Supporting Information

Synthesis of the Naphthalene Portion of the Rubromycins

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General Experimental Information. Unless otherwise stated, all non-aqueous reactions and distillations were carried out under an atmosphere of dry N_2 in dried glassware. When necessary, solvents and reagents were dried prior to use. Toluene, THF, Et_2O, and CH_2Cl_2 were de-oxygenated by purging with Ar and then dried by passing through activated alumina.

Analytical thin layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light. Chromatography on silica gel was performed using a forced flow of the indicated solvent system on EM Reagents Silica Gel 60 (230-400 mesh). Melting points were obtained on Thomas Scientific Unimelt apparatus and are uncorrected.

^1H NMR spectra were recorded on Bruker AM-500 (500 MHz), AM-250 (250 MHz), AM-360 (360 MHz) or AM-200 (200 MHz) spectrometers. ^{13}C NMR spectra were recorded on a Bruker AM-500 (125 MHz), AM-360 (90 MHz) or AM-250 (62.5 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane (0 ppm) or with the solvent resonance as the internal standard ($CDCl_3$ 7.26 ppm, DMSO-d_6 2.49 ppm, D_2O 4.80 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. Mass spectra were obtained on a low resonance Micromass Platform LC in electrospray mode and high resonance VG autospec with an ionization mode of either CI or ES. IR spectra were taken on a Perkin-Elmer FT-IR spectrometer.

4-Benzyloxy-3-bromo-5-methoxy-benzaldehyde. To a mixture of vanillin (15.2 g, 100 mmol) in HOAc (30 mL) was added Br_2 (5.5 mL) in HOAc (20 mL). The mixture was stirred at rt for an additional 10 min then poured into water (300 mL). The solid was filtered with suction to give an orange solid which was recrystallized from EtOH to afford yellow crystals (21.1 g). A solution of this material (21.1 g, 91.3 mmol) and *n*Bu_4NI (3.37 g, 9.1 mmol) in DMF (100 mL) at 0 °C was treated with NaH (60%, 4.4 g, 109 mmol). The resultant mixture was stirred at rt for 10 min, recooled to 0 °C, treated with BnBr (13.9 mL 116.7 mmol), and stirred at rt overnight. The mixture was poured into ice-water (600 mL) and extracted with CH_2Cl_2 (3 x 200 mL). The combined organic phases were washed with brine and dried over Na_2SO_4. Concentration followed by chromatography (8% EtOAc/hexanes) provided the product (27.6 g) as a pale yellow solid in 86% overall yield: m.p. 47-49 °C; $R_f = 0.3$ (8% EtOAc/hexanes); ^1H NMR (200 MHz, $CDCl_3$) δ 3.94 (s, 3H), 5.16 (s, 2H), 7.34-7.66 (m, 7H), 9.84 (s, 1H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 56.1, 74.8, 110.0, 118.3, 128.2, 128.4, 128.6, 133.0, 136.4, 150.4, 154.2, 189.7; IR (film) 1696, 1415 cm^{-1}; HRMS (ES) calcd for $C_{15}H_{13}O_3BrNa$ (MNa^+) 342.9946, found 342.9960.

4-Benzyloxy-3-bromo-5-methoxy-phenol. To a solution of 4-benzyloxy-3-bromo-5-methoxy-benzaldehyde (16.05 g, 50 mmol) in CH_2Cl_2 (100 mL) was added 60% *m*CPBA (21.5 g, 75 mmol),. After stirring overnight at rt, the mixture was diluted with EtOAc (400 mL), washed with saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in MeOH (100 mL) and was treated with 10% KOH (30 mL). The mixture was stirred 10 min at rt, then neutralized with 1N HCl. After evaporating most of the solvent, the residue was diluted with EtOAc (400 mL), washed with brine, and dried over Na_2SO_4. Concentration and chromatography (12% EtOAc/hexanes) provided 4-benzyloxy-3-bromo-5-methoxy-phenol (11.2 g) as a yellow oil in 73% yield: $R_f = 0.3$ (12% EtOAc/hexanes); ^1H NMR (360 MHz, $CDCl_3$) δ 3.72 (s, 3H), 4.68 (s, 2H), 6.31 (d, J = 2.7 Hz, 1H), 6.42 (brs, 1H), 6.55 (d, J = 2.7 Hz, 1H), 7.32-7.41 (m, 3H) 7.56 (d, J = 6.6 Hz, 2H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 55.8, 65.3, 100.2, 110.8, 117.7, 128.3, 128.7, 136.5, 138.3, 152.9, 154.0; IR (film) 3380, 1468 cm^{-1}; HRMS (ES) calcd for $C_{14}H_{13}O_3BrNa$ (MNa^+) 330.9946, found 330.9933.

2,5-Bis-benzyloxy-1-bromo-3-methoxy-benzene (8). To a solution of 4-benzyloxy-3-bromo-5-methoxy-phenol (1.04 g, 3.37 mmol) and nBu$_4$NI (0.125 g, 0.34 mmol) in DMF (5 mL) at 0 °C was added NaH (60%, 0.156 g, 3.7 mmol). The resultant mixture was stirred at rt for 10 min then recooled to 0 °C, treated with BnBr (0.6 mL, 5.1 mmol), and stirred at rt overnight. The mixture was poured into ice-water (30 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phases were washed with brine and dried over Na_2SO_4. The solvent was evaporated and the residue was chromatographed (8% EtOAc/hexanes) to provide **8** (27.6 g) as a white solid in 83% yield: m.p. 69-71 °C; R_f = 0.3 (9% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.83 (s, 3H), 4.98 (s, 2H), 5.01 (s, 2H), 6.56 (d, J = 2.8 Hz, 1H), 6.77 (d, J = 2.8 Hz, 1H), 7.32-7.58 (m, 10 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 55.8, 70.4, 76.5, 100.6, 108.8, 117.7, 127.4, 127.8, 128.0, 128.1, 128.3, 128.5, 136.3, 137.1, 139.6, 154.1, 155.5; IR (film) 2934, 1486 cm^{-1}; HRMS (ES) calcd for $C_{21}H_{19}O_3BrNa$ (MNa^+) 421.0415, found 421.0422.

Chromium carbene complex (9). To a solution of **8** (0.399 g, 1 mmol) in dry Et_2O (5 mL) was added a solution of nBuLi in hexanes (0.44 mL, 2.4 M, 1.05 mmol) at -78 °C. After stirring an additional 15 min, $Cr(CO)_6$ was added. The reaction mixture was warmed to ambient temperature over 3 h. The resultant deep brown solution was concentrated and then dissolved in CH_2Cl_2 (5 mL). To the mixture was added Me_3OBF_4 (0.25 g, 2 mmol) at 0 °C, which was allowed to warm to rt over 1.5 h. The resultant solution was stirred an additional 1 h at rt and then concentrated. Chromatography (8% EtOAc/hexanes) gave **9** (0.542 g) as a red oil in 97% yield: R_f = 0.27 (8% EtOAc/hexanes); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.86 (s, 3H), 4.17 (brs, 3H), 5.04 (brs, 4H), 6.14 (d, J = 2.7 Hz, 1H), 6.56 (d, J = 2.7 Hz, 1H), 7.28-7.46 (m, 10 H); IR (film) 2062 (sharp), 1988, 1935, 1594, 1454 cm^{-1}. The IR spectrum indicates that **9** is a stable pentacarbonyl complex.

5,8-Bis-benzyloxy-2,3-bis-(*tert*-butyldimethylsiloxymethyl)-4,6-dimethyoxy-naphthalen-1-ol (11). A solution of carbene **9** (0.554 g, 1 mmol), **10** (0.942 g, 3 mmol) and Ac_2O (0.09 mL, 1 mmol) in THF (6 mL) was heated at 50 °C for 17 h. After cooling, the reaction mixture was concentrated and chromatographed (8% EtOAc/hexanes) to afford **11** (0.376 g) as a yellow oil in 53% yield: R_f = 0.25 (8% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.11 (s, 6H), 0.17 (s, 6H), 0.94 (s, 9H), 0.95 (s, 9H), 3.72 (s, 3H), 3.87 (s, 3H), 4.88 (s, 2H), 5.02 (s, 2H), 5.08 (s, 2H), 5.29 (s, 2H), 6.74 (s, 1H), 7.41-7.48 (m, 10H), 9.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -5.3, -5.2, 18.3, 18.4, 25.9, 26.0, 56.0, 56.6, 56.8, 63.7, 72.6, 76.6, 97.6, 112.6, 119.7, 125.2, 127.6, 127.8, 127.9, 128.1, 128.7, 128.8, 128.9, 132.8, 134.9, 136.8, 138.1, 145.8, 148.8, 150.0, 152.3; IR (film) 1609, 1356 cm^{-1}; HRMS (ES) calcd for $C_{40}H_{56}O_7Si_2Na$ (MNa^+) 727.3463, found 727.3494.

5,8-Bis-benzyloxy-2,3-bis-hydroxymethyl-4,6-dimethyoxy-naphthalen-1-ol (12). To a solution of **11** (0.285 g, 0.4 mmol) in THF (4 mL) was added TBAF/THF (1.6 mL, 1.6 mmol). The mixture was stirred at rt for 1 h, diluted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After the solvent was evaporated, the residue was chromatographed (60% EtOAc/hexanes) to afford **12** (0.060 g) as a yellow oil in 31% yield: R_f = 0.3 (60 % EtOAc/hexanes); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.86 (s, 3H), 4.88 (s, 2H), 4.93 (s, 2H), 4.97 (s, 2H), 5.25 (s, 2H), 6.77 (s, 1 H), 7.33-7.60 (m, 10H), 9.83 (s, 1H).

1,4-Bis-benzyloxy-2,11-dimethoxy-8,8-dimethyl-6,10-dihydro-7,9-dioxa-cyclohepta[*b*]naphthalen-5-ol (13). A solution of **12** (0.058 g, 0.20 mmol), PPTS (10 mg), 2,2-dimethoxypropane (0.1 mL, 0.8 mmol) in anhydrous acetone (2 mL) was stirred at rt for 1 h. The mixture was concentrated and chromatographed (15% EtOAc/hexanes) to provide **13** as a pale yellow oil: R_f = 0.3 (14 % EtOAc/hexanes); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.54 (s, 6H), 3.64 (s, 3H), 3.88 (s, 3H), 4.86 (s, 2H), 5.03 (s, 2H), 5.16 (s, 2H), 5.26 (s, 2H), 6.72 (s, 1H), 7.32-7.58 (m, 10H), 9.59 (s, 1H).

1,5,8-Tris-benzyloxy-2,3-bis(*tert*-butyldimethylsiloxymethyl)-4,6-dimethoxy-naphthalene (17). A mixture of **11** (1.11 g, 1.57 mmol), K_2CO_3 (2.16 g, 15.7 mmol), nBu$_4$NI (0.579 g, 1.57 mmol) and BnBr (0.56 mL, 4.71 mmol) in acetone (12 mL) was heated to 50 °C for 48 h. After cooling, the mixture was filtered and concentrated to give a yellow oil which was chromatographed (7% EtOAc/hexanes) to provide **17** (1.02 g) as a pale yellow oil in 81% yield: R_f = 0.25 (7% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.10 (s, 6H), 0.22 (s, 6H), 0.92 (s, 9H), 0.98 (s, 9H), 3.81 (s, 3H), 3.86 (s, 3H), 4.95 (s, 2H), 5.07 (s, 2H), 5.11 (s, 2H), 5.12 (s, 2H), 5.17 (s, 2H), 6.81 (s, 1H), 7.24-7.67 (m, 15H); ^{13}C NMR (90 MHz, $CDCl_3$) δ -5.3, -5.1, 18.7, 18.8, 26.4, 26.6, 56.9, 57.0, 57.1, 64.2, 73.8, 77.2, 78.1, 100.1, 118.7, 126.5, 127.4, 127.5, 127.8, 128.1, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 128.9, 129.4, 129.5, 132.4, 134.9, 137.4, 138.6, 138.7; IR (film) 2927, 1456 cm^{-1}; HRMS (ES) calcd for $C_{47}H_{62}O_7Si_2Na$ (MNa^+) 817.3931, found 817.3957.

1,5,8-Tris-benzyloxy-3-(*tert*-butyldimethylsiloxymethyl)-4,6-dimethoxy-naphthalene-2-carbaldehyde (18). To a mixture of **17** (0.07 g, 0.088 mmol) in CH_2Cl_2 (4 mL) and H_2O (0.4 mL) was added DDQ (0.02 g, 0.088 mmol). The resultant mixture was stirred at rt for 1 h, diluted with CH_2Cl_2 (20 mL), washed with aqueous $NaHCO_3$, brine, and dried over Na_2SO_4. Concentration and chromatography afforded **18** (0.048 g) as a yellow oil in 80% yield: R_f = 0.27 (9% EtOAc/hexanes); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.15 (s, 6H), 0.91 (s, 9H), 3.77 (s, 3H), 3.88 (s, 3H), 4.90 (s, 2H), 5.01 (s, 2H), 5.18 (s, 2H), 5.21 (s, 2H), 6.82 (s, 1H), 7.26-7.57 (m, 15H), 10.51 (s, 1H); ^{13}C NMR (90 MHz, $CDCl_3$) δ -5.4, 18.4, 25.9, 55.4, 56.3, 63.7, 72.8, 76.6, 79.2, 100.4, 116.7, 124.7, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.5, 128.9, 130.1, 136.2, 136.4, 137.7, 149.9, 152.8, 153.6, 157.4, 192.5; IR (film) 2929, 1682, 1597 cm^{-1}; HRMS (ES) calcd for $C_{41}H_{46}O_7SiNa$ (MNa^+) 701.2910, found 701.2932.

1,5,8-Tris-benzyloxy-3-(*tert*-butyldimethylsiloxymethyl)-4,6-dimethoxy-naphthalen-2-yl]-methanol. To a solution of **18** (0.476 g, 0.7 mmol) in THF (6 mL) and MeOH (1.5 mL) was added $NaBH_4$ (0.04 g, 1.05 mmol) at 0 °C. The mixture was warmed to rt and stirred for additional 1.5 h. 1N HCl was added and the solvent was removed. The residue was diluted with CH_2Cl_2 (50 mL), washed with brine, and dried over Na_2SO_4. Chromatography provided the product (0.461 g) as a yellow oil in 96% yield: R_f = 0.26 (9% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.22 (s, 6H), 0.95 (s, 9H), 3.72 (s, 3H), 3.74 (t, J = 6.7 Hz, 1H), 3.84 (s, 3H), 4.88 (s, 2H), 4.93 (d, J = 6.7 Hz, 2H), 5.04 (s, 2H), 5.10 (s, 2H), 5.14 (s, 2H), 6.80 (s, 1H), 7.27-7.60 (m, 15H); ^{13}C NMR (90 MHz, $CDCl_3$) δ -5.5, 18.1, 25.8, 56.4, 57.2, 57.7, 63.6, 72.9, 76.6, 77.9, 101.2, 118.1, 125.5, 127.3, 127.6, 127.7, 127.8, 128.0, 128.3, 128.8, 129.6, 130.4, 136.1, 136.6, 137.7, 137.9, 149.4, 150.2, 150.3, 152.5; IR (film) 3472, 1341 cm^{-1}; HRMS (ES) calcd for $C_{41}H_{48}O_7SiNa$ (MNa^+) 703.3067, found 703.3092.

4,5,8-Tris-benzyloxy-2-*tert*-butyldimethylsiloxymethyl-1,7-dimethoxy-3-methoxymethoxy-methyl-naphthalene (19). To a solution of 1,5,8-tris-benzyloxy-3-(*tert*-butyldimethylsiloxymethyl)-4,6-dimethoxy-naphthalen-2-yl]-methanol (0.720 g, 1.07 mmol) and iPr_2NEt (0.93 mL, 5.4 mmol) in CH_2Cl_2 (5 mL) was added MOMCl (0.40 mL, 5.4 mmol) at 0 °C. After stirring at 0 °C for 30 min, the mixture was warmed to rt and stirred overnight. Chromatography provided **19** (0.676g) as a pale yellow oil in 87% yield: R_f = 0.26 (9% EtOAc/hexanes); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.20 (s, 6H), 0.96 (s, 9H), 3.38 (s, 3H), 3.79 (s, 3H), 3.85 (s, 3H), 4.73 (s, 2H), 4.91 (s, 2H), 5.01 (s, 2H), 5.04 (s, 2H), 5.09 (s, 2H), 5.12 (s, 2H), 6.79 (s, 1H), 7.24-7.63 (m, 15H); ^{13}C NMR (90 MHz, $CDCl_3$) δ -5.3, 18.3, 25.9, 55.4, 56.4, 56.6, 61.6, 63.7, 73.3, 76.7, 77.6, 96.6, 101.5, 118.1, 125.7, 126.3, 127.1, 127.2, 127.7, 128.1, 128.2, 128.3, 128.9, 131.5, 136.3, 136.7, 138.0, 138.1, 150.0, 150.3, 151.1, 152.4; IR (film) 2930, 1342 cm^{-1}; HRMS (ES) calcd for $C_{43}H_{52}O_8SiNa$ (MNa^+) 747.3328 , found 747.3330.

(4,5,8-Tris-benzyloxy-1,7-dimethoxy-3-methoxymethoxymethyl-naphthalen-2-yl)-methanol. To a solution of **19** (0.676 g, 0.93 mmol) in THF (5 mL) was added TBAF/THF (1 M, 1.86 mL, 1.86 mmol). The resultant solution was stirred at rt for 3 h. The solvent was evaporated and the residue chromatographed (30% EtOAc/hexanes) to afford the product (0.563 g) as a pale yellow oil in 99% yield: R_f = 0.28 (30% EtOAc/hexanes); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.40 (s, 3H), 3.44 (t, J = 6.6 Hz, 1H), 3.85 (s, 6H), 4.71 (s, 2H), 4.93 - 4.97 (m, 8H), 5.12 (s, 2H), 6.81 (s, 1H), 7.23-7.62 (m, 15H); ^{13}C NMR (90 MHz, $CDCl_3$) δ55.6, 56.3, 57.1, 62.1, 63.6, 73.0, 76.5, 77.7, 96.4, 101.2, 117.6, 124.5, 126.3, 127.1, 127.2, 127.6, 127.7, 128.1, 128.2, 128.7, 132.2, 136.1, 136.5, 137.5, 137.8, 150.3, 150.5, 150.6, 152.3; IR (film) 3493, 1344 cm^{-1}; HRMS (ES) calcd for $C_{37}H_{38}O_8Na$ (MNa^+) 633.2464 , found 633.2477.

4,5,8-Tris-benzyloxy-1,7-dimethoxy-3-methoxymethoxymethyl-naphthalene-2-carbaldehyde (20). To a solution of 4,5,8-tris-benzyloxy-1,7-dimethoxy-3-methoxymethoxymethyl-naphthalen-2-yl)-methanol (0.337 g, 0.55 mmol) in CH_2Cl_2 (10 mL)was added Dess-Martin periodinane (0.352 g, 0.83 mmol). The resultant mixture was stirred at rt for 30 min, filtered and concentrated to give a yellow oil which was chromatographed (20% EtOAc/hexanes) to afford **20** (0.302 g) as a yellow oil in 90% yield: R_f = 0.26 (20% EtOAc/hexanes); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.36 (s, 3H), 3.86 (s, 6H), 4.73 (s, 2H), 4.95 (s, 2H), 5.02 (s, 2H), 5.10 (s, 2H), 5.13 (s, 2H), 6.92 (s, 1H), 7.26-7.58 (m, 15H), 10.77 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 55.4, 56.4, 60.4, 65.1, 73.4, 76.8, 77.9, 97.0, 103.8, 119.9, 123.4, 125.8, 127.0, 127.1, 127.4, 127.7, 127.9, 128.1, 128.2, 128.4, 128.8, 136.3, 137.0, 137.5, 151.1, 151.2, 152.5, 158.1, 193.0; IR (film) 1688, 1342 cm^{-1}; HRMS (ES) calcd for $C_{37}H_{36}O_8Na$ (MNa^+) 631.2308 found 631.2313.

4,5,8-Tris-benzyloxy-1,7-dimethoxy-3-methoxymethoxymethyl-naphthalen-2-ol (21). To a mixture of **20** (0.122 g, 0.20 mmol) and $NaHCO_3$ (0.038 g, 0.45 mmol) in CH_2Cl_2 (5 mL) was added *m*CPBA (50-80%, 0.086 g). After stirring overnight at rt, the mixture was diluted with CH_2Cl_2 (20 mL), washed with brine, and dried over Na_2SO_4. After evaporation, the residue was dissolved in a saturated solution of NH_3 in EtOH (4 mL). After stirring for 5 min, the mixture was concentrated to provide crude **21**. While **21** could be isolated as a yellow oil and characterized, this was accompanied by rapid decomposition. As such, crude **21** was normally taken on to the next step without purification. R_f = 0.25 (20% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.40 (s, 3H), 3.80 (s, 3H), 3.85 (s, 3H), 4.74 (s, 2H), 4.85 (s, 2H), 4.89(s, 2H), 5.01 (s, 2H), 5.13 (s, 2H), 6.63 (s, 1H), 6.74 (s, 1H), 7.24-7.60 (m, 15H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 55.4, 56.5, 62.6, 65.3, 72.9, 76.6, 78.1, 96.3, 98.1, 116.6, 125.8, 127.4, 127.7, 127.8, 128.1, 128.2, 128.4, 128.5, 128.9, 132.5, 134.3, 135.6, 136.8, 137.8, 138.0, 147.1, 150.5, 151.8, 153.0; IR (film) 3400 1347 cm^{-1}; HRMS (ES) calcd for $C_{36}H_{36}O_8Na$ (MNa^+) 619.2298 found 619.2307.

2,4,5,8-Tetrakis-benzyloxy-1,7-dimethoxy-3-methoxymethoxymethyl-naphthalene (22). Crude **21** was dissolved in acetone (4 mL), then treated with K_2CO_3 (0.276 g, 2 mmol), *n*Bu_4NI (0.073 g, 0.2 mmol), and BnBr (0.05 mL, 0.3 mmol). After stirring overnight at 55 °C , the mixture was filtered, concentrated, and chromatographed (15% EtOAc/hexanes) to provide **22** (0.076 g) as a yellow oil in 55% total yield from **20**: R_f = 0.27 (15% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.23 (s, 3H), 3.84 (s, 3H), 3.85 (s, 3H), 4.63 (s, 2H), 4.74 (s, 2H), 4.96 (s, 2H), 5.02 (s, 2H), 5.12 (s, 2H), 5.29 (s, 2H), 6.70 (s, 1H), 7.22-7.63 (m, 20H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 55.3, 56.6, 60.4, 62.0, 73.0, 75.8, 76.4, 78.0, 96.7, 99.7, 115.4, 117.4, 122.3, 127.2, 127.71, 127.74, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 128.9, 135.8, 136.8, 138.0, 138.3, 143.9, 149.8, 150.3, 151.5, 152.6; IR (film) 1602, 1345 cm^{-1}; HRMS (ES) calcd for $C_{43}H_{42}O_8Na$ (MNa^+) 709.2777 found 709.2764.

4,5,8-Tris-benzyloxy-2-*tert*-butyldimethylsiloxymethyl-1,7-dimethoxy-naphthalen-3-ol (23). To a solution of **18** (0.03g, 0.044 mmol) and bis(2-nitrobenzene)diselenide (0.002 g, 0.005 mmol) in PhH (2 mL) was added H_2O_2 (30%, 0.1 mL). After stirring overnight at rt, the mixture was diluted with CH_2Cl_2 (20 mL), washed with Na_2SO_3 followed by brine, and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in methanol (1 mL) and treated with 10% KOH (0.01 mL). After stirring for 5 min, the mixture was diluted with CH_2Cl_2 (20 mL), washed with brine, and dried over Na_2SO_4. While **23** could be isolated as a yellow oil and partially characterized, this material was particularly unstable. As such, crude **23** was normally taken on to the next step without purification. R_f = 0.25 (15% EtOAc/hexanes); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.16 (s, 6H), 0.91 (s, 9H), 3.74 (s, 3H), 3.84 (s, 3H), 4.88 (s, 2H), 4.93 (s, 2H), 5.12 (s, 2H), 5.13 (s, 2H), 6.78 (s, 1H), 7.26-7.59 (m, 16H).

3,4,5,8-Tetrakis-benzyloxy-2-*tert*-butyldimethylsiloxymethyl-1,7-dimethoxy-naphthalene (24). Crude **23** was dissolved in acetone (2 mL), treated with K_2CO_3 (0.11 g, 0.8 mmol), *n*Bu_4NI (0.014 g, 0.04 mmol) and BnBr (0.01 mL, 0.08 mmol). After stirring overnight at 55 ^{o}C , the mixture was filtered, concentrated and chromatographed (12% EtOAc/hexanes) to provide **24** (0.016 g) as a yellow oil in 48% overall yield from **18**. R_f = 0.27 (15% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.12 (s, 6H), 0.86 (s, 9H), 3.79 (s, 3H), 3.83 (s, 3H), 4.89 (s, 2H), 4.95 (s, 2H), 5.03 (s, 2H), 5.17 (s, 2H), 5.20 (s, 2H), 6.76 (s, 1H), 7.19-7.41 (m, 18H), 7.59 (d, J= 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -.5.23, 18.35, 25.99, 55.43, 56.93, 64.01, 72.89, 76.03, 76.66, 76.82, 101.40, 119.10, 123.29, 127.30, 127.61, 127.75, 127.86, 128.04, 128.16, 128.19, 128.22, 128.59, 128.61, 129.07, 136.43, 137.05, 138.08, 138.13, 138.18, 144.60, 147.63, 149.20, 150.89, 152.16; IR (film) 1592, 1344 cm^{-1}; HRMS (ES) calcd for $C_{47}H_{52}O_{7Si}Na$ (MNa^+) 779.3380 found 779.3407.