Supporting Information

A gold-catalyzed cycloisomerization/aerobic oxidation cascade strategy for 2-aryl indenones from 1,5-enynes

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1. 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 Dynamic adsorbents 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.

2. Preparation of 7 and Characterization Data

To a solution of compound 9[21] (1 mmol, 287 mg), (PPh$_3$)$_2$PdCl$_2$ (0.05 mmol, 35.1 mg), CuI (0.1 mmol, 19.1 mg) and Et$_3$N (5 mmol, 0.7 mL) in dry THF was added trimethylsilylacetylene (1.2 mmol, 0.17 mL). The resulting mixture was stirred at room temperature and the reaction progress was monitored by TLC. When all of compound 9 had been consumed, the reaction mixture was quenched by saturated aq. NH$_4$Cl (10 mL) and extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo.

The crude product obtained above was dissolved in MeOH (10 mL) and K$_2$CO$_3$ (3 mmol, 0.41 g) was added. The reaction mixture was stirred at room temperature for 2 h and quenched by saturated aq. NH$_4$Cl (10 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by a flash column chromatography (petroleum ether:ethyl acetate, 20:1, v/v) on silica gel to afford the desired product 7 as a yellowish oil (139 mg) with a yield of 75%; $^1$H NMR (600 MHz, CDCl$_3$) δ = 6.94 (s, 1H), 6.69 (s, 1H), 3.90 (s, 3H), 3.87 (s, 2H), 3.59 (s, 1H), 2.39 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 161.3, 141.3, 134.1, 121.1, 117.6, 111.3, 107.9, 87.0, 77.3, 56.2, 22.7, 22.1; HRMS (ESI): m/z: Calcd for C$_{12}$H$_{12}$ON [M+H]$^+$ 186.0913, Found 186.0916; IR (thin film, cm$^{-1}$): 3445, 3254, 2924, 1608, 1575, 1303, 1147, 1079, 832.

3. General Preparation of 6-6s and Characterization Data
To a solution of the corresponding 2-bromobenzaldehyde \(8-8s\) (1 mmol), 
\((\text{PPh}_3)_2\text{PdCl}_2\) (0.05 mmol, 35.1 mg), CuI (0.1 mmol, 19.1 mg) and \(\text{Et}_3\text{N}\) (5 mmol, 0.7 mL) in dry THF was added the appropriate acetylene (1.2 mmol). The resulting mixture was heated at 50 \(^\circ\text{C}\) for 12 h. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with \(\text{CH}_2\text{Cl}_2\) (3 × 20 mL). The combined organic layer was washed with brine, dried over anhydrous \(\text{Na}_2\text{SO}_4\), and concentrated \textit{in vacuo}. The residue was purified by column chromatography on silica gel to afford the desired products \(6-6s\).

Spectral data were consistent with those reported in the literature.\(^{[1]}\)

\(\text{N}-(4-(2\text{-formylphenyl})\text{ethynyl} \text{phenyl})\text{acetamide}(6c)\)

TLC (petroleum ether:ethyl acetate, 3:1, v/v): \(R_f=0.3\); yellowish solid, Mp 202–203 \(^\circ\text{C}\); 76%; \(^1\text{H}\) NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) 10.50 (s, 1H), 10.18 (s, 1H), 7.88 (d, \(J = 7.6\) Hz, 1H), 7.73 – 7.72 (m, 2H), 7.67 (d, \(J = 8.6\) Hz, 2H), 7.59 – 7.57 (m, 3H), 2.07 (s, 3H); \(^{13}\text{C}\) NMR (150 MHz, DMSO-\(d_6\)) \(\delta\) 191.37, 168.67, 140.34, 135.29, 134.36, 133.17, 132.43, 128.98, 127.61, 125.58, 118.81, 115.65, 96.16, 84.46, 24.15; HRMS (ESI): \(m/z\): Calcd for \(\text{C}_{17}\text{H}_{14}\text{NO}_2\) 264.1019 [M+H]\(^+\), Found 264.1021; IR (thin film, cm\(^{-1}\)): 3321, 2212, 1685, 1590, 1526, 1307, 835, 767.

\(\text{N}-(3-(2\text{-formylphenyl})\text{ethynyl} \text{phenyl})\text{acetamide}(6d)\)

TLC (petroleum ether:ethyl acetate, 3:1, v/v): \(R_f=0.3\); yellowish solid, Mp 168–169 \(^\circ\text{C}\); 85%; \(^1\text{H}\) NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) 10.48 (s, 1H), 10.10 (s, 1H), 7.92 (s, 1H), 7.90 (d, \(J = 7.6\) Hz, 1H), 7.78 – 7.71 (m, 2H), 7.63 – 7.57 (m, 2H), 7.38 (t, \(J = 7.9\) Hz, 1H), 7.32 (d, \(J = 7.6\) Hz, 1H), 2.06 (s, 3H); \(^{13}\text{C}\) NMR (150 MHz, DMSO-\(d_6\)) \(\delta\) 191.19, 168.62, 139.63, 135.51, 134.35, 133.38, 129.33, 127.86, 126.26, 124.98, 121.89, 121.57, 120.00, 95.67, 85.02, 24.06; HRMS (ESI): \(m/z\): Calcd for \(\text{C}_{17}\text{H}_{14}\text{NO}_2\) 264.1019, Found 264.1014; IR (thin film, cm\(^{-1}\)): 3425, 3255, 3080, 2208, 1699, 1591, 1425, 1264, 883, 757.

\(\text{Ethyl 2}-(4-(2\text{-formylphenyl})\text{ethynyl} \text{phenyl})\text{acetate}(6e)\)
TLC (petroleum ether:ethyl acetate, 20:1, v/v): Rf=0.3; yellowish oil, 80%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 10.64 (d, $J = 0.6$ Hz, 1H), 7.95 (dd, $J = 7.8$, 0.9 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.59 (td, $J = 7.6$, 1.4 Hz, 1H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.31 (d, $J = 8.2$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.64 (s, 2H), 1.26 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 191.89, 171.19, 135.96, 135.41, 133.95, 133.37, 133.37, 131.99, 129.67, 128.77, 127.41, 127.02, 121.25, 96.24, 85.14, 77.37, 77.16, 76.95, 61.22, 41.48, 14.31; HRMS (ESI): m/z: Calcd for C$_{18}$H$_{15}$O$_3$ [M+H]$^+$ 279.1016, Found 279.1023; IR (thin film, cm$^{-1}$): 3425, 2923, 1732, 1631, 1387, 1008, 832, 760, 703.

2-((4-Chlorophenyl)ethynyl)-5-fluorobenzaldehyde (6m)
TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.3; yellowish solid, Mp 130–131 °C; 85%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 10.50 (s, 1H), 7.95 (dd, $J = 8.7$ Hz, 5.9 Hz, 1H), 7.47 (d, $J = 8.6$ Hz, 2H), 7.35 (d, $J = 8.6$ Hz, 2H), 7.28 (dd, $J = 8.9$ Hz, 2.5 Hz, 1H), 7.19 – 7.06 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 189.8 (d, $J = 8.1$ Hz), 165.7 (d, $J = 257.0$ Hz), 135.7, 133.1, 133.1, 132.7 (d, $J = 2.6$ Hz), 130.4 (d, $J = 10.2$ Hz), 129.1, 129.1, 128.9 (d, $J = 11.0$ Hz), 120.4, 119.8 (d, $J = 23.6$ Hz), 116.8 (d, $J = 22.1$ Hz), 96.2, 84.8 (d, $J = 2.9$ Hz); HRMS (ESI): m/z: Calcd for C$_{15}$H$_9$OCIF [M+H]$^+$ 259.0320, Found 259.0315; IR (thin film, cm$^{-1}$): 3422, 3038, 2922, 2210, 1694, 1602, 1568, 1491, 1401, 1207, 869, 820, 649.

1-((4-Chlorophenyl)ethynyl)-2-naphthaldehyde (6r)
TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.3; yellowish solid, Mp 130–131 °C; 83%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 10.83 (s, 1H), 8.58 – 8.51 (m, 1H), 7.97 (d, $J = 8.6$ Hz, 1H), 7.92 – 7.84 (m, 2H), 7.70 – 7.65 (m, 2H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 192.0, 135.9, 135.6, 134.4, 133.1, 133.1, 129.6, 129.3, 129.2, 129.2, 128.7, 127.9, 127.2, 127.1, 122.2, 120.9, 101.2, 84.0; HRMS (ESI): m/z: Calcd for C$_{19}$H$_{11}$OClNa [M+Na]$^+$ 313.0391, Found 313.0398; IR (thin film, cm$^{-1}$): 3423, 3038, 2922, 2210, 1694, 1602, 1568, 1491, 1401, 1207, 869, 820, 649.
2-(2-(2-Formyl-3-methoxyphenyl)ethynyl)-3-methoxy-5-methylphenyl)acetonitrile (6s)

TLC (petroleum ether:ethyl acetate, 5:1, v/v): $R_f = 0.3$; yellowish oil, 75%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 10.56$ (s, 1H), 7.39 ($J = 8.1$ Hz, 1H), 7.18 (d, $J = 6.7$ Hz, 1H), 6.88 (d, $J = 6.1$ Hz, 2H), 6.61 (s, 1H), 4.07 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta = 189.8$, 161.7, 161.1, 141.4, 134.5, 134.2, 126.6, 125.3, 124.7, 121.2, 118.2, 111.7, 111.2, 109.0, 97.1, 88.8, 56.2, 56.1, 22.7, 22.2. HRMS (ESI): $m/z$: Calcld for C$_{20}$H$_{18}$O$_3$N [M+H]$^+$ 320.1281, Found 320.1280; IR (thin film, cm$^{-1}$): 3395, 2922, 2851, 2195, 1687, 1566, 1465, 1258, 1065, 793, 542.

4. General Preparation of 1-1s and Characterization Data

To a suspension of (methoxymethyl)triphenylphosphonium chloride (2 mmol, 685.6 mg) in anhydrous THF was added 1 M solution of KHMDS in anhydrous THF (1.8 mmol, 1.8 mL) at $-78 \, ^\circ\text{C}$. The mixture was stirred at $-78 \, ^\circ\text{C}$ for 0.5 h, then a solution of 2-phenylethynyl benzaldehyde 6-6s (1 mmol) in anhydrous THF was added. The reaction was allowed to warm up to 0 $^\circ\text{C}$ 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 triphenylphosphine oxide. After evaporation to dryness, the crude vinyl ether was purified by silica gel chromatography eluting with petroleum ether/ethyl acetate to yield the products 1-1s.

Spectral data were consistent with those reported in the literature.$^{[3]}$

1-(2-Methoxyvinyl)-2-(phenylethynyl)benzene (1)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): $R_f=0.3$; yellowish oil, (1:0.38 $E/Z$), 75%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 8.09$ (d, $J = 8.0$ Hz, 1H, Z), 7.52 – 7.46 (m, 2H,
Z + 2H, E), 7.45 (d, J = 7.9 Hz, 1H, E), 7.32 – 7.20 (m, 5H, Z + 4H, E), 7.15 (t, J = 7.6 Hz, 1H, E), 7.12 (d, J = 13.0 Hz, 1H, E), 7.05 (q, J = 7.2 Hz, 1H, Z + 1H, E), 6.32 (d, J = 13.0 Hz, 1H, E), 6.18 (d, J = 7.2 Hz, 1H, Z), 5.87 (d, J = 7.2 Hz, 1H, Z), 3.68 (s, 1H, Z), 3.65 (s, 3H, E); 13C NMR (150 MHz, CDCl3) δ = 150.3 (E), 149.2 (Z), 138.2 (E), 137.4 (Z), 135.2 (E), 131.6 (Z), 131.5 (E), 128.7 (Z), 128.6 (E), 128.5 (E), 128.4 (E), 128.3 (Z), 128.3 (Z), 128.2 (Z), 125.5 (Z), 125.5 (E), 123.7 (E), 123.6 (Z), 123.6 (E), 120.9 (Z), 120.6 (E), 103.7 (E), 103.3 (Z), 93.8 (E), 93.6 (Z), 88.5 (E), 60.8 (Z), 56.5 (E); HRMS (ESI): m/z: Calcd for C17H15O [M+H]+ 265.1117, Found 265.1125; IR (thin film, cm⁻¹): 3430, 2850, 1697, 1493, 1446, 1124, 757, 690.

1-(4-Methoxyphenyl)ethynyl)-2-(2-methoxyvinyl)benzene (1a)
TLC (petroleum ether:ethyl acetate, 30:1, v/v): Rf=0.25; yellowish oil (1:0.56 E/Z), 72%; 1H NMR (600 MHz, CDCl3) δ = 8.17 (d, J = 8.0 Hz, 1H, Z), 7.57 – 7.47 (m, 3H, Z + 3H, E), 7.39 (t, J = 8.0 Hz, 1H, E), 7.31 (t, J = 7.6 Hz, 1H, Z), 7.25 (s, 1H, E), 7.22 (d, J = 13.1 Hz, 1H, E), 7.15 (dt, J = 11.1 Hz, 5.5 Hz, 1H, Z + 1H, E), 6.94 – 6.88 (m, 2H, Z + 2H, E), 6.41 (d, J = 13.0 Hz, 1H, E), 6.29 (d, J = 7.2 Hz, 1H, Z), 5.96 (d, J = 7.2 Hz, 1H, Z), 3.83 (s, 3H, E), 3.83 (s, 3H, Z), 3.81 (s, 3H, Z), 3.77 (s, 3H, E); 13C NMR (150 MHz, CDCl3) δ = 159.7 (E), 159.6 (Z), 150.2 (E), 149.1 (Z), 137.9 (E), 137.14 (Z), 133.0 (Z), 132.9 (E), 132.9 (E), 132.4 (E), 132.0 (Z), 128.6 (Z), 128.3 (E), 128.0 (Z), 125.5 (Z), 125.5 (E), 123.7 (E), 121.3 (Z), 121.0 (E), 115.8 (Z), 115.7 (E), 114.1 (E), 114.1 (E), 114.1 (Z), 110.3 (E), 103.4 (Z), 93.8 (E), 93.6 (Z), 87.3 (Z), 87.2 (E), 60.9 (Z), 56.6 (E), 55.3 (E + Z); HRMS (ESI): m/z: Calcd for C17H17O2 [M+H]+ 265.1223, Found 265.1249; IR (thin film, cm⁻¹): 3426, 2934, 1638, 1606, 1249, 832, 755.

1-(4-Chlorophenyl)ethynyl)-2-(2-methoxyvinyl)benzene (1b)
TLC (petroleum ether:ethyl acetate, 10:1, v/v): Rf=0.3; yellowish oil (1:0.60 E/Z), 72%; 1H NMR (600 MHz, CDCl3) δ = 8.00 (d, J = 8.0 Hz, 1H, Z), 7.36 (t, J = 7.3 Hz, 1H, Z + 1H, E), 7.32 (dd, J = 8.4 Hz, 3.6 Hz, 2H, Z + 2H, E), 7.23 (d, J = 7.9 Hz, 1H, E), 7.20 – 7.14 (m, 2H, E + 3H, Z), 7.10 (t, J = 7.5 Hz, 1H, E), 7.03 (d, J = 13.0 Hz, 1H, E), 6.99 (dt, J = 11.7 Hz, 5.9 Hz, 1H, Z + 1H, E), 6.20 (d, J = 13.0 Hz, 1H, E), 6.12 (d, J = 7.2 Hz, 1H, Z), 5.74 (d, J = 7.2 Hz, 1H, Z), 3.64 (s, 3H, Z), 3.59 (s, 3H, E); 13C NMR
(150 MHz, CDCl$_3$) $\delta$ = 150.4 (E), 149.3 (Z), 138.3 (E), 137.4 (Z), 134.3 (E), 134.2 (Z), 132.8 (Z), 132.8 (E), 132.7 (E), 132.7 (E), 132.2 (Z), 128.8 (E), 128.8 (E), 128.8 (E), 128.7 (Z), 128.7 (Z), 128.6, (Z) 125.6 (Z), 125.5 (E), 123.8 (E), 122.2 (Z), 122.1 (E), 120.6 (Z), 120.3 (E), 103.6 (E), 103.2 (Z), 92.6 (E), 92.4 (Z), 89.6 (Z), 89.5 (E), 60.9 (Z), 56.7 (E); HRMS (ESI): m/z: Calcd for C$_{17}$H$_{14}$ClO [M+H]$^+$ 269.0728, Found 269.0742; IR (thin film, cm$^{-1}$): 3434, 2932, 1727, 1638, 1492, 1091, 828, 758.

**N-(4-((2-(2-Methoxyvinyl)phenyl)ethynyl)phenyl)acetamide (1c)**

TLC (petroleum ether:ethyl acetate, 2:1, v/v): R$_f$=0.3; yellowish solid, Mp 137–138 °C; (1/0.3 E/Z), 76%; $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 10.14 (s, 1H, E+ 1H, Z), 8.02 (d, $J$ = 7.8 Hz, 1H, Z), 7.66 – 7.64 (m, 1H, E + 1H, Z), 7.55 (d, $J$ = 7.9 Hz, 1H, Z), 7.50 – 7.47 (m, 2H, E + 2H, Z), 7.46 – 7.43 (m, 1H, E), 7.41 (d, $J$ = 12.9 Hz, 1H, E), 7.33 – 7.29 (m, 1H, Z), 7.29 – 7.25 (m, 1H, E), 7.16 – 7.13 (m, 1H, E + 1H, Z), 6.48 (d, $J$ = 7.2 Hz, 1H, Z), 6.25 (d, $J$ = 12.9 Hz, 1H, E), 5.75 (d, $J$ = 7.2 Hz, 1H, Z), 3.79 (s, 2H, Z), 3.71 (s, 2H, E), 2.07 (s, 3H, E + 3H, Z); $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$ 168.57 (E), 151.08 (E), 150.42 (Z), 139.73 (E), 137.61 (E), 136.88 (Z), 131.98 (Z), 131.78 (Z), 128.67 (E), 128.38 (Z), 128.14 (Z), 125.53 (Z), 125.50 (E), 123.51 (E), 119.90 (Z), 119.53 (E), 118.91 (E), 118.84 (Z), 116.55 (E), 102.66 (E), 101.67 (Z), 93.80 (E), 93.62 (Z), 87.34 (Z), 87.30 (E), 60.89 (Z), 56.62 (E), 24.12 (E); HRMS (ESI): m/z: Calcd for C$_{19}$H$_{18}$NO$_2$ [M+H]$^+$ 292.1332, Found 292.1335; IR (thin film, cm$^{-1}$): 3424, 3247, 1665, 1596, 1367, 1239, 1129, 836, 753.

**N-(4-((2-(2-Methoxyvinyl)phenyl)ethynyl)phenyl)acetamide (1d)**

TLC (petroleum ether:ethyl acetate, 2:1, v/v): R$_f$=0.3; yellowish solid, Mp 129–130 °C; 75%; $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 10.08 (s, 1H), 7.90 (s, 1H), 7.57 (d, $J$ = 8.0 Hz, 1H), 7.54 (dd, $J$ = 8.2, 1.0 Hz, 1H), 7.49 (dd, $J$ = 7.7, 1.0 Hz, 1H), 7.44 (d, $J$ = 12.9 Hz, 1H), 7.36 (t, $J$ = 7.9 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.23 (d, $J$ = 7.7 Hz, 1H), 7.17 (td, $J$ = 7.6, 1.0 Hz, 1H), 6.26 (d, $J$ = 12.9 Hz, 1H), 3.73 (s, 3H), 2.07 (s, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$ 168.61, 151.24, 139.66, 137.87, 132.11, 129.31, 129.00, 125.75, 125.55, 123.55, 122.67, 121.20, 119.28, 119.12, 102.97, 93.62, 87.90, 56.67, 24.09; HRMS (ESI): m/z: Calcd for C$_{19}$H$_{18}$NO$_2$ [M+H]$^+$ 292.1332, Found 292.1331; IR (thin film, cm$^{-1}$): 3293, 3137, 2930, 1668, 1637, 1427, 1235, 1154, 753.
Ethyl 2-(4-((2-(2-methoxyvinyl)phenyl)ethynyl)phenyl)acetate (1e)

TLC (petroleum ether:ethyl acetate, 20:1, v/v): Rf = 0.3; yellowish oil, (1/0.8 E/Z) 91%;

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 7.5$ Hz, 1H, Z), 7.51 – 7.48 (m, 3H, E + 3H, Z), 7.37 (d, $J = 7.9$ Hz, 1H, Z), 7.30 – 7.26 (m, 2H, E + 3H, Z), 7.23 (d, $J = 0.9$ Hz, 1H, E), 7.18 (d, $J = 13.0$ Hz, 1H, E), 7.12 (dd, $J = 7.6$, 3.8 Hz, 1H, E + 1H, Z), 6.34 (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), 4.16 (q, $J = 7.1$, 2H, E), 3.81 (s, 3H, Z), 3.75 (s, 3H, E), 3.63 (s, 2H, E + 2H, Z), 1.29 – 1.24 (m, 3H, E + 3H, Z); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.24 (E), 171.23 (Z), 150.21 (E), 149.10 (Z), 148.5 (E), 134.31 (E), 134.22 (Z), 132.53 (E), 132.10 (Z), 131.68 (Z), 131.63 (E), 129.39 (E), 129.31 (Z), 128.57 (E), 128.30 (Z), 128.46 (E), 123.62 (E), 122.38 (Z), 122.30 (E), 120.81 (Z), 120.52 (E), 103.53 (E), 103.19 (Z), 93.45 (E), 93.21 (Z), 88.61 (Z), 88.48 (E), 61.04 (E), 61.02 (Z), 56.54 (E), 41.36 (Z), 41.34 (E), 14.20 (E); HRMS (ESI): m/z: Calcd for C$_{20}$H$_{19}$O$_3$ [M+H]$^+$ 307.1329, Found 307.1327; IR (thin film, cm$^{-1}$): 3438, 2981, 2935, 1732, 1639, 1237, 1031, 937, 755.

1-(2-Methoxyvinyl)-4-methyl-2-(phenylethynyl)benzene (1f)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf = 0.2; yellowish oil (1:0.3 E/Z), 72%;

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 8.14 (d, $J = 8.1$ Hz, 1H, Z), 7.67 – 7.61 (m, 2H, Z + 2H, E), 7.46 – 7.38 (m, 4H, Z + 4H, E), 7.35 (d, $J = 8.1$ Hz, 1H, E), 7.24 (d, $J = 13.0$ Hz, 1H, E), 7.20 (dd, $J = 8.2$ Hz, 1.3 Hz, 1H, Z), 7.12 (dd, $J = 8.1$ Hz, 1.2 Hz, 1H, E), 6.45 (d, $J = 13.0$ Hz, 1H, E), 6.29 (d, $J = 7.2$ Hz, 1H, Z), 6.00 (d, $J = 7.2$ Hz, 1H, Z), 3.82 (s, 3H, Z), 3.80 (s, 3H, E), 2.40 (s, 3H, Z), 2.38 (s, 3H, E); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 149.6 (E), 148.5 (Z), 135.3 (E), 135.1 (Z), 134.6 (Z), 132.9 (E), 132.5 (Z), 131.5 (Z), 131.5 (Z), 131.5 (E), 131.5 (E), 129.7 (E), 129.4 (Z), 128.6 (Z), 128.4 (E), 128.4 (E), 128.2 (E), 128.2 (E), 128.1 (Z), 123.7 (Z), 123.6 (E), 120.7 (Z), 120.4 (E), 103.5 (E), 103.2 (E), 93.4 (E), 93.2 (Z), 88.8 (Z), 88.7 (E), 60.7 (Z), 56.4 (E), 21.0 (Z), 20.8 (E); HRMS (ESI): m/z: Calcd for C$_{18}$H$_{17}$O [M+H]$^+$ 249.1274, Found 249.1277; IR (thin film, cm$^{-1}$): 3438, 2931, 1639, 1237, 1103, 756, 690.
2-((4-Methoxyphenyl)ethynyl)-1-(2-methoxyvinyl)-4-methylbenzene (1g)
TLC (petroleum ether:ethyl acetate, 30:1, v/v): Rf=0.25; yellowish oil (1:0.46 E/Z), 72%;
1H NMR (600 MHz, CDCl₃) δ = 8.01 (d, J = 8.1 Hz, 1H, Z), 7.48 (dd, J = 8.9 Hz, 2.5 Hz, 2H, Z + 2H, E), 7.32 (s, 1H, E), 7.27 (d, J = 8.1 Hz, 1H, E), 7.15 (d, J = 13.0 Hz, 1H, E), 7.10 (d, J = 8.1 Hz, 1H, Z), 7.04 (d, J = 8.0 Hz, 1H, E), 6.94 – 6.82 (m, 3H, Z + 2H, E), 6.34 (d, J = 13.0 Hz, 1H, E), 6.22 (d, J = 7.2 Hz, 1H, Z), 5.88 (d, J = 7.1 Hz, 1H, Z), 3.83 (s, 3H, E), 3.82 (s, 3H, Z), 3.79 (s, 3H, Z), 3.74 (s, 3H, E), 2.32 (s, 3H, Z), 2.31 (s, 3H, E); 13C NMR (150 MHz, CDCl₃) δ = 159.7 (E), 159.6 (Z), 149.6 (E), 148.4 (Z), 135.2 (Z), 135.1 (E), 135.1 (E), 134.4 (Z), 133.0 (Z), 133.0 (Z), 133.0 (E), 133.0 (E), 132.8 (E), 132.4 (Z), 129.4 (E), 129.1 (Z), 128.6 (Z), 123.7 (E), 121.2 (Z), 120.8 (E), 115.9 (Z), 115.8 (E), 114.1 (E), 114.1 (E), 114.1 (Z), 114.1 (Z), 103.7 (E), 103.3 (Z), 93.4 (E), 93.2 (Z), 87.4 (Z), 87.3 (E), 68.1 (Z), 60.8 (Z), 56.6 (E), 55.4 (E), 21.1 (Z), 20.9 (E); HRMS (ESI): m/z: Calcd for C₁₉H₁₉O₂ [M+H]+ 279.1380, Found 279.1371; IR (thin film, cm⁻¹): 3441, 2921, 2851, 1637, 1512, 1384, 1249, 1161, 830, 619.

4-Fluoro-2-(2-methoxyvinyl)-1-(phenylethynyl)benzene (1I)
TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.3; yellowish oil (1:0.5 E/Z), 75%;
1H NMR (600 MHz, CDCl₃) δ = 8.19 (dd, J = 8.8 Hz, 6.0 Hz, 1H, Z), 7.61 (m, 6H, Z), 7.41 (m, 5H, E), 7.34 (dd, J = 8.7 Hz, 5.6 Hz, 1H, E), 7.30 – 7.24 (m, 1H, E), 7.15 (d, J = 13.0 Hz, 1H, E), 7.07 (td, J = 8.6 Hz, 2.7 Hz, 1H, Z), 7.00 (td, J = 8.5 Hz, 2.7 Hz, 1H, E), 6.37 (d, J = 13.0 Hz, 1H, E), 6.28 (d, J = 7.2 Hz, 1H, Z), 5.93 (d, J = 7.2 Hz, 1H, Z), 3.81 (s, 3H, Z), 3.77 (s, 3H, E); 13C NMR (150 MHz, CDCl₃) δ = 160.6 (d, J = 254 Hz, E), 159.9 (d, J = 254 Hz, Z), 150.0 (d, J = 1.4 Hz, E), 148.7 (d, J = 2.0 Hz, Z), 134.5 (d, J = 3.2 Hz), 133.8 (d, J = 3.2 Hz), 131.6 (Z), 131.6 (Z), 131.6 (E), 131.6 (E), 131.5 (d, J = 9.5 Hz), 130.3 (d, J = 8.1 Hz), 128.6 (E), 128.5 (Z), 128.5 (E), 128.5 (Z), 128.4 (Z), 125.3 (d, J = 8.2 Hz), 123.1 (Z), 123.08 (E), 122.5 (d, J = 9.2 Hz, Z), 121.9 (d, J = 9.2 Hz, E), 118.6 (d, J = 22.7 Hz, E), 118.3 (d, J = 22.8 Hz, Z), 116.1 (d, J = 21.7 Hz, E), 115.7 (d, J = 21.0 Hz, Z), 102.8 (E), 102.3 (Z), 94.6 (E), 94.4 (Z), 87.5 (d, J = 3.2 Hz, Z), 87.4 (d, J = 3.2 Hz, E), 60.8 (Z), 56.5 (E); HRMS (ESI): m/z: Calcd for C₁₇H₁₄FO [M+H]+ 253.1023, Found 253.1036; IR (thin film, cm⁻¹): 3447, 2938, 1696, 1604, 1573, 1497, 1217, 757, 690.
1-((4-Chlorophenyl)ethynyl)-4-fluoro-2-(2-methoxyvinyl)benzene (1m)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.3; yellowish oil (0.6:1 E/Z), 74%; 
^1H NMR (600 MHz, CDCl_3) δ = 8.18 (dd, J = 8.8 Hz, 6.0 Hz, 1H, Z), 7.52 – 7.46 (m, 2H, Z + 2H, E), 7.38 – 7.34 (m, 2H, Z + 2H, E), 7.32 (dd, J = 8.7 Hz, 5.6 Hz, 1H, E), 7.24 (m, 1H, Z + 1H, E), 7.12 (d, J = 13.0 Hz, 1H, E), 7.06 (td, J = 8.6 Hz, 2.7 Hz, 1H, Z), 6.99 (td, J = 8.5 Hz, 2.7 Hz, 1H, E), 6.31 (d, J = 13.0 Hz, 1H, E), 6.28 (d, J = 7.1 Hz, 1H, Z), 5.87 (d, J = 7.1 Hz, 1H, Z), 3.81 (s, 3H, Z), 3.76 (s, 3H, E); ^13C NMR (150 MHz, CDCl_3) δ = 160.5 (d, J = 243.0 Hz, E), 159.9 (d, J = 243.0 Hz, Z), 150.1 (d, J = 1.3 Hz, E), 148.8 (d, J = 1.9 Hz, Z), 137.3 (d, J = 11.2 Hz, Z), 134.58 (E, 134.49 (Z), 134.49 (Z), 133.8 (E), 133.8 (d, J = 3.2 Hz, Z), 133.7 (E), 132.77 (Z), 132.72 (E), 130.4 (d, J = 8.1 Hz, Z), 128.80 (E), 128.74 (Z), 128.5 (d, J = 6.8 Hz, E), 125.3 (d, J = 8.2 Hz, E), 122.1 (d, J = 9.1 Hz, Z), 121.58 (Z), 121.54 (E), 121.52 (Z), 118.59 (d, J = 22.7 Hz, E), 118.3 (d, J = 22.7 Hz, Z), 116.3 (d, J = 21.7 Hz, E), 115.9 (d, J = 21.7 Hz, Z), 102.72 (E), 102.21 (Z), 93.33 (E), 93.13 (Z), 88.5 (d, J = 3.1 Hz, Z), 88.4 (d, J = 3.1 Hz, E), 60.78 (Z), 56.56 (E); HRMS (ESI): m/z: Calcd for C_{17}H_{14}ClOClF [M+H]^+ 287.0633, Found 287.0666; IR (thin film, cm^{-1}): 3677, 2962, 1640, 1491, 1240, 1089, 930, 824, 694.

4-Fluoro-1-(2-methoxyvinyl)-2-(phenylethynyl)benzene (1n)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.2; yellowish oil (1:0.44 E/Z), 72%; ^1H NMR (600 MHz, CDCl_3) δ = 8.13 (dd, J = 8.9 Hz, 6.0 Hz, 1H, Z), 7.59 – 7.55 (m, 2H, Z + 2H, E), 7.40 – 7.35 (m, 4H, Z + 3H, E), 7.32 (dd, J = 8.7 Hz, 5.6 Hz, 1H, E), 7.22 (dd, J = 9.2 Hz, 2.8 Hz, 1H, E), 7.12 (d, J = 13.0 Hz, 1H, E), 7.02 (td, J = 8.6 Hz, 2.8 Hz, 1H, Z), 6.98 (td, J = 8.5 Hz, 2.8 Hz, 1H, E), 6.32 (d, J = 13.0 Hz, 1H, E), 6.26 (d, J = 7.2 Hz, 1H, Z), 5.87 (d, J = 7.2 Hz, 1H, Z), 3.81 (s, 3H, Z), 3.75 (s, 3H, E); ^13C NMR (150 MHz, CDCl_3) δ = 160.7 (d, J = 254 Hz, E), 160.0 (d, J = 254 Hz, Z), 150.05 (d, J = 1.5 Hz, E), 148.7 (d, J = 2.1 Hz, Z), 134.5 (d, J = 3.2 Hz, E), 133.9 (E), 133.8 (E), 133.75 (d, J = 3.2 Hz), 131.7 (Z), 131.7 (Z), 131.6 (E), 131.6 (E), 130.3 (E), 128.8 (Z), 128.7 (Z), 128.6 (Z), 128.6 (E), 128.6 (E), 128.5 (E), 125.3 (d, J = 8.2 Hz, E), 123.2 (Z), 123.1 (E), 122.5 (d, J = 9.3 Hz, Z), 122.0 (d, J = 9.3 Hz, E), 118.7 (d, J = 22.7 Hz, E), 118.3 (d, J = 22.8 Hz, Z), 116.2 (d, J = 21.7 Hz, E), 115.7 (d, J = 21.1 Hz, Z), 102.9 (E), 102.4 (Z), 94.6 (E), 94.3 (Z), 87.5 (d, J = 3.3 Hz, Z), 87.4 (d, J = 3.2 Hz, E), 60.9 (Z), 56.6 (E); HRMS (ESI): m/z: Calcd for C_{17}H_{14}FO
4-Fluoro-2-((4-methoxyphenyl)ethyl)-1-(2-methoxyvinyl)benzene (1o)
TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rr=0.25; yellowish oil (1:0.57 E/Z), 74%; 
1H NMR (600 MHz, CDCl3) δ = 8.13 (dd, J = 8.8 Hz, 6.1 Hz, 1H, Z), 7.54 - 7.46 (m, 2H, Z + 2H, E), 7.30 (dd, J = 8.7 Hz, 5.6 Hz, 1H, E), 7.24 - 7.17 (m, 1H, Z + 1H, E), 7.11 (d, J = 13.0 Hz, 1H, E), 7.01 (td, J = 8.6 Hz, 2.7 Hz, 1H, Z), 6.95 (td, J = 8.5 Hz, 2.6 Hz, 1H, E), 6.91 (dd, J = 8.6 Hz, 3.5 Hz, 2H, Z + 2H, E), 6.86 (d, J = 8.6 Hz, 1H, E), 6.32 (d, J = 13.0 Hz, 1H, E), 6.25 (d, J = 7.2 Hz, 1H, Z), 5.88 (d, J = 7.1 Hz, 1H, Z), 3.82 (s, 3H, E), 3.80 (s, 3H, Z), 3.79 (s, 3H, Z), 3.74 (s, 3H, E); 13C NMR (150 MHz, CDCl3) δ = 160.5 (d, J = 238.5 Hz, E), 160.3 (E), 160.1 (d, J = 238.5 Hz, Z), 159.9 (E), 159.9 (Z), 149.9 (d, J = 1.2 Hz), 148.6 (d, J = 1.9 Hz), 134.2 (d, J = 3.2 Hz, E), 134.1 (E), 133.5 (d, J = 3.1 Hz, Z), 133.1 (Z), 133.1 (Z), 133.0 (E), 133.0 (E), 130.3 (d, J = 8.1 Hz, Z), 125.2 (d, J = 8.3 Hz, E), 122.9 (d, J = 9.3 Hz, Z), 122.3 (d, J = 9.3 Hz, E), 118.4 (d, J = 22.7 Hz, E), 118.1 (d, J = 22.3 Hz, Z), 115.7 (d, J = 21.7 Hz, E), 115.4 (Z), 115.2 (d, J = 4.2 Hz, Z), 115.1 (Z), 114.2 (Z), 114.2 (Z), 114.2 (E), 114.2 (E), 114.1 (E), 113.9 (Z), 102.9 (E), 102.4 (Z), 94.7 (E), 94.5 (Z), 86.2 (d, J = 3.1 Hz, Z), 86.1 (d, J = 3.1 Hz, E), 60.8 (Z), 56.5 (E), 55.3 (Z + E); HRMS (ESI): m/z: Calcd for C18H18FO2 [M+H]+ 283.1129, Found 283.1129; IR (thin film, cm−1): 3431, 2935, 1639, 1601, 1512, 1250, 830, 535.

2-(2-Methoxyvinyl)-1-(phenylethynyl)naphthalene (1p)
TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rr=0.2; yellowish oil (1:0.7 E/Z), 71%; 
1H NMR (600 MHz, CDCl3) δ = 8.46 - 8.40 (m, 1H, Z + 1H, E), 8.30 (d, J = 8.8 Hz, 1H, Z), 7.79 (t, J = 8.2 Hz, 1H, Z + 1H, E), 7.76 (d, J = 8.8 Hz, 1H, Z), 7.72 (d, J = 8.7 Hz, 1H, E), 7.67 (m, 5H, Z), 7.59 - 7.56 (m, 1H, E), 7.56 - 7.51 (m, 3H, Z), 7.46 (d, J = 6.8 Hz, 2H, E), 7.42 (m, 5H, E), 7.34 (d, J = 13.0 Hz, 1H, E), 6.68 (d, J = 13.0 Hz, 1H, E), 6.35 (d, J = 7.2 Hz, 1H, Z), 6.16 (d, J = 7.2 Hz, 1H, Z), 3.86 (s, 3H, Z), 3.82 (s, 3H, E); 13C NMR (150 MHz, CDCl3) δ = 151.1 (E), 149.7 (Z), 136.9 (E), 136.7 (Z), 134.0 (E), 133.7 (Z), 131.7 (Z), 131.7 (Z), 131.7 (E), 131.6 (E), 131.6 (E), 128.7 (E), 128.6 (E), 128.6 (Z), 128.6 (Z), 128.4 (E), 128.4 (Z), 128.2 (E), 128.1 (Z), 128.1 (Z), 127.2 (E), 126.8 (Z), 126.7 (Z), 126.6 (Z), 126.3 (E), 125.8 (Z), 125.6 (E), 125.6 (E), 123.9 (Z), 123.9 (E), 121.9 (E), 117.2 (Z), 116.5 (E), 104.7 (E), 104.3 (Z),
99.6 (E), 99.5 (Z), 86.8 (Z), 86.5 (E), 61.1 (Z), 56.8 (E); HRMS (ESI): m/z: Calcd for C₂₁H₁₇O [M+H]⁺ 285.1274, Found 285.1276; IR (thin film, cm⁻¹): 3432, 2931, 1634, 1490, 1201, 753, 689.

1-((4-Methoxyphenyl)ethynyl)-2-(2-methoxyvinyl)naphthalene (1q)
TLC (petroleum ether:ethyl acetate, 15:1, v/v): Rᵣ=0.3; yellowish oil (1:0.5 E/Z), 65%;
¹H NMR (600 MHz, CDCl₃) δ = 8.44 (s, 1H, Z), 8.41 (d, J = 8.7 Hz, 1H, Z), 7.78 (t, J = 8.3 Hz, 1H, Z + 1H, E), 7.74 (d, J = 8.8 Hz, 1H, Z), 7.70 (d, J = 8.7 Hz, 1H, E), 7.60 (dd, J = 8.4 Hz, 3.5 Hz, 2H, Z + 2H, E), 7.57 – 7.51 (m, 2H, Z + 2H, E), 7.49 – 7.42 (m, 2H, Z + 2H, E), 7.32 (d, J = 13.0 Hz, 1H, E), 6.94 (d, J = 8.6 Hz, 2H, Z + 2H, E), 6.86 (d, J = 8.7 Hz, 1H, E), 6.67 (d, J = 13.0 Hz, 1H, E), 6.34 (d, J = 7.2 Hz, 1H, Z), 6.15 (d, J = 7.2 Hz, 1H, Z), 3.86 (3H, E), 3.85 (3H, S), 3.81 (s, 3H, Z + 3H, E); ¹³C NMR (150 MHz, CDCl₃) δ = 160.4(Z), 159.8 (E), 151.0 (E), 149.6 (Z), 136.5 (E), 136.4 (Z), 134.2 (E), 134.0 (Z), 133.7 (Z), 133.1 (Z), 133.1 (E), 133.1 (E), 131.7 (E), 131.6 (Z), 128.4 (E), 128.1 (E), 128.1 (Z), 127.8 (Z), 127.1 (E), 126.7 (Z), 126.7 (E), 126.4 (E), 125.7 (Z), 125.6 (E), 121.9 (E), 117.6 (Z), 116.9 (E), 116.0 (Z), 114.3 (E), 114.3 (E), 114.2 (Z), 114.2 (Z), 114.1 (Z), 104.8 (E), 104.4 (Z), 99.6 (E), 99.5 (Z), 85.4 (Z), 85.2 (E), 61.1 (Z), 56.8 (E), 55.5 (E), 55.5 (Z); HRMS (ESI): m/z: Calcd for Cₓ₂ᵧHᵧₐO_y [M+H]⁺ 315.1380, Found 315.1370; IR (thin film, cm⁻¹): 3429, 2932, 1634, 1603, 1509, 1248, 829.

1-((4-Chlorophenyl)ethynyl)-2-(2-methoxyvinyl)naphthalene (1r)
TLC (petroleum ether:ethyl acetate, 20:1, v/v): Rᵣ=0.25; yellowish oil (1:0.7 E/Z), 63%;
¹H NMR (600 MHz, CDCl₃) δ = 8.41 (d, J = 8.5 Hz, 1H, Z), 8.39 (d, J = 8.4 Hz, 1H, E), 8.32 (d, J = 8.8 Hz, 1H, Z), 7.81 (d, J = 8.2 Hz, 1H, Z), 7.78 (m, 4H, Z), 7.72 (d, J = 8.7 Hz, 1H, E), 7.59 (d, J = 6.7 Hz, 2H, E), 7.57 (d, J = 6.7 Hz, 2H, E), 7.53 (d, J = 8.7 Hz, 1H, E), 7.47 (q, J = 7.4 Hz, 3H, Z), 7.39 (dd, J = 8.4 Hz, 2.7 Hz, 3H, E), 7.32 (d, J = 13.0 Hz, 1H, E), 6.65 (d, J = 13.0 Hz, 1H, E), 6.36 (d, J = 7.2 Hz, 1H, Z), 6.13 (d, J = 7.2 Hz, 1H, Z), 3.85 (s, 3H, Z), 3.82 (s, 3H, E); ¹³C NMR (150 MHz, CDCl₃) δ = 151.1 (E), 149.7 (Z), 136.9 (E), 136.7 (Z), 134.0 (E), 133.7 (Z), 131.7 (Z), 131.6 (E), 131.6 (E), 128.7 (E), 128.6 (E), 128.6 (Z), 128.6 (Z), 128.4 (E), 128.4 (Z), 128.2 (E), 128.1 (Z), 128.1 (Z), 127.2 (E), 126.8 (Z), 126.7 (Z), 126.6 (Z), 126.3 (E), 125.8 (Z), 125.6 (E), 123.9 (Z), 123.9 (E), 121.9 (E), 117.2 (Z), 116.5 (Z), 104.7 (E), 104.3 (Z), 99.6 (E), 99.5 (Z), 86.8 (Z), 86.5 (E), 61.1 (Z), 56.8 (E); HRMS
(ESI): m/z: Calcd for C21H16OCl [M+H]+ 319.0884, Found 319.0901; IR (thin film, cm⁻¹) 3419, 2921, 1634, 1488, 1204, 1089, 826.

**E**-2-(3-Methoxy-2-((3-methoxy-2-(2-methoxyvinyl)phenyl)ethynyl)-5-methylphenyl)acetonitrile (1s)

TLC (petroleum ether:ethyl acetate, 8:1, v/v): Rf=0.25; yellowish oil (E); 73%; ¹H NMR (600 MHz, CDCl₃) δ = 7.76 (d, J = 12.8 Hz, 1H), 7.18 (dd, J = 7.7 Hz, 1.0 Hz, 1H), 7.07 (t, J = 8.0 Hz, 1H), 6.96 (s, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.71 (s, 1H), 6.37 (d, J = 12.8 Hz, 1H), 3.96 (s, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 3.76 (s, 3H), 2.40 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 160.7, 156.7, 153.7, 140.5, 132.9, 126.8, 125.6, 125.5, 121.8, 121.1, 117.8, 111.3, 111.1, 109.7, 100.5, 99.1, 87.0, 56.3, 56.0, 55.6, 22.8, 22.1; HRMS (ESI): m/z: Calcd for C₂₂H₂₂O₃N [M+H]+ 348.1594, Found 348.1593; IR (thin film, cm⁻¹) 3442, 2960, 2925, 1639, 1460, 1384, 1260, 1088, 1033, 802.

### 5. General Preparation of 3-3s and Characterization Data

The 1,5-enyne substrates 1-1s (1 mmol) and the Ph₃PAuNTf₂ (0.1 mmol, 73.8 mg) in toluene (2 mL) were placed in a screw-cap vial containing a stirring bar. The reaction vial was fitted with a cap, evacuated, filled with oxygen, bubbled over all the time, and heated with stirring at 80 °C for 10-20 h. 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 indenones 3-3s. Spectral data were consistent with those reported in the literature.[⁴]

2-(4-Chlorophenyl)-1-oxo-1H-indene-3-carbaldehyde (3b)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.2; red solid, Mp 143–145 °C; 75%; ¹H NMR (600 MHz, CDCl₃) δ = 10.30 (s, 1H), 7.98 (d, J = 7.4 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.52 – 7.45 (m, 5H), 7.34 (t, J = 7.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ = 196.7, 190.5, 144.0, 143.7, 142.3, 137.2, 135.0, 132.0, 129.7, 129.6, 129.3, 129.3, 126.7, 124.5, 124.5; HRMS (ESI): m/z: Calcd for C₁₆H₁₀O₂Cl [M+H]+
N-(4-(3-Formyl-1-oxo-1H-inden-2-yl)phenyl)acetamide (3c)
TLC (petroleum ether:ethyl acetate, 1:1, v/v): Rf=0.3; red solid, Mp 223–225 °C; 57%;
^1H NMR (600 MHz, DMSO-d_6) δ 10.25 (s, 1H), 10.19 (s, 1H), 7.90 (d, J = 7.4 Hz, 1H),
7.75 (d, J = 8.6 Hz, 2H), 7.63 – 7.59 (m, 3H), 7.57 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 7.3 Hz,
1H), 2.10 (s, 3H); ^13C NMR (150 MHz, DMSO-d_6) δ 196.88, 191.11, 168.81,
143.46, 142.44, 141.59, 141.45, 134.87, 131.71, 129.20, 129.17, 123.92, 123.43,
122.47, 118.60, 24.18; HRMS (ESI): m/z: Calcd for C_{18}H_{14}NO_3 [M+H]^+ 292.0968,
Found 292.0970; IR (thin film, cm\(^{-1}\)): 3381, 2922, 1701, 1664, 1370, 1184, 826, 746.

N-(3-(3-Formyl-1-oxo-1H-inden-2-yl)phenyl)acetamide (3d)
TLC (petroleum ether:ethyl acetate, 1:1, v/v): Rf=0.3; red solid, Mp 188–189 °C; 46%;
^1H NMR (600 MHz, DMSO-d_6) δ 10.20 (s, 1H), 10.15 (s, 1H), 7.89 (d, J = 7.3 Hz, 1H),
7.77 (d, J = 6.7 Hz, 2H), 7.63 (d, J = 7.1 Hz, 1H), 7.59 (td, J = 7.6, 1.0 Hz, 1H), 7.46
(t, J = 8.2 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.30 (d, J = 7.6 Hz, 1H), 2.07 (s, 3H); ^13C NMR (150 MHz, DMSO-d_6) δ 196.88, 191.11, 168.61, 143.62, 143.13, 142.03, 139.41,
134.84, 129.66, 129.51, 129.22, 128.97, 128.32, 125.47, 123.99, 123.60, 120.97,
120.79, 24.18; HRMS (ESI): m/z: Calcd for C_{18}H_{14}NO_3 [M+H]^+ 292.0968, Found
292.0970; IR (thin film, cm\(^{-1}\)): 3394, 3246, 2922, 1677, 1660, 1385, 1014, 758.

Ethyl 2-(4-(3-formyl-1-oxo-1H-inden-2-yl)phenyl)acetate (3e)
TLC (petroleum ether:ethyl acetate, 15:1, v/v): Rf=0.3; red oil, 61%; ^1H NMR (600 MHz, CDCl_3) δ 10.31 (s, 1H), 7.98 (d, J = 7.4 Hz, 1H), 7.62 (d, J = 7.1 Hz, 1H), 7.54
– 7.50 (m, 2H), 7.48 (td, J = 7.6, 1.1 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.35 – 7.30 (m, 1H),
4.18 (q, J = 7.1 Hz, 2H), 3.69 (s, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^13C NMR (150 MHz, CDCl_3) δ 196.92, 190.99, 170.96, 144.59, 143.54, 142.31, 136.86, 134.72, 130.86,
129.74, 129.50, 129.31, 126.94, 124.26, 124.18, 61.16, 41.28, 14.19; HRMS (ESI): m/z:
Calcd for C_{19}H_{15}O_4 [M+H]^+ 307.0965, Found 307.0970; IR (thin film, cm\(^{-1}\)): 3425,
2981, 2932, 1732, 16373, 1460, 1369, 1156, 1029, 758.
2-(4-Methoxyphenyl)-6-methyl-1-oxo-1H-indene-3-carbaldehyde (3f)
TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f = 0.2; red solid, Mp 166–167 °C; 82%;
^1H NMR (600 MHz, CDCl_3) δ = 10.27 (s, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 8.6 Hz, 2H), 7.42 (s, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.02 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H), 2.37 (s, 3H); ^13C NMR (150 MHz, CDCl_3) δ = 197.9, 191.2, 161.8, 144.3, 142.5, 140.1, 139.4, 134.9, 132.5, 123.0, 125.2, 123.8, 121.0, 114.5, 55.6, 21.5; HRMS (ESI): m/z: Calcd for C_{18}H_{15}O_3 [M+H]^+ 279.1016, Found 279.1016; IR (thin film, cm\(^{-1}\)): 3442, 2924, 1716, 1667, 1507, 1458, 1383, 1256, 1115, 825.

5-Methoxy-2-(4-methoxyphenyl)-1-oxo-1H-indene-3-carbaldehyde (3i)
TLC (petroleum ether:ethyl acetate, 5:1, v/v): R_f = 0.3; red solid, Mp 178–180 °C; 82%;
^1H NMR (600 MHz, CDCl_3) δ = 10.25 (s, 1H), 7.57 (m, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 6.70 (dd, J = 8.2 Hz, 2.2 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H); ^13C NMR (150 MHz, CDCl_3) δ = 195.6, 191.0, 165.4, 162.0, 146.8, 145.8, 140.3, 132.7, 132.7, 126.4, 122.3, 121.1, 114.5, 114.5, 112.4, 111.6, 56.1, 55.6; HRMS (ESI): m/z: Calcd for C_{18}H_{14}O_4Na [M+Na]^+ 317.0784, Found 317.0777; IR (thin film, cm\(^{-1}\)): 3422, 2924, 1666, 1601, 1475, 1290, 1262, 1181, 1025, 831.

2-(4-Chlorophenyl)-5-methoxy-1-oxo-1H-indene-3-carbaldehyde (3j)
TLC (petroleum ether:ethyl acetate, 15:1, v/v): R_f = 0.2; red solid, Mp 152–154 °C; 79%;
^1H NMR (600 MHz, CDCl_3) δ = 10.25 (s, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.49 (s, 4H), 6.73 (dd, J = 8.1 Hz, 2.1 Hz, 1H), 3.92 (s, 3H); ^13C NMR (150 MHz, CDCl_3) δ = 194.9, 190.4, 165.4, 145.7, 145.1, 142.1, 137.2, 132.1, 132.1, 129.2, 129.2, 126.9, 126.6, 122.2, 112.8, 112.2, 56.1; HRMS (ESI): m/z: Calcd for C_{17}H_{10}ClO_3 [M-H]^− 297.0324, Found 297.0360; IR (thin film, cm\(^{-1}\)): 3421, 2923, 1700, 1676, 1599, 1470, 1221, 1183, 890, 793, 526.
5,6-Dimethoxy-1-oxo-2-phenyl-1H-indene-3-carbaldehyde (3k)
TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rf=0.25; red solid, Mp 179–181 °C; 77%; 1H NMR (600 MHz, CDCl3) δ = 10.24 (s, 1H), 7.60 (s, 1H), 7.51 (m, 5H), 7.19 (s, 1H), 4.02 (s, 3H), 3.92 (s, 3H); 13C NMR (150 MHz, CDCl3) δ = 196.0, 191.2, 153.9, 149.5, 145.4, 142.5, 137.8, 130.7, 130.7, 130.5, 128.8, 128.8, 128.5, 121.9, 108.3, 108.1, 56.7, 56.5; HRMS (ESI): m/z: Calcd for C_{18}H_{15}O_{4} [M+H]^+ 295.0965, Found 295.0970; IR (thin film, cm\(^{-1}\)): 3424, 2923, 1702, 1664, 1466, 1366, 1124, 1022, 692.

![3k](image)

5-Fluoro-1-oxo-2-phenyl-1H-indene-3-carbaldehyde (3l)
TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.3; red solid, Mp 130–132 °C; 70%; 1H NMR (600 MHz, CDCl3) δ = 10.29 (s, 1H), 7.97 (dd, J = 8.1 Hz, 4.7 Hz, 1H), 7.55 – 7.50 (m, 5H), 7.32 (dd, J = 7.0 Hz, 2.3 Hz, 1H), 7.14 (td, J = 8.5 Hz, 2.3 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ = 195.76, 190.96, 163.8 (d, J = 251.5 Hz), 145.16 (d, J = 4.7 Hz), 143.52 (d, J = 1.8 Hz), 138.0 (d, J = 3.3 Hz), 131.9 (d, J = 7.2 Hz), 130.8, 130.7, 130.7, 128.9, 128.9, 128.0, 125.7 (d, J = 7.7 Hz), 120.3 (d, J = 22.5 Hz), 112.5 (d, J = 24.6 Hz); HRMS (ESI): m/z: Calcd for C_{16}H_{10}O_{2}F [M+H]^+ 253.0659, Found 253.0680; IR (thin film, cm\(^{-1}\)): 3418, 2923, 1724, 1672, 1469, 1260, 1013, 803, 692.

![3l](image)

2-(4-Chlorophenyl)-5-fluoro-1-oxo-1H-indene-3-carbaldehyde (3m)
TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.2; red solid, Mp 153–155 °C; 77%; 1H NMR (600 MHz, CDCl3) δ = 10.28 (s, 1H), 7.97 (dd, J = 8.2 Hz, 4.7 Hz, 1H), 7.52 – 7.46 (m, 5H), 7.33 (dd, J = 7.0 Hz, 2.4 Hz, 1H), 7.15 (td, J = 8.6 Hz, 2.5 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ = 195.4, 190.4, 163.9 (d, J = 251.9 Hz), 143.7, 137.8 (d, J = 3.3 Hz), 137.3, 132.1, 131.9, 131.9, 129.4, 129.4, 129.4, 126.4, 125.8 (d, J = 7.7 Hz), 120.5 (d, J = 22.5 Hz), 112.7 (d, J = 24.6 Hz); HRMS (ESI): m/z: Calcd for C_{16}H_{10}ClFO_{2} [M+H]^+ 287.0270, Found 287.0302; IR (thin film, cm\(^{-1}\)): 3417, 2923, 1724, 1672, 1590, 1474, 1224, 1007, 833, 795.

![3m](image)

6-Fluoro-2-(4-methoxyphenyl)-1-oxo-1H-indene-3-carbaldehyde (3n)

![3n](image)
TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rf=0.3; red solid, Mp 168–170 °C; 75%;

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 10.28\) (s, 1H), 7.95 (dd, \(J = 8.1\) Hz, 4.7 Hz, 1H), 7.53 (d, \(J = 8.7\) Hz, 2H), 7.30 (dd, \(J = 7.0\) Hz, 2.4 Hz, 1H), 7.13 (dd, \(J = 8.6\) Hz, 2.4 Hz, 1H), 7.03 (d, \(J = 8.7\) Hz, 2H), 3.89 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 196.2, 190.8, 163.3\) (d, \(J = 250.9\) Hz), 161.8, 144.6 (d, \(J = 4.7\) Hz), 141.6, 138.2 (d, \(J = 3.3\) Hz), 132.3, 131.6 (d, \(J = 7.1\) Hz), 125.1 (d, \(J = 7.7\) Hz), 120.3, 120.2 (d, \(J = 22.5\) Hz), 114.4, 114.4, 112.2 (d, \(J = 24.5\) Hz), 55.4; HRMS (ESI): \(m/z\): Calcd for C\(_{17}\)H\(_{12}\)O\(_3\) F \([M+H]^+\) 283.0700, Found 283.0692; IR (thin film, cm\(^{-1}\)): 3420, 2924, 1723, 1671, 1607, 1468, 1253, 1176, 1020, 797.

1-Oxo-2-phenyl-1H-cyclopenta[a]naphthalene-3-carbaldehyde (3p)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.2; red solid, Mp 153–154 °C; 56%; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 10.33\) (s, 1H), 8.76 (d, \(J = 8.5\) Hz, 1H), 8.20 (d, \(J = 8.2\) Hz, 1H), 8.00 (d, \(J = 8.2\) Hz, 1H), 7.80 (d, \(J = 8.3\) Hz, 1H), 7.61 – 7.57 (m, 3H), 7.54 (dd, \(J = 8.8\) Hz, 1.8 Hz, 3H), 7.45 – 7.40 (m, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 198.4, 191.0, 145.2, 142.7, 135.8, 134.7, 130.9, 130.9, 130.7, 130.0, 129.8, 128.9, 128.8, 128.3, 126.6, 123.8, 121.8, 121.8; HRMS (ESI): \(m/z\): Calcd for C\(_{20}\)H\(_{13}\)O\(_2\) [M+H]^+ 285.0910, Found 285.0946; IR (thin film, cm\(^{-1}\)): 3395, 2925, 1700, 1670, 1464, 1443, 1384, 825, 694.

2-(4-Methoxyphenyl)-1-oxo-1H-cyclopenta[a]naphthalene-3-carbaldehyde (3q)

TLC (petroleum ether:ethyl acetate, 50:1, v/v): Rf=0.3; brown solid, Mp 163–166 °C; 59%; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 10.31\) (s, 1H), 8.76 (d, \(J = 8.5\) Hz, 1H), 8.20 (d, \(J = 8.2\) Hz, 1H), 7.98 (d, \(J = 8.2\) Hz, 1H), 7.79 (d, \(J = 8.3\) Hz, 1H), 7.60 (d, \(J = 8.8\) Hz, 2H), 7.58 – 7.56 (m, 1H), 7.41 (m, 1H), 7.05 (d, \(J = 8.8\) Hz, 2H), 3.90 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 198.9, 190.9, 162.1, 145.8, 144.9, 140.9, 135.8, 134.5, 132.8, 132.8, 129.9, 129.8, 128.8, 126.4, 123.8, 121.8, 121.6, 120.9, 114.6, 114.6, 55.7, 53.6; HRMS (ESI): \(m/z\): Calcd for C\(_{21}\)H\(_{15}\)O\(_3\) [M+H]^+ 315.1016, Found 315.1029; IR (thin film, cm\(^{-1}\)): 3405, 2925, 1700, 1670, 1459, 1384, 1255, 832.
2-(4-Chlorophenyl)-1-oxo-1H-cyclopenta[a]naphthalene-3-carbaldehyde (3r)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): Rf=0.2; brown solid, Mp 101–102 °C; 52%; 
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 10.31 (s, 1H), 8.74 (d, J = 8.5 Hz, 1H), 8.19 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.58 (t, J = 7.3 Hz, 1H), 7.54 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 198.0, 190.4, 145.0, 143.7, 142.9, 137.2, 135.9, 134.8, 132.1, 132.1, 130.1, 129.8, 129.3, 129.3, 128.8, 126.7, 126.7, 123.8, 121.9, 121.7; HRMS (ESI): m/z: Calcd for C\(_{20}\)H\(_{12}\)O\(_2\)Cl [M+H]\(^+\) 319.0520, Found 319.0561; IR (thin film, cm\(^{-1}\)): 3395, 2956, 2924, 1709, 1672, 1465, 1383, 1090, 1078, 828, 739.

2-(2-(3-Formyl-4-methoxy-1-oxo-1H-inden-2-yl)-3-methoxy-5-methylphenyl)acetonitrile (3s)

TLC (petroleum ether:ethyl acetate, 3:1, v/v): Rf=0.25; red solid, Mp 188–191 °C; 61%; 
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 10.39 (s, 1H), 7.33 (dd, J = 8.4, 7.1 Hz, 1H), 7.25 (s, 1H), 7.10 (d, J = 8.4 Hz, 1H), 6.97 (s, 1H), 6.71 (s, 1H), 3.95 (s, 3H), 3.70 (s, 3H), 3.68 (d, J = 18.7 Hz, 1H), 3.62 (d, J = 18.6 Hz, 1H), 2.39 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 195.5, 190.8, 157.9, 153.7, 149.9, 141.4, 133.6, 132.0, 131.9, 131.5, 128.7, 121.7, 119.1, 118.0, 117.7, 115.6, 111.6, 56.0, 56.0, 22.5, 22.0; HRMS (ESI): m/z: Calcd for C\(_{21}\)H\(_{18}\)O\(_4\)N [M+H]\(^+\) 348.1158, Found 348.1177; IR (thin film, cm\(^{-1}\)): 3398, 2922, 2855, 2195, 1687, 1601, 1568, 1465, 1260, 1065, 793.

6. Preparation of 4i and Characterization Data

To a solution of 4-methoxy-1-((4-methoxyphenyl)ethynyl)-2-(2-methoxyvinyl)benzene 1i (1 mmol, 294.3 mg) and Ph\(_3\)PAuNTf\(_2\) (0.1 mmol, 73.8 mg) in toluene was added three drops of water. The resulting mixture was stirred at 80 °C for 9 h under a nitrogen atmosphere. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH\(_2\)Cl\(_2\) (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether:ethyl acetate, 20:1, v/v) on silica gel to afford the desired product 4i (230 mg) as a yellowish solid with a yield of 82%; Mp 151–152 °C; 82%; 
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 10.15 (s, 1H), 7.85 (d, J = 2.2 Hz, 1H), 7.46 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.2 Hz, 1H), 7.26 (s, 1H), 7.01 (d, J = 8.6 Hz, 2H), 6.85 (dd, J = 8.2 Hz, 2.3 Hz, 1H), 3.92 (s,
2H), 3.88 (s, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 189.8, 164.5, 161.2, 159.5, 142.8, 136.0, 132.9, 131.0, 127.1, 124.0, 114.5, 114.5, 113.4, 107.5, 55.8, 55.6, 42.4; HRMS (ESI): $m/z$: Calcd for C$_{18}$H$_{16}$O$_3$Na [M+Na]$^+$ 303.0992, Found 303.0993; IR (thin film, cm$^{-1}$): 3441, 2924, 2852, 1656, 1600, 1474, 1262, 1105, 1022, 803.

7. Preparation of 2 and Characterization Data

To a solution of 1-(2-methoxyvinyl)-2-(phenylethynyl)benzene 1 (1 mmol, 234.3 mg) in toluene was added Ph$_3$PAuNTf$_2$ (0.1 mmol, 73.8 mg). The resulting mixture was stirred at 80 °C for 1 h under a nitrogen atmosphere. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether:ethyl acetate, 100:1, v/v) on silica gel to afford the desired product 2 (223 mg) as a yellowish oil with a yield of 95%; $^1$H NMR (600 MHz, DMSO-$d_6$) δ = 7.87 (d, $J = 7.4$ Hz, 1H), 7.49 (dd, $J = 8.1$ Hz, 1.1 Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.36 (d, $J = 7.3$ Hz, 2H), 7.24 (s, 1H), 7.19 (td, $J = 7.4$ Hz, 1.2 Hz, 1H), 7.15 (td, $J = 7.4$ Hz, 1.2 Hz, 1H), 6.74 (s, 1H), 4.04 (s, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ = 155.6, 141.4, 140.2, 135.7, 134.2, 128.8, 128.8, 128.6, 128.6, 127.2, 125.9, 124.2, 123.9, 123.4, 120.3, 117.8, 62.4; HRMS (ESI): $m/z$: Calcd for C$_{17}$H$_{13}$O [M+H]$^+$ 235.1117, Found 235.1125; IR (thin film, cm$^{-1}$): 3329, 2852, 1695, 1493, 1449, 1126, 757, 690.

8. X-Ray Structure of 3o

![Figure S1. Single crystal structure of 3o.](image_url)
Table 1 Crystal data and structure refinement for exp_5652.

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9. Detailed Information on Control Experiments under $^{18}\text{O}_2$ Atmosphere

$^{18}\text{O}_2$ (1 mmol) and the Ph$_3$PAuNTf$_2$ (0.1 mmol, 73.8 mg) in toluene (2 mL) were placed in a screw-cap vial containing a stirring bar. The reaction vial was fitted with a cap, filled with $^{18}\text{O}_2$ and heated with stirring at 80 °C for 10 h. 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 indenones 3i-1 and 3i-2 with a yield of 60%.
1i (1 mmol) and the Ph₃PAuNTf₂ (0.1 mmol, 73.8 mg) in toluene (2 mL) were placed in a screw-cap vial containing a stirring bar. The reaction vial was fitted with a cap, filled with O₂ and heated with stirring at 80 °C for 10 h. 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 desired
product 4i with a yield of 75%.

10. Preparation of 5 and Characterization Data
To a stirred solution of the aldehyde 3s (0.21 mmol, 74 mg) in t-BuOH (0.8 mL) was added phosphate buffer (0.4 mL) (pH ~ 3.6) and 2-methyl-2-butene (1.06 mmol, 0.11 mL) at room temperature. After that a solution of NaClO₂ (0.32 mmol, 29 mg) in H₂O (0.40 mL) was added to the reaction mixture and stirred at room temperature for 3 h. After completion of the reaction it was acidified with 1 N HCl to pH 4. Most of the solvent was evaporated off and EtOAc (10 mL) and brine (8 mL) were added to the residue. The organic layer was separated off and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic extracts were dried over anhydrous Na₂SO₄ and the crude acid thus obtained after evaporation of the solvent was mixed in MeOH/toluene (v:v = 1:1) at 0 °C, and a solution of (trimethylsilyl)diazomethane (2.0 M in hexanes) was slowly added dropwise via syringe over 30 min until effervescence ceased. The reaction mixture was stirred for 1 h and then concentrated under reduced pressure to afford the crude ester as a pale yellowish oil. The resulting oil was purified by chromatography (3:1 to 1:1 petroleum ether:EtOAc). Pure fractions were evaporated to dryness to afford compound 5 as a yellowish solid (64 mg, 80%); Data were in agreement with those reported previously.[2]

TLC (petroleum ether:ethyl acetate, 3:1, v/v): Rf = 0.3; yellowish solid, 80%; 1H NMR (600 MHz, CDCl₃) δ = 7.29 (m, 1H), 7.21 (d, J = 6.0 Hz, 1H), 7.04 (d, J = 6.0 Hz, 1H), 6.97 (s, 1H), 6.69 (s, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 3.76 (d, J = 18.0 Hz, 1H), 3.72 (s, 3H), 3.66 (d, J = 18.0 Hz, 1H), 2.38 (s, 3H); 13C NMR (150 MHz, CDCl₃) δ = 195.2, 166.1, 158.3, 153.0, 148.4, 141.2, 131.9, 131.2, 131.0, 130.6, 128.2, 121.4, 119.1, 118.1, 117.2, 115.2, 111.5, 56.3, 55.9, 52.5, 22.1, 21.9.

11. References


12. NMR Spectra
$^1$H NMR Spectrum of Compound 6c (DMSO-$d_6$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 6c (DMSO-$d_6$, 150 MHz)
$^1\text{H}$ NMR Spectrum of Compound $6\text{d}$ (DMSO-$d_6$, 600 MHz)

$^{13}\text{C}$ NMR Spectrum of Compound $6\text{d}$ (DMSO-$d_6$, 150 MHz)
**1H NMR Spectrum of Compound 6a (CDCl$_3$, 600 MHz)**

**13C NMR Spectrum of Compound 6a (CDCl$_3$, 150 MHz)**
$^1$H NMR Spectrum of Compound 6m (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 6m (CDCl$_3$, 150 MHz)
**1H NMR Spectrum of Compound 6r (CDCl₃, 600 MHz)**

**13C NMR Spectrum of Compound 6r (CDCl₃, 150 MHz)**
$^1$H NMR Spectrum of Compound 6s (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 6s (CDCl$_3$, 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 1b (CDCl$_3$, 600 MHz)

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

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

$^{13}$C NMR Spectrum of Compound 1d (DMSO-$d_6$, 150 MHz)
\( ^1 \text{H NMR Spectrum of Compound 1e (CDCl}_3, 600 \text{ MHz)} \)

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

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

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

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

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

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

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

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

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

13C NMR Spectrum of Compound 1s (CDCl₃, 150 MHz)
$^1$H NMR Spectrum of Compound 3b (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 3b (CDCl$_3$, 150 MHz)
H NMR Spectrum of Compound 3c (DMSO-$d_6$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 3c (DMSO-$d_6$, 150 MHz)
$^1$H NMR Spectrum of Compound 3d (DMSO-$d_6$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 3d (DMSO-$d_6$, 150 MHz)
1H NMR Spectrum of Compound 3e (CDCl₃, 600 MHz)

13C NMR Spectrum of Compound 3e (CDCl₃, 150 MHz)
1H NMR Spectrum of Compound 3f (CDCl₃, 600 MHz)

13C NMR Spectrum of Compound 3f (CDCl₃, 150 MHz)
1H NMR Spectrum of Compound 3i (CDCl$_3$, 600 MHz)

13C NMR Spectrum of Compound 3i (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 3j (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 3j (CDCl$_3$, 150 MHz)
HSQC Spectrum of Compound 3j (CDCl₃, 600 MHz)

HMBC Spectrum of Compound 3j (CDCl₃, 600 MHz)
HSQC Spectrum of Compound 3j (CDCl₃, 600 MHz)

NOESY Spectrum of Compound 3j (CDCl₃, 600 MHz)
$^1$H NMR Spectrum of Compound 3k (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 3h (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 3i (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 3i (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 3m (CDCl$_3$, 600 MHz)

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

13C NMR Spectrum of Compound 3o (CDCl₃, 150 MHz)
$^1$H NMR Spectrum of Compound 3p (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 3p (CDCl$_3$, 150 MHz)
$^1\text{H NMR Spectrum of Compound 3q (CDCl}_3, 600 \text{ MHz)}$

$^{13}\text{C NMR Spectrum of Compound 3q (CDCl}_3, 150 \text{ MHz)}$
$^1$H NMR Spectrum of Compound 3o (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 3o (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound 3p (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 3p (CDCl$_3$, 150 MHz)
$^1$H NMR Spectrum of Compound $4i$ (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound $4i$ (CDCl$_3$, 150 MHz)
\( ^1H \) NMR Spectrum of Compound 2 (CDCl\(_3\), 600 MHz)

\( ^{13}C \) NMR Spectrum of Compound 2 (CDCl\(_3\), 150 MHz)
$^1$H NMR Spectrum of Compound 7 (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectrum of Compound 7 (CDCl$_3$, 150 MHz)
$^1$H-NMR Spectrum of Compound 5 and Dmitrienko’s Key Intermediate
$^{13}$C-NMR Spectrum of Compound 5 and Dmitrienko’s Key Intermediate