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Supporting Information

General Information. Unless otherwise noted all commercial materials were used without purification. Small scale reactions (< 4 mL) were carried out in Fisher Scientific disposable scintillation vials. Nitromethane (MeNO₂) and hexafluorophosphate salts were obtained from Aldrich Chemical Company. Catalyst **1**, (dppm)Re(O)Cl₃, can be prepared by two different methods: i) from ammonium perrhenate via (PPh₃)₂Re(O)Cl₃,¹ or, ii) from rhenium pentachloride via (MeCN)₂ReCl₄.² Propargyl alcohols were prepared from the corresponding benzaldehydes by addition of the requisite organometallic reagent. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F₂₅₄ TLC plates. Chromatography was carried out on Merck 60 silica gel (32-63 μm). ¹H and ¹³C NMR spectra were recorded with Bruker AMX-300, AV-300, AMX-400, AVB-400, and AVQ-400 spectrometers and referenced to CDCl₃ unless otherwise noted. Mass spectral and analytical data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

General procedure for Rhenium catalyzed propargylation. To a small screw-cap scintillation vial equipped with a magnetic stir bar and charged with a solution of propargyl alcohol (100 mg, 1 eq) in MeNO₂ (0.5M) was added aromatic nucleophile (1.05 eq – 10 eq) followed by catalyst **1** (5 mol%) and KPF₆ (5 mol%). The reaction mixture was placed in a pre-heated oil bath (65 °C) and monitored periodically by TLC. Upon completion the reaction mixture was cooled to ambient temperature, loaded directly on to a silica gel column and chromatographed with the appropriate mixture of hexanes and EtOAc to give the propargylation products described below.

Bromo piperonal propargyl alcohol - 1,2,3-Trimethoxybenzene product (3). Prepared with 1.5 eq. nucleophile and isolated as a clear oil. ¹H NMR (300 MHz, CDCl₃) δ 7.06 (d, *J* = 8.7, 1H), 6.99 (s, 1H), 6.88 (s, 1H), 6.61 (d, *J* = 8.7, 1H), 5.95 (d, *J* = 1.5, 1H), 5.94 (d, *J* = 1.5, 1H), 5.60 (s, 1H), 3.85 (s, 3H),

¹ (a) Chatt, J.; Rowe, G.A. *J. Chem Soc.* **1962**, 4019. (b) Rossi, R.; Marchi, A.; Marvelli, L.; Magon, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta.* **1993**, 204, 63.

² (a) Rouschias, G.; Wilkinson, G. *J. Chem Soc. (A)* **1968**, 489. (b) Myers, R.E.; Walton, R.A. *Inorg. Chem.* **1976**, 15, 3065.

3.84 (s, 3H), 3.75 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.1, 151.3, 147.3, 147.1, 142.2, 134.0, 126.5, 122.7, 114.3, 112.6, 109.9, 106.7, 106.1, 101.7, 88.3, 60.7, 60.6, 55.9, 37.8, 00.1; HRMS (EI) calc. for $[\text{C}_{22}\text{H}_{25}\text{BrO}_5\text{Si}]^+$ 476.0655, found 476.0652; Anal. calcd.: C, 55.35; H, 5.28, found: C, 53.30; H, 5.20.

1,2,4-Trimethoxybenzene addition product (6a). Prepared with 1.05 eq. nucleophile and isolated as a pale yellow solid (mp 92-94 °C). ^1H NMR (300 MHz, CDCl_3) δ 7.48 (m, 4H), 7.34-7.17 (m, 7H), 6.54 (s, 1H), 5.68 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 148.7, 143.3, 141.9, 131.7, 128.4, 128.3, 127.9, 127.7, 126.6, 123.7, 121.7, 112.9, 97.4, 91.0, 83.7, 56.6, 56.2, 36.2, 1 –OMe C unresolved at 56.6; HRMS (EI) calc. for $[\text{C}_{24}\text{H}_{22}\text{O}_3]^+$ 358.1569, found 358.1574; Anal. calcd.: C, 80.42; H, 6.19, found: C, 80.19; H, 6.27.

1,3-Dimethoxybenzene addition product (6b). Prepared with 5 eq. nucleophile and isolated as a white solid (mp 101 °C). ^1H NMR (300 MHz, CDCl_3) δ 7.46 (m, 5H), 7.31-7.16 (m, 6H), 6.47 (m, 2H), 5.59 (s, 1H), 3.81 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 157.1, 142.1, 131.7, 129.5, 128.3, 128.2, 127.7, 126.4, 126.4, 123.8, 122.9, 104.5, 98.6, 91.1, 83.4, 55.5, 55.3, 36.1, 1 Ar C unresolved; HRMS (EI) calc. for $[\text{C}_{23}\text{H}_{20}\text{O}_2]^+$ 328.1463, found 328.1463; Anal. calcd.: C, 84.12; H, 6.14, found: C, 84.10; H, 6.22.

Anisole addition product (6c). Prepared with 1.05 eq. nucleophile and isolated as a clear oil. ^1H NMR (300 MHz, CDCl_3) δ 7.51-7.24 (m, 12H), 6.89 (d, $J = 8.4$, 2H), 5.21 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 142.1, 133.9, 131.7, 128.9, 128.6, 128.2, 128.0, 127.8, 126.8, 123.5, 114.0, 90.5, 84.7, 55.3, 42.9; HRMS (EI) calc. for $[\text{C}_{22}\text{H}_{18}\text{O}]^+$ 298.1358, found 298.1356.

1-Bromo-2,4-dimethoxybenzene addition product (6d). Prepared with 1.05 eq. nucleophile and isolated as a white solid (mp 132 °C). ^1H NMR (300 MHz, CDCl_3) δ 7.70 (s, 1H), 7.46 (m, 4H), 7.32-7.18 (m, 6H), 6.46 (s, 1H), 5.56 (s, 1H), 3.89 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.3, 155.6, 141.4, 132.8, 131.7, 128.4, 128.2, 128.0, 127.7, 126.7, 124.1, 123.5, 102.2, 96.6, 90.3, 83.9, 56.4, 55.9, 35.9; HRMS (EI) calc. for $[\text{C}_{23}\text{H}_{19}\text{BrO}_2]^+$ 406.0568, found 406.0574; Anal. calcd.: C, 67.82; H, 4.70, found: C, 67.37; H, 4.73.

Phenol addition product (7a). Prepared with 1.5 eq. nucleophile and isolated as a waxy yellow solid (mp 82-87 °C). ^1H NMR (300 MHz, CDCl_3) δ 7.49-7.21 (m, 12H), 6.79 (d, J = 8.4, 1H), 5.16 (s, 1H), 4.88 (bs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 142.0, 134.1, 131.7, 129.1, 128.6, 128.2, 128.0, 127.8, 126.9, 123.5, 115.4, 90.5, 84.8, 42.9; HRMS (EI) calc. for $[\text{C}_{21}\text{H}_{16}\text{O}]^+$ 284.1201, found 284.1201.

2-Napthol addition product (7b). Prepared with 1.5 eq. nucleophile and isolated as an off white foam. ^1H NMR (300 MHz, CDCl_3) δ 8.03 (d, J = 8.4, 1H), 7.78 (m, 2H), 7.49-7.08 (m, 13H), 6.37 (s, 1H), 6.27 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.5, 138.9, 131.6, 131.1, 129.1, 128.9, 128.1, 128.0, 127.7, 127.6, 126.5, 126.3, 126.1, 122.6, 122.4, 121.9, 118.3, 117.0, 87.8, 85.2, 32.9; HRMS (EI) calc. for $[\text{C}_{25}\text{H}_{18}\text{O}]^+$ 334.1358, found 334.1360.

Sesamol addition product (7c). Prepared with 1.05 eq. nucleophile and isolated as a yellow solid (mp 142 °C). ^1H NMR (300 MHz, CDCl_3) δ 7.47 (m, 4H), 7.36-7.23 (m, 6H), 6.85 (s, 1H), 6.42 (s, 1H), 5.90 (s, 1H), 5.89 (s, 1H), 5.38 (s, 1H), 5.17 (bs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 147.2, 141.7, 140.4, 131.7, 128.7, 128.3, 127.6, 127.1, 122.8, 119.6, 108.7, 101.2, 99.1, 89.0, 85.2, 38.0; HRMS (EI) calc. for $[\text{C}_{22}\text{H}_{16}\text{O}_3]^+$ 328.1100, found 328.1100.

Furan addition product (9a). Prepared with 10 eq. nucleophile and isolated as a yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.48 (m, 4H), 7.38-7.25 (m, 7H), 6.29 (m, 2H), 5.26 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.8, 142.3, 138.9, 131.8, 128.7, 128.3, 127.9, 127.5, 123.2, 110.4, 106.7, 87.5, 84.0, 37.9; HRMS (EI) calc. for $[\text{C}_{19}\text{H}_{14}\text{O}]^+$ 258.1045, found 258.1047.

Thiophene addition product (9b). Prepared with 10 eq. nucleophile and isolated as a yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.49 (m, 4H), 7.38-7.19 (m, 7H), 7.01-6.92 (m, 2H), 5.43 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.8, 141.2, 131.7, 128.8, 128.3, 128.2, 127.7, 127.4, 126.7, 125.1, 124.8, 123.2, 89.5, 84.4, 39.2; HRMS (EI) calc. for $[\text{C}_{19}\text{H}_{14}\text{S}]^+$ 274.0816, found 274.0818.

N-tosyl-indole addition product (9c). Prepared with 1.05 eq. nucleophile and isolated as an off white foam. ^1H NMR (300 MHz, CDCl_3) δ 7.95 (d, $J = 8.4$, 1H), 7.75 (d, $J = 8.4$, 1H), 7.53 (s, 1H), 7.45 (m, 5H), 7.35-7.13 (m, 10H), 5.33 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 139.5, 135.7, 135.1,

131.7, 129.9, 129.3, 128.7, 128.3, 128.2, 127.9, 127.3, 126.8, 124.8, 124.3, 123.3, 123.2, 123.1, 120.4, 113.8, 88.8, 84.3, 35.4, 21.6; HRMS (EI) calc. for $[C_{30}H_{23}NO_2S]^+$ 461.1450, found 461.1454.

Methyl propargyl alcohol - 1,2,3-Trimethoxybenzene product (10a). Prepared with 1.05 eq. nucleophile and isolated as a clear oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.18 (m, 6H), 6.68 (d, $J=8.7$, 1H), 5.34 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 1.92 (d, $J=2.4$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 150.9, 142.6, 142.0, 128.6, 128.3, 127.8, 126.4, 123.2, 107.2, 80.2, 79.3, 60.8, 60.7, 55.9, 36.5, 3.8; HRMS (EI) calc. for $[C_{19}H_{20}O_3]^+$ 296.1412, found 296.1410.

Diphenyl propargyl alcohol - 1,2,3-Trimethoxybenzene product (10b). Prepared with 1.5 eq. nucleophile and isolated as a clear oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.45 (m, 4H), 7.32-7.18 (m, 7H), 6.66 (d, $J = 8.7$, 1H), 5.55 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 151.0, 142.1, 142.0, 131.6, 128.4, 128.2, 128.0, 127.9, 126.6, 123.6, 123.2, 107.2, 90.9, 83.8, 60.9, 60.7, 55.9, 37.0, 1 Ar C unresolved; HRMS (EI) calc. for $[C_{24}H_{22}O_3]^+$ 358.1569, found 358.1575; Anal. calcd.: C, 80.42; H, 6.19, found: C, 80.13; H, 6.36.

Propenyl propargyl alcohol - 1,2,3-Trimethoxybenzene product (10c). Prepared with 1.05 eq. nucleophile and isolated as a clear oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.14 (m, 6H), 6.66 (d, $J = 8.1$, 1H), 5.41 (s, 1H), 5.29 (s, 1H), 5.19 (t, $J=1.7$, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.76 (s, 3H), 1.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 151.0, 142.1, 128.4, 128.0, 127.8, 127.1, 126.6, 123.2, 121.1, 107.3, 89.9, 85.1, 60.8, 60.7, 55.9, 36.9, 29.7, 23.8; HRMS (EI) calc. for $[C_{21}H_{22}O_3]^+$ 322.1569, found 322.1563.

2,5-Dimethoxy-4-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynyl]-phenol (12). Prepared with 1.2 eq. nucleophile and isolated as a white solid that slowly yellows over time (mp 121-123 °C). ¹H NMR (300 MHz, CDCl₃) δ 7.46-7.15 (m, 5H), 7.10 (s, 1H), 6.53 (s, 1H), 5.60 (s, 1H), 5.44 (s, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 0.20 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 145.2, 141.7, 140.4, 128.2, 127.5, 126.4, 120.8, 111.8, 107.9, 99.4, 87.7, 56.4, 56.2, 36.5, 0.1.

2,5-Dimethoxy-4-(1-phenyl-prop-2-ynyl)-phenol. To a solution of coupling product **12** (1.18 g, 3.45 mmol) in THF (35 mL) at 0 °C was added TBAF in THF (3.80 mL, 1M, 3.80 mmol) dropwise. After 30 min. the reaction mixture was quenched with 10% HCl (10 mL), diluted with Et₂O (150 mL), and washed with H₂O and then brine. The organic layer was separated, dried (MgSO₄), concentrated *in vacuo*, and chromatographed (1:9 EtOAc / Hexanes) to give terminal alkyne (shown above) (853 mg, 92%) as a yellow orange wax. ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.16 (m, 5H), 7.01 (s, 1H), 6.54 (s, 1H), 5.58 (s, 1H), 5.44 (d, *J* = 2.7, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 2.39 (d, *J* = 2.7, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 145.4, 141.4, 140.5, 128.3, 127.5, 126.6, 120.4, 111.9, 99.5, 85.5, 71.5, 56.6, 56.2, 35.3.

(±)-Mimosifoliol. To a solution of terminal alkyne (100 mg, 0.37 mmol) and EtOAc (7 mL) in a large scintillation vial was added quinoline (220 μ L, 1.86 mmol) and 5% palladium on barium sulfate. The vial was sealed with a rubber septum and with rapid stirring the mixture was placed under an atmosphere of H₂ gas. The reaction mixture was carefully monitored by TLC, and after exactly 20 min. opened to the atmosphere and degassed with N₂ gas. The mixture was then filtered over celite, concentrated *in vacuo*, and chromatographed directly (1:30 $\rightarrow$ 1:10 EtOAc / Hexanes) to give (±)-mimosifoliol (shown above) (91 mg, 91%) as an off white solid (mp 70-72 °C). ¹H NMR (300 MHz, CDCl₃) δ 7.29-7.17 (m, 5H), 6.64 (s, 1H), 6.57 (s, 1H), 6.27 (ddd, *J* = 17.4, 10.2, 6.6, 1H), 5.57 (s, 1H), 5.19 (d, *J* = 10.2, 1H), 5.10 (d, *J* = 6.6,

1H), 4.92 (d, $J = 17.4$, 1H), 3.78 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 144.7, 143.3, 140.6, 140.2, 128.5, 128.1, 126.0, 122.6, 116.0, 112.6, 99.8, 56.7, 56.3, 47.1.

[3-(2-Methoxy-5-methyl-phenyl)-3-phenyl-prop-1-ynyl]-trimethyl-silane (13). Prepared with 2 eq. nucleophile and isolated as an off white crystalline solid (mp 70-72 °C). ^1H NMR (300 MHz, CDCl_3) δ 7.43-7.15 (m, 6H), 7.00 (m, 1H), 7.00 (m, 1H), 6.74 (m, 1H), 5.49 (s, 1H), 3.79 (s, 3H), 2.29 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.1, 141.7, 130.1, 129.9, 129.6, 128.5, 128.3, 127.8, 126.5, 110.8, 107.8, 87.6, 55.7, 36.9, 20.7, 0.2; HRMS (EI) calc. for $[\text{C}_{20}\text{H}_{24}\text{O}_1\text{Si}]^+$ 308.1596, found 308.1593; Anal. calcd.: C, 77.87; H, 7.84, found: C, 77.61; H, 8.06.

***N,N*-Diisopropyl-3-(2-methoxy-5-methyl-phenyl)-3-phenyl-propionamide.** To a stirred solution of $\text{BH}_3 \cdot \text{THF}$ (3.90 mL, 1M, 3.9 mmol) at 0 °C was added cyclohexene (0.88 mL, 8.66 mmol) dropwise over 5 min. Stirring was continued and the reaction mixture slowly became thick and white. After 2 h at 0 °C, a solution of coupling product **13** (485 mg, 1.57 mmol) in THF (8 mL) was added dropwise over 5 min. Within 45 min the reaction mixture clarified. Stirring was continued for 1.5 h upon which MeOH (4 mL) was carefully added, followed by NaOH (4 mL, 3M), and H_2O_2 (4 mL). This mixture was rapidly stirred for 15 min, and then another volume of NaOH (4 mL, 3M) was added. The reaction mixture was extracted with Et_2O (2 x 30 mL). The aqueous layer was separated, acidified with concentrated HCl until a white precipitate formed, and extracted with Et_2O (3 x 30 mL). The organic layer was dried (MgSO_4) and concentrated *in vacuo*, to give the crude carboxylic acid **14** (383 mg, ca. 90%). This material was dissolved in benzene (7 mL), a catalytic amount of pyridine (1 drop) was added, followed by neat SOCl_2 (0.57 mL, 7.76 mmol) and the mixture was heated to 50 °C. After 1 h the reaction mixture was concentrated *in vacuo*, Et_2O (7 mL) was added and the mixture concentrated. The residue obtained was again dissolved in Et_2O (7 mL) and diisopropylamine (2 mL, 14.1 mmol) was added. After stirring the reaction mixture for 2 h the solvent was removed *in vacuo*. The residue obtained was chromatographed directly (1:7 EtOAc / Hexanes) to give amide (382 mg, 69%) as a pale yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.26-7.11 (m, 5H), 6.96 (m, 2H), 6.72 (app d, $J = 8.6$, 1H), 4.96 (t, $J = 7.4$, 1H), 4.05 (m, $J = 6.6$, 1H), 3.70 (s, 3H), 3.35 (bs, 1H), 2.99 (m, 2H), 2.25 (s, 3H), 1.28 (d, $J = 4.6$, 3H), 1.26 (d, $J = 4.6$, 3H), 1.12 (d, $J = 6.6$, 3H), 1.06 (d, $J = 6.6$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 155.0, 144.2, 132.6, 129.4, 129.0, 128.1, 128.0, 127.6, 125.8,

110.9, 55.6, 48.7, 45.7, 41.2, 39.8, 21.0, 20.9, 20.7, 20.6; HRMS (EI) calc. for $[C_{23}H_{31}NO_2]^+$ 353.2355, found 353.2357; Anal. calcd.: C, 78.15; H, 8.84; N, 3.96; found: C, 78.04; H, 9.15; N, 3.89.

4-Hydroxy-4-(3,4,5-trimethoxy-phenyl)-but-2-ynoic acid ethyl ester (15). To a stirred solution of ethyl propiolate (14.9 mL, 147 mmol) in THF (490 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*BuLi (55.4 mL, 2.5 M, 139 mmol) dropwise. The reaction mixture was stirred for 30 min at which point a solution of 3,4,5-trimethoxybenzaldehyde (16 g, 81.5 mmol) in THF (160 mL) was added via cannula over 1 h. The resulting orange solution was stirred an additional 2 h, before being quenched with AcOH (15 mL). The reaction mixture was diluted with Et₂O (1.5 L) and washed with a saturated solution of NaHCO₃ and then brine. The organic layer was separated and dried with MgSO₄ before being concentrated *in vacuo* and chromatographed (1:4 $\rightarrow$ 1:1 EtOAc / Hexanes) to give propargyl alcohol **15** (18.5 g, 77%) as an orange syrup. ¹H NMR (300 MHz, CDCl₃) δ 6.74 (s, 2H), 5.52 (d, *J* = 5.9, 2H), 4.29 (q, *J* = 7.1, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 2.51 (d, *J* = 5.9, 1H), 1.26 (t, *J* = 7.1, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.5, 153.3, 138.0, 134.4, 103.6, 86.3, 77.6, 64.2, 62.4, 60.9, 56.1, 14.0; HRMS (EI) calc. for $[C_{15}H_{18}O_6]^+$ 294.1103, found 294.1109; Anal. calcd.: C, 61.22; H, 6.16; found: C, 61.14; H, 6.25.

4-(6-Allyl-benzo[1,3]dioxol-5-yl)-3-iodo-4-(3,4,5-trimethoxy-phenyl)-but-2-enoic acid ethyl ester (16). To a small round bottom flask equipped with a magnetic stir bar and charged with a solution of safrole (1 mL, 6.80 mmol), catalyst **1** (11.8 mg, 0.017 mmol), and AgPF₆ (4.3 mg, 0.017 mmol) in MeNO₂ (15 mL) at $50\text{ }^{\circ}\text{C}$ was slowly added a solution of propargyl alcohol **15** (100 mg, 0.340 mmol) in MeNO₂ (1.5 mL) dropwise. After 4 h the reaction mixture was concentrated *in vacuo* and chromatographed (1:14 $\rightarrow$ 1:6 EtOAc / Hexanes) to give coupled product **16** (84 mg, 56%) as a yellow syrup, its corresponding regioisomer (15 mg, 10%), and the propargyl alcohol homocoupling dimer (12 mg, data below). **Coupling product 16:** ¹H NMR (300 MHz, CDCl₃) δ 6.85 (s, 1H), 6.68 (s, 1H), 6.50 (s, 2H), 5.92 (m, 3H), 5.22 (s, 1H), 5.1 (dq, *J* = 10.1, 1.6, 1H), 5.1 (dq, *J* = 17.0, 1.7, 1H), 4.23 (q, *J* = 7.1, 2H), 3.83 (s, 3H), 3.81 (s, 6H), 3.33 (m, 2H), 1.31 (t, *J* = 7.1, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.7, 153.4, 147.1, 146.5, 137.2, 136.6, 134.4, 130.8, 130.3, 116.3, 110.2, 109.1, 105.1, 101.2, 88.0, 76.7, 62.0, 60.9, 56.1, 38.8, 37.0, 14.0; HRMS

(EI) calc. for $[C_{25}H_{28}O_7]^+$ 438.1679, found 438.1686; Anal. calcd.: C, 68.48; H, 5.98, found: C, 67.44; H, 5.95.

(10-Ethoxycarbonyl-1,2,3,5,6,7-hexamethoxy-9,10-dihydro-anthracen-9-yl)-propynoic acid ethyl ester. 1H NMR (300 MHz, $CDCl_3$) δ 6.91 (s, 2H), 5.24 (s, 2H), 4.16 (q, $J = 7.2$, 4H), 4.06 (s, 6H), 3.90 (s, 6H), 3.88 (s, 6H), 1.24 (t, $J = 7.2$, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.6, 151.2, 141.6, 127.1, 117.7, 107.1, 90.1, 73.2, 61.8, 61.0, 60.7, 56.1, 30.6, 14.0; HRMS (EI) calc. for $[C_{30}H_{32}O_{10}]^+$ 552.1996, found 552.1994.

4-(6-Allyl-benzo[1,3]dioxol-5-yl)-3-iodo-4-(3,4,5-trimethoxy-phenyl)-but-2-enoic acid ethyl ester. To a small round bottom flask, equipped with a magnetic stir bar, containing coupling product **16** (7.00 g, 16.0 mmol) was added AcOH (9 mL) followed by NaI (7.18 g, 47.9 mmol). This mixture was heated, with stirring, to 115 °C until judged complete by TLC (4.5 h). After cooling, the mixture was diluted with Et₂O (200 mL), washed with sat. Na₂S₂O₃ and brine. The organic layer was then separated, dried over MgSO₄, concentrated *in vacuo*, and chromatographed (1:8 EtOAc / Hexanes) to give vinyl iodide (shown above) (6.87g, 76%) that solidified to a white solid (mp 139 °C) upon reconcentration in ether. 1H NMR (300 MHz, $CDCl_3$) δ 6.69 (s, 1H), 6.52 (s, 1H), 6.30 (s, 2H), 6.30 (s, 1H), 5.92 (m, 3H), 5.36 (s, 1H), 5.07 (m, 2H), 4.18 (q, $J = 7.2$, 2H), 4.06 (s, 6H), 3.83 (s, 3H), 3.77 (s, 6H), 3.20 (d, $J = 6.0$, 2H), 1.27 (t, $J = 7.2$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 153.4, 146.8, 146.3, 137.3, 136.6, 135.4, 132.2, 131.7, 128.3, 121.4, 116.3, 110.5, 109.4, 106.6, 101.2, 63.6, 60.9, 56.2, 37.4, 14.2, 1 C unresolved; HRMS (EI) calc. for $[C_{25}H_{27}IO_7]^+$ 566.0802, found 566.0794; Anal. calcd.: C, 53.02; H, 4.80, found: C, 52.84; H, 4.86.

4-(6-Allyl-benzo[1,3]dioxol-5-yl)-3-iodo-4-(3,4,5-trimethoxy-phenyl)-but-2-en-1-ol. To a stirred solution of vinyl iodide (6.00 g, 10.6 mmol) in CH_2Cl_2 (105 mL) at 0 °C was added DIBAL-H (32.0 mL of a 1M solution, 32.0 mmol) dropwise over 5 min. The reaction mixture was immediately warmed to room temperature stirred for 2 h at which point 10% NaOH (16 mL) was slowly added. The reaction mixture was diluted with Et_2O (150 mL), and then washed with H_2O , followed by brine. The organic layer was separated and dried with MgSO_4 before being concentrated *in vacuo* and chromatographed (1:4 EtOAc / Hexanes) to give iodo alcohol (shown above) (4.27 g, 77%) as a white foam. ^1H NMR (300 MHz, CDCl_3) δ 6.68 (s, 1H), 6.60 (s, 1H), 6.33 (s, 2H), 5.92 (m, 3H), 5.60 (dt, $J = 5.7, 1.2$, 1H), 5.07 (m, 3H), 4.26 (t, $J = 4.8, 2\text{H}$), 3.83 (s, 3H), 3.78 (s, 6H), 3.22 (d, $J = 5.1, 2\text{H}$), 1.63 (bs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 146.6, 146.1, 137.5, 137.0, 136.9, 136.1, 132.7, 131.5, 116.1, 110.4, 110.1, 109.4, 106.6, 101.1, 67.8, 61.1, 60.9, 56.1, 37.2; HRMS (EI) calc. for $[\text{C}_{23}\text{H}_{25}\text{IO}_6]^+$ 524.0696, found 524.0698; Anal. calcd.: C, 52.68; H, 4.81, found: C, 52.91; H, 4.90.

2-[7-Methylene-5-(3,4,5-trimethoxy-phenyl)-7,8-dihydro-5H-naphtho[2,3-d][1,3]dioxol-6-ylidene]-ethanol (17). To a solution of iodo alcohol (1.75 g, 3.34 mmol) in benzene (70 mL) was added PPh_3 (88.0 mg, 0.334 mmol) and Ag_2CO_3 (1.84 g, 6.68 mmol). The resulting grey slurry was degassed with a rapid stream of N_2 in the dark for 15 min. $\text{Pd}(\text{OAc})_2$ was added under N_2 and the reaction mixture placed in a preheated 50 °C oil bath for 1 h. Upon completion, the reaction mixture was cooled and poured over a short pad of celite, concentrated *in vacuo*, and chromatographed (2:3 EtOAc / Hexanes) to give somewhat sensitive dienyl alcohol **17** (1.21 g, 91%) as a white foam. ^1H NMR (300 MHz, CDCl_3) δ 6.59 (s, 1H), 6.52 (s, 1H), 6.26 (s, 2H), 5.89 (d, $J = 1.2$, 1H), 5.88 (d, $J = 1.2$, 1H), 5.75 (dd, $J = 7.8, 5.1$, 1H), 5.21 (d, $J = 1.5$, 1H), 4.74 (d, $J = 1.5$, 1H), 4.53 (s, 1H), 4.41 (dd, $J = 13.2, 7.8$, 1H), 4.22 (dd, $J = 13.2, 4.8$, 1H), 3.78 (s, 3H), 3.73 (s, 6H), 3.52 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 146.5, 146.2, 142.3, 140.2, 139.8, 136.4, 131.5, 128.6, 126.9, 115.0, 109.0, 107.8, 105.1, 100.9, 60.8, 60.2, 56.1, 55.2, 37.8; HRMS (EI) calc. for $[\text{C}_{23}\text{H}_{24}\text{O}_6]^+$ 396.1573, found 396.1570.

***tert*-Butyl-dimethyl-[2-[7-methylene-5-(3,4,5-trimethoxy-phenyl)-7,8-dihydro-5H-naphtho[2,3-d][1,3]dioxol-6-ylidene]-ethoxy]-silane.** To a solution of dienyl alcohol **17** (1.16 g, 2.92 mmol) in CH₂Cl₂ (15 mL) was added TEA (4.07 mL, 29.2 mmol) and a catalytic amount of DMAP (4 small chip). This solution was cooled to 0 °C and TBSCl (670 mg, 4.45 mmol) was added in one portion. The resulting solution slowly thickened and the reaction was complete in 2 h. At this point Et₂O (200 mL) was added, and the organic layer extracted with H₂O, washed with brine, dried (MgSO₄), and concentrated *in vacuo* to give a thick syrup. This residue was then chromatographed (1:14 → 1:6 EtOAc / Hexanes) to give somewhat sensitive TBS ether (shown above) (1.32 g, 89%) as a clear syrup. ¹H NMR (300 MHz, CDCl₃) δ 6.59 (s, 1H), 6.53 (s, 1H), 6.28 (s, 2H), 5.90 (d, *J* = 2.1, 2H), 5.70 (dd, *J* = 7.5, 4.5, 1H), 5.21 (d, *J* = 1.5, 1H), 4.73 (d, *J* = 1.5, 1H), 4.53 (s, 1H), 4.40 (dd, *J* = 13.5, 7.8, 1H), 4.27 (dd, *J* = 13.5, 4.5, 1H), 3.79 (s, 3H), 3.74 (s, 6H), 3.51 (s, 2H), 0.86 (s, 9H), 0.02 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 152.9, 146.4, 146.1, 140.4, 140.3, 140.0, 136.4, 131.6, 128.7, 128.3, 114.8, 109.0, 107.8, 105.1, 100.8, 60.9, 60.8, 56.0, 55.0, 37.8, 26.0, 18.3, -5.0, -5.1; HRMS (EI) calc. for [C₂₉H₃₈O₆Si]⁺ 510.2438, found 510.2441.

***tert*-Butyl-dimethyl-[5-(3,4,5-trimethoxy-phenyl)-5,6,9,10-tetrahydro-1,3,7,8-tetraoxa-cyclopenta[b]anthracen-6-ylmethoxy]-silane.** To a solution of the TBS ether (1.16 g, 2.92 mmol) in CCl₄ (65 mL) was added TPP (50 mg, 0.478 mmol) and the resulting pinkish purple solution was vigorously saturated with dry O₂ gas at 0 °C. After 15 min, the O₂ flow was reduced to a gentle stream and the solution irradiated with a halogen overhead projector lamp at a 4" distance. CCl₄ was added periodically to maintain the approximate volume of solvent. After 7 h, the reaction mixture was concentrated *in vacuo* at 20 °C and chromatographed directly (1:14 → 1:5 EtOAc / Hexanes) to give peroxide (shown above) (845 mg, 80%) as an off-white foam and recovered starting material (71.0 mg, 7%). ¹H NMR (300 MHz, CDCl₃) δ 6.61 (s, 2H), 6.35 (s, 2H), 5.87 (dd, *J* = 13.8, 0.9, 2H), 4.84 (d, *J* = 15.9, 1H), 4.37 (d, *J* = 15.9, 1H), 4.28 (bs, 2H), 3.80 (s, 6H), 3.77 (s, 3H), 3.59 (dd, *J* = 11.9, 9.0, 1H), 3.49 (d, *J* = 21.0, 1H), 3.19 (d, *J* = 21.0, 1H), 2.97 (dd, *J* = 11.8, 2.4, 1H), 0.79 (s, 9H), -0.09 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 153.6, 146.5, 146.3, 140.6, 137.2, 131.5, 128.3, 127.6, 124.2, 108.0, 107.6, 104.6, 100.9, 84.6, 71.6, 62.7, 60.9, 56.2, 49.6, 30.3, 26.0, 18.5, -5.2, -5.5, 1 peak artifact; HRMS (EI) calc. for [C₂₉H₃₈O₈Si]⁺ 542.2336, found 542.2347; Anal. calcd.: C, 64.18; H, 7.06, found: C, 64.34; H, 7.27.

2-(*tert*-Butyl-dimethyl-silanyloxy)-1-[7-hydroxymethyl-5-(3,4,5-trimethoxy-phenyl)-5,8-dihydro-naphtho[2,3-*d*][1,3]dioxol-6-yl]-ethanol (18). To a solution of peroxide (445 mg, 0.820 mmol) in 15:1 THF/H₂O (320 mL) was added 4 freshly prepared pieces of aluminum amalgam over 20 min. Each piece of amalgam was prepared as follows: a 4" square of aluminum foil was loosely rolled up and dipped into aq. NaOH (3M) for approximately 15 s, rinsed with H₂O, then dipped into aq. HgCl₂ (3%) for 30 s, and again rinsed with H₂O. This process was repeated once and the material finally rinsed with EtOH. As each piece of amalgam broke down in solution the reaction mixture became grey in color and Hg⁰ began to build up on the bottom of the flask. After 2.5 h the reaction mixture was poured over a silica gel plug and concentrated *in vacuo*. The residue obtained was redissolved in EtOAc (200 mL) washed with brine, dried (MgSO₄), and concentrated *in vacuo*, and chromatographed (1:2 EtOAc / Hexanes) to give diol **17** (428 mg, 96%) as a white foam. ¹H NMR (300 MHz, CDCl₃) δ 6.63 (s, 1H), 6.55 (s, 1H), 6.37 (s, 2H), 5.89 (d, *J* = 1.2, 1H), 5.84 (d, *J* = 1.2, 1H), 4.53 (m, 3H), 3.99 (d, *J* = 11.7, 1H), 3.79 (s, 6H), 3.76 (s, 3H), 3.61 (d, *J* = 3.3, 2H), 3.53 (dd, *J* = 9.9, 8.7, 1H), 3.10 (dd, *J* = 9.9, 5.1, 1H), 0.79 (s, 9H), -0.08 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 146.2, 146.1, 143.1, 141.3, 136.6, 135.6, 134.0, 131.3, 126.0, 107.5, 107.3, 104.6, 100.7, 74.3, 65.7, 62.3, 60.7, 56.0, 50.1, 35.0, 25.7, 19.1, 18.2, -5.6, 1 peak artifact; HRMS (EI) calc. for [C₂₉H₄₀O₈Si]⁺ 544.2492, found 544.2481; Anal. calcd.: C, 63.94; H, 7.40, found: C, 63.65; H, 7.54.

1-[7-Hydroxymethyl-5-(3,4,5-trimethoxy-phenyl)-5,8-dihydro-naphtho[2,3-*d*][1,3]dioxol-6-yl]-ethane-1,2-diol. To a solution of diol **17** (300 mg, 0.551 mmol) in THF (11 mL) at 0 °C was added TBAF in THF (0.725 mL, 1M, 0.725 mmol). After 1 h the reaction mixture was concentrated *in vacuo*, and chromatographed (1:14 MeOH / CHCl₃) to give triol (shown above) (236 mg, 99%) as a white foam. ¹H NMR (300 MHz, CDCl₃) δ 6.63 (s, 1H), 6.62 (s, 1H), 6.42 (s, 2H), 5.89 (d, *J* = 1.2, 1H), 5.85 (d, *J* = 1.2, 1H), 5.89 (d, *J* = 1.2, 1H), 4.75 (dd, *J* = 7.5, 5.7, 1H), 4.52 (bs, 1H), 4.43 (d, *J* = 11.7, 1H), 4.20 (d, *J* = 11.7, 1H), 3.78 (s, 6H), 3.76 (s, 3H), 3.62 (m, 3H), 3.33 (dd, *J* = 10.8, 5.4, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 146.3, 146.2, 141.5, 136.5, 135.2, 135.0, 131.8, 126.2, 107.5, 104.5, 100.8, 99.1, 73.3, 67.9, 64.9, 64.4, 61.9, 60.8, 56.1, 49.2, 34.8, 1 C unresolved; HRMS (FAB+) calc. for [C₂₃H₂₆O₈]⁺ 430.1628, found 430.1624; Anal. calcd. for M·H₂O: C, 61.60; H, 6.29, found: C, 61.42; H, 6.33.

(+)-apopicropodophyllin. To a stirred solution of triol (115 mg, 0.267 mmol) in CH_2Cl_2 (9 mL) buffered with solid NaHCO_3 (115 mg, 1.34 mmol) at 0 °C was added $\text{Pb}(\text{OAc})_4$ (118 mg, 0.267 mmol). After 15 min, PDC (121 mg, 0.320 mmol) was added and the rate of stirring was increased. After 30 min the reaction mixture was diluted with CH_2Cl_2 (20 mL), poured over a short plug of silica gel, and washed with another volume of CH_2Cl_2 . Concentration of this solution *in vacuo*, followed by chromatography yielded apopicropodophyllin (41 mg, 39%) and the corresponding furan (37 mg, 36%, data below) resulting from dehydration of the intermediate lactol. **apopicropodophyllin:** ^1H NMR (300 MHz, CDCl_3) δ 6.71 (s, 1H), 6.62 (s, 1H), 6.36 (s, 2H), 5.94 (d, $J = 1.2$, 1H), 5.93 (d, $J = 1.2$, 1H), 4.82 (m, 3H), 3.85 (dd, $J = 22.5$, 4.5, 1H), 3.78 (s, 3H), 3.77 (s, 6H), 3.63 (dd, $J = 22.5$, 4.5, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.2, 157.3, 153.2, 147.2, 147.0, 138.2, 136.9, 129.6, 128.0, 123.7, 109.5, 107.7, 105.4, 101.3, 71.0, 60.7, 56.1, 42.7, 29.2; HRMS (EI) calc. for $[\text{C}_{22}\text{H}_{20}\text{O}_7]^+$ 396.1209, found 396.1214.

5-(3,4,5-Trimethoxy-phenyl)-5,9-dihydro-furo[3',4':6,7]naphtho[2,3-d][1,3]dioxole. ^1H NMR (300 MHz, CDCl_3) δ 7.32 (app d, $J = 2.1$, 2H), 7.15 (s, 1H), 6.75 (s, 1H), 6.56 (s, 1H), 6.37 (s, 2H), 5.91 (s, 2H), 4.92 (s, 1H), 3.83 (m, 5H), 3.72 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 146.2, 140.3, 137.9, 136.6, 136.5, 132.0, 128.2, 126.2, 120.5, 109.1, 108.5, 105.2, 102.7, 101.0, 60.8, 56.0, 25.8, 1 C unresolved; HRMS (EI) calc. for $[\text{C}_{22}\text{H}_{20}\text{O}_6]^+$ 380.1260, found 380.1267.