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Novel Substitutions of 1-Alkoxy- and 1-Arylsulfonyloxy-η^3-allylmolybdenum Complexes. A Case for η^1-Alkenyl Carbene Complexes as Intermediates†

Thomas C. Coombs,‡ Wenwei Huang,§ Ethel C. Garnier-Amblard, and Lanny S. Liebeskind*

Sanford S. Atwood Chemistry Center, Emory University, 1515 Dickey Drive, Atlanta, Georgia 30322. ‡*Current address: Department of Medicinal Chemistry, University of Kansas, 1251 Wescoe Hall Dr., Lawrence, KS 66045-7582.* §*Current address: National Institutes of Health, NIH Chemical Genomics Center, 9800 Medical Center Dr. MSC: 3370, Bethesda, MD 20892-3370*

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A series of acyclic and cyclic 1-alkoxy- and 1-arylsulfonyloxy-substituted TpMo(CO)$_2$(η^3-allyl) complexes was synthesized and characterized, and exchange of the oxygenated substituent was investigated under a variety of reaction conditions. 1-Alkoxy-substituted η^3-allyl and η^3-butenyl complexes participated in direct, uncatalyzed exchange of the alkoxy substituent with benzylamine, but required a Lewis acid for exchange with alcohols. The 1-alkoxy-substituted η^3-cyclohexenyl complex was unreactive toward exchange under all conditions investigated. The corresponding acyclic arylsulfonyloxy-substituted complexes underwent direct, uncatalyzed exchange with both benzylamine and alcohols, while the arylsulfonyloxy-substituted cyclohexenyl compounds participated in direct substitution with benzylamine, but not alcohols. High enantiopurity acyclic and cyclic alkoxy- and arylsulfonyloxy-substituted complexes provided exchange products with predominant, but incomplete, losses in enantiomeric excess in all cases examined. Mechanisms accounting for the observed reactivity trends and for the losses in enantiomeric excess are discussed. Reactions of alkoxy-substituted complexes through an associative mechanism and of arylsulfonyloxy-substituted compounds through a dissociative mechanism are suggested.

Introduction

TpMo(CO)$_2$(η^3-pyranyl) and TpMo(CO)$_2$(η^3-pyridinyl) complexes are versatile organometallic enantiomeric scaffolds (Tp = hydridotris(pyrazolyl)borate).[1] Single enantiomers of these readily available and easily synthesized organometallic π-complexes function as scaffolds from which widely differing families of complex and biologically significant oxa- and aza-heterocyclic organic structures can be elaborated in an enantiospecific fashion.

An earlier study described the rapid enantiocontrolled construction of substituted oxabicyclo[3.2.1]octenes via a stepwise [5+2] cycloaddition pathway through the reaction of a highly enantioenriched TpMo(CO)$_2$(η^3-pyranyl) complex with a number of electron-deficient alkenes in the presence of EtAlCl$_2$ (Scheme 1).[1r] For most olefinic substrates the cycloaddition reaction was rapid at room temperature in the presence of catalytic quantities of EtAlCl$_2$ and delivered cycloadducts of high enantiopurity. However, less reactive alkenes such as acrylonitrile required larger amounts of EtAlCl$_2$ and led to an unexpected slight racemization of the product.[1r] Control experiments traced the lower enantiopurity to a slow racemization of the high enantiopurity TpMo(CO)$_2$(η^3-pyranyl) complex in the presence of EtAlCl$_2$. Racemization was easily eliminated for the less reactive alkenes, as long as the alkene was present in greater amount than the Lewis acid. An analogous racemization of TpMo(CO)$_2$(η^3-pyridinyl) complexes was also observed under similar reaction conditions.[1p,q]

Racemization requires a π-face migration of the TpMo(CO)$_2$ moiety. In appropriate *acyclic* systems this can occur by a sequential slippage from η^3 to η^1, rotation about the newly generated Csp^3−Csp^2 bond, and re-formation of a η^3-complex. However, in *cyclic* π-systems this cannot occur: slippage of the allyl from η^3 to η^1 is feasible, but full rotation about the newly generated Csp^3−Csp^2 bond is restricted by

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*To whom correspondence should be addressed. E-mail: chemLL1@emory.edu.

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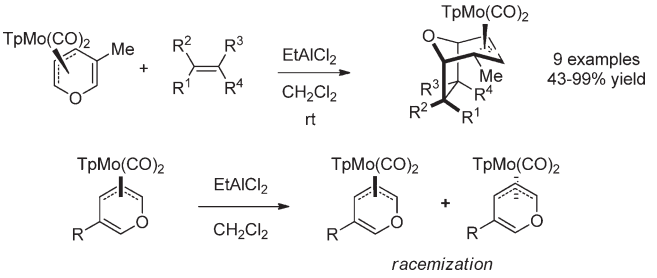
Scheme 1. Stereocontrol during [5+2] Cycloaddition Reactions of Pyranylmolybdenum Complexes



its inclusion within a ring. By what mechanism then do the η^3-pyranyl- and η^3-pyridinylmolybdenum complexes racemize? Given the generally very robust nature of the molybdenum π-complexes, it seems unlikely that π-face migration of the $TpMo(CO)_2$ moiety takes place by homo- or heterolytic cleavage of the Mo−allyl bond or even via a bimolecular exchange process. If those assumptions are true, then π-face migration (racemization) must occur by a reversible *opening of the pyranyl ring* proceeding through an achiral intermediate.

In the original disclosure of the [5+2] cycloaddition chemistry of $TpMo(CO)_2(\eta^3$-pyranyl) complexes,[1r] it was proposed that the $TpMo(CO)_2$ fragment slipped from η^3 to η^1 at the carbon atom adjacent to the pyran ring oxygen. This would allow reversible, Lewis acid-assisted opening of the pyran ring (Scheme 2). Cleavage of the ring carbon−oxygen bond would reversibly generate the acyclic $TpMo(CO)_2$ carbene complex **A**, from which racemization would ensue. As a related precedent, Green and co-workers have described a ring-opening of η^3-γ-lactonylmolybdenum complexes.[2]

The postulated reversible opening of the η^3-pyranyl ring shown in Scheme 2 should represent a specific case of a more general family of exchange reactions of 1-alkoxy-η^3-allylmetals. Little is known about the chemical reactivity of seemingly simple 1-alkoxy-η^3-allylmetal or related complexes.[2] Synthesis and structural studies have been carried out on a variety of 1-alkoxy-η^3-allylmetal complexes of nickel,[3] palladium,[4] platinum,[4b,d,5] iron,[6] cobalt,[7] and molybdenum,[1s] but no fundamental studies of the exchange chemistry of the alkoxy substituent have been described. Herein we describe a study of the synthesis, characterization, and exchange reactions of acyclic and cyclic enantiomerically enriched 1-alkoxy- and 1-sulfonyloxy-η^3-allylmolybdenum complexes. Through this study we have explored the properties and reaction chemistry of 1-alkoxy-η^3-allylmetals and have probed for the intermediacy of vinylcarbene complexes along the reaction pathways.

Scheme 2. η^3-Pyranylmolybdenum Complex Racemization

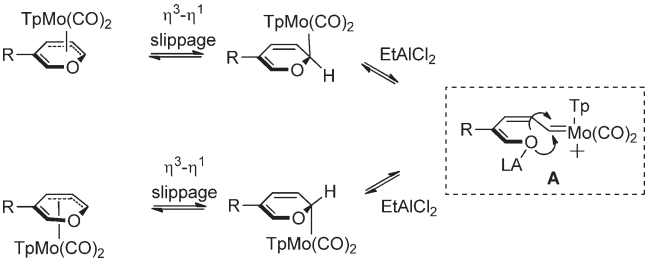
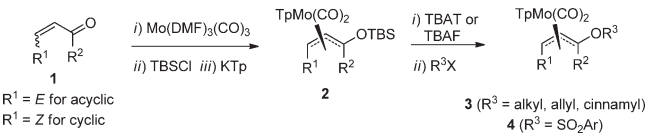


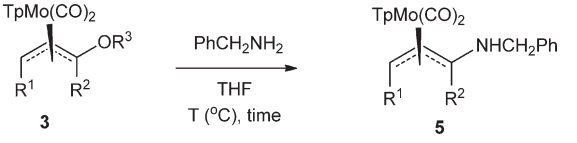
Table 1. Synthesis of 1-Alkoxy and 1-Sulfonyloxy Substrates



entry	cmpd	R^1	R^2	cmpd, yield (%)	R^3	yield (%)
1	**1a**	H	H	**2a**, 54%	Me	80, **3a**
2	**1a**	H	H	**2a**, 54%	*i*Pr	76, **3b**
3	**1a**	H	H	**2a**, 54%	SO_2Ar[a]	92, **4a**
4	**1b**	*E*-CH_3	H	**2b**, 83%	Me	72, **3c**
5	**1b**	*E*-CH_3	H	**2b**, 83%	tosyl	−[b], **4b**
6	**1b**	*E*-CH_3	H	**2b**, 83%	SO_2Ar[a]	70, **4c**
7	**1b**	*E*-CH_3	H	**2b**, 83%	allyl	81, **3d**
8	**1b**	*E*-CH_3	H	**2b**, 83%	cinnamyl	80, **3e**
9	**1c**	$-(CH_2)_3-$		**2c**, 65%	Me	83, **3f**
10	**1c**	$-(CH_2)_3-$		**2c**, 65%	tosyl	32, **4d**
11	**1c**	$-(CH_2)_3-$		**2c**, 65%	SO_2Ar[a]	65, **4e**

[a] Ar = 2,4,6-triisopropylphenyl. [b] The 2-butenyl tosylate could not be isolated due to its instability.

Table 2. Exchange Reactions of Alkoxy-Substituted Complexes with Benzylamine



entry	cmpd	R^1	R^2	R^3	*T* (°C)	time	cmpd	yield (%)
1	**3a**	H	H	Me	23	20 h	**5a**	95
2	**3c**	CH_3	H	Me	reflux	20 h	**5b**	74
3	**3e**	CH_3	H	cinnamyl	reflux	24 h	**5b**	58
4	**3f**	$-(CH_2)_3-$		Me	reflux	48 h	**5c**	NR[a]

[a] NR: no reaction took place.

Results and Discussion

A series of acyclic and cyclic 1-alkoxy and 1-arylsulfonyloxyallylmolybdenum complexes was prepared, and the substitution chemistry of these materials was studied. The substitution investigation fell into three categories: (1) direct nucleophilic exchange of alkoxy substituents with external amines (Table 2), (2) Lewis acid-catalyzed exchange of alkoxy substituents with external alcohols (Table 3), and (3) direct nucleophilic exchange of arylsulfonate ester substituents with both alcohols and amines (Table 4).

Racemic Substrate Synthesis. η^3-Allylmolybdenum complexes bearing oxygenated substituents at the 1-position were synthesized according to previously published protocols or

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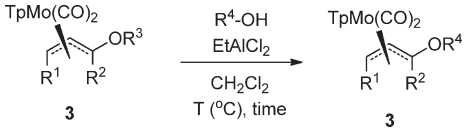
Table 3. Exchange Reactions of Alkoxy-Substituted Complexes with Alcohols



entry	cmpd	R^1	R^2	R^3	R^4–OH	T (°C)	time	cmpd	yield (%)
1	**3a**	H	H	Me	*i*PrOH	23	26 h	**3b**	72
2	**3b**	H	H	*i*Pr	MeOH	23	4 h	**3a**	87
3	**3c**	CH_3	H	Me	*i*PrOH	23	days	**3g**	–[a]
4	**3f**	$-(CH_2)_3-$		Me	*i*PrOH	reflux	24 h	**3h**	NR[b]

[a] The reaction took place very slowly. HPLC analysis showed (time/reactant/product): 30 h/70/30; 52 h/56/44; 6 d/45/54; 11 d/37/62. [b] NR: no reaction took place.

by slight modifications thereof.[1s] Thus, monosubstituted-(propenyl), 1,3-disubstituted- (2-butenyl), and cyclic (cyclohexenyl) 1-alkoxy and 1-arylsulfonyloxy compounds were prepared from the corresponding 1-*tert*-butyldimethylsiloxy complexes **2a**–**2c** by treatment with tetrabutylammonium fluoride (TBAF) or tetrabutylammonium triphenyldifluorosilicate (TBAT), followed by addition of the appropriate alkylating agent or $ArSO_2Cl$ (Table 1). In turn, the *tert*-butyldimethylsiloxy complexes **2a**–**2c** were synthesized by addition of the appropriate α,β-unsaturated aldehyde or ketone to a solution of $Mo(DMF)_3(CO)_3$[8] in CH_2Cl_2 followed by reaction with TBSCl and then ligand exchange with potassium hydridotrispyrazolylborate, KTp.[9] The alkoxy-substituted complexes could also be prepared in one pot from the requisite α,β-unsaturated aldehyde or ketone without isolating the intermediate silyl ethers. With the exception of sulfonate esters **4a**–**4d**, which were found to partly decompose during routine purification techniques, the other complexes were obtained as easily manipulated, air- and moisture-stable materials. The problematic arylsulfonate esters **4a**–**4d** were isolable in low yields, but were typically generated and used *in situ*, making isolation unnecessary.

Direct Exchange of Alkoxy Substituents with Amines and Alcohols. Alkoxy-substituted complexes **3a**, **3c**, and **3e** reacted directly with benzyl amine in the absence of a catalyst, providing benzylamino-substituted complexes **5a** and **5b**, in which the alkoxy group had been replaced by a benzyl amine substituent (Table 2). For example, stirring monosubstituted methoxy complex **3a** in THF in the presence of 30 equiv of benzyl amine at room temperature for 20 h produced the desired amino-substituted complex **5a** in 95% yield as a bright red solid (Table 2, entry 1). The disubstituted 2-butenyl methoxy complex **3c** underwent a similar substitution of the methoxy substituent by benzylamine when stirred with excess benzyl amine in THF at room temperature (Table 2, entry 2). However, this reaction required several days to reach completion, and over that period of time significant decomposition occurred. Alternatively, refluxing complex **3c** (and **3e**) in THF with 30 equiv of benzyl amine for 20 h provided the desired benzylamino-substituted complex **5b** in 74% (and 58%) yield as a bright red solid (Table 2, entries 2 and 3). In contrast to the acyclic η^3-allylmolybdenum complexes, cyclic methoxy complex **3f** failed to react with benzyl amine, even at elevated temperatures (Table 2, entry 4),

^{1}H NMR analysis of the amino-substituted complex **5a** supports assignment of the *syn*-configuration to the amino substituent (Figure 1). In a prior publication,[1v] it was shown that *syn* protons exhibit coupling constants ranging from 5.4 to 8.1 Hz, while *anti* protons have consistently larger coupling constants ranging from 8.7 to 12.2 Hz. The benzylamino-substituted η^3-allylmolybdenum complex **5a** shown in Figure 1 displayed one large coupling constant for H_a (J = 9.6 Hz), supporting assignment of its *anti* configuration. IR spectroscopy of **5a** also showed a significant shift to lower wavenumbers for the metal carbonyl stretches (1903, 1783 cm^{-1}) relative to the methoxy-substituted starting material **3a** (1930, 1832 cm^{-1}, Figure 1),[1s] indicating a large contribution from zwitterionic resonance structure **5a′**.

For disubstituted complexes, again, ^{1}H NMR spectroscopy revealed two large coupling constants (J = 11.2 and 9.2 Hz) for H_a and one smaller coupling constant (J = 6.8 Hz) for H_b, thus confirming the *anti*-Me, *syn*-NHBn configuration assigned to **5b** (Figure 1). IR spectroscopy also showed the same shift of the metal carbonyls to lower wavenumbers (1899, 1783 cm^{-1}) relative to the methoxy-substituted starting material **3c** (1925, 1826 cm^{-1}, Figure 1),[1s] again indicating significant zwitterionic character.

Previous structural studies of methoxy-substituted η^3-allylmolybdenum complexes such as **3a** showed that the methoxy substituent was oriented in the plane of the allyl moiety and that significant double-bond character existed between the oxygen atom and the attached allyl carbon.[1s,v] These properties were attributed to resonance overlap of the oxygen lone pairs with the π-system of the allyl. Oxygen lone pair overlap with the π-system of the η^3-allyl was most efficient when the methoxy substituent occupied a *syn* position on the η^3-allyl since substituents occupying *anti* positions bend out of the plane of the allyl in order to minimize unfavorable nonbonded interactions. Resonance delocalization as in structure **3a′** is reinforced by the tendency of $TpMo(CO)_2$ systems to favor six-coordinate over seven-coordinate structures[10] and by the ability of the six-coordinate canonical structure to delocalize its negative charge buildup at molybdenum with three good π-back-bonding ligands: two terminal CO's and an *O*-alkylated η^2-enone ligand. The same arguments would apply to the benzylamino-substituted complexes **5a** and **5b**.

Lewis Acid-Catalyzed Exchange of Alkoxy Substituents with Alcohols. In contrast to the direct substitution of the acyclic methoxy-substituted η^3-allylmolybdenum complexes with benzyl amine, no reaction occurred upon exposure of the same complexes to 2-propanol in the absence of a catalyst. However, upon stirring monosubstituted methoxy complex **3a** at room temperature with 20 equiv of 2-propanol in the presence of 0.4 equiv of $EtAlCl_2$, a facile exchange took place, allowing isolation of isopropyloxy-substituted complex **3b** in 72% yield after 26 h (Table 3, entry 1). Conversely, reaction of isopropyloxy-substituted complex **3b** with MeOH, a much smaller nucleophile than 2-propanol, in the presence of $EtAlCl_2$ produced **3a** in 87% yield after just 4 h (Table 3, entry 2). The disubstituted 2-butenyl methoxy complex **3c** also reacted with 2-propanol under similar Lewis acid catalysis to produce **3g**, but the transformation was exceedingly

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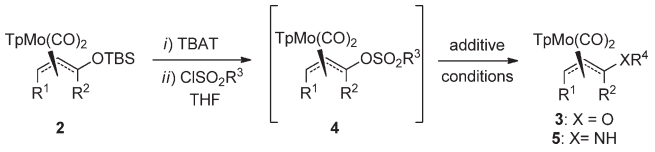
Table 4. Exchange Reactions of Sulfonate Ester-Substituted Complexes



entry	cmpd	R^1	R^2	R^3	yield (%), cmpd	additive	conditions	time (h)	XR^4	yield (%), cmpd
1	**2a**	H	H	Ar[a]	–[b], **4a**	$BnNH_2$ (30 equiv)	THF/MeOH (1:1), reflux	2	NHBn	78,[c] **5a**
2	**2b**	CH_3	H	*p*-tolyl	–[b], **4b**	$BnNH_2$ (30 equiv)	THF/MeOH (1:1), reflux	2	NHBn	53,[c] **5b**
3	**2b**	CH_3	H	Ar[a]	--[b], **4c**	$BnNH_2$ (30 equiv)	THF/MeOH (1:1), reflux	2	NHBn	74,[c] **5b**
4	**2c**	$-(CH_2)_3-$		*p*-tolyl	32, **4d**	$BnNH_2$ (15 equiv)	THF reflux	18	NHBn	45, **5c**
5	**2c**	$-(CH_2)_3-$		Ar[a]	65, **4e**	$BnNH_2$ (30 equiv)	THF reflux	17	NHBn	32, **5c**
6	**2a**	H	H	Ar[a]	–[b], **4a**		THF/MeOH (1:1), 23 °C	17	OMe	73,[c] **3a**
7	**2b**	CH_3	H	Ar[a]	–[b], **4c**		THF/MeOH (1:1), 23 °C	14	OMe	72,[c] **3c**
8	**2c**	$-(CH_2)_3-$		Ar[a]	65, **4e**		THF/MeOH (1:1), reflux		OMe	dec[d]

[a] Ar = 2,4,6-triisopropylphenyl. [b] Sulfonate ester was not isolated, but generated and used *in situ*. [c] Isolated yield over 2 steps. [d] Decomposition.

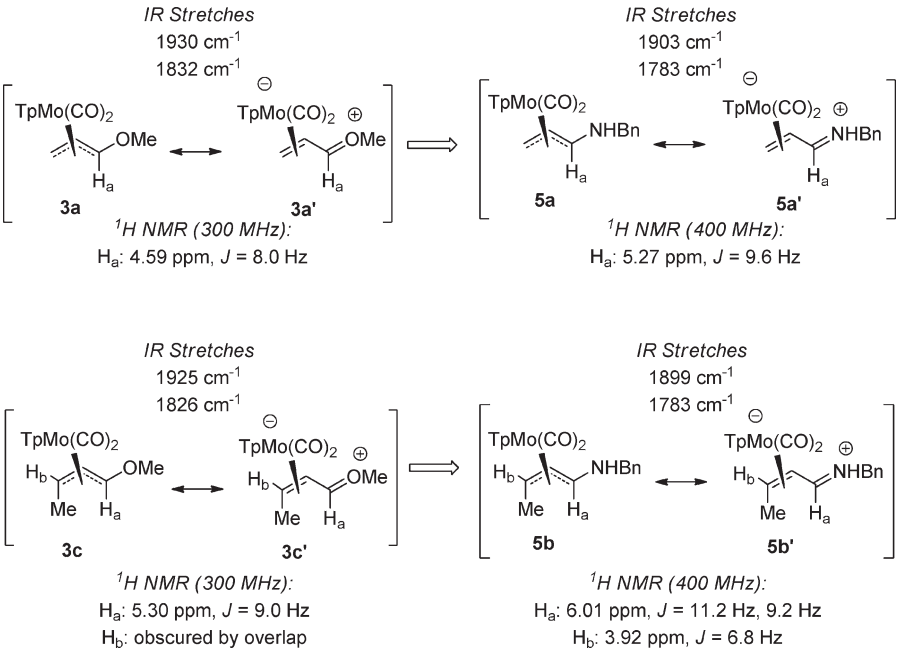


Figure 1. Structural implications from spectroscopic data.

slow (Table 3, entry 3). Heating did not have a significant effect on the reaction. Again, in contrast to the acyclic η^3-allylmolybdenum complexes, cyclohexenyl complex **3f** showed no evidence of exchange with 2-propanol in the presence of $EtAlCl_2$, even at elevated temperatures.

Direct Exchange of Sulfonate Esters with Amines and Alcohols. The sulfonate ester complexes analogous to the methoxy-substituted complexes discussed in Tables 2 and 3 also reacted directly with benzyl amine in the absence of a catalyst, providing amino-substituted complexes **5a**, **5b**, and **5c** (Table 4, entries 1–5). As noted above, sulfonate ester-substituted complexes proved challenging to work with, as most attempts at isolation and purification led to significant decomposition. However, when synthesized on a large scale, samples of pure material could be crystallized from the bulk material and used for characterization and small-scale reactions. The tosyloxy esters **4b** and **4d** led to more severe decomposition during isolation than did the corresponding 2,4,6-triisopropylbenzenesulfonate-substituted complexes **4a**, **4c**, and **4e**, and so the 2,4,6-triisopropylbenzene sulfonate ester group was chosen for most purposes in this study. Instabilities notwithstanding, once purified, both the toluene-substituted sulfonate esters and 2,4,6-triisopropylbenzene sulfonate esters were reasonably stable in solution and exhibited similar reactivities.

It also proved possible to generate the desired sulfonate esters *in situ* in THF by treating silyloxy complexes **2a** and **2b** with tetrabutylammonium triphenyldifluorosilicate (TBAT) followed by the requisite sulfonyl chloride (tolyl- or 2,4,6-triisopropylphenyl). These reactant solutions could be treated with benzyl amine in methanol, providing a simple method for accessing amino-substituted complexes **5a** and **5b** without the need for isolating the sensitive intermediates. In these cases reactivity trends were such that the methanol appears to function solely as a solvent and not as a reactant (see below).

For example, the monosubstituted allyl complex **4a** (2,4,6-triisopropylphenylsulfonyloxy) and the 2-butenyl allyl complexes **4b** (*p*-toluenesulfonyloxy) and **4c** (2,4,6-triisopropylphenylsulfonyloxy) were generated *in situ* from the siloxy η^3-allylmolybdenum complexes **2a** and **2b** in THF. Addition

of benzylamine in MeOH/THF (1:1) gave the corresponding substitution products after 2 h at reflux (Table 4, entries 1−3). These reactions did proceed at room temperature in the absence of MeOH using THF alone, but the best yields for these acyclic complexes were obtained at reflux in the THF/MeOH mixture.

The *in situ* generated *monosubstituted* sulfonate ester **4a** reacted very slowly with benzylamine at room temperature in THF/MeOH (1:1) (after two days significant quantities of unreacted **4a** remained), while the *in situ* generated 1,3-*disubstituted* sulfonate ester **4c** was completely consumed after 19 h under identical conditions and produced **5b** in 35% isolated yield. Similar results were obtained using other solvents at room temperature.

In those reactions that use 1:1 THF/MeOH as cosolvents, we cannot rule out the intermediacy of a methoxy-substituted η^3-allylmolybdenum complex that then reacts with benzylamine. For example, in THF/methanol, in the absence of benzylamine, the acyclic mono- and 1,3-disubstituted sulfonate ester complexes **4a** and **4c** undergo substitution with methanol to afford the corresponding methoxy-substituted complexes **3a** and **3c** (Table 4, entries 6 and 7). However, various observations suggest that the sulfonate esters react directly with benzylamine and do not proceed through methoxy intermediates when MeOH is present. First, the acyclic 1,3-disubstituted *alkoxy* complexes required prolonged times for the reaction with benzyl amine to reach completion (20−24 h in refluxing THF; see Table 2, entries 2 and 3), while the 1,3-disubstituted *arylsulfonyloxy* complexes reacted with benzylamine in just 2 h in refluxing THF/MeOH (Table 4, entries 2 and 3). If the arylsulfonyloxy substituent was first replaced by OMe, a much slower reaction would result. Also, the methoxy-substituted cyclohexenyl complex **3f** did not react with benzylamine in refluxing THF (Table 2, entry 4), while the corresponding arylsulfonyloxy-substituted cyclohexenyl complexes did (Table 4, entries 4 and 5). Additionally, the arylsulfonyloxy-substituted cyclohexenyl complexes failed to react with MeOH in refluxing THF/MeOH (Table 4, entry 8). Collectively, these observations imply the direct reaction of the arylsulfonyloxy-substituted complexes by benzyl amine even when MeOH is used as a cosolvent.

In contrast to the *acyclic* sulfonate-ester-substituted complexes **4a** and **4c**, which were unstable and required *in situ* generation, cyclohexenyl complex **4e**, possessing a 2,4,6-triisopropylbenzenesulfonyloxy substituent, was quite stable and easily isolated. The corresponding tosyloxy-substituted cyclohexenyl complex **4d**, while still isolable, was much less stable (Table 4, entry 4). As listed in Table 4 (entries 4 and 5), the isolable sulfonate ester-substituted cyclohexenyl complexes **4d** and **4e** underwent reaction with benzyl amine in refluxing THF (the methoxy-substituted cyclohexenyl complex **3f** does not react with benzylamine), producing the benzylamino-substituted complex **5c** in 45% and 32% yields, respectively. The remainder of the mass in these reactions was lost to decomposition. Reactions run in THF/MeOH mixtures did not provide improved results.

The structural features of the sulfonate ester complexes were assessed through X-ray diffraction analysis of a single crystal of **4e** that was grown from dichloromethane/hexanes (Figure 2). Very little lengthening of the Mo(1)−C(17) bond is observed relative to related methoxy-substituted allyl complexes. The Mo(1)−C(17) bond length is 2.407(5) Å, while the Mo(1)−C(12) and Mo(1)−C(13) bond lengths are 2.213(5) and 2.362 Å, respectively. This observation contrasts with

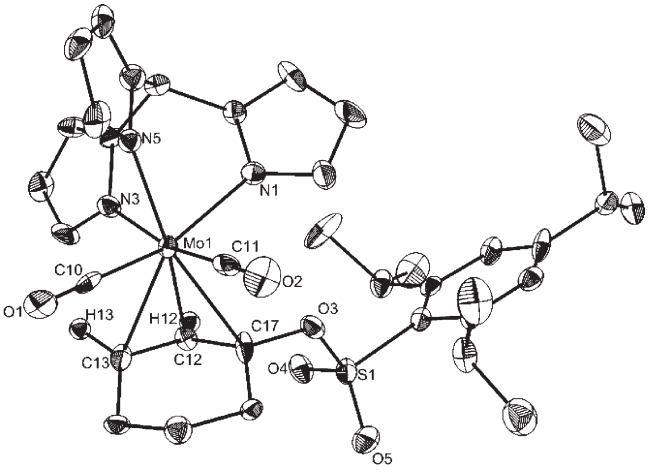


Figure 2. ORTEP view of the arylsulfonyloxy-substituted cyclohexenyl complex (±)-**4e**. Key bond lengths (Å): Mo(1)−C(17), 2.407(5); Mo(1)−C(12), 2.213(5); Mo(1)−C(13), 2.361(5); C(13)−C(12), 1.429(7); C(12)−C(17), 1.405(7); C(17)−O(3), 1.436(5).

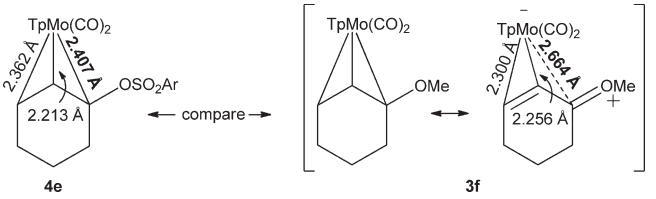


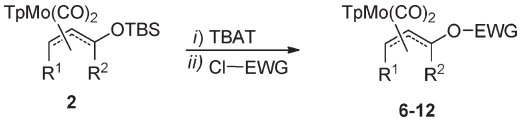
Figure 3. Bond length comparisons between arylsulfonyloxy- and methoxy-substituted complexes **4e** and **3f**.

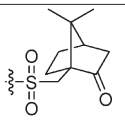
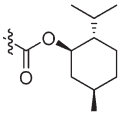
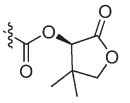
the results from a prior X-ray crystallography study carried out on methoxy-substituted cyclohexenyl complex **3f** (see Figure 3).[1s] In that study, the Mo−C bond for the carbon bearing the methoxy substituent was significantly longer (2.664(4) Å) than the remaining two molybdenum allyl Mo−C bonds (2.256(4) and 2.300(4) Å). This lengthening was attributed to resonance donation from the oxygen atom into the metal allyl (see Figure 1 for related spectroscopic details).

Exchange Reactions with Chiral, Nonracemic Complexes. By what mechanism(s) do the reactions depicted in Tables 2−4 occur? Do the alkoxy and sulfonate ester substitution reactions take place with retention of π-complex stereochemistry, or does the mechanism of substitution allow racemization? To address these questions, enantiomerically enriched versions of 1-substituted cyclohexenyl- and 2-butenyl molybdenum complexes were prepared. To accomplish this task, a chiral auxiliary screen was conducted in order to find a suitable auxiliary for efficient resolution of both cyclohexenyl and 2-butenyl diastereomeric molybdenum complexes. The results are listed in Table 5.

The Cyclohexenyl Series. Camphorsulfonyl-substituted cyclohexenyl complexes **6** proved too reactive to isolate (Table 5, entry 1), while the analogous diastereomeric mixtures of both (*S*)-(−)-2-acetoxypropionyl-substituted complexes **8** (Table 5, entry 2) and (−)-menthyl-substituted complexes **10** (Table 5, entry 5) were isolable, but the diastereomers could not be separated. (*R*)-(−)-Pantolactone derivatives of the cyclohexenyl system, however, proved quite useful, allowing both diastereomers of the cyclohexenyl complex to be isolated in good yields (Table 5, entry 7). Once separated via a combination of chromatography and recrystallization

Table 5. Chiral Auxiliary Screen



entry	cmpd	R^1	R^2	EWG	cpd #	yld/dr
1	**2c**	$-CH_2CH_2CH_2-$			**6**	decomp
2	**2b**	$-CH_3$	-H		**7**	decomp
3	**2c**	$-CH_2CH_2CH_2-$			**8**	89/1:1
4	**2b**	$-CH_3$	-H		**9**	decomp
5	**2c**	$-CH_2CH_2CH_2-$			**10**	90/1:1
6	**2b**	$-CH_3$	-H		NA[a]	NA[a]
7	**2c**	$-CH_2CH_2CH_2-$			**11**	75/1.1:1
8	**2b**	$-CH_3$	-H		**12**	22/1:1[b]

[a] NA: not attempted. [b] The diastereomers are formed in a roughly 1:1 ratio, but one decomposes upon purification of the mixture. Refer to text for details.

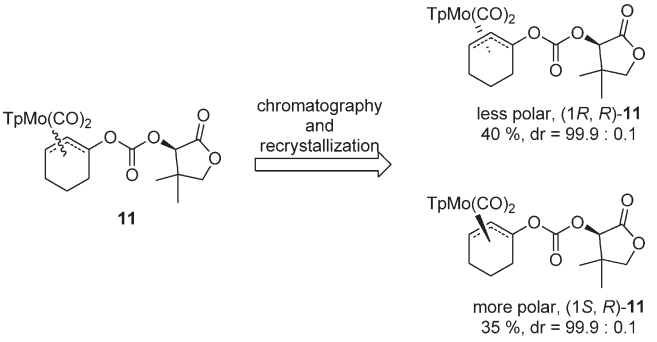


Figure 4. Pantolactone-based resolution of the cyclohexenyl complex diastereomers **11**.

(Figure 4), the products showed excellent diastereomeric ratios (up to 99.9:0.1). Of the two, only the more polar diastereomer provided crystals of suitable quality for analysis. A single-crystal X-ray diffraction analysis of the more polar diastereomer confirmed the relative and absolute configuration as (*1S*, *R*)-**11**[11] (Figure 5).

The 2-Butenyl Series. Diastereomeric arylsulfonyloxy and carboxylic ester complexes **7** (Table 5, entry 2) and **9** (Table 5, entry 4) could be generated from the acyclic 2-butenyl system using camphorsulfonyl chloride and (*S*)-(−)-2-acetoxypropionyl chloride, respectively, but in both cases the diastereomers decomposed during attempts at isolation. However, (*R*)-(−)-pantolactone could be used to produce a mixture of stable diastereomeric carbonates **12**. Of these, only one of the diastereomers could be isolated; the other decomposed during processing (Figure 6). The decomposition product from this unstable diastereomer partly overlapped with the stable diastereomer, making purification particularly tedious.

(11) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1–36.

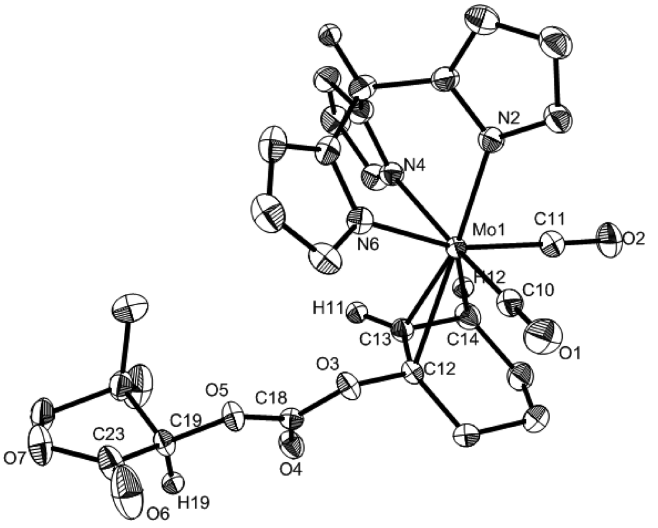


Figure 5. ORTEP view of the pantolactonecarbonyloxy-substituted cyclohexenyl complex (1*S*, *R*)-**11** (more polar diastereomer). Key bond lengths (Å): Mo(1)−C(12), 2.4055(14); Mo(1)−C(13), 2.2144(14); Mo(1)−C(14), 2.3595(15); C(14)−C(13), 1.435(2); C(13)−C(12), 1.405(2); C12−O3, 1.4290(17).

Figure 6. Accessing diastereomerically pure 2-butenyl complex **12**.

However, repeated iterations of silica gel column chromatography and recrystallization from dichloromethane/hexanes

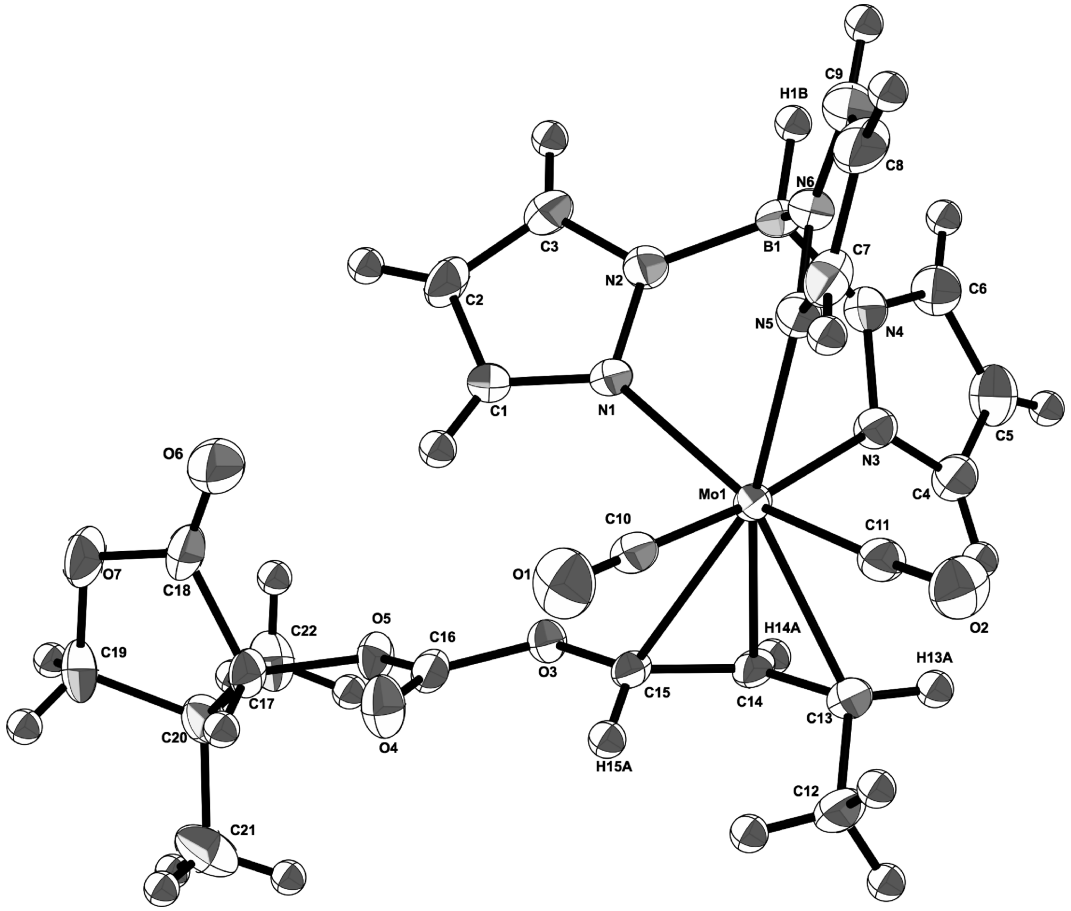
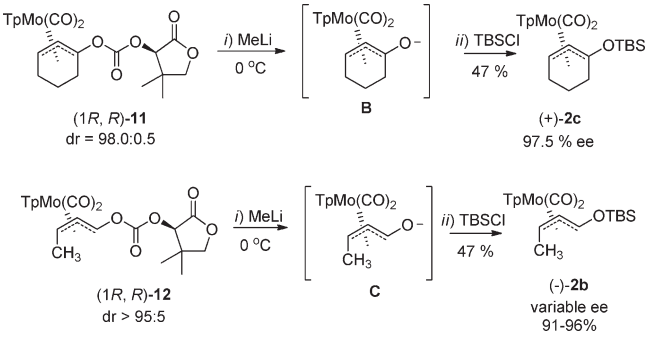


Figure 7. ORTEP view of pantolactonecarbonyloxy-substituted 2-butenyl complex (1*R*, *R*)-**12**. Selected bond lengths (Å): Mo(1)−C(13), 2.364(4); Mo(1)−C(14), 2.241(4); Mo(1)−C(15), 2.395(4); C(13)−C(14), 1.415(5); C(14)−C(15), 1.390(5); C15−O3, 1.416(4). Crystallized from EtOAc/hexanes. EtOAc solvate molecule not shown.

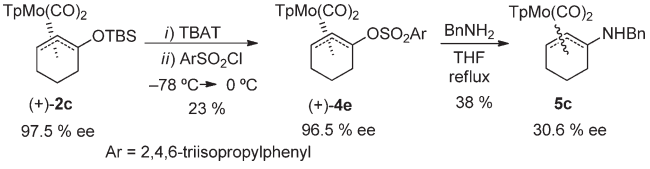
Scheme 3



provided (1*R*, *R*)-**12** in a low, but useful 22% yield. The absolute configuration of **12** was determined to be (1*R*, *R*)[11] by single-crystal X-ray diffraction (Figure 7). In the ^{1}H NMR spectrum of the **12** only one set of peaks was observed, so the diastereomeric ratio of the purified material was determined to be >95:5 (1*R*, *R*).

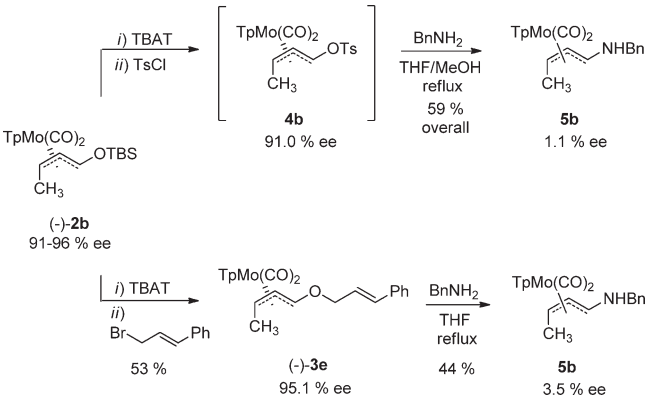
With single diastereomers of both the cyclohexenyl (**11**) and 2-butenyl (**12**) complexes in hand, attention was turned to converting these complexes into simpler high-enantiopurity alkoxy- and arylsulfonyloxy-substituted variants for an investigation of the exchange reactions. To accomplish this task, the carbonates were cleaved to oxidic intermediates (**B** and **C** in Scheme 3) with excess MeLi, and the anionic species was trapped. Unfortunately, direct exposure of the MeLi-treated reaction mixtures to arylsulfonyl chlorides led only to decomposition. Instead, the anions **B** and **C** generated upon cleavage of the carbonate with excess MeLi were successfully trapped as the corresponding *tert*-butyldimethylsilyl ether using TBSCl. Unexpectedly, the anionic intermediates **B** and **C** generated upon treatment of the pantolactone-derived complexes with excess MeLi were prone to racemization, but it was easily minimized either by using low reaction temperatures or by rapid reaction processing.[12] For example, when diastereomerically enriched carbonate (1*R*,*R*)-**11** (98.0:0.5 dr) was treated with 5 equiv of MeLi at 0 °C and the reaction mixture immediately quenched with 10 equiv of TBSCl, the silyl ether (+)-**2c** was produced in 47% yield and 97.5% ee (Scheme 3). Similarly, upon cleaving the carbonate of the

Scheme 4. Amino Exchange of Enantioenriched Cyclohexenyl Sulfonate Ester 4e

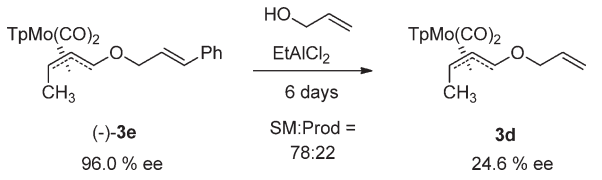


(12) Racemization of the anionic intermediate generated by cleavage of the η^3-allylmolybdenum complexes bearing the pantolactone carbonate is intriguing, but its detailed study was beyond the scope of this initial exploration of the substitution chemistry of 1-alkoxy- and 1-arylsulfonyloxy-substituted η^3-allylmolybdenum complexes.

Scheme 5. Asymmetric Amino Exchange of Complexes 4b and 3e



Scheme 6. Slow Exchange of Enantioenriched Cinnamyloxy Complex (−)-3e



diastereomerically enriched 2-butenyl complex **12** (dr > 95:5) under the same reaction conditions used above for **11**, the silyl ether (−)-**2b** was obtained in 47% yield and 96.2% ee.

Conversion of the *tert*-butyldimethylsiloxy-substituted η^3-allylmolybdenum complexes to the desired alkoxy- and arylsulfonyloxy-substituted complexes was achieved through fluoride activation of the silyloxide and quenching with an appropriate electrophile. Although yields are modest because of the inherent reactivity of the arylsulfonyloxy-substituted complexes, minimal loss of enantiomeric purity was observed in the conversion of cyclohexenyl carbonate (1*R*, *R*)-**11** to the corresponding sulfonate ester complex (+)-**4e** (Scheme 4). In this series of transformations, treatment of **2c** with TBAT at room temperature followed by low-temperature (−78 °C) addition of 2,4,6-triisopropylbenzenesulfonyl chloride yielded sulfonate ester (+)-**4e** in 96.5% ee as measured by chiral HPLC. The sulfonate ester (+)-**4e** was then refluxed in THF for 16 h in the presence of 30 equiv of benzyl amine, providing a largely racemized benzylamino-substituted complex **5c** (30.6% ee). We could not determine if the sulfonate ester (+)-**4e** racemized during the reaction, because heating the sulfonate ester complex in THF in the absence of amine led only to decomposition.

Along similar lines, activation of the silyl ether (−)-**2b** with TBAT at room temperature and trapping with 2,4,6-triisopropylbenzenesulfonyl chloride at room temperature provided the 2-butenyl sulfonate ester **4c**. Unfortunately, its enantiomers could not be separated under any of the conditions explored with available chiral HPLC columns. Nevertheless the enantiomers of the simpler but less stable tosyloxy-substituted 2-butenyl complex **4b** were resolvable via chiral HPLC. Due to the instability of tosylate **4b** to isolation procedures, it was generated *in situ* from (−)-**2b** of 96.2% ee (Scheme 5), and its ee was determined by directly analyzing a sample of the reaction mixture by chiral HPLC. The reaction mixture containing the enantioenriched tosylate (91.0% ee) was then heated at reflux in the presence of 30 equiv of benzylamine in THF/MeOH (1:1) for 3 h, delivering

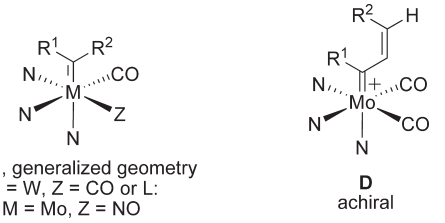


Figure 8

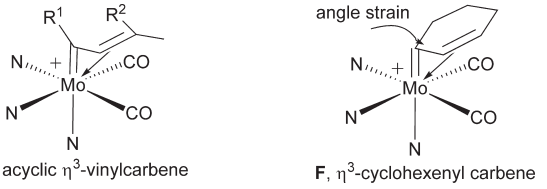
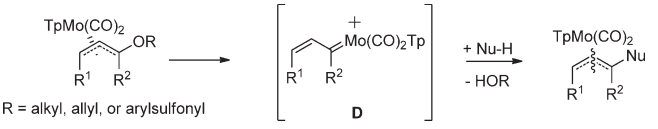


Figure 9

Scheme 7. Carbene Intermediates in Exchange Reactions



racemic amino-substituted complex **5b** (1.1% ee) in 59% yield.

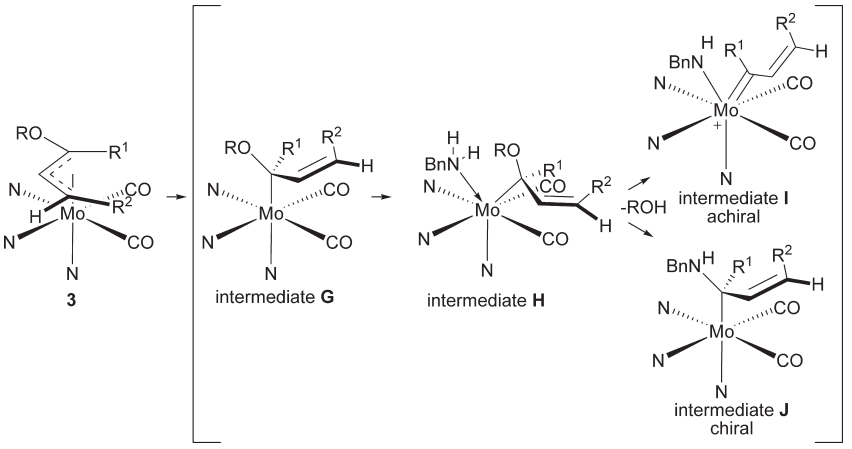
The previously prepared methoxy- and isopropyloxy-substituted 2-butenylmolybdenum complexes were not suitable to probe the stereochemical outcome of the substitution of an acyclic alkoxyl-substituted complex, because their enantiomers could not be resolved by chiral HPLC. Since the enantiomers of the related cinnamyloxy- and allyloxy-substituted 2-butenyl complexes were resolvable by chiral HPLC, these latter systems were chosen for study.

The silyl ether (−)-**2b** (91.1% ee) was activated with TBAT at −78 °C and then treated with cinnamyl bromide at −78 °C to generate the cinnamyloxy-substituted complex (−)-**3e** in 53% yield and 95.1% ee[13] (Scheme 5). The cinnamyloxy-substituted complex was then subjected to the exchange reaction by refluxing in THF with $BnNH_2$ (30 equiv). After 23 h, racemic benzylamino-substituted complex **5b** was isolated in 44% yield and 3.5% ee. Thus, the uncatalyzed exchange of sulfonate ester and alkoxy groups with benzylamine occurs with almost complete racemization.

A sample of the enantio-enriched cinnamyloxy-substituted complex (−)-**3e** (96.0% ee) was also subjected to Lewis acid-catalyzed alkoxy exchange (Scheme 6). When stirred in the presence of allyl alcohol (25 equiv) and $EtAlCl_2$ (0.5 equiv), an exceedingly slow reaction ensued, producing allyloxy-substituted complex **3d**. After six days, analysis of the crude reaction mixture by chiral HPLC showed a 22:78 ratio of the desired allyloxy-substituted exchange product **3d** (24.6% ee) to the starting cinnamyloxy complex **3e**. While the enantiomeric excess of the allyloxy-substituted exchange product **3g** had degraded to 24.6% over the course of the 6 days, the enantiopurity of the cinnamyloxy-substituted starting material

(13) These enantiomeric excesses were obtained by integrating the appropriate HPLC peaks for both (−)-**2b** and (−)-**3e**. The slight gain in enantiomeric excess is likely the result of a small impurity coeluting with the product peak.

Scheme 8. Suggested Associative Mechanism for Substitution of 1-Alkoxy η^3-Allylmolybdenum Complexes by $PhCH_2NH_2$



was unchanged. This latter observation is important. It provides strong support for the notion that the low ee's of the substitution products described within are not caused by racemization of the starting materials under the reaction conditions.

Mechanistic Rationale. For the purpose of this descriptive study of the substitution chemistry of alkoxy and arylsulfonyloxy η^3-allylmolybdenum complexes, the discussion of mechanism is restricted to reasonable suggestions that are consistent with observations. A more detailed analysis will require additional experimentation that is beyond the scope of this disclosure.

As described above, varying degrees of racemization are observed when enantiomerically enriched 1-alkoxy and 1-sulfonyloxy η^3-allylmolybdenum complexes are subjected to substitution reactions. To accommodate these observations, we suggest that the substitution reactions proceed through an achiral molybdenum carbene intermediate from which stereochemical information can be lost. A generic representation is depicted in Scheme 7.

Support for this mechanistic assumption comes from the published structures of known TpM(CO)(Z)(carbene) complexes (M = Mo, W; Z = CO, NO, other L:),[14] which, in each case, depict the Mo=CR_2 plane bisecting the plane defined by the Mo and the two basal plane pyrazole ligands (Figure 8). If the substitution reactions investigated here pass through a carbene complex that possesses the same geometry (**D**, Figure 8), then full racemization must ensue when these achiral cationic complexes are attacked by the incoming nucleophile from either equivalent π-face.

However, the isolation of substitution products that are significantly, but not fully, racemic requires the presence of a reactive chiral, nonracemic intermediate that can also be intercepted by the nucleophile. An obvious candidate is a η^3-vinylcarbene[14d−f,15] for which the π-facial information of the reactant would be retained (Figure 9, E and F). However, only the acyclic 2-butenyl reactants can form η^3-vinylcarbenes such as **E** in Figure 9. Significant geometric constraints make this pathway highly unlikely for the cyclohexenyl complexes (**F** in Figure 9), which implies that nonracemic products must result by an alternate mechanism.

Insight into possible mechanistic pathways comes from a comparison of the reactivity of the alkoxy- and arylsulfonyloxy-substituted η^3-allyl complexes. For the alkoxy-substituted η^3-allylmolybdenum complexes, the less substituted systems undergo substitution reactions much faster than the more substituted systems, with the cyclohexenyl complexes being completely unreactive under the experimental conditions explored. In contrast, for the arylsulfonyloxy-substituted η^3-allylmolybdenum complexes, the less substituted systems undergo substitution reactions much slower than the more substituted systems, with the cyclohexenyl systems bordering on being too unstable to handle. Therefore, the alkoxy- and arylsulfonyloxy-substituted η^3-allylmolybdenum complexes react by different mechanisms: the arylsulfonyloxy-bearing substrates display S_N1-like (dissociative) reactivity patterns, while the alkoxy-bearing substrates show S_N2-like (associative) reactivity patterns.

Alkoxy-Substituted Complexes. In order to accommodate the different reactivity profiles as well as the isolation of substitution products that are partly, but not fully, racemic, we suggest that the observations are consistent with reaction of the alkoxy-substituted complexes through an associative mechanism. The specific case of reaction of the alkoxy-substituted η^3-allylmolybdenum complexes with benzylamine is depicted in Scheme 8.

In lieu of generating a η^3-vinylcarbene to explain the residual stereoselectivity, the data are consistent with association of the incoming nucleophile at molybdenum, either coincident with or subsequent to $\eta^3-\eta^1$ slippage of the allyl (complex **3** → intermediate **G** → intermediate **H**). This will generate an intermediate seven-coordinate η^1-allyl **H** that retains the stereochemical information of its precursor η^3-allyl complex. Intermediate **H** can subsequently partition along two pathways. Ionization of the alkoxy substituent generates an achiral η^1-vinylcarbene intermediate **I**, which

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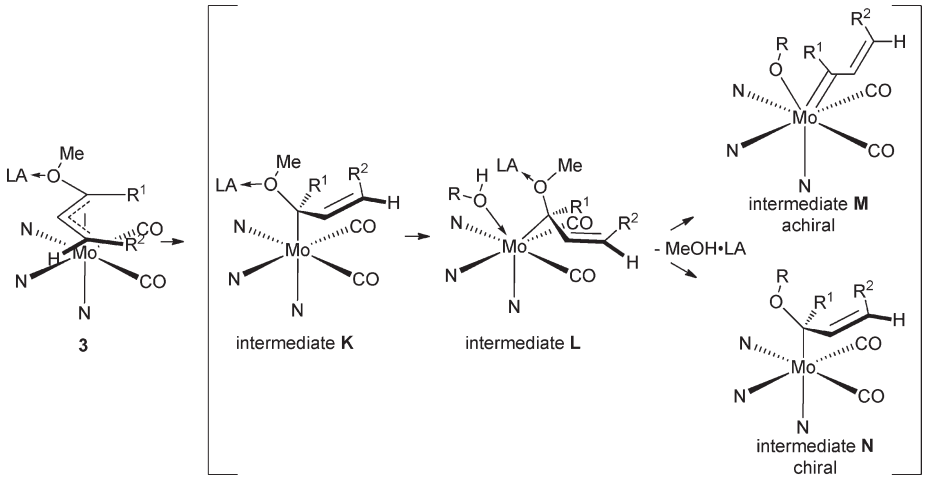
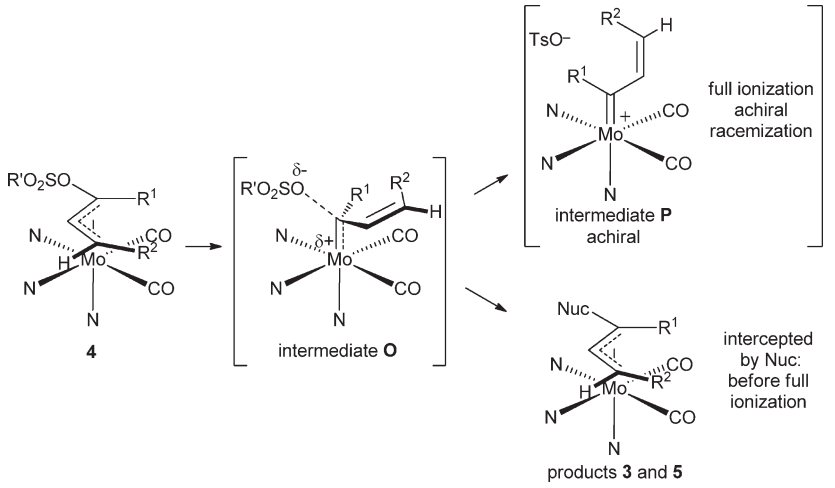
(15) (a) Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Organometallics* **2001**, *20*, 3845–3847. (b) Mistudo, T.-a. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1525–1538. (c) Hofmann, P.; Hammerle, M.; Unfried, G. *New J. Chem.* **1991**, *15*, 769–789. (d) Fischer, H.; Hofmann, J.; Mauz, E. *Angew. Chem., Int. Ed.* **1991**, *30*, 998–999. (e) Harvey, D.; Brown, M. *J. Am. Chem. Soc.* **1990**, *112*, 7806. (f) Feng, S. G.; Gamble, A. S.; Templeton, J. L. *Organometallics* **1989**, *8*, 2024–2031. (g) Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383–8391. (h) Mayr, A.; Asaro, M. F.; Glines, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2215–2216. (i) Stone, K. C.; Jamison, G. M.; White, P. S.; Templeton, J. L. *Organometallics* **2003**, *22*, 3083–3095.

Scheme 9. Lewis Acid-Catalyzed Exchange of Alkoxy Complexes with External Alcohols



Scheme 10. Suggested Dissociative Mechanism for Substitution of 1-Sulfonyloxy η^3-Allylmolybdenum Complexes



would react with the coordinate nucleophile to produce fully racemic product. Alternatively, a concerted displacement of the alkoxy leaving group from the η^1-allyl by the molybdenum-coordinated nucleophile (intermediate **H** → intermediate **J**) would deliver nonracemic product at $\eta^1 \rightarrow \eta^3$ slippage. The actual degree of racemization will reflect the relative rates of reaction of the nucleophile through these two different pathways: via the achiral η^1-vinylcarbene **I** would lead to full racemization, while the internal displacement on the η^1-allyl would proceed with stereocontrol. Whether the residual enantiomeric excess in the substitution product is due to retention or inversion has not yet been determined. Enantiomerically enriched samples of the amino substitution products **5** are not available by the procedures described within, and the enantiomers of methoxy- and isopropyloxy-substituted complexes could not be resolved by chiral HPLC. However, the enantiomers of the allyloxy-substituted complex depicted in Scheme 6 are resolvable on chiral HPLC columns. With additional work this system may allow us to determine if the residual enantiopurity in the product is due to retention or inversion of the original stereochemistry

This proposed associative pathway is consistent with the poor leaving group ability of an alkoxide, unassisted by protic or Lewis acids. It is therefore likely that a molecule of benzyl amine must first fill an empty coordination site at molybdenum, generating a (still chiral) η^1-allyl. This ligand coordination will increase the electron density at Mo and promote a metal-assisted ionization of the alkoxy group. As the alkoxyl group departs, it can pick up a proton from the amine as the intermediate partitions, whether following the racemization or the stereospecific substitution pathway. The observed relative rates of reaction of the alkoxyl-substituted η^3-allylmolybdenum complexes (the less substituted η^3-allyl complexes displace faster than more substituted complexes) are also fully consistent with the requirement for association of the nucleophile at molybdenum prior to ionization and the increased steric demand that accrues in the intermediate.

In contrast to the reaction of the alkoxy-substituted η^3-allylmolybdenum complexes with benzylamine, the necessary requirement of a Lewis acid for exchange of alkoxy substituents with external alcohols aligns with the decreased Lewis basicity of alcohols relative to amines. Prior coordination of the Lewis acid to the alkoxy substituent removes electron density from the molybdenum atom (see the electron-donating attribute of the alkoxy-substituted η^3-allylmolybdenum complexes described in Figures 1 and 3), which would facilitate both slippage to the η^1-allyl and coordination of an alcohol at the molybdenum atom (Scheme 9, Lewis acid-coordinated complex **3** → intermediate **K** → intermediate **L**). The stereochemistry of this process would reflect partitioning

of the chiral, seven-coordinate, η^1-allylmolybdenum intermediate **L** to either the chiral η^1-allyl intermediate **N**, resulting from concerted internal displacement of the alkoxy leaving group by the molybdenum-coordinated nucleophile, or the achiral η^1-vinylcarbene **M**, from which racemic product would result.

Arylsulfonyloxy-Substituted Complexes. Since the more substituted arylsulfonyloxy-substituted complexes show greater reactivity toward substitution than the less substituted relatives, a dissociative mechanism is likely (Scheme 10). These observations are consistent with a solvolysis-like reaction wherein η^3-to-η^1 slippage of the $TpMo(CO)_2$ fragment occurs in concert with departure of the sulfonate leaving group (**4** → **O**). The degree of racemization would then be determined by partitioning between complete ionization to the discrete achiral η^1-carbene **P** or interception of the still chiral, partially ionized intermediate **O** by the incoming nucleophile.

Conclusions

1-Alkoxy- and 1-arylsulfonyloxy-η^3-allylmolybdenum complexes participate in exchange reactions with external amine and alcohol nucleophiles. Acyclic alkoxyl-substituted complexes (η^3-allyl and η^3-butenyl) react directly with benzylamine to generate benzylamino-substituted η^3-allylmolybdenum complexes, but a Lewis acid catalyst is required to facilitate the substitution reaction with alcohols. The corresponding cyclohexenyl system did not participate in substitution reactions. Both acyclic (η^3-allyl and η^3-butenyl) and cyclic (η^3-cyclohexenyl) 1-arylsulfonyloxy complexes react directly with both amines and alcohols in the absence of any catalyst to provide the substitution products. In all cases studied, high enantiopurity starting materials provided substitution products that were significantly racemized. The reactivity order of each family of complexes suggests that the alkoxy-substituted η^3-allylmolybdenum complexes react via an associative process, while the 1-arylsulfonyloxy complexes react via a dissociative process. The loss of enantiopurity in the substitution products suggests a mechanism proceeding via an achiral η^1-vinylcarbene in each case. While additional studies are required to tease out the mechanistic details of these interesting processes, the results disclosed within highlight a new reactivity principle for η^3-allylmetal complexes bearing substituents that can function as leaving groups. It is suggested that useful stereocontrol emanating from enantiomerically enriched complexes could result either (1) by using an internally tethered nucleophile that is attached to the π-complex via a preexisting stereocenter (cf., earlier studies of the stereocontrolled functionalization of η^3-pyranyl- and η^3-pyridinylmolybdenum complexes)[1] or (2) by exploring reaction variables that can inhibit the partitioning of the substitution reaction pathway through an achiral η^1-vinylcarbene. Finally, the chemistry described within, when extended from molybdenum to tungsten, is likely to provide a useful procedure to generate stable vinylcarbene complexes.[14]

Experimental Section

General Methods. Details of the general methods are provided in the Supporting Information. Compounds **2a**−**2c**, **3a**−**3c**, and **3f** were synthesized according to previously published protocols.[1s] The absorption that appears near 2400 cm^{-1} in the infrared spectra of some of the complexes is due to the B−H stretch of the hydridotrispyrazolylborate ligand. This absorption is not always sufficiently strong to allow designation.

Synthetic Protocols and Characterization Data. (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-1,2,3)-1-(2,4,6-triisopropylbenzenesulfonyloxy)-2-propen-1-yl]molybdenum (*syn*-OSO_2Ar), 4a. Complex **2a** (50.0 mg, 0.093 mmol, 1.0 equiv) was dissolved in THF (2 mL), and TBAT (55.4 mg, 0.10 mmol, 1.1 equiv) was added in one portion at room temperature. After 15 min 2,4,6-triisopropylbenzenesulfonyl chloride (30.3 mg, 0.10 mmol, 1.10 equiv) was added in one portion at room temperature. The solution was stirred for 15 min at room temperature before being passed through a short pad of silica gel with hexanes−EtOAc (2:1) and concentrated on a rotary evaporator. Flash chromatography over silica gel with hexanes−EtOAc (2:1) provided **4a** (58.6 mg, 0.085 mmol, 92%) as a yellow solid. *Due to the sensitivity of **4a** to purification techniques, it was usually generated and used in situ.* (±)-**4a**: TLC: R_f = 0.60 (hexanes−EtOAc, 2:1). IR (cm^{-1}): 2964 (m), 1949 (s), 1864 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.75−8.55 (br m, 3 H), 7.54 (br s, 3 H), 7.16 (s, 2 H), 6.18 (br s, 3 H), 4.30 (d, J = 6.8 Hz, 1 H), 4.07 (hep, J = 6.8 Hz, 2 H), 3.70−3.76 (m, 1 H), 3.27 (dd, J = 7.6 Hz, 2.8 Hz, 1 H), 2.92 (hep, J = 6.8 Hz, 1 H), 1.25 (d, J = 6.8 Hz, 6 H), 1.20 (d, J = 6.4 Hz, 6 H), 1.08 (dd, J = 9.2 Hz, 3.2 Hz, 1 H), 0.98 (d, J = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 228.9, 225.9, 154.5, 151.8, 128.9, 124.1, 105.7, 98.7, 69.5, 45.2, 34.5, 25.0, 24.3, 23.8, 23.6. HRMS (ESI): calcd for $C_{29}H_{38}BMoN_6O_5S$ ($[M + H]^+$) 691.1766, found 691.1796.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-1,2,3)-1-(*p*-toluenesulfonyloxy)-2-buten-1-yl]molybdenum (*anti*-methyl/*syn*-OTs), 4b. Tosyloxy-substituted complex **4b** was synthesized in an analogous manner to 2,4,6-triisopropylbenzenesulfonyloxy-substituted complex **4c**, described below. However, instead of performing an aqueous workup, the crude reaction mixture was filtered through a short column of basic alumina and concentrated. Spectroscopic data were then gathered on this crude material. The use of silica gel and/or $CDCl_3$ for purification and characterization resulted in rapid decomposition of **4b**. Therefore, for synthetic purposes, **4b** was generated and used *in situ* without isolation. (±)-**4b**: TLC: R_f = 0.47 (hexanes−EtOAc, 2:1). IR (cm^{-1}): 2964 (m), 1942 (s), 1857 (s), 1594 (m), 1505 (m), 1432 (m). ^1H NMR (C_6D_6, 400 MHz): δ 8.49 (d, J = 2.0 Hz, 1 H), 8.41 (d, J = 2.0 Hz, 1 H), 7.71 (d, J = 8.4 Hz, 2 H), 7.22 (d, J = 2.0 Hz, 1 H), (1 proton obscured by C_6H_6), 7.01 (d, J = 1.6 Hz, 1 H), 6.98 (d, J = 2.0 Hz, 1 H), 6.64 (d, J = 8.4 Hz, 2 H), 5.86 (t, J = 2.0 Hz, 1 H), 5.72 (t, J = 2.4 Hz, 1 H), 5.65 (t, J = 2.4 Hz, 1 H), 5.36 (d, J = 7.2 Hz, 1 H), 3.78 (t, J = 8.4 Hz, 1 H), 3.54−3.61 (m, 1 H), 1.78 (s, 3 H), 1.10 (d, J = 6.4 Hz, 3 H). ^{13}C NMR (C_6D_6, 100 MHz): δ 230.9, 227.0, 147.8, 147.6, 145.2, 141.1, 136.5, 136.2, 134.5, 133.6, 130.2 (2), 129.1 (2), 106.6, 106.1, 106.0, 99.3, 71.9, 58.6, 30.8, 21.5, 17.5. HPLC: Daicel Chiralcel OJ-RH column, gradient solvent system was used (% CH_3CN in H_2O with 0.1% TFA) 0−20 min (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-**4b**: $t_{(S)}$ = 10.31 min; (*R*)-**4b**: $t_{(R)}$ = 10.88 min.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-1,2,3)-1-(2,4,6-triisopropylbenzenesulfonyloxy)-2-buten-1-yl]molybdenum (*anti*-methyl/*syn*-OSO_2Ar), 4c. Complex **2b** (500 mg, 0.91 mmol, 1.0 equiv) was dissolved in THF (10 mL), and TBAT (540 mg, 1.00 mmol, 1.1 equiv) was added in one portion at room temperature. After 15 min, 2,4,6-triisopropylbenzenesulfonyl chloride (606 mg, 2.00 mmol, 2.2 equiv) was added in one portion at room temperature. The solution was stirred for one hour at room temperature before it was poured into a separatory funnel containing water (20 mL) and CH_2Cl_2 (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was then subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1). The bright yellow band was collected and concentrated without heat on a rotary evaporator (slight decomposition observed). Compound **4c** was obtained as a yellow-brown solid (447 mg, 0.64 mmol, 70%). A sample for characterization was obtained by crystallization from the material isolated after chromatography. *Due to the sensitivity of **4c** to*

purification techniques, it was usually generated and used in situ. (±)-**4c**: TLC: R_f = 0.69 (hexanes−EtOAc, 2:1). IR (cm^{-1}): 1964 (m), 1945 (s), 1861 (s), 1598 (m), 1463 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.51 (s, 1 H), 8.10 (s, 1 H), 7.53 (s, 2 H), 7.48 (s, 1 H), 7.36 (s, 1 H), 7.12 (s, 2 H), 6.26 (s, 1 H), 6.14 (s, 1 H), 6.11 (s, 1 H), 5.00 (d, J = 7.2 Hz, 1 H), 3.97 (hep, J = 6.6 Hz, 2 H), 3.88 (pent, J = 6.6 Hz, 1 H), 3.62 (t, J = 7.8 Hz, 1 H), 2.91 (hep, J = 6.6 Hz, 1 H), 1.25 (d, J = 7.2 Hz, 6 H), 1.17 (d, J = 7.2 Hz, 6 H), 1.11 (d, J = 6.6 Hz, 3 H), 0.86 (d, J = 6.6 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 231.8, 225.5, 154.4, 151.6 (2), 147.3, 147.0, 139.6, 135.9 (2), 134.6, 129.2, 123.9 (2), 106.0, 105.6, 105.2, 97.7, 73.9, 56.5, 34.5, 29.9, 29.8, 25.1 (2), 23.8 (3), 23.6, 17.5. HRMS (ESI): calcd for $C_{30}H_{39}BMoN_6O_5S$ ($[M+H]^+$) 705.1926, found 705.1926.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-1,2,3)-1-(prop-2-en-1-oxy)-2-buten-1-yl]molybdenum (*anti*-methyl/*syn*-allyloxy), 3d. Silyl ether **2b** (1.00 g, 1.82 mmol, 1.0 equiv) was dissolved in THF (10 mL), and TBAT (1.08 g, 2.00 mmol, 1.1 equiv) was added in one portion. The solution was stirred for 55 min at room temperature before allyl bromide (1.57 mL, 18.2 mmol, 10.0 equiv) was added. After 20 h, the solution was concentrated and the crude product was subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1), affording **3d** as a yellow solid (699 mg, 1.47 mmol, 81%). (±)-**3d**: TLC: R_f = 0.70 (hexanes−EtOAc, 2:1). IR (cm^{-1}): 2872 (m), 1918 (s), 1818 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.48 (d, J = 2.0 Hz, 1 H), 8.09 (d, J = 2.0 Hz, 1 H), 7.72 (d, J = 2.0 Hz, 1 H), 7.55 (dd, J = 2.0 Hz, 0.4 Hz, 2 H), 7.50 (dd, J = 2.0 Hz, 0.4 Hz, 1 H), 6.25 (t, J = 2.0 Hz, 1 H), 6.16 (t, J = 2.0 Hz, 1 H), 6.12 (t, J = 2.4 Hz, 1 H), 5.94−6.04 (m, 1 H), 5.39 (dq, J = 17.2 Hz, 1.6 Hz, 1 H), 5.27−5.31 (m, 2 H), 4.54 (ddt, J = 12.8 Hz, 5.6 Hz, 1.6 Hz, 1 H), 4.33 (ddt, J = 12.8 Hz, 5.6 Hz, 1.6 Hz, 1 H), 3.86−3.93 (m, 2 H), 1.33 (d, J = 6.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 232.8, 229.5, 147.2, 145.0, 141.6, 135.9, 135.8, 134.4, 132.7, 118.8, 117.5, 105.8, 105.3, 105.0, 72.8, 66.0, 58.2, 17.9. HRMS (ESI): calcd for $C_{18}H_{22}BMoN_6O_3$ ($[M+H]^+$) 479.0895, found 479.0900.

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

Complex (−)-**2b** (32.4 mg, 0.059 mmol, 1.0 equiv, 91.1% ee) was dissolved in THF (2 mL), and the solution was cooled to −78 °C. TBAT (35.0 mg, 0.065 mmol, 1.1 equiv) was added in one portion, and the solution was stirred for 15 min. Cinnamyl bromide (11 μL, 0.071 mmol, 1.2 equiv) was added, and the solution was stirred for 2 h at −78 °C before being concentrated. Flash chromatography over silica gel with hexanes−EtOAc (4:1) afforded (−)-**3e** (17.1 mg, 0.031 mmol, 53%, 95.1% ee)[13] ($[\alpha]^{25}_D$ −212 (*c* 1.01, CH_2Cl_2)) as a yellow solid.

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

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-1,2,3)-1-(*p*-toluenesulfonyloxy)-2-cyclohexen-1-yl]molybdenum, 4d. Complex **2c** (300 mg, 0.52 mmol, 1.0 equiv) was dissolved in THF (10 mL), and TBAT (338 mg, 0.63 mmol, 1.2 equiv) was added in one portion. The solution was stirred for 25 min at room temperature and cooled to 0 °C, and then *p*-toluenesulfonyl chloride (120 mg, 0.63 mmol, 1.2 equiv) was added in one portion. The solution was stirred for 4 h at 0 °C and then concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1), affording **4d** (104 mg, 0.17 mmol, 32%) as a yellow-brown solid. (±)-**4d**: TLC: R_f = 0.56 (hexanes−EtOAc, 4:1). IR (cm^{-1}): 3150−2853 (m), 1934 (s), 1849 (s), 1409 (s), 1505 (m), 1598 (w). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.49 (d, J = 1.8 Hz, 1 H), 7.90 (d, J = 2.4 Hz, 1 H), 7.57 (d, J = 1.8 Hz, 1 H), 7.56 (d, J = 1.8 Hz, 1 H), 7.46 (d, J = 2.4 Hz, 1 H), 7.39 (d, J = 2.4 Hz, 1 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.00 (d, J = 8.4 Hz, 2 H), 6.24 (t, J = 2.4 Hz, 1 H), 6.13 (t, J = 2.4 Hz, 1 H), 6.10 (t, J = 2.4 Hz, 1 H), 3.92 (s, 2 H), 2.69−2.64 (m, 1 H), 2.31 (s, 3 H), 2.24−2.21 (m, 1 H), 2.10 (dt, J = 13.8 H, 5.4 Hz, 1 H), 1.84−1.81 (m, 1 H), 1.26−1.20 (m, 1 H), 0.58−0.52 (m, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 229.0, 226.1, 146.9, 146.8, 144.6, 139.0, 136.0, 135.9, 135.2, 134.4, 129.5 (2), 127.6 (2), 114.4, 105.9, 105.4, 105.3, 66.0, 58.6, 30.0, 22.4, 21.7, 20.5. HRMS (ESI): calcd for $C_{24}H_{26}BMoN_6O_5S$ ($[M+H]^+$) 619.0827, found 619.0829.

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

Similar treatment of (+)-**2c** (199 mg, 0.34 mmol, 1.0 equiv, 97.5% ee) with TBAT (202 mg, 0.37 mmol, 1.1 equiv) and 2,4,6-triisopropylbenzenesulfonyl chloride (112 mg, 0.37 mmol, 1.1 equiv) in THF (5 mL) afforded (+)-**4e** (56.6 mg, 0.078 mmol, 23%, 96.5% ee) [$[\alpha]^{25}_D$ +82 (*c* 0.18, CH_2Cl_2)] as a bright yellow solid.

(±)-**4e**: TLC: R_f = 0.72 (hexanes−EtOAc, 2:1). IR (cm^{-1}): 2961 (m), 1938 (s), 1849 (s), 1602 (m), 1505 (m), 1463 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.53 (d, J = 1.8 Hz, 1 H), 7.69 (d, J = 2.4 Hz, 1 H), 7.62 (d, J = 1.8 Hz, 1 H), 7.57 (d, J = 2.4 Hz, 1 H), 7.47 (d, J = 2.4 Hz, 1 H), 7.42 (d, J = 2.4 Hz, 1 H), 7.11 (s, 2 H), 6.25 (t, J = 2.4 Hz, 1 H), 6.19 (t, J = 2.4 Hz, 1 H), 5.69 (t, J = 2.4 Hz, 1 H), 4.36 (d, J = 7.8 Hz, 1 H), 4.10 (hep, J = 6.6 Hz, 2 H), 4.03 (br d, J = 8.4 Hz, 1 H), 2.89 (hep, J = 6.6 Hz, 1 H), 2.59−2.64 (m, 1 H), 2.21 (dd, J = 15.0 Hz, 6.0 Hz, 1 H), 2.11 (dt, J = 13.2 Hz, 6.0 Hz, 1 H), 1.87 (dt, J = 14.4 Hz, 4.8 Hz, 1 H), 1.25 (d, J = 6.6 Hz, 6 H), 1.19−1.21 (m, 1 H), 1.17 (d, J = 6.6 Hz, 6 H), 1.00 (d, J = 6.6 Hz, 6 H), 0.52−0.59 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 229.0, 226.5, 154.1, 150.8 (2), 146.9, 146.1, 139.5, 136.2, 135.8, 134.3, 131.4, 123.9 (2), 114.7, 105.9, 105.6, 104.4, 66.9, 59.6, 34.4, 29.8 (3), 24.5 (2), 24.4 (2), 23.7 (2), 22.6, 20.7.

HRMS (ESI): calcd for $C_{32}H_{41}BMoN_6O_5S$ ([M]$^+$) 731.2079, found 731.2079. HPLC: Daicel Chiralcel OJ-RH column, gradient solvent system was used (% CH_3CN in H_2O with 0.1% TFA) 0−20 min (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-(−)-**4e**: $t_{(S)}$ = 18.36 min; (*R*)-(+)-**4e**: $t_{(R)}$ = 17.32 min.

Direct Exchange of Alkoxy Substituents with Amines. (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-propen-1-yl]molybdenum (*syn*-benzylamino), 5a. Methoxy-substituted complex **3a** (100 mg, 0.23 mmol, 1.0 equiv) was dissolved in THF (3 mL), and benzyl amine (0.75 mL, 6.88 mmol, 30.0 equiv) was added. After 20 h, the reaction mixture was concentrated and the crude material was subjected to flash chromatography over silica gel with hexanes−ethyl acetate (4:1). The red band was collected, affording **5a** (112 mg, 0.22 mmol, 95%) as a red solid. (±)-**5a**: TLC: R_f = 0.45 (hexanes−EtOAc, 2:1). IR (cm^{-1}): 3397 (m), 3034 (w), 2478 (m), 1903 (s), 1783 (s), 1698 (m), 1571 (s), 1502 (s), 1455 (m). ^{1}H NMR (400 MHz, C_6D_6): δ 8.41 (d, J = 1.6 Hz, 1 H), 7.51 (d, J = 1.2 Hz, 1 H), 7.46 (d, J = 2.0 Hz, 1 H), 7.39 (d, J = 2.0 Hz, 1 H), 7.30 (d, J = 2.0 Hz, 1 H), 7.23 (d, J = 2.4 Hz, 1 H), 7.03−7.07 (m, 3 H), 6.75−6.77 (m, 2 H), 5.88 (t, J = 2.0 Hz, 1 H), 5.85 (t, J = 2.0 Hz, 1 H), 5.74 (t, J = 2.0 Hz, 1 H), 5.27 (app t, J = 9.6 Hz, 1 H), 3.36−3.41 (m, 1 H), 3.24−3.32 (m, 3 H), 2.57−2.63 (m, 1 H), 1.48 (dd, J = 8.8 Hz, 4.8 Hz, 1 H). ^{13}C NMR (100 MHz, C_6D_6): δ 234.5, 231.9, 147.5, 144.7, 140.1, 137.7, 136.2, 135.6, 134.9, 133.1, 129.1 (2), 128.5 (2), 106.3, 105.7, 105.6, 77.9, 57.1, 49.5, 44.9. HRMS (ESI): calcd for $C_{21}H_{23}BMoN_7O_2$ ([M + H]$^+$) 514.1054, found 514.1060.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-buten-1-yl]molybdenum (*anti*-methyl/*syn*-benzylamino), 5b. Methoxy-substituted molybdenum complex **3c** (25.0 mg, 0.056 mmol, 1.0 equiv) was dissolved in THF (2 mL), benzyl amine (0.18 mL, 1.7 mmol, 30 equiv) was added, and the solution was heated to reflux. After refluxing for 20.5 h, the solution was concentrated and the residue was subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1). The red band was collected to afford **5b** as a red solid (21.8 mg, 0.042 mmol, 74%). (±)-**5b**: TLC: R_f = 0.53 (hexanes−EtOAc, 2:1). IR (cm^{-1}): 3401 (br), 2922 (m), 1899 (s), 1783 (s), 1575 (s), 1502 (s), 1455 (m). ^{1}H NMR (400 MHz, C_6D_6): δ 8.42 (d, J = 2.0 Hz, 1 H), 7.48 (d, J = 2.0 Hz, 1 H), 7.45 (d, J = 2.0 Hz, 1 H), 7.39 (d, J = 2.0 Hz, 1 H), 7.23−7.24 (m, 2 H), 7.03−7.08 (m, 3 H), 6.71−6.73 (m, 2 H), 6.01 (dd, J = 11.2 Hz, 9.2 Hz, 1 H), 5.87 (q, J = 2.4 Hz, 2 H), 5.74 (t, J = 2.4 Hz, 1 H), 3.92 (app pent, J = 6.8 Hz, 1 H), 3.38−3.40 (m, 1 H), 3.27 (dd, J = 14.4 Hz, 4.8 Hz, 1 H), 3.04 (dd, J = 14.4 Hz, 5.2 Hz, 1 H), 2.84 (dd, J = 11.2 Hz, 8.4 Hz, 1 H), 1.73 (d, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, C_6D_6): δ 235.6, 232.1, 147.4, 145.1, 140.3, 137.6, 136.2, 135.5, 135.0, 130.9, 129.0 (2), 128.4 (2), 106.2, 105.7, 105.6, 62.4, 54.3, 48.9, 19.7. HRMS (ESI): calcd for $C_{22}H_{25}BMoN_7O_2$ ([M + H]$^+$) 528.1211, found 528.1217. HPLC: Daicel Chiralcel OD-RH column, gradient solvent system was used (% CH_3CN in H_2O with 0.1% TFA) 0−20 min (50% to 75%), 1.5 mL/min, λ = 254 nm, enantiomer 1: t_1 = 13.55 min; enantiomer 2: t_2 = 15.21 min.

Conversion of 3e to 5b and (−)-3e to 5b. Cinnamyloxy-substituted molybdenum complex **3e** (25.0 mg, 0.045 mmol, 1.0 equiv) was dissolved in THF (2 mL), benzyl amine (0.15 mL, 1.4 mmol, 30 equiv) was added, and the solution was heated to reflux. After 24 h, the solution was concentrated and the crude material was subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1). The red band was collected, affording **5b** (13.7 mg, 0.026 mmol, 58%) as a red solid.

Similar treatment of (−)-**3e** (17.1 mg, 0.031 mmol, 1.0 equiv, 95.1% ee) with $BnNH_2$ (0.10 mL, 0.93 mmol, 30 equiv) in THF (1 mL) afforded **5b** (7.2 mg, 0.014 mmol, 44%, 3.5% ee) as a red solid.

Lewis Acid-Catalyzed Exchange of Alkoxy Substituents with Alcohols. Conversion of 3a to 3b. Methoxy-substituted complex **3a** (100 mg, 0.23 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (3 mL), and *i*-PrOH (0.35 mL, 4.59 mmol, 20 equiv) and $EtAlCl_2$ (1.0 M in hexanes, 0.092 mL, 0.092 mmol, 0.40 equiv) were added sequentially. The flask was sealed and the solution was stirred overnight at room temperature. After 26 h, the solution was concentrated and the crude reaction mixture was subjected to flash chromatography over silica gel with hexanes−EtOAc (9:1). The yellow band was collected, affording **3b** (79.6 mg, 0.17 mmol, 72%) as a yellow solid.

Conversion of 3b to 3a. Isopropyloxy-substituted complex **3b** (43.0 mg, 0.093 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2 mL), and MeOH (75 μL, 1.85 mmol, 20 equiv) and $EtAlCl_2$ (1.0 M in hexanes, 0.037 mL, 0.037 mmol, 0.4 equiv) were added sequentially. The solution was stirred 4 h at room temperature and then concentrated. Flash chromatography over silica gel with hexanes−EtOAc (4:1) afforded **3a** (35.1 mg, 0.080 mmol, 87%) as a yellow solid.

Direct Exchange of Sulfonate Ester Substituents with Amines and Alcohols. Conversion of 2a to 5a through Intermediate 4a. Complex **2a** (50.0 mg, 0.093 mmol, 1.0 equiv) was dissolved in THF (2 mL), and TBAT (55.4 mg, 0.10 mmol, 1.1 equiv) was added in one portion at room temperature. The solution was stirred for 5 min before 2,4,6-triisopropylbenzenesulfonyl chloride (30.3 mg, 0.10 mmol, 1.1 equiv) was added in one portion at room temperature. The reaction mixture was stirred for 10 min before benzyl amine (0.31 mL, 2.79 mmol, 30 equiv) and MeOH (2 mL) were added, and the solution was refluxed for 2 h. The reaction mixture was concentrated on a rotary evaporator and then subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1). The red band was collected, affording **5a** (37.2 mg, 0.073 mmol, 78%) as a red solid.

Conversion of (±)-2b to 5b and (−)-2b to 5b through Intermediate 4b. Silyl ether (±)-**2b** (100 mg, 0.18 mmol, 1.0 equiv) was dissolved in THF (2 mL), and TBAT (108 mg, 0.20 mmol, 1.1 equiv) was added in one portion. After 5 min, the reaction mixture was cooled to 0 °C and *p*-TsCl (38.1 mg, 0.20 mmol, 1.1 equiv) was added. After 10 min, MeOH (2 mL) and benzyl amine (0.59 mL, 5.40 mmol, 30 equiv) were added, and the solution was heated to reflux for 2 h and concentrated. Flash chromatography over silica gel with hexanes−EtOAc (4:1) afforded **5b** (50.2 mg, 0.096 mmol, 53%) as a red solid.

Silyl ether (−)-**2b** (50.0 mg, 0.091 mmol, 1.0 equiv, 96.2% ee) was dissolved in THF (1.5 mL), and TBAT (54.0 mg, 0.10 mmol, 1.1 equiv) was added in one portion. After 5 min, the reaction was cooled to 0 °C and *p*-TsCl (19.1 mg, 0.10 mmol, 1.1 equiv) was added. After 10 min, a sample of the crude reaction mixture was analyzed by chiral HPLC, and tosylate **4b** was determined to have a 91.0% ee. MeOH (1.5 mL) and benzyl amine (0.30 mL, 2.73 mmol, 30 equiv) were added to the reaction, and the solution was heated to reflux for 3 h and then concentrated. Flash chromatography over silica gel with hexanes−EtOAc (4:1) afforded **5b** (28.3 mg, 0.054 mmol, 59%, 1.1% ee) as a red solid.

Conversion of (±)-2b to 5b through Intermediate 4c. Complex **2b** (100 mg, 0.18 mmol, 1.0 equiv) was dissolved in THF (2 mL), and tetrabutylammonium triphenyldifluorosilicate (TBAT) (108 mg, 0.20 mmol, 1.1 equiv) was added in one portion at room temperature. The solution was stirred for 5 min before 2,4,6-triisopropylbenzenesulfonyl chloride (60.6 mg, 0.20 mmol, 1.1 equiv) was added in one portion at room temperature. After stirring for 10 min, MeOH (2 mL) and benzyl amine (0.59 mL, 5.4 mmol, 30 equiv) were added and the solution was refluxed for 2 h. The reaction mixture was then concentrated under reduced pressure and passed through a short pad of silica gel. The solution was again concentrated and subjected to flash chromatography over silica gel with hexanes−EtOAc (2:1). The red band was collected, affording **5b** as a red solid (70.1 mg, 0.13 mmol, 74%).

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-1,2,3)-1-benzylamino-2-cyclohexen-1-yl]molybdenum, 5c. Complex **4d** (52.0 mg, 0.084 mmol, 1.0 equiv) was dissolved in THF (2 mL), benzyl amine (0.14 mL, 1.27 mmol, 15 equiv) was added, and the solution was heated to reflux. After 18 h, the solution was concentrated and the

crude reaction mixture was subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1). The red band was collected, affording **5c** as a red solid (20.9 mg, 0.038 mmol, 45%). (±)-**5c**: TLC: R_f = 0.53 (hexanes−EtOAc, 4:1). IR (cm^{-1}): 3374 (br, w), 2930 (m), 2478 (m), 1888 (s), 1772 (s). ^{1}H NMR (C_6D_6, 400 MHz): δ 8.45 (d, J = 1.2 Hz, 1 H), 7.52 (s, 1 H), 7.50 (d, J = 2.0 Hz, 1 H), 7.45 (d, J = 2.0 Hz, 1 H), 7.37 (d, J = 1.2 Hz, 1 H), 7.26 (d, J = 2.0 Hz, 1 H), 7.02−7.06 (m, 3 H), 6.70 (d, J = 6.4 Hz, 2 H), 5.88−5.90 (m, 2 H), 5.74 (t, J = 1.6 Hz, 1 H), 3.93−3.98 (m, 2 H), 3.18−3.44 (m, 2 H), 2.50−2.53 (m, 1 H), 2.35−2.38 (m, 1 H), 2.17−2.22 (m, 1 H), 1.70−1.84 (m, 2 H), 1.23−1.37 (m, 2 H). ^{13}C NMR (C_6D_6, 100 MHz): δ 233.9 (2), 147.5, 144.2, 140.3, 137.7, 136.2, 135.9, 134.8, 129.1 (2), 128.9 (2), 127.7, 106.2, 105.6, 105.5, 56.7, 53.1, 47.1, 26.3, 25.2, 19.0. HRMS (ESI): calcd for $C_{24}H_{27}BMoN_7O_2$ ([M + H]$^+$): 554.1368, found 554.1361. HPLC: Daicel Chiralcel OD-RH column, gradient solvent system was used (% CH_3CN in H_2O with 0.1% TFA) 0−20 min (50% to 75%), 1.5 mL/min, λ = 254 nm, enantiomer 1: t_1 = 14.37 min; enantiomer 2: t_2 = 15.84 min.

Conversion of (±)-4e to 5c and (+)-4e to 5c. Complex **4e** (50.0 mg, 0.069 mmol, 1.0 equiv) was dissolved in THF (2 mL), benzyl amine (0.23 mL, 2.06 mmol, 30 equiv) was added, and the solution was heated to reflux. After 17 h, the solution was concentrated and the crude reaction mixture was subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1). The red band was collected, affording **5c** as a red solid (12.1 mg, 0.022 mmol, 32%).

Similar treatment of (+)-**4e** (56.0 mg, 0.077 mmol, 1.0 equiv) with $BnNH_2$ (0.25 mL, 2.31 mmol, 30 equiv) in THF (1 mL) afforded **5c** (16.1 mg, 0.029 mmol, 38%, 30.6% ee) as a red solid.

Conversion of 2a to 3a through Intermediate 4a. Complex **2a** (50.0 mg, 0.093 mmol, 1.0 equiv) was dissolved in THF (2 mL), and TBAT (55.4 mg, 0.10 mmol, 1.1 equiv) was added in one portion. After 5 min, 2,4,6-triisopropylbenzenesulfonyl chloride (30.3 mg, 0.10 mmol, 1.0 equiv) was added in one portion. After 10 min, MeOH (2 mL) was added, and the solution was stirred 17 h at room temperature and concentrated. Flash chromatography over silica gel with hexanes−EtOAc (4:1) afforded **3a** (29.7 mg, 0.068 mmol, 73%) as a yellow solid.

Conversion of 2b to 3c through Intermediate 4c. Complex **2b** (100 mg, 0.18 mmol, 1.0 equiv) was dissolved in THF (2 mL), and TBAT (108 mg, 0.20 mmol, 1.10 equiv) was added in one portion at room temperature. After 5 min, 2,4,6-triisopropylbenzenesulfonyl chloride (60.6 mg, 0.20 mmol, 1.1 equiv) was added in one portion at room temperature. The solution was stirred for 10 min before MeOH (2 mL) was added. After 14 h, the reaction mixture was poured into a separatory funnel containing water (10 mL) and CH_2Cl_2 (10 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography over silica gel with hexanes−EtOAc (9:1) afforded **3c** (59.5 mg, 0.13 mmol, 72%) as a yellow solid.

Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(1,2,3)-1-((*S*)-(−)-2-acetoxypropionyloxy)-2-cyclohexen-1-yl]molybdenum, 8. Complex **2c** (1.75 g, 3.05 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10 mL), and TBAT (1.98 g, 3.66 mmol, 1.2 equiv) was added in one portion. The solution was stirred 30 min at room temperature before (*S*)-(−)-acetoxypropionyl chloride (0.42 mL, 3.36 mmol, 1.1 equiv) was added dropwise. After stirring 10 min at room temperature, the solution was concentrated and the crude product was subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1). Recrystallization from dichloromethane and hexanes provided **8**, a 1:1 mixture of two diastereomers (1.56 g, 2.71 mmol, 89%), as a yellow solid. (±)-**8**: TLC: R_f = 0.51 (hexanes−EtOAc, 4:1). IR (cm^{-1}): 2941 (m), 2849 (w), 2482 (m), 2258 (w), 1934 (s), 1849 (s), 1749 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.55 (d, J = 2.0 Hz, 1 H), 8.54 (d, J = 2.0 Hz, 1 H), 8.04 (d, J = 1.6 Hz, 1 H), 8.03 (d, J = 2.0 Hz, 1 H), 7.66 (d, J = 2.0 Hz, 1 H), 7.63 (d, J = 1.6 Hz, 1 H), 7.60 (d, J = 2.4 Hz, 2 H), 7.56 (d, J = 2.4 Hz, 2 H), 7.50 (dd, J = 2.4 Hz, 0.8 Hz, 1 H), 7.48 (d, J = 2.0 Hz, 1 H), 6.25−6.27 (m, 2 H), 6.20−6.21 (dd, J = 4.0 Hz, 2.4 Hz, 2 H), 6.13−6.15 (dd, J = 4.0 Hz, 2.4 Hz, 2 H), 5.00 (m, 2 H), 4.04−4.12 (m, 3 H), 3.91 (m, 1 H), 2.59−2.41 (m, 2 H), 2.23−2.14 (m, 2 H), 2.12 (s, 3 H), 2.10 (s, 3 H), 2.05−1.85 (m, 4 H), 1.47 (d, J = 7.2 Hz, 3 H), 1.20−1.29 (m, 2 H), 1.13 (d, J = 6.8 Hz, 3 H), 0.66 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 229.0, 228.5, 226.7, 226.4, 170.6, 170.4, 170.3, 169.8, 147.0, 146.8, 146.3, 140.0, 139.6, 136.4, 134.4, 111.5, 111.1, 106.0, 105.6, 105.0, 104.8, 69.3, 69.1, 67.5, 66.6, 60.3, 59.0, 27.8, 22.7, 22.7, 20.8, 20.1, 20.0, 17.1, 16.4. HRMS (ESI): calcd for $C_{22}H_{26}BMoN_6O_6$ ([M + H]$^+$) 579.1055, found 579.1058.

Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(1,2,3)-1-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanoxycarbonyl)-2-cyclohexen-1-yl]molybdenum, 10. Complex **2c** (672 mg, 1.17 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (6 mL), and TBAT (756 mg, 1.40 mmol, 1.2 equiv) was added in one portion at room temperature. The solution was stirred for 30 min before (−)-menthyl chloroformate (0.27 mL, 1.29 mmol, 1.1 equiv) was added dropwise. After 3 h, the solution was concentrated and the crude product was subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1), affording **10**, a 1:1 mixture of two diastereomers (677 mg, 1.05 mmol, 90%), as a yellow solid. (±)-**10**: TLC: R_f = 0.27 (hexanes−EtOAc, 4:1). IR (cm^{-1}): 2957 (m), 2872 (m), 2478 (m), 1938 (s), 1849 (s), 1749 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56 (br s, 1 H), 8.14 (d, J = 2.0 Hz, 0.5 H), 8.12 (d, J = 2.0 Hz, 0.5 H), 7.72 (d, J = 2.0 Hz, 0.5 H), 7.70 (d, J = 1.6 Hz, 0.5 H), 7.63−7.65 (m, 2 H), 7.61 (br s, 1 H), 7.54 (d, J = 2.0 Hz, 0.5 H), 7.53 (d, J = 2.0 Hz, 0.5 H), 7.49−7.50 (m, 2 H), 7.37−7.48 (m, 3 H), 6.26−6.28 (m, 2 H), 6.19−6.21 (m, 2 H), 6.09 (t, J = 2.4 Hz, 1 H), 6.04 (t, J = 2.4 Hz, 1 H), 4.52 (dt, J = 10.8 Hz, 4.8 Hz, 1 H), 4.42 (dt, J = 10.8 Hz, 4.8 Hz, 1 H), 4.21 (d, J = 7.6 Hz, 1 H), 4.16 (d, J = 8.0 Hz, 1 H), 4.06−4.12 (m, 2 H), 2.47−2.58 (m, 2 H), 2.11−2.24 (m, 4 H), 1.86−2.02 (m, 4 H), 1.62−1.71 (m, 6 H), 1.22−1.50 (m, 6 H), 0.78−1.13 (m, 6 H), 0.94 (d, J = 1.2 Hz, 3 H), 0.93 (s, 3 H), 0.85 (d, J = 6.4 Hz, 3 H), 0.83 (d, J = 6.8 Hz, 3 H), 0.76 (d, J = 6.8 Hz, 3 H), 0.57−0.68 (m, 2 H), 0.55 (d, J = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 228.5, 228.4, 226.9, 226.8, 153.7, 153.6, 147.1, 146.5, 140.4, 140.2, 136.3, 136.2, 136.1, 135.2, 134.3, 131.1, 130.3, 128.3, 128.2, 112.6, 112.3, 106.0, 105.5, 104.9, 104.7, 79.3, 79.1, 65.7, 65.6, 61.5, 60.9, 47.4, 47.3, 40.9, 40.8, 34.3 (2), 31.6, 28.2, 28.1, 26.5, 25.9, 23.7, 23.4, 22.7, 22.2, 22.1, 21.0 (2), 20.1 (2), 16.7, 16.3. HRMS (ESI): calcd for $C_{28}H_{38}BMoN_6O_5$ ([M + H]$^+$) 647.2045, found 647.2054.

(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*R*)-(η-1,2,3)-1-(((*R*)-3-hydroxycarbonyl-4,4-dimethyldihydrofuran-2(3*H*)-one)-oxy)-2-cyclohexen-1-yl]molybdenum, (+)-(1*R*,*R*)-11, and (−)-Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1*S*)-(η-1,2,3)-1-(((*R*)-3-hydroxycarbonyl-4,4-dimethyldihydrofuran-2(3*H*)-one)oxy)-2-cyclohexen-1-yl]molybdenum, (−)-(1*S*,*R*)-11. Complex **2c** (2.00 g, 3.47 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (15 mL), and TBAT (2.25 g, 4.17 mmol, 1.2 equiv) was added in one portion at room temperature. After 15 min, (*R*)-(−)-pantolactone chloroformate (735 mg, 3.82 mmol, 1.1 equiv) was added dropwise. The solution was stirred for 45 min, concentrated under reduced pressure, and subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1). The unseparated portion of the diastereomeric mixture was subjected to a second chromatography under the same conditions. Highly diastereomerically enriched samples of each diastereomer were thus obtained. Recrystallization of the *R*,*R* diastereomer from CH_2Cl_2/hexanes improved the dr of the crystals from 98.5:1.5 to >99.9:0.1 (supernatant dr = 96.2:3.8). Recrystallization of the supernatant from CH_2Cl_2/hexanes brought the dr of the crystals to >99.9:0.1. The supernatant (dr = 90.2:9.8) was set aside. The *S*,*R* diastereomer was recrystallized from CH_2Cl_2/hexanes, improving the dr of the crystals from 88.8:11.2 to >99.9:0.1. The supernatant (dr = 80.4:19.6) was combined with the supernatant from the *R*,*R* diastereomer and again chromatographed with hexanes−EtOAc (4:1). Recrystallization from CH_2Cl_2/hexanes provided additional *R*,*R* diastereomer in dr >99.9:0.1. Following this protocol, (1*R*,*R*)-**11** (850 mg, 1.38 mmol, 40%) {$[\alpha]^{25}_D$ +54 (*c* 1.05, CH_2Cl_2)} and (1*S*,*R*)-**11** (741 mg, 1.20 mmol, 35%) {$[\alpha]^{25}_D$ −36 (*c* 1.02, CH_2Cl_2)} were obtained as bright yellow solids.

HPLC: Agilent Eclipse XDB-C8 column (% CH_3CN in H_2O with 0.1% TFA) 0−10 min (50% to 75%), 10−12 min (75% to 90%), 1.5 mL/min, λ = 254 nm, (−)-(1*S*,*R*)-**11**: $t_{(1S,R)}$ = 10.16 min; (+)-(1*R*, *R*)-**11**: $t_{(1R,R)}$ = 10.79 min.

(+)-(1*R*,*R*)-**11**: TLC: R_f = 0.60 (hexanes−EtOAc, 4:1). IR (cm^{-1}): 3146 (w), 2941 (m), 2482 (m), 2258 (w), 1938 (s), 1849 (s), 1791 (s), 1756 (s). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.56 (d, J = 1.8 Hz, 1 H), 8.15 (d, J = 2.4 Hz, 1 H), 7.70 (d, J = 1.8 Hz, 1 H), 7.62 (d, J = 1.8 Hz, 1 H), 7.54 (d, J = 1.8 Hz, 1 H), 7.50 (d, J = 1.8 Hz, 1 H), 6.28 (t, J = 2.4 Hz, 1 H), 6.22 (t, J = 1.8 Hz, 1 H), 6.07 (t, J = 2.4 Hz, 1 H), 5.30 (s, 1 H), 5.12 (s, 1 H), 4.15 (d, J = 7.8 Hz, 1 H), 4.09−4.10 (m, 1 H), 4.01 (dd, J = 9.0 Hz, 2.4 Hz, 2 H), 2.63−2.58 (m, 1 H), 2.20−2.16 (m, 1 H), 1.95−1.91 (dt, J = 13.8 Hz, 4.8 Hz, 1 H), 1.32−1.28 (dt, J = 14.4 Hz, 5.4 Hz, 1 H), 1.12 (s, 3 H), 1.03 (s, 3 H), 0.65−0.59 (m, 1 H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 228.2, 225.8, 171.7, 153.2, 147.1, 146.7, 139.9, 136.4, 136.3, 134.4, 111.7, 106.0, 105.5, 104.8, 97.9, 78.7, 76.2, 65.1, 40.2, 27.7, 23.1, 22.6, 20.1, 19.9. HRMS (ESI): calcd for $C_{24}H_{27}BMoN_6O_7$ ($[M + H]^+$) 621.1161, found 621.1163.

(−)-(1*S*, *R*)-**11**: TLC: R_f = 0.62 (hexanes−EtOAc, 4:1). IR (cm^{-1}): 3146 (w), 2941 (m), 2482 (m), 2258 (w), 1938 (s), 1849 (s), 1791 (s), 1756 (s). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.56 (d, J = 1.8 Hz, 1 H), 8.15 (d, J = 2.4 Hz, 1 H), 7.70 (d, J = 1.8 Hz, 1 H), 7.62 (d, J = 1.8 Hz, 1 H), 7.54 (d, J = 1.8 Hz, 1 H), 7.50 (d, J = 1.8 Hz, 1 H), 6.28 (t, J = 2.4 Hz, 1 H), 6.22 (t, J = 1.8 Hz, 1 H), 6.07 (t, J = 2.4 Hz, 1 H), 5.30 (s, 1 H), 5.12 (s, 1 H), 4.15 (d, J = 7.8 Hz, 1 H), 4.09−4.11 (m, 1 H), 4.01 (dd, J = 20.4 Hz, 9.0 Hz, 2 H), 2.63−2.58 (m, 1 H), 2.20−2.16 (m, 1 H), 1.95−1.91 (dt, J = 13.8 Hz, 4.8 Hz, 1 H), 1.32−1.28 (dt, J = 14.4 Hz, 5.4 Hz, 1 H), 1.12 (s, 3 H), 1.03 (s, 3 H), 0.65−0.59 (m, 1 H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 228.2, 225.8, 171.7, 153.2, 147.1, 146.7, 139.9, 136.4, 134.4, 111.7, 106.0, 105.5, 104.8, 97.9, 78.7, 76.2, 65.1, 60.5, 40.2, 27.7, 23.1, 22.6, 20.1, 19.9. HRMS (ESI): calcd for $C_{24}H_{27}BMoN_6O_7$ ($[M + H]^+$) 621.1161, found 621.1164.

(−)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*R*)-(η-1,2,3)-1-(((*R*)-3-hydroxycarbonyl-4,4-dimethyldihydrofuran-2(3*H*)-one)-oxy)-2-buten-1-yl]molybdenum (*anti*-methyl/*syn*-pantolactonecarbonyloxy), (−)-(1*R*,*R*)-12. Complex **2b** (2.04 g, 37.0 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (100 mL), and TBAT (2.40 g, 44.4 mmol, 1.2 equiv) was added in one portion. The solution was stirred 20 min at room temperature, and (*R*)-(−)-pantolactone chloroformate (7.84 g, 40.7 mmol, 1.1 equiv) was added dropwise. The solution was stirred for 1 h and then concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes−EtOAc (9:1 and slowly ramping to 0:1), followed by a second chromatography under the same conditions. Iterations of recrystallization from CH_2Cl_2/hexanes and further chromatography allowed one diastereomer, (1*R*,*R*)-**12** (4.76 g, 8.0 mmol, 22%, dr > 95:5) {$[\alpha]^{25}_D$ −149 (*c* 1.04, CH_2Cl_2)}, to be isolated as a yellow solid. The second diastereomer, (1*S*,*R*)-**12**, decomposed, producing a byproduct that partly overlapped with the stable diastereomer during chromatography. (−)-(1*R*, *R*)-**12**: TLC: R_f = 0.34 (hexanes−EtOAc, 2:1). IR (cm^{-1}): 2968 (w), 2930 (w), 2486 (w), 1938 (s), 1849 (s), 1803 (s), 1760 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (d, J = 1.6 Hz, 1 H), 7.79 (d, J = 2.0 Hz, 1 H), 7.60 (d, J = 1.6 Hz, 1 H), 7.58 (d, J = 2.4 Hz, 1 H), 7.57 (d, J = 2.4 Hz, 1 H), 7.48 (d, J = 2.4 Hz, 1 H), 6.27 (t, J = 2.0 Hz, 1 H), 6.23 (t, J = 2.0 Hz, 1 H), 6.18 (t, J = 2.0 Hz, 1 H), 5.99 (d, J = 7.6 Hz, 1 H), 5.34 (s, 1 H), 4.18 (t, J = 7.6 Hz, 1 H), 4.05−4.07 (m, 1 H), 4.03 (s, 2 H), 1.28 (d, J = 6.4 Hz, 3 H), 1.25 (s, 3 H), 1.11 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 231.9, 226.1, 171.3, 153.4, 146.9, 146.5, 139.8, 136.1, 135.9, 134.5, 106.1, 105.8, 105.5, 100.6, 79.2, 76.1, 70.4, 55.0, 40.1, 22.8, 19.8, 17.9. HRMS (ESI): calcd for $C_{22}H_{26}BMoN_6O_7$ ($[M + H]^+$) 595.1005, found 595.1005.

Conversion of (1*R*,*R*)-11 to (+)-2c. Complex (1*R*,*R*)-**11** (448 mg, 0.73 mmol, 1.0 equiv, 97.5% de) was dissolved in THF (10 mL) and cooled to 0 °C. MeLi (1.6 M in diethyl ether, 2.28 mL, 3.65 mmol, 5.0 equiv) was quickly added dropwise. TBSCl (1.10 g, 7.30 mmol, 10.0 equiv) was added in one portion, and the solution was warmed to room temperature. After 1.5 h, the reaction mixture was poured into a separatory funnel containing H_2O (20 mL) and CH_2Cl_2 (20 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was subjected to flash chromatography over silica gel with hexanes−EtOAc (4:1), affording (+)-**2c** (199 mg, 0.34 mmol, 47%, 97.5% ee) [$[\alpha]^{25}_D$ +418 (*c* 0.47, CH_2Cl_2)] as an orange solid. HPLC: Daicel Chiralcel OD-RH column (% CH_3CN in H_2O with 0.1% TFA) 0−20 min (50−75%), 20−30 min (75−85%), 1.5 mL/min, λ = 254 nm, (*S*)-(−)-**2c**: $t_{(S)}$ = 19.29 min; (*R*)-(+)-**2c**: $t_{(R)}$ = 20.19 min.

Conversion of (−)-(1*R*,*R*)-12 to (−)-2b. Complex (−)-(1*R*,*R*)-**12** (500 mg, 0.84 mmol, 1.0 equiv, dr > 95:5) was dissolved in THF (10 mL) and cooled to 0 °C. MeLi (1.6 M in Et_2O, 2.64 mL, 4.22 mmol, 5.0 equiv) was quickly added dropwise, and then TBSCl (1.27 g, 8.40 mmol, 10.0 equiv) was immediately added. The reaction was stirred for 2 h at 0 °C and then poured into a separatory funnel containing H_2O (20 mL) and CH_2Cl_2 (20 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography over silica gel with hexanes−EtOAc (4:1) afforded (−)-**2b** (217 mg, 0.39 mmol, 47%, 96.2% ee) {$[\alpha]^{25}_D$ −128 (*c* 1.04, CH_2Cl_2)} as a bright yellow solid. HPLC: Daicel Chiralcel OD-RH column (% CH_3CN in H_2O with 0.1% TFA) 0−20 min (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-(+)-**2b**: $t_{(S)}$ = 18.48 min; (*R*)-(−)-**2b**: $t_{(R)}$ = 17.73 min.

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Supporting Information Available: General experimental methods and X-ray crystallographic studies of **4e**, (1*S*,*R*)-**11**, and (1*R*,*R*)-**12** and copies of ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.