry out allylic hydrogenolysis[141] using $Pd(OAc)_2$, PPh_3, and $Na(CN)BH_3$ failed in both refluxing THF and refluxing dioxane (Scheme 3.33), leading only to recovered starting material. While allylic acetates typically undergo hydrogenolytic cleavage under similar conditions, the unreactive nature of this particular allylic acetate was not surprising in hindsight. Oxidative addition of an allylic acetate to Pd(0) proceeds with inversion of configuration and favorable reaction conditions are those in which the Pd(0) can coordinate to the alkene in an orientation antiperiplanar to the acetate.[142] This geometry cannot be achieved in rigid bicycle **3.125** (Scheme 3.33). Additionally, disolving metal reduction of allylic acetate **3.125** with Li(0) in $THF/NH_{3(l)}$ also failed, leading only to decomposition.

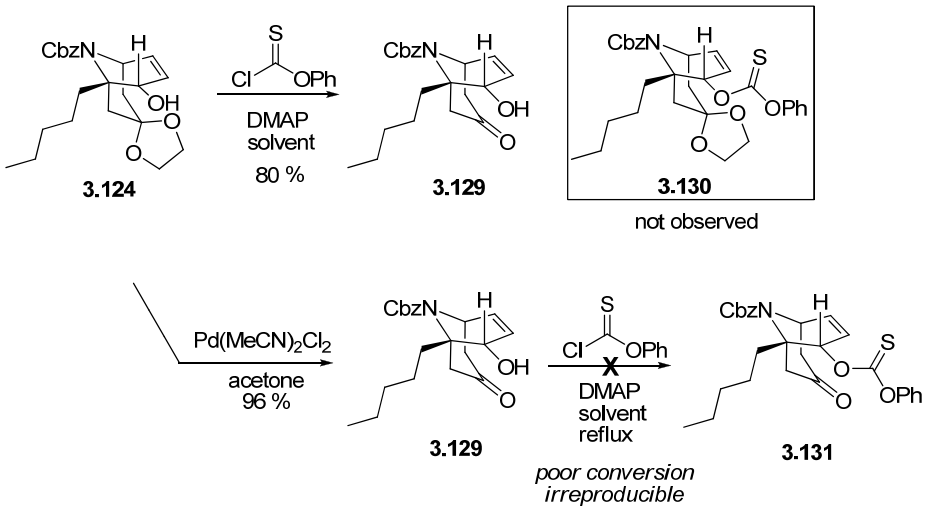
[141] Hutchins, R. O.; Learn, K.; Fulton, R. P. *Tetrahedron Lett.* **1980**, *21*, 27-30.
[142] Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994.

Scheme 3.33. Attempt at Allylic Acetate Hydrogenolysis



With the intent to switch tactics and carry out Barton-McCombie dehydroxylation, allylic alcohol **3.124** was stirred at room temperature with phenyl chlorothionoformate and DMAP. Instead of the desired thionocarbonate **3.130**, ketone **3.129** was unexpectedly isolated in 80 % yield, resulting from loss of the ketal protecting group (Scheme 3.34). Revising the route to incorporate this unanticipated deprotection, other conditions for the transformation were explored. While 1N HCl in THF delivered ketone **3.129** in 49 %, $Pd(MeCN)_2Cl_2$ in wet acetone gave the desired ketone in a significantly-improved 96 % yield. At this point, the thionocarbonate **3.131** could be made by refluxing allylic alcohol **3.129** in 1,2-dichloroethane with phenyl chlorothionoformate and DMAP. However, the conversion was poor and irreproducible. A slightly different approach would be required.

Scheme 3.34. Attempted Barton-McCombie Precursor Synthesis

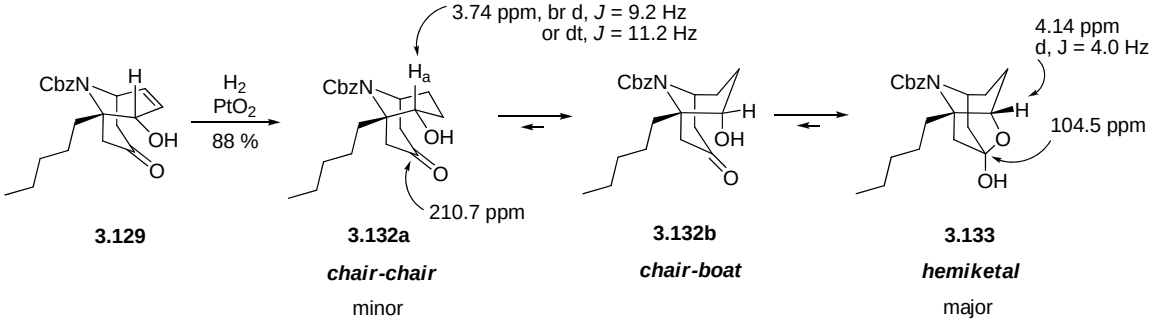


To confirm the configuration of the stereocenter formed in the Luche reduction of enone **3.120**, hydrogenation of the alkene in allylic alcohol **3.129** was carried out using PtO_2 (Table 3.1). It was anticipated that the coupling constant between H_a (compound **3.132a**) and the adjacent methylene hydrogens would confirm the configuration of the stereocenter created in the Luche reduction. A coupling constant larger than 8 Hz would indicate axial-axial coupling,[143] confirming hydride delivery to the convex face of bicycle **3.120**. Instead of isolating a single compound, however, an equilibrium mixture of keto-alcohol **3.132a** and hemiketal **3.133** were unexpectedly obtained in which **3.132a** was the minor component. The existence of hemiketal **3.133** was confirmed by a peak in the ^{13}C NMR at 104.5 ppm. The formation of hemiketal **3.133** requires a chair-chair to chair-boat conversion of **3.132a** to **3.132b**, followed by intramolecular attack of the alcohol onto the ketone. Thus, the configuration of the new stereocenter was confirmed as hemiketal **3.133** could only form from an equatorially-disposed alcohol.

[143] Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Structural Spectroscopy*; Prentice Hall: Upper Saddle River, NJ, 1998.

In $CDCl_3$ at room temperature (20 °C), the ratio of **3.132a**:**3.133** was 22:78 (Table 3.1). At 50 °C, the ratio became 27:73. In d_3-MeCN at 20 °C, the ratio of **3.132a**:**3.133** was a much closer 39:61, and upon heating to 65 °C it was nearly 1:1.

Table 3.1. Equilibrium Mixture from Hydrogenation of 3.129

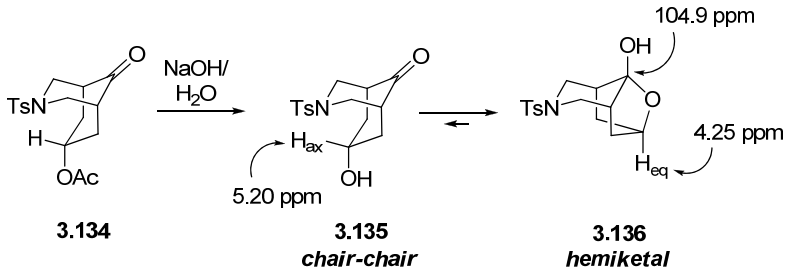


Solvent/Temperature	Chair-Chair : Hemiketal
$CDCl_3$, 20 °C	22:78
$CDCl_3$, 50 °C	27:73
D_3-MeCN, 20 °C	39:61
D_3-MeCN, 65 °C	46:54

Speckamp and co-workers observed a similar phenomenon when acetate **3.134** was hydrolyzed with $NaOH/H_2O$ in MeOH (Table 3.2).[144] The result was an equilibrium mixture of **3.135** and **3.136**, whose position shifted with changes in solvent and temperature. In this case, the axial hydrogen highlighted in chair-chair structure **3.135** was further downfield than the equatorial hydrogen highlighted in hemiketal **3.136** due to the deshielding effect of the tosyl protecting group.

[144] Bok, T. R.; Kruk, C.; Speckamp, W. N. *Tetrahedron Lett.* **1978**, *7*, 657-660.

Table 3.2. Related Hemiketal Formation Reported by Speckamp

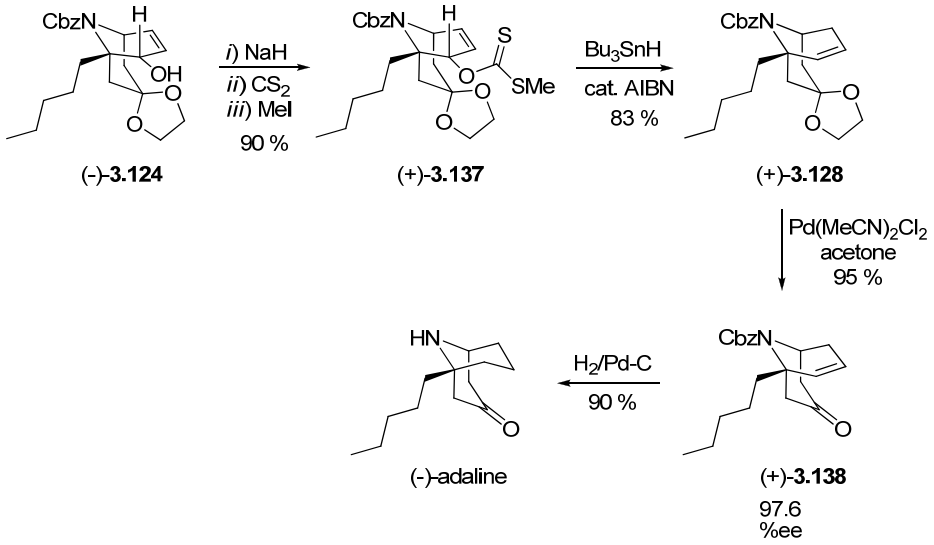


3.134 **3.135** ***chair-chair*** **3.136** ***hemiketal***

Solvent/Temperature	Chair-Chair : Hemiketal
$CDCl_3/C_5D_5N$, -60 °C	15:85
$CDCl_3$, 35 °C	45:55
Ph_2O, 35 °C	30:70
Ph_2O, 130 °C	Coalescence
d_8-toluene, 90 °C	50:50

To finish the synthesis of adaline, allylic alcohol **3.124** was deprotonated with NaH and then treated with CS_2 and MeI to form allylic xanthate **3.137** in 90 % (Scheme 3.35). Refluxing **3.137** in benzene with Bu_3SnH and AIBN carried out Barton-McCombie dehydroxylation, delivering a single alkene isomer **3.128** in 83 %, whose structure was confirmed by COSY NMR. Hydrolysis of the ketal protecting group with $Pd(MeCN)_2Cl_2$ in wet acetone produced ketone **3.138**, and concomitant hydrogenation/hydrogenolysis of the alkene and Cbz protecting group provided adaline in 90 % after work-up with aqueous NaOH, $[\alpha]_D^{25}$ = -13.0 (*c* 0.73, $CHCl_3$), [lit. $[\alpha]_D$ = -13 ($CHCl_3$)]. The spectral properties of the compound produced in this manner matched those reported in the literature. The enantiomeric excess of (+)-**3.138** was determined to be 97.6 % by HPLC, so (-)-adaline produced by this method is assumed to also have a 97.6 % ee.

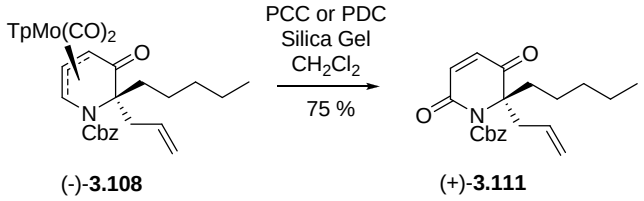
Scheme 3.35. Finishing the Total Synthesis of (-)-Adaline



Synthesis of (-)-Adalinine

Using quaternary-center-bearing complex **3.108** employed in the synthesis of (-)-adaline, the synthesis of (-)-adalinine was undertaken. Known oxidative demetalation conditions using PDC or PCC and silica gel provided α,β-unsaturated keto-lactam **3.111** (Table 3.3).

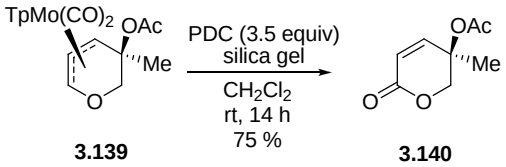
Table 3.3. Oxidative Demetalation to Lactam 3.111



PCC/Silica Gel		PDC/Silica Gel	
Equivs	**Yield (%)**	**Equivs**	**Yield (%)**
3.2	32	3.2	6
5.0	43	6.0	63
7.0	52	7.0	66
10.0	37	8.0	75

Previous work by the Liebeskind laboratory showed that (η-2,3,4-pyranyl) molybdenum complexes such as **3.139** undergo oxidative demetalation to the corresponding 5,5-disubstituted dihydropyranones in good yields with 3.5 equivalents of PDC and silica gel (Scheme 3.36).

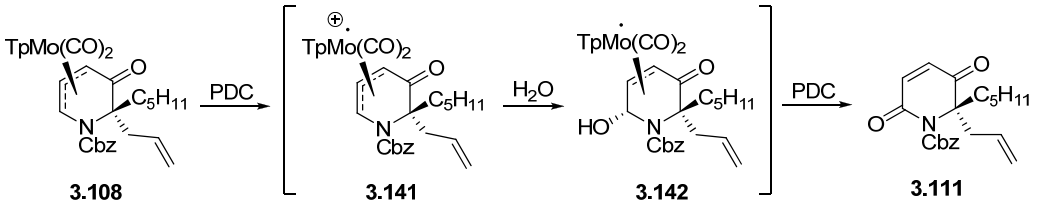
Scheme 3.36. Oxidative Demetalation Precedent



3.139 **3.140**

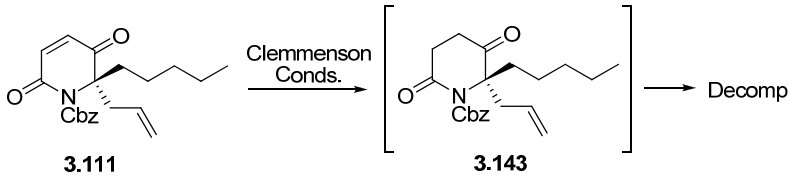
However, in the present case 3.2 equivalents of PDC/silica gel were insufficient to drive the demetalation of compound **3.108** to completion. A meager 6 % of the desired **3.111** was isolated, with most of the starting material remaining after prolonged reaction times. Switching to PCC/silica gel led to a significant improvement in yield (32 %), but the best yield (52 %) was obtained using 7.0 equivalents of PCC/silica gel. Reinvestigating PDC, the yield of unsaturated keto-lactam **3.111** could be improved to 75 % with 8.0 equivalents of the reagent. Scheme 3.37 shows the proposed mechanism of this oxidative demetalation: A one-electron oxidation of **3.108** to radical cation **3.141**, followed by nucleophilic addition of water to the 2-position of the pyridinyl ligand, provides η^2-alkenyl molybdenum complex **3.142**. Decomplexation of the metal and further PDC oxidation of the aminal affords lactam **3.111**.

Scheme 3.37. Proposed Mechanism of Oxidative Demetalation



With unsaturated keto-lactam **3.111** in hand, attention was turned to chemoselective reduction of the ketone. Attempts to deoxygenate the enone under Clemmenson reduction conditions provided instead **3.143** (identified by crude ^{1}H NMR), in which the alkene was reduced, and the ketone remained untouched (Scheme 3.38). Forcing the reduction with harsher conditions and higher temperatures led only to decomposition.

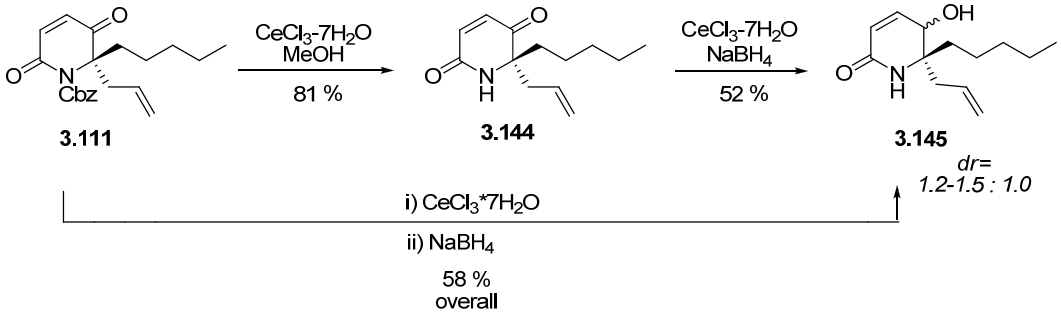
Scheme 3.38. Attempted Clemmenson Reduction



Reducing the ketone of **3.111** with DIBAL-H was also briefly explored, but led to a complex mixture of products. After extended reaction times, most of the starting material still remained. Turning instead to the Luche reduction, **3.111** was stirred with $CeCl_3$-$7H_2O$ for 30 minutes before the addition of $NaBH_4$ in one portion at 0 ^{o}C (Scheme 3.39). Allylic alcohols **3.145**, in which the Cbz protecting group had been removed, were isolated as a 1.2-1.5 : 1.0 mixture of diastereomers in 58 % yield. Another 19 % of what appeared to be a complex mixture of diastereomers resulting from hydride addition to both the ketone and lactam carbonyl was also isolated.

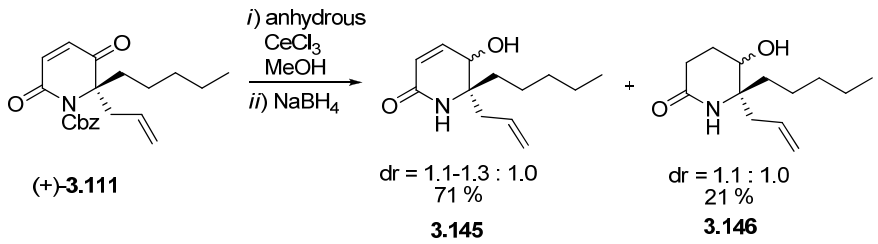
Simply stirring compound **3.111** with $CeCl_3$-$7H_2O$ in MeOH led to the isolation of compound **3.144** in which the Cbz protecting group had been removed (Scheme 3.39). This result suggested that the $CeCl_3$-$7H_2O$ promoted MeOH addition to the urethane carbonyl, resulting in loss of the protecting group. Thus, it was determined that the deprotected lactam was the species undergoing 1,2-reduction upon addition of $NaBH_4$. Therefore, attempts to improve the yield of this one-pot deprotection/reduction were made by separating the transformation into two steps. Subjecting purified lactam **3.144** to the Luche reduction conditions described above provided allylic alcohols **3.145** in 52 %. Thus, the 2-step procedure did not provide any improvement in yield over the direct one-pot deprotection/reduction sequence and the one-pot sequence was kept.

Scheme 3.39. Deprotection/Luche Reduction Sequence



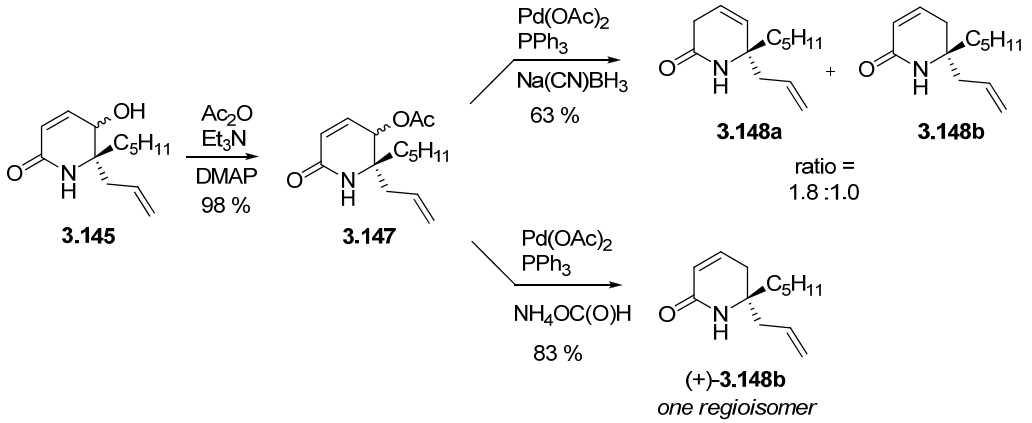
The yield of the deprotection/reduction sequence was moderate and difficult to reproduce, and this was traced back to the $CeCl_3$-$7H_2O$. Using anhydrous $CeCl_3$ in the one-pot reduction protocol reliably delivered compound **3.145** in a significantly-improved 71 % yield (dr = 1.1-1.3 : 1.0). Another 21 % of **3.146** (dr = 1.1 : 1.0) could also be isolated, resulting from 1,4- followed by 1,2-hydride addition (Scheme 3.40).

Scheme 3.40. Luche Reduction with Anhydrous $CeCl_3$



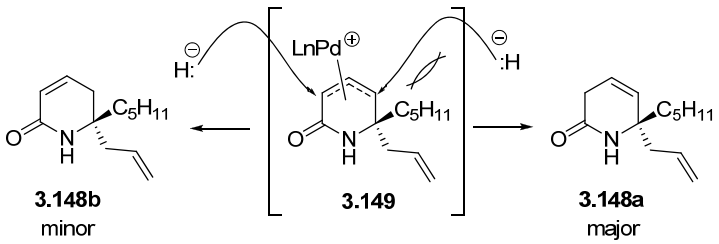
Acylation of allylic alcohols **3.145** provided the corresponding acetates in 98 % yield. Hydrogenolysis of the allylic acetates of **3.147** with $Pd(OAc)_2$, PPh_3, and $Na(CN)BH_3$ in refluxing THF was carried out and a 1.8 : 1.0 mixture of regioisomeric alkenes was obtained in approximately 63 % yield, containing a small quantity of an inseparable impurity (Scheme 3.41).

Scheme 3.41. Acylation and Allylic Hydrogenolysis



The major product **3.148a** resulted from hydride addition to the end of the Pd-allyl of intermediate **3.149** furthest from the sterically-congested quaternary center (Scheme 3.42).

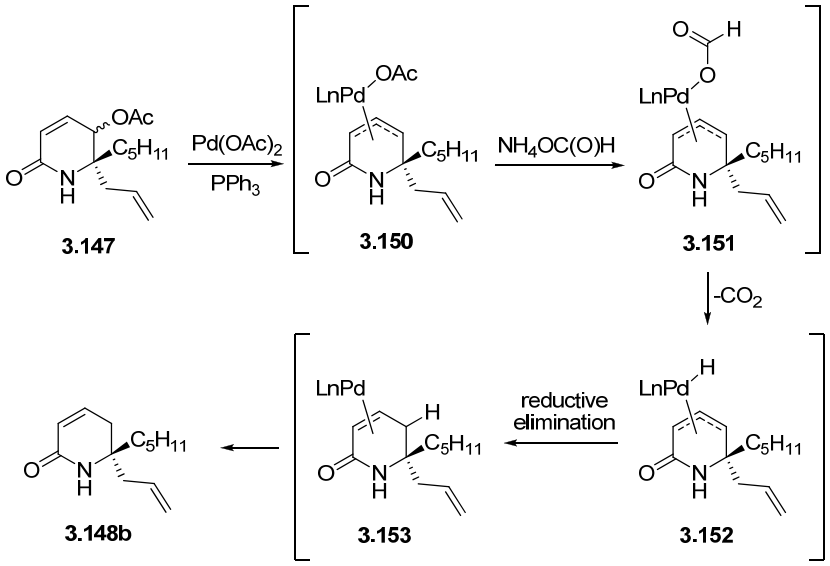
Scheme 3.42. Hydride Addition to Pd-allyl



Using ammonium formate as the hydride source,[145] a single alkene isomer **3.148b** was obtained in 83 % yield. The mechanism of this reaction again begins with oxidative addition of allylic acetate **3.147** to Pd(0). Exchanging the acetate ligand for a formate on palladium, and elimination of CO_2 leads to palladium hydride **3.152**. Reductive elimination and decomplexation of PdL_n affords the α,β-unsaturated lactam **3.148b**. Two factors are likely responsible for the regio-outcome of this reaction: 1) the η^3-allyl palladium intermediate **3.152** likely tips away from the sterically-bulky quaternary center giving the intermediate an enhanced degree of α,β-unsaturated lactam character before the reductive elimination, and 2) the α,β-unsaturated lactam **3.148b** is thermodynamically more stable then the regioisomeric alkene **3.148a** that would result from reductive elimination of the hydride to the opposite end of the palladium allyl.

[145] Tsuji, J.; Yamakawa, T. *Tetrahedrdon Lett.* **1979**, *7*, 613-616.

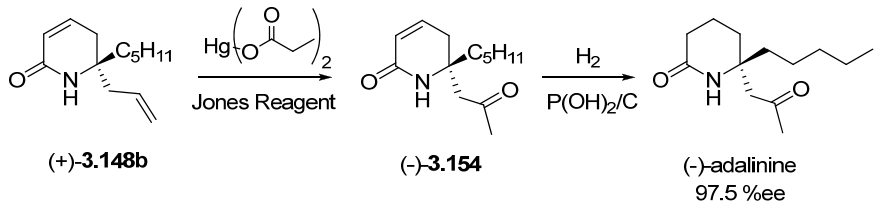
Scheme 3.43. Ammonium Formate Hydrogenolysis Mechanism



To finish the synthesis of adalinine, oxidation of terminal alkene **3.148b** to the corresponding methyl ketone **3.154** was carried out (Scheme 3.44). Wacker oxidation provided the desired product in low yield, accompanied by several byproducts. Alternatively, an oxymercuration/oxidation protocol developed by Whitesides[146] and employing mercury(II) propionate/Jones reagent delivered **3.154** as the sole product of the reaction in 68 %. Hydrogenation of the alkene in **3.154** afforded (-)-adalinine (88 % yield, 97.5 % ee), whose spectral data matched that reported for the natural product, $[\alpha]_D^{25}$ = -22.1 (*c* 0.92, CH_2Cl_2), [lit. $[\alpha]_{579}^{20}$ -26 (*c* 0.13, CH_2Cl_2)].

[146] Rogers, H. R.; McDermott, J. X.; Whitesides, G. M. *J. Org. Chem.* **1975**, *40*, 3577-3580.

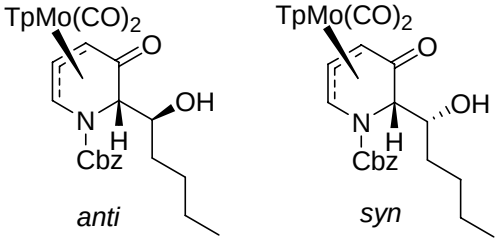
Scheme 3.44. Finishing the Synthesis of (-)-Adalinine



In conclusion, asymmetric syntheses of (-)-adaline and (-)-adalinine have been carried out using a common quaternary-center-bearing intermediate **3.108**, derived from enantiomerically-enriched 5-oxo-η^3-allylmolybdenum pyridinyl complex (-)-**1.5**. The synthesis of (-)-adalinine highlights the synthetic utility of the semipinacol rearrangement and also employs an oxidative demetalation protocol previously developed by the Liebeskind group. The synthesis of (-)-adaline showcases the power of coupling the semipinacol rearrangement and 1,5-Michael-like reaction to access quaternary-center-bearing bicyclic compounds. Key to finishing both syntheses were deoxygenation protocols: Barton-McCombie dehydroxylation for (-)-adaline and Pd-catalyzed hydrogenolysis of an allylic acetate for (-)-adalinine.

Experimental Section:

General Methods: Refer to Chapter One.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-1-(benzyloxycarbonyl)-6-(1-hydroxypentyl)-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-3.112; and (-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-1-(benzyloxycarbonyl)-6-(1-hydroxypentyl)-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (-)-3.112. Molybdenum complex (±)-**1.5** (10.0 g, 16.8 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (125 mL), and Et_3N (3.17 mL, 22.8 mmol, 1.4 equiv) and TBSOTf (5.02 mL, 21.8 mmol, 1.3 equiv) were added successively. The reaction mixture was stirred at room temperature for 30 minutes before it was cooled to -78 ^oC and a pre-mixed solution of $TiCl_4$ (21.8 mL, 21.8 mmol, 1.0 M in CH_2Cl_2, 1.3 equiv) and valeraldehyde (2.50 mL, 23.5 mmol, 1.4 equiv) in CH_2Cl_2 (10 mL) at -78 ^oC was added *via* cannula. The mixture was stirred for 15 minutes at -78 ^oC before it was quenched with 5 mL of aqueous NH_4Cl and warmed to room temperature. The solution was transferred to a separatory funnel containing 150 mL of water. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes-

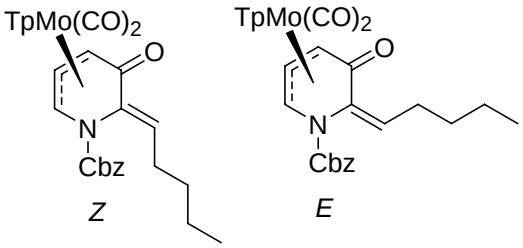
EtOAc (4:1). Overlapping fractions were subjected to a second chromatography under the same conditions, affording (±)-*anti*-**3.112** (6.47 g, 9.49 mmol, 57 %), (±)-*syn*-**3.112** (808 mg, 1.19 mmol, 7 %), and recovered (±)-**1.5** (1.11 g, 1.87 mmol, 11 %), all orange solids.

Similar treatment of complex (-)-**1.5** (11.9 g, 20.0 mmol, 1.0 equiv, 97.5 %ee) in CH_2Cl_2 (200 mL) with Et_3N (3.77 mL, 27.2 mmol, 1.4 equiv) and TBSOTf (5.98 mL, 26.0 mmol, 1.3 equiv), and then with $TiCl_4$ (1.0 M in CH_2Cl_2, 26.0 mL, 26.0 mmol, 1.3 equiv) and valeraldehyde (2.98 mL, 28.0 mmol, 1.4 equiv) in CH_2Cl_2 (10 mL), afforded (-)-*anti*-**3.112** (9.55 g, 14.0 mmol, 70 %, 97.3 %ee) $[[\alpha]_D^{25}$ -566 (*c* 0.12, $CH_2Cl_2)]$. Additionally, *syn*-**3.112** and (-)-**1.5** were collected together (1.98 g, HPLC ratio = 8:92).

(±)-*Anti*-**3.112**: TLC: R_f = 0.67 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3459 (br m), 3123 (w), 2957 (m), 2486 (m), 1969 (s), 1864 (s), 1702 (s), 1664 (s), 1505 (m), 1409 (s). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 2.0 Hz, 0.4 H), 8.40 (d, *J* = 1.6 Hz, 0.6 H), 8.36 (d, *J* = 1.6 Hz, 0.4 H), 7.68 (d, *J* = 2.0 Hz, 0.6 H), 7.64 (d, *J* = 1.6 Hz, 1.0 H), 7.63 (d, *J* = 2.0 Hz, 0.4 H), 7.60 (d, *J* = 2.0 Hz, 0.4 H), 7.57 (d, *J* = 2.0 Hz, 0.6 H), 7.48-7.51 (m, 2.8 H), 7.40-7.42 (m, 2.2 H), 7.31-7.37 (m, 2.0 H), 7.15 (dd, *J* = 6.4 Hz, 1.6 Hz, 0.6 H), 6.25-6.28 (m, 1.4 H), 6.18-6.21 (m, 1.0 H), 5.76 (t, *J* = 2.0 Hz, 0.6 H), 5.13-5.29 (m, 2.0 H), 4.81 (dd, *J* = 6.0 Hz, 2.0 Hz, 0.4 H), 4.77 (dd, *J* = 5.6 Hz, 1.6 Hz, 0.6 H), 4.04-4.10 (m, 1.0 H), 3.87-3.94 (m, 1.0 H), 3.85 (d, *J* = 2.4 Hz, 0.6 H), 3.60 (d, *J* = 2.4 Hz, 0.4 H), 2.97 (br s, 0.6 H), 1.98 (br s, 0.4 H), 1.48-1.72 (m, 2.0 H), 1.15-1.43 (m, 4.0 H), 0.91 (t, *J* = 7.2 Hz, 1.8 H), 0.81 (t, *J* = 7.2 Hz, 1.2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 226.0, 225.0, 222.7, 221.9, 195.4, 195.3, 155.7, 154.9, 147.6, 147.5, 146.1, 144.6, 140.6, 140.3, 136.7, 136.5, 136.4, 136.3, 129.8, 129.0, 128.8, 128.7, 128.6,

106.4, 106.3, 106.0, 99.5, 96.1, 75.5, 75.4, 69.8, 68.9, 66.0, 64.8, 62.8, 62.3, 60.9, 60.2, 33.4, 32.9, 28.3, 28.2, 22.8, 22.6, 14.2, 14.1. HRMS (ESI) Calcd for $C_{29}H_{33}BMoN_7O_6$ ($[M+H]^+$): 684.1634. Found: 684.1656. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-(-)-*anti*-**3.112**: t_S = 9.16 min; (*R*)-(+)-*anti*-**3.112**: t_R = 8.44 min.

(±)-*Syn*-**3.112**: TLC: R_f = 0.75 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3459 (br), 2957 (m), 1969 (s), 1868 (s), 1710 (s), 1664 (m), 1505 (m), 1455 (w). ^1H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 1.6 Hz, 0.6 H), 8.41 (d, *J* = 2.0 Hz, 0.4 H), 8.36 (d, *J* = 1.6 Hz, 0.6 H), 7.70 (d, *J* = 1.6 Hz, 0.4 H), 7.67 (d, *J* = 1.6 Hz, 0.6 H), 7.63 (d, *J* = 2.0 Hz, 1.0 H), 7.61 (d, *J* = 2.4 Hz, 0.6 H), 7.58 (d, *J* = 2.4 Hz, 0.4 H), 7.48-7.52 (m, 2.2 H), 7.40-7.42 (m, 1.8 H), 7.29-7.36 (m, 3.0 H), 7.17 (d, *J* = 6.4 H, 0.4 H), 6.26-6.28 (m, 1.5 H), 6.22 (br s, 0.6 H), 6.20 (br s, 0.5 H), 5.79 (br s, 0.4 H), 5.19-5.31 (m, 2.0 H), 4.77 (t, *J* = 6.0 Hz, 1.0 H), 4.06 (t, *J* = 6.0 Hz, 0.6 H), 4.00 (br s, 0.4 H), 3.93 (t, *J* = 6.0 Hz, 1.0 H), 3.77 (d, *J* = 5.2 Hz, 0.4 H), 3.68 (d, *J* = 4.4 Hz, 0.6 H), 3.13 (d, *J* = 9.6 Hz, 0.6 H), 3.01 (d, *J* = 9.6 Hz, 0.4 H), 1.45-1.67 (m, 2.0 Hz), 1.23-1.37 (m, 4.0 H), 0.84-0.95 (m, 3.0 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.6, 225.0, 222.7, 221.5, 198.1, 197.6, 154.9, 154.2, 147.1, 147.0, 145.6, 144.2, 140.6, 140.3, 136.5, 136.4, 136.3, 136.2, 135.2, 134.9 (2), 134.7, 129.4, 128.7, 128.4, 128.2, 128.0, 106.1, 105.8, 105.7, 99.4, 96.2, 73.0, 72.6, 69.3, 68.4, 65.6, 64.8, 61.2, 61.1, 60.7, 59.8, 32.8, 32.5, 28.3, 28.2, 22.5, 22.4, 14.0, 13.9. HRMS (ESI) Calcd for $C_{29}H_{33}BMoN_7O_6$ ($[M+H]^+$): 684.1634. Found: 684.1663.



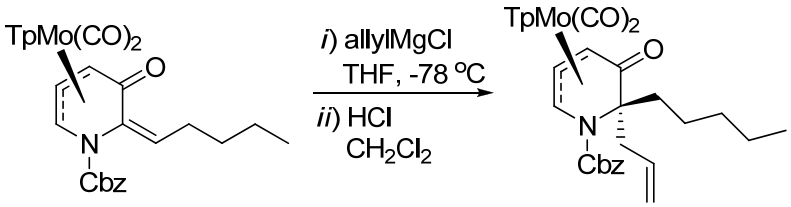
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-1-(benzyloxycarbonyl)-5-oxo-6-pentylene-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-3.110; and (-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-1-(benzyloxycarbonyl)-5-oxo-6-pentylene-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (-)-3.110. To a solution of (±)-*anti*-**3.112** (133 mg, 0.19 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added DMAP (11.9 mg, 0.098 mmol, 0.5 equiv), Et_3N (40.8 μL, 0.29 mmol, 1.5 equiv), and methanesulfonyl chloride (20.7 μL, 0.25 mmol, 1.3 equiv). The reaction mixture was stirred 1 h at room temperature and then passed through a short pad of silica gel with hexanes-EtOAc (1:1). The solvents were completely removed on a rotary evaporator, the residue was dissolved in CH_2Cl_2 (5 mL), and DBU (22.5 μL, 0.15 mmol, 0.8 equiv) was slowly added *via* syringe. The reaction mixture was stirred overnight at room temperature. HPLC analysis of the reaction mixture showed a ratio of *E*-(±)-**3.110a**/*Z*-(±)-**3.110b**/(±)-**3.110c** = 79:4:17 (HPLC yield: 89%). Careful chromatography provided pure *Z*-(±)-**3.110b**, while *E*-(±)-**3.110a** and (±)-**3.110c** could not be separated.

Similarly, (-)-*anti*-**3.112** (5.01 g, 7.35 mmol, 1.0 equiv, 97.3 %ee) was dissolved in CH_2Cl_2 (100 mL) and DMAP (449 mg, 3.68 mmol, 0.5 equiv), Et_3N (1.53 mL, 11.0 mmol, 1.5 equiv), and methanesulfonyl chloride (0.75 mL, 9.56 mmol, 1.3 equiv) were added in succession. After 2 hours, the solution was passed through a short pad of silica gel (100 % ethyl acetate) and concentrated. The residue was dissolved in CH_2Cl_2 (100

mL), the solution was cooled to 0 ^{o}C, and DBU (1.10 mL, 7.35 mmol, 1.0 equiv) was added dropwise. The solution was warmed to room temperature and stirred 16 hours before it was poured into H_2O (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 X 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *Z*-(-)-**3.110b** (259 mg, 0.39 mmol, 5 %) $[[\alpha]_D^{25}$ -370 (*c* 0.090, CH_2Cl_2)], and an 83:17 mixture of *E*-(-)-**3.110a**/**3.110c** (3.36 g, 5.06 mmol, 69 %, 97.8 %ee) $[[\alpha]_D^{25}$ -775 (*c* 0.16, CH_2Cl_2)].

E-(±)-**3.110a**: TLC: R_f = 0.57 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1969 (s), 1876 (s), 1710 (s), 1660 (s), 1602 (m), 1505 (m), 1467 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 2.0 Hz, 1 H), 7.72 (d, *J* = 2.4 Hz, 1 H), 7.58 (d, *J* = 2.0 Hz, 1 H), 7.55 (br s, 1 H), 7.49 (d, *J* = 2.4 Hz, 1 H), 7.42 (br s, 2 H), 7.37-7.41 (m, 4 H), 7.24 (br s, 1 H), 6.48 (br s, 1 H), 6.27 (t, *J* = 2.4 Hz, 1 H), 6.20 (t, *J* = 2.0 Hz, 1 H), 5.97 (br s, 1 H), 5.24 (s, 2 H), 4.80 (dd, *J* = 6.0 Hz, 2.4 Hz, 1 H), 3.98 (br s, 1 H), 2.54-2.68 (m, 2 H), 1.25-1.44 (m, 4 H), 0.88 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.1, 223.0, 187.7, 153.9, 147.3, 144.1, 140.9, 136.5, 136.3, 135.3, 135.1, 134.8, 129.0, 128.8 (3), 128.7, 128.1, 106.3, 106.0, 105.8, 92.0, 69.0, 65.7, 65.0, 32.0, 28.3, 22.5, 14.1. HRMS (ESI) Calcd for $C_{29}H_{31}BMoN_7O_5$ ($[M+H]^+$): 666.1528. Found: 666.1550. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-(-)-*E*-**3.110a**: t_S = 15.36 min; (*R*)-(+)-*E*-**3.110a**: t_R = 14.36 min; unconjugated alkene-**3.110c**: t_C = 16.41 min.

Z-(±)-**3.110b**: TLC: R_f = 0.54 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1969 (s), 1880 (s), 1702 (s), 1668 (s), 1613 (m), 1505 (m), 1455 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.2 Hz, 1 H), 7.77 (d, *J* = 1.6 Hz, 1 H), 7.58-7.59 (m, 2 H), 7.50 (d, *J* = 2.0 Hz, 1 H), 7.34-7.43 (m, 6 H), 7.21 (br s, 1 H), 6.28 (br s, 1 H), 6.25 (t, *J* = 6.8 Hz, 1 H), 6.20 (br s, 1 H), 6.15 (br s, 1 H), 5.22 (br s, 2 H), 4.82 (dd, *J* = 6.4 Hz, 2.0 Hz, 1 H), 4.25 (br s, 1 H), 1.68-2.00 (m, 2 H), 1.18-1.38 (m, 4 H), 0.84 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.4, 223.7, 186.8, 147.4, 143.3, 142.0, 136.5, 136.4, 135.3, 134.9, 130.6, 130.1, 128.9 (2), 128.8, 128.7 (2), 128.6, 106.4, 106.1, 105.9, 88.8, 68.9, 68.2 (2), 30.8, 29.9, 22.6, 14.0. HRMS (ESI) Calcd for $C_{29}H_{31}BMoN_7O_5$ ($[M+H]^+$): 666.1528. Found: 666.1498.



E-**3.110a** **3.108**

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-allyl-1-(benzyloxycarbonyl)-5-oxo-6-pentyl-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-3.108; and (-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-allyl-1-(benzyloxycarbonyl)-5-oxo-6-pentyl-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (-)-3.108. *E*-(±)-**3.110a/3.110c** (approx. 83:17) (7.97 g, 12.0 mmol, 1.0 equiv) was dissolved in THF (100 mL) and cooled to -78 °C. AllylMgCl (2.0 M in THF, 12.0 mL, 24.0 mmol, 2.0 equiv) was added dropwise. After 15 minutes, and then again after 25 minutes, 0.2 equiv of additional allylMgBr (2.4 mmol, 1.2 mL) was added, consuming

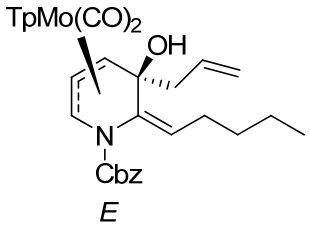
the remainder of *E*-(±)-**3.110a**. After 10 minutes, aqueous saturated NH_4Cl (5 mL) was added, and the solution warmed to room temperature and poured into H_2O (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and HCl (3.3 mL, 13.2 mmol, 4.0 M in dioxane, 1.1 equiv) was added dropwise at room temperature. After 55 minutes, the solution was poured into H_2O (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1), affording (±)-**3.108** (6.63g, 9.4 mmol, 78 %) as an orange solid.

Similar treatment of *E*-(-)-**3.110a/3.110c** (approx. 83:17) (6.46 g, 9.74 mmol, 1.0 equiv, 97.8 %ee) in THF (100 mL) with allylMgBr (1.0 M in Et_2O, 21.4 mL, 21.4 mmol, 2.2 equiv) and then HCl (4.0 M in dioxane, 2.68 mL, 10.7 mmol, 1.1 equiv) in CH_2Cl_2 (100 mL) afforded (-)-**3.108** (5.31 g, 7.53 mmol, 77 %, 97.7 %ee) $[[\alpha]_D^{25}$ -437 (*c* 0.15, $CH_2Cl_2)]$.

(±)-**3.108**: TLC: R_f = 0.52 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2957 (m), 2486 (m), 1969 (s), 1884 (s), 1710 (s), 1664 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 2.0 Hz, 1 H), 7.80 (d, *J* = 2.4 Hz, 1 H), 7.48-7.59 (m, 5 H), 7.38 (br s, 5 H), 7.17 (br s, 1 H), 6.27 (t, *J* = 2.4 Hz, 1 H), 6.20 (t, *J* = 2.4 Hz, 1 H), 5.85 (br s, 1 H), 5.14-5.25 (m, 2 H), 5.02-5.10 (m, 2 H), 4.66 (dd, *J* = 6.0 Hz, 2.0 Hz, 1 H), 3.79 (br s, 1 H), 2.77 (br s, 1 H), 2.56 (br s, 1 H), 2.26 (br s, 2 H), 1.18-1.32 (m, 6 H), 0.88 (br s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 224.8, 223.7, 199.8, (156.2), 153.3, 147.1, (143.5), 143.0, 141.3, 136.5 (2),

135.7, 134.8, 133.5, 129.2, 128.8 (2), 128.6 (2), 118.4, 106.2, 105.9, 105.7, (92.5), 91.7, 69.0, 68.6, (63.2), 62.4 (2), (43.7), 42.7, (35.4), 33.9, 32.1, 23.9, 22.5, 14.1. HRMS (ESI) Calcd for $C_{32}H_{37}BMoN_7O_5$ ($[M+H]^+$): 708.1998. Found: 708.1993. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-(-)-**3.108**: t_S = 14.26 min; (*R*)-(+)-**3.108**: t_R = 14.91 min.

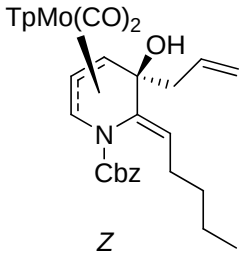
Intermediate allylic alcohol *E*-(-)-**3.109**, containing an inseparable impurity, could be isolated and characterized:



***E*-(-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-5-allyl-1-(benzyloxycarbonyl)-5-hydroxy-6-pentylene-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, *E*-(-)-3.109**. *E*-(-)-**3.110a/3.110c** (approx. 83:17) (194 mg, 0.29 mmol, 1.0 equiv, 97.8 %ee) was dissolved in THF (5 mL) and cooled to -78 °C. AllylMgBr (1.0 M in Et_2O, 0.32 mL, 0.32 mmol, 1.1 equiv) was added dropwise. After 15 minutes, an additional 1.1 equiv of allylMgBr was added. After an additional 15 minutes, 1 mL of H_2O was added and the reaction mixture was warmed to room temperature. The solution was poured into a separatory funnel containing H_2O (10 mL) and CH_2Cl_2 (10 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 X 5 mL), dried over $MgSO_4$, filtered and concentrated. Flash chromatography over silica gel with

hexanes-EtOAc (4:1) afforded *E*-(-)-**3.109** (188 mg, 0.27 mmol, 92 %, 97.7 %ee) [$[\alpha]_D^{25}$ -115 (*c* 0.40, CH_2Cl_2)], containing 12 % impurity by HPLC, as a yellow solid.

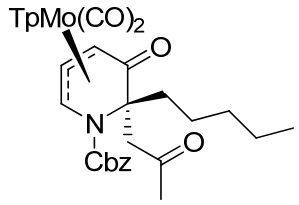
E-(-)-**3.109**: TLC: R_f = 0.49 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3601 (m), 3474 (br w), 3123 (w), 2957 (w), 2930 (m), 2860 (w), 2482 (m), 1945 (s), 1845 (s), 1687 (s), 1505 (w), 1455 (w), 1409 (s), 1293 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.6 Hz, 1 H), 7.86 (d, *J* = 1.9 Hz, 1 H), 7.84 (br s, 1 H), 7.55 (d, *J* = 2.2 Hz, 2 H), 7.47 (d, *J* = 2.5 Hz, 1 H), 7.31-7.36 (m, 5 H), 6.97 (br s, 1 H), 6.26 (t, *J* = 2.2 Hz, 1 H), 6.17 (t, *J* = 2.2 Hz, 1 H), 6.16 (br s, 1 H), 5.85-5.95 (m, 1 H), 5.20-5.29 (m, 3 H), 5.07-5.11 (m, 2 H), 4.60 (dd, *J* = 7.3 Hz, *J* = 2.5 Hz, 1 H), 3.53-3.55 (m, 1 H), 3.20 (s, 1 H), 2.31-2.59 (m, 4 H), 1.10-1.30 (br s, 4 H), 0.81 (br s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 231.8, 224.4, 147.1 (2), 142.9, 142.1, 136.3, 136.1, 134.6, 133.9, 133.0, 128.6 (2), 128.3, 128.2 (2), 127.1, 118.6, 106.2, 105.8, 105.6, 83.3, 78.2, 68.1, 60.1, 49.9, 32.4, 26.9, 22.4, 14.2. HRMS (ESI) Calcd for $C_{32}H_{37}BMoN_7O_5$ ($[M+H]^+$): 708.1998. Found: 708.2029. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-(-)-*E*-**3.109**: t_S = 15.90 min; (*R*)-(+)-*E*-**3.109**: t_R = 15.17 min.



***Z*-(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(η-2,3,4)-5-allyl-1-(benzyloxycarbonyl)-5-hydroxy-6-pentylene-5,6-dihydro-2*H*-pyridin-2-**

yl]molybdenum, *Z*-(±)-3.109. *Z*-(±)-**3.110b** (108 mg, 0.16 mmol, 1.0 equiv) was dissolved in THF (10 mL) and cooled to -78 ^{o}C. AllylMgBr (1.0 M in Et_2O, 0.33 mL, 0.33 mmol, 2.0 equiv) was added. After 5 minutes, 1 mL of saturated aq. NH_4Cl and the reaction mixture was warmed to room temperature. The solution was poured into H_2O (20 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1, then 2:1) afforded *Z*-(±)-**3.109** (104 mg, 0.15 mmol, 93 %) as a yellow solid.

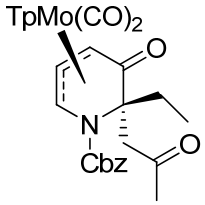
Z-(±)-**3.109**: TLC: R_f = 0.48 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3466 (br w), 2930 (m), 1949 (s), 1872 (s), 1853 (s), 1691 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (br s, 1 H), 7.91 (d, *J* = 2.0 Hz, 1 H), 7.89 (br s, 1 H), 7.57 (t, *J* = 2.0 Hz, 2 H), 7.49 (d, *J* = 2.4 Hz, 1 H), 7.30-7.40 (m, 5 H), 6.89-6.93 (m, 1 H), 6.28 (t, *J* = 2.4 Hz, 1 H), 6.21 (br s, 1 H), 6.19 (t, *J* = 1.6 Hz, 1 H), 5.78-5.95 (m, 1 H), 5.24-5.34 (m, 2 H), 5.04-5.16 (m, 3 H), 4.60-4.68 (m, 1 H), 3.54-3.68 (m, 1 H), 3.05 (s, 1 H), 2.58 (dd, *J* = 13.6 Hz, 8.4 Hz, 1 H), 2.41-2.48 (m, 1 H), 1.82-1.98 (m, 1 H), 1.62-1.73 (m, 1 H), 1.23-1.43 (m, 4 H), 0.82-0.93 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 231.3, 224.8, 155.7, 147.0, 143.2, 141.9, 136.3, 136.1, 134.7, 134.6, 134.0, 128.6 (2), 128.4, 128.3, 127.7, 121.1, 118.4, 106.2, 105.8, 105.6, 83.4, 83.1, 76.2, 68.2, 61.1, 49.6, 31.3, 28.5, 22.8, 14.2. HRMS (ESI) Calcd for $C_{32}H_{37}BMoN_7O_5$ ($[M+H]^+$): 708.1997. Found: 708.1994.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-1-(benzyloxycarbonyl)-5-oxo-6-(2-oxopropyl)-6-pentyl-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-3.114; and (-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-acetonyl-1-(benzyloxycarbonyl)-5-oxo-6-pentyl-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (-)-3.114. Terminal alkene complex (±)-**3.108** (1.0 g, 1.42 mmol, 1.0 equiv) was dissolved in DMF (40 mL) and H_2O (2 mL), $PdCl_2$ (101 mg, 0.57 mmol, 0.4 equiv), and CuCl (70 mg, 0.71 mmol, 0.5 equiv) were added in succession. The reaction was stirred open to air for 38 hours and then poured into CH_2Cl_2 (100 mL). The layers were separated and the organic layer was washed with brine (3 X 100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford (±)-**3.114** (710 mg, 0.98 mmol, 69 %) as an orange solid. Some starting material (±)-**3.108** was recovered but not quantified.

Similar treatment of (-)-**3.108** (1.50 g, 2.13 mmol, 1.0 equiv) with $PdCl_2$ (151 mg, 0.85 mmol, 0.4 equiv) and CuCl (106 mg, 1.07 mmol, 0.5 equiv) in DMF (50 mL)/H_2O (2.5 mL) was carried out in triplicate. After 74 hours, the three reactions were combined and purified as described for the racemate above. (-)-**3.114** was obtained (4.3 g, 5.96 mmol, 93 %) [$[\alpha]_D^{25}$ -434 (*c* 0.095, CH_2Cl_2)] along with recovered (-)-**3.108** (98 mg, 0.14 mmol, 6 %).

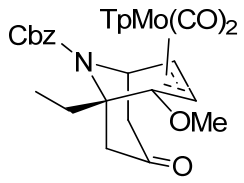
(±)-**3.114**: TLC: R_f = 0.49 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2926 (s), 1965 (s), 1880 (s), 1710 (s), 1668 (m). ^1H NMR (600 MHz, $CDCl_3$): δ 8.47 (br s, 0.9 H), 8.29 (br s, 0.1 H), 7.79 (d, *J* = 1.8 Hz, 0.9 H), 7.77 (br s, 0.1 H), 7.57-7.64 (m, 1.2 H), 7.45-7.54 (m, 4.4 H), 7.35-7.42 (m, 3.4 H), 7.21 (d, *J* = 5.4 Hz, 1 H), 6.27 (t, *J* = 2.4 Hz, 1 H), 6.19 (br s, 1 H), 5.84 (br s, 1 H), 5.28-5.30 (m, 0.4 H), 5.18 (AB quartet, *J* = 11.4 Hz, 1.6 H), 4.63 (d, *J* = 4.8 Hz, 1 H), 4.03-4.07 (br s, 0.2 H), 3.96 (t, *J* = 6.0 Hz, 0.8 H), 3.65 (d, *J* = 16.2 Hz, 1 H), 3.11 (d, *J* = 16.2 Hz, 0.8 H), 2.92 (d, *J* = 14.4 Hz, 0.2 H), 2.30 (dt, *J* = 13.8 Hz, 4.2 Hz, 1 H), 2.13 (s, 2.4 H), 1.99 (s, 0.6 H), 1.65 (dt, *J* = 12.6 Hz, 4.2 Hz, 1.2 H), 1.44-1.60 (m, 0.8 H), 1.16-1.36 (m, 4.6 H), 0.96-1.06 (br s, 0.4 H), 0.80-0.90 (t + br s, *J* = 7.2 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 225.1, 224.1, 206.3, 201.4, 153.4, 146.9, 142.6, 141.2, 136.3, 136.2, 135.3, 134.5, 128.9, 128.6 (3), 128.4, 106.0, 105.6, 105.5, 90.5, 68.5, 65.1, 62.9, 62.0, 49.1, 35.8, 31.9, 31.0, 24.4, 22.4, 13.9. HRMS (ESI) Calcd for: $C_{32}H_{37}BMoN_7O_6$ ($[M+H]^+$): 724.1947. Found: 724.1939.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-1-(benzyloxycarbonyl)-6-ethyl-5-oxo-6-(2-oxopropyl)-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-3.114. Terminal alkene (±)-**3.108** (194 mg, 0.29 mmol, 1.0 equiv) was completely dissolved in DMF (5 mL), and to this solution was added $PdCl_2$ (20.7 mg, 0.12 mmol, 0.4 equiv), CuCl (14.5 mg, 0.15 mmol, 0.5 equiv) and H_2O (0.5 mL). The mixture was stirred open to air for 24 hours and then poured into a separatory funnel

containing CH_2Cl_2 (10 mL) and 10 mL of H_2O. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were washed with H_2O (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford (±)-**3.114** (168 mg, 0.25 mmol, 85%) and the recovered starting material (±)-**3.108** (15 mg, 8%).

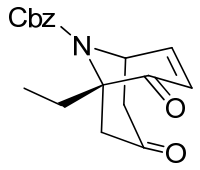
(±)-**3.114**: TLC: R_f = 0.49 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3127 (w), 2968 (w), 2486 (m), 1961 (s), 1876 (s), 1702 (s), 1664 (s), 1505 (m), 1409 (m), 1301 (s), 1254 (s), 1220 (s), 1127 (m), 1054 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.9 Hz, 1 H), 7.81 (d, *J* = 2.2 Hz, 1 H), 7.59 (d, *J* = 1.9 Hz, 1 H), 7.53 (br s, 2 H), 7.47-7.49 (m, 3 H), 7.39-7.41 (m, 3 H), 7.22-7.23 (m, 1 H), 6.29 (t, *J* = 2.2 Hz, 1 H), 6.21 (t, *J* = 1.9 Hz, 1 H), 5.87 (br s, 1 H), 5.18-5.19 (m, 2 H), 4.65 (d, *J* = 4.4 Hz, 1 H), 3.98 (d, *J* = 4.0 Hz, 1 H), 3.61 (d, *J* = 15.9 Hz, 1 H), 3.12 (d, *J* = 16.2 Hz, 1 H), 2.41 (qd, *J* = 14.0 Hz, 7.6 Hz, 1 H), 2.16 (s, 3 H), 1.79 (qd, *J* = 14.0 Hz, 7.3 Hz, 1 H), 1.26-1.31 (m, 2 H), 0.93 (t, *J* = 7.0 Hz, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 225.2, 224.4, 206.6, 201.4, 153.8, 147.2, 143.0, 141.6, 136.6, 136.5, 135.6, 134.8, 129.2, 128.9 (3), 128.7, 106.3, 105.9, 105.8, 90.8, 68.8, 65.7, 63.2, 62.4, 49.2, 31.4, 29.2, 9.97. HRMS (ESI) Calcd for $C_{29}H_{31}BMoN_7O_6$ ($[M+H]^+$): 682.1499. Found: 682.1499.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*S*,2*S*,5*R*)-(η^3-2,3,4)-9-benzyloxycarbonyl-1-ethyl-2-methoxy-7-oxo-9-azabicyclo[3.3.1]non-3-en-2-yl]molybdenum, (±)-3.117. To a solution of (±)-**3.115** (270 mg, 0.40 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was added $KOSiMe_3$ (153 mg, 1.19 mmol, 3.0 equiv). The reaction mixture was stirred at room temperature for 10 min and then Me_3OBF_4 (158 mg, 1.11 mmol, 2.8 equiv) was added. The reaction mixture was stirred at room temperature overnight and then passed through a short pad of silica gel. The solvents were completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (4:1) to afford (±)-**3.117** (245 mg, 0.35 mmol, 89%) as an orange solid.

(±)-**3.117**: TLC: R_f = 0.45 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3127 (w), 2926 (m), 2482 (w), 1930 (s), 1837 (s), 1710 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1119 (s), 1073 (s), 1050 (s). ^{1}H NMR (600MHz, $CDCl_3$): δ 8.35 (d, *J* = 1.9 Hz, 1 H), 7.81 (d, *J* = 1.4 Hz, 1 H), 7.64 (d, *J* = 2.4 Hz, 1 H), 7.60 (d, *J* = 21.9 Hz, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 7.46 (d, *J* = 1.4 Hz, 1 H), 7.43 (d, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 7.1 Hz, 1 H), 6.24 (t, *J* = 1.9 Hz, 1 H), 6.21 (t, *J* = 1.9 Hz, 1 H), 6.20 (t, *J* = 1.9 Hz, 1 H), 5.21 (AB quartet, *J* = 12.4 Hz, 2 H), 5.02-5.04 (m, 1 H), 3.95 (dd, *J* = 8.1 Hz, 2.8 Hz, 1 H), 3.55 (d, *J* = 8.1 Hz, 1 H), 2.95 (qd, *J* = 15.2 Hz, 7.6 Hz, 1 H), 2.89 (d, *J* = 14.8 Hz, 1 H), 2.82 (s, 3 H), 2.59-2.67 (m, 4 H), 1.11 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 230.0, 227.9, 208.9, 154.7, 146.3, 145.1, 142.8, 139.5, 136.54, 136.51, 135.9,

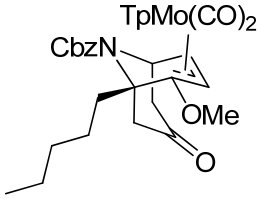
134.8, 128.6 (2), 128.27 (2), 128.22, 105.9, 105.78, 105.76, 67.7, 65.7, 57.8, 57.4, 55.5, 53.8, 50.5, 49.2, 25.4, 11.5. HRMS (ESI) Calcd for $C_{30}H_{32}BMoN_7O_6$ ($[M]^+$): 695.1561. Found: 695.1589.



(±)-(1*S*,5*R*)-9-Benzyloxycarbonyl-1-ethyl-7-oxo-9-azabicyclo[3.3.1]non-3-en-2-one, (±)-3.118. To an orange solution of molybdenum complex (±)-**3.117** (259 g, 0.37 mmol, 1.0 equiv) and Et_3N (78.2 μL, 0.56 mmol, 1.5 equiv) in a 3:2 mixture of THF/H_2O (25 mL) at 0 °C open to air was added a solution of CAN (1.64 g, 2.99 mmol, 8.0 equiv) in H_2O (5 mL) dropwise over 5 min. After complete addition, the color of the solution had faded to a light yellow. The reaction mixture was warmed to room temperature and stirred for an additional 10 min, before it was partitioned between CH_2Cl_2 (10 mL) and water (10 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford (±)-**3.118** (79 mg, 0.25 mmol, 68%) as a colorless oil.

(±)-**3.118**: TLC: R_f = 0.50 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 2968 (m), 2941 (m), 2482 (w), 1718 (s), 1687 (s), 1455 (s), 1397 (s), 1297 (s), 1224 (s), 1123 (m), 1069 (s), 1038 (m). ^1H NMR (600 MHz, $CDCl_3$): δ 7.37-7.47 (m, 5 H), 7.02 (dd, *J* = 10.0 Hz, 6.2 Hz, 1 H), 6.15 (d, *J* = 10.0 Hz, 1 H), 5.46 (dt, *J* = 6.2 Hz, 0.9 Hz, 1 H), 5.22 (AB quartet, *J* = 11.9 Hz, 2 H), 2.69 (the left side of AB quartet, *J* = 15.2 Hz, 1 H), 2.69 (doublets of the left side of AB quartet, *J* = 14.8 Hz, 6.7 Hz, 1 H), 2.56 (qd, *J* = 13.8 Hz, 7.1 Hz, 1 H),

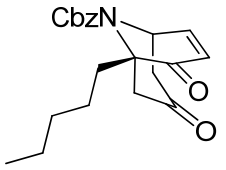
2.40-2.44 (m, 2 H), 2.37 (doublets of the right side of AB quartet, J = 15.2 Hz, 1.9 Hz, 1 H), 0.87 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 204.3, 195.6, 155.1, 148.4, 135.8, 128.9 (2), 128.8, 128.6 (2), 128.1, 71.3, 68.3, 51.6, 51.4, 43.1, 28.4, 8.9. HRMS (ESI) Calcd for $C_{18}H_{19}NO_4$ ([M]$^+$): 313.1314. Found: 313.1316.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*S*,2*S*,5*R*)-(η-2,3,4)-9-benzyloxycarbonyl-1-pentyl-2-methoxy-7-oxo-9-azabicyclo[3.3.1]non-3-en-2-yl]molybdenum, (±)-3.105. Methyl ketone (±)-**3.114** (139 mg, 0.19 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (7 mL) and $KOSiMe_3$ (74 mg, 0.58 mmol, 3.0 equiv) was added. After stirring one hour at room temperature, Me_3OBF_4 (86 mg, 0.58 mmol, 3.0 equiv) was added. The solution was stirred overnight, passed through a short pad of silica gel and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded (±)-**3.105** (102 mg, 0.14 mmol, 73 %) as an orange solid.

(±)-**3.105**: TLC: R_f = 0.40, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2957 (m), 1930 (s), 1841 (s), 1702 (s), 1505 (m), 1455 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 2.0 Hz, 1 H), 7.79 (d, J = 1.6 Hz, 1 H), 7.63 (d, J = 2.4 Hz, 1 H), 7.59 (d, J = 2.0 Hz, 1 H), 7.49 (d, J = 2.0 Hz, 1 H), 7.45 (d, J = 1.6 Hz, 1 H), 7.28-7.42 (m, 5 H), 6.22 (t, J = 2.4 Hz, 1 H), 6.18-6.21 (m, 2 H), 5.19 (AB quartet, J = 12.4 Hz, 2 H), 5.02-5.06 (m, 1 H), 3.94 (dd, J = 8.0 Hz, 3.2 Hz, 1 H), 3.53 (d, J = 8.4 Hz, 1 H), 2.89 (d, J = 14.8 Hz, 1 H), 2.81 (s, 3 H), 2.76-2.86 (m, 1 H), 2.47-2.68 (m, 4 H), 1.18-1.40 (m, 6 H), 0.88 (t, J = 7.6 Hz, 3 H).

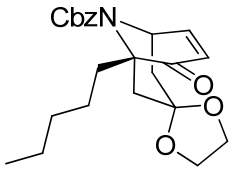
^{13}C NMR (100 MHz, $CDCl_3$): δ 230.0, 227.7, 208.9, 154.8, 146.2, 145.0, 142.8, 139.5, 136.4, 135.9, 134.8, 128.6 (2), 128.3 (2), 128.2, 105.9, 105.7 (2), 67.7, 65.5, 57.7, 57.4, 55.4, 53.7, 51.0, 49.1, 32.5 (2), 26.5, 23.0, 14.3. HRMS (ESI) Calcd for $C_{33}H_{38}BMoN_7O_6$ (M^+): 737.2025. Found: 737.2011.



(±)-(1*S*,5*R*)-9-Benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-one, (±)-3.104; and (-)-(1*S*,5*R*)-9-Benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-one, (-)-3.104. Molybdenum complex (±)-**3.114** (350 mg, 0.50 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10 mL) and $KOSiMe_3$ (191 mg, 1.49 mmol, 3.0 equiv) was added in one portion. The reaction mixture was stirred for 35 minutes, during which time it turned from dull orange to bright red. The mixture was passed through a pad of silica gel and concentrated. The red residue was dissolved in DME (10 mL) and cooled to 0 ^oC before $NOPF_6$ (91.1 mg, 0.50 mmol, 1.0 equiv) was added in one portion causing the solution to bubble and darken to black. After 25 minutes, the crude reaction mixture was passed through a pad of silica gel and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)-**3.104** (142 mg, 0.40 mmol, 80 %, 97.7 %ee) as a clear, light yellow oil.

Similar treatment of (-)-**3.114** (4.14 g, 5.87 mmol, 1.0 equiv) with $KOSiMe_3$ (2.26 g, 17.6 mmol, 3.0 equiv) in CH_2Cl_2 (60 mL) and then $NOPF_6$ (1.07 g, 5.87 mmol, 1.00 equiv) in DMF (60 mL) afforded (-)-**3.104** (1.46 g, 4.12 mmol, 70 %) $[[\alpha]_D^{25}$ -110 (*c* 0.67, CH_2Cl_2)].

(±)-**3.104**: TLC: R_f = 0.30, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2957 (m), 1718 (s), 1687 (s), 1640 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.38 (m, 5 H), 7.01 (dd, *J* = 10.4 Hz, 6.0 Hz, 1 H), 6.12 (d, *J* = 10.0 Hz, 1 H), 5.44 (t, *J* = 6.0 Hz, 1 H), 5.19 (dd, *J* = 12.0 Hz, 9.2 Hz, 2 H), 2.68 (d, *J* = 15.6 Hz, 1 H), 2.62 (dd, *J* = 15.2 Hz, 6.8 Hz, 1 H), 2.26-2.50 (m, 4 H), 1.26-1.38 (m, 1 H), 1.12-1.25 (m, 4 H), 1.00-1.11 (m, 1 H), 0.83 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.3, 195.7, 155.2, 148.3, 135.7, 128.9 (2), 128.8, 128.6 (2), 128.0, 70.9, 68.3, 51.9, 51.3, 43.1, 35.4, 32.0, 24.1, 22.6, 14.1. HRMS (ESI) Calcd for $C_{21}H_{26}NO_4$ ($[M+H]^+$): 356.1856. Found: 356.1865. HPLC: Daicel® Chiralcel OJ-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (20% to 50%), 20-30 mins (50%-85%), 1.5 mL/min, λ = 254 nm, (1*S*,5*R*)-(-)-**3.104**: $t_{(1S,5R)}$ = 23.50 min; (1*R*,5*S*)-(+)-**3.104**: $t_{(1R,5S)}$ = 25.27 min.

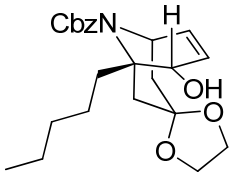


(±)-(1*S*,5*R*)-9-Benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-one, (±)-3.120; and (-)-(1*S*,5*R*)-9-Benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-one, (-)-3.120. Ketone (±)-**3.104** (638.1 mg, 1.80 mmol, 1.00 equiv, 97.7 %ee) was dissolved in $CHCl_3$ (15 mL) before 2-ethyl-2-methyl-1,3-dioxolane (1.35 mL, 10.8 mmol, 6.0 equiv), ethylene glycol (0.020 mL, 0.36 mmol, 0.2 equiv), and BF_3-OEt_2 (0.25 mL, 1.98 mmol, 1.1 equiv) were added in succession. The flask was sealed and the reaction stirred overnight at room temperature. After 12.5 hours, the solution was poured into a separatory funnel containing H_2O (15 mL), and the flask was rinsed with CH_2Cl_2 (10 mL). The layers were

separated and the aqueous layer was extracted with CH_2Cl_2 (2 X 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded (±)-**3.120** (601 mg, 1.50 mmol, 84 %) as a white solid (mp 104-106 ^oC).

Similar treatment of (-)-**3.104** (1.44 g, 4.07 mmol, 1.0 equiv) with 2-ethyl-2-methyl-1,3-dioxolane (3.05 mL, 24.4 mmol, 6.0 equiv), ethylene glycol (46 μL, 0.81 mmol, 0.2 equiv), and BF_3-OEt_2 (0.57 mL, 4.48 mmol, 1.1 equiv) in $CHCl_3$ (30 mL) afforded (-)- **3.120** (1.38 g, 3.46 mmol, 85 %) $[[\alpha]_D^{25}$ -116 (*c* 1.33, CH_2Cl_2)].

(±)-**3.120**: TLC: R_f = 0.25, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1718 (s), 1687 (s), 1455 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26-7.39 (m, 5 H), 7.01 (dd, *J* = 9.6 Hz, 6.6 Hz, 1 H), 6.18 (d, *J* = 10.2 Hz, 1 H), 5.22 (t, *J* = 6.6 Hz, 1 H), 5.13 (AB quart, *J* = 12.6 Hz, 2 H), 3.86-3.88 (m, 1 H), 3.76-3.83 (m, 3 H), 2.43 (dt, *J* = 12.6 Hz, 3.6 Hz, 1 H), 2.19 (dt, *J* = 12.0 Hz, 4.2 Hz, 1 H), 2.03 (dd, *J* = 14.4 Hz, 7.2 Hz, 1 H), 1.90-1.95 (m, 2 H), 1.78 (d, *J* = 13.8 Hz, 1 H), 1.25-1.32 (m, 1 H), 1.08-1.23 (m, 4 H), 0.96-1.03 (m, 1 H), 0.81 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 154.7, 147.8, 136.0, 129.4, 128.6 (2), 128.3 (3), 106.3, 69.6, 67.6, 64.9, 63.3, 50.2, 45.0, 36.3, 36.1, 32.0, 23.8, 22.5, 14.0. HRMS (ESI) Calcd for $C_{23}H_{30}NO_5$ ($[M+H]^+$): 400.2119. Found: 400.2116.

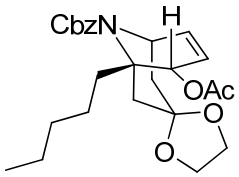


(±)-(1*S*,2*S*,5*R*)-9-Benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-ol, (±)-3.124; and (-)-(1*S*,2*S*,5*R*)-9-Benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-ol, (-)-3.124. Enone

(±)-**3.120** (521 mg, 1.30 mmol, 1.0 equiv) was dissolved in THF (10 mL) and MeOH (20 mL), and $CeCl_3$-$7H_2O$ (1.02 g, 2.74 mmol, 2.1 equiv) was added. The solution was stirred at room temperature for 30 minutes before it was cooled to 0 ^oC and $NaBH_4$ (98.3 mg, 2.60 mmol, 2.0 equiv) was added in one portion. After 45 minutes at 0 ^oC, the solution was transferred to a separatory funnel containing H_2O (20 mL) and CH_2Cl_2 (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 X 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded a single diastereomer (±)-**3.124** (493 mg, 1.23 mmol, 94 %) as a clear, colorless oil.

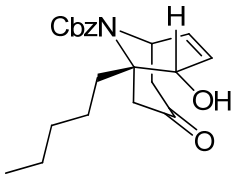
Similar treatment of (-)-**3.120** (1.30 g, 3.26 mmol, 1.0 equiv) with $CeCl_3$-$7H_2O$ (2.55 g, 6.85 mmol, 2.1 equiv) and $NaBH_4$ (247 mg, 6.52 mmol, 2.0 equiv) in THF (20 mL)/MeOH (40 mL) afforded (-)-**3.124** (1.28 g, 3.19 mmol, 98 %) $[[\alpha]_D^{25}$ -8.8 (*c* 1.05, $CH_2Cl_2)]$.

(±)-**3.124**: TLC: R_f = 0.19, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3489 (br), 2957 (m), 1710 (s), 1455 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.27-7.37 (m, 5 H), 5.87 (dd, *J* = 9.6 Hz, 5.2 Hz, 1 H), 5.71 (dd, *J* = 9.6, 2.8 Hz, 1 H), 5.08 (s, 2 H), 4.88 (t, *J* = 4.8 Hz, 1 H), 4.29 (d, *J* = 11.2, 1 H), 3.97-4.02 (m, 1 H), 3.85-3.93 (m, 3 H), 2.63 (d, *J* = 11.2 Hz, 1 H), 2.20-2.27 (m, 1 H), 2.07 (dd, *J* = 14.4 Hz, 2.4 Hz, 1 H), 1.91-2.00 (m, 3 H), 1.78 (d, *J* = 14.0 Hz, 1 H), 1.28-1.37 (m, 2 H), 1.16-1.28 (m, 4 H), 0.84 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 136.6, 130.3, 129.9, 128.7 (2), 128.3 (3), 107.8, 72.4, 67.4, 65.1, 63.5, 62.1, 50.8, 40.8, 40.0, 38.3, 32.4, 23.9, 22.9, 14.3. HRMS (ESI) Calcd for $C_{23}H_{32}NO_5$ ($[M+H]^+$): 402.2275. Found: 402.2272.



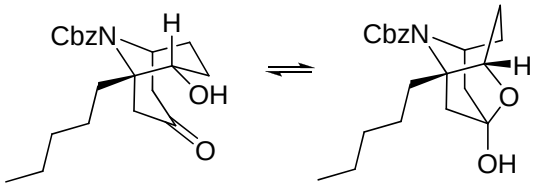
(±)-(1*S*,2*S*,5*R*)-2-Acetoxy-9-benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-3-ene, (±)-3.125. Allylic alcohol (±)-**3.124** (34.4 mg, 0.086 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (4 mL) and Et_3N (24 μL, 0.17 mmol, 2.0 equiv), Ac_2O (16 μL, 0.17 mmol, 2.0 equiv), and a crystal of DMAP were added in succession. The flask was sealed and the solution stirred at room temperature. After 12.5 hours, the solution was concentrated and subjected to flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford (±)-**3.125** (28.1 mg, 0.063 mmol, 74 %) as a clear, colorless oil.

(±)-3.125: TLC: R_f = 0.29, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1741 (s), 1710 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.36 (m, 5 H), 5.82-5.87 (m, 1 H), 5.59-5.61 (m, 2 H), 5.09 (dd, *J* = 19.6 Hz, 12.0 Hz, 2 H), 4.93 (br s, 1 H), 3.96 (t, *J* = 6.4 Hz, 2 H), 3.79-3.91 (m, 2 H), 2.10-2.27 (m, 3 H), 2.08 (s, 3 H), 1.89 (d, *J* = 14.8 Hz, 1 H), 1.84 (dt, *J* = 14.0, 2.4 Hz, 1 H), 1.53-1.61 (m, 1 H), 1.25-1.38 (m, 2 H), 1.17-1.24 (m, 2 H), 1.12 (hex, *J* = 7.6 Hz, 2 H), 0.83 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 155.8, 136.4, 132.0, 128.7 (2), 128.3 (3), 125.8, 107.3, 73.3, 67.5, 64.5, 63.4, 59.5, 51.2, 39.1, 39.0, 38.5, 32.4, 23.4, 22.9, 21.4, 14.3. HRMS (ESI) Calcd for $C_{25}H_{34}NO_6$ ($[M+H]^+$): 444.2381. Found: 444.2384.



(±)-(1*S*,2*S*,5*R*)-9-Benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-ol, (±)-3.129. Ketal (±)-**3.124** (493 mg, 1.23 mmol, 1.0 equiv) was dissolved in acetone (50 mL) and $Pd(MeCN)_2Cl_2$ (25.5 mg, 0.098 mmol, 0.080 equiv) was added. The flask was sealed and the solution stirred at room temperature. After 20.5 hours, the solution was concentrated and subjected to flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford (±)-**3.129** (422 mg, 1.18 mmol, 96 %) as a clear, colorless oil.

(±)-**3.129**: TLC: R_f = 0.27, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3443 (br), 2930 (m), 1706 (s), 1455 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34-7.38 (m, 5 H), 5.73 (ddd, *J* = 10.2 Hz, 4.2 Hz, 1.8 Hz, 1 H), 5.67 (dd, *J* = 11.4 Hz, 1.2 Hz, 1 H), 5.17 (br s, 1 H), 5.14 (dd, *J* = 18.6 Hz, 12.6 Hz, 2 H), 4.50 (d, *J* = 4.8 Hz, 1 H), 2.71-2.75 (m, 2 H), 2.33-2.41 (m, 3 H), 1.88 (d, *J* = 6.0 Hz, 1 H), 1.70-1.75 (m, 1 H), 1.18-1.41 (m, 6 H), 0.86 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.5, 155.7, 136.2, 130.4, 129.7, 128.8 (2), 128.5, 128.3 (2), 70.8, 67.8, 63.1, 52.4, 44.8, 44.2, 37.4, 32.2, 23.4, 22.8, 14.3. HRMS (ESI) Calcd for $C_{21}H_{28}NO_4$ ($[M+H]^+$): 358.2013. Found: 358.2015.

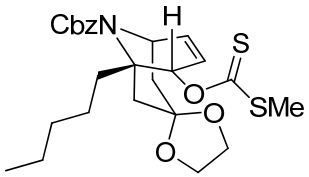


3.132a, minor **3.132b, major**

(±)-(1*S*,2*S*,5*R*)-9-Benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]nonan-2-ol, (±)-3.132a; and (±)-3.132b. Allylic alcohol (±)-**3.129** (97.1 mg, 0.27 mmol, 1.0 equiv) was dissolved in MeOH (5 mL) and PtO_2 (6.2 mg, 0.027 mmol, 0.1 equiv) was added to the solution. The reaction mixture was stirred for 9.5 hours under an atmosphere of hydrogen before it was concentrated under reduced pressure. Flash chromatography over

silica gel with hexanes-EtOAc (2:1) afforded (±)-**3.132a**/(±)-**3.132b** (85 mg, 0.24 mmol, 88%), a 1.0:4.0-4.5 equilibrium mixture of isomers at room temperature (20 ^{o}C) in $CDCl_3$, as a clear, colorless oil. Note: Carbon peaks from the minor compound (±)-**3.132a** are shown in parentheses.

(±)-**3.132a/3.132b**: TLC: R_f = 0.20, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3374 (br), 2934 (m), 1702 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.37 (m, 5 H), 5.14 (d, *J* = 12.0 Hz, 1 H), 5.05 (d, *J* = 12.4 Hz, 1 H), 4.87 (br s, 0.2 H), 4.72 (t, *J* = 6.8 Hz, 0.8 H), 4.27 (br s, 0.8 H), 4.13 (d, *J* = 4.0 Hz, 0.8 H), 3.74 (br d, *J* = 9.2 Hz, 0.2 H), 2.51-2.70 (m, 1.6 H), 2.27-2.38 (m, 0.6 H), 2.09-2.19 (m, 1 H), 1.81-2.00 (m, 4 H), 1.54-1.73 (m, 3 H), 1.04-1.44 (m, 6 H), 0.81-0.86 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 155.8, 136.6, (136.3), (128.7), 128.6 (3), (128.4), (128.3), 128.2, 128.1, 104.5, 81.5, (71.3), (67.6), 67.4, 67.2, (64.3), (51.3), 48.9, 47.7, (44.9), (44.7), 44.3, (37.3), (36.0), 32.3, (32.2), (29.5), (27.2), 24.8, 24.2, (23.5), 23.1, (22.9), 22.7, 14.2. HRMS (ESI) Calcd for $C_{21}H_{30}NO_4$ ($[M+H]^+$): 360.2169. Found: 360.2166.



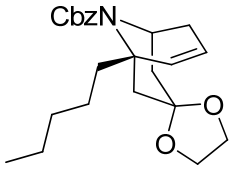
(±)-(1*S*,2*S*,5*R*)-9-benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-2-methylthiocarbonothioyloxy-1-pentyl-9-azabicyclo[3.3.1]non-3-ene, (±)-3.137; and (+)-(1*S*,2*S*,5*R*)-9-benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-2-methylthiocarbonothioyloxy-1-pentyl-9-azabicyclo[3.3.1]non-3-ene, (+)-3.137. Allylic alcohol (±)-**3.124** (454 mg, 1.13 mmol, 1.0 equiv) in THF (2 mL) was added dropwise to a suspension of NaH (60 % dispersion in mineral oil, washed twice with 2

mL of hexanes, 453 mg, 11.3 mmol, 10.0 equiv) in THF (15 mL) at -78 ^{o}C. The solution was warmed to 0 ^{o}C over 30 minutes, CS_2 (1.36 mL, 22.6 mmol, 20.0 equiv) and imidazole (38.5 mg, 0.57 mmol, 0.5 equiv) were added, and the solution was warmed to room temperature. After 15 minutes, the solution was heated to reflux. After 45 minutes, MeI (1.41 mL, 22.6 mmol, 20.0 equiv) was added. The solution was refluxed for an additional 30 minutes, cooled to room temperature, and then poured into a separatory funnel containing CH_2Cl_2 (20 mL) and H_2O (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 X 20 mL). The organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded (±)-**3.137** (490 mg, 0.99 mmol, 88 %) as a clear, yellow oil.

Similar treatment of (-)-**3.124** (754 mg, 1.88 mmol, 1.0 equiv) with NaH (752 mg, 18.8 mmol, 10.0 equiv), CS_2 (2.27 mL, 37.6 mmol, 20.0 equiv), imidazole (64 mg, 0.94 mmol, 0.5 equiv), and MeI (2.34 mL, 37.6 mmol, 20.0 equiv) afforded (+)-**3.137** (835 mg, 1.70 mmol, 90 %) [$[\alpha]_D^{25}$ +40.5 (*c* 1.07, CH_2Cl_2)].

(±)-**3.137**: TLC: R_f = 0.55, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2957 (m), 1710 (s), 1455 (m), 1393 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.39 (m, 5 H), 6.45 (d, *J* = 1.2 Hz, 1 H), 5.91 (ddd, *J* = 10.0 Hz, 4.8 Hz, 1.6 Hz, 1 H), 5.75 (dd, *J* = 10.0 Hz, 1.2 Hz, 1 H), 5.07-5.14 (m, 2 H), 4.97 (br s, 1 H), 3.95-4.04 (m, 2 H), 3.87-3.92 (m, 1 H), 3.80-3.85 (m, 1 H), 2.57 (s, 3 H), 2.14-2.28 (m, 3 H), 1.95 (d, *J* = 16.0 Hz, 1 H), 1.86 (d, *J* = 14.0 Hz, 1 H), 1.62-1.69 (m, 1 H), 1.29-1.37 (m, 2 H), 1.19-1.25 (m, 2 H), 1.08-1.17 (m, 2 H), 0.82 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.4, 155.8, 136.4, 132.8, 128.7 (2), 128.3 (3), 124.5, 107.2, 81.8, 67.6, 64.6, 63.4, 59.9, 51.4, 39.7, 39.2, 38.4, 32.3,

23.5, 22.9, 19.2, 14.2. HRMS (ESI) Calcd for $C_{25}H_{34}NO_5S_2$ ([M+H]$^+$): 492.1872. Found: 492.1867.

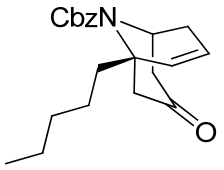


(±)-(1*S*,5*R*)-9-benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-2-ene, (±)-3.128; and (+)-(1*S*,5*R*)-9-benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-2-ene, (+)-3.128. Xanthate (±)-**3.137** (471 mg, 0.96 mmol, 1.0 equiv) was dissolved in benzene (10 mL). AIBN (15.8 mg, 0.096 mmol, 0.1 equiv) and Bu_3SnH (0.76 mL, 2.88 mmol, 3.0 equiv) were added in succession and the solution was refluxed for 6 hours. The solution was concentrated and subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). Product fractions were collected and concentrated. The residue was passed through a short pad of silica gel impregnated with 10 % of powdered KF using hexanes-EtOAc (4:1), affording (±)-**3.128** (309 mg, 0.80 mmol, 83 %) as a clear, colorless oil.

Similar treatment of (+)-**3.137** (835 mg, 1.70 mmol, 1.0 equiv) with AIBN (28 mg, 0.17 mmol, 0.10 mmol) and Bu_3SnH (1.35 mL, 5.10 mmol, 3.0 equiv) in benzene (11 mL) afforded (+)-**3.128** (528 mg, 1.37 mmol, 81 %) [$[\alpha]_D^{25}$ +17.8 (*c* 0.98, CH_2Cl_2)].

(±)-**3.128**: TLC: R_f = 0.52, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2953 (m), 1710 (s), 1455 (m), 1397 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.37 (m, 5 H), 5.75 (ddd, *J* = 10.0 Hz, 5.2 Hz, 1.6 Hz, 1 H), 5.32 (dt, *J* = 10.0 Hz, 1.6 Hz, 1 H), 5.14 (d, *J* = 12.4 Hz, 1 H), 5.07 (d, *J* = 12.4 Hz, 1 H), 4.80-4.83 (m, 1 H), 3.86-3.95 (m, 2 H), 3.76-3.84 (m, 2 H), 2.51-2.67 (m, 2 H), 2.05 (d, *J* = 13.6 Hz, 1 H), 1.91-1.99 (m, 2 H), 1.66-1.73 (m, 2 H),

1.12-1.33 (m, 7 H), 0.84 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 137.0, 134.8, 128.6 (2), 128.3 (2), 128.1, 124.1, 108.3, 67.1, 64.8, 63.3, 58.2, 48.1, 44.4, 41.2, 39.1, 32.3, 30.9, 23.5, 22.8, 14.3. HRMS (ESI) Calcd for $C_{23}H_{32}NO_4$ ($[M+H]^+$): 386.2325. Found: 386.2321.

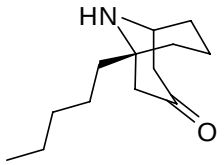


(±)-(1*S*,5*R*)-9-benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]non-2-ene, (±)-3.138; and (+)-(1*S*,5*R*)-9-benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]non-2-ene, (+)-3.138. Ketal (±)-**3.128** (291 mg, 0.75 mmol, 1.0 equiv) was dissolved in acetone (20 mL) and $Pd(MeCN)_2Cl_2$ (15.7 mg, 0.060 mmol, 0.080 equiv) was added. The solution was stirred for 14 hours and then concentrated. Flash chromatography over silica gel with hexanes-EtOAc afforded (±)-**3.138** (244 mg, 0.71 mmol, 95 %) as a clear, colorless oil.

Similar treatment of (+)-**3.128** (500 mg, 1.30 mmol, 1.0 equiv) with $Pd(MeCN)_2Cl_2$ (27 mg, 0.10 mmol, 0.08 equiv) in acetone (30 mL) afforded (+)-**3.138** (394 mg, 1.15 mmol, 89 %, 97.6 %ee) [$[\alpha]_D^{25}$ +8.3 (*c* 0.84, CH_2Cl_2)].

(±)-**3.138**: TLC: R_f = 0.55, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1710 (s), 1455 (w), 1390 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.37 (m, 5 H), 5.76-5.80 (m, 1 H), 5.11-5.26 (m, 3 H), 5.06 (t, J = 6.8 Hz, 1 H), 2.78-2.86 (m, 1 H), 2.70 (d, J = 14.8 Hz, 1 H), 2.57-2.63 (m, 1 H), 2.47 (dd, J = 16.4 Hz, 8.4 Hz, 1 H), 2.14-2.24 (m, 2 H), 1.93 (dd, J = 18.4 Hz, 6.0 Hz, 1 H), 1.13-1.32 (m, 7 H), 0.84 (t, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 155.7, 136.4, 134.3, 128.8 (2), 128.5, 128.4 (2), 124.0, 67.6,

60.0, 50.5, 49.4, 46.4, 39.8, 32.1, 31.0, 23.5, 22.8, 14.2. HRMS (ESI) Calcd for $C_{21}H_{28}NO_3$ ($[M+H]^+$): 342.2063. Found: 342.2063. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (20% to 50%), 20-30 mins (50%-85%), 1.5 mL/min, λ = 254 nm, (1*S*,5*R*)-(+)-**3.138**: $t_{(1S,5R)}$ = 27.11 min; (1*R*,5*S*)-(-)-**3.138**: $t_{(1R,5S)}$ = 25.96 min.

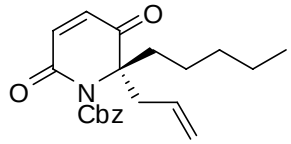


(±)-(1*S*,5*R*)-1-pentyl-9-azabicyclo[3.3.1]nonan-3-one, (±)-Adaline; and (-)-(1*S*,5*R*)-1-pentyl-9-azabicyclo[3.3.1]nonan-3-one, (-)-Adaline. Compound (±)-**3.138** (25 mg, 0.073 mmol, 1.0 equiv) was dissolved in MeOH (2 mL) and $Pd(OH)_2/C$ (7.7 mg, 0.011 mmol, 0.15 equiv) was added. The mixture was stirred under an atmosphere of hydrogen for 11 hours before it was passed through a plug of cotton and concentrated. The residue was dissolved in Et_2O (10 mL) and washed with 20 % aqueous NaOH saturated with NaCl (2 X 5 mL) and H_2O (2 X 10 mL). The solution was dried over $MgSO_4$, filtered and concentrated to afford (±)-adaline (11.8 mg, 0.056 mmol, 77 %) as a clear, colorless oil.

Similar treatment of (+)-**3.138** (332 mg, 0.97 mmol, 1.0 equiv) with $Pd(OH)_2/C$ (102 mg, 0.15 mmol, 0.15 equiv) in MeOH (20 mL) was carried out. In this case, the mixture was stirred under an atmosphere of hydrogen for 13 hours before it was passed through a plug of Celite with Et_2O (30 mL). The solution was washed with 20 % aqueous NaOH saturated with NaCl (2 X 50 mL) and H_2O (4 X 50 mL), dried over

$MgSO_4$, filtered and concentrated to afford (-)-adaline (183 mg, 0.87 mmol, 90 %) [$[\alpha]_D^{25}$ -13.0 (*c* 0.73, $CHCl_3$)], [lit. $[\alpha]_D$ = -13 ($CHCl_3$)].

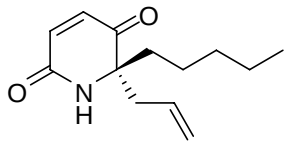
(±)-adaline: TLC: R_f = 0.17, ($CHCl_3$-MeOH = 15:1). IR (cm^{-1}): 3304 (br w), 2930 (s), 1706 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.68-3.69 (m, 1 H), 2.53 (dd, *J* = 16.8 Hz, 6.8 Hz, 1 H), 2.39 (d, *J* = 16.4 Hz, 2 H), 2.19 (d, *J* = 16.8 Hz, 1 H), 1.25-1.75 (m, 15 H), 0.89 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 54.7, 51.8, 49.8, 46.8, 44.9, 36.8, 32.5, 31.8, 22.7, 22.4, 18.0, 14.2. HRMS (ESI) Calcd for $C_{13}H_{24}NO$ ($[M+H]^+$): 210.1852. Found: 210.1850.



(±)-(6*S*)-6-allyl-1-(benzyloxy carbonyl)-6-pentyl-5-oxo-5,6-dihydropyridin-2(1*H*)-one, 3.111; and (+)-(6*S*)-6-allyl-1-(benzyloxy carbonyl)-6-pentyl-5-oxo-5,6-dihydropyridin-2(1*H*)-one, (+)-3.111. Complex (±)-**3.108** (5.82 g, 8.25 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (200 mL) before PDC (24.8 g, 66.0 mmol, 8.0 equiv) and silica gel (24.8 g) were added to the solution. The flask was sealed and the reaction mixture was stirred overnight at room temperature. After 18 hours, the dark orange-brown reaction mixture was passed through a pad of Celite and concentrated. The solution was then passed through a pad of silica gel and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded (±)-**3.111** (2.20 g, 6.19 mmol, 75 %) as a clear, light yellow oil.

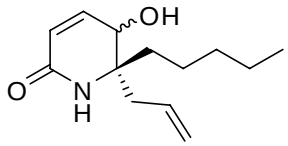
Similar treatment of (-)-**3.108** (1.02 g, 1.44 mmol, 1.0 equiv) with PDC (4.34 g, 11.5 mmol, 8.0 equiv) and silica gel (4.34 g) in CH_2Cl_2 (50 mL) for 36 hours afforded (+)-**3.111** (321 mg, 0.90 mmol, 63 %) [$[\alpha]_D^{25}$ +11.1 (*c* 1.15, CH_2Cl_2)].

(±)-**3.111**: TLC: R_f = 0.64, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1745 (s), 1683 (s), 1621 (m). ^1H NMR (600 MHz, $CDCl_3$): δ 7.44-7.45 (m, 2 H), 7.34-7.39 (m, 3 H), 6.84 (d, *J* = 10.2 Hz, 1 H), 6.61 (d, *J* = 10.2 Hz, 1 H), 5.52-5.58 (m, 1 H), 5.37 (d, *J* = 12.0 Hz, 1 H), 5.28 (d, *J* = 12.0 Hz, 1 H), 5.03 (s, 1 H), 5.00 (d, *J* = 1.8 Hz, 1 H), 2.95 (dd, *J* = 13.8 Hz, 7.8 Hz, 1 H), 2.61 (dd, *J* = 13.8 Hz, 7.8 Hz, 1 H), 1.92-2.00 (m, 2 H), 1.21-1.27 (m, 2 H), 1.06-1.17 (m, 2 H), 0.91-1.04 (m, 2 H), 0.78 t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 162.3, 153.7, 139.8, 136.7, 134.7, 130.9, 129.0, 128.9 (2), 128.8 (2), 120.9, 75.4, 70.0, 44.6, 39.1, 31.7, 23.9, 22.4, 14.0. HRMS (ESI) Calcd for $C_{21}H_{26}NO_4$ ($[M+H]^+$): 356.1856. Found: 356.1856.



(±)-(6*S*)-6-allyl-6-pentyl-5-oxo-5,6-dihydropyridin-2(1*H*)-one, (±)-3.144. Compound (±)-**3.111** (31.0 mg, 0.087 mmol, 1.0 equiv) was dissolved in MeOH (3 mL) and $CeCl_3$-$7H_2O$ was added in one portion. The solution was stirred for 2.5 hours at room temperature before it was poured into a separatory funnel containing H_2O (5 mL) and ethyl acetate (3 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (3 X 3 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)-**3.144** (15.6 mg, 0.071 mmol, 81 %) as a white solid (mp 98-101 ^oC).

(±)-**3.144**: TLC: R_f = 0.21, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2957 (s), 1729 (m), 1675 (s), 1606 (s), 1490 (s), 1440 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (br s, 1 H), 6.81 (dd, *J* = 10.0 Hz, 2.8 Hz, 1 H), 6.54 (d, *J* = 10.4 Hz, 1 H), 5.58-5.69 (m, 1 H), 5.13 (s, 1 H), 5.09 (dd, *J* = 9.2 Hz, 1.6 Hz, 1 H), 2.60 (dd, *J* = 13.6 Hz, 7.6 Hz, 1 H), 2.34 (dd, *J* = 13.6 Hz, 7.2 Hz, 1 H), 1.93-2.01 (m, 1 H), 1.52 (dt, *J* =12.4 Hz, 4.0 Hz, 1 H), 1.29-1.39 (m, 1 H), 1.14-1.28 (m, 4 H), 1.04-1.11 (m, 1 H), 0.83 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 162.9, 140.3, 136.5, 130.7, 121.1, 68.3, 45.9, 41.1, 31.9, 23.6, 22.5, 14.1. HRMS (ESI) Calcd for $C_{13}H_{20}NO_2$ ($[M+H]^+$): 222.1488. Found: 222.1489.



(5*R*,6*S*)-6-allyl-5-hydroxy-6-pentyl-5,6-dihydro-2*H*-pyridin-2-one and (5*S*,6*S*)-6-allyl-5-hydroxy-6-pentyl-5,6-dihydro-2*H*-pyridin-2-one, 3.145. Compound (±)-**3.111** (2.20 g, 6.19 mmol, 1.0 equiv) was dissolved in MeOH (50 mL) and $CeCl_3$-$7H_2O$ was added in one portion. After stirring for 30 minutes at room temperature, the solution was cooled to 0 ^oC and $NaBH_4$ (257 mg, 6.81 mmol, 1.1 equiv) was added in one portion. After 1.3 hours, the solution was warmed to room temperature and stirred for 20 minutes before additional $NaBH_4$ (58.5 mg, mmol, 0.25 equiv) was added. After another 20-minute interval, $NaBH_4$ (58.5 mg, 1.55 mmol, 0.25 equiv) was again added, resulting in the disappearance of all starting material. The solution was stirred for 15 minutes and then transferred to a separatory funnel containing water (75 mL) and dichloromethane (75 mL). The layers were separated and the aqueous layer was extracted with

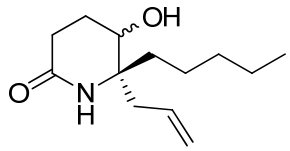
dichloromethane (3 X 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (1:1), and ramping to 100 % EtOAc, provided (±)-**3.145** (734 mg, 3.29 mmol, 53 %), a 1.5:1.0 mixture of diastereomers, as a clear, colorless oil. Note: The diastereomeric ratio ranged from 1.2-1.5:1.0 for this reaction.

Higher yields and a more reliable reaction were achieved using anhydrous $CeCl_3$ according to the following procedure: Compound (±)-**3.111** (511 mg, 1.44 mmol, 1.0 equiv) was dissolved in MeOH (15 mL) and anhydrous $CeCl_3$ (426 mg, 1.73 mmol, 1.2 equiv) was added. The solution was stirred for 40 minutes, cooled to 0 ^oC, and $NaBH_4$ (60 mg, 1.58 mmol, 1.10 equiv) was added in one portion. When bubbling had subsided, the reaction mixture was warmed to room temperature and stirred for one hour. The solution was transferred to a separatory funnel containing CH_2Cl_2 (30 mL) and H_2O (30 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 X 15 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (1:1, then 0:1) followed by $CHCl_3$-MeOH (15:1) provided (±)-**3.145** (229 mg, 1.02 mmol, 71 %) as 1.3:1.0 mixture of diastereomers. (±)-**3.146** (68 mg, 0.30 mmol, 21 %) was also obtained as an approximately 1.2:1.0 mixture of diastereomers. Both (±)-**3.145** and (±)-**3.146** were obtained as clear, colorless oils. Note: The diastereomeric ratios ranged from 1.1-1.3:1.0 for this reaction.

Similar treatment of (+)-**3.111** (302 mg, 0.85 mmol, 1.0 equiv) with anhydrous $CeCl_3$ (252 mg, 1.02 mmol, 1.2 equiv) and $NaBH_4$ (35 mg, 0.94 mmol, 1.1 equiv) in MeOH (10 mL) afforded chiral, non-racemic-**3.145** (132 mg, 0.59 mmol, 70 %) as a

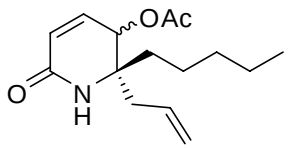
1.1:1.0 mixture of diastereomers and chiral, non-racemic-**3.146** (46 mg, 0.20 mmol, 24 %) as a 1.1:1.0 mixture of diastereomers.

(±)-**3.145**: TLC: R_f = 0.29, (hexanes-EtOAc = 0:1). IR (cm^{-1}): 3273 (br), 2930 (m), 1671 (s), 1610 (s), 1436 (m). ^1H NMR (600 MHz, $CDCl_3$): δ 6.65 (dt, *J* = 11.4 Hz, 4.8 Hz, 2.5 H), 5.91-5.94 (m, 2.5 H), 5.72-5.85 (m, 2.5 H), 5.63 (d, *J* = 14.4 Hz, 2.5 H), 5.16-5.22 (m, 3.5 H), 5.11 (dd, *J* = 16.2 Hz, 1.2 Hz, 1.5 H), 4.13 (d, *J* = 4.2 Hz, 1.5 H), 4.08 (d, *J* = 4.2 Hz, 1.0 H), 2.53 (dd, *J* = 13.2 Hz, 6.6 Hz, 1.0 H), 2.31-2.40 (m, 3.0 H), 2.23 (dd, *J* = 13.8 Hz, 7.8 Hz, 2.0 H), 1.71 (dt, *J* = 12.6 Hz, 4.8 Hz, 1.5 H), 1.50-1.58 (m, 2.5 H), 1.36-1.45 (m, 2.5 H), 1.19-1.33 (m, 15 H), 0.84-0.89 (m, 7.5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 142.5, 142.2, 132.7, 132.6, 124.4, 124.2, 119.7, 119.4, 67.3, 66.9, 60.2, 60.0, 40.2, 37.3, 35.4, 32.9, 32.3, 32.1, 23.3, 22.9, 22.6, 22.5, 14.1, 14.0. HRMS (ESI) Calcd for $C_{13}H_{22}NO_2$ ($[M+H]^+$): 224.1645. Found: 224.1645.



(5*S*,6*S*)-6-allyl-5-hydroxy-6-pentyl-piperidin-2-one and (5*S*,6*S*)-6-allyl-5-hydroxy-6-pentyl-piperidin-2-one, 3.146. TLC: R_f = 0.17, (hexanes-EtOAc = 0:1). IR (cm^{-1}): 3312 (br), 2934 (m), 1637 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 6.10 (br s, 1.1 H), 6.02 (br s, 1.0 H), 5.68-5.83 (m, 2.1 H), 5.10-5.18 (m, 4.2 H), 3.81-3.83 (m, 2.1 H), 3.16 (br s, 1.0 H), 3.03 (br s, 1.1 H), 2.41-2.54 (m, 3.1 H), 2.23-2.33 (m, 5.2 H), 1.88-2.00 (m, 4.2 H), 1.61-1.69 (m, 1.1 H), 1.18-1.51 (m, 15.8 H), 0.83-0.87 (m, 6.3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 132.6, 132.4, 120.0, 119.8, 68.4, 67.7, 60.2, 60.1, 42.2, 39.1, 37.8, 34.5,

32.4, 32.2, 27.4, 27.1, 24.9, 24.8, 22.8, 22.6, 14.1. HRMS (ESI) Calcd for $C_{13}H_{24}NO_2$ ($[M+H]^+$): 226.1801. Found: 226.1801.

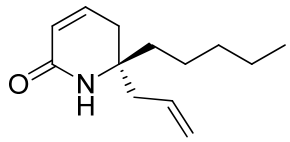


(5*R*,6*S*)-5-acetoxy-6-allyl-6-pentyl-5,6-dihydro-2*H*-pyridin-2-one and (5*S*,6*S*)-5-acetoxy-6-allyl-6-pentyl-5,6-dihydro-2*H*-pyridin-2-one, 3.147. Allylic alcohol (±)-**3.145** (734 mg, 3.29 mmol, 1.0 equiv, dr = 1.5:1.0) was dissolved in CH_2Cl_2 (20 mL) before Et_3N (0.91 mL, 6.58 mmol, 2.0 equiv), acetic anhydride (0.62 mL, 6.58 mmol, 2.0 equiv), and several crystals of DMAP were added in succession. The flask was sealed and the reaction mixture was allowed to stir overnight at room temperature. After 16 hours, the solution was transferred to a separatory funnel containing water (40 mL) and CH_2Cl_2 (10 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 X 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) and ramping to hexanes-EtOAc (1:1) provided (±)-**3.147** (852 mg, 3.21 mmol, 98 %), a white solid, as a 1.4:1.0 mixture of diastereomers.

Similar treatment of chiral, non-racemic **3.145** (115 mg, 0.52 mmol, 1.0 equiv) (dr = 1.1:1.0) with Et_3N (0.14 mL, 1.04 mmol, 2.0 equiv), Ac_2O (0.10 mL, 1.04 mmol, 2.0 equiv) and several crystals of DMAP in CH_2Cl_2 (5 mL) afforded chiral, non-racemic **3.147** (135 mg, 0.51 mmol, 98 %, dr = 1.1:1.0).

(±)-**3.147**: TLC: R_f = 0.21, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3200 (m), 2934 (m), 1741 (s), 1683 (s), 1621 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 6.53-6.58 (m, 2.2 H), 6.10

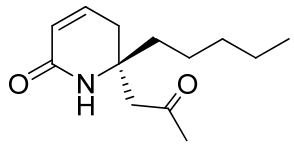
(br s, 1.2 H), 6.08 (br s, 1.0 H), 6.05 (dt, *J* = 2.8 Hz, 0.8 Hz, 1.2 Hz), 6.03 (dt, *J* = 2.0, 0.4 Hz, 1.0 H), 5.65-5.78 (m, 2.2 H), 5.26-5.29 (m, 2.2 H), 5.07-5.21 (m, 4.4 H), 2.23-2.46 (m, 4.4 H), 2.09 (s, 3.0 H), 2.08 (s, 3.6 H), 1.43-1.68 (m, 4.4 H), 1.18-1.35 (m, 13.2 H), 0.84-0.90 (m, 6.6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1 (2), 164.4, 137.5, 137.1, 131.9, 131.7, 127.1, 126.9, 120.2, 120.0, 68.7, 68.3, 59.0, 58.6, 40.5, 37.8, 35.9, 33.3, 32.2, 32.0, 23.2, 22.7, 22.5, 20.9, 14.0. HRMS (ESI) Calcd for $C_{15}H_{24}NO_3$ ($[M+H]^+$): 266.1751. Found: 266.1751.



(±)-(6*S*)-6-allyl-6-pentyl-5,6-dihydropyridin-2(1*H*)-one, (±)-3.148b; and (+)-(6*S*)-6-allyl-6-pentyl-5,6-dihydropyridin-2(1*H*)-one, (+)-3.148b. Allylic acetate (±)-**3.147** (50 mg, 0.19 mmol, 1.0 equiv, dr = 1.3 : 1.0) was dissolved in dioxane (3 mL) and $Pd(OAc)_2$ (4.3 mg, 0.019 mmol, 0.10 equiv), PPh_3 (10 mg, 0.038 mmol, 0.20 equiv) and $NH_4OC(O)H$ (24 mg, 0.38 mmol, 2.0 equiv) were added in succession. The solution was refluxed for one hour, cooled to room temperature, passed through a short pad of silica gel with hexanes-EtOAc (0:1), and concentrated. The residue was subjected to flash chromatography over silica gel with hexanes-EtOAc (1:1), affording (±)-**3.148b** (33 mg, 0.16 mmol, 83 %) as a clear, yellow oil.

Similar treatment of chiral, non-racemic **3.147** (108 mg, 0.41 mmol, 1.0 equiv, dr = 1.1:1.0) with $Pd(OAc)_2$ (9.2 mg, 0.041 mmol, 0.1 equiv), PPh_3 (22 mg, 0.082 mmol, 0.2 equiv), and $NH_4OC(O)H$ (52 mg, 0.82 mmol, 2.0 equiv) in refluxing dioxane (5 mL) provided (+)-**3.148b** (69 mg, 0.33 mmol, 81 %) $[[\alpha]_D^{25}$ +4.7 (*c* 1.61, CH_2Cl_2)].

(±)-**3.148b**: TLC: R_f = 0.17, (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3204 (w), 2934 (m), 1679 (s), 1617 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 6.50 (dt, *J* = 10.0 Hz, 4.0 Hz, 1 H), 5.88 (dq, *J* = 9.6 Hz, 1.6 Hz, 1 H), 5.68-5.78 (m, 1 H), 5.55 (br s, 1 H), 5.15 (dd, *J* = 10.0 Hz, 1.6 Hz, 1 H), 5.10 (dd, *J* = 16.8 Hz, 1.6 Hz, 1 H), 2.32 (dd, *J* = 4.0 Hz, 1.6 Hz, 2 H), 2.29 (d, *J* = 7.6 Hz, 2 H), 1.44-1.58 (m, 2 H), 1.19-1.35 (m, 6 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 139.8, 132.5, 124.0, 119.9, 56.5, 43.7, 39.3, 33.4, 32.2, 23.4, 22.7, 14.1. HRMS (ESI) Calcd for ($[M+H]^+$): 208.1695. Found: 208.1696.

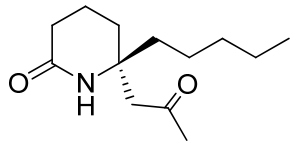


(±)-(6*R*)-6-(2-oxopropyl)-6-pentyl-5,6-dihydropyridin-2(1*H*)-one, (±)-3.154; and (-)-(6*R*)-6-(2-oxopropyl)-6-pentyl-5,6-dihydropyridin-2(1*H*)-one, (-)-3.154. To a solution of mercury(II) propionate (31 mg, 0.089 mmol, 1.0 equiv) in acetone (1 mL) was added terminal alkene (±)-**3.148b** (18.5 mg, 0.089 mmol, 1.0 equiv) in acetone (1 mL). The solution was cooled to 0 ^oC and Jones reagent (1.3 M in H_2O, 0.68 mL, 0.89 mmol, 10.0 equiv) was added dropwise. The reaction mixture was warmed to room temperature and stirred 25 hours before it was passed directly through a short pad of silica gel with hexanes-EtOAc (1:1) and concentrated. Flash chromatography over silica gel with $CHCl_3$-MeOH (10:1) afforded (±)-**3.154** (10.1 mg, 0.045 mmol, 51 %) as a clear, colorless oil.

Similar addition of (+)-**3.148b** (33 mg, 0.16 mmol, 1.0 equiv) in acetone (1 mL) to a solution of mercury(II) propionate (55 mg, 0.16 mmol, 1.0 equiv) in acetone (1 mL),

followed by addition of Jones reagent (1.3 M in H_2O, 1.23 mL, 1.60 mmol, 10.0 equiv) at 0 ^oC, afforded (-)-**3.154** (24.4 mg, 0.11 mmol, 68 %) [$[\alpha]_D^{25}$ -30.6 (*c* 1.22, CH_2Cl_2)].

(±)-**3.154**: TLC: R_f = 0.22, (hexanes-EtOAc = 0:1). IR (cm^{-1}): 3231 (w), 2930 (m), 1710 (m), 1675 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 6.50 (dt, *J* = 10.0, 4.8 Hz, 1 H), 6.09 (br s, 1 H), 5.90 (d, *J* = 8.8 Hz, 1 H), 2.78 (d, *J* = 17.2 Hz, 1 H), 2.68 (d, *J* = 17.2 Hz, 1 H), 2.44 (dm, *J* = 18.4 Hz, 1 H), 2.30 (dd, *J* = 18.0 Hz, 4.0 Hz, 1 H), 2.13 (s, 3 H), 1.73 (app t, *J* = 7.6 Hz, 2 H), 1.16-1.34 (m, 6 H), 0.87 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.1, 165.3, 139.3, 124.2, 56.1, 50.2, 38.7, 33.8, 32.1, 31.8, 24.1, 22.7, 14.1. HRMS (ESI) Calcd for $C_{13}H_{22}NO_2$ ($[M+H]^+$): 224.1645. Found: 224.1645.



(±)-(6*R*)-6-(2-oxopropyl)-6-pentyl-piperidin-2-one, (±)-Adalinine; and (-)-(6*R*)-6-(2-oxopropyl)-6-pentyl-piperidin-2-one, (-)-Adalinine. Dihydropyridinone (±)-**3.154** (13.4 mg, 0.060 mmol, 1.0 equiv) was dissolved in MeOH (2 mL), and $Pd(OH)_2/C$ (6.3 mg, 0.0090 mmol, 0.15 equiv) was added. The mixture was stirred under an atmosphere of hydrogen for 12 hours before it was concentrated. Flash chromatography over silica gel with 100 % EtOAc afforded (±)-adalinine (9.4 mg, 0.042 mmol, 70 %) as a clear, colorless oil.

Similar treatment of (-)-**3.154** (20.6 mg, 0.092 mmol, 1.0 equiv) with $Pd(OH)_2/C$ (9.8 mg, 0.014 mmol, 0.15 equiv) in MeOH (2 mL) under an atmosphere of hydrogen afforded (-)-adaline (18.3 mg, 0.081 mmol, 88 %, 97.5 %ee) [$[\alpha]_D^{25}$ -22.1 (*c* 0.92,

CH_2Cl_2)], [lit. $[\alpha]_{579}{}^{20}$ -26 (*c* 0.13, CH_2Cl_2)], after flash chromatography over silica gel with $CHCl_3$-MeOH (10:1).

(±)-adalinine: TLC: R_f = 0.42, ($CHCl_3$-MeOH = 10:1). IR (cm^{-1}): 3076-3459 (br), 2926 (m), 1710 (m), 1660 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.59 (br s, 1 H), 2.66 (AB q, *J* = 18.0 Hz, 2 H), 2.24-2.34 (m, 2 H), 2.14 (s, 3 H), 1.53-1.82 (m, 6 H), 1.20-1.32 (m, 5 H), 1.08-1.15 (m, 1 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 171.7, 56.3, 51.4, 39.4, 32.1, 32.0, 31.6, 31.4, 24.1, 22.7, 17.4, 14.1. HRMS (ESI) Calcd for $C_{13}H_{24}NO_2$ ($[M+H]^+$): 226.1802. Found: 226.1796. HPLC: Daicel® Chiralpak AS-RH column, % CH_3CN : H_2O (with 0.1 % TFA) = 30 : 70, 1.5 mL/min, λ = 210 nm, (*R*)-(-)-adalinine: t_R = 9.47 min; (*S*)-(+)-adalinine: t_S = 7.44 min.

Crystal Structure Analysis

A suitable crystal of **3.116** was obtained by diffusion recrystallization from CH_2Cl_2/hexanes. The crystal was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated MoK_α (0.71073Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3^o frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART[147] software. Frame integration and final cell refinements were done using SAINT[148] software. The final cell parameters

[147] SMART Version 5.628, **2003**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[148] SAINT Version 6.36A, **2002**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.

were determined from least-squares refinement on 5664 reflections. The SADABS[149] program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).[150] Hydrogen atoms were placed their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij} 's related to the atom's ridden upon. The C-H distances were fixed at 0.93 Å(aromatic and amide), 0.98 Å (methine), 0.97 Å (methylene), or 0.96 Å (methyl). All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography* [151] . Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V6.12 software.

Table 3.4. Crystal data and structure refinement for 3.116

Identification code	**3.116**	
Empirical formula	C29 H29 B Mo N7 O6	
Formula weight	678.34	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I-4	
Unit cell dimensions	a = 21.1763(14) Å	α= 90°.
	b = 21.1763(14) Å	β= 90°.
	c = 12.8350(10) Å	γ = 90°.
Volume	5755.7(7) Å^3	

[149] SADABS Version 2.10, **2003**, George Sheldrick, University of Göttingen.
[150] SHELXTL V6.12, **2002**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[151] A. J. C. Wilson (ed), *International Tables for X-ray Crystallography, Volume C.* Kynoch, Academic Publishers, Dordrecht, **1992**, Tables 6.1.1.4 (pp. 500-502) and 4.2.6.8 (pp. 219-222).

Z	8
Density (calculated)	1.566 Mg/m^3
Absorption coefficient	0.513 mm^{-1}
F(000)	2776
Crystal size	0.26 x 0.17 x 0.14 mm^3
Theta range for data collection	1.86 to 28.36°.
Index ranges	-28<=h<=28, -28<=k<=28, -17<=l<=17
Reflections collected	29240
Independent reflections	6173 [R(int) = 0.0590]
Completeness to theta = 28.36°	86.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.828000
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6173 / 0 / 398
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0801
R indices (all data)	R1 = 0.0492, wR2 = 0.0814
Absolute structure parameter	-0.01(3)
Largest diff. peak and hole	0.555 and -0.542 $e.Å^{-3}$

Table 3.5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3.116. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Mo(1)	8744(1)	7133(1)	9046(1)	25(1)
B(1)	9394(2)	5901(2)	10239(4)	36(1)
C(1)	7784(2)	5924(2)	9324(4)	37(1)
C(2)	7791(2)	5318(2)	9719(4)	46(1)
C(3)	8376(2)	5227(2)	10085(4)	40(1)
C(4)	9329(2)	7448(2)	11393(3)	35(1)
C(5)	9644(2)	7147(2)	12201(4)	40(1)
C(6)	9699(2)	6538(2)	11910(4)	39(1)
C(7)	9981(2)	6625(2)	7852(4)	34(1)
C(8)	10413(2)	6148(2)	7905(4)	42(1)
C(9)	10275(2)	5820(2)	8785(4)	37(1)
C(10)	7715(2)	8176(2)	8174(3)	26(1)
C(11)	7762(2)	7553(2)	8739(3)	27(1)
C(12)	7885(2)	7553(2)	9830(3)	29(1)
C(13)	7949(2)	8141(2)	10405(3)	28(1)
C(14)	7909(2)	8777(2)	9793(3)	27(1)
C(16)	8338(2)	9137(2)	8103(3)	29(1)

C(17)	8735(2)	9374(2)	6418(4)	40(1)
C(18)	8772(2)	9092(2)	5365(4)	32(1)
C(19)	8763(2)	8453(2)	5199(4)	35(1)
C(20)	8807(2)	8216(2)	4203(4)	45(1)
C(21)	8870(2)	8607(3)	3392(4)	53(2)
C(22)	8886(3)	9244(3)	3533(4)	54(2)
C(23)	8851(2)	9491(2)	4511(4)	41(1)
C(24)	7016(2)	8401(2)	8103(3)	33(1)
C(25)	6761(2)	8621(2)	9151(4)	37(1)
C(26)	7211(2)	8989(2)	9816(3)	33(1)
C(27)	8300(2)	9269(2)	10381(3)	36(1)
C(28)	9010(2)	9173(2)	10403(4)	43(1)
C(29)	8534(2)	7089(2)	7565(3)	30(1)
C(30)	9207(2)	7904(2)	8574(3)	27(1)
N(1)	8343(2)	6194(2)	9464(3)	34(1)
N(2)	8713(2)	5753(2)	9955(3)	34(1)
N(3)	9184(2)	7036(2)	10646(3)	31(1)
N(4)	9415(2)	6467(2)	10965(3)	34(1)
N(5)	9582(2)	6584(2)	8658(3)	30(1)
N(6)	9763(2)	6072(2)	9245(3)	32(1)
N(7)	8089(2)	8667(2)	8688(3)	25(1)
O(1)	7979(2)	8150(2)	11347(2)	36(1)
O(2)	6221(2)	8531(2)	9395(3)	60(1)
O(3)	8531(2)	9646(1)	8377(3)	44(1)
O(4)	8384(1)	8952(1)	7080(2)	33(1)
O(5)	8438(2)	7074(2)	6681(3)	46(1)
O(6)	9502(1)	8296(2)	8182(3)	40(1)

Table 3.6. Bond lengths [Å] and angles [°] for 3.116

Mo(1)-C(29)	1.955(4)	C(10)-N(7)	1.463(5)
Mo(1)-C(30)	1.998(4)	C(10)-C(11)	1.508(6)
Mo(1)-N(5)	2.178(4)	C(10)-C(24)	1.558(5)
Mo(1)-N(1)	2.229(4)	C(11)-C(12)	1.425(6)
Mo(1)-C(12)	2.261(4)	C(12)-C(13)	1.454(6)
Mo(1)-N(3)	2.264(4)	C(13)-O(1)	1.211(5)
Mo(1)-C(11)	2.296(4)	C(13)-C(14)	1.563(6)
B(1)-N(4)	1.519(6)	C(14)-N(7)	1.486(5)
B(1)-N(2)	1.521(7)	C(14)-C(27)	1.529(6)
B(1)-N(6)	1.540(6)	C(14)-C(26)	1.545(6)
C(1)-N(1)	1.327(5)	C(16)-O(3)	1.206(5)
C(1)-C(2)	1.379(6)	C(16)-N(7)	1.353(5)
C(2)-C(3)	1.339(7)	C(16)-O(4)	1.375(5)
C(3)-N(2)	1.332(6)	C(17)-O(4)	1.441(5)
C(4)-N(3)	1.331(5)	C(17)-C(18)	1.480(6)
C(4)-C(5)	1.389(6)	C(18)-C(19)	1.369(6)
C(5)-C(6)	1.349(7)	C(18)-C(23)	1.394(7)
C(6)-N(4)	1.361(6)	C(19)-C(20)	1.377(7)
C(7)-N(5)	1.339(5)	C(20)-C(21)	1.336(7)
C(7)-C(8)	1.364(7)	C(21)-C(22)	1.362(8)
C(8)-C(9)	1.359(6)	C(22)-C(23)	1.361(7)
C(9)-N(6)	1.345(5)	C(24)-C(25)	1.523(6)

C(25)-O(2)	1.200(5)
C(25)-C(26)	1.498(6)
C(27)-C(28)	1.516(7)
C(29)-O(5)	1.153(5)
C(30)-O(6)	1.154(5)
N(1)-N(2)	1.372(5)
N(3)-N(4)	1.364(4)
N(5)-N(6)	1.374(5)
C(29)-Mo(1)-C(30)	81.72(17)
C(29)-Mo(1)-N(5)	86.40(16)
C(30)-Mo(1)-N(5)	88.18(16)
C(29)-Mo(1)-N(1)	95.96(16)
C(30)-Mo(1)-N(1)	171.63(16)
N(5)-Mo(1)-N(1)	83.63(13)
C(29)-Mo(1)-C(12)	105.59(16)
C(30)-Mo(1)-C(12)	102.01(16)
N(5)-Mo(1)-C(12)	165.14(14)
N(1)-Mo(1)-C(12)	86.36(15)
C(29)-Mo(1)-N(3)	166.26(15)
C(30)-Mo(1)-N(3)	98.51(15)
N(5)-Mo(1)-N(3)	79.88(13)
N(1)-Mo(1)-N(3)	81.81(14)
C(12)-Mo(1)-N(3)	87.86(14)
C(29)-Mo(1)-C(11)	69.24(16)
C(30)-Mo(1)-C(11)	94.30(16)
N(5)-Mo(1)-C(11)	154.82(14)
N(1)-Mo(1)-C(11)	92.38(14)
C(12)-Mo(1)-C(11)	36.42(15)
N(3)-Mo(1)-C(11)	124.27(13)
N(4)-B(1)-N(2)	109.7(4)
N(4)-B(1)-N(6)	107.9(4)
N(2)-B(1)-N(6)	109.4(4)
N(1)-C(1)-C(2)	109.9(4)
C(3)-C(2)-C(1)	105.9(4)
N(2)-C(3)-C(2)	109.2(4)
N(3)-C(4)-C(5)	110.4(4)
C(6)-C(5)-C(4)	105.8(4)
C(5)-C(6)-N(4)	108.3(4)
N(5)-C(7)-C(8)	109.7(4)
C(9)-C(8)-C(7)	106.0(4)
N(6)-C(9)-C(8)	109.5(4)
N(7)-C(10)-C(11)	111.7(3)
N(7)-C(10)-C(24)	108.8(3)
C(11)-C(10)-C(24)	111.0(3)
C(12)-C(11)-C(10)	119.0(4)
C(12)-C(11)-Mo(1)	70.4(2)
C(10)-C(11)-Mo(1)	118.7(3)
C(11)-C(12)-C(13)	121.0(4)
C(11)-C(12)-Mo(1)	73.1(2)
C(13)-C(12)-Mo(1)	119.2(3)
O(1)-C(13)-C(12)	121.8(4)
O(1)-C(13)-C(14)	119.4(4)
C(12)-C(13)-C(14)	118.6(3)
N(7)-C(14)-C(27)	116.1(4)
N(7)-C(14)-C(26)	108.0(3)
C(27)-C(14)-C(26)	108.1(3)
N(7)-C(14)-C(13)	109.3(3)
C(27)-C(14)-C(13)	108.0(3)
C(26)-C(14)-C(13)	107.0(3)
O(3)-C(16)-N(7)	128.9(4)
O(3)-C(16)-O(4)	120.6(4)
N(7)-C(16)-O(4)	110.4(4)
O(4)-C(17)-C(18)	108.4(4)
C(19)-C(18)-C(23)	118.6(4)
C(19)-C(18)-C(17)	122.7(4)
C(23)-C(18)-C(17)	118.6(4)
C(18)-C(19)-C(20)	120.2(5)
C(21)-C(20)-C(19)	120.3(5)
C(20)-C(21)-C(22)	120.9(5)
C(23)-C(22)-C(21)	120.0(5)
C(22)-C(23)-C(18)	120.0(5)
C(25)-C(24)-C(10)	112.3(3)
O(2)-C(25)-C(26)	122.7(5)
O(2)-C(25)-C(24)	121.3(4)
C(26)-C(25)-C(24)	115.9(4)
C(25)-C(26)-C(14)	116.5(3)
C(28)-C(27)-C(14)	117.0(4)
O(5)-C(29)-Mo(1)	176.7(4)
O(6)-C(30)-Mo(1)	170.1(4)
C(1)-N(1)-N(2)	106.1(4)
C(1)-N(1)-Mo(1)	133.8(3)
N(2)-N(1)-Mo(1)	120.1(3)
C(3)-N(2)-N(1)	108.8(4)
C(3)-N(2)-B(1)	130.5(4)
N(1)-N(2)-B(1)	120.7(4)
C(4)-N(3)-N(4)	106.3(4)
C(4)-N(3)-Mo(1)	133.5(3)
N(4)-N(3)-Mo(1)	120.0(3)
C(6)-N(4)-N(3)	109.2(4)
C(6)-N(4)-B(1)	130.3(4)
N(3)-N(4)-B(1)	120.2(4)
C(7)-N(5)-N(6)	107.3(3)
C(7)-N(5)-Mo(1)	131.0(3)
N(6)-N(5)-Mo(1)	121.5(3)
C(9)-N(6)-N(5)	107.4(4)
C(9)-N(6)-B(1)	132.7(4)
N(5)-N(6)-B(1)	119.9(3)
C(16)-N(7)-C(10)	118.9(3)
C(16)-N(7)-C(14)	120.9(3)
C(10)-N(7)-C(14)	113.8(3)
C(16)-O(4)-C(17)	115.0(3)

Symmetry transformations used to generate equivalent atoms:

Table 3.7. Anisotropic displacement parameters ($Å^2 x 10^3$) for 3.116. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mo(1)	23(1)	23(1)	29(1)	-1(1)	1(1)	1(1)
B(1)	39(3)	25(3)	45(3)	8(2)	1(2)	6(2)
C(1)	26(2)	28(2)	57(3)	-3(2)	8(2)	-2(2)
C(2)	37(3)	36(3)	63(3)	1(2)	12(2)	-10(2)
C(3)	48(3)	27(2)	45(3)	4(2)	13(2)	2(2)
C(4)	37(3)	37(2)	31(2)	-2(2)	2(2)	3(2)
C(5)	40(3)	52(3)	29(2)	-5(2)	0(2)	7(2)
C(6)	44(3)	39(3)	34(3)	8(2)	0(2)	-2(2)
C(7)	29(2)	39(3)	35(2)	-6(2)	7(2)	-4(2)
C(8)	28(2)	48(3)	50(3)	-17(2)	11(2)	-1(2)
C(9)	29(2)	33(2)	51(3)	-9(2)	1(2)	4(2)
C(10)	21(2)	28(2)	28(2)	1(2)	-2(2)	2(2)
C(11)	21(2)	22(2)	37(3)	-3(2)	5(2)	2(2)
C(12)	22(2)	27(2)	38(3)	9(2)	6(2)	0(2)
C(13)	20(2)	32(2)	31(2)	0(2)	5(2)	5(2)
C(14)	23(2)	23(2)	33(2)	-4(2)	3(2)	5(2)
C(16)	28(2)	31(2)	28(2)	1(2)	2(2)	3(2)
C(17)	48(3)	32(3)	40(3)	7(2)	10(2)	-10(2)
C(18)	24(2)	36(3)	36(2)	-5(2)	3(2)	-1(2)
C(19)	32(2)	36(3)	36(3)	7(2)	0(2)	-1(2)
C(20)	30(2)	45(3)	61(4)	-15(3)	4(2)	-2(2)
C(21)	40(3)	83(5)	35(3)	-16(3)	-2(2)	12(3)
C(22)	51(3)	75(4)	37(3)	13(3)	6(2)	9(3)
C(23)	42(3)	31(2)	50(3)	8(2)	6(2)	1(2)
C(24)	25(2)	30(2)	44(3)	3(2)	-4(2)	3(2)
C(25)	28(2)	37(2)	44(3)	8(2)	-2(2)	8(2)
C(26)	37(3)	28(2)	34(2)	1(2)	10(2)	12(2)
C(27)	43(3)	39(3)	25(2)	-7(2)	2(2)	-1(2)
C(28)	47(3)	39(3)	42(3)	-1(2)	-5(2)	-6(2)
C(29)	27(2)	25(2)	36(2)	-4(2)	-1(2)	2(2)
C(30)	26(2)	26(2)	29(2)	2(2)	0(2)	2(2)
N(1)	30(2)	25(2)	48(2)	-2(2)	4(2)	4(2)
N(2)	38(2)	24(2)	40(2)	2(2)	5(2)	5(2)
N(3)	29(2)	30(2)	36(2)	1(2)	4(2)	4(2)
N(4)	39(2)	30(2)	34(2)	3(2)	3(2)	7(1)
N(5)	28(2)	28(2)	34(2)	-3(2)	-1(2)	0(2)
N(6)	30(2)	29(2)	36(2)	-6(2)	-3(2)	4(1)
N(7)	21(2)	23(2)	30(2)	-1(1)	0(1)	0(1)
O(1)	39(2)	35(2)	35(2)	2(1)	4(1)	2(1)
O(2)	26(2)	90(3)	63(3)	-12(2)	7(2)	0(2)
O(3)	69(2)	30(2)	32(2)	-5(1)	6(2)	-12(2)
O(4)	42(2)	30(2)	29(2)	0(1)	0(1)	-7(1)
O(5)	57(2)	47(2)	35(2)	-5(2)	-7(2)	3(2)
O(6)	32(2)	39(2)	50(2)	7(2)	4(2)	-3(2)

Table 3.8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 3.116

	x	y	z	U(eq)
H(1)	9592	5527	10584	43
H(1A)	7431	6119	9001	44
H(2)	7451	5026	9728	55
H(3)	8528	4847	10390	48
H(4)	9230	7885	11375	42
H(5)	9791	7333	12830	48
H(6)	9901	6213	12297	47
H(7)	9966	6938	7323	41
H(8)	10743	6063	7425	51
H(9)	10504	5466	9038	45
H(10)	7881	8118	7451	31
H(11)	7440	7235	8515	32
H(12)	7630	7230	10213	35
H(17A)	9165	9438	6701	48
H(17B)	8521	9790	6383	48
H(19)	8725	8172	5773	42
H(20)	8793	7773	4091	54
H(21)	8903	8438	2709	63
H(22)	8923	9517	2948	65
H(23)	8880	9934	4611	49
H(24A)	6987	8752	7596	39
H(24B)	6752	8050	7841	39
H(26A)	7061	8968	10546	40
H(26B)	7192	9437	9599	40
H(27A)	8214	9687	10068	43
H(27B)	8147	9282	11110	43
H(28A)	9182	9240	9703	64
H(28B)	9104	8742	10633	64
H(28C)	9201	9475	10888	64

Table 3.9. Torsion angles [°] for 3.116

N(1)-C(1)-C(2)-C(3)	-1.0(6)
C(1)-C(2)-C(3)-N(2)	1.6(6)
N(3)-C(4)-C(5)-C(6)	1.3(5)
C(4)-C(5)-C(6)-N(4)	-1.2(5)
N(5)-C(7)-C(8)-C(9)	-1.3(5)
C(7)-C(8)-C(9)-N(6)	1.8(5)
N(7)-C(10)-C(11)-C(12)	27.5(5)
C(24)-C(10)-C(11)-C(12)	-94.1(5)
N(7)-C(10)-C(11)-Mo(1)	-54.8(4)
C(24)-C(10)-C(11)-Mo(1)	-176.5(3)
C(29)-Mo(1)-C(11)-C(12)	176.1(3)
C(30)-Mo(1)-C(11)-C(12)	-104.4(3)
N(5)-Mo(1)-C(11)-C(12)	160.7(3)
N(1)-Mo(1)-C(11)-C(12)	80.6(3)
N(3)-Mo(1)-C(11)-C(12)	-1.1(3)

C(29)-Mo(1)-C(11)-C(10)	-70.8(3)
C(30)-Mo(1)-C(11)-C(10)	8.7(3)
N(5)-Mo(1)-C(11)-C(10)	-86.2(4)
N(1)-Mo(1)-C(11)-C(10)	-166.3(3)
C(12)-Mo(1)-C(11)-C(10)	113.1(4)
N(3)-Mo(1)-C(11)-C(10)	112.0(3)
C(10)-C(11)-C(12)-C(13)	1.6(6)
Mo(1)-C(11)-C(12)-C(13)	114.3(4)
C(10)-C(11)-C(12)-Mo(1)	-112.7(3)
C(29)-Mo(1)-C(12)-C(11)	-3.8(3)
C(30)-Mo(1)-C(12)-C(11)	80.8(3)
N(5)-Mo(1)-C(12)-C(11)	-146.7(5)
N(1)-Mo(1)-C(12)-C(11)	-99.0(3)
N(3)-Mo(1)-C(12)-C(11)	179.1(3)
C(29)-Mo(1)-C(12)-C(13)	-120.4(3)
C(30)-Mo(1)-C(12)-C(13)	-35.8(3)
N(5)-Mo(1)-C(12)-C(13)	96.7(6)
N(1)-Mo(1)-C(12)-C(13)	144.4(3)
N(3)-Mo(1)-C(12)-C(13)	62.5(3)
C(11)-Mo(1)-C(12)-C(13)	-116.6(4)
C(11)-C(12)-C(13)-O(1)	171.1(4)
Mo(1)-C(12)-C(13)-O(1)	-101.8(5)
C(11)-C(12)-C(13)-C(14)	-2.6(6)
Mo(1)-C(12)-C(13)-C(14)	84.5(4)
O(1)-C(13)-C(14)-N(7)	161.4(4)
C(12)-C(13)-C(14)-N(7)	-24.7(5)
O(1)-C(13)-C(14)-C(27)	34.3(5)
C(12)-C(13)-C(14)-C(27)	-151.8(4)
O(1)-C(13)-C(14)-C(26)	-81.9(5)
C(12)-C(13)-C(14)-C(26)	92.0(4)
O(4)-C(17)-C(18)-C(19)	-28.8(7)
O(4)-C(17)-C(18)-C(23)	154.4(4)
C(23)-C(18)-C(19)-C(20)	-2.4(7)
C(17)-C(18)-C(19)-C(20)	-179.2(4)
C(18)-C(19)-C(20)-C(21)	1.1(7)
C(19)-C(20)-C(21)-C(22)	-0.5(8)
C(20)-C(21)-C(22)-C(23)	1.2(9)
C(21)-C(22)-C(23)-C(18)	-2.6(8)
C(19)-C(18)-C(23)-C(22)	3.1(7)
C(17)-C(18)-C(23)-C(22)	-180.0(5)
N(7)-C(10)-C(24)-C(25)	-51.5(4)
C(11)-C(10)-C(24)-C(25)	71.8(4)
C(10)-C(24)-C(25)-O(2)	-144.5(4)
C(10)-C(24)-C(25)-C(26)	39.3(5)
O(2)-C(25)-C(26)-C(14)	146.6(4)
C(24)-C(25)-C(26)-C(14)	-37.2(5)
N(7)-C(14)-C(26)-C(25)	45.1(5)
C(27)-C(14)-C(26)-C(25)	171.4(4)
C(13)-C(14)-C(26)-C(25)	-72.4(4)
N(7)-C(14)-C(27)-C(28)	-55.2(5)
C(26)-C(14)-C(27)-C(28)	-176.7(4)
C(13)-C(14)-C(27)-C(28)	67.8(5)
C(30)-Mo(1)-C(29)-O(5)	34(7)
N(5)-Mo(1)-C(29)-O(5)	-55(7)
N(1)-Mo(1)-C(29)-O(5)	-138(7)
C(12)-Mo(1)-C(29)-O(5)	134(7)

N(3)-Mo(1)-C(29)-O(5)	-58(8)
C(11)-Mo(1)-C(29)-O(5)	132(7)
C(29)-Mo(1)-C(30)-O(6)	-44(2)
N(5)-Mo(1)-C(30)-O(6)	43(2)
N(1)-Mo(1)-C(30)-O(6)	31(3)
C(12)-Mo(1)-C(30)-O(6)	-148(2)
N(3)-Mo(1)-C(30)-O(6)	123(2)
C(11)-Mo(1)-C(30)-O(6)	-112(2)
C(2)-C(1)-N(1)-N(2)	0.0(5)
C(2)-C(1)-N(1)-Mo(1)	178.5(3)
C(29)-Mo(1)-N(1)-C(1)	-53.5(4)
C(30)-Mo(1)-N(1)-C(1)	-127.0(11)
N(5)-Mo(1)-N(1)-C(1)	-139.1(4)
C(12)-Mo(1)-N(1)-C(1)	51.8(4)
N(3)-Mo(1)-N(1)-C(1)	140.2(4)
C(11)-Mo(1)-N(1)-C(1)	15.9(4)
C(29)-Mo(1)-N(1)-N(2)	124.8(3)
C(30)-Mo(1)-N(1)-N(2)	51.3(13)
N(5)-Mo(1)-N(1)-N(2)	39.1(3)
C(12)-Mo(1)-N(1)-N(2)	-129.9(3)
N(3)-Mo(1)-N(1)-N(2)	-41.5(3)
C(11)-Mo(1)-N(1)-N(2)	-165.8(3)
C(2)-C(3)-N(2)-N(1)	-1.7(5)
C(2)-C(3)-N(2)-B(1)	179.6(5)
C(1)-N(1)-N(2)-C(3)	1.0(5)
Mo(1)-N(1)-N(2)-C(3)	-177.7(3)
C(1)-N(1)-N(2)-B(1)	179.9(4)
Mo(1)-N(1)-N(2)-B(1)	1.2(5)
N(4)-B(1)-N(2)-C(3)	-121.9(5)
N(6)-B(1)-N(2)-C(3)	119.9(5)
N(4)-B(1)-N(2)-N(1)	59.5(5)
N(6)-B(1)-N(2)-N(1)	-58.7(5)
C(5)-C(4)-N(3)-N(4)	-0.8(5)
C(5)-C(4)-N(3)-Mo(1)	-174.9(3)
C(29)-Mo(1)-N(3)-C(4)	132.2(7)
C(30)-Mo(1)-N(3)-C(4)	42.2(4)
N(5)-Mo(1)-N(3)-C(4)	128.8(4)
N(1)-Mo(1)-N(3)-C(4)	-146.2(4)
C(12)-Mo(1)-N(3)-C(4)	-59.6(4)
C(11)-Mo(1)-N(3)-C(4)	-59.0(4)
C(29)-Mo(1)-N(3)-N(4)	-41.2(8)
C(30)-Mo(1)-N(3)-N(4)	-131.2(3)
N(5)-Mo(1)-N(3)-N(4)	-44.6(3)
N(1)-Mo(1)-N(3)-N(4)	40.4(3)
C(12)-Mo(1)-N(3)-N(4)	127.0(3)
C(11)-Mo(1)-N(3)-N(4)	127.7(3)
C(5)-C(6)-N(4)-N(3)	0.7(5)
C(5)-C(6)-N(4)-B(1)	173.3(4)
C(4)-N(3)-N(4)-C(6)	0.1(5)
Mo(1)-N(3)-N(4)-C(6)	175.1(3)
C(4)-N(3)-N(4)-B(1)	-173.4(4)
Mo(1)-N(3)-N(4)-B(1)	1.6(5)
N(2)-B(1)-N(4)-C(6)	127.4(5)
N(6)-B(1)-N(4)-C(6)	-113.4(5)
N(2)-B(1)-N(4)-N(3)	-60.6(5)
N(6)-B(1)-N(4)-N(3)	58.5(5)

C(8)-C(7)-N(5)-N(6)	0.3(5)
C(8)-C(7)-N(5)-Mo(1)	-175.7(3)
C(29)-Mo(1)-N(5)-C(7)	41.6(4)
C(30)-Mo(1)-N(5)-C(7)	-40.3(4)
N(1)-Mo(1)-N(5)-C(7)	138.0(4)
C(12)-Mo(1)-N(5)-C(7)	-174.1(5)
N(3)-Mo(1)-N(5)-C(7)	-139.2(4)
C(11)-Mo(1)-N(5)-C(7)	56.0(6)
C(29)-Mo(1)-N(5)-N(6)	-134.0(3)
C(30)-Mo(1)-N(5)-N(6)	144.2(3)
N(1)-Mo(1)-N(5)-N(6)	-37.6(3)
C(12)-Mo(1)-N(5)-N(6)	10.3(7)
N(3)-Mo(1)-N(5)-N(6)	45.2(3)
C(11)-Mo(1)-N(5)-N(6)	-119.6(4)
C(8)-C(9)-N(6)-N(5)	-1.6(5)
C(8)-C(9)-N(6)-B(1)	179.6(4)
C(7)-N(5)-N(6)-C(9)	0.8(4)
Mo(1)-N(5)-N(6)-C(9)	177.3(3)
C(7)-N(5)-N(6)-B(1)	179.8(4)
Mo(1)-N(5)-N(6)-B(1)	-3.7(5)
N(4)-B(1)-N(6)-C(9)	120.1(5)
N(2)-B(1)-N(6)-C(9)	-120.5(5)
N(4)-B(1)-N(6)-N(5)	-58.5(5)
N(2)-B(1)-N(6)-N(5)	60.8(5)
O(3)-C(16)-N(7)-C(10)	161.7(4)
O(4)-C(16)-N(7)-C(10)	-21.5(5)
O(3)-C(16)-N(7)-C(14)	11.6(7)
O(4)-C(16)-N(7)-C(14)	-171.6(3)
C(11)-C(10)-N(7)-C(16)	150.1(3)
C(24)-C(10)-N(7)-C(16)	-87.0(4)
C(11)-C(10)-N(7)-C(14)	-57.8(4)
C(24)-C(10)-N(7)-C(14)	65.1(4)
C(27)-C(14)-N(7)-C(16)	-30.7(5)
C(26)-C(14)-N(7)-C(16)	90.9(4)
C(13)-C(14)-N(7)-C(16)	-153.1(4)
C(27)-C(14)-N(7)-C(10)	177.8(4)
C(26)-C(14)-N(7)-C(10)	-60.6(4)
C(13)-C(14)-N(7)-C(10)	55.4(4)
O(3)-C(16)-O(4)-C(17)	6.6(6)
N(7)-C(16)-O(4)-C(17)	-170.5(4)
C(18)-C(17)-O(4)-C(16)	176.7(4)

Symmetry transformations used to generate equivalent atoms:

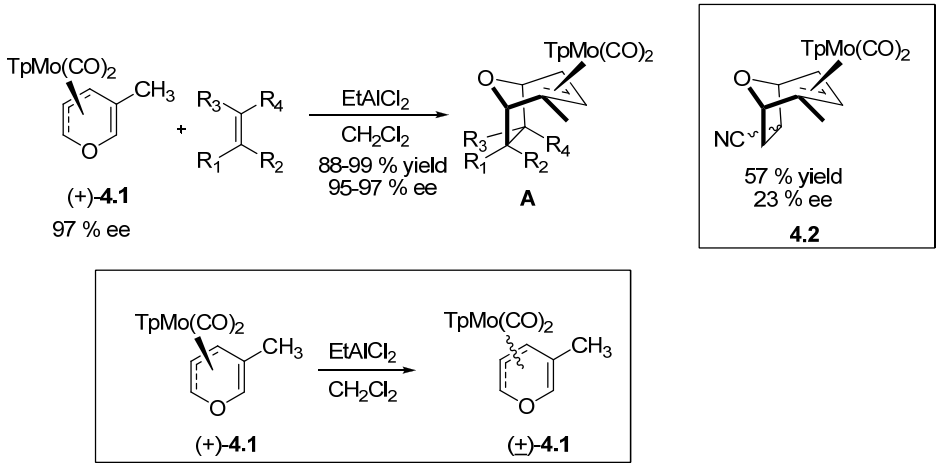
Chapter 4:

Novel Substitutions of 1-Alkoxy- and 1-Sulfonyloxy-η^3-Allylmolybdenum Complexes: Mechanism, Scope, and Limitations

Introduction

As part of an exploratory study of the reactivity of η^3-pyranylmolybdenum π-complex **4.1** (Scheme 4.1), Dr. Jingjun Yin, a former graduate student in the Liebeskind group, found that it underwent rapid [5+2] cycloaddition with a variety of electron-deficient dienophiles in the presence of catalytic $EtAlCl_2$ (0.1-0.2 equiv).[152] Using highly enantioenriched samples of complex (+)-**4.1 (**97 % ee), cycloadducts **A** were obtained in high yields (88-99 %) and high enantiomeric excesses (95-97 % ee) in most cases. However, cycloadditions of the less reactive dienophiles required greater quantities of $EtAlCl_2$ (1.1-1.2 equiv). In the case of of acrylonitrile, the least reactive alkene studied, a partially racemized cycloadduct **4.2** was unexpectedly obtained (57 % yield, 23 % ee). This surprising result was traced back to a slow racemization of complex (+)-**4.1** in the presence of the Lewis acid, $EtAlCl_2$ (Scheme 4.1, inset). Racemization was dramatically reduced or eliminated when more reactive alkenes were used, provided the alkene was present in greater quantity than the Lewis acid.

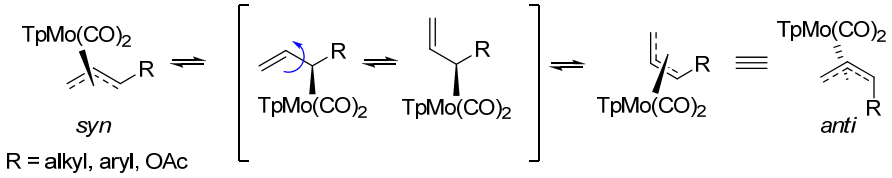
Scheme 4.1. Lewis acid-Catalyzed Cycloadditions and Racemization



[152] Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1999**, *121*, 5811-5812.

In other studies by the Liebeskind group,[153] it was demonstrated that acyclic mono-substituted alkyl-, aryl-, and acetoxy-substituted $TpMo(CO)_2$ η^3-allyl complexes underwent *syn*/*anti* isomerization at elevated temperatures (120 ^oC), while the corresponding 1,3-disubstituted complexes isomerized at room temperature. To explain this *syn*/*anti* isomerization, a π-σ-π mechanism was invoked in which an η^3 to η^1 slippage of the metal allows rotation about the C(1)-C(2) bond (Scheme 4.2). Reformation of the η^3-allyl, now in the *endo* configuration, results in a net *syn* to *anti* conversion of the substituent on C(1) and a migration of the $TpMo(CO)_2$ moiety from one face to the other of the η^3-allyl.

Scheme 4.2. Mechanism of *Syn*/*Anti* Isomerization

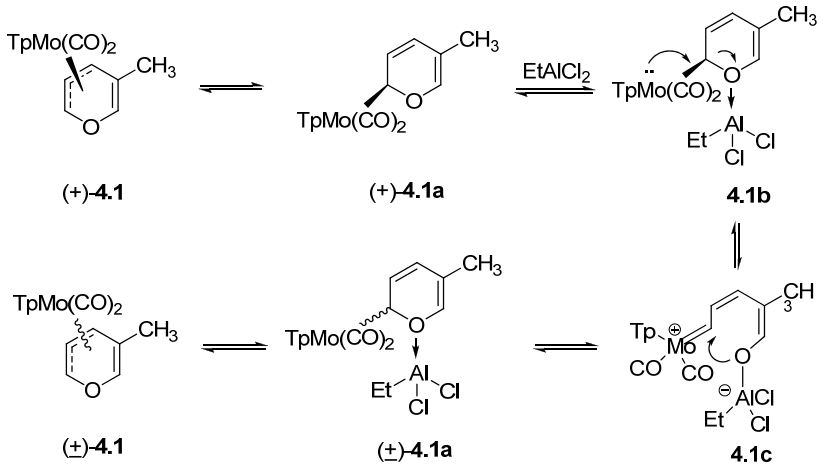


The racemization of cyclic π-complex (+)-**4.1** highlighted in Scheme 1 requires migration of the $TpMo(CO)_2$ fragment from one face to the other. This migration cannot simply occur by the slippage/rotation mechanism shown in Scheme 4.2 as the C(1)-C(2) bond is constrained within a heterocyclic ring and, therefore, cannot rotate. It is assumed that cleavage of the Mo-allyl bond by homo- or heterolytic cleavage, or bimolecular exchange, is unlikely due to the general stability of these complexes. Therefore, it is postulated that facial migration of the $TpMo(CO)_2$ fragment (ie. racemization) occurs by Lewis-acid-assisted opening of the pyran, proceeding through a carbene intermediate. Scheme 4.3 shows the proposed mechanism: Complex (+)-**4.1** undergoes an η^3-to-η^1 slippage, followed by reversible molybdenum-promoted

[153] Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132-4156.

and Lewis-acid-assisted opening of the pyran to carbene **4.1c**. At this point, stereochemical information is lost as intermediate Lewis-acid-bound alkoxide can reform pyran **4.1a** by adding to either face of the carbene.

Scheme 4.3. Mechanism Explaining the Observed Racemization

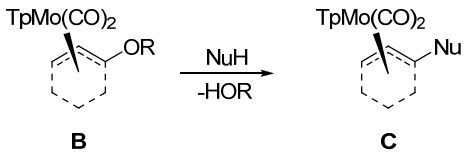


Based on these observations and mechanistic rationale, it was hypothesized that 1-alkoxy-η^3-allylmetals might participate in novel substitution reactions that proceed through carbene intermediates as suggested in Scheme 4.4. The reactivity profile of such 1-alkoxy-η^3-allylmetals has not been thoroughly explored, and so, little is known about these complexes. Synthesis and structural studies have been carried out on a variety of 1-alkoxy-η^3-allylmetal complexes using nickel,[154,155] palladium,[156,157,158,159] platinum,[160,157,158] cobalt,[161] iron,[162,163] and

[154] Johnson, J. R.; Tully, P. S.; Mackenzie, P. B.; Sabat, M. *J. Am. Chem. Soc.* **1991**, *113*, 6172-6177.
[155] Krysan, D. J.; Mackenzie, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 6273-6274.
[156] Kjellgren, J.; Kritikos, M.; Szabo, K. J. *J. Organomet. Chem.* **2006**, *691*, 3640-3645.
[157] Morita, M.; Inoue, K.; Ogoshi, S.; Kurosawa, H. *Organometallics* **2003**, *22*, 5468-5472.
[158] Ogoshi, S.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2003**, *125*, 9020-9021.
[159] Vicart, N.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1995**, *36*, 535-538.
[160] Morita, M.; Inoue, K.; Yoshida, T.; Ogoshi, S.; Kurosawa, H. *J. Organomet. Chem.* **2004**, *689*, 894-898.
[161] Chatani, N.; Yamasaki, Y.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1983**, *24*, 5649-5652.
[162] Ito, K.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1988**, 473-476.
[163] Ito, K.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1987**, 2103-2106.

molybdenum.[164] However, no fundamental studies on exchange of the alkoxy substituent have yet been published.

Scheme 4.4. Proposal for Intermolecular Exchange Reactions



Results and Discussion

Using the knowledge described above and the mechanistic proposals outlined in Scheme 4.3, the substitution investigation of 1-alkoxy- and 1-sulfonyloxy-η^3-allylmolybdenum complexes was carried out. Preliminary studies were done by Dr. Wenwei Huang. The results fell into three categories: 1) direct nucleophilic exchange of alkoxy substituents with external amines (Table 4.2), 2) protic/Lewis acid-catalyzed exchange of alkoxy substituents with external alcohols (Table 4.3), and 3) direct nucleophilic exchange of sulfonate ester substituents with both alcohols and amines (Table 4.3).

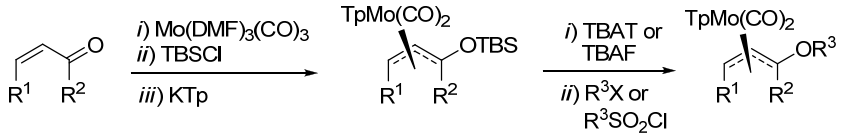
Substrate Synthesis

Substrates for the investigation bearing oxygenated substituents at the 1-position were synthesized according to previously published protocols or slight modifications thereof. Thus, monosubstituted- (propenyl-) (**4.5a**-**4.5c**); 1,3-disubstituted- (2-butenyl-) (**4.5d**-**4.5h**); and cyclic (cyclohexenyl-) (**4.5i**-**4.5k**) 1-alkoxy and 1-sulfonyloxy compounds were made from the corresponding 1-siloxy complexes **4.4a**-**4.4c** by treatment with tetrabutylammonium fluoride (TBAF) or tetrabutylammonium triphenyldifluorosilicate (TBAT), followed by addition of the

[164] Ward, Y. D.; Vellanueva, L. A.; Allred, G. D.; Liebeskind, L. S. *Organometallic* **1996**, *15*, 4201-4210.

appropriate alkyl halide or $ArSO_2Cl$ (Table 4.1). Siloxy complexes **4.4a**-**4.4c** were synthesized by addition of the appropriate α,β-unsaturated aldehyde or ketone to a solution of $Mo(DMF)_3(CO)_3$ in CH_2Cl_2 followed by TBSCl and then KTp. The alkoxy complexes could also be prepared in one pot from the requisite α,β-unsaturated aldehyde or ketone without isolating the intermediate silyl ethers. These complexes were air- and moisture-stable and easily manipulated, with the exception of sulfonate esters **4.5c**, **4.5e**, **4.5f**, and **4.5j**, which were found to partly decompose using routine purification techniques. These sulfonate esters could be carefully isolated, but were typically generated and used *in situ*, making isolation unnecessary.

Table 4.1. Synthesis of 1-Alkoxy and 1-Sulfonyloxy Substrates



4.3 **4.4** **4.5**

Entry	SM	R^1	R^2	Yld (%)	R^3	Yld (%)
1	**4.3a**	H	H	**4.4a**	OMe	80, **4.5a**
2	**4.3a**	H	H	54 %, **4.4a**	O*i*Pr	76, **4.5b**
3	**4.3a**	H	H	**4.4a**	OSO_2Ar[a]	92, **4.5c**
4	**4.3b**	CH_3	H	**4.4b**	OMe	64, **4.5d**
5	**4.3b**	CH_3	H	**4.4b**	OTs	--[b], **4.5e**
6	**4.3b**	CH_3	H	83 %, **4.4b**	OSO_2Ar[a]	70, **4.5f**
7	**4.3b**	CH_3	H	**4.4b**	Allyl	81, **4.5g**
8	**4.3b**	CH_3	H	**4.4b**	Cinnamyl	80, **4.5h**
9	**4.3c**	$-(CH_2)_3-$		**4.4c**	OMe	83, **4.5i**
10	**4.3c**	$-(CH_2)_3-$		65 %, **4.4c**	OTs	32, **4.5j**
11	**4.3c**	$-(CH_2)_3-$		**4.4c**	OSO_2Ar[a]	65, **4.5k**

[a]Ar = 2,4,6-triisopropylbenzene

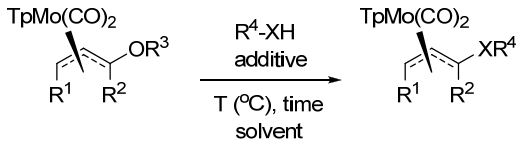
[b]The 2-butenyl tosylate could not be routinely isolated due to its instability.

Direct Exchange of Alkoxy Substitutents with Amines

Alkoxy-substituted complexes **4.5a**, **4.5d** and **4.5h** reacted directly with benzyl amine in the absence of a catalyst, providing amino-substituted complexes **4.6a** and **4.6b** in which the alkoxy group had been replaced by benzyl amine (Table 4.2). Stirring monosubstituted methoxy

complex **4.5a** in THF in the presence of 30 equivalents of benzyl amine at room temperature for 20 hours produced the desired amino-substituted complex **4.6a** in 95 % yield as a bright red solid (Entry 1).

Table 4.2. Exchange Reactions of Methoxy-substituted Complexes



Entry	SM	R^1	R^2	R^3	R^4-XH	Additive	Solvent	T (°C)	Time	Cpd. No.	Yld %
1	**4.5a**	H	H	OMe	$BnNH_2$	--	THF	Reflux	20 hrs	**4.6a**	95
2	**4.5d**	CH_3	H	OMe	$BnNH_2$	--	THF	Reflux	20 hrs	**4.6b**	74
3	**4.5h**	CH_3	H	OCinnamyl	BnNH2	--	THF	Reflux	24 hrs	**4.6b**	58
4	**4.5i**	$-(CH_2)_3-$		OMe	$BnNH_2$	--	THF	Reflux	NR	**4.6c**	NR
5	**4.5a**	H	H	OMe	*i*PrOH	$EtAlCl_2$	CH_2Cl_2	23	26 hrs	**4.5b**	72
6	**4.5b**	H	H	O*i*Pr	MeOH	$EtAlCl_2$	CH_2Cl_2	23	4 hrs	**4.5a**	87
7	**4.5d**	CH_3	H	OMe	*i*PrOH	$EtAlCl_2$	CH_2Cl_2	23	v. slow	**4.5l**	--
8	**4.5i**	$-(CH_2)_3-$		OMe	*i*PrOH	$EtAlCl_2$	CH_2Cl_2	Reflux	NR	**4.5m**	NR

NMR analysis of the amino-substituted complex **4.6a** confirmed the *syn*-configuration assigned to the amino substituent (Figure 4.1). In a prior publication from the Liebeskind group, it was shown that *syn* protons exhibit coupling constants ranging from 5.4-8.1 Hz, while *anti* protons have larger coupling constants ranging from 8.7-12.2 Hz. IR spectroscopy of **4.6a** also showed a significant shift to lower wavenumbers for the metal carbonyl stretches (1903 cm^{-1}, 1783 cm^{-1}) relative to the methoxy-substituted starting material **4.5a** (1918 cm^{-1}, 1818 cm^{-1}, Figure 4.1), indicating a large contribution from zwitterionic resonance structure **4.6a-I**. Previous studies showed that the methoxy substituent of **4.5a** was oriented in the plane of the allyl moiety and that significant double bond character existed between the oxygen atom and the allyl carbon. These properties were attributed to resonance overlap of the oxygen lone pairs with the π-system of the allyl. Overlap was most efficient when the methoxy substituent occupied a *syn* position on the η^3-allyl. Substituents occupying *anti* positions were found to bend out of the

plane of the allyl to minimize nonbonded interactions with the nearby metal carbonyl. This out-of-plane bending decreases the efficiency of resonance delocalization.

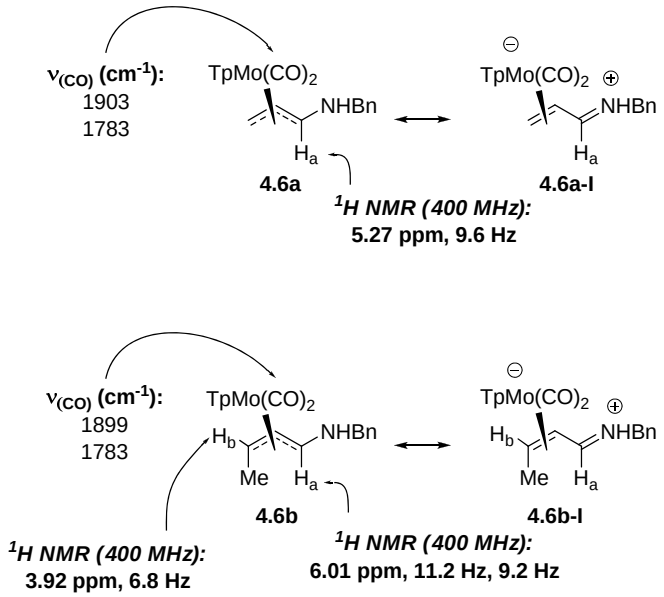


Figure 4.1. Structural Implications From Spectral Data

Disubstituted 2-butenyl methoxy complex **4.5d** underwent similar substitution of the methoxy substituent for a benzyl amine substituent when stirred with excess benzyl amine in THF at room temperature (Table 4.2). However, the reaction required several days to go to completion, and over that period of time significant decomposition occurred. Alternatively, refluxing complex **4.5d** in THF with 30 equivalents of benzyl amine for 20 hours provided the desired amino-substituted complex **4.6b** in 74 % yield as a bright red solid (Table 4.2, Entry 2). Again, NMR spectroscopy confirmed the *anti*-Me, *syn*-NHBn configuration assigned to **4.6b** (Figure 4.1). IR spectroscopy also showed the same shift of the metal carbonyls to lower wavenumbers (1899 cm^{-1}, 1783 cm^{-1}) relative to the methoxy-substituted starting material **4.5d** (1918 cm^{-1}, 1818 cm^{-1}), indicating significant zwitterionic character. Cyclic methoxy complex **4.5i** failed to react with benzyl amine, even at elevated temperatures.

Lewis acid-Catalyzed Exchange of Alkoxy Substituents with Alcohols

Stirring monosubstituted methoxy complex **4.5a** at room temperature with 20 equivalents of isopropanol in the presence of 0.4 equivalents of $EtAlCl_2$ led to the isolation of isopropyloxy-substituted complex **4.5b** in 72 % yield after 26 hours. (Table 4.2, Entry 5). Conversely, reaction of isopropyloxy-substituted complex **4.5b** with MeOH, a much smaller nucleophile than isopropanol, in the presense of $EtAlCl_2$ produced **4.5a** in 87 % yield after just 4 hours (Entry 6). The disubstituted 2-butenyl methoxy complex **4.5d** also reacted with isopropanol under similar Lewis acid catalysis to produce **4.5l**, but the transformation was exceedingly slow (Entry 7). Heating the reaction did not have a significant effect. Cyclohexenyl complex **4.5i** did not exchange with isopropanol at all in the presence of $EtAlCl_2$, even at elevated temperatures.

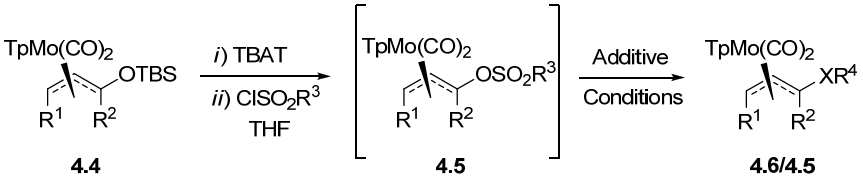
Direct Exchange of Sulfonate Esters with Amines and Alcohols

Sulfonate ester complexes analogous to the methoxy-substituted complexes discussed in Table 4.2 also reacted directly with benzyl amine in the absence of a catalyst, providing amino-substituted complexes **4.6a**, **4.6b**, and **4.6c** (Table 4.3, Entries 1-5). As previously noted, sulfonate ester-substituted complexes proved especially challenging to work with as most attempts at isolation led to significant decomposition. When synthesized on large scale, samples could be crystallized from the bulk material and used for characterization and small-scale reactions. Toluene-substituted sulfonate esters **4.5e** and **4.5j** led to more severe decomposition during isolation than did the corresponding 2,4,6-triisopropylbenzenesulfonate-substituted complexes **4.5c**, **4.5f**, and **4.5k**, and so the 2,4,6-triisopropylbenzene sulfonate ester group was chosen for most purposes in this study. However, in solution, both toluene-substituted sulfonate esters and 2,4,6-triisopropylbenzene sulfonate esters were stable and exhibited similar reactivities. Generating the desired sulfonate esters *in situ* by treating silyloxy complexes **4.4a**

and **4.4b** with tetrabutylammonium triphenyldifluorosilicate (TBAT) and the requisite sulfonyl chloride (tolyl- or 2,4,6-triisopropylbenzyl-) in THF, followed by addition of methanol and benzyl amine, was found to be a practical method for accessing amino-substituted complexes **4.6a** and **4.6b** without the need for isolating the sensitive intermediates.

In these cases, both monosubstituted complex **4.5a** and 2-butenyl complexes **4.5d** and **4.5h** reacted at room temperature to provide the desired amino-substituted complexes, but the best yields for both reactions were achieved when they were run in 1:1 mixtures of methanol and THF at reflux for 2-3 hours (Table 4.3, Entries 1-3). At room temperature, amino substitution of monosubstituted sulfonate ester **4.5c** in THF/MeOH (1:1) proceeded very slowly, and after stirring two days in the presence of $BnNH_2$, significant quantities of unreacted **4.5c** remained. At room temperature, amino substitution of 1,3-disubstituted sulfonate ester **4.5f** produced **4.6b** in 35 % yield after stirring 19 hours. No unreacted **4.5f** remained. Similar results were obtained using other solvents at room temperature.

Table 4.3. Exchange Reactions of Sulfonate Ester-Substituted Complexes



Entry	SM	R^1	R^2	R^3	Yld (%) Cpd. ID	Additive	Conditions	Time (hrs)	XR^4	Yld (%) Cpd. ID
1	**4.4a**	H	H	Ar[a]	--[b], **4.5c**	$BnNH_2$ (30 equiv)	THF/MeOH (1:1), reflux	2	NHBn	78, **4.6a**
2	**4.4b**	CH_3	H	Ts	--[b], **4.5e**	$BnNH_2$ (30 equiv)	THF/MeOH (1:1), reflux	2	NHBn	53, **4.6b**
3	**4.4b**	CH_3	H	Ar[a]	--[b], **4.5f**	$BnNH_2$ (30 equiv)	THF/MeOH (1:1), reflux	2	NHBn	74, **4.6b**
4	**4.4c**	$-(CH_2)_3-$		Ts	32, **4.5j**	$BnNH_2$ (15 equiv)	THF, Reflux	18	NHBn	45, **4.6c**
5	**4.4c**	$-(CH_2)_3-$		Ar[a]	65, **4.5k**	$BnNH_2$ (30 equiv)	THF, Reflux	17	NHBn	32, **4.6c**
6	**4.4a**	H	H	Ar[a]	--[b], **4.5c**	--	THF/MeOH (1:1), 23 °C	17	OMe	73, **4.5a**
7	**4.4b**	CH_3	H	Ar[a]	--[b], **4.5f**	--	THF/MeOH (1:1), 23 °C	14	OMe	72, **4.5d**
8	**4.4c**	$-(CH_2)_3-$		Ar[a]	65, **4.5k**	--	THF/MeOH (1:1), reflux	--	OMe	Decomp

[a]Ar = 2,4,6-Triisopropylbenzene

[b]Sulfonate ester not isolated; generated and used *in situ*

Unlike their methoxy-substituted counterpart **4.5i**, sulfonate ester-substituted cyclohexenyl complexes **4.5j** and **4.5k** underwent substitution with benzyl amine in refluxing THF, producing amino-substituted complex **4.6c** in 45 % and 32 % yields, respectively. The remainder of the mass was lost to decomposition. In contrast to acyclic sulfonate-ester-substituted complexes **4.5c** and **4.5f**, cyclohexenyl complex **4.5k** was quite stable once formed and easily isolated. The tosyl-substituted cyclohexenyl complex **4.5j** was much less stable.

To study the structural features of these sulfonate ester complexes, a single crystal of **4.5k** was grown from dichloromethane/hexanes and submitted to X-ray diffraction analysis. The structure is shown in Figure 4.2. It is interesting to note that very little lengthening of the Mo(1)-C(17) bond is observed which would have been due to resonance donation from the oxygen atom

of the electron-withdrawing sulfonate ester. The Mo(1)-C(17) bond length is 2.407(5) Å, while the Mo(1)-C(12) and Mo(1)-C(13) bond lengths are 2.213(5) Å and 2.362 Å, respectively. This observation contrasts with the results from a prior X-ray crystallography study carried out on methoxy-substituted cyclohexenyl complex **4.5i**. In that study, the Mo-C bond for the carbon bearing the methoxy substituent was significantly longer (2.664(4) Å) than the remaining two molybdenum allyl Mo-C bonds (2.256(4) Å and 2.300(4) Å). This lengthening was attributed to resonance donation from the oxygen atom into the metal allyl. Additionally, the O(3)-S(1) bond of sulfonate ester **4.5k** is rotated away from the $TpMo(CO)_2$ fragment, presumably to minimize nonbonded interactions between the SO_2 moiety and the proximal pyrazole hydrogen.

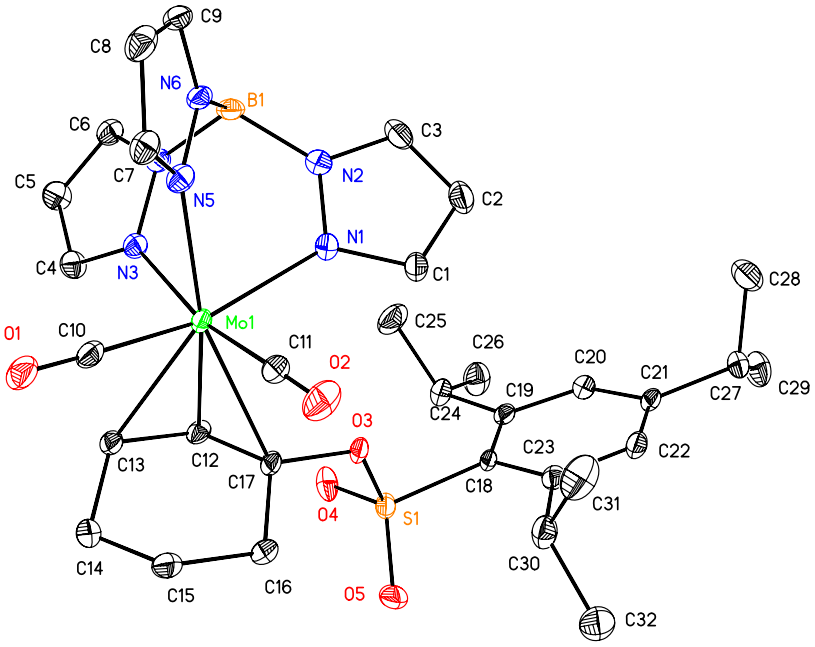


Figure 4.2. ORTEP View of (±)-4.5k

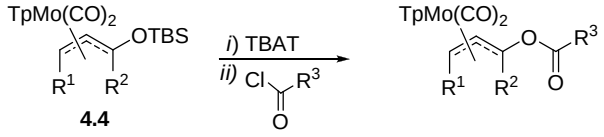
Acyclic mono- and disubstituted sulfonate ester complexes **4.5c** and **4.5f** also underwent substitution with methanol in THF, affording the corresponding methoxy-substituted complexes

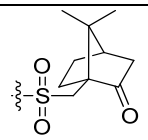
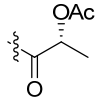
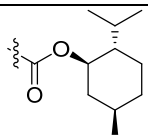
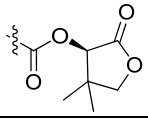
4.5a and **4.5d** (Table 4.3, Entries 6 and 7). Cyclohexenyl complex **4.5k**, however, did not react with methanol, even at elevated temperatures. Instead, the complex simply decomposed.

Accessing Chiral, Non-racemic Complexes

The results in Table 4.2 and Table 4.3 prompt the mechanistic question: Do the alkoxy and sulfonate ester substitution reactions occur with retention of π-complex stereochemistry or does the mechanism of substitution allow racemization? To address this question, a chiral auxiliary screen was conducted to find a suitable auxiliary for efficient resolution of both cyclohexenyl- and 2-butenyl- diastereomeric molybdenum complexes (Table 4.4).

Table 4.4. Chiral Auxiliary Screen



Entry	SM	R^1	R^2	R^3	Cpd. No.	Yld/dr
1	**4.4c**	$-CH_2CH_2CH_2-$			**4.7**	Decomp
2	**4.4b**	$-CH_3$	-H		**4.8**	Decomp
3	**4.4c**	$-CH_2CH_2CH_2-$			**4.9**	89/1:1
4	**4.4b**	$-CH_3$	-H		**4.10**	Decomp
5	**4.4c**	$-CH_2CH_2CH_2-$			**4.11**	90/1:1
6	**4.4b**	$-CH_3$	-H		NA	NA
7	**4.4c**	$-CH_2CH_2CH_2-$			**4.12**	75/1.1:1
8	**4.4b**	$-CH_3$	-H		**4.13**	22/1:0

Beginning with cyclohexenyl compounds, camphorsulfonyl-substituted complexes **4.7** proved too reactive to isolate, while the diastereomeric mixtures of both (*S*)-(-)-2-acetoxypropionyl-substituted complexes **4.9** and (-)-menthyl-substituted complexes **4.11** could not be resolved. (*R*)-(-)-pantolactone, however, proved quite useful allowing both diastereomers to be isolated in good yields and excellent diastereomeric ratios (up to 99.9 : 0.1) *via* a combination of chromatography and recrystallization (Figure 4.3).

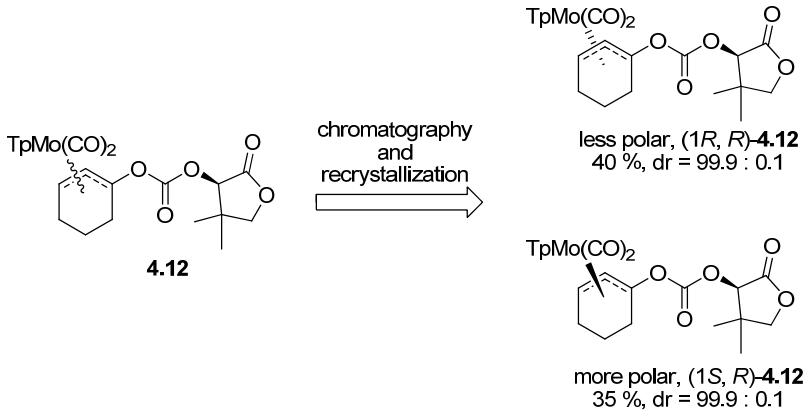


Figure 4.3. Pantolactone-based Cyclohexenyl Diastereomer Resolution

Single crystal X-ray diffraction confirmed the absolute configuration of the more polar diastereomer (*1S*, *R*)-**4.12** (Figure 4.4).

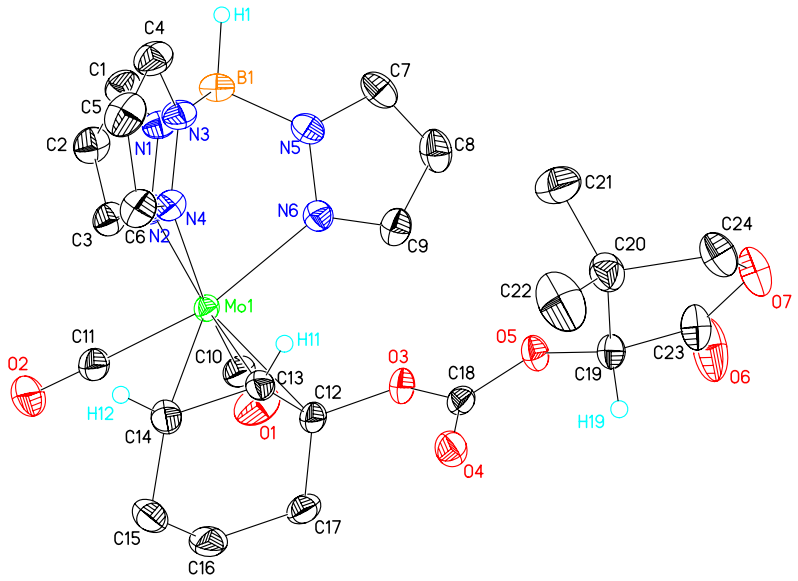


Figure 4.4. ORTEP View of Compound (1*S*, *R*)-4.12

In the case of 2-butenyl molybdenum complexes, camphorsulfonylchloride and (*S*)-(-)-2-acetoxypropionyl chloride produced diastereomeric sulfonate ester and carboxylic ester complexes **4.8** and **4.10**, respectively, in which both diastereomers decomposed during attempts at isolation (Table 4.4). However, (*R*)-(-)-pantolactone produced a mixture of diastereomeric carbonates **4.13**, of which one diastereomer could be isolated, while the second decomposed (Figure 4.5). The decomposition product from this unstable diastereomer partly overlapped with the stable diastereomer, making purification particularly tedious. However, repeated iterations of silica gel column chromatography and recrystallization from dichloromethane/hexanes provided (1*R*, *R*)-**4.13** in a low, but useful 22 % yield. The (1*R*, *R*) diastereomer of **4.13** was the only compound observed by ^{1}H NMR, so its diastereomeric ratio was determined to be >95:5.

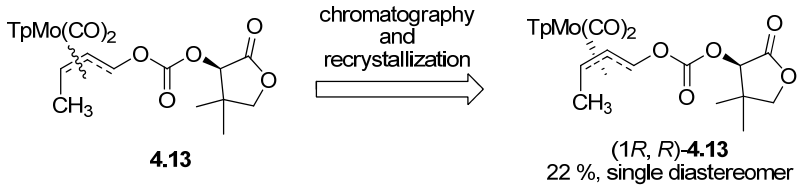


Figure 4.5. Accessing Diastereomerically-pure 2-Butenyl Complex

The absolute configuration of **4.13** was determined to be (1*R*, *R*) by single crystal X-ray diffraction (Figure 4.6).

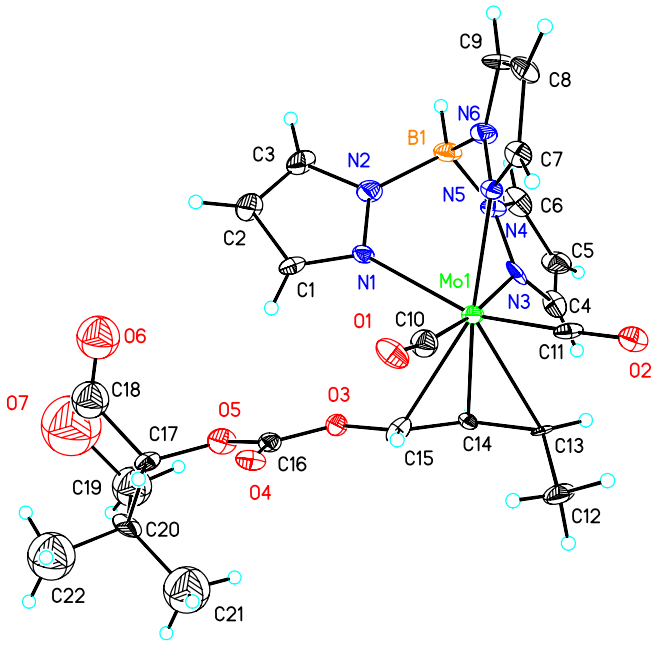


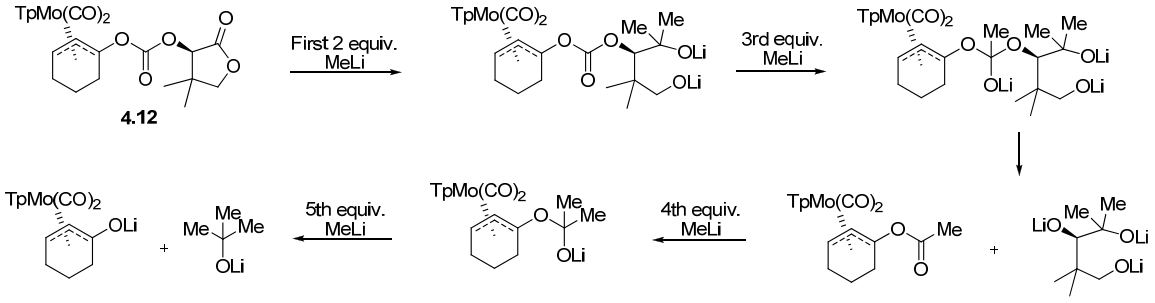
Figure 4.6. ORTEP View of Compound (1*R*, *R*)-4.13

Exchange Reactions with Chiral, Non-racemic Substrates

With single diastereomers of both cyclohexenyl and 2-butenyl complexes **4.12** and **4.13**, respectively, attention was turned to carrying out the exchange reactions. Cleavage of the carbonates and direct conversion to sulfonate esters could not be achieved, leading only to

decomposition, but the carbonates could be cleaved with MeLi and trapped as the corresponding silyl ethers with TBSCl. Scheme 4.5 shows how five equivalents of MeLi could be consumed during cleavage of the pantolactone carbonate.

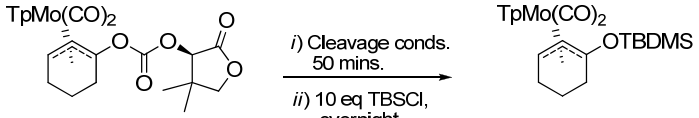
Scheme 4.5. Cleavage of the Pantolactone Carbonate with 5 Equivalents of MeLi



This analysis led to the use of 10 equivalents of MeLi in the initial cleavage reactions, which were carried out at room temperature. Following the addition of MeLi and stirring at room temperature for 50 minutes, the reaction was quenched by addition of TBSCl. Unexpectedly, these conditions led to the isolation of completely racemic silyloxy complex **4.4c** (Table 4.5, Entry 1). This racemization was traced back to the MeLi cleavage step, where it was determined that cooling the reaction to -78 ^{o}C before the addition of MeLi followed by TBSCl suppressed the undesired racemization almost entirely. Even with 10 equivalents of MeLi, very little racemization was observed at -78 ^{o}C (Entry 2). Under the optimized conditions, 5.0 equivalents of MeLi were added at -78 ^{o}C and the reaction was stirred for 50 minutes at -78 ^{o}C before TBSCl was added (Entry 3). Using (1*S*, *R*)-**4.12** (99.8 % de) and 5 equivalents of MeLi at -78 ^{o}C, a 59 % yield of (-)-**4.4c** (99.2 % ee) could be achieved. It was later determined that using 5.0 equivalents of MeLi at room temperature or 0 ^{o}C, followed by an immediate quench with TBSCl, also led to minimal losses in enantiomeric excess (Entry 4). In this case, reacting (1*R*,

R)-**4.12** (97.5 % de) with 5 equivalents of MeLi followed by immediate addition of TBSCl at room temperature afforded (+)-**4.4c** (97.0 % ee). Using 10.0 equivalents of *n*-BuLi at room temperature, complete racemization was again observed (Entry 5). However, when $KOSiMe_3$ was used to cleave the carbonate, even in excess and in the presence of LiCl, no racemization was observed (Entries 6 and 7). Difficulties achieving reliable yields of **4.4c** with $KOSiMe_3$ prevented its regular use.

Table 4.5. Cleavage of the Pantolactone Carbonate Auxiliary



(1*R*, *R*)-**4.12** (+)-**4.4c**

Entry	Cleavage Conditions	Enantiomeric Ratio (HPLC)
1	10.0 equiv MeLi (23 °C)	51:49
2	10.0 equiv MeLi (-78 °C)	99:1
3	5.0 equiv MeLi (-78 °C)	>99:1[a]
4	5.0 equiv MeLi (0 °C)/immediate TBSCl add'n.	98.5:1.5[b]
5	10.0 equiv *n*-BuLi (23 °C)	51:49
6	10.0 equiv $KOSiMe_3$	99:1
7	6.0 equiv $KOSiMe_3$ + 20.0 equiv LiCl	99:1

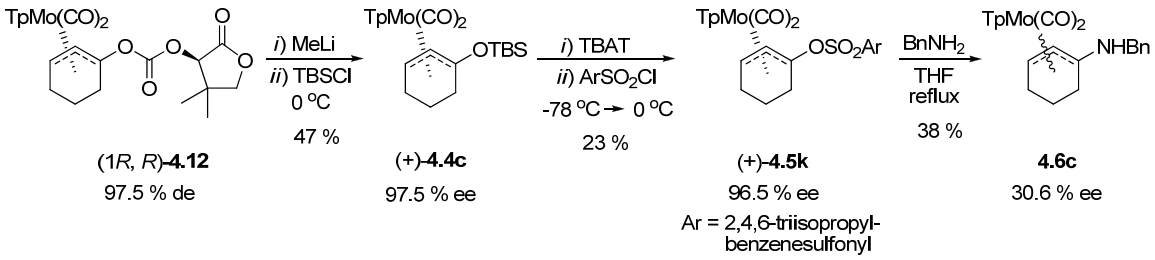
[a]Used (1*S*, *R*)-**4.12**, dr > 99.9:0.1
[b]Used (1*R*, *R*)-**4.12**, dr = 98.75:1.25

Conversion of silyl ethers **4.4b** and **4.4c** to the desired sulfonate esters **4.5e**/**4.5f** and **4.5j**/**4.5k** was carried out by first treating the silyl ethers with TBAT at low temperature and then adding the requisite sulfonyl chloride (Schemes 4.6 and 4.7). While conditions for chiral HPLC separation of the enantiomers of the 2,4,6-triisopropylbenzenesulfonyl-substituted cyclohexenyl complex **4.5k** were developed, enantiomers of the corresponding 2-butenyl complex **4.5f** could not be separated under any of the conditions explored with the available chiral columns.

However, the enantiomers of tosyloxy-substituted 2-butenyl complex **4.5e** could be resolved *via* chiral HPLC, and so, this complex was used in the investigation (Scheme 4.7).

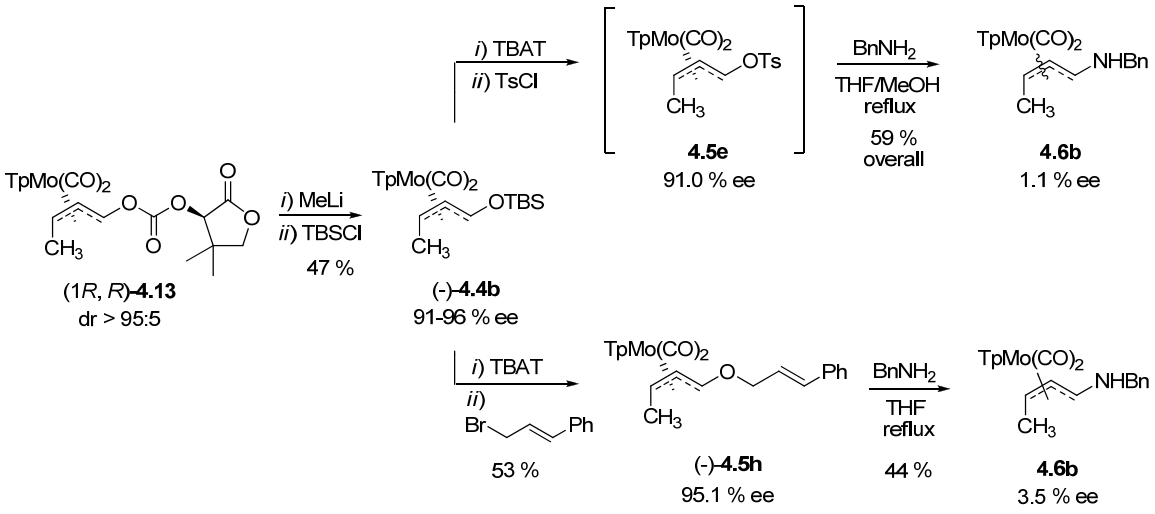
Minimal loss of enantiomeric excess was observed in the conversion of cyclohexenyl carbonate (1*R*, *R*)-**4.12** to the corresponding sulfonate ester complex (+)-**4.5k** (Scheme 4.6). In this series of transformations, diastereomerically-enriched carbonate (1*R*, *R*)-**4.12** (97.5 % ee) was first treated with 5 equivalents of MeLi at 0 ^{o}C. Immediate trapping of the alkoxide intermediate with 10 equivalents of TBSCl produced silyl ether (+)-**4.4c** (97.5 % ee). Treating **4.4c** with TBAT, followed by low-temperature (-78 ^{o}C) addition of 2,4,6-triisopropylbenzenesulfonyl chloride yielded sulfonate ester (+)-**4.5k** in 96.5 % ee. The sulfonate ester (+)-**4.5k** was refluxed in THF for 16 hours in the presence of 30 equivalents of benzyl amine, providing a largely-racemized amino-substituted complex **4.6c** (30.6 % ee). It should be noted that the HPLC behavior of amino-substituted complex **4.6c** is unusual as the racemic sample produced an HPLC measurement indicating a 12.8 % ee. Thus, the degree of confidence in the accuracy of this measurement is low. However, it is clear that exchange of enantiomerically-enriched sulfonate ester (+)-**4.5k** with benzyl amine occurred with significant racemization.

Scheme 4.6. Amino Exchange of Enantioenriched Cyclohexenyl Sulfonate Ester



Cleaving the carbonate of diastereomerically-enriched 2-butenyl complex **4.13** (dr > 95:5) under the same reaction conditions used above for **4.12**, silyl ether (-)-**4.4b** was obtained in 91-96 % ee (Scheme 4.7). Due to the sensitivity of tosylate **4.5e** to isolation, it was generated *in situ* from (-)-**4.4b** (96.2 % ee), and its ee was determined by directly analyzing a sample of the reaction mixture by chiral HPLC. The enantioenriched tosylate (91.0 % ee) was then heated to reflux in the presence of 30 equivalents of benzyl amine in a 1:1 mixture of THF and MeOH for 3 hours, delivering racemic amino-substituted complex **4.6b** (1.1 % ee) in 59 % yield. Silyl ether (-)-**4.4b** (91.1 % ee) was also converted to cinnamyl-substituted complex (-)-**4.5h** (95.1 % ee) and then subjected to exchange by refluxing in THF with $BnNH_2$ (30 equiv). After 23 hours, racemic amino-substituted complex **4.6b** (3.5 % ee) was isolated in 44 % yield. Thus, uncatalyzed amino exchange of both sulfonate esters and alkoxy groups occurred with complete racemization.

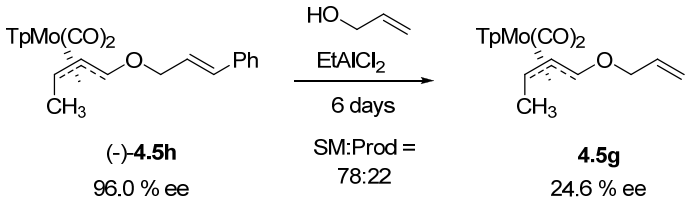
Scheme 4.7. Asymmetric Amino Exchange of Complexes 4.5e and 4.5h



Enantioenriched cinnamyloxy-substituted complex (-)-**4.5h** (96.0 % ee) was also subjected to Lewis acid-catalyzed exchange (Scheme 4.8). When stirred in the presence of allyl

alcohol (25 equiv) and $EtAlCl_2$ (0.5 equiv), an exceedingly slow reaction ensued, producing allyloxy-substituted complex **4.5g**. After six days, analysis of the crude reaction mixture by chiral HPLC showed a 22:78 ratio of desired allyloxy-substituted exchange product **4.5g** (24.6 % ee) to starting cinnamyloxy complex **4.5h**. Methoxy- and isopropyloxy-substituted complexes were not suitable for this study as their enantiomers could not be resolved by chiral HPLC.

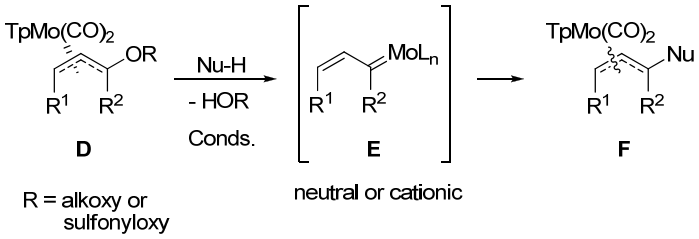
Scheme 4.8. Slow Exchange of Enantioenriched Cinnamyloxy Complex (-)-4.5h



Mechanistic Rationale

For all exchange reactions of 1-alkoxy and 1-sulfonyloxy η^3-allylmolybdenum complexes investigated, racemization was observed when enantiomerically-enriched substrates were used. These results suggest that in all cases exchange proceeds through carbene intermediates. A general mechanism is shown in Scheme 4.9.

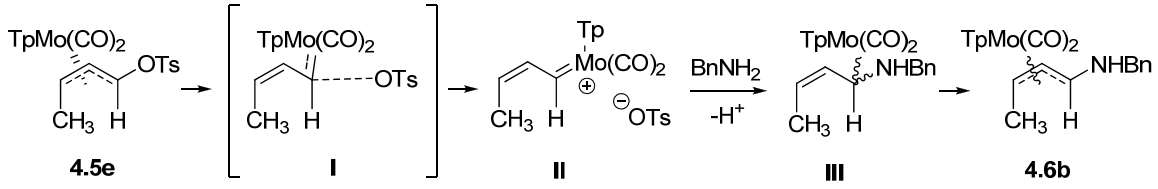
Scheme 4.9. General Mechanism of Exchange Reactions



The extreme sensitivity and reactivity of sulfonate ester complexes is consistent with a solvolysis reaction wherein η^3-to-η^1 slippage of the $TpMo(CO)_2$ fragment occurs in concert with ionization of the sulfonate leaving group, delivering carbene **II** (Scheme 4.10). This carbene may then be intercepted by an external nucleophile from either face, delivering a racemic substitution product after η^1-to-η^3 conversion.

The observation that 1,3-disubstituted sulfonate ester complexes **4.5e** and **4.5f** were more reactive than the corresponding monosubstituted complex **4.5c** may be explained by the lower barrier for η^3-to-η^1 slippage that is attributed to the ground state energy-raising effect of the *anti*-oriented methyl group. As the transformation proceeds from the ground-state η^3-allyl complex, through the transition state to carbene intermediate **II**, an overall decrease in steric strain occurs. The reactivity of cyclohexenyl sulfonate esters towards substitution with amines also supports reaction *via* a synchronous η^3-to-η^1 conversion/ionization event. In this way, a discrete η^1 intermediate never has to form.

Scheme 4.10. Exchange Mechanism for Sulfonate Esters

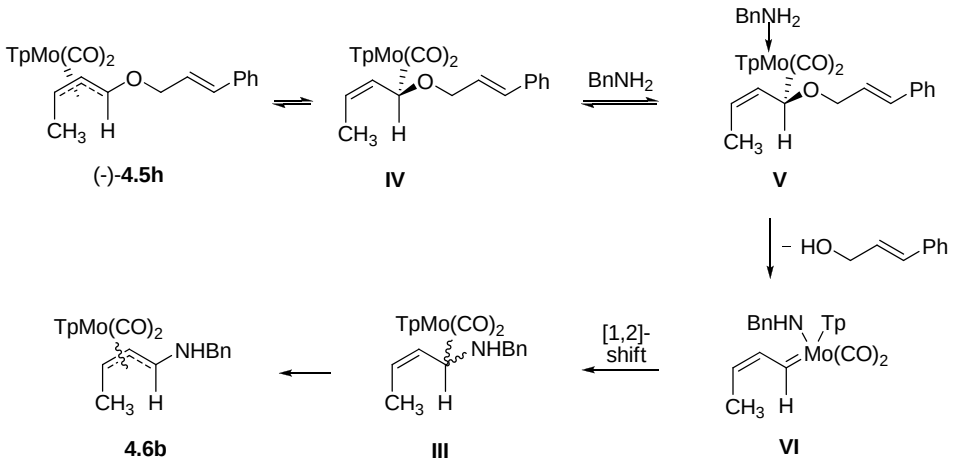


Alkoxy complexes must also undergo η^3-to-η^1 slippage of the $TpMo(CO)_2$ fragment in order to exchange (Scheme 4.11). However, unlike sulfonate ester-substituted complexes, these complexes do not undergo concomitant ionization of the alkoxy group and carbene formation as alkoxides are much poorer leaving groups than sulfonates. Instead, it is more likely that a molecule of benzyl amine fills the empty coordination site, increasing the electron density on the

metal. This increase in electron density promotes metal-assisted ionization of the alkoxy group, delivering carbene **VI**. A 1,2-shift of the amino group from molybdenum to carbon, followed by an η^1-to-η^3 conversion, would deliver substitution product **4.6b**. Enantioenrichment is likely lost upon formation of carbene **VI**, as the barrier to rotation about transition metal-carbene carbon bonds is usually low.[165,166,167,168]

The increase in steric bulk, and therefore, nonbonded interactions, that build up in the transition state when proceeding from η^3-allyl complex **4.5h** to amine-coordinated intermediate **V** explains why the bulkier 1,3-disubstituted complexes **4.5e** and **4.5f** react more slowly than the monosubstituted complex **4.5c**.

Scheme 4.11. Exchange of Alkoxy Substituents With Amines



The eclipsing and gauche interactions which develop between the $TpMo(CO)_2$ fragment and the adjacent methylene on the cyclohexane ring of methoxy complex **4.5i** (Figure 4.7) in the η^3-to-η^1 conversion may present a significant barrier to buildup of the η^1-intermediate as no

[165] Gunnoe, T. B.; White, P. S.; Templeton, J. L. *Organometallics* **1997**, *16*, 370-377.
[166] Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1995**, *14*, 1567-1577.
[167] Adams, H.; Bailey, N. A.; Bentley, G. W.; Hough, G.; Winter, M. J.; Woodward, S. *J. Chem. Soc., Dalton Trans.* **1991**, 749-758.
[168] Manganiello, F. J.; Radcliffe, M. D.; Jones, W. M. *J. Organomet. Chem.* **1982**, *228*, 273-279.

exchange with amines occurred for methoxy-substituted cyclohexenyl complex **4.5i**. Alternatively, η^3-to-η^1 conversion may occur, but the amine and Lewis acid adducts are too hindered to form.

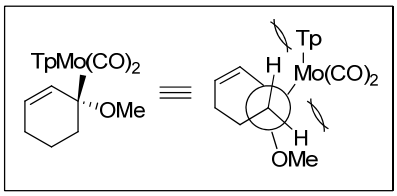
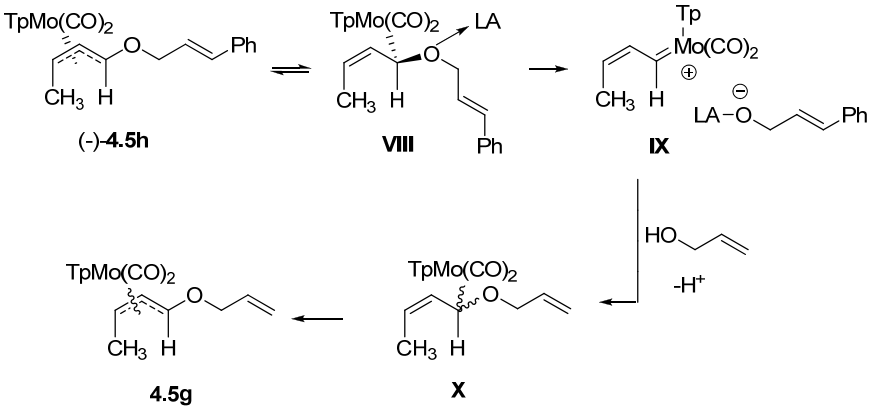


Figure 4.7. Barrier to Cyclohexenyl Exchange

Amines are better ligands for metals than alcohols, making a Lewis acid necessary for exchange of alkoxy substituents with alcohols. The Lewis acid likely facilitates ionization of the alkoxy group, delivering a cationic carbene intermediate **IX** to which the external alcohol nucleophile may add (Scheme 4.12). The increase in nonbonded interactions that again build up in the transition to Lewis acid-bound η^1-intermediate **VIII** explains why 1,3-disubstituted complexes react more slowly than the monosubstituted complex.

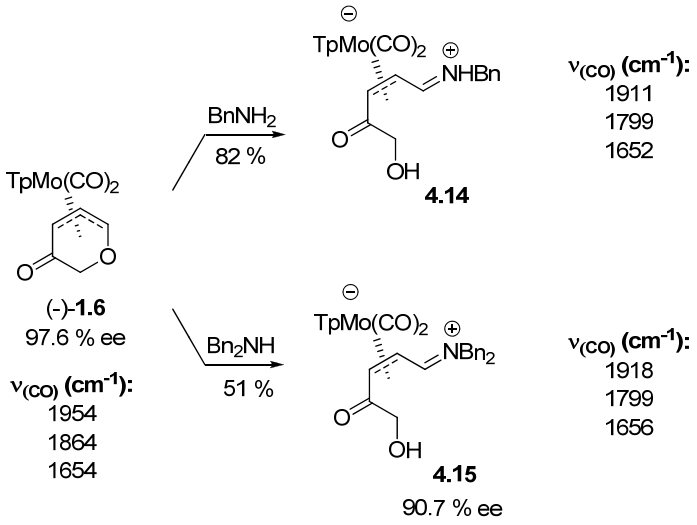
Scheme 4.12. Lewis acid-Catalyzed Exchange of Alkoxy Complexes With External Alcohols



Ring-opening Amination of TpMo(CO)$_2$ 5-Oxo-pyranyl Complex

In addition to the amino exchange reactions described above, TpMo(CO)$_2$ 5-oxo-pyranyl complex **1.6**, a bright orange solid, was found to react with both primary and secondary amine nucleophiles. Rapid ring-opening amination reactions provided dark purple complexes **4.14** and **4.15** in which the oxygen atom of the pyran was substituted by the amine on the metal allyl (Scheme 4.13). IR analysis of the metal carbonyls again showed a shift to lower wavenumbers for the amino-substituted complexes relative to the 5-oxo-pyranyl starting material. These reactions proceeded in excellent yields and with only small loss of enantiomeric excess. Subjecting enantiomerically-enriched 5-oxo-pyranyl complex (-)-**1.6** (97.6 % ee) to reaction with dibenzyl amine delivered ring-opened amination complex **4.15** in 90.7 % ee. These reactions likely follow the mechanism described in Scheme 4.16, which was proposed for similar transformations of related compounds. As the metal remains on the same face of the formal η^3-allyl moiety throughout, enantioenrichment is maintained.

Scheme 4.13. Ring-opening Aminations of Pyranyl Scaffold 1.6



The structure of complex **4.15** was confirmed by single-crystal X-ray crystallography (Figure 4.8). It is of interest to note that as suggested for acyclic amino-substituted complexes **4.6a** and **4.6b**, ring-opened complex **4.15** exhibits significant zwitterionic character. Notable structural features include an η^2-alkenyl molybdenum bonding motif resulting from lengthening of the Mo(1)-C(14) bond. (The Mo(1)-C(14) bond length is 3.007(15) Å compared to 2.368(14) Å and 2.314(15) Å for Mo(1)-C(13) and Mo(1)-C(12), respectively.) This lengthening is attributed to resonance donation from N(7) into the metal allyl. The *syn*-amino/*anti*-keto configuration of **4.15** is consistent with that of other heteroatom-bearing 1,3-disubstituted complexes, including methoxy-substituted complex **4.5d** and benzyl amine-substituted complex **4.6b**.

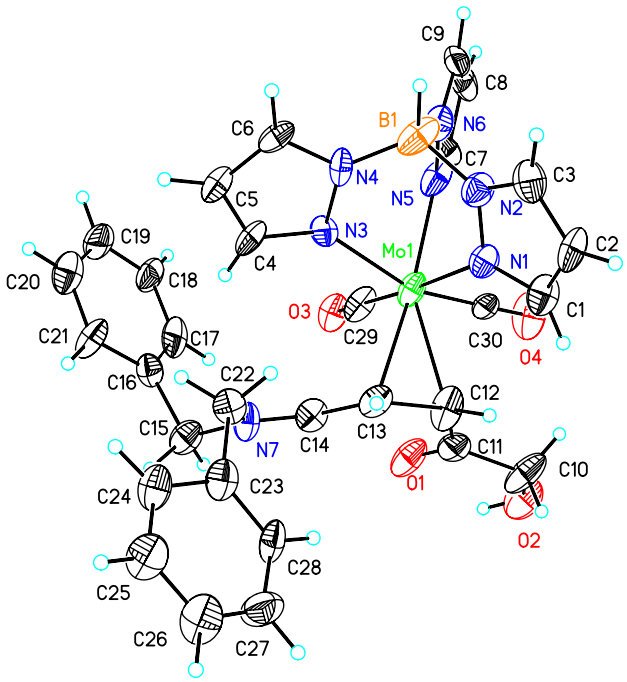
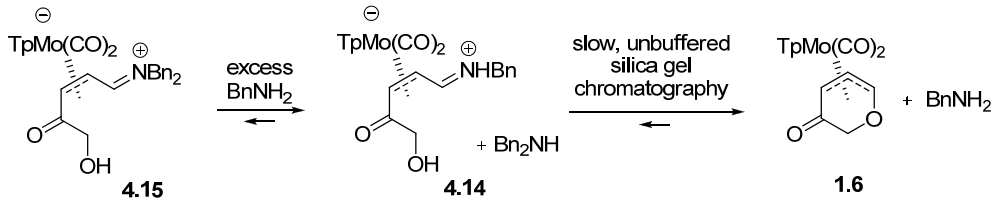


Figure 4.8. ORTEP View of (±)-4.15.

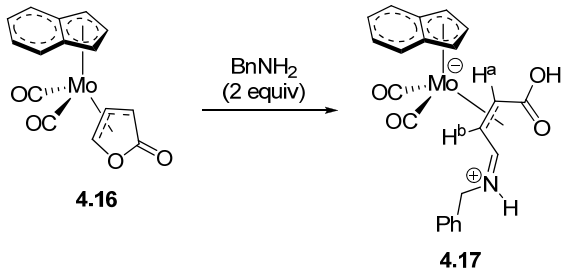
The amino component of the ring-opened amination products was found to undergo further reversible exchange. When stirred in the presence of excess benzyl amine, dibenzylamine adduct **4.15** was slowly converted to benzyl amine adduct **4.14**, and when subjected to slow, unbuffered silica gel column chromatography, 5-oxo-pyranyl complex **1.6** was formed (Scheme 4.14).

Scheme 4.14. Illustration of Amino Substitution Reversibility



Green and co-workers[169] have reported a similar transformation in which η^5-indenyl-η^3-γ-lactonyl complex **4.16** underwent reaction with two equivalents of an external amine nucleophile, delivering ring-opened amino-substituted complex **4.17** (Scheme 4.15). A similar transformation was also carried out with the Cp analog of **4.16**.

Scheme 4.15. Ring-opening Amination of Lactonyl Complexes

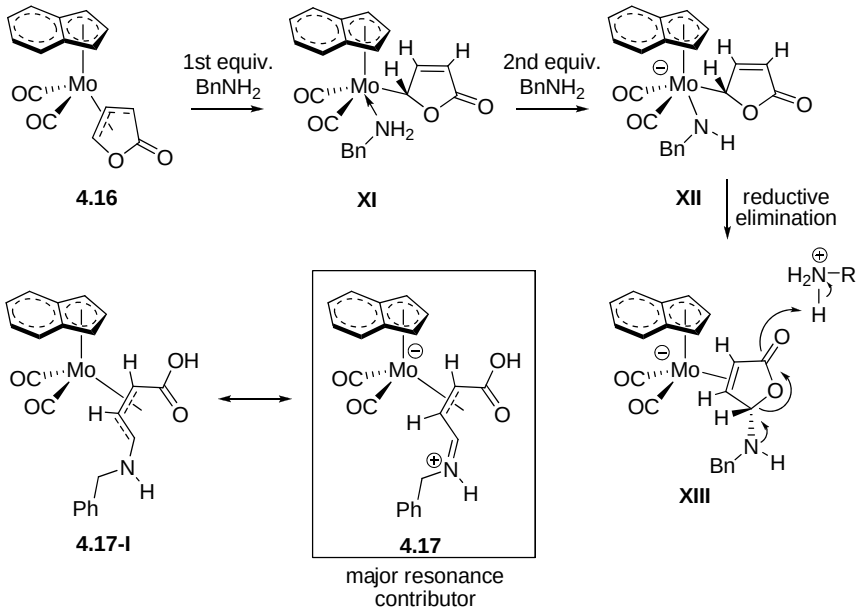


The requirement for at least two molar equivalents of the amine, coupled with the results of an extended Hückel molecular orbital (EHMO) calculation incorporating bond parameters

[169] Butters, C.; Carr, N.; Deeth, R. J.; Green, M.; Green, S. M.; Mahon, M. F. *J. Chem. Soc., Dalton Trans.* **1996**, 2299-2308.

derived from X-ray crystallographic analysis of the lactonyl complex **4.16**, prompted the mechanistic proposal shown in Scheme 4.16. The EHMO calculations provide an image of the relative charge distribution over complex **4.16**. As expected, the carbonyl carbon was a site of localized positive charge (+1.180), as was the γ-carbon C^4 (+0.404) to which the nucleophile had overall added. Interestingly, however, the molybdenum atom was dramatically more electropositive (+1.106) than the γ-carbon C^4. This calculation suggested to Green that the overall transformation of **4.16** to **4.17** proceeds by coordination of the primary amine to the molybdenum atom after it undergoes an η^3-to-η^1 conversion, opening a coordination site and providing an energetically-appropriate LUMO. Deprotonation of the coordinated amine leads to amido-substituted anionic complex **XII**, which undergoes reductive elimination transferring the amido species to C^4 and providing the anionic η^2-alkenyl complex **XIII**. Nitrogen-assisted opening of the lactone delivers zwitterionic η^2-alkene complex **4.17**. Zwitterion **4.17** is a resonance structure of the neutral η^3-allyl complex **4.17-I**. Structure **4.17** is apparently the major contributor.

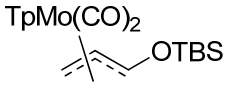
Scheme 4.16. Proposed Mechanism of Ring-opening Amination



In conclusion, a family of related 1-alkoxy and 1-sulfonyloxy-η^3-allylmolybdenum complexes has been shown to undergo a series of exchange reactions with external amines and alcohol nucleophiles. Alkoxy complexes reacted directly with amines, but required the participation of a Lewis acid catalyst to undergo substitution with alcohols. Sulfonyloxy complexes reacted directly with both amines and alcohols in the absence of any catalyst. In all cases, optically active starting materials racemized when subjected to exchange conditions. The reactivity order of each family of complexes suggests that 1-sulfonyloxy complexes react via a synchronous η^3-to-η^1 slippage/ionization event leading to an electrophilic carbene intermediate. Alkoxy-substituted complexes appear to undergo a stepwise η^3-to-η^1 slippage followed by amine or Lewis acid coordination. This coordination enables molybdenum-assisted ejection of the alkoxide and carbene formation. Additionally, 5-oxo-pyranyl complex **1.6** was found to undergo rapid ring-opening amination reactions with both primary and secondary amines. Using enantiomerically-enriched samples of (-)-**1.6**, only relatively small degredation of the enantiomeric purity was observed. These amination reactions have literature precedent.

Experimental Section:

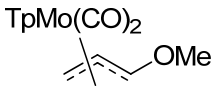
General Methods: Refer to Chapter One.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-(*tert*-butyldimethylsilyloxy)-2-propen-1-yl]molybdenum, (*syn*-OTBS), 4.4a. To a solution of $Mo(DMF)_3(CO)_3$ (6.18 g, 15.5 mmol, 1.1 equiv) in dry, degassed CH_2Cl_2 (20 mL) was added acrolein (90 %, 1.0 mL, 14.1

mmol, 1.0 equiv) and TBSCl (2.34 g, 15.5 mmol, 1.1 equiv). The solution was stirred at room temperature for 1.75 hours before KTp (3.90 g, 15.5 mmol, 1.1 equiv) was added. After stirring an additional 1 hour at room temperature, the solution was passed through a pad of silica gel and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.4a** (4.08 g, 7.60 mmol, 54 %) as a yellow solid.

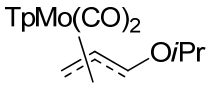
(±)-**4.4a**: IR (cm^{-1}): 1926 (s), 1833 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (br s, 1 H), 8.29 (br s, 1 H), 7.81 (br s, 1 H), 7.58 (br s, 2 H), 7.53 (br s, 1 H), 6.26 (br s, 1 H), 6.18 (br s, 1 H), 6.12 (br s, 1 H), 4.60 (d, *J* = 7.6 Hz, 1 H), 3.80 (dt, *J* = 9.2 Hz, 7.6 Hz, 1 H), 3.27 (dd, *J* = 7.2 Hz, 3.2 Hz, 1 H), 1.24 (dd, *J* = 9.2 Hz, 3.2 Hz, 1 H), 1.04 (s, 9 H), 0.35 (s, 3 H), 0.30 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 231.7, 228.5, 147.3, 145.0, 141.7, 135.7, 134.3, 113.4, 105.8, 105.2, 104.5, 65.0, 47.0, 26.0 (3), 25.9, 18.8, -4.5, -5.4.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-methoxy-2-propen-1-yl]molybdenum, (*syn*-Methoxy), 4.5a. Complex **4.4a** (100 mg, 0.19 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2 mL) and TBAT (111 mg, 0.21 mmol, 1.1 equiv) was added in one portion. After 5 minutes, MeI (0.24 mL, 3.8 mmol, 20.0 equiv) was added. The solution was stirred 14 hours and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.5a** (66.2 mg, 0.15 mmol, 80 %) as an orange solid.

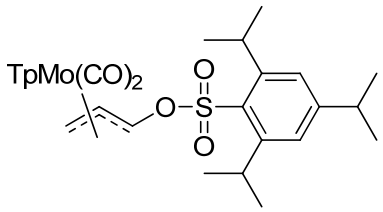
(±)-**4.5a**: IR (cm^{-1}): 1918 (s), 1818 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (br s, 1 H), 8.09 (br s, 1 H), 7.79 (br s, 1 H), 7.56 (br s, 2 H), 7.52 (br s, 1 H), 6.27 (br s, 1 H), 6.16 (br s, 1 H), 6.14 (br s, 1 H), 4.57 (d, *J* = 8.0 Hz, 1 H), 3.84 (s, 3 H), 3.74-3.81 (m, 1 H), 3.29 (dd, *J* = 7.6

Hz, 3.2 Hz, 1 H), 1.25 (dd, *J* = 9.2 Hz, 3.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 232.7, 227.9, 147.2, 144.5, 141.9, 135.8, 134.4, 120.5 (2), 105.9, 105.2, 105.0, 61.9, 59.9, 47.6.



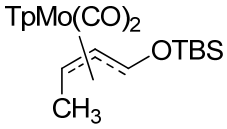
(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-((1-methylethyl)oxy)-2-propen-1-yl]molybdenum, (*syn*-Isopropoxy), 4.5b. Complex **4.4a** (100 mg, 0.19 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2 mL) and TBAT (111 mg, 0.21 mmol, 1.1 equiv) was added in one portion. After 5 minutes, MeI (0.24 mL, 3.8 mmol, 20.0 equiv) was added. The solution was stirred 14 hours and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.5b** (69.4 mg, 0.14 mmol, 76 %) as an orange solid.

(±)-**4.5b**: IR (cm^{-1}): 1918 (s), 1822 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1 H), 8.36 (s, 1 H), 7.82 (s, 1 H), 7.58 (s, 2 H), 7.54 (s, 1 H), 6.27 (s, 1 H), 6.16 (s, 1 H), 6.14 (s, 1 H), 4.69 (d, *J* = 8.0 Hz, 1 H), 4.52-4.58 (m, 1 H), 3.75 (app q, *J* = 7.6 Hz, 1 H), 3.29 (dd, *J* = 7.2 Hz, 2.8 Hz, 1 H), 1.44 (d, *J* = 6.8 Hz, 3 H), 1.42 (d, *J* = 6.4 Hz, 3 H), 1.32 (dd, *J* = 9.2 Hz, 2.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 233.7, 228.0, 147.3, 144.7, 142.2, 135.7 (2), 134.3, 119.4, 105.8, 105.2, 104.7, 76.6, 61.6, 48.2, 22.5, 22.3.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-(2,4,6-triisopropylbenzenesulfonyloxy)-2-propen-1-yl]molybdenum, (*syn*-OSO_2Ar), 4.5c. Complex **4.4a** (50.0 mg, 0.093 mmol, 1.0 equiv) was dissolved in THF (2 mL) and TBAT (55.4 mg, 0.10 mmol, 1.1 equiv) was added in one portion at room temperature. After 15 minutes 2,4,6-triisopropylbenzenesulfonylchloride (30.3 mg, 0.10 mmol, 1.10 equiv) was added in one portion at room temperature. The solution was stirred for 15 minutes at room temperature before being passed through a short pad of silica gel (33 % ethyl acetate in hexanes) and concentrated on a rotary evaporator. Silica gel column chromatography (33 % ethyl acetate in hexanes) provided **4.5c** (58.6 mg, 0.085 mmol, 92 %) as a yellow solid. *Due to the sensitivity of **4.5c** to purification techniques, it was usually generated and used in situ.*

(±)-4.5c: TLC: R_f = 0.60 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2964 (m), 1949 (s), 1864 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.75-8.55 (br, 3 H), 7.54 (br s, 3 H), 7.16 (s, 2 H), 6.18 (br s, 3 H), 4.30 (d, *J* = 6.8 Hz, 1 H), 4.07 (hep, *J* = 6.8 Hz, 2 H), 3.70-3.76 (m, 1 H), 3.27 (dd, *J* = 7.6 Hz, 2.8 Hz, 1 H), 2.92 (hep, *J* = 6.8 Hz, 1 H), 1.25 (d, *J* = 6.8 Hz, 6 H), 1.20 (d, *J* = 6.4 Hz, 6 H), 1.08 (dd, *J* = 9.2 Hz, 3.2 Hz, 1 H), 0.98 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 228.9, 225.9, 154.5, 151.8, 128.9, 124.1, 105.7, 98.7, 69.5, 45.2, 34.5, 25.0, 24.3, 23.8, 23.6. HRMS (ESI) Calcd for $C_{29}H_{38}BMoN_6O_5S$ ($[M+H]^+$): 691.1766. Found: 691.1796.



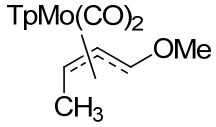
(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-(*tert*-butyldimethylsilyloxy)-2-buten-1-yl]molybdenum, (*anti*-Me/*syn*-OTBS), 4.4b. To a solution of $Mo(DMF)_3(CO)_3$ (14.1 g, 35.4 mmol, 1.2 equiv) in dry, degassed CH_2Cl_2 (60 mL) was added (*E*)-2-butenal (2.4 mL, 29.5 mmol, 1.0 equiv) and TBSCl (4.9 g, 32.4 mmol, 1.1 equiv). The deep red solution was stirred for 30 minutes at room temperature and then KTp (8.9 g, 35.4 mmol, 1.2 equiv) was added in one portion. After stirring an additional 30 minutes at room temperature, the solution was concentrated. The crude product was purified by flash chromatography over silica gel with hexanes-EtOAc (2:1) affording **4.4b** (13.5 g, 24.6 mmol, 83 %).

(±)-**4.4b**: IR (cm^{-1}): 1922 (s), 1830 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 2.0 Hz, 1 H), 8.11 (d, *J* = 1.6 Hz, 1 H), 7.69 (d, *J* = 2.0 Hz, 1 H), 7.56 (d, *J* = 2.0 Hz, 1 H), 7.55 (d, *J* = 2.4 Hz, 1 H), 7.49 (d, *J* = 2.4 Hz, 1 H), 6.24 (t, *J* = 2.0 Hz, 1 H), 6.16 (t, *J* = 2.4 Hz, 1 H), 6.09 (t, *J* = 2.0 Hz, 1 H), 5.28 (d, *J* = 7.6 Hz, 1 H), 3.84-3.87 (m, 2 H), 1.32 (d, *J* = 6.4 Hz, 3 H), 1.00 (s, 9 H), 0.28 (s, 3 H), 0.24 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 231.6, 230.4, 147.3, 145.4, 141.2, 135.8 (2), 134.4, 112.6, 105.8, 105.3, 104.5, 69.7, 57.1, 26.1 (3), 18.9, 17.8, -4.4, -5.3. HPLC: Daicel® Chiralcel OD-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-(+)-**4.4b**: $t_{(+)}$ = 18.48 min; (*R*)-(-)-**4.4b**: $t_{(-)}$ = 17.73 min.

(1*R*, *R*)-**4.13** (-)-**4.4b**

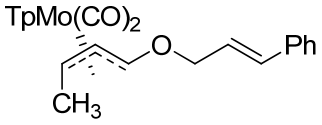
(-)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1*R*)-(η-1,2,3)-1-(*tert*-butyldimethylsilyloxy)-2-buten-1-yl]molybdenum, (*anti*-Me/*syn*-OTBS), (-)-4.4b.

Complex (-)-(1*R*, *R*)-**4.13** (500 mg, 0.84 mmol, 1.0 equiv, dr>95:5) was dissolved in THF (10 mL) and cooled to 0 ^{o}C. MeLi (1.6 M in Et_2O, 2.64 mL, 4.22 mmol, 5.0 equiv) was added dropwise fast and then TBSCl (1.27 g, 8.40 mmol, 10.0 equiv) was immediately added. The reaction was stirred for two hours at 0 ^{o}C and then poured into a separatory funnel containing H_2O (20 mL) and CH_2Cl_2 (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded (-)-**4.4b** (217 mg, 0.39 mmol, 47 %, 96.2 % ee) $[\alpha]_D^{25}$ -128 (*c* 1.04, CH_2Cl_2)] as a bright yellow solid.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-methoxy-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Methoxy), 4.5i. Complex **4.4b** (50 mg, 0.091 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2 mL) and TBAT (54 mg, 0.10 mmol, 1.1 equiv) was added in one portion. The solution was stirred for 5 mins and then MeI (0.11 mL, 1.82 mmol, 20.0 equiv) was added. The solution was stirred for 4.5 hours and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.5i** (29.5 mg, 0.066 mmol, 72 %) as a yellow solid.

(±)-**4.5i**: IR (cm^{-1}): 1918 (s), 1818 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.8 Hz, 1 H), 8.04 (d, *J* = 1.8 Hz, 1 H), 7.71 (d, *J* = 1.8 Hz, 1 H), 7.57 (d, *J* = 1.8 Hz, 1 H), 7.55 (d, *J* = 2.4 Hz, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 6.25 (app t, *J* = 2.4 Hz, 1 H), 6.16 (app t, *J* = 1.8 Hz, 1 H), 6.15 (app t, *J* = 2.4 Hz, 1 H), 5.29 (d, *J* = 8.4 Hz, 1 H), 3.88-3.93 (m, 1 H), 3.83-3.86 (m, 1 H), 3.66 (s, 3 H), 1.34 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 232.5, 229.8, 147.2, 144.8, 141.6, 136.0, 135.8, 134.5, 119.6, 105.9, 105.3, 105.1, 66.0, 59.0, 57.8, 18.0.

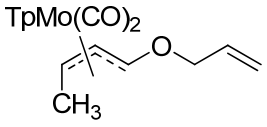


(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-((*E*)-3-phenylprop-2-en-1-oxy)-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Cinnamyloxy), (±)-4.5h and (-)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1*R*)-(η-1,2,3)-1-((*E*)-3-phenylprop-2-en-1-oxy)-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Cinnamyloxy), (-)-4.5h. Complex (±)-**4.4b** (1.00 g, 1.82 mmol, 1.0 equiv) was dissolved in THF (10 mL) and TBAT (1.08 g, 2.00 mmol, 1.1 equiv) was added in one portion. The solution was stirred 55 minutes at room temperature before cinnamyl bromide (1.79 g, 9.10 mmol, 5.0 equiv) was added. After 21 hours, the solution was concentrated and the crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1), affording (±)-**4.5h** (809 mg, 1.46 mmol, 80 %) as a yellow solid.

Complex (-)-**4.4b** (32.4 mg, 0.059 mmol, 1.0 equiv, 91.1 % ee) was dissolved in THF (2 mL) and the solution was cooled to -78 ^{o}C. TBAT (35.0 mg, 0.065 mmol, 1.1 equiv) was added in one portion and the solution was stirred for 15 minutes. Cinnamyl bromide (11 μL, 0.071

mmol, 1.2 equiv) was added and the solution was stirred for 2 hours at -78 °C before being concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded (-)-**4.5h** (17.1 mg, 0.031 mmol, 53 %, 95.1 % ee) $[\alpha]_D^{25}$ -212 (*c* 1.01, CH_2Cl_2)] as a yellow solid.

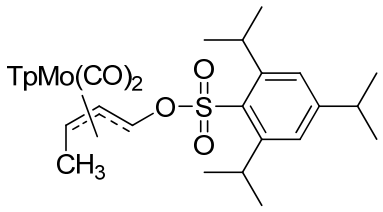
(±)-4.5h: TLC: R_f = 0.67 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3030 (m), 1918 (s), 1818 (s), 1505 (s), 1409 (s). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.49 (d, *J* = 1.8 Hz, 1 H), 8.15 (d, *J* = 1.8 Hz, 1 H), 7.73 (d, *J* = 1.8 Hz, 1 H), 7.57 (d, *J* = 2.4 Hz, 2 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 7.41 (d, *J* = 7.2 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 2 H), 7.28 (t, *J* = 7.2 Hz, 1 H), 6.68 (d, *J* = 16.2 Hz, 1 H), 6.35 (dt, *J* = 16.2 Hz, 6.6 Hz, 1 H), 6.26 (t, *J* =2.4 Hz, 1 H), 6.17 (t, *J* = 2.4 Hz, 1 H), 6.12 (t, *J* = 2.4 Hz, 1 H), 5.38-5.39 (m, 1 H), 4.69 (ddd, *J* = 12.6 Hz, 6.0 Hz, 1.2 Hz, 1 H), 4.49 (ddd, *J* = 13.2 Hz, 6.6 Hz, 1.8 Hz, 1 H), 3.91-3.95 (m, 2 H), 1.34 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 232.9, 229.6, 147.2, 145.1, 141.6, 136.4, 136.0, 135.8, 134.4, 134.3, 128.8 (2), 128.3, 126.8 (2), 123.7, 117.5, 105.9, 105.3, 105.1, 72.7, 66.2, 58.2, 18.0. HRMS (ESI) Calcd for $C_{24}H_{25}BMoN_6O_3$ (M^+): 554.1130. Found: 554.1129. HPLC: Daicel® Chiralcel OJ-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 55%), 20-30 mins (55 % to 60 %), 30-40 mins (60 % to 65 %), 1.5 mL/min, λ = 254 nm, (*S*)-(+)-**4.5h**: $t_{(+)}$ = 33.19 min; (*R*)-(-)-**4.5h**: $t_{(-)}$ = 35.24 min.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-(prop-2-en-1-oxy)-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Allyloxy), 4.5g. Silyl ether **4.4b** (1.00 g, 1.82 mmol, 1.0

equiv) was dissolved in THF (10 mL) and TBAT (1.08 g, 2.00 mmol, 1.1 equiv) was added in one portion. The solution was stirred 55 minutes at room temperature before allyl bromide (1.57 mL, 18.2 mmol, 10.0 equiv) was added. After 20 hours, the solution was concentrated and the crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1), affording **4.5g** as a yellow solid (699 mg, 1.47 mmol, 81 %).

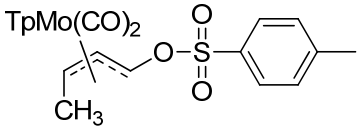
(±)-4.5g: TLC: R_f = 0.70 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2872 (m), 1918 (s), 1818 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.48 (d, *J* = 2.0 Hz, 1 H), 8.09 (d, *J* = 2.0 Hz, 1 H), 7.72 (d, *J* = 2.0 Hz, 1 H), 7.55 (dd, *J* = 2.0 Hz, 0.4 Hz, 2 H), 7.50 (dd, *J* = 2.0 Hz, 0.4 Hz, 1 H), 6.25 (t, *J* = 2.0 Hz, 1 H), 6.16 (t, *J* = 2.0 Hz, 1 H), 6.12 (t, *J* = 2.4 Hz, 1 H), 5.94-6.04 (m, 1 H), 5.39 (dq, *J* = 17.2 Hz, 1.6 Hz, 1 H), 5.27-5.31 (m, 2 H), 4.54 (ddt, *J* = 12.8 Hz, 5.6 Hz, 1.6 Hz, 1 H), 4.33 (ddt, *J* = 12.8 Hz, 5.6 Hz, 1.6 Hz, 1 H), 3.86-3.93 (m, 2 H), 1.33 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 228.5, 225.2, 142.9, 140.7, 137.3, 131.6, 131.5, 130.1, 128.4, 114.5, 113.2, 101.5, 101.0, 100.7, 68.5, 61.7, 53.9, 13.6. HRMS (ESI) Calcd for $C_{18}H_{22}BMoN_6O_3$ ($[M+H]^+$): 479.0895. Found: 479.0900.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-(2,4,6-triisopropylbenzenesulfonyloxy)-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-OSO_2Ar), 4.5f. Complex **4.4b** (500 mg, 0.91 mmol, 1.0 equiv) was dissolved in THF (10 mL) and TBAT (540 mg, 1.00 mmol, 1.1 equiv) was added in one portion at room temperature. After 15 minutes,

2,4,6-triisopropylbenzenesulfonylchloride (606 mg, 2.00 mmol, 2.2 equiv) was added in one portion at room temperature. The solution was stirred for one hour at room temperature before it was poured into a separatory funnel containing water (20 mL) and CH_2Cl_2 (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was then subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). The bright yellow band was collected and concentrated without heat on a rotary evaporator, where some decomposition was observed, providing **4.5f** as a yellow-brown solid (447 mg, 0.64 mmol, 70 %). A sample for characterization was obtained by crystallization from the material isolated after chromatography. *Due to the sensitivity of **4.5f** to purification techniques, it was usually generated and used in situ.*

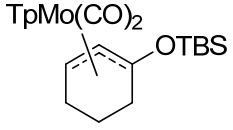
(±)-4.5f: TLC: R_f = 0.69 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 1964 (m), 1945 (s), 1861 (s), 1598 (m), 1463 (m). ^1H NMR (600 MHz, $CDCl_3$): δ 8.51 (s, 1 H), 8.10 (s, 1 H), 7.53 (s, 2 H), 7.48 (s, 1 H), 7.36 (s, 1 H), 7.12 (s, 2 H), 6.26 (s, 1 H), 6.14 (s, 1 H), 6.11 (s, 1 H), 5.00 (d, *J* = 7.2 Hz, 1 H), 3.97 (hep, *J* = 6.6 Hz, 2 H), 3.88 (pent, *J* = 6.6 Hz, 1 H), 3.62 (t, *J* = 7.8 Hz, 1 H), 2.91 (hep, *J* = 6.6 Hz, 1 H), 1.25 (d, *J* = 7.2 Hz, 6 H), 1.17 (d, *J* = 7.2 Hz, 6 H), 1.11 (d, *J* = 6.6 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 231.8, 225.5, 154.4, 151.6 (2), 147.3, 147.0, 139.6, 135.9 (2), 134.6, 129.2, 123.9 (2), 106.0, 105.6, 105.2, 97.7, 73.9, 56.5, 34.5, 29.9, 29.8, 25.1 (2), 23.8 (3), 23.6, 17.5. HRMS (ESI) Calcd for $C_{30}H_{39}BMoN_6O_5S$ ($[M+H]^+$): 705.1926. Found: 705.1926.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-(*p*-toluenesulfonyloxy)-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-OTs), 4.5e.

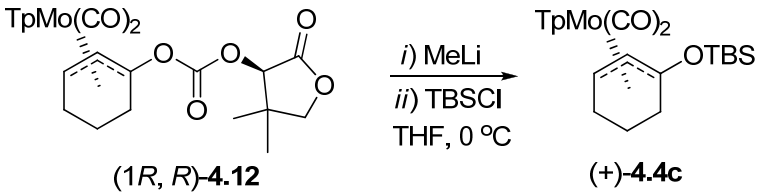
Tosyloxy-substituted complex **4.4b** was synthesized in an analogous manner to 2,4,6-triisopropylbenzenesulfonyloxy-substituted complex **4.5f**, above. However, instead of performing an aqueous work-up, the crude reaction mixture was filtered through a short column of basic alumina and concentrated. Spectroscopic data was then gathered on this material. The use of silica gel and/or $CDCl_3$ for purification and characterization resulted in rapid decomposition of **4.5e**. For synthetic purposes, **4.5e** was generated and used *in situ* without isolation.

(±)-4.5e: TLC: R_f = 0.47 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2964 (m), 1942 (s), 1857 (s), 1594 (m), 1505 (m), 1432 (m). ^{1}H NMR (C_6D_6, 400 MHz): δ 8.49 (d, *J* = 2.0 Hz, 1 H), 8.41 (d, *J* = 2.0 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 2.0 Hz, 1 H), (1 proton obscured by C_6H_6), 7.01 (d, *J* = 1.6 Hz, 1 H), 6.98 (d, *J* = 2.0 Hz, 1 H), 6.64 (d, *J* = 8.4 Hz, 2 H), 5.86 (t, *J* = 2.0 Hz, 1 H), 5.72 (t, *J* = 2.4 Hz, 1 H), 5.65 (t, *J* = 2.4 Hz, 1 H), 5.36 (d, *J* = 7.2 Hz, 1 H), 3.78 (t, *J* = 8.4 Hz, 1 H), 3.54-3.61 (m, 1 H), 1.78 (s, 3 H), 1.10 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (d_6-benzene, 100 MHz): δ 230.9, 227.0, 147.8, 147.6, 145.2, 141.1, 136.5, 136.2, 134.5, 133.6, 130.2 (2), 129.1 (2), 106.6, 106.1, 106.0, 99.3, 71.9, 58.6, 30.8, 21.5, 17.5. HPLC: Daicel® Chiralcel OJ-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-**4.5e**: $t_{(S)}$ = 10.31 min; (*R*)-**4.5e**: $t_{(R)}$ = 10.88 min.

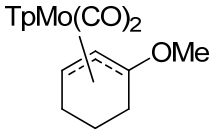


(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-(*tert*-butyldimethylsilyloxy)-2-cyclohexen-1-yl]molybdenum, 4.4c. To a solution of $Mo(DMF)_3(CO)_3$ (12.7 g, 31.8 mmol, 1.1 equiv) in dry, degassed CH_2Cl_2 (100 mL) was added cyclohexenone (2.81 mL, 28.9 mmol, 1.0 equiv) and TBSCl (4.79 g, 31.8 mmol, 1.1 equiv). The solution was stirred at room temperature for 1.5 hours before KTp (8.01 g, 31.8 mmol, 1.1 equiv) was added. The solution was stirred for an additional 45 minutes at room temperature, filtered through a short pad of silica gel, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.4c** (10.8 g, 18.7 mmol, 65 %) as a red-orange solid.

(±)-**4.4c**: IR (cm^{-1}): 1915 (s), 1822 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 1.6 Hz, 1 H), 7.83 (d, *J* = 1.6 Hz, 1 H), 7.61 (br s, 2 H), 7.58 (d, *J* = 2.0 Hz, 1 H), 7.48 (d, *J* = 2.0 Hz, 1 H), 6.21 (app t, *J* = 2.0 Hz, 1 H), 6.19 (app t, *J* = 2.0 Hz, 1 H), 6.09 (app t, *J* = 2.4 Hz, 1 H), 3.90-3.93 (m, 1 H), 3.50 (d, *J* = 8.0 Hz, 1 H), 2.39 (dd, *J* = 16.8 Hz, 6.8 Hz, 1 H), 2.22-2.31 (m, 1 H), 2.04-2.12 (m, 1 H), 1.89-1.97 (m, 1 H), 1.20-1.28 (m, 1 H), 0.78-0.98 (m, 1 H), 0.92 (s, 9 H), 0.06 (s, 3 H), -0.49 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 230.5, 230.2, 146.8, 146.5, 139.3, 135.9 (2), 134.8, 134.5, 105.7, 105.4, 104.9, 64.6, 55.8, 32.0, 26.1 (3), 23.3, 19.8, 18.7, -3.7, -5.4. HPLC: Daicel® Chiralcel OD-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 20-30 mins (75%-85%), 1.5 mL/min, λ = 254 nm, (*S*)-(-)-**4.4c**: $t_{(-)}$ = 19.29 min.; (*R*)-(+)-**4.4c**: $t_{(+)}$ = 20.19 min.



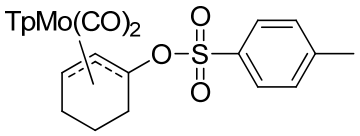
(+)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1*R*)-(η-1,2,3)-1-(*tert*-butyldimethylsilyloxy)-2-cyclohexen-1-yl]molybdenum, (+)-4.4c. Complex (1*R*, *R*)-**4.12** (448 mg, 0.73 mmol, 1.0 equiv, 97.5 % de) was dissolved in THF (10 mL) and cooled to 0 ^{o}C. MeLi (1.6 M in diethyl ether, 2.28 mL, 3.65 mmol, 5.0 equiv) was added dropwise fast. TBSCl (1.10 g, 7.30 mmol, 10.0 equiv) was added in one portion and the solution was warmed to room temperature. After 1.5 hours, the reaction mixture was poured into a separatory funnel containing H_2O (20 mL) and CH_2Cl_2 20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1), affording (+)-**4.4c** (199 mg, 0.34 mmol, 47 %, 97.5 % ee) [$[\alpha]_D^{25}$ +418 (*c* 0.47, CH_2Cl_2)] as an orange solid.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-methoxy-2-cyclohexen-1-yl]molybdenum, 4.5i. Complex **4.4c** (500 mg, 0.87 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (5 mL) and TBAF (1.0 M in THF, 2.17 mL, 2.17 mmol, 2.5 equiv) and MeI (1.08 mL, 17.4 mmol, 20 equiv) were added in succession. The solution was stirred at room temperature for 23 hours and then concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.5i** (342 mg, 0.72 mmol, 83 %) as an orange solid.

(±)-**4.5i**: IR (cm^{-1}): 1907 (s), 1810 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.42 (d, *J* = 1.8 Hz, 1 H), 7.85 (d, *J* = 1.2 Hz, 1 H), 7.65 (d, *J* = 1.2 Hz, 1 H), 7.62 (d, *J* = 1.8 Hz, 2 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 6.20-6.22 (m, 2 H), 6.15 (app t, *J* = 1.8 Hz, 1 H), 3.94 (br d, *J* = 8.4 Hz, 1 H), 3.64

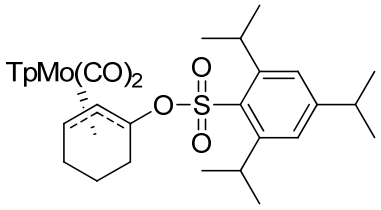
(d, J = 8.4 Hz, 1 H), 3.13 (s, 3 H), 2.52 (dd, J = 16.8 Hz, 6.6 Hz, 1 H), 2.37 (ddd, J = 18.0 Hz, 11.4 Hz, 7.2 Hz, 1 H), 2.10-2.16 (m, 1 H), 1.99-2.02 (m, 1 H), 1.27-1.32 (m, 1 H), 0.90-0.98 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 230.5, 230.2, 146.7, 144.5, 140.7, 139.7, 136.2, 135.9, 134.5, 105.6, 105.4, 105.3, 58.2, 56.3, 54.9, 28.7, 23.4, 19.1.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-(*p*-toluenesulfonyloxy)-2-cyclohexen-1-yl]molybdenum, 4.5j. Complex **4.4c** (300 mg, 0.52 mmol, 1.0 equiv) was dissolved in THF (10 mL) and TBAT (338 mg, 0.63 mmol, 1.2 equiv) was added in one portion. The solution was stirred 25 minutes at room temperature, cooled to 0 ^{o}C, and then *p*-toluenesulfonyl chloride (120 mg, 0.63 mmol, 1.2 equiv) was added in one portion. The solution was stirred 4 hours at 0 ^{o}C and then concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1) affording **4.5j** (104 mg, 0.17 mmol, 32 %) as a yellow-brown solid.

(±)-4.5j: TLC: R_f = 0.56 (hexanes-EtOAc = 4:1). IR (cm^{-1}): 3150-2853 (m), 1934 (s), 1849 (s), 1409 (s), 1505 (m), 1598 (w). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.49 (d, J = 1.8 Hz, 1 H), 7.90 (d, J = 2.4 Hz, 1 H), 7.57 (d, J = 1.8 Hz, 1 H), 7.56 (d, J = 1.8 Hz, 1 H), 7.46 (d, J = 2.4 Hz, 1 H), 7.39 (d, J = 2.4 Hz, 1 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.00 (d, J = 8.4 Hz, 2 H), 6.24 (t, J = 2.4 Hz, 1 H), 6.13 (t, J = 2.4 Hz, 1 H), 6.10 (t, J = 2.4 Hz, 1 H), 3.92 (s, 2 H), 2.69-2.64 (m, 1 H), 2.31 (s, 3 H), 2.24-2.21 (m, 1 H), 2.10 (dt, J = 13.8 H, 5.4 Hz, 1 H), 1.84-1.81 (m, 1 H), 1.26-1.20 (m, 1 H), 0.58-0.52 (m, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 229.0, 226.1, 146.9, 146.8, 144.6, 139.0, 136.0, 135.9, 135.2, 134.4, 129.5 (2), 127.6 (2), 114.4, 105.9, 105.4, 105.3, 66.0,

58.6, 30.0, 22.4, 21.7, 20.5. HRMS (ESI) Calcd for $C_{24}H_{26}BMoN_6O_5S([M+H]^+)$: 619.0827. Found: 619.0829.



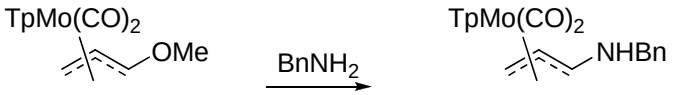
(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-(2,4,6-triisopropylbenzenesulfonyloxy)-2-cyclohexen-1-yl]molybdenum, (±)-4.5k and (+)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1*R*)-(η-1,2,3)-1-(2,4,6-triisopropylbenzenesulfonyloxy)-2-cyclohexen-1-yl]molybdenum, (+)-4.5k. Complex **4.4c** (500 mg, 0.87 mmol, 1.0 equiv) was dissolved in THF (10 mL) and TBAT (516 mg, 0.96 mmol, 1.1 equiv) was added in one portion at room temperature. After 15 minutes, the solution was cooled to -78 ^{o}C, and 2,4,6-triisopropylbenzenesulfonylchloride (291 mg, 0.96 mmol, 1.1 equiv) was added in one portion. (*Note: It is important that 2,4,6-triisopropylbenzenesulfonylchloride be added to the solution at -78 ^{o}C. Addition at higher temperatures leads to severe decomposition.*) The reaction mixture was immediately warmed to 0 ^{o}C, where it was maintained for 4.5 hours before being passed through a short pad of silica gel and concentrated. The crude material was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1) and the yellow band was collected to afford (±)-**4.5k** (411 mg, 0.56 mmol, 65 %) as a yellow solid.

Similar treatment of (+)-**4.4c** (199 mg, 0.34 mmol, 1.0 equiv, 97.5 % ee) with TBAT (202 mg, 0.37 mmol, 1.1 equiv) and 2,4,6-triisopropylbenzenesulfonylchloride (112 mg, 0.37

mmol, 1.1 equiv) in THF (5 mL) afforded (+)-**4.5k** (56.6 mg, 0.078 mmol, 23 %, 96.5 % ee) [$[\alpha]_D^{25}$ +82 (*c* 0.18, CH_2Cl_2)] as a bright yellow solid.

(±)-4.5k: TLC: R_f = 0.72 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2961 (m), 1938 (s), 1849 (s), 1602 (m), 1505 (m), 1463 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.53 (d, *J* = 1.8 Hz, 1 H), 7.69 (d, *J* = 2.4 Hz, 1 H), 7.62 (d, *J* = 1.8 Hz, 1 H), 7.57 (d, *J* = 2.4 Hz, 1 H), 7.47 (d, *J* = 2.4 Hz, 1 H), 7.42 (d, *J* = 2.4 Hz, 1 H), 7.11 (s, 2 H), 6.25 (t, *J* = 2.4 Hz, 1 H), 6.19 (t, *J* = 2.4 Hz, 1 H), 5.69 (t, *J* = 2.4 Hz, 1 H), 4.36 (d, *J* = 7.8 Hz, 1 H), 4.10 (hep, *J* = 6.6 Hz, 2 H), 4.03 (br d, *J* = 8.4 Hz, 1 H), 2.89 (hep, *J* = 6.6 Hz, 1 H), 2.59-2.64 (m, 1 H), 2.21 (dd, *J* = 15.0 Hz, 6.0 Hz, 1 H), 2.11 (dt, *J* = 13.2 Hz, 6.0 Hz, 1 H), 1.87 (dt, *J* = 14.4 Hz, 4.8 Hz, 1 H), 1.25 (d, *J* = 6.6 Hz, 6 H), 1.19-1.21 (m, 1 H), 1.17 (d, *J* = 6.6 Hz, 6 H), 1.00 (d, *J* = 6.6 Hz, 6 H), 0.52-0.59 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 229.0, 226.5, 154.1, 150.8 (2), 146.9, 146.1, 139.5, 136.2, 135.8, 134.3, 131.4, 123.9 (2), 114.7, 105.9, 105.6, 104.4, 66.9, 59.6, 34.4, 29.8 (3), 24.5 (2), 24.4 (2), 23.7 (2), 22.6, 20.7. HRMS (ESI) Calcd for $C_{32}H_{41}BMoN_6O_5S$ ($[M]^+$): 731.2079. Found: 731.2079. HPLC: Daicel® Chiralcel OJ-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-(-)-**4.5k**: $t_{(S)}$ = 18.36 min; (*R*)-(+)-**4.5k**: $t_{(R)}$ = 17.32 min.

Procedures For Direct Exchange of Alkoxy Substitutents with Amines:

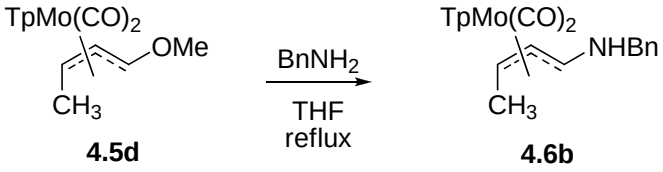


4.5a **4.6a**

(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-propen-1-yl]molybdenum, (*syn*-Benzylamino), 4.6a. Methoxy-substituted complex **4.5a** (100 mg, 0.23 mmol, 1.0 equiv) was dissolved in THF (3 mL) and benzyl amine (0.75 mL, 6.88 mmol, 30.0

equiv) was added. After 20 hours, the reaction mixture was concentrated and the crude material was subjected to flash chromatography over silica gel with hexanes-ethyl acetate (4:1). The red band was collected, affording **4.6a** (112 mg, 0.22 mmol, 95 %) as a red solid.

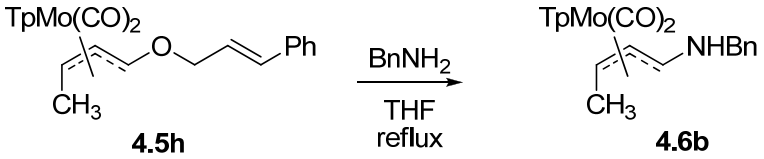
(±)-4.6a: TLC: R_f = 0.45 (hexanes-EtOAc =). IR (cm^{-1}): 3397 (m), 3034 (w), 2478 (m), 1903 (s), 1783 (s), 1698 (m), 1571 (s), 1502 (s), 1455 (m). ^{1}H NMR (400 MHz, C_6D_6): δ 8.41 (d, *J* = 1.6 Hz, 1 H), 7.51 (d, *J* = 1.2 Hz, 1 H), 7.46 (d, *J* = 2.0 Hz, 1 H), 7.39 (d, *J* = 2.0 Hz, 1 H), 7.30 (d, *J* = 2.0 Hz, 1 H), 7.23 (d, *J* = 2.4 Hz, 1 H), 7.03-7.07 (m, 3 H), 6.75-6.77 (m, 2 H), 5.88 (t, *J* = 2.0 Hz, 1 H), 5.85 (t, *J* = 2.0 Hz, 1 H), 5.74 (t, *J* = 2.0 Hz, 1 H), 5.27 (app t, *J* = 9.6 Hz, 1 H), 3.36-3.41 (m, 1 H), 3.24-3.32 (m, 3 H), 2.57-2.63 (m, 1 H), 1.48 (dd, *J* = 8.8 Hz, 4.8 Hz, 1 H). ^{13}C NMR (100 MHz, C_6D_6): δ 234.5, 231.9, 147.5, 144.7, 140.1, 137.7, 136.2, 135.6, 134.9, 133.1, 129.1 (2), 128.5 (2), 106.3, 105.7, 105.6, 77.9, 57.1, 49.5, 44.9. HRMS (ESI) Calcd for $C_{21}H_{23}BMoN_7O_2$ ($[M+H]^+$): 514.1054. Found: 514.1060.



4.5d **4.6b**

(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Benzylamino), 4.6b. Methoxy-substituted molybdenum complex **4.5d** (25.0 mg, 0.056 mmol, 1.0 equiv) was dissolved in THF (2 mL), benzyl amine (0.18 mL, 1.7 mmol, 30 equiv) was added, and the solution was heated to reflux. After refluxing for 20.5 hours, the solution was concentrated and the residue was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). The red band was collected to afford **4.6b** as a red solid (21.8 mg, 0.042 mmol, 74 %).

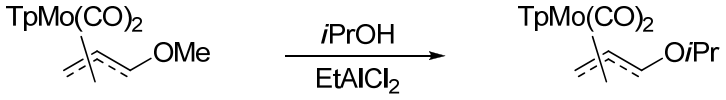
(±)-4.6b: TLC: R_f = 0.53 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3401 (br), 2922 (m), 1899 (s), 1783 (s), 1575 (s), 1502 (s), 1455 (m). ^{1}H NMR (400 MHz, C_6D_6): δ 8.42 (d, *J* = 2.0 Hz, 1 H), 7.48 (d, *J* = 2.0 Hz, 1 H), 7.45 (d, *J* = 2.0 Hz, 1 H), 7.39 (d, *J* = 2.0 Hz, 1 H), 7.23-7.24 (m, 2 H), 7.03-7.08 (m, 3 H), 6.71-6.73 (m, 2 H), 6.01 (dd, *J* = 11.2 Hz, 9.2 Hz, 1 H), 5.87 (q, *J* = 2.4 Hz, 2 H), 5.74 (t, *J* = 2.4 Hz, 1 H), 3.92 (app pent, *J* = 6.8 Hz, 1 H), 3.38-3.40 (m, 1 H), 3.27 (dd, *J* = 14.4 Hz, 4.8 Hz, 1 H), 3.04 (dd, *J* = 14.4 Hz, 5.2 Hz, 1 H), 2.84 (dd, *J* = 11.2 Hz, 8.4 Hz, 1 H), 1.73 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, C_6D_6): δ 235.6, 232.1, 147.4, 145.1, 140.3, 137.6, 136.2, 135.5, 135.0, 130.9, 129.0 (2), 128.4 (2), 106.2, 105.7, 105.6, 62.4, 54.3, 48.9, 19.7. HRMS (ESI) Calcd for $C_{22}H_{25}BMoN_7O_2$ ($[M+H]^+$): 528.1211. Found: 528.1217. HPLC: Daicel® Chiralcel OD-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, Enantiomer 1: t_1 = 13.55 min.; Enantiomer 2: t_2 = 15.21 min.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Benzylamino), 4.6b. Cinnamyloxy-substituted molybdenum complex **4.5h** (25.0 mg, 0.045 mmol, 1.0 equiv) was dissolved in THF (2 mL), benzyl amine (0.15 mL, 1.4 mmol, 30 equiv) was added, and the solution was heated to reflux. After 24 hours, the solution was concentrated and the crude material was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). The red band was collected, affording **4.6b** (13.7 mg, 0.026 mmol, 58 %) as a red solid.

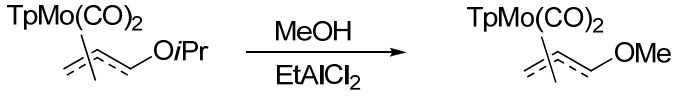
Similar treatment of (-)-**4.5h** (17.1 mg, 0.031 mmol, 1.0 equiv, 95.1 % ee) with $BnNH_2$ (0.10 mL, 0.93 mmol, 30 equiv) in THF (1 mL) afforded **4.6b** (7.2 mg, 0.014 mmol, 44 %, 3.5 % ee) as a red solid.

Procedures For Lewis acid-Catalyzed Exchange of Alkoxy Substituents with Alcohols:



4.5a **4.5b**

(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-((1-methylethyl)oxy)-2-propen-1-yl]molybdenum, (*syn*-Isopropoxy), 4.5b. Methoxy-substituted complex **4.5a** (100 mg, 0.23 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (3 mL), and *i*PrOH (0.35 mL, 4.59 mmol, 20 equiv) and $EtAlCl_2$ (1.0 M in hexanes, 0.092 mL, 0.092 mmol, 0.40 equiv) were added in succession. The flask was sealed and the solution was stirred overnight at room temperature. After 26 hours, the solution was concentrated and the crude reaction mixture was subjected to flash chromatography over silica gel with hexanes-EtOAc (9:1). The yellow band was collected, affording **4.5b** (79.6 mg, 0.17 mmol, 72 %) as a yellow solid.

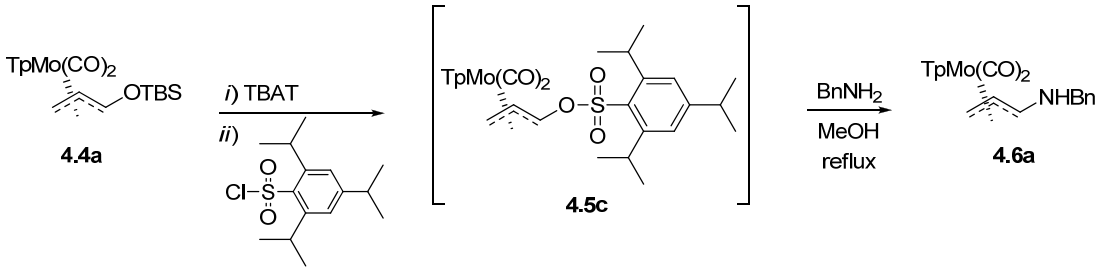


4.5b **4.5a**

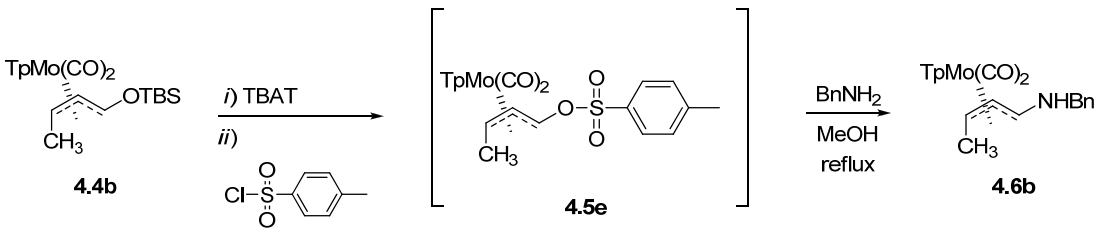
(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-methoxy-2-propen-1-yl]molybdenum, (*syn*-Methoxy), 4.5a. Isopropyloxy-substituted complex **4.5b** (43.0 mg, 0.093 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2 mL) and MeOH (75 μL, 1.85 mmol, 20 equiv) and $EtAlCl_2$ (1.0 M in hexanes, 0.037 mL, 0.037 mmol, 0.4 equiv) were added in succession. The

solution was stirred 4 hours at room temperature and then concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.5a** (35.1 mg, 0.080 mmol, 87 %) as a yellow solid.

Procedures For Direct Exchange of Sulfonate Ester Substituents with Amines and Alcohols:

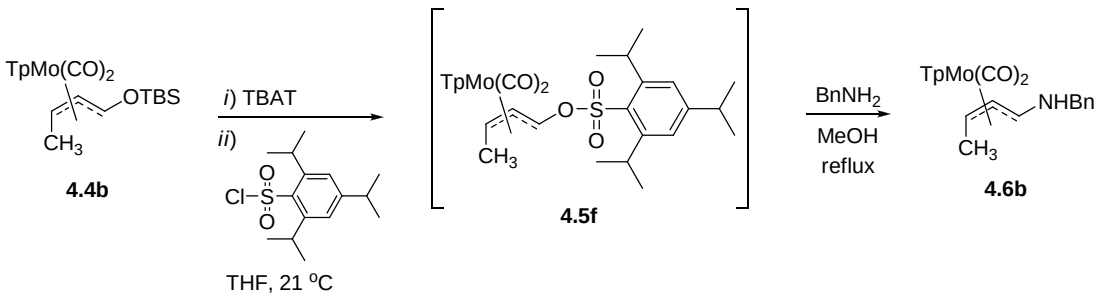


(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-propen-1-yl]molybdenum, (*syn*-Benzylamino), 4.6a. Complex **4.4a** (50.0 mg, 0.093 mmol, 1.0 equiv) was dissolved in THF (2 mL) and TBAT (55.4 mg, 0.10 mmol, 1.1 equiv) was added in one portion at room temperature. The solution was stirred for 5 minutes before 2,4,6-triisopropylbenzenesulfonylchloride (30.3 mg, 0.10 mmol, 1.1 equiv) was added in one portion at room temperature. The reaction mixture was stirred for 10 minutes before benzyl amine (0.31 mL, 2.79 mmol, 30 equiv) and MeOH (2 mL) were added and the solution was refluxed for two hours. The reaction mixture was concentrated on a rotary evaporator and then subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). The red band was collected, affording **4.6a** (37.2 mg, 0.073 mmol, 78 %) as a red solid.

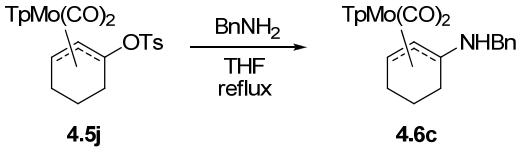


(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Benzylamino), 4.6b. Silyl ether (±)-**4.4b** (100 mg, 0.18 mmol, 1.0 equiv) was dissolved in THF (2 mL) and TBAT (108 mg, 0.20 mmol, 1.1 equiv) was added in one portion. After 5 minutes, the reaction mixture was cooled to 0 ^{o}C and *p*-TsCl (38.1 mg, 0.20 mmol, 1.1 equiv) was added. After 10 minutes, MeOH (2 mL) and benzyl amine (0.59 mL, 5.40 mmol, 30 equiv) were added and the solution was heated to reflux for 2 hours and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.6b** (50.2 mg, 0.096 mmol, 53 %) as a red solid.

Silyl ether (-)-**4.4b** (50.0 mg, 0.091 mmol, 1.0 equiv, 96.2 % ee) was dissolved in THF (1.5 mL) and TBAT (54.0 mg, 0.10 mmol, 1.1 equiv) was added in one portion. After 5 minutes, the reaction was cooled to 0 ^{o}C and *p*-TsCl (19.1 mg, 0.10 mmol, 1.1 eq) was added. After 10 minutes, a sample of the crude reaction mixture was analyzed by chiral HPLC and tosylate **4.5e** was determined to have a 91.0 % ee). MeOH (1.5 mL) and benzyl amine (0.30 mL, 2.73 mmol, 30 equiv) were added to the reaction and the solution was heated to reflux for 3 hours and then concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.6b** (28.3 mg, 0.054 mmol, 59 %, 1.1 % ee) as a red solid.



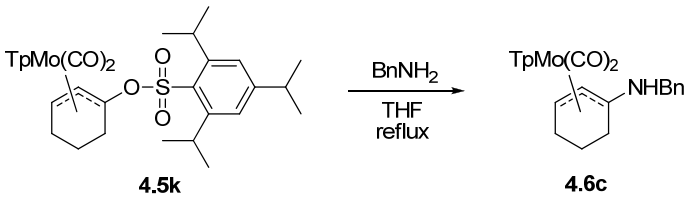
(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Benzylamino), 4.6b. Complex **4.4b** (100 mg, 0.18 mmol, 1.0 equiv) was dissolved in THF (2 mL) and tetrabutylammonium triphenyldifluorosilicate (TBAT) (108 mg, 0.20 mmol, 1.1 equiv) was added in one portion at room temperature. The solution was stirred for 5 minutes before 2,4,6-triisopropylbenzenesulfonylchloride (60.6 mg, 0.20 mmol, 1.1 equiv) was added in one portion at room temperature. After stirring 10 minutes, MeOH (2 mL) and benzyl amine (0.59 mL, 5.4 mmol, 30 equiv) were added and the solution was refluxed for 2 hours. The reaction mixture was then concentrated under reduced pressure and passed through a short pad of silica gel. The solution was again concentrated and subjected to flash chromatography over silica gel with hexanes-EtOAc (2:1). The red band was collected, affording **4.6b** as a red solid (70.1 mg, 0.13 mmol, 74 %).



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-cyclohexen-1-yl]molybdenum, 4.6c. Complex **4.5j** (52.0 mg, 0.084 mmol, 1.0 equiv) was dissolved in THF (2 mL), benzyl amine (0.14 mL, 1.27 mmol, 15 equiv) was added, and the solution was heated to reflux. After 18 hours, the solution was concentrated and the crude reaction mixture was

subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). The red band was collected, affording **4.6c** as a red solid (20.9 mg, 0.038 mmol, 45 %).

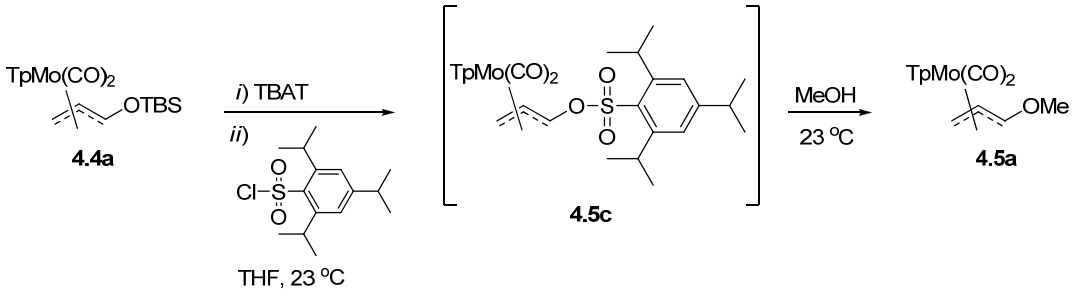
(±)-4.6c: TLC: R_f = 0.53 (hexanes-EtOAc = 4:1). IR (cm^{-1}) 3374 (br, w), 2930 (m), 2478 (m), 1888 (s), 1772 (s). ^1H NMR (C_6D_6, 400 MHz): δ 8.45 (d, *J* = 1.2 Hz, 1 H), 7.52 (s, 1 H), 7.50 (d, *J* = 2.0 Hz, 1 H), 7.45 (d, *J* = 2.0 Hz, 1 H), 7.37 (d, *J* = 1.2 Hz, 1 H), 7.26 (d, *J* = 2.0 Hz, 1 H), 7.02-7.06 (m, 3 H), 6.70 (d, *J* = 6.4 Hz, 2 H), 5.88-5.90 (m, 2 H), 5.74 (t, *J* = 1.6 Hz, 1 H), 3.93-3.98 (m, 2 H), 3.18-3.44 (m, 2 H), 2.50-2.53 (m, 1 H), 2.35-2.38 (m, 1 H), 2.17-2.22 (m, 1 H), 1.70-1.84 (m, 2 H), 1.23-1.37 (m, 2 H). ^{13}C NMR (C_6D_6, 100 MHz): δ 233.9 (2), 147.5, 144.2, 140.3, 137.7, 136.2, 135.9, 134.8, 129.1 (2), 128.9 (2), 127.7, 106.2, 105.6, 105.5, 56.7, 53.1, 47.1, 26.3, 25.2, 19.0. HRMS (ESI) Calcd for $C_{24}H_{27}BMoN_7O_2([M+H]^+)$: 554.1368. Found: 554.1361. HPLC: Daicel® Chiralcel OD-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, Enantiomer 1: t_1 = 14.37 min.; Enantiomer 2: t_2 = 15.84 min.



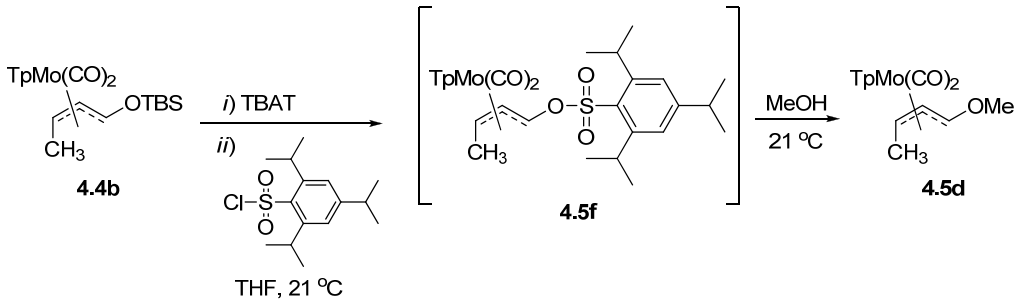
4.5k **4.6c**

(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-cyclohexen-1-yl]molybdenum, 4.6c. Complex **4.5k** (50.0 mg, 0.069 mmol, 1.0 equiv) was dissolved in THF (2 mL), benzyl amine (0.23 mL, 2.06 mmol, 30 equiv) was added, and the solution was heated to reflux. After 17 hours, the solution was concentrated and the crude reaction mixture was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). The red band was collected, affording **4.6c** as a red solid (12.1 mg, 0.022 mmol, 32 %).

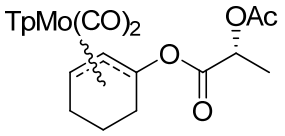
Similar treatment of (+)-**4.5k** (56.0 mg, 0.077 mmol, 1.0 equiv) with $BnNH_2$ (0.25 mL, 2.31 mmol, 30 equiv) in THF (1 mL) afforded **4.6c** (16.1 mg, 0.029 mmol, 38 %, 30.6 % ee) as a red solid.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-methoxy-2-propen-1-yl]molybdenum, (*syn*-Methoxy), 4.5a. Complex **4.4a** (50.0 mg, 0.093 mmol, 1.0 equiv) was dissolved in THF (2 mL) and TBAT (55.4 mg, 0.10 mmol, 1.1 equiv) was added in one portion. After 5 minutes, 2,4,6-triisopropylbenzenesulfonylchloride (30.3 mg, 0.10 mmol, 1.0 equiv) was added in one portion. After 10 minutes, MeOH (2 mL) was added, the solution was stirred 17 hours at room temperature, and the solution was concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded **4.5a** (29.7 mg, 0.068 mmol, 73 %) as a yellow solid.



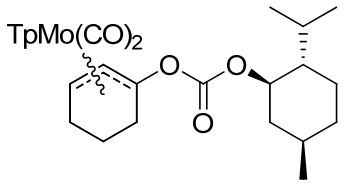
(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-methoxy-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Methoxy), 4.5d. Complex **4.4b** (100 mg, 0.18 mmol, 1.0 equiv) was dissolved in THF (2 mL) and TBAT (108 mg, 0.20 mmol, 1.10 equiv) was added in one portion at room temperature. After 5 minutes, 2,4,6-triisopropylbenzenesulfonylchloride (60.6 mg, 0.20 mmol, 1.1 equiv) was added in one portion at room temperature. The solution was stirred for 10 minutes before MeOH (2 mL) was added. After 14 hours, the reaction mixture was poured into a separatory funnel containing water (10 mL) and CH_2Cl_2 (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (9:1) afforded **4.5d** (59.5 mg, 0.13 mmol, 72 %) as a yellow solid.



Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-1-((*S*)-(-)-2-acetoxypropionyloxy)-2-cyclohexen-1-yl]molybdenum, 4.9. Complex **4.4c** (1.75 g, 3.05 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10 mL) and TBAT (1.98 g, 3.66 mmol, 1.2 equiv) was added in one portion. The solution was stirred 30 minutes at room temperature before (*S*)-(-)-acetoxypropionyl chloride (0.42 mL, 3.36 mmol, 1.1 equiv) was added dropwise. After stirring 10 minutes at room temperature, the solution was concentrated and the crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). Recrystallization from

dichloromethane and hexanes provided **4.9**, a 1:1 mixture of two diastereomers (1.56 g, 2.71 mmol, 89 %), as a yellow solid.

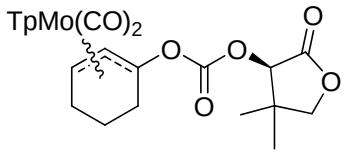
(±)-4.9: TLC: R_f = 0.51 (hexanes-EtOAc = 4:1). IR (cm^{-1}): 2941 (m), 2849 (w), 2482 (m), 2258 (w), 1934 (s), 1849 (s), 1749 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.55 (d, *J* = 2.0 Hz, 1 H), 8.54 (d, *J* = 2.0 Hz, 1 H), 8.04 (d, *J* = 1.6 Hz, 1 H), 8.03 (d, *J* = 2.0 Hz, 1 H), 7.66 (d, *J* = 2.0 Hz, 1 H), 7.63 (d, *J* = 1.6 Hz, 1 H), 7.60 (d, *J* = 2.4 Hz, 2 H), 7.56 (d, *J* = 2.4 Hz, 2 H), 7.50 (dd, *J* = 2.4 Hz, 0.8 Hz, 1 H), 7.48 (d, *J* = 2.0 Hz, 1 H), 6.25-6.27 (m, 2 H), 6.20-6.21 (dd, *J* = 4.0 Hz, 2.4 Hz, 2 H), 6.13-6.15 (dd, *J* = 4.0 Hz, 2.4 Hz, 2 H), 5.00 (m, 2 H), 4.04-4.12 (m, 3 H), 3.91 (m, 1 H), 2.59-2.41 (m, 2 H), 2.23-2.14 (m, 2 H), 2.12 (s, 3 H), 2.10 (s, 3 H), 2.05-1.85 (m, 4 H), 1.47 (d, *J* = 7.2 Hz, 3 H), 1.20-1.29 (m, 2 H), 1.13 (d, *J* = 6.8 Hz, 3 H), 0.66 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 229.0, 228.5, 226.7, 226.4, 170.6, 170.4, 170.3, 169.8, 147.0, 146.8, 146.3, 140.0, 139.6, 136.4, 134.4, 111.5, 111.1, 106.0, 105.6, 105.0, 104.8, 69.3, 69.1, 67.5, 66.6, 60.3, 59.0, 27.8, 22.7, 22.7, 20.8, 20.1, 20.0, 17.1,16.4. HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_6O_6$([M+H]$^+$): 579.1055. Found: 579.1058.



Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-1-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanoxycarbonyl)-2-cyclohexen-1-yl]molybdenum, 4.11. Complex **4.4c** (672 mg, 1.17 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (6 mL) and TBAT (756 mg, 1.40 mmol, 1.2 equiv) was added in one portion at room temperature. The solution was stirred for 30 minutes before (-)-menthyl chloroformate (0.27 mL, 1.29 mmol, 1.1 equiv) was added dropwise. After 3 hours, the solution was concentrated and the crude product was subjected to flash

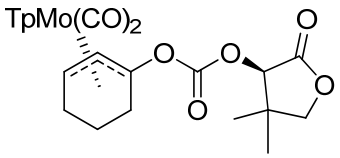
chromatography over silica gel with hexanes-EtOAc (4:1), affording **4.11**, a 1:1 mixture of two diastereomers (677 mg, 1.05 mmol, 90 %), as a yellow solid.

(±)-4.11: TLC: R_f = 0.27 (hexanes-EtOAc = 4:1). IR (cm^{-1}) 2957 (m), 2872 (m), 2478 (m), 1938 (s), 1849 (s), 1749 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.56 (br s, 1 H), 8.14 (d, *J* = 2.0 Hz, 0.5 H), 8.12 (d, *J* = 2.0 Hz, 0.5 H), 7.72 (d, *J* = 2.0 Hz, 0.5 H), 7.70 (d, *J* = 1.6 Hz, 0.5 H), 7.63-7.65 (m, 2 H), 7.61 (br s, 1 H), 7.54 (d, *J* = 2.0 Hz, 0.5 H), 7.53 (d, *J* = 2.0 Hz, 0.5 H), 7.49-7.50 (m, 2 H), 7.37-7.48 (m, 3 H), 6.26-6.28 (m, 2 H), 6.19-6.21 (m, 2 H), 6.09 (t, *J* = 2.4 Hz, 1 H), 6.04 (t, *J* = 2.4 Hz, 1 H), 4.52 (dt, *J* = 10.8 Hz, 4.8 Hz, 1 H), 4.42 (dt, *J* = 10.8 Hz, 4.8 Hz, 1 H), 4.21 (d, *J* = 7.6 Hz, 1 H), 4.16 (d, *J* = 8.0 Hz, 1 H), 4.06-4.12 (m, 2 H), 2.47-2.58 (m, 2 H), 2.11-2.24 (m, 4 H), 1.86-2.02 (m, 4 H), 1.62-1.71 (m, 6 H), 1.22-1.50 (m, 6 H), 0.78-1.13 (m, 6 H), 0.94 (d, *J* = 1.2 Hz, 3 H), 0.93 (s, 3 H), 0.85 (d, *J* = 6.4 Hz, 3 H), 0.83 (d, *J* = 6.8 Hz, 3 H), 0.76 (d, *J* = 6.8 Hz, 3 H), 0.57-0.68 (m, 2 H), 0.55 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 228.5, 228.4, 226.9, 226.8, 153.7, 153.6, 147.1, 146.5, 140.4, 140.2, 136.3, 136.2, 136.1, 135.2, 134.3, 131.1, 130.3, 128.3, 128.2, 112.6, 112.3, 106.0, 105.5, 104.9, 104.7, 79.3, 79.1, 65.7, 65.6, 61.5, 60.9, 47.4, 47.3, 40.9, 40.8, 34.3 (2), 31.6, 28.2, 28.1, 26.5, 25.9, 23.7, 23.4, 22.7, 22.2, 22.1, 21.0 (2), 20.1 (2), 16.7, 16.3. HRMS (ESI) Calcd for $C_{28}H_{38}BMoN_6O_5$([M+H]$^+$): 647.2045. Found: 647.2054.

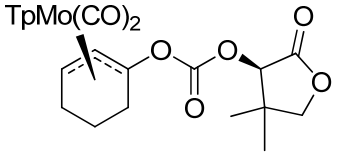


(+)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1*R*)-(η-1,2,3)-1-(((*R*)-3-hydroxycarbonyl-4,4-dimethyldihydrofuran-2(3*H*)-one)oxy)-2-cyclohexen-1-yl]molybdenum, (+)-(1*R*, *R*)-4.12

and (-)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1*S*)-(η-1,2,3)-1-(((*R*)-3-hydroxycarbonyl-4,4-dimethyldihydrofuran-2(3*H*)-one)oxy)-2-cyclohexen-1-yl]molybdenum, (-)-(1*S*, *R*)-4.12. Complex **4.4c** (2.00 g, 3.47 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (15 mL) and TBAT (2.25 g, 4.17 mmol, 1.2 equiv) was added in one portion at room temperature. After 15 minutes, (*R*)-(-)-pantolactone chloroformate (735 mg, 3.82 mmol, 1.1 equiv) was added dropwise. The solution was stirred 45 minutes, concentrated under reduced pressure, and subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). The unseparated portion of the diastereomeric mixture was subjected to a second chromatography under the same conditions. Highly diastereomerically-enriched samples of each diastereomer were thus obtained. Recrystallization of the *R*,*R* diastereomer from CH_2Cl_2/hexanes improved the de of the crystals from 97.1 % to > 99.9 % (supernatant de = 92.4 %). Recrystallization of the supernatant from CH_2Cl_2/hexanes brought the de of the crystals to > 99.9 %. The supernatant (de = 80.4 %) was set aside. The *S*,*R* diastereomer was recrystallized from CH_2Cl_2/hexanes, improving the de of the crystals from 77.7 % to >99.9 %. The supernatant (de = 60.8 %) was combined with the supernatant from the *R*,*R* diastereomer and again chromatographed with hexanes-EtOAc (4:1). Recrystallization from CH_2Cl_2/hexanes provided additional *R*,*R* diastereomer in >99.9 % de. Following this protocol, (1*R*, *R*)-**4.12** (850 mg, 1.38 mmol, 40 %) $[\alpha]_D^{25}$ +54 (*c* 1.05, CH_2Cl_2), and (1*S*, *R*)-**4.12** (741 mg, 1.20 mmol, 35 %) $[\alpha]_D^{25}$ -36 (*c* 1.02, CH_2Cl_2) were obtained as bright yellow solids. HPLC: Agilent Eclipse XDB-C8 column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-10 mins (50% to 75%), 10-12 mins (75 % to 90 %), 1.5 mL/min, λ = 254 nm, (-)-(1*S*, *R*)-**4.12**: $t_{(1S,R)}$ = 10.16 min; (+)-(1*R*, *R*)-**4.12**: $t_{(1R,R)}$ = 10.79 min.

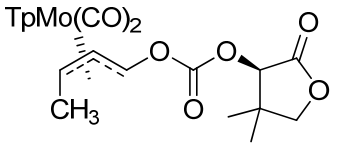


(+)-(1*R*, *R*)-**4.12**: TLC: R_f = 0.60 (hexanes-EtOAc = 4:1). IR (cm^{-1}) 3146 (w), 2941 (m), 2482 (m), 2258 (w), 1938 (s), 1849 (s), 1791 (s), 1756 (s). ^1H NMR ($CDCl_3$, 600 MHz): δ 8.56 (d, *J* = 1.8 Hz, 1 H), 8.15 (d, *J* = 2.4 Hz, 1 H), 7.70 (d, *J* = 1.8 Hz, 1 H), 7.62 (d, *J* = 1.8 Hz, 1 H), 7.54 (d, *J* = 1.8 Hz, 1 H), 7.50 (d, *J* = 1.8 Hz, 1 H), 6.28 (t, *J* = 2.4 Hz, 1 H), 6.22 (t, *J* = 1.8 Hz, 1 H), 6.07 (t, *J* = 2.4 Hz, 1 H), 5.30 (s, 1 H), 5.12 (s, 1 H), 4.15 (d, *J* = 7.8 Hz, 1 H), 4.09-4.10 (m, 1 H), 4.01 (dd, *J* = 9.0 Hz, 2.4 Hz, 2 H), 2.63-2.58 (m, 1 H), 2.20-2.16 (m, 1 H), 1.95-1.91 (dt, *J* = 13.8 Hz, 4.8 Hz, 1 H), 1.32-1.28 (dt, *J* = 14.4 Hz, 5.4 Hz, 1 H), 1.12 (s, 3 H), 1.03 (s, 3 H), 0.65-0.59 (m, 1 H). ^{13}C ($CDCl_3$, 150 MHz): δ 228.2, 225.8, 171.7, 153.2, 147.1, 146.7, 139.9, 136.4, 136.3, 134.4, 111.7, 106.0, 105.5, 104.8, 97.9, 78.7, 76.2, 65.1, 40.2, 27.7, 23.1, 22.6, 20.1, 19.9. HRMS (ESI) Calcd for $C_{24}H_{27}BMoN_6O_7$([M+H]$^+$): 621.1161. Found: 621.1163.



(-)-(1*S*, *R*)-**4.12**: TLC: R_f = 0.62 (hexanes-EtOAc = 4:1). IR (cm^{-1}) 3146 (w), 2941 (m), 2482 (m), 2258 (w), 1938 (s), 1849 (s), 1791 (s), 1756 (s). ^1H ($CDCl_3$, 600 MHz): δ 8.56 (d, *J* = 1.8 Hz, 1 H), 8.15 (d, *J* = 2.4 Hz, 1 H), 7.70 (d, *J* = 1.8 Hz, 1 H), 7.62 (d, *J* = 1.8 Hz, 1 H), 7.54 (d, *J* = 1.8 Hz, 1 H), 7.50 (d, *J* = 1.8 Hz, 1 H), 6.28 (t, *J* = 2.4 Hz, 1 H), 6.22 (t, *J* = 1.8 Hz, 1 H), 6.07 (t, *J* = 2.4 Hz, 1 H), 5.30 (s, 1 H), 5.12 (s, 1 H), 4.15 (d, *J* = 7.8 Hz, 1 H), 4.09-4.11 (m, 1 H), 4.01 (dd, *J* = 20.4 Hz, 9.0 Hz, 2 H), 2.63-2.58 (m, 1 H), 2.20-2.16 (m, 1 H), 1.95-1.91 (dt, *J* =

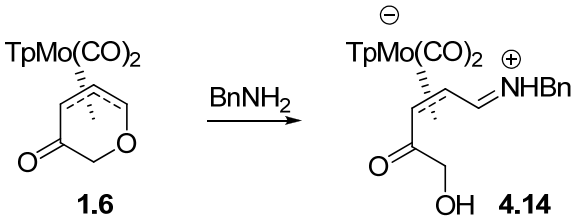
13.8 Hz, 4.8 Hz, 1 H), 1.32-1.28 (dt, *J* = 14.4 Hz, 5.4 Hz, 1 H), 1.12 (s, 3 H), 1.03 (s, 3 H), 0.65-0.59 (m, 1 H). ^{13}C ($CDCl_3$, 150 MHz): δ 228.2, 225.8, 171.7, 153.2, 147.1, 146.7, 139.9, 136.4, 134.4, 111.7, 106.0, 105.5, 104.8, 97.9, 78.7, 76.2, 65.1, 60.5, 40.2, 27.7, 23.1, 22.6, 20.1, 19.9. HRMS (ESI) Calcd for $C_{24}H_{27}BMoN_6O_7$([M+H]$^+$): 621.1161. Found: 621.1164.



(-)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1*R*)-(η-1,2,3)-1-(((*R*)-3-hydroxycarbonyl-4,4-dimethyldihydrofuran-2(3*H*)-one)oxy)-2-buten-1-yl]molybdenum, (*anti*-Methyl/*syn*-Pantolactonecarbonyloxy), (-)-(1*R*, *R*)-4.13. Complex **4.4b** (2.04 g, 37.0 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (100 mL) and TBAT (2.40 g, 44.4 mmol, 1.2 equiv) was added in one portion. The solution was stirred 20 minutes at room temperature and (*R*)-(-)-pantolactone chloroformate (7.84 g, 40.7 mmol, 1.1 equiv) was added dropwise. The solution was stirred one hour and then concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (9:1 and slowly ramping to 0:1), followed by a second chromatography under the same conditions. Iterations of recrystallization from CH_2Cl_2/hexanes and further chromatography allowed one diastereomer, (1*R*, *R*)-**4.13** (4.76 g, 8.0 mmol, 22 %, de = 98.7 %) $[\alpha]_D^{25}$ -149 (*c* 1.04, CH_2Cl_2) to be isolated as a yellow solid. The second diastereomer (1*S*, *R*)-**4.13** decomposed, producing a byproduct that partly overlapped with the stable diastereomer during chromatography.

(-)-(1*R*, *R*)-**4.13**: TLC: R_f = 0.34, (hexanes-EtOAc = 2:1). IR (cm^{-1}) 2968 (w), 2930 (w), 2486 (w), 1938 (s), 1849 (s), 1803 (s), 1760 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.50 (d, *J* = 1.6

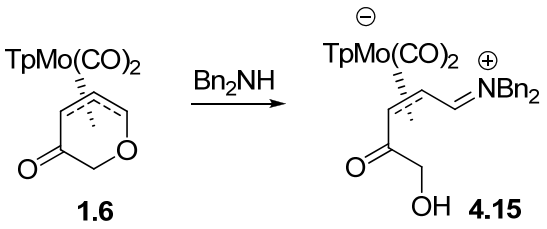
Hz, 1 H), 7.79 (d, *J* = 2.0 Hz, 1 H), 7.60 (d, *J* = 1.6 Hz, 1 H), 7.58 (d, *J* = 2.4 Hz, 1 H), 7.57 (d, *J* = 2.4 Hz, 1 H), 7.48 (d, *J* = 2.4 Hz, 1 H), 6.27 (t, *J* = 2.0 Hz, 1 H), 6.23 (t, *J* = 2.0 Hz, 1 H), 6.18 (t, *J* = 2.0 Hz, 1 H), 5.99 (d, *J* = 7.6 Hz, 1 H), 5.34 (s, 1 H), 4.18 (t, *J* = 7.6 Hz, 1 H), 4.05-4.07 (m, 1 H), 4.03 (s, 2 H), 1.28 (d, *J* = 6.4 Hz, 3 H), 1.25 (s, 3 H), 1.11 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 231.9, 226.1, 171.3, 153.4, 146.9, 146.5, 139.8, 136.1, 135.9, 134.5, 106.1, 105.8, 105.5, 100.6, 79.2, 76.1, 70.4, 55.0, 40.1, 22.8, 19.8, 17.9. HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_6O_7$([M+H]$^+$): 595.1005. Found: 595.1005.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-3-(2-hydroxyacetyl)-propen-1-yl]molybdenum, (*anti*-2-Hydroxyacetyl/*syn*-Benzylamino), 4.14. Complex **1.6** (200 mg, 0.43 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (5 mL) and $BnNH_2$ (0.24 mL, 2.16 mmol, 5.0 equiv) was added. The solution was stirred *open to air* for 1.25 hours and then concentrated. Rapid flash chromatography over silica gel with hexanes-EtOAc (1:1) afforded **4.14** (201 mg, 0.35 mmol, 82 %) as a dark purple solid.

(±)-4.14: TLC: R_f = 0.37, (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3034-3377 (br w), 2482 (m), 1911 (s), 1799 (s), 1652 (m), 1575 (s), 1502 (m), 1405 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (t, *J* = 10.8 Hz, 1 H), 7.44-8.06 (br m, 6 H), 7.30-7.39 (m, 3 H), 7.21-7.26 (m, 2 H), 6.18 (br s, 3 H), 5.79 (br s, 1 H), 4.53 (d, *J* = 16.8 Hz, 1 H), 4.30-4.42 (m, 2 H), 4.08 (d, *J* = 14.0 Hz, 1 H), 3.92 (d, *J* = 14.8 Hz, 1 H), 3.41 (br s, 1 H), 3.16 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

240.7, 231.6, 210.5, 147.0, 135.9, 129.1, 128.3, 128.0, 105.6, 68.5, 60.1, 56.1, 48.8. HRMS (ESI) Calcd for $C_{23}H_{25}BMoN_7O_4$ ($[M+H]^+$): 572.1109. Found: 572.1109.



(±)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-1-dibenzylamino-3-(2-hydroxyacetyl)-propen-1-yl]molybdenum, (*anti*-2-Hydroxyacetyl/*syn*-Dibenzylamino), (±)-4.15 and (-)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1*R*)-η-(1,2,3)-1-dibenzylamino-3-(2-hydroxyacetyl)-propen-1-yl]molybdenum, (*anti*-2-Hydroxyacetyl/*syn*-Dibenzylamino), (-)-4.15. Complex **1.6** (200 mg, 0.43 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (5 mL) and Bn_2NH (0.41 mL, 2.16 mmol, 5.0 equiv) was added. The solution was stirred *open to air* for 1.25 hours and then concentrated. Rapid flash chromatography over silica gel with hexanes-EtOAc (1:1) afforded (±)-**4.15** (146 mg, 0.22 mmol, 51 %) as a dark purple solid.

Similar treatment of (-)-**1.6** (25.0 mg, 0.054 mmol, 1.0 equiv, 97.6 % ee) with Bn_2NH (0.051 mL, 0.27 mmol, 5.0 equiv) in CH_2Cl_2 (1.5 mL) afforded (-)-**4.15** (32.2 mg, 0.049 mmol, 90 %, 90.7 % ee) $[\alpha]_D^{25}$ - 559 (*c* 0.005, CH_2Cl_2) as a dark purple solid.

(±)-4.15: TLC: R_f = 0.55, (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3451 (br w), 3034 (w), 2482 (m), 1918 (s), 1799 (s), 1656 (m), 1571 (s), 1498 (m), 1409 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 11.2 Hz, 1 H), 7.58-8.52 (br s, 3 H), 7.50-7.54 (m, 5 H), 7.40-7.46 (m, 3 H), 7.29-7.35 (m, 3 H), 7.13 (d, *J* = 6.8 Hz, 2 H), 6.08 (br s, 3 H), 4.69 (d, *J* = 14.4 Hz, 1 H), 4.56 (dd, *J* = 20.0 Hz, 17.6 Hz, 2 H), 4.39-4.43 (m, 2 H), 4.03 (d, *J* = 16.0 Hz, 1 H), 3.82 (d, *J* = 16.0 Hz, 1 H), 3.37 (dd, *J* = 11.2 Hz, 7.2 Hz, 1 H), 3.31 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 241.3,

231.6, 210.9, 153.9, 135.8, 133.9, 133.6, 130.4, 129.4, 129.2, 128.8, 128.3, 127.4, 105.3, 68.7, 60.7, 57.1, 56.9, 49.8. HRMS (ESI) Calcd for $C_{30}H_{30}BMoN_7O_4$ (M^+): 661.1500. Found: 661.1501. HPLC: Daicel® Chiralcel OD-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (20% to 50%), 20-30 mins (50% to 80%), 1.5 mL/min, λ = 254 nm, (*S*)-(+)-**4.15**: $t_{(+)}$ = 27.91 min; (*R*)-(-)-**4.15**: $t_{(-)}$ = 27.51 min.

Crystal Structure Analyses

Suitable crystals of **4.5k**, (1*S*, *R*)-**4.12**, (1*R*, *R*)-**4.13**, and **4.15** were obtained by diffusion recrystallization from CH_2Cl_2/hexanes. These crystals were coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 APEX II CCD sealed tube diffractometer with graphite monochromated CuK_α (1.54178 Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 - 30 s frame exposures and 0.5° frame widths. Data collection, indexing and initial cell refinements were all carried out using APEX II[170] software. Frame integration and final cell refinements were done using SAINT[171] software. The final cell parameters were determined from least-squares refinement on 6333 reflections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).[172] Hydrogen atoms were placed their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij} 's related to the atom's ridden upon. All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables*

[170] APEX II, **2005**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[171] SAINT Version 6.45A, **2003**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[172] SHELXTL V6.12, **2002**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.

for X-ray Crystallography[173]. Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V6.12 software.

Table 4.6. Crystal data and structure refinement for 4.5k

Identification code	**4.5k**	
Empirical formula	C32 H41 B Mo N6 O5 S	
Formula weight	728.52	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2747(5) Å	α= 117.430(2)°.
	b = 14.2031(7) Å	β= 91.938(2)°.
	c = 15.1516(7) Å	γ = 103.496(2)°.
Volume	1699.35(15) $Å^3$	
Z	2	
Density (calculated)	1.424 Mg/m^3	
Absorption coefficient	4.128 mm^{-1}	
F(000)	756	
Crystal size	0.29 x 0.19 x 0.08 mm^3	
Theta range for data collection	8.14 to 65.79°.	
Index ranges	-9<=h<=9, -16<=k<=14, 0<=l<=17	
Reflections collected	7555	
Independent reflections	7555 [R(int) = 0.0284]	
Completeness to theta = 65.79°	76.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7336 and 0.3807	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7555 / 0 / 422	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0939, wR2 = 0.2227	
R indices (all data)	R1 = 0.0953, wR2 = 0.2246	

[173] A. J. C. Wilson (ed), *International Tables for X-ray Crystallography, Volume C.* Kynoch, Academic Publishers, Dordrecht, **1992**, Tables 6.1.1.4 (pp. 500-502) and 4.2.6.8 (pp. 219-222).

Extinction coefficient	0.0013(7)
Largest diff. peak and hole	2.189 and -1.364 e.Å^{-3}

Table 4.7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 4.5k. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	4104(7)	12334(5)	3712(5)	23(1)
C(1)	1593(7)	9855(5)	3541(4)	29(1)
C(2)	2921(7)	9777(5)	3915(4)	34(1)
C(3)	4026(7)	10638(5)	3967(4)	31(1)
C(4)	2652(6)	11988(5)	1302(4)	25(1)
C(5)	4159(6)	12399(5)	1306(4)	29(1)
C(6)	4881(6)	12572(4)	2189(4)	26(1)
C(7)	1431(7)	13831(5)	4887(5)	27(1)
C(8)	2661(7)	14584(5)	5589(5)	32(1)
C(9)	3833(6)	14121(5)	5268(4)	28(1)
C(10)	-703(6)	12508(4)	2865(4)	25(1)
C(11)	-1115(6)	11184(4)	3619(4)	25(1)
C(12)	-451(6)	10134(4)	1255(4)	20(1)
C(13)	-934(6)	11019(4)	1255(4)	21(1)
C(14)	-2607(6)	10880(5)	1073(5)	28(1)
C(15)	-3483(6)	10449(5)	1707(5)	28(1)
C(16)	-2995(6)	9493(4)	1707(4)	23(1)
C(17)	-1310(6)	9662(4)	1772(4)	20(1)
C(18)	-334(6)	7002(4)	1517(4)	19(1)
C(19)	977(6)	6654(4)	1272(4)	21(1)
C(20)	1431(6)	6135(4)	1763(4)	24(1)
C(21)	686(6)	5968(4)	2486(4)	22(1)
C(22)	-579(6)	6328(5)	2704(4)	25(1)
C(23)	-1130(6)	6855(4)	2241(4)	21(1)
C(24)	1947(6)	6848(5)	534(5)	26(1)
C(25)	2975(7)	8019(5)	1052(5)	41(2)
C(26)	2865(7)	6018(6)	76(5)	39(2)
C(27)	1254(6)	5451(5)	3064(4)	27(1)
C(28)	2349(7)	6330(6)	3994(5)	41(2)
C(29)	1914(7)	4512(5)	2424(5)	40(2)
C(30)	-2550(6)	7211(5)	2574(4)	29(1)
C(31)	-2354(8)	7931(5)	3714(5)	45(2)
C(32)	-3907(7)	6186(6)	2211(5)	41(2)
Mo(1)	376(1)	11476(1)	2825(1)	17(1)
N(1)	1875(5)	10720(4)	3351(3)	24(1)
N(2)	3404(5)	11203(4)	3630(3)	25(1)
N(3)	2440(5)	11911(4)	2136(3)	22(1)
N(4)	3852(5)	12276(4)	2683(3)	22(1)
N(5)	1787(5)	12957(4)	4173(3)	24(1)
N(6)	3304(5)	13152(4)	4425(3)	22(1)
O(1)	-1345(4)	13146(3)	2958(3)	34(1)

O(2)	-2006(5)	11023(3)	4086(3)	38(1)
O(3)	-864(4)	8811(3)	1876(3)	21(1)
O(4)	-233(4)	7781(3)	192(3)	30(1)
O(5)	-2679(4)	7073(3)	543(3)	32(1)
S(1)	-1107(1)	7619(1)	900(1)	22(1)

Table 4.8. Bond lengths [Å] and angles [°] for 4.5k.

B(1)-N(2)	1.530(7)	C(21)-C(22)	1.378(8)
B(1)-N(4)	1.529(7)	C(21)-C(27)	1.524(7)
B(1)-N(6)	1.539(7)	C(22)-C(23)	1.397(7)
B(1)-H(1)	1.0000	C(22)-H(22)	0.9500
C(1)-N(1)	1.358(6)	C(23)-C(30)	1.538(7)
C(1)-C(2)	1.386(8)	C(24)-C(25)	1.516(8)
C(1)-H(1)	0.9500	C(24)-C(26)	1.534(7)
C(2)-C(3)	1.368(8)	C(24)-H(24)	1.0000
C(2)-H(2)	0.9500	C(25)-H(25A)	0.9800
C(3)-N(2)	1.345(7)	C(25)-H(25B)	0.9800
C(3)-H(3)	0.9500	C(25)-H(25C)	0.9800
C(4)-N(3)	1.334(6)	C(26)-H(26A)	0.9800
C(4)-C(5)	1.382(8)	C(26)-H(26B)	0.9800
C(4)-H(4)	0.9500	C(26)-H(26C)	0.9800
C(5)-C(6)	1.363(8)	C(27)-C(28)	1.505(9)
C(5)-H(5)	0.9500	C(27)-C(29)	1.524(8)
C(6)-N(4)	1.342(7)	C(27)-H(27)	1.0000
C(6)-H(6)	0.9500	C(28)-H(28A)	0.9800
C(7)-N(5)	1.341(7)	C(28)-H(28B)	0.9800
C(7)-C(8)	1.370(9)	C(28)-H(28C)	0.9800
C(7)-H(7)	0.9500	C(29)-H(29A)	0.9800
C(8)-C(9)	1.387(8)	C(29)-H(29B)	0.9800
C(8)-H(8)	0.9500	C(29)-H(29C)	0.9800
C(9)-N(6)	1.338(7)	C(30)-C(31)	1.525(9)
C(9)-H(9)	0.9500	C(30)-C(32)	1.538(9)
C(10)-O(1)	1.156(6)	C(30)-H(30)	1.0000
C(10)-Mo(1)	1.939(5)	C(31)-H(31A)	0.9800
C(11)-O(2)	1.156(7)	C(31)-H(31B)	0.9800
C(11)-Mo(1)	1.957(6)	C(31)-H(31C)	0.9800
C(12)-C(17)	1.405(7)	C(32)-H(32A)	0.9800
C(12)-C(13)	1.429(7)	C(32)-H(32B)	0.9800
C(12)-Mo(1)	2.213(5)	C(32)-H(32C)	0.9800
C(12)-H(12)	0.9500	Mo(1)-N(5)	2.210(5)
C(13)-C(14)	1.517(8)	Mo(1)-N(1)	2.265(4)
C(13)-Mo(1)	2.361(5)	Mo(1)-N(3)	2.306(4)
C(13)-H(13)	0.9500	N(1)-N(2)	1.378(6)
C(14)-C(15)	1.524(7)	N(3)-N(4)	1.373(6)
C(14)-H(14A)	0.9900	N(5)-N(6)	1.373(6)
C(14)-H(14B)	0.9900	O(3)-S(1)	1.611(4)
C(15)-C(16)	1.528(7)	O(4)-S(1)	1.434(4)
C(15)-H(15A)	0.9900	O(5)-S(1)	1.433(4)
C(15)-H(15B)	0.9900	N(2)-B(1)-N(4)	110.5(5)
C(16)-C(17)	1.517(7)	N(2)-B(1)-N(6)	108.2(4)
C(16)-H(16A)	0.9900	N(4)-B(1)-N(6)	107.6(4)
C(16)-H(16B)	0.9900	N(2)-B(1)-H(1)	110.2
C(17)-O(3)	1.436(5)	N(4)-B(1)-H(1)	110.2
C(17)-Mo(1)	2.407(5)	N(6)-B(1)-H(1)	110.2
C(18)-C(23)	1.409(7)	N(1)-C(1)-C(2)	110.2(5)
C(18)-C(19)	1.416(7)	N(1)-C(1)-H(1)	124.9
C(18)-S(1)	1.777(5)	C(2)-C(1)-H(1)	124.9
C(19)-C(20)	1.380(7)	C(3)-C(2)-C(1)	105.6(5)
C(19)-C(24)	1.540(7)	C(3)-C(2)-H(2)	127.2
C(20)-C(21)	1.395(7)	C(1)-C(2)-H(2)	127.2
C(20)-H(20)	0.9500	N(2)-C(3)-C(2)	109.0(5)

N(2)-C(3)-H(3)	125.5	O(3)-C(17)-Mo(1)	113.0(3)
C(2)-C(3)-H(3)	125.5	C(16)-C(17)-Mo(1)	119.7(3)
N(3)-C(4)-C(5)	111.2(5)	C(23)-C(18)-C(19)	122.4(4)
N(3)-C(4)-H(4)	124.4	C(23)-C(18)-S(1)	115.9(4)
C(5)-C(4)-H(4)	124.4	C(19)-C(18)-S(1)	121.7(4)
C(6)-C(5)-C(4)	105.2(5)	C(20)-C(19)-C(18)	116.6(4)
C(6)-C(5)-H(5)	127.4	C(20)-C(19)-C(24)	118.4(4)
C(4)-C(5)-H(5)	127.4	C(18)-C(19)-C(24)	124.9(4)
N(4)-C(6)-C(5)	108.5(5)	C(19)-C(20)-C(21)	123.4(5)
N(4)-C(6)-H(6)	125.8	C(19)-C(20)-H(20)	118.3
C(5)-C(6)-H(6)	125.8	C(21)-C(20)-H(20)	118.3
N(5)-C(7)-C(8)	111.8(5)	C(22)-C(21)-C(20)	117.9(4)
N(5)-C(7)-H(7)	124.1	C(22)-C(21)-C(27)	119.5(5)
C(8)-C(7)-H(7)	124.1	C(20)-C(21)-C(27)	122.6(5)
C(7)-C(8)-C(9)	104.2(5)	C(21)-C(22)-C(23)	122.9(5)
C(7)-C(8)-H(8)	127.9	C(21)-C(22)-H(22)	118.6
C(9)-C(8)-H(8)	127.9	C(23)-C(22)-H(22)	118.6
N(6)-C(9)-C(8)	109.2(5)	C(22)-C(23)-C(18)	116.9(5)
N(6)-C(9)-H(9)	125.4	C(22)-C(23)-C(30)	116.3(4)
C(8)-C(9)-H(9)	125.4	C(18)-C(23)-C(30)	126.8(4)
O(1)-C(10)-Mo(1)	175.3(5)	C(25)-C(24)-C(26)	110.2(5)
O(2)-C(11)-Mo(1)	178.9(4)	C(25)-C(24)-C(19)	110.0(5)
C(17)-C(12)-C(13)	112.3(4)	C(26)-C(24)-C(19)	113.5(4)
C(17)-C(12)-Mo(1)	80.0(3)	C(25)-C(24)-H(24)	107.6
C(13)-C(12)-Mo(1)	77.5(3)	C(26)-C(24)-H(24)	107.6
C(17)-C(12)-H(12)	123.8	C(19)-C(24)-H(24)	107.6
C(13)-C(12)-H(12)	123.8	C(24)-C(25)-H(25A)	109.5
Mo(1)-C(12)-H(12)	110.5	C(24)-C(25)-H(25B)	109.5
C(12)-C(13)-C(14)	118.6(4)	H(25A)-C(25)-H(25B)	109.5
C(12)-C(13)-Mo(1)	66.3(3)	C(24)-C(25)-H(25C)	109.5
C(14)-C(13)-Mo(1)	122.9(3)	H(25A)-C(25)-H(25C)	109.5
C(12)-C(13)-H(13)	120.7	H(25B)-C(25)-H(25C)	109.5
C(14)-C(13)-H(13)	120.7	C(24)-C(26)-H(26A)	109.5
Mo(1)-C(13)-H(13)	82.1	C(24)-C(26)-H(26B)	109.5
C(13)-C(14)-C(15)	113.2(4)	H(26A)-C(26)-H(26B)	109.5
C(13)-C(14)-H(14A)	108.9	C(24)-C(26)-H(26C)	109.5
C(15)-C(14)-H(14A)	108.9	H(26A)-C(26)-H(26C)	109.5
C(13)-C(14)-H(14B)	108.9	H(26B)-C(26)-H(26C)	109.5
C(15)-C(14)-H(14B)	108.9	C(28)-C(27)-C(21)	110.2(5)
H(14A)-C(14)-H(14B)	107.8	C(28)-C(27)-C(29)	111.6(5)
C(14)-C(15)-C(16)	111.6(4)	C(21)-C(27)-C(29)	113.6(5)
C(14)-C(15)-H(15A)	109.3	C(28)-C(27)-H(27)	107.0
C(16)-C(15)-H(15A)	109.3	C(21)-C(27)-H(27)	107.0
C(14)-C(15)-H(15B)	109.3	C(29)-C(27)-H(27)	107.0
C(16)-C(15)-H(15B)	109.3	C(27)-C(28)-H(28A)	109.5
H(15A)-C(15)-H(15B)	108.0	C(27)-C(28)-H(28B)	109.5
C(17)-C(16)-C(15)	113.1(4)	H(28A)-C(28)-H(28B)	109.5
C(17)-C(16)-H(16A)	109.0	C(27)-C(28)-H(28C)	109.5
C(15)-C(16)-H(16A)	109.0	H(28A)-C(28)-H(28C)	109.5
C(17)-C(16)-H(16B)	109.0	H(28B)-C(28)-H(28C)	109.5
C(15)-C(16)-H(16B)	109.0	C(27)-C(29)-H(29A)	109.5
H(16A)-C(16)-H(16B)	107.8	C(27)-C(29)-H(29B)	109.5
C(12)-C(17)-O(3)	117.2(4)	H(29A)-C(29)-H(29B)	109.5
C(12)-C(17)-C(16)	122.2(4)	C(27)-C(29)-H(29C)	109.5
O(3)-C(17)-C(16)	112.0(4)	H(29A)-C(29)-H(29C)	109.5
C(12)-C(17)-Mo(1)	64.9(3)	H(29B)-C(29)-H(29C)	109.5

C(31)-C(30)-C(23)	111.9(5)
C(31)-C(30)-C(32)	110.3(5)
C(23)-C(30)-C(32)	110.0(4)
C(31)-C(30)-H(30)	108.2
C(23)-C(30)-H(30)	108.2
C(32)-C(30)-H(30)	108.2
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(30)-C(32)-H(32A)	109.5
C(30)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(30)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(10)-Mo(1)-C(11)	83.0(2)
C(10)-Mo(1)-N(5)	82.4(2)
C(11)-Mo(1)-N(5)	92.0(2)
C(10)-Mo(1)-C(12)	100.4(2)
C(11)-Mo(1)-C(12)	105.8(2)
N(5)-Mo(1)-C(12)	162.15(18)
C(10)-Mo(1)-N(1)	160.0(2)
C(11)-Mo(1)-N(1)	90.04(18)
N(5)-Mo(1)-N(1)	79.14(17)
C(12)-Mo(1)-N(1)	99.57(18)
C(10)-Mo(1)-N(3)	102.05(17)
C(11)-Mo(1)-N(3)	169.8(2)
N(5)-Mo(1)-N(3)	79.95(16)
C(12)-Mo(1)-N(3)	82.24(17)
N(1)-Mo(1)-N(3)	82.29(15)
C(10)-Mo(1)-C(13)	65.0(2)
C(11)-Mo(1)-C(13)	107.6(2)
N(5)-Mo(1)-C(13)	138.65(16)
C(12)-Mo(1)-C(13)	36.24(17)
N(1)-Mo(1)-C(13)	134.91(17)
N(3)-Mo(1)-C(13)	82.61(16)
C(10)-Mo(1)-C(17)	105.9(2)
C(11)-Mo(1)-C(17)	72.2(2)
N(5)-Mo(1)-C(17)	160.74(16)
C(12)-Mo(1)-C(17)	35.10(17)
N(1)-Mo(1)-C(17)	89.60(16)
N(3)-Mo(1)-C(17)	114.24(16)
C(13)-Mo(1)-C(17)	59.19(16)
C(1)-N(1)-N(2)	105.7(4)
C(1)-N(1)-Mo(1)	133.2(4)
N(2)-N(1)-Mo(1)	120.9(3)
C(3)-N(2)-N(1)	109.5(4)
C(3)-N(2)-B(1)	128.9(5)
N(1)-N(2)-B(1)	120.6(4)
C(4)-N(3)-N(4)	105.2(4)
C(4)-N(3)-Mo(1)	135.3(4)
N(4)-N(3)-Mo(1)	119.3(3)
C(6)-N(4)-N(3)	109.9(4)
C(6)-N(4)-B(1)	128.2(5)
N(3)-N(4)-B(1)	121.9(4)
C(7)-N(5)-N(6)	105.7(5)
C(7)-N(5)-Mo(1)	130.6(4)
N(6)-N(5)-Mo(1)	123.7(3)
C(9)-N(6)-N(5)	109.1(4)
C(9)-N(6)-B(1)	131.6(5)
N(5)-N(6)-B(1)	119.1(4)
C(17)-O(3)-S(1)	119.6(3)
O(5)-S(1)-O(4)	116.6(2)
O(5)-S(1)-O(3)	110.2(2)
O(4)-S(1)-O(3)	107.6(2)
O(5)-S(1)-C(18)	109.8(2)
O(4)-S(1)-C(18)	113.8(2)
O(3)-S(1)-C(18)	97.0(2)

Symmetry transformations used to generate equivalent atoms:

Table 4.9. Anisotropic displacement parameters ($Å^2$x 10^3)for 4.5k. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	21(3)	23(4)	19(4)	8(3)	-3(2)	-1(3)
C(1)	39(4)	22(3)	25(4)	14(3)	-2(3)	2(3)
C(2)	49(4)	27(3)	30(4)	16(3)	-3(3)	12(3)
C(3)	38(4)	33(4)	25(4)	14(3)	-2(3)	14(3)
C(4)	28(3)	30(3)	20(3)	14(3)	5(2)	7(3)
C(5)	25(3)	39(4)	28(4)	21(3)	9(2)	7(3)
C(6)	24(3)	24(3)	28(4)	13(3)	5(2)	4(2)
C(7)	30(3)	25(3)	27(4)	14(3)	9(3)	7(3)
C(8)	46(4)	20(3)	25(4)	9(3)	8(3)	5(3)
C(9)	27(3)	24(4)	25(4)	13(3)	-4(2)	-6(2)
C(10)	20(3)	20(3)	33(4)	15(3)	4(2)	0(2)
C(11)	28(3)	17(3)	27(4)	10(3)	-1(3)	3(2)
C(12)	26(3)	14(3)	13(3)	4(3)	0(2)	-1(2)
C(13)	26(3)	16(3)	19(3)	8(3)	-2(2)	0(2)
C(14)	27(3)	24(3)	36(4)	18(3)	-2(3)	5(2)
C(15)	19(3)	25(3)	38(4)	15(3)	-1(2)	2(2)
C(16)	23(3)	17(3)	25(3)	9(3)	1(2)	1(2)
C(17)	25(3)	11(3)	20(3)	7(3)	-1(2)	2(2)
C(18)	23(3)	13(3)	19(3)	11(3)	-3(2)	-2(2)
C(19)	24(3)	15(3)	18(3)	8(3)	-1(2)	-2(2)
C(20)	23(3)	23(3)	25(3)	14(3)	3(2)	3(2)
C(21)	26(3)	14(3)	22(3)	10(3)	-1(2)	-1(2)
C(22)	29(3)	23(3)	25(3)	16(3)	4(2)	2(2)
C(23)	26(3)	14(3)	17(3)	6(3)	0(2)	2(2)
C(24)	29(3)	24(3)	31(4)	17(3)	8(2)	7(3)
C(25)	36(4)	40(4)	47(4)	26(4)	11(3)	-3(3)
C(26)	40(4)	48(4)	42(4)	29(4)	19(3)	17(3)
C(27)	28(3)	31(3)	31(4)	21(3)	2(2)	7(3)
C(28)	49(4)	40(4)	33(4)	17(4)	-7(3)	12(3)
C(29)	52(4)	36(4)	46(4)	26(4)	8(3)	21(3)
C(30)	28(3)	34(3)	38(4)	25(3)	14(3)	13(3)
C(31)	53(4)	37(4)	48(5)	20(4)	26(3)	15(3)
C(32)	27(3)	52(4)	54(5)	32(4)	13(3)	13(3)
Mo(1)	19(1)	14(1)	19(1)	10(1)	3(1)	2(1)
N(1)	27(3)	21(3)	25(3)	14(2)	1(2)	4(2)
N(2)	25(3)	25(3)	23(3)	12(2)	0(2)	4(2)
N(3)	19(3)	23(3)	25(3)	14(2)	4(2)	5(2)
N(4)	19(2)	23(3)	23(3)	13(2)	2(2)	2(2)
N(5)	22(3)	24(3)	28(3)	15(3)	6(2)	3(2)
N(6)	24(3)	20(3)	18(3)	11(3)	0(2)	-3(2)
O(1)	29(2)	19(2)	52(3)	16(2)	4(2)	6(2)
O(2)	38(3)	39(3)	36(3)	21(2)	19(2)	3(2)
O(3)	27(2)	15(2)	23(2)	13(2)	1(2)	2(2)
O(4)	47(2)	30(2)	24(2)	18(2)	10(2)	18(2)
O(5)	31(2)	24(2)	33(3)	12(2)	-12(2)	1(2)

S(1)	29(1)	17(1)	19(1)	11(1)	1(1)	4(1)

Table 4.10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 4.5k.

	x	y	z	U(eq)
H(1)	5203	12592	3980	28
H(1)	626	9372	3434	35
H(2)	3039	9239	4096	41
H(3)	5064	10810	4204	38
H(4)	1868	11787	775	30
H(5)	4597	12532	802	35
H(6)	5936	12854	2416	31
H(7)	446	13917	4904	32
H(8)	2703	15266	6164	39
H(9)	4850	14441	5596	33
H(12)	359	9892	941	24
H(13)	-223	11680	1366	25
H(14A)	-3009	10361	351	34
H(14B)	-2765	11602	1226	34
H(15A)	-4570	10196	1437	33
H(15B)	-3322	11056	2408	33
H(16A)	-3319	9403	2286	28
H(16B)	-3509	8802	1083	28
H(20)	2296	5878	1602	28
H(22)	-1100	6214	3191	30
H(24)	1253	6767	-32	31
H(25A)	3694	8115	1597	62
H(25B)	2375	8542	1332	62
H(25C)	3522	8157	562	62
H(26A)	3720	6201	580	58
H(26B)	3234	6053	-510	58
H(26C)	2228	5271	-135	58
H(27)	368	5129	3296	33
H(28A)	3263	6636	3797	62
H(28B)	2606	6006	4405	62
H(28C)	1892	6921	4386	62
H(29A)	2803	4799	2195	60
H(29B)	1162	3944	1839	60
H(29C)	2201	4189	2828	60
H(30)	-2753	7651	2251	35
H(31A)	-3239	8203	3890	68
H(31B)	-1456	8560	3941	68
H(31C)	-2242	7494	4045	68
H(32A)	-3731	5742	2521	61
H(32B)	-4041	5743	1476	61
H(32C)	-4813	6420	2405	61

Table 4.11. Torsion angles [°] for 4.5k.

N(1)-C(1)-C(2)-C(3)	1.2(7)
C(1)-C(2)-C(3)-N(2)	-0.8(7)
N(3)-C(4)-C(5)-C(6)	0.2(6)
C(4)-C(5)-C(6)-N(4)	0.1(6)
N(5)-C(7)-C(8)-C(9)	-0.1(6)
C(7)-C(8)-C(9)-N(6)	0.1(6)
C(17)-C(12)-C(13)-C(14)	-42.3(7)
Mo(1)-C(12)-C(13)-C(14)	-115.8(4)
C(17)-C(12)-C(13)-Mo(1)	73.5(4)
C(12)-C(13)-C(14)-C(15)	47.7(7)
Mo(1)-C(13)-C(14)-C(15)	-31.1(6)
C(13)-C(14)-C(15)-C(16)	-44.7(7)
C(14)-C(15)-C(16)-C(17)	40.0(7)
C(13)-C(12)-C(17)-O(3)	-176.1(4)
Mo(1)-C(12)-C(17)-O(3)	-104.2(4)
C(13)-C(12)-C(17)-C(16)	38.7(7)
Mo(1)-C(12)-C(17)-C(16)	110.6(5)
C(13)-C(12)-C(17)-Mo(1)	-71.9(4)
C(15)-C(16)-C(17)-C(12)	-39.2(7)
C(15)-C(16)-C(17)-O(3)	174.0(4)
C(15)-C(16)-C(17)-Mo(1)	38.2(6)
C(23)-C(18)-C(19)-C(20)	1.4(8)
S(1)-C(18)-C(19)-C(20)	-176.8(4)
C(23)-C(18)-C(19)-C(24)	-176.3(5)
S(1)-C(18)-C(19)-C(24)	5.5(7)
C(18)-C(19)-C(20)-C(21)	-1.3(8)
C(24)-C(19)-C(20)-C(21)	176.5(5)
C(19)-C(20)-C(21)-C(22)	0.9(8)
C(19)-C(20)-C(21)-C(27)	-176.5(5)
C(20)-C(21)-C(22)-C(23)	-0.5(8)
C(27)-C(21)-C(22)-C(23)	177.0(6)
C(21)-C(22)-C(23)-C(18)	0.5(8)
C(21)-C(22)-C(23)-C(30)	-179.7(5)
C(19)-C(18)-C(23)-C(22)	-1.0(8)
S(1)-C(18)-C(23)-C(22)	177.3(4)
C(19)-C(18)-C(23)-C(30)	179.3(5)
S(1)-C(18)-C(23)-C(30)	-2.4(7)
C(20)-C(19)-C(24)-C(25)	-97.9(6)
C(18)-C(19)-C(24)-C(25)	79.8(7)
C(20)-C(19)-C(24)-C(26)	26.1(8)
C(18)-C(19)-C(24)-C(26)	-156.2(6)
C(22)-C(21)-C(27)-C(28)	-89.7(6)
C(20)-C(21)-C(27)-C(28)	87.6(6)
C(22)-C(21)-C(27)-C(29)	144.2(5)
C(20)-C(21)-C(27)-C(29)	-38.4(8)
C(22)-C(23)-C(30)-C(31)	54.4(6)
C(18)-C(23)-C(30)-C(31)	-125.9(6)
C(22)-C(23)-C(30)-C(32)	-68.6(6)
C(18)-C(23)-C(30)-C(32)	111.1(6)
O(1)-C(10)-Mo(1)-C(11)	45(5)
O(1)-C(10)-Mo(1)-N(5)	-48(5)
O(1)-C(10)-Mo(1)-C(12)	149(5)
O(1)-C(10)-Mo(1)-N(1)	-26(6)

O(1)-C(10)-Mo(1)-N(3)	-126(5)
O(1)-C(10)-Mo(1)-C(13)	158(5)
O(1)-C(10)-Mo(1)-C(17)	114(5)
O(2)-C(11)-Mo(1)-C(10)	4(31)
O(2)-C(11)-Mo(1)-N(5)	86(31)
O(2)-C(11)-Mo(1)-C(12)	-95(31)
O(2)-C(11)-Mo(1)-N(1)	165(31)
O(2)-C(11)-Mo(1)-N(3)	124(30)
O(2)-C(11)-Mo(1)-C(13)	-57(31)
O(2)-C(11)-Mo(1)-C(17)	-105(31)
C(17)-C(12)-Mo(1)-C(10)	-102.9(3)
C(13)-C(12)-Mo(1)-C(10)	12.8(3)
C(17)-C(12)-Mo(1)-C(11)	-17.4(3)
C(13)-C(12)-Mo(1)-C(11)	98.4(3)
C(17)-C(12)-Mo(1)-N(5)	159.7(5)
C(13)-C(12)-Mo(1)-N(5)	-84.6(6)
C(17)-C(12)-Mo(1)-N(1)	75.4(3)
C(13)-C(12)-Mo(1)-N(1)	-168.9(3)
C(17)-C(12)-Mo(1)-N(3)	156.2(3)
C(13)-C(12)-Mo(1)-N(3)	-88.1(3)
C(17)-C(12)-Mo(1)-C(13)	-115.8(4)
C(13)-C(12)-Mo(1)-C(17)	115.8(4)
C(12)-C(13)-Mo(1)-C(10)	-166.1(3)
C(14)-C(13)-Mo(1)-C(10)	-56.3(4)
C(12)-C(13)-Mo(1)-C(11)	-92.9(3)
C(14)-C(13)-Mo(1)-C(11)	16.9(4)
C(12)-C(13)-Mo(1)-N(5)	152.5(3)
C(14)-C(13)-Mo(1)-N(5)	-97.7(4)
C(14)-C(13)-Mo(1)-C(12)	109.8(5)
C(12)-C(13)-Mo(1)-N(1)	15.6(4)
C(14)-C(13)-Mo(1)-N(1)	125.4(4)
C(12)-C(13)-Mo(1)-N(3)	86.9(3)
C(14)-C(13)-Mo(1)-N(3)	-163.3(4)
C(12)-C(13)-Mo(1)-C(17)	-37.1(3)
C(14)-C(13)-Mo(1)-C(17)	72.7(4)
C(12)-C(17)-Mo(1)-C(10)	85.4(3)
O(3)-C(17)-Mo(1)-C(10)	-164.1(3)
C(16)-C(17)-Mo(1)-C(10)	-28.8(4)
C(12)-C(17)-Mo(1)-C(11)	162.4(3)
O(3)-C(17)-Mo(1)-C(11)	-87.2(3)
C(16)-C(17)-Mo(1)-C(11)	48.2(4)
C(12)-C(17)-Mo(1)-N(5)	-161.2(4)
O(3)-C(17)-Mo(1)-N(5)	-50.7(7)
C(16)-C(17)-Mo(1)-N(5)	84.6(6)
O(3)-C(17)-Mo(1)-C(12)	110.4(5)
C(16)-C(17)-Mo(1)-C(12)	-114.2(5)
C(12)-C(17)-Mo(1)-N(1)	-107.4(3)
O(3)-C(17)-Mo(1)-N(1)	3.0(3)
C(16)-C(17)-Mo(1)-N(1)	138.4(4)
C(12)-C(17)-Mo(1)-N(3)	-26.0(3)
O(3)-C(17)-Mo(1)-N(3)	84.4(3)
C(16)-C(17)-Mo(1)-N(3)	-140.3(3)
C(12)-C(17)-Mo(1)-C(13)	38.3(3)
O(3)-C(17)-Mo(1)-C(13)	148.7(4)
C(16)-C(17)-Mo(1)-C(13)	-75.9(4)

C(2)-C(1)-N(1)-N(2)	-1.2(6)
C(2)-C(1)-N(1)-Mo(1)	-176.1(4)
C(10)-Mo(1)-N(1)-C(1)	105.6(7)
C(11)-Mo(1)-N(1)-C(1)	36.5(5)
N(5)-Mo(1)-N(1)-C(1)	128.6(5)
C(12)-Mo(1)-N(1)-C(1)	-69.5(5)
N(3)-Mo(1)-N(1)-C(1)	-150.3(5)
C(13)-Mo(1)-N(1)-C(1)	-78.8(6)
C(17)-Mo(1)-N(1)-C(1)	-35.7(5)
C(10)-Mo(1)-N(1)-N(2)	-68.7(6)
C(11)-Mo(1)-N(1)-N(2)	-137.8(4)
N(5)-Mo(1)-N(1)-N(2)	-45.7(4)
C(12)-Mo(1)-N(1)-N(2)	116.2(4)
N(3)-Mo(1)-N(1)-N(2)	35.5(4)
C(13)-Mo(1)-N(1)-N(2)	106.9(4)
C(17)-Mo(1)-N(1)-N(2)	150.0(4)
C(2)-C(3)-N(2)-N(1)	0.1(7)
C(2)-C(3)-N(2)-B(1)	168.0(5)
C(1)-N(1)-N(2)-C(3)	0.7(6)
Mo(1)-N(1)-N(2)-C(3)	176.4(4)
C(1)-N(1)-N(2)-B(1)	-168.4(5)
Mo(1)-N(1)-N(2)-B(1)	7.3(6)
N(4)-B(1)-N(2)-C(3)	130.2(6)
N(6)-B(1)-N(2)-C(3)	-112.3(6)
N(4)-B(1)-N(2)-N(1)	-63.0(6)
N(6)-B(1)-N(2)-N(1)	54.5(6)
C(5)-C(4)-N(3)-N(4)	-0.4(6)
C(5)-C(4)-N(3)-Mo(1)	173.7(4)
C(10)-Mo(1)-N(3)-C(4)	-54.3(5)
C(11)-Mo(1)-N(3)-C(4)	-172.9(9)
N(5)-Mo(1)-N(3)-C(4)	-134.2(5)
C(12)-Mo(1)-N(3)-C(4)	44.7(5)
N(1)-Mo(1)-N(3)-C(4)	145.5(5)
C(13)-Mo(1)-N(3)-C(4)	8.1(5)
C(17)-Mo(1)-N(3)-C(4)	59.4(5)
C(10)-Mo(1)-N(3)-N(4)	119.1(4)
C(11)-Mo(1)-N(3)-N(4)	0.6(11)
N(5)-Mo(1)-N(3)-N(4)	39.2(3)
C(12)-Mo(1)-N(3)-N(4)	-141.9(4)
N(1)-Mo(1)-N(3)-N(4)	-41.1(3)
C(13)-Mo(1)-N(3)-N(4)	-178.5(4)
C(17)-Mo(1)-N(3)-N(4)	-127.1(3)
C(5)-C(6)-N(4)-N(3)	-0.3(6)
C(5)-C(6)-N(4)-B(1)	-179.0(5)
C(4)-N(3)-N(4)-C(6)	0.4(6)
Mo(1)-N(3)-N(4)-C(6)	-174.8(3)
C(4)-N(3)-N(4)-B(1)	179.2(4)
Mo(1)-N(3)-N(4)-B(1)	4.0(6)
N(2)-B(1)-N(4)-C(6)	-125.6(5)
N(6)-B(1)-N(4)-C(6)	116.6(6)
N(2)-B(1)-N(4)-N(3)	55.9(6)
N(6)-B(1)-N(4)-N(3)	-61.9(6)
C(8)-C(7)-N(5)-N(6)	0.1(6)
C(8)-C(7)-N(5)-Mo(1)	-178.9(3)
C(10)-Mo(1)-N(5)-C(7)	31.7(4)

C(11)-Mo(1)-N(5)-C(7)	-50.9(5)
C(12)-Mo(1)-N(5)-C(7)	131.9(6)
N(1)-Mo(1)-N(5)-C(7)	-140.6(4)
N(3)-Mo(1)-N(5)-C(7)	135.4(4)
C(13)-Mo(1)-N(5)-C(7)	68.9(5)
C(17)-Mo(1)-N(5)-C(7)	-85.4(6)
C(10)-Mo(1)-N(5)-N(6)	-147.2(4)
C(11)-Mo(1)-N(5)-N(6)	130.2(4)
C(12)-Mo(1)-N(5)-N(6)	-46.9(7)
N(1)-Mo(1)-N(5)-N(6)	40.6(3)
N(3)-Mo(1)-N(5)-N(6)	-43.4(3)
C(13)-Mo(1)-N(5)-N(6)	-109.9(4)
C(17)-Mo(1)-N(5)-N(6)	95.8(6)
C(8)-C(9)-N(6)-N(5)	0.0(5)
C(8)-C(9)-N(6)-B(1)	175.2(5)
C(7)-N(5)-N(6)-C(9)	-0.1(5)
Mo(1)-N(5)-N(6)-C(9)	179.0(3)
C(7)-N(5)-N(6)-B(1)	-175.9(4)
Mo(1)-N(5)-N(6)-B(1)	3.1(5)
N(2)-B(1)-N(6)-C(9)	124.1(5)
N(4)-B(1)-N(6)-C(9)	-116.5(5)
N(2)-B(1)-N(6)-N(5)	-61.1(6)
N(4)-B(1)-N(6)-N(5)	58.2(5)
C(12)-C(17)-O(3)-S(1)	-70.5(5)
C(16)-C(17)-O(3)-S(1)	78.1(5)
Mo(1)-C(17)-O(3)-S(1)	-143.1(2)
C(17)-O(3)-S(1)-O(5)	-66.6(4)
C(17)-O(3)-S(1)-O(4)	61.5(4)
C(17)-O(3)-S(1)-C(18)	179.2(3)
C(23)-C(18)-S(1)-O(5)	-49.0(5)
C(19)-C(18)-S(1)-O(5)	129.3(4)
C(23)-C(18)-S(1)-O(4)	178.2(4)
C(19)-C(18)-S(1)-O(4)	-3.5(5)
C(23)-C(18)-S(1)-O(3)	65.5(4)
C(19)-C(18)-S(1)-O(3)	-116.2(4)

Symmetry transformations used to generate equivalent atoms:

Table 4.12. Crystal data and structure refinement for (1*S*, *R*)-4.12.

Identification code	(1*S*, *R*)-**4.12**
Empirical formula	C24 H27 B Mo N6 O7
Formula weight	618.27
Temperature	173(2) K
Wavelength	0.71073 Å

Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.9080(6) Å	α= 90°.
	b = 15.9173(12) Å	β= 90°.
	c = 21.9238(17) Å	γ = 90°.
Volume	2759.6(4) $Å^3$	
Z	4	
Density (calculated)	1.488 Mg/m^3	
Absorption coefficient	0.528 mm^{-1}	
F(000)	1264	
Crystal size	0.45 x 0.43 x 0.28 mm^3	
Theta range for data collection	1.58 to 28.31°.	
Index ranges	-10<=h<=10, -21<=k<=21, -29<=l<=29	
Reflections collected	38329	
Independent reflections	6861 [R(int) = 0.0272]	
Completeness to theta = 28.31°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.855595	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6861 / 0 / 460	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0186, wR2 = 0.0479	
R indices (all data)	R1 = 0.0191, wR2 = 0.0481	
Absolute structure parameter	0.001(15)	
Largest diff. peak and hole	0.235 and -0.312 $e.Å^{-3}$	

Table 4.13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (1*S*, *R*)-4.12. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	-1048(2)	5352(1)	8486(1)	24(1)
C(1)	-2607(2)	5022(1)	9516(1)	31(1)
C(2)	-2570(2)	4366(1)	9929(1)	35(1)
C(3)	-1285(2)	3843(1)	9725(1)	29(1)
C(4)	1466(2)	6389(1)	8400(1)	28(1)
C(5)	3197(2)	6328(1)	8375(1)	31(1)
C(6)	3519(2)	5472(1)	8444(1)	26(1)
C(7)	-2635(2)	4742(1)	7545(1)	30(1)
C(8)	-2680(2)	3984(1)	7247(1)	35(1)
C(9)	-1410(2)	3513(1)	7518(1)	29(1)
C(10)	524(2)	2495(1)	8733(1)	27(1)
C(11)	2522(2)	3395(1)	9415(1)	28(1)
C(12)	2737(2)	2766(1)	7861(1)	21(1)
C(13)	3617(2)	3509(1)	8000(1)	21(1)
C(14)	4411(2)	3481(1)	8587(1)	26(1)
C(15)	5319(2)	2679(1)	8771(1)	34(1)
C(16)	4286(3)	1887(1)	8648(1)	35(1)
C(17)	3403(3)	1906(1)	8025(1)	29(1)
C(18)	2640(2)	2891(1)	6786(1)	20(1)
C(19)	2111(2)	3202(1)	5756(1)	22(1)
C(20)	2324(2)	4151(1)	5651(1)	29(1)
C(21)	965(4)	4647(1)	5992(1)	48(1)
C(22)	4087(3)	4488(2)	5783(1)	48(1)
C(23)	774(2)	2945(1)	5292(1)	33(1)
C(24)	1988(2)	4167(1)	4959(1)	34(1)
Mo(1)	1445(1)	3630(1)	8631(1)	17(1)
N(1)	-1417(2)	4883(1)	9089(1)	25(1)
N(2)	-582(2)	4155(1)	9215(1)	24(1)
N(3)	816(2)	5612(1)	8476(1)	23(1)
N(4)	2093(2)	5033(1)	8507(1)	21(1)
N(5)	-1388(2)	4723(1)	7963(1)	24(1)
N(6)	-603(2)	3957(1)	7948(1)	23(1)
O(1)	-23(2)	1828(1)	8793(1)	44(1)
O(2)	3073(2)	3242(1)	9892(1)	43(1)
O(3)	1793(1)	2747(1)	7306(1)	23(1)
O(4)	4142(1)	2938(1)	6721(1)	26(1)
O(5)	1471(1)	2969(1)	6348(1)	23(1)
O(6)	-126(2)	2342(1)	5302(1)	55(1)
O(7)	715(2)	3523(1)	4846(1)	38(1)

Table 4.14. Bond lengths [Å] and angles [°] for (1*S*, *R*)-4.12.

B(1)-N(3)	1.531(2)	B(1)-N(1)	1.547(2)
B(1)-N(5)	1.544(2)	B(1)-H(1)	1.12(2)

C(1)-N(1)	1.345(2)	C(21)-H(22)	0.99(2)
C(1)-C(2)	1.382(3)	C(22)-H(23)	0.92(3)
C(1)-H(2)	0.91(2)	C(22)-H(24)	0.92(3)
C(2)-C(3)	1.388(2)	C(22)-H(25)	1.03(3)
C(2)-H(3)	0.95(2)	C(23)-O(6)	1.196(2)
C(3)-N(2)	1.3434(19)	C(23)-O(7)	1.344(2)
C(3)-H(4)	0.98(2)	C(24)-O(7)	1.458(2)
C(4)-N(3)	1.3493(19)	C(24)-H(26)	1.01(2)
C(4)-C(5)	1.374(2)	C(24)-H(27)	0.99(2)
C(4)-H(5)	0.96(2)	Mo(1)-N(2)	2.2143(13)
C(5)-C(6)	1.395(2)	Mo(1)-N(6)	2.2663(13)
C(5)-H(6)	0.87(2)	Mo(1)-N(4)	2.3075(12)
C(6)-N(4)	1.334(2)	N(1)-N(2)	1.3625(18)
C(6)-H(7)	0.88(2)	N(3)-N(4)	1.3696(18)
C(7)-N(5)	1.348(2)	N(5)-N(6)	1.3694(18)
C(7)-C(8)	1.371(3)	N(3)-B(1)-N(5)	109.43(13)
C(7)-H(8)	0.92(2)	N(3)-B(1)-N(1)	108.94(13)
C(8)-C(9)	1.388(3)	N(5)-B(1)-N(1)	106.80(12)
C(8)-H(9)	0.89(2)	N(3)-B(1)-H(1)	109.3(11)
C(9)-N(6)	1.341(2)	N(5)-B(1)-H(1)	109.8(11)
C(9)-H(10)	0.91(2)	N(1)-B(1)-H(1)	112.5(11)
C(10)-O(1)	1.154(2)	N(1)-C(1)-C(2)	108.49(15)
C(10)-Mo(1)	1.9609(16)	N(1)-C(1)-H(2)	117.5(14)
C(11)-O(2)	1.159(2)	C(2)-C(1)-H(2)	134.0(14)
C(11)-Mo(1)	1.9530(17)	C(1)-C(2)-C(3)	104.89(15)
C(12)-C(13)	1.405(2)	C(1)-C(2)-H(3)	130.3(14)
C(12)-O(3)	1.4290(17)	C(3)-C(2)-H(3)	124.6(14)
C(12)-C(17)	1.510(2)	N(2)-C(3)-C(2)	110.48(15)
C(12)-Mo(1)	2.4055(14)	N(2)-C(3)-H(4)	115.2(14)
C(13)-C(14)	1.435(2)	C(2)-C(3)-H(4)	134.2(14)
C(13)-Mo(1)	2.2144(14)	N(3)-C(4)-C(5)	108.64(15)
C(13)-H(11)	0.951(18)	N(3)-C(4)-H(5)	119.7(13)
C(14)-C(15)	1.519(2)	C(5)-C(4)-H(5)	131.6(13)
C(14)-Mo(1)	2.3595(15)	C(4)-C(5)-C(6)	104.31(15)
C(14)-H(12)	0.99(2)	C(4)-C(5)-H(6)	127.3(14)
C(15)-C(16)	1.527(3)	C(6)-C(5)-H(6)	128.4(14)
C(15)-H(13)	0.90(2)	N(4)-C(6)-C(5)	111.60(16)
C(15)-H(14)	0.98(2)	N(4)-C(6)-H(7)	123.3(14)
C(16)-C(17)	1.533(3)	C(5)-C(6)-H(7)	125.0(14)
C(16)-H(15)	0.94(2)	N(5)-C(7)-C(8)	108.84(16)
C(16)-H(16)	0.94(3)	N(5)-C(7)-H(8)	119.3(13)
C(17)-H(17)	0.95(2)	C(8)-C(7)-H(8)	131.8(13)
C(17)-H(18)	0.95(2)	C(7)-C(8)-C(9)	104.73(15)
C(18)-O(4)	1.1984(18)	C(7)-C(8)-H(9)	127.6(14)
C(18)-O(5)	1.3398(18)	C(9)-C(8)-H(9)	127.6(15)
C(18)-O(3)	1.3404(18)	N(6)-C(9)-C(8)	111.10(15)
C(19)-O(5)	1.4400(17)	N(6)-C(9)-H(10)	122.2(14)
C(19)-C(23)	1.523(2)	C(8)-C(9)-H(10)	126.6(14)
C(19)-C(20)	1.537(2)	O(1)-C(10)-Mo(1)	179.77(17)
C(19)-H(19)	0.905(19)	O(2)-C(11)-Mo(1)	176.16(17)
C(20)-C(22)	1.522(3)	C(13)-C(12)-O(3)	117.38(12)
C(20)-C(21)	1.529(3)	C(13)-C(12)-C(17)	122.61(14)
C(20)-C(24)	1.540(2)	O(3)-C(12)-C(17)	111.53(12)
C(21)-H(20)	0.96(3)	C(13)-C(12)-Mo(1)	64.99(8)
C(21)-H(21)	0.98(3)	O(3)-C(12)-Mo(1)	112.82(9)

C(17)-C(12)-Mo(1)	119.92(9)	C(20)-C(22)-H(25)	108.1(16)
C(12)-C(13)-C(14)	112.61(13)	H(23)-C(22)-H(25)	106(2)
C(12)-C(13)-Mo(1)	79.90(9)	H(24)-C(22)-H(25)	113(2)
C(14)-C(13)-Mo(1)	77.32(8)	O(6)-C(23)-O(7)	122.83(17)
C(12)-C(13)-H(11)	122.0(11)	O(6)-C(23)-C(19)	128.05(16)
C(14)-C(13)-H(11)	125.3(11)	O(7)-C(23)-C(19)	109.11(14)
Mo(1)-C(13)-H(11)	108.9(11)	O(7)-C(24)-C(20)	106.01(13)
C(13)-C(14)-C(15)	118.15(14)	O(7)-C(24)-H(26)	107.3(13)
C(13)-C(14)-Mo(1)	66.29(8)	C(20)-C(24)-H(26)	113.0(12)
C(15)-C(14)-Mo(1)	122.93(11)	O(7)-C(24)-H(27)	106.6(14)
C(13)-C(14)-H(12)	116.0(13)	C(20)-C(24)-H(27)	115.4(14)
C(15)-C(14)-H(12)	112.8(12)	H(26)-C(24)-H(27)	108.0(18)
Mo(1)-C(14)-H(12)	113.3(12)	C(11)-Mo(1)-C(10)	83.41(7)
C(14)-C(15)-C(16)	113.22(14)	C(11)-Mo(1)-N(2)	83.10(6)
C(14)-C(15)-H(13)	105.3(13)	C(10)-Mo(1)-N(2)	90.73(6)
C(16)-C(15)-H(13)	107.6(13)	C(11)-Mo(1)-C(13)	101.26(6)
C(14)-C(15)-H(14)	111.4(13)	C(10)-Mo(1)-C(13)	106.22(6)
C(16)-C(15)-H(14)	111.2(13)	N(2)-Mo(1)-C(13)	162.82(5)
H(13)-C(15)-H(14)	107.9(19)	C(11)-Mo(1)-N(6)	159.46(6)
C(15)-C(16)-C(17)	112.66(15)	C(10)-Mo(1)-N(6)	91.23(6)
C(15)-C(16)-H(15)	111.4(13)	N(2)-Mo(1)-N(6)	77.15(5)
C(17)-C(16)-H(15)	108.3(13)	C(13)-Mo(1)-N(6)	99.27(5)
C(15)-C(16)-H(16)	110.7(14)	C(11)-Mo(1)-N(4)	101.08(6)
C(17)-C(16)-H(16)	108.4(15)	C(10)-Mo(1)-N(4)	171.02(6)
H(15)-C(16)-H(16)	105.0(19)	N(2)-Mo(1)-N(4)	82.17(5)
C(12)-C(17)-C(16)	112.91(13)	C(13)-Mo(1)-N(4)	80.69(5)
C(12)-C(17)-H(17)	104.8(13)	N(6)-Mo(1)-N(4)	81.87(5)
C(16)-C(17)-H(17)	112.2(14)	C(11)-Mo(1)-C(14)	65.36(6)
C(12)-C(17)-H(18)	110.5(12)	C(10)-Mo(1)-C(14)	106.34(6)
C(16)-C(17)-H(18)	112.4(12)	N(2)-Mo(1)-C(14)	141.35(5)
H(17)-C(17)-H(18)	103.2(18)	C(13)-Mo(1)-C(14)	36.39(5)
O(4)-C(18)-O(5)	126.32(14)	N(6)-Mo(1)-C(14)	134.98(5)
O(4)-C(18)-O(3)	127.37(14)	N(4)-Mo(1)-C(14)	82.64(5)
O(5)-C(18)-O(3)	106.31(12)	C(11)-Mo(1)-C(12)	108.82(6)
O(5)-C(19)-C(23)	106.75(12)	C(10)-Mo(1)-C(12)	73.20(6)
O(5)-C(19)-C(20)	115.25(12)	N(2)-Mo(1)-C(12)	158.22(5)
C(23)-C(19)-C(20)	103.81(13)	C(13)-Mo(1)-C(12)	35.11(5)
O(5)-C(19)-H(19)	110.4(11)	N(6)-Mo(1)-C(12)	88.36(5)
C(23)-C(19)-H(19)	109.9(11)	N(4)-Mo(1)-C(12)	112.11(5)
C(20)-C(19)-H(19)	110.3(11)	C(14)-Mo(1)-C(12)	59.45(5)
C(22)-C(20)-C(21)	111.63(18)	C(1)-N(1)-N(2)	109.78(13)
C(22)-C(20)-C(19)	114.70(16)	C(1)-N(1)-B(1)	130.35(14)
C(21)-C(20)-C(19)	110.94(15)	N(2)-N(1)-B(1)	119.47(12)
C(22)-C(20)-C(24)	109.83(16)	C(3)-N(2)-N(1)	106.36(13)
C(21)-C(20)-C(24)	110.62(16)	C(3)-N(2)-Mo(1)	129.88(11)
C(19)-C(20)-C(24)	98.38(13)	N(1)-N(2)-Mo(1)	123.72(9)
C(20)-C(21)-H(20)	110.9(15)	C(4)-N(3)-N(4)	110.03(13)
C(20)-C(21)-H(21)	111.3(17)	C(4)-N(3)-B(1)	128.08(13)
H(20)-C(21)-H(21)	112(2)	N(4)-N(3)-B(1)	121.76(12)
C(20)-C(21)-H(22)	111.4(13)	C(6)-N(4)-N(3)	105.42(12)
H(20)-C(21)-H(22)	110(2)	C(6)-N(4)-Mo(1)	134.95(11)
H(21)-C(21)-H(22)	102(2)	N(3)-N(4)-Mo(1)	119.62(9)
C(20)-C(22)-H(23)	111.3(16)	C(7)-N(5)-N(6)	109.59(13)
C(20)-C(22)-H(24)	110.1(16)	C(7)-N(5)-B(1)	128.18(14)
H(23)-C(22)-H(24)	109(2)	N(6)-N(5)-B(1)	121.06(12)

C(9)-N(6)-N(5)	105.72(13)	C(18)-O(3)-C(12)	117.33(11)
C(9)-N(6)-Mo(1)	133.16(11)	C(18)-O(5)-C(19)	115.33(12)
N(5)-N(6)-Mo(1)	120.85(10)	C(23)-O(7)-C(24)	109.41(13)

Symmetry transformations used to generate equivalent atoms:

Table 4.15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (1*S*, *R*)-4.12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	23(1)	20(1)	30(1)	2(1)	2(1)	2(1)
C(1)	26(1)	34(1)	33(1)	-6(1)	7(1)	3(1)
C(2)	34(1)	41(1)	29(1)	0(1)	12(1)	1(1)
C(3)	35(1)	30(1)	22(1)	2(1)	8(1)	0(1)
C(4)	36(1)	19(1)	30(1)	1(1)	4(1)	-1(1)
C(5)	36(1)	24(1)	33(1)	-1(1)	6(1)	-11(1)
C(6)	25(1)	26(1)	27(1)	-2(1)	3(1)	-4(1)
C(7)	21(1)	39(1)	31(1)	10(1)	-2(1)	-1(1)
C(8)	24(1)	53(1)	30(1)	-2(1)	-5(1)	-7(1)
C(9)	24(1)	36(1)	27(1)	-6(1)	2(1)	-5(1)
C(10)	34(1)	24(1)	22(1)	3(1)	6(1)	1(1)
C(11)	36(1)	28(1)	20(1)	0(1)	0(1)	5(1)
C(12)	26(1)	23(1)	14(1)	0(1)	2(1)	2(1)
C(13)	21(1)	23(1)	18(1)	0(1)	0(1)	2(1)
C(14)	24(1)	31(1)	22(1)	-3(1)	-2(1)	3(1)
C(15)	32(1)	44(1)	26(1)	2(1)	-5(1)	14(1)
C(16)	47(1)	30(1)	28(1)	5(1)	0(1)	16(1)
C(17)	41(1)	21(1)	24(1)	-1(1)	4(1)	8(1)
C(18)	25(1)	16(1)	18(1)	-2(1)	0(1)	1(1)
C(19)	25(1)	25(1)	16(1)	1(1)	1(1)	-1(1)
C(20)	36(1)	25(1)	24(1)	3(1)	-3(1)	-2(1)
C(21)	70(2)	33(1)	42(1)	-2(1)	3(1)	17(1)
C(22)	53(1)	43(1)	47(1)	13(1)	-13(1)	-21(1)
C(23)	38(1)	41(1)	21(1)	-1(1)	-4(1)	-7(1)
C(24)	39(1)	38(1)	26(1)	10(1)	-3(1)	-1(1)
Mo(1)	22(1)	16(1)	14(1)	0(1)	1(1)	0(1)
N(1)	24(1)	22(1)	28(1)	-1(1)	4(1)	3(1)
N(2)	29(1)	20(1)	22(1)	1(1)	4(1)	-1(1)
N(3)	26(1)	17(1)	26(1)	2(1)	1(1)	0(1)
N(4)	23(1)	20(1)	22(1)	-1(1)	1(1)	0(1)
N(5)	23(1)	24(1)	26(1)	5(1)	-1(1)	0(1)
N(6)	23(1)	23(1)	23(1)	0(1)	-1(1)	-1(1)
O(1)	58(1)	23(1)	53(1)	3(1)	17(1)	-9(1)
O(2)	56(1)	51(1)	21(1)	4(1)	-7(1)	12(1)
O(3)	26(1)	28(1)	15(1)	-2(1)	1(1)	-3(1)
O(4)	21(1)	37(1)	20(1)	0(1)	1(1)	3(1)
O(5)	22(1)	31(1)	16(1)	2(1)	0(1)	-2(1)
O(6)	70(1)	63(1)	33(1)	3(1)	-16(1)	-36(1)
O(7)	41(1)	49(1)	23(1)	7(1)	-9(1)	-6(1)

Table 4.16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (1*S*, *R*)-4.12.

	x	y	z	U(eq)
H(1)	-1860(30)	5921(13)	8426(9)	34(5)
H(2)	-3250(30)	5493(13)	9478(10)	34(5)
H(3)	-3300(30)	4244(14)	10263(10)	43(6)
H(4)	-850(30)	3293(14)	9854(10)	40(6)
H(5)	730(30)	6866(13)	8396(9)	31(5)
H(6)	3920(30)	6736(13)	8321(9)	32(5)
H(7)	4540(30)	5244(13)	8470(9)	33(5)
H(8)	-3300(30)	5218(13)	7510(9)	34(5)
H(9)	-3340(30)	3837(14)	6940(11)	43(6)
H(10)	-1160(30)	2962(13)	7442(9)	32(5)
H(11)	3620(20)	3978(11)	7731(8)	19(4)
H(12)	5030(30)	3993(14)	8712(10)	40(6)
H(13)	6250(30)	2658(13)	8534(9)	31(5)
H(14)	5690(30)	2702(13)	9197(10)	39(6)
H(15)	4960(30)	1404(14)	8666(9)	39(5)
H(16)	3460(30)	1810(14)	8950(11)	43(6)
H(17)	4150(30)	1762(13)	7702(11)	40(6)
H(18)	2530(30)	1498(13)	7994(9)	29(5)
H(19)	3090(20)	2930(11)	5678(8)	20(4)
H(20)	1000(30)	5228(16)	5882(11)	53(7)
H(21)	-170(40)	4405(18)	5926(13)	66(9)
H(22)	1090(30)	4589(14)	6440(11)	43(6)
H(23)	4900(30)	4163(16)	5603(12)	48(7)
H(24)	4270(30)	4501(15)	6196(12)	51(7)
H(25)	4190(40)	5070(17)	5583(13)	65(8)
H(26)	1510(30)	4718(13)	4814(10)	39(5)
H(27)	2970(30)	4026(15)	4698(11)	46(6)

Table 4.17. Torsion angles [°] for (1*S*, *R*)-4.12.

N(1)-C(1)-C(2)-C(3)	0.6(2)
C(1)-C(2)-C(3)-N(2)	-0.4(2)
N(3)-C(4)-C(5)-C(6)	-0.24(18)
C(4)-C(5)-C(6)-N(4)	-0.07(19)
N(5)-C(7)-C(8)-C(9)	0.8(2)
C(7)-C(8)-C(9)-N(6)	-1.2(2)
O(3)-C(12)-C(13)-C(14)	175.51(12)
C(17)-C(12)-C(13)-C(14)	-39.20(19)
Mo(1)-C(12)-C(13)-C(14)	71.59(11)
O(3)-C(12)-C(13)-Mo(1)	103.91(11)
C(17)-C(12)-C(13)-Mo(1)	-110.80(13)
C(12)-C(13)-C(14)-C(15)	42.8(2)
Mo(1)-C(13)-C(14)-C(15)	116.00(14)
C(12)-C(13)-C(14)-Mo(1)	-73.23(11)
C(13)-C(14)-C(15)-C(16)	-46.9(2)
Mo(1)-C(14)-C(15)-C(16)	31.78(19)

C(14)-C(15)-C(16)-C(17)	43.0(2)
C(13)-C(12)-C(17)-C(16)	38.1(2)
O(3)-C(12)-C(17)-C(16)	-174.83(14)
Mo(1)-C(12)-C(17)-C(16)	-39.7(2)
C(15)-C(16)-C(17)-C(12)	-38.0(2)
O(5)-C(19)-C(20)-C(22)	94.44(19)
C(23)-C(19)-C(20)-C(22)	-149.19(17)
O(5)-C(19)-C(20)-C(21)	-33.2(2)
C(23)-C(19)-C(20)-C(21)	83.19(17)
O(5)-C(19)-C(20)-C(24)	-149.13(13)
C(23)-C(19)-C(20)-C(24)	-32.76(16)
O(5)-C(19)-C(23)-O(6)	-36.0(3)
C(20)-C(19)-C(23)-O(6)	-158.2(2)
O(5)-C(19)-C(23)-O(7)	143.28(14)
C(20)-C(19)-C(23)-O(7)	21.09(18)
C(22)-C(20)-C(24)-O(7)	154.98(16)
C(21)-C(20)-C(24)-O(7)	-81.35(19)
C(19)-C(20)-C(24)-O(7)	34.84(17)
O(2)-C(11)-Mo(1)-C(10)	-51(2)
O(2)-C(11)-Mo(1)-N(2)	41(2)
O(2)-C(11)-Mo(1)-C(13)	-156(2)
O(2)-C(11)-Mo(1)-N(6)	25(2)
O(2)-C(11)-Mo(1)-N(4)	121(2)
O(2)-C(11)-Mo(1)-C(14)	-162(2)
O(2)-C(11)-Mo(1)-C(12)	-120(2)
O(1)-C(10)-Mo(1)-C(11)	120(24)
O(1)-C(10)-Mo(1)-N(2)	37(24)
O(1)-C(10)-Mo(1)-C(13)	-141(100)
O(1)-C(10)-Mo(1)-N(6)	-41(24)
O(1)-C(10)-Mo(1)-N(4)	-1(25)
O(1)-C(10)-Mo(1)-C(14)	-179(100)
O(1)-C(10)-Mo(1)-C(12)	-128(84)
C(12)-C(13)-Mo(1)-C(11)	106.77(9)
C(14)-C(13)-Mo(1)-C(11)	-9.35(10)
C(12)-C(13)-Mo(1)-C(10)	20.44(10)
C(14)-C(13)-Mo(1)-C(10)	-95.68(9)
C(12)-C(13)-Mo(1)-N(2)	-149.98(16)
C(14)-C(13)-Mo(1)-N(2)	93.90(18)
C(12)-C(13)-Mo(1)-N(6)	-73.58(9)
C(14)-C(13)-Mo(1)-N(6)	170.30(8)
C(12)-C(13)-Mo(1)-N(4)	-153.67(9)
C(14)-C(13)-Mo(1)-N(4)	90.20(9)
C(12)-C(13)-Mo(1)-C(14)	116.12(12)
C(14)-C(13)-Mo(1)-C(12)	-116.12(12)
C(13)-C(14)-Mo(1)-C(11)	169.90(11)
C(15)-C(14)-Mo(1)-C(11)	60.67(13)
C(13)-C(14)-Mo(1)-C(10)	95.33(9)
C(15)-C(14)-Mo(1)-C(10)	-13.90(14)
C(13)-C(14)-Mo(1)-N(2)	-151.85(8)
C(15)-C(14)-Mo(1)-N(2)	98.92(14)
C(15)-C(14)-Mo(1)-C(13)	-109.23(16)
C(13)-C(14)-Mo(1)-N(6)	-13.60(12)
C(15)-C(14)-Mo(1)-N(6)	-122.83(12)
C(13)-C(14)-Mo(1)-N(4)	-84.28(8)
C(15)-C(14)-Mo(1)-N(4)	166.48(13)
C(13)-C(14)-Mo(1)-C(12)	36.84(8)

C(15)-C(14)-Mo(1)-C(12)	-72.39(13)
C(13)-C(12)-Mo(1)-C(11)	-82.76(10)
O(3)-C(12)-Mo(1)-C(11)	166.49(10)
C(17)-C(12)-Mo(1)-C(11)	31.92(14)
C(13)-C(12)-Mo(1)-C(10)	-159.50(10)
O(3)-C(12)-Mo(1)-C(10)	89.75(10)
C(17)-C(12)-Mo(1)-C(10)	-44.81(13)
C(13)-C(12)-Mo(1)-N(2)	156.53(12)
O(3)-C(12)-Mo(1)-N(2)	45.78(18)
C(17)-C(12)-Mo(1)-N(2)	-88.78(17)
O(3)-C(12)-Mo(1)-C(13)	-110.75(13)
C(17)-C(12)-Mo(1)-C(13)	114.69(16)
C(13)-C(12)-Mo(1)-N(6)	108.73(9)
O(3)-C(12)-Mo(1)-N(6)	-2.02(10)
C(17)-C(12)-Mo(1)-N(6)	-136.58(13)
C(13)-C(12)-Mo(1)-N(4)	28.19(9)
O(3)-C(12)-Mo(1)-N(4)	-82.56(10)
C(17)-C(12)-Mo(1)-N(4)	142.88(12)
C(13)-C(12)-Mo(1)-C(14)	-38.21(8)
O(3)-C(12)-Mo(1)-C(14)	-148.96(12)
C(17)-C(12)-Mo(1)-C(14)	76.48(13)
C(2)-C(1)-N(1)-N(2)	-0.6(2)
C(2)-C(1)-N(1)-B(1)	171.95(16)
N(3)-B(1)-N(1)-C(1)	126.52(17)
N(5)-B(1)-N(1)-C(1)	-115.39(18)
N(3)-B(1)-N(1)-N(2)	-61.52(17)
N(5)-B(1)-N(1)-N(2)	56.57(17)
C(2)-C(3)-N(2)-N(1)	0.03(19)
C(2)-C(3)-N(2)-Mo(1)	-177.49(12)
C(1)-N(1)-N(2)-C(3)	0.36(18)
B(1)-N(1)-N(2)-C(3)	-173.13(14)
C(1)-N(1)-N(2)-Mo(1)	178.07(11)
B(1)-N(1)-N(2)-Mo(1)	4.58(19)
C(11)-Mo(1)-N(2)-C(3)	-44.34(15)
C(10)-Mo(1)-N(2)-C(3)	38.93(15)
C(13)-Mo(1)-N(2)-C(3)	-150.27(17)
N(6)-Mo(1)-N(2)-C(3)	130.02(15)
N(4)-Mo(1)-N(2)-C(3)	-146.58(15)
C(14)-Mo(1)-N(2)-C(3)	-78.87(17)
C(12)-Mo(1)-N(2)-C(3)	80.6(2)
C(11)-Mo(1)-N(2)-N(1)	138.52(13)
C(10)-Mo(1)-N(2)-N(1)	-138.21(12)
C(13)-Mo(1)-N(2)-N(1)	32.6(2)
N(6)-Mo(1)-N(2)-N(1)	-47.12(11)
N(4)-Mo(1)-N(2)-N(1)	36.28(12)
C(14)-Mo(1)-N(2)-N(1)	103.99(13)
C(12)-Mo(1)-N(2)-N(1)	-96.54(16)
C(5)-C(4)-N(3)-N(4)	0.46(17)
C(5)-C(4)-N(3)-B(1)	-175.50(15)
N(5)-B(1)-N(3)-C(4)	119.28(16)
N(1)-B(1)-N(3)-C(4)	-124.29(15)
N(5)-B(1)-N(3)-N(4)	-56.24(17)
N(1)-B(1)-N(3)-N(4)	60.18(17)
C(5)-C(6)-N(4)-N(3)	0.34(17)
C(5)-C(6)-N(4)-Mo(1)	179.29(10)
C(4)-N(3)-N(4)-C(6)	-0.49(16)

B(1)-N(3)-N(4)-C(6)	175.77(13)
C(4)-N(3)-N(4)-Mo(1)	-179.64(10)
B(1)-N(3)-N(4)-Mo(1)	-3.38(17)
C(11)-Mo(1)-N(4)-C(6)	63.21(15)
C(10)-Mo(1)-N(4)-C(6)	-177.4(3)
N(2)-Mo(1)-N(4)-C(6)	144.55(15)
C(13)-Mo(1)-N(4)-C(6)	-36.55(14)
N(6)-Mo(1)-N(4)-C(6)	-137.41(15)
C(14)-Mo(1)-N(4)-C(6)	0.19(14)
C(12)-Mo(1)-N(4)-C(6)	-52.53(15)
C(11)-Mo(1)-N(4)-N(3)	-117.95(11)
C(10)-Mo(1)-N(4)-N(3)	1.4(4)
N(2)-Mo(1)-N(4)-N(3)	-36.61(10)
C(13)-Mo(1)-N(4)-N(3)	142.29(11)
N(6)-Mo(1)-N(4)-N(3)	41.43(10)
C(14)-Mo(1)-N(4)-N(3)	179.03(11)
C(12)-Mo(1)-N(4)-N(3)	126.31(10)
C(8)-C(7)-N(5)-N(6)	-0.15(19)
C(8)-C(7)-N(5)-B(1)	-167.75(15)
N(3)-B(1)-N(5)-C(7)	-130.64(16)
N(1)-B(1)-N(5)-C(7)	111.58(17)
N(3)-B(1)-N(5)-N(6)	63.01(17)
N(1)-B(1)-N(5)-N(6)	-54.76(17)
C(8)-C(9)-N(6)-N(5)	1.11(18)
C(8)-C(9)-N(6)-Mo(1)	175.02(12)
C(7)-N(5)-N(6)-C(9)	-0.59(17)
B(1)-N(5)-N(6)-C(9)	168.05(14)
C(7)-N(5)-N(6)-Mo(1)	-175.42(10)
B(1)-N(5)-N(6)-Mo(1)	-6.78(18)
C(11)-Mo(1)-N(6)-C(9)	-109.4(2)
C(10)-Mo(1)-N(6)-C(9)	-35.05(15)
N(2)-Mo(1)-N(6)-C(9)	-125.52(15)
C(13)-Mo(1)-N(6)-C(9)	71.60(15)
N(4)-Mo(1)-N(6)-C(9)	150.72(15)
C(14)-Mo(1)-N(6)-C(9)	79.73(16)
C(12)-Mo(1)-N(6)-C(9)	38.11(15)
C(11)-Mo(1)-N(6)-N(5)	63.8(2)
C(10)-Mo(1)-N(6)-N(5)	138.12(11)
N(2)-Mo(1)-N(6)-N(5)	47.65(11)
C(13)-Mo(1)-N(6)-N(5)	-115.23(11)
N(4)-Mo(1)-N(6)-N(5)	-36.11(11)
C(14)-Mo(1)-N(6)-N(5)	-107.10(12)
C(12)-Mo(1)-N(6)-N(5)	-148.72(11)
O(4)-C(18)-O(3)-C(12)	9.4(2)
O(5)-C(18)-O(3)-C(12)	-170.75(11)
C(13)-C(12)-O(3)-C(18)	57.98(17)
C(17)-C(12)-O(3)-C(18)	-90.98(15)
Mo(1)-C(12)-O(3)-C(18)	130.62(10)
O(4)-C(18)-O(5)-C(19)	-5.5(2)
O(3)-C(18)-O(5)-C(19)	174.70(11)
C(23)-C(19)-O(5)-C(18)	159.36(13)
C(20)-C(19)-O(5)-C(18)	-85.95(17)
O(6)-C(23)-O(7)-C(24)	-178.9(2)
C(19)-C(23)-O(7)-C(24)	1.82(19)
C(20)-C(24)-O(7)-C(23)	-24.25(19)

Symmetry transformations used to generate equivalent atoms:

Table 4.18. Crystal data and structure refinement for (1*R*, *R*)-4.13.

Identification code	(1*R*, *R*)-**4.13**	
Empirical formula	C22 H25 B Mo N6 O7	
Formula weight	592.23	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.8097(14) Å	α= 90°.
	b = 10.2212(14) Å	β= 101.890(7)°.
	c = 15.1441(18) Å	γ = 90°.
Volume	1485.9(3) $Å^3$	
Z	2	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	4.011 mm^{-1}	
F(000)	604	
Crystal size	0.45 x 0.18 x 0.16 mm^3	
Theta range for data collection	8.98 to 66.46°.	
Index ranges	-10<=h<=8, -10<=k<=10, -15<=l<=17	
Reflections collected	6245	
Independent reflections	3289 [R(int) = 0.0306]	
Completeness to theta = 66.46°	78.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5662 and 0.2655	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3289 / 1 / 299	
Goodness-of-fit on F^2	1.102	
Final R indices [I>2sigma(I)]	R1 = 0.0735, wR2 = 0.1864	
R indices (all data)	R1 = 0.0755, wR2 = 0.1886	
Absolute structure parameter	0.14(3)	
Largest diff. peak and hole	1.075 and -1.216 $e.Å^{-3}$	

Table 4.19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (1*R*, *R*)-4.13. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	5360(20)	1524(16)	7322(11)	48(5)
C(1)	8539(15)	3360(20)	7383(9)	54(3)
C(2)	8450(20)	2789(17)	6519(9)	66(5)
C(3)	7244(18)	2119(16)	6371(8)	52(4)
C(4)	3539(15)	4051(15)	8280(11)	46(4)
C(5)	2500(20)	3739(14)	7610(13)	60(5)
C(6)	3047(17)	2740(17)	7147(12)	59(5)
C(7)	7320(13)	288(14)	9430(9)	39(3)
C(8)	6873(18)	-906(16)	9026(11)	57(4)
C(9)	6114(17)	-616(14)	8229(10)	49(4)
C(10)	8842(13)	3340(30)	9624(8)	49(3)
C(11)	6716(15)	2960(11)	10243(8)	38(4)
C(12)	6980(20)	5586(15)	10754(10)	71(6)
C(13)	6115(16)	5133(13)	9892(9)	39(3)
C(14)	6393(19)	5524(14)	9019(10)	31(3)
C(15)	7842(17)	5559(14)	8927(9)	44(4)
C(16)	9251(15)	6241(14)	7991(8)	38(3)
C(17)	10365(16)	7208(14)	6933(9)	41(4)
C(18)	10600(30)	6580(30)	6022(19)	109(8)
C(19)	9080(30)	8770(30)	5787(19)	137(11)
C(20)	10220(20)	8742(15)	6653(13)	69(6)
C(21)	9960(40)	9390(40)	7590(30)	175(15)
C(22)	11830(40)	9050(40)	6690(30)	180(15)
Mo(1)	6931(1)	3393(1)	9071(1)	33(1)
N(1)	7446(12)	3070(9)	7682(6)	35(3)
N(2)	6616(13)	2313(13)	7071(7)	51(3)
N(3)	4667(10)	3334(18)	8267(6)	42(3)
N(4)	4335(11)	2534(10)	7549(7)	37(3)
N(5)	6822(14)	1230(14)	8902(8)	38(4)
N(6)	5967(12)	708(11)	8137(7)	42(3)
O(1)	10083(10)	3129(11)	9981(7)	56(3)
O(2)	6619(10)	2623(10)	11008(6)	49(2)
O(3)	7974(10)	6009(9)	8104(5)	40(2)
O(4)	10359(10)	6048(9)	8499(6)	42(2)
O(5)	9121(12)	6825(10)	7173(6)	56(3)
O(6)	10450(20)	5460(20)	5893(15)	145(7)
O(7)	10220(40)	7550(40)	5460(30)	310(20)

Table 4.20. Bond lengths [Å] and angles [°] for (1*R*, *R*)-4.13.

B(1)-N(6)	1.51(2)	C(2)-C(3)	1.35(2)
B(1)-N(4)	1.53(2)	C(2)-H(2)	0.9500
B(1)-N(2)	1.59(2)	C(3)-N(2)	1.346(18)
B(1)-H(1)	1.0000	C(3)-H(3)	0.9500
C(1)-N(1)	1.283(17)	C(4)-C(5)	1.32(2)
C(1)-C(2)	1.420(19)	C(4)-N(3)	1.33(2)
C(1)-H(1)	0.9500	C(4)-H(4)	0.9500

C(5)-C(6)	1.41(2)	N(6)-B(1)-N(2)	106.2(13)
C(5)-H(5)	0.9500	N(4)-B(1)-N(2)	106.8(12)
C(6)-N(4)	1.302(18)	N(6)-B(1)-H(1)	110.9
C(6)-H(6)	0.9500	N(4)-B(1)-H(1)	110.9
C(7)-N(5)	1.283(19)	N(2)-B(1)-H(1)	110.9
C(7)-C(8)	1.39(2)	N(1)-C(1)-C(2)	109.4(15)
C(7)-H(7)	0.9500	N(1)-C(1)-H(1)	125.3
C(8)-C(9)	1.31(2)	C(2)-C(1)-H(1)	125.3
C(8)-H(8)	0.9500	C(3)-C(2)-C(1)	104.4(14)
C(9)-N(6)	1.365(18)	C(3)-C(2)-H(2)	127.8
C(9)-H(9)	0.9500	C(1)-C(2)-H(2)	127.8
C(10)-O(1)	1.245(15)	C(2)-C(3)-N(2)	108.9(13)
C(10)-Mo(1)	1.890(12)	C(2)-C(3)-H(3)	125.6
C(11)-O(2)	1.232(16)	N(2)-C(3)-H(3)	125.6
C(11)-Mo(1)	1.883(14)	C(5)-C(4)-N(3)	111.6(15)
C(12)-C(13)	1.48(2)	C(5)-C(4)-H(4)	124.2
C(12)-H(12A)	0.9800	N(3)-C(4)-H(4)	124.2
C(12)-H(12B)	0.9800	C(4)-C(5)-C(6)	104.2(16)
C(12)-H(12C)	0.9800	C(4)-C(5)-H(5)	127.9
C(13)-C(14)	1.460(19)	C(6)-C(5)-H(5)	127.9
C(13)-Mo(1)	2.401(12)	N(4)-C(6)-C(5)	108.5(16)
C(13)-H(13)	1.0000	N(4)-C(6)-H(6)	125.7
C(14)-C(15)	1.46(2)	C(5)-C(6)-H(6)	125.7
C(14)-Mo(1)	2.239(16)	N(5)-C(7)-C(8)	109.7(13)
C(14)-H(14)	1.0000	N(5)-C(7)-H(7)	125.1
C(15)-O(3)	1.358(16)	C(8)-C(7)-H(7)	125.1
C(15)-Mo(1)	2.414(16)	C(9)-C(8)-C(7)	105.9(13)
C(15)-H(15)	0.9500	C(9)-C(8)-H(8)	127.1
C(16)-O(4)	1.212(16)	C(7)-C(8)-H(8)	127.1
C(16)-O(3)	1.320(16)	C(8)-C(9)-N(6)	110.2(13)
C(16)-O(5)	1.357(15)	C(8)-C(9)-H(9)	124.9
C(17)-O(5)	1.400(17)	N(6)-C(9)-H(9)	124.9
C(17)-C(18)	1.58(3)	O(1)-C(10)-Mo(1)	172(2)
C(17)-C(20)	1.62(2)	O(2)-C(11)-Mo(1)	176.7(11)
C(17)-H(17)	1.0000	C(13)-C(12)-H(12A)	109.4
C(18)-O(6)	1.17(3)	C(13)-C(12)-H(12B)	109.1
C(18)-O(7)	1.31(4)	H(12A)-C(12)-H(12B)	109.5
C(19)-C(20)	1.54(3)	C(13)-C(12)-H(12C)	109.9
C(19)-O(7)	1.81(5)	H(12A)-C(12)-H(12C)	109.5
C(19)-H(19A)	0.9900	H(12B)-C(12)-H(12C)	109.5
C(19)-H(19B)	0.9900	C(14)-C(13)-C(12)	122.3(13)
C(20)-C(22)	1.60(4)	C(14)-C(13)-Mo(1)	65.7(8)
C(20)-C(21)	1.64(4)	C(12)-C(13)-Mo(1)	119.9(11)
C(21)-H(21A)	0.9800	C(14)-C(13)-H(13)	113.6
C(21)-H(21B)	0.9800	C(12)-C(13)-H(13)	113.6
C(21)-H(21C)	0.9800	Mo(1)-C(13)-H(13)	113.6
C(22)-H(22A)	0.9800	C(13)-C(14)-C(15)	117.5(14)
C(22)-H(22B)	0.9800	C(13)-C(14)-Mo(1)	77.8(8)
C(22)-H(22C)	0.9800	C(15)-C(14)-Mo(1)	78.4(9)
Mo(1)-N(5)	2.226(15)	C(13)-C(14)-H(14)	120.9
Mo(1)-N(1)	2.286(9)	C(15)-C(14)-H(14)	120.9
Mo(1)-N(3)	2.303(9)	Mo(1)-C(14)-H(14)	120.9
N(1)-N(2)	1.344(15)	O(3)-C(15)-C(14)	112.0(12)
N(3)-N(4)	1.345(17)	O(3)-C(15)-Mo(1)	120.0(9)
N(5)-N(6)	1.390(17)	C(14)-C(15)-Mo(1)	65.3(8)
N(6)-B(1)-N(4)	111.0(12)	O(3)-C(15)-H(15)	124.0

C(14)-C(15)-H(15)	124.0
Mo(1)-C(15)-H(15)	85.8
O(4)-C(16)-O(3)	129.8(11)
O(4)-C(16)-O(5)	123.6(13)
O(3)-C(16)-O(5)	106.5(11)
O(5)-C(17)-C(18)	113.9(15)
O(5)-C(17)-C(20)	107.8(12)
C(18)-C(17)-C(20)	100.5(15)
O(5)-C(17)-H(17)	111.4
C(18)-C(17)-H(17)	111.4
C(20)-C(17)-H(17)	111.4
O(6)-C(18)-O(7)	129(3)
O(6)-C(18)-C(17)	121(3)
O(7)-C(18)-C(17)	101(3)
C(20)-C(19)-O(7)	81(2)
C(20)-C(19)-H(19A)	115.2
O(7)-C(19)-H(19A)	115.2
C(20)-C(19)-H(19B)	115.2
O(7)-C(19)-H(19B)	115.2
H(19A)-C(19)-H(19B)	112.2
C(19)-C(20)-C(22)	125(2)
C(19)-C(20)-C(17)	104.4(16)
C(22)-C(20)-C(17)	98.4(19)
C(19)-C(20)-C(21)	121(2)
C(22)-C(20)-C(21)	103(2)
C(17)-C(20)-C(21)	100.6(18)
C(20)-C(21)-H(21A)	102.8
C(20)-C(21)-H(21B)	114.6
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	110.8
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	89.8
C(20)-C(22)-H(22B)	117.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	118.9
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(11)-Mo(1)-C(10)	82.4(6)
C(11)-Mo(1)-N(5)	82.1(5)
C(10)-Mo(1)-N(5)	92.3(9)
C(11)-Mo(1)-C(14)	101.0(5)
C(10)-Mo(1)-C(14)	104.5(9)
N(5)-Mo(1)-C(14)	163.2(5)
C(11)-Mo(1)-N(1)	157.3(4)
C(10)-Mo(1)-N(1)	90.9(5)
N(5)-Mo(1)-N(1)	76.4(4)
C(14)-Mo(1)-N(1)	101.8(4)
C(11)-Mo(1)-N(3)	102.1(5)
C(10)-Mo(1)-N(3)	173.7(7)
N(5)-Mo(1)-N(3)	84.0(6)
C(14)-Mo(1)-N(3)	79.2(6)
N(1)-Mo(1)-N(3)	83.2(4)
C(11)-Mo(1)-C(13)	64.6(5)
C(10)-Mo(1)-C(13)	101.5(7)
N(5)-Mo(1)-C(13)	141.5(4)
C(14)-Mo(1)-C(13)	36.5(5)
N(1)-Mo(1)-C(13)	138.1(4)
N(3)-Mo(1)-C(13)	84.6(5)
C(11)-Mo(1)-C(15)	114.6(5)
C(10)-Mo(1)-C(15)	73.5(9)
N(5)-Mo(1)-C(15)	155.6(5)
C(14)-Mo(1)-C(15)	36.3(5)
N(1)-Mo(1)-C(15)	83.9(4)
N(3)-Mo(1)-C(15)	108.1(6)
C(13)-Mo(1)-C(15)	62.4(5)
C(1)-N(1)-N(2)	108.8(11)
C(1)-N(1)-Mo(1)	130.6(9)
N(2)-N(1)-Mo(1)	119.9(8)
N(1)-N(2)-C(3)	108.5(13)
N(1)-N(2)-B(1)	121.3(11)
C(3)-N(2)-B(1)	128.3(13)
C(4)-N(3)-N(4)	106.5(10)
C(4)-N(3)-Mo(1)	133.8(11)
N(4)-N(3)-Mo(1)	119.3(10)
C(6)-N(4)-N(3)	109.2(13)
C(6)-N(4)-B(1)	128.5(14)
N(3)-N(4)-B(1)	122.2(11)
C(7)-N(5)-N(6)	108.6(13)
C(7)-N(5)-Mo(1)	132.1(11)
N(6)-N(5)-Mo(1)	119.0(10)
C(9)-N(6)-N(5)	105.2(11)
C(9)-N(6)-B(1)	130.5(12)
N(5)-N(6)-B(1)	122.7(12)
C(16)-O(3)-C(15)	116.9(11)
C(16)-O(5)-C(17)	116.0(11)
C(18)-O(7)-C(19)	117(4)

Symmetry transformations used to generate equivalent atoms:

Table 4.21. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for (1*R*, *R*)-4.13. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	76(13)	25(10)	42(8)	1(7)	7(8)	-2(9)
C(1)	65(9)	39(8)	64(8)	-28(12)	27(7)	-6(12)
C(2)	113(16)	65(11)	25(6)	-3(7)	30(8)	-13(10)
C(3)	86(12)	51(11)	18(6)	-2(6)	5(6)	7(9)
C(4)	32(9)	43(9)	63(9)	18(7)	8(7)	6(7)
C(5)	53(10)	33(12)	95(12)	-2(8)	14(9)	9(7)
C(6)	38(10)	64(11)	68(10)	19(9)	-7(8)	-3(7)
C(7)	22(7)	39(9)	52(8)	5(7)	-1(6)	6(6)
C(8)	77(13)	30(8)	67(10)	19(8)	22(9)	-2(8)
C(9)	61(11)	20(9)	58(9)	-13(7)	-8(8)	-6(7)
C(11)	53(9)	18(9)	38(7)	-9(5)	-1(6)	6(5)
C(12)	149(19)	24(9)	47(9)	-7(7)	39(11)	-4(10)
C(13)	54(9)	23(8)	46(7)	-28(6)	24(6)	-11(6)
C(14)	42(9)	20(8)	32(7)	-1(6)	12(6)	-9(7)
C(15)	53(10)	50(10)	29(6)	1(6)	9(6)	20(7)
C(16)	51(9)	37(8)	24(6)	-6(6)	6(6)	-12(7)
C(17)	76(11)	15(8)	38(7)	6(6)	21(7)	9(7)
C(20)	108(15)	30(14)	74(10)	10(8)	34(10)	-32(9)
Mo(1)	41(1)	26(1)	32(1)	-4(1)	8(1)	-3(1)
N(1)	54(7)	30(9)	23(4)	-5(4)	9(4)	-15(5)
N(2)	72(9)	49(8)	31(6)	-12(6)	10(5)	-17(7)
N(3)	36(6)	41(7)	49(5)	8(9)	7(4)	-27(9)
N(4)	44(7)	24(6)	40(6)	-1(5)	-2(5)	0(5)
N(5)	53(10)	25(8)	38(6)	-3(6)	17(6)	-7(6)
N(6)	35(7)	41(8)	45(6)	-12(5)	-2(5)	-12(5)
O(1)	40(6)	53(10)	69(6)	6(6)	-6(4)	-15(5)
O(2)	54(7)	39(6)	51(6)	0(5)	5(5)	-4(5)
O(3)	53(6)	42(6)	27(4)	-2(4)	11(4)	-9(5)
O(4)	51(6)	29(5)	39(5)	-1(4)	-6(4)	-4(4)
O(5)	83(8)	56(7)	24(4)	7(4)	1(5)	-11(6)

Table 4.22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 x\ 10^3$) for (1*R*, *R*)-4.13.

	x	y	z	U(eq)
H(1)	4896	957	6808	58
H(1)	9292	3882	7691	65
H(2)	9096	2862	6132	79
H(3)	6893	1594	5857	63
H(4)	3487	4705	8718	56

H(5)	1591	4106	7472	73
H(6)	2559	2292	6628	71
H(7)	7904	388	10010	46
H(8)	7075	-1754	9275	68
H(9)	5725	-1239	7782	59
H(12A)	7960	5576	10712	106
H(12B)	6837	4998	11238	106
H(12C)	6707	6477	10885	106
H(13)	5100	5073	9900	47
H(14)	5634	5880	8535	37
H(15)	8605	5298	9387	53
H(17)	11185	7053	7436	50
H(19A)	9006	9599	5442	165
H(19B)	8156	8442	5856	165
H(21A)	10153	10318	7517	262
H(21B)	10579	9059	8141	262
H(21C)	8989	9279	7646	262
H(22A)	11764	8616	6107	270
H(22B)	12516	8585	7150	270
H(22C)	12125	9956	6652	270

Table 4.23. Torsion angles [°] for (1*R*, *R*)-4.13.

N(1)-C(1)-C(2)-C(3)	-2(2)
C(1)-C(2)-C(3)-N(2)	2(2)
N(3)-C(4)-C(5)-C(6)	0.1(18)
C(4)-C(5)-C(6)-N(4)	-0.6(17)
N(5)-C(7)-C(8)-C(9)	1.2(19)
C(7)-C(8)-C(9)-N(6)	-4.8(19)
C(12)-C(13)-C(14)-C(15)	41(2)
Mo(1)-C(13)-C(14)-C(15)	-69.9(12)
C(12)-C(13)-C(14)-Mo(1)	111.3(14)
C(13)-C(14)-C(15)-O(3)	-176.4(12)
Mo(1)-C(14)-C(15)-O(3)	114.1(10)
C(13)-C(14)-C(15)-Mo(1)	69.5(11)
O(5)-C(17)-C(18)-O(6)	-48(3)
C(20)-C(17)-C(18)-O(6)	-163(3)
O(5)-C(17)-C(18)-O(7)	100(3)
C(20)-C(17)-C(18)-O(7)	-15(3)
O(7)-C(19)-C(20)-C(22)	58(3)
O(7)-C(19)-C(20)-C(17)	-53(2)
O(7)-C(19)-C(20)-C(21)	-165(2)
O(5)-C(17)-C(20)-C(19)	-66.3(18)
C(18)-C(17)-C(20)-C(19)	53(2)
O(5)-C(17)-C(20)-C(22)	164.5(17)
C(18)-C(17)-C(20)-C(22)	-76(2)
O(5)-C(17)-C(20)-C(21)	60(2)
C(18)-C(17)-C(20)-C(21)	179(2)
O(2)-C(11)-Mo(1)-C(10)	-55(21)
O(2)-C(11)-Mo(1)-N(5)	39(21)
O(2)-C(11)-Mo(1)-C(14)	-158(21)

O(2)-C(11)-Mo(1)-N(1)	19(22)
O(2)-C(11)-Mo(1)-N(3)	121(21)
O(2)-C(11)-Mo(1)-C(13)	-161(21)
O(2)-C(11)-Mo(1)-C(15)	-123(21)
O(1)-C(10)-Mo(1)-C(11)	77(7)
O(1)-C(10)-Mo(1)-N(5)	-4(7)
O(1)-C(10)-Mo(1)-C(14)	177(7)
O(1)-C(10)-Mo(1)-N(1)	-81(7)
O(1)-C(10)-Mo(1)-N(3)	-58(12)
O(1)-C(10)-Mo(1)-C(13)	140(7)
O(1)-C(10)-Mo(1)-C(15)	-164(7)
C(13)-C(14)-Mo(1)-C(11)	-4.9(10)
C(15)-C(14)-Mo(1)-C(11)	116.9(9)
C(13)-C(14)-Mo(1)-C(10)	-89.8(9)
C(15)-C(14)-Mo(1)-C(10)	32.0(9)
C(13)-C(14)-Mo(1)-N(5)	94.2(16)
C(15)-C(14)-Mo(1)-N(5)	-144.0(15)
C(13)-C(14)-Mo(1)-N(1)	176.1(8)
C(15)-C(14)-Mo(1)-N(1)	-62.1(8)
C(13)-C(14)-Mo(1)-N(3)	95.5(9)
C(15)-C(14)-Mo(1)-N(3)	-142.7(8)
C(15)-C(14)-Mo(1)-C(13)	121.8(13)
C(13)-C(14)-Mo(1)-C(15)	-121.8(13)
C(14)-C(13)-Mo(1)-C(11)	174.7(11)
C(12)-C(13)-Mo(1)-C(11)	60.0(12)
C(14)-C(13)-Mo(1)-C(10)	98.9(11)
C(12)-C(13)-Mo(1)-C(10)	-15.8(13)
C(14)-C(13)-Mo(1)-N(5)	-152.4(8)
C(12)-C(13)-Mo(1)-N(5)	93.0(13)
C(12)-C(13)-Mo(1)-C(14)	-114.7(15)
C(14)-C(13)-Mo(1)-N(1)	-5.7(12)
C(12)-C(13)-Mo(1)-N(1)	-120.3(11)
C(14)-C(13)-Mo(1)-N(3)	-79.2(9)
C(12)-C(13)-Mo(1)-N(3)	166.1(12)
C(14)-C(13)-Mo(1)-C(15)	34.6(9)
C(12)-C(13)-Mo(1)-C(15)	-80.1(12)
O(3)-C(15)-Mo(1)-C(11)	-176.5(11)
C(14)-C(15)-Mo(1)-C(11)	-74.3(10)
O(3)-C(15)-Mo(1)-C(10)	110.1(12)
C(14)-C(15)-Mo(1)-C(10)	-147.7(9)
O(3)-C(15)-Mo(1)-N(5)	53.5(19)
C(14)-C(15)-Mo(1)-N(5)	155.7(9)
O(3)-C(15)-Mo(1)-C(14)	-102.2(14)
O(3)-C(15)-Mo(1)-N(1)	17.3(11)
C(14)-C(15)-Mo(1)-N(1)	119.5(8)
O(3)-C(15)-Mo(1)-N(3)	-63.4(12)
C(14)-C(15)-Mo(1)-N(3)	38.8(9)
O(3)-C(15)-Mo(1)-C(13)	-137.0(13)
C(14)-C(15)-Mo(1)-C(13)	-34.8(8)
C(2)-C(1)-N(1)-N(2)	1(2)
C(2)-C(1)-N(1)-Mo(1)	171.3(10)
C(11)-Mo(1)-N(1)-C(1)	-100.1(19)
C(10)-Mo(1)-N(1)-C(1)	-27.7(18)
N(5)-Mo(1)-N(1)-C(1)	-119.9(16)
C(14)-Mo(1)-N(1)-C(1)	77.3(16)
N(3)-Mo(1)-N(1)-C(1)	154.7(16)

C(13)-Mo(1)-N(1)-C(1)	80.7(17)
C(15)-Mo(1)-N(1)-C(1)	45.6(16)
C(11)-Mo(1)-N(1)-N(2)	69.7(17)
C(10)-Mo(1)-N(1)-N(2)	142.1(12)
N(5)-Mo(1)-N(1)-N(2)	50.0(10)
C(14)-Mo(1)-N(1)-N(2)	-112.9(10)
N(3)-Mo(1)-N(1)-N(2)	-35.4(10)
C(13)-Mo(1)-N(1)-N(2)	-109.5(10)
C(15)-Mo(1)-N(1)-N(2)	-144.6(10)
C(1)-N(1)-N(2)-C(3)	0.9(17)
Mo(1)-N(1)-N(2)-C(3)	-171.0(9)
C(1)-N(1)-N(2)-B(1)	166.1(15)
Mo(1)-N(1)-N(2)-B(1)	-5.8(16)
C(2)-C(3)-N(2)-N(1)	-2.2(17)
C(2)-C(3)-N(2)-B(1)	-166.0(14)
N(6)-B(1)-N(2)-N(1)	-54.9(17)
N(4)-B(1)-N(2)-N(1)	63.6(16)
N(6)-B(1)-N(2)-C(3)	107.1(16)
N(4)-B(1)-N(2)-C(3)	-134.4(15)
C(5)-C(4)-N(3)-N(4)	0.5(18)
C(5)-C(4)-N(3)-Mo(1)	172.4(11)
C(11)-Mo(1)-N(3)-C(4)	66.2(14)
C(10)-Mo(1)-N(3)-C(4)	-159(8)
N(5)-Mo(1)-N(3)-C(4)	146.8(14)
C(14)-Mo(1)-N(3)-C(4)	-32.8(14)
N(1)-Mo(1)-N(3)-C(4)	-136.2(14)
C(13)-Mo(1)-N(3)-C(4)	3.6(13)
C(15)-Mo(1)-N(3)-C(4)	-55.0(14)
C(11)-Mo(1)-N(3)-N(4)	-122.8(10)
C(10)-Mo(1)-N(3)-N(4)	12(9)
N(5)-Mo(1)-N(3)-N(4)	-42.2(10)
C(14)-Mo(1)-N(3)-N(4)	138.2(11)
N(1)-Mo(1)-N(3)-N(4)	34.8(10)
C(13)-Mo(1)-N(3)-N(4)	174.7(11)
C(15)-Mo(1)-N(3)-N(4)	116.1(11)
C(5)-C(6)-N(4)-N(3)	1.0(16)
C(5)-C(6)-N(4)-B(1)	177.9(13)
C(4)-N(3)-N(4)-C(6)	-0.9(16)
Mo(1)-N(3)-N(4)-C(6)	-174.2(10)
C(4)-N(3)-N(4)-B(1)	-178.1(12)
Mo(1)-N(3)-N(4)-B(1)	8.7(16)
N(6)-B(1)-N(4)-C(6)	-126.4(15)
N(2)-B(1)-N(4)-C(6)	118.3(16)
N(6)-B(1)-N(4)-N(3)	50.2(18)
N(2)-B(1)-N(4)-N(3)	-65.2(15)
C(8)-C(7)-N(5)-N(6)	2.7(17)
C(8)-C(7)-N(5)-Mo(1)	175.8(10)
C(11)-Mo(1)-N(5)-C(7)	-39.0(14)
C(10)-Mo(1)-N(5)-C(7)	43.0(14)
C(14)-Mo(1)-N(5)-C(7)	-140.9(15)
N(1)-Mo(1)-N(5)-C(7)	133.4(14)
N(3)-Mo(1)-N(5)-C(7)	-142.2(14)
C(13)-Mo(1)-N(5)-C(7)	-68.8(16)
C(15)-Mo(1)-N(5)-C(7)	96.3(15)
C(11)-Mo(1)-N(5)-N(6)	133.5(11)
C(10)-Mo(1)-N(5)-N(6)	-144.5(10)

C(14)-Mo(1)-N(5)-N(6)	32(2)
N(1)-Mo(1)-N(5)-N(6)	-54.1(10)
N(3)-Mo(1)-N(5)-N(6)	30.4(10)
C(13)-Mo(1)-N(5)-N(6)	103.8(11)
C(15)-Mo(1)-N(5)-N(6)	-91.2(16)
C(8)-C(9)-N(6)-N(5)	6.4(18)
C(8)-C(9)-N(6)-B(1)	171.4(16)
C(7)-N(5)-N(6)-C(9)	-5.5(16)
Mo(1)-N(5)-N(6)-C(9)	-179.6(10)
C(7)-N(5)-N(6)-B(1)	-172.0(14)
Mo(1)-N(5)-N(6)-B(1)	13.8(17)
N(4)-B(1)-N(6)-C(9)	132.0(16)
N(2)-B(1)-N(6)-C(9)	-112.2(16)
N(4)-B(1)-N(6)-N(5)	-65.1(18)
N(2)-B(1)-N(6)-N(5)	50.7(17)
O(4)-C(16)-O(3)-C(15)	4(2)
O(5)-C(16)-O(3)-C(15)	-172.8(11)
C(14)-C(15)-O(3)-C(16)	171.5(12)
Mo(1)-C(15)-O(3)-C(16)	-115.2(12)
O(4)-C(16)-O(5)-C(17)	0.0(19)
O(3)-C(16)-O(5)-C(17)	177.4(11)
C(18)-C(17)-O(5)-C(16)	122.3(17)
C(20)-C(17)-O(5)-C(16)	-127.1(12)
O(6)-C(18)-O(7)-C(19)	123(4)
C(17)-C(18)-O(7)-C(19)	-22(4)
C(20)-C(19)-O(7)-C(18)	51(3)

Symmetry transformations used to generate equivalent atoms:

Table 4.24. Crystal data and structure refinement for 4.15

Identification code	**4.15**	
Empirical formula	C30.70 H31.40 B Cl1.40 Mo N7 O4	
Formula weight	718.81	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.988(3) Å	α= 90°.
	b = 11.0479(16) Å	β= 90.869(10)°.
	c = 15.429(2) Å	γ = 90°.
Volume	3236.2(9) Å^3	
Z	4	
Density (calculated)	1.475 Mg/m^3	

Absorption coefficient	4.769 mm^{-1}
F(000)	1470
Crystal size	0.24 x 0.19 x 0.03 mm^3
Theta range for data collection	13.73 to 65.52°.
Index ranges	-21<=h<=17, -10<=k<=13, -13<=l<=15
Reflections collected	6717
Independent reflections	3373 [R(int) = 0.1822]
Completeness to theta = 65.52°	60.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3373 / 0 / 417
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0848, wR2 = 0.1619
R indices (all data)	R1 = 0.2039, wR2 = 0.2059
Largest diff. peak and hole	0.667 and -0.544 e.$Å^{-3}$

Table 4.25. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 4.15. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	4635(13)	5948(14)	7267(10)	64(6)
C(1)	3656(9)	3926(11)	8621(9)	54(4)
C(2)	4068(10)	4437(11)	9279(9)	59(5)
C(3)	4500(10)	5241(12)	8872(12)	60(5)
C(4)	3214(10)	7098(11)	5964(9)	54(5)
C(5)	3531(11)	8190(11)	6125(10)	53(5)
C(6)	4115(10)	7926(10)	6667(11)	55(5)
C(7)	4881(10)	3648(11)	5622(8)	43(4)
C(8)	5576(13)	3951(15)	5705(10)	67(5)
C(9)	5608(10)	4853(13)	6343(10)	56(4)
C(10)	2117(11)	1071(11)	7006(10)	77(6)
C(11)	2095(10)	2303(12)	6608(14)	52(5)
C(12)	2406(10)	3292(9)	7111(9)	57(5)
C(13)	2211(8)	4560(10)	6948(9)	45(4)
C(14)	1865(8)	5001(12)	6262(9)	45(4)
C(15)	1218(9)	6385(11)	5368(10)	56(5)
C(16)	1697(9)	6992(11)	4730(9)	48(4)
C(17)	2100(10)	6303(12)	4167(8)	58(5)
C(18)	2602(10)	6820(12)	3670(9)	57(5)
C(19)	2710(10)	8046(15)	3712(10)	68(5)
C(20)	2287(11)	8762(12)	4236(9)	64(5)
C(21)	1776(10)	8250(11)	4718(9)	60(5)

C(22)	1656(9)	7055(11)	6789(8)	48(4)
C(23)	1018(10)	7223(11)	7365(8)	53(5)
C(24)	756(10)	8424(11)	7495(9)	59(5)
C(25)	203(11)	8582(14)	8035(11)	74(6)
C(26)	-126(12)	7644(14)	8419(10)	78(6)
C(27)	104(11)	6507(15)	8247(11)	75(6)
C(28)	667(10)	6280(11)	7738(9)	57(5)
C(29)	3103(9)	3951(9)	5309(10)	49(4)
C(30)	3533(8)	2450(14)	6345(8)	48(4)
Mo(1)	3370(1)	4186(1)	6470(1)	47(1)
N(1)	3784(7)	4433(9)	7849(7)	46(3)
N(2)	4337(7)	5230(9)	8021(9)	52(4)
N(3)	3534(7)	6189(9)	6386(7)	41(3)
N(4)	4108(8)	6717(9)	6820(8)	48(4)
N(5)	4503(8)	4252(10)	6195(7)	58(4)
N(6)	4934(8)	5012(9)	6608(8)	56(4)
N(7)	1579(7)	6085(9)	6167(7)	47(4)
O(1)	1835(7)	2389(7)	5899(9)	69(4)
O(2)	1876(8)	200(8)	6409(7)	85(4)
O(3)	2954(6)	3714(7)	4565(7)	59(3)
O(4)	3641(7)	1388(8)	6271(6)	79(4)
C(1S)	1199(14)	2106(15)	3992(13)	63(7)
Cl(1S)	808(3)	3554(4)	3991(3)	65(2)
Cl(2S)	608(3)	1079(3)	4536(3)	66(2)

Table 4.26. Bond lengths [Å] and angles [°] for 4.15.

B(1)-N(4)	1.48(3)	C(10)-O(2)	1.404(19)
B(1)-N(2)	1.52(2)	C(10)-C(11)	1.49(2)
B(1)-N(6)	1.56(2)	C(10)-H(10A)	0.9900
B(1)-H(1)	1.0000	C(10)-H(10B)	0.9900
C(1)-N(1)	1.342(16)	C(11)-O(1)	1.197(19)
C(1)-C(2)	1.39(2)	C(11)-C(12)	1.46(3)
C(1)-H(1)	0.9500	C(12)-C(13)	1.469(19)
C(2)-C(3)	1.37(2)	C(12)-Mo(1)	2.314(15)
C(2)-H(2)	0.9500	C(12)-H(12)	1.0000
C(3)-N(2)	1.344(19)	C(13)-C(14)	1.33(2)
C(3)-H(3)	0.9500	C(13)-Mo(1)	2.368(14)
C(4)-N(3)	1.338(19)	C(13)-H(13)	1.0000
C(4)-C(5)	1.37(2)	C(14)-N(7)	1.322(17)
C(4)-H(4)	0.9500	C(14)-H(14)	0.9500
C(5)-C(6)	1.41(2)	C(15)-N(7)	1.441(19)
C(5)-H(5)	0.9500	C(15)-C(16)	1.51(2)
C(6)-N(4)	1.356(16)	C(15)-H(15A)	0.9900
C(6)-H(6)	0.9500	C(15)-H(15B)	0.9900
C(7)-N(5)	1.328(18)	C(16)-C(17)	1.39(2)
C(7)-C(8)	1.36(2)	C(16)-C(21)	1.398(18)
C(7)-H(7)	0.9500	C(17)-C(18)	1.36(2)
C(8)-C(9)	1.40(2)	C(17)-H(17)	0.9500
C(8)-H(8)	0.9500	C(18)-C(19)	1.37(2)
C(9)-N(6)	1.36(2)	C(18)-H(18)	0.9500
C(9)-H(9)	0.9500	C(19)-C(20)	1.39(2)

C(19)-H(19)	0.9500	N(4)-C(6)-H(6)	126.4
C(20)-C(21)	1.36(2)	C(5)-C(6)-H(6)	126.4
C(20)-H(20)	0.9500	N(5)-C(7)-C(8)	110.3(14)
C(21)-H(21)	0.9500	N(5)-C(7)-H(7)	124.9
C(22)-N(7)	1.444(17)	C(8)-C(7)-H(7)	124.9
C(22)-C(23)	1.53(2)	C(7)-C(8)-C(9)	105.8(15)
C(22)-H(22A)	0.9900	C(7)-C(8)-H(8)	127.1
C(22)-H(22B)	0.9900	C(9)-C(8)-H(8)	127.1
C(23)-C(28)	1.367(19)	N(6)-C(9)-C(8)	105.7(17)
C(23)-C(24)	1.433(18)	N(6)-C(9)-H(9)	127.1
C(24)-C(25)	1.36(2)	C(8)-C(9)-H(9)	127.1
C(24)-H(24)	0.9500	O(2)-C(10)-C(11)	110.3(16)
C(25)-C(26)	1.35(2)	O(2)-C(10)-H(10A)	109.6
C(25)-H(25)	0.9500	C(11)-C(10)-H(10A)	109.6
C(26)-C(27)	1.36(2)	O(2)-C(10)-H(10B)	109.6
C(26)-H(26)	0.9500	C(11)-C(10)-H(10B)	109.6
C(27)-C(28)	1.36(2)	H(10A)-C(10)-H(10B)	108.1
C(27)-H(27)	0.9500	O(1)-C(11)-C(12)	125.8(13)
C(28)-H(28)	0.9500	O(1)-C(11)-C(10)	117.2(15)
C(29)-O(3)	1.206(15)	C(12)-C(11)-C(10)	117.0(19)
C(29)-Mo(1)	1.873(17)	C(11)-C(12)-C(13)	121.5(17)
C(30)-O(4)	1.197(14)	C(11)-C(12)-Mo(1)	114.0(9)
C(30)-Mo(1)	1.954(16)	C(13)-C(12)-Mo(1)	73.7(7)
Mo(1)-N(5)	2.201(14)	C(11)-C(12)-H(12)	113.8
Mo(1)-N(3)	2.238(10)	C(13)-C(12)-H(12)	113.8
Mo(1)-N(1)	2.273(11)	Mo(1)-C(12)-H(12)	113.8
N(1)-N(2)	1.393(17)	C(14)-C(13)-C(12)	127.3(12)
N(3)-N(4)	1.398(17)	C(14)-C(13)-Mo(1)	105.4(8)
N(5)-N(6)	1.329(19)	C(12)-C(13)-Mo(1)	69.8(8)
O(2)-H(2A)	0.8400	C(14)-C(13)-H(13)	114.5
C(1S)-Cl(1S)	1.76(2)	C(12)-C(13)-H(13)	114.5
C(1S)-Cl(2S)	1.81(2)	Mo(1)-C(13)-H(13)	114.5
C(1S)-H(1S1)	0.9900	N(7)-C(14)-C(13)	128.1(12)
C(1S)-H(1S2)	0.9900	N(7)-C(14)-H(14)	116.0
N(4)-B(1)-N(2)	113.5(16)	C(13)-C(14)-H(14)	116.0
N(4)-B(1)-N(6)	109.1(13)	N(7)-C(15)-C(16)	112.2(14)
N(2)-B(1)-N(6)	107.2(11)	N(7)-C(15)-H(15A)	109.2
N(4)-B(1)-H(1)	109.0	C(16)-C(15)-H(15A)	109.2
N(2)-B(1)-H(1)	109.0	N(7)-C(15)-H(15B)	109.2
N(6)-B(1)-H(1)	109.0	C(16)-C(15)-H(15B)	109.2
N(1)-C(1)-C(2)	111.7(14)	H(15A)-C(15)-H(15B)	107.9
N(1)-C(1)-H(1)	124.1	C(17)-C(16)-C(21)	118.4(13)
C(2)-C(1)-H(1)	124.1	C(17)-C(16)-C(15)	120.5(11)
C(3)-C(2)-C(1)	105.3(13)	C(21)-C(16)-C(15)	121.1(12)
C(3)-C(2)-H(2)	127.4	C(18)-C(17)-C(16)	121.3(13)
C(1)-C(2)-H(2)	127.4	C(18)-C(17)-H(17)	119.3
N(2)-C(3)-C(2)	108.2(14)	C(16)-C(17)-H(17)	119.3
N(2)-C(3)-H(3)	125.9	C(17)-C(18)-C(19)	119.6(15)
C(2)-C(3)-H(3)	125.9	C(17)-C(18)-H(18)	120.2
N(3)-C(4)-C(5)	112.2(19)	C(19)-C(18)-H(18)	120.2
N(3)-C(4)-H(4)	123.9	C(18)-C(19)-C(20)	120.1(15)
C(5)-C(4)-H(4)	123.9	C(18)-C(19)-H(19)	120.0
C(4)-C(5)-C(6)	105.4(13)	C(20)-C(19)-H(19)	120.0
C(4)-C(5)-H(5)	127.3	C(21)-C(20)-C(19)	120.3(13)
C(6)-C(5)-H(5)	127.3	C(21)-C(20)-H(20)	119.8
N(4)-C(6)-C(5)	107.3(12)	C(19)-C(20)-H(20)	119.8

C(20)-C(21)-C(16)	120.0(14)
C(20)-C(21)-H(21)	120.0
C(16)-C(21)-H(21)	120.0
N(7)-C(22)-C(23)	113.8(13)
N(7)-C(22)-H(22A)	108.8
C(23)-C(22)-H(22A)	108.8
N(7)-C(22)-H(22B)	108.8
C(23)-C(22)-H(22B)	108.8
H(22A)-C(22)-H(22B)	107.7
C(28)-C(23)-C(24)	118.3(14)
C(28)-C(23)-C(22)	123.3(11)
C(24)-C(23)-C(22)	118.3(12)
C(25)-C(24)-C(23)	118.5(14)
C(25)-C(24)-H(24)	120.8
C(23)-C(24)-H(24)	120.8
C(26)-C(25)-C(24)	122.4(14)
C(26)-C(25)-H(25)	118.8
C(24)-C(25)-H(25)	118.8
C(25)-C(26)-C(27)	118.1(14)
C(25)-C(26)-H(26)	121.0
C(27)-C(26)-H(26)	121.0
C(26)-C(27)-C(28)	122.8(15)
C(26)-C(27)-H(27)	118.6
C(28)-C(27)-H(27)	118.6
C(27)-C(28)-C(23)	119.6(12)
C(27)-C(28)-H(28)	120.2
C(23)-C(28)-H(28)	120.2
O(3)-C(29)-Mo(1)	175.1(10)
O(4)-C(30)-Mo(1)	179.3(13)
C(29)-Mo(1)-C(30)	79.0(5)
C(29)-Mo(1)-N(5)	94.0(6)
C(30)-Mo(1)-N(5)	81.7(5)
C(29)-Mo(1)-N(3)	96.8(4)
C(30)-Mo(1)-N(3)	160.4(4)
N(5)-Mo(1)-N(3)	79.5(4)
C(29)-Mo(1)-N(1)	175.3(6)
C(30)-Mo(1)-N(1)	99.0(5)
N(5)-Mo(1)-N(1)	81.4(4)
N(3)-Mo(1)-N(1)	83.6(4)
C(29)-Mo(1)-C(12)	98.4(6)
C(30)-Mo(1)-C(12)	75.6(4)
N(5)-Mo(1)-C(12)	151.4(5)
N(3)-Mo(1)-C(12)	124.0(4)
N(1)-Mo(1)-C(12)	85.2(5)
C(29)-Mo(1)-C(13)	94.8(6)
C(30)-Mo(1)-C(13)	110.6(5)
N(5)-Mo(1)-C(13)	166.0(4)
N(3)-Mo(1)-C(13)	88.7(4)
N(1)-Mo(1)-C(13)	89.9(5)
C(12)-Mo(1)-C(13)	36.6(5)
C(1)-N(1)-N(2)	103.9(12)
C(1)-N(1)-Mo(1)	135.7(11)
N(2)-N(1)-Mo(1)	120.2(8)
C(3)-N(2)-N(1)	110.7(11)
C(3)-N(2)-B(1)	131.2(14)
N(1)-N(2)-B(1)	118.1(14)
C(4)-N(3)-N(4)	105.3(11)
C(4)-N(3)-Mo(1)	135.0(12)
N(4)-N(3)-Mo(1)	119.6(8)
C(6)-N(4)-N(3)	109.8(12)
C(6)-N(4)-B(1)	129.7(15)
N(3)-N(4)-B(1)	120.1(11)
C(7)-N(5)-N(6)	107.5(14)
C(7)-N(5)-Mo(1)	130.8(11)
N(6)-N(5)-Mo(1)	121.7(10)
N(5)-N(6)-C(9)	110.5(13)
N(5)-N(6)-B(1)	120.2(15)
C(9)-N(6)-B(1)	129.3(15)
C(14)-N(7)-C(15)	119.5(11)
C(14)-N(7)-C(22)	124.2(14)
C(15)-N(7)-C(22)	116.1(11)
C(10)-O(2)-H(2A)	109.5
Cl(1S)-C(1S)-Cl(2S)	107.8(11)
Cl(1S)-C(1S)-H(1S1)	110.2
Cl(2S)-C(1S)-H(1S1)	110.2
Cl(1S)-C(1S)-H(1S2)	110.2
Cl(2S)-C(1S)-H(1S2)	110.2
H(1S1)-C(1S)-H(1S2)	108.5

Symmetry transformations used to generate equivalent atoms:

Table 4.27. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 4.15. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	100(20)	54(10)	37(11)	-11(8)	7(11)	-36(11)
C(1)	81(15)	53(8)	29(10)	-3(6)	-3(9)	-1(7)
C(2)	97(15)	45(8)	36(10)	13(7)	2(9)	-3(8)
C(3)	72(15)	59(9)	48(13)	-2(7)	-8(10)	11(8)
C(4)	77(15)	45(8)	40(9)	17(6)	12(9)	-14(8)
C(5)	77(16)	38(8)	44(10)	9(5)	6(10)	-13(8)
C(6)	66(15)	26(7)	72(12)	-4(6)	2(11)	-22(7)
C(7)	37(13)	57(8)	33(9)	-2(6)	-7(8)	11(8)
C(8)	63(17)	104(12)	35(10)	15(8)	-9(9)	25(11)
C(9)	39(14)	76(10)	54(11)	27(8)	-7(9)	5(8)
C(10)	126(18)	34(8)	72(11)	-8(6)	49(11)	-18(8)
C(11)	49(13)	71(11)	37(11)	3(7)	17(10)	1(7)
C(12)	109(16)	18(6)	45(9)	-20(5)	12(9)	11(7)
C(13)	62(12)	42(8)	32(10)	-8(6)	15(9)	-5(7)
C(14)	60(13)	54(9)	20(9)	-8(6)	5(8)	-1(8)
C(15)	70(14)	42(7)	56(11)	-2(6)	8(9)	-8(7)
C(16)	52(13)	49(8)	41(9)	4(6)	-2(8)	12(7)
C(17)	90(16)	58(8)	27(8)	11(6)	-21(9)	5(9)
C(18)	74(15)	53(9)	43(9)	19(6)	0(9)	-7(8)
C(19)	78(16)	77(12)	51(11)	33(8)	0(10)	-9(10)
C(20)	99(17)	49(8)	44(9)	0(6)	-9(10)	0(9)
C(21)	99(16)	39(8)	43(9)	8(6)	14(9)	-13(8)
C(22)	56(13)	56(8)	34(9)	-4(6)	7(8)	9(7)
C(23)	77(15)	53(9)	31(9)	-2(6)	-3(8)	4(8)
C(24)	90(16)	35(7)	52(9)	-8(5)	-1(9)	4(8)
C(25)	98(17)	61(9)	64(11)	-6(7)	28(11)	11(9)
C(26)	113(19)	63(10)	59(11)	-10(7)	27(11)	19(10)
C(27)	68(15)	71(11)	86(12)	11(8)	34(12)	-3(9)
C(28)	86(15)	32(7)	52(9)	11(5)	5(9)	12(7)
C(29)	85(14)	35(7)	28(10)	-10(5)	13(8)	-10(7)
C(30)	41(12)	72(10)	32(9)	22(6)	10(8)	-4(8)
Mo(1)	72(1)	31(1)	37(1)	-1(1)	10(1)	-1(1)
N(1)	57(10)	45(6)	37(8)	2(5)	3(6)	-2(6)
N(2)	61(11)	51(7)	43(10)	2(5)	-2(7)	-8(7)
N(3)	44(11)	59(7)	21(7)	5(5)	-13(7)	-3(6)
N(4)	65(12)	38(7)	42(8)	14(5)	0(8)	13(7)
N(5)	98(12)	41(6)	34(7)	0(5)	-17(7)	-29(7)
N(6)	68(13)	48(7)	50(8)	11(5)	9(8)	6(7)
N(7)	73(11)	37(6)	32(8)	0(5)	-1(7)	11(6)
O(1)	106(11)	36(5)	66(9)	-4(4)	27(8)	-13(5)
O(2)	115(13)	49(5)	92(9)	-7(5)	9(7)	-16(6)
O(3)	88(10)	43(5)	48(7)	-4(4)	8(6)	5(5)
O(4)	127(12)	32(5)	78(8)	-16(4)	9(7)	29(6)
C(1S)	90(20)	52(11)	50(13)	-10(8)	38(12)	-1(11)
Cl(1S)	92(5)	33(2)	69(4)	12(2)	-5(3)	-7(3)

Cl(2S)	114(6)	32(2)	51(3)	-3(2)	-4(3)	-19(2)

Table 4.28. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 4.15.

	x	y	z	U(eq)
H(1)	5029	6470	7487	76
H(1)	3324	3295	8708	65
H(2)	4053	4265	9881	71
H(3)	4854	5723	9143	72
H(4)	2814	6997	5594	65
H(5)	3388	8962	5915	63
H(6)	4452	8490	6886	66
H(7)	4696	3085	5213	51
H(8)	5959	3619	5395	81
H(9)	6016	5267	6549	67
H(10A)	2606	877	7191	92
H(10B)	1818	1057	7526	92
H(12)	2481	3097	7739	68
H(13)	2183	5072	7480	54
H(14)	1819	4472	5779	54
H(15A)	818	6931	5493	67
H(15B)	1023	5637	5105	67
H(17)	2022	5455	4130	70
H(18)	2877	6335	3296	68
H(19)	3073	8408	3384	82
H(20)	2357	9613	4255	77
H(21)	1471	8746	5048	72
H(22A)	1742	7820	6473	58
H(22B)	2074	6892	7161	58
H(24)	963	9095	7211	71
H(25)	44	9381	8146	89
H(26)	-508	7776	8798	93
H(27)	-139	5842	8492	90
H(28)	817	5471	7643	68
H(2A)	1629	538	6023	128
H(1S1)	1660	2131	4300	75
H(1S2)	1276	1832	3390	75

Table 4.29. Hydrogen bonds for 4.15 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2A)...O(1)	0.84	2.09	2.544(13)	113.4

Symmetry transformations used to generate equivalent atoms: