Supplementary Information

Au(I)-Catalyzed Triple Bond Alkoxylation/Vinyl-Vinyl Aromaticity-Driven Cascade Cyclization to Naphthalenes

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I. General Information
Unless otherwise noted, reagents were obtained commercially and used without further purification. THF was distilled from sodium-benzophenone under a nitrogen atmosphere. TLC analysis of reaction mixtures was performed on Dynamicadsorbents silica gel F-254 TLC plates. Flash chromatography was carried out on Zeoprep 60 ECO silica gel. $^1$H and $^{13}$C NMR spectra were recorded with Bruker Avance-III 600 spectrometers and referenced to CDCl$_3$. HR-ESI-MS was recorded on a Bruker micro-TOFQ-Q instrument. IR spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer. Melting points were tested on Thomas Hoover capillary melting point apparatus. Compounds were detected by monitoring UV absorbance at 254 nm.
II. General Preparation of 2-Ethynylbenzaldehyde Derivatives (7a-7g)

\[
\begin{align*}
\text{R}^1 & \quad \text{CHO} \\
\text{R}^2 & \quad \text{Br} \\
\text{R}^3 & \quad \text{TMS, Pd(PPh}_3\text{)}_2\text{Cl}_2, \text{Cul, Et}_3\text{N, THF, 50 °C} \\
\text{R}^1 & \quad \text{CHO} \\
\text{R}^2 & \quad \text{Br} \\
\text{R}^3 & \quad \text{TMS, K}_2\text{CO}_3, \text{MeOH, rt} \\
\end{align*}
\]

To a solution of the corresponding 2-bromobenzaldehyde (1 mmol), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (0.05 mmol, 35.1 mg), CuI (0.1 mmol, 19.1 mg) and Et\textsubscript{3}N (5 mmol, 0.7 mL) in dry THF was added the appropriate acetylene (2 mmol, 0.3 mL). The resulting mixture was heated at 50 °C for 12 hours. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH\textsubscript{2}Cl\textsubscript{2} (three times). The combined organic layer was washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product 2-[(trimethylsilyl)ethynyl]benzaldehyde. Then the product obtained above was dissolved in MeOH and treated with K\textsubscript{2}CO\textsubscript{3} (2 mmol, 276.4 mg). After being stirred at room temperature for 1 hour, the reaction mixture was diluted with water and extracted with CH\textsubscript{2}Cl\textsubscript{2} (three times). The combined organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo. The residue was purified by column chromatography on silica gel to yield products 7a-7g. Spectral data were consistent with those reported in the literatures. 1-6

III. General Preparation of 2-Alkynylbenzaldehyde Derivatives (7h-7l) and Characterization Data

\[
\begin{align*}
\text{R}^1 & \quad \text{CHO} \\
\text{R}^2 & \quad \text{Br} \\
\text{R}^3 & \quad \text{R}^4, \text{Pd(PPh}_3\text{)}_2\text{Cl}_2, \text{Cul, Et}_3\text{N, THF, 50 °C} \\
\text{R}^1 & \quad \text{CHO} \\
\text{R}^2 & \quad \text{Br} \\
\text{R}^3 & \quad \text{R}^4 = \text{aryl} \\
\end{align*}
\]

To a solution of the corresponding 2-bromobenzaldehyde (1 mmol), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (0.05 mmol, 35.1 mg), CuI (0.1 mmol, 19.1 mg) and Et\textsubscript{3}N (5 mmol, 0.7 mL) in dry THF was added the appropriate acetylene (1.2 mmol). The resulting mixture was heated at 50 °C for 12 hours. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH\textsubscript{2}Cl\textsubscript{2} (three times). The combined organic layer was washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired products 7h-7l. Spectral data were consistent with those reported in the literature. 1

4, 5-Methylenedioxy-2-(2-phenylethynyl) benzaldehyde (7l): TLC (petroleum ether: ethyl acetate, 30:1, v/v): R=0.3; yellowish solid, Mp 138–139 °C; 85%; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \( \delta = 10.44 \) (s, 1H), 7.51 (dd, \( J = 8.4 \) Hz, 5.5 Hz, 2H), 7.35 (s, 1H), 7.06 (t, \( J = 8.6 \) Hz, 2H), 6.99 (s, 1H), 6.08 (s, 2H); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \( \delta = 190.0, 163.0 \) (d, \( J = 249.4 \) Hz), 152.5, 148.9, 133.7 (d, \( J = 8.4 \) Hz), 133.7 (d, \( J = 8.4 \) Hz), 132.3, 123.5, 118.6 (d, \( J = 3.5 \) Hz), 116.0 (d, \( J = 22.0 \) Hz), 112.1, 106.3, 102.6, 94.2, 84.7; HRMS (ESI): \( m/z \): Calcd for C\textsubscript{16}H\textsubscript{10}O\textsubscript{3}F [M+H]\textsuperscript{+} 269.0608. Found 269.0608; IR (thin film, cm\textsuperscript{-1}): 3712, 3816, 3734, 3619, 1542, 1457, 805.
IV. General Preparation of 1, 5-Enyne Substrates (1-1k) and Characterization Data

To a suspension of (methoxymethyl)triphenylphosphonium chloride (2 mmol, 685.6 mg) in anhydrous THF was added 1 M solution of KHMD (1.8 mmol, 1.8 mL) at −78 °C. The mixture was stirred at −78 °C for 0.5 h, and then a 2-alkynylbenzaldehyde (1 mmol) in anhydrous THF was added. The reaction was allowed to warm up to 0 °C over 3 h, and then hexane was added. The resulting mixture was filtered through Celite and thoroughly washed with hexane. The filtrate was concentrated in vacuo and the residue was diluted with hexane. The resulting mixture was filtered through Celite again to remove the remaining triphenylphosphate oxide. After evaporation to dryness, the crude product was purified by silica gel chromatography eluting with petroleum ether/ethyl acetate (30:1, v/v). The crude vinyl ether was purified by silica gel chromatography eluting with petroleum ether/ethyl acetate to yield the product. Spectral data were consistent with those reported in the literature.7-8

2-Ethynyl-1-(2-methoxyvinyl)-4-methylbenzene (1a): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R=0.2; yellowish oil, 75%; 1H NMR (600 MHz, CDCl3) δ = 7.97 (d, J = 8.2 Hz, 1H, Z), 7.29 (s, 1H, Z + 1H, E), 7.25 (d, J = 8.1 Hz, 1H, E), 7.13 – 7.09 (m, 1H, Z + 1H, E), 7.06 (d, J = 8.0 Hz, 1H, E), 6.24 (d, J = 13.0 Hz, 1H, E), 6.20 (d, J = 7.2 Hz, 1H, Z), 5.77 (d, J = 7.2 Hz, 1H, Z), 3.78 (s, 3H, Z), 3.72 (s, 3H, E), 3.28 (s, 1H, E), 3.26 (s, 1H, Z), 2.29 (s, 3H, Z), 2.29 (s, 3H, E); 13C NMR (150 MHz, CDCl3) δ = 149.9 (E), 148.6 (Z), 136.0 (E), 135.2 (Z), 135.2 (E), 133.7 (E), 133.2 (Z), 130.2 (E), 129.8 (Z), 128.6 (Z), 123.6 (E), 119.7 (Z), 119.4 (E), 103.2 (E), 103.0 (Z), 83.0 (Z), 82.8 (Z), 81.1 (E), 80.8 (E), 60.9 (Z), 59.7 (E), 21.0 (Z), 20.9 (E); HRMS (ESI): m/z: Calcd for C12H13O [M+H]+ 173.0961, Found 173.0962; IR (thin film, cm−1): 3854, 3807, 3675, 2923, 1700,1652, 1638, 1635, 1558, 1465, 1457, 1090, 833, 748, 682.

1-Ethynyl-4-methoxy-2-(2-methoxyvinyl)benzene (1b): TLC (petroleum ether:ethyl acetate, 30:1, v/v): R=0.25; yellowish oil (1: 0.5 E/Z), 72%; 1H NMR (600 MHz, CDCl3) δ = 7.68 (d, J = 2.6 Hz, 1H, Z), 7.40 (d, J = 8.5 Hz, 1H, E + 1H, Z), 7.15 (d, J = 13.0 Hz, 1H, E), 6.86 (d, J = 2.5 Hz, 1H, E), 6.66 (dd, J = 8.5 Hz, 2.4 Hz, 1H, Z + 1H, E), 6.24 (dd, J = 10.1 Hz, 5.5 Hz, 1H, Z + 1H, E), 5.79 (d, J = 7.2 Hz, 1H, Z), 3.82 (s, 3H, Z), 3.81 (s, 3H, E), 3.80 (s, 3H, Z), 3.73 (s, 3H, E), 3.24 (s, 1H, E), 3.22 (s, 1H, Z); 13C NMR (150 MHz, CDCl3) δ = 160.1 (E), 159.9 (Z), 150.6 (E), 149.6 (Z), 140.5 (E), 139.4 (Z), 134.7 (E), 134.0 (Z), 113.9 (Z), 112.5 (Z), 112.2 (E), 111.8 (Z), 111.7 (E), 108.8 (E), 103.4 (E), 103.1 (Z), 82.9 (Z), 82.7 (Z), 80.1 (E), 79.9 (E), 61.1 (Z), 56.7 (E), 55.4(E), 55.3 (Z); HRMS (ESI): m/z: Calcd for C12H13O2 [M+H]+ 189.0909, Found 189.0909; IR (thin film, cm−1): 3744, 3628, 1700, 1652, 1507, 720, 688, 676.

1c
1-Ethynyl-4,5-dimethoxy-2-(2-methoxyvinyl)benzene (1c): TLC (petroleum ether:ethyl acetate, 10:1): Rf=0.3; yellowish solid (1: 0.6 E/Z, Mp 80–82 °C; 71%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.68 (s, 1H, Z), 7.06 (d, $J$ = 13.0 Hz, 1H, E), 6.94 (s, 1H, Z), 6.93 (s, 1H, E), 6.79 (s, 1H, E), 6.21 (d, $J$ = 13.0 Hz, 1H, E), 6.16 (d, $J$ = 7.2 Hz, 1H, Z), 5.74 (d, $J$ = 7.2 Hz, 1H, Z), 3.89 (s, 3H, E + H, Z), 3.85 (s, 3H, Z), 3.85 (s, 3H, E), 3.79 (s, 3H, Z), 3.71 (s, 3H, E), 3.25 (s, 1H, E), 3.24 (s, 1H, Z); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 150.1 (E), 149.5 (Z), 149.4 (E), 147.9 (E), 147.1 (Z), 146.7 (Z), 132.7 (E), 132.2 (Z), 115.2 (E), 114.8 (Z), 112.1 (Z), 111.5 (Z), 111.5 (E), 106.4 (E), 103.4 (E), 103.1 (Z), 82.9 (Z), 82.8 (Z), 80.2 (E), 79.9 (E), 61.0 (Z), 56.6 (E), 56.1 (E), 56.0 (Z), 56.0 (E), 55.9 (Z); HRMS (ESI): m/z: Calcd for C$_{13}$H$_{15}$O$_3$ [M+H]$^+$ 219.1016, Found 219.1016; IR (thin film, cm$^{-1}$): 3874, 3850, 3821, 3750, 1685, 1652, 1560, 744, 683.

![Chemical Structure](image1c)

4-Chloro-1-ethynyl-2-(2-methoxyvinyl) benzene (1e): TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.3; yellowish solid (1: 0.5 E/Z, Mp 91–93 °C; 70%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 8.09 (d, $J$ = 2.1 Hz, 1H, Z), 7.37 (d, $J$ = 8.3 Hz, 1H, E + 1H, Z), 7.33 (d, $J$ = 2.0 Hz, 1H, E), 7.14 (d, $J$ = 13.0 Hz, 1H, E), 7.06 (dt, $J$ = 8.3Hz, 2.3 Hz, 1H, E + 1H, Z), 6.28 (d, $J$ = 7.2 Hz, 1H, Z), 6.19 (d, $J$ = 13.0 Hz, 1H, E), 5.75 (d, $J$ = 7.2 Hz, 1H, Z), 3.83 (s, 3H, Z), 3.73 (s, 3H, E), 3.33 (s, 1H, E), 3.31 (s, 1H, Z); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 151.4 (E), 150.4 (Z), 140.6 (E), 139.5 (Z), 135.1 (E), 134.8 (Z), 134.4 (E), 133.8 (Z), 128.5 (Z), 125.6 (E), 123.6 (E), 118.2 (Z), 118.0 (E), 102.6 (E), 102.1 (Z), 82.3 (Z + E), 82.1 (E), 81.7 (Z), 61.3 (Z), 56.9 (E); HRMS (ESI): m/z: Calcd for C$_{11}$H$_{10}$ClO [M+H]$^+$ 193.0414, Found 193.0415; IR (thin film, cm$^{-1}$): 3854, 3670, 1734, 1700, 1685, 1539, 841, 754, 676.

![Chemical Structure](image1e)

1-Ethynyl-2-(2-methoxyvinyl) naphthalene (1f): TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.25; yellowish oil (1: 0.5 E/Z, 74%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 8.37 (d, $J$ = 8.6 Hz, 1H, Z), 8.35 (d, $J$ = 8.4 Hz, 1H, E), 8.27 (d, $J$ = 8.8 Hz, 1H, Z), 7.79 (d, $J$ = 8.8 Hz, 1H, E), 7.77 (d, $J$ = 8.6 Hz, 1H, E + 1H, Z), 7.72 (d, $J$ = 8.7 Hz, 1H, E), 7.58 – 7.53 (m, 1H, E + 1H, Z), 7.52 (d, $J$ = 8.7 Hz, 1H, E), 7.45 (m, 1H, E + 1H, Z), 7.31 (d, $J$ = 13.0 Hz, 1H, E), 6.59 (d, $J$ = 13.0 Hz, 1H, E), 6.33 (d, $J$ = 7.2 Hz, 1H, Z), 6.08 (d, $J$ = 7.2 Hz, 1H, Z), 3.84 (s, 3H, Z), 3.80 (s, 3H, E), 3.78 (s, 1H, E), 3.77 (s, 1H, Z); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 151.4 (E), 149.9 (Z), 137.8 (E), 137.6 (Z), 134.3 (E) 134.0 (Z), 131.5 (E), 131.4 (Z), 129.1 (E), 128.5 (Z), 128.1 (E), 128.1 (Z), 127.3 (E), 127.0 (Z), 126.5 (Z), 126.4 (Z), 126.1 (E), 125.8 (Z), 125.6 (E), 121.6 (E), 116.0 (Z), 115.4 (E), 104.3 (E), 104.0 (Z), 87.2 (E), 87.1 (E), 80.8 (Z), 80.6 (Z), 61.1 (Z), 56.8 (E); HRMS (ESI): m/z: Calcd for C$_{15}$H$_{13}$O [M+H]$^+$ 209.0961, Found 209.0962; IR (thin film, cm$^{-1}$): 3852, 3650, 1717, 1696, 1653, 1534, 1520, 720, 684.

![Chemical Structure](image1f)

4-Methoxy-2-(2-methoxyvinyl)-1-(phenylethynyl)benzene (1g): TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rf=0.3; yellowish oil (0.6: 1 E/Z, 74%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.72 (d, $J$ = 2.6 Hz, 1H, Z), 7.56 – 7.49 (m, 2H, Z + 2H E), 7.44 (d, $J$ = 8.5 Hz, 1H, Z + 1H, E), 7.38 – 7.29 (m, 3H, Z + 3H, E), 7.20 (d, $J$ = 13.0 Hz, 1H, E), 6.89 (d, $J$ = 2.5 Hz, 1H, E), 6.72 – 6.70 (m, 1H, Z + 1H, E), 6.34 (d, $J$ = 13.0 Hz, 1H, E),
6.28 (d, J = 7.2 Hz, 1H, Z), 5.89 (d, J = 7.2 Hz, 1H, Z), 3.84 (s, 3H, Z), 3.83 (s, 3H, E), 3.82 (s, 3H, Z), 3.76 (s, 3H, E); $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 159.9 (E), 159.6 (Z), 150.5 (E), 149.5 (Z), 139.8 (E), 138.8 (Z), 134.0 (E), 133.4 (Z), 131.5 (Z), 131.5 (Z), 131.4 (E), 131.4 (E), 128.5 (E), 128.5 (E), 128.4 (Z), 128.4 (Z), 128.0 (E), 127.9 (Z), 124.0 (Z), 124.0 (E), 113.9 (Z), 113.7 (E), 113.4 (E), 111.9 (Z), 111.8 (E), 109.0 (Z), 103.7 (E), 103.4 (Z), 92.5 (Z), 92.2 (Z), 88.7 (E), 88.6 (E), 61.1 (Z), 56.7 (E), 55.4 (E), 55.4 (Z); HRMS (ESI): $m/z$: Calcd for C$_{18}$H$_{17}$O$_2$ [M+H]$^+$ 265.1223, Found 265.1221; IR (thin film, cm$^{-1}$): 3838, 3676, 2921, 1734, 1700, 1560, 1540, 767, 679.

1-((4-Chlorophenyl)ethynyl)-4-methoxy-2-(2-methoxyvinyl)benzene (1H): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R$_f$=0.2; yellowish solid (1: 0.7 E/Z), Mp 77–79 °C; 71%; $^1$H NMR (600 MHz, CDCl$_3$) δ = 7.72 (d, J = 2.5 Hz, 1H, Z), 7.45 – 7.41 (m, 2H, E + 2H, Z), 7.37 – 7.29 (m, 3H, E + 3H, Z), 7.18 (d, J = 12.9 Hz, 1H, E), 6.89 (d, J = 2.5 Hz, 1H, E), 6.71 (ddd, J = 8.5 Hz, 2.4 Hz, 1.2 Hz, 1H, Z + 1H, E), 6.29 (d, J = 12.0 Hz, 7.7 Hz, 1H, E + 1H, Z), 5.84 (d, J = 7.2 Hz, 1H, Z), 3.84 (s, 3H, Z), 3.83 (s, 3H, E), 3.82 (s, 3H, Z), 3.75 (s, 3H, E); $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 160.0 (E), 159.8 (Z), 150.6 (E), 149.6 (Z), 139.9 (E), 138.8 (Z), 134.0 (E), 133.4 (Z), 132.7 (Z), 132.6 (E), 132.7 (Z), 132.6 (E), 128.8 (E), 128.7 (Z), 128.8 (E), 128.7 (Z), 128.6 (Z), 128.6 (E), 122.5 (Z), 122.5 (E), 114.0 (Z), 113.3 (Z), 113.0 (E), 111.9 (Z), 111.9 (E), 109.0 (E), 103.7 (E), 103.2 (Z), 91.4 (E), 91.1 (E), 89.7 (Z), 89.6 (Z), 61.1 (Z), 56.8 (E), 55.4 (E), 55.3 (Z); HRMS (ESI): $m/z$: Calcd for C$_{18}$H$_{16}$O$_2$Cl [M+H]$^+$ 299.0833, Found 299.0856; IR (thin film, cm$^{-1}$): 3852, 3815, 3744, 3668, 3646, 1696, 1675, 1576, 1560, 1558, 696, 678.

4-Methoxy-1-((4-methoxyphenyl)ethynyl)-2-(2-methoxyvinyl)benzene (1i): TLC (petroleum ether:ethyl acetate, 15:1, v/v): R$_f$=0.3; yellowish solid (1: 0.5 E/Z), Mp 83–85 °C; 65%; $^1$H NMR (600 MHz, CDCl$_3$) δ = 7.71 (d, J = 2.6 Hz, 1H, Z), 7.47 – 7.44 (m, 2H, E + 2H, Z), 7.42 (d, J = 8.5 Hz, 1H, E + 1H, Z), 7.18 (d, J = 13.0 Hz, 1H, E), 6.91 – 6.85 (m, 3H, E + 2H, Z), 6.70 (dd, J = 8.5, 2.4 Hz, 1H, E + 1H, Z), 6.33 (d, J = 13.0 Hz, 1H, E), 6.27 (d, J = 7.2 Hz, 1H, Z), 5.88 (d, J = 7.2 Hz, 1H, Z), 3.83 (s, 3H, Z), 3.83 (s, 3H, E), 3.81 (s, 3H, Z), 3.75 (s, 3H, E); $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 159.6 (E), 159.5 (E), 159.4 (Z), 159.4 (E), 150.4 (E), 149.4 (Z), 139.5 (E), 138.6 (Z), 133.8 (E), 133.2 (Z), 132.9 (Z), 132.9 (E), 132.8 (E), 116.2 (Z), 116.1 (E), 114.1 (E), 114.1 (Z), 114.1 (E), 114.0 (Z), 113.9 (E), 113.7 (Z), 111.8 (Z), 111.6 (E), 108.9 (E), 103.8 (E), 103.5 (Z), 92.4 (E), 92.1 (Z), 87.2 (Z), 87.1 (E), 61.0 (Z), 56.7 (E), 55.4 (E + Z), 55.4 (E), 55.3 (Z); HRMS (ESI): $m/z$: Calcd for C$_{19}$H$_{19}$O$_3$ [M+H]$^+$ 295.1329, Found 295.1300; IR (thin film, cm$^{-1}$): 3891, 3854, 3744, 3735, 3674, 2920, 1701, 1695, 1685, 718, 676.
1, 2-Dimethoxy-4-(2-methoxyvinyl)-5-(phenylethenyl) benzene (1j): TLC (petroleum ether:ethyl acetate, 20:1, v/v): Rf=0.25; yellowish oil (1: 0.7 E/Z); 63% 1H NMR (600 MHz, CDCl3) δ = 7.72 (s, 1H, Z), 7.54 – 7.49 (m, 5H, Z), 7.33 (m, 5H, E), 7.09 (d, J = 13.0 Hz, 1H, E), 6.98 (s, 1H, Z), 6.98 (s, 1H, E), 6.82 (s, 1H, E), 6.30 (d, J = 13.0 Hz, 1H, E), 6.18 (d, J = 7.2 Hz, 1H, Z), 5.83 (d, J = 7.2 Hz, 1H, Z), 3.90 (s, 3H, E), 3.90 (s, 3H, Z), 3.88 (s, 3H, E), 3.88 (s, 3H, Z), 3.80 (s, 3H, Z), 3.73 (s, 3H, E); 13C NMR (150 MHz, CDCl3) δ = 149.8 (E), 149.2 (Z), 149.2 (E), 147.8 (E), 147.2 (Z), 146.9 (Z), 132.0 (E), 131.7 (Z), 131.5 (Z), 131.5 (Z), 131.4 (E), 131.4 (E), 128.5 (E), 128.5 (E), 128.4 (Z), 128.4 (Z), 128.1 (E), 128.0 (Z), 123.9 (Z), 123.8 (E), 114.7 (E), 114.2 (Z), 113.3 (Z), 112.7 (E), 111.6 (Z), 106.7 (E), 103.8 (E), 103.5 (Z), 92.6 (E), 92.3 (Z), 88.7 (E), 88.6 (Z), 60.9 (Z), 56.6 (E), 56.1 (E), 56.0 (Z), 56.0 (E), 55.9 (Z); HRMS (ESI): m/z: Calcd for C19H19O3 [M+H]+ 295.1329, Found 295.1331; IR (thin film, cm⁻¹): 3838, 3816, 3676, 1700, 1696, 1576, 1560, 1540, 747, 683.

5-((4-Fluorophenyl)ethynyl)-6-(2-methoxyvinyl)benzo[d][1,3]dioxole (1k): TLC (petroleum ether:ethyl acetate, 30:1, v/v): Rf=0.2; yellowish solid (1: 0.4 E/Z), Mp 97–98 °C; 71%; 1H NMR (600 MHz, CDCl3) δ 7.67 (s, 1H, Z), 7.51 – 7.45 (m, 2H, E + 2H, Z), 7.07 – 7.00 (m, 3H, E + 2H, Z), 6.92 (s, 1H, Z), 6.91 (s, 1H, E), 6.83 (s, 1H, E), 6.31 (d, J = 12.9 Hz, 1H, E), 6.18 (d, J = 7.2 Hz, 1H, Z), 5.96 (s, 2H, Z), 5.95 (s, 2H, E), 5.81 (d, J = 7.2 Hz, 1H, Z), 3.79 (s, 3H, Z), 3.72 (s, 3H, E); 13C NMR (150 MHz, CDCl3) δ = 162.5 (d, J = 247.8 Hz, E), 149.5 (E), 148.6 (E), 148.1 (Z), 148.0 (Z), 145.7 (E), 145.3 (Z), 133.6 (E), 133.3 (d, J = 8.3 Hz, Z), 133.3 (d, J = 8.3 Hz, Z), 133.2 (d, J = 8.3 Hz, E), 133.2 (d, J = 8.3 Hz, E), 132.9 (Z), 119.9 (d, J = 3.5 Hz, Z), 119.8 (d, J = 3.5 Hz, E), 115.8 (d, J = 21.9 Hz, E), 115.8 (d, J = 21.9 Hz, E), 115.7 (d, J = 21.9 Hz, Z), 115.7 (d, J = 21.9 Hz, Z), 114.1 (Z), 113.5 (E), 111.6 (E), 111.3 (Z), 108.9 (Z), 103.9 (E), 103.8 (E), 103.4 (Z), 101.4 (E), 101.4 (Z), 91.6 (E), 91.3 (Z), 88.4 (Z), 88.1 (E), 60.9 (Z), 56.8 (E); HRMS (ESI): m/z: Calcd for C19H13O3Na [M+Na]+ 319.0741, Found 319.0738; IR (thin film, cm⁻¹): 3854, 3821, 3802, 3752, 3671, 1700, 1684, 1653, 1635, 694, 686.

V. Characteration Data of Naphthalenes

![Diagram of naphthalene synthesis](image)

General procedure for Au(I)-catalyzed cascade cyclization for the synthesis of naphthalenes: The 1,5-enyne substrate (1 mmol) and the [[IPr]AuSbF6] (0.05 mmol, 36.9 mg) in ROH (2 mL) were placed in a screw-cap vial containing a stirring bar. The reaction vial was fitted with a cap, evacuated, filled with nitrogen, and heated with stirring at 80–150 °C for 30–120h. The reaction mixture was cooled, filtered through a plug of silica gel. The filtrate was concentrated and the obtained residue was purified by flash column chromatography to afford the naphthalene.
6-Chloro-1-methoxynaphthalene (5e): TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rf=0.2; white solid, Mp 46–47 °C; 75%; 1H NMR (600 MHz, CDCl3) δ = 8.20 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 1.6 Hz, 1H), 7.41 (m, 2H), 7.33 (d, J = 8.3 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 4.00 (s, 3H); 13C NMR (150 MHz, CDCl3) δ = 155.6, 135.3, 132.5, 127.4, 126.3, 126.1, 124.1, 124.0, 119.4, 104.2, 55.7; HRMS (ESI): m/z: Calcd for C11H10Cl [M+H]+ 193.0414, Found 193.0417; IR (thin film, cm⁻¹): 3750, 3745, 1701, 1653, 1558, 1507, 761, 749, 676.

1,6-Dimethoxy-2-phenynaphthalene (5g): TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rf=0.2; yellowish solid, Mp 112–114 °C; 50%; 1H NMR (600 MHz, CDCl3) δ = 8.15 (d, J = 9.1 Hz, 1H), 7.68 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.48 – 7.45 (m, 3H), 7.36 (t, J = 7.3 Hz, 1H), 7.20 (dd, J = 9.1 Hz, 2.0 Hz, 1H), 7.17 (br.s, 1H), 3.95 (s, 3H), 3.57 (s, 3H); 13C NMR (150 MHz, CDCl3) δ = 158.2, 153.6, 139.0, 135.8, 129.5, 129.5, 129.5, 128.5, 128.5, 127.7, 127.0, 124.4, 123.9, 122.9, 119.0, 106.0, 61.3, 55.5; HRMS (ESI): m/z: Calcd for C18H17O2 [M+H]+ 265.1223, Found 265.1199; IR (thin film, cm⁻¹): 3854, 3821, 3752, 1700, 1685, 1653, 1635, 1507, 743, 728, 687.

2-(4-Chlorophenyl)-1,6-dimethoxynaphthalene (5h): TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rf=0.3; yellowish solid, Mp 118–120 °C; 51%; 1H NMR (600 MHz, CDCl3) δ = 8.13 (d, J = 9.1 Hz, 1H), 7.63 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.42 (m, 3H), 7.21 (dd, J = 9.1 Hz, 2.1 Hz, 1H), 7.16 (s, 1H), 3.95 (s, 3H), 3.57 (s, 3H); 13C NMR (150 MHz, CDCl3) δ = 158.4, 153.6, 137.3, 136.0, 133.0, 130.8, 130.8, 129.0, 128.7, 128.7, 126.5, 124.4, 123.9, 123.1, 119.2, 106.0, 61.4, 55.5; HRMS (ESI): m/z: Calcd for C18H16O2Cl [M+H]+ 299.0833, Found 299.0728; IR (thin film, cm⁻¹): 3852, 3815, 3744, 3734, 3688, 3674, 1700, 1695, 1652, 1558, 1507, 714, 678.

1,6-Dimethoxy-2-(4-methoxyphenyl)naphthalene (5i): TLC (petroleum ether:ethyl acetate, 20:1, v/v): Rf=0.2; yellowish solid, Mp 107–108 °C; 30%; 1H NMR (600 MHz, CDCl3) δ = 8.13 (d, J = 9.1 Hz, 1H), 7.64 – 7.60 (dd, J = 8.4 Hz, 1.8 Hz, 2H), 7.54 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.19 (dd, J = 9.1 Hz, 2.5 Hz, 1H), 7.15 (d, J = 2.5 Hz, 1H), 7.02 – 6.97 (dd, J = 8.4 Hz, 1.8 Hz, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 3.57 (s, 3H); 13C NMR (150 MHz, CDCl3) δ = 158.8, 158.1, 153.3, 135.5, 131.3, 130.5, 130.5, 129.5, 128.8, 124.3, 124.0, 122.9, 118.9, 114.0, 114.0, 106.0, 61.1, 55.5, 55.4; HRMS (ESI): m/z: Calcd for C19H19O3 [M+H]+ 295.1328, Found 295.1330; IR (thin film, cm⁻¹): 3837, 3832, 3647, 1696, 1675, 1558, 1542, 747, 728, 688.
1, 6, 7-Trimethoxy-2-phenynaphthalene (5j): TLC (petroleum ether:ethyl acetate, 20:1, v/v): Rf=0.3; yellowish solid, Mp 101–103 °C; 50%; 1H NMR (600 MHz, CDCl3) δ = 7.68 (d, J = 7.4 Hz, 2H), 7.52 (m, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.37 (m, 2H), 7.15 (s, 1H), 4.05 (s, 3H), 4.03 (s, 3H), 3.56 (s, 3H); 13C NMR (150 MHz, CDCl3) δ = 152.3, 150.1, 150.0, 139.1, 130.3, 129.5, 129.5, 128.5, 128.3, 127.1, 127.0, 124.1, 122.5, 106.5, 101.3, 60.9, 56.1. HRMS (ESI): m/z: Calcd for C19H18O3Na [M+Na]+ 317.1148, Found 317.1150; IR (thin film, cm⁻¹): 3891, 3854, 3821, 3752, 3744, 1700, 1685, 1653, 1635, 1506, 743, 745, 677.

6-(4-Fluorophenyl)-5-methoxynaptho[2,3-d][1,3]dioxole (5k): TLC (petroleum ether:ethyl acetate, 40:1, v/v): Rf=0.3; yellow solid, Mp 120–122 °C; 50%; 1H NMR (600 MHz, CDCl3) δ = 7.64 (m, 2H), 7.50 (s, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.14 (m, 3H), 6.07 (s, 2H), 3.52 (s, 3H); 13C NMR (150 MHz, CDCl3) δ = 162.2 (d, J = 244.8 Hz), 152.8, 148.4, 148.2, 134.8 (d, J = 3.5 Hz), 131.7, 131.0 (d, J = 7.8 Hz), 131.0 (d, J = 7.8 Hz), 127.8, 127.0, 125.5, 123.3, 115.4 (d, J = 21 Hz), 115.4 (d, J = 21 Hz), 104.1, 101.3, 99.2, 60.9; HRMS (ESI): m/z: Calcd for C18H14O3F [M+H]+ 297.0921, Found 297.0915; IR (thin film, cm⁻¹): 3854, 3821, 3816, 3801, 3671, 1700, 1696, 1653, 1560, 1539, 835, 694, 686.

1-Ethoxy-6-methoxynaphthalene (5l): TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rf=0.2; white solid, Mp 63–65 °C; 88%; 1H NMR (600 MHz, CDCl3) δ = 8.21 (d, J = 9.1 Hz, 1H), 7.39 – 7.28 (m, 1H), 7.16 – 7.07 (m, 1H), 6.68 (dd, J = 7.0 Hz, 0.9 Hz, 1H), 4.20 (q, J = 7.0 Hz, 1H), 3.92 (s, 1H), 1.54 (t, J = 7.0 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ = 158.2, 155.1, 136.0, 126.8, 124.0, 121.0, 119.2, 117.5, 105.8, 103.0, 63.8, 55.3, 15.0; HRMS (ESI): m/z: Calcd for C13H15O2 [M+H]+ 203.1067, Found 203.1010; IR (thin film, cm⁻¹): 3854, 3821, 1685, 1653, 1617, 1596, 1432, 1373, 747, 696.

1-Ethoxy-6, 7-dimethoxynaphthalene (5m): TLC (petroleum ether:ethyl acetate, 15:1, v/v): Rf=0.2; white solid, Mp 103–104 °C; 80%; 1H NMR (600 MHz, CDCl3) δ = 7.56 (s, 1H), 7.28 (d, J = 8.1 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.09 (s, 1H), 6.72 (d, J = 7.5 Hz, 1H), 4.21 (q, J = 7.0 Hz, 2H), 4.03 (s, 3H), 4.00 (s, 3H), 1.55 (d, J = 6.9 Hz, 3H); 13C NMR (150 MHz, CDCl3) δ = 153.9, 149.9, 149.0, 130.5, 124.4, 120.9, 118.8, 106.4, 103.8, 101.2, 63.8, 56.0, 55.9, 15.1; HRMS (ESI): m/z: Calcd for C14H12O2 [M+H]+ 233.1200, Found 233.1200; IR (thin film, cm⁻¹): 3860, 3854, 3836, 3732, 3611, 1683, 1558, 835, 743, 728, 681.

4-Ethoxyphenanthrene (5n): TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.3; colorless oil, 75%; 1H NMR (600 MHz, CDCl3) δ = 9.80 (d, J = 8.6 Hz, 1H), 7.89 (dd, J = 7.8 Hz, 1.4 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.64 (ddd, J = 8.6 Hz, 7.0 Hz, 1.6 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.52 (d, J =
6.9 Hz, 2H), 7.16 (t, J = 6.6 Hz, 1H), 4.36 (q, J = 6.9 Hz, 2H), 1.72 (t, J = 6.9 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 158.3, 134.8, 132.9, 130.7, 128.8, 128.4, 128.1, 127.3, 126.6, 126.5, 125.9, 121.6, 120.9, 109.3, 64.8, 15.3; HRMS (ESI): m/z: Calcd for C$_{16}$H$_{14}$OK [M+K]$^+$ 261.1271, Found 261.1271; IR (thin film, cm$^{-1}$): 3881, 3854, 3749, 3646, 3612, 1675, 1559, 1539, 792, 683.

6-Chloro-1-ethoxynaphthalene (5o): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R$_f$=0.2; white solid, Mp 51–52 ºC; 82%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 8.23 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 1.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.31 (d, J = 8.2 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 4.20 (q, J = 6.9 Hz, 2H), 1.55 (t, J = 6.9 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 155.0, 135.4, 132.4, 127.4, 126.2, 125.9, 124.2, 124.1, 119.2, 105.0, 63.9, 15.0; HRMS (ESI): m/z: Calcd for C$_{12}$H$_{12}$OCl [M+H]$^+$ 207.0571, Found 207.0571; IR (thin film, cm$^{-1}$): 3851, 3801, 3749, 3647, 1700, 1635, 1539, 1505, 746, 729, 679.

1-Butoxy-6-methoxynaphthalene (5p): TLC (petroleum ether:ethyl acetate, 50:1, v/v): R$_f$=0.25; white solid, Mp 46–47 ºC; 65%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 8.20 (d, J = 9.0 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.11 (m, 1H), 6.69 – 6.67 (m, 1H), 4.13 (t, J = 6.4 Hz, 1H), 3.92 (s, 1H), 1.90 (tt, J = 12.7 Hz, 6.4 Hz, 1H), 1.65 – 1.56 (m, 1H), 1.03 (t, J = 7.4 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 152.9, 149.9, 149.0, 130.7, 124.4, 126.2, 125.9, 124.2, 124.1, 119.2, 104.9, 68.1, 31.5, 19.6, 14.1; HRMS (ESI): m/z: Calcd for C$_{15}$H$_{19}$O$_2$ [M+H]$^+$ 231.1380, Found 231.1377; IR (thin film, cm$^{-1}$): 3870, 3807, 3801, 3750, 1653, 1557, 774, 685.

1-Butoxy-6-chloronaphthalene (5q): TLC (petroleum ether:ethyl acetate, 100:1, v/v): R$_f$=0.2; colorless oil, 60%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 8.22 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 1.8 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.31 (d, J = 8.2 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 4.14 (t, J = 6.4 Hz, 1H), 1.97 – 1.82 (m, 1H), 1.60 (dd, J = 15.0 Hz, 7.5 Hz, 1H), 1.03 (t, J = 7.4 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 155.1, 135.4, 132.4, 127.5, 126.2, 125.9, 124.2, 124.1, 119.2, 104.9, 68.1, 31.5, 19.6, 14.1; HRMS (ESI): m/z: Calcd for C$_{14}$H$_{16}$OCl [M+H]$^+$ 235.0884, Found 235.0885; IR (thin film, cm$^{-1}$): 3815, 3743, 3674, 1652, 780, 675.

1-Isopropoxy-6,7-dimethoxynaphthalene (5r): TLC (petroleum ether:ethyl acetate, 20:1, v/v): R$_f$=0.2; white solid, Mp 71–73 ºC; 50%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.54 (s, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.09 (s, 1H), 6.76 (d, J = 7.4 Hz, 1H), 4.73 (dt, J = 12.1 Hz, 6.0 Hz, 1H), 4.02 (s, 3H), 3.99 (s, 3H), 1.46 (s, 3H), 1.45 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 152.9, 149.9, 149.0, 130.7, 124.4, 121.8, 118.7, 106.3, 105.6, 101.5, 70.6, 56.0, 55.9, 22.4, 22.4; HRMS (ESI): m/z: Calcd for C$_{15}$H$_{18}$O$_3$Na [M+Na]$^+$ 269.1148, Found 269.1152; IR (thin film, cm$^{-1}$): 3734, 3711, 1652, 1635, 1542, 1507, 841, 743.
**d5-1,6,7-Trimethoxynaphthalene (5c-D):** TLC (petroleum ether:ethyl acetate, 15:1, v/v): Rₜ=0.3; white solid, Mp 120–121 °C; 79%; ¹H NMR (600 MHz, CDCl₃) δ = 7.54 (s, 1H), 7.25 (s, 1H), 7.10 (s, 1H), 4.02 (s, 3H), 4.00 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 154.6, 149.9, 149.1, 130.4, 124.2, 120.7, 118.7 (t), 106.3, 102.5 (t), 101.1, 56.0, 55.9; HRMS (ESI): m/z: Calcd for C₁₃H₁₀O₃D₅ [M+H]+ 224.1330, Found 224.1310; IR (thin film, cm⁻¹): 3891, 3854, 3821, 3752, 3744, 1700, 1653, 1635, 1506, 826, 745, 677.

**d2-1,6,7-Trimethoxynaphthalene (5c-D-1):** TLC (petroleum ether:ethyl acetate, 15:1, v/v): Rₜ=0.3; white solid, Mp 120–121 °C; 70%; ¹H NMR (600 MHz, CDCl₃) δ = 7.54 (s, 1H), 7.29 (br.d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 6.88 (dd, J = 5.5 Hz, 1.5 Hz, 1H), 6.48 (dd, J = 5.6 Hz, 1.8 Hz, 1H), 4.02 (s, 3H), 4.00 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 154.6, 149.9, 149.1, 130.4, 124.2, 120.7, 118.7 (t), 106.4, 102.5 (t), 101.1, 56.0, 55.9, 55.6; HRMS (ESI): m/z: Calcd for C₁₃H₁₀O₃D₂ [M+H]+ 221.1147, Found 221.1151; IR (thin film, cm⁻¹): 3890, 3855, 3821, 3752, 3744, 1700, 1655, 1635, 1506, 826, 745, 679.

**d3-1,6,7-Trimethoxynaphthalene (5c-D-2):** TLC (petroleum ether:ethyl acetate, 15:1, v/v): Rₜ=0.3; white solid, Mp 120–121 °C; 74%; ¹H NMR (600 MHz, CDCl₃) δ = 7.54 (s, 1H),7.29 (br.d. J = 8.0 Hz, 1H), 7.26 (m, 1H), 7.10 (s, 1H), 6.72 (dd, J = 7.4, 0.8 Hz, 3H), 4.02 (s, 3H), 4.00 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 154.6, 149.9, 149.1, 130.4, 124.4, 120.7, 118.79, 106.4, 102.8, 101.1, 56.0, 55.9, 54.8 (t); HRMS (ESI): m/z: Calcd for C₁₃H₁₀O₃D₂ [M+H]+ 222.1209, Found 222.1209; IR (thin film, cm⁻¹): 3891, 3853, 3821, 3755, 3744, 1700, 1653, 1636, 1506, 826, 745, 677.

**1-(Dimethoxymethyl)-1H-indene (3):** TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rₜ=0.2; yellowish oil, 42%; ¹H NMR (600 MHz, CDCl₃) δ = 7.60 (d, J = 7.4 Hz, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 6.88 (dd, J = 5.5 Hz, 1.5 Hz, 1H), 6.48 (dd, J = 5.6 Hz, 1.8 Hz, 1H), 4.07 (d, J = 8.0 Hz, 1H), 3.83 (d, J = 8.0 Hz, 1H), 3.48 (s, 3H), 3.45 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 145.1, 143.2, 135.0, 133.1, 127.2, 125.1, 125.0, 121.1, 105.7, 54.5, 53.8, 53.7; HRMS (ESI): m/z: Calcd for C₁₂H₁₄O₂Na [M+Na]+ 213.0886, Found 213.0874; IR (thin film, cm⁻¹): 3400, 2880, 2700, 1696, 1476, 1400, 748.
(E)-1-(2-(2-Methoxyvinyl) phenyl)ethanone (6): TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rf=0.25; colorless oil, 61%; 1H NMR (600 MHz, DMSO-d6) δ = 7.71 (dd, J = 7.8 Hz, 1.2 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.41 (td, J = 7.8 Hz, 1.1 Hz, 1H), 7.25 (td, J = 7.7 Hz, 1.1 Hz, 1H), 7.14 (d, J = 12.9 Hz, 1H), 6.38 (d, J = 12.9 Hz, 1H), 3.63 (s, 3H), 2.53 (s, 3H); 13C NMR (150 MHz, DMSO-d6) δ = 202.1, 150.9, 135.9, 134.8, 131.4, 129.3, 125.7, 125.4, 103.2, 56.5, 30.0; HRMS (ESI): m/z: Calcd for C11H13O2 [M+H]+ 177.0910, Found 177.0913; IR (thin film, cm⁻¹): 3675, 3668, 3647, 1696, 1576, 1558, 1539, 748, 680.

(E/Z)-1-(4, 5-Dimethoxy-2-(2-methoxyvinyl) phenyl)ethanone (6c): TLC (petroleum ether:ethyl acetate, 10:1, v/v): Rf=0.3; white solid (1: 0.4 E/Z), Mp 66–68 °C; 93%; 1H NMR (600 MHz, CD3OD) δ = 7.56 (s, 1H, Z), 7.29 (s, 1H, E), 7.22 (s, 1H, Z), 6.98 (d, J = 12.9 Hz, 1H, E), 6.94 (s, 1H, E), 6.55 (d, J = 12.8 Hz, 1H, E), 6.19 (d, J = 7.3 Hz, 1H, Z), 5.83 (d, J = 7.3 Hz, 1H, Z), 3.88 (s, 3H, E), 3.85 (s, 3H, E), 3.85 (s, 3H, Z), 3.84 (s, 3H, Z), 3.74 (s, 3H, Z), 3.67 (s, 3H, E), 2.54 (s, 3H, E), 2.53 (s, 3H, Z); 13C NMR (150 MHz, CD3OD) δ = 203.7 (Z), 202.9 (E), 153.6 (Z), 152.6 (E), 151.5 (E), 149.4 (E), 148.2 (E), 147.8 (Z), 132.9 (E), 130.9 (Z), 130.8 (Z), 129.2 (E), 114.8 (E), 114.4 (Z), 113.8 (Z), 110.5 (E), 105.4 (E), 103.9 (Z), 60.9 (Z), 56.9 (E), 56.7 (E), 56.6 (Z), 56.4 (E), 56.2 (Z), 29.9 (E), 29.9 (Z); HRMS (ESI): m/z: Calcd for C13H16O4Na [M+Na]+ 259.0941, Found 259.0939; IR (thin film, cm⁻¹): 3890, 3864, 3853, 3836, 3751, 3690, 3668, 3687, 1750, 1729, 1695, 1560, 1558, 1541, 786, 683.

d3-(E/Z)-1-(4,5-Dimethoxy-2-(2-methoxyvinyl)phenyl)ethanone (6c-D): TLC (petroleum ether:ethyl acetate, 10:1, v/v): Rf=0.25; white solid (1: 0.4 E/Z), Mp 58–59 °C; 90%; 1H NMR (600 MHz, CD3OD) δ = 7.56 (s, 1H, Z), 7.29 (s, 1H, E), 7.22 (s, 1H, Z), 6.98 (d, J = 12.9 Hz, 1H, E), 6.94 (s, 1H, E), 6.56 (d, J = 12.8 Hz, 1H, E), 6.19 (d, J = 7.3 Hz, 1H, Z), 5.84 (d, J = 7.3 Hz, 1H, Z), 3.89 (s, 3H, E), 3.85 (s, 3H, E), 3.85 (s, 3H, Z), 3.84 (s, 3H, Z), 3.74 (s, 3H, Z), 3.68 (s, 3H, E); 13C NMR (150 MHz, CD3OD) δ = 203.8 (Z), 203.0 (E), 153.7 (Z), 152.7 (Z), 151.5 (E), 149.4 (E), 148.2 (E), 147.8 (Z), 132.9 (E), 130.9 (Z), 130.7 (Z), 129.2 (E), 114.8 (E), 114.4 (Z), 113.8 (Z), 110.5 (E), 105.4 (E), 103.9 (Z), 60.9 (Z), 56.9 (E), 56.7 (E), 56.6 (Z), 56.4 (E), 56.2 (Z), 30.5 (hepta, E), 29.3 (hepta, Z); HRMS (ESI): M/Z: Calcd for C13H16O4D3Na [M+Na]+ 262.1129, Found 262.1125; IR (thin film, cm⁻¹): 3821, 3752, 1700, 1652, 1635, 706, 693.

References
VII. NMR Spectra

**1H NMR Spectrum of Compound 7I (CDCl₃, 600 MHz)**

**13C NMR Spectrum of Compound 7I (CDCl₃, 150 MHz)**
$^1$H NMR Spectrum of Compound 1 (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 1 (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 1a (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 1a (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 1b (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 1b (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 1c (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 1c (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound $1d$ (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound $1d$ (CDCl$_3$, 150 MHz)
$\text{H NMR Spectrum of Compound 1e (CDCl}_3$, 600 MHz$)$

$\text{13C NMR Spectrum of Compound 1e (CDCl}_3$, 150 MHz$)$
$^1$H NMR Spectrum of Compound 1f (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 1f (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 1g (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 1g (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound $1h$ (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound $1h$ (CDCl$_3$, 150 MHz)
$^{1}H$ NMR Spectrum of Compound 1i (CDCl$_3$, 600 MHz)

$^{13}C$ NMR Spectrum of Compound 1i (CDCl$_3$, 150 MHz)
1H NMR Spectrum of Compound 1j (CDCl₃, 600 MHz)

13C NMR Spectrum of Compound 1j (CDCl₃, 150 MHz)
$^1$H NMR Spectrum of Compound 1k (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 1k (CDCl$_3$, 150 MHz)
$^{1}H$ NMR Spectrum of Compound 5 (CDCl$_3$, 600 MHz)

$^{13}C$ NMR Spectrum of Compound 5 (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 5a (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5a (CDCl$_3$, 150 MHz)
1H NMR Spectrum of Compound 5b (CDCl₃, 600 MHz)

2H NMR Spectrum of Compound 5b in CDCl₃

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$^{13}$C NMR Spectrum of Compound 5b (CDCl$_3$, 150 MHz)

Dept135 $^{13}$C NMR Spectrum of Compound 5b (CDCl$_3$, 150 MHz)

H-H COSY Spectrum of Compound 5b (CDCl$_3$, 600 MHz)
HSQC Spectrum of Compound 5b (CDCl₃, 600 MHz)

HMBC Spectrum of Compound 5b (CDCl₃, 600 MHz)
HMBC Spectrum of Compound 5b (CDCl₃, 600 MHz)

NOESEY Spectrum of Compound 5b (CDCl₃, 600 MHz)
$^1$H NMR Spectrum of Compound 5c (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5c (CDCl$_3$, 150 MHz)
$^{1}$H NMR Spectrum of Compound 5d (CDCl$_3$, 600 MHz)
$^{13}$C NMR Spectrum of Compound 5d (CDCl$_3$, 150 MHz)

$^1$H NMR Spectrum of Compound 5e (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5e (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 5f (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5f (CDCl$_3$, 150 MHz)
1H NMR Spectrum of Compound 5g (CDCl3, 600 MHz)

13C NMR Spectrum of Compound 5g (CDCl3, 150 MHz)
1H NMR Spectrum of Compound 5h (CDCl₃, 600 MHz)

13C NMR Spectrum of Compound 5h (CDCl₃, 150 MHz)
H NMR Spectrum of Compound 5i (CDCl₃, 600 MHz)

13C NMR Spectrum of Compound 5i (CDCl₃, 150 MHz)
$^1$H NMR Spectrum of Compound 5j (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5j (CDCl$_3$, 150 MHz)
$^{1}$H NMR Spectrum of Compound 5k (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5k (CDCl$_3$, 150 MHz)
**1H NMR Spectrum of Compound 5l (CDCl₃, 600 MHz)**

**13C NMR Spectrum of Compound 5l (CDCl₃, 150 MHz)**
$^1$H NMR Spectrum of Compound 5m (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5m (CDCl$_3$, 150 MHz)
\(^1\)H NMR Spectrum of Compound 5n (CDCl₃, 600 MHz)

\(^{13}\)C NMR Spectrum of Compound 5n (CDCl₃, 150 MHz)
$^{1}H$ NMR Spectrum of Compound 5o (CDCl$_3$, 600 MHz)

$^{13}C$ NMR Spectrum of Compound 5o (CDCl$_3$, 150 MHz)
1H NMR Spectrum of Compound 5p (CDCl$_3$, 600 MHz)

$^1$H NMR Spectrum of Compound 5p (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5p (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 5q (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5q (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 5r (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5r (CDCl$_3$, 150 MHz)
**1H NMR Spectrum of Compound 3 (CDCl₃, 600 MHz)**

**13C NMR Spectrum of Compound 3 (CDCl₃, 150 MHz)**
$^1$H NMR Spectrum of Compound 6 (DMSO-$d_6$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 6 (DMSO-$d_6$, 150 MHz)
$^{1}H$ NMR Spectrum of Compound 6c (CD$_3$OD, 600 MHz)

$^{13}C$ NMR Spectrum of Compound 6c (CD$_3$OD, 150 MHz)
$^1$H NMR Spectrum of Compound 6c-D (CD$_3$OD, 600 MHz)

$^{13}$C NMR G2-M-4-1-D in MeOD
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$^1$H NMR Spectrum of Compound 6c-D (CD$_3$OD, 600 MHz)
$^1$H NMR Spectrum of Compound $5c$-D (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound $5c$-D (CDCl$_3$, 150 MHz)
$^{1}$H NMR Spectrum of Compound 5c-D-1 (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 5c-D-1 (CDCl$_3$, 150 MHz)
\(^1\)H NMR Spectrum of Compound 5c-D-2 (CDCl\(_3\), 600 MHz)

\(^{13}\)C NMR Spectrum of Compound 5c-D-2 (CDCl\(_3\), 150 MHz)