Electrophilic Carbon–Carbon Bond Forming Reaction of Molybdenum–η^3-Cyclohexadienyl Complexes

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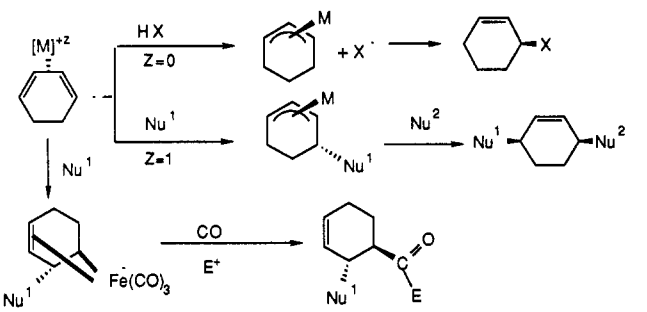
BF_3-catalyzed electrophilic addition of aldehydes to $CpMo(CO)_2(\eta^3$-6-R-cyclohexadien-1-yl) (R = H, Me, Ph) in cold toluene produced isolable Mo–η^4-diene cationic salts (**I**). Demetalation of these salts by Me_3NO in CH_2Cl_2 gave functionalized cyclohexadiene compounds in good yields. The stereochemistry of this carbon–carbon bond forming reaction has been clarified. Methods to utilize these cationic salts (**I**) for stereoselective syntheses of highly substituted cyclohexene compounds are demonstrated.

Introduction

Stereoselective functionalization of a metal–cyclohexane ring has become a useful reaction in organic synthesis.[1] Metal-promoted addition to a η^4-cyclohexadiene ring is of special interest because it can be directed with a high 1,4-selectivity. Although such an addition is facilitated by complexes of various metals[2–4] including Pd(II), Ni(0), Co(I), Hg(II), Rh(I), and Fe(II), their reaction pathways follow exclusively a double addition by two nucleophiles or by H–X via a π-allyl intermediate, as illustrated in Scheme I. $Fe(CO)_3(\eta^4$-cyclohexadiene)[5] may represent an exception which enables 1,2-addition to the ring. Nevertheless the reaction is made to proceed only with special nucleophiles such as cyano-stabilized carbanions.

Functionalization of the $CpMo(CO)_2(\eta^4$-diene)$^+$ cation[6] is interesting because the η^4-diene cation can be regenerated from Ph_3C^+-promoted hydride abstraction of a Mo–η^3-cyclohexen-1-yl ring after their nucleophilic attack, which thus allows a double nucleophilic addition on the six-membered ring. In this paper, we report a new controlled functionalization of molybdenum–η^3-cyclohexadien-1-yl complexes, which involves a BF_3-promoted electrophilic addition of aldehydes to the cyclohexadienyl ring. These reactions enable stereoselective syntheses of highly functionalized 1,3-cyclohexadiene and cyclohexene compounds.

Scheme I



Stereoselective Syntheses of Cyclohexadiene Compounds

The starting cyclohexadienyl compounds **2–4** were easily prepared from $CpMo(CO)_2(\eta^3$-cyclohexen-1-yl) (**1**) according to the method of Pearson et al.,[7] which involves RMgBr addition to the $CpMo(CO)_2(\eta^4$-cyclohexadiene) cation, then hydride abstraction by Ph_3CBF_4, and finally deprotonation with Et_3N (Chart I). Similar to their acyclic η^3-pentadienyl analogues,[8] compounds **2–4** are capable of undergoing BF_3-promoted carbon–carbon bond forming reactions with various aldehydes. In a typical reaction, the Mo–η^3-allyl complex was treated with equimolar proportions of $BF_3{\cdot}Et_2O$ and aldehydes in cold toluene (−40 °C), which gradually deposited a highly hydroscopic dark-red gum. Unlike their acyclic Mo–η^4-trimethylenemethane analogues,[8b] fractional crystallization of these salts failed to give a well-defined solid form. ^1H NMR characterization of these salts was not successful even for those cases which proceeded in good diastereoselectivities, e.g. entry 5 in Scheme II. In this particular case, the resonances of the corresponding diene cation were broad and severely overlapped with those of the protonation product in a minor amount (ca. 10%). We attribute the observed broad proton NMR resonances partly to the chemical instability of the initial BF_3O^- salt which was prone to hydrolysis to give the corresponding BF_4^- salt. The η^4-cyclohexadiene cationic structures were deduced

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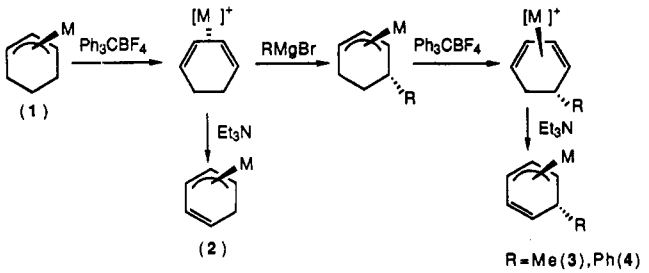
Chart I[a]



[a] M = $CpMo(CO)_2$.

either from their ν(CO) absorption bands[9] at 2080 (s) and 2010 (s) cm^{-1} or by their subsequent reaction with nucleophiles to give η^3-allyl compounds (*vide post*). After precipitation three times in diethyl ether/hexane to remove residual acid, the cationic salts (**I**) were stirred with anhydrous Me_3NO in CH_2Cl_2 (23 °C, 4 h), to cause demetalation, after which substituted cyclohexadienes were isolated in reasonable yields (ca. 50–60%) following purification through a preparative SiO_2 TLC plate. When excess Me_3NO was used, e.g. 5 molar proportions, the dehydrogenation products, i.e. benzyl alcohol compounds, were produced in 8–12% yields. Two diastereomeric products **a** and **b** were produced in the reactions between **2** and various aldehydes, and the diastereomeric selectivity **a**/**b** improved with increasing sizes of aldehydes whereas only one single diastereomer was detectable for disubstituted cyclohexadiene compounds **9**–**14** (entries 5–10). The two diastereomers of **5**–**8** were clearly distinguished by ^{1}H-NMR spectra in $CDCl_3$ which showed the C*H*(OH) proton resonances of the major isomer **a** slightly more downfield than those of the minor isomer **b**.

The *cis*-related R^1 and $CH(OH)R^2$ substituents were confirmed by ^{1}H-NMR NOE-difference spectra. Irradiation of the H^6-proton resonance (δ 3.73 ppm) of **13** gave rise to a 4.4% increase in the H^5-proton signal (δ 2.94 ppm) whereas the C*H*(OH) proton signal (δ 3.29 ppm) was unaffected. Furthermore, irradiation of the CH^7(OH)-proton resonance caused a 3.6% increase in the phenyl ortho proton (δ 7.39 ppm) but the H^6-proton was unaffected. We examined the BF_3-promoted addition of CH_3-CHO to **2**, which after demetalation gave two diastereomeric cyclohexadiene derivatives in equal proportions (50%). Nevertheless, in this case, assignment of the ^{1}H-NMR spectra of the two isomers is difficult because of the severe overlap of their proton NMR signals. The spectral data for these dienes are not thus given in this paper.

Functionalization of the Salts (I)

For the Mo-η^4-cyclohexadiene salts (**I**), the CH_2 methylene protons[6a,7,10] adjacent to the π-diene fragment are highly acidic and readily deprotonated by Et_3N. As shown in Scheme III, treatment of **I**, derived from **2** and benzaldehyde or isobutyraldehyde (entries 1 and 3, scheme II) with a 10-fold excess of Et_3N in CH_2Cl_2, gave the η^3-cyclohexadien-1-yl alcohols **15** and **16** as a mixture of two diastereomers, further separated by a preparative SiO_2 TLC plate.

$NaBH_4$ reduction of the salt (**I**) (entries 3 and 4, Scheme II) gave the 1,4-addition allyl compounds **17** and **18** in two diastereomers. Slow addition of a THF solution of PhMgBr, MeMgBr, and $LiCH(COOMe)_2$ to the salts (**I**) (entries 2–4, Scheme II) produced the 4,6-disubstituted η^3-cyclohexen-1-yl compounds **19**–**22**, as illustrated in Scheme III. In all cases, the reported diastereomeric ratios for compounds **17**–**22a**/**b** were estimated from the ^{1}H NMR spectra of the product mixtures after elution through a SiO_2 column. For **17**–**22**, the major isomer **a** was separated from the minor isomer **b** either by elution through a preparative SiO_2 TLC plate or by fractional crystallization from a saturated ether/hexane solution. All nucleophiles unambiguously attack at the less hindered carbon terminus of the η^4-diene moiety, and the proposed structures in Scheme III are supported by sequential proton-decoupled NMR experiments as well as 2D-COSEY ^{1}H-NMR spectra. There exist some discrepancies among the diastereomeric ratios **a**/**b** reported for Schemes II and III, which are attributed to either some absorption of the η^3-allyl products on the SiO_2 column, or partial decomposition of the crude products during workup.

To clarify the stereochemistries of the two isomers **a** and **b** given in Schemes II and III, we determined the molecular structure of **21a** by X-ray diffraction measurement; the ORTEP drawing is provided in Figure 1. The selected bond distances, bond angles, and atomic coordinates are given in Tables I and II, respectively. According to the ORTEP drawing, the six-membered ring approximates a chairlike conformation, with the two axial $CH(OH)CHMe_2$ and $CH(COOMe)_2$ substituents lying on the non-metal face of the ring. The Mo–C(3) (2.379(9) Å), MO–C(4), (2.191(10) Å), and Mo–C(5) (2.366(11) Å) bond lengths are similar to the corresponding values (2.371(3), 2.206(3), and 2.381(3) Å) reported for $CpMo(CO)_2(\eta^3$-cyclohexen-1-yl).[6a] Consistent with this solid-state structure, the two axial R^2 and $CH(OH)R^1$ groups of the chairlike conformation of **19**–**22** are also indicated by proton NOE-difference spectra. For example, irradiation of the methyl proton resonance (δ 1.10 ppm) of **22a** gave rise to a 3.0% increase in the CH^7(OH) signal (δ 3.34 ppm) whereas the H^4-proton signal (δ 2.11 ppm) was unaffected. For compounds **17**–**22**, additional support for the chairlike cyclohexenyl ring is provided by proton-coupling parameters $J_{6'5}$(a–a) = 10–11 Hz, $J_{5'6} = J_{5'4}$(e–e) = 0–3 Hz, and $J_{56} = J_{54} = J_{a-e}$ = 4–5 Hz (a = axial, e = equatorial). These values are similar to those reported for the related compounds $CpMo(CO)_2(\eta^3$-4-R-cyclohexenyl),[6a] which similarly adopt chairlike six-membered rings.

To ensure that the stereochemistries of **9**–**14** are identical to that of **21a**, we treated the salts (**I**) (entry 11, Scheme II) with 1.5 equimolar proportions of $LiHBEt_3$ in cold THF (−78 °C, 1 h) which gave **23** exclusively. In the ^{1}H NMR spectra, there is a small amount of unknown organomolybdenum (ca. 5% of **23**) in the crude products. Recrystallization from a saturated ether/hexane solution afforded **23** in pure form in overall 53% yield. The compound crystallizes in a rare space group $P1$ (Z = 1). Its molecular structure is presented in Figure 2, and Table III lists the selected bond distances and angles; the atomic coordinates are summarized in Table IV. Similar to that in **21a**, the η^3-cyclohexadienyl ring adopts a chairlike conformation which has phenyl and CH(OH)Ph groups in the equatorial and axial positions, respectively. Both substituents are in the non-metal face of the dienyl ring. The Mo–C(3) (2.362(5) Å), Mo–C(4) (2.212(5) Å), and Mo–C(5) (2.392-(6) Å) bond lengths are similar to those of **21a**. The

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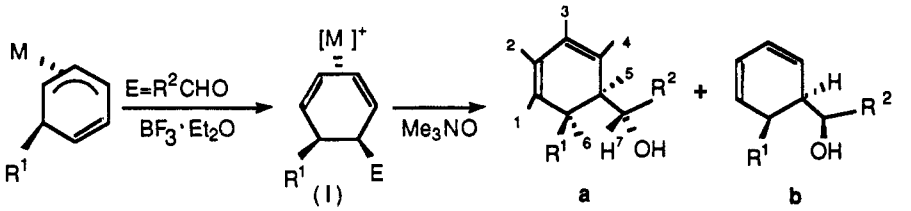
Scheme II[a]

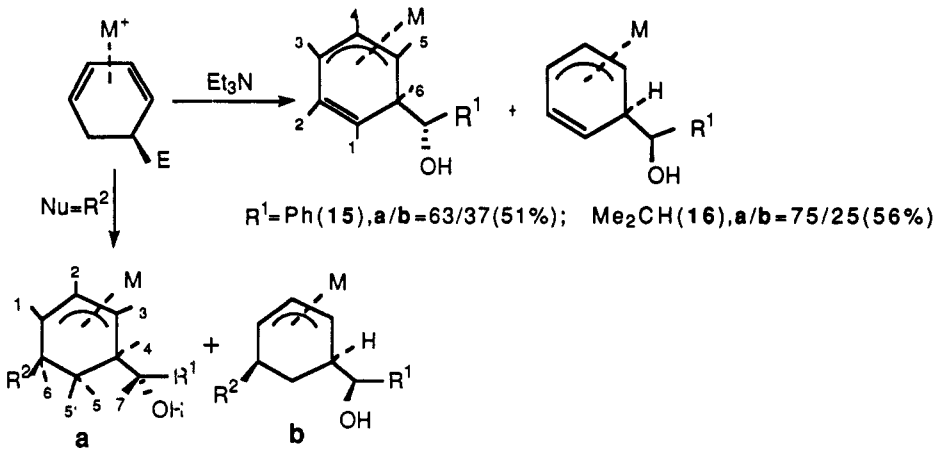


R^1=H (**2**), Me (**3**), Ph (**4**)

entry#	R^1	R^2	a/b (yield)	compd. no.
1	H	Ph	63/37 (61%)	**5**
2	H	Me_2CHCH_2	61/39 (58%)	**6**
3	H	Me_2CH	80/20 (63%)	**7**
4	H	Me_3C	92/8 (67%)	**8**
5	Me	Ph	**a** (52%) only	**9**
6	Me	Me_2CH	**a** (56%) only	**10**
7	Me	Me_2CHCH_2	**a** (54%) only	**11**
8	Ph	Me	**a** (51%) only	**12**
9	Ph	Me_2CH	**a** (48%) only	**13**
10	Ph	Ph	**a** (49%) only	**14**

[a] M = $CpMo(CO)_2$.

Scheme III



R^1=Ph (**15**), **a**/**b**=63/37 (51%); Me_2CH (**16**), **a**/**b**=75/25 (56%)

Nu	R^2	R^1	a/b (yield)	compd. no.
$NaBH_4$	$H^{6'}$	Me_2CH	85/15 (62%)	**17**
$NaBH_4$	$H^{6'}$	Me_3C	88/12 (52%)	**18**
PhMgBr	Ph	Me_2CHCH_2	90/10 (53%)	**19**
PhMgBr	Ph	Me_2CH	85/15 (63%)	**20**
$LiCH(COOMe)_2$	$CH(COOMe)_2$	Me_2CH	85/15 (65%)	**21**
MeMgBr	Me	Me_3C	only **a** (54%)	**22**

chairlike conformation of the ring is also shown by proton NOE-difference spectra. Irradiation of the $H^{6'}$ proton resonance (δ 1.95 ppm) led to a 3.0% increase in the CH^7-(OH) resonance whereas the H^4 (δ 2.45 ppm) and H^5 (δ 2.18 ppm) proton signals were unaffected. Compounds **21a** and **23** have identical configurations at the asymmetric CH^4 and CH^7(OH) carbons, indicative of an identical mechanism in the carbon–carbon bond forming reaction.

To account for the stereochemical outcome, we propose the two most likely transition states A and B,[11,12] in which the aldehyde carbonyl group lies *trans* to the η^3-cyclohexenyl C=C double bond to minimize steric hindrance.

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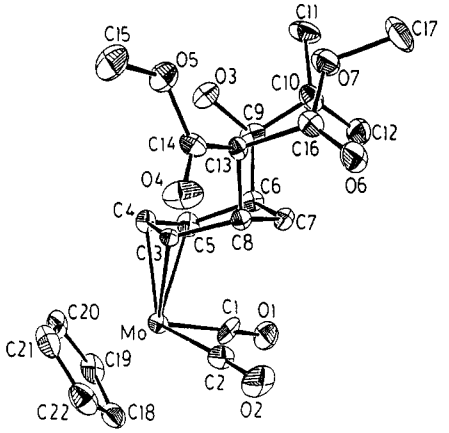


Figure 1. ORTEP drawing of compound **21a**.

Table I. Selected Bond Distances (Å) and Angles (deg) of 21a

Mo–C(1)	1.925(10)	C(6)–C(9)	1.531(14)
Mo–C(2)	1.940(9)	C(7)–C(8)	1.517(14)
Mo–C(3)	2.379(9)	C(8)–C(13)	1.551(13)
Mo–C(4)	2.191(10)	C(9)–O(3)	1.471(12)
Mo–C(5)	2.366(11)	C(13)–C(14)	1.514(13)
C(1)–O(1)	1.164(13)	C(13)–C(16)	1.523(13)
C(2)–O(2)	1.134(12)	C(14)–O(4)	1.199(12)
C(3)–C(4)	1.401(12)	C(14)–O(5)	1.317(12)
C(3)–C(8)	1.524(12)	C(15)–O(5)	1.438(12)
C(4)–C(5)	1.388(14)	C(16)–O(6)	1.196(12)
C(5)–C(6)	1.500(14)	C(16)–O(7)	1.302(12)
C(6)–C(7)	1.566(14)	C(17)–O(7)	1.479(14)
C(1)–Mo–C(2)	80.3(5)	C(4)–C(5)–C(6)	121.0(8)
C(1)–Mo–C(3)	111.9(5)	C(5)–C(6)–C(7)	110.2(8)
C(1)–Mo–C(4)	105.3(5)	C(5)–C(6)–C(9)	109.4(8)
C(1)–Mo–C(5)	71.1(4)	C(7)–C(6)–C(9)	116.1(8)
C(2)–Mo–C(3)	74.8(4)	C(6)–C(7)–C(8)	117.8(8)
C(2)–Mo–C(4)	107.9(4)	C(3)–C(8)–C(7)	112.7(7)
C(2)–Mo–C(5)	109.3(4)	C(3)–C(8)–C(13)	106.6(7)
C(3)–Mo–C(4)	35.4(3)	C(7)–C(8)–C(13)	112.0(7)
C(3)–Mo–C(5)	60.1(3)	C(6)–C(9)–O(3)	111.5(8)
C(4)–Mo–C(5)	35.2(3)	C(8)–C(13)–C(14)	113.0(7)
Mo–C(1)–O(1)	176.1(12)	C(8)–C(13)–C(16)	110.8(7)
Mo–C(2)–O(2)	176.8(9)	C(14)–C(13)–C(16)	105.2(7)
Mo–C(3)–C(4)	64.9(5)	C(13)–C(14)–O(4)	125.2(9)
Mo–C(3)–C(8)	116.9(6)	C(13)–C(14)–O(5)	111.2(8)
C(4)–C(3)–C(8)	120.9(8)	O(4)–C(14)–O(5)	123.5(9)
Mo–C(4)–C(3)	79.7(5)	C(13)–C(16)–O(6)	124.5(9)
Mo–C(4)–C(5)	79.3(6)	C(13)–C(16)–O(7)	111.9(8)
C(3)–C(4)–C(5)	116.8(8)	O(6)–C(16)–O(7)	123.6(9)
Mo–C(5)–C(4)	65.5(6)	C(14)–O(5)–C(15)	117.1(8)
Mo–C(5)–C(6)	122.0(7)	C(16)–O(7)–C(17)	116.7(9)

State A is the preferable conformation because the R^1 and R^2 groups are mutually staggered. This conformation is particularly favored with increasing sizes of R^1 and R^2, which are expected to contribute to greater stereoselection of the major isomer, compatible with our observations.

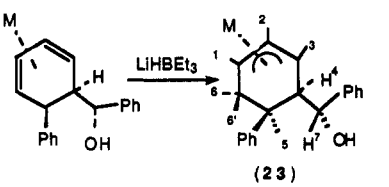
Stereoselective Syntheses of Cyclohexene Compounds

An interesting feature in the chemistry of molybdenum–π-allyl complexes is the versatility in removal of the metal fragment.[13,14] The dicarbonyl Mo–π-allyl compounds are converted to $CpMo(CO)NO(allyl)^+$ by $NOBF_4$, which in synthetic equivalence functions as an allyl cation.[15,16] On the basis of this method, the new η^3-allyl compounds were utilized for syntheses of cyclohexene compounds. As depicted in Scheme IV, heating **21a** with Bu_4NOH (1.2 equimolar) in refluxing THF (0.5 h) gave monoacid **24** as a single stereoisomer (94%).[6b] Further treatment of **24** with $NOBF_4$ (1.0 equimolar) in CH_3CN (0 °C, 20 min), followed by demetalation with Na_2CO_3(s) in air gave a bicyclic lactone **25** in 50% yield. Similarly, further treatment of **17a** and **18a** with $NOBF_4$ (1.0 equimolar), followed by addition of PhSNa, gave the difunctionalized

Table II. Atomic Parameters (x, y, z) of 21a

	x	y	z	B_{iso} (Å^2)
Mo	0.00000	0.10555(3)	0.25000	2.49(3)
C(1)	–0.0229(13)	0.1729(4)	0.2259(14)	3.5(6)
C(2)	–0.0307(10)	0.1104(4)	0.0016(12)	3.4(5)
C(3)	0.2011(9)	0.0796(3)	0.1586(11)	2.0(4)
C(4)	0.2133(9)	0.0949(4)	0.3293(11)	2.9(5)
C(5)	0.2028(10)	0.1433(3)	0.3558(13)	3.0(4)
C(6)	0.2673(9)	0.1782(3)	0.2503(12)	2.6(4)
C(7)	0.2502(10)	0.1619(3)	0.0581(13)	2.8(4)
C(8)	0.2546(9)	0.1093(3)	0.0222(11)	2.3(4)
C(9)	0.4100(10)	0.1874(3)	0.3352(13)	3.1(4)
C(10)	0.4970(17)	0.2191(3)	0.2489(24)	3.8(6)
C(11)	0.6331(10)	0.2245(4)	0.3417(19)	5.2(7)
C(12)	0.4325(12)	0.2675(4)	0.2098(16)	4.8(6)
C(13)	0.3981(9)	0.0918(3)	0.0141(11)	2.3(4)
C(14)	0.4044(9)	0.0400(4)	–0.0326(13)	2.8(4)
C(15)	0.5367(12)	–0.0285(4)	0.0022(17)	4.8(6)
C(16)	0.4589(10)	0.1181(3)	–0.1246(13)	2.8(4)
C(17)	0.6351(12)	0.1674(5)	–0.1842(17)	6.0(7)
C(18)	–0.2112(11)	0.0868(4)	0.2906(15)	4.5(6)
C(19)	–0.1398(11)	0.0964(4)	0.4602(14)	4.2(6)
C(20)	–0.0391(12)	0.0637(4)	0.4999(13)	4.1(5)
C(21)	–0.0477(13)	0.0300(4)	0.3653(18)	5.0(6)
C(22)	–0.1540(13)	0.0450(5)	0.2444(16)	5.3(7)
O(1)	–0.0402(7)	0.2136(3)	0.2198(13)	5.2(5)
O(2)	–0.0539(9)	0.1120(3)	–0.1436(9)	5.8(5)
O(3)	0.4831(7)	0.14294(25)	0.3753(9)	3.8(3)
O(4)	0.3175(7)	0.0183(3)	–0.1181(11)	4.9(4)
O(5)	0.5189(7)	0.02111(23)	0.0327(9)	3.6(3)
O(6)	0.4083(7)	0.1216(3)	–0.2708(9)	4.6(4)
O(7)	0.5718(7)	0.1377(3)	–0.0641(10)	4.2(4)

Chart II[a]



(23)

[a] M = $CpMo(CO)_2$.

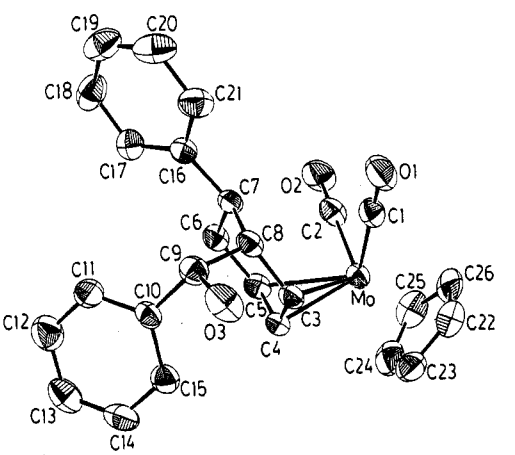


Figure 2. ORTEP drawing of compound **23**.

(13) Faller, J. W.; Rosan, A. M. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 18.
(14) (a) Faller, J. W.; John, J. A.; Mazzieri, M. R. *Tetrahedron Lett.* **1989**, *30*, 1769. (b) Faller, J. W.; Linebarrier, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937.
(15) Hansson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9660.
(16) Pearson, A. J. *SynLett* **1990**, 10.

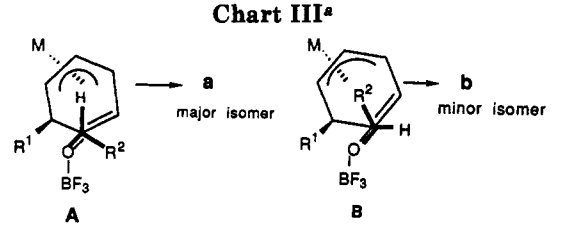
Table III. Selected Bond Distances (Å) and Angles (deg) of 23

Mo–C(1)	1.952(6)	C(4)–C(5)	1.430(8)
Mo–C(2)	1.922(6)	C(5)–C(6)	1.499(8)
Mo–C(3)	2.362(5)	C(6)–C(7)	1.534(7)
Mo–C(4)	2.212(5)	C(7)–C(8)	1.544(7)
Mo–C(5)	2.392(6)	C(7)–C(16)	1.531(8)
C(1)–O(1)	1.144(7)	C(8)–C(9)	1.551(7)
C(2)–O(2)	1.170(7)	C(9)–C(10)	1.530(7)
C(3)–C(4)	1.394(8)	C(9)–O(3)	1.416(7)
C(3)–C(8)	1.531(8)		
C(1)–Mo–C(2)	83.07(24)	Mo–C(4)–C(5)	78.9(3)
C(1)–Mo–C(3)	72.56(21)	C(3)–C(4)–C(5)	115.8(5)
C(1)–Mo–C(4)	106.24(22)	Mo–C(5)–C(4)	65.1(3)
C(1)–Mo–C(5)	109.93(21)	Mo–C(5)–C(6)	119.3(3)
C(2)–Mo–C(3)	112.07(22)	C(4)–C(5)–C(6)	118.3(5)
C(2)–Mo–C(4)	106.38(22)	C(5)–C(6)–C(7)	113.6(4)
C(2)–Mo–C(5)	71.52(22)	C(6)–C(7)–C(8)	113.5(4)
C(3)–Mo–C(4)	35.29(19)	C(6)–C(7)–C(16)	115.5(4)
C(3)–Mo–C(5)	60.41(18)	C(8)–C(7)–C(16)	113.8(4)
C(4)–Mo–C(5)	35.92(20)	C(3)–C(8)–C(7)	111.5(4)
Mo–C(1)–O(1)	179.2(5)	C(3)–C(8)–C(9)	110.7(4)
Mo–C(2)–O(2)	178.5(6)	C(7)–C(8)–C(9)	115.9(4)
Mo–C(3)–C(4)	66.5(3)	C(8)–C(9)–C(10)	116.2(4)
Mo–C(3)–C(8)	119.4(3)	C(8)–C(9)–O(3)	105.7(4)
C(4)–C(3)–C(8)	120.2(5)	C(10)–C(9)–O(3)	111.1(4)
Mo–C(4)–C(3)	78.2(3)		

Table IV. Atomic Parameters (*x*, *y*, *z*) of 23

	x	*y*	*z*	B_{iso} (Å^2)
Mo	0.00000	0.00000	0.00000	2.707(13)
C(1)	0.0972(8)	–0.2104(7)	–0.0764(7)	3.10(22)
C(2)	0.2351(8)	–0.0123(7)	0.0639(7)	3.43(23)
C(3)	–0.1550(7)	–0.1959(7)	0.1470(6)	2.70(20)
C(4)	–0.1718(7)	–0.0512(7)	0.2175(6)	2.87(20)
C(5)	–0.0166(7)	–0.0220(6)	0.2821(6)	2.93(22)
C(6)	0.0939(7)	–0.1622(7)	0.3679(6)	2.87(21)
C(7)	0.1196(7)	–0.3196(6)	0.2863(6)	2.63(19)
C(8)	–0.0508(7)	–0.3522(7)	0.2222(6)	2.71(20)
C(9)	–0.1742(7)	–0.4453(6)	0.3405(6)	2.89(20)
C(10)	–0.2592(7)	–0.3581(6)	0.4840(6)	2.70(20)
C(11)	–0.1973(7)	–0.4091(7)	0.6313(7)	3.35(23)
C(12)	–0.2807(9)	–0.3420(9)	0.7647(8)	4.4(3)
C(13)	–0.4266(9)	–0.2169(9)	–0.7522(8)	4.2(3)
C(14)	–0.4884(8)	–0.1700(8)	0.6086(8)	4.0(3)
C(15)	–0.4066(7)	–0.2360(7)	0.4718(7)	3.13(21)
C(16)	0.2215(7)	–0.4691(7)	0.3749(6)	2.86(21)
C(17)	0.2709(8)	–0.4634(7)	0.5279(7)	3.24(23)
C(18)	0.3808(9)	–0.5942(9)	0.5985(8)	4.3(3)
C(19)	0.4384(9)	–0.7298(8)	0.5222(9)	4.5(3)
C(20)	0.3874(9)	–0.7400(8)	0.3752(10)	4.7(3)
C(21)	0.2815(8)	–0.6072(8)	0.3027(8)	3.9(3)
C(22)	–0.1319(10)	0.0917(8)	–0.2356(8)	4.4(3)
C(23)	–0.2542(9)	0.1572(9)	–0.1132(9)	4.5(3)
C(24)	–0.1722(12)	0.2628(9)	–0.0421(9)	5.3(4)
C(25)	–0.0031(11)	0.2650(9)	–0.1140(9)	5.0(3)
C(26)	0.0211(10)	0.1622(10)	–0.2364(8)	5.4(3)
O(1)	0.1556(7)	–0.3330(6)	–0.1221(5)	4.78(22)
O(2)	0.3787(6)	–0.0169(7)	0.1006(6)	5.05(25)
O(3)	–0.3051(6)	–0.4819(6)	0.2507(5)	4.22(19)

Chart III[a]



A B

[a] M = $CpMo(CO)_2$.

cyclohexenes **26** and **27** in 60% and 65% yields, respectively. A method applicable to the stereoselective syntheses of highly functionalized cyclohexene compounds is thus established.

Experimental Section

All operations were carried out under argon in a Schlenk apparatus or in a glovebox. The solvents benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane and chloroform were dried over calcium hydride and distilled. Anhydrous trimethylamine oxide was prepared by subliming its dihydrate (Aldrich) at 110 °C. $Mo(CO)_6$, $NOBF_4$, RCHO (R = Ph, Me_2CH, Me_2CHCH_2, Me_3C, Me) were obtained commercially (Aldrich) and used without further purification. $CpMo(CO)_2(\eta^3$-cyclohexenyl) (**1**) and $CpMo(CO)_2$(6-R-η^3-cyclohexadien-1-yl) [(R = H (**2**), Me (**3**), and Ph (**4**)] were prepared according to the procedures in the literature.[6b]

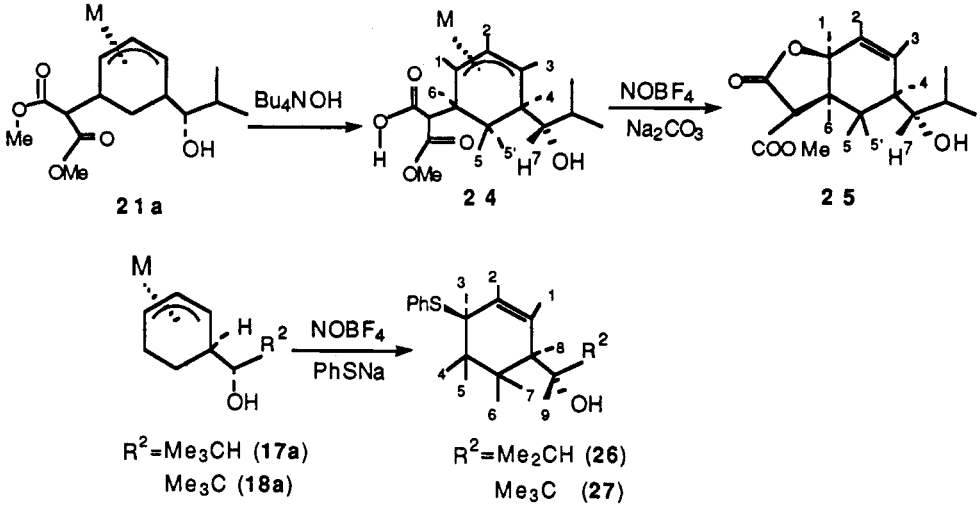
All ^{1}H-NMR (400 and 300 MHz) and ^{13}C-NMR (100 and 75 MHz) spectra were obtained on either a Bruker AM-400 or a Varian Gemini-300 spectrometer; the chemical shifts of ^{1}H- and ^{13}C-NMR spectra were referred to tetramethylsilane. Microanalyses were performed at National Cheng Kung University, Tainan. Infrared spectra were recorded on a Perkin-Elemer 781 spectrophotometer. High-resolution mass spectra were recorded on a JEOL HX 110 spectrometer.

(a) (i) Synthesis of 5-(Hydroxyphenylmethyl)-1,3-cyclohexadiene (5). To a toluene solution (10 mL) of **2** (0.30 g, 1.00 mmol) was added benzaldehyde (0.161 g, 1.50 mmol) and BF_3·Et_2O (0.149 g, 1.05 mmol) at –40 °C, which gradually deposited a dark-red gum. After stirring for 2 h, toluene was decanted away and the residues were dissolved in CH_2Cl_2 (5 mL). Diethyl ether (20 mL) was added to produce a viscous oil, and the organic layer was decanted away. After two more repetitions of this procedure, the acid-free gum was dissolved in CH_2Cl_2 (5 mL), and stirred with anhydrous trimethylamine oxide for 2 h at 23 °C. TLC monitoring (SiO_2, ether/hexane = 1/2) showed the formation of a new organic compound (UV, R_f = 0.32). The solution was washed with water (2 mL), and the CH_2Cl_2 layer was evaporated to dryness. The residues were chromatographed through a preparative TLC plate (SiO_2, $60F_{254}$) using ether/hexane (1/2) as the eluting solvent which provided **5** (113 mg, 0.61 mmol) as a mixture of two diastereomers (**a**/**b** = 63/37). The following dienes **6**–**14** were prepared in a similar method. Compound **5**: IR (Nujol): ν(OH) 3402 (br vs) cm^{-1}; ν(C=C) 1615 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): diastereomer **a** δ 7.25–7.34 (5H, m Ph), 6.05 (1H, dd, J = 8.2, 4.2 Hz, H^3) 5.82–6.05 (2H, m, H^2 + H^4), 5.70 (1H, dt, J = 10.0, 4.0 Hz, H^1), 4.61 (1H, d, J = 7.6 Hz, H^7), 2.60 (1H, q, J = 7.6 Hz, H^5), 2.35 (1H, m, C*H*^{6}H), 2.10 (1H, m, CH^6*H*); diastereomer **b** δ 5.82–6.02 (2H, m, H^2 + H^3, overlapped with the H^2 and H^4 proton resonances of **a**), 5.78 (1H, dt, J = 10.0, 4.1 Hz, H^1), 5.35 (1H, dd, J = 10.5, 3.8 Hz, H^4), 4.58 (1H, d, J = 7.0 Hz, H^7), 2.35–2.38 (2H, m, H^5 + C*H*^{6}H, overlapped with the CH^6 resonances of **a**), 2.28 (1H, ddd, J = 11.2, 8.2, 7.8 Hz, CH^6*H*). HRMS Calcd for $C_{13}H_{14}O$: 186.1044. Found: 186.1040.

(ii) Synthesis of 5-(1′-Hydroxy-3-methylbutyl)-1,3-cyclohexadiene (6). A mixture of two diastereomers (**a**/**b** = 61/39) was obtained after elution through a preparative TLC plate (SiO_2, $_{60}F_{254}$); the yield is 58%. IR (neat): ν(OH) 3400 (br, s) cm^{-1}; ν(C=C) 1609 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): diastereomer **a** (61%) δ 5.93 (1H, dd, J = 10.0, 6.6 Hz, H^3), 5.82 (1H, dd, J = 9.2, 6.6 Hz, H^2), 5.74 (1H, m, H^1), 5.61 (1H, dd, J = 10.0, 3.0 Hz, H^4), 3.66 (1H, td, J = 5.6, 3.7 Hz, H^7), 2.15–2.28 (3H, m, H^5 + CH^{6}H), 1.70 (m, 1H, C*H*Me$_2$), 1.36 (1H, m, C*H*H″), 1.23 (1H, m, CH*H*′), 0.90 (3H, d, J = 6.5 Hz, Me), 0.86 (3H, d, J = 6.5 Hz, Me); diastereomer **b** (39%) δ 6.00 (1H, dd, J = 10.0, 6.2 Hz, H^3), 5.80 (1H, m, H^2, overlapped with the H^2 resonance of isomer **a**), 5.74 (1H, m, H^1 + H^4, overlapped with the H^1 resonances of **a**), 3.58 (1H, td, J = 9.3, 3.7 Hz, H^7), 2.16–2.24 (3H, m, H^5 + CH^{6}H), 1.70 (m, 1H, CHMe$_2$, overlapped with the C*H*Me$_2$ resonance of **a**), 1.40 (1H, ddd, m, C*H*H′), 1.20 (1H, m, CH*H*′), 0.90, 0.86 (3H, 3H, 2Me, overlapped with the methyl resonances of **a**). ^{13}C NMR (100 MHz, $CDCl_3$): diastereomer **a** δ 127.8, 126.2, 125.4, 123.8, 71.3, 43.3, 39.2, 24.4, 23.4, 23.0, 21.5. HRMS Calcd for $C_{11}H_{18}O$: 166.1358. Found: 166.1349.

(iii) Synthesis of 5-(1-hydroxy-2-methylpropyl)-1,3-cyclohexadiene (7): 63% yield; IR (neat) ν(OH) 3415 (br, vs) ν-

Scheme IV[a]



[a] M = $CpMo(CO)_2$.

(C=C) 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) diastereomer **a** (80%) δ 5.39 (1H, dd, J = 9.0, 4.9 Hz, H^3), 5.83 (1H, m, H^2), 5.75 (1H, m, H^1), 5.57 (1H, dt, J = 9.0, 4.0 Hz, H^4), 3.34 (1H, t, J = 5.8 Hz, H^7), 2.48 (1H, m, H^5), 2.18–2.28 (2H, m, C*H*^{6}*H*), 1.53 (1H, m, C*H*Me_2), 0.91, 0.80 (3H, 3H, d, d, J = 6.8 Hz, 2Me). ^1H NMR (400 MHz, $CDCl_3$) diastereomer **b** (20%) δ 6.00 (1H, dd, J = 8.8, 5.2 Hz, H^3), 5.80–5.86 (3H, m, H^2 + H^1 + H^4, overlapped with the H^1 and H^2 resonances of isomer **a**), 3.18 (1H, t, J = 4.8 Hz, H^7), 1.54 (1H, m, $CHMe_2$), 0.96, 0.74 (3H, 3H, d, d, J = 6.8 Hz, 2Me); ^{13}C NMR (100 MHz, $CDCl_3$) diastereomer **a** δ 127.8, 126.2, 125.6, 123.6, 77.6, 35.7, 29.6, 22.5, 19.3, 16.5. HRMS Calcd for $C_{10}H_{16}O$: 152.1201. Found: 152.1190.

(iv) Synthesis of 5-(1-hydroxy-2,2-dimethylpropyl)-1,3-cyclohexadiene (8): 67% yield; IR (neat) ν(OH) 3408 (br, vs) ν(C=C) 1620 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) diastereomer **a** (88%) δ 5.92 (1H, dd, J = 9.1, 3.0 Hz, H^3), 5.80 (1H, dd, J = 9.3, 3.0 Hz, H^2), 5.72 (1H, dt, J = 9.3, 3.9 Hz, H^1), 5.53 (1H, dd, J = 9.1, 3.4 Hz, H^4), 3.37 (1H, d, J = 3.4 Hz, H^7), 2.60 (1H, td, J = 11.0, 3.9 Hz, C*H*^{6}H), 2.40 (1H, m, H^5), 2.25 (1H, td, J = 11.0, 3.9 Hz, CH^6*H*), 0.90 (9H, s, 3Me); ^1H NMR, (400 MHz, $CDCl_3$) diastereomer **b** (12%) 5.96 (1H, dd, J = 8.0, 2.0 Hz, H^3), 3.12 (1H, d, J = 2.1 Hz, H^7), 2.21 (1H, m, CH^6*H*), 0.89 (9H, s, 3Me), the remaining proton signals were masked by overwhelming resonances of isomer **a**; ^{13}C NMR (100 MHz, $CDCl_3$) diastereomer **a** δ 127.5, 126.2, 123.8, 120.6, 83.4, 35.5, 34.1, 29.7, 25.5. HRMS Calcd for $C_{11}H_{18}O$: 166.1358. Found: 166.1369.

(v) Synthesis of 5-(hydroxyphenylmethyl)-6-methyl-1,3-cyclohexadiene (9): 52% yield; IR (neat) ν(OH) 3410 (br, vs) ν(C=C) 1630 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) diastereomer **a** only δ 7.27–7.39 (5H, m, Ph), 5.75–5.96 (3H, m, H^1 + H^2 + H^3), 4.99 (1H, dd, J = 9.0, 1.6 Hz, H^4), 4.69 (1H, d, J = 10.9 Hz, H^7), 2.87 (1H, m, H^5), 2.70 (1H, m, H^6), 0.98 (3H, d, J = 7.0 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 133.8, 128.6, 128.1, 127.4, 126.3, 124.7, 122.8, 74.5, 45.0, 28.2, 10.7. HRMS Calcd for $C_{14}H_{18}O$: 200.1201. Found: 200.1194.

(vi) Synthesis of 5-(1-hydroxy-2-methylpropyl)-6-methyl-1,3-cyclohexadiene (10): 56% yield; IR (neat) ν(OH) 3308 (br, vs) ν(C=C) 1620 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) diastereomer **a** only δ 5.84–5.92 (3H, m, H^1 + H^2 + H^3), 5.43 (1H, dd, J = 9.3, 2.5 Hz, H^4), 3.59 (1H, d, J = 11.2 Hz, H^7), 2.56 (1H, m, H^5), 2.48 (1H, m, H^6), 1.98 (1H, m, C*H*Me_2), 1.02 (3H, d, J = 6.8 Hz, Me), 0.89, 0.85 (6H, 2d, J = 6.8 Hz, 2Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 125.2, 124.4, 122.7, 75.0, 41.2, 29.0, 28.3, 20.4, 14.3, 10.9. HRMS Calcd for $C_{11}H_{18}O$: 166.1358. Found: 166.1346.

(vii) Synthesis of 5-(1-hydroxy-3-methylbutyl)-6-methyl-1,3-cyclohexadiene (11): 54% yield; IR (neat) ν(OH) 3408 (br, vs) ν(C=C) 1620 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) diastereomer **a** only δ 5.84–5.92 (3H, m, H^1 + H^2 + H^3), 5.41 (1H, dd, J = 10.4, 2.7 Hz, H^4), 3.76 (1H, td, J = 8.9, 2.1 Hz, H^7), 2.53 (1H, m, H^5), 2.38 (1H, m, H^6), 1.84 (1H, m, C*H*Me_2); 1.29–1.40 (2H, m, CH_2), 0.98 (1H, d, J = 6.8 Hz, Me), 0.90–0.88 (6H, 2d, J = 6.8 Hz, 2Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 125.6, 124.9, 122.8, 69.6, 44.6, 44.3, 28.4, 24.6, 24.0, 21.6, 11.2. HRMS Calcd for $C_{12}H_{20}O$: 180.1514. Found: 180.1490.

(viii) Synthesis of 5-(1-hydroxyethyl)-6-methyl-1,3-cyclohexadiene (12): 51% yield; IR (neat) ν(OH) 3440 (br, vs) ν(C=C) 1620 (m), 1590 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) diastereomer **a** only δ 7.17–7.39 (5H, m, Ph), 5.97–6.09 (3H, m, H^1 + H^2 + H^3), 5.77 (1H, dd, J = 9.5, 3.0 Hz, H^4), 3.79 (1H, dd, J = 9.2, 5.3 Hz, H^6), 3.57 (1H, dq, J = 6.2, 3.0 Hz, H^7), 2.76 (1H, m, H^5), 1.17 (3H, d, J = 6.2 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 131.4, 129.2, 128.5, 127.1, 126.5, 125.6, 124.1, 67.3, 47.4, 40.9, 21.2. HRMS Calcd for $C_{14}H_{16}O$: 200.1201. Found: 200.1190.

(ix) Synthesis of 5-(1-hydroxy-2-methylpropyl)-6-methyl-1,3-cyclohexadiene (13): 48% yield; IR (neat) ν(OH) 3420 (br, vs) ν(C=C) 1618 (m), 1570 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) diastereomer **a** only δ 7.17–7.40 (5H, m, Ph), 5.99–6.10 (3H, m, H^1 + H^2 + H^3), 5.60 (1H, dd, J = 9.2, 3.0 Hz, H^4), 3.73 (1H, dd, J = 9.0, 5.5 Hz, H^6), 3.29 (1H, dd, J = 10.2, 2.9 Hz, H^7), 2.94 (1H, ddd, J = 10.2, 9.0, 3.0 Hz, H^5), 1.94 (1H, m, C*H*Me_2), 0.89, 0.83 (6H, 2d, J = 6.8 Hz, 2Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 129.2, 128.4, 127.9, 127.0, 126.1, 125.7, 124.0, 74.7, 43.0, 40.6, 29.1, 20.2, 14.4. HRMS Calcd for $C_{16}H_{20}O$: 228.1514. Found: 228.1509.

(x) Synthesis of 5-(hydroxyphenylmethyl)-6-phenyl-1,3-cyclohexadiene (14): 49% yield; IR (neat) ν(OH) 3380 (br, vs), ν(C=C) 1618 (m), 1590 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) diastereomer **a** only δ 7.23–7.47 (10H, m, 2Ph), 6.10 (1H, dd, J = 9.2, 4.8 Hz, H^2), 6.04 (1H, dd, J = 9.2, 5.3 Hz, H^1), 5.90 (1H, dd, J = 9.7, 4.8 Hz, H^3), 5.01 (1H, dd, J = 9.7, 2.6 Hz, H^4), 4.24 (1H, d, J = 10.8 Hz, H^7), 3.91 (1H, dd, J = 9.0, 5.3 Hz, H^6), 3.23 (1H, ddd, J = 10.8, 9.0, 2.6 Hz, H^5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 138.4, 131.4, 129.6, 128.5, 128.2, 128.0, 127.5, 127.0, 125.8, 125.3, 124.2, 74.4, 46.5, 40.2. HRMS Calcd for $C_{19}H_{18}O$: 262.1358. Found: 262.1355.

(b) (i) Synthesis of $CpMo(CO)_2$[(1,2,3-η)-6-(hydroxyphenylmethyl)cyclohexadien-1-yl] (15). To the salt (**I**) (ca. 1.0 mmol) in section a(i) in CH_2Cl_2 (10 mL) was added Et_3N (1.0 mL, 7.2 mmol), and the mixture was stirred at 23 °C for 2 h. TLC monitoring (SiO_2, ether/hexane = 1/2) showed the formation of two new organometallic compounds (UV, R_f = 0.45 for **b**, R_f = 0.50 for **a**). The solution was evaporated to dryness and chromatographed through a SiO_2 column (ether/hexane = 1/2) to produce a yellow band, which was collected, and concentrated to give 18 as a viscous solid (206 mg, 0.51 mmol, **a**/**b** = 63/37). Elution through a preparative TLC plate (SiO_2, $_{60}F_{254}$, ether/hexane = 1/2) provided separation of the two isomers. IR (Nujol): ν(OH) 3408 (br, vs) cm^{-1}; ν(CO) 1934 (S) and 1853 (S)

cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): isomer **a** δ 7.30–7.41 (5H, m, Ph), 6.28 (1H, dd, J = 9.0, 5.0 Hz, H^2), 5.29 (5H, s, Cp), 4.75 (1H, d, J = 9.0 Hz, H^7), 4.42 (1H, dd, J = 9.0, 6.0 Hz, H^1), 4.33 (1H, t, J = 6.0 Hz, H^4), 4.05 (2H, m, H^3 + H^5), 2.80 (1H, ddd, J = 9.0, 6.0, 4.2 Hz, H^6): isomer **b** δ 7.30–7.63 (5H, m, Ph), 6.25 (1H, dd, J = 9.0, 3.0 Hz, H^2), 5.28 (5H, s, Cp), 4.62 (1H, d, J = 8.0 Hz, H^7), 4.30 (1H, dd, J = 9.0, 5.4 Hz, H^1), 4.15 (1H, t, J = 7.0 Hz, H^4), 4.00 (2H, m, H^3 + H^5), 2.95 (1H, m, H^6). Mass (12 eV, EI): m/z 376 (M^+ – CO). Anal. Calcd for $C_{20}H_{18}MoO_3$: C, 59.71; H, 4.51. Found: C, 59.44; H, 4.56.

(ii) Synthesis of CpMo(CO)$_2$[(1,2,3-η)-6-(1-hydroxy-2-methylpropyl)cyclohexadien-1-yl] (16). This compound was prepared similarly to the procedure in section b(i) except that the salt (**I**) in entry 3, Scheme II was used; the combined yields of the two isomers were 56% with **a**/**b** = 75/25. Separation of the two isomers was conducted by elution through a preparative TLC plate (SiO_2, $_{60}F_{254}$, ether/hexane = 1/2, R_f = 0.50 for **a**, 0.46 for **b**). IR (Nujol): ν(OH) 3380 (br, vs) cm^{-1}; ν(CO) 1928 (s) and 1843 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): isomer **a** δ 6.25 (1H, dd, J = 9.0, 7.0 Hz, H^2), 5.28 (5H, s, Cp), 4.42 (1H, dd, J = 9.0, 6.0 Hz, H^1), 4.30 (1H, t, J = 7.0 Hz, H^4), 4.11 (1H, dd, J = 7.0, 2.5 Hz, H^5), 3.95 (1H, t, J = 7.0 Hz, H^3), 3.17 (1H, dd, J = 9.5, 6.5 Hz, H^7), 2.51 (1H, ddd, J = 9.5, 6.0, 2.5 Hz, H^6), 1.62 (1H, m, C*H*Me$_2$), 1.04, 0.95 (6H, 2d, J = 7.0 Hz, 2Me); isomer **b** δ 6.25 (1H, dd, J = 9.0, 7.0 Hz, H^2), 5.29 (5H, s, Cp), 4.50 (1H, dd, J = 9.0, 6.0 Hz, H^1), 4.30 (1H, t, J = 7.0 Hz, H^4), 3.95 (1H, dd, J = 7.0, 3.0 Hz, H^5), 3.88 (1H, t, J = 7.0 Hz, H^3), 3.02 (1H, dd, J = 6.0, 4.0 Hz, H^7), 2.63 (1H, ddd, J = 6.0, 4.0, 3.0 Hz, H^6), 1.84 (1H, m, C*H*Me$_2$), 0.97, 0.91 (6H, 2d, J = 7.0 Hz, 2Me). Mass (12 eV, EI): 370 (M^+). Anal. Calcd for $C_{17}H_{20}MoO_3$: C, 55.44; H, 5.74. Found: C, 55.21; H, 5.84.

(c) (i) Synthesis of CpMo(CO)$_2$[(1,2,3-η)-4-(1-hydroxy-2-methylpropyl)cyclohexen-1-yl] (17). To the salt (**I**) in entry 3, Scheme II (ca. 1.00 mmol) in THF (15 mL) was added $NaBH_4$ (0.18 g, 5.00 mmol) at 23 °C, and the mixture was stirred for 6 h. TLC monitoring (SiO_2, ether/hexane = 1/2) showed the formation of two new organometallic compounds which have very close values of R_f (R_f = 0.50, 0.47). The solution was neutralized with 1 M HCl, and the volume was reduced to 10 mL before addition to an ether (15 mL)/water (10 mL) mixture. The organic layer was concentrated; the residues were chromatographed through a SiO_2 column to give a yellow band which was collected to give a yellow solid as a mixture of two isomers (0.23 g, 0.62 mmol) with **a**/**b** = 85/15. Separation of the two isomers was conducted on a preparative TLC plate (SiO_2, $_{60}F_{254}$, ether/hexane = 1/2). IR (Nujol): ν(OH) 3408 (br, s); ν(CO) 1927 (s), 1846 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): major isomer **a** δ 5.26 (5H, s, Cp), 4.14 (1H, t, J = 7.0 Hz, H^2), 3.69 (2H, m, H^1 + H^3), 2.81 (1H, t, J = 5.8 Hz, H^7), 1.70–1.78 (3H, m, $H^{6'}$ + H^6 + H^5), 1.62 (1H, ddd, J = 6.0, 5.8, 3.4 Hz, H^4), 1.52 (1H, m, C*H*Me$_2$), 0.78 (6H, 2d, J = 6.8 Hz, 2Me), 0.50 (1H, ddd, J = 14.0, 11.0, 5.8 Hz, H^5); minor isomer **b** δ 5.27 (5H, s, Cp), 4.25 (1H, t, J = 7.1 Hz, H^2), 3.72 (1H, ddd, J = 7.1, 4.6, 2.1 Hz, H^1), 3.40 (1H, dd, J = 7.1, 5.7 Hz, H^3), 3.15 (1H, t, J = 5.7 Hz, H^7), 1.95 (2H, m, $H^{6'}$ + C*H*Me$_2$), 1.79 (1H, m, H^4), 1.55 (1H, ddd, J = 15.0, 6.1, 2.1 Hz, H^6), 1.16 (1H, br dd, J = 14.0, 5.8 Hz, $H^{5'}$), 0.91 (6H, 2d, J = 6.8 Hz, 2Me), 0.32 (1H, ddt, J = 14.0, 10.8, 6.1 Hz, H^5). ^{13}C NMR (100 MHz, $CDCl_3$): isomer **a** δ 235.6, 235.5, 92.0, 80.1, 60.0, 56.9, 54.6, 54.3, 33.5, 29.8, 25.0, 22.7, 19.5, 16.8; isomer **b** δ 236.0, 235.2, 92.1, 81.6, 57.8, 56.0, 54.8, 34.9, 30.3, 19.9, 19.8, 17.8, 16.7. Mass (12 eV, EI): m/z 372 (M^+). Anal. Calcd for $C_{17}H_{22}MoO_3$: C, 55.14; H, 5.99. Found: C, 55.31; H, 6.10.

(ii) Synthesis of CpMo(CO)$_2$[(1,2,3-η)-4-(1-hydroxy-2,2-dimethylpropyl)cyclohexen-1-yl] (18). This compound was prepared similarly to the procedure in section c(i) except that the salt (**I**) in entry 4, Scheme II was used; the combined yields of the two isomers were 52% with **a**/**b** = 88/12. Separation of the two isomers was conducted on a preparative TLC plate (SiO_2, $_{60}F_{254}$, ether/hexane = 1/2, R_f = 0.49 for **b**, 0.46 for **a**). IR (Nujol): ν(OH) 3380 (br, s) cm^{-1}; ν(CO) 1929 (s), 1848 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): major isomer **a** δ 5.27 (5H, s, Cp), 4.13 (1H, t, J = 7.0 Hz, H^2), 3.70 (2H, m, H^1 + H^3), 2.78 (1H, d, J = 2.0 Hz, H^7), 1.95 (2H, m, $H^{6'}$ + H^4), 1.73 (1H, ddd, J = 14.3, 6.0, 3.4 Hz, H^6), 1.56 (1H, br dd, J = 14.0, 5.9 Hz, $H^{5'}$), 0.81 (9H, s, 3Me), 0.67 (1H, ddt, J = 14.0, 11.0, 6.0 Hz, H^5); minor isomer **b** δ 5.26 (5H, s, Cp), 4.27 (1H, t, J = 7.2 Hz, H^2), 3.76 (1H, ddd, J = 7.2, 4.6, 2.0 Hz, H^1), 3.43 (1H, dd, J = 7.0, 1.5 Hz, H^3), 3.39 (1H, d, J = 1.6 Hz, H^7), 2.10 (1H, m, $H^{6'}$), 2.03 (1H, m, H^4), 1.58 (1H, m, H^6), 1.15 (1H, dd, J = 14.5, 6.2, 5.1 Hz, $H^{5'}$), 0.90 (9H, s, 3Me), 0.36 (1H, m, H^5). ^{13}C NMR (100 MHz, $CDCl_3$): isomer **a** δ 235.8, 235.6, 90.0, 82.3, 56.8, 55.4, 55.1, 35.6, 32.8, 27.7, 26.8, 21.7; isomer **b** δ 236.2, 235.2, 92.1, 86.3, 58.8, 56.7, 55.6, 36.3, 32.8, 26.7, 21.3, 18.6. Mass (12 eV, EI): m/z 386 (M^+). Anal. Calcd for $C_{18}H_{24}MoO_3$: C, 56.25; H, 6.29. Found: C, 56.41; H, 6.40.

(iii) Synthesis of CpMo(CO)$_2$[(1,2,3-η)-4-(1-hydroxy-3-methylbutyl)-6-phenylcyclohexen-1-yl] (19). This compound was similarly prepared from the reaction between the salt (**I**) in entry 2, Scheme II and PhMgBr (4 equimolar) in THF; the combined yields of the two diastereomeric products were 53% with **a**/**b** = 90/10. Attempts to separate the two isomers by preparative SiO_2 TLC plate were unsuccessful. The major isomer **19a** was obtained in pure form by recrystallization from ether/hexane. IR (Nujol): ν(OH) 3402 (br, s) cm^{-1}; ν(CO) 1930 (s), 1850 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): major isomer **a** δ 7.14–7.43 (5H, m, Ph), 5.31 (5H, s, Cp), 4.63 (1H, t, J = 7.0 Hz, H^2), 3.84 (2H, m, H^1 + H^3), 3.42 (1H, ddd, J = 8.9, 5.5, 3.6 Hz, H^7), 3.03 (1H, ddd, J = 5.6, 4.9, 1.8 Hz, H^6), 1.73 (1H, m, H^4), 1.65 (1H, m, CH^7CHH'), 1.25 (2H, m, $H^{6'}$ + CH^7HH'), 1.19 (1H, m, C*H*Me$_2$), 0.92 (1H, m, H^5), 0.88, 0.79 (6H, 2d, J = 6.8 Hz, 2Me); minor isomer **b** (selected peaks) δ 5.26 (5H, s, Cp), 4.64 (1H, t, J = 7.0 Hz, H^2), 4.16 (2H, m, H^1 + H^3), 3.28 (1H, m, H^7), 3.23 (1H, m, H^6), 1.82 (1H, m, CH^7CHH'), 1.08 (2H, m, $CH^5H^{5'}$), 0.78, 0.66 (6H, 2d, J = 7.0 Hz, 2Me). The remaining peaks were masked by the overwhelming resonances of isomer **a**. Mass (12 eV, EI): m/z 462 (M^+). Anal. Calcd for $C_{24}H_{28}MoO_3$: C, 62.61; H, 6.13. Found: C, 62.47; H, 6.40.

(iv) Synthesis of CpMo(CO)$_2$[(1,2,3-η)-4-(1-hydroxy-2-methylpropyl)-6-phenylcyclohexen-1-yl] (20). This compound was similarly prepared from the reaction between the salt (**I**) in entry 3, Scheme II, and PhMgBr (4 equimolar) in THF at –78 °C for 3 h; the combined yields of **20a** and **20b** were 63% with **a**/**b** = 85/15 after being chromatographed through a SiO_2 column. Pure isomer **a** was obtained in 51% yield by cooling a concentrated ether/hexane solution at –20 °C for 2 days. IR (Nujol): ν(OH) 3400 (br, s) cm^{-1}; ν(CO) 1930 (s), 1848 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): major isomer **a** δ 7.18–7.49 (5H, m, Ph), 5.29 (5H, s, Cp), 4.63 (1H, t, J = 6.9 Hz, H^2), 3.87 (1H, dd, J = 6.9, 2.0 Hz, H^3), 3.76 (1H, dd, J = 6.9, 2.5 Hz, H^1), 3.05 (2H, m, H^6 + H^7), 1.87 (2H, m, H^4 + C*H*Me$_2$), 1.32 (1H, dt, J = 13.3, 3.0 Hz, $H^{5'}$), 1.17 (1H, dt, J = 13.3, 5.8 Hz, H^5), 0.86, 0.83 (6H, 2d, J = 6.5 Hz, 2Me); minor isomer **b** (selected peaks) δ 5.25 (5H, s, Cp), 4.26 (1H, t, J = 7.0 Hz, H^2), 3.70 (2H, m, H^1 + H^3), 3.10 (2H, m, H^7 + H^6), 2.86 (1H, t, J = 6.0 Hz, H^7), 1.94 (2H, m, H^4 + H^5), 1.53 (1H, m, C*H*Me$_2$), 0.78, 0.66 (6H, 2d, J = 6.5 Hz, 2Me); the remaining resonances were masked by the overwhelming peaks of **a**. Mass (12 eV, EI): m/z 448 (M^+). Anal. Calcd for $C_{23}H_{26}MoO_3$: C, 61.89; H, 5.87. Found: C, 61.90; H, 5.47.

(v) Synthesis of CpMo(CO)$_2$[(1,2,3-η)-4-(1-hydroxy-2-methylpropyl)-6-(bis(carbomethoxy)methyl)cyclohexen-1-yl] (21). This compound was similarly prepared from the salt (**I**) in entry 3, Scheme II, and LiCH(COOMe)$_2$ (4 equimolar) in THF; the combined yields of **21a** and **21b** were 65% with **a**/**b** = 85/15 after elution through a SiO_2 column. Cooling a saturated ether/hexane solution at –20 °C for 2 days gave pure **21a** in block-shaped crystals (51%). IR (Nujol): ν(OH) 3350 (br, s) cm^{-1}; ν(CO) 1938 (s), 1852 (s), 1711 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): major isomer **a** δ 5.24 (5H, s, Cp), 4.21 (1H, t, J = 7.1 Hz, H^2), 3.80, 3.73 (6H, 2s, 2 OMe), 3.63 (3H, m, H^1 + H^3 + C*H*(COOMe)$_2$), 3.16 (1H, dd, J = 8.8, 5.8 Hz, H^7), 2.51 (1H, ddd, J = 5.8, 2.9, 2.5 Hz, H^6), 2.43 (1H, s, H^9), 1.90 (2H, m, H^4 + C*H*Me$_2$), 0.90–0.92 (7H, 2d + m, J = 6.7Hz, 2Me + H^5), 0.62 (1H, dt, J = 14.6, 5.8 Hz, H^5); minor isomer **b** selected peaks δ 5.23 (5H, s, Cp), 4.31 (1H, t, J = 7.2, Hz, H^2), 3.60 (2H, m, H^1 + H^3), 3.53, 3.54 (6H, 2s, 2OMe), 3.15 (1H, dd, J = 8.2, 5.6 Hz, H^7), 2.10

(1H, m, H^6), 1.75 (1H, m, C*H*Me_2); the rest of the peaks were masked by the overwhelming resonances of **a**. ^{13}C NMR (100 MHz, $CDCl_3$): isomer **a** δ 235.7, 234.9, 169.7, 168.9, 92.3, 81.5, 61.2, 57.9, 56.8, 54.2, 52.7, 52.5, 35.2, 33.0, 30.2, 21.0, 20.3, 16.0. Mass (12 eV, EI): *m/z* 502 (M^+). Anal. Calcd for $C_{22}H_{28}MoO_7$: C, 52.81; H, 5.64. Found: C, 52.91; H, 5.58.

(vi) Synthesis of $CpMo(CO)_2$[(1,2,3-η)-4-(1-hydroxy-2,2-dimethylpropyl)-5-methylcyclohexen-1-yl] (22). This compound was prepared similarly from the salt (**I**) in entry 4, Scheme II and MeMgBr (5 equimolar amount) in THF at −78 °C for 3 h, and only one isomer **a** was detected by ^1H-NMR spectra for the crude yellow solid (54% yield) after elution through a SiO_2 column. Recrystallization from a saturated ether/hexane solution (−20 °C, 3 days) gave **22** as a yellow crystalline solid in 48% overall yield. IR (Nujol): ν(OH) 3360 (br, s) cm^{-1}; ν(CO) 1948 (s), 1830 (s), 1715 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): diastereomer **a** only δ 5.25 (5H, s, Cp), 4.34 (1H, t, J = 7.2 Hz, H^2), 3.71 (1H, dd, J = 7.2, 2.8 Hz, H^3), 3.65 (1H, dd, J = 7.2, 2.8 Hz H^1), 3.34 (1H, d, J = 3.2 Hz, H^7), 2.11 (1H, ddd, J = 6.0, 3.2, 2.8 Hz, H^4), 1.76 (1H, ddd, J = 5.0, 2.8, 2.0 Hz, H^6), 1.56 (2H, m, $H^{5'}$ + H^6), 1.10 (3H, d, J = 7.0 Hz, 1Me), 0.89 (9H, s, 3Me), 0.80 (1H, dt, J = 14.0, 5.0 Hz, H^5). Mass (12 eV, EI): *m/z* 400 (M^+). Anal. Calcd for $C_{19}H_{26}MoO_3$: C, 57.29; H, 6.58. Found: C, 54.51; H, 6.82.

(d) Synthesis of $CpMo(CO)_2$[(1,2,3-η)-4-(1-hydroxyphenylmethyl)-5-phenylcyclohexen-1-yl] (23). This compound was similarly prepared from the salt (**I**) in entry 10, Scheme II, and $LiHBEt_3$ (1.5 equimolar) in THF at −40 °C for 4 h. After elution through a SiO_2 column, the resultant crude yellow product consisted mainly of **23**, according to ^1H-NMR spectra. Recrystallization from a saturated ether/hexane solution (−20 °C, 3 days) gave **23** as block-shaped crystals (53%). IR (Nujol): ν(OH) 3410 (br, s) cm^{-1}; ν(CO) 1938 (s), 1845 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.03–7.11 (10H, m, 2Ph), 5.15 (5H, s, Cp), 4.37 (1H, d, J = 6.8 Hz, H^7), 3.96 (1H, t, J = 7.0 Hz, H^2), 3.58 (1H, ddd, J = 7.0, 3.0, 2.5 Hz, H^1), 3.02 (1H, dd, J = 7.0, 3.0 Hz, H^3), 2.45 (1H, ddd, J = 6.8, 6.0, 3.0 Hz, H^4), 2.18 (1H, ddd, J = 11.0, 6.0, 3.0 Hz, H^5), 1.95 (1H, ddd, J = 14.0, 11.0, 2.5 Hz, $H^{6'}$), 1.67 (1H, dt, J = 14.0, 3.0 Hz, H^6). Mass (12 eV, EI): 482 *m/z* (M^+). Anal. Calcd for $C_{26}H_{24}MoO_3$: C, 65.00; H, 5.04. Found: C, 65.23; H, 5.28.

(e) Synthesis of $CpMo(CO)_2$[(1,2,3-η)-4-(1-hydroxy-2-methylpropyl)-6-((carbomethoxy)(hydroxycarbonyl)-methyl)cyclohexen-1-yl] (24). To compound **21a** (0.22 g, 0.44 mmol) in THF (20 mL) was added 40% aqueous Bu_4NOH (0.30 mL, 0.44 mmol), and the mixture was refluxed for 0.5 h. After the solution was neutralized to pH = 7.0 by HCl (0.1 M), the solution was extracted with diethyl ether (15 mL) three times, and the ethereal layer was dried over $MgSO_4$, concentrated, and finally eluted through a SiO_2 column with diethyl ether/CH_2Cl_2 (1/1) as eluent. A dark-yellow band was developed, collected, and evaporated to give yellow plate-shaped solid (0.18 g, 0.37 mmol, 86%). IR (Nujol): ν(CO) 1930 (s), 1840 (s), 1701 (s) cm^{-1}. ^1H NMR (300 MHz, CD_3OD): major isomer **a** (93%) δ 5.40 (5H, s, Cp), 4.33 (1H, t, J = 7.0 Hz, H^2), 3.73 (3H, s, OMe), 3.69 (1H, br d, J = 7.0 Hz, H^3), 3.62 (1H, br d, J = 7.1 Hz, H^1), 3.32 (2H, m, H^7 + C*H*COO), 2.46 (1H, br d, J = 7.0 Hz, H^6), 2.18 (1H, m, C*H*Me_2), 1.81 (1H, dd, J = 7.0, 6.5 Hz, H^4), 1.30 (1H, br d, J = 13.2 Hz, $H^{5'}$), 1.03, 0.88 (6H, 2d, J = 6.7 Hz, 2Me), 0.55 (1H, dt, J = 13.2, 7.0 Hz, H^5); minor isomer **b** (7%) δ 5.38 (5H, s, Cp), 4.37 (1H, t, J = 7.0 Hz, H^2), 3.91 (1H, br d, J = 7.0 Hz, H^3), 3.71 (3H, s, OMe), 2.00 (1H, br t, J = 7.0 Hz, H^4), 0.96, 0.90 (6H, 2d, J = 6.7 Hz, 2Me); the remaining peaks were masked by the overwhelming resonances of the major isomer. Mass (12 eV, EI): *m/z* 442 (M^+ − COOH − 1). Anal. Calcd for $C_{21}H_{26}MoO_7$: C, 51.86; H, 5.39. Found: C, 51.45; H, 5.62.

(f) Lactonization of 24. To compound **24** (0.22 g, 0.48 mmol) in CH_3CN (4 mL) was added $NOBF_4$ (58 mg, 0.50 mmol) at 0 °C, and the mixture was stirred for 30 min before addition of Na_2CO_3(s) (0.40 g). The solution continued to stir for 2 h before exposure to air. After stirring for 2 h in air, to this dark brown suspension was added H_2O (5 mL), and the mixture was extracted with diethyl ether (4 mL) three times. The organic layer was concentrated and eluted through a preparative SiO_2 TLC plate, and an organic band (hexane/ether = 4/1, R_f = 0.25) was collected to give **25** as a colorless oil (50 mg, 0.24 mmol). IR (neat): ν(CO) 1773 (s), 1730 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.78 (1H, dd, J = 10.0, 4.2 Hz, H^2), 5.56 (1H, dd, J = 10.0, 2.0 Hz, H^3), 4.83 (1H, t, J = 4.2 Hz, H^1), 3.37 (3H, s, OMe), 3.27 (1H, s, C*H*$(COOMe)_2$), 2.87 (1H, t, J = 5.5 Hz, H^7), 2.31 (1H, ddd, J = 11.0, 4.9, 4.2 Hz, H^6), 1.80 (1H, m, H^4), 1.55 (1H, m, C*H*Me_2), 1.32 (1H, dt, J = 14.4, 4.9, Hz, H^5), 1.06 (1H, td, J = 14.4, 11.0 Hz, H^5), 0.97, 0.82 (6H, 2d, J = 6.7 Hz, 2Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 167.8, 137.9, 123.7, 79.0, 75.0, 55.2, 53.1, 37.9, 37.7, 30.3, 23.9, 19.4, 18.0. HRMS Calcd for $C_{14}H_{20}O_5$: 268.1311. Found: 268.1309.

(g) (i) Synthesis of 3-Thiophenoxy-6-(1-hydroxy-2-methylpropyl)cyclohexene (26). To compound **17a** (130 mg, 0.35 mmol) in CH_3CN (5 mL) was added $NOBF_4$ (50 mg, 0.40 mmol) at 0 °C, and the mixture was stirred for 20 min before a THF solution (2 mL) of PhSNa (66 mg, 0.50 mmol) was added. After stirring for 2 h, to the solution was added $(NH_4)_2Ce(NO_3)_6{\cdot}H_2O$(s) (0.21 g, 0.38 mmol), and TLC monitoring (SiO_2, ether/hexane = 1/2) showed the formation of a new organic compound (UV, R_f = 0.40). The solution was concentrated and extracted with ether (5 mL) three times. After evaporation to dryness, and residues were chromatographed through a preparative TLC plate (SiO_2, $_{60}F_{254}$) with diethyl ether/hexane = 1/2 as the eluent to give **26** (55 mg, 0.21 mmol) as a colorless oil. IR (neat): ν(OH) 3451 (br s) cm^{-1}; ν(C=C) 1650 (s), 1590 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.15–7.45 (5H, m, Ph), 5.78 [1H, ddd, J = 9.9, 5.2, 2.7(J_{24}) Hz, H^2], 5.68 (1H, br d, J = 9.9 Hz, H^1), 3.86 (1H, ddd, J = 6.4, 5.2, 3.0Hz, H^3), 3.11 (1H, dd, J = 6.7, 5.8 Hz, H^9), 2.08 (1H, m, H^4), 1.92–1.98 (2H, m, H^6 + H^5), 1.83 (1H, ddd, J = 8.0, 6.7, 3.6 Hz, H^8), 1.74 (1H, octet, J = 6.7 Hz, C*H*Me_2), 1.52 (1H, m, H^7), 0.90, 0.88 (6H, 2d, J = 6.6 Hz, 2Me). ^{13}C NMR (100 MHz, $CDCl_3$): 134.7, 131.8, 128.8, 128.0, 126.8, 80.4, 44.7, 37.1, 33.9, 30.3, 25.4, 19.5, 17.5. HRMS Calcd for $C_{16}H_{22}OS$: 262.1391. Found: 262.1385.

Table V. Crystal Data and Data Collection Parameters for 21a and 23

compd	**21a**	**23**
empirical formula	$MoC_{22}H_{28}O_7$	$MoC_{26}H_{24}O_3$
fw	500.4	480.4
space group	*Cc*	*P*1
a (Å)	10.173(2)	7.674(2)
b (Å)	28.265(5)	8.380(2)
c (Å)	7.870(2)	8.554(2)
α (deg)		83.70(2)
β (deg)	98.21(2)	84.10(2)
γ (deg)		80.46(2)
vol (Å^3)	2239.8(9)	537.2(2)
Z	4	1
D_{calc} (g/cm^{-3})	1.484	1.485
μ (cm^{-1})	6.1 (Mo Kα)	6.2 (Mo Kα)
cell dimens (mm)	0.05 × 0.15 × 0.50	0.30 × 0.30 × 0.50
collcn range	$2\theta_{max}$ = 50, $\pm h,k,l$	$2\theta_{max}$ = 55, $\pm h,k,\pm l$
scan mode	$\theta/2\theta$	$\theta/2\theta$
scan speed (deg min^{-1})	16.48(8)–16.48(2)	16.48(7)–16.48(2)
scan width (deg)	0.90 + 0.35 tan θ	0.65 + 0.35 tan θ
collcn *T* (K)	298	298
decay correcn	no (<6%)	no (<2%)
abs correcn	yes	yes
min and max transition factors	0.92, 1.00	0.91, 1.00
no. of ind reflns	1982	2454
no. of reflns with $I > 2\sigma(I)$	1661	2451
weighting scheme	$w^{-1} = \sigma^2 + 0.0001F^2$	$w^{-1} = \sigma^2 + 0.00005F^2$
R_F[a] (all data)	0.045 (0.057)	0.028 (0.028)
R_w[b] (all data)	0.044 (0.045)	0.041 (0.041)
S[c]	1.66	2.89
residual extrema in final diff map (e Å^{-3})	−0.58, 0.94	−0.52, 0.46

[a] $R = \sum|F_o - F_c|/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. [c] $S = [\sum w(|F_o| - |F_c|)^2/(m - p)]^{1/2}$.

(ii) Synthesis of 3-Thiophenoxy-6-(1-hydroxy-2,2-dimethylpropyl)cyclohexene (27). This compound was similarly prepared from **18a**, $NOBF_4$, and PhSNa in the procedure described in section g(i); the yield of **27** was 65%. IR (neat): ν(OH) 3480 (br s) cm^{-1}; ν(C=C) 1670 (s), 1590 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.17–7.55 (5H, m, Ph), 5.75 [1H, ddd, J = 9.9, 4.7, 2.7 (J_{24}) Hz, H^2], 5.67 (1H, dd, J = 9.9, 1.0 Hz, H^1), 3.85 (1H, ddd, J = 7.8, 4.7, 3.6 Hz, H^3), 3.07 (1H, d, J = 2.0 Hz, H^9), 2.26 (1H, m, H^4), 2.10 (1H, m, H^5), 1.85–1.90 (2H, m, H^6 + H^8), 1.49 (1H, m, H^7), 0.92 (9H, s, 3Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 131.6, 129.4, 128.8, 128.4, 82.4, 44.8, 35.9, 32.1, 31.4, 26.5. HRMS Calcd for $C_{17}H_{24}SO$: 276.1548. Found: 276.1539.

(h) X-ray Diffraction Measurement. A single crystal of each of **21a** and **23** was sealed in a glass capillary under an inert atmosphere. Data were collected on a Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation, and the structures were solved by heavy-atom methods; all data reduction and structural refinement were performed with the NRCCSDP package. Crystal data and details of the data collection and structure analysis[17,18] are summarized in Table V. For all structures, all non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms included in structure factor calculations were placed in idealized positions.

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Supplementary Material Available: Tables of crystal data, all bond distances and angles, positional parameters, and thermal parameters for compounds **21a** and **23** (9 pages). Ordering information is given on any current masthead page.

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