Synthesis of Mono- and Dialkylsubstituted 1,10-Phenanthrolines

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Abstract: Starting from o-anisidine, alkylated 8-hydroxyquinolines 2 and 8-aminoquinolines 3 were obtained. From the latter, dialkylsubstituted 1,10-phenanthrolines 5 have been prepared in good yields. Reaction of unsubstituted 8-aminoquinoline under the same conditions, yielded monoalkylated 1,10-phenanthrolines 4.

INTRODUCTION

Substituted 1,10-phenanthrolines are known as important complexing agents in the analysis of transition metal ions, such as iron(II) and copper(I). In recent years substituted 1,10-phenanthrolines have also been used in homogenous catalysis. A large number of studies on supramolecular assemblies involving 1,10-phenanthroline derivatives, have been made over the last decade. For instance Sauvage prepared the "molecular knot", Chandler studied crown-ether substituted derivatives, while others have used 1,10-phenanthroline functions in enzyme mimics. Additionally substituted Fe/Ru/Os-phenanthroline complexes have been investigated as potential electron and energy transfer species. An excellent review over the uses and properties of 1,10-phenanthrolines and derivatives has been written by Sammes and Yahioglu.

Case and co-workers prepared disubstituted 1,10-phenanthrolines by a three-step synthesis. Condensation of an α,β-unsaturated ketone or aldehyde with o-nitroaniline and reduction of the resulting 8-nitroquinoline gave a monosubstituted 8-aminoquinoline. Condensation of the latter with a second α,β-unsaturated ketone or aldehyde yielded the disubstituted 1,10-phenanthroline, using arsenic acid as the oxidizing agent for the condensations. However, the overall yields for the procedure were generally very low (Scheme 1).
RESULTS AND DISCUSSION

Recently O’Murchu showed an easy way to condense 3-substituted quinolines from anilines and 2-substituted acroleins with sodium iodide as catalyst. Unfortunately attempts to prepare substituted 8-nitroquinolines under the same conditions proved unsuccessful. Consequently p-anisidine was used to synthesize substituted 8-hydroxyquinolines 2 (Scheme 2).

To examine the generality of this procedure, a series of 2-, 3- and 4-substituted 8-hydroxyquinolines 2 were prepared with unsaturated carbonyl compounds 1 in good yields. The 8-hydroxyquinolines 2 were then transformed to the desired 8-aminoquinolines 3 by the Bucherer reaction in excellent yields.
The synthesis of substituted 1,10-phenanthrolines under the condensation conditions described above were subsequently attempted. 2-, 3- and 4-monomethyl-substituted 1,10-phenanthrolines 4 (Scheme 3) can be prepared from commercially available 8-aminoquinoline and crotonic aldehyde 1a, methacrolein 1b or methylvinylketone 1c respectively.

\[
\begin{array}{c}
\text{H}_2\text{N} & \text{N} \\
\text{H}_2\text{N} & \text{N} \\
\end{array}
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{R}^3 \\
\end{array}
\begin{array}{c}
\text{Nal (cat.)} \\
\text{H}_2\text{SO}_4 \text{70\%,} \\
\text{110\°C, 5 h} \\
\end{array}
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{R}^3 \\
\end{array}
\begin{array}{c}
\text{H}_2\text{N} & \text{N} \\
\text{H}_2\text{N} & \text{N} \\
\end{array}
\begin{array}{c}
\text{H}_2\text{N} & \text{N} \\
\text{H}_2\text{N} & \text{N} \\
\end{array}
\begin{array}{c}
\text{R}^4 \\
\text{R}^5 \\
\text{R}^6 \\
\end{array}
\begin{array}{c}
\text{4} \\
\text{4} \\
\text{4} \\
\end{array}
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{R}^3 \\
\end{array}
\begin{array}{c}
\text{Yield} \text{ (\%)} \\
\text{Yield} \text{ (\%)} \\
\text{Yield} \text{ (\%)} \\
\end{array}
\begin{array}{c}
\text{a} \\
\text{b} \\
\text{c} \\
\end{array}
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\end{array}
\begin{array}{c}
\text{55} \\
\text{81} \\
\text{51} \\
\end{array}
\]

Scheme 3

Similarly a series of disubstituted 1,10-phenanthrolines can be synthesized using the appropriate substituted 8-aminoquinolines and by varying the carbonyl functionalized reagent 1. Both, symmetrically and unsymmetrically substituted 1,10-phenanthrolines were prepared in yields of up to 70% (Scheme 4). With 8-aminoquinolines 3d and 3e, poor solubility was overcome using additional solvent (H$_2$SO$_4$ 70%). However, working under more dilute conditions decreases the yields dramatically.

\[
\begin{array}{c}
\text{H}_2\text{N} & \text{N} \\
\text{H}_2\text{N} & \text{N} \\
\end{array}
\begin{array}{c}
\text{R}^2 \\
\text{R}^3 \\
\text{R}^4 \\
\end{array}
\begin{array}{c}
\text{Nal (cat.)} \\
\text{H}_2\text{SO}_4 \text{70\%,} \\
\text{110\°C, 5 h} \\
\end{array}
\begin{array}{c}
\text{R}^4 \\
\text{R}^5 \\
\text{R}^6 \\
\end{array}
\begin{array}{c}
\text{H}_2\text{N} & \text{N} \\
\text{H}_2\text{N} & \text{N} \\
\end{array}
\begin{array}{c}
\text{R}^4 \\
\text{R}^5 \\
\text{R}^6 \\
\end{array}
\begin{array}{c}
\text{5} \\
\text{5} \\
\text{5} \\
\end{array}
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{R}^3 \\
\text{R}^4 \\
\text{R}^5 \\
\text{R}^6 \\
\end{array}
\begin{array}{c}
\text{Yield} \text{ (\%)} \\
\text{Yield} \text{ (\%)} \\
\text{Yield} \text{ (\%)} \\
\text{Yield} \text{ (\%)} \\
\text{Yield} \text{ (\%)} \\
\text{Yield} \text{ (\%)} \\
\end{array}
\begin{array}{c}
\text{a} \\
\text{b} \\
\text{c} \\
\text{d} \\
\text{e} \\
\text{f} \\
\text{g} \\
\end{array}
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\begin{array}{c}
\text{75} \\
\text{70} \\
\text{81} \\
\text{70} \\
\text{82} \\
\text{70} \\
\text{91} \\
\end{array}
\]

Scheme 4

**EXPERIMENTAL**

$^1$H NMR (300 MHz) and $^{13}$C NMR (75.4 MHz) spectra were recorded in CDCl$_3$ on a Varian Gemini 300, using solvent as the internal standard. Chemical shifts are reported in ppm on the δ scale. Mass spectral data were obtained with a VG Instruments 7070E mass spectrometer. The melting points were measured on a Büchi 520 and are uncorrected. All reagents and solvents were obtained from either Fluka Chemie AG or Aldrich and unless otherwise stated used as supplied. 2-tert-Butylacrolein 1d was prepared by the method of Fujii. 9
8-Hydroxyquinolines 2a-e, General Procedure:

The unsaturated carbonyl compound 1 (40 mmol) was added over 5 h to a stirred solution of o-anisidine (2.96 g, 24 mmol) and NaI (0.035 g, 0.23 mmol) in H₂SO₄ 70% (8.7 ml, 100 mmol) at 110°C. After 1 h at 110 °C the dark brown reaction mixture was cooled to r. t., poured into 1 M Na₂CO₃ (150 ml) and extracted with CH₂Cl₂ (2a-2c, 3 x 100 ml) or diethyl ether (2d+2e, 3 x 100 ml). The combined organic layers were extracted with 12 M HCl (5x40 ml), the acidic solution was neutralized (3 M NaOH and 1 M Na₂CO₃) and extracted with CH₂Cl₂. Removal of the solvent in vacuo afforded a brown oil. HBr 62% (50 ml) was added and the resulting mixture refluxed for 30 h, cooled and neutralized (3 M NaOH and 1 M Na₂CO₃). The yellow suspension was extracted with CH₂Cl₂ (3 x 100 ml) and the combined organic layers dried, treated with charcoal and filtered through silica gel. The silica gel was rinsed with additional CH₂Cl₂ until no product was detectable in the eluent by TLC. Removal of the solvent in vacuo affords the quinolinols in good yields (Table 1) as yellow solids.

Table 1. Yields and Spectroscopic Data of the Prepared 8-Hydroxyquinolines 2 (Scheme 2)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Substrate</th>
<th>Yield (%)</th>
<th>mp / (°C) (Lit)</th>
<th>δ (Hz)</th>
<th>¹H NMR (CDCl₃ / TMS)</th>
<th>¹³C NMR (CDCl₃ / TMS)</th>
<th>MS (70 eV) m/z (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1a</td>
<td>95</td>
<td>73-75</td>
<td>2.71 (s, 3H), 7.13 (d, J = 7.3, 1H), 7.22-7.30 (m, 2H), 7.32-7.41 (m, 1H), 8.00 (d, J = 8.5, 1H)</td>
<td>156.8, 151.6, 137.5, 136.1, 159 (M⁺,100), 126.6, 126.5, 122.6, 117.5, 131 (73)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(72-73)¹⁰</td>
<td></td>
<td></td>
<td>109.8, 24.8</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>1b</td>
<td>88</td>
<td>111-114</td>
<td>2.51 (s, 3H), 7.10 (d, J = 7.5, 1H), 7.22-7.25 (m, 1H), 7.38-7.43 (m, 1H), 7.90 (d, J = 1.0, 1H), 8.61 (d, J = 2.0, 1H)</td>
<td>152.2, 149.7, 136.6, 134.8, 159 (M⁺,100), 131.2, 128.4, 127.7, 117.2, 131 (82)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(112-113)¹¹</td>
<td></td>
<td></td>
<td>109.2, 18.7</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>1c</td>
<td>86</td>
<td>135-137</td>
<td>2.68 (s, 3H), 7.12-7.28 (m, 2H), 7.43-7.45 (m, 2H), 8.61 (d, J = 4.4, 1H)</td>
<td>152.5, 147.3, 144.9, 138.0, 159 (M⁺,100), 128.4, 127.2, 122.4, 114.0, 131 (77)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(138-140)¹²</td>
<td></td>
<td></td>
<td>109.6, 18.7</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>1d</td>
<td>67</td>
<td>74-75</td>
<td>1.44 (s, 9H), 7.10 (d, J = 7.5, 1H), 7.28 (d, J = 8.3, 1H), 7.39-7.44 (m, 1H), 8.03 (d, J = 2.3, 1H), 8.88 (d, J = 2.3, 1H)</td>
<td>151.9, 147.3, 144.2, 136.1, 201 (M⁺, 70), 131.1, 128.1, 127.7, 117.7, 186 (100), 158 (32)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>109.3, 33.8, 30.9</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>1e</td>
<td>91</td>
<td>73-77</td>
<td>0.95 (t, J = 7.3, 3H), 1.33-1.46 (m, 2H), 1.64-1.73 (m, 2H), 2.79 (t, J = 8.0, 2H), 7.10 (d, J = 7.5, 1H), 7.25 (d, J = 8.1, 1H), 7.38-7.43 (m, 1H), 7.89 (d, J = 2.0, 1H), 8.62 (d, J = 2.0, 1H)</td>
<td>152.2, 149.5, 136.8, 136.2, 201 (M⁺, 100), 134.3, 128.5, 127.7, 117.4, 158 (80), 130 (59)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>109.3, 33.2, 32.9, 22.2</td>
<td></td>
</tr>
</tbody>
</table>

Table notes:

¹a HRMS for 2d: C₁₃H₁₅NO, calculated: 201.1154, found: 201.1162
¹b HRMS for 2e: C₁₃H₁₅NO, calculated: 201.1154, found: 201.1161
8-Aminoquinolines 3a-e, General Procedure:

2 (10 mmol (2a-2c) or 5 mmol (2d+2e)), ammonium sulfite monohydrate (NH₄)₂SO₃·H₂O (6.7 g, 20 mmol) and ammonia solution 32% (9 ml) were added to a teflon coated autoclave (23 ml capacity, Parr Instrument Company). The mixture was heated at 170°C for 2 days (2a-2c) or 7 days (2d+2e). After cooling the autoclave was rinsed with water and CH₂Cl₂. The CH₂Cl₂ was separated and the aqueous layer washed twice with CH₂Cl₂ (50 ml). The combined organic layers were dried (MgSO₄) and the solvent removed in vacuo. Yields and analytical data are given in Table 2.

Table 2. Yields and Spectroscopic Data of the Prepared 8-Aminoquinolines 3 (Scheme 2)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Substrate</th>
<th>Yield (%)</th>
<th>mp / (°C) (Lit)</th>
<th>¹H NMR (CDCl₃ / TMS) δ, J (Hz)</th>
<th>¹³C NMR (CDCl₃ / TMS) δ</th>
<th>MS (70 eV) m/z (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>2a</td>
<td>95</td>
<td>51-52</td>
<td>2.71 (s, 3H), 5.0 (bs, 2H), 6.89 (d, J = 7.4, 1H), 7.11 (d, J = 8.2, 1H), 7.19-7.30 (m, 1H), 7.92 (d, J = 8.3, 1H)</td>
<td>156.0, 143.4, 137.8, 136.0, 158 (M⁺, 100), 126.9, 126.3, 122.1, 115.8, 131 (22)</td>
<td>110.1, 25.2</td>
</tr>
<tr>
<td>3b</td>
<td>2b</td>
<td>97</td>
<td>58-60</td>
<td>2.47 (s, 3H), 4.9 (bs, 2H), 6.84 (d, J = 7.5, 1H), 7.05 (d, J = 8.1, 1H) 7.25-7.31 (m, 1H), 7.81 (d, J = 1.0, 1H), 8.59 (d, J = 2.0, 1H)</td>
<td>149.2, 143.8, 136.7, 134.7, 158 (M⁺, 100), 130.6, 128.6, 127.4, 115.4, 130 (29)</td>
<td>109.2, 18.6</td>
</tr>
<tr>
<td>3c</td>
<td>2c</td>
<td>96</td>
<td>80-81</td>
<td>2.62 (s, 3H), 5.0 (bs, 2H), 6.90 (d, J = 7.1, 1H), 7.17 (d, J = 4.4, 1H), 7.24-7.36 (m, 2H), 8.60 (d, J = 4.4, 1H)</td>
<td>146.9, 144.4, 144.2, 138.0, 158 (M⁺, 100), 128.8, 127.0, 122.1, 112.0, 131 (23)</td>
<td>109.9, 18.9</td>
</tr>
<tr>
<td>3d</td>
<td>2d</td>
<td>90</td>
<td>50-53</td>
<td>1.43 (s, 9H), 6.86 (d, J = 7.5, 1H), 7.11 (d, J = 8.1, 1H) 7.24-7.33 (m, 1H), 7.96 (d, J = 2.4, 1H), 8.86 (d, J = 2.4, 1H)</td>
<td>146.9, 143.6, 143.4, 136.5, 200 (M⁺, 70), 130.8, 128.4, 127.3, 115.9, 185 (100), 157</td>
<td>109.4, 33.7, 30.9 (28)²</td>
</tr>
<tr>
<td>3e</td>
<td>2e</td>
<td>93</td>
<td>oil</td>
<td>0.94 (t, J = 7.3, 3H), 1.32-1.45 (m, 2H), 1.63-1.73 (m, 2H), 2.76 (t, J = 8.0, 2H), 5.0 (bs, 2H), 6.85 (d, J = 7.4, 1H), 7.08 (d, J = 8.2, 1H) 7.26-7.32 (m, 1H), 7.81 (d, J = 2.1, 1H), 8.60 (d, J = 2.1, 1H)</td>
<td>148.8, 143.7, 136.7, 135.5, 200 (M⁺, 84), 134.3, 128.7, 127.4, 115.5, 157 (100), 130</td>
<td>109.3, 33.2, 32.8, 22.2, 13.8 (28)</td>
</tr>
</tbody>
</table>

a HRMS for 3d: C₁₃H₁₆N₂ calc’d : 200.1313 found : 200.1313
b HRMS for 3e: C₁₃H₁₆N₂ calc’d : 200.1313 found : 200.1324
Mono- and Dialkylsubstituted 1,10-Phenanthrolines 4a-c, 5a-g, General Procedure:

The unsaturated carbonyl compound 1 (40 mmol) was added over 5 h to a stirred solution of the 8-aminoquinoline 3 (24 mmol) and NaI (0.035 g, 0.23 mmol) in H₂SO₄ 70% (8.7 ml, 100 mmol) at 110°C (In the case of 3d and 3e further H₂SO₄ 70% was added until the mixture dissolved). After 1 h at 110°C the dark brown reaction mixture was cooled to r. t., poured into 1 M Na₂CO₃ (100 ml) and extracted with CH₂Cl₂ (3 x 100 ml). The combined organic layers were extracted with 12 M HCl (5x50 ml), the acidic solution was neutralized (3 M NaOH and 1 M Na₂CO₃) and extracted with CH₂Cl₂. Removal of the solvent in vacuo afforded the appropriate 1,10-phenanthroline. The products were purified by filtration through silica gel using CH₂Cl₂ or THF as solvent. Schemata 3 and 4 indicate the yields obtained, Tables 3 and 4 give the analytical data for the respective compounds.

Table 3. Spectroscopic Data of the Prepared Methyl-1,10-phenanthrolines 4 (Scheme 3)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Substrate</th>
<th>mp / °C</th>
<th>1H NMR (CDCl₃ / TMS) δ, J (Hz)</th>
<th>13C NMR (CDCl₃ / TMS) δ</th>
<th>MS (70 eV) m/z (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>1a</td>
<td>53 (51-52)¹⁶</td>
<td>2.91 (s, 3H), 7.46 (d, J = 8.2, 1H), 7.57 (dd, J = 8.1, 4.4, 1H), 7.66 (d, J = 8.8, 1H), 7.72 (d, J = 8.8, 1H), 8.07 (d, J = 8.2, 1H), 8.18 (dd, J = 9.1, 1.8, 1H), 9.17 (dd, J = 4.4, 1.8, 1H)</td>
<td>159.5, 150.1, 145.8, 145.5, 136.1, 136.0, 128.7, 126.6, 126.4, 125.3, 123.6, 122.6, 25.7</td>
<td>194 (M⁺, 100), 166</td>
</tr>
<tr>
<td>4b</td>
<td>1b</td>
<td>158-159 (151-152)¹⁴</td>
<td>2.57 (s, 3H), 7.57 (dd, J = 8.1, 4.4, 1H), 7.69 (d, J = 8.8, 1H), 7.74 (d, J = 8.8, 1H), 7.99 (d, J = 2.2, 1H), 8.20 (dd, J = 8.1, 1.8, 1H), 9.01 (dd, J = 2.2, 1H), 9.15 (dd, J = 4.3, 1.8, 1H)</td>
<td>151.7, 150.1, 146.1, 144.0, 135.9, 135.2, 132.8, 128.4, 128.1, 126.4, 126.2, 122.6, 18.6</td>
<td>194 (M⁺, 100), 167</td>
</tr>
<tr>
<td>4c</td>
<td>1c</td>
<td>146-150 (144-145)¹⁷</td>
<td>2.73 (s, 3H), 7.47 (dd, J = 4.4, 0.8, 1H), 7.58 (dd, J = 8.1, 4.3, 1H), 7.76 (d, J = 9.1, 1H), 7.95 (d, J = 9.1, 1H), 8.20 (dd, J = 8.1, 1.8, 1H), 9.01 (dd, J = 4.5, 1H), 9.15 (dd, J = 4.3, 1.7, 1H)</td>
<td>150.2, 149.7, 146.3, 145.7, 144.4, 135.7, 128.1, 126.0, 125.4, 124.1, 122.8, 122.4, 19.0</td>
<td>194 (M⁺, 100), 167</td>
</tr>
<tr>
<td>Compound</td>
<td>Substrate 1</td>
<td>Substrate 3</td>
<td>mp / (°C) (Lit)</td>
<td>1H NMR (CDCl₃ / TMS) δ, J (Hz)</td>
<td>13C NMR (CDCl₃/TMS) δ</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
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<td>--------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>5a</td>
<td>1a</td>
<td>3c</td>
<td>145-147</td>
<td>2.73 (s, 3H), 2.91 (s, 3H), 7.39 (d, J = 3.8, 1H), 7.45 (d, J = 8.2, 1H), 7.72 (d, J = 9.0, 1H), 7.89 (d, J = 9.0, 1H), 8.07 (d, J = 8.2, 1H), 9.01 (d, J = 4.5, 1H)</td>
<td>159.3, 149.6, 145.7, 145.4</td>
</tr>
<tr>
<td>5b</td>
<td>1a</td>
<td>3b</td>
<td>122-124</td>
<td>2.55 (s, 3H), 2.91 (s, 3H), 7.43 (d, J = 8.2, 1H), 7.61 (d, J = 8.8, 1H), 7.67 (d, J = 8.8, 1H), 7.95 (d, J = 1.9, 1H), 8.05 (d, J = 8.2, 1H), 9.01 (d, J = 1.9, 1H)</td>
<td>159.3, 151.6, 145.6, 143.8</td>
</tr>
<tr>
<td>5c</td>
<td>1b</td>
<td>3b</td>
<td>194-196</td>
<td>2.57 (s, 3H), 7.68 (s, 1H), 7.96 (d, J = 1.8, 1H), 8.99 (d, J = 1.7, 1H)</td>
<td>151.5, 144.2, 135.1, 132.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(209-212)(^14)</td>
<td></td>
<td>127.9, 126.2, 18.6</td>
</tr>
<tr>
<td>5d</td>
<td>1c</td>
<td>3b</td>
<td>129-134</td>
<td>2.56 (s, 3H), 2.74 (s, 3H), 7.39 (d, J = 4.5, 1H), 7.70 (d, J = 9.1, 1H), 7.93 (d, J = 9.1, 1H), 7.96 (d, J = 11.1, 1H), 8.98-9.00 (m, 2H)</td>
<td>151.6, 149.5, 145.8, 144.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(137-138)(^14)</td>
<td></td>
<td>124.1, 134.8, 132.4, 127.8</td>
</tr>
<tr>
<td>5e</td>
<td>1d</td>
<td>3d</td>
<td>44-47</td>
<td>1.47 (s, 9H), 7.72 (s, 1H), 8.08 (d, J = 2.5, 1H), 9.21 (d, J = 2.4, 1H)</td>
<td>149.2, 145.1, 143.8, 131.2</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>127.7, 126.5, 33.8, 31.0</td>
</tr>
<tr>
<td>5f</td>
<td>1e</td>
<td>3e</td>
<td>112-115</td>
<td>0.95 (t, J = 7.4, 3H), 1.35-1.49 (m, 2H), 1.68-1.78 (m, 2H), 2.86 (t, J = 7.6, 2H), 7.72 (s, 1H), 7.99 (d, J = 2.0, 1H), 9.02 (d, J = 2.0, 1H)</td>
<td>151.3, 144.4, 137.1, 134.4</td>
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<td>128.0, 126.2, 33.2, 32.7</td>
</tr>
<tr>
<td>5g</td>
<td>1b</td>
<td>3d</td>
<td>75-80</td>
<td>1.48 (s, 9H), 2.57 (s, 3H), 7.68 (d, J = 8.8, 1H), 7.73 (d, J = 8.8, 1H), 7.98 (d, J = 1.2, 1H), 8.11 (d, J = 1.4, 1H), 9.00 (d, J = 1.2), 9.24 (d, J = 1.4)</td>
<td>151.6, 149.2, 145.0, 144.1</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>144.0, 135.0, 132.2, 131.2</td>
</tr>
</tbody>
</table>

\(^a\) HRMS for 5a: C₁₄H₁₂N₂ calcd.: 208.1000 found: 208.1002
\(^b\) HRMS for 5b: C₁₄H₁₂N₂ calcd.: 208.1000 found: 208.1013
\(^c\) HRMS for 5e: C₂₀H₂₄N₂ calcd.: 292.1939 found: 292.1941
\(^d\) HRMS for 5f: C₂₀H₂₄N₂ calcd.: 292.1939 found: 292.1943
\(^e\) HRMS for 5g: C₁₇H₁₄N₂ calcd.: 250.1470 found: 250.1475
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