Supporting Information

Copper-Catalyzed Three-Component Carboiodination of Arynes: Expeditious Synthesis of o-Alkynyl Aryl Iodides

Wenxuan Cao, Sheng-Li Niu, Li Shuai and Qing Xiao*

College of Pharmacy, Third Military Medical University, Chongqing 400038, China

Table of Contents

Materials and Methods ........................................................................................................ S2
Cu-Catalyzed 1-Iodo-2-phenylethynyl-benzene Synthesis .................................................. S3
Cross-Coupling Reactions of Products .................................................................................. S19
mechanism research ........................................................................................................... S23
References .......................................................................................................................... S25

^1H and ^13C NMR Spectra .................................................................................................. S26
Materials and Methods

General. All reactions dealing with air- and moisture-sensitive compounds were carried out in dry reaction vessels under a nitrogen atmosphere. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on Agilent 600 MHz NMR spectrometer. $^1$H and $^{13}$C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and CHCl$_3$ (77.0 ppm), respectively. ESI high-resolution mass spectra (HRMS) were recorded on a Waters SYNPAT G2. Melting points were determined using a capillary melting point apparatus and are uncorrected.

Materials. Unless otherwise noted, materials were purchased from commercial suppliers and were used as received. Anhydrous MeCN was distilled over Calcium hydride and stored under N$_2$. 
Cu-Catalyzed 1-Iodo-2-phenylethynyl-benzene Synthesis

General Procedure

A 10 mL of Schlenk tube equipped with a stirrer bar was charged with 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol), aryl acetylene (0.3 mmol), N-Iodosuccinimide (0.3 mmol), [1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]chlorocopper(I) (IMesCuCl) (10 mol %), CsF (0.4 mmol), and Cs₂CO₃ (0.4 mmol). Then, the Schlenk tube was quickly evacuated and refilled with Ar for three times, followed by the addition of MeCN (0.8 mL). The Schlenk tube was sealed with a Teflon screwcap under Ar flow and the reaction mixture was stirred at 60 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with ethyl acetate (20 mL). Subsequently, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired products.

1-Iodo-2-phenylethynyl-benzene (4a): According to the general procedure, a mixture consisting 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 30.6 mg), N-Iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4a (45.1 mg). Yellow oil; (74% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.70 – 7.64 (m, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.40 (m, 1H), 7.36 – 7.32 (m, 2H), 7.29 (dd, J = 6.6, 2.7 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 138.87, 132.54, 131.76, 129.89, 129.50, 128.79, 128.52, 127.96, 123.04, 101.32, 93.18, 91.75. (Spectral properties were identical to those previously reported).

4-((2-Iodophenyl)ethynyl)-N,N-dimethylaniline (4b): According to the general procedure, a mixture consisting 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 4-ethynyl-N,N-dimethylaniline (0.3 mmol, 43.5 mg), N-Iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4b (43.1 mg). Black solid; (62% yield, eluent = petroleum ether/EtOAc (100:1)); Mp = 73–74 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.85 (d, J = 7.9 Hz, 1H), 7.48 (t, J = 8.7 Hz, 3H), 7.29 (t, J = 7.5 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 8.6 Hz, 2H), 3.00 (s, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 150.50, 138.73, 132.92, 132.00, 128.63, 127.87, 111.93, 101.11, 94.82, 90.11, 40.36; HRMS (ESI): Caled for [C₁₆H₁₄N⁺H⁺] 348.0244, found 348.0248.
4-((2-Iodophenyl)ethynyl)-N,N-diphenylaniline (4c): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 4-ethynyl-N,N-diphenylaniline (0.3 mmol, 80.7 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4c (57.5 mg). Yellow oil; (61% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.86 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.33–7.26 (m, 5H), 7.12 (d, J = 7.9 Hz, 4H), 7.07 (t, J = 7.3 Hz, 2H), 7.01 (dd, J = 16.3, 8.0 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 148.40, 147.25, 138.81, 132.71, 132.30, 130.23, 129.55, 129.13, 127.93, 125.18, 123.77, 122.32, 115.71, 101.23, 93.66, 91.13; HRMS (ESI): Caled for [C₉₊H₁₈N⁺]+ 472.0557, found 472.0564.

-\begin{center}
\includegraphics[width=0.4\textwidth]{structure4c}
\end{center}

1-Iodo-2-((4-methoxyphenyl)ethynyl)benzene (4d): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 39.7 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4d (42.2 mg). White solid; (63% yield, eluent = petroleum ether); Mp = 86-87°C; ¹H NMR (600 MHz, CDCl₃): δ 7.87 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 6.99 (t, J = 7.7 Hz, 1H), 6.90 (d, J = 8.6 Hz, 2H), 3.84 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 160.08, 138.81, 133.25, 131.58, 130.21, 129.15, 127.93, 115.15, 114.19, 101.19, 93.36, 90.64, 55.48. (Spectral properties were identical to those previously reported).

-\begin{center}
\includegraphics[width=0.4\textwidth]{structure4d}
\end{center}

1-Iodo-2-((4-phenoxyphenyl)ethynyl)benzene (4e): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 58.2 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4e (52.3 mg). Colorless oil; (66% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.88 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.34–7.31 (m, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.8 Hz, 2H), 6.99 (p, J = 8.8, 8.3 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 158.09, 156.47, 138.85, 133.40, 132.40, 131.65, 130.04, 129.37, 128.48, 127.96, 124.06, 119.62, 118.52, 117.35, 110.23, 92.86, 91.23; HRMS (ESI): Caled for [C₂₀H₁₈I₂O⁺]+ 397.0084, found 397.0089.

-\begin{center}
\includegraphics[width=0.4\textwidth]{structure4e}
\end{center}

1-((4-(Tert-butyl)phenyl)ethynyl)-2-iodobenzene (4f): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl
acetylene (0.3 mmol, 47.4 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4f (41.2 mg). Colorless oil; (81% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDC1₃): δ 7.87 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 8.2 Hz, 3H), 7.40 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.00 (t, J = 7.7 Hz, 1H), 1.33 (s, 9H); ¹³C NMR (150 MHz, CDC1₃): δ 152.12, 138.83, 131.50, 130.10, 129.31, 127.93, 125.54, 120.01, 101.35, 93.41, 91.18, 34.99, 31.31. (Spectral properties were identical to those previously reported).

**1-Iodo-2-(p-tolylethynyl)benzene (4g)**[4]: According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4g (49.8 mg). White solid; (78% yield, eluent = petroleum ether): Mp = 88-90 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.53 (dd, J = 7.9, 1.5 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.16 (d, J = 8.1 Hz, 2H), 2.38 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 139.00, 138.84, 132.44, 131.66, 130.11, 129.30, 129.29, 127.93, 119.98, 101.29, 93.47, 91.20, 21.72. (Spectral properties were identical to those previously reported).

**1-Iodo-2-((4-(trifluoromethoxy)phenyl)ethynyl)benzene (4h)**: According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 55.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4h (47.1 mg). Colorless oil; (61% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.89 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 7.03 (t, J = 7.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ149.30 (d, J = 2.3 Hz), 138.94, 133.28, 132.60, 132.50 (d, J = 219.9 Hz), 129.50, 128.91 (d, J = 267.6 Hz), 128.62 (d, J = 21.9 Hz), 121.85, 121.07, 120.52 (d, J = 257.8 Hz), 101.28, 92.08 (d, J = 133.5 Hz); HRMS (ESI): Caled for [C₁₃H₁₄F₂I+H⁺] 388.9645, found 388.9650.

**4-((2-Iodophenyl)ethynyl)-1,1’-biphenyl (4i)**: According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 53.2 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4i (61.6 mg). White solid; (81% yield, eluent = petroleum ether): Mp =
80–81 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.89 (d, \(J = 8.0\) Hz, 1H), 7.68 (d, \(J = 8.2\) Hz, 2H), 7.62 (dt, \(J = 5.8, 3.7\) Hz, 4H), 7.56 (d, \(J = 7.7\) Hz, 1H), 7.47 (t, \(J = 7.6\) Hz, 2H), 7.36 (dt, \(J = 19.3, 7.4\) Hz, 2H), 7.03 (t, \(J = 7.6\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 141.53, 140.47, 138.90, 132.54, 132.19, 129.94, 129.51, 129.02, 127.98, 127.85, 127.22, 127.19, 121.94, 101.35, 93.14, 92.46; HRMS (ESI): Caled for [C\(_{20}\)H\(_{13}\)I +H\(^+\)] 381.0135, found 381.0138.

\[\text{Methyl 4-((2-iodophenyl)ethynyl)benzoate (4l)}\]

According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifuoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 54.3 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs\(_2\)CO\(_3\) (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4l (57.0 mg). White solid; (78% yield, eluent = petroleum ether/EtOAc (80:1)); Mp = 122-124 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.04 (d, \(J = 8.2\) Hz, 2H), 7.89 (d, \(J = 8.0\) Hz, 1H), 7.66 (d, \(J = 8.2\) Hz, 2H), 7.55 (d, \(J = 7.7\) Hz, 1H), 7.35 (t, \(J = 7.6\) Hz, 1H), 7.05 (t, \(J = 7.7\) Hz, 1H), 3.94 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 166.66, 138.98, 132.78, 131.66, 130.01, 129.69, 129.37, 128.05, 127.72, 101.36, 94.51, 92.24, 52.44. (Spectral properties were identical to those previously reported.)
identical to those previously reported).

1-(4-((2-Iodophenyl)ethynyl)phenyl)ethan-1-one (4m): According to the general procedure, a mixture consisting 2-((trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 43.5 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4m (47.1 mg). White solid; (68% yield, eluent = petroleum ether/EtOAc (50:1)); Mp = 70–71 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.96 (d, J = 8.3 Hz, 2H), 7.90 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 7.3 Hz, 1H), 7.38–7.34 (m, 1H), 7.05 (t, J = 7.7 Hz, 1H), 2.63 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 197.47, 139.00, 136.61, 132.79, 132.44, 131.87, 130.16, 129.33, 128.44, 128.07, 101.39, 94.85, 92.20, 26.83; HRMS (ESI): Caled for [C₁₆H₁₁O₂⁺H⁺] 346.9927, found 346.9931.

1-Iodo-2-(((4-(trifluoromethyl)phenyl)ethynyl)benzene (4n) [3]: According to the general procedure, a mixture consisting 2-((trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 51 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4n (48.4 mg). White solid; (65% yield, eluent = petroleum ether); Mp = 61–63 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.90 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 149.93, 139.04, 132.98, 131.17, 130.44, 128.77, 128.09, 125.58, 101.38, 95.92, 90.10. (Spectral properties were identical to those previously reported).

4-((2-Iodophenyl)ethynyl)benzonitrile (4o) [3]: According to the general procedure, a mixture consisting 2-((trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 38.1 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4w (53.1 mg). White solid; (81% yield, eluent = petroleum ether/EtOAc (80:1)); Mp = 101–103 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.90 (d, J = 8.0 Hz, 1H), 7.69–7.64 (m, 4H), 7.54 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 139.07, 132.88, 132.24, 132.23, 130.37, 128.93, 128.12, 127.99, 118.63, 112.01, 101.38, 95.85, 91.20. (Spectral properties were identical to those previously reported).
1-Iodo-2-((4-nitrophenyl)ethynyl)benzene (4p): According to the general procedure, a mixture consisting 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 37.6 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4p (56.1 mg). Yellow solid; (80% yield, eluent = petroleum ether/EtOAc (80:1)); Mp = 92–93 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.24 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 147.36, 139.10, 132.95, 132.45, 130.51, 129.97, 128.81, 128.15, 123.83, 101.43, 96.69, 90.97; HRMS (ESI): Caled for [C₁₄H₁₃NO₂⁺H⁺] 349.9672, found 349.9673.

1-Iodo-2-((2-methoxyphenyl)ethynyl)benzene (4q): According to the general procedure, a mixture consisting 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 39.7 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4q (44.1 mg). Colorless oil; (66% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.87 (d, J = 7.9 Hz, 1H), 7.58 (t, J = 7.8 Hz, 2H), 7.33 (q, J = 7.4 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 3.93 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 160.23, 138.84, 133.81, 132.53, 132.28, 130.00, 129.71, 129.42, 128.87, 128.42, 127.95, 122.84, 101.32, 93.41, 91.42, 21.41. (Spectral properties were identical to those previously reported).

1-Iodo-2-(m-tolyethyl)benzene (4r): According to the general procedure, a mixture consisting 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4r (45.1 mg). Colorless oil; (71% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.89 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.45 − 7.41 (m, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.02 (t, J = 7.7 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 138.85, 138.22, 132.53, 132.28, 130.00, 129.71, 129.42, 128.87, 128.42, 127.95, 122.84, 101.32, 93.41, 91.42, 21.41. (Spectral properties were identical to those previously reported).
1-((3-Bromophenyl)ethynyl)-2-iodobenzene (4s) \(^{[5]}\): According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 54.3 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs\(_2\)CO\(_3\) (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4s (55.9 mg). White solid; (73% yield, eluent = petroleum ether); Mp = 58–59 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): δ 7.88 (d, \(J = 8.0\) Hz, 1H), 7.74 (s, 1H), 7.51 (dd, \(J = 17.6, 7.5\) Hz, 3H), 7.34 (t, \(J = 7.6\) Hz, 1H), 7.24 (t, \(J = 7.9\) Hz, 1H), 7.04 (t, \(J = 7.7\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): δ 138.94, 134.39, 132.68, 131.91, 130.32, 129.98, 129.41, 128.02, 125.06, 122.35, 101.31, 92.92, 91.45. (Spectral properties were identical to those previously reported).

1-((3-Chlorophenyl)ethynyl)-2-iodobenzene (4t): According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 30.6 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 43.7 mg), and Cs\(_2\)CO\(_3\) (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4t (52.8 mg). White solid; (78% yield, eluent = petroleum ether); Mp = 54–55 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): δ 7.88 (d, \(J = 8.0\) Hz, 1H), 7.58 (s, 1H), 7.53 (d, \(J = 7.6\) Hz, 1H), 7.48 (d, \(J = 7.5\) Hz, 1H), 7.36 – 7.32 (m, 2H), 7.30 (t, \(J = 7.8\) Hz, 1H), 7.04 (t, \(J = 7.7\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): δ 138.94, 134.38, 132.68, 131.54, 129.88, 129.86, 129.77, 129.42, 129.03, 128.02, 124.77, 101.31, 92.80, 91.60; HRMS (ESI): Caled for [C\(_{14}\)H\(_8\)CI+H\(^+\)] 338.9432, found 338.9434.

1-((3-Fluorophenyl)ethynyl)-2-iodobenzene (4u): According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 36.0 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs\(_2\)CO\(_3\) (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4u (46.4 mg). Colorless oil; (72% yield, eluent = petroleum ether); \(^1\)H NMR (600 MHz, CDCl\(_3\)): δ 7.89 (d, \(J = 8.0\) Hz, 1H), 7.53 (d, \(J = 7.7\) Hz, 1H), 7.39 (d, \(J = 7.6\) Hz, 1H), 7.34 (t, \(J = 7.3\) Hz, 2H), 7.32 – 7.28 (m, 1H), 7.11 – 7.01 (m, 2H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): δ 162.52 (d, \(J = 246.7\) Hz), 138.94, 132.66, 130.12 (d, \(J = 8.6\) Hz), 129.83, 129.44, 128.01, 127.64 (d, \(J = 3.1\) Hz), 124.88 (d, \(J = 9.5\) Hz), 118.50 (d, \(J = 22.8\) Hz), 116.13 (d, \(J = 21.2\) Hz), 101.31, 92.54, 91.78 (d, \(J = 3.5\) Hz); HRMS (ESI): Caled for [C\(_{14}\)H\(_8\)FI+H\(^+\)] 322.9727, found 322.9730.
Methyl 3-((2-iodophenyl)ethynyl)benzoate (4v): According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 30.6 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 51.2 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4v (63.0 mg). Colorless oil; (83% yield, eluent = petroleum ether/EtOAc (80:1)); ¹H NMR (600 MHz, CDCl₃): δ 8.26 (s, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.7 Hz, 1H), 3.94 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 166.52, 138.93, 135.91, 132.79, 132.70, 130.64, 129.80, 129.73, 129.52, 128.70, 128.02, 123.52, 101.26, 92.51, 91.99, 52.49; HRMS (ESI): Caled for [C₁₆H₁₁IO₂⁺ H⁺] 362.9876, found 362.9880.

1-Iodo-2-((2-methoxyphenyl)ethynyl)benzene (4w): According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 39.7 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4w (46.2 mg). Colorless oil; (69% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.87 (d, J = 7.9 Hz, 1H), 7.58 (t, J = 7.8 Hz, 2H), 7.33 (q, J = 7.4 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 3.93 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 160.23, 138.84, 133.81, 132.71, 130.29, 129.32, 127.86, 120.66, 110.95, 101.09, 95.57, 89.78, 56.03. (Spectral properties were identical to those previously reported).

1-Iodo-2-((o-tolyethynyl)benzene (4x): According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4x (40.0 mg). Colorless oil; (63% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.88 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 13.0, 7.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.01 (t, J = 7.7 Hz, 1H), 2.59 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 140.67, 138.91, 132.81, 132.30, 130.29, 129.69, 129.38, 128.81, 127.94, 125.72, 122.80, 100.78, 95.19, 92.28, 21.40. (Spectral properties were identical to those previously reported).
1-Bromo-2-((2-iodophenyl)ethynyl)benzene (4y)<sup>[5]</sup>: According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 54.3 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs<sub>2</sub>CO<sub>3</sub> (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4y (53.6 mg). White solid; (70% yield, eluent = petroleum ether); Mp = 68–70 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.89 (d, J = 8.0 Hz, 1H), 7.68 – 7.57 (m, 3H), 7.33 (dt, J = 20.5, 7.5 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 138.96, 136.13, 133.67, 133.11, 129.85, 129.75, 129.67, 129.53, 129.76, 126.62, 125.62, 125.28, 100.73, 95.66, 91.56. (Spectral properties were identical to those previously reported).

1-Chloro-2-((2-iodophenyl)ethynyl)benzene (4z): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 41.0 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs<sub>2</sub>CO<sub>3</sub> (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4z (48.1 mg). Yellow oil; (71% yield, eluent = petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.89 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.28 (dd, J = 17.4, 8.8 Hz, 2H), 7.04 (t, J = 7.7 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 138.96, 136.13, 133.67, 133.11, 129.85, 129.75, 129.67, 129.53, 127.96, 126.62, 123.03, 100.81, 96.28, 89.84; HRMS (ESI): Caled for [C<sub>14</sub>H<sub>12</sub>F<sub>2</sub>C<sub>2</sub>H<sub>2</sub>]+ 338.9432, found 338.9432.

1-Fluoro-2-((2-iodophenyl)ethynyl)benzene (4aa): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 36.0 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs<sub>2</sub>CO<sub>3</sub> (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4aa (47.1 mg). Colorless oil; (73% yield, eluent = petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.89 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.18 – 7.09 (m, 2H), 7.03 (t, J = 7.7 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ162.79 (d, J = 252.7 Hz), 138.93, 133.67 (d, J = 0.9 Hz), 132.83, 130.51 (d, J = 7.9 Hz), 129.80, 129.63, 127.95, 124.14 (d, J = 3.7 Hz), 115.75 (d, J = 20.7 Hz), 111.71 (d, J = 15.7 Hz), 100.97, 96.36 (d, J = 3.1 Hz), 86.56; HRMS (ESI): Caled for [C<sub>14</sub>H<sub>12</sub>F<sub>3</sub>I+H<sup>+</sup>]<sup>[14]</sup> 322.9727, found 322.9731.
Methyl 2-((2-iodophenyl)ethynyl)benzoate (4ab): According to the general procedure, a mixture consisting 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 30.6 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 51.2 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ab (57.1 mg). Yellow oil (75% yield, eluent = petroleum ether/Dichloromethane (10:1)); ¹H NMR (600 MHz, CDCl₃): δ 7.99 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.03 (t, J = 7.7 Hz, 1H), 3.97 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 166.77, 138.85, 134.41, 133.09, 131.90, 131.83, 130.64, 130.01, 129.77, 128.42, 127.99, 123.48, 100.93, 96.37, 91.91, 52.51; HRMS (ESI): Caled for [C₁₆H₁₁IO₂⁺H⁺] 362.9876, found 362.9879.

1-Iodo-2-((2-nitrophenyl)ethynyl)benzene (4ac): According to the general procedure, a mixture consisting 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 37.6 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ac (49.2 mg). Yellow solid; (71% yield, eluent = petroleum ether/EtOAc (80:1)); Mp = 82–83 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.12 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.63 (dd, J = 12.5, 7.4 Hz, 2H), 7.50 (t, J = 7.8 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 138.97, 135.05, 133.58, 133.08, 130.47, 129.07, 128.10, 118.68, 100.95, 98.96, 88.25. (Spectral properties were identical to those previously reported).

2-((2-Iodophenyl)ethynyl)-1,3,5-trimethylbenzene (4ad): According to the general procedure, a mixture consisting 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), aryl acetylene (0.3 mmol, 37.6 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ad (39.5 mg). Colorless oil; (57% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.88 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.00 (t, J = 7.7 Hz, 1H), 6.91 (s, 2H), 2.55 (s, 6H), 2.31 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 140.83, 138.90, 138.42, 132.85, 130.85, 129.08, 127.89, 127.83, 119.69, 100.21, 98.75, 91.51, 21.61, 21.54. (Spectral properties were identical to those
5-((2-Iodophenyl)ethynyl)benzo[cd][1,3]dioxole (4ae): According to the general procedure, a mixture consisting 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 5-ethynylbenzo[cd][1,3]dioxole (0.3 mmol, 43.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ae (50.1 mg). White solid; (71% yield, eluent = petroleum ether); Mp = 92–93 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.86 (d, $J$ = 8.0 Hz, 1H), 7.50 (d, $J$ = 7.7 Hz, 1H), 7.32 (t, $J$ = 7.5 Hz, 1H), 7.14 (d, $J$ = 8.0 Hz, 1H), 7.05 (s, 1H), 7.00 (t, $J$ = 7.7 Hz, 1H), 6.81 (d, $J$ = 8.0 Hz, 1H), 6.00 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 148.39, 147.63, 138.84, 132.33, 129.98, 129.30, 127.95, 126.56, 116.29, 111.66, 108.72, 101.53, 101.23, 93.22, 90.34; HRMS (ESI): Caled for [C$_{15}$H$_{13}$O$_2$+H$^+$] 348.9720, found 348.9724.

6-((2-Iodophenyl)ethynyl)-4,4-dimethylthiochromane (4af): According to the general procedure, a mixture consisting 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 6-ethynyl-4,4-dimethylthiochromane (0.3 mmol, 60.6 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4af (43.6 mg). Green oil; (54% yield, eluent = petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$): δ 7.88 (d, $J$ = 8.0 Hz, 1H), 7.58 (s, 1H), 7.53 (d, $J$ = 7.7 Hz, 1H), 7.33 (t, $J$ = 7.5 Hz, 1H), 7.27 (s, 1H), 7.08 (d, $J$ = 8.1 Hz, 1H), 7.01 (t, $J$ = 7.6 Hz, 1H), 3.09 – 3.04 (m, 2H), 2.00 – 1.94 (m, 2H), 1.36 (s, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 142.20, 138.84, 133.74, 132.37, 130.10, 129.72, 129.26, 129.12, 127.94, 126.71, 118.30, 101.25, 93.73, 91.14, 37.34, 33.12, 30.12, 23.38; HRMS (ESI): Caled for [C$_{15}$H$_{15}$S+H$^+$] 405.0168, found 405.0170.

2-((2-Iodophenyl)ethynyl)naphthalene (4ag): According to the general procedure, a mixture consisting 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 2-ethynyl)naphthalene (0.3 mmol, 45.7 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ag (47.5 mg). White solid; (67% yield, eluent = petroleum ether); Mp = 86–88 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 8.12 (s, 1H), 7.90 (d, $J$ = 7.9 Hz, 1H), 7.83 (d, $J$ = 7.6 Hz, 3H), 7.65 (d, $J$ = 8.4 Hz, 1H), 7.58 (d, $J$ = 7.7 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.36 (t, $J$ = 7.4 Hz, 1H), 7.03 (t, $J$ = 7.7 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 138.91, 133.13, 133.11, 132.60, 131.72, 129.92, 129.55, 128.39, 128.21, 128.00, 127.95, 126.98, 126.75,
9-((2-Iodophenyl)ethynyl)phenanthrene (4ah): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 9-ethynylphenanthrene (0.3 mmol, 60.7 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ah (55.8 mg). White solid; (69% yield, eluent = petroleum ether); Mp = 111–112 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.73 (ddd, $J$ = 22.5, 5.8, 3.3 Hz, 2H), 8.68 (d, $J$ = 8.3 Hz, 1H), 8.16 (s, 1H), 7.94 (d, $J$ = 8.0 Hz, 1H), 7.90 (d, $J$ = 7.8 Hz, 1H), 7.75 – 7.67 (m, 4H), 7.62 (t, $J$ = 7.4 Hz, 1H), 7.40 (t, $J$ = 7.5 Hz, 1H), 7.07 (t, $J$ = 7.7 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 138.99, 133.06, 132.49, 131.34, 131.20, 130.57, 130.26, 130.14, 129.65, 128.80, 128.05, 127.78, 127.30, 127.14, 122.88, 122.80, 119.51, 100.94, 95.77, 91.63; HRMS (ESI): Caled for [C$_{18}$H$_{11}$I + H$^+$] 354.9978, found 354.9983.

1-((2-Iodophenyl)ethynyl)pyrene (4ai): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 1-ethynylpyrene (0.3 mmol, 67.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ai (54.8 mg). Yellow solid; (64% yield, eluent = petroleum ether); Mp = 103–105 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.88 (d, $J$ = 9.1 Hz, 1H), 8.28 (d, $J$ = 7.9 Hz, 1H), 8.23 (dd, $J$ = 14.4, 8.0 Hz, 3H), 8.15 (d, $J$ = 7.9 Hz, 1H), 8.12 (d, $J$ = 8.8 Hz, 1H), 8.08 – 8.02 (m, 2H), 7.96 (d, $J$ = 8.0 Hz, 1H), 7.73 (d, $J$ = 7.6 Hz, 1H), 7.42 (t, $J$ = 7.5 Hz, 1H), 7.08 (t, $J$ = 7.6 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 138.99, 133.06, 132.49, 131.34, 131.20, 130.57, 130.26, 130.14, 129.98, 129.57, 128.62, 128.51, 128.08, 127.39, 126.43, 126.08, 125.85, 125.79, 124.68, 124.42, 117.51, 100.98, 97.04, 92.61; HRMS (ESI): Caled for [C$_{22}$H$_{13}$I + H$^+$] 405.0135, found 405.0140.

8-((2-Iodophenyl)ethynyl)quinoline (4aj): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 8-ethynylquinoline (0.3 mmol, 45.9 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was
stirred at 60 °C for 12 h to afford 4aj (39.1 mg). Yellow oil; (55% yield, eluent = petroleum ether); 1H NMR (600 MHz, CDCl3): δ 9.07 – 9.01 (m, 1H), 8.17 (dd, J = 8.0, 2.8 Hz, 1H), 8.12 – 8.08 (m, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.82 (dd, J = 7.2, 3.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.54 (td, J = 7.8, 3.3 Hz, 1H), 7.45 (dt, J = 8.0, 4.0 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.02 (td, J = 6.9, 6.2, 2.1 Hz, 1H); 13C NMR (150 MHz, CDCl3): δ 151.26, 148.12, 138.78, 136.57, 134.59, 133.13, 129.60, 128.84, 128.47, 127.85, 126.27, 123.23, 121.83, 101.58, 97.46, 91.10, 83.19; HRMS (ESI): Caled for [C13H10IN]+: 355.9931, found 355.9935.

4-((2-Iodophenyl)ethynyl)pyridine (4ak): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 4-ethynylpyridine (0.3 mmol, 30.9 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs2CO3 (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ak (31.1 mg). Black solid; (57% yield, eluent = petroleum ether/EtOAc (10:1)); Mp = 56–57 °C; 1H NMR (600 MHz, CDCl3): δ 8.62 (d, J = 4.5 Hz, 2H), 7.89 (d, J = 7.9 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 4.6 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H); 13C NMR (150 MHz, CDCl3): δ 149.93, 139.04, 132.98, 131.17, 130.44, 128.77, 128.09, 125.58, 101.38, 95.92, 90.10; HRMS (ESI): Caled for [C13H8IN]+: 305.9774, found 305.9777.

3-((2-Iodophenyl)ethynyl)thiophene (4am): According to the general procedure, a mixture consisting 2- (trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 3-ethynylthiophene (0.3 mmol, 32.4 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs2CO3 (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4am (38.2 mg). Colorless oil; (61% yield, eluent = petroleum ether/EtOAc (10:1)); Mp = 56-57 °C; 1H NMR (600 MHz, CDCl3): δ 8.83 (s, 1H), 8.58 (d, J = 4.7 Hz, 1H), 7.95 – 7.83 (m, 2H), 7.55 (d, J = 7.5 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.31 (dd, J = 7.7, 5.0 Hz, 1H), 7.05 (t, J = 7.7 Hz, 1H); 13C NMR (150 MHz, CDCl3): δ 152.17, 148.88, 138.83, 138.45, 132.56, 131.66, 129.89, 127.90, 123.07, 120.12, 101.06, 94.65, 89.46; HRMS (ESI): Caled for [C13H8IN]+: 305.9774, found 305.9777.
ether); \textbf{1H NMR} (600 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 8.0$ Hz, 1H), 7.63 – 7.57 (m, 1H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.35 – 7.30 (m, 2H), 7.26 (d, $J = 3.1$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H); \textbf{13C NMR} (150 MHz, CDCl$_3$): $\delta$ 138.85, 132.48, 129.90, 129.44, 129.25, 127.95, 125.63, 122.08, 101.09, 91.18, 88.40; \textbf{HRMS} (ESI): Caled for [C$_{12}$H$_7$IS$^+$] 310.9386, found 310.9389.

2-((2-Iodophenyl)ethynyl)thiophene (4an): According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 2-ethynylthiophene (0.3 mmol, 32.4 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4an (44.1 mg). Colorless oil; (71% yield, eluent = petroleum ether); \textbf{1H NMR} (600 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.38 – 7.31 (m, 3H), 7.07 – 6.99 (m, 2H); \textbf{13C NMR} (150 MHz, CDCl$_3$): $\delta$ 138.89, 132.45, 132.39, 129.68, 129.62, 128.05, 127.98, 127.36, 122.98, 100.86, 95.29, 86.53; \textbf{HRMS} (ESI): Caled for [C$_{12}$H$_7$IS$^+$] 310.9386, found 310.9388.

1-(Cyclohex-1-en-1-ylethynyl)-2-iodobenzene (4ao): According to the general procedure, a mixture consisting 2-((trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), 1-ethylcy-clohexene (0.3 mmol, 31.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 90 °C for 12 h to afford 4ao (34.5 mg). Colorless oil; (56% yield, eluent = petroleum ether); \textbf{1H NMR} (600 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 7.3$ Hz, 1H), 7.31 – 7.27 (m, 1H), 6.95 (t, $J = 7.7$ Hz, 1H), 6.31 (s, 1H), 2.32 – 2.11 (m, 4H), 1.74 – 1.59 (m, 4H); \textbf{13C NMR} (150 MHz, CDCl$_3$): $\delta$ 138.72, 136.16, 132.77, 131.57, 128.97, 128.35, 127.86, 101.28, 95.24, 89.35, 29.05, 25.97, 22.41, 21.64. (Spectral properties were identical to those previously reported.)

1-Iodo-4,5-dimethoxy-2-(p-tolylethynyl)benzene (4ap): According to the general procedure, a mixture consisting 4,5-dimethoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (0.2 mmol, 71.6 mg), 1-ethyl-4-methyl-benzene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ap (51.4 mg). White solid; (68% yield, eluent = petroleum ether/EtOAc (25:1)); Mp = 115–116 °C; \textbf{1H NMR} (600 MHz, CDCl$_3$): $\delta$ 7.47 (d, $J = 7.7$ Hz, 2H), 7.25 (s, 1H), 7.17 (d, $J = 7.7$ Hz, 2H), 7.02 (s, 1H), 3.88 (s, 6H), 2.37 (s, 3H); \textbf{13C NMR} (150 MHz, CDCl$_3$): $\delta$ 149.64, 149.08, 138.71, 131.50, 129.27, 122.32, 121.07, 120.14, 16
114.63, 91.78, 91.25, 90.38, 56.32, 56.15, 21.71; **HRMS** (ESI): Caled for [C_{17}H_{15}O_{2}H^+] 379.0189, found 379.0195.

![Chemical structure](image)

**1-Iodo-4,5-dimethyl-2-(p-tolythynyl)benzene (4aq):** According to the general procedure, a mixture consisting 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.2 mmol, 65.2 mg), 1-ethynyl-4-methyl-benzene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol%, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs_{2}CO_{3} (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4aq (47.8 mg). White solid; (69% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.62 (s, 1H), 7.47 (d, J = 7.9 Hz, 2H), 7.30 (s, 1H), 7.16 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H), 2.21 (d, J = 14.8 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 139.51, 138.95, 138.69, 136.77, 133.37, 131.58, 129.25, 127.26, 120.25, 97.46, 92.29, 91.26, 77.37, 77.16, 76.95, 21.71, 19.46, 19.39; **HRMS** (ESI): Caled for [C_{16}H_{13}I+H^+] 347.0291 found 347.0287.

![Chemical structure](image)

**2-Iodo-3-(p-tolythynyl)naphthalene (4ar):** According to the general procedure, a mixture consisting 3-(trimethylsilyl)-2-naphthyl trflate (0.2 mmol, 69.6 mg), 1-ethynyl-4-methyl-benzene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol%, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs_{2}CO_{3} (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4ar (49.4 mg). White solid; (67% yield, eluent = petroleum ether); Mp = 103–105 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.40 (s, 1H), 8.05 (s, 1H), 7.77 (d, J = 7.0 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.54 (d, J = 7.9 Hz, 2H), 7.52 – 7.48 (m, 2H), 7.20 (d, J = 7.8 Hz, 2H), 2.39 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 139.01 (s), 138.15 (s), 134.04 (s), 132.46 (s), 131.81 (s), 131.67 (s), 129.33 (s), 127.75 (s), 127.41 (s), 127.15 (s), 126.77 (s), 126.53 (s), 120.04 (s), 97.65 (s), 93.27 (s), 91.43 (s), 77.37 (s), 77.16 (s), 76.95 (s), 21.76 (s); **HRMS** (ESI): Caled for [C_{16}H_{13}I+H^+] 369.0135, found 369.0139.

![Chemical structure](image)

**1-Iodo-2-(p-tolythynyl)naphthalene (4as):** According to the general procedure, a mixture consisting 1-(trimethylsilyl)-2-naphthyl trflate (0.2 mmol, 69.6 mg), 1-ethynyl-4-methyl-benzene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol%, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs_{2}CO_{3} (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4as (52.3 mg). White solid; (71% yield, eluent = petroleum ether); Mp = 76–77 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.21 (d, J = 8.5 Hz, 1H), 7.77 (dd, J = 13.9, 8.2 Hz, 2H), 7.59 – 7.54 (m, 4H), 7.51 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.8 Hz, 2H), 2.40 (s, 3H); ¹³C
**NMR** (150 MHz, CDCl$_3$): $\delta$ 139.10, 135.10, 133.39, 133.02, 131.69, 129.35, 128.72, 128.66, 128.47, 128.39, 127.15, 120.10, 107.16, 94.29, 93.09, 21.77; **HRMS** (ESI): Caled for $[C_{16}H_{13}I+H^+]$ 369.0135, found 369.0141.

**2-Iodo-1-methoxy-3-(p-tolylenyl)benzene (4at):** According to the general procedure, a mixture consisting (3-methoxy-2-trimethylsilylphenyl) trifluoromethanesulfonate (0.2 mmol, 65.6 mg), 1-ethynyl-4-methyl-benzene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford 4at (52.2 mg). White solid; (75% yield, eluent = petroleum ether); Mp $= 92–93^\circ$C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.50 (d, $J = 7.8$ Hz, 2H), 7.28 (d, $J = 7.9$ Hz, 1H), 7.17 (t, $J = 7.3$ Hz, 3H), 6.76 (d, $J = 8.0$ Hz, 1H), 3.90 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 158.77, 138.90, 133.39, 133.02, 131.69, 129.35, 128.72, 128.66, 120.05, 110.37, 93.45, 91.46, 56.70, 31.10, 21.73; **HRMS** (ESI): Caled for $[C_{16}H_{13}I+H^+]$ 349.0084, found 349.0088.

**2-Iodo-1-methyl-3-(p-tolylenyl)benzene and 1-Iodo-3-methyl-2-(p-tolylenyl)benzene (4au and 4av):** According to the general procedure, a mixture consisting (2-methyl-6-trimethylsilylphenyl) trifluoromethanesulfonate (0.2 mmol, 62.4 mg), 1-ethynyl-4-methyl-benzene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs$_2$CO$_3$ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford the products (39.2 mg). Colorless oil; (59% yield, eluent = petroleum ether); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.50 (d, $J = 7.9$ Hz, 2H), 7.31 (t, $J = 7.3$ Hz, 3H), 7.18 (dt, $J = 15.5$, 9.0 Hz, 4H), 2.56 (s, 1H), 2.50 (s, 2H), 2.38 (d, $J = 5.9$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 142.71, 138.86, 132.26, 131.59, 129.86, 129.27, 128.75, 127.76, 120.19, 107.90, 93.08, 92.30, 29.77, 21.73; **HRMS** (ESI): Caled for $[C_{16}H_{13}I+H^+]$ 333.0135, found 333.0138.

**2-Iodo-4-methyl-1-(p-tolylenyl)benzene and 1-Iodo-4-methyl-2-(p-tolylenyl)benzene (4av and 4av′):** According to the general procedure, a mixture consisting (4-methyl-2-trimethylsilylphenyl) trifluoromethanesulfonate (0.2 mmol, 62.4 mg), 1-ethynyl-4-methyl-benzene (0.3 mmol, 34.8 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol %, 8 mg), CsF
(0.4 mmol, 60.8 mg), and Cs₂CO₃ (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 12 h to afford the products (42.5 mg). Colorless oil; (64% yield, eluent = petroleum ether); \(^1\)H NMR (600 MHz, CDCl₃): \(\delta\) 7.75 – 7.69 (m, 2H), 7.49 (dd, \(J = 7.8, 2.7\) Hz, 4H), 7.40 (d, \(J = 7.9\) Hz, 1H), 7.36 (s, 1H), 7.19 – 7.15 (m, 4H), 7.12 (d, \(J = 7.9\) Hz, 1H), 6.83 (d, \(J = 8.0\) Hz, 1H), 2.38 (s, 6H), 2.32 (s, 3H), 2.30 (s, 3H); \(^1\)C NMR (150 MHz, CDCl₃): \(\delta\) 139.36, 138.56, 137.97, 133.17, 132.07, 131.64, 130.56, 129.27, 120.16, 101.21, 93.02, 91.25, 21.72, 20.96; HRMS (ESI): Caled for \([\text{C}_{16}\text{H}_{13}I^+ + \text{H}^+]\) 333.0135, found 333.0139.

**Cross-Coupling Reactions of Products**

1. **General Procedure for the Synthesis of 5**

A 10 mL of Schlenk tube equipped with a stirrer bar was charged with 4-cyanophenylboronic acid (0.3 mmol, 44 mg), K₂CO₃ (0.6 mmol, 82.8 mg), [1,1'-Bis(diphenylphosphino)ferrocene]-dichloropalladium(II) (PdCl₂(dppf)) (0.01 mmol, 7.3 mg) in DMF (1 ml). The resulting solution was further degassed for 15 min and 1-iodo-2-phenylethynyl-benzene 4a (0.2 mmol, 60.8 mg) was added to it under an argon atmosphere. The Schlenk tube was sealed with a Teflon screwcap under Ar flow and the reaction mixture was stirred at 100 °C for 4 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate, washed with brine and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the desired products 5.

2. **General Procedure for the Synthesis of 6**

A 10 mL of Schlenk tube equipped with a stirrer bar was charged with (tris(isopropylsilyl)acetylene (0.24 mmol, 43.7 mg), 1-iodo-2-phenylethynyl-benzene 4a (0.2 mmol, 60.8 mg), CuI (0.02 mmol, 3.8 mg), bis(triphenylphosphine)palladium(II) -chloride (Pd(PPh₃)₂Cl₂) (0.01 mmol, 7.0 mg) in THF (1 ml) mixed with Et₃N (1 ml). The Schlenk tube was sealed with a Teflon screwcap under Ar flow and the reaction mixture was stirred at 50 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate, washed with brine and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the desired products 6.
3. General Procedure for the Synthesis of 7

A 10 mL of Schlenk tube equipped with a stirrer bar was charged with 1-iodo-2-phenylethynylbenzene 4a (0.4 mmol, 121.6 mg), CuI (0.02 mmol, 3.8 mg), Na₂S·9H₂O (0.8 mmol, 192 mg) in DMF (1.0 mL). The Schlenk tube was sealed with a Teflon screwcap under Ar flow and the reaction mixture was stirred at 120 °C for 10 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate, washed with brine and extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the desired products 7.

4. General Procedure for the Synthesis of 10 and 11

A 10 mL of Schlenk tube equipped with a stirrer bar was charged with benzo[b]thiophen-3-ylboronic acid (0.6 mmol, 107 mg), K₂CO₃ (1.2 mmol, 166 mg), [1,1’-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (PdCl₂(dppf)) (0.02 mmol, 14.6 mg) in DMF (2 mL). The resulting solution was further degassed for 15 min and 1,4-bis((2-iodophenyl)ethynyl)benzene 9 (0.2 mmol, 106 mg) was added to it under an argon atmosphere. The Schlenk tube was sealed with a Teflon screwcap under Ar flow and the reaction mixture was stirred at 100 °C for 4 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, washed with brine and extracted with ethyl acetate (3×20 mL).
The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford the desired products 10.

A 10 mL of Schlenk tube equipped with a stirrer bar was charged with 1,4-bis((2-(benzo[b]thiophen-3-yl)phenyl)ethynyl)benzene 10 (0.1 mmol, 54.2 mg, N-bromosuccinimide (NBS) (0.3 mmol, 53.4 mg) in CH₂Cl₂ (1 ml). The reaction mixture was stirred at room temperature for 72 h. The reaction mixture was then diluted with diethyl ether (20 mL), washed with satd aq Na₂S₂O₃ (25 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford the desired product 11.

![N,N'-Phenylethynyl-biphenyl-4-carbonitrile (5):](image)

According to the general procedure for the synthesis of 5, compound 5 was afforded. Yellow oil; (40.7 mg, 73% yield, eluent = petroleum ether/EtOAc (50:1)); ³¹H NMR (600 MHz, CDCl₃): δ 7.77 (q, J = 8.2 Hz, 4H), 7.68 (d, J = 7.2 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.32 (s, 5H); ¹³C NMR (150 MHz, CDCl₃): δ 145.34, 141.84, 133.26, 131.84, 131.41, 130.25, 129.35, 128.88, 128.66, 128.55, 128.35, 122.97, 121.69, 119.15, 111.27, 93.14, 88.47; HRMS (ESI): Caled for [C₂₁H₁₃N⁺Na⁺] 302.0940, found 302.0939.

![Triisopropyl-(2-phenylethynyl-phenylethynyl)-silane (6):](image)

According to the general procedure for the synthesis of 6, compound 6 was afforded. Yellow oil; (56.6 mg, 79% yield, eluent = petroleum ether); ¹H NMR (600 MHz, CDCl₃): δ 7.60 – 7.50 (m, 4H), 7.39 – 7.33 (m, 3H), 7.32 – 7.25 (m, 2H), 1.15 (s, 18H); ¹³C NMR (150 MHz, CDCl₃): δ 132.93, 132.24, 131.87, 128.42, 128.28, 128.13, 127.95, 125.99, 125.93, 123.45, 105.50, 95.16, 93.28, 88.35, 18.84, 11.47; HRMS (ESI): Caled for [C₂₅H₃₀Si⁺H⁺] 359.2190, found 359.2188.

![2-Phenylbenzo[b]thiophene (7):](image)

According to the general procedure for the synthesis of 7, compound 7 was afforded. White solid; (79.0 mg, 94% yield, eluent = petroleum ether); Mp = 174.8–175.3°C; ¹H NMR (600 MHz, CDCl₃): δ 7.84 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.56 (s, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.34 (ddd, J = 19.3, 13.9, 7.0 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 144.38 (s), 140.82 (s), 139.63 (s), 134.43 (s), 129.09 (s), 128.41 (s), 126.64 (s), 124.65 (s), 124.46 (s), 123.70 (s), 122.41 (s), 119.59 (s), 77.37 (s), 77.16 (s), 76.95 (s). (Spectral properties were identical to those previously reported).
1,4-Bis((2-iodophenyl)ethynyl)benzene (9): According to the general procedure, a mixture consisting of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (2.0 mmol, 596 mg), 1,4-diethynylbenzene (1.5 mmol, 189.4 mg), N-iodosuccinimide (3.0 mmol, 675 mg), IMesCuCl (20 mol %, 80 mg), CsF (4 mmol, 610 mg), and Cs₂CO₃ (4 mmol, 1.31 g) in MeCN (8 mL) was stirred at 60 °C for 12 h to afford 9 (381.6 mg). White solid; (381.6 mg, 72% yield, eluent = petroleum ether); Mp = 144–145 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.89 (d, J = 8.0 Hz, 1H), 7.59 (s, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 138.94 (s), 132.63 (s), 131.72 (s), 129.70 (d, J = 13.5 Hz), 128.02 (s), 123.27 (s), 101.33 (s), 77.37 (s), 77.16 (s), 76.95 (s); HRMS (ESI): Caled for [C₂₂H₁₂I₂⁺] 530.9101, found 530.9110.

1,4-Bis((2-(benzo[b]thiophen-3-yl)phenyl)ethynyl)benzene (10): According to the general procedure for the synthesis of 10, compound 10 was afforded. Red solid; (91.1 mg, 84% yield, eluent = petroleum ether); Mp = 182–183 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.95 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.57 (s, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.44 (t, J = 7.1 Hz, 1H), 7.39 (dd, J = 15.6, 7.8 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 6.83 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 23.83 (s), 138.50 (s), 138.24 (s), 136.25 (s), 132.76 (s), 131.12 (s), 130.24 (s), 128.63 (s), 127.71 (s), 125.48 (s), 124.37 (s), 124.23 (s), 123.64 (s), 123.04 (m), 92.93 (s), 91.01 (s), 77.37 (s), 77.16 (s), 76.95 (s); HRMS (ESI): Caled for [C₃₈H₂₂S₂⁺] 543.1236, found 543.1244.

1,4-Bis(5-bromobenzo[b]naphtho[1,2-d]thiophen-6-yl)benzene (11): According to the general procedure for the synthesis of 11, compound 11 was afforded. Yellow solid; (43.4 mg, 62% yield, eluent = petroleum ether); Mp = 304–305 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.13 (d, J = 8.4 Hz, 1H), 8.92 (dd, J = 8.2, 3.9 Hz, 1H), 8.71 (dd, J = 8.2, 4.9 Hz, 1H), 7.99 (dd, J = 22.3, 7.9 Hz, 1H),
7.85 (t, J = 7.6 Hz, 1H), 7.76 (t, J = 7.2 Hz, 1H), 7.71 (d, J = 2.2 Hz, 2H), 7.65 (dd, J = 12.6, 7.5 Hz, 1H), 7.54 (dd, J = 15.2, 7.7 Hz, 1H);\(^{13}\)C {\text{NMR}} (150 MHz, CDCl\(_3\)): \(\delta\) 140.97 (s), 140.57 (s), 130.96 (s), 130.06 (s), 129.79 (s), 128.93 (s), 127.95 (s), 126.46 (s), 125.84 (s), 125.04 (s), 123.59 (s), 123.32 (s), 77.37 (s), 77.16 (s), 76.95 (s); \text{HRMS (ESI)}: Caled for [C\(_{38}\)H\(_{20}\)Br\(_2\)S\(_2\) + Na\(^+\)] 720.9265, found 720.9251.

\textbf{Mechanism Research}

\textbf{General Procedure for the Synthesis of 12, 13, 14 and 16}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.5\textwidth]{diagram}};
\end{tikzpicture}
\end{center}

\textbf{1,2-Diphenylethynyl (12)}\(^{10}\): According to the general procedure, a mixture consisting 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.2 mmol, 59.6 mg), phenylacetylene (0.3 mmol, 30.6 mg), IMesCuCl (10 mol \%, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs\(_2\)CO\(_3\) (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for the stated time to afford 12. Colorless oil; (eluent = petroleum ether); \(^1\)H {\text{NMR}} (600 MHz, CDCl\(_3\)): \(\delta\) 7.56 (dd, J = 7.5, 2.0 Hz, 2H), 7.40 – 7.33 (m, 3H); \(^{13}\)C {\text{NMR}} (150 MHz, CDCl\(_3\)) \(\delta\) 131.74, 128.47, 128.39, 123.41, 89.51. (Spectral properties were identical to those previously reported).

\textbf{(Iodoethynyl)benzene (13)}\(^{11}\): According to the general procedure, a mixture consisting phenylacetylene (0.3 mmol, 30.6 mg), N-iodosuccinimide (0.3 mmol, 67.5 mg), IMesCuCl (10 mol \%, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs\(_2\)CO\(_3\) (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 1 h to afford 13 and 14. Yellow oil; (eluent = petroleum ether); \(^1\)H {\text{NMR}} (600 MHz, CDCl\(_3\)): \(\delta\) 7.47 – 7.43 (m, 2H), 7.36 – 7.30 (m, 3H); \(^{13}\)C {\text{NMR}} (150 MHz, CDCl\(_3\)) \(\delta\) 132.44, 128.93, 128.36, 123.48, 94.25, 6.37. (Spectral properties were identical to those previously reported).

\textbf{1,4-Diphenylbuta-1,3-diyne (14)}\(^{12}\): According to the previous procedure, compound 14 was
afforded. White solid; (7.3 mg, 12% yield, eluent = petroleum ether); Mp = 87–88 °C; \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)): \(\delta\) 7.57 – 7.52 (m, 2H), 7.40 – 7.33 (m, 3H); \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 132.63, 129.35, 128.58, 121.91, 81.69, 74.04. (Spectral properties were identical to those previously reported).

(Bromoethynyl)benzene (16) \(^{13}\): According to the general procedure, a mixture consisting phenylacetylene (0.3 mmol, 30.6 mg), N-bromosuccinimide (0.3 mmol, 53.4 mg), IMesCuCl (10 mol %, 8 mg), CsF (0.4 mmol, 60.8 mg), and Cs\(_2\)CO\(_3\) (0.4 mmol, 130.4 mg) in MeCN (0.8 mL) was stirred at 60 °C for 20 min to afford 16. Yellow oil; (11.9 mg, 22% yield, eluent = petroleum ether); \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)): \(\delta\) 7.46 (dt, \(J = 6.8, 1.5\) Hz, 2H), 7.38 – 7.29 (m, 3H); \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 132.12, 128.81, 128.46, 122.81, 80.17, 49.89. (Spectral properties were identical to those previously reported).
References


$^1$H and $^{13}$C NMR Spectra

$^1$H NMR Spectrum of 4a

$^{13}$C NMR Spectrum of 4a
$^1$H NMR Spectrum of 4b

$^{13}$C NMR Spectrum of 4b
$^1$H NMR Spectrum of 4c

$^{13}$C NMR Spectrum of 4c
$^1$H NMR Spectrum of 4d

$^{13}$C NMR Spectrum of 4d
$^1$H NMR Spectrum of 4e

$^{13}$C NMR Spectrum of 4e
$^1$H NMR Spectrum of 4f

$^{13}$C NMR Spectrum of 4f
$^1$H NMR Spectrum of 4g

$^{13}$C NMR Spectrum of 4g
$^1$H NMR Spectrum of 4h

$^{13}$C NMR Spectrum of 4h
$^1$H NMR Spectrum of 4i

$^{13}$C NMR Spectrum of 4i
$^1\text{H NMR Spectrum of 4j}$

$^{13}\text{C NMR Spectrum of 4j}$
$^{1}$H NMR Spectrum of 4k

$^{13}$C NMR Spectrum of 4k
$^1$H NMR Spectrum of 4l

$^{13}$C NMR Spectrum of 4l
$^1$H NMR Spectrum of 4m

$^{13}$C NMR Spectrum of 4m
$^1$H NMR Spectrum of 4n

$^{13}$C NMR Spectrum of 4n
$^{1}H$ NMR Spectrum of 4o

$^{13}C$ NMR Spectrum of 4o
$^1$H NMR Spectrum of 4p

$^{13}$C NMR Spectrum of 4p
$^1$H NMR Spectrum of 4q

$^{13}$C NMR Spectrum of 4q
$^1$H NMR Spectrum of 4r

$^{13}$C NMR Spectrum of 4r
$^1$H NMR Spectrum of 4s

$^{13}$C NMR Spectrum of 4s
$^1$H NMR Spectrum of 4t

$^{13}$C NMR Spectrum of 4t
$^1$H NMR Spectrum of 4u

![H NMR Spectrum of 4u](image)

$^{13}$C NMR Spectrum of 4u

![C NMR Spectrum of 4u](image)
$^{1}H$ NMR Spectrum of 4v

$^{13}C$ NMR Spectrum of 4v
$^1$H NMR Spectrum of 4w

$^{13}$C NMR Spectrum of 4w
$^{1}$H NMR Spectrum of 4x

$^{13}$C NMR Spectrum of 4x
$^1$H NMR Spectrum of 4y

$^{13}$C NMR Spectrum of 4y
$^1$H NMR Spectrum of 4z

$^{13}$C NMR Spectrum of 4z
$^1$H NMR Spectrum of 4aa

$^{13}$C NMR Spectrum of 4aa
$^1$H NMR Spectrum of 4ac

$^{13}$C NMR Spectrum of 4ac
$^1$H NMR Spectrum of 4ad

$^{13}$C NMR Spectrum of 4ad
$^1$H NMR Spectrum of 4ae

$^{13}$C NMR Spectrum of 4ae
$^1$H NMR Spectrum of 4af

$^{13}$C NMR Spectrum of 4af
$^1$H NMR Spectrum of 4ag

$^{13}$C NMR Spectrum of 4ag
$^1$H NMR Spectrum of 4ah

$^{13}$C NMR Spectrum of 4ah
$^1$H NMR Spectrum of 4ai

$^{13}$C NMR Spectrum of 4ai
$^1$H NMR Spectrum of 4aj

$^{13}$C NMR Spectrum of 4aj
$^1$H NMR Spectrum of 4ak

$^{13}$C NMR Spectrum of 4ak
$^1$H NMR Spectrum of 4al

$^{13}$C NMR Spectrum of 4al
$^1$H NMR Spectrum of 4am

$^{13}$C NMR Spectrum of 4am
$^1$H NMR Spectrum of 4an

$^{13}$C NMR Spectrum of 4an
$^{1}$H NMR Spectrum of 4ao

$^{13}$C NMR Spectrum of 4ao
$^1$H NMR Spectrum of 4ap

$^{13}$C NMR Spectrum of 4ap
$^1$H NMR Spectrum of 4aq

$^{13}$C NMR Spectrum of 4aq
$^1$H NMR Spectrum of 4ar

$^{13}$C NMR Spectrum of 4ar
$^1$H NMR Spectrum of 4as

$^{13}$C NMR Spectrum of 4as
$^1$H NMR Spectrum of 4at

$^{13}$C NMR Spectrum of 4at
$^1$H NMR Spectrum of 4au

$^{13}$C NMR Spectrum of 4au
$^1$H NMR Spectrum of 4av

$^{13}$C NMR Spectrum of 4av
$^1$H NMR Spectrum of 5

$^{13}$C NMR Spectrum of 5
$^1$H NMR Spectrum of 6

$^{13}$C NMR Spectrum of 6
$^1$H NMR Spectrum of 7

$^{13}$C NMR Spectrum of 7
$^1$H NMR Spectrum of 9

$^{13}$C NMR Spectrum of 9
$^1$H NMR Spectrum of 10

$^{13}$C NMR Spectrum of 10
$^1$H NMR Spectrum of 11

$^{13}$C NMR Spectrum of 11
$^1$H NMR Spectrum of 12

$^{13}$C NMR Spectrum of 12
$^1$H NMR Spectrum of 13

$^{13}$C NMR Spectrum of 13
1H NMR Spectrum of 14

13C NMR Spectrum of 14
$^1$H NMR Spectrum of 16

$^{13}$C NMR Spectrum of 16