Siloxy Effect on Intramolecular Cyclization of Tungsten−η^1-Siloxypropargyl Complexes: Formation of 2,5-Dihydrofurans versus γ-Lactones

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Treatment of tungsten−η^1-4-(triethylsiloxy)propargyl and η^1-4-(tripropylsiloxy)propargyl compounds **8a**−**d** and **9a**−**d** with CF_3CO_2H in cold CH_2Cl_2 yielded a mixture of tungsten η^1-2,5-dihydrofurans **10a**−**d** and η^3-*syn*-γ-lactones **4a**−**d**. The product ratios depend on the types of alkyl and siloxy substituents of the propargyl ligand; η^1-2,5-dihydrofurans **10a**−**d** were formed in significant amount when the substituent is a secondary alkyl group. This cyclization pathway is in sharp contrast to our previous report that the dimethyl-*tert*-butylsiloxy group yielded only η^3-*syn*-γ-lactones **4a**−**d**. To validate this reaction on a complex system, we prepared the chiral tungsten−η^1-4-(triethylsiloxy)propargyl species **12b**, which ultimately gave optically active tungsten η^1-2,5-dihydrofuran **13** in 68% yields. In connection with our previous report, we elaborated three types of cyclization reactions on chiral tungsten η^1-propargylic triols **12a**−**c**, to afford chiral η^1-2,5-dihydrofurans and unsaturated γ- and δ-lactones in reasonable yields.

Introduction

Acid-promoted intramolecular alkoxycarbonylations of tungsten−η^1-propargyl complexes **1**−**3** led to formation of η^3-γ, η^3-δ-, and η^3-ϵ-lactones **4**−**6** in good yields;[1,2] the reaction involved the tungsten−η^2-allene cationic intermediates **A**.[1−5] Among these cyclizations, δ- and ϵ-lactones **5** and **6** followed *anti* and *syn* stereoselections[1,2] respectively, whereas the η^3-γ-lactone **4** was formed in 1:1 diastereomeric mixtures.[1,2] The selectivity problem of **4** can be circumvented by introduction of a dimethyl-*tert*-butylsiloxy group on these η^1-propargyl species such as **7** (Scheme 1, path 2), leading to *syn* stereoselection of η^3-γ-lactone **4**;[1,2] the reaction requires small amounts of H_2O and CF_3SO_3H (optimum conditions: H_2O, 0.8−1.0 equiv; CF_3SO_3H, 0.30 equiv). The overall reaction is shown in path 2 of Scheme 1; the proposed formation mechanism of *syn* η^3-γ-lactones **4** is supported by results obtained from isotopic H_2O^* ($O^* = {}^{18}O$) labeling as well as by isolation of the key η^3-2-carboxyallyl intermediate.[1,2] To study thoroughly the drastic impact of the siloxy group, we report here a new cyclization of these propargyl complexes with alteration of their tethered siloxy groups.

Results and Discussion

As shown in Scheme 2, tungsten−η^1-propargyl compounds **1a**−**d** were readily converted to their triethyl- and tripropylsiloxy derivatives **8a**−**d** and **9a**−**d** in high yields (>90%). We previously reported[1,2] that CF_3SO_3H acidification of tungsten−η^1-(dimethyl-*tert*-butylsiloxy)-propargyl species **7a**−**d** afforded the *syn* isomers of tungsten η^3-γ-lactones **4a**−**d** in yields exceeding 80% (Scheme 2). We now expand this reaction to those tungsten complexes having different siloxy derivatives. Scheme 3 shows the results for acidification of **8a** and **9a** under various conditions. An interesting finding here is the formation of tungsten η^1-2,5-dihydrofuran **10a** in addition to the expected *syn*-η^3-γ-lactone **4a**. These two compounds were easily separable on a silica column; the isolated yields are provided in Scheme 3. Both triethylsiloxy and tripropylsiloxy derivatives **8a** and **9a** gave the products **10a** and **4a** with close **10a**/**4a** ratios, i. e. 1.42 and 1.42, respectively (entries 1 and 4). When the reactions were performed with CF_3SO_3H or in CH_3CN (entries 2 and 3), the resulting ratios **10a**/**4b** were 1.47 and 1.40, respectively, similar to that (1.42) in entry 1.

We extended the reactions to other tungsten triethylsiloxy and tripropylsiloxy complexes **8b**−**d** and **9b**−**d;** the results were summarized in Scheme 4. Entries 1−3 show the product ratios of **10n**/**4n** (n = b−d) for η^1-triethylsiloxy derivatives **8b**−**d** having different alkyl substituents R′. A small ethyl group as in compound **8a** gave a low **10b**/**4b** ratio, ca. 0.44 (entry 1) in favor of the η^3-γ-lactone. The **10b**/**4b** ratio increases gradually with increasing alkyl sizes, i.e. 0.65 for **8b** (entry 2, R′ = MeC=CH_2) and 0.90 for **8c** (entry 3, R′ = cyclohexyl). Entries 4−6 show the results for the tripropylsiloxy derivatives **9b**−**d**; the **10b**/**4b** ratio was 1.2 for compound **9b** (R′ = Et), significantly larger than that (**10b**/**4b** = 0.43) for its triethylsiloxy analogue **8b**. In entries 5 and 6, attempts to improve the selectivity of η^1-2,5-dihydrofuran were less pronounced for **9c** and **9d**; the product ratios **10c**/**4c** = 0.64 and **10d**/**4d** = 0.93 were very close to those of their triethylsiloxy analogues **8c** and **8d** (entries 2 and 3).

The siloxy effect on these cyclization reactions could be potentially useful for the synthesis of various lactones

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

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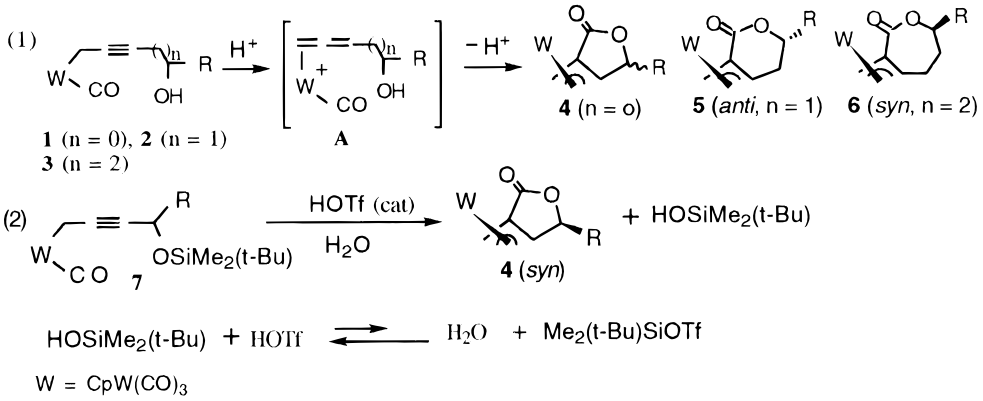
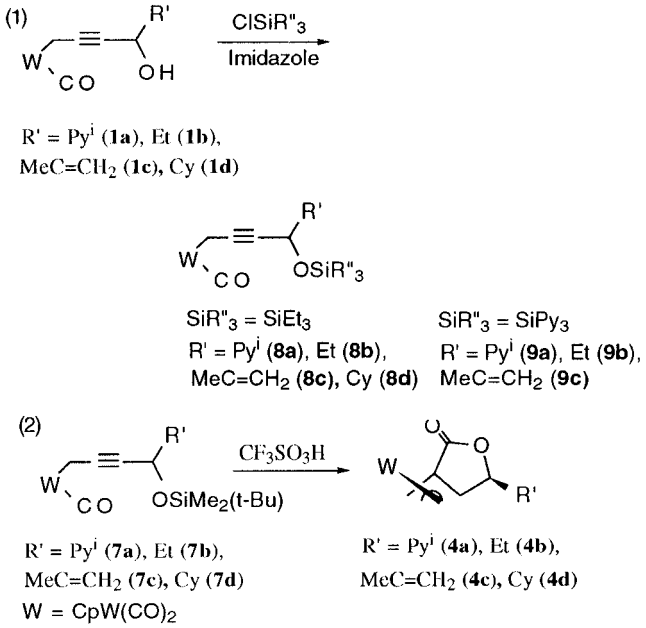
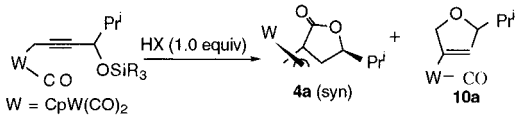
Scheme 1



Scheme 2



Scheme 3



Entry	η^1-Propargyl	HX	Solvent	Products (Isolated Yields)
1	R = Et (**8a**)	CF_3CO_2H	CH_2Cl_2	**4a** (26%) **10a** (37%)
2	R = Et (**8a**)	CF_3CO_2H	CH_3CN	**4a** (21 %) **10a** (31 %)
3	R = Et (**8a**)	CF_3SO_3H	CH_2Cl_2	**4a** (24 %) **10a** (34 %)
4	R = Py (**9a**)	CF_3CO_2H	CH_2Cl_2	**4a** (25 %) **10a** (35%)

and dihydrofurans. Toward this direction, we prepared the chiral chloropropargylic triol[6] **11a**, which was subsequently transformed into **11b** and **11c** in 92% and 96% yields, respectively. As shown in Scheme 5, treatment of **11a**−**c** with $CpW(CO)_3Na$[7] afforded η^1-(triethylsiloxy)propargyl species **12a**−**c** in good yields (>85%). In contrast with **8a**−**d**, the triethylsiloxy effect was very significant in acidification of **12b** with CF_3CO_2H (0.25 equiv), so that chiral 2,5-dihydrofuran **13** was formed as the major product (68% yield) in addition to a small amount of the η^3-γ-lactone **14-*syn*** (5% yield). If one equiv of CF_3CO_2H was used, the yields of **13** and **14** were 61% and 10%, respectively. The X-ray structure[8] of **13** is given in Figure 1 to confirm its absolute configuration. By our previous method given in Scheme 1 (path 1), CF_3SO_3H-promoted lactonization of **12a** afforded the two diastereomers **14-*syn*** and **14-*anti*** that were separable on a silica column in 33% and 38% yields, respectively. Figure 2 shows the X-ray structure[9] of **14-*anti*** to confirm its configuration. Treatment of

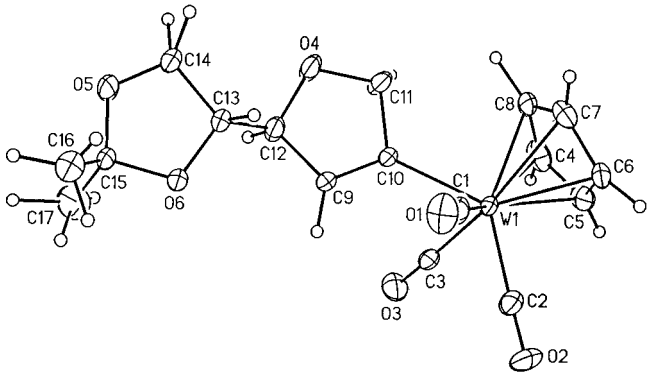


Figure 1. ORTEP drawing of compound **13.** Selected bond lengths (Å): W(1)−C(10) = 2.247(4), C(9)−C(10) = 1.330 (7), C(10)−C(11) = 1.501(7), C(11)−O(4) = 1.441(7), C(12)−O(4) = 1.410 (7).

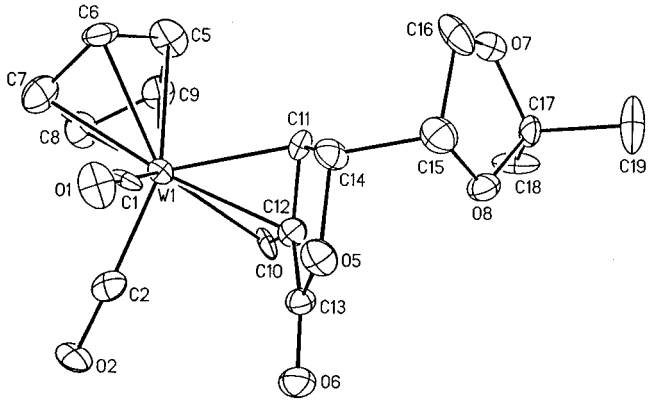


Figure 2. ORTEP drawing of compound **14-*anti*.** Selected bond lengths (Å): W(1)−C(10) = 2.301(15), W(1)−C(12) = 2.287(16), W(1)−C(10) = 2.301(15), C(10)−C(12) = 1.418-(20), C(11)−C(12) = 1.416(21), C(13)−O(6) = 1.190(19).

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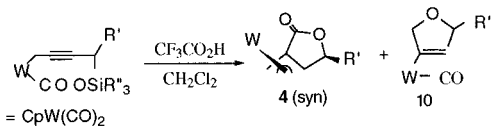
(8) Crystal data for compound **13**: orthorhombic, space group $P2_12_12_1$, a = 7.1921(3) Å, b = 10.1576(5) Å, c = 23.9737(11) Å, Z = 4, V = 1751.37(23) Å^3, final R = 0.0186, R_w = 0.0193.

(9) Crystal data for compound **14-*anti***: orthorhombic, space group $P2_12_12$, a = 21.7945(4) Å, b = 21.8583(2) Å, c = 7.1876(1) Å, Z = 8, V = 3424.1(11) Å^3, final R = 0.0465, R_w = 0.0434.

Scheme 4



W = CpW(CO)$_2$

Entry	η^1-Propargyl	Products (Isolated Yields)
	SiR"$_3$ =SiEt$_3$	
1	R' = Et (**8b**)	**4b** (48%) **10b** (21%)
2	R' = MeC=CH$_2$ (**8c**)	**4c** (40 %) **10c** (26 %)
3	R' = Cy (**8d**)	**4d** (30 %) **10d** (27 %)
	SiR"$_3$ =SiPy$_3$	
4	R' = Et (**9b**)	**4b** (30 %) **10b** (36%)
5	R' = MeC=CH$_2$ (**9c**)	**4c** (42 %) **10c** (27 %)
6	R' = Cy (**9d**)	**4d** (33 %) **10d** (31 %)

the methyl ether species **12c** with CF_3SO_3H (0.25 equiv) under similar conditions afforded the η^3-δ-lactone **15-*anti*** exclusively in 76% yield. The *anti* and *syn* configurations of **15** refer to the orientation of the methoxy group relative to CpW(CO)$_2$. Characterization of the structure of **15-*anti*** relies on the X-ray diffraction study[10] of its acetyl derivative **16** that has better crystal quality; the molecular structure of **16** is shown in Figure 3 to reveal that the methoxy group of **15-*anti*** lies away from the bulky CpW(CO)$_2$ fragment to minimize their mutual steric interactions. In contrast with **10a**−**d**, compound **13** was obtained in high yields (68%); this is probably due to steric interaction of dioxolane group that forces triethylsiloxy group tilt toward the tungsten−allene carbon to induce a cyclization reaction. According to this conformation effect, we propose that tungsten-η^1-2,5-dihydrofurans are formed more favorably when the starting propargyl species **8a**−**d** and **9a**−**d** have a sterically demanding alkyl substituent R′ and siloxy group OSiR″$_3$. This model accounts for most of the product ratios shown in Scheme 4 as R′ and OSiR″$_3$ were modified.

The X-ray structure of optically active η^1-2,5-dihydrofuran **13** enables us to propose its formation mechanism as shown in Scheme 6. The C_δ carbon of **13** has an *S* configuration, implying retention of stereochemistry with respect to the C_δ carbon of **12b**. The cyclization reaction can be envisaged to proceed via protonation at the $\equiv C_\gamma$ carbon[11−13] of **12b,** yielding the η^2-allene cationic intermediate **A**. We believe that the the η^2-allene carbon of **A** is highly electrophilic,[10−12] reacting with its siloxy oxygen to yield the trioxonium species **B**; further cleavage of the Si−O bond of **B** is achieved by counterion X. A competitive reaction here is the formation of the γ-lactone **14-*syn*** that was very difficult to annihilate because the formation is accelerated by a catalytic amount of water; elucidation of the mechanism including the intermediate **C** has been described in our previous study.[1,2]

Scheme 5 shows the formation of the three tungsten η^1-heterocycles **13**, **14-*syn*,*anti***, and **15**, derived from the chiral chloropropargylic triol **11a**; these organometallics ultimately provide optically active 2,5-dihydrofurans, unsaturated γ- and δ-lactones, and demetalation reactions. As shown in Scheme 7, I_2 oxidative demetalation[14] of chiral η^1-2,5-dihydrofuran **13** in MeOH afforded unsaturated ester **17** in 45% yield. Treatment of a *syn* and *anti* diastereomeric mixture of η^3-γ-lactone **14** with $NOBF_4$ yielded an allyl cation[15−17] that reacted with Bu_4NBH_4 to afford chiral furanone **18** in 58% yield. A similar transformation of chiral η^3-δ-lactone **16** into unsaturated δ-lactone **19** was achieved in 63% yield.

In conclusion, we have reported the effect of the siloxy group in the intramolecular cyclization of tungsten propargylic alcohol. The products may be *syn*-η^3-γ-lactones and η^3-2,5-dihydrofuran. As described before, utilization of the dimethyl-*tert*-butylsiloxy group only yielded an η^3-γ-lactone. Formation of η^1-2,5-dihydrofuran was favored by increasing sizes of siloxy groups and alkyl substituents of the propargyl ligands. Toward this direction, we prepared the large chiral chloropropargylic alcohol **11**, which afforded chiral η^1-2,5-dihydrofuran in good yield. In connection with our previous investigation, we also demonstrated that this chiral chloropropargylic alcohol **11** could ultimately give optically active unsaturated γ- and ϵ-lactones in reasonable yields.

Experimental Section

Unless otherwise noted, all reactions were carried out under a nitrogen atomsphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over CaH_2 and distilled before use. $W(CO)_6$, CF_3CO_2H, CF_3SO_3H, propargyl chloride, and sodium were obtained commercially and used without purification. Syntheses of compounds **1**−**6** were reported in our previous paper. Elemental analyses were performed at National Cheng Kung University, Taiwan. The synthetic scheme and characterization of **11a**−**c** were provided in the Supporting Information of our previous paper.

(1) General Procedure for Syntheses of Tungsten−η^1-(Triethylsiloxy)propargyl Complexes. Synthesis of 8a. To a DMF solution (30 mL) of **1a** (1.20 g, 2.70 mmol) and imidazole (370 mg, 5.40 mmol) was added triethylsilyl chloride (450 mg, 3.00 mmol); the mixture was stirred for 8 h before sequential addition of aqueous NaCl (25 mL). The solution was extracted with diethyl ether (3 × 20 mL) and flash-chromatographed through a short silica column to yield **8a** as a yellow oil (1.50 g, 2.56 mmol, 95%). IR (neat, cm^{-1}): ν(CO) 2018 (vs), 1921 (vs). ^{1}H NMR (300 MHz; $CDCl_3$): δ 5.48 (s, 5H, Cp), 4.15 (m 1H, OCH), 2.01 (d, J = 2.1 Hz, 2H, W−CH_2), 1.76 (m, 1H, C*H*Me$_2$), 0.94 (m, 15H, CH*Me*$_2$ + SiCH$_2$C*H*$_3$), 0.64 (m, 6H, Si(C*H*$_2$CH$_3$)$_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ 229.1, 216.2, 93.8, 92.5, 80.6, 68.1, 18.4, 17.6, 6.8, 4.9, −32.1. MS (75 eV; *m*/*e*): 530 (M^+ − 28).

(2) Synthesis of 8b. Compound **1b** (1.50 g, 3.50 mmol), imidazole (480 mg, 7.00 mmol), and triethylsilyl chloride (580 mg, 3.80 mmol) afforded **8b** as a yellow oil (1.83 g, 3.36 mmol, 96%). IR (neat, cm^{-1}): ν(CO) 2018 (vs), 1921 (vs). ^{1}H NMR (300 MHz; $CDCl_3$): δ 5.49 (s, 5H, Cp), 4.30 (m, 1H, OCH), 1.99 (d, J = 2.2 Hz, 2H, W−CH_2), 1.63 (m; 2H, CH_2), 0.95 (m, 12H, CH_2CH_3 + SiCH$_2$C*H*$_3$), 0.63 (m, 6H, SiC*H*$_2$CH$_3$). ^{13}C NMR (75

(10) Crystal data for compound **16**: monoclinic, space group $P2_1$, a = 8.0692(2) Å, b = 9.5150(2) Å, c = 12.0951(4) Å, z = 2, V = 879.6(3) Å^3, final R = 0.0396, R_w = 0.0420.

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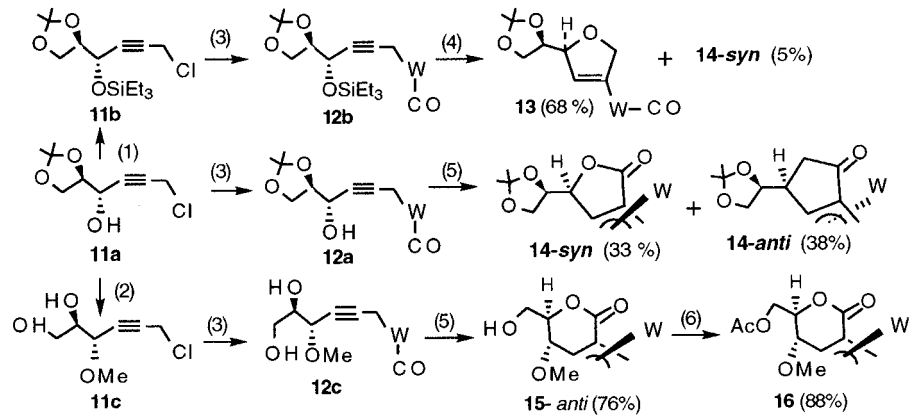
Scheme 5



W =$CpW(CO)_2$ (1) $ClSiEt_3$ (1.0 equiv), imidazole, 2.0 equiv) (2) NaH(1.0 equiv), MeI (2.0 equiv); CH_3CO_2H (60 wt%) (3) $NaCpW(CO)_3$ (1.0 equiv) (4) CF_3CO_2H (0.25 equiv), - 40 ^{0}C) (5) CF_3SO_3H (0.25 equiv) (6) Ac_2O/DMAP

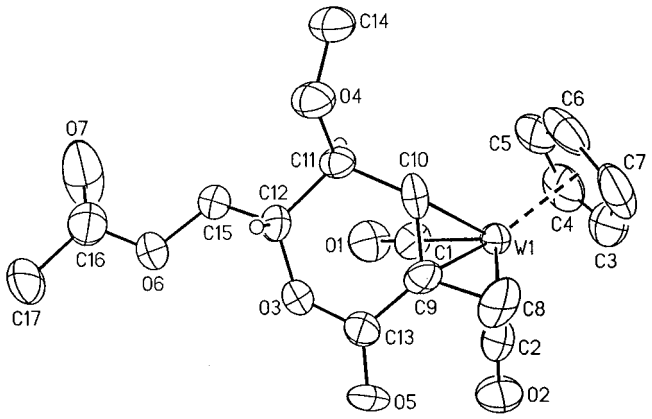
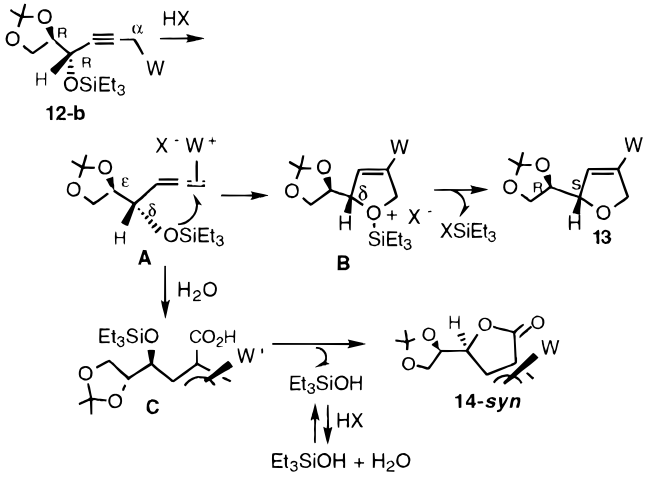


Figure 3. ORTEP drawing of compound **16.** Selected bond lengths (Å): W(1)−C(8) = 2.285(11), W(1)−C(1) = 1.994-(11), W(1)−C(10) = 2.267(11), C(9)−C(8) = 1.416(16), C(9)−C(10) = 1.413(17), C(13)−O(5) = 1.206(14).

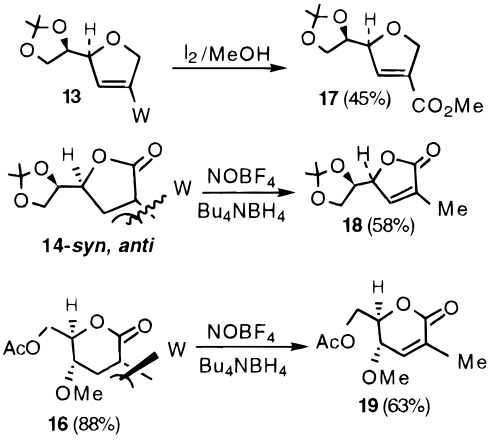
Scheme 6



MHz; $CDCl_3$): δ 229.1, 216.3, 93.2, 92.6, 81.8, 64.6, 32.6, 9.7, 6.8, 4.8, −32.3. MS (75 eV; *m*/*e*): 544 (M^+).

(3) Synthesis of 8c. Compound **1c** (1.20 g, 2.70 mmol), imidazole (370 mg, 5.40 mmol), and triethylsilyl chloride (450 mg, 3.00 mmol) afforded **8c** as a yellow oil (1.40 g, 2.52 mmol, 93%). IR (neat, cm^{-1}): ν(CO) 2020 (s), 1918 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.48 (s, 5H, Cp), 5.04 (s, 1H, =C*H*′), 4.80 (s, 1H, =C*H*H′); 4.78 (d, *J* = 2.2 Hz, 1H, OCH), 1.98 (d, *J* = 2.2 Hz, 2H, W−CH_2), 1.82 (s, 3H, Me), 0.95 (m, 9H, $SiCH_2CH_3$), 0.64 (m, 6H, $SiCH_2CH_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ 229.0, 216.3, 216.2, 146.2, 110.3, 94.3, 92.6, 81.6, 67.1, 17.8 (C_7), 6.8, 4.8, −32.3. MS (75 eV; *m*/*e*): 556 (M^+).

Scheme 7



(4) Synthesis of 8d. Compound **1d** (2.00 g, 4.1 mmol), imidazole (560 mg, 8.2 mmol), and triethylsilyl chloride (680 mg, 4.5 mmol) afforded **8d** as a yellow oil (2.32 g, 3.89 mmol, 95%). IR (neat, cm^{-1}): ν(CO) 2018 (s), 1921 (s). ^{1}H NMR (300 MHz; $CDCl_3$): δ 5.48 (s, 5H, Cp), 4.15 (m, 1H, OCH), 2.01 (d, *J* = 2.2 Hz, 2H, W−CH_2), 1.83−1.63, 1.23−1.03 (m, 11H, cyclohexyl), 0.96 (m, 9H, $SiCH_2CH_3$), 0.62 (m, 6H, $Si(CH_2CH_3)_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ 229.1, 216.2, 93.9, 92.6, 81.1, 68.1, 45.7, 29.0, 28.4, 26.6, 26.1, 6.9, 4.9, −32.0. MS (75 eV; *m*/*e*): 570 (M^+ − 28).

(5) Synthesis of 9a. Compound **1a** (1.50 g, 3.37 mmol), imidazole (460 mg, 6.74 mmol), and tripropylsilyl chloride (710 mg, 3.7 mmol) afforded **9a** as a yellow oil (1.94 g, 3.24 mmol, 96%). IR (neat, cm^{-1}): ν(CO) 2019 (s), 1931 (s). ^{1}H NMR (300 MHz; $CDCl_3$): δ 5.46 (s, 5H, Cp), 4.15 (m, 1H, OCH), 2.00 (d, *J* = 2.2 Hz, 2H, W−CH_2), 1.73 (m, 1H, C*H*Me_2), 1.43−1.33 (m, 6H, $(SiCH_2CH_2CH_3)$), 0.97−0.91 (m, 15H, $Si(CH_2CH_2CH_3)$ + 2Me), 0.66−0.59 (m, 6H, $SiCH_2CH_2CH_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ 229.1, 216.2, 93.9, 92.6, 80.6, 68.8, 35.9, 18.6, 18.4, 16.7, −32.1. MS (75 eV; *m*/*e*): 600 (M^+).

(6) Synthesis of 9b. Compound **1b** (1.50 g, 3.48 mmol), imidazole (475 mg, 6.96 mmol), and tripropylsilyl chloride (736 mg, 3.83 mmol) afforded **9b** as a yellow oil (1.98 g, 3.37 mmol, 97%). IR (neat, cm^{-1}): ν(CO) 2012 (s), 1912 (s). ^{1}H NMR (300 MHz; $CDCl_3$): δ 5.47 (s, 5H, Cp), 4.25 (m, 1H, OCH), 1.98 (d, *J* = 2.2 Hz, 2H, W−CH_2), 1.62 (m, 2H, CH_2), 1.43−1.33 (m, 6H, $SiCH_2CH_2CH_3$, 0.94 (m, 12H, $SiCH_2CH_2CH_3$ + Me), 0.64−0.58 (m, 6H, $SiCH_2CH_2CH_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ

228.9, 216.1, 93.2, 92.5, 81.8, 64.6, 32.6, 18.5, 18.3, 17.0, 9.6, −32.3. MS (75 eV; *m*/*e*): 586 (M^+).

(7) Synthesis of 9c. Compound **1c** (1.40 g, 3.16 mmol), imidazole (430 mg, 6.32 mmol), and tripropylsilyl chloride (670 mg, 3.47 mmol) afforded **9c** as a yellow oil (1.8 g, 3.0 mmol, 95%). IR (neat, cm^{-1}): ν(CO) 2021 (s), 1923 (s). ^1H NMR (300 MHz; $CDCl_3$): δ 5.46 (s, 5H, Cp), 5.45 (s, 1H, =CH*H*′), 5.02 (s, 1H, C*H*H′), 4.78 (s, 1H, OCH), 1.98 (d, J = 2.2 Hz, 2H, W−CH_2), 1.82 (s, 3H, C_5H), 1.44−1.28 (m, 6H, $SiCH_2CH_2CH_3$), 0.97−0.91 (m, 9H, $SiCH_2CH_2CH_3$), 0.65−0.60 (m, 6H, $SiCH_2CH_2CH_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ 228.9, 216.1, 146.2, 110.2, 94.2, 92.5, 80.4, 67.1, 18.6, 18.3, 17.7, 16.7, −32.3. MS (75 eV; *m*/*e*): 598 (M^+).

(8) Synthesis of 9d. Compound **1d** (1.6 g, 3.3 mmol), imidazole (450 mg, 6.6 mmol), and tripropylsilyl chloride (700 mg, 3.63 mmol) afforded **9d** as a yellow oil (2.05 g, 3.2 mmol, 97%). IR (neat, cm^{-1}): ν(CO) 2023 (s), 1927 (s). ^1H NMR (300 MHz; $CDCl_3$): δ 5.46 (s, 5H, Cp), 4.12 (m, 1H, C_4H), 2.00 (d, J_{14} = 2.0 Hz, 2H, C_1H), 1.75−1.65, 1.42−1.27, 1.25−1.01, 0.96−0.90, 0.65−0.58 (m, 32H, cyclohexyl + OTPS). ^{13}C NMR (75 MHz; $CDCl_3$): δ 229.1, 216.2 (3W−CO), 93.9 (C_3), 92.6 (Cp), 81.0 (C_2), 68.1 (C_4), 45.7 (C_5), 28.9, 28.2, 26.6, 26.1, 25.9 (cyclohexyl), 18.6 ($Si(CH_2CH_2CH_3)_3$), 18.5 ($Si(CH_2CH_2CH_3)_3$), 16.8 ($Si(CH_2CH_2CH_3)_3$), −32.0 (C_1). MS (75 eV; *m*/*e*): 640 (M^+).

(9) General Procedure for Syntheses of $CpW(CO)_3$(η^1-2,5-dihydrofuran) Compounds. Synthesis of 10a. In a typical reaction, to a cold CH_2Cl_2 (−40 °C) solution (20 mL) of **8a** (480 mg, 0.86 mmol) was added CF_3CO_2H (98 mg, 0.86 mmol), and the mixture was stirred for 4 h before the temperature was raised to 0 °C. To this solution was added a saturated $NaHCO_3$ solution, followed by evaporation to half its volume. The organic layer was extracted with diethyl ether (2 × 20 mL), concentrated, and eluted through a silica column (diethyl ether/hexane, 1/1) to give **10a** (R_f 0.4, 141 mg, 0.32 mmol, 37%) and **4a** (R_f 0.60, 99 mg, 0.22 mmol, 26%). Spectral data for **10a**: IR (Nujol, cm^{-1}) ν(CO) 2023 (s), 1930 (s); ^1H NMR (300 MHz; C_6D_6) δ 5.70 (br s, 1H, =CH), 4.7 (m, 1H, OCH), 4.63 (m, 2H, OCH_2), 4.50 (s, 5H, Cp), 1.85 (m, 1H, C*H*Me_2), 1.02 (t, J = 6.8 Hz, 3H, Me), 1.00 (t, J = 6.8 Hz, 3H, Me); ^{13}C NMR (75 MHz; C_6D_6) δ 228.4, 216.9, 216.8, 141.6, 118.7, 92.7, 90.9, 89.2, 34.6, 18.6, 18.1; MS (EI, 12 eV; *m*/*e*) 472 (M^+). Anal. Calcd for $C_{15}H_{16}WO_4$: C, 40.57; H, 3.67. Found: C, 40.68; H, 3.70.

(10) Synthesis of 10b. Compound **8b** (510 mg, 0.94 mmol) and CF_3CO_2H (107 mg, 0.94 mmol) in cold CH_2Cl_2 (−40 °C) afforded **10b** (86 mg, 0.20 mmol, 21%) and **4b** (194 mg, 0.45 mmol, 48%). IR (neat, cm^{-1}): ν(CO) 2012 (s), 1912 (s). ^1H NMR (300 MHz; $CDCl_3$): δ 5.65 (br s, 1H, =CH), 5.48 (s, 5H, Cp), 4.65 (m, 1H, OCH), 4.50 (m, 2H, OCH_2), 1.48 (m, 2H, CH_2), 0.85 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (75 MHz; $CDCl_3$) δ 227.1, 216, 142.7, 117.5, 91.2, 88.6, 88.3, 29.1, 9.1. MS (EI, 12 eV; *m*/*e*): 430 (M^+). Anal. Calcd for $C_{14}H_{14}WO_4$: C, 39.10; H, 3.28. Found: C, 39.28; H, 3.17.

(11) Synthesis of 10c. Compound **8c** (500 mg, 0.90 mmol), and CF_3CO_2H (103 mg, 0.90 mmol) in cold CH_2Cl_2 (−40 °C) afforded **10c** (104 mg, 0.23 mmol, 26%) and **4c** (160 mg, 0.36 mol, 40%). IR (neat, cm^{-1}): ν(CO) 2013 (s), 1912 (s). ^1H NMR (300 MHz; $CDCl_3$): δ 5.54 (br s, 1H, =CH), 5.49 (s, 5H, Cp), 4.87 (s, 1H, =C*H*H′), 4.74 (s, 1H, =CH*H*′), 4.57 (m, 2H, C_1H), 1.59 (s, 3H, C_7H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 226.8, 216.0, 147.1, 141.1, 118.7, 110.8, 93.9, 91.0, 89.5, 17.0. MS (EI, 12 eV; *m*/*e*): 442 (M^+). Anal. Calcd for $C_{15}H_{14}WO_4$: C, 40.75; H, 3.19. Found: C, 40.45; H, 3.11.

(12) Synthesis of 10d. Compound **8d** (600 mg, 1.00 mmol) and CF_3CO_2H (114.0 mg, 1.00 mmol) in cold CH_2Cl_2 (−40 °C) afforded **10d** (145.6 mg, 0.30 mmol, 30%) and **4d** (131 mg, 0.27 mmol, 27%). IR (neat, cm^{-1}): ν(CO) 2012 (s), 1912 (s). ^1H NMR (300 MHz; $CDCl_3$): δ 5.64 (d, J = 2.0 Hz, 1H, =CH), 5.46 (s, 5H, Cp), 4.45 (m, 3H, OCH + OCH_2), 1.69−0.91 (m, 11H, cyclohexyl). ^{13}C NMR (75 MHz; $CDCl_3$): δ 227.1, 216.1, 141.3, 117.3, 91.7, 91.1, 88.6, 44.1, 28.7, 28.3, 26.6, 26.2. MS (75 eV; *m*/*e*): 484 (M^+). Anal. Calcd for $C_{18}H_{20}WO_4$: C, 44.65; H, 4.16. Found: C, 44.80; H, 4.22.

(13) Synthesis of Chiral Tungsten−η^1-Propargyl Complex 12a. To a THF solution (50 mL) of $CpW(CO)_3Na$ (5.25 g, 14.7 mmol) was slowly added the chloropropargylic triol[6] **11a** (3.00 g, 14.7 mmol) in THF (5.0 mL); the mixture was stirred for 5 h at 23 °C. The solution was evaporated to dryness, and the residue was chromatographed on a silica column to yield **12a** as a yellow solid (6.50 mg, 13.1 mmol). [α] = 7.20° (*c* = 0.50, CH_2Cl_2). IR (Nujol, cm^{-1}): 3445 (vs), ν(CO) 2015 (s), 1920 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 5.48 (s, 5H, Cp), 4.39 (dt, J = 4.7, 2.3 Hz, 1H, OCH), 4.08 (ddd, J = 11.2, 6.1, 4.7 Hz, 1H, OCH), 4.02−3.92 (m, 2H, OCH_2), 1.91 (d, J = 2.3 Hz, 2H, W−CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 228.6, 216.5, 109.6, 95.9, 91.2, 78.9, 77.9, 65.5, 62.8, 26.5, 26.2, −33.2. MS (EI, 12 eV; *m*/*e*): 502 (M^+).

(14) Synthesis of 12b. Optically active chloropropargylic triol **11b** (2.00 g, 6.30 mmol) and $CpW(CO)_3Na$ (2.30 g, 6.30 mmol) afforded **12b** (3.56 g, 5.78 mol) as a yellow solid. [α] = 33.5° (*c* = 0.33, CH_2Cl_2). IR (Nujol, cm^{-1}): ν(CO) 2013 (s), 1918 (s). ^1H NMR (400 MHz, C_6D_6): δ 4.78 (s, 5H, Cp), 4.52 (dt, J = 5.3, 2.1 Hz, 1H, SiOCH), 4.10−4.06 (m, 3H, OCH + OCH_2), 1.93 (d, J = 2.1 Hz, 2H, W−CH_2), 1.45 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.07 (t, J = 8.0 Hz, 9H, $SiCH_2CH_3$), 0.74 (q, J = 8.0 Hz, 6H, $SiCH_2CH_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 229.4, 216.6, 100.6, 92.5, 95.3, 79.9, 80.3, 66.6, 64.9, 27.0, 25.7, 6.9, 5.5, −32.5. MS (EI, 12 eV; *m*/*e*): 616 (M^+), 588 (M^+ − CO), 560 (M^+ − 2CO).

(15) Synthesis of 12c. Optically active chloropropargylic triol **11c** (2.00 g, 6.30 mmol) and $CpW(CO)_3Na$ (4.00 g, 11.23 mmol) afforded **12c** (4.38 g, 9.21 mmol) as a yellow solid. [α] = 29.5° (*c* = 0.25, CH_2Cl_2). IR (Nujol, cm^{-1}): ν(OH) 3444 (vs), ν(CO) 2016 (s), 1915 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 5.47 (s, 5H, Cp), 4.13 (dt, J = 5.5, 2.3 Hz, 1H, OCH), 3.83 (q, J = 6.0 Hz, 1H, OCH), 3.75−3.69 (m, 2H, OCH_2), 3.39 (s, 3H, OCH_3), 1.97(d, J = 2.3 Hz, 2H, W−CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 228.1, 216.7, 92.4, 92.0, 74.9, 74.6, 73.3, 63.4, 56.6. −32.1. MS (EI, 12 eV; *m*/*e*): 476 (M^+).

(16) Intramolecular Cyclization of 12a. Compound **12a** (2.50 g, 4.98 mmol) and CF_3CO_2H (1.25 mmol) in cold CH_2Cl_2 (−40 °C) afforded ***14-anti*** (825 mg, 1.64 mmol, 33%) and ***14-syn*** (950 mg, 1.89 mol, 38%) after chromatographic separation.

Spectral data for ***14-syn***: [α] = −47.5° (*c* = 0.10, CH_2Cl_2); IR (neat, cm^{-1}) ν(CO) 2018 (s), 1917 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 5.32 (s, 5H, Cp), 4.86 (dd, J = 9.2, 3.9 Hz, 1H, OCH), 4.11−4.00 (m, 2H, OCH_2), 3.76 (d, J = 3.9 Hz, 1H, η^3-CH), 3.48 (dt, J = 9.2, 5.0 Hz, 1H, OCH), 3.05 (d, J = 4.0 Hz, 1H, η^3-C*H*H′), 1.49 (d, J = 4.0 Hz, 1H, η^3-CH*H*′), 1.45 (s, 3H, CH_3), 1.36 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 221.9, 220.5, 176.1, 110.0, 93.5, 81.0, 79.5, 68.8, 67.4, 65.4, 27.0, 25.3, 20.0; MS (75 eV; *m*/*e*) 502 (M^+), 474 (M^+ − CO). Anal. Calcd for $C_{17}H_{18}WO_6$: C, 40.66; H, 3.61. Found: C, 40.65; H, 3.77.

Spectral data for ***14-anti***: [α] = 66.9° (*c* = 0.25, CH_2Cl_2); IR (neat, cm^{-1}): ν(CO) 1956 (vs), 1887 (vs); ^1H NMR (400 MHz, $CDCl_3$) δ 5.33 (s, 5H, Cp), 4.42 (d, J = 6.8 Hz, 1H, OCH), 4.16−4.02 (m, 3H, OCH + OCH_2), 3.65 (s, 1H, η^3-CH), 3.05 (d, J = 4.0 Hz, 1H, η^3-C*H*H′), 1.47 (d, J = 4.0 Hz, 1H, η^3-CH*H*′), 1.41 (s, 3H, CH_3), 1.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 224.7, 218.8, 176.0, 110.4, 93.8, 83.0, 82.8, 78.1, 68.1, 62.9, 26.7, 24.9, 20.9; MS (75 eV; *m*/*e*) 502 (M^+), 474 (M^+ − CO). Anal. Calcd for $C_{17}H_{18}WO_6$: C, 40.66; H, 3.61. Found: C, 40.55; H, 3.76.

(17) Intramolecular Cyclization of 12b. Compound **12b** (3.00 g, 4.87 mmol) and CF_3CO_2H (0.10 mL, 1.22 mmol) in cold CH_2Cl_2 (−40 °C) afforded **13** (1.66 g, 3.31 mmol, 68%) and ***14-syn*** (0.12, 0.24 mmol, 5%) after chromatographic separation. [α] = −9.5° (*c* = 0.44, $CHCl_3$). IR (neat, cm^{-1}): ν(CO) 2025 (s), 1919 (s), 1457, 1371. ^1H NMR (400 MHz, $CDCl_3$): δ 5.71 (t, J = 1.5 Hz, 1H, =CH), 5.45 (s, 5H, Cp), 4.64 (dd, J = 6.0, 1.5 Hz, 1H, OCH), 4.50 (dd, J = 4.4, 2.2 Hz, 2H, OCH_2), 3.98 (dd, J = 7.7, 6.4 Hz, 1H, OCH), 3.88 (q, J = 6.2 Hz, 1H, OC*H*H′), 3.78 (dd, J = 7.7, 5.8 Hz, 1H, OCH*H*′), 1.40 (s, 3H,

CH_3), 1.33 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 226.6, 216.0, 138.9, 120.9, 109.8, 91.2, 89.4, 87.7, 78.7, 66.5, 26.6, 25.3. MS (75 eV; *m/e*): 502 (M^+). Anal. Calcd for $C_{17}H_{18}WO_6$: C, 40.66; H, 3.61. Found: C, 40.75; H, 3.77.

(18) Intramolecular Cyclization of 12c. Compound **12c** (1.00 g, 2.10 mmol) and CF_3CO_2H (40 μL, 0.53 mmol) in cold CH_2Cl_2 (−40 °C) afforded **15-*anti*** (0.81 g, 1.60 mmol, 76%). $[\alpha] = -103.7°$ (*c* = 0.4, $CDCl_3$). IR (neat, cm^{-1}): ν(CO) 3423 (vs), 1970 (vs), 1898 (vs). ^1H NMR (400 MHz, $CDCl_3$): *endo* form, δ 5.35 (s, 5H, Cp), 4.54 (dd, *J* = 10.4, 1.5 Hz, 1H, C*H*OCH$_3$), 4.28 (dt, *J* = 10, 3.5 Hz, 1H, OCH), 3.89−3.74 (dd, *J* = 12.5, 3.5 Hz, 2H, CH_2OH), 3.42 (s, 3H, OCH_3), 3.17 (d, *J* = 1.5 Hz, 1H, η^3-CH), 2.93 (s, 1H, η^3-C*H*H′), 1.62 (s, 1H, η^3-CH*H*′); *exo* form, 5.44 (s, 5H, Cp), 4.35 (dt, *J* = 10.2, 3.2 Hz, 1H, OCH), 3.99 (dd, *J* = 10.2, 1.5 Hz, 1H, C*H*OCH$_3$), 3.89−3.74 (dd, *J* = 12.5, 3.5 Hz, 2H, OCH_2), 3.54 (s, 3H, OCH_3), 3.17 (d, *J* = 1.5 Hz, 1H, η^3-CH), 2.32 (d, *J* = 2.2 Hz, 1H, η^3-C*H*H′), 1.06 (d, *J* = 2.2 Hz, 1H, η^3-CH*H*′). ^{13}C NMR (100 MHz, $CDCl_3$): *endo* form, δ 223.6, 219.2, 169.7, 88.7, 83.3, 74.5, 72.5, 61.3, 57.6, 46.0, 23.6; *exo*-form, 244.0, 216.6, 172.6, 94.7, 83.5, 73.5, 73.6, 60.6, 58.2, 57.9, 55.6, 29.5. MS (75 eV; *m/e*): 502 (M^+). Anal. Calcd for $C_{17}H_{18}WO_6$: C, 40.66; H, 3.61. Found: C, 40.88; H, 3.77.

(19) Synthesis of Compound 16. To **15-*anti*** (1,00 g, 1.99 mL) in CH_2Cl_2 (10 mL) was added Ac_2O (0.28 mL, 2.99 mmol) and DMAP (0.48 g, 3.98 mL) at 23 °C; the mixture was stirred for 1 h. The solution was concentrated and eluted through a silica column to afford **16** (0.96 mg, 1.77 mmol, 89%) as a yellow solid. $[\alpha] = -172.5°$ (*c* = 1.0, $CDCl_3$). IR (neat, cm^{-1}): ν(CO) 1969 (vs), 1804 (vs), 1742 (s), 1708 (s). ^1H NMR (400 MHz, $CDCl_3$): *endo* form, δ 5.34 (s, 5H, Cp), 4.36−4.25 (m, 3H, OCH + OCH_2), 3.78 (d, *J* = 8.5 Hz, 1H, C*H*OMe), 3.40 (s, 3H, OCH_3), 3.17 (1H, s, η^3-C*H*H′), 2.65 (s, 1H, η^3-C*H*H′), 2.03 (s, 3H, OAc), 1.62 (s, 1H, η^3-CH*H*′); *exo* form, 5.39 (s, 5H, Cp), 4.54 (d, *J* = 6.2 Hz, 1H, CHOCH$_3$), 4.37−4.22 (3H, m), 3.46 (s, 3H, OCH_3), 3.17 (1H, s, η^3-C*H*H′), 2.38 (1H, s, η^3-CH), 2.07 (s, 3H, OAc), 1.11 (1H, s, η^3-CH*H*′). ^{13}C NMR (100 MHz, $CDCl_3$): *endo* form, δ 223.4, 220.7, 170.7, 169.8, 88.8, 80.5, 75.7, 72.9, 62.5, 57.6, 45.6, 23.9, 20.6; *endo* form, 223.7, 216.5, 171.5, 168.0, 94.3, 80.7, 75.0, 62.6, 59.1, 58.6, 55.2, 29.6, 20.6. MS (75 eV; *m/e*): 518 (M^+). Anal. Calcd for $C_{17}H_{18}O_7W$: C, 39.41; H, 3.5. Found: C, 39.46; H, 3.5.

(20) I_2 Oxidation of Compound 13. To compound **13** (200 mg, 0.44 mmol) in MeOH (3.0 mL) was added I_2 (120 mg, 0.48 mmol) at −40 °C, and the mixture was stirred for 4 h before an aqueous $NaHSO_3$ (2.00 M) solution (5.00 mL) was added. The solution was reduced to ca. 5 mL, and the remaining solution was extracted with diethyl ether (2 × 10 mL). The solution was concentrated and chromatographed by a preparative silica TLC to yield **17** (37.2 mg, 0.20 mmol, 45%) as an oil. $[\alpha] = -15.5°$ (*c* = 0.5, $CHCl_3$). IR (neat, cm^{-1}): ν(OH) 3450 (vs), ν(CO) 1700 (s), ν(C=C) 1624 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 6.84 (s, 1H, =C*H*H′), 4.96(dd, 1H, *J* = 9.6, 4.4 Hz, OCH), 4.78−4.85 (m, 2H, OCH_2), 3.76 (s, 3H, OMe), 3.67−3.78 (m, 3H, OCH+OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 155.1, 121.3, 89.4, 87.3, 78.6, 66.5, 51.2. MS (75 eV; *m/e*): 186 (M^+). HRMS: calcd for $C_8H_{10}O_5$ 186.0528, found 186.0497.

(21) Synthesis of Unsaturated γ-Lactone 18. To a mixture of **14-*syn*** and **14-*anti*** (500 mg, 0.996 mmol) in CH_3CN (5.0 mL, 0 °C) was added $NOBF_4$ (115 mg, 0.996 mmol), and the mixture was stirred for 20 min. To the resulting solution was added Bu_4NBH_4 (320 mg, 1.25 mmol) at 23 °C, and after 1 h $Ce(NH_4)_2(NO_3)_6$ (1.10 g, 1.99 mmol) was added to the mixture. The solution was concentrated and chromatographed by a preparative silica TLC to yield **18** as an oil (158 mg, 0.80 mmol, 58%). $[\alpha] = -45.4°$ (*c* = 1.0, $CHCl_3$). IR (neat, cm^{-1}): ν(CO) 1765 (s), ν(C=C) 1644 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.10 (t, *J* = 1.7 Hz, 1H, =CH), 4.69 (dd, *J* = 8.5, 1.7 Hz, 1H, OCH), 4.13−4.03 (dd, *J* = 9.4, 6.0 Hz, 2H, OCH_2), 3.83 (m, 1H, OCH), 1.91 (t, *J* = 1.6 Hz, 3H, =CCH_3), 1.43 (s, 3H, CH_3), 1.32 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 146.8, 131.2, 110.3, 80.9, 76.6, 67.2, 26.7, 25.0, 10.5. MS (75 eV; *m/e*): 198 (M^+). HRMS: calcd for $C_{10}H_{14}O_4$ 198.0892, found 198.0890.

(22) Synthesis of Unsaturated δ-Lactone 19. Compound **16** (0.50 g, 0.92 mmol), $NOBF_4$ (107 mg, 0.92 mmol), and Bu_4NBH_4 (237 mg, 0.92 mmol) afforded **19** as an oil (123 mg, 0.58 mmol, 63%). $[\alpha] = 30.5°$ (*c* = 1, $CHCl_3$). IR (neat, cm^{-1}): ν(CO) 1745 (s), ν(C=C) 1634 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 6.61 (d, *J* = 1.5 Hz, 1H, =CH), 4.43 (ddd, *J* = 8.7, 4.7, 3.2 Hz, 1H, OCH), 4.36−4.26 (dd, *J* = 12.3, 4.7, 3.2 Hz, 2H, CH_2-OAc), 3.42 (s, 3H, OCH_3), 2.07 (s, 3H, OAc), 1.93 (t, *J* = 1.6 Hz, =CMe, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 163.3, 138.5, 129.1, 78.2, 71.9, 62.8, 57.0, 20.5, 16.8; MS (75 eV *m/e*): 214 (M^+). HRMS: calcd for $C_{10}H_{14}O_5$ 214.0814, found 214.0812.

X-ray Diffraction Studies of 13, 14-*anti*, and 16. Single crystals of **13**, **14-*anti***, and **16** were sealed in glass capillaries under an inert atmosphere. Data for **13**, **14-*anti***, and **16** were collected on a Siemens SMART CCD diffractometer using graphite monochromated Mo Kα radiation. The structures of **13**, **14-*anti***, and **16** were solved by direct methods; all data reduction and structural refinements were performed with the Siemens SHELXTL-PLUS package. Crystal data, details of data collection and structural analysis of these three compounds are provided in the Supporting Information. For all structures, all non-hydrogen atoms were refined with anisotropic parameters, and all hydrogen atoms included in the structure factors were placed in idealized positions.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for compounds **13**, **14-*anti***, and **16** and an additional ORTEP drawing for **14-*syn*** (23 pages). Ordering information is given on any current masthead page.

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