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

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Contents

1. General information
2. Experimental procedure for copper(I)-catalyzed tandem reactions of gem-dihaloolefins
3. Experimental procedure for Pd/C-catalyzed environmentally benign process for the oxidation of 2-alkynylbenzofuran to corresponding benzil derivatives.
4. Experiments on investigation of mechanism
5. Characterization data for products
6. $^1$H NMR and $^{13}$C NMR copies of products
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 $^1$H 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$_2$CO$_3$ (2.0 equiv), and DMF (5.0 mL) in a Schlenk tube was stirred under N$_2$ at 140 ºC (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$_2$SO$_4$, 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 ºC (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$_2$SO$_4$, 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$_2$CO$_3$ (2.0 equiv), and DMF (5.0 mL) in a Schlenk tube was
stirred under N₂ 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 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 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 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

\[ \text{Structure diagram} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 156.77, 140.63, 133.53, 131.01, 130.35, 129.60, 127.46, 125.16, 123.70, 123.06, 113.45, 96.92, 81.55. HRMS, calculated for C$_{16}$H$_{11}$O (M+H$^+$): 219.0804, found: 219.0808 (M+H$^+$).

2-(p-tolylethynyl)benzofuran

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 C$_{17}$H$_{13}$O (M+H$^+$): 233.0961, found: 233.0962 (M+H$^+$).

2-((4-methoxyphenyl)ethynyl)benzofuran

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 C$_{17}$H$_{12}$Na$_2$ (M+Na$^+$): 271.0730, found: 271.0727 (M+Na$^+$).

2-((4-chlorophenyl)ethynyl)benzofuran

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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
$^1$H 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 C$_{16}$H$_{10}$FO (M+H$^+$): 237.0710, found: 237.0741 (M+H$^+$).

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

$^1$H 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 C$_{20}$H$_{19}$O (M+H$^+$): 275.1430, found: 275.1413 (M+H$^+$).

5-methyl-2-(phenylethynyl)benzofuran

$^1$H 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 C$_{17}$H$_{13}$O (M+H$^+$): 233.0961, found: 233.0972 (M+H$^+$).

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

$^1$H 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 C$_{18}$H$_{15}$O$_2$ (M+H$^+$): 263.1067, found: 263.1074 (M+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). **13C NMR (100 MHz, CDCl$_3$)** δ 155.29, 140.30, 137.03, 134.72, 134.63, 130.72, 129.58, 128.98, 122.81, 122.6, 113.60, 112.60, 95.60, 82.65, 23.16. HRMS, calculated for C$_{17}$H$_{12}$ClO (M+H$^+$):267.0571, found: 267.0601 (M+H$^+$).

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

![Image](image.png)

$^1$H 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). **13C 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 C$_{17}$H$_{12}$FO (M+H$^+$):251.0867, found: 251.0867 (M+H$^+$).

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

![Image](image.png)

$^1$H 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). **13C 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 C$_{21}$H$_{21}$O (M+H$^+$):289.1587, found: 289.1595 (M+H$^+$).

**6-methoxy-2-(phenylethynyl)benzofuran**

![Image](image.png)

$^1$H 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). **13C 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 C$_{17}$H$_{13}$O$_2$ (M+H$^+$):249.0910, found: 249.0897 (M+H$^+$).

**6-methoxy-2-(p-tolylethynyl)benzofuran**

![Image](image.png)

$^1$H 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). **13C NMR (100 MHz,
CDCl$_3$ $\delta$ 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 C$_{18}$H$_{15}$O$_2$ (M+H$^+$):263.1067, found: 263.1056 (M+H$^+$).

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

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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 C$_{18}$H$_{15}$O$_3$ (M+H$^+$):279.1016, found: 279.0992 (M+H$^+$).

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

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (ddddd, $J = 7.0$, 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). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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 C$_{17}$H$_{12}$FO$_2$ (M+H$^+$):267.0810, found: 267.0804 (M+H$^+$).

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

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta 7.62-7.51 (m, 3H), 7.39 (dd, J = 8.8, 3.4 Hz, 4H), 7.34-7.27 (m, 1H), 6.94 (s, 1H). \\
\text{C NMR (100 MHz, CDCl}_3\text{)} & \delta 155.06, 142.07, 133.59, 131.23, 130.95, 130.80, 130.40, 127.62, 123.41, 122.50, 114.03, 112.81, 97.56, 81.09. \\
\end{align*}
\]

ESI-MS: 252

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

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta 7.53 (d, J = 2.1 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.7 Hz, 1H), 7.28 (dd, J = 8.7, 2.2 Hz, 1H), 7.19 (d, J = 7.9 Hz, 2H), 6.92 (s, 1H), 2.39 (s, 3H). \\
\text{C NMR (100 MHz, CDCl}_3\text{)} & \delta 155.00, 142.26, 141.61, 133.49, 131.14, 131.00, 130.72, 127.46, 122.41, 120.28, 113.98, 112.42, 97.79, 80.41, 23.48. \\
\end{align*}
\]

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

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta 7.55-7.49 (m, 3H), 7.38 (dt, J = 8.8, 0.7 Hz, 1H), 7.30-7.25 (m, 1H), 6.93-6.87 (m, 3H), 3.84 (s, 3H). \\
\text{C NMR (100 MHz, CDCl}_3\text{)} & \delta 162.32, 154.95, 142.41, 135.20, 131.06, 130.68, 127.35, 122.35, 116.05, 115.35, 113.93, 112.11, 97.71, 79.86, 57.19. \\
\end{align*}
\]

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

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta 7.62-7.47 (m, 4H), 7.43-7.26 (m, 3H), 6.95 (s, 1H). \\
\text{C NMR (100 MHz, CDCl}_3\text{)} & \delta 155.09, 141.71, 137.38, 134.72, 130.87, 130.81, 130.77, 127.77, 122.54, 121.86, 114.05, 113.07, 96.32, 81.91. \\
\end{align*}
\]

5-chloro-2-((4-fluorophenyl)ethynyl)benzofuran
$^{1}$H 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

$^{1}$H 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, 98.71, 83.38, 80.43, 75.37, 36.79, 36.76, 32.98, 32.96. HRMS, calculated for C$_{32}$H$_{31}$O (M+H$^+$):431.2369, found: 431.2369 (M+H$^+$).

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

$^{1}$H 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 C$_{20}$H$_{13}$O (M+H$^+$): 269.0961, found: 269.0952 (M+H$^+$).

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

$^{1}$H 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

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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
$^1$H 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 C$_{24}$H$_{21}$O (M+H$^+$): 325.1587, found: 325.1606 (M+H$^+$).

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

![Structure of 1-(benzofuran-2-yl)-2-phenylethane-1, 2-dione]

$^1$H 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 C$_{16}$H$_{10}$NaO$_3$ (M+Na$^+$): 273.0522, found: 273.0546 (M+Na$^+$).
6. $^1$H NMR and $^{13}$C NMR copies of products