Dearomatization-Bis-alkylation of Aromatic and Heteroaromatic Diesters Promoted by Me₃SnLi via a Stanna-Brook Rearrangement

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Supporting Information

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General Methods. All reactions were performed under an inert atmosphere of Argon in glassware that had been oven- or flame-dried. Reaction temperatures are reported as the temperature of the bath surrounding the vessel. Solvents were distilled immediately prior to use: Tetrahydrofuran (THF) from sodium/benzophenone, methylene chloride (CH₂Cl₂) and triethylamine from CaH₂; isopropanol (*i*PrOH) from Mg(OMe)₂. NMR spectra were recorded in CDCl₃ on a 250, 300 or 500 MHz spectrometer. Chemical shifts are reported in ppm (δ) relative to the internal TMS (tetramethylsilane) reference signal. *J* values are reported in hertz (Hz).

Diisopropyl terephthalate (4). Triethylamine (4.8 mL, 34.5 mmol) was added to a 0 °C solution of terephthaloyl dichloride (2.0 g, 9.9 mmol), 4-dimethylaminopyridine (60 mg, 0.5 mmol) and *i*PrOH (2.6 mL, 34.5 mmol) in CH₂Cl₂ (50 mL). The resulting orange mixture was stirred at rt for 30 min and then poured over 2 N HCl (20 mL) and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic phase was washed with 1 M NaOH (2 x 15 mL) and H₂O (20 mL), dried with anhydrous Na₂SO₄, filtered and concentrated. The resulting residue was purified by column chromatography (SiO₂, EtOAc/hexane 1/6) to give 1.80 g (72%) of **4** as a white solid: mp: 56-57 °C (MeOH); IR (KBr) 1716 cm⁻¹; ¹H NMR δ 7.93 (s, 4H), 5.11 (hept, *J* = 6.2, 2H), 1.23 (d, *J* = 6.2, 12H); ¹³C NMR δ 164.7, 134.1, 129.0, 68.4, 21.5. Anal. Calcd for C₁₄H₁₈O₄: C, 67.18; H, 7.25. Found: C, 66.88; H, 7.37.

Diisopropyl pyridine-2,3-dicarboxylate (22). *i*PrOH (2.8 mL, 36.0 mmol) was added to a solution of dicyclohexylcarbodiimide (5.2 g, 25.0 mmol), 4-dimethylaminopyridine (244 mg, 2.0 mmol) and quinolinic acid (2.0 g, 12.0 mmol) in CH₂Cl₂. The resulting mixture was stirred in a sealed tube at 60 °C overnight and then poured over cold Et₂O, filtered and concentrated. The reaction mixture was partitioned between CH₂Cl₂ (15 mL) and 2 N HCl (2 x 10 mL). The organic layer was washed with satd aq NaHCO₃ (10 mL) and H₂O (10 mL), dried with Na₂SO₄, filtered and evaporated. The residue was chromatographed through a short column of SiO₂ (EtOAc/hexane 1/3) to give **22** in 70% yield (2.1 g) as a pale yellow solid: mp: 39-40 °C (MeOH); IR (KBr) 1725 and 1658 cm⁻¹; ¹H NMR δ 8.74 (dd, *J* = 1.6, 4.8, 1H), 8.17 (dd, *J* = 1.6, 7.9, 1H), 7.45 (dd, *J* = 4.8, 7.9, 1H), 5.31 (m, 2H), 1.42 (d, *J* = 6.3, 6H), 1.36 (d, *J* = 6.3, 6H); ¹³C NMR δ 165.0, 163.5, 151.0, 150.8, 136.7, 125.2, 123.7, 68.8, 20.7. Anal. Calcd for C₁₃H₁₇NO₄: C, 62.14; H, 6.82; N, 5.57. Found: C, 61.74; H, 6.91; N, 5.61.

Diisopropyl pyridine-2,5-dicarboxylate (23). Following the same procedure as for **22**, 1.0 g of pyridine-2,5-dicarboxylic acid (7.31 mmol) afforded 1.63 g (89%) of **23** as a white solid: mp: 68-69 °C (MeOH); IR (KBr) 1724 and 1712 cm⁻¹; ¹H NMR δ 9.29 (s, 1H), 8.39 (dd, *J* = 1.7, 8.1, 1H), 8.15 (d, *J* = 8.1, 1H), 5.30 (m, 2H), 1.42 (d, *J* = 6.3, 6H), 1.38 (d, *J* = 6.3, 6H); ¹³C NMR δ 163.3, 163.2, 150.8, 150.2, 137.4, 128.3, 123.9, 69.3, 69.0, 21.2. Anal. Calcd for C₁₃H₁₇NO₄: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.08; H, 6.96; N, 5.54.

General Procedure for the Addition of Me₃SnLi to Aromatic Diesters. Dearomatization-Bis-alkylation Process. MeLi (331 μL, 0.53 mmol, 1.6 M in Et₂O) was added to a 0 °C solution of Me₆Sn₂ (126 μL, 0.53 mmol) in THF (2.0 mL) and the mixture was stirred for 15 min. After cooling at -78 °C, a solution of the corresponding diester (0.21 mmol) in THF (2.0 mL) was added and the mixture stirred for further 1 h. The corresponding electrophile (0.53 mmol) was added and the reaction mixture was stirred at the temperature and for the time indicated below for each electrophile. 1 mL of pH 7.0 phosphate buffer was added and then partitioned between CH₂Cl₂ (10 mL) and phosphate buffer (10 mL). The aqueous phase was extracted with CH₂Cl₂ (5 mL) and the combined organic phase was washed with brine (10 mL), dried with anhydrous Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography (SiO₂, EtOAc/hexane 1/6).

Diisopropyl cyclohexa-2,4-diene-1,2-dicarboxylate (2). Following the general procedure, starting from **1** and using *i*PrOH (250 μL) as the electrophile, and allowing the bath to reach -30 °C for 3 h, 300 μL of diisopropyl phthalate (**1**, 1.27 mmol) afforded 250 mg (78%) of **2**: IR (KBr) 1734 cm⁻¹; ¹H NMR δ 7.13 (t, *J* = 3.3, 1H), 5.82 (s, 2H), 5.07 (hept, *J* = 6.2, 1H), 5.00 (hept, *J* = 6.2, 1H), 4.04 (m, 1H), 2.92 (m, 2H), 1.26, 1.25 and 1.22 (3 d, *J* = 6.2, 12H); ¹³C NMR δ 170.9, 165.1, 137.0, 126.7, 124.5, 122.4, 67.8, 67.5, 42.2, 26.7, 21.5, 21.4, 21.3, 21.2. Anal. Calcd for C₁₄H₂₀O₄: C, 66.65; H, 7.99. Found: C, 66.96; H, 7.85.

Diisopropyl cyclohexa-3,5-diene-1,2-dicarboxylate (3). Following the general procedure, starting from **1** and using acetic acid (250 μL) as the electrophile for 1 min at -78 °C, 300 μL of diisopropyl phthalate (1.27 mmol) afforded 145 mg (45%) of a more polar colorless oil (**3a**) and 64 mg (20%) of a less polar colorless oil (**3b**):

3a: IR (KBr) 1728 cm^{-1} ; ^1H NMR δ 6.05 (m, 2H), 5.96 (m, 2H), 5.01 (hept, $J = 6.3$, 2H), 3.57 (m, 2H), 1.21 (d, $J = 6.3$, 6H), 1.20 (d, $J = 6.3$, 6H); ^{13}C NMR δ 170.6, 124.4, 124.1, 68.0, 40.9, 21.6, 21.5. Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$: C, 66.65; H, 7.99. Found: C, 66.91; H, 8.07.

3b: IR (KBr) 1729 cm^{-1} ; ^1H NMR δ 5.97 (m, 2H), 5.80 (m, 2H), 5.04 (hept, $J = 6.3$, 2H), 3.73 (m, 2H), 1.25 (d, $J = 6.3$, 6H), 1.24 (d, $J = 6.3$, 6H); ^{13}C NMR δ 172.4, 123.9, 123.5, 68.6, 41.9, 21.7, 21.6. Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$: C, 66.65; H, 7.99. Found: C, 66.44; H, 8.26.

Diisopropyl cyclohexa-2,5-diene-1,4-dicarboxylate (5). Following the general procedure, starting from **4** and using trifluoroacetic acid (100 μL) as the electrophile, for 1 min at -78°C , 62 mg of diisopropyl terephthalate (**4**, 0.25 mmol) gave 50 mg (81%) of **5** as a white solid: mp: $49\text{--}50^\circ\text{C}$ (MeOH); IR (KBr) 1727 cm^{-1} ; ^1H NMR δ 5.99 (m, 4H), 5.01 and 5.00 (hept, $J = 6.3$, 2H), 3.66 (m, 2H), 1.24 and 1.23 (2 d, $J = 6.3$, 12H); ^{13}C NMR δ 171.1, 124.1, 124.0, 68.5, 68.4, 42.0, 41.9, 21.7. Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$: C, 66.65; H, 7.99. Found: C, 66.88; H, 7.37.

Diisopropyl 2,3-dihydro-1H-indene-3a,7a-dicarboxylate (14). Following the general procedure, starting from **1** and using 1,3-diiodopropane (62 μL , 0.55 mmol) as the electrophile for 1 h at -78°C , 50 μL of diisopropyl phthalate (0.21 mmol) afforded 61 mg (99%) of **14** as a colorless oil: IR (KBr) 1728 cm^{-1} ; ^1H NMR δ 5.84 (s, 4H), 4.93 (hept, $J = 6.3$, 2H), 2.45 (m, 2H), 1.98 (m, 2H), 1.62 (m, 2H), 1.18 (d, $J = 6.3$, 6H), 1.17 (d, $J = 6.3$, 6H); ^{13}C NMR δ 173.5, 130.2, 121.0, 67.9, 55.9, 39.9, 21.5, 21.4, 21.2. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$: C, 69.84; H, 8.27. Found: C, 69.58; H, 8.44.

Diisopropyl 1,2,3,4-tetrahydronaphthalene-4a,8a-dicarboxylate (15). Following the general procedure, starting from **1** and using 1,4-diiodobutane (70 μL , 0.55 mmol) as the electrophile for 1 h at -78°C , 50 μL of diisopropyl phthalate (0.21 mmol) afforded 55 mg (85%) of **15** as a colorless oil: IR (KBr) 1725 cm^{-1} ; ^1H NMR δ 5.82 (m, 4H), 4.96 (hept, $J = 6.2$, 2H), 2.11 (m, 2H), 1.75 (m, 2H), 1.38 (bs, 4H), 1.19 (d, $J = 6.2$, 6H), 1.17 (d, $J = 6.2$, 6H); ^{13}C NMR δ 173.4, 132.3, 122.1, 67.7, 48.6, 32.6, 21.6, 21.5, 20.6. Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_4$: C, 70.56; H, 8.55. Found: C, 70.58; H, 8.84.

Diisopropyl 5,6,7,8,9a-hexahydro-4aH-benzo[7]annulene-4a,9a-dicarboxylate (16). Following the general procedure, starting from **1** but using only 110 mol % of 1,5-diiodopentane (104 μL , 0.70 mmol) as the electrophile and allowing the bath to reach rt for 3 h, 150 μL of diisopropyl phthalate (0.64 mmol) afforded 146 mg (71%) of **16** as a colorless oil: IR (KBr) 1726 cm^{-1} ; ^1H NMR δ 5.84 (m, 2H), 5.64 (m, 2H), 4.93 (hept, $J = 6.3$, 2H), 2.17 (m, 2H), 2.02 (m, 2H), 1.63 (m, 4H), 1.37 (m, 2H), 1.19 (d, $J = 6.4$, 6H), 1.16 (d, $J = 6.4$, 6H); ^{13}C NMR δ 174.1, 130.8, 121.2, 67.8, 53.4, 34.7, 29.1, 22.2, 21.5, 21.3. Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_4$: C, 71.22; H, 8.81. Found: C, 71.26; H, 9.00.

Diisopropyl 1,4-dihydronaphthalene-4a,8a-dicarboxylate (17). Following the general procedure, starting from **1** and using *cis*-1,4-dichlorobut-2-ene (56 μL , 0.55 mmol) as the electrophile for 10 h while warming to rt, 50 μL of diisopropyl phthalate (0.21 mmol) afforded 39 mg (60%) of **17** as a colorless oil: IR (KBr) 1726 cm^{-1} ; ^1H NMR δ 5.89 (m, 4H), 5.75 (s, 2H), 4.99 (hept, $J = 6.2$, 2H), 2.67 (d, $J = 17.5$, 2H), 2.35

(d, $J = 17.5$, 2H), 1.19 (d, $J = 6.2$, 12H); ^{13}C NMR δ 173.0, 134.3, 125.8, 122.8, 67.9, 46.5, 34.6, 21.5. Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$: C, 71.03; H, 7.95. Found: C, 70.64; H, 8.14.

Diisopropyl 1,2,3,7a-tetrahydroindene-3a,6-dicarboxylate (18). Following the general procedure, starting from **4** and using 1,3-dibromopropane (53 μL , 0.55 mmol) as the electrophile for 10 h while warming to rt, 50 μL of diisopropyl terephthalate (0.21 mmol) afforded 55 mg (89%) of **18** as a colorless oil: IR (KBr) 1719 cm^{-1} ; ^1H NMR δ 6.88 (dt, $J = 1.1$, 5.2, 1H), 6.34 (dd, $J = 1.3$, 9.9, 1H), 5.77 (dd, $J = 0.8$, 9.9, 1H), 5.07 (hept, $J = 6.3$, 1H), 4.96 (hept, $J = 6.3$, 1H), 3.36 (m, 1H), 2.23 (m, 2H), 1.73 (m, 1H), 1.47 (m, 3H), 1.26 (d, $J = 6.3$, 6H), 1.21 (d, $J = 6.3$, 3H), 1.20 (d, $J = 6.3$, 3H); ^{13}C NMR δ 175.2, 165.3, 139.4, 128.6, 124.4, 119.0, 68.2, 67.8, 51.8, 41.4, 41.0, 34.8, 22.2, 21.8, 21.6. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$: C, 69.84; H, 8.27. Found: C, 69.58; H, 8.45.

Diisopropyl 2,3-dihydro-5-methyl-1H-indene-3a,7a-dicarboxylate (19). Following the general procedure, starting from **12** and using 1,3-diiodopropane (50 μL , 0.44 mmol) as the electrophile for 3 h while warming to rt, 46 mg of diisopropyl 4-methylbenzene-1,2-dioate (0.17 mmol) afforded 32 mg (60%) of **19** as a colorless oil: IR (KBr) 1726 cm^{-1} ; ^1H NMR δ 5.95 (d, $J = 9.7$, 1H), 5.71 (dd, $J = 1.2$, 9.7, 1H), 5.42 (m, 1H), 4.94 (oct, $J = 6.4$, 2H), 2.42 (m, 2H), 1.95 (m, 2H), 1.76 (d, $J = 1.5$, 3H), 1.61 (m, 2H), 1.20 and 1.18 (2 d, $J = 6.0$, 6H), 1.19 and 1.17 (2 d, $J = 6.2$, 6H); ^{13}C NMR δ 173.8, 173.7, 130.4, 129.1, 124.7, 124.5, 67.8, 67.7, 56.5, 55.7, 40.4, 39.6, 21.6, 21.54, 21.51, 21.4, 21.2. Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_4$: C, 70.56; H, 8.55. Found: C, 70.58; H, 8.85.

Trimethyl 2,3,3a,7a-tetrahydro-1H-indene-3a,5,7a-tricarboxylate (20). Following the general procedure, starting from **13** and using 1,3-diiodopropane (50 μL , 0.44 mmol) as the electrophile for 3 h while warming to rt, 44 mg of trimethyl benzene-1,2,4-tricarboxylate (0.17 mmol) afforded 51 mg (99%) of **20** as a pale yellow oil. IR (KBr) 1731 cm^{-1} ; ^1H NMR δ 7.13 (s, 1H), 6.39 (dd, $J = 9.8$, 1.2, 1H), 5.74 (d, $J = 9.8$, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 3.59 (s, 3H), 2.63 (m, 1H), 2.40 (m, 1H), 2.00 (m, 2H), 1.77 (m, 1H), 1.55 (m, 1H); ^{13}C NMR δ 173.6, 173.5, 165.7, 138.7, 130.5, 124.7, 119.9, 56.7, 56.4, 52.4, 52.1, 51.9, 40.5, 39.1, 21.6. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_6$: C, 61.22; H, 6.16. Found: C, 60.93; H, 6.23.

Trimethyl 4a,5,6,7,8,8a-hexahydronaphthalene-2,4a,8a-tricarboxylate (21). Following the general procedure, starting from **13** and using 1,4-diiodobutane (83 μL , 0.63 mmol) as the electrophile and stirring at 35 $^\circ\text{C}$ for 12 h, 63 mg of trimethyl benzene-1,2,4-tricarboxylate (0.25 mmol) gave 77 mg (99%) of **21** as a pale yellow oil. IR (KBr) 1728 cm^{-1} ; ^1H NMR δ 7.15 (s, 1H), 6.42 (dd, $J = 9.7$, 1.2, 1H), 5.73 (d, $J = 9.7$, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.61 (s, 3H), 2.25 (m, 1H), 2.08 (m, 1H), 1.88 (m, 1H), 1.60 (m, 1H), 1.34 (m, 4H); ^{13}C NMR δ 173.7, 173.3, 165.7, 142.1, 132.0, 125.5, 121.8, 52.3, 52.0, 51.9, 50.0, 48.4, 32.0, 31.8, 20.8, 20.0. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_6$: C, 62.33; H, 6.54. Found: C, 62.43; H, 6.73.

Diisopropyl 1,2,3,8a-tetrahydroindolizidine-8,8a-dicarboxylate (24). Following the general procedure, starting from **22** and using 1,3-dibromopropane (62 μL , 0.55 mmol) as the electrophile for 16 h while warming to rt, 53 mg of diisopropylpyridine-2,3-dicarboxylate (0.21 mmol) afforded 54 mg (86%) of **24** as a pale yellow oil: IR (KBr) 1728 and 1696 cm^{-1} ; ^1H NMR (CD_2Cl_2) δ 7.05 (d, $J = 6.7$, 1H), 6.62 (d, $J = 6.7$, 1H), 4.87 (m, 3H), 3.65 (dt, $J = 3.5$, 9.8, 1H), 3.48 (m, 1H), 2.67 (ddd, $J = 1.8$, 7.3, 13.5, 1H), 2.44 (m,

1H), 1.89 (m, 2H), 1.17 (d, $J = 6.1$, 6H), 1.10 and 1.09 (2 d, $J = 6.1$, 6H); ^{13}C NMR (CD_2Cl_2) δ 174.2, 166.2, 140.1, 135.7, 110.2, 95.3, 68.9, 68.8, 67.1, 51.1, 38.1, 22.4, 22.2, 22.0. Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_4$: C, 65.51; H, 7.90; N, 4.77. Found: C, 65.67; H, 8.10; N, 4.64.

Diisopropyl 7,8,9,9a-tetrahydro-6H-quinolizine-1,9a-dicarboxylate (25). Following the general procedure, starting from **22** and using 1,4-diiodobutane (70 μL , 0.55 mmol) as the electrophile and stirring for 16 h while warming to rt, 53 mg of diisopropylpyridine-2,3-dicarboxylate (0.21 mmol) afforded 56 mg (86%) of **25** as a pale yellow oil after FCC (SiO_2 , EtOAc/hexane 1/6, 5% Et_3N): IR (KBr) 1734 and 1693 cm^{-1} ; ^1H NMR ($\text{C}_5\text{D}_5\text{N}$) δ 7.28 (dd, $J = 0.8$, 6.6, 1H), 6.45 (d, $J = 6.8$, 1H), 5.24 (hept, $J = 6.3$, 1H), 5.12 (hept, $J = 6.3$, 1H), 4.73 (t, $J = 6.7$, 1H), 3.22 (dt, $J = 2.9$, 12.8, 1H), 3.09 (m, 1H), 2.81 (d, $J = 12.8$, 1H), 2.19 (m, 2H), 1.56 (m, 3H), 1.27 (d, $J = 6.3$, 3H), 1.25 (d, $J = 6.3$, 3H), 1.21 (d, $J = 6.2$, 6H); ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$) δ 171.4, 165.8, 145.5, 136.4, 115.0, 91.7, 69.0, 67.4, 67.3, 52.2, 32.1, 26.5, 22.5, 22.4, 22.3, 22.2, 21.3. Anal. Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_4$: C, 66.43; H, 8.20; N, 4.56. Found: C, 66.27; H, 8.29; N, 4.66.

Diisopropyl 6,7,8,9,10,10a-hexahydropyrido[1,2-a]azepine-1,10a-dicarboxylate (26). Following the general procedure, starting from **22** and using 1,5-diiodopentane (79 μL , 0.55 mmol) as the electrophile and stirring for 16 h while warming to rt, 53 mg of diisopropylpyridine-2,3-dicarboxylate (0.21 mmol) afforded 55 mg (81%) of **26** as a pale yellow oil after FCC (SiO_2 , EtOAc/hexane 1/6, 5% Et_3N): IR (KBr) 1731 and 1703 cm^{-1} ; ^1H NMR ($\text{C}_5\text{D}_5\text{N}$) δ 7.47 (d, $J = 6.6$, 1H), 6.60 (d, $J = 6.8$, 1H), 5.16 (m, 2H), 4.85 (t, $J = 6.7$, 1H), 3.37 (m, 1H), 3.20 (dt, $J = 3.7$, 14.8, 1H), 2.79 (m, 1H), 2.48 (m, 1H), 1.81 (m, 2H), 1.50 (m, 4H), 1.22 and 1.21 (2 d, $J = 6.2$, 12H); ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$) δ 172.7, 166.2, 144.3, 137.3, 114.0, 92.2, 69.7, 69.2, 67.3, 51.5, 38.3, 30.8, 29.1, 24.6, 22.5, 22.1. Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_4$: C, 67.26; H, 8.47; N, 4.36. Found: C, 67.63; H, 8.28; N, 4.25.

Diisopropyl 1,2,3,8a-tetrahydroindolizine-6,8a-dicarboxylate (27).¹ Following the general procedure, starting from **23** and using 1,3-diiodopropane (62 μL , 0.55 mmol) as the electrophile for 16 h while warming to rt, 53 mg of diisopropylpyridine-2,5-dicarboxylate (0.21 mmol) afforded 60 mg (96%) of **27** as a white solid: mp: 59-60 $^\circ\text{C}$ (MeOH).

Diisopropyl 7,8,9,9a-tetrahydro-6H-quinolizine-3,9a-dicarboxylate (28).¹ Following the general procedure, starting from **23** and using 1,4-diiodobutane (70 μL , 0.55 mmol) as the electrophile and stirring for 16 h while warming to rt, 53 mg of diisopropylpyridine-2,5-dicarboxylate (0.21 mmol) afforded 50 mg (77%) of **28** as a pale yellow solid: mp: 73-74 $^\circ\text{C}$ (MeOH).

Diisopropyl 6,7,8,9,10,10a-hexahydropyrido[1,2-a]azepine-3,10a-dicarboxylate (29).¹ Following the general procedure, starting from **23** and using 1,5-diiodopentane (79 μL , 0.55 mmol) the electrophile and heating the resulting mixture overnight at 45 $^\circ\text{C}$, 53 mg of diisopropylpyridine-2,5-dicarboxylate (0.21 mmol) afforded 50 mg (73%) of **29** as a white solid: mp: 89-90 $^\circ\text{C}$ (MeOH).

Preparation of diols.

(7a-Hydroxymethyl-1,2,3,7a-tetrahydro-inden-3a-yl)-methanol (30). A solution of **14** (100 mg, 0.34 mmol) in THF (0.5 mL) was added over a suspension of LiAlH_4 (13 mg, 0.34 mmol) in THF (0.5 mL) at 0 $^\circ\text{C}$. The reaction mixture was stirred for 3h at 0 $^\circ\text{C}$ and EtOAc (0.5 mL) was added carefully, followed by

CHCl₃ (2 mL), satd aq Na₂CO₃ (1 mL), KH₂PO₄ and Na₂SO₄. The resulting suspension was stirred at rt for 1h, then filtered over celite and evaporated. The residue was chromatographed through a short column of SiO₂ (5% *i*PrOH-CH₂Cl₂) to give **30** in 90% yield (55 mg) as a white solid: mp: 119-120 °C (hexane); ¹H NMR δ 5.87 (m, 2H), 5.46 (m, 2H), 3.83 (bs, 2H), 3.66 (dd, *J* = 1.5, 11.6, 2H), 3.42 (d, *J* = 11.6, 2H), 1.66 (m, 6H); ¹³C NMR δ 133.5, 122.7, 66.5, 50.3, 37.8, 21.7. Anal. Calcd for C₁₁H₁₆O₂: C, 73.30; H, 8.95. Found: C, 73.15; H, 9.29.

(8a-Hydroxymethyl-1,3,4,8a-tetrahydro-2H-naphthalen-4a-yl)-methanol (31). Following the above procedure, 160 mg of **15** (1.27 mmol) gave 100 mg (99%) of **31** as a white solid: mp: 127-128 °C (hexane); ¹H NMR δ 5.87 (m, 2H), 5.43 (dd, *J* = 2.7, 7.8, 2H), 4.19 (bs, 2H), 3.53 (m, 4H), 1.60 (m, 2H), 1.39 (bs, 6H); ¹³C NMR δ 133.9, 123.1, 65.3, 42.9, 30.9, 21.4. Anal. Calcd for C₁₂H₁₈O₂: C, 74.19; H, 9.34. Found: C, 74.01; H, 9.37.

ORTEP of (7a-Hydroxymethyl-1,2,3,7a-tetrahydro-inden-3a-yl)-methanol (30).

ORTEP of (8a-Hydroxymethyl-1,3,4,8a-tetrahydro-2H-naphthalen-4a-yl)-methanol (31).

¹ Donohoe, T. J.; McRiner, A. J.; Helliwell, M.; Sheldrake, P. J. *Chem. Soc., Perkin Trans. 1*, **2001**, 1435.