Supporting Information

for Unique Synthetic Utility of BF_3•OEt_2 in the Highly Diastereoselective Reduction of Hydroxy Carbonyl and Dicarbonyl Substrates

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Typical Procedure of BF_3•OEt_2-Promoted Reduction of α-Hydroxy Ketone 1a with Bu_3SnH (Table 1, entry 1). To a solution of α-hydroxy ketone **1a** (45.0 mg, 0.3 mmol) in toluene (3 mL) was added BF_3•OEt_2 (45.6 µL, 0.36 mmol) dropwise at -78 °C under argon and the solution was stirred for 5 min at the same temperature. Then Bu_3SnH (98.8 µL, 0.36 mmol) was added dropwise and the reaction mixture was stirred for 2 h at -78 °C, and poured into ice-cooled saturated $NaHCO_3$. The whole mixture was stirred for several hours and extracted three times with EtOAc. The combined organic extracts were dried over Na_2SO_4 and K_2CO_3. Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (EtOAc/hexane = 1:1 as eluant) gave the corresponding diol **2a** and **3a** (80% yield, **2a**:**3a** = 13:1 by ^{1}H NMR analysis).

Typical Procedure of $TiCl_4$-Promoted Reduction of α-Hydroxy Ketone 1a with Et_3SiH (Table 1, entry 3). To a solution of α-hydroxy ketone **1a** (45.0 mg, 0.3 mmol) in CH_2Cl_2 (3 mL) was added a 1 M CH_2Cl_2 solution of $TiCl_4$ (0.36 mL, 0.36 mmol) dropwise at -78 °C under argon and the solution was stirred for 5 min at the same temperature. Then Et_3SiH (57.5 µL, 0.36 mmol) was added dropwise and the reaction mixture was stirred at -78 °C for 1 h and at 25 °C for additional 8 h. The mixture was poured into ice-cooled 1*N* HCl and extracted with EtOAc. The organic extracts were sequentially washed with saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. After the similar purification by column chromatography as described above gave the diol **2a** and **3a** (75% yield, **2a**:**3a** = 1:1.6 by ^{1}H NMR analysis).

Typical Procedure of TiF_4-Promoted Reduction of α-Hydroxy Ketone 1a with Bu_3SnH (Table 1, entry 5). TiF_4 powder (44.6 mg, 0.36 mmol) was placed in a dry, two-neck flask with stirring bar under argon atmosphere. Then CH_2Cl_2 (3 mL) was introduced at ambient temperature. α-Hydroxy ketone **1a** (45.0 mg, 0.3 mmol) was added at -78 °C and the suspension was stirred for 5 min at the same temperature. Then Bu_3SnH (98.8 µL, 0.36 mmol) was added dropwise and the reaction mixture was stirred at -78 °C for 5 min and at 25 °C for additional 20 h.

The similar workup and purification procedure as described for the $TiCl_4$-promoted reduction gave the diol **2a** and **3a** (87% yield, **2a**:**3a** = 1:1.8 by ^{1}H NMR analysis).

Typical Procedure of $SnCl_4$-Promoted Reduction of α-Hydroxy Ketone 1a with Et_3SiH (Table 1, entry 6). The procedure was exactly the same as described for $TiCl_4$-Et_3SiH system except for the reaction condition, which was at -78 °C for 5 min and at 25 °C for 20 h, and only a trace amount of the diol was obtained.

Other hydroxy ketones and γ-keto aldehydes were reduced as described for each Lewis acid under the conditions given in the Tables..

Characterization of Unknown Compounds.

γ-Hydroxy Ketone 1c: 300 MHz ^{1}H NMR ($CDCl_3$) δ 8.00 (2H, m, Ph), 7.44-7.62 (3H, m, Ph), 3.75 (1H, ddd, J = 6.0, 6.9, 7.2 Hz, O=CCH), 3.70 (2H, t, J = 6.0 Hz, CH_2O), 2.13 (1H, ddt, J = 6.0, 6.9, 12.0 Hz, CH_2), 1.72 (1H, dq, J = 6.0, 12.0 Hz, CH_2), 1.62 (1H, br, OH), 1.24 (3H, d, J = 7.2 Hz, CH_3); IR (liquid film) 3429, 3061, 2970, 2934, 2878, 1682, 1597, 1580, 1448, 1377, 1231, 1049, 974, 704 cm^{-1}. MS: 178 (M$^+$) (100%), 161, 134. FD-HRMS Calcd for $C_{11}H_{14}O_2$: 178.0994 (M$^+$). Found:178.0976 (M$^+$).

γ-Keto Aldehyde 5b: 300 MHz ^{1}H NMR ($CDCl_3$) δ 9.69 (1H, t, J = 1.8 Hz, CHO), 7.24-7.67 (15H, m, Ph), 5.43 (1H, t, J = 6.0 Hz, O=CCH), 2.89 (1H, ddd, J = 1.8, 6.0, 16.8 Hz, CH_2), 2.78 (1H, ddd, J = 1.8, 6.0, 16.8 Hz, CH_2), 1.03 (9H, s, *t*-Bu); IR (KBr) 3053, 2936, 2860, 1722, 1693, 1595, 1475, 1448, 1429, 1258, 1138, 1113, 1070, 1005, 982, 824, 739, 692 cm^{-1}. MS: 359 ([M-*t*-Bu]$^+$), 281, 199 (100%). Anal. Calcd for $C_{26}H_{28}O_3Si$: C, 74.96; H, 6.77. Found: C, 74.81; H, 6.90.

Silyloxy Diol 6b: 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.65-7.71 (2H, m, Ph), 7.26-7.50 (13H, m, Ph), 4.74 (1H, t, J = 4.8 Hz, PhCH-O), 4.12 (1H, dt, J = 2.1, 4.2 Hz, CHOSi), 3.52 (1H, m, CH_2O), 3.41 (1H, m, CH_2O), 3.11 (1H, br, OH), 1.45-1.74 (2H, m, CH_2), 1.00 (9H, s, *t*-Bu); IR (liquid film) 3323, 3071, 2932, 2858, 1495, 1472, 1452, 1427, 1192, 1082, 1028, 999, 822, 741, 700, 611 cm^{-1}. MS: 421 ([M+H]$^+$) (100%), 363, 345, 313, 255, 107. FD-HRMS Calcd for $C_{26}H_{33}O_3Si$: 421.2200 ([M+H]$^+$). Found: 421.2229 ([M+H]$^+$).

Dihydroxy Ketone 9: 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.92-7.98 (2H, m, Ph), 7.60-7.67 (1H, m, Ph), 7.48-7.56 (2H, m, Ph), 5.30 (1H, ddd, J = 3.0, 5.4, 9.3 Hz, O=CCH), 3.93 (2H, dd, J = 5.7, 14.7 Hz, CH_2O), 3.91 (1H, br, OH), 2.34 (1H, br, OH), 2.16 (1H, dddd, J = 3.3, 5.4, 6.9, 14.7 Hz, CH_2), 1.74 (1H, dddd, J = 3.3, 4.5, 5.7, 9.3 Hz, CH_2); IR (KBr) 3350, 3275, 1684, 1595, 1452, 1373, 1317, 1246, 1109, 1051, 986, 864, 787, 760, 691, 662 cm^{-1}. MS: 181 ([M+H]$^+$), 162, 105 (100%), 77, 75. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.45; H, 6.71.

α-Hydroxy Ketone 10: 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.98-8.04 (2H, m, Ph), 7.58-7.76 (5H, m, Ph), 7.30-7.52 (8H, m, Ph), 5.41 (1H, ddd, J = 2.4, 6.6, 9.0 Hz, O=CCH), 4.01 (1H, ddd, J = 3.9, 9.3, 9.9 Hz, CH_2OSi), 3.86 (1H, ddd, J = 4.8, 5.1, 9.9 Hz, CH_2OSi), 3.72 (1H, d, J = 6.6, OH), 2.17 (1H, dddd, J = 2.4, 5.1, 9.3, 15.0 Hz, CH_2), 1.63 (1H, dddd, J = 3.9, 4.8, 9.0, 15.0 Hz, CH_2), 1.09 (9H, s, *t*-Bu); IR (KBr) 3501, 3069, 2955, 2932, 2856, 1680, 1600, 1472, 1425, 1377, 1306, 1273, 1113, 1078, 1059, 984, 949, 820, 741, 694 cm^{-1}. MS: 400 ([M-H_2O]$^+$), 359, 345, 329, 283 (100%), 199. Anal. Calcd for $C_{24}H_{30}O_3Si$: C, 74.60; H, 7.22. Found: C, 74.54; H, 7.19.

γ-Hydroxy Ketone 11: The complete structural assignment has been performed after conversion to the corresponding acetate. 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.73 (2H, m, Ph), 7.64 (2H, m, Ph), 7.57 (2H, m, Ph), 7.22-7.53 (9H, m, Ph), 5.40 (1H, t, *J* = 6.0 Hz, O=CCH), 4.17 (1H, dt, *J* = 6.0, 11.1 Hz, CH_2OAc), 4.11 (1H, dt, *J* = 6.0, 11.1 Hz, CH_2OAc), 2.10 (2H, q, *J* = 6.0 Hz, CH_2), 1.84 (3H, s, Ac), 1.08 (9H, s, *t*-Bu); IR (liquid film) 2961, 2934, 2858, 1742, 1701, 1597, 1427, 1366, 1240, 1113, 1045, 966, 824, 741, 702, 613 cm^{-1}. MS: 461 ([M+H]$^+$), 403 (100%), 383, 256, 57. FD-HRMS Calcd for $C_{28}H_{33}O_4Si$: 461.2148 ([M+H]$^+$). Found: 461.2118 ([M+H]$^+$).

Silyloxy Diol 12: 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.62-7.68 (4H, m, Ph), 7.23-7.48 (11H, m, Ph), 4.84 (1H, dd, *J* = 3.3, 3.6 Hz, PhCH-O), 4.13 (1H, m, CH-O), 3.83 (1H, dt, *J* = 4.8, 10.2 Hz, CHOSi), 3.78 (1H, ddd, *J* = 3.3, 9.3, 10.2 Hz, CHOSi), 3.75 (1H, br, OH), 2.83 (1H, br, OH), 1.79 (1H, dddd, *J* = 3.6, 9.3, 10.2, 10.4 Hz, CH_2), 1.48 (1H, m, CH_2), 1.05 (9H, s, *t*-Bu); IR (KBr) 3360, 3339, 3071, 2930, 2856, 1472, 1427, 1391, 1207, 1113, 1088, 1049, 939, 824, 756, 737, 702, 615 cm^{-1}. MS: 421 ([M+H]$^+$) (100%), 363, 345, 313, 255, 107. FD-HRMS Calcd for $C_{26}H_{33}O_3Si$: 421.2200 ([M+H]$^+$). Found: 421.2205 ([M+H]$^+$).