Supporting information.

C-N bond formation between alcohols and amines using an iron catalyst

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General Procedure for the alkylation of amines with alcohols.

Aniline (0.069 mL, 0.76 mmol), benzyl alcohol (0.157 mL, 1.52 mmol), trimethylamine N-oxide dihydrate (5.7 mg, 0.076 mmol), 1 (40 mg, 0.076 mmol) were placed in a pressure tube which was flushed with nitrogen. Degassed toluene or xylene (0.40 mL) was added and the pressure tube was sealed and heated at 110 °C (in toluene) or 110 °C (in xylene) for the time indicated. Once the reaction was complete an additional excess of trimethylamine N-oxide dihydrate was added and reacted for a further 0.5 hours after which time the mixture was filtered through celite using 100% EtOAc and the solvent was removed under reduced pressure. Purification is as described below for each product.

N-Benzylaniline 6.

(Toluene, 110 °C, 48h)

This compound has been reported and fully characterised.¹ The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a pale yellow oil (133.7 mg, 0.731 mmol, 95 %). δ_H (400 MHz, CDCl₃) 7.30-7.40 (4H, m, ArH), 7.24-7.29 (1H, m, ArH), 7.12-7.20 (2H, m, ArH), 6.68-6.74 (1H, m, ArH), 6.61-6.65 (2H, m, ArH), 4.32 (2H, s, NHCH₂), 4.00 (1H, s, NH); δ_C (100 MHz, CDCl₃) 148.20 (C), 139.48 (C), 129.30 (CH), 128.67 (CH), 127.55 (CH), 127.27 (CH), 117.60 (CH), 112.49 (CH), 48.36 (CH₂); m/z (ESMS+) [M+H]+ 184.1. C₁₃H₁₄N+. Conversion was determined by chiral GC analysis: Chrompac cyclodextrin-β-236M-19, 50 m x 0.25 mm x 0.25 μM, T = 140 °C, 10 min, 5 °C /min, P = 15 psi H₂, det = FID 220 °C, inj = 220 °C, aniline 5.8 min, benzyl alcohol 7.9 min, imine 31.2 min, amine 39.9 min.
N-(2-Methoxybenzyl)aniline 9.

(Toluene, 110 °C, 48h)

This compound has been reported and fully characterised.\textsuperscript{2} The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give a pale yellow oil (136.6 mg, 0.641 mmol, 84 %). $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 7.27-7.36 (2H, m, ArH), 7.12-7.20 (2H, m, ArH), 6.84-6.91 (2H, m, ArH), 6.71-6.78 (3H, m, ArH), 5.35-6.17 (1H, br s, NH), 4.33 (2H, s, NHCH$_2$), 3.83 (3H, s, OCH$_3$); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 157.52 (C), 146.61 (C), 129.40 (CH), 129.22 (CH), 128.69 (CH), 126.18 (C), 120.55 (CH), 118.89 (CH), 114.53 (CH), 110.28 (CH), 55.35 (CH$_3$), 44.48 (CH$_2$); $m/z$ (ESMS+) [M+H]$^+$ 214.1. C$_{14}$H$_{16}$NO$^+$. 

![N-(2-Methoxybenzyl)aniline](image)
N-(4-Methoxybenzyl)aniline 10.

(Toluene, 110 °C, 48h)

This compound has been reported and fully characterized\(^1\). The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. Ether to give the product as a brown oil (103.5 mg, 0.486 mmol, 64%). After purification there was still presence of starting material but the characteristic peaks could be identified from 1H NMR. 

\[\delta^H (400 \text{ MHz, CDCl}_3) \ 7.16-7.23 \ (2\text{H, Ar}H), \ 7.08-7.15 \ (3\text{H, Ar}H), \ 6.79-6.84 \ (2\text{H, Ar}H), \ 6.70-6.77 \ (2\text{H, Ar}H), \ 4.27-4.33 \ (1\text{H, br s, NH}), \ 3.78 \ (3\text{H, s, OCH}_3), \ 3.70 \ (2\text{H, s, NHCH}_2); \ m/z \ (\text{ESMS}^+) \ [\text{M+H}]^+ \ 214.1. \ C_{13}H_{13}ClN^+ \].
13C NMR could be added:
**N-(4-Chlorobenzyl)aniline, 11.**

(Toluene, 110 °C, 48h)

This compound has been reported and fully characterised.\(^1\) The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. Ether to give the product as a pale yellow oil (100.0 mg, 0.461 mmol, 60 %). \(\delta_H\) (400 MHz, CDCl\(_3\)) 7.22-7.36 (4H, m, ArH), 7.09-7.19 (2H, m, ArH), 6.67-6.75 (1H, m, ArH), 6.53-6.61 (2H, m, ArH), 4.26 (2H, s, NHCH\(_2\)), 4.01 (1H, br s, NH); \(\delta_C\) (100 MHz, CDCl\(_3\)) 147.86 (C), 138.05 (C), 132.90 (C), 129.34 (CH), 128.79 (CH), 128.73 (CH), 117.84 (CH), 112.93 (CH), 47.64 (CH\(_2\)); m/z (ESMS+) [M+H]\(^+\) 218.1. C\(_{13}\)H\(_{13}\)ClN\(^+\).
This compound has been reported and fully characterised. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a light brown oil (93.0 mg, 0.429 mmol, 56 %). $\delta_H$ (400 MHz, CDCl$_3$) 7.34-7.42 (2H, m, ArH), 7.11-7.20 (4H, m, ArH), 6.68-6.73 (1H, m, ArH), 6.57-6.62 (2H, m, ArH), 4.41 (2H, s, NHCH$_2$), 4.12 (1H, br s, NH); $\delta_C$ (100 MHz, CDCl$_3$) 147.81 (C), 136.72 (C), 133.28 (C), 129.57 (CH), 129.33 (CH), 129.06 (CH), 128.41 (CH), 126.97 (CH), 117.79 (CH), 112.97 (CH), 45.94 (CH$_2$); $m/z$ (ESMS+) [M+H]$^+$ 218.1. C$_{13}$H$_{15}$ClN$^+$. 

$N$-(2-Chlorobenzyl)aniline 12.

\[
\begin{align*}
\text{\text{H}} & \quad \text{\text{N}} \\
\text{\text{Cl}} & 
\end{align*}
\]

(Toluene, 110 °C, 48h)
N-Benzyl-4-methoxyaniline 13.
This compound has been reported and fully characterized. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a brown oil (140.6 mg, 0.660 mmol, 87%). $\delta_H$ (400 MHz, CDCl$_3$) 7.31-7.39 (3H, m, ArH), 7.11-7.29 (1H, m, ArH), 6.75-6.80 (2H, m, ArH), 6.57-6.63 (2H, m, ArH), 4.28 (2H, s, NHCH$_2$), 3.74 (3H, s, OCH$_3$); $\delta_C$ (100 MHz, CDCl$_3$) 152.22 (C), 142.48 (C), 139.71 (C), 128.62 (CH), 127.57 (CH), 127.19 (CH), 114.94 (CH), 114.13 (CH), 55.84 (CH$_3$), 49.27 (CH$_2$); m/z (ESMS+) [M+H]$^+$ 214.1. C$_{14}$H$_{16}$NO$^+$. 

![NMR spectrum](Image)
**N-Hexylaniline 14 and di(n-hexyldiamine) 15.**

(Xylene, 140 °C):

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Mol% catalyst</th>
<th>Time/h</th>
<th>Eq. amine</th>
<th>Eq. Alcohol</th>
<th>Monoalkylated 14</th>
<th>Dialkylated 15</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>088</td>
<td>10</td>
<td>24</td>
<td>1</td>
<td>2</td>
<td>51%</td>
<td>Not determined</td>
<td>Isolated yield.</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>24</td>
<td>1</td>
<td>3</td>
<td>72%</td>
<td>13%</td>
<td>Isolated yield.</td>
</tr>
<tr>
<td>104</td>
<td>10</td>
<td>24</td>
<td>1</td>
<td>1.1</td>
<td>67%</td>
<td>0%</td>
<td>Isolated yield, no dialk seen.</td>
</tr>
<tr>
<td>105</td>
<td>10</td>
<td>48</td>
<td>1</td>
<td>3</td>
<td>96</td>
<td>4</td>
<td>Ratio in crude 1H NMR only.</td>
</tr>
<tr>
<td>134</td>
<td>20</td>
<td>24</td>
<td>1</td>
<td>3</td>
<td>87.5%</td>
<td>12.5%</td>
<td>Ratio in crude 1H NMR only.</td>
</tr>
<tr>
<td>138</td>
<td>20</td>
<td>48</td>
<td>1</td>
<td>3</td>
<td>72%</td>
<td>28%</td>
<td>Ratio in crude 1H NMR only.</td>
</tr>
</tbody>
</table>
This compound has been reported and fully characterised. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a pale yellow oil (110.0 mg, 0.623 mmol, 82%). $\delta_H$ (400 MHz, CDCl$_3$) 7.13-7.19 (2H, m, ArH), 6.65-6.70 (1H, m, ArH), 6.56-6.61 (2H, m, ArH), 3.57 (1H, br s, NH), 3.09 (2H, t, $J$ 8.0 NHCH$_2$), 1.61 (2H, quin, $J$ 8.0 NHCH$_2$CH$_2$), 1.26-1.44 (6H, m, hex), 0.85-0.94 (3H, m, CH$_2$CH$_3$); $\delta_C$ (100 MHz, CDCl$_3$) 148.58 (C), 129.24 (CH), 117.08 (CH), 112.71 (CH), 44.04 (CH$_2$), 31.69 (CH$_2$), 29.59 (CH$_2$), 26.90 (CH$_2$), 22.67 (CH$_2$), 14.08 (CH$_3$); m/z (ESMS+) [M+H]$^+$ 178.1. C$_{12}$H$_{19}$N$^+$. 
The dialkylation product 15 was formed in low conversion as a mixture with 14 however sufficient could be isolated to characterize the product by 1H NMR:

\[
\delta_{\text{H}} (400 \text{ MHz, CDCl}_3) 7.25-7.15 (2\text{H, M, ArH}), 6.65-6.55 (3\text{H, m, ArH}), 3.22 (4\text{H, t, } J = 6.5, 2 \times \text{NCH}_2), 1.60-1.50 (4\text{H, m, 2 x CH}_2), 1.30-1.20 (12\text{H, m, 6 x CH}_2), 0.85 (6\text{H, t, } J = 6.5, 2 \times \text{CH}_3).
\]
Fraction containing 16% mono and 11% dialkylated:
N-Cyclohexylaniline 16.

\[
\begin{align*}
&\text{(Xylene, 140 °C, 24h)} \\
\text{This compound has been reported and fully characterised.}^1 \text{ The compound was purified by} \\
\text{column chromatography on silica with a gradient elution 0-20% EtOAc in pet. Ether to give} \\
\text{the product as a pale yellow oil (102.8 mg, 0.587 mmol, 77 %).} \\
\text{\(\delta_H(400 \text{ MHz, CDCl}_3\)) 7.11-7.18 (2H, m, ArH), 6.62-6.67 (1H, m, ArH), 6.55-6.60 (2H, m, ArH), 3.49 (1H, br s, NH),} \\
\text{3.20-3.28 (1H, m, NHCHCH}_2\text{), 2.01-2.09 (2H, m, c-Hex), 1.70-1.80 (2H, m, c-Hex), 1.60-1.69 (1H, m, c-Hex), 1.29-1.43 (2H, m, c-Hex), 1.08-1.28 (3H, m, c-Hex);} \\
\text{\(\delta_C(100 \text{ MHz, CDCl}_3\)) 147.43 (C), 129.28 (CH), 116.84 (CH), 113.16 (CH), 51.71 (CH), 33.54 (CH}_2\text{), 25.98 (CH}_2\text{), 25.07 (CH}_2\text{);} \\
\text{\(m/z\) (ESMS+) [M+H]+ 176.1.} \\
\end{align*}
\]
\[\text{C}_{12}\text{H}_{18}\text{N}^+\]
Examples which worked poorly:

*N*-Benzyl-2-chloroaniline.

(Toluene, 110 °C, 48h)

This compound has been reported and fully characterised. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. ether to give the product as a brown oil (6.60 mg, 0.03 mmol, 4 %). After purification there was still presence of starting material but most of the characteristic peaks could be identified from 1H NMR. $\delta$H (400 MHz, CDCl$_3$) 7.32-7.39 (4H, m, ArH), 7.24-7.31 (2H, m, ArH), 7.06-7.12 (1H, m, ArH), 6.60-6.67 (2H, m, ArH), 4.67-4.81 (1H, br s, NH), 4.38-4.43 (2H, s, NHCH$_2$); m/z (ESMS+) [M+H]$^+$ 218.1. C$_{13}$H$_{13}$ClN$^+$. 

![N-Benzylic-2-chloroaniline.png](attachment://N-Benzylic-2-chloroaniline.png)
N-Benzyl-3-chloroaniline.
This compound has been reported and fully characterised. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. Ether to give the product as a brown oil (57.7 mg, 0.266 mmol, 35%). After purification there was still presence of starting material but most of the characteristic peaks could be identified from $^1$H NMR. $\delta_H$ (400 MHz, CDCl$_3$) 7.07-7.12 (2H, m, ArH), 6.50-6.56 (2H, m, ArH), 4.29 ((2H, s, NHCH$_2$), 3.96-4.14 (1H, br s, NH); $m/z$ (ESMS+) [M+H]$^+$ 218.1. C$_{13}$H$_{13}$ClN.$^+$
Benzyl(2-methoxyphenyl)amine.

(Toluene, 110 °C, 48h)
This compound has been reported and fully characterised. The compound was purified by column chromatography on silica with a gradient elution 0-20% EtOAc in pet. Ether to give the product as a pale brown oil (37.3 mg, 0.175 mmol, 23 %). After purification there was still presence of starting material but most of the characteristic peaks could be identified from 1H NMR. \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 6.64-6.70 (1H, m, Ar\( \text{H} \)), 6.57-6.61 (1H, m, Ar\( \text{H} \)), 4.57-4.69 (1H, br s, NH), 4.35 (2H, s, NHCH\(_2\)), 3.84 (3H, s, OCH\(_3\)); \( m/z \) (ESMS+) [M+H]\(^+\) 214.1. C\(_{14}\)H\(_{16}\)NO\(^+\).
References


