

Supporting Information

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Asymmetric Catalysis of Intramolecular Cyclopropanation of 5-Aryl-1-diazo-1-mesitylsulfonyl-5-hexene-2-ones

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Supporting Information

General Information. ¹H and ¹³C NMR spectra were recorded on a JEOL AL-400 spectrometer. ¹H and ¹³C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, d scale) with the solvent resonances as internal standards. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; band, several overlapping signals; b, broad. IR spectra were recorded on a JASCO FT/IR-8300. Melting points (mp) are uncorrected, recorded on a Yamato capillary melting point apparatus. Optical rotations were measured using a 2 mL cell with a 1 dm path length on a JASCO DIP-1000. Chiral HPLC analysis was performed on a JASCO PU-980 and UV-970. Mass spectra and elemental analyses were provided at the Materials Characterization Central Laboratory, Waseda University. All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and phosphomolybdic acid and heat as developing agents. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on self-made 0.3 mm E. Merck silica gel plates (60F-254). Materials. THF was distilled from sodium/benzophenone ketyl, and methylene chloride (CH₂Cl₂), benzene, and toluene from calcium hydride.. Toluene was distilled from sodium. DMF was distilled from CaH₂ under reduced pressure. (CuOTf)₂C₆H₆ and all other reagents were purchased from

Ethyl 4-(3,4-Dimethoxyphenyl)-5-pentenoate (11)

Aldrich, TCI, or Kanto Chemical Co. ltd.

To a solution of **10** (2.87 g, 13.9 mmol) in DME/H₂O (1/1.5, 140 mL) was added 3, 4-dimethoxyphenylboric acid (3.03 g, 16.6 mmol), Pd(OAc)₂ (155.6 mg, 0.70 mmol), P(o-tol)₃ (421.9 mg, 1.39 mmol), and Ba(OH)₂·H₂O (3.16 g, 16.6 mmol) successively, and the mixture was stirred at 50°C. After the starting material disappeared, the precipitate was filtered through a pad of Celite, and washed with ethyl acetate (100 mL). The filtrate was concentrated under vacuum, and the residue was diluted with CH₂Cl₂ (80 mL), washed with H₂O (40 mL). The aqueous layer was extracted with CH₂Cl₂ (50 mL × 3), and the combined organic layer was washed with brine (40 mL), dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane / ethyl acetate = 15 / 1) to afford **11** (5.65 g, 13.6 mmol, 98 %) as a white

solid: R_f = 0.25 (hexane / ethyl acetate = 4 / 1); mp = 44 - 45 °C; IR(KBr): 2984, 1734, 1604, 1582, 1522, 1472, 1438, 1418, 1382, 1316, 1252, 1220, 1172, 1150, 1112, 1026, 886, 796 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): d = 6.97 (dd, J = 8.3, 2.0 Hz, 1H), 6.94 (d, J = 2.0 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H), 5.24 (s, 1H), 5.03 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 2.81 (t, J = 7.7 Hz, 2H), 2.48 (t, J = 7.7 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); ¹³C-NMR (100 Hz, CDCl₃): d = 173.0, 148.5, 146.3, 133.3, 118.3, 111.4, 110.7, 109.3, 60.3, 55.8, 55.8, 33.3, 30.5, 14.2; HRMS (FAB): m/z calcd for $C_{15}H_{20}O_4$ 264.1362, found 264.1343.

5-(3,4-Dimethoxyphenyl)-1-(2,4,6-trimethylphenylsulfonyl)-5-hexen-2-one (12)

To a solution of methyl-2, 4, 6-trimethylphenylsulfone (638.7 mg, 3.93 mmol) in THF (20 mL) was added n-BuLi (1.57 M, 12.3 mL, 7.86 mmol) at 0°C, and stirred at room tepmerature for 1 h. To the resultant stirred orange suspension was added **11** (207.1 mg, 3.96 mmol) in THF (2 mL \times 2) via a canula at 0°C. The reaction mixture was stirred at 0 °C for 1h, and quenched with saturated aqueous NH₄Cl solution (20 mL), extracted with Et₂O (5 mL \times 1), and CH₂Cl₂(10 mL \times 3). The combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane / ethyl acetate = 6 / 1) to afford **12** (1.34 g, 3.22 mmol, 82 %) as a white solid: R_f=0.28 (hexane / ethyl acetate = 2 / 1); mp = 87-88 °C; IR(KBr): 2940, 1716, 1604, 1520, 1462, 1316, 1254, 1216, 1172, 1148, 1028, 890, 746, 518 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): d = 6.97 (s, 2H), 6.95-6.89 (m, 2H), 6.83 (d, J = 8.3 Hz, 1H), 5.24 (s, 1H), 5.01 (s, 1H), 4.10 (s, 2H), 3.89 (s, 6H), 2.90 (t, J = 7.6 Hz, 2H), 2.77 (t, J = 7.6 Hz, 2H), 2.60 (s, 6H), 2.31 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): d = 197.7, 148.7, 148.7, 145.8, 143.9, 139.9, 132.9, 132.8, 132.3, 118.3, 111.9, 110.8, 109.3, 66.9, 55.9, 55.9, 43.7, 29.0, 22.9, 21.1; HRMS (FAB) : m/z calcd for C₂₃H₂₈O₅S 416.1657, found 416.1657.

2-Diazo-5-(3, 4-dimethoxyphenyl)-1-(2,4,6-trimethylphenylsulfonyl)-5-hexen-2-one (9)

To a solution of **10** (598.3 mg, 1.56 mmol) in CH₃CN (15 mL) was added triethylamine (0.64 mL, 4.62 mmol) at 0°C, and then a solution of *p*-toluenesulfonylazide (615.9 mg, 4.60 mmol) in CH₃CN (2.0 mL × 2) via a cannula. The reaction mixture was stirred at room temperature for 3 h. The light yellow reaction mixture was quenched with 3N KOH aqueous solution (15 mL), extracted with ether (15 mL), and CH₂Cl₂ (10 mL × 3). The combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography (hexane / ethyl acetate = 12 / 1) to afford **9** (643.4 mg, 1.45 mmol, 93 %) as an yellow solid: R_f = 0.40 (hexane / ethyl acetate = 1 / 1); mp = 107-108 °C; IR (KBr) : 2120, 1666, 1602, 1520, 1454, 1416, 1328, 1278, 1256, 1230, 1178, 1150, 1028, 886, 678, 666, 596, 538 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): d = 6.93 (s, 2H), 6.87-6.77 (m, 3H), 5.16 (s, 1H), 4.87 (s, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.57 (s, 6H), 2.52 (t, *J* = 7.7 Hz, 2H), 2.30 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): d = 188.2, 148.7, 148.7, 145.9, 144.1, 139.9, 134.8, 132.9, 132.4, 118.3, 111.8, 110.9, 109.2, 55.9, 55.8, 38.0, 29.2, 22.5, 21.1; HRMS(FAB):*m/z* calcd for C₁₆H₁₈N₂O₃H⁺ 287.1395, found 287.1410.

5-(3,4-Dimethoxyphenyl)-2-oxo-1-(2,4,6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (8)

The same procedure as that for **14** in Experimental Section of text, and purification by flash chromatography (hexane / ethyl acetate = 4 / 1) afforded **8** as a white solid: Ee (0 % ee) was determined by HPLC (254 nm); Daicel Chiral Cell AS-H 0.46 cm? × 25 cm; hexane / 2-propanol = 3 / 1; flow rate = 0.4 mL / min); retention time : 27.0 min for *ent-8*, 27.0 min for **8**: R_f = 0.14 (hexane / ethyl acetate = 2 / 1); mp = 110-111 °C; IR (KBr): 2940, 1734, 1606, 1522, 1434, 1314, 1272, 1256, 1238, 1142, 1028, 984, 804, 656, 514cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): d = 7.18-7.13 (m, 2H), 6.95 (s, 2H), 6.89 (d, J = 7.8 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.00 (d, J = 4.9 Hz, 1H), 2.59-2.20 (m, 4H), 2.29 (s, 3H), 2.07 (d, J = 4.9 Hz, 1H); ¹³C-NMR (100 MHz, CDCl₃): d = 203.9, 148.8, 148.4, 142.8, 140.5, 135.3, 131.9, 129.1, 121.7, 113.2, 110.5, 59.3, 56.0, 55.7, 48.4, 34.0, 30.8, 27.2, 23.5, 21.0; HRMS(FAB): m/z calcd for m/z calcd for $C_{21}H_{22}O_3SH^+$ 355.1368, found 355.1339.

2-Diazo-5-phenyl-1-(2,4,6-trimethylphenylsulfonyl)-5-hexen-2-one (13)

The same procedure as that for **9**, and purification by flash chromatography (hexane / ethyl acetate = 30 / 1) afforded **13** (1.22 g, 89 %) as an yellow solid: $R_f = 0.64$ (hexane / ethyl acetate = 2 / 1); mp = 87-88 °C; IR (KBr) : 2104, 1684, 1602, 1462, 1322, 1262, 1244, 1188, 1172, 1142, 914, 782, 714, 700, 668, 594 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): d = 7.33-7.24 (m, 5H), 6.92 (s, 2H), 5.22 (s, 1H), 4.93 (s, 1H), 2.71 (t, J = 7.7 Hz, 2H), 2.57 (s, 6H), 2.52 (t, J = 7.7 Hz, 2H), 2.29 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): d = 188.2, 146.3, 144.0, 140.0, 134.8, 132.5, 128.3, 127.6, 125.9, 113.0, 37.8, 29.0, 22.5, 21.1; HRMS(FAB):m/z calcd for $C_{16}H_{18}N_2O_3H^+$ 287.1395, found 287.1410.

2-Diazo-5-(3,4-methylenedioxyphenyl)-1-(2,4,6-trimethylphenylsulfonyl)-5-hexen-2-one (15)

The same procedure as that for **9**, and purification by flash chromatography (hexane / ethyl acetate = 30/1) afforded **15** (0.35 g, 72 %) as an yellow solid: R_f = 0.33 (hexane / ethyl acetate = 4/1); mp = 77-78 °C; IR (KBr) : 2180, 1676, 1508, 1494, 1446, 1326,1242, 1224, 1180, 1148, 1036, 668, 600cm^{-1} ; ¹H-NMR (400 MHz, CDCl₃): d = 6.94 (s, 2H) ,6.81-6.69 (m, 3H), 5.97 (s, 2H), 5.12 (s, 1H), 4.85 (s, 1H), 2.64 (t, J = 7.4 Hz, 2H), 2.58 (s, 6H), 2.51 (t, J = 7.4 Hz, 2H), 2.31 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): d = 188.1, 147.6, 147.0, 145.8, 144.1, 139.9, 134.8, 134.2, 132.4, 119.4, 112.1, 108.0, 106.5, 101.0, 37.9, 29.3, 22.5, 21.1; HRMS(FAB):m/z calcd for $C_{16}H_{18}N_2O_3H^+$ 287.1395, found 287.1410.

$(1R,5R)-5-(3,4-Methylenedioxyphenyl)-1-(2,4,6-trimethylphenylsulfonyl) bicyclo [3.1.0] hexane \\ (16)$

The same procedure as that for **8** in Experimental Section of text, and purification by flash chromatography (hexane / ethyl acetate = 4 / 1) afforded **16** as a white solid: Ee was determined by HPLC (254 nm); Daicel Chiral Cell OD-H 0.46 cm ? × 25 cm; hexane / 2-propanol = 3 / 1; flow rate = 0.5 mL / min); retention time : 29.0 min for **16**, 34.0 min for *ent-16*: R_f = 0.30 (hexane / ethyl acetate = 2 / 1); mp = 145-146 °C; $[a]_D^{23}$ -89.0 (c 0.28, CHCl₃, 67 % ee); IR (KBr): 2944, 1732, 1606, 1508, 1462, 1446, 1360, 1312, 1266, 1240, 1202, 1142, 1036, 988, 854, 804, 652, 614, 556, 518cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): d = 7.10 (d, *J* = 1.7 Hz, 1H), 7.08 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.94 (s, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.97 (s, 2H), 2.98 (d, *J* = 5.1 Hz, 1H), 2.65 (s, 6H), 2.55-2.18 (m, 4H), 2.29 (s, 3H). 2.04 (d, *J* = 5.1 Hz, 1H); ¹³C-NMR (100 MHz, CDCl₃): d = 203.7, 147.6, 147.5, 142.9, 140.6, 135.3, 132.0, 130.3, 123.2, 110.4, 108.1, 101.2, 59.4, 48.2, 34.1, 30.8, 27.2, 23.5, 21.1; HRMS(FAB):*m/z* calcd for C₂₂H₂₂O₅S 398.1188, found 399.1266

Ethyl 4-(3,4-Di-tert-butyldimethylsilyloxyphenyl)-5-pentenoate (19)

The same procedure as that for **11**, and purification by flash chromatography (hexane / ethyl acetate = 30 / 1) afforded **19** (2.03 g, 99 %) as a colorless oil: $R_f = 0.25$ (hexane / ethyl acetate = 4 / 1); IR(KBr): 2960, 2936, 2860, 1740, 1512, 1474, 1306, 1290, 1256, 976, 906, 840, 782 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): d = 6.89 (d, d = 2.0 Hz, 1H), d = 2.0 Hz, 1H, d = 2.0 Hz, 2H, d = 2.0 Hz, 2H,

5-(3,4-Di-tert-butyldimethylsilyloxyphenyl)-1-(2,4,6-trimethylphenylsulfonyl)-5-hexen-2-one (20)

The same procedure as that for **12**, and purification by flash chromatography (hexane / ethyl acetate = 40 / 1) afforded **20** (1.01 g, 81 %) as a white solid: $R_f = 0.36$ (hexane / ethyl acetate = 4/1); IR (neat): 2960, 2936, 2864, 1722, 1514, 1474, 1324, 1254, 1152, 976, 910, 840, 784, 736cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): d = 6.97 (s, 2H), 6.85 (s, 1H), 6.82 (d, J = 8.3 Hz, 1H), 6.76 (d, J = 8.3 Hz, 1H), 5.18 (s, 1H), 4.95 (s, 1H), 4.10 (s, 2H), 2.87 (t, J = 7.3 Hz, 2H), 2.73 (s, J = 7.3 Hz, 2H), 2.61 (s, 6H), 2.31 (s,3H), 0.98 (s, 18H), 0.20 (s, 6H), 0.19 (s, 6H); ¹³C-NMR (100 MHz, CDCl₃): d = 197.7, 146.6, 146.5, 145.5, 143.9, 139.9, 133.4, 132.8, 132.3, 120.7, 119.0, 118.9, 111.5, 66.9, 43.7, 28.9, 26.0, 26.0, 22.9, 21.1, 18.5, -4.0; HRMS (FAB) : m/z calcd for $C_{33}H_{52}O_5SSi_2H^+$ 617.3152, found 617.3127.

2-Diazo-5-(3,4-di-*tert*-butyldimethylsilyloxyphenyl)-1-(2,4,6-trimethylphenylsulfonyl)-5-hexen-2-one (21)

The same procedure as that for **9**, and purification by flash chromatography (hexane / ethyl acetate = 50 / 1) afforded **15** (756.3 mg, 67 %) as an yellow oil: R_f = 0.56 (hexane / ethyl acetate = 4 / 1); IR (neat): 2960, 2936, 2860, 2128, 2104, 1668, 1336, 1292, 1256, 1216, 1152, 908, 838, 786, 668, 598cm^{-1} ; $^{1}\text{H-NMR}$ (400 MHz, CDCl₃): d = 6.95 (s, 2H), 6.83-6.72 (m, 3H), 5.11 (s, 1H), 4.79 (s, 1H), 2.69-2.40 (m, 4H), 2.60 (s, 6H), 2.30 (s, 3H), 0.99 (s, 18H), 0.20 (s, 6H), 0.18 (s, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl₃): d = 188.2, 146.6, 146.5, 145.5, 144.1, 140.0, 134.8, 133.2, 132.4, 120.7, 118.9,118.7, 111.3, 38.0, 29.1, 26.0, 22.5, 21.1, 18.5, -4.0; HRMS (FAB) : m/z calcd for $C_{33}H_{50}N_2O_5SSi$ 642.2979, found 642.2966.

(1*R*,5*R*)-5-(3,4-Di-*tert*-butyldimethylsilyloxyphenyl)-1-(2,4,6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (22)

The same procedure as that for **8** in Experimental Section of text, and purification by flash chromatography (hexane / ethyl acetate = 20 / 1) afforded **22** as a white solid: Ee was determined by HPLC (254 nm); Daicel Chiral Cell AS-H 0.46 cm ? × 25 cm; hexane / 2-propanol = 9 / 1; flow rate = 0.1 mL / min); retention time : 37.0 min for *ent-22*, 41.0 min for **22**: $R_f = 0.29$ (hexane / ethyl acetate = 4 / 1); mp = 145-146 °C; $[a]_D^{27}$ -45.5 (c 0.55, CHCl₃, 64 % ee); IR (KBr): 2936, 2860, 1738, 1518, 1318, 1304, 1256, 1144, 908, 842, 826, 784cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): d = 7.07-7.03 (m ,2H), 6.92 (s, 2H), 6.82 (d, J = 8.8 Hz, 1H), 2.93 (d, J = 5.1 Hz, 1H), 2.64 (s, 6H), 2.54-2.15 (m, 4H), 2.28 (s, 3H), 2.01 (d, J = 5.1 Hz, 1H), 1.00 (s, 6H), 0.99 (s, 6H), 0.23 (s, 3H), 0.22 (s, 3H), 0.21 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): d = 204.1, 147.0, 146.3, 142.6, 140.5, 135.6, 131.9, 129.4, 122.9, 122.8, 120.5, 59.6, 48.1, 34.1, 30.6, 27.0, 26.1, 26.0, 23.5, 21.0, 18.5, 18.5, -3.9, -4.0, -4.0, -4.1; HRMS(FAB):m/z calcd for $C_{33}H_{50}O_5SSi_2$ 614.2917, found 615.2996.

2-Diazo-5-(3,4-dibenzoyloxyphenyl)-1-(2,4,6-trimethylphenylsulfonyl)-5-hexen-2-one (23)

The same procedure as that for **9**, and purification by flash chromatography (hexane / ethyl acetate = 30 / 1) afforded **23** (347.4 mg, 75 %) as an yellow solid: $R_f = 0.48$ (hexane / ethyl acetate = 2 / 1); mp = 139-140 °C; IR (KBr): 2928, 2100, 1742, 1678, 1512, 1334, 1260, 1180, 1152, 1122, 1090, 1054, 1024, 722, 702, 664, 596cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl₃): d = 8.10-8.03 (m, 4H), 7.60-7.52 (m, 2H), 7.49-7.23 (m, 7H), 6.98 (s, 2H), 5.23 (s, 1H), 4.99 (s, 1H), 2.72 (t, J=7.6 Hz, 2H), 2.63 (t, J=7.6 Hz, 2H), 2.61 (s, 6H), 2.29 (s, 3H); $^{13}\text{C-NMR}$ (100 MHz, CDCl₃): d = 187.8, 164.0, 144.7,

144.1, 142.3, 141.9, 139.9, 138.8, 133.6, 132.5, 130.0, 128.6, 128.4, 123.9, 123.2, 121.1, 114.0, 37.7, 28.8, 22.5, 21.1; HRMS (FAB) : m/z calcd for $C_{35}H_{30}N_2O_7SH^+$ 623.1852, found 623.1876.

(1R,5R)-5-(3,4-Dibenzoyloxyphenyl)-1-(2,4,6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (24)

The same procedure as that for **8** in Experimental Section of text, and purification by flash chromatography (hexane / ethyl acetate = 4 / 1) afforded **24** as a white solid: Ee was determined by HPLC (254 nm); Daicel Chiral Cell OD-H 0.46 cm ? × 25 cm; hexane / 2-propanol = 1 / 1; flow rate = 0.4 mL / min); retention time : 24.0 min for **24**, 32.0 min for *ent-24*: $R_f = 0.14$ (hexane / ethyl acetate = 2 / 1); mp = 193-194 °C; $[a]_D^{27}$ -124.5 (c 0.51, CHCl₃, 100 % ee); IR (KBr):2928, 1742, 1604, 1508, 1452, 1316, 1262, 1202, 1172, 1144, 1120, 1102, 1080, 1060, 1024, 708, 652, 522cm⁻¹; 1 H-NMR (400 MHz, CDCl₃): d = 8.06 (dd, J = 9.0, 9.6 Hz, 4H), 7.68 (d, J = 2.0 Hz, 1H), 7.63 (dd, J = 8.5, 2.0 Hz, 1H), 7.54 (dd, J = 7.3, 7.3 Hz, 2H), 7.46 (d, J = 8.5 Hz, 1H), 7.38 (dd, J = 7.3, 7.3 Hz, 2H), 6.95 (s, 2H), 3.03 (d, J = 5.4 Hz, 1H), 2.66 (s, 6H), 2.65-2.25 (m, 4H), 2.29 (s, 3H), 2.09 (d, J = 5.4 Hz, 1H); 13 C-NMR (100 MHz, CDCl₃): d = 203.4, 163.8, 163.7, 143.0, 142.2, 142.0, 140.6, 135.1, 133.5, 132.0, 130.1, 130.0, 128.7, 128.3, 128.1, 125.0, 123.3, 59.6, 47.2, 34.1, 30.6, 26.8, 23.6, 21.1; HRMS(FAB): m/z calcd for $C_{35}H_{30}O_7SH^+$ 595.1790, found 595.1820.