Supporting Information

A Novel Titanium-Catalyzed Cyclization of Olefinic Iodoethers to Tetrahydrofurans

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General Procedure for the Preparation of 1a – 1j. The olefinic iodoether **1** was prepared according to the literature procedure.¹ Under argon, an allyl alcohol (7.52 mmol) was added to a solution of an olefin (3.76 mmol) in dry CH₂Cl₂ (25 mL) at room temperature. After stirring for 5 min, the reaction mixture was cooled to -78 °C. *N*-Iodosuccinimide (1.27 g, 5.64 mmol) was then added to the mixture, which was allowed to reach 0 °C within 6 h. A saturated aqueous solution of Na₂S₂O₃ was added to the reaction mixture, which was stirred vigorously for 5 min. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂.

The combined organic layer was dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluting with hexane/Et₂O (20:1 – 1:1) to give the iodide **1**.

Representative Procedure for the Intramolecular Cyclization of 1. To a mixture of Cp₂TiCl₂ (12.5 mg, 0.050 mmol) and manganese powder (220 mg, 4.0 mmol) in THF (6 mL) was added Me₃SiCl (0.13 mL, 1.0 mmol) at room temperature under argon. After stirring for 30 min, a solution of **1** (0.5 mmol) in THF (3 mL) was added to the mixture. The mixture was kept at the indicated temperature with magnetic stirring for the time indicated in the table. Then, the reaction mixture was subjected to workup with 1 M HCl (3 mL) and ether (50 mL). The organic layer was washed with saturated aqueous Na₂S₂O₃ (10 mL), water (10 mL), and brine (10 mL), dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography on silica gel (20 g; eluent, hexane/ethyl acetate = 50:0, 48:2, 46:4, 44:6, 42:8, 40:10, 38:12, 35:15, 32:18, 28:22, 25:25, 50 mLxeach), giving **2**.

2a:¹ colorless oil. *trans*: ¹H NMR (CDCl₃) δ 1.09 (d, 3H, *J* = 6.9 Hz), 1.85 ~ 2.04 (m, 2H), 2.36 ~ 2.50 (m, 1H), 3.45 (dd, 1H, *J* = 8.1, 6.9 Hz), 3.80 (s, 3H), 4.20 (dd, 1H, *J* = 8.4, 6.9 Hz), 4.97 (t, 1H, *J* = 6.9 Hz), 6.85 ~ 6.89 (m, 2H), 7.23 ~ 7.29 (m, 2H); ¹³C NMR (CDCl₃) 17.9, 33.3, 42.6, 55.2, 75.5, 79.7, 113.5, 126.7, 135.6, 158.5 ppm. *cis*: ¹H NMR (CDCl₃) δ 1.10 (d, 3H, *J* = 6.9 Hz), 1.88 ~ 2.04 (m, 1H), 2.39 ~ 2.50 (m, 2H), 3.57 (t, 1H, *J* = 8.1 Hz), 3.80 (s, 3H), 4.07 (t, 1H, *J* = 8.1 Hz), 4.86 (dd, 1H, *J* = 10.0, 5.7 Hz), 6.85 ~ 6.89 (m, 2H), 7.23 ~ 7.29 (m, 2H); ¹³C NMR (CDCl₃) 17.6, 34.9, 43.8, 55.2, 75.2, 81.3, 113.6, 126.8, 135.1, 158.6 ppm.

MS (EI): 192 (M^+ , 64), 191 (73), 161 (35), 135 (100). HRMS (EI) Calcd for $C_{12}H_{16}O_2$ (M^+): 192.1150. Found: 192.1144.

2b: colorless oil. *trans*: 1H NMR ($CDCl_3$) δ 0.97 (d, 3H, J = 6.9 Hz), 1.01 (s, 3H), 1.36 (s, 3H), 2.00 ~ 2.11 (m, 3H), 3.78 (s, 3H), 4.97 (t, 1H, J = 7.0 Hz), 6.82 ~ 6.87 (m, 2H), 7.23 ~ 7.27 (m, 2H); ^{13}C NMR ($CDCl_3$) 14.6, 21.5, 27.7, 42.0, 42.5, 55.2, 76.8, 83.2, 113.4, 126.7, 137.1, 158.3 ppm. *cis*: 1H NMR ($CDCl_3$) δ 0.99 (d, 3H, J = 6.9 Hz), 1.12 (s, 3H), 1.31 (s, 3H), 2.00 ~ 2.11 (m, 3H), 3.78 (s, 3H), 4.87 (dd, 1H, J = 10.2, 5.4 Hz), 6.82 ~ 6.87 (m, 2H), 7.23 ~ 7.27 (m, 2H); ^{13}C NMR ($CDCl_3$) 14.6, 24.3, 28.1, 43.7, 44.2, 55.2, 78.4, 83.2, 113.4, 126.8, 137.1, 158.3 ppm. MS (EI): 220 (M^+ , 78), 219 (36), 162 (53), 147 (71), 137 (71), 135 (100), 108 (68), 84 (35), 69 (49). HRMS (EI) Calcd for $C_{14}H_{20}O_2$ (M^+): 220.1463. Found: 220.1474.

2c: colorless oil. *trans*: 1H NMR ($CDCl_3$) δ 0.90 (t, 3H, J = 6.9 Hz), 1.24 ~ 1.46 (m, 6H), 1.93 ~ 2.10 (m, 3H), 3.48 (t, 1H, J = 8.0 Hz), 3.80 (s, 3H), 4.21 (t, 1H, J = 8.0 Hz), 4.94 (t, 1H, J = 6.9 Hz), 6.85 ~ 6.89 (m, 2H), 7.22 ~ 7.26 (m, 2H); ^{13}C NMR ($CDCl_3$) 14.1, 22.8, 30.8, 33.0, 39.0, 40.8, 55.2, 74.1, 79.7, 113.5, 126.6, 135.7, 158.5 ppm. *cis*: 1H NMR ($CDCl_3$) δ 0.98 (t, 3H, J = 7.5 Hz), 1.24 ~ 1.46 (m, 6H), 2.25 ~ 2.33 (m, 3H), 3.60 (t, 1H, J = 8.1 Hz), 3.80 (s, 3H), 4.07 (t, 1H, J = 8.0 Hz), 4.83 (dd, 1H, J = 10.2, 5.7 Hz), 6.85 ~ 6.89 (m, 2H), 7.22 ~ 7.26 (m, 2H); ^{13}C NMR ($CDCl_3$) 13.9, 25.8, 30.7, 33.1, 40.5, 42.1, 55.2, 73.9, 81.3, 113.5, 126.8, 135.7, 158.5 ppm. MS (EI): 234 (M^+ , 69), 233 (84), 203 (40), 137 (30), 136 (69), 135 (100), 134 (24), 121 (24). HRMS (EI) Calcd for $C_{15}H_{22}O_2$ (M^+): 234.1620 Found: 234.1620.

2e: colorless oil. 2,3-*trans*-3,5-*trans*-2,5-*cis*: 1H NMR ($CDCl_3$) δ 1.05 (d, 3H, J = 6.3 Hz),

1.30 (d, 3H, $J = 6.0$ Hz), 1.53 ~ 2.48 (m, 3H), 3.54 ~ 3.81 (m, 1H), 3.79 (s, 3H), 4.90 ~ 4.99 (m, 1H), 6.84 ~ 6.89 (m, 2H), 7.23 ~ 7.28 (m, 2H); ^{13}C NMR (CDCl_3) 16.8, 19.4, 40.2, 43.1, 55.2, 78.8, 79.3, 113.5, 126.7, 135.9, 158.5 ppm. 2,3-*trans*-3,5-*cis*-2,5-*trans*: ^1H NMR (CDCl_3) δ 1.07 (d, 3H, $J = 6.6$ Hz), 1.35 (d, 3H, $J = 6.0$ Hz), 1.53 ~ 2.48 (m, 3H), 3.54 ~ 3.81 (m, 1H), 3.79 (s, 3H), 4.90 ~ 4.99 (m, 1H), 6.84 ~ 6.89 (m, 2H), 7.23 ~ 7.28 (m, 2H); ^{13}C NMR (CDCl_3) 16.0, 19.3, 42.7, 44.8, 55.2, 82.0, 82.5, 113.5, 126.8, 136.0, 158.5 ppm. 2,3-*cis*-3,5-*trans*-2,5-*trans*: ^1H NMR (CDCl_3) δ 1.01 (d, 3H, $J = 7.2$ Hz), 1.20 (d, 3H, $J = 7.2$ Hz), 1.53 ~ 2.48 (m, 3H), 3.54 ~ 3.81 (m, 1H), 3.79 (s, 3H), 5.08 (t, 1H, $J = 7.2$ Hz), 6.84 ~ 6.89 (m, 2H), 7.23 ~ 7.28 (m, 2H); ^{13}C NMR (CDCl_3) 14.0, 16.3, 36.6, 42.6, 55.2, 78.0, 78.1, 113.5, 126.5, 136.4, 158.5 ppm. MS (EI): 206 (M^+ , 73), 205 (61), 175 (24), 162 (36), 137 (30), 136 (63), 135 (100), 134 (39), 121 (19), 108 (27), 55 (18). HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ (M^+): 206.1307. Found: 206.1295.

2f:¹ colorless oil. ^1H NMR (CDCl_3) δ 1.15 (s, 3H), 1.19 (s, 3H), 1.67 (dd, 1H, $J = 12.3, 9.3$ Hz), 2.08 (dd, 1H, $J = 12.3, 6.6$ Hz), 3.64 (d, 1H, $J = 8.1$ Hz), 3.74 (d, 1H, $J = 7.8$ Hz), 3.80 (s, 3H), 4.99 (dd, 1H, $J = 9.3, 6.6$ Hz), 6.86 ~ 6.89 (m, 2H), 7.26 ~ 7.28 (m, 2H). ^{13}C NMR (CDCl_3) 26.5, 26.8, 40.1, 49.7, 55.2, 80.5, 80.8, 113.6, 126.7, 135.4, 158.5 ppm. MS (EI): 206 (M^+ , 88), 205 (77), 175 (44), 161 (40), 137 (59), 136 (54), 135 (100), 121 (22), 55 (20). HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ (M^+): 206.1307. Found: 206.1320.

2g:¹ colorless oil. *endo*: ^1H NMR (CDCl_3) δ 1.21 ~ 2.42 (m, 11H), 3.79 (s, 3H), 4.22 (dd, 1H, $J = 7.5, 3.9$ Hz), 5.12 (t, 1H, $J = 7.8$ Hz), 6.84 ~ 6.89 (m, 2H), 7.24 ~ 7.33 (m, 2H). *exo*: ^1H

NMR (CDCl₃) δ 1.21 ~ 2.42 (m, 11H), 3.79 (s, 3H), 4.00 (dd, 1H, J = 9.6, 4.5 Hz), 4.90 (t, 1H, J = 7.8 Hz), 6.84 ~ 6.89 (m, 2H), 7.24 ~ 7.33 (m, 2H). mixture: ¹³C NMR (CDCl₃) 19.8, 20.6, 21.6, 23.8, 24.1, 26.2, 27.4, 28.5, 28.6, 29.0, 38.1, 38.7, 39.0, 40.5, 41.9, 42.0, 55.2, 77.8, 78.5, 79.2, 79.6, 113.5, 113.6, 126.5, 126.7, 126.8, 127.8, 128.6, 135.5, 136.1, 137.1, 158.3, 158.4, 158.6 ppm. MS (EI): 232 (M⁺, 49), 231 (M⁺-1, 44), 187 (31), 147 (20), 136 (47), 135 (100), 134 (64), 121 (23), 108 (30), 81 (15). HRMS (EI) Calcd for C₁₅H₂₀O₂ (M⁺): 232.1463. Found: 232.1463.

2h: colorless oil. *trans*: ¹H NMR (CDCl₃) δ 0.89 (d, 3H, J = 7.5 Hz), 0.92 (t, 3H, J = 6.3 Hz), 1.01 (s, 3H), 1.30 (s, 3H), 1.24 ~ 1.73 (m, 5H), 1.85 ~ 2.02 (m, 1H), 2.15 ~ 2.40 (m, 1H), 3.27 ~ 3.37 (m, 1H), 3.62 ~ 3.73 (m, 1H), 4.94 (d, 1H, J = 4.8 Hz); ¹³C NMR (CDCl₃) 13.9, 14.3, 19.5, 23.4, 29.2, 31.9, 40.0, 40.9, 66.5, 83.7, 101.7 ppm. *cis*: ¹H NMR (CDCl₃) δ 0.89 (d, 3H, J = 7.5 Hz), 0.94 (t, 3H, J = 6.3 Hz), 1.12 (s, 3H), 1.20 (s, 3H), 1.24 ~ 1.73 (m, 5H), 1.85 ~ 2.02 (m, 1H), 2.15 ~ 2.40 (m, 1H), 3.27 ~ 3.37 (m, 1H), 3.62 ~ 3.73 (m, 1H), 5.03 (dd, 1H, J = 6.0, 4.5 Hz); ¹³C NMR (CDCl₃) 13.9, 14.4, 19.4, 22.7, 27.7, 32.0, 41.0, 42.6, 66.5, 83.7, 101.7 ppm. MS (CI): 187 (M⁺+1, 16), 169 (20), 113 (100). HRMS (CI) Calcd for C₁₁H₂₃O₂ (M⁺+1): 187.1698. Found: 187.1702.

2i: colorless oil. ¹H NMR (CDCl₃) δ 0.91 (t, 3H, J = 7.5 Hz), 1.06 (s, 3H), 1.13 (s, 3H), 1.24 ~ 1.93 (m, 6H), 3.24 ~ 3.69 (m, 4H), 5.12 ~ 5.15 (dd, 1H, J = 5.4, 3.0 Hz). ¹³C NMR (CDCl₃) 14.0, 19.4, 25.9, 27.9, 31.9, 47.4, 67.5, 78.6, 81.5, 105.0 ppm. MS (CI): 173 (M⁺+1, 100), 99 (97). HRMS (CI) Calcd for C₁₀H₂₁O₂ (M⁺+1): 173.1542. Found: 173.1546.

2j:² colorless oil. *trans*: ¹H NMR (CDCl₃) δ 0.91 (t, 3H, *J* = 7.5 Hz), 1.02 (d, 3 H, *J* = 6.6 Hz), 1.22 ~ 1.59 (m, 6H), 2.23 ~ 2.25 (m, 1H), 3.33 ~ 3.43 (m, 2H), 3.63 ~ 3.69 (m, 1H), 3.90 ~ 4.05 (m, 1H), 5.08 ~ 5.19 (m, 1H). *cis*: ¹H NMR (CDCl₃) δ 0.90 (d, 3H, *J* = 7.5 Hz), 1.07 (d, 3 H, *J* = 6.0 Hz), 1.22 ~ 1.59 (m, 6H), 2.23 ~ 2.25 (m, 1H), 3.33 ~ 3.43 (m, 2H), 3.63 ~ 3.69 (m, 1H), 3.90 ~ 4.05 (m, 1H), 5.08 ~ 5.19 (m, 1H). mixture: ¹³C NMR (CDCl₃) 13.9, 17.4, 19.4, 31.9, 32.9, 40.8, 67.4, 73.2, 104.7 ppm. MS (CI): 159 (M⁺+1, 100), 85 (93). HRMS (CI) Calcd for C₉H₁₉O₂ (M⁺+1): 159.1385. Found: 159.1387.

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