SUPPLEMENTARY MATERIAL

Synthesis of Highly Oxygenated Dinaphthyl Ethers *via* S_NAr Reactions Promoted by Barton's Base

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Experimental parts and spectral data for all new compounds. ¹H and ¹³C NMR spectra for **9**, **11**, **13**, **15**, **17**, **19**, **21**, **23**, **25**, **27** and **29–33**.

General: All reactions were performed in flame-dried or oven-dried glassware under a dry nitrogen atmosphere. THF and ether were distilled over Na/benzophenone; CH₂Cl₂ was purified by passage through a column of activated alumina. All other reagents and solvents were used as received unless otherwise noted. NMR spectra were recorded in CDCl₃ (unless otherwise noted) at either 300 MHz (¹H NMR) or 75 MHz (¹³C NMR) using Bruker Avance 300 with XWIN-NMR software. Melting points were determined on a Mel-Temp II and are uncorrected.

4-(Naphthalen-1-yloxy)-naphthalene-1-carbaldehyde (9). To a solution of 1-naphthol (**7**, 158 mg, 1.10 mmol) and 4-fluoro-1-naphthalenecarbaldehyde¹ (**8**, 174 mg, 1.00 mmol) in CH₃CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine² (0.24 mL, 1.20 mmol). The reaction mixture was heated at 70 °C for 1 h, cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Chromatography on SiO₂ (hexanes/EtOAc, 4:1) afforded 293 mg (98%) of **9** as a yellow oil: IR (neat) 2851, 2725, 1684, 1568, 1510, 1429, 1388, 1240 cm⁻¹; ¹H NMR δ 10.17 (s, 1 H), 9.47 (d, 1 H, *J* = 8.4 Hz), 8.68 (d, 1 H, *J* = 8.4 Hz), 8.01 (d, 1 H, *J* = 8.4 Hz), 7.96 (d, 1 H, *J* = 8.2 Hz), 7.82-7.78 (m, 1 H), 7.81 (d, 1 H, *J* = 8.2 Hz), 7.73-7.67 (m, 1 H), 7.64 (d, 1 H, *J* = 8.0 Hz), 7.58-7.48 (m, 2 H), 7.45-7.40 (m, 1 H), 7.25 (d, 1 H, *J* = 7.4 Hz), 6.63 (d, 1 H, *J* = 8.0 Hz); ¹³C NMR δ 192.3, 160.2, 150.7, 138.9, 135.2, 132.3, 130.0, 128.2, 127.1, 127.0, 126.7,

126.2, 126.0, 125.6, 125.2, 122.4, 121.7, 116.9, 108.3; MS (EI) m/z (rel intensity) 298 (M^+ , 100), 269 (24), 239 (22), 134 (12), 127 (28), 115 (23); HRMS (EI) calcd for $C_{21}H_{14}O_2$ 298.0994, found 298.0993.

4-(5-Methoxy-8-formylnaphthalen-1-yloxy)-naphthalene-1-carbaldehyde

(11). To a solution of 8-hydroxy-4-methoxynaphthalene-1-carbaldehyde³ (**10**, 127 mg, 0.63 mmol) and 4-fluoro-1-naphthalenecarbaldehyde (**8**, 100 mg, 0.57 mmol) in CH_3CN (2 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (0.14 mL, 0.68 mmol). The reaction mixture was heated at 70 °C for 1 h, additional Barton's base (0.06 mL, 0.28 mmol) was added, and heating was continued for 2 h. The reaction mixture was then cooled to room temperature, poured into 1.0 M HCl (8 mL), and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layer was washed with H_2O (10 mL), dried (MgSO_4), and concentrated under reduced pressure. The residue was passed through a 1" pad of SiO_2 (CH_2Cl_2) to provide 173 mg (85%) of **11** as a yellow solid: mp 181-182 °C (CH_2Cl_2); IR (neat) 2729, 1678, 1573, 1508, 1411, 1320, 1220 cm^{-1} ; ^1H NMR δ 10.89 (s, 1 H), 10.22 (s, 1 H), 9.35 (d, 1 H, $J = 8.4$ Hz), 8.48 (d, 1 H, $J = 8.4$ Hz), 8.32 (dd, 1 H, $J = 8.4, 1.1$ Hz), 8.19 (d, 1 H, $J = 8.3$ Hz), 7.80-7.75 (m, 1 H), 7.78 (d, 1 H, $J = 8.0$ Hz), 7.70-7.64 (m, 1 H), 7.52 (t, 1 H, $J = 8.0$ Hz), 7.30 (dd, 1 H, $J = 7.6, 1.1$ Hz), 6.98 (d, 1 H, $J = 8.3$ Hz), 6.75 (d, 1 H, $J = 8.0$ Hz), 4.10 (s, 3 H); ^{13}C NMR δ 192.4, 192.3, 160.3, 159.0, 151.9, 138.3, 132.6, 131.4, 130.3, 128.0, 127.7, 127.2, 126.6, 126.4, 126.2, 126.1, 125.3, 122.3, 120.7, 120.3, 109.9,

104.5, 56.4; MS (EI) m/z (rel intensity) 356 (M^+ , 8), 302 (8), 287 (13), 252 (8), 200 (11), 185 (23), 149 (40); HRMS (EI) calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1037.

4-(Naphthalen-2-yloxy)-naphthalene-1-carbaldehyde (13). To a solution of 2-naphthol (**12**, 158 mg, 1.10 mmol) and 4-fluoro-1-naphthalenecarbaldehyde (**8**, 174 mg, 1.00 mmol) in CH₃CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (0.24 mL, 1.20 mmol). The reaction mixture was heated at 70 °C for 1 h, cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Chromatography on SiO₂ (hexanes/EtOAc, 4:1) afforded 290 mg (97%) of **13** as a pale yellow solid: mp 74-75 °C (hexanes/EtOAc); IR (neat) 2853, 2726, 1684, 1571, 1509, 1461, 1430, 1244 cm⁻¹; ¹H NMR δ 10.24 (s, 1 H), 9.40 (d, 1 H, J = 8.5 Hz), 8.54 (d, 1 H, J = 8.5 Hz), 7.95 (d, 1 H, J = 8.9 Hz), 7.94-7.89 (m, 1 H), 7.82-7.76 (m, 2 H), 7.81 (d, 1 H, J = 8.0 Hz), 7.67 (ddd, 1 H, J = 8.4, 6.9, 1.2 Hz), 7.59 (d, 1 H, J = 2.4 Hz), 7.57-7.48 (m, 2 H), 7.35 (dd, 1 H, J = 8.9, 2.4 Hz), 6.84 (d, 1 H, J = 8.0 Hz); ¹³C NMR δ 192.4, 160.0, 153.0, 138.7, 134.5, 132.5, 131.3, 130.6, 130.1, 128.1, 127.6, 127.1, 127.0, 126.5, 126.2, 125.8, 125.2, 122.6, 120.8, 117.4, 109.2; MS (EI) m/z (rel intensity) 298 (M^+ , 100), 269

(23), 241 (34), 134 (13), 127 (39), 115 (27); HRMS (EI) calcd for $C_{21}H_{14}O_2$ 298.0994, found 298.0991.

4-(5-Methoxynaphthalen-1-yloxy)-naphthalene-1-carbaldehyde (15). To a solution of 5-methoxy-1-naphthol³ (**14**, 191 mg, 1.10 mmol) and 4-fluoro-1-naphthalenecarbaldehyde (**8**, 174 mg, 1.00 mmol) in CH_3CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (0.24 mL, 1.20 mmol). The reaction mixture was heated at 70 °C for 1 h, cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layer was washed with H_2O (10 mL), dried (MgSO_4), and concentrated under reduced pressure. Trituration of the residue with cold hexanes/EtOAc (4:1) afforded 275 mg (84%) of **15** as a beige solid: mp 132-133 °C (hexanes/EtOAc); IR (neat) 2851, 2726, 1682, 1570, 1505, 1398, 1261 cm^{-1} ; ^1H NMR δ 10.20 (s, 1 H), 9.40 (d, 1 H, $J = 8.5$ Hz), 8.67 (d, 1 H, $J = 8.4$ Hz), 8.24 (d, 1 H, $J = 8.5$ Hz), 7.83-7.78 (m, 1 H), 7.73 (d, 1 H, $J = 8.1$ Hz), 7.73-7.68 (m, 1 H), 7.53 (d, 1 H, $J = 8.4$ Hz), 7.50 (d, 1 H, $J = 8.4$ Hz), 7.37-7.27 (m, 2 H), 6.88 (d, 1 H, $J = 7.6$ Hz), 6.62 (d, 1 H, $J = 8.1$ Hz), 4.05 (s, 3 H); ^{13}C NMR δ 192.5, 160.6, 155.9, 150.6, 139.1, 132.5, 130.1, 128.3, 127.7, 127.2, 127.1, 126.3, 125.7, 125.4, 122.6, 120.1, 118.0, 114.0, 108.3, 105.0, 55.9; MS (EI) m/z (rel intensity) 328 (M^+ , 100), 285 (17), 255 (10), 239 (8), 142 (9), 127 (15), 114 (14); HRMS (EI) calcd for $C_{22}H_{16}O_3$ 328.1099, found 328.1106.

4-(4-Methoxynaphthalen-1-yloxy)-naphthalene-1-carbaldehyde (17). To a solution of 4-methoxy-1-naphthol (**16**, 191 mg, 1.10 mmol) and 4-fluoro-1-naphthalenecarbaldehyde (**8**, 174 mg, 1.00 mmol) in CH₃CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (0.24 mL, 1.2 mmol). The reaction mixture was heated at 70 °C for 1 h, cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Trituration of the residue with cold hexanes/EtOAc (4:1) afforded 251 mg (77%) of **17** as a light brown solid: mp 174-175 °C (hexanes/EtOAc); IR (neat) 2841, 2729, 1683, 1570, 1509, 1460, 1385, 1234 cm⁻¹; ¹H NMR δ 10.18 (s, 1 H), 9.40 (dd, 1 H, *J* = 8.5, 0.6 Hz), 8.71 (d, 1 H, *J* = 8.5 Hz), 8.35 (dd, 1 H, *J* = 8.4, 0.6 Hz), 7.84-7.78 (m, 2 H), 7.73-7.69 (m, 1 H), 7.70 (d, 1 H, *J* = 8.0 Hz), 7.54-7.51 (m, 1 H), 7.46-7.41 (m, 1 H), 7.22 (d, 1 H, *J* = 8.3 Hz), 6.83 (d, 1 H, *J* = 8.3 Hz), 6.59 (d, 1 H, *J* = 8.0 Hz), 4.06 (s, 3 H); ¹³C NMR δ 192.4, 161.2, 153.6, 143.7, 139.2, 132.5, 130.1, 127.9, 127.4, 127.1, 127.0, 126.4, 126.0, 125.5, 125.3, 122.8, 122.6, 121.6, 117.6, 107.5, 103.4, 56.0; MS (EI) *m/z* (rel intensity) 328 (M⁺, 100), 313 (20), 268 (6), 239 (8), 174 (19), 127 (32); HRMS (EI) calcd for C₂₂H₁₆O₃ 328.1099, found 328.1099.

4-(2-Methoxynaphthalen-1-yloxy)-naphthalene-1-carbaldehyde (19). To a solution of 2-methoxy-1-naphthol⁴ (**18**, 191 mg, 1.10 mmol) and 4-fluoro-1-naphthalenecarbaldehyde (**8**, 174 mg, 1.00 mmol) in CH₃CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (0.24 mL, 1.20 mmol). The reaction mixture was heated at 70 °C for 1 h, cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Chromatography on SiO₂ (hexanes/EtOAc, 7:3) afforded 260 mg (79%) of **19** as a white solid: mp 112-113 °C (hexanes/EtOAc); IR (neat) 2841, 2726, 1682, 1570, 1510, 1377, 1276, 1218 cm⁻¹; ¹H NMR δ 10.18 (s, 1 H), 9.41 (dd, 1 H, *J* = 8.4, 1.2 Hz), 8.78 (dt, 1 H, *J* = 8.4, 0.8 Hz), 7.91-7.78 (m, 4 H), 7.76-7.70 (m, 1 H), 7.71 (d, 1 H, *J* = 8.1 Hz), 7.46-7.39 (m, 3 H), 6.48 (d, 1 H, *J* = 8.1 Hz), 3.89 (s, 3 H); ¹³C NMR δ 192.5, 160.0, 148.7, 139.4, 135.9, 132.5, 130.0, 129.9, 128.6, 128.2, 127.4, 127.2, 127.0, 126.0, 125.3, 124.8, 122.8, 120.9, 115.0, 106.4, 57.1; MS (EI) *m/z* (rel intensity) 328 (M⁺, 100), 285 (23), 268 (37), 257 (17), 239 (27), 228 (22), 173 (17), 127 (37); HRMS (EI) calcd for C₂₂H₁₆O₃ 328.1099, found 328.1092.

4-(4,8-Dimethoxynaphthalen-1-yloxy)-naphthalene-1-carbaldehyde (21).

To a solution of 4,8-dimethoxy-1-naphthol³ (**20**, 180 mg, 0.88 mmol) and 4-fluoro-1-naphthalenecarbaldehyde (**8**, 140 mg, 0.80 mmol) in CH₃CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (0.20 mL, 0.96 mmol). The reaction mixture was heated at 70 °C for 1 h, additional Barton's base (0.09 mL, 0.44 mmol) was added, and heating was continued for 2 h. The reaction mixture was then cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Trituration of the residue with cold hexanes/EtOAc (4:1) afforded 159 mg (56%) of **21** as a beige solid: mp 203-204 °C (hexanes/EtOAc); IR (neat) 2835, 2723, 1680, 1599, 1570, 1510, 1410, 1269 cm⁻¹; ¹H NMR δ 10.14 (s, 1 H), 9.37 (d, 1 H, *J* = 8.4 Hz), 8.67 (d, 1 H, *J* = 8.4 Hz), 7.94 (d, 1 H, *J* = 8.5 Hz), 7.80-7.74 (m, 1 H), 7.71-7.65 (m, 1 H), 7.68 (d, 1 H, *J* = 8.1 Hz), 7.41 (t, 1 H, *J* = 8.3 Hz), 7.19 (d, 1 H, *J* = 8.3 Hz), 6.87 (d, 1 H, *J* = 8.3 Hz), 6.75 (d, 1 H, *J* = 7.8 Hz), 6.39 (d, 1 H, *J* = 8.1 Hz), 4.05 (s, 3 H), 3.22 (s, 3 H); ¹³C NMR δ 192.6, 162.6, 155.5, 153.5, 142.9, 139.7, 132.4, 129.8, 129.1, 126.6, 126.5, 125.6, 125.0, 123.2, 119.9, 119.6, 114.9, 107.2, 106.4, 104.3, 56.1, 55.7; MS (EI) *m/z* (rel intensity) 358 (M⁺, 100), 343 (24), 299 (7), 283 (9), 271 (6), 157 (11), 127 (20); HRMS (EI) calcd for C₂₃H₁₈O₄ 358.1205, found 358.1204.

4-(5,8-Dimethoxynaphthalen-1-yloxy)-naphthalene-1-carbaldehyde (23).

To a solution of 5,8-dimethoxy-1-naphthol⁵ (**22**, 133 mg, 0.65 mmol) and 4-fluoro-1-naphthalenecarbaldehyde (**8**, 103 mg, 0.59 mmol) in CH₃CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (0.14 mL, 0.71 mmol). The reaction mixture was heated at 70 °C for 1 h, additional Barton's base (0.06 mL, 0.33 mmol) was added, and heating was continued for 2 h. The reaction mixture was then cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Trituration of the residue with cold hexanes/EtOAc (4:1) afforded 86 mg (41%) of **23** as a beige solid: mp 165-166 °C (hexanes/EtOAc); IR (neat) 2835, 2725, 1680, 1598, 1571, 1507, 1409, 1267 cm⁻¹; ¹H NMR δ 10.14 (s, 1 H), 9.39 (d, 1 H, *J* = 8.4 Hz), 8.68 (d, 1 H, *J* = 8.4 Hz), 8.27 (dd, 1 H, *J* = 8.5, 1.2 Hz), 7.81-7.75 (m, 1 H), 7.71-7.66 (m, 1 H), 7.67 (d, 1 H, *J* = 8.1 Hz), 7.56 (dd, 1 H, *J* = 8.4, 7.5 Hz), 7.32 (dd, 1 H, *J* = 7.5, 1.2 Hz), 6.74 (d, 1 H, *J* = 8.5 Hz), 6.62 (d, 1 H, *J* = 8.5 Hz), 6.34 (d, 1 H, *J* = 8.1 Hz), 3.98 (s, 3 H), 3.20 (s, 3 H); ¹³C NMR δ 192.6, 162.2, 149.6, 149.5, 149.4, 139.6, 132.4, 129.8, 129.3, 126.7, 126.2, 125.6, 125.2, 125.0, 123.2, 121.0, 120.6, 120.2, 106.5, 106.4, 104.6, 56.2, 56.0; MS (EI) *m/z* (rel intensity) 358 (M⁺, 100), 327 (7), 311 (28), 283 (18), 255 (6), 171 (9), 115 (10); HRMS (EI) calcd for C₂₃H₁₈O₄ 358.1205, found 358.1215.

1-(Naphthalen-1-yloxy)-naphthalene-2-carbaldehyde (25). To a solution of 1-naphthol (**7**, 158 mg, 1.10 mmol) and 1-fluoro-2-naphthalenecarbaldehyde⁶ (**24**, 174 mg, 1.00 mmol) in CH₃CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (0.24 mL, 1.20 mmol). The reaction mixture was heated at 70 °C for 1 h, cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Chromatography on SiO₂ (hexanes/EtOAc, 4:1) afforded 240 mg (81%) of **25** as a yellow solid: mp 103-104 °C (hexanes/EtOAc); IR (neat) 2855, 2741, 1697, 1679, 1626, 1597, 1572, 1376, 1230 cm⁻¹; ¹H NMR δ 10.45 (s, 1 H), 8.73 (d, 1 H, *J* = 7.7 Hz), 8.07 (d, 1 H, *J* = 8.6 Hz), 8.03 (d, 1 H, *J* = 8.4 Hz), 7.95 (d, 2 H, *J* = 8.6 Hz), 7.86 (d, 1 H, *J* = 8.6 Hz), 7.72-7.61 (m, 3 H), 7.55 (d, 1 H, *J* = 8.3 Hz), 7.45-7.41 (m, 1 H), 7.17 (t, 1 H, *J* = 8.0 Hz), 6.36 (dd, 1 H, *J* = 7.7, 0.8 Hz); ¹³C NMR δ 189.4, 156.8, 156.3, 138.4, 135.0, 129.8, 128.5, 128.0, 127.7, 127.5, 127.3, 126.6, 126.3, 125.8, 124.6, 123.6, 122.7, 122.6, 121.6, 108.5; MS (EI) *m/z* (rel intensity) 298 (M⁺, 43), 281 (6), 268 (8), 239 (12), 170 (100), 128 (92), 115 (22); HRMS (EI) calcd for C₂₁H₁₄O₂ 298.0994, found 298.0998.

1-[4-(Naphthalen-1-yloxy)-naphthalen-1-yl]-ethanone (27). To a solution of 1-naphthol (**7**, 158 mg, 1.10 mmol) and 1-(4-fluoronaphthalen-1-yl)-ethanone⁷ (**26**, 188 mg, 1.00 mmol) in CH₃CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (0.24 mL, 1.20 mmol). The reaction mixture was heated at 70 °C for 1 h, additional Barton's base (0.10 mL, 0.50 mmol) was added, and heating was continued for 2 h. The reaction mixture was then cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Chromatography on SiO₂ (hexanes/EtOAc, 4:1) followed by recrystallization (hexanes/EtOAc, 9:1) afforded 250 mg (80%) of **27** as a white solid: mp 103-104 °C (hexanes/EtOAc); IR (neat) 3055, 1670, 1569, 1507, 1424, 1388, 1231 cm⁻¹; ¹H NMR δ 9.08 (d, 1 H, *J* = 8.3 Hz), 8.61 (dd, 1 H, *J* = 8.3, 0.9 Hz), 8.06 (d, 1 H, *J* = 8.3 Hz), 7.95 (d, 1 H, *J* = 8.2 Hz), 7.82 (d, 1 H, *J* = 8.2 Hz), 7.79-7.71 (m, 2 H), 7.67-7.61 (m, 1 H), 7.58-7.53 (m, 1 H), 7.48-7.43 (m, 1 H), 7.47 (d, 1 H, *J* = 8.2 Hz), 7.18 (dd, 1 H, *J* = 7.5, 0.9 Hz), 6.61 (d, 1 H, *J* = 8.2 Hz), 2.68 (s, 3 H); ¹³C NMR δ 200.4, 158.5, 151.6, 135.3, 132.5, 131.1, 129.5, 129.2, 128.2, 127.0, 126.7, 126.2, 126.1, 125.2, 122.3, 122.0, 116.3, 108.5, 29.7; MS (EI) *m/z* (rel intensity) 312 (M⁺, 78), 297 (100), 268 (13), 239 (17), 149 (12), 127 (18), 115 (11); HRMS (EI) calcd for C₂₂H₁₆O₂ 312.1150, found 312.1154.

4-(Naphthalen-1-yloxy)-1-nitronaphthalene (29). To a solution of 1-naphthol (**7**, 158 mg, 1.10 mmol) and 4-fluoro-1-nitronaphthalene⁸ (**28**, 191 mg, 1.00 mmol)

in CH₃CN (3 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3,-tetramethylguanidine (0.24 mL, 1.20 mmol). The reaction mixture was stirred at room temperature for 1 h, cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Chromatography on SiO₂ (hexanes/EtOAc, 4:1) followed by recrystallization (hexanes/EtOAc, 9:1) afforded 278 mg (88%) of **29** as a yellow solid: mp 104-105 °C (hexanes/EtOAc); IR (neat) 3061, 1567, 1511, 1425, 1322, 1261, 1240 cm⁻¹; ¹H NMR δ 8.83 (d, 1 H, *J* = 8.7 Hz), 8.71 (d, 1 H, *J* = 8.5 Hz), 8.19 (d, 1 H, *J* = 8.7 Hz), 7.97-7.92 (m, 2 H), 7.88-7.81 (m, 2 H), 7.77-7.71 (m, 1 H), 7.59-7.43 (m, 2 H), 7.55 (d, 1 H, *J* = 7.5 Hz), 7.25 (dd, 1 H, *J* = 7.5, 1.0 Hz), 6.57 (d, 1 H, *J* = 8.7 Hz); ¹³C NMR δ 160.1, 150.7, 140.7, 135.4, 130.6, 128.4, 127.5, 127.4, 127.2, 127.0, 126.6, 126.1, 126.0, 125.9, 123.9, 122.9, 121.7, 117.1, 107.5; MS (EI) *m/z* (rel intensity) 315 (M⁺, 100), 285 (11), 268 (37), 239 (38), 134 (17), 127 (47), 115 (26); HRMS (EI) calcd for C₂₀H₁₃NO₃ 315.0895, found 315.0898.

8-Methoxy-4-(naphthalen-1-yloxy)-naphthalene-1-carbaldehyde (31). To a solution of 1-naphthol (**7**, 158 mg, 1.10 mmol) and fluoronaphthalene **30** (204 mg, 1.00 mmol) in CH₃CN (4 mL) was added at room temperature 2-*tert*-butyl-1,1,3,3,-tetramethylguanidine (0.24 mL, 1.20 mmol). The reaction mixture was heated at 70 °C for 1 h, additional Barton's base (0.10 mL, 0.50 mmol) was added, and heating

was continued for 2 h. The reaction mixture was then cooled to room temperature, poured into 1.0 M HCl (10 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with H₂O (10 mL), dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue on SiO₂ (hexanes/EtOAc, 7:3) afforded 284 mg (87%) of **31** as a beige solid: mp 125-126 °C (hexanes/EtOAc); IR (neat) 2965, 2837, 1674, 1513, 1390, 1324, 1260, 1226 cm⁻¹; ¹H NMR δ 11.09 (d, 1 H, *J* = 0.6 Hz), 8.23 (dd, 1 H, *J* = 8.5, 0.9 Hz), 8.04 (d, 1 H, *J* = 7.9 Hz), 7.93 (d, 1 H, *J* = 8.9 Hz), 7.90 (d, 1 H, *J* = 8.3 Hz), 7.76 (d, 1 H, *J* = 8.3 Hz), 7.57 (d, 1 H, *J* = 8.3 Hz), 7.57-7.52 (m, 1 H), 7.48-7.42 (m, 1 H), 7.46 (d, 1 H, *J* = 8.2 Hz), 7.14 (dd, 1 H, *J* = 7.5, 0.9 Hz), 7.11 (d, 1 H, *J* = 8.9 Hz), 6.73 (d, 1 H, *J* = 8.2 Hz), 4.06 (s, 3 H); ¹³C NMR δ 194.7, 158.7, 156.8, 151.6, 135.3, 129.8, 128.9, 128.3, 127.6, 127.0, 126.8, 126.6, 126.1, 125.4, 125.2, 121.9, 116.1, 115.5, 110.5, 108.2, 56.0; MS (EI) *m/z* (rel intensity) 328 (M⁺, 66), 272 (67), 159 (52), 134 (83), 121 (100), 115 (28); HRMS (EI) calcd for C₂₂H₁₆O₃ 328.1099, found 328.1107.

4-(5-Methoxy-8-hydroxynaphthalen-1-yloxy)-naphth-1-ol (32). To a solution of dialdehyde **11** (770 mg, 2.16 mmol) in CH₂Cl₂ (40 mL) was added 70% *m*-CPBA (1.60 g, 6.48 mmol). The reaction mixture was stirred at room temperature for 15 h, then a solution of 10% Na₂S₂O₃ (40 mL) was added and stirring was continued for 1 h. The organic phase was separated and diluted with CH₂Cl₂,

washed with saturated aqueous NaHCO_3 , dried (MgSO_4), and concentrated under reduced pressure. The residue was dissolved in 1:1 MeOH/THF (30 mL) and cooled to 0 °C. A solution of KOH (730 mg, 12.9 mmol) in MeOH (3 mL) was added dropwise. After stirring at 0 °C for 15 min, the reaction mixture was acidified with 10% HCl, poured into H_2O (40 mL), and extracted with CH_2Cl_2 . The organic layer was washed with H_2O , dried (MgSO_4), and concentrated under reduced pressure. Chromatography on SiO_2 (hexanes/EtOAc, 7:3) gave 460 mg (64%) of **32** as a white solid: mp 218-219 °C (hexanes/EtOAc); IR (neat) 3440 (br), 1609, 1461, 1404, 1263, 1230, 1066 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.29 (s, 1 H), 8.87 (s, 1 H), 8.36-8.33 (m, 1 H), 7.91-7.85 (m, 2 H), 7.58-7.48 (m, 2 H), 7.25 (d, 1 H, J = 8.2 Hz), 7.19 (dd, 1 H, J = 8.4, 7.8 Hz), 7.00 (d, 1 H, J = 8.2 Hz), 6.94 (d, 1 H, J = 8.4 Hz), 6.86 (d, 1 H, J = 8.4 Hz), 6.52 (dd, 1 H, J = 7.8, 1.0 Hz), 3.97 (s, 3 H); ^{13}C NMR (acetone- d_6) δ 157.3, 152.1, 149.1, 148.5, 143.0, 129.0, 128.8, 127.9, 126.9, 126.4, 126.0, 123.7, 122.1, 119.4, 117.5, 116.5, 110.3, 108.3, 107.0, 56.2; MS (EI) m/z (rel intensity) 332 (M^+ , 100), 317 (11), 299 (15), 271 (7), 189 (43), 159 (12), 144 (57), 131 (12), 115 (37); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{16}\text{O}_4$ 332.1049, found 332.1057.

1-Oxo-1,4-dihydronaphthalene-4-spiro-2'-naphtho[4"-methoxy-1",8"-de][1',3'] dioxin (33). To a suspension of diol **32** (50 mg, 0.15 mmol) in dry CH_3CN (5 mL) at room temperature was added $\text{PhI}(\text{OAc})_2$ (58 mg, 0.18 mmol) in one portion. The reaction mixture was stirred for 30 min, then concentrated under

reduced pressure. The residue was dissolved in EtOAc (20 mL) and washed with H₂O (10 mL), dried (MgSO₄) and concentrated under reduced pressure. Chromatography on SiO₂ (hexanes/EtOAc, 4:1) gave 27 mg (55%) of **33** as a yellow-green solid: mp 190-191°C (hexanes/EtOAc, dec); IR (neat) 1675, 1612, 1417, 1386, 1299, 1266, 1060 cm⁻¹; ¹H NMR δ 8.17 (dd, 1 H, *J* = 7.8, 1.0 Hz), 7.98 (dd, 1 H, *J* = 7.8, 0.8 Hz), 7.90 (dd, 1 H, *J* = 8.5, 0.8 Hz), 7.77 (td, 1 H, *J* = 7.6, 1.4 Hz), 7.63 (td, 1 H, 7.6, 1.2 Hz), 7.47 (dd, 1 H, *J* = 8.4, 7.6 Hz), 7.02 (dd, 1 H, *J* = 7.6, 0.7 Hz), 7.01 (d, 1 H, *J* = 10.6 Hz), 6.90 (d, 1 H, *J* = 8.3 Hz), 6.79 (d, 1 H, *J* = 8.3 Hz), 6.38 (d, 1 H, *J* = 10.6 Hz), 4.00 (s, 3 H); ¹³C NMR δ 183.7, 151.0, 147.7, 141.0, 139.0, 138.9, 134.0, 130.5, 130.3, 130.2, 128.1, 127.1, 126.6, 126.2, 116.5, 113.9, 111.1, 109.6, 105.3, 93.2, 56.1; MS (EI) *m/z* (rel intensity) 330 (M⁺, 100), 315 (81), 287 (8), 241 (8), 202 (7), 172 (12), 158 (14), 129 (40), 115 (16); HRMS (EI) calcd for C₂₁H₁₄O₄ 330.0892, found 330.0904.

5-Fluoro-8-methylnaphthalen-1-ol (34). To a solution of 5-fluoro-8-methyl-1-tetralone⁹ (1.67 g, 9.40 mmol) in THF (40 mL) was slowly added phenyltrimethylammonium tribromide (3.52 g, 9.4 mmol). The reaction mixture was stirred at room temperature for 30 min as a thick white precipitate was formed then quenched by addition of H₂O and extracted with EtOAc. The combined organic layer was washed with H₂O, dried (MgSO₄), and concentrated under reduced pressure. The pale orange residue was dissolved in DMF (40 mL) and LiBr (1.71 g, 19.7 mmol) and Li₂CO₃ (2.22 g, 30.0 mmol) were added. The suspension was heated at 130 °C for 1 h, and cooled to room temperature. The solids were

removed via filtration and rinsed with EtOAc (3 x 40 mL). The filtrate was washed with H₂O (3 x 40 mL), dried (MgSO₄), and concentrated under reduced pressure. Chromatography on SiO₂ (hexanes/EtOAc, 4:1) afforded 1.47 g (89%) of **34** as a light brown solid: mp 102-103 °C (hexanes/EtOAc); IR (neat) 3299 (br), 1604, 1521, 1417, 1331, 1262, 1217 cm⁻¹; ¹H NMR δ 7.70 (dt, 1 H, *J* = 8.4, 0.9 Hz), 7.32 (t, 1 H, *J* = 7.9 Hz), 7.12-7.07 (m, 1 H), 7.01 (dd, 1 H, *J* = 10.2, 7.9 Hz), 6.77 (dd, 1 H, *J* = 7.4, 0.7 Hz), 5.29 (s, 1 H), 2.91 (s, 3 H); ¹³C NMR δ 157.5 (d, *J* = 246.1 Hz), 153.9 (d, *J* = 4.2 Hz), 130.8 (d, *J* = 4.3 Hz), 127.2 (d, *J* = 8.0 Hz), 126.7 (d, *J* = 16.4 Hz), 126.2 (s), 125.1 (d, *J* = 4.3 Hz), 113.9 (d, *J* = 7.4 Hz), 111.5 (s), 109.5 (d, *J* = 19.4 Hz), 24.3 (s); MS (EI) *m/z* (rel intensity) 176 (M⁺, 100), 157 (20), 147 (23), 133 (24), 127 (9), 120 (7); HRMS (EI) calcd for C₁₁H₉OF 176.0637, found 176.0635.

1-Fluoro-5-methoxy-4-methylnaphthalene (35). To a solution of **34** (1.45 g, 8.20 mmol) in DMF (35 mL) at 0 °C was slowly added NaH (60% dispersion in mineral oil; 0.36 g, 9.00 mmol). The reaction mixture was warmed to room temperature and stirred for 30 min, then cooled to 0 °C and MeI (0.77 mL, 12.3 mmol) was added dropwise. The reaction mixture was again warmed to room temperature and stirred for 30 min then quenched at 0 °C by careful addition of H₂O and extracted with EtOAc (3 x 40 mL). The combined organic layer was washed with H₂O (3 x 40 mL), dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue on SiO₂ (hexanes/EtOAc, 9:1) afforded 1.46 g (94%) of **35** as a yellow-green solid: mp 38-39 °C (hexanes/EtOAc); IR (neat) 2966, 2935, 1605, 1586, 1511, 1456, 1413, 1268, 1036 cm⁻¹; ¹H NMR δ 7.69

(dt, 1 H, $J = 8.4, 1.0$ Hz), 7.41 (t, 1 H, $J = 8.0$ Hz), 7.12-7.07 (m, 1 H), 7.01 (dd, 1 H, $J = 10.1, 7.9$ Hz), 6.86 (d, 1 H, $J = 7.7$ Hz), 3.93 (s, 3 H), 2.85 (s, 3 H); ^{13}C NMR δ 158.1 (d, $J = 3.4$ Hz), 157.4 (d, $J = 245.4$ Hz), 131.2 (d, $J = 4.1$ Hz), 127.4 (d, $J = 7.9$ Hz), 126.3 (s), 126.1 (s), 113.4 (d, $J = 7.7$ Hz), 109.5 (d, $J = 19.4$ Hz), 106.3 (s), 55.5 (s), 25.0 (s); MS (EI) m/z (rel intensity) 190 (M^+ , 100), 175 (67), 157 (18), 147 (33), 133 (17), 127 (14); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{11}\text{OF}$ 190.0794, found 190.0792.

4-Bromomethyl-1-fluoro-5-methoxynaphthalene (36). To a solution of naphthalene **35** (1.0 g, 5.2 mmol) in CCl_4 (30 mL) was added NBS (1.0 g, 5.7 mmol) followed immediately by benzoyl peroxide (50 mg, 0.2 mmol). The reaction mixture was heated at reflux for 1 h then cooled to room temperature. The resulting white precipitate was removed *via* filtration and the filtrate was concentrated under reduced pressure. Chromatography of the residue on SiO_2 (hexanes/EtOAc, 4:1) afforded 1.35 g (96%) of **36** as a yellow solid: mp 57-59 °C (hexanes/EtOAc); IR (neat) 2962, 2935, 1605, 1513, 1463, 1413, 1385, 1270, 1048 cm^{-1} ; ^1H NMR δ 7.72 (dt, 1 H, $J = 8.4, 1.0$ Hz), 7.48 (t, 1 H, $J = 8.0$ Hz), 7.37 (dd, 1 H, $J = 8.0, 5.7$ Hz), 7.07 (dd, 1 H, $J = 9.8, 8.0$ Hz), 6.99 (d, 1 H, $J = 7.8$ Hz), 5.25 (s, 2 H), 4.04 (s, 3 H); ^{13}C NMR δ 159.3 (d, $J = 251.3$ Hz), 157.0 (d, $J = 3.8$ Hz), 130.3 (d, $J = 4.7$ Hz), 129.8 (d, $J = 8.9$ Hz), 127.1 (s), 126.5 (d, $J = 16.5$ Hz), 124.7 (d, $J = 4.0$ Hz), 113.7 (d, $J = 7.8$ Hz), 109.7 (d, $J = 20.4$ Hz), 107.9 (s), 56.0 (s), 37.0 (s); MS (EI) m/z (rel intensity) 270 (M^+ , 20), 189 (100), 173 (36), 159 (52), 145 (21), 133 (23), 125 (15); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{10}\text{OBrF}$ 267.9899, found 267.9886.

(4-Fluoro-8-methoxynaphthalen-1-yl)-methanol (37). To a solution of bromide **36** (1.35 g, 5.0 mmol) in 2:1 CH₃CN/DMF (24 mL) was added NaOAc (0.82 g, 10.0 mmol). The reaction mixture was heated at 80 °C for 3 h, cooled to room temperature and diluted with Et₂O (25 mL). The insoluble white solid present was removed *via* filtration and rinsed with Et₂O (3 x 15 mL). The filtrate was washed with H₂O (3 x 20 mL), dried (MgSO₄), and concentrated under reduced pressure. The crude solid residue was dissolved in 1:1 MeOH/THF (24 mL) and a solution of KOH (0.84 g, 15.0 mmol) in MeOH (3 mL) was added dropwise. After stirring at room temperature for 15 min, the reaction mixture was acidified with 10% HCl, poured into H₂O (40 mL), and extracted with Et₂O. The organic layer was washed with H₂O, dried (MgSO₄), and concentrated under reduced pressure to afford 0.82 g (80%) of **37** as a pale yellow solid: mp 88-89 °C; IR (neat) 3358 (br), 2960, 1607, 1514, 1413, 1387, 1266, 1039 cm⁻¹; ¹H NMR δ 7.76 (dt, 1 H, *J* = 8.4, 0.9 Hz), 7.46 (t, 1 H, *J* = 8.0 Hz), 7.35 (dd, 1 H, *J* = 7.9, 5.8 Hz), 7.08 (dd, 1 H, *J* = 10.0, 7.9 Hz), 6.97 (d, 1 H, *J* = 7.8 Hz), 5.00 (s, 2 H), 4.03 (s, 3 H), 3.19 (s, 1 H); ¹³C NMR δ 158.6 (d, *J* = 248.9 Hz), 156.0 (d, *J* = 3.9 Hz), 133.0 (d, *J* = 4.4 Hz), 127.6 (d, *J* = 8.6 Hz), 126.6 (s), 126.4 (s), 125.2 (d, *J* = 4.4 Hz), 114.4 (d, *J* = 7.7 Hz), 109.6 (d, *J* = 19.7 Hz), 107.3 (s), 66.8 (s), 56.2 (s); MS (EI) *m/z* (rel intensity) 206 (M⁺, 100), 189 (22), 177 (65), 173 (52), 162 (42), 145 (55), 133 (45), 125 (24); HRMS (EI) calcd for C₁₂H₁₁O₂F 206.0743, found 206.0739.

4-Fluoro-8-methoxynaphthalene-1-carbaldehyde (30). To a solution of alcohol **37** (0.82 g, 4.00 mmol) in CH_2Cl_2 (30 mL) was added PCC (1.72 g, 8.00 mmol) in one portion. The reaction mixture was stirred at room temperature for 1 h then filtered directly through a 1" pad of SiO_2 and rinsed with CH_2Cl_2 (150 mL). The filtrate was concentrated under reduced pressure to give 0.77 g (95%) of **30** as a white solid: mp 141-142 °C (CH_2Cl_2); IR (neat) 2919, 2842, 1678, 1515, 1414, 1329, 1229, 1039 cm^{-1} ; ^1H NMR δ 11.01 (d, 1 H, $J = 0.6$ Hz), 7.95 (dd, 1 H, $J = 8.1, 5.9$ Hz), 7.75 (d, 1 H, $J = 8.4$ Hz), 7.49 (t, 1 H, $J = 8.1$ Hz), 7.19 (dd, 1 H, $J = 9.3, 8.5$ Hz), 7.02 (d, 1 H, $J = 7.8$ Hz), 4.01 (s, 3 H); ^{13}C NMR δ 194.4 (s), 161.9 (d, $J = 257.4$ Hz), 156.4 (d, $J = 3.1$ Hz), 131.4 (d, $J = 3.8$ Hz), 128.5 (d, $J = 9.8$ Hz), 127.3 (s), 125.5 (d, $J = 17.1$ Hz), 125.3 (d, $J = 5.6$ Hz), 114.0 (d, $J = 7.3$ Hz), 110.1 (d, $J = 20.9$ Hz), 108.1 (s), 55.9 (s); MS (EI) m/z (rel intensity) 204 (M^+ , 100), 189 (49), 173 (43), 161 (23), 145 (31), 133 (73), 125 (20); HRMS (EI) calcd for $\text{C}_{12}\text{H}_9\text{O}_2\text{F}$ 204.0587, found 204.0588.

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1-SML-133 300 MHz

1-SML-171 300 MHz

3.2776

1.54811