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Stereocontrolled Synthesis of Tungsten−π-Allyl Complexes Comprising Two Remoted Alcohols

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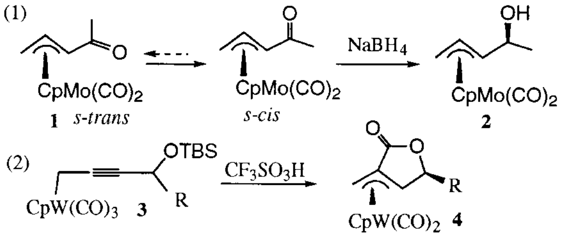
Organic lithium reagents add to the carbonyl group of $CpW(CO)_2(\eta^3$-γ-lactonyl) **4a** to give the π-allyl η^3-hydroxycarbonyl tungsten complexes **5a**−**5d** with good yields (79−94%). An X-ray study of compound **5a** revealed the acetyl group has π-delocalization with a tungsten−π-allyl group. A subsequent reaction of **5a** with DIBAL-H, RMgBr (R = Ph, Et), and ^{n}BuLi gave the diols $CpW(CO)_2[(3R^*,4S^*)$-π-2-$CMe(OH)R-CH_2CCHCMe(OH)]$ (R = H **6a**, Ph **6b**, Et **6c**, ^{n}Bu **6d**) as a single diastereomer; the yields were 64%−86%. The acyl group of $CpW(CO)_2[(3R^*,4S^*)$-π-2-$COMe-CH_2CCHCMe(OTBS)]$ **(7)** was deprotonated by LDA at −78 °C to form an enolate that condensed with RCHO (R = ^{i}Pr, ^{i}Bu) to form a pair of aldol products **8a**,**8b** and **9a**,**9b**, which were separated by column chromatography. In the presence of ^{n}-Bu_2BOTf, the diastereoselectivities of **8b** and **9b** were improved significantly. The structures of these aldol products were elucidated by X-ray diffraction study of the representative product **8b**.

Introduction

Nucleophilic addition of a C═X group (X = O, NR) adjacent to a metal fragment ML_n normally proceeds with high diastereoselectivities due to steric and electronic effects.[1,2] Sterically, a metal fragment can block nucleophilic attack from the metal side, and this phenomenon allows only anti-addition of nucleophiles.[1−3] For electron-rich metal fragments,[1−3] the orbital overlap between the metal fragment and the C═X group is significant, and in most cases only one confomer exists predominantly in both solution and solid structure. Scheme 1 (eq 1) shows an instance where the s-cis-conformer is the observed species for $CpMo(CO)_2(\pi$-1-$C_3H_4COMe)$[3b] (**1**) in solution, and its reaction with $NaBH_4$ and Grignard reagents gave only one stereoisomeric product. The resulting η^3-allyl alcohol (**2**) is subsequently transformed into various 1,3-diols on further functionalization.[3b] Recently, we reported an acid-catalyzed intramolecular carbonylation of tungsten−propargyl species (**3**) (eq 2), leading to a tungsten−syn-butyrolactonyl compound (**4**).[4,5] As a continuing work on functionalization of tungsten−allyl complexes, we report stereocontrolled synthesis of acyclic diols starting from tungsten π-butyrolactone complex **4**. Stereocontrolled synthesis of an acyclic molecule comprising two remoted alcohols is an intriguing topic in synthetic chemistry.

Scheme 1



Results and Discussions

Shown in Scheme 2 is ring-opening of compound **4a** effected by various organic lithium reagents to afford the alcohols **5a**−**5d**. The molecular structure of **5a**[6] was characterized by an X-ray diffraction study (Figure 1). The acetyl group is quite coplanar with the allyl fragment, and the dihedral angle between the two planes is ca. 4.5°. The ν(CO) frequency of the acetyl group is observed at 1660 cm^{-1}. This information suggests that the acetyl group forms partial π-overlap with its π-allyl group. Compound **5a** also retains the same conformation in solution according to its proton NOE NMR spectra. With the tungsten−π-allyl fragment as a stereotemplate, compound **5a** is transformed into acyclic diols **6a**−**6d** in the reactions with DIBAL-H, RMgBr (R = Ph, Et), and RLi (R = ^{n}Bu). The reactions proceed with excellent diastereoselectivities to give one

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(1) (a) Gree, R. *Synthesis* **1989**, 341. (b) Wada, C. K.; Roush, W. R. *Tetrahedron Lett.* **1994**, *35*, 7351. (c) Uemura, M. In *Advances in Metal-Organic Chemistry*; 1991; Vol. 2, p 1.

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(4) Chen, C.-C.; Fan, J. S.; Lee, G. H.: Peng, S. M.; Wang, S. L.; Liu, R. S. *J. Am. Chem. Soc.* **1995**, *117*, 2933.

(5) Chen, C.-C.; Fan J.-S.; Shieh, S.-J.; Lee G.-H.; Peng S.-M.; Wang S.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 9279.

(6) Crystal data for **5a**: tetragonal *P*-421*c*, a = 13.988(5) Å, c = 14.338(7) Å, V = 2809.4(17) A^3, Z = 8, final R = 0.025 and R_w = 0.0025 for 1210 observed reflections ($I > 2\sigma I$) out of 1396.

10.1021/om000556v CCC: $19.00

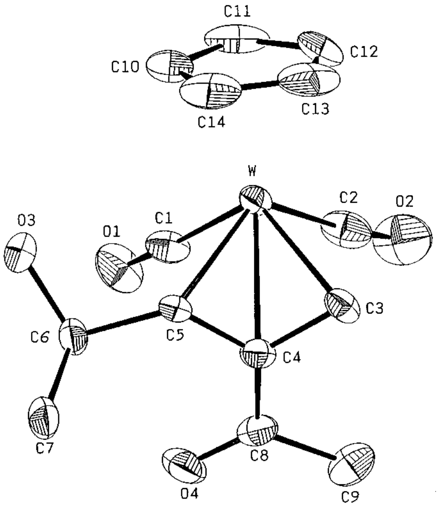
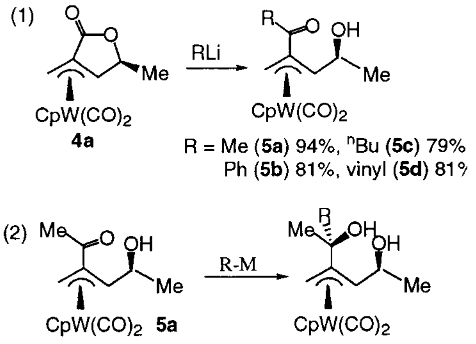


Figure 1. Molecular structure of compound **5a**. Selected bond distances (Å): C(3)−C(4) 1.434(15), C(4)−C(5) 1.437(14), C(4)−C(8) 1.490(16), C(8)−O(4) 1.216(15), C(6)−O(3) 1.436(14).

Scheme 2



entry	R-M	yields
1	DIBAL-H	R = H (**6a**) 65%
2	PhMgBr	R = Ph (**6b**) 85%
3	^{n}BuLi	R = ^{n}Bu (**6c**) 68%
4	EtMgBr	R = Et (**6d**) 68%

diastereomeric product in 65−86% yield. Clarification of the structures of **6a**−**6d** relies on X-ray diffraction studies of the representative compound **6a** (Figure 2).[7] The ORTEP drawing reveals that compound **6a** is produced via attack of hydride at the ketone group of **5a** anti to the tungsten−π-allyl fragment.

We also examined the aldol reaction of the *tert*-butyldimethylsilyloxy derivative **7** that was prepared in 89% yield from its parent alcohol **5a**. The enolate of compound **7** was generated by LDA at −78 °C in THF, and its reaction with aldehydes RCHO (R = ^{i}Pr, ^{i}Bu) at this temperature afforded two aldol products (R = ^{i}Pr, **8a** and **8b**; R = ^{i}Bu, **9a** and **9b**), respectively. These two diastereomers were separable on a silica column, and their isolated yields are shown in Scheme 3 (entries 1 and 3). Compounds **8a** and **9a** are distinguishable from **8b** and **9b** in their proton NMR spectra. The CH_2 protons of **8a** and **9a** show an AB pattern in the ^{1}H NMR spectra, whereas those of **8b** and **9b** show a simple doublet resonance. The structure of compound **8b** was determined by X-ray diffraction study (Figure 3).[9] The aldol diastereoselectivities can be improved significantly by the presence of ^{n}Bu$_2$BOTf, and the results are given in entries 2 and 4. The diastereomeric ratios of **8b**/**8a** (61/19) and **9b**/**9a** (70/13) were estimated on the basis of the yields of isolated products. The improving effect of ^{n}Bu$_2$BOTf suggests that the major diastereomers **8b** and **9b** are produced via a chairlike transition state **A**.[8−10] Such a transition state was previouly proposed for aldol reactions of molybdenum−π-allyl enolates.[3] To realize the synthetic utility of these complexes, com-

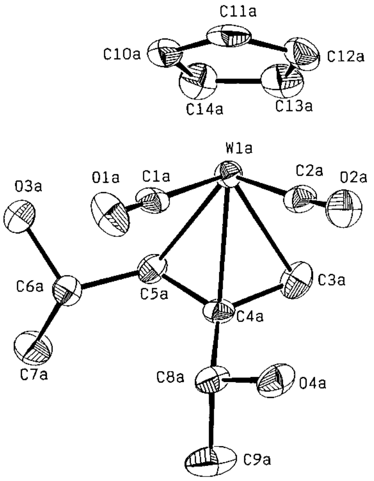
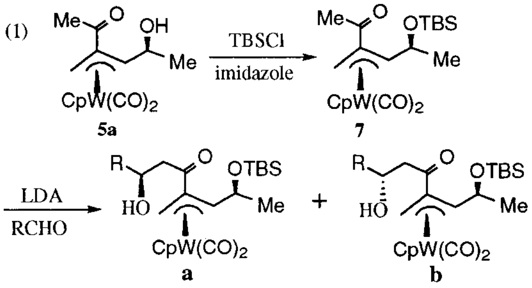
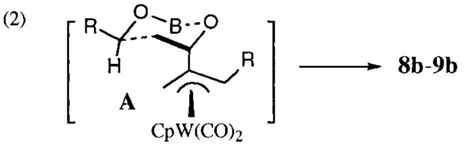


Figure 2. Molecular structure of compound **6a**. Selected bond distances (Å): C(3a)−C(4a) 1.453(15), C(4a)−C(5a) 1.438(13), C(4a)−C(8a) 1.513(14), C(8a)−O(4a) 1.411(12), C(6a)−O(3a) 1.447(12).

Scheme 3



entry	RCHO	L.A.	Yields
1	^{i}PrCHO	—	**8a** (37%), **8b** (45%)
2	^{i}PrCHO	Bu$_2$BOTf	**8a** (19%), **8b** (61%)
3	^{i}BuCHO	—	**9a** (33%), **9b** (50%)
4	^{i}BuCHO	Bu$_2$BOTf	**9a** (13%), **9b** (70%)



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[7] Crystal data for **6a**: monoclinic *P*21/*c*, *a* = 7.789(5) Å, *b* = 25.508(8) Å, *c* = 14.817(4) Å, *V* = 2931.1(22) A^3, *Z* = 8, final *R* = 0.035 and R_w = 0.035 for 3650 observed reflections ($I > 2\sigma I$) out of 5146 reflections.

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[10] Fellman, P.; Dubois, J. E. *Tetrahedron* **1978**, *34*, 1349.

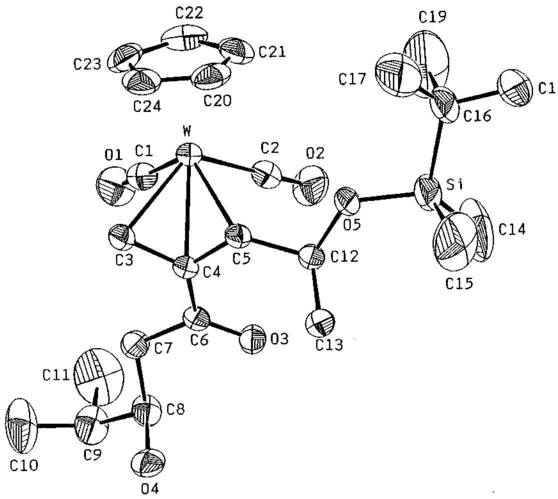
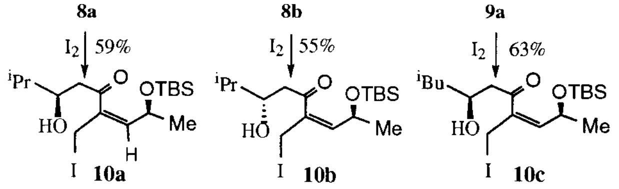


Figure 3. Molecular structure of compound **8b**. Selected bond distances (Å): C(3)–C(4) 1.413(7), C(4)–C(5) 1.417(7), C(4)–C(6) 1.496(7), C(6)–O(3) 1.220(6), C(8)–O(4) 1.422(7).

Scheme 4



pounds **8a**,**8b** and **9a** were demetalated smoothly by I_2 (1.0–1.1 equiv) in CH_2Cl_2 to afford the iodoallyl derivatives **10a**–**10c** in 55–63% yield (Scheme 4). The structures of **10a**,**10b** were determined by proton NOE NMR spectra. Irradation of the CHH′I signal (δ 4.33 ppm) of **10a** gives an increase in the intensity of the =CH proton (δ 6.32 ppm) by 2.0%. In contrast with **8a**, **9b**, and **9a**, I_2-oxidative demetalation of the π-allyl diols **6a**–**6d** gave a complicated mixture of products. This may be attributed to the vulnerability of the central alcohol, which easily undergoes ionization to form a tungsten–η^4-trimethylenemethane cation in acidic medium.[12] Treatment of **8a**,**8b** and **9a** with Ce(IV)-salt, $NOBF_4$/PhSNa,[13,14] and $NOBF_4/NaBH_4$ was also unsuccessful.

A metal fragment comprising two stereogenic alcohols, amines, and phosphines can be utilized as a ligand.[15] Compound **4a** can be prepared in enantiomerically pure form via chiral chloropropargyl alcohol.[4,5] In principle, chiral tungsten–π-allyl complexes having diols, diamines, and diphosphines can be prepapred using the allyl diols **6a**–**6d** as starting materials. These chiral compounds may be useful as a ligand in asymmetric catalysis. Studies toward this direction are currently underway.

Experimental Section

Unless otherwise noted, all reactions were carried out under 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 CaH_2 and distilled before use. $W(CO)_6$, sodium, dicyclopentadiene, propargyl bromide, methanesulfonamide, *p*-toluenesulfonamide, and benzaldehyde were obtained commercially and used without purification. Spectral data of compound **4a** were published previously.[5]

Reaction of MeLi with 4a. To a THF solution (12 mL) of compound **4a** (1.00 g, 2.40 mmol) was added MeLi (1.6 M, 1.60 mL, hexane) at −78 °C, and the mixture was stirred for 2 h before addition of a saturated NH_4Cl solution (2.0 mL). The organic layer was extracted with diethyl ether and eluted through a silica column (diethyl ether/hexane = 1/1) to give compound **5a** (0.97 g, 2.25 mmol, 94%) as a yellow solid. IR (CH_2Cl_2): ν(CO) 1969 (vs), 1897 (vs), 1661 (m) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$): δ 5.35 (s, 5H), 4.85 (m, 1H), 2.54 (s, 1H), 2.12 (s, 4H), 1.33 (d, J = 6.0 Hz, 3H), 1.11 (s, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 224.4; 220.2, 201.8, 93.7, 88.1, 83.9, 67.8, 61.8, 25.8, 25.4, 21.5. Mass (EI, 75 eV): 432 (M^+). Anal. Calcd for $C_{13}H_{14}WO_4$: C 38.91; H 3.73. Found: C 38.82; H 3.77.

Synthesis of Compound 5b. This compound was prepared similarly from the reaction between **4a** and PhLi. The crude product was purified by column chromatography (silica, diethyl ether/hexane = 1/1) to afford **5b** as a yellow solid (81% yield). IR (neat): ν(CO) 1964 (vs); 1895 (vs); 1620 (m) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$): δ 7.71–7.33 (m, 5H), 5.31 (s, 5H), 4.98 (m, 1H), 2.56 (s, 1H), 2.31 (d, J = 6.2 Hz,1H), 1.36 (d, J = 6.0 Hz, 3H), 1.24 (s, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 221.4; 221.1, 199.5, 139.5, 131.7, 128.6, 127.8, 87.9, 83.4, 68.0, 63.0, 25.6, 24.3. Mass (EI^+, 75 eV): 494 (M^+). Anal. Calcd for $C_{19}H_{18}WO_4$: C 46.18; H 3.67. Found: C 45.92; H 3.71.

Synthesis of Compound 5c. The reaction of **4a** and BuLi, followed by chromatographic purification (silica, diethyl ether/hexane = 1/1), gave **5c** as a yellow solid (79% yield). IR (CH_2Cl_2): ν(CO) 1967 (vs), 1899 (vs); 1659 (m) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$): δ 5.35 (s, 5H), 4.89 (m, 1H), 2.57 (s, 1H), 2.46–2.20 (m, 4H), 2.12 (d, J = 6.4 Hz, 1H), 1.59–1.54 (m, 2H), 1.32–1.22 (m, 2H), 1.36 (d, J = 6.4 Hz, 3H), 1.23 (s, 1H), 0.89 (t, J = 7.4 Hz). ^{13}C NMR (75 MHz; $CDCl_3$): δ 224.4; 220.4, 204.4, 88.1, 83.8, 67.9, 61.9, 37.2, 26.7, 25.3, 22.3, 22.2, 13.9. Mass (EI^+, 75 eV/m): 474 (M^+). Anal. Calcd for $C_{17}H_{22}WO_4$: C 43.06; H 4.68. Found. C 43.00; H 4.66.

Synthesis of Compound 5d. The reaction of **4a** with vinyllithium, followed by chromatographic purification (silica, diethyl ether/hexane = 2/5), gave **5d** as a yellow solid (81% yield). IR (CH_2Cl_2): ν(CO) 1968 (vs), 1898 (vs), 1658 (m) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$): δ 6.48 (d, 1H, J = 17.2 Hz), 6.30 (d, 1H, J = 10.2 Hz), 5.60 (d, J = 17.2. 10.2 Hz, 1H), 5.36 (s, 5H), 4.91 (m, 1H), 2.62 (s, 1H), 2.18 (d, J = 6.4 Hz, 1H), 1.39 (d, J = 6.1 Hz, 3H), 1.12 (s, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 224.9; 221.5, 192.4, 140.7, 128.7, 89.6, 85.0, 68.0, 63.0, 25.6, 22.3. Mass (EI^+, 75 eV): 444 (M^+).

Reaction of 5a with DIBAL-H. To a THF (12 mL) solution of **5a** (0.25 g, 0.58 mmol) was added DIBAL-H (1.0 M, 0.58 mL) at −78 °C, and the mixture was stirred for 2 h before it was warmed to 23 °C. The solution was quenched with a saturated NH_4Cl solution, and the organic layer was extracted with diethyl ether. The extract was dried in vacuo and eluted through a silica column (diethyl ether/hexane = 1/1) to give compound **6a** as a yellow solid (0.16 g, 0.37 mmol, 65%). IR (neat) ν(CO) 1960(s); 1894(s) cm^{-1}. ^1H NMR (300 MHz; C_6D_6): δ 4.58 (s, 5H), 4.25 (m, 2H), 2.99 (s, 1H), 2.36 (d, J = 9.4 Hz, 1H), 1.38 (t, J = 7.4 Hz, 3H), 1.36 (t, J = 7.4 Hz, 3H), 0.98 (s, 1H). ^{13}C NMR (75 MHz; toluene-d_8): δ 219.8; 219.6, 111.3, 89.9, 67.7; 67.2, 61.5, 28.8; 26.1, 24.3. Mass (EI^+, 75 eV): 433

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(11) Crystal data for **8b**: triclinic $P\bar{1}$, a = 8.554(3) Å, b = 11.988(3) Å, c = 13.859(4) Å, V = 1368.2(7) A^3, Z = 2, final R = 0.030 and R_w = 0.032 for 4264 observed reflections ($I > 2\sigma I$) out of 4820 reflections.

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(M^+). Anal. Calcd for $C_{14}H_{18}WO_4$: C 38.70; H 4.18. Found: C 38.0.66; H 4.25.

Synthesis of Compound 6b. The reaction of **5a** and PhMgBr, followed by chromatographic purification (silica, diethyl ether/hexane = 2/3), gave **6b** as a yellow solid (85% yield). IR (CH_2Cl_2): ν(CO) 1971 (vs), 1899 (vs), 1643 (m) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$): δ 5.33 (s, 5H), 4.92 (m, 1H), 4.02 (m, 1H), 2.54 (d, $J = 1.76$ Hz, 1H), 2.50 (d, $J = 2.1$ Hz, 1H), 2.48 (s, 1H), 2.25 (d, $J = 8.3$ Hz, 1H), 1.78 (m, 1H), 1.44 (m, 1H), 1.39 (d, $J = 5.7$ Hz, 3H), 1.11 (m, 2H), 0.89−0.86 (br s, 12H), 0.09 (s, 3H); 0.08 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 225.3; 220.9, 203.5, 88.6, 83.0, 70.0, 66.4, 62.9, 45.8, 43.9, 27.9, 26.0, 24.3, 23.4; 22.3, 22.0, 17.9, −3.9, −4.2. Mass (EI^+, 75 eV): 632 (M^+). Anal. Calcd for $C_{25}H_{40}WSiO_5$: 47.47; H 6.37. Found: C 47.58; H 6.29.

Synthesis of Compound 6c. The reaction of BuLi and **5a**, followed by chromatographic purification (silica, diethyl ether/hexane = 2/3), gave **6c** as a yellow solid (68% yield). IR (neat): ν(CO) 1967(s); 1892 (s) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$): δ 7.65−7.20 (m, 5H), 5.33 (s, 5H), 4.16 (m, 2H), 3.04 (s, 1H), 2.13 (d, $J = 5.1$ Hz, 1H), 1.73 (s, 1H), 1.49 (s, 1H), 0.74 (d, $J = 6.1$ Hz, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 219.8; 219.6, 111.3, 89.9, 67.7; 67.2, 61.5, 28.8; 26.1, 24.3. Mass (EI^+, 75 eV): 510 (M^+). Anal. Calcd for $C_{20}H_{22}O_4W$: C 47.08; H 4.35. Found: C 47.86; H 4.54.

Synthesis of Compound 6d. The reaction of EtMgBr and **5a**, followed by chromatographic purification (silica, diethyl ether/hexane = 1/1), gave **6d** as a yellow solid (68% yield). IR (neat): ν(CO) 1965(s); 1897 (s) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$): δ 5.31 (s, 5H), 4.82 (m, $J = 5.6$, 4.9 Hz, 1H), 2.50 (s, 1H), 2.24 (d, $J = 4.9$ Hz, 1H), 1.91 (m, 2H), 1.33 (s, 1H), 1.30 (d, $J = 5.6$ Hz, 3H), 1.23 (s, 1H), 0.98 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 229.7; 228.6, 110.6, 89.1, 77.4, 67.0, 58.1, 37.5, 25.8, 25.4, 22.7, 9.9. Mass (EI^+, 75 eV): 462 (M^+). Anal. Calcd for $C_{16}H_{22}WO_4$: C 41.58; H 4.80. Found: C 41.93; H 4.75.

Synthesis of the *tert*-Butyldimethylsilyloxy Derivative 7. To a *N*,*N*-dimethylformarmide solution (20 mL) of **5a** (5.10 g, 11.8 mmol) and imidazole (1.61 g, 23.6 mmol) was added *tert*-butyldimethylsilyl chloride (1.95 g, 12.9 mmol), and the mixture was stirred for 12 h before it was quenched with water (2.0 mL). The organic layer was extracted with diethyl ether (3 × 50 mL). The ether extract was dried over $CaCl_2$ and eluted through a silica column (diethyl ether/hexane = 1/2) to afford compound **7** as a yellow solid (5.72 g, 10.5 mmol, 89%). IR (CH_2Cl_2): ν(CO) 1968 (vs); 1897 (vs); 1660 (m) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$): δ 5.32 (s, 5H), 4.91 (m, 1H), 2.57 (d, $J = 1.6$ Hz, 1H), 2.31 (d, $J = 8.4$ Hz, 1H), 1.39 (d, $J = 5.8$ Hz, 3H), 1.24 (d, $J = 1.6$ Hz, 1H), 0.89 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 221.4, 221.1, 199.5, 139.5, 131.7, 128.6, 127.8, 87.9, 83.4, 68.0, 63.0, 25.6, 24.3. Mass (EI^+, 75 eV): 546 (M^+). Anal. Calcd for $C_{20}H_{30}WSiO_4$: C 43.97; H 5.53. Found: C 44.06; H 5.54.

Condensation of the Enolate of 7 with ^{i}PrCHO. To a THF solution (20 mL) of **7** (400 mg, 0.73 mmol) was added LDA (1.6 M, 6.8 mL, 1.1 mmol) at −78 °C, and the mixture was stirred for 1 h before addition of isopropyl aldehyde (80 mg, 1.1 mmol). The solution was stirred for 2 h before it was quenched with water. The organic layer was extracted with diethyl ether, dried over $CaCl_2$, and eluted through a silica column (diethyl ether/hexane = 1/1) to give **8a** (167 mg, 0.27 mmol, 37%) and **8b** (197 mg, 0.32 mmol, 45%), respectively.

Spectral data for **8a**: IR (CH_2Cl_2) ν(CO) 1971; 1901; 1644 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 5.32 (s, 5H), 4.90 (m, 1H), 3.81 (m, 1H), 2.64 (dd, $J = 17.0$, 2.0 Hz, 1H), 2.51 (d, $J = 1.7$ Hz), 2.32 (dd, $J = 17.0$, 10 Hz, 1H), 2.25 (d, $J = 8.4$ Hz, 1H), 1.66 (m, 1H), 1.39 (d, $J = 5.8$ Hz, 3H), 1.10 (d, $J = 1.7$ Hz, 1H), 0.89 (br s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 224.6; 220.8, 202.9, 88.5, 83.2, 72.5, 70.1, 63.0, 40.7, 33.1, 27.9, 26.0, 22.1, 18.4; 17.8, 17.9, −3.9, −4.2; Mass (EI^+, 75 eV) 618 (M^+). Anal. Calcd for $C_{24}H_{38}WSiO_5$: C 46.61; H 6.19. Found. C 46.71; H 6.18.

Spectral data for **8b**: IR (CH_2Cl_2) ν(CO) 1972 (vs); 1900 (vs); 1644 (m) cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 5.30 (s, 5H), 4.90 (m, 1H), 3.70 (q, $J = 5.8$ Hz, H), 2.54 (d, $J = 1.8$ Hz, 1H), 2.48 (d, $J = 5.8$ Hz, 2H), 2.25 (d, $J = 8.3$ Hz, 1H), 1.63 (m, 1H), 1.36 (d, $J = 5.8$ Hz, 3H), 1.09 (d, $J = 1.8$ Hz, 1H), 0.87 (br s, 12H,), 0.07 (s, 3H); 0.05 (s, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 225.2; 220.9, 203.8, 88.5, 83.1, 72.7, 70.0, 62.9, 40.2, 33.1, 27.9, 25.9, 22.3, 18.3; 17.7, 17.9, −3.9, −4.2; Mass (EI^+, 75 eV) 618 (M^+). Anal. Calcd for $C_{24}H_{38}WSiO_5$ C 46.61; H 6.19. Found: C 46.76; H 6.20.

Aldol Reaction in the Presence of Bu_2BOTf. The enolate generated from LDA and **7** was added a THF solution of isopropyl aldehyde (80 mg, 1.1 mmol) and Bu_2BOTf (1.1 mmol) at −78 °C, and the mixture was stirred for 2 h before it was quenched with water. Workup of the solution gave **8a** and **8b** in 19% and 61%, respectively.

Syntheses of Compounds 9a and 9b. These two compounds were prepared similarly from the enolate of **7** with isobutylaldehyde; the yields of **9a** and **9b** were 32% and 50%, respectively.

Spectral data for **9a**: IR(CH_2Cl_2) ν(CO) 1974 (vs); 1901(vs), 1644 (m) cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 5.32 (s, 5H), 4.90 (m, 1H), 4.10 (m, 1H), 2.64 (dd, $J = 17.1$, 2.5 Hz, 1H), 2.50 (d, $J = 1.7$ Hz, 1H), 2.35 (dd, $J = 17.1$, 8.9 Hz, 1H), 2.24 (d, $J = 8.34$ Hz, 1H), 1.80 (m, 1H), 1.45 (m, 1H), 1.38 (d, $J = 5.8$ Hz, 3H), 1.09 (m, 2H), 0.88 (br s, 12H), 0.08 (s, 3H); 0.06 (s; 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 224.7; 220.8, 202.8, 88.5, 83.0, 70.1, 66.1, 63.0, 45.7, 44.3, 27.9, 26.0, 24.4, 23.4; 22.0, 21.9, 17.9, −3.9; −4.2; Mass (EI^+, 75 eV) 632 (M^+). Anal. Calcd for $C_{25}H_{40}O_5SiW$: C 47.47; H 6.37. Found: C 47.40; H 6.43.

Spectral Data for **9b**: IR (CH_2Cl_2) ν(CO) 1971 (vs), 1899 (vs), 1643 (m) cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 5.33 (s, 5H), 4.92 (m, 1H), 4.02 (m, 1H), 2.54 (d, $J = 1.8$ Hz, 1H), 2.50 (d, $J = 2.1$ Hz, 1H), 2.48 (s, 1H), 2.25 (d, $J = 8.3$ Hz, 1H), 1.78 (m, 1H), 1.44 (m, 1H), 1.39 (d, $J = 5.7$ Hz, 3H), 1.11 (m, 2H), 0.89 (s, 3H); 0.86 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 225.3; 220.9, 203.5, 88.6, 83.0, 70.0, 66.4, 62.9, 45.8, 43.9, 27.9, 26.0, 24.3, 23.4; 22.3, 22.0, 17.9, −3.9, −4.2; Mass (EI^+, 75 eV) 632 (M^+). Anal. Calcd for $C_{25}H_{40}WO_5Si$: C 47.47; H 6.37. Found: C 47.58; H 6.29.

I_2-Demetalation of 8a. To a CH_2Cl_2 solution (5.0 mL) of **8a** (167 mg, 0.27 mmol) was added I_2 (76.2 mg, 0.30 mmol) at −40 °C, and the mixture was slowly warmed to 0 °C over a period of 8 h. To the solution was added $Na_2S_2O_3$ (20 mg), and the mixture was filtered and concentrated to leave an oil. Elution of this residue over a preparative TLC plate afforded **10a** as an oil (49.8 mg, 0.16 mmol, 59%). ^1H NMR (300 MHz; $CDCl_3$): δ 6.32 (d, $J = 2.0$.Hz, 1H), 4.33 (d, $J = 9.0$ Hz, 1H), 4.23 (q, $J = 6$.Hz, 1H), 3.75 (d, $J = 9.0$ Hz, 1H), 3.48 (m, 1H), 2.77 (m, 2H), 1.68 (m, 1H), 1.25 (d, $J = 6.8$ Hz), 0.94 (d $J = 6.6$ Hz, 3H), 0.86 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 200.8, 143.3, 137.2, 79.3, 76.7, 50.1, 33.3, 21.1, 18.6, 18.1, 4.8. Mass (EI^+ , *m*/*e*): 313 (M^+). Anal. Calcd for $C_{11}H_{19}IO_3$: C, 58.12; H, 8.43. Found: C, 58.24; H, 8.43.

Synthesis of Compound 10b. The reaction of **8b** and I_2, followed by purification on a silica TLC plate, gave **10b** as a colorless oil (55% yield). ^1H NMR (300 MHz; $CDCl_3$): δ 6.52 (d, $J = 3.1$ Hz, 1H), 4.62 (dq, $J = 6.8$, 3.1 Hz, 1H), 4.04 (s, 2H), 3.65 (m, 1H), 2.77 (m, 2H), 1.75 (m, 1H), 1.35 (d, $J = 6.8$ Hz, 1H), 0.94 (d $J = 6.6$ Hz, 3H), 0.86 (d,$J = 6.6$ Hz, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 199.6, 146.1, 139.2, 74.2, 69.3, 48.9, 32.5, 20.5, 18.7, 2.65. Mass (EI^+ , *m*/*e*): 313 (M^+). Anal. Calcd for $C_{11}H_{19}IO_3$: C, 58.12; H, 8.43. Found: C, 58.04; H, 8.40.

Synthesis of Compound 10c. The reaction of **9a** and I_2, followed by purification on a silica TLC plate, gave **10c** as a colorless oil (63% yield). ^1H NMR (300 MHz; $CDCl_3$): δ 6.38 (d, $J = 2.2$ Hz, 1H), 4.33 (d, $J = 8.9$ Hz, 1H), 4.29 (q, $J = 6.4$ Hz, 1H), 3.89 (m, 1H), 3.77 (d, $J = 8.9$ Hz, 1H), 2.76

(d, $J = 6.7$ Hz, 2H), 1.75 (m, 1H), 1.48 (m, 1H), 1.25 (d, $J = 6.8$ Hz), 1.18 (m, 1H), 0.89 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 200.0, 144.1, 137.5, 75.9, 72.5, 52.5, 44.8, 24.7, 23.2, 22.3, 21.4, 4.0.44. Mass (EI$^+$, m/e): 327 (M$^+$).

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Supporting Information Available: X-ray data of **5a**, **6a**, and **8b** including an ORTEP drawing, bond distances and angles, atomic coordinates, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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