

Highly Diastereoselective Synthesis of Tetrahydrofurans via Lewis Acid Catalyzed Cyclopropane/Aldehyde Cycloadditions

Patrick D. Pohlhaus and Jeffrey S. Johnson*

Department of Chemistry, University of North Carolina at Chapel Hill,

Chapel Hill, North Carolina 27599-3290

Supporting Information

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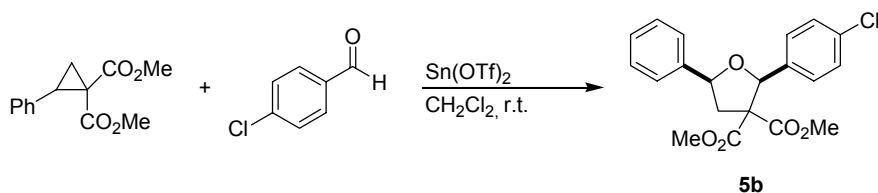
Experimental Section

Materials and Methods: General. Proton and carbon nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded with tetramethylsilane (TMS) as the internal standard for ^1H NMR at 0.00 ppm and CDCl_3 solvent resonance as the internal standard for ^{13}C NMR at 77.16 ppm. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constants (Hz), and integration. Structural assignments were made using NOESY experiments (see Appendix for spectra). Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 plates. Visualization was accomplished with UV light and aqueous ceric ammonium molybdate solution followed by heating. Purification of the reaction products was carried out by flash chromatography using silica gel 60 (32-63 μm). All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring. Yield refers to isolated yield of analytically pure material. Yields are reported for a specific experiment and as a result may differ slightly from those found in the tables and equations, which are averages of at least two experiments. Methylene chloride was dried by passage through a column of neutral alumina under nitrogen prior to use. Cyclopropanes were prepared using Wood's procedure from the corresponding benzyldiene malonate and trimethylsulphoxonium iodide.¹ Benzyldiene malonates were prepared via Knoevenagel condensations.¹ Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Solid aldehydes, 4-nitrobenzaldehyde and 4-chlorobenzaldehyde were purified by sublimation prior to use. All other aldehydes were distilled from CaSO_4 prior to use.

General procedure (A) for the Lewis acid catalyzed cycloaddition. In an inert atmosphere glovebox, a flame-dried vial was charged with 0.017 mmol of $\text{Sn}(\text{OTf})_2$ (0.050 equiv), 0.34 mmol of the cyclopropane (1.0 equiv), and a magnetic stir bar. Outside of the glove box, the vial was placed under an argon atmosphere and charged with 0.5 mL of CH_2Cl_2 followed by 1.0 mmol of the aldehyde (3.0 equiv). The reaction

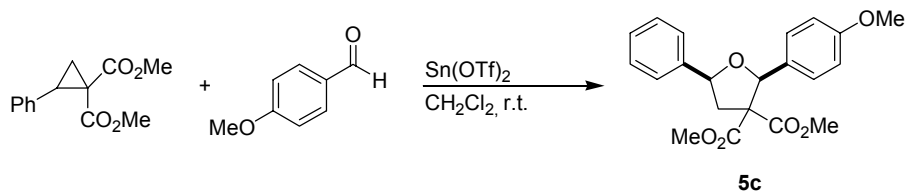
was stirred at room temp (23 °C - 29 °C) until the disappearance of starting material was confirmed by TLC. The reaction mixture was then passed over a plug of silica with 50 mL of Et₂O, the solvent removed with a rotary evaporator, and the residue placed under vacuum (< 0.1 torr) overnight. The product was purified by flash chromatography, eluting with the indicated solvent system to afford the pure tetrahydrofuran.

General procedure (B) for the Lewis acid catalyzed cycloaddition. In an inert atmosphere glovebox, a flame-dried vial was charged with 0.017 mmol of Sn(OTf)₂ (0.050 equiv) and a magnetic stir bar. Outside of the glove box, the vial was placed under an argon atmosphere, charged with 0.5 mL of CH₂Cl₂ and cooled to -10 °C with stirring. After 5 min, the stirring suspension was charged with 0.34 mmol of the cyclopropane (1.0 equiv) via syringe, followed by 1.0 mmol of the aldehyde (3.0 equiv). The reaction was stirred at -10 °C until the disappearance of starting material was confirmed by TLC. The reaction mixture was then passed over a plug of silica with 50 mL of Et₂O, the solvent removed with a rotary evaporator, and the residue placed under vacuum (< 0.1 torr) overnight. The product was purified by flash chromatography, eluting with the indicated solvent system to afford the pure tetrahydrofuran.



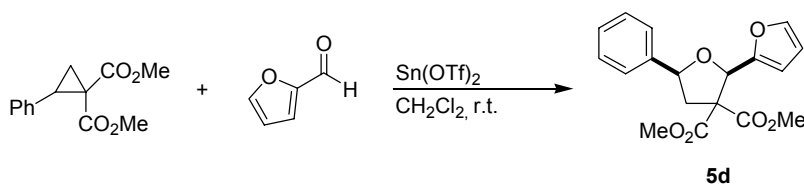
2-(4-chlorophenyl)-5-phenyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (5b, Table 1, entry 2). In an inert atmosphere glovebox, a flame-dried vial was charged with Sn(OTf)₂ (7.1 mg, 0.017 mmol, 0.050 equiv), the cyclopropane (80.0 mg, 0.34 mmol, 1.0 equiv), and a stir bar. Outside of the glovebox, the vial was placed under argon and charged with the aldehyde (144 mg, 1.0 mmol, 3.0 equiv) in 0.5 mL of CH₂Cl₂. The reaction was stirred at room temperature. After 4.75 h the reaction was passed over a small plug of silica with 50 mL of Et₂O, and the solvent was removed by rotary evaporation. ¹H NMR analysis of the unpurified product (δ 5.73 vs. δ 3.70) gave the diastereomeric ratio: >69:1. The crude product was purified by flash chromatography with a 2.5% to 5% acetone/petroleum ether gradient to afford 125 mg (97%) of the product as a slightly yellow oil.

Analytical data for **5b**: **IR** (thin film, cm⁻¹) 3034, 2953, 2883, 1732, 1599, 1491, 1435, 1385, 1348, 1271, 1232, 1209, 1198, 1176, 1089, 1057, 1028, 1015, 941, 906, 843, 800, 760, 700; **¹H NMR** (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.2 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 7.1, 7.1 Hz, 2H), 7.36-7.25 (m, 3H), 5.74 (s, 1H), 4.94 (dd, *J* = 10.4, 6.0 Hz, 1H), 3.81 (s, 3H), 3.16 (s, 3H), 2.97 (dd, *J* = 13.6, 10.8 Hz, 1H), 2.74 (dd, *J* = 13.6, 6.0 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.3, 169.2, 139.8, 136.3, 134.0, 128.6, 128.6, 128.3, 128.1, 126.6, 83.9, 80.1, 66.3, 53.1, 52.4, 42.8; **TLC** (80% CH₂Cl₂/petroleum ether) R_f 0.56; **Anal.** Calcd. for C₂₀H₁₉ClO₅: C, 64.09; H, 5.11. Found: C, 64.20; H, 5.16.



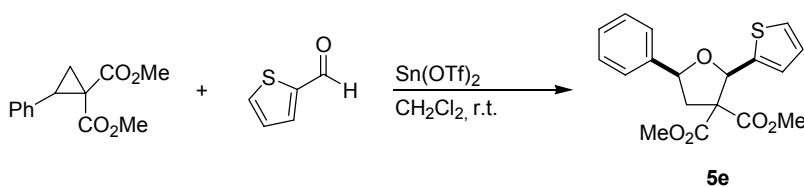
2-(4-methoxyphenyl)-5-phenyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (5c, Table 1, entry 3). The title compound was prepared according to General Procedure A using 7.1 mg of $\text{Sn}(\text{OTf})_2$, 80.0 mg of the cyclopropane, and 140 mg of the aldehyde. After 3.75 h at room temperature and workup, ^1H NMR analysis of the unpurified product (δ 5.75 vs. δ 3.65) gave the diastereomeric ratio: >81:1. The crude product was purified by flash chromatography with a 2.5% to 5% to 10% acetone/petroleum ether gradient to afford 127 mg (100%) of the product as a slightly yellow oil.

Analytical data for **5c**: **IR** (thin film, cm^{-1}) 3003, 2953, 2839, 1732, 1614, 1585, 1514, 1435, 1387, 1358, 1273, 1250, 1211, 1174, 1092, 1057, 1032, 939, 904, 841, 804, 760, 700; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, J = 7.2 Hz, 2H), 7.48-7.29 (m, 5H), 6.84 (d, J = 8.8 Hz, 2H), 5.74 (s, 1H), 4.93 (dd, J = 10.4, 6.0 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.15 (s, 3H), 2.98 (dd, J = 13.2, 10.8 Hz, 1H), 2.72 (dd, J = 13.6, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 169.4, 159.6, 140.1, 129.8, 128.6, 128.4, 128.1, 126.5, 113.3, 84.4, 79.8, 66.3, 55.3, 52.9, 52.3, 42.8; TLC (20% EtOAc/petroleum ether) R_f 0.37; **Anal.** Calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_6$: C, 68.10; H, 5.99. Found: C, 68.07; H, 5.94.



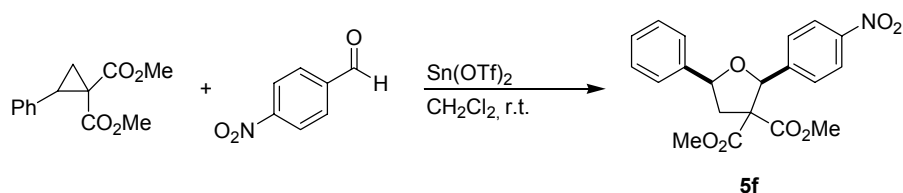
5-phenyl-1,2,3,4-tetrahydro[2,2']bifuryl-3,3-dicarboxylic acid dimethyl ester (5d, Table 1, entry 4). The title compound was prepared according to General Procedure A using 7.1 mg of $\text{Sn}(\text{OTf})_2$, 80.0 mg of the cyclopropane, and 99 mg of the aldehyde. After 2.75 h at room temperature and workup, ^1H NMR analysis of the unpurified product (δ 4.93 vs. δ 3.67) gave the diastereomeric ratio: 25.9:1. The crude product was purified by flash chromatography with 5% acetone/petroleum ether to afford 94 mg (83%) of the product as a colorless oil.

Analytical data for **5d**: **IR** (thin film, cm^{-1}) 2954, 2359, 2343, 1736, 1497, 1450, 1435, 1333, 1273, 1232, 1209, 1173, 1151, 1093, 1051, 1011, 945, 895, 808, 746, 700, 669; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, J = 7.2 Hz, 2H), 7.43-7.27 (m, 4H), 6.38 (d, J = 3.1 Hz, 1H), 6.35-6.29 (m, 1H), 5.85 (s, 1H), 4.93 (dd, J = 11.2, 5.6 Hz, 1H), 3.83 (s, 3H), 3.44 (s, 3H), 3.04 (dd, J = 13.2, 11.6 Hz, 1H), 2.72 (dd, J = 13.6, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 168.3, 151.5, 142.8, 139.9, 128.5, 128.1, 126.5, 110.4, 109.1, 80.2, 78.1, 65.2, 53.3, 52.8, 41.9; TLC (5% acetone/petroleum ether) R_f 0.11; **Anal.** Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_6$: C, 65.45; H, 5.49. Found: C, 65.73; H, 5.56.



5-phenyl-2-(2-thienyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (5e, Table 1, entry 5). The title compound was prepared according to General Procedure A using 7.1 mg of $\text{Sn}(\text{OTf})_2$, 80.0 mg of the cyclopropane, and 115 mg of the aldehyde. After 3 h at room temperature and workup, ^1H NMR of the unpurified product (δ 6.07 vs. δ 3.68) gave the diastereomeric ratio: >76:1. The crude product was purified by flash chromatography with 7.5% acetone/petroleum ether to afford 116 mg (98%) of the product as a colorless oil.

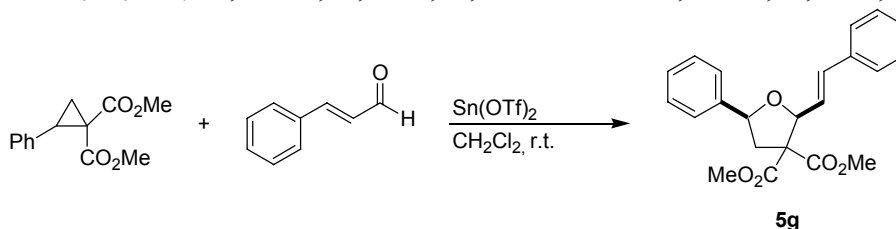
Analytical data for **5e**: **IR** (thin film, cm^{-1}) 3068, 3034, 3007, 2953, 2359, 1732, 1498, 1439, 1367, 1321, 1273, 1236, 1213, 1198, 1174, 1092, 1072, 1051, 1024, 943, 899, 858, 841, 825, 806, 758, 700; **^1H NMR** (400 MHz, CDCl_3) δ 7.52 (d, J = 7.2 Hz, 2H), 7.38 (dd, J = 7.2, 7.2 Hz, 2H), 7.34-7.28 (m, 1H), 7.24 (d, J = 4.8 Hz, 1H), 7.10 (d, J = 3.2 Hz, 1H), 6.95 (dd, J = 4.6, 3.7 Hz, 1H), 6.06 (s, 1H), 4.94 (dd, J = 10.8, 6.0 Hz, 1H), 3.83 (s, 3H), 3.32 (s, 3H), 2.96 (dd, J = 13.6, 10.8 Hz, 1H), 2.74 (dd, J = 13.6, 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 171.0, 168.8, 141.0, 139.7, 128.5, 128.2, 126.5, 126.4, 125.7, 125.3, 81.1, 80.1, 66.5, 53.2, 52.6, 42.1; **TLC** (80% CH_2Cl_2 /petroleum ether) R_f 0.37; **Anal.** Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_5\text{S}$: C, 62.41; H, 5.24. Found: C, 62.20; H, 5.28.



2-(4-nitrophenyl)-5-phenyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (5f, Table 1, entry 6). In an inert atmosphere glovebox, a flame-dried vial was charged with $\text{Sn}(\text{OTf})_2$ (28.5 mg, 0.0684 mmol, 0.200 equiv), the cyclopropane (80.0 mg, 0.34 mmol, 1.0 equiv), and a stir bar. Outside of the glovebox, the vial was placed under argon and charged with the aldehyde (155 mg, 1.0 mmol, 3.0 equiv) in 1.0 mL of CH_2Cl_2 . The reaction was stirred at room temperature. After 15 h the reaction was passed over a small plug of silica with 50 mL of Et_2O , and the solvent was removed by rotary evaporation. ^1H NMR analysis of the unpurified product (δ 5.83 vs. δ 3.73) gave the diastereomeric ratio: >15:1. The crude product was purified by flash chromatography with a 40% to 50% to 60% CH_2Cl_2 /petroleum ether gradient to afford 120 mg (91%) of the product as a white solid.

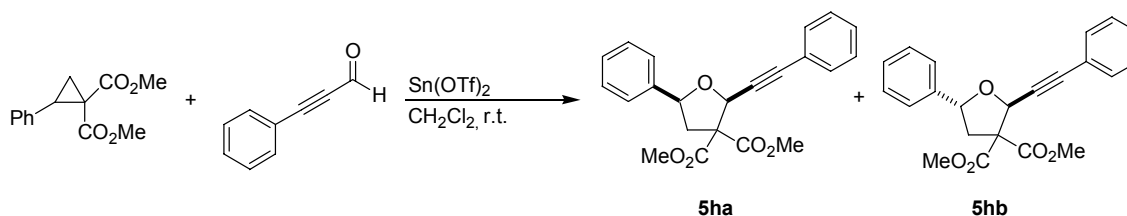
Analytical data for **5f**: mp 112-115 $^\circ\text{C}$; **IR** (thin film, cm^{-1}) 2954, 1732, 1606, 1524, 1495, 1435, 1387, 1348, 1313, 1273, 1232, 1209, 1176, 1109, 1092, 1059, 1030, 1016, 941, 862, 845, 806, 762, 746, 698; **^1H NMR** (400 MHz, CDCl_3) δ 8.18 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.2 Hz, 2H), 7.42 (dd, J = 7.2, 7.2 Hz, 2H),

7.39-7.31 (m, 1H), 5.82 (s, 1H), 4.99 (dd, $J = 10.0, 6.8$ Hz, 1H), 3.85 (s, 3H), 3.15 (s, 3H), 3.00 (dd, $J = 13.2, 10.8$ Hz, 1H), 2.81 (dd, $J = 13.2, 6.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 169.0, 147.8, 145.0, 139.3, 128.7, 128.5, 128.1, 126.6, 123.0, 83.5, 80.4, 66.4, 53.3, 52.5, 42.9; TLC (20% EtOAc/petroleum ether) R_f 0.36; **Anal.** Calcd. for $\text{C}_{20}\text{H}_{19}\text{NO}_7$: C, 62.33; H, 4.97; N, 3.63. Found: C, 62.05; H, 4.96; N, 3.65.



5-phenyl-2-styryltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (5g, Table 1, entry 7). The title compound was prepared according to General Procedure A using 7.1 mg of $\text{Sn}(\text{OTf})_2$, 80.0 mg of the cyclopropane, and 137 mg of the aldehyde. After 2.5 h at room temperature and workup, ^1H NMR of the unpurified product (δ 4.91 vs. δ 3.69) gave the diastereomeric ratio: 17.8:1. The isomers were separated and purified by flash chromatography with 5% acetone/petroleum ether to afford 119 mg (95%) of the products as yellow oils.

Analytical data for **5g**: **IR** (thin film, cm^{-1}) 3084, 3057, 3030, 3003, 2953, 2927, 2848, 1732, 1657, 1601, 1578, 1497, 1450, 1435, 1387, 1354, 1335, 1273, 1225, 1198, 1176, 1140, 1090, 1086, 1043, 1005, 970, 945, 914, 845, 818, 796, 760, 748, 696; ^1H NMR (500 MHz, CDCl_3) δ 7.50-7.45 (m, 2H), 7.40-7.20 (m, 8H), 6.80 (d, $J = 16.0$ Hz, 1H), 6.23 (dd, $J = 16.0, 7.0$ Hz, 1H), 5.28 (dd, $J = 7.0, 1.0$ Hz, 1H), 4.91 (dd, $J = 10.5, 6.5$ Hz, 1H), 3.84 (s, 3H), 3.62 (s, 3H), 2.85 (dd, $J = 13.5, 10.0$ Hz, 1H), 2.77 (dd, $J = 13.5, 6.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.0, 169.4, 140.2, 136.5, 133.1, 128.7, 128.6, 128.2, 128.0, 126.8, 126.6, 125.0, 83.2, 80.2, 65.3, 53.2, 52.9, 42.3; TLC (80% CH_2Cl_2 /petroleum ether) R_f 0.38; **Anal.** Calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_5$: C, 72.12; H, 6.05. Found: C, 72.25; H, 6.20.

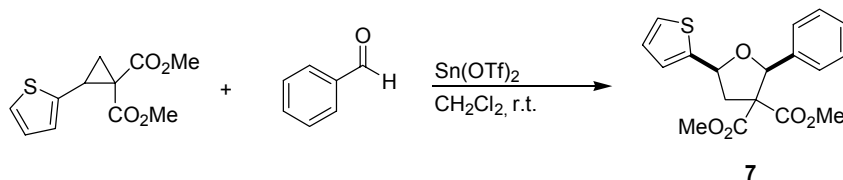


cis-5-phenyl-2-phenylethynyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (5ha, Table 1, entry 8). In an inert atmosphere glovebox, a flame-dried vial was charged with $\text{Sn}(\text{OTf})_2$ (14.2 mg, 0.034 mmol, 0.10 equiv), the cyclopropane (80.0 mg, 0.34 mmol, 1.0 equiv), and a stir bar. Outside of the glovebox, the vial was placed under argon and charged with 0.5 mL of CH_2Cl_2 and the aldehyde (133 mg, 1.0 mmol, 3.0 equiv). The reaction was stirred at room temperature. After 5.5 h the reaction was passed over a small plug of silica with 50 mL of Et_2O , the solvent removed by rotary evaporation, and the residue placed under vacuum (<0.1 torr) overnight. ^1H NMR analysis of the unpurified product (δ 5.67 vs. δ 5.93) gave the diastereomeric ratio: 1.5:1.

The isomers were separated and purified by flash chromatography with 7.5% acetone/petroleum ether to afford 118 mg (94%) of the products as yellow oils.

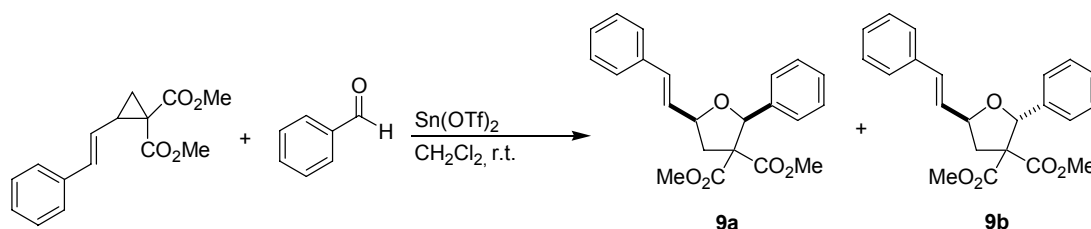
Analytical data for **5ha**: **IR** (thin film, cm^{-1}) 3064, 3032, 3005, 2953, 2231, 1738, 1599, 1574, 1491, 1435, 1383, 1354, 1327, 1273, 1228, 1196, 1173, 1092, 1070 1049, 1028, 1001, 989, 955, 914, 887, 843, 804, 758, 692; **^1H NMR** (400 MHz, CDCl_3) δ 7.60-7.23 (m, 10H), 5.66 (s, 1H), 4.96 (dd, $J = 10.8, 6.0$ Hz, 1 H), 3.86 (s, 3H), 3.77 (s, 3H), 2.93 (dd, $J = 13.2, 10.8$ Hz, 1H), 2.82 (dd, $J = 13.2, 5.6$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 169.8, 168.0, 140.3, 131.8, 128.8, 128.6, 128.4, 128.1, 126.5, 122.2, 87.8, 85.2, 81.1, 73.0, 66.6, 53.5, 53.1, 41.5; TLC (10% acetone/petroleum ether) R_f 0.17; **Anal.** Calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_5$: C, 72.51; H, 5.53. Found: C, 72.79; H, 5.48.

Analytical data for **trans-5-phenyl-2-phenylethynyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (5hb, Table 1, entry 8)**: **IR** (thin film, cm^{-1}) 3064, 3034, 3003, 2953, 2850, 2227, 1740, 1599, 1491, 1435, 1331, 1269, 1228, 1198, 1171, 1109, 1049, 1001, 987, 970, 939, 916, 889, 758, 692; **^1H NMR** (400 MHz, CDCl_3) δ 7.50-7.24 (m, 10H), 5.91 (s, 1H), 5.41 (dd, $J = 7.6, 7.6$ Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.40 (dd, $J = 13.2, 7.2$ Hz, 1H), 2.23 (dd, $J = 13.6, 8.4$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.1, 168.4, 140.5, 132.0, 128.9, 128.6, 128.4, 128.0, 126.0, 122.2, 87.8, 84.6, 80.4, 73.3, 66.6, 53.3 (two overlapping signals), 41.5; TLC (10% acetone/petroleum ether) R_f 0.24; **Anal.** Calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_5$: C, 72.51; H, 5.53. Found: C, 72.63; H, 5.49.



2-phenyl-5-(2-thienyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (7). The title compound was prepared according to General Procedure **B** using 7.1 mg of $\text{Sn}(\text{OTf})_2$, 81.5 mg of the cyclopropane, and 110 mg of benzaldehyde. After 45 min at -10°C and workup, ^1H NMR of the unpurified product (δ 5.22 vs. δ 2.58) gave the diastereomeric ratio: 21.7:1. The crude product was purified by flash chromatography with 10% acetone/petroleum ether to afford 113.5 mg (97%) of the product as a slightly yellow oil.

Analytical data for **7**: **IR** (thin film, cm^{-1}) 2953, 1732, 1497, 1456, 1435, 1387, 1365, 1327, 1273, 1232, 1207, 1174, 1107, 1076, 1053, 1028, 1022, 933, 922, 897, 852, 833, 814, 752, 700; **^1H NMR** (400 MHz, CDCl_3) δ 7.50-7.43 (m, 2H), 7.37-7.23 (m, 4H), 7.14 (d, $J = 3.6$ Hz, 1H), 7.00 (dd, $J = 5.2, 3.6$ Hz, 1H), 5.79 (s, 1H), 5.22 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.81 (s, 3H), 3.15-3.09 (m, 4H), 2.76 (dd, $J = 13.6, 6.0$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 171.2, 168.9, 142.7, 137.6, 128.3, 127.9, 127.1, 126.7, 125.7, 125.5, 84.5, 75.8, 66.4, 53.1, 52.3, 42.9; TLC (80% CH_2Cl_2 /petroleum ether) R_f 0.43; **Anal.** Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_5\text{S}$: C, 62.41; H, 5.24. Found: C, 62.32; H, 5.23.



2-phenyl-5-styryltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (9a). The title compound was prepared according to General Procedure **B** using 7.1 mg of $\text{Sn}(\text{OTf})_2$, 89 mg of the cyclopropane, and 110 mg of benzaldehyde. After 1 h at $-10\text{ }^\circ\text{C}$ and workup, ^1H NMR of the unpurified product (δ 5.73 vs. δ 5.87) gave the diastereomeric ratio: 2.4:1. The crude product was purified by flash chromatography with a 5% to 10% acetone/petroleum ether gradient to afford 123.1 mg (98%) of the product (inseparable diastereomers) as a colorless oil.

Analytical data for combined **9a/9b**: **IR** (thin film, cm^{-1}) 3082, 3062, 3001, 2953, 1732, 1601, 1578, 1497, 1452, 1435, 1360, 1335, 1269, 1228, 1207, 1174, 1109, 1090, 1070, 1049, 1028, 968, 916, 881, 845, 825, 814, 752, 698; **^1H NMR** (300 MHz, CDCl_3) δ 7.54–7.18 (m, 20H, major/minor), 6.72 (d, $J = 15.9$ Hz, 1H, major), 6.68 (d, $J = 15.6$ Hz, 1H, minor), 6.44 (dd, $J = 15.9, 6.9$ Hz, 1H, major), 6.25 (dd, $J = 15.9, 6.6$ Hz, 1H, minor), 5.87 (s, 1H, minor), 5.73 (s, 1H, major), 5.27 (ddd, $J = 7.2, 7.2, 7.2$ Hz, 1H, minor), 4.59 (ddd, $J = 9.9, 6.6, 6.6$ Hz, 1H, major), 3.80 (s, 3H, major), 3.74 (s, 3H, minor), 3.17 (s, 3H, minor), 3.11 (s, 3H, major), 3.08 (dd, $J = 13.2, 6.9$ Hz, 1H, minor), 2.87 (dd, $J = 13.2, 10.2$ Hz, 1H, major), 2.55 (dd, $J = 13.5, 6.0$ Hz, 1H, major), 2.28 (dd, $J = 13.2, 7.5$ Hz, 1H, minor); **^{13}C NMR** (75 MHz, CDCl_3) δ 171.2, 170.4, 169.2, 169.1, 138.3, 137.8, 136.5, 136.4, 133.0, 131.5, 129.4, 128.6, 128.2, 128.1, 128.03, 127.95, 127.89, 127.86, 127.6, 127.0, 126.8, 126.62, 126.55, 84.3, 83.6, 79.9, 79.2, 66.29, 66.26, 53.0, 52.9, 52.3, 52.2, 41.1, 40.7 (2 overlapping sp^2 signals); **TLC** (80% CH_2Cl_2 /petroleum ether) R_f 0.43; **Anal.** Calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_5$: C, 72.12; H, 6.05. Found: C, 72.40; H, 6.15.

Reference

- (1) Fraser, W.; Suckling, C. J.; Wood, H. C. S. *J. Chem. Soc. Perkin Trans. I.* 1990, 3137–3144.

Appendix. NMR spectra

