Conjugated Addition of Organocopper Reagents to the Enone Group Adjacent to a $CpMo(CO)_2(\pi$-allyl) Fragment

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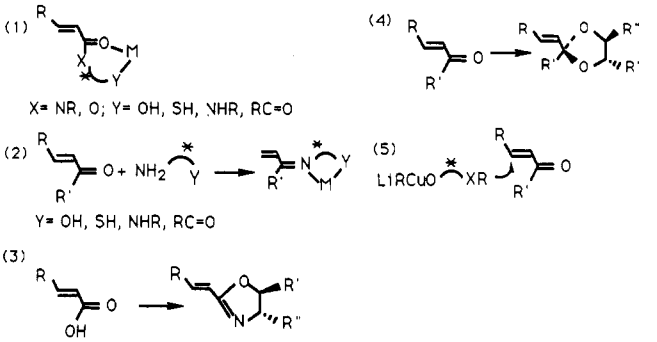
1,4-Addition of organocopper reagents to $CpMo(CO)_2(\eta^3$-1-*trans*-COCH=CHR-allyl) (R = Ph (**1**), 2-furyl (**2**), methyl (**3**)) proceeded in reasonable diastereoselectivities that can be improved to excellent levels in the presence of $BF_3{\cdot}Et_2O$ at one equimolar proportion. The stereochemistry of the major diastereomeric products was elucidated from X-ray structural analysis, which indicated that the minor species of **1–3** in solution, the s-trans-enone conformer, is the active species. The cis-enolates of these major products were selectively generated by $LiN(SiMe_3)_2$ which condensed with aldehydes in excellent diastereoselectivities, and X-ray structures of representative products were determined. Further utilization of these aldol products for stereoselective synthesis of 2,3,4,5-tetrahydrofurans is demonstrated.

Introduction

The stereochemical course of the conjugated addition of an organocopper reagent to an α,β-unsaturated carbonyl group is a problem in synthetic organic chemistry,[1-4] particularly challenging when the organic molecule is acyclic because of it is more conformationally flexible than its cyclic counterpart. To achieve a high diastereomeric synthesis, one may attach to the acyclic unsaturated amide or ester[2,5,6] (C=CR—CO—XR*, XR*=OR*, NR′R″*$_2$) a chiral auxiliary (XR*) that generally contains a heteroatom, e.g. oxygen, nitrogen, and sulfur to chelate a metal ion to form a more conformationally rigid structure, as shown in Scheme 1; in this manner, organometallic reagents attack at the unsaturated C_β carbon from the less hindered face. Unsaturated enones, acids, and aldehydes are typically transformed to enamine, oxazolidines, and acetals with a similar chiral functionality that likewise tends to chelate a metal ion to direct the diastereofacial nucleophilic attack. Utilization of an organocopper reagent, complexed with a chiral chelated ligand, induces enantiomeric excess with an acyclic unsaturated enone and ester group, but the ee values are commonly small compared to those of their cyclic enone compounds.[5,6]

Utilization of an organometallic fragment as a chiral auxiliary in a Michael reaction is an alternative method, and its effectiveness is shown by compounds such as $CpFeCO(PPh_3)(\eta^1$-*trans*-COCH=CHR)[7,8] and $Cr(CO)_3$-(1-*trans*-COCH=CHR-2-OR-benzene).[9-11] The enone

Scheme 1



group adjacent to an asymmetric π-complexed metal fragment deserves special attention because of delocalization between the π-enone and π-metal–organic fragment that makes the enone conformationally more rigid; one expects a highly diastereomeric Michael reaction if the metal approaches the enone opposite the metal fragment.

We and others[12,13] are currently investigating the application of molybdenum– and tungsten–π-allyl compounds of the type $CpMo(CO)_2(\pi$-allyl) for organic reactions. As there are only a few cases of transition-metal–enone compounds used for the diastereoselective Michael reaction, we report here[14] the stereochemical outcome of the addition of organocopper reagents to the enone group adjacent to $CpMo(CO)_2(\pi$-allyl).

Results and Discussion

Diastereofacial Conjugated Addition. The starting enone compounds $CpMo(CO)_2(\eta^1$-1-*trans*-COCH=CHR-

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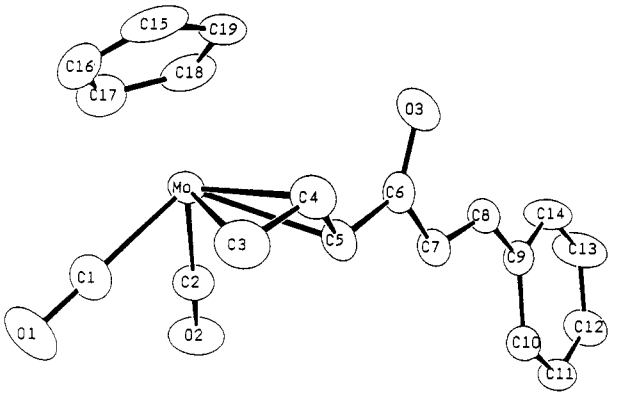


Figure 1. ORTEP drawing of compound 1.

Table 1. Selected Bond Distances (Å) and Angles (deg) of Compound 1

Mo–C(1)	1.949(4)	C(3)–C(4)	1.385(6)
Mo–C(2)	1.933(5)	C(4)–C(5)	1.384(6)
Mo–C(3)	2.359(5)	C(5)–C(6)	1.476(6)
Mo–C(4)	2.208(4)	C(6)–C(7)	1.485(7)
Mo–C(5)	2.336(4)	C(6)–O(3)	1.233(6)
C(1)–O(1)	1.149(5)	C(7)–C(8)	1.305(6)
C(2)–O(2)	1.163(6)	C(8)–C(9)	1.446(6)
C(1)–Mo–C(2)	79.67(19)	Mo–C(3)–C(4)	66.5(3)
C(1)–Mo–C(3)	72.13(19)	Mo–C(4)–C(3)	78.4(3)
C(1)–Mo–C(4)	106.05(19)	Mo–C(4)–C(5)	77.39(24)
C(1)–Mo–C(5)	114.23(17)	C(3)–C(4)–C(5)	120.1(4)
C(2)–Mo–C(3)	110.75(16)	Mo–C(5)–C(4)	67.29(24)
C(2)–Mo–C(4)	108.76(17)	Mo–C(5)–C(6)	115.3(3)
C(2)–Mo–C(5)	76.51(16)	C(4)–C(5)–C(6)	121.1(4)
C(3)–Mo–C(4)	35.11(16)	C(5)–C(6)–C(7)	117.1(4)
C(3)–Mo–C(5)	61.45(15)	C(5)–C(6)–O(3)	121.1(4)
C(4)–Mo–C(5)	35.32(16)	C(7)–C(6)–O(3)	121.7(4)
Mo–C(1)–O(1)	178.3(4)	C(6)–C(7)–C(8)	122.5(4)
Mo–C(2)–O(2)	179.0(4)	C(7)–C(8)–C(9)	128.3(4)

allyl) (R = phenyl (1), 2-furyl (2), methyl (3)) were obtained from the anion $CpMo(CO)_2(\eta^3\text{-}C_3H_4COCH_2Li)$ *via* an aldol reaction with the corresponding aldehydes, followed by subsequent dehydration with Ac_2O/Et_3N;[15] the overall yields were 70–80%. If one regards $CpMo(CO)_2$(1-R-allyl) as an asymmetric unit to direct diastereofacial attack, the conformation of the allyl–enone fragment becomes ultimately important for the outcome. We therefore determined the molecular structure of 1; its ORTEP drawing appears in Figure 1, and selected bond distances and angles are provided in Table 1. According to the ORTEP drawing, the compound adopts a sickle-shaped arrangement of the allyl ketone group, and an s-cisoid conformation of the CO/C=C fragment. The five carbon C(3)–C(7) and O(3) atoms form a planar system within a maximum deviation of 1.129(6) Å, indicating the resonance structure **A**. Further indication of this resonance is provided from the small value (1645 cm^{-1}) of the ketone ν(CO) stretching frequency, and also from the distances C(6)—O(3) (1.233(6) Å) and C(5)—C(6) (1.476(6) Å) that deviate from the normal values of the double C=O (1.20(1) Å) and single C—C (1.54(1) Å) bonds.

The sickle-shaped allyl ketone conformation of 1 is consistent with all reported molybdenum–π-allyl ketone

Chart 1

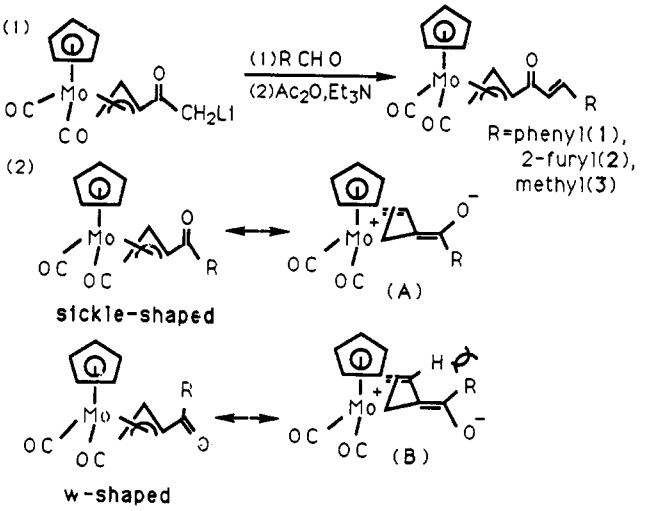
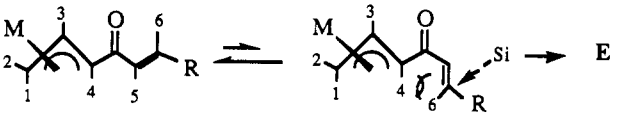


Chart 2 [a]



s -cis -enone (**C**) *s -trans*-enone (**D**)

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

and ester and –π-allylamide compounds $CpMo(CO)_2(\pi$-1-COX-allyl)[16] (X = alkyl, OR, NR_2) except for the aldehyde compound[17] (X = H) that adopts a W-shaped conformation of the allyl ketone fragment. Although the W-shaped allyl/CO conformation is superior to its sickled conformer because of a transoid arrangement between the π-allyl fragment and ketone group, this superiority is offset by the increasing sizes of R groups that exert steric hindrance with the central allyl proton, as in structure **B**. The s-cisoid conformation of the CO/C=C fragment is similar to that in other metal–enone compounds such as $CpFe(CO)PPh_3(\eta^1$-*trans*-COCH=CHR)[7,8] and $Cr(CO)_3$-(1-enone-2-OR-benzene).[9,10] This conformation is the preferable form for iron–η^1-enone complexes according to an extended Huckel calculation.[7] For compound 1, steric interaction between the H^4 and H^6 hydrogens tends to destabilize the s-transoid CO/C=C conformation (**D**) (see Chart 2).

We examined the conformation of 1 in solution by ^{1}H-NOE NMR spectra in $CDCl_3$ at –60 °C which show only one enone species to exist there. At this temperature, irradiation of the H^4 signal (δ 2.25 ppm) causes an increased intensities of signals of H^1 (δ 1.41), H^3 (δ 5.17), H^5 (δ 6.85), and H^6 (δ 7.60) by 2.1%, 1.4%, 5.2%, and 2.2%, respectively. Likewise, irradiation of the H^5 proton shows increased intensities of the H^4 and H^6 proton signals by 4.8% and 2.5%, respectively. Finally, irradiation of the H^6 proton produces an increase in the intensities of the H^5 and H^4 signals by 2.9% and 1.2%, respectively. This information indicates that the s-cisoid conformer (**C**) is still the major species in solution. For the s-transoid

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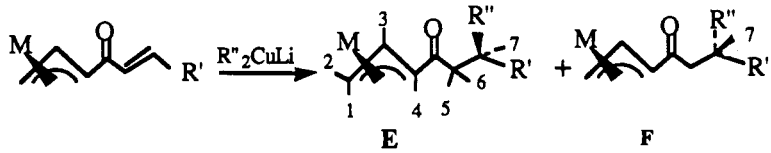
Scheme 2



E **F**

Entry	Enone	R_2"CuM	L. A.	E/F(Yields)[a]	E/F(Yields)[b]	Prod. No
1	1	Me_2CuLi	-	4 / 1(65%)	4E(45%), 4F(10%)	4
2	1	Me_2CuLi	$BF_3 \cdot Et_2O$	14 / 1(90%)	4E(78%), 4F(3%)	4
3	1	$(C_2H_3)_2CuMgBr$	-	6 / 1(70%)	5E(55%)[c]	5
4	1	$(C_2H_3)_2CuMgBr$	$BF_3 \cdot Et_2O$	>20 / 1(88%)	5E(64%)[c]	5
5	2	Me_2CuLi	-	3 / 1(80%)	6E(52%), 6F(7%)	6
6	2	Me_2CuLi	$BF_3 \cdot Et_2O$	16 / 1(88%)	6E(75%), 6F(3%)	6
7	2	$(C_2H_3)_2CuMgBr$	-	5 / 1(74%)	7E(50%)[c]	7
8	2	$(C_2H_3)_2CuMgBr$	$BF_3 \cdot Et_2O$	>20 / 1(85%)	7E(78%)[c]	7
9	3	Ph_2CuLi	-	5 / 2(80%)	4*E(48%),4*F(16%)	4*
10	3	Ph_2CuLi	$BF_3 \cdot Et_2O$	14 / 1(88%)	4*E(70%), 4*F(3%)	4*

[a] These product ratioes and yields are estimated by proton NMR spectra before separation by preparative TLC plate or by fractional crystallization(see experimental section)

[b] These values represent the isolated yields after separation of the two diastereomers.

[c] Only major isomer is isolated by fractional crystallization method.

conformer (**D**), the H^4 proton signal is expected to exert a greater Overhauser effect on the H^6 proton than the H^5 proton, which is inconsistent with our observations. Nevertheless, the increased intensity of the H^6 proton (2.2%) on irradiation of the H^4-proton indicates that the s-transoid conformer (**D**) is likely to exist but equilibrates rapidly with the major conformer (**C**) in solution (Chart 2).

Additions of organocopper reagents to compounds **1–3** were carried out in THF at −40 °C. The copper reagents were prepared by mixing CuI and RLi (R = Me, Ph) or vinylmagnesium bromide in double molar proportions. In a typical run, organocopper reagents in 4–5 fold molar proportions were required to achieve satisfactory yields. The two diastereomeric products **E** and **F** were separated either on a conventional silica column (entries 1,2, 5,6, and 9,10) or by fractional crystallization (entries 3,4 and 7,8). The product ratios and combined yields of crude products, indicated in Scheme 2, were estimated from ^1H NMR spectra before separation. These values deviate somewhat from the respective yields after isolation. Although the selectivities failed to achieve the excellent level of $CpFe(CO)PPh_3(\eta^1$-(E)-COCH=CHR),[7,8] they are better than those of $Cr(CO)_3$(*trans*-1-COCH=CHR-2-OR-benzene).[9] The major isomers in entries 1,2 and 9,10 (Scheme 2) have reverse configuration in the major products, i.e. **4E** = **4F*** and **4F** = **4E***, providing stereocontrol of the desired structures. To elucidate the reaction stereochemistry, we performed X-ray structural analyses of **5E** and aldol derivatives of **3E** and **4E** (compounds **12** and **13**; *vide ante*). The molecular drawing of **5E** appears in Figure 2, and selected bond distances and angles are presented in Table 2.

According to the ORTEP drawing (Figure 2), the π-allyl and ketone conformation of **5E** likewise adopts a sickle

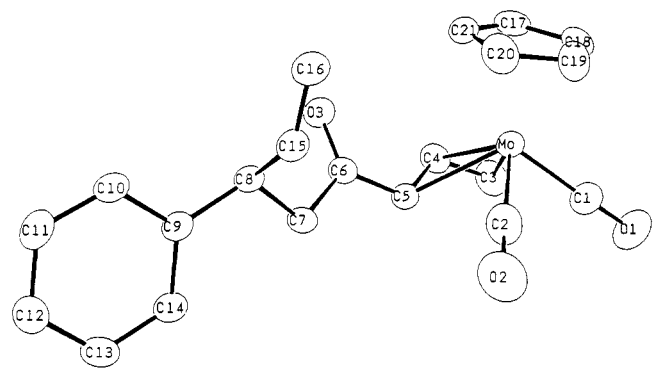


Figure 2. ORTEP drawing of compound **5E**.

shape, and delocalization between the π-allyl and ketone fragments is shown by the lengths C(5)—C(6) (1.459(7) Å) and C(6)—O(3) (1.222(6) Å) and by the planarity of the five allyl ketone atoms that have a maximum deviation of 0.071(6) Å. Similar to **1**, the main (C(3)–C(9)) carbon skeleton retains a zigzag shape to achieve the most stable conformation, and the vinyl group lies toward the $CpMo(CO)_2$ fragment. If the π-allyl C(5) carbon (ORTEP labeling) of **5E** is designated to have the *S** configuration, the molecule has the 3*S**,6*R** configuration. In connecting this stereochemistry with two possible enone conformations, we conclude that the minor conformer **D** is responsible for the observed major products if one assumes that organocopper reagents approach the enone C=C double bond opposite the metal fragment. As the $CpMo(CO)_2$ fragment is regarded as an electron-rich group, for cuprates to approach the major conformer **C** on the same side as the metal fragment is unlikely. For compound **1**, conjugated addition of $(C_2H_3)_2CuLi$ to s-cis enone conformer **C** is expected to give molybdenum–π-allyl compounds in

Table 2. Selected Bond Distances (Å) and Angles (deg) of Compound 5E

Mo–C(1)	1.916(6)	C(4)–C(5)	1.403(7)
Mo–C(2)	1.911(6)	C(5)–C(6)	1.459(7)
Mo–C(3)	2.349(5)	C(6)–C(7)	1.495(6)
Mo–C(4)	2.214(5)	C(6)–O(3)	1.222(6)
Mo–C(5)	2.350(4)	C(7)–C(8)	1.534(6)
C(1)–O(1)	1.157(7)	C(8)–C(9)	1.510(6)
C(2)–O(2)	1.142(7)	C(8)–C(15)	1.510(6)
C(3)–C(4)	1.374(7)	C(15)–C(16)	1.306(7)
C(1)–Mo–C(2)	79.0(3)	Mo–C(4)–C(5)	77.5(3)
C(1)–Mo–C(3)	72.41(22)	C(3)–C(4)–C(5)	121.4(4)
C(1)–Mo–C(4)	105.67(21)	Mo–C(5)–C(4)	66.9(3)
C(1)–Mo–C(5)	113.29(19)	Mo–C(5)–C(6)	115.8(3)
C(2)–Mo–C(3)	112.03(22)	C(4)–C(5)–C(6)	120.3(4)
C(2)–Mo–C(4)	108.98(21)	C(5)–C(6)–C(7)	118.0(4)
C(2)–Mo–C(5)	76.34(20)	C(5)–C(6)–O(3)	121.4(4)
C(3)–Mo–C(4)	34.90(18)	C(7)–C(6)–O(3)	120.5(4)
C(3)–Mo–C(5)	62.04(17)	C(6)–C(7)–C(8)	113.5(3)
C(4)–Mo–C(5)	35.66(17)	C(7)–C(8)–C(9)	115.4(3)
Mo–C(1)–O(1)	179.1(5)	C(7)–C(8)–C(15)	109.7(3)
Mo–C(2)–O(2)	177.7(6)	C(9)–C(8)–C(15)	110.8(3)
Mo–C(3)–C(4)	67.1(3)	C(8)–C(15)–C(16)	124.9(4)
Mo–C(4)–C(3)	78.0(3)		

3*S**,6*S** configuration like the minor isomer **5F**. This result is distinct from other metal–η^1-enone compounds (M=CpFe(CO)PPh$_3$,[7,8] (2-XC$_6$H$_4$)Cr(CO)$_3$)[9-11] in which the cis-enone conformer **C** applies in both the crystal and the species active in solution. To assure the reaction role of conformer **D**, we added BF_3·Et_2O in an equimolar proportion to **1–3** before addition to the organocopper reagents. The presence of BF_3·Et_2O is expected to increase the concentration of conformer **D** because of increasing steric hindrance between the coordinated BF_3·O=C fragment and the enone C=C double bond in conformer **C**. Under these conditions, excellent diastereoselectivities of products **4–7E** and **4*E** were achieved; this result again supports the dominant role of conformer **D**. Sterically, the enone group of conformer **C** is farther from the CpMo(CO)$_2$ fragment relative to conformer **D**, and thus stereochemical control by conformer **D** in the conjugated addition is superior to that in conformer **C**. Hence the Michael reaction of conformer **C** is less sterically hindered because of its more remote enone group. The electronic effect must be favorable for **D** to account for its higher reactivity, and its origin is unclear at this stage.

Stereoselective Synthesis of 2,3,4,5-Tetrahydrofuran. We previously utilized aldol reaction products of the enolate anion CpMo(CO)$_2$(π-1-COCH$_2$Li-allyl) for diastereoselective synthesis of tetrahydrfuran compounds.[13] The cis-enolates of compounds **4E** and **6E** were selectively generated by LiN(SiMe$_3$)$_2$ that further reacted with ICH$_2$COOEt to give the alkylation products **8** and **9** as a single diastereomer (yields >80%), Scheme 3. The enolate underwent a highly diastereoselective condensation with aldehydes, selectively giving **10–13** exclusively (yields >75%) after purification with column chromatography. We attempted to use other bases such as lithium diisopropylamide and potassium *tert*-butoxide; the enolates generated therefrom reacted with aldehydes to give mixtures of diastereomers that were difficult to separate and to characterize. For LDA and potassium *tert*-butoxide, the occurrence of further diastereomeric products is probably due not only to the generation of both s-cis- and trans-enolates but also to their subsequent additions to aldehyde. We performed X-ray diffraction measurements on **10** and **12**. For both compounds, each asymmetric unit contains two independent molecules. The structures of representative independent molecules appear in Figures 3 and 4, and selected bond distances and angles are given in Tables 3 and 4, respectively.

Similar to **1** and **5E**, the π-allyl/C=O conformations of **10** and **12** adopt a sickle-shaped conformation. This conformation is expected to be favorable for bulky π-ketone compounds like **10** and **12** (*vide ante*). According to ORTEP drawings in Figures 3 and 4, if the asymmetric Mo–π-allyl C^3 carbon is taken to have the *R** configuration shown in Scheme 3, the two molecules have the 3*R**,5*R**,6*R**,1′*R** configuration. The 6*R** configurations of the *C*^{7}HMe carbons of **10** and **12** are consistent with the stereochemistry of the major isomers **4–7E**, and the 5*R** configurations of their asymmetric COC^{5}H carbons confirm formation of the cis-enolate that selectively condensed with the *si*-face of aldehyde to give the products in the 5*R**,1′*R** configuration. As the main carbon skeletons of **4E** and **6E** are zigzag, formation of the cis-enolate is attributed to deprotonation of one methylene proton (COCHH′) either exo or endo to the metal fragment. The two O(3)—O(4) distances of the two molecules are small, i.e. 2.82 Å for **12** and 3.03 Å for **10**; this information indicates that an intramolecular hydrogen bond exists between the C=O and CH(OH)Ph fragments. Further structural analysis of the two dependent molecules of **12** by a Fourier difference map confirms such a hydrogen bond that locks the remaining C(15)—C(14)—C(17) into a boatlike conformation. A similar hydrogen bond of one independent molecule of **10** was refined from a Fourier difference map, which also forms a boat-like conformation with the O(3)—C(11)—C(12)—C(14)—O(4) atoms. These structural features help one to understand the stereochemical course of the reaction. In aldol reactions, metal ions such as Li^+, Mg^{2+}, and B^{3+} are commonly used to improve diastereoselectivities[18] because they tend to form a cyclic transition-state structure. Once Li^+ replaces H^+, and a cyclic transition structure in either the boat or chair form, represented by structure **G** (Scheme 3), is generated[18] that has two mutually trans R and S (S = CHMePh) substituents to minimize steric hindrance, selectively generating products **10**.

The ketone groups of **10** and **12** were reducible with DIBAL-H, of which 4–5-fold molar proportions were required to ensure complete reaction. Here the hydride attacked at the ketone group opposite the metal fragment to give **14** and **15** as only one diastereomer, and the yields exceeded 80% after purification with silica column chromatography. In contrast to **14**, compound **15** exists as two conformers, endo and exo forms (endo/exo = 1/2), which were readily distinguished by their distinct NMR chemical shifts of the two anti allyl H^1 and H^4 protons.[19,20] The crystal structures of **1**, **5E**, **10**, and **12** are examples of exo conformers; i.e. the allyl mouth faces away from the CpMo(CO)$_2$ fragment. Further treatment of **14** and **15** with $NOBF_4$ generated an electrophilic allyl cation[21,22] that in the presence of Na_2CO_3 underwent intramolecular cyclization,[23,24] finally liberating tetrasubstituted tetrahy-

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(19) Davison, A.; Rode, W. C. *Inorg. Chem.* **1967**, *6*, 2125.
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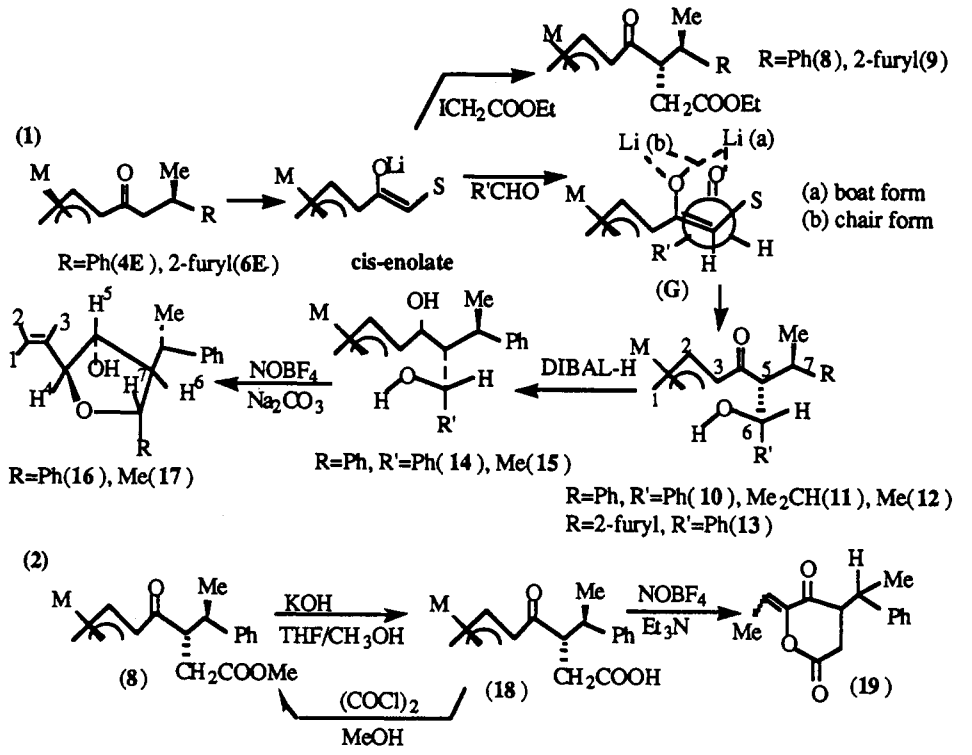
Scheme 3 [a]



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

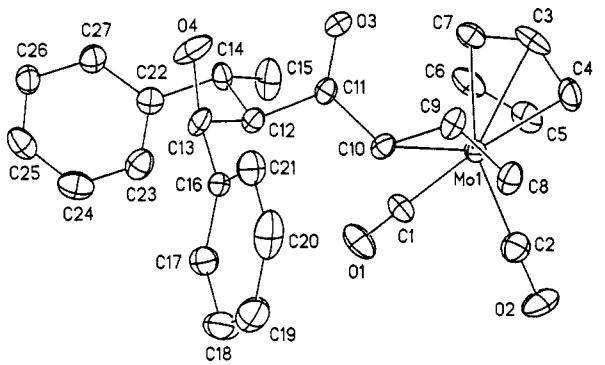


Figure 3. ORTEP drawing of one independent molecule of **10**.

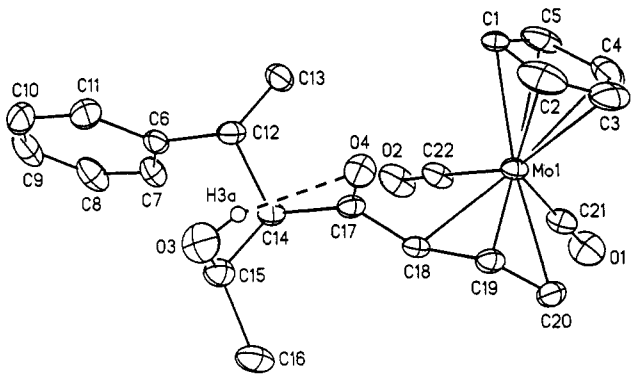


Figure 4. ORTEP drawing of one independent molecule of **12**.

drofuran compounds **16** and **17** in 50–55% yield after demetalation by air oxidation. The specific proton positions of the ring were determined by proton NOE-difference spectra. In the case of **17**, irradiation of the H^3 proton signal (δ 5.92 ppm) led to intensities of the H^7 (δ 4.68 ppm) and H^5 (δ 4.04 ppm) signals increased by 3.9% and 3.6%, respectively. Likewise irradiation of the H^7 proton caused an increased signals of the CH*Me*Ph proton (δ 2.74) by 1.8%. These results indicate an all cis relationship between the CH_2=CH, H^5, H^7, and CHMePh groups. Formation of **16** and **17** proceeds evidently via intramolecular attack of the C(Ph)HO$^-$ terminus at the molybdenum–π-allyl moiety opposite the metal fragment.

Stirring of **8** with KOH in THF/CH_3OH at 23 °C for 5 h produced its acidic form **18** in 93% yield after workup. To assure that the new product has the same configuration in the COC^5H carbon as **8**, we succeeded in reconverting **18** to **8** with oxalyl chloride and methanol in 70% yield.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of One Independent Molecule of 10

Mo(1)–C(1)	1.942(10)	Mo(1)–C(2)	1.957(9)
Mo(1)–C(8)	2.341(8)	Mo(1)–C(9)	2.215(7)
Mo(1)–C(10)	2.347(7)	O(1)–C(1)	1.159(12)
O(2)–C(2)	1.140(11)	O(3)–C(11)	1.225(9)
O(4)–C(13)	1.399(9)	C(8)–C(9)	1.389(10)
C(9)–C(10)	1.412(12)	C(10)–C(11)	1.468(9)
C(11)–C(12)	1.517(11)	C(12)–C(13)	1.556(9)
C(12)–C(14)	1.546(10)	C(13)–C(16)	1.511(9)
C(14)–C(15)	1.528(11)	C(14)–C(22)	1.523(14)
C(1)–Mo(1)–C(2)	77.3(4)	C(1)–Mo(1)–C(8)	115.2(3)
C(2)–Mo(1)–C(8)	73.6(3)	C(2)–Mo(1)–C(9)	105.9(3)
C(1)–Mo(1)–C(10)	75.4(3)	C(2)–Mo(1)–C(10)	108.9(3)
C(8)–Mo(1)–C(10)	62.2(3)	C(9)–Mo(1)–C(10)	35.9(3)
Mo(1)–C(1)–O(1)	178.5(7)	Mo(1)–C(2)–O(2)	176.4(8)
Mo(1)–C(8)–C(9)	67.3(4)	Mo(1)–C(9)–C(8)	77.3(4)
Mo(1)–C(9)–C(10)	77.2(4)	C(8)–C(9)–C(10)	119.6(7)
Mo(1)–C(10)–C(9)	66.9(4)	Mo(1)–C(10)–C(11)	115.3(4)
C(9)–C(10)–C(11)	121.2(7)	O(3)–C(11)–C(10)	122.1(7)
O(3)–C(11)–C(12)	120.3(6)	C(10)–C(11)–C(12)	117.7(6)
C(11)–C(12)–C(13)	109.2(6)	C(11)–C(12)–C(14)	111.5(6)
C(13)–C(12)–C(14)	111.7(5)	O(4)–C(13)–C(12)	113.4(6)
O(4)–C(13)–C(16)	108.4(6)	C(12)–C(13)–C(16)	113.7(5)
C(12)–C(14)–C(15)	111.6(6)	C(15)–C(14)–C(22)	110.5(7)
C(13)–C(16)–C(21)	122.9(7)		

(24) Pearson, A. J.; Khan, Md. N. I. *J. Am. Chem. Soc.* 1984, *106*, 1872.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of One Independent Molecule of 12

Mo(1)–C(18)	2.342(6)	Mo(1)–C(19)	2.209(7)
Mo(1)–C(20)	2.339(7)	Mo(1)–C(21)	1.946(7)
Mo(1)–C(22)	1.961(6)	O(1)–C(21)	1.140(9)
O(2)–C(22)	1.148(8)	O(3)–C(15)	1.421(8)
O(4)–C(17)	1.218(7)	C(6)–C(12)	1.503(8)
C(12)–C(13)	1.503(10)	C(12)–C(14)	1.555(9)
C(14)–C(15)	1.538(10)	C(14)–C(17)	1.518(7)
C(15)–C(16)	1.513(10)	C(17)–C(18)	1.485(7)
C(18)–C(19)	1.408(7)	C(19)–C(20)	1.420(8)
C(2)–Mo(1)–C(4)	54.9(4)	C(18)–Mo(1)–C(21)	110.7(3)
C(20)–Mo(1)–C(21)	71.7(3)	C(18)–Mo(1)–C(22)	74.7(3)
C(20)–Mo(1)–C(22)	111.9(3)	C(21)–Mo(1)–C(22)	77.5(3)
C(6)–C(12)–C(13)	109.2(5)	C(6)–C(12)–C(14)	112.1(6)
C(13)–C(12)–C(14)	113.4(5)	C(12)–C(14)–C(15)	111.4(4)
C(12)–C(14)–C(17)	112.2(5)	C(15)–C(14)–C(17)	107.7(5)
O(3)–C(15)–C(14)	112.0(6)	O(3)–C(15)–C(16)	110.2(6)
C(14)–C(15)–C(16)	112.5(5)	O(4)–C(17)–C(14)	120.2(5)
O(4)–C(17)–C(18)	121.8(5)	C(14)–C(17)–C(18)	117.9(5)
Mo(1)–C(18)–C(17)	117.4(5)	Mo(1)–C(18)–C(19)	66.9(3)
C(17)–C(18)–C(19)	119.0(5)	Mo(1)–C(19)–C(20)	76.9(4)
C(18)–C(19)–C(20)	119.4(6)	Mo(1)–C(20)–C(19)	66.9(4)
Mo(1)–C(21)–O(1)	177.9(7)	Mo(1)–C(22)–O(2)	178.3(6)

Further treatment of **18** with $NOBF_4$, followed by addition of Et_3N, likewise induced intramolecular cyclization that after air oxidation liberated organic δ-valerolactone compound **19** as a 5/1 mixture of two diastereomers (56% yields). We were unable to determine the specific configuration of **19** because of possible epimerization at the COC^5H carbon by Na_2CO_3.

In conclusion, this work shows the diastereofacial Michael reactions of organocopper reagents to molybdenum–π-1-*trans*-enone allyl compounds, and the cis-enolates of the resulting major diastereomeric products were selectively generated by $LiN(SiMe_3)_2$ which provides a stereocontrolled carbon–carbon bond formation reaction through alkylation and aldol reaction. Utilization of these enolates for stereoselective synthesis of highly substituted furans was achieved.

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 was dried over calcium hydride and distilled. Compounds **1–3** were prepared according to the procedures in the literature.[15,16]

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

(a) (i) Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)-((3*R,6*R**)-(1,2,3-η)-*syn*-4-oxo-6-phenyl-2-hepten-1-yl)molybdenum (4E) and Its 3*R**,6*S** Epimer (4F).** To a diethyl ether solution (40 mL) of CuI (0.60 g, 3.15 mmol) was added a hexane solution of MeLi (4 mL, 1.5 M, 6.0 mmol) at −40 °C, and the mixtures were stirred to 30 min before a diethyl ether solution (10 mL) of **1** (0.29 g, 0.75 mmol) was slowly added. After stirring for 6 h at −40 °C, the solution was slowly brought to 0 °C before a saturated NH_4Cl solution (10 mL) was added; the organic layer was extracted with ether (2 × 30 mL). The ether extract was washed with water (10 mL), dried with $MgSO_4$, and finally eluted through a short silica column with hexane/ether = 3/1 as the eluting solvent, which developed a yellow band of **4E** and **4F** (0.22 g, 0.49 mmol, 65%) consisting of a ratio of **4E**/**4F** = 4/1. Further elution of the mixture through a long silica column with hexane/ether = 3/1 produced two yellow bands (R_f = 0.29 for **4E**, R_f = 0.34 for **4F**) that gave **4E** (0.150 g, 0.34 mmol, 45%) and **4F** (0.030 g, 0.076 mmol, 10%) as yellow crystalline solids. IR (Nujol): ν(CO) 1951 (s), 1872 (s), 1665 (s) cm^{-1}. ^1H NMR (400 MHz, δ, $CDCl_3$): (**4E**) 7.30–7.15 (5H, Ph, m), 5.22 (5H, Cp, s), 4.99 (1H, H^3, ddd, *J* 10.9, 9.5, 7.5 Hz), 3.34 (1H, H^7, m), 2.97 (1H, H^2, d, *J* 7.5 Hz), 2.82 (1H, H^5, dd, *J* 16.2, 6.0 Hz), 2.76 (1H, H^6, dd, *J* 16.2, 8.5 Hz), 1.80 (1H, H^4, d, *J* 9.5 Hz), 1.28 (3H, Me, d, *J* 6.9 Hz), 1.23 (1H, H^1, d, *J* 10.9 Hz); (**4F**) 7.30–7.15 (5H, Ph, m), 4.92 (1H, H^3, ddd, *J* 10.6, 9.5, 7.5 Hz), 4.83 (5H, Cp, s), 3.36 (1H, H^7, m), 2.92–2.72 (3H, H^2 + H^5 + H^6, m), 1.84 (1H, H^4, d, *J* 9.5 Hz), 1.27–1.23 (4H, Me + H^1, m). ^{13}C NMR (100 MHz, δ, $CDCl_3$): (**4E**) 239.2, 236.5, 205.5, 146.3, 128.4, 126.8, 126.1, 93.7, 71.1, 56.2, 50.6, 39.9, 35.4, 21.5. Mass (75 eV, *m*/*z*): 406 (M^+), 378 (M^+ − CO), 350 (M^+ − 2CO). Anal. Calcd for $C_{20}H_{20}O_3Mo$: C, 59.41; H, 4.99. Found: C, 59.06; H, 5.00.

(ii) In the Presence of BF_3·Et_2O. This procedure was analogous to that in section (a)(i) except that compound **1** (0.30 g, 0.77 mmol) was mixed with BF_3·Et_2O (0.11 g, 0.75 mmol) before addition to the ether solution of Me_2CuLi (3.10 mmol). The combined yields (0.28 g, 0.69 mmol) of **4E** and **4F** were 90% with **4E**/**4F** = 14/1 after elution through a short silica column. Further elution through a long silica column afforded **4E** (0.24 g, 0.60 mmol, 78%) and **4F** (9.4 mg, 0.023 mmol, 3%) as yellow solids.

(b) (i) Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)-((3*R,6*S**)-(1,2,3-η)-*syn*-4-oxo-6-phenyl-2,7-octadien-1-yl)molybdenum (5E) and Its 3*R**,6*R** Epimer (5F).** Synthesis of this compound was similar to those of **4E** and **4F** as described in section (a)(i) except that **1** (0.30 g, 0.77 mmol) and $(C_2H_3)_2$-CuLi (3.15 mmol) were used, and the combined yields (0.23 g, 0.54 mmol) were 70% with **5E**/**5F** = 6/1 after elution through a short silica column. Attempts to separate the two diastereomers on a long silica column were unsuccessful. Cooling the mixtures in a saturated ether/hexane solution at −30 °C produced orange crystals of **5E** in an overall yield of 55% (0.175 g, 0.42 mmol). IR (Nujol): ν(CO) 1953 (s), 1873 (s), 1665 (s) cm^{-1}. ^1H NMR (400 MHz, δ, $CDCl_3$): (**5E**) 7.29–7.18 (5H, Ph, m), 6.01 (1H, CH=, ddd, *J* 17.1, 11.3, 7.2 Hz), 5.21 (5H, Cp, s), 5.13–5.07 (2H, CH_2=, m), 4.98 (1H, H^3, ddd, *J* 10.9, 9.3, 7.8 Hz), 3.99 (1H, H^7, m), 3.03 (1H, H^5, dd, *J* 16.3, 8.7 Hz), 2.99 (1H, H^2, d, *J* 7.8 Hz), 2.87 (1H, H^6, dd, *J* 16.3, 5.8 Hz), 1.81 (1H, H^4, d, *J* 9.3 Hz), 1.24 (1H, H^1, d, *J* 10.9 Hz); (**5F**) 7.29–7.18 (5H, Ph, m), 5.89 (1H, CH=, ddd, *J* 16.8, 11.3, 7.2 Hz), 5.12 (5H, Cp, s), 5.00 (1H, H^3, ddd, *J* 11.2, 9.2, 7.8 Hz), 4.00 (1H, H^7, m), 3.04–2.98 (3H, H^2 + H^6 + H^5, m), 1.82 (1H, H^4, d, *J* 9.2 Hz), 1.23 (1H, H^1, d, *J* 11.2 Hz). ^{13}C NMR (100 MHz, δ, $CDCl_3$): (**5E**) 239.1, 236.6, 203.8, 156.0, 141.3, 138.0, 116.1, 110.1, 105.0, 93.7, 71.0, 55.7, 45.2, 40.1, 38.3. Mass (75 eV, *m*/*z*) 418 (M^+). Anal. Calcd for $C_{21}H_{20}O_3Mo$: C, 60.58; H, 4.84. Found: C, 60.72; H, 4.78.

(ii) In the Presence of BF_3·Et_2O. This procedure was analogous to that in section (b)(i) except that compound **1** (0.30 g, 0.77 mmol) was first mixed with BF_3·Et_2O (0.11 g, 0.75 mmol) before addition of $(C_2H_3)_2CuLi$ (3.16 mmol) in ether (15 mL, −40 °C). The combined yields (0.28 g, 0.68 mmol) were 88% with **5E**/**5F** > 20/1 after elution through a short silica column. Recrystallization of the mixtures in a saturated ether/hexane solution at −30 °C gave **5E** in 64% yield (0.20 g, 0.49 mmol) as a yellow solid.

(c) (i) Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)-((3*R,6*R**)-(1,2,3-η)-*syn*-6-(2′-furyl)-4-oxo-2-hepten-1-yl)molybdenum (6E) and Its 3*R**,6*S** Epimer (6F).** Synthesis of this compound was similar to those of **4E** and **4F** as described in section (a)(i) except that **2** (0.30 g, 0.78 mmol) and Me_2CuLi (3.20 mmol) were used; the combined yields (0.27 g, 0.62 mmol) were 80% with **6E**/**6F** = 6/1 after elution through a short silica column (ether/hexane = 1/3). Further separation of **6E** and **6F** was achieved by elution through a long silica column (ether/hexane = 1/3) which produced two yellow bands of **6E** (R_f = 0.28) and **6F** (R_f = 0.33) to give yellow solids **6E** (0.16 g, 0.40 mmol, 52%) and **6F** (0.021 g, 0.055 mmol, 7% yield). IR (Nujol): ν(CO) 1953 (s), 1873 (s), 1665 (s) cm^{-1}. ^1H NMR (400 MHz, δ, $CDCl_3$): (**6E**) 7.28 (1H, C_4H_3O, d, *J* 1.0 Hz), 6.25 (1H, d, C_4H_3O, d, *J* 2.8

Hz), 5.98 (1H, C_4H_3O, dd, *J* 2.8, 1.0 Hz), 5.24 (5H, Cp, s), 5.02 (1H, H^3, ddd, *J* 10.6, 9.3, 7.2 H), 3.42 (1H, H^7, m), 2.99 (1H, H^2, d, *J* 7.2 Hz), 2.92 (1H, H^5, dd, *J* 16.5, 5.4 Hz), 2.67 (1H, H^6, dd, *J* 16.5, 8.6 Hz), 1.80 (1H, H^4, d, *J* 9.3 Hz), 1.28–1.22 (4H, H^1 + Me, m); (**6F**) 7.31 (1H, C_4H_3O, t *J* 1.0 Hz), 6.25 (1H, d, C_4H_3O, *J* 2.8 Hz), 6.01 (1H, C_4H_3O, dd, *J* 2.8, 1.0 Hz), 5.12 (5H, Cp, s), 4.98 (1H, H^3, ddd, *J* 10.6, 9.3, 7.2 H), 3.45 (1H, H^7, m), 3.02–2.93 (2H, H^2 + H^5, m), 2.62 (1H, H^6, dd, *J* 16.6, 5.0 Hz), 1.86 (1H, H^4, d, *J* 9.3 Hz), 1.28–1.22 (4H, H^1 + Me, m). ^{13}C NMR (100 MHz, δ, $CDCl_3$): (**6E**) 239.6, 237.2, 205.6, 159.1, 141.1, 110.1, 103.8, 93.8, 71.2, 56.0, 47.7, 39.7, 28.8, 18.5; (**6F**) 238.9, 237.0, 205.0, 159.3, 140.9, 110.0, 103.9, 93.8, 70.9, 55.6, 47.7, 40.3, 28.8, 19.6. Mass (75 eV, *m/z*): 396 (M^+), 368 (M^+ – CO), 340 (M^+ – 2CO). Anal. Calcd for $C_{18}H_{18}O_4Mo$: C, 54.83; H, 4.60. Found: C, 54.75; H, 4.56.

(ii) In the Presence of BF_3·Et_2O. This procedure was analogous to that in section (i) except that compound **2** (0.30 g, 0.78 mmol) was first mixed with BF_3·Et_2O (0.11 g, 0.75 mmol) before addition of Me_2CuLi (3.20 mmol) in ether (10 mL, –40 °C). The combined yields (0.27 g, 0.68 mmol) were 88% with **6E**/**6F** = 16/1 after elution through a short silica column (ether/hexane = 1/3). Separation of the two diastereomers was conducted on a long silica column (ether/hexane = 1/3) that gave **6E** (0.23 g, 0.59 mmol, 75%) and **6F** (9.2 mg, 0.023 mmol, 3%) as a yellow solid.

(d) (i) Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)-((3*R,6*S**)-(1,2,3-η)-*syn*-6-(2′-furyl)-4-oxo-2,7-octadien-1-yl)-molybdenum (7E) and Its 3*R**,6*S** Epimer (7F).** Synthesis of this compound was similar to those of **4E** and **4F** as described in section (a)(i) except that **2** (0.30 g, 0.78 mmol) and $(C_2H_3)_2$-CuLi (3.20 mmol) were used; and the combined yields (0.23 g, 0.57 mmol) were 74% with **7E**/**7F** = 5/1 after elution through a short silica column. Separation of the two diastereomers by a long silica column was unsuccessful. Cooling the mixtures in a saturated ether/hexane solution at –30 °C for 2 days produced orange crystals of **7E** (0.16 g, 0.39 mmol) in 50% overall yield. IR (Nujol): ν(CO) 1954 (s), 1872 (s), 1666 (s) cm^{-1}. ^1H NMR (400 MHz, δ, $CDCl_3$): (**7E**) 7.25 (1H, C_4H_3O, d, *J* 1.4 Hz), 6.21 (1H, d, C_4H_3O, *J* 2.8 Hz), 5.97 (1H, C_4H_3O, dd, *J* 2.8, 1.4 Hz), 5.86 (1H, CH=, ddd, *J* 17.2, 9.9, 7.2 Hz), 5.16 (5H, Cp, s), 5.12–5.07 (2H, CH_2=, m), 4.95 (1H, H^3, ddd, *J* 11.3, 9.6, 7.4 Hz), 4.01 (1H, H^7, ddd, *J* 8.6, 7.5, 4.2 Hz), 2.96–2.82 (3H, H^2 + H^5 + H^6, m), 1.80 (1H, H^4, d, *J* 9.6 Hz), 1.22 (1H, H^1, d, *J* 11.3 Hz); (**7F**) 7.20 (1H, C_4H_3O, d, *J* 1.4 Hz), 6.20 (1H, d, C_4H_3O, *J* 2.8 Hz), 5.97 (1H, C_4H_3O, dd, *J* 2.8, 1.4 Hz), 5.77 (1H, CH=, ddd, *J* 17.2, 9.9, 7.2 Hz), 5.12 (1H, CH_2=, d, *J* 17.2 Hz), 5.08 (5H, Cp, s), 4.98 (1H, CH_2=, d, *J* 9.9 Hz), 4.88 (1H, H^3, ddd, *J* 11.3, 9.2, 7.8 Hz), 3.99 (1H, H^7, m), 2.84 (1H, H^6, dd, *J* 16.8, 7.6 Hz), 2.78–2.73 (2H, H^5 + H^2, m), 1.75 (1H, H^4, d, *J* 9.2 Hz), 1.20 (1H, H^1, d, *J* 11.3 Hz). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 239.1, 236.5, 203.8, 156.0, 141.3, 138.0, 116.1, 110.1, 105.0, 93.7, 71.0, 55.7, 45.2, 40.1, 38.3. Mass (75 eV, *m/z*): 408 (M^+), 380 (M^+ – CO), 352 (M^+ – 2CO). Anal. Calcd for $C_{19}H_{18}O_4Mo$: C, 56.17; H, 4.47. Found: C, 56.30; H, 4.70.

(ii) In the Presence of BF_3·Et_2O. This procedure was analogous to that in section (i) except that compound **2** (0.30 g, 0.78 mmol) was mixed with BF_3·Et_2O (0.11 g, 0.75 mmol) before addition of $(C_2H_3)_2CuLi$ (3.4 mmol) in ether (10 mL, –40 °C). The combined yields (0.27 g, 0.66 mmol) were 85% with **7E**/**7F** > 20/1 after elution through a short silica column (ether/hexane = 1/3). Recrystallization of the mixtures from a saturated ether/hexane solution at –30 °C for 2 days gave **7E** (0.25 g, 0.61 mmol, 78%) as a yellow solid.

(e) (i) Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)-((3*R,6*S**)-(1,2,3-η)-*syn*-4-oxo-6-phenyl-2-hepten-1-yl)molybdenum (4E* = 4F) and Its 3*R**,6*S** Epimer (4F* = 4E).** Synthesis of this compound was similar to those of **4E** and **4F** as described in section (a)(i) except that **3** (0.30 g, 0.92 mmol) and Ph_2CuLi (3.90 mmol) were used, and the combined yields (0.28 g, 0.68 mmol) were 74% with **4E***/**4F*** = 2.5/1. Separation of these two products was identical to those of **4E** and **4F** (section (a)(i)); the isolated yields of **4E*** (0.178 g, 0.44 mmol) and **4F*** (0.056 g, 0.14 mmol) were 48% and 16%, respectively. Spectral data for **4E*** and **4F*** are identical to those of **4F** and **4E**, respectively.

(ii) In the Presence of BF_3·Et_2O. This procedure was analogous to that in section (e)(i) except that compound **3** (0.30 g, 0.92 mmol) was first mixed with BF_3·Et_2O (0.13 g, 0.92 mmol) before addition to $(C_2H_3)_2CuLi$ (4.0 mmol) in ether (10 mL, –40 °C). The combined yields (0.33 g, 0.81 mmol) were 88% with **4E***/**4F*** = 14/1 after elution through a short silica column (ether/hexane = 1/3). Further elution through a long silica column (ether/hexane = 1/3) gave **4E*** (0.26 g, 0.64 mmol, 70%) and **4F*** (11 mg, 0.028 mmol, 3%) as yellow solids.

(f) Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)-((3*R,5*S**,6*R**)-(1,2,3-η)-*syn*-5-[(methoxycarbonyl)methyl]-4-oxo-6-phenyl-2-hepten-1-yl)molybdenum (8).** BuLi (1.7M, 4.7 mL, 7.2 mmol) was slowly added to a THF solution (5 mL) of $(Me_3Si)_2NH$ (1.20 g, 7.43 mmol) at –78 °C and the mixture was stirred for 30 min before the temperature was raised to 23 °C. Transfer of this solution to **4E** (1.50 g, 3.71 mmol) in THF (5 mL) at –40 °C produced a slightly red color; after stirring for 5 h, ethyl iodoacetate (0.80 g, 3.74 mmol) was added. After stirring for 1 h, the solution was treated with a saturated NH_4Cl solution (15 mL) with stirring for a further 20 min. The organic layer was extracted with ether (2 × 20 mL), filtered, and dried with $MgSO_4$. Elution through a silica column with ether/hexane (1/2) produced a yellow band of **8** (1.20 g, 2.45 mmol, 66%) as a yellow crystalline solid. IR (Nujol): ν(CO) 1953 (s), 1875 (s), 1731 (s), 1664 (s) cm^{-1}. ^1H NMR (400 MHz, δ, $CDCl_3$): 7.26–7.12 (5H, Ph, m), 5.24 (5H, s Cp), 5.02 (1H, H^3, ddd, *J* 11.0, 9.5, 6.8 Hz), 3.86 (2H, OCH_2, q, *J* 6.9 Hz), 3.20 (1H, COCH, m), 2.98 (1H, C*H*Me, dq, *J* 10.4, 6.9 Hz), 2.95 (1H, H^2, d, *J* 6.8 Hz), 2.31 (1H, COC*H*H′, dd, *J* 16.1, 8.8 Hz), 2.18 (1H, COC*H*H′, *J* 16.1, 4.6 Hz), 1.97 (1H, H^4, *J* 9.5 Hz), 1.27 (1H, H^1, d, *J* 11.0 Hz), 1.24 (3H, Me, d, *J* 6.9 Hz), 1.07 (3H, Me, d, *J* 7.3). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 239.1, 236.7, 205.5, 173.4, 144.4, 136.5, 128.6, 127.6, 127.3, 126.5, 126.4, 117.2, 85.9, 83.4, 80.0, 61.2, 41.3, 19.1. Mass (75 eV, *m/z*) 492 (M^+). Anal. Calcd for $C_{24}H_{26}MoO_5$: C, 58.78; H, 5.34. Found: C, 58.70; H, 5.36.

(g) Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)-((3*R,5*S**,6*R**)-(1,2,3-η)-*syn*-6-furyl-5-[(methoxycarbonyl)-methyl]-4-oxo-2-hepten-1-yl)molybdenum (9).** This compound was similarly prepared from the enolate of **6E** (3.70 mmol) and ICH_2COOMe (0.80 g, 3.74 mmol) according to the procedure in (f), and the yield of **9** (1.51 g, 3.14 mmol) was 84%. IR (Nujol): ν(CO) 1954 (s), 1875 (s), 1730 (s), 1685 (s) cm^{-1}. ^1H NMR (400 MHz, δ, $CDCl_3$): 7.28 (1H, C_3H_3O, d, *J* 1.0 Hz), 6.24 (1H, C_3H_3O, dd, *J* 2.8, 1.0 Hz), 6.03 (1H, C_3H_3O, d, *J* 2.8 Hz), 5.25 (5H, Cp, s), 5.02 (1H, H^3, ddd, *J* 11.0, 9.4, 7.4 Hz), 3.97 (2H, OCH_2, q, *J* 7.0 Hz), 3.32 (1H, C*H*Me, dq, *J* 8.1, 7.0 Hz), 3.23 (1H, COC*H*, ddd, *J* 8.6, 8.1, 4.6 Hz), 3.00 (1H, H^2, d, *J* 7.4 Hz), 2.45 (1H, COCH*H*, dd, *J* 16.4, 8.6 Hz), 2.31 (1H, CO*H*H′, *J* 16.4, 4.6 Hz), 1.97 (1H, H^4, d, *J* 9.4 Hz), 1.28 (3H, Me, d, *J* 7.0 Hz), 1.20–1.12 (4H, Me+H^1, m). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 239.1, 236.7, 208.4, 171.7, 156.7, 141.1, 109.9, 106.0, 93.8, 73.1, 60.5, 55.7, 52.6, 39.9, 35.2, 34.2, 18.4, 14.0. Mass (75 eV, *m/z*): 482 (M^+). Anal. Calcd for $C_{22}H_{24}MoO_6$: C, 55.01; H, 5.04. Found: C, 55.17; H, 5.20.

(h) Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)-((3*R,5*R**,6*R**,1′*R**)-(1,2,3-η)-*syn*-5-(1-hydroxybenzyl)-4-oxo-6-phenyl-2-hepten-1-yl)molybdenum (10).** To the enolate generated in section (f) were slowly added **4E** (0.25 g, 0.62 mmol), $HN(SiMe_3)_2$ (0.40 g, 1.90 mmol), BuLi (1.7 M, 1.1 mL, 1.9 mmol), and THF (10 mL) with PhCHO (0.18 g, 1.70 mmol) at –40 °C, and the mixtures were stirred for 4 h at this temperature before addition of a saturated NH_4Cl solution. The organic layer was extracted with diethyl ether (2 × 10 mL), dried with $MgSO_4$, and evaporated to dryness. Elution through a silica column with ether/hexane (1/2) produced on orange band that gave **10** (0.25 g, 0.49 mmol, 79%) as an orange solid. IR (Nujol): ν(CO) 1951 (vs), 1873 (vs), 1647 (s) cm^{-1}. ^1H NMR (400 MHz, δ, $CDCl_3$): 7.33–7.01 (10H, Ph, m), 5.19 (5H, Cp, s), 4.75 (1H, H^3, ddd, *J* 11.2, 9.4, 7.0 Hz), 4.41 (1H, CHPh, d, *J* 2.6 Hz), 3.41 (1H, CHMe,

m), 3.16 (1H, s, OH), 3.07 (1H, COCH, dd, *J* 11.3, 2.6 Hz), 2.69 (1H, H^2, d, *J* 7.0 Hz), 1.25 (3H, Me, d, *J* 6.9 Hz), 0.79 (1H, H^1, d, *J* 11.2 Hz), 0.74 (1H, H^4, d, *J* 9.4 Hz). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 239.9, 236.9, 211.7, 144.6, 143.1, 128.9, 128.2, 127.9, 127.1, 126.8, 125.1, 93.9, 72.3, 72.0, 66.1, 59.1, 39.0, 38.5, 20.5. Mass (12 eV, *m/z*): −512 (M$^+$). Anal. Calcd for $C_{27}H_{26}MoO_4$: C, 63.53; H, 5.13. Found: C, 63.40; H, 5.14.

(i) Synthesis of Dicarbonyl(η^5-cyclopentadienyl)-((3*R,5*R**,6*R**,1′*R**)-(1,2,3-η)-*syn*-5-(1′-hydroxyisobutyl)-4-oxo-6-phenyl-2-hepten-1-yl)molybdenum (11).** Synthesis of this compound followed the procedure described in section (h) [**4E** (0.25 g, 0.62 mmol), $HN(SiMe_3)_2$ (0.40 g, 1.90 mmol), BuLi (1.7 M, 1.1 mL, 1.9 mmol), THF (10 mL)] except that isobutyraldehyde (0.130 g, 1.80 mmol) was used; an orange crystalline solid **11** (0.21 g, 0.44 mmol) was obtained in 71% yield. IR (Nujol): ν(CO) 1953 (vs), 1878 (vs), 1642 (vs) cm^{-1}. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.32–7.20 (5H, Ph, m), 5.32 (5H, Cp, s), 5.12 (1H, H^3, ddd, *J* 11.0, 9.4, 7.7 Hz), 3.36 (1H, CHPh, dq, *J* 11.0, 7.0 Hz), 3.13 (1H, COC*H*, dd, *J* 11.0, 2.1 Hz), 3.03 (1H, H^2, *J* 7.7 Hz), 2.65 (1H, OH, s), 2.45 (1H, CH(OH), dd, *J* 7.0, 2.1 Hz), 1.89 (1H, H^4, d, *J* 9.4 Hz), 1.58 (1H, m, $CHMe_2$), 1.36 (1H, H^1, d, *J* 11.0 Hz), 1.29 (3H, d, *J* 7.0 Hz), 0.84 (3H, Me, d, *J* 6.3 Hz), 0.72 (3H, Me, d, *J* 6.6 Hz). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 236.5, 232.7, 211.9, 144.8, 128.7, 127.7, 126.5, 94.2, 77.3, 73.3, 59.7, 59.2, 39.7, 39.3, 32.8, 21.1, 19.6. Mass (75 eV, *m/z*): 478 (M$^+$). Anal. Calcd for $C_{24}H_{28}MoO_4$: C, 60.51; H, 5.92. Found: C, 60.44; H, 6.15.

(j) Synthesis of Dicarbonyl(η^5-cyclopentadienyl)-((3*R,5*R**,6*R**,1′*R**)-(1,2,3-η)-*syn*-5-(1′-hydroxyethyl)-4-oxo-6-phenyl-2-hepten-1-yl)molybdenum (12).** Synthesis of this compound followed the procedure described in section (h) except that acetaldehyde was used; orange crystalline solid **12** was obtained in yield 81%. IR (Nujol): ν(CO) 1953 (vs), 1876 (vs), 1646 (s) cm^{-1}. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.32–7.20 (5H, Ph, m), 5.32 (5H, Cp, s), 5.12 (1H, H^3, ddd, *J* 11.4, 9.4, 7.6 Hz), 3.47 (1H, C*H*Me, dq, *J* 6.5, 2.4 Hz), 3.35 (1H, C*H*Ph, dq, *J* 11.1, 7.0 Hz), 3.02 (1H, H^2, d, *J* 7.6 Hz), 2.84 (1H, COC*H*, dd, *J* 11.1, 2.4 Hz), 2.35 (1H, OH, s), 1.88 (1H, H^4, d, *J* 9.4 Hz), 1.36 (1H, H^1, d, *J* 11.4 Hz), 1.28 (3H, Me, d, *J* 7.0 Hz), 1.13 (3H, Me, d, *J* 6.5 Hz). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 240.1, 236.9, 212.2, 144.9, 128.7, 127.8, 126.6, 94.1, 72.5, 66.7, 64.1, 59.7, 39.4, 38.3, 22.8, 20.5. Mass (75 eV, *m/z*): 450 (M$^+$). Anal. Calcd for $C_{22}H_{24}MoO_4$: C, 58.93; H, 5.40. Found: C, 58.94; H, 5.41.

(k) Synthesis of Dicarbonyl(η^5-cyclopentadienyl)-((3*R,5*R**,6*R**,1′*R**)-(1,2,3-η)-*syn*-6-(2′-furyl)-5-(1′-hydroxybenzyl)-4-oxo-2-hepten-1-yl)molybdenum (13).** This compound was similarly prepared from the enolate of **6E** and PhCHO according to the procedure of section (h); a dark orange crystalline solid **13** was obtained in yield 75%. IR (Nujol): ν(CO) 1953 (s), 1874 (s), 1651 (s) cm^{-1}. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.36 (1H, C_3H_3O, s), 7.16–7.07 (5H, Ph, m), 6.27 (1H, C_3H_3O, d, *J* 3.1 Hz), 6.18 (1H, C_3H_3O, d, *J* 3.1 Hz), 5.18 (5H, Cp, s), 4.75 (1H, H^3, ddd, *J* 11.0, 9.4, 7.4 Hz), 4.53 (1H, CHPh, d, *J* 2.9 Hz), 3.55 (1H, CHMe, dq, *J* 10.5, 7.2 Hz), 3.15 (1H, COCH, dd, *J* 10.5, 2.9 Hz), 2.70 (1H, H^2, d, *J* 7.4 Hz), 1.24 (3H, Me, d, *J* 7.2 Hz), 0.79 (1H, H^1, d, *J* 11.0 Hz), 0.77 (1H, H^4, d, *J* 9.4 Hz). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 238.7, 236.4, 210.1, 157.1, 142.5, 141.4, 128.0, 127.0, 125.1, 110.1, 106.2, 93.8, 72.9, 64.1, 58.9, 58.4, 39.3, 32.5, 18.3. Mass (12 eV, *m/z*): 502 (M$^+$). Anal. Calcd for $C_{25}H_{24}MoO_5$: C, 60.01; H, 4.83. Found: C, 59.71; H, 4.86.

(l) Synthesis of Dicarbonyl(η^5-cyclopentadienyl)-((3*R,4*S**,5*R**,6*R**,1′*R**)-(1,2,3-η)-*syn*-4-hydroxy-5-(1′-hydroxybenzyl)-6-phenyl-2-hepten-1-yl)molybdenum (14).** To compound **10** (180 mg, 0.35 mmol) in diethyl ether (20 mL) was added a hexane solution of DIBAL-H (1.0 M, 1.6 mL, 1.6 mmol) at 0 °C, and the solution first turned from yellow into red and finally back to yellow. After stirring for 4 h, the solution was quenched with a saturated NH_4Cl solution (5 mL), and the organic layer was extracted with diethyl ether (2 × 10 mL), dried over $MgSO_4$, and concentrated. Elution of the residues through a silica column (ether/hexane = 1/2) produced a yellow band that gave **14** as a yellow oil (0.154 g, 0.30 mmol). IR (Nujol): ν(CO) 1943 (vs), 1860 (vs) cm^{-1}. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.36–7.21 (6H, Ph, m), 5.05 (5H, Cp, s), 4.61 (1H, C*H*Ph(OH), d, *J* 1.0 Hz), 3.64 (1H, C*H*(OH), d, *J* 9.4 Hz), 3.47 (1H, C*H*Me, m), 3.34 (1H, H^3, ddd, *J* 10.3, 9.4, 7.2 Hz), 2.55 (1H, H^2, d, *J* 7.2 Hz), 2.31 (1H, C*H*CHMePh, m), 2.13 (1H, H^4, t, *J* 9.4 Hz), 1.50 (3H, Me, d, *J* 7.0 Hz), 0.70 (1H, H^1, d, *J* 10.3 Hz). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 230.5, 236.2, 146.7, 144.9, 128.6, 128.1, 127.5, 126.8, 126.2, 125.1, 91.9, 74.9, 74.4, 72.3, 66.5, 61.0, 38.1, 35.1, 22.4. Mass (75 eV, *m/z*): 514 (M$^+$). Anal. Calcd for $C_{27}H_{28}MoO_4$: C, 63.28; H, 5.51. Found: C, 63.31; H, 5.62.

(m) Synthesis of Dicarbonyl(η^5-cyclopentadienyl)-((3*R,4*S**,5*R**,6*R**,1′*R**)-(1,2,3-η)-*syn*-4-hydroxy-5-(1′-hydroxyethyl)-6-phenyl-2-hepten-1-yl)molybdenum (15).** This compound was similarly prepared from reduction of **12** with DIBAL-H (4.8 equimolar) according to the procedure in section (l), and the yield was 86% (yellow oil). IR (Nujol): ν(CO) 1943 (vs), 1860 (vs) cm^{-1}. ^{1}H NMR (400 MHz, δ, $CDCl_3$): (exo isomer) 7.30–7.18 (5H, Ph, m), 5.31 (5H, Cp, s), 4.06 (1H, H^3, ddd, *J* 10.4, 9.8, 7.2 Hz), 3.95 (1H, C*H*Me, dq, *J* 7.1, 3.8 Hz), 3.73 (1H, CH(OH), dd, *J* 9.8, 1.7 Hz), 3.31 (1H, C*H*Ph, m), 2.73 (1H, H^2, *J* 7.2 Hz), 2.29 (1H, H^4, t, *J* 9.8 Hz), 2.01 (1H, C*H*CMe, ddd, *J* 7.2, 3.8, 1.7 Hz), 1.42 (3H, Me, d, *J* 7.1 Hz), 1.16 (3H, Me, d, *J* 6.3 Hz), 0.84 (1H, H^1, d, *J* 10.4 Hz); (endo isomer) 7.30–7.18 (5H, Ph, m), 5.30 (5H, s, Cp), 4.15 (1H, C*H*(OH), dd, *J* 9.6, 2.0 Hz), 3.88 (1H, C*H*Me, dq, *J* 6.8, 4.0 Hz), 3.72 (1H, H^3, ddd, *J* 10.2, 9.6, 6.3 Hz), 3.30 (1H, CHPh, m), 3.18 (1H, H^4, t, *J* 9.6, 9.4 Hz), 2.63 (1H, H^2, d, *J* 6.3 Hz), 1.97 (1H, C*H*CPh, ddd, *J* 7.2, 4.0, 2.0 Hz), 1.78 (1H, H^1, d, *J* 10.2 Hz), 1.38 (3H, Me, d, *J* 7.1 Hz), 1.13 (3H, Me, d, *J* 6.8 Hz). ^{13}C NMR (100 MHz, δ, $CDCl_3$): (exo isomer) 238.7, 236.7, 146.1, 128.4, 127.6, 126.1, 91.7, 75.0, 70.8, 69.4, 68.2, 57.7, 38.3, 35.5, 22.9, 20.5; (endo isomer) 241.0, 239.8, 146.1, 128.4, 127.6, 126.1, 90.3, 73.9, 70.8, 68.6, 67.6, 57.3, 38.5, 32.0, 23.0, 20.6. Mass (75 eV, *m/z*): 452 (M$^+$). Anal. Calcd for $C_{22}H_{26}MoO_4$: C, 58.67; H, 5.83. Found: C, 58.49; H, 5.91.

(n) Synthesis of (2*R,3*R**,4*R**,5*S**,1′*S**)-3-Hydroxy-4-(1′-methylbenzyl)-5-phenyl-2-vinyltetrahydrofuran (16).** To a CH_3CN (10-mL) solution of **14** (0.20 g, 0.39 mmol) was added $NOBF_4$ (0.050 g, 0.43 mmol) at 0 °C, and the mixture was stirred for 5 min before Na_2CO_3 solid was added (0.10 g). After stirring for 2 h, the resulting dark red solution was exposed to air for 3 h, concentrated, and finally eluted on a SiO_2 preparative TLC plate (ether/hexane = 1/1) that afforded an organic band (R_f = 0.52) which afforded **16** as a colorless oil (70 mg, 0.24 mmol). IR (neat): ν(OH) 3405 (br s) cm^{-1}; ν(C=C) 1645 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.24–7.00 (10H, Ph, m), 5.92 (1H, H^3, ddd, *J* 17.1, 10.4, 6.0 Hz), 5.39 (1H, H^1, d, *J* 17.1 Hz), 5.24 (1H, H^2, d, *J* 10.4 Hz), 4.68 (1H, H^7, d, *J* 7.3 Hz), 4.43 (1H, H^4, t, *J* 6.0 Hz), 4.04 (1H, H^5, dd, *J* 11.1, 6.0 Hz), 2.91 (1H, C*H*Ph, dq, *J* 7.0, 6.5 Hz), 2.50 (1H, H^6, ddd, *J* 11.1, 7.3, 7.0 Hz), 1.58 (1H, OH, s). 1.37 (3H, Me, d, *J* 6.5 Hz). ^{13}C NMR (75 MHz, δ, $CDCl_3$) 145.1, 145.0, 138.4, 136.4, 128.5, 128.1, 127.3, 126.5, 125.5, 117.4, 80.9, 78.3, 60.6, 42.8, 21.7, 19.9. HRMS Calcd for $C_{20}H_{22}O_2$: 294.1620. Found: 294.1613.

(o) Synthesis of (2*R,3*R**,4*R**,5*S**,1′*S**)-3-Hydroxy-4-(1′-methylbenzyl)-5-methyl-2-vinyltetrahydrofuran (17).** This compound was similarly prepared from **15**, $NOBF_4$ (equimolar), and Na_2CO_3 (see section (**n**)); the yield of **17** was 50%. IR (neat): ν(OH) 3405 (br s) cm^{-1}; ν(C=C) 1645 (m) cm^{-1}. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.36–7.21 (5H, Ph, m), 5.84 (1H, H^3, ddd, *J* 17.2, 10.2, 6.6 Hz), 5.34 (1H, H^1, d, *J* 17.2 Hz), 5.21 (1H, H^2, d, *J* 10.2 Hz), 4.14 (1H, H^4, t, *J* 6.6 Hz), 3.84 (1H, H^5, dd, *J* 6.6. 6.0 Hz), 3.80 (1H, H^7, m), 2.74 (1H, CHMe, dq, *J* 9.6, 6.7 Hz), 1.94 (1H, H^6, ddd, *J* 9.6, 6.6, 6.0 Hz), 1.39 (3H, Me, d, *J* 6.7 Hz), 0.85 (3H, Me, d, *J* 6.6 Hz). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 145.1, 136.4, 128.5, 127.3, 126.5, 117.4, 80.2, 80.9, 78.3, 60.6, 42.8, 21.7, 19.9. HRMS Calcd for $C_{15}H_{20}O_2$: 232.1463. Found: 232.1465.

(p) Synthesis of Dicarbonyl(η^5-cyclopentadienyl)-((3*R,5*S**,6*R**)-(1,2,3-η)-*syn*-5-(carboxymethyl)-4-oxo-6-phenyl-2-hepten-1-yl)molybdenum (18).** To a THF/MeOH (1/1, 20-mL) solution of **8** (0.50 g, 1.06 mmol) was added an aqueous KOH solution (0.20 g, 2 mL), and the mixture was stirred at 23 °C for 5 h. The solution was neutralized by HCl (1 M, 2 mL),

Table 5. Crystal Data and Data Collection Parameters for 1, 5E, 10, and 12

compd	**10**	**12**	**1**	**5E**
empirical formula	$MoC_{27}H_{26}O_4$	$MoC_{22}H_{24}O_4$	$MoC_{19}H_{16}O_3$	$MoC_{21}H_{20}O_3$
fw	510.4	448.4	388.27	396.17
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a (Å)	18.223(3)	24.059(5)	10.957(3)	26.560(10)
b (Å)	11.179(3)	11.310(3)	12.843(2)	7.195(3)
c (Å)	24.027(4)	15.877(3)	12.758(4)	21.236(5)
β (deg)	101.82(1)	108.85(2)	111.26(3)	112.35(3)
vol (Å^3)	4790.8(15)	4088.5(14)	1673.1(8)	3753.4(22)
Z	8	8	4	8
D_{calcd} (g/cm^{-3})	1.415	1.457	1.541	1.402
μ (cm^{-1})	5.62 (Mo Kα)	6.47 (Mo Kα)	7.8 (Mo Kα)	7.0 (Mo Kα)
cell dimens (mm)	0.24 × 0.28 × 0.32	0.16 × 0.27 × 0.48	0.10 × 0.40 × 0.50	0.13 × 0.13 × 0.50
collcn range	$2\theta_{max}$ = 50, $\pm h,k,l$	$2\theta_{max}$ = 50, $\pm h,k,l$	$2\theta_{max}$ = 45, $\pm h,k,l$	$2\theta_{max}$ = 45, $\pm h,k,l$
scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan speed (deg min^{-1})	2.93–14.65	2.93–14.65	2.35–8.24	2.06–8.24
collcn T (K)	298	298	298	298
abs corr	yes	yes	yes	yes
no. of ind reflns	8496	7248	2180	2451
no. of obsd reflns, m	3685 ($I > 3\sigma(I)$)	4217 ($I > 3\sigma(I)$)	1788 ($I > 2\sigma(I)$)	1943 ($I > 2\sigma(I)$)
no. of variables, p	578	488	209	227
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0007F^2$	$w^{-1} = \sigma^2(F) + 0.0006F^2$	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$
R_F[a]	0.0404	0.0410	0.027	0.032
R_w[b]	0.0401	0.0429	0.022	0.022
S[c]	1.11	1.43	2.17	2.02
residual extrema in final diff map (e Å^{-3})	–0.40, 0.37	–0.52, 1.02	–0.34, 0.28	–0.31, 0.28

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

and the organic layer was extracted with diethyl ether (2 × 20 mL), washed with 5 mL of water, dried over $MgSO_4$, and concentrated. The residues were first eluted with ether/hexane (1/2) to remove impurities, and finally eluted with THF to produce a yellow band that gave **18** (0.44 g, 0.95 mmol, 90%) as a yellow crystalline solid. IR (Nujo): ν(CO) 1954 (vs), 1876 (vs), 1710 (s), 1659 (s) cm^{-1}. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.23–7.11 (5H, Ph, m), 5.21 (5H, Cp, s), 5.01 (1H, H^3, m), 3.14 (1H, COC*H*, ddd, *J* 9.0, 6.8, 4.1 Hz), 3.00–2.93 (2H, C*H*Me + H^4, m), 2.36 (1H, C*H*H'COOH, dd, *J* 16.5, 9.0 Hz), 2.21 (1H, CH*H'*COOH, dd, *J* 16.5, 4.1 Hz), 1.93 (1H, H^4, d, *J* 9.4 Hz), 1.28–1.19 (4H, H^1 + Me, m). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 239.4, 236.5, 209.7, 176.7, 143.8, 128.6, 127.8, 93.9, 73.3, 56.3, 54.2, 41.0, 39.8, 36.7, 20.8. Mass (75 eV, *m/z*): 464 (M$^+$). Anal. Calcd for $C_{22}H_{22}MoO_5$: C, 56.89; H, 4.78. Found: C, 57.09; H, 4.82.

(q) 4-(α-Methylbenzyl)-6-(1′-ethylidene)-2,5-dioxo-1-oxacyclohexane (19). To a CH_3CN solution (5 mL) of **18** (0.20 g, 0.43 mmol) was added $NOBF_4$ (0.10 g, 0.85 mmol) at 0 °C; the mixture was stirred for 10 min before addition of Et_3N (0.25 g, 2.50 mmol). The solution was further stirred for 2 h and then exposed to air for 2 h; water was added (2 mL). The organic layer was extracted with ether (2 × 10 mL), dried over $MgSO_4$, and eluted through a preparative TLC plate (ether/hexane = 1/2) to yield **19** as a 5/1 mixture of isomers (52 mg, 0.22 mol). IR (Nujol): ν(CO) 1760 (s), 1714 (s) cm^{-1}; ν(C=C) 1636 (m) cm^{-1}. ^{1}H NMR (400 MHz, δ, $CDCl_3$): (major isomer) 7.33–7.13 (5H, Ph, m), 6.29 (1H, MeC*H*=, q, *J* 7.6 Hz), 3.11 (1H, C*H*Me, qd, *J* 7.0, 4.7 Hz), 2.74 (1H, COCH, m), 2.68 (1H, COCH*H'*, *J* 16.7, 5.0 Hz), 2.40 (1H, CO*H*H', *J* 16.7, 6.7 Hz), 1.83 (3H, Me, d, *J* 7.6 Hz), 1.33 (3H, Me, d, 7.0 Hz); (minor isomer) 7.33–7.14 (5H, Ph, m), 6.27 (1H, MeC*H*=, q, *J* 7.6 Hz), 3.54 (1H, C*H*Ph, m), 2.77–2.58 (3H, COC*H*—C*HH'*, m), 1.81 (3H, Me, d, *J* 7.6 Hz), 1.26 (3H, Me, d, 7.1 Hz). ^{13}C NMR (75 MHz, δ, $CDCl_3$): (major isomer) 191.1, 166.2, 146.4, 141.8, 128.9, 127.6, 127.3, 119.7, 49.5, 39.0, 31.8, 20.0, 10.9. HRMS Calcd for $C_{15}H_{16}O_3$: 244.1099. Found: 244.1091.

(r) X-ray Diffraction Measurement. A single crystal of **1**, **5E**, **10**, or **12** was sealed in a glass capillary under an inert atmosphere. Data for **1** and **5E** were collected on a Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation, and the structures were solved by the heavy-atom method; all data reduction and structural refinements were performed with the NRCCSDP package. Data for **10** and **12** were collected on Siemens R3m/V diffractometer, using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods, and all data reduction and structural refinements were performed on SHELXTL PLUS. Crystal data and details of the data collection and structural analysis are summarized in Table 5. For **1** and **5E**, all non-hydrogen atoms were refined with anisotropic parameters, and their hydrogen atoms included in the structure factor calculations were placed in idealized positions. For **10** and **12**, the non-hydrogen atoms and the O(3)–H(3a)···O(4) hydrogen were refined with anisotropic parameters, and the remaining hydrogens included in the structure factor calculation were placed in idealized positions.

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Supplementary Material Available: Tables of crystal data, positional parameters, isotropic thermal parameters, anisotropic thermal parameters of non-hydrogen atoms, and all bond distances and angles for **1**, **5E**, **10**, and **12** (21 pages). Ordering information is given on any current masthead page.

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