Supporting Information

for

Expedient Copper-Free One-Pot Alkynylation-Cyclization Sequence for the Preparation of 2-Substituted 7-Azaindoles

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1. General considerations

All reactions were performed using Schlenk-tubes, septa, and syringes under nitrogen atmosphere. Reagents were purchased from standard sources such as ABCR GmbH & Co. KG, Alfa Aesar GmbH & Co. KG, Fisher Scientific GmbH, Merck KGaA, Sigma-Aldrich Chemie GmbH, VWR International GmbH, and used without further purification or were prepared using literature known procedures. The progress of all reactions was monitored using TLC silica gel 60 F254 aluminum sheets supplied by Merck KGaA (Darmstadt). The spots were detected using UV light at 254 nm and aqueous potassium permanganate solution. Crude products were adsorbed onto Celite® 545. Column chromatographic purification has been performed on a Biotage SP1 Flash Chromatography Purification system using SNAP 100 g cartridges and silica gel 60 M (0.040 – 0.063 mm), supplied by Macherey Nagel (Düren). Melting points (uncorrected) were measured on a Büchi Melting Point B-540. All NMR spectra were recorded on a Bruker AVIII 300 or Bruker AVIII 600 spectrometer, respectively. Chloroform-d with TMS, dimethylsulfoxide-d₆ and dimethylsulfoxide-d₆ with CS₂ have been used as deuterated solvents. The resonances of TMS or the non-deuterated (¹H NMR) or deuterated solvents (¹³C NMR), respectively have been used as internal standards (TMS: ¹H, δ 0.00, ¹³C, δ 0.00, CDCl₃: ¹H, δ 7.26, ¹³C, δ 77.16, DMSO-d₆: ¹H, δ 2.50, ¹³C, δ 39.52). To describe multiplicities, standard abbreviations were used. The type of carbon nuclei was determined by using 135-DEPT NMR spectroscopy. EI mass spectra were measured on a Finnigan TSQ 7000. IR spectra were measured on a Shimadzu IRAffinity-1 using ATR technique. Standard abbreviations were used to describe signal strength. HRMS was performed using a Bruker maxis 4G. Combustion analyses were performed on an Elementar vario MICRO cube in the microanalytical laboratory of the Institut für Medizinische und Pharmazeutische Chemie at the Heinrich-Heine-Universität Düsseldorf.
In a flame-dried Schlenk flask, di(1-adamantyl)phosphinic chloride (6.00 g, 16.5 mmol) was dissolved in 60.0 mL THF and the solution was cooled to -14 °C. Lithiumaluminiumhydride (1.50 g, 39.0 mmol) was added in three portions within 15 min and the solution was stirred at room temperature for 16 h. Afterwards, the reaction mixture was cooled to -14 °C and 30.0 mL of a 1 M HCl solution were slowly added. The aqueous phase was extracted three times with THF and the combined organic phases were dried with anhydrous sodium sulfate. The solvents were removed under reduced pressure to give 4.54 g of a colorless solid. Without further purification, di(1-adamantyl)phosphane (3.02 g, 10.0 mmol) was treated with benzylbromide (6.00 mL, 50.0 mmol) and the suspension was stirred at room temperature for 2 h. The crude product was filtered, washed three times with cold diethylether before removal of residual solvent under reduced pressure within 1 h to give di(1-adamantyl)benzyl-phosphonium bromide as a colorless solid; yield 3.3 g (70%).

\begin{align*}
{^1}H-\text{NMR} (300 \text{ MHz, CDCl}_3): & = 1.65-2.43 \text{ (m, 30 H), 3.74 (dd, } J = 13.3, 6.1 \text{ Hz, 2 H), 7.29-7.44 (m, 3 H), 7.65 (d, } J = 8.0 \text{ Hz, 2 H), 9.13 (t, } J = 6.1 \text{ Hz, 1 H).} \\
{^{13}}C-\text{NMR} (75 \text{ MHz, CDCl}_3): & = 19.7 (d, } J = 37.4 \text{ Hz, CH}_2, 27.7 (d, } J = 9.3 \text{ Hz, CH), 35.7 (d, } J = 1.5 \text{ Hz, CH}_2, 38.3 (d, } J = 2.8 \text{ Hz, CH}_2, 38.4 (d, } J = 30.9 \text{ Hz, C}_\text{quat}, 128.3 (d, } J = 2.2 \text{ Hz, CH), 129.7 (d, } J = 1.4 \text{ Hz, CH), 130.3 (d, } J = 5.9 \text{ Hz, CH), 130.6 (d, } J = 7.7 \text{ Hz, C}_\text{quat}. \\
\text{MS (EI\textsuperscript{+}, 70 eV): m/z (%) = 393 (8, 392 ([M\textsuperscript{+}-HBr, 27], 136 (11), 135 (100), 107 (5), 93 (10), 91 (5), 79 (9). IR (ATR): = 2901 (s), 2853 (m), 1497 (m), 1454 (m), 762 (m), 716 (m), 694 cm\textsuperscript{-1} (s).}
\end{align*}

\[ C_{27}H_{38}BrP \]
3. Analytical Data for compounds 4

Table 1. Experimental details for the preparation and purification of 2-substituted 7-azaindoles 4.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bromide 1 (1.00 mmol)</th>
<th>Alkyne 2 (1.20 mmol)</th>
<th>Product 4 (isolated yield)</th>
<th>Chromatographic purification ( R_f ) (eluent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-Bromopyridine-2-amine 1a</td>
<td>Phenylacetylene 2a</td>
<td>4a 173mg (0.89 mmol, 89%)</td>
<td>Ethyl acetate/( n )-hexane = 33% ( R_f ) (ethyl acetate/( n )-hexane = 50%) = 0.54</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>4-Ethynyl-1,2-dimethoxybenzene 2b</td>
<td>4b 214 mg (0.84 mmol, 84%)</td>
<td>Ethyl acetate/( n )-hexane = 45%—60% ( R_f ) (ethyl acetate/( n )-hexane = 50%) = 0.38</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>1-((\text{tert}-\text{Butyl})-4)-ethynylbenzene 2c</td>
<td>4c 225 mg (0.90 mmol, 90%)</td>
<td>Ethyl acetate/( n )-hexane = 25%—60% ( R_f ) (ethyl acetate/( n )-hexane = 33%) = 0.33</td>
</tr>
<tr>
<td>4</td>
<td>1a</td>
<td>(Prop-2-yn-1-yloxy)benzene 2d</td>
<td>4d 40 mg (0.18 mmol, 18%)</td>
<td>Ethyl acetate/( n )-hexane = 25%—60% ( R_f ) (ethyl acetate/( n )-hexane = 50%) = 0.60</td>
</tr>
<tr>
<td>5</td>
<td>1a</td>
<td>2-Ethynylpyridine 2e</td>
<td>4e 76 mg (0.39 mmol, 39%)</td>
<td>Methanol/DCM = 5% ( R_f ) (ethyl acetate/( n )-hexane = 50%) = 0.24</td>
</tr>
<tr>
<td>6</td>
<td>3-Bromo-5-methylpyridin-2-amine 1b</td>
<td>1-Hexyne 2f</td>
<td>4f 149 mg (0.79 mmol, 79%)</td>
<td>Ethyl acetate/( n )-hexane = 27% ( R_f ) (ethyl acetate/( n )-hexane = 50%) = 0.53</td>
</tr>
<tr>
<td>7</td>
<td>1a</td>
<td>But-3-yn-1-ol 2g</td>
<td>4g 32 mg (0.22 mmol, 22%)</td>
<td>Ethyl acetate/( n )-hexane = 20%—25% ( R_f ) (ethyl acetate/( n )-hexane = 33%) = 0.31</td>
</tr>
</tbody>
</table>
Table 1 (continuation). Experimental details for the preparation and purification of 2-substituted 7-azaindoles 4.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bromide 1 (1.00 mmol)</th>
<th>Alkyne 2 (1.20 mmol)</th>
<th>Product 4 (isolated yield)</th>
<th>Chromatographic purification Rf (eluent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1b</td>
<td>2a</td>
<td>4h</td>
<td>Ethyl acetate/n-hexane = 30% Rf (ethyl acetate/n-hexane = 50%) = 0.50</td>
</tr>
<tr>
<td>9</td>
<td>1a 1-Ethynyl-4-methoxybenzene 2h</td>
<td>4i</td>
<td>114 mg (0.51 mmol, 51%)</td>
<td>Ethyl acetate/n-hexane = 20% Rf (ethyl acetate/n-hexane = 50%) = 0.32</td>
</tr>
<tr>
<td>10</td>
<td>1b</td>
<td>2c</td>
<td>4j</td>
<td>Ethyl acetate/n-hexane = 33% Rf (ethyl acetate/n-hexane = 50%) = 0.52</td>
</tr>
<tr>
<td>11</td>
<td>1b</td>
<td>2h</td>
<td>4k</td>
<td>Ethyl acetate/n-hexane = 35% Rf (ethyl acetate/n-hexane = 50%) = 0.26</td>
</tr>
<tr>
<td>12</td>
<td>1a 5-Ethynyl-1,2,3-trimethoxybenzene 2i</td>
<td>4l</td>
<td>113 mg (0.40 mmol, 40%)</td>
<td>Ethyl acetate/n-hexane = 75% Rf (ethyl acetate/n-hexane = 75%) = 0.43</td>
</tr>
<tr>
<td>13</td>
<td>1b 5-Ethynyl-1,2,3-trimethoxybenzene 2i</td>
<td>4m</td>
<td>163 mg (0.55 mmol, 55%)</td>
<td>Ethyl acetate/n-hexane = 75% Rf (ethyl acetate/n-hexane = 75%) = 0.35</td>
</tr>
<tr>
<td>14</td>
<td>1a 1-Ethynyl-2-fluorobenzene 2j</td>
<td>4n</td>
<td>144 mg (0.68 mmol, 68%)</td>
<td>Ethyl acetate/n-hexane = 29% Rf (ethyl acetate/n-hexane = 50%) = 0.44</td>
</tr>
</tbody>
</table>

**Table 1 (continuation).** Experimental details for the preparation and purification of 2-substituted 7-azaindoles 4.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bromide 1 (1.00 mmol)</th>
<th>Alkyne 2 (1.20 mmol)</th>
<th>Product 4 (isolated yield)</th>
<th>Chromatographic purification Rf (eluent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>3-Bromo-5-chloropyridin-2-amine 1c³</td>
<td>2c</td>
<td><img src="image" alt="4o" /> 245 mg (0.86 mmol, 86%)</td>
<td>Ethyl acetate/n-hexane = 20% Rf (ethyl acetate/n-hexane = 20%) = 0.46</td>
</tr>
<tr>
<td>16</td>
<td>1c</td>
<td>2h</td>
<td><img src="image" alt="4p" /> 96 mg (0.37 mmol, 37%)</td>
<td>Ethyl acetate/n-hexane = 21% Rf (ethyl acetate/n-hexane = 50%) = 0.58</td>
</tr>
<tr>
<td>17</td>
<td>1a</td>
<td>1-ethynlnaphthalene 2k⁴</td>
<td><img src="image" alt="4q" /> 172 mg (0.70 mmol, 70%)</td>
<td>Ethyl acetate/n-hexane = 33% Rf (ethyl acetate/n-hexane = 50%) = 0.49</td>
</tr>
<tr>
<td>18</td>
<td>3-bromo-5-(trifluoromethyl)pyridin-2-amine 1d</td>
<td>2a</td>
<td><img src="image" alt="4r" /> 172 mg (0.66 mmol, 66%)</td>
<td>Ethyl acetate/n-hexane = 20% Rf (ethyl acetate/n-hexane = 33%) = 0.57</td>
</tr>
<tr>
<td>19</td>
<td>1d</td>
<td>2c</td>
<td><img src="image" alt="4s" /> 172 mg (0.54 mmol 54%)</td>
<td>Ethyl acetate/n-hexane = 18% Rf (ethyl acetate/n-hexane = 33%) = 0.85</td>
</tr>
</tbody>
</table>

3.1 2-Phenyl-1H-pyrrolo[2,3-b]pyridine (4a)

![Chemical Structure of 2-Phenyl-1H-pyrrolo[2,3-b]pyridine (4a)](image)

C$_{13}$H$_{10}$N$_2$ (194.23)

By following the general procedure, 173 mg (89%) were obtained as a colorless solid. Mp.: 204.3 °C. 1H-NMR (600 MHz, CDCl$_3$): $\delta$ = 6.79 (s, 1 H), 7.10 (d, $J$ = 4.8 Hz, 7.7 Hz, 1 H), 7.40 (t, $J$ = 7.4 Hz, 1 H), 7.52 (t, $J$ = 7.6 Hz, 2 H), 7.92 (d, $J$ = 7.8 Hz, 2 H), 7.96 (d, $J$ = 7.7 Hz, 1 H), 8.3 (d, $J$ = 4.8 Hz, 1 H), 12.94 (br s, 1 H). 13C-NMR (150 MHz, CDCl$_3$): $\delta$ = 97.4 (CH), 116.1 (CH), 122.4 (C$_{quat}$), 126.0 (CH), 128.2 (CH), 128.7 (CH), 129.0 (CH), 132.5 (C$_{quat}$), 139.7 (C$_{quat}$), 142.1 (CH), 150.1 (C$_{quat}$). MS (EI+, 70 eV): $m/z$ (%) = 195 (14), 194 ([M]+, 100), 193 (14), 192 (6), 167 (16), 166 (8), 139 (5), 97 (7), 91 (8) IR (ATR): $\tilde{\nu}$ = 1456 (m), 1281 (m), 750 (s), 685 (m), 675 (m), 648 (m), 625 cm$^{-1}$ (m). Anal. calcd. for C$_{13}$H$_{10}$N$_2$ (194.2): C 80.39; H 5.19; N 14.42. Found: C 80.16; H 4.92; N 14.21.

3.2 2-(3,4-Dimethoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4b)

![Chemical Structure of 2-(3,4-Dimethoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4b)](image)

C$_{15}$H$_{14}$N$_2$O$_2$ (254.28)

By following the general procedure, 214 mg (84%) were obtained as a yellow solid. Mp.: 190.5 °C. 1H NMR (600 MHz, CDCl$_3$): $\delta$ = 3.95 (s, 3 H), 3.97 (s, 3 H), 6.68 (s, 1 H), 7.02 (d, $J$ = 8.3 Hz, 1 H), 7.08 (dd, $J$ = 7.7, 4.8 Hz, 1 H), 7.35 (d, $J$ = 1.6 Hz, 1 H), 7.48 (d, $J$ = 8.3 Hz, 1 H), 7.93 (dd, $J$ = 7.7, 1.2 Hz, 1 H), 8.24 (dd, $J$ = 4.7, 1.2 Hz, 1 H), 12.82 (br s, 1 H). 13C NMR (150 MHz, CDCl$_3$): $\delta$ = 56.1 (CH$_3$), 56.1 (CH$_3$), 96.5 (CH), 109.5 (CH), 111.6 (CH), 116.0 (CH), 118.7 (CH), 122.6 (C$_{quat}$), 125.6 (C$_{quat}$), 128.4 (CH), 140.0 (C$_{quat}$), 141.6 (CH), 149.5 (C$_{quat}$), 149.5 (C$_{quat}$), 150.0 (C$_{quat}$). MS (EI+, 70 eV): $m/z$ (%) = 255 (18), 254 ([M]+, 100), 240 (5), 239 (31), 212 (7), 211 (48), 210 (7), 209 (6), 196 (10), 193 (9), 192 (5), 183 (10), 182 (7), 181 (19), 179 (8), 169 (8), 168 (21), 167 (7), 166 (8), 142 (9), 141 (8), 140 (11), 127 (11), 114 (8), 113 (6), 111 (8), 97 (11), 95 (7), 85 (10), 83 (12), 81 (8), 71 (15), 70 (7), 69 (10), 57 (18), 55 (14), 43 (12), 41 (8). IR (ATR): $\tilde{\nu}$ =1497 (m), 1546 (m), 1441 (m), 1233 (s), 1142 (m), 1022 (m), 853 (m), 795 (s), 785 (m), 764 (s), 745 (s), 667 (m), 638 cm$^{-1}$ (m). Anal. calcd. for C$_{15}$H$_{14}$N$_2$O$_2$ (254.3): C 70.85; H 5.55; N 11.02. Found: C 70.93; H 5.48; N 10.73.

3.3 2-(4-((tert-Butyl)phenyl)-1H-pyrrolo[2,3-b]pyridine (4c)

![Chemical Structure of 2-(4-((tert-Butyl)phenyl)-1H-pyrrolo[2,3-b]pyridine (4c)](image)
C_{17}H_{18}N_{2} (250.34)

By following the general procedure 225 mg (90%) were obtained as a yellow solid. Mp.: 220.5 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 1.42\) (s, 9 H), 6.78 (s, 1 H), 7.13 (dd, \(J = 7.7, 4.7\) Hz, 1 H), 7.56 (d, \(J = 8.4\) Hz, 2 H), 7.87 (dd, \(J = 8.4, 3.0\) Hz, 2 H), 7.97 (dd, \(J = 7.7, 1.2\) Hz, 1 H), 8.34 (d, \(J = 4.7\) Hz, 1 H), 12.81 (br s, 1 H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 31.5\) (CH\(_3\)), 34.9 (C_quat), 97.1 (CH), 116.2 (CH), 122.7 (C_quat), 125.8 (CH), 126.1 (CH), 128.7 (CH), 129.7 (C_quat), 139.9 (C_quat), 141.9 (CH), 150.1 (C_quat), 151.6 (C_quat). MS (EI+, 70 eV): \(m/z\) (%) = 251 (11), 250 ([M] +, 58), 236 (17), 235 (100), 220 (9), 219 (10), 218 (6), 207 (20), 206 (5), 194 (7), 149 (6), 148 (14), 104 (10), 103 (24), 97 (7), 95 (6), 91 (5), 81 (6), 71 (9). IR (ATR): \(\tilde{\nu} = 1279\) (m), 828 (m), 799 (s), 764 (s), 735 (m), 723 (m), 621 cm\(^{-1}\) (m). Anal. calcd. for C\(_{17}H\_18N\_2\) (250.3): C 81.56; H 7.25; N 11.19. Found: C 81.46; H 7.33; N 11.01.

3.4 2-(Phenoxy)methyl-1H-pyrrolo[2,3-b]pyridine (4d)

\[
\text{C}_{14}\text{H}_{12}\text{N}_{2}\text{O} (224.26)
\]

By following the general procedure 40 mg (18%) were obtained as a yellow solid. Mp.: 169.9 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 5.30\) (s, 2 H), 6.50 (s, 1 H), 6.97-7.00 (m, 1 H), 7.02 7.05 (m, 3 H), 7.30 (dd, \(J = 8.7, 7.4\) Hz, 2 H), 7.91 (dd, \(J = 7.8, 1.5\) Hz, 1 H), 8.27 (dd, \(J = 4.8, 1.5\) Hz, 1 H), 11.94 (br s, 1 H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 63.9\) (CH\(_2\)), 99.6 (CH), 114.9 (CH), 115.9 (CH), 120.9 (C_quat), 121.4 (CH), 129.0 (CH), 129.7 (CH), 135.2 (C_quat), 142.5 (CH), 149.2 (C_quat), 158.4 (C_quat). MS (EI+, 70 eV): \(m/z\) (%) = 224 ([M]+, 3), 132 (9), 131 (100), 104 (12), 77 (9), 65 (6). IR (ATR): \(\tilde{\nu} = 1425\) (m), 1238 (m), 1223 (m), 1211 (m), 1173 (m), 1028 (m), 1005 (m), 991 (m), 764 (m), 745 (m), 685 (m), 646 (m). Anal. calcd. for C\(_{14}H\_12N\_2O\) (224.3): C 74.98; H 5.39; N 12.49. Found: C 74.98; H 5.30; N 12.20.

3.5 2-(Pyridin-2-yl)-1H-pyrrolo[2,3-b]pyridine (4e)

\[
\text{C}_{12}\text{H}_{9}\text{N}_{3} (195.22)
\]

By following the general procedure 76 mg (39%) were obtained as a white solid. Mp.: 215.2 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 6.98\) (s, 1 H), 7.11 (dd, \(J = 7.8, 4.8\) Hz, 1 H), 7.19-7.24 (m, 1 H), 7.74 (td, \(J = 7.8, 1.6\) Hz, 1 H), 7.84 (d, \(J = 8.0, 1\) H), 7.97 (dd, \(J = 7.8, 1.3\) Hz, 1 H), 8.44 (dd, \(J = 4.7, 1.3\) Hz, 1 H), 8.68 (d, \(J = 4.8\) Hz, 1 H), 10.99 (br s, 1 H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 98.8\) (CH),
116.5 (CH), 120.1 (CH), 121.9 (Cquat), 122.7 (CH), 129.5 (CH), 136.7 (CH), 137.6 (Cquat), 144.2 (CH), 148.9 (Cquat), 149.7 (CH), 150.1 (Cquat). MS (EI+, 70 eV): \( m/z \) (%) = 196 (15), 195 ([M]+, 100), 194 (27), 169 (7), 168 (7), 167 (5), 97 (8), 91 (9), 71 (5). IR (ATR): \( \tilde{\nu} = 1582 \) (m), 1560 (m), 1445 (m), 1425 (m), 1325 (m), 916 (m), 812 (m), 787 (m), 770 (m), 756 (s), 731 (m), 689 (m), 656 (m), 619 cm\(^{-1}\) (m). Anal. calcd. for C\(_{12}\)H\(_9\)N\(_3\) (195.2): C 73.83; H 4.65; N 21.52. Found: C 73.27; H 4.60; N 21.16.

3.6 2-Butyl-5-methyl-1H-pyrrolo[2,3-b]pyridine (4f)

\[
\begin{align*}
\text{C}_{12}\text{H}_{16}\text{N}_{2} & \quad (188.27) \\
\end{align*}
\]

By following the general procedure 149 mg (79%) were obtained as a yellow solid. Mp.: 89.0 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 0.98 \) (dd, \( J = 7.7, 7.0 \) Hz, 3 H), 1.41-1.52 (m, 2 H), 1.77-1.86 (m, 2 H), 2.44 (s, 3 H), 2.86 (t, \( J = 7.7 \) Hz, 2 H), 6.12 (s, 1 H), 7.64 (d, \( J = 0.9 \) Hz, 1 H), 8.04 (s, 1 H), 11.72 (br s, 1 H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \( \delta = 14.0 \) (CH\(_3\)), 18.7 (CH\(_3\)), 22.6 (CH\(_2\)), 28.6 (CH\(_2\)), 31.3 (CH\(_2\)), 96.7 (CH), 121.9 (Cquat), 124.4 (Cquat), 128.0 (CH), 141.1 (CH), 142.1 (Cquat), 147.9 (Cquat). MS (EI+, 70 eV): \( m/z \) (%) = 189 (5), 188 ([M]+, 37), 147 (6), 146 (58), 145 (100), 40 (6). IR (ATR): \( \tilde{\nu} = 2965 \) (m), 2953 (m), 2926 (m), 1447 (m), 1408 (m), 1375 (m), 1277 (s), 1225 (m), 980 (m), 870 (s), 800 (s), 789 (m), 777 (m), 760 (s), 741 (s), 696 cm\(^{-1}\) (m). Anal. calcd. for C\(_{12}\)H\(_{16}\)N\(_2\) (188.3): C 76.55; H 8.57; N 14.99. Found: C 76.46; H 8.39; N 14.79.

3.7 2-Vinyl-1H-pyrrolo[2,3-b]pyridine (4g)

\[
\begin{align*}
\text{C}_9\text{H}_8\text{N}_2 & \quad (144.17) \\
\end{align*}
\]

By using 3.40 equivalents of KO\(_t\)Bu (382 mg, 3.40 mmol) and otherwise following the general procedure 32 mg (22%) were obtained as a yellow solid. Mp.: 150.5 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 5.36 \) (d, \( J = 11.2 \) Hz, 1 H), 5.86 (d, \( J = 17.7 \) Hz, 1 H), 6.37 (s, 1 H), 6.73 (dd, \( J = 11.2 \) Hz, 17.7 Hz, 1 H), 6.98 (dd, \( J = 4.9 \) Hz, 7.8 Hz, 1 H), 7.81 (dd, \( J = 1.5 \) Hz, 7.8 Hz, 1 H), 8.23 (dd, \( J = 1.5 \) Hz, 7.8 Hz, 1 H), 12.3 (br s, 1 H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 100.7 \) (CH), 114.4 (CH\(_2\)), 115.9 (CH), 121.9 (Cquat), 127.9 (CH), 128.8 (CH), 137.9 (Cquat), 142.5 (CH), 149.8 (Cquat). MS (EI+, 70 eV): \( m/z \) (%) = 145, (11), 144 ([M]+, 100), 143 (50), 142 (5), 131 (5), 118 (21), 117 (6), 116 (16), 91 (6), 90 (6), 89 (10), 63 (6). IR (ATR): \( \tilde{\nu} = 1582 \) (m), 1418 (m), 1279 (m), 1265 (m), 1140 (m), 1109 (m), 1047
3.8 5-Methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine (4h)

By following the general procedure 165 mg (79%) were obtained as a yellow solid. Mp.: 254.5 °C. \(^1\)H NMR (600 MHz, DMSO-d6): \(\delta = 2.36\) (s, 3 H), 6.82 (d, \(J = 2.1\) Hz, 1 H), 7.31 – 7.35 (m, 1 H), 7.43 – 7.47 (m, 2 H), 7.71 (s, 1 H), 7.90 – 7.93 (m, 2 H), 8.06 (d, \(J = 1.9\) Hz, 1 H), 11.99 (br s, 1 H). \(^{13}\)C NMR (150 MHz, DMSO-d6): \(\delta = 18.1\) (CH\(_3\)), 96.5 (CH), 120.8 (C\(_{\text{quat}}\)), 124.4 (C\(_{\text{quat}}\)), 125.2 (CH), 127.6 (CH), 127.9 (CH), 128.9 (CH), 131.7 (C\(_{\text{quat}}\)), 138.3 (C\(_{\text{quat}}\)), 143.6 (CH), 148.3 (C\(_{\text{quat}}\)). MS (EI+, 70 eV): \(m/z\) (%) = 209 (14), 208 ([M]+, 100), 207 (50), 192 (6), 180 (11), 153 (5), 152 (9), 104 (11), 77 (7), 69 (7), 40 (6). IR (ATR): \(\nu = 1279\) (m), 870 (m), 748 (s), 687 (m), 679 (m), 644 (m), 625 cm\(^{-1}\) (m). Anal. calcd. for C\(_{14}H_{12}N_2\) (208.3): C 80.74; H 5.81; N 13.45. Found: C 80.48; H 5.95; N 13.36.

3.9 2-(4-Methoxyphenyl)-5-methyl-1H-pyrrolo[2,3-b]pyridine (4i)

By following the general procedure 114 mg (51%) were obtained as a yellow solid. Mp.: 212.5 °C. \(^1\)H \(^1\)H-NMR (600 MHz, DMSO-d6): \(\delta = 3.80\) (s, 3 H), 6.77 (s, 1 H), 7.02 – 7.04 (m, 3 H), 7.87 – 7.88 (m, 3 H), 8.16 (d, \(J = 4.0\) Hz, 1 H), 12.02 (br s, 1 H). \(^{13}\)C NMR (150 MHz, DMSO-d6): \(\delta = 55.2\) (CH\(_3\)), 95.7 (CH), 114.4 (CH), 115.9 (CH), 121.1 (C\(_{\text{quat}}\)), 124.2 (C\(_{\text{quat}}\)), 126.7 (CH), 127.3 (CH), 138.4 (C\(_{\text{quat}}\)), 142.1 (CH), 149.6 (C\(_{\text{quat}}\)), 159.2 (C\(_{\text{quat}}\)). EI MS (70eV): \(m/z\) (%) = 225 (16), 224 ([M]+, 100), 210 (11), 209 (76), 182 (6), 181 (36), 180 (5), 179 (8), 149 (5), 127 (11), 112 (7), 97 (6), 85 (5), 83 (7), 71 (6), 69 (6), 57 (7), 40 (8). IR (ATR): \(\nu = 1491\) (m), 1441 (m), 1248 (m), 1277 (m), 1221 (m), 1182 (m), 1030 (m), 827 (m), 799 (s), 785 (m), 762 (s), 727 (m), 714 (m), 629 (m), 617 cm\(^{-1}\) (m). Anal. calcd. for C\(_{14}H_{12}N_2O\) (224.3): C 74.98; H 5.39; N 12.49. Found: C 74.71; H 5.39; N 12.20.

3.10 2-(4-(tert-Butyl)phenyl)-5-methyl-1H-pyrrolo[2,3-b]pyridine (4j)
C_{18}H_{20}N_{2} (264.36)

By following the general procedure 169 mg (64%) were obtained as a yellow solid. Mp.: 238.7 °C. \(^1H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 1.39\ (s, \; 9\ H), 2.45\ (s, \; 3\ H), 6.67\ (s, \; 1\ H), 7.52 – 7.53\ (m, \; 2\ H), 7.73\ (d, \; J = 0.92\ Hz, \; 1\ H), 7.79 – 7.81\ (m, \; 2\ H), 8.13\ (s, \; 1\ H), 12.12\ (br\ s, \; 1\ H). \(^13\)C-NMR (150 MHz, CDCl\(_3\)): \(\delta = 18.8\ (CH_3), 31.5\ (CH_3), 34.9\ (C_{quat}), 96.5\ (CH), 122.4\ (C_{quat}), 125.0\ (C_{quat}), 125.7\ (CH), 126.0\ (CH), 128.7\ (CH), 129.8\ (C_{quat}), 139.8\ (C_{quat}), 142.9\ (CH), 148.6\ (C_{quat}), 151.4\ (C_{quat})\) MS (EI+, 70 eV): \(m/z\ (% = 277\ (6), 265\ (13), 264\ ([M]^+, 63), 250\ (19), 149\ (100), 234\ (10), 233\ (8), 221\ (12), 125\ (5), 110\ (27). IR (ATR): \(v = 1281\ (m), 876\ (m), 839\ (m), 797\ (m), 758\ (s), 748\ (m), 733\ (m), 725\ (m), 638\ cm^{-1}\ (m).\) Anal. calcd. for C_{18}H_{20}N_{2} (264.4): C 81.78; H 7.63; N 10.60. Found: C 81.53; H 7.81; N 10.34.

3.11 2-(4-Methoxyphenyl)-5-methyl-1H-pyrrolo[2,3-b]pyridine (4k)

By following the general procedure 173 mg (73%) were obtained as a yellow solid. Mp.: 243.3 °C. \(^1H\) NMR (600 MHz, DMSO-d\(_6\) and 17% CS\(_2\)): \(\delta = 2.39\ (s, \; 3\ H), 3.82\ (s, \; 3\ H), 6.61\ (d, \; J = 2.1\ Hz, \; 1\ H), 6.97 – 6.99\ (m, \; 2\ H), 7.62\ (s, \; 1\ H), 7.81 – 7.83\ (m, \; 2\ H), 7.98\ (d, \; J = 1.5\ Hz, \; 1\ H), 11.81\ (br\ s, \; 1\ H). \(^13\)C NMR (150 MHz, DMSO-d\(_6\) and 17% CS\(_2\)): \(\delta = 18.2\ (CH_3), 55.0\ (CH_3), 95.0\ (CH), 114.0\ (CH), 121.0\ (C_{quat}), 123.9\ (C_{quat}), 124.3\ (C_{quat}), 126.5\ (CH), 126.8\ (CH), 138.4\ (C_{quat}), 142.7\ (CH), 148.2\ (C_{quat}), 158.9\ (C_{quat}).\) MS (EI+, 70 eV): \(m/z\ (% = 277\ (7), 239\ (18), 238\ ([M]^+, 100), 224\ (12), 223\ (77), 196\ (6), 195\ (29)\) MS (EI+, 70 eV): \(m/z\ (% = 277\ (7), 239\ (18), 238\ ([M]^+, 100), 224\ (12), 223\ (77), 196\ (6), 195\ (29)\) IR (ATR): \(v = 1501\ (m), 1491\ (m), 1458\ (m), 1439\ (m), 1391\ (m), 1290\ (m), 1277\ (m), 1248\ (s), 1169\ (m), 1109\ (m), 1026\ (m), 881\ (m), 824\ (s), 758\ (s), 773\ (m), 716\ cm^{-1}\ (m).\) Anal. calcd. for C_{13}H_{14}N_{2}O (238.3): C 75.61; H 5.92; N 11.76. Found: C 75.32; H 5.81; N 11.46.

3.12 2-(4-Methoxyphenyl)-5-methyl-1H-pyrrolo[2,3-b]pyridine (4l)

By using DCM instead of ethyl acetate for extraction and otherwise following the general procedure 113 mg (40%) were obtained as a yellow solid. Mp.: 177.4 °C. \(^1H\) NMR (600 MHz, DMSO-d\(_6\)): \(\delta = 3.70\ (s, \; 3\ H), 3.89\ (s, \; 6\ H), 6.95\ (s, \; 1\ H), 7.04 – 7.06\ (m, \; 1\ H), 7.28\ (s, \; 2\ H), 7.91\ (d, \; J = 7.4\ Hz, \; 1\ H), 8.12\ (s, \; 1\ H), 12.17\ (br\ s, \; 1\ H). \(^13\)C NMR (150 MHz, DMSO-d\(_6\)): \(\delta = 18.8\ (CH_3), 55.0\ (CH_3), 95.0\ (CH), 114.0\ (CH), 121.0\ (C_{quat}), 123.9\ (C_{quat}), 124.3\ (C_{quat}), 126.5\ (CH), 126.8\ (CH), 138.4\ (C_{quat}), 142.7\ (CH), 148.2\ (C_{quat}), 158.9\ (C_{quat}).\) MS (EI+, 70 eV): \(m/z\ (% = 277\ (7), 239\ (18), 238\ ([M]^+, 100), 224\ (12), 223\ (77), 196\ (6), 195\ (29)\) IR (ATR): \(v = 1501\ (m), 1491\ (m), 1458\ (m), 1439\ (m), 1391\ (m), 1290\ (m), 1277\ (m), 1248\ (s), 1169\ (m), 1109\ (m), 1026\ (m), 881\ (m), 824\ (s), 758\ (s), 773\ (m), 716\ cm^{-1}\ (m).\) Anal. calcd. for C_{16}H_{16}N_{2}O_{3} (284.31): C 78.03; H 5.70; N 11.36. Found: C 78.01; H 5.70; N 11.36.
8.20 (d, $J = 3.3$ Hz, 1 H), 12.11 (br s, 1 H). $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta = 56.1$ (CH$_3$), 60.1 (CH$_3$), 96.9 (CH), 102.9 (CH), 116.0 (CH), 121.0 (C$_{quat}$), 127.1 (C$_{quat}$), 127.6 (CH), 137.5 (C$_{quat}$), 138.4 (C$_{quat}$), 142.6 (CH), 149.6 (C$_{quat}$), 153.3 (C$_{quat}$). MS (EI+, 70 eV): $m/z$ (%) = 285 (19), 284 ([M]$^+$, 100), 270 (11), 269 (60), 241 (10), 226 (11), 211 (8), 209 (9), 181 (7), 155 (9), 142 (12), 127 (9). IR (ATR): $\tilde{\nu} = 1485$ (m), 1431 (m), 1398 (m), 1273 (m), 1256 (m), 1242 (m), 1099 (s), 1080 (m), 1030 (m), 997 (m), 912 (w), 841 (m), 820 (s), 772 (s), 760 (m), 721 (m), 652 (m), 625 cm$^{-1}$ (m). Anal. calcd. for C$_{16}$H$_{16}$N$_2$O$_3$ (284.3): C 67.59; H 5.67; N 9.85. Found: C 67.31; H 5.73; N 9.48.

3.13 5-Methyl-2-(3,4,5-trimethoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4m)

\[
\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3 (298.34)
\]

By following the general procedure 163 mg (55%) were obtained as a yellow solid. Mp.: 180.9 °C. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 2.36$ (s, 3 H), 3.69 (s, 3 H), 3.88 (s, 6 H), 6.86 (d, $J = 2.0$ Hz, 1 H), 7.25 (s, 2 H), 7.69 (s, 1 H), 8.04 (d, $J = 1.6$ Hz, 1 H), 11.95 (br s, 1 H). $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta = 18.2$ (CH$_3$), 56.1 (CH$_3$), 60.1 (CH$_3$), 96.4 (CH), 102.9 (CH), 120.9 (C$_{quat}$), 124.4 (C$_{quat}$), 127.3 (C$_{quat}$), 127.4 (CH), 137.4 (C$_{quat}$), 138.5 (C$_{quat}$), 143.5 (CH), 148.3 (C$_{quat}$), 153.3 (C$_{quat}$). MS (EI+, 70 eV): $m/z$ (%) = 299 (22), 298 ([M]$^+$, 100), 284 (12), 283 (65), 255 (7), 240 (10), 225 (8), 223 (9), 195 (6), 169 (9), 149 (20), 134 (14), 84 (6), 43 (8). IR (ATR): $\tilde{\nu} = 1589$ (m), 1464 (m), 1449 (m), 1427 (m), 1414 (m), 1279 (m), 1240 (m), 1132 (m), 1119 (s), 1005 (m), 845 (m), 831 (m), 822 (m), 793 (m), 756 (s), 629 cm$^{-1}$ (m). HRMS: $m/z$ calcd. for C$_{17}$H$_{19}$N$_2$O$_3$ $^+$: 299.1390. Found: 299.1392.

3.14 2-(2-Fluorophenyl)-1H-pyrrolo[2,3-b]pyridine (4n)

\[
\text{C}_{13}\text{H}_9\text{FN}_2 (212.22)
\]

By following the general procedure 144 mg (68%) were obtained as an off-white solid. Mp.: 176.1 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 6.94$ (d, $J = 1.6$ Hz, 1 H), 7.11 (dd, $J = 7.8, 4.8$ Hz, 1 H), 7.23 (ddd, $J = 11.7, 8.1, 1.1$ Hz, 1 H), 7.28 – 7.32 (m, 1 H), 7.33 – 7.37 (m, 1 H), 7.91 (td, $J = 7.7, 1.7$ Hz, 1 H), 7.98 (dd, $J = 7.9, 1.3$ Hz, 1 H), 8.31 (d, $J = 4.0$ Hz, 1 H), 11.61 (br s, 1 H). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 100.8$ (d, $J_{CF} = 6.6$ Hz, CH), 116.4 (CH), 116.8 (d, $J_{CF} = 22.3$ Hz, CH), 120.2 (d, $J_{CF} = 11.4$ Hz, C$_{quat}$), 121.7 (C$_{quat}$), 124.9 (d, $J_{CF} = 3.3$ Hz, CH), 128.3 (d, $J_{CF} = 3.6$ Hz, CH), 129.2 (CH), 129.7 (d, $J_{CF} = 8.9$ Hz, CH), 133.4 (d, $J = 2.0$ Hz, C$_{quat}$), 143.0 (CH), 149.3 (C$_{quat}$), 159.9 (d, $J_{CF} = 249.0$, C$_{quat}$). MS (EI+, 70 eV): $m/z$ (%) = 213 (15), 212 ([M]$^+$, 100), 211 (10), 184 (7), 164 (5), 106
3.15 2-(4-(tert-Butyl)phenyl)-5-chloro-1H-pyrrolo[2,3-b]pyridine (4o)

By following the general procedure 245 mg (86%) were obtained as a yellow solid. Mp.: 261.7 °C. $^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ = 1.30 (s, 9 H), 6.84 (s, 1 H), 7.49 (d, $J$ = 8.1 Hz, 2 H), 7.86 (d, $J$ = 8.0 Hz, 2 H), 8.00 (s, 1 H), 8.17 (s, 1 H), 12.33 (br s, 1 H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): $\delta$ = 31.0 (CH$_3$), 34.4 (C$_{quat}$), 96.3 (CH), 122.0 (C$_{quat}$), 122.7 (C$_{quat}$), 125.3 (CH), 125.7 (CH), 126.6 (CH), 128.3 (C$_{quat}$), 140.5 (C$_{quat}$), 140.5 (CH), 147.9 (C$_{quat}$), 151.1 (C$_{quat}$). MS (EI+, 70 eV): $m/z$ (%) = 286 (20), 285 (12), 284 ([M]$^+$, 63), 272 (6), 271 (33), 270 (19), 269 (100), 254 (7), 243 (6), 241 (17), 234 (8), 134 (5), 121 (9), 120 (33), 102 (6). IR (ATR): $\bar{\nu}$ = 2967 (m), 2901 (m), 2868 (m), 1472 (m), 1435 (m), 1393 (m), 1281 (m), 1267 (m), 1182 (m), 1086 (m), 941 (s), 928 (m), 883 (s), 839 (s), 826 (m), 793 (s), 764 (s), 737 (m), 700 cm$^{-1}$ (m). HRMS: $m/z$ calced. for C$_{17}$H$_{17}$ClN$_2$+: 285.1152. Found: 285.1153.

3.16 5-Chloro-2-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4p)

By following the general procedure 96 mg (37%) were obtained as a dark-yellow solid. Mp.: Decomposition at 284.3 °C. $^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ = 3.81 (s, 3 H), 6.77 (s, 1 H), 7.04 (d, $J$ = 8.4 Hz, 2 H), 7.88 (d, $J$ = 8.4 Hz, 2 H), 7.96 (s, 1 H), 8.14 (d, $J$ = 1.6 Hz, 1 H), 12.25 (br s, 1 H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): $\delta$ = 55.3 (CH$_3$), 95.4 (CH), 114.4 (CH), 122.2 (C$_{quat}$), 122.7 (C$_{quat}$), 123.7 (C$_{quat}$), 126.3 (CH), 127.0 (CH), 140.1 (CH), 140.5 (C$_{quat}$), 147.9 (C$_{quat}$), 159.6 (C$_{quat}$). MS (EI+, 70 eV): $m/z$ (%) = 278 (7), 277 (17), 261 (5), 260 (34), 259 (17), 258 ([M]$^+$, 100), 245 (20), 244 (11), 243 (64), 217 (6), 215 (21), 179 (7), 153 (7), 152 (8), 149 (20), 135 (10), 129 (7), 85 (6), 71 (6), 57 (9), 55 (5). IR (ATR): $\bar{\nu}$ = 1609 (m), 1497 (m), 1456 (m), 1439 (m), 1283 (m), 1277 (m), 1256 (m), 1177 (m), 1028 (m), 941 (m), 924 (m), 899 (m), 868 (m), 829 (s), 820 (m), 789 (s), 760 (s), 721 (m), 694 (m), 645 cm$^{-1}$ (m). HRMS: $m/z$ calced. for C$_{14}$H$_{11}$ClN$_2$O$: 259.0633. Found: 259.0638.

3.17 2-(Naphthalen-1-yl)-1H-pyrrolo[2,3-b]pyridine (4q)
3.18 2-Phenyl-5-(trifluoromethyl)-1H-pyrrolo[2,3-b]pyridine (4r)

\[
\text{C}_{17}\text{H}_{12}\text{N}_{2} (244.29)
\]

By following the general procedure 172 mg (70%) were obtained as a yellow solid. Mp.: 227.9 °C. \(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \(\delta = 6.74\) (s, 1 H), 7.12 (s, 1 H), 7.59 – 7.64 (m, 3 H), 7.74 (d, \(J = 5.5\) Hz, 1 H), 8.01 – 8.02 (m, 3 H), 8.27 (s, 2 H), 12.16 (br s, 1 H). \(^1\)C NMR (150 MHz, DMSO-\(d_6\)): \(\delta = 101.0\) (CH), 115.9 (CH), 120.5 (C quat), 125.3 (CH), 125.5 (CH), 126.2 (CH), 126.8 (CH), 127.6 (CH), 127.9 (CH), 128.4 (CH), 128.6 (CH), 130.3 (C quat), 130.8 (C quat), 133.5 (C quat), 137.2 (C quat), 142.7 (CH), 149.1 (C quat). MS (EI+, 70 eV): \(m/z (\%) = 245 (18), 244 ([M]+, 100), 243 (90), 242 (23), 212 (35), 108 (6), 94 (6), 61 (28).\) IR (ATR): \(v = 1282\) (m), 810 (m), 789 (m), 770 (s), 758 (s), 735 (m), 656 (m), 627 cm\(^{-1}\) (m). HRMS: \(m/z\) calcd. for C\(_{17}\)H\(_{13}\)N\(_2\): 245.1073. Found: 245.1071.

3.19 2-(4-(tert-Butyl)phenyl)-5-(trifluoromethyl)-1H-pyrrolo[2,3-b]pyridine (4s)

\[
\text{C}_{18}\text{H}_{17}\text{F}_{3}\text{N}_{2} (318.34)
\]

By following the general procedure 172 mg (54%) were obtained as a yellow solid. Mp.: 239.9 °C. \(^1\)H NMR (600 MHz, DMSO-\(d_6\) and 17% CS\(_2\)): \(\delta = 7.45\) (d, \(J = 1.9\) Hz, 1 H), 7.83 (t, \(J = 7.4\) Hz, 1 H), 7.93 (d, \(J = 7.7\) Hz, 2 H), 8.42 – 8.44 (m, 2 H), 8.65 (m, 1 H), 8.93 (d, \(J = 1.5\) Hz, 1 H), 12.50 (br s, 1 H). \(^1\)C NMR (150 MHz, DMSO-\(d_6\) and 17% CS\(_2\)): \(\delta = 108.5\) (CH), 129.1 (q, \(J_{CF} = 31.6\) Hz, C quat), 130.9 (C quat), 135.4 (q, \(J_{CF} = 3.8\) Hz, CH), 135.7 (q, \(J_{CF} = 270.9\) Hz, C quat), 136.3 (CH), 139.0 (CH), 139.4 (CH), 141.8 (C quat), 149.9 (q, \(J_{CF} = 4.0\) Hz, CH), 151.7 (C quat), 161.7 (C quat). MS (EI+, 70 eV): \(m/z (\%) = 263 (16), 262 ([M]+, 100), 261 (11), 243 (5), 131 (7).\) IR (ATR): \(v = 1339\) (m), 1304 (m), 1290 (m), 1269 (m), 1142 (m), 1105 (s), 1074 (m), 951 (m), 905 (m), 754 (s), 687 (m), 656 cm\(^{-1}\) (m). HRMS: \(m/z\) calcd. for C\(_{18}\)H\(_{19}\)F\(_3\)N\(_2\): 263.0791. Found: 263.0791.
= 31.7 Hz, C quat), 131.2 (C quat), 135.4 (q, J CF = 3.8 Hz, CH), 135.8 (q, J CF = 270.2 Hz, C quat), 136.1
(CH), 136.5 (CH), 139.0 (C quat), 149.9 (q, J CF = 4.0 Hz, CH), 151.8 (C quat), 161.7 (C quat), 162.2 (C quat).
MS (EI+, 70 eV): m/z (%) = 319 (12), 318 ([M]+, 61), 312 (9), 304 (19), 303 (100), 288 (6), 287 (7),
276 (5), 275 (26), 263 (5), 262 (5), 151 (8). IR (ATR): ν = 1337 (m), 1308 (m), 1296 (m), 1269 (s),
758 (m), 1175 (m), 1148 (m), 1117 (s), 1076 (m), 951 (m), 903 (m), 839 (m), 797 (m), 758 (m), 662
cm⁻¹ (m). HRMS: m/z calcd. for C₁₈H₁₈F₃N₂⁺: 319.1417. Found: 319.1414.
4. NMR Spectra of compounds 4

3.1 2-Phenyl-1H-pyrrolo[2,3-b]pyridine (4a)

$^1$H NMR of 4a in CDCl$_3$ at 298 K.
$^{13}$C NMR of $4a$ in CDCl$_3$ at 298 K.

$^{13}$C DEPT-135 NMR of $4a$ in CDCl$_3$ at 298 K.
4.2 2-(3,4-Dimethoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4b)

$^1$H NMR of 4b in CDCl$_3$ at 298 K.

$^{13}$C NMR of 4b in CDCl$_3$ at 298 K.
$^{13}$C DEPT-135 NMR of 4b in CDCl$_3$ at 298 K.
4.3 2-(4-(tert-Butyl)phenyl)-1H-pyrrolo[2,3-b]pyridine (4c)

$^{1}H$ NMR of 4c in CDCl$_3$ at 298 K.

$^{13}C$ NMR of 4c in CDCl$_3$ at 298 K.
$^{13}$C DEPT-135 NMR of 4e in CDCl$_3$ at 298 K.
4.4 2-(Phenoxy)methyl-1H-pyrrolo[2,3-b]pyridine (4d)

$^1$H NMR of 4d in CDCl$_3$ at 298 K. * Residual solvent impurities.

$^{13}$C NMR of 4d in CDCl$_3$ at 298 K.
$^{13}$C DEPT-135 NMR of 4d in CDCl$_3$ at 298 K.
4.5 2-(Pyridin-2-yl)-1H-pyrrolo[2,3-b]pyridine (4e)

$^1$H NMR of 4e in CDCl$_3$ at 298 K. * Residual solvent impurities.

$^{13}$C NMR of 4e in CDCl$_3$ at 298 K.
$^{13}$C DEPT-135 NMR of 4e in CDCl$_3$ at 298 K.
4.6 2-Butyl-5-methyl-1H-pyrrolo[2,3-b]pyridine (4f)

$^1$H NMR of 4f in CDCl$_3$ at 298 K.
$^{13}$C NMR of 4f in CDCl$_3$ at 298 K.

$^{13}$C DEPT-135 NMR of 4f in CDCl$_3$ at 298 K.
4.7 2-Vinyl-1H-pyrrolo[2,3-b]pyridine (4g)

$^1$H NMR of 4g in CDCl$_3$ at 298 K. * Residual solvent impurities.
13C NMR of 4g in CDCl$_3$ at 298 K.

13C DEPT-135 NMR of 4g in CDCl$_3$ at 298 K.
4.8 5-Methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine (4h)

$^{1}H$ NMR of 4h in DMSO-d$_{6}$ at 298 K.

$^{13}C$ NMR of 4h in DMSO-d$_{6}$ at 298 K.
$^{13}$C DEPT-135 NMR of 4h in DMSO-d$_6$ at 298 K.
4.9 2-(4-Methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4i)

$^{1}H$ NMR of 4i in DMSO-d$_6$ at 298 K.

$^{13}C$ NMR of 4i in DMSO-d$_6$ at 298 K.
$^{13}$C DEPT-135 NMR of 4i in DMSO-$d_6$ at 298 K.
4.10 2-(4-(tert-Butyl)phenyl)-5-methyl-1H-pyrrolo[2,3-b]pyridine (4j)

$^1$H NMR of 4j in CDCl$_3$ at 298 K.

$^{13}$C NMR of 4j in CDCl$_3$ at 298 K.
$^{13}$C DEPT-135 NMR of 4j in CDCl$_3$ at 298 K.
4.11 2-(4-Methoxyphenyl)-5-methyl-1H-pyrrolo[2,3-b]pyridine (4k)

\[ \text{\( ^{1}H \) NMR of 4k in DMSO-\( d_6 \) with 17\% CS}_2 \text{ at 298 K.} \]

\[ \text{\( ^{13}C \) NMR of 4k in DMSO-\( d_6 \) with 17\% CS}_2 \text{ at 298 K.} \]
$^{13}$C DEPT-135 NMR of 4k in DMSO-d$_6$ with 17% CS$_2$ at 298 K.
4.12 2-(3,4,5-Trimethoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (41)

$^1$H NMR of 41 in DMSO-d$_6$ at 298 K.

$^{13}$C NMR of 41 in DMSO-d$_6$ at 298 K.
$^{13}$C DEPT-135 NMR of 4l in DMSO-d$_6$ at 298 K
4.13 5-Methyl-2-(3,4,5-trimethoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4m)

$^1$H NMR of 4m in DMSO-d$_6$ at 298 K.
$^{13}$C NMR of 4m in DMSO-d$_6$ at 298 K.

$^{13}$C DEPT-135 NMR of 4m in DMSO-d$_6$ at 298 K.
4.14 2-(2-Fluorophenyl)-1H-pyrrolo[2,3-b]pyridine (4n)

$^1$H NMR of 4n in CDCl$_3$ at 298 K. * Residual solvent impurities.

$^{13}$C NMR of 4n in CDCl$_3$ at 298 K.
$^{13}$C DEPT-135 NMR of 4n in CDCl$_3$ at 298 K.
4.15 2-(4-(tert-Butyl)phenyl)-5-chloro-1H-pyrrolo[2,3-b]pyridine (4o)

$^{1}$H NMR of 4o in DMSO-d$_6$ at 298 K.
$^{13}$C NMR of 4o in DMSO-$d_6$ at 298 K.

$^{13}$C DEPT-135 NMR of 4o in DMSO-$d_6$ at 298 K.
4.16 5-Chloro-2-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4p)

$^1$H NMR of 4p in DMSO-d$_6$ at 298 K.
$^{13}$C NMR of 4p in DMSO-$d_6$ at 298 K.

$^{13}$C DEPT-135 NMR of 4p in DMSO-$d_6$ at 298 K.
4.17 2-(Naphthalen-1-yl)-1H-pyrrolo[2,3-b]pyridine (4q)

$^1$H NMR of 4q in DMSO-d$_6$ at 298 K.
$^{13}$C NMR of 4q in DMSO-d$_6$ at 298 K.

$^{13}$C DEPT-135 NMR of 4q in DMSO-d$_6$ at 298 K.
4.18 2-Phenyl-5-(trifluoromethyl)-1H-pyrrolo[2,3-b]pyridine (4r)

$^1$H NMR of 4r in DMSO-$d_6$ with 17% CS$_2$ at 298 K.
$^{13}$C NMR of 4r in DMSO-d$_6$ with 17% CS$_2$ at 298 K. * Residual dithiocarbonates from CS$_2$.

$^{13}$C DEPT-135 NMR of 4r in DMSO-d$_6$ with 17% CS$_2$ at 298 K.
4.19  2-(4-(tert-Butyl)phenyl)-5-(trifluoromethyl)-1H-pyrrolo[2,3-b]pyridine (4s)

$^{1}$H NMR of 4s in DMSO-d$_6$ with 17% CS$_2$ at 298 K.
$^{13}$C NMR of 4s in DMSO-$_2$ with 17% CS$_2$ at 298 K. * Residual dithiocarbonates from CS$_2$.

$^{13}$C DEPT-135 NMR of 4s in DMSO-$_2$ with 17% CS$_2$ at 298 K.