Supporting information

Size- and support-dependent selective amine cross-coupling with platinum nanocluster catalysts

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1. TEM
Transmission electron microscopy (TEM) measurement was carried out using a JEOL JEM-2100F TEM operated at 200 kV. The average Pt particle size from TEM (2.43 ± 0.65 nm) was consistent with that from CO adsorption (2.5 nm) within the experimental error. Based on the result, we adopted Pt particle sizes from CO adsorption (Table 1) in this study.

Fig. S1. TEM image and particle size distribution of Pt/SiO2-2.5.
2. EXAFS curve-fitting

Fig. S2. The inverse Fourier transform of $k^3$-weighted Pt L3-edge EXAFS spectrum of (solid line) Pt/Al2O3-0.8 and (●) its best fit derived from curve-fitting analysis.

Table S1. N-alkylation of aniline with various amines by Pd/Al2O3-1.8.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine donor</th>
<th>Product</th>
<th>Conversion / %</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
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<td>0</td>
</tr>
<tr>
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<td></td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
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<td></td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td></td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Et3N</td>
<td></td>
<td>93</td>
<td>79</td>
</tr>
</tbody>
</table>

*Yields of product determined by GC are based on aniline. Conditions are shown in Table 4.*
Scheme S1. N-alkylation of p-methoxyaniline with iPr₂NH by Pd/Al₂O₃-1.8.

Scheme S2. N-alkylation of benzylamine with iPr₂NH by Pd/Al₂O₃-1.8.

Fig. S3. Yields of (△) unreacted aniline 1, (○) N-isopropylaniline 3 and (●) isopropylidene-phenylamine 4 for the reaction of aniline with iPr₂NH by Pt/CeO₂-1.8 vs. reaction time. Reaction conditions are shown in Table 3.
3. ¹H-NMR and GC/MS Analysis

¹H-NMR spectra were recorded in CDCl₃ with TMS as an internal standard at ambient temperature on a Varian INOVA-500 operating at 500 MHz. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

N-Isopropylaniline: (Table 2, Entry 1)

\[
\text{H}N\text{H}
\]

¹H NMR (CDCl₃): δ 7.37-7.31 (m, 2H), 6.88-6.82 (m, 1H), 6.76-6.73 (m, 2H), 3.82-3.75 (m, 1H), 3.55 (br, s, 1H), 1.36 (d, \( J = 6.3 \) Hz, 6H).

MS: \( m/z \) (relative intensity) 135 (M⁺,27), 120 (100).

N-sec-Butylaniline: (Table 2, Entries 7)

\[
\text{H}N\text{H}
\]

¹H NMR (CDCl₃): δ 7.33-7.40 (m, 2H), 6.74-6.90 (m, 3H), 3.71 (m, 1H), 3.39 (br, s, 1H), 1.62 (m, 2H), 1.23 (d, \( J = 7.1 \) Hz, 3H), 1.00 (t, \( J = 7.2 \) Hz, 3H).

MS: \( m/z \) (relative intensity) 149 (M⁺,28), 120 (100).

N-(pentan-3-yl)aniline: (Table 2, Entry 8)

\[
\text{H}N\text{H}
\]

MS: \( m/z \) (relative intensity) 163 (M⁺,16), 134 (100).

N-Ethylaniline: (Table 2, Entry 10)

\[
\text{H}N\text{H}
\]

¹H NMR (CDCl₃): δ 6.79(m, 2H), 6.57 (m, 3H), 3.27 (br, s, 1H), 3.09 (q, \( J = 7.2 \) Hz, 2H), 1.23(t, \( J = 7.2 \) Hz, 3H).

MS: \( m/z \) (relative intensity) 121 (M⁺,36), 106 (100).
\textbf{\textit{N-Isopropyl-4-methoxyaniline:}} (Table 3, Entry 1)

\begin{center}
\includegraphics[width=0.2\textwidth]{n-isopropyl-4-methoxyaniline.png}
\end{center}

$^1$H NMR (CDCl$_3$): $\delta$ 6.81 (d, $J = 9.0$ Hz, 2H), 6.60 (d, $J = 8.7$ Hz, 2H), 3.77 (s, 3H), 3.57 (heptet, $J = 6.3$ Hz, 1H), 3.16 (br, s, 1H), 1.22 (d, $J = 6.3$ Hz, 6H).

MS: $m/z$ (relative intensity) 165 (M$^+$,33), 150 (100).

\textbf{\textit{N-Isopropyl-4-methylaniline:}} (Table 3, Entry 2)

\begin{center}
\includegraphics[width=0.2\textwidth]{n-isopropyl-4-methylaniline.png}
\end{center}

$^1$H NMR (CDCl$_3$): $\delta$ 7.06 (d, $J = 8.1$ Hz, 2H), 6.59 (d, $J = 8.4$ Hz, 2H), 3.67 (heptet, $J = 6.3$ Hz, 1H), 3.32 (br, 1H), 2.32 (s, 3H), 1.27 (d, $J = 6.3$ Hz, 6H).

MS: $m/z$ (relative intensity) 149 (M$^+$,31), 134 (100).

\textbf{\textit{4-\textit{t}-Butyl-N-isopropylaniline:}} (Table 3, Entry 3)

\begin{center}
\includegraphics[width=0.2\textwidth]{4-t-butyl-n-isopropylaniline.png}
\end{center}

$^1$H NMR (CDCl$_3$): $\delta$7.39 (d, $J = 8.4$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 2H), 3.79 (heptet, $J = 6.3$ Hz, 1H), 3.50 (br, s, 1H), 1.49 (s, 9H), 1.38 (d, $J = 6.3$ Hz, 6H).

MS: $m/z$ (relative intensity) 191 (M$^+$,31), 176 (100).

\textbf{\textit{4-Chloro-N-isopropylaniline:}} (Table 3, Entry 4)

\begin{center}
\includegraphics[width=0.2\textwidth]{4-chloro-n-isopropylaniline.png}
\end{center}

MS: $m/z$ (relative intensity) 169 (M$^+$,25), 154 (100).
**N-Benzylpropan-2-amine:** (Table 3, Entry 5)

![N-Benzylpropan-2-amine structure](image)

$^1$H NMR (CDCl$_3$): δ 7.28-7.15 (m, 5H), 3.73 (s, 2H), 2.80 (heptet, $J = 6.3$ Hz, 1H), 1.39 (br, s, 1H), 1.04 (d, $J = 6.3$ Hz, 6H).

MS: $m/z$ (relative intensity) 149 (M$^+$,8), 91 (100).

**N-Phenethylpropan-2-amine:** (Table 3, Entry 6)

![N-Phenethylpropan-2-amine structure](image)

$^1$H NMR (CDCl$_3$): δ 7.35-7.18 (m, 5H), 2.91-2.83 (m, 5H), 1.08 (d, $J = 6.0$ Hz, 6H).

MS: $m/z$ (relative intensity) 162 (M$^+$,1), 72 (100).

**N-Isopropyl-2,3-dihydro-1H-inden-5-amine:** (Table 3, Entry 8)

![N-Isopropyl-2,3-dihydro-1H-inden-5-amine structure](image)

$^1$H NMR (CDCl$_3$): δ 7.08 (d, $J = 8.1$ Hz, 2H), 6.57 (s, 1H), 6.47 (d, $J = 8.1$ Hz, 2H), 3.66 (heptet, $J = 6.3$ Hz, 1H), 3.29 (br, s, 1H), 2.88 (q, $J = 7.8$ Hz, 2H), 2.11 (sextet, $J = 7.5$ Hz, 2H), 1.26 (d, $J = 6.3$ Hz, 6H).

MS: $m/z$ (relative intensity) 175 (M$^+$,24), 86(100).

**N-Isopropyl-6-methylheptan-2-amine:** (Table 3, Entry 8)

![N-Isopropyl-6-methylheptan-2-amine structure](image)

$^1$H NMR (CDCl$_3$): δ 2.81 (heptet, $J = 6.3$ Hz, 1H), 2.60-2.40 (m, 1H), 1.45 (heptet, $J = 6.6$ Hz, 1H), 1.32-1.00 (m, 6H), 0.97-0.90 (m, 9H), 0.78 (d, $J = 6.6$ Hz, 6H), 0.63 (br, s, 1H).

MS: $m/z$ (relative intensity) 171 (M$^+$,1), 86 (100).