Quantitating the Effect of an Ortho Substituent on Cyclization and Intramolecular Hydrogen Transfer Reactions of Aryl Radicals

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Supporting Information

Purities of all authentic samples and isolated products were excellent (>95%, typically >98%) as assessed by GC (see Appendix A below for column and conditions).

(2-Iodo-3-methylphenyl)methanol:[1] To a stirred solution of 2-iodo-3-methyl benzoic acid (4.57 g, 17.4 mmol) and triethylamine (2.70 mL, 19.4 mmol) in THF (12 mL) at 0 °C was added dropwise ethyl chloroformate (1.90 mL, 19.9 mmol) over 30 min. The reaction mixture was stirred for 30 min followed by filtration to remove the solid precipitate. The precipitate was washed with additional THF (2 x 10 mL). Sodium borohydride (2.57 g, 67.8 mmol) was then added to the filtrate in one portion followed by the dropwise addition of methanol (30 mL) over 45 min at 0 °C. The mixture was stirred for an additional 40 min followed by quenching with 6 N HCl. The layers were separated and the aqueous layer was extracted with Et_2O (2 x 40 mL). The combined organic layers were dried over $MgSO_4$ and concentrated on a rotary evaporator. The residue was purified by silica gel chromatography (20% EtOAc in hexanes) to provide the product as a white solid: (7.19 g, 74%) mp 75-76 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.17-7.22 (m, 3 H), 4.73 (d, 1 H, *J* = 6.5 Hz), 2.48 (s, 3 H), 2.12 (t, *J* = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.3, 142.2, 129.1, 128.2, 125.8, 104.8, 70.4, 29.2; IR (KBr) 3275, 2899, 2839, 1583, 1447, 1403, 1314, 1169, 1059, 1002, 765 cm^{-1}; EIMS 248 (M^+, 100), 231 (7), 127 (14), 119

(119), 103 (20), 91 (59), 77 (61), 65 (30), 54 (18); HRMS calcd for C_8H_9OI (M^+) 247.9698, found 247.9696.

2-Iodo-3-methylbenzyl bromide:[2] To a stirred solution of (2-iodo-3-methylphenyl)methanol (0.84 g, 3.41 mmol) in CH_2Cl_2 (15 mL) was added PPh_3 (0.98 g, 3.74 mmol) in one portion. The mixture was stirred for 45 min prior to the portionwise addition of NBS (0.67 g, 3.75 mmol). The mixture was stirred for 3 h followed by quenching with sat. $NaHCO_3$. The layers were separated and the aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with sat. $NaHCO_3$ (20 mL), H_2O (30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator. The residue was purified by silica gel chromatography (hexanes) to provide the product as a clear oil (0.84 g, 79%). Data from the obtained product was in direct agreement to published characterization data[3]: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29-7.18 (m, 3 H), 4.65 (s, 2 H), 2.44 (s, 3 H); HRMS calcd for $C_8H_8Br_2$ (M^+) 261.8993, found 261.9002.

2-Allylmalonic acid dimethyl ester (CAS # 40637-57-7). (General Procedure for Alkylations of Malonates): To a stirred suspension of NaH (0.21 g, 8.5 mmol) in THF (15.0 mL) at 25 ^{o}C was added dropwise dimethyl malonate (1.3 mL, 11.4 mmol). The mixture was stirred for 30 min prior to the dropwise addition of allyl bromide (0.95 g, 7.9 mmol) in THF (3.0 mL). The solution was stirred at room temperature for 14 h followed by quenching with H_2O. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with H_2O (30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator. The residue was purified by silica gel chromatography

(15% EtOAc in hexanes) to provide the product as a clear oil (0.95 g, 49%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.77 (ddt, 1 H, *J* = 17.0, 10.3, 7.0 Hz), 5.12 (dq, 1 H, *J* = 17.0, 1.3 Hz), 5.06 (dq, 1 H, *J* = 10.3, 1.1 Hz), 3.74 (s, 6 H), 3.47 (t, 1 H, *J* = 7.3 Hz), 2.65 (t, 2 H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.2, 133.9, 117.6, 52.5, 51.4, 32.8; IR 3083, 3004, 2956, 2847, 1746, 1643, 1438, 1347, 1201 cm^{-1}; LRMS 172 (M^+, 20), 157 (10), 141 (10), 112 (100), 81 (100), 59 (65), 53 (30); EIMS calcd for $C_8H_{12}O_4$ (M^+) 172.0736, found 172.0730.

2-Allyl-2-(2-iodobenzyl)malonic acid dimethyl ester (1a): The reaction was carried out as above with NaH (0.088 g, 3.7 mmol), 2-allyldimethyl malonate (0.57 g, 3.3 mmol) and 2-iodobenzyl bromide (1.08 g, 3.7 mmol) in THF (9.0 mL). Purification by silica gel chromatography (20% EtOAc in hexanes) provided the product as a clear oil (1.13 g, 88%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (d, 1 H, *J* = 7.9 Hz), 7.27-7.19 (m, 2 H), 6.92-6.87 (m, 1 H), 5.83 (ddt, 1 H, *J* = 19.6, 9.6, 7.2 Hz), 5.14-5.07 (m, 2 H), 3.70 (s, 6 H), 3.51 (s, 2 H), 2.67 (d, 2 H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.7, 139.6, 139.3, 132.6, 129.8, 127.8, 118.7, 102.5, 58.8, 52.2, 42.3, 37.8; IR 3077, 2951, 2841, 1740, 1640, 1562, 1434 cm^{-1}; LRMS 388 (M^+, 20), 357 (25), 315 (20), 261 (100), 217 (65), 201 (30), 139 (30), 128 (20), 115 (25); EIMS calcd for $C_{15}H_{17}O_3I$ (M^+) 388.0172, found 388.0165.

2-Allyl-2-(2-iodo-3-methylbenzyl)malonic acid dimethyl ester (1b): The reaction was carried out as above with NaH (0.027 g, 1.8 mmol), 2-allyl-dimethyl malonate (0.17 g, 1.0 mmol) in THF (0.5 mL) and 2-iodo-3-methylbenzyl bromide (0.36 g, 1.2 mmol) in THF (3.5 mL). Purification by silica gel chromatography (20% EtOAc in hexanes) provided the product as a clear oil (0.32 g, 80%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12-7.10 (m, 2 H), 7.00-6.97 (m, 1 H),

5.43 (ddt, 1 H, *J* = 17.5, 9.6, 7.3 Hz), 5.12-5.06 (m, 2 H), 3.69 (s, 6 H), 3.62 (s, 2 H), 2.67 (d, 2 H, *J* = 7.3 Hz), 2.48 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.2, 142.6, 140.3, 133.1, 128.2, 127.5, 127.0, 118.9, 110.3, 59.4, 52.4, 43.7, 38.1, 30.7; IR 3082, 2953, 2839, 1731, 1632, 1575, 1451 cm^{-1}; LRMS 402 (M^+, 5), 371 (10), 339 (40), 329 (75), 275 (100), 231 (55), 215 (20), 155 (20), 139 (20), 115 (25), 104 (30), 59 (25); EIMS calcd for $C_{16}H_{19}O_4I$ (M^+) 402.0328, found 402.0337.

Representative Procedure for Kinetic Experiments with Ph_3SnH: To a stirred solution of 2-allyl-2-(2-iodo-3-methylbenzyl)malonic acid dimethyl ester **1b** (0.11 g, 0.27 mmol) in benzene (11 mL) was added Ph_3SnH (0.19 g, 0.55 mmol) and a catalytic amount of AIBN. The mixture was heated to reflux for 3 h followed by cooling to room temperature and concentration on a rotary evaporator to yield a crude oil. An aliquot from the crude reaction mixture was then diluted in CH_2Cl_2 for analysis by GC/MS and GC. A mixture of four products (**2b**, **3b**, **4b** and **5b**) with *m/e* = 276 (GC/MS) was obtained. GC product ratios as a function of concentration are listed in Table 1. A representative chromatogram is shown in Appendix A.

2-Allyl-2-(3-methylbenzyl)malonic acid dimethyl ester (2b): The reaction was carried out as above with NaH (0.031 g, 1.3 mmol), 2-allyl dimethyl malonate (0.20 g, 1.2 mmol) and 3-methylbenzyl bromide (0.17 mL, 1.3 mmol) in THF (6.0 mL). Purification by silica gel chromatography (20% EtOAc in hexanes) provided the product as a clear oil (0.28 g, 88%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.16 (t, 1 H, *J* = 7.6 Hz), 7.03 (d, 1 H, *J* = 7.7 Hz), 6.88 (d, 2 H, *J* = 7.5 Hz), 5.77 (ddt, 1 H, *J* = 14.9, 11.1, 7.3 Hz), 5.16 (bd, 1 H, *J* = 10.6 Hz), 5.13 (bd, 1 H, *J* = 5.7 Hz), 3.73 (s, 6 H), 3.21 (s, 2 H), 2.55 (d, 2 H, *J* = 7.2 Hz), 2.31 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75

MHz) δ 171.1, 137.7, 135.7, 132.7, 130.7, 128.1, 127.7, 126.9, 119.1, 59.1, 52.2, 38.1, 36.5, 21.3; IR 3078, 3025, 2952, 2359, 2342, 1738, 1641, 1608, 1435 cm^{-1}; EIMS 276 (M^+, 35), 244 (45), 235 (65), 203 (70), 157 (45), 105 (100), 59 (10); HRMS calcd for $C_{16}H_{20}O_4$ (M^+) 276.1362, found 276.1363.

Product **2b** was injected into the GC and it coeluted the second peak from the radical cyclizations of **1b**.

2-(3-Methylbenzyl)-2-propenylmalonic acid dimethyl ester (3b):[3] To a stirred solution of 2-allyl-2-(3-methylbenzyl)malonic acid dimethyl ester **2b** (0.102 g, 0.37 mmol) in EtOH (3.5 mL) was added a catalytic amount of $RhCl_3$. This mixture was heated to reflux for 20 h followed by cooling to room temperature. The crude reaction mixture was filtered through a plug of Celite (1:1 CH_2Cl_2:hexanes) and concentrated on a rotary evaporator. The residue was purified by column chromatography (20% EtOAc in hexanes) to yield the product as a clear oil (0.078 g, 77%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.21 (m, 1 H), 7.18-7.15 (m, 1 H), 7.03-7.01 (m, 2 H), 5.96 (dq, 1 H, *J* = 16.1, 1.6 Hz), 5.73 (dq, 1 H, *J* = 16.1, 6.3 Hz), 3.87 (s, 6 H), 3.46 (s, 2 H), 2.44 (s, 3 H), 1.90 (dd, 3 H, *J* = 6.4, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1137.2, 135.6, 130.9, 128.2, 128.1, 127.9, 127.8, 127.1, 60.7, 52.4, 42.3, 21.3, 18.1; IR 3010, 2952, 2703, 2342, 1730, 1606, 1434, 1274, 1194, 966, 806, 778, 705 cm^{-1}; EIMS 276 (M^+, 20), 244 (35), 216 (90), 203 (80), 185 (65), 171 (80), 157 (100), 141(70), 106 (80), 77 (95), 59 (65); HRMS calcd for $C_{16}H_{20}O_4$ (M^+) 276.1362, found 276.1356.

Product **3b** was injected into the GC and it coeluted with the first peak from the radical cyclizations of **1b**.

4,5-Dimethyl-3,4-dihydro-1*H*-napthalene-2,2-dicarboxylic acid dimethyl ester (4b) and 1-Methyl-8,9-dihydro-5*H*,7*H*-benzocycloheptene-6,6-dicarboxylic acid dimethyl ester (5b): To a stirred solution of 2-allyl-2-(2-iodo-3-methylbenzyl)malonic acid dimethyl ester **1b** (0.19 g, 0.41 mmol) in benzene (9.0 mL) was added Ph_3SnH (0.22 g, 0.62 mmol) and a catalytic amount of AIBN. The mixture was heated to reflux for 3 h followed by cooling to room temperature and concentration on a rotary evaporator to yield a crude oil. The crude oil was dissolved in Et_2O followed by the addition of DBU. A saturated solution of I_2 in Et_2O was then added until a dark brown color persisted. The mixture was then filtered through a plug of silica eluting with Et_2O followed by concentration on a rotary evaporator. Ozone was bubbled for 30 min through a stirred solution of the crude products in MeOH:CH_2Cl_2 (15 mL : 11 mL) at –78 ^oC. Pyridine (0.10 mL, 1.2 mmol) and Me_2S (1.2 mL, 16.3 mmol) were added followed by warming the mixture to room temperature. The mixture was stirred for 16 h followed by concentration on a rotary evaporator. The residue was purified by column chromatography (15% EtOAc in hexanes) to yield the products as an inseparable mixture in approximately a 5:1 ratio in favor of the 6-*exo* product **4b** over **5b** (0.023 g, 18% from **1b**). **4,5-Dimethyl-3,4-dihydro-1*H*-napthalene-2,2-dicarboxylic acid dimethyl ester (4b):** ^1H NMR ($CDCl_3$, 300 MHz) δ 7.09-6.94 (m, 3 H), 3.75 (s, 3 H), 3.57 (s, 3 H), 3.19-3.12 (m, 2 H), 2.69 (ddd, 1 H, *J* = 14.0, 7.8, 1.8 Hz), 2.29 (s, 3 H), 2.05 (dd, 2 H, *J* = 14.0, 4.9 Hz), 1.17 (d, 3 H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.7, 171.6, 138.8, 135.5, 133.1, 129.0, 126.8, 53.7, 52.2, 36.9, 35.5, 28.8, 21.9, 19.3; **1-Methyl-8,9-dihydro-5*H*,7*H*-benzocycloheptene-6,6-dicarboxylic acid dimethyl ester (5b):** ^1H NMR ($CDCl_3$, 300 MHz) δ 7.09-6.94 (m, 3 H), 3.64 (s, 6 H), 3.35 (s, 2 H), 2.83-2.79 (m, 2 H), 2.16 (t, 2 H, *J* = 6.5 Hz), 1.88-1.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.8, 141.2, 135.9, 134.5, 129.1, 128.9, 125.3, 55.5, 52.6, 39.4, 36.0, 28.2, 22.6, 20.3; Mixture, IR

3142, 2992, 2953, 2863, 2356, 2340, 1735, 1435, 1257, 1204, 1105, 957, 774 cm^{-1}; EIMS 276 (M^+, 40), 216 (85), 201 (60), 157 (100), 142 (60), 128 (35), 115 (35), 59 (25); HRMS calcd for $C_{16}H_{20}O_4$ (M^+) 276.1362, found 276.1362.

Products **4b** and **5b** were injected into the GC and coeluted with the third and fourth peaks from the radical cyclizations of **1b**.

2-Allyl-2-benzylmalonic acid dimethyl ester (2a):[4] The reaction was carried out as above with NaH (0.011 g, 0.46 mmol), 2-allyldimethyl malonate (0.069 g, 0.40 mmol) and benzyl bromide (0.060 mL, 0.44 mmol) in THF (1.5 mL). Purification by silica gel chromatography (20% EtOAc in hexanes) provided the product as a clear oil (0.078 g, 75%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27-7.25 (m, 3 H), 7.10-7.08 (m, 2 H), 5.76 (ddt, 1 H, *J* = 18.7, 11.4, 7.1 Hz), 5.16 (bd, 1 H, *J* = 10.2 Hz), 5.13 (bd, 1 H, *J* = 5.9 Hz), 3.71 (s, 6 H), 3.24 (s, 3 H), 2.55 (d, 2 H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 135.8, 132.6, 130.0, 128.3, 127.0, 119.2, 51.1, 52.2, 38.2, 36.5; IR 3405, 3288, 3181, 3029, 2953, 2358, 2340, 1733, 1640, 1436 cm^{-1}; EIMS 262 (M^+, 30), 231 (25), 221 (35), 189 (65), 143 (40), 91 (100); HRMS calcd for $C_{15}H_{18}O_4$ (M^+) 262.1205, found 262.1208.

Product **2a** was injected into the GC and coeluted with the second peak from the radical cyclizations of **1a**.

2-Benzyl-2-propenylmalonic acid dimethyl ester (3a): To a stirred solution of 2-allyl-2-benzylmalonic acid dimethyl ester **2a** (0.063 g, 0.24 mmol) in EtOH (2.0 mL) was added a catalytic amount of $RhCl_3$. This mixture was heated to reflux for 21 h followed by cooling to room temperature. The crude reaction mixture was filtered through a plug of Celite (1:1 CH_2Cl_2 : hexanes) and concentrated on a rotary evaporator. The residue was purified by column

chromatography (20% EtOAc in hexanes) to yield the product as a clear oil (0.048 g, 77%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26-7.22 (m, 3 H), 7.10-7.02 (m, 2 H), 5.82 (dq, 1 H, *J* = 16.1, 1.6 Hz), 5.60 (dq, 1 H, *J* = 16.1, 6.4 Hz), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.36 (s, 2 H), 1.75 (dd, 3 H, *J* = 6.5, 1.4 Hz) ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 135.8, 130.1, 129.9, 128.3, 128.0, 127.8, 127.7, 126.8, 60.7, 52.5, 42.4, 18.2; IR 3031, 2952, 2855, 1738, 1604, 1444, 1224, 967, 744, 702 cm^{-1}; EIMS 262 (M^+, 35), 171 (30), 143(25), 91 (100), 65 (20); HRMS calcd for $C_{15}H_{18}O_4$ (M^+) 262.1205, found 262.1207.

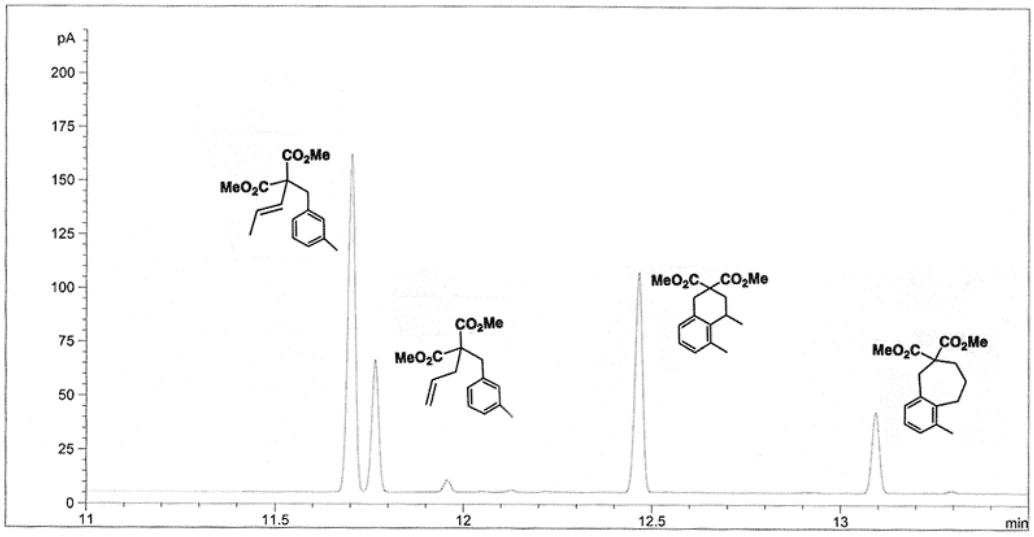
Product **3a** was injected into the GC and coeluted with the first peak from the radical cyclizations of **1a**.

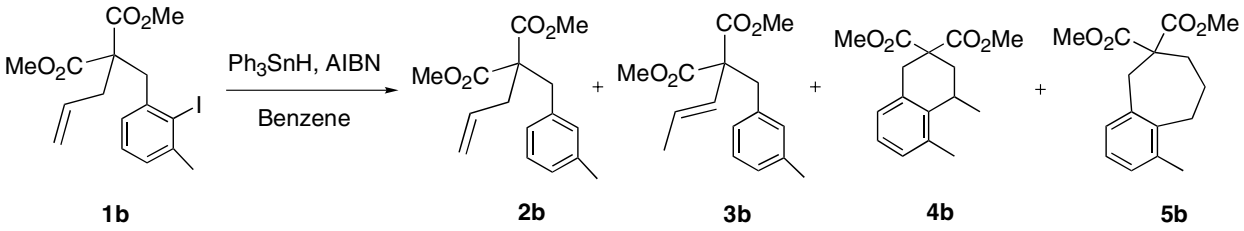
4-Methyl-3,4-dihydro-1*H*-napthalene-2,2-dicarboxylic acid dimethyl ester (4a) and 5,7,8,9-Tetrahydrobenzocycloheptene-6,6-dicarboxylic acid dimethyl ester (5a): To a stirred solution of 2-allyl-2-(2-iodobenzyl)malonic acid dimethyl ester (0.28 g, 0.73 mmol) in benzene (14.0 mL) was added Ph_3SnH (0.51 g, 1.5 mmol) and a catalytic amount of AIBN. The mixture was heated to reflux for 3 h followed by cooling to room temperature and concentration on a rotary evaporator to yield a crude oil. The crude oil was dissolved in Et_2O followed by the addition of DBU. A saturated solution of I_2 in Et_2O was then added until a dark brown color persists. The mixture was then filtered through a plug of silica eluting with Et_2O followed by concentration on a rotary evaporator. Ozone was bubbled for 30 min through a stirred solution of the crude products in MeOH:CH_2Cl_2 (20 mL : 15 mL) at –78 ^{o}C. Pyridine (0.20 mL, 2.5 mmol) and Me_2S (2.5 mL, 34.0 mmol) were added followed by warming the mixture to room temperature. The mixture was stirred for 16 h followed by concentration on a rotary evaporator. The residue was purified by column chromatography (15% EtOAc in hexanes) to yield the

products as an inseparable mixture along with benzyl dimethylmalonate. The mixture of three products was dissolved in DMF (2.5 mL) and heated to 180 ºC in a microwave for 30 min. This converted benzyl dimethylmalonate to $PhCH_2CH_2CO_2$ Me without reacting the cyclized (disubstituted) malonates. Purification by column chromatography (10% EtOAc in hexanes) yielded the cyclized products as an inseparable mixture in approximately a 3:1 ratio in favor of the 6-*exo* product (**4a** over **5a**) (0.044 g, 23% from **1a**). **4,5-Dimethyl-3,4-dihydro-1*H*-napthalene-2,2-4-Methyl-3,4-dihydro-1*H*-napthalene-2,2-dicarboxylic acid dimethyl ester (4a):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25-7.05 (m, 4 H), 3.75 (s, 3 H), 3.67 (s, 3 H), 3.38 (d, 1 H, *J* = 16.3 Hz), 3.17 (d, 1 H, *J* = 16.3 Hz), 2.59 (ddd, 1 H, *J* = 13.6, 5.9, 2.2 Hz), 1.83 (dd, 2 H, *J* = 13.5, 11.3 Hz), 1.36 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.3, 171.4, 139.7, 133.3, 128.6, 126.5, 125.9, 55.7, 52.8, 37.3, 35.3, 29.9, 21.3; **5,7,8,9-Tetrahydrobenzocycloheptene-6,6-dicarboxylic acid dimethyl ester (5a):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25-7.05 (m, 4 H), 3.64 (s, 6 H), 3.34 (s, 2 H), 2.79 (t, 2 H, *J* = 5.5 Hz), 2.21 (t, 2 H, *J* = 5.6 Hz), 1.92-1.86 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.7, 143.1, 135.8, 131.0, 128.5, 127.0, 53.8, 52.6, 52.3, 35.3, 29.9; Mixture: IR 3023, 2953, 2852, 1737, 1449, 1263, 1210, 755 cm^{-1}; LRMS 262 (M^+, 25), 202 (55), 187 (25), 143 (100), 128 (55), 115 (30), 91 (15), 59 (30); HRMS calcd for $C_{15}H_{18}O_4$ (M^+) 262.1205, found 262.1197.

Products **4a** and **4b** were injected into the GC and coeluted with the third and fourth peaks from the radical cyclizations of **1a**.

Appendix A. A Representative GC Chromatogram from the Radical Cyclization of 1b.





1b **2b** **3b** **4b** **5b**

GC Parameters:

Column: Agilent 190091Z-413E, Crosslinked Methyl Siloxane Stationary Phase
30 m x 0.320 mm x 0.25 μm
Initial Temp: 60 ˚C
Ramp Temp: 12 ˚C/min
Final Temp: 300 ˚C
Detector: FID
Gas Flow Rate: 34 cm/s

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[2] Yokohama, S.; Mochida, K. *Synthesis*, **1987**, 647.

[3] Grieco, P. A. Nishizawa, M.; Mariovic, N.; Ehmann, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 7102-7104.

[4] 2-Allyl-2-benzylmalonic acid dimethyl ester **104** has been reported in the literature without spectral data. Please see: a) Wang, S. F.; Chuang, C. P.; Lee, J. H.; Liu, S. T. *Tetrahedron* **1999**, *55*, 2273-2288. b) Chuang, C. P. *Tetrahedron Lett.* **1992**, *33*, 6311-6314.