

A Simple and Efficient Approach to 2-Alkynylbenzofurans under Mild Copper (I)-Catalyzed Conditions

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1. General information

All the chemicals and solvents were used as received without further purification. Silica gel was purchased from Qing Dao Hai Lang Chemical Industry Co. NMR spectra of the products were recorded using a Bruker Avance TM spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C in CDCl_3 unless otherwise noted. High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics microTOF-Q spectrometer.

2. Experimental procedure for copper(I)-catalyzed tandem reactions of gem-dihaloolefins

A mixture of gem-dihaloolefins (1.0 mmol), phenylacetylenes (1.5 mmol), CuI (15 mol %), DABCO (30 mol %), Cs_2CO_3 (2.0 equiv), and DMF (5.0 mL) in a Schlenk tube was stirred under N_2 at 140 °C (oil bar temperature) for 24h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na_2SO_4 , and concentrated in vacuum. The residue was purified by flash column chromatography (hexane or hexane /ethyl acetate) to afford the corresponding coupled products.

3. Experimental procedure for the oxidation of 2-alkynylbenzofuran to corresponding benzil derivatives.

A mixture of 2-alkynylbenzofuran (1.0 mmol), 10% Pd/C (0.10 mmol), and DMSO (3.0 mL), was stirred under an oxygen (balloon) atmosphere at 120 °C (oil bar temperature) for 24h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na_2SO_4 , and concentrated in vacuum. The residue was purified by flash column chromatography (hexane or hexane /ethyl acetate) to afford the corresponding coupled products.

4. Experiments on investigation of mechanism

4.1 Copper(I)-catalyzed tandem reactions of gem-dihaloolefins and (phenylethynyl)copper.

A mixture of gem-dihaloolefins (1.0 mmol), (phenylethynyl)copper (1.5 mmol), CuI (15 mol %), DABCO (30 mol %), Cs_2CO_3 (2.0 equiv), and DMF (5.0 mL) in a Schlenk tube was

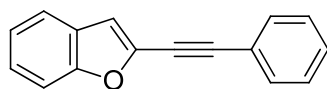
stirred under N₂ at 140 °C (oil bath temperature) for 24h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na₂SO₄, and concentrated in *vacuum*. The residue was purified by flash column chromatography (hexane or hexane /ethyl acetate) to afford the corresponding coupled products.

4.2 Copper(I)-catalyzed tandem reactions of 2-bromobenzofuran and (phenylethynyl)copper.

A mixture of 2-bromobenzofuran (1.0 mmol), (phenylethynyl)copper (1.5 mmol), CuI (15 mol %), DABCO (30 mol %), Cs₂CO₃ (2.0 equiv), and DMF (5.0 mL) in a Schlenk tube was stirred under N₂ at 140 °C (oil bath temperature) for 24h. After cooling to room temperature, water (30 mL) was added and the aqueous phase was extracted by EtOAc (5×30 mL). The combined organic phases were dried over Na₂SO₄, and concentrated in *vacuum*. The residue was purified by flash column chromatography (hexane or hexane /ethyl acetate) to afford the corresponding coupled products.

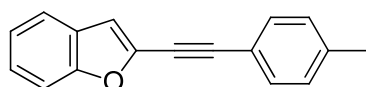
5. Characterization data for products

2-(phenylethynyl)benzofuran



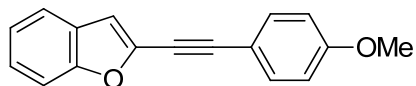
^1H NMR (400 MHz, CDCl_3) δ 7.62 (dt, $J = 6.9, 2.8$ Hz, 3H), 7.52 (d, $J = 8.3$ Hz, 1H), 7.46-7.33 (m, 4H), 7.33-7.26 (m, 1H), 7.06 (d, $J = 2.7$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.77, 140.63, 133.53, 131.01, 130.35, 129.60, 127.46, 125.16, 123.70, 123.06, 113.45, 113.10, 96.92, 81.55. HRMS, calculated for $\text{C}_{16}\text{H}_{11}\text{O}$ ($\text{M}+\text{H}^+$):219.0804, found: 219.0808 ($\text{M}+\text{H}^+$).

2-(p-tolyethynyl)benzofuran



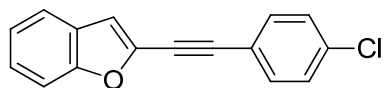
^1H NMR (400 MHz, CDCl_3) δ 7.58 (dq, $J = 7.7, 1.1$ Hz, 1H), 7.48 (dt, $J = 8.2, 1.6$ Hz, 3H), 7.34 (tt, $J = 8.4, 1.4$ Hz, 1H), 7.29-7.16 (m, 3H), 6.99 (t, $J = 1.2$ Hz, 1H), 2.39 (d, $J = 1.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.70, 141.33, 140.81, 133.44, 131.11, 129.65, 127.31, 125.09, 122.97, 120.58, 113.08, 113.05, 97.15, 80.89, 23.47. HRMS, calculated for $\text{C}_{17}\text{H}_{13}\text{O}$ ($\text{M}+\text{H}^+$):233.0961, found: 233.0962 ($\text{M}+\text{H}^+$).

2-((4-methoxyphenyl)ethynyl)benzofuran



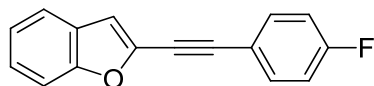
^1H NMR (400 MHz, CDCl_3) δ 7.63-7.46 (m, 4H), 7.37 (t, $J = 7.8$ Hz, 1H), 7.29 (dd, $J = 9.0, 5.6$ Hz, 1H), 7.02-6.88 (m, 3H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.18, 156.69, 140.99, 135.15, 129.73, 127.26, 125.11, 122.96, 116.04, 115.68, 113.04, 112.83, 97.11, 80.37, 57.18. HRMS, calculated for $\text{C}_{17}\text{H}_{12}\text{Na}_2$ ($\text{M}+\text{Na}^+$):271.0730, found: 271.0727 ($\text{M}+\text{Na}^+$).

2-((4-chlorophenyl)ethynyl)benzofuran



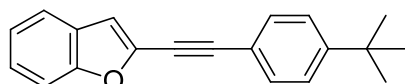
^1H NMR (400 MHz, CDCl_3) δ 7.58 (dq, $J = 7.8, 1.1$ Hz, 1H), 7.53-7.46 (m, 3H), 7.39-7.33 (m, 3H), 7.29-7.24 (m, 1H), 7.03 (t, $J = 1.1$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.80, 140.28, 137.11, 134.67, 130.74, 129.48, 127.60, 125.22, 123.11, 122.18, 113.76, 113.11, 95.74, 82.44. ESI-MS: 252

2-((4-fluorophenyl)ethynyl)benzofuran



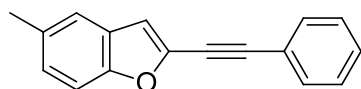
^1H NMR (400 MHz, CDCl_3) δ 7.61 (t, $J = 7.1$ Hz, 3H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.39 (t, $J = 7.8$ Hz, 1H), 7.34-7.26 (m, 1H), 7.12 (t, $J = 8.4$ Hz, 2H), 7.05 (d, $J = 3.1$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.10, 163.60, 156.75, 140.43, 135.57, 129.52, 127.50, 125.18, 123.06, 119.83, 117.86, 113.48, 95.79, 81.27. HRMS, calculated for $\text{C}_{16}\text{H}_{10}\text{FO}$ ($\text{M}+\text{H}^+$):237.0710, found: 237.0741($\text{M}+\text{H}^+$).

2-((4-(tert-butyl)phenyl)ethynyl)benzofuran



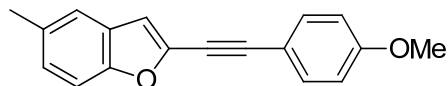
^1H NMR (400 MHz, CDCl_3) δ 7.56 (td, $J = 18.7, 8.0$ Hz, 4H), 7.44 (dd, $J = 7.5, 3.1$ Hz, 2H), 7.37 (t, $J = 7.9$ Hz, 1H), 7.32-7.28 (m, 1H), 7.03 (d, $J = 2.7$ Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.70, 154.42, 140.85, 133.29, 129.66, 127.37, 127.31, 125.09, 122.97, 120.63, 113.12, 113.05, 97.17, 80.91, 36.77, 33.00. HRMS, calculated for $\text{C}_{20}\text{H}_{19}\text{O}$ ($\text{M}+\text{H}^+$):275.1430, found: 275.1413 ($\text{M}+\text{H}^+$).

5-methyl-2-(phenylethynyl)benzofuran



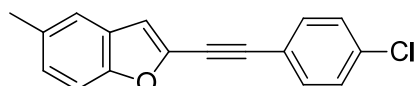
^1H NMR (400 MHz, CDCl_3) δ 7.65-7.57 (m, 2H), 7.41 (dq, $J = 9.2, 3.5, 2.8$ Hz, 5H), 7.19 (d, $J = 8.5$ Hz, 1H), 6.98 (d, $J = 3.4$ Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.24, 140.63, 134.64, 133.49, 130.92, 130.33, 129.68, 128.81, 123.77, 122.76, 113.26, 112.58, 96.74, 81.69, 23.16. HRMS, calculated for $\text{C}_{17}\text{H}_{13}\text{O}$ ($\text{M}+\text{H}^+$):233.0961, found: 233.0972 ($\text{M}+\text{H}^+$).

2-((4-methoxyphenyl)ethynyl)-5-methylbenzofuran



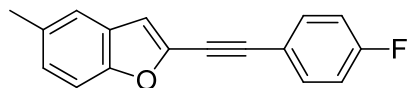
^1H NMR (400 MHz, CDCl_3) δ 7.55 (dt, $J = 8.8, 2.4$ Hz, 2H), 7.38 (t, $J = 4.1$ Hz, 2H), 7.21-7.14 (m, 1H), 6.97-6.89 (m, 3H), 3.87 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.12, 155.14, 140.98, 135.10, 134.55, 129.79, 128.58, 122.66, 116.01, 115.76, 112.63, 112.50, 96.88, 80.49, 57.18, 23.16. HRMS, calculated for $\text{C}_{18}\text{H}_{15}\text{O}_2$ ($\text{M}+\text{H}^+$):263.1067, found: 263.1074 ($\text{M}+\text{H}^+$).

2-((4-chlorophenyl)ethynyl)-5-methylbenzofuran



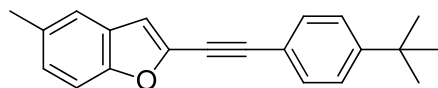
^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.9$ Hz, 2H), 7.43-7.32 (m, 4H), 7.20 (d, $J = 8.4$ Hz, 1H), 6.98 (s, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.29, 140.30, 137.03, 134.72, 134.63, 130.72, 129.58, 128.98, 122.81, 122.26, 113.60, 112.60, 95.60, 82.65, 23.16. HRMS, calculated for $\text{C}_{17}\text{H}_{12}\text{ClO}$ ($\text{M}+\text{H}^+$):267.0571, found: 267.0601 ($\text{M}+\text{H}^+$).

2-((4-fluorophenyl)ethynyl)-5-methylbenzofuran



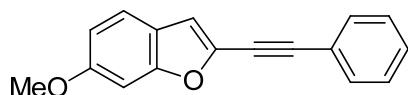
^1H NMR (400 MHz, CDCl_3) δ 7.59 (ddd, $J = 8.6, 4.7, 1.8$ Hz, 2H), 7.43-7.35 (m, 2H), 7.22-7.16 (m, 1H), 7.15-7.05 (m, 2H), 6.97 (d, $J = 3.4$ Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.06, 163.56, 155.24, 140.45, 135.56, 134.68, 129.62, 128.87, 122.77, 119.94, 117.84, 117.62, 95.64, 81.45, 23.15. HRMS, calculated for $\text{C}_{17}\text{H}_{12}\text{FO}$ ($\text{M}+\text{H}^+$):251.0867, found: 251.0867 ($\text{M}+\text{H}^+$).

2-((4-(tert-butyl)phenyl)ethynyl)-5-methylbenzofuran



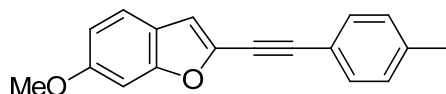
^1H NMR (400 MHz, CDCl_3) δ 7.56-7.48 (m, 2H), 7.44-7.32 (m, 4H), 7.19-7.11 (m, 1H), 6.93 (dd, $J = 4.1, 2.0$ Hz, 1H), 2.45 (d, $J = 3.2$ Hz, 3H), 1.40-1.29 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.19, 154.34, 140.88, 134.57, 133.28, 129.77, 128.68, 127.36, 122.71, 120.72, 112.97, 112.54, 97.02, 81.11, 36.77, 33.01, 23.17. HRMS, calculated for $\text{C}_{21}\text{H}_{21}\text{O}$ ($\text{M}+\text{H}^+$):289.1587, found: 289.1595 ($\text{M}+\text{H}^+$).

6-methoxy-2-(phenylethynyl)benzofuran



^1H NMR (400 MHz, CDCl_3) δ 7.63-7.54 (m, 2H), 7.48-7.34 (m, 4H), 7.05-6.87 (m, 3H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.02, 157.91, 139.77, 133.38, 130.79, 130.32, 123.91, 123.17, 122.80, 114.59, 113.45, 97.40, 96.76, 81.73, 57.55. HRMS, calculated for $\text{C}_{17}\text{H}_{13}\text{O}_2$ ($\text{M}+\text{H}^+$):249.0910, found: 249.0897 ($\text{M}+\text{H}^+$).

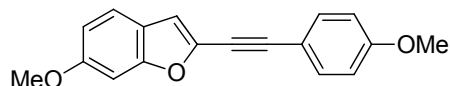
6-methoxy-2-(p-tolyethynyl)benzofuran



^1H NMR (400 MHz, CDCl_3) δ 7.47 (dd, $J = 8.2, 2.0$ Hz, 2H), 7.42 (d, $J = 8.5$ Hz, 1H), 7.21 – 7.16 (m, 2H), 7.00 (d, $J = 2.3$ Hz, 1H), 6.94 – 6.86 (m, 2H), 3.86 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz,

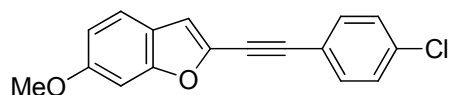
CDCl₃) δ 160.91, 157.83, 141.09, 139.96, 133.31, 131.09, 123.08, 122.85, 120.79, 114.49, 113.08, 97.40, 96.97, 81.07, 57.55, 23.45. HRMS, calculated for C₁₈H₁₅O₂ (M+H⁺):263.1067, found: 263.1056 (M+H⁺).

6-methoxy-2-((4-methoxyphenyl)ethynyl)benzofuran



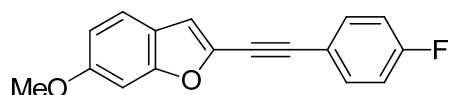
¹H NMR (400 MHz, CDCl₃) δ 7.55-7.49 (m, 2H), 7.42 (dd, *J* = 8.6, 1.4 Hz, 1H), 6.99 (dt, *J* = 2.3, 1.0 Hz, 1H), 6.95-6.87 (m, 4H), 3.86 (d, *J* = 1.3 Hz, 3H), 3.84 (d, *J* = 1.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.02, 160.86, 157.78, 140.11, 134.99, 123.02, 122.90, 115.99, 115.90, 114.42, 112.78, 97.41, 96.82, 80.46, 57.54, 57.17. HRMS, calculated for C₁₈H₁₅O₃ (M+H⁺):279.1016, found: 279.0992 (M+H⁺).

2-((4-chlorophenyl)ethynyl)-6-methoxybenzofuran



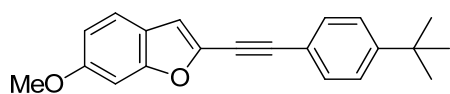
¹H NMR (400 MHz, CDCl₃) δ 7.53-7.46 (m, 2H), 7.43 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.37-7.32 (m, 2H), 7.01-6.94 (m, 2H), 6.90 (ddd, *J* = 8.6, 2.3, 1.3 Hz, 1H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.13, 157.96, 139.42, 136.85, 134.52, 130.68, 123.21, 122.68, 122.40, 114.68, 113.77, 97.38, 95.61, 82.66, 57.54. ESI-MS: 282

2-((4-fluorophenyl)ethynyl)-6-methoxybenzofuran



¹H NMR (400 MHz, CDCl₃) δ 7.55 (dddd, *J* = 7.0, 5.3, 3.3, 1.5 Hz, 2H), 7.43 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.07 (ddd, *J* = 8.7, 7.7, 1.7 Hz, 2H), 7.00 (t, *J* = 2.2 Hz, 1H), 6.97-6.87 (m, 2H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.97, 163.48, 161.05, 157.90, 139.58, 135.33, 123.16, 122.72, 117.80, 114.61, 113.46, 97.39, 95.62, 81.42, 57.54. HRMS, calculated for C₁₇H₁₂FO₂ (M+H⁺):267.0810, found: 267.0804 (M+H⁺).

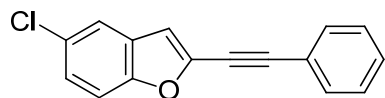
2-((4-(tert-butyl)phenyl)ethynyl)-6-methoxybenzofuran



¹H NMR (400 MHz, CDCl₃) δ 7.54-7.48 (m, 2H), 7.45-7.37 (m, 3H), 7.01-6.98 (m, 1H), 6.94-6.87 (m, 2H), 3.86 (s, 3H), 1.33 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 160.91, 157.83, 154.18, 139.99, 133.15,

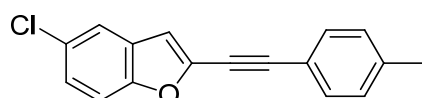
127.33, 123.08, 122.87, 120.83, 114.48, 113.11, 97.40, 96.97, 81.07, 57.55, 36.75, 33.00. HRMS, calculated for $C_{21}H_{21}O_2$ ($M+H^+$):305.1536, found: 305.1521 ($M+H^+$).

5-chloro-2-(phenylethynyl)benzofuran



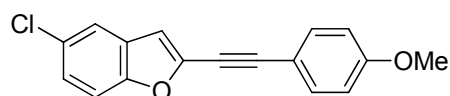
1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.51 (m, 3H), 7.39 (dd, $J = 8.8, 3.4$ Hz, 4H), 7.34-7.27 (m, 1H), 6.94 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.06, 142.07, 133.59, 131.23, 130.95, 130.80, 130.40, 127.62, 123.41, 122.50, 114.03, 112.81, 97.56, 81.09. ESI-MS: 252

5-chloro-2-(p-tolyethynyl)benzofuran



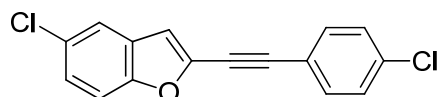
1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, $J = 2.1$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.7$ Hz, 1H), 7.28 (dd, $J = 8.7, 2.2$ Hz, 1H), 7.19 (d, $J = 7.9$ Hz, 2H), 6.92 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.00, 142.26, 141.61, 133.49, 131.14, 131.00, 130.72, 127.46, 122.41, 120.28, 113.98, 112.42, 97.79, 80.41, 23.48. HRMS, calculated for $C_{17}H_{12}ClO$ ($M+H^+$):267.0571, found: 267.0575 ($M+H^+$). ESI-MS: 264

5-chloro-2-((4-methoxyphenyl)ethynyl)benzofuran



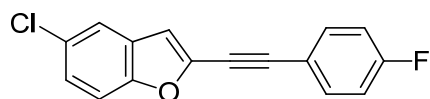
1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.49 (m, 3H), 7.38 (dt, $J = 8.8, 0.7$ Hz, 1H), 7.30-7.25 (m, 1H), 6.93-6.87 (m, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.32, 154.95, 142.41, 135.20, 131.06, 130.68, 127.35, 122.35, 116.05, 115.35, 113.93, 112.11, 97.71, 79.86, 57.19. HRMS, calculated for $C_{17}H_{12}ClO_2$ ($M+H^+$):283.0520, found: 283.0523 ($M+H^+$).

5-chloro-2-((4-chlorophenyl)ethynyl)benzofuran



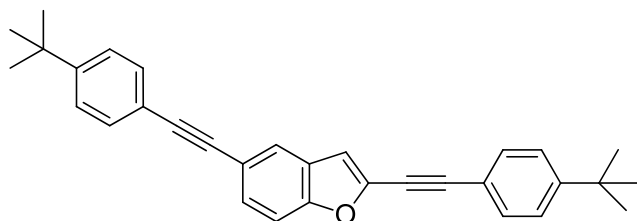
1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.47 (m, 4H), 7.43-7.26 (m, 3H), 6.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.09, 141.71, 137.38, 134.72, 130.87, 130.81, 130.77, 127.77, 122.54, 121.86, 114.05, 113.07, 96.32, 81.91.

5-chloro-2-((4-fluorophenyl)ethynyl)benzofuran



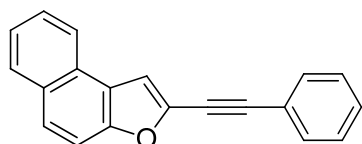
^1H NMR (400 MHz, CDCl_3) δ 7.57 (ddt, $J = 11.1, 5.0, 2.4$ Hz, 3H), 7.44-7.34 (m, 1H), 7.34-7.24 (m, 1H), 7.15-7.04 (m, 2H), 6.94 (d, $J = 2.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.21, 163.71, 155.04, 141.86, 135.65, 130.82, 127.66, 122.49, 119.52, 117.69, 114.02, 112.80, 96.38, 80.75.

2-((4-(tert-butyl)phenyl)ethynyl)-5-chlorobenzofuran



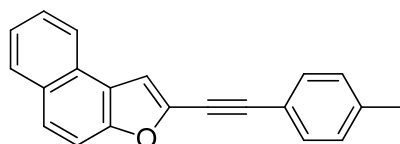
^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.49 (m, 3H), 7.47 (d, $J = 8.1$ Hz, 2H), 7.44 – 7.39 (m, 3H), 7.36 (t, $J = 6.3$ Hz, 3H), 7.29 (s, 1H), 6.92 (s, 1H), 1.34 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.01, 154.69, 154.40, 142.30, 134.11, 133.36, 131.03, 130.73, 127.46, 127.41, 127.32, 122.41, 120.69, 120.33, 113.98, 112.46, 97.81, 83.38, 80.43, 75.37, 36.79, 36.76, 32.98, 32.96. HRMS, calculated for $\text{C}_{32}\text{H}_{31}\text{O}$ ($\text{M}+\text{H}^+$): 431.2369, found: 431.2369 ($\text{M}+\text{H}^+$).

2-(phenylethynyl)naphtho[2,1-b]furan



^1H NMR (400 MHz, CDCl_3) δ 8.13 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.98 – 7.93 (m, 1H), 7.79 (d, $J = 8.9$ Hz, 1H), 7.67 – 7.59 (m, 4H), 7.56 – 7.49 (m, 2H), 7.40 (dp, $J = 4.8, 1.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.56, 140.03, 133.45, 132.31, 130.91, 130.68, 130.37, 129.22, 128.59, 128.54, 126.77, 125.27, 125.04, 123.85, 114.02, 112.53, 97.04, 81.76. HRMS, calculated for $\text{C}_{20}\text{H}_{13}\text{O}$ ($\text{M}+\text{H}^+$): 269.0961, found: 269.0952 ($\text{M}+\text{H}^+$).

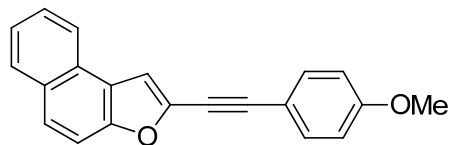
2-(p-tolyethynyl)naphtho[2,1-b]furan



^1H NMR (400 MHz, CDCl_3) δ 8.16 – 8.10 (m, 1H), 7.95 (d, $J = 8.1$ Hz, 1H), 7.78 (d, $J = 8.9$ Hz, 1H), 7.67 – 7.58 (m, 2H), 7.55 – 7.47 (m, 4H), 7.24 – 7.18 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.47, 141.23, 140.23, 133.37, 132.29, 131.13, 130.65, 129.20, 128.48, 128.43, 126.72,

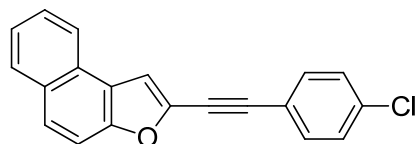
125.27, 125.08, 120.73, 114.01, 112.19, 97.26, 81.11, 23.48. HRMS, calculated for $C_{21}H_{14}NaO_2$ (M+Na):305.0937, found: 305.0926 (M+Na).

2-((4-methoxyphenyl)ethynyl)naphtho[2,1-b]furan



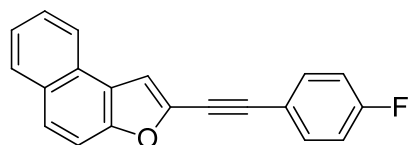
1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.2$ Hz, 1H), 7.94 (d, $J = 8.3$ Hz, 1H), 7.77 (d, $J = 8.9$ Hz, 1H), 7.67-7.45 (m, 6H), 6.97-6.88 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.10, 154.40, 140.38, 135.07, 132.29, 130.65, 129.19, 128.45, 128.32, 126.70, 125.27, 125.11, 116.04, 115.83, 113.99, 111.89, 97.12, 80.52, 57.19. HRMS, calculated for $C_{21}H_{15}O_2$ (M+H $^+$):299.1067, found: 299.1060 (M+H $^+$).

2-((4-chlorophenyl)ethynyl)naphtho[2,1-b]furan



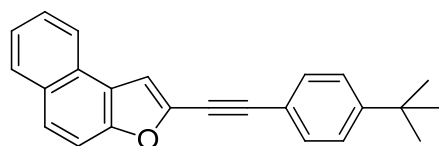
1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.1$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 1H), 7.79 (d, $J = 8.8$ Hz, 1H), 7.68-7.58 (m, 2H), 7.53 (dd, $J = 8.8, 2.1$ Hz, 4H), 7.41-7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.64, 139.68, 136.99, 134.59, 132.31, 130.74, 130.68, 129.19, 128.77, 128.60, 126.83, 125.23, 124.96, 122.32, 113.98, 112.83, 95.88, 82.68. HRMS, calculated for $C_{20}H_{12}ClO$ (M+H $^+$):303.0571, found: 303.0573 (M+H $^+$).

2-((4-fluorophenyl)ethynyl)naphtho[2,1-b]furan



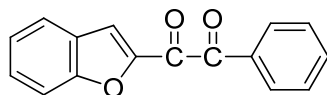
1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.0$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.78 (d, $J = 8.9$ Hz, 1H), 7.60 (dddd, $J = 14.3, 6.7, 3.5, 2.1$ Hz, 4H), 7.55-7.47 (m, 2H), 7.14-7.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.05, 163.55, 154.57, 139.84, 135.49, 135.40, 132.31, 130.67, 129.20, 128.64, 128.55, 126.79, 125.24, 117.64, 113.98, 112.55, 95.90, 81.48. ESI-MS: 286

2-((4-(tert-butyl)phenyl)ethynyl)naphtho[2,1-b]furan



^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 8.1$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 1H), 7.78 (d, $J = 9.0$ Hz, 1H), 7.68-7.59 (m, 2H), 7.59-7.47 (m, 4H), 7.46-7.39 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.47, 154.32, 140.26, 133.24, 132.30, 130.66, 129.21, 128.49, 128.44, 127.40, 126.73, 125.28, 125.09, 120.78, 114.01, 112.23, 97.29, 81.14, 36.78, 33.02. HRMS, calculated for $\text{C}_{24}\text{H}_{21}\text{O}$ ($\text{M}+\text{H}^+$):325.1587, found: 325.1606 ($\text{M}+\text{H}^+$).

1-(benzofuran-2-yl)-2-phenylethane-1, 2-dione



^1H NMR (400 MHz, CDCl_3) δ 8.14-8.03 (m, 2H), 7.79-7.61 (m, 4H), 7.54 (tt, $J = 7.7, 4.1$ Hz, 3H), 7.35 (dq, $J = 7.3, 4.6, 4.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 193.12, 184.36, 158.48, 151.46, 136.88, 134.33, 132.10, 131.62, 130.84, 128.64, 126.26, 125.82, 121.41, 114.58. HRMS, calculated for $\text{C}_{16}\text{H}_{10}\text{NaO}_3$ ($\text{M}+\text{Na}^+$):273.0522, found: 273.0546 ($\text{M}+\text{Na}^+$).

6. ^1H NMR and ^{13}C NMR copies of products

