

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 $\text{CF}_3\text{CO}_2\text{H}$ 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 alkoxy-carbonylations 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 $\text{CF}_3\text{SO}_3\text{H}$ (optimum conditions: H_2O , 0.8–1.0 equiv; $\text{CF}_3\text{SO}_3\text{H}$, 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^* ($\text{O}^* = ^{18}\text{O}$) 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 $\text{CF}_3\text{SO}_3\text{H}$

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 $\text{CF}_3\text{SO}_3\text{H}$ 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, $\text{R}' = \text{MeC}=\text{CH}_2$) and 0.90 for **8c** (entry 3, $\text{R}' = \text{cyclohexyl}$). Entries 4–6 show the results for the tripropylsiloxy derivatives **9b–d**; the **10b/4b** ratio was 1.2 for compound **9b** ($\text{R}' = \text{Et}$), 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

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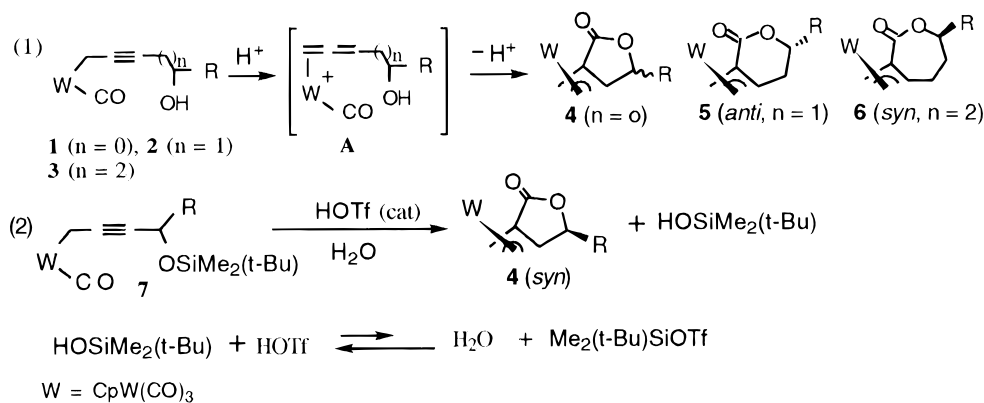
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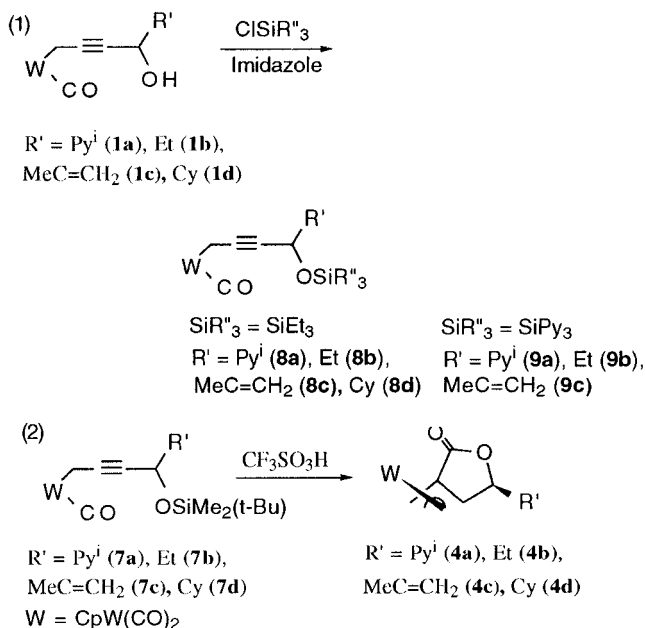
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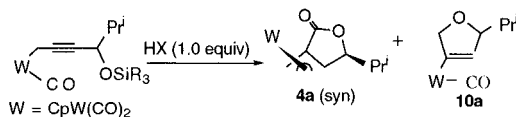
Scheme 1



Scheme 2



Scheme 3



Entry	η^1 -Propargyl	HX	Solvent	Products (Isolated Yields)
1	R = Et (8a)	CF ₃ CO ₂ H	CH ₂ Cl ₂	4a (26%) 10a (37%)
2	R = Et (8a)	CF ₃ CO ₂ H	CH ₃ CN	4a (21%) 10a (31%)
3	R = Et (8a)	CF ₃ SO ₃ H	CH ₂ Cl ₂	4a (24%) 10a (34%)
4	R = Py (9a)	CF ₃ CO ₂ H	CH ₂ Cl ₂	4a (25%) 10a (35%)

and dihydrofurans. Toward this direction, we prepared the chiral chloropropargylic triol⁶ **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)₃Na⁷ 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 CF₃CO₂H (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

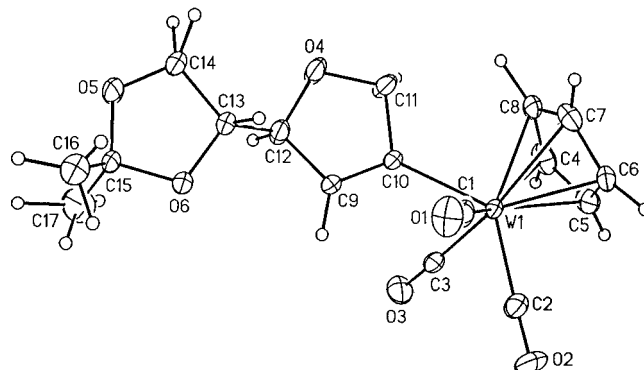


Figure 1. ORTEP drawing of compound **13**. Selected bond lengths (Å): W(1)–C(10) = 2.247(4), C(9)–C(10) = 1.330(7), C(10)–C(11) = 1.501(7), C(11)–O(4) = 1.441(7), C(12)–O(4) = 1.410(7).

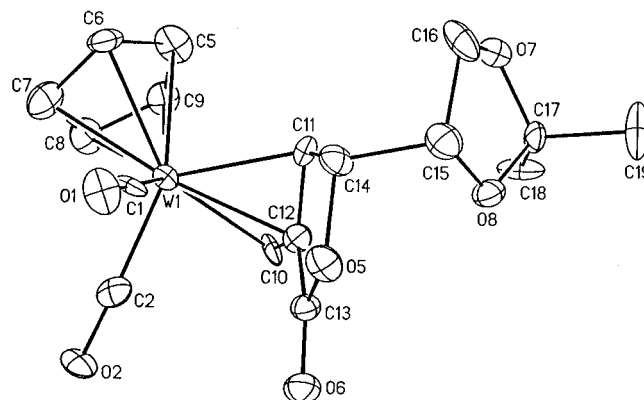


Figure 2. ORTEP drawing of compound **14-anti**. Selected bond lengths (Å): W(1)–C(10) = 2.301(15), W(1)–C(12) = 2.287(16), W(1)–C(10) = 2.301(15), C(10)–C(12) = 1.418(20), C(11)–C(12) = 1.416(21), C(13)–O(6) = 1.190(19).

equiv of CF₃CO₂H was used, the yields of **13** and **14** were 61% and 10%, respectively. The X-ray structure⁸ of **13** is given in Figure 1 to confirm its absolute configuration. By our previous method given in Scheme 1 (path 1), CF₃SO₃H-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 structure⁹ of **14-anti** to confirm its configuration. Treatment of

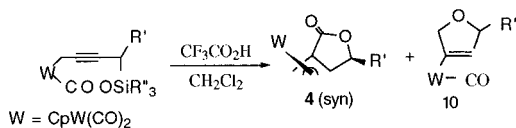
(8) Crystal data for compound **13**: orthorhombic, space group $P2_12_12_1$, $a = 7.1921(3)$ Å, $b = 10.1576(5)$ Å, $c = 23.9737(11)$ Å, $Z = 4$, $V = 1751.37(23)$ Å³, final $R = 0.0186$, $R_w = 0.0193$.

(9) Crystal data for compound **14-anti**: orthorhombic, space group $P2_12_12_1$, $a = 21.7945(4)$ Å, $b = 21.8583(2)$ Å, $c = 7.1876(1)$ Å, $Z = 8$, $V = 3424.1(11)$ Å³, final $R = 0.0465$, $R_w = 0.0434$.

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Scheme 4



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 CF₃SO₃H (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 study¹⁰ 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 than 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_γ carbon¹¹⁻¹³ of **12b**, yielding the η^2 -allene cationic intermediate **A**. We believe that 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, I₂ oxidative demetalation¹⁴ 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 NOBF₄ yielded an allyl cation¹⁵⁻¹⁷ that reacted with Bu₄NBH₄ 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 atmosphere 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 CaH₂ and distilled before use. W(CO)₆, CF₃CO₂H, CF₃SO₃H, 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). ¹H NMR (300 MHz; CDCl₃): δ 5.48 (s, 5H, Cp), 4.15 (m, 1H, OCH), 2.01 (d, *J* = 2.1 Hz, 2H, W-CH₂), 1.76 (m, 1H, CHMe₂), 0.94 (m, 15H, CHMe₂ + SiCH₂CH₃), 0.64 (m, 6H, Si(CH₂CH₃)₃). ¹³C NMR (75 MHz; CDCl₃): 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). ¹H NMR (300 MHz; CDCl₃): δ 5.49 (s, 5H, Cp), 4.30 (m, 1H, OCH), 1.99 (d, *J* = 2.2 Hz, 2H, W-CH₂), 1.63 (m; 2H, CH₂), 0.95 (m, 12H, CH₂CH₃ + SiCH₂CH₃), 0.63 (m, 6H, SiCH₂CH₃). ¹³C NMR (75

(10) Crystal data for compound **16**: monoclinic, space group *P*2₁, *a* = 8.0692(2) Å, *b* = 9.5150(2) Å, *c* = 12.0951(4) Å, *z* = 2, *V* = 879.6(3) Å³, final *R* = 0.0396, *R*_w = 0.0420.

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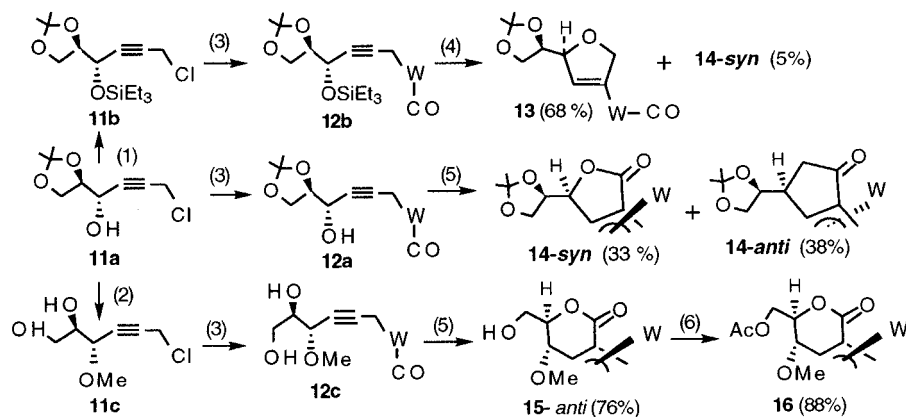
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Scheme 5



W = CpW(CO)₂ (1) C₁SiEt₃ (1.0 equiv), imidazole, 2.0 equiv (2) NaH (1.0 equiv), MeI (2.0 equiv); CH₃CO₂H (60 wt%) (3) NaCpW(CO)₃ (1.0 equiv) (4) CF₃CO₂H (0.25 equiv), -40 °C (5) CF₃SO₃H (0.25 equiv) (6) Ac₂O/DMAP

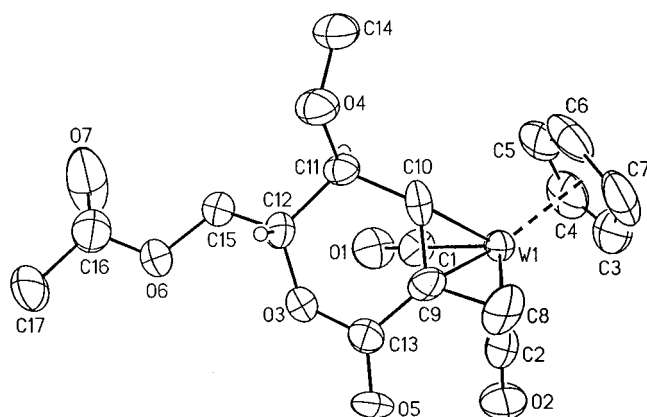
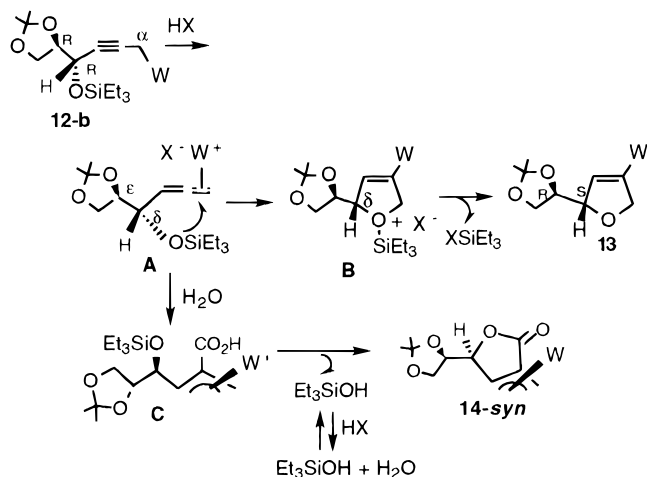


Figure 3. ORTEP drawing of compound **16**. Selected bond lengths (Å): W(1)–C(8) = 2.285(11), W(1)–C(1) = 1.994(11), W(1)–C(10) = 2.267(11), C(9)–C(8) = 1.416(16), C(9)–C(10) = 1.413(17), C(13)–O(5) = 1.206(14).

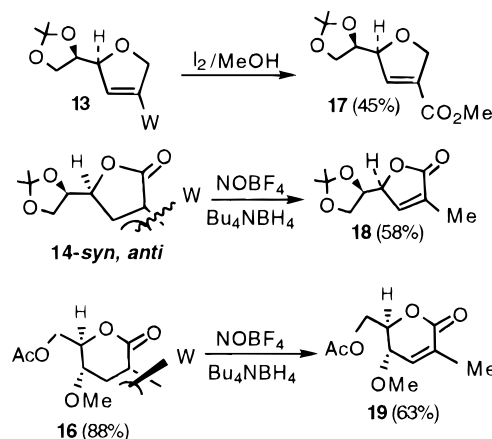
Scheme 6



MHz; CDCl₃): 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). ¹H NMR (300 MHz; CDCl₃): δ 5.48 (s, 5H, Cp), 5.04 (s, 1H, =CHH), 4.80 (s, 1H, =CHH); 4.78 (d, *J* = 2.2 Hz, 1H, OCH), 1.98 (d, *J* = 2.2 Hz, 2H, W–CH₂), 1.82 (s, 3H, Me), 0.95 (m, 9H, SiCH₂CH₃),

Scheme 7



0.64 (m, 6H, SiCH₂CH₃). ¹³C NMR (75 MHz; CDCl₃): δ 229.0, 216.3, 216.2, 146.2, 110.3, 94.3, 92.6, 81.6, 67.1, 17.8 (C₇), 6.8, 4.8, -32.3. MS (75 eV; *m/e*): 556 (M⁺).

(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). ¹H NMR (300 MHz; CDCl₃): δ 5.48 (s, 5H, Cp), 4.15 (m, 1H, OCH), 2.01 (d, *J* = 2.2 Hz, 2H, W–CH₂), 1.83–1.63, 1.23–1.03 (m, 11H, cyclohexyl), 0.96 (m, 9H, SiCH₂CH₃), 0.62 (m, 6H, Si(CH₂CH₃)₃). ¹³C NMR (75 MHz; CDCl₃): 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). ¹H NMR (300 MHz; CDCl₃): δ 5.46 (s, 5H, Cp), 4.15 (m, 1H, OCH), 2.00 (d, *J* = 2.2 Hz, 2H, W–CH₂), 1.73 (m, 1H, CHMe₂), 1.43–1.33 (m, 6H, (SiCH₂CH₂CH₃)), 0.97–0.91 (m, 15H, Si(CH₂CH₂CH₃) + 2Me), 0.66–0.59 (m, 6H, SiCH₂CH₂CH₃). ¹³C NMR (75 MHz; CDCl₃): 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). ¹H NMR (300 MHz; CDCl₃): δ 5.47 (s, 5H, Cp), 4.25 (m, 1H, OCH), 1.98 (d, *J* = 2.2 Hz, 2H, W–CH₂), 1.62 (m, 2H, CH₂), 1.43–1.33 (m, 6H, SiCH₂CH₂CH₃), 0.94 (m, 12H, SiCH₂CH₂CH₃ + Me), 0.64–0.58 (m, 6H, SiCH₂CH₂CH₃). ¹³C NMR (75 MHz; CDCl₃): 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}): $\nu(CO)$ 2021 (s), 1923 (s). 1H NMR (300 MHz; $CDCl_3$): δ 5.46 (s, 5H, Cp), 5.45 (s, 1H, =CHH), 5.02 (s, 1H, CHH'), 4.78 (s, 1H, OCH), 1.98 (d, $J = 2.2$ Hz, 2H, W-CH₂), 1.82 (s, 3H, C₅H), 1.44-1.28 (m, 6H, SiCH₂CH₂CH₃), 0.97-0.91 (m, 9H, SiCH₂CH₂CH₃), 0.65-0.60 (m, 6H, SiCH₂CH₂CH₃). ^{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}): $\nu(CO)$ 2023 (s), 1927 (s). 1H NMR (300 MHz; $CDCl_3$): δ 5.46 (s, 5H, Cp), 4.12 (m, 1H, C₄H), 2.00 (d, $J_{14} = 2.0$ Hz, 2H, C₁H), 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 (C₃), 92.6 (Cp), 81.0 (C₂), 68.1 (C₄), 45.7 (C₅), 28.9, 28.2, 26.6, 26.1, 25.9 (cyclohexyl), 18.6 (Si(CH₂CH₂CH₃)), 18.5 (Si(CH₂CH₂CH₃)), 16.8 (Si(CH₂CH₂CH₃)), -32.0 (C₁). 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 \times 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}) $\nu(CO)$ 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, OCH₂), 4.50 (s, 5H, Cp), 1.85 (m, 1H, CHMe₂), 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}): $\nu(CO)$ 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, OCH₂), 1.48 (m, 2H, CH₂), 0.85 (t, $J = 7.4$ Hz, 3H, CH₃). ^{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}): $\nu(CO)$ 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, =CHH'), 4.74 (s, 1H, =CHH'), 4.57 (m, 2H, C₁H), 1.59 (s, 3H, C₇H). ^{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}): $\nu(CO)$ 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 + OCH₂), 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 triol⁶ **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). $[\alpha] = 7.20^\circ$ ($c = 0.50$, CH_2Cl_2). IR (Nujol, cm^{-1}): 3445 (vs), $\nu(CO)$ 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, OCH₂), 1.91 (d, $J = 2.3$ Hz, 2H, W-CH₂). ^{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. $[\alpha] = 33.5^\circ$ ($c = 0.33$, CH_2Cl_2). IR (Nujol, cm^{-1}): $\nu(CO)$ 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 + OCH₂), 1.93 (d, $J = 2.1$ Hz, 2H, W-CH₂), 1.45 (s, 3H, CH₃), 1.30 (s, 3H, CH₃), 1.07 (t, $J = 8.0$ Hz, 9H, SiCH₂CH₃), 0.74 (q, $J = 8.0$ Hz, 6H, SiCH₂CH₃). ^{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. $[\alpha] = 29.5^\circ$ ($c = 0.25$, CH_2Cl_2). IR (Nujol, cm^{-1}): $\nu(OH)$ 3444 (vs), $\nu(CO)$ 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, OCH₂), 3.39 (s, 3H, OCH₃), 1.97 (d, $J = 2.3$ Hz, 2H, W-CH₂). ^{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**: $[\alpha] = -47.5^\circ$ ($c = 0.10$, CH_2Cl_2); IR (neat, cm^{-1}) $\nu(CO)$ 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, OCH₂), 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 -CHH'), 1.49 (d, $J = 4.0$ Hz, 1H, η^3 -CHH'), 1.45 (s, 3H, CH₃), 1.36 (s, 3H, CH₃); ^{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**: $[\alpha] = 66.9^\circ$ ($c = 0.25$, CH_2Cl_2); IR (neat, cm^{-1}) $\nu(CO)$ 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 + OCH₂), 3.65 (s, 1H, η^3 -CH), 3.05 (d, $J = 4.0$ Hz, 1H, η^3 -CHH'), 1.47 (d, $J = 4.0$ Hz, 1H, η^3 -CHH'), 1.41 (s, 3H, CH₃), 1.33 (s, 3H, CH₃); ^{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. $[\alpha] = -9.5^\circ$ ($c = 0.44$, $CHCl_3$). IR (neat, cm^{-1}): $\nu(CO)$ 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, OCH₂), 3.98 (dd, $J = 7.7$, 6.4 Hz, 1H, OCH), 3.88 (q, $J = 6.2$ Hz, 1H, OCHH'), 3.78 (dd, $J = 7.7$, 5.8 Hz, 1H, OCHH'), 1.40 (s, 3H,

CH₃), 1.33 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 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 C₁₇H₁₈WO₆: 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 CF₃CO₂H (40 μL, 0.53 mmol) in cold CH₂Cl₂ (−40 °C) afforded **15-anti** (0.81 g, 1.60 mmol, 76%). [α] = −103.7° (*c* = 0.4, CDCl₃). IR (neat, cm^{−1}): ν(CO) 3423 (vs), 1970 (vs), 1898 (vs). ¹H NMR (400 MHz, CDCl₃): *endo* form, δ 5.35 (s, 5H, Cp), 4.54 (dd, *J* = 10.4, 1.5 Hz, 1H, CHOCH₃), 4.28 (dt, *J* = 10, 3.5 Hz, 1H, OCH), 3.89–3.74 (dd, *J* = 12.5, 3.5 Hz, 2H, CH₂OH), 3.42 (s, 3H, OCH₃), 3.17 (d, *J* = 1.5 Hz, 1H, η³-CH), 2.93 (s, 1H, η³-CHH), 1.62 (s, 1H, η³-CHH); *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, CHOCH₃), 3.89–3.74 (dd, *J* = 12.5, 3.5 Hz, 2H, OCH₂), 3.54 (s, 3H, OCH₃), 3.17 (d, *J* = 1.5 Hz, 1H, η³-CH), 2.32 (d, *J* = 2.2 Hz, 1H, η³-CHH), 1.06 (d, *J* = 2.2 Hz, 1H, η³-CHH). ¹³C NMR (100 MHz, CDCl₃): *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 C₁₇H₁₈WO₆: 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 CH₂Cl₂ (10 mL) was added Ac₂O (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. [α] = −172.5° (*c* = 1.0, CDCl₃). IR (neat, cm^{−1}): ν(CO) 1969 (vs), 1804 (vs), 1742 (s), 1708 (s). ¹H NMR (400 MHz, CDCl₃): *endo* form, δ 5.34 (s, 5H, Cp), 4.36–4.25 (m, 3H, OCH + OCH₂), 3.78 (d, *J* = 8.5 Hz, 1H, CHOMe), 3.40 (s, 3H, OCH₃), 3.17 (1H, s, η³-CHH), 2.65 (s, 1H, η³-CHH), 2.03 (s, 3H, OAc), 1.62 (s, 1H, η³-CHH); *exo* form, 5.39 (s, 5H, Cp), 4.54 (d, *J* = 6.2 Hz, 1H, CHOCH₃), 4.37–4.22 (3H, m), 3.46 (s, 3H, OCH₃), 3.17 (1H, s, η³-CHH), 2.38 (1H, s, η³-CH), 2.07 (s, 3H, OAc), 1.11 (1H, s, η³-CHH). ¹³C NMR (100 MHz, CDCl₃): *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; *exo* 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 C₁₇H₁₈O₇W: C, 39.41; H, 3.5. Found: C, 39.46; H, 3.5.

(20) I₂ Oxidation of Compound 13. To compound **13** (200 mg, 0.44 mmol) in MeOH (3.0 mL) was added I₂ (120 mg, 0.48 mmol) at −40 °C, and the mixture was stirred for 4 h before an aqueous NaHSO₃ (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. [α] = −15.5° (*c* = 0.5, CHCl₃). IR (neat, cm^{−1}): ν(OH) 3450 (vs), ν(CO) 1700 (s), ν(C=C) 1624 (m). ¹H NMR (400 MHz, CDCl₃): δ 6.84 (s, 1H, =CHH), 4.96 (dd, 1H, *J* = 9.6, 4.4 Hz, OCH), 4.78–4.85 (m, 2H, OCH₂), 3.76 (s, 3H, OMe), 3.67–3.78 (m, 3H, OCH+OCH₂). ¹³C NMR (100 MHz, CDCl₃): 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 C₈H₁₀O₅ 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 CH₃CN (5.0 mL, 0 °C) was added NOBF₄ (115 mg, 0.996 mmol), and the mixture was stirred for 20 min. To the resulting solution was added Bu₄NBH₄ (320 mg, 1.25 mmol) at 23 °C, and after 1 h Ce(NH₄)₂(NO₃)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%). [α] = −45.4° (*c* = 1.0, CHCl₃). IR (neat, cm^{−1}): ν(CO) 1765 (s), ν(C=C) 1644 (m). ¹H NMR (400 MHz, CDCl₃): 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, OCH₂), 3.83 (m, 1H, OCH), 1.91 (t, *J* = 1.6 Hz, 3H, =CCH₃), 1.43 (s, 3H, CH₃), 1.32 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 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 C₁₀H₁₄O₄ 198.0892, found 198.0890.

(22) Synthesis of Unsaturated δ-Lactone 19. Compound **16** (0.50 g, 0.92 mmol), NOBF₄ (107 mg, 0.92 mmol), and Bu₄NBH₄ (237 mg, 0.92 mmol) afforded **19** as an oil (123 mg, 0.58 mmol, 63%). [α] = 30.5° (*c* = 1, CHCl₃). IR (neat, cm^{−1}): ν(CO) 1745 (s), ν(C=C) 1634 (m). ¹H NMR (400 MHz, CDCl₃): 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, CH₂OAc), 3.42 (s, 3H, OCH₃), 2.07 (s, 3H, OAc), 1.93 (t, *J* = 1.6 Hz, =CMe, 3H). ¹³C NMR (100 MHz, CDCl₃): 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 C₁₀H₁₄O₅ 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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