

Silver-Catalyzed Synthesis of 4-Substituted Benzofurans via a Cascade Oxidative Coupling-Annulation Protocol

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Supporting Information

1. General experimental methods (S2)
2. General experimental procedure and characterization data. (S2-S7)
3. Copies of ^1H , ^{13}C NMR spectra of products (S8-S48)

General experimental methods:

All reactions were performed in Schlenk tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μm , standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~ 20 Torr (house vacuum) at 25–35 $^{\circ}\text{C}$. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

General Experimental procedure:

The mixture of 4-alkyl-2-ynylphenol **1** (0.5 mmol) with AgOTf (13 mg, 0.05 mmol) in MeOH (2 mL) was treated with $\text{PhI}(\text{OAc})_2$ (177 mg, 0.55 mmol) at 0 $^{\circ}\text{C}$. After 2 min, indole **2** (1 mmol) was added. The reaction mixture was warmed up to 25 $^{\circ}\text{C}$, and allowed to stir at 25 $^{\circ}\text{C}$. Upon completion by TLC, the reaction was quenched with saturated NaHCO_3 , and extracted by ethyl acetate (100 mL x 3). The organic layer was dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by column chromatography on silica gel (15% ethyl acetate in hexanes) to give the corresponding product **3**.

3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3aa: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.32 (br, 1 H), 7.74–7.77 (m, 2 H), 7.48 (d, $J = 7.8$ Hz, 1 H), 7.42 (t, $J = 8.2$ Hz, 2 H), 7.37 (t, $J = 7.8$ Hz, 2 H), 7.23–7.30 (m, 4 H), 7.12 (td, $J = 7.3, 0.9$ Hz, 1 H), 6.76 (d, $J = 0.9$ Hz, 1 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.6, 153.3, 136.1, 131.3, 130.8, 130.6, 128.8, 128.3, 127.3, 126.9, 126.8, 124.9, 123.5, 122.3, 120.7, 120.0, 114.8, 111.3, 109.6, 102.1, 20.3; IR (KBr) 3410, 2922, 1668, 1604, 1546, 1455, 1413 cm^{-1} ; HRMS m/z calcd for $\text{C}_{23}\text{H}_{18}\text{NO}$ ($[\text{M}+\text{H}]^+$): 324.1383, found 324.1387.

1-methyl-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3ab: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 7.8$ Hz, 2 H), 7.38–7.42 (m, 3 H), 7.33–7.37 (m, 2 H), 7.19–7.30 (m,

3 H), 7.08-7.13 (m, 2 H), 6.78 (s, 1 H), 3.86 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 153.2, 136.8, 131.0, 130.7, 130.4, 128.6, 128.1, 127.9, 127.6, 126.9, 126.7, 124.7, 121.7, 120.7, 119.4, 113.1, 109.3, 109.2, 102.1, 32.9, 20.2; IR (KBr) 2922, 2854, 1732, 1610, 1549, 1479, 1443, 1421 cm^{-1} ; HRMS m/z calcd for $\text{C}_{24}\text{H}_{19}\text{NNaO}$ ($[\text{M}+\text{Na}]^+$): 360.1359, found 360.1352.

1-benzyl-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3ac: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.73-7.76 (m, 2 H), 7.16-7.43 (m, 14 H), 7.10 (t, $J = 7.6$ Hz, 1 H), 6.77 (s, 1 H), 5.38 (s, 2 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 153.2, 137.5, 136.4, 131.0, 130.7, 130.3, 128.8, 128.6, 128.2, 127.9, 127.7, 127.5, 126.8, 126.7, 124.7, 121.9, 120.8, 119.7, 113.7, 109.8, 109.4, 102.0, 50.1, 20.2; IR (KBr) 2918, 2848, 1601, 1549, 1463, 1453, 1421 cm^{-1} ; HRMS m/z calcd for $\text{C}_{30}\text{H}_{23}\text{NNaO}$ ($[\text{M}+\text{Na}]^+$): 436.1672, found 436.1663.

1-allyl-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3ad: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.8$ Hz, 2 H), 7.33-7.42 (m, 5 H), 7.19-7.28 (m, 3 H), 7.16 (s, 1 H), 7.10 (t, $J = 7.6$ Hz, 1 H), 6.77 (s, 1 H), 6.02-6.12 (m, 1 H), 5.24 (d, $J = 10.1$ Hz, 1 H), 5.16 (d, $J = 17.0$ Hz, 1 H), 4.81 (d, $J = 4.5$ Hz, 2 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 153.2, 136.2, 133.5, 131.0, 130.7, 130.4, 128.6, 128.2, 127.8, 127.0, 126.8, 126.7, 124.7, 121.7, 120.8, 119.5, 117.4, 113.5, 109.7, 109.3, 102.0, 48.8, 20.2; IR (KBr) 3052, 2920, 2857, 1610, 1549, 1464, 1442, 1421 cm^{-1} ; HRMS m/z calcd for $\text{C}_{26}\text{H}_{21}\text{NNaO}$ ($[\text{M}+\text{Na}]^+$): 386.1515, found 386.1510.

5-fluoro-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3af: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.33 (br, 1 H), 7.74-7.78 (m, 2 H), 7.43 (d, $J = 8.2$ Hz, 1 H), 7.34-7.39 (m, 3 H), 7.21-7.31 (m, 3 H), 6.96-7.06 (m, 2 H), 6.74 (s, 1 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.3, 156.9, 155.7, 153.2, 132.5, 131.2, 130.6, 130.3, 128.7, 128.3, 127.7, 127.6, 126.7, 126.1, 125.0, 124.8, 114.9, 111.9, 111.8, 110.9, 110.6, 109.7, 105.4, 105.1, 101.7, 20.0; IR (KBr) 3424, 2924, 2851, 1629, 1581, 1484, 1451 cm^{-1} ; HRMS m/z calcd for $\text{C}_{23}\text{H}_{16}\text{FNNaO}$ ($[\text{M}+\text{Na}]^+$): 364.1108, found 364.1097.

5-chloro-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3ag: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.39 (br, 1 H), 7.75-7.78 (m, 2 H), 7.43 (d, $J = 8.2$ Hz, 1 H), 7.34-7.40 (m, 4 H), 7.18-7.31 (m, 4 H), 6.72 (s, 1 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 153.1,

134.3, 131.3, 130.6, 130.5, 128.7, 128.3, 126.7, 125.9, 125.8, 124.8, 124.5, 122.6, 119.7, 114.5, 112.3, 109.8, 101.5, 20.0; IR (KBr) 3413, 2921, 2851, 1619, 1558, 1456, 1444, 1409 cm^{-1} ; HRMS m/z calcd for $\text{C}_{23}\text{H}_{16}\text{ClNNaO}$ ($[\text{M}+\text{Na}]^+$): 380.0813, found 380.0826.

5-bromo-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3ah: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.37 (br, 1 H), 7.75-7.78 (m, 2 H), 7.51 (s, 1 H), 7.43 (d, $J = 8.2$ Hz, 1 H), 7.35-7.40 (m, 2 H), 7.21-7.34 (m, 5 H), 6.71 (s, 1 H), 2.31 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.8, 153.1, 134.6, 131.3, 130.6, 130.5, 128.9, 128.7, 128.3, 126.6, 125.8, 125.2, 124.8, 124.4, 122.8, 114.4, 113.3, 112.7, 109.8, 101.5, 20.0; IR (KBr) 3413, 2915, 1577, 1558, 1450 cm^{-1} ; HRMS m/z calcd for $\text{C}_{23}\text{H}_{16}\text{BrNNaO}$ ($[\text{M}+\text{Na}]^+$): 424.0307, found 424.0310.

1-allyl-5-methyl-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3ak: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.75-7.78 (m, 2 H), 7.41 (d, $J = 8.7$ Hz, 1 H), 7.34-7.39 (m, 2 H), 7.20-7.31 (m, 3 H), 7.17 (s, 1 H), 7.12 (s, 1 H), 7.09 (dd, $J = 8.2, 1.4$ Hz, 1 H), 6.78 (s, 1 H), 6.01- 6.11 (m, 1 H), 5.23 (dd, $J = 10.5, 1.4$ Hz, 1 H), 5.14 (dd, $J = 16.9, 1.4$ Hz, 1 H), 4.78 (d, $J = 5.0$ Hz, 2 H), 2.39 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 153.2, 134.6, 133.6, 131.1, 130.7, 130.4, 128.9, 128.6, 128.1, 128.0, 127.1, 127.0, 126.6, 124.7, 123.4, 120.2, 117.2, 112.9, 109.4, 109.3, 102.0, 48.9, 21.4, 20.2; IR (KBr) 2919, 2863, 1607, 1549, 1485, 1444, 1420 cm^{-1} ; HRMS m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NNaO}$ ($[\text{M}+\text{Na}]^+$): 400.1672, found 400.1693.

1-allyl-5-methoxy-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3al: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.77-7.80 (m, 2 H), 7.42 (d, $J = 8.2$ Hz, 1 H), 7.35-7.40 (m, 2 H), 7.22-7.32 (m, 3 H), 7.15 (s, 1 H), 6.93 (dd, $J = 9.2, 2.3$ Hz, 1 H), 6.82 (d, $J = 2.3$ Hz, 1 H), 6.81 (s, 1 H), 6.02- 6.12 (m, 1 H), 5.25 (dd, $J = 10.5, 1.4$ Hz, 1 H), 5.16 (dd, $J = 17.0, 1.4$ Hz, 1 H), 4.79 (d, $J = 5.5$ Hz, 2 H), 3.71 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 154.2, 153.2, 133.6, 131.5, 131.0, 130.7, 130.3, 128.7, 128.2, 128.1, 127.6, 126.9, 126.7, 124.7, 117.3, 113.0, 112.4, 110.5, 109.3, 102.0, 101.9, 55.8, 49.1, 20.2; IR (KBr) 2921, 1610, 1546, 1482, 1452, 1421 cm^{-1} ; HRMS m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NNaO}_2$ ($[\text{M}+\text{Na}]^+$): 416.1621, found 416.1615.

1-allyl-6-methoxy-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3am: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.3$ Hz, 1 H), 7.34-7.41 (m, 3 H), 7.21-7.30 (m, 3 H), 7.06 (s, 1 H), 6.87 (d, $J = 1.8$ Hz, 1 H), 6.76-6.80 (m, 2 H), 6.02- 6.13 (m, 1 H), 5.26 (dd, $J = 10.1, 1.4$ Hz, 1 H), 5.17 (dd, $J = 17.4, 1.4$ Hz, 1 H), 4.76 (d, $J = 5.5$ Hz, 2 H), 3.88 (s, 3 H), 2.36

(s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 155.4, 153.2, 136.9, 133.4, 130.9, 130.7, 130.3, 128.6, 128.2, 126.9, 126.7, 125.9, 124.7, 122.3, 121.4, 117.3, 113.4, 109.3, 109.2, 102.1, 93.4, 55.7, 48.8, 20.2; IR (KBr) 2924, 2829, 1738, 1621, 1556, 1489, 1463, 1420 cm^{-1} ; HRMS m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NNaO}_2$ ($[\text{M}+\text{Na}]^+$): 416.1621, found 416.1637.

1-allyl-5-fluoro-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3an: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.76-7.79 (m, 2 H), 7.41 (d, $J = 8.2$ Hz, 1 H), 7.35-7.40 (m, 2 H), 7.28-7.33 (m, 2 H), 7.20-7.25 (m, 2 H), 6.97-7.05 (m, 2 H), 6.75 (s, 1 H), 6.02- 6.12 (m, 1 H), 5.26 (dd, $J = 10.5, 0.9$ Hz, 1 H), 5.16 (dd, $J = 17.0, 0.9$ Hz, 1 H), 4.80 (d, $J = 5.0$ Hz, 2 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 156.8, 155.6, 153.2, 133.2, 132.8, 131.0, 130.6, 130.2, 128.6, 128.5, 128.3, 128.2, 128.1, 126.7, 126.2, 124.8, 117.6, 113.5, 110.5, 110.4, 110.1, 109.5, 105.5, 105.3, 101.7, 49.2, 20.1; IR (KBr) 2922, 2848, 1619, 1604, 1580, 1549, 1485, 1443 cm^{-1} ; HRMS m/z calcd for $\text{C}_{26}\text{H}_{20}\text{FNNaO}$ ($[\text{M}+\text{Na}]^+$): 404.1421, found 404.1439.

1-allyl-5-chloro-3-(5-methyl-2-phenylbenzofuran-4-yl)-1H-indole 3ao: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.76-7.80 (m, 2 H), 7.18-7.45 (m, 9 H), 6.73 (s, 1 H), 6.01- 6.11 (m, 1 H), 5.27 (dd, $J = 10.1, 0.9$ Hz, 1 H), 5.14 (dd, $J = 17.0, 0.9$ Hz, 1 H), 4.80 (d, $J = 5.5$ Hz, 2 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 153.2, 134.6, 133.1, 131.2, 130.6, 130.4, 128.8, 128.7, 128.3, 128.2, 126.7, 125.9, 125.5, 124.8, 122.2, 119.9, 117.6, 113.2, 110.8, 109.7, 101.6, 49.1, 20.1; IR (KBr) 2918, 2850, 1607, 1549, 1470, 1446, 1420 cm^{-1} ; HRMS m/z calcd for $\text{C}_{26}\text{H}_{20}\text{ClNNaO}$ ($[\text{M}+\text{Na}]^+$): 420.1126, found 420.1130.

1-allyl-3-(5-butyl-2-phenylbenzofuran-4-yl)-1H-indole 3bd: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 7.3$ Hz, 2 H), 7.32-7.45 (m, 5 H), 7.23-7.27 (m, 3 H), 7.14 (s, 1 H), 7.08 (t, $J = 7.6$ Hz, 1 H), 6.70 (s, 1 H), 6.01- 6.11 (m, 1 H), 5.23 (dd, $J = 10.5, 1.4$ Hz, 1 H), 5.12 (dd, $J = 16.9, 1.4$ Hz, 1 H), 4.75-4.87 (m, 2 H), 2.61-2.77 (m, 2 H), 1.44-1.53 (m, 2 H), 1.14-1.26 (m, 2 H), 0.76 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.3, 153.0, 136.4, 136.2, 133.5, 130.7, 130.6, 128.6, 128.2, 128.1, 126.7, 126.4, 125.9, 124.7, 121.7, 120.6, 119.5, 117.2, 113.3, 109.6, 102.2, 48.7, 34.5, 32.8, 22.4, 13.9; IR (KBr) 2955, 2925, 2857, 1607, 1549, 1463, 1420 cm^{-1} ; HRMS m/z calcd for $\text{C}_{29}\text{H}_{27}\text{NNaO}$ ($[\text{M}+\text{Na}]^+$): 428.1985, found 428.2006.

2-(4-(1-allyl-1H-indol-3-yl)-2-phenylbenzofuran-5-yl)ethyl acetate 3cd: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.74-7.77 (m, 2 H), 7.47 (d, $J = 7.8$ Hz, 1 H), 7.42 (d, $J = 8.2$ Hz, 1 H),

7.34-7.39 (m, 3 H), 7.24-7.30 (m, 3 H), 7.22 (s, 1 H), 7.10 (t, $J = 8.0$ Hz, 1 H), 6.71 (s, 1 H), 6.04- 6.15 (m, 1 H), 5.26 (dd, $J = 10.1, 1.4$ Hz, 1 H), 5.17 (dd, $J = 17.0, 1.4$ Hz, 1 H), 4.84 (d, $J = 5.5$ Hz, 2 H), 4.06-4.24 (m, 2 H), 2.96-3.12 (m, 2 H), 1.91 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 155.7, 153.4, 136.2, 133.4, 131.1, 130.8, 130.5, 128.6, 128.3, 128.0, 127.3, 126.9, 126.2, 124.8, 121.9, 120.4, 119.7, 117.4, 112.6, 109.8, 109.7, 102.0, 65.4, 48.9, 32.3, 20.9; IR (KBr) 3055, 2955, 2866, 1735, 1610, 1546, 1464, 1421 cm^{-1} ; HRMS m/z calcd for $\text{C}_{29}\text{H}_{25}\text{NNaO}_3$ ($[\text{M}+\text{Na}]^+$): 458.1727, found 458.1716.

1-allyl-3-(5,6-dimethyl-2-phenylbenzofuran-4-yl)-1H-indole 3fd: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 7.3$ Hz, 2 H), 7.32-7.43 (m, 5 H), 7.22-7.29 (m, 2 H), 7.15 (s, 1 H), 7.10 (t, $J = 7.6$ Hz, 1 H), 6.71 (s, 1 H), 6.03-6.14 (m, 1 H), 5.25 (d, $J = 10.1$ Hz, 1 H), 5.17 (d, $J = 17.0$ Hz, 1 H), 4.82 (d, $J = 5.5$ Hz, 2 H), 2.46 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 153.0, 136.2, 134.1, 133.5, 130.9, 130.2, 128.6, 128.4, 128.1, 127.9, 127.1, 126.6, 124.6, 121.7, 120.8, 119.5, 117.4, 114.0, 110.7, 109.7, 102.0, 48.8, 21.7, 17.0; IR (KBr) 2914, 1610, 1560, 1547, 1465, 1435 cm^{-1} ; HRMS m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NNaO}$ ($[\text{M}+\text{Na}]^+$): 400.1672, found 400.1675.

1-allyl-3-(2-tert-butyl-5-methylbenzofuran-4-yl)-1H-indole 3hd: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 8.0$ Hz, 1 H), 7.37 (d, $J = 8.0$ Hz, 1 H), 7.31 (d, $J = 8.0$ Hz, 1 H), 7.24 (t, $J = 7.8$ Hz, 1 H), 7.16 (d, $J = 8.0$ Hz, 1 H), 7.13 (s, 1 H), 7.10 (t, $J = 7.8$ Hz, 1 H), 6.01-6.11 (m, 2 H), 5.23 (dd, $J = 10.1, 1.4$ Hz, 1 H), 5.14 (dd, $J = 16.9, 1.4$ Hz, 1 H), 4.80 (d, $J = 5.0$ Hz, 2 H), 2.32 (s, 3 H), 1.31 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 152.8, 136.2, 133.5, 130.5, 130.0, 127.8, 126.9, 126.2, 125.3, 121.6, 120.8, 119.4, 117.2, 113.8, 109.6, 109.0, 99.3, 48.8, 32.9, 28.8, 20.2; IR (KBr) 2960, 1573, 1463, 1421 cm^{-1} ; HRMS m/z calcd for $\text{C}_{24}\text{H}_{25}\text{NNaO}$ ($[\text{M}+\text{Na}]^+$): 366.1828, found 366.1848.

1-allyl-3-(5-methylbenzofuran-4-yl)-1H-indole 3id: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 1.8$ Hz, 1 H), 7.39 (d, $J = 8.2$ Hz, 2 H), 7.36 (d, $J = 7.8$ Hz, 1 H), 7.22-7.27 (m, 2 H), 7.14 (s, 1 H), 7.07-7.12 (m, 1 H), 6.50 (d, $J = 0.9$ Hz, 1 H), 6.01-6.11 (m, 1 H), 5.23 (dd, $J = 10.5, 1.4$ Hz, 1 H), 5.13 (dd, $J = 17.0, 1.4$ Hz, 1 H), 4.80 (d, $J = 5.0$ Hz, 2 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 144.4, 136.2, 133.5, 130.8, 128.5, 127.7, 127.0, 126.9, 126.6, 121.7, 120.7, 119.4, 117.3, 113.5, 109.7, 109.5, 107.1, 48.8, 20.1; IR (KBr) 2922, 1613, 1552, 1532, 1464, 1419 cm^{-1} ; HRMS m/z calcd for $\text{C}_{20}\text{H}_{17}\text{NNaO}$ ($[\text{M}+\text{Na}]^+$): 310.1202, found 310.1202.

1-allyl-3-(2-tert-butyl-5-methylbenzofuran-4-yl)-5-methyl-1H-indole 3hk: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 8.4$ Hz, 1 H), 7.29 (d, $J = 8.8$ Hz, 1 H), 7.16 (d, $J = 8.8$ Hz, 1 H), 7.15 (s, 1 H), 7.09 (s, 1 H), 7.07 (d, $J = 8.4$ Hz, 1 H), 6.01-6.11 (m, 2 H), 5.23 (d, $J = 10.4$ Hz, 1 H), 5.14 (d, $J = 17.2$ Hz, 1 H), 4.79 (d, $J = 5.6$ Hz, 2 H), 2.39 (s, 3 H), 2.31 (s, 3 H), 1.31 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 152.8, 136.6, 133.7, 130.5, 130.0, 128.7, 128.0, 127.0, 126.4, 125.2, 123.2, 120.4, 117.1, 113.3, 109.3, 109.0, 99.3, 48.9, 32.9, 28.8, 21.4, 20.2; IR (KBr) 2964, 2921, 2866, 1607, 1577, 1484, 1458, 1422 cm^{-1} ; HRMS m/z calcd for $\text{C}_{25}\text{H}_{27}\text{NNaO}$ ($[\text{M}+\text{Na}]^+$): 380.1985, found 380.1987.

4-methoxy-4-methyl-2-(phenylethynyl)cyclohexa-2,5-dienone 4a: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.56 (m, 2 H), 7.32-7.35 (m, 3 H), 7.09 (d, $J = 1.8$ Hz, 0.5 H), 7.08 (d, $J = 1.8$ Hz, 0.5 H), 6.80 (dd, $J = 2.3, 3.2$ Hz, 0.5 H), 6.77 (dd, $J = 2.3, 3.2$ Hz, 0.5 H), 6.40 (d, $J = 2.3$ Hz, 0.5 H), 6.37 (d, $J = 2.3$ Hz, 0.5 H), 3.24 (s, 1.5 H), 3.23 (s, 1.5 H), 1.48 (s, 1.5 H), 1.47 (s, 1.5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 181.6, 154.0, 151.3, 131.8, 129.9, 128.8, 128.2, 125.9, 122.2, 94.1, 82.5, 72.8, 53.5, 26.3; HRMS m/z calcd for $\text{C}_{16}\text{H}_{14}\text{NaO}_2$ ($[\text{M}+\text{Na}]^+$): 261.0886, found 261.0881.

4-methoxy-5-methyl-2-phenylbenzofuran 5a: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.88 (m, 2 H), 7.43-7.48 (m, 2 H), 7.32-7.38 (m, 1 H), 7.17 (d, $J = 8.2$ Hz, 1 H), 7.14 (s, 1 H), 7.08 (d, $J = 8.2$ Hz, 1 H), 4.07 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 155.0, 151.0, 130.5, 128.9, 128.6, 127.1, 124.9, 122.5, 120.9, 105.8, 99.1, 60.2, 15.8; IR (KBr) 2924, 1597, 1479, 1436 cm^{-1} ; HRMS m/z calcd for $\text{C}_{16}\text{H}_{15}\text{O}_2$ ($[\text{M}+\text{H}]^+$): 239.1067, found 239.1071.

6a: yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.75-7.78 (m, 2 H), 7.34-7.43 (m, 5 H), 7.22-7.30 (m, 3 H), 7.18 (s, 1 H), 7.11 (t, $J = 7.8$ Hz, 1 H), 6.77 (s, 0.15 H), 6.03-6.14 (m, 1 H), 5.26 (dd, $J = 10.1, 1.4$ Hz, 1 H), 5.17 (dd, $J = 17.0, 1.4$ Hz, 1 H), 4.83 (d, $J = 5.5$ Hz, 2 H), 2.36 (s, 3 H).

















































































