Supporting Information For:

Highly Diastereoselective 5-Hexenyl Radical Cyclizations With Lewis Acids and Carbohydrate Scaffolds

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General Methods: Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer and are reported in wave numbers (cm^{-1}). ^{1}H Nuclear magnetic resonance spectra were recorded on a Varian Gemini-300 at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz. Chemical shifts are reported in ppm downfield relative to tetramethylsilane as an internal standard. All mass spectroscopy was performed by the Mass Spectroscopy Service at the University of Florida Department of Chemistry. Elemental analysis was performed by Atlantic Microlab Inc. in Norcross, GA. All reactions were run under an inert atmosphere of argon using clean, dry glassware. Solvents were freshly distilled before use. All yields reported refer to isolated material determined to be pure by NMR spectroscopy and thin layer chromatography.

Monobenzylated Isosorbide 3a.[9] Sodium hydride (60% in oil) (15.0 mmol, 0.6 g) was added to a flask flushed with argon. The gray powder was washed three times with pentane to remove the oil. A dilute solution of isosorbide (13.7 mmol, 2.0 g) in DMF (30 mL) was added to the sodium hydride. The mixture was stirred for 20 min. Benzylbromide (14.0 mmol, 1.7 mL) was added to the reaction flask and allowed to stir for 15 h at ambient temperature. The reaction was monitored by TLC. Workup entailed an extraction with brine and diethyl ether. The organic layer was dried with anhydrous magnesium sulfate and the solution concentrated. Compound **3a** was isolated by flash chromatography with silica gel (hexane/ether 35:65) as a colorless oil (2.7 g, 82%): $R_f = 0.08$ (35:65 EtOAc:Hex). All spectral data is in agreement with known literature values.[9]

Isosorbide Ylide 4a.[10] The monobenzylated isosorbide **3a** (17.2 mmol, 4.07 g) was dissolved in chloroform (80mL). The solution was cooled to 0^{o}C in an ice-bath and allowed to stir for 10 minutes. After addition of pyridine (60.3 mmol, 4.9 mL), the reaction was stirred at 0^{o}C for 15 minutes. In a seperate vessel, chloroacetic anhydride (34.5 mmol, 5.9 g) was dissolved in chloroform (70 mL). This solution was added dropwise to the above reaction mixture. The reaction was stirred at room temperature for 12 hours. After consumption of starting material, dilute HCl was added to neutralize the pH. Workup entailed an extraction with brine and chloroform. The organic layer was dried with anhydrous magnesium sulfate and the solution was concentrated. The chloride was isolated by flash chromatography on silica gel (hexane/ether 45 : 55), leaving a residual oil (4.5 g, 84%): $R_f = 0.46$ (35:65 EtOAc:Hex); $[\alpha]^{25}_{D} = +1.77$ (c = 2.8, chloroform); ^{1}H NMR ($CDCl_3$) 7.35 (m, 5H), 5.25 (d, 3.5 Hz, 1H), 4.75 (d, 11.9 Hz, 1H), 4.67 (t, 4.6 Hz, 1H), 4.55 (d, 11.9 Hz, 1H), 4.5 (m, 1H), 4.1 (m, 5H), 3.86 (dd, 8.8 Hz, 1H), 3.65 (dd, 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) 166.3, 137.5, 128.4, 127.8, 127.7, 85.4, 80.5, 80.0, 78.8, 73.2, 72.3, 70.4, 40.5 ; IR (neat): 2877.7, 1757.8, 1174.1, 699.8 cm^{-1}; HRMS calcd for $C_{15}H_{17}O_5Cl$ 312.0764, found 312.0764; Anal. Calcd for $C_{15}H_{17}O_5Cl$: C, 57.61; H, 5.48. Found : C, 57.73; H, 5.49.

The chloride (39.4 mmol, 12.3 g) was mixed with triphenylphosphine (118.2 mmol, 31.0 g) and benzene (50 mL) and allowed to reflux for 15 h. The resulting solution was cooled to room temperature. Benzene (20 mL) was added to the mixture to dissolve the excess triphenylphosphine. This procedure was repeated 3 times, discarding the benzene layer. Hot water was added to dissolve the salt formed in the flask. Once dissolved, 0.1 M NaOH was added dropwise until no further white ppt. was formed. More ppt. was observed upon cooling of the flask in an ice-bath for 1 hour. Workup entailed an extraction with brine and methylene chloride. The organic layer was dried with anhydrous magnesium sulfate and the solution was concentrated. Product **4a** was concentrated with a vacuum pump to a brown oil (17.2 g, 81%): R_f = 0.054 (35:65 EtOAc:Hex); $[\alpha]^{25}_{D}$ = + 39.7 (c = 3.2, chloroform); ^{1}H NMR ($CDCl_3$) 7.63 (m, 5H), 7.42 (m, 10H), 7.29 (m, 5H), 5.1 (d, 12 Hz, 1H), 4.77-4.4 (m, 4H), 4.07-3.4 (m, 6H), 1.98 (d, 13 Hz, 1H); ^{13}C NMR ($CDCl_3$) 137.4, 133.4, 133.1, 132.9, 132.5, 132.4, 131.7, 131.6, 131.56, 131.5, 131.35, 131.3, 130.1, 129.9, 128.5, 128.3, 128.2, 128.14, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.3, 127.23, 127.2, 85.4, 80.5, 80.0, 78.8, 73.2, 70.4, 69.4; IR (neat): 3048.5, 2954.5, 2355.1, 1619.3, 1434.3, 1190.4, 1108.1, 884.8, 743.8, 696.8 cm^{-1}; HRMS calcd for $C_{33}H_{31}PO_5$ 538.1909, found 538.1987.

1,2-O-Isopropylidene-5-O-Benzyl-(D)-xylofuranose (3b).[9] Sodium hydride (60% in oil) (26.7 mmol, 1.07 g) was added to a flask flushed with argon. The gray powder was washed three times with pentane to remove the protective oil. Commercial 1,2-O-isopropylidene-D-xylofuranose (26.4 mmol, 5.03 g), diluted in DMF (30 mL), was slowly added. The mixture was stirred for 20 min. Benzylbromide (26.7 mmol, 3.2 mL) was added to the reaction flask and allowed to stir for 15 h at room temperature. Workup entailed an extraction with brine and diethyl ether. The organic layer was dried with anhydrous magnesium sulfate and concentrated. Product **4b** was isolated by flash chromatography with silica gel (hexane/ether 35:65) as a colorless oil. All spectral data is in agreement with known literature values.[9]

(D)-Xylose Ylide 4b[10]. Monobenzylated xylose compound **4b** (14.3 mmol, 4.0 g) was dissolved in chloroform (80 mL). The solution was cooled to 0°C in an ice-bath and allowed to stir for 10 minutes. After addition of pyridine (57.1 mmol, 4.7 mL), the reaction was stirred at 0°C for 15 minutes. In a separate flask, chloroacetic anhydride (42.8 mmol, 7.3 g) was dissolved in chloroform (70 mL). This solution was added dropwise to the above reaction mixture. The reaction was stirred at room temperature for 12 hours. Workup entailed extraction with brine and chloroform. The organic layer was dried with anhydrous magnesium sulfate and the solution was concentrated. The chloride product was isolated by flash chromatography on silica gel (hexane/ether 45 : 55), as a clear oil (4.0 g, 78 %): R_f = 0.11 (35:65 EtOAc:Hex); $[\alpha]^{25}_{D}$ = - 40.8 (c = 3.2, chloroform); ^{1}H NMR ($CDCl_3$) 7.35 (m, 5H), 5.96 (d, 3.9 Hz, 4H), 4.7 (d, 12 Hz, 1H), 4.63 (d, 3.7 Hz, 1H), 4.4 (d, 12 Hz, 1H), 4.42-4.38 (m, 4H), 4.0 (s, 2H), 3.9 (d, 2.5 Hz, 1H), 1.5 (s, 3H), 1.3 (s, 3H); ^{13}C NMR ($CDCl_3$) 166.9, 136.9, 128.4, 128.0, 127.7, 111.8, 105.2, 81.9, 81.3, 77.6, 71.7, 63.7, 40.6, 26.7, 26.1; IR (neat): 2989.1, 2936.5, 2254.3, 1759.8, 1454.9, 1375.4, 1015.8, 735.7, 700.1 cm^{-1}; HRMS calcd for $C_{17}H_{21}ClO_6$ 356.1027, found 356.1105; Anal. Calcd for $C_{17}H_{21}ClO_6$: C, 57.23; H, 5.93. Found : C, 56.95; H, 5.79.

The chloride (48.2 mmol, 17.2 g) was mixed with triphenylphosphine (144.0 mmol, 37.8 g) and benzene (96 mL) and allowed to reflux for 15 h. The resulting solution was cooled to room temperature. Benzene (20 mL) was added to the mixture to solubilize the excess triphenylphosphine. This procedure was repeated 3 times, disgarding the benzene layer. Hot water was added to dissolve the salt formed in the flask. Once dissolved, 0.1 M NaOH was added dropwise until no further white ppt was formed. More ppt was observed upon cooling of the flask in an ice-bath for 1 h. Workup entailed an extraction with brine and methylene chloride. The organic layer was dried with anhydrous magnesium sulfate and the solution was concentrated. Ylide **4b** was thoroughly dried by a vacuum pump (23.7 g, 85 %): R_f = 0.054 (35:65 EtOAc:Hex); $[\alpha]^{25}_D$ = - 8.9 (c = 5.7, chloroform); ^{1}H NMR ($CDCl_3$) 7.9-7.6 (m, 15H), 7.28 (m, 5H), 5.85 (d, 3.6 Hz, 1H), 4.6 (d, 12 Hz, 1H), 4.57 (d, 3.7 Hz, 1H), 4.4 (d, 12 Hz, 1H), 4.28 (m, 1H), 4.17 (m, 2H), 3.85 (d, 3.0 Hz, 1H), 3.3 (d, 13.5 Hz, 2H), 1.4 (s, 3H), 1.3 (s, 3H); ^{13}C NMR ($CDCl_3$) 136.6, 134.8, 134.7, 133.6, 133.5, 132.9, 132.8, 130.2, 130.0, 129.9, 129.8, 128.2, 127.7, 127.4, 119.4, 111.5, 104.8, 81.5, 81.0, 71.4, 26.5, 25.8; IR (neat): 3354.1, 3060.3, 2990.5, 2712.2, 2173.7, 1736.5, 1710.5, 1588.0, 1439.0, 1374.4, 1115.2, 927.4, 737.8, 638.4 cm^{-1}; HRMS calcd for $C_{35}H_{35}O_6P$ 582.2171, found 582.2265.

Aldehyde 6. Isochroman (75 mmol, 10 g) was dissolved in freshly distilled methylene chloride (150 mL) and stirred under argon. To the solution, 1 equiv. of pyridinium chlorochromate (PCC) (75 mmol, 16 g) was added. After the mixture was stirred for 2 h at reflux, more PCC (32 g) was added. The reaction was monitored by TLC. Upon completion, the reaction was cooled and filtered through a plug of silica. The product lactone[19] was isolated by flash chromatography on silica gel (hexane/ether 70:30), leaving a residual oil (7.9 g, 72%): R_f = 0.47 (35:65 EtOAc:Hex) ^{1}H NMR ($CDCl_3$) 8.1 (d, 7.8 Hz, 1H), 7.5 (m, 1H), 7.4 (m, 1H), 7.3 (m, 1H), 4.5 (t, 5.9 Hz, 2H), 3.1 (t, 5.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) 164.7, 139.3, 133.3, 129.7, 127.2, 127.0, 124.8, 67.0, 27.3, 28.0; IR (neat): 2899.5, 1725.1, 1605.2, 1294.6, 1120.3, 744.3 cm^{-1}; HRMS calcd for $C_9H_8O_2$ 148.0524, found 148.0524; Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found : C, 72.73; H, 5.51.

The lactone (47.8 mmol, 7.1 g) was dissolved in methylene chloride (96 mL) and cooled in a round bottom flask to –78°C in a dry ice/acetone bath. Diisobutylaluminium hydride (DIBAL) (47.8 mmol, 6.8 g) was added to the reaction dropwise. The reaction was monitored by TLC. The reaction mixture was quenched with 5 mL of methanol at -78°C. The mixture was then poured into a flask and stirred rapidly with Rochelle's salt. Workup entailed an extraction with brine and methylene chloride. The organic layer was dried with anhydrous magnesium sulfate. The solution was concentrated and further purified by flash chromatography on silica gel (hexane/ether 55:45), producing the lactol as a white crystalline solid (mp 73-74 °C) (6.1 g, 84.5%): R_f = 0.47 (35:65 EtOAc:Hex) ^{1}H NMR ($CDCl_3$) 7.3 (m, 1H), 7.25 (m, 2H), 7.14 (m, 1H), 5.9 (d, 5.4 Hz, 1H), 4.2 (ddd, 3.7 Hz, 3.5 Hz, 3.7 Hz, 1H), 3.95 (dddd, 2.7 Hz, 1H), 3.0 (m, 2H), 2.7 (dt, 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) 135.0, 134.1, 128.5, 128.2, 127.3, 126.5, 91.5, 58.4, 28.0; IR (neat):

3356.1, 2932.1, 1724.1, 1606.3, 1459.1, 740.6 cm^{-1}; HRMS calcd for $C_9H_{10}O_2$ 150.0681, found 150.0681; Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found : C, 72.04; H, 6.60.

The lactol (33 mmol, 5.0 g) was dissolved in DMF (0.5 M) in a round bottom flask. Imidazole (167 mmol, 11.3 g) and DMAP (3.3 mmol, 0.41 g) were added to the reaction mixture. The solution was degassed with argon for 20 min at room temperature. Slowly, *t*-butylchlorodiphenylsilane was added dropwise and the resulting solution was allowed to stir overnight (12 h). Workup entailed an extraction with brine and diethyl ether. The organic layer was dried with anhydrous magnesium sulfate and concentrated. Aldehyde **6** was isolated by flash chromatography on silica gel (hexane/ether 65:35), as a tan oil (10.3 g, 80%): R_f = 0.84 (35:65 EtOAc:Hex) ^{1}H NMR ($CDCl_3$) 10.2 (s, 1H), 7.5 (m, 4H), 7.33 (m, 10H), 3.9 (t, 6.36 Hz, 2H), 3.3 (t, 6.36 Hz, 2H), 0.98 (s, 9H); ^{13}C NMR ($CDCl_3$) 192.3, 135.5, 133.5, 133.4, 132.1, 131.1, 129.6, 127.7, 127.6, 126.8, 64.6, 35.2, 26.7, 26.5, 19.0; IR (neat): 3073.7, 2855.8, 1692.3, 1599.7, 1109.3, 1016.7, 744.2, 700.6 cm^{-1}; HRMS calcd for $C_{25}H_{28}SiO_2$ 388.1859, found 388.1859.

Isosorbide Wittig Adduct 7a. Aldehyde **6** (10.3 mmol, 4.0 g) and Wittig reagent **4a** (20.6 mmol, 11.1 g) were combined in a oven dried flask and dissolved in freshly distilled methylene chloride (to 1M in aldehyde). The reaction was stirred for 15 h at room temperature. After completion of the reaction, the solvent was evaporated and the remaining residue was purified with column chromatography (hexane/ether 50:50) to give **7a** as a clear oil (3.1 g, 46%): R_f = 0.64 (35:65 EtOAc:Hex); $[\alpha]^{25}_D$ = +34.8 (c = 1.3, chloroform); ^{1}H NMR ($CDCl_3$) 8.1 (d, 15.8 Hz, 1H), 7.55 (m, 5H), 7.35 (m, 14H), 6.32 (d, 15.8 Hz, 1H), 5.3 (d, 3.5 Hz, 1H), 4.79 (d, 12 Hz, 1H), 4.7 (t, 4.3 Hz, 1H), 4.58 (d, 11.8 Hz, 1H), 4.54 (s, 1H), 4.18 (dd, 3.7 Hz, 1 H), 4.1 (m, 2H), 3.9 (dd, 6.6 Hz, 1H), 3.8 (m, 2H), 3.68 (dd, 8.2 Hz, 1H), 3.02 (t, 6.6 Hz, 2H), 0.97 (s, 9 H); ^{13}C NMR ($CDCl_3$) 165.8, 143.5, 139.1, 137.6, 135.4, 133.3, 131.1, 130.0, 129.4, 128.4, 127.9, 127.5, 126.7, 126.3, 118.5, 85.9, 80.5, 79.0, 78.5, 73.8, 72.4, 70.2, 64.5, 35.9, 26.8, 26.7, 19.0; IR (neat): 3063.1, 2931.1, 2858.0, 1716.0, 1632.8, 1167.6, 1106.6, 702.6 cm^{-1}; HRMS calcd for $C_{40}H_{44}SiO_6$ 648.2907, found 648.2907; Anal. Calcd for $C_{40}H_{44}SiO_6$: C, 74.04; H, 6.83. Found : C, 73.80; H, 6.86.

Bromide 8a. Wittig adduct **7a** (0.54 mmol, 0.35 g) was dissolved in acetonitrile (0.5 M) and cooled to 0^{o}C. To this solution, 49% HF (0.54 mmol) was added by syringe. The reaction was monitored by TLC. Workup entailed an extraction with brine and chloroform. The organic layer was dried with anhydrous magnesium sulfate and the solution was concentrated. The alcohol product was isolated by flash chromatography on silica gel (hexane/ether 10:90), leaving a colorless, residual oil (0.20 g, 90%): R_f = 0.13 (35:65 EtOAc:Hex); $[\alpha]^{25}_D$ = + 2.48 (c = 2.5, chloroform); ^{1}H NMR ($CDCl_3$) 8.05 (d, 15.9 Hz, 1H), 7.55 (m, 4H), 7.2-7.4 (m, 15H), 6.32 (d, 15.8 Hz, 1H), 5.9 (d, 3.9 Hz, 1H), 4.68 (d, 11.9 Hz, 1H), 4.6 (d, 3.9 Hz, 1H), 4.55-4.4 (m, 4H), 4.5 (d, 12.0 Hz, 1H), 4.0 (d, 2.5 Hz, 1H), 3.8 (t, 6.4 Hz, 2H), 3.0 (t, 6.4 Hz, 2H), 1.49 (s, 3H), 1.32 (s, 3H), 0.98 (s, 9H); ^{13}C NMR ($CDCl_3$) 166.5, 142.8, 138.9, 137.1, 135.5, 135.4, 134.7, 133.5, 133.4, 131.1, 129.8, 129.5, 129.4, 128.5, 128.0, 127.7, 127.6, 127.57, 127.53, 126.7, 126.4, 119.0, 111.8, 105.2, 82.1, 81.5, 78.1, 71.8, 64.5, 62.2, 35.9, 26.8, 26.7, 26.5, 26.1, 19.0; IR (neat): 3054.3, 2937.8, 2856.2, 1711.5, 1635.7, 1216.2, 1012.3, 703.5, 616.1 cm^{-1}; HRMS calcd for $C_{24}H_{26}O_6$ 410.1729, found 410.1808.

The alcohol (0.85 mmol, 0.35 g) was dissolved in distilled methylene chloride and cooled to 0^{o}C. The reaction flask was purged with argon for 10 minutes. Triphenylphosphine (1.0 mmol, 0.27 g) was added and allowed to dissolve into solution. Carbon tetrabromide (0.94 mmol, 0.31 g) was slowly added in parts. The reaction was monitored by TLC. Workup entailed an extraction with brine and methylene chloride. The organic layer was dried with anhydrous magnesium sulfate and concentrated. Bromide **8a** was isolated by flash chromatography on silica gel (hexane/ether 65:35), leaving a residual oil (0.33 g, 82%): R_f = 0.53 (35:65 EtOAc:Hex); $[\alpha]^{25}_D$ = + 111.7 (c = 0.12, chloroform); ^{1}H NMR ($CDCl_3$) 7.98 (d, 15.8 Hz, 1H), 7.6 (m, 1H), 7.4-7.2 (m, 7H), 6.4 (d, 15.6Hz, 1H), 5.33 (d, 3.5 Hz, 1H), 4.79 (d, 11.9 Hz, 1H), 4.7 (m, 1H), 4.55 (d, 11.7 Hz, 1H), 4.5 (m, 1H), 4.2-4.06 (m, 3H), 3.9 (dd, 8.8 Hz, 1H), 3.7 (dd, 8 Hz, 1H), 3.5 (t, 7.4 Hz, 2H), 3.3 (t, 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) 165.7, 142.3, 138.4, 137.6, 133.0, 130.6, 130.5. 129.1, 128.5, 128.0, 127.7, 127.0, 119.5, 86.0, 80.6, 79.1, 78.7, 73.8, 72.5, 70.4, 36.4, 32.1; IR (neat): 2953.8, 2877.6, 1714.1, 1626.9, 1169.2, 1054.8, 727.9 cm^{-1}; HRMS calcd for $C_{24}H_{25}O_5Br$ 472.1085, found 472.0964.

(D)-Xylose Wittig Adduct 7b. Aldehyde **6** (2.6 mmol, 1.0 g) and Wittig reagent **4b** (5.2 mmol, 3.0 g) were combined in a oven dried flask. The reaction was stirred for 15 h at room temperature. After the reaction was complete by TLC, the remaining residue was subjected directly to column chromatography (hexane/ether 50:50). Wittig adduct **7b** was obtained as a tan oil (1.0 g, 56 %): R_f = 0.73 (35:65 EtOAc:Hex); $[\alpha]^{25}_D$ = - 20.4 (c = 1.7, chloroform); ^{1}H NMR ($CDCl_3$) 8.05 (d, 15.9 Hz, 1H), 7.55 (m, 4H), 7.2-7.4 (m, 15H), 6.32 (d, 15.8 Hz, 1H), 5.9 (d, 3.9 Hz, 1H), 4.68 (d, 11.9 Hz, 1H), 4.6 (d, 3.9 Hz, 1H), 4.55-4.4 (m, 4H), 4.5 (d, 12.0 Hz, 1H), 4.0 (d, 2.5 Hz, 1H), 3.8 (t, 6.4 Hz, 2H), 3.0 (t, 6.4 Hz, 2H), 1.49 (s, 3H), 1.32 (s, 3H), 0.98 (s, 9H); ^{13}C NMR ($CDCl_3$) 166.5, 142.8, 138.9, 137.1, 135.5, 135.4, 134.7, 133.5, 133.4, 131.1, 129.8, 129.5, 129.4, 128.5, 128.0, 127.7, 127.6, 127.57, 127.53, 126.7, 126.4, 119.0, 111.8, 105.2, 82.1, 81.5, 78.1, 71.8, 64.5, 62.2, 35.9, 26.8, 26.7, 26.5, 26.1, 19.0; IR (neat): 3054.3, 2937.8, 2856.2, 1711.5, 1635.7, 1216.2, 1012.3, 703.5, 616.1 cm^{-1} ; HRMS calcd for $C_{42}H_{48}SiO_7$ 692.3169, found 692.3248; Anal. Calcd for $C_{42}H_{48}SiO_7$: C, 72.80; H, 6.98. Found : C, 72.65; H, 7.09.

Bromide 8b. Wittig adduct **7b** (1.4 mmol, 1.0 g) was dissolved in pyridine (0.5 M) and cooled to 0^{o}C. To this mixture, a 65% hydrogen flouride/pyridine solution (1.5 mmol) was added by syringe. The reaction was monitored by TLC. Workup entailed an extraction with brine and chloroform. The organic layer was dried with anhydrous magnesium sulfate and the solution was concentrated. The alcohol product was isolated by flash chromatography on silica gel (hexane/ether 10:90), as a colorless, residual oil (0.55 g, 86 %): R_f = 0.19 (35:65 EtOAc:Hex); $[\alpha]^{25}_D$ = - 28.6 (c = 2.5, chloroform); ^{1}H NMR ($CDCl_3$) 8.03 (d, 15.8 Hz, 1H), 7.58 (m, 1H), 7.4-7.23 (m, 8H), 6.4 (d, 15.8 Hz, 1H), 6.0 (d, 3.9 Hz, 1H), 4.72 (d, 11.9 Hz, 1H), 4.65 (d, 3.85 Hz, 1H), 4.55 (d, 11.9 Hz, 1H), 4.49-4.3 (m, 3H), 4.0 (d, 2.3 Hz, 1H), 3.8 (t, 6.75 Hz, 2H), 3.0 (t, 6.75 Hz, 2H), 1.5 (s, 3H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$) 166.6, 142.5, 138.1, 137.1, 133.4, 130.8, 130.2, 128.5, 128.0, 127.7, 127.1, 126.8, 119.3, 111.9, 105.3, 82.1, 81.6, 78.2, 71.9, 63.3, 62.4, 36.4, 26.8, 26.2; IR (neat): 3474.2, 2939.0, 2869.1, 1713.2, 1631.7, 1596.6, 1375.7, 1166.3, 1079.0, 1012.3, 738.0, 699.4 cm^{-1}; HRMS calcd for $C_{26}H_{30}O_7$ for 454.1992, found 454.2070.

The alcohol (0.22 mmol, 0.10 g) was dissolved in distilled methylene chloride (0.44 mL) and cooled to 0^{o}C. The reaction flask was purged with argon for 10 minutes. Triphenylphosphine (0.26 mmol, 0.07 g) was added and allowed to dissolve into solution. Carbon tetrabromide (0.24 mmol, 0.08 g) was slowly added in parts. The reaction was monitored by TLC. Workup entailed an extraction with brine and methylene chloride. The organic layer was dried with anhydrous magnesium sulfate and the solution was concentrated. Bromide product **8b** was isolated by flash chromatography on silica gel (hexane/ether 65:35), leaving a residual oil (0.10 g, 90 %): R_f = 0.65 (35:65 EtOAc:Hex); $[\alpha]^{25}_D$ = - 26.9 (c = 2.1, chloroform); ^{1}H NMR ($CDCl_3$) 7.95 (d, 15.8 Hz, 1H), 7.58 (m, 1H), 7.4-7.2 (m, 8H), 6.4 (d, 15.8 Hz, 1H), 6.0 (d, 3.7 Hz, 1H), 4.71 (d, 11.9 Hz, 1H), 4.64 (d, 3.85 Hz, 1H), 4.5-4.4 (m, 5H), 4.0 (d, 2.3 Hz, 1H), 3.5 (t, 7.9, 7.3 Hz, 2H), 3.3 (t, 7.3, 7.7 Hz, 2H), 1.5 (s, 3H), 1.3 (s, 3H); ^{13}C NMR ($CDCl_3$) 166.4, 141.6, 138.2, 137.1, 133.1, 130.5, 130.2. 128.5, 128.0, 127.7, 127.6, 126.9, 119.9, 111.8, 105.3, 82.1, 81.6, 78.1, 71.9, 62.4, 36.4, 32.0, 26.8, 26.2; IR (neat): 2931.0, 1713.4, 1361.1, 1454.8, 1319.7, 1166.9, 1072.9, 1014.1, 767.3, 696.8 cm^{-1}; HMRS (CI) for $C_{26}H_{29}O_6Br$ calcd 516.1348, found 516.1221.

General Procedure for Radical Cyclizations. Bromide **8a** or **8b** (0.13 mmol) and methylene chloride (to 0.5 M in bromide) were added to an argon flushed, oven-dried, round bottom flask. The Lewis acid (2 equiv.) was also added to the reaction vessel and allowed to stir under argon at room temperature for 15 min. The reaction mixture was then cooled to –78 ^{o}C with a dry ice/acetone bath. Tributyltin hydride (0.63 mmol, 0.17 mL) and triethylborane (1M in hexane) (0.32 mmol, 0.32 mL) were then added to the solution in that order. After all the reagents were allowed to stir at –78 ^{o}C for 10 min, oxygen was bubbled into the mixture for five minute intervals every 3h. The reaction was monitored by TLC until completion. Workup entailed concentrating the mixture and applying it to a pad of potassium flouride on top of a column of silica gel. After leaving the residue on the pad for 30 min, the cyclized product was eluted (30:60 ether:hexane) yielding **9a** or **9b** (75-87 %): Spectral data for **9a**: R_f = 0.50 (35:65 EtOAc:Hex); ^{1}H NMR ($CDCl_3$) 7.35 (m, 5H), 7.1 (m, 4H), 5.23 (d, 3.7 Hz, 1H), 4.7-4.5 (dd, 12 Hz, 2H), 4.65 (t, 4.4 Hz, 1H), 4.47 (t, 5 Hz, 1H), 4.15-3.97 (m, 4H), 3.9 (t, 8.9 Hz, 2H), 3.9 (d, 2.5 Hz, 1H), 1.5 (s, 3H), 1.3 (s, 3H); ^{13}C NMR($CDCl_3$) 171.5, 143.0, 135.1, 128.5, 127.9, 126.8, 126.3, 124.6, 123.4, 85.9, 80.6, 79.1, 78.5, 73.8, 72.5, 70.4, 41.2, 39.7, 32.2, 31.2; IR (neat): 2927.7, 2847.8, 2358.6, 1735.0, 1660.2, 1635.2, 1455.5, 1365.6, 1255.8, 1161.0, 1101.1, 1056.1, 986.3, 746.6, 691.7 cm^{-1} ; HRMS calcd for $C_{24}H_{26}O_5$ 394.1780, found 394.2185; Spectral data for **9b**: R_f = 0.59 (35:65 EtOAc:Hex); ^{1}H NMR ($CDCl_3$) 7.31 (m, 5H), 7.15 (m, 4H), 5.96 (d, 3.7 Hz, 1H), 4.70 (d, 11.9 Hz, 1H), 4.62 (d, 3.67 Hz, 1H), 4.5-4.3 (m, 4H), 3.95 (d, 1.7 Hz, 1H), 3.57 (t, 6.7, 7.5 Hz, 1H), 2.8 (m, 3H), 2.4 (m, 2H), 1.7 (m, 1H), 1.49 (s, 3H), 1.32 (s, 3H); ^{13}C NMR($CDCl_3$) 172.5, 143.8, 137.2, 128.5, 128.1, 127.7, 126.7, 126.3, 124.5, 123.4, 111.8, 105.3, 82.1, 81.6, 78.1, 71.9, 62.2, 41.2, 39.7, 32.3, 31.2, 26.8, 26.2; IR (neat): 2957.6, 2917.7, 2348.6, 1730.0, 1455.5, 1370.6, 1260.8, 1210.9, 1161.0, 1071.1, 1011.2, 856.5, 746.6, 691.7 cm^{-1} ; HRMS calcd for $C_{26}H_{30}O_6$ 438.2042, found 438.2036.

(S)-(+)-Indan Acid 10.[13] Indanate ester **9a** or **9b** (0.14 mmol) was dissolved in a 5:1 THF:H_2O solution and stirred at room temperature. To this flask, LiOH (140 mmol) was added. The resulting reaction mixture was heated at reflux for 3h. Reaction progress was monitored by TLC. The reaction mixture was first washed with ether to remove any organic contaminants, followed by neutralization of the basic solution with 2M HCl. An ethyl acetate wash removed the reprotonated alcohol product. Further acidification to pH = 2 provided acid **10** (10.0 mgs): R_f = 0.53 (35:65 EtOAc:Hex); $[\alpha]^{25}_D$ (isosorbide) = + 5.5 (c = 0.5, benzene); $[\alpha]^{25}_D$ (xylose) = + 3.5 (c = 0.9, benzene); ^{1}H NMR ($CDCl_3$) 7.25-7.1 (m, 4H), 3.58 (q, 7.5 Hz, 1H), 2.87 (m, 2H), 2.47 (m, 2H), 1.76 (m, 1H); ^{13}C NMR ($CDCl_3$) 178.5, 145.7, 144.1, 126.9, 126.5, 124.8, 123.6, 41.2, 39.8, 32.5, 31.3; IR (neat): 2943.5, 2849.5, 2673.2, 1707.9, 1408.2, 1267.2, 1190.8, 750.1 cm^{-1}; HRMS calcd for $C_{11}H_{12}O_2$ 176.0837, found 176.0840. The (+)-acid had ^{1}H NMR, ^{13}C NMR and IR identical to that previously reported.[13]