# Dirhodium Tetraprolinates Catalyzed Asymmetric Cyclopropanations with High Turnover Numbers

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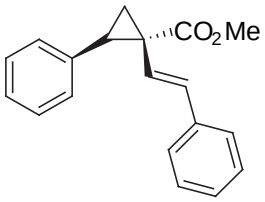
**Supporting Information:**

Experimental data for the cyclopropanation reactions.

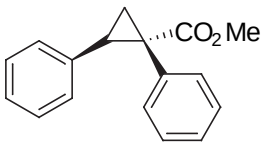
General: All reactions were carried out under an argon atmosphere and anhydrous conditions unless otherwise noted. Methyl benzoate was distilled from calcium hydride and stored over 3Å molecular sieves. 4Å molecular sieves were dried under vacuum at 150 $^{o}$C over 12 h before each reaction. Reagents were purchased from Aldrich Chemical Company and Acros Organics at the highest commercial quality and used without further purification unless otherwise stated. Analytical TLC was performed on 250μm Whatman silica gel (Aluminium backing, UV 254 nm) plates. Column chromatography was carried out using E. Merck silica 60 (230-400 mesh). $^{1}$H NMR spectra were recorded on a Varian Nuclear Magnetic Resonance spectrometer at 300, 400, or 500 MHz and $^{13}$C spectra were recorded at 75 or 125 MHz, with the sample solvent being $CDCl_3$, unless otherwise noted. Infrared spectra were obtained on a Nicolet Impact 420 FT-IR spectrometer. Mass spectra were recorded on a Hewlett-Packard GC-MS system using 70 eV electron impact (EI) ionization. High-resolution mass spectra were obtained from the Mass Spectroscopy Facility at the University at Buffalo, The State University of New York. Elemental analyses were determined by Atlantic Microlab, Inc., Norcross, GA.

$Rh_2$(*S*-DOSP)$_4$ (**1**)[1] and $Rh_2$(*S*-biTISP)$_2$ (**2**)[7] catalyst were prepared by following the literature procedure.[1,7]



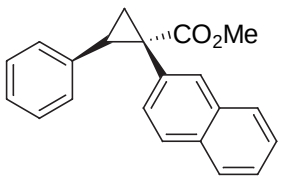

**2*R*-Phenyl-1*R*-styryl-cyclopropanecarboxylic acid methyl ester (4)[1]:**

Methyl *E*-2-diazo-4-phenyl-3-butenoate[2] (101 mg, 0.5 mmol) in $CH_2Cl_2$ (3 mL) was added dropwise over 1.5 h, to a stirred solution of $Rh_2$(*S*-biTISP)$_2$ (0.5 mL from 0.0001M $CH_2Cl_2$ solution , 0.01 mol%), styrene (0.3 mL, 2.5 mmol), methyl benzoate (68 mg, 0.5 mmol), 4Å activated molecular sieves (500 mg) in $CH_2Cl_2$ (3 mL), under an argon atmosphere and the resulting red slurry was stirred at 23 ºC. After 26 h at 23 ºC, the resulting white slurry was filtered through celite (1 g) washed with $CH_2Cl_2$ (10 mL) and concentrated under pressure to give the **4**.[1] The product was purified by flash chromatography ($SiO_2$, $Et_2O$/Pentane = 5:95) to give the title compound (107 mg, 0.384 mmol, 77% yield); 85% ee (HPLC, Whelk column, 1.0% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 13.64 (minor) and 17.31 (major) min, UV 254 nm); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.25 - 7.11 (m, 10 H), 6.36 (d, *J* = 16.2 Hz, 1 H), 6.14 (d, *J* = 16.2 Hz, 1 H), 3.75 (s, 3 H), 3.03 (t, *J* = 8.1 Hz, 1 H), 2.05 - 1.99 (dd, *J* = 5.1, 9.3 Hz, 1 H), 1.84 - 1.80 (dd, *J* = 5.4, 7.2 Hz, 1 H).[1]




**(1*S*,2*R*)-Diphenylcyclopropanecarboxylic acid methyl ester (6)[1]:**

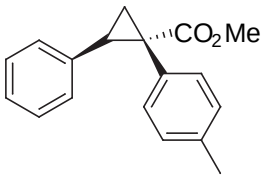
Methyl phenyldiazoacetate[2] (35.2 g, 200 mmol) in $CH_2Cl_2$ (120 mL) was added dropwise over 30 min, to a stirred solution of $Rh_2$(*S*-biTISP)$_2$ (3.8 mg, 0.001 mol%), styrene (57.3 mL, 500 mmol), methyl benzoate (27.2 g, 200 mmol), 4Å activated molecular sieves (10.1 g) in $CH_2Cl_2$ (120 mL), under an argon atmosphere and the resulting yellow slurry was stirred at 23 °C. After 26 h at 23 °C, the resulting white slurry was filtered through celite (4 g), washed with $CH_2Cl_2$ (50 mL) and concentrated under pressure. The excess of styrene and methylbenzoate was removed by bulb-to-bulb distillation (85 °C, 2 mm Hg) to give **6** (46 g, 180 mmol, 92% yield); 85% ee (HPLC, Whelk column, 1.5% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 11.05 (minor) and 12.19 (major) min, UV 254 nm); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.12 (m, 3 H), 7.04 (m, 5 H), 6.76 (m, 2 H), 3.65 (s, 3 H), 3.12 - 3.09 (dd, *J* = 4.0, 9.0 Hz, 1 H), 2.14 - 2.11 (dd, *J* = 5.0, 9.5 Hz, 1 H), 1.88 - 1.86 (dd, *J* = 5.0, 7.5 Hz, 1 H). Recrystallization using hexanes (500 mL) gave **6** (37.8 g, 75% yield) and 99.3% ee (HPLC, Whelk column, 1.5% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 11.05 (minor) and 12.19 (major) min, UV 254 nm).[1]




**1*S*-Naphthalen-2-yl-2*R*-phenyl-cyclopropanecarboxylic acid methyl ester (7a):**

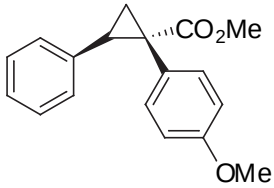
Methyl-2-naphthyldiazoacetate[3] (113 mg, 0.5 mmol) in $CH_2Cl_2$ (3 mL) was added dropwise over 1.5 h, to a stirred solution of $Rh_2$(*S*-biTISP)$_2$ (0.05 mL from 0.0001M $CH_2Cl_2$ solution , 0.001 mol%), styrene (0.3 mL, 2.5 mmol), methyl benzoate (68 mg, 0.5 mmol), 4Å activated molecular sieves (500 mg) in $CH_2Cl_2$ (3 mL), under an argon atmosphere and the resulting yellow slurry was stirred at 23 °C. After 26 h at 23 °C, the resulting white slurry was filtered through celite (1 g) washed with $CH_2Cl_2$ (10 mL) and

concentrated under pressure to give **7a**. The product was purified by flash chromatography ($SiO_2$, $Et_2O$/Pentane = 10:90) to give the title compound (130 mg, 0.430 mmol, 86% yield); 94% ee (HPLC, Whelk column, 4.0% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 15.33 (minor) and 25.75 (major) min, UV 254 nm); $[\alpha]^{25}_D$ = -91.8° (c 1.42, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 - 7.67 (dd, *J* = 5.0, 9.0 Hz, 2 H), 7.59 (s, 1 H), 7.53 (d, *J* = 8.5 Hz, 1 H), 7.39 (m, 2 H), 7.04 (m, 1 H), 6.98 (m, 3 H), 6.80 (m, 2 H), 3.63 (s, 3 H), 3.19 - 3.16 (dd, *J* = 7.5, 9.0 Hz, 1 H), 2.22 - 2.19 (dd, *J* = 5.0, 9.0 Hz, 1 H), 2.01 - 1.99 (dd, *J* = 5.5, 7.5 Hz, 1 H); $^{13}$C NMR (DEPT) (125 MHz, $CDCl_3$) δ 174.7 (C), 136.4 (C), 133.3 (C), 132.9 (C), 132.7 (C), 130.8 (CH), 130.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.4 (CH), 126.6 (CH), 126.1 (CH), 125.9 (CH), 52.9 ($CH_3$), 37.8 (C), 33.5 (CH), 20.8 ($CH_2$); IR (neat): 3054, 3027, 2949, 1717, 1500, 1432, 1250, 1160, 969 $cm^{-1}$; Anal. Calcd for $C_{18}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.28; H, 6.04.




**2*R*-Phenyl-1*S*-*p*-tolyl-cyclopropanecarboxylic acid methyl ester (7b):** Methyl-4-methylphenyldiazoacetate[4] (95 mg, 0.5 mmol) in $CH_2Cl_2$ (3 mL) was added dropwise over 1.5 h, to a stirred solution of $Rh_2$(*S*-biTISP)$_2$ (0.05 mL from 0.0001M $CH_2Cl_2$ solution , 0.001 mol%), styrene (0.3 mL, 2.5 mmol), methyl benzoate (68 mg, 0.5 mmol), 4Å activated molecular sieves (500 mg) in $CH_2Cl_2$ (3 mL), under an argon atmosphere and the resulting yellow slurry was stirred at 23 °C. After 26 h at 23 °C, the resulting white slurry was filtered through celite (1 g) washed with $CH_2Cl_2$ (10 mL) and concentrated under pressure to give **7b**. The product was purified by flash chromatography ($SiO_2$, $Et_2O$/Pentane = 10:90) to give the title compound (121 mg, 0.454

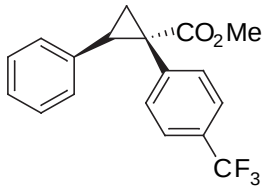
mmol, 91% yield); 82% ee (HPLC, Whelk column, 2.0% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 8.41 (minor) and 10.05 (major) min, UV 254 nm); $[\alpha]^{25}_D$ = +22.0° (c 1.62, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.07 (m, 3 H), 6.94 - 6.89 (m, 4 H), 6.78 (m, 2 H), 3.65 (s, 3 H), 3.09 - 3.06 (dd, *J* = 7.0, 9.0 Hz, 1 H), 2.24 (s, 3 H), 2.12 - 2.09 (dd, *J* = 4.5, 9.5 Hz, 1 H), 1.85 - 1.82 (dd, *J* = 5.0, 7.5 Hz, 1 H); $^{13}$C NMR (DEPT) (125 MHz, $CDCl_3$) δ 174.5 (C), 136.5 (C), 136.4 (C), 131.6 (CH), 131.5 (CH), 128.4 (CH), 128.0 (C), 127.6 (CH), 126.5 (CH), 52.5 ($CH_3$), 36.9 (C), 33.1 (CH), 21.1 ($CH_3$), 20.5 ($CH_2$); IR (neat): 3088, 3028, 2950, 2921, 1717, 1517, 1433, 1258, 1161, 1091, 966 $cm^{-1}$; Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.29; H, 7.02.




**1*S*-(4-Methoxyphenyl)-2*R*-phenylcyclopropanecarboxylic acid methyl ester (7c):**

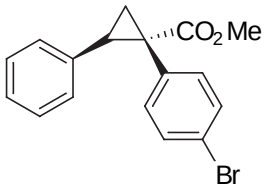
Methyl-4-methoxyphenyldiazoacetate[4] (103 mg, 0.5 mmol) in $CH_2Cl_2$ (3 mL) was added dropwise over 1.3 h, to a stirred solution of $Rh_2$(*S*-biTISP)$_2$ (0.05 mL from 0.0001M $CH_2Cl_2$ solution , 0.001 mol%), styrene (0.3 mL, 2.5 mmol), methyl benzoate (68 mg, 0.5 mmol), 4Å activated molecular sieves (500 mg) in $CH_2Cl_2$ (3 mL), under an argon atmosphere and the resulting yellow slurry was stirred at 23 °C. After 24 h at 23 °C, the resulting white slurry was filtered through celite (1 g) washed with $CH_2Cl_2$ (10 mL) and concentrated under pressure to give **7c**. The product was purified by flash chromatography ($SiO_2$, $Et_2O$/Pentane = 10:90) to give the title compound (129 mg, 0.457 mmol, 91% yield); 80% ee (HPLC, Whelk column, 4.0% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 12.77 (minor) and 17.20 (major) min, UV 254 nm); $[\alpha]^{25}_D$ = +7.36° (c 1.82, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.11 (m, 3 H), 6.98 (m, 2 H), 6.82 (m, 2 H), 6.71 (m, 2 H), 3.75 (s, 3 H), 3.69 (s, 3 H), 3.13 (dd, *J* = 7.5, 9.0 Hz, 1 H), 2.18 -

2.15 (dd, *J* = 5.0, 9.0 Hz, 1 H), 1.88 - 1.85 (dd, *J* = 5.0, 7.5 Hz, 1 H); $^{13}$C NMR (DEPT) (125 MHz, $CDCl_3$) δ 174.6 (C), 158.4 (C), 136.4 (C), 132.8 (C), 128.0 (CH), 127.6 (CH), 126.7 (CH), 126.2 (C), 113.1 (CH), 54.9 ($CH_3$), 52.5 ($CH_3$), 36.6 (C), 33.1 (CH), 20.7 ($CH_2$); IR (neat): 3033, 3004, 2951, 2836, 1717, 1612, 1516, 1267, 1259, 1161, 1033 cm$^{-1}$; Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.34; H, 6.41.



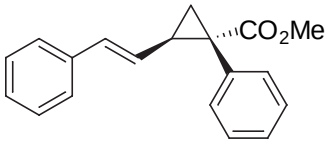

**2*R*-Phenyl-1*S*-(4-trifluoromethylphenyl)cyclopropanecarboxylic acid methyl ester (7d):** Methyl-4-triflourophenyldiazoacetate[4] (122 mg, 0.5 mmol) in $CH_2Cl_2$ (3 mL) was added dropwise over 1.5 h, to a stirred solution of $Rh_2$(*S*-biTISP)$_2$ (0.05 mL from 0.0001M $CH_2Cl_2$ solution , 0.001 mol%), styrene (0.3 mL, 2.5 mmol), methyl benzoate (68 mg, 0.5 mmol), 4Å activated molecular sieves (500 mg) in $CH_2Cl_2$ (3 mL), under an argon atmosphere and the resulting yellow slurry was stirred at 23 $^o$C. After 36 h at 23 $^o$C, the resulting white slurry was filtered through celite (1 g) washed with $CH_2Cl_2$ (10 mL) and concentrated under pressure to give **7d**. The product was purified by flash chromatography ($SiO_2$, $Et_2O$/Pentane = 10:90) to give the title compound (123 mg, 0.384 mmol, 77% yield); 88% ee (HPLC, Whelk column, 2.0% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 7.14 (minor) and 8.42 (major) min, UV 254 nm); $[\alpha]^{25}_D$ = +21.6$^o$ (c 2.36, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.5 Hz, 2 H), 7.06 (m, 3 H), 6.77 (m, 2 H), 3.66 (s, 3 H), 3.17 - 3.14 (dd, *J* = 7.0, 9.0 Hz, 1 H), 2.19 - 2.16 (dd, *J* = 5.0, 9.0 Hz, 1 H), 1.91 - 1.88 (dd, *J* = 5.0, 7.5 Hz, 1 H); $^{13}$C NMR (DEPT) (125 MHz, $CDCl_3$) δ 173.5 (C), 138.9 (C), 138.9 (C), 135.5 (CH), 132.2 (CH), 129.2 (q, *J* = 32.0 Hz), 127.9 (CH), 125.2 (q, *J* = 270.9 Hz, $CF_3$), 124.6 (q, *J* = 4.0 Hz,

CH), 52.7 ($CH_3$), 36.9 (C), 33.2 (CH), 20.1 ($CH_2$); IR (neat): 3031, 2954, 1722, 1619, 1435, 1325, 1260, 1164, 1124, 1020 $cm^{-1}$; Anal. Calcd for $C_{18}H_{15}F_3O_2$: C, 67.50; H, 4.72. Found: C, 67.52; H, 4.83.



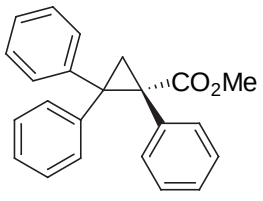

**1*S*-(4-Bromophenyl)-2*R*-phenylcyclopropanecarboxylic acid methyl ester (7e):**

Methyl 4-bromophenyldiazoacetate[4] (128 mg, 0.5 mmol) in $CH_2Cl_2$ (3 mL) was added dropwise over 1.5 h, to a stirred solution of $Rh_2$(*S*-biTISP)$_2$ (0.05 mL from 0.0001M $CH_2Cl_2$ solution , 0.001 mol%), styrene (0.3 mL, 2.5 mmol), methyl benzoate (68 mg, 0.5 mmol), 4Å activated molecular sieves (500 mg) in $CH_2Cl_2$ (3 mL), under an argon atmosphere and the resulting yellow slurry was stirred at 23 $^oC$. After 22 h at 23 $^oC$, the resulting white slurry was filtered through celite (1 g) washed with $CH_2Cl_2$ (10 mL) and concentrated under pressure to give **7e**. The product was purified by flash chromatography ($SiO_2$, $Et_2O$/Pentane = 10:90) to give the title compound (146 mg, 0.437 mmol, 87% yield); 86% ee (HPLC, Whelk column, 2.0% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 9.41 (minor) and 11.31 (major) min, UV 254 nm); $[\alpha]^{25}_D$ = +0.64$^o$ (c 1.91, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2 H), 7.08 (m, 3 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 6.77 (m, 2 H), 3.64 (s, 3 H), 3.12 (dd, *J* = 7.5, 9.0 Hz, 1 H), 2.14 - 2.11 (dd, *J* = 5.0, 9.0 Hz, 1 H), 1.84 (dd, *J* = 5.0, 7.0 Hz, 1 H); $^{13}$C NMR (DEPT) (125 MHz, $CDCl_3$) δ 173.7 (C), 138.9 (C), 135.8 (C), 133.9 (C), 133.5 (CH), 130.8 (CH), 127.9 (CH), 127.8 (CH), 126.5 (CH), 121.1 (C), 52.6 ($CH_3$), 36.9 (C), 33.1 (CH), 20.2 ($CH_2$); IR (neat): 3105, 3062, 3030, 2950, 1719, 1488, 1257, 1162 $cm^{-1}$; Anal. Calcd for $C_{17}H_{15}BrO_2$: C, 61.65; H, 4.56. Found: C, 67.87; H, 4.62.



**1*S*-Phenyl-2*R*-styrylcyclopropanecarboxylic acid methyl ester (8):**

Methyl phenyldiazoacetate[2] (88 mg, 0.5 mmol) in $CH_2Cl_2$ (4 mL) was added dropwise over 2 h, to a stirred solution of $Rh_2$(*S*-biTISP)$_2$ (0.05 mL from 0.0001M $CH_2Cl_2$ solution, 0.001 mol%), buta-1,3-dienyl-benzene[5] (326 mg, 2.5 mmol), methyl benzoate (68 mg, 0.5 mmol), 4Å activated molecular sieves (500 mg) in $CH_2Cl_2$ (3 mL), under an argon atmosphere and the resulting yellow slurry was stirred at 23 °C. After 26 h at 23 °C, the resulting white slurry was filtered through celite (1 g) washed with $CH_2Cl_2$ (10 mL) and concentrated under pressure to give **8**. The product was purified by flash chromatography ($SiO_2$, $Et_2O$/Pentane = 20:80) to give the title compound (128 mg, 0.460 mmol, 92% yield); 78% ee (HPLC, Whelk column, 1.0% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 18.14 (minor) and 24.36 (major) min, UV 254 nm); $[\alpha]^{25}_D$ = +173.9° (c 1.03, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.30 - 7.09 (m, 10 H), 6.59 (d, *J* = 15.6 Hz, 1 H), 5.22 - 5.17 (dd, *J* = 9.6, 15.6 Hz, 1 H), 3.63 (s, 3 H), 2.71 - 2.63 (m, 1 H), 2.07 - 2.02 (dd, *J* = 4.5, 9.3 Hz, 1 H), 1.49 (m, 1 H); $^{13}$C NMR (DEPT) (125 MHz, $CDCl_3$) δ 174.1 (C), 137.2 (C), 135.8 (C), 131.6 (CH), 128.8 (CH), 128.4 (CH), 128.1 (CH), 127.4 (CH), 127.1 (CH), 125.9 (CH), 52.7 ($CH_3$), 35.7 (C), 31.9 (CH), 22.6 ($CH_2$); IR (neat): 3058, 3027, 2950, 1717, 1602, 1496, 1446, 1271, 1245, 1159 cm$^{-1}$; Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.77; H, 6.58.




**(1*R*,2,2)-Triphenylcyclopropanecarboxylic acid methyl ester (9)** [6]**:** Methyl phenyldiazoacetate[2] (88 mg, 0.5 mmol) in $CH_2Cl_2$ (4 mL) was added dropwise over 2 h, to a stirred solution of $Rh_2$(*S*-biTISP)$_2$ (0.05 mL from 0.0001M $CH_2Cl_2$ solution , 0.001

mol%), diphenylethylene (451 mg, 500 mmol), methyl benzoate (68 mg, 0.5 mmol), 4Å activated molecular sieves (500 mg) in $CH_2Cl_2$ (3 mL), under an argon atmosphere and the resulting yellow slurry was stirred at 23 °C. After 26 h at 23 °C, the resulting white slurry was filtered through celite (1 g) washed with $CH_2Cl_2$ (10 mL) and concentrated under pressure to give **9**. The product was purified by flash chromatography ($SiO_2$, $Et_2O$/Pentane = 10:90) to give the title compound (147 mg, 0.45 mmol, 90% yield); 79% ee (HPLC, Whelk column, 15% 2-PrOH in hexanes, 1.0 mL/min, 1mg/mL, $t_R$ = 5.19 (minor) and 9.91 (major) min, UV 254 nm); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.33 (m, 4 H), 6.97 - 6.90 (m, 5 H), 3.34 (s, 3 H), 2.69 (d, *J* = 5.5 Hz, 1 H), 2.42 (d, *J* = 5.5 Hz, 1 H).[6]

**References:**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