Supporting Information
for DOI: 10.1055/s-0037-1611639
© Georg Thieme Verlag KG Stuttgart · New York 2018
Reduction of Nitroarenes to Anilines with a Benzothiazoline: Application of Enantioselective Synthesis of 2-Arylquinoline Derivatives

Masamichi Miyagawa, Ryota Yamamoto, Nanako Kobayashi and Takahiko Akiyama

*Department of Chemistry, Faculty of Science, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171-8588, Japan*
General experimental procedures

All reactions were performed in dried glassware under an atmosphere of dry nitrogen. Toluene was distilled over CaH$_2$, and stored over 4A molecular sieves. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F254, Art 5715, 0.25 mm) were used. Column chromatography and preparative TLC (PTLC) were performed on PSQ 60B, Fuji Silysia Chemical Ltd. and Wakogel B-5F, Wako pure Chemical Industries, respectively. $^1$H NMR and $^{13}$C NMR were measured on an Ascend$^{TM}$ 400 (Bruker Ltd, 400 MHz) spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane for $^1$H, 0.00 ppm in chloroform-d) and coupling constants are reported as hertz (Hz). $^{13}$C NMR spectra taken in CDCl$_3$ ($\delta$ 77.0) were referenced to the residual solvents. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet.

General procedures of reduction

Under a nitrogen atmosphere, a mixture of nitroarene 1a (0.080 mmol), benzothiazoline 2e (0.32 mmol, 4.0 equiv) and MS4A (100 mg, activated) in toluene (0.80 mL) was heated at reflux for 0.5 h, and the reaction was monitored with TLC. After completion of the reaction, the reaction mixture was filtered with dichloromethane through Celite pad. Then, the filtrate was concentrated in vacuo and the residue was purified by preparative TLC to give aniline 3a (98%).

Compound data

Spectroscopic data of 3a-n and 4aa-ae were consistent with commercially available materials.

2-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinoline (10b).$^{1)}$

White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.91-2.00 (m, 1H), 2.06-2.13 (m, 1H), 2.71 (dt, 1H, $J =$ 4.8, 16.4 Hz), 2.91 (ddd, 1H, $J =$ 5.4, 10.8, 16.4 Hz), 4.00 (brs, 1H), 4.43 (dd, 1H, $J =$ 3.2, 9.2 Hz), 6.55 (dd, 1H, $J =$ 1.2, 8.0 Hz), 6.66 (dt, 1H, $J =$ 1.2, 7.6 Hz), 6.96-7.04 (m, 2H), 7.31 (s, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 26.2, 31.0, 55.6, 114.1, 117.4, 120.8, 127.0, 127.9, 128.7, 129.3, 133.0, 143.4, 144.4.
2-Naphthyl-1,2,3,4-tetrahydroquinoline (10c).\(^2\)

White solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.04-2.20 (m, 2H), 2.77 (dt, 1H, \(J = 16.4\) Hz), 2.95 (ddd, 1H, \(J = 5.6, 10.8, 16.4\) Hz), 4.14 (brs, 1H), 4.61 (dd, 1H, \(J = 3.6, 9.2\) Hz), 6.59 (d, 1H, \(J = 8.0\) Hz), 6.70 (dt, 1H, \(J = 1.2, 7.6\) Hz), 7.01-7.05 (m, 2H), 7.44-7.52 (m, 3H), 7.80-7.84 (m, 4H)

\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 26.4, 31.0, 56.4, 114.0, 117.2, 121.0, 124.9, 125.1, 125.8, 126.2, 127.0, 127.7, 127.9, 128.4, 129.3, 133.0, 133.4, 142.2, 144.7.

\([\alpha]_D^{24} -33\) (c 0.54, CHCl\(_3\)).

References

HPLC analyses

(±)-10a

HPLC: DAICEL CHIRALPAK® OD-H; hexane/i-PrOH = 9:1, flow rate = 1.0 mL/min, UV = 315 nm, $t_{\text{major}}$ = 9.4 min, $t_{\text{minor}}$ = 12.7 min.

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Retention time</th>
<th>Type</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.533</td>
<td>BB</td>
<td>35444746</td>
<td>50.039</td>
</tr>
<tr>
<td>2</td>
<td>14.007</td>
<td>BB</td>
<td>35389904</td>
<td>49.961</td>
</tr>
</tbody>
</table>

(-)-10a

HPLC: DAICEL CHIRALPAK® OD-H; hexane/i-PrOH = 9:1, flow rate = 1.0 mL/min, UV = 315 nm, $t_{\text{major}}$ = 9.4 min, $t_{\text{minor}}$ = 12.7 min.

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Retention time</th>
<th>Type</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.400</td>
<td>BB</td>
<td>43719832</td>
<td>95.905</td>
</tr>
<tr>
<td>2</td>
<td>12.653</td>
<td>BB</td>
<td>1866308</td>
<td>4.094</td>
</tr>
</tbody>
</table>
HPLC: DAICEL CHIRALPAK® OD-H; hexane/i-PrOH = 9:1, flow rate = 1.0 mL/min, UV = 300 nm, $t_{\text{major}} = 11.0$ min, $t_{\text{minor}} = 20.4$ min.
HPLC: DAICEL CHIRALPAK® OJ-H; hexane/i-PrOH = 9:1, flow rate = 1.0 mL/min, UV = 290 nm, $t_{\text{major}}$ = 14.0 min, $t_{\text{minor}}$ = 24.9 min.
NMR spectra