Diversity Synthesis Using the Complimentary Reactivity of Rhodium(II)- and Palladium(II)-Catalyzed Reactions

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Methyl 4-iodophenylacetate (1a): This was prepared according to a modified procedure of Togo.¹ Sulfuric acid (0.4 mL, 795 mg, 8.1 mmol) was added dropwise to a solution of 4-iodoacetophenone (1.0 g, 4.1 mmol) and iodobenzene diacetate (1.6 g, 4.9 mmol) in methanol (10 mL) at 0 °C. The reaction mixture was stirred under reflux for 1 h. The reaction was cooled and then quenched with water (50 mL). The mixture was extracted with Et₂O (3 x 100 mL). The combined Et₂O layers were washed with brine (100 mL) and then dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Et₂O/Pentane = 1/9) to give the title compound **1a** (706 mg, 62% yield) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.69 (s, 3H), 3.57 (s, 2H). The spectroscopic data are consistent with the previously reported data.²

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylacetate (1b): This was prepared according to a modified procedure of Robichaud.³ Potassium acetate (15.3 g,

155.8 mmol) was added to a thoroughly degassed solution of methyl 4-bromophenylacetate (11.9 g, 51.9 mmol), bis(pinacolato)diboron (15.8 g, 62.3 mmol), and [1,1'-bis(diphenylphosphino)-ferrocene]dichloropalladium (1.3 g, 1.6 mmol) in DMF (150 mL). The reaction was heated at 100 °C for 2 h. An additional amount of [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (1.3 g, 1.6 mmol) was added and the reaction heated at 100 °C for another 2 h. The reaction was cooled and poured into water (250 mL), then extracted with Et₂O (3 x 150 mL). The combined Et₂O layers were washed with water (150 mL) and brine (150 mL), and then dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Et₂O/Pentane = 1/20) to give the title compound **1b** (11.37 g, 79% yield) as a white solid. mp = 41-45 °C; IR (neat): 2978, 1737, 1610, 1354, 1253, 1139, 1087, 1013 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 3.68 (s, 3H), 3.64 (s, 2H), 1.34 (s, 12H); ¹³C NMR DEPT (125 MHz, CDCl₃) δ 171.6 (C), 137.0 (C), 135.0 (CH), 128.6 (CH), 83.7 (C), 52.0 (CH₃), 41.3 (CH₂), 24.8 (CH₃), C-B signal not observed; LRMS (ESI) *m/z* (relative intensity): 299 (100), 277 (31), 276 (9); Anal. calcd for C₁₅H₂₁BO₄: C, 65.24; H, 7.67. Found: C, 65.35; H, 7.82.

Methyl 4-(tributylstannyl)phenylacetate (1c): This was prepared according to a modified procedure of Dowden.² Tetrakis(triphenylphosphine)palladium(0) (2.0 g, 1.7 mmol) was added to a thoroughly degassed solution of methyl 4-bromophenylacetate (4.0

g, 17.3 mmol) and bis(tributyltin) (17.5 mL, 20.1 g, 34.6 mmol) in toluene (4 mL). The reaction mixture was heated to reflux and stirred for 5 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (petroleum ether to EtOAc/petroleum ether (0.5/99.5) to give the title compound **1c** (4.6 g, 61% yield) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.69 (s, 3H), 3.61 (s, 2H), 1.56-1.50 (m, 6H), 1.36-1.29 (m, 6H), 1.04 (m, 6H), 0.88 (t, *J* = 8.0 Hz, 9H). The spectroscopic data are consistent with the previously reported data.²

Methyl 4-(trifluoromethanesulfonyloxy)phenylacetate: To a stirred solution of methyl 4-hydroxyphenylacetate (1.66 g, 10 mmol) and triethylamine (2 mL) in dichloromethane (15 mL) at 0 °C, trifluoromethanesulfonic anhydride (3.24 g, 11.5 mmol) was added slowly and the mixture was then stirred at room temperature for 1.5 h. The mixture was then poured into sat. NaHCO₃ solution (30 mL), the aqueous layer was extracted with ether (15 mL x 3) and the combined organic layers were dried over MgSO₄. The solvent was removed and the residue was diluted with petroleum ether and ether, filtered through a pad of silica and the residue was purified by flash chromatography on silica gel. Flash chromatography (petroleum ether/ether = 1/1) gave the title compound **1d** (2.74 g, 91% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 3.69 (s, 3H), 3.64 (s, 2H). The spectroscopic data are consistent with the previously reported data.⁴

Methyl 2-(trifluoromethanesulfonyloxy)phenylacetate (1e): To a stirred solution of methyl 2-hydroxyphenylacetate (9.72 g, 58.6 mmol) and triethylamine (12 mL) in dichloromethane (45 mL) at 0 °C, trifluoromethanesulfonic anhydride (10.5 mL, 62.2 mmol) was added slowly and the mixture was stirred at room temperature overnight. The mixture was then poured into sat. NaHCO₃ solution (30 mL). The aqueous layer was extracted with ether (25 mL x 3) and the combined organic layers were dried over MgSO₄. The solvent was removed and the residue was diluted with petroleum ether and ether, filtered through a pad of silica and the residue was purified by flash chromatography on silica gel. Flash chromatography (petroleum ether/ether = 1/1) gave the title compound **1e** (14.3 g, 82% yield) as a colorless liquid. IR (neat) 1742, 1418, 1250, 1135, 889, 766 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (dd, *J* = 6.7, 2.2 Hz, 1H), 7.38-7.31 (m, 3H), 3.75 (s, 2H), 3.71 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.1, 148.0, 132.4, 129.2, 128.3, 127.2, 121.3, 118.5(CF₃), 52.1, 35.4; HRMS (ESI) calcd. for C₁₀H₉O₅F₃NaS (MNa⁺) 321.0015; Found 321.0016.

Methyl 3-hydroxyphenylacetate: 3-Hydroxyphenylacetic acid (4.57 g, 30 mmol) was dissolved into methanol (30 mL) containing 5 drops of conc. sulfuric acid, and the mixture was stirred for 4 h. The solution was concentrated and diluted with ethyl acetate,

and washed with brine until neutral, then dried over MgSO_4 . The solution was concentrated in *vacuum* and purified through a short column (petroleum ether/ether = 4/1) which gave 4.8 g of product. ^1H NMR (500 MHz, CDCl_3) δ 7.17 (m, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.76 - 6.72 (m, 2H), 5.85 (br, 1H), 3.70 (s, 3H), 3.58 (s, 2H). The spectra data are consistent with previously reported data.⁵

To a stirred solution of methyl 3-hydroxyphenylacetate (4.8 g, 28.8 mmol) and triethyl amine (5.6 ml, 40mmol) in dichloromethane (40 ml) at -78°C , trifluoromethanesulfonic anhydride (5 ml, 30 mmol) was added slowly, then warmed up to room temperature and stirred for 2h. It was then poured into 20 ml sat. NaHCO_3 solution. The aqueous layer was extracted with ether (25 mL x 3) and the combined organic layers were dried on MgSO_4 . The solvent was removed and the residue was purified by flash chromatography (petroleum ether/ether = 4/1) to give **1f** (8.31 g, 93% yield for two steps) as colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.41 (m, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.23 (s, 1H), 7.20 (dd, J = 8.2, 2.2 Hz, 1H), 3.72 (s, 3H), 3.67 (s, 2H). The spectra data are consistent with previously reported data.⁴

2a

Methyl 4-iodophenyldiazoacetate (2a): DBU (3.3 mL, 22.2 mmol) was added in one portion to a solution of **1a** (5.1 g, 18.5 mmol) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (5.3 g, 22.2 mmol) in CH_3CN (50 mL) at 0°C . The reaction mixture was stirred for 16 h at 23°C . The solvent was removed under reduced pressure and the residue was

dissolved in Et₂O (200 mL) and washed with water (2 x 50 mL) and brine (50 mL), then dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Et₂O/Pentane = 1/9) to give the title compound **2a** (5.0 g, 89% yield) as an orange solid. IR (neat): 2949, 2090, 1701, 1688, 1486, 1435, 1350, 1273, 1242, 1189, 1153, 1065, 1041 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H); ¹³C NMR DEPT (75 MHz, CDCl₃) δ 165.1 (C), 137.9 (CH), 125.5 (CH), 125.4 (C), 90.2 (C), 52.1 (CH₃), C-N₂ signal not observed; LRMS (EI) *m/z* (relative intensity): 302 (49), 244 (50), 231 (100), 203 (57), 76 (50); HRMS (EI) calcd for C₉H₇IN₂O₂ (M⁺): 301.9547. Found: 301.9536.

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyldiazoacetate (2b): DBU (5.2 mL, 35.0 mmol) was added in one portion to a solution of **1b** (8.07 g, 29.2 mmol) and *p*-ABSA (8.41 g, 35.0 mmol) in CH₃CN (100 mL) at 0 °C. The reaction mixture was stirred for 16 h at 23 °C. The solvent was removed under reduced pressure and the residue was dissolved in Et₂O (400 mL) and washed with water (2 x 100 mL) and brine (100 mL), then dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Et₂O/Pentane = 1/9) to give the title compound **2b** (7.10 g, 81% yield) as an orange solid. IR (neat): 2980, 2091, 1703, 1608, 1357, 1271, 1245, 1144, 1092, 1038 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 1.34 (s, 12H); ¹³C NMR

(125 MHz, CDCl₃) δ 165.2, 135.3, 128.6, 122.6, 83.8, 52.0, 24.8, C-B signal not observed, C-N₂ signal not observed; LRMS (ESI) m/z (relative intensity): 302 (26), 231 (100); HRMS (ESI) calcd for C₁₅H₁₉O₄N₂B (M⁺): 302.1437. Found: 302.1432.

Methyl 4-(tributylstannyl)phenyldiazoacetate (2c): DBU (1.3 mL, 8.5 mmol) was added in one portion to a solution of **1c** (1.56 g, 3.5 mmol) and *p*-ABSA (2.04 g, 8.5 mmol) in CH₃CN (50 mL) at 0 °C. The reaction mixture was stirred for 16 h at 23 °C. The solvent was removed under reduced pressure and the residue was dissolved in Et₂O (200 mL) and washed with water (2 x 50 mL) and brine (50 mL), then dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Et₂O/pentane = 1/20) to give the title compound **2c** (1.09 g, 66% yield) as an orange oil. IR (neat): 2955, 2924, 2871, 2852, 2084, 1707, 1435, 1348, 1266, 1241, 1190, 1154, 1039 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 1.56-1.50 (m, 6H), 1.36-1.29 (m, 6H), 1.05 (t, *J* = 8.0 Hz, 6H), 0.90-0.88 (m, 9H); ¹³C NMR DEPT (75 MHz, CDCl₃) δ 166.1 (C), 139.9 (C), 137.5 (CH), 125.6 (C), 124.0 (CH), 52.4 (CH₃), 29.6 (CH₂), 27.9 (CH₂), 14.2 (CH₃), 10.2 (CH₂), C-N₂ signal not observed; LRMS (ESI) m/z (relative intensity): 489 (83, MNa⁺), 413 (100), 301 (47); HRMS (ESI) calcd for C₂₁H₃₄O₂N₂NaSn (MNa⁺): 489.1554. Found: 489.1534.

Methyl 4-(trifluoromethanesulfonyloxy)phenyldiazo acetate (2d) To a stirred solution of **1d**⁵ (2.98 g, 10.0 mmol) and *p*-ABSA (2.88 g, 12.0 mmol) in acetonitrile (20 mL) at 0 °C, was added DBU (1.80 mL, 12.0 mmol) in one portion. The reaction mixture was stirred overnight at room temperature. The reaction mixture was then quenched with sat. ammonium chloride solution (20 mL). The aqueous layer was extracted with ether (15 mL x 3) and the combined organic layers were dried over MgSO₄. The solvent was removed and the residue was diluted with petroleum ether and ether, filtered through a pad of silica and the residue was purified by flash chromatography on silica gel. Flash chromatography (petroleum ether/ether = 4/1) gave **2d** (2.36 g, 73% yield) as a yellow solid. IR (neat) 2960, 2096, 1708, 1504, 1426, 1251, 1212, 1141, 886 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 164.9, 147.1, 126.7, 125.2, 121.9, 118.7(CF₃), 52.2, C-N₂ signal not observed; Anal. Calcd for C₁₀H₇F₃N₂O₅S C, 37.04; H, 2.18; Found: C, 37.27; H, 2.11.

Methyl 2-(trifluoromethanesulfonyloxy)phenyldiazoacetate (2e) To a stirred solution of **1e** (8.94 g, 30.0 mmol) and *p*-ABSA (8.64 g, 36.0 mmol) in acetonitrile (60 mL) at 0 °C, was added DBU (5.4 mL, 36.0 mmol) in one portion. The reaction mixture was

stirred overnight at room temperature. The reaction mixture was then quenched with sat. ammonium chloride solution (60 mL). The aqueous layer was extracted with ether (30 mL x 3) and the combined organic layers were dried over MgSO₄. The solvent was removed and the residue was diluted with petroleum ether and ether, filtered through a pad of silica and the residue was purified by flash chromatography on silica gel. Flash chromatography (petroleum ether/ether = 4/1) gave 7.12g of **2e** as a yellow liquid, yield 73%. IR (neat) 3005, 2959, 2104, 1712, 1494, 1425, 1291, 1213, 1140, 877, 767 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, *J* = 7.3 Hz, 1H), 7.42-7.34 (m, 3H), 3.83 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 164.8, 146.3, 131.6, 129.6, 128.6, 121.9, 119.6, 118.5 (CF₃), 52.2, C-N₂ signal not observed. Anal. Calcd for C₁₀H₇F₃N₂O₅S: C, 37.04; H, 2.18; Found: C, 37.07; H, 2.05.

Methyl 3-(trifluoromethanesulfonyloxy)phenyldiazoacetate (2f) To a stirred solution of **1f**⁷ (8.0 g, 26.8 mmol) and *p*-ABSA (7.2 g, 30 mmol) in acetonitrile (50 mL) at 0 °C, was added DBU (4.5 mL, 30 mmol) in one portion. The reaction mixture was stirred overnight at room temperature. The reaction mixture was then quenched with sat. ammonium chloride solution (30 mL). The aqueous layer was extracted with ether (30 mL x 3) and the combined organic layers were dried on MgSO₄. The solvent was removed and the residue was diluted with petroleum ether and ether, filtered through a pad of silica and the residue was purified by flash chromatography (petroleum ether/ether = 4/1) to give **2f** (7.14g, 83%) as yellow liquid. IR (neat): 2090, 1703, 1421, 1205, 1137,

880 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.63 (t, J = 2.1 Hz, 1H), 7.45 (t, J = 8.2 Hz, 1H), 7.34 (m, 1H), 7.08 (dd, J = 8.2, 1.9 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.6, 150.1, 130.4, 129.0, 122.5, 118.0, 118.7 (CF_3), 116.7, 52.2, C- N_2 signal not observed; Anal. Calcd for $\text{C}_{10}\text{H}_7\text{F}_3\text{N}_2\text{O}_5\text{S}$ C, 37.04; H, 2.18; Found: C, 37.16; H, 2.07.

(1R,2S)-Methyl 1-(4-iodophenyl)-2-phenylcyclopropanecarboxylate (9a): A solution of **2a** (151 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) and styrene (260 mg, 2.5 mmol) in hexanes (5 mL) at $-40\text{ }^\circ\text{C}$. After the addition was complete, the reaction was warmed to $23\text{ }^\circ\text{C}$ and stirred for 1 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be $>94\%$ de by ^1H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et_2O /pentane = 1/20) to give the title compound **9a** (160 mg, 84% yield) as a colorless oil. $[\alpha]_{\text{D}}^{25} = +9^\circ$ (c = 1.0, CHCl_3); 97% ee (R,R -Whelk column, 2% i -PrOH in hexanes, 1.0 mL/min, λ = 254 nm, t_{R} = 9.4, minor; 11.4, major); IR (neat): 3033, 2951, 2852, 1720, 1490, 1435, 1260 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, J = 7.5 Hz, 2H), 7.10-7.08 (m, 3H), 6.78-6.75 (m, 4H), 3.66 (s, 3H), 3.10 (dd, J = 9.0, 7.5 Hz, 1H), 2.13 (dd, J = 9.0, 5.0 Hz, 1H), 1.83 (dd, J = 7.5, 5.0 Hz, 1H); ^{13}C NMR DEPT (75 MHz, CDCl_3) δ 173.6 (C), 136.8 (CH), 135.8 (C), 134.6 (C), 133.8 (CH), 127.9 (CH), 127.8 (CH), 126.5 (CH), 92.9 (C), 52.6 (CH_3), 36.8 (C), 33.0 (CH), 20.2 (CH_2); LRMS (ESI) m/z (relative intensity): 378

(100); HRMS (EI) calcd for $C_{17}H_{15}IO_2$ (M^+): 378.0111. Found: 378.0118; Anal. Calcd for $C_{17}H_{15}IO_2$: C, 53.99; H, 4.00. Found: C, 54.21; H, 4.14.

(1*R*,2*S*)-Methyl 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2-phenylcyclopropanecarboxylate (9b): A solution of **2b** (151 mg, 0.5 mmol) in hexanes (10 mL) was added dropwise over 1 h using a syringe pump to a stirred solution of $Rh_2(S-DOSP)_4$ (9.4 mg, 1 mol%) and styrene (260 mg, 2.5 mmol) in hexanes (5 mL) at $-40\text{ }^{\circ}C$. After the addition was complete, the reaction was warmed to $23\text{ }^{\circ}C$ and stirred for 16 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be $>94\%$ de by 1H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et_2O /pentane = 1/20) to give the title compound **9b** (152 mg, 80% yield) as a white solid. mp = $148\text{--}151\text{ }^{\circ}C$; $[\alpha]_D^{25} = -6^{\circ}$ ($c = 1.17$, $CHCl_3$); 90% ee (S,S -Whelk column, 2% i -PrOH in hexanes, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 14.9$, minor; 18.4, major); IR (neat): 2976, 2929, 1721, 1613, 1363 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, $J = 8.0$ Hz, 2H), 7.10–7.08 (m, 5H), 6.83–6.81 (m, 2H), 3.67 (s, 3H), 3.17 (dd, $J = 9.0, 8.0$ Hz, 1H), 2.18 (dd, $J = 9.0, 5.0$ Hz, 1H), 1.93 (dd, $J = 7.5, 5.0$ Hz, 1H), 1.35 (s, 12H); ^{13}C NMR DEPT (75 MHz, $CDCl_3$) δ 174.0 (C), 137.8 (C), 136.0 (C), 134.0 (CH), 131.2 (CH), 127.9 (CH), 127.7 (CH), 126.3 (CH), 83.6 (C),

52.5 (CH₃), 37.4 (C), 33.1 (CH), 24.8 (CH₃), 24.7 (CH₃), 20.3 (CH₂), C-B signal not observed; LRMS (ESI) *m/z* (relative intensity): 779 (100), 778 (60), 401 (18), 379 (34); HRMS (ESI) calcd for C₂₃H₂₇BNaO₄ (MNa⁺): 401.1895. Found: 401.1882; Anal. Calcd for C₂₃H₂₇BO₄: C, 73.03; H, 7.19. Found: C, 72.84; H, 7.26.

(1R,2S)-Methyl 2-phenyl-1-(4-(tributylstannyl)phenyl)cyclopropanecarboxylate

(9c): A solution of **2c** (233 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of Rh₂(*S*-DOSP)₄ (9.4 mg, 1 mol%) and styrene (260 mg, 2.5 mmol) in hexanes (5 mL) at −40 °C. After the addition was complete, the reaction was warmed to 23 °C and stirred for 16 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ¹H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et₂O/Pentane = 1/20) to give the title compound **9c** (227 mg, 84% yield) as a colorless oil. [α]_D²⁵ = −40° (*c* = 1.22, CHCl₃); 94% ee (*S,S*-Whelk column, 2% *i*-PrOH in hexanes, 0.8 mL/min, λ = 254 nm, *t*_R = 9.1, minor; 12.0, major); IR (neat): 2952, 2924, 2871, 2852, 1719, 1456, 1433, 1261, 1211, 1161 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.03–7.01 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.73–6.71 (m, 2H), 3.67 (s, 3H), 3.08 (dd, *J* = 9.0, 7.5 Hz, 1H), 2.13 (dd, *J* = 9.0, 5.0 Hz, 1H), 1.86 (dd, *J* = 7.5, 5.0 Hz, 1H), 1.48–1.43 (m, 6H), 1.33–1.25 (m, 6H), 0.99–0.94 (t, *J* = 7.5 Hz 6H), 0.88–0.85 (m, 9H); ¹³C NMR DEPT (75 MHz, CDCl₃) δ 174.9 (C), 140.9 (C), 137.0 (C), 136.3 (CH),

134.8 (C), 132.0 (CH), 128.6 (CH) 128.1 (CH), 126.7 (CH), 53.1 (CH₃), 38.0 (C), 33.7 (CH), 29.6 (CH₂), 27.8 (CH₂), 21.1 (CH₂), 14.2 (CH₃), 10.1 (CH₂); LRMS (ESI) *m/z* (relative intensity): mass ion not observed, 485 (100), 376 (61), 170 (57); HRMS (EI) calcd for C₂₉H₄₂O₂Sn (M⁺): 542.2201. Found: 542.2186.

(1*R*,2*S*)-Methyl 2-phenyl-1-((4-trifluoromethanesulfonyloxy)phenyl)-cyclopropanecarboxylate (9d): Styrene (260 mg, 2.5 mmol) and Rh₂(*S*-DOSP)₄ (9.4 mg, 1 mol%) were dissolved into degassed hexanes (5 mL). Then **2d** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h via syringe pump at -40 °C and then warmed to rt. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ¹H NMR analysis of the crude reaction mixture. Purification by flash chromatography (petroleum ether/ether = 4/1) on silica gel gave **9d** (184 mg, 92% yield) as white solid. mp = 46-48 °C; 97% ee (*S,S*-Whelk column, 1% *i*-PrOH in hexanes, 1.0 mL/min, λ = 254 nm, t_R = 15.4, minor; 20.7, major); [α]_D²⁵ = -5° (*c* = 1.0, CHCl₃); IR (neat) 3034, 2958, 1723, 1504, 1424, 1212, 1141, 890 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.07-6.99 (m, 7H), 6.71 (m, 2H), 3.66 (s, 3H), 3.11 (dd, *J* = 9.2, 7.3 Hz, 1H), 2.16 (dd, *J* = 9.5, 5.2 Hz, 1H), 1.85 (dd, *J* = 7.3, 5.2 Hz, 1H); ¹³C NMR DEPT (125 MHz, CDCl₃) δ 173.3 (C), 148.3 (C), 135.6 (C), 135.4 (C), 133.7 (CH), 127.83 (CH), 127.81 (CH), 126.6 (CH), 120.4 (CH), 118.6 (CF₃), 52.6 (CH₃), 36.5 (C), 33.2 (CH), 20.1 (CH₂); Anal. Calcd for C₁₈H₁₅F₃O₅S C, 54.00; H, 3.78; Found: C, 54.19; H, 3.76.

9e

(1R,2S)-Methyl 2-phenyl-1-((2-(trifluoromethanesulfonyloxy)phenyl)-

cyclopropanecarboxylate (9e): Styrene (260 mg, 2.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) were dissolved into degassed hexanes (5 mL). Then **2e** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h via syringe pump at $-40\text{ }^\circ\text{C}$ and warmed to rt. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ^1H NMR analysis of the crude reaction mixture. Purification by flash chromatography (petroleum ether/ether = 4/1) on silica gel gave **9e** (131 mg, 64% yield) as a white solid. mp = $70\text{--}72\text{ }^\circ\text{C}$; 92% ee (OD-H column, 1.0 mL/min, 1% *i*-PrOH in hexanes, $\lambda = 254\text{ nm}$, $t_R = 7.7$, major; 8.7, minor); $[\alpha]_D^{25} = -87^\circ$ ($c = 1.0$, CHCl_3); IR (neat) :3018, 2956, 1738, 1502, 1426, 1215, 1141, 890 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.27–7.24 (m, 1H), 7.09–7.03 (m, 2H), 6.78–6.76 (m, 1H), 3.67 (s, 3H), 3.24–3.21 (m, 1H), 2.24 (br, 1H), 1.92 (dd, $J = 7.1, 5.3\text{ Hz}$, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.5, 150.0, 135.2, 133.9, 129.3, 128.2, 127.7, 127.6, 127.3, 126.7, 120.2, 118.1(CF_3), 52.5, 33.5, 20.3; Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{O}_5\text{S}$: C, 54.00; H, 3.78; Found: C, 54.00; H, 3.70.

9f

(1R,2S)-Methyl

2-phenyl-1-((3-

trifluoromethanesulfonyloxy)phenyl)cyclopropanecarboxylate (9f): Styrene (260 mg,

2.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) were dissolved into degassed hexanes (5 mL). Then **2f** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h via syringe pump at $-40\text{ }^\circ\text{C}$ and then warmed to rt. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be 90% de by ^1H NMR analysis of the crude reaction mixture. Purification by flash chromatography (petroleum ether/ether = 4/1) on silica gel gave **9f** (156 mg, yield 76%). mp $58\text{--}60\text{ }^\circ\text{C}$; 90% ee (OD-H column, 1.0 mL/min, 1% *i*-PrOH in hexanes, $\lambda = 254\text{ nm}$, $t_R = 9.3$, major; 11.3, minor); $[\alpha]_D^{25} = -21^\circ$ ($c = 1.05$, CHCl_3); IR (neat): 1721, 1420, 1208, 1138, 913, 694 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.21–7.18 (m, 1H), 7.08–7.03 (m, 5H), 6.96 (m, 1H), 6.78–6.76 (m, 1H), 3.68 (s, 3H), 3.16 (dd, $J = 9.1, 7.3\text{ Hz}$, 1H), 2.18 (dd, $J = 9.1, 5.2\text{ Hz}$, 1H), 1.92 (dd, $J = 7.2, 5.2\text{ Hz}$, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.1, 148.9, 137.9, 135.1, 131.8, 129.2, 127.9, 127.8, 126.7, 124.6, 119.8, 118.8(CF_3), 52.6, 36.8, 33.4, 19.8; Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{O}_5\text{S}$ C, 54.00; H, 3.78; Found: C, 53.96; H, 3.74.

(1*R*,2*S*)-Methyl 2-(4-bromophenyl)-1-(4-iodophenyl)cyclopropanecarboxylate (10a):

A solution of **2a** (151 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) and 4-bromostyrene (457 mg, 2.5 mmol) in hexanes (5 mL) at $-40\text{ }^\circ\text{C}$. After the addition was complete, the reaction was warmed to $23\text{ }^\circ\text{C}$ and stirred for 1 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ^1H NMR

analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et₂O/pentane = 1/20) to give the title compound **10a** (189 mg, 83% yield) as a white solid. mp = 49-51 °C; $[\alpha]_D^{25} = +12^\circ$ ($c = 1.15$, CHCl₃); 92% ee (*S,S*-Whelk column, 2% *i*-PrOH in hexanes, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 15.8$, minor; 21.7 major); IR (neat): 3033, 2960, 1720, 1489, 1437, 1260 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.75 (d, $J = 8.0$ Hz, 2H), 6.63 (d, $J = 8.0$ Hz, 2H), 3.65 (s, 3H), 3.05 (dd, $J = 9.0, 7.3$ Hz, 1H), 2.13 (dd, $J = 9.0, 5.0$ Hz, 1H), 1.77 (dd, $J = 7.3, 5.0$ Hz, 1H); ¹³C NMR DEPT (125 MHz, CDCl₃) δ 173.4 (C), 137.0 (CH), 135.0 (C), 134.1 (C), 133.7 (CH), 131.0 (CH), 129.6 (CH), 120.4 (C), 93.2 (C), 52.7 (CH₃), 36.9 (C), 32.4 (CH), 20.4 (CH₂); LRMS (EI) m/z (relative intensity): 458 (35), 189 (100); HRMS (EI) calcd for C₁₇H₁₄BrIO₂ (M⁺): 455.9216. Found: 455.9231.

(1*R*,2*S*)-Methyl 2-(4-bromophenyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropanecarboxylate (10b): A solution of **2b** (151 mg, 0.5 mmol) in hexanes (10 mL) was added dropwise over 1 h using a syringe pump to a solution of Rh₂(*S*-DOSP)₄ (9.4 mg, 1 mol%) and 4-bromostyrene (457 mg, 2.5 mmol) in hexanes (5 mL) at -40 °C. After the addition was complete, the reaction was warmed to 23 °C and stirred for 2 h. The solvent was removed under reduced pressure and the

diastereoselectivity was determined to be >94% de by ^1H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography ($\text{Et}_2\text{O}/\text{Pentane} = 1/10$) to give the title compound **10b** (136 mg, 59% yield) as a white solid. mp = 50-52 °C; $[\alpha]_{\text{D}}^{22} = -1^\circ$ ($c = 1.30$, CHCl_3); 91% ee (*R,R*-Whelk column, 2% *i*-PrOH in hexanes, 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{R}} = 9.0$, major; 11.0 minor); IR (neat): 2976, 1721, 1610, 1363 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 7.5$ Hz, 2H), 6.63 (d, $J = 8.0$ Hz, 2H), 3.63 (s, 3H), 3.06 (dd, $J = 9.0, 7.5$ Hz, 1H), 2.13 (dd, $J = 9.0, 5.0$ Hz, 1H), 1.83 (dd, $J = 7.5, 5.0$ Hz, 1H), 1.32 (s, 12H); ^{13}C NMR DEPT (125 MHz, CDCl_3) δ 173.8 (C), 137.3 (C), 135.3 (C), 134.2 (CH), 131.1 (CH), 130.8 (CH), 129.5 (CH), 120.1 (C), 83.6 (C), 52.6 (CH_3), 37.4 (C), 32.4 (CH), 24.8 (CH_3), 24.7 (CH_3), 20.5 (CH_2), C-B signal not observed; LRMS (EI) m/z (relative intensity): 456 (10), 298 (75), 217 (84), 191 (100); Anal. calcd for $\text{C}_{23}\text{H}_{26}\text{BrO}_4$: C, 60.43; H, 5.73. Found: C, 60.42; H, 5.78.

(1*R*,2*S*)-Methyl 2-(4-bromo-phenyl)-2-phenyl-1-(4-trifluoromethanesulfonyloxyphenyl)cyclopropanecarboxylate (10d) 4-Bromostyrene (457 mg, 2.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) were dissolved into degassed hexanes (5 mL). Then **2d** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h via syringe pump at -40 °C and warmed to rt. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ^1H NMR analysis of the crude

reaction mixture. Purification by flash chromatography (petroleum ether/ether = 4/1) on silica gel gave of **10d** (174 mg, 73% yield) as a colorless oil. 96% ee (*S,S*-Whelk column, 1.0 mL/min, 1% *i*-PrOH in hexanes, λ = 254 nm, t_R = 19.4, minor; 27.2, major); $[\alpha]_D^{25}$ = +3° (c = 1.0, CHCl₃); IR (neat) 2958, 1723, 1504, 1424, 1211, 1141, 888 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.12 (d, J = 7.2 Hz, 2H), 7.03-6.98 (m, 4H), 6.53 (d, J = 8.5 Hz, 2H), 3.61(s, 3H), 3.01 (dd, J = 9.3, 7.3 Hz, 1H), 2.12 (dd, J = 9.3, 5.2 Hz, 1H), 1.75 (dd, J = 7.3, 5.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 173.0, 148.4, 135.2, 134.7, 133.6, 130.9, 129.4, 120.6, 120.5, 118.6(CF₃), 52.7, 36.6, 32.5, 20.2; Anal. Calcd for C₁₈H₁₄BrF₃O₅S: C, 45.11; H, 2.94; Found: C, 45.56; H, 2.94.

(1R,2S)-Methyl 1-(4-iodophenyl)-2-styrylcyclopropanecarboxylate (11a): A solution of **2a** in hexanes (5 mL) was added over 1 h using a syringe pump to a solution of Rh₂(*S*-DOSP)₄ (9.4 mg, 1 mol%) and (*E*)-1-phenyl-1,3-butadiene (325 mg, 2.5 mmol) in hexanes (5 mL) at -40 °C. After the addition was complete, the reaction was warmed to 23 °C and stirred for 16 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ¹H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et₂O/pentane = 1/20) to give the title compound **11a** (160 mg, 84% yield) as a colorless oil. $[\alpha]_D^{25}$ = -109° (c = 1.03, CHCl₃); 91ee % (*S,S*-Whelk column, 2% *i*-PrOH in hexanes, 1.0 mL/min, λ = 254 nm, t_R = 17.8, minor; 28.0, major); IR (neat): 3032, 2954, 2855, 1720 cm⁻¹; ¹H

NMR (500 MHz, CDCl₃) δ 7.64 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 7.5 Hz, 2H), 7.19-7.13 (m, 3H), 7.04 (d, J = 8.0 Hz, 2H), 6.58 (d, J = 16.0 Hz, 1H), 5.18 (dd, J = 16.0, 10.0 Hz, 1H), 3.64 (s, 3H), 2.69-2.64 (m, 1H), 2.05 (dd, J = 9.0, 4.5 Hz, 1H), 1.42 (dd, J = 6.5, 4.5 Hz, 1H); ¹³C NMR DEPT (125 MHz, CDCl₃) δ 173.5 (C), 137.2 (CH), 136.9 (C), 135.6 (C), 133.6 (CH), 131.8 (CH), 128.5 (CH), 128.1 (CH), 127.3 (CH), 125.9 (CH), 93.3 (C), 52.6 (CH₃), 35.2 (CH), 31.9 (C), 22.5 (CH₂); LRMS (EI) m/z (relative intensity): 404 (43), 345 (100); HRMS (EI) calcd for C₁₉H₁₇IO₂ (M⁺): 404.0268. Found: 404.0269.

(1R,2S)-Methyl 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2-styrylcyclopropanecarboxylate (11b): A solution of **2b** (151 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of Rh₂(S-DOSP)₄ (9.4 mg, 1 mol%) and (*E*)-1-phenyl-1,3-butadiene (325 mg, 2.5 mmol) in hexanes (5 mL) at –40 °C. After the addition was complete, the reaction was warmed to 23 °C and stirred for 16 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ¹H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et₂O/pentane = 1/9) to give the title compound **11b** (162 mg, 80% yield) as a white gum. $[\alpha]_D^{25}$ = –105° (c = 1.20, CHCl₃); 89% ee (*R,R*-Whelk column, 2% *i*-PrOH in hexanes, 1.0 mL/min, λ = 254 nm, t_R = 10.3, major; 13.8 minor); IR (neat): 3028, 2981, 2929, 1721, 1612, 1363 cm^{–1}; ¹H NMR (500

MHz, CDCl₃) δ 7.78 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.23-7.11 (m, 5H), 6.59 (d, J = 16.0 Hz, 1H), 5.21 (dd, J = 16.0, 10.0 Hz, 1H), 3.63 (s, 3H), 2.72-2.67 (m, 1H), 2.06 (dd, J = 9.0, 4.5 Hz, 1H), 1.49 (dd, J = 6.5, 4.5 Hz, 1H), 1.35 (s, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 174.0, 138.9, 137.0, 134.5, 131.4, 131.0, 128.5, 128.4, 127.0, 125.9, 83.7, 52.5, 35.7, 32.1, 24.8 (2C), 22.5, C-B signal not observed; LRMS (EI) m/z (relative intensity): 404 (82), 345 (100) 245 (80), 217 (59), 115 (55), 91 (57); HRMS (EI) calcd for C₂₅H₂₉BO₄ (M⁺): 404.2153. Found: 404.2158.

(1R,2S)-Methyl 2-Styryl-1-((4-trifluoromethanesulfonyloxy)phenyl)cyclopropane-carboxylate (11d) (*E*)-1-Phenyl-1,3-butadiene (325 mg, 2.5 mmol) and Rh₂(*S*-DOSP)₄ (9.4 mg, 1 mol%) were dissolved into degassed hexanes (5 mL). Then **2d** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h via syringe pump at -40°C and warmed to rt. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ¹H NMR analysis of the crude reaction mixture. Purification by flash chromatography (petroleum ether/ether = 4/1) on silica gel gave **11d** (193 mg, 90% yield) as a white gum. 94% ee (*S,S*-Whelk, 1.0 mL/min, 1% *i*-PrOH in hexanes, λ = 254 nm, t_R = 20.7, minor; 32.7, major); [α]_D²⁵ = -97° (c = 1.25, CHCl₃); IR (neat): 2962, 1721, 1505, 1423, 1212, 1141, 889 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, J = 8.8 Hz, 2H), 7.23 (dd, J = 15.6, 7.0 Hz, 4H), 7.18-7.16 (m, 1H), 7.10 (d, J = 7.0 Hz, 2H), 6.58 (d, J = 15.9 Hz, 1H), 5.11 (dd, J = 15.9, 9.8 Hz, 1H), 3.66 (s, 3H), 2.70

(m, 1H), 2.11 (dd, $J = 8.8, 4.9$ Hz, 1H), 1.48 (dd, $J = 6.7, 4.9$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.1, 148.6, 136.7, 136.6, 133.5, 132.0, 128.4, 127.7, 127.3, 125.8, 120.8, 119.0(CF_3), 52.5, 34.9, 31.8, 22.3; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{O}_5\text{F}_3\text{NS}$ (M^+): 449.0641. Found 449.0642.

(1*S*,2*R*)-Methyl 2-butoxy-1-(4-iodophenyl)cyclopropanecarboxylate (12a): **2a** (151 mg, 0.5 mmol) in hexanes (10 mL) was added dropwise over 1 h using a syringe pump to a solution of $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) and butyl vinyl ether (251 mg, 2.5 mmol) in hexanes (5 mL) at -40 °C. After the addition was complete, the reaction was warmed to 23 °C and stirred for 1 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be $>94\%$ de by ^1H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et_2O /pentane = 1/20) to give the title compound **12a** (149 mg, 79% yield) as a colorless oil. $[\alpha]_D^{25} = +18^\circ$ ($c = 1.11$, CHCl_3); 82% ee (*S,S*-Whelk column, 2% *i*-PrOH in hexanes, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 11.0$, minor; 15.4 major); IR (neat): 2956, 2874, 1732 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 3.89 (dd, $J = 7.0, 4.5$ Hz, 1H), 3.63 (s, 3H), 3.50 - 3.46 (m, 2H), 1.78 (t, $J = 6.5$ Hz, 1H), 1.55 (t, $J = 5.0$ Hz, 1H), 1.39 - 1.32 (m, 2H), 1.16-1.08 (m, 2H), 0.79 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR DEPT (75 MHz, CDCl_3) δ 172.9 (C), 136.9 (CH), 134.2 (C), 133.4 (CH), 92.8 (C), 70.8 (CH_2), 64.7 (CH), 52.3 (CH_3), 34.6 (C), 31.4 (CH_2), 21.1 (CH_2), 18.9 (CH_2), 13.7 (CH_3); LRMS

(ESI) m/z (relative intensity): 429 (100), 397 (83); HRMS (ESI) calcd for $C_{15}H_{19}IO_3$ (MNa^+): 397.0271. Found: 397.0267. Anal. Calcd for $C_{15}H_{19}IO_3$: C, 48.14; H, 5.12. Found: C, 47.95; H, 5.06.

(1S,2R)-Methyl 2-butoxy-1-(4-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropanecarboxylate (12b): A solution of **2b** (151 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of $Rh_2(S-DOSP)_4$ (9.4 mg, 1 mol%) and butyl vinyl ether (251 mg, 2.5 mmol) in hexanes (5 mL) at $-40\text{ }^{\circ}C$. After the addition was complete, the reaction was warmed to $23\text{ }^{\circ}C$ and stirred for 1 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be $>94\%$ de by 1H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et_2O /pentane = 1/10) to give the title compound **12b** (130 mg, 69% yield) as a colorless oil. $[\alpha]_D^{25} = +15^{\circ}$ ($c = 1.56$, $CHCl_3$); 70% ee (S,S -Whelk column, 4% i -PrOH in hexanes, 0.9 mL/min, $\lambda = 254\text{ nm}$, $t_R = 8.9$, minor; 11.1 major); IR (neat): 2965, 2873, 1721, 1610, 1364 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 3.92 (dd, $J = 7.0, 5.0$ Hz, 1H), 3.62 (s, 3H), 3.54 - 3.45 (m, 2H), 1.78 (t, $J = 6.0$ Hz, 1H), 1.64 (t, $J = 5.0$ Hz, 1H), 1.36-1.31 (m, 2H), 1.34 (s, 12H), 1.14-1.07 (m, 2H), 0.77 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR DEPT (125 MHz, $CDCl_3$) δ 173.3 (C), 137.4 (C), 134.2 (CH), 130.8 (CH), 83.6 (C), 70.8 (CH_2), 65.1 (CH), 52.2 (CH_3), 35.1 (C), 31.3 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 21.0 (CH_2), 18.9 (CH_2), 13.7 (CH_3),

C-B signal not observed; LRMS (ESI) m/z (relative intensity): 397 (100), 392 (67), 375 (66); HRMS (ESI) calcd for $C_{21}H_{31}BNaO_5$ (M^+): 397.2157. Found: 397.2165; Anal. Calcd for $C_{21}H_{31}BO_5$: C, 67.39; H, 8.35. Found: C, 67.47; H, 8.51.

(1*S*,2*R*)-Methyl 2-Butoxy-1-((4-trifluoromethanesulfonyloxy)phenyl)-cyclopropanecarboxylate (12d) Butyl vinyl ether (251 mg, 2.5 mmol) and $Rh_2(S-DOSP)_4$ (9.4 mg, 1 mol %) were dissolved into degassed hexanes (5 mL). Then **2d** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h via syringe pump at $-40\text{ }^{\circ}\text{C}$ and warmed to rt. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be $>94\%$ de by ^1H NMR analysis of the crude reaction mixture. Purification by flash chromatography (petroleum ether/ether = 4/1) on silica gel gave **12d** (160 mg, 81% yield) as colorless oil. 87% ee (*S,S*-Whelk, 1.0 mL/min, 1% *i*-PrOH in hexanes, $\lambda = 254\text{ nm}$, $t_R = 11.5$, minor; 26.5, major); $[\alpha]_D^{25} = +21^{\circ}$ ($c = 1.18$, CHCl_3); IR (neat): 2960, 2875, 1723, 1505, 1425, 1214, 1142, 890 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40 (d, $J = 8.5\text{ Hz}$, 2H), 7.20 (d, $J = 8.5\text{ Hz}$, 2H), 3.89 (dd, $J = 7.0$, 4.8 Hz, 1H), 3.62 (s, 3H), 3.44 (t, $J = 6.4\text{ Hz}$, 2H), 1.81 (t, $J = 6.4\text{ Hz}$, 1H), 1.57 (m, 1H), 1.28 (m, 2H), 1.04 (m, 2H), 0.73 (t, $J = 7.3\text{ Hz}$, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.6, 148.6, 135.2, 133.3, 120.5, 118.7(CF_3), 70.8, 64.7, 52.3, 34.4, 31.4, 21.2, 19.0, 13.6; Anal. Calcd for $C_{18}H_{15}F_3O_5S$ C, 48.48; H, 4.83; Found: C, 48.70; H, 4.91.

(S)-Methyl-1-(4-iodophenyl)-2,2-diphenylcyclopropanecarboxylate (13a): A solution of **2a** (151 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) and 1,1-diphenylethylene (451 mg, 2.5 mmol) in hexanes (5 mL) at $-40\text{ }^\circ\text{C}$. After the addition was complete, the reaction was warmed to $23\text{ }^\circ\text{C}$ and stirred for 1 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be $>94\%$ de by ^1H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et_2O /pentane = 1/20) to give the title compound **13a** (195 mg, 86% yield) as a white solid. mp = $101\text{--}104\text{ }^\circ\text{C}$; $[\alpha]_D^{25} = +249^\circ$ ($c = 1.23$, CHCl_3); 99% ee (*R,R*-Whelk column, 15% *i*PrOH in hexanes, 0.8 mL/min, $\lambda = 254\text{ nm}$, $t_R = 8.6$, major; 23.0, minor); IR (neat): 2981, 2366, 2329, 1726, 1605, 1362 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.51 (d, $J = 7.5\text{ Hz}$, 2H), 7.42 (d, $J = 7.5\text{ Hz}$, 2H), 7.27–7.21 (m, 4H), 7.13 (t, $J = 7.0\text{ Hz}$, 1H), 6.91–6.81 (m, 5H), 3.24 (s, 3H), 2.60 (d, $J = 5.0\text{ Hz}$, 1H), 2.33 (d, $J = 5.0\text{ Hz}$, 1H), 1.20 (s, 12H); ^{13}C NMR DEPT (125 MHz, CDCl_3) δ 171.0 (C), 141.9 (C), 139.4 (C), 138.7 (C), 133.8 (CH), 131.2 (CH), 129.8 (CH), 128.6 (CH), 128.2 (CH), 127.6 (CH), 126.8 (CH), 126.1 (CH), 83.6 (C), 52.1 (CH_3), 44.5 (C), 43.1 (C), 24.8 (CH_3), 24.7 (CH_3), 22.7 (CH_2), C-B signal not observed; LRMS (ESI) m/z (relative intensity): 455 (100); HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{31}\text{BNaO}_4$ (MNa^+): 477.2208. Found: 477.2221; Anal. Calcd for $\text{C}_{29}\text{H}_{31}\text{BO}_4$: C, 76.66; H, 6.88. Found: C, 76.41; H, 6.98.

(S)-Methyl 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2-diphenylcyclopropanecarboxylate (13b): **2b** (151 mg, 0.5 mmol) in hexanes (10 mL) was added dropwise over 1 h using a syringe pump to a solution of $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) and 1,1-diphenylethylene (451 mg, 2.5 mmol) in hexanes (5 mL) at -40°C . After the addition was complete, the reaction was warmed to 23°C and stirred for 16 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography ($\text{Et}_2\text{O}/\text{Pentane} = 1/10$) to give the title compound **13b** (192 mg, 84% yield) as a white solid. mp = $147\text{--}149^\circ\text{C}$; $[\alpha]_D^{25} = +213^\circ$ ($c = 2.36$, CHCl_3); 98% ee (*R,R*-Whelk column, 15% *i*PrOH in hexanes, 0.8 mL/min, $\lambda = 254\text{ nm}$, $t_R = 8.6$, major; 23.0, minor); IR (neat): 2981, 2366, 2329, 1726, 1605, 1362 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.63 (d, $J = 7.5\text{ Hz}$, 2H), 7.54 (d, $J = 7.5\text{ Hz}$, 2H), 7.39–7.33 (m, 4H), 7.25 (t, $J = 7.0\text{ Hz}$, 1H), 7.03–6.93 (m, 5H), 3.36 (s, 3H), 2.72 (d, $J = 5.0\text{ Hz}$, 1H), 2.45 (d, $J = 5.0\text{ Hz}$, 1H), 1.32 (s, 12H); ^{13}C NMR DEPT (125 MHz, CDCl_3) δ 171.0 (C), 141.9 (C), 139.4 (C), 138.7 (C), 133.8 (CH), 131.2 (CH), 129.8 (CH), 128.6 (CH), 128.2 (CH), 127.6 (CH), 126.8 (CH), 126.1 (CH), 83.6 (C), 52.1 (CH_3), 44.5 (C), 43.1 (C), 24.8 (CH_3), 24.7 (CH_3), 22.7 (CH_2), C-B signal not observed; LRMS (ESI) m/z (relative intensity): 455 (100); HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{31}\text{BNaO}_4$ (MNa^+): 477.2208. Found: 477.2221; Anal. calcd for $\text{C}_{29}\text{H}_{31}\text{BO}_4$: C, 76.66; H, 6.88. Found: C, 76.41; H, 6.98.

(S)-Methyl 2,2-Diphenyl-1-((4-trifluoromethanesulfonyloxy)phenyl)cyclopropanecarboxylate (13d): 1,1-Diphenylethylene (451 mg, 2.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) were dissolved into degassed hexanes (5 mL). Then **2d** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h via syringe pump at -40°C and warmed to rt. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ^1H NMR analysis of the crude reaction mixture. Purification by flash chromatography (petroleum ether/ether = 4/1) on silica gel gave **13d** (191 mg, 80% yield) as a white solid. 99% ee (*S,S*-Whelk column, 10% *i*-PrOH in hexanes, $\lambda = 254$ nm, 0.8 mL/min, $t_R = 7.1$, minor; 27.0, major); mp = $56 - 59^\circ\text{C}$; $[\alpha]_D^{25} = +180^\circ$ ($c = 1.11$, CHCl_3); IR (neat): 3050, 2949, 1728, 1503, 1423, 1216, 1141, 890 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.47 (d, $J = 7.6$ Hz, 2H), 7.40-7.33 (m, 4H), 7.28-7.25 (m, 1H), 7.03-6.91 (m, 7H), 3.36 (s, 3H), 2.72 (d, $J = 5.8$ Hz, 1H), 2.44 (d, $J = 5.8\text{ Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.6, 148.3, 141.4, 138.8, 136.6, 133.6, 129.8, 128.4, 128.3, 127.7, 127.1, 126.4, 120.2, 118.8 (CF_3), 52.1, 44.8, 42.2, 22.6; HRMS (EI) calcd. for $\text{C}_{24}\text{H}_{19}\text{O}_5\text{F}_3\text{S}$ (M^+): 476.0900. Found 476.0908.

(S)-Methyl 2-(4-iodophenyl)-2-((R)-pyrrolidin-2-yl)acetate (18a): A solution of **2a** (151 mg, 0.5 mmol) in hexanes (10 mL) was added over 3 h using a syringe pump to a solution of $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) and *tert*-butyl pyrrolidine-1-carboxylate (428 mg, 2.5 mmol) in hexanes (5 mL) at $-40\text{ }^\circ\text{C}$. After the addition was complete, the reaction was warmed to $23\text{ }^\circ\text{C}$ and stirred for 16 h. The solvent was removed under reduced pressure and the excess *tert*-butyl pyrrolidine-1-carboxylate was removed by bulb to bulb distillation using a Kugelrohr apparatus ($80\text{ }^\circ\text{C}$). The residue was dissolved in DCM (2 mL), and then trifluoroacetic acid (0.2 mL, 2.5 mmol) was added and the reaction was stirred for 16 h. The solvent was removed under reduced pressure and the residue was dissolved in Et_2O (30 mL), extracted with 10% HCl (3 x 15 mL). The combined aqueous layers were basified to pH 8-9 (NaHCO_3 , 1M NaOH) and extracted with EtOAc (3 x 30 mL). The combined EtOAc layers were washed with water (30 mL) and brine (30 mL), then dried over Na_2SO_4 . The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ^1H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et_2O /pentane/triethylamine = 50/50/2) to give the title compound **18a** (70 mg, 41% yield) as a light brown oil. $[\alpha]_{\text{D}}^{25} = -34^\circ$ ($c = 1.45$, CHCl_3); IR (neat): 2949, 2869, 1730, 1484, 1433, 1403, 1300, 1202, 1152, 1006 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.66 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.5$ Hz, 2H), 3.71-3.61 (m, 4H), 3.44 (d, $J = 9.5$ Hz, 1H), 2.95-2.89 (m, 1H), 2.83-2.77 (m, 1H), 2.07-1.99 (m, 1H), 1.88-1.72 (m, 2H), 1.52-1.43 (m, 1H), N-H proton not observed; ^{13}C NMR DEPT (75 MHz, CDCl_3) δ 172.7 (C), 137.7 (CH), 137.3 (C), 130.4 (CH), 93.1 (C), 61.0 (CH), 57.2 (CH), 51.9 (CH_3), 45.8 (CH_2), 29.9

(CH₂), 24.6 (CH₂); LRMS (ESI) m/z (relative intensity): 346 (100, MH⁺); HRMS (EI) calcd for C₁₃H₁₇O₂Ni (MH⁺): 346.0298, found: 346.0287.

The above compound **18a** was converted to the trifluoroacetamide in order to measure the enantiomeric excess. Acylation: A small sample of the free amine (5 mg) was dissolved in DCM (1 mL). Pyridine (2 drops) and TFAA (2 drops) were added and the reaction was stirred for 3 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (EtOAc/Pentane = 1/9) to give the amide. 70% ee (*S,S*-Whelk column, 10% *i*-PrOH in hexanes, 0.8 mL/min, λ = 254 nm, t_R = 15.7, major; 23.9 minor).

18d

(*S*)-Methyl 2-(4-trifluoromethanesulfonyloxy-phenyl)-2-((*R*)-pyrrolidin-2-yl)acetate (18d**)** A solution of **2d** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 3 h using a syringe pump to a solution of Rh₂(*S*-DOSP)₄ (9.4 mg, 1 mol%) and *tert*-butyl pyrrolidine-1-carboxylate (428 mg, 2.5 mmol) in hexanes (5 mL) at –40 °C. After the addition was complete, the reaction was warmed to 23 °C. The solvent was removed under reduced pressure and the excess *tert*-butyl pyrrolidine-1-carboxylate was removed by bulb to bulb distillation using a Kugelrohr apparatus (80 °C). The residue was dissolved in DCM (2 mL), then trifluoroacetic acid (0.2 mL, 2.5 mmol) was added and the reaction was stirred for 16 h. The solvent was removed under reduced pressure and the residue was dissolved in Et₂O (30 mL) and extracted with 10% HCl (3 x 15 mL). The combined aqueous layers were basified to pH 8-9 (NaHCO₃, 1M NaOH) and extracted

with EtOAc (3 x 30 mL). The combined EtOAc layers were washed with water (30 mL) and brine (30 mL), then dried over Na₂SO₄. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ¹H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (EtOAc/triethylamine = 19/1) to give the title compound **18d** (89 mg, 48% yield) as a light brown oil. [α]_D²⁵ = -28.9° (*c* = 1.06, CHCl₃); IR (neat): 2954, 1733, 1419, 1205, 1137, 883 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 3.68 (s, 3H), 3.64 (t, *J* = 7.2 Hz, 1H), 3.49 (d, *J* = 9.8 Hz, 1H), 2.95-2.91 (m, 1H), 2.85-2.80 (m, 1H), 2.06-1.99 (m, 1H), 1.83-1.75 (m, 2H), 1.51-1.42 (m, 2H); ¹³C NMR DEPT (75 MHz, CDCl₃) δ 172.6, 148.8, 138.2, 130.4, 121.4, 118.7 (CF₃), 61.2, 57.3, 52.0, 46.0, 30.0, 24.8; HRMS (ESI) calcd for C₁₄H₁₇O₅NF₃S (MH⁺): 368.0774. Found: 368.0764.

The above compound **18d** was converted to the trifluoroacetamide in order to measure the enantiomeric excess. Acylation: A small sample of the free amine (5 mg) was dissolved in DCM (1 mL). Pyridine (2 drops) and TFAA (2 drops) were added and the reaction was stirred for 3 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ether = 2/1) to give the amide. 85% ee (*S,S*-Whelk column, 10% *i*-PrOH in hexanes, 1 mL/min, λ = 254 nm, *t*_R = 9.0, major; 12.0 minor).

(*R*)-Methyl 2-(cyclohexa-2,5-dienyl)-2-(4-iodophenyl)acetate (19a): A solution of **2a** (151 mg, 0.5 mmol) in hexanes (10 mL) was added dropwise over 1 h using a syringe pump to a solution of Rh₂(*S*-DOSP)₄ (9.4 mg, 1 mol%) and 1,4-cyclohexadiene (200 mg, 2.5 mmol) in hexanes (5 mL) at –40 °C. After the addition was complete, the reaction was warmed to 23 °C and stirred for 2 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Et₂O/pentane = 1/20) to give the title compound **19a** (132 mg, 74% yield) as colorless oil. $[\alpha]_D^{25} = -119^\circ$ ($c = 1.66$, CHCl₃); 95% ee (*R,R*-Whelk column, 0.7% iPrOH in hexanes, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 8.5$, major; 10.7, minor); IR (neat): 2361, 2339, 1738, 1689, 1580 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, $J = 8.5$ Hz, 2H), 7.08 (d, $J = 8.5$ Hz, 2H), 5.81-5.79 (m, 1H), 5.71-5.66 (m, 2H), 5.28-5.26 (m, 1H), 3.68 (s, 3H), 3.46-2.42 (m, 1H), 3.37 (d, $J = 10.0$ Hz, 1H), 2.60-2.58 (m, 2H); ¹³C NMR DEPT (75 MHz, CDCl₃) δ 172.9 (C), 137.5 (CH), 136.3 (C), 130.6 (CH), 126.5 (CH), 126.3 (CH), 126.2 (CH), 125.3 (CH), 93.0 (C), 57.6 (CH), 52.0 (CH₃), 38.4 (CH), 26.3 (CH₂); LRMS (EI) m/z (relative intensity): mass ion not observed, 276 (100), 244 (41), 79 (61), 77 (42); HRMS (EI) calcd for C₁₅H₁₃O₂I (M-2H⁺): 351.9955. Found: 351.9957.

(*R*)-Methyl 2-(cyclohexa-2,5-dienyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetate (19b): A solution of **2b** (151 mg, 0.55 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of Rh₂(*S*-DOSP)₄ (9.4 mg, 1 mol%) and 1,4-cyclohexadiene (200 mg, 2.5 mmol) in hexanes (5 mL) at –40 °C. After the

addition was complete, the reaction was warmed to 23 °C and stirred for 16 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Et₂O/pentane = 1/10) to give the title compound **19b** (110 mg, 62% yield) as white solid. mp = 90-93 °C; $[\alpha]_D^{25} = -109^\circ$ ($c = 1.00$, CHCl₃); 89% ee (AD-RH column, 1% *i*PrOH in hexanes, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 4.2$, minor; 4.6, major); IR (neat): 3045, 2981, 2861, 1737, 1269 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 5.81-5.63 (m, 3H), 5.25-5.23 (m, 1H), 3.66 (s, 3H), 3.51-3.49 (m, 1H), 3.43 (d, $J = 10.5$ Hz, 1H), 2.61-2.59 (m, 2H), 1.34 (s, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 173.1, 139.8, 134.9, 128.0, 126.5, 126.3, 125.9, 125.7, 83.7, 58.4, 51.9, 38.9, 26.3, 24.8 (2C), C-B signal not observed; LRMS (EI) m/z (relative intensity): 354 (2), 293 (100), 193 (35), 165 (46); Anal. Calcd for C₂₁H₂₇BO₄: C, 71.20; H, 7.68. Found: C, 70.95; H, 7.66.

(R)-Methyl 2-(cyclohexa-2,5-dienyl)-2-(4-trifluoromethanesulfonyloxyphenyl)acetate (19d) 1,4-Cyclohexadiene (200 mg, 2.5 mmol) and Rh₂(*S*-DOSP)₄ (9.4 mg, 1 mol%) were dissolved into degassed hexanes (5 mL). A solution of **2d** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h via syringe pump at -40°C and warmed to rt. The solution was concentrated in *vacuum* followed by flash chromatography (petroleum ether/ether = 9/1) on silica gel gave **19d** (111 mg, 59% yield) as white solid. mp = 34–35 °C; 94% ee (OD-H column, 1.0 mL/min, 1% *i*-PrOH in hexanes, $\lambda = 254$ nm,

$t_R = 6.0$, minor; 8.6 , major); $[\alpha]_D^{25} = -80^\circ$ ($c = 1.3$, CHCl_3); IR (neat): $3028, 2957, 2866, 1737, 1501, 1427, 1215, 1141, 890 \text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3) δ 7.40 (d, $J = 8.9$ Hz, 2H), 7.21 (d, $J = 8.9$ Hz, 2H), 5.78 (d, $J = 10.0$ Hz, 1H), 5.70 (d, $J = 10.4$ Hz, 1H), 5.63 (d, $J = 10.1$ Hz, 1H), 5.24 (d, $J = 10.0$ Hz, 1H), 3.68 (s, 3H), 3.46 (m, 2H), 2.55 (m, 2H); ^{13}C NMR DEPT (125 MHz, CDCl_3) δ 172.7 (C), 148.8 (C), 137.1 (C), 130.6 (CH), 126.8 (CH), 126.7 (CH), 125.9 (CH), 124.9 (CH), 121.2 (CH), 118.7 (CF_3), 57.3 (CH), 52.1 (CH_3), 38.7 (CH), 26.2 (CH_2); HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{15}\text{O}_5\text{F}_3\text{NaS}$ (M^+): 399.0485. Found: 399.0485.

(R)-Methyl-2-(cyclohepta-2,4,6-trienyl)-2-(4-iodophenyl)acetate (20a): A solution of **2a** (151 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) and 1,3,5-cycloheptatriene (230 mg, 2.5 mmol) in hexanes (5 mL) at -40°C . After the addition was complete, the reaction was warmed to 23°C and stirred for 2 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography ($\text{Et}_2\text{O}/\text{Pentane} = 1/20$) to give the title compound **20a** (106 mg, 58% yield) as a light yellow oil. $[\alpha]_D^{25} = +7^\circ$ ($c = 0.38$, CHCl_3); 91% ee (*S,S*-Whelk column, 0.3% iPrOH in hexanes, 1.0 mL/min, $\lambda = 254 \text{ nm}$, $t_R = 27.2$, major; 31.6 , minor); IR (neat): $3017, 2950, 2362, 2329, 1736, 1484 \text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 8.5$ Hz, 2H), 7.04 (d, $J = 8.5$ Hz, 2H), 6.72-6.64 (m, 2H), 6.27 (dd, $J = 9.5, 5.5$ Hz, 1H), 6.12 (dd, $J = 9.5, 5.5$ Hz, 1H), 5.36 (dd, $J = 9.0$,

6.5 Hz, 1H), 4.96 (dd, $J = 9.0, 6.5$ Hz, 1H), 3.77 (d, $J = 12.0$ Hz, 1H), 3.67 (s, 3H), 2.68-2.63 (m, 1H); ^{13}C NMR DEPT (75 MHz, CDCl_3) δ 172.9 (C), 137.7 (CH), 136.6 (C), 131.0 (CH), 130.8 (CH), 130.5 (CH), 125.7 (CH), 125.6 (CH), 123.8 (CH), 122.7 (CH), 93.2 (C), 52.1 (2C; CH, CH_3), 41.5 (CH); LRMS (EI) m/z (relative intensity): 366 (20), 307 (100), 165 (84); Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{IO}_2$: C, 52.48; H, 4.13. Found: C, 52.53; H, 4.23.

(*R*)-Methyl 2-(cyclohepta-2,4,6-trienyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)phenyl)acetate (20b): A solution of **2b** (151 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of $\text{Rh}_2(\text{S-DOSP})_4$ (9.4 mg, 1 mol%) and 1,3,5-cycloheptatriene (230 mg, 2.5 mmol) in hexanes (5 mL) at -40 °C. After the addition was complete, the reaction was warmed to 23 °C and stirred for 16 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Et_2O /pentane = 1/10) to give the title compound **20b** (106 mg, 58% yield) as a white gum. $[\alpha]_D^{25} = -37^\circ$ ($c = 2.13$, CHCl_3); 88% ee (*R,R*-Whelk column, 0.3% *i*PrOH in hexanes, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 17.4$, minor; 23.8, major); IR (neat): 2982, 1738, 1363 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.71-6.63 (m, 2H), 6.26 (dd, $J = 9.5, 5.5$ Hz, 1H), 6.08 (dd, $J = 9.5, 6.0$ Hz, 1H), 5.37 (dd, $J = 9.0, 6.0$ Hz, 1H), 4.97 (dd, $J = 9.5, 6.5$ Hz, 1H), 3.83 (d, $J = 11.9$ Hz, 1H), 3.65 (s, 3H), 2.72-2.68 (m, 1H), 1.33 (s, 12H); ^{13}C NMR DEPT (125 MHz, CDCl_3) δ 173.2 (C), 140.1 (C), 135.1 (CH), 131.0 (CH), 130.9 (CH), 128.0 (CH),

125.6 (CH), 125.5 (CH), 124.2 (CH), 123.0 (CH), 83.8 (C), 53.0 (CH), 52.1 (CH₃), 41.6 (CH), 24.8 (2C; CH₃, CH₃), C-B signal not observed; LRMS (EI) *m/z* (relative intensity): mass ion not observed, 91 (100); HRMS (EI) calcd for C₂₂H₂₇BO₄ (M⁺): 366.1997. Found: 366.2003.; Anal. Calcd for C₂₂H₂₇BO₄: C, 72.14; H, 7.43. Found: C, 71.83; H, 7.39.

(R)-Methyl-2-(cyclohepta-2,4,6-trienyl)-2-(4-(trifluoromethanesulfonyl)-

xyphenyl)acetate (20d) 1,3,5-Heptatriene (230 mg, 2.5 mmol) and Rh₂(S-DOSP)₄ (9.4 mg, 1 mol%) were dissolved into degassed hexanes (5 mL). Then a solution of **2d** (162 mg, 0.5 mmol) in hexanes (10 mL) was added over 1 h via syringe pump at -40 °C and then the mixture was warmed to rt. The solution was concentrated in *vacuum* followed by flash chromatography (pet ether/ether = 9/1) on silica gel to give **20d** (125 mg, 52% yield) as a white gum. 95% ee (*S,S*-Whelk, 1.0 mL/min, 1% *i*-PrOH in hexanes, λ = 254 nm, t_R = 11.0, minor; 13.4, major; [α]_D²⁵ = +10° (*c* = 1.43, CHCl₃); IR (neat): 3018, 2956, 1738, 1502, 1426, 1215, 1141, 890 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.73-6.64 (m, 2H), 6.28 (dd, *J* = 9.4, 6.0 Hz, 1H), 6.13 (dd, *J* = 9.4, 6.0 Hz, 1H), 5.38 (dd, *J* = 9.3, 6.5 Hz, 1H), 4.94 (dd, *J* = 9.3, 6.5 Hz, 1H), 3.84 (d, *J* = 11.9 Hz, 1H), 3.67 (s, 3H), 2.72-2.67 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 172.8, 148.9, 137.6, 131.2, 130.9, 130.4, 126.01, 125.96, 123.6, 122.4, 121.5, 118.7(CF₃), 52.2, 51.8, 41.9; HRMS (EI) calcd. for C₁₇H₁₅O₅F₃S (M⁺): 388.0587. Found: 388.0593.

(*E*)-(2*S*,3*R*)-3-(*tert*-Butyldimethylsilanyloxy)-2-(4-iodophenyl)-5-phenylpent-4-enoic

acid methyl ester (21a): A solution of **2a** (302 mg, 1.0 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of $\text{Rh}_2(\text{S-DOSP})_4$ (18.8 mg, 1 mol%) and (*E*)-1-(*tert*-Butyldimethylsiloxy)-3-phenyl-2-butene (125 mg, 0.5 mmol) in hexanes (5 mL) at -40°C . After the addition was complete, the reaction was warmed to 23°C and stirred for 2 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be $>94\%$ de by ^1H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography ($\text{Et}_2\text{O}/\text{Pentane} = 1/10$) to give the title compound **21a** (248 mg, 95% yield) as a white gum. $[\alpha]_D^{25} = -45^\circ$ ($c = 1.67$, CHCl_3); 84% ee (AD-RH column, 1% *i*-PrOH in hexanes, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 3.8$, major; 5.4 minor); IR (neat): 3028, 2953, 2893, 2858, 1737, 1484, 1255 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.68 (d, $J = 8.0$ Hz, 2H), 7.38-7.27 (m, 5H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.61 (d, $J = 16.0$ Hz, 1H), 6.13 (dd, $J = 16.0, 7.3$ Hz, 1H), 4.78 (t, $J = 7.5$ Hz, 1H), 3.68 (d, $J = 8.0$ Hz, 1H), 3.65 (s, 3H), 0.77 (s, 9H), -0.06 (s, 3H), -0.19 (s, 3H); ^{13}C NMR DEPT (125 MHz, CDCl_3) δ 171.1 (C), 137.2 (CH), 136.5 (C), 135.7 (C), 131.7 (CH), 131.5 (CH), 130.2 (CH), 128.6 (CH), 127.8 (CH), 126.5 (CH), 93.0 (C), 75.6 (CH), 59.1 (CH), 51.9 (CH_3), 25.6 (CH_3), 17.9 (C), -4.3 (CH_3), -5.4 (CH_3); LRMS (EI) m/z (relative intensity): mass ion not observed, 465 (5), 247 (100), 204 (19), 89 (30), 73 (41); Anal. Calcd for $\text{C}_{24}\text{H}_{31}\text{IO}_3\text{Si}$: C, 55.17; H, 5.98. Found: C, 55.29; H, 6.05.

21b

(*E*)-(2*S*,3*R*)-3-(*tert*-Butyldimethylsilanyloxy)-5-phenyl-2-[4-(4,4,5,5-tetramethyl-

1,3,2-dioxaborolan-2-yl)phenyl]pent-4-enoic acid methyl ester (21b**):** A solution of **2b** (302 mg, 1 mmol) in hexanes (10 mL) was added over 1 h using a syringe pump to a solution of Rh₂(*S*-DOSP)₄ (18.8 mg, 1 mol%) and (*E*)-1-(*tert*-Butyldimethylsiloxy)-3-phenyl-2-butene (125 mg, 0.5 mmol) in hexanes (5 mL) at −40 °C. After the addition was complete, the reaction was warmed to 23 °C and stirred for 1 h. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by ¹H NMR analysis of the crude reaction mixture. The residue was purified by flash chromatography (Et₂O/pentane = 1/10) to give the title compound **21b** (195 mg, 74% yield) as a white gum. [α]_D²⁵ = −41° (*c* = 1.25, CHCl₃); 89% ee (AD-RH column, 0.7% *i*-PrOH in hexanes, 1.0 mL/min, λ = 254 nm, *t*_R = 4.2, major; 6.3 minor); IR (neat): 2980, 2953, 2931, 2858, 1739, 1400, 1362 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.40–7.23 (m, 5H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.81 (t, *J* = 8.0 Hz, 1H), 3.72 (d, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 1.35 (s, 12H), 0.72 (s, 9H), −0.11 (s, 3H), −0.26 (s, 3H); ¹³C NMR DEPT (75 MHz, CDCl₃) δ 172.0 (C), 139.1 (C), 136.7 (C), 134.6 (CH), 131.4 (CH), 130.6 (CH), 128.9 (CH), 128.5 (CH), 127.6 (CH), 126.6 (CH), 83.7 (C), 75.6 (CH), 59.8 (CH), 51.8 (CH₃), 25.6 (CH₃), 24.9 (CH₃), 24.8 (CH₃), 17.9 (C), −4.4 (CH₃), −5.4 (CH₃), C-B signal not observed;

LRMS (ESI) m/z (relative intensity): 545 (100, MNa^+); HRMS (EI) calcd for $C_{30}H_{34}BNaO_5Si$ (MNa^+): 545.2865. Found: 545.2856.

(*E*)-(2*S*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(4-trifluoromethanesulfonyloxyphenyl)-5-phenyl-pent-4-enoic acid methyl ester (21d) (*E*)-1-(*tert*-Butyldimethylsilyloxy)-3-phenyl-2-butene (125 mg, 0.5 mmol) and $Rh_2(S-DOSP)_4$ (37.6 mg, 2 mol%) were dissolved into degassed hexanes (5 mL). Then a solution of **2d** (324 mg, 1 mmol) in hexanes (10 mL) was added over 2 h via syringe pump at 50°C and stirred for another 10 min. The solvent was removed under reduced pressure and the diastereoselectivity was determined to be >94% de by 1H NMR analysis of the crude reaction mixture. Purification by flash chromatography (petroleum ether/ether = 20/1) on silica gel gave **21d** (161 mg, 59% yield) as a white gum. (ee was determined from the corresponding alcohol, 74% ee, *R,R*-Whelk column, 1.0 mL/min, 5% *i*-PrOH in hexanes, λ = 254 nm, t_R = 14.6, minor; 18.6, major); $[\alpha]_D^{25} = +28^\circ$ (c = 1.0, $CHCl_3$); IR (neat) 2956, 2930, 2859, 1738, 1501, 1427, 1214, 1142, 889, 838 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.8 Hz, 2H), 7.33-7.23 (m, 7H), 6.58 (d, J = 15.8 Hz, 1H), 6.09 (dd, J = 15.9, 7.6 Hz, 1H), 4.73 (t, J = 7.6 Hz, 1H), 3.73 (d, J = 8.2 Hz, 1H), 3.63 (s, 3H), 0.71 (s, 9H), -0.10 (s, 3H), -0.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 149.0, 136.8, 136.5, 132.0, 131.3,

130.0, 128.6, 127.9, 126.6, 121.0, 118.7 (CF₃), 75.9, 59.0, 52.0, 25.5, 17.9, , -4.3, -5.5;
 HRMS (ESI) calcd.for C₂₅H₃₁O₆F₃NaSSi (M⁺): 567.1455. Found: 567.1451.

(E)-(2S,3R)-2-(4-trifluoromethanesulfonyloxyphenyl)-5-phenyl-3-hydroxy-pent-4-enoic acid methyl ester 21d (25 mg, 0.1 mmol) was dissolved into methanol (5mL) at 0°C, then 2 drops of con. HCl was added and stirred for 2 min, then solvent was removed, flash chromatography (petroleum ether/ether = 1/1) gave 17.7 mg product, yield 99%. mp = 100-103 °C; $[\alpha]_D^{25} = +47^\circ$ ($c = 1.3$, CHCl₃); IR (neat) 1734, 1423, 1213, 1140, 889 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, $J = 8.9$ Hz, 2H), 7.32-7.25 (m, 7H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.10 (dd, $J = 15.9, 6.7$ Hz, 1H), 4.87 (m, 1H), 3.82 (d, $J = 6.4$ Hz, 1H), 3.69 (s, 3H), 2.49 (d, $J = 3.4$ Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 172.2, 149.1, 136.2, 135.4, 132.8, 131.2, 128.6, 128.1, 127.8, 126.6, 121.4, 118.7 (CF₃), 73.6, 57.1, 52.4; HRMS (ESI) calcd.for C₁₉H₂₇O₆F₃NaSSi (M⁺): 453.0590. Found 453.0593.

(1R,2S)-1-(4'-Methoxybiphenyl-4-yl)-2-phenylcyclopropanecarboxylic acid methyl ester (22) To a 25 ml flask **9d** (121 mg, 0.3 mmol), *p*-methoxyphenylboronic acid (69 mg, 0.45 mmol), palladium acetate (1.3 mg, 2 mol%), PPh₃ (6.1 mg, 8 mol%), K₃PO₄ (258 mg, 0.9 mmol) and degassed THF (5 mL) were added, and heated to reflux for 12 h. The

mixture was concentrated and washed through a pad of silica with ether. Flash chromatography (pet ether/ether = 4/1) gave **22** (97 mg, 90% yield) as white solid. mp = 100-104 °C; IR (neat): 3034, 2953, 2839, 1719, 1606, 1500, 1456, 1162, 1091, 818 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.06-7.01 (m, 5H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.79 (m, 2H), 3.81 (s, 3H), 3.67 (s, 3H), 3.12 (dd, *J* = 9.1, 7.3 Hz, 1H), 2.15 (dd, *J* = 9.1, 4.9 Hz, 1H), 1.87 (dd, *J* = 7.3, 4.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 174.6, 159.3, 139.4, 136.6, 133.4, 133.3, 132.5, 128.3, 128.2, 128.0, 126.6, 126.1, 114.3, 55.6, 52.9, 37.3, 33.5, 20.9; HRMS (ESI) calcd. for C₂₄H₂₂O₃Na (MNa⁺): 381.1461. Found 381.1466.

(1R,2S)-1-[4'-(1R,2S)-(1-Methoxycarbonyl-2-phenylcyclopropyl)biphenyl-4-yl]-2-phenylcyclopropanecarboxylic acid methyl ester (23) To a 25 mL flask **9d** (80 mg, 0.2 mmol), **9b** (76 mg, 0.2 mmol), palladium acetate (4.5 mg, 10 mol%), PPh₃ (21 mg, 40 mol%), K₃PO₄ (127.2 mg, 0.6 mmol) and degassed THF (5 mL) were added, and heated to reflux for 20 h. The mixture was concentrated and washed through a pad of silica with ether. Flash chromatography (pet ether: ether = 4/1, then 1/1) gave **23** (69 mg, 68% yield) as white solid. mp = 155-158 °C; [α]_D²⁵ = +50° (*c* = 1.0, CHCl₃); IR (neat): 3046, 2956, 1723, 1504, 1424, 1251, 1213, 1142, 891 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 8.3 Hz, 4H), 7.05-7.03 (m, 10H), 6.79-6.77 (m, 4H), 3.66 (s, 6H), 3.12 (dd, *J* = 8.9, 7.5

Hz, 2H), 2.15 (dd, $J = 8.8, 4.9$ Hz, 2H), 1.88 (dd, $J = 7.5, 4.9$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 174.2, 139.0, 136.2, 133.7, 132.1, 128.0, 127.7, 126.3, 126.1, 52.6, 37.0, 33.2, 20.4; HRMS (ESI) calcd. for $\text{C}_{34}\text{H}_{30}\text{O}_4\text{Na}$ (MNa^+): 525.2036. Found 525.2034.

(1R,2S)-1-[4'-(1S)-(1-Methoxycarbonyl-2-phenylcyclopropyl)biphenyl-4-yl]-2,2-diphenylcyclopropanecarboxylic acid methyl ester (24) To a 25 mL flask **13b** (91 mg, 0.2 mmol), **9d** (80 mg, 0.2 mmol), palladium acetate (4.5 mg, 10 mol%), PPh_3 (21 mg, 40 mol%), K_3PO_4 (127 mg, 0.6 mmol) and degassed THF (5 mL) were added, and heated to reflux for 20 h. The mixture was concentrated and washed through a pad of silica with ether. Flash chromatography (petroleum ether/ether = 4/1-1/1) gave **24** (96 mg, 83% yield) as white solid. mp = 89-91 $^\circ\text{C}$; $[\alpha]_D^{25} = +226^\circ$ ($c = 1.0$, CHCl_3); IR (neat): 3028, 2949, 2855, 1717, 1256, 1216, 696 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, $J = 7.0$ Hz, 2H), 7.35 - 7.23 (m, 9H), 7.06 - 6.93 (m, 10H), 6.79-6.77 (m, 2 H), 3.67 (s, 3H), 3.36 (s, 3H), 3.11 (dd, $J = 9.1, 7.3$ Hz, 1H), 2.70 (d, $J = 5.5$ Hz, 1H), 2.42 (d, $J = 5.5$ Hz, 1H), 2.15 (dd, $J = 9.1, 4.9$ Hz, 1H), 1.87 (dd, $J = 7.3, 4.9$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 174.3, 171.3, 141.9, 139.5, 139.02, 138.96, 136.2, 134.6, 133.7, 132.13, 133.11, 129.9, 128.7, 128.3, 128.0, 127.7, 127.6, 126.9, 126.3, 126.1, 125.9, 52.6, 52.2, 44.5, 42.8, 37.0, 33.2, 22.8, 20.5; Anal. Calcd for $\text{C}_{40}\text{H}_{34}\text{O}_4$ C, 83.02; H, 5.92; Found: C, 82.96, H, 6.12; HRMS (EI) calcd. for $\text{C}_{40}\text{H}_{34}\text{O}_4$ (M^+): 578.2452. Found 578.2444.

(1*R*,2*S*)-1-[3'-(1*S*)-(1-Methoxycarbonyl-2-phenylcyclopropyl)biphenyl-4-yl]-2,2-diphenylcyclopropanecarboxylic acid methyl ester (25**)** To a 25 mL flask **13b** (91 mg, 0.2 mmol), **9f** (80 mg, 0.2 mmol), palladium acetate (4.5 mg, 10 mol%), PPh₃ (21 mg, 40 mol%), K₃PO₄ (127 mg, 0.6 mmol) and degassed THF (5 mL) were added, and heated to reflux for 20 h. The mixture was concentrated and washed through a pad of silica with ether. Flash chromatography (petroleum ether: ether = 4/1-1/1) gave **25** (106 mg, 92% yield) as white solid. mp = 199-201 °C; [α]_D²⁵ = +87° (*c* = 1.03, CHCl₃); IR (neat): 3022, 1717, 1261, 1217, 750 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, *J* = 7.0 Hz, 2H), 7.35 - 7.31 (m, 4H), 7.26-7.23 (m, 2H), 7.15-6.94 (m, 13H), 6.78 (dd, *J* = 3.4, 5.2 Hz, 2 H), 3.64 (s, 3H), 3.34 (s, 3H), 3.12 (dd, *J* = 9.1, 7.3 Hz, 1H), 2.70 (d, *J* = 5.5 Hz, 1H), 2.40 (d, *J* = 5.5 Hz, 1H), 2.14 (dd, *J* = 9.1, 4.9 Hz, 1H), 1.88 (dd, *J* = 7.3, 4.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 174.2, 171.4, 142.0, 140.1, 139.7, 139.5, 136.4, 135.2, 134.6, 132.0, 130.9, 130.7, 129.9, 128.8, 128.3, 128.1, 127.9, 127.8, 127.6, 126.9, 126.4, 126.13, 126.06, 125.8, 76.6, 52.6, 52.1, 44.5, 42.8, 37.3, 33.1, 22.9, 20.5; HRMS (EI) calcd. for C₄₀H₃₄O₄ (M⁺): 578.2452. Found 578.2456.

(1*R*,2*S*)-1-[4'-((*R*)-Cycloheptatrienylmethoxycarbonylmethyl)biphenyl-4-yl]-2-

phenylcyclopropanecarboxylic acid methyl ester (26**)** To a 25 ml flask **11b** (73 mg, 0.2

mmol), **9d** (80 mg, 0.2 mmol), palladium acetate (4.5 mg, 10 mol%), PPh₃ (21 mg, 40 mol%), K₃PO₄ (127 mg, 0.6 mmol) and degassed THF (5 ml) were added, and heated to

reflux for 20 h. The mixture was concentrated and washed through a pad of silica gel with ether. Flash chromatography (petroleum ether/ether = 4/1) gave **26** (56.2 mg, 57%

yield) as white gum. $[\alpha]_D^{25} = +61.5^\circ$ ($c = 1.05$, CHCl₃); IR (neat): 3022, 1717, 1499, 1255,

1159, 751, 696 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 7.9$ Hz, 2H), 7.08 - 7.04 (m, 5H), 6.79-6.78 (m, 2H), 6.68 (ddd,

$J = 13.3, 11.0, 5.5$ Hz, 2H), 6.27 (dd, $J = 9.5, 5.5$ Hz, 1H), 6.11 (dd, $J = 9.4, 5.5$ Hz, 1H),

5.37 (dd, $J = 9.4, 6.1$ Hz, 1H), 5.01 (dd, $J = 9.5, 6.4$ Hz, 1H), 3.84 (d, $J = 11.9$ Hz, 1H),

3.69 (s, 3H), 3.68 (s, 3H), 3.13 (dd, $J = 9.3, 7.4$ Hz, 2H), 2.68 (m, 1H), 2.17 (dd, $J = 9.3,$

5.0 Hz, 1H), 1.90 (dd, $J = 7.3, 5.0$ Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 174.2, 173.4,

139.9, 139.0, 136.2, 136.0, 133.9, 132.3, 131.0, 130.9, 128.9, 128.0, 127.7, 127.2, 126.3,

126.2, 125.7, 125.5, 124.2, 123.2, 52.60, 52.58, 52.1, 41.7, 37.0, 33.2, 20.4; HRMS (EI)

calcd. for C₃₃H₃₀O₄ (M⁺): 490.2139. Found 490.2130.

(1R,2S)-1-[4'-(1R,2S)-(1-Methoxycarbonyl-2-phenylcyclopropyl)biphenyl-4-yl]-2-

phenylvinylcyclopropanecarboxylic acid methyl ester (27) To a 25 ml flask **9b** (75 mg, 0.2 mmol), **11d** (85.3 mg, 0.2 mmol), palladium acetate (4.5 mg, 10 mol%), PPh₃ (21 mg, 40mol%), K₃PO₄ (127 mg, 0.6 mmol) were added, then flushed with argon, then THF (5 ml) were added. The reaction was refluxed for 16 h. The mixture was concentrated and washed through a pad of silica with ether. Flash chromatography (petroleum ether/ether = 2/1) gave **27** (78 mg, 74% yield) as white gum. $[\alpha]_D^{25} = -48.2^\circ$ ($c = 1.15$, CHCl₃); IR (neat): 3029, 2951, 2929, 2855, 1718, 1434, 1255, 1161, 834, 776, 732 cm⁻¹; ¹H NMR (500 Mz, CDCl₃) δ 7.49 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 6.3$ Hz, 2H), 7.23-7.02 (m, 11H), 6.79 (dd, $J = 7.6, 2.8$ Hz, 1H), 6.58 (d, $J = 16.1$ Hz, 1H), 5.22 (dd, $J = 16.1, 9.8$ Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 3.13 (dd, $J = 9.2, 7.5$ Hz, 1H), 2.69 (dd, $J = 9.0, 6.6$ Hz, 1H), 2.15 (dd, $J = 9.1, 5.0$ Hz, 1H), 2.06 (dd, $J = 9.0, 4.5$ Hz, 1H), 1.90 (dd, $J = 7.5, 5.0$ Hz, 1H), 1.48 (dd, $J = 6.6, 4.6$ Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 174.2, 174.1, 139.5, 139.1, 137.1, 136.2, 134.8, 133.9, 132.2, 131.9, 131.3, 128.7, 128.4, 128.0, 127.7, 127.1, 126.5, 126.3, 126.2, 125.9, 52.6, 52.5, 37.0, 35.4, 33.2, 32.0, 22.6, 20.4; HRMS (ESI) calcd. for C₃₆H₃₃O₄ (M⁺): 529.2373. Found 529.2385;

(S)-1-[4'-((R)-Cycloheptatrienylmethoxycarbonylmethyl)biphenyl-4-yl]-2,2-diphenylcyclopropanecarboxylic acid methyl ester (28):

This was prepared according to a modified procedure of Tao.⁵ **13a** (91 mg, 0.20 mmol), (*R*)-methyl **20b** (74 mg, 0.20 mmol), DAPCy (6 mg, 0.01 mmol), and potassium phosphate (127 mg, 0.60 mmol) were dissolved in EtOH (5mL). The reaction was stirred for 16 h at rt. The mixture was extracted with Et₂O (3 x 50 mL) and the combined Et₂O layers were washed with brine (50 mL), then dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Et₂O/Pentane = 1/9) to give the title compound **221** (88 mg, 0.16 mmol, 79% yield) as a white gum. $[\alpha]_D^{25} = +168^\circ$ (*c* 1.31, CHCl₃); IR (neat): 3024, 2954, 1726, 1497, 1448, 1434, 1217, 1156, 1007 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.38-7.30 (m, 10H), 7.01-6.92 (m, 4H), 6.26 (dd, *J* = 9.0, 5.5 Hz, 1H), 6.11 (dd, *J* = 9.0, 5.5 Hz, 1H), 5.37 (dd, *J* = 9.0, 6.0 Hz, 1H), 5.01 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.84 (d, *J* = 11.5 Hz, 1H), 3.68 (s, 3H), 3.50-3.46 (m, 1H), 3.37 (s, 3H), 2.72-2.66 (m, 1H), 2.45 (d, *J* = 5.5 Hz, 1H); ¹³C NMR DEPT (75 MHz, CDCl₃) δ 173.4 (C), 171.3 (C), 141.9 (C), 139.9 (C), 139.5 (C), 138.9 (C), 135.9 (C), 134.8 (C), 132.2 (CH), 131.0 (CH), 130.8 (CH), 129.9 (CH), 128.8 (CH), 128.7 (CH), 128.3 (CH), 127.6 (CH), 127.1 (CH), 126.9 (CH), 126.1 (CH), 126.0 (CH), 125.6 (CH), 125.5 (CH), 124.1 (CH),

123.1 (CH), 52.5 (CH), 52.1 (CH₃), 52.0 (CH₃), 44.5 (C), 42.7 (C), 41.7 (CH), 22.7 (CH₂); LRMS (EI) *m/z* (relative intensity): 566 (24), 475 (87), 250 (53), 191 (76), 165 (46), 91(100); HRMS (EI) calcd for C₃₉H₃₄O₄ (M⁺): 566.2452. Found: 566.2451.

(1*R*,2*S*)-1-{4'-[(1*S*,2*R*)-2-(tert-Butyldimethylsilyloxy)-1-methoxycarbonyl-4-phenylbut-3-enyl]biphenyl-4-yl}-2-phenylcyclopropanecarboxylic acid methyl ester (29)

This was prepared according to a modified procedure of Tao.⁵ To a 25 ml flask **9b** (75 mg, 0.2 mmol), **21a** (104 mg, 0.2 mmol), DAPCy (5.9 mg, 5 mol%), K₃PO₄ (127 mg, 0.6 mmol) and EtOH (5 ml) were added, and stirred at room temperature for 16 h. The mixture was concentrated and washed through a pad of silica with ether. Flash chromatography (petroleum ether/ether = 4/1) gave **29** (85 mg, 66% yield) as white solid. mp = 141-144 °C; [α]_D²⁵ = -13.7° (*c* = 1.05, CHCl₃); IR (neat): 3028, 2951, 1714, 1247, 1161, 908, 728 cm⁻¹; ¹H NMR (500 Mz, CDCl₃) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.37 - 7.29 (m, 6H), 7.25-7.22 (m, 2H), 7.09-7.05 (m, 5 H), 6.81-6.79 (m, 2H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.78 (t, *J* = 7.6 Hz, 1H), 3.71 (d, *J* = 7.7 Hz, 1H), 3.69 (s, 3H), 3.62 (s, 3H), 3.13 (dd, *J* = 9.3, 7.5 Hz, 1H), 2.17 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.90 (dd, *J* = 7.5, 4.9 Hz, 1H), 0.72 (s, 9H), -0.11 (s, 3H), -0.26 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 174.3, 172.2, 139.8, 139.4, 136.7, 136.3, 135.0,

133.8, 132.2, 131.4, 130.6, 129.8, 128.5, 128.1, 127.73, 127.66, 126.7, 126.5, 126.34, 126.26, 75.7, 59.3, 52.6, 51.8, 37.1, 33.2, 25.6, 20.5, 17.9, -4.4, -5.4; HRMS (ESI) calcd. for $C_{41}H_{46}O_5NaSi$ (MNa^+): 669.3007. Found 669.3007.

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