Catalytic Asymmetric Synthesis of Diarylacetates and 4,4-Diarylbutanoates. A Formal Asymmetric Synthesis of (+)-Sertraline

Huw M. L. Davies*, Douglas G. Stafford and Tore Hansen

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14260

hdavies@acsu.buffalo.edu

Supporting Information.

Full experimental data for compounds **13**, **15-21**, **23** and **25**.

Experimental Section

^{1}H NMR spectra were run at either 300, 400, or 500 MHz, and ^{13}C NMR at either 75 or 125 MHz in $CDCl_3$ unless otherwise noted. Mass spectral determinations were carried out at 70 eV. Melting points are uncorrected. IR spectra were obtained using a Nicolet Impact series 420 IR. Optical rotations were measured using a Jasco DIP-370 digital polarimeter. Glassware was flame dried prior to use. Solvent hexanes was distilled over sodium with triglyme and benzophenone. Reactions were carried out under an atmosphere of argon. Hydrogenations were carried out using a Parr hydrogenation apparatus. Ozonolyses were carried out using a Welbash T-408 ozone generator. Elemental analysis performed by Atlantic Microlab, Inc.; Norcross, Georgia. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). Commercially available reagents were used without additional purification unless noted. *p*-Acetamidobenzenesulfonyl azide (*p*-ABSA),[1] and vinyldiazoacetates **14**, **20** and **22** were prepared from known procedures.[1,2]

Formation of the Aryldiazomethanes.

Methyl 1-(4-Cl-phenyl)-1-phenyl acetate (13a). A degassed solution of methyl 4-Cl-phenyldiazoacetate (211 mg, 1.00 mmol), in hexane (10 mL) was added dropwise over 1 h to a degassed, – 50 ˚C solution of Rh_2(*S*-DOSP)$_4$ (19 mg, 0.010 mmol) and 1,4-cyclohexadiene (400 mg, 5.0 mmol) in hexane (5 mL). The solvent was removed under reduced pressure and flash chromatography with 2 % Et_2O / petroleum ether gave **12a** (220 mg) in 84 % as a colorless oil. 94 % ee, Daicel-OD, 0.6 % IPA / hex., 1.0 mL / min, T_R = 6.5 min and 9.8 min. The product **12a** (210 mg, 0.80 mmol) was dissolved in benzene (25 mL), treated with DDQ (380 mg, 1.67 mmol) for 2 h at ambient temperature. The solution was filtered, concentrated and the product purified through silica (2 % Et_2O / petroleum ether) to give **13a** (180 mg) in 86 % yield. $[\alpha]^{25}_D$ = 11.5˚ (*c* = 3.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (1,4-diene) δ 7.28 (m, 4H), 5.80 (m, 1H), 5.69 (m, 2H), 5.27 (d, 1H, *J* = 9.9 Hz), 3.67 (s, 3H), 3.42 (m, 2H), 2.59 (s, 2H); (DDQ-product) _ 7.36–7.26 (m, 9H), 5.04 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (DDQ product) δ 172.5 (C), 138.1 (C), 137.0 (C), 133.2 (C), 130.0 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 127.4 (CH), 56.2 (CH), 52.4 (CH_3); IR (cm^{-1}, DDQ-product, neat): 3087, 3062, 3028, 2951, 2922, 1737, 1601, 1491, 1452, 1432, 1199, 1150, 1089, 1012. HRMS calcd for $C_{16}H_{13}O_2$, 260.0600, found, 260.0604.

Methyl 1−(4-Me-phenyl)-1-phenyl acetate (13b). A degassed solution of methyl 4-Me-phenyldiazoacetate (192 mg, 1.01 mmol), in hexane (10 mL) was added dropwise over 1 h to a degassed, – 50 ˚C solution of Rh_2(*S*-DOSP)$_4$ (19 mg, 0.010 mmol) and 1,4-cyclohexadiene (400 mg, 5.0 mmol) in hexane (5 mL). The solvent was removed under reduced pressure, and flash chromatography with 2 % Et_2O / petroleum ether gave **12b** (203 mg) in 84 % yield as a colorless oil. 94 % ee, Daicel-OD, 1.0 % IPA / hex., 1.0 mL / min, T_R = 6.0 min and 6.5 min. The product **12b** (199 mg, 0.82 mmol) was dissolved in benzene (25 mL), treated with DDQ (378 mg, 1.66 mmol) for 2 h at ambient temperature. The solution was filtered, concentrated and the product purified through silica (2 % Et_2O / petroleum ether) to give **13b** (176 mg) in 89 % yield. $[\alpha]^{25}_D$ = - 6.1˚ (*c* = 5.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (1,4-diene) δ 7.22 (d, 2H, *J* = 8.0 Hz), 7.13 (d, 2H, *J* = 8.0 Hz), 5.82 (m, 1H), 5.69 (m, 2H), 5.27 (d, 1H, *J* = 10.2 Hz), 3.66 (s, 3H), 3.45 (m, 1H), 3.37 (d, 1H, *J* = 10.2 Hz), 2.60 (s, 2H), 2.33 (s, 3H); (DDQ-product) δ 7.40–7.32 (m, 5H), 7.29 (d, 2H, *J* = 4.8 Hz), 7.21 (d, 2H, *J* = 4.8 Hz), 5.09 (s, 1H), 3.81 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (DDQ product) δ 173.0 (C), 138.7 (C), 136.9 (C), 135.6 (C), 129.2 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.1 (CH), 56.6 (CH), 52.2 (CH_3), 21.0 (CH_3); IR (cm^{-1}, DDQ-product, neat): 3059, 3026, 3004, 2950, 2922, 1738, 1512, 1494, 1453, 1433, 1307, 1276, 1233, 1196, 1152. HRMS calcd for $C_{16}H_{16}O_2$, 240.1156, found, 240.1150.

Methyl 1-(4-MeO-phenyl)-1-phenyl acetate (13c). A degassed solution of methyl 4-MeO-phenyldiazoacetate (206 mg, 1.00 mmol), in hexane (5 mL) and F_3C-Ph (5 mL) was added dropwise over 1 h to a degassed, – 50 ˚C solution of Rh_2(*S*-DOSP)$_4$ (19 mg, 0.010 mmol) and 1,4-cyclohexadiene (400 mg, 5.0 mmol) in hexane (5 mL). The solvent was removed under reduced pressure, and flash chromatography with 2 % Et_2O / petroleum ether gave **12c** (179 mg) in 69 % yield as a colorless oil. 93 % ee, Daicel-OD, 0.7 % IPA / hex., 1.0 mL / min, T_R = 12.6 min and 16.1 min). The product **12c** (179 mg, 0.69 mmol) was dissolved in benzene (25 mL), treated with DDQ (204 mg, 0.90 mmol) for 2 h at ambient temperature. The solution was filtered, concentrated and the product purified through silica (2 % Et_2O / petroleum ether) to give **13c** (154 mg) in 87 % yield. $[\alpha]^{25}_D$ = 5.6˚ (*c* = 1.6, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) (1,4-diene) δ 7.25 (d, 2H, *J* = 8.4 Hz), 6.85 (d, 2H, *J* = 8.4 Hz), 5.80 (m, 1H), 5.69 (m, 2H), 5.27 (d, 1H, *J* = 10.3 Hz), 3.79 (s, 3H), 3.66 (s, 3H), 3.42 (m, 1H), 3.37 (d, 1H, *J* = 10.6 Hz), 2.60 (s, 2H); (DDQ-product) δ 7.36 (m, 5H), 7.29 (d, 2H, *J* = 9.0 Hz), 6.91 (d, 2H, *J* = 9.0 Hz), 5.05 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (DDQ product) δ 173.2 (C), 158.7 (C), 138.9 (C), 130.7 (C), 129.6 (CH), 128.5 (CH), 128.4 (CH), 127.1 (CH), 113.9 (CH), 56.1 (CH), 55.1 (CH_3), 52.2 (CH_3); IR (cm^{-1}, DDQ-product, neat): 3061, 3028, 3000, 2950, 2937, 1736, 1607, 1584, 1511, 1459, 1433, 1302, 1251, 1150. HRMS calcd for $C_{16}H_{16}O_3$, 256.1101, found, 256.1099.

Methyl 1-(2-naphthyl)-1-phenyl acetate (13d). A degassed solution of methyl 2-naphthyldiazoacetate (226 mg, 1.00 mmol), in hexane (7 mL) and F_3C-Ph (3 mL) was added dropwise over 1 h to a degassed, – 50 ˚C solution of Rh_2(*S*-DOSP)$_4$ (19 mg, 0.010 mmol) and 1,4-cyclohexadiene (400 mg, 5.0 mmol) in hexane (5 mL). The solvent was removed under reduced pressure, and flash chromatography with 2 % Et_2O / petoleum ether gave **12d** in 64 % yield (178 mg) as a colorless oil. 92 % ee, Daicel-OD, 0.7 % IPA / hex., 1.0 mL / min, T_R = 9.4 min and 10.4 min. The product (172 mg, 0.62 mmol) was dissolved in benzene (25 mL), treated with DDQ (204 mg, 0.90 mmol) for 2 h at ambient temperature. The solution was filtered, concentrated and the product purified through silica (5 % Et_2O / petroleum ether) to give **13d** (150 mg) in 88 % yield as a white solid. 92 % ee, Daicel-OD, 0.7 % IPA / hex., 1.0 mL / min,

T_R = 14.7 min and 15.9 min, $[\alpha]^{25}_D$ = -24.3° (c = 2.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) (1,4-diene) δ 7.81 (m, 4H), 7.49 (m, 3H), 5.81 (m, 2H), 5.68 (d, 2H, J = 9.9 Hz), 5.27 (d, 1H, J = 9.9 Hz), 3.69 (s, 3H), 3.61 (s, 2H), 2.63 (s, 2H); (DDQ-product) δ 7.81 (m, 4H), 7.49 (m, 3H), 7.47–7.33 (m, 5H), 5.28 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (DDQ product) δ 172.9 (C), 138.5 (C), 136.0 (C), 133.3 (C), 132.5 (C), 128.6 (CH), 128.30 (CH), 128.28 (CH), 127.9 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 126.7 (CH), 126.2 (CH), 126.0 (CH), 57.0 (CH), 52.3 (CH_3); IR (cm^{-1}, DDQ-product, neat): 3085, 3058, 3026, 2950, 2940, 1736, 1598, 1509, 1492, 1432, 1308, 1197, 1156. HRMS calcd for $C_{19}H_{16}O_2$, 276.1150, found, 276.1150.

Formation of the Arylvinyldiazomethanes. General Procedure.

Methyl (E)-4-(3,4-dichlorophenyl)-3-butenoate. The acid was prepared following the literature procedure of Minami *et. al*.[3] A solution of potassium *tert*-butoxide (5.28 g, 47 mmol) in tetrahydrofuran (50 mL) was added dropwise, over 1 h, to a stirring solution of 3,4-dichlorobenzaldehyde (3.90 g, 22 mmol) and (2-carboxyethyl)-triphenylphosphonium chloride (8.66 g, 23 mmol) in tetrahydrofuran (60 mL) at 0 °C. After 0.5 h the reaction was allowed to warm to room temperature and let react 12 h. The reaction mixture was added to 1 L of ice water/sat. sodium bicarbonate (1:1) and extracted with ether (3 x 150 mL). The aqueous layer was acidified with HCl (6 M) to ~ pH 1 and extracted with EtOAc (3 x 150 mL). The combined oganics were dried over magnesium sulfate and concentrated under reduced pressure. Products were esterified without further purification. The residue was dissolved in methanol (150 mL), benzene (10 mL), and conc. sulfuric acid (0.5 mL) and refluxed. After 15 h the reaction was added to sat. sodium bicarbonate solution (400 mL) and extracted with ether (3 x 75 mL). The combined organics were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. The residue was chromatographed over silica gel using petroleum ether/Et_2O (9:1) as eluent (R_f = 0.21) to give Methyl (E)-4-(3,4-dichlorophenyl)-3-butenoate in

69% yield (3.77 g) (for two steps) as a clear oil. IR (neat) 3029, 2994, 2954, 2846, 1743 cm^{-1}; ^{1}H NMR (300 MHz) _ 7.43 (d, 1 H, *J* = 2.0 Hz), 7.36 (d, 1 H, *J* = 8.5 Hz), 7.18 (dd, 1 H, *J* = 8.5, 2.0 Hz), 6.39 (d, 1 H, *J* = 16.0 Hz), 6.30 (dt, 1 H, *J* = 16.0, 7.0 Hz), 3.72 (s, 3 H), 3.25 (d, 2 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, DEPT) _ 171.5 (4˚), 136.8 (4˚), 132.6 (4˚), 131.12 (4˚), 131.10 (3˚), 130.4 (3˚), 127.9 (3˚), 125.4 (3˚), 123.8 (3˚), 52.0 (1˚), 37.9 (2˚); MS m/z (relative intensity): 248 (6) M + 4, 246 (36) M + 2, 245 (7) M + 1, 244 (57), 204 (15), 202 (19), 187 (64), 185 (100), 152 (27), 151 (30), 150 (71), 149 (68), 115 (87), 59 (19). Anal. Calcd for $C_{11}H_{10}O_2Cl_2$: C, 53.90; H, 4.11. Found: C, 54.07; H, 4.15.

Methyl (E)-2-diazo-4-(3,4-dichlorophenyl)-3-butenoate (18b). DBU (2.2 mL, 15 mmol) was added drop wise to a solution of methyl (E)-4-(3,4-dichlorophenyl)-3-butenoate (3.46 g, 14 mmol) and *p*-ABSA (4.13 g, 17 mmol) in CH_3CN (110 mL) at 0 ˚C. After 0.5 h the reaction was alowed to warm to room temerature and stirred for an additional 2 h. The resulting red solution was quenched with aqueous NH_4Cl soln. (750 mL) and extracted into ether (3 x 100 mL). The combined organics were dried with magnesium sulfate and concentrated under reduced pressure. The resulting red solid was triturated and filtered twice, first with ether then with petroleum ether/ether (1:1). The filtrate was concentrated and the residue was chromatographed over silica gel using petroleum ether/Et_2O (9:1) as eluent (R_f = 0.30) to give **18b** in 68% yield (2.58 g) as a red solid. IR (neat) 3051, 3000, 2954, 2149, 2086, 1697 cm^{-1}; ^{1}H NMR (500 MHz) δ 7.36 (d, 1 H, *J* = 2.0 Hz), 7.32 (d, 1 H, *J* = 8.5 Hz), 7.12 (dd, 1 H, *J* = 8.5, 2.0 Hz), 6.45 (d, 1 H, *J* = 16.5 Hz), 6.06 (d, 1 H, *J* = 16.5 Hz), 3.85 (s, 3 H); ^{13}C NMR (50 MHz, DEPT) δ 164.9 (4˚), 136.8 (4˚), 132.6 (4˚), 130.35 (3˚), 130.28 (4˚), 127.2 (3˚), 124.7 (3˚), 120.1 (3˚), 113.6 (3˚), 52.3 (1˚). The product was insufficiently stable for elemental analysis.

Methyl (E)-4-(4-methoxyphenyl)-3-butenoate. Purification by silica gel column chromatography (pentane/Et_2O, 9:1, R_f = 0.22) gave Methyl (E)-4-(4-methoxyphenyl)-3-butenoate in 44% yield (2.38 g) (for two steps) as a white solid (mp 41-42 ˚C). IR (neat) 3037, 2995, 2959, 2859, 1724, 1610 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.28 (d, 2 H, *J* = 8.6 Hz), 6.82 (d, 2

H, *J* = 8.6 Hz), 6.40 (d, 1 H, *J* = 15.9 Hz), 6.13 (dt, 1 H, *J* = 15.9, 6.9 Hz), 3.75 (s, 3 H), 3.68 (s, 3 H), 3.20 (d, 2 H, *J* = 6.9 Hz); ^{13}C NMR (75 MHz, DEPT) δ 172.0 (4˚), 159.0 (4˚), 132.7 (3˚), 129.4 (4˚), 127.2 (3˚), 119.2 (3˚), 113.7 (3˚), 54.9 (1˚), 51.6 (1˚), 37.9 (2˚); MS m/z (relative intensity): 207 (6) M + 1, 206 (46), 147 (100), 132 (10), 131 (10), 115 (17), 107 (4), 103 (13), 91 (21). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.63; H, 6.84.

Methyl (E)-2-diazo-4-(4-methoxyphenyl)-3-butenoate (18a). Purification by silica gel column chromatography (pentane/Et_2O, 9:1, R_f = 0.23) gave **18a** in 70% yield as a red solid. IR (neat) 3041, 3009, 2956, 2834, 2072, 1694 cm^{-1}; ^{1}H NMR (300 MHz, TMS); δ 7.29 (d, 2 H, *J* = 8.9 Hz), 6.86 (d, 2 H, *J* = 8.9 Hz), 6.30 (d, 1 H, *J* = 16.5 Hz), 6.14 (d, 1 H, *J* = 16.5 Hz), 3.84 (s, 3 H), 3.80 (s, 3 H); ^{13}C NMR (75 MHz, DEPT) δ 165.8 (4˚), 158.8 (4˚), 129.6 (4˚), 127.0 (3˚), 122.7 (3˚), 114.1 (3˚), 108.5 (3˚), 55.2 (1˚), 52.2 (1˚). The product was insufficiently stable for elemental analysis.

Methyl (E)-4-(2-methoxyphenyl)-3-butenoate. Purification by silica gel column chromatography (pentane/Et_2O, 9:1, R_f = 0.24) gave Methyl (E)-4-(2-methoxyphenyl)-3-butenoate in 55% yield (2.42 g) (for two steps) as a clear oil. IR (neat) 3004, 2951, 2839, 1742, 1598 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.43 (dd, 1 H, *J* = 7.5, 1.5 Hz), 7.19 (ddd, 1 H, *J* = 8.6, 8.1, 1.5 Hz), 6.90 (dd, 1 H, *J* = 8.1, 7.5 Hz), 6.82 (d, 1 H, *J* = 8.6 Hz), 6.81 (d, 1 H, *J* = 16.2 Hz), 6.29 (dd, 1 H, *J* = 16.2, 7.2 Hz), 3.79 (s, 3 H), 3.68 (s, 3 H), 3.25 (dd, 2 H, *J* = 7.2, 1.5 Hz); ^{13}C NMR (75 MHz, DEPT) δ 172.0 (4˚), 156.4 (4˚), 128.4 (3˚), 128.1 (3˚), 126.6 (3˚), 125.7 (4˚), 122.1 (3˚), 120.5 (3˚), 110.6 (3˚), 55.2 (1˚), 51.6 (1˚), 38.4 (2˚). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.86; H, 6.83.

Methyl (E)-2-diazo-4-(2-methoxyphenyl)-3-butenoate (18d). Purification by silica gel column chromatography (pentane/Et_2O, 9:1, R_f = 0.33) gave **18d** in 65% yield (1.14 g) as a red solid. IR (neat) 3004, 2951, 2839, 2088, 1704 cm^{-1}; ^{1}H NMR (400 MHz, TMS); δ 7.41 (dd, 1 H, *J* = 7.6, 1.6 Hz), 7.18 (ddd, 1 H, *J* = 8.2, 7.6, 1.6 Hz), 6.92 (dd, 1 H, *J* = 7.6, 7.6 Hz), 6.85 (d, 1 H, *J* = 8.2 Hz), 6.51 (d, 2 H, *J* = 1.2 Hz), 3.84 (s, 3 H), 3.83 (s, 3 H); ^{13}C NMR (75 MHz, DEPT) δ 165.4 (4˚), 155.8 (4˚), 127.9 (3˚), 126.1 (3˚), 125.5 (4˚), 120.5 (3˚), 117.7 (3˚), 111.2 (3˚), 110.5 (3˚), 55.0 (1˚), 51.9 (1˚). The product was insufficiently stable for elemental analysis.

Methyl (E)-4-(2-naphthyl)-3-butenoate. Purification by silica gel column chromatography (petroleum ether /Et$_2$O, 9:1, R$_f$ = 0.19) gave Methyl (E)-4-(2-naphthyl)-3-butenoate in 44% yield (1.82 g) (for two steps) as a white solid (mp 70-71 ˚C). IR (neat) 3052, 2988, 2951, 2898, 2844, 1742, 1593 cm^{-1}; ^{1}H NMR (300 MHz, TMS) δ 7.76-7.71 (m, 3 H), 7.65 (Br. s, 1 H), 7.55 (dd, 1 H, *J* = 9.0, 1.5 Hz), 7.44-7.36 (m, 2 H), 6.58 (d, 1 H, *J* = 16.2 Hz), 6.38 (dt, 1 H, *J* = 16.2, 7.2 Hz), 3.69 (s, 3 H), 3.25 d, 2 H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, DEPT) δ 171.8 (4˚), 134.1 (4˚), 133.41 (4˚), 133.40 (3˚), 132.8 (4˚), 128.0 (3˚), 127.8 (3˚), 127.5 (3˚), 126.1 (3˚), 126.0 (3˚), 125.7 (3˚), 123.3 (3˚), 121.9 (3˚), 51.8 (1˚), 38.1 (2˚); MS m/z (relative intensity): 227 (8), 226 (46), 168 (14), 167 (100), 166 (23), 165 (51), 152 (29), 139 (5), 115 (6). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.75; H, 6.29.

Methyl (E)-2-diazo-4-(2-naphthyl)-3-butenoate (18c). Purification by silica gel column chromatography (pentane/Et$_2$O, 9:1, R$_f$ = 0.31) gave **18c** in 52% yield (1.01 g) as a red solid. IR (neat) 3057, 3020, 2946, 2120, 2093, 1705 cm^{-1}; ^{1}H NMR (500 MHz, TMS); δ 7.73-7.70 (m, 3 H), 7.59 (s, 1 H), 7.52 (dd, 1 H, *J* = 9.0, 1.5 Hz), 7.42-7.35 (m, 2 H), 6.52 (d, 1 H, *J* = 16.5 Hz), 6.26 (d, 1 H, *J* = 16.5 Hz), 3.79 (s, 3 H); ^{13}C NMR (75 MHz, DEPT) δ 165.4 (4˚), 134.2 (4˚), 133.5 (4˚), 132.5 (4˚), 128.2 (3˚), 127.8 (3˚), 127.5 (3˚), 126.2 (3˚), 125.6 (3˚), 125.3 (3˚), 122.99 (3˚), 122.95 (3˚), 111.3 (3˚), 52.1 (1˚). The product was insufficiently stable for elemental analysis.

Methyl (E)-4-(1-naphthyl)-3-butenoate. Purification by silica gel column chromatography (petroleum ether /Et$_2$O, 9:1, R$_f$ = 0.24) gave Methyl (E)-4-(1-naphthyl)-3-butenoate in 41% yield (1.82 g) (for two steps) as a white solid (mp ˚C). IR (neat) 3043, 2999, 2955, 2846, 1732 cm^{-1}; ^{1}H NMR (400 MHz, TMS) δ 8.11-8.09 (m, 1 H), 7.86-7.83 (m, 1 H), 7.78 (d, 1 H, *J* = 8.4 Hz), 7.60 (d, 1 H, *J* = 6.8 Hz), 7.53-7.42 (m, 3 H), 7.24 (d, 1 H, *J* = 15.6 Hz), 6.33 (dt, 1 H, *J* = 15.6, 6.8 Hz), 3.75 (s, 3 H), 3.39 (dd, 2H, *J* = 6.8, 1.4 Hz); ^{13}C NMR (75 MHz, DEPT) δ 172.0 (4˚), 134.5 (4˚), 133.5 (4˚), 131.0 (4˚), 130.7 (3˚), 128.5 (3˚), 127.9 (3˚), 126.0 (3˚), 125.7 (3˚), 125.6 (3˚), 124.9 (3˚), 123.9 (3˚), 123.7 (3˚), 51.9 (1˚), 38.5 (2˚); MS m/z (relative intensity): 227 (5), 226 (29), 167 (51), 166 (28), 165 (65), 153 (34), 152 (100), 139 (5), 115 (5), 82 (6). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.90; H, 6.31.

Methyl (E)-2-diazo-4-(1-naphthyl)-3-butenoate (18e). Purification by silica gel column chromatography (petroleum ether/Et_2O, 9:1, R_f = 0.16) gave **18e** in 57% yield as a red solid. IR (neat) 3086, 3064, 3003, 2952, 2083, 1693 cm^{-1}; ^{1}H NMR (300 MHz, TMS) δ 8.04-8.01 (m, 1 H), 7.79-7.76 (m, 1 H), 7.70-7.67 (m, 1 H), 7.55-7.53 (m, 1 H), 7.46-7.35 (m, 3 H), 6.94 (d, 1 H, *J* = 16.2 Hz), 6.48 (d, 1 H, *J* = 16.2 Hz), 3.79 (s, 3 H); ^{13}C NMR (75 MHz, DEPT) δ 165.4 (4˚), 134.1 (4˚), 133.6 (4˚), 130.6 (4˚), 128.5 (3˚), 127.5 (3˚), 125.9 (3˚), 125.7 (3˚), 125.5 (3˚), 123.3 (3˚), 123.1 (3˚), 119.9 (3˚), 113.8 (3˚), 52.1 (1˚). HRMS calcd for $C_{15}H_{12}N_2O_2$, 252.0899, found, 252.0900.

Rh_2(*S*-DOSP)$_4$ Catalyzed Decomposition of Vinyldiazomethanes in the Presence of Cyclohexadienes. **General Procedure**. A solution of vinyldiazoacetate **14** (0.5-1.5 mmol) in dry hexanes (20 mL) was added dropwise over 15-30 minutes to a round bottom flask containing a stirred solution of Rh_2(*S*-DOSP)$_4$ (0.01 equiv) and the diene (5-10 equiv) in dry hexane (30 mL) at room temperature. (Final concentration ~ 0.02 M based on amount of diazo.) After 16-48 h the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel. Enantioselectivities were determined either by GC using an Astec Chiraldex β-TA column (20m x 0.25mm), or by HPLC using a Daicel OJ or OD analytical column (25 cm length).

Methyl (E,4*R*)-4-(2,5-cyclohexadienyl)-4-(3,4-dichlorophenyl)-2-butenoate (19b). Purification by silica gel column chromatography (petroleum ether/Et_2O, 9:1, R_f = 0.24) gave

19b in 59% yield as a clear oil. 99% ee (determined by HPLC: OD, 0.8% *i*-Pr-OH in hexanes, 0.8 mL/min; T_R = 12.06 min (minor), 23.73 min (major)). $[\alpha]^{25}_D$ = +4° (*c* 2.08, $CHCl_3$). IR (neat) 3029, 2954, 2863, 2817, 1726, 1651 cm^{-1}; ^1H NMR (300 MHz) δ 7.36 (d, 1 H, *J* = 8.0 Hz), 7.27 (d, 1 H, *J* = 2.5 Hz), 7.10 (dd, 1 H, *J* = 15.5, 8.5 Hz), 7.02 (dd, 1 H, *J* = 8.0, 2.5 Hz), 5.81 (d, 1 H, *J* = 15.5 Hz), 5.75 (Br. d, 2 H, *J* = 12.0 Hz), 5.57 (Br. d, 1 H, *J* = 10.0 Hz), 5.43 (Br. d, 1 H, *J* = 10.0 Hz), 3.71 (s, 3 H), 3.38 (dd, 1 H, *J* = 8.5, 8.0 Hz), 3.17-3.15 (m, 1 H), 2.62-2.48 (m, 2 H); ^{13}C NMR (125 MHz) δ 166.5, 148.1, 140.7, 132.4, 130.8, 130.4, 130.2, 127.6, 126.83, 126.79, 125.7, 125.3, 122.9, 53.6, 51.6, 40.1, 26.3. HRMS calcd for $C_{17}H_{16}O_2Cl_2$, 322.0527, found, 322.0504.

Methyl (E,4*R*)-4-(2,5-cyclohexadienyl)-4-(4-methoxyphenyl)-2-butenoate (19a). Purification by silica gel column chromatography (pentane/Et_2O, 9:1, R_f = 0.26) gave **19a** in 58% yield as a white solid (mp 61-65 °C). 99% ee (determined by HPLC: OD, 1.0% *i*-Pr-OH in hexanes, 1.0 mL/min; T_R = 16.76 min (major), 24.45 min (minor)). $[\alpha]^{26}_D$ = +16° (*c* 2.04, $CHCl_3$). IR (neat) 3029, 2956, 2836, 1709, 1652 cm^{-1}; ^1H NMR (300 MHz, TMS) δ 7.18 (dd, 1 H, *J* = 15.6, 8.7 Hz), 7.12 (d, 2 H, *J* = 8.4 Hz), 6.86 (d, 2 H, *J* = 8.4 Hz), 5.83 (d, 1 H, *J* = 15.6 Hz), 5.77-5.64 (m, 3 H), 5.49-5.45 (m, 1 H), 3.79 (s, 3 H), 3.71 (s, 3 H), 3.37 (dd, 1 H, *J* = 8.7, 8.3 Hz), 3.18-3.15 (m, 1 H), 2.60-2.58 (m, 2 H); ^{13}C NMR (75 MHz, DEPT) δ 166.9 (4°), 158.3 (4°), 149.9 (3°), 132.6 (4°), 129.1 (3°), 126.6 (3°), 126.13 (3°), 126.08 (3°), 125.9 (3°), 121.7 (3°), 113.9 (3°), 55.2 (1°), 53.9 (3°), 51.4 (1°), 40.1 (3°), 26.3 (2°). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.20; H, 7.12.

Methyl (E,4*R*)-4-(2,5-cyclohexadienyl)-4-(2-methoxyphenyl)-2-butenoate (19d). Purification by silica gel column chromatography (petroleum ether/Et_2O, 19:1, R_f = 0.18) gave **19d** in 17% yield as a clear oil. 86% ee (determined by HPLC: OD, 1.2% *i*-Pr-OH in hexanes, 0.8 mL/min; T_R = 15.2 min (major), 17.1 min (minor)). $[\alpha]^{25}_D$ = +7° (*c* 1.02, $CHCl_3$). IR (neat) 3025, 2951, 2839, 1726, 1657 cm^{-1}; ^1H NMR (500 MHz, TMS) δ 7.25 (dd, 1 H, *J* = 16.0, 9.0 Hz), 7.21 (dd, 1 H, *J* = 7.0, 7.0 Hz), 7.15 (d, 1 H, *J* = 7.0 Hz), 6.91 (dd, 1 H, *J* = 7.5, 7.0 Hz), 6.87 (d, 1 H, *J* = 7.5 Hz), 5.85 (d, 1 H, *J* = 16.0 Hz), 5.78 (Br. d, 1 H, *J* = 10.5 Hz), 5.71 (Br. d, 1 H, *J* = 10.5 Hz), 5.65 (Br. d, 1 H, *J* = 10.5 Hz), 5.47 (Br. d, 1 H, *J* = 10.5 Hz), 3.87 (dd, 1 H, *J* = 9.0, 8.0 Hz), 3.82 (s, 3 H), 3.71 (s, 3 H), 3.31 (m, 1 H), 2.62 (dd, 2 H, *J* = 5.5, 2.5 Hz); ^{13}C NMR (75 MHz, DEPT) δ 167.1 (4˚), 156.9 (4˚), 149.7 (3˚), 128.92 (3˚), 128.88 (4˚), 127.7 (3˚), 127.2 (3˚), 126.4 (3˚), 125.7 (3˚), 125.4 (3˚), 121.9 (3˚), 120.5 (3˚), 110.8 (3˚), 55.3 (1˚), 51.3 (1˚), 48.0 (3˚), 38.1 (3˚), 26.3 (2˚). HRMS calcd for $C_{18}H_{20}O_3$, 284.14125, found, 284.13994. Also, HRMS calcd for $C_{18}H_{18}O_3$, 282.1256, found, 282.1257. (M-2)

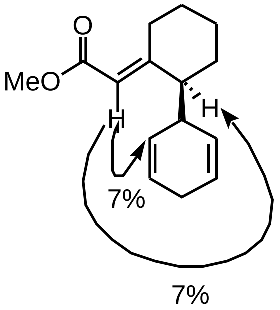
Methyl (E,4*R*)-4-(2,5-cyclohexadienyl)-4-(2-naphthyl)-2-butenoate (19c). Purification by silica gel column chromatography (petroleum ether/Et_2O, 9:1, R_f = 0.29) gave **19c** in 50% yield as a white solid (mp 92-93 ˚C). 99% ee (determined by HPLC: OD, 1.0% *i*-Pr-OH in hexanes, 1.0 mL/min; T_R = 13.8 min (minor), 16.8 min (major)). $[\alpha]^{25}_D$ = +9˚ (*c* 1.70, $CHCl_3$). IR (neat) 3057, 3031, 2962, 2844, 2818, 1715, 1651 cm^{-1}; ^{1}H NMR (500 MHz, TMS) δ 7.82-7.79 (m, 3 H), 7.64 (Br. s, 1 H), 7.49-7.43 (m, 2 H), 7.36 (dd, 1 H, *J* = 8.0, 1.5 Hz), 7.30 (dd, 1 H, *J* = 15.5, 9.0 Hz), 5.89 (dd, 1 H, *J* = 15.5, 1.0 Hz), 5.82-5.79 (m, 1 H), 5.75-5.69 (m, 2 H), 5.49-5.46 (m, 1 H), 3.72 (s, 3 H), 3.59 (dd, 1 H, *J* = 9.0, 8.5 Hz), 3.34-3.31 (m, 1 H), 2.62-2.60 (m, 2 H); ^{13}C NMR (75 MHz, DEPT) δ 166.9 (4˚), 149.5 (3˚), 138.1 (4˚), 133.5 (4˚), 132.4 (4˚), 128.3 (3˚), 127.7 (3˚), 127.6 (3˚), 126.9 (3˚), 126.7 (3˚), 126.3 (3˚), 126.2 (3˚), 126.1 (3˚), 126.03 (3˚), 125.97 (3˚), 125.7 (3˚), 122.3 (3˚), 54.9 (3˚), 51.5 (1˚), 40.1 (3˚), 26.4 (2˚). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.87; H, 6.62. Found: C, 82.78; H, 6.68.

Methyl (E,4*R*)-4-(2,5-cyclohexadienyl)-4-(1-naphthyl)-2-butenoate (19e). Purification by silica gel column chromatography (petroleum ether/Et_2O, 9:1, R_f = 0.23) gave **19e** in 22% yield as a lite yellow solid (mp 97-100 ˚C). 83% ee (determined by HPLC: OD, 1.0% *i*-Pr-OH in hexanes, 1.0 mL/min; T_R = 14.1 min (minor), 35.9 min (major)). $[\alpha]^{25}_D$ = -62˚ (*c* 1.20, $CHCl_3$). IR (neat) 3036, 2951, 2860, 1726, 1657 cm^{-1}; ^{1}H NMR (400 MHz, TMS) δ 8.07-8.05 (m, 1 H), 7.89-7.87 (m, 1 H), 7.77-7.75 (m, 1 H), 7.55-7.43 (m, 4 H), 7.35 (dd, 1 H, *J* = 15.6, 8.4 Hz), 5.90 (d, 1 H, *J* = 15.6 Hz), 5.86-5.84 (m, 1 H), 5.74-5.67 (m, 2 H), 5.53-5.51 (m, 1 H), 4.33 (dd, 1 H, *J* = 8.4, 8.0 Hz), 3.71 (s, 3 H), 3.43-3.41 (m, 1 H), 3.67 (m, 2 H); ^{13}C NMR (75 MHz, DEPT) δ 166.9 (4˚), 149.4 (3˚), 136.8 (4˚), 134.1 (4˚), 131.5 (4˚), 129.1 (3˚), 127.3 (3˚), 126.9 (3˚), 126.4 (3˚), 126.2 (3˚), 126.0 (3˚), 125.9 (3˚), 125.6 (3˚), 125.3 (3˚), 125.1 (3˚), 122.9 (3˚), 122.4 (3˚), 51.4 (1˚), 48.6 (3˚), 39.5 (3˚), 26.4 (2˚). HRMS calcd for $C_{15}H_{14}O_2$ (M^+ -78), 226.0994, found, 226.0981.

Methyl (E,4*R*)-4-(2,5-cyclohexadienyl)-4-phenyl-2-butenoate (15). Purification by silica gel column chromatography (petroleum ether/Et_2O, 19:1, R*f* = 0.20) gave **15** in 55% yield as a white solid (mp 60-63 ˚C). >99% ee (determined by HPLC: OD, 1.0% *i*-Pr-OH in hexanes, 1.0 mL/min; T_R = 13.5 min (major), 27.5 min (minor)). $[\alpha]^{26}_D = +30^\circ$ (*c* 4.08, $CHCl_3$). IR (neat) 3028, 2942, 2841, 1715, 1646 cm^{-1}; ^{1}H NMR (500 MHz, TMS) δ 7.32 (m, 2 H), 7.25-7.16 (m, 3 H), 7.20 (dd, 1 H, *J* = 15.5, 8.5 Hz), 5.84 (d, 1 H, *J* = 15.5 Hz), 5.81-5.79 (m, 1 H), 5.75-5.72 (m, 1 H), 5.68-5.66 (m, 1 H), 5.46-5.44 (m, 1 H), 3.72 (s, 3 H), 3.41 (dd, 1 H, *J* = 8.5, 8.5 Hz), 3.22-3.20 (m, 1 H), 2.61-2.59 (m, 2 H); ^{13}C NMR (75 MHz, DEPT) δ 166.9 (4˚), 149.6 (3˚), 140.6 (4˚), 128.6 (3˚), 128.2 (3˚), 126.8 (3˚), 126.6 (3˚), 126.2 (3˚), 126.01 (3˚), 125.98 (3˚), 122.1 (3˚), 54.8 (3˚), 51.5 (1˚), 40.1 (3˚), 26.3 (2˚). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.38; H, 7.19.

Methyl 4-phenylbicyclo[3.2.2]nona-2,6-diene-2-carboxylate (16). Purification by silica gel column chromatography (petroleum ether/Et_2O, 19:1, R*f* = 0.27) gave **16** in 14% yield as a clear oil. 40% ee for -78 ˚C reaction (determined by GC: β-TA, 145 ˚C, 22.2 psi, 1.8 mL/min, 46 cm/sec average velocity; T_R = 40.9 min (minor), 44.1 min (major)). IR (neat) 3041, 2946, 2871, 1710, 1641 cm^{-1}; ^{1}H NMR (500 MHz, TMS) δ 7.28 (t, 2 H, *J* = 7.0 Hz), 7.22 (t, 1 H, *J* = 7.0 Hz), 7.14 (d, 2 H, *J* = 7.0 Hz), 6.73 (d, 1 H, *J* = 4.0 Hz), 6.43 (dd, 1 H, *J* = 8.5, 8.0 Hz), 5.64 (dd, 1 H, *J* = 8.0, 7.5 Hz), 3.74 (s, 3 H), 3.66 (dd, 1 H, *J* = 4.0, 3.5 Hz), 3.56-3.54 (m, 1 H), 2.73 (m, 1 H), 2.10-2.05 (m, 1 H), 1.99-1.92 (m, 2 H), 1.83-1.76 (m, 1 H); ^{13}C NMR (75 MHz, DEPT) δ 168.1 (4˚), 141.74 (4˚), 141.71 (3˚), 137.3 (3˚), 136.6 (4˚), 130.0 (3˚), 128.3 (3˚), 128.1 (3˚), 126.6 (3˚), 51.9 (1˚), 51.6 (3˚), 38.4 (3˚), 31.1 (3˚), 29.8 (2˚), 26.0 (2˚); MS m/z (relative intensity): 255 (14), 254 (73), 195 (86), 194 (42), 178 (31), 167 (34), 165 (54), 128 (25), 117 (52), 116 (36), 115 (100), 103 (30), 91 (73), 77 (39). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.29; H, 7.13. Found: C, 80.37; H, 7.01.

Methyl (2E,5E)-4-(2,5-cyclohexadienyl)-6-phenyl-2,5-hexadienoate (25). Purification by silica gel column chromatography (pentane/Et_2O, 9:1, R_f = 0.38) gave **25** in 60% yield as a clear oil. 99% ee (determined by HPLC: OD, 1.0% *i*-Pr-OH in hexanes, 1.0 mL/min; T_R = 12.6 min (major), 13.8 min (minor)). $[\alpha]^{25}_D$ = +17° (*c* 1.38, $CHCl_3$). IR (neat) 3031, 2951, 2860, 2818, 1721, 1651 cm^{-1}; ^1H NMR (300 MHz, TMS) δ 7.36-7.20 (m, 5 H), 7.06 (dd, 1 H, *J* = 15.9, 7.7 Hz), 6.41 (d, 1 H, *J* = 16.2 Hz), 6.18 (dd, 1 H, *J* = 16.2, 7.7 Hz), 5.88 (d, 1 H, *J* = 15.9 Hz), 5.82 (m, 2 H), 5.66 (Br. d, 2 H, *J* = 10.8 Hz), 3.74 (s, 3 H), 3.12 (m, 1 H), 3.07 (m, 1 H), 2.64 (dd, 2 H, *J* = 5.4, 2.1 Hz); ^{13}C NMR (125 MHz, DEPT) δ 166.8 (4°), 149.2 (3°), 137.0 (4°), 132.2 (3°), 128.5 (3°), 128.3 (3°), 127.4 (3°), 126.5 (3°), 126.4 (3°), 126.2 (3°), 125.99 (3°), 125.98 (3°), 121.9 (3°), 51.4 (1°), 51.2 (3°), 39.8 (3°), 26.3 (2°). HRMS calcd for $C_{19}H_{20}O_2$, 280.1463, found, 280.1455.



Methyl 2-[(2S)-2-(2,5-cyclohexadienyl)cyclohexyliden]acetate (23). Purification by silica gel column chromatography (petroleum ether/Et_2O, 19:1, R_f = 0.30) gave **23** in 73% yield as a clear oil. 97% ee (determined by HPLC: OD, 0.7% *i*-Pr-OH in hexanes, 1.0 mL/min; T_R = 7.0 min (minor), 7.4 min (major)). $[\alpha]^{25}_D$ = - 6° (*c* 5.88, PhH). IR (neat) 3025, 2929, 2860, 1720, 1646 cm^{-1}; ^{1}H NMR (400 MHz) δ 5.77 (m, 2 H), 5.74 (Br. d, 1 H, *J* = 10.4 Hz), 5.63 (s, 1 H), 5.49 (Br. d, 1 H, *J* = 10.4 Hz), 3.66 (s, 3 H), 3.11-3.07 (m, 1 H), 2.91 (ddd, 1 H, *J* = 13.4, 6.4, 4.8 Hz), 2.77 (ddd, 1 H, *J* = 13.4, 8.6, 4.4 Hz), 2.62-2.61 (m, 2 H), 2.06 (ddd, 1 H, *J* = 11.2, 6.8, 4.4 Hz), 1.78-1.54 (m, 5 H), 1.53-1.48 (m, 1 H); ^{13}C NMR (75 MHz, DEPT) δ 167.2 (4˚), 164.6 (4˚), 128.0 (3˚), 126.2 (3˚), 125.7 (3˚), 125.0 (3˚), 113.1 (3˚), 51.5 (3˚), 50.8 (1˚), 34.7 (3˚), 29.8 (2˚), 28.1 (2˚), 27.9 (2˚), 26.3 (2˚), 23.1 (2˚). HRMS calcd for $C_{15}H_{20}O_2$, 232.1463, found, 232.1461.

Methyl (E)-2-(2,4-cyclohexadienyl)-4-phenyl-3-butenoate (17). A 0.03 M solution of **14** in hexanes with **5** (*S*-DOSP) (0.5 mol%) was refluxed for 60 h. Solvent was removed under reduced pressure. Purification by silica gel column chromatography (pentane/Et$_2$O, 9:1, R$_f$ = 0.46) gave **17** in 81% yield as a clear oil. 99% ee (determined by HPLC: OD, 0.7% *i*-Pr-OH in hexanes, 1.0 mL/min; T_R = 8.3 min (major), 10.3 min (minor)). $[\alpha]^{26}_D$ = +30˚ (*c* 1.88, CHCl$_3$). IR (neat) 3036, 2950, 2860, 1736 cm^{-1}; ^{1}H NMR (300 MHz, TMS) δ 7.39-7.24 (m, 5 H), 6.48 (d, 1 H, *J* = 16.2 Hz), 6.13 (dd, 1 H, *J* = 16.2, 9.6 Hz), 6.00-5.90 (m, 2 H), 5.77-5.68 (m, 2 H), 3.70 (s, 3 H), 3.26 (dd, 1 H, *J* = 9.6, 9.1 Hz), 2.71 (dddd, 1 H, *J* = 18.3, 9.1, 4.2, 1.5 Hz), 2.30 (dddd, 1 H, *J* = 17.7, 8.4, 4.2, 2.1 Hz), 2.17 (dddd, 1 H, *J* = 17.7, 8.4, 4.8, 1.5 Hz); ^{13}C NMR (75 MHz, DEPT) δ 173.7 (4˚), 136.6 (4˚), 133.7 (3˚), 128.6 (3˚), 127.7 (3˚), 127.4 (3˚), 126.4 (3˚), 126.1 (3˚), 125.4 (3˚), 125.2 (3˚), 124.3 (3˚), 52.5 (3˚), 51.8 (1˚), 35.0 (3˚), 25.5 (2˚). HRMS calcd for $C_{17}H_{18}O_2$, 254.1307, found, 254.1303.

(2S)-2-phenylcyclohexan-1-one. DDQ (0.54 g, 2.4 mmol) was added to a stirred solution of **21** (284 mg, 1.2 mmol) in benzene (30 mL). After 2 h the reaction was filtered and the solvent removed under reduced pressure. The crude reaction mixture was flushed through a silica plug (petroleum ether/ether, 4:1, R$_f$ = 0.59) and the solvent was removed under reduced pressure. The residue in a solution of CH$_2$Cl$_2$ (18 mL) and EtOH (12 mL) was cooled to –78 ˚C and treated with ozone for 1 h. The solution was purged with oxygen, dimethylsulfide (0.2 mL, 2.2 mmol) was added, and the reaction was allowed to warm to room temperature. After 16 h the solvent was removed under reduced pressure. Purification by silica gel column chromatography (pentene/Et_2O, 4:1, R_f = 0.29) gave (2S)-2-phenylcyclohexan-1-one in 56% yield (120 mg, 0.69 mmol) as a white solid (mp 45-51 ˚C) whose ^1H and ^{13}C NMR and IR spectra matched that of the known compound.[4] $[\alpha]^{26}_D$ = -17˚ (*c* 1.66, PhH). For the *S*-enantiomer (lit.; mp 38-39, $[\alpha]^{24}_D$ = -113.5˚ (*c* 0.60, PhH)[5]). IR (neat) 3089, 3063, 3036, 2960, 2934, 2866, 2855, 1699 cm^{-1}; ^1H NMR (300 MHz, TMS) δ 7.35-7.12 (m, 5 H), 3.60 (dd, 1 H, *J* = 12.0, 5.4 Hz), 2.54-2.38 (m, 2 H), 2.28-2.22 (m, 1 H), 2.15-2.07 (m, 1 H), 2.04-1.97 (m, 2 H), 1.87-1.76 (m, 2 H); ^{13}C NMR (75 MHz) δ 210.2, 138.7, 128.4, 128.2, 126.8, 57.2, 42.0, 35.0, 27.7, 25.2.

Methyl (4R)-4-(3,4-dichlorophenyl)-4-phenylbutanoate (20). The reaction solution containing **19b** was concentrated under reduced pressure then disolved in benzene (30 mL). DDQ (0.518 g, 2 eq.) was added to the stirring solution. After 2 h the solution was filtered and concentrated under reduced pressure. To remove the rhodium catalyst the residue was run through a plug of silica with pentane/Et_2O (2:1) as eluent. Solvent was removed under reduced pressure and the residue was added to a hydrogenation vessel with ethanol (30 mL). Palladium on activated carbon (42 mg, 3 mol %) was added and the reaction was hydrogenated at 55 psi of H_2. After 2.5 h the reaction was filtered and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (pentane/Et_2O, 9:1, R_f = 0.22) gave **20** in 52% yield as a clear oil. 96% ee (determined by HPLC: OD, 1.2% *i*-Pr-OH in hexanes, 0.8 mL/min; T_R = 22.0 min (minor), 25.6 min (major)). $[\alpha]^{25}_D$ = -8˚ (*c* 2.55, $CHCl_3$). IR (neat) 3061, 3025, 2953, 1736 cm^{-1}; ^1H NMR (300 MHz, TMS) δ 7.35-7.18 (m, 7 H), 7.09-7.05 (m, 1 H), 3.89 (t, 1 H, *J* = 7.7 Hz), 3.64 (s, 3 H), 2.38 (m, 4 H); ^{13}C NMR (75 MHz, DEPT) δ 173.5 (4˚), 144.5 (4˚), 142.7 (4˚), 132.5 (4˚), 130.4 (3˚), 130.3 (4˚), 129.7 (3˚), 128.8 (3˚), 127.7 (3˚), 127.2 (3˚), 126.9 (3˚), 51.6 (1˚), 49.5 (3˚), 32.2 (2˚), 30.2 (2˚); MS m/z (relative intensity): 326 (1), 324 (6), 322 (9), 290 (18), 248 (64), 235 (88), 165 (100), 74 (32). Anal. Calcd for $C_{17}H_{16}O_2Cl_2$: C, 63.17; H, 4.99. Found: C, 63.38; H, 5.12.

(*S*)-4-(3,4-Dichlorophenyl)-1-tetralone (21). A procedure similar to that of Corey and Gant was used for the conversion of ester **20** to the tetralone **21**.[6] A round bottom flask was charged with **20** (0.177 g, 0.55 mmol) and 6 M HCl (20 mL) and the solution was heated at reflux. After 23 h the reaction was added to cool H_2O (20 mL) and extracted with EtOAc (3 x 10 mL). The combined organics were dried over $MgSO_4$ and concentrated under reduced pressure. Spectral data of crude material matched that of the known acid.[6] $[\alpha]^{25}_{D}$ = -13˚ (*c* 3.54, $CHCl_3$). IR (neat) 2972, 2663, 1715, 1470, 1406 cm^{-1}; ^1H NMR (300 MHz, TMS) δ 10.39 (Br. s, 1 H), 7.35-7.28 (m, 4 H), 7.24-7.18 (m, 3 H), 6.98 (dd, 1 H, *J* = 8.1, 2.1 Hz), 3.91 (t, 1 H, *J* = 6.9 Hz), 2.38-2.29 (m, 4 H); ^{13}C NMR (75 MHz, DEPT) δ 179.6 (4˚), 144.4 (4˚), 142.5 (4˚), 132.5 (4˚), 130.5 (3˚), 130.4 (4˚), 129.7 (3˚), 128.8 (3˚), 127.7 (3˚), 127.2 (3˚), 126.9 (3˚), 49.4 (3˚), 32.2 (2˚), 29.9 (2˚). The acid was then dissolved in CH_2Cl_2 (10 mL) and $ClSO_3H$ was added. After 45 minutes the cloudy solution was added to a saturated $NaHCO_3$ solution (75 mL) and extracted with CH_2Cl_2 (2 x 30 mL) then ether (1 x 30 mL). The combined organics were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by silica gel column chromatography (petroleum ether/Et_2O, 9:1, R_f = 0.13) gave **21** in 79% yield (126 mg, 0.433 mmol) from the ester (**20**) as a white solid (mp 84-85 ˚C) whose ^1H and ^{13}C NMR and IR spectra matched that of the known compound.[6] 94% ee (determined by HPLC: OD, 2.0% *i*-Pr-OH in hexanes, 1.0 mL/min; T_R = 13.5 min (major), 15.9 min (minor)). $[\alpha]^{25}_{D}$ = +66˚ (*c* 2.04, PhH). For the (*S*) enantiomer (lit.; mp 84 ˚C, $[\alpha]^{23}_{D}$ = +71.3˚ (*c* 1.1, PhH)[6]). IR (neat) 3063, 3025, 2946, 2871, 1689, 1598 cm^{-1}; ^1H NMR (300 MHz, TMS) δ 8.13 (d, 1 H, *J* = 7.2 Hz), 7.50-7.37 (m, 3 H), 7.23 (d, 1 H, *J* = 1.5 Hz), 6.96 (d, 2 H, *J* = 7.8 Hz), 4.28 (dd, 1 H, *J* = 7.8, 4.8 Hz), 2.77-2.58 (m, 2 H), 2.52-2.42 (m, 1 H), 2.32-2.20 (m, 1 H); ^{13}C NMR (75 MHz) δ 197.3, 144.8, 144.0, 133.8, 132.7, 132.6, 130.8, 130.5, 130.4, 129.2, 128.2, 127.9, 127.4, 127.3, 44.4, 36.4, 31.5; MS *m/z* (relative intensity): 294 (7), 292 (40), 290 (63), 250 (19), 248 (30), 229 (34), 227 (100), 201 (19), 199 (58), 163 (41), 115 (20).

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