Supporting Information for:

Application of Aryl Siloxane Cross-Coupling to the Synthesis of Allocolchicinoids

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GENERAL EXPERIMENTAL

Thin-layer chromatography (TLC) was performed on 0.25 mm Merck silica gel coated plates treated with a UV-active binder with compounds being identified by UV (254 nm). Flash chromatography was performed using thick walled columns and medium pressure silica gel (Whatman 200-425 mesh), with column length and diameter being determined by the method of Still.¹

Melting points were taken in Kimax soft glass capillary tubes using a Thomas-Hoover Uni-Melt capillary melting point apparatus (Model 6406K) equipped with a calibrated thermometer. Infrared spectra band positions are reported in reciprocal centimeters (cm^{-1}) and relative intensities are listed as br (broad), s (strong), m (medium), or w (weak).

Nuclear magnetic resonance (^1H , ^{13}C NMR) spectra were recorded on a 400 MHz spectrometer at 400 and 200 Hz respectively. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS). Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br s (broad singlet).

Low resolution mass spectrometry (LRMS) and high resolution mass spectrometry (HRMS) data are reported in the form of m/z (intensity relative to base peak = 100). The matrix used for fast atom bombardment (FAB) was ethylene glycol.

All compounds were determined to be >95% pure by ^1H NMR or GC analysis, unless otherwise noted. Previously reported compounds were characterized *via* ^1H and ^{13}C NMR and IR and compared to literature values. All new compounds were characterized using ^1H NMR, ^{13}C NMR, IR, low resolution and high resolution mass spectrometry.

CROSS COUPLING REACTIONS

2-Bromo-3,4,5-trimethoxy-benzaldehyde (6). Title compound was prepared according to the procedure of Fukuyama.² The ^1H , and ^{13}C NMR, and IR match that reported by Fukuyama.²

6-Carbaldehyde-2,3,4-trimethoxy-biphenyl (16). To a 250 mL round bottom flask was added 2-bromo-3,4,5-trimethoxybenzaldehyde (5.00 g, 18.2 mmol), $\text{Pd}(\text{OAc})_2$ (204 mg, 0.910 mmol), and PPh_3 (1.19 g, 4.55 mmol). The flask was placed under argon and 100 mL of THF was added *via* syringe. Phenyltrimethoxysilane (6.75 mL, 36.4 mmol) was added to the yellow solution, followed by 36.4 mL of a 1.0 M solution of TBAF in THF (36.4 mmol). The reaction was heated to reflux for 18 h, at which time, the reaction was cooled to room temperature, poured through a short pad of silica gel, and diluted with ether (100 mL). The organic layer was washed with water (100 mL x2), dried (MgSO_4), and evaporated to yield a yellow oil. Column chromatography (TLC R_f = 0.24, 9:1 hexanes/EtOAc) yielded 4.66 g of a white solid (94%) mp 91.2-92.4 °C. IR (CCl_4) 3085 (w) 3067 (w), 3009 (w), 2960 (m), 2933 (m), 2857 (m), 1683 (s), 1587 (m), 1328 (s), 1193 (m), 1141 (s), 1096 (s); ^1H NMR (CDCl_3) δ 3.59 (s, 3H), 3.94 (s, 3H), 3.99 (s, 3H), 7.30-7.35 (m, 3H), 7.42-7.43 (m, 2H), 9.63 (s, 1H); ^{13}C NMR (CDCl_3) δ 56.6, 61.4, 61.5, 105.6, 110.2, 127.5, 128.1, 123.3, 128.4, 129.9, 130.1, 131.4, 133.2, 191.8; LRMS (FAB^+) m/z 273 ($\text{M}^+ + \text{H}$, 100), 272 (80), 255 (42), 230 (24), 214 (19), 151 (18), 135 (24), 119 (25), 85 (29), 55 (34), 43 (25); HRMS (FAB^+ , M^+) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$ 272.1049, found 272.1045.

6-Carbaldehyde-2,3,4,4'-tetramethoxy-biphenyl (25). Title compound was prepared according to the cross-coupling procedure for biaryl **16**. Column chromatography (TLC R_f = 0.25, 4:1 hexanes/EtOAc) yielded a pale yellow oil.

Recrystallization (hexane/EtOAc) provided 5.12 g of a white solid (93%) mp 68.0-69.0 °C. IR (CCl₄) 3002 (m), 2954 (s), 2933 (s), 2874 (s), 2853 (m), 2836 (m), 1745 (s), 1690 (s), 1587 (s), 1480 (s), 1462 (s), 1331 (s), 1252 (s), 1152 (s), 1100 (s); ¹H NMR (CDCl₃) δ 3.60 (s, 3H), 3.87 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 6.98 (d, *J*=8.8, 2H), 7.25 (d, *J*=8.8, 2H), 7.35 (s, 1H), 9.68 (s, 1H); ¹³C NMR (CDCl₃) δ 55.3, 56.1, 61.0, 61.1, 105.2, 113.5, 124.8, 129.9, 132.2, 134.3, 147.7, 151.3, 152.9, 159.4, 191.5; LRMS (FAB⁺) *m/z* 303 (M⁺ + H, 100), 302 (65), 285 (20); HRMS (FAB⁺, M⁺) *m/z* calcd for C₁₇H₁₈O₅ 302.1154, found 302.1154.

6-Carbaldehyde-4'-methyl-2,3,4-trimethoxy-biphenyl (Table 1, entry 3). Title compound was prepared according to the cross-coupling procedure for biaryl **16**. Column chromatography (TLC R_f = 0.23, 9:1 hexanes/EtOAc) yielded 4.53 g of a white solid (87%) mp 58.0-59.0 °C. IR (CCl₄) 3087 (w), 3054 (w), 3007 (m), 2967 (m), 2937 (s), 2856 (m), 1689 (s), 1586 (s), 1482 (s), 1331 (s), 1137 (s), 1097 (s), 1004 (s); ¹H NMR (CDCl₃) δ 2.43 (s, 3H), 3.61 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 7.21 (d, *J*=8.0, 2H), 7.25 (d, *J*=8.0, 2H), 7.36 (s, 1H), 9.66 (s, 1H); ¹³C NMR (CDCl₃) δ 21.3, 56.0, 56.1, 61.1, 105.1, 128.7, 129.7, 129.8, 130.9, 134.6, 137.7, 147.6, 151.2, 153.0, 191.5; LRMS (EI⁺) *m/z* 286 (M⁺, 100), 271 (20), 129 (20); HRMS (FAB⁺, M⁺) *m/z* calcd for C₁₇H₁₈O₄ 286.1205, found 286.1205.

6-Carbaldehyde-4'-carboethoxy-2,3,4-trimethoxy-biphenyl (Table 1, entry 4). Title compound was prepared according to the cross-coupling procedure for biaryl **16**. Column chromatography (TLC R_f = 0.28, 4:1 hexanes/EtOAc) yielded 5.89 g of a colorless oil (94%). IR (CCl₄) 3004 (w), 2979 (m), 2939 (m), 2841 (m), 1711 (s), 1679 (s), 1588 (s), 1319 (s), 1268 (s), 1145 (s), 1086 (s), 1000 (s); ¹H NMR (CDCl₃) δ 1.41 (t, *J*=7.2, 3H), 3.58 (s, 3H), 3.95 (s, 3H), 3.99 (s, 3H), 4.40 (q, *J*=7.2, 2H), 7.24 (s, 1H), 7.40 (d, *J*=8.0, 2H), 8.11 (d, *J*=8.0, 2H), 9.61 (s, 3H); ¹³C NMR (CDCl₃) δ 14.4, 29.0, 56.2, 61.1, 61.2, 105.5, 129.2, 129.5, 130.1, 131.1, 133.3, 137.8, 147.7, 151.0, 153.5, 166.3, 190.6; LRMS (FAB⁺) *m/z* 345 (M⁺ + H, 100), 327 (55), 299 (30), 55 (30); HRMS (FAB⁺, M⁺) *m/z* calcd for C₁₉H₂₀O₆ 344.1260, found 344.1275.

CARBENE-RING EXPANSION REACTIONS

Model System

9-(Methoxymethoxy)-phenanthrene (9). 9-Phenanthrol (1.00 g, 3.09 mmol) was dissolved in 25 mL of CH₂Cl₂. Chloromethylmethyl ether (1.26 mL, 10.3 mmol) was added *via* syringe, followed by 1.12 mL (10.3 mmol) of Hunig's base. The brown solution was stirred at room temperature for 12 h to consume all of the starting material. After 12 h, the reaction was diluted with 25 mL of CH₂Cl₂. The organic phase was washed with water (50 mL), 1M HCl (50 mL) and brine (50 mL), dried (MgSO₄), and evaporated to yield a brown oil. Column chromatography (TLC R_f = 0.41, 9:1 hexanes/EtOAc) yielded 0.894 g of a white solid (89%) mp 55.0-56.0 °C. IR (CCl₄) 3077 (m), 3060 (s), 3010 (m), 2960 (s), 2983 (s), 2850 (w), 2823 (m), 1632 (s), 1606 (s), 1452 (s), 1315 (s), 1147 (s); ¹H NMR (CDCl₃) δ 3.58 (s, 3H), 5.48 (s, 2H), 7.49-7.79 (m, 6H), 8.37 (d, *J*=8.0, 1H), 8.58 (d, *J*=8.4, 1H), 8.65 (d, *J*=8.4, 1H); ¹³C NMR (CDCl₃) δ 56.3, 94.6, 105.9, 122.4, 122.5, 122.6, 124.6, 126.4, 126.6, 126.9, 127.0, 127.1, 127.7, 131.3, 132.7, 150.9; LRMS (FAB⁺) *m/z* 238 (M⁺, 100), 207 (45), 165 (22), 45 (65); HRMS (FAB⁺, M⁺) *m/z* calcd for C₁₆H₁₄O₂ 238.0994, found 238.0999.

7,7-Dichlorodibenzo[a,c]bicyclo(4.1.0)-6-(methoxymethoxy)-heptane (10). To a solution of 9-(methoxymethoxy)-phenanthrene (238 mg, 1.00 mmol) in 10 mL of CHCl_3 was added 22.7 mg (0.100 mmol) of benzyltriethylammonium chloride and 2.00 mL of a 50% solution of NaOH. The colorless biphasic mixture was stirred for 5 h at room temperature, during which time the reaction changed from colorless, to orange, to brown. The brown suspension was diluted with 50 mL of CH_2Cl_2 and poured into 50 mL of water. The layers were separated and the aqueous phase extracted with CH_2Cl_2 (3 x 50 mL). The organic extracts were combined, washed with brine (50 mL), dried (MgSO_4), and evaporated to yield a brown oil. Column chromatography (TLC R_f = 0.32, 9:1 hexanes/EtOAc) yielded 296 mg of an off white solid (92%) mp 91-92 °C. IR (CCl_4) 3077 (w), 3037 (w), 2997 (w), 2963 (m), 2927 (m), 2896 (m), 2843 (m), 2826 (w), 1492 (m), 1455 (m), 1157 (s), 1030 (s); ^1H NMR (CDCl_3) δ 3.44 (s, 3H), 3.64 (s, 1H), 4.79 (dd, J =6.8, 3.8, 2H), 7.35-7.49 (m, 4H), 7.86-7.88 (m, 1H), 8.04-8.07 (m, 3H); ^{13}C NMR (CDCl_3) δ 41.6, 56.7, 62.3, 66.4, 96.3, 122.6, 122.9, 123.1, 127.4, 128.1, 128.2, 128.3, 128.8, 128.9, 130.4, 130.9, 132.5; LRMS (FAB^+) m/z 320 (M^+ , 10), 285 (15), 259 (100), 241 (35), 194 (40), 154 (38), 45 (90); HRMS (FAB^+ , M^+) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{Cl}_2$ 320.0371, found 320.0367.

6-Chloro-5H-dibenzo[a,c]cyclohepten-5-one (11). 7,7-Dichlorodibenzo[a,c]bicyclo(4.1.0)-6-(methoxymethoxy)-heptane (813 mg, 2.53 mmol) in 30 mL of IPA, 30 mL of THF and 30 mL of 2.0 M HCl was heated to 100 °C for 5 h. The solution was cooled to room temperature and the organic solvents were removed *in vacuo*. The remaining mixture was partitioned between 75 mL of ether and water. The aqueous phase was extracted three times with ether (50 mL) and the combined organic extracts were dried (MgSO_4), and evaporated to yield a yellow oil. Column chromatography (TLC R_f = 0.41, 4:1 hexanes/EtOAc) yielded 579 mg of a white solid (95%) mp 100.0-100.8 °C (lit. 98.0-98.8 °C).³ IR (CCl_4) 3100 (w), 3070 (m), 3030 (m), 1672 (s), 1592 (m); ^1H NMR (CDCl_3) δ 7.52-7.63 (m, 4H), 7.72-7.89 (m, 2H), 7.90-7.96 (m, 3H); ^{13}C NMR (CDCl_3) δ 128.6, 128.8, 129.6, 129.7, 130.0, 130.9, 131.0, 131.4, 131.9, 134.1, 136.6, 137.2, 137.7, 139.1, 187.3; LRMS (FAB^+) m/z 241 (M^+ , 100), 154 (60), 136 (55); HRMS (FAB^+ , M^+) m/z calcd for $\text{C}_{15}\text{H}_{10}\text{OCl}$ 241.0420, found 241.0419.

6,7-Dihydro-5H-dibenzo[a,c]cyclohepten-5-one (12). 6-Chloro-5H-dibenzo[a,c]cyclohepten-5-one (75.0 mg, 0.312 mmol), sodium acetate (79.3 mg, 0.967 mmol), and palladium on carbon (5%, 65.8 mg, 16.8 μmol) were stirred in 10 mL of EtOH under 1 ATM of hydrogen for 1 h. The reaction mixture was filtered, and poured into 50 mL of ether. The organic layer was washed with water (50 mL x2) and brine (50 mL). The ethereal phase was dried (MgSO_4), and evaporated to yield a yellow oil. Column chromatography (TLC R_f = 0.21, 4:1 hexanes/EtOAc) yielded 46.8 mg of a white solid (72%) mp 84.5-85.6 °C (lit. 85-86 °C).³ IR (CCl_4) 3074 (m), 3027 (m), 2957 (m), 2927 (w), 2863 (w), 1689 (s), 1596 (m), 1448 (m), 1271 (s); ^1H NMR (CDCl_3) δ 2.99 (s, 4H), 7.27-7.46 (m, 6H), 7.58-7.67 (m, 2H); ^1H NMR (benzene d_6) δ 2.45 (t, J =6.8, 2H), 2.63 (t, J =6.8, 2H), 6.85-6.87 (m, 1H), 7.05-7.16 (m, 6H), 7.80-7.82 (m, 1H); ^{13}C NMR (CDCl_3) δ 29.5, 47.6, 127.6, 127.9, 128.0, 128.4, 128.6, 129.6, 130.0, 132.2, 138.8, 138.9, 139.0, 139.5, 206.2; LRMS (EI^+) m/z 208 (M^+ , 100), 180 (90), 179 (70), 165 (39), 152 (25); HRMS (EI^+ , M^+) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{O}$ 208.0888, found 208.0895.

6,7-Dihydro-5H-dibenzo[a,c]cyclohepten-5-ol (13). 6-Chloro-5H-dibenzo[a,c]cyclohepten-5-one (75.0 mg, 0.312 mmol), sodium acetate (79.3 mg, 0.967 mmol), and palladium on carbon (5%, 65.8 mg, 0.0168 mmol) were stirred in 10 mL of EtOH under 1 ATM of hydrogen for 24 h. The reaction mixture was filtered, and poured into 50 mL of ether. The organic layer

was washed with water (50 mL x2) and brine (50 mL). The ethereal phase was dried (MgSO_4), and evaporated to yield a yellow oil. Column chromatography (TLC R_f = 0.25, 4:1 hexanes/EtOAc) yielded 43.0 mg of a white solid (66%) mp 114.5-115.0 °C. IR (CCl_4) 3619 (s), 3070 (m), 3020 (m), 2940 (s), 2860 (m), 1482 (m), 1455 (m), 1047 (s); ^1H NMR (CDCl_3) δ 2.08-2.10 (m, 1H), 2.46-2.67 (m, 4H), 4.65-4.67 (m, 1H), 7.25-7.64 (m, 7H), 7.64-7.65 (m, 1H); ^{13}C NMR (CDCl_3) δ 30.1, 41.9, 70.6, 123.1, 123.2, 126.9, 127.3, 127.6, 127.8, 128.2, 128.3, 137.9, 139.4, 139.8, 141.5; LRMS (EI^+) m/z 210 (M^+ , 100), 192 (90), 191 (40), 165 (30), 152 (20); HRMS (EI^+ , M^+) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{O}$ 210.1045, found 210.1035.

5H-dibenzo[a,c]cyclohepten-5-one (14). Title compound was prepared according to a procedure by Jones and coworkers³ starting with 150 mg (0.623 mmol) of 6-chloro-5H-dibenzo[a,c]cyclohepten-5-one and yielding 102 mg of the title compound as a white solid (79%) mp 82.3-83.7 °C (lit. 83-84.5 °C).³ IR (CCl_4) 3060 (w), 3031 (m), 2953 (s), 2921 (m), 2847 (w), 1658 (s); ^1H NMR (CDCl_3) δ 6.66 (d, J =12.0, 1H), 7.35 (d, J =12.0, 1H), 7.47-7.59 (m, 4H), 7.65-7.69 (m, 1H), 7.88-7.96 (m, 3H); ^{13}C NMR (CDCl_3) δ 110.8, 128.2, 128.5, 129.0, 129.4, 130.3, 131.1, 131.5, 131.6, 133.1, 137.0, 138.2, 139.9, 141.2, 192.6; LRMS (EI^+) m/z 206 (M^+ , 40), 178 (100), 176 (30), 88 (30); HRMS (EI^+ , M^+) m/z calcd for $\text{C}_{15}\text{H}_{10}\text{O}$ 206.732, found 206.0728.

6-Phenyl-5H-dibenzo[a,c]cyclohepten-5-one (15). 6-Chloro-5H-dibenzo[a,c]cyclohepten-5-one (240 mg, 1.00 mmol) was weighed into a 25 mL round bottom flask and placed under argon. Tetrakis(triphenylphosphine)palladium(0) (116 mg, 0.100 mmol) was added, followed by 10 mL of benzene, and 1.50 mL (3.00 mmol) of a 2M aqueous solution of Na_2CO_3 . Phenyl boronic acid (377 mg, 3.00 mmol) in 3 mL of EtOH was added *via* syringe. The reaction mixture was brought to reflux for 72 h to consume all of the α -chloro enone. The reaction was cooled to room temperature and diluted with water (30 mL), and ether (30 mL). The layers were separated and the aqueous phase extracted twice with 30 mL of ether. The organic phases were combined and dried (MgSO_4) and evaporated to yield a yellow solid. Column chromatography (TLC R_f = 0.31, 9:1 hexanes/EtOAc) yielded 200 mg of a white solid (71%) mp 136.8-138.2 °C. IR (CCl_4) 3030 (m), 3023 (w), 2921 (s), 2843 (m), 1670 (s), 1368 (m), 1290 (s); ^1H NMR (CDCl_3) δ 7.36-7.68 (m, 10H), 7.77-7.90 (m, 1H), 7.85-7.89 (m, 2H); ^{13}C NMR (CDCl_3) δ 127.6, 127.9, 128.1, 128.4, 128.5, 128.7, 129.2, 130.4, 131.0, 133.3, 135.2, 136.2, 137.1, 138.4, 143.4, 144.4, 196.2; LRMS (EI^+) m/z 282 (M^+ , 30), 254 (100), 252 (60); HRMS (EI^+ , M^+) m/z calcd for $\text{C}_{21}\text{H}_{14}\text{O}$ 282.1045, found 282.1036.

Phenyl System

2,3,4-Trimethoxy-6-((E/Z)-2-methoxyvinyl)biphenyl. Sodium hydride (60% dispersion in mineral oil, 2.15 g, 53.6 mmol) was added to a 250 mL round bottom flask and placed under argon. The sodium hydride was washed three times with dry pentane to remove the mineral oil. Ether was added (130 mL), followed by methoxymethyltriphenylphosphonium chloride (20.2 g, 57.6 mmol), which was added in three portions over 10 min. The reaction mixture was brought to reflux for 30 min and cooled to room temperature. 2,3,4-Trimethoxy-6-carbaldehyde-biphenyl (3.64 g, 13.4 mmol) was added in one portion. The reaction was heated to reflux for 12 h to consume all of the aldehyde, after which time the reaction was filtered, and diluted with 100 mL of ether. The organic layer was washed with water (100 mL x2), 1 M HCl (100 mL), brine (100 mL),

dried (MgSO_4), and evaporated to yield a white solid. Column chromatography (TLC R_f = 0.34, 4:1 hexanes/EtOAc) yielded 3.90 g of a white solid (97%) mp 105-108 °C as a 60:40 mixture of E/Z isomers which were not separated. IR (CCl_4) 3060 (m), 3003 (m), 2957 (s), 2930 (s), 2903 (m), 2830 (m), 1639 (s), 1489 (s), 1398 (s), 1328 (s), 1147 (s), 1101 (s); LRMS (FAB^+) m/z 300 (M^+ , 100), 269 (60), 238 (29), 89 (22), 45 (35); HRMS (FAB^+ , M^+) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4$ 300.1362, found 300.1367.

6-Acetylaldehyde-2,3,4-trimethoxybiphenyl. 2,3,4-Trimethoxy-6-((E/Z)-2-methoxyvinyl)biphenyl (5.25 g, 17.5 mmol) was dissolved in 50 mL of THF. A 2.0 M HCl (0.600 mL, 13.1 mmol) solution was added and the reaction was refluxed for 1.5 h. The pale yellow solution was diluted with 75 mL of ethyl acetate, washed twice with 50 mL of a sat. solution of NaHCO_3 , water (50 mL), brine (50 mL), dried (MgSO_4), and evaporated to yield a yellow solid. Column chromatography (TLC R_f = 0.28, 4:1 hexanes/EtOAc) yielded a viscous oil which crystallized upon cooling to provide 3.58 g of the title compound as white needles (97%) mp 56.0-56.5 °C. IR (CCl_4) 3064 (w), 2993 (m), 2963 (m), 2940 (s), 2833 (m), 2719 (w), 1733 (s), 1489 (s), 1147 (s), 1101 (s); ^1H NMR (CDCl_3) δ 3.47 (s, 2H), 3.61 (s, 3H), 3.89 (s, 3H), 3.92 (s, 3H), 6.55 (s, 1H), 7.17-7.19 (m, 2H), 7.34-7.43 (m, 3H), 9.55 (s, 1H); ^{13}C NMR (CDCl_3) δ 48.4, 56.1, 60.9, 61.0, 109.2, 126.1, 127.4, 128.3, 130.0, 130.2, 136.5, 141.6, 151.9, 152.9, 199.4; LRMS (FAB^+) m/z 286 (M^+ , 40), 269 (100), 258 (60), 242 (43), 226 (40); HRMS (FAB^+ , M^+) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4$ 286.1205, found 286.1217.

6-(Acetic acid)-2,3,4-trimethoxybiphenyl (17). A stock solution of Jones reagent was prepared by dissolving 5.0 g of CrO_3 in 7 mL of water. The red solution was cooled to 0 °C and sulfuric acid (4.21 mL) was added dropwise, followed by an additional 18 mL of water. 6-Acetylaldehyde-2,3,4-trimethoxybiphenyl (3.76 g, 13.1 mmol) was dissolved in 130 mL of acetone and the colorless solution was cooled to 0 °C. Jones reagent was added dropwise until the persistence of a deep red color. Isopropanol was added dropwise to quench the excess Jones reagent, forming a dark green reaction mixture. The solvents were removed *in vacuo* and the residue was dissolved in 100 mL of 1 M NaOH. The aqueous layer was washed with ether (50 mL x2) and acidified with concentrated HCl. The aqueous suspension was extracted with CH_2Cl_2 (75 mL x3). The combined organic extracts were dried (MgSO_4), and evaporated to yield 3.76 g of a white solid (95%) mp 108.0-108.5 °C. IR (CCl_4) 3528 (m), 3060 (m), 3007 (m), 2960 (m), 2933 (m), 2840 (m), 1709 (s), 1489 (m), 1395 (m), 1147 (s), 1104 (s); ^1H NMR (CDCl_3) δ 3.43 (s, 2H), 3.60 (s, 3H), 3.90 (s, 3H), 3.91 (s, 3H), 6.68 (s, 1H), 7.22-7.24 (m, 2H), 7.35-7.42 (m, 3H), 9.20 (br, 1H); ^{13}C NMR (CDCl_3) δ 38.1, 56.0, 60.9, 61.0, 108.9, 127.2, 127.8, 128.2, 129.9, 130.1, 136.4, 136.7, 151.6, 152.7, 175.0; LRMS (FAB^+) m/z 302 (M^+ , 100), 257 (25), 226 (20); HRMS (FAB^+ , M^+) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_5$ 302.1154, found 302.1144.

2,3,4-Trimethoxy-9-phenanthrol (18). 6-(Acetic acid)-2,3,4-trimethoxybiphenyl (3.76 g, 12.4 mmol) was dissolved in 36.0 mL SOCl_2 and brought to a gentle reflux for 2 h. Excess thionyl chloride was removed *in vacuo*. The residue was dissolved in 50 mL of benzene and added dropwise to a stirred, cooled (5 °C) mixture of AlCl_3 (3.31 g, 24.8 mmol) in benzene (80 mL). The reaction mixture was allowed to warm to room temperature, at which time 100 mL of a 1.0 M HCl solution was added in one portion. The phases were separated and the aqueous layer extracted with EtOAc (75 mL x3). The combined organic extracts were dried (MgSO_4), and evaporated to yield a brown oil. Column chromatography (TLC R_f =

0.31, 1:1 hexanes/EtOAc) yielded 2.19 g of an air sensitive off-white solid which was immediately stored under argon (62%) mp 130-132 °C (decomp). IR (CCl₄) 3609 (m), 3064 (w), 2997 (m), 2960 (m), 2933 (s), 2876 (m), 2856 (m), 1746 (m), 1609 (m), 1469 (s), 1221 (s), 1101 (s); ¹H NMR (CDCl₃) δ 3.99 (s, 3H), 4.01 (s, 3H), 4.02 (s, 3H), 5.22 (s, 1H), 6.91 (s, 1H), 6.92 (s, 1H), 7.59-7.66 (m, 2H), 8.29 (d, *J*=8.0, 1H), 9.52 (d, *J*=8.0, 1H); ¹³C NMR (CDCl₃) δ 56.4, 60.9, 61.9, 104.1, 106.8, 115.7, 122.3, 125.5, 125.9, 127.3, 128.0, 131.2, 131.9, 141.6, 149.9, 153.2, 153.4; LRMS (FAB⁺) *m/z* 284 (M⁺, 100), 154 (30), 136 (40); HRMS (FAB⁺, M⁺) *m/z* calcd for C₁₆H₁₆O₄ 284.1049, found 284.1050.

2,3,4-Trimethoxy-9-(methoxymethoxy)-phenanthrene (19). 3,4,5-Trimethoxy-9-phenanthrol (2.19 g, 7.71 mmol) was dissolved in 40 mL of CH₂Cl₂. To this dark brown solution was added 1.88 mL (15.4 mmol) of chloromethylmethyl ether, followed by 1.67 mL of Hunig's base (15.4 mmol). The light brown solution was stirred at room temperature for 12 h to consume all of the starting material (TLC). The reaction was diluted with ether (150 mL), washed with water (100 mL), 1M HCl (100 mL), brine (100 mL), dried (MgSO₄), and evaporated to yield a brown oil. Column chromatography (TLC R_f = 0.27, 4:1 hexanes/EtOAc) yielded 2.13 g of a white solid (84%) mp 91.1-92.5 °C. IR (CCl₄) 3074 (w), 3000 (m), 2963 (m), 2933 (s), 2903 (m), 2826 (m), 1632 (s), 1612 (s), 1502 (s), 1462 (s), 1351 (s), 1144 (s), 1064 (s); ¹H NMR (CDCl₃) δ 3.58 (s, 3H), 4.00 (s, 3H), 4.01 (s, 3H), 4.02 (s, 3H), 5.47 (s, 2H), 7.02 (s, 1H), 7.20 (s, 1H), 7.55-7.67 (m, 2H), 8.36 (d, *J*=8.0, 1H), 9.50 (d, *J*=8.0, 1H); ¹³C NMR (CDCl₃) δ 55.8, 56.2, 60.3, 61.3, 94.6, 104.5, 106.0, 115.2, 121.9, 125.3, 125.9, 126.6, 127.2, 130.6, 131.0, 141.3, 150.7, 152.4, 152.7; LRMS (FAB⁺) *m/z* 328 (M⁺, 100), 297 (20), 283 (25); HRMS (FAB⁺, M⁺) *m/z* calcd for C₁₉H₂₀O₅ 328.1311, found 328.1318.

1,1-Dichloro-1a,9b-dihydro-6,7,8-trimethoxy-1a-(methoxymethoxy)-1H-cyclopropa[*l*]phenanthrene (20). 2,3,4-Trimethoxy-9-(methoxymethoxy)-phenanthrene (2.13 g, 6.49 mmol) and 148 mg (0.649 mmol) of benzyltriethylammonium chloride were dissolved in 65 mL of CHCl₃. To this colorless solution was added 13 mL of 50% NaOH in one portion. The biphasic reaction mixture was stirred vigorously at room temperature for 6 h during which time the reaction changed from pale yellow to orange to brown. The reaction mixture was diluted with CH₂Cl₂ (100 mL) and water (100 mL). The layers were separated and the aqueous phase was extracted with CH₂Cl₂ (75 mL x3). The combined organic extracts were dried (MgSO₄), and evaporated to yield a brown oil. Column chromatography (TLC R_f = 0.26, 4:1 hexanes/EtOAc) yielded 1.95 g of a yellow oil (73%) which was used without further purification. IR (CCl₄) 3137 (w), 3064 (w), 2997 (m), 2957 (s), 2937 (s), 2846 (m), 1596 (s), 1492 (s), 1328 (s), 1161 (s); ¹H NMR (CDCl₃) δ 3.45 (s, 3H), 3.56 (s, 1H), 3.85 (s, 3H), 3.93 (s, 3H), 3.96 (s, 3H), 4.78 (q_{AB}, *J*=6.8, 7.2, 2H), 6.80 (s, 1H), 7.26-7.42 (m, 2H), 7.84-7.85 (m, 1H), 8.94-8.96 (m, 1H); ¹³C NMR (CDCl₃) δ 42.1, 55.9, 56.7, 60.4, 61.0, 62.4, 66.6, 96.2, 109.8, 117.7, 125.1, 126.9, 127.0, 128.5, 129.0, 132.5, 143.2, 152.9, 153.8; LRMS (FAB⁺) *m/z* 410 (M⁺, 10), 349 (100), 331 (70), 283 (90), 154 (65), 136 (50), 45 (85); HRMS (FAB⁺, M⁺) *m/z* calcd for C₂₀H₂₀O₅Cl₂ 410.0688, found 410.0687.

6-Chloro-1,2,3-trimethoxy-5H-dibenzo[*a,c*]cyclohepten-7-one (22). 1,1-Dichloro-1a,9b-dihydro-6,7,8-trimethoxy-1a-(methoxymethoxy)-1H-cyclopropa[*l*]phenanthrene (757 mg, 1.84 mmol) was dissolved in 12 mL of THF, 12 mL of *i*PrOH, and 12 mL of 2 M HCl. The reaction mixture was heated to 100 °C for 5 h. The solution was cooled to room temperature and the organic solvents were removed *in vacuo*. The remaining mixture was partitioned between 50 mL of ether and 50 mL

of water. The aqueous phase was extracted three times with ether (30 mL) and the combined organic extracts were dried, (MgSO_4), and evaporated to yield a yellow oil. Column chromatography (TLC R_f = 0.26, 4:1 hexanes/EtOAc) yielded a light yellow solid. Recrystallization (benzene/pentane) provided 407 mg of colorless crystals (67%) mp 141.1-141.8 °C. IR (CCl_4) 3064 (w), 3007 (m), 2963 (s), 2927 (s), 2850 (s), 1733 (m), 1672 (s), 1592 (s), 1492 (s), 1338 (s), 1151 (s), 1121 (s); ^1H NMR (CDCl_3) δ 3.44 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 6.75 (s, 1H), 7.50-7.59 (m, 2H), 7.57 (s, 1H), 7.78-7.80 (m, 1H), 8.02-8.04 (m, 1H); ^{13}C NMR (CDCl_3) δ 56.1, 61.2, 61.4, 108.6, 124.7, 127.8, 128.2, 128.4, 130.0, 131.7, 132.1, 133.1, 137.0, 139.6, 144.1, 152.9, 153.0, 188.3; LRMS (FAB^+) m/z 331 (M^+ , 30), 307 (22), 154 (35), 137 (100); HRMS (FAB^+ , M^+) m/z calcd for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Cl}$ 331.0737, found 331.0733.

5,6-Dihydro-1,2,3-trimethoxy-5H-dibenzo[a,c]cyclohepten-7-one (23). 6-Chloro-1,2,3-trimethoxy-5H-dibenzo[a,c]cyclohepten-7-one (36.5 mg, 0.110 mmol), sodium acetate (22.6 mg, 0.275 mmol), and palladium on carbon (5%, 11.7 mg, 5.52 μmol) were stirred in 5 mL of EtOH under 1 ATM of hydrogen for 1 h. The reaction mixture was filtered, and poured into 25 mL of ether. The organic layer was washed with water (25 mL x2) and brine (25 mL). The ethereal phase was dried (MgSO_4), and evaporated to yield a yellow oil. Column chromatography (TLC R_f = 0.21, 4:1 hexanes/EtOAc) yielded a colorless oil, which was recrystallized from hexane to provide 26.0 mg of white crystals (72%) mp 79.0-80.0 °C. IR (CCl_4) 3067, (w), 3000 (m), 2957 (m), 2933 (s), 2863 (m), 2836 (m), 1689 (s), 1599 (s), 1405 (s), 1348 (s), 1114 (s); ^1H NMR (CDCl_3) δ 2.64-2.67 (m, 1H), 2.88-3.09 (m, 3H), 3.50 (s, 3H), 3.90 (s, 3H), 3.91 (s, 3H), 6.61 (s, 1H), 7.37-7.41 (m, 1H), 7.51-7.79 (m, 3H); ^{13}C NMR (CDCl_3) δ 31.3, 48.4, 56.5, 61.4, 61.6, 107.4, 124.7, 127.8, 128.0, 131.2, 131.7, 134.4, 136.2, 139.9, 142.0, 152.7, 153.5, 207.5; LRMS (EI^+) m/z 298 (M^+ , 100), 283 (10), 241 (10); HRMS (EI^+ , M^+) m/z calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4$ 298.1205, found 298.1203.

5-Acetamido-5,6-dihydro-1,2,3-trimethoxy-5H-dibenzo[a,c]cycloheptene (24). Title compound was prepared from 114 mg (0.380 mmol) of 5,6-dihydro-1,2,3-trimethoxy-5H-dibenzo[a,c]cyclohepten-7-one according to the reductive amination/acylation protocol of Wulff and coworkers⁴ to yield 73.9 mg (57%) of the titled compound as a white solid mp 184.3-187.1 (lit. 185.2-187.6).⁵ The ^1H and ^{13}C NMR, and IR spectral data match those reported by Fagnou and coworkers.⁵

NCME System

2,3,4,4'-Tetramethoxy-6-(methanol)-biphenyl. Sodium borohydride (843 mg, 22.3 mmol) was added in small portions at 0 °C to a stirred solution of 6-carbaldehyde-2,3,4,4'-tetramethoxy-biphenyl (5.39 mg, 18.6 mmol) in 75 mL of MeOH. The reaction was stirred at room temperature overnight to consume all of the aldehyde, at which time the reaction mixture was poured into 100 mL of cold 1M HCl and extracted with ether (100 mL x3). The combined organic extracts were dried (MgSO_4), and evaporated to yield a yellow oil. Column chromatography (TLC R_f = 0.32, 1:1 hexanes/EtOAc) yielded 4.81 g of a white solid (85%) mp 81.0-82.0 °C. IR (CCl_4) 3613 (m), 3002 (w), 2957 (m), 2937 (m), 2902 (w), 2833 (m), 1597 (m), 1494 (s), 1245 (s); ^1H NMR (CDCl_3) δ 3.60 (s, 3H), 3.86 (s, 3H), 3.91 (s, 3H), 3.93 (s, 3H), 4.42 (s, 2H), 6.90 (s, 1H), 6.96 (d, J =8.4, 2H), 7.18 (d, J =8.4, 2H); ^{13}C NMR (CDCl_3) δ 55.2, 56.0, 60.9, 61.0, 63.2, 106.9, 113.6, 127.8, 128.0, 131.0, 134.7,

141.2, 151.3, 153.4, 158.7; LRMS (EI^+) m/z 304 (M^+ , 100), 287 (80), 256 (50); HRMS (EI^+ , M^+) m/z calcd for $\text{C}_{17}\text{H}_{20}\text{O}_5$ 304.1311, found 304.1324.

2,3,4,4'-Tetramethoxy-6-(bromomethyl)-biphenyl. Phosphorous tribromide (1.40 mL, 14.7 mmol) in 30 mL of CH_2Cl_2 was added dropwise to a cold (0 °C), stirred solution of 2,3,4,4'-tetramethoxy-6-(methanol)-biphenyl (6.05 g, 19.9 mmol) in 90 mL of CH_2Cl_2 . The reaction was stirred for 45 min at 0 °C, at which time the solution was poured into ice water and extracted with CH_2Cl_2 (50 mL, x2). The combined organic extracts were dried (MgSO_4), and evaporated to yield a yellow oil. Column chromatography (TLC R_f = 0.31, 4:1 hexanes/EtOAc) yielded 6.50 g of a white solid (89%) mp 73.0-74.0 °C. IR (CCl_4) 3037 (w), 2997 (m), 2957 (s), 2940 (s), 2903 (m), 2836 (s), 1599 (s), 1489 (s), 1335 (s), 1238 (s); ^1H NMR (CDCl_3) δ 3.58 (s, 3H), 3.87 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 4.29 (s, 2H), 6.82 (s, 1H), 6.97 (d, J =8.4, 2H), 7.25 (d, J =8.4, 2H); ^{13}C NMR (CDCl_3) δ 32.8, 55.2, 56.1, 60.9, 109.1, 113.6, 127.6, 129.4, 131.0, 131.5, 142.6, 151.7, 152.8, 158.8; LRMS (EI^+) m/z 366 (M^+ , 70), 287 (90), 256 (100), 241 (60); HRMS (EI^+ , M^+) m/z calcd for $\text{C}_{17}\text{H}_{19}\text{O}_4\text{Br}$ 366.0467, found 366.0484.

6-Acetonitrile-2,3,4,4'-tetramethoxy-biphenyl. 6-Carbaldehyde-2,3,4,4'-tetramethoxy-biphenyl (885 mg, 2.41 mmol) and potassium cyanide (188 mg, 2.89 mmol) were added to a round bottom flask. DMSO (15 mL) and water (2.5 mL) were added and the reaction heated to 60 °C for 3 h to consume all of the starting material (TLC). After cooling to room temperature, the reaction mixture was diluted with 75 mL of ether, and washed with water (75 mL x3) and once with brine. The ethereal phase was dried (MgSO_4), and evaporated to yield a yellow solid. Column chromatography (TLC R_f = 0.29, 4:1 hexanes/EtOAc) yielded 673 mg of a white solid (89%) mp 99-100 °C. IR (CCl_4) 3000 (s), 2971 (s), 2939 (s), 2835 (s), 2252 (m), 1595 (s), 1495 (s), 1456 (s), 1398 (m), 1333 (s), 1239 (s), 1100 (s); ^1H NMR (CDCl_3) δ 3.44 (s, 2H), 3.60 (s, 3H), 3.86 (s, 3H), 3.91 (s, 3H), 3.91 (s, 3H), 6.83 (s, 1H), 6.98 (d, J =8.0, 2H), 7.14 (d, J =8.0, 2H); ^{13}C NMR (CDCl_3) δ 22.1, 55.3, 56.2, 60.9, 61.0, 107.5, 114.1, 118.3, 124.1, 127.5, 128.8, 130.9, 142.1, 152.1, 153.1, 159.0; LRMS (EI^+) m/z 313 (M^+ , 100), 255 (10); HRMS (EI^+ , M^+) m/z calcd for $\text{C}_{18}\text{H}_{19}\text{O}_4\text{N}$ 313.1314, found 313.1311.

6-Acetic acid-2,3,4,4'-tetramethoxy-biphenyl (26). To 6-acetonitrile-2,3,4,4'-tetramethoxy-biphenyl (3.34 g, 11.0 mmol) in a round bottom flask was added 45 mL of 40% KOH and 45 mL of EtOH. The yellow solution was heated to 100 °C for 12 h. After cooling to room temperature, the reaction was poured into a separatory funnel and washed twice with 50 mL portions of ether. The aqueous layer was acidified with conc. HCl and extracted with 50 mL of CH_2Cl_2 three times. The combined CH_2Cl_2 extracts were dried (MgSO_4), and evaporated to yield 2.88 g of a white solid (79%) mp 144-146 °C. IR (CCl_4) 3300 (w), 3006 (m), 2958 (m), 2939 (m), 2835 (m), 1706 (s), 1489 (s), 1246 (s), 1107 (m); ^1H NMR (CDCl_3) δ 3.44 (s, 2H), 3.58 (s, 3H), 3.84 (s, 3H), 3.89 (s, 3H), 3.90 (s, 3H), 6.66 (s, 1H), 6.93 (d, J =8.0, 2H), 7.14 (d, J =8.0, 2H), 10.9 (br, 1H); ^{13}C NMR (CDCl_3) δ 38.5, 55.2, 56.0, 60.9, 61.0, 108.9, 113.6, 127.5, 128.5, 129.6, 131.2, 141.5, 151.8, 152.5, 158.7, 177.1; LRMS (EI^+) m/z 334 (M^+ + H, 25), 333 (M^+ , 100), 319 (10), 287 (10), 242 (15); HRMS (EI^+ , M^+) m/z calcd for $\text{C}_{18}\text{H}_{21}\text{O}_6$ 333.1338, found 333.1333.

2,3,4,4'-Tetramethoxy-9-phenanthrol (27). 6-Acetic acid-2,3,4,4'-tetramethoxy-biphenyl (1.00 g, 3.00 mmol) was stirred under argon in 12 mL of methanesulfonic acid for 2.5 h at room temperature. The reaction was then poured into 100 mL of

ice water and extracted three times with 75 mL of ether. The combined ether extracts were dried (MgSO_4), and evaporated to yield a brown solid which was quickly purified via column chromatography (TLC R_f = 0.39, 1:1 hexanes/EtOAc) to yield 707 mg of an off white solid (75%) mp 145-148 °C (decomp). IR (CCl_4) 3608 (m), 3505 (w), 3006 (w), 2964 (w), 2935 (w), 2828 (w), 1612 (s), 1476 (s), 1430 (m), 1278 (s), 1220 (s), 1100 (s); ^1H NMR (CDCl_3) δ 3.97, (s, 3H), 3.98 (s, 3H), 4.00 (s, 6H), 5.37 (s, 1H), 6.87 (s, 1H), 6.91 (s, 1H), 7.27-7.30 (d, J =9.6, 1H), 7.68 (s, 1H), 9.42 (s, J =9.6, 1H); ^{13}C NMR (CDCl_3) δ 55.3, 55.8, 60.2, 61.3, 102.4, 103.5, 106.6, 115.3, 117.5, 125.6, 126.4, 128.4, 129.4, 141.0, 148.9, 151.9, 152.1, 157.2; LRMS (EI^+) m/z 315 ($\text{M}^+ + \text{H}$, 100), 284 (15); HRMS (EI^+ , $\text{M}^+ + \text{H}$) m/z calcd for $\text{C}_{18}\text{H}_{19}\text{O}_5$ 315.1233, found 315.1228.

2,3,4,4'-Tetramethoxy-9-(methoxymethoxy)-phenanthrene (28). 2,3,4,4'-Tetramethoxy-9-phenanthrol (611 mg, 1.94 mmol) was dissolved in 10 mL of CH_2Cl_2 . To this solution was added 711 μL (5.83 mmol) of chloromethylmethyl ether, followed by 633 μL (5.83 mmol) of diisopropylethylamine. The reaction was stirred for 12 h, at which time it was diluted with 50 mL of CH_2Cl_2 and washed with 50 mL of 1M HCl, 50 mL of water, and 50 mL of brine. The organic phase was dried (MgSO_4), and evaporated to yield a yellow solid. Column chromatography (TLC R_f = 0.21, 4:1 hexanes/EtOAc) yielded 459 mg of a white solid (66%) mp 109-110 °C. IR (CCl_4) 3000 (w), 3958 (m), 2932 (m), 2903 (w), 2841 (w), 1615 (s), 1498 (m), 1466 (s), 1272 (s), 1227 (s), 1155 (s), 1058 (s); ^1H NMR (CDCl_3) δ 3.58 (s, 3H), 3.98 (s, 6H), 3.99 (s, 3H), 4.00 (s, 3H), 5.47 (s, 2H), 7.01 (s, 1H), 7.22 (s, 1H), 7.28 (d, J =9.2, 1H), 7.74 (s, 1H), 9.42 (d, J =9.2, 1H); ^{13}C NMR (CDCl_3) δ 55.3, 55.8, 56.2, 60.2, 61.3, 94.7, 102.6, 104.5, 106.6, 115.4, 117.1, 125.3, 127.5, 128.3, 129.4, 141.3, 150.3, 151.7, 151.9, 157.2; LRMS (EI^+) m/z 359 ($\text{M}^+ + \text{H}$, 50), 252 (100), 136 (90); HRMS (EI^+ , $\text{M}^+ + \text{H}$) m/z calcd for $\text{C}_{20}\text{H}_{23}\text{O}_6$ 359.1495, found 359.1508.

5,6-Dihydro-1,2,3,4'-tetramethoxy-5H-dibenzo[a,c]cyclohepten-7-one (29). 2,3,4,4'-Tetramethoxy-9-(methoxymethoxy)-phenanthrene (286 mg, 0.798 mmol) and 18.1 mg (0.0798 mmol) of benzyltriethylammonium chloride were vigorously stirred in 8 mL of CHCl_3 . To this suspension was added 1.6 mL of 50% NaOH and the reaction was stirred for a further 6 h to consume all of the starting material. The reaction was then partitioned between 75 mL of CH_2Cl_2 and 50 mL of water. The aqueous layer was subsequently extracted with three 50 mL portions of CH_2Cl_2 . The combined organic extracts were dried (MgSO_4) and filtered through a short pad of silica gel. Evaporation of the solvent yielded a yellow oil that was dissolved in 3 mL of THF. Isopropyl alcohol (3 mL) was added, followed by 3 mL of 2M HCl. The yellow solution was heated to 100 °C for 12 h. The THF and isopropyl alcohol were removed in vacuo, and 50 mL of ether and water were added. The aqueous phase was extracted twice with ether. The combined organic extracts were dried (MgSO_4) and filtered through a short pad of silica gel. Evaporation of the solvent yielded a yellow oil which was dissolved in 10 mL of EtOH. Sodium acetate (164 mg, 1.99 mmol) and palladium on carbon (5%, 84.9 mg, 0.0399 mmol) were added and the reaction mixture was stirred under 1 ATM of hydrogen for 1 h. The reaction mixture was filtered, and poured into 25 mL of ether. The organic layer was washed with water (25 mL x2) and brine (25 mL). The ethereal phase was dried (MgSO_4), and evaporated to yield a colorless oil. Column chromatography (TLC R_f = 0.15, 4:1 hexanes/EtOAc) yielded a colorless oil, which crystallized on standing to provide 139 mg of white crystals (53%, 3 steps) mp 135-136 °C (lit. 134-135 °C).⁶ The ^1H NMR matched that reported by Lee and coworkers. IR (CCl_4) 3006 (w), 2961 (m), 2932 (s), 2861 (w), 2832 (m), 1686 (s), 1605 (s), 1489 (s), 1408 (s), 1104 (s); ^{13}C NMR (CDCl_3) δ 30.5, 49.5, 56.2, 57.1, 61.2, 61.9, 109.2, 111.5, 117.8, 118.5, 119.8, 120.2, 127.1,

129.2, 133.1, 134.2, 135.1, 137.2, 207.2; LRMS (EI^+) m/z 329 ($\text{M}^+ + \text{H}$, 100), 279 (10), 242 (10); HRMS (EI^+ , $\text{M}^+ + \text{H}$) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{O}_5$ 329.1389, found 329.1391.

***N*-Acetylcolchinol methyl ether (2).** Title compound was prepared from 114 mg (0.347 mmol) of 5,6-dihydro-1,2,3,4'-tetramethoxy-5*H*-dibenzo[*a,c*]cyclohepten-7-one according to the reductive amination/acylation protocol of Wulff and coworkers.⁴ Column chromatography (TLC R_f = 0.27 40% acetone/pentane) yielded 78.7 mg (61%) of a white solid mp 203-204 °C (lit. 204-205 °C).⁶ In CDCl_3 , two atropisomers were observed in approximately a 5:2 ratio, however, only one isomer is observed in DMSO. IR (CCl_4) 3447 (m), 3000 (w), 2929 (m), 2861 (w), 2838 (w), 1699 (s), 1686 (s), 1485 (s), 1246 (m), 1110 (m); ^1H NMR (DMSO) δ 1.81-1.89 (m, 2H), 1.88 (s, 3H), 2.00-2.19 (m, 2H), 3.46 (s, 3H), 3.77 (s, 3H), 3.79 (s, 3H), 3.82 (s, 3H), 4.48-4.56 (m, 1H), 6.77 (s, 1H), 6.88 (s, 1H), 7.09 (br, 1H, D_2O exchangeable) 7.24 (d, $J=8.4$, 1H), 8.38 (d, $J=8.4$, 1H); ^{13}C NMR (DMSO) δ 23.5, 31.0, 49.0, 55.8, 56.7, 61.4, 61.4, 80.1, 108.9, 110.3, 111.6, 125.2, 127.0, 131.4, 135.6, 141.4, 142.7, 151.2, 153.0, 159.2, 169.2; LRMS (EI^+) m/z 372 ($\text{M}^+ + \text{H}$, 100), 314 (10), 313 (40); HRMS (EI^+ , $\text{M}^+ + \text{H}$) m/z calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_5$ 372.1811, found 372.1812. The ^1H NMR spectral data matched that reported by Lee and coworkers.⁶

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¹H NMR spectrum (CDCl₃) of compound 9. The spectrum shows peaks in the aromatic region (7.240–8.668 ppm) and two aliphatic singlets (3.580 and 5.481 ppm). Integration values are provided for the aromatic signals.

Chemical Shift (ppm)	Integration
8.668, 8.647, 8.594, 8.573, 8.386, 8.366	2.0861
7.787, 7.782, 7.765, 7.677, 7.656, 7.640, 7.621, 7.533, 7.529, 7.521, 7.515, 7.510, 7.505, 7.280, 7.240	5.9971
5.481	2.1985
3.580	3.0000

Chemical structure of compound 9: COc1ccc2cc3ccccc3cc2c1

S14

S17

Integral
S19

ppm

S20

S22

S24

S25

200 180 160 140 120 100 80 60 40 20

ppm

19

152.674
152.472
150.747

141.265

131.046
130.635
127.242
126.579
125.963
125.331
121.905
115.209

106.030
104.479

94.618

77.333
77.015
76.698

61.304
60.288
56.248
55.810

S30

ppm

180

160

140

120

100

80

60

40

20

0

93.1

22

188.334

153.022
152.996

144.063
139.616
137.044
133.115
132.110
131.661
130.005
128.410
128.202
127.752
124.740

108.649

77.366
77.253
77.048
76.730

61.395
61.201
56.097

0.001

S34

180

160

140

120

100

80

60

40

20

24

207

169.988
167.967153.024
152.722
151.289
142.347
138.912
135.994
134.715
134.418
131.351
130.217
129.059
127.500
127.304
127.251
126.538
125.871
124.973
121.978
107.941
107.59177.340
77.224
77.022
75.70561.312
61.243
61.111
60.585
56.104
52.531
49.24040.997
39.79630.797
30.55423.408
23.324

S36

ppm
S41
180
160
140
120
100
80
60
40
20
0

157.245
151.969
151.721
150.301

141.325

129.377
128.313
127.480
125.319

117.144
115.392

106.633
104.487
102.595

94.691

77.334
77.219
77.016
76.698

61.291
60.229
56.231
55.801
55.338

30.941

0.248
-0.003
-0.256

S44

ppm

180

160

140

120

100

80

60

40

20

0

169.233

159.223

152.958

151.188

142.681

141.419

135.610

131.449

127.005

125.150

111.592

110.311

108.947

80.061

61.406

61.356

56.685

55.841

48.958

41.021

40.812

40.603

40.394

40.185

39.977

39.768

39.376

31.002

23.544