Supporting Information

Rhodium-Catalyzed Synthesis of Quinolines and Imines under Mild Condition

Dilip Kumar T. Yadav and Bhalchandra M. Bhanage*

Department of Chemistry, Institute of Chemical Technology,
N. Parekh Marg, Matunga, Mumbai 400019, India.
Tel.: +91-22-33612601; fax: +91-22-33611020;
E-mail: bm.bhanage@ictmumbai.edu.in, bm.bhanage@gmail.com

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Contents</th>
<th>Page no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>General information</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>General procedure for the synthesis of quinolines</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>General procedure for the synthesis of imines</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Spectral data of compounds</td>
<td>4-5</td>
</tr>
<tr>
<td>5</td>
<td>References</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Spectra</td>
<td>6-15</td>
</tr>
</tbody>
</table>
1. General information:

**Materials and Method:**

All chemicals and reagents were purchased from Alfa Aesar, Sigma Aldrich and commercial suppliers. Solvents were acquired from commercial suppliers and used without further purification. Reaction monitor was done by using Perkin Elmer Clarus 400 gas chromatography equipped with flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm). GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df) = 0.25 μm, column flow 2 mLmin⁻¹, 80 °C to 240 °C at 10 °C/min rise) was employed for the mass analysis of the products. Products were purified by column chromatography on silica (100-200 mesh) and basic alumina. The ¹H NMR spectrum was recorded on Bruker-400 MHz spectrometer in CDCl₃ using tetramethylsilane (TMS) as internal standard. The ¹³C NMR spectrum was recorded on Bruker-100 MHz spectrometer in CDCl₃. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as internal standard. J (coupling constant) values were reported in Hz. Splitting patterns of proton are described as s (singlet), d (doublet), t (triplet) and m (multiplet). The products were confirmed by the comparison of their GC-MS spectra, and/or ¹H and ¹³C NMR spectra with those of authentic data.
2. General procedure for the synthesis of quinolines:

In oven-dried sealed tube equipped with magnetic stirring bar, 4 mL of deionised water was charged and dry nitrogen gas was purged for 1 h. Next, 1a (1 mmol), 2a (2.5 mmol), rhodium acetate dimer (0.03 mmol) and triphenylphosphine trisulfonate sodium salt (0.06 mmol) were charged to the above degassed deionised water and then refluxed for 6 h under nitrogen atmosphere. On completion of reaction, it was cooled to room temperature and extracted with ethyl acetate (3×5 mL). The combined ethyl acetate layers were dried over anhydrous Na₂SO₄ and solvent was evaporated under reduce pressure. The obtained crude product was directly purified by column chromatography (silica gel, 100-200 mesh, PE–EtOAc) to afford the pure product. The identity of product was confirmed by ¹H and ¹³C NMR spectroscopic analysis.

3. General procedure for the synthesis of imines:

The benzyl amine (4a, 2 mmol) and rhodium acetate dimer (0.03 mmol) were mixed in an oven-dried sealed tube with a magnetic stirrer bar and the reaction mixture was heated at 100 °C for 10 h. After cooling the reaction mixture to room temperature, the crude product was purified by column chromatography (basic alumina saturated with Et₃N, 100-200 mesh, PE) to provide the desired pure product. The identity of product was confirmed by comparison with those of authentic compounds from literature.
4. Spectral data of compounds:

**2-ethyl-3,8-dimethylquinoline (3b)**

\[
\text{\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.76 \text{ (s, 1H)}, 7.53 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 7.44 \text{ (d, } J = 6.9 \text{ Hz, 1H)}, 7.31 \text{ (t, } J = 7.7 \text{ Hz, 1H)}, 2.97 \text{ (q, } J = 7.4 \text{ Hz, 2H), 2.79 \text{ (s, 3H), 2.44 \text{ (s, 3H), 1.42 (t, } J = 7.4 \text{ Hz, 3H)) ppm; }

\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } & \delta 161.48, 145.60, 136.68, 135.47, 129.10, 128.23, 127.10, 125.23, 124.61, 29.23, 19.00, 17.82, 12.12 \text{ ppm. HRMS (ESI): calc. for [(C}_{13}\text{H}_{15}\text{N})\text{H} \text{ (M+H)} 186.1283, measured 186.1257.}
\end{align*}}
\]

**2-ethyl-3,6-dimethylquinoline (3c)**

\[
\text{\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.90 \text{ (d, } J = 8.3 \text{ Hz, 1H)}, 7.72 \text{ (s, 1H)}, 7.43-7.41 \text{ (m, 2H), 2.96 \text{ (q, } J = 7.5 \text{ Hz, 2H), 2.49 \text{ (s, 3H), 2.45 \text{ (s, 3H), 1.36 (t, } J = 7.6 \text{ Hz, 3H)) ppm; }

\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } & \delta 162.34, 145.24, 135.26, 135.19, 130.52, 129.32, 128.20, 127.35, 125.59, 29.43, 21.52, 19.13, 12.92 \text{ ppm. HRMS (ESI): calc. for [(C}_{13}\text{H}_{15}\text{N})\text{H} \text{ (M+H)} 186.1283, measured 186.1255.}
\end{align*}}
\]

**2-ethyl-3,6,8-trimethylquinoline (3d)**

\[
\text{\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.65 \text{ (s, 1H)}, 7.27 \text{ (s, 2H), 2.94 (q, } J = 7.4 \text{ Hz, 2H), 2.75 \text{ (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H), 1.39 (t, } J = 7.8 \text{ Hz, 3H)) ppm; }

\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } & \delta 160.53, 144.21, 136.26, 134.90, 134.71, 130.53, 129.03, 127.19, 123.50, 29.14, 21.54, 19.01, 17.71, 12.19 \text{ ppm. HRMS (ESI): calc. for [(C}_{14}\text{H}_{17}\text{N})\text{H} \text{ (M+H)} 200.1439, measured 200.1425.}
\end{align*}}
\]
2-ethyl-6-methoxy-3-methylquinoline (3f)\textsuperscript{2}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{compound_3f}
\caption{Structural formula of 2-ethyl-6-methoxy-3-methylquinoline (3f).}
\end{figure}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.84 (d, \(J = 9.1\) Hz, 1H), 7.66 (s, 1H), 7.19 (dd, \(J = 9.1, 2.8\) Hz, 1H), 6.90 (d, \(J = 2.8\) Hz, 1H), 3.83 (s, 3H), 2.88 (q, \(J = 7.5\) Hz, 2H), 2.39 (s, 3H), 1.27 (t, \(J = 7.5\) Hz, 3H) ppm; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 160.74, 157.17, 142.68, 134.83, 129.96, 129.68, 128.15, 120.68, 104.53, 55.47, 29.26, 19.14, 14.05 ppm. HRMS (ESI): calc. for [(C\textsubscript{13}H\textsubscript{15}NO)H] (M+H) 202.1232, measured 202.1228.

6-chloro-2-ethyl-3-methylquinoline (3i)\textsuperscript{1}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{compound_3i}
\caption{Structural formula of 6-chloro-2-ethyl-3-methylquinoline (3i).}
\end{figure}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.79 (d, \(J = 8.8\) Hz, 1H), 7.76 (d, \(J = 2.1\) Hz, 1H), 7.63 (s, 1H), 7.58 (dd, \(J = 8.9, 2.2\) Hz, 1H), 2.88 (q, \(J = 7.5\) Hz, 2H), 2.39 (s, 3H), 1.28 (t, \(J = 7.5\) Hz, 3H) ppm; \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 163.79, 145.21, 134.59, 131.65, 130.55, 130.35, 128.70, 128.47, 119.26, 29.37, 19.14, 12.57 ppm.

5. References:

6. Copies of $^1$H NMR and $^{13}$C NMR Spectra:

2-ethyl-3,8-dimethylquinoline (3b) $^1$H NMR
2-ethyl-3,8-dimethylquinoline (3b) $^{13}$C NMR
2-ethyl-3,6-dimethylquinoline (3c) $^1$H NMR
2-ethyl-3,6-dimethylquinoline (3c) $^{13}$C NMR
2-ethyl-3,6,8-trimethylquinoline (3d) $^1$H NMR
2-ethyl-3,6,8-trimethylquinoline (3d) $^{13}$C NMR
2-ethyl-6-methoxy-3-methylquinoline (3f) $^1$H NMR
2-ethyl-6-methoxy-3-methylquinoline (3f) $^{13}$C NMR
6-chloro-2-ethyl-3-methylquinoline (3f) $^1$H NMR
6-chloro-2-ethyl-3-methylquinoline (3f) $^{13}\text{C}$ NMR