Supporting Information

Heterogeneous Cobalt Catalysts for the Reductive Amination with H₂: General Synthesis of Secondary and Tertiary Amines

Fei Mao a, Dejun Sui a, Zhengliang Qi a, Haipeng Fan a, Rizhi Chen a and Jun Huang a

a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009 (P. R. China), Fax: (+86) 25-83172261; E-mail: junhuang@njtech.edu.cn
Experimental section

General Methods and Reagents

All reagents were purchased from Aladdin Reagent Company, Sigma-Aldrich Company and Alfa-Aesar Company and used without further purification. $^1$H-NMR spectra were measured with a Bruker AVANCE 400D spectrometer in CDCl$_3$ using tetramethylsilane (TMS) as internal reference. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKa radiations. X-ray diffraction (XRD) patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu Kα radiation source at 40 kV and 20 mA, from 5°C to 80°C with a scan rate of 0.5 °C/min. The base pressure was about 3x10$^{-9}$ mbar. SEM images were performed on a HITACHI S-4800 field-emission scanning electron microscope and TEM images were obtained using a JEOL JEM-2010 (200 kV) TEM instrument. BET surface areas were measured at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer. The samples were degassed at 150 °C to vacuum of 10$^{-3}$ Torr before analysis. The amount of Co was measured using a Jarrell-Ash 1100 ICP-AES spectrometer (Inductively Coupled Plasma-Atomic Emission Spectrometry).

The synthesis of [MCNIm]Cl

The ionic liquid [MCNIm]Cl was synthesized as following:

\[ \text{N} = \text{C} = \text{N}\]  \[\text{CH}_2\text{CN}\]

A mixture of 1-methylimidazole (8.21 g, 100 mmol) and CH$_2$CN (9.06 g, 120 mmol) was stirred at room temperature for 24 hours, the solid could be formed in the process of reaction. The formed solid was then washed with diethyl ether (3*50 mL) and dried under vacuum for 24 hours. Finally, the [MCNIm]Cl was synthesized with 96% yield (15.1 g).

Procedure for the preparation of the Co@NC catalyst

The typical procedure for the preparation of the catalysts is described as follows: A mixture of Co(OAc)$_2$.4H$_2$O (0.249 g, 1.0 mmol) and [MCNIm]Cl (0.772 g, 3.0 mmol) in methanol was stirred for 30 minutes at room temperature. Then, the activated carbon powder (0.75 g) was added and the whole reaction mixture was stirred at 50 °C for 5 hours. The reaction mixture was cooled to room temperature and methanol was removed slowly under vacuum. The remaining solid sample obtained was dried at 60 °C for 12 hours. The dried sample was grinded to a powder. Then, the grinded powder was pyrolyzed at 600 °C - 800 °C for 2-3 hours under nitrogen atmosphere. The yield of Co@NC (800-2h) catalyst was 0.985g after pyrolysis at 800 °C for 2 hours. Yields of other catalysts were listed in Table S1. The Co/C(800-2h) catalyst was synthesized without adding [MCNIm]Cl with the same others conditions as above. The IL/C(800-2h) catalyst was synthesized without adding Co(OAc)$_2$.4H$_2$O with similar conditions. The Co-IL/C catalyst was synthesized without pyrolysis.

ICP-AES analysis of Co@NC (800-2h): Co = 5.95
XPS data of Co@NC (800-2h) (Atom%): C = 92.47, N = 2.86, O = 4.28, Co = 0.39
Table S1 the pyrolysis condition of the Co@NC catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>pyrolysis temperature (°C)</th>
<th>pyrolysis time (h)</th>
<th>Yield of the Co catalyst (g)</th>
<th>Co content (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co@NC (600-2h)</td>
<td>600</td>
<td>2</td>
<td>0.993</td>
<td>5.93</td>
</tr>
<tr>
<td>2</td>
<td>Co@NC (700-2h)</td>
<td>700</td>
<td>2</td>
<td>0.985</td>
<td>5.98</td>
</tr>
<tr>
<td>3</td>
<td>Co@NC (800-2h)</td>
<td>800</td>
<td>2</td>
<td>0.984</td>
<td>5.95</td>
</tr>
<tr>
<td>4</td>
<td>Co@NC (800-3h)</td>
<td>800</td>
<td>3</td>
<td>0.977</td>
<td>6.03</td>
</tr>
<tr>
<td>5</td>
<td>Co/C(800-2h)</td>
<td>800</td>
<td>2</td>
<td>0.902</td>
<td>6.53</td>
</tr>
<tr>
<td>6</td>
<td>IL/C(800-2h)</td>
<td>800</td>
<td>2</td>
<td>0.934</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>Co-IL/C</td>
<td>no</td>
<td>no</td>
<td>1.885</td>
<td>0.312</td>
</tr>
</tbody>
</table>

* without adding [MCNim]Cl.  
* without adding Co(OAc)₂·4H₂O.  
* without pyrolyzing.

Characterization of the Co@NC (800-2h) catalyst

![Graph (a)](image1)

![Graph (b)](image2)

![Graph (c)](image3)

![Graph (d)](image4)
Figure S1 (a) XPS survey spectrum for Co@NC (800-2h). High-resolution XPS survey spectra of (b) Co 2p: 780.91 eV is CoO, 778.12 eV is Co and (c) N 1s for Co@NC (800-2h): 398.3 eV is pyridine-type nitrogen, 400.4 eV is pyrrole-type nitrogen, 402.4 eV is carbon nitrogen. (d) A close look at the XPS spectrum of Co 2p in Co@NC (800-2h).

Figure S2 The peak locations of catalyst comparing with standard of Co/CoO/Co$_3$O$_4$: (a) Co@NC (800-2h), (b) recycled Co@NC (800).

Figure S3 (a) Nitrogen adsorption-desorption isotherms at 77 K of AC (top): ADS(♦) and DES(▼); Co@NC (800-2h) (bottom): ADS(■) and DES(●). (b) pore size distribution curves of AC (■) and Co@NC (800-2h) (●).
Figure S4 TEM images for Co@NC (800-2h).

Figure S5 SEM images for Co@NC (800-2h)

Figure S6 EDX analysis for the Co@NC (800-2h)

Table S2 The optimization of reaction conditions for the reductive amination of benzaldehyde with aniline.

<table>
<thead>
<tr>
<th>Element Line</th>
<th>Weight %</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>85.84</td>
<td>89.05</td>
</tr>
<tr>
<td>N K</td>
<td>11.05</td>
<td>9.83</td>
</tr>
<tr>
<td>O K</td>
<td>0.80</td>
<td>0.63</td>
</tr>
<tr>
<td>CoK</td>
<td>2.3</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Table S3: The optimization of reaction conditions for the reductive amination of benzaldehyde with N-methylaniline

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp (℃)</th>
<th>Time (h)</th>
<th>H₂ pressure (bar)</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>acetonitrile</td>
<td>120</td>
<td>18</td>
<td>10</td>
<td>85</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>1,4-dioxane</td>
<td>120</td>
<td>18</td>
<td>10</td>
<td>83</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>o-xylene</td>
<td>120</td>
<td>18</td>
<td>10</td>
<td>93</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>toluene</td>
<td>120</td>
<td>18</td>
<td>10</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>toluene</td>
<td>110</td>
<td>18</td>
<td>10</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>toluene</td>
<td>90</td>
<td>18</td>
<td>10</td>
<td>87</td>
<td>74</td>
</tr>
<tr>
<td>7</td>
<td>toluene</td>
<td>110</td>
<td>14</td>
<td>10</td>
<td>99</td>
<td>63</td>
</tr>
<tr>
<td>8</td>
<td>toluene</td>
<td>110</td>
<td>18</td>
<td>5</td>
<td>90</td>
<td>46</td>
</tr>
</tbody>
</table>

* Reaction conditions: 1.0 mmol aniline, 1.5 mmol benzaldehyde; Co 2.0 mol% added; solvent (2.0 mL).  
  b Determined by GC. In case of lower yields, the imine was detected as the by-product.

Table S3: The optimization of reaction conditions for the reductive amination of benzaldehyde with N-methylaniline

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp (℃)</th>
<th>Time (h)</th>
<th>H₂ pressure (bar)</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>acetonitrile</td>
<td>140</td>
<td>18</td>
<td>30</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>1,4-dioxane</td>
<td>140</td>
<td>18</td>
<td>30</td>
<td>84</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>o-xylene</td>
<td>140</td>
<td>18</td>
<td>30</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>toluene</td>
<td>140</td>
<td>18</td>
<td>30</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>toluene</td>
<td>130</td>
<td>18</td>
<td>30</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>toluene</td>
<td>130</td>
<td>24</td>
<td>30</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>7</td>
<td>toluene</td>
<td>140</td>
<td>18</td>
<td>20</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>8</td>
<td>toluene</td>
<td>140</td>
<td>18</td>
<td>10</td>
<td>17</td>
<td>17</td>
</tr>
</tbody>
</table>

* Reaction conditions: 1.0 mmol N-methylaniline, 1.5 mmol benzaldehyde; Co 3.0 mol% added; solvent (2.0 mL).  
  b Determined by GC.
**Scheme S1** Control reactions for the reductive amination of benzaldehyde with benzylamine

Reaction conditions for (i): Co@NC(800-2h), 3.0 mol% 110 °C, 10 bar H₂, 18h, (ii): 140 °C, 30 bar H₂, 18h, (iii): Co@NC(800-2h), 3.0 mol% 140 °C, 30 bar H₂, 18h.

**Reaction (i):** Reactions were performed in a 30 mL stainless steel autoclave equipped with a stirring bar. Benzylamine (1.0 mmol), benzaldehyde (2.25 mmol), toluene (2.0 mL) and 3.0 mol % Co@NC(800-2h) were placed into the autoclave. Then, the autoclave was purged with hydrogen three times, and pressurized to 10 bar hydrogen and heated at 110 °C for 18 h. After the autoclave was cooled to room temperature, the sample was analyzed by GC. **Reaction (ii):** Then, the reactor was purged with hydrogen and pressurized to 30 bar hydrogen and heated at 140 °C for another 18 h. After the autoclave was cooled to room temperature, the sample was analyzed by GC.

**Reaction (iii):** Benzylamine (1.0 mmol), benzaldehyde (2.25 mmol), toluene (2.0 mL) and 3.0 mol % Co@NC(800-2h) were added to the autoclave. Then, the autoclave was purged with hydrogen three times and pressurized to 30 bar hydrogen and heated to 140 °C for 18 h. After the autoclave was cooled to room temperature, the sample was analyzed by GC.

**Typical procedure for the reductive amination of benzaldehyde and aniline over Co@NC(800-2h) catalyst (Table 1)**

Reactions were performed in a 30 mL stainless steel autoclave equipped with a stirring bar. Aniline (1.0 mmol), benzaldehyde (1.5 mmol), toluene (2 mL) and Co catalyst containing Co 2.0 mol % were added into the autoclave. Then, the autoclave was purged with hydrogen three times, and pressurized to 10 bar hydrogen and heated to 110 °C for 18 h. After the autoclave was cooled to room temperature, the sample was analyzed by GC.

**General procedure for the reductive amination of aldehydes and ketones with primary amines (Table 2 and Table S2)**

Reactions were performed in a 30 mL stainless steel autoclave equipped with a stirring bar. Amine (1.0 mmol), aldehyde/ketone (1.5 mmol), toluene (2.0 mL) and 2.0 mol % Co@NC(800-2h)
were added into the autoclave. Then, the autoclave was purged with hydrogen three times, and pressurized to 10 bar hydrogen and heated to 110 °C for 18 h. After the autoclave was cooled to room temperature, the solution was filtered and concentrated, and the product was isolated by chromatography on a silica gel column with hexane and ethyl acetate.

**General procedure for the reductive amination of aldehydes and ketones with secondary amines (Table 3 and Table S3)**

Reactions were performed in a 30 mL stainless steel autoclave equipped with a stirring bar. Amine (1.0 mmol), aldehyde/ketone (1.5 mmol), toluene (2.0 mL) and 3.0 mol % Co@NC(800-2h) were added into the autoclave. Then, the autoclave was purged with hydrogen three times, and pressurized to 30 bar hydrogen and heated to 140 °C for 18 h. After the autoclave was cooled to room temperature, the solution was filtered and concentrated, and the product was isolated by chromatography on a silica gel column with hexane and ethyl acetate.

**Scheme S2** Proposed mechanism of the reductive amination of aldehydes and ketones with amines over Co@NC(800-2h).

**General procedure for the synthesis of N-substituted isoindolinones (Scheme 2)**

Amine (1.0 mmol), 2-carboxybenzaldehyde (1.0 mmol), toluene (2.0 mL) and 3.0 mol % Co@NC (800-2h) were added into the autoclave. Then, the autoclave was purged with hydrogen three times, and pressurized to 30 bar hydrogen and heated to 140 °C for 18 h. After the autoclave was cooled to room temperature, the solution was filtered and concentrated, and the product was isolated by chromatography on a silica gel column with hexane and ethyl acetate.

**Recycling Procedure**

**The reductive amination of benzaldehyde with aniline**

Initially, the stainless steel autoclave equipped with a stirring bar was added in aniline (0.093 g, 1.0 mmol), benzaldehyde (0.159 g, 1.5 mmol), toluene (2.0 mL) and Co@NC (800-2h) (20mg, 2.0 mol% Co). Then, the autoclave was purged with hydrogen three times and pressurized to 10 bar hydrogen and heated at 110 °C for 18 h. After the autoclave was cooled to room temperature,
the reaction mixture was extracted with ethyl acetate (3 × 6 mL). The organic extract was dried with
anhydrous MgSO₄ and analyzed by GC to determine the yield. The catalyst Co@NC (800-2h) was
collected by centrifugation and washed with ethyl acetate. The recovered Co@NC (800-2h) was used
again for the reaction under the same action conditions.

The reductive amination of benzaldehyde and N-methylaniline
The stainless steel autoclave equipped with a stirring bar was added in N-methylaniline (0.107 g,
1.0 mmol), benzaldehyde (0.159 g, 1.5 mmol), toluene (2.0 mL) and Co@NC (800-2h) (30 mg, 3.0
mol% Co). Then the autoclave was purged with hydrogen three times and pressurized to 30 bar
hydrogen and heated at 140 °C for 18 h. After the autoclave was cooled to room temperature,
the reaction mixture was extracted with ethyl acetate (3 × 6 mL). The organic extract was dried with
anhydrous MgSO₄ and analyzed by GC to determine the yield. The catalyst Co@NC (800-2h) was
collected by centrifugation and washed with ethyl acetate. The recovered Co@NC (800-2h) was used
again for the reaction under the same action conditions.

The product data.

Secondary amines:

N-benzylaniline (Table 2, entry 1)

\(^1\)H NMR (400 MHz, CDCl₃): δ 4.36 (s, 2H), 6.67-7.77 (m, 3H), 7.21 (t, J = 8.4 Hz, 2H), 7.30-7.42 (m,
5H); \(^13\)C NMR (100 MHz, CDCl₃): 6 148.4, 139.8, 129.6, 128.9, 127.8, 127.6, 117.9, 113.1,
48.7; IR (neat): 3419, 3026, 2924, 2853, 1949, 1602, 1505, 1324, 1267, 989, 749.

N-(4-fluorobenzyl)aniline (Table 2, entry 2)

\(^1\)H NMR (500 MHz, CDCl₃): δ 4.81 (s, 2H), 7.23 (t, J = 8.3Hz, 3H), 7.48 (t, J = 6.8Hz, 2H), 7.55-7.58
(m, 1H), 7.72 (d, J = 8.5Hz, 2H), 7.91 (t, J = 7.4Hz, 1H); \(^13\)C NMR (75 MHz, CDCl₃): δ 163.7, 160.5,
148.0, 135.2, 129.4, 129.1, 129.0, 117.8, 115.6, 115.4, 112.9, 47.7; IR (neat): 3416, 1600, 1504,
1220.

N-(2-Chlorobenzyl)aniline (Table 2, entry 3)

\(^1\)H NMR (500 MHz, CDCl₃): δ 4.50 (s, 2H), 6.68-6.75 (m, 2H), 7.21-7.27 (m, 5H), 7.42-7.57 (m, 2H);

\(^13\)C NMR (75 MHz, CDCl₃): δ 147.8, 136.7, 133.2, 129.6, 129.4, 129.0, 128.4, 127.0, 117.8, 112.9,
N-(4-methoxybenzyl)aniline (Table 2, entry 4)

$^1$H NMR (400 MHz, CDCl$_3$): δ 3.84 (s, 3H), 4.29 (s, 2H), 6.67-6.78 (m, 3H), 6.92 (d, $J = 8.4$ Hz, 2H), 7.22 (t, $J = 7.6$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.1, 148.4, 131.6, 129.5, 129.1, 117.8, 114.3, 113.1, 55.5, 48.1; IR (neat): 3416, 3019, 2930, 2835, 1922, 1603, 1508, 1321, 1247, 1177, 1034, 824, 750, 692.

N-(3-methoxybenzyl)aniline (Table 2, entry 5)

$^1$H NMR (400 MHz, CDCl$_3$): δ 3.83 (s, 3H), 4.34 (s, 2H), 6.69-6.86 (m, 4H), 6.99 (d, $J = 11.6$ Hz, 2H), 7.20-7.29 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.9, 148.1, 141.2, 129.6, 129.2, 119.7, 117.6, 113.0, 112.8, 112.6, 55.2, 48.3; IR (neat): 3417, 3015, 2920, 2833, 1912, 1600, 1518, 1311, 1227, 1177, 1035, 826, 752, 694.

N-(4-methylbenzyl)aniline (Table 2, entry 6)

$^1$H NMR (400 MHz, CDCl$_3$): δ 2.39 (s, 3H), 4.33 (s, 2H), 6.69-6.79 (m, 3H), 7.20-7.32 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.3, 136.9, 136.5, 129.6, 129.3, 127.8, 117.7, 113.2, 48.3, 21.2; IR (neat): 3418, 2920, 1603, 1507, 1322, 1255, 1179, 749.

N-(2-methylbenzyl)aniline (Table 2, entry 7)

$^1$H NMR (400 MHz, CDCl$_3$): δ 2.32 (s, 3H), 4.32 (s, 2H), 6.86 (s, 3H), 7.22 (t, $J = 15.0$ Hz, 5H), 7.41 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 148.3, 137.1, 136.3, 130.4, 129.3, 128.3, 127.4, 126.2, 117.5, 112.7, 46.4, 18.9; IR (neat): 3419, 2930, 1934, 1603, 1507, 1321, 1245, 1177, 749.

N-(4-Chlorophenyl)benzylamine (Table 2, entry 8)

$^1$H NMR (500 MHz, CDCl$_3$): δ 4.29 (s, 2H), 6.54 (t, $J = 8.8$ Hz, 2H), 7.10 (t, $J = 8.8$ Hz, 2H), 7.25-7.29
(m, 1H), 7.32 (t, J = 8.6 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 146.9, 139.2, 129.3, 128.9, 127.7, 127.5, 122.4, 114.3, 48.6; IR (neat): 3427, 3028, 2924, 2853, 1952, 1864, 1600, 1502, 1453, 1401, 1321, 1177, 1094, 815, 733, 698, 505.

**N-(4-cyanophenyl)benzylamine (Table 2, entry 9)**

$^1$H NMR (400 MHz, CDCl$_3$): δ 4.40 (s, 2H), 6.62 (d, J=8.6 Hz, 2H), 7.34-7.45 (m, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 151.1, 137.8, 133.6, 128.8, 127.6, 127.2, 120.4, 112.3, 98.9, 47.4; IR (neat): 3357, 3018, 2914, 2843, 1942, 1864, 1600, 1502, 1443, 1407, 1325, 1177, 1084, 916, 817, 734, 698, 506.

**N-(4-methylphenyl)benzylamine (Table 2, entry 10)**

$^1$H NMR (400 MHz, CDCl$_3$): δ 2.27 (s, 3H), 4.34 (s, 2H), 6.60 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 4.8 Hz, 1H), 7.35-7.41 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 146.1, 139.9, 130.0, 128.9, 127.8, 127.4, 127.0, 113.3, 48.9, 20.7; IR (neat): 3445, 3027, 2918, 2763, 1951, 1865, 1701, 1618, 1522, 1452, 1302, 1126, 807, 742, 697, 511.

**N-(3-Methylphenyl)benzylamine (Table 2, entry 11)**

$^1$H NMR (400 MHz, CDCl$_3$): δ 2.18 (s, 3H), 4.23 (s, 2H), 6.50 (d, J = 36.2 Hz, 3H), 6.92 (d, J = 74.9 Hz, 1H), 7.20 (d, J = 34.3 Hz, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.2, 139.5, 139.2, 129.4, 128.9, 119.0, 114.1, 110.3, 48.8, 21.7; IR (neat): 3446, 3029, 2915, 2767, 1950, 1815, 1704, 1615, 1523, 1452, 1302, 1126, 805, 742, 693, 511.

**N-(4-methoxyphenyl)benzylamine (Table 2, entry 12)**

$^1$H NMR (400 MHz, CDCl$_3$): δ 3.84 (s, 3H), 4.29 (s, 2H), 6.67-6.78 (m, 3H), 6.92 (d, J = 8.4 Hz, 2H), 7.22 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 152.5, 142.4, 139.7, 128.8, 127.8, 127.4, 115.1, 114.5, 56.0, 49.5; IR (neat): 3375, 2944, 1629, 1511, 1456, 1236, 1033.
N-(2-methoxyphenyl)benzylamine (Table 2, entry 13)

$^1$H NMR (400 MHz, CDCl$_3$): δ 3.79 (s, 3H), 4.29 (s, 2H), 6.45-6.83 (m, 4H), 7.23 (d, $J = 39.3$Hz, 5H);

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 146.8, 139.6, 138.1, 128.6, 127.5, 127.1, 121.3, 116.6, 110.1, 109.4, 55.4, 48.0; IR (neat): 3376, 1607, 1512, 1403, 1239, 1177, 1076.

N-[2,6-Bis(1-methylethyl)phenyl]benzylamine (Table 2, entry 14)

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.17 (d, $J = 6.9$Hz, 12H), 2.94-3.02 (m, 2H), 4.29 (s, 2H), 7.08-7.11 (m, 1H), 7.15 (d, $J = 7.2$Hz, 2H), 7.50 (d, $J = 1.5$Hz, 3H), 7.90-7.92 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 143.2, 140.1, 129.0, 128.1, 126.6, 122.7, 56.1, 29.2, 23.4; IR (neat): 3419, 3016, 2931, 2843, 1929, 1602, 1505, 1324, 1277, 1177, 1092, 989, 814, 749, 692.

N-(2-pyridylmethyl)aniline (Table 2, entry 15)

$^1$H NMR (400 MHz, CDCl$_3$): δ 1.17 (d, $J = 6.9$Hz, 12H), 2.94-3.02 (m, 2H), 4.29 (s, 2H), 7.08-7.11 (m, 1H), 7.71 (t, $J = 6.2$Hz, 1H), 8.61 (d, $J = 4.8$Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 158.6, 149.1, 147.9, 136.7, 129.2, 122.1, 121.6, 117.5, 113.0, 49.2; IR (neat): 3416, 3028, 2972, 2843, 2788, 1566, 1542, 1028, 737, 700.

N-Isopropylaniline (Table 2, entry 16)

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.27 (d, $J = 6.3$Hz, 6H), 3.65-3.72 (m, 1H), 6.65-6.75 (m, 3H), 7.22 (t, $J = 7.5$Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 147.4, 129.1, 116.7, 113.1, 43.9, 22.7; IR (neat): 3400, 3050, 3018, 2964, 2828, 2869, 1596, 1600, 1503, 1314, 1254, 1176, 745, 691.

N-Cyclopentylaniline (Table 2, entry 17)

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.50-1.56 (m, 2H), 1.67-1.82 (m, 4H), 2.05-2.11 (m, 2H), 3.82-3.87 (m, 1H), 6.66 (d, $J = 8$Hz, 2H), 6.73 (t, $J = 7.3$Hz, 1H), 7.22 (t, $J = 7.5$Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$):
N-Cyclohexylaniline (Table 2, entry 18)

$^1$H NMR (500 MHz, CDCl₃): δ 1.19-1.48 (m, 5H), 1.71-1.86 (m, 3H), 2.12-2.15 (m, 2H), 3.30-3.36 (m, 1H), 6.66-6.75 (m, 3H), 7.21-7.24 (m, 2H); $^{13}$C NMR (75 MHz, CDCl₃): δ 147.4, 129.2, 116.8, 113.1, 51.6, 33.5, 25.9, 25.0; IR (neat): 3399, 3050, 2929, 2853, 1912, 1731, 1601, 1502, 1449, 1320, 1255, 1177, 1147, 1117, 887, 749, 692.

N-Cyclohexylethylaniline (Table 2, entry 19)

$^1$H NMR (500 MHz, CDCl₃): δ 1.01-1.09 (m, 2H), 1.23-1.34 (m, 3H), 1.62-1.90 (m, 6H), 3.02 (d, $J$ = 6.7Hz, 2H), 6.66-6.76 (m, 3H), 7.21-7.25 (m, 2H); $^{13}$C NMR (75 MHz, CDCl₃): δ 148.0, 129.3, 116.9, 112.7, 50.7, 37.7, 31.4, 26.7, 26.1.; IR (neat): 3408, 1600, 1505, 1470, 1447, 745, 691.

N-hexylaniline (Table 2, entry 20)

$^1$H NMR (500 MHz, CDCl₃): δ 0.89 (t, $J$ = 7.0Hz, 3H), 1.30-1.33 (m, 4H), 1.37-1.43 (m, 2H), 1.58-1.64 (m, 2H), 3.10 (t, $J$ = 7.2Hz, 2H), 6.60 (d, $J$ = 7.7Hz, 2H), 6.68 (m, $J$ = 7.3Hz, 1H), 7.15-7.18 (m, 2H);

$^{13}$C NMR (100 MHz, CDCl₃): δ 148.7, 129.3, 117.3, 113.0, 44.2, 31.8, 29.7, 27.0, 22.7, 14.7; IR (neat): 3412, 2956, 2928, 1603, 1507, 1321, 1259, 748, 692.

N-butylbenzylamine (Table 2, entry 21)

$^1$H NMR (500 MHz, CDCl₃): δ 0.91 (t, $J$ = 7.4Hz, 3H), 1.32-1.39 (m, 2H), 1.47-1.51 (m, 2H), 2.63 (t, $J$ = 7.3Hz, 2H), 3.79 (s, 2H), 7.22-7.26 (m, 1H), 7.31 (t, $J$ = 8.6Hz, 4H); $^{13}$C NMR (100 MHz, CDCl₃): δ 140.9, 128.6, 128.3, 127.0, 54.4, 49.5, 32.6, 20.8, 14.4; IR (neat): 3322, 3067, 2957, 2871, 1870, 1719, 1646, 1495, 1028, 732, 466.

N-Phenylbenzylimine
Tertiary amines:

N-Benzyl-N-methylaniline (Table 3, entry 1)

$^1$H NMR (400 MHz, CDCl$_3$): δ 2.40 (s, 3H), 4.33 (s, 2H), 6.69-6.79 (m, 3H), 7.20-7.32 (m, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 150.2, 134.6, 131.7, 130.1, 128.0, 117.4, 114.8, 56.7, 39.2; IR (neat): 3067, 3017, 2893, 2817, 1597, 1507, 1424, 1371, 1292, 1213, 1114, 1036, 950, 749, 692.

4-fluoro-N-methyl-N-phenylbenzylamine (Table 3, entry 2)

$^1$H NMR (500 MHz, CDCl$_3$): δ 3.07 (s, 3H), 4.57 (s, 2H), 6.81-6.85 (m, 3H), 7.08 (t, $J = 8.7$Hz, 2H), 7.26-7.33 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 161.3, 150.2, 134.6, 131.7, 130.1, 128.0, 117.4, 114.8, 56.7, 39.2; IR (neat): 3067, 3017, 2893, 2817, 1597, 1507, 1424, 1371, 1292, 1213, 1114, 1036, 950, 749, 692.

4-Chloro-N-methyl-N-phenylbenzylamine (Table 3, entry 3)

$^1$H NMR (500 MHz, CDCl$_3$): δ 3.07 (s, 3H), 4.55 (s, 2H), 6.80-6.82 (m, 3H), 7.24 (d, $J = 8.35$Hz, 2H), 7.28-7.31 (m, 2H), 7.35 (d, $J = 8.5$Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.9, 137.7, 132.9, 129.5, 129.1, 128.4, 117.2, 112.8, 56.5, 38.8; IR (neat): 3061, 3027, 2896, 2817, 1599, 1575, 1505, 1448, 1427, 1406, 1371, 1347, 1292, 1251, 1213, 1114, 1094, 1034, 1013, 950, 927, 804, 749, 692.

2-Chloro-N-methyl-N-phenylbenzylamine (Table 3, entry 4)

$^1$H NMR (500 MHz, CDCl$_3$): δ 3.16 (s, 3H), 4.68 (s, 2H), 6.76-6.82 (m, 3H), 7.26 (d, $J = 6.5$Hz, 3H),
7.28-7.31 (m, 2H), 7.45-7.49 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.1, 136.8, 134.0, 130.7, 129.5, 128.7, 118.0, 112.5, 56.8, 38.8; IR (neat): 3067, 3017, 2895, 2815, 1589, 1565, 1501, 1449, 1427, 1371, 1347, 1292, 1213, 1114, 1084, 1033, 950, 804, 748, 692.

2-bromo-N-methyl-N-phenylbenzylamine (Table 3, entry 5)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.15 (s, 3H), 4.61 (s, 2H), 6.74-6.80 (m, 3H), 7.16-7.23 (m, 2H), 7.26-7.29 (m, 3H), 7.63 (d, $J$ = 7.9Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 149.1, 137.3, 132.7, 129.2, 128.3, 127.8, 122.6, 116.6, 111.9, 57.3, 38.6; IR (neat): 2920, 1599, 1502, 1440, 1025, 747, 687.

N-methyl-N-phenyl-4-methylaniline (Table 3, entry 6)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.41 (s, 3H), 3.08 (s, 3H), 4.57 (s, 2H), 6.79 (t, $J$ = 7.3Hz, 1H), 6.84 (d, $J$ = 8.2Hz, 2H), 7.21 (t, $J$ = 8.7Hz, 4H), 7.28-7.32 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 150.2, 137.5, 136.4, 128.9, 128.3, 117.4, 112.0, 57.6, 39.1, 20.6; IR (neat): 3062, 2973, 2861, 1597, 1504, 1451, 1393, 1356, 1245, 1198, 1180, 1126, 1074, 987, 908, 862, 799, 747, 727, 693.

N-methyl-N-phenyl-2-methylaniline (Table 3, entry 7)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.38 (s, 3H), 3.09 (s, 3H), 4.53 (s, 2H), 6.77-6.80 (m, 3H), 7.20 (d, $J$ = 3Hz, 2H), 7.24-7.31 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 149.8, 141.0, 138.2, 129.5, 129.0, 128.3, 127.5, 126.3, 117.5, 112.9, 56.8, 39.4, 19.6; IR (neat): 3065, 2976, 2871, 1599, 1504, 1441, 1391, 1356, 1198, 1074, 985, 906, 863, 795, 748, 722, 694.

N-methyl-N-phenyl-3-phenylpropylamine (Table 3, entry 8)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.99-2.05 (m, 2H), 2.75 (t, $J$ = 7.8Hz, 2H), 3.01 (s, 3H), 3.44 (t, $J$ = 7.5 Hz, 2H), 6.78 (t, $J$ = 8.3 Hz, 3H), 7.28-7.33 (m, 5H), 7.38 (t, $J$ = 7.5Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 150.3, 141.5, 129.5, 129.0, 126.6, 118.2, 113.1, 54.2, 39.6, 35.7, 29.4; IR (neat): 3065, 3022.
2931, 2871, 1599, 1504, 1453, 1394, 1357, 1271, 1198, 1125, 1071, 1030, 987, 908, 889, 862, 799, 746, 727, 764, 505.

**N-methyl-N-pentylbenzenamine (Table 3, entry 9)**

$^1$H NMR (500 MHz, CDCl$_3$): δ 0.95-0.98 (m, 4H), 1.35-1.42 (m, 3H), 1.61-1.67 (m, 2H), 2.98 (s, 3H), 3.36 (t, $J = 7.6$Hz, 2H), 6.72-6.78 (m, 3H), 7.29-7.31 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 149.7, 129.6, 116.0, 112.1, 52.3, 39.1, 29.6, 26.4, 22.3, 14.4; IR (neat): 3072, 2956, 2928, 1603, 1507, 1321, 1259, 748, 692.

**N-methyl-N-phenyl-Cyclohexanemethylamine (Table 3, entry 10)**

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.01 (t, $J = 11$Hz, 2H), 1.23-1.32 (m, 3H), 1.74-1.81 (m, 6H), 3.01 (s, 3H), 1.81 (d, $J = 6.7$Hz, 2H), 6.71-6.75 (m, 3H), 7.26-7.31 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 149.1, 129.5, 118.0, 114.5, 59.3, 40.1, 37.2, 34.0, 26.2, 24.6; IR (neat): 3058, 2966, 1600, 1505, 1470, 1447, 745, 691.

**N-benzyl-N-ethylaniline (Table 3, entry 11)**

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.29 (t, $J = 7.1$Hz, 3H), 3.54-3.58 (m, 2H), 4.61 (s, 2H), 6.75-6.81 (m, 3H), 7.26-7.29 (m, 2H), 7.31-7.34 (m, 3H), 7.38-7.42 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.42, 139.22, 128.50, 126.69, 126.49, 115.96, 112.07, 53.85, 45.08, 12.09; IR (neat): 3061, 3027, 2971, 2927, 2871, 1599, 1504, 1451, 1393, 1356, 1272, 1245, 1198, 1180, 1126, 1074, 1037, 987, 908, 879, 862, 799, 747, 727, 693.

**Tribenzylamine (Table 3, entry 12)**

$^1$H NMR (400 MHz, CDCl$_3$): δ 3.57 (s, 6H), 7.26 (t, $J = 41.2$ Hz,15H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 139.8, 128.9, 128.6,127.1, 58.2; IR (neat): 3102, 3082, 3061, 3025, 2932, 2880, 2836, 2798, 2749, 2714, 1601, 1492, 1449, 1365, 1307, 1245, 1205, 1119, 1070, 1027, 988, 971, 903, 879, 824, 740,
N,N-Dibutylbenzylamine (Table 3, entry 13)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.93 (t, $J = 7.35$Hz, 6H), 1.31-1.37 (m, 4H), 1.48-1.54 (m, 4H), 2.47 (t, $J = 7.1$ Hz, 4H), 3.62 (s, 2H), 7.27 (t, $J = 7.1$Hz, 1H), 7.33-7.40 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$140.5, 128.8, 128.2, 126.6, 58.7, 53.8, 29.4, 20.7, 14.1; IR (neat): 1492, 1451, 1365, 741, 696.

N-Benzylmorpholine (Table 3, entry 14)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.49 (t, $J = 4.5$Hz, 4H), 3.55 (s, 2H), 3.75 (t, $J = 4.7$Hz, 4H), 7.28-7.31 (m, 1H), 7.35-7.39 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 140.5, 129.4, 128.1, 126.9, 66.3, 64.9, 60.4; IR (neat): 3034, 2986, 2631, 1717, 1377, 1245, 1045, 939, 750, 716, 699, 609.

N-benzylpyrrolidine (Table 3, entry 15)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.86 (s, 4H), 2.62 (s, 4H), 3.72 (s, 2H), 7.30 (d, $J = 5.1$Hz, 1H), 7.35-7.41 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.5, 128.9, 128.2, 126.8, 60.7, 54.3, 23.6; IR (neat): 3054, 2965, 2784, 1454, 1348, 1125.

Tributylamine (Table 3, entry 16)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.95 (t, $J = 7.3$Hz, 9H), 1.30-1.37 (m, 6H), 1.42-1.48 (m, 6H), 2.43 (t, $J = 7.7$Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 54.0, 29.5, 20.8, 13.3; IR (neat): 2967, 2873, 2798, 1468, 1377, 1307, 1183, 1086, 996, 901, 785, 733.

N-methyl-N-isopropylaniline (Table 3, entry 17)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.23 (d, $J = 6.6$Hz, 6H), 2.80 (s, 3H), 4.11-4.19 (m, 1H), 6.76 (t, $J = 7.3$Hz, 1H), 6.87 (d, $J = 8.2$Hz, 2H), 7.27-7.31 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.4, 129.3, 116.6, 113.6, 49.1, 30.0, 19.5; IR (neat): 2917, 2849, 1713, 1673, 1598, 1503, 1450, 1287, 1232, 1111, 749, 698.
**N-cyclopentyl-N-methyl-Benzamine (Table 3, entry 18)**

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.63-1.71 (m, 4H), 1.75-1.79 (m, 2H), 1.89-1.96 (m, 2H), 2.87 (s, 3H), 4.15-4.22 (m, 1H), 6.80 (t, $J = 7.3$Hz, 1H), 6.93 (d, $J = 8.2$Hz, 2H), 7.27-7.30 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.2, 130.1, 117.0, 113.6, 61.2, 38.7, 29.8, 20.4; IR (neat): 2946, 2861, 1597, 1504.

**N-methyl-N-cyclohexylaniline (Table 3, entry 19)**

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.19-1.24 (m, 1H), 1.40-1.57 (m, 4H), 1.75-1.93 (m, 5H), 2.86 (s, 3H), 3.61-3.67 (m, 1H), 6.75-6.87 (m, 3H) 7.28-7.32 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.3, 129.2, 116.3, 113.3, 58.2, 30.2, 30.1, 26.3, 26.1; IR (neat): 2946, 2861, 1597, 1504.

**4-tert-butyl-N-methyl-N-phenylCyclohexylamine (Table 3, entry 20)**

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.93 (s, 13H), 1.51-1.59 (m, 5H), 2.84 (s, 1H), 2.89 (s, 3H), 7.01 (d, $J =$ 8Hz, 2H), 7.28-7.32 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.4, 130.1, 117.4, 115.8, 58.2, 48.1, 30.6, 27.2, 21.0; IR (neat): 2956, 2867, 1597, 1504,1409, 889, 783, 633, 507 .

**N-methyl-N-phenyl-2-Pyridinemethanamine (Table 3, entry 21)**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.14 (s, 3H), 4.82 (s, 2H), 6.58-6.89 (m, 3H), 7.09-7.29 (m, 4H), 7.63-8.02 (m, 1H), 8.67 (t, $J = 29.7$Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.0, 149.3, 148.5, 137.1, 130.2, 123.8, 122.3, 117.2, 112.4, 59.2, 39.5; IR (neat): 3056, 3018, 2952, 2833, 2768, 1566, 1542, 1028, 737, 700.

**N-substituted isoindolinones:**

**N-Phenylisoindolin-1-one (Scheme 2)**

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.91 (s, 2H), 7.23 (t, $J = 7.4$Hz, 1H), 7.48 (t, $J = 8.1$Hz, 2H), 7.56 (d, $J =$
7.7 Hz, 2H), 7.63 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.98 (d, J = 7.5 Hz, 1H); 13C NMR (75 MHz, CDCl3): δ 168.0, 140.5, 139.9, 133.6, 132.4, 129.5, 128.7, 124.8, 124.5, 123.0, 119.8, 51.1; IR (neat): 3026, 2922, 2851, 1686, 1595, 1501, 1464, 1440, 732.

N-(4-methylphenyl)isoindolin-1-one (Scheme 2)

1H NMR (500 MHz, CDCl3): δ 2.40 (s, 3H), 4.97 (s, 2H), 7.23 (t, J = 7.5 Hz, 3H), 7.37 (t, J = 5.5 Hz, 3H), 7.88 (d, J = 8.9 Hz, 2H); 13C NMR (75 MHz, CDCl3): δ 167.7, 140.5, 137.3, 134.5, 133.7, 132.3, 130.0, 128.7, 124.4, 122.9, 119.9, 51.2, 21.2; IR (neat): 2921, 1683, 1513, 1447, 1390, 1305, 1159.

N-(4-chlorophenyl)isoindolin-1-one (Scheme 2)

1H NMR (500 MHz, CDCl3): δ 4.88 (s, 2H), 7.43 (t, J = 9.0 Hz, 2H), 7.53-7.57 (m, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.88 (d, J = 8.9 Hz, 2H), 7.97 (d, J = 7.7 Hz, 1H); 13C NMR (75 MHz, CDCl3): δ 167.7, 139.9, 138.2, 133.1, 132.5, 129.6, 129.4, 128.6, 124.4, 122.8, 120.5, 50.7; IR (neat): 3056, 2952, 2871, 1685, 1599, 1503, 1466, 1441, 733.