SUPPORTING INFORMATION

Heterocycles by $PtCl_2$-Catalyzed Intramolecular Carboalkoxylation or Carboamination of Alkynes

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General: Unless stated otherwise, all reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF, DMA (Desmodur®, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Gallenkamp melting point apparatus (uncorrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received. NMR: Spectra were recorded on a Bruker DPX 300, AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.24$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ ppm).

STARTING MATERIALS

All the alkynylphenol derivatives were prepared according to Scheme S-1 using a modified variant of the method reported by Takahashi.[1]

Scheme S-1

2-(Methoxymethoxy)iodobenzene. MOMCl (5.5 g, 1.5 equiv) was added to a mixture of 2-iodophenol (10 g, 45.5 mmol) and K_2CO_3 (25 g, 182 mmol) in DMF (50 mL) with ice-cooling. The mixture was then stirred at room temperature until the phenol was consumed, after which the mixture was diluted with water (900 mL) and *tert*-butyl methyl ether (300 mL). The layers were separated and the organic phase washed with water (2 × 900 mL) and brine before being dried over Na_2SO_4, filtered and the solvent removed under reduced pressure to afford the iodide as a bronze oil (11.6 g, 97%) with data matching that previously reported.[2]

Sonagashira Reaction: Standard Procedure (SP1). $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (2 mol%) are added to a solution of alkyne (1.1 eq.) and aryl iodide (1.0 eq.) in triethylamine (0.1 M). The resulting mixture is stirred at 50 °C until the reaction is complete as determined by GC/MS or TLC. On completion, the mixture is allowed to cool to room temperature, *tert*-butyl methyl ether or hexanes are added, and the mixture is filtered through a plug of cotton wool. Removal of solvent under reduced pressure affords a residue which is purified by flash chromatography in *tert*-butyl methyl ether/hexanes to afford the analytically pure arylated alkynes.

The following compounds were prepared by this method:

1-(Methoxymethoxy)-2-(1-pentynyl)benzene. Pale brown oil (1.14 g, 93%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.21 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 1H), 7.08 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.94 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 5.24 (s, 2H), 3.53 (s, 3H), 2.44 (t, *J* = 7.0 Hz, 2H), 1.65 (qt, *J* = 7.3, 7.1 Hz, 2H), 1.07 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 133.5, 128.7, 121.8, 115.5, 114.7, 95.1, 94.3, 76.8, 56.2, 22.2, 21.7, 13.5; IR (neat): 2962, 2933, 1596, 1575, 1489, 1450 1440, 1254, 1227, 1196, 1152, 1113, 1078, 1043, 991, 921, 751; MS (EI): *m/z* (%): 204 (37) $[M\text{-}H]^+$, 173

[1] Yoneda, E.; Sugioka, T.; Hirao, K.; Zhang, S.-W.; Takahashi, S. *J. Chem. Soc., Perkin Trans 1* **1998**, 477.

[2] Labrosse, J. -R.; Poncet, C.; Lhoste, P.; Sinou, D. *Tetrahedron: Asymmetry* **1999**, *10*, 1069.

(23), 145 (28), 131 (31), 45 (100); HR-MS (EI): *m/z*: calcd for $C_{13}H_{16}O_2$: 204.1150, found 204.1150 [*M*].

1-(1-Heptynyl)-2-(methoxymethoxy)benzene. Colorless oil (3.20 g, 91%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 (m, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.93 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 5.24 (s, 2H), 3.53 (s, 3H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.63 (quin, *J* = 7.3 Hz, 2H), 1.48 (m, 2H), 1.39 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.6, 133.5, 128.6, 121.8, 115.5, 114.8, 95.1, 94.5, 76.6, 56.1, 31.0, 28.5, 22.2, 19.6, 14.0; IR (neat): 2956, 2931, 2859, 1596, 1575, 1489, 1450, 1440, 1255, 1228, 1196, 1152, 113, 1079, 1045, 991, 922, 751; MS (EI): *m/z* (%): 232 (20) $[M\text{-}H]^+$, 201 (5), 187 (8), 171 (15), 145 (29), 131 (25), 45 (100); HR-MS (EI): *m/z*: calcd for $C_{15}H_{20}O_2$: 232.1463, found 232.1461 [*M*].

1-(Cyclopropylethynyl)-2-(methoxymethoxy)benzene. Colorless oil (345 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.6, 1.6 Hz, 1H), 7.20 (m, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.92 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 1H), 5.23 (s, 2H), 3.52 (s, 3H), 1.50 (m, 1H), 0.87 (m, 2H), 0.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.8, 133.6, 128.7, 121.8, 115.6, 114.7, 97.4, 95.2, 71.8, 55.2, 8.7 (2C), 0.5; IR (neat): ν 3009, 2956, 2826, 2231, 1596, 1572, 1490, 1451, 1439, 1278, 1227, 1197, 1151, 1121, 1077, 1043, 987, 951, 921, 839, 811, 751; MS (EI): *m/z* (%): 202 (34) $[M]^+$, 187 (17), 171 (33), 128 (27), 45 (100); HR-MS (EI): *m/z*: calcd for $C_{13}H_{14}O_2$: 202.0994, found 202.0997 [*M*].

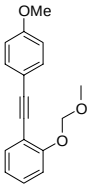
1-(Methoxymethoxy)-2-(4-phenyl-1-butynyl)benzene. Pale yellow oil (906 mg, 90%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.31 (m, 4H), 7.23 (m, 2H), 7.09 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.95 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 5.22 (s, 2H), 3.51 (s, 3H), 2.96 (t, *J* 7.3 Hz, 2H), 2.77 (t, *J* 7.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 140.7, 133.6, 128.9, 128.5 (2C), 128.3 (2C), 126.2, 121.8, 115.4, 114.4, 95.0, 93.5, 77.4, 56.1, 35.2, 21.9; IR (neat): 3027, 2904, 1596, 1574, 1489, 1451, 1439, 1255, 1228, 1197, 1151, 1112, 1077, 991, 921, 748, 697; MS (EI): *m/z* (%): 266 (18) $[M]^+$, 233 (57), 219 (17), 145 (15), 115 (13), 91 (40), 45 (100); HR-MS (EI): *m/z*: calcd for $C_{18}H_{18}O_2$: 266.1307, found 266.1304 [*M*].

Dimethyl 2-{3-[2-(methoxymethoxy)phenyl]-2-propynyl}malonate. Colorless oil (1.11 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.21 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 1H), 7.06 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.92 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 5.21 (s, 2H), 3.78 (s, 6H), 3.71 (t, *J* = 7.7 Hz, 1H), 3.50 (s, 3H), 3.05 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3 (2C), 157.7, 133.6, 129.3, 121.8, 115.4, 113.8, 95.0, 89.2, 78.7, 56.1, 52.7 (2C), 51.3, 19.8; IR (neat): 2955,

2917, 2849, 1735, 1490, 1436, 1340, 1232, 1197, 1150, 1113, 1078, 1031, 992, 920, 755; MS (EI): *m/z* (%): 306 (13) $[M]^+$, 275 (11), 215 (19), 174 (15), 161 (13), 115 (11), 45 (100); HR-MS (ESI+): *m/z*: calcd for $C_{16}H_{18}NaO_6$: 329.1001, found 329.1003 $[M+Na]^+$.

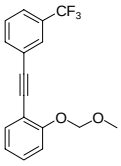
1-(Methoxymethoxy)-2-(phenylethynyl)benzene. Yellow oil. The analytical and spectroscopic data match those previously reported in the literature.[4] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (m, 2H), 7.51 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.36-7.24 (m, 4H), 7.13 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.00 (td, *J* = 7.5, 1.1 Hz, 1H), 5.29 (s, 2H), 3.55 (s, 3H).

1-(Methoxymethoxy)-2-[(4-methoxyphenyl)ethynyl]benzene. Colorless oil (747 mg, 93%);



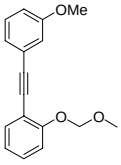
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (m, 3H), 7.27 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.13 (dd, *J* 8.3, 0.6 Hz, 1H), 7.0 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 1H), 6.88 (m, 2H), 5.29 (s, 2H), 3.83 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 157.6, 133.3, 133.0 (2C), 129.3, 121.9, 115.7, 115.6, 114.4, 113.2 (2C), 95.2, 93.3, 84.3, 56.2, 55.2; IR (neat): 2957, 2837, 2214, 1606, 1594, 1570, 1509, 1486, 1450, 1439, 1286, 1245, 1231, 1197, 1174, 1152, 1103, 1076, 1029, 982, 920, 829, 751; MS (EI): *m/z* (%): 268 (37) $[M-H]^+$, 237 (100); HR-MS (EI): *m/z*: calcd for $C_{17}H_{16}O_3$: 268.1099, found 268.1102 [*M*].

1-(Methoxymethoxy)-2-{[3-(trifluoromethyl)phenyl]ethynyl}benzene. Colorless oil (1.53



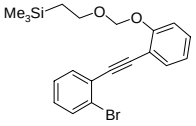
g, 94%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.32 (ddd, *J* = 8.6, 7.5, 1.8 Hz, 1H), 7.17 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.02 (ddd, *J* = 7.5, 1.1 H, 1H), 5.31 (s, 2H), 3.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$,): δ 157.9, 134.6, 133.6, 130.9 (q, *J* = 33 Hz), 130.2 (2C), 128.8, 128.3 (q, *J* = 4 Hz), 124.6 (q, *J* = 4 Hz), 123.8 (q, *J* = 272 Hz), 121.9, 115.2, 113.2, 95.0, 91.6, 87.4, 56.3; IR (neat): 2958, 2217, 1596, 1586, 1575, 1494, 1482, 1431, 1338, 1296, 1268, 1232, 1199, 1147, 1123, 1105, 1069, 1043, 984, 922, 893, 799, 751, 693; MS (EI): *m/z* (%): 306 (43) $[M]^+$, 275 (100); HR-MS (EI): *m/z*: calcd for $C_{17}H_{13}F_3O_2$: 306.0868, found 306.0867 [*M*].

1-(Methoxymethoxy)-2-[(3-methoxyphenyl)ethynyl]benzene. Colorless oil (1.20 g, 84%);



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.27 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.13 (m, 2H), 7.07 (d, *J* = 2.6, 1.4 Hz, 1H), 6.99 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 6.88 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 5.27 (s, 2H), 3.81 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.3, 157.8, 133.5, 129.7, 129.3, 124.6, 124.2, 121.9, 116.4, 115.5, 114.7, 114.0, 95.2, 93.2, 85.5, 56.3, 55.3; IR (neat): 2956, 2829, 1593, 1573, 1494, 1484, 1451, 1322, 1282, 1236, 1223, 1197, 1152, 1103, 1077, 1041, 982, 921, 853, 779, 750, 685; MS (EI): *m/z* (%): 268 (51) $[M]^+$, 237 (100); HR-MS (EI): *m/z*: calcd for $C_{17}H_{16}O_3$: 268.1099, found 268.1102 [*M*].

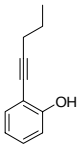
[2-({2-[(2-Bromophenyl)ethynyl]phenoxy}methoxy)ethyl](trimethyl)silane, 9 (Scheme 5).



Colorless oil; ^{1}H NMR (400 MHz, toluene-d_8): δ 7.62 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.39 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.20-7.06 (m, 2H), 6.86 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 1H), 6.81 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 6.70 (ddd, *J* = 8.0, 7.5, 1.2 Hz, 1H), 5.17 (s, 2H), 3.82 (t, *J* = 8.0 Hz, 2H), 0.96 (t, *J* = 8.0 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, toluene-d_8): δ 159.9, 135.0, 134.5, 133.7, 131.1, 130.2, 128.0, 127.6, 127.0, 127.7, 116.3, 115.2, 94.4, 93.4, 92.6, 67.6, 19.3, -0.4 (3C); IR (neat): 2952, 2895, 2220, 1597, 1574, 1492, 1466, 1446, 1248, 1228, 1148, 1085, 986, 855, 833, 749; MS (EI): *m/z* (%): 402 (7) [*M*]$^+$, 345 (20), 331 (100); HR-MS (EI): *m/z*: calcd for $C_{20}H_{23}Br_1O_2Si$: 402.0651, found 402.0652 [*M*]; elemental analysis calcd (%) for $C_{20}H_{23}Br_1O_2Si$: C 59.55, H 5.75; found: C 59.64, H 5.82.

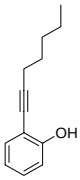
MOM deprotection. Standard Procedure (SP2). HCl (6 N) is added to a solution of the MOM protected phenol in THF/^{i}PrOH (1:1) and the mixture stirred at room temperature until deprotection is complete. Dilution with water and *tert*-butyl methyl ether and extraction of the aqueous layer with *tert*-butyl methyl ether is followed by washing of the combined organic phases with brine, drying over Na_2SO_4, and removing the solvent under reduced pressure to afford a residue which can be purified by flash chromatography in *tert*-butyl methyl ether/hexanes if necessary.

2-(1-Pentynyl)phenol. Colorless oil (734 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d,

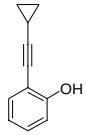


J = 7.7 Hz, 1H), 7.20 (dd, *J* = 7.7, 7.5 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.84 (dd, *J* = 8.0, 7.5 Hz, 1H), 5.80 (s, 1H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.67 (qt, *J* = 7.4, 7.1 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.5, 131.4, 129.6, 120.1, 114.3, 110.2, 97.8, 74.6, 22.2, 21.6, 13.6; IR (neat): 3502, 2963, 2933, 2872, 1613, 1574, 1485, 1461, 1379, 1340, 1286, 1234, 1205, 1176, 1151, 1100, 1030, 937, 824, 749; MS (EI): *m/z* (%): 160 (56) [*M-H*]$^+$, 131 (100); HR-MS (EI): *m/z*: calcd for $C_{11}H_{12}O$: 160.0888, found 160.889 [*M*].

2-(1-Heptynyl)phenol. Colorless oil (2.15 g, 90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd,



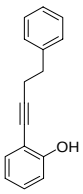
J = 7.6, 1.6 Hz, 1H), 7.20 (m, 1H), 7.08 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.84 (ddd, *J* = 7.6, 7.5, 1.1 Hz, 1H), 5.81 (s, 1H), 2.48 (t, *J* = 7.1 Hz, 2H), 1.63 (tt, *J* = 7.3, 7.1 Hz, 2H), 1.41 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.5, 131.4, 129.5, 120.1, 114.2, 110.2, 98.0, 74.5, 31.1, 28.4, 22.2, 19.6, 13.9; IR (neat): 3505, 2956, 2930, 2860, 1576, 1485, 1462, 1346, 1287, 1234, 1206, 1234, 1206, 1177, 1151, 1031, 822, 749; MS (EI): *m/z* (%): 188 (73) [*M-H*]$^+$, 173 (8), 159 (52), 145 (33), 131 (100); HR-MS (ESI+): *m/z*: calcd for $C_{13}H_{16}O$: 188.1201, found 188.1203 [*M*].



2-(Cyclopropylethynyl)phenol. Colorless oil (150 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.19 (m, 1H), 6.92 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.83 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 5.80 (s, 1H), 1.51 (m, 1H), 0.93 (m, 2H), 0.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.8, 131.6, 129.6, 120.1, 114.3,

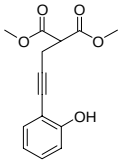
110.1, 101.0, 69.6, 9.0 (2C), 0.2; IR (neat): 3497, 3013, 2215, 1612, 1571, 1486, 1460, 1450, 1343, 1286, 1235, 1174, 1152, 1029, 953, 849, 809, 749; MS (EI): *m/z* (%): 158 (100) $[M]^+$; HR-MS (EI): *m/z*: calcd for $C_{11}H_{10}O$: 158.0732, found 158.0730 [*M*].

2-(4-Phenyl-1-butynyl)phenol. Pale yellow oil (546 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$):



δ 7.38 (m, 2H), 7.30 (m, 4H), 7.21 (m, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.85 (ddd, *J* = 7.6, 7.6, 0.9 Hz, 1H), 5.52 (s, 1H), 2.97 (t, *J* = 7.1 Hz, 2H), 2.84 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.7, 140.2, 131.3, 129.7, 128.6 (2C), 128.4 (2C), 126.6, 120.1, 114.4, 109.9, 96.7, 75.7, 34.8, 21.7; IR (neat): 3490, 3027, 2926, 1603, 1578, 1484, 1461, 1453, 1339, 1286, 1234, 1176, 1151, 1077, 1031, 817, 747, 697; MS (EI): *m/z* (%): 222 (69) $[M]^+$, 207 (13), 194 (9), 131 (100); HR-MS (EI): *m/z*: calcd for $C_{16}H_{14}O$: 222.1045, found 222.1042 [*M*].

Dimethyl 2-[3-(2-hydroxyphenyl)-2-propynyl]malonate. Colorless oil (260 mg, 88%); ^{1}H

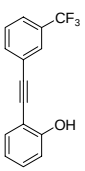


NMR (400 MHz, $CDCl_3$): δ 7.26 (m, 1H), 7.24 (m, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.85 (m, 1H), 6.36 (brd, OH), 3.83 (s, 6H), 3.74 (t, *J* = 7.2 Hz, 1H), 3.08 (d, *J* = 7.2 H, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.5 (2C), 157.6, 131.1, 130.1, 119.9, 114.8, 109.2, 92.3, 77.6, 53.0 (2C), 50.6, 19.7; IR (neat): 3450, 2956, 2918, 2849, 1728, 1573, 1486, 1436, 1340, 1288, 1265, 1236, 1152, 1029, 910, 828, 753, 732; MS (EI): *m/z* (%): 262 (45) $[M\text{-}H]^+$, 203 (100); HR-MS (ESI+): *m/z*: calcd for $C_{14}H_{14}NaO_5$: 285.07333, found 285.0733 $[M+Na]^+$.

2-(2-Phenylethynyl)phenol. Yellow solid. The analytical and spectroscopic data match those previously reported in the literature.[3] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (m, 2H), 7.39 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.32 (m, 3H) 7.23 (m, 1H) 6.95 (d, *J* 8.2 Hz, 1H), 6.87 (m, 1H), 5.82 (s, 1H).

2-[(4-Methoxyphenyl)ethynyl]phenol. Yellow solid. The analytical and spectroscopic data match those previously reported in the literature.[1] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.41 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.27 (m, 1H), 7.00-6.89 (m, 4H), 5.89 (s, 1H), 3.84 (s, 3H).

2-{[3-(Trifluoromethyl)phenyl]ethynyl}phenol. Yellow solid (875 mg, 87%); mp 77.3-78.7



°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.31 (ddd, *J* = 8.4, 7.5, 1.6 Hz, 1H), 7.01 (dd, *J* = 8.3, 0.7 Hz, 1H), 6.94 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 5.81 (s 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.6, 134.6, 131.9, 131.2 (q, *J* = 33 Hz), 131.0, 129.0, 128.3 (q, *J* = 4 Hz), 125.2 (q, *J* = 4 Hz), 123.6 (q, *J* = 272 Hz), 123.4, 120.6, 115.0, 109.0, 94.5, 84.8; IR (neat): 3428, 3053,1603, 1587, 1571, 1494, 1482, 1460, 1432, 1342, 1301, 1293, 1276, 1193, 1176, 1167, 1153, 1142, 1113, 1093, 1071,

[3] Kondo, Y.; Shiga, S.; Murata, N.; Sakamoto, T.; Yamanaka, H. *Tetrahedron*, **1994**, *50*, 11803.

1030, 904, 897, 801, 828, 749, 691; MS (EI): *m/z* (%): 262 (100) $[M]^+$; HR-MS (EI): *m/z*: calcd for $C_{15}H_9F_3O$: 261.0533, found 261.0536 [M^+].

2-[(3-Methoxyphenyl)ethynyl]phenol. White solid (717 mg, 99%); mp 81.8-83.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.29 (m, 2H), 7.13 (ddd, *J* = 7.6, 1.1, 1.1 Hz, 1H), 7.06 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.98 (ddd, *J* = 7.5, 7.5, 0.7 Hz, 1H), 6.88 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H), 6.88 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 5.85 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4, 156.5, 131.7, 130.5, 129.6, 124.1, 123.4, 120.4, 116.4, 115.4, 114.7, 109.5, 96.3, 82.9, 55.3; IR (neat): 3400, 2940, 1594, 1583, 1573, 1489, 1482, 1460, 1450, 1419, 1321, 1289, 1246, 1230, 1193, 1172, 1154, 1134, 1027, 992, 927, 846, 840, 780, 769, 759, 682; MS (EI): *m/z* (%): 224 (100) $[M]^+$; HR-MS (ESI+): *m/z*: calcd for $C_{15}H_{12}O_2$: 223.0765, found 223.0762 [M-H^+].

O-Alkylation. General Procedure (SP3). The alkylating agent (1.1-1.2 eq.) and K_2CO_3 (2 eq.) are added to a solution of the phenol (1 eq.) in CH_3CN (~1 M) and the mixture is stirred at room temperature until the phenol is consumed. The mixture is diluted with *tert*-butyl methyl ether and washed with water and brine before being dried over Na_2SO_4, filtered and the solvent removed under reduced pressure to afford a residue which is purified by flash chromatography in *tert*-butyl methyl ether/hexanes.

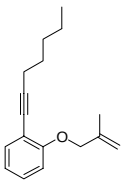
1-[(Benzyloxy)methoxy]-2-iodobenzene. Colorless oil (1.44 g, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.40-7.27 (m, 6H), 7.17 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.79 (ddd, *J* = 7.7, 7.7, 1.5 Hz, 1H), 5.37 (s, 2H), 4.78 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.0, 139.5, 136.9, 129.4, 128.4 (2C), 128.1 (2C), 127.9, 123.7, 115.0, 92.6, 87.2, 70.3; IR (neat): 3062, 3030, 2902, 1582, 1496, 1470, 1439, 1407, 1382, 1300, 1270, 1224, 1156, 1118, 1089, 1044, 1016, 975, 904, 745, 695; MS (EI): *m/z* (%): 340 (7) $[M]^+$, 310 (34), 91 (100); HR-MS (EI): *m/z*: calcd for $C_{14}H_{13}IO_2$: 339.9960, found 339.9956 [*M*].

{2-[(2-Iodophenoxy)methoxy]ethyl}(trimethyl)silane. Colorless oil (564 mg, 95%); ^{1}H NMR (300 MHz, C_6D_6): δ 7.65 (m, 1H), 6.94 (m, 2H), 6.38 (ddd, *J* = 7.9, 5.7, 3.0 Hz, 1H), 4.91 (s, 2H), 3.63 (t, *J* = 8.2 Hz, 2H), 0.81 (t, *J* = 8.2 Hz, 2H), -0.11 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6): δ 156.8, 139.8, 129.4, 123.5, 115.0, 93.3, 87.5, 66.6, 18.1, -1.4 (3C); IR (neat): 2952, 2898, 1583, 1471, 1440, 1408, 1380, 1248, 1230, 1152, 1091, 1045, 1017, 982, 916, 856, 831, 747, 692; MS (EI): *m/z* (%): 350 (4) [*M*-*H*]$^+$, 292 (48), 277 (100); HR-MS (EI): *m/z*: calcd for $C_{12}H_{19}IO_2Si$: 350.0199, found 350.0201 [*M*].

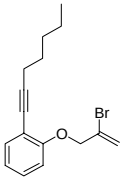
1-(Allyloxy)-2-(1-pentynyl)benzene. Colorless oil (196 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.20 (ddd, *J* = 8.5, 7.6, 1.7 Hz, 1H), 6.88 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.08 (ddt, *J* = 17.3, 10.5, 5.0 Hz, 1H), 5.48 (ddt, *J* = 17.3, 1.6, 1.7 Hz, 1H), 5.28 (ddt, *J* = 10.5, 1.6, 1.5 Hz, 1H), 4.60 (ddd, *J* = 5.0, 1.7, 1.5 Hz, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.66 (qt, *J* 7.2,

7.1 Hz, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 133.5, 133.3, 128.7, 120.7, 117.1, 114.0, 112.6, 94.6, 77.4, 69.4, 22.3, 21.8, 13.6; IR (neat): 2970, 2934, 2871, 1738, 1595, 1574, 1490, 1444, 1424, 1365, 1259, 1228, 1217, 1116, 1018, 996, 924, 827, 747; MS (EI): *m/z* (%): 200 (100) $[M\text{-}H]^+$, 185 (10), 171 (60), 157 (87); HR-MS (EI): *m/z*: calcd for $C_{14}H_{16}O$: 200.1201, found 200.1202 [*M*].

1-(1-Heptynyl)-2-[(2-methyl-2-propenyl)oxy]benzene. Colorless oil (286 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.20 (ddd, *J* = 8.5, 7.5, 1.7 Hz, 1H), 6.87 (m, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 5.17 (m, 1H), 4.99 (m, 1H), 4.49 (s, 2H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.86 (s, 3H), 1.63 (tt, *J* = 7.4, 7.4 Hz, 2H), 1.46 (m, 2H), 1.37 (tt, *J* = 7.4, 7.4 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.2, 140.7, 133.4, 128.6, 120.5, 114.0, 112.4, 112.3, 94.6, 76.6, 72.1, 31.1, 28.6, 22.3, 19.7, 19.3, 14.0; IR (neat): 2930, 2859, 1658, 1596, 1574, 1490, 1443, 1376, 1290, 1258, 1233, 1161, 1116, 1055, 1014, 900, 747; MS (EI): *m/z* (%): 242 (81) $[M\text{-}H]^+$, 227 (34), 201 (44), 185 (99), 171 (100); HR-MS (EI): *m/z*: calcd for $C_{17}H_{22}O$: 242.1671, found 242.1670 [*M*].



1-[(2-Bromo-2-propenyl)oxy]-2-(1-heptynyl)benzene. Colorless oil (290 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.21 (m, 1H), 6.92 (ddd, *J* = 7.5, 7.5, 0.9 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.14 (dt, *J* = 1.8, 1.8 Hz, 1H), 5.68 (dt, *J* = 1.8, 1.5 Hz, 1H), 4.69 (t, *J* = 1.5 Hz, 2H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.63 (tt, *J* = 7.4, 7.4 Hz, 2H), 1.46 (m, 2H), 1.37 (tt, *J* = 7.4, 7.4 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.2, 133.6, 128.7, 126.6, 121.5, 117.3, 114.2, 113.1, 95.1, 76.3, 72.1, 31.1, 28.5, 22.2, 19.7, 14.0; IR (neat): 2956, 2930, 2858, 1640, 1597, 1575, 1490, 1444, 1290, 1261, 1221, 1208, 1161, 1113, 1050, 1032, 896, 830, 747; MS (EI): *m/z* (%): 306 (30) $[M\text{-}H]^+$, 227 (29), 171 (44), 131 (100); HR-MS (EI): *m/z*: calcd for $C_{16}H_{19}{}^{81}BrO$: 308.0599, found 308.0602 [*M*].



1-(1-Heptynyl)-2-{[(2*E*)-3-phenyl-2-propenyl]oxy}benzene. White solid (112 mg, 28%); mp 45.3-47.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.24 (m, 7H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.48 (dt, *J* = 15.9, 0.5 Hz, 1H), 6.46 (dt, *J* = 15.9, 5.5 Hz, 1H), 4.80 (dd, *J* = 5.5, 0.5 Hz, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.70-1.29 (m, 6H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 137.0, 134.0, 132.9, 129.1, 129.0 (2C), 128.2, 126.9 (2C), 125.0, 121.2, 114.4, 113.1, 95.2, 77.0, 69.7, 31.5, 29.0, 22.6, 20.2, 14.4; IR (neat): 2963, 2952, 2936, 2854, 1595, 1575, 1491, 1448, 1384, 1289, 1278, 1263, 1232, 1205, 1118, 1067, 971, 929, 746, 78, 687; MS (EI): *m/z* (%): 304 (2) $[M]^+$, 233 (6), 117 (100); HR-MS (ESI+): *m/z*: calcd for $C_{22}H_{24}O$: 304.1823, found 304.1823 [*M*].

1-(Benzyloxy)-2-(1-heptynyl)benzene. Colorless oil (276 mg, 75%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (m, 2H), 7.40 (m, 1H), 7.38 (m, 1H), 7.32 (m, 2H), 7.20 (ddd, *J* = 8.2, 7.5, 1.3 Hz, 1H), 6.90 (m, 2H), 5.17 (s, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.64 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.47 (m, 2H), 1.36 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 137.2, 133.4, 128.7 (2C), 128.4 (2C), 127.6, 126.9, 120.8, 114.2, 112.9, 94.9, 76.7, 70.4, 31.1, 28.5, 22.2, 19.7, 14.0; IR (neat): 2955, 2930, 2858, 1596, 1574, 1489, 1444, 1379, 1290, 1260, 1227, 1161, 1116, 1048, 1022, 748, 732, 694; MS (EI): *m/z* (%): 278 (16) $[M\text{-}H]^+$, 221 (25), 91 (100); HR-MS (EI): *m/z*: calcd for $C_{20}H_{22}O$: 278.1671, found 278.1670 [*M*].

1-(1-Heptynyl)-2-[(4-methoxybenzyl)oxy]benzene. Colorless oil (351 mg, 86%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (m, 3H), 7.20 (m, 1H), 6.90 (m, 4H), 5.09 (s, 2H), 3.82 (s, 3H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.62 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.45 (m, 2H), 1.35 (m, 2H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 159.2, 133.4, 129.2 (2C), 128.6, 128.6, 120.8, 114.2, 113.8 (2C), 113.1, 94.8, 76.7, 70.3, 55.2, 31.1, 28.5, 22.2, 19.7, 14.0; IR (neat): 2955, 2931, 2858, 1613, 1595, 1574, 1514, 1490, 1464, 1444, 1378, 1301, 1288, 1246, 1173, 1114, 1034, 1005, 867, 818, 747; MS (EI): *m/z* (%): 308 (5) $[M\text{-}H]^+$, 121 (100); HR-MS (EI): *m/z*: calcd for $C_{21}H_{24}O_2$: 308.1776, found 308.1773 [*M*].

1-(Allyloxy)-2-(4-phenyl-1-butynyl)benzene. Colorless oil (143 mg, 91%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.31 (m, 2H), 7.30 (m, 2H), 7.22 (m, 2H), 6.88 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.08 (ddt, *J* = 17.3, 10.6, 5.0 Hz, 1H), 5.47 (ddt, *J* = 17.3, 1.7, 1.6 Hz, 1H), 5.29 (ddt, *J* = 10.6, 1.7, 1.5 Hz, 1H), 4.62 (dt, *J* = 5.0, 1.6 Hz, 2H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 140.8, 133.6, 133.2, 128.8, 128.5 (2C), 128.3 (2C), 126.2, 120.6, 117.2, 113.6, 112.5, 93.7, 77.3, 69.3, 35.3, 22.0; IR (neat): 3026, 2925, 1595, 1574, 1489, 1444, 1424, 1290, 1261, 1225, 1161, 1116, 1017, 995, 925, 746, 697; MS (EI): *m/z* (%): 262 (100) $[M]^+$; HR-MS (EI): *m/z*: calcd for $C_{19}H_{18}O$: 262.1358, found 262.1354 [*M*].

2-Methyl-2-propenyl 2-(4-phenyl-1-butynyl)phenyl ether. Colorless oil (165 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.30 (m, 4H), 7.22 (m, 2H), 6.88 (m, 1H), 6.86 (m, 1H), 5.17 (s, 1H), 5.00 (s, 1H), 4.50 (s, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.2, 140.9, 140.7, 133.4, 128.8, 128.5 (2C), 128.4 (2C), 126.2, 120.6, 113.7, 112.4, 112.3, 93.6, 77.4, 72.1, 35.3, 22.0, 19.3; IR (neat): 3027, 2923, 1658, 1595, 1573, 1489, 1444, 1290, 1258, 1221, 1161, 1116, 1054, 1012, 901, 747, 696; MS (EI): *m/z* (%): 276 (37) $[M]^+$, 261 (14), 233 (12), 221 (23), 185 (100); HR-MS (EI): *m/z*: calcd for $C_{20}H_{20}O$: 276.1514, found 276.1515 [*M*].

1-[(Benzyloxy)methoxy]-2-(4-phenyl-1-butynyl)benzene. Following SP3 with BOMCl (tech.) the product was obtained as a colorless oil contaminated with {[(benzyloxy)methoxy]methyl}benzene (23 mol%) which was used in the subsequent cyclisation step; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.20 (multiple m, 12H), 7.16 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.95 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H), 5.33 (s, 2H), 4.77 (s, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.7, 140.8, 137.3, 133.6, 128.9, 128.5 (2C), 128.4 (2C), 128.3 (2C), 128.1 (2C), 127.8, 126.3, 121.9, 115.6, 114.5, 93.6, 93.0, 77.4, 70.1, 35.2, 21.9; IR (neat): 3063, 3029, 2904, 1596, 1575, 1489, 1453, 1382, 1253, 1209, 1159, 1076, 1045, 1027, 992, 905, 734, 695; MS (EI): *m/z* (%): 342 (7) $[M]^+$, 312 (18), 221 (55), 91 (100); HR-MS (EI): *m/z*: calcd for $C_{24}H_{22}O_2$: 342.1620, found 342.1617 [*M*].

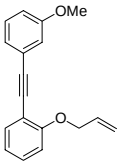
Trimethyl(2-{[2-(4-phenyl-1-butynyl)phenoxy]methoxy}ethyl)silane. Pale yellow oil (350 mg, 98%); ^{1}H NMR (300 MHz, C_6D_6): δ 7.48 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.10 (m, 6H), 6.99 (m, 1H), 6.71 (dd, *J* = 7.5, 1.1 Hz, 1H), 5.06 (s, 2H), 3.69 (t, *J* = 8.0 Hz, 2H), 2.73 (t, *J* = 7.3 Hz, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 0.85 (t, *J* = 8.0 Hz, 2H), -0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, C_6D_6): δ 158.9, 141.1, 134.0, 129.1, 128.9 (2C), 128.6 (2C), 126.5, 121.7, 115.3, 115.1, 93.5, 93.8, 78.5, 66.5, 35.6, 22.4, 18.2, -1.4 (3C); IR (neat): 2951, 1597, 1575, 1490, 1448, 1248, 1211, 1146, 1113, 1085, 1046, 991, 936, 917, 856, 832, 748, 696; MS (EI): *m/z* (%): 352 (5) $[M]^+$, 294 (100); HR-MS (EI): *m/z*: calcd for $C_{22}H_{28}O_2Si$: 352.1859, found 352.1861 [*M*].

1-(Allyloxy)-2-{[3-(trifluoromethyl)phenyl]ethynyl}benzene. Yellow oil (300 mg, 98%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.51 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 (dd, *J* = 7.8, 7,8 Hz, 1H), 7.31 (ddd, *J* = 8.5, 7.5, 1.8 Hz, 1H), 6.96 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.12 (ddt, *J* = 17.2, 10.6, 4.8 Hz, 1H), 5.54 (ddt, *J* = 17.2, 1.7, 1.7 Hz, 1H), 5.32 (ddt, *J* = 10.6, 1.7, 1.7 Hz, 1H), 4.65 (dt, *J* = 4.8, 1.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 134.6, 134.6, 133.5, 132.9, 130.9 (q, *J* = 32 Hz), 130.1, 128.8, 128.3 (q, *J* = 4 Hz), 124.7, 124.5 (q, *J* = 4 Hz), 123.5 (q, *J* = 272 Hz), 120.8, 117.2, 112.5, 91.9, 87.5, 69.3; IR (neat): 1595, 1574, 1495, 1482, 1446, 1430, 1338, 1296, 1278, 1269, 1241, 1227, 1164, 1123,1069, 996, 926, 893, 799, 747, 693; MS (EI): *m/z* (%): 302 (94) $[M]^+$, 275 (63), 261 (24), 233 (100); HR-MS (EI): *m/z*: calcd for $C_{18}H_{13}F_3O$: 302.0918, found 302.0915 [*M*].

1-[(Benzyloxy)methoxy]-2-{[3-(trifluoromethyl)phenyl]ethynyl}benzene. Following SP3 with BOMCl (tech.) a colorless oil contaminated with {[(benzyloxy)-methoxy]methyl}benzene (9 mol%) was obtained which was used in the subsequent cyclisation step; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.48 (dd, *J* = 7.8 Hz, 1H), 7.34 (m, 6H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.04 (ddd, *J*

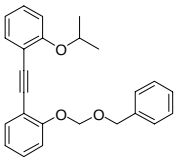
= 7.5, 7.4, 1.1 Hz, 1H), 5.42 (s, 2H), 4.82 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.9, 137.0, 134.6, 133.5, 130.9 (q, *J* = 33 Hz), 130.2, 130.2, 128.8, 128.4 (2C), 128.3 (q, *J* = 4 Hz), 128.1 (2C), 127.9, 124.6 (q, *J* = 4 Hz), 123.8 (q, *J* = 272 Hz), 121.9, 115.2, 113.2, 92.7, 91.7, 87.4, 70.2; IR (neat): 2906, 2217, 1596, 1575, 1495, 1482, 1451, 1430, 1338, 1296, 1267, 1223, 1164, 1124, 1087, 1069, 1043, 986, 893, 800, 748, 693; MS (EI): *m/z* (%): 382 (9) $[M]^+$, 352 (58), 275 (17), 207 (13), 91 (100); HR-MS (EI): *m/z*: calcd for $C_{23}H_{17}F_3O_2$: 382.1181, found 382.1184 [*M*].

1-(Allyloxy)-2-[(3-methoxyphenyl)ethynyl]benzene. Colorless oil (527 mg, 98%); ^{1}H NMR



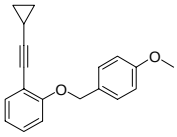
(300 MHz, $CDCl_3$): δ 7.49 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.24 (m, 2H), 7.14 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.08 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.93 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 6.88 (m, 2H), 6.09 (ddt, *J* = 17.2, 10.6, 4.8 Hz, 1H), 5.54 (ddt, *J* = 17.2, 1.7, 1.6 Hz, 1H), 5.29 (ddt, *J* = 10.6, 1.5, 1.6 Hz, 1H), 4.63 (dt, *J* = 4.8, 1.7 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 159.1, 133.4, 133.0, 129.6, 129.3, 124.7, 124.1, 120.7, 117.1, 116.3, 114.7, 113.0, 112.5, 93.4, 85.6, 69.2, 55.2; IR (neat): 3071, 2937, 2835, 1593, 1572, 1494, 1444, 1422, 1322, 1278, 1223, 1161, 1135, 1104, 1040, 1016, 992, 927, 853, 777, 748, 684; MS (EI): *m/z* (%): 264 (100) $[M]^+$; HR-MS (EI): *m/z*: calcd for $C_{18}H_{16}O_2$: 264.1150, found 264.1151 [*M*].

1-[(Benzyloxy)methoxy]-2-[(2-isopropoxyphenyl)ethynyl]benzene. Colorless oil (363 mg,



98%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (m, 2H), 7.43-7.23 (m, 8H), 7.08 (ddd, *J* = 7.4, 7.3, 1.2 Hz, 1H), 7.00 (m, 2H), 5.50 (s, 2H), 4.88 (s, 2H), 4.71 (sept, *J* = 6.1 Hz, 1H), 1.45 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.7, 157.6, 137.2, 133.5, 133.5, 129.4, 129.4, 128.4 (2C), 128.1 (2C), 127.8, 122.0, 120.8, 115.8, 115.5, 114.8, 114.6, 93.0, 90.4, 89.5, 71.9, 70.1, 22.2 (2C); IR (neat): 2976, 1591, 1573, 1495, 1480, 1447, 1383, 1372, 1276, 1240, 1221, 1160, 1117, 1107, 1084, 1043, 987, 951, 746; MS (EI): *m/z* (%): 372 (17) $[M]^+$, 327 (9), 299 (44), 152 (15), 181 (22), 209 (21), 91 (100); HRMS (ESI+): *m/z*: calcd for $C_{25}H_{24}Na_1O_3$: 395.1618, found 395.1613 $[M+Na]^+$.

1-(Cyclopropylethynyl)-2-[(4-methoxybenzyl)oxy]benzene. Colorless oil (245 mg, 88%);

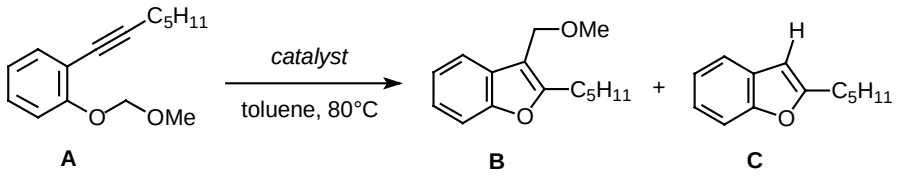


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.37 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.19 (m, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.90-6.85 (m, 2H), 5.08 (s, 2H), 3.82 (s, 3H), 1.56-1.46 (m 1H), 0.91-0.78 (4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 159.2, 133.4, 129.2, 128.6 (2C), 128.5, 120.8, 114.1, 113.8 (2C), 113.1, 97.7, 71.9, 70.3, 55.3, 8.7 (2C), 0.5; IR (neat): 3008, 283, 2229, 1613, 1594, 1573, 1513, 1490, 1447, 1378, 1301, 1288, 1245, 1173, 1123, 1094, 1030, 1006, 952, 808, 748, 734; MS (EI): *m/z* (%): 278 (11) $[M]^+$, 121 (100).

1-[(4-Methoxybenzyl)oxy]-2-{[3-(trifluoromethyl)phenyl]ethynyl}benzene. Pale yellow solid (348 mg, 91%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.59-7.43 (m, 5H), 7.32 (m, 1H), 7.00-6.90 (m, 4H), 5.13 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.5, 159.4, 134.5, 133.2, 130.8 (q, *J* = 32 Hz), 130.1, 128.9, 128.8, 128.5 (2C), 128.3 (q, *J* = 4 Hz), 124.7, 124.4 (q, *J* = 4 Hz), 123.8 (q, *J* = 272 Hz), 120.9, 113.9 (2C), 112.9, 112.7, 92.1, 87.6, 70.4, 55.2; IR (neat): 2959, 2835, 2214, 1614, 1585, 1574, 1514, 1495, 1463, 1448, 1428, 1339, 1295, 1282, 1243, 1163 1152, 1116, 1070, 1033, 936, 893, 853, 813, 802, 747, 692; MS (EI): *m/z* (%): 382 (10) $[M]^+$, 121 (100).

BENZOFURAN DERIVATIVES

Scheme S-2. Preliminary Screening of Different Catalysts



Entry	Catalyst	Reaction Time	Product Distribution (GC %)
1	$PtCl_2$ (5 mol%)	2h	**A** (< 1%), **B** (> 95%), **C** (< 1%)
2	AuCl (10 mol%)	3h	**A** (66%), **B** (26%), **C** (9%)
3	$IrCl_3$ (10 mol%)	3h	**A** (42%), **B** (--), **C** (58%)
4	$RhCl_3$ (10 mol%)	3h	*no conversion*
5	$RuCl_3$ (10 mol%)	3h	*no conversion*
6	$FeCl_3$ (10 mol%)	3h	*complex mixture*
7	$CrCl_3 \cdot 6\ H_2O$ (10 mol%)	3h	*no conversion*
8	$InCl_3$ (10 mol%)	3h	*no conversion*
9	$CuCl_2$ (10 mol%)	3h	*no conversion*
10	$CoCl_2 \cdot 6\ H_2O$ (10 mol%)	3h	*no conversion*

Standard Procedure for $PtCl_2$ Catalysed Cyclisation Reactions (SP4). The substrate (generally 0.2-0.4 mmol, however **10** was prepared on a 1.75 mmol scale with no reduction in yield) is weighed into a Schlenk tube and toluene added (0.2 M). $PtCl_2$ is then added to the tube as a solid before the tube is sealed and the mixture stirred at the appropriate temperature. For reactions under a CO atmosphere, after addition of $PtCl_2$ to the reaction mixture a CO balloon fitted to a needle was placed through a septum into the reaction mixture and CO bubbled through for ~ 30 seconds before the needle was removed from the mixture and

heating commenced under a CO atmosphere. When the reaction is complete, the solution is allowed to cool before being placed directly onto a column and product eluted in *tert*-butyl methyl ether/hexanes.

2-Propyl-1-benzofuran (Table 1, entry 1). Colorless oil. The analytical and spectroscopic data match those previously reported in the literature.[4] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (m, 1H), 7.43 (m, 1H), 7.21 (m, 2H), 6.40 (s, 1H), 2.77 (t, *J* = 7.4 Hz, 2H), 1.81 (qt, *J* = 7.4 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

2-Pentyl-1-benzofuran (Table 1, entry 2). Colorless oil. The analytical and spectroscopic data match those previously reported in the literature.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.22 (m, 2H), 6.40 (s, 1H), 2.79 (t, *J* = 7.7 Hz, 2H), 1.79 (m, 2H), 1.42 (m, 4H), 0.96 (t, *J* = 7.1 Hz, 3H).

2-**Cyclopropyl-1-benzofuran (Table 1, entry 3)**. Colorless oil. The analytical and spectroscopic data match those previously reported in the literature.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (m, 1H), 7.38 (m, 1H), 7.18 (m, 2H), 6.36 (s, 1H), 2.04 (tt, *J* = 8.1, 5.2 Hz, 1H), 0.99 (m, 4H).

2-(2-Phenylethyl)-1-benzofuran (Table 1, entry 4). Colorless oil. The analytical and spectroscopic data match those previously reported in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.31-7.15 (m, 7H), 6.36 (s, 1H), 3.08 (s, 4H).

Dimethyl 2-(1-benzofuran-2-ylmethyl)malonate (Table 1, entry 5). Colorless oil. The analytical and spectroscopic data match those previously reported in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.26-7.16 (m, 2H), 6.48 (s, 1H), 3.90 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 6H), 3.42 (d, *J* = 7.6 Hz, 2H).

2-Phenyl-1-benzofuran (Table 1, entry 6). Yellow solid. The analytical and spectroscopic data match those previously reported in the literature.[9] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (m, 2H), 7.66-7.24 (m, 7H), 7.07 (s, 1H).

2-(4-Methoxyphenyl)-1-benzofuran (Table 1, entry 7). Yellow solid. The analytical and spectroscopic data match those previously reported in the literature.[10] ^{1}H NMR (300 MHz,

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[4] Fujimura, O.; Fu, G. C.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 4029.

[5] Ledoussal, B.; Gorgues, A.; Le Coq, A. *Tetrahedron* **1987**, *43*, 5841.

[6] Hercouet, A.; Le Corre, M. *Tetrahedron* **1981**, *37*, 2867.

[7] Macleod, C.; McKiernan, G. J.; Guthrie, E. J.; Farrugia, L. J.; Hamprecht, D. W.; Macritchie, J.; Hartley, R. C. *J. Org. Chem.* **2003**, *68*, 387.

[8] Primault, G.; Legros, J.-Y.; Fiaud, J.-C. *J. Organomet. Chem.* **2003**, *687*, 353.

[9] Becht, J. –M.; Gissot, A.; Wagner, A.; Miokowski, C. *Chem. Eur. J.* **2003**, *9*, 3209.

[10] Kabalka, G. W.; Wang, L.; Pagni, R. M, *Tetrahedron*, **2001**, *57*, 8017.

$CDCl_3$): δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.51 (m, 2H), 7.22 (m, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.86 (s, 1H), 3.83 (s, 3H).

2-[3-(Trifluoromethyl)phenyl]-1-benzofuran (Table 1, entry 8). Yellow solid; mp 67.2-67.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.58 (m, 4H), 7.34 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.27 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 7.11 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.0, 154.2, 131.5 (q, *J* = 32 Hz), 131.3, 129.3, 128.9, 127.9, 124.9, 124.9 (q, *J* = 4 Hz), 123.2, 121.8 (q, *J* = 272 Hz), 121.6 (q, *J* = 4 Hz), 121.2, 111.3, 102.6; IR (neat): 2927, 1485, 1471, 1451, 1421, 1329, 1310, 1282, 1273, 1259, 1208, 1167, 1113, 1095, 1072, 1042, 927, 895, 827, 814, 799, 754, 693; MS (EI): *m/z* (%): 262 (100) $[M]^+$; HR-MS (EI): *m/z*: calcd for $C_{15}H_9F_3O$: 262.0606, found 262.0608 [*M*]; elemental analysis calcd (%) for $C_{15}H_9F_3O$: C 68.70, H 3.46; found: C 68.81, H 3.42.

3-Allyl-2-propyl-1-benzofuran. (Table 2, entry 1) Colorless oil. The analytical and spectroscopic data match those previously reported in the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.38 (m, 2H), 7.22-7.15 (m, 2H), 5.96 (m, 1H), 5.14-5.04 (m, 2H), 3.39 (dd, *J* = 6.0, 1.4 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 1.78 (tq, *J* = 7.4, 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

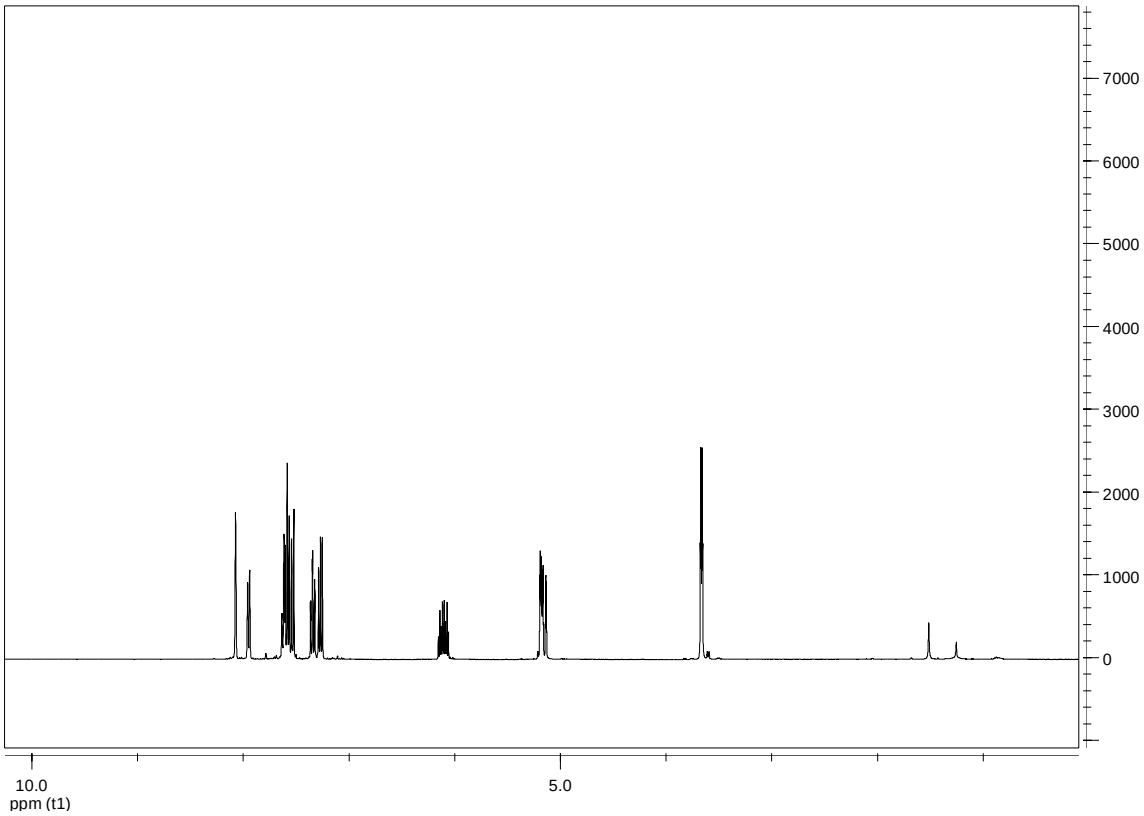
3-Allyl-2-(2-phenylethyl)-1-benzofuran (Table 2, entry 2). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (m, 2H), 7.26 (m, 7H), (ddt, *J* = 17.0, 10.0, 6.2 Hz, 1H), 5.07 (m, 1H), 5.04 (m, 1H), 3.27 (dt, *J* = 6.2, 1.5 Hz, 2H), 3.07 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0, 153.7, 141.1, 135.8, 129.5, 128.4 (2C), 128.4 (2C), 126.1, 123.2, 122.0, 119.2, 115.5, 112.4, 110.7, 34.6, 28.6, 27.8; IR (neat): 3062, 3027, 2925, 1639, 1604, 1496, 1474, 1454, 1254, 1182, 1092, 1068, 992, 913, 867, 742, 697; MS (EI): *m/z* (%): 262 (46) $[M]^+$, 171 (100); HR-MS (EI): *m/z*: calcd for $C_{19}H_{18}O$: 262.1358, found 262.1360 [*M*]; elemental analysis calcd (%) for $C_{19}H_{18}O$: C 86.99, H 6.92; found: C 86.75, H 6.84.

3-Allyl-2-[3-methoxyphenyl]-1-benzofuran (Table 2, entry 3). Following SP4 a mixture of compounds was obtained as a colorless oil in a 7.75:1 ratio. Separation by HPLC obtained the main compound in pure form with the minor product decomposing; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.41 (m, 2H), 7.37 (brd, 1H), 7.36 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.27 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.96 (m, 1H), 6.15 (ddt, *J* = 16.9, 10.8, 5.5 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 5.17 (d, *J* = 16.9 Hz, 1H), 3.90 (s, 3H), 3.70 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 153.9, 151.4, 135.1, 123.1, 130.3, 129.7, 124.4, 122.4, 119.7, 119.4, 116.2, 114.2, 113.2, 112.1, 111.0, 55.3, 28.4; IR (neat): 3078, 3003, 2938, 2834, 1638, 1598, 1575, 1490, 1454, 1431, 1287, 1267, 1234, 1218, 1176, 1115, 1039, 993, 915,

[11] Chaplin, J. H.; Flynn, B. L. *Chem. Commun.*, **2001**, 1594.

869, 776, 742; MS (EI): *m/z* (%): 264 (91) $[M]^+$, 249 (100); elemental analysis calcd (%) for $C_{18}H_{16}O_2$: C 81.79, H 6.10; found: C 81.71, H 6.16.

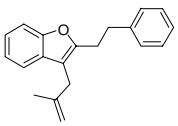
3-Allyl-2-[3-(trifluoromethyl)phenyl]-1-benzofuran (Table 2, entry 4). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.61 (m, 3H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.5, 1.3 Hz, 1H), 7.28 (m, 1H), 6.12 (ddt, *J* = 17.0, 10.3, 5.6 Hz, 1H), 5.17 (m, 2H), 3.65 (dt, *J* = 5.6, 1.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1, 149.9, 134.6, 131.7, 131.2 (q, *J* = 32 Hz), 130.1, 129.8, 129.2, 125.0, 124.7 (q, *J* = 4 Hz), 124.0 (q, *J* = 272 Hz), 123.7 (q, *J* = 4 Hz), 122.8, 119.9, 116.5, 114.5, 111.0, 28.4; IR (neat): 1639, 1615, 1453, 1425, 1325, 1278, 1226, 1166, 1120, 1092, 1074, 993, 908, 838, 802, 743, 695; MS (EI): *m/z* (%): 302 (100) $[M]^+$; HR-MS (ESI+): *m/z*: calcd for $C_{18}H_{13}F_3O$: 302.0918, found 302.0915 [*M*].



3-(2-Methyl-2-propenyl)-2-pentyl-1-benzofuran (Table 2, entry 5). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (m, 1H), 7.40 (m, 1H), 7.19 (m, 2H), 4.81 (centre of AB, *J* = 18.3 Hz, 2H), 3.34 (s, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 1.75 (s, 3H), 1.7.3 (m, 2H), 1.36 (m, 4H), 0.92 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.5, 153.9, 143.4, 129.8, 122.9, 121.9, 119.3, 111.5, 111.4, 110.5, 32.2, 31.5, 27.9, 26.3, 22.4, 22.3, 14.0; IR (neat): 2955, 2929, 2859, 1653, 1454, 1375, 1250, 1202, 1167, 1009, 890, 740; MS (EI): *m/z* (%): 242 (84) $[M]^+$, 199 (37), 185 (100); HR-MS (EI): *m/z*: calcd for

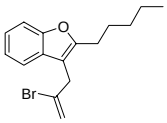
$C_{17}H_{22}O$: 242.1671, found 242.1670 [*M*]; elemental analysis calcd (%) for $C_{17}H_{22}O$: C 84.25, H 9.15; found: C 84.19, H 9.06.

3-(2-Methyl-2-propenyl)-2-(2-phenylethyl)-1-benzofuran (Table 2, entry 6). Colorless oil;



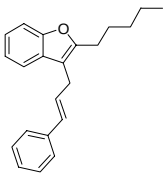
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.22 (m, 7H), 4.77 (s, 1H), 4.73 (s, 1H), 3.20 (s, 2H), 3.03 (s, 4H), 1.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.1, 154.0, 143.3, 141.1, 129.7, 128.4 (2C), 128.4 (2C), 126.1, 123.1, 122.0, 119.4, 112.2, 111.5, 110.6, 34.5, 32.0, 28.7, 22.1; IR (neat): 3064, 3027, 2925, 1652, 1604, 1496, 1473, 1454, 1374, 1249, 1180, 1068, 1009, 890, 740, 696; MS (EI): *m/z* (%): 276 (47) $[M]^+$, 185 (100); HR-MS (EI): *m/z*: calcd for $C_{20}H_{20}O$: 276.1514, found 276.1511 [*M*]; elemental analysis calcd (%) for $C_{20}H_{20}O$: C 86.92, H 7.29; found: C 86.85, H 7.21.

3-(2-Bromo-2-propenyl)-2-pentyl-1-benzofuran (Table 2, entry 7). Colorless oil; ^{1}H NMR



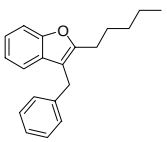
(400 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.21 (m, 2H), 5.57 (m, 2H), 3.77 (s, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 1.75 (m, 2H), 1.36 (m, 4H), 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 56.5, 153.9, 131.2, 129.0, 123.3, 122.3, 119.0, 117.4, 110.8, 110.2, 36.1, 31.5, 27.8, 26.4, 22.4, 14.0; IR (neat): 2954, 2928, 2859, 1631, 1454, 1274, 1250, 1170, 1106, 1011, 888, 740; MS (EI): *m/z* (%): 308 (68) $[M]^+$, 306 (68), 227 (29), 170 (100); HR-MS (EI): *m/z*: calcd for $C_{16}H_{19}{}^{81}BrO$: 308.0599, found 308.0602 [*M*]. elemental analysis calcd (%) for $C_{16}H_{19}BrO$: C 62.55, H 6.23; found: C 62.46, H 6.21.

2-Pentyl-3-[(2*E*)-3-phenyl-2-propenyl]-1-benzofuran (Table 2, entry 8). Colorless oil; ^{1}H



NMR (300 MHz, $CDCl_3$): δ 7.50-7.10 (m, 9H), 8.47 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.8, 6.0 Hz, 1H), 3.53 (dd, *J* = 6.0, 1.1 Hz, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 1.72 (m, 2H), 1.33 (m, 4H), 0.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.23, 153.9, 137.4, 130.6, 129.6, 128.5 (2C), 127.9, 127.1, 126.1 (2C), 123.1, 122.0, 119.1, 111.8, 110.6, 31.4, 28.1, 27.2, 26.4, 22.4, 14.0; IR (neat): 2955, 2927, 2858, 1703, 1599, 1455, 1250, 1202, 1167, 1103, 1072, 1010, 963, 864, 743, 692; MS (EI): *m/z* (%):304 (100) $[M]^+$; HR-MS (ESI+): *m/z*: calcd for $C_{22}H_{24}O_1$: 304.1827, found 304.1825 $[M+Na]^+$; elemental analysis calcd (%) for $C_{22}H_{24}O$: C 86.80, H 7.95; found: C 86.72, H 7.88.

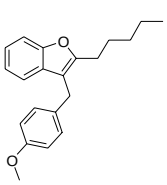
3-Benzyl-2-pentyl-1-benzofuran (Table 2, entry 9). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.1 Hz, 1H), 7.29 (m, 5H), 7.23 (m, 2H), 7.15 (ddd, *J* = 7.6, 0.9 Hz, 1H), 4.04 (s, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 1.77 (m, 2H), 1.38 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.6, 154.1, 139.9, 129.6, 128.4 (2C), 128.3 (2C),



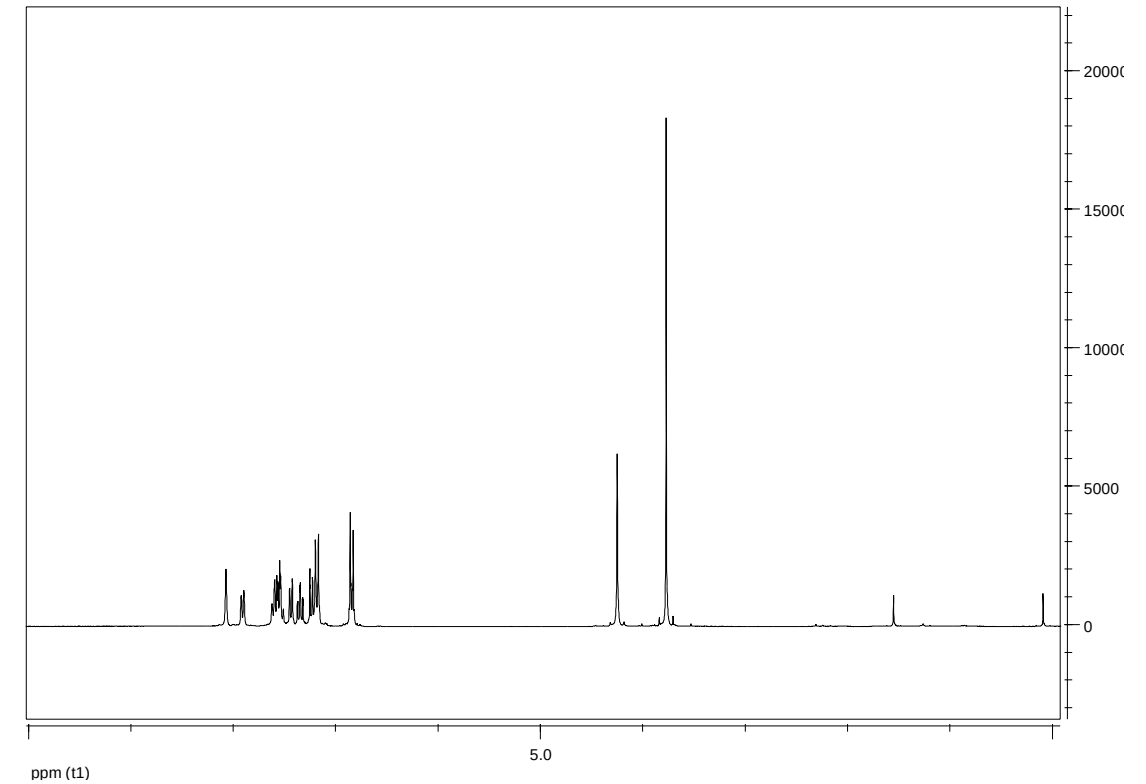
126.1, 123.1, 122.0, 119.3, 112.7, 110.6, 31.5, 29.6, 28.0, 26.4, 22.4, 14.0 ; IR (neat): 3028, 2954, 2927,2858, 1739, 1603, 1494, 1454, 1429, 1250, 1166, 742, 718, 695; MS (EI): *m/z* (%): 278 (100) $[M]^+$; HR-MS (EI): *m/z*: calcd for $C_{20}H_{22}O$: 278.1670, found 278.1668 [*M*]; elemental analysis calcd (%) for

$C_{20}H_{22}O$: C 86.29, H 7.97; found: C 86.14, H 7.88.

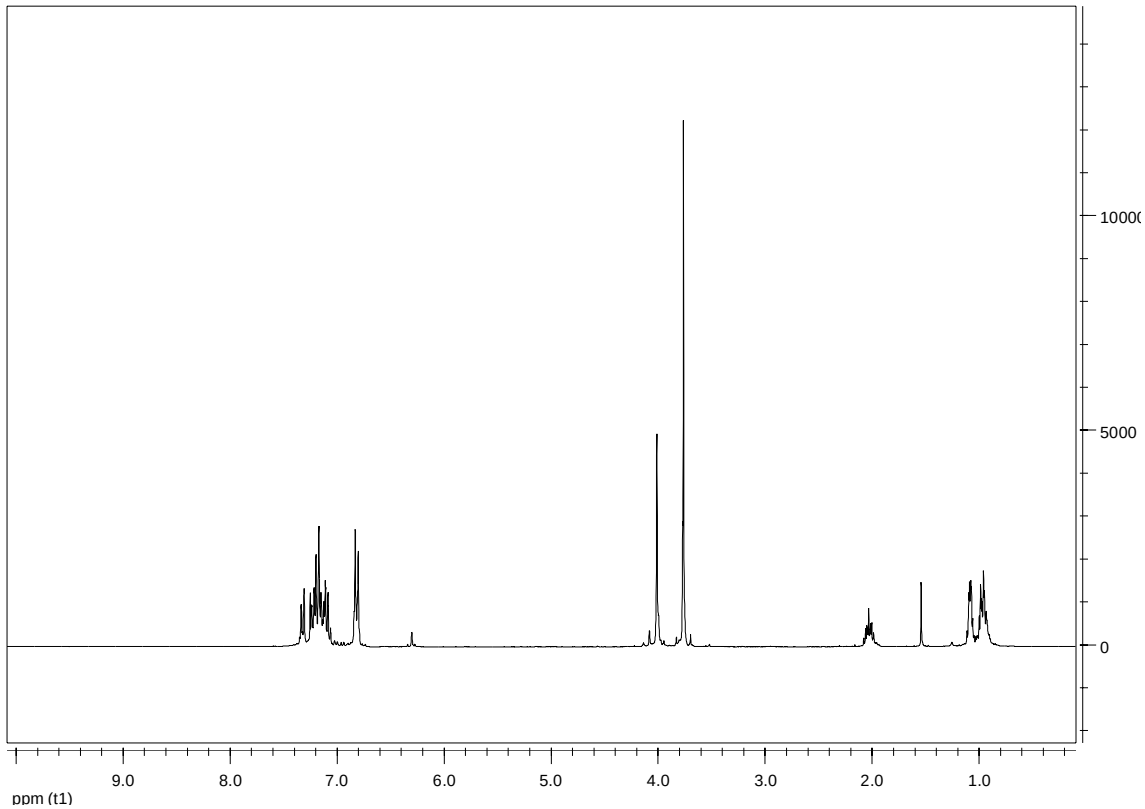
3-(4-Methoxybenzyl)-2-pentyl-1-benzofuran (Table 2, entry 10). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.0 Hz, 1H), 7.15 (m, 1H), 7.09 (m, 3H), 6.78 (m, 2H), 3.90 (s, 2H), 3.74 (s, 3H), 2.72 (t, *J* = 7.5 Hz, 2H), 1.70 (m, 2H), 1.31 (m, 4H), 0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.0, 155.4, 154.0, 132.0, 129.6, 129.2 (2C), 123.0, 122.0, 119.3, 113.8 (2C), 113.1, 110.6, 55.2, 31.5, 28.7, 28.0, 26.4, 22.4, 13.6; IR (neat): 2953, 2929, 2858, 1611, 1509, 1454, 1301, 1243, 1174, 1106, 1036, 1011, 817, 739; MS (EI): *m/z* (%): 308 (100) $[M]^+$; HR-MS (EI): *m/z*: calcd for $C_{21}H_{24}O_2$: 308.1776, found 308.1778 [*M*]; elemental analysis calcd (%) for $C_{21}H_{24}O_2$: C 81.78, H 7.84; found: C 81.70, H 7.94.



3-(4-Methoxybenzyl)-2-[3-(trifluoromethyl)phenyl]-1-benzofuran (Table 2, entry 11). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.65-7.51 (m, 3H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.35 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.27 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 154.1, 150.1, 131.6, 131.2 (q, *J* = 32 Hz), 130.7, 130.3, 129.7, 129.2, 129.0 (2C), 125.0, 124.7 (q, *J* = 4 Hz), 124.0 (q, *J* = 272 Hz), 123.6 (q, *J* = 4 Hz), 122.8, 120.2, 115.7, 114.1 (2C), 111.2, 55.2, 29.2; IR (neat): 2935, 2836, 1611, 1584, 1509, 1453, 142, 1324, 1281, 1244, 1165, 1120, 1075, 1061, 1034, 1009, 904, 841, 802, 745, 695; MS (EI): *m/z* (%): 382 (100) $[M]^+$.



2-Cyclopropyl-3-(4-methoxybenzyl)-1-benzofuran (Table 2, entry 12). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.2 Hz, 1H), 7.26-7.07 (m, 5H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.03 (s, 2H), 3.78 (s, 3H), 2.06 (m, 1H), 1.14-0.95 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.9, 154.9, 153.3, 132.0, 130.0, 129.2, (2C), 122.8, 122.1, 118.7, 113.1 (2C), 113.1, 110.4, 55.2, 28.5, 7.8, 6.8 (2C); IR (neat): 3008, 2834, 1610, 1584, 1509, 1456, 1301, 1243, 1174, 1090, 1034, 976, 810, 738; MS (EI): *m/z* (%): 278 (85) $[M]^+$, 249 (100).



Methyl (2-pentyl-1-benzofuran-3-yl)methyl ether (Table 3, entry 1). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (m, 1H), 7.41 (m, 1H), 7.25 (m, 2H), 4.56 (s, 2H), 3.38 (s, 3H), 2.80 (t, *J* = 7.4 Hz, 2H), 1.75 (m, 2H), 1.36 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.3, 154.0, 128.9, 123.4, 122.4, 119.3, 111.4, 110.6, 64.6, 57.7, 31.4, 28.0, 26.5, 22.4, 13.9; IR (neat): 2927, 2859, 1717, 1673, 1625, 1454, 1378, 1276, 1248, 1191, 1172, 1093, 1073, 952, 908, 743; MS (EI): *m/z* (%): 232 (65) $[M\text{-}H]^+$, 200 (32), 171 (30), 145 (100); HR-MS (EI): *m/z*: calcd for $C_{15}H_{20}O_2$: 232.1463, found 232.1460 [*M*]; elemental analysis calcd (%) for $C_{15}H_{20}O_2$: C 77.55, H 8.68; found: C 77.36, H 8.58.

3-(Methoxymethyl)-2-(2-phenylethyl)-1-benzofuran (Table 3, entry 2). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (m, 1H), 7.40 (m, 1H), 7.25-7.10 (7H), 4.34 (s, 2H), 3.20 (s, 3H), 3.04 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.7, 154.0, 140.8, 128.8, 128.4 (2C), 128.4 (2C), 126.2, 123.6, 122.5, 119.4, 112.1, 110.7, 64.4, 57.5, 34.5, 28.8; IR (neat): 3027, 2925, 1603, 1496, 1475, 1453, 1247, 1189, 1084, 1068, 1008, 907, 743, 697; MS (EI): *m/z* (%): 266 (86) $[M]^+$, 234 (21), 175 (80), 145 (100); HR-MS (EI): *m/z*: calcd for $C_{18}H_{18}O_2$: 266.1307, found 266.1309 [*M*]; elemental analysis calcd (%) for $C_{18}H_{18}O_2$: C 81.17, H 6.81; found: C 81.10, H 6.76.

3-[(Benzyloxy)methyl]-2-(2-phenylethyl)-1-benzofuran (Table 3, entry 3). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (m, 1H), 7.47 (m, 1H), 7.29 (m, 11H), 7.15 (m 1H), 4.49 (s, 2H), 4.43 (s, 2H), 3.08 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.5, 153.8, 140.5, 137.9, 128.5, 128.1 (2C), 128.1 (2C), 128.0 (2C), 127.5 (2C), 127.3, 125.9, 123.3, 122.2, 119.3, 111.9, 110.4, 71.3, 61.7, 34.2, 28.5; IR (neat): 3062, 3028, 2924, 2855, 1626, 1604, 1495, 1453, 1359, 1248, 1186, 1084, 1063, 1028, 1007, 741, 695; MS (EI): *m/z* (%): 342 (55) $[M]^+$, 234 (26), 145 (84), 91 (100); HR-MS (EI): *m/z*: calcd for $C_{24}H_{22}O_2$: 342.1620, found 342.1618 [*M*]; elemental analysis calcd (%) for $C_{24}H_{22}O_2$: C 84.18, H 6.48; found: C 84.22, H 6.50.

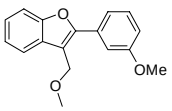
[2-(2-Phenylethyl)-1-benzofuran-3-yl]methyl 2-(trimethylsilyl)ethyl ether (Table 3, entry 4). Pale yellow oil; ^{1}H NMR (400 MHz, C_6D_6): δ 7.68 (m, 1H), 7.38 (m, 1H), 7.16-6.95 (m, 7H), 4.28 (s, 2H), 3.41 (t, *J* = 7.7 Hz, 2H), 2.91 (brd s, 4H), 0.91 (t, *J* = 7.7 Hz, 2H), -0.04 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6): δ 155.5, 154.7, 141.2, 129.6, 128.7 (2C), 128.7 (2C), 126.4, 124.0, 122.8, 120.2, 113.4, 111.0, 67.3, 62.7, 34.9, 29.1, 18.4, -1.2 (3C); IR (neat): 2952, 2855, 1605, 1496, 1475, 1454, 1373, 1247, 1184, 1079, 1065, 937, 857, 832, 743, 696; MS (EI): *m/z* (%): 352 (42) $[M]^+$, 234 (49), 145 (100); HR-MS (EI): *m/z*: calcd for $C_{22}H_{28}O_2Si$: 352.1859, found 352.1861 [*M*]; elemental analysis calcd (%) for $C_{22}H_{28}O_2Si$: C 74.95, H 8.01; found: C 75.04, H 7.96.

2-Cyclopropyl-3-(methoxymethyl)-1-benzofuran (Table 3, entry 5). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (m, 1H), 7.33 (m, 1H), 7.20 (m, 2H), 4.66 (s, 2H), 3.41 (s, 3H), 2.20 (tt, *J* = 8.3, 5.5 Hz, 1H), 1.13 (m, 2H), 1.03 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.2, 153.2, 129.4, 123.2, 122.5, 118.7, 111.2, 110.5, 64.4, 57.7, 7.9 (2C), 7.2; IR (neat): 3012, 2924, 2816, 1626, 1611, 1475, 1458, 1330, 1259, 1182, 1128, 1081, 1043, 1025, 950, 911, 812, 742; MS (EI): *m/z* (%): 202 (95) $[M]^+$, 187 (48), 171 (100); HR-MS (ESI+): *m/z*: calcd for $C_{13}H_{14}O_2$: 202.0994, found 202.0996 [*M*]; elemental analysis calcd (%) for $C_{13}H_{14}O_2$: C 77.20, H 6.98; found: C 77.11, H 7.04.

Methyl (2-phenyl-1-benzofuran-3-yl)methyl ether (Table 3, entry 6). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (m, 2H), 7.71 (m, 1H), 7.51 (m, 2H), 7.42 (m, 2H), 7.31 (m, 2H), 4.75 (s, 2H), 3.48 (s, 3H); ^{13}C NMR (101 MHz,

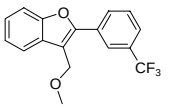
$CDCl_3$): δ 154.1, 154.0, 130.4, 129.9, 128.8, 128.7 (2C), 127.5 (2C), 124.5, 122.9, 119.8, 112.6, 111.1, 64.7, 58.0; IR (neat): 3062, 2923, 2889, 2814, 1591, 1569, 1494, 1475, 1454, 1443, 1255, 1182, 1130, 1084, 1066, 1031, 1004, 948, 903, 877; *m/z* (%): 238 (76) $[M\text{-}H]^+$, 207 (100); HR-MS (EI): *m/z*: calcd for $C_{16}H_{14}O_2$: 238.0994, found 238.0992 [*M*]; elemental analysis calcd (%) for $C_{16}H_{14}O_2$: C 80.65, H 5.92; found: C 80.48, H 6.11.

3-(Methoxymethyl)-2-(3-methoxyphenyl)-1-benzofuran (Table 3, entry 7). Colorless oil;



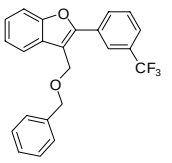
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (m, 1H), 7.48 (m, 1H), 7.38 (m, 3H), 7.26 (m, 2H), 6.93 (ddd, *J* = 7.8, 2.6, 1.3 Hz, 1H), 4.71 (s, 2H), 3.86 (s, 3H), 3.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 154.0, 153.9, 131.6, 129.9, 129.8, 124.6, 122.9, 119.9, 119.8, 115.0, 112.8, 112.6, 111.1, 64.7, 58.0, 55.3; IR (neat): 2935, 2834, 1598, 1571, 1489, 1452, 1283, 1258, 1234, 1162, 1048, 1032, 848, 777, 744; MS (EI): *m/z* (%): 268 (90) $[M]^+$, 237 (100); HR-MS (EI): *m/z*: calcd for $C_{17}H_{16}O_3$: 268.1099, found 268.1102 [*M*]; elemental analysis calcd (%) for $C_{17}H_{16}O_3$: C 76.10, H 6.01; found: C 75.97, H 5.93.

3-(Methoxymethyl)-2-(3-trifluoromethylphenyl)-1-benzofuran (Table 3, entry 8). Pale

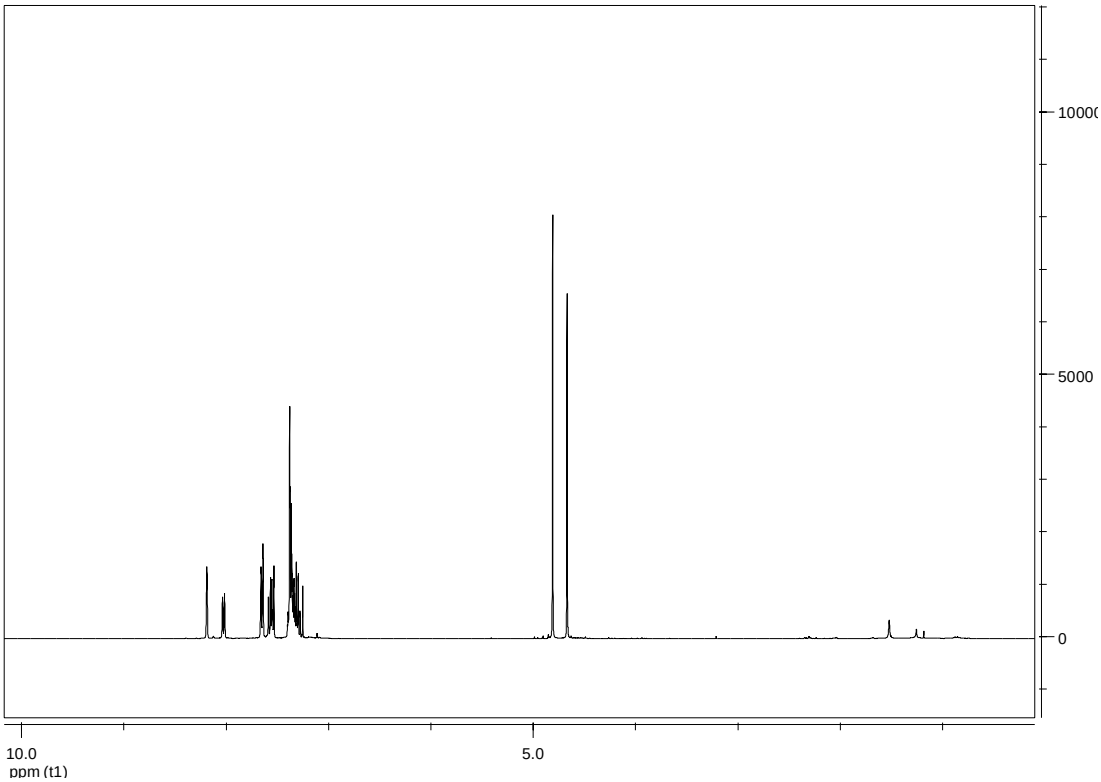


yellow solid; mp 55.3-56.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.62 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.37 (ddd, *J* = 7.9, 7.3, 1.4 Hz, 1H), 7.32 (ddd, *J* = 7.6, 7.3, 1.0 Hz, 1H), 4.73 (s, 2H), 3.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$,): δ 154.0, 152.5, 131.3 (q, *J* = 32 Hz), 131.1, 130.3, 129.6, 129.2, 125.4, 125.2 (q, *J* = 4 Hz), 124.1 (q, *J* = 4 Hz), 124.0 (q, *J* = 272 Hz), 123.2, 119.9, 113.9, 111.3, 64.4, 58.1; IR (neat): 2927, 2895, 2877, 2816, 1728, 1607, 1478, 1452, 1347, 1326, 1286, 1265, 1240, 1199, 1189, 1164, 1135, 1111, 1095, 1085, 1069, 1020, 943, 916, 878, 843, 804, 785, 742, 696; MS (EI): *m/z* (%): 306 (67) $[M]^+$, 275 (100); HR-MS (EI): *m/z*: calcd for $C_{17}H_{13}F_3O_2$: 306.0868, found 306.0865 [*M*]; elemental analysis calcd (%) for $C_{17}H_{13}F_3O_2$: C 66.67, H 4.28; found: C 66.86, H 4.25.

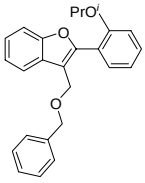
{2-[3-(Trifluoromethyl)phenyl]-1-benzofuran-3-yl}methyl 2-(trimethylsilyl)ethyl ether



(Table 3, entry 9). White solid; mp 60.0-61.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.4, 2H), 7.56 (m, 2H), 7.41-7.28 (m, 7H), 4.83 (s, 2H), 4.69 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1, 152.5, 137.8, 131.2 (q, *J* = 32 Hz), 131.2, 130.4, 129.6, 129.2, 128.5 (2C), 128.0 (2C), 127.9, 125.2, 125.2 (q, *J* = 4 Hz), 124.1 (q, *J* = 272 Hz), 124.1 (q, *J* = 4 Hz), 123.2, 119.9, 113.9, 111.3, 72.4, 61.9; IR (neat): 3073, 3038, 2893, 2369, 1749, 1603, 1478, 1450, 1338, 1320, 1281, 1183, 1171, 1127, 1080, 1071, 1155, 1021, 997, 908, 817, 742, 696; MS (EI): *m/z* (%): 382 (86) $[M]^+$, 291 (20), 275 (100); HR-MS (EI): *m/z*: calcd for $C_{23}H_{17}F_3O_2$: 382.1181, found 382.1177 [*M*]; elemental analysis calcd (%) for $C_{23}H_{17}F_3O_2$: C 72.24, H 4.48; found: C 72.18, H 4.40.

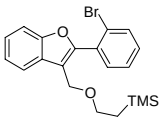


3-[(Benzyloxy)methyl]-2-(2-isopropoxyphenyl)-1-benzofuran (Table 3, entry 10).

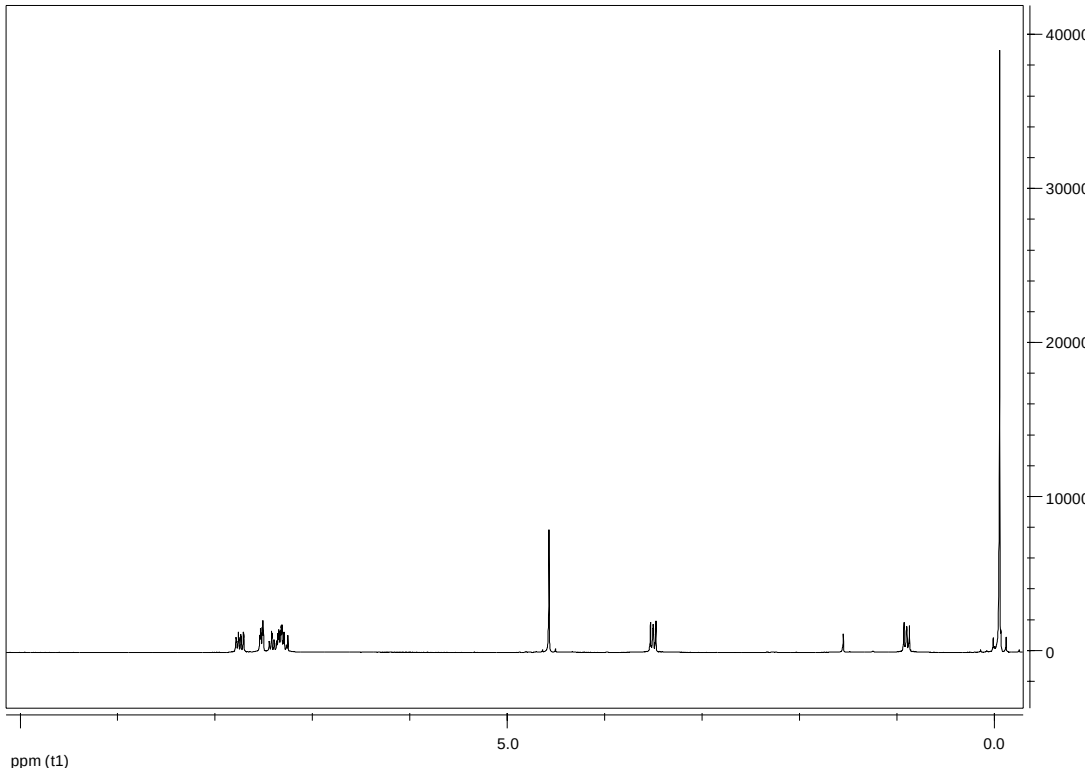


Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (m, 1H), 7.54 (m, 2H), 7.42-7.25 (m, 8H), 7.04 (m, 2H), 4.74 (s, 2H), 4.52 (sept, *J* = 6.1 Hz, 1H), 4.48 (s, 2H), 1.25 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 154.7, 151.1, 138.3, 131.6, 130.5, 129.2, 128.2 (2C), 127.9 (2C), 124.0, 122.5, 120.8, 120.6, 120.6, 120.6, 114.6, 114.3, 111.0, 71.8, 70.9, 63.7, 21.9 (2C); IR (neat): 2976, 2930, 2855, 1591, 1489, 1452, 1384, 1372, 1277, 1239, 110, 1057, 949, 742; MS (EI): *m/z* (%): 372 (51) $[M]^+$, 239 (24), 221 (100); HR-MS (ESI+): *m/z*: calcd for $C_{25}H_{24}Na_1O_3$: 395.1618, found 395.1615 $[M+Na]^+$; elemental analysis calcd (%) for $C_{25}H_{24}O_3$: C 80.62, H 6.49; found: C 80.55, H 6.42.

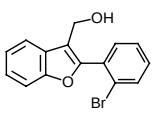
[2-(2-Bromophenyl)-1-benzofuran-3-yl]methyl 2-(trimethylsilyl)ethyl ether (10) (Scheme 5).



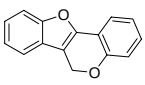
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (m, 2H), 7.53 (m, 2H), 7.43 (ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H), 7.32 (m, 3H), 4.59 (s, 2H), 3.52 (m, 2H), 0.93 (m, 2H), -0.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.5, 152.2, 133.3, 132.6, 131.6, 130.8, 128.5, 127.1, 124.7, 124.1, 122.8, 120.7, 115.4, 111.3, 67.5, 63.0, 18.2, -1.4 (3C); IR (neat): 3059, 2951, 2856, 1475, 1449, 1432, 1371, 1246, 1199, 1069, 1026, 1006, 857, 832, 744,692; MS (EI): *m/z* (%): 404 (20) $[M]^+$, 286 (29), 206 (100); HR-MS (EI): *m/z*: calcd for $C_{20}H_{23}Br_1O_2Si$: 402.0651, found 402.0658 [*M*]; elemental analysis calcd (%) for $C_{20}H_{23}Br_1O_2Si$: C 59.55, H 5.75; found: C 59.65, H 5.85.



[2-(2-Bromophenyl)-1-benzofuran-3-yl]methanol (Scheme 5). White gum ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (m, 1H), 7.73 (8.0, 1.1 Hz, 1H), 7.53 (m, 2H), 7.43 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.34 (m, 3H), 4.79 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.6, 151.7, 133.3, 132.6, 131.4, 131.0, 128.1, 127.3, 124.9, 123.9, 123.0, 120.4, 117.4, 111.4, 56.3; IR (neat): 3337, 3055, 2924, 2876, 1626, 1580, 1560, 1474, 1448, 1431, 1295, 1268, 1239, 1195, 1127, 1104, 1078, 1041, 1024, 1006, 906, 881, 819, 745, 697; MS (EI): *m/z* (%): 304 (100) $[M]^+$; HR-MS (EI): *m/z*: calcd for $C_{15}H_{11}BrNaO_2$: 324.9825, found 324.9840 $[M+Na]^+$; elemental analysis calcd (%) for $C_{15}H_{11}Br_1O_2$: C 59.43, H 3.66; found: C 59.56, H 3.73.



6*H*-[1]Benzofuro[3,2-*c*]chromene (11) (Scheme 5). $Pd(OAc)_2$ (0.4 mg), di(*t*-butyl)biphenyl phosphine (0.7 mg)[12] and Cs_2CO_3 were weighed into a Schlenk tube before the addition of [2-(2-bromophenyl)-1-benzofuran-3-yl]methanol (25 mg, 0.082 mmol) and toluene (0.35 mL). After heating the mixture at 80 °C for 1 h, the mixture was allowed to cool and then placed on a column eluting with 2.5% *tert*-butyl methyl ether in hexanes to afford **11** as a white solid (9.0 mg, 0.041 mmol, 50%), mp 76.0-76.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.54 (brd d, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.31 (ddd, *J* = 7.3, 7.3, 1.4 Hz, 1H), 7.26 (ddd, *J* = 7.6, 7.3, 1.4 Hz, 1H), 7.20 (ddd, *J* = 8.1, 7.6, 1.6 Hz, 1H), 7.00 (ddd, *J* = 7.6, 7.5, 0.6 Hz, 1H), 6.93 (dd, *J*

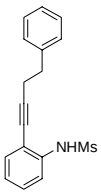


[12] Kuwabe, S-I.; Torraca, K. E.; Buchwald, S. L.; *J. Am. Chem. Soc*. **2001**, *123*, 12202.

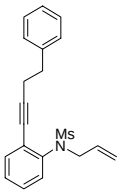
= 8.1, 0.6 Hz, 1H), 5.64 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.5, 154.1, 147.8, 129.8, 125.6, 124.4, 123.3, 121.5, 120.7, 118.8, 116.3, 116.2, 115.6, 108.2, 65.3; IR (neat): 2853, 1640, 1493, 1454, 1383, 1300, 1278, 1213, 1189, 1142, 1043, 1034, 982, 831, 812, 739; MS (EI): *m/z* (%): 221 (100) $[M\text{-}H]^+$; elemental analysis calcd (%) for $C_{15}H_{10}O_2$: C 81.07, H 4.54; found: C 80.97, H 4.46.

OTHER SUBSTRATES AND HETEROCYCLES

***N*-[2-(4-Phenyl-1-butynyl)phenyl]methanesulfonamide (5a).** Mesylchloride (1.14 g, 10 mmol) was added to a solution of crude 2-(4-phenyl-1-butynyl)aniline[13] prepared using SP3 (modified using 3 mol% of $PdCl_2(PPh_3)_2$ and 10 mol% of CuI) in pyridine (5 mL) and THF (10 mL) and the mixture was stirred at room temperature overnight. Water and EtOAc were added and the aqueous phase extracted with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified by flash chroatography eluting in 25% EtOAc/hexanes (1:3) affording **5a** as a light brown oil (2.00 g, 73% over 2 steps); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.42-7.25 (m, 7H), 7.11 (ddd, *J* = 7.6, 1.1 Hz, 1H), 6.89 (brd, 1H), 2.97 (t, *J* = 6.8 Hz, 2H), 2.89 (s, 3H), 2.83 (t, *J* = 6.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.0, 137.6, 132.3, 129.2, 128.6 (2C), 128.4 (2C), 126.6, 124.5, 119.5, 114.7, 97.1, 76.2, 39.3, 34.7, 21.6; IR (neat): 3268, 2929, 1602, 1575, 1489, 1453, 1393, 1333, 1289, 1153, 1103, 1043, 964, 902, 816, 749; MS (EI): *m/z* (%): 299 (14) $[M]^+$, 220 (100); HR-MS (ESI+): *m/z*: calcd for $C_{17}H_{17}N_1Na_1O_2S_1$: 322.0872, found 322.0871 $[M+Na]^+$.



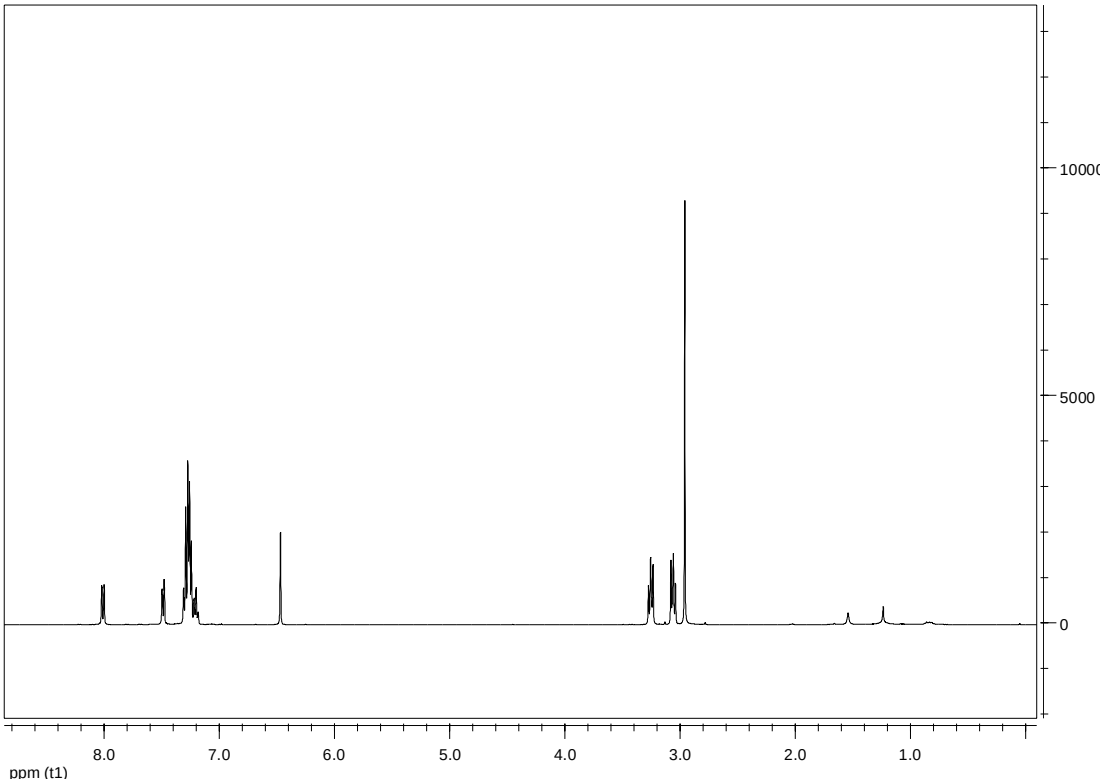
***N*-Allyl-*N*-[2-(4-phenyl-1-butynyl)phenyl]methanesulfonamide (5b).** DEAD (348 mg, 2 mmol) was slowly added to a solution of allyl alcohol (174 mg, 3 mmol), **5a** (299 mg, 1 mmol) and PPh_3 (524 mg, 2 mmol) in THF (10 mL) cooled to 0 °C. After stirring overnight at ambient temperature, the solvent was removed under reduced pressure and the residue purified by flash chromatography to afford **5b** as a light brown oil (282 mg, 83%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (1H, m), 7.24 (m, 8H), 5.74 (ddt, *J* = 17.0, 10.2, 6.4 Hz, 1H), 5.02 (m, 1H), 5.01 (m, 1H), 4.12 (d, *J* = 6.4 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.1, 139.4, 133.7, 133.5, 133.0, 128.6, 128.5 (2C), 128.4 (2C), 128.2, 126.6, 123.5, 118.4, 95.2, 78.6, 53.0, 40.1, 34.6, 21.4; IR (neat): 2926, 1485, 1445, 1335, 1213, 1152, 1107, 1075, 1040, 958, 924, 856, 775, 747; MS (EI): *m/z* (%): 338 (0.4%) $[M]^+$,



[13] Li, H.; Yang, H.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.*, **2004**, *69*, 4500.

312 (30), 260 (100); HR-MS (ESI+): *m/z*: calcd for $C_{20}H_{21}N_1Na_1O_2S_1$: 362.1185, found 362.1183 $[M+Na]^+$.

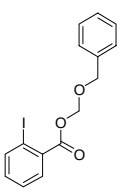
1-(Methylsulfonyl)-2-(2-phenylethyl)-1*H*-indole (6a). Following SP4, product **6a** was isolated as a white solid; mp 111.2-112.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.49 (m, 1H), 7.28 (m, 6H), 7.21 (m, 1H), 6.48 (s, 1H), 3.27 (t, *J* = 7.8 Hz, 2H), 3.07 (t, *J* = 7.8 Hz, 2H), 2.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.3, 141.0, 136.8, 129.7, 128.5 (2C), 128.5 (2C), 126.2, 124.2, 123.7, 120.4, 114.2, 109.2, 40.4, 35.6, 30.9; IR (neat): 3059, 3008, 2926, 2860, 1593, 1570, 1496, 1452, 1357, 1331, 1297, 1264, 1217, 1167, 1138, 1042, 1019, 969, 818, 772, 751, 740; MS (EI): *m/z* (%): 299 (30) $[M]^+$, 208 (100); HR-MS (ESI+): *m/z*: calcd for $C_{17}H_{17}N_1Na_1O_2S_1$: 322.0872, found 322.0874 $[M+Na]^+$.



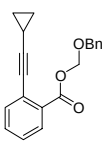
3-Allyl-1-(methylsulfonyl)-2-(2-phenylethyl)-1*H*-indole (6b). Following SP4, product **6b** was isolated as a white solid; mp 111.7-113.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (m, 1H), 7.28 (m, 5H), 7.22 (m, 3H), 5.92 (ddt, *J* = 17.1, 10.4, 4.9 Hz, 1H), 5.23 (brd d, *J* = 10.4 Hz, 1H), 4.92 (brd d, *J* = 17.1 Hz, 1H), 4.65 (dt, *J* = 4.7, 1.8 Hz, 2H), 3.43 (m, 2H), 3.02 (m, 2H), 3.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.7, 140.3, 135.8, 131.8, 128.6 (2C), 128.6 (2C), 126.5, 125.0, 123.2, 122.4, 119.6, 117.6, 110.7, 110.3, 45.6, 45.6, 36.6, 27.0; IR (neat): 2926, 1521, 1464, 1452, 1401, 1350, 1324, 1286, 1263, 1152, 1129, 1112, 977, 946, 925, 786, 767, 751, 702; MS (EI):

m/z (%): 339 (80) $[M]^+$, 260 (58), 248 (80), 169 (100); HR-MS (ESI+): *m/z*: calcd for $C_{20}H_{21}N_1Na_1O_2S_1$: 362.1185, found 362.1188 $[M+Na]^+$; elemental analysis calcd (%) for $C_{20}H_{21}NO_2S$: C 70.77, H 6.24, N 4.13; found: C 70.57, H 6.36, N 4.07.

(Benzyloxy)methyl 2-iodobenzoate. A solution of 2-iodobenzoic acid (2.48 g, 10 mmol) in DMF (20 mL) was added dropwise to a stirring suspension of NaH (0.3 g, 12 mmol) in DMF (20 mL) and the mixture stirred for 1 h at ambient temperature before BOMCl (12mmol) was added. The mixture was then stirred at room temperature until the carboxylic acid was consumed, after which the mixture was diluted with water (300 mL) and *tert*-butyl methyl ether (150 mL). The layers were separated and the organic phase washed with water (2 × 300 mL) and brine before being dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. Flash chromotography eluting in *tert*-butyl methyl ether/hexanes afforded the title compound as a colorless oil (2.67 g, 73%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.78 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.44-7.29 (m, 6H), 7.17 (ddd, *J* = 7.7, 7.7, 1.5 Hz, 1H), 5.63 (s, 2H), 4.84 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8, 141.4, 136.8, 134.5, 132.9, 131.1, 128.5 (2C), 128.0, 127.9 (2C), 127.9, 127.7, 89.6, 72.3; IR (neat): 1727, 1582, 1285, 1244, 1162, 1068, 1010, 904, 734; MS (EI): *m/z* (%): 368 (2) $[M]^+$, 231 (42), 120 (100); HR-MS (ESI+): *m/z*: calcd for $C_{15}H_{13}I_1Na_1O_3$: 390.9802, found 390.9800 $[M+Na]^+$.



(Benzyloxy)methyl-2-(cyclopropylethynyl)benzoate. Following SP1, the title compound was isolated as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 7.9, 1,3 Hz, 1H), 7.51-7.26 (m, 8H), 5.61 (s, 2H), 4.82 (s, 2H), 1.49 (m, 1H), 0.90-0.85 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.7, 137.0, 134.3, 131.8, 131.3, 130.4, 128.5 (2C), 127.9, 127.9 (2C), 127.0, 124.7, 99.5, 89.1, 74.5, 71.9, 8.9 (2C), 0.7; IR (neat): 2228, 1722, 1484, 1284, 1240, 1161, 1097, 1063, 1027, 954, 909, 754, 731, 695; MS (EI): *m/z* (%): 276 (7), 185 (85), 91 (100); HR-MS (ESI+): *m/z*: calcd for $C_{20}H_{21}N_1Na_1O_2S_1$: 329.1148, found $[M+Na]^+$ 329.1151.



4-[(Benzyloxy)methyl]-3-cyclopropyl-1*H*-isochromen-1-one. Following SP4, the title compound was isolated as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.71 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.46-7.28 (m, 6H), 4.71 (s, 2H), 4.64 (s, 2H), 1.98 (tt, *J* = 8.3, 5.0 Hz, 1H), 1.20 (m, 2H), 0.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9, 160.0, 137.8, 137.8, 134.8, 129.5, 128.5 (2C), 128.0 (2C), 127.9, 127.0, 122.8, 120.0, 108.6, 72.0, 63.6, 10.9, 7.6 (2C); IR (neat): 2922, 2852, 1726, 1634, 1605, 1564, 1481, 1454, 1364, 1320, 1259, 1213, 1056, 1025, 919, 811, 771, 691; MS (EI): *m/z* (%): 306 (47) $[M]^+$, 199 (19), 173 (21), 91 (100); HR-MS (ESI+): *m/z*: calcd for $C_{20}H_{18}Na_1O_3$: 329.1148, found 329.1146 $[M+Na]^+$; elemental analysis calcd (%) for $C_{20}H_{18}O_3$: C 78.41, H 5.92; found: C 78.29, H 6.04.