SUPPORTING INFORMATION

Solvent-free amination catalysed by [Pd(NHC)] complexes

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General informations

- All aryl halides and amines were used as received.
- KO\textsubscript{t}Am was received as a solution in toluene (1.7 M), dried on a Schlenk line, stored in a glovebox and used as a dried white powder.
- KO\textsubscript{t}Bu and LiHMDS were used as received and stored in a glovebox.
- \[\text{Pd(IPr*)}(\text{cin})\text{Cl}\], \[\text{Pd(IPr*}\text{Tol})(\text{cin})\text{Cl}\], \[\text{Pd(IPr*)}(\text{acac})\text{Cl}\], \[\text{Pd(IPr*)}(\text{PEPPSI})\] and \[\text{Pd(IPr)(acac})\text{Cl}\] were prepared according to procedures reported in the literature.
- \[\text{Pd(IPr)(cin})\text{Cl}\], \[\text{Pd(SIPr)(cin})\text{Cl}\], \[\text{Pd(IPr)}(\text{PEPPSI})\] and \[\text{Pd(SIPr)}(\text{PEPPSI})\] were commercially available from Umicore.
- Flash chromatography was performed on silica gel 60 Å pore diameter and 40-63 µm particles size.
- \textsuperscript{1}H and \textsuperscript{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker-400 MHz or 300 MHz spectrometer at ambient temperature in CDCl\textsubscript{3} using the residual chloroform peak as a reference.
- Elemental analyses were performed at London Metropolitan University 166-220 Holloway Road, London, N7 8DB.
- High resolution mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre (NMSSC), Grove Building Extn., Swansea University, Singleton Park, Swansea, SA2 8PP, UK.


Optimisation of the solvent-free amination (complete table).\(^{a}\)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd] (mol%)</th>
<th>Base</th>
<th>Solvent</th>
<th>Conversion(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{c})</td>
<td><a href="cin">Pd(IPr*)</a>Cl</td>
<td>KOtAm</td>
<td>DME</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td><a href="cin">Pd(IPr*)</a>Cl</td>
<td>KOtAm</td>
<td>-</td>
<td>74%</td>
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<tr>
<td>3(^{d})</td>
<td><a href="cin">Pd(IPr*)</a>Cl</td>
<td>KOtAm</td>
<td>-</td>
<td>&gt;99% (98%)</td>
</tr>
<tr>
<td>4</td>
<td>[Pd(IPr*)(cin)Cl] (0.5)</td>
<td>KOtAm</td>
<td>-</td>
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<tr>
<td>5</td>
<td>[Pd(IPr*)(cin)Cl] (0.25)</td>
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<td>KOtAm</td>
<td>-</td>
<td>11%</td>
</tr>
<tr>
<td>7</td>
<td>[Pd(IPr)(cin)Cl]</td>
<td>KOtAm</td>
<td>-</td>
<td>11%</td>
</tr>
<tr>
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</tr>
<tr>
<td>9</td>
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<td>-</td>
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</tr>
<tr>
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<td>-</td>
<td>6%</td>
</tr>
<tr>
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<tr>
<td>12(^{d})</td>
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<td>13</td>
<td>[Pd(IPr)(PEPPSI)]</td>
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<td>14</td>
<td>[Pd(IPr)(PEPPSI)]</td>
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<td>15</td>
<td>[Pd(SIPr)(PEPPSI)]</td>
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<td>KOtAm</td>
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<tr>
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<td>21</td>
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<td>LiHMDS</td>
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<td>23</td>
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<td>24</td>
<td>[Pd(IPr)(acac)Cl]</td>
<td>LiHMDS</td>
<td>-</td>
<td>2%</td>
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\(^{a}\) Reagents and conditions: \(i\) 2-chloro-1,3-dimethylbenzene (1 mmol), base (1.1 mmol), [Pd] (mol%), 25°C, 5 min. \(ii\) 2,6-dimethylaniline (1.1 mmol), 25°C, 30 min. \(^{b}\) Conversion to coupling product based on starting material determined by GC. \(^{d}\) Conversion was complete after 5 minutes. \(^{e}\) Isolated yield after chromatography on silica gel, average of two runs.
Scope of the solvent-free amination reaction (complete table).^a

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Time</th>
<th>Product</th>
<th>Conversion^b / Yield^c</th>
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</thead>
<tbody>
<tr>
<td>1d</td>
<td>Cl</td>
<td>5 min</td>
<td>&gt;99% / 98%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Br</td>
<td>3 min</td>
<td>&gt;99% / 93%</td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>Cl</td>
<td>5 min</td>
<td>&gt;99% / 96%</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Br</td>
<td>5 min</td>
<td>&gt;99% / 99%</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Cl</td>
<td>5 min</td>
<td>&gt;99% / 99%</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Cl</td>
<td>10 min</td>
<td>99% / 99%</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Br</td>
<td>3 min</td>
<td>&gt;99% / 94%</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Cl</td>
<td>5 min</td>
<td>&gt;99% / 97%</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Cl</td>
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<td>&gt;99% / 93%</td>
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<td>10 min</td>
<td>0% / -</td>
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</tr>
<tr>
<td>11d</td>
<td>Cl</td>
<td>24 h</td>
<td>&gt;99% / 95%</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Cl</td>
<td>10 min</td>
<td>22% / -</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Cl</td>
<td>24 h</td>
<td>95% / 94%</td>
<td></td>
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<tr>
<td>14</td>
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<td>10 min</td>
<td>8% / -</td>
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<tr>
<td>15</td>
<td>Cl</td>
<td>24 h</td>
<td>&gt;99% / 98%</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Cl</td>
<td>1 h</td>
<td>67% / -</td>
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<tr>
<td>17</td>
<td>Cl</td>
<td>24 h</td>
<td>95% / 93%</td>
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</tr>
<tr>
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<td>Cl</td>
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<tr>
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<td>Cl</td>
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<td>&gt;99% / 94%</td>
<td></td>
</tr>
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</tr>
<tr>
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<td>95% / 83%</td>
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<tr>
<td>25</td>
<td>Br</td>
<td>24 h</td>
<td>73% / 66%</td>
<td></td>
</tr>
</tbody>
</table>

^a Reagents and conditions: i) ArX (1 mmol), I (1 mol%), KOAm (1.1 mmol), 25°C, 5 min. ii) Amine (1.1 mmol), 25°C, Time. ^b Conversion to coupling product based on starting material determined by GC. ^c Isolated yield after chromatography on silica gel, average of two runs. ^d Reaction performed in DME (1M) at 25°C for 24 h does not lead to any significant conversion of the starting materials.
Solvent-free amination of aryl halides with primary and secondary amines.

**General procedure using [Pd(IPr*)(cin)Cl] 1**: In a glovebox, in a vial equipped with a stirring bar and sealed with a screw cap fitted with a septum were added KOtAm (139 mg, 1.1 mmol) and [Pd(IPr*)(cin)Cl] (11.7 mg, 1 mol%). Both powders were next ground with a spatula and homogeneously mixed. Outside the glovebox, was added the aryl halide (1.0 mmol) under inert atmosphere. If the aryl halide was a solid, it was loaded inside the glovebox. The reaction mixture was then stirred (800 rpm) at room temperature (25°C) during 5 minutes. Then the amine (1.1 mmol) was finally added and the mixture was further stirred (800 rpm) at room temperature (25°C) during 3 min to 24 h. In most cases, the reaction medium was becoming solid after a short time. In the cases where the reaction was really fast to reach completion (5-10min), a strong exotherm was observed visually in the vial by the formation of fumes. After this time (3 min to 24 h), the crude product was solubilised in DCM, filtered through Celite® and eluted with DCM. The filtrate was evaporated in vacuo. The crude product was finally purified by flash chromatography on silica gel. The reported yields are the average of two runs.

**Bis(2,6-dimethylphenyl)amine** (Table 2, entries 1-2)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 99/1), 221 mg or 210 mg (98% starting from ArCl ; 93% starting from ArBr) of the title compound as a white powder.

![Bis(2,6-dimethylphenyl)amine](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.00 (d, $J = 7.4$ Hz, 4H), 6.86 (t, $J = 7.4$ Hz, 2H), 4.81 (s broad, 1H), 2.03 (s, 12H).

$^{13}$C {1H} NMR (75 MHz, CDCl$_3$): $\delta$ 141.9, 129.7, 128.8, 121.9, 19.3.

**2,6-Dimethyl-N-(o-tolyl)aniline** (Table 2, entries 3-4)

---


The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 99/1), 203 mg or 209 mg (96% starting from ArCl; 99% starting from ArBr) of the title compound as a yellow powder.

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.18-7.08 \text{ (m, 4H), 7.00 (t, } J = 7.7 \text{ Hz, 1H), 6.74 (t, } J = 7.4 \text{ Hz, 1H), 6.18 (d, } J = 8.0 \text{ Hz, 1H), 4.97 (s broad, 1H), 2.36 (s, 3H), 2.22 (s, 6H).} \\
\text{13C \{1H\} NMR (100 MHz, CDCl}_3\text{): } & \delta 144.3, 138.9, 135.6, 130.4, 128.7, 127.0, 125.7, 122.6, 118.2, 111.9, 18.4, 17.8.
\end{align*}
\]

2,6-Dimethyl-N-(p-tolyl)aniline\(^8\) (Table 2, entry 5)
The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 99/1), 209 mg (99% starting from ArCl) of the title compound as a yellow oil.

\[
\begin{align*}
\text{1H NMR (300 MHz, CDCl}_3\text{): } & \delta 7.25-7.13 \text{ (m, 3H), 7.08 (d, } J = 7.9 \text{ Hz, 2H), 6.54 (d, } J = 8.2 \text{ Hz, 2H), 5.17 (s broad, 1H), 2.36 (s, 3H), 2.32 (s, 6H).} \\
\text{13C \{1H\} NMR (100 MHz, CDCl}_3\text{): } & \delta 144.0, 138.8, 135.6, 129.8, 128.6, 127.5, 125.5, 113.9, 20.6, 18.5.
\end{align*}
\]

Dimesitylamine\(^9\) (Table 2, entries 6-7)
The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 99/1), 251 mg or 238 mg (99% starting from ArCl; 94% starting from ArBr) of the title compound as a white powder.

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3\text{): } & \delta 6.80 \text{ (s, 4H), 4.58 (s broad, 1H), 2.25 (s, 6H), 1.99 (s, 12H).} \\
\text{13C \{1H\} NMR (100 MHz, CDCl}_3\text{): } & \delta 139.6, 130.9, 129.6, 129.5, 20.7, 19.2.
\end{align*}
\]


**N-(2,6-diethylphenyl)-2,4,6-trimethylaniline** (Table 2, entry 8)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 99/1), 259 mg (97% starting from ArCl) of the title compound as a yellow powder.

\begin{center}
\begin{tikzpicture}
  \node[shape=circle,draw,scale=0.5] at (0,0) {N};
  \node[shape=circle,draw,scale=0.5] at (1.5,0) {H};
  \node[shape=circle,draw,scale=0.5] at (0,-1.5) {H};
  \node[shape=circle,draw,scale=0.5] at (1.5,-1.5) {H};
  \node[shape=circle,draw,scale=0.5] at (0,-3) {H};
  \node[shape=circle,draw,scale=0.5] at (1.5,-3) {H};
  \node[shape=circle,draw,scale=0.5] at (3,0) {H};
  \node[shape=circle,draw,scale=0.5] at (4.5,0) {H};
  \node[shape=circle,draw,scale=0.5] at (3,-1.5) {H};
  \node[shape=circle,draw,scale=0.5] at (4.5,-1.5) {H};
  \node[shape=circle,draw,scale=0.5] at (3,-3) {H};
  \node[shape=circle,draw,scale=0.5] at (4.5,-3) {H};
\end{tikzpicture}
\end{center}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \( \delta \) 7.12-6.98 (m, 3H), 6.84 (s, 2H), 4.82 (s broad, 1H), 2.47 (q, \( J = 7.6 \) Hz, 4H), 2.30 (s, 3H), 2.02 (s, 6H), 1.22-1.15 (m, 6H).

\textsuperscript{13}C \{1H\} NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 141.0, 139.5, 136.0, 130.5, 129.7, 128.6, 126.3, 122.5, 24.9, 20.7, 19.3, 14.0.

HRMS: calcld for C\textsubscript{19}H\textsubscript{26}N (M + H\textsuperscript{+}) 268.2065, found 268.2061.

**N-(2,6-diisopropylphenyl)-2,6-dimethylaniline\textsuperscript{10}** (Table 2, entry 9)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 99/1), 261 mg (93% starting from ArCl) of the title compound as an orange oil.

\begin{center}
\begin{tikzpicture}
  \node[shape=circle,draw,scale=0.5] at (0,0) {N};
  \node[shape=circle,draw,scale=0.5] at (1.5,0) {H};
  \node[shape=circle,draw,scale=0.5] at (0,-1.5) {H};
  \node[shape=circle,draw,scale=0.5] at (1.5,-1.5) {H};
  \node[shape=circle,draw,scale=0.5] at (3,0) {H};
  \node[shape=circle,draw,scale=0.5] at (4.5,0) {H};
  \node[shape=circle,draw,scale=0.5] at (3,-1.5) {H};
  \node[shape=circle,draw,scale=0.5] at (4.5,-1.5) {H};
\end{tikzpicture}
\end{center}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.18-7.09 (m, 3H), 6.94 (d, \( J = 7.5 \) Hz, 2H), 6.73 (t, \( J = 7.4 \) Hz, 1H), 4.79 (s, 1H), 3.15 (septet, \( J = 6.9 \) Hz, 2H), 1.98 (s, 6H), 1.12 (d, \( J = 6.8 \) Hz, 12H).

\textsuperscript{13}C \{1H\} NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 144.3, 143.3, 138.9, 129.6, 125.8, 125.0, 123.4, 119.7, 28.2, 23.6, 19.5.

**2,6-Dimethyl-N-phenylaniline\textsuperscript{11}** (Table 2, entry 10)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 98/2), 187 mg (95% starting from ArCl) of the title compound as a yellow solid.

\begin{itemize}
\end{itemize}
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.20-7.05 (m, 5H), 6.79-6.72 (m, 1H), 6.54-6.49 (m, 2H), 5.18 (s broad, 1H), 2.23 (s, 6H).

$^{13}$C {1H} NMR (75 MHz, CDCl$_3$): $\delta$ 146.4, 138.3, 136.0, 129.4, 128.7, 125.9, 118.3, 113.6, 18.5.

N-(2-methoxyphenyl)-2,6-dimethylaniline$^6$ (Table 2, entry 11)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 95/5), 214 mg (94% starting from ArCl) of the title compound as a white powder.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.16-7.07 (m, 3H), 6.90-6.86 (m, 1H), 6.77-6.70 (m, 2H), 6.18-6.14 (m, 1H), 3.97 (s, 3H), 2.23 (s, 6H).

$^{13}$C {1H} NMR (100 MHz, CDCl$_3$): $\delta$ 146.9, 138.5, 136.3, 136.1, 128.6, 125.8, 121.2, 117.4, 111.2, 110.0, 55.8, 18.4.

N-(4-methoxyphenyl)-2,6-dimethylaniline$^7$ (Table 2, entry 12)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 95/5), 223 mg (98% starting from ArCl) of the title compound as an orange oil.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.16-7.04 (m, 3H), 6.78 (d, $J = 9.0$ Hz, 2H), 6.52 (m broad, 2H), 3.77 (s, 3H), 2.23 (s, 6H).

$^{13}$C {1H} NMR (100 MHz, CDCl$_3$): $\delta$ 152.8, 140.2, 139.3, 135.0, 128.7, 125.1, 115.4, 114.8, 55.8, 18.5.

N-isobutyl-2-methylaniline (Table 2, entry 13)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 99/1), 152 mg (93% starting from ArCl) of the title compound as a yellow oil.
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.06 (d, $J = 7.2$ Hz, 2H), 6.87 (t, $J = 7.5$ Hz, 1H), 3.11 (s, 1H), 2.87 (d, $J = 6.7$ Hz, 2H), 2.36 (s, 6H), 1.97-1.84 (m, 1H), 1.09 (d, $J = 6.7$ Hz, 6H).

$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 146.5, 129.2, 128.9, 121.6, 56.5, 29.7, 20.6, 18.6.

HRMS: calcd for C$_{12}$H$_{20}$N (M + H)$^+$ 178.1596, found 178.1589.

$N,N$-dimethyl-$N$-phenylaniline$^{12}$ (Table 2, entry 14)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 99/1), 191 mg (92% starting from ArCl) of the title compound as a yellow oil.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.31-7.25 (m, 2H), 7.19-7.14 (m, 2H), 7.07-7.02 (m, 2H), 7.00-6.88 (m, 3H), 3.34 (s, 3H), 2.37 (s, 3H).

$^{13}$C {$^1$H} NMR (75 MHz, CDCl$_3$): $\delta$ 149.4, 146.7, 132.2, 130.0, 129.1, 122.7, 119.9, 118.3, 40.4, 20.9.

$N$-$2,4,6$-tetramethyl-$N$-phenylaniline$^{13}$ (Table 2, entry 15)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 98/2), 219 mg (97% starting from ArCl) of the title compound as a yellow liquid.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.31-7.25 (m, 2H), 7.07 (s, 2H), 6.82-6.74 (m, 1H), 6.54 (m broad, 2H), 3.28 (s, 3H), 2.44 (s, 3H), 2.18 (s, 6H).

$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 148.4, 141.7, 137.6, 136.6, 129.7, 129.3, 115.9, 111.1, 37.3, 21.1, 18.0.

4-Methoxy-$N$-methyl-$N$-phenylaniline$^{14}$ (Table 2, entry 16)


The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 98/2), 201 mg (94% starting from ArCl) of the title compound as a colorless oil.

\[ \text{MeO} \quad \text{N} \]

\[^1\text{H} \text{ NMR (300 MHz, CDCl}_3\): \delta 7.24-7.17 (m, 2H), 7.13-7.07 (m, 2H), 6.93-6.87 (m, 2H), 6.82-6.76 (m, 3H), 3.82 (s, 3H), 3.27 (s, 3H). \]

\[^{13}\text{C} \{^{1}\text{H}\} \text{ NMR (75 MHz, CDCl}_3\): \delta 156.4, 149.8, 142.3, 129.0, 126.3, 118.5, 115.9, 114.9, 55.6, 40.6. \]

4-(2-Methoxyphenyl)morpholine\(^{15}\) (Table 2, entry 17)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 90/10 to 80/20), 160 mg (83% starting from ArCl) of the title compound as a yellow oil.

\[ \text{O} \quad \text{N} \quad \text{O} \]

\[^1\text{H} \text{ NMR (300 MHz, CDCl}_3\): \delta 7.05-6.98 (m, 1H), 6.96-6.92 (m, 2H), 6.90-6.86 (m, 1H), 3.90 (t, \( J = 4.5 \) Hz, 4H), 3.87 (s, 3H), 3.07 (t, \( J = 4.5 \) Hz, 4H). \]

\[^{13}\text{C} \{^{1}\text{H}\} \text{ NMR (75 MHz, CDCl}_3\): \delta 152.2, 141.1, 123.1, 121.0, 117.9, 111.3, 67.1, 55.3, 51.1. \]

N-(2,6-dimethylphenyl)-2,3,4,5,6-pentamethylaniline (Table 2, entry 18)

The general procedure yielded, after flash chromatography on silica gel (Pentane/AcOEt: 99/1), 177 mg (66% starting from ArBr) of the title compound as a yellow powder.

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

\[^1\text{H} \text{ NMR (400 MHz, CDCl}_3\): \delta 6.97 (d, \( J = 7.3 \) Hz, 2H), 6.74 (t, \( J = 7.3 \) Hz, 1H), 4.85 (s, 1H), 2.27 (s, 3H), 2.24 (s, 6H), 2.08 (s, 6H), 1.97 (s, 6H). \]

\[^{13}\text{C} \{^{1}\text{H}\} \text{ NMR (100 MHz, CDCl}_3\): \delta 143.4, 139.0, 132.7, 130.7, 129.3, 129.1, 125.8, 119.4, 19.4, 17.0, 16.8, 15.8. \]

**HRMS:** calcd for C\(_{19}\)H\(_{26}\)N (M + H\(^+\)) 268.2065, found 268.2062.


Copy of NMR spectra for all compounds