Supporting Information

N-Methyl Transfer Induced Copper-mediated Oxidative Diamination of Alkynes

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General Information. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded on JEOL JNM AL 400 (400 MHz), JEOL JNM AL 700 (700 MHz), and JNM ECA 700 (700MHz) spectrometers. $^1$H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl$_3$ at 7.26 ppm, CD$_2$Cl$_2$ at 5.32 ppm, acetone-$d_6$ at 2.04 ppm, THF-$d_8$ at 3.58 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broadened), and coupling constants (Hz). $^{13}$C NMR spectra were recorded on JEOL JNM AL 400 (100.5 MHz) and JEOL JNM AL 400 (176.0 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line for CDCl$_3$ at 77 ppm, CD$_2$Cl$_2$ at 53.8 ppm, Acetone-$d_6$ at 29.8 ppm, and THF-$d_8$ at 66.5 ppm. $^{19}$F NMR were recorded on JNM ECA-700 (658.8 MHz, ppm) spectrophotometer with chemical shift reported in ppm (δ) relative to CFCl$_3$ as an external standard (δ = 0 ppm). High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer and JEOL JMS-70 MStation operator. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40~63 μm, Merck Chemicals) and basic silica gel NH-DM1020 (Fuji Silysia Chemical Ltd). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials. The commercially available chemicals were used as received. Structures of the products were identified by $^1$H NMR, $^{13}$C NMR, HRMS, and compared with 2a which was confirmed unambiguously by X-ray crystallography: CCDC 1469095 contains the supplementary crystallography data of 2a. This data can be download free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Representative procedure for Cu-mediated synthesis of 5,10-dimethyl-5,10-dihydropyrido[3,2-b]indole 2a

To a solution of starting material 1a (47.2 mg, 0.2 mmol) in MeCN (1.0 mL) were added Cu(hfacac)$_2$•xH$_2$O (95.5 mg, 0.2 mmol) and K$_2$CO$_3$ (82.8 mg, 0.6 mmol). The reaction mixture was stirred for 3 h at 80 °C under O$_2$ balloon. The resulting mixture was filtered through a short basic silica pad (Fuji Silysis) using Et$_2$O or hexane/EtOAc as eluent. After concentration, the residue was purified by quick column chromatography using basic silica gel (hexane:EtOAc = 10:1) to give 2a (37.5 mg, 0.16 mmol) in 80% yield as white solid.

Representative procedure for synthesis of 2-((2-aminophenyl)ethynyl)-N,N-dimethylaniline 1a

To a mixture of 2-ethynyl-N,N-dimethylaniline (1.59 g, 11 mmol), 2-idoaniline (2.19 g, 10 mmol), PdCl$_2$(PPh$_3$)$_3$ (210 mg, 0.3 mmol), and Cu (5.7 mg, 0.3 mmol) was added triethylamine (0.3 M, 33 mL) in a 50 mL of Schlenk tube under Ar atmosphere. The reaction mixture was stirred for 12 h at room temperature. The resulting mixture was washed with Et$_2$O and filtered through a Celite pad. The filtrate was concentrated under reduced pressure to afford crude product, which was purified by silica gel chromatography (hexane:EtOAc = 7:1) to give 1a (2.24 g, 9.5 mmol) in 95% yield as pale yellow oil.
Table S1. Optimization of bases for catalytic reaction conditions\textsuperscript{a}

<table>
<thead>
<tr>
<th>entry</th>
<th>Base (0.6 equiv)</th>
<th>2a (%)\textsuperscript{b}</th>
<th>1a (%)\textsuperscript{b}</th>
</tr>
</thead>
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<tr>
<td>1\textsuperscript{c}</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>31</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>50</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>K\textsubscript{3}PO\textsubscript{4}</td>
<td>35</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>Cs\textsubscript{2}CO\textsubscript{3}</td>
<td>30</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>Na\textsubscript{2}CO\textsubscript{3}</td>
<td>37</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Ag\textsubscript{2}CO\textsubscript{3}</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Na(hfacac)\textsubscript{2}</td>
<td>18</td>
<td>0</td>
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<tr>
<td>8</td>
<td>KBF\textsubscript{4}</td>
<td>27</td>
<td>10</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 1a (0.2 mmol), Cu(hfacac)\textsubscript{2}∙xH\textsubscript{2}O (0.2 equiv), base (0.6 equiv), DTBP (2 equiv) in MeCN (0.2 M) at 100 °C for 12 h. \textsuperscript{b}\textsuperscript{1}H NMR yield determined using CH\textsubscript{3}Br\textsubscript{2} as an internal standard. \textsuperscript{c}O\textsubscript{2} was used instead of DTBP at 80 °C.

Table S2. Optimization of stoichiometric reaction conditions\textsuperscript{a}

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<tr>
<th>entry</th>
<th>metal salt (1.0 equiv)</th>
<th>base (3 equiv)</th>
<th>2a (%)\textsuperscript{b}</th>
<th>1a (%)\textsuperscript{b}</th>
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<tbody>
<tr>
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<td>Cu(hfacac)\textsubscript{2}</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>85 (80)</td>
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</tr>
<tr>
<td>2</td>
<td>Cu(tfacac)\textsubscript{2}</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
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<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Cu(acac)\textsubscript{2}</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
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<td>80</td>
</tr>
<tr>
<td>4</td>
<td>Cu(OAc)\textsubscript{2}</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
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</tr>
<tr>
<td>5</td>
<td>CuBr</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
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<td>0</td>
</tr>
<tr>
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<td>CuBr\textsubscript{2}</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
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<td>0</td>
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<td>K\textsubscript{2}CO\textsubscript{3}</td>
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<td>K\textsubscript{2}CO\textsubscript{3}</td>
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<tr>
<td>9</td>
<td>Ni(hfacac)\textsubscript{2}</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>0</td>
<td>99</td>
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<tr>
<td>10</td>
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<tr>
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<td>K\textsubscript{2}CO\textsubscript{3}</td>
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<td>80</td>
</tr>
<tr>
<td>12</td>
<td>Cu(hfacac)\textsubscript{2}</td>
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<td>0</td>
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<tr>
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<td>Cu(hfacac)\textsubscript{2}</td>
<td>Cs\textsubscript{2}CO\textsubscript{3}</td>
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<tr>
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<tr>
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<td>Cu(hfacac)\textsubscript{2}</td>
<td>K\textsubscript{3}PO\textsubscript{4}</td>
<td>45</td>
<td>15</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 1a (0.2 mmol), metal salt (1.0 equiv), base (6.0 equiv), O\textsubscript{2} balloon in MeCN (0.2 M) at 80 °C for 3 h. \textsuperscript{b}\textsuperscript{1}H NMR yield determined using CH\textsubscript{3}Br\textsubscript{2} as an internal standard. Isolated is shown in parenthesis.
Figure S1. ORTEP drawing of the DHII compound 2a. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Scheme S1. Crossover experiments with the protonated 1d' and the deuterated 1s

\[
\begin{align*}
1s & \quad \text{D}_{3}C \quad 1d' \\
\text{Cu(hfacac)}_{2} (1 \text{ equiv}) & \quad \text{O}_{2} (1 \text{ atm}) \\
\text{K}_{2}\text{CO}_{3} (3 \text{ equiv}) & \quad \text{MeCN, 80 °C, 3 h} \\
2s:2s' &= -1:1 \ (80\%)
\end{align*}
\]

\[
\begin{align*}
2d & + \\
2s' &= -1:1 \ (82\%)
\end{align*}
\]

$^1$H NMR spectra of the crossover products: 2s and 2s' mixture was measured in THF-d$_8$
\(^1\)H NMR spectra of the crossover products: 2d and 2d' mixture was measured in acetone-\(d_6\)

Scheme S2. Radical scavenging experiments in the presence of TEMPO or BHT.
Analytical data for compounds.

**5,10-Dimethyl-5,10-dihydroindolo[3,2-b]indole, (2a)**
![Chemical structure of 5,10-Dimethyl-5,10-dihydroindolo[3,2-b]indole]

White solid (80%, 0.16 mmol, 37.5 mg); $^1$H NMR (400 MHz, THF-d$_8$) $\delta$ 7.89 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.22 (t, $J = 8.0$ Hz, 2H), 7.06 (t, $J = 8.0$ Hz, 2H), 4.10 (s, 6H); $^{13}$C NMR (100 MHz, THF-d$_8$) $\delta$ 141.42, 126.28, 121.33, 117.82, 117.19, 115.02, 109.28, 30.72; HRMS (APCI) calcd for C$_{16}$H$_{14}$N$_2$, [M+H]$^+$: 235.12297, found: 235.12290.

**3-(tert-Butyl)-5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole, (2b)**
![Chemical structure of 3-(tert-Butyl)-5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole]

White solid (78%, 0.156 mmol, 45.3 mg); $^1$H NMR (400 MHz, THF-d$_8$) $\delta$ 7.89 (d, $J = 0.8$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.38-7.31 (m, 2H), 7.18 (t, $J = 8.0$ Hz, 1H), 7.05 (d, $J = 8.0$ Hz, 1H), 4.10 (s, 3H), 4.05 (s, 3H), 1.42 (s, 9H); $^{13}$C NMR (100 MHz, THF-d$_8$) $\delta$ 141.33, 140.47, 139.87, 126.50, 126.44, 121.09, 119.54, 117.71, 117.08, 115.11, 114.82, 113.09, 109.24, 108.92, 34.27, 31.05, 30.80, 30.76; HRMS (APCI) calcd for C$_{20}$H$_{22}$N$_2$, [M+H]$^+$: 291.18558, found: 291.18560.

**3,5,10-Trimethyl-5,10-dihydroindolo[3,2-b]indole, (2c)**
![Chemical structure of 3,5,10-Trimethyl-5,10-dihydroindolo[3,2-b]indole]

White solid (from 1c: 81%, 0.162 mmol, 40.2 mg; from 1c': 45%, 0.09 mmol, 22.3 mg); $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.90 (d, $J = 8.0$ Hz, 1H), 7.71 (s, 1H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 1H), 7.29 (t, $J = 8.0$ Hz, 1H), 7.18-7.13 (m, 2H), 4.09 (s, 3H), 4.07 (s, 3H), 2.54 (s, 3H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) 141.39, 140.00, 127.57, 126.74, 126.24, 123.41, 121.74, 118.20, 117.57, 117.45, 115.09, 115.06, 109.71, 109.48, 31.95, 31.89, 21.59; HRMS (APCI) calcd for C$_{17}$H$_{16}$N$_2$, [M+H]$^+$: 249.13862, found: 249.13865.

**Methyl 5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole-3-carboxylate, (2d)**
![Chemical structure of Methyl 5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole-3-carboxylate]

White solid (from 1d: 70%, 0.14 mmol, 40.9 mg; from 1d': 80%, 0.16 mmol, 46.7 mg); $^1$H NMR (400 MHz, Acetone-d$_6$) $\delta$ 8.60 (d, $J = 1.6$ Hz, 1H), 7.98-7.91 (m, 2H), 7.56 (d, $J = 8.8$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.33-7.28 (m, 1H), 7.15 (td, $J = 8.4, 1.2$ Hz, 1H), 4.15 (s, 3H), 4.14 (s, 3H), 3.90 (s, 3H); $^{13}$C NMR (100 MHz, Acetone-d$_6$) 168.10, 143.85, 142.26, 127.99, 127.13, 123.43, 123.05, 120.81, 120.75, 119.26, 118.47, 115.40, 115.03, 110.69, 110.06, 51.90, 31.97, 31.84; HRMS (APCI) calcd for C$_{18}$H$_{16}$N$_2$O$_2$, [M+H]$^+$: 293.12845, found: 293.12846.

**3-Bromo-5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole, (2e)**
White solid (from 1e: 75%, 0.15 mmol, 46.8 mg; from 1e': 87%, 0.174 mmol, 54.3 mg); \(^1\)H NMR (400 MHz, Acetone-\(d_2/\text{CD}_2\text{Cl}_2\)) \(\delta\) 8.01 (d, \(J = 2.0\) Hz, 1H), 7.91 (d, \(J = 7.6\) Hz, 1H), 7.47 (d, \(J = 8.4\) Hz, 1H), 7.39 (d, \(J = 8.8\) Hz, 1H), 7.34-7.27 (m, 2H), 7.15-7.11 (t, \(J = 8.0\) Hz, 1H), 4.06 (s, 3H), 4.05 (s, 3H); \(^{13}\)C NMR (100 MHz, Acetone-\(d_2/\text{CD}_2\text{Cl}_2\)) \(\delta\) 142.13, 140.20, 127.89, 125.61, 124.44, 122.89, 120.29, 118.82, 118.29, 116.50, 115.01, 111.77, 111.01, 110.28, 31.74, 31.61.

HRMS (APCI) calcd for \(\text{C}_{16}\text{H}_{13}\text{BrN}_2\), [M+H]+: 313.03349, found: 313.03351.

3-Chloro-5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole, (2f)

White solid (80%, 0.16 mmol, 42.9 mg); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.88 (d, \(J = 8.0\) Hz, 1H), 7.83 (d, \(J = 2.0\) Hz, 1H), 7.43 (d, \(J = 8.4\) Hz, 1H), 7.35-7.30 (m, 2H), 7.23 (dd, \(J = 8.8, 2.0\) Hz, 1H), 7.17 (t, \(J = 7.6\) Hz, 1H), 4.03 (s, 3H), 4.00 (s, 3H); \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 141.66, 139.55, 127.71, 125.49, 123.60, 122.52, 121.59, 118.48, 117.86, 116.97, 115.42, 114.67, 110.71, 109.87, 31.98, 31.82.; HRMS (APCI) calcd for \(\text{C}_{16}\text{H}_{13}\text{ClN}_2\), [M+H]+: 269.08400, found: 269.08403.

3-Fluoro-5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole, (2g)

White solid (73%, 0.146 mmol, 36.8 mg); \(^1\)H NMR (400 MHz, THF-\(d_8\)) \(\delta\) 7.89 (d, \(J = 7.6\) Hz, 1H), 7.60 (dd, \(J = 9.6, 2.4\) Hz, 1H), 7.43 (d, \(J = 8.4\) Hz, 1H), 7.38 (dd, \(J = 8.8, 4.4\) Hz, 1H), 7.23 (dd, \(J = 8.8, 2.0\) Hz, 1H), 7.17 (t, \(J = 7.6\) Hz, 1H), 6.98 (td, \(J = 9.2, 2.4\) Hz, 1H), 4.05 (s, 3H), 4.03 (s, 3H); \(^{13}\)C NMR (100 MHz, THF-\(d_8\)) \(\delta\) 157.00 (d, \(J_1 = 230.5\) Hz), 141.84, 137.98, 128.02, 125.90 (d, \(J_6 = 4.2\) Hz), 121.96, 117.90, 117.48, 114.81, 114.38 (d, \(J = 10.7\) Hz), 109.90 (d, \(J = 9.1\) Hz), 109.38, 108.94 (d, \(J = 25.5\) Hz), 102.35 (d, \(J = 24.7\) Hz), 30.83, 30.53; \(^{19}\)F NMR (658.8 MHz, THF-\(d_8\)) \(\delta\) -130.90; HRMS (MALDI) calcd for \(\text{C}_{16}\text{H}_{13}\text{FN}_2\), [m/z]: 252.10573, found: 252.10574.

3,5,8,10-Tetramethyl-5,10-dihydroindolo[3,2-b]indole, (2h)

White solid (80%, 0.16 mmol, 41.9 mg); \(^1\)H NMR (400 MHz, THF-\(d_8\)) \(\delta\) 7.67 (s, 2H), 7.29 (d, \(J = 8.4\) Hz, 2H), 7.02 (d, \(J = 8.0\) Hz, 2H), 4.04 (s, 6H), 2.47 (s, 6H); \(^{13}\)C NMR (100 MHz, THF-\(d_8\)) \(\delta\) 140.06, 126.61, 126.31, 122.71, 117.00, 115.26, 108.95, 83.90, 30.74, 20.76; HRMS (APCI) calcd for \(\text{C}_{18}\text{H}_{18}\text{N}_2\), [M+H]+: 263.15428, 263.15430.

3,8-Difluoro-5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole, (2i)
White solid (72%, 0.144 mmol, 38.9 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (dd, $J = 9.2, 2.4$ Hz, 2H), 7.31 (dd, $J = 8.8, 4.4$ Hz, 2H), 7.06 (td, $J = 9.2, 2.4$ Hz, 2H), 4.03 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.74 (d, $J^1 = 231.8$ Hz), 137.93, 127.43 (d, $J^5 = 4.1$ Hz), 113.98 (d, $J^4 = 10.7$ Hz), 105.10 (d, $J^3 = 18.2$ Hz), 109.92 (d, $J^6 = 1.7$ Hz), 102.77 (d, $J^2 = 21.7$ Hz), 31.69; $^{19}$F NMR (658.8 MHz, CDCl$_3$) $\delta$ -127.46; HRMS (APCI) calcd for C$_{16}$H$_{12}$F$_2$N$_2$ $[M+H]^+$: 271.1041, found: 271.1041.

Methyl 5,8,10-trimethyl-5,10-dihydroindolo[3,2-b]indole-3-carboxylate, (2j)

White solid (80%, 0.16 mmol, 49.0 mg); $^1$H NMR (400 MHz, THF-d$_8$) $\delta$ 8.60 (s, 1H), 7.91 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.71 (d, $J = 0.8$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.09 (d, $J = 8.4$ Hz, 1H), 4.10 (s, 3H), 4.07 (s, 3H), 3.87 (s, 3H), 2.49 (s, 3H); $^{13}$C NMR (100 MHz, THF-d$_8$) $\delta$ 167.01, 143.05, 140.12, 127.18, 126.87, 126.46, 122.48, 119.99, 119.77, 117.13, 114.83, 114.39, 109.27, 108.70, 50.74, 30.87, 30.82, 20.74; HRMS (APCI) calcd for C$_{19}$H$_{18}$N$_2$O$_2$, [M+H]$^+$: 307.1441, found: 307.1441.

3-Fluoro-5,8,10-trimethyl-5,10-dihydroindolo[3,2-b]indole, (2k)

White solid (73%, 0.146 mmol, 38.9 mg); $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.55 (s, 1H), 7.38 (dd, $J = 9.6, 2.4$ Hz, 1H) 7.20-7.16 (m, 2H), 7.02 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.90 (td, $J = 9.2, 2.4$ Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) $\delta$ 156.97 (d, $J^1 = 230.2$ Hz), 140.24, 137.94, 127.90, 127.63, 126.28 (d, $J^6 = 4.2$ Hz), 124.00, 117.65, 114.86, 114.38 (d, $J^3 = 10.8$ Hz), 110.18 (d, $J^5 = 9.9$ Hz), 109.50, 109.28 (d, $J^2 = 26.4$ Hz), 102.63 (d, $J^4 = 24.7$ Hz), 31.96, 31.72, 21.56; $^{19}$F NMR (658.8 MHz, CD$_2$Cl$_2$) $\delta$ -128.65; HRMS (APCI) calcd for C$_{17}$H$_{15}$FN$_2$, [M+H]$^+$: 267.1292, found: 267.1292.

7,14-Dimethyl-7,14-dihydrobenzo[g]benzo[6,7]indolo[3,2-b]indole, (2l)

Yellow solid(50%, 0.1 mmol, 33.4 mg); $^1$H NMR (400 MHz, CD$_2$Cl$_2$/CS$_2$) $\delta$ 8.68 (d, $J = 8.8$ Hz, 2H), 8.13 (d, $J = 8.8$ Hz, 2H), 8.00 (d, $J = 8.8$ Hz, 2H), 7.61 (d, $J = 9.2$ Hz, 2H), 7.60 (td, $J = 8.4, 1.6$ Hz, 2H), 7.49-7.45 (m, 2H), 4.71 (s, 6H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$/CS$_2$) $\delta$ 135.05, 131.51, 129.56, 127.45, 125.57, 124.18, 123.76, 121.55, 120.19, 117.71, 111.46, 37.55; HRMS (APCI) calcd for C$_{24}$H$_{18}$N$_2$, [M]: 335.15428, found: 335.15430.

5-Ethyl-10-methyl-5,10-dihydroindolo[3,2-b]indole, (2m)
White solid (75%, 0.15 mmol, 37.2 mg); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.94 (d, \(J = 7.6\) Hz, 1H), 7.88 (d, \(J = 8.0\) Hz, 1H), 7.48 (t, \(J = 8.0, 2H\)), 7.35-7.29 (m, 2H), 7.22-7.16 (m, 2H), 4.55 (q, \(J = 7.2\) Hz, 2H), 4.11 (s, 3H), 1.51 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 141.55, 140.39, 126.92, 125.51, 121.97, 121.94, 118.48, 118.34, 117.84, 114.90, 109.86, 40.18, 31.89, 15.40, 15.35; HRMS (APCI) calcd for C\(_{17}\)H\(_{16}\)N\(_2\), [M+H]+: 249.1386, found: 249.13869.

5-Benzyl-10-methyl-5,10-dihydroindolo[3,2-b]indole, (2n)

Yellow solid (25%, 0.05 mmol, 16.2 mg); \(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 8.01 (d, \(J = 7.2\) Hz, 1H), 7.75 (d, \(J = 7.2\) Hz, 1H), 7.61 (d, \(J = 8.4\) Hz, 1H), 7.52 (d, \(J = 8.4\) Hz, 1H), 7.25-7.12 (m, 7H), 7.14 (t, \(J = 8.0\) Hz, 1H), 5.82 (s, 2H), 4.17 (s, 3H); \(^{13}\)C NMR (100 MHz, Acetone-\(d_6\)) \(\delta\) 142.19, 141.88, 139.62, 129.41, 128.08, 127.51, 122.71, 122.52, 119.31, 118.97, 118.51, 118.48, 116.02, 115.56, 111.02, 110.51, 49.02, 31.78; HRMS (APCI) calcd for C\(_{22}\)H\(_{18}\)N\(_2\), [m/z]: 311.15428, found: 311.15428.

5,10-Diethyl-5,10-dihydroindolo[3,2-b]indole, (2o)

White solid (40%, 0.08 mmol, 20.9 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 7.6\) Hz, 2H), 7.06 (t, \(J = 8.0\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.40, 126.27, 121.31, 117.79, 117.19, 114.99, 109.28, 30.01 (m); HRMS (APCI) calcd for C\(_{15}\)H\(_8\)D\(_2\)N\(_2\), [m/z]: 240.15281, found: 240.15284.

5,10-Bis(methyl-d\(_3\))-5,10-dihydroindolo[3,2-b]indole, (2s)

White solid (70%, 0.14 mmol, 33.6 mg); \(^1\)H NMR (400 MHz, THF-d\(_6\)) \(\delta\) 7.89 (d, \(J = 7.6\) Hz, 2H), 7.43 (d, \(J = 8.8\) Hz, 2H), 7.06 (t, \(J = 8.0\) Hz, 2H); \(^{13}\)C NMR (100 MHz, THF-d\(_6\)) \(\delta\) 141.40, 126.27, 121.31, 117.79, 117.19, 114.99, 109.28, 30.01 (m); HRMS (APCI) calcd for C\(_{15}\)H\(_8\)D\(_3\)N\(_2\), [m/z]: 240.15281, found: 240.15284.

2-(1-Methyl-1H-indol-2-yl)aniline, (4c)
Yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 8.4$ Hz, 1H), 7.29-7.23 (m, 2H). 7.20-7.14 (m, 2H), 6.86-6.80 (m, 2H), 6.55 (s, 1H), 3.84 (bs, 2H, -NH$_2$), 3.61 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.21, 137.91, 137.72, 131.60, 129.05, 121.53, 120.43, 119.71, 118.24, 118.06, 115.44, 109.57, 101.84, 30.46; HRMS (APCI) calcd for C$_{15}$H$_{14}$N$_2$: [M+H]$^+$: 223.12297, found: 223.12297.

$\text{N-Methyl-2-[1-methyl-1H-indol-2-yl]aniline}$

Pale yellow oil (70%, 0.14 mmol, 33.1 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (td, $J = 8.0$, 0.8 Hz, 1H), 7.39-7.34 (m, 2H), 7.29-7.25 (m, 1H), 7.17 (td, $J = 7.2$, 1.6 Hz, 2H), 6.79 (td, $J = 7.2$, 0.8 Hz, 1H), 6.73 (d, $J = 8.4$ Hz, 1H), 6.54 (s, 1H), 4.02 (bs, 1H), 3.60 (s, 3H), 2.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.04, 137.94, 137.65, 131.31, 130.10, 128.05, 121.50, 120.40, 119.70, 117.51, 116.23, 109.65, 101.92, 30.45, 30.34.

$\text{2-((2-Aminophenyl)ethynyl)-N,N-dimethylaniline (1a)}$

Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.39 (dd, $J = 8.0$, 2.0 Hz, 1H), 7.28 (td, $J = 8.8$, 2.0 Hz, 1H), 7.14 (td, $J = 8.4$, 1.6 Hz, 1H), 6.99 (d, $J = 8.4$ Hz, 1H), 6.95 (td, $J = 8.0$, 1.2 Hz, 1H), 6.74-6.71 (m, 2H), 4.46 (bs, 2H), 2.97 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.58, 147.67, 133.51, 131.50, 129.40, 129.01, 121.06, 117.66, 117.37, 116.15, 114.11, 108.45, 94.00, 91.24, 43.97. HRMS (ESI positive) calcd for C$_{16}$H$_{16}$N$_2$: [M+Na]$^+$: 259.1188, found: 259.1188.

$\text{2-((2-Aminophenyl)ethynyl)-4-(tert-butyl)-N,N-dimethylaniline (1b)}$

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, $J = 2.4$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.34 (dd, $J = 8.8$, 2.4 Hz, 1H), 7.16 (t, $J = 8.0$ Hz, 1H), 6.98 (d, $J = 8.8$ Hz, 1H), 6.77-6.74 (m, 2H), 4.53 (bs, 2H), 2.96 (s, 6H), 1.36 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.29, 147.71, 143.81, 131.38, 130.16, 129.26, 126.08, 117.51, 117.05, 115.83, 114.02, 108.42, 94.42, 90.65, 44.05, 34.00, 31.31. HRMS (ESI positive) calcd for C$_{20}$H$_{24}$N$_2$: [M+Na]$^+$: 315.1832, found: 315.1832.

$\text{2-((2-Aminophenyl)ethynyl)-N,N-4-trimethylaniline, (1c)}$

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J = 8.0$ Hz, 1H), 7.34 (s, 1H), 7.17-7.09 (m, 2H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.75-6.72 (m, 2H), 4.50 (bs, 2H), 2.93 (s, 6H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.55, 147.83, 133.72, 131.47, 130.67, 129.76, 129.38, 117.60, 117.44, 116.42, 114.08, 108.47, 94.06, 90.92, 44.13, 20.28; HRMS (ESI) calcd for C$_{17}$H$_{18}$N$_2$: [M+Na]$^+$: 273.1362, found: 273.1362.
Methyl 3-[(2-aminophenyl)ethynyl]-4-(dimethylamino)benzoate, (1d)

\[
\text{MeO}_2\text{C} \quad \text{H}_2\text{N} \\
\text{Me} \quad \equiv \quad \equiv \\
\text{Me} \\
\]

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.13\) (d, \(J = 2.8\) Hz, 1H), 7.87 (dd, \(J = 8.8, 2.0\) Hz, 1H), 7.35 (d, 8.0 Hz, 1H), 7.13 (td, \(J = 8.0, 1.6\) Hz, 1H), 6.86 (d, \(J = 8.8\) Hz, 1H), 6.74-6.70 (m, 2H), 4.34 (bs, 2H), 3.89 (s, 3H), 3.10 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 166.51, 157.21, 147.63, 136.16, 131.66, 130.55, 129.63, 120.80, 117.83, 115.73, 114.28, 112.84, 108.18, 93.61, 91.37, 51.82; HRMS (ESI) calcd for C\(_{18}\)H\(_{18}\)N\(_2\)O\(_2\), [M+Na]\(^+\): 317.1260, found: 317.1260.

2-[(2-Aminophenyl)ethynyl]-4-bromo-N,N-dimethylaniline, (1e)

\[
\text{Br} \\
\text{H}_2\text{N} \\
\text{Me} \\
\text{Me} \\
\equiv \equiv \\
\text{Me} \\
\]

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.57\) (d, \(J = 2.4\) Hz, 1H), 7.36-7.32 (m, 2H), 7.14 (td, \(J = 8.0, 1.6\) Hz, 2H), 6.83 (d, \(J = 8.0\) Hz, 1H), 6.73-6.70 (m, 2H), 4.40 (bs, 2H), 2.94 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 153.58, 147.86, 135.72, 131.77, 131.71, 129.87, 118.94, 117.84, 117.82, 114.26, 112.94, 107.91, 92.60, 92.49, 43.73; HRMS (ESI) calcd for C\(_{16}\)H\(_{15}\)BrN\(_2\), [M+Na]\(^+\): 337.0311, found 337.0311.

2-[(2-Amino-5-methylphenyl)ethynyl]-N,N-dimethylaniline, (1c’)

\[
\text{H}_2\text{N} \\
\text{Me} \\
\equiv \equiv \\
\text{Me} \\
\text{Me} \\
\]

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.48\) (dd, \(J = 7.6, 1.2\) Hz, 1H), 7.28 (m, 1H), 7.19 (s, 1H), 6.99-6.91 (m, 3H), 6.84 (d, \(J = 8.0\) Hz, 1H), 4.24 (bs, 2H), 2.94 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 154.50, 145.33, 133.51, 131.56, 130.22, 128.91, 126.83, 120.96, 117.28, 116.13, 114.30, 108.44, 93.70, 91.44, 43.89, 20.32; HRMS (ESI) calcd for C\(_{17}\)H\(_{15}\)N\(_2\), [M+H]\(^+\): 251.1543, found 251.1543.

Methyl 4-amino-3-[(2-(dimethylamino)phenyl)ethynyl]benzoate, (1d’)

\[
\text{N} \quad \equiv \quad \equiv \\
\text{Me} \quad \text{CO}_2\text{Me} \\
\text{Me} \\
\text{Me} \\
\]

Pale yellow solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.06\) (d, \(J = 2.0\) Hz, 1H), 7.81 (dd, \(J = 8.4, 2.0\) Hz, 1H), 7.48, (dd, \(J = 7.6, 1.6\) Hz, 1H), 7.28 (td, \(J = 8.8, 1.6\) Hz, 1H), 7.02 (d, \(J = 8.0\) Hz, 1H), 6.97 (t, \(J = 7.6\) Hz, 1H), 6.69 (d, \(J = 8.4\) Hz, 1H), 4.94 (bs, 2H), 3.87 (s, 3H), 2.95 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 166.56, 151.48, 133.60, 133.49, 131.21, 129.33, 121.48, 119.07, 117.64, 115.98, 113.03, 107.58, 94.36, 90.19, 51.75, 44.13; HRMS (ESI) calcd for C\(_{18}\)H\(_{18}\)N\(_2\O_2\), [M+H]\(^+\): 295.1441, found 295.1441.

2-[(2-Amino-5-bromophenyl)ethynyl]-N,N-dimethylaniline, (1e’)

\[
\text{N} \quad \equiv \quad \equiv \\
\text{Br} \quad \text{Me} \\
\text{Me} \\
\text{Me} \\
\]


Pale yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49-7.46 (m, 2H), 7.31-7.27 (m, 1H), 7.20 (dd, \(J = 8.8, 2.4\) Hz, 1H), 6.99 (d, \(J = 8.4\) Hz, 1H), 6.95 (td, \(J = 7.6, 1.2\) Hz, 1H), 6.59 (d, \(J = 8.8\) Hz, 1H), 4.48 (br, 2H), 2.95 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.76, 146.76, 133.48, 133.36, 132.00, 129.35, 121.03, 117.37, 115.54, 115.48, 110.25, 108.60, 95.15, 89.73, 43.92; HRMS (ESI) calcd for \(\text{C}_{16}\text{H}_{15}\text{BrN}_{2}\), [M+Na]\(^+\): 337.0311, found: 337.0311.

2-[(2-Amino-5-chlorophenyl)ethynyl]-\(N,N\)-dimethylaniline, (1f)

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.41 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.26 (d, \(J = 2.4\) Hz, 1H), 7.22 (t, \(J = 8.0\) Hz, 1H), 7.01 (dd, \(J = 8.8, 2.4\) Hz, 1H), 6.93 (d, \(J = 8.0\) Hz, 1H), 6.88 (t, \(J = 7.6\) Hz, 1H), 6.58 (d, \(J = 8.4\) Hz, 1H), 4.39 (bs, 2H), 2.89 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.73, 146.29, 133.56, 130.62, 129.38, 129.28, 121.92, 121.14, 117.46, 115.63, 115.17, 109.79, 95.00, 89.94, 43.99; HRMS (ESI) calcd for \(\text{C}_{16}\text{H}_{15}\text{ClN}_{3}\), [M+Na]\(^+\): 293.0816, found: 293.0816.

2-[(2-Amino-5-fluorophenyl)ethynyl]-\(N,N\)-dimethylaniline, (1g)

Pale yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.48 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.30-7.26 (m, 1H), 7.01 (dd, \(J = 8.8, 3.2\) Hz, 1H), 6.99 (d, \(J = 7.6\) Hz, 1H), 6.94 (td, \(J = 8.0, 1.2\) Hz, 1H), 6.86 (td, \(J = 8.8, 2.8\) Hz, 1H), 6.65 (dd, \(J = 8.4, 4.0\) Hz, 1H), 4.31 (bs, 2H), 2.95 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 155.16 (d, \(J^\prime = 234.7\) Hz), 154.88, 144.17 (d, \(J^\prime = 1.7\) Hz), 133.67, 129.43, 121.09, 117.45, 117.20 (d, \(J^\prime = 23.1\) Hz), 116.54 (d, \(J^\prime = 23.1\) Hz), 115.64, 115.06 (d, \(J^\prime = 8.2\) Hz), 109.2 (d, \(J^\prime = 9.0\) Hz), 94.76, 90.26 (d, \(J^\prime = 3.3\) Hz), 43.90; \(^{19}\)F NMR (658.8 MHz, CDCl\(_3\)), \(\delta\) -128.87; HRMS (ESI) calcd for \(\text{C}_{16}\text{H}_{15}\text{FN}_{3}\), [M+Na]\(^+\): 255.1292, found: 255.1292.

2-[(2-Amino-5-methylphenyl)ethynyl]-\(N,N\)-4-trimethylaniline, (1h)

Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31 (d, \(J = 2.0\) Hz, 1H), 7.18, (s, 1H), 7.07 (dd, \(J = 8.4, 2.0\) Hz, 1H), 6.95 (dd, \(J = 8.4, 2.0\) Hz, 1H), 6.91 (d, \(J = 8.0\) Hz, 1H), 6.65 (d, \(J = 8.0\) Hz, 1H), 4.34 (bs, 2H), 2.92 (s, 6H), 2.29 (s, 3H), 2.25 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.36, 145.40, 133.77, 131.56, 130.61, 130.19, 129.66, 126.83, 117.39, 116.40, 114.28, 108.52, 93.76, 91.16, 44.19, 20.39, 20.35; HRMS (ESI) calcd for \(\text{C}_{18}\text{H}_{16}\text{N}_{3}\), [M+H]\(^+\): 265.1699, found: 265.1699.

2-[(2-Amino-5-fluorophenyl)ethynyl]-4-fluoro-\(N,N\)-dimethylaniline, (1i)

Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.17 (dd, \(J = 8.4, 2.8\) Hz, 1H), 7.05 (dd, \(J = 8.8, 3.2\) Hz, 1H), 7.01-6.92 (m, 2H), 6.87 (td, \(J = 8.4, 2.8\) Hz, 1H), 6.65 (dd, \(J = 8.8, 4.4\) Hz, 1H), 4.35 (bs, 2H), 2.88 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.19 (d, \(J^\prime = 239.2\) Hz), 154.93 (d, \(J^\prime = 233.5\) Hz), 151.42 (d, \(J^{12} = 16\))
2.5 Hz), 144.39 (d, $J^2 = 1.6$ Hz), 119.53 (d, $J^3 = 24.0$ Hz), 118.87 (d, $J^p = 8.3$ Hz), 117.66 (d, $J'^{p} = 9.1$ Hz), 117.10 (d, $J'^3 = 23.1$ Hz), 116.92 (d, $J'^2 = 23.1$ Hz), 115.97 (d, $J'^{b} = 21.5$ Hz), 115.05 (d, $J'^{p} = 8.2$ Hz), 108.41 (d, $J'^b = 9.1$ Hz), 93.387 (d, $J^{1} = 2.5$ Hz), 91.02 (d, $J^{2} = 2.4$ Hz), 44.35; $^{19}$F NMR (658.8 MHz, CDCl$_3$) δ -128.77; HRMS (ESI) calcld for C$_{18}$H$_{14}$F$_2$N$_2$: 273.1198, found: 273.1198.

**Methyl 4-amino-3-((2-(dimethylamino)-5-methylphenyl)ethynyl)benzoate, (1j)**

Yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, $J = 1.6$ Hz, 1H), 7.80 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.30 (s, 1H), 7.08 (dd, $J = 8.4$, 2.0 Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.67 (d, $J = 8.8$ Hz, 1H), 5.05 (bs, 2H), 3.87 (s, 3H), 2.87 (s, 6H), 2.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.61, 152.69, 151.70, 133.52, 133.42, 131.09, 130.91, 130.01, 118.78, 117.58, 116.16, 112.91, 107.53, 94.53, 89.70, 51.55, 44.17, 20.22; HRMS (ESI) calcld for C$_{18}$H$_{20}$N$_2$O$_2$: 331.1417, found: 331.1417.

**2-((2-Amino-5-fluorophenyl)ethynyl)-N,N-4-trimethylaniline, (1k)**

Bright yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (s, 1H), 7.12-7.07 (m, 2H), 6.92 (d, $J = 8.4$, 1H), 6.86 (td, $J = 8.8$, 2.8 Hz, 1H), 6.65 (dd, $J = 8.8$, 4.0 Hz, 1H), 4.30 (bs, 2H), 2.92 (s, 6H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.99 (d, $J = 233.5$ Hz), 152.54, 144.16 (d, $J = 1.6$ Hz), 133.74. 130.72, 130.08, 117.49, 116.73 (d, $J = 24.0$ Hz), 116.41 (d, $J = 23.1$ Hz), 115.83, 114.95 (d, $J = 8.3$ Hz), 109.15 (d, $J = 9.9$ Hz), 94.75, 89.96 (d, $J = 3.3$ Hz), 44.18, 20.33; $^{19}$F NMR (658.8 MHz, CDCl$_3$) δ -128.93; HRMS (ESI) calcld for C$_{18}$H$_{21}$F$_{2}$N$_{2}$: 269.1449, found: 269.1449.

**2-((1-Aminonaphthalen-2-yl)ethynyl)-N,N-dimethynaphthalen-1-amine, (1l)**

Yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, $J = 8.0$ Hz, 1H), 7.76 (t, $J = 8.0$, 3H), 7.56-7.41 (m, 7H), 7.24-7.19 (m, 1H), 4.95 (bs, 2H), 3.18 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.37, 144.46, 134.30, 133.97, 131.84, 130.28, 128.56, 127.95, 126.54, 126.45, 126.08, 125.35, 124.62, 124.55, 122.49, 120.87, 118.09, 116.75, 102.61, 95.26, 92.49, 44.07; HRMS (ESI) calcld for C$_{28}$H$_{20}$N$_2$: 359.1519, found: 359.1519.

**2-((2-Aminophenyl)ethynyl)-N-ethyl-N-methylaniline, (1m)**

Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (dd, $J = 7.6$, 2.0 Hz, 1H), 7.40 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.29 (td, $J = 8.0$, 1.2 Hz, 1H), 7.15 (td, $J = 7.6$, 1.6 Hz, 1H), 7.02 (d, $J = 8.4$ Hz, 1H), 6.96 (td, $J = 8.0$, 0.8 Hz, 1H), 6.75-6.72 (m, 2H), 4.49 (bs, 2H), 3.37 (q, $J = 7.2$ Hz, 2H), 2.89 (s, 3H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.22, 147.80, 133.54, 131.45, 129.37, 128.90, 121.02, 118.49, 117.59,
116.66, 114.06, 108.42, 94.11, 90.74, 50.15, 39.87, 12.55; HRMS (ESI) calcd for C_{17}H_{18}N_{2}, [M+Na]^+: 273.1362, found: 273.1363.

2-((2-Aminophenyl)ethynyl)-N-benzyl-N-methylaniline, (1n)

Yellow oil; 1H NMR (400 MHz, CDCl₃) δ 7.53 (dd, J = 8.0, 2.0 Hz, 1H), 7.39-7.23 (m, 6H), 7.12-7.08 (m, 2H), 6.01-6.95 (m, 2H), 4.52 (s, 2H), 4.26 (bs, 2H), 2.81 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 153.89, 147.66, 138.56, 133.90, 131.72, 129.39, 128.34, 127.02, 121.18, 118.58, 117.64, 116.34, 114.04, 108.34, 93.90, 91.26, 59.90, 40.17; HRMS (ESI) calcd for C_{22}H_{20}N_{2}, [M+Na]^+: 335.1519, found: 335.1519.

2-((2-Aminophenyl)ethynyl)-N,N-diethylaniline, (1o)

Pale yellow oil; 1H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 6.8 Hz, 1H), 7.34 (dd, J = 7.6, 1.6 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.73-6.68 (m, 2H), 4.58 (bs, 2H), 3.30 (q, J = 6.8 Hz, 4H), 1.07 (t, J = 6.8 Hz, 6H); 13C NMR (100 MHz, CDCl₃) δ 152.41, 147.97, 133.11, 131.23, 129.33, 128.50, 121.70, 120.95, 118.90, 117.51, 113.95, 108.51, 94.50, 90.41, 46.61, 12.27; HRMS (ESI) calcd for C_{18}H_{20}N_{2}, [M+H]^+: 265.1699, found: 265.1700.

2-((2-Aminophenyl)ethynyl)-N-methyl-N-phenylaniline, (1p)

Yellow solid; 1H NMR (400 MHz, CDCl₃) δ 7.63 (dd, J = 8.0, 1.6 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.28-7.20 (m, 5H), 7.07 (t, J = 8.0 Hz, 1H), 6.81 (td, J = 7.6, 1.2 Hz, 1H), 6.76 (dd, J = 8.0, 1.2 Hz, 2H), 6.65 (t, J = 8.0 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 3.79 (bs, 2H), 3.38 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 149.23, 148.90, 147.95, 133.41, 131.84, 129.63, 129.00, 127.93, 125.74, 122.67, 117.67, 117.34, 113.97, 113.81, 107.51, 92.25, 90.85, 39.58.

2-((2-Aminophenyl)ethynyl)-N,N-diphenylaniline, (1q)

Pale yellow solid; 1H NMR (400 MHz, CDCl₃) δ 7.52 (dd, J = 8.0, 1.6 Hz, 1H), 7.23 (td, J = 7.6, 1.6 Hz, 1H), 7.18-7.05 (m, 6H), 7.00-6.93 (m, 6H), 6.89 (t, J = 7.6 Hz, 2H), 6.55-6.48 (m, 2H), 3.68 (bs, 2H); 13C NMR (100 MHz, CDCl₃) δ 147.64, 147.60, 147.30, 134.18, 132.25, 129.61, 129.54, 129.29, 129.11, 125.19, 122.40, 122.33, 122.00, 117.64, 114.18, 107.95, 92.42, 91.20.

2,2'-(Ethynyl-1,2-diyl)dianiline, (1r)

Pale yellow flake; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, $J = 8.0$ Hz, 2H), 7.16 (t, $J = 8.0$ Hz, 2H), 6.75-6.72 (m, 4H), 4.14 (bs, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.48, 131.93, 129.63, 117.93, 114.33, 108.00, 91.02.

$2'$-((2-Aminophenyl)ethynyl)-$N,N$-bis(methyl-$d_3$)aniline (1s)

Pale yellow oil; $^1$H NMR R (400 MHz, CDCl$_3$) δ 7.50 (dd, $J = 7.2, 1.6$ Hz, 1H), 7.39 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.28 (td, $J = 8.0, 1.6$ Hz, 1H), 7.14 (td, $J = 8.0, 1.6$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.95 (t, $J = 8.0$ Hz, 1H), 6.75-6.71 (m, 2H), 4.56 (bs, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.70, 147.75, 133.58, 131.53, 129.43, 129.06, 120.95, 117.67, 117.27, 116.05, 114.13, 108.47, 94.05, 91.19, 42.90 (m); HRMS (ESI) calcd for C$_{16}$H$_{10}$D$_6$N$_2$, [M+Na]$^+$: 265.1582, found: 265.1582.

$2'$-(2-Aminophenyl)ethynyl)-$N$-methylaniline, (3c)

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.36 (m, 2H), 7.26 (t, $J = 8.0$ Hz, 1H), 7.15 (td, $J = 8.0, 1.6$ Hz, 1H), 6.77-6.62 (m, 4H), 4.73 (bs, 1H), 4.27 (bs, 2H), 2.92 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.67, 147.60, 131.99, 130.06, 129.68, 117.94, 116.18, 114.34, 109.01, 108.03, 107.35, 91.29, 91.10, 30.27; HRMS (APCI positive) calcd for C$_{16}$H$_{14}$N$_2$, [M+H]$^+$: 237.13862, found 237.13865.

$N,N$-Dimethyl-$2'$-((2-(methylamino)phenyl)ethynyl)aniline, (3e)

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.37 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.28-7.21 (m, 2H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.95 (td, $J = 7.6, 0.8$ Hz, 1H), 6.65 (td, $J = 7.6, 0.8$ Hz, 1H), 6.61 (d, $J = 8.0$ Hz, 1H), 5.19 (bs, 1H), 2.95 (s, 3H), 2.93 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.66, 149.74, 133.20, 131.19, 129.74, 128.91, 121.25, 117.46, 116.50, 115.82, 108.66, 107.80, 94.29, 91.40, 44.08, 30.37.
NMR spectra

![NMR spectrum of compound 2a](image)

2a