Supporting Information

Room-Temperature Copper-Catalyzed Synthesis of Primary Arylamines from Aryl Halides and Aqueous Ammonia

Chuanzhou Tao, a Weiwei Liu, a Aifeng Lv, b Mingming Sun, a Ying Tian, a Qi Wang, a Jing Zhao, a,b

a School of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P. R. of China
Fax +86(518)85895121; E-mail: cztao@mail.ustc.edu.cn
b State Key Laboratory of Pharmaceutical Biotechnology, School of Life Sciences, Nanjing University, Nanjing 210093, P. R. of China
Fax +86(25)83592672; E-mail: jingzhao@nju.edu.cn

General experimental procedures

All reactions were carried out in an oven-dried Schlenk tube under nitrogen atmosphere. All chemicals were obtained from commercial source and used without further purification. Flash column chromatography was performed on silica 230–400 mesh. 1H-NMR, 13C-NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature in CDCl3. Chemical shifts are reported in ppm relative to TMS.

Coupling of aryl halides with aqueous ammonia at room temperature; General procedure

An oven-dried Schlenk tube was charged with CuI (18 mg, 10 mol%), K3PO4 (424 mg, 2.0 mmol) and aryl halide (1.0 mmol). The tube was evacuated and backfilled with nitrogen. Then, aqueous ammonia (6.5 mmol, 0.5 mL) and DMF (1.0 mL) were added under nitrogen. The tube was sealed and the reaction mixture was stirred at room temperature for 36-48 hours. The reaction mixture was quenched with water, extracted with diethyl ether and dried over anhydrous MgSO4. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, EtOAc-PE) to afford the product. The products obtained herein are all known compounds, and 1H NMR and 13C NMR are presented below.

Aniline (2a):

1H NMR (400 MHz, CDCl3) δ 7.14 (t, J = 8.0, 2H), 6.74 (t, J = 8.0 Hz, 1H), 6.65 (d, J = 8.1 Hz, 2H), 3.56 (s, br, 2H).

13C NMR (100 MHz, CDCl3) δ 146.5, 129.4, 118.6, 115.2.

p-toluidine (2b):

1H NMR (400 MHz, CDCl3) δ 6.96 (d, J = 7.9 Hz, 2H), 6.60 (d, J = 8.1 Hz, 2H), 3.46 (s, br, 2H), 2.23 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 143.9, 129.8, 127.9, 115.4, 20.5.

4-methoxyaniline (2c):

1H NMR (400 MHz, CDCl3) δ 6.74 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 3.74 (s, 3H), 3.34 (s,
br, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.9, 140.1, 116.5, 114.9, 55.9.

4-chloroaniline (2d)$^3$:
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.09 (d, $J = 8.6$ Hz, 2H), 6.60 (d, $J = 8.6$ Hz, 2H), 3.63 (s, br, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.1, 129.2, 123.3, 116.3.

4-bromoaniline (2e)$^3$:
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 (d, $J = 7.9$ Hz, 2H), 6.55 (d, $J = 7.8$ Hz, 2H), 3.64 (s, br, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.6, 132.1, 116.8, 110.3.

1-(4-aminophenyl)ethanone (2f)$^3$:
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J = 7.7$ Hz, 2H), 6.65 (d, $J = 7.7$ Hz, 2H), 4.11 (s, br, 2H), 2.50 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.5, 151.2, 130.9, 128.2, 113.9, 26.2.

ethyl 4-aminobenzoate (2g)$^3$:
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, $J = 7.8$ Hz, 2H), 6.64 (d, $J = 7.8$ Hz, 2H), 4.32 (q, $J = 7.1$ Hz, 2H), 4.04 (s, br, 2H), 1.36 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.8, 150.8, 131.7, 120.4, 113.9, 60.4, 14.6.

4-aminobenzonitrile (2h)$^3$:
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 (d, $J = 7.8$ Hz, 2H), 6.64 (d, $J = 7.8$ Hz, 2H), 4.15 (s, br, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.5, 133.9, 120.2, 114.6, 100.4.

4-aminobenzoic acid (2i)$^3$:
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, $J = 8.4$ Hz, 2H), 6.66 (d, $J = 8.4$ Hz, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.9, 151.6, 132.5, 118.8, 113.9.

4-nitroaniline (2j)$^3$:
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, $J = 8.8$ Hz, 2H), 6.63 (d, $J = 8.8$ Hz, 2H), 4.37 (s, br, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.6, 139.4, 126.5, 113.5.

3-chloroaniline (2k)$^3$:
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.04 (t, $J = 8.0$ Hz, 1H), 6.71 (d, $J = 7.9$ Hz, 1H), 6.64 (s, 1H), 6.52 (d, $J = 8.1$ Hz, 1H), 3.63 (s, br, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.7, 134.9, 130.4, 118.5, 115.0, 113.3.
methyl 3-aminobenzoate (2i):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 7.7$ Hz, 1H), 7.36 (s, 1H), 7.21 (t, $J = 7.8$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 3.89 (s, 3H), 3.55 (s, br, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 146.4, 131.3, 129.4, 119.9, 119.6, 116.0, 52.2.

3-nitroaniline (2m):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 8.1$ Hz, 1H), 7.49 (s, 1H), 7.31 – 7.24 (m, 1H), 6.94 (d, $J = 8.0$ Hz, 1H), 3.98 (s, br, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.5, 147.5, 130.7, 120.7, 113.4, 109.2.

2-aminobenzoic acid (2p):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 8.2$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 6.67 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.2, 151.3, 135.3, 132.3, 116.9, 116.6, 109.6.

3-aminobenzonitrile (2r):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (t, $J = 7.9$ Hz, 1H), 7.01 (d, $J = 7.5$ Hz, 1H), 6.92 – 6.83 (m, 2H), 3.87 (s, br, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.1, 130.2, 122.1, 119.3, 119.1, 117.6, 113.1.

References

Table 2: Copper Iodide-Catalyzed Cross-Coupling Aryl Halides (1) with Aqueous Ammonia at Room Temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl halide</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="" /> 1a</td>
<td><img src="image2" alt="" /> 2a</td>
<td>48</td>
<td>69</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="" /> 1b</td>
<td><img src="image4" alt="" /> 2b</td>
<td>48</td>
<td>61</td>
</tr>
</tbody>
</table>
Isolated yields.

* Reaction conditions: aryl halide (1.0mmol), 25% aqueous ammonia (6.5mmol, 0.5mL), Cul (10mol%), K$_3$PO$_4$ (2.0mmol), DMP (1mL), room temperature, nitrogen atmosphere.

* Isolated yields.