Supporting Information

Synthesis of Fused Chromenes by Indium(III)-Catalyzed Cascade Hydroarylation/Cycloisomerization Reactions of Polyyne-Type Aryl Propargyl Ethers

Lorena Alonso-Marañón, Luis A. Sarandeses, M. Montserrat Martínez,* José Pérez Sestelo*

Centro de Investigaciones Científicas Avanzadas (CICA) and Departamento de Química, Universidade da Coruña, E-15071 A Coruña, Spain

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Reaction of 1a with InBr$_3$ monitored by $^1$H NMR measurements.

The reaction of 1a (20 mg, 0.054 mmol) with InBr$_3$ (0.082 mL, 0.0027 mmol, 5 mol %) in CD$_2$Cl$_2$ (0.5 mL) was monitored by analysis of the $^1$H NMR spectra at different time intervals (4 h, 8 h, 12 h, 18 h and 24 h).
Reaction of 1b with InBr₃ monitored by ¹H NMR measurements.
Monitoring of the reaction of 1b (22.6 mg, 0.067 mmol) with InBr₃ (0.100 mL, 0.0033 mmol, 5 mol %) in CD₂Cl₂ (0.5 mL) was carried out by analysis of the ¹H NMR spectra at different time intervals (30 min, 60 min, 120 min, 180 min and 360 min).
General methods.
All reactions were carried out in flame-dried glassware, under argon atmosphere, using standard gastight syringes, cannulae and septa. Toluene and THF were distilled from sodium/benzophenone. Dry MeOH, DCE, Et₃N, piperidine and other commercially available reagents were used as received. Reaction temperatures refer to external bath temperatures. Butyllithium was titrated prior to use. Indium(III) iodide (99.998%), indium(III) bromide (99.999%), were purchased from Aldrich and used as received under argon. 1-Methoxy-4-(prop-1-yn-1-iloxy)benzene (S6) was prepared according to previous reported method.¹ Reactions were monitored by TLC using pre-coated silica gel plates (Alugram® Xtra SIL G/UV₂₅₄, 0.20 mm thick), UV light as the visualizing agent and ethanolic phosphomolybdic acid as the developing agent. Flash column chromatography was performed with 230–400 mesh silica gel packed in glass columns.¹H and ¹³C NMR spectra were recorded in CDCl₃ at 300 MHz and 75 MHz, respectively, in a Bruker Avance 300 spectrometer at ambient temperature, and calibrated to the solvent peak. DEPT data were used to assign carbon types. The low resolution EIMS were measured on a Thermo Finnigan Trace MS spectrometer at 70 eV. The HRMS were measured on a Thermo Finnigan MAT 95XP spectrometer or in a QSTAR LC/MS Turbo Spray. Melting points were measured in a Stuart Scientific melting point apparatus SMP3 and are uncorrected.

Preparation of compounds S1–S5.
1-Iodo-2-((4-methoxyphenyl)ethynyl)benzene (S1).²

To a room temperature solution of 4-methoxyphenylacetylene (485 mg, 3.67 mmol, 120 mol %) in Et₃N (8 mL), Pd(PPh₃)₂Cl₂ (42.8 mg, 0.061 mmol, 2 mol %), CuI (5.9 mg, 0.031 mmol, 1 mol %) and 1,2-diiodobenzene (1.0 g, 3.06 mmol) were added and the resulting mixture was stirred overnight. After the reaction was completed, the mixture was diluted with EtOAc (20 mL) and saturated aqueous NH₄Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and

the combined organic layer was dried (MgSO₄), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95–10:90) to afford S1 (594 mg, 58%) as a white solid. Rf = 0.38 (EtOAc/hexane 10:90); mp 108–110 °C (lit.² 86–87 °C); ¹H NMR (CDCl₃, 300 MHz) δ 7.87 (dd, J = 8.0, 1.0 Hz, 1H), 7.55 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 7.7 Hz, 1H), 7.32 (td, J = 7.6, 1.1 Hz, 1H), 6.98 (td, J = 7.7, 1.7 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 160.0 (C), 138.7 (CH), 133.1 (2 × CH), 132.1 (CH), 130.1 (C), 129.0 (CH), 127.8 (CH), 115.1 (C), 114.1 (2 × CH), 101.0 (C), 93.2 (C), 90.5 (C), 55.3 (CH₃) ppm; MS (EI) m/z (%): 335 [M⁺] (100), 319 [M – CH₃⁺] (20). HRMS (EI) calcd for C₁₅H₁₁IO [M⁺] 333.9849, found 333.9850.

1-Bromo-(2-phenylethynyl)benzene (S2).³

\[
\text{Br} + \text{Ph} \equiv \xrightarrow{\text{Pd(PPh₃)₂Cl₂ (5 mol %)}} \xrightarrow{\text{CuI (10 mol %)}} \xrightarrow{\text{Et₃N, rt, 16 h}} \text{S2} \\
\text{Br}
\]

To a room temperature solution of 2-bromoiodobenzene (0.7 mL, 5.45 mmol) in Et₃N (12 mL), Pd(PPh₃)₂Cl₂ (0.191 mg, 0.272 mmol, 5 mol %), CuI (0.104 mg, 0.545 mmol, 10 mol %) and phenylacetylene (0.660 mL 6.00 mmol, 110 mol %) were added and the resulting mixture was stirred overnight. After the reaction was completed, the mixture was diluted with EtOAc (20 mL) and saturated aqueous NH₄Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layer was dried (MgSO₄), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 2:98) to afford S2 (1.58 g, 99%) as a yellow oil. Rf = 0.41, (EtOAc/hexane 2:98); ¹H NMR (CDCl₃, 300 MHz) δ 7.64–7.55 (m, 4H), 7.39–7.36 (m, 3H), 7.30 (td, J = 7.5, 1.7 Hz, 1H), 7.19 (td, J = 7.7, 1.7 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 133.2 (CH), 132.4 (CH), 131.7 (2 × CH), 129.4 (CH), 128.6 (CH), 128.4 (2 × CH), 127.0 (CH), 125.6 (C), 125.4 (C), 122.9 (C), 93.9 (C), 88.0 (C) ppm; MS (EI) m/z (%) 258 [M, ⁸¹Br⁺] (98), 256 [M, ⁷⁹Br⁺] (100); HRMS (EI) calcd for C₁₄H₉Br [M⁺] 255.9882, found 255.9888.

((2-Bromophenyl)ethynyl)trimethylsilane (S3).\(^4\)

\[
\begin{align*}
\text{Br} & \quad \text{TMS} & \quad \text{Pd(PPh}_3\text{)}_2\text{Cl}_2 (5 \text{ mol \%}) \quad \text{CuI (10 \text{ mol \%})}
\end{align*}
\]

To a solution of 2-bromiodobenzene (1.0 mL, 7.79 mmol) in Et\(_3\)N (15 mL), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (0.273 mg, 0.389 mmol, 5 mol \%), CuI (0.148 mg, 0.778 mmol, 10 mol \%) and ethynyltrimethylsilane (1.20 mL 8.57 mmol, 110 mol \%) were added and the resulting mixture was stirred at room temperature overnight. After the reaction was completed, the mixture was diluted with EtOAc (20 mL) and saturated aqueous NH\(_4\)Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layer was dried (MgSO\(_4\)), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 2:98) to afford S3 (1.92 g, 97\%) as a yellow oil. \(R_f = 0.50\), EtOAc/hexane (2:98); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta 7.58 (d, J = 7.9 \text{ Hz, 1H}), 7.50 (dd, J = 7.6 \text{ Hz, 1H}), 7.24 (d, J = 7.5 \text{ Hz, 1H}), 7.17 (td, J = 7.7, 1.5 \text{ Hz, 1H}), 0.29 (s, 9H) \text{ ppm}; \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta 133.6 (\text{CH}), 132.3 (\text{CH}), 129.5 (\text{CH}), 126.9 (\text{CH}), 125.8 (\text{C}), 125.2 (\text{C}), 103.0 (\text{C}), 99.6 (\text{C}), -0.17 (3 \times \text{CH}_3) \text{ ppm}; \text{MS (EI) } m/z (\%) 254 [\text{M, } ^{81}\text{Br}]^{+} (22), 252 [\text{M, } ^{79}\text{Br}]^{+} (21), 239 [\text{M – CH}_3, ^{81}\text{Br}]^{+} (100), 237 [\text{M – CH}_3, ^{79}\text{Br}]^{+} (98); \text{HRMS (EI) } \text{calcd for } C_{11}H_{13}BrSi [\text{M}]^{+} 251.9964, \text{ found } 251.9971.\)

1-Iodo-2-(phenylethynyl)benzene (S4).\(^5\)

\[
\begin{align*}
\text{Ph} \quad \text{TMS} & \quad n-\text{BuLi (120 mol \%)} \\
\text{Br} & \quad \text{I}_2 (140 \text{ mol \%})
\end{align*}
\]

To a –78 °C solution of S2 (1.58 g, 6.15 mmol) in dry THF (30 mL), n-BuLi (3.10 mL, 7.37 mmol, 120 mol \%) was added dropwise, and the resulting mixture was stirred 30 minutes. Then I\(_2\) (2.18 g, 8.60 mmol, 140 mol \%) was added in one portion and the mixture was stirred for 2 hours and warmed to room temperature. The reaction was quenched by the addition H\(_2\)O (10 mL) and poured into a sepratory funnel over Na\(_2\)S\(_2\)O\(_3\) (50 mL) and the aqueous layer was extracted with EtOAc (3 × 40 mL), dried (MgSO\(_4\)), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 2:98) to afford S4 (1.62 g, 88\%) as a yellow oil. \(R_f = 0.50\)


(EtOAc/hexane 2:98); $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.90 (d, $J = 8.4$ Hz, 1H), 7.64–7.60 (m, 4H), 7.03 (dt, $J = 7.7$, 1.4 Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 138.7 (CH), 132.4 (CH), 131.6 (2 × CH), 129.8 (C), 129.3 (CH), 128.6 (CH), 128.4 (2 × CH), 127.8 (CH), 122.9 (C), 101.2 (C), 93.0 (C), 91.6 (C) ppm; MS (EI) $m/z$ (%) 305 [M, $^{128}$I]$^+$ (15), 304 [M, $^{127}$I]$^+$ (100); HRMS (EI) calcd for C$_{14}$H$_9$I [M]$^+$ 303.9743, found 303.9774.

((2-Iodophenyl)ethyl)trimethylsilane (S5).$^6$

According to the known procedure,$^6$ to a solution of S3 (1.92 g, 7.58 mmol) in dry THF (40 mL) at $-78$ °C, n-BuLi (3.90 mL, 9.10 mmol, 120 mol %) was added dropwise, and the resulting mixture was stirred for 30 minutes. Then I$_2$ (2.70 g, 10.6 mmol, 140 mol %) was added in one portion and the mixture was stirred for 2 hours at $-78$ °C and warmed to room temperature. The reaction was quenched by the addition H$_2$O (10 mL) and poured into a separatory funnel over Na$_2$S$_2$O$_3$ (50 mL) and the aqueous layer was extracted with EtOAc (3 × 40 mL), dried (MgSO$_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 2:98) to afford S5 (2.01 g, 88%) as a yellow oil. $R_f = 0.36$ (hexane); $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.84 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.47 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.28 (dt, $J = 7.6$, 1.1 Hz, 1H), 6.98 (dt, $J = 7.7$, 1.7 Hz, 1H), 0.29 (s, 9H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 138.7 (CH), 132.7 (CH), 129.6 (C), 129.5 (CH), 127.7 (CH), 106.5 (C), 101.2 (C), 98.8 (C), −0.20 (3 × CH$_3$) ppm; MS (EI) $m/z$ (%) 301 [M, $^{128}$I]$^+$ (6), 300 [M, $^{127}$I]$^+$ (37), 285 [M − CH$_3$]$^+$ (100); HRMS (EI) calcd for C$_{11}$H$_{13}$Si [M]$^+$ 299.9826, found 299.9826.

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Preparation of diynes 1a–b, S7 and compound S8.

1-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)-2-((4-methoxyphenyl)ethynyl)benzene (1a).

To a solution of S6 (291 mg, 1.80 mmol) in Et$_3$N (3 mL), Pd(PPh$_3$)$_2$Cl$_2$ (52.5 mg, 0.075 mmol, 5 mol%), CuI (14.3 mg, 0.075 mmol, 5 mol%) and a solution of S1 (720 mg, 2.16 mmol, 120 mol%) in Et$_3$N (2 mL) were added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc (10 mL) and saturated aqueous NH$_4$Cl (10 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layer was dried (MgSO$_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford 1a (596 mg, 90%) as a brown solid. R$_f$ = 0.12 (EtOAc/hexane 5:95); mp 86–88 °C; $^{1}$H NMR (CDCl$_3$, 300 MHz) δ 7.51–7.43 (m, 4H), 7.42–7.21 (m, 2H), 7.01 (d, $J$ = 9.0 Hz, 2H), 6.86 (d, $J$ = 8.9 Hz, 2H), 6.77 (d, $J$ = 9.1 Hz, 2H), 4.95 (s, 2H), 3.84 (s, 3H), 3.73 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 159.8 (C), 154.3 (C), 152.1 (C), 133.2 (2 × CH), 132.1 (CH), 131.5 (CH), 128.3 (CH), 127.5 (CH), 126.4 (C), 124.6 (C), 116.2 (2 × CH), 115.3 (C), 114.6 (2 × CH), 114.0 (2 × CH), 93.6 (C), 88.2 (C), 86.8 (C), 85.8 (C), 57.6 (CH$_2$), 55.6 (CH$_3$), 55.3 (CH$_3$) ppm; MS (EI) m/z (%) 368 [M]$^{+}$ (137), 245 [M – C$_7$H$_7$O$_2$]$^{+}$ (61), 230 [M – C$_8$H$_9$O$_2$]$^{+}$ (52), 202 [M – C$_9$H$_{11}$O$_3$]$^{+}$ (100); HRMS (EI) calcd for C$_{25}$H$_{20}$O$_3$ [M]$^{+}$ 368.1407, found 368.1401.

1-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)-2-(phenylethynyl)benzene (1b).

To a solution of S6 (291 mg, 1.80 mmol) in Et$_3$N (3 mL), Pd(PPh$_3$)$_2$Cl$_2$ (52.5 mg, 0.075 mmol, 5 mol%), CuI (14.3 mg, 0.075 mmol, 5 mol%) and a solution of S3 (656 mg, 2.16 mmol, 120 mol%), in Et$_3$N (2 mL) were added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc (10 mL) and saturated aqueous NH$_4$Cl (10 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layer was dried (MgSO$_4$), filtered and concentrated under reduced pressure. The crude was purified by flash
chromatography (EtOAc/hexane 2:98) to afford 1b (577 mg, 95%) as a brown solid. \( R_f = 0.20 \) (EtOAc/hexane 2:98); mp 66–68 °C; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.55–7.47 (m, 4H), 7.36–7.28 (m, 5H), 7.02 (d, \( J = 9.1 \) Hz, 2H), 6.77 (d, \( J = 9.1 \) Hz, 2H), 4.95 (s, 2H), 3.73 (s, 3H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \( \delta \) 154.3 (C), 152.1 (C), 132.2 (CH), 131.8 (3 × CH), 128.4 (CH), 128.3 (3 × CH), 127.9 (CH), 126.0 (C), 124.8 (C), 123.1 (C), 116.2 (2 × CH), 114.6 (2 × CH), 93.5 (C), 88.4 (C), 88.0 (C), 57.6 (CH\(_2\)), 55.6 (CH\(_3\)) ppm; MS (EI) \( m/z \) 338 [M\(^+\)] (32), 215 [M – C\(_7\)H\(_2\)O\(_2\)]\(^+\) (100); HRMS (EI) calcd for C\(_{24}\)H\(_{18}\)O\(_2\) [M\(^+\)] 338.1300, found 338.1300.

\[(2\text{-}(3\text{-}(4\text{-}\text{Methoxyphenoxy})\text{prop-1-yn-1-yl})\text{phenyl})\text{ethynyl}]\text{trimethylsilane (S7).}

To a solution of S6 (500 mg, 3.08 mmol) in Et\(_3\)N (5 mL), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (43.3 mg, 0.062 mmol, 2 mol %), CuI (23.4 mg, 0.123 mmol, 4 mol %) and a solution of S5 (1.02, 3.39 mmol, 110 mol %), in Et\(_3\)N (2 mL) were added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc (20 mL) and saturated aqueous NH\(_4\)Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layer was dried (MgSO\(_4\)), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford S7 (763 mg, 74%) as a viscose colorless oil. \( R_f = 0.22 \) (EtOAc/hexane 5:95); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.48–7.41 (m, 2H), 7.27–7.24 (m, 2H), 7.02 (d, \( J = 9.1 \) Hz, 2H), 6.87 (d, \( J = 9.1 \) Hz, 2H), 4.91 (s, 2H), 3.79 (s, 3H), 0.27 (s, 9H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \( \delta \) 154.4 (C), 152.1 (C), 138.7 (CH), 133.0 (CH), 129.8 (CH), 125.8 (C), 125.3 (C), 116.3 (2 × CH), 114.6 (2 × CH), 103.2 (C), 98.4 (C), 88.2 (C), 85.5 (C), 57.6 (CH\(_2\)), 55.7 (CH\(_3\)), –0.06 (3 × CH\(_3\)) ppm; MS (EI) \( m/z \) (%) 334 [M\(^+\)] (100), 211 [M – C\(_7\)H\(_2\)O\(_2\)]\(^+\) (20); HRMS (EI) calcd for C\(_{21}\)H\(_{22}\)O\(_2\)Si [M\(^+\)] 334.1384, found 334.1376.

1-Iodo-2-[3-(4-methoxyphenoxy)prop-1-yn-1-yl]benzene (S8).

To a solution of S6 (500 mg, 3.08 mmol) in Et\(_3\)N (6 mL), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (108 mg, 0.154 mmol, 5 mol %), CuI (29.3 mg, 0.154 mmol, 5 mol %) and 1,2-diiodobenzene (0.405 mL, 3.08 mmol, 100 mol %) were added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc (20 mL) and saturated aqueous NH\(_4\)Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layer was dried (MgSO\(_4\)), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95–10:90) to afford S8 (741 mg, 66%) as a yellow oil. \( R_f = 0.28 \) (EtOAc/hexane 5:95); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.84 (d, \( J = 8.0 \) Hz, 1H), 7.44 (dd, \( J = 7.7, 1.2 \) Hz, 1H), 7.31–7.27 (m, 1H), 7.06–6.98 (m, 3H), 6.87 (d, \( J = 9.1 \) Hz, 2H), 4.93 (s, 2H), 3.79 (s, 3H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \( \delta \) 154.5 (C), 151.9 (C), 138.7 (CH), 133.0 (CH), 129.8 (CH), 128.6 (C), 128.3 (C), 116.2 (2 × CH), 115.3 (C), 105.7 (C), 99.7 (C), 88.2 (C), 85.5 (C), 55.7 (CH\(_3\)), –0.06 (3 × CH\(_3\)) ppm; MS (EI) \( m/z \) (%) 334 [M\(^+\)] (100), 211 [M – C\(_7\)H\(_2\)O\(_2\)]\(^+\) (20); HRMS (EI) calcd for C\(_{24}\)H\(_{18}\)O\(_2\)Si [M\(^+\)] 334.1384, found 334.1376.
129.0 (C), 127.7 (CH), 116.4 (2 × CH), 114.6 (2 × CH), 100.7 (C), 88.8 (C), 88.2 (C), 57.4 (CH₂), 55.7 (CH₃) ppm; MS (EI) m/z (%) 364 [M⁺, ¹²⁷I]⁺ (32), 365 [M⁺, ¹²⁸I]⁺ (5), 241 [M – C₇H₇O₂]⁺ (96), 123 [M – C₃H₆I]⁺ (48); HRMS (EI) calc'd for C₁₆H₁₃O₂ [M⁺] 363.9955, found 363.9952.

4-(2-Iodophenyl)-6-methoxy-2H-chromene (S9).

To a solution of S₈ (98.0 mg, 0.269 mmol) in dry DCE (3 mL) placed in a Schlenk tube, InBr₃ (0.410 mL, 0.013 mmol, 0.033M in DCE) was added and the reaction was stirred at room temperature for 16 h. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (EtOAc/hexane 5:95) to afford S₉ (88.1 mg, 90%) as a colorless oil. Rᵓ = 0.35 (EtOAc/hexane 5:95); ¹H NMR (CDCl₃, 300 MHz) δ 7.93 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 6.3 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 6.84 (d, J = 8.7 Hz, 1H), 6.71 (dd, J = 8.7, 2.6 Hz, 1H), 6.17 (d, J = 2.6 Hz, 1H), 5.74 (t, J = 3.5 Hz, 1H), 4.96 – 4.81 (m, 2H), 3.65 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 154.0 (C), 148.0 (C), 142.9 (C), 139.42 (C), 139.40 (CH), 130.3 (CH), 129.3 (CH), 128.3 (CH), 123.7 (C), 122.5 (CH), 116.4 (CH), 113.9 (CH), 111.7 (CH), 99.5 (C), 65.2 (CH₂), 55.7 (CH₃) ppm; MS (EI) m/z (%) 364 [M⁺] (100); HRMS (EI) calc'd for C₁₆H₁₃O₂ [M⁺] 363.9955, found 363.9939.

Preparation of diynes 1c–k.

1-[4-((2-(3-(4-Methoxyphenoxy)prop-1-yn-yl)phenyl)ethynyl)phenyl]ethan-1-one (1c).

To a solution of diine 1k (200 mg 0.762 mmol) in Et₃N (2 mL), Pd(PPh₃)₂Cl₂ (26.8 mg, 0.038 mmol, 5 mol %) and CuI (7.2 mg, 0.038 mmol, 5 mol %) were added. Then a solution of 4-iodoacetophenone (225 mg, 0.914 mmol, 120 mol %) in Et₃N (2 mL) was added and the mixture was stirred at room temperature overnight. The reaction was quenched by addition of saturated
aqueous NH₄Cl (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 10:90) to afford 1c (287 mg, 99%) as a brown solid. Rf = 0.13, 10% EtOAc/hexane; mp 73–75 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.89 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 3H), 7.50–7.47 (m, 1H), 7.32–7.27 (m, 2H), 7.01 (d, J = 9.1 Hz, 2H), 6.78 (d, J = 9.1 Hz, 2H), 4.94 (s, 2H), 3.70 (s, 3H), 2.59 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 197.2 (C), 154.4 (C), 152.0 (C), 136.3 (C), 132.2 (CH), 131.9 (CH), 131.8 (2 × CH), 128.5 (CH), 128.4 (CH), 128.2 (2 × CH), 127.9 (C), 125.3 (C), 125.1 (C), 116.1 (2 × CH), 114.6 (2 × CH), 92.6 (C), 91.2 (C), 88.8 (C), 85.5 (C), 57.5 (CH₂), 55.5 (CH₃), 26.6 (CH₃) ppm; MS (El) m/z (%) 380 [M⁺] (100); HRMS (El) calcd for C₂₆H₂₀O₃ [M⁺] 380.1407, found 380.1408.

General Procedure for diynes 1d–h.

To a solution of aryl propargyl ether (0.419 mmol) in Et₃N (2 mL), Pd(PPh₃)₂Cl₂ (0.021 mmol, 5 mol %), CuI (0.021 mmol, 5 mol %) and the alkyne (0.419 mmol, 100 mol %) were added at room temperature and the resulting mixture was stirred for 18 hours. The mixture was diluted with EtOAc (10 mL) and saturated aqueous NH₄Cl (10 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layer was dried (MgSO₄), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane) to afford the corresponding diyne.

3-[2-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)phenyl]ethynyl]tiophene (1d).

Following the General Procedure, the reaction of aryl propargyl ether S8 (150 mg, 0.419 mmol) in Et₃N (2 mL) with Pd(PPh₃)₂Cl₂ (14.7 mg, 0.021 mmol, 5 mol %), CuI (4.0 mg, 0.021 mmol, 5 mol %) and 3-ethynyltiophene (0.045 mL, 0.419 mmol, 100 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound 1d (143 mg, 99%) as a yellow viscose oil. Rf =
Following the General Procedure, the reaction of aryl propargyl ether S8 (275 mg, 0.755 mmol) in Et3N (5 mL) with Pd(PPh3)2Cl2 (26.5 mg, 0.038 mmol, 5 mol %) and ethynylcyclohexene (0.093 mL, 0.793 mmol, 105 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound 1e (191 mg, 74%) as a yellow oil. Rf = 0.35 (EtOAc/hexane 10:90); 1H NMR (CDCl3, 300 MHz) δ 7.44 (d, J = 7.4 Hz, 2H), 7.26–7.21 (m, 2H), 7.04 (d, J = 9.4 Hz, 1H), 6.87 (d, J = 9.0 Hz, 2H), 6.22 (s, 1H), 4.92 (s, 2H), 3.78 (s, 3H), 2.25–2.16 (m, 4H), 1.68–1.64 (m, 4H) ppm; 13C NMR (CDCl3, 75 MHz) δ 154.4 (C), 152.2 (C), 135.8 (CH), 132.1 (CH), 131.6 (CH), 128.3 (CH), 127.4 (CH), 126.6 (C), 124.6 (C), 120.8 (CH), 116.2 (2 × CH), 114.6 (2 × CH), 95.6 (C), 88.1 (C), 85.8 (C), 85.5 (C), 57.6 (CH2), 55.6 (CH3), 29.2 (CH2), 25.9 (CH2), 22.4 (CH2), 21.5 (CH2) ppm; MS (EI) m/z (%) 342 [M]+ (100); HRMS (EI) calcd for C23H18O2S [M]+ 342.1614, found 342.1618.

1-Cyclohexyl-2-[3-(4-methoxyphenoxy)prop-1-yn-1-yl]benzene (If).

Following the General Procedure, the reaction of aryl propargyl ether S8 (275 mg, 0.755 mmol) in Et3N (5 mL) with Pd(PPh3)2Cl2 (26.5 mg, 0.038 mmol, 5 mol %), Cul (7.2 mg, 0.038 mmol, 5 mol %) and cyclopropylacetylene (0.067 mL, 0.793 mmol, 105 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound 1f (228 mg, 99%) as an orange oil. Rf = 0.33 (EtOAc/hexane 10:90); 1H NMR (CDCl3, 300 MHz) δ 7.41 (d, J = 7.0 Hz, 2H), 7.21 (t, J = 6.3 Hz, 2H), 7.06 (d, J = 8.9 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 4.93 (s, 2H), 3.77 (s, 3H), 1.49–1.44 (m, 1H), 0.90–0.85 (m, 4H) ppm; 13C NMR (CDCl3, 75 MHz) δ 154.4 (C), 152.1 (C), 132.0 (CH), 131.8 (CH), 128.3 (CH), 127.1 (CH), 126.7 (C), 124.8 (C), 116.2 (2 × CH), 114.6 (2 × CH), 98.2 (C), 87.8 (C), 85.9 (C), 74.3 (C), 57.6 (CH2), 55.7 (CH3), 9.0 (2 × CH2), 0.49 (CH) ppm; MS (EI) m/z (%) 302 [M]+ (16), 192 [M – C6H4O]+ (24), 178 [M – C8H12O]+ (82), 69 [M – C17H15O]+ (100); HRMS (EI) calcd for C23H18O2S [M]+ 302.1301, found 302.1306.
1-(Hex-1-yn-1-yl)-2-[3-(4-methoxyphenoxy)prop-1-yn-1-yl]benzene (1g).

Following the General Procedure, the reaction of propargyl ether S8 (275 mg, 0.755 mmol) in Et₃N (5 mL) with Pd(PPh₃)₂Cl₂ (26.5 mg, 0.038 mmol, 5 mol %), Cul (7.2 mg, 0.038 mmol, 5 mol %) and hexyne (0.092 mL, 0.793 mmol, 105 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 10:90) to afford 1g (154 mg, 65%) as an orange viscous oil. R_f = 0.40 (EtOAc/hexane 10:90); ¹H NMR (CDCl₃, 300 MHz) δ 7.42 (d, J = 6.2 Hz, 2H), 7.27–7.18 (m, 2H), 7.04 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 4.92 (s, 2H), 3.78 (s, 3H), 2.43 (t, J = 6.6 Hz, 2H), 1.63–1.49 (m, 4H) ppm, 0.97 (t, J = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 154.4 (C), 152.1 (C), 132.1 (CH), 131.8 (CH), 128.2 (CH), 127.1 (CH), 126.8 (C), 124.7 (C), 116.2 (2 × CH), 114.6 (2 × CH), 94.9 (C), 87.7 (C), 86.0 (C), 79.2 (C), 57.6 (CH₂), 55.7 (CH₃), 30.8 (CH₂), 22.0 (CH₂), 19.3 (CH₂), 13.7 (CH₃) ppm; MS (EI) m/z (%) 318 [M⁺] (42), 195 [M – C₇H₇O₂]⁺ (50), 181 [M – C₈H₉O₂]⁺ (60); HRMS (EI) calcd for C₂₂H₂₂O₂ [M⁺] 318.1614, found 318.1630.

6-[2-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)phenyl]hex-5-yenonitrile (1h).

Following a General Procedure, the reaction of aryl propargyl ether S8 (275 mg, 0.755 mmol) in Et₃N (5 mL) with Pd(PPh₃)₂Cl₂ (26.5 mg, 0.038 mmol, 5 mol %), Cul (7.2 mg, 0.038 mmol, 5 mol %) and 5-hexynenitrile (0.085 mL, 0.793 mmol, 105 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 20:80) compound 1h (184 mg, 99%) as a yellow viscous oil. R_f = 0.16 (EtOAc/hexane 20:80); ¹H NMR (CDCl₃, 300 MHz) δ 7.45–7.38 (m, 2H), 7.25–7.23 (m, 2H), 7.02 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 4.92 (s, 2H), 3.75 (s, 3H), 2.54 (t, J = 6.5 Hz, 4H), 1.86 (t, J = 6.9 Hz, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 154.4 (C), 150.0 (C), 132.1 (CH), 131.8 (CH), 128.4 (CH), 127.7 (CH), 125.8 (C), 124.8 (C), 119.4 (C), 116.2 (2 × CH), 114.7 (2 × CH), 91.5 (C), 88.0 (C), 85.8 (C), 80.9 (C), 57.6 (CH₂), 55.7 (CH₃), 24.5 (CH₂), 18.6 (CH₂), 16.0 (CH₂) ppm; MS (EI) m/z (%) 239 [M⁺] (11), 277 [M – C₆H₆]⁺ (42), 206 [M – C₇H₇O₂]⁺ (63); HRMS (EI) calcd for C₂2H₁₉O₂ [M⁺] 329.1410, found 329.1403.

3-[2-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)phenyl]prop-2-yn-1-yl acetate (1i).
To a solution of the aryl propargyl ether S7 (275 mg, 0.755 mmol) in Et3N (5 mL) and THF (4 mL) Pd(PPh3)2Cl2 (106 mg, 0.151 mmol, 20 mol %) and propargyl acetate (0.080 mL, 0.793 mmol, 105 mol %) were added at room temperature. The mixture was stirred for additional 5 minutes and CuI (14.4 mg, 0.076 mmol, 10 mol %) was added. The reaction mixture was stirred for 3 hours at room temperature and quenched by addition of saturated aqueous NH4Cl (10 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic layers were dried (MgSO4), filtered, and concentrated in vacuo. The crude was purified by flash chromatography (EtOAc/hexane 20:80) to afford 1i (245 mg, 97%) as an orange oil. 

Methyl 3-(2-(3-(4-methoxyphenoxy)prop-1-yn-1-yl)phenyl)propiolate (1j).

To a solution of diene 1k (250 mg, 0.381 mmol) in dry THF (8 mL) at −78 °C n-BuLi (0.190 mL, 0.400 mmol, 105 mol %) was added dropwise. After 30 minutes, methyl chloroformate (0.150 mL, 1.91 mmol, 200 mol %) was added and the mixture was stirred at room temperature overnight. The solvent was concentrated under reduced pressure and the residue was redissolved in Et2O (10 mL). The organic layer was washed with H2O (5 mL), then dried (MgSO4), filtered and concentrated in vacuo. The crude was purified by flash chromatography (EtOAc/hexane 10:90) to afford 1j (102 mg, 83%) as a yellow oil.
(CH₃) ppm; MS (EI) m/z (%) 320 [M⁺] (45), 261 [M – C₂H₅O₂]⁺ (42), 123 [M – C₁₃H₉O₂]⁺ (100); HRMS (EI) calcd for C₂₀H₁₆O₄ [M⁺] 320.1043, found 320.1055.

**1-Ethynyl-2-[3-(4-methoxyphenoxy)prop-1-yn-1-yl]benzene (1k).**

![Chemical Structure of 1k]

To a solution of diyne S7 (318 mg, 0.951 mmol) in MeOH (5 mL), K₂CO₃ (158 mg, 1.14 mmol, 120 mol %) was added and the mixture was stirred at room temperature for 1 hour. The reaction mixture was diluted with EtOAc (15 mL) and H₂O (15 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layer was dried (MgSO₄), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford 1k (241 mg, 97%) as a viscous white oil. Rₛ = 0.15 (EtOAc/hexane 5:95); ¹H NMR (CDCl₃, 300 MHz) δ 7.49–7.43 (m, 2H), 7.30–7.27 (m, 2H), 7.04 (d, J = 9.1 Hz, 2H), 6.87 (d, J = 9.1 Hz, 2H), 4.93 (s, 2H), 3.79 (s, 3H), 3.23 (s, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 154.4 (C), 152.0 (C), 132.5 (CH), 132.2 (CH), 128.5 (CH), 128.3 (CH), 125.4 (C), 124.8 (C), 116.4 (2 × CH), 114.5 (2 × CH), 88.4 (C), 85.3 (C), 81.9 (C), 81.1 (CH), 57.4 (CH₂), 55.7 (CH₃) ppm; MS (EI) m/z (%) 262 [M⁺] (21), 139 [M – C₇H₇O₂]⁺ (100); HRMS (EI) calcd for C₁₈H₁₄O₂ [M⁺] 262.0988, found 262.0970.

**6-Methoxy-4-[2-(4-(methoxyphenyl)ethynyl]phenyl-2H-chromene (2a).**

![Chemical Structure of 2a]

To a solution of S9 (88.1 mg 0.242 mmol) in Et₃N (2 mL), Pd(PPh₃)₂Cl₂ (8.5 mg 0.012 mmol, 5 mol %), CuI (2.3 mg, 0.012 mmol, 5 mol %) and 4-methoxyphenylacetylene (0.040 mL, 0.290 mmol, 120 mol %) were added at room temperature and the resulting mixture was stirred for 18 hours. The reaction was diluted with EtOAc (10 mL) and saturated aqueous NH₄Cl (10 mL). The aqueous layer was extracted with AcOEt (2 × 10 mL), dried (MgSO₄), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford 2a (72.2 mg, 81%) as a viscous orange oil. Rₛ = 0.20 (EtOAc/hexane 5:95); ¹H NMR
(CDCl₃, 300 MHz) δ 7.60 (d, J = 8.7 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.13 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.7 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 6.70 (dd, J = 8.7, 3.0 Hz, 1H), 6.44 (d, J = 3.0 Hz, 1H), 5.93 (t, J = 3.9 Hz, 1H), 4.89 (d, J = 3.9 Hz, 2H), 3.79 (s, 3H), 3.63 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 159.5 (C), 154.0 (C), 148.2 (C), 140.2 (C), 136.3 (CH), 132.9 (2 × CH), 132.0 (CH), 129.7 (CH), 128.0 (CH), 127.7 (CH), 124.5 (C), 123.3 (C), 122.5 (CH), 116.3 (CH), 115.4 (C), 114.0 (CH), 113.8 (2 × CH), 111.8 (CH), 93.8 (C), 87.2 (C), 65.3 (CH₂), 55.8 (CH₃), 55.2 (CH₃) ppm; MS (EI) m/z (%) 368 [M]+ (100); HRMS (EI) calcd for C₂₅H₂₀O₃ [M]+ 368.1407, found 368.1392.

6-Methoxy-4-[2-(4-(phenyl)ethynyl)phenyl-2H-chromene (2b).

To a solution of S9 (103 mg 0.283 mmol) in Et₃N (2 mL), Pd(PPh₃)₂Cl₂ (9.9 mg 0.014 mmol, 5 mol %), CuI (2.3 mg, 0.014 mmol, 5 mol %) and phenylacetylene (0.032 mL, 0.339 mmol, 120 mol %) were added at room temperature and the resulting mixture was stirred for 18 hours. The reaction was diluted with EtOAc (10 mL) and saturated aqueous NH₄Cl (10 mL). The aqueous layer was extracted with AcOEt (2 × 10 mL), dried (MgSO₄), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford 2b (39.4 mg, 41%) as a yellow oil. Rf = 0.43 (EtOAc/hexane 10:90); ¹H NMR (CDCl₃, 300 MHz) δ 7.64 – 7.61 (m, 1H), 7.39 – 7.35 (m, 3H), 7.27 – 7.19 (m, 5H), 6.88 (d, J = 8.7 Hz, 1H), 6.71 (dd, J = 8.8, 2.9 Hz, 2H), 6.43 (d, J = 2.8 Hz, 1H), 5.94 (t, J = 3.8 Hz, 1H), 4.89 (d, J = 3.8 Hz, 2H), 3.63 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 154.0 (C), 148.2 (C), 140.5 (C), 136.2 (C), 132.3 (CH), 131.4 (2 × CH), 129.7 (CH), 128.3 (CH), 128.1 (2 × CH), 128.09 (CH), 127.7 (CH), 124.5 (C), 123.2 (C), 122.9 (C), 122.5 (CH), 116.3 (CH), 114.0 (CH), 111.8 (CH), 93.6 (C), 88.5 (C), 65.3 (CH₂), 55.8 (CH₃) ppm.

General Procedure for indium(III)-catalyzed cascade cycloisomerization (3a–g).
To a solution of diyne (100 mg) in dry dichloroethane (3 mL) placed in an argon filled Schlenk tube, 5 mol % of a solution of InBr₃ in DCE 0.033M (5 mol %) was added, and the resulting mixture was stirred at the adequate temperature until the starting material has been consumed. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (EtOAc/hexane) to afford the corresponding polycyclization product.

**Synthesis of naphtho[c]chromenes 3a–g and 2H-chromenes 2h–k.**

**2-Methoxy-7-(4-methoxyphenyl)-6H-naphtho[2,1-c]chromene (3a).**

Following the General Procedure, the reaction of 1a (100 mg, 0.271 mmol) with InBr₃ (0.410 mL, 0.014 mmol, 5 mol %) at room temperature for 24 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound 3a (84.7 mg, 85%) as a yellow solid. R_f = 0.20 (EtOAc/hexane 10:90); mp 142–144 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.63 (d, J = 9.2 Hz, 1H), 7.93–7.90 (m, 1H), 7.75 (s, 1H), 7.64 (d, J = 2.9 Hz, 1H), 7.58–7.51 (m, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 8.7 Hz, 2H), 6.90 (dd, J = 8.8, 2.9 Hz, 1H), 5.05 (s, 2H), 3.91 (s, 3H), 3.90 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 159.2 (C), 154.3 (C), 150.6 (C), 136.8 (C), 134.0 (C), 132.4 (C), 132.0 (C), 130.4 (2 × CH), 128.9 (CH), 128.6 (CH), 128.3 (C), 127.8 (C), 126.6 (CH), 125.9 (CH), 125.2 (C), 125.1 (CH), 117.8 (CH), 114.2 (CH), 113.9 (2 × CH), 113.8 (CH), 68.3 (CH₂), 55.9 (CH₃), 55.4 (CH₃) ppm; MS (EI) m/z (%) 368 [M]+ (100); HRMS (EI) calcd for C₂₅H₂₀O₂ [M]+ 368.1407, found 368.1403.

**2-Methoxy-7-phenyl-6H-naphtho[2,1-c]chromene (3b).**

Following the General Procedure, the reaction of 1b (100 mg, 0.295 mmol) with InBr₃ (0.450 mL, 0.015 mmol, 5 mol %) at room temperature for 4 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound 3b (90.8 mg, 91%) as a beige solid. R_f = 0.41 (EtOAc/hexane 10:90); mp 150–152 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.64 (d, J = 7.7 Hz, 1H), 7.93 (dd, J = 6.8, 2.6 Hz, 1H), 7.78 (s, 1H), 7.63 (d, J = 2.9 Hz, 1H), 7.58–7.55 (m, 2H), 7.51–7.47 (m, 3H), 7.4 (d, J = 6.4 Hz, 2H), 7.11 (d, J = 8.8 Hz, 1H), 6.91 (dd, J = 8.8, 2.9 Hz, 1H), 5.04 (s, 2H), 3.91 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 154.3 (C), 150.6 (C), 139.7 (C), 137.1 (C), 133.9 (C), 132.1 (C), 129.3 (2 × CH), 129.0 (CH), 128.7 (CH), 128.5 (2 × CH), 128.4 (C), 127.9
Following the General Procedure, the reaction of 1c (100 mg, 0.263 mmol) with InBr₃ (0.400 mL, 0.013 mmol, 5 mol %) at 80 °C for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 20:80) compound 3e (85.2 mg, 85%) as a red solid. Rₛ = 0.25 (EtOAc/hexane 20:80); mp 187–189 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.63 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 7.1 Hz, 1H), 7.75 (s, 1H), 7.62 (d, J = 2.7 Hz, 1H), 7.56 (t, J = 6.6 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.8 Hz, 1H), 6.91 (dd, J = 8.7, 2.7 Hz, 1H), 5.01 (s, 2H), 3.91 (s, 3H), 2.69 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 197.6 (C), 154.4 (C), 150.5 (C), 144.5 (C), 136.3 (C), 135.9 (C), 133.8 (C), 131.6 (C), 129.5 (2 × CH), 129.0 (CH), 128.7 (CH), 128.6 (C), 128.5 (2 × CH), 128.2 (C), 127.1 (CH), 126.2 (CH), 125.2 (CH), 124.9 (CH), 117.8 (CH), 114.3 (CH), 114.0 (CH), 68.0 (CH₂), 55.9 (CH₃), 26.7 (CH₃) ppm; MS (EI) m/z (%) 380 [M⁺] (100), 322 [M – C₃H₆O]⁺ (41); HRMS (EI) calcd for C₂₆H₂₃O₃ [M⁺] 380.1407, found 380.1406.

Following the General Procedure, the reaction of 1d (100 mg, 0.290 mmol) with InBr₃ (0.440 mL, 0.015 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound 3d as a yellow solid (90.1 mg, 90%). Rₛ = 0.33 (EtOAc/hexane 10:90); mp 170–172 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.63 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.63 (d, J = 2.6 Hz, 1H), 7.59–7.51 (m, 2H), 7.45 (dd, J = 4.7, 3.0 Hz, 1H), 7.27 (d, J = 2.6 Hz, 1H), 7.18 (d, J = 4.2 Hz, 1H), 7.13 (dd, J = 8.8, 2.8 Hz, 1H), 6.91 (dd, J = 8.7, 2.8 Hz, 1H), 5.11 (s, 2H), 3.90 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 154.3 (C), 150.6 (C), 140.1 (C), 133.9 (C), 132.4 (C), 131.6 (C), 128.9 (CH), 128.8 (CH and C), 128.6 (CH), 128.5 (C), 127.9 (C), 126.8 (CH), 126.0 (CH), 125.9 (CH), 125.1 (CH), 123.5 (CH), 117.8 (CH), 114.2 (CH), 113.9 (CH), 68.1 (CH₂), 55.9 (CH₃) ppm; MS (EI) m/z (%) 344 [M⁺] (100); HRMS (EI) calcd for C₂₃H₁₈O₂S [M⁺] 344.0866, found 344.0859.

Following the General Procedure, the reaction of 1e (100 mg, 0.292 mmol) with InBr₃ (0.440 mL, 0.015 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound 3e (87.4 mg, 87%) as a yellow oil. Rₛ = 0.40
(EtOAc/hexane 10:90); mp 148–150 °C; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 8.62 (d, \(J = 7.9\) Hz, 1H), 7.88 (d, \(J = 8.5\) Hz, 1H), 7.64 (s, 2H), 7.53–7.51 (m, 2H), 7.15 (d, \(J = 8.7\) Hz, 1H), 6.91 (dd, \(J = 8.7, 2.6\) Hz, 1H), 5.70 (s, 1H), 5.10 (s, 2H), 3.90 (s, 3H), 2.33–2.25 (m, 4H), 1.86–1.76 (m, 4H) ppm; \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 154.3 (C), 150.6 (C), 139.5 (C), 136.7 (C), 134.0 (C), 132.3 (C), 128.7 (CH), 128.0 (C), 127.9 (CH), 127.4 (C), 126.9 (CH), 126.3 (CH), 125.7 (CH), 125.3 (C), 125.0 (CH), 117.7 (CH), 114.1 (CH), 113.7 (CH), 68.0 (CH\(_2\)), 55.9 (CH\(_3\)), 30.7 (CH\(_2\)), 25.5 (CH\(_2\)), 23.1 (CH\(_3\)), 22.1 (CH\(_2\)) ppm; MS (El) \(m/z\) (%) 342 [M]\(^+\) (34); HRMS (El) calcd for C\(_{24}\)H\(_{22}\)O\(_2\) [M]\(^+\) 342.1614, found 342.1606.

7-Cyclopropyl-2-methoxy-6\(H\)-naphtho[2,1-c]chromene (3f).

Following the General Procedure, the reaction of 1f (100 mg, 0.331 mmol) with InBr\(_3\) (0.500 mL, 0.017 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound 3f (85.8 mg, 86%) as a yellow oil. \(R_f = 0.36\) (EtOAc/hexane 10:90); mp 99–101 °C; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 8.59 (d, \(J = 7.8\) Hz, 1H), 7.84 (d, \(J = 8.9\) Hz, 1H), 7.61 (d, \(J = 2.6\) Hz, 1H), 7.55 (s, 1H), 7.50 (t, \(J = 3.7\) Hz, 2H), 7.16 (d, \(J = 8.6\) Hz, 1H), 6.90 (dd, \(J = 8.7, 2.8\) Hz, 1H), 5.36 (s, 2H), 3.88 (s, 3H), 2.00–1.95 (m, 1H), 1.03 (d, \(J = 8.2\) Hz, 2H), 0.81 (d, \(J = 4.6\) Hz, 2H) ppm; \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 154.3 (C), 150.4 (C), 135.9 (C), 134.7 (C), 134.1 (C), 128.5 (CH), 127.9 (C), 126.9 (C), 126.1 (CH), 125.7 (CH), 125.6 (CH), 125.1 (C), 125.0 (CH), 117.8 (CH), 114.1 (CH), 113.6 (CH), 67.0 (CH\(_2\)), 55.9 (CH\(_3\)), 13.1 (CH\(_2\)), 6.3 (2 \(\times\) CH\(_2\)) ppm; MS (El) \(m/z\) (%) 302 [M]\(^+\) (100); HRMS (El) calcd for C\(_{21}\)H\(_{18}\)O\(_2\) [M]\(^+\) 302.1301, found 302.1307.

7-Butyl-2-methoxy-6\(H\)-naphtho[2,1-c]chromene (3g).

Following the General Procedure, the reaction of 1g (100 mg, 0.314 mmol) with InBr\(_3\) (0.480 mL, 0.016 mmol, 5 mol %) at 80 °C for 6 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound 3g (92.3 mg, 92%) as a yellow oil. \(R_f = 0.38\) (EtOAc/hexane 10:90); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 8.61 (d, \(J = 8.8\) Hz, 1H), 7.86 (d, \(J = 8.8\) Hz, 1H), 7.63 (broad s, 2H), 7.51 (d, \(J = 8.3\) Hz, 2H), 7.16 (d, \(J = 8.7\) Hz, 1H), 6.91 (dd, \(J = 8.7, 2.6\) Hz, 1H), 5.16 (s, 2H), 3.90 (s, 3H), 2.79 (t, \(J = 7.6\) Hz, 2H), 1.69–1.64 (m, 2H), 1.67–1.42 (m, 2H), 0.98 (t, \(J = 7.2\) Hz, 3H) ppm; \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 154.3 (C), 150.4 (C), 135.6 (C), 134.1 (C), 133.1 (C), 128.3 (CH), 127.8 (C), 127.7 (CH), 127.3 (C), 125.9 (CH), 125.6 (CH), 125.2 (C), 125.1 (CH), 117.7 (CH), 114.1 (CH), 113.6 (CH), 67.0 (CH\(_2\)), 55.9 (CH\(_3\)), 32.9 (CH\(_2\)), 32.7 (CH\(_2\)), 22.6 (CH\(_2\)), 14.0 (CH\(_3\)) ppm; MS (El) \(m/z\) (%) 318 [M]\(^+\) (100); HRMS (El) calcd for C\(_{22}\)H\(_{21}\)O\(_2\) [M]\(^+\) 318.1614, found 318.1612.
6-(2-(6-Methoxy-2H-chromen-4-yl)phenyl)hex-5-ynenitrile (2h).

Following the General Procedure, the reaction of 1h (100 mg, 0.304 mmol) with InBr₃ (0.920 mL, 0.030 mmol, 10 mol %) at 80 °C for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 20:80) compound 2h (79.3 mg, 79%) as a red oil. R_f = 0.23 (EtOAc/hexane 20:80); ^1H NMR (CDCl₃, 300 MHz) δ 7.46 (d, J = 7.5 Hz, 1H), 7.36–7.26 (m, 3H), 6.85 (d, J = 8.7 Hz, 1H), 6.29 (d, J = 2.7 Hz, 1H), 5.82 (t, J = 3.6 Hz, 1H), 4.85 (d, J = 3.5 Hz, 2H), 3.66 (s, 3H), 2.38 (t, J = 6.4 Hz, 2H), 2.17 (t, J = 7.2 Hz, 2H), 1.60 (t, J = 6.6 Hz, 2H) ppm; ^13C NMR (CDCl₃, 75 MHz) δ 154.0 (C), 147.9 (C), 140.5 (C), 136.6 (C), 132.2 (CH), 129.7 (CH), 128.2 (CH), 127.8 (CH), 124.5 (C), 122.9 (C), 122.2 (CH), 119.4 (C), 116.4 (CH), 113.6 (CH), 111.9 (CH), 91.3 (C), 81.2 (C), 65.3 (CH₂), 55.7 (CH₃), 24.4 (CH₂), 18.5 (CH₂), 15.7 (CH₂) ppm; MS (EI) m/z (%) 329 [M⁺] (5), 83 [M – C₁₇H₁₀O₂]⁺ (100); HRMS (EI) calcd for C₂₂H₁₉O₂N [M⁺] 329.1410, found 329.1403.

3-(2-(6-Methoxy-2H-chromen-4-yl)phenyl)prop-2-yn-1-yl acetate (2i).

Following the General Procedure, the reaction of 1i (100 mg, 0.300 mmol) with InBr₃ (0.450 mL, 0.015 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 20:80) compound 2i (64.8 mg, 65%) as a yellow oil. R_f = 0.25 (EtOAc/hexane 20:80); ^1H NMR (CDCl₃, 300 MHz) δ 7.54 (d, J = 8.0 Hz, 1H), 7.37–7.26 (m, 3H), 6.82 (d, J = 8.7 Hz, 1H), 6.69 (dd, J = 8.7, 2.8 Hz, 1H), 6.32 (d, J = 2.7 Hz, 1H), 5.87 (t, J = 3.8 Hz, 1H), 4.85 (d, J = 3.8 Hz, 2H), 4.69 (s, 2H), 3.65 (s, 3H), 2.04 (s, 3H) ppm; ^13C NMR (CDCl₃, 75 MHz) δ 170.1 (C), 153.9 (C), 148.2 (C), 140.7 (C), 135.5 (C), 132.7 (CH), 129.6 (CH), 128.7 (CH), 127.6 (CH), 124.4 (C), 122.7 (CH), 121.9 (C), 116.3 (CH), 113.9 (CH), 111.6 (CH), 86.8 (C), 85.2 (C), 65.2 (CH₂), 55.7 (CH₃), 52.6 (CH₂), 20.7 (CH₃) ppm; MS (EI) m/z (%) 334 [M⁺] (42), 274 [M – C₂H₄O₂]⁺ (80) 243 [M – C₃H₇O₂]⁺ (95); HRMS (EI) calcd for C₂₁H₁₉O₄ [M⁺] 334.1200, found 334.1187.

Methyl 3-[2-(6-methoxy-2H-chromen-4-yl)phenyl]propiolate (2j).

Following the General Procedure, the reaction of 1j (100 mg, 0.312 mmol) with InBr₃ (0.470 mL, 0.016 mmol, 5 mol %) at room temperature for 48 hours afforded, after purification by flash chromatography (EtOAc/hexane 5:95) compound 2j (71.3 mg, 71%) as a red oil. R_f = 0.33 (EtOAc/hexane 5:95); ^1H NMR (CDCl₃, 300 MHz) δ 7.68 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.3 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 6.2 Hz, 1H), 6.85 (d, J = 8.7 Hz, 1H), 6.74 (dd, J = 8.7, 2.8 Hz, 1H), 6.28 (d, J = 2.7 Hz, 1H), 5.93 (t, J = 3.8 Hz, 1H), 4.87 (d, J = 3.8 Hz, 2H), 3.74 (s,
3H), 3.66 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 154.0 (2 × C), 148.3 (C), 142.0 (C), 134.5 (C), 134.1 (CH), 130.5 (CH), 129.8 (CH), 127.8 (CH), 124.2 (C), 123.6 (CH), 119.4 (C), 116.5 (CH), 114.0 (CH), 111.5 (CH), 85.4 (C), 83.4 (C), 65.1 (CH$_2$), 55.7 (CH$_3$), 52.6 (CH$_3$) ppm; MS (EI) $m/z$ (%) 320 [M$^+$] (67), 305 [M – CH$_3$]$^+$ (100), 261 [M – C$_2$H$_5$O]$^+$ (54), 83 [M – C$_{16}$H$_{13}$O$_2$]$^+$ (100); HRMS (EI) calcd for C$_{20}$H$_{16}$O$_4$ [M$^+$] 320.1043, found 320.1040.

4-(2-Ethynlyphenyl)-6-methoxy-2H-chromene (2k).

Following the General Procedure, the reaction of 1k (100 mg, 0.381 mmol) with InBr$_3$ (0.580 mL, 0.019 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 5:95–10:90) compound 2k (48.2 mg, 48%) as a yellow oil. R$_f$ = 0.30 (EtOAc/hexane 10:90). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.60 (d, $J$ = 7.2 Hz, 1H), 7.41 – 7.26 (m, 3H), 6.84 (d, $J$ = 8.7 Hz, 1H), 6.70 (dd, $J$ = 8.5, 2.2 Hz, 1H), 6.32 (d, $J$ = 2.0 Hz, 1H), 5.89 (t, $J$ = 3.3 Hz, 1H), 4.87 (d, $J$ = 3.4 Hz, 2H), 3.65 (s, 3H), 3.04 (s, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 153.9 (C), 148.1 (C), 140.9 (C), 135.5 (C), 133.4 (CH), 129.6 (CH), 128.7 (CH), 127.6 (CH), 124.5 (C), 122.6 (CH), 121. (C), 116.3 (CH), 113.8 (CH), 111.6 (CH), 82.2 (C), 80.7 (CH), 65.3 (CH$_2$), 55.7 (CH$_3$) ppm. MS (EI) $m/z$ (%) 262 [M$^+$] (98), 261 [M – H$^+$] (100). HRMS (EI) calcd for C$_{18}$H$_{14}$O$_2$ [M$^+$] 262.0988, found 262.0984.

1-[3-(4-Methoxyphenoxy)prop-1-yn-1-yl)-2-((2-(phenylethynyl)phenyl)ethynyl]benzene (4).

To a solution of aryl diyne 1k (471 mg, 1.80 mmol) in Et$_3$N (3 mL), Pd(PPh$_3$)$_2$Cl$_2$ (52.5 mg, 0.075 mmol, 5 mol %), CuI (14.3 mg, 0.075 mmol, 5 mol %) and a solution of S4 (656 mg, 2.16 mmol, 120 mol %) in Et$_3$N (2 mL) were added and stirred at room temperature 18 h. The resulting mixture was quenched by addition of saturated aqueous NH$_4$Cl (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried (MgSO$_4$), filtered, and concentrated in vacuo. The crude was purified by flash chromatography (EtOAc/hexane 10:90) to afford 4 (577 mg, 95%) as a brown viscous oil. R$_f$ = 0.19 (EtOAc/hexane 10:90); $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.63–7.50 (m,
6H), 7.37–7.30 (m, 7H), 6.97 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 9.0 Hz, 2H), 4.78 (s, 2H), 3.70 (s, 3H) ppm; 13C NMR (CDCl3, 75 MHz) δ 154.2 (C), 152.0 (C), 132.3 (CH), 132.2 (CH), 132.0 (CH), 131.9 (CH), 131.8 (2 × CH), 128.5 (CH), 128.4 (3 × CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 126.1 (C), 125.8 (C), 125.7 (C), 124.9 (C), 123.3 (C), 116.1 (2 × CH), 114.5 (2 × CH), 93.7 (C), 92.2 (C), 92.0 (C), 88.6 (C), 88.4 (C), 85.5 (C), 57.4 (CH2), 55.6 (CH3) ppm; MS (EI) m/z (%) 438 [M]+ (21), 315 [M – C7H7O2]+ (97), 313 [M – C7H9O2]+ (100); HRMS (EI) calcd for C32H22O2 [M]+ 438.1614, found 438.1599.


Following the General Procedure, the reaction of 4 (100 mg, 0.228 mmol) with InBr3 (0.690 mL, 0.023 mmol, 10 mol %) at room temperature for 24 hours afforded, after purification by flash chromatography (EtOAc/hexane 5:95) compound 6 (71.4 mg, 70%) as a light green oil. Rf = 0.15 (EtOAc/hexane 5:95); 1H NMR (CDCl3, 300 MHz) δ 8.69 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 7.3 Hz, 1H), 7.81 (s, 1H), 7.69 (d, J = 2.6 Hz, 2H), 7.62–7.52 (m, 3H), 7.43–7.45 (m, 3H), 7.15–7.05 (m, 3H), 6.99 (d, J = 7.0 Hz, 2H), 6.91 (dd, J = 8.8, 2.8Hz, 1H), 5.11 (d, J = 13.7 Hz, 1H), 4.91 (d, J = 13.7 Hz, 1H), 3.92 (s, 3H) ppm. 13C NMR (CDCl3, 75 MHz) δ 154.3 (C), 150.8 (C), 142.2 (C), 135.7 (C), 133.8 (C), 133.2 (C), 131.9 (CH), 131.3 (2 × CH), 129.9 (CH), 129.1 (CH), 129.0 (CH), 128.6 (C), 128.4 (CH), 128.1 (3 × CH), 127.9 (CH), 127.3 (C), 126.8 (CH), 125.8 (CH), 125.2 (C), 125.1 (CH), 123.4 (C), 122.8 (C), 117.9 (CH), 114.1 (CH), 113.8 (CH), 93.2 (C), 88.5 (C), 68.3 (CH2), 56.0 (CH3) ppm; MS (EI) m/z (%) 438 [M]+ (100); HRMS (EI) calcd for C32H22O2 [M]+ 438.1614, found 438.1599.


Following the General Procedure, the reaction of 4 (100 mg, 0.228 mmol) with InBr3 (0.690 mL, 0.023 mmol, 10 mol %) at room temperature for 24 hours followed by 16 hours at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 10%) compound 7 (60.2 mg, 60%) as a yellow solid. Rf = 0.20 (EtOAc/hexane 10:90); mp 88–90 °C; 1H NMR (CDCl3, 300 MHz) δ 8.71 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.85 (s, 1H), 7.68–7.60 (m, 3H), 7.50–7.43 (m, 6H), 7.23 (d, J = 8.8 Hz, 1H), 7.11 (t, J = 7.7 Hz, 1H), 6.97 (dd, J = 8.8, 2.8 Hz, 1H), 5.74 (s, 2H), 3.93 (s, 3H) ppm; 13C NMR (CDCl3, 75 MHz) δ 154.4 (C), 150.8 (C), 145.2 (C), 138.0 (C), 132.5 (C), 131.7 (C), 130.9 (CH), 130.6 (C), 129.9 (CH), 129.14 (2 × CH), 129.09 (C), 128.9 (2 × CH), 128.88 (C), 128.8 (2 × C), 128.4 (CH), 128.0 (C), 127.4 (CH), 127.0 (CH), 126.6 (CH), 126.1 (CH), 125.6 (CH), 125.4 (C), 125.0 (CH), 123.9 (CH),
117.4 (CH), 114.6 (CH), 114.0 (CH), 70.9 (CH), 56.0 (CH) ppm; MS (EI) m/z (%) 438 [M]+ (100); HRMS (EI) calcd for C₃₂H₂₂O₂ [M]+ 438.1614, found 438.1605.

2-[(Trimethylsilyl)ethynyl]aniline (S10).\(^7\)

\[
\begin{align*}
\text{NH}_2
\end{align*}
\]
\[
\begin{align*}
\text{Pd} & \text{(PPh}_3\text{)}_2\text{Cl}_2 \text{ (5 mol %)} \\
\text{Cul (5 mol %)} \\
\text{piperidine, rt, 18 h} \\
\text{73%}
\end{align*}
\]

According to the known procedure,\(^7\) on a round-bottomed flask coupled with a Liebig refrigerant, 2-iodoaniline (1.50 g, 6.85 mmol), Pd(PPh₃)₂Cl₂ (0.240 g, 0.342 mmol, 5 mol %), CuI (0.065 g, 0.342 mmol, 5 mol %) and Et₃N (30 mL) were successively added. Then, trimethylsilylacetylene (1.20 mL, 8.22 mmol, 120 mol %) was added and the reaction mixture was heated to reflux for 5 hours. The reaction mixture was diluted with CH₂Cl₂ (30 mL) and H₂O (30 mL) and the aqueous layer was extracted with CH₂Cl₂ (2 × 30 mL). The combined organic layer was dried (MgSO₄), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford S10 (1.19 g, 91%) as a yellow oil. Rᵢ = 0.30 (EtOAc/hexane 5:95); \(^1\)H NMR (CDCl₃, 300 MHz) δ 7.31 (d, J = 7.6 Hz, 1H), 7.13 (t, J = 7.1 Hz, 1H), 6.70 (d, J = 8.6 Hz, 2H), 4.24 (br s, 2H), 0.29 (s, 9H) ppm; \(^13\)C NMR (CDCl₃, 75 MHz) δ 148.3 (C), 132.3 (CH), 130.0 (CH), 117.7 (CH), 114.2 (CH), 107.8 (C), 101.8 (C), 99.7 (C), 0.16 (3 × CH₃) ppm; MS (EI) m/z (%) 189 [M]+ (82), 174 [M – CH₃]+ (100); HRMS (EI) calcd for C₁₁H₁₅NSi [M]+ 189.0968, found 189.0971.

2-Ethynylaniline (S11).\(^7\)

\[
\begin{align*}
\text{NH}_2
\end{align*}
\]
\[
\begin{align*}
\text{K}_2\text{CO}_3 \text{ (200 mol %)} \\
\text{MeOH, rt, 18 h} \\
\text{87%}
\end{align*}
\]

According to the known procedure,\(^7\) to a solution of aniline S10 (1.19 g, 6.27 mmol) in MeOH (15 mL), K₂CO₃ (1.74 g, 12.6 mmol, 200 mol %) was added and the mixture was stirred at room temperature for 30 minutes. The reaction mixture was diluted with EtOAc (30 mL) and H₂O (30 mL) and the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic layer was dried with MgSO₄, filtered and concentrated under reduced pressure. The crude was purified by

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flash chromatography (EtOAc/hexane 10:90) to afford S11 (735 mg, 99%) as a yellow oil. Rf = 0.25 (Et2O/hexane 10:90); 1H NMR (CDCl3, 300 MHz) δ 7.35 (d, J = 7.8 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 6.71 (d, J = 7.8 Hz, 2H), 4.26 (br s, 2H), 3.40 (s, 1H) ppm; 13C NMR (CDCl3, 75 MHz) δ 148.5 (C), 132.6 (CH), 130.1 (CH), 117.8 (CH), 114.3 (CH), 106.6 (C), 82.4 (CH), 80.6 (C) ppm; MS (EI) m/z (%) 117 [M]+ (100); HRMS (EI) calcd for C8H7N [M]+ 117.0573, found 117.0562.

2-[(Trimethylsilyl)ethynyl]phenol (S12). 8

\[
\begin{align*}
\text{To a solution of 2-iodophenol (1.00 g, 4.54 mmol) in THF (40 mL) and Et}_3\text{N (10 mL), CuI (35 mg, 0.182 mmol, 4 mol %), Pd(PPh}_3\text{)}_2\text{Cl}_2 (64 mg, 0.091 mmol, 2 mol %) and ethynyltrimethylsilane (1.28 mL, 9.09 mmol, 200 mol %) were added at room temperature and stirred 18 h. The resulting mixture was diluted with CH}_2\text{Cl}_2 (30 mL) and saturated aqueous NH}_4\text{Cl (20 mL). The aqueous layer was extracted with CH}_2\text{Cl}_2 (2} \times 30 \text{mL} \rightleftharpoons \text{and the combined organic layer was washed with H}_2\text{O (20 mL), dried (MgSO}_4\text{), filtrated, and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography with silica gel (EtOAc/hexane 5:95) to afford S12 (830 mg, 96%) as an orange viscous oil. Rf = 0.25 (EtOAc/hexane 5:95); 1H NMR (300 MHz, CDCl3) δ 7.36 (dd, J = 7.7, 1.6 Hz, 1H), 7.26 (dd, J = 7.4, 1.6 Hz, 1H), 6.95 (d, J = 8.3, 0.8 Hz, 1H), 6.87 (td, J = 7.5, 1.0 Hz, 1H), 5.85 (s, 1H), 0.30 (s, 9H) ppm; 13C NMR (75 MHz, CDCl3) δ 157.1 (C), 131.6 (CH), 130.6 (CH), 120.2 (CH), 114.5 (CH), 109.5 (C), 102.4 (C), 98.9 (C), -0.04 (3 × CH3) ppm.}
\end{align*}
\]

2-Ethynylphenol (S13). 9

\[
\begin{align*}
\text{To a solution of S12 (830 mg, 4.36 mmol) in dry THF (35 mL) a solution of TBAF (5.25 mL, 125 mol %, 1.0 M in THF) was added and the resulting mixture was stirred at room temperature for 2 hours. The reaction mixture was diluted with Et}_2\text{O (20 mL) and brine (20 mL) and the aqueous}
\end{align*}
\]

layer was extracted with Et$_2$O (2 × 20 mL). The combined organic layers were dried (MgSO$_4$), filtered and concentrated under reduced pressure to afford, after purification by flash chromatography (Et$_2$O/hexane 20:80) compound S13 (426 mg, 86%) as a brown oil. R$_f$ = 0.26 (EtOAc/hexane 10:90); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.38 (dd, $J$ = 7.7, 1.6 Hz, 1H), 7.28 (td, $J$ = 7.4, 1.7 Hz, 1H), 6.96 (dd, $J$ = 8.3, 0.8 Hz, 1H), 6.88 (td, $J$ = 7.5, 1.1 Hz, 1H), 5.80 (br s, 1H), 3.47 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 157.4 (C), 132.0 (CH), 130.9 (CH), 120.3 (CH), 114.8 (CH), 108.2 (C), 84.3 (CH), 78.3 (C) ppm; MS (EI) m/z 118 [M]+ (40); HRMS (EI) calcd for C$_8$H$_6$O [M]+ 118.0413 found 118.0415.

2-[(2-(Phenylethynyl)phenyl)ethynyl]aniline (8).$^{10}$

\[ \text{Pd(PPh}_3)_2\text{Cl}_2 (5 \text{ mol \%}), \text{CuI (5 \text{ mol \%}), Et}_3\text{N, rt, 18 h}} \]

In a round-bottom flask coupled with a Liebig refrigerant, compound S3 (371 mg, 1.22 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (42.8 mg, 0.061 mmol, 5 mol %), CuI (11.6 mg, 0.061 mmol, 5 mol %) and Et$_3$N (3 mL) were added at room temperature. After 5 minutes a solution of 2-ethynylaniline (S11, 150 mg, 1.28 mmol, 105 mol %) in THF (2 mL) was added at room temperature and the reaction mixture was heated at 80 °C during 18 hours. The reaction was quenched by addition of an aqueous saturated solution of NH$_4$Cl (10 mL) and was extracted with EtOAc (3 × 10 mL), dried with MgSO$_4$, filtered and concentrated in vacuo to afford, after purification by flash chromatography (EtOAc/hexane 10:90–20:80) compound 8 (304 mg, 85%) as a brown solid. R$_f$ = 0.20 (EtOAc/hexane 2:98); mp 95–97 °C (lit.,$^{10}$ 90–91 °C); $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.62–7.59 (m, 4H), 7.45–7.32 (m, 6H), 7.17 (dt, $J$ = 7.8, 1.4 Hz, 1H), 6.75–6.68 (m, 2H), 4.40 (br s, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 148.2 (C), 132.1 (CH), 132.0 (C), 131.9 (2 × CH), 131.4 (CH), 130.0 (CH), 128.6 (CH), 128.4 (2 × CH), 128.2 (CH), 127.8 (CH), 125.9 (C), 125.0 (C), 123.0 (C), 117.6 (CH), 114.1 (C), 107.5 (C), 93.7 (C), 93.1 (C), 90.5 (C), 88.9 (C) ppm; MS (EI) m/z (%) 293 [M]+ (100); HRMS (EI) calcd for C$_{22}$H$_{15}$N [M]+ 293.1199, found 293.1186.

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2-[(2-((4-Methoxyphenyl)ethynyl)phenyl)ethynyl]phenol (10).

![Reaction Diagram]

To a solution of S1 (659 mg, 1.97 mmol) in Et₃N (4 mL), Pd(PPh₃)₂Cl₂ (69.2 mg, 0.098 mmol, 5 mol%), CuI (18.8 mg, 0.098 mmol, 5 mol%) and a solution of 2-ethynylphenol (S11, 280 mg, 2.37 mmol, 120 mol%) in Et₃N (3 mL) were added at room temperature, and the reaction mixture was stirred overnight. The reaction was quenched by addition of an aqueous saturated solution of NH₄Cl (10 mL) and was extracted with EtOAc (3 × 20 mL), dried with MgSO₄, filtered and concentrated under reduced pressure to afford, after purification by flash chromatography (EtOAc/hexane 5:95–10:90) compound 10 (230 mg, 50%) as a yellow solid. Rf = 0.15 (EtOAc/hexane 10:90); mp 87–89 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.62–7.54 (m, 4H), 7.47 (dd, J = 7.7, 1.5 Hz, 1H), 7.36–7.26 (m, 3H), 7.02 (dd, J = 8.3, 0.8 Hz, 1H), 6.95–6.90 (m, 3H), 6.43 (s, 1H), 3.85 (s, 3H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 160.0 (C), 157.1 (C), 133.5 (2 × CH), 132.2 (CH), 131.3 (CH), 131.1 (CH), 130.6 (CH), 128.4 (CH), 127.9 (CH), 125.8 (C), 124.4 (C), 120.2 (CH), 114.8 (C), 114.6 (C), 114.1 (2 × CH), 109.5 (C), 95.7 (C), 94.2 (C), 87.4 (C), 87.1 (C), 55.3 (CH₃) ppm; MS (EI) m/z (%) 324 [M]+ (100); HRMS (EI) calcd for C₂₃H₁₆O₂ [M]+ 324.1145, found 324.1156.

General Procedure for indium(III)-catalyzed cascade cycloisomerization (9 and 11).

To a solution of diyne (100 mg scale) in dry toluene or DCE (6 mL) placed in a Schlenk tube, 5 mol% of InX₃ was added, and the resulting mixture was stirred at the adequate temperature until the starting material has been consumed. The mixture was concentrated under reduced pressure to remove the solvent and the residue was purified by flash chromatography (EtOAc/hexane) to afford the corresponding polycyclization product.

6-Phenyl-11H-benzo[a]carbazole (9).¹⁰

Following the General Procedure, the reaction of diyne 8 (90.4 mg, 0.308 mmol) with InBr₃ (5.3 mg, 0.015 mmol, 5 mol%) in toluene (4 mL) at 110 °C for 24 hours, afforded after purification by flash chromatography (EtOAc/hexane 20:80) compound 9 (73.2 mg, 81%) as an orange solid. Rf = 0.33 (EtOAc/hexane 20:80); mp 120–123 °C (lit.,¹⁰ 164–165 °C); ¹H NMR (CDCl₃, 300 MHz) δ
8.91 (s, 1H), 8.16 (d, J = 7.4 Hz, 1H), 8.03 (d, J = 6.9 Hz, 1H), 7.73 (d, J = 7.4 Hz, 2H), 7.60 – 7.55 (m, 6H), 7.48 (d, J = 8.1 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 141.3 (C), 138.7 (C), 136.6 (C), 135.3 (C), 132.1 (C), 129.4 (2 × CH), 128.9 (CH), 128.4 (2 × CH), 127.6 (CH), 125.7 (CH), 125.4 (CH), 124.7 (C), 123.9 (C), 122.1 (CH), 120.9 (CH), 120.4 (CH), 120.2 (C), 119.3 (CH), 116.8 (C), 111.0 (CH) ppm; MS (EI) m/z (%) 293 [M]$^+$ (100); HRMS (EI) calcd for C$_{22}$H$_{15}$N [M]$^+$ 293.1199, found 293.1194.

6-(4-Methoxyphenyl)indene[1,2-c]chromene (11).

Following the General Procedure, the reaction of diyne 10 (100 mg, 0.308 mmol) with InI$_3$ (7.6 mg, 0.015 mmol, 5 mol %) in DCE (4 mL) at 80 °C for 4 hours, afforded after purification by flash chromatography (EtOAc/hexane 5:95) compound 11 (67.8 mg, 68%) as a yellow solid. R$_f$ = 0.30 (EtOAc/hexane 5:95); mp 143–145 °C; $^1$H NMR δ 8.07 (dd, J = 7.1, 2.2 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 6.8 Hz, 2H), 7.51 (dd, J = 8.0, 1.5 Hz, 1H), 7.46–7.36 (m, 3H), 7.20 (s, 1H), 7.13 (d, J = 8.8 Hz, 3H), 3.96 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 161.4 (C), 152.8 (C), 149.7 (C), 143.3 (C), 131.1 (2 × CH), 130.7 (C), 129.7 (C), 127.9 (CH), 126.6 (CH), 126.0 (C), 124.7 (CH), 124.1 (CH), 122.2 (CH), 121.7 (CH), 120.5 (CH), 119.8 (C), 117.7 (CH), 116.9 (C), 114.1 (2 × CH), 106.9 (CH), 55.5 (CH$_3$) ppm; MS (EI) m/z (%) 324 [M]$^+$ (100); HRMS (EI) caleed for C$_{23}$H$_{16}$O$_2$ [M]$^+$ 324.1145, found 324.1148.
300 MHz $^1H$ NMR Spectrum of compound S1 (CDCl$_3$, 300 K)

75 MHz $^{13}C$ NMR Spectrum of compound S1 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S2 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S2 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S3 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S3 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S4 (CDCl$_3$, 300 K)

![300 MHz $^1$H NMR Spectrum of compound S4](image)

75 MHz $^{13}$C NMR Spectrum of compound S4 (CDCl$_3$, 300 K)

![75 MHz $^{13}$C NMR Spectrum of compound S4](image)
300 MHz $^1$H NMR Spectrum of compound S5 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S5 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 1a (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 1a (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 1b (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 1b (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S7 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S7 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S8 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S8 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S9 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S9 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 1c (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 1c (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 1d (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 1d (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 1e (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 1e (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound If (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound If (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 1g (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 1g (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound $1h$ (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound $1h$ (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 1i (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 1i (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 1j (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 1j (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 1k (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 1k (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 2a (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 2a (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 2b (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 2b (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 3a (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 3a (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 3b (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 3b (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 3c (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 3c (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 3d (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 3d (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 3e (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 3e (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 3f (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 3f (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 3g (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 3g (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 2h (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 2h (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 2i (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 2i (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 2j (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 2j (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 2k (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 2k (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 4 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 4 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 6 (CDCl₃, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 6 (CDCl₃, 300 K)
300 MHz $^1$H NMR Spectrum of compound 7 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 7 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S10 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S10 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S11 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S11 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S12 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S12 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound S13 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound S13 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 8 (CDCl$_3$, 300 K)

![NMR Spectrum Image]

75 MHz $^{13}$C NMR Spectrum of compound 8 (CDCl$_3$, 300 K)

![NMR Spectrum Image]
300 MHz $^1$H NMR Spectrum of compound 10 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 10 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 9 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 9 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of compound 11 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of compound 11 (CDCl$_3$, 300 K)