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Maurice duPont Lee, IV

Organometallic Scaffolding as a Practical Approach to Diversity-Oriented Synthesis: Stereo- and Regiocontrolled Sequential Functionalization of Pyranylalkylidene Allylmolybdenum Complexes

By

Maurice duPont Lee, IV
Doctor of Philosophy

Department of Chemistry

_____
Lanny S. Liebeskind, Ph.D.
Advisor

_____
Frank E. McDonald, Ph.D.
Committee Member

_____
Simon B. Blakey, Ph.D.
Committee Member

Accepted:

_____
Lisa A. Tedesco, Ph.D.
Dean of the Graduate School

_____
Date

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An Abstract of
A dissertation submitted to the Faculty of the Graduate School of Emory University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry
Graduate School of Arts and Sciences

2008

Abstract

Organometallic enantiomeric scaffolding is a powerful and versatile tool for enantiocontrolled bond construction. $Tp(CO)_2$allylmolybdenum complexes of pyrans and piperidines are noteworthy examples of this approach to synthesis. A streamlined procedure for the construction of the key η^3(2,3,4)-5-oxopyranyl molybdenum complex was developed, facilitating scale up, and making these scaffolds more available to the synthetic community.

The key scaffold was derivatized to include an alkylidene moiety that provided new opportunities for synthesis of heterocyclic skeletons and stereochemical relationships not accessible with existing methods. An unprecedented intermolecular 1,5-Michael reaction of this substrate was evaluated for its scope and mechanism, whereby the addition of alkoxide nucleophiles to neutral allyl molybdenum complexes is apparently favorable, and likely goes through an anionic molybdenum intermediate.

The products of this reaction were studied for use in a novel and general sequential functionalization protocol, whereby iterative leaving group abstraction/nucleophilic addition sequences afford highly substituted pyran architectures with divergent, yet predictable regiochemical outcomes, notably those bearing 2,6-*trans* and 2,2,6-functionality. Other highlights include a [5+2] cycloaddition reaction to 5,6-disubstituted pyranyl complexes, and hetero Diels-Alder reaction to form spiroketals.

The full utility of the method is ultimately demonstrated by the synthesis of highly functionalized enantiomerically pure pyran rings bearing functionality equipped for further manipulations.

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To Erin

The person to whom I most look up for inspiration, advice and a good laugh.

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Special thanks must also be paid to my committee members Dr. Frank McDonald and Dr. Simon Blakey, who are incredibly apt at dissecting the issue at hand, and asking thought provoking questions. Their helpful discussions and suggestions about my project over the years, not to mention their extremely valuable comments, and encouraging enthusiasm regarding my research proposal made me actually look forward to giving presentations in front of them.

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List of Abbreviations

[α]	specific rotation
Ac	acetyl
anal.	analysis
Aq	aqueous
Ar	argon
Bn	benzyl
br	broad
bu	butyl
^{o}C	degree Celsius
calcd	calculated
CAN	ceric ammonium nitrate
Cbz	benzyloxycarbonyl
cod	1,5-cyclooctadiene
Cy	cyclohexyl
δ	chemical shift(s)
d	doublet
DMAP	dimethylamino pyridine
Decomp	decomposed
DMSO	dimethyl sulfoxide
DMS	dimethyl sulfide
E	entgegen
ee	enantiomeric excess
ESI	electrospray ionization
Et	ethyl
FAB	fast atom bombardment
fod	tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate)
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
LDA	lithium diisopropylamide
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
MVK	methyl vinyl ketone

nbd	norbornadiene
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
nm	nanometer(s)
PG	protecting group
Ph	phenyl
ppm	parts per million
pr	propyl
py	pyridine
q	quartet
R_f	retention factor
rt	room temperature
s	singlet
SAR	structure activity relationship
t	triplet
t	tertiary
TBME	*tert*-butyl methyl ether
TBS	*tert*-butyl dimethyl silyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
Tp	hydridotris(1-pyrazolyl)borate
Tr	triphenylcarbenium
UV	ultraviolet
Z	zusammen

Chapter 1: Highlights of recent developments in the synthesis of 2,6-cis and 2,6-trans substituted pyrans. Introduction to organometallic scaffolding as a means of generating highly functionalized pyran architectures

Introduction:

The development of mild, efficient and selective synthetic transformations remains one of the major challenges of contemporary organic chemistry. The incredible structural and functional group diversity of natural products continues to challenge the synthetic chemist to pursue more concise approaches to these complex targets, especially those which have demonstrated pharmacological relevance.[1] Functionalized pyrans represent one particularly important substructure of many biologically relevant natural and unnatural products, and so the need to develop new stereoselective approaches to this architecture has driven the considerable advances in this field.

The construction of substituted pyrans was comprehensively reviewed over 20 years ago,[2] but a more recent review has highlighted some contemporary advances and their application to natural product synthesis.[3] It is the purpose of this introduction to highlight a few of the most interesting and important contributions to the stereocontrolled synthesis of 2,6-*cis* and 2,6-*trans* substituted pyrans, emphasizing in particular the generality of certain methods and their applicability to a range of substrates.

Considerable effort has been made to functionalize (new C-C bonds) the anomeric position of carbohydrates,[4,5,6,7,8,9,10,11,12] but a critical examination of these methods suggests that

---

[1] a) Faulkner, D. J. *Nat. Prod. Rep.* **2000**, *17*, 7-55. b) Faulkner, D. J. *Nat. Prod. Rep.* **1998**, *15*, 113-158. b) Class, Y. J.; DeShong, P. *Chem. Rev.* **1995**, *95*, 1843-1857. c) Norcross, R. D.; Patterson, I. *Chem. Rev.* **1995**, *95*, 2041-2114.

[2] a) Boivin, T. L. *Tetrahedron* **1987**, *43*, 3309-3362. b) Baliah, V.; Jeyaraman, R.; Chankdrasedaran, L. *Chem. Rev.* **1983**, *83*, 379-423.

[3] Clarke, P. A.; Santos, S. *Eur. J. Org. Chem.* **2006**, 2045-2053.

[4] For a comprehensive review on the stereoselective synthesis of *C*-glycosides see: Du, Y.; Linhardt, R. J.; Vlahov, I. R. *Tetrahedron* **1998**, *54*, 9913-9959.

[5] Reed, L. A. III; Ito, Y.; Masamune, S.; Sharpless, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 6468-6470.

[6] Kraus, G. A.; Molina, M. T. *J. Org. Chem.* **1988**, *53*, 752-753.

[7] Czernecki, S.; Ville, G. *J. Org. Chem.* **1989**, *54*, 610-612.

[8] Panek, J. S.; Sparks, M. A. *J. Org. Chem.* **1989**, *54*, 2034-2038.

[9] Boschetti, A.; Nicotra, F.; Panza, L.; Russo, G. *J. Org. Chem.* **1988**, *53*, 4181-4185.

[10] Ireland, R. E.; Norbeck, D. W.; Mandel, G. S.; Mandel, N. S. *J. Am. Chem. Soc.* **1985**, *107*, 3285-3294.

[11] Tius, M. A.; Gomez-Galeno, J.; Gu, X.-Q.; Zaidi, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 5775-5783.

carbohydrate templating for synthesis of non-sugar targets is often not practical for use in total synthesis because of the amount of de-functionalization required.[13] Because of this, *de novo* syntheses, focusing on either construction of the heterocycle or manipulating the relative stereochemical relationship between various substituents on the ring, tend to be more practical from a synthetic perspective.

In discussing these methods, the focus will be on the efficiency and selectivity (regio-, enantio-, diastereo-) of each transformation and the ease of generating the requisite starting materials. Also important, is the generality of these methods with regard to functional group tolerance, and control of relative stereochemistry. Some methods may only be applicable to generating 2,6-*cis* or 2,6-*trans*- pyrans, while others, by changing the catalyst or changing the geometry or stereochemistry of the reactants may selectively generate either.

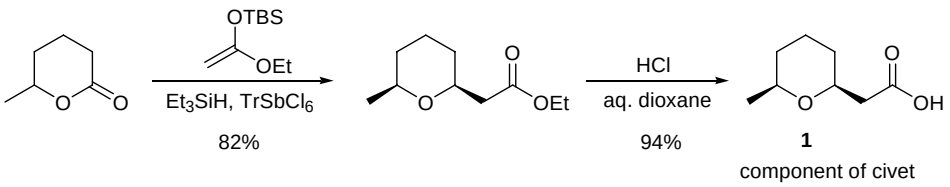
Reductions of Hemiketals

The reduction of hemiketals is one method that provides expedient access to 2,6-*cis* stereochemistry in substituted pyrans. The two major strategies for this approach involve addition to lactones (pre-existing heterocycle), and cyclization of alcohols onto ketones to form the hemiketal. In 1989, Mukaiyama developed what is probably the simplest and most expedient synthesis of (*cis*-6-methyltetrahydropyran-2-yl)acetic acid, **1** (**Scheme 1**), a component of the glandular secretion of the civet cat, and an apparent litmus test for the efficacy of 2,6-*cis* substituted pyran methodology.[14] Addition of the silyl ketene acetal to the commercially available 6-methylvalerolactone and subsequent reduction of the hemiacetal under Lewis acidic conditions provided the 2,6-*cis* substituted pyran. Hydrolysis of the ester provided the natural product.

---

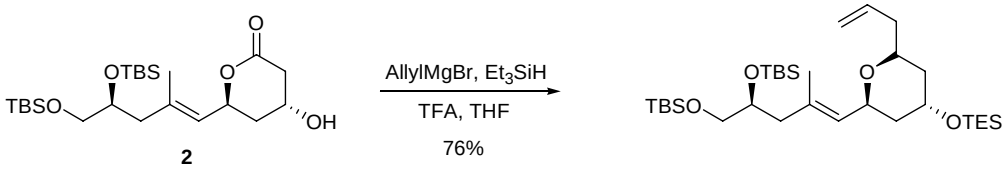
[12] Stork, G.; Suh, H. S.; Kim, G. *J. Am. Chem. Soc.* **1991**, *113*, 7054-7056.
[13] See: Hanessian, S. Total Synthesis of Natural Products: the 'Chiron' Approach; Pergamon Press: Oxford, UK, 1983.
[14] Homma, K.; Mukaiyama, T. *Chem. Lett.* **1989**, 893-894.

Scheme 1: Reduction of hemiacetal provides 2,6-*cis*-disubstituted tetrahydropyrans



The reaction proceeds in very good yields with excellent *cis* selectivity (>99:1), and the reaction pathway lends itself to non-racemic syntheses as well if enantioenriched starting material is used. The authors demonstrate only the use of silyl nucleophiles (allyl silanes, silyl enol ethers, etc.), but other nucleophiles are applicable to this transformation as well. Jennings used this reaction type with chiral, non-racemic lactone **2** to construct the tetrahydropyran ring of (-)-dactylolide (**Scheme 2**).[15] The addition of allyl Grignard reagent to the lactone, and subsequent pseudo-axial attack of the silane onto the oxocarbenium ion intermediate formed by ionization of the resulting hemiacetal provides the 2,6-*cis* stereochemistry.

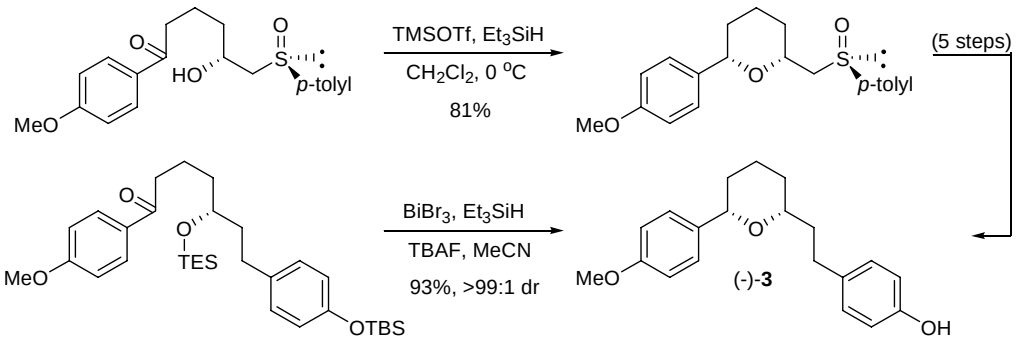
Scheme 2: Reduction of hemiketal toward synthesis of (-)-dactylolide



Among acids used to promote the formation of cyclic hemiketals, trimethylsilyl triflate was used by Colobert,[16] and a $BiBr_3$ precatalyst system has been used by Evans[17] both for the syntheses of (-)-centrolobine, (-)-**3** (**Scheme 3**).

[15] Ding, F.; Jennings, M. P. *Org. Lett.* **2005**, *7*, 2321-2324.
[16] a) Colobert, F.; Des Mazery, R.; Solladie, G.; Carreno, M. C. *Org. Lett.* **2002**, *4*, 1723-1725. b) Carreno, M. C.; Des Mazery, R.; Urbano, A.; Colobert, F.; Solladie, G. *J. Org. Chem.* **2003**, *68*, 7779-7787.
[17] Evans, P. A.; Cui, J.; Gharpure, S. J. *Org. Lett.* **2004**, *5*, 3883-3885. For a discussion on the role of $BiBr_3$ in this reaction see: Evans, P. A. Cui, J.; Gharpure, S. J.; Hinkle, R. J. *J. Am. Chem. Soc.* **2003**, *125*, 11456-11457.

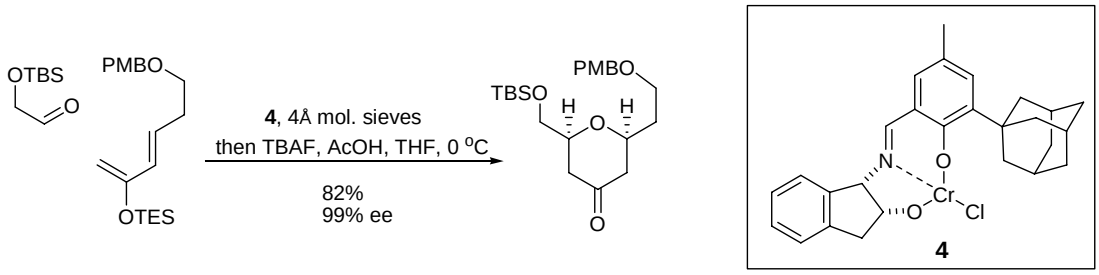
Scheme 3: Enantioselective syntheses of 2,6-*cis* natural product, (-)-centrolobine



Hetero Diels-Alder Cycloadditions

The use of the hetero Diels-Alder reaction has been prevalent in the synthesis of pyrans. In the synthesis of (-)-dactylolide, McLeod and co-workers used a Jacobsen catalytic enantioselective hetero Diels-Alder reaction[18] to establish the absolute and relative stereochemistry of the pyran moiety (**Scheme 4**).[19] This method is efficient, highly selective and scalable to many grams.

Scheme 4: Catalytic asymmetric hetero Diels Alder reaction

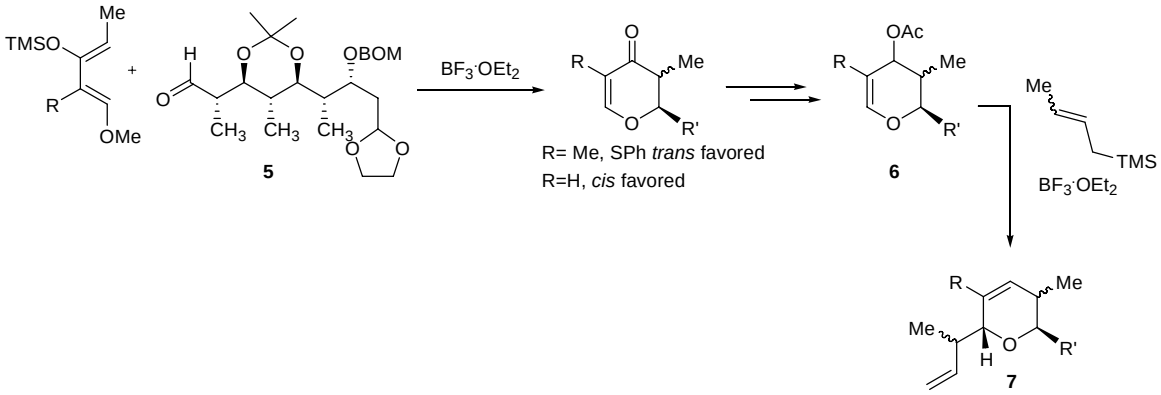


A diastereoselective hetero Diels-Alder reaction was used by Danishefsky in his approach to zincophorin. The reaction was utilized at a late stage to set the appropriate relative 5,6-stereochemistry (**Scheme 5**).[20] After a few simple functional group manipulations, the stage was set for a diastereoselective (3.5:1) carbon Ferrier reaction of glycal acetate **6** with crotyltrimethylsilane. This step allowed for complete control of the 2,6-pyran stereochemistry,

[18] Dossetter, A. G.; Jamison, T. F.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2398-2400.
[19] Louis, I.; Hungerford, N. L.; Humphries E. J.; McLeod, M. D. *Org. Lett*. **2006**, *8*, 1117-1120.
[20] Danishefsky, S. J.; Selnick, H. G.; Zelle, R. E.; DeNinno, M. P. *J. Am. Chem. Soc.* **1988**, *110*, 4368-4378.

while the stereochemistry of the butenyl side chain depended on the *E*/*Z* stereochemistry of the silane reagent. The product **7** was elaborated into zincophorin.

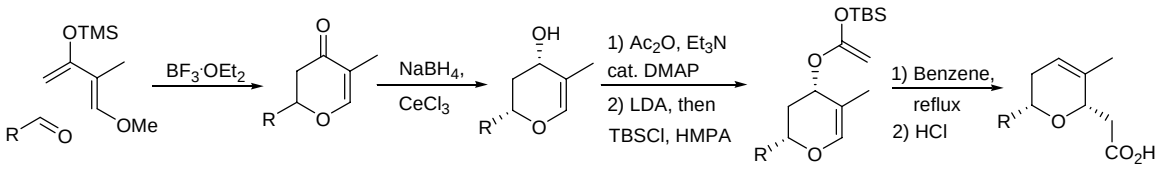
Scheme 5: Diastereoselective hetero Diels-Alder en route to Zincophorin



The advantage of using Danishefsky's diene is that the Diels-Alder cycloadducts allow for further functionalization of the ring through conjugate addition, or through analogous reactions as shown. In this case, the absolute stereochemistry of the hetero Diels-Alder cycloadduct is controlled by the aldehyde, while the relative stereochemistry appears to be influenced by the R group.[21] Adding to the generality of this method, replacing R with a thioether moiety (~SPh), the cycloaddition favors the 5,6-*trans* relationship while providing a hydrogen surrogate that may be required of the final target. Given the tunability of the aldehyde **5**, and the *trans*-selectivity of the second step, this method is eminently useful. However, because the selectivity of each step depends strongly on the relative stereochemistry of the reactants, each step must be carefully modeled to ensure the acquisition of desired products. A similar reaction sequence was used by Varelis and Johnson[22] using an ester enolate Claisen reaction to establish a 2,6-*cis* relationship (**Scheme 6**).

[21] This phenomenon was first observed here: Danishefsky, S. J.; Myles, D. C.; Harvey, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 862-867.
[22] Varelis, P.; Johnson, B. L. *Aust. J. Chem.* **1997**, *50*, 43-51

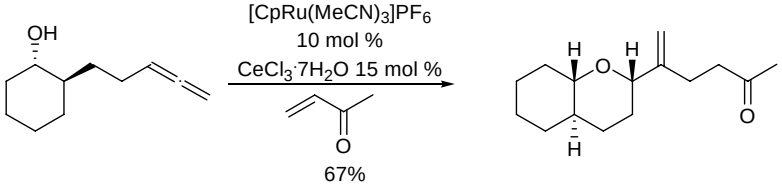
Scheme 6: Hetero Diels-Alder/ester enolate Claisen reaction sequence



Metal-Catalyzed Cycloetherification Reactions

Trost and Pinkerton have developed a ruthenium-catalyzed cycloetherification that uses a chiral, tethered alcohol as a nucleophile in an allenic substitution reaction.[23] The reaction is terminated through conjugate addition to an α,β-unsaturated ketone (**Scheme 7**). This method establishes considerable molecular complexity very quickly, and works with both primary and secondary alcohols. The role of cerium chloride is not explained by the authors,[24] but likely acts as a Lewis acid, coordinating to the carbonyl of the unsaturated ketone, and increasing its reactivity towards the coulpling.

Scheme 7: Ruthenium catalyzed allenic cycloetherification

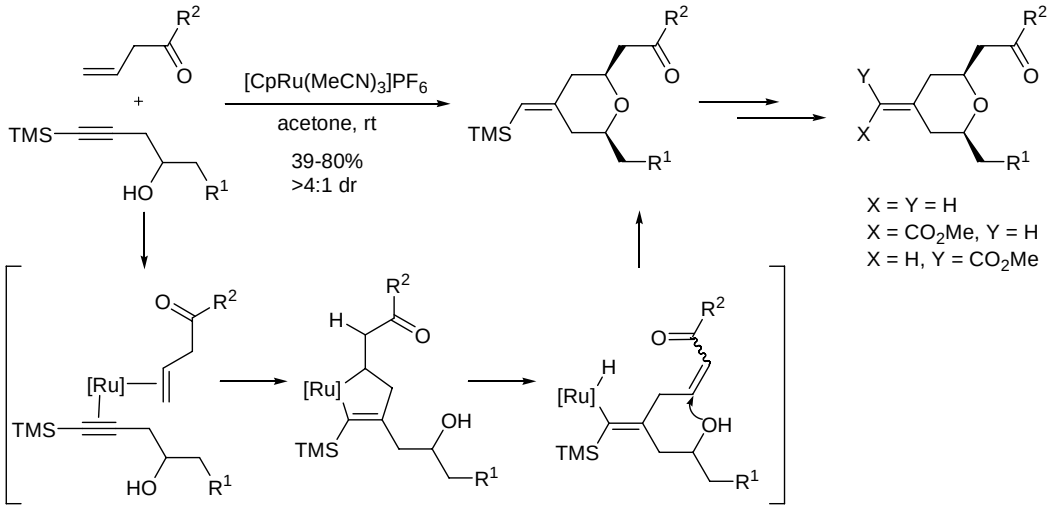


Similarly, a one pot protocol involving a ruthenium-catalyzed tandem ene-yne coupling/Michael addition sequence has been found to be general for the stereocontrolled construction of 4-methylene-2,6-*cis*-tetrahydropyrans (**Scheme 8**). The authors also demonstrate that the stereodefined trimethylsilyl group is a versatile handle for installing additional functionality on the methylene group with complete stereocontrol. Presumably, the mechanism involves an intermediate 5-membered ruthenacycle, which after β-hydride elimination, generates the Michael

[23] Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **1999**, *121*, 10842-10843.
[24] Nor is its purpose explained in earlier work that details optimization of conditions: Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **1999**, *121*, 4068-4069.

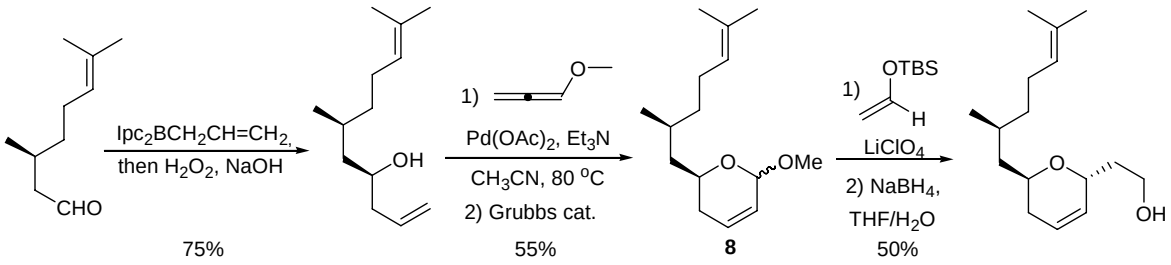
acceptor. Cyclization by the hydroxyl group and reductive elimination of the ruthenium hydride forms the vinylsilane with retention of olefin geometry and regenerates the catalyst.

Scheme 8: Ruthenium-catalyzed ene-yne coupling/Michael addition cascade sequence



Researchers at the Eisai Research Institute[25] modified a protocol used by Davidson[26] to create the pyran acetal **8** on the way to synthesizing Laulimalide, and analogs. The key step was a palladium-catalyzed etherification of the secondary alcohol with methoxyallene, followed by ring-closing metathesis.[27] Further functionalization at the anomeric center gave only the *trans*-disubstituted dihydropyran (**Scheme 9**).

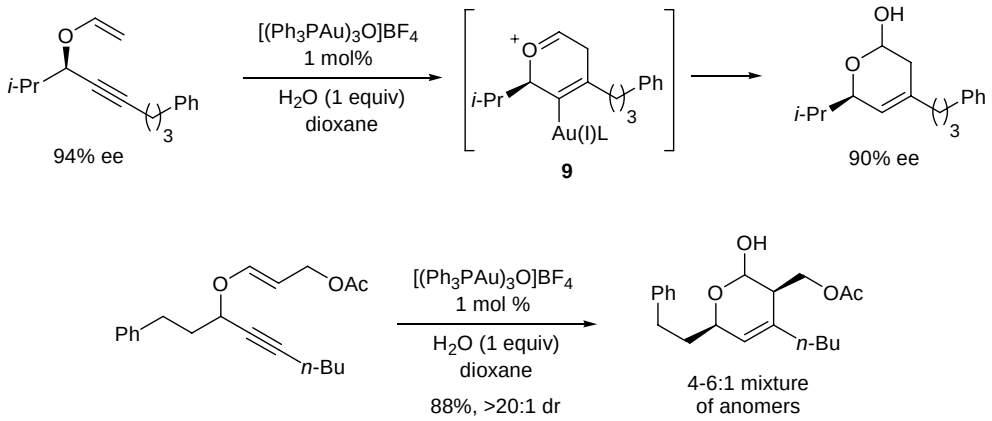
Scheme 9: Palladium-catalyzed etherification



[25] Gallagher, B. M.; Fang, F. G.; Johannes, C. W.; Pesant, M.; Tremblay, M. R.; Zhao, H.; Akasaka, K.; Li, X.-Y.; Liu, J.; Littlefield, B. A. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 575-579.
[26] Nadolski, G. T.; Davidson, B. S. *Tetrahedron Lett.* **2001**, *42*, 797-800.
[27] Rutjes, F. P. J. T.; Kooistra, T. M.; Hiemstra, H.; Shoemaker, H. E. *Synlett* **1998**, 193-194.

The Toste group found that propargyl vinyl ethers undergo a gold-catalyzed Claisen rearrangement to form homoallenic alcohols after reduction.[28] By running the reaction in wet dioxane, the oxocarbenium intermediate **9** could be intercepted with water to form the substituted dihydropyran with minimal loss of ee, when starting with enantioenriched propargylic ethers. The reaction is run under very mild conditions, and is diastereoselective.

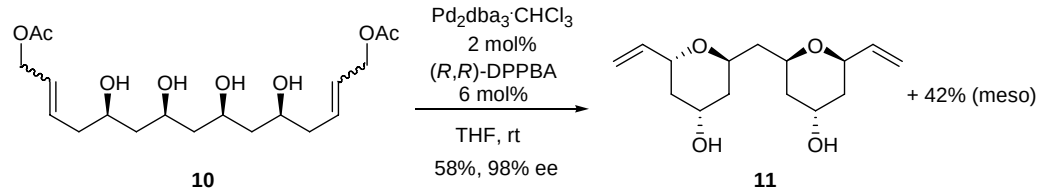
Scheme 10: Toste's propargyl Claisen Rearrangement/heterocyclization



Steven Burke has utilized a two-directional allylic substitution reaction (based on Trost's catalyst system[29]) to the tetraol **10** to form the desired bis-pyran unit of phorboxazole **11**.[30] Also formed in the reaction was the *meso* compound in 42% yield. The explanation for the excellent enantioselectivity and poor diastereoselectivity is based on competitive rates of cyclization, the first of which is a matched case, forming the first ring very quickly, and preventing the formation of the other enantiomer, and then a subsequent competition between substrate control (matched) and ligand control (mismatched) in the second cyclization to form a nearly 3:2 ratio.

[28] Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 15978-15979.
[29] Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327-9343.
[30] Lucas, B. S.; Burke, S. D. *Org. Lett.* **2003**, *5*, 3915-3918. See also: Lucas, B. S.; Luther, L. M.; Burke, S. D. *Org. Lett.* **2004**, *6*, 2965-2968.

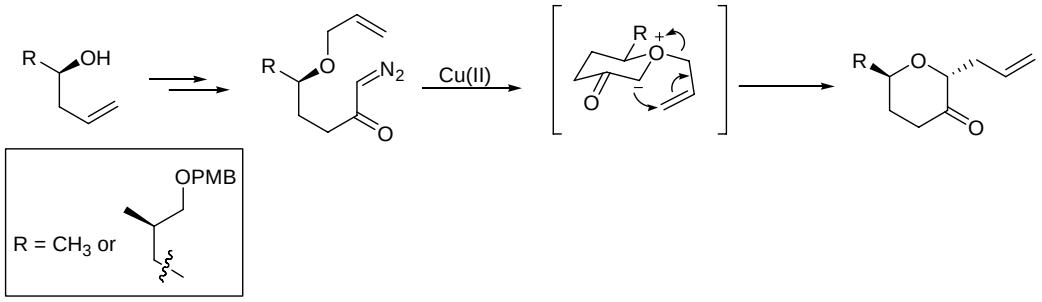
Scheme 11: Palladium catalyzed allylic substitution reaction



DPPBA = (*R*,*R*)-*N*-[2,(2'-diphenylphosphino)benzamido cyclohexyl] (2'-dipheylphosphino)benzamide

The use of carbenoid chemistry to form heterocycles[31] is also prevalent in the literature for formation of substituted pyrans. This reaction type has been exploited very recently in the asymmetric syntheses of Decarestrictine L[32] and the tetrahydropyran unit of Laulimalide,[33] whereby copper catalyzed decomposition of the α-diazo ketone formed the intermediate carbenoid. The *trans*-stereochemistry is formed with high selectivity due to the proposed oxonium ylide intermediate shown in **Scheme 12**.

Scheme 12: Copper carbenoid/oxonium ylide cyclization onto allylic ethers



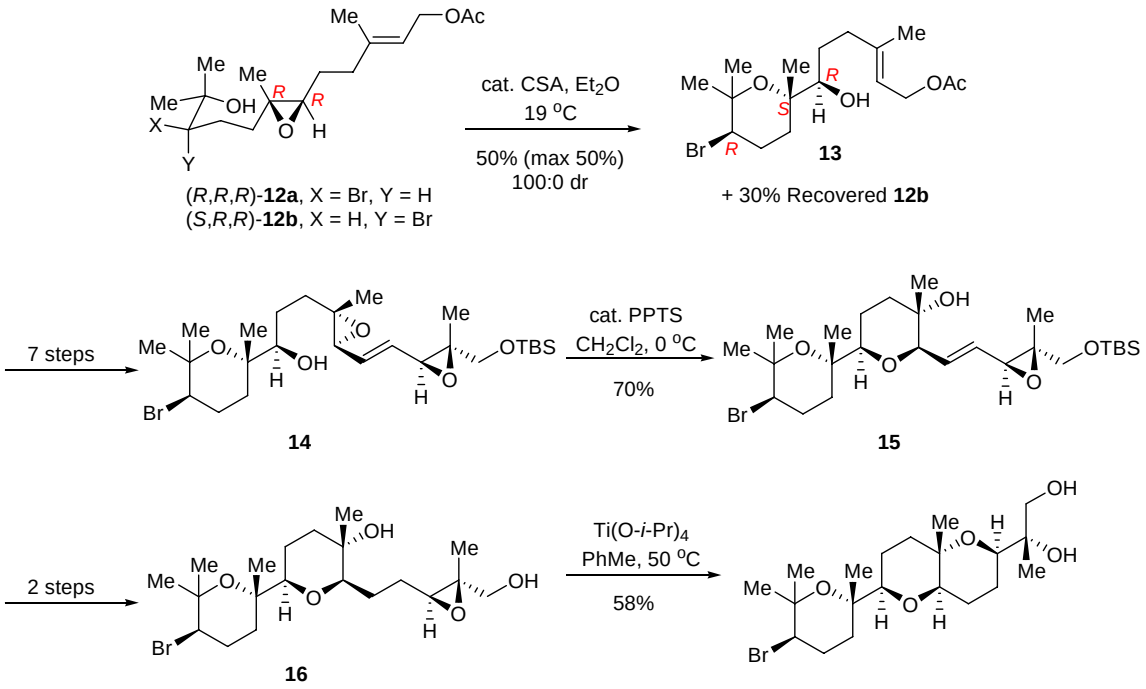
Ring Opening/Cyclization onto Epoxides

McDonald and coworkers have utilized the ring opening of chiral nonracemic epoxides with tethered alcohols as a means of forming highly substituted pyrans with excellent stereocontrol.[34] In the synthesis of the ABC rings of thyrsiferol and venustatriol, they achieved a dynamic kinetic resolution of bromohydrin diastereomers **12a** and **12b** using careful temperature control. Only

[31] Padwa, A. *J. Organomet. Chem.* **2005**, *690*, 5533-5540.
[32] Clark, J. S.; Fessard, T. C.; Whitlock, G. A. *Tetrahedron* **2006**, *62*, 73-78.
[33] Yakura, T.; Muramatsu, W.; Uenishi, J. *Chem. Pharm. Bull.* **2005**, *53*, 989-994.
[34] McDonald, F. E.; Wei, X. *Org. Lett.* **2002**, *4*, 593-595.

12a reacted in the cyclization, to form **13** in the maximum theoretical yield (50% isolated) with 100:0 dr owing to *anti*-attack on the acid-activated epoxide, which inverts the stereochemistry at that center. Subsequent manipulations, including a Sharpless asymmetric epoxidation[35] provided **14** in only 7 linear steps, after which cyclization onto the proximal epoxide provided **15** with perfect *endo*-selectivity that is attributed to stabilization of the ensuing positive charge by the π-orbitals of the adjacent olefin.[36] Diimide reduction of the olefin, and deprotection of the primary alcohol provided **16**, which underwent a cyclization by activation of the epoxide with titanium isopropoxide to provide the ABC rings of thyrsiferol and venustatriol in good yields.

Scheme 13: Acid-promoted diastereoselective ring opening onto chiral nonracemic epoxides

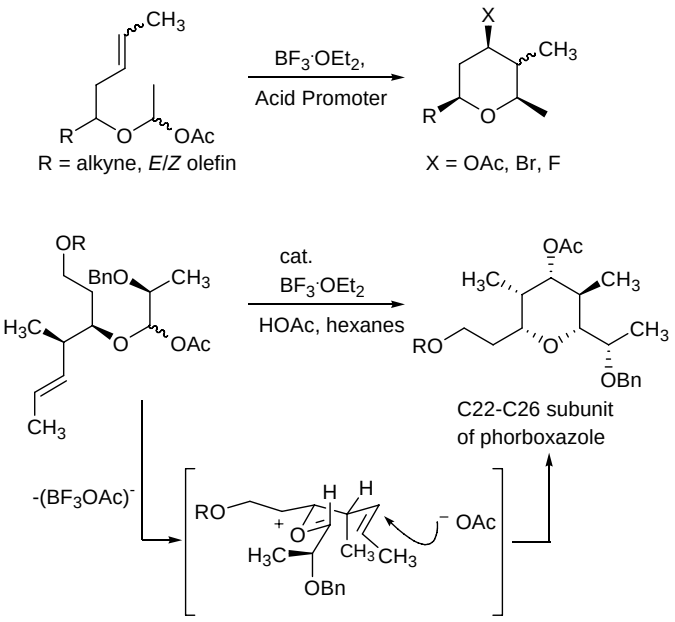


[35] Gao, Y.; Klunder, J. M.; Hanson, R. M.; Masamune, H.; Ko, S. Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765-5780.
[36] Nicolaou, K. C.; Prasad, C. V. C.; Somers, P. K.; Hwang, C.-K. *J. Am. Chem. Soc.* **1989**, *111*, 5330-5334.

Prins Cyclizations and Related Reactions

One very significant method for the construction of substituted pyrans that has seen a marked amount of attention from the synthetic world is the use of the Prins reaction to make pyrans.[37] Rychnovsky developed the "segment coupling Prins cyclization" in 1998[38] and applied it to a synthesis of the pentasubstituted pyran subunit of phorboxazole (**Scheme 14**).[39] The counterion of the acid promoter is essential to speeding the rate of the Prins reaction, and avoiding the competitive oxonia-Cope rearrangement, that would racemize the stereochemistry at the chiral alcohol center in the starting material.

Scheme 14: Lewis Acid initiated Prins Cyclization, application to phorboxazole unit



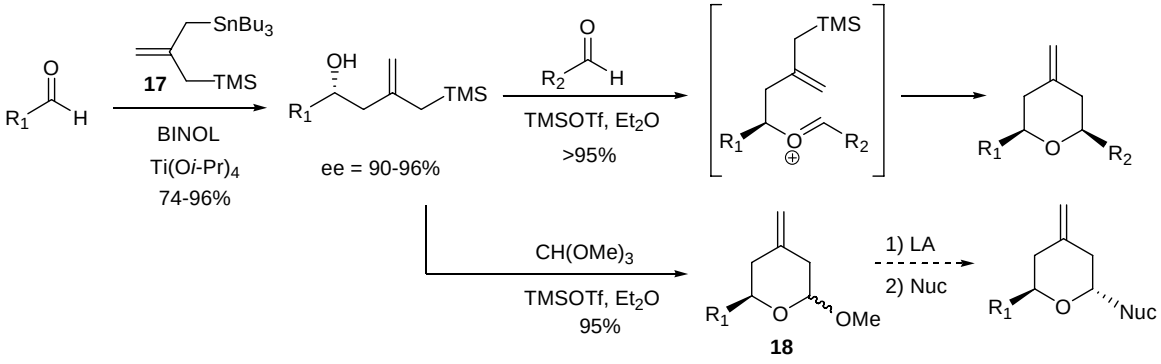
This synthesis is dramatic in many ways because it demonstrates the range of tolerated functionality, and resistance to epimerization. This particular variation of the method is only useful for the preparation of 2,6-*cis*-substituted pyrans.

---

[37] a) Adams, D. R.; Bhaynagar, S. D. *Synthesis* **1977**, 661-672. b) Cloninger, M. J.; Overman, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 1092-1093.
[38] Rychnovsky, S. D.; Hu. Y.; Ellsworth, B. *Tetrahedron Lett.* **1998**, *39*, 7271-7274. See also: Jaber, J. J.; Mitsui, K.; Rychnovsky, S. D. *J. Org. Chem.* **2001**, *66*, 4679-4686.
[39] Rychnovsky, S. D.; Thomas, C. R. *Org. Lett.* **2000**, *2*, 1217-1219.

Keck and co-workers have demonstrated an allylsilane-terminated Prins cascade procedure, that allows for the simple installation of a 4-methylene unit in 2,6-*cis*-substituted tetrahydropyrans.[40] The method is similar to one described by Rychnovsky and Kopecky,[41] but they also describe a facile entrance into the requisite starting material using a stereoselective BINOL/Ti(O*i*-Pr)$_4$ catalyzed addition of the silyl-stannane reagent **17** to aldehydes. Then, a second aldehyde converges on the newly formed alcohol in the presence of TMSOTf setting up the annulation step (**Scheme 15**). Although not explicitly demonstrated, the facile formation of **18** suggests that this procedure is amenable to formation of the 2,6-*trans*-substitution pattern as well.

Scheme 15: Allylsilane terminated Prins cyclization

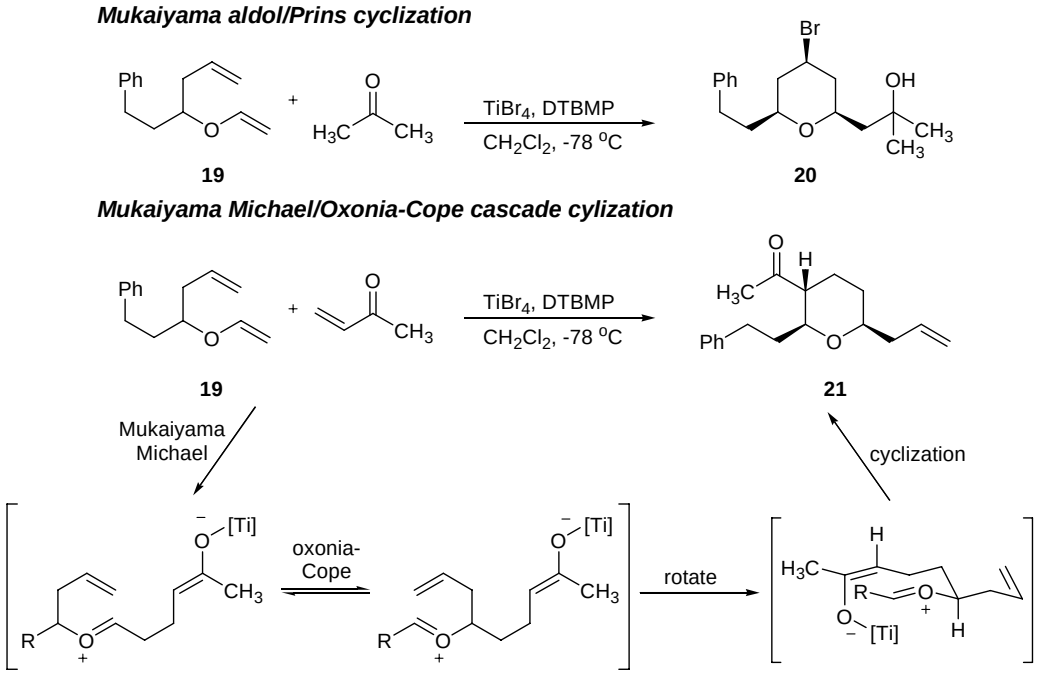


Rychnovsky and co-workers have also demonstrated that homoallylic enol ethers, such as **19** react with aldehydes in the presence of titanium tetrabromide to initiate a bromide terminated Prins cyclization to form compound **20**.[42] A similar intiation step occurs with $TiBr_4$ and unsaturated ketones and esters, which undergo a Mukaiyama Michael reaction.[43] However, under these conditions, the oxonium intermediate does not undergo a Prins cyclization, but rather, after

[40] Keck, G. E.; Covel, J. A.; Schiff, T.; Yu, T. *Org. Lett.* **2002**, *4*, 1189-1192.
[41] Kopecky, D. J.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **2001**, *123*, 8420-8421.
[42] a) Patterson, B.; Marumoto, S.; Rychnovsky, S. D. *Org. Lett.* **2003**, *5*, 3163-3166. b) Patterson, B.; Rychnovsky, S. D. *Synlett* **2004**, 543-545.
[43] Bolla, M. L.; Patterson, B.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **2005**, *127*, 16044-16045.

facile oxonia-Cope rearrangement, the oxonium intermediate is terminated by the aldol condensation to form the *trans-trans* tetrahydropyran **21** as a single diastereomer.

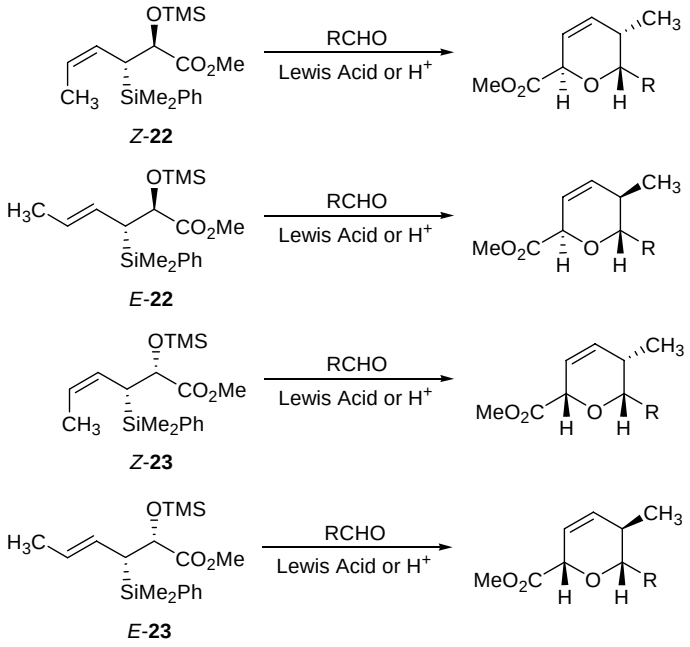
Scheme 16: Mukaiyama aldol and Mukaiyama Michael initiated cyclizations



Recently Panek has developed a very versatile method for the formation of both *cis* and *trans C*-pyranosides. The method involves a [4+2]-annulation of (*E*)-[44] and (*Z*)-crotylsilanes.[45] The relative stereochemistry of the vicinal silane and protected alcohol predetermine the *cis* or *trans* relationship between the 2- and 6-substituents (**Scheme 17**). In addition, the 5,6-relationship is controlled by the geometry of the crotylsilane, with (*E*)-favoring a *trans*-relationship and (*Z*)-favoring a *cis*-relationship. A wide variety of functional groups ("R") on the aldehyde are tolerated; among them are aliphatic ketones and bromides, activated aryl groups and olefins. The downside of this method appears only to be that while the routes toward the starting materials (**22** and **23**) are high-yielding and selective, they are very long (twelve steps to **22** and ten steps to **23** from commercially available starting materials).

[44] Huang, H.; Panek, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 9836-9837.
[45] Lowe, J. T.; Panek, J. S. *Org. Lett.* **2005**, *7*, 3231-3234.

Scheme 17: Diastereoselective [4+2]-annulation of crotyl silanes and aldehydes



Enantiomeric Scaffolding Approach to Stereocontrolled Synthesis

While the majority of the reactions described above are high-yielding, selective, and proceed under generally mild conditions, there is a single commonality among them that certain circles of the synthetic community might consider to be a drawback. In each reaction type the starting materials always contain pre-installed carbon functional groups that "decorate" the periphery of the pyran ring. To the target-directed synthetic chemist, this is no problem, because each carbon functional group is strategically installed to access a desired substitution pattern, and each set of reaction conditions is optimized for that particular substrate. However, to the researcher interested in the exploration of chemical space through diversity-oriented synthesis, many of these methods would not be expeditious for predictable access to a library of compounds bearing different functional groups, with deliberate control over stereochemistry. This is because catalyst and substrate control are paramount to the selectivity enjoyed by so much of the chemistry

discussed above that even minor alterations in the starting substrates may require re-optimization of reaction conditions to achieve high selectivity.

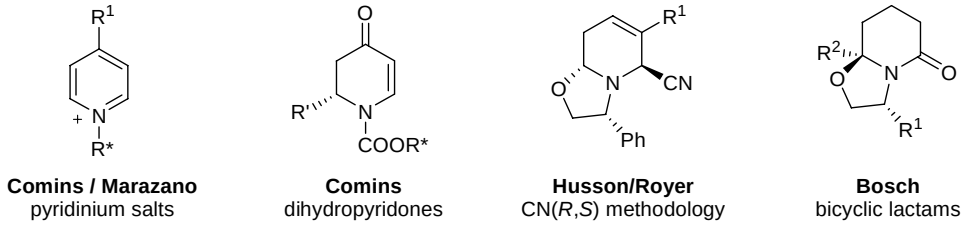
It is with this general problem that the Liebeskind laboratory has been concerned for the last 15 years: how to generate complex molecules of varying carbon and heterocyclic skeletons with the flexibility to install a variety of functional groups while controlling the absolute and relative stereochemistry of all chiral centers over multiple steps using only a single auxiliary. Any synthetic approach that addresses each and all of these requirements would be a very powerful and strategic tool for the synthetic chemist.

The dominant force in the published approaches to enantiocontrolled bond construction in recent decades has been catalysis in its many forms (metallo-[46] or organo-[47]). Other approaches have utilized the chiral pool, either as chirons[13, 48] or auxiliaries[49] for classical resolutions, and enzymatic resolutions.[50,51]

Another strategic approach to enantiocontrolled synthesis which is less well studied is that of enantiomeric scaffolding. In enantiomeric scaffolding, a simple molecule of high enantiopurity serves as a core for the construction of various families of important molecules. These scaffolds bear simple yet versatile functionality that permits stereocontrolled elaboration of the core into molecules of increasing complexity and skeletal diversity. The most prominent examples of *organic enantiomeric scaffolding* in complex molecule synthesis are in the elegant work of

[46] Ojima, I. *Catalytic Asymmetric Synthesis*, 2nd ed.; Wiley: New Yort, 2000; p864.
[47] Seayad, J.; List, B. *Org. Biomol. Chem.* **2005**, *3*, 719-724.
[48] Hanessian, S. *Pure Appl. Chem.* **1993**, *65*, 1189-1204.
[49] Blaser, H. U. *Chem. Rev.* **1992**, *92*, 935-952.
[50] Mulzer, J. Enzymes in Organic Synthesis. 2. In *Organic Synthesis Highlights*; Mulzer, J., Altenbach, H. J., Braun, M., Krohn, K., Reissig, H. U., Eds.; VCH Verlagsgesellschaft: Weinheim, Germany, 1991; pp 216-223.
[51] Mulzer, J. Enzymes in Organic Synthesis. 1. In *Organic Synthesis Highlights*; Mulzer, J., Altenbach, H. J., Braun, M., Krohn, K., Reissig, H. U., Eds.; VCH Verlagsgesellschaft: Weinheim, Germany, 1991; pp 207-215.

Comins,[52] Marazano,[53] Husson and Royer,[54] and Bosch[55] (**Figure 1**). Other examples of enantiomeric scaffolds used in total synthesis are the Wieland-Miescher ketone[56,57] and the Roche ester,[58] both of which are commercially available. To date, the majority of work in heterocyclic enantiomeric scaffolding has been restricted to nitrogen heterocycles.



Comins / Marazano pyridinium salts | **Comins** dihydropyridones | **Husson/Royer** CN(*R*,*S*) methodology | **Bosch** bicyclic lactams

Figure 1: Organic enantiomeric scaffolds

Comins has nicely demonstrated how enantiomeric scaffolding can be used for the construction of a variety of different families of molecules (**Figure 2**).

[52] Selected examples: (a) Comins, D. L.; King, L. S.; Smith E. D.; Fevrier, F. C. *Org. Lett.* **2005**, *7*, 5059-5062. (b) Comins, D. L.; Kuethe, J. T.; Miller, T. M.; Fevrier, F. C.; Brooks, C. A. *J. Org. Chem.* **2005**, *70*, 5221-5234. (c) Joseph, S.; Comins, D. L. *Curr. Opin. Drug Discovery Dev.* **2002**, *5*, 870-880.

[53] Selected examples: (a) Viana, G. H. R.; Santos, I. C.; Alves, R. B.; Gil, L.; Marazano, C.; de Freitas Gil, R. P. *Tetrahedron Lett.* **2005**, *46*, 7773-7776. (b) dos Santos, D. C.; de Freitas Gil, R. P.; Gil, L.; Marazano, C. *Tetrahedron Lett.* **2001**, *42*, 6109-6111.

[54] Husson, H.-P.; Royer, J. *Chem. Soc. Rev.* **1999**, *28*, 383-394.

[55] Selected examples: Escolano, C.; Amat, M.; Bosch, J. *Chem. Eur. J.* **2006**, *12*, 8198-8207. (b) Amat, M.; Perez, M.; Minaglia, A. T.; Casamitjana, N.; Bosch, J. *Org. Lett.* **2005**, *7*, 3653-3656.

[56] Wieland, P.; Miescher, K. *Helv. Chim. Acta* **1950**, *33*, 2215-2228.

[57] For an example of the use of the Wieland-Miescher ketone in total synthesis see: Danishefsky, S. J.; Masters, J. J.; Young, W. B.; Link, J. T.; Snyder, L. B.; Magee, T. V.; Jung, D. K.; Isaacs, R. C. A.; Bornmann, W. G.; Alaimo, C. A.; Coburn, C. A.; Di Grandi, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 2843–2859.

[58] For an example of the use of the Roche ester in total synthesis see: Smith, A. B., III; Adams, C. M.; Lodise Barbosa, S. A.; Degnan, A. P. *Proc. Natl. Acad. Sci. USA*, **2004**, *101*, 12042-12047.

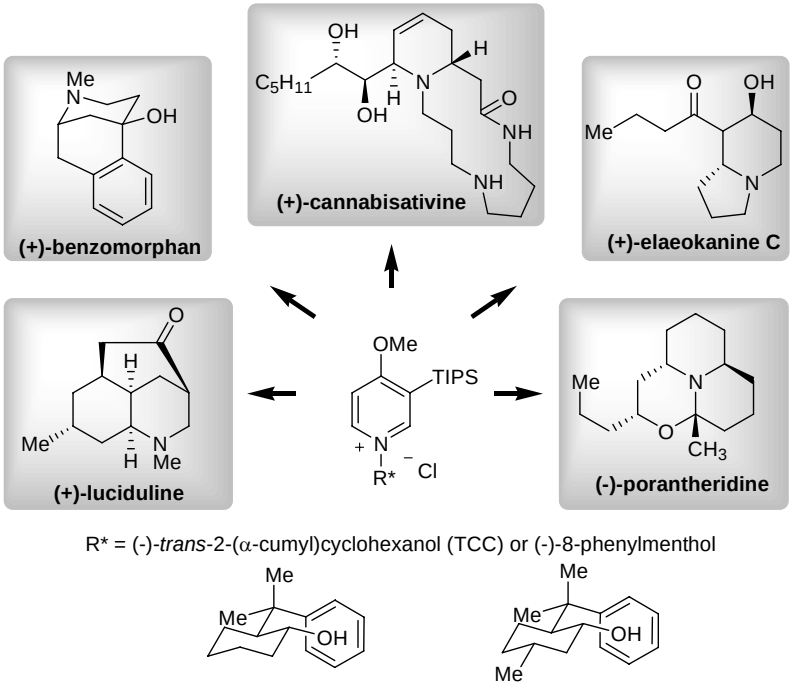


Figure 2: Comins' acylpyridinium scaffolds[59]

Over the last decade, the Liebeskind laboratory has demonstrated the utility of *organometallic enantiomeric scaffolds*. In organometallic enantiomeric scaffolding, single enantiomers of transition metal π-complexes of unsaturated organic ligands serve as the core off of which diverse families of organic molecules of high enantiopurity are constructed. In this scaffolding approach, the metal and its ligands direct the elaboration of the core organic ligand by providing a dominant stereo and regiocontrol element, and also providing the opportunity for strategic bond connections not otherwise available with traditional organic systems. Additionally, the use of a single stoichiometric metal is mitigated by predictably and effectively controlling the introduction of multiple sterecenters over multiple steps.

The Liebeskind laboratory has focused on the use of four main molybdenum-based organometallic enantiomeric scaffolds based on oxygen and nitrogen-containing heterocyles

[59] Shown in **Figure 2**: (a) Comins, D. L.; Brooks, C. A.; Al-awar, R. S.; Goehring, R. R. *Org Lett*. **1999**, *1*, 229-232. (b) Comins, D. L.; Zhang, Y.-M.; Joseph, S. P. *Org. Lett.* **1999**, *1*, 657-660. (c) Kuethe, J. T.; Comins, D. L. *J. Org. Chem.* **2004**, *69*, 5219-5231. (d) Comins, D. L.; Hong, H. *J. Am. Chem. Soc.* **1991**, *113*, 6672-6673. (e) Comins, D. L.; Hong, H. *J. Am. Chem. Soc.* **1993**, *115*, 8851-8852.

(**Figure 3**). These metal π-complexes are air and moisture stable solids that are easily handled on the benchtop without dry boxes or Schlenk lines. Both antipodes of each scaffold are readily available on large scale and in high enantiomeric excess from inexpensive organic precursors and an inexpensive, non-toxic metal source.

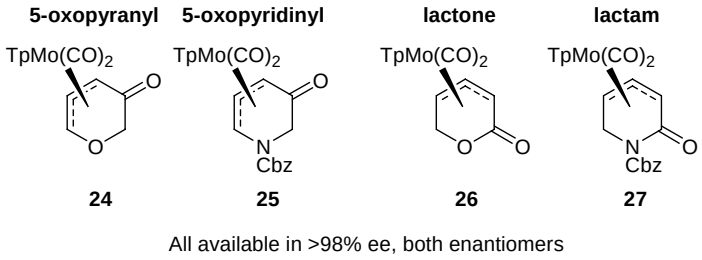


Figure 3: Liebeskind organometallic enantiomeric scaffolds

The $TpMo(CO)_2(\eta^3$-5-oxo-pyranyl)[60] and $TpMo(CO)_2(\eta^3$-5-oxo-pyridinyl) complexes **24** and **25** respectively have been elaborated into diverse families of heterocyclic compounds of high enantiopurity utilizing a range of novel methodologies and bond connections (**Figure 4**).

[60] Tp = hydridotrispyrazolylborato

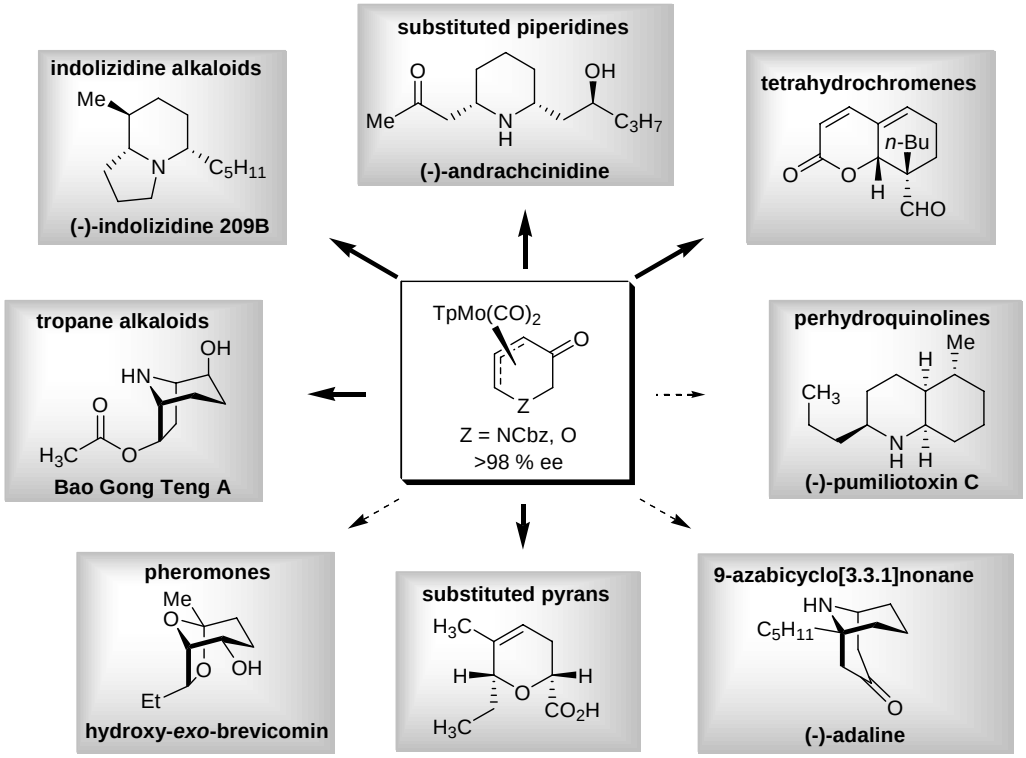
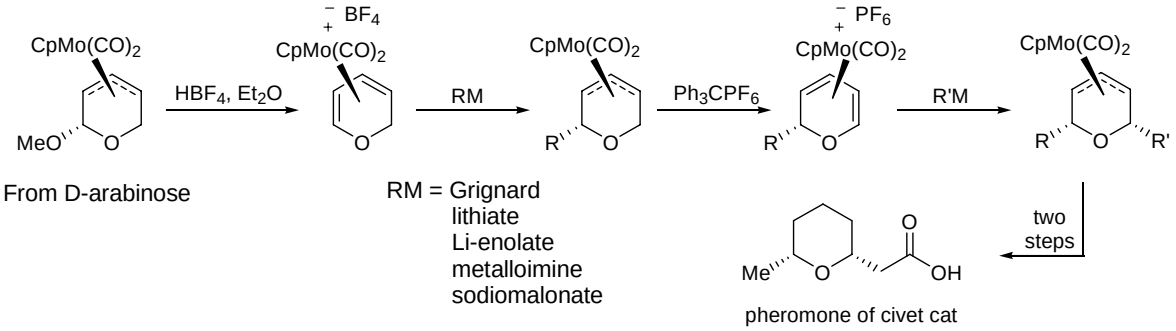


Figure 4: Organometallic Enantiomeric Scaffolding Revealed[61]

The use of these scaffolds for the stereocontrolled synthesis of substituted pyran architectures has been demonstrated through a variety of different methods. In 1990, the preamble to what was to become bedrock of the Liebeskind group's chemistry was published. Two enantiopure molybdenum π-complexes derived from *D*- and *L*-arabinose were created, and through the sequential abstraction of leaving groups adjacent to the η^3-allyl moiety, followed by nucleophilic addition with complete stereoselectivity *anti* to the metal moiety, a general method for the enantiocontrolled 2,6-*cis* functionalization of pyrans was developed.[62]

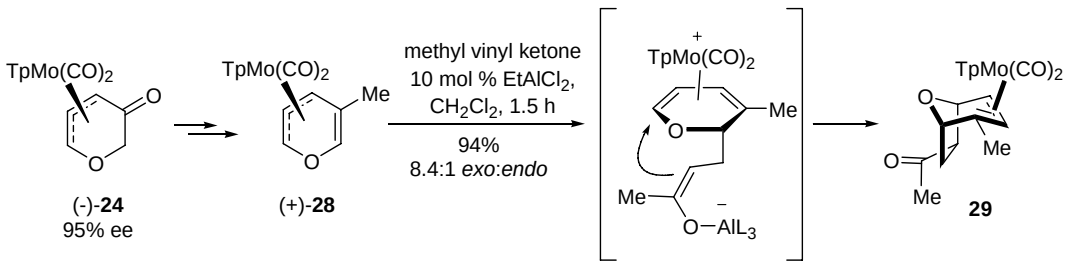
[61] Dashed arrows represent currently unpublished work.
[62] Hansson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9960-9961.

Scheme 18: Synthesis of 2,6-*cis* disubstituted pyrans *via* $CpMo(CO)_2$ complexes derived from arabinose



A number of years later, the synthesis of the 5-oxopyranyl scaffold **24** was accomplished in high enantiopurity *via* a diastereoselective metalation protocol of pantolactone-resolved pyranones (*vide infra*).[63] Addition to the ketone, followed by elimination of the resulting alcohol provided the fully unsaturated complex **28** (**Scheme 19**). In the presence of $EtAlCl_2$, and a conjugated electrophile, the complex reacted to form the bicyclic complex **29** resulting from a formal [5+2] cycloaddition. A stepwise mechanism was proposed whereby conjugate addition to the Lewis acid complexed electrophile occurred creating a molybdenum-stabilized cationic diene. The incipient enolate then attacks back at the terminus of the diene adjacent to the pyran ring oxygen, forming the bicyclo-[3.2.1]-octane in excellent yield and in high enantiopurity after decomplexation.

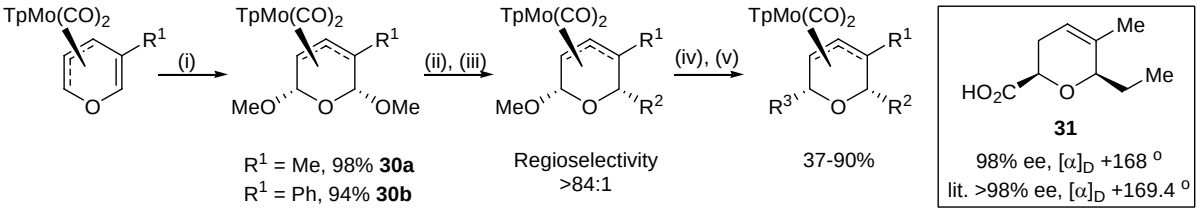
Scheme 19: [5 + 2] Cycloaddition to unsaturated pyranyl complexes



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

The fully-unsaturated complexes have also been used in a sequential functionalization protocol, similar to that demonstrated on the $CpMo(CO)_2$ complex in **Scheme 18**.[64] In this more general procedure, the complexes undergo oxidative bromination, with methoxide quench to provide the stable dimethoxy complexes **30a-b**. These complexes undergo selective ionization of the methoxide on the carbon adjacent to the group R^1 to form intermediate molybdenum-stabilized cations followed by a stereoselective nucleophilic addition *anti* to the metal moiety to provide the intermediate disubstituted complexes,[65] which could be subsequently treated with tetrafluoroboric acid, and a second nucleophile to provide the 2,3,6-trisubstituted complexes, with 2,6-*cis* relative stereochemistry. This protocol was used to synthesize **31** in high ee, an intermediate in Kende's synthesis of ambruticin.[66]

Scheme 20: Sequential functionalization protocol provides 2,6-*cis* trisubstituted compounds



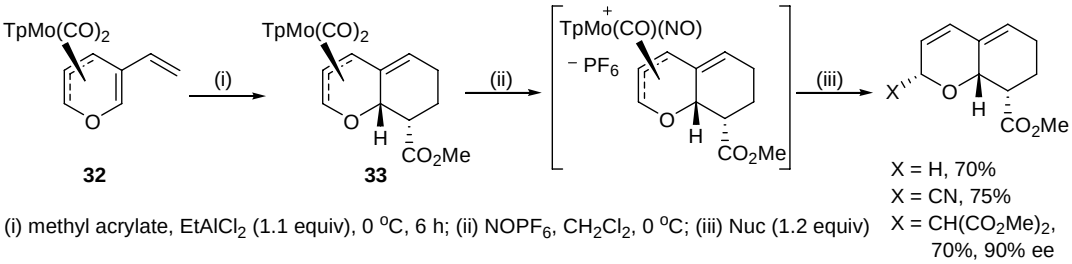
(i) Br_2, -78 °C, then NaOMe/MeOH; (ii) $TrPF_6$, CH_2Cl_2, -78 to 0 °C; (iii) R^2M, THF; (iv) HBF_4, THF; (v) R^3M, -78 °C

One other method that provided functionalized pyrans took advantage of a [4+2] reaction of olefin-substituted complex **32**.[67] The Lewis acid-catalyzed cycloaddition proceeded smoothly with *endo*-selectivity to provide **33**, which could undergo ligand exchange with nitrosonium hexafluorophosphate, creating an intermediate η^3-cationic complex, to which was added various nucleophiles. The product in each case was a functionalized fused bicycle with 2,6-*cis* stereochemistry at the pyran ring.

---

[64] Yin, J.; Llorente, I.; Villanueva, L. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2000**, *122*, 10458-10459.
[65] For an in depth discussion on the selectivity of ionization, see chapter 4.
[66] Kende, A. S.; Mendoza, J. S.; Fujii, Y. *Tetrahedron* **1993**, *49*, 8015-8038.
[67] Arrayás, R. G.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 6185-6186.

Scheme 21: [4+2] cycloaddition/demetalation sequence provides 2,6-*cis* tetrahydrochromenes



These examples highlight the power of the organometallic enantiomeric scaffolding strategy: the enantiocontrolled synthesis of a diverse range of highly functionalized molecules originating from a common starting material. It is evident from the discussion above, however that each example presented only provided the 2,6-*cis* stereochemistry about the pyran ring. The projects described in this dissertation are the efforts to expand the utility of the Liebeskind organometallic enantiomeric scaffolds toward the synthesis of spiroketals and 2,6-*trans* susbstituted pyrans, both of which would be of significant utility and a boon to the project.

Results and Discussion:

Improved Synthetic routes to 5-oxopyranyl scaffold

The reported synthesis of the 5-oxopyranyl scaffold is based on the Achmatowicz reaction[68] (**Scheme 22**). In this three step sequence, oxidation of furfuryl alcohol with *m*-CPBA provides the 6-hydroxypyranone **34**, which, is acetylated under standard conditions. Oxidative addition to the allylic acetate with $Mo(CO)_3(DMF)_3$,[69] followed by ligand exchange with potassium hydridotris(1-pyrazolyl)borate (KTp)[70] provided the racemic scaffold **24** in 72% yield from **35**. Paramount to the utility of organometallic enantiomeric scaffolding is the relative ease of generating the starting materials on multi-gram scale, and while this reaction is high yielding and

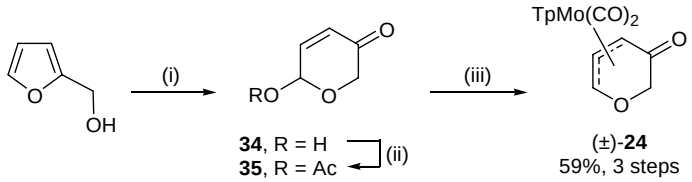
[68] Achmatowicz, O., Jr.; Bukowski, P.; Szechner, B.; Zwierzchowska, Z.; Zamojski, A. *Tetrahedron* **1971**, *27*, 1973-1996.

[69] This reagent is trivially prepared on several hundred gram scale by heating $Mo(CO)_6$ in DMF and toluene. See: Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Gazz. Chim. Ital.* **1992**, *122*, 275-277.

[70] KTp is also simple to prepare on mole scale by heating pyrazole and KBH_4 without solvent. See: a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943-980. b) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170-3177.

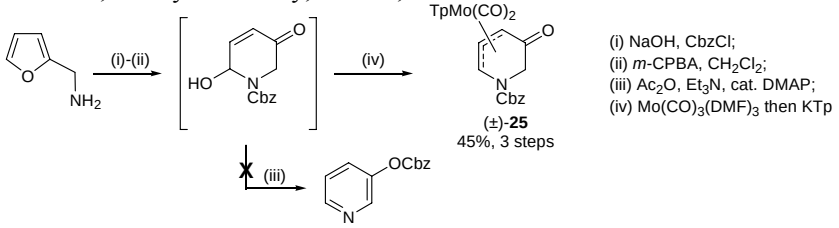
procedurally simple, the drawback of this sequence is that it suggests the requirement of isolating and purifying the intermediates **34** and **35**. With a mind toward streamlining the synthesis of the key pyranyl scaffold **24**, it was hoped that bypassing the acetylation step by direct metalation of the Achmatowicz product **34** would provide complex **24**.[71] Unfortunately all attempts to directly metalate **34** gave low yields, as did metalation of the acetate **35** with the more air stable $Mo(CO)_3(py)_3$. It was discovered, however that a related three operation synthetic sequence provided the target complex **24** in 59% yield from furfuryl alcohol without isolation of intermediates.[72] By this improved protocol the reaction mixture from the Achmatowicz (oxidation) step is vacuum filtered to remove precipitated 3-chlorobenzoic acid byproduct. The filtrate is then used directly in the acetylation step. This reaction mixture is subjected to an aqueous wash, and the resulting crude product is metalated directly. A single chromatography is required at the end of this sequence, and the majority of the product can be further purified by trituration with ether.

Scheme 22: Synthesis of racemic 5-oxopyranyl scaffold



(i) *m*-CPBA, CH_2Cl_2; (ii) Ac_2O, Et_3N, cat. DMAP; (iii) $Mo(CO)_3(DMF)_3$ then KTp

[71] Thomas Coombs had discovered that an aza-Achmatowicz approach to the key nitrogen scaffold (±)-**25** was possible through direct metalation of the 6-hydroxypyridinone. Acetylation of this intermediate caused aromatization, and *N* to *O* protecting group migration, and thus precluded metalation. For a detailed discussion of this, see (a) Moretto, A. F. Ph.D. Dissertation, Emory University, Atlanta, 1999. (b) Coombs, T. C. Ph.D. Dissertation, Emory University, Atlanta, 2008.



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

This new streamlined protocol produces 13.6 g of pure product from 4.9 g of furfuryl alcohol, and expedites the scale up of starting material (**Figure 5**).

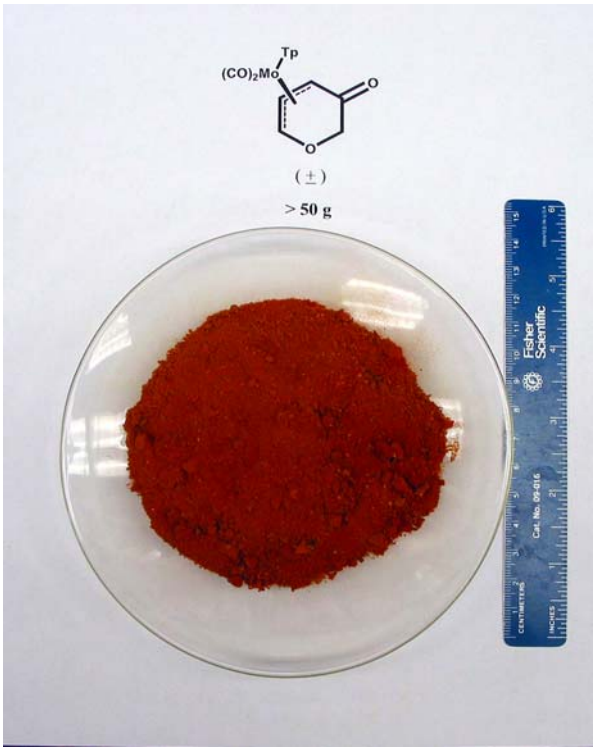
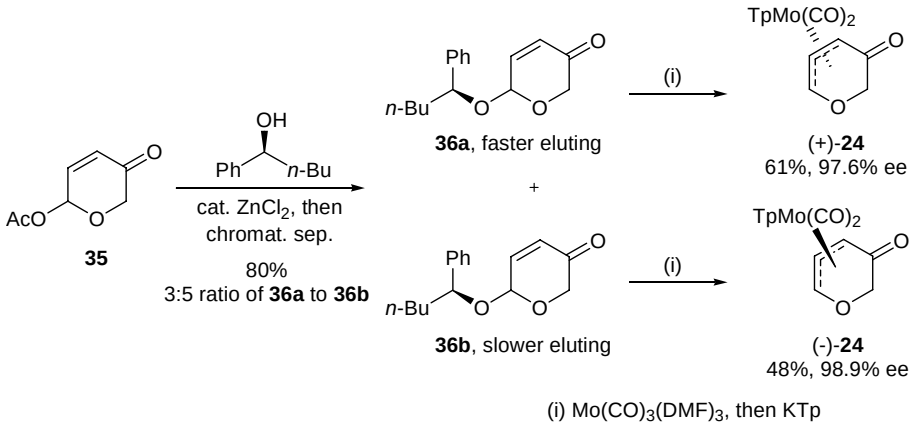


Figure 5: Simple three-operation sequence facilitates scale up

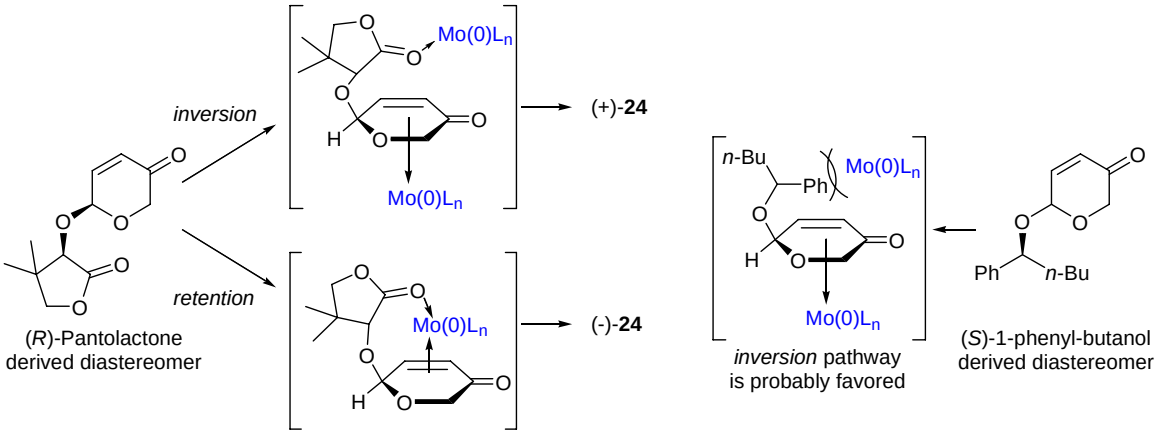
A further improvement to the synthesis of chiral, non-racemic oxopyranyl scaffolds was made by Bo Cheng. It was discovered that the crude acetate **35** could be resolved by metathesis of the anomeric acetate with commercially available (*S*)-(-)-1-phenyl-1-butanol with catalytic $ZnCl_2$ (**Scheme 23**). After chromatographic separation of the diastereomers, each could be metalated stereospecifically to provide both antipodes of **24** in good yields with high enantiopurity.

Scheme 23: Four step synthesis of chiral, non-racemic oxopyranyl scaffolds



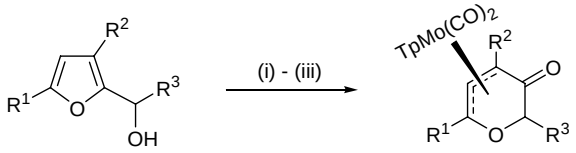
The enantiomeric excesses using this protocol were an improvement over those in a previous report in which (*R*)-pantolactone-derived pyranones were found to undergo oxidative addition with predominantly *inversion* of configuration to form both antipodes of **24** in 95% ee. While the relative stereochemistry of the two diastereomers formed in **Scheme 23** is unknown, it is assumed that the lack of coordinating functionality in the 1-phenyl-1-butanol auxiliary probably minimizes oxidative addition with retention of configuration. This would account for the slightly higher enantioselectivity observed in the metalation (**Scheme 24**).

Scheme 24: Origins of selectivity of oxidative addition,



The new protocol used to generate (±)-**24** was also used to generate 2-,[73] 4-,[74] and 6-methyl substituted scaffolds as well. Under identical conditions, each appropriately substituted furan afforded the corresponding pyranyl-complexes (**Table 1**).

Table 1: Synthesis of substituted scaffolds



(i) *m*-CPBA, CH_2Cl_2; (ii) Ac_2O, Et_3N, cat. DMAP; (iii) $Mo(CO)_3(DMF)_3$ then KTp

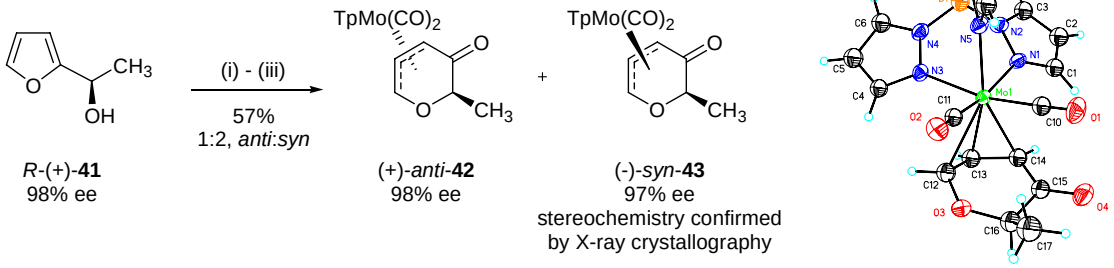
Entry	Substrate	R^1	R^2	R^3	Product	% Yield (3 steps)[a]
1	**37**	Me	H	H	**38**	32
2	**39**	H	Me	H	**40**	41
3	**41**	H	H	Me	*anti*-**42** *syn*-**43**	57 (1:2, *anti* :*syn*)[b]

a) isolated yield; b) separable by chromatography

While not investigated here, it is expected that after Achmatowicz rearrangement of **37** and **39**, resolution of the intermediate pyranones with a chiral alcohol in a manner similar to that shown in **Scheme 25**, would provide access to enantioenriched substituted pyranyl-complexes **38** and **40**. However, the rearrangement and metalation of 1-furan-2-yl-ethanol **41** afforded a 1:2 mixture of diastereomers (*anti* : *syn*), which were found to be separable by chromatography. Thus, the opportunity to synthesize enantioenriched 6-methyl substituted scaffolds from enantioenriched 1-furan-2-yl-ethanol was seized. Asymmetric reduction of acetylfuran following Noyori's protocol[75] provided the known compound (*R*)-(+)-**41** in 98% ee, which was metalated under the now standard conditions to provide (+)-*anti*-**42** in 98% ee, and (-)-*syn*-**43** in 97% ee. Enantiomeric excesses were determined by comparison of chiral HPLC data to that of the racemic compounds. The stereochemistry of (-)-*syn*-**43** was confirmed by X-ray crystallography.

[73] Synthesis of the 2-methyl substituted oxopyranyl scaffolds was investigated by Bo Cheng.
[74] Synthesis of the 4-methyl substituted oxopyranyl scaffolds was investigated by Wenyong Chen.
[75] Fujii, A.; Hashigucki, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521-2522.

Scheme 25: Synthesis of enantiopure *anti*-42 and *syn*-43



R-(+)-**41**
98% ee

(+)-*anti*-**42**
98% ee

(-)-*syn*-**43**
97% ee
stereochemistry confirmed
by X-ray crystallography

(i) *m*-CPBA, CH_2Cl_2; (ii) Ac_2O, Et_3N, cat. DMAP; (iii) $Mo(CO)_3(DMF)_3$ then KTp

Conclusions:

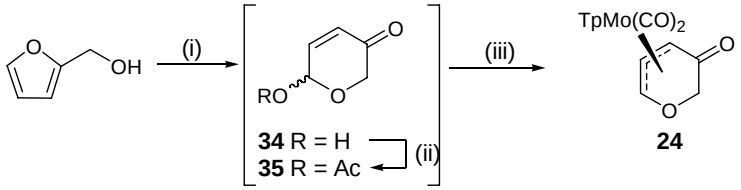
Many recent developments in organic methodology have demonstrated a number of highly selective and efficient methods for the construction of functionalized pyrans, particularly those bearing stereocenters at the 2- and 6-positions. The argument was made that while extremely useful for target-directed synthesis, some of these new methods rely heavily enough on substrate control or catalyst/substrate interactions to provide the degree of selectivity that is observed, that their utility in diversity-oriented synthesis may be compromised. A conceptual approach to diversity-oriented synthesis was presented by the enantiomeric scaffolding strategy. A streamlined route for the synthesis of the Liebeskind 5-oxopyranylmolybdenum scaffold **24** was developed, and the new protocol was applied to the racemic and enantiopure synthesis of substituted scaffolds.

Experimental Details:

GENERAL INFORMATION

Unless otherwise indicated, all ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 400 MHz (400 MHz ^{1}H, 100 MHz ^{13}C) or Varian Inova 600 MHz (600 MHz ^{1}H, 150 MHz ^{13}C) at room temperature in $CDCl_3$ with internal $CHCl_3$ as the reference (7.26 ppm for ^{1}H and 77.23 ppm for ^{13}C). IR spectra were recorded on ASI ReactIR® 1000 FT-IR spectrometer, equipped with a silicon probe or a Nicolet 380 FT-IR with a Smart Orbit diamond crystal plate. Peaks are reported (cm^{-1}) 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 ^{o}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. Analytical thin-layer chromatography (TLC) was carried out on commercial aluminum-backed silica gel plates (thickness: 200 μm) with fluorescent indicator (F-254). Visualization was accomplished by UV light or staining with 5% phosphomolybdic acid (PMA) in ethanol. Flash column chromatography was performed with 32-63 μm silica gel. Unless otherwise specified, all reactions were carried out under a nitrogen or argon atmosphere using solvents dried over molecular sieves or dispensed and used directly from a Seca Solvent System purchased from Glass Contour. Solvents were degassesed by bubbling through argon for 10 minutes All reaction flasks were flame or oven dried prior to use. The nomenclature for determining the chirality of the molybdenum complexes is straightforward.[76]

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



i) *m*-CPBA, CH_2Cl_2; ii) Ac_2O, Et_3N, cat. DMAP;
iii) $Mo(CO)_3(DMF)_3$ then KTp

(±)-6-Hydroxy-6*H*-pyran-3-one, 34

Furfuryl alcohol (4.90 g, 50.0 mmol, 1.0 equiv) was dissolved in 100 mL of dry dichloromethane and cooled to 0 °C. To this solution was added 77% *m*-CPBA (12.3 g, 55.0 mmol, 1.1 equiv) in two equal portions with 15 minutes in between. The reaction was stirred for an additional 60 minutes and TLC revealed that nearly complete consumption of starting material had occurred. The solid byproducts were filtered off by vacuum filtration (Note: *do not wash this solid with additional CH_2Cl_2*). The filtrate was placed in the refrigerator overnight and the additional solid that formed was filtered off by vacuum filtration (Note: *do not wash this solid with additional CH_2Cl_2*). While this solution of crude product was taken on directly, an analytical sample can be obtained by flash chromatography using 33% EtOAc in hexanes to give the pure product **34** as a yellow oil (R_f = 0.15, 33% EtOAc in hexanes) which solidifies at low temperature. Spectroscopic information was in agreement with published data.

(±)-6-Acetoxy-6*H*-pyran-3-one, 35

The solution of crude material from above was cooled to 0 °C. To the reaction was added acetic anhydride (7.14 mL, 75.0 mmol, 1.5 equiv), and 4-(dimethylamino)-pyridine (610 mg, 5.00 mmol, 0.10 equiv), followed by triethylamine dropwise (14.04 mL, 100 mmol, 2.0 equiv). The reaction was stirred for 5 minutes, after which TLC showed complete consumption of starting material, and then quenched with 50 mL saturated $NaHCO_3$ solution. The organic layer was then washed with a 50/50 mixture of saturated $NaHCO_3$ and H_2O (2 x 150 mL). The combined aqueous layers were then extracted with CH_2Cl_2 (2 x 75 mL). Finally, the combined organic

layers were washed with 100 mL of H_2O, then dried on $MgSO_4$, and concentrated under reduced pressure to give **35** as a dark orange oil. This product was used in the next step without further purification (R_f = 0.37, 33% EtOAc in hexanes). Spectroscopic information was in agreement with published data.

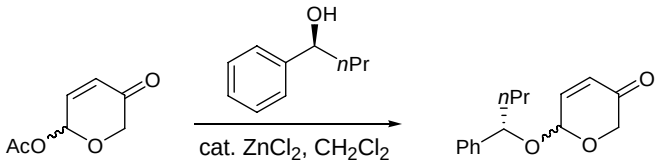
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η^3-2,3,4)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]-molybdenum, 24

The crude product **35** from above was placed under vacuum for approximately 30 minutes while a clean, flame-dried Schlenk flask was charged with $Mo(CO)_3(DMF)_3$ (21.9 g, 55.0 mmol, 1.1 equiv) under argon. The molybdenum reagent was dissolved in 100 mL of dry, degassed CH_2Cl_2 at room temperature, and a solution of **35** in 50 mL of dry, degassed CH_2Cl_2 was added using an argon-flushed syringe. The reaction mixture quickly turned from dark green/black to dark red/black. The mixture was stirred for 2.5 hours at room temperature and then potassium hydridotris(1-pyrazolyl)borate (KTp)[77] (14.5 g, 57.5 mmol, 1.15 equiv) was added in one portion and stirred for 1 hour. The reaction mixture was added directly to a short plug of silica gel (5x15 cm) and eluted with 50% EtOAc in hexanes to collect the orange product band, which was concentrated to reveal an orange/brown solid. This material was purified by trituration with ether to give the majority of pure product **24** as an orange solid. Flash chromatography on silica gel of the condensed trituration solution fractions in 25% EtOAc in hexanes gave some additional product (13.6 g total, 59% over 3 steps).

24: TLC: R_f = 0.47 (50% ethyl acetate in hexanes). IR (cm^{-1}): 2489 (w), 1954 (vs), 1864 (vs), 1654 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.50 (d, *J* = 2.2 Hz, 1H), 7.92 (d, *J* = 1.7 Hz, 1H), 7.67 (d, *J* = 2.2 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.40 (dd, *J* = 4.4, 2.2 Hz, 1H), 6.30 (t, *J* = 1.7 Hz, 1H), 6.26 (t, *J* = 2.2 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 4.80 (dd, *J* = 6.1, 2.2 Hz, 1H), 4.17 (dd, *J* = 6.1, 4.4 Hz, 1H), 3.68 (d, *J* = 18.2 Hz, 1H),

[77] Mole Scale Preparation: Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170-3177.

3.44 (d, J = 18.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 HMz): δ 224.8, 223.7, 193.4, 147.6, 143.8, 141.8, 136.5 (2), 134.9, 108.7, 106.5, 106.2, 106.0 69.2, 66.7, 65.3. Anal Calcd for $C_{16}H_{15}BMoN_6O_4$: C, 41.59; H, 3.27; N, 18.19. Found: C, 41.44; H, 3.35; N, 18.02.



35 **36a-b**

[(*S*)-1-Phenyl-butoxy]-6*H*-pyran-3-one, 36a

and

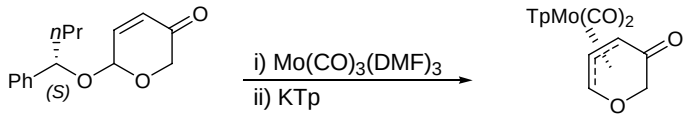
[(*S*)-1-Phenyl-butoxy]-6*H*-pyran-3-one, 36b

To a 250-mL flask charged with 2-acetoxy-5-oxo-5,6-dihydro-2*H*-pyran, **35** (4.0 g, 25.6 mmol, 1 equiv) and (*S*)-(-)-1-phenyl-1-butanol (98% ee, 3.85 g, 25.6 mmol, 1 equiv) in 30 mL CH_2Cl_2 under argon was added $ZnCl_2$ (1.0 M in Et_2O, 7.7 mL, 7.7 mmol, 0.3 equiv). The solution was stirred at room temperature for 67 hours, after which TLC indicated no starting material was left. The mixture was transferred into a separatory funnel containing 50 mL of H_2O and 50 mL of CH_2Cl_2. The organic layer was collected, washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated. The crude material was further purified by column chromatography (10% EtOAc in hexanes) to afford the less polar diastereomer **36a** (1.8 g, 29%), and more polar diastereomer **36b** (3.2 g, 51%) as colorless liquids.

36a: TLC: R_f = 0.66 (20% EtOAc in hexanes). $[\alpha]_D^{20}$ -90.1 (*c* 0.754, CH_2Cl_2). IR (cm^{-1}): 2934 (m), 1702 (s), 1455 (s), 1397(s), 1262(s). ^{1}H NMR (400 MHz, $CDCl_3$): 7.34 (m, 5H), 6.76 (dd, J = 10.2 Hz, 3.4 Hz, 1H), 6.12 (d, J = 10.0 Hz, 1H), 5.00 (d, J = 3.2 Hz, 1H), 4.76 (dd, J = 8.0 Hz, 5.6 Hz, 1H), 4.56 (d, J = 16.8 Hz, 1H), 4.12 (d, J = 16.8 Hz, 1H), 1.88 (m, 1H), 1.66 (m, 1H), 1.47 (m, 1H), 1.32 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): 194.9,

144.8, 141.4, 128.6, 128.6, 128.0, 127.6, 126.9, 126.9, 89.9, 79.2, 66.4, 40.1, 19.3, 13.8. HRMS (FAB) Calcd for $C_{15}H_{19}O_3$ ([M + H]$^+$): 247.1329. Found: 247.1326.

36b: TLC: R_f = 0.57 (20% EtOAc in hexanes). $[\alpha]_D^{20}$ -113.3 (*c* 0.444, CH_2Cl_2). IR (cm^{-1}): 2934 (m), 1702 (s), 1455 (s), 1393(s), 1262(s). ^{1}H NMR (400 MHz, $CDCl_3$): 7.30 (m, 5H), 6.93 (dd, *J* = 10.2 Hz, 3.4 Hz, 1H), 6.12 (d, *J* = 10.4 Hz, 1H), 5.39 (d, *J* = 3.2 Hz, 1H), 4.59 (t, *J* = 6.8 Hz, 1H), 3.95 (d, *J* = 17.2 Hz, 1H), 3.72 (d, *J* = 17.2 Hz, 1H), 1.88 (m, 1H), 1.72 (m, 1H), 1.32 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 195.0, 144.1, 142.4, 128.3, 128.3, 127.7, 127.6, 126.4(2), 93.4, 82.3, 66.1, 39.3, 18.9, 13.9. HRMS (ESI) Calcd for $C_{15}H_{19}O_3$ [M + H]$^+$: 247.1329. Found: 247.1336.



Fast Eluting Diastereomer-**36a**

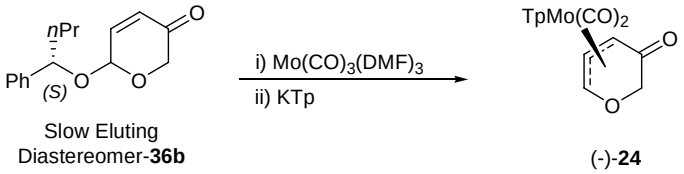
(+)-**24**

(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*)-(η-2,3,4)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (+)-**24**

To a Schlenk flask charged with a solution of $Mo(CO)_3(DMF)_3$ (7.52 g, 18.80 mmol, 2 equiv) in 40 mL of degassed dry CH_2Cl_2 under argon at -40 ^{o}C was slowly added a solution of **36a** (2.32 g, 9.42 mmol, 1 equiv) in 10 mL of degassed CH_2Cl_2 . The reaction mixture was allowed to warm up to -20 ^{o}C over 1 hour, and then warmed to -10 ^{o}C over 30 min. The reaction was warmed to 0 ^{o}C and stirred for 2 hours before allowing the reaction to warm to room temperature over 30 min. Solid potassium hydridotris(1-pyrazolyl)borate (KTp) (5.22 g, 20.70 mmol, 2.2 equiv) was added in one portion and the reaction was stirred for 1 hour at room temperature. The solution was then passed through a pad of silica gel, eluting with EtOAc. Solvents were completely removed on a rotary evaporator, and the residue was further purified by column chromatography (50% EtOAc in hexanes) to afford a yellow solid (+)-**24** (2.1 g, 48%) in 98.9% ee. *This compound tends to crystallize as a racemate, and therefore slow crystallization in hexanes/CH_2Cl_2 afforded the*

product in >99% ee when the first few crystals that formed were removed, and the filtrate was collected.

(+)-**24:** $[\alpha]_D^{20}$ +447.8 (*c* 0.090, CH_2Cl_2). HPLC: CHIRALPAK AS-RH column, CH_3CN : H_2O = 55 : 45, 1.0 mL/min., λ = 254 nm, t_r = 11.43 min, >99% e.e.



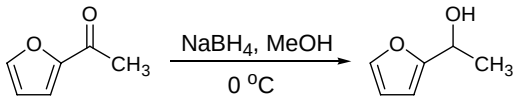
Slow Eluting Diastereomer-**36b**

(-)-**24**

(–)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-η-(2,3,4)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (–)-**24**

To a Schlenk flask charged with a solution of $Mo(CO)_3(DMF)_3$ (4.63 g, 11.6 mmol, 2 equiv) in 30 mL degassed, dry CH_2Cl_2 under argon at -40 ^oC was slowly added a solution of **36b** (1.43 g, 5.80 mmol, 1 equiv) in 10 mL degassed CH_2Cl_2 . The reaction mixture was allowed to warm up to -20 ^oC over 1 hour, and then warmed to 0 ^oC over 30 min. After the reaction was slowly warmed to room temperature over 30 min, solid potassium hydridotris(1-pyrazolyl)borate (KTp) (3.22 g, 12.77 mmol, 2.2 equiv) was added in one portion. After stirring for 1 hour at room temperature, the solution was passed through a pad of silica gel, eluting with EtOAc. The solvents were completely removed on a rotary evaporator, and the residue was further purified by column chromatography (50% EtOAc in hexanes) to afford a yellow solid product (-)-**24** (1.64 g, 61%) in 97.6% ee. *This compound tends to crystallize as a racemate, and therefore slow crystallization in hexanes/CH_2Cl_2 afforded the product in >99% ee when the first few crystals that formed were removed, and the filtrate was collected.*

(-)-**24:** $[\alpha]_D^{20}$ -525.8 (*c* 0.095, CH_2Cl_2). HPLC: CHIRALPAK AS-RH column, CH_3CN : H_2O = 55 : 45, 1.0 mL/min., λ = 254 nm, t_r = 14.62 min, >99% e.e.

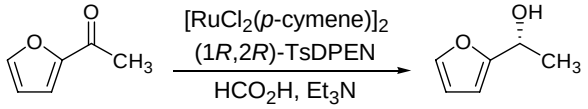


(±)-**41**

(±)-1-Furan-2-yl-ethanol, 41

Acetylfuran (20.0 g, 182 mmol, 1.0 equiv) was dissolved in 200 mL of methanol, and cooled to 0 °C. Solid sodium borohydride (7.56 g, 200 mmol, 1.1 equiv) was added in small portions over 10 minutes. When addition was complete, the reaction was stirred for one hour until TLC revealed that all starting material was consumed and a new spot had formed. The reaction mixture was poured into a separatory funnel containing 150 mL of H_2O and 100 mL of ethyl acetate. These layers were separated and the aqueous phase was extracted with EtOAc (4 x 125 mL). The combined organic layers were then washed with brine, and the brine layer was extracted with EtOAc (7 x 125 mL). All organic layers were concentrated to give pure **41** as a yellow oil (18.4 g, 90%).

41: TLC: R_f = 0.42 (33% EtOAc in hexanes). IR (cm^{-1}): 3336 (bm), 2980 (w), 1148 (s), 1066 (s), 1008 (s) 735 (s). ^{1}H NMR [$CDCl_3$, 400 MHz]: δ 7.37 (d, *J* = 1.9 Hz, 1H), 6.32 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 4.88 (app pentet, *J* = 6.0 Hz, 1H), 1.99 (br s, 1H), 1.54 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR [$CDCl_3$, 100 MHz]: δ 157.8, 142.1, 110.3, 105.3, 63.8, 21.5.



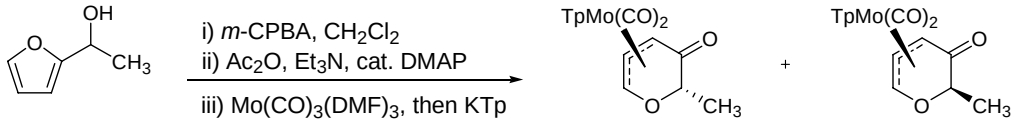
R-(+)-**41**

(*R*)-1-Furan-2-yl-ethanol, *R*-(+)-41

Acetylfuran (1.65 g, 15.0 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (45.9 mg, 0.749 mmol, 0.5 mol%), and (1*R*,2*R*)-*N*-(*p*-tolylsulfonyl)-1,2-diphenylethylenediamine (TsDPEN) (54.9 mg, 0.150 mmol, 0.01 equiv) were added to a 50 mL round bottom flask and cooled to 0 °C. A 5:2 mixture of HCO_2H and Et_3N was added and the reaction was stirred at 0 °C for 15 minutes, and then warmed to room temperature and stirred overnight (24 hours). The reaction was then diluted with

20 mL water and extracted with ethyl acetate (3 x 25 mL). Organic layers were washed with saturated $NaHCO_3$ solution (20 mL) and brine (20 mL). The organic layers were dried on $MgSO_4$ and filtered. Concentration of the filtrate gave the crude product, which was purified by flash chromatography on silica gel (25% EtOAc in hexanes) to give the pure product *R*-(+)-**41** as a clear oil (1.34 g, 80%, 98% ee).

R-(+)-**41**: $[\alpha]_D^{20}$ +17.4 (*c* 0.510, CH_2Cl_2). HPLC: CHIRALPAK AD-RH column, CH_3CN : H_2O = 3 : 97, 0.4 mL/min., λ = 230 nm, t_r = 39.7 min. Enantiomer: t_r = 36.8 min



(±)-**41** (±)-*anti*-**42** (±)-*syn*-**43**

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-η-(2,3,4)-5-oxo-6-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *anti*-**42**

and

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)-5-oxo-6-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *syn*-**43**

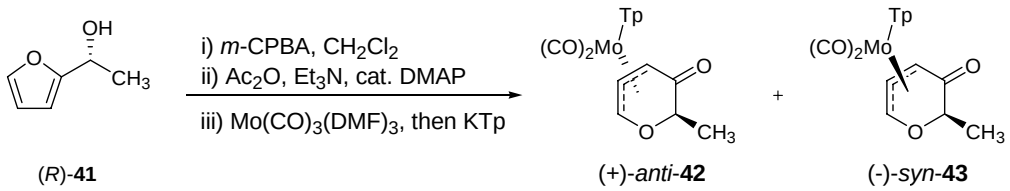
1-Furan-2-yl-ethanol **41** (1.68 g, 15.0 mmol, 1.0 equiv) was dissolved in 30 mL of dry, dichloromethane and cooled to 0 °C. To this solution was added 77% *m*-CPBA (3.70 g, 16.5 mmol, 1.1 equiv) in two equal portions with 15 minutes in between. The reaction was stirred for an additional 65 minutes and TLC revealed that complete consumption of starting material had occurred. The reaction was warmed to room temperature and potassium fluoride (1.31 g, 22.5 mmol, 1.5 equiv) was added in one portion and the reaction was stirred vigorously for 80 minutes. The solid byproducts were removed by vacuum filtration, and the filtrate was concentrated under reduced pressure to give the crude product as a yellow oil (R_f = 0.22, 33% EtOAc in hexanes). This material was redissolved in 30 mL of dry, degassed dichloromethane and cooled to 0 °C. To the reaction was added acetic anhydride (2.14 mL, 22.5 mmol, 1.5 equiv),

and 4-(dimethylamino)-pyridine (183 mg, 1.50 mmol, 0.10 equiv), followed by triethylamine dropwise (4.21 mL, 30.0 mmol, 2.0 equiv). The reaction was stirred for 5 minutes and then quenched with 25 mL saturated $NaHCO_3$ solution. The organic layer was washed with a 50/50 mixture of saturated $NaHCO_3$ and H_2O (3 x 100 mL). The aqueous layers were then extracted with CH_2Cl_2 (4 x 50 mL). Finally the combined organic layers were washed with 100 mL of H_20, then dried on $MgSO_4$, and concentrated under reduced pressure to give a dark orange oil. This mixture of diastereomers was used in the next step without further purification (R_f = 0.35 and 0.42, 33% EtOAc in hexanes). The crude product was placed under vacuum for approximately 30 minutes while a clean, flame-dried Schlenk flask was charged with $Mo(CO)_3(DMF)_3$ (8.37 g, 21.0 mmol, 1.4 equiv) under argon. The molybdenum reagent was dissolved, stirring in 25 mL of dry, degassed CH_2Cl_2 at room temperature, and to this was added a solution of the crude allylic acetate dissolved in 10 mL of dry, degassed CH_2Cl_2 using an argon-flushed syringe. The reaction mixture quickly turned from dark green/black to dark red/black. The mixture was stirred for 3 hours at room temperature and then potassium hydridotris(1-pyrazolyl)borate (KTp) (5.66 g, 22.5 mmol, 1.5 equiv) was added in one portion and stirred for 1 hour more. The reaction mixture was added directly to a short plug of silica gel (3 x 10 cm) and eluted with 50% EtOAc in hexanes. Pure product was obtained by flash chromatography (25% EtOAc in hexanes) as a 2:1 (*syn*:*anti*) mixture of diastereomers (3.29 g, 46%). The two diastereomers were separated by gravity chromatography on silica gel eluting with 10% ethyl acetate in hexanes. The *anti*-isomer eluted first, followed by the *syn*-isomer.

anti-**42**: TLC: R_f = 0.18 (25% EtOAc in hexanes). IR (cm^{-1}): 2495 (w), 1955 (s), 1869 (s), 1653 (m). ^1H NMR [$CDCl_3$, 400 MHz]: δ 8.49 (d, *J* = 1.9 Hz, 1H), 7.91 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 1.9 Hz, 1H), 7.38 (dd, *J* = 4.8, 2.2 Hz, 1H). 6.26 (t, *J* = 2.2 Hz, 1H), 6.24 (t, *J* = 2.2 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H), 4.72 (dd, *J* = 6.4, 2.2 Hz, 1H), 4.14 (dd, *J* = 6.0, 4.4 Hz, 1H), 3.52 (q, *J* = 7.0 Hz, 1H), 1.31 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR [$CDCl_3$, 100 MHz]: δ 225.4, 224.1, 196.7, 147.5, 143.7,

141.7, 136.4, 134.8, 108.2, 106.4, 106.2, 105.9, 73.3, 67.9, 64.9, 18.4. HRMS (ESI) Calcd for $C_{17}H_{18}BMoN_6O_4^+$ $[M + H]^+$: 479.05312. Found: 479.05169.

syn-**43**: TLC: R_f = 0.15 (25% EtOAc in hexanes). IR (cm^{-1}): 2486 (w), 1956 (s), 1870 (s), 1658 (m). ^1H NMR [$CDCl_3$, 400 MHz]: δ 8.50 (d, *J* = 1.9 Hz, 1H), 7.95 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.55 (dd, *J* = 4.8, 2.2 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 6.26 (t, *J* = 2.2 Hz, 1H), 6.24 (t, *J* = 1.9 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 4.87 (dd, *J* = 6.0, 2.2 Hz, 1H), 4.11 (dd, *J* = 6.0, 4.8 Hz, 1H), 3.64 (q, *J* = 6.7 Hz, 1H), 1.19 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR [$CDCl_3$, 100 MHz]: δ 226.5, 223.9, 197.8, 147.5, 143.4, 141.7, 136.5 (2), 134.8, 110.4, 106.4, 106.1, 105.8, 73.5, 66.9, 65.7, 16.2. HRMS (ESI) Calcd for $C_{17}H_{18}BMoN_6O_4^+$ $[M + H]^+$: 479.05312. Found: 479.05163.



(*R*)-**41** (+)-*anti*-**42** (-)-*syn*-**43**

(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,6*R*)-η-(2,3,4)-5-oxo-6-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (+)-*anti*-**42,**

and

(-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)-5-oxo-6-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)-*syn*-**43**

(*R*)-1-Furan-2-yl-ethanol (*R*)-**41** (98% ee, 571 mg, 5.10 mmol, 1.0 equiv) was dissolved in 10 mL of dry, degassed dichloromethane and cooled to 0 °C. To this solution was added 77% *m*-CPBA (1.26 g, 5.61 mmol, 1.1 equiv) in two equal portions with 15 minutes in between. The reaction was stirred for an additional 65 minutes and TLC revealed that complete consumption of starting material had occurred. The reaction was cooled to -78 °C, and stirred for 5 minutes. The solid byproducts were removed by vacuum filtration, and the filtrate was concentrated under reduced pressure to give the crude product as a yellow oil (R_f = 0.22, 33% EtOAc in hexanes).

This material was redissolved in 10 mL of dry, degassed dichloromethane and cooled to 0 ^{o}C. To the reaction was added acetic anhydride (0.73 mL, 7.65 mmol, 1.5 equiv), and 4-(dimethylamino)-pyridine (62 mg, 0.51 mmol, 0.10 equiv), followed by triethylamine dropwise (1.43 mL, 10.2 mmol, 2.0 equiv). The reaction was stirred for 5 minutes and then quenched with 25 mL saturated $NaHCO_3$ solution. The organic layer was diluted with 20 mL CH_2Cl_2 and washed with a 50/50 mixture of saturated $NaHCO_3$ and H_2O (2 x 50 mL). The aqueous layers were then extracted with CH_2Cl_2 (2 x 25 mL). Finally the combined organic layers were washed with 25 mL of H_20, then dried on $MgSO_4$, and concentrated under reduced pressure to give a dark orange oil. This mixture of diastereomers was used in the next step without further purification (R_f = 0.35 and 0.42, 33% EtOAc in hexanes). The crude product was placed under vacuum for approximately 30 minutes while a clean, flame-dried Schlenk flask was charged with $Mo(CO)_3(DMF)_3$ (2.85 g, 7.14 mmol, 1.4 equiv) under argon. The molybdenum reagent was dissolved, stirring in 15 mL of dry, degassed CH_2Cl_2 at room temperature, and to this was added a solution of the crude allylic acetate dissolved in 10 mL of dry, degassed CH_2Cl_2 using an argon-flushed syringe. The reaction mixture quickly turned from dark green/black to dark red/black. The mixture was stirred for 3 hours at room temperature and then potassium hydridotris(1-pyrazolyl)borate (KTp) (1.93 g, 7.65 mmol, 1.5 equiv) was added in one portion and stirred for 1 hour more. The reaction mixture was added directly to a short plug of silica gel (3 x 10 cm) and eluted with 50% EtOAc in hexanes. Pure product was obtained by flash chromatography (25% EtOAc in hexanes) as a 1:2 (*anti*:*syn*) mixture of diastereomers (1.39 g, 57%). The two enantio-enriched diastereomers were separated by gravity chromatography on silica gel eluting with 10% ethyl acetate in hexanes. The *anti*-isomer eluted first, followed by the *syn*-isomer.

(+)-*anti*-**42**: $[\alpha]_D^{20}$ +507 (*c* 0.510, CH_2Cl_2). HPLC: CHIRALPAK OJ-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1% TFA) 0-5 min (20%), 5-15 min (30%), 15-20 min (40%), 20-30 min (50%); 1.0 mL/min., λ = 254 nm, t_r = 26.93 min, 98% e.e. Enantiomer: t_r = 22.33 min

(-)-*syn*-**43**: $[\alpha]_D^{20}$ -606 (*c* 0.165, CH_2Cl_2). HPLC: CHIRALPAK OJ-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1% TFA) 0-5 min (20%), 5-15 min (30%), 15-20 min (40%), 20-30 min (50%); 1.0 mL/min., λ = 254 nm, t_r = 20.87 min, >97% e.e. Enantiomer: t_r = 24.88 min. X-Ray diffraction study is detailed below.

X-Ray Crystallographic Study:

Crystals of enantiopure (-)-*syn*-**43** were obtained by diffusion recrystallization from CH_2Cl_2 and hexanes. A suitable crystal of (-)-*syn*-**43** 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 APEX II CCD sealed tube diffractometer with graphite monochromated MoK_α (0.71073 Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.5° frame widths. Data collection, indexing and initial cell refinements were all carried out using APEX II[78] software. Frame integration and final cell refinements were done using SAINT[79] software. The final cell parameters were determined from least-squares refinement on 9842 reflections. .

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).[80] 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 for X-ray Crystallography*.[81] Structure solution, refinement, graphics and generation of publication

[78] APEX II, **2005**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[79] SAINT Version 6.45A, **2003**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[80] SHELXTL V6.12, **2002**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[81] 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).

materials were performed by using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Table 1.

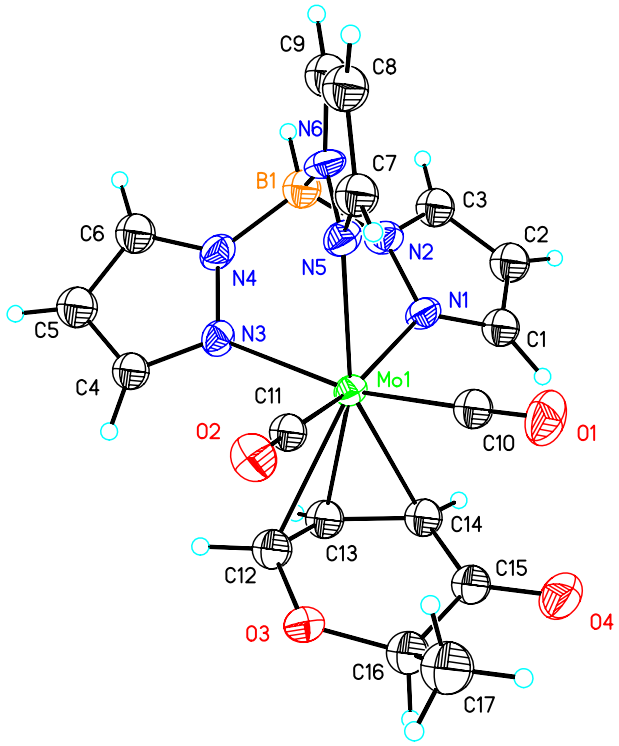


Figure 6: ORTEP of complex (-)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)-5-oxo-6-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)-*syn*-43

Table 2: Crystal data and structure refinement for (-)-*syn*-43

Identification code	(-)-*syn*-**43**	
Empirical formula	C17.25 H17.50 B Cl0.50 Mo N6 O4	
Formula weight	497.35	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.9826(4) Å	α= 90°.
	b = 10.7528(4) Å	β= 92.992(2)°.
	c = 34.9644(12) Å	γ = 90°.
Volume	4123.4(3) Å^3	
Z	8	

Density (calculated)	1.602 Mg/m^3
Absorption coefficient	0.738 mm^{-1}
F(000)	2004
Crystal size	0.35 x 0.35 x 0.15 mm^3
Theta range for data collection	1.86 to 34.92°.
Index ranges	-17<=h<=17, -17<=k<=16, -56<=l<=56
Reflections collected	73316
Independent reflections	32017 [R(int) = 0.0503]
Completeness to theta = 34.92°	99.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8974 and 0.7823
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	32017 / 1 / 1103
Goodness-of-fit on F^2	1.145
Final R indices [I>2sigma(I)]	R1 = 0.0609, wR2 = 0.1492
R indices (all data)	R1 = 0.0705, wR2 = 0.1547
Absolute structure parameter	0.01(3)
Largest diff. peak and hole	2.683 and -1.178 $e.Å^{-3}$

Table 3: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (-)-*syn*-43. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	10643(5)	1093(6)	2060(2)	33(1)
C(1)	9229(4)	3115(5)	2736(1)	32(1)
C(2)	10219(5)	2733(6)	2976(1)	39(1)
C(3)	10826(5)	1860(6)	2759(1)	37(1)
C(4)	7954(5)	-449(4)	1654(1)	30(1)
C(5)	8740(5)	-1466(5)	1655(1)	37(1)
C(6)	9830(5)	-1013(5)	1816(1)	36(1)
C(7)	10168(4)	3461(5)	1330(1)	33(1)
C(8)	11400(5)	3257(6)	1281(2)	41(1)
C(9)	11757(4)	2395(6)	1549(2)	37(1)
C(10)	7895(4)	4408(5)	1841(1)	29(1)
C(11)	7309(4)	2799(4)	1339(1)	25(1)
C(12)	5906(4)	1830(5)	1760(2)	33(1)
C(13)	6376(4)	1803(5)	2140(2)	34(1)
C(14)	6547(4)	2978(6)	2313(1)	33(1)
C(15)	5783(4)	4024(5)	2183(1)	32(1)
C(16)	4869(4)	3804(6)	1849(2)	35(1)

C(17)	4801(6)	4880(7)	1573(2)	50(1)
Mo(1)	7999(1)	2578(1)	1859(1)	20(1)
N(1)	9229(3)	2514(4)	2401(1)	26(1)
N(2)	10222(3)	1741(4)	2419(1)	30(1)
N(3)	8520(3)	542(4)	1812(1)	25(1)
N(4)	9679(3)	172(4)	1909(1)	28(1)
N(5)	9792(3)	2740(4)	1614(1)	26(1)
N(6)	10782(3)	2086(4)	1748(1)	30(1)
O(1)	7863(4)	5476(4)	1807(1)	43(1)
O(2)	6927(3)	3011(4)	1030(1)	34(1)
O(3)	5043(3)	2700(4)	1630(1)	33(1)
O(4)	5780(4)	5033(5)	2348(1)	46(1)
B(1B)	865(5)	2670(5)	77(1)	28(1)
C(1B)	3710(4)	3428(5)	600(1)	30(1)
C(2B)	3274(5)	4634(5)	548(2)	37(1)
C(3B)	2202(5)	4500(5)	337(1)	35(1)
C(4B)	2187(4)	403(5)	-551(1)	32(1)
C(5B)	1505(5)	1059(6)	-830(1)	39(1)
C(6B)	934(5)	1961(5)	-633(1)	36(1)
C(7B)	266(4)	326(5)	789(1)	30(1)
C(8B)	-893(4)	861(6)	772(1)	37(1)
C(9B)	-825(4)	1781(5)	505(1)	33(1)
C(10B)	3249(4)	198(4)	948(1)	30(1)
C(11B)	2387(4)	-1269(4)	438(1)	27(1)
C(12B)	4122(5)	-936(5)	65(1)	35(1)
C(13B)	4537(4)	295(5)	70(1)	36(1)
C(14B)	4978(4)	711(5)	427(2)	35(1)
C(15B)	5535(4)	-218(5)	704(2)	35(1)
C(16B)	5575(4)	-1563(5)	569(2)	35(1)
C(17B)	5427(6)	-2444(6)	899(2)	45(1)
Mo(1B)	2859(1)	477(1)	397(1)	22(1)
N(1B)	2940(3)	2584(4)	430(1)	26(1)
N(2B)	2005(3)	3293(4)	268(1)	27(1)
N(3B)	2031(3)	901(4)	-202(1)	27(1)
N(4B)	1252(4)	1869(4)	-261(1)	29(1)
N(5B)	993(3)	881(4)	544(1)	25(1)

N(6B)	304(3)	1798(4)	370(1)	29(1)
O(1B)	3413(4)	2(5)	1266(1)	47(1)
O(2B)	2098(4)	-2285(4)	480(1)	40(1)
O(3B)	4680(3)	-1901(4)	269(1)	37(1)
O(4B)	6062(4)	89(5)	1000(1)	50(1)
B(1C)	4472(5)	9986(6)	2934(2)	33(1)
C(1C)	7282(5)	11359(5)	3324(1)	31(1)
C(2C)	6535(5)	12393(5)	3364(2)	38(1)
C(3C)	5399(5)	12032(5)	3201(1)	36(1)
C(4C)	5698(5)	8002(5)	2215(1)	34(1)
C(5C)	4729(5)	8471(6)	1988(1)	42(1)
C(6C)	4192(5)	9317(6)	2219(2)	39(1)
C(7C)	4996(4)	7638(5)	3664(1)	32(1)
C(8C)	3794(4)	7883(6)	3738(2)	39(1)
C(9C)	3427(4)	8768(5)	3470(2)	37(1)
C(10C)	7893(3)	8248(4)	3595(1)	25(1)
C(11C)	7096(4)	6555(5)	3144(1)	28(1)
C(12C)	8336(4)	7318(5)	2651(1)	32(1)
C(13C)	8407(4)	8634(5)	2637(1)	32(1)
C(14C)	8973(4)	9167(5)	2963(1)	29(1)
C(15C)	9920(3)	8469(5)	3177(1)	28(1)
C(16C)	10209(4)	7183(5)	3035(1)	30(1)
C(17C)	10610(6)	6290(6)	3350(2)	51(2)
Mo(1C)	7058(1)	8370(1)	3084(1)	19(1)
N(1C)	6668(3)	10436(4)	3142(1)	27(1)
N(2C)	5507(3)	10867(4)	3067(1)	30(1)
N(3C)	5747(3)	8508(4)	2563(1)	26(1)
N(4C)	4790(3)	9314(4)	2565(1)	30(1)
N(5C)	5339(3)	8316(4)	3367(1)	25(1)
N(6C)	4356(3)	9011(4)	3248(1)	30(1)
O(1C)	8333(3)	8127(4)	3900(1)	38(1)
O(2C)	7127(4)	5513(4)	3212(1)	39(1)
O(3C)	9257(3)	6584(4)	2810(1)	36(1)
O(4C)	10557(3)	8925(4)	3440(1)	41(1)
B(1D)	4032(5)	-1341(5)	4904(2)	34(1)
C(1D)	2503(5)	990(6)	5449(1)	40(1)

C(2D)	3098(6)	377(7)	5756(1)	46(1)
C(3D)	3749(6)	-546(7)	5596(1)	45(1)
C(4D)	1290(4)	-2160(4)	4344(1)	29(1)
C(5D)	1638(5)	-3361(5)	4447(2)	36(1)
C(6D)	2709(5)	-3213(5)	4668(1)	36(1)
C(7D)	4914(4)	937(5)	4202(1)	35(1)
C(8D)	6040(5)	374(7)	4257(2)	47(1)
C(9D)	5881(5)	-536(6)	4524(2)	42(1)
C(10D)	2589(5)	2587(5)	4503(1)	35(1)
C(11D)	2148(4)	1198(4)	3949(1)	29(1)
C(12D)	168(4)	680(5)	4162(1)	32(1)
C(13D)	155(4)	549(5)	4558(1)	35(1)
C(14D)	432(5)	1642(6)	4766(1)	36(1)
C(15D)	116(5)	2858(5)	4594(2)	38(1)
C(16D)	-555(5)	2788(5)	4199(1)	35(1)
C(17D)	-364(6)	3936(6)	3962(2)	45(1)
Mo(1D)	2160(1)	810(1)	4491(1)	24(1)
N(1D)	2740(4)	459(4)	5119(1)	33(1)
N(2D)	3532(4)	-502(4)	5215(1)	35(1)
N(3D)	2093(3)	-1303(4)	4489(1)	26(1)
N(4D)	2974(4)	-1991(4)	4687(1)	31(1)
N(5D)	4096(4)	412(4)	4428(1)	30(1)
N(6D)	4713(4)	-511(4)	4626(1)	33(1)
O(1D)	2890(5)	3616(4)	4494(2)	55(1)
O(2D)	2222(3)	1519(4)	3631(1)	38(1)
O(3D)	-256(3)	1732(4)	3973(1)	35(1)
O(4D)	218(5)	3863(5)	4751(1)	57(1)
C(1S)	2079(8)	5958(10)	1831(3)	34(2)
C(2S)	3955(8)	5182(8)	3083(3)	29(2)
Cl(1)	738(2)	5906(3)	2075(1)	40(1)
Cl(2)	1913(3)	6711(3)	1393(1)	42(1)
Cl(3)	2988(2)	4407(4)	2759(1)	56(1)
Cl(4)	3799(3)	4627(2)	3553(1)	37(1)

Table 4: Bond lengths [Å] and angles [°] for (-)-*syn*-43

B(1)-N(4)	1.523(7)	C(13)-C(14)	1.409(8)
B(1)-N(2)	1.530(7)	C(13)-Mo(1)	2.242(4)
B(1)-N(6)	1.541(7)	C(13)-H(13)	1.0000
B(1)-H(1)	1.0000	C(14)-C(15)	1.462(7)
C(1)-N(1)	1.338(6)	C(14)-Mo(1)	2.349(4)
C(1)-C(2)	1.401(7)	C(14)-H(14)	1.0000
C(1)-H(1)	0.9500	C(15)-O(4)	1.229(7)
C(2)-C(3)	1.399(8)	C(15)-C(16)	1.517(7)
C(2)-H(2)	0.9500	C(16)-O(3)	1.431(6)
C(3)-N(2)	1.335(6)	C(16)-C(17)	1.506(8)
C(3)-H(3)	0.9500	C(16)-H(16)	1.0000
C(4)-N(3)	1.339(6)	C(17)-H(17A)	0.9800
C(4)-C(5)	1.393(7)	C(17)-H(17B)	0.9800
C(4)-H(4)	0.9500	C(17)-H(17C)	0.9800
C(5)-C(6)	1.384(8)	Mo(1)-N(5)	2.194(3)
C(5)-H(5)	0.9500	Mo(1)-N(1)	2.269(3)
C(6)-N(4)	1.328(6)	Mo(1)-N(3)	2.271(4)
C(6)-H(6)	0.9500	N(1)-N(2)	1.370(5)
C(7)-N(5)	1.343(6)	N(3)-N(4)	1.360(5)
C(7)-C(8)	1.390(7)	N(5)-N(6)	1.358(5)
C(7)-H(7)	0.9500	B(1B)-N(6B)	1.540(6)
C(8)-C(9)	1.360(9)	B(1B)-N(4B)	1.540(6)
C(8)-H(8)	0.9500	B(1B)-N(2B)	1.541(6)
C(9)-N(6)	1.348(6)	B(1B)-H(1B)	1.0000
C(9)-H(9)	0.9500	C(1B)-N(1B)	1.357(6)
C(10)-O(1)	1.155(7)	C(1B)-C(2B)	1.391(8)
C(10)-Mo(1)	1.972(5)	C(1B)-H(1B)	0.9500
C(11)-O(2)	1.159(5)	C(2B)-C(3B)	1.364(8)
C(11)-Mo(1)	1.948(4)	C(2B)-H(2B)	0.9500
C(12)-O(3)	1.391(6)	C(3B)-N(2B)	1.336(6)
C(12)-C(13)	1.402(7)	C(3B)-H(3B)	0.9500
C(12)-Mo(1)	2.444(4)	C(4B)-N(3B)	1.351(5)
C(12)-H(12)	1.0000	C(4B)-C(5B)	1.391(7)

C(4B)-H(4B)	0.9500	Mo(1B)-N(3B)	2.284(3)
C(5B)-C(6B)	1.361(8)	N(1B)-N(2B)	1.377(5)
C(5B)-H(5B)	0.9500	N(3B)-N(4B)	1.356(5)
C(6B)-N(4B)	1.335(6)	N(5B)-N(6B)	1.367(5)
C(6B)-H(6B)	0.9500	B(1C)-N(6C)	1.528(7)
C(7B)-N(5B)	1.341(5)	B(1C)-N(2C)	1.534(7)
C(7B)-C(8B)	1.395(7)	B(1C)-N(4C)	1.535(7)
C(7B)-H(7B)	0.9500	B(1C)-H(1C)	1.0000
C(8B)-C(9B)	1.364(8)	C(1C)-N(1C)	1.343(6)
C(8B)-H(8B)	0.9500	C(1C)-C(2C)	1.393(7)
C(9B)-N(6B)	1.349(6)	C(1C)-H(1C)	0.9500
C(9B)-H(9B)	0.9500	C(2C)-C(3C)	1.399(8)
C(10B)-O(1B)	1.135(6)	C(2C)-H(2C)	0.9500
C(10B)-Mo(1B)	1.976(4)	C(3C)-N(2C)	1.344(7)
C(11B)-O(2B)	1.150(6)	C(3C)-H(3C)	0.9500
C(11B)-Mo(1B)	1.955(5)	C(4C)-N(3C)	1.334(6)
C(12B)-O(3B)	1.385(6)	C(4C)-C(5C)	1.387(7)
C(12B)-C(13B)	1.401(8)	C(4C)-H(4C)	0.9500
C(12B)-Mo(1B)	2.398(5)	C(5C)-C(6C)	1.370(8)
C(12B)-H(12B)	1.0000	C(5C)-H(5C)	0.9500
C(13B)-C(14B)	1.390(7)	C(6C)-N(4C)	1.346(6)
C(13B)-Mo(1B)	2.228(4)	C(6C)-H(6C)	0.9500
C(13B)-H(13B)	1.0000	C(7C)-N(5C)	1.338(6)
C(14B)-C(15B)	1.499(8)	C(7C)-C(8C)	1.385(6)
C(14B)-Mo(1B)	2.338(4)	C(7C)-H(7C)	0.9500
C(14B)-H(14B)	1.0000	C(8C)-C(9C)	1.383(9)
C(15B)-O(4B)	1.204(6)	C(8C)-H(8C)	0.9500
C(15B)-C(16B)	1.523(8)	C(9C)-N(6C)	1.340(6)
C(16B)-O(3B)	1.445(6)	C(9C)-H(9C)	0.9500
C(16B)-C(17B)	1.508(8)	C(10C)-O(1C)	1.155(5)
C(16B)-H(16B)	1.0000	C(10C)-Mo(1C)	1.968(4)
C(17B)-H(17D)	0.9800	C(11C)-O(2C)	1.146(7)
C(17B)-H(17E)	0.9800	C(11C)-Mo(1C)	1.963(5)
C(17B)-H(17F)	0.9800	C(12C)-O(3C)	1.377(6)
Mo(1B)-N(5B)	2.183(3)	C(12C)-C(13C)	1.418(8)
Mo(1B)-N(1B)	2.270(4)	C(12C)-Mo(1C)	2.401(4)

C(12C)-H(12C)	1.0000	C(5D)-H(5D)	0.9500
C(13C)-C(14C)	1.393(7)	C(6D)-N(4D)	1.346(7)
C(13C)-Mo(1C)	2.228(4)	C(6D)-H(6D)	0.9500
C(13C)-H(13C)	1.0000	C(7D)-N(5D)	1.353(6)
C(14C)-C(15C)	1.457(6)	C(7D)-C(8D)	1.381(8)
C(14C)-Mo(1C)	2.331(4)	C(7D)-H(7D)	0.9500
C(14C)-H(14C)	1.0000	C(8D)-C(9D)	1.372(9)
C(15C)-O(4C)	1.227(6)	C(8D)-H(8D)	0.9500
C(15C)-C(16C)	1.509(7)	C(9D)-N(6D)	1.349(7)
C(16C)-O(3C)	1.430(6)	C(9D)-H(9D)	0.9500
C(16C)-C(17C)	1.509(8)	C(10D)-O(1D)	1.156(7)
C(16C)-H(16C)	1.0000	C(10D)-Mo(1D)	1.968(6)
C(17C)-H(17G)	0.9800	C(11D)-O(2D)	1.171(6)
C(17C)-H(17H)	0.9800	C(11D)-Mo(1D)	1.941(5)
C(17C)-H(17I)	0.9800	C(12D)-O(3D)	1.379(6)
Mo(1C)-N(5C)	2.176(3)	C(12D)-C(13D)	1.392(7)
Mo(1C)-N(3C)	2.267(3)	C(12D)-Mo(1D)	2.421(4)
Mo(1C)-N(1C)	2.273(4)	C(12D)-H(12D)	1.0000
N(1C)-N(2C)	1.369(5)	C(13D)-C(14D)	1.406(8)
N(3C)-N(4C)	1.362(5)	C(13D)-Mo(1D)	2.243(5)
N(5C)-N(6C)	1.360(5)	C(13D)-H(13D)	1.0000
B(1D)-N(4D)	1.524(7)	C(14D)-C(15D)	1.472(8)
B(1D)-N(2D)	1.535(7)	C(14D)-Mo(1D)	2.348(5)
B(1D)-N(6D)	1.542(7)	C(14D)-H(14D)	1.0000
B(1D)-H(1D)	1.0000	C(15D)-O(4D)	1.214(7)
C(1D)-N(1D)	1.324(6)	C(15D)-C(16D)	1.534(7)
C(1D)-C(2D)	1.394(8)	C(16D)-O(3D)	1.431(6)
C(1D)-H(1D)	0.9500	C(16D)-C(17D)	1.507(8)
C(2D)-C(3D)	1.361(10)	C(16D)-H(16D)	1.0000
C(2D)-H(2D)	0.9500	C(17D)-H(17J)	0.9800
C(3D)-N(2D)	1.343(6)	C(17D)-H(17K)	0.9800
C(3D)-H(3D)	0.9500	C(17D)-H(17L)	0.9800
C(4D)-N(3D)	1.356(6)	Mo(1D)-N(5D)	2.192(4)
C(4D)-C(5D)	1.389(7)	Mo(1D)-N(3D)	2.274(4)
C(4D)-H(4D)	0.9500	Mo(1D)-N(1D)	2.286(4)
C(5D)-C(6D)	1.384(8)	N(1D)-N(2D)	1.380(6)

N(3D)-N(4D)	1.376(5)	C(8)-C(7)-H(7)	125.1
N(5D)-N(6D)	1.368(6)	C(9)-C(8)-C(7)	105.7(4)
C(1S)-Cl(2)	1.735(11)	C(9)-C(8)-H(8)	127.2
C(1S)-Cl(1)	1.740(9)	C(7)-C(8)-H(8)	127.2
C(1S)-H(1S1)	0.9900	N(6)-C(9)-C(8)	108.4(4)
C(1S)-H(1S2)	0.9900	N(6)-C(9)-H(9)	125.8
C(2S)-Cl(3)	1.727(10)	C(8)-C(9)-H(9)	125.8
C(2S)-Cl(4)	1.764(9)	O(1)-C(10)-Mo(1)	175.5(4)
C(2S)-H(2S1)	0.9900	O(2)-C(11)-Mo(1)	175.5(4)
C(2S)-H(2S2)	0.9900	O(3)-C(12)-C(13)	122.3(4)
N(4)-B(1)-N(2)	110.3(4)	O(3)-C(12)-Mo(1)	116.4(3)
N(4)-B(1)-N(6)	107.3(4)	C(13)-C(12)-Mo(1)	64.8(2)
N(2)-B(1)-N(6)	108.2(4)	O(3)-C(12)-H(12)	114.7
N(4)-B(1)-H(1)	110.3	C(13)-C(12)-H(12)	114.7
N(2)-B(1)-H(1)	110.3	Mo(1)-C(12)-H(12)	114.7
N(6)-B(1)-H(1)	110.3	C(12)-C(13)-C(14)	115.0(4)
N(1)-C(1)-C(2)	110.4(4)	C(12)-C(13)-Mo(1)	80.7(3)
N(1)-C(1)-H(1)	124.8	C(14)-C(13)-Mo(1)	76.3(3)
C(2)-C(1)-H(1)	124.8	C(12)-C(13)-H(13)	121.9
C(3)-C(2)-C(1)	104.3(4)	C(14)-C(13)-H(13)	121.9
C(3)-C(2)-H(2)	127.8	Mo(1)-C(13)-H(13)	121.9
C(1)-C(2)-H(2)	127.8	C(13)-C(14)-C(15)	119.7(4)
N(2)-C(3)-C(2)	108.6(4)	C(13)-C(14)-Mo(1)	68.0(2)
N(2)-C(3)-H(3)	125.7	C(15)-C(14)-Mo(1)	109.2(3)
C(2)-C(3)-H(3)	125.7	C(13)-C(14)-H(14)	116.7
N(3)-C(4)-C(5)	110.4(4)	C(15)-C(14)-H(14)	116.7
N(3)-C(4)-H(4)	124.8	Mo(1)-C(14)-H(14)	116.7
C(5)-C(4)-H(4)	124.8	O(4)-C(15)-C(14)	123.2(5)
C(6)-C(5)-C(4)	104.4(4)	O(4)-C(15)-C(16)	118.8(5)
C(6)-C(5)-H(5)	127.8	C(14)-C(15)-C(16)	117.8(5)
C(4)-C(5)-H(5)	127.8	O(3)-C(16)-C(17)	107.3(4)
N(4)-C(6)-C(5)	108.7(5)	O(3)-C(16)-C(15)	116.0(4)
N(4)-C(6)-H(6)	125.6	C(17)-C(16)-C(15)	112.4(5)
C(5)-C(6)-H(6)	125.6	O(3)-C(16)-H(16)	106.9
N(5)-C(7)-C(8)	109.8(5)	C(17)-C(16)-H(16)	106.9
N(5)-C(7)-H(7)	125.1	C(15)-C(16)-H(16)	106.9

C(16)-C(17)-H(17A)	109.5	N(2)-N(1)-Mo(1)	119.7(3)
C(16)-C(17)-H(17B)	109.5	C(3)-N(2)-N(1)	110.0(4)
H(17A)-C(17)-H(17B)	109.5	C(3)-N(2)-B(1)	128.1(4)
C(16)-C(17)-H(17C)	109.5	N(1)-N(2)-B(1)	120.7(4)
H(17A)-C(17)-H(17C)	109.5	C(4)-N(3)-N(4)	106.1(4)
H(17B)-C(17)-H(17C)	109.5	C(4)-N(3)-Mo(1)	133.2(3)
C(11)-Mo(1)-C(10)	80.22(19)	N(4)-N(3)-Mo(1)	120.0(3)
C(11)-Mo(1)-N(5)	86.53(15)	C(6)-N(4)-N(3)	110.3(4)
C(10)-Mo(1)-N(5)	87.75(17)	C(6)-N(4)-B(1)	128.0(4)
C(11)-Mo(1)-C(13)	100.12(18)	N(3)-N(4)-B(1)	121.3(4)
C(10)-Mo(1)-C(13)	109.81(19)	C(7)-N(5)-N(6)	106.4(4)
N(5)-Mo(1)-C(13)	161.97(16)	C(7)-N(5)-Mo(1)	130.7(3)
C(11)-Mo(1)-N(1)	165.62(15)	N(6)-N(5)-Mo(1)	122.9(3)
C(10)-Mo(1)-N(1)	95.01(18)	C(9)-N(6)-N(5)	109.8(4)
N(5)-Mo(1)-N(1)	79.70(13)	C(9)-N(6)-B(1)	130.3(4)
C(13)-Mo(1)-N(1)	94.26(16)	N(5)-N(6)-B(1)	119.7(3)
C(11)-Mo(1)-N(3)	97.89(15)	C(12)-O(3)-C(16)	119.4(4)
C(10)-Mo(1)-N(3)	166.95(16)	N(6B)-B(1B)-N(4B)	107.8(4)
N(5)-Mo(1)-N(3)	79.24(14)	N(6B)-B(1B)-N(2B)	108.7(3)
C(13)-Mo(1)-N(3)	83.24(16)	N(4B)-B(1B)-N(2B)	109.0(4)
N(1)-Mo(1)-N(3)	83.67(14)	N(6B)-B(1B)-H(1B)	110.4
C(11)-Mo(1)-C(14)	111.35(16)	N(4B)-B(1B)-H(1B)	110.4
C(10)-Mo(1)-C(14)	78.4(2)	N(2B)-B(1B)-H(1B)	110.4
N(5)-Mo(1)-C(14)	154.72(17)	N(1B)-C(1B)-C(2B)	111.4(4)
C(13)-Mo(1)-C(14)	35.7(2)	N(1B)-C(1B)-H(1B)	124.3
N(1)-Mo(1)-C(14)	80.60(14)	C(2B)-C(1B)-H(1B)	124.3
N(3)-Mo(1)-C(14)	114.07(17)	C(3B)-C(2B)-C(1B)	104.7(4)
C(11)-Mo(1)-C(12)	65.82(17)	C(3B)-C(2B)-H(2B)	127.7
C(10)-Mo(1)-C(12)	105.78(19)	C(1B)-C(2B)-H(2B)	127.7
N(5)-Mo(1)-C(12)	145.84(16)	N(2B)-C(3B)-C(2B)	109.1(5)
C(13)-Mo(1)-C(12)	34.49(18)	N(2B)-C(3B)-H(3B)	125.4
N(1)-Mo(1)-C(12)	128.51(15)	C(2B)-C(3B)-H(3B)	125.4
N(3)-Mo(1)-C(12)	84.89(15)	N(3B)-C(4B)-C(5B)	110.1(4)
C(14)-Mo(1)-C(12)	59.27(17)	N(3B)-C(4B)-H(4B)	124.9
C(1)-N(1)-N(2)	106.7(4)	C(5B)-C(4B)-H(4B)	124.9
C(1)-N(1)-Mo(1)	133.6(3)	C(6B)-C(5B)-C(4B)	104.6(4)

C(6B)-C(5B)-H(5B)	127.7	C(14B)-C(15B)-C(16B)	116.7(4)
C(4B)-C(5B)-H(5B)	127.7	O(3B)-C(16B)-C(17B)	107.4(5)
N(4B)-C(6B)-C(5B)	109.6(5)	O(3B)-C(16B)-C(15B)	115.8(4)
N(4B)-C(6B)-H(6B)	125.2	C(17B)-C(16B)-C(15B)	110.6(5)
C(5B)-C(6B)-H(6B)	125.2	O(3B)-C(16B)-H(16B)	107.6
N(5B)-C(7B)-C(8B)	111.2(5)	C(17B)-C(16B)-H(16B)	107.6
N(5B)-C(7B)-H(7B)	124.4	C(15B)-C(16B)-H(16B)	107.6
C(8B)-C(7B)-H(7B)	124.4	C(16B)-C(17B)-H(17D)	109.5
C(9B)-C(8B)-C(7B)	104.3(4)	C(16B)-C(17B)-H(17E)	109.5
C(9B)-C(8B)-H(8B)	127.9	H(17D)-C(17B)-H(17E)	109.5
C(7B)-C(8B)-H(8B)	127.9	C(16B)-C(17B)-H(17F)	109.5
N(6B)-C(9B)-C(8B)	109.4(4)	H(17D)-C(17B)-H(17F)	109.5
N(6B)-C(9B)-H(9B)	125.3	H(17E)-C(17B)-H(17F)	109.5
C(8B)-C(9B)-H(9B)	125.3	C(11B)-Mo(1B)-C(10B)	80.08(19)
O(1B)-C(10B)-Mo(1B)	176.1(5)	C(11B)-Mo(1B)-N(5B)	85.33(17)
O(2B)-C(11B)-Mo(1B)	176.8(4)	C(10B)-Mo(1B)-N(5B)	87.61(16)
O(3B)-C(12B)-C(13B)	124.5(5)	C(11B)-Mo(1B)-C(13B)	100.5(2)
O(3B)-C(12B)-Mo(1B)	118.5(3)	C(10B)-Mo(1B)-C(13B)	110.16(19)
C(13B)-C(12B)-Mo(1B)	65.9(3)	N(5B)-Mo(1B)-C(13B)	161.93(16)
O(3B)-C(12B)-H(12B)	113.3	C(11B)-Mo(1B)-N(1B)	164.72(16)
C(13B)-C(12B)-H(12B)	113.3	C(10B)-Mo(1B)-N(1B)	95.51(16)
Mo(1B)-C(12B)-H(12B)	113.3	N(5B)-Mo(1B)-N(1B)	79.85(14)
C(14B)-C(13B)-C(12B)	114.4(5)	C(13B)-Mo(1B)-N(1B)	94.70(18)
C(14B)-C(13B)-Mo(1B)	76.6(3)	C(11B)-Mo(1B)-N(3B)	99.49(17)
C(12B)-C(13B)-Mo(1B)	79.1(3)	C(10B)-Mo(1B)-N(3B)	168.55(16)
C(14B)-C(13B)-H(13B)	122.3	N(5B)-Mo(1B)-N(3B)	80.96(13)
C(12B)-C(13B)-H(13B)	122.3	C(13B)-Mo(1B)-N(3B)	81.22(16)
Mo(1B)-C(13B)-H(13B)	122.3	N(1B)-Mo(1B)-N(3B)	81.92(14)
C(13B)-C(14B)-C(15B)	118.5(5)	C(11B)-Mo(1B)-C(14B)	111.54(19)
C(13B)-C(14B)-Mo(1B)	68.0(2)	C(10B)-Mo(1B)-C(14B)	78.90(19)
C(15B)-C(14B)-Mo(1B)	109.2(3)	N(5B)-Mo(1B)-C(14B)	155.85(17)
C(13B)-C(14B)-H(14B)	117.1	C(13B)-Mo(1B)-C(14B)	35.35(18)
C(15B)-C(14B)-H(14B)	117.1	N(1B)-Mo(1B)-C(14B)	81.60(17)
Mo(1B)-C(14B)-H(14B)	117.1	N(3B)-Mo(1B)-C(14B)	111.57(16)
O(4B)-C(15B)-C(14B)	122.2(5)	C(11B)-Mo(1B)-C(12B)	65.74(19)
O(4B)-C(15B)-C(16B)	120.5(5)	C(10B)-Mo(1B)-C(12B)	105.99(18)

N(5B)-Mo(1B)-C(12B)	144.55(17)	N(2C)-C(3C)-C(2C)	107.9(4)
C(13B)-Mo(1B)-C(12B)	35.0(2)	N(2C)-C(3C)-H(3C)	126.0
N(1B)-Mo(1B)-C(12B)	129.40(17)	C(2C)-C(3C)-H(3C)	126.0
N(3B)-Mo(1B)-C(12B)	83.98(15)	N(3C)-C(4C)-C(5C)	111.5(5)
C(14B)-Mo(1B)-C(12B)	59.38(18)	N(3C)-C(4C)-H(4C)	124.3
C(1B)-N(1B)-N(2B)	104.1(4)	C(5C)-C(4C)-H(4C)	124.3
C(1B)-N(1B)-Mo(1B)	135.4(3)	C(6C)-C(5C)-C(4C)	104.3(4)
N(2B)-N(1B)-Mo(1B)	120.4(3)	C(6C)-C(5C)-H(5C)	127.9
C(3B)-N(2B)-N(1B)	110.7(4)	C(4C)-C(5C)-H(5C)	127.9
C(3B)-N(2B)-B(1B)	128.4(4)	N(4C)-C(6C)-C(5C)	108.8(4)
N(1B)-N(2B)-B(1B)	120.5(4)	N(4C)-C(6C)-H(6C)	125.6
C(4B)-N(3B)-N(4B)	106.0(4)	C(5C)-C(6C)-H(6C)	125.6
C(4B)-N(3B)-Mo(1B)	133.2(3)	N(5C)-C(7C)-C(8C)	110.6(5)
N(4B)-N(3B)-Mo(1B)	120.7(3)	N(5C)-C(7C)-H(7C)	124.7
C(6B)-N(4B)-N(3B)	109.7(4)	C(8C)-C(7C)-H(7C)	124.7
C(6B)-N(4B)-B(1B)	129.7(4)	C(9C)-C(8C)-C(7C)	104.5(4)
N(3B)-N(4B)-B(1B)	120.6(3)	C(9C)-C(8C)-H(8C)	127.8
C(7B)-N(5B)-N(6B)	105.7(4)	C(7C)-C(8C)-H(8C)	127.8
C(7B)-N(5B)-Mo(1B)	131.3(3)	N(6C)-C(9C)-C(8C)	108.9(4)
N(6B)-N(5B)-Mo(1B)	123.0(3)	N(6C)-C(9C)-H(9C)	125.6
C(9B)-N(6B)-N(5B)	109.4(4)	C(8C)-C(9C)-H(9C)	125.6
C(9B)-N(6B)-B(1B)	130.4(4)	O(1C)-C(10C)-Mo(1C)	176.0(4)
N(5B)-N(6B)-B(1B)	120.2(3)	O(2C)-C(11C)-Mo(1C)	174.0(4)
C(12B)-O(3B)-C(16B)	116.8(4)	O(3C)-C(12C)-C(13C)	123.1(4)
N(6C)-B(1C)-N(2C)	107.1(4)	O(3C)-C(12C)-Mo(1C)	117.2(3)
N(6C)-B(1C)-N(4C)	108.1(4)	C(13C)-C(12C)-Mo(1C)	65.6(2)
N(2C)-B(1C)-N(4C)	110.4(4)	O(3C)-C(12C)-H(12C)	114.1
N(6C)-B(1C)-H(1C)	110.4	C(13C)-C(12C)-H(12C)	114.1
N(2C)-B(1C)-H(1C)	110.4	Mo(1C)-C(12C)-H(12C)	114.1
N(4C)-B(1C)-H(1C)	110.4	C(14C)-C(13C)-C(12C)	113.9(4)
N(1C)-C(1C)-C(2C)	110.8(5)	C(14C)-C(13C)-Mo(1C)	76.3(2)
N(1C)-C(1C)-H(1C)	124.6	C(12C)-C(13C)-Mo(1C)	79.0(3)
C(2C)-C(1C)-H(1C)	124.6	C(14C)-C(13C)-H(13C)	122.6
C(1C)-C(2C)-C(3C)	104.8(4)	C(12C)-C(13C)-H(13C)	122.6
C(1C)-C(2C)-H(2C)	127.6	Mo(1C)-C(13C)-H(13C)	122.6
C(3C)-C(2C)-H(2C)	127.6	C(13C)-C(14C)-C(15C)	119.0(4)

C(13C)-C(14C)-Mo(1C)	68.2(2)	C(10C)-Mo(1C)-C(14C)	78.89(16)
C(15C)-C(14C)-Mo(1C)	110.1(3)	N(5C)-Mo(1C)-C(14C)	154.81(17)
C(13C)-C(14C)-H(14C)	116.7	C(13C)-Mo(1C)-C(14C)	35.50(18)
C(15C)-C(14C)-H(14C)	116.7	N(3C)-Mo(1C)-C(14C)	111.77(15)
Mo(1C)-C(14C)-H(14C)	116.7	N(1C)-Mo(1C)-C(14C)	80.35(15)
O(4C)-C(15C)-C(14C)	122.9(5)	C(11C)-Mo(1C)-C(12C)	65.67(18)
O(4C)-C(15C)-C(16C)	119.4(4)	C(10C)-Mo(1C)-C(12C)	106.28(16)
C(14C)-C(15C)-C(16C)	117.4(4)	N(5C)-Mo(1C)-C(12C)	145.37(17)
O(3C)-C(16C)-C(15C)	115.7(3)	C(13C)-Mo(1C)-C(12C)	35.44(19)
O(3C)-C(16C)-C(17C)	107.0(5)	N(3C)-Mo(1C)-C(12C)	83.77(14)
C(15C)-C(16C)-C(17C)	113.7(4)	N(1C)-Mo(1C)-C(12C)	129.42(17)
O(3C)-C(16C)-H(16C)	106.6	C(14C)-Mo(1C)-C(12C)	59.72(18)
C(15C)-C(16C)-H(16C)	106.6	C(1C)-N(1C)-N(2C)	106.2(4)
C(17C)-C(16C)-H(16C)	106.6	C(1C)-N(1C)-Mo(1C)	132.3(3)
C(16C)-C(17C)-H(17G)	109.5	N(2C)-N(1C)-Mo(1C)	119.5(3)
C(16C)-C(17C)-H(17H)	109.5	C(3C)-N(2C)-N(1C)	110.4(4)
H(17G)-C(17C)-H(17H)	109.5	C(3C)-N(2C)-B(1C)	127.1(4)
C(16C)-C(17C)-H(17I)	109.5	N(1C)-N(2C)-B(1C)	121.1(4)
H(17G)-C(17C)-H(17I)	109.5	C(4C)-N(3C)-N(4C)	105.6(4)
H(17H)-C(17C)-H(17I)	109.5	C(4C)-N(3C)-Mo(1C)	134.6(3)
C(11C)-Mo(1C)-C(10C)	80.32(19)	N(4C)-N(3C)-Mo(1C)	119.7(3)
C(11C)-Mo(1C)-N(5C)	86.52(17)	C(6C)-N(4C)-N(3C)	109.8(4)
C(10C)-Mo(1C)-N(5C)	87.76(14)	C(6C)-N(4C)-B(1C)	129.2(4)
C(11C)-Mo(1C)-C(13C)	100.92(19)	N(3C)-N(4C)-B(1C)	120.9(4)
C(10C)-Mo(1C)-C(13C)	110.46(16)	C(7C)-N(5C)-N(6C)	106.6(3)
N(5C)-Mo(1C)-C(13C)	161.14(14)	C(7C)-N(5C)-Mo(1C)	130.7(3)
C(11C)-Mo(1C)-N(3C)	99.13(17)	N(6C)-N(5C)-Mo(1C)	122.6(3)
C(10C)-Mo(1C)-N(3C)	168.38(14)	C(9C)-N(6C)-N(5C)	109.4(4)
N(5C)-Mo(1C)-N(3C)	80.62(13)	C(9C)-N(6C)-B(1C)	130.1(4)
C(13C)-Mo(1C)-N(3C)	81.09(15)	N(5C)-N(6C)-B(1C)	120.2(3)
C(11C)-Mo(1C)-N(1C)	164.90(16)	C(12C)-O(3C)-C(16C)	117.7(4)
C(10C)-Mo(1C)-N(1C)	93.80(17)	N(4D)-B(1D)-N(2D)	109.2(4)
N(5C)-Mo(1C)-N(1C)	79.32(15)	N(4D)-B(1D)-N(6D)	109.5(4)
C(13C)-Mo(1C)-N(1C)	94.16(17)	N(2D)-B(1D)-N(6D)	108.1(4)
N(3C)-Mo(1C)-N(1C)	83.82(14)	N(4D)-B(1D)-H(1D)	110.0
C(11C)-Mo(1C)-C(14C)	111.75(18)	N(2D)-B(1D)-H(1D)	110.0

N(6D)-B(1D)-H(1D)	110.0	C(12D)-C(13D)-C(14D)	114.6(5)
N(1D)-C(1D)-C(2D)	111.2(6)	C(12D)-C(13D)-Mo(1D)	79.8(3)
N(1D)-C(1D)-H(1D)	124.4	C(14D)-C(13D)-Mo(1D)	76.3(3)
C(2D)-C(1D)-H(1D)	124.4	C(12D)-C(13D)-H(13D)	122.2
C(3D)-C(2D)-C(1D)	105.2(5)	C(14D)-C(13D)-H(13D)	122.2
C(3D)-C(2D)-H(2D)	127.4	Mo(1D)-C(13D)-H(13D)	122.2
C(1D)-C(2D)-H(2D)	127.4	C(13D)-C(14D)-C(15D)	119.5(4)
N(2D)-C(3D)-C(2D)	108.2(6)	C(13D)-C(14D)-Mo(1D)	68.1(3)
N(2D)-C(3D)-H(3D)	125.9	C(15D)-C(14D)-Mo(1D)	110.5(3)
C(2D)-C(3D)-H(3D)	125.9	C(13D)-C(14D)-H(14D)	116.4
N(3D)-C(4D)-C(5D)	111.7(4)	C(15D)-C(14D)-H(14D)	116.4
N(3D)-C(4D)-H(4D)	124.2	Mo(1D)-C(14D)-H(14D)	116.4
C(5D)-C(4D)-H(4D)	124.2	O(4D)-C(15D)-C(14D)	126.4(5)
C(6D)-C(5D)-C(4D)	104.6(5)	O(4D)-C(15D)-C(16D)	118.6(5)
C(6D)-C(5D)-H(5D)	127.7	C(14D)-C(15D)-C(16D)	114.5(5)
C(4D)-C(5D)-H(5D)	127.7	O(3D)-C(16D)-C(17D)	107.7(4)
N(4D)-C(6D)-C(5D)	108.4(5)	O(3D)-C(16D)-C(15D)	115.0(4)
N(4D)-C(6D)-H(6D)	125.8	C(17D)-C(16D)-C(15D)	112.3(5)
C(5D)-C(6D)-H(6D)	125.8	O(3D)-C(16D)-H(16D)	107.1
N(5D)-C(7D)-C(8D)	110.7(5)	C(17D)-C(16D)-H(16D)	107.1
N(5D)-C(7D)-H(7D)	124.7	C(15D)-C(16D)-H(16D)	107.1
C(8D)-C(7D)-H(7D)	124.7	C(16D)-C(17D)-H(17J)	109.5
C(9D)-C(8D)-C(7D)	105.2(5)	C(16D)-C(17D)-H(17K)	109.5
C(9D)-C(8D)-H(8D)	127.4	H(17J)-C(17D)-H(17K)	109.5
C(7D)-C(8D)-H(8D)	127.4	C(16D)-C(17D)-H(17L)	109.5
N(6D)-C(9D)-C(8D)	108.8(5)	H(17J)-C(17D)-H(17L)	109.5
N(6D)-C(9D)-H(9D)	125.6	H(17K)-C(17D)-H(17L)	109.5
C(8D)-C(9D)-H(9D)	125.6	C(11D)-Mo(1D)-C(10D)	78.6(2)
O(1D)-C(10D)-Mo(1D)	176.0(5)	C(11D)-Mo(1D)-N(5D)	84.35(16)
O(2D)-C(11D)-Mo(1D)	173.6(4)	C(10D)-Mo(1D)-N(5D)	87.7(2)
O(3D)-C(12D)-C(13D)	122.6(4)	C(11D)-Mo(1D)-C(13D)	99.93(18)
O(3D)-C(12D)-Mo(1D)	117.0(3)	C(10D)-Mo(1D)-C(13D)	110.8(2)
C(13D)-C(12D)-Mo(1D)	65.8(3)	N(5D)-Mo(1D)-C(13D)	161.54(19)
O(3D)-C(12D)-H(12D)	114.2	C(11D)-Mo(1D)-N(3D)	102.38(17)
C(13D)-C(12D)-H(12D)	114.2	C(10D)-Mo(1D)-N(3D)	168.0(2)
Mo(1D)-C(12D)-H(12D)	114.2	N(5D)-Mo(1D)-N(3D)	80.55(15)

C(13D)-Mo(1D)-N(3D)	80.99(18)	C(4D)-N(3D)-N(4D)	104.5(4)
C(11D)-Mo(1D)-N(1D)	164.01(17)	C(4D)-N(3D)-Mo(1D)	134.4(3)
C(10D)-Mo(1D)-N(1D)	94.86(18)	N(4D)-N(3D)-Mo(1D)	121.0(3)
N(5D)-Mo(1D)-N(1D)	80.79(14)	C(6D)-N(4D)-N(3D)	110.8(4)
C(13D)-Mo(1D)-N(1D)	96.03(16)	C(6D)-N(4D)-B(1D)	129.0(4)
N(3D)-Mo(1D)-N(1D)	81.05(15)	N(3D)-N(4D)-B(1D)	120.1(4)
C(11D)-Mo(1D)-C(14D)	110.69(18)	C(7D)-N(5D)-N(6D)	105.8(4)
C(10D)-Mo(1D)-C(14D)	79.6(2)	C(7D)-N(5D)-Mo(1D)	130.9(4)
N(5D)-Mo(1D)-C(14D)	157.58(17)	N(6D)-N(5D)-Mo(1D)	123.3(3)
C(13D)-Mo(1D)-C(14D)	35.6(2)	C(9D)-N(6D)-N(5D)	109.5(5)
N(3D)-Mo(1D)-C(14D)	110.79(18)	C(9D)-N(6D)-B(1D)	130.8(5)
N(1D)-Mo(1D)-C(14D)	82.00(16)	N(5D)-N(6D)-B(1D)	119.6(4)
C(11D)-Mo(1D)-C(12D)	65.71(17)	C(12D)-O(3D)-C(16D)	117.9(4)
C(10D)-Mo(1D)-C(12D)	106.0(2)	Cl(2)-C(1S)-Cl(1)	113.3(6)
N(5D)-Mo(1D)-C(12D)	143.00(15)	Cl(2)-C(1S)-H(1S1)	108.9
C(13D)-Mo(1D)-C(12D)	34.46(17)	Cl(1)-C(1S)-H(1S1)	108.9
N(3D)-Mo(1D)-C(12D)	85.02(15)	Cl(2)-C(1S)-H(1S2)	108.9
N(1D)-Mo(1D)-C(12D)	130.28(15)	Cl(1)-C(1S)-H(1S2)	108.9
C(14D)-Mo(1D)-C(12D)	59.13(17)	H(1S1)-C(1S)-H(1S2)	107.7
C(1D)-N(1D)-N(2D)	105.2(4)	Cl(3)-C(2S)-Cl(4)	111.2(5)
C(1D)-N(1D)-Mo(1D)	135.0(4)	Cl(3)-C(2S)-H(2S1)	109.4
N(2D)-N(1D)-Mo(1D)	119.8(3)	Cl(4)-C(2S)-H(2S1)	109.4
C(3D)-N(2D)-N(1D)	110.1(5)	Cl(3)-C(2S)-H(2S2)	109.4
C(3D)-N(2D)-B(1D)	129.1(5)	Cl(4)-C(2S)-H(2S2)	109.4
N(1D)-N(2D)-B(1D)	120.8(4)	H(2S1)-C(2S)-H(2S2)	108

Symmetry transformations used to generate equivalent atoms:

Table 5: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (-)-*syn*-43. 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)	24(2)	35(3)	39(3)	-3(2)	4(2)	5(2)
C(1)	29(2)	40(3)	29(2)	-6(2)	2(2)	2(2)
C(2)	34(2)	47(3)	34(2)	-7(2)	-8(2)	-2(2)
C(3)	28(2)	47(3)	34(2)	4(2)	-7(2)	-3(2)

C(4)	42(2)	26(2)	22(2)	-1(1)	-1(2)	-1(2)
C(5)	50(3)	23(2)	37(2)	-4(2)	6(2)	5(2)
C(6)	49(3)	26(2)	35(2)	-1(2)	8(2)	12(2)
C(7)	36(2)	35(2)	31(2)	1(2)	14(2)	-7(2)
C(8)	36(2)	47(3)	42(2)	-10(2)	21(2)	-14(2)
C(9)	22(2)	45(3)	46(3)	-13(2)	14(2)	-6(2)
C(10)	30(2)	27(2)	29(2)	1(2)	4(2)	2(2)
C(11)	25(2)	23(2)	28(2)	-1(1)	7(1)	1(1)
C(12)	24(2)	30(2)	43(2)	-1(2)	3(2)	-4(2)
C(13)	24(2)	34(2)	44(2)	14(2)	13(2)	2(2)
C(14)	24(2)	50(3)	26(2)	1(2)	6(1)	6(2)
C(15)	24(2)	40(3)	32(2)	-5(2)	5(2)	5(2)
C(16)	28(2)	40(3)	37(2)	-4(2)	-2(2)	6(2)
C(17)	54(3)	43(3)	52(3)	4(3)	-15(3)	7(3)
Mo(1)	20(1)	20(1)	21(1)	1(1)	4(1)	2(1)
N(1)	24(1)	30(2)	26(1)	-3(1)	2(1)	7(1)
N(2)	24(2)	35(2)	31(2)	0(1)	-1(1)	5(1)
N(3)	29(2)	18(2)	28(2)	0(1)	2(1)	2(1)
N(4)	28(2)	24(2)	33(2)	0(1)	4(1)	7(1)
N(5)	26(2)	24(2)	28(2)	1(1)	7(1)	2(1)
N(6)	19(1)	33(2)	39(2)	-1(2)	7(1)	5(1)
O(1)	57(2)	21(2)	51(2)	1(2)	10(2)	2(2)
O(2)	37(2)	37(2)	29(2)	3(1)	0(1)	-4(1)
O(3)	25(1)	36(2)	37(2)	-5(1)	0(1)	3(1)
O(4)	45(2)	48(2)	47(2)	-14(2)	3(2)	9(2)
B(1B)	30(2)	27(2)	26(2)	-1(2)	-3(2)	6(2)
C(1B)	27(2)	31(2)	33(2)	-2(2)	9(2)	-8(2)
C(2B)	43(3)	24(2)	44(3)	-6(2)	14(2)	-6(2)
C(3B)	49(3)	21(2)	36(2)	2(2)	12(2)	1(2)
C(4B)	40(2)	29(2)	27(2)	-5(2)	3(2)	4(2)
C(5B)	51(3)	42(3)	24(2)	-6(2)	0(2)	3(2)
C(6B)	47(3)	33(2)	26(2)	1(2)	-6(2)	2(2)
C(7B)	27(2)	34(2)	30(2)	-4(2)	7(1)	-7(2)
C(8B)	28(2)	43(3)	40(2)	-10(2)	11(2)	-3(2)
C(9B)	23(2)	38(3)	38(2)	-6(2)	4(2)	6(2)
C(10B)	33(2)	25(2)	32(2)	0(2)	-3(2)	7(2)

C(11B)	24(2)	27(2)	31(2)	0(2)	2(1)	0(2)
C(12B)	34(2)	39(3)	31(2)	-6(2)	2(2)	11(2)
C(13B)	27(2)	44(3)	36(2)	4(2)	12(2)	7(2)
C(14B)	22(2)	36(3)	48(2)	-5(2)	8(2)	-1(2)
C(15B)	22(2)	39(3)	44(2)	-5(2)	-4(2)	5(2)
C(16B)	26(2)	33(2)	45(2)	-3(2)	1(2)	8(2)
C(17B)	52(3)	38(3)	45(3)	4(2)	-4(2)	8(3)
Mo(1B)	20(1)	20(1)	25(1)	1(1)	2(1)	1(1)
N(1B)	27(2)	24(2)	26(2)	2(1)	4(1)	1(1)
N(2B)	32(2)	22(2)	28(2)	1(1)	4(1)	4(1)
N(3B)	31(2)	27(2)	24(1)	-2(1)	2(1)	7(1)
N(4B)	33(2)	30(2)	25(2)	-1(1)	-1(1)	7(2)
N(5B)	25(2)	24(2)	26(1)	0(1)	2(1)	-1(1)
N(6B)	24(2)	34(2)	28(2)	0(1)	3(1)	6(1)
O(1B)	58(2)	49(2)	32(2)	4(2)	-7(2)	15(2)
O(2B)	39(2)	28(2)	55(2)	1(2)	2(2)	-2(2)
O(3B)	35(2)	38(2)	38(2)	-4(1)	-4(1)	12(2)
O(4B)	43(2)	48(3)	56(2)	-10(2)	-17(2)	8(2)
B(1C)	21(2)	34(3)	45(3)	-2(2)	1(2)	11(2)
C(1C)	38(2)	25(2)	31(2)	0(2)	4(2)	-4(2)
C(2C)	52(3)	24(2)	38(2)	-6(2)	8(2)	-1(2)
C(3C)	45(3)	24(2)	39(2)	3(2)	11(2)	12(2)
C(4C)	34(2)	37(2)	29(2)	-4(2)	-8(2)	5(2)
C(5C)	43(3)	52(3)	31(2)	-2(2)	-12(2)	6(2)
C(6C)	27(2)	44(3)	43(3)	4(2)	-10(2)	10(2)
C(7C)	28(2)	34(2)	35(2)	0(2)	7(2)	-4(2)
C(8C)	29(2)	44(3)	45(3)	-7(2)	18(2)	-8(2)
C(9C)	21(2)	41(3)	49(3)	-15(2)	14(2)	-3(2)
C(10C)	21(2)	27(2)	28(2)	2(1)	3(1)	-4(2)
C(11C)	25(2)	30(2)	28(2)	-4(2)	1(1)	4(2)
C(12C)	27(2)	44(3)	25(2)	-6(2)	-1(1)	9(2)
C(13C)	22(2)	47(3)	26(2)	9(2)	8(1)	9(2)
C(14C)	19(2)	28(2)	41(2)	5(2)	9(2)	0(1)
C(15C)	17(1)	34(2)	34(2)	0(2)	7(1)	-1(2)
C(16C)	21(2)	30(2)	39(2)	0(2)	4(2)	7(2)
C(17C)	59(4)	40(3)	51(3)	0(2)	-14(3)	11(3)

Mo(1C)	17(1)	20(1)	21(1)	1(1)	2(1)	2(1)
N(1C)	27(2)	21(2)	32(2)	0(1)	3(1)	4(1)
N(2C)	27(2)	26(2)	37(2)	-1(1)	4(1)	8(1)
N(3C)	24(2)	27(2)	28(2)	1(1)	-2(1)	6(1)
N(4C)	24(2)	32(2)	34(2)	1(1)	-2(1)	8(1)
N(5C)	20(1)	26(2)	28(1)	5(1)	4(1)	1(1)
N(6C)	17(1)	34(2)	39(2)	-2(2)	5(1)	3(1)
O(1C)	29(2)	53(2)	31(2)	5(2)	-2(1)	-6(2)
O(2C)	44(2)	28(2)	45(2)	1(2)	0(1)	2(2)
O(3C)	26(1)	39(2)	41(2)	-11(2)	-1(1)	13(1)
O(4C)	25(2)	52(2)	44(2)	-14(2)	-1(1)	-2(2)
B(1D)	37(3)	28(3)	34(2)	2(2)	-5(2)	5(2)
C(1D)	49(3)	45(3)	27(2)	-6(2)	1(2)	-16(2)
C(2D)	51(3)	60(4)	27(2)	-5(2)	-4(2)	-14(3)
C(3D)	54(3)	56(4)	26(2)	3(2)	-10(2)	-14(3)
C(4D)	33(2)	21(2)	32(2)	1(1)	5(2)	-2(2)
C(5D)	43(3)	23(2)	42(2)	2(2)	2(2)	0(2)
C(6D)	49(3)	23(2)	35(2)	6(2)	2(2)	-2(2)
C(7D)	34(2)	34(2)	37(2)	-4(2)	7(2)	-6(2)
C(8D)	40(3)	52(4)	50(3)	-13(3)	11(2)	-11(3)
C(9D)	32(2)	51(3)	42(3)	-3(2)	1(2)	0(2)
C(10D)	43(3)	31(2)	32(2)	-2(2)	0(2)	-1(2)
C(11D)	28(2)	25(2)	34(2)	3(2)	0(2)	1(2)
C(12D)	31(2)	27(2)	37(2)	-3(2)	-2(2)	1(2)
C(13D)	31(2)	38(3)	37(2)	10(2)	7(2)	3(2)
C(14D)	39(2)	45(3)	25(2)	0(2)	9(2)	6(2)
C(15D)	42(3)	36(3)	37(2)	-5(2)	9(2)	9(2)
C(16D)	36(2)	31(3)	37(2)	-1(2)	5(2)	5(2)
C(17D)	54(3)	38(3)	43(3)	2(2)	3(2)	10(3)
Mo(1D)	30(1)	21(1)	20(1)	0(1)	3(1)	0(1)
N(1D)	38(2)	33(2)	26(2)	-1(2)	0(1)	-4(2)
N(2D)	43(2)	37(2)	24(2)	3(2)	-4(2)	-5(2)
N(3D)	31(2)	25(2)	21(1)	1(1)	1(1)	2(1)
N(4D)	40(2)	22(2)	29(2)	5(1)	-2(1)	2(2)
N(5D)	35(2)	30(2)	24(2)	2(1)	-1(1)	-1(2)
N(6D)	33(2)	34(2)	32(2)	0(2)	-5(1)	2(2)

O(1D)	60(3)	28(2)	76(3)	-3(2)	-4(2)	-8(2)
O(2D)	43(2)	43(2)	27(2)	7(1)	2(1)	1(2)
O(3D)	38(2)	31(2)	35(2)	-3(1)	-2(1)	6(1)
O(4D)	71(3)	46(3)	55(3)	-23(2)	0(2)	18(2)
C(1S)	31(4)	27(4)	45(5)	-9(4)	9(3)	2(3)
C(2S)	28(4)	21(4)	38(4)	-2(3)	10(3)	-1(3)
Cl(1)	28(1)	41(1)	51(1)	3(1)	14(1)	5(1)
Cl(2)	52(1)	38(1)	35(1)	3(1)	7(1)	21(1)
Cl(3)	25(1)	105(3)	38(1)	-15(2)	-3(1)	-10(1)
Cl(4)	54(1)	21(1)	35(1)	-4(1)	2(1)	13(1)

Table 6: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (-)-*syn*-43

	x	y	z	U(eq)
H(1)	11436	658	2117	39
H(1)	8641	3715	2801	39
H(2)	10431	3005	3229	46
H(3)	11547	1424	2839	44
H(4)	7132	-458	1555	36
H(5)	8568	-2285	1566	44
H(6)	10565	-1474	1853	44
H(7)	9668	4026	1184	40
H(8)	11892	3641	1099	49
H(9)	12556	2066	1589	45
H(12)	5826	996	1634	39
H(13)	6423	1015	2293	40
H(14)	6848	2986	2588	40
H(16)	4049	3733	1959	42
H(17A)	5495	4844	1408	75
H(17B)	4826	5663	1717	75
H(17C)	4039	4832	1415	75
H(1B)	259	3313	-13	33
H(1B)	4452	3222	737	36
H(2B)	3642	5385	639	44
H(3B)	1679	5160	253	42

H(4B)	2688	-294	-598	38
H(5B)	1450	910	-1098	47
H(6B)	392	2565	-744	43
H(7B)	508	-345	953	36
H(8B)	-1574	637	914	44
H(9B)	-1473	2324	426	40
H(12B)	3755	-1199	-190	42
H(13B)	4657	775	-170	43
H(14B)	5303	1579	443	42
H(16B)	6400	-1712	469	42
H(17D)	4567	-2475	960	68
H(17E)	5919	-2153	1123	68
H(17F)	5697	-3277	827	68
H(1C)	3690	10457	2893	40
H(1C)	8112	11314	3414	38
H(2C)	6750	13172	3477	45
H(3C)	4680	12523	3186	43
H(4C)	6257	7398	2131	40
H(5C)	4492	8255	1732	51
H(6C)	3508	9822	2147	46
H(7C)	5507	7068	3804	39
H(8C)	3326	7524	3931	47
H(9C)	2643	9143	3446	44
H(12C)	7882	6936	2425	39
H(13C)	8216	9117	2397	38
H(14C)	9056	10093	2964	35
H(16C)	10913	7274	2867	36
H(17G)	10030	6320	3554	76
H(17H)	11422	6526	3455	76
H(17I)	10637	5445	3246	76
H(1D)	4603	-1971	5024	40
H(1D)	1994	1697	5472	48
H(2D)	3057	564	6021	56
H(3D)	4268	-1122	5731	54
H(4D)	577	-1963	4190	34
H(5D)	1230	-4116	4380	43

H(6D)	3178	-3862	4787	43
H(7D)	4739	1601	4028	42
H(8D)	6769	575	4135	56
H(9D)	6493	-1092	4622	50
H(12D)	19	-110	4016	38
H(13D)	-181	-208	4681	42
H(14D)	410	1582	5050	43
H(16D)	-1447	2736	4242	41
H(17J)	489	3976	3893	68
H(17K)	-559	4676	4111	68
H(17L)	-897	3904	3729	68
H(1S1)	2713	6390	1993	41
H(1S2)	2363	5098	1789	41
H(2S1)	3770	6083	3074	34
H(2S2)	4809	5068	3012	34

Chapter 2: Efforts toward the synthesis of non-anomeric spiroketals using pyranylalkylidene η^3-allylmolybdenum complexes

Introduction:

Spiroketals and the Anomeric Effect

Spiroketals are some of the most important and synthetically challenging pyran-containing substructures of complex natural products.[82,83] Spiroketals possess a bicyclic core fused at a single carbon where one of the atoms at the spirocenter of each ring is oxygen. While many of the simplest spiroketals are components of insect secretions,[84] extremely complex molecules such as the spongistatins,[85] pectenotoxins[86] (marine), and spirofungins[87] (bacterial) are natural products of varying origins (**Figure 7**). The [6,6]-spiroketals are among the most prevalent in the family, although [5,5] and [6,5] and even higher order spiroketals can be found in numerous naturally occurring substances as well.

[82] Perron, F.; Albizati, K. F. *Chem. Rev.* **1989**, *89*, 1617-1661.
[83] Mead, K. T.; Brewer, B. N. *Curr. Org. Chem.* **2003**, *7*, 227-256.
[84] Francke, W.; Kitching, W. *Curr. Org. Chem.* **2001**, *5*, 233-251.
[85] Pettit, G. R. Chichacz, Z, A. Gao, F.; Herald, C. L. Boyd, M. R.; Schmidt, J. M. Hooper, J. N. A. *J. Org. Chem.* **1993**, *58*, 1302. b) Fusetani, N.; Shinoda, K.; Matsunaga, S. *J. Am. Chem.. Soc.* **1993**, *115*, 3977. c) Kobayashi, M. Aoki, S.; Sakai, H.; Kawazoe, K.; Kihara, N.; Sasaki, T.;Kitagawa, I. *Tetrahedron Lett.* **1993**, *35*, 1243.
[86] a) Yasumoto, T.; Murata, M.; Oshima, Y.; Sano, M.; Matsumoto, G. K.; Clardy, J. *Tetrahedron* **1985**, *41*, 1019. b) Sasaki, K.; Wright, J. L. C.; Yasumoto, T. *J. Org. Chem.* **1998**, *63*, 2475. c) Kaiguji, M.; Satake, M.; James, K. J.; Bishop, A.; Mackenzie, L.; Naoki, H.; Yasumoto, T. *Chem. Lett.* **1998**, *7*, 653. d) Jung, J. H.; Sim, C. J.; Lee, C.-O. *J. Nat. Prod.* **1995**, *58*, 1722.
[87] (a) Holtzel, A.; Kempter, C.; Metzger, J. W.; Jung, G.; Groyh, I.; Fritz, T.; Fiedler, H.-P. *J. Antibiot.* **1998**, *51*, 699. (b) Zanatta, S. D.; White, J. M.; Rizzacasa, M. A. *Org. Lett.* **2004**, *6*, 1041.

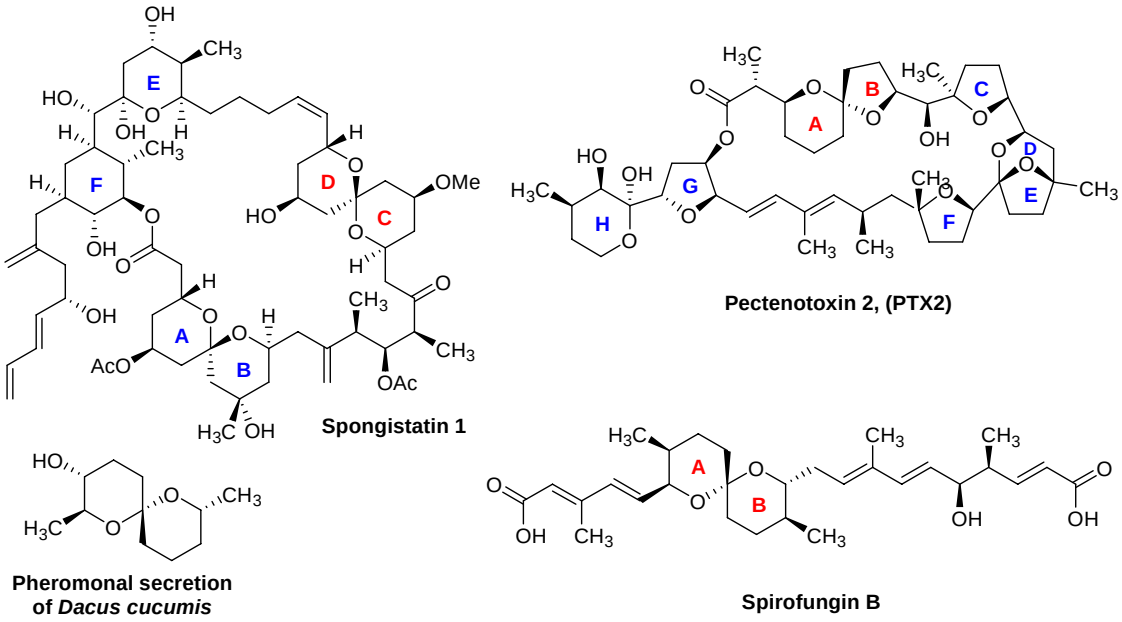


Figure 7: Selected examples of spiroketal natural products bearing non-anomeric spiroketals (in red)

Because the conformation of spiroketals at the spiro-ring junction is typically governed by the anomeric effect,[88] a broad understanding of this concept is essential to the importance of the chemistry described below. The anomeric effect is the term given to the observation that pyran rings with alpha-heteroatom substitution will typically adopt (in the absence of another, more dominant conformational bias) the chair conformation which places the heteroatom in an axial position (**Figure 8**). The stabilizing effect of an axial heteroatom has been attributed to a range of influences. While the relative importance of some of these influences is under dispute, the overall effect is probably a weighted average of all or many of them. One simple explanation is that an equatorial heteroatom possesses a dipole that is roughly aligned to that of the pyran oxygen creating a destabilizing repulsive interaction. This is mitigated by ring flipping to the axial conformation where the dipoles point in roughly opposite directions, which creates a lower energy state. Similarly, an electron rich heteroatom in an equatorial orientation feels the

[88] Deslongchamps, P. In *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: New York, 1983.

electrostatic repulsion of two gauche non-bonded electron pairs, which should be disfavored relative to the single gauche interaction observed in the axial configuration.

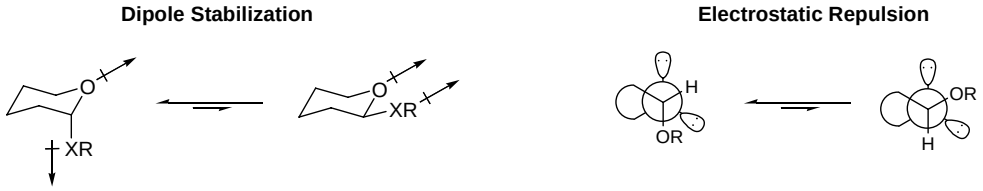


Figure 8: Contributing explanations for anomeric stabilization

Another very widely accepted factor in explaining the stability of the anomeric effect is the ability of non-bonded electron pairs in each heteroatom to donate through hyperconjugation into the $\sigma^*_{C\text{-}X}$ orbital of the adjacent carbon-heteroatom bond (**Figure 9**). Donating ability is maximized in the anomeric conformation because the lone pairs of each heteroatom are antiperiplanar to the adjacent carbon heteroatom bond. In the equatorial conformation, only electron donation by the α-heteroatom into the $\sigma^*_{C\text{-}O}$ is possible because the lone pairs of the pyran ring-oxygen are not antiperiplanar to the α-heteroatom. The dominance of the axial conformer is thus rationalized by the favorable contribution of two "resonance" forms over the single resonance form of the equatorial conformer. A stabilizing energy of approximately 2.4 kcal/mole has been estimated for the anomeric conformation.[89]

[89] Deslongchamps, P.; Rowan, D. D.; Pothier, N.; Sauve, T.; Saunders, J. K. *Can. J. Chem.* **1981**, *59*, 1105-1121.

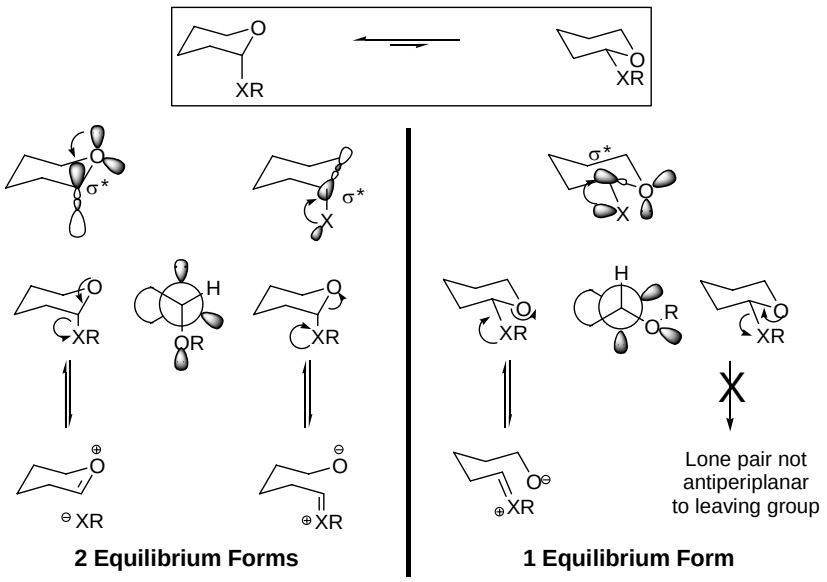


Figure 9: Hyperconjugative resonance forms in the anomeric conformation

It is important, at this point, to emphasize the difference between conformation and stereochemistry in spiroketals. In the absence of acid, the stereochemistry of the spiro ring junction on the pyran ring is set in a given molecule, but the conformation of a pyran ring can change to accommodate the most stable arrangement of substituents to satisfy electronic and steric concerns. The conformations of spiroketals are especially illustrative of this point. Because each pyran ring has the α-oxygen substitution of its neighboring pyran ring, each ring can afford anomeric stabilization to the other. This provides a substituted spiroketal with four possible chair conformations, with varying levels of anomeric stabilization as illustrated in **Figure 10** for a generically disubstituted spiroketal. At the [6,6] ring size, the preferred conformation adopted by most substituted spiroketal natural products is such that the spirocenter is doubly stabilized by the anomeric effect.

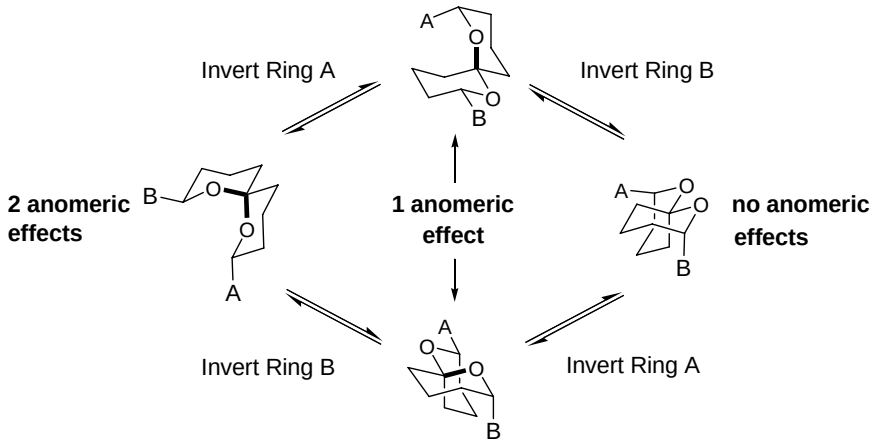


Figure 10: The four possible chair conformers of disubstituted spiroketals

In some diastereochemical relationships, steric interactions observed in the anomerically favored conformation outweigh the stabilizing energy of the anomeric effect. In these cases, the spiroketals will undergo ring flips until steric congestion is avoided at the expense of the anomeric effect.[90] "Non-anomeric spiroketals,"--defined as *those bearing fewer than the maximum number of anomeric interactions*--are difficult to synthesize under equilibrating reaction conditions because of the tendency to epimerize at the spirocenter, often forming the more stable diastereomer.[91] A simple example of this phenomenon is observed in the 1,7-dioxaspiro[5,5]undecane family of spiroketals.[92] Kitching and co-workers have done extensive work to characterize the 2,8-dimethyl-1,7-dioxaspiro-[5,5]-undecane spirocycles[93,94,95] and their stable conformations. The three diastereomers of this molecule are components of the rectal gland pheromonal secretion of the cucumber fly *Dacus cucumis*, and are depicted in **Figure 11**. The (*E,E*) component **44** is epimeric at the spirocenter with the (*Z,Z*) component **46**, and both

[90] Spiroketals of this type have been termed "contrathermodynamic spiroacetals," although the implication that these configurations are either always not the thermodynamically favored product—or even less true, in opposition to the laws of thermodynamics—makes the term "non-anomeric spiroketals" preferential, and it will be used throughout the remainder of this chapter.
[91] For an excellent review on non-anomeric spiroacetals in natural products see: Aho, J. E.; Pihko, P. M.; Rissa, T. K. *Chem. Rev.* **2005**, *105*, 4406-4440.
[92] Kluge, A. F. *Heterocycles* **1986**, *24*, 1699-1740.
[93] Mori, K.; Tanida, K. *Tetrahedron* **1981**, *37*, 3221-3225.
[94] Kitching, W.; Lewis, J. A.; Perkinds, M. V.; Drew, R.; Moore, C. J.; Schurig, V.; Konig, W. A.; Francke, W. *J. Org. Chem.* **1989**, *54*, 3893-3902.
[95] Chen, J.; Fletcher, M. T.; Kitching, W. *Tetrahedron: Asymmetry* **1995**, *6*, 967-972.

enantiomers of the (*E,Z*) component **45** have also been described. According to Kitching, the conformation adopted by **3** places both oxygens of the spiroketal in equatorial positions. Indeed, as shown in **Figure 11**, significant steric interactions are produced by adopting the doubly anomeric conformation, causing the molecule to preferentially adopt the completely non-anomeric conformation shown. The steric interactions are apparently less favorable than the 4.8 kcal/mole stabilization estimated from the contribution of two anomeric effects. Owing to its higher energy, the treatment of non-anomeric diastereomer **46** with trifluoroacetic acid under equilibrating conditions yields a complete epimerization at the spirocenter to produce the more stable diastereomer **44**.

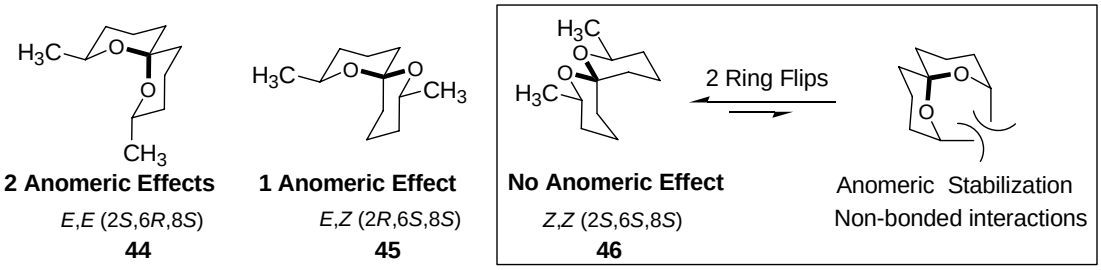


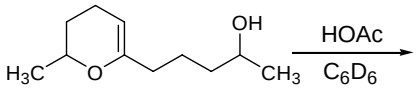
Figure 11: Three pheromonal secretion components of the cucumber fly and their most stable conformations

Synthesis of non-anomeric spiroketals

As expected, the thermodynamic deficit of these products is felt in the transition state, and as such, acid-catalyzed cyclization of the appropriate dimethyl keto-diol forms **44** to a much greater extent than its epimer **46**.[93,95,96,97,98,99,100] Despite efforts by Deslongchamps[101] to increase the ratio of the non-anomeric stereoisomer by treatment of the dihydropyran precursor with acid under kinetic conditions, the thermodynamic product **44** is produced in greater yield than **46** (**Scheme 1**).

[96] Mori, K.; Watanabe, H. *Tetrahedron* **1986**, *42*, 295-304.
[97] Yadav, J. S.; Gadgil, V. R. *Tetrahedron Lett.* **1990**, *31*, 6217-6218.
[98] Solladie, G.; Huser, N. *Tetrahedron: Asymmetry* **1994**, *5*, 255-260.
[99] Cohen, T.; Tong, S. *Tetrahedron* **1997**, *53*, 9487-9496.
[100] Brown, H. C.; Kulkarni, S. V.; Racherla, U. S.; Dhokte, U. P. *J. Org. Chem.* **1998**, *63*, 7030-7036.
[101] Pothier, N.; Goldstein, S.; Deslongchamps, P. *Helv. Chim. Acta.* **1992**, *75*, 604-620.

Scheme 26: Kinetic cyclization leads predominantly to the anomerically stabilized diastereoisomers



44 (*E*,*E*) **45** (*E*,*Z*) **46** (*Z*,*Z*)

1.5 : 2.5 : 1

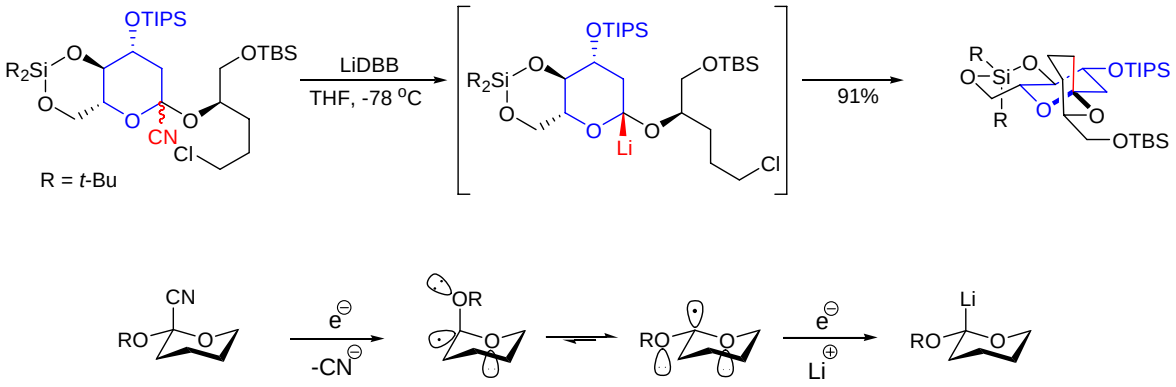
To our knowledge no method has been described which synthesizes the (*Z*,*Z*)-isomer **46** exclusively, or in greater yield than the (*E*,*E*)-isomer **44**. This observation is not surprising considering the implications of selectively synthesizing the thermodynamically least stable diastereomer. A few, highly innovative methods, taking advantage of the tendency of either a radical[102,103] or lithiate (anion)[104,105] to adopt the anomeric position at the tertiary α-center, have permitted stereoselective formation of spiroketals possessing only one anomeric relationship (*E*,*Z*-type spiroketals). In all cases, a means of stabilizing the conformation of high energy intermediates in the ring forming step is required. This is usually achieved by locking the conformation of one ring with bulky substituents or fused rings while the second ring forms, or by hydrogen or metal ion bonding in the transition state.

Scheme 27 highlights Rychnovsky's reductive cyclization strategy toward non-anomeric spiroacetals. Treatment of the mixture of cyanoacetals with LiDBB creates an intermediate organolithiate, which ring closes on the tethered alkyl halide. The mechanism of this reaction, shown in the bottom of **Scheme 27** is demonstrative of the utility of the anomeric effect. In this case, reduction of the oxonium cation generates a radical intermediate, which can freely equilibrate to either the equatorial or axial position, potentially inverting the stereochemistry. However, the axial radical is favored by the anomeric effect,[106] permitting a second reduction to the α-alkoxy alkyllithiate, which are known to be conformationally stable.

---

[102] Kahne, D.; Yang, D.; Lim, J. J.; Miller, R.; Paguaga, E. *J. Am. Chem. Soc.* **1988**, *110*, 8716-8717.
[103] Ferrier, R. J.; Hall, D. W. *J. Chem. Soc. Perkin Trans. 1* **1992**, 3029-3034.
[104] Rychnovsky, S. D.; Hata, T.; Kim, A. I.; Buckmelter, A. J. *Org. Lett.* **2001**, *3*, 807-810.
[105] Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201-1202.
[106] Rychnovsky, S. D.; Powers, J. P.; LePage, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 8375-8384.

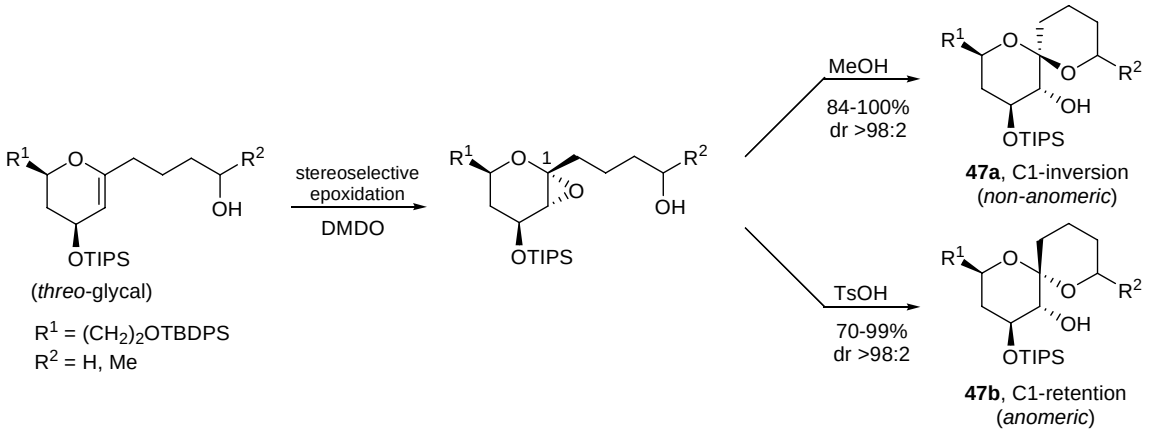
Scheme 27: Rychnovsky's reductive cyclization strategy and proposed mechanism



The Tan group has recently reported unique and highly stereoselective approaches to the synthesis of stereochemically diverse non-anomeric spiroketals *via* kinetic spirocyclizations of glycal epoxides. The initial report detailed that after stereoselective *anti*-epoxidation[107] of a trisubstituted *threo*-glycal, spontaneous epoxide opening upon warming gave a mixture of the possible spiroketals possessing C^1-inversion (**47a**) and C^1-retention (**47b**) of configuration (**Scheme 28**).[108] The authors discovered that spirocyclization with inversion of configuration (products bearing one anomeric relationship) could be favored (up to 100:0 dr) through the addition of excess methanol at low temperature after epoxidation, while the addition of TsOH equilibrated the mixture to the thermodynamically favored "retention" spiroketal possessing double anomeric stabilization.

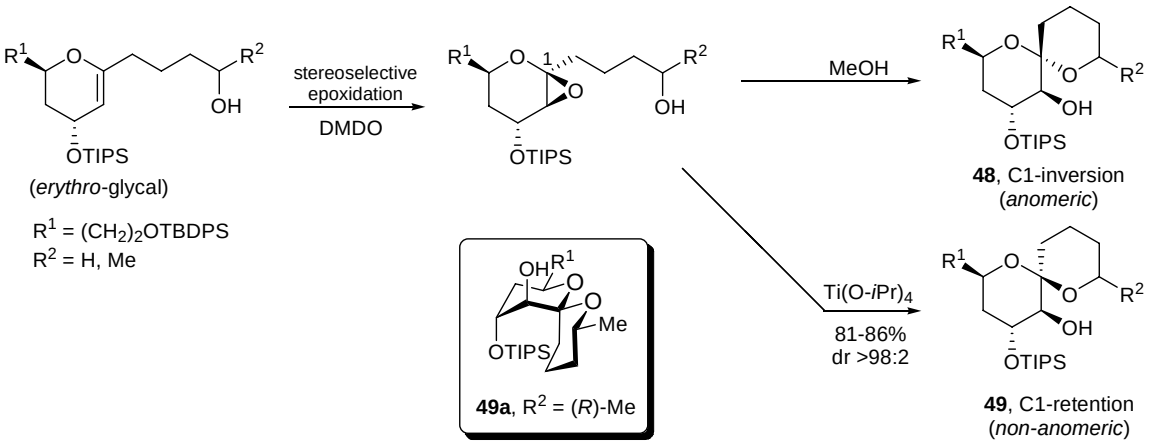
[107] Halcomb, R. L.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6661-6666.
[108] Potuzak, J. S.; Moilanen, S. B.; Tan, D. S. *J. Am. Chem. Soc.* **2005**, *127*, 13796-13797.

Scheme 28: Non-anomeric spiroacetals *via* methanol-induced kinetic spirocyclization of *threo*-glycal epoxides



In the *erythro*-glycal series,[109] the products of spontaneous spirocyclization under methanolic conditions yielded the thermodynamically favored C^1-inversion pathway resulting in spiroketals **48** (possessing two anomeric relationships); while a multidentate Lewis acid-mediated spirocyclization favors the C^1-retention products **49** (non-anomeric) (See **Scheme 29**). Significantly, when the stereochemistry at R^2 = (*R*)-Me, the product formed demonstrates significant steric interaction in the mono-anomeric conformation to undergo a single ring flip at the newly-formed ring to yield the *doubly* non-anomeric spiroketal **49a**.

Scheme 29: Non-anomeric spiroacetals *via* Ti(O-*i*Pr)$_4$-mediated kinetic spirocyclization of *erythro*-glycal epoxides

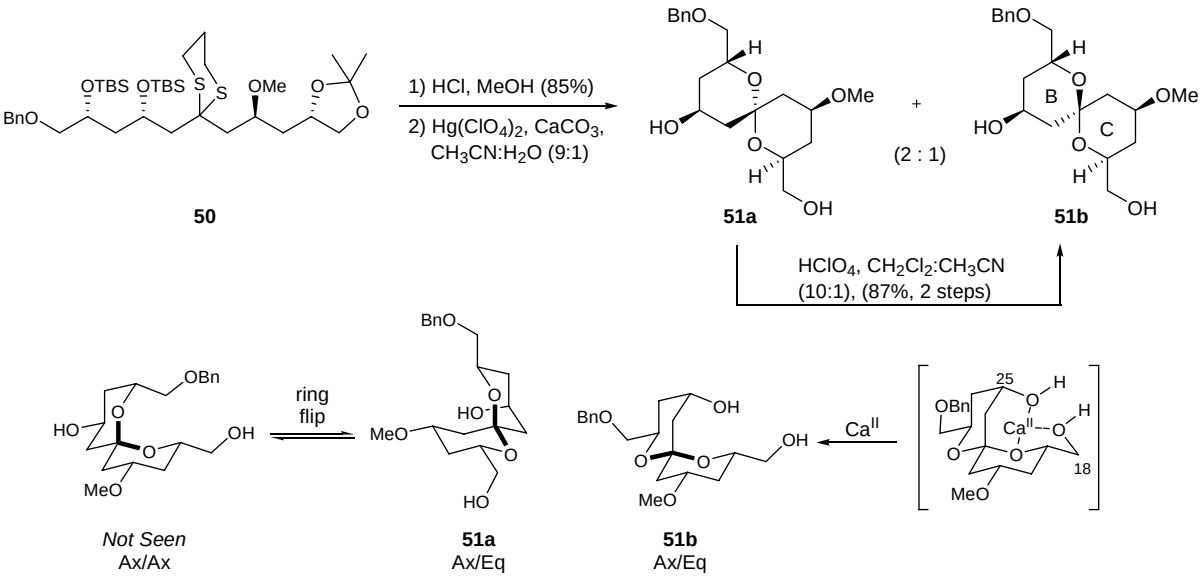


[109] Moilanen, S. B.; Potuzak, J. S.; Tan, D. S. *J. Am. Chem. Soc.* **2006**, *128*, 1792-1793.

During the construction of the ABCD fragment of Spongistatin 1, a marine macrolide antibiotic containing 2 spiroketal subunits, the Smith group was challenged by the complex subunit containing the CD spiroketal moiety, which possesses only one anomeric relationship (**Scheme 30**).[110] The construction of this fragment involved removal of both TBS and acetonide protecting groups of **50** with HCl/MeOH, followed by treatment with mercury perchlorate/calcium carbonate buffer to produce the singly anomeric products **51a** and **51b** in a 2:1 ratio. While the stereochemistry of substituents around the rings is such that the favored conformation of both products resides in only the single anomeric conformation (the axial/axial conformer of **51a** was not observed by NOE), only diastereomer **51b** possesses the requisite stereochemistry of the natural product. Fortunately, the mixture could be completely converted to the desired isomer **51b** by treating the reaction mixture with perchloric acid prior to purification. The success of the conversion was attributed to residual calcium ions in the reaction mixture coordinating to the C-18 and C-25 hydroxyl groups and the C-ring pyran oxygen, which presumably stabilizes the structure. This discovery proved extremely useful at a later stage in the synthesis of Spongistatin 2 when epimerization to the undesired stereochemistry at the spirocenter occurred unexpectedly. Simply re-subjecting the C-23-epimer of the natural product to perchloric acid in the presence of Ca^{II} ions equilibrated the mixture in favor of the desired stereoisomer.[111]

[110] Smith, A. B., III; Doughty, V. A.; Lin, Q.; Zhuang, L.; McBriar, M. D.; Boldi, A. M.; Moser, W. H.; Murase, N.; Nakayama, K.; Sobukawa, M. *Angew. Chem., Int. Ed.*, **2001**, *40*, 191-195.
[111] Smith, A. B., III; Lin, Q.; Doughty, V. A.; Zhuang, L.; McBriar, M. D.; Kerns, J. K.; Brook, C. S.; Murase, N.; Nakayama, K. *Angew. Chem., Int. Ed.*, **2001**, *40*, 196-199.

Scheme 30: Smith's synthesis of the non-anomeric CD spiroketal fragment of Spongistatin 1

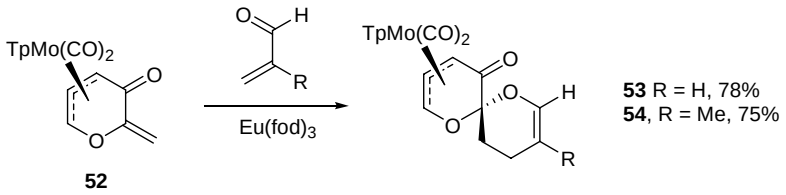


In all examples described above, the stereochemistry at the spirocenter , and the number of anomeric interactions in the preferred conformation of the product are dependant upon both the conformational bias in the transition state of the ring-forming step, and the preset stereochemistry of the substituents around the rings. Because of this, variation of stereochemistry and substituent size at other locations on the ring will invariably influence the selectivity of the ring-forming step.

Project Design

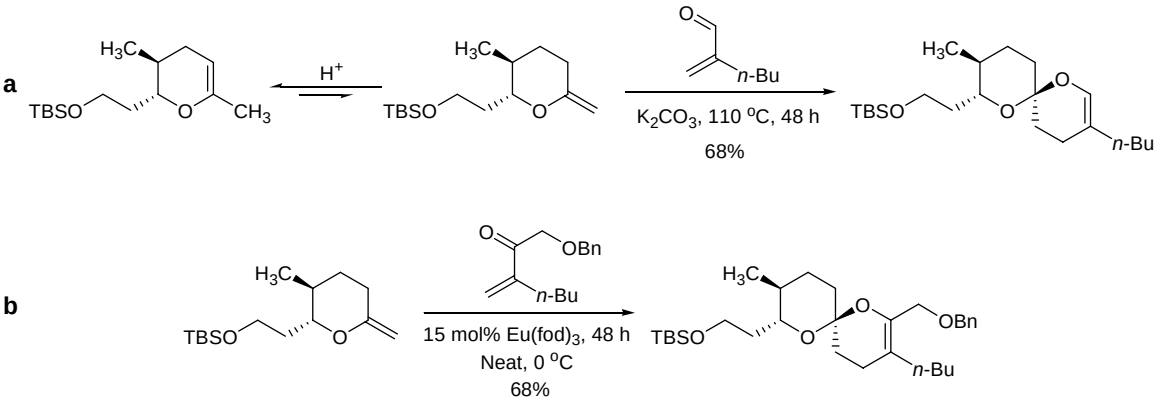
In reviewing some unpublished preliminary results obtained by Drs. Ramón Gómez Arrayás and Ana Alcudia in the Liebeskind group, the possibility of using the organometallic enantiomeric chiron strategy for spiroketal synthesis was recognized. They had found that exocyclic enone scaffold **52** underwent inverse electron demand hetero-Diels-Alder cycloaddition with unsaturated aldehydes in the presence of catalytic Lewis acid to yield spirocycloadducts in good yields (**Scheme 31**). Unfortunately, no detailed experimental remained from this work, and we have been forced to re-investigate the appropriate conditions.

Scheme 31: Unpublished preliminary results of hetero Diels-Alder cycloadditions



The synthesis of spiroketals *via* inverse electron demand HDA is known.[82, 112] Thermal cycloadditions are known, however the harsh conditions required to promote cyclization (>110 ^{o}C) typically cause competitive oligomerization of the α,β-unsaturated carbonyls decreasing the yields of cycloadducts. Additionally, the exocyclic vinyl ether starting materials for these reactions are generally unstable and must be generated *in situ*. Rapid double bond isomerization to the *endo*-isomer is extremely facile, even in base washed glassware, and so the cycloaddition requires the presence of base (**Scheme 32a**).[113] Lewis acid catalyzed inverse electron demand hetero Diels-Alder cycloadditions are also known, and allow the reactions to occur at lower temperatures (**Scheme 32b**).[114]

Scheme 32: Inverse electron demand HDA, under thermal and Lewis acid catalyzed reaction conditions



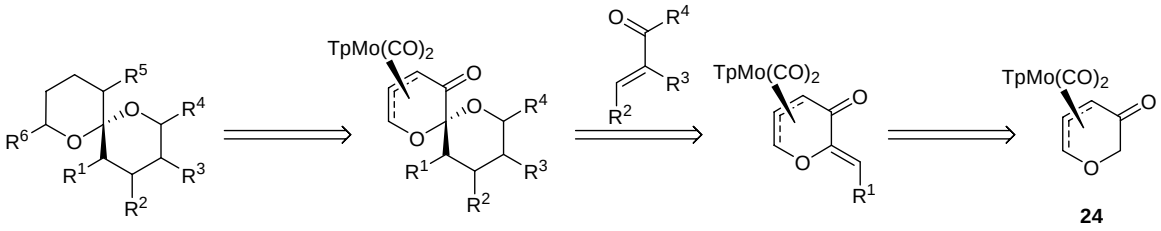
[112] For examples see: (a) El Sous, M.; Rizzacasa, M. A. *Tetrahedron Lett.* **2000**, *41*, 8591-8594. (b) Zhuang, W.; Thorhauge, J.; Jorgensen, K. A. *Chem. Commun.* **2000**, 459-460. (c) McRae, K. J.; Rizzacasa, M. A. *J. Org, Chem.* **1997**, *62*, 1196-1197. (e) Ireland, R. E.; Daub, J. P. *J. Org. Chem.* **1983**, *48*, 1303-1312.

[113] Cuzzupe, A. N.; Hutton, C. A.; Lilly, M. J.; Mann, R. K.; McRae, K. J.; Zammit, S. C.; Rizzacasa, M. A. *J. Org. Chem*. **2001**, *66*, 2382-2393.

[114] El Sous, M.; Ganame, D.; Tregloan, P. A.; Rizzacasa, M. A. *Org. Lett.*, **2004**, *6*, 3001-3004.

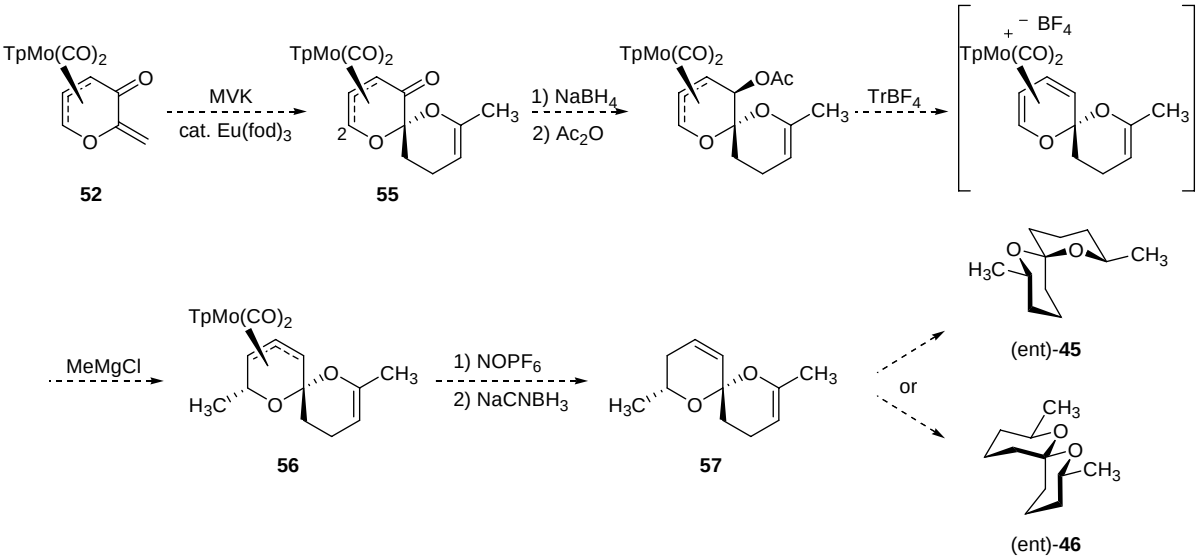
It was hypothesized that if the scope of this reaction could be generalized, then the organometallic enantiomeric chiron strategy would be readily applicable to the synthesis of highly functionalized spiroketals, further extending the utility of the Liebeskind molybdenum scaffolds in diversity oriented synthesis (**Scheme 33**). Tantamount to the cycloaddition step, however, is the need to develop a general method to functionalize other positions around the initial pyran ring (R^5 and R^6) as well.

Scheme 33: Hetero Diels-Alder cycloaddition provides access to diverse spiroketal structures



The goal to create a general protocol for the synthesis of highly functionalized pyrans thus presented three major methodological challenges: 1) development of a general reaction protocol for hetero Diels-Alder spirocycloaddition to enone **52**; 2) further functionalize the scaffold ring; 3) decomplex the metal moiety under conditions that maintain the stereochemical integrity of the chiral centers set earlier including the spirocenter. Upon a detailed evaluation of the likely stereochemical outcome of some proposed transformations, it was reasoned that the $TpMo(CO)_2$ moiety would supply the appropriate stereochemical and conformational bias in the HDA cycloaddition step, along with a subsequent stereospecific functionalization to provide access to non-anomeric pheromonal spiroketals **45** and **46** (**Scheme 34**).

Scheme 34: Proposed synthesis of non-anomeric spiroketal pheromones



Novel aspects of the proposed methodology would be the stereo- and regioselective hetero Diels-Alder reaction of methyl vinyl ketone to the exocyclic enone **52**, providing spiroketal **55**. The stability of enone **52** offers an advantage over the alkylidene substrates used by Rizzacasa in **Scheme 32** because equilibration of the vinyl ether is not observed. Stereoselective functionalization of the 2-position of **55** could be accomplished by reduction and protection of the ketone followed by ionization of the resulting acetoxy group,[115] creating a molybdenum stabilized cation-diene intermediate. To this electrophilic species would be added methyl Grignard reagent, which should install the methyl group stereoselectively *anti* to the metal moiety to provide compound **56**. Subsequent reductive demetalation following a well-established protocol would provide **57**.[116] It was expected that reduction would provide access to mono-anomeric spiroketal **45** or doubly non-anomeric **46** depending on the stereoselectivity of the reduction (recall **Figure 11**).

This chapter initially details the effort toward development of a general protocol for the synthesis of functionalized spiroketals. As the investigation progressed, however, the focus of the study

[115] Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1999**, *121*, 5811-5812.
[116] Shu, C.; Alcudia, A.; Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 12477-12487.

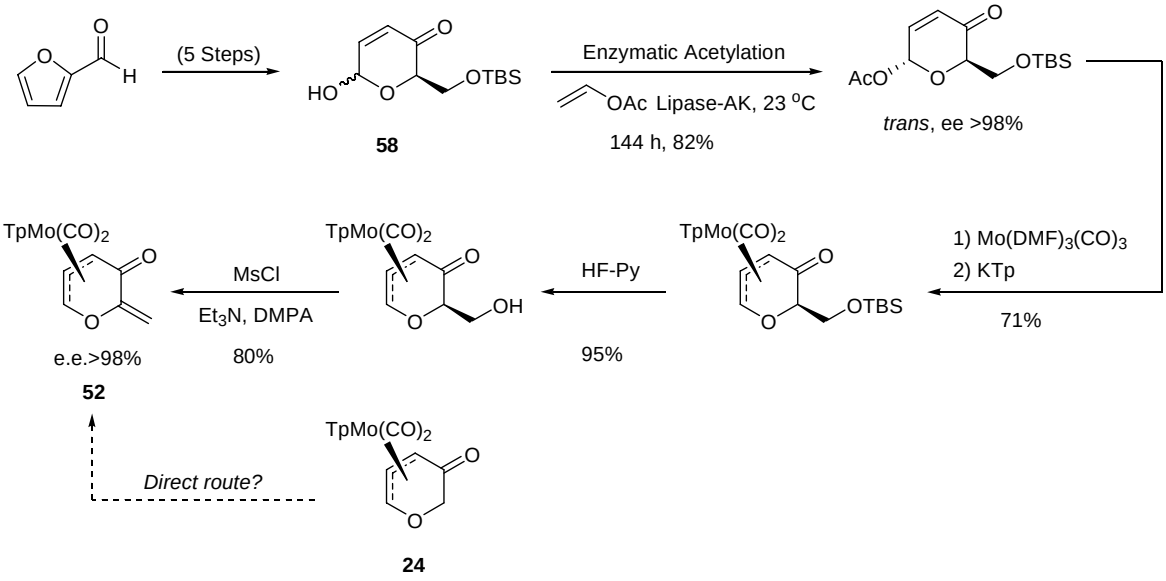
changed considerably as new results opened up novel applications of the chemistry beyond simply construction of spiroketals. The results in this chapter and the next, thus, demonstrate the evolution of a narrowly focused (and applicable) project into an idea of higher conceptual value, the successful application of which will be demonstrated in the final chapter.

Results and Discussion:

Improved Synthetic routes to enone complexes

The synthesis of exocyclic enone **52** by the procedure utilized by Dr. Arrayás is shown in **Scheme 35**.[117] The synthesis up to compound **58** is high yielding and follows literature precedent established by O'Doherty and coworkers.[118] Unfortunately, the protocol is lengthy and a direct route to exocyclic enone **52** (and its substituted analogs) from the more readily available 5-oxo pyranyl scaffold **24** would be preferable.

Scheme 35: Previous synthesis of enone complex 9 in high ee

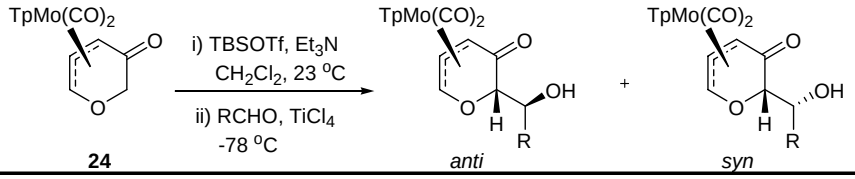


An alternative and general approach to α-substituted 5-oxopyranylmolybdenum complexes *via* an aldol/dehydration sequence was investigated by Dr. Heilam Wong and Dr. Yongqiang Zhang in

[117] Arrayás, R. G.; Alcudia, A. Liebeskind Group, unpublished results.
[118] Harris, J. M.; Keranen, M. D.; O'Doherty, G. A. *J. Am. Chem. Soc.* **1999**, *64*, 2982-2983.

the Liebeskind group. They independently found that aldol condensation of TMEDA-stabilized lithium enolates of **24** yielded aldol products in moderate yields and with significant decomposition.[119] Fortunately, scaffold **24** reacted with Et_3N and TBSOTf to generate the sily enol ether in excellent yield (99%). Generated *in situ*, the silyl enol ether underwent $TiCl_4$-mediated Mukaiyama aldol reaction with various aldehydes in excellent yields with *anti*-selectivity (**Table 7, Entries 1-5**).

Table 7: Mukaiyama aldol reactions of oxopyranyl scaffold 24[120]



24 *anti* *syn*

Entry	Ketone	R =	*anti* :*syn*	% Yield	%ee
1	(? -**24**	Ph	7:1	90	--
2	(? -**24**	*i* -Pr	>10:1	84	--
3	(? -**24**	Me	2:1 (**59a**:**59b**)	91	--
4	(-)-**24**	Ph	7:1	93	99
5	(-)-**24**	*i* -Pr	>10:1	85	99
6	(? -**24**	H[a]	N/A **59c**	23	--

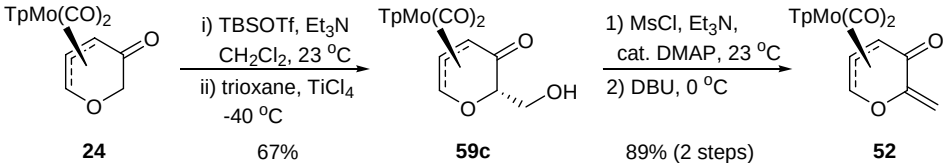
a) *s*-trioxane used as a formaldehyde equivalent

Unfortunately, while various aldehydes can undergo Mukaiyama aldol reactions, the yield of the reaction with the formaldehyde equivalent *s*-trioxane was very low as initially reported (**Table 7, Entry 6**). Attempts to improve the reaction using various other aldehyde/ester equivalents resulted in lower yields or no reaction. After optimization, it was discovered that reaction with three equivalents of *s*-trioxane and 1.5 equivalents of $TiCl_4$ at -40 °C would provide **59** in 67% yield on 3 grams scale (**Scheme 36**). An alternative two-step procedure for elimination of the primary alcohol was found to be higher yielding and procedurally faster than that used in **Scheme 35**. Isolation of the mesylate, followed by elimination with DBU provided the enone in 89%

[119] Wong, Heilam. Ph.D. Thesis. Emory University, 2006, p75.
[120] Wong, Heilam. Ph.D. Thesis. Emory University, 2006, p79.

yield over two steps. This three pot synthesis of unsubstituted enone **52** is a drastic improvement over the previous synthesis, and also represents a more general route to substituted enones as well (*vide infra*).

Scheme 36: Improved synthesis of unsubstituted enone 9

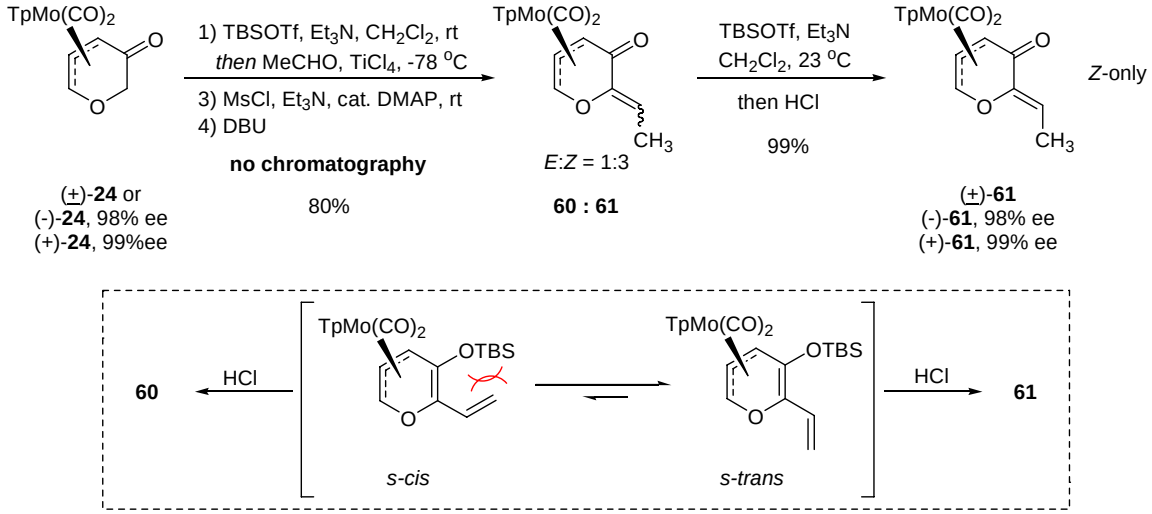


This two step dehydration sequence was also applicable to the other Mukaiyama aldol products from **Table 7**,[121] however, even the three step protocol was laborious to perform on large scale, separating each product at each step. It was discovered that the aldol/dehydration sequence could be performed iteratively, and without separation of the aldol products or mesylates and only requires an extraction and filtration through silica plug. This streamlined protocol is of considerable utility during the scale-up procedures required for total synthesis or method development using later stage starting materials. Using this procedure, the elimination of unpurified mesylates yields a mixture of *E*- and *Z*-isomers **60** and **61** in a 1:3 ratio (**Scheme 37**). Fortunately, the mixture of isomers could be quantitatively converted into a single conjugated silyl enol ether using TBSOTf and Et_3N, which was reprotonated with HCl (solution in dioxane) to immediately provide only the *Z*-isomer **61** (to the limits of ^1H NMR detection) in 99% yield based on the mixture of starting isomers.[122] Under these non-equilibrating conditions (the pure *E*-isomer is unreactive to 1 equivalent of HCl in CH_2Cl_2) the protonation must reflect the equilibrium position of the two rotational isomers. Given that only the *Z*-isomer is formed, it is assumed that the *s-trans* conformation, which should lead to the *Z*-isomer upon reprotonation,

[121] Zhang, Y. Liebeskind Group, unpublished results.
[122] It was found that the silyl enol ether required a full equivalent of HCl for complete conversion, unless washed with water first, after which 0.2 equivalent was sufficient for complete conversion. Curiously, washing the silyl enol ether with 5% aqueous HCl solution did not initiate hydrolysis.

must dominate the equilibrium (>20:1). This reaction sequence consistently provides approximately 4.20 grams of **61** from 5.00 grams of starting scaffold **24** (79.4% over 4 steps), and proceeds without loss of enantiomeric purity.

Scheme 37: Optimized procedure for the synthesis of substituted enones

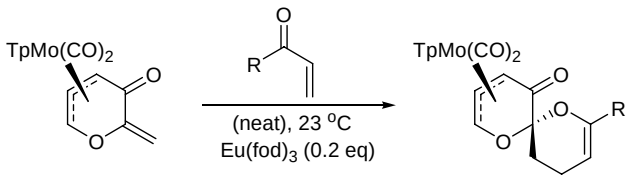


Hetero Diels-Alder Cycloadditions

When **52** was reacted with 1.5-2.0 equivalents of acrolein in CH_2Cl_2 with catalytic $Eu(fod)_3$, no reaction was observed after 24 hours. Stronger Lewis acids such as $ZnCl_2$ and Et_2AlCl provided the target compound **53**, but in low yields (<25%). However, it was discovered that running the reaction with acrolein as solvent (~77 equiv) with 20 mol% $Eu(fod)_3$ [123] provided the spirocycloadduct in 54% yield after 91 hours at room temperature (**Scheme 38**). Encouragingly, the new reaction conditions proved effective for the HDA cycloaddition of ketones as well. Methyl vinyl ketone undergoes HDA cycloaddition under similar conditions to yield spirocycloadduct **55** in 44% after 3 days at room temperature.

[123] Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 3716-3717.

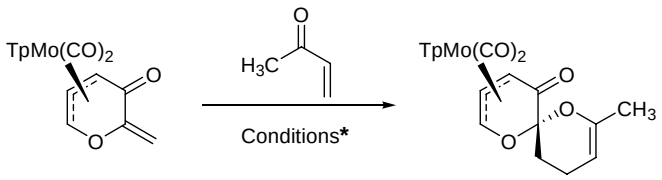
Scheme 38: Lewis Acid-catalyzed Hetero Diels-Alder reaction



R = H, 91 h **53** 54%
R = Me, 72 h **55**, 44%

Table 8 summarizes the results of the optimization study of the cycloaddition of MVK with **52**. Increasing the amount of catalyst did not increase the yield of the reaction, and catalyst decomposition is apparently not the reason for low yields (**Table 8,** compare **Entries 2 and 3**). The reaction also works with $Yb(fod)_3$, but purification was more difficult since minor impurities remained and could not be removed. Triflate ligands cause rapid decomposition (**Entries 5 and 6**). Fortunately, at higher temperatures the reaction was completed faster and with improved yields (**Entries 7-11**). The reaction could be run much more rapidly under microwave irradiation (**Entry 12**) as the cycloadduct was obtained in 59% yield after 90 minutes at 70 °C.

Table 8: Optimization study of Hetero Diels-Alder Cycloaddition

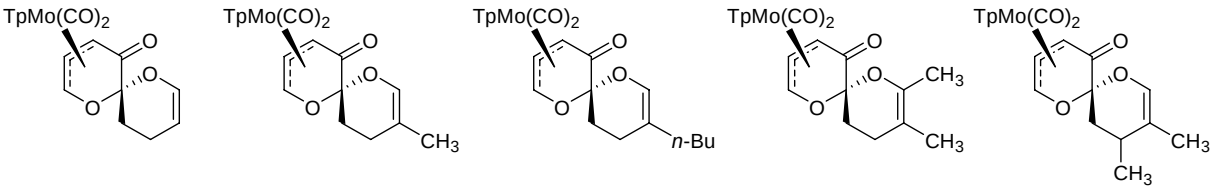


52 55

Entry	Catalyst (Equiv)	Temp (^{o}C)	Time (h)	Yield[a]
1	$Eu(fod)_3$ (0.2)	23	72	44%
2	$Eu(fod)_3$ (0.4)	23	67	47%
3	$Eu(fod)_3$ (0.2 then 0.2 after 24h)	23	64	50%
4	$Yb(fod)_3$ (0.2)	23	63	~50%[b]
5	$Sc(OTf)_3$ (0.2)	23	18.5	Decomp.
6	$Yb(OTf)_3$ (0.2)	23	23	Decomp.
7	$Eu(fod)_3$ (0.2)	30	44	58%
8	$Eu(fod)_3$ (0.2)	40	24	52%
9	$Eu(fod)_3$ (0.2)	50	23	65%
10	$Eu(fod)_3$ (0.2)	60	24	68%
11	$Eu(fod)_3$ (0.2)	60	36	80%
12	$Eu(fod)_3$ (0.2)	70 (w)	1.5	59%

Conditions:* Compound **52 and catalyst were dissolved in minimum amount of methyl vinyl ketone, and heated in a sealed tube for the indicated amount of time. a) Isolated yields; b) Purification difficulties precluded accurate yield

Under these optimized conditions, the scope of the cycloaddition reaction was briefly investigated for various substituted ketones and aldehydes, the products of which are shown in **Figure 12**. Ketones and aldehydes reacted similarly, and substitution at the α-position of the aldehyde (compounds **54**, **62** and **63**) did not dramatically affect the reaction. On the contrary, β-substitution slowed the reaction considerably. After 50 hours at 60 ^{o}C, cycloadduct **64** was collected in only trace amounts (< 10%) as a 1:1 mixture of diastereomers by ^{1}H NMR. No reaction was observed with methyl acrylate, or the vinylogous ester 4-methoxy-3-butene-2-one.



67%[a] **53** | 57%[a] **54** | 56%[b] **62** | 51%[c] **63** | trace[d] **64**

Conditions: a)50 °C, 24 h; b) 60 °C, 68 h; c) 60 °C, 24 h; d) 60 °C, 50 h

Figure 12: Scope of hetero Diels-Alder cycloaddition

It was of paramount importance to this study to determine the relative stereochemistry of the spirocycle, and with no other spectroscopic method capable of providing this information for this particular set of compounds, we turned to X-ray crystallography. Fortunately, unique among the family of compounds in **Figure 12** cycloadduct **62** was found to be crystalline, and a single-crystal X-ray diffraction study unequivocally established the regiochemistry and relative stereochemistry of the cycloadducts (**Figure 13**). As predicted, the unsaturated carbonyl group approaches the alkylidene from the face opposite to the metal moiety, with regiochemistry that places the oxygen at the spirocenter.

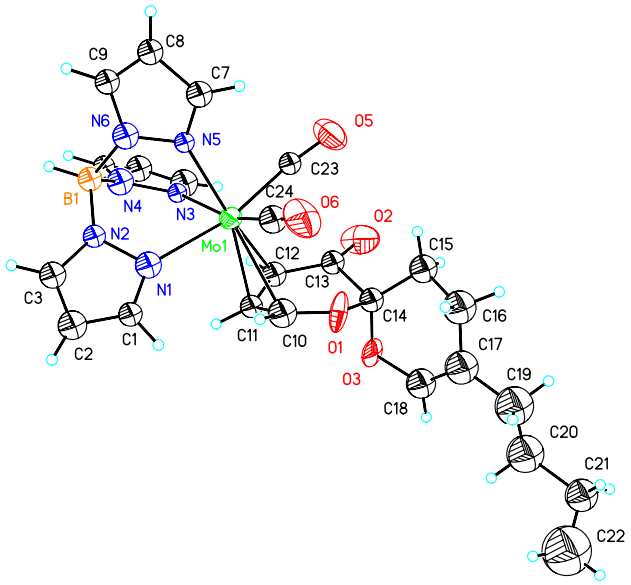
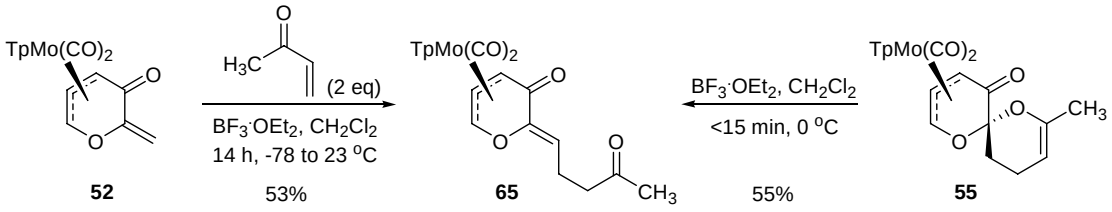


Figure 13: ORTEP of Spirocycloadduct 62

During the course of this study it was noticed that when **52** was reacted with methyl vinyl ketone under stronger Lewis acidic conditions ($BF_3{\cdot}OEt_2$, $TiCl_4$) **65** was formed as the major product, and no spirocycloadduct was ever isolated under these conditions (**Scheme 39**).[124] Because a Michael addition/deprotonation sequence seems a plausible mechanism, it is unclear whether the cycloadduct **55** is an intermediate in this reaction. A control experiment revealed, however, that it can be converted to the ring-opened product under the reaction conditions.

Scheme 39: Ring opening of cycloadduct

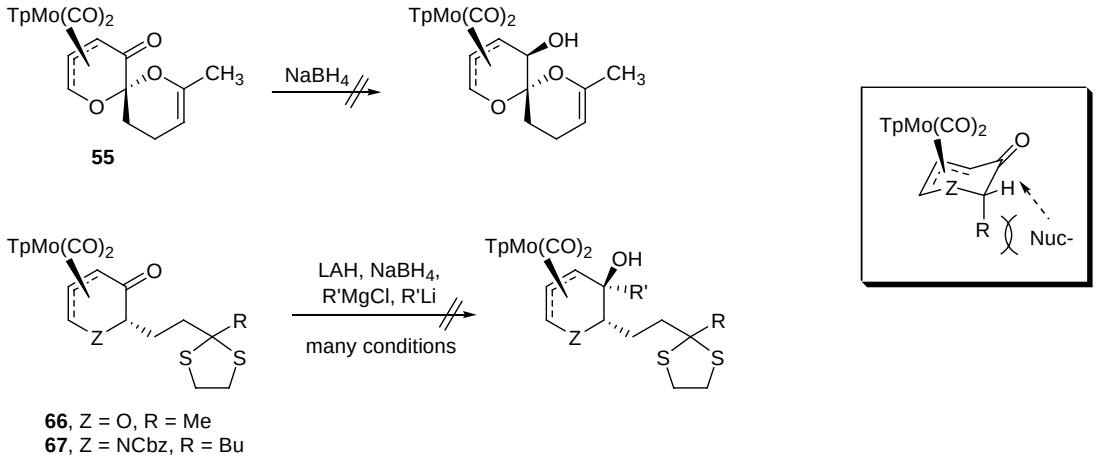


Attempts to Functionalize the 2-Position of Spiroketal Complex

Functionalization of the 2-position of **55** was envisioned through reduction of the ketone, followed by ionization of the secondary acetoxy group to create a cationic diene, followed by nucleophilic addition (recall **Scheme 34**). Unfortunately, reduction of the ketone failed, and only starting material was recovered. Precedent from our group corroborated this difficulty.[125] Dr. Heilam Wong found during his graduate study that reduction of ketones **66** and **67** did not occur with various nucleophiles under many conditions (**Scheme 40**). The lack of reactivity was attributed to the chair-like conformation adopted by the pyran and piperidine rings, which places an α-substituent (*anti* to Mo-moiety) in a pseudo-axial orientation, effectively blocking nucleophilic attack of the ketone.

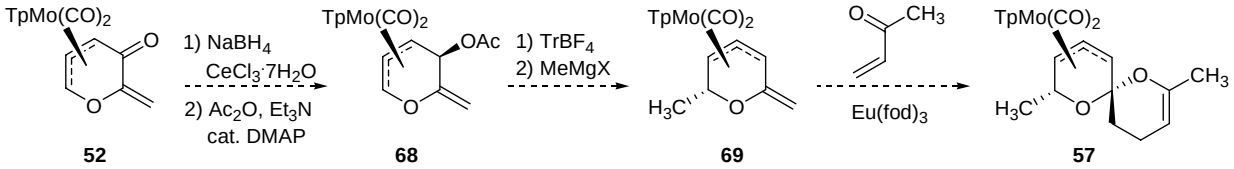
[124] This product was not observed using $Eu(fod)_3$ as catalyst.
[125] Wong, H. Ph.D. Thesis. 2006, Emory University.

Scheme 40: Hindered ketones of 6-*anti*-substituted 5-oxo complexes



This result suggested that the proposed pathway to functionalization at C^2 was not feasible, and so a new approach was devised, which would rely upon functionalization of the 2-position *first* followed by cycloaddition (**Scheme 41**). In this proposal, Luche reduction and protection of **52** would provide access to allylic acetate **68**. Subsequent ionization/nucleophilic addition of the acetate should provide compound **69**, which was expected to be even more electron rich than enone **52**, and thus more reactive to inverse electron demand hetero Diels-Alder cycloaddition.

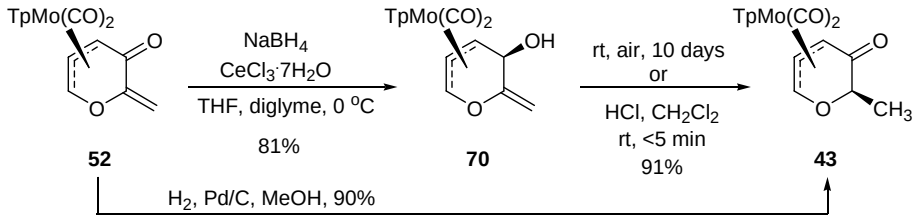
Scheme 41: Second generation synthesis of functionalized spiroketals



When reacted under standard Luche conditions (sodium borohydride, $CeCl_3 \cdot 7H_2O$, methanol), compound **52** gave an inseparable mixture of 1,2 and 1,4-addition products. Similar results were obtained with other reducing agents known to provide selective 1,2-addition (DIBAL, LAH, 9-BBN) possibly owing to the six-atom transition state of a carbonyl-coordinated metal hydride. Fortunately, it was discovered that using a solution of $NaBH_4$ in diglyme, under methanol-free conditions provided clean formation of the allylic alcohol **70** in good yield (**Scheme 42**).

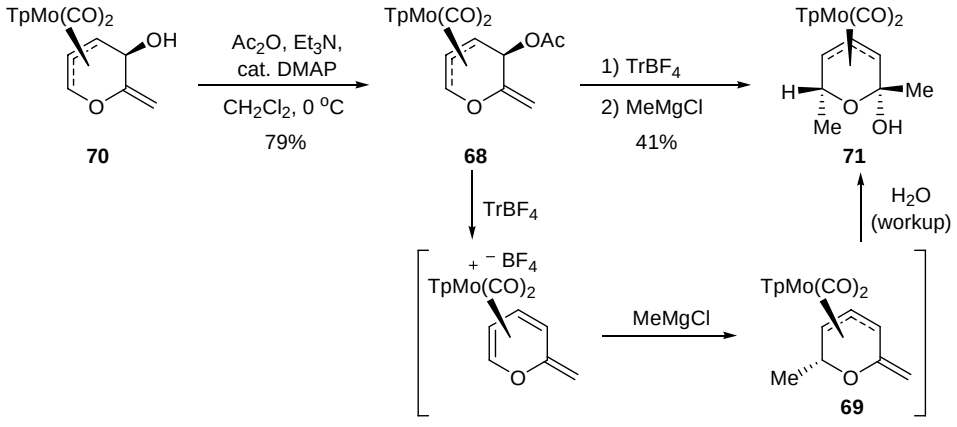
Interestingly, the Luche reduction product was found to undergo slow, but spontaneous and stereoselective semi-pinacol rearrangement[126] over 10 days in air to compound **43**. In the presence of one equivalent of HCl, the semi-pinacol reaction rapidly occurs in 91% yield. The stereochemistry of the migration was supported by the hydrogenation of **52** (presumed to occur *via* reduction of the olefin from the face opposite the metal moiety), which provided the spectroscopically identical product in 90% yield.

Scheme 42: Luche reduction of 52, and facile semi-pinacol rearrangement



Because of its instability, the allylic alcohol was immediately protected as the acetate in excellent yield. Under the ionization/nucleophilic addition reaction sequence, the target material was not obtained, however its hydrated analog **71** was isolated in moderate yield (**Scheme 43**). Presumably, the product **69** was formed during the reaction sequence, but was hydrated upon workup.

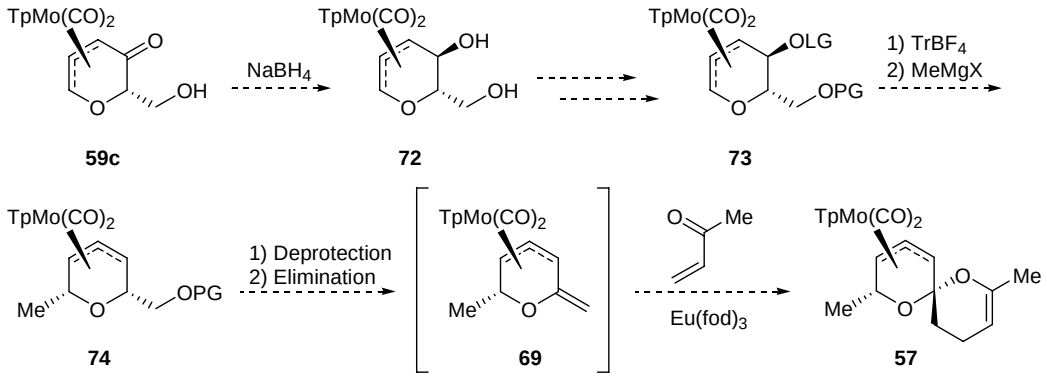
Scheme 43: Ionization/nucleophilic addition to alkylidene scaffold



[126] Coveney, D. J. In *Comprehensive Organic Synthesis*; Trost, B. M; Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, p777-801.

The success of the reaction was mitigated by the destruction of the alkylidene moiety, which must stay intact to undergo HDA cycloaddition. Unfortunately, the reaction conditions under which the nucleophilic addition occurs are not compatible with an *in situ* nucleophilic addition/cycloaddition sequence. Because of this, another alternative sequence was developed that proposes to generate the alkylidene moiety *in situ* after functionalization. Reduction of alcohol **59c** and derivitization of the diol into **73** with a leaving group adjacent to the metal allyl would permit an ionization/nucleophilic addition sequence to provide **74**. With compound **69** generated *in situ* by elimination of the alkoxymethyl moiety, cycloaddition would provide the desired cycloadduct **57** (**Scheme 44**).

Scheme 44: Third Generation synthesis of functionalized spiroketals

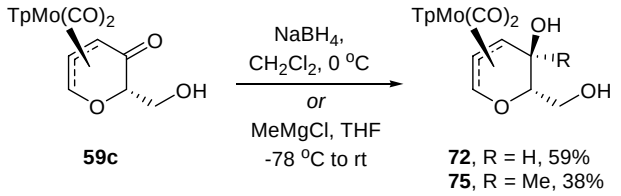


Somewhat surprisingly, reduction of *anti*-α-hydroxymethyl ketone **59c** with sodium borohydride occurred reliably and in good yields (**Scheme 45)**. This result contrasts with those in **Scheme 40**, but holds some literature precedent. Liotta and Maryanoff and coworkers have demonstrated that hydroxyl groups are well suited to stereo- and regioselectively direct nucleophilic additions.[127] The hydroxyl group was also found to direct addition of methyl Grignard reagent in modest,

[127] (a) Solomon, M.; Jamison, W. C. L.; McCormick, M.; Liotta, D.; Cherry, D. A.; Mills, J. E.; Shah, R. D.; Rodgers, J. D.; Maryanoff, C. A. *J. Am. Chem. Soc.* **1988**, *110*, 3702-3704. (b) Ganem, B. *Chemtracts: Organic Chemistry* **1988**, *1*, 458-460. (c) Swiss, K. A.; Liotta, D. C.; Maryanoff, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9393-9394.

albeit unoptimized yield. The various derivatives of the diol were synthesized using standard techniques and are shown at the bottom of **Scheme 45**.

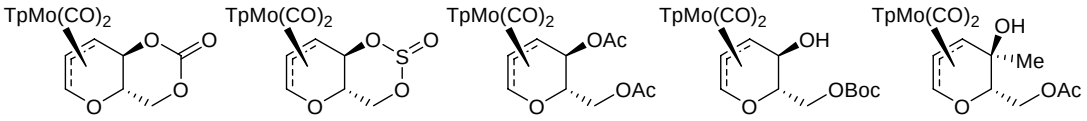
Scheme 45: Hydroxyl-directed reduction of ketone 59c and derivatization



59c

72, R = H, 59%
75, R = Me, 38%

Protected Diols:



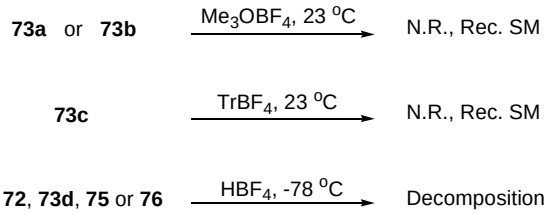
73a **73b** **73c** **73d** **76**

Alkylation of carbonate **73a** and sulfite **73b** with Meerwein reagent (Me_3OBF_4) did not occur (as monitored by IR spectroscopy of an aliquot of the reaction mixtures) even after stirring for several hours at room temperature. Similarly, treatment of **73c** with $TrBF_4$ gave no reaction, and only starting material was recovered. It was hypothesized that formation of a secondary cation was unfavorable, because ionization of tertiary acetates at that position of the ring with $TrPF_6$ is known. When secondary alcohols **72** and **73d** were treated with HBF_4 at low temperature, the reactions immediately changed color from yellow/orange to deep purple, usually a sign of decomposition.[128] No additional reaction was observed after adding MeMgCl. Under identical conditions (HBF_4, CH_2Cl_2, low temperature) tertiary alcohols **75** and **76** underwent the same decomposition, characterized by change to dark purple color (and loss of the metal carbonyls by IR analysis of an aliquot of the reaction mixture). The decomposition pathway is thus

[128] Analysis of the reaction mixture using ReactIR showed a loss of metal carbonyl stretches, and TLC analysis showed a dark purple spot at the origin, and a streak up the plate.

independent of the degree of substitution at the leaving group, and the primary alcohol is not solely responsible for the decomposition.[129]

Scheme 46: Functionalization attempts

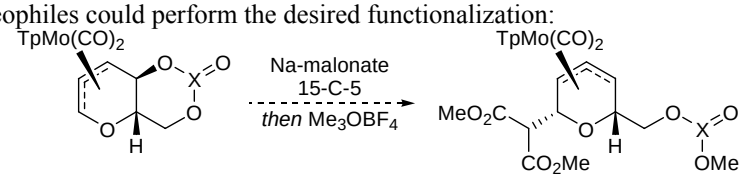


It was clear from the failure of all these various reactions that it would be advantageous to consider an entirely new approach toward functionalization of the 2-position of our scaffolds.

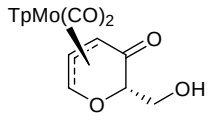
Conclusions:

A streamlined synthesis of unsubstituted and β-substituted exocyclic enone pyranylmolybdenum scaffolds was accomplished with high enantiopurity. These scaffolds underwent a Lewis acid catalyzed hetero Diels-Alder cycloaddition with unsaturated ketones and aldehydes to provide spiroketal complexes in good yields. Functionalization of the 2-position of these complexes was problematic. A series of alternative approaches geared toward functionalizing the 2-position of 6-substituted complexes first followed by cycloaddition also proved difficult.

[129] Interesting recent results in our laboratory by Wenyong Chen suggest that *direct* nucleophilic addition by stabilized nucleophiles could perform the desired functionalization:



Experimental Procedures:

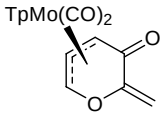


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-η-(2,3,4)-5-oxo-6-hydroxymethyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 59c

Starting material **24** (3.00 g, 6.49 mmol, 1.0 equiv) was dissolved/suspended in CH_2Cl_2 (15mL) under nitrogen in a flame-dried 250 mL Schlenk flask at room temperature. *Tert*-Butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) (2.13 mL, 9.09 mmol, 1.4 equiv) and Et_3N (1.55 mL, 11.0 mmol, 1.7 equiv) were added dropwise simultaneously and the resulting solution was stirred for 10 minutes until TLC (buffered with triethylamine) showed complete consumption of starting material and the formation of a new less polar spot. This reaction mixture was cooled to -78 ^oC. In a separate flame-dried 50 mL round bottom flask a solution of *s*-trioxane (1.75 g, 19.5 mmol, 3.0 equiv) and CH_2Cl_2 (10 mL) was stirred vigorously under argon. This solution was cooled to -40 ^oC and $TiCl_4$ (1.0 M in CH_2Cl_2, 9.75 mL, 9.75 mmol, 1.5 equiv) was added slowly. The bright yellow Lewis acid complex was then transferred *via* nitrogen-flushed syringe to the previously prepared silyl enol ether. Complete transfer of the entire solution was facilitated with more CH_2Cl_2 (10 mL). The reaction was allowed to stir for 15 hours before it was quenched with water (50 mL). The organic layer was separated and washed again with water (50 mL) and then with saturated $NaHCO_3$ solution (50 mL), dried ($MgSO_4$), filtered and concentrated under low pressure. Flash chromatography eluting with 50% EtOAc in hexanes gave the pure alcohol **59c** as a bright yellow solid (2.13 g, 67 %).

59c: TLC: R_f = 0.15 (50% EtOAc in hexanes). IR (cm^{-1}): 3417 (b), 3136 (w), 2490 (w), 1961 (s), 1872 (s), 1640 (m). ^1H NMR [600 MHz, $CDCl_3$]: δ 8.51 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 2.2 Hz, 1H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.51 (d, *J* = 1.9, 1H), 7.39 (dd, *J* = 4.8, 1.9 Hz, 1H), 6.30 (t, *J* = 2.2 Hz, 1H), 6.26 (t, *J* = 2.2 Hz, 1H),

6.21 (t, *J* = 2.2 Hz, 1H), 4.80 (dd, *J* = 6.4, 2.2 Hz, 1H), 4.20 (dd, *J* = 6.4, 4.8 Hz, 1H), 3.89 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.73 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.43 (t, *J* = 4.5 Hz, 1H), 2.50 (bs, 1H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 224.6, 223.6, 194.4, 147.7, 144.0, 141.8, 136.6 (2), 135.0, 107.6, 106.6, 106.3, 106.0, 76.9, 70.2, 65.2, 63.3. HRMS (ESI) Calcd for $C_{17}H_{18}BMoN_6O_5$ $[M + H]^+$: 495.0480. Found: 495.0484.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-η-(2,3,4)-5-oxo-6-methylene-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 52

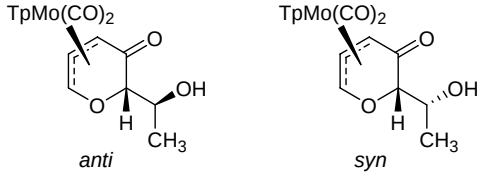
Alcohol **59** (50 mg, 0.102 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (5 mL) with a catalytic amount of DMAP (10 mg) at room temperature in a flame-dried Schlenk flask under nitrogen. The solution was cooled to 0 ^oC before adding methanesulfonyl chloride (15 μL, 0.132 mmol, 1.3 equiv) and Et_3N (0.04 mL, 0.305 mmol, 3.0 equiv). The reaction was stirred for one hour, after which the mesylate was isolated by flash chromatography (50% EtOAc in hexanes) as an orange/yellow solid.

The mesylate was re-dissolved in CH_2Cl_2 (5 mL). The solution was cooled to 0 ^oC and distilled diazabicyclo-[5.4.0]-undec-7-ene (DBU) (23 μL, 0.152 mmol, 1.5 equiv.) was added. After stirring for 10 minutes, the reaction was quenched with water (3 mL), extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated. Pure enone **52** was collected after purification by flash chromatography (50% EtOAc in hexanes) as an orange solid (43 mg, 89% over two steps).

Mesylate intermediate: TLC: R_f = 0.41 (50% EtOAc in hexanes). IR (cm^{-1}): 3146 (w), 2494 (w), 1961 (s), 1876 (s), 1656 (s). ^{1}HNMR [600 MHz, $CDCl_3$]: δ 8.50 (d, *J* = 1.4 Hz, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.52 (d, *J* = 1.4 Hz, 1H), 7.34 (dd, *J* = 4.8, 1.9 Hz, 1H), 6.31 (t, *J* = 2.4 Hz, 1H), 6.27 (t, *J* = 2.4 Hz, 1H), 6.22 (t, *J* = 2.4 Hz, 1H), 4.82 (dd, *J* = 6.2, 1.9 Hz, 1H), 4.49 (dd, *J* = 9.5, 3.8 Hz,

1H), 4.39 (dd, *J* = 9.5, 2.8 Hz, 1H), 4.25 (dd, *J* = 6.2, 4.8 Hz, 1H), 3.56 (t, *J* = 3.3 Hz, 1H), 3.05 (s, 3H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 224.4, 223.4, 190.9, 147.6, 144.0, 141.8, 136.7 (2), 135.0, 106.7, 106.6, 106.4, 106.1, 74.5, 70.3, 69.8, 65.6, 37.7. HRMS (ESI) Calcd for $C_{18}H_{20}BMoN_6O_7S$ $[M + H]^+$: 573.0256. Found: 573.0258.

52: TLC: R_f = 0.64 (50% EtOAc in hexanes). IR (cm^{-1}): 3127 (w), 2490 (w), 1965 (s), 1884 (s), 1660 (s), 1606 (s). ^{1}HNMR [400 MHz, $CDCl_3$]: δ 8.52 (d, *J* = 2.2 Hz, 1H), 7.93 (d, *J* = 2.2 Hz, 1H), 7.65 (d, *J* = 1.9Hz, 1H), 7.62 (d, *J* = 2.22 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.16 (dd, *J* = 4.8, 2.5 Hz, 1H), 6.32 (t, *J* = 2.2 Hz, 1H), 6.27 (t, *J* = 2.2 Hz, 1H), 6.23 (t, *J* = 2.2 Hz, 1H), 5.46 (s, 1H), 4.96 (dd, *J* = 6.4, 2.2 Hz, 1H), 4.67 (s, 1H), 4.38 (dd, *J* = 6.4, 4.8 Hz, 1H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 224.4, 222.5, 196.7, 180.6, 150.2, 147.7, 144.0, 141.7, 136.7, 136.6, 135.0, 106.7, 106.4, 106.1, 103.7, 97.9, 72.3, 67.4. HRMS (ESI) Calcd for $C_{17}H_{16}BMoN_6O_4$ $[M + H]^+$: 477.0375. Found: 477.0387.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1-hydroxylethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 59a-b

(-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1-(*S*)-hydroxylethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)**-59a**

and

(-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1-(*R*)-hydroxylethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)**-59b**

To a Schlenk flask charged with a solution of **24** (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 *tert*-butyldimethylsilyl

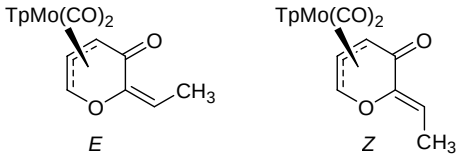
trifluoromethanesulfonate (TBSOTf) (1.74 mL, 7.6 mmol, 1.15 equiv). The reaction mixture was stirred for 10 mins at room temperature, after which TLC (neutralized with Et_3N) indicated that complete conversion had occurred. The solution was then cooled to –78 ºC. To this mixture was slowly added a low-temperature (–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 min 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 and then poured into 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 resulting 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 **59a** (2.12 g, 65%) as a yellow solid. The filtrates were combined, concentrated, and purified by column chromatography (50% EtOAc in hexanes) to give pure *syn*-**59b** (1.08 g, 33%) as a yellow solid after solvent removal.

Under the exact same conditions, (-)-**24** (98% ee) was converted to (-)-**59a** and (-)-**59b** which were assumed to be of 98% ee because the subsequent transformations provided enone (-)-**52** in 98% ee.

(-)-**59a**: TLC: R_f = 0.39 (50% EtOAc in hexanes). $[\alpha]_D^{20}$ -490 (98% ee, *c* 0.22, CH_2Cl_2). 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 8.53 (d, *J* = 1.9 Hz, 1H), 7.91 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.53 (d, *J* = 2.2 Hz, 1H), 7.37 (dd, *J* = 1.91, 4.76 Hz, 1H), 6.33 (t, *J* = 2.2 Hz, 1H), 6.28 (t, *J* = 2.2 Hz, 1H), 6.23 (t, *J* = 2.2 Hz, 1H), 4.78 (dd, *J* = 2.22, 6.04 Hz, 1H), 4.21 (dd, *J* = 4.76, 6.35 Hz, 1H), 3.95 (m, 1H), 3.27 (d, *J* = 6.35 Hz, 1H), 3.08 (d, *J* = 4.76 Hz, 1H), 0.99 (d, *J* = 6.35 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 224.5, 223.6, 195.1, 147.7, 143.9,

141.8, 136.65, 136.62, 135.0, 107.5, 106.6, 106.4, 106.1, 79.0, 69.5, 68.8, 65.0, 18.7. 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.

(-)-**59b**: TLC: R_f = 0.31 (50% EtOAc in hexanes). $[\alpha]_D^{20}$ -512 (98% ee, *c* 0.27, CH_2Cl_2). 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 8.53 (d, *J* = 1.9 Hz, 1H), 7.91 (d, *J* = 2.2 Hz, 1H), 7.67 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.42 (dd, *J* = 2.2, 4.8 Hz, 1H), 6.33 (t, *J* = 2.2 Hz, 1H), 6.28 (t, *J* = 2.2 Hz, 1H), 6.23 (t, *J* = 2.2 Hz, 1H), 4.78 (dd, *J* = 2.2, 6.0 Hz, 1H), 4.20 (dd, *J* = 4.8, 6.4 Hz, 1H), 4.15 (m, 1H), 3.31 (d, *J* = 3.2 Hz, 1H), 2.39 (d, *J* = 8.9 Hz, 1H), 1.25 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 224.7, 223.7, 195.0, 147.7, 144.0, 141.8, 136.63, 136.61, 135.0, 108.0, 106.6, 106.3 106.1, 78.9, 70.4, 68.8, 65.1, 19.2. 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.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-6-(*E*)-ethylidene-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-**60**

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-6-(*Z*)-ethylidene-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-**61**

(-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-(2*S*)-6-(*E*)-ethylidene-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)-**60**

(-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-(2*S*)-6-(*Z*)-ethylidene-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)-**61**

(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-(2*R*)-6-(*Z*)-ethylidene-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (+)-**61**

There are two different methods to perform mesylation-elimination reactions.[130]

To a solution of **59b** (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, 6.0 equiv), and methanesulfonyl chloride (11 μL, 0.14 mmol, 1.3 equiv). The reaction mixture was stirred 4 days at room temperature. TLC monitoring the reaction indicated almost completion of the reaction. The solution was concentrated and directly purified by column chromatography (30% EtOAc in hexanes) to afford the major isomer **61** (45 mg, 85%) and the minor isomer **60** (less than 1 mg).

Alternatively, to a solution of **59a** (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 (43 μL, 0.53 mmol, 1.3 equiv). The reaction mixture was stirred 10 min at room temperature. TLC monitoring the reaction indicated the disappearance of the starting material and formation of the mesylated product. The solution was passed through a short pad of silica gel with 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 down 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 h at room temperature. TLC monitoring the reaction indicated the completion of the reaction. The solution was again passed through a short pad of silica gel with 50% EtOAc in hexanes, concentrated, and purified by column chromatography (30% EtOAc in hexanes) to afford the major isomer **60** (125 mg, 63%) and the minor isomer **61** (61 mg, 31%) both as orange solids.

*A streamlined procedure from starting scaffold **24** to pure Z-enone **61** was developed that requires only one true chromatographic separation over four steps.*

To a Schlenk flask charged with a solution of **24** (5.00 g, 10.8 mmol, 1.0 equiv) in CH_2Cl_2 (70 mL) was successively added Et_3N (1.75 mL, 12.4 mmol, 1.15 equiv) and TBSOTf (2.86 mL,

[130] Both of the following elimination procedures were devised and written by Dr. Yongqiang Zhang.

12.4 mmol, 1.15 equiv). The reaction mixture was stirred for 10 mins at room temperature, after which TLC (neutralized with Et_3N) indicated that complete conversion had occurred. The solution was then cooled to –78 ºC. To this mixture was slowly added a low-temperature (–78 ºC) premixed solution of acetaldehyde (0.98 mL, 17.3 mmol, 1.6 equiv) and $TiCl_4$ (1.0 M in CH_2Cl_2, 14.1 mL, 14.1 mmol, 1.3 equiv) in CH_2Cl_2 (20 mL) *via* syringe (using an extra 5 mL of CH_2Cl_2 for quantitation). The mixture was stirred for 10 min at –78 ºC and then quenched with water (25 mL). The cold bath was removed, and the reaction mixture was allowed to warm to room temperature and then poured into a separatory funnel containing CH_2Cl_2 (100 mL) and water (100 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (2x100mL, then 2x50 mL). The combined organic phases were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated. The residue was then redissolved in CH_2Cl_2 (70 mL) at room temperature, and DMAP (132 mg, 1.08 mmol, 0.1 equiv), Et_3N (2.28 mL, 16.2 mmol, 1.5 equiv) and methanesulfonylchloride dropwise (1.37 mL, 14.1 mmol, 1.3 equiv) were added sequentially. The reaction was stirred at room temperature for 10 minutes after which TLC indicated complete consumption of the alcohol products. The reaction mixture was passed through a short plug of silica gel using 50% EtOAc in hexanes, collecting the large orange band. The solution was concentrated, and immediately redissolved in CH_2Cl_2 (70 mL). This solution was cooled to 0 ^oC, and DBU (2.43 mL, 16.2 mmol, 1.5 equiv) was added dropwise over 3 minutes. The reaction was stirred for 10 minutes, after which TLC revealed that no mesylate remained. The reaction mixture was again passed through a plug of silica gel with 50% EtOAc in hexanes collecting the large orange band. The residue was purified by flash chromatography eluting with 25% EtOAc in hexanes to afford 2.10 g of a mixture of **60** and **61**, and 2.10 g of pure **61**.[131] To the mixture of **60** and **61** (2.10 g, 4.30 mmol, 1.0 equiv) redissolved in CH_2Cl_2 (40 mL) at room temperature was added successively triethylamine (0.69 mL, 4.94 mmol, 1.15 equiv), then TBSOTf (1.13 mL, 4.94

[131] It has since been determined that if only the *Z*-isomer is desired, then this purification step may be performed after the final isomerization step instead.

mmol, 1.15 equiv) dropwise after which TLC (neutralized with Et_3N) revealed that complete consumption of starting material had occurred. The reaction mixture was poured into a separatory funnel and washed with H_2O (50 mL). To the organic layer was added HCl (4.0 M in dioxane, 0.21 mL, 0.86 mmol, 0.2 equiv), and the reaction was stirred for 5 minutes after which TLC revealed that complete hydrolysis had occurred, and only one spot remained. The reaction mixture was concentrated to ~50% on rotavap, and then passed through a silica gel plug to give only **61** in 99% yield. The reaction sequence provided 4.19 g total of **61** (79% yield over 4 steps).

The exact same reaction protocol was used to generate (-)-**61** in 98% ee from (-)-**24** of 98% ee.

The exact same reaction protocol was used to generate (+)-**61** in 99% ee from (+)-**24** of 99% ee.

(-)-**60**: TLC: R_f = 0.57 (25% EtOAc in hexanes). $[\alpha]_D^{20}$ -516 (98% ee, *c* 0.16, CH_2Cl_2). IR (cm^{-1}): 3127 (w), 2490 (w), 2494 (w), 1965 (s), 1880 (s), 1671 (m), 1617 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.50 (d, *J* = 1.9 Hz, 1H), 7.94 (d, *J* = 2.2 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.24 (dd, *J* = 4.8, 2.5 Hz, 1H), 6.31 (t, *J* = 2.2 Hz, 1H), 6.27 (t, *J* = 2.2 Hz, 1H), 6.23 (t, *J* = 2.2 Hz, 1H), 5.51 (qd, *J* = 7.9, 0.6 Hz, 1H), 4.87 (dd, *J* = 6.7, 2.6 Hz, 1H), 4.17 (dd, *J* = 6.4, 4.8 Hz, 1H), 2.03 (d, *J* = 7.9 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 224.7, 223.4, 184.1, 147.4, 143.8, 142.8, 141.7, 136.5, 136.4, 134.9, 117.5, 106.5, 106.2, 106.0, 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.

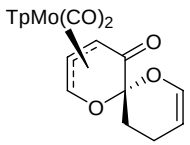
(-)-**61**: TLC: R_f = 0.49 (25% EtOAc in hexanes). $[\alpha]_D^{20}$ -263 (98% ee, *c* 0.21, CH_2Cl_2). IR (cm^{-1}): 3127 (w), 2918 (w), 2490 (m), 1965 (s), 1880 (s), 1671 (m), 1617 (s), 1505 (m), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.51 (d, *J* = 1.9 Hz, 1H), 7.93 (d, *J* = 2.2 Hz, 1H), 7.72 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 2.2

Hz, 1H), 7.53 (d, *J* = 2.2 Hz, 1H), 7.31 (dd, *J* = 4.8, 2.2 Hz, 1H), 6.32 (t, *J* = 2.2 Hz, 1H), 6.28 (t, *J* = 2.2 Hz, 1H), 6.22 (t, *J* = 2.2 Hz, 1H), 6.05 (q, *J* = 7.6 Hz, 1H), 4.90 (dd, *J* = 6.4, 2.2 Hz, 1H), 4.28 (dd, *J* = 6.4, 4.8 Hz, 1H), 1.63 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 224.2, 223.2, 181.3, 147.5, 144.8, 143.6, 141.8, 136.6, 136.5, 134.9, 111.4, 106.5, 106.3, 105.9, 104.7, 71.3, 66.0, 10.3. HRMS (ESI) Calcd for $C_{18}H_{17}BMoN_6O_4$ $[M]^+$: 490.0458. Found: 490.0480. HRMS (FAB) Calcd for $C_{16}H_{17}BMoN_6O_2$ ($[M-2CO]^+$): 434.0560. Found: 434.0565. HPLC: Daicel Chiralcel AS-RH, MeCN:H_2O (w/0.1% TFA) = 55:45, 1.0 mL/min, 254 nm, t_t = 8.76 min, 97.5% ee. Enantiomer: t_r = 7.07 min.

(+)-**61**: $[\alpha]_D^{20}$ +217 (99% ee, *c* 0.14, CH_2Cl_2).

General protocol for hetero-Diels-Alder cycloadditions:

The enone **52** and catalytic Europium tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) [$Eu(fod)_3$] were dissolved in the indicated amount of α,β-unsaturated aldehyde or ketone in a pressure tube under argon. The tube was sealed, and was heated in an oil bath to the indicated temperature for the indicated period of time. Then the crude reaction mixture was pipetted into a flask of cold hexanes (0 °C), which caused the product to crash out. The solvent was decanted off, and the crude material was dissolved in dichloromethane and dried onto a small amount of silica gel on the rotavap. This material was added dry to the top of a silica gel column packed with 20% EtOAc in hexanes, and eluted with this solvent system to provide the pure products, all as red-orange or yellow solids.

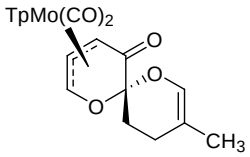


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)-1,7-dioxa-spiro-[5.5]-undeca-8-ene-5-one-2-yl]molybdenum, 53

Following the general reaction protocol enone **52** (30 mg, 0.063 mmol, 1.0 equiv) and

$Eu(fod)_3$ (13 mg, 0.013 mmol, 0.2 equiv) were dissolved in acrolein (0.33 mL, 4.90 mmol, 78 equiv), in a flame-dried pressure tube under nitrogen while stirring. The reaction was heated to 50 °C and stirred for 24 hours. The usual workup and purification by chromatography provided pure product **53** (22.5 mg, 67%) as a yellow-orange solid.

53: TLC: R_f = 0.40, (33% EtOAc in hexanes). IR (cm^{-1}): 3127 (w), 2922 (w), 2490 (w), 1965 (s), 1880 (s), 1725 (w), 1675 (s). ^1H NMR [600 MHz, $CDCl_3$]: δ 8.57 (d, *J* = 1.9 Hz, 1H), 7.97 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 2H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.30 (dd, *J* = 4.8, 2.4 Hz, 1H), 6.32 (t, *J* = 2.4 Hz, 1H), 6.27 (apparent s, 1H), 6.25 (t, *J* = 2.4 Hz, 1H), 6.23 (t, *J* = 2.4 Hz, 1H), 4.96 (dd, *J* = 5.7, 2.4 Hz, 1H), 4.85 (t, *J* = 5.7 Hz, 1H), 4.62 (dd, *J* = 5.7, 4.8 Hz, 1H), 2.12 (m, 2H), 1.95 (m, 1H), 1.42 (m, 1H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 226.8, 223.4, 191.9, 148.0, 143.7, 141.6, 140.9, 136.6, 136.5, 134.9, 106.7, 106.3, 106.1, 104.5, 102.3, 93.7, 70.2, 66.6, 25.0, 15.2. HRMS (ESI) Calcd for $C_{20}H_{19}BMoN_6O_5$ $[M + H]^+$: 533.0637. Found: 533.0637.

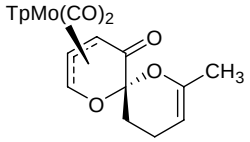


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)- 5-oxo-9-methyl-1,7-dioxa-spiro-[5.5]-undec-8-ene-2-yl]molybdenum, 54

Following the general reaction protocol enone **53** (30 mg, 0.063 mmol, 1.0 equiv) and $Eu(fod)_3$ (13 mg, 0.013 mmol, 0.2 equiv) were dissolved in methacrolein (0.40 mL, 4.88 mmol, 77 equiv), in a flame-dried pressure tube under nitrogen while stirring. The reaction was heated to 50 °C and stirred for 24 hours. The usual workup and purification by chromatography provided pure product **54** (19.5 mg, 57%) as a yellow-orange solid.

54: TLC: R_f = 0.40, (33% EtOAc in hexanes). IR (cm^{-1}): 2923 (w), 2491 (w), 1965 (s), 1881 (s), 1677 (m), 1407 (m), 1306 (m), 1218 (m), 1126 (m), 1501 (s). ^1H NMR [600 MHz, $CDCl_3$]: δ

8.57 (d, J = 1.9 Hz, 1H), 7.97 (d, J = 1.9 Hz, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.59 (m, 2H), 7.50 (d, J = 2.4 Hz, 1H), 7.29 (dd, J = 4.8, 2.4 Hz, 1H), 6.31 (t, J = 2.4 Hz, 1H), 6.24 (t, J = 1.9 Hz, 1H), 6.22 (t, J = 1.9 Hz, 1H), 6.07 (s, 1H), 4.96 (dd, J = 6.2, 2.4 Hz, 1H), 4.61 (t, J = 5.2 Hz, 1H), 2.17 (ddd, J = 13.3, 13.3, 6.7 Hz, 1H), 2.08 (m, 1H), 1.80 (dd, J = 16.2, 5.7 Hz, 1H), 1.57 (s, 3H), 1.42 (ddd, J = 12.9, 5.7, 1.9 Hz, 1H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 226.9, 223.4, 192.1, 148.0, 143.7, 141.6, 136.6, 136.5, 135.2, 135.0, 110.4, 106.7, 106.3, 106.1, 104.7, 93.2, 70.2, 66.7, 24.9, 20.8, 18.5. HRMS (ESI) Calcd for $C_{21}H_{22}BMoN_6O_5$ $[M + H]^+$: 547.0793. Found: 547.0794.



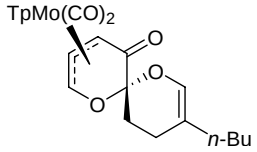
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)- 5-oxo-8-methyl-1,7-dioxa-spiro-[5.5]-undec-8-ene-2-yl]molybdenum, 55

Following the general reaction protocol enone **52** (100 mg, 0.211 mmol, 1.0 equiv) and $Eu(fod)_3$ (44 mg, 0.042 mmol, 0.2 equiv) were dissolved in methyl vinyl ketone (0.80 mL, 9.70 mmol, 46 equiv), in a flame-dried pressure tube under nitrogen while stirring. The reaction was heated to 70 ^{o}C and stirred for 36 hours. The usual workup and purification by chromatography provided 91.8 mg (80%) of pure product **55** as an orange solid.

Alternatively, the enone **52** (100 mg, 0.211 mmol, 1.0 equiv) and $Eu(fod)_3$ (44 mg, 0.042 mmol, 0.2 equiv) were dissolved in methyl vinyl ketone (1.00 mL, 11.98 mmol, 57 equiv), in a microwave reactor tube. The reaction mixture was heated to 70 ^{o}C under 300 watts of power for 1.5 hours, monitoring by TLC at 15-20 minute intervals until the reaction did not appear to change anymore. The usual workup and purification provided pure product **55** (68.1 mg, 59%) as a yellow solid.

55: TLC: R_f = 0.41, (33% EtOAc in hexanes). IR (cm^{-1}): 2922 (w), 2487 (w), 1962 (s), 1879 (s), 1675 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.57 (d, J = 1.9 Hz, 1H), 7.99 (d, J = 2.2 Hz, 1H),

7.61 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.32 (dd, *J* = 4.8, 2.2 Hz, 1H), 6.32 (t, *J* = 2.2 Hz, 1H), 6.24 (t, *J* = 2.2 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 5.01 (dd, *J* = 6.0, 2.5 Hz, 1H), 4.61 (apparent dd, *J* = 6.0, 4.8 Hz, 2H), 2.09 (m, 2H), 1.92 (m, 1H), 1.76 (s, 3H), 1.40 (m, 1H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 226.7, 223.6, 192.2, 148.2, 148.0, 143.7, 141.6, 136.6, 136.5, 134.9, 106.7, 106.3, 106.0, 105.0, 97.0, 94.3, 70.0, 66.6, 24.7, 20.2, 15.9. HRMS (ESI) Calcd for $C_{21}H_{22}BMoN_6O_5$ $[M + H]^+$: 547.0793. Found: 547.0791.

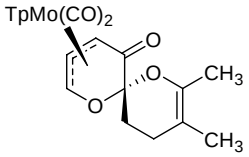


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)-9-butyl-5-oxo-1,7-dioxa-spiro-[5.5]-undec-8-ene-2-yl]molybdenum, 62

Following the general reaction protocol enone **52** (100 mg, 0.211 mmol, 1.0 equiv) and $Eu(fod)_3$ (44 mg, 0.042 mmol, 0.2 equiv) were dissolved in 2-butylacrolein (1.60 mL, 11.98 mmol, 57 equiv), in a flame-dried pressure tube under nitrogen while stirring. The reaction was heated to 60 ^{o}C and stirred for 68 hours. The usual workup and purification by chromatography provided pure product **62** (69.2 mg, 56%) as a yellow-orange solid.

62: TLC: R_f = 0.47, (33% EtOAc in hexanes). IR (cm^{-1}): 2928 (w), 2858 (w), 1963 (s), 1880 (s), 1670 (m), 1407 (m), 1304 (m), 1217 (m), 1125 (s), 1050 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.57 (d, *J* = 1.9 Hz, 1H), 7.97 (d, *J* = 1.9 Hz, 1H), 7.61 (app s, 2H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.30 (dd, *J* = 4.4, 2.2 Hz, 1H), 6.31 (t, *J* = 2.2 Hz, 1H), 6.24 (t, *J* = 2.2 Hz, 1H), 6.22 (t, *J* = 1.9 Hz, 1H), 6.07 (s, 1H), 4.96 (dd, *J* = 6.0, 2.2 Hz), 4.60 (dd, *J* = 6.0, 4.8 Hz, 1H), 2.09 (m, 1H), 1.87 (m, 2H), 1.44-1.27 (m, 9H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 226.9, 223.4, 192.1, 147.9, 143.7, 141.5, 136.5, 136.4, 135.2, 134.8, 114.3, 106.6, 106.2, 106.0, 104.8, 93.3, 70.1, 66.6, 32.5, 30.0, 24.9, 22.4, 28.7, 14.1. HRMS (ESI) Calcd for $C_{21}H_{21}BMoN_6O_5$ [M +

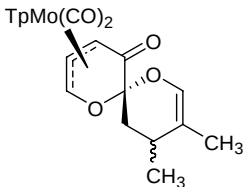
H]$^+$: 589.1263. Found: 589.1261. X-Ray Diffraction data is included at the end of this experimental section.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)- 5-oxo-8,9-dimethyl-1,7-dioxa-spiro-[5.5]-undec-8-ene-2-yl]molybdenum, 63

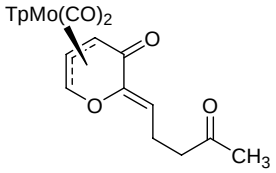
Following the general reaction protocol enone **52** (30 mg, 0.063 mmol, 1.0 equiv) and $Eu(fod)_3$ (13 mg, 0.013 mmol, 0.2 equiv) were dissolved in 3-methyl-3-buten-2-one (0.48 mL, 4.88 mmol, 77 equiv), in a flame-dried pressure tube under nitrogen while stirring. The reaction was heated to 60 ^oC and stirred for 24 hours. The usual workup and purification by chromatography provided 18 mg (51%) of pure product **63** as an orange solid.

63: IR (cm^{-1}): 3123 (w), 2926 (m), 2490 (w), 1965 (s), 1880 (s), 1702 (s), 1675 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.57 (d, *J* = 1.9 Hz, 1H), 7.98 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 2.2 Hz, 2H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 2.2 Hz, 1H), 7.31 (dd, *J* = 4.8, 2.5 Hz, 1H), 6.31 (t, *J* = 2.2 Hz, 1H), 6.24 (t, *J* = 2.2 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 4.98 (dd, *J* = 6.0, 2.2 Hz, 1H), 4.58 (dd, *J* = 6.0, 4.8 Hz, 1H), 2.22-2.06 (m, 3H), 1.76 (s, 3H), 1.60 (s, 3H), 1.38 (m, 1H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 226.9, 223.7, 192.5, 148.0, 143.7, 141.6, 141.5, 136.6, 136.5, 134.9, 106.7, 106.2, 106.0, 105.2, 103.2, 93.9, 70.0, 66.6, 25.3, 22.1, 18.0, 16.5.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*,10*R/S*)-η-(2,3,4)- 5-oxo-9,10-dimethyl-1,7-dioxa-spiro-[5.5]-undec-8-ene-2-yl]molybdenum, 64

Following the general reaction protocol enone **52** (30 mg, 0.063 mmol, 1.0 equiv) and $Eu(fod)_3$ (13 mg, 0.013 mmol, 0.2 equiv) were dissolved in 2-methyl-2-butenal (0.40 mL, 4.14 mmol, 65 equiv), in a flame-dried pressure tube under nitrogen while stirring. The reaction was heated to 60 ^{o}C and stirred for 50 hours, after which a very small amount of product was visible by TLC. The usual workup and purification by chromatography provided a trace amount of slightly impure product ~4.0 mg (11%) **64**, which was determined to be a 1:1 mixture of diastereomers by ^{1}H NMR.



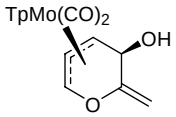
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-η-(2,3,4)-5-oxo-6-(*Z*)-(4-oxo-pentylidene)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 65

Enone **52** (40 mg, 0.0844 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (4 mL) in a flame-dried schlenk flask under nitrogen while stirring, then cooled to -78 ^{o}C. A separate flask was prepared with a solution of methyl vinyl ketone (0.014 mL, 0.169 mmol, 2.0 equiv) in CH_2Cl_2 (1 mL) under nitrogen. The vial was cooled to -78 ^{o}C, and subsequently borontrifluoride diethyletherate ($BF_3{\cdot}OEt_2$) (90 μL, 0.093 mmol, 1.1 equiv) was added and the Lewis acid complex was mixed thoroughly. The cold complex was then transferred to the stirring enone solution with a syringe. The reaction was stirred for 14 hours (-78 ^{o}C to rt), after which it was quenched with water (5 mL), extracted with CH_2Cl_2 (2x5 mL), dried over $MgSO_4$, and concentrated. Column

chromatography (33% EtOAc in hexanes) gave the cycloadduct (24 mg, 52%) as a yellow-orange solid.

Alternatively, spirocycloadduct **55** (20 mg, 0.037 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (1.0 mL) and cooled to 0 ^oC. Borontrifluoride diethyletherate (5 μL, 0.037 mmol, 1.0 equiv) was added dropwise and the reaction was stirred for 15 minutes, after which TLC revealed the formation of a new, much more polar spot. The reaction mixture was concentrated, and added directly to a silica gel column, and eluted with 50% EtOAc in hexanes to provide pure product **65** (10.9 mg, 55%) as an orange solid.

65: TLC: R_f = 0.13, (33% EtOAc in hexanes). IR (cm^{-1}): 3127 (w), 2926 (w), 2494 (w), 1969 (s), 1884 (s), 1714 (m), 1668 (w), 1621 (m). ^1H NMR [600 MHz, $CDCl_3$]: δ 8.50 (d, *J* = 1.9 Hz, 1H), 7.91 (d, *J* = 1.9 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.26 (obscured dd, 1H), 6.31 (t, *J* = 2.4 Hz, 1H), 6.27 (t, *J* = 2.4 Hz, 1H), 6.21 (t, *J* = 2.4 Hz, 1H), 5.95 (t, *J* = 7.6 Hz, 1H), 4.90 (dd, *J* = 6.7, 2.4 Hz, 1H), 4.29 (dd, *J* = 6.2, 4.8 Hz), 2.51 (m, 2H), 2.32 (m, 2H), 2.13 (s, 3H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 224.3, 223.0, 208.1, 181.0, 147.6, 144.6, 143.8, 141.8, 136.7, 136.6, 135.0, 114.3, 106.6, 106.3, 106.0, 104.5, 71.5, 66.4, 42.6, 30.1, 19.3. HRMS (ESI) Calcd for $C_{21}H_{22}BMoN_6O_5$ $[M + H]^+$: 547.0793. Found: 547.0792.

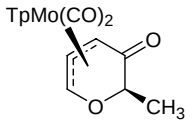


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-5-hydroxy-6-methylene-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 70

Enone **52** (50 mg, 0.105 mmol, 1.0 equiv) was dissolved in THF (2 mL) and $CeCl_3 \cdot 7H_2O$ (41 mg, 0.111 mmol, 1.05 equiv) was added in one portion. The mixture was stirred for 30 minutes at room temperature. The reaction was then cooled to 0 ^oC, and $NaBH_4$ was added dropwise (0.5 M in 2-methoxy ethyl ether, 0.46 mL, 0.232 mmol, 1.1 equiv). The reaction was stirred at 0 ^oC

for 10 minutes, and then concentrated to dryness on a rotary evaporator. The crude mixture was then redissolved in a small amount of dichloromethane and added directly to a column. The pure product was eluted with 33% EtOAc in hexanes, and concentrated as 41 mg of yellow solid (81% yield).

70: TLC: R_f = 0.40, (33% EtOAc in hexanes). IR (cm^{-1}): 3455 (w), 3146 (w), 2486 (m), 1945 (s), 1849 (s), 1656 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.46 (d, *J* = 1.9 Hz, 1H), 7.94 (d, *J* = 1.9 Hz, 1H), 7.68 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.49 (dd, *J* = 2.2, 0.6 Hz, 1H), 6.96 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.28 (t, *J* = 2.2 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 5.22 (d, *J* = 8.6 Hz, 1H), 4.80 (dt, *J* = 7.3, 2.5 Hz, 1H), 4.60 (t, *J* = 1.6 Hz, 1H), 4.47 (t, *J* = 1.0 Hz, 1H), 3.57 (ddd, *J* = 7.3, 4.4, 0.6 Hz, 1H)), 2.99 (br d, *J* = 11.1 Hz, 1H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 231.8, 224.5, 157.2, 147.0, 142.7, 141.9, 136.4, 136.3, 134.8, 106.7, 106.3, 106.0, 105.7, 92.8, 73.2, 70.3, 60.4.

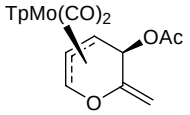


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)-5-oxo-6-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 43

Allylic alcohol **70** (41 mg, 0.086 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.0 mL) at room temperature. Hydrochloric acid (4.0 M in dioxane, 22 μL, 0.086 mmol, 1.0 equiv) was added dropwise, and the reaction was stirred for 5 minutes, after which TLC revealed the formation of a new product. Aqueous workup, followed by flash chromatography on silica gel eluting with 50% EtOAc in hexanes provided 37.4 mg of product **43** (91%) as an orange solid.

Alternatively, exocyclic enone **52** (50 mg, 0.105 mmol, 1.0 equiv.) and 10 mol % palladium on activated carbon (116.8 mg, 0.158 mmol, 15 mol %), was added to a clean, dry Schlenk flask. The flask was evacuated and then placed under hydrogen atmosphere three times, after which the reaction mixture was dissolved in methanol (2 mL), and stirred for 3 hours. The reaction mixture

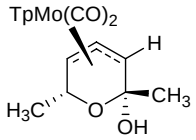
was filtered over a small pad of celite, eluting with ethyl acetate. The filtrate was then concentrated and purified by flash chromatography on silica gel, eluting with (50 % ethyl acetate in hexanes) to provide the product as an orange solid (45 mg, 90 %), which was spectroscopically identical to the complex described in chapter 1.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-5-acyloxy-6-methylene-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 68

Allylic alcohol **70** (171 mg, 0.359 mmol, 1.0 equiv) was dissolved in dichloromethane (5 mL), and triethylamine (151 μL, 1.08 mmol, 3.0 equiv), and a catalytic amount of DMAP were added to the stirring solution at room temperature. The reaction mixture was then cooled to 0 ^{o}C, and acetic anhydride (86 μL, 0.898 mmol, 2.5 equiv) was added dropwise over 1 minute. The solution was stirred for 1.5 hours until the starting material had disappeared by TLC. The reaction mixture was concentrated and added directly to column using a small amount of dichloromethane. Isolation by flash chromatography (33% EtOAc in hexanes) afforded 147 mg of the allylic acetate , **68** (79%).

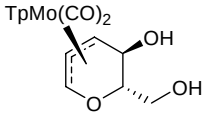
68: TLC: R_f = 0.52, (33% EtOAc in hexanes). IR (cm^{-1}): 3127 (w), 2922 (m), 2853 (m), 2486 (m), 1957 (s), 1872 (s), 1733 (s), 1656 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.50 (d, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 4.4, 2.5 Hz, 1H), 6.26 (t, *J* = 1.9 Hz, 1H), 6.22 (d, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 1.9 Hz, 1H), 6.17 (t, *J* = 1.9 Hz, 1H), 4.74 (dt, *J* = 7.6, 2.5, 2.5 Hz, 1H), 4.48 (s, 1H), 4.40 (s, 1H), 3.51 (dd, *J* = 7.6, 4.4 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 226.8, 225.1, 171.0, 151.6, 146.9, 142.3, 142.0, 136.3 (2), 134.7, 107.5, 106.2, 105.9, 105.6, 93.5, 70.6, 65.8, 59.1, 21.2. HRMS (ESI) Calcd for $C_{19}H_{20}BMoN_6O_5$ $[M + H]^+$: 521.0637. Found: 521.0636.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-6-hydroxy-2,6-dimethyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 71

Allylic acetate **68** (47 mg, 0.091 mmol, 1.0 equiv) was dissolved in CH_2Cl_2, and the solution was cooled to -78 °C before adding triphenylcarbenium tetrafluoroborate (33 mg, 0.100 mmol, 1.1 equiv). The reaction was stirred for 1 hour at -78 °C and then the cold bath was removed, the reaction stirred for 1 hour more, warming to room temperature. The reaction was again cooled to -78 °C, and methylmagnesium chloride was added dropwise (2.5 M in THF, 73 μL, 0.181 mmol, 2.0 equiv). The reaction mixture was purified directly by flash chromatography on a silica gel column neutralized with 5% Et_3N and eluted with 25% EtOAc in hexanes, which provided 18.5 mg (41%) of the pure product, **71** as an orange solid.

71: TLC: R_f = 0.17 (33% EtOAc in hexanes). IR (cm^{-1}): 1945 (s), 1185 (s), 1660 (w), 1408 (m), 1305 (m), 1219 (m), 1125 (m), 1049 (s). ^1H NMR [400 MHz, C_6D_6]: δ 8.51-7.30 (br s, 4H), 7.10-6.90 (br s, 2H), 5.70 (br s, 3H), 4.73 (dd, *J* = 10.8, 8.6 Hz, 1H), 4.47 (t, *J* = 7.9 Hz, 1H), 3.19 (app pentet, *J* = 7.0 Hz, 1H), 3.12 (d, *J* = 11.1 Hz, 1H), 2.75 (br s, 1H), 1.59 (s, 3H), 1.18 (d, *J* = 6.4 Hz, 3H). HRMS (ESI) Calcd for $C_{18}H_{20}BMoN_6O_3$ $[M - OH]^+$: 477.0739. Found: 477.0737.

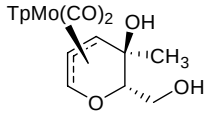


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*,6*S*)-η-(2,3,4)-5-hydroxy-6-hydroxymethyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 72

The α-hydroxymethyl ketone **59c** (1.09 g, 2.21 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10 mL), cooled to 0 °C and stirred for 30 minutes. Sodium borohydride (88 mg, 2.32 mmol, 1.05 equiv) was added in small portions as a solid with 5 minutes in between each. Then methanol (5

mL) was added slowly and the reaction mixture was stirred for 12 hours at room temperature. The reaction was diluted with CH_2Cl_2 (10 mL), and washed with water (10 mL). The organic layer was collected and dried with $MgSO_4$, filtered and concentrated under reduced pressure. Flash chromatography on silica gel eluting with 50% EtOAc in hexanes provided 646 mg (59%) of pure product **72** as a bright yellow solid.

72: TLC: R_f = 0.21, (50% EtOAc in hexanes). IR (cm^{-1}): 3389 (m), 2926 (m), 2856 (w), 2486 (w), 1942 (s), 1849 (s). ^1H NMR [600 MHz, $CDCl_3$]: δ 8.49 (s, 1H), 7.89 (s, 1H), 7.71 (s, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.58 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H) 7.01 (d, *J* = 1.9 Hz, 1H), 6.30 (t, *J* = 1.9 Hz, 1H), 6.22 (t, *J* = 1.9 Hz, 1H), 6.20 (t, *J* = 1.4 Hz, 1H), 4.70 (d, *J* = 7.6 Hz, 1H), 4.57 (d, *J* = 10.0 Hz, 1H), 3.76 (m, 2H), 3.45 (dd, *J* = 7.1, 4.7 Hz, 1H), 2.65 (br s, 1H), 2.49 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.3, 224.0, 147.0, 142.3, 141.9, 136.4 (2), 134.7, 109.7, 106.3, 105.9, 105.6, 79.2, 72.1, 68.2, 62.0, 58.1. HRMS (ESI) Calcd for $C_{17}H_{19}BMoN_6O_5$ $[M - H]^+$: 496.0480. Found: 495.0482.

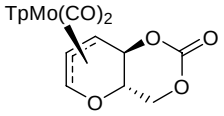


(±)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*,6*S*)-η-(2,3,4)-6-hydroxymethyl-5-hydroxy-5-methyl-5,6-dihydro-2H-pyran-2-yl]molybdenum, 75

The α-hydroxymethyl ketone **59c** (150 mg, 0.305 mmol, 1.0 equiv) was dissolved in THF (4.5 mL), and cooled to -78 °C. Methylmagnesium bromide (3.0 M in Et_2O, 0.23 mL, 0.671 mmol, 2.2 equiv) was added dropwise and the reaction was stirred for 100 minutes after which more MeMgBr was added (0.12 mL, 1.1 equiv). The reaction was warmed to room temperature and stirred for 17 hours after which more MeMgBr was added (0.12 mL, 1.1 equiv—Total = 4.4 equiv). The reaction was quenched with brine, and the aqueous layer was extracted with CH_2Cl_2 (2x10 mL). Concentration of the combined organic layers, and purification by flash chromatography on silica gel provided 59 mg of pure product **75** (38%) as a yellow solid.

75: TLC: R_f = 0.35, (50% EtOAc in hexanes). IR (cm^{-1}): 3424 (m), 3401 (m), 3127 (w), 2930 (w), 2482 (m), 1942 (s), 1849 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.49 (d, *J* = 1.6 Hz, 1H), 7.88 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.58 (t, *J* = 2.5 Hz, 2H), 7.51 (d, *J* = 2.2 Hz, 1H), 6.95 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.29 (t, *J* = 1.9 Hz, 1H), 6.20 (m, 2H), 4.50 (dd, *J* = 7.6, 2.2 Hz, 1H), 3.81 (dd, *J* = 11.1, 4.4 Hz, 1H), 3.67 (dd, *J* = 11.1, 7.0 Hz, 1H), 3.40 (dd, *J* = 7.3, 4.1 Hz, 1H), 3.01 (br s, 1H), 2.62 (dd, *J* = 7.0, 4.7 Hz, 1H), 1.9 (br s, 1H), 1.47 (s, 3H).

Protection of diols:

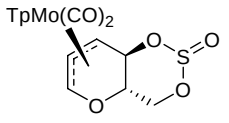


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(4a*S*,8a*S*,6*S*)-η-(6,7,8)-4,4a,7,8a-tetrahydro-pyrano-[3,2-*d*]-[1,3]dioxin-2-one-6-yl]molybdenum, 73a

Diol **72** (150 mg, 0.303 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (9 mL) at room temperature. Pyridine (51 μL, 0.638 mmol, 2.1 equiv) and a catalytic amount of DMAP were added to the reaction mixture, which was stirred at room temperature for 1 hour. The reaction was cooled to 0 ^oC, and triphosgene was added (95 mg, 0.319 mmol, 1.05 equiv). The reaction was stirred at 0 ^oC until almost no starting material remained by TLC. The reaction mixture was washed with brine and water, the organic layer was collected and dried on $MgSO_4$, filtered and concentrated. Purification by chromatography on silica gel provided pure product **73a** (10 mg, 6.3%).

73a: TLC: R_f = 0.57, (50% EtOAc in hexanes). IR (cm^{-1}): 2922 (m), 2853 (w), 2486 (w), 1949 (s), 1864 (s), 1760 (s). ^1H NMR [300 MHz, $CDCl_3$]: δ 8.52 (d, *J* = 1.9 Hz, 1H), 7.82 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 6.96 (d, *J* = 4.4, 1.9 Hz, 1H), 6.32 (t, *J* = 2.2 Hz, 1H), 6.23 (t, *J* = 2.2 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 4.91 (dd, *J* = 9.2, 1.9 Hz, 1H), 4.48 (dt, *J* = 7.6, 2.2, 2.2 Hz, 1H), 4.36 (dd, *J* = 9.2, 5.7 Hz, 1H), 4.25 (dd, *J* = 10.8, 9.2 Hz, 1H), 3.46 (dd, *J* = 7.6, 4.4 Hz, 1H), 2.77

(ddd, *J* = 10.5, 10.5, 5.7 Hz, 1H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 225.2, 223.8, 148.0, 147.1, 142.4, 142.0, 136.6 (2), 134.9, 109.4, 106.5, 106.1, 105.9, 76.7, 69.6, 67.9, 62.7, 55.5. HRMS (ESI) Calcd for $C_{18}H_{18}BMoN_6O_6$ $[M + H]^+$: 523.0429. Found: 523.0431.



\+ Unidentified product

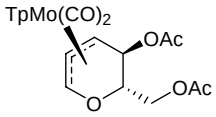
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(4a*S*,8a*S*,6*S*)-η-(6,7,8)-2-oxo-4,4a,6,8a-tetrahydro-pyrano-[3,2-*d*]-[1,3,2]dioxathiin-6-yl]molybdenum, 73b

Diol **72** (100 mg, 0.202 mmol, 1.0 equiv), triethylamine (0.14 mL, 1.01 mmol, 5.0 equiv), and a catalytic amount of DMAP were dissolved in CH_2Cl_2 (6 mL) at 0 °C. Thionyl chloride (37 μL, 0.506 mmol, 2.5 equiv) was added dropwise over 1 minute and stirred for 2.5 hours, after which the reaction mixture was concentrated and purified directly by chromatography on silica gel, eluting with 33% EtOAc in hexanes to provide pure product **73b** (27 mg 25%) as a yellow solid, along with another unidentified product (10 mg).

73b: TLC: R_f = 0.61, (33% EtOAc in hexanes). IR (cm^{-1}): 2926 (w), 2853 (w), 2486 (w), 1953 (s), 1864 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.55 (d, *J* = 1.9 Hz, 1H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 2.5 Hz, 1H), 6.90 (dd, *J* = 4.4, 2.2 Hz, 1H), 6.32 (t, *J* = 2.2 Hz, 1H), 6.22 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 5.69 (dd, *J* = 9.8, 1.6 Hz, 1H), 4.72 (t, *J* = 10.5 Hz, 1H), 4.28 (dt, *J* = 7.6, 2.2 Hz, 1H), 3.87 (dd, *J* = 10.2, 4.1 Hz, 1H), 3.47 (dd, *J* = 7.6, 4.7 Hz, 1H), 2.86 (ddd, *J* = 10.5, 9.8, 4.1 Hz). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 225.9, 224.1, 147.0, 142.1 (2), 136.5 (2), 134.8, 110.4, 106.4, 106.0, 105.7, 71.1, 69.3, 63.2, 61.8, 56.8. HRMS (ESI) Calcd for $C_{17}H_{17}BMoN_6O_6S$ $[M + H]^+$: 542.0077. Found: 542.0072.

Unidentified Product: TLC: R_f = 0.49, (33% EtOAc in hexanes). IR (cm^{-1}): 2922 (w), 2853 (w), 2486 (w), 1957 (s), 1864 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.55 (d, *J* = 1.9 Hz, 1H), 7.80 (d, *J* = 1.9 Hz, 1H), 7.68 (d, *J* = 1.9 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 1.9 Hz, 1H),

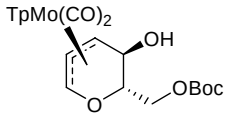
7.51 (d, J = 2.2 Hz, 1H), 6.88 (dd, J = 4.4, 2.2 Hz, 1H), 6.32 (t, J = 2.2 Hz, 1H), 6.22 (t, J = 2.2 Hz, 1H), 6.19 (t, J = 2.2 Hz, 1H), 4.93 (dd, J = 9.8, 1.6 Hz, 1H), 4.38 (m, 2H), 4.20 (t, J = 9.8 Hz, 1H), 3.44 (dd, J = 7.6, 4.4 Hz, 1H), 3.08 (ddd, J = 9.8, 9.8, 6.7 Hz, 1H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 224.8, 223.9, 147.1, 142.2, 142.0, 136.5 (2), 134.8, 109.4, 106.4, 106.0, 105.7, 74.8, 69.6, 65.9, 63.2, 55.8.

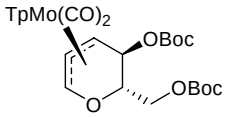


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*,6*S*)-η-(2,3,4)-5-acyloxy-6-acyloxymethyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 73c

Diol **72** (50 mg, 0.101 mmol, 1.0 equiv), triethylamine (58 μL, 0.415 mmol, 4.1 equiv) and a catalytic amount of DMAP were dissolved in CH_2Cl_2 (6 mL) at 0 ^{o}C. Acetic anydride (39 μL, 0.405 mmol, 4.0 equiv) was added dropwise over 1 minute and stirred for 15 hours, after which the reaction mixture was concentrated and purified directly by chromatography on silica gel, eluting with 50% EtOAc in hexanes to provide 53 mg (91%) of pure product **73c** as a yellow solid.

73c: TLC: R_f = 0.72, (50% EtOAc in hexanes). IR (cm^{-1}): 3127 (w), 2922 (w), 2482 (w), 1949 (s), 1864 (s), 1737 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.51 (d, J = 1.9 Hz, 1H), 7.72 (d, J = 2.2 Hz, 1H), 7.70 (d, J = 1.9 Hz, 1H), 7.58 (d, J = 2.2 Hz, 1H), 7.56 (d, J = 1.9 Hz, 1H), 7.50 (d, J = 1.9 Hz, 1H), 7.04 (dd, J = 4.4, 2.2 Hz, 1H), 6.29 (t, J = 2.2 Hz, 1H), 6.20 (t, J = 2.2 Hz, 1H), 6.17 (t, J = 2.2 Hz, 1H), 5.45 (dd, J = 9.5, 2.5 Hz, 1H), 4.73 (dt, J = 7.6, 2.5, 2.5 Hz, 1H), 4.11 (d, J = 3.5 Hz, 2H), 3.42 (dd, J = 7.6, 4.1 Hz, 1H), 2.78 (dt, J = 9.8, 3.5 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.7, 224.2, 171.09, 171.01, 146.9, 142.1, 142.0 136.4, 136.3, 134.7, 110.3, 106.2, 105.9, 105.6, 73.5, 69.2, 65.2, 62.6, 57.1, 21.1, 21.0. HRMS (ESI) Calcd for $C_{21}H_{23}BMoN_6O_7$ $[M]^+$: 580.0770. Found: 580.0769.





(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*,6*S*)-η-(2,3,4)-5-hydroxy-6-*tert*-butoxycarbonyloxymethyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 73d

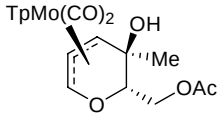
Diol **72** (50 mg, 0.101 mmol, 1.0 equiv), pyridine (16 μL, 0.202 mmol, 2.0 equiv) and a catalytic amount of DMAP were dissolved in CH_2Cl_2 (3 mL) at 0 °C. Di-*tert*-butyldicarbonate (23 mg, 0.106 mmol, 1.05 equiv) was added dropwise over 1 minute and stirred for 14 hours, after which purification by preparatory TLC eluting with 33% EtOAc in hexanes provided the di-protected product (10 mg, 14%), and the mono-protected product **73d** (48 mg, 80%), both as yellow solids.

73d: TLC: R_f = 0.40, (33% EtOAc in hexanes). IR (cm^{-1}): 3520 (m), 3127 (w), 2980 (m), 2926 (m), 2482 (m), 1942 (s), 1849 (s), 1741 (s). ^{1}H NMR [300 MHz, $CDCl_3$]: δ 8.48 (d, *J* = 1.9 Hz, 1H), 7.88 (d, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 4.1, 1.9 Hz, 1H), 6.28 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H) 4.65 (d, *J* = 7.6 Hz, 1H), 4.47 (d, *J* = 8.3 Hz, 1H), 4.28 (dd, *J* = 12.1, 4.1 Hz, 1H), 4.20 (dd, *J* = 12.1, 2.2 Hz, 1H), 3.42 (dd, *J* = 7.3, 4.4 Hz, 1H) 2.81 (br s, 1H), 2.57 (ddd, *J* = 9.5, 3.8, 2.2 Hz), 1.49 (s, 9H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 231.7, 223.8, 153.8, 147.0, 142.2, 142.0, 136.38, 136.33, 134.7, 109.9, 106.2, 105.9, 105.6, 82.7, 77.3, 71.1, 67.6, 65.5, 57.8, 27.9 (3). HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_7O_6$ $[M - H]^+$: 595.1004. Found: 595.1002.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*,6*S*)-η-(2,3,4)-5-*tert*-butoxycarbonyloxy-6-*tert*-butoxycarbonyloxymethyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum

Diprotected product: TLC: R_f = 0.63, (33% EtOAc in hexanes). IR (cm^{-1}): 3146 (w), 2980 (m), 2926 (m), 2482 (m), 1953 (s), 1864 (s), 1741 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.51 (d, *J*

= 1.9 Hz, 1H), 7.73 (d, *J* = 2.2 Hz, 1H), 7.71 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.04 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.29 (t, *J* = 2.2 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 6.17 (t, *J* = 2.2 Hz, 1H), 5.30 (dd, *J* = 10.2, 2.9 Hz, 1H), 4.86 (dt, *J* = 7.6, 2.5 Hz, 1H), 4.15 (d, *J* = 3.2 Hz, 2H), 3.41 (dd, *J* = 7.6, 4.4 Hz, 1H), 2.78 (dt, *J* = 9.8, 3.2 Hz, 1 H), 1.52 (s, 9H), 1.49 (s, 9H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.4, 224.1, 153.5, 153.1, 147.0, 142.1, 141.9, 136.3, 136.2, 134.6, 110.6, 106.2, 105.9, 105.6, 82.7, 82.5, 73.3, 71.5, 64.9, 64.8, 57.2, 27.9 (6). HRMS (ESI) Calcd for $C_{27}H_{35}BMoN_6O_6$ $[M]^+$: 696.1607. Found: 696.1602.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-5-hydroxy-5-methyl-6-acyloxymethyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 76

Diol **75** (59 mg, 0.116 mmol, 1.0 equiv), triethylamine (67 μL, 0.476 mmol, 4.1 equiv) and a catalytic amount of DMAP were dissolved in CH_2Cl_2 (6 mL) at 0 °C. Acetic anhydride (44 μL, 0.465 mmol, 4.0 equiv) was added dropwise over 1 minute and stirred for 5 hours, after which the reaction mixture was concentrated and purified directly by chromatography on silica gel, eluting with 50% EtOAc in hexanes to provide 56 mg (88%) of pure product **76** as a yellow solid.

76: TLC: R_f = 0.72, (50% EtOAc in hexanes). IR (cm^{-1}): 3489 (w), 3146 (w), 3127 (w), 2964 (w), 2926 (w), 2486 (m), 1942 (s), 1849 (s), 1737 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.48 (d, *J* = 2.2 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.58 (t, *J* = 2.2 Hz, 2H), 7.51 (d, *J* = 2.2 Hz, 1H), 6.98 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.28 (t, *J* = 2.2 Hz, 1H), 6.20 (m, 2H), 4.51 (dd, *J* = 7.6, 2.5 Hz, 1H), 4.37 (dd, *J* = 11.8, 1.9 Hz, 1H), 4.06 (dd, *J* = 11.4, 8.6 Hz, 1H), 4.10 (dd, *J* = 7.3, 4.1 Hz, 1H), 2.94 (br s, 1H), 2.71 (dd, *J* = 8.6, 1.6 Hz, 1H), 2.08 (s, 3H), 1.46 (s, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.6, 223.3, 171.3, 147.0, 142.1, 142.0, 136.4, 136.3, 134.7, 109.2, 106.3, 105.9, 105.6, 79.4, 77.4, 71.4, 62.9, 56.9, 28.2, 21.1. HRMS (ESI) Calcd for $C_{20}H_{24}BMoN_6O_6$ $[M + H]^+$: 553.0899. Found: 553.0899.

X-Ray Crystallographic Study:

A suitable crystal of **62** was coated with a small amount of Paratone N oil, suspended in a small fiber loop and placed on a Bruker D8 APEX II CCD sealed tube diffractometer with graphite monochromated CuK_α (1.54178 Å) radiation. Data were measured at 296 K using a series of combinations of phi and omega scans with 10 s frame exposures and 0.5^o frame widths. Data collection, indexing and initial cell refinements were all carried out using APEX II[132] software. Frame integration and final cell refinements were done using SAINT[133] software. The final cell parameters were determined from least-squares refinement on 1390 reflections. .

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).[134] 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. Only the molybdenum and oxygen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*.[135] Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Table 1.

Table 9: Crystal data and structure refinement for 62

Identification code	**62**
Empirical formula	$C_{24}\ H_{27}\ B\ Mo\ N_6\ O_5$
Formula weight	586.27
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic

[132] APEX II, **2005**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[133] SAINT Version 6.45A, **2003**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[134] SHELXTL V6.12, **2002**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[135] 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).

Space group	P1	
Unit cell dimensions	a = 9.6927(10) Å	α= 72.134(7)°.
	b = 11.2825(12) Å	β= 76.552(8)°.
	c = 13.9298(16) Å	γ = 65.766(6)°.
Volume	1312.1(2) $Å^3$	
Z	2	
Density (calculated)	1.484 Mg/m^3	
Absorption coefficient	4.478 mm^{-1}	
F(000)	600	
Crystal size	0.15 x 0.09 x 0.05 mm^3	
Theta range for data collection	3.36 to 52.88°.	
Index ranges	-9<=h<=10, -10<=k<=11, -14<=l<=11	
Reflections collected	5582	
Independent reflections	3490 [R(int) = 0.0261]	
Completeness to theta = 52.88°	91.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8071 and 0.5532	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3490 / 14 / 359	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R_1 = 0.0652, wR_2 = 0.1628	
R indices (all data)	R_1 = 0.0891, wR_2 = 0.2110	
Absolute structure parameter	0.26(6)	
Largest diff. peak and hole	0.953 and -0.938 $e.Å^{-3}$	

Figure 14: ORTEP of (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*R*)-η-(2,3,4)-9-butyl-5-oxo-1,7-dioxa-spiro-[5.5]-undec-8-ene-2-yl]molybdenum, 62

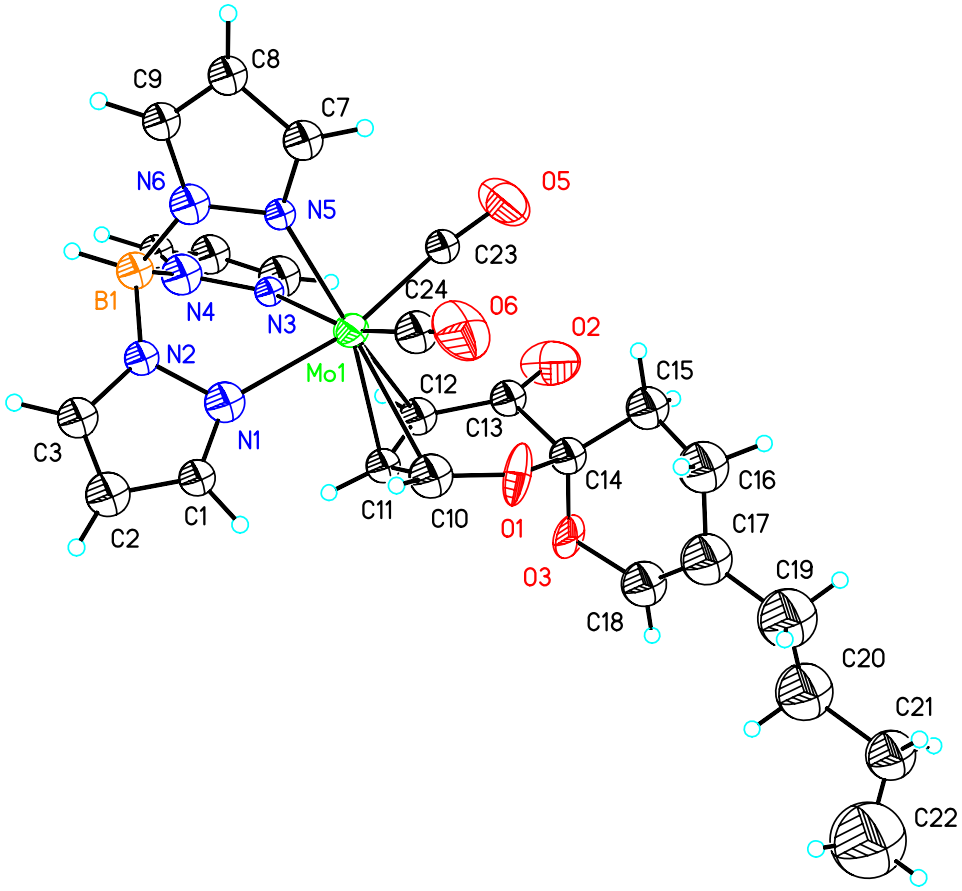


Table 10: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 62. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	4390(40)	-3670(30)	4290(30)	52(9)
C(1)	1060(30)	-3150(20)	3340(20)	48(7)
C(2)	1350(40)	-4440(40)	3650(30)	70(10)
C(3)	2610(30)	-4770(30)	3950(20)	59(8)
C(4)	3080(40)	-850(40)	5240(30)	79(11)
C(5)	3790(40)	-1730(30)	6090(30)	71(10)
C(6)	4270(30)	-2760(30)	5840(20)	48(7)
C(7)	5690(30)	-1800(30)	1880(20)	56(8)

C(8)	7080(30)	-2920(30)	1970(20)	53(8)
C(9)	6710(30)	-3700(30)	2720(20)	50(7)
C(10)	-360(40)	310(30)	2443(19)	74(10)
C(11)	-210(30)	20(20)	3477(17)	48(7)
C(12)	160(30)	860(20)	3830(20)	59(8)
C(13)	-80(30)	2230(30)	3270(20)	55(8)
C(14)	-1070(30)	2650(30)	2230(20)	54(8)
C(15)	-690(30)	3720(30)	1530(20)	72(9)
C(16)	-1710(40)	4140(40)	780(30)	101(12)
C(17)	-3310(50)	4370(40)	1160(30)	103(12)
C(18)	-3650(40)	3850(30)	2140(30)	84(11)
C(19)	-4550(50)	5320(50)	500(40)	136(15)
C(20)	-6040(50)	5860(50)	900(40)	131(15)
C(21)	-7300(40)	6810(40)	140(30)	97(11)
C(22)	-8470(80)	6430(70)	350(60)	230(40)
C(23)	3000(30)	850(20)	2660(20)	46(7)
C(24)	2200(40)	-290(30)	1520(30)	64(10)
Mo(1)	2273(2)	-652(1)	2983(1)	51(1)
N(1)	1980(30)	-2640(30)	3370(20)	61(8)
N(2)	3080(20)	-3750(20)	3916(18)	44(6)
N(3)	3080(20)	-1340(20)	4532(17)	35(5)
N(4)	3880(30)	-2660(30)	4990(20)	69(8)
N(5)	4610(20)	-1931(19)	2568(16)	34(5)
N(6)	5240(30)	-3140(30)	3180(20)	59(7)
O(1)	-770(30)	1478(17)	1822(16)	75(8)
O(2)	90(30)	3160(20)	3410(30)	126(12)
O(3)	-2570(30)	2920(20)	2785(17)	79(8)
O(5)	3390(30)	1700(30)	2140(30)	112(11)
O(6)	2160(30)	20(30)	700(20)	106(10)
B(1B)	-4090(40)	11130(40)	5680(30)	55(10)
C(1B)	-2660(30)	8140(30)	4660(20)	41(7)
C(2B)	-3350(40)	8990(30)	3880(30)	66(10)
C(3B)	-3930(40)	10370(30)	4200(30)	70(10)
C(4B)	-590(40)	10430(30)	6870(30)	74(10)
C(5B)	-1110(40)	11930(40)	6260(30)	70(10)
C(6B)	-2380(40)	12330(30)	5710(30)	72(10)
C(7B)	-5250(40)	9200(30)	8170(30)	62(9)
C(8B)	-6620(50)	10210(40)	8000(30)	85(12)
C(9B)	-6430(30)	11130(30)	6930(20)	67(9)
C(10B)	-30(30)	6380(30)	6140(20)	65(9)
C(11B)	530(30)	7300(30)	6210(20)	65(9)
C(12B)	630(30)	7240(30)	7205(19)	57(8)
C(13B)	1440(40)	4790(30)	7500(30)	56(9)
C(14B)	520(40)	5000(30)	6920(30)	69(9)
C(15B)	1390(40)	3690(30)	8600(30)	77(10)
C(16B)	2690(40)	3290(30)	9260(30)	88(10)
C(17B)	4130(20)	3290(30)	8530(30)	90(11)
C(18B)	4130(40)	3840(40)	7540(30)	85(11)
C(19B)	5720(30)	2660(20)	9070(20)	100(10)
C(20B)	6170(30)	1180(20)	9480(30)	200(30)
C(21B)	7410(30)	860(40)	10110(20)	180(30)

C(22B)	9090(40)	600(50)	9390(30)	126(15)
C(23B)	-1720(40)	7600(30)	8380(30)	54(9)
C(24B)	-2520(40)	6500(30)	7470(30)	65(9)
Mo(1B)	-1890(2)	8048(1)	6933(1)	53(1)
N(1B)	-2700(30)	8760(30)	5450(20)	59(8)
N(2B)	-3530(20)	10110(20)	5087(18)	45(6)
N(3B)	-1630(30)	10100(30)	6500(20)	55(7)
N(4B)	-2590(30)	11170(30)	5940(20)	60(8)
N(5B)	-4270(40)	9430(30)	7210(30)	83(10)
N(6B)	-5000(30)	10580(20)	6634(19)	47(7)
O(1B)	1040(30)	5910(20)	7928(16)	66(7)
O(2B)	180(40)	4240(30)	6620(30)	122(12)
O(3B)	2880(20)	4430(20)	7020(20)	80(8)
O(4B)	-1920(30)	7400(30)	9310(30)	98(10)
O(5B)	-3020(30)	5650(20)	7560(20)	78(8)

Table 11: Bond lengths [Å] and angles [°] for 62.

B(1)-N(2)	1.52(5)	C(11)-H(11)	0.9300
B(1)-N(4)	1.57(5)	C(12)-C(13)	1.45(4)
B(1)-N(6)	1.64(4)	C(12)-Mo(1)	2.40(2)
B(1)-H(1)	0.9800	C(12)-H(12)	0.9300
C(1)-N(1)	1.25(4)	C(13)-O(2)	1.20(4)
C(1)-C(2)	1.32(4)	C(13)-C(14)	1.76(4)
C(1)-H(1)	0.9300	C(14)-C(15)	1.42(4)
C(2)-C(3)	1.25(5)	C(14)-O(3)	1.44(4)
C(2)-H(2)	0.9300	C(14)-O(1)	1.49(4)
C(3)-N(2)	1.39(4)	C(15)-C(16)	1.45(5)
C(3)-H(3)	0.9300	C(15)-H(15A)	0.9700
C(4)-N(3)	1.28(5)	C(15)-H(15B)	0.9700
C(4)-C(5)	1.39(5)	C(16)-C(17)	1.46(5)
C(4)-H(4)	0.9300	C(16)-H(16A)	0.9700
C(5)-C(6)	1.19(4)	C(16)-H(16B)	0.9700
C(5)-H(5)	0.9300	C(17)-C(18)	1.33(5)
C(6)-N(4)	1.29(4)	C(17)-C(19)	1.51(6)
C(6)-H(6)	0.9300	C(18)-O(3)	1.40(4)
C(7)-N(5)	1.27(4)	C(18)-H(18)	0.9300
C(7)-C(8)	1.42(4)	C(19)-C(20)	1.37(6)
C(7)-H(7)	0.9300	C(19)-H(19A)	0.9700
C(8)-C(9)	1.23(4)	C(19)-H(19B)	0.9700
C(8)-H(8)	0.9300	C(20)-C(21)	1.61(6)
C(9)-N(6)	1.39(3)	C(20)-H(20A)	0.9700
C(9)-H(9)	0.9300	C(20)-H(20B)	0.9700
C(10)-O(1)	1.29(3)	C(21)-C(22)	1.31(7)
C(10)-C(11)	1.40(2)	C(21)-H(21A)	0.9700
C(10)-Mo(1)	2.52(3)	C(21)-H(21B)	0.9700
C(10)-H(10)	0.9300	C(22)-H(22A)	0.9600
C(11)-C(12)	1.39(2)	C(22)-H(22B)	0.9600
C(11)-Mo(1)	2.21(2)	C(22)-H(22C)	0.9600

C(23)-O(5)	1.16(4)	C(15B)-H(15C)	0.9700
C(23)-Mo(1)	1.98(3)	C(15B)-H(15D)	0.9700
C(24)-O(6)	1.09(4)	C(16B)-C(17B)	1.52(5)
C(24)-Mo(1)	1.97(4)	C(16B)-H(16C)	0.9700
Mo(1)-N(5)	2.187(18)	C(16B)-H(16D)	0.9700
Mo(1)-N(3)	2.26(2)	C(17B)-C(18B)	1.32(5)
Mo(1)-N(1)	2.27(3)	C(17B)-C(19B)	1.667(12)
N(1)-N(2)	1.41(3)	C(18B)-O(3B)	1.38(5)
N(3)-N(4)	1.38(3)	C(18B)-H(18B)	0.9300
N(5)-N(6)	1.34(3)	C(19B)-C(20B)	1.496(14)
B(1B)-N(2B)	1.47(4)	C(19B)-H(19C)	0.9700
B(1B)-N(6B)	1.52(5)	C(19B)-H(19D)	0.9700
B(1B)-N(4B)	1.60(5)	C(20B)-C(21B)	1.507(14)
B(1B)-H(1B)	0.9800	C(20B)-H(20C)	0.9700
C(1B)-C(2B)	1.32(4)	C(20B)-H(20D)	0.9700
C(1B)-N(1B)	1.46(4)	C(21B)-C(22B)	1.667(12)
C(1B)-H(1B)	0.9300	C(21B)-H(21C)	0.9700
C(2B)-C(3B)	1.59(5)	C(21B)-H(21D)	0.9700
C(2B)-H(2B)	0.9300	C(22B)-H(22D)	0.9600
C(3B)-N(2B)	1.30(4)	C(22B)-H(22E)	0.9600
C(3B)-H(3B)	0.9300	C(22B)-H(22F)	0.9600
C(4B)-N(3B)	1.45(5)	C(23B)-O(4B)	1.24(4)
C(4B)-C(5B)	1.56(5)	C(23B)-Mo(1B)	1.94(4)
C(4B)-H(4B)	0.9300	C(24B)-O(5B)	1.20(4)
C(5B)-C(6B)	1.44(5)	C(24B)-Mo(1B)	1.96(4)
C(5B)-H(5B)	0.9300	Mo(1B)-N(1B)	2.18(3)
C(6B)-N(4B)	1.34(4)	Mo(1B)-N(5B)	2.22(3)
C(6B)-H(6B)	0.9300	Mo(1B)-N(3B)	2.31(3)
C(7B)-C(8B)	1.36(5)	N(1B)-N(2B)	1.39(3)
C(7B)-N(5B)	1.47(5)	N(3B)-N(4B)	1.33(4)
C(7B)-H(7B)	0.9300	N(5B)-N(6B)	1.30(4)
C(8B)-C(9B)	1.55(5)	N(2)-B(1)-N(4)	114(2)
C(8B)-H(8B)	0.9300	N(2)-B(1)-N(6)	97(2)
C(9B)-N(6B)	1.29(4)	N(4)-B(1)-N(6)	112(3)
C(9B)-H(9B)	0.9300	N(2)-B(1)-H(1)	110.8
C(10B)-C(11B)	1.39(2)	N(4)-B(1)-H(1)	110.8
C(10B)-C(14B)	1.56(4)	N(6)-B(1)-H(1)	110.8
C(10B)-Mo(1B)	2.36(3)	N(1)-C(1)-C(2)	122(3)
C(10B)-H(10B)	0.9300	N(1)-C(1)-H(1)	119.0
C(11B)-C(12B)	1.38(2)	C(2)-C(1)-H(1)	118.9
C(11B)-Mo(1B)	2.24(3)	C(3)-C(2)-C(1)	97(3)
C(11B)-H(11B)	0.9300	C(3)-C(2)-H(2)	131.3
C(12B)-O(1B)	1.48(4)	C(1)-C(2)-H(2)	131.3
C(12B)-Mo(1B)	2.31(3)	C(2)-C(3)-N(2)	117(3)
C(12B)-H(12B)	0.9300	C(2)-C(3)-H(3)	121.4
C(13B)-C(14B)	1.25(5)	N(2)-C(3)-H(3)	121.4
C(13B)-O(3B)	1.35(4)	N(3)-C(4)-C(5)	117(3)
C(13B)-O(1B)	1.42(4)	N(3)-C(4)-H(4)	121.3
C(13B)-C(15B)	1.66(5)	C(5)-C(4)-H(4)	121.3
C(14B)-O(2B)	1.25(5)	C(6)-C(5)-C(4)	101(4)
C(15B)-C(16B)	1.57(5)	C(6)-C(5)-H(5)	129.4

C(4)-C(5)-H(5)	129.4	H(16A)-C(16)-H(16B)	107.4
C(5)-C(6)-N(4)	113(3)	C(18)-C(17)-C(16)	118(4)
C(5)-C(6)-H(6)	123.3	C(18)-C(17)-C(19)	121(4)
N(4)-C(6)-H(6)	123.3	C(16)-C(17)-C(19)	121(4)
N(5)-C(7)-C(8)	115(3)	C(17)-C(18)-O(3)	124(3)
N(5)-C(7)-H(7)	122.6	C(17)-C(18)-H(18)	117.8
C(8)-C(7)-H(7)	122.6	O(3)-C(18)-H(18)	117.8
C(9)-C(8)-C(7)	101(3)	C(20)-C(19)-C(17)	123(4)
C(9)-C(8)-H(8)	129.5	C(20)-C(19)-H(19A)	106.7
C(7)-C(8)-H(8)	129.5	C(17)-C(19)-H(19A)	106.7
C(8)-C(9)-N(6)	113(3)	C(20)-C(19)-H(19B)	106.7
C(8)-C(9)-H(9)	123.4	C(17)-C(19)-H(19B)	106.7
N(6)-C(9)-H(9)	123.4	H(19A)-C(19)-H(19B)	106.6
O(1)-C(10)-C(11)	127(3)	C(19)-C(20)-C(21)	119(4)
O(1)-C(10)-Mo(1)	118(2)	C(19)-C(20)-H(20A)	107.5
C(11)-C(10)-Mo(1)	61.0(14)	C(21)-C(20)-H(20A)	107.5
O(1)-C(10)-H(10)	116.3	C(19)-C(20)-H(20B)	107.4
C(11)-C(10)-H(10)	116.3	C(21)-C(20)-H(20B)	107.4
Mo(1)-C(10)-H(10)	90.7	H(20A)-C(20)-H(20B)	107.0
C(12)-C(11)-C(10)	119(3)	C(22)-C(21)-C(20)	111(4)
C(12)-C(11)-Mo(1)	79.9(15)	C(22)-C(21)-H(21A)	109.5
C(10)-C(11)-Mo(1)	85.3(17)	C(20)-C(21)-H(21A)	109.5
C(12)-C(11)-H(11)	120.3	C(22)-C(21)-H(21B)	109.5
C(10)-C(11)-H(11)	120.3	C(20)-C(21)-H(21B)	109.5
Mo(1)-C(11)-H(11)	104.8	H(21A)-C(21)-H(21B)	108.0
C(11)-C(12)-C(13)	121(3)	C(21)-C(22)-H(22A)	109.5
C(11)-C(12)-Mo(1)	65.3(13)	C(21)-C(22)-H(22B)	109.4
C(13)-C(12)-Mo(1)	110.0(18)	H(22A)-C(22)-H(22B)	109.5
C(11)-C(12)-H(12)	119.3	C(21)-C(22)-H(22C)	109.5
C(13)-C(12)-H(12)	119.3	H(22A)-C(22)-H(22C)	109.5
Mo(1)-C(12)-H(12)	94.5	H(22B)-C(22)-H(22C)	109.5
O(2)-C(13)-C(12)	135(3)	O(5)-C(23)-Mo(1)	156(3)
O(2)-C(13)-C(14)	114(3)	O(6)-C(24)-Mo(1)	174(4)
C(12)-C(13)-C(14)	110(2)	C(24)-Mo(1)-C(23)	87.1(14)
C(15)-C(14)-O(3)	119(2)	C(24)-Mo(1)-N(5)	81.8(11)
C(15)-C(14)-O(1)	116(3)	C(23)-Mo(1)-N(5)	88.1(9)
O(3)-C(14)-O(1)	105(3)	C(24)-Mo(1)-C(11)	98.0(11)
C(15)-C(14)-C(13)	105(3)	C(23)-Mo(1)-C(11)	110.9(9)
O(3)-C(14)-C(13)	97(2)	N(5)-Mo(1)-C(11)	161.0(8)
O(1)-C(14)-C(13)	113(2)	C(24)-Mo(1)-N(3)	163.6(11)
C(14)-C(15)-C(16)	102(3)	C(23)-Mo(1)-N(3)	89.0(10)
C(14)-C(15)-H(15A)	111.3	N(5)-Mo(1)-N(3)	82.1(8)
C(16)-C(15)-H(15A)	111.3	C(11)-Mo(1)-N(3)	98.3(8)
C(14)-C(15)-H(15B)	111.3	C(24)-Mo(1)-N(1)	94.9(13)
C(16)-C(15)-H(15B)	111.3	C(23)-Mo(1)-N(1)	167.7(10)
H(15A)-C(15)-H(15B)	109.2	N(5)-Mo(1)-N(1)	80.2(9)
C(15)-C(16)-C(17)	116(3)	C(11)-Mo(1)-N(1)	80.9(9)
C(15)-C(16)-H(16A)	108.2	N(3)-Mo(1)-N(1)	85.7(9)
C(17)-C(16)-H(16A)	108.2	C(24)-Mo(1)-C(12)	114.1(12)
C(15)-C(16)-H(16B)	108.2	C(23)-Mo(1)-C(12)	80.7(9)
C(17)-C(16)-H(16B)	108.2	N(5)-Mo(1)-C(12)	159.7(9)

C(11)-Mo(1)-C(12)	34.8(6)	N(4B)-C(6B)-C(5B)	100(3)
N(3)-Mo(1)-C(12)	80.9(8)	N(4B)-C(6B)-H(6B)	130.2
N(1)-Mo(1)-C(12)	109.4(9)	C(5B)-C(6B)-H(6B)	130.2
C(24)-Mo(1)-C(10)	64.3(12)	C(8B)-C(7B)-N(5B)	103(3)
C(23)-Mo(1)-C(10)	107.1(11)	C(8B)-C(7B)-H(7B)	128.3
N(5)-Mo(1)-C(10)	141.5(9)	N(5B)-C(7B)-H(7B)	128.3
C(11)-Mo(1)-C(10)	33.7(6)	C(7B)-C(8B)-C(9B)	109(3)
N(3)-Mo(1)-C(10)	132.0(8)	C(7B)-C(8B)-H(8B)	125.7
N(1)-Mo(1)-C(10)	84.7(11)	C(9B)-C(8B)-H(8B)	125.7
C(12)-Mo(1)-C(10)	58.6(9)	N(6B)-C(9B)-C(8B)	102(3)
C(1)-N(1)-N(2)	102(2)	N(6B)-C(9B)-H(9B)	129.0
C(1)-N(1)-Mo(1)	142(2)	C(8B)-C(9B)-H(9B)	129.0
N(2)-N(1)-Mo(1)	116(2)	C(11B)-C(10B)-C(14B)	114(3)
C(3)-N(2)-N(1)	101(2)	C(11B)-C(10B)-Mo(1B)	67.7(15)
C(3)-N(2)-B(1)	135(2)	C(14B)-C(10B)-Mo(1B)	111(2)
N(1)-N(2)-B(1)	125(3)	C(11B)-C(10B)-H(10B)	122.8
C(4)-N(3)-N(4)	96(3)	C(14B)-C(10B)-H(10B)	122.8
C(4)-N(3)-Mo(1)	139(2)	Mo(1B)-C(10B)-H(10B)	90.7
N(4)-N(3)-Mo(1)	124.5(18)	C(12B)-C(11B)-C(10B)	113(3)
C(6)-N(4)-N(3)	112(2)	C(12B)-C(11B)-Mo(1B)	75.1(16)
C(6)-N(4)-B(1)	132(3)	C(10B)-C(11B)-Mo(1B)	77.3(16)
N(3)-N(4)-B(1)	115(3)	C(12B)-C(11B)-H(11B)	123.5
C(7)-N(5)-N(6)	104(2)	C(10B)-C(11B)-H(11B)	123.5
C(7)-N(5)-Mo(1)	135.8(19)	Mo(1B)-C(11B)-H(11B)	115.6
N(6)-N(5)-Mo(1)	119.6(16)	C(11B)-C(12B)-O(1B)	118(2)
N(5)-N(6)-C(9)	106(2)	C(11B)-C(12B)-Mo(1B)	69.5(16)
N(5)-N(6)-B(1)	123(2)	O(1B)-C(12B)-Mo(1B)	110.7(18)
C(9)-N(6)-B(1)	130(2)	C(11B)-C(12B)-H(12B)	121.1
C(10)-O(1)-C(14)	117(2)	O(1B)-C(12B)-H(12B)	121.1
C(18)-O(3)-C(14)	110(2)	Mo(1B)-C(12B)-H(12B)	89.8
N(2B)-B(1B)-N(6B)	105(3)	C(14B)-C(13B)-O(3B)	110(3)
N(2B)-B(1B)-N(4B)	105(3)	C(14B)-C(13B)-O(1B)	112(3)
N(6B)-B(1B)-N(4B)	112(3)	O(3B)-C(13B)-O(1B)	114(3)
N(2B)-B(1B)-H(1B)	111.7	C(14B)-C(13B)-C(15B)	116(3)
N(6B)-B(1B)-H(1B)	111.7	O(3B)-C(13B)-C(15B)	109(3)
N(4B)-B(1B)-H(1B)	111.7	O(1B)-C(13B)-C(15B)	96(2)
C(2B)-C(1B)-N(1B)	113(3)	C(13B)-C(14B)-O(2B)	133(4)
C(2B)-C(1B)-H(1B)	123.3	C(13B)-C(14B)-C(10B)	119(3)
N(1B)-C(1B)-H(1B)	123.3	O(2B)-C(14B)-C(10B)	105(3)
C(1B)-C(2B)-C(3B)	102(3)	C(16B)-C(15B)-C(13B)	116(3)
C(1B)-C(2B)-H(2B)	129.0	C(16B)-C(15B)-H(15C)	108.2
C(3B)-C(2B)-H(2B)	129.0	C(13B)-C(15B)-H(15C)	108.2
N(2B)-C(3B)-C(2B)	107(3)	C(16B)-C(15B)-H(15D)	108.2
N(2B)-C(3B)-H(3B)	126.3	C(13B)-C(15B)-H(15D)	108.2
C(2B)-C(3B)-H(3B)	126.3	H(15C)-C(15B)-H(15D)	107.4
N(3B)-C(4B)-C(5B)	95(3)	C(17B)-C(16B)-C(15B)	107(3)
N(3B)-C(4B)-H(4B)	132.3	C(17B)-C(16B)-H(16C)	110.4
C(5B)-C(4B)-H(4B)	132.4	C(15B)-C(16B)-H(16C)	110.4
C(6B)-C(5B)-C(4B)	114(4)	C(17B)-C(16B)-H(16D)	110.4
C(6B)-C(5B)-H(5B)	123.0	C(15B)-C(16B)-H(16D)	110.4
C(4B)-C(5B)-H(5B)	123.0	H(16C)-C(16B)-H(16D)	108.6

C(18B)-C(17B)-C(16B)	124(3)	N(1B)-Mo(1B)-C(11B)	90.6(10)
C(18B)-C(17B)-C(19B)	121(3)	N(5B)-Mo(1B)-C(11B)	159.3(11)
C(16B)-C(17B)-C(19B)	115(3)	C(23B)-Mo(1B)-N(3B)	98.1(12)
C(17B)-C(18B)-O(3B)	126(3)	C(24B)-Mo(1B)-N(3B)	167.6(11)
C(17B)-C(18B)-H(18B)	117.1	N(1B)-Mo(1B)-N(3B)	82.8(11)
O(3B)-C(18B)-H(18B)	117.1	N(5B)-Mo(1B)-N(3B)	77.5(11)
C(20B)-C(19B)-C(17B)	111(2)	C(11B)-Mo(1B)-N(3B)	85.1(10)
C(20B)-C(19B)-H(19C)	109.5	C(23B)-Mo(1B)-C(12B)	69.4(11)
C(17B)-C(19B)-H(19C)	109.5	C(24B)-Mo(1B)-C(12B)	105.0(12)
C(20B)-C(19B)-H(19D)	109.5	N(1B)-Mo(1B)-C(12B)	125.1(10)
C(17B)-C(19B)-H(19D)	109.5	N(5B)-Mo(1B)-C(12B)	149.4(12)
H(19C)-C(19B)-H(19D)	108.1	C(11B)-Mo(1B)-C(12B)	35.4(6)
C(19B)-C(20B)-C(21B)	102.3(17)	N(3B)-Mo(1B)-C(12B)	83.5(10)
C(19B)-C(20B)-H(20C)	111.3	C(23B)-Mo(1B)-C(10B)	111.2(12)
C(21B)-C(20B)-H(20C)	111.3	C(24B)-Mo(1B)-C(10B)	75.4(11)
C(19B)-C(20B)-H(20D)	111.3	N(1B)-Mo(1B)-C(10B)	80.9(10)
C(21B)-C(20B)-H(20D)	111.3	N(5B)-Mo(1B)-C(10B)	151.2(12)
H(20C)-C(20B)-H(20D)	109.2	C(11B)-Mo(1B)-C(10B)	35.1(6)
C(20B)-C(21B)-C(22B)	110(3)	N(3B)-Mo(1B)-C(10B)	116.9(10)
C(20B)-C(21B)-H(21C)	109.6	C(12B)-Mo(1B)-C(10B)	59.4(10)
C(22B)-C(21B)-H(21C)	109.6	N(2B)-N(1B)-C(1B)	104(2)
C(20B)-C(21B)-H(21D)	109.6	N(2B)-N(1B)-Mo(1B)	120(2)
C(22B)-C(21B)-H(21D)	109.6	C(1B)-N(1B)-Mo(1B)	136(2)
H(21C)-C(21B)-H(21D)	108.1	C(3B)-N(2B)-N(1B)	113(2)
C(21B)-C(22B)-H(22D)	109.5	C(3B)-N(2B)-B(1B)	122(3)
C(21B)-C(22B)-H(22E)	109.5	N(1B)-N(2B)-B(1B)	125(3)
H(22D)-C(22B)-H(22E)	109.5	N(4B)-N(3B)-C(4B)	112(3)
C(21B)-C(22B)-H(22F)	109.5	N(4B)-N(3B)-Mo(1B)	121(2)
H(22D)-C(22B)-H(22F)	109.5	C(4B)-N(3B)-Mo(1B)	126(2)
H(22E)-C(22B)-H(22F)	109.5	N(3B)-N(4B)-C(6B)	119(3)
O(4B)-C(23B)-Mo(1B)	168(3)	N(3B)-N(4B)-B(1B)	121(3)
O(5B)-C(24B)-Mo(1B)	163(3)	C(6B)-N(4B)-B(1B)	120(3)
C(23B)-Mo(1B)-C(24B)	77.2(15)	N(6B)-N(5B)-C(7B)	109(3)
C(23B)-Mo(1B)-N(1B)	165.4(12)	N(6B)-N(5B)-Mo(1B)	129(2)
C(24B)-Mo(1B)-N(1B)	98.9(13)	C(7B)-N(5B)-Mo(1B)	122(2)
C(23B)-Mo(1B)-N(5B)	89.6(13)	C(9B)-N(6B)-N(5B)	116(3)
C(24B)-Mo(1B)-N(5B)	91.0(13)	C(9B)-N(6B)-B(1B)	127(3)
N(1B)-Mo(1B)-N(5B)	76.3(12)	N(5B)-N(6B)-B(1B)	117(3)
C(23B)-Mo(1B)-C(11B)	104.1(11)	C(13B)-O(1B)-C(12B)	116(2)
C(24B)-Mo(1B)-C(11B)	107.0(11)	C(13B)-O(3B)-C(18B)	122(3)

Symmetry transformations used to generate equivalent atoms:

Table 12: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 62. 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)	41(1)	43(1)	66(2)	-16(1)	-1(1)	-12(1)
O(1)	111(16)	30(9)	48(14)	-12(9)	-19(11)	16(10)
O(2)	80(16)	87(15)	240(30)	-97(19)	3(18)	-23(14)
O(3)	69(13)	88(15)	42(14)	37(11)	-25(11)	-20(12)
O(5)	103(18)	86(16)	140(30)	-32(16)	31(17)	-53(15)
O(6)	120(20)	120(20)	60(18)	-25(15)	35(15)	-56(17)
Mo(1B)	42(1)	45(1)	69(2)	-14(1)	-3(1)	-14(1)
O(1B)	72(12)	96(16)	42(13)	-8(12)	-44(10)	-30(12)
O(2B)	160(30)	84(19)	130(30)	-24(18)	-60(20)	-40(20)
O(3B)	37(11)	67(13)	120(20)	-56(13)	-4(12)	16(10)
O(4B)	72(15)	95(18)	120(30)	-34(17)	3(16)	-24(14)
O(5B)	92(15)	54(12)	100(20)	0(12)	-36(14)	-40(12)

Table 13: Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for 62

	x	y	z	U(eq)
H(1)	5038	-4561	4633	63
H(1)	136	-2588	3086	58
H(2)	802	-4951	3650	84
H(3)	3203	-5665	4194	71
H(4)	2629	70	5199	95
H(5)	3872	-1558	6678	85
H(6)	4866	-3569	6231	57
H(7)	5577	-1037	1355	68
H(8)	8023	-3025	1574	64
H(9)	7356	-4578	2955	60
H(10)	-130	-413	2174	89
H(11)	-364	-733	3922	57
H(12)	572	544	4442	70
H(15A)	364	3417	1239	86
H(15B)	-892	4431	1856	86
H(16A)	-1347	3471	386	121
H(16B)	-1651	4966	315	121
H(18)	-4665	4135	2419	101
H(19A)	-4238	6066	120	163
H(19B)	-4530	4859	12	163
H(20A)	-6082	6363	1358	157
H(20B)	-6354	5119	1300	157
H(21A)	-7646	7727	194	116
H(21B)	-6851	6782	-558	116

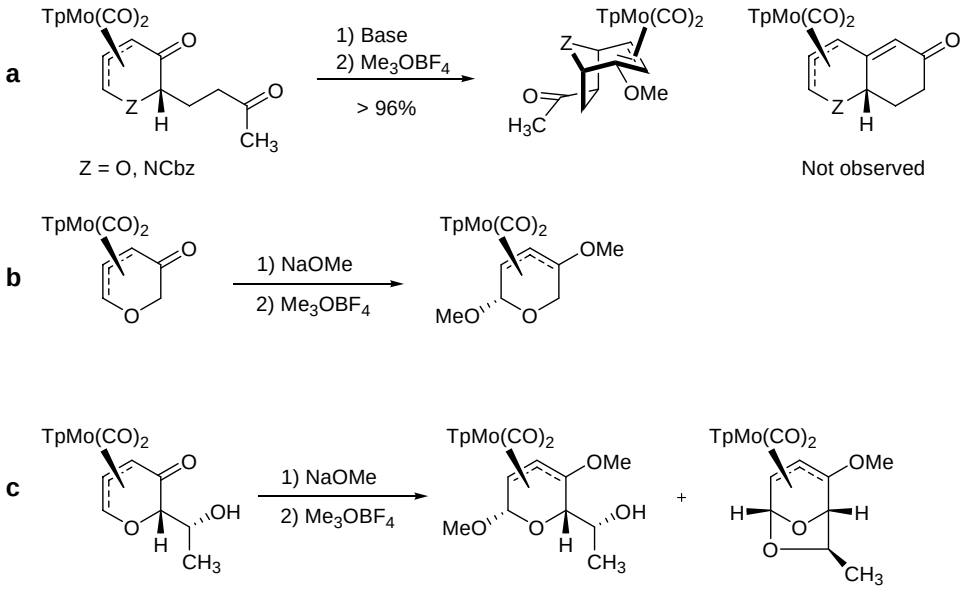
H(22A)	-8112	5486	415	338
H(22B)	-9106	6896	-185	338
H(22C)	-9043	6640	979	338
H(1B)	-4716	12000	5304	66
H(1B)	-2187	7221	4704	49
H(2B)	-3475	8835	3293	79
H(3B)	-4456	11212	3814	84
H(4B)	144	9924	7314	89
H(5B)	-650	12505	6261	84
H(6B)	-2899	13159	5303	86
H(7B)	-4997	8530	8759	74
H(8B)	-7513	10322	8444	102
H(9B)	-7163	11885	6589	80
H(10B)	-671	6568	5669	78
H(11B)	805	7902	5654	78
H(12B)	455	8002	7410	68
H(15C)	420	4055	8999	92
H(15D)	1425	2887	8467	92
H(16C)	2428	3930	9673	106
H(16D)	2856	2411	9715	106
H(18B)	5068	3823	7167	102
H(19C)	6536	2852	8576	120
H(19D)	5561	3083	9620	120
H(20C)	6559	714	8939	242
H(20D)	5321	953	9896	242
H(21C)	7453	68	10655	215
H(21D)	7169	1598	10420	215
H(22D)	9149	136	8900	190
H(22E)	9890	74	9810	190
H(22F)	9186	1446	9045	190

Chapter 3: The intermolecular 1,5-Michael Reaction: Mechanistic studies, and efforts toward its application to spiroketal synthesis

Introduction:

In 2003, Dr. Yongqiang Zhang discovered that enolates of 5-oxo-6-*anti*-(3-oxobutyl)-pyranyl molybdenum complexes do not add directly to the ketone to form the Robinson annulation product as expected, but instead performed a homo-conjugate addition to the neutral molybdenum allyl (**Scheme 47a**). When quenched with Meerwein reagent, the reaction provided clean access to oxa- and aza-[3.2.1]-bicyclic complexes as shown.[136] Preliminary studies by Dr. Zhang also demonstrated that this "1,5-Michael-like" reaction could be extended to inter- and intramolecular alkoxide nucleophiles (**Scheme 47b and c**).

Scheme 47: Preliminary studies of 1,5-Michael-like reaction



Results and Discussion:

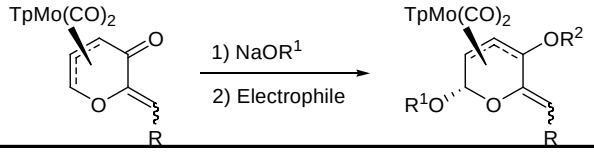
Investigating the scope of the intermolecular 1,5-Michael reaction:

With a mind toward applying this new reaction to the synthesis of spiroketals, and to extend the scope of the reaction, a number of 1,5-Michael-like products were synthesized using various enone substrates, nucleophiles and electrophiles (**Table 14**). Sodium alkoxides were excellent

[136] (a) Zhang, Y. Liebeskind, L. S. *J. Am. Chem. Soc.* **2005**, *127*, 11258-11259. (b) Zhang, Y.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2006**, *128*, 465-472.

nucleophiles for both substituted and unsubstituted enones (Entries 1, 3-8), but the less nucleophilic sodium acetate gave no reaction and only starting material was recovered (Entry 2). Both isomers of the methyl-substituted enone **60** and **61** could be converted to the product with retention of stereochemistry, but the dimethoxy *E*-alkylidene complex **79** was very sensitive completely converted into its stereoisomer **78** within one hour (Entry 4). Various electrophiles could be used to quench the reaction as well. Meerwein reagents (Me_3OBF_4 and Et_3OPF_6) were effective, as were chloroformates and diphenylphosphoryl chloride, but acetyl chloride gave the product **83** in low yield, and that reaction was not repeatable on larger scale, as only starting material was recovered.

Table 14: Intermolecular 1,5-Michael-like reaction



Entry	R =	R^1 =	Electrophile	R^2 =	% Yield[a]
1	**24**, H	Me	Me_3OBF_4	Me	**77**, 76
2	**24**, H	Ac	Me_3OBF_4	Me	NR, Rec SM
3	**61**, *Z*-Me	Me	Me_3OBF_4	Me	**78**, 76
4	**60**, *E*-Me	Me	Me_3OBF_4	Me	**79**, 77[b]
5	**61**, *Z*-Me	Et	Et_3OPF_6	Et	**80**, 71
6	**61**, *Z*-Me	Me	$ClCO_2Et$	CO_2Et	**81**, 84
7	**61**, *Z*-Me	Me	$ClPO(OPh)_2$	$P(O)(OPh)_2$	**82**, 51
8	**61**, *Z*-Me	Me	ClCOMe	COMe	**83**, 29

a) isolated yields; b) Product isomerized completely to **37** in $CDCl_3$ within an hour.

There is a pronounced structural difference in the 1,5-Michael products bearing different groups in the 5-position. While unable to obtain a crystal structure of either of compounds **78** or **81**, some information can be gleaned from the spectroscopic data (**Figure 15**). The electronic differences between the donating methoxy group and withdrawing carbonate group on the allyl moiety are reflected in the ^1H and ^{13}C resonances of the allyl protons and IR stretches, and the

metal carbonyls. These differences give clues as to the structural characteristics of these complexes.

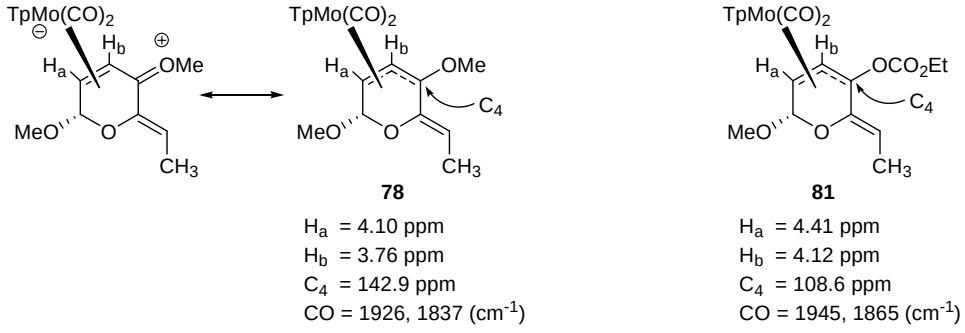


Figure 15: Electronic differences in substituents on neutral allyl-Mo are reflected spectroscopically

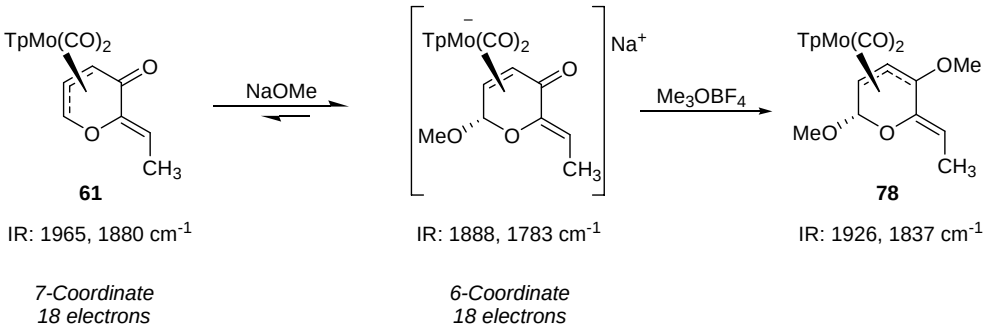
The higher field resonances of H_a and H_b in **84** are not necessarily surprising, given the electron withdrawing nature of a carbonate relative to a methoxy group. Interestingly, however, the ^{13}C resonance of C_4 in **78** (142.9 ppm) appears to be very enol ether like in character, whereas that in **81** is shielded upfield beyond the range expected by the electronic changes (108.6 ppm). These data suggest that there may be considerable oxonium character in the 5-methoxy group of **78**, and therefore a long C_4-Mo bond (relative to the other C-Mo bonds of the allyl).[137] On the other hand, the electron withdrawing nature of the carbonate in **81** causes the metal moiety to donate electron density into C_4, accounting for the low field resonance, and presumably shortening the Mo-C_4 bond length. The electronic deficiency this creates on the metal center is reflected in its decreased backbonding into its ancilliary carbon monoxide ligands leading to the observed higher frequency IR stretches. The importance of these structural characteristics will become very important in the next chapter, as it will be argued that the Mo-C_4 bond length is related to the regioselectivity of nucleophilic additions.

[137] This assumption would be in accord with crystallographic data obtained for other allylmolybdenum complexes bearing an alkoxy group at the terminal position. See: Ward, Y. D.; Villavueva, L. A.; Allred, G. D.; Liebeskind, L. S. *Organometallics* **1996**, *15*, 4201-4210.

The mechanism of the 1,5 Michael reaction has become the focus of intense interest in our group because mounting evidence suggests that the reaction proceeds through an anionic molybdenum intermediate, which is quenched with an electrophile to form the product (**Scheme 48**). The first experimental step of the reaction requires stirring the neutral allyl-molybdenum complex in excess sodium methoxide for several hours, with longer reaction times and high concentration of methoxide being essential to obtaining good yields. A drastic color change from bright orange to dark red or purple is observed over the first step, and infrared analysis of an aliquot of the reaction mixture revealed a red-shift of the carbonyl stretches (from 1965 and 1880 cm^{-1} in the starting material to 1888 and 1783 cm^{-1} in the reaction mixture) indicating increased backbonding character into the metal carbonyls, which reflects an electron-rich metal center. TLC analysis of the reaction during this step shows only starting material, which suggests that the first step is reversible upon workup, and the long reaction times suggest a relatively high activation energy of the forward reaction (i.e. the reaction is slow to reach equilibrium). Meerwein quench of the reaction provides excellent yields of product, and typically ~10% recovered starting material, the yields of which probably reflect the position of the equilibrium. The implication of a favorable equilibrium position before quench is that *the intermediate must be thermodynamically downhill*. Curtis and coworkers have observed that the sterically bulky 7-coordinate $TpMo(CO)_3X$ undergoes a thermodynamically favorable orbital distortion, compressing the CO and X ligands closer together.[138] It is argued that this distortion could favor rearrangement to a "quasi-six-coordinate" octahedral geometry [i.e. $TpMo(CO)_2(\eta^2\text{-COX})$].[139] It follows that the neutral, 18 electron 7-coordinate starting complex may be less stable than an anionic 18 electron 6-coordinate η^2-complex under the reaction conditions.

[138] Curtis, M. D.; Shiu, K.-B. *Inorg. Chem.* **1985**, *24*, 1213-1218.
[139] Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550-1561.

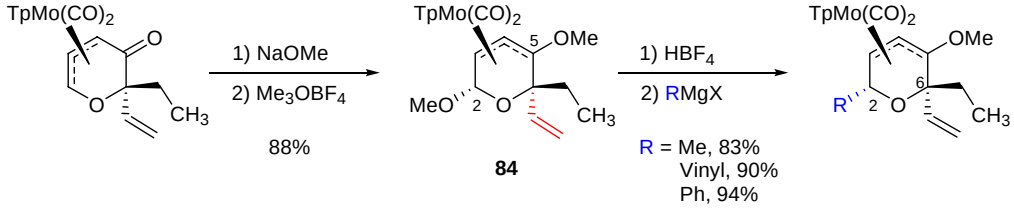
Scheme 48: Proposed mechanism of intermolecular 1,5-Michael reaction



Synthetic Applications of the Intermolecular 1,5-Michael Reaction

A synthetic application of the products of the intermolecular variant of the 1,5-Michael reaction was first demonstrated by Bo Cheng in late 2005. She discovered that 6,6-disubstituted-5-oxo-pyranyl molybdenum complexes could be converted cleanly through the 1,5-Michael reaction to the dimethoxy complex **84** (**Scheme 49**).[140] Subsequent ionization of the 2-*anti*-methoxy group with tetrafluoroboric acid, followed by nucleophilic addition with Grignard reagents formed the 2,6,6-trisubstituted products[141] in excellent yields. The ionization/nucleophilic addition reaction presumably proceeds through a cationic diene, which is activated for nucleophilic addition at the 2-position.

Scheme 49: Ionization/nucleophilic addition sequence to 6,6-disubstituted compounds



The obvious potential of the "Ionization/Nucleophilic Addition" (henceforth, this reaction sequence will be abbreviated "INA" for simplification) sequence is that the reactive dimethoxy compound generated possesses a leaving group both farther away from the sterically bulky

[140] Cheng, B., Liebeskind Lab, unpublished results.
[141] While the exchange of substituents in this case should invert the numbering around the ring (by IUPAC standards), for simplicity, the numbering has been kept constant throughout the scheme.

quaternary center (in contrast to the encumbered acetates and hydroxyl groups of compounds **68** and **73** discussed in the previous chapter), and in an orientation that is close to antiperiplanar to the metal moiety (**Figure 16**). This suggests that ionization should be kinetically favored over that of the *syn*-leaving groups discussed in Chapter 2.

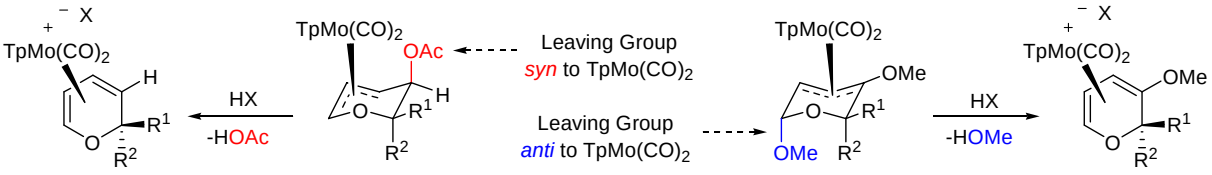
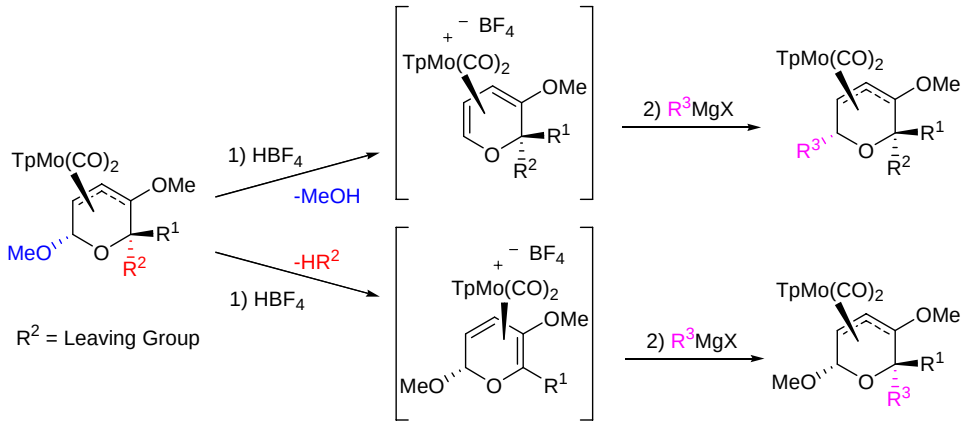


Figure 16: Favorable stereoelectronics in ionization of 1,5-Michael product

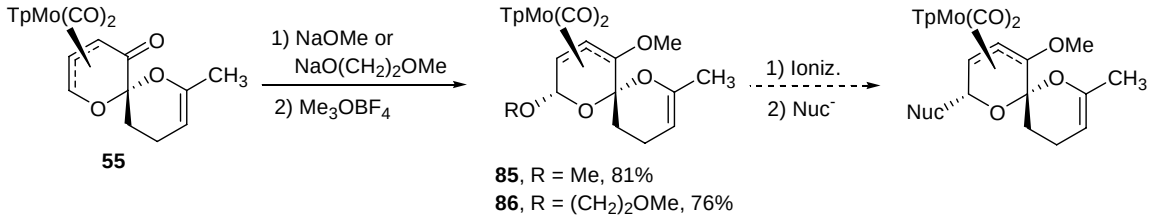
The high reactivity and selectivity of complex **84** in **Scheme 49** can be attributed to a dearth of competing pathways. Even the cationic diene electrophile formed in the ionization step of **Scheme 49** should be electrophilic at both termini of the diene, but presumably steric interaction between an incoming nucleophile and the *anti* vinyl group (in red) preclude addition to the 5-position. A foreseeable problem with the application of the INA sequence to the synthesis of spiroketals is the selectivity of ionization if R^2 is *also* a leaving group (**Scheme 50**). If R^2 is a suitable leaving group, then there could be competition between the two possible ionization pathways. Subsequent nucleophilic addition to the different diene electrophiles would produce different products. We hoped that the reactivity profile of these dialkoxy complexes could be investigated, and applied further to useful and general synthetic applications.

Scheme 50: Competing ionization pathways expected to form different products



Spiroketal **55** was also found to be a suitable substrate for the 1,5-Michael reaction. The dialkoxy spirocycles **85** and **86** could be isolated in very good yields, but were unstable in solution over long periods and were therefore used right away. We hoped that the INA sequence would thus provide the 2-functionalized complexes (**Scheme 51**).

Scheme 51: 1,5-Michael reaction of spirocycloadduct

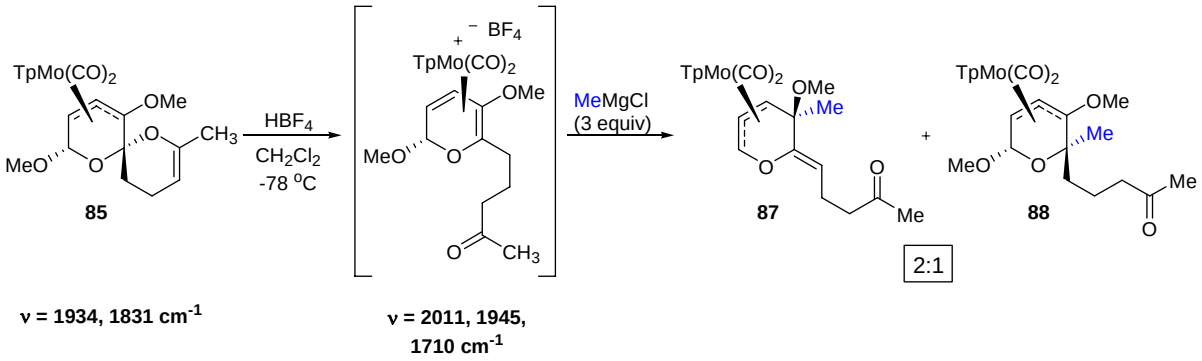


85, R = Me, 81%
86, R = $(CH_2)_2OMe$, 76%

Unfortunately, when compound **85** was subject to the INA sequence with $TrBF_4$ or HBF_4, followed by Grignard or organolithium reagents, the desired 2-functionalized product was not observed, but rather only ring opened products **87** and **88** were observed in approximately 2:1 ratio by crude ^1H NMR (**Scheme 52**). While the possibility of competing ionization of the ring oxygen was anticipated (recall **Scheme 50**), the complete selectivity of ionization was surprising. The reactions were monitored by ReactIR during the ionization step. Infrared analysis of an aliquot of the reaction mixture after the addition of HBF_4 indicated a blue shift in the carbonyl stretches from 1934 and 1831 cm^{-1} in the starting material to 2007 and 1942 cm^{-1} in the

intermediate, typical of increased positive character at the metal center. Importantly, a new carbonyl stretch at 1710 cm^{-1} was also observed in the intermediate, suggesting that the ketone had already formed from ring opening of the spirocycle. It is important to note that this conclusion must be qualified by the manner in which the experiment was run, because the aliquot obtained for this measurement was exposed to air, it is reasonable to suggest that the infrared signals observed represent those of a "worked up" product, and may not accurately represent what is actually present in the reaction mixture.

Scheme 52: INA sequence of spirocycle provides only ring-opened products



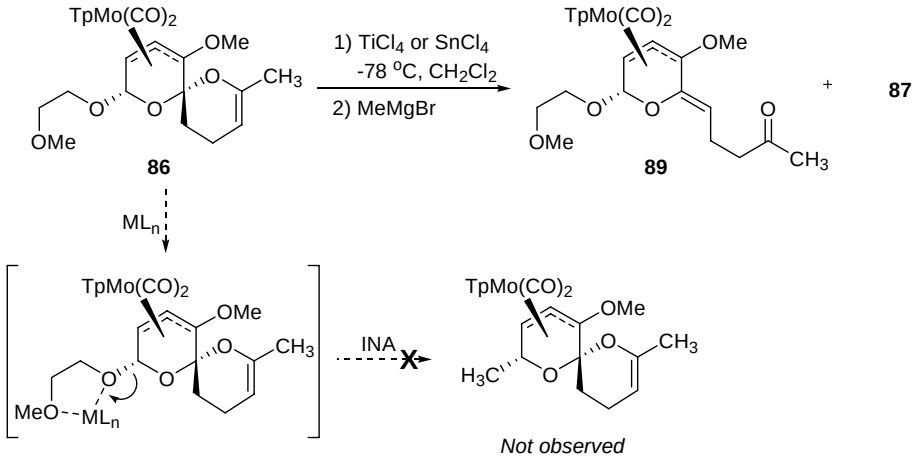
85 ν = 1934, 1831 cm^{-1}

ν = 2011, 1945, 1710 cm^{-1}

87 **88**

It was thought that the use of a chelating alkoxide group and a multidentate Lewis acid could outweigh the preference for the selectivity described above, however, similar results were observed when 1,5-Michael product **86** was subjected to chelating Lewis acids $TiCl_4$ and $SnCl_4$ even at low temperatures (**Scheme 53**). The same INA product **87** was observed in the crude ^1H NMR, as was ring opened adduct **89**, a similar structure to that observed in the strong Lewis acid mediated ring opening shown in **Scheme 39**.

Scheme 53: Proposed chelation-assisted ionization only yields ring opened products



Because the enol ether character was thought to increase the leaving group ability of the spiro-ring in **85**, attempts to hydrogenate the enol ether of the spiro ring of **55** were made, but using a variety of catalysts (Pd/C, $Rh(PPh_3)_3Cl$, $[Ir(cod)(PCy_3)(py)]PF_6$,[142] $[Rh(cod)(diphos)]PF_6$[143]) no reaction was observed after several days under 880 psi H_2 pressure (60 atm) owing to the electron-rich nature of the double bond.[144] Hydroboration/oxidation of the enol ether moiety was also attempted, but under various conditions did not provide suitable amounts of product for further study.

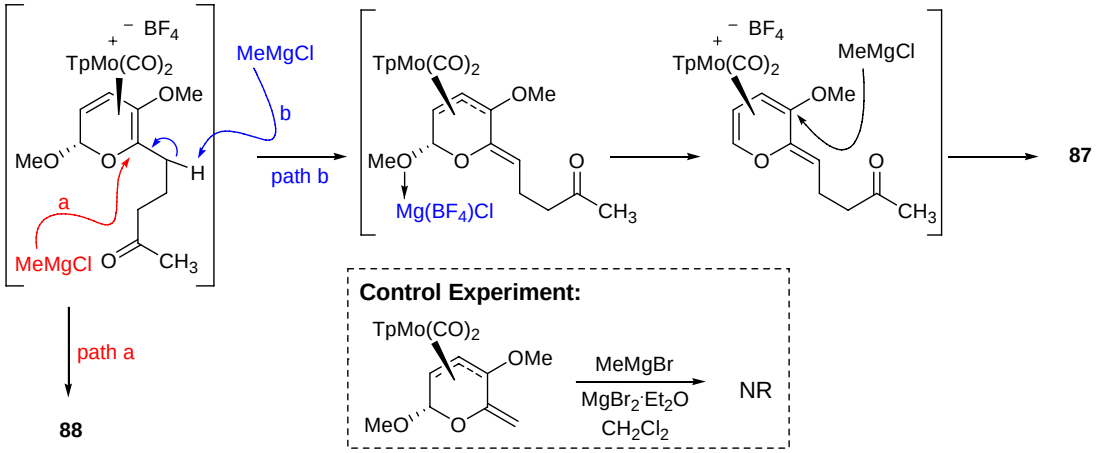
Rationalizing the Ionization Selectivity

The structure of the observed product **87** was still interesting from a mechanistic perspective because it foreshadowed the curious nature of some future results described in detail in Chapter 4. A mechanistic proposal for the reaction is shown in **Scheme 54**. While ionization of the methoxy group apparently took place, we know from **Scheme 49** that nucleophilic addition to 6,6-disubstituted complexes only occurs at the 2-position. Therefore, in accord with the IR data, ring opening must occur first. However, once the ring opens, and the alkylidene forms *via*

[142] Schultz, A. G.; McCloskey, P. J. *J. Org. Chem.* **1985**, *50*, 5905-5907.
[143] Evans, D. A.; Morrissey, M. M. *J. Am. Chem. Soc.* **1984**, *106*, 3866-3868.
[144] While not many examples were found in the literature, hydrogenation of enol ethers is known: Poss, A. J.; Smyth, M. S. *Tetrahedron Lett.* **1988**, *29*, 5723-5724.

deprotonation of the methylene unit (path b), ionization of the methoxy group must then occur under the basic reaction conditions, which conceivably could be accomplished by magnesium salts in the reaction mixture.[145] The nucleophile then selectively attacks the 5-position of the pyran-ring (as opposed to the 2-position), forming the 3° methoxy compound **87**. The regioselectivity of nucleophilic addition will be addressed in more detail in the next chapter. A control experiment testing the ability of magnesium salts to ionize the methoxy group gave no reaction. The experiment is not totally conclusive, however because the tethered carbonyl group in the original substrate may contribute to ionization by increasing local concentrations of Mg^{2+} salts around the molecule. Additionally, the absence of a better stabilizing, non-coordinating ion (BF_4^-) may be required for ionization. The control experiment definitively rules out a direct nucleophilic addition to the neutral allyl, followed by expulsion of the leaving group in an S_N2'-like pathway.

Scheme 54: Mechanistic Hypothesis for INA products

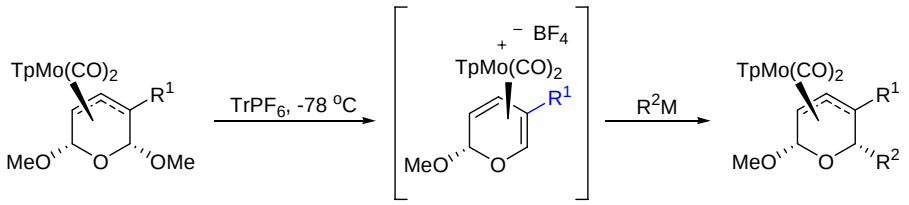


The preference of the spiro-ring to ionize over the methoxy group was attributed ultimately to two major factors. First, the enol ether character of the spiro-ring presumably makes it a better leaving group than the alkoxide, favoring its selective ionization. Secondly, the regioselectivity

[145] Ionization of alkoxides at carbons adjacent to an allyl-molybdenum moiety by magnesium salts has been proposed in: Wong, H. Ph.D. Thesis, **2006**, Emory University, pp120-122.

mirrors that of the known dimethoxy molybdenum complex **90**, which undergoes regioselective ionization in favor of the cationic diene with non-hydrogen substituents R^1 in the internal position (**Scheme 55**).[146] The regioisomeric ratios were determined by analysis of product mixtures, and were found to be on the order of 49:1 and 84:1, depending on the size of the substituent R^1.

Scheme 55: Regioselective ionization favors substituents at internal position of cation-diene



90

Regioselectivity
R^1 = Me, >49:1
R^1 = Ph, >84:1

The rationale for this high selectivity seen in **Scheme 55** was initially attributed to the ground state energy steric acceleration of the ionization of the more hindered methoxy group or to the improved bonding interaction between the HOMO/LUMO orbitals of the product diene with an internal substituent whose stability is reflected in a late transition state. Our group has shown that the two equatorial pyrazoles of the Tp ligand are highly sensitive to steric bulk at the termini of simple allyls, and that non-hydrogen *syn*-substituents at these positions experience unfavorable eclipsing interactions with the protons of the pyrazole ligands.[147] These interactions are alleviated in the ground state by rotation of the $TpMo(CO)_2$ moiety which places the *syn*-substituent into the cleft in between the equatorial pyrazole ligands. The same observation could be assumed for the system above, in which the non-hydrogen substituent R^1 is located in the cleft between the two pyrazole ligands (**Figure 17a**). Ionization of the less hindered methoxy group would require rotation of the pyrazole unit past R^1 in the transition state presenting a potentially formidable kinetic barrier, while the observed ionization pathway would experience no such

[146] Yin, J.; Llorente, I.; Villanueva, L.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2000**, *122*, 10458-10459.
[147] Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132-4156.

interactions. This rationale extends to the observation that ionization of the enol ether of **44** selectively forms the cationic diene shown in **Scheme 52**. In this reaction, however there may be another complementary explanation. The fast and selective ionization could also be accounted for by steric acceleration, owing to the relief of steric strain in the transition state as the *syn* methylene unit of the spiro-ring moves away from the metal moiety and into the plane of the pyran ring (**Figure 17b**).

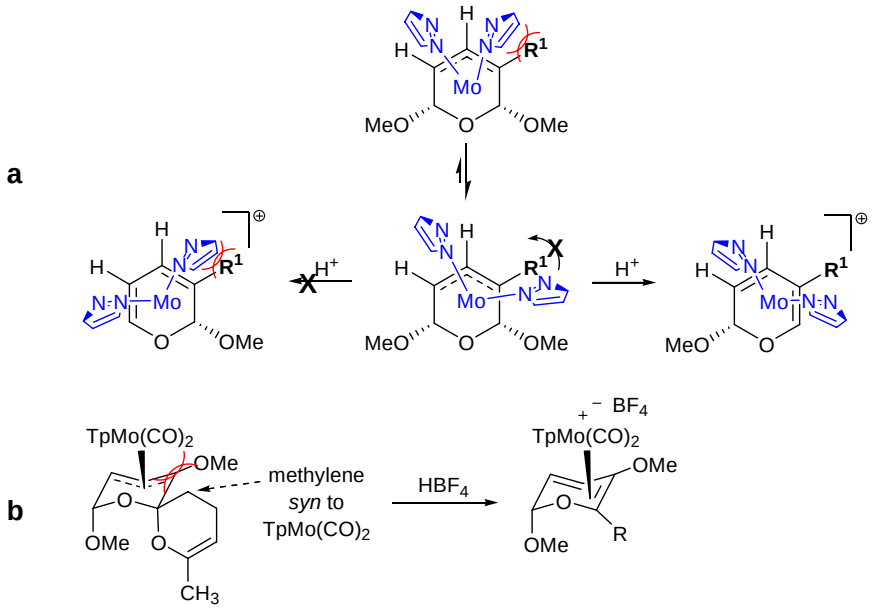


Figure 17: Steric rationale for ionization selectivity

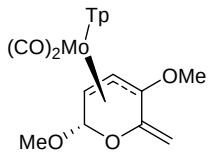
Knowing that the selectivity for opening the spiro-ring, over ionization of the alkoxide was unlikely to be overcome, a complete re-evaluation of the project goals was made. It was known that the intermolecular 1,5-Michael reaction still offered ample opportunity for the stereocontrolled functionalization of pyrans, but with such reactive competing functionality, the substrates were too sensitive to be worth further study. Fortunately, the full scope of the synthetic utility of the alkylidene moiety in the compounds formed in **Table 14** had not been investigated. An in depth study on the reactivity of these compounds brought to light the broad synthetic potential of the products of the 1,5-Michael reaction and particularly the alkylidene moiety, the

result of this was a project of greater conceptual value than the narrowly applicable goals of the spiroketal study. The results to this end will be discussed in detail in the next chapter.

Conclusions:

The scope of the intermolecular 1,5-Michael reaction of sodium alkoxides to enone complexes was investigated. The reaction conditions and spectroscopic evidence suggest that a thermodynamically favored anionic molybdenum salt is a likely intermediate. Molybdenum complexed spiroketals were also found to be suitable substrates for the intermolecular 1,5-Michael reaction, however, attempts to use these reactive compounds to functionalize the pyran-core at C^2 only resulted in the ring-opening of the spiroketal moiety. A rationale for the observed selectivity is presented. Because all attempts to overcome this undesired reactivity were unsuccessful, it was decided that a re-direction of the project goals could open up the other possible uses for the 1,5-Michael reaction and the exocyclic alkylidene moiety.

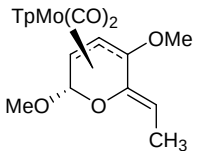
Experimental Details:



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][((2*S*, 3*R*)-η-(3,4,5)- 2,5-dimethoxy-6-methylene-5,6-dihydro-2*H*-pyran-3-yl]molybdenum, 77

Enone **52** (60 mg, 0.127 mmol, 1.0 equiv) and sodium methoxide (68 mg, 1.27 mmol, 10.0 equiv) were dissolved in THF (4 mL). The solution was stirred at room temperature for 130 mins during which the yellow-orange solution turned dark red. The solution was cooled to 0 ^{o}C, after which trimethyloxonium tetrafluoroborate (187 mg, 1.27 mmol, 10.0 equiv) was added in one portion and stirred for 30 mins. The reaction was quenched at 0 ^{o}C with triethylamine (0.5 mL), and then added directly to a short silica gel column packed with ether and neutralized with 5% Et_3N. The product was eluted with ether and concentrated. The oily substance was dissolved in a 1:1 mixture of CH_2Cl_2 and hexanes and concentrated on rotavap to provide compound **77** (49.7 mg, 76%) as a red-brown solid.

77: TLC: R_f = 0.55, (33% EtOAc in hexanes). IR (cm^{-1}): 2482 (w), 1926 (s), 1840 (s), 1616 (w), 1502 (w) 1406 (m), 1304 (m), 1208 (m), 1117 (m), 1046 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.35 (d, *J* = 2.2 Hz, 1H), 7.68 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.63 (d, *J* = 2.5 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 6.23 (t, *J* = 2.2 Hz, 1H), 6.22 (t, *J* = 2.2 Hz, 1H), 6.17 (t, *J* = 1.9 Hz, 1H), 5.00 (s, 1H), 4.84 (s, 1H), 4.68 (s, 1H), 4.09 (dd, *J* = 8.3, 1.6 Hz, 1H), 3.91 (d, *J* = 8.3 Hz, 1H), 3.48 (s, 3H), 3.01 (s, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 231.5, 226.4, 149.3, 147.0, 144.4, 139.6, 136.6, 136.0, 134.9, 130.2, 105.9, 105.8, 105.7, 99.7, 92.1, 59.2, 56.6, 55.1, 52.4. HRMS (ESI) Calcd for $C_{19}H_{22}BMoN_6O_5$ $[M + H]^+$: 523.0793. Found: 523.0792.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*)-η-(3,4,5)-6-(*Z*)-ethylidene-2,5-dimethoxy-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 78.

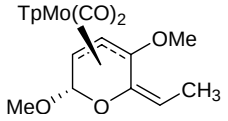
(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*)-η-(3,4,5)-6-(*Z*)-ethylidene-2,5-dimethoxy-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, (+)-**78**.

The starting enone (±)-**61** (2.00 g, 4.10 mmol, 1.0 equiv) and sodium methoxide (1.99 g, 36.9 mmol, 9.0 equiv) were dissolved in THF (75 mL) at room temperature, and stirred for 16 hours, after which the reaction was cooled to 0 ^{o}C with an ice bath. Trimethyloxonium tetrafluoroborate (5.46 g, 36.9 mmol, 9.0 equiv) was then added in one portion, and the reaction was stirred for one hour, after which TLC showed complete conversion. The reaction was quenched by quickly passing the reaction mixture through a silica plug buffered with Et_3N, and eluting with 33% EtOAc in hexanes. The residue was purified by flash chromatography on silica gel neutralized with Et_3N, eluting with 17% EtOAc in hexanes to give pure product **78** (1.69 g, 76%) as a dark red/brown solid.

Enantiopure procedure (Discussed in Chapter 4):

The starting enone (-)-**61** (98% ee, 200 mg, 0.410 mmol, 1.0 equiv) was dissolved in dry THF (2.0 mL) and cooled to 0 ^{o}C. Sodium methoxide (443 mg, 8.20 mmol, 20.0 equiv) was added followed by more THF (0.2 mL) to dissolve the remaining solid. The reaction was stirred for 115 mins, after which trimethyloxonium tetrafluoroborate (1.21 g, 8.20 mmol, 20.0 equiv) was added in one portion followed shortly by more THF (2 mL), and the reaction was stirred for 45 mins at 0 ^{o}C. The reaction was quenched by quickly passing the reaction mixture through a silica plug buffered with Et_3N, eluting with 50% EtOAc in hexanes. The residue was purified by flash chromatography on silica gel neutralized with Et_3N, eluting with 25% EtOAc in hexanes to give pure product (+)-**78** (166 mg, 76%) of as a dark red/brown solid.

(+)-**78:** TLC: R_f = 0.37 (25% EtOAc in hexanes). $[\alpha]_D^{20}$ +1947 (97.3-98.3% ee, *c* = 0.0124, CH_2Cl_2). IR (cm^{-1}): 2930 (w), 2482 (w), 1926 (s), 1837 (s), 1505 (m), 1409 (m), 1305 (m), 1239 (m), 1216 (m), 1119 (m), 1050 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.29 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.17 (t, *J* = 2.2 Hz, 1H), 5.62 (q, *J* = 7.3 Hz, 1H), 4.98 (s, 1H), 4.11 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.76 (d, *J* = 7.3 Hz, 1H), 3.48 (s, 3H), 3.01 (s, 3H), 1.80 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.4, 227.7, 146.8, 144.2, 142.4, 139.6, 136.5, 135.9, 134.9 (2), 105.8, 105.7, 105.6, 105.4, 100.0, 57.6, 56.3, 55.1, 52.6, 10.2. HRMS (ESI) Calcd for $C_{20}H_{24}BMoN_6O_5$ $[M + H]^+$: 537.0950. Found: 537.0955.

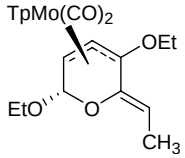


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*)-η-(3,4,5)-6-(*E*)-ethylidene-2,5-dimethoxy-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 79

Enone **60** (129 mg, 0.264 mmol, 1.0 equiv) and sodium methoxide (143 mg, 2.64 mmol, 10.0 equiv) were dissolved in THF (5 mL) at room temperature. The reaction was stirred for 5.5 h, after which it was cooled to 0 °C, and trimethyloxonium tetrafluoroborate (391 mg, 2.64 mmol, 10.0 equiv) was added in one portion. The reaction was stirred for 35 minutes, quenched with Et_3N (0.5 mL), and the reaction mixture was concentrated on under reduced pressure. The residue was added to a silica gel column neutralized with 5% Et_3N and the product was eluted with 33% EtOAc in hexanes to provide product **79** (108.4 mg, 77%). The product completely converted to pure **78** within one hour in $CDCl_3$, and could only be characterized as a mixture. Representative ^{1}H NMR peaks are tabulated below, although some resonances were obscured by those of compound **78**.

79: TLC: R_f = 0.47 (33% EtOAc in hexanes). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.33 (d, *J* =

1.6 Hz, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 6.66 (obscured d, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 6.24-6.15 (obscured m, 3H), 5.35 (q, *J* = 7.9 Hz, 1H), 4.83 (s, 1H), 4.09 (d, *J* = 9.5 Hz, 1H), 3.84 (d, *J* = 8.3 Hz, 1H), 3.46 (s, 3H), 3.01 (s, 3H), 2.08 (d, *J* = 7.9 Hz, 3H).

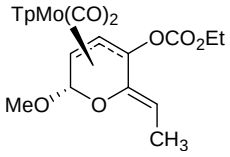


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*)-η-(3,4,5)-2,5-diethoxy-6-(*Z*)-ethylidene-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 80

Complex **61** (200 mg, 0.410 mmol, 1.0 equiv), and sodium ethoxide (251 mg, 3.69 mmol, 9.0 equiv) were dissolved in dry THF (12 mL) at room temperature and the reaction was stirred for six hours. The reaction was then cooled to 0 ^{o}C and triethyloxonium hexafluorophosphate (915 mg, 3.69 mmol, 9.0 equiv) was added as a solid in one portion, and it was stirred for 30 min after which TLC revealed the formation of a new spot. The reaction mixture was added directly to a silica gel column neutralized with 5% Et_3N and the product was eluted with 25% EtOAc in hexanes to provide compound **80** (163 mg, 71%) as a reddish brown solid. An impurity in the ^{13}C NMR spectrum precluded assigning appropriate carbon resonances. The compound will not be published in any peer reviewed journals unless fully characterized.

80: TLC: R_f = 0.45 (25% EtOAc in hexanes). IR (cm^{-1}): 2927 (w), 2856 (w), 1924 (s), 1839 (s), 1406 (m), 1306 (m), 1215 (m), 1117 (m), 1049 (s). ^{1}H NMR [600 MHz, $CDCl_3$]: δ 8.29 (d, *J* = 1.9 Hz, 1H), 7.71 (d, *J* = 1.9 HZ, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 6.196 (t, *J* = 2.4 Hz, 1H), 6.192 (t, *J* = 2.4 Hz, 1H), 6.16 (t, *J* = 2.4 Hz, 1H), 5.66 (q, *J* = 7.1 Hz, 1H), 5.10 (s, 1H), 4.10 (dd, *J* = 8.1, 1.4 Hz, 1H), 3.80 (dq, *J* = 9.5, 7.1 Hz, 1H), 3.77 (d, *J* = 8.1 Hz, 1H), 3.64 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.47 (m, 1H), 2.82 (dq, *J* = 9.1, 7.1 Hz, 1H), 1.78 (d, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1

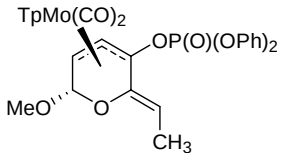
Hz, 3H). HRMS (ESI) Calcd for $C_{22}H_{27}BMoN_6O_5$ $[M]^+$: 564.1185. Found: 564.1188.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*)-η-(3,4,5)-5-ethoxycarbonyloxy-6-(*Z*)-ethylidene-2-methoxy-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 81

The starting enone **61** (1.00 g, 2.05 mmol, 1.0 equiv) and sodium methoxide (996 mg, 18.4 mmol, 9.0 equiv) were dissolved in THF (40 mL) at room temperature, and stirred for 19 hours, after which the reaction was cooled to 0 ^oC in an ice bath. Ethyl chloroformate (1.76 mL, 18.4 mmol, 9.0 equiv) was then added in one portion, and the reaction was stirred for one hour, after which TLC showed complete conversion. The reaction was quenched by quickly passing the reaction mixture through a silica plug buffered with 5% Et_3N (eluting with 50% EtOAc in hexanes). The residue was purified by flash chromatography on silica gel neutralized with 5% Et_3N, eluting with 33% EtOAc in hexanes to afford compound **81** (1.02 g, 84%) as an orange/brown solid.

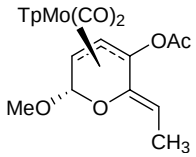
81: TLC: R_f = 0.32 (25% EtOAc in hexanes). IR (cm^{-1}): 2930 (w), 2482 (w), 1945 (s), 1865 (s), 1763 (s), 1408 (m), 1303 (m), 1242 (s), 1198 (s), 1048 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.49 (d, *J* = 1.9 Hz, 1H), 8.01 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 2.5 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 2.2 Hz, 1H), 6.26 (t, *J* = 2.2 Hz, 1H), 6.21 (t, *J* = 1.9 Hz, 1H), 6.15 (t, *J* = 2.2 Hz, 1H), 5.12 (q, *J* = 7.0 Hz, 1H), 4.93 (d, *J* = 1.0 Hz, 1H), 4.41 (d, *J* = 7.9 Hz, 1H), 4.28-4.19 (m, 1H), 4.19-4.10 (m, 2H), 3.50 (s, 3H), 1.71 (d, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 229.6, 224.7, 153.2, 147.2, 146.5, 143.3, 139.7, 136.3 (2), 134.6, 108.6, 106.2, 105.7, 105.1, 101.7, 99.3, 66.4, 65.1, 56.6, 53.8, 14.3, 10.0. HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_6O_7$ $[M + H]^+$: 595.1005. Found: 595.1015.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*)-η-(3,4,5)-6-(*Z*)-ethylidene-2-methoxy-5-(diphenoxy-phosphoryloxy)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 82

Starting material **61** (200 mg, 0.410 mmol, 1.0 equiv) and sodium methoxide (199 mg, 3.69 mmol, 9.0 equiv) were dissolved in dry THF (12 mL) at room temperature. The reaction was stirred for 5 hours, after which it was cooled to 0 ^{o}C, and diphenyl chlorophosphate was added (0.76 mL, 3.69 mL, 9.0 equiv). The reaction was stirred for 30 minutes, after which TLC revealed that all starting material had been consumed. The mixture was passed through a silica gel plug neutralized with 5% Et_3N and eluting with 50% EtOAc in hexanes. The crude material was purified by gravity chromatography on buffered silica gel eluting with 17% EtOAc in hexanes to provide pure product **82** (156 mg, 51%) as a bright orange solid.

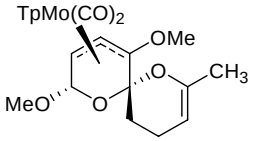
82: ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.42 (d, *J* = 1.9 Hz, 1H), 7.82 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.53 (dd, *J* = 2.2, 0.6 Hz, 1H), 7.51 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.18-7.12 (m, 4H), 7.09-7.07 (m, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.24 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 6.07 (t, *J* = 2.2 Hz, 1H), 5.34 (q, *J* = 7.0 Hz, 1H), 4.89 (d, *J* = 0.6 Hz, 1H), 4.32 (d, *J* = 7.9 Hz, 1H), 4.07 (dd, *J* = 7.9, 1.6 Hz, 1H), 3.48 (s, 3H), 1.64 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 230.3, 224.7, 150.2 (2), 147.0, 146.3, 142.9, 139.4, 136.3, 136.0, 134.7, 129.7 (4), 125.5, 125.4, 120.2 (2), 119.9 (2), 111.5, 106.1, 105.9, 105.5, 103.7, 99.2, 65.6, 56.3, 52.8, 10.0.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*)-η-(3,4,5)-5-acetoxy-6-(*Z*)-ethylidene-2-methoxy-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 83

Complex **61** (50 mg, 0.102 mmol, 1.0 equiv) and sodium methoxide (44 mg, 0.820 mmol, 8.0 equiv) were dissolved in THF (2 mL) at room temperature and stirred for 200 minutes, after which the reaction was cooled to 0 °C. Acetyl chloride (60 μL, 0.820 mmol, 8.0 equiv) was added in one portion, and the reaction was diluted with more THF (1 mL) and stirred for 1 hour. The reaction was concentrated and the residue was purified by chromatography on neutralized silica gel, which provided pure product **83** (16.6 mg, 29%) as a yellow/orange solid. No ^{13}C NMR was obtained for this compound—it will not be published in any peer reviewed journals unless fully characterized.

83: TLC: R_f = 0.27 (25% EtOAc in hexanes). IR (cm^{-1}): 2923 (m), 2853 (w), 1944 (s), 1864 (s), 1772 (m), 1408 (m), 1304 (m), 1208 (m), 1123 (s), 1050 (s). ^1H NMR [600 MHz, $CDCl_3$]: δ 8.47 (d, *J* = 1.9 Hz, 1H), 7.96 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 6.26 (t, *J* = 1.9 Hz, 1H), 6.20 (t, *J* = 1.9 Hz, 1H), 6.16 (t, *J* = 1.9 Hz, 1H), 5.02 (q, *J* = 7.1 Hz, 1H), 4.93 (d, *J* = 1.0 Hz, 1H), 4.27 (d, *J* = 8.1 Hz, 1H), 4.15 (dd, *J* = 8.1, 1.9 Hz, 1H), 3.50 (s, 3H), 2.11 (s, 3H), 1.70 (d, *J* = 7.1 Hz, 3H). HRMS (ESI) Calcd for $C_{21}H_{24}BMoN_6O_6$ $[M + H]^+$: 565.0899. Found: 565.0899.

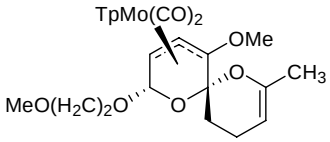


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*,6*R*)-η-(3,4,5)-2,5-dimethoxy-8-methyl-1,7-dioxa-spiro-[5.5]-undec-8-ene-3-yl]molybdenum, 85

Spirocycle **55** (60 mg, 0.110 mmol, 1.0 equiv) and sodium methoxide (60 mg, 1.10 mmol,

10.0 equiv) were dissolved in THF (4.0 mL) at room temperature. The solution was stirred for 200 mins during which the orange-yellow solution turned dark red. The solution was cooled to 0 ^{o}C, after which trimethyloxonium tetrafluoroborate (163 mg, 1.10 mmol, 10.0 equiv) was added in one portion and stirred for 40 mins. The reaction mixture was added directly to a silica gel column neutralized with 5% Et_3N. The product was eluted with 33% EtOAc in hexanes collecting the red band. The oily substance was dissolved in a 1:1 mixture of CH_2Cl_2 and hexanes and concentrated under reduced pressure to provide compound **85** (52.4 mg, 81%) as a red-orange solid. The product was unstable over prolonged periods in solution, however, and was therefore used directly after its synthesis.

55: TLC: R_f = 0.50 (33% EtOAc in hexanes). IR (cm^{-1}): 2930 (w), 1934 (s), 1841 (s), 1409 (w), 1309 (w), 1227 (w), 1119 (w), 1050 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.33 (dd, *J* = 2.2, 0.6 Hz, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.63 (dd, *J* = 1.9, 0.6 Hz, 1H), 7.60 (dd, *J* = 1.9, 0.6 Hz, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.49 (dd, *J* = 2.5, 0.6 Hz, 1H), 6.22 (t, *J* = 1.9 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 4.72 (s, 1H), 4.58 (dd, *J* = 5.7, 1.0 Hz, 1H), 4.21 (dd, *J* = 7.9, 1.0 Hz, 1H), 4.03 (d, *J* = 7.9 Hz, 1H), 3.43 (s, 3H), 2.75 (s, 3H), 2.59-2.52 (m, 1H), 2.30-2.22 (m, 2H), 2.00-1.91 (m, 1H), 1.78 (s, 3H).

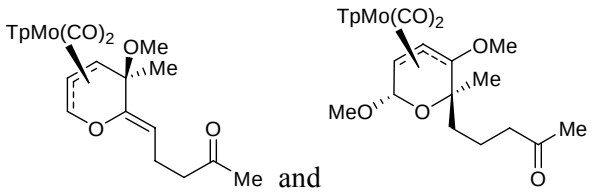


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*,6*R*)-η-(3,4,5)-5-methoxy-2-(2-methoxyethoxy)-8-methyl-1,7-dioxa-spiro-[5.5]-undec-8-ene-3-yl]molybdenum, 86

To a solution of spirocycle **55** (30 mg, 0.055 mmol, 1.0 equiv) in THF (1.0 mL) at room temperature was added a solution of sodium (2-methoxy)-ethoxide [prepared from sodium hydride (13.3 mg, 0.55 mmol, 10.0 equiv) and 2-methoxyethanol (43 μL, 0.55 mmol, 10.0 equiv) in THF (1.0 mL)]. The solution was stirred for 7 h during which the orange-yellow solution

turned dark red. The solution was cooled to 0 °C, after which trimethyloxonium tetrafluoroborate (81.5 mg, 0.55 mmol, 10.0 equiv) was added as a solid in one portion and the reaction was stirred for 1 hour. The reaction mixture was added directly to a silica gel column neutralized with 5% Et_3N. The product was eluted with 33% EtOAc in hexanes collecting the red band. The oily substance was dissolved in a 1:1 mixture of CH_2Cl_2 and hexanes and concentrated on rotavap to provide compound **86** (26.6 mg, 76%) as a red-orange solid. The product was unstable over prolonged periods in solution, however, and was therefore used directly after its synthesis.

86: ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.32 (d, *J* = 1.9 Hz, 1H), 7.76 (d, *J* = 1.9 Hz, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H), 4.86 (s, 1H), 4.56 (d, *J* = 5.4 Hz, 1H), 4.28 (d, *J* = 7.9 Hz, 1H), 4.04 (d, *J* = 8.3 Hz, 1H), 3.88-3.79 (m, 1H), 3.68-3.50 (m, 4H), 3.39 (s, 3H), 2.73 (s, 3H), 2.56-2.48 (m, 1H), 2.26-2.18 (m, 2H), 1.98-1.87 (m 1H), 1.76 (s, 3H).



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-5-methoxy-5-methyl-6-(*Z*)-(4-oxo-pentylidene)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 87

and

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*,6*R*)-η-(3,4,5)-2,5-dimethoxy-6-methyl-6-(4-oxo-pentyl)-3,6-dihydro-2*H*-pyran-3-yl]molybdenum, 88

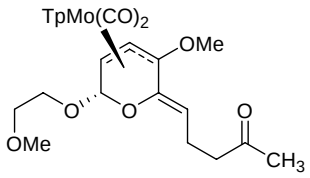
Starting material **85** (23 mg, 0.040 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.0 mL) and the reaction was cooled to 0 °C. Tetrafluoroboric acid (54 wt% in Et_2O, 10 μL, 0.060 mmol, 1.5

equiv) was then added dropwise.[148] After 25 minutes at 0 °C the reaction was cooled to -78 °C and methylmagnesium chloride (2.5 M in Et_2O, 48 μL, 0.119 mmol, 3.0 equiv) was added. After stirring for 30 minutes, water (10 mL) was added to quench the reaction, and the mixture was extracted with CH_2Cl_2 (20 mL). The organic layer was dried, concentrated and evaluated by crude NMR, which revealed the formation of products **87** and **88** in ~ 2:1 ratio. Purification by chromatography on a silica gel column neutralized with 5% Et_3N eluting with 33% EtOAc in hexanes provided very small amounts (<5 mg each) of the two products.

87: TLC: R_f = 0.25 (25% EtOAc in hexanes). IR (cm^{-1}): 2923 (w), 2851 (w), 2481 (w), 1949 (s), 1859 (s), 1710 (s), 1406 (m), 1302 (m), 1217 (m), 1123 (m), 1049 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.51 (d, *J* = 2.0 Hz, 1H), 7.84 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.56 (s, 2H), 7.48 (d, *J* = 2.3 Hz, 1H), 7.02 (dd, *J* = 4.3, 2.3 Hz, 1H), 6.27 (t, *J* = 2.0 Hz, 1H), 6.20 (t, *J* = 2.0 Hz, 1H), 6.19 (t, *J* = 2.3 Hz, 1H), 4.84 (t, *J* = 7.4 Hz, 1H), 4.67 (dd, *J* = 7.8, 2.3 Hz, 1H), 3.59 (s, 3H), 3.40 (dd, *J* = 7.8, 4.3 Hz, 1H), 2.55-2.20 (m, 4H), 2.12 (s, 3H), 1.63 (s, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.1, 226.1, 209.7, 151.5, 147.0, 142.1, 142.0, 136.3, 136.1, 134.6, 108.2, 106.2, 105.8, 105.5, 105.1, 76.4, 69.3, 57.5, 49.3, 43.9, 31.6, 29.9, 19.2. HRMS (ESI) Calcd for $C_{23}H_{28}BMoN_6O_5$ $[M + H]^+$: 577.1263. Found: 577.1265.

88: TLC: R_f = 0.19 (25% EtOAc in hexanes). IR (cm^{-1}): 2922 (m), 2851 (w), 1944 (m), 1827 (m), 1711 (m), 1405 (m), 1308 (m), 1217 (m), 1118 (m), 1050 (s). ^{1}H NMR [600 MHz, $CDCl_3$]: δ 8.27 (s, 1H), 7.70 (s, 1H), 7.64 (s, 1H), 7.58 (s, 1H), 7.49 (s, 1H), 7.42 (s, 1H), 6.19, (s, 3H), 4.98 (s, 1H), 4.29 (d, *J* = 8.6 Hz, 1H), 3.51 (d, *J* = 8.1 Hz, 1H), 3.46 (s, 3H), 2.58 (s, 3H), 2.54 (dd, *J* = 8.6, 6.2 Hz, 1H), 2.47-2.42 (m, 1H), 2.32 (dt, *J* = 12.4, 4.3 Hz, 1H), 2.12 (s, 3H), 2.02 (dt, *J* = 11.4, 4.8 Hz, 1H), 1.91-1.82 (m, 1H), 1.73-1.65 (m, 1H), 1.50 (s, 3H). HRMS (ESI) Calcd for $C_{24}H_{31}BMoN_6O_6$ $[M + H]^+$: 608.1447. Found: .

[148] Infrared analysis of an aliquot of the reaction mixture after 10 minutes indicated new carbonyl stretches at 2061, 2011, 1945, 1710 cm^{-1}



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*)-η-(3,4,5)-5-methoxy-2-(2-methoxyethoxy)-6-(*Z*)-(4-oxo-pentylidene)-3,6-dihydro-2*H*-pyran-3-yl]molybdenum, 89

Representative protocol for attempted chelation-controlled ionization.

Starting material **86** (13.3 mg, 0.021 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 (1.5 mL) and the solution was cooled to -78 ^oC. Titanium tetrachloride (1.0 M in CH_2Cl_2, 21 μL, 0.021 mmol, 1.0 equiv) was added dropwise, and the reaction mixture was stirred for 15 minutes.[149] Methylmagnesium bromide (3.0 M in Et_2O, 14 μL, 0.042 mmol, 2.0 equiv) was then added, and the reaction was stirred for 1 hour, after which Grignard reagent was added again (14 μL, 2.0 equiv—4.0 equiv total). The reaction mixture was added directly to a column of neutralized silica gel and eluted with 25% EtOAc in hexanes to provide very small amounts (< 5 mg) of the two products **87** and **89**.

89: TLC: R_f = 0.11 (33% EtOAc in hexanes). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.28 (d, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 1.9 Hz, 2H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.48 (d, *J* = 1.6 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 6.16 (t, *J* = 2.2 Hz, 1H), 5.54 (t, *J* = 7.9 Hz, 1H), 5.07 (s, 1H), 4.16 (dd, *J* = 8.3, 1.3 Hz, 1H), 3.88-3.72 (m, 3H), 3.68-3.49 (m, 2H), 3.41 (s, 3H), 2.97 (s, 3H), 2.57 (d, *J* = 7.3 Hz, 1H), 2.50 (app sextet, *J* = 7.0 Hz, 1H), 2.33 (app sextet, *J* = 6.4 Hz, 1H), 2.11 (s, 3H).

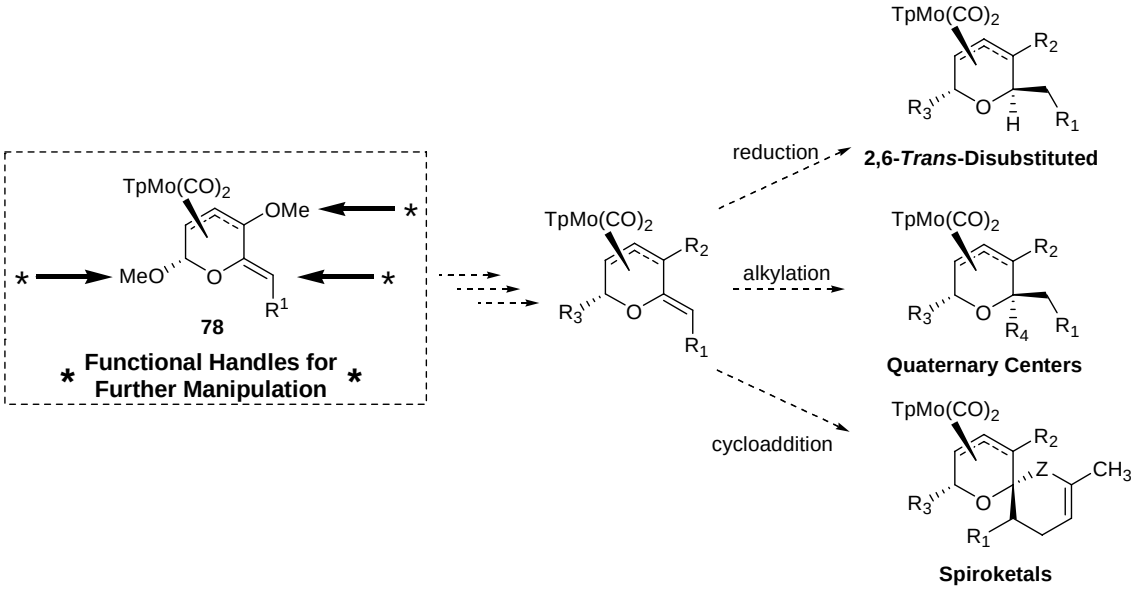
[149] Infrared analysis of an aliquot of the reaction mixture after 2 minutes revealed new carbonyl stretches at 2054, 2003, 1942 and 1714 cm^{-1}

Chapter 4: A highly regio- and stereoselective ionization/nucleophilic addition sequence leading to the construction of functionalized pyrans bearing, stereochemical substituent and skeletal diversity

Introduction:

The observations discussed in the previous chapter led us to a reorganization and revision of the goals of the project. The spiroketal products were so susceptible to ring opening that their synthetic potential was minimal unless the cycloaddition could be performed at a later stage. More importantly however, we recognized that the alkylidene moiety provides a unique opportunity for the stereoselective functionalization of the pyran ring beyond the narrow focus of spiroketal synthesis. As such, this chapter highlights how the sequential functionalization of 2,5-dimethoxy-6-alkylidenes permits access, not only to functionalized spiroketals, but also to the previously inaccessible 2,6-*trans*-substituted pyrans, and other bicyclic compounds. The combined result of the diverse array of products accessible through the methodology developed here serves to highlight organometallic enantiomeric scaffolding as a conceptual and practical approach to a variety of pyran architectures with considerable stereochemical and substituent diversity (**Scheme 56**).

Scheme 56: Potential synthetic versatility of dimethoxy alkylidene complexes



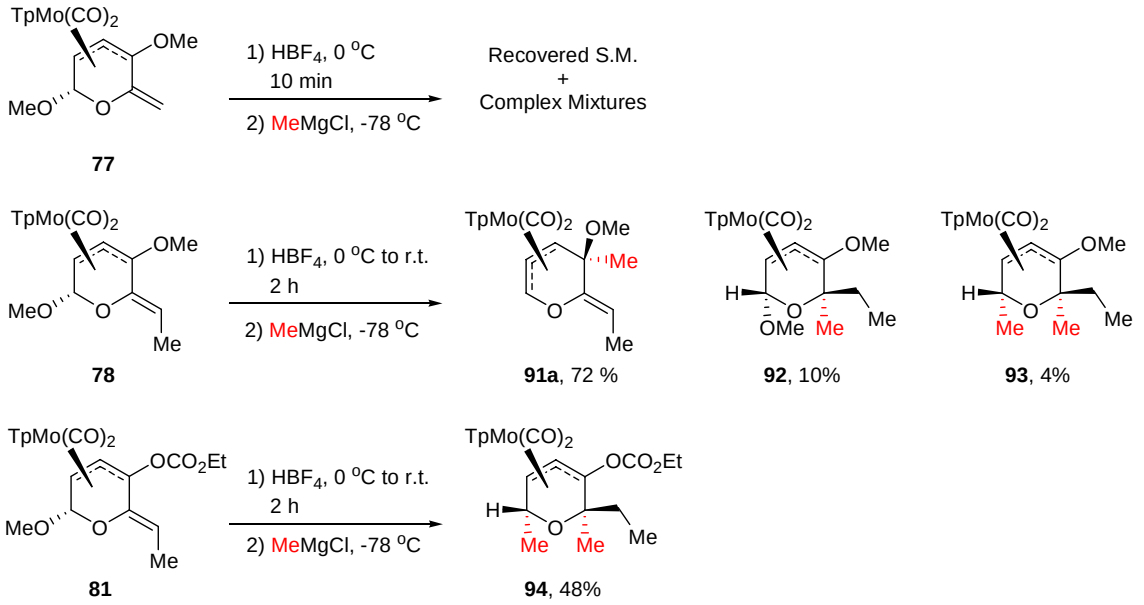
The inception of the idea of these dimethoxy alkylidene compounds as versatile intermediates in scaffolding came from the recognition that the methoxy groups are poised to be excellent handles for the elaboration of substituent diversity, and that the alkylidene moiety should be a versatile handle for manipulating stereochemical, and skeletal diversity.

Results and Discussion:

Investigation into INA reaction of 78

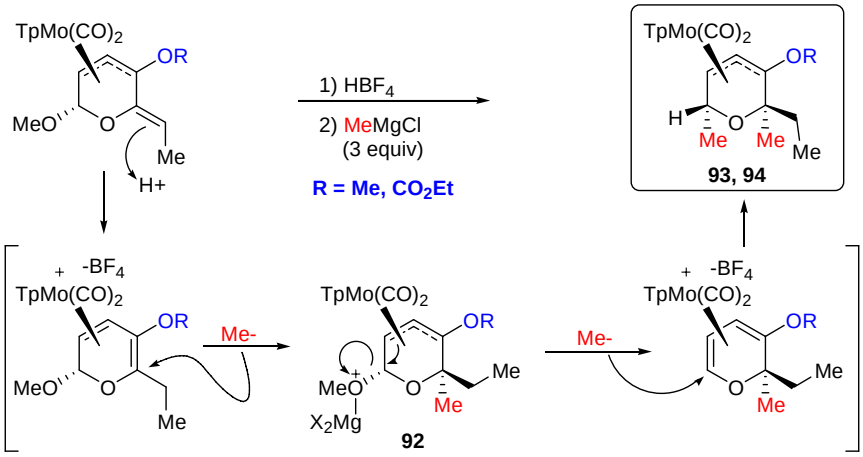
When dimethoxy compound **77** was subjected to INA conditions, only starting material could be recovered cleanly, along with a complex mixture of unidentifiable side products. Interestingly, however, under the same conditions **78** was found to undergo relatively clean conversion to the tertiary methoxy compound **91a** in 72% isolated yield, along with two other minor products shown in **Scheme 57**. Under identical conditions, the reaction with carbonate **81** provided only the double addition product **94**.

Scheme 57: Divergent reactivity in INA sequence of various dimethoxy substrates



Because of their quaternary centers, **92**, **93** and **94** must come from a competing protonation pathway and a subsequent nucleophilic addition, the likely mechanism of which is shown in **Scheme 58**.[150]

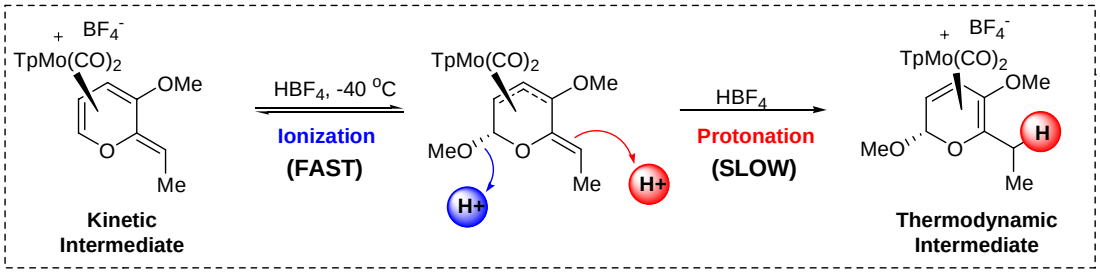
Scheme 58: Proposed mechanism for minor products formation



A short optimization study revealed that temperature control was essential to controlling selectivity for ionization over protonation of the alkylidene (**Scheme 59**). Under low temperature (-40 °C) and short reaction time (<10 min), ionization of the methoxy group occurs selectively over protonation, and *the byproducts **92** and **93** are not formed*. From these data, it is clear that ionization is kinetically favored over protonation. The ionization pathway is probably reversible, but at low temperatures, protonation does not occur. As the temperature increases, protonation of the alkylidene occurs irreversibly, leading to the unwanted byproducts. While the slight increase in yield under these optimized conditions was seemingly trivial (72% increased to 79%), the absence of these byproducts made purification much easier; the only other significant isolated compound was starting material, which could be recycled.

[150] This mechanism is not dissimilar to that proposed in **Scheme 54**. (See also reference 145).

Scheme 59: Low temperatures are essential for controlling ionization selectivity

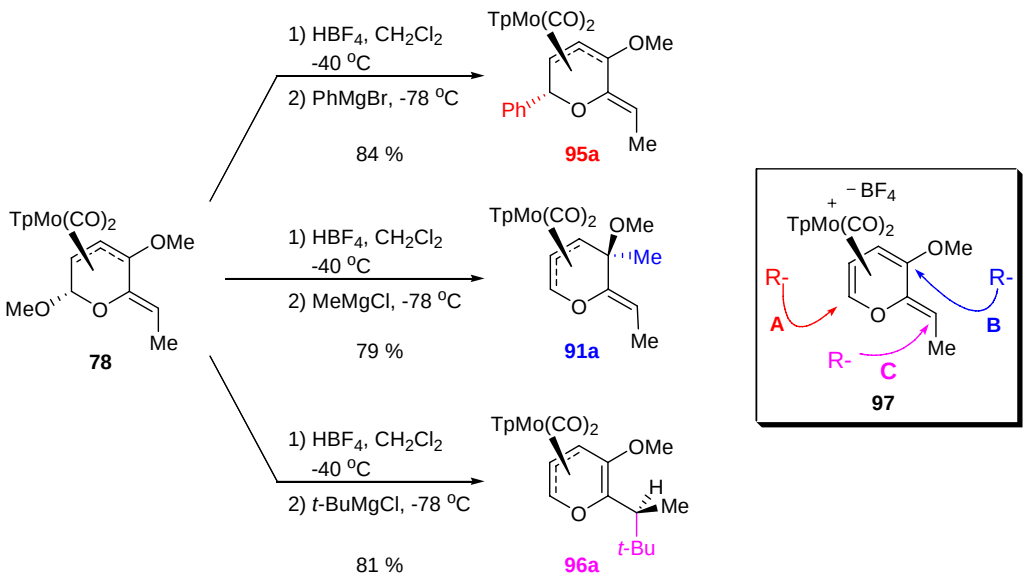


With optimized conditions in hand, the INA sequence was performed with different Grignard reagents (PhMgBr and *t*-BuMgCl), and the results were compared to that of the reaction using methyl Grignard reagent. To our surprise, the major product isolated in each case demonstrated *completely different regioselectivity* in the nucleophilic addition step (**Scheme 60**). Clearly these nucleophiles are adding selectively to each of the three electrophilic sites of the diene intermediate **97**. Control experiments helped to determine that the regioselectivity pattern was not dependent upon the nature of the Grignard halide (Cl *vs* Br), Grignard composition (based on the Schlenk equilibrium[151]), and Grignard solvent (THF *vs* Et_2O). All control experiments provided the same products shown in **Scheme 60** in similar (or slightly decreased) yields. The yield suffered significantly when the reaction was run in THF instead of dichloromethane.[152]

[151] Two control experiments were run in which either $MgCl_2 \cdot OEt_2$ or 1,4-dioxane were added to a solution of phenylmagnesium bromide prior to reaction with the electrophilic diene complex. Both reactions provided greater than 70% yield of the product, with recovered starting material as the only major side product.

[152] Dichloromethane does not react with Grignard reagents at low temperature (-78 °C). See: *Organomagnesium Methods in Organic Synthesis*, Wakefield, B. J., Ed. Academic Press, London, 1995.

Scheme 60: Divergent regioselective addition of different nucleophiles to common diene intermediate

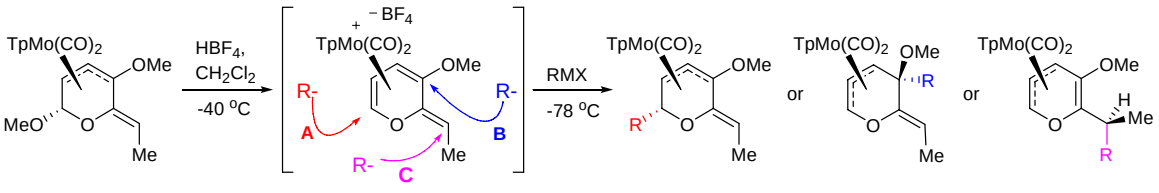


With no obvious way to rationalize these results based on few examples, an extensive and systematic investigation into the regioselectivity of nucleophilic addition by various nucleophiles[153] was undertaken under these optimized conditions, and the results are summarized in **Table 15**. In every case but one only one major product is formed and usually accounts for the bulk of the mass balance with recovered starting material and very polar decomposition products accounting for the rest. In each reaction the cation-diene complex was formed in exactly the same manner and concentration was kept constant. A careful examination of the results suggests a few clear trends. Grignard reagents with sp^2-hybridized substituents appear to undergo nucleophilic addition following only pathway A, forming compounds **95a-e** (**Table 15**, Entries 8-12), while those Grignard reagents with sp^3-hybridized alkyl substituents only add to the diene

[153] Because 1.3 equivalent of HBF_4 is used in the first step, up to 0.3 equivalent of H^+ still exists in the reaction mixture, along with 1 equivalent of methanol that is formed through ionization. For this reason, at least 2.3 equivalents are required for the reaction, but 3.0 equivalents were used to ensure complete conversion.
Given the broad scope of this study, the diversity of reagents employed, and the number of times each reaction was repeated, it was experimentally simpler to use commercially available reagents when possible. It should be noted that the quality of the Grignard reagent is very important in this reaction. While commercially available Grignard reagents were often titrated prior to use (Love, B. E.; Jones, E. G. *J. Org. Chem.* **1999**, *64*, 3755-3756), newer bottles of reagent usually gave better yields.

following pathway B, forming compounds **91a-g** (Entries 1-6). Organolithium reagents and lithium enolates also follow pathway B providing **91a** and **91i-l** in moderate to good yields (Entries 13-17). Finally, *t*-butylmagnesium chloride and copper-modified Grignard reagents gave products resulting from nucleophilic addition to the off-ring position following pathway C, forming the fully unsaturated complexes **96a-c** (Entries 18-20).

Table 15: Investigation into the regioselectivity of INA using various nucleophiles



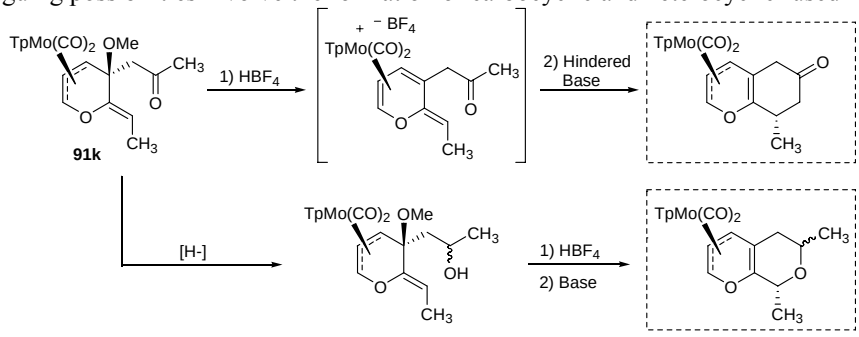
Entry	RMX[a]	Yield 95[b] (%)	Yield 91[b] (%)	Yield 96[b] (%)
1	MeMgCl	--	79, **91a**	--
2	EtMgBr	--	83, **91b**	--
3	HexylMgBr	--	59, **91c**	--
4	*i*-PrMgCl	--	92, **91d**	--
5	AllylMgCl	--	71, **91e**	--
6	BnMgCl	--	95, **91f**	--
7	$NaCNBH_3$	--	78, **91g**	--
8	PhMgBr	84, **95a**	--	--
9	*m*-MeO-C_6H_4MgBr	56, **95b**	--	--
10	*p*-F-C_6H_4MgBr	56, **95c**	--	--
11	MesitylMgBr	50, **95d**	--	--
12	VinylMgCl	45, **95e**[c]	**91h**[c]	--
13	MeLi	--	73, **91a**	--
14	PhLi	--	53, **91i**	--
15	PhCCLi	--	29, **91j**	--
16	CH_3COCH_2Li	--	61, **91k**	--
17	$PhCOCH_2Li$	--	69, **91l**	--
18	*t*-BuMgCl	--	--	81, **96a**
19	MeMgCl/CuBr·DMS	--	--	48, **96b**
20	PhMgCl/CuBr·DMS	--	--	66, **96c**

a) Grignards, lithiates and $NaCNBH_3$ were purchased commercially as solutions (typically of THF or Et_2O); enolates were prepared from the corresponding ketones and LiHMDS. See experimental details for more information. b) isolated yields. c) collected as an inseparable mixture 1.4:1 **95e**:**91h**

There are several highlights of the study worth noting. Primary and secondary aliphatic nucleophiles are excellent reagents for nucleophilic addition. Electron rich and electron deficient aryl rings (Entries 9 and 10) work equally well, as do very bulky aryl nucleophiles (Entry 11). Ketone enolates also work very well, and will provide ample opportunity for the elaboration of the products into skeletally diverse frameworks.[154] Nucleophilic additions by cuprates and *t*-BuMgCl to the off-ring position formed only one diastereoisomer in all cases, which is presumed to be that arising from attack at the *Z*-alkylidene *anti* to the metal moiety.

The simple steric argument that the 2-position of the cation diene is less hindered (relative to the 5-position), and therefore the bulkier sp^2-aryl nucleophiles would preferentially add following pathway A, does not account for the discrepancy between vinyl Grignard and its bulkier saturated ethyl and isopropyl analogs.[155] Additionally, if steric effects were a strong determining factor for influencing regioselectivity, then one would expect to isolate some products resulting from addition following pathway C (presumably the least hindered electrophilic site) in most of these reactions. If hybridization is the over-riding factor in influencing the regioselectivity of Grignard addition, it has no discernible effect within the subclass of organolithium reagents (compare Entries 13-15), or organocuprates (compare Entries 19 and 20). However, the identity of the metallic species in each reagent clearly has a dramatic effect on the regioselectivity of addition

[154] Some intriguing possibilities involve the formation of carbocyclic and heterocyclic fused ring systems:



[155] While not a perfect measure of steric bulk, the conformational energies (A-Values) of ethyl and isopropyl (1.8 and 2.1 kcal/mol respectively) are larger than that of vinyl (1.7 kcal/mol). Source: Advanced Organic Chemistry Part A: Structure and Mechanisms. 4th Ed. Carey, F. A. and Sundberg, R. J. Eds. Kluwer Academic/Plenum Publishers, New York, 2000, p140.

(compare Entries 8, 14 and 20).[156] A more cohesive series of observations and rationale for the observed trends will be discussed later in the chapter.

Synthetic Elaboration of INA Products to Diverse and Highly Functionalized Pyrans:

The synthetic utility of this reaction should be apparent from **Table 15** as yields are good to excellent in most cases, and judicious selection of organometallic reagent should permit access to considerably diverse structures from the same starting material (**Figure 18**). These three different product types became the centerpieces for the application of this ionization nucleophilic addition (INA) methodology to diversity-oriented synthesis (*vide infra*).

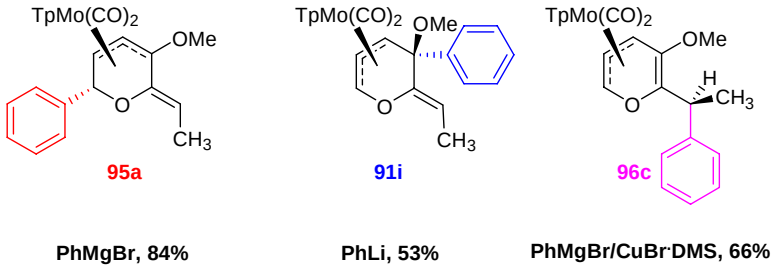


Figure 18: Judicious reagent selection allows predictable, yet diverse regiochemical outcome

Compound **95a**, a representative example of the products resulting from the INA sequence following pathway A was considered as a test bed for the elaboration of this class of products into functionally and stereochemically diverse organic molecules. While direct hydrogenation of the alkylidene with palladium on activated carbon gave no product, it was discovered that under similar conditions to those of the INA sequence, the alkylidene of **95a** could be protonated with HBF_4, creating a cation-diene, to which was added various nucleophiles (**Scheme 61**). Sodium cyanoborohydride delivered a hydride to the diene opposite the molybdenum moiety, giving the

[156] The stark regioselectivity differences for addition to unsaturated electrophiles by organolithiates, organomagnesium and organocuprates are well documented. See: House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Org. Chem.* **1966**, *31*, 3128-3141. For a review on conjugate addition reactions by organocopper reagents see: Posner, G. H. *Org. React. (N.Y.)*, **1972**, *19*, 1-113.

overall reduction product **98** possessing the 2,6-*trans* relationship.[157] Addition of allylmagnesium chloride formed the 2,2,3,6-tetrasubstituted complex **100**. Confirmation of the relative stereochemistry of these complexes was confirmed through the single crystal X-ray diffraction study of complex **100** (see experimental details). Both products could also be oxidatively decomplexed with CAN and triethylamine to provide the enones **99** and **101** in very good yields and with complete regioselectivity. Unfortunately, nucleophilic addition with aryl Grignard reagents (phenyl or 3-methoxyphenyl) gave only recovered starting material. Presumably nucleophilic addition is slowed by the sterically bulky *anti* phenyl group, which allows the Grignard to act only as a base, providing recovered starting material. On the other hand, using benzylmagnesium chloride as a nucleophile provided compound **102** with excellent conversion by TLC, but it was unstable, and underwent rearrangement during purification to form compound **104** in significant amounts.[158] The rearrangement presumably goes through a metal-mediated 1,4-hydride migration mechanism that has been observed in other trisubstituted pyranyl complexes.[159] By subjecting the crude reaction mixture to demetalation conditions, the enone product **103** could be isolated in 42% yield over two steps. It was discovered that several iterations of heating the product in dichloromethane until all solvent had evaporated converted **102** completely into its isomer **104**.[160] This isomerization, if general, could permit access to other highly substituted 4-pyranones such as **105**. The modular nature of the sequential

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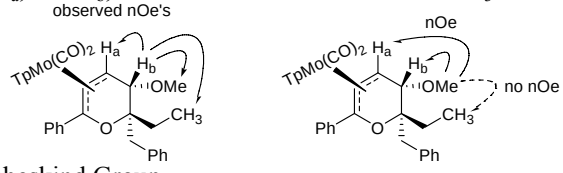
[157] The formal reduction and oxidative demetalation of compound **95a** was first demonstrated by Bo Cheng in 2007. The general procedure has changed, and yields have been optimized since her initial preliminary study.

[158] This type of rearrangement has been seen before by other group members. The stereochemistry of **104** was supported by two separate nOe studies, which showed H_b in proximity to the adjacent allyl proton H_a, the geminal methoxy group, and the CH_3 of the *syn* ethyl group. On the contrary, while the methoxy group did demonstrate nOe with H_a, and H_b, no nOe was observed with the CH_3 of the adjacent ethyl group:

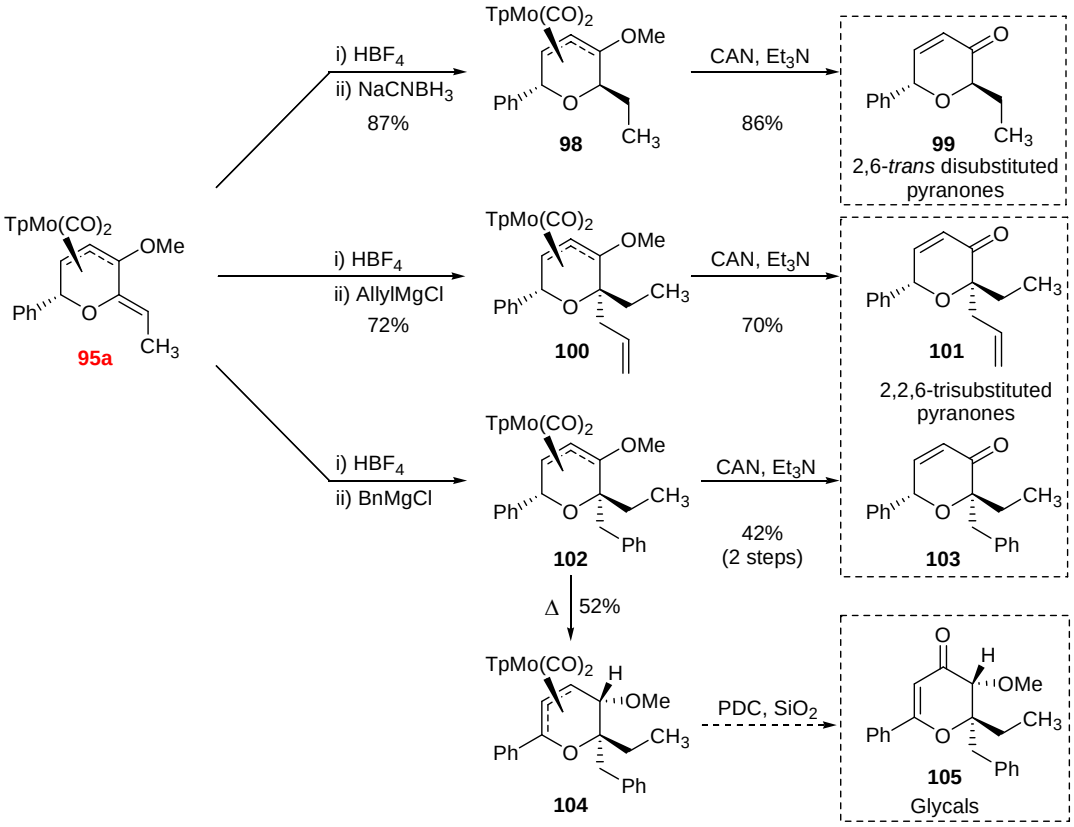


[159] Unpublished results, Liebeskind Group.

[160] Efforts are still underway to devise a more practical approach to initiating this rearrangement.

functionalization methodology and its application to diversity-oriented synthesis is nicely highlighted by the variety of structures shown in **Scheme 61**.

Scheme 61: Elaboration of substituent diversity and stereochemical space *via* functionalization and demetalation of alkylidene complex 95a

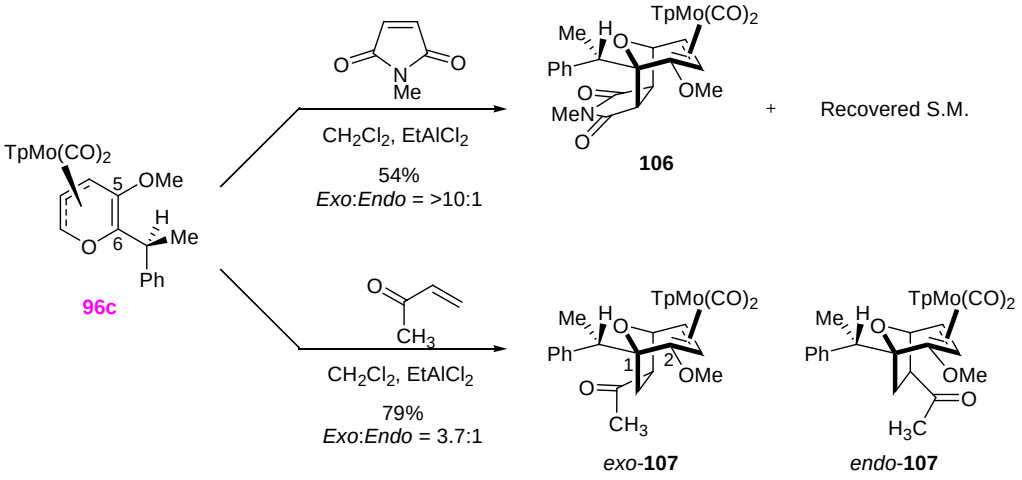


It was found that compound **96c** underwent [5+2]-cycloaddition[115, 161] in the presence of *N*-methylmaleimide and $EtAlCl_2$ to provide the tricyclic compound **106** in 54% yield (>10:1 *exo:endo*) (**Scheme 62**). Similarly, methyl vinyl ketone underwent cycloaddition to form the bicyclo-[3.2.1]-octane complexes **107** in very good yield with 3.7:1 *exo*:*endo* selectivity. The *exo*/*endo* stereochemistry was determined in accordance with coupling constants as previously described. This represents the first general route to 1,2-disubstituted [5+2] cycloadducts

[161] a) Garnier, E.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2008**, in press. b) Zhang, Y.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2006**, *128*, 465-472. c) Malinakova, H. C.; Liebeskind, L. S. *Org. Lett.* **2000**, *2*, 4083-4086. e) Malinakova, H. C.; Liebeskind, L. S. *Org. Lett.* **2000**, *2*, 3909-3911.

developed in our laboratory,[162] and uniquely provides another point of stereochemical and substituent diversity (by the presence of the chiral substituent off the ring). Dr. Ethel Garnier has discovered that 5-hydro-6-aryl substituted complexes require a catalytic amount of acetic acid in addition to the Lewis acid to undergo cycloaddition[161a] (the analogous 5-R, 6-H substitution pattern does not require this[115,161b-e]). As this is not a requirement in the system below, these results suggest that only those complexes lacking substitution in the 5-position require the additional co-catalyst.

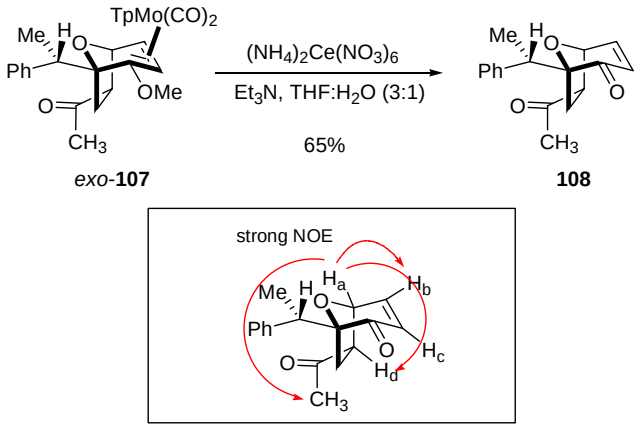
Scheme 62: [5+2]-Cycloaddition to 5,6-disubstituted complex 96c



The isomer *exo*-**107** could be easily decomplexed under oxidative conditions with ammonium cerium nitrate (CAN) to provide the bicyclic enone **108** in good yields (**Scheme 63**) with complete regioselectivity that was determined by an nOe study. Irradiation of H_a demonstrated the strongest nOe with H_b, while moderate intensity nOe was observed with H_d and the acetyl methyl group. Very small nOe was observed between H_a and H_c, and none was observed between H_a and either the benzylic proton or the benzyl methyl group. These data strongly indicate that the carbonyl group resulting from the oxidation is adjacent to the quaternary ring fused carbon.

[162] A few isolated examples have been observed: a) Yin, J. Ph.D Thesis, 1999, Emory University, p 219. b) Arrayás, R. G. Annual Report, Liebeskind Lab.

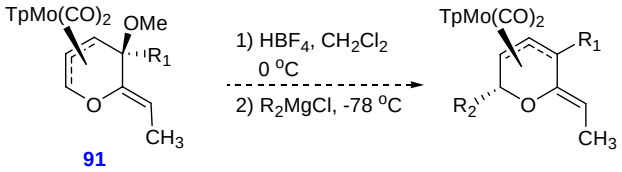
Scheme 63: Oxidative demetalation of [5+2]-cycloadduct



Second INA Sequence to Provide Trifunctionalized Pyrans

Having demonstrated that representative examples of products from the INA sequence of dimethoxy alkylidene following pathways A (**95a**) and C (**96c**) (recall **Figure 18**) could be elaborated in diverse and efficient ways, we sought to further functionalize those compounds resulting from the INA sequence following pathway B. It was thought that ionization of the tertiary methoxy group in **91**, followed by nucleophilic addition would provide trifunctionalized pyrans (**Scheme 64**).[163]

Scheme 64: Proposed second INA sequence should provide trifunctionalized pyrans

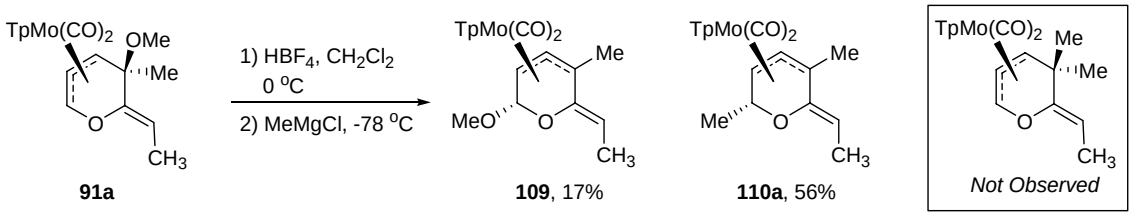


In the preliminary investigation of the INA sequence to compound **91a**, two major products were formed, the major being that product resulting from methyl Grignard addition to the 2-position, and the minor product resulting from methoxide (presumably formed from deprotonation of the methanol formed in the first step) addition (**Scheme 65**). It was interesting that the major product formed in this INA reaction sequence (**110a**) resulted from nucleophilic addition of methyl

[163] This idea was initially proposed and preliminarily investigated by Bo Cheng in 2006.

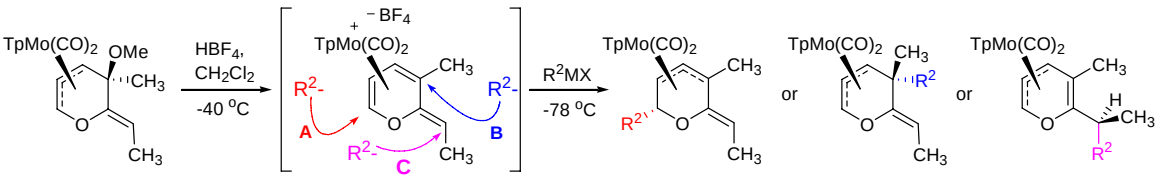
Grignard to the 2-position of the pyran, which contrasts with the result shown in **Table 15 (Entry 1)**.

Scheme 65: Significant byproduct formation observed in second INA sequence



Isolation of the diene intermediate by removing the reaction solvent under vacuum and washing the residue with *tert*-butyl methyl ether (TBME) helped to remove some of the methanol formed in the first step, and as such, gave the product **110a** in slightly improved yield (62%, up from 56%). Using the optimized conditions, another comprehensive study of this second INA sequence with various nucleophiles provided some very interesting results (**Table 16**). By comparison to the results in **Table 15** it is easy to see that, at first glance, the major trends of each table are the same with a few exceptions. As with the first INA sequence, sp^2-hybridized Grignard reagents add selectively only to the 2-position of the diene following pathway A (Entries 8-12), while sp^3-hybridized Grignard reagents preferentially add to the 5-position following pathway B (Entries 2-6). Also similar to the first INA sequence, *t*-butyl Grignard and copper-modified Grignard reagents add selectively to the off ring-position following pathway C (Entries 18-20). Interestingly, however, organolithium reagents, regardless of hybridization all add selectively following pathway A (rather than pathway B as in **Table 15**, Entries 13-15). Lithium enolates, which also previously provided only products resulting from pathway B, provide mixtures of products from pathways A and B in this reaction. Another result worth highlighting is the tendency for sp^3-hybridized Grignards to form small amounts of products **113**. The most surprising change is the preference for pathway A of methyl Grignard, with no similar shift in selectivity for the structurally similar ethyl Grignard.

Table 16: Second INA sequence provides trifunctionalized pyrans



91a 111 110 112 113

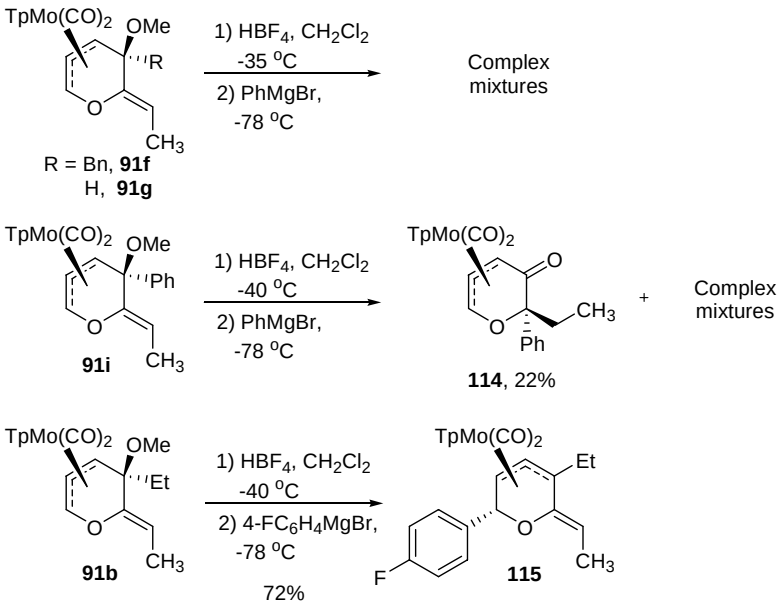
	Entry	RMX[a]	Yield 110[b] (%)	Yield 112[b] (%)	Yield 113[b] (%)
{	1	MeMgCl	62, **110a**	--	--
	2	EtMgBr	--	62, **112a**	trace
	3	HexylMgBr	--	70, **112b**	trace
	4	*i*-PrMgCl	--	93, **112c**	--
	5	AllylMgCl	--	76, **112d**	trace
	6	BnMgCl	--	87, **112e**	trace
{	7	$NaCNBH_3$	59, **110b**[c]	--	trace
	8	PhMgBr	77, **110c**	--	--
	9	*m*-MeO-C_6H_4MgBr	61, **110d**	--	--
	10	*p*-F-C_6H_4MgBr	81, **110e**	--	--
	11	MesitylMgBr	64, **110f**	--	--
	12	VinylMgCl	99, **110g**	--	--
{	13	MeLi	43, **110a**	--	--
	14	PhLi	62, **110c**	--	--
	15	PhCCLi	71, **110h**	--	--
	16	CH_3COCH_2Li	15, **110i**	26, **112f**	--
	17	$PhCOCH_2Li$	48, **110j**	28, **112g**	--
	18	*t*-BuMgCl	--	--	30, **113a**
	19	MeMgCl/CuBr·DMS	--	--	39, **113b**
	20	PhMgCl/CuBr·DMS	--	--	79, **113c**

a) Grignards, lithiates and $NaCNBH_3$ were purchased commercially as solutions (typically of THF or Et_2O); enolates were prepared from the corresponding ketones and LiHMDS. See experimental details for more information. b) isolated yield. c) In the major product the ethylidene had been fully reduced to an ethyl group (See experimental section).

The scope of the reaction is broad, but there are currently some limitations. The reaction works well using starting complex **91a**, however attempts to perform this second ionization reaction with other starting complexes gave poor results (**Scheme 66**). Starting complexes **91f** and **91g** gave a complex mixture of products. From the INA reaction of starting complex **91i**, a complex mixture was also obtained, however 20% of the semi-pinacol product **114** was isolated. The formation of this product was surprising, but its spectroscopic data exactly matches that of the

known compound.[164] Presumably, steric hinderance from the bulky phenyl group in **91i** slows ionization of the tertiary methoxy group enough that initiation of the semipinacol reaction is faster.[165] Apparently other alkyl groups are not as problematic, however, as the INA sequence to complex **91b** provides the expected product in good yields with no major side products. Further study would be beneficial to expanding the scope of this reaction to other substrates.

Scheme 66: Second INA sequence with different starting substrates

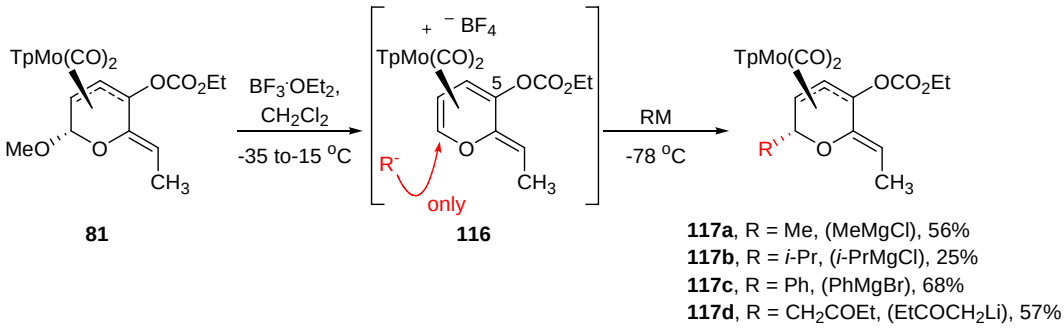


To investigate the extent of the electronic influences on the selectivity of this INA sequence another short study was performed on the carbonate **81**. The diene **116**, formed after ionization of the *anti*-methoxy group[166] possesses an electron-withdrawing group at the 5-position (**Scheme 67**). Interestingly, all Grignard reagents studied, regardless of their hybridization added to the 2-position of the diene, giving the products shown. The kinetic enolate of methyl ethyl ketone, as well, only gave the product shown. While the yields were lower in all of these reactions, analysis

[164] Zhang,Y.; Coombs, T. Liebeskind group, unpublished results.
[165] It is unclear at this time whether the semipinacol reaction of these substrates is a general phenomenon, that competes with ionization when the substrate possesses a good migrating group (such as phenyl), or whether, this particular reactivity is unique to this starting complex.
[166] As shown previously for dimethoxy alkylidene **78** (recall **Scheme 59**), an optimization study revealed that temperature control in the ionization step could favor ionization of the methoxy group over protonation of the alkylidene. The use of $BF_3{\cdot}OEt_2$ in the first step gave better yields than HBF_4.

of the crude mixtures in each case showed no trace of products resulting from nucleophilic addition to the 5-position of the pyranyl (corresponding to C_4). Typically, significant decomposition was observed in these reactions and probably accounts for the majority of the remainder of the mass balance.

Scheme 67: Regioselectivity study of nucleophilic additions to cationic diene of carbonate 81

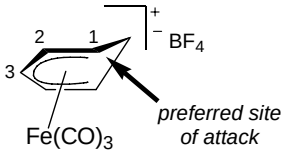


It was discussed in Chapter 3 (recall **Figure 15**, and related text) that the electronic differences between the methoxy and carbonate substituents in **78** and **81** are reflected in the spectroscopic data of each compound. Consistent with ^{13}C NMR shifts, and carbon monoxide stretches, the electron withdrawing nature of the carbonate group appears to cause the metal to donate more electron density into the π-system, particularly at C_4 (the 5-position of the pyranyl). If this assumption is correct, then we can conclude that the Mo-C_4 bond in **81** is of higher order than the Mo-C_4 bond of **78**. It has been shown computationally by Kane-Maguire[167] that in iron and chromium dienyl complexes $[(C_6H_7)M(CO)_3]^+$ (where M = Fe or Cr) the bond indices[168] of the terminal carbons of the dienyl are lower than those of the internal carbons, which suggests lower metal carbon bond order at the teminal positions. These data correlate with the known tendency of nucleophiles to attack the termini of the dienyl in these complexes.

[167] a) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1976**, *120*, C25-C27. b) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1976**, *107*, C40-C42.

[168] Bond index is a computational value representative of overall bonding of an atom. A lower bond index signifies that the atom shows lower overall bonding character (i.e. weaker existing bonding interactions). It is argued then, that low bond index will lead to more facile new bond formation because of the increased "free valence" available for formation of a new bond.

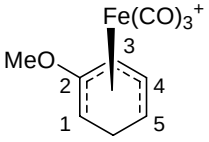
Figure 19: Kane-Maguire's INDO calculations of bond index in $[(C_6H_7)Fe(CO)_3]BF_4$[167b]



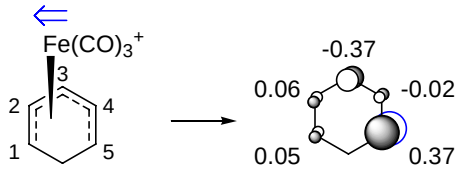
σ-bond index	π-bond index
C_1 = 1.582	C_1 = 0.364
C_2 = 1.690	C_2 = 0.378
C_3 = 1.702	C_3 = 0.376

Eisenstein, Butler and Pearson have used molecular orbital calculations of asymmetrically substituted cationic cyclohexadienyliron complexes to derive orbital overlap population figures.[169] Two separate computational studies demonstrate how 1) the effect of an electron donating substituent on the dienyl causes the metal fragment to bond more strongly to one side of the dienyl over the other (although in this case the metal fragment shifts toward the donating group, which is the opposite of what we observe in our neutral molybdenum complexes) and 2) if the iron fragment is theoretically shifted to one side of the mirror plane of an unsubstituted dienyl fragment, the resulting orbital distortion indicates that C_5 will be activated toward nucleophilic attack compared to C_1 (**Figure 20**). The data reflect how weaker orbital overlap (and crystallographically-verified longer Fe-C bond lengths) at one end of the dienyl compared to the other accurately correlate to the preferred site of nucleophilic attack.

Figure 20: Molecular orbital calculations of cyclohexadienyl iron complexes



better orbital overlap when metal fragment shifted toward C_1, C_2



orbital analysis of unsubstituted dienyl with metal fragment shifted 0.1Å perpendicular to mirror plane

The reaction described in this study could be reflecting a similar trend. As the electron withdrawing nature of the substituent on the allyl increases, the Mo-C_4 bond length in the ground state appears to decrease. If this disparity in bond lengths is reflected in the cation-dienes of each

[169] Eisenstein, O.; Butler, W. M.; Pearson, A. J. *Organometallics* **1984**, *3*, 1150-1157.

substrate as well,[170] then it could account for the decreased preference for nucleophilic attack at C_4 (5-position of pyranyl), and the increased tendency for nucleophiles to add to C_1 and the off-ring position (alkylidene).

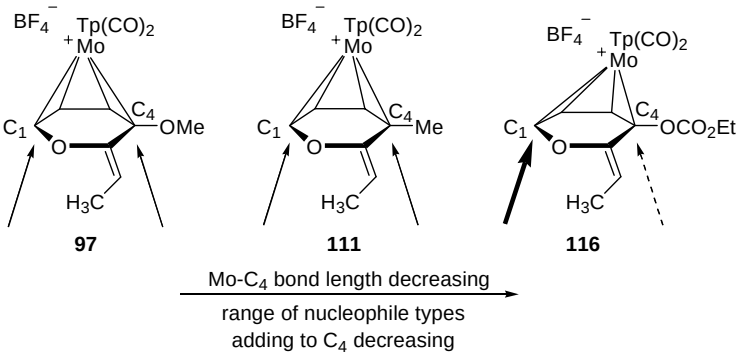


Figure 21: Disparity in C-Mo bond lengths could account for the change in regioselectivity of attack by some nucleophiles

It follows that as the electron donating capability of the substituent at C_4 increases from OCO_2Et (**Scheme 67**), to Me (**Table 16**) to OMe (**Table 15**) the strength of the Mo-C_4 bond is weakened, and thus increases the tendency to add to the 5-position. An overall evaluation of this trend suggests that an inherent change in the nature of the different electrophilic sites is occurring. In any nucleophile/electrophile interaction, the appropriate HOMO/LUMO overlap must be favorable. Because we must assume that the HOMO of each nucleophile used in this study does not change from one reaction to another, we must conclude that—in order to obtain different products—the LUMO of the diene electrophile must be different. Therefore, if it is assumed that along the continuum of reactivity, the most favorable pairing of each electrophilic site on the various cationic dienes will demonstrate a preference for the nucleophile with which it is most electronically compatible. The results of the three studies are summarized in **Figure 22**. While this is not an explanation for the observed trend, it can serve as a predictive model for the expected regioselectivity of nucleophilic addition.

[170] Unfortunately all attempts to crystallize the diene intermediates have been unsuccessful.

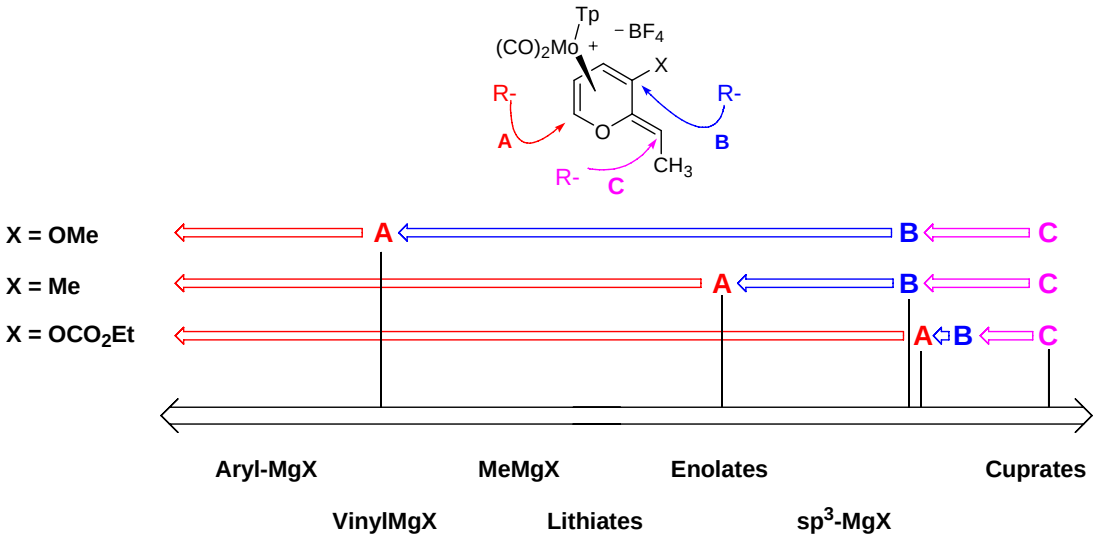


Figure 22: Graphical description of the regioselectivity of nucleophilic addition to different diene electrophiles

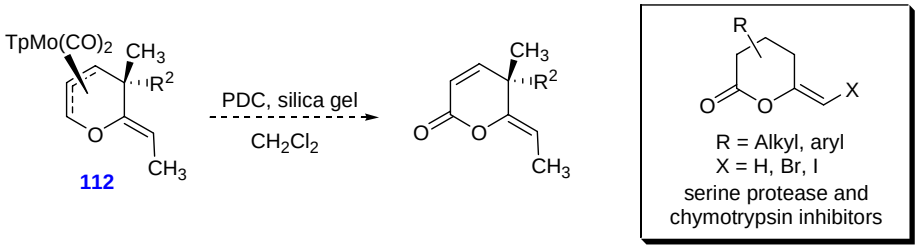
While there remain a number of unanswered questions, the ultimate origins of the selectivity observed in this study were *intentionally not pursued*, in favor of a more general investigation of the reactivity and utility of the products. Because of this, the inherent reasons for the observed selectivity are not well understood at this time. However, a qualitative evaluation of the trends observed has permitted the development of a predictive model for the reactivity, and the scope of the investigation has laid ample groundwork for a detailed mechanistic study, and potentially, a computational investigation.

Synthetic elaboration and demetalation of products:

It was hoped that oxidative demetalation of the products resulting from INA following pathway B using conditions previously described by our group for formation of lactones[171] would provide stereocontrolled access to the biologically relevant enol lactone motif.[172]

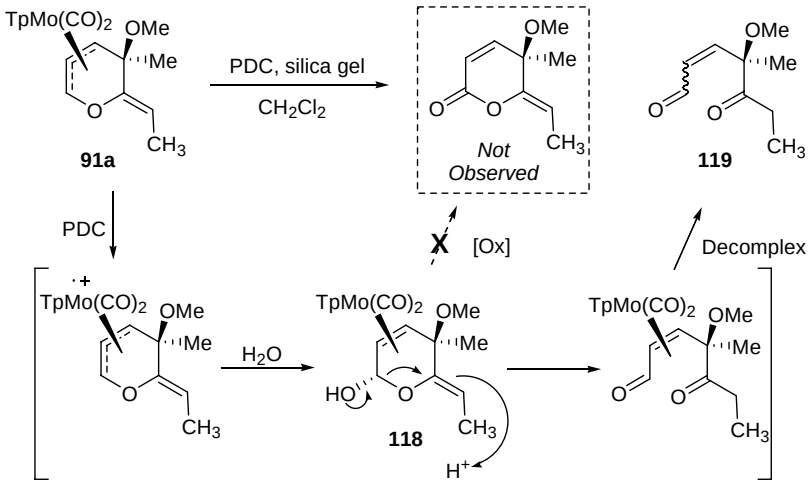
[171] Alcudia, A.; Arrayás, R. G.; Liebeskind, L. S. *J. Org. Chem.* **2002**, *67*, 5773-5778.
[172] For relevant examples see: Dai, W.; Katzenellenbogen, J. A. *J. Org. Chem.* **1993**, *58*, 1900-1908, and references within.

Scheme 68: Oxidative decomplexation could lead to enol lactones



Using substrate **91a** as a model study, however, the only products formed were those resulting from ring opening (**Scheme 69**). The working mechanism for these oxidation reactions is initial oxidation of the metal by PDC, then water present in the silica gel adds to the allyl moiety, in this case creating the highly reactive hemiacetal, **118**. Apparently, before the second oxidation to form the desired lactone can occur, protonation of the enol moiety causes the ring to open, after which no further reaction takes place, and decomplexation of the metal leads to the aldehyde **119** as an inseparable mixture of *cis* and *trans* isomers. Attempts to speed the second oxidation using more equivalents of oxidant or to inhibit the rapid protonation of the enol ether moiety by adding triethylamine provided only the ring opened product as well.

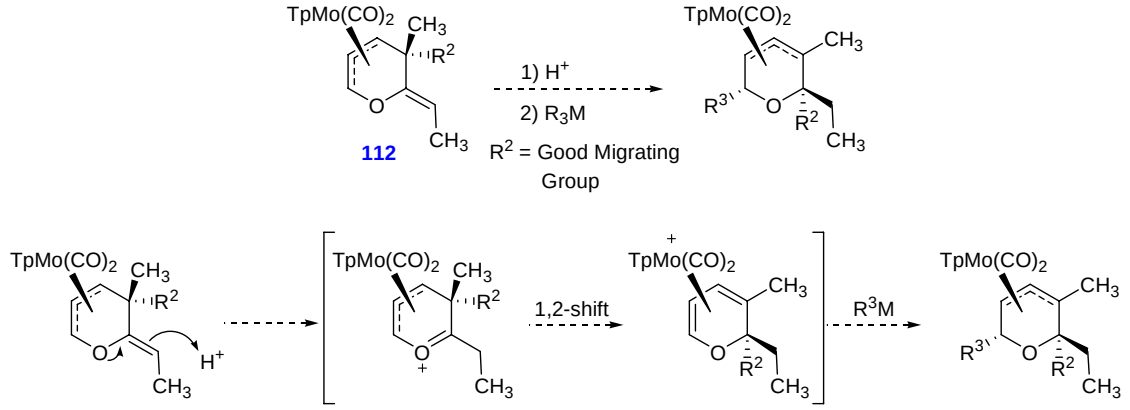
Scheme 69: Attempts to access enol lactone structure leads only to ring-opened products



While this particular reaction pathway was not fruitful, the potential of the products **112a-e** for use in a molybdenum-mediated semipinacol reaction is an intriguing possibility. In this reaction

1,2-migration must be facilitated by formation of a cationic molybdenum intermediate [173] (**Scheme 70**). Quench of the electrophilic intermediate with an organometallic nucleophile would provide access to 2,2,3,6-tetrasubstituted pyrans.

Scheme 70: Proposed application of products 112 to molybdenum-mediated semi-pinacol reaction



The synthetic elaboration of those trisubstituted compounds resulting from nucleophilic addition following pathway A was accomplished in a similar manner as in **Scheme 61**. It was found that substituted alkylidenes underwent a protonation/hydride delivery sequence to provide the 2,6-*trans*-trisubstituted compounds in excellent yields (**Table 17**).

[173] The molybdenum-mediated semipinacol reaction highlighted below and in **Scheme 42** has been studied extensively by Thomas Coombs and Dr. Yongqiang Zhang in our laboratory. These reactions require a full equivalent of acid (in contrast to the well known organic transformation—see reference 126), which was rationalized by the proposed intermediacy of a molybdenum-stabilized oxonium. The extent to which molybdenum is actually involved in facilitating the 1,2-shift, however, is unknown at this writing.

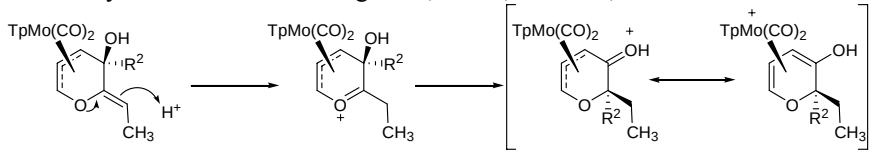
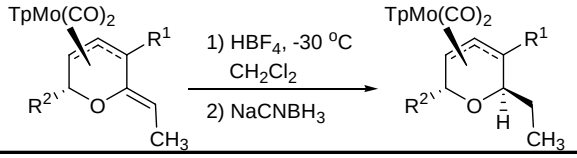


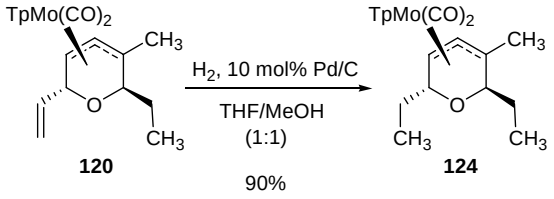
Table 17: Protonation/hydride delivery sequence provides 2,6-*trans* trisubstituted complexes



Entry	Substrate	R^1 =	R^2 =	Yield
1	**110g**	Me	Vinyl	**120**, 80%
2	**110h**	Me	PhC≡C	**121**, 87%
3	**110e**	Me	*p*-F-C_6H_4	**122**, 88%
4	**115**	Et	*p*-F-C_6H_4	**123**, 80%

Saturated alkyl functionality in the 2-position can be accessed *via* addition of organolithiates as described in **Table 16**, or by hydrogenation of the unsaturated analogs accessible *via* Grignard addition (**Scheme 71**). To this end, the 2,6-*trans* diethyl substituted complex **124** was obtained in excellent yield from the 2-ethyl-6-vinyl complex **120**.

Scheme 71: Hydrogenation unmasks target saturated functional groups

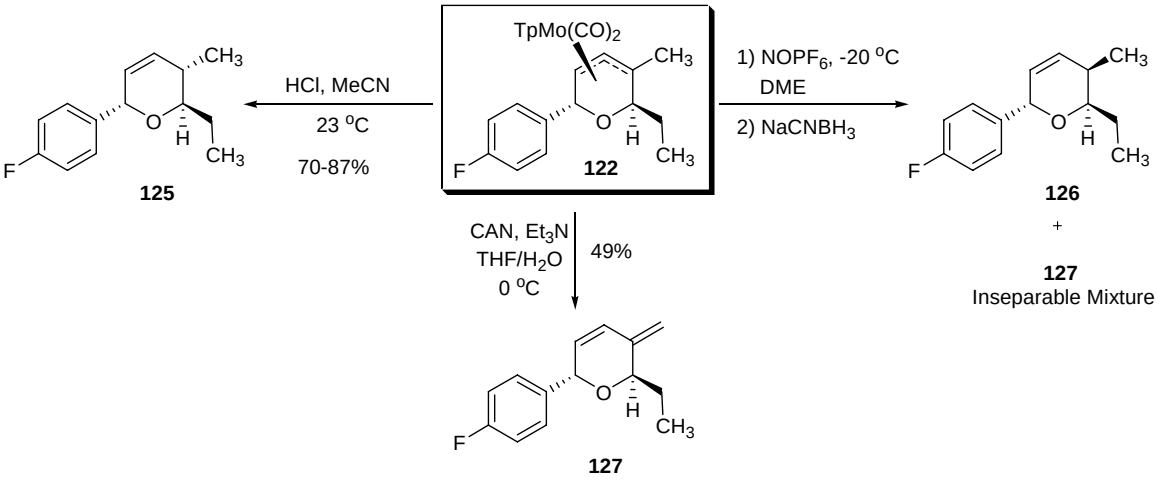


The products of the study in **Table 17** were excellent substrates for further diversification through several known demetalation protocols. Stereodivergent decomplexation of **124** following known protocols permits access to the four possible isomeric products. Protodemetalation with TFA in acetonitrile provides the product **125** resulting from internal hydride delivery to the more substituted end of the allyl,[115, 116] while ligand exchange with nitrosonium hexafluorophosphate followed by addition of sodium cyanoborohydride promotes external hydride delivery to the same position, forming **126**.[174 175] The result of these stereodivergent demetalations is effective control

[174] a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388-3389. b) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858-4859. c) Villanueva, L. A.; Ward, Y. D.; Lachicotte, R.; Liebeskind, L. S. *Organometallics* **1996**, *15*, 4190-4200.

of the relative stereochemistry of the substituent on the allyl. Further diversity was obtained through oxidative demetallation with CAN, which provided the diene **127**[115,176] in moderate yield. The application of these demetalation protocols to substrate **122** serves only to highlight the elaborative potential of any and all of the many substrates synthesized in this study, suggesting that even from a small and focused library of compounds generated using this methodology, a large number of stereochemically and peripherally diverse organic structures can be obtained through the many permutations of substituents and accessible stereochemistries at the various positions around the pyran ring.

Scheme 72: Further diversity through stereo and regiocontrolled demetalations

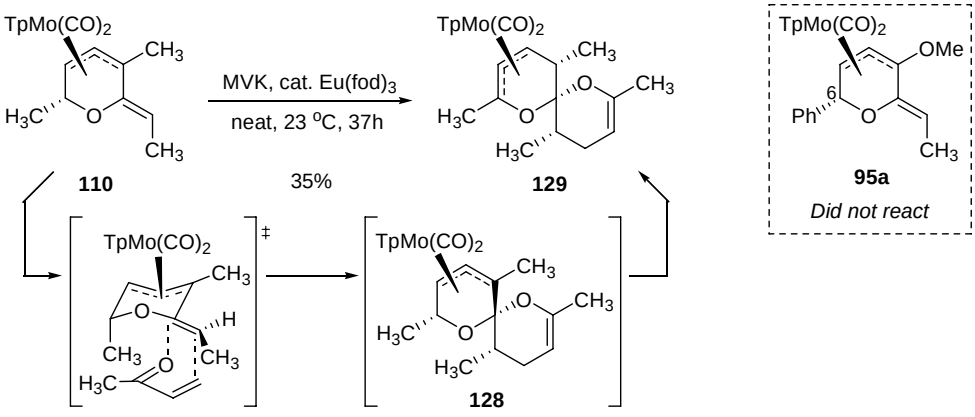


A preliminary investigation into the synthesis of spirocycloadducts *via* hetero Diels-Alder reactions to the 6-functionalized-2-alkylidene products **110** revealed that the cycloaddition does occur, although not completely as expected (**Scheme 73**). Compound **110a** was stirred with $Eu(fod)_3$ in methyl vinyl ketone for 37 hours at room temperature, and provided the spirocycloadduct **130** in 35% yield with recovered starting material, and decomposition. Because only one stereoisomer was formed, it is assumed that the stereochemistry of the methyl group in

[175] Unfortunately, the targer could only be isolated in low yield as mixture of the two products **126** and **127**. Further optimization of the reaction conditions is required.
[176] Arrayás, R. G.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 9026-9027.

the spiro-ring resulted from cycloaddition to the *Z*-alkylidene, opposite the face of the metal, however the spectroscopic data for **129** is consistant with the structure having undergone a 1,4-hydride shift. Presumably the expected product **128** was formed as an intermediate in the reaction, but was thermally unstable (recall from **Scheme 61** that the 2,2,6-substituted complex **102** was also thermally unstable and underwent a 1,4-hydride shift), and rearranged under the reaction conditions. Cycloaddition did not occur with substrate **95a**. Even after several days under identical reaction conditions only starting material was recovered. Presumably, the cyclization is slowed or inhibited by non-bonded interactions between the substituent in the 6-position of the alkylidene starting material that are amplified with increasing steric bulk of the substituent. While this investigation was only preliminary, and only one example was generated, further study in this area could expand the methodology to include cycloadditions to other substituted aldehydes and ketones, and presumably a wider variety of substituted alkylidene complexes. The application of the cycloaddition reaction to the pyranyl alkylidenes provides yet another example of heterocyclic skeletal diversity accessible through the organometallic chiron strategy.

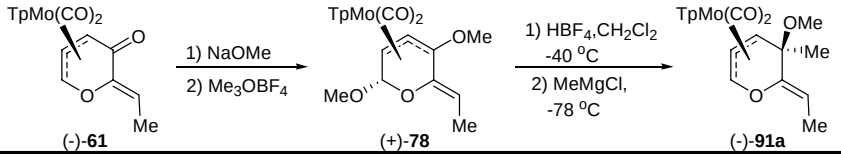
Scheme 73: Spiroketals through hetero Diels Alder cycloaddition to functionalized products



Stereo- and Regiocontrolled Synthesis of Functionalized Pyrans of High Enantiopurity

The final test of the methodology developed and highlighted in this chapter was its application to the synthesis of products of high enantiopurity to ensure that at no point in the multi-step process does racemization occur. It was determined in Chapter 2, **Scheme 37** that the four step process (Mukaiyama aldol, mesylation, elimination, isomerization) for converting the starting scaffold (-)-**24** entirely to *Z*-enone (-)-**61** occurs without loss of enantiopurity. The 1,5 Michael like reaction was investigated next. The two enantiomers of the 1,5-Michael product **78** could not be separated by HPLC, but could be converted to **91a**, whose enantiomers were separable by chiral HPLC. Subjecting an enantioenriched sample (80.4% ee) of enone (-)-**61** to abbreviated, but otherwise identical 1,5-Michael reaction conditions as used for racemic mixtures (6 hours in first step, as opposed to the usual 16 hours) provided the 1,5-Michael product in 24% yield. A subsequent INA sequence with methyl Grignard provided the product (-)-**91a** in 39% ee. The low yield of the 1,5-Michael step was certainly due to the short reaction time in the first step, the length of which is critical for achieving high yields as discussed earlier. It was unclear after this experiment in which step racemization was occurring, but because the loss of enantiopurity was not complete, we rationalized that racemization was a slow process, which suggested that it was most likely occurring during the 1,5-Michael reaction's first step and could be controlled by altering the reaction conditions. The results of the optimization study are included in **Table 18**. The INA sequence was performed in an identical manner in each entry, and so only the yields of the 1,5-Michael product are included and relevant.

Table 18: Development of non-racemizing 1,5-Michael reaction conditions



(-)-**61** (+)-**78** (-)-**91a**

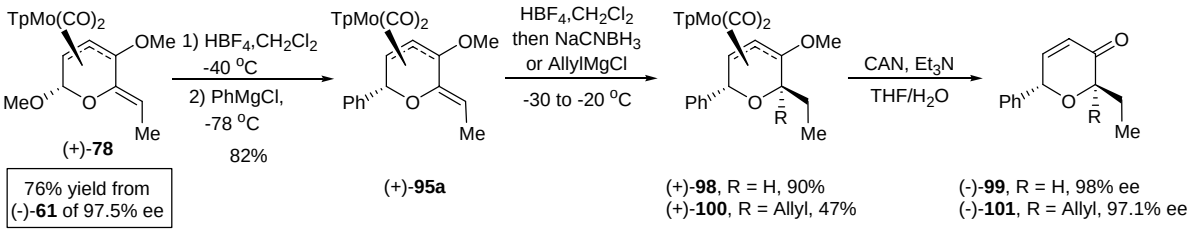
Entry	% ee (-)-**61**	Equiv NaOMe	Time of Step 1 (min)	Temp (^{o}C)	Conc. (M)	Equiv Me_3OBF_4	Yield (%) (+)-**78**	% ee (-)-**91a**
1	80.4	9.0	360	23	0.04	9.0	24	39.1
2	80.4	20.0	45	0	0.04	20.0	14	79.2
3	80.4	20.0	45	0	0.19	20.0	39	81.4
4	80.4	20.0	90	0	0.19	20.0	64	80.8
5	97.5	20.0	105	0	0.19	20.0	70	98.0, (-)-**99**
6	97.5	20.0	120	0	0.19	20.0	76	97.1, (-)-**101**

Fortunately it was discovered that by running the 1,5-Michael reaction at lower temperature (0 ^{o}C), for a shorter time, and with more equivalents of NaOMe in the first step, racemization of the reaction could be completely suppressed (Compare Entries 1 and 2). Additionally, the starting material recovered was of exactly the same enantiopurity as before the reaction. This experiment tells us that the *racemization occurs only in the first step of the 1,5-Michael reaction, and that no racemization occurs during the INA sequence*. Unfortunately, under these non-racemizing conditions, the yield of the 1,5-Michael product suffered greatly. The yield could be increased dramatically by running the reaction at higher concentration (Entry 3). Further improvements could be achieved by longer reaction times in the first step without loss of enantiopurity (Entries 4-6). The yield of the reaction in Entry 6 is identical to that obtained under the optimized conditions used for the racemic substrate (recall **Table 14**). The enantiopurity of the products in Entries 5 and 6 were determined by their subsequent conversion to demetalated products (-)-**99** and (-)-**101** (*vide infra*).

Gratifyingly, the optimization study also provided the significant result that the conditions used for the INA sequence do not racemize the products. With this result in hand, the synthesis of high enantiopurity compounds (-)-**99** and (-)-**101** were achieved using conditions identical to those using racemic material (**Scheme 74**). The demetalated products were found to be of > 97.1% ee

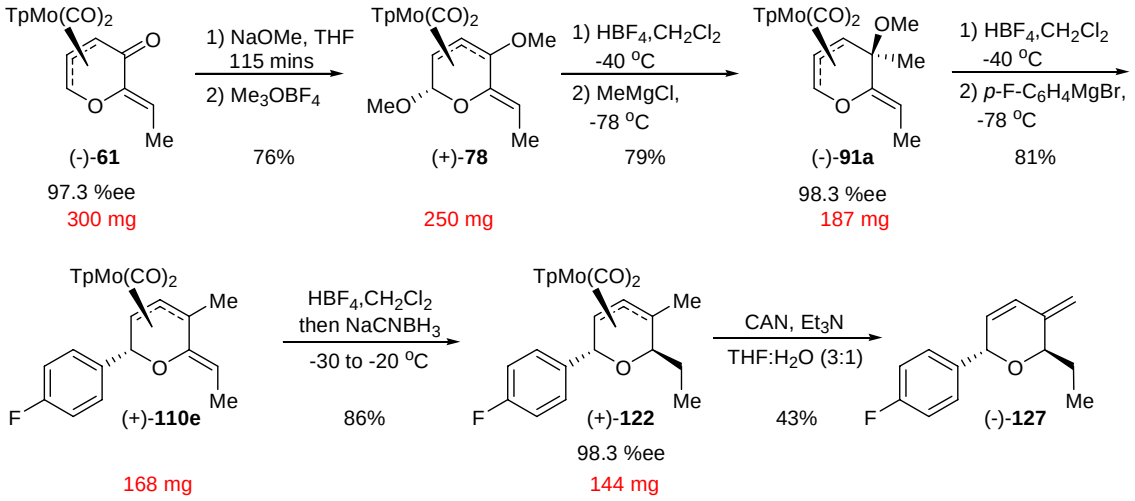
by comparison of chiral HPLC data to that of the racemic products first synthesized in **Scheme 61**.

Scheme 74: Synthesis of high enantiopurity di- and tri-substituted pyranones using INA methodology



The synthesis of high-enantiopurity trisubsituted compound (-)-**127** was also achieved following the same exact procedures used to synthesize the racemic material. The enantiopurity of complex (+)-**122** was determined by comparison to the chiral HPLC data obtained from (±)-**122**. The practical utility of this methodology is demonstrated in this multistep reaction sequence, whereby 300 mg of enantioenriched enone (-)-**61** was converted to 144 mg of (+)-**122** over 4 steps, each of which builds the simple starting material into one of increasing complexity. Decomplexation provides a highly enantioenriched organic product, with functional groups in place for further elaboration.

Scheme 75: Enantiocontrolled synthesis of trisubstituted dihydropyrans using INA methodology

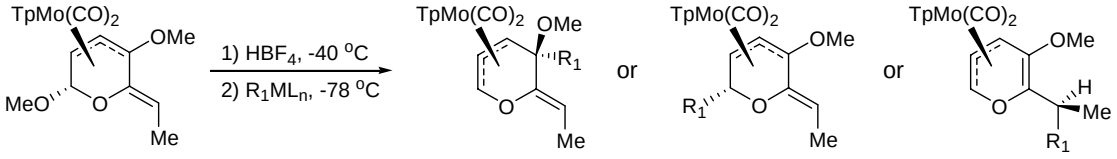


Conclusions:

A novel, and general sequential functionalization of $TpMo(CO)_2$ pyranyl alkylidenes has been developed. Synthetic elaboration of these complexes *via* an ionization/nucleophilic addition sequence provided access to 3-distinct regioisomeric products. The selectivity for one regioisomer over the other is predictable and is related to the nature of the organometallic reagent, including a curious dependence upon the hybridization of Grignard reagents. The 3 regioisomers were elaborated in ways that offer diverse exploration of chemical space by accessing various structural types from common intermediates including oxabicyco-[3.2.1]-nonanes, 2,6-*trans*-disubstituted and 2,2,6-trisubstituted pyranones. The further elaboration of one of the regioisomeric products *via* another INA sequence provided access to 2,3,6-trisubstituted pyrans with complete control over the stereochemical relationships between substituents. The full scope of the utility of the organometallic enantiomeric chiron strategy is ultimately demonstrated by the synthesis of diverse pyran architectures of high enantiopurity.

Experimental Details:

General reaction procedure for the given transformation:



1) Preparation of Diene:

Preparation of the diene was constant for every nucleophile. Starting material was dissolved in dry, degassed CH_2Cl_2, and cooled to -40 °C. A solution of tetrafluoroboric acid (HBF_4, 54 wt% in Et_2O) was added dropwise, and the reaction was stirred for 3 minutes after which TLC showed *almost* complete disappearance of starting material. Immediately, the reaction was cooled to -78 °C and allowed to stir for 3 minutes.

2) Procedure A: *R_1ML_n = Commercially available Grignard or organolithiium reagent:*

The indicated Grignard or organolithium reagent was added as a solution dropwise to the diene and the reaction was stirred for 3 minutes after which TLC indicated the appearance of a new product. The reaction was quenched with water, and diluted with three times the starting solvent volume of CH_2Cl_2. The organic layer was washed two times with a 1:1 mixture of water and saturated aqueous NH_4Cl solution (2 x 20 mL), dried ($MgSO_4$), filtered and concentrated under low pressure. The resulting residue was purified by gravity chromatography (10% EtOAc in hexanes) on silica gel neutralized with 5% Et_3N. In some cases, recrystalization from dichloromethane and hexanes was required to obtain analytically pure material.

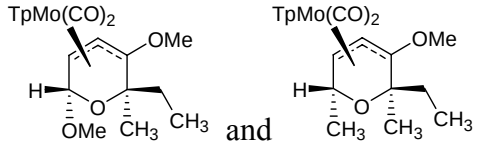
Procedure B: *R_1ML_n = Cuprate or Enolate*

Cuprates were prepared as follows: To 1 mL of THF cooled to -70 °C was added the indicated amount of CuBr·DMS and the grayish-white suspension was stirred for 3 minutes before adding the indicated Grignard reagent dropwise to the mixture. This solution was then warmed to -45 °C over 20 to 30 minutes producing a yellow (or yellow-brown or orange) solution, which was

recooled to -78 ^{o}C.

Enolates were prepared as follows: To 1.0 mL of THF cooled to -78 ^{o}C was added the indicated amount of lithium hexamethyldisilazide (LiHMDS) solution. This was stirred for 3 minutes before adding the ketone dropwise over 5 minutes. This solution was stirred at -78 ^{o}C for 20 minutes.

The solution of diene was then cannulated directly into the stirring solution of cuprate or enolate, using a small of amount of extra CH_2Cl_2 to complete the transfer. The reaction was stirred for 3 minutes after which TLC indicated the appearance of a new product. The reaction was quenched with water, and diluted with 15 mL of CH_2Cl_2. The organic layer was washed two times with a 1:1 mixture of water and saturated aqueous NH_4Cl solution (2x20 mL), dried ($MgSO_4$), filtered and concentrated under low pressure. The resulting residue was purified by gravity chromatography (10% EtOAc in hexanes) on silica gel neutralized with 5% Et_3N. In some cases, recrystalization from dichloromethane and hexanes was required to obtain analytically pure material.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*R*,6*R*)-η-(2,3,4)-6-ethyl-2,5-dimethoxy-6-methyl-3,6-dihydro-2*H*-pyran-3-yl]molybdenum, 92

and

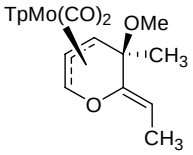
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-2-ethyl-3-methoxy-2,6-dimethyl-3,6-dihydro-2*H*-pyran-3-yl]molybdenum, 93

Compounds **92** and **93** were isolated from a modified version of the reaction as that described below for the synthesis of **91a**. Under the *un*optimized conditions, to a solution of **78** (40 mg,

0.0749 mmol, 1.0 equiv) in CH_2Cl_2 (2.5 mL) at 0 °C was added tetrafluoroboric acid (54 wt% in Et_2O, 16 μL, 0.0974 mmol, 1.3 equiv). The reaction was stirred for 2 hours, allowing the mixture to warm from 0 °C to 23 °C. It was then cooled to -78°C, and methylmagnesium chloride (3.0 M in THF, 75 μL, 0.225 mmol, 3.0 equiv) was added. The reaction was worked up in the usual manner, and chromatography on neutralized silica gel provided **91a** (28 mg, 72%, *see below for optimized reaction, and spectroscopic data*) and the two byproducts **92** (3.8 mg, 10%) and **93** (1.5 mg, 4%) as orange oily solids.

92: TLC: R_f = 0.51 (25% EtOAc in hexanes). IR (cm^{-1}): 2922 (w), 2852 (w), 1941 (m), 1828 (m), 1502 (w), 1405 (m), 1307 (m), 1217 (m), 1117 (m), 1049 (s). ^1H NMR [600 MHz, $CDCl_3$]: δ 8.28 (d, *J* = 1.4 Hz, 1H), 7.74 (d, *J* = 1.4 Hz, 1H), 7.64 (d, *J* = 1.9 Hz, 1H), 7.58 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.42 (s, 1H), 6.18 (m, 3H), 4.98 (d, *J* = 1.4 Hz, 1H), 4.29 (dd, *J* = 8.1, 1.4 Hz, 1H), 3.52 (d, *J* = 8.1 Hz, 1H), 3.47 (s, 3H), 2.57 (s, 3H), 2.44 (app sextet, *J* = 7.6 Hz, 1H), 1.90 (app sextet, *J* = 7.6 Hz, 1H), 1.46 (s, 3H), 0.98 (t, *J* = 7.6 Hz, 3H). HRMS (ESI) Calcd for $C_{21}H_{27}BMoN_6O_5$ $[M]^+$: 552.1185. Found: 552.1185.

93: ^1H NMR [600 MHz, $CDCl_3$]: δ 8.27 (s, 1H), 7.77 (s, 1H), 7.64 (s, 1H), 7.59 (s, 1H), 7.49 (d, *J* = 1.0 Hz, 1H), 7.43 (s, 1H), 6.19 (m, 3H), 4.17 (q, *J* = 6.7 Hz, 1H), 4.07 (d, *J* = 8.1 Hz, 1H), 3.61 (d, *J* = 8.1 Hz, 1H), 2.62 (s, 3H), 2.37 (app sextet, *J* = 7.1 Hz, 1H), 2.04 (app sextet, *J* = 6.2 Hz, 1H), 1.55 (s, 3H), 1.52 (d, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.6 Hz, 3H).



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methoxy-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91a

(-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methoxy-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)**-91a**

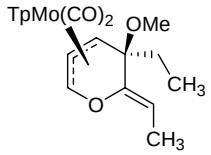
This compound was successfully prepared using methylmagnesium chloride or methyllithium. Following the *general procedure A,* starting material **78** (500 mg, 0.936 mmol, 1.0 equiv) was dissolved in 30 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 200 μL, 1.22 mmol, 1.3 equiv) and methylmagnesium chloride (3.0 M in THF, 940 μL, 2.81 mmol, 3.0 equiv). Purification by gravity chromatography gave 385 mg (79%) of pure product **91a** as a yellow solid.[177]

The exact same procedure was used in the conversion of (+)-**78** (97.3-98.3% ee) to (-)-**91a**, which was determined to be 98.3% ee by chiral HPLC.

Alternatively, following the *general procedure A*, starting material **78** (50 mg, 0.094 mmol, 1.0 equiv) was dissolved in 3.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 20 μL, 0.122 mmol, 1.3 equiv) and methyllithium (1.4 M in Et_2O, 200 μL, 0.281 mmol, 3.0 equiv). Purification by gravity chromatography gave 35.4 mg (73%) of pure product **91a** as a yellow solid.

(-)-**91a:** TLC: R_f = 0.45 (25% EtOAc in hexanes). $[\alpha]_D^{20}$ -187 (98.3% ee, *c* 0.105, CH_2Cl_2). IR (cm^{-1}): 2925 (w), 1951 (vs), 1863 (vs), 1407 (m), 1218 (m), 1125 (m), 1049 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.52 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 1.9 Hz, 1H), 7.57 (s, 2H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.06 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.26 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 4.95 (q, *J* = 7.0 Hz, 1H), 4.68 (dd, *J* = 7.6, 2.2 Hz, 1H), 3.60 (s, 3H), 3.40 (dd, *J* = 7.9, 4.4 Hz, 1H), 1.65 (s, 3H), 1.53 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.4, 225.7, 151.3, 147.0, 142.1, 142.0, 136.2, 136.1, 134.5, 108.8, 106.1, 105.7, 105.5, 101.3, 76.5, 69.0, 57.3, 49.3, 31.5, 9.7. HRMS (ESI) Calcd for $C_{20}H_{24}BMoN_6O_4$ [M + H]$^+$: 521.1001. Found: 521.1023. HPLC: Daicel Chiralpak OJ-RH, gradient solvent system was used (% MeCN in H_2O w/0.1% TFA) = 0-20 mins, 20% to 80%, 1.0 ml/min, 254 nm, t_r = 21.86 min. Enantiomer: t_r = 19.84 min.

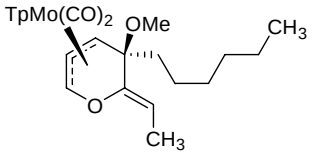
[177] Note: scale up to 1.5 g of starting material **78** and all other reagents in the same proportions gave slightly decreased yields of product 1.07 g (74%) using an identical procedure.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-5-ethyl-6-(*Z*)-ethylidene-5-methoxy-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91b

Following the *general procedure A*, starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved CH_2Cl_2 (2.5 mL), and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and ethylmagnesuim bromide (1.0 M in THF, 225 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 33.0 mg (83%) of pure product **91b** as a yellow solid.

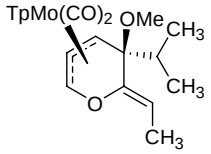
91b: TLC: R_f = 0.49 (25% EtOAc in hexanes). IR (cm^{-1}): 2931 (w), 2490 (w), 1945 (s), 1864 (s), 1406 (m), 1301 (m), 1216 (m), 1123 (m), 1048 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.53 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 2H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.01 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.27 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.5 Hz, 1H), 4.85 (q, *J* = 7.0 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.2 Hz, 1H), 3.52 (s, 3H), 3.42 (dd, *J* = 7.9, 4.4 Hz, 1H), 2.21 (app sextet, *J* = 7.3 Hz, 1H), 1.58 (app sextet, *J* = 7.3 Hz, 1H), 1.55 (d, *J* = 7.0 Hz, 3H), 0.79 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.4, 225.9, 147.6, 147.1, 142.0 (2), 136.2, 136.1, 134.5, 108.5, 106.1, 105.7, 105.5, 103.7, 79.0, 69.1, 57.6, 48.7, 34.3, 9.7, 8.7. HRMS (ESI) Calcd for $C_{21}H_{26}BMoN_6O_4$ $[M + H]^+$: 535.1157. Found: 535.1172.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-hexyl-5-methoxy-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91c

Following the *general procedure A,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and hexylmagnesium bromide (2.0 M in Et_2O, 110 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 25.8 mg (59%) of pure product **91c** as a yellow oil.

91c: TLC: R_f = 0.51 (25% EtOAc in hexanes). IR (cm^{-1}): 2932 (w), 1955 (vs), 1868 (vs), 1407 (w), 1219 (w), 1125 (w), 1050 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.53 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 2H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.01 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.26 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 4.85 (q, *J* = 7.0 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.5 Hz, 1H), 3.52 (s, 3H), 2.42 (dd, *J* = 7.9, 4.4 Hz, 1H), 2.17 (m, 1H), 1.60 (m, 1H), 1.54 (d, *J* = 7.0, 3H), 1.28 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.4, 225.9, 148.2, 147.0, 142.0 (2), 136.2, 136.1, 134.5, 108.6, 106.1, 105.7, 105.5, 103.4, 78.7, 69.2, 57.6, 48.8, 42.0, 32.1, 29.5, 24.1, 22.9, 14.3, 9.8. HRMS (ESI) Calcd for $C_{25}H_{34}BMoN_6O_4$ $[M + H]^+$: 591.1783. Found: 591.1804.

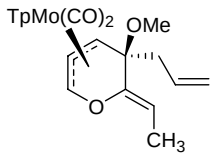


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-isopropyl-5-methoxy-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91d

Following the *general procedure A,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and isopropylmagnesium chloride (2.0 M in Et_2O, 110 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 37.6 mg (92%) of pure product **91d** as a yellow solid.

91d: TLC: R_f = 0.48 (25% EtOAc in hexanes). IR (cm^{-1}): 2933 (w), 1951 (vs), 1863 (vs), 1406 (m), 1217 (m), 1123 (m), 1049 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.55 (d, *J* = 1.9 Hz,

1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 2H), 7.48 (dd, *J* = 2.2, 0.6 Hz, 1H), 6.99 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.27 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 4.83 (q, *J* = 6.7 Hz, 1H), 4.52 (dd, *J* = 7.9, 2.2 Hz, 1H), 3.71 (dd, *J* = 7.9, 4.4 Hz, 1H), 3.56 (s, 3H), 2.26 (septet, *J* = 6.7 Hz, 1H), 1.56 (d, *J* = 7.0 Hz, 3H), 1.14 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 228.6, 226.3, 147.1, 146.7, 142.4, 141.7, 136.2, 136.1, 134.5, 106.3, 106.2, 105.7, 105.5, 105.1, 81.1, 68.9, 60.7, 49.2, 36.5, 17.9, 17.6, 9.7. HRMS (ESI) Calcd for $C_{22}H_{28}BMoN_6O_4$ $[M + H]^+$: 549.1313. Found: 549.1330.

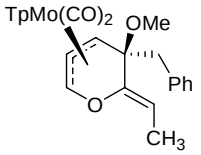


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-5-allyl-6-(*Z*)-ethylidene-5-methoxy-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91e

Following the *general procedure A*, starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and allylmagnesium chloride (1.5 M in THF, 150 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 28.7 mg (71%) of pure product **91e** as a yellow solid.

91e: TLC: R_f = 0.43 (25% EtOAc in hexanes). IR (cm^{-1}): 1944 (vs), 1851 (vs), 1407 (w), 1216 (w), 1045 (w). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.52 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 2H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.03 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.27 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 5.74 (m, 1H), 5.05 (m, 2H), 4.89 (q, *J* = 7.0 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.5 Hz, 1H), 3.57 (s, 3H), 3.44 (dd, *J* = 7.9, 4.4 Hz, 1H), 2.94 (dd, *J* = 14.6, 7.6 Hz, 1H), 2.46 (dd, *J* = 14.9, 6.4 Hz, 1H), 1.54 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.2, 225.8, 148.0, 147.1, 142.1, 142.0, 136.3,

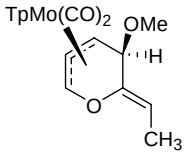
136.1, 134.6, 134.4, 116.9, 108.5, 106.2, 105.8, 105.5, 103.7, 78.7, 68.4, 57.6, 49.0, 46.6, 9.7. HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_6O_4$ $[M + H]^+$: 547.1157. Found: 547.1180.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-5-benzyl-6-(*Z*)-ethylidene-5-methoxy-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91f

Following the *general procedure, A* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and benzylmagnesium chloride (1.0 M in Et_2O, 225 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 42.1 mg (95%) of pure product **91f** as a yellow solid.

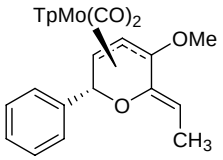
91f: TLC: R_f = 0.44 (25 % EtOAc in hexanes). IR (cm^{-1}): 2916 (w), 2480 (w), 1948 (vs), 1861 (vs), 1406 (m), 1302 (m), 1218 (m), 1121 (m), 1049 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.53 (d, *J* = 1.9 Hz, 1H), 7.92 (d, *J* = 1.9 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H) 7.59 (d, *J* = 2.2 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.20 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.00 (dd, *J* = 4.4, 2.5 Hz, 1H), 6.26 (t, *J* = 2.2 Hz, 1H), 6.22 (t, *J* = 1.9 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 4.75 (dd, *J* = 7.9, 2.2 Hz, 1H), 4.42 (q, *J* = 7.0, 1H), 3.77 (s, 3H), 3.49 (dd, *J* = 7.9, 4.4 Hz, 1H), 3.47 (d, *J* = 13.3 Hz, 1H), 2.95 (d, *J* = 13.3 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.5, 225.9, 147.2, 147.1, 142.1, 141.9, 137.5, 136.3, 136.1, 134.6, 130.9 (2), 127.4 (2), 126.2, 108.3, 106.2, 105.8, 105.5, 104.5, 80.2, 68.7, 58.1, 49.7, 48.5, 9.5. HRMS (ESI) Calcd for $C_{26}H_{28}BMoN_6O_4$ $[M + H]^+$: 597.1314. Found: 597.1314.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methoxy-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91g

Following the *general procedure A,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and sodium cyanoborohydride (1.0 M in THF, 225 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 29.5 mg (78%) of pure product **91g** as a yellow solid.

91g: TLC: R_f = 0.44 (25% EtOAc in hexanes). IR (cm^{-1}): 2925 (w), 2482 (w), 2359 (w), 1949 (vs), 1860 (vs), 1503 (w), 1406 (m), 1303 (m), 1217 (m), 1118 (m), 1049 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.51 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.74 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.55 (d, *J* = 2.5 Hz, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.03 (dd, *J* = 4.4, 2.5 Hz, 1H), 6.27 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 1.9 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H), 4.92 (dq, *J* = 7.0, 1.9 Hz, 1H), 4.76 (d, *J* = 2.2 Hz, 1H), 4.71 (dt, *J* = 7.3, 2.5, 2.5 Hz, 1H), 3.66 (s, 3H), 3.43 (dd, *J* = 7.6, 4.4 Hz, 1H), 1.54 (dd, *J* = 7.0, 1.9 Hz, 3H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 226.7, 225.7, 147.0, 146.4, 142.2, 142.1, 136.2, 136.1, 134.6, 108.7, 106.7, 105.8, 105.5, 102.8, 77.9, 66.8, 58.2, 57.9, 9.6. HRMS (ESI) Calcd for $C_{19}H_{22}BMoN_6O_4$ $[M + H]^+$: 507.0844. Found: 507.0848.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methoxy-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 95a

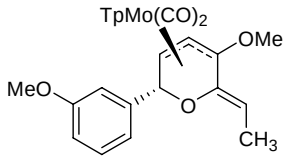
(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-

methoxy-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, (+)-**95a**

Following the *general procedure A,* starting material **78** (500 mg, 0.936 mmol, 1.0 equiv) was dissolved in 30 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 198 μL, 1.22 mmol, 1.3 equiv) and phenylmagnesium bromide (3.0 M in Et_2O, 940 μL, 2.81 mmol, 3.0 equiv). Purification by gravity chromatography gave 455 mg (84%) of pure product **95a** as an orange solid.

The exact same procedure was used to convert (+)-**78** (of 97.5-98.0% ee) to (+)-**95a** in what was determined after conversion to (-)-**99** to be of 98% ee.

(+)-**95a:** TLC: R_f = 0.39 (25% EtOAc in hexanes). $[\alpha]_D^{20}$ +590 (98% ee, *c* 0.050, CH_2Cl_2). IR (cm^{-1}): 2481 (w), 1921 (s), 1837 (s), 1406 (m), 1305 (m), 1234 (m), 1119 (m), 1049 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.35 (d, *J* = 1.6 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.51 (app t, *J* = 2.0 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 6.22 (t, *J* = 2.0 Hz, 1H), 6.19 (t, *J* = 2.0 Hz, 1H), 6.18 (t, *J* = 2.3 Hz, 1H), 5.50 (q, *J* = 7.4 Hz, 1H), 5.23 (s, 1H), 4.25 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.70 (d, *J* = 8.2 Hz, 1H), 2.93 (s, 3H), 1.80 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.0, 227.5, 146.9, 145.7, 144.6, 144.4, 139.5, 136.5, 135.8, 134.9, 131.8, 128.7 (2), 127.5, 125.7 (2), 105.8, 105.6 (2), 102.2, 75.9, 57.5, 56.9, 54.9, 10.3. HRMS (ESI) Calcd for $C_{25}H_{26}BMoN_6O_4$ $[M + H]^+$: 583.1157. Found: 583.1162.

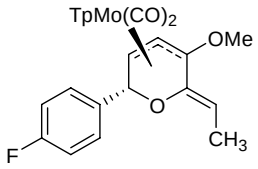


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methoxy-6-(3-methoxyphenyl)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 95b

Following the *general procedure A,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 3.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3

equiv) and 3-methoxyphenylmagnesium bromide (1.0 M in THF, 225 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 25.6 mg (56%) of pure product **95b** as an orange solid.

95b: TLC: R_f = 0.39 (25% EtOAc in hexanes). IR (cm^{-1}): 2482 (w), 1920 (s), 1835 (s), 1406 (m), 1305 (m), 1231 (m), 1119 (m), 1048 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.35, (d, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 2.3 Hz, 1H), 7.51 (s, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.99 (s, 1H), 6.83 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 6.18 (t, *J* = 2.0 Hz, 2H), 5.50 (q, *J* = 7.4 Hz, 1H), 5.19 (s, 1H), 4.24 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.83 (s, 3H), 3.69 (d, *J* = 8.2 Hz, 1H), 2.93 (s, 3H), 1.81 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.0, 227.5, 159.8, 147.4, 146.9, 144.58, 144.50, 139.5, 136.5, 135.9, 134.9, 131.8, 129.7, 118.1, 112.6, 111.5, 105.8, 105.7, 105.6, 102.4, 75.7, 57.3, 57.0, 55.4, 55.0, 10.3. HRMS (ESI) Calcd for $C_{26}H_{28}BMoN_6O_5$ $[M + H]^+$: 613.1263. Found: 613.1265.

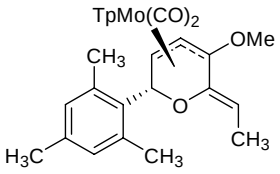


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methoxy-6-(4-fluorophenyl)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 95c

Following the *general procedure A,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 3.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and 4-fluorophenylmagnesium bromide (1.0 M in THF, 225 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 25.0 mg (56%) of pure product **95c** as an orange solid.

95c: TLC: R_f = 0.42 (25% EtOAc in hexanes). IR (cm^{-1}): 2486 (w), 1922 (s), 1838 (s), 1506 (m), 1407 (m), 1305 (m), 1221 (m), 1049 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.35 (d, *J* = 2.2 Hz, 1H), 7.73 (d, *J* = 2.2 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.51 (d, *J* =

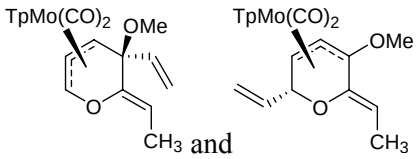
2.2 Hz, 2H), 7.42 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.22 (t, *J* = 2.2 Hz, 1H), 6.28 (s, 2H), 5.50 (q, *J* = 7.0 Hz, 1H), 5.19 (s, 1H), 4.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 3.70 (d, *J* = 8.3 Hz, 1H), 2.94 (s, 3H), 1.77 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.0, 227.4, 163.4, 161.0, 146.9, 144.4, 144.2, 141.3, 139.4, 136.5, 135.9, 134.9, 131.8, 127.58, 127.50, 115.6, 115.3, 105.9, 105.6 (2), 102.7, 75.3, 57.1, 56.9, 55.0, 10.3. HRMS (ESI) Calcd for $C_{25}H_{25}BFMoN_6O_4$ $[M + H]^+$: 601.1063. Found: 601.1072.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methoxy-6-(2,4,6-trimethyl-phenyl)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 95d

Following the *general procedure A,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and mesitylmagnesium bromide (1.0 M in Et_2O, 225 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 23.4 mg (50 %) of pure product **95d**.

95d: TLC: R_f = 0.58 (25 % EtOAc in hexanes). IR (cm^{-1}): 2922 (w), 2484 (w), 1925 (s), 1839 (s), 1405 (m), 1306 (m), 1217 (m), 1119 (m), 1049 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.33 (d, *J* = 1.9 Hz, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 2.2 Hz, 1H), 7.41 (d, *J* = 1.9 Hz 1H), 6.89 (s, 2H), 6.21 (t, *J* = 1.9 Hz, 2H), 6.15 (t, *J* = 2.2 Hz, 1H), 5.81 (s, 1H), 5.29 (q, *J* = 7.3 Hz, 1H), 4.21 (d, *J* = 8.6 Hz, 1H), 3.81 (d, *J* = 8.3 Hz, 1H), 2.83 (s, 3H), 2.46 (s, 6H), 2.30 (s, 3H), 1.77 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 234.9, 226.5, 146.7, 146.3, 145.0, 139.6, 138.0, 137.1, 136.5, 136.3 (2), 135.8, 134.9, 130.8 (2), 127.1, 105.8, 105.7, 105.6, 98.2, 76.6, 61.2, 55.5, 54.4, 21.2 (2), 20.9, 10.1. HRMS (ESI) Calcd for $C_{28}H_{32}BMoN_6O_4$ $[M + H]^+$: 625.1627. Found: 625.1630.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methoxy-5-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91h

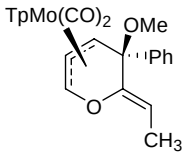
and

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methoxy-6-vinyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 95e

Following the *general procedure A,* starting material **78** (80 mg, 0.150 mmol, 1.0 equiv) was dissolved in 5.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 32 μL, 0.195 mmol, 1.3 equiv) and vinylmagnesium chloride (1.6 M in THF, 280 μL, 0.449 mmol, 3.0 equiv). Purification by gravity chromatography gave 35.8 mg (45%) of an inseparable mixture of the two regioisomers **91h** and **95e** in a 1:1.4 ratio as an orange solid. All spectroscopic data was collected using the mixture of regioisomers, although the ratio of products permitted assignment of individual signals in the ^{1}H NMR.

91h and 95e: TLC: R_f = 0.39 (17% EtOAc in hexanes). IR (cm^{-1}): 1955 (w), 1918 (s), 1866 (m), 1832 (s), 1502 (w), 1406 (m), 1303 (m), 1217 (m), 1120 (m), 1048 (s). ^{1}H NMR [400 MHz, $CDCl_3$], **91h**: δ 8.54 (d, *J* = 1.6 Hz, 1H), 7.85 (d, *J* = 1.6 Hz, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 2H), 7.49 (d, *J* = 2.7 Hz, 1H), 7.05 (dd, *J* = 4.3, 2.3 Hz, 1H), 6.28 (t, *J* = 2.0 Hz, 1H), 6.20 (m, 2H), 5.93 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.68 (dd, *J* = 17.2, 0.8 Hz, 1H), 5.33 (d, *J* = 10.2 Hz, 1H), 5.04 (q, *J* = 7.0 Hz, 1H), 4.58 (dd, *J* = 7.8, 2.3 Hz, 1H), 3.68 (dd, *J* = 7.8, 4.3 Hz, 1H), 3.57 (s, 3H), 1.54 (d, *J* = 7.0 Hz, 3H). [**95e**]: δ 8.32 (d, *J* = 2.0 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.63 (d, *J* = 2.3 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 6.20 (m, 2H), 6.17 (t, *J* = 2.3 Hz, 1H), 6.00 (ddd, *J* = 16.8, 10.6, 5.9 Hz, 1H), 5.49 (q, *J* = 7.4 Hz, 1H), 5.30 (dt, *J* = 16.8, 1.2, 1.2 Hz, 1H), 5.14 (dt, *J* = 10.2, 1.2, 1.2 Hz, 1H), 4.59 (dd, *J*

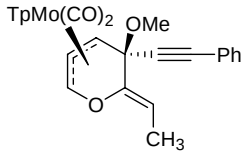
= 7.4, 2.0 Hz, 1H), 4.03 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.67 (d, *J* = 8.6 Hz, 1H), 2.96 (s, 3H), 1.79 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$] mixture of regioisomers: δ 231.5, 227.7, 227.6, 225.9, 148.7, 147.1, 146.8, 145.1, 144.3, 143.8, 142.2, 141.9, 140.8, 139.4, 136.4, 136.3, 136.2, 135.9, 134.8, 134.6, 132.8, 116.2, 114.9, 108.0, 106.2, 105.8, 105.64, 105.60, 103.2, 103.1, 79.8, 74.9, 65.4, 59.0, 56.6, 55.9, 55.1, 50.3, 10.3, 9.9. HRMS (ESI) Calcd for $C_{21}H_{23}BMoN_6O_4$ [M + H]$^+$: 533.1001. Found: 533.1002.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methoxy-5-phenyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91i

Following the *general procedure A,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 3.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and phenyllithium (1.8 M in Bu_2O, 125 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 23.2 mg (53%) of pure product **91i** as a yellow solid.

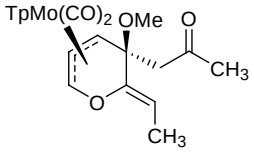
91i: TLC: R_f = 0.43 (25% EtOAc in hexanes). IR (cm^{-1}): 2487 (w), 1944 (s), 1851 (s), 1406 (w), 1300 (w), 1214 (w), 1121 (w), 1047 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.59 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 2H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.59 (app t, *J* = 1.9 Hz, 2H), 7.51 (d, *J* = 2.2 Hz, 1H), 7.37 (t, *J* = 7.3, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.09 (dd, *J* = 4.4, 2.5 Hz, 1H), 6.30 (t, *J* = 2.2 Hz, 1H), 6.22 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 5.27 (q, *J* = 7.0 Hz, 1H), 4.81 (dd, *J* = 7.6, 2.2 Hz, 1H), 3.91 (dd, *J* = 7.6, 4.1 Hz, 1H), 3.38 (s, 3H), 1.53 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.8, 226.5, 150.6, 147.1, 145.1, 142.5, 141.8, 136.3, 136.1, 134.6, 128.2 (2), 127.9 (2), 127.5, 108.2, 106.2, 105.9, 105.6, 103.0, 80.8, 67.4, 59.9, 50.7, 10.0. HRMS (ESI) Calcd for $C_{25}H_{26}BMoN_6O_4$ [M + H]$^+$: 583.1157. Found: 583.1158.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methoxy-5-phenylethynyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91j

Following the *general procedure A,* starting material **78** (40 mg, 0.75 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and lithiumphenylacetylide (1.0 M in THF, 225 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 13.3 mg (29%) of pure product **91j**.

91j: TLC: R_f = 0.41 (25% EtOAc in hexanes). IR (cm^{-1}): 2923 (w), 2480 (w), 1858 (s), 1871 (s), 1406 (m), 1303 (m), 1219 (m), 1122 (m), 1050 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.52 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 2H), 7.49 (m, 3H), 7.31 (t, *J* = 3.2 Hz, 3H), 7.16 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.28 (t, *J* = 2.2 Hz, 1H), 6.21 (m, 2H), 5.19 (q, *J* = 7.0 Hz, 1H), 4.92 (dd, *J* = 7.9, 2.5 Hz, 1H), 3.80 (s, 3H), 3.56 (dd, *J* = 7.6, 4.1 Hz, 1H), 1.60 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.0, 225.5, 147.0 (2), 142.2, 142.1, 136.3, 136.2, 134.6, 132.0 (2), 128.5 (2), 128.4, 122.9, 109.2, 106.2, 105.8, 105.6, 104.0, 91.6, 85.1, 73.6, 68.1, 57.6, 51.6, 10.1. HRMS (ESI) Calcd for $C_{27}H_{26}BMoN_6O_4$ $[M + H]^+$: 607.1157. Found: 607.1160.

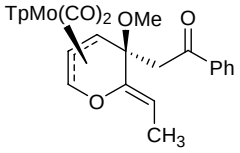


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methoxy-5-(2-oxo-propyl)-3,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91k

Following the *general procedure B,* compound **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 1.5 mL of dry CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol,

1.3 equiv). In a separate flask, the enolate was prepared in THF (1 mL) with LiHMDS (1.0 M in THF) (240 μL, 0.240 mmol, 3.2 equiv) and acetone (16.5 μL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography on silica gel neutralized with 5% Et_3N afforded 25.4 mg (61%) of pure product **91k** as a yellow solid.

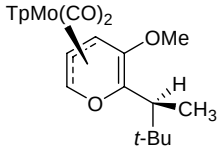
91k: TLC: R_f = 0.19 (25% EtOAc in hexanes). IR (cm^{-1}): 2921 (w), 2483 (w), 1952 (s), 1864 (s), 1702 (m), 1406 (m), 1302 (m), 1217 (m), 1121 (m), 1049 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.52 (d, *J* = 2.0 Hz, 1H), 7.84 (d, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 2H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.05 (dd, *J* = 4.3, 2.3 Hz, 1H), 6.28 (t, *J* = 2.3 Hz, 1H), 6.21 (t, *J* = 2.3 Hz, 1H), 6.20 (t, *J* = 2.0 Hz, 1H), 4.98 (q, *J* = 7.0 Hz, 1H), 4.69 (dd, *J* = 7.8, 2.3 Hz, 1H), 3.69 (s, 3H), 3.45 (dd, *J* = 7.8, 4.3 Hz, 1H), 3.23 (d, *J* = 12.5 Hz, 1H), 2.90 (d, *J* = 12.1 Hz, 1H), 2.10 (s, 3H), 1.54 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [400 MHz, $CDCl_3$]: δ 226.8, 225.6, 206.2, 147.7, 147.0, 142.2, 141.9, 136.4, 136.2, 134.6, 108.5, 106.2, 105.8, 105.6, 104.6, 78.2, 68.3, 57.2, 55.8, 49.9, 31.9, 9.8. HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_6O_5$ $[M + H]^+$: 563.1106. Found: 563.1115.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methoxy-5-(2-oxo-2-phenyl-ethyl)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 91l

Following the *general procedure B,* compound **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 1 mL of dry CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv). In a separate flask, the enolate was prepared in THF (1 mL) with LiHMDS (1.0 M in THF) (380 μL, 0.380 mmol, 5.1 equiv) and acetophenone (44 μL, 0.374 mmol, 5.0 equiv). Purified by gravity chromatography on silica gel neutralized with 5% Et_3N afforded 32.1 mg (69%) of pure product **91l** as a yellow solid.

91l: TLC: R_f = 0.28 (25% EtOAc in hexanes). IR (cm^{-1}): 1955 (s), 1868 (s), 1670 (w), 1050 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.50 (d, *J* = 1.6 Hz, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.87 (s, 1H), 7.85 (s, 1H), 7.72 (d, *J* = 1.2 Hz, 1H), 7.58 (s, 2H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.10 (dd, *J* = 3.9, 2.3 Hz, 1H), 6.27 (s, 1H), 6.22 (app d, *J* = 2.0 Hz, 2H), 4.83 (dd, *J* = 7.8, 2.3 Hz, 1H), 4.66 (q, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 3.67 (d, *J* = 12.5 Hz, 1H), 3.53 (dd, *J* = 7.8, 4.3 Hz, 1H), 3.47 (d, *J* = 12.5 Hz, 1H), 1.09 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 226.6, 225.4, 197.6, 147.0, 146.9, 142.2, 141.8, 138.5, 136.3, 136.2, 134.6, 132.6, 128.6 (2), 128.2 (2), 108.0, 106.2, 105.8, 105.6, 105.3, 78.6, 68.7, 57.4, 50.2, 49.8, 9.3. HRMS (ESI) Calcd for $C_{27}H_{27}BMoN_6O_5$ $[M]^+$: 624.1185. Found: 624.1182.

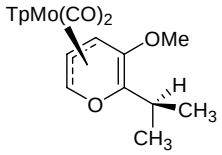


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-η-(2,3,4)-5-methoxy-6-((*S*)-1,2,2-trimethyl-propyl)-2*H*-pyran-2-yl]molybdenum, 96a

Following the *general procedure A,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv) and *tert*-butylmagnesium chloride (2.0 M in Et_2O, 0.124 mL, 0.225 mmol, 3.0 equiv). Purification by gravity chromatography gave 34.1 mg (81%) of pure product **96a** as a bright yellow solid.

96a: TLC: R_f = 0.51 (25% EtOAc in hexanes). IR (cm^{-1}): 2958 (w), 1937 (s), 1855 (s), 1407 (w), 1303 (w), 1221 (w), 1126 (w), 1050 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.23 (d, *J* = 2.0 Hz, 1H), 7.89 (app t, *J* = 2.3 Hz, 2H), 7.60 (app t, *J* = 2.0 Hz, 2H), 7.57 (dd, *J* = 3.9, 2.0 Hz, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 6.23 (t, *J* = 2.0 Hz, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 6.19 (t, *J* = 2.3 Hz, 1H), 4.91 (dd, *J* = 6.7, 2.3 Hz, 1H), 3.84 (s, 3H), 2.56 (q, *J* = 7.4 Hz, 1H), 2.46 (dd, *J* = 6.7, 4.3 Hz, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.92 (s, 9H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 228.3, 224.6, 146.0,

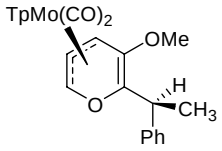
141.9, 141.6, 140.2, 138.6, 136.1, 134.6, 107.8, 105.7, 105.6, 105.5, 62.1, 58.5, 46.6, 39.7, 33.6, 28.6 (3), 13.6. HRMS (ESI) Calcd for $C_{23}H_{30}BMoN_6O_4$ $[M + H]^+$: 563.1470. Found: 563.1471.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-η-(2,3,4)-6-isopropyl-5-methoxy-2*H*-pyran-2-yl]molybdenum, 96b

Following the *general procedure B,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 1.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv). The cuprate was prepared according to the *general procedure B* using copper bromide-dimethylsulfide complex (46.2 mg, 0.225 mmol, 3.0 equiv), and methylmagnesium chloride (3.0 M in THF, 75 μL, 0.225 mmol, 3.0 equiv). The solution of diene was then cannulated into the stirring cuprate (using an additional 0.5 mL CH_2Cl_2 for quantitation). Purification by gravity chromatography gave 18.7 mg (48%) of pure product **96b** as a yellow/orange solid.

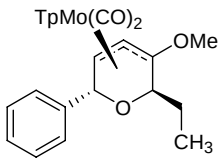
96b: TLC: R_f = 0.44 (25% EtOAc in hexanes). IR (cm^{-1}): 2964 (w), 2928 (w), 2481 (w), 1932 (s), 1850 (s), 1406 (m), 1302 (m), 1219 (m), 1123 (m), 1048 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.23 (d, *J* = 2.0 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.60 (s, 2H), 7.56 (dd, *J* = 4.3, 2.3 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 6.24 (t, *J* = 2.0 Hz, 1H), 6.21 (t, *J* = 2.0 Hz, 1H), 6.19 (t, *J* = 2.0 Hz, 1H), 4.86 (dd, *J* = 7.0, 2.3 Hz, 1H), 3.79 (s, 3H), 2.84 (septet, *J* = 7.0 Hz, 1H), 2.46 (dd, *J* = 6.7, 4.3 Hz, 1H), 1.05 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 228.3, 224.0, 146.1, 142.0, 141.5, 140.3, 139.1, 136.2, 136.1, 134.6, 108.1, 105.8, 105.7, 105.5, 63.0, 59.9, 46.3, 25.6, 20.9, 20.3. HRMS (ESI) Calcd for $C_{20}H_{24}BMoN_6O_4$ $[M + H]^+$: 521.1001. Found: 521.1001.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-η-(2,3,4)-5-methoxy-6-[(*S*)-(1-phenyl-ethyl)]-2*H*-pyran-2-yl]molybdenum, 96c

Following the *general procedure B,* starting material **78** (40 mg, 0.075 mmol, 1.0 equiv) was dissolved in 2.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.097 mmol, 1.3 equiv). The cuprate was prepared according to the *general procedure B* using copper bromide-dimethylsulfide complex (46.2 mg, 0.225 mmol, 3.0 equiv), and phenylmagnesium chloride (1.8 M in THF, 225 μL, 0.125 mmol, 3.0 equiv). The solution of diene was then cannulated into the stirring cuprate (using an additional 0.5 mL CH_2Cl_2 for quantitation). Purification by gravity chromatography gave 28.8 mg (66%) of pure product **96c** as a yellow solid.

96c: TLC: R_f = 0.40 (25% EtOAc in hexanes). IR (cm^{-1}): 2482 (m), 1934 (s), 1852 (s), 1406 (m), 1302 (m), 1218 (m), 1126 (m), 1049 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.26 (d, *J* = 2.0 Hz, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 2H), 7.56 (dd, *J* = 4.3, 2.3 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.35-7.27 (m, 4H), 7.21 (m, 1H), 6.23 (t, *J* = 2.0 Hz, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 6.20 (t, *J* = 2.3 Hz, 1H), 4.86 (dd, *J* = 6.7, 2.3 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 2.45 (dd, *J* = 6.7, 4.7 Hz, 1H), 1.37 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 228.3, 224.0, 146.1, 144.3, 142.0, 141.5, 140.1, 137.8, 136.25, 135.20, 134.6, 128.4 (2), 127.8 (2), 126.3, 108.0, 105.8, 105.7, 105.5, 62.3, 59.7, 46.5, 36.0, 19.1. HRMS (ESI) Calcd for $C_{25}H_{26}BMoN_6O_4$ $[M + H]^+$: 583.1157. Found: 583.1159.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-2-ethyl-3-methoxy-6-

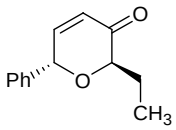
phenyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 98

(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-2-ethyl-3-methoxy-6-phenyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, (+)-**98**

Starting material **95a** (455 mg, 0.784 mmol, 1.0 equiv) was dissolved in 25 mL of dichloromethane and cooled to -40 ^{o}C. Tetrafluoroboric acid (54 wt% in Et_2O, 166 μL, 1.02 mmol, 1.3 equiv) was added dropwise and the reaction was stirred for 3 minutes. Then sodium cyanoborohydride was added dropwise (1.0 M in THF, 1.57 mL, 1.57 mmol, 2.0 equiv) and the reaction was stirred for an additional 3 minutes after which, TLC revealed the formation of a new product. The reaction was quenched with 15 mL of water and the organic layer was washed with water (2 x 50 mL), dried over $MgSO_4$, filtered and concentrated under low pressure. The crude material was purified by flash chromatography on silica gel neutralized with 5% Et_3N (eluting with 10% EtOAc in hexanes) to provide 396 mg of pure product **98** (87%) as an orange solid.

The exact same procedure was used to convert (+)-**95a** of 98% ee to (+)-**98** which was converted to (-)-**99** of 98% ee.

(+)-**98** TLC: R_f = 0.45 (25% EtOAc in hexanes). $[\alpha]_D^{20}$ +665 (98% ee, *c* 0.09, CH_2Cl_2). IR (cm^{-1}): 2480 (w), 1917 (s), 1825 (s), 1406 (m), 1304 (m), 1220 (m), 1117 (m), 1047 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.39 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 2.3 Hz, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 1H), 6.25 (t, *J* = 2.0 Hz, 1H), 6.21 (app d, *J* = 1.2 Hz, 2H), 5.09 (s, 1H), 4.35 (dd, *J* = 7.8, 0.8 Hz, 1H), 3.95 (d, *J* = 8.2 Hz, 1H), 3.72 (dd, *J* = 8.2, 4.3 Hz, 1H), 2.80 (s, 3H), 2.20 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.3, 229.6, 146.1, 145.2, 142.4, 141.5, 139.3, 136.3, 135.7, 134.7, 128.4 (2), 128.3 (2), 127.8, 105.7 (3), 74.1, 71.5, 59.8, 55.3, 54.3, 22.2, 11.0. HRMS (ESI) Calcd for $C_{25}H_{28}BMoN_6O_4$ $[M + H]^+$: 585.1314. Found: 585.1320.



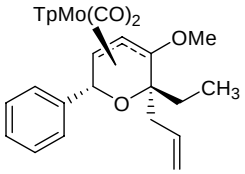
(±)-(2*R*,6*S*)-2-Ethyl-6-phenyl-6*H*-pyran-3-one, 99

(-)-(2*R*,6*S*)-2-Ethyl-6-phenyl-6*H*-pyran-3-one, (-)**-99**

Starting material (±)**-98** (58.2 mg, 0.100 mmol, 1.0 equiv) was dissolved in 2.5 mL THF/H_2O (3:1) and Et_3N (21 μL, 0.150 mmol, 1.5 equiv) at 0 ^oC. A solution of ceric ammonium nitrate (439 mg, 0.800 mmol, 8.0 equiv) in 2.5 mL of water was added dropwise over 5 minutes. When addition was complete, the dark orange/red solution had changed to light yellow. The reaction was allowed to stir at room temperature for 10 minutes, and then partitioned between 10 mL each of CH_2Cl_2 and water. The organic layer was collected and washed with brine, dried over $MgSO_4$, concentrated and chromatographed on silica gel (25% EtOAc in hexanes) to afford the product **99** as a clear oil (17.3 mg, 86%).

The exact same procedure was used to convert (+)**-98** of 98 %ee to (-)**-99**, which was determined to be 98% ee by HPLC.

(-)**-99:** TLC: R_f = 0.54 (25% EtOAc in hexanes, $KMnO_4$ stain). $[\alpha]_D^{20}$ -186.2 (98% ee, *c* 0.305, CH_2Cl_2). IR (cm^{-1}): 2967 (w), 2932 (w), 1685 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 7.39 (m, 5H), 7.13 (dd, *J* = 10.6, 3.1 Hz, 1H), 6.21 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.48 (t, *J* = 2.7 Hz, 1H), 4.05 (dd, *J* = 8.2, 5.5 Hz, 1H), 1.83 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 196.8, 149.4, 137.5, 129.0, 128.9 (2), 128.0 (2), 126.3, 78.8, 72.3, 22.8, 10.1. HRMS (ESI) Calcd for $C_{13}H_{15}O_2$ $[M + H]^+$: 203.1067. Found: 203.1065. HPLC: Daicel Chiralpak AS-RH, gradient solvent system was used (% MeCN in H_2O w/0.1% TFA) = 0-20 mins, 20% to 80%, 1.0 ml/min, 254 nm, t_r = 16.77 min. Enantiomer: t_r = 14.59 min.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*S*,6*R*)-η-(3,4,5)-2-allyl-2-ethyl-3-methoxy-6-phenyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 100

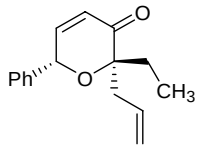
(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*S*,6*R*)-η-(3,4,5)-2-allyl-2-ethyl-3-methoxy-6-phenyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, (+)-**100**

Starting material **95a** (100 mg, 0.172 mmol, 1.0 equiv) was dissolved in 10 mL of dichloromethane and cooled to -40 °C. Tetrafluoroboric acid (54 wt% in Et_2O, 37 μL, 0.224 mmol, 1.3 equiv) was added dropwise and the reaction was stirred for 5 minutes as the temperature was allowed to warm to -30 °C. Then allylmagnesium chloride was added dropwise (1.5 M in THF, 230 μL, 0.345 mmol, 2.0 equiv) and the reaction was stirred for an additional 5 minutes after which, TLC revealed the formation of a new product. The reaction was washed with 25 mL of water, and the organic layer was dried over $MgSO_4$, filtered and concentrated under low pressure. The crude material was purified by flash chromatography on silica gel neutralized with 5% Et_3N (eluting with 10% EtOAc in hexanes) to provide 77 mg of pure product **100** (72%) as an orange solid.

The exact same procedure was used to convert (+)-**95a** of 98% ee to (+)-**100** which was later converted to (-)-**101** of 97.1% ee.

100: TLC: R_f = 0.48 (25% EtOAc in hexanes). $[\alpha]_D^{20}$ +499 (97.1-98% ee, *c* 0.022, CH_2Cl_2). IR (cm^{-1}): 2478 (w), 2360 (w), 1917 (s), 1823 (s), 1506 (w), 1406 (m), 1305 (m), 1220 (m), 1118 (m), 1048 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.30 (d, *J* = 1.6 Hz, 1H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 6.24 (t, *J* = 2.0 Hz, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 6.21 (t, *J* = 2.3 Hz, 1H), 5.55 (m, 1H), 5.13 (s, 1H), 4.73 (dd, *J*

= 10.2, 0.8 Hz, 1H), 4.63 (d, *J* = 19.2 Hz, 1H), 4.62 (d, *J* = 7.4 Hz, 1H), 3.91 (d, *J* = 8.2 Hz, 1H), 2.58 (s, 3H), 2.23 (m, 2H), 2.16 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.03 (dd, *J* = 14.1, 8.2 Hz, 1H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 233.6, 229.3, 151.0, 146.2, 145.6 (2), 139.3, 136.3, 135.6, 135.2, 134.9, 128.5 (2), 128.2 (2), 127.6, 115.5, 105.7 (3), 78.9, 74.1, 61.3, 54.9, 52.9, 47.1, 28.5, 7.7. HRMS (ESI) Calcd for $C_{28}H_{31}BMoN_6O_4$ $[M]^+$: 624.1548. Found: 624.1546.



(±)-(2*S*,6*S*)-2-Allyl-2-ethyl-6-phenyl-6*H*-pyran-3-one, 101

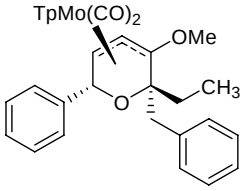
(-)-(2*S*,6*S*)-2-Allyl-2-ethyl-6-phenyl-6*H*-pyran-3-one, (-)-**101**.

Starting material **100** (61.6 mg, 0.099 mmol, 1.0 equiv) was dissolved in 2.5 mL THF/H_2O (3:1) and Et_3N (21 μL, 0.149 mmol, 1.5 equiv) at 0 °C. A solution of ceric ammonium nitrate (434 mg, 0.792 mmol, 8.0 equiv) in 2.5 mL of water was added dropwise over 5 minutes. When addition was complete, the dark orange/red solution had changed to light yellow. The reaction was allowed to stir at room temperature for 10 minutes, and then partitioned between 10 mL each of CH_2Cl_2 and water. The organic layer was washed with brine, dried over $MgSO_4$, concentrated and chromatographed on silica gel (25% EtOAc in hexanes) to afford the product **101** as a clear oil (16.6 mg, 70%).

The exact same procedure was used to convert (+)-**100** of 97.1-98% ee to (-)-**101**, which was determined to be 97.1% ee by HPLC.

(-)-101: TLC: R_f = 0.58 (25% EtOAc in hexanes, $KMnO_4$ stain). $[\alpha]_D^{20}$ -192.2 (98% ee, *c* 0.49, CH_2Cl_2). IR (cm^{-1}): 2975 (w), 2925 (w), 1685 (s), 1064 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 7.40 (d, *J* = 4.4 Hz, 4H), 7.35 (m, 1H), 6.87 (dd, *J* = 10.2, 1.6 Hz, 1H), 6.03 (dd, *J* = 10.2, 2.5 Hz, 1H), 5.90 (m, 1H), 5.43 (t, *J* = 1.9 Hz, 1H), 5.12 (dd, *J* = 17.8, 1.3 Hz, 1H), 5.09 (dd, *J* =

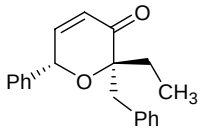
10.1, 1.0 Hz, 1H), 2.66 (ddt, *J* = 15.2, 7.0, 1.0, 1.0 Hz, 1H), 2.49 (dd, *J* = 14.3, 7.0 Hz, 1H), 1.94 (dq, *J* = 14.3, 7.3 Hz, 1H), 1.75 (dq, *J* = 14.3, 7.3 Hz, 1H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 198.3, 150.0, 139.7, 133.5, 129.0 (2), 128.6, 127.2 (2), 124.9, 118.3, 83.8, 71.6, 38.6, 26.2, 7.9. HRMS (ESI) Calcd for $C_{16}H_{19}O_2$ $[M + H]^+$: 243.1380. Found: 243.1375. HPLC: Daicel Chiralpak OJ-RH, gradient solvent system was used (% MeCN in H_2O w/0.1% TFA) = 0-20 mins, 20% to 80%, 1.0 ml/min, 254 nm, t_r = 18.02 min. Enantiomer: t_r = 19.04 min.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*S*,6*R*)-η-(3,4,5)-2-benzyl-2-ethyl-3-methoxy-6-phenyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 102

Due to its instability, this compound was not isolated, but rather was synthesized as an intermediate. See experimental details for compounds **103** and **104** below.

102: TLC: R_f = 0.49 (25% EtOAc in hexanes).

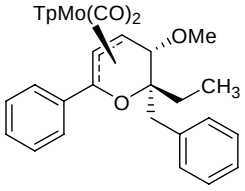


(±)-(2*S*,6*S*)-2-Benzyl-2-ethyl-6-phenyl-6H-pyran-3-one, 103

Starting material **95a** (65 mg, 0.112 mmol, 1.0 equiv) was dissolved in 5 mL of dichloromethane and cooled to -30 °C. Tetrafluoroboric acid (54 wt% in Et_2O, 24 μL, 0.146 mmol, 1.3 equiv) was added dropwise and the reaction was stirred for 3 minutes. The temperature was maintained between -30 and -20 °C. Then benzylmagnesium chloride was added dropwise (1.0 M in Et_2O, 224 μL, 0.224 mmol, 2.0 equiv) and the reaction was stirred for an additional 3 minutes after which, TLC revealed the formation of a new product. The reaction was washed 2 times with a 1:1 mixture of water and saturated aqueous ammonium chloride (2x10

mL), and the organic layer was dried over $MgSO_4$, filtered and concentrated under low pressure. The crude material was passed through a very short plug of silica gel neutralized with 5% Et_3N (eluting with 25% EtOAc in hexanes). The dark red crude product **102** was collected and the solvent was removed. The crude material was then dissolved in 2.5 mL of THF:H_2O (3:1) and Et_3N (24 μL, 0.168 mmol, 1.5 equiv) at 0 °C. A solution of ceric ammonium nitrate (491 mg, 0.897 mmol, 8.0 equiv) in 2.5 mL of water was added dropwise over 5 minutes, and stirred at 0 °C for an additional 5 minutes. When addition was complete, the dark red solution had changed to bright yellow. The reaction was allowed to stir at room temperature for 20 minutes, and then partitioned between 10 mL each of CH_2Cl_2 and water. The organic layer was washed with brine, dried over $MgSO_4$, concentrated and chromatographed on silica gel (25% EtOAc in hexanes) to afford the product **103** as a clear/yellow oil (13.8 mg, 42% over 2 steps).

103: TLC: R_f = 0.48 (17% EtOAc in hexanes). IR (cm^{-1}): 2971 (w), 2931 (w), 1683 (s), 1495 (w), 1454 (w), 1175 (w), 1061 (m), 698 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 7.37-7.30 (m, 3H), 7.28-7.17 (m, 7H), 6.73 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.92 (dd, *J* = 10.6, 2.7 Hz, 1H), 5.42 (t, *J* = 2.0 Hz, 1H), 3.30 (d, *J* = 13.3 Hz, 1H), 2.97 (d, *J* = 14.1 Hz, 1H), 1.97 (app sextet, *J* = 7.8 Hz, 1H), 1.84 (app sextet, *J* = 7.4 Hz, 1H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 198.0, 149.9, 139.7, 137.1, 131.6 (2), 128.8 (2), 128.5, 127.7 (2), 127.3 (2), 126.3, 124.8, 84.7, 71.8, 40.0, 26.9, 8.1. HRMS (ESI) Calcd for $C_{20}H_{21}O_2$ $[M + H]^+$: 293.1536. Found: 293.1533.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*R*,6*S*)-η-(2,3,4)-6-benzyl-6-ethyl-5-methoxy-1-phenyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 104

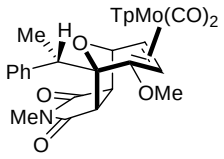
Starting material **95a** (65 mg, 0.112 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (5.0 mL) and cooled to -30 °C. Tetrafluoroboric acid (54 wt% in Et_2O, 24 μL, 0.146 mmol, 1.3 equiv) was

added dropwise and the reaction was stirred for 3 minutes. The temperature was maintained between -30 and -20 ^{o}C. Then benzylmagnesium chloride was added dropwise (1.0 M in Et_2O, 224 μL, 0.224 mmol, 2.0 equiv) and the reaction was stirred for an additional 3 minutes after which, TLC revealed the formation of a new product. The reaction was washed 2 times with a 1:1 mixture of water and saturated aqueous ammonium chloride (2x10 mL), and the organic layer was dried over $MgSO_4$, filtered and concentrated under low pressure. The crude material was passed through a very short plug of silica gel neutralized with 5% Et_3N (eluting with 25% EtOAc in hexanes). The rearrangement was initiated by dissolving the compound in dichloromethane, and then heating the solution on the rotavap at 50 ^{o}C without vacuum until all of the solvent had evaporated. This process was repeated with 10 mL of CH_2Cl_2 ten times, after which the original product had almost completely converted to the rearranged complex. The crude material was chromatographed on silica gel, eluting with 10% EtOAc in hexanes to provide the pure product **104** as a brown oily residue (39.3 mg, 52% over 2 steps).

The product was tentatively assigned as structure **104**. Presumably due to hindered rotation of the phenyl group, the the protons of the aryl group exhibit a very broad resonance in the region from 7.3-7.0 ppm in the ^{1}H NMR. Similarly, in the ^{13}C NMR, two carbons in the aromatic region are accounted for at 131.1 and 125.1 ppm that were much smaller than the other resonances in the spectrum, and do not appear to be from an impurity.

104: TLC: R_f = 0.34 (25% EtOAc in hexanes). IR (cm^{-1}): 2927 (w), 1920 (s), 1832 (s), 1048 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.28 (d, *J* = 1.9 Hz, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 2.2 Hz, 1H), 7.27-7.22 (m, 1H), 7.30-7.01 (br, 3H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.92 (t, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 7.0 Hz, 2H), 6.30 (t, *J* = 2.2 Hz, 1H), 6.15 (t, *J* = 2.2 Hz, 1H), 5.96 (d, *J* = 2.2 Hz, 1H), 5.60 (t, *J* = 2.2 Hz, 1H), 4.68 (d, *J* = 7.0 Hz, 1H), 4.44 (d, *J* = 7.0 Hz, 1H), 4.14 (s, 1H), 3.69 (s, 3H), 3.59 (d, *J* = 14.9 Hz, 1H), 2.89 (d, *J* = 14.9 Hz, 1H), 1.64-1.53 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ

239.2, 228.5, 147.1, 145.6, 139.6, 138.9, 137.1, 136.7, 136.2, 135.9, 134.7, 131.6 (2), 131.1, 128.7, 128.2, 127.4 (2), 125.9, 125.4, 125.1, 105.7, 105.6, 104.6, 84.4, 83.1, 67.8, 56.9, 53.6, 34.3, 29.7, 8.3. HRMS (ESI) Calcd for $C_{32}H_{33}BMoN_6O_4$ $[M]^+$: 674.1705. Found: 674.1704.

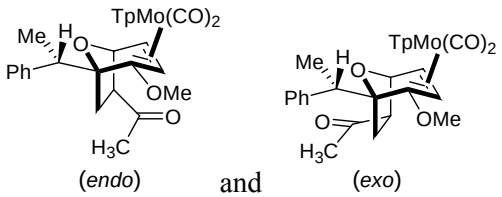


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*S*,2*S*,6*R*,8*R*)-η-(8,9,10)-10-methoxy-4-methyl-1-(1-phenyl-ethyl)-11-oxa-4-aza-tricyclo[5.3.1.0^{2,6}]undec-9-ene-3,5-dion-8-yl]molybdenum, 106

Starting material **96c** (63 mg, 0.109 mmol, 1.0 equiv) was dissolved in 2.0 mL dichloromethane and cooled to 0 °C. To this solution was added *N*-methylmaleimide (54 mg, 0.489 mmol, 4.5 equiv), followed by $EtAlCl_2$ dropwise (1.0 M in hexanes, 120 μL, 0.12 mmol, 1.1 equiv). The reaction was stirred for 10 minutes, and TLC revealed near complete consumption of starting material. The reaction mixture was passed through a short plug of silica gel with 50% EtOAc in hexanes, concentrated on rotavap, and the resulting residue was purified by flash chromatography in 33% EtOAc in hexanes to provide product **106** (40.7 mg, 54%) with >10:1 *exo*:*endo* selectivity as determined by ^{1}H NMR.

106: TLC: R_f = 0.46 (33% EtOAc in hexanes). IR (cm^{-1}): 2935 (w), 1922 (s), 1829 (s), 1701 (s), 1406 (m), 1304 (m), 1214 (m), 1117 (m), 1048 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.28 (d, *J* = 1.6 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 2.3 Hz, 1H), 7.61 (d, *J* = 2.3 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.23 (m, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.22 (t, *J* = 2.0 Hz, 1H), 6.20 (t, *J* = 2.0 Hz, 1H), 4.75 (d, *J* = 6.7 Hz, 1H), 3.92 (q, *J* = 7.0 Hz, 1H), 3.91 (dd, *J* = 7.4, 2.0 Hz, 1H), 3.42-3.32 (m, 2H), 3.31 (d, *J* = 7.0 Hz, 1H), 2.96 (s, 3H), 2.76 (s, 3H), 1.71 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 231.4, 229.3, 176.1, 174.8, 156.9, 146.3, 144.5, 142.4, 139.1, 136.6, 135.8, 135.0,

130.5 (2), 128.3 (2), 127.0, 106.0, 105.96, 105.90, 88.3, 76.8, 58.7, 55.9, 55.1, 52.8, 52.1, 43.0, 24.8, 19.2. HRMS (ESI) Calcd for $C_{30}H_{30}BMoN_7O_6$ $[M]^+$: 693.1399. Found: 693.1404.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*S*,2*S*,5*R*,6*S*)-η-(2,3,4)-6-acetyl-2-methoxy-1-(*S*-1-phenyl-ethyl)-8-oxa-bicyclo[3.2.1]oct-3-en-2-yl]molybdenum, *endo*-**107**

and

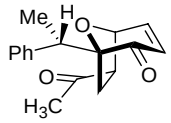
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*S*,2*S*,5*R*,6*R*)-η-(2,3,4)-6-acetyl-2-methoxy-1-(*S*-1-phenyl-ethyl)-8-oxa-bicyclo[3.2.1]oct-3-en-2-yl]molybdenum, *exo*-**107**

To a solution of complex **96c** (20 mg, 0.035 mmol, 1.0 equiv) in CH_2Cl_2 (1.0 mL) at room temperature was added successively methyl vinyl ketone (9.0 μL, 0.103 mmol, 3.0 equiv) and ethylaluminum dichloride (1.0 M in hexanes, 40 μL, 0.038 mmol, 1.1 equiv) and the yellow solution immediately turned a dark red. The reaction mixture was stirred for 3 minutes and then passed through a silica gel plug buffered with 5% Et_3N, eluting with 50% EtOAc in hexanes. The crude mixture was purified by chromatography on silica gel, eluting with 25% EtOAc in hexanes to provide *endo*-**107** (3.7 mg, 17%), followed by *exo*-**107** (13.8 mg, 62%) as orange solids. The stereochemistry of the cycloadducts was determined by coupling constants as previously described.

Endo-**107:** TLC: R_f = 0.45 (33% EtOAc in hexanes). IR (cm^{-1}): 2934 (w), 2479 (w), 1912 (s), 1829 (s), 1709 (m), 1501 (m), 1406 (m), 1304 (m), 1215 (m), 1116 (m), 1046 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.32 (d, *J* = 1.6 Hz, 1H), 7.84 (d, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.28-7.24 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.20 (t, *J* = 2.0 Hz, 1H), 6.15 (t, *J* = 2.3 Hz, 1H),

4.79 (d, *J* = 5.1 Hz, 1H), 3.78 (q, *J* = 7.0 Hz, 1H), 3.47 (d, *J* = 7.0 Hz, 1H), 3.44 (dd, *J* = 11.0, 6.3 Hz, 1H), 3.30 (d, *J* = 7.4 Hz, 1H), 2.82 (s, 3H), 2.41 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.33 (s, 3H), 2.03 (dd, *J* = 12.5, 10.2 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 231.9, 229.8, 205.7, 157.6, 146.1, 144.7, 144.5, 139.3, 136.3, 135.7, 134.8, 129.7 (2), 127.8 (2), 126.1, 105.8, 105.67, 105.63, 86.7, 77.0, 58.3, 57.1, 55.9, 54.5, 42.1, 36.6, 31.2, 18.7. HRMS (ESI) Calcd for $C_{29}H_{31}BMoN_6O_5$ $[M]^+$: 652.1498. Found: 652.1504.

Exo-**107:** TLC: R_f = 0.33 (33% EtOAc in hexanes). IR (cm^{-1}): 2932 (w), 2480 (w), 1914 (s), 1823 (s), 1709 (m), 1502 (m), 1407 (m), 1304 (m), 1221 (m), 1124 (m), 1048 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.34 (d, *J* = 1.6 Hz, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.46 (d, *J* = 1.9 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.237 (*J*, J = 2.2 Hz, 1H), 6.232 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 1.9 Hz, 1H), 4.49 (s, 1H), 3.91 (dd, *J* = 7.6, 2.2 Hz, 1H), 3.84 (d, *J* = 7.3 Hz, 1H), 3.33 (d, *J* = 7.6 Hz, 1H), 3.18 (dd, *J* = 8.9, 4.4 Hz, 1H), 2.80 (s, 3H), 2.44 (dd, *J* = 13.0, 4.4 Hz, 1H), 2.02 (dd, *J* = 13.0, 8.9 Hz, 1H), 1.89 (s, 3H), 1.51 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 230.9, 229.4, 208.1, 156.3, 146.2, 144.5, 144.4, 139.4, 136.4, 135.8, 134.8, 130.1 (2), 127.7 (2), 126.3, 105.8, 105.7, 105.6, 86.6, 78.5, 59.6, 59.4, 55.7, 55.6, 42.2, 38.9, 26.8, 18.3. HRMS (ESI) Calcd for $C_{29}H_{31}BMoN_6O_5$ $[M]^+$: 652.1498. Found: 652.1505.



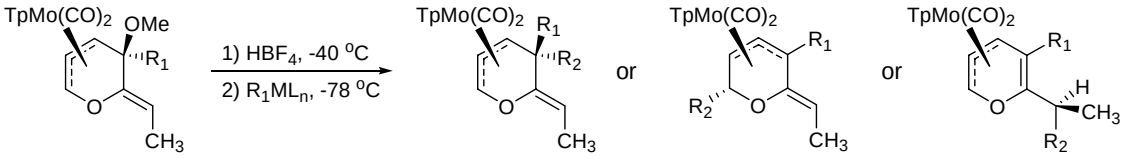
(±)-(1*R*,5*S*,6*R*)-6-Acetyl-1-(*S*-1-phenyl-ethyl)-8-oxa-bicyclo[3.2.1]oct-3-en-2-one, 108

Starting material *exo*-**107** (20.0 mg, 0.0308 mmol, 1.0 equiv) was dissolved in 2.0 mL THF/H_2O (3:1) and Et_3N (7.0 μL, 0.0462 mmol, 1.5 equiv) at 0 °C. A solution of ceric ammonium nitrate (135 mg, 0.246 mmol, 8.0 equiv) in 1.0 mL of water was added dropwise over 5 minutes. When addition was complete, the dark orange/red solution had changed to light yellow. The reaction was allowed to stir at room temperature for 10 minutes, and then partitioned

between 5 mL each of CH_2Cl_2 and water. The organic layer was washed with brine, dried over $MgSO_4$, concentrated and chromatographed on silica gel (25% EtOAc in hexanes) to afford the product as a white solid (5.4 mg, 65%).

108: TLC: R_f = 0.25 (33% EtOAc in hexanes). mp = 132-134 °C. IR (cm^{-1}): 2922 (m), 2852 (w), 1714 (m), 1685 (s), 1451 (w), 1358 (w), 1173 (m), 1050 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 7.28 (m, 5H), 7.23 (m, 1H), 6.09 (d, *J* = 9.8 Hz, 1H), 5.15 (d, *J* = 4.7 Hz, 1H), 3.61 (q, *J* = 7.0 Hz, 1H), 2.80 (dd, *J* = 9.4, 4.3 Hz, 1H), 1.96 (dd, *J* = 14.1, 4.3 Hz, 1H), 1.90 (dd, *J* = 14.1, 9.4 Hz, 1H), 1.58 (s, 3H), 1.35 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 205.5, 198.0, 151.5, 141.8, 129.7 (2), 128.4 (2), 127.5, 127.1, 92.3, 73.8, 55.4, 40.3, 31.7, 27.2, 17.5. HRMS (ESI) Calcd for $C_{17}H_{19}O_3$ $[M + H]^+$: 271.1329. Found: 271.1329.

General reaction procedure for the given transformation:



Preparation of Diene:

Starting material was dissolved in dry, degassed CH_2Cl_2, and cooled to -40 °C. A solution of tetrafluoroboric acid (HBF_4) was added dropwise, and the reaction was stirred for 3 minutes after which TLC showed complete disappearance of starting material. The reaction was placed under vacuum until all solvent had evaporated (T = -40 °C → -10 °C). The resulting residue was washed with dry *t*-butyl methyl ether (TBME) (2x10 mL), decanting off the solvent each time. The brownish-red solid product was then placed under vacuum again, to remove any remaining solvent, then redissolved in CH_2Cl_2 at low temperature (~-20 °C), cooled further to -78 °C and allowed to stir for 5 minutes.

Procedure A: *R_2ML_n = Commercially available Grignard or organolithium reagent:*

The indicated Grignard or lithium reagent was added dropwise as a solution to the diene and the reaction was stirred for 3 minutes, after which TLC indicated the appearance of a new product. The reaction was quenched with water, and diluted with three times the starting solvent volume of CH_2Cl_2. The organic layer was washed two times with a 1:1 mixture of water and saturated aqueous NH_4Cl solution (2x20 mL), dried ($MgSO_4$), filtered and concentrated on rotavap. The resulting residue was purified by gravity chromatography (10% EtOAc in hexanes) on silica gel neutralized with 5% Et_3N. In some cases recrystalization from dichloromethane and hexanes was required to obtain analytically pure product.

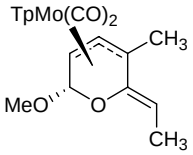
Procedure B: *R_2ML_n = Cuprate or Enolate*

Cuprates were prepared as follows: To 1 mL of THF cooled to -70 ^oC was added the indicated amount of CuBr·DMS and the grayish-white suspension was stirred for 3 minutes before adding the indicated Grignard reagent dropwise to the mixture. This solution was then warmed to -45 ^oC over 20 to 30 minutes producing a yellow (or yellow-brown or orange) solution, which was recooled to -78 ^oC.

Enolates were prepared as follows: To 1 mL of THF cooled to -78 ^oC was added the indicated amount of lithium hexamethyldisilazide (LiHMDS) solution. This was stirred for 3 minutes before adding the ketone dropwise over 5 minutes. This solution was stirred at -78 ^oC for 20 minutes.

The solution of diene was then cannulated directly into the stirring solution of cuprate or enolate, using a small of amount of extra CH_2Cl_2 to complete the transfer. The reaction was stirred for 3 minutes, after which TLC indicated the appearance of a new product. The reaction was quenched with water, and diluted with three times the starting solvent volume of CH_2Cl_2. The organic layer was washed two times with a 1:1 mixture of water and saturated aqueous NH_4Cl solution (2x20

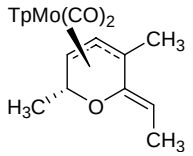
mL), dried ($MgSO_4$), filtered and concentrated on rotavap. The resulting residue was purified by gravity chromatography (10% EtOAc in hexanes) on silica gel neutralized with 5% Et_3N. In some cases, recrystalization from dichloromethane and hexanes was required to obtain analytically pure material.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*S*)-η-(3,4,5)-2-(*Z*)-ethylidene-6-methoxy-3-methyl-3,6-dihydro-2*H*-pyran-3-yl]molybdenum, 109

Compound **109** appears as a minor byproduct in many of the INA reactions of **91a**, but was usually not quantified.

109: TLC: R_f = 0.44 (25% EtOAc in hexanes). IR (cm^{-1}): 2924 (w), 2486 (w), 1931 (s), 1848 (s), 1503 (w), 1405 (s), 1308 (m), 1216 (m), 1118 (m), 1050 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.42 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.61 (app t, *J* = 2.0 Hz, 2H), 7.46 (d, *J* = 2.3 Hz, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 6.21 (t, *J* = 2.3 Hz, 1H), 6.19 (t, *J* = 2.3 Hz, 1H), 5.10 (q, *J* = 7.0 Hz, 1H), 4.99 (s, 1H), 4.09 (s, 2H), 3.48 (s, 3H), 1.89 (s, 3H), 1.74 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 233.4, 226.5, 147.4, 147.1, 145.7, 139.5, 136.7, 136.1, 134.7, 105.9, 105.8, 105.4, 104.4, 100.0, 99.0, 75.8, 56.4, 54.1, 22.5, 10.5. HRMS (ESI) Calcd for $C_{20}H_{24}BMoN_6O_4$ $[M + H]^+$: 521.1001. Found: 521.1001.



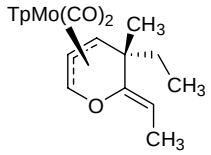
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-3,6-dimethyl-2-(*Z*)-ethylidene-2,6-dihydro-6*H*-pyran-3-yl]molybdenum, 110a

Compound **110a** was successfully prepared using methylmagnesium chloride or

methyllithium. Following the *general procedure A,* starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.5 mL), and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in 3 mLCH_2Cl_2 was added methylmagnesium chloride (3.0 M in THF, 58 μL, 0.175 mmol, 3.0 equiv). Purification by gravity chromatography gave 18.1 mg (62%) of pure product **110a** as a reddish-orange solid.

Alternatively, following the *general procedure A,* starting material **91a** (40 mg, 0.077 mmol, 1.0 equiv) was dissolved in 2.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.100 mmol, 1.3 equiv). To the isolated diene salt dissolved in 2.5 mL CH_2Cl_2 was added methyllithium (1.4 M in Bu_2O, 165 μL, 0.232 mmol, 3.0 equiv). Purification by gravity chromatography gave 16.8 mg (43%) of pure product, which was spectroscopically identical to that prepared using the procedure above.

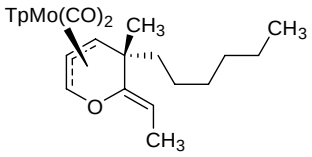
110a: TLC: R_f = 0.48 (25% EtOAc in hexanes). IR (cm^{-1}): 2484 (w), 1924 (s), 1841 (s), 1405 (s), 1306 (m), 1216 (m), 1118 (m), 1048 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.45 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.62 (s, 2H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.46 (d, *J* = 2.3 Hz, 1H), 6.22 (t, *J* = 2.0 Hz, 1H), 6.20 (t, *J* = 2.0 Hz, 1H), 6.16 (t, *J* = 2.0 Hz, 1H), 5.00 (q, *J* = 6.7 Hz, 1H), 4.33 (q, *J* = 6.3 Hz, 1H), 4.00 (dd, *J* = 7.4, 1.6 Hz, 1H), 3.94 (d, *J* = 7.4 Hz, 1H), 1.84 (s, 3H), 1.69 (d, *J* = 7.0 Hz, 3H), 1.46 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.9, 226.7, 148.6, 147.0, 145.6, 139.3, 136.6, 136.0, 134.5, 105.8, 105.6, 105.3, 102.8, 96.4, 74.6, 69.9, 60.3, 25.3, 22.4, 10.5. HRMS (ESI) Calcd for $C_{20}H_{24}BMoN_6O_3$ $[M + H]^+$: 505.1052. Found: 505.1052.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*R*)-η-(2,3,4)-5-ethyl-6-(*Z*)-ethylidene-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 112a

Following the *general procedure A,* starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in 3 mL CH_2Cl_2 was added ethylmagnesium bromide (1.0 M in THF, 175 μL, 0.175 mmol, 3.0 equiv). Purification by gravity chromatography gave 18.6 mg (62%) of pure product **112a** as a yellow solid.

112a: TLC: R_f = 0.55 (25% EtOAc in hexanes). IR (cm^{-1}): 2922 (w), 2482 (w), 1937 (s), 1850 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.49 (d, *J* = 1.9 Hz, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.55 (d, *J* = 2.4 Hz, 2H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 3.9, 2.7 Hz, 1H), 6.25 (t, *J* = 1.9 Hz, 1H), 6.19 (t, *J* = 2.4 Hz, 1H), 6.18 (t, *J* = 1.9 Hz, 1H), 4.45 (q, *J* = 7.0 Hz, 1H), 4.40 (dd, *J* = 7.4, 2.7 Hz, 1H), 3.52 (dd, *J* = 7.4, 4.3 Hz, 1H), 1.75 (m, *J* = 7.0 Hz, 1H), 1.67 (m, *J* = 7.0 Hz, 1H), 1.55 (d, *J* = 6.7 Hz, 3H), 1.41 (s, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 230.2, 227.8, 151.9, 146.9, 143.3, 141.5, 136.1, 135.9, 134.5, 107.0, 106.1, 105.8, 105.4, 102.5, 80.7, 60.3, 43.0, 41.9, 20.7, 9.88, 9.84. HRMS (ESI) Calcd for $C_{21}H_{26}BMoN_6O_3$ $[M + H]^+$: 519.1208. Found: 519.1212.

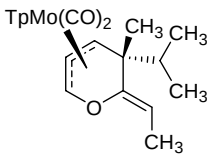


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*R*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-hexyl-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 112b

Following the *general procedure A,* starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv)

was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in 2.5 mL CH_2Cl_2 was added hexylmagnesium bromide (2.0 M in Et_2O, 87 μL, 0.174 mmol, 3.0 equiv). Purification by gravity chromatography gave 23.1 mg (70%) of product **112b** [as an inseparable mixture with the regioisomer resulting from addition of hexylmagnesium bromide to the alkylidene location (pathway C) (<10% of total)] as a yellow oil.

112b: TLC: R_f = 0.66 (25% EtOAc in hexanes). IR (cm^{-1}): 2928 (m), 2856 (w), 2477 (w), 1938 (s), 1852 (s), 1406 (m), 1303 (m), 1217 (m), 1121 (m), 1049 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.49 (d, *J* = 1.9 Hz, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.55 (d, *J* = 1.9 Hz, 2H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.03 (dd, *J* = 4.1, 2.5 Hz, 1H), 6.25 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H), 4.45 (q, *J* = 6.7 Hz, 1H), 4.41 (dd, *J* = 7.6, 2.9 Hz, 1H), 3.51 (dd, *J* = 7.6, 4.4 Hz, 1H), 1.73 (m, 1H), 1.59 (m, 1H), 1.54 (d, *J* = 6.7, 3H), 1.44 (s, 3H), 1.28 (br s, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 230.2, 227.8, 152.4, 146.9, 143.3, 141.5, 136.1, 135.9, 134.4, 107.0, 106.0, 105.7, 105.4, 102.2, 80.9, 60.3, 49.8, 42.7, 32.1, 30.0, 25.2, 22.9, 21.5, 14.3, 9.9. HRMS (ESI) Calcd for $C_{25}H_{34}BMoN_6O_3$ [M + H]$^+$: 575.1834. Found: 575.1827.

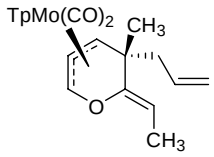


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*R*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methyl-5-(2-propyl)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 112b

Following the *general procedure A,* starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in 3 mL CH_2Cl_2 was added isopropylmagnesium chloride (2.0 M in Et_2O, 87 μL, 0.174 mmol, 3.0 equiv). Purification by gravity chromatography

gave 28.6 mg (93%) of pure product **121c** as a yellow solid.

112c: TLC: R_f = 0.54 (25% EtOAc in hexanes). IR (cm^{-1}): 2925 (w), 2479 (w), 1938 (s), 1852 (s), 1405 (m), 1303 (m), 1217 (m), 1121 (m), 1049 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.50 (d, *J* = 1.9 Hz, 1H), 7.88 (d, *J* = 1.6 Hz, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.56 (app t, *J* = 2.5 Hz, 2H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.02 (app t, *J* = 3.8 Hz, 1H), 6.25 (t, *J* = 2.2 Hz, 1H), 6.19 (s, 2H), 4.56 (dd, *J* = 7.6, 2.9 Hz, 1H), 4.45 (q, *J* = 6.7 Hz, 1H), 3.59 (dd, *J* = 7.3, 4.1 Hz, 1H), 1.91 (septet, *J* = 7.0 Hz, 1H), 1.56 (d, *J* = 7.0 Hz, 3H), 1.32 (s, 3H), 1.17 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 230.3, 228.2, 152.1, 146.9, 143.4, 141.4, 136.2, 135.8, 134.5, 106.9, 106.0, 105.8, 105.5, 103.2, 81.1, 60.7, 45.2, 42.8, 19.7, 16.8, 15.6, 9.8. HRMS (ESI) Calcd for $C_{22}H_{28}BMoN_6O_3$ $[M + H]^+$: 533.1365. Found: 533.1364.

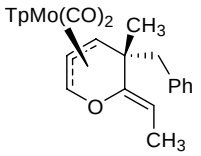


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*R*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methyl-5-(2-propene)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 112d

Following the *general procedure A,* starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in 2.5 mL CH_2Cl_2 was added allylmagnesium chloride (1.0 M in Et_2O, 174 μL, 0.174 mmol, 3.0 equiv). Purification by gravity chromatography gave 23.2 mg (76%) of pure product **112d** as a yellow solid.

112d: TLC: R_f = 0.55 (25% EtOAc in hexanes). IR (cm^{-1}): 2481 (w), 1938 (s), 1852 (s), 1406 (m), 1305 (m), 1217 (m), 1121 (m), 1049 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.49 (d, *J* = 1.9 Hz, 1H), 7.86 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.55 (d, *J* = 1.9 Hz, 2H), 7.47 (d, *J* = 1.9 Hz, 1H), 7.05 (dd, *J* = 4.1, 3.1 Hz, 1H), 6.26 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H), 5.84 (m, 1H), 5.08 (s, 1H), 5.05 (d, *J* = 2.5 Hz, 1H), 4.47 (q, *J* = 6.7 Hz,

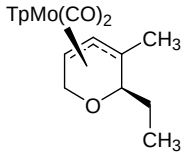
1H), 4.35 (dd, *J* = 7.3, 2.5 Hz, 1H), 3.54 (dd, *J* = 7.3, 4.4 Hz, 1H), 2.43 (m, 2H), 1.55 (d, *J* = 6.7 Hz, 3H), 1.43 (s, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 230.1, 227.5, 152.0, 146.9, 143.3, 141.5, 136.1, 135.9, 135.4, 134.5, 117.6, 107.2, 106.1, 105.8, 105.4, 102.4, 79.8, 60.2, 53.8, 42.8, 21.6, 9.8. HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_6O_3$ $[M + H]^+$: 531.1208. Found: 531.1207.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*R*)-η-(2,3,4)-5-benzyl-6-(*Z*)-ethylidene-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 112e

Following the *general procedure A*, starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in 3 mL CH_2Cl_2 was added benzylmagnesium chloride (1.0 M in Et_2O, 175 μL, 0.175 mmol, 3.0 equiv). Purification by gravity chromatography gave 29.1 mg (87%) of pure product **112e** as a yellow solid.

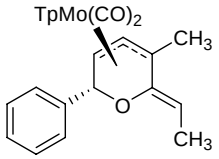
112e: TLC: R_f = 0.49 (25% EtOAc in hexanes). IR (cm^{-1}): 2480 (w), 1939 (s), 1853 (s), 1406 (m), 1303 (m), 1217 (m), 1121 (m), 1049 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.49 (d, *J* = 1.9 Hz, 1H). 7.80 (d, *J* = 1.6 Hz, 1H), 7.67 (d, *J* = 1.6 Hz, 1H). 7.57 (d, *J* = 2.2 Hz, 1H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.27-7.21 (m, 2H), 7.17-7.13 (m, 3H), 6.25 (t, *J* = 2.2 Hz, 1H), 6.22 (t, *J* = 2.2 Hz, 1H), 6.16 (t, *J* = 2.2 Hz, 1H), 4.36 (dd, *J* = 7.3, 2.9 Hz, 1H), 4.19 (q, *J* = 6.7 Hz, 1H), 3.62 (dd, *J* = 7.3, 4.4 Hz, 1H), 3.02 (d, *J* = 12.7 Hz, 1H), 2.97 (d, *J* = 12.7 Hz, 1H), 1.52 (d, *J* = 7.0 Hz, 3H), 1.35 (s, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 230.3, 227.4, 151.2, 146.9, 143.2, 141.6, 138.4, 136.1, 135.9, 134.5, 131.1 (2), 127.5 (2), 126.3, 107.6, 106.1, 105.8, 105.5, 103.4, 79.7, 60.3, 55.3, 44.2, 21.4, 9.8. HRMS (ESI) Calcd for $C_{26}H_{28}BMoN_6O_3$ $[M + H]^+$: 581.1365. Found: 581.1366.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*)-η-(3,4,5)-2-ethyl-3-methyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 110b

Following the *general procedure A,* starting material **91a** (40 mg, 0.077 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.5 mL) and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.100 mmol, 1.3 equiv). To the isolated diene salt dissolved in CH_2Cl_2 (3.0 mL) was added sodium cyanoborohydride solution (1.0 M in THF, 230 μL, 0.232 mmol, 3.0 equiv). Purification by gravity chromatography gave 22.3 mg (59%) of the fully reduced complex **110b** as a reddish-orange solid.

110b: TLC: R_f = 0.51 (25% EtOAc in hexanes). IR (cm^{-1}): 1923 (s), 1838 (s), 1407 (m), 1304 (m), 1207 (w), 1116 (m), 1048 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.45 (d, *J* = 1.9 Hz, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 1.9 Hz, 1H), 7.46 (d, *J* = 1.9 Hz, 1H), 6.21 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H), 3.96-3.89 (m, 3H), 3.86 (t, *J* = 6.7 Hz, 1H), 3.43 (dd, *J* = 9.5, 3.2 Hz, 1H), 2.01 (m, 1H), 1.90 (m, 1H), 1.74 (s, 3H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.4, 228.6, 146.4 (2), 139.5, 136.1, 135.8, 134.4, 105.7, 105.6, 105.3, 99.5, 79.7, 77.1, 64.7, 58.8, 24.7, 24.0, 11.5. HRMS (ESI) Calcd for $C_{19}H_{24}BMoN_6O_3$ $[M + H]^+$: 493.1052. Found: 493.1056.



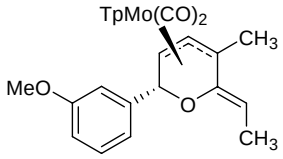
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methyl-6-phenyl-2,6-dihydro-6*H*-pyran-3-yl]molybdenum, 110c

This compound was successfully prepared using phenylmagnesium chloride or phenyllithium. Following the *general procedure A,* starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.5 mL), and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in 3 mL CH_2Cl_2 was added phenylmagnesium chloride (1.8 M in THF, 97 μL, 0.174 mmol, 3.0 equiv). Purification by gravity chromatography gave 25.0 mg (77%) of pure product **110c** as an orange solid.

Alternatively, following the *general procedure A,* starting material **91a** (40 mg, 0.077 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.5 mL), and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.10 mmol, 1.3 equiv). To the isolated diene salt dissolved in 2.5 mL CH_2Cl_2 was added phenyllithium (1.8 M in Bu_2O, 130 μL, 0.232 mmol, 3.0 equiv). Purification by gravity chromatography gave 26.8 mg (62%) of pure product, which was spectroscopically identical to that prepared using the procedure above.

110c: TLC: R_f = 0.47 (25% EtOAc in hexanes). IR (cm^{-1}): 2924 (w), 2486 (w), 1928 (s), 1846 (s), 1405 (s), 1307 (m), 1217 (m), 1118 (m), 1050 (s). ^{1}H NMR [600 MHz, $CDCl_3$]: δ 8.49 (d, *J* = 1.9 Hz, 1H), 7.71 (d, *J* = 1.4 Hz, 1H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.1 Hz, 1H), 6.23 (t, *J* = 1.9 Hz, 1H), 6.18 (t, *J* = 1.9 Hz, 2H), 5.23 (s, 1H), 5.01 (q, *J* = 7.1 Hz, 1H), 4.21 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.98 (d, *J* = 7.6 Hz, 1H), 1.88 (s, 3H), 1.73 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 233.2, 226.3, 149.7, 147.1, 145.9, 145.7, 139.4, 136.7, 136.0, 134.6, 128.7 (2), 127.5, 125.8 (2), 105.8, 105.6, 105.4, 101.6, 95.6, 75.6, 74.6, 59.5,

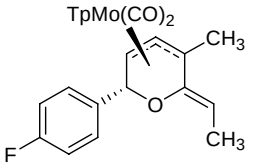
22.7, 10.6. HRMS (ESI) Calcd for $C_{25}H_{26}BMoN_6O_3$ $[M + H]^+$: 567.1208. Found: 567.1209.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methyl-6-(3-methoxyphenyl)-2,6-dihydro-6*H*-pyran-3-yl]molybdenum, 110d

Following the *general procedure A,* starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in CH_2Cl_2 (3 mL) was added 3-methoxyphenylmagnesium chloride (1.0 M in THF, 175 μL, 0.175 mmol, 3.0 equiv). Purification by gravity chromatography gave 20.9 mg (61%) of pure product **110d** as an orange solid.

110d: TLC: R_f = 0.36 (25% EtOAc in hexanes). IR (cm^{-1}): 2923 (w), 2481 (w), 1926 (s), 1844 (s), 1406 (m), 1304 (m), 1207 (m), 1118 (m), 1048 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.48 (d, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.54 (d, *J* = 1.6 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.85 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.23 (t, *J* = 2.2 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H), 6.18 (t, *J* = 1.9 Hz, 1H), 5.20 (s, 1H), 5.01 (q, *J* = 6.9 Hz, 1H), 4.21 (dd, *J* = 7.6, 1.9 Hz, 1H), 3.98 (d, *J* = 7.3 Hz, 1H), 3.83 (s, 3H), 1.87 (s, 3H), 1.74 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 233.2, 226.3, 159.8, 149.7, 147.7, 147.1, 145.7, 139.4, 136.7, 136.0, 134.6, 129.7, 118.2, 112.8, 111.4, 105.8, 105.7, 105.4, 101.6, 95.5, 75.4, 74.7, 59.4, 55.4, 22.7, 10.6. HRMS (ESI) Calcd for $C_{26}H_{28}BMoN_6O_4$ $[M + H]^+$: 597.1314. Found: 597.1317.



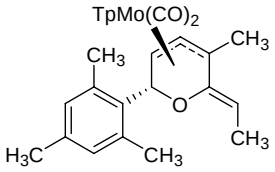
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methyl-6-(4-fluorophenyl)-2,6-dihydro-6*H*-pyran-3-yl]molybdenum, 110e

(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methyl-6-(4-fluorophenyl)-2,6-dihydro-6*H*-pyran-3-yl]molybdenum, (+)-**110e**

Following the *general procedure A,* starting material **91a** (1.60 g, 3.09 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (15.0 mL) and reacted with HBF_4 (54 wt% in Et_2O, 0.65 mL, 4.02 mmol, 1.3 equiv). To the isolated diene salt dissolved in 15 mL CH_2Cl_2 was added 4-fluorophenylmagnesium bromide (1.0 M in THF, 9.27 mL, 9.27 mmol, 3.0 equiv). Purification by gravity chromatography gave pure product **110e (**1.41 g, 81%) as an orange solid.

The exact same procedure was used to convert (-)-**91a** (98.3% ee) to (+)-**110e** in what was determined after conversion to (+)-**122** to be of 98.3 %ee.

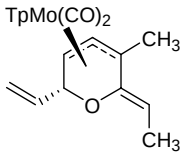
(+)-**110e:** TLC: R_f = 0.49 (25% EtOAc in hexanes). $[\alpha]_D^{20}$ +1129 (98.3% ee, *c* 0.09, CH_2Cl_2). IR (cm^{-1}): 1923 (w), 2481 (w), 1928 (s), 1846 (s), 1506 (m), 1407 (m), 1304 (m), 1219 (m), 1123 (m), 1049 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.48 (d, *J* = 2.0 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.23 (t, *J* = 2.0 Hz, 1H), 6.19 (t, *J* = 2.0 Hz, 1H), 6.18 (t, *J* = 2.0 Hz, 1H), 5.20 (s, 1H), 5.02 (q, *J* = 7.0 Hz, 1H), 4.17 (dd, *J* = 7.4, 2.0 Hz, 1H), 3.99 (d, *J* = 7.4 Hz, 1H), 1.88 (s, 3H), 1.70 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 233.2, 226.1, 163.5, 161.0, 149.3, 147.1, 145.7, 141.5, 139.3, 136.8, 136.1, 134.6, 127.6, 127.5, 115.6, 115.4, 105.9, 105.7, 105.4, 102.0, 95.5, 75.0, 74.5, 59.2, 22.6, 10.5. HRMS (ESI) Calcd for $C_{25}H_{25}BFMoN_6O_3$ $[M + H]^+$: 585.1114. Found: 585.1121.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methyl-6-(2,4,6-trimethyl-phenyl)-2,6-dihydro-6*H*-pyran-3-yl]molybdenum, 110f

Following the *general procedure A,* starting material **91a** (80 mg, 0.154 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (4.0 mL), and reacted with HBF_4 (54 wt% in Et_2O, 32 μL, 0.201 mmol, 1.3 equiv). To the isolated diene salt dissolved in 5 mL CH_2Cl_2 was added 2,4,6-trimethylphenylmagnesium bromide (1.0 M in Et_2O, 175 μL, 0.175 mmol, 3.0 equiv). Purification by gravity chromatography gave 71.3 mg (76%) of pure product **110f** as an orange solid.

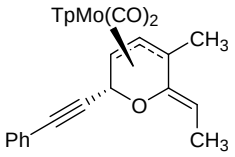
110f: TLC: R_f = 0.63 (25% EtOAc in hexanes). IR (cm^{-1}): 1931 (s), 1850 (s), 1407 (w), 1304 (w), 1206 (w), 1123 (w), 1049 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.45 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.47 (app t, *J* = 2.5 Hz, 2H), 6.91 (s, 2H), 6.22 (t, *J* = 2.2 Hz, 2H), 6.17 (t, *J* = 2.2 Hz, 1H), 5.83 (s, 1H), 4.86 (q, *J* = 7.0 Hz, 1H), 4.23 (d, *J* = 7.6 Hz, 1H), 4.09 (d, *J* = 7.6 Hz, 1H), 2.44 (s, 6H), 2.31 (s, 3H), 1.84 (s, 3H), 1.72 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 236.2, 225.5, 151.5, 146.9, 146.0, 139.6, 138.1, 137.0, 136.9, 136.4 (2), 135.9, 134.6, 130.8 (2), 105.7, 105.6, 105.5, 97.9, 91.0, 78.3, 75.4, 57.7, 23.7, 20.9, 20.8 (2), 10.4. HRMS (ESI) Calcd for $C_{28}H_{32}BMoN_6O_3$ $[M + H]^+$: 609.1678. Found: 609.1700.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methyl-6-vinyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 110g

Following the *general procedure A,* starting material **91a** (200 mg, 0.386 mmol, 1.0 equiv) was dissolved in 16.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 82 μL, 0.502 mmol, 1.3 equiv). To the isolated diene salt dissolved in 16 mL CH_2Cl_2 was added vinylmagnesium chloride (1.6 M in THF, 440 μL, 0.708 mmol, 1.8 equiv). Purification by gravity chromatography (33% EtOAc in hexanes) gave 196 mg (99%) of pure product **110g** as an orange solid.

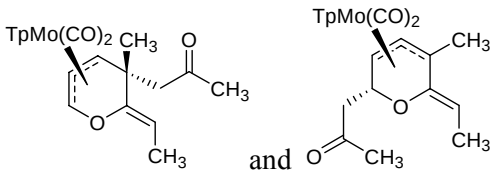
110g: TLC: R_f = 0.50 (25% EtOAc in hexanes). IR (cm^{-1}): 2483 (m), 1922 (vs), 1840 (vs), 1406 (m), 1304 (m), 1117 (m), 1049 (s). ^{1}H NMR [600 MHz, $CDCl_3$]: δ 8.45, (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.62 (app t, *J* = 2.4 Hz, 2H), 7.60 (d, *J* = 1.4 Hz, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 6.22 (t, *J* = 2.4 Hz, 1H), 6.21 (t, *J* = 2.4 Hz, 1H), 6.16 (t, *J* = 1.9 Hz, 1H), 6.02 (ddd, *J* = 16.7, 10.0, 5.7 Hz, 1H), 5.30 (d, *J* = 15.1 Hz, 1H), 5.15 (d, *J* = 10.5 Hz, 1H), 4.98 (q, *J* = 7.1 Hz, 1H), 4.58 (d, *J* = 5.7 Hz, 1H), 4.01 (dd, *J* = 7.1, 1.4 Hz, 1H), 3.95 (d, *J* = 7.6 Hz, 1H), 1.84 (s, 3H), 1.72 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 232.7, 226.5, 148.9, 147.1, 145.7, 141.2, 139.3, 136.7, 136.0, 134.6, 114.8, 105.8, 105.7, 105.3, 102.4, 96.8, 74.5, 74.4, 57.9, 22.5, 10.6. HRMS (ESI) Calcd for $C_{21}H_{24}BMoN_6O_3$ $[M + H]^+$: 517.1052. Found: 517.1052.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methyl-6-phenylethynyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 110h

Following the *general procedure A,* starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in 3.0 mL CH_2Cl_2 was added lithiumphenylacetylide (1.0 M in THF, 175 μL, 0.175 mmol, 3.0 equiv). Purification by gravity chromatography gave 24.0 mg (71%) of pure product **110h** as an orange solid.

110h: TLC: R_f = 0.57 (25% EtOAc in hexanes). IR (cm^{-1}): 2480 (w), 1928 (s), 1847 (s), 1407 (m), 1304 (m), 1207 (m), 1118 (m), 1049 (s). ^{1}H NMR [600 MHz, $CDCl_3$]: δ 8.45 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 1.4 Hz, 1H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.64 (app s, 2H), 7.51-7.48 (m, 3H), 7.33 (m, 3H), 6.25 (t, *J* = 1.9 Hz, 1H), 6.22 (t, *J* = 2.4 Hz 1H), 6.18 (t, *J* = 1.9 Hz, 1H), 5.15 (q, *J* = 7.1 Hz, 1H), 5.04 (d, *J* = 1.9 Hz, 1H), 4.28 (dd, *J* = 7.1, 1.9 Hz, 1H), 4.06 (d, *J* = 7.6 Hz, 1H), 1.91 (s, 3H), 1.77 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 232.2, 226.5, 148.1, 147.0, 145.6, 139.6, 136.7, 136.1, 134.7, 132.0 (2), 128.5 (2), 128.4, 123.0, 105.9, 105.7, 105.3, 104.8, 98.6, 90.6, 84.9, 74.3, 64.2, 57.4, 22.5, 10.7. HRMS (ESI) Calcd for $C_{27}H_{26}BMoN_6O_3$ [M + H]$^+$: 591.1208. Found: 591.1210.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*R*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-methyl-5-(2-oxo-propyl)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 112f

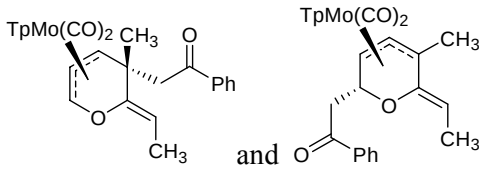
and

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-methyl-6-(2-oxo-propyl)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 110i

Following the *general procedure B,* starting material **91a** (100 mg, 0.193 mmol, 1.0 equiv) was dissolved in 4.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 41 μL, 0.251 mmol, 1.3 equiv). The isolated diene salt dissolved in 2.0 mL CH_2Cl_2 (and an additional 0.5 mL for quantitation) was cannulated into the enolate prepared by the *general procedure B* using lithiumhexamethyldisilazide (1.0 M in THF, 990 μL, 0.985 mmol, 5.1 equiv), and acetone (71 μL, 0.965 mmol, 5.0 equiv). Purification by gravity chromatography gave 27.2 mg (26%) of pure product **112f** as a yellow solid followed by 16.0 mg (15%) of pure product **110i** as an orange solid.

112f: TLC: R_f = 0.33 (25% EtOAc in hexanes). IR (cm^{-1}): 2480 (w), 1940 (s), 1854 (s), 1701 (w), 1407 (m), 1303 (m), 1218 (m), 1122 (m), 1049 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.48 (d, *J* = 1.9 Hz 1H), 7.89 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.55 (app t, *J* = 2.2 Hz, 2H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.07 (dd, *J* = 4.1, 2.9 Hz, 1H), 6.26 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 1.9 Hz, 1H), 6.18 (t, *J* = 2.2 Hz, 1H), 4.64 (dd, *J* = 7.3, 2.5 Hz, 1H), 4.55 (q, *J* = 6.7 Hz, 1H), 3.50 (dd, *J* = 7.3, 4.1 Hz, 1H), 2.84 (s, 2H), 2.12 (s, 3H), 1.60 (s, 3H), 1.54 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 229.7, 227.2, 208.1, 151.5, 146.9, 143.4, 141.4, 136.2, 136.0, 134.5, 107.1, 106.1, 105.8, 105.6, 103.2, 78.6, 61.5, 59.8, 42.4, 32.2, 21.5, 9.9. HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_6O_4$ $[M + H]^+$: 547.1157. Found: 547.1174.

110i: TLC: R_f = 0.25 (25% EtOAc in hexanes). IR (cm^{-1}): 2921 (w), 2487 (w), 1927 (s), 1845 (s), 1711 (w), 1406 (m), 1305 (m), 1216 (w), 1118 (m), 1049 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.44 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 2.3 Hz, 2H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 2.3 Hz, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.21 (t, *J* = 2.0 Hz, 1H), 6.16 (t, *J* = 2.3 Hz, 1H), 5.01 (q, *J* = 7.0 Hz, 1H), 4.63 (t, *J* = 6.3 Hz, 1H), 4.07 (dd, *J* = 7.4, 2.0 Hz, 1H), 3.92 (d, *J* = 7.0 Hz, 1H), 2.82 (m, 2H), 2.25 (s, 3H), 1.84 (s, 3H), 1.63 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.4, 226.4, 206.9, 147.8, 147.1, 145.7, 139.3, 136.7, 136.1, 134.6, 105.9, 105.7, 105.3, 103.6, 96.3, 74.0, 70.8, 57.9, 53.6, 30.6, 22.4, 10.5. HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_6O_4$ $[M + H]^+$: 547.1157. Found: 547.1158.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*R*)-η-(2,3,4)-6-(*Z*)-ethylidene-5-(2-oxo-2-phenyl-ethyl)-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 112g

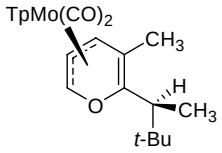
and

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-6-(2-oxo-2-phenyl-ethyl)-3-methyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 110j

Following the *general procedure B,* starting material **91a** (40 mg, 0.077 mmol, 1.0 equiv) was dissolved in 3.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.10 mmol, 1.3 equiv). The isolated diene salt dissolved in 1.5 mL CH_2Cl_2 (and an additional 0.5 mL for quantitation) was cannulated into the enolate prepared by the *general procedure B* using lithiumhexamethyldisilazide (1.0 M in THF, 390 μL, 0.392 mmol, 5.1 equiv), and acetophenone (45 μL, 0.386 mmol, 5.0 equiv). Purification by gravity chromatography gave 13 mg (28%) of pure product **112g** as a yellow solid followed by 22.2 mg (48%) of pure product **110j** as an orange solid.

112g: TLC: R_f = 0.40 (25% EtOAc in hexanes). IR (cm^{-1}): 2921 (w), 2481 (w), 1939 (s), 1852 (s), 1668 (m), 1406 (m), 1303 (m), 1217 (m), 1121 (m), 1048 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.48 (d, *J* = 2.0 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 2H), 7.92 (d, *J* = 1.2 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.11 (dd, *J* = 3.9, 2.7 Hz, 1H), 6.26 (t, *J* = 2.0 Hz, 1H), 6.20 (t, *J* = 2.3 Hz, 1H), 6.19 (t, *J* = 2.3 Hz, 1H), 4.80 (dd, *J* = 7.4, 2.7 Hz, 1H), 4.4 (q, *J* = 6.7 Hz, 1H), 3.52 (dd, *J* = 7.4, 4.3 Hz, 1H), 3.44 (d, *J* = 14.5 Hz, 1H), 3.32 (d, *J* = 14.1 Hz, 1H), 1.67 (s, 3H), 1.37 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 229.8, 227.2, 199.3, 151.4, 146.9, 143.4, 141.4, 138.3, 136.2, 135.9, 134.5, 132.9, 128.5 (4), 107.0, 106.1, 105.8, 105.6, 103.4, 78.9, 60.1, 56.2, 42.8, 29.9, 21.6, 9.8. HRMS (ESI) Calcd for $C_{27}H_{28}BMoN_6O_4$ $[M + H]^+$: 609.1314. Found: 609.1316.

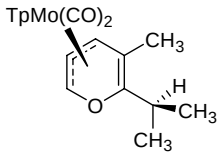
110j: TLC: R_f = 0.35 (25% EtOAc in hexanes). IR (cm^{-1}): 2925 (w), 2488 (w), 1928 (s), 1845 (s), 1681 (m), 1405 (m), 1307 (m), 1214 (m), 1118 (m), 1049 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.44 (d, *J* = 2.0 Hz, 1H), 8.00 (d, *J* = 7.0 Hz, 2H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.57 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 1.6 Hz, 1H), 6.21 (t, *J* = 2.3 Hz, 1H), 6.20 (t, *J* = 2.3 Hz, 1H), 6.15 (t, *J* = 2.0 Hz, 1H), 4.99 (q, *J* = 7.0 Hz, 1H), 4.79 (t, *J* = 6.3 Hz, 1H), 4.23 (dd, *J* = 7.4, 1.9 Hz, 1H), 3.95 (d, *J* = 7.4 Hz, 1H), 3.51 (dd, *J* = 14.9, 6.7 Hz, 1H), 3.28 (dd, *J* = 15.3, 6.3 Hz, 1H), 1.87 (s, 3H), 1.51 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.1, 226.5, 198.3, 148.1, 147.1, 145.6, 139.4, 137.3, 136.7, 136.0, 134.6, 133.4, 128.8 (2), 128.6 (2), 105.8, 105.7, 105.3, 103.5, 96.1, 74.2, 71.4, 58.2, 48.3, 22.4, 10.4. HRMS (ESI) Calcd for $C_{27}H_{28}BMoN_6O_4$ $[M + H]^+$: 609.1316. Found: 609.1317.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-η-(2,3,4)-5-methyl-6-((*S*)-1,2,2-trimethyl-propyl)-2*H*-pyran-2-yl]molybdenum, 113a

Following the *general procedure A,* starting material **91a** (30 mg, 0.058 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 12 μL, 0.075 mmol, 1.3 equiv). To the isolated diene salt dissolved in 3.0 mL CH_2Cl_2 was added *tert*-butylmagnesium chloride (2.0 M in Et_2O, 87 μL, 0.174 mmol, 3.0 equiv). Purification by gravity chromatography gave pure product **113a** (9.5 mg, 30%) as a yellow solid.

113a: TLC: R_f = 0.57 (25% EtOAc in hexanes). IR (cm^{-1}): 2922 (w), 1929 (s), 1847 (s), 1406 (m), 1303 (m), 1217 (m), 1123 (m), 1049 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.21 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.59 (d, *J* = 2.5 Hz, 2H), 7.57 (dd, *J* = 4.4, 2.5 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 6.22 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 1.9 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 4.68 (dd, *J* = 6.4, 2.5 Hz, 1H), 2.46 (d, *J* = 6.4, 4.4 Hz, 1H), 2.25 (q, *J* = 7.0 Hz, 1H), 2.02 (s, 3H), 0.96 (d, *J* = 7.3 Hz, 3H), 0.89 (s, 9H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 228.7, 225.1, 146.0, 144.8, 141.9, 141.6, 136.0 (2), 134.5, 111.8, 107.6, 105.65, 105.61, 105.4, 70.5, 47.5, 42.4, 34.6, 28.4 (3), 18.9, 13.6. HRMS (ESI) Calcd for $C_{23}H_{29}BMoN_6O_3$ $[M]^+$: 546.1443. Found: 546.1442.

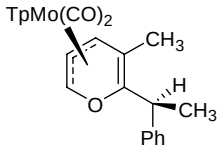


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-η-(2,3,4)-6-isopropyl-5-methyl-2*H*-pyran-2-yl]molybdenum, 113b

Following the *general procedure B,* starting material **91a** (40 mg, 0.077 mmol, 1.0 equiv)

was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.10 mmol, 1.3 equiv). The isolated diene salt dissolved in 1.5 mL CH_2Cl_2 (and an additional 0.5 mL for quantitation) was cannulated into the cuprate prepared by the *general procedure B* using copper bromide-dimethylsulfide complex (48 mg, 0.232 mmol, 3.0 equiv), and methylmagnesium chloride (3.0 M in THF, 77 μL, 0.232 mmol, 3.0 equiv). Purification by gravity chromatography gave 15.3 mg (39%) of pure product **113b** as a yellow solid.

113b: TLC: R_f = 0.53 (25% EtOAc in hexanes). IR (cm^{-1}): 2967 (w), 2478 (w), 1926 (s), 1843 (s), 1406 (m), 1302 (m), 1218 (m), 1119 (m), 1048 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.21 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.59 (m, 3H), 7.48 (d, *J* = 2.3 Hz, 1H), 6.23 (t, *J* = 2.0 Hz, 1H), 6.20 (t, *J* = 2.0 Hz, 1H), 6.19 (t, *J* = 2.3 Hz, 1H), 4.69 (dd, *J* = 6.3, 2.3 Hz, 1H), 2.61 (septet, *J* = 7.0 Hz, 1H), 2.47 (dd, *J* = 6.3, 4.7 Hz, 1H), 2.01 (s, 3H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 228.8, 224.8, 146.0, 145.5, 141.9, 141.6, 136.1, 136.0, 134.5, 109.6, 107.8, 105.7, 105.6, 105.4, 70.8, 47.3, 27.9, 20.9, 19.9, 17.7. HRMS (ESI) Calcd for $C_{20}H_{24}BMoN_6O_3$ $[M + H]^+$: 505.1052. Found: 505.1053.

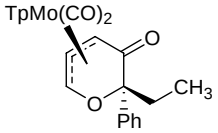


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-η-(2,3,4)-5-methyl-6-[(*S*)-(1-phenyl-ethyl)]-2*H*-pyran-2-yl]molybdenum, 113c

Following the *general procedure B,* starting material **91a** (40 mg, 0.077 mmol, 1.0 equiv) was dissolved in 2.5 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 16 μL, 0.10 mmol, 1.3 equiv). The isolated diene salt dissolved in 1.5 mL CH_2Cl_2 (and an additional 0.5 mL for quantitation) was cannulated into the cuprate prepared by the *general procedure B* using copper bromide-dimethylsulfide complex (48 mg, 0.232 mmol, 3.0 equiv), and phenylmagnesium

chloride (3.0 M in Et_2O, 77 μL, 0.232 mmol, 3.0 equiv). Purification by gravity chromatography gave 34.2 mg (79%) of pure product **113c** as a yellow solid.

113c: TLC: R_f = 0.49 (25% EtOAc in hexanes). IR (cm^{-1}): 2475 (w), 1926 (s), 1843 (s), 1406 (m), 1302 (m), 1217 (m), 1124 (m), 1048 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.25 (d, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.59 (s, 2H), 7.56 (dd, *J* = 4.3, 2.5 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.30 (m, 4H), 7.21 (m, 1H), 6.20 (m, 3H), 4.68 (dd, *J* = 6.3, 2.3 Hz, 1H), 3.81 (q, *J* = 7.4 Hz, 1H), 2.45 (dd, *J* = 6.3, 4.3 Hz, 1H), 2.12 (s, 3H), 1.39 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 228.9, 224.6, 146.0, 144.2, 143.3, 141.9, 141.5, 136.1, 136.0, 134.6, 128.4 (2), 127.6 (2), 126.3, 111.4, 107.9, 105.7, 105.6, 105.4, 70.1, 47.5, 38.5, 18.9, 18.1. HRMS (ESI) Calcd for $C_{25}H_{26}BMoN_6O_3$ $[M + H]^+$: 567.1208. Found: 567.1207.

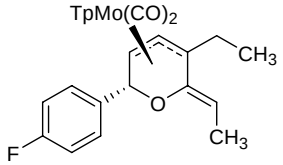


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(6*S*,6*S*)-η-(2,3,4)-6-ethyl-5-oxo-6-phenyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, 114

Following the *general procedure A,* starting material **91i** (100 mg, 0.173 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (4.0 mL) and reacted with HBF_4 (54 wt% in Et_2O, 36 μL, 0.224 mmol, 1.3 equiv). To the isolated diene salt redissolved in CH_2Cl_2 (4.0 mL) was added 4-fluorophenylmagnesium bromide (1.0 M in THF, 0.52 mL, 0.517 mmol, 3.0 equiv). Purification by gravity chromatography gave a complex mixture of products, of which, only **114** (21 mg, 22%) was isolated cleanly as a yellow solid (Note: The product **114** did not incorporate the Grignard reagent, and as such, its inclusion in the reaction sequence may not be necessary).

114: TLC: R_f = 0.47 (25% EtOAc in hexanes). IR (cm^{-1}): 3146 (w), 3127 (w), 2980 (w), 2490 (m), 1961 (s), 1876 (s), 1660 (s), 1505 (m), 1447 (m),1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.58 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.71

(d, *J* = 1.9 Hz, 1H), 7.68 (dd, *J* = 4.4, 2.2 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 2.2 Hz, 1H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.31 (t, *J* = 2.2 Hz, 1H), 6.24 (t, *J* = 2.2 Hz, 1H), 6.16 (t, *J* = 2.2 Hz, 1H), 4.69 (dd, *J* = 5.7, 2.2 Hz, 1H), 1.92 (app sextet, *J* = 7.6 Hz, 1H), 1.80 (app sextet, *J* = 7.3 Hz, 1H), 0.68 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 226.5, 223.8, 198.5, 147.7, 143.1, 141.6, 139.1, 136.5, 134.8, 128.6 (2), 127.7, 125.5 (2), 108.4, 106.5, 106.1, 105.8, 85.1, 65.7, 65.0, 31.8, 7.6. HRMS (ESI) Calcd for $C_{24}H_{23}BMoN_6O_4$ $[M + H]^+$: 568.0928. Found: 568.0949.



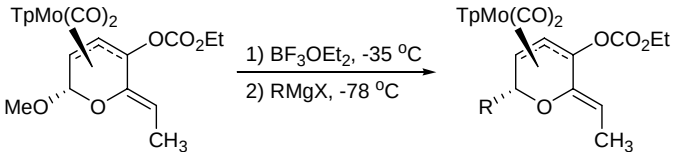
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-3-ethyl-2-(*Z*)-ethylidene-6-(4-fluorophenyl)-2,6-dihydro-6*H*-pyran-3-yl]molybdenum, 115

Following the *general procedure A,* starting material **91b** (152 mg, 0.286 mmol, 1.0 equiv) was dissolved in 4.0 mL CH_2Cl_2, and reacted with HBF_4 (54 wt% in Et_2O, 60 μL, 0.371 mmol, 1.3 equiv). To the isolated diene salt dissolved in 10 mL CH_2Cl_2 was added 4-fluorophenylmagnesium bromide (1.0 M in THF, 860 μL, 0.857 mmol, 3.0 equiv). After concentration of the washed organic layer, some of the pure product crashed out of solution before being loaded onto the column (with a minimal amount of CH_2Cl_2). Purification of the remaining material by gravity chromatography (33% EtOAc in hexanes) gave 123 mg total (72%) of pure product **115** as an orange solid.

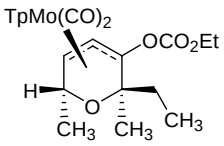
115: TLC: R_f = 0.51 (25% EtOAc in hexanes). IR (cm^{-1}): 2925 (w), 2484 (w), 1928 (s), 1843 (s), 1506 (m), 1406 (m), 1303 (m), 1216 (m), 1117 (m), 1048 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.45 (d, *J* = 1.6 Hz, 1H), 7.66 (d, *J* = 1.6 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 7.39 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.06 (t, *J* = 9.0 Hz, 2H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.18 (m, 2H), 5.19 (s, 1H), 5.05 (q, *J* = 6.7 Hz,

1H), 4.20 (dd, *J* = 7.4, 1.6 Hz, 1H), 4.00 (d, *J* = 7.4 Hz, 1H), 2.50 (app sextet, *J* = 7.4 Hz, 1H), 1.73 (d, *J* = 7.0 Hz, 3H), 1.51 (app sextet, *J* = 7.4 Hz, 1H), 1.24 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 233.4, 226.2, 163.4, 161.0, 147.3, 147.1, 145.9, 141.9, 139.3, 136.6, 136.0, 134.7, 127.5, 127.4, 115.6, 115.3, 105.9, 105.7, 105.5, 103.4, 101.1, 74.9, 74.5, 59.6, 29.5, 16.7, 10.6. HRMS (ESI) Calcd for $C_{26}H_{27}BFMoN_6O_3$ $[M + H]^+$: 599.1270. Found: 599.1268.

General reaction procedure for INA sequence with carbonates:



Starting material was dissolved in dry, degassed CH_2Cl_2, and cooled to -35 °C. Freshly distilled $BF_3{\cdot}OEt_2$ was added dropwise, and the reaction was stirred for 20-30 minutes allowing the temperature to remain above -15 °C. The reaction was cooled to -78 °C and allowed to stir for 3 minutes for equilibration. Then the indicated Grignard was added dropwise to the diene, the reaction was stirred for 3 minutes after which TLC indicated the appearance of a new product. The reaction mixture was washed two times with a 1:1 mixture of water and aqueous ammonium chloride solution (2x20 mL), dried ($MgSO_4$), filtered and concentrated on rotavap. The resulting residue was purified by gravity chromatography (10% EtOAc in hexanes) on silica gel neutralized with 5% Et_3N.

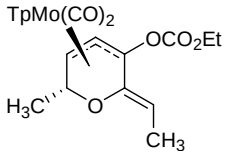


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-2-ethyl-3-ethoxycarbonyloxy-2,6-dimethyl-3,6-dihydro-2*H*-pyran-3-yl]molybdenum, 94

This product was formed as the undesired major compound using unoptimized conditions.

Carbonate **81** (30 mg, 0.051 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 at room temperature, and cooled to 0 ^oC. Tetrafluoroboric acid was added (54 wt% in Et_2O, 14 μL, 0.85 mmol, 1.7 equiv), and the reaction was stirred for 2 hours before being cooled to -78 ^oC. Methylmagnesium bromide was then added (68 μL, 0.17 mmol, 3.4 equiv) dropwise, and the reaction was stirred for three minutes. The reaction was quenched with ice, diluted with water (10 mL), and CH_2Cl_2 (10 mL). The organic layer was dried over $MgSO_4$, and concentrated, and the resulting residue was purified by flash chromatography on silica gel neutralized with 5% Et_3N, eluting with 10% EtOAc in hexanes to afford pure product **94** (14.4 mg, 48%) as a yellow solid.

94: TLC: R_f = 0.47 (25% EtOAc in hexanes). IR (cm^{-1}): 2924 (m), 1940 (s), 1855 (s), 1754 (m), 1406 (s), 1308 (m), 1219 (s), 1120 (m), 1051 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.42 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 1.9 Hz, 1H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.46 (d, *J* = 1.6 Hz, 1H), 6.22 (t, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.14 (t, *J* = 2.2 Hz, 1H), 4.95 (d, *J* = 8.3 Hz, 1H), 4.12 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.07 (q, *J* = 6.7 Hz, 1H), 3.92 (dq, *J* = 10.8, 7.3 Hz, 1H), 3.80 (dq, *J* = 10.8, 7.3 Hz, 1H), 2.25 (app sextet, *J* = 6.7 Hz, 1H), 1.97 (app sextet, *J* = 7.3 Hz, 1H), 1.61 (s, 3H), 1.59 (s, 3H), 1.08 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H).. HRMS (ESI) Calcd for $C_{23}H_{30}BMoN_6O_6$ $[M + H]^+$: 595.1368. Found: 595.1380.

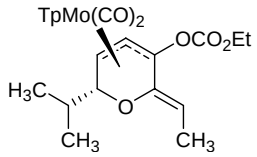


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-ethoxycarbonyloxy-6-methyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 117a

Following the *general procedure A*, starting material **81** (80 mg, 0.135 mmol, 1.0 equiv) was dissolved in 4.0 mL CH_2Cl_2, and reacted with freshly distilled $BF_3{\cdot}OEt_2$ (51 μL, 0.405 mmol, 3.0 equiv) and methylmagnesium chloride (3.0 M in THF, 160 μL, 0.473 mmol, 3.5 equiv).

Purification by gravity chromatography gave 43.6 mg (56%) of pure product **117a** as an orange solid.

117a: TLC: R_f = 0.45 (25% EtOAc in hexanes). IR (cm^{-1}): 2923 (w), 1940 (s), 1858 (s), 1758 (s), 1408 (m), 1241 (s), 1196 (s), 1123 (m), 1048 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.52 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 7.61 (app t, *J* = 2.7 Hz, 2H), 7.58 (d, *J* = 2.3 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 6.27 (t, *J* = 2.3 Hz, 1H), 6.21 (t, *J* = 2.0 Hz, 1H), 6.19 (t, *J* = 2.3 Hz, 1H), 5.02 (q, *J* = 7.0 Hz, 1H), 4.25 (m, 2H), 4.21 (d, *J* = 8.2 Hz, 1H), 4.15 (m, 1H), 4.06 (dd, *J* = 7.8, 1.6 Hz, 1H), 1.66 (d, *J* = 7.0 Hz, 3H), 1.60 (d, *J* = 6.3 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 229.0, 224.9, 153.9, 147.2, 146.5, 144.3, 139.5, 136.2, 136.1, 134.5, 107.2, 106.1, 105.6, 105.1, 100.4, 69.7, 65.3, 65.0, 59.9, 25.0, 14.3, 10.0. HRMS (ESI) Calcd for $C_{22}H_{26}BMoN_6O_6$ $[M + H]^+$: 579.1055. Found: 579.1058.

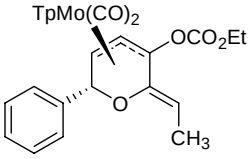


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-ethoxycarbonyloxy-6-(2-propyl)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 117b

Following the *general procedure A,* starting material **81** (50 mg, 0.084 mmol, 1.0 equiv) was dissolved in 3.0 mL CH_2Cl_2, and reacted with freshly distilled $BF_3{\cdot}OEt_2$ (32 μL, 0.253 mmol, 3.0 equiv) and isopropylmagnesium chloride (2.0 M in Et_2O, 150 μL, 0.295 mmol, 3.5 equiv). Purification by gravity chromatography gave 12.7 mg (25%) of pure product **117b** as an orange solid.

117b: TLC: R_f = 0.25 (17% EtOAc in hexanes). IR (cm^{-1}): 2959 (w), 2924 (w), 1946 (s), 1865 (s), 1762 (m), 1408 (m), 1304 (m), 1242 (s), 1213 (m), 1199 (m), 1050 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.51 (d, *J* = 1.9 Hz, 1H), 8.02 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 6.27 (t, *J* = 2.2 Hz, 1H),

6.22 (t, *J* = 2.2 Hz, 1H), 6.15 (t, *J* = 2.2 Hz, 1H), 4.92 (q, *J* = 7.0 Hz, 1H), 4.26-4.20 (m, 2H), 4.17-4.10 (m, 2H), 3.70 (d, *J* = 7.9 Hz, 1H), 1.98 (m, 1H), 1.69 (d, *J* = 7.0, 3H), 1.28 (d, *J* = 7.3 Hz, 3H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.12 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 229.2, 225.0, 153.8, 147.2, 146.5, 145.1, 139.4, 136.2, 136.1, 134.5, 106.9, 106.1, 105.7, 105.0, 99.1, 78.9, 65.8, 64.9, 57.0, 36.9, 20.1, 19.8, 14.3, 10.1. HRMS (ESI) Calcd for $C_{24}H_{30}BMoN_6O_6$ $[M + H]^+$: 607.1368. Found: 607.1373.

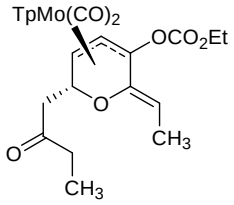


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-ethoxycarbonyloxy-6-phenyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 117c

Following the *general procedure A,* starting material **81** (100 mg, 0.169 mmol, 1.0 equiv) was dissolved in 5.0 mL CH_2Cl_2, and reacted with freshly distilled $BF_3{\cdot}OEt_2$ (64 μL, 0.507 mmol, 3.0 equiv) and phenylmagnesium bromide (3.0 M in Et_2O, 200 μL, 0.591 mmol, 3.5 equiv). Purification by gravity chromatography gave 73.8 mg (68%) of pure product **117c** as an orange solid.

117c: TLC: R_f = 0.35 (25 % EtOAc in hexanes). IR (cm^{-1}): 1948 (s), 1868 (s), 1761 (m), 1408 (w), 1303 (w), 1243 (m), 1198 (m), 1050 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.56 (d, *J* = 2.0 Hz, 1H), 8.08 (d, *J* = 2.0 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.29 (t, *J* = 2.3 Hz, 1H), 6.18 (t, *J* = 2.3 Hz, 1H), 6.17 (t, *J* = 2.3 Hz, 1H), 5.13 (s, 1H), 5.04 (q, *J* = 7.0 Hz, 1H), 4.33-4.15 (m, 2H), 4.30 (d, *J* = 7.8 Hz, 1H), 4.17 (d, *J* = 7.4 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 229.6, 224.5, 153.8, 147.2, 146.7, 145.1, 144.1, 139.7, 136.2 (2), 134.6, 128.8 (2), 128.1, 126.8 (2), 106.5, 106.1, 105.7, 105.1, 99.4, 76.1, 65.0, 64.8, 59.2, 14.4, 10.0. HRMS (ESI) Calcd for

$C_{27}H_{28}BMoN_6O_6$ $[M + H]^+$: 641.1212. Found: 641.1215.

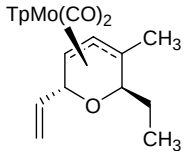


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(3*S*,6*R*)-η-(3,4,5)-2-(*Z*)-ethylidene-3-ethoxycarbonyloxy-6-(2-oxo-butyl)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 117d

To a solution of carbonate **81** (44 mg, 0.743 mmol, 1.0 equiv) in CH_2Cl_2 (1.0 mL) at -50 °C was added borontrifluoride diethyletherate (42 μL, 0.334 mmol, 4.5 equiv), and the reaction was stirred for 20 mins, and then cooled to -78 °C. To a separate flask of THF (1.0 mL) at -78 °C was added lithium hexamethyldisilazide (1.0 M in THF, 0.38 mL, 0.38 mmol, 5.1 equiv), followed by very slow addition of methyl ethyl ketone (33.5 mL, 0.372 mmol, 5.0 equiv). The enolate was stirred for 10 minutes. Then the solution of the molybdenum complex was cannulated into stirring enolate. The reaction was stirred for an additional 10 minutes, then poured directly into a separatory funnel containing CH_2Cl_2 (10 mL) and a 1:1 mixture of aqueous ammonium chloride and water (15 mL). The organic layer was washed once more, dried, filtered and concentrated under reduced pressure. Purification by chromatography on silica gel neutralized with 5% Et_3N, and eluting with 10% EtOAc in hexanes provided pure product **117d** (26.6 mg, 57%) as an orange solid.

117d: TLC: R_f = 0.27 (25% EtOAc in hexanes). IR (cm^{-1}): 2978 (w), 2482 (w), 1943 (s), 1861 (s), 1757 (m), 1711 (m), 1407 (m), 1303 (m), 1241 (s), 1194 (s), 1121 (m), 1048 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.51 (d, *J* = 1.6 Hz, 1H), 8.00 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.50 (d, *J* = 2.7 Hz, 1H), 6.27 (t, *J* = 2.3 Hz, 1H), 6.21 (t, *J* = 2.0 Hz, 1H), 6.15 (t, *J* = 2.3 Hz, 1H), 5.01 (q, *J* = 7.0 Hz, 1H), 4.54 (ddd, *J* = 7.0, 5.5, 1.6 Hz, 1H), 4.28-4.14 (m, 4H), 3.12 (dd, *J* = 15.7, 7.4 Hz, 1H), 2.89 (dd, *J* = 15.5, 5.5 Hz, 1H), 2.53 (q, *J* = 7.4 Hz, 2H), 1.60 (d, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.08 (t, *J*

= 7.0 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 227.9, 224.8, 209.5, 154.0, 147.2, 146.4, 144.0, 139.8, 136.3, 136.2, 134.5, 106.7, 106.1, 105.7, 105.1, 100.8, 70.4, 65.1, 64.9, 58.2, 51.3, 37.2, 14.3, 10.0, 7.7. HRMS (ESI) Calcd for $C_{25}H_{30}BMoN_6O_7$ $[M + H]^+$: 635.1318. Found: 635.1322.

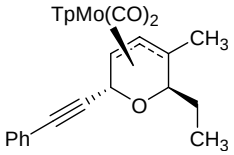


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-2-ethyl-3-methyl-6-vinyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 120

Starting material **110g** (198 mg, 0.385 mmol, 1.0 equiv) was dissolved in 16 mL of dichloromethane and cooled to -40 °C. Tetrafluoroboric acid (54 wt% in Et_2O, 81.5 μL, 0.501 mmol, 1.3 equiv) was added dropwise and the reaction was stirred for 3 minutes. Then sodium cyanoborohydride was added dropwise (1.0 M in THF, 770 μL, 0.770 mmol, 2.0 equiv) and the reaction was stirred for an additional 3 minutes, after which TLC revealed the formation of a new product. The reaction was quenched with 10 mL of water and the organic layer was washed with water (2x50 mL), dried over $MgSO_4$, filtered and concentrated under low pressure. The crude material was purified by chromatography on silica gel neutralized with 5% Et_3N (gravity flow, eluting with 10% EtOAc in hexanes) to provide pure product **120** (157 mg, 80%) as an orange solid.

120: TLC: R_f = 0.56 (25% EtOAc in hexanes). IR (cm^{-1}): 2359 (w), 1925 (vs), 1839 (vs), 1407 (w), 1304 (w), 1117 (w), 1048 (m). ^{1}H NMR [600 MHz, $CDCl_3$]: δ 8.47 (s, 1H), 7.80 (s, 1H), 7.63 (s, 1H), 7.61 (s, 1H), 7.54 (s, 1H), 7.47 (s, 1H), 6.20 (m, 3H), 6.17 (ddd, *J* = 17.4, 11.4, 7.1 Hz, 1H), 5.49 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.31 (dd, *J* = 10.5, 1.0 Hz, 1H), 5.29 (s, 1H), 4.43 (d, *J* = 5.7 Hz, 1H), 3.99 (s, 2H), 3.70 (dd, *J* = 9.5, 2.4 Hz, 1H), 1.99 (m, 1H), 1.91 (m, 1H), 1.75 (s, 3H), 0.96 (t, *J* = 8.1 Hz, 3H). ^{13}C NMR [150 MHz, $CDCl_3$]: δ 233.2, 228.8, 146.4, 146.3, 139.7,

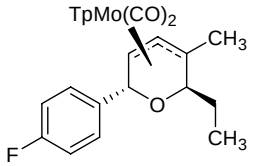
139.3, 136.6, 135.9, 134.4, 117.2, 105.7, 105.6, 105.3, 99.2, 78.0, 74.0, 73.1, 61.7, 24.6, 23.9, 11.6. HRMS (ESI) Calcd for $C_{21}H_{26}BMoN_6O_3$ $[M + H]^+$: 519.1208. Found: 519.1221.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-2-ethyl-6-ethynylphenyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 121

Starting material **110h** (169 mg, 0.286 mmol, 1.0 equiv) was dissolved in 16 mL of dichloromethane and cooled to -40 °C. Tetrafluoroboric acid (54 wt% in Et_2O, 60 μL, 0.371 mmol, 1.3 equiv) was added dropwise and the reaction was stirred for 3 minutes. Then sodium cyanoborohydride was added dropwise (1.0 M in THF, 570 μL, 0.570 mmol, 2.0 equiv) and the reaction was stirred for an additional 3 minutes, after which TLC revealed the formation of a new product. The reaction mixture was washed with water (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated under low pressure. The crude material was purified by flash chromatography on silica gel eluting with 25% EtOAc in hexanes) to provide 148 mg of product **121** (87%) as an orange solid. Recrystalization from CH_2Cl_2 and hexanes provided analytically pure material.

121: TLC: R_f = 0.46 (25% EtOAc in hexanes). IR (cm^{-1}): 2480 (w), 1927 (s), 1841 (s), 1407 (m), 1304 (m), 1207 (w), 1117 (w), 1048 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.46 (d, *J* = 1.6 Hz, 1H), 7.81 (d, *J* = 1.9 Hz, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 1.6 Hz, 1H), 7.54 (m, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 7.35 (m, 3H), 6.22 (app s, 2H), 6.20 (t, *J* = 1.9 Hz, 1H), 4.86 (d, *J* = 1.6 Hz, 1H), 4.18 (dd, *J* = 7.3, 1.9 Hz, 1H), 3.98 (br d, *J* = 7.6 Hz, 2H), 2.07 (m, 1H), 1.97 (m, 1H), 1.81 (s, 3H), 1.02 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 232.6, 228.2, 146.5, 146.3, 139.8, 136.6, 135.9, 134.5, 132.0 (2), 128.4 (3), 123.1, 105.8, 105.7, 105.4, 101.0, 89.8, 85.4, 77.4, 74.8, 64.1, 61.1, 24.3, 24.0, 11.4. HRMS (ESI) Calcd for $C_{27}H_{28}BMoN_6O_3$ $[M + H]^+$: 593.1365. Found: 593.1367.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-6-ethyl-2-(4-fluorophenyl)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 122

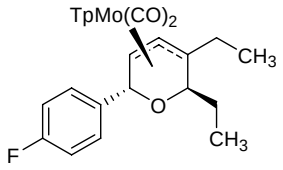
(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-6-ethyl-2-(4-fluorophenyl)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, (+)-**122**

Starting material **110e** (1.41 g, 2.42 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (15.0 mL), and cooled to -30 ^oC. To the solution was added HBF_4 (54 wt% in Et_2O, 0.51 mL, 3.15 mmol, 1.3 equiv), and the reaction was stirred for 3 minutes. To the reaction mixture was added sodium cyanoborohydride solution (1.0 M in THF, 4.85 mL, 4.85 mmol, 2.0 equiv), maintaining the temperature between -30 and -20 ^oC. The reaction was stirred for 3 minutes, after which TLC revealed formation of a new product, and complete disappearance of starting material. The reaction mixture was poured into a separatory funnel containing a 1:1 mixture of water and aqueous saturated NH_4Cl solution, and the organic layer was washed (2 x 15 mL), then dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified by gravity chromatography on silica gel buffered with 5% Et_3N (eluting with 10% EtOAc in hexanes) to afford the pure product **122** (1.24 g, 88%) of as an orange solid.

The exact same procedure was used in the conversion of (+)-**110e** (98.3% ee) to (+)-**122**, which was determined to be 98.3% ee by chiral HPLC.

(+)-**122:** TLC: R_f = 0.39 (17% EtOAc in hexanes). $[\alpha]_D^{20}$ +332 (98.3% ee, *c* 0.06, CH_2Cl_2). IR (cm^{-1}): 2931 (w), 2478 (w), 2358 (w), 1925 (s), 1839 (s), 1505 (m), 1406 (m), 1304 (m), 1218 (m), 1117 (m), 1048 (m). ^1H NMR [400 MHz, $CDCl_3$]: δ 8.50 (d, *J* = 1.9 Hz, 1H), 7.81 (d, *J* = 1.9 Hz, 1H), 7.68 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.10 (t, *J* = 8.9 Hz, 2H), 6.24 (t, *J* = 2.2 Hz,

1H), 6.23 (t, *J* = 1.9 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 5.04 (s, 1H), 4.25 (dd, *J* = 7.3, 1.9 Hz, 1H), 4.20 (d, *J* = 7.3 Hz, 1H), 3.28 (dd, *J* = 9.8, 2.5 Hz, 1H), 2.00 (m, 1H), 1.83 (m, 1H), 1.74 (s, 3H), 0.84 (s, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 233.5, 229.0, 163.7, 161.2, 146.5, 146.3, 139.6, 137.6, 136.7, 136.0, 134.5, 130.2, 130.1, 115.2, 115.0, 105.8, 105.7, 105.4, 99.8, 78.3, 73.3, 60.3, 24.1, 23.9, 11.3. HRMS (ESI) Calcd for $C_{25}H_{26}BFMoN_6O_3$ $[M]^+$: 586.1192. Found: 586.1198. HPLC: Daicel Chiralpak AS-RH, gradient solvent system was used (% MeCN in H_2O w/0.1% TFA) = 0-40 mins, 50%; 40-60 mins, 50% to 60%, 1.0 mL/min, 254 nm, t_r = 45.65 min. Enantiomer: t_r = 49.52 min.

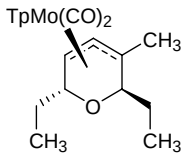


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-5,6-diethyl-2-(4-fluorophenyl)-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 123

Starting material **115** (123 mg, 0.206 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10.0 mL) and cooled to -30 °C. To the solution was added HBF_4 (54 wt% in Et_2O, 44 μL, 0.268 mmol, 1.3 equiv), and the reaction was stirred for 3 minutes. To the reaction mixture was added sodium cyanoborohydride solution (1.0 M in THF, 410 μL, 0.413 mmol, 2.0 equiv), maintaining the temperature between -30 °C and -25 °C. The reaction was stirred for 3 minutes, after which TLC revealed formation of a new product, and complete disappearance of starting material. The reaction mixture was poured into a separatory funnel containing a 1:1 mixture of water and aqueous saturated NH_4Cl solution, and the organic layer was washed (2 X 20 mL), then dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified by gravity chromatography on silica gel (eluting with 33% EtOAc in hexanes) to afford 98.9 mg (80%) of the product **123** as an orange solid.

123: TLC: R_f = 0.52 (25% EtOAc in hexanes). IR (cm^{-1}): 2968 (w), 2930 (w), 1925 (s),

1838 (s), 1504 (m), 1407 (m), 1304 (m), 1216 (m), 1117 (m), 1048 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.48 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 1.6 Hz, 1H), 7.69 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.10 (t, *J* = 8.6 Hz, 2H), 6.23 (t, *J* = 2.0 Hz, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 6.20 (t, *J* = 2.0 Hz, 1H), 4.99 (s, 1H), 4.36 (d, *J* = 7.4 Hz, 1H), 4.26 (dd, *J* = 7.4, 1.6 Hz, 1H), 3.43 (dd, *J* = 10.6, 2.7 Hz, 1H), 2.37 (app sextet, *J* = 7.0 Hz, 1H), 2.03 (m, 1H), 1.85 (m, 1H), 1.54 (app sextet, *J* = 7.4 Hz, 1H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 234.3, 228.8, 163.7, 161.3, 146.49, 146.45, 139.5, 137.3, 136.6, 135.9, 134.5, 130.3, 130.2, 115.2, 115.0, 108.4, 105.8 (2), 105.5, 78.7, 73.4, 70.4, 59.6, 31.0, 23.5, 15.6, 11.0. HRMS (ESI) Calcd for $C_{26}H_{29}BFMoN_6O_3$ $[M + H]^+$: 601.1427. Found: 601.1423.

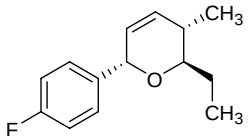


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,3*S*,6*R*)-η-(3,4,5)-2,6-diethyl-3-methyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 124

Starting material **120** (24.0 mg, 0.0469 mmol, 1.0 equiv) and 10 mol% palladium on activated carbon (10.0 mg, 0.094 mmol, 0.20 equiv), were added to a round bottom flask, which was placed under vacuum. The flask was then placed under hydrogen atmosphere, and 1 mL each of THF and methanol were added in succession to dissolve the complex. The reaction was stirred under H_2 atmosphere for 24 hours, and then filtered over Celite with dichloromethane and 50% EtOAc in hexanes. The mixture was concentrated to provide pure product **124**(21.6 mg 90%) as an orange solid.

124: TLC: R_f = 0.62 (25% EtOAc in hexanes). IR (cm^{-1}): 2927 (w), 1910 (vs), 1808 (vs), 1406 (w), 1303 (m), 1116 (m), 1049 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.46 (d, *J* = 1.9 Hz, 1H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.51 (d, *J* = 1.9 Hz,

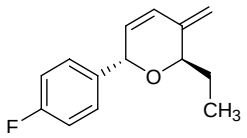
1H), 7.45 (d, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 1.9 Hz, 1H), 6.17 (t, *J* = 2.2 Hz, 1H), 3.96 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.90 (d, *J* = 7.3 Hz, 1H), 3.81 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.62 (d, *J* = 7.6 Hz, 1H), 1.99 (m, 1H), 1.89 (m, 1H), 1.80-1.71 (m, 2H), 1.74 (s, 3H), 1.04 (t, *J* = 7.6, 3H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 233.4, 229.0, 146.4, 146.3, 139.6, 136.5, 135.8, 134.3, 105.7, 105.6, 105.3, 99.0, 78.1, 73.8, 73.0, 63.6, 28.9, 24.3, 23.9, 11.6, 11.5. HRMS (ESI) Calcd for $C_{21}H_{28}BMoN_6O_3$ $[M + H]^+$: 521.1365. Found: 521.1342.



(±)-(2*R*,3*S*,6*S*)-2-Ethyl-6-(4-fluoro-phenyl)-3-methyl-3,6-dihydro-2*H*-pyran, 125

To a solution of the starting complex **122** (50 mg, 0.0856 mmol, 1.0 equiv) in acetonitrile (2.0 mL) at room temperature was added concentrated HCl (12 M, 0.10 mL, 1.20 mmol, 14 equiv) dropwise. The reaction was stirred for 5 minutes, and then diluted with dichloromethane (10 mL) and washed with saturated $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with dichloromethane (10 mL), and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Chromatography on silica gel, eluting with 25% EtOAc in hexanes provided pure product **125** (16.5 mg, 88%) as a clear oil.

125: TLC: R_f = 0.66 (17% EtOAc in hexanes). IR (cm^{-1}): 2962 (m), 2928 (m), 2875 (w), 1603 (m), 1507 (s), 1222 (s). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 7.36 (dd, *J* = 8.6, 5.7 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.92 (dt, *J* = 10.2, 3.2, 3.2 Hz, 1H), 5.84 (dt, *J* = 10.2, 1.9, 1.9 Hz, 1H), 5.18 (d, *J* = 1.9 Hz, 1H), 3.01 (dt, *J* = 8.3, 8.3, 2.9 Hz 1H), 2.14 (m, 1H), 1.60 (m, 1H), 1.47 (m, 1H), 0.97 (d, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 163.6, 161.2, 137.3, 132.8, 129.9, 129.8, 126.6, 115.2, 115.0, 75.9, 72.7, 34.1, 25.9, 18.0, 10.3. HRMS (ESI) Calcd for $C_{14}H_{16}FO$ $[M - H]^+$: 219.1179. Found: 219.1180.



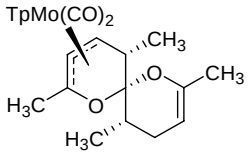
(±)-(2*R*,6*S*)-2-Ethyl-6-(4-fluoro-phenyl)-3-methylene-3,6-dihydro-2*H*-pyran, 127

(-)-(2*R*,6*S*)-2-Ethyl-6-(4-fluoro-phenyl)-3-methylene-3,6-dihydro-2*H*-pyran, (-)-**127**

Starting material **122** (75 mg, 0.128 mmol, 1.0 equiv) was dissolved in a 3:1 solution of THF/H_2O (2.5 mL) and Et_3N (27 μL, 0.193 mmol, 1.5 equiv) at 0 ^oC. A solution of ceric ammonium nitrate (563 mg, 1.03 mmol, 8.0 equiv) in 2.5 mL of water was added dropwise over 5 minutes. When addition was complete, the dark orange/red solution had changed to light yellow. The reaction was allowed to stir at room temperature for 10 minutes, and then partitioned between CH_2Cl_2 and water (10 mL each). The organic layer was washed with brine, dried over $MgSO_4$, concentrated and chromatographed on silica gel (10% EtOAc in hexanes) to afford the product **127** as a clear oil (13.6 mg, 49%).

The exact same procedure was used to convert (+)-**122** of 98.3 %ee to (-)-**127**.

(-)-**127:** TLC: R_f = 0.70 (17% EtOAc in hexanes). $[\alpha]_D^{20}$ -85.5 (*c* 0.565, CH_2Cl_2). IR (cm^{-1}): 2959 (m), 2924 (s), 2852 (m), 1604 (w), 1509 (s), 1462 (w), 1222 (s). ^1H NMR [400 MHz, $CDCl_3$]: δ 7.35 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.03 (t, *J* = 9.0 Hz, 2H), 6.33 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.89 (d, *J* = 10.2 Hz, 1H), 5.22 (s, 1H), 4.94 (s, 1H), 4.87 (s, 1H), 4.19 (dd, *J* = 8.6, 5.5 Hz, 1H), 1.83 (m, 1H), 1.68 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 163.8, 161.4, 141.8, 136.6, 129.9, 129.7, 129.6, 126.7, 115.5, 115.3, 111.0, 75.9, 71.1, 25.6, 10.3. HRMS (ESI) Calcd for $C_{14}H_{14}FO$ $[M - H]^+$: 217.1023. Found: 217.1023.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*R*,6*R*,11*S*)-η-(2,3,4)-2,5,8,11-tetramethyl-1,7-dioxa-spiro-[5,5]-undec-3,8-diene-3-yl]molybdenum, 129

Starting material **110a** (30 mg, 0.0598 mmol, 1.0 equiv) and $Eu(fod)_3$ (9.3 mg, 0.090 mmol, 0.15 equiv) were dissolved in 1.2 mL methyl vinyl ketone (14.6 mmol, 244 equiv) and stirred at room temperature for 37 h. The reaction mixture was diluted with 0.5 mL of a solution of 10% EtOAc in hexanes, and added directly to a column prepared using this solvent (and neutralized with 5% Et_3N). Elution by flash chromatography provided 12.0 mg of the product **130** (35%) as a red/orange solid.

130: TLC: R_f = 0.43 (17% EtOAc in hexanes). IR (cm^{-1}): 2920 (w), 1917 (s), 1827 (s), 1407 (m), 1304 (m), 1213 (w), 1172 (w), 1122 (m), 1048 (m). ^{1}H NMR [400 MHz, $CDCl_3$]: δ 8.37 (d, *J* = 1.9 Hz, 1H), 7.95 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 1.9 Hz,1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.45 (d, *J* = 2.5 Hz, 1H), 6.22-6.16 (m, 3H), 4.53 (br s, 1H), 4.10 (d, *J* = 6.7 Hz, 1H), 3.83 (dd, *J* = 7.0, 1.0 Hz, 1H), 2.66 (q, *J* = 7.3 Hz, 1H), 2.11 (s, 3H), 2.05-1.93 (m, 1H), 1.86-1.78 (m, 2H), 1.75 (s, 3H), 1.24 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 235.8, 228.4, 147.1, 147.0, 145.7, 139.2, 136.6, 135.7, 134.8, 134.5, 105.7, 105.4, 105.3, 102.8, 97.2, 72.6, 57.2, 38.7, 31.0, 26.1, 26.0, 19.8, 18.4, 15.8. HRMS (ESI) Calcd for $C_{24}H_{29}BMoN_6O_4$ $[M + H]^+$: 574.1392. Found: 574.1388.

X-Ray Crystallographic Study

Table 19: Crystal data and structure refinement for 100

Identification code	100	
Empirical formula	C28 H31 B Mo N6 O4	
Formula weight	622.34	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.8810(3) Å	α= 113.808(1)°.
	b = 14.0338(5) Å	β= 92.394(2)°.
	c = 14.3864(5) Å	γ = 103.445(2)°.
Volume	1399.30(9) $Å^3$	
Z	2	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	4.207 mm^{-1}	
F(000)	640	
Crystal size	0.23 x 0.22 x 0.03 mm^3	
Theta range for data collection	3.40 to 65.89°.	
Index ranges	-9<=h<=9, -16<=k<=16, -16<=l<=16	
Reflections collected	13963	
Independent reflections	4392 [R(int) = 0.0271]	
Completeness to theta = 65.89°	90.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8842 and 0.4446	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4392 / 0 / 363	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0207, wR2 = 0.0515	
R indices (all data)	R1 = 0.0213, wR2 = 0.0518	
Largest diff. peak and hole	0.316 and -0.347 $e.Å^{-3}$	

Figure 23: ORTEP of (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,3*S*,6*R*)-η-(3,4,5)-2-allyl-2-ethyl-3-methoxy-6-phenyl-2,6-dihydro-2*H*-pyran-3-yl]molybdenum, 100

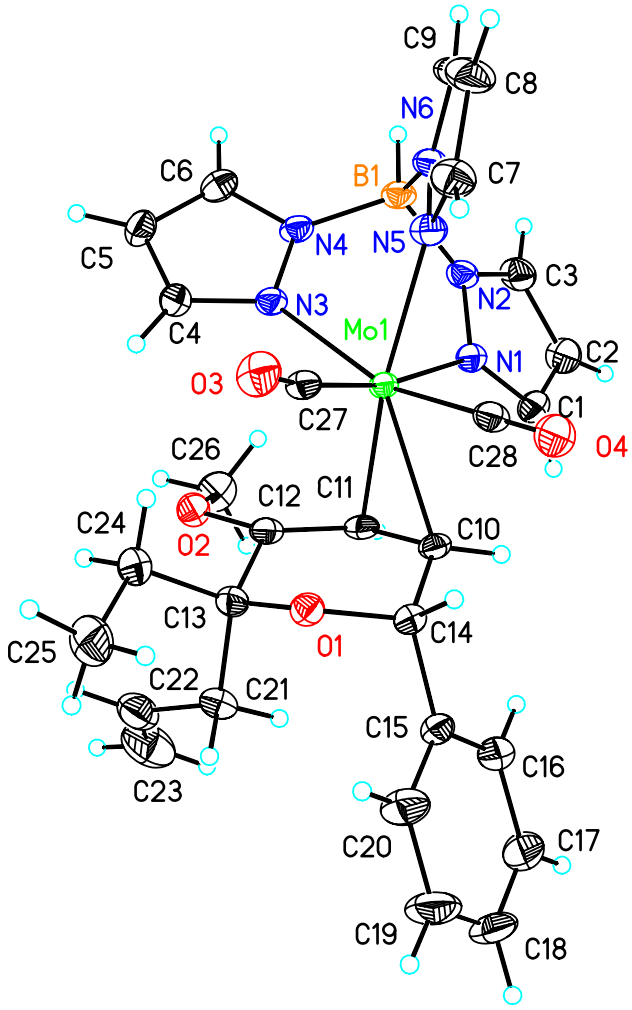


Table 20: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 100. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	4914(3)	12928(2)	3768(2)	22(1)
C(1)	3959(3)	11197(2)	5100(2)	24(1)

C(2)	5440(3)	11952(2)	5779(2)	29(1)
C(3)	5993(3)	12676(2)	5362(2)	27(1)
C(4)	3881(3)	10885(2)	1149(1)	23(1)
C(5)	5356(3)	11563(2)	1022(2)	27(1)
C(6)	6010(3)	12366(2)	1993(2)	25(1)
C(7)	333(3)	12921(2)	3379(2)	30(1)
C(8)	1054(3)	14024(2)	3694(2)	36(1)
C(9)	2839(3)	14186(2)	3912(2)	29(1)
C(10)	530(2)	9244(1)	3274(1)	19(1)
C(11)	2102(3)	9185(1)	2810(1)	19(1)
C(12)	1876(2)	8785(1)	1747(1)	19(1)
C(13)	195(2)	7933(1)	1083(1)	20(1)
C(14)	-1179(3)	8401(1)	2662(1)	20(1)
C(15)	-1603(3)	7385(2)	2867(2)	23(1)
C(16)	-729(3)	7315(2)	3681(2)	31(1)
C(17)	-1278(4)	6397(2)	3870(2)	42(1)
C(18)	-2686(4)	5553(2)	3242(2)	45(1)
C(19)	-3562(3)	5612(2)	2423(2)	46(1)
C(20)	-3029(3)	6526(2)	2240(2)	35(1)
C(21)	402(3)	6812(2)	963(2)	25(1)
C(22)	1732(3)	6384(2)	318(2)	34(1)
C(23)	2917(3)	5997(2)	604(2)	49(1)
C(24)	-182(3)	7946(2)	33(2)	26(1)
C(25)	-1834(3)	7089(2)	-659(2)	38(1)
C(26)	4991(3)	9033(2)	1745(2)	30(1)
C(27)	-260(3)	10352(1)	1748(2)	21(1)
C(28)	-629(3)	10716(1)	3590(2)	23(1)
N(1)	3620(2)	11445(1)	4314(1)	20(1)
N(2)	4905(2)	12363(1)	4487(1)	21(1)
N(3)	3666(2)	11237(1)	2137(1)	20(1)
N(4)	5005(2)	12163(1)	2662(1)	21(1)
N(5)	1594(2)	12438(1)	3400(1)	22(1)
N(6)	3155(2)	13233(1)	3738(1)	22(1)
O(1)	-1311(2)	8135(1)	1581(1)	20(1)
O(2)	3245(2)	8737(1)	1198(1)	22(1)
O(3)	-1338(2)	10257(1)	1109(1)	31(1)

O(4)	-1932(2)	10709(1)	3938(1)	33(1)
Mo(1)	1475(1)	10716(1)	2916(1)	16(1)

Table 21: Bond lengths [Å] and angles [°] for 100

B(1)-N(2)	1.535(3)	C(11)-C(12)	1.387(3)
B(1)-N(4)	1.535(3)	C(11)-Mo(1)	2.2622(18)
B(1)-N(6)	1.547(3)	C(11)-H(11)	1.0000
B(1)-H(1)	1.1146	C(12)-O(2)	1.362(2)
C(1)-N(1)	1.343(2)	C(12)-C(13)	1.527(3)
C(1)-C(2)	1.390(3)	C(13)-O(1)	1.437(2)
C(1)-H(1)	0.9500	C(13)-C(24)	1.536(3)
C(2)-C(3)	1.376(3)	C(13)-C(21)	1.559(3)
C(2)-H(2)	0.9500	C(14)-O(1)	1.439(2)
C(3)-N(2)	1.342(3)	C(14)-C(15)	1.535(2)
C(3)-H(3)	0.9500	C(14)-H(14)	1.0000
C(4)-N(3)	1.337(3)	C(15)-C(16)	1.383(3)
C(4)-C(5)	1.391(3)	C(15)-C(20)	1.392(3)
C(4)-H(4)	0.9500	C(16)-C(17)	1.398(3)
C(5)-C(6)	1.373(3)	C(16)-H(16)	0.9500
C(5)-H(5)	0.9500	C(17)-C(18)	1.376(4)
C(6)-N(4)	1.347(3)	C(17)-H(17)	0.9500
C(6)-H(6)	0.9500	C(18)-C(19)	1.383(4)
C(7)-N(5)	1.333(3)	C(18)-H(18)	0.9500
C(7)-C(8)	1.388(3)	C(19)-C(20)	1.385(3)
C(7)-H(7)	0.9500	C(19)-H(19)	0.9500
C(8)-C(9)	1.373(3)	C(20)-H(20)	0.9500
C(8)-H(8)	0.9500	C(21)-C(22)	1.498(3)
C(9)-N(6)	1.343(3)	C(21)-H(21A)	0.9900
C(9)-H(9)	0.9500	C(21)-H(21B)	0.9900
C(10)-C(11)	1.435(3)	C(22)-C(23)	1.312(4)
C(10)-C(14)	1.519(3)	C(22)-H(22)	0.9500
C(10)-Mo(1)	2.2953(17)	C(23)-H(23A)	0.9500
C(10)-H(10)	1.0000	C(23)-H(23B)	0.9500

C(24)-C(25)	1.526(3)	N(3)-C(4)-H(4)	124.6
C(24)-H(24A)	0.9900	C(5)-C(4)-H(4)	124.6
C(24)-H(24B)	0.9900	C(6)-C(5)-C(4)	104.52(17)
C(25)-H(25A)	0.9800	C(6)-C(5)-H(5)	127.7
C(25)-H(25B)	0.9800	C(4)-C(5)-H(5)	127.7
C(25)-H(25C)	0.9800	N(4)-C(6)-C(5)	109.14(17)
C(26)-O(2)	1.437(2)	N(4)-C(6)-H(6)	125.4
C(26)-H(26A)	0.9800	C(5)-C(6)-H(6)	125.4
C(26)-H(26B)	0.9800	N(5)-C(7)-C(8)	110.67(19)
C(26)-H(26C)	0.9800	N(5)-C(7)-H(7)	124.7
C(27)-O(3)	1.169(2)	C(8)-C(7)-H(7)	124.7
C(27)-Mo(1)	1.935(2)	C(9)-C(8)-C(7)	104.77(19)
C(28)-O(4)	1.161(3)	C(9)-C(8)-H(8)	127.6
C(28)-Mo(1)	1.956(2)	C(7)-C(8)-H(8)	127.6
N(1)-N(2)	1.365(2)	N(6)-C(9)-C(8)	108.85(18)
N(1)-Mo(1)	2.2804(16)	N(6)-C(9)-H(9)	125.6
N(3)-N(4)	1.370(2)	C(8)-C(9)-H(9)	125.6
N(3)-Mo(1)	2.2371(15)	C(11)-C(10)-C(14)	117.56(16)
N(5)-N(6)	1.367(2)	C(11)-C(10)-Mo(1)	70.39(9)
N(5)-Mo(1)	2.2052(15)	C(14)-C(10)-Mo(1)	118.32(12)
N(2)-B(1)-N(4)	111.11(15)	C(11)-C(10)-H(10)	114.5
N(2)-B(1)-N(6)	108.72(16)	C(14)-C(10)-H(10)	114.5
N(4)-B(1)-N(6)	106.61(16)	Mo(1)-C(10)-H(10)	114.5
N(2)-B(1)-H(1)	112.8	C(12)-C(11)-C(10)	116.17(17)
N(4)-B(1)-H(1)	106.1	C(12)-C(11)-Mo(1)	89.96(11)
N(6)-B(1)-H(1)	111.2	C(10)-C(11)-Mo(1)	72.90(10)
N(1)-C(1)-C(2)	110.88(17)	C(12)-C(11)-H(11)	120.7
N(1)-C(1)-H(1)	124.6	C(10)-C(11)-H(11)	120.7
C(2)-C(1)-H(1)	124.6	Mo(1)-C(11)-H(11)	120.7
C(3)-C(2)-C(1)	104.58(17)	O(2)-C(12)-C(11)	123.21(17)
C(3)-C(2)-H(2)	127.7	O(2)-C(12)-C(13)	110.35(15)
C(1)-C(2)-H(2)	127.7	C(11)-C(12)-C(13)	121.23(16)
N(2)-C(3)-C(2)	108.80(17)	O(1)-C(13)-C(12)	110.11(14)
N(2)-C(3)-H(3)	125.6	O(1)-C(13)-C(24)	105.69(15)
C(2)-C(3)-H(3)	125.6	C(12)-C(13)-C(24)	113.05(15)
N(3)-C(4)-C(5)	110.89(17)	O(1)-C(13)-C(21)	109.49(14)

C(12)-C(13)-C(21)	107.10(15)	C(22)-C(23)-H(23B)	120.0
C(24)-C(13)-C(21)	111.40(16)	H(23A)-C(23)-H(23B)	120.0
O(1)-C(14)-C(10)	112.59(14)	C(25)-C(24)-C(13)	114.45(17)
O(1)-C(14)-C(15)	111.93(15)	C(25)-C(24)-H(24A)	108.6
C(10)-C(14)-C(15)	114.77(16)	C(13)-C(24)-H(24A)	108.6
O(1)-C(14)-H(14)	105.5	C(25)-C(24)-H(24B)	108.6
C(10)-C(14)-H(14)	105.5	C(13)-C(24)-H(24B)	108.6
C(15)-C(14)-H(14)	105.5	H(24A)-C(24)-H(24B)	107.6
C(16)-C(15)-C(20)	118.85(19)	C(24)-C(25)-H(25A)	109.5
C(16)-C(15)-C(14)	123.36(18)	C(24)-C(25)-H(25B)	109.5
C(20)-C(15)-C(14)	117.61(18)	H(25A)-C(25)-H(25B)	109.5
C(15)-C(16)-C(17)	120.3(2)	C(24)-C(25)-H(25C)	109.5
C(15)-C(16)-H(16)	119.8	H(25A)-C(25)-H(25C)	109.5
C(17)-C(16)-H(16)	119.8	H(25B)-C(25)-H(25C)	109.5
C(18)-C(17)-C(16)	120.2(2)	O(2)-C(26)-H(26A)	109.5
C(18)-C(17)-H(17)	119.9	O(2)-C(26)-H(26B)	109.5
C(16)-C(17)-H(17)	119.9	H(26A)-C(26)-H(26B)	109.5
C(17)-C(18)-C(19)	119.9(2)	O(2)-C(26)-H(26C)	109.5
C(17)-C(18)-H(18)	120.1	H(26A)-C(26)-H(26C)	109.5
C(19)-C(18)-H(18)	120.1	H(26B)-C(26)-H(26C)	109.5
C(18)-C(19)-C(20)	120.0(2)	O(3)-C(27)-Mo(1)	171.64(16)
C(18)-C(19)-H(19)	120.0	O(4)-C(28)-Mo(1)	176.02(17)
C(20)-C(19)-H(19)	120.0	C(1)-N(1)-N(2)	105.76(15)
C(19)-C(20)-C(15)	120.8(2)	C(1)-N(1)-Mo(1)	134.74(13)
C(19)-C(20)-H(20)	119.6	N(2)-N(1)-Mo(1)	119.47(11)
C(15)-C(20)-H(20)	119.6	C(3)-N(2)-N(1)	109.98(15)
C(22)-C(21)-C(13)	117.15(17)	C(3)-N(2)-B(1)	128.75(16)
C(22)-C(21)-H(21A)	108.0	N(1)-N(2)-B(1)	121.17(15)
C(13)-C(21)-H(21A)	108.0	C(4)-N(3)-N(4)	106.27(15)
C(22)-C(21)-H(21B)	108.0	C(4)-N(3)-Mo(1)	131.97(13)
C(13)-C(21)-H(21B)	108.0	N(4)-N(3)-Mo(1)	121.15(11)
H(21A)-C(21)-H(21B)	107.3	C(6)-N(4)-N(3)	109.17(15)
C(23)-C(22)-C(21)	124.1(2)	C(6)-N(4)-B(1)	128.86(16)
C(23)-C(22)-H(22)	117.9	N(3)-N(4)-B(1)	119.94(15)
C(21)-C(22)-H(22)	117.9	C(7)-N(5)-N(6)	106.41(16)
C(22)-C(23)-H(23A)	120.0	C(7)-N(5)-Mo(1)	131.20(13)

N(6)-N(5)-Mo(1)	122.26(12)	N(5)-Mo(1)-C(11)	161.93(7)
C(9)-N(6)-N(5)	109.29(17)	N(3)-Mo(1)-C(11)	97.48(6)
C(9)-N(6)-B(1)	130.79(17)	C(27)-Mo(1)-N(1)	170.01(6)
N(5)-N(6)-B(1)	119.64(15)	C(28)-Mo(1)-N(1)	100.15(7)
C(13)-O(1)-C(14)	118.30(14)	N(5)-Mo(1)-N(1)	81.39(6)
C(12)-O(2)-C(26)	117.88(15)	N(3)-Mo(1)-N(1)	84.18(6)
C(27)-Mo(1)-C(28)	81.18(8)	C(11)-Mo(1)-N(1)	80.69(6)
C(27)-Mo(1)-N(5)	88.99(7)	C(27)-Mo(1)-C(10)	101.11(7)
C(28)-Mo(1)-N(5)	82.66(7)	C(28)-Mo(1)-C(10)	66.19(7)
C(27)-Mo(1)-N(3)	91.24(7)	N(5)-Mo(1)-C(10)	144.94(6)
C(28)-Mo(1)-N(3)	159.61(7)	N(3)-Mo(1)-C(10)	134.13(6)
N(5)-Mo(1)-N(3)	78.28(6)	C(11)-Mo(1)-C(10)	36.70(7)
C(27)-Mo(1)-C(11)	108.77(7)	N(1)-Mo(1)-C(10)	88.40(6)
C(28)-Mo(1)-C(11)	102.87(7)		

Symmetry transformations used to generate equivalent atoms:

Table 22: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for 100. 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)	25(1)	15(1)	22(1)	8(1)	-1(1)	0(1)
C(1)	30(1)	24(1)	21(1)	13(1)	3(1)	7(1)
C(2)	37(1)	28(1)	21(1)	12(1)	-4(1)	8(1)
C(3)	29(1)	22(1)	23(1)	7(1)	-4(1)	2(1)
C(4)	28(1)	21(1)	19(1)	9(1)	2(1)	7(1)
C(5)	31(1)	30(1)	24(1)	15(1)	12(1)	10(1)
C(6)	21(1)	26(1)	30(1)	17(1)	5(1)	3(1)
C(7)	30(1)	28(1)	34(1)	14(1)	1(1)	12(1)
C(8)	45(1)	24(1)	42(1)	15(1)	3(1)	18(1)
C(9)	44(1)	15(1)	27(1)	8(1)	1(1)	7(1)
C(10)	23(1)	15(1)	20(1)	10(1)	2(1)	3(1)
C(11)	20(1)	14(1)	23(1)	11(1)	-1(1)	3(1)

C(12)	20(1)	14(1)	24(1)	9(1)	4(1)	3(1)
C(13)	20(1)	17(1)	20(1)	6(1)	3(1)	2(1)
C(14)	21(1)	18(1)	20(1)	9(1)	4(1)	3(1)
C(15)	26(1)	20(1)	26(1)	11(1)	11(1)	5(1)
C(16)	44(1)	22(1)	27(1)	12(1)	7(1)	7(1)
C(17)	68(2)	31(1)	36(1)	22(1)	16(1)	18(1)
C(18)	63(2)	25(1)	58(2)	27(1)	28(1)	9(1)
C(19)	42(1)	26(1)	62(2)	19(1)	11(1)	-6(1)
C(20)	31(1)	29(1)	43(1)	18(1)	3(1)	-1(1)
C(21)	26(1)	17(1)	27(1)	7(1)	2(1)	3(1)
C(22)	37(1)	23(1)	37(1)	7(1)	9(1)	8(1)
C(23)	38(1)	35(1)	63(2)	8(1)	8(1)	14(1)
C(24)	29(1)	25(1)	20(1)	8(1)	2(1)	5(1)
C(25)	37(1)	41(1)	27(1)	10(1)	-7(1)	4(1)
C(26)	20(1)	37(1)	36(1)	18(1)	6(1)	7(1)
C(27)	23(1)	16(1)	24(1)	10(1)	6(1)	3(1)
C(28)	29(1)	15(1)	22(1)	7(1)	1(1)	3(1)
N(1)	23(1)	17(1)	19(1)	8(1)	2(1)	3(1)
N(2)	23(1)	15(1)	19(1)	5(1)	-1(1)	1(1)
N(3)	22(1)	15(1)	19(1)	7(1)	0(1)	0(1)
N(4)	21(1)	17(1)	22(1)	10(1)	0(1)	-1(1)
N(5)	24(1)	19(1)	23(1)	9(1)	-1(1)	4(1)
N(6)	28(1)	14(1)	21(1)	7(1)	1(1)	2(1)
O(1)	18(1)	20(1)	20(1)	9(1)	0(1)	2(1)
O(2)	18(1)	23(1)	23(1)	8(1)	5(1)	3(1)
O(3)	29(1)	36(1)	27(1)	16(1)	-5(1)	7(1)
O(4)	29(1)	31(1)	38(1)	13(1)	14(1)	8(1)
Mo(1)	17(1)	13(1)	16(1)	7(1)	1(1)	2(1)

Table 23: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 100.

	x	y	z	U(eq)
H(1)	3278	10589	5180	29
H(2)	5954	11964	6395	34
H(3)	6983	13295	5646	32
H(4)	3128	10255	606	27
H(5)	5809	11489	402	32
H(6)	7011	12968	2166	30
H(7)	-892	12561	3176	35
H(8)	447	14551	3747	43
H(9)	3708	14862	4147	35
H(10)	696	9412	4022	23
H(11)	3212	9221	3200	22
H(14)	-2139	8756	2904	24
H(16)	249	7894	4114	37
H(17)	-677	6357	4433	50
H(18)	-3057	4929	3372	55
H(19)	-4528	5027	1985	55
H(20)	-3644	6566	1681	42
H(21A)	715	6863	1658	30
H(21B)	-763	6274	664	30
H(22)	1716	6394	-338	41
H(23A)	2966	5976	1256	59
H(23B)	3725	5737	158	59
H(24A)	-307	8669	146	31
H(24B)	847	7839	-329	31
H(25A)	-1663	6367	-851	57
H(25B)	-2050	7197	-1280	57
H(25C)	-2849	7152	-289	57
H(26A)	5279	9785	2265	46
H(26B)	5844	8963	1262	46

H(26C)	5040	8555	2082	46
H(1)	6070	13650	3993	19

Table 24: Torsion angles [°] for 100

N(1)-C(1)-C(2)-C(3)	-0.2(2)	C(16)-C(17)-C(18)-C(19)	0.0(4)
C(1)-C(2)-C(3)-N(2)	-0.2(2)	C(17)-C(18)-C(19)-C(20)	-0.5(4)
N(3)-C(4)-C(5)-C(6)	-1.2(2)	C(18)-C(19)-C(20)-C(15)	0.8(4)
C(4)-C(5)-C(6)-N(4)	1.2(2)	C(16)-C(15)-C(20)-C(19)	-0.4(3)
N(5)-C(7)-C(8)-C(9)	-0.1(3)	C(14)-C(15)-C(20)-C(19)	-175.7(2)
C(7)-C(8)-C(9)-N(6)	-0.2(2)	O(1)-C(13)-C(21)-C(22)	170.92(17)
C(14)-C(10)-C(11)-C(12)	31.2(2)	C(12)-C(13)-C(21)-C(22)	-69.7(2)
Mo(1)-C(10)-C(11)-C(12)	-81.26(14)	C(24)-C(13)-C(21)-C(22)	54.4(2)
C(14)-C(10)-C(11)-Mo(1)	112.47(15)	C(13)-C(21)-C(22)-C(23)	131.6(2)
C(10)-C(11)-C(12)-O(2)	176.17(15)	O(1)-C(13)-C(24)-C(25)	-60.6(2)
Mo(1)-C(11)-C(12)-O(2)	105.31(16)	C(12)-C(13)-C(24)-C(25)	178.86(17)
C(10)-C(11)-C(12)-C(13)	-31.8(2)	C(21)-C(13)-C(24)-C(25)	58.2(2)
Mo(1)-C(11)-C(12)-C(13)	-102.68(16)	C(2)-C(1)-N(1)-N(2)	0.5(2)
O(2)-C(12)-C(13)-O(1)	-167.53(14)	C(2)-C(1)-N(1)-Mo(1)	-177.70(14)
C(11)-C(12)-C(13)-O(1)	37.2(2)	C(2)-C(3)-N(2)-N(1)	0.5(2)
O(2)-C(12)-C(13)-C(24)	-49.6(2)	C(2)-C(3)-N(2)-B(1)	176.9(2)
C(11)-C(12)-C(13)-C(24)	155.19(18)	C(1)-N(1)-N(2)-C(3)	-0.6(2)
O(2)-C(12)-C(13)-C(21)	73.50(18)	Mo(1)-N(1)-N(2)-C(3)	177.92(13)
C(11)-C(12)-C(13)-C(21)	-81.7(2)	C(1)-N(1)-N(2)-B(1)	-177.30(17)
C(11)-C(10)-C(14)-O(1)	-37.6(2)	Mo(1)-N(1)-N(2)-B(1)	1.2(2)
Mo(1)-C(10)-C(14)-O(1)	43.88(19)	N(4)-B(1)-N(2)-C(3)	125.1(2)
C(11)-C(10)-C(14)-C(15)	92.0(2)	N(6)-B(1)-N(2)-C(3)	-117.9(2)
Mo(1)-C(10)-C(14)-C(15)	173.49(12)	N(4)-B(1)-N(2)-N(1)	-58.9(2)
O(1)-C(14)-C(15)-C(16)	142.69(19)	N(6)-B(1)-N(2)-N(1)	58.1(2)
C(10)-C(14)-C(15)-C(16)	12.8(3)	C(5)-C(4)-N(3)-N(4)	0.6(2)
O(1)-C(14)-C(15)-C(20)	-42.2(2)	C(5)-C(4)-N(3)-Mo(1)	171.49(14)
C(10)-C(14)-C(15)-C(20)	-172.15(18)	C(5)-C(6)-N(4)-N(3)	-0.9(2)
C(20)-C(15)-C(16)-C(17)	-0.2(3)	C(5)-C(6)-N(4)-B(1)	-164.36(19)
C(14)-C(15)-C(16)-C(17)	174.8(2)	C(4)-N(3)-N(4)-C(6)	0.2(2)
C(15)-C(16)-C(17)-C(18)	0.4(4)	Mo(1)-N(3)-N(4)-C(6)	-171.89(12)

C(4)-N(3)-N(4)-B(1)	165.34(17)	O(4)-C(28)-Mo(1)-C(10)	-113(2)
Mo(1)-N(3)-N(4)-B(1)	-6.7(2)	C(7)-N(5)-Mo(1)-C(27)	38.71(18)
N(2)-B(1)-N(4)-C(6)	-135.59(19)	N(6)-N(5)-Mo(1)-C(27)	-136.53(14)
N(6)-B(1)-N(4)-C(6)	106.1(2)	C(7)-N(5)-Mo(1)-C(28)	-42.53(18)
N(2)-B(1)-N(4)-N(3)	62.5(2)	N(6)-N(5)-Mo(1)-C(28)	142.23(15)
N(6)-B(1)-N(4)-N(3)	-55.8(2)	C(7)-N(5)-Mo(1)-N(3)	130.19(18)
C(8)-C(7)-N(5)-N(6)	0.4(2)	N(6)-N(5)-Mo(1)-N(3)	-45.05(13)
C(8)-C(7)-N(5)-Mo(1)	-175.43(15)	C(7)-N(5)-Mo(1)-C(11)	-151.8(2)
C(8)-C(9)-N(6)-N(5)	0.4(2)	N(6)-N(5)-Mo(1)-C(11)	33.0(3)
C(8)-C(9)-N(6)-B(1)	174.18(19)	C(7)-N(5)-Mo(1)-N(1)	-144.02(18)
C(7)-N(5)-N(6)-C(9)	-0.5(2)	N(6)-N(5)-Mo(1)-N(1)	40.74(13)
Mo(1)-N(5)-N(6)-C(9)	175.78(13)	C(7)-N(5)-Mo(1)-C(10)	-69.4(2)
C(7)-N(5)-N(6)-B(1)	-175.06(17)	N(6)-N(5)-Mo(1)-C(10)	115.38(15)
Mo(1)-N(5)-N(6)-B(1)	1.2(2)	C(4)-N(3)-Mo(1)-C(27)	-32.97(18)
N(2)-B(1)-N(6)-C(9)	126.5(2)	N(4)-N(3)-Mo(1)-C(27)	136.76(14)
N(4)-B(1)-N(6)-C(9)	-113.6(2)	C(4)-N(3)-Mo(1)-C(28)	-100.5(2)
N(2)-B(1)-N(6)-N(5)	-60.3(2)	N(4)-N(3)-Mo(1)-C(28)	69.2(2)
N(4)-B(1)-N(6)-N(5)	59.6(2)	C(4)-N(3)-Mo(1)-N(5)	-121.68(18)
C(12)-C(13)-O(1)-C(14)	-44.4(2)	N(4)-N(3)-Mo(1)-N(5)	48.05(13)
C(24)-C(13)-O(1)-C(14)	-166.80(14)	C(4)-N(3)-Mo(1)-C(11)	76.15(18)
C(21)-C(13)-O(1)-C(14)	73.11(18)	N(4)-N(3)-Mo(1)-C(11)	-114.13(14)
C(10)-C(14)-O(1)-C(13)	46.0(2)	C(4)-N(3)-Mo(1)-N(1)	155.93(18)
C(15)-C(14)-O(1)-C(13)	-85.04(18)	N(4)-N(3)-Mo(1)-N(1)	-34.34(13)
C(11)-C(12)-O(2)-C(26)	5.3(2)	C(4)-N(3)-Mo(1)-C(10)	73.86(19)
C(13)-C(12)-O(2)-C(26)	-149.37(16)	N(4)-N(3)-Mo(1)-C(10)	-116.41(14)
O(3)-C(27)-Mo(1)-C(28)	64.3(11)	C(12)-C(11)-Mo(1)-C(27)	34.12(13)
O(3)-C(27)-Mo(1)-N(5)	-18.4(11)	C(10)-C(11)-Mo(1)-C(27)	-83.37(12)
O(3)-C(27)-Mo(1)-N(3)	-96.6(11)	C(12)-C(11)-Mo(1)-C(28)	119.05(12)
O(3)-C(27)-Mo(1)-C(11)	165.0(11)	C(10)-C(11)-Mo(1)-C(28)	1.55(12)
O(3)-C(27)-Mo(1)-N(1)	-34.1(13)	C(12)-C(11)-Mo(1)-N(5)	-134.80(19)
O(3)-C(27)-Mo(1)-C(10)	127.8(11)	C(10)-C(11)-Mo(1)-N(5)	107.7(2)
O(4)-C(28)-Mo(1)-C(27)	-7(2)	C(12)-C(11)-Mo(1)-N(3)	-59.76(12)
O(4)-C(28)-Mo(1)-N(5)	83(2)	C(10)-C(11)-Mo(1)-N(3)	-177.26(10)
O(4)-C(28)-Mo(1)-N(3)	62(2)	C(12)-C(11)-Mo(1)-N(1)	-142.57(12)
O(4)-C(28)-Mo(1)-C(11)	-114(2)	C(10)-C(11)-Mo(1)-N(1)	99.93(11)
O(4)-C(28)-Mo(1)-N(1)	163(2)	C(12)-C(11)-Mo(1)-C(10)	117.50(17)

C(1)-N(1)-Mo(1)-C(27)	152.0(4)	C(11)-C(10)-Mo(1)-C(27)	106.57(12)
N(2)-N(1)-Mo(1)-C(27)	-26.0(5)	C(14)-C(10)-Mo(1)-C(27)	-4.89(15)
C(1)-N(1)-Mo(1)-C(28)	55.2(2)	C(11)-C(10)-Mo(1)-C(28)	-178.34(13)
N(2)-N(1)-Mo(1)-C(28)	-122.80(14)	C(14)-C(10)-Mo(1)-C(28)	70.19(14)
C(1)-N(1)-Mo(1)-N(5)	136.09(19)	C(11)-C(10)-Mo(1)-N(5)	-149.03(12)
N(2)-N(1)-Mo(1)-N(5)	-41.91(13)	C(14)-C(10)-Mo(1)-N(5)	99.50(16)
C(1)-N(1)-Mo(1)-N(3)	-144.93(19)	C(11)-C(10)-Mo(1)-N(3)	3.79(14)
N(2)-N(1)-Mo(1)-N(3)	37.07(13)	C(14)-C(10)-Mo(1)-N(3)	-107.68(14)
C(1)-N(1)-Mo(1)-C(11)	-46.34(19)	C(14)-C(10)-Mo(1)-C(11)	-111.47(18)
N(2)-N(1)-Mo(1)-C(11)	135.66(14)	C(11)-C(10)-Mo(1)-N(1)	-76.51(11)
C(1)-N(1)-Mo(1)-C(10)	-10.26(19)	C(14)-C(10)-Mo(1)-N(1)	172.02(14)
N(2)-N(1)-Mo(1)-C(10)	171.74(14)		

Symmetry transformations used to generate equivalent atoms: