Manganese Catalyzed $N$-Alkylation of Amines with Alcohols:
Ligand Enabled Selectivity

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Contents

1. General Information S2
2. Experimental Section S3-S6
3. Mechanistic Studies S6-S10
4. Characterization Data S11-S25
5. References S25
6. Copy of NMR Spectra S26-S97
1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. Toluene was refluxed over sodium/benzophenone and followed by distilled under argon atmosphere and stored over sodium. Metal complexes and other chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO$_2$ (SilicycleSiliaflash F60 (230-400 mesh). $^1$H NMR (400 or 500 MHz), $^{13}$C{$^1$H} NMR (100 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for $^1$H (chloroform-d), δ 77.2 for $^{13}$C{$^1$H} (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer). HPLC analysis was performed on Agilent Technologies 1260 Infinity with UV detector.
2. Experimental Section

2.1 Reaction Optimization

Table S1: Screening of ligands

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,2'-Bipyridine</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>2,2'-Bipyridine-4,4'-dicarboxylic acid</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>1,10-Phenanthroline</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>1,1'-Binaphthyl-2,2'-diamine</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>L1</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>L2</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>L3</td>
<td>74</td>
</tr>
<tr>
<td>8</td>
<td>L4</td>
<td>80</td>
</tr>
<tr>
<td>9</td>
<td>L5</td>
<td>91</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{Me}_2\text{N} & \quad \text{Me}_2\text{N} \\
\text{L1} & \quad \text{L2} \\
\text{Me}_2\text{S} & \quad \text{Me}_2\text{S} \\
\text{L3} & \quad \text{L4} \\
\text{Me}_2\text{NH} & \quad \text{Me}_2\text{NH} \\
\text{L5} & \quad \text{L5}
\end{align*}
\]
"Reaction conditions: aniline 1a (0.5 mmol), alcohol 2a (0.55 mmol), Mn catalyst (5 mol%), Ligand (5 mol%), KOrBu (0.55 mmol), 1 mL toluene, 140 °C (oil-bath temperature), 18 h. \(^b\) Yield determined by GC using dibromobutane as an internal standard. L1 = N\(^1\)-(3-(dimethylamino)propyl)-N\(^3\),N\(^3\)-dimethylpropane-1,3-diamine; \(\text{L2} = 2,2'\)-oxybis(N,N-dimethylethanamine); \(\text{L3} = \\text{bis}(2-\text{(methylthio)}\text{ethyl})\text{amine}; \(\text{L4} = \\text{bis}(2\text{(isopropylthio)}\text{ethyl})\text{amine.}\)

**Table S2: Screening of base\(^a\)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiO(^t)Bu</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>NaO(^t)Bu</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>KO(^t)Bu</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>NaO(^i)Pr</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>KOH</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>K(_2)CO(_3)</td>
<td>NR</td>
</tr>
<tr>
<td>7</td>
<td>CsOAc</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>KO(^t)Bu (50 mol%)</td>
<td>45</td>
</tr>
<tr>
<td>9</td>
<td>KO(^t)Bu (25 mol%)</td>
<td>23</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: aniline 1a (0.5 mmol), alcohol 2a (0.55 mmol), MnBr(CO)\(_5\) (5 mol%), L1 (5 mol%), base (0.55 mmol), 1 mL solvent, 140 °C (oil-bath temperature), 18 h. \(^b\) Yield determined by GC using dibromobutane as an internal standard. NR = No reaction.
Table S3: Screening of solvent

![Reaction scheme](attachment:image.png)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Xylene</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>Mesitylene</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td><strong>Toluene</strong></td>
<td><strong>85</strong></td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>MeCN</td>
<td>NR</td>
</tr>
<tr>
<td>6</td>
<td>n-Octane</td>
<td>44</td>
</tr>
<tr>
<td>7</td>
<td>1,4 Dioxane</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>1,4 Dioxane + Toluene</td>
<td>77</td>
</tr>
</tbody>
</table>

*aReaction conditions: aniline 1a (0.5 mmol), alcohol 2a (0.55 mmol), MnBr(CO)$_5$ (5 mol%), L1 (5 mol%), KO$_t$Bu (0.55 mmol), 1 mL solvent, 140 °C (oil-bath temperature), 18 h. *b Yield determined by GC using dibromobutane as an internal standard. NR = No reaction.*

Table S4: Screening of temperature

![Reaction scheme](attachment:image.png)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>120</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td><strong>140</strong></td>
<td><strong>92</strong></td>
</tr>
</tbody>
</table>

*aReaction conditions: aniline 1a (0.5 mmol), alcohol 2a (0.55 mmol), MnBr(CO)$_5$ (5 mol%), L1 (5 mol%), KO$_t$Bu (0.55 mmol), 1 mL solvent, 140 °C (oil-bath temperature), 18 h. *b Yield determined by GC using dibromobutane as an internal standard. NR = No reaction.*
Reaction conditions: aniline 1a (0.5 mmol), alcohol 2a (0.55 mmol), MnBr(CO)₅ (5 mol%), Ligand (5 mol%), KOrBu (0.55 mmol), 1 mL toluene, temperature (oil-bath temperature), 18 h. Yield determined by GC using dibromobutane as an internal standard. NR = No reaction.

2.2 General Procedure for the Manganese-Catalyzed N-Alkylation of anilines

To an oven-dried 10 mL screw-capped vial, MnBr(CO)₅ (0.025 mmol, 5 mol%), ligand L₁ or L₅ (0.025 mmol, 5mol%), alcohol 2 (0.55 mmol, 1.1 equivalent), amine 1 (0.5 mmol), KOrBu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 °C for 18 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

3. Mechanistic studies

2.2.1. Identification of Mn-Complex:

To an oven-dried 10 mL screw-capped vial, MnBr(CO)₅ (0.01 mmol), ligand L₁ (0.01 mmol, 5mol%), KOrBu (0.01 mmol), toluene (2 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 °C for 2 h. Then, the reaction mixture was passed through celite and submitted for HRMS.
2.2.2 Homogeneous nature of Mn-catalysis

a) To an oven-dried 10 mL screw-capped vial, MnBr(CO)$_5$ (0.025 mmol, 5 mol%), ligand L1 (0.025 mmol, 5 mol%), mercury (300 equivalent with respect to catalyst), benzyl alcohol 2a (0.55 mmol, 1.1 equivalent), m-toludine 1a (0.5 mmol), KOtBu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 °C for 18 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.
b) To an oven-dried 10 mL screw-capped vial, MnBr(CO)$_5$ (0.025 mmol, 5 mol%), ligand L1 (0.025 mmol, 5 mol%), tetra-butyl ammonium bromide (0.025 mmol, 5 mol%), benzyl alcohol 2a (0.55 mmol, 1.1 equivalent), m-toludine 1a (0.5 mmol), KOtBu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 ºC for 18 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

\[
\text{NH}_2\text{H}_2\text{O} \quad \text{MnBr(CO)}_5, \text{L1, TBAB} \\
\begin{array}{c}
\text{N} \\
\end{array} \text{Me} \text{H} \\
\begin{array}{c}
\text{NH} \\
\end{array} \text{Me} \\
\text{Me} \\
\begin{array}{c}
\text{N} \\
\end{array} \text{Me} \\
\begin{array}{c}
\text{N} \\
\end{array} \text{Me} \\
\text{Me} \\
\begin{array}{c}
\text{H} \\
\end{array} \\
\begin{array}{c}
\text{MnBr(CO)}_5, \text{L1} \\
\end{array} \\
\begin{array}{c}
\text{TBAB} \\
\text{KOTBu, toluene} \\
140 ^\circ \text{C, 18h} \\
\end{array} \\
\begin{array}{c}
\text{4a, 65}\% \\
\end{array}
\]

\[
\text{NH}_2\text{H}_2\text{O} \quad \text{MnBr(CO)}_5, \text{L1, TEMPO} \\
\begin{array}{c}
\text{N} \\
\end{array} \text{Me} \text{H} \\
\begin{array}{c}
\text{NH} \\
\end{array} \text{Me} \\
\text{Me} \\
\text{Me} \\
\begin{array}{c}
\text{N} \\
\end{array} \text{Me} \\
\begin{array}{c}
\text{H} \\
\end{array} \\
\begin{array}{c}
\text{MnBr(CO)}_5, \text{L1} \\
\end{array} \\
\begin{array}{c}
\text{TEMPO} \\
\text{KOTBu, toluene} \\
140 ^\circ \text{C, 18h} \\
\end{array} \\
\begin{array}{c}
\text{4a, 56}\% \\
\end{array}
\]

c) To an oven-dried 10 mL screw-capped vial, MnBr(CO)$_5$ (0.025 mmol, 5 mol%), ligand L1 (0.025 mmol, 5 mol%), TEMPO (1 equivalent), benzyl alcohol 2a (0.55 mmol, 1.1 equivalent), m-toludine 1a (0.5 mmol), KOtBu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 ºC for 18 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.
2.2.3 Qualitative analysis of hydrogen gas and aldehyde intermediate

To an oven-dried 10 mL screw-capped vial, MnBr(CO)$_5$ (0.025 mmol, 5 mol%), ligand L1 (0.025 mmol, 5 mol%), benzyl alcohol 2a (0.50 mmol), KOtBu (0.55 mmol), and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 140 °C for 12 h. GC analysis showed the formation of dihydrogen gas (TCD detector).

![Figure S2. Hydrogen gas detection (GC Analysis)](image)

2.2.4 Reaction kinetics

To an oven-dried 10 mL screw-capped vial, seven parallel reaction carried out using MnBr(CO)$_5$ (0.025 mmol, 5 mol%), ligand L1 or L5 (0.025 mmol, 5 mol%), benzyl alcohol 2a (0.55 mmol, 1.1 equivalent), m-toludine 1a (0.5 mmol), KOtBu (0.55 mmol, 1.1 equivalent), n-decane (0.25 mmol) as internal standard and toluene (2 mL) were added under a gentle stream of argon. The mixture was stirred at 140 °C (oil-bath temperature). At regular time intervals, the reaction vessel was cooled to 28 °C and 15 µL of the sample was diluted with 0.5 mL of CH$_2$Cl$_2$, and subjected to GC analysis. The concentration of the product 4a obtained in each sample was determined with respect to the internal standard n-decane.
Figure S3. Reaction profile for the manganese-catalyzed formation of 4a by using L1 and L5 ligand.
4. Characterization Data

*N*-benzylaniline (3a)

73 mg, 80% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. The spectral data is consistent with the literature compound. \(^1\)H NMR (200 MHz, \textit{CHLOROFORM}-d) \( \delta = 7.54 - 7.23 \) (m, 5H), 7.21 - 7.01 (m, 2H), 6.53 - 6.25 (m, 3H), 4.33 (s, 2 H), 4.19 (brs, 1H). \(^{13}\)C NMR (50 MHz, \textit{CHLOROFORM}-d) \( \delta = 148.12, 139.41, 129.23, 128.60, 127.48, 127.19, 117.53, 112.81, 48.29. 

*N*-benzyl-4-methoxyaniline (3b)

71 mg, 67% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \(^1\)H NMR (500 MHz, \textit{CHLOROFORM}-d) \( \delta = 7.45 - 7.31 \) (m, 4H), 7.29 (s, 1H), 6.85 - 6.71 (m, 2H), 6.67 - 6.53 (m, 2H), 4.30 (s, 2H), 3.76 (s, 3H). \(^{13}\)C NMR (126 MHz, \textit{CHLOROFORM}-d) \( \delta = 152.2, 142.4, 139.7, 128.6, 127.5, 127.1, 114.9, 114.1, 55.8, 49.2. \) HRMS (EI): \( m/z \) Calcd for [M-H] 

\( \text{C}_{14}\text{H}_{14}\text{NO}: 212.1070; \) Found: 212.1072.

*N*-benzyl-4-chloroaniline (3c)

70 mg, 65% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \(^1\)H NMR (500 MHz, \textit{CHLOROFORM}-d) \( \delta = 7.45 - 7.37 \) (m, 4H), 7.37 - 7.30 (m, 1H), 7.20 - 7.11 (m, \( J = 8.5 \) Hz, 2H), 6.63 - 6.54 (m, \( J = 8.5 \) Hz, 2H), 4.34 (s, 2H), 4.10 (brs, 1H). \(^{13}\)C NMR (126 MHz,
**CHLOROFORM-d** \( \delta = 146.6, 138.9, 129.0, 128.7, 127.4, 127.3, 122.0, 113.9, 48.3. \) HRMS (EI): 
\[ m/z \text{ Calcd for [M+H]} \ C_{13}H_{13}NCl: 218.0731; \text{ Found: 218.0730.} \]

*N*-benzyl-3-(trifluoromethyl)aniline (3d)

![Chemical structure of N-benzyl-3-(trifluoromethyl)aniline (3d)](image)

102 mg, 81% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \(^1\)H NMR (500 MHz, \textit{CHLOROFORM-d}) \( \delta = 7.39 \) (brs, 4H), 7.33 (brs, 1H), 6.98 (brs, 1H), 6.87 (brs, 1H), 6.78 (brs, 1H), 4.37 (brs, 2H), 4.24 (brs, 1H). \(^{13}\)C NMR (126 MHz, \textit{CHLOROFORM-d}) \( \delta = 148.2, 138.5, 131.5 \) (q, \( J_{C-F} = 31.5 \) Hz), 129.6, 128.7, 127.5, 123.3 (q, \( J_{C-F} = 272 \) Hz), 115.7, 113.9 (q, \( J_{C-F} = 3.81 \) Hz), 109.0 (q, \( J_{C-F} = 3.81 \) Hz), 48.1. HRMS (EI): \( m/z \text{ Calcd for [M+H]} \ C_{14}H_{13}NF_3: 252.0995; \text{ Found: 252.0993.} \)

*N*-benzyl-3-fluoroaniline (3e)

![Chemical structure of N-benzyl-3-fluoroaniline (3e)](image)

60 mg, 60% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \(^1\)H NMR (500 MHz, \textit{CHLOROFORM-d}) \( \delta = 7.38 \) (brs, 4H), 7.32 (brs, 1H), 7.17 - 7.04 (m, 1H), 6.42 (brs, 2H), 6.34 (d, \( J = 11.0 \) Hz, 1H), 4.33 (brs, 2H), 4.19 (brs, 1H). \(^{13}\)C NMR (126 MHz, \textit{CHLOROFORM-d}) \( \delta = 164.1 \) (q, \( J_{C-F} = 240 \) Hz), 149.9, 149.8, 138.8, 130.3, 130.2, 128.7, 127.4, 108.7, 103.9 (q, \( J_{C-F} = 22 \) Hz), 99.5 (q, \( J_{C-F} = 25.7 \) Hz), 48.2. HRMS (EI): \( m/z \text{ Calcd for [M+H]} \ C_{13}H_{13}NF: 202.1027; \text{ Found: 202.1025.} \)
N-benzyl-2-chloroaniline (3f)

\[
\begin{align*}
&\text{70 mg, 65\% isolated yield. } R_f = 0.32 \text{ (hexane/EtOAc = 90/1). Yellow liquid. } \\
&\text{1}^1\text{H NMR (500 MHz, CHLOROFORM-}d\text{) } \delta = 7.45 - 7.39 \text{ (m, 3H), 7.38 - 7.29 \text{ (m, 2H), 7.14 \text{ (t, } J = 7.6 \text{ Hz, 1H),} } \\
&6.76 - 6.57 \text{ (m, 2H), 4.79 \text{ (brs, 1H), 4.45 \text{ (s, 2H). } } ^13\text{C NMR (126 MHz, CHLOROFORM-}d\text{) } \delta =} \\
&143.8, 138.7, 129.1, 128.7, 127.8, 127.3, 127.2, 119.1, 117.4, 111.5, 47.8. \text{ HRMS (EI): } m/z \text{ Calcd for } [\text{M+H}] C_{13}H_{13}NCl: 218.0731; \text{ Found: } 218.0730. 
\end{align*}
\]

N-benzylbiphenyl-2-amine (3g)

\[
\begin{align*}
&\text{101 mg, 78\% isolated yield. } R_f = 0.32 \text{ (hexane/EtOAc = 90/1). Yellow liquid. } \\
&\text{1}^1\text{H NMR (500 MHz, CHLOROFORM-}d\text{) } \delta = 7.57 - 7.45 \text{ (m, 4H), 7.45 - 7.32 \text{ (m, 5H), 7.29 \text{ (d, } J = 3.1 \text{ Hz, 1H),} } \\
&7.24 \text{ (s, 1H), 7.16 \text{ (d, } J = 7.2 \text{ Hz, 1H), 6.83 \text{ (s, 1H), 6.72 \text{ (d, } J = 8.0 \text{ Hz, 1H),} } 4.53 \text{ (brs, 1H), 4.38 \text{ (s, 2H). } } ^13\text{C NMR (126 MHz, CHLOROFORM-}d\text{) } \delta =} \\
&144.8, 139.4, 130.2, 129.4, 128.9, 128.7, 128.6, 127.2, 127.1, 117.3, 110.9, 48.2. \text{ HRMS (EI): } m/z \text{ Calcd for } [\text{M+H}] C_{19}H_{18}N: 260.1434; \text{ Found: } 260.1433. 
\end{align*}
\]

N-benzyl-3,5-bis(trifluoromethyl)aniline (3h)

\[
\begin{align*}
&\text{151 mg, 95\% isolated yield. } R_f = 0.32 \text{ (hexane/EtOAc = 90/1). Yellow liquid. } \\
&\text{1}^1\text{H NMR (500 MHz, CHLOROFORM-}d\text{) } \delta = 7.47 - 7.30 \text{ (m, 5H), 7.20 \text{ (s, 1H), 7.00 \text{ (s, 2H),} } \\
&4.47 \text{ (brs, 1H), 4.39 \text{ (d, } J = 5.0 \text{ Hz, 2H). } ^13\text{C NMR (126MHz, CHLOROFORM-}d\text{) } \delta =} \\
&148.6, 137.6, 132.4 \text{ (q, } J_{CF} = 153.6). 
\end{align*}
\]
33.9 Hz), 128.9, 127.9, 127.5, 124.5 (q, J_C-F = 273 Hz), 112.0, 110.5, 110.4, 110.4, 48.0. HRMS (EI): m/z Calcd for [M+H] C_{15}H_{12}NFe: 320.0868; Found: 320.0863.

N-benzyl-2,4-dimethoxyaniline (3i)

\[ \text{MeO} \begin{array}{c} \text{H} \text{N} \\ \text{Me} \text{N} \text{O} \end{array} \text{OMe} \]

55 mg, 45% isolated yield. R_f = 0.32 (hexane/EtOAc = 90/1). Yellow liquid. ¹H NMR (500 MHz, CHLOROFORM-d) δ = 7.41 - 7.35 (m, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.28 - 7.23 (m, 1H), 6.51 (d, J = 8.4 Hz, 1H), 6.46 (d, J = 2.3 Hz, 1H), 6.36 (dd, J = 2.5, 8.6 Hz, 1H), 4.30 (s, 3H), 3.86 - 3.80 (m, 3H), 3.74 (s, 3H). ¹³C NMR (126 MHz, CHLOROFORM-d) δ = 152.1, 147.9, 139.8, 128.5, 127.6, 127.1, 110.5, 103.7, 99.2, 55.8, 55.5, 48.9.

N-benzylpyridin-2-amine (3j)

\[ \text{N} \begin{array}{c} \text{H} \\ \text{N} \text{H} \text{N} \text{Me} \end{array} \]

78 mg, 85% isolated yield. R_f = 0.32 (hexane/EtOAc = 90/1). Yellow liquid. ¹H NMR (500 MHz, CHLOROFORM-d) δ = 8.09 (brs, 1H), 7.49 - 7.31 (m, 6H), 6.58 (brs, 1H), 6.36 (d, J = 7.3 Hz, 1H), 5.02 (brs, 1H), 4.50 (brs, 2H). ¹³C NMR (126 MHz, CHLOROFORM-d) δ = 158.6, 148.2, 139.2, 137.4, 128.6, 127.4, 127.2, 113.1, 106.7, 46.3. HRMS (EI): m/z Calcd for [M+H] C_{12}H_{13}N_{2}: 185.1073; Found: 185.1072.

N-benzylquinolin-8-amine (3k)

\[ \text{N} \begin{array}{c} \text{H} \\ \text{N} \text{H} \text{N} \text{Me} \end{array} \]

S14
84 mg, 72% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \( ^1\)H NMR (500 MHz, CHLOROFORM-\( d \)) \( \delta = 8.77 \) (d, \( J = 3.1 \) Hz, 1H), 8.10 (d, \( J = 7.3 \) Hz, 1H), 7.49 (d, \( J = 7.3 \) Hz, 2H), 7.45 - 7.35 (m, 4H), 7.35 - 7.30 (m, 1H), 7.10 (d, \( J = 8.5 \) Hz, 1H), 6.77 - 6.56 (m, 2H), 4.61 (d, \( J = 5.5 \) Hz, 2H). \( ^{13}\)C NMR (126 MHz, CHLOROFORM-\( d \)) \( \delta = 146.9, 144.5, 139.2, 138.2, 136.0, 128.6, 127.7, 127.4, 127.1, 121.4, 114.1, 105.1, 47.6. \) HRMS (EI): \( m/z \) Calcd for [M+H] \( C_{16}H_{15}N_2 \): 235.1230; Found: 235.1229.

\( N \)-benzylquinolin-6-amine (3I)

\[ \text{N-benzylquinolin-6-amine (3I)} \]

87 mg, 75% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \( ^1\)H NMR (500 MHz, CHLOROFORM-\( d \)) \( \delta = 8.64 \) (s, 1H), 7.91 (s, 2H), 7.40 (s, 2H), 7.43 (s, 2H), 7.34 (brs, 1H), 7.16 (d, \( J = 7.3 \) Hz, 1H), 6.74 (brs, 1H), 4.46 (brs, 3H). \( ^{13}\)C NMR (126 MHz, CHLOROFORM-\( d \)) \( \delta = 146.2, 145.9, 143.2, 138.6, 133.8, 130.2, 130.0, 128.7, 127.5, 127.4, 121.3, 121.3, 103.2, 48.2. \) HRMS (EI): \( m/z \) Calcd for [M+H] \( C_{16}H_{15}N_2 \): 235.1230; Found: 235.1229.

\( N \)-benzyl-3-methylaniline (4a)

\[ \text{N-benzyl-3-methylaniline (4a)} \]

91 mg, 92% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \( ^1\)H NMR (200 MHz, CHLOROFORM-\( d \)) \( \delta = 7.54 - 7.29 \) (m, 5H), 7.13 (t, \( J = 7.6 \) Hz, 1H), 6.61 (d, \( J = 7.3 \) Hz, 1H), 6.56 - 6.43 (m, 2H), 4.37 (s, 2H), 4.01 (brs, 1H), 2.34 (s, 3H). \( ^{13}\)C NMR (50 MHz, CHLOROFORM-\( d \)) \( \delta = 148.2, 139.5, 139.0, 129.1, 128.6, 127.5, 127.1, 118.5, 113.6, 109.9, 48.3, 21.6. \) HRMS (EI): \( m/z \) Calcd for [M+H] \( C_{16}H_{16}N \): 198.1277; Found: 198.1278.
3-methyl-N-(4-methylbenzyl)aniline (4b)

71 mg, 67% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \(^1\)H NMR (500 MHz, CHLOROFORM-\(d\)) \( \delta = 7.34 - 7.26 \) (m, 2H), 7.19 (d, \( J = 7.6 \) Hz, 2H), 7.10 (t, \( J = 7.6 \) Hz, 1H), 6.58 (d, \( J = 7.6 \) Hz, 1H), 6.53 - 6.44 (m, 2H), 4.30 (s, 2H), 2.38 (s, 3H), 2.31 (s, 3H). \(^{13}\)C NMR (126 MHz, CHLOROFORM-\(d\)) \( \delta = 148.3, 139.0, 136.8, 136.4, 129.3, 129.1, 127.5, 118.4, 113.6, 109.9, 48.1, 21.6, 21.1 \). HRMS (EI): \( m/z \) Calcd for [M+H] \( C_{15}H_{18}N \): 212.1434; Found: 212.1433.

\( N\)-(4-chlorobenzyl)-3-methylaniline (4c)

39 mg, 45% isolated yield. \(^1\)H NMR (200 MHz, CHLOROFORM-\(d\)) \( \delta = 7.31 \) (m, 4H), 7.07 (t, \( J = 8 \) Hz, 1H), 6.57 (d, \( J = 7 \) Hz, 1H), 6.49 - 6.36 (m, 2H), 4.31 (s, 2H), 4.01 (s, br, 1H), 2.28 (s, 3H). \(^{13}\)C NMR (50 MHz, CHLOROFORM-\(d\)) \( \delta = 147.88, 139.10, 138.10, 132.83, 129.17, 128.69, 118.77, 113.68, 109.98, 47.64, 21.60 \).

\( N\)-(2-methoxybenzyl)-3-methylaniline (4d)

88 mg, 78% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \(^1\)H NMR (500 MHz, CHLOROFORM-\(d\)) \( \delta = 7.38 \) (d, \( J = 7.2 \) Hz, 1H), 7.31 (t, \( J = 7.6 \) Hz, 1H), 7.12 (t, \( J = 7.6 \) Hz, 2H), 6.75 (t, \( J = 7.4 \) Hz, 2H), 6.54 (s, 2H), 4.13 (s, 1H), 4.03 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.40 (s, 3H).
Hz, 1H), 7.01 - 6.90 (m, 2H), 6.59 (d, J = 7.6 Hz, 1H), 6.58 - 6.50 (m, 2H), 4.39 (s, 2H), 3.92 (s, 3H), 2.34 (s, 3H). ¹³C NMR (126 MHz, CHLOROFORM-d) δ = 157.3, 148.4, 138.8, 129.0, 128.8, 128.2, 127.4, 120.5, 118.2, 113.8, 110.1, 110.1, 55.2, 43.4, 21.6. HRMS (EI): m/z Calcd for [M+H] C₁₅H₁₈NO: 228.1383; Found: 228.1382.

N-(furan-2-ylmethyl)-3-methylaniline (4e)

![Chemical structure](image)

69 mg, 74% isolated yield. Rₓ = 0.32 (hexane/EtOAc = 90/1). Yellow liquid. ¹H NMR (500 MHz, CHLOROFORM-d) δ = 7.38 (dd, J = 0.6, 1.8 Hz, 1H), 7.12 - 7.05 (m, 1H), 6.58 (d, J = 7.0 Hz, 1H), 6.55 - 6.47 (m, 2H), 6.33 (dd, J = 2.0, 3.2 Hz, 1H), 6.24 (dd, J = 0.6, 3.4 Hz, 1H), 4.32 (s, 2H), 3.98 (brs 1H), 2.29 (s, 3H). ¹³C NMR (126 MHz, CHLOROFORM-d) δ = 152.8, 147.6, 141.9, 139.0, 129.1, 119.0, 114.0, 110.3, 110.2, 106.9, 41.5, 21.6. HRMS (EI): m/z Calcd for [M+H] C₁₂H₁₄NO: 188.1070; Found: 188.1068.

N-butyl-3-methylaniline (4f)

![Chemical structure](image)

27 mg, 33% isolated yield. Rₓ = 0.32 (hexane/EtOAc = 90/1). Yellow liquid. ¹H NMR (500 MHz, CHLOROFORM-d) δ = 7.14 - 6.98 (m, 1H), 6.53 (d, J = 7.2 Hz, 1H), 6.49 - 6.35 (m, 2H), 3.12 (t, J = 7.1 Hz, 2H), 2.29 (s, 3H), 1.66 - 1.55 (m, 2H), 1.53 - 1.38 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CHLOROFORM-d) δ = 148.5, 139.0, 129.1, 118.1, 113.5, 109.9, 43.7, 31.7, 21.6, 20.3, 13.9. HRMS (EI): m/z Calcd for [M+H] C₁₁H₁₈N: 164.1434; Found: 164.1432.
3-methyl-N-octylaniline (4g)

46 mg, 42% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \( ^1 \)H NMR (500 MHz, CHLOROFORM-d) \( \delta = 7.08 \) (t, \( J = 7.4 \) Hz, 1H), 6.54 (d, \( J = 7.2 \) Hz, 1H), 6.49 - 6.38 (m, 2H), 3.11 (t, \( J = 7.2 \) Hz, 2H), 2.30 (s, 3H), 1.66 - 1.57 (m, 2H), 1.44 - 1.35 (m, 3H), 1.35 - 1.26 (m, 7H), 1.01 - 0.84 (m, 3H). \( ^{13} \)C NMR (126 MHz, CHLOROFORM-d) \( \delta = 148.4, 139.0, 129.1, 118.2, 113.6, 110.0, 31.8, 29.5, 29.4, 29.3, 27.2, 22.6, 21.6, 14.1 \). HRMS (EI): \( m/z \) Calcd for [M+H] \( C_{15}H_{26}N: 220.2060 \); Found: 220.2060.

N-decyl-3-methylaniline (4h)

71 mg, 58% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 90/1). Yellow liquid. \( ^1 \)H NMR (200 MHz, CHLOROFORM-d) \( \delta = 7.05 \) (d, \( J = 8.5 \) Hz, 1H), 6.52 (d, \( J = 7.3 \) Hz, 1H), 6.47 - 6.36 (m, 2H), 3.10 (t, \( J = 7.0 \) Hz, 2H), 2.29 (s, 3H), 1.60 (d, \( J = 6.6 \) Hz, 3H), 1.28 (brs, 13H), 0.96 - 0.84 (m, 4H). \( ^{13} \)C NMR (50 MHz, CHLOROFORM-d) \( \delta = 139.0, 129.1, 118.0, 113.5, 109.9, 44.0, 31.9, 29.6, 29.4, 29.3, 27.2, 22.7, 21.6, 14.1 \). HRMS (EI): \( m/z \) Calcd for [M+H] \( C_{17}H_{30}N: 248.2373 \); Found: 248.2375.

(R)-N-(3,7-dimethyloct-6-enyl)-3-methylaniline (4i)
92 mg, 75% isolated yield. $R_f = 0.32$ (hexane/EtOAc = 90/1). Yellow liquid. $^1$H NMR (500 MHz, CHLOROFORM-d) $\delta = 7.11$ (t, $J = 7.8$ Hz, 1H), 6.56 (d, $J = 7.6$ Hz, 1H), 6.50 - 6.40 (m, 2H), 5.16 (t, $J = 7.1$ Hz, 1H), 3.25 - 3.06 (m, 2H), 2.33 (s, 3H), 2.15 - 1.93 (m, 2H), 1.79 - 1.70 (m, 4H), 1.70 - 1.57 (m, 5H), 1.52 - 1.35 (m, 2H), 1.34 - 1.21 (m, 1H), 1.04 - 0.94 (m, 3H). $^{13}$C NMR (126 MHz, CHLOROFORM-d) $\delta = 148.6, 138.9, 131.2, 129.0, 124.6, 118.0, 113.4, 109.8, 41.9, 37.1, 36.7, 30.4, 25.7, 25.4, 21.6, 19.6, 17.6$. HRMS (EI): $m/z$ Calcd for [M+H] $C_{17}H_{18}N$: 246.2216; Found: 246.2216.

2-(4-(benzylamino)phenyl)ethanol (6a)

91 mg, yellow liquid, 80% isolated yield. $R_f = 0.32$ (hexane/EtOAc = 70/30). Yellow liquid. $^1$H NMR (500 MHz, CHLOROFORM-d) $\delta = 7.46 - 7.23$ (m, 5H), 7.09 - 7.01 (m, $J = 8.0$ Hz, 2H), 6.68 - 6.56 (m, $J = 8.4$ Hz, 2H), 4.34 (s, 2H), 4.02 (brs, 1H), 3.80 (t, $J = 6.5$ Hz, 2H), 2.78 (t, $J = 6.7$ Hz, 2H), 1.69 (brs, 1H). $^{13}$C NMR (126 MHz, CHLOROFORM-d) $\delta = 146.7, 139.4, 129.8, 128.6, 127.4, 127.1, 127.0, 113.0, 63.8, 48.4, 38.2$. HRMS (EI): $m/z$ Calcd for [M+H] $C_{15}H_{18}NO$: 228.1383; Found: 228.1381.

2-(4-(4-methylbenzylamino)phenyl)ethanol (6b)

94 mg, yellow liquid, 78% isolated yield. $R_f = 0.32$ (hexane/EtOAc = 70/30). Yellow liquid. $^1$H NMR (500 MHz, CHLOROFORM-d) $\delta = 7.29$ (s, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.08 - 6.85 (m, $J = 8.4$ Hz, 2H), 6.71 - 6.48 (m, $J = 8.0$ Hz, 2H), 4.29 (s, 2H), 3.81 (t, $J = 6.5$ Hz, 2H), 2.77 (t, $J = 6.5$ Hz, 2H), 2.37 (s, 3H). $^{13}$C NMR (126 MHz, CHLOROFORM-d) $\delta = 146.9, 136.8, 136.3, 129.8, 129.7, 127.5, 126.9, 113.1, 63.9, 48.2, 38.3, 21.1$. HRMS (EI): $m/z$ Calcd for [M+H] $C_{16}H_{20}NO$: 242.1539; Found: 242.1533.
2-(4-(4-methoxybenzylamino)phenyl)ethanol (6c)

\[
\begin{align*}
\text{HO-} & \quad \text{N} \quad \text{OMe} \\
\end{align*}
\]

92 mg, yellow liquid, 72% isolated yield. R_f = 0.32 (hexane/EtOAc = 60/40). \(^1\)H NMR (500 MHz, CHLOROFORM-d) \(\delta = 7.41 - 7.18 (m, J = 8.4 \text{ Hz}, 2H), 7.10 - 6.97 (m, J = 8.0 \text{ Hz}, 2H), 6.97 - 6.75 (m, J = 8.8 \text{ Hz}, 2H), 6.66 - 6.54 (m, J = 8.4 \text{ Hz}, 2H), 4.25 (s, 2H), 3.88 - 3.64 (m, 5H), 2.77 (t, J = 6.5 \text{ Hz}, 2H), 1.61 (brs, 1H). \(^{13}\)C NMR (126 MHz, CHLOROFORM-d) \(\delta = 158.9, 146.9, 131.4, 129.8, 128.8, 127.0, 114.0, 113.1, 63.9, 55.3, 48.0, 38.3. \) HRMS (EI): \(m/z \) Calcd for [M+H] \(\text{C}_{16}\text{H}_{20}\text{NO}_2\): 258.1489; Found: 258.1486.

2-(4-(4-chlorobenzylamino)phenyl)ethanol (6d)

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

110 mg, 85% isolated yield. R_f = 0.32 (hexane/EtOAc = 70/30). \(^1\)H NMR (400 MHz, CHLOROFORM-d) \(\delta = 7.31 (s, 4H), 7.12 - 6.97 (m, J = 8.2 \text{ Hz}, 2H), 6.66 - 6.45 (m, J = 8.7 \text{ Hz}, 2H), 4.30 (s, 2H), 3.80 (t, J = 6.4 \text{ Hz}, 2H), 2.76 (t, J = 6.6 \text{ Hz}, 2H). \(^{13}\)C NMR (50 MHz, CHLOROFORM-d) \(\delta = 146.4, 138.0, 132.9, 129.9, 128.7, 128.7, 127.4, 113.2, 63.9, 47.8, 38.2. \) HRMS (EI): \(m/z \) Calcd for [M+H] \(\text{C}_{15}\text{H}_{17}\text{NOCl}\): 262.0993; Found: 262.0991.

2-(4-(4-bromobenzylamino)phenyl)ethanol (6e)

\[
\begin{align*}
\text{HO-} & \quad \text{N} \quad \text{Br} \\
\end{align*}
\]

96 mg, yellow liquid, 63% isolated yield. R_f = 0.32 (hexane/EtOAc = 70/30). \(^1\)H NMR (500 MHz, CHLOROFORM-d) \(\delta = 7.47 (d, J = 8.0 \text{ Hz}, 2H), 7.25 (d, J = 8.4 \text{ Hz}, 2H), 7.14 - 6.98 (m, J = 8.4 \text{ Hz}, 2H), 6.65 - 6.50 (m, J = 8.4 \text{ Hz}, 2H), 4.29 (s, 2H), 3.80 (t, J = 6.5 \text{ Hz}, 2H), 2.76 (t, J
\[
\begin{align*}
\text{13C NMR (126 MHz, CHLOROFORM-}d\text{) }\delta &= \text{ 146.7, 138.8, 131.9, 130.1, 129.3, 127.6, 121.2, 113.4, 64.1, 48.0, 38.5. HRMS (EI): } m/z \text{ Calcd for [M+H] C}_{15}\text{H}_{17}\text{NOBr: 306.0488; Found: 306.0490.}
\end{align*}
\]

2-(4-(biphenyl-4-ylmethylamino)phenyl)ethanol (6f)

\[
\begin{align*}
\text{113 mg, yellow solid, 75% isolated yield. } R_f &= 0.32 \text{ (hexane/EtOAc = 70/30). } ^1\text{H NMR (500 MHz, CHLOROFORM-}d\text{) }\delta &= 7.67 - 7.52 \text{ (m, 4H), 7.49 - 7.39 \text{ (m, 4H), 7.39 - 7.31 (m, 1H), 7.12 - 6.98 \text{ (m, } J = 8.0 \text{ Hz, 2H), 6.75 - 6.53 \text{ (m, } J = 8.4 \text{ Hz, 2H), 4.38 (s, 2H), 3.81 (t, } J = 6.5 \text{ Hz, 2H), 2.78 (t, } J = 6.5 \text{ Hz, 2H). } ^1\text{C NMR (126 MHz, CHLOROFORM-}d\text{) }\delta &= 146.8, 140.8, 140.2, 138.5, 129.9, 128.8, 127.9, 127.4, 127.2, 127.1, 127.0, 113.2, 63.9, 48.2, 38.3. HRMS (EI): } m/z \text{ Calcd for [M+H] C}_{21}\text{H}_{22}\text{NO: 304.1696; Found: 304.1693.}
\end{align*}
\]

2-(4-(3-methylbenzylamino)phenyl)ethanol (6g)

\[
\begin{align*}
\text{87 mg, yellow liquid, 72% isolated yield. } R_f &= 0.32 \text{ (hexane/EtOAc = 70/30). } ^1\text{H NMR (500 MHz, CHLOROFORM-}d\text{) }\delta &= 7.34 \text{ (d, } J = 7.2 \text{ Hz, 1H), 7.25 - 7.14 \text{ (m, 3H), 7.11 - 7.02 \text{ (m, } J = 8.4 \text{ Hz, 2H), 6.66 - 6.58 \text{ (m, } J = 8.4 \text{ Hz, 2H), 4.27 (s, 2H), 3.81 (t, } J = 6.5 \text{ Hz, 3H), 2.78 (t, } J = 6.5 \text{ Hz, 2H), 2.38 (s, 3H). } ^1\text{C NMR (126 MHz, CHLOROFORM-}d\text{) }\delta &= 147.0, 137.0, 136.3, 130.4, 129.9, 128.2, 127.4, 126.9, 126.1, 113.0, 63.9, 46.5, 38.3, 18.9. HRMS (EI): } m/z \text{ Calcd for [M+H] C}_{16}\text{H}_{20}\text{NO: 242.1545; Found: 242.1540.}
\end{align*}
\]
2-(4-(3-methoxybenzylamino)phenyl)ethanol (6h)

87 mg, yellow liquid, 68% isolated yield. 

$R_f = 0.32$ (hexane/EtOAc = 70/30). 

$^1$H NMR (500 MHz, CHLOROFORM-d) $\delta = 7.32$ - 7.25 (m, 1H), 7.11 - 7.02 (m, $J = 8.4$ Hz, 2H), 7.02 - 6.91 (m, 2H), 6.84 (dd, $J = 2.1, 8.2$ Hz, 1H), 6.68 - 6.59 (m, $J = 8.4$ Hz, 2H), 4.32 (s, 2H), 3.87 - 3.78 (m, 5H), 2.78 (t, $J = 6.7$ Hz, 2H). 

$^{13}$C NMR (126 MHz, CHLOROFORM-d) $\delta = 159.9, 146.8, 141.2, 129.8, 129.6, 127.1, 119.7, 113.1, 113.0, 112.6, 63.9, 55.2, 48.4, 38.2$. 

HRMS (EI): $m/z$ Calcd for [M+H] $C_{16}H_{20}O_2$: 258.1489; Found: 258.1486.

2-(4-(2-methoxybenzylamino)phenyl)ethanol (6i)

80 mg, white solid, 63% isolated yield. 

$R_f = 0.32$ (hexane/EtOAc = 70/30). 

$^1$H NMR (500 MHz, CHLOROFORM-d) $\delta = 7.33$ (d, $J = 7.2$ Hz, 1H), 7.30 - 7.27 (m, 1H), 7.10 - 6.99 (m, $J = 8.4$ Hz, 2H), 6.92 (t, $J = 7.4$ Hz, 2H), 6.75 - 6.60 (m, $J = 8.4$ Hz, 2H), 4.34 (s, 2H), 3.89 (s, 3H), 3.81 (t, $J = 6.5$ Hz, 2H), 2.78 (t, $J = 6.5$ Hz, 2H). 

$^{13}$C NMR (126 MHz, CHLOROFORM-d) $\delta = 157.4, 147.0, 129.8, 128.9, 128.3, 127.3, 126.8, 120.5, 113.4, 110.2, 63.9, 55.3, 43.6, 38.3$. 

HRMS (EI): $m/z$ Calcd for [M+H] $C_{16}H_{20}NO_2$: 258.1489; Found: 258.1486.

2-(4-(3,4-dimethoxybenzylamino)phenyl)ethanol (6j)

109 mg, white solid, 76% isolated yield. 

$R_f = 0.32$ (hexane/EtOAc = 60/30). 

$^1$H NMR (500 MHz, CHLOROFORM-d) $\delta = 7.05$ (d, $J = 8.4$ Hz, 2H), 6.92 (brs, 2H), 6.85 (s, 1H), 6.63 (d, $J = 8.4$ Hz,
2H), 4.25 (s, 2H), 3.88 (d, \( J = 2.3 \) Hz, 6H), 3.80 (t, \( J = 6.7 \) Hz, 3H), 2.77 (t, \( J = 6.5 \) Hz, 2H). \(^{13}\)C NMR (126 MHz, CHLOROFORM-\( d \)) \( \delta = 149.1, 146.8, 131.9, 129.8, 127.1, 119.7, 113.2, 113.1, 111.1, 110.8, 63.9, 55.9, 55.8, 48.4, 38.2.\) HRMS (EI): \( m/z \) Calcd for [M+H] \( C_{17}H_{22}NO_3 \): 288.1594; Found: 288.1592.

2-(4-(furan-2-ylmethylamino)phenyl)ethanol (6k)

\[ \text{HO} \quad \begin{array}{c}
\text{N}
\end{array} \quad \begin{array}{c}
\text{CH}
\end{array} \quad \begin{array}{c}
\text{O}
\end{array} \]

68 mg, yellow liquid, 63% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 70/30). \(^1\)H NMR (500 MHz, CHLOROFORM-\( d \)) \( \delta = 7.38 \) (s, 1H), 7.12 - 6.98 (m, \( J = 8.0 \) Hz, 2H), 6.69 - 6.60 (m, \( J = 8.4 \) Hz, 2H), 6.35 - 6.30 (m, 1H), 6.24 (d, \( J = 2.7 \) Hz, 1H), 4.31 (s, 2H), 3.80 (t, \( J = 6.7 \) Hz, 2H), 2.77 (t, \( J = 6.5 \) Hz, 2H). \(^{13}\)C NMR (126 MHz, CHLOROFORM-\( d \)) \( \delta = 152.7, 146.3, 141.9, 129.8, 127.5, 113.4, 110.3, 106.9, 63.9, 41.6, 38.2.\) HRMS (EI): \( m/z \) Calcd for [M+H] \( C_{13}H_{16}NO_2 \): 218.1176; Found: 218.1174.

\( N^1 \)-benzylbenzene-1,3-diamine (7b)

\[ \begin{array}{c}
\text{NH}_2
\end{array} \quad \begin{array}{c}
\text{CH}
\end{array} \quad \begin{array}{c}
\text{NH}
\end{array} \quad \begin{array}{c}
\text{CH}
\end{array} \]

64 mg, yellow liquid, 65% isolated yield. \( R_f = 0.32 \) (hexane/EtOAc = 70/30). \(^1\)H NMR (500 MHz, CHLOROFORM-\( d \)) \( \delta = 7.49 - 7.34 \) (m, 4H), 7.34 - 7.27 (m, 1H), 7.00 (t, \( J = 7.8 \) Hz, 1H), 6.17 - 6.09 (m, 2H), 6.01 (t, \( J = 1.9 \) Hz, 1H), 4.33 (s, 2H), 3.51 (brs, 3H). \(^{13}\)C NMR (126 MHz, CHLOROFORM-\( d \)) \( \delta = 149.3, 147.5, 139.6, 130.1, 128.6, 127.5, 127.1, 105.1, 104.0, 99.5, 48.3.\) HRMS (EI): \( m/z \) Calcd for [M+H] \( C_{13}H_{15}N_2 \): 199.1230; Found: 199.1227.
$N^1$-benzyl-$N^3$-octylbenzene-1,2-diamine (7c)

![Chemical structure of 7c](image)

93 mg, yellow liquid, 60% isolated yield. $R_f = 0.32$ (hexane/EtOAc = 70/30). $^1$H NMR (500 MHz, CHLOROFORM-d) $\delta = 7.42 - 7.32$ (m, 4H), 7.29 - 7.24 (m, 1H), 6.98 (t, $J = 8.0$ Hz, 1H), 6.07 - 5.99 (m, 2H), 5.91 (s, 1H), 4.33 - 4.25 (m, 2H), 3.10 - 3.00 (m, 2H), 1.62 - 1.54 (m, 2H), 1.39 - 1.26 (m, 12H), 0.89 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (126 MHz, CHLOROFORM-d) $\delta =$ 149.6, 149.4, 139.7, 130.0, 128.6, 127.5, 127.1, 103.1, 102.7, 97.2, 48.4, 44.1, 31.8, 29.6, 29.4, 29.2, 27.2, 22.6, 14.1. HRMS (EI): m/z Calcd for [M+H] $C_{21}H_{31}N_2$: 311.2482; Found: 311.2480.

(R)-$N^1$-(3,7-dimethyloct-6-enyl)benzene-1,3-diamine (7d)

![Chemical structure of 7d](image)

95 mg, yellow liquid, 78% isolated yield. $R_f = 0.32$ (hexane/EtOAc = 70/30). $^1$H NMR (400 MHz, CHLOROFORM-d) $\delta = 6.97$ (t, $J = 8.0$ Hz, 1 H), 6.08 (dd, $J = 2.3, 7.6$ Hz, 2 H), 5.97 (t, $J = 1.9$ Hz, 1 H), 5.19 - 5.06 (m, 1 H), 3.35 (brs, 2 H), 3.16 - 3.03 (m, 3 H), 2.10 - 1.94 (m, 2 H), 1.75 - 1.68 (m, 3 H), 1.66 - 1.54 (m, 5 H), 1.48 - 1.36 (m, 2 H), 1.27 - 1.18 (m, 1 H), 0.99 - 0.92 (m, 3 H). $^{13}$C NMR (101MHz, CHLOROFORM-d) $\delta =$ 149.7, 147.4, 131.3, 130.0, 124.6, 104.7, 104.0, 99.3, 77.3, 76.7, 41.9, 37.0, 36.7, 30.4, 25.7, 25.4, 19.5, 17.6. HRMS (EI): m/z Calcd for [M+H] $C_{16}H_{27}N_2$: 247.2169; Found: 247.2167.
(R)-N³-(3,7-dimethyloct-6-enyl)-N³-(4-methylbenzyl)benzene-1,3-diamine (7e)

113 mg, yellow liquid, 65% isolated yield. R_f = 0.32 (hexane/EtOAc = 70/30). ^1H NMR (400 MHz, CHLOROFORM-d) δ = 7.35 - 7.28 (m, J = 7.6 Hz, 2 H), 7.24 - 7.13 (m, J = 7.6 Hz, 2 H), 7.03 (dt, J = 1.5, 8.0 Hz, 1 H), 6.12 - 6.03 (m, 2 H), 5.95 (s, 1 H), 5.21 - 5.05 (m, 1 H), 4.30 (s, 2 H), 3.69 (brs, 2 H), 3.20 - 3.01 (m, 2 H), 2.39 (s, 3 H), 2.12 - 1.99 (m, 2 H), 1.75 (s, 3 H), 1.72 - 1.58 (m, 5 H), 1.50 - 1.40 (m, 2 H), 1.30 - 1.18 (m, 1 H), 0.98 (dd, J = 1.9, 6.5 Hz, 4 H). ^13C NMR (101 MHz, CHLOROFORM-d) δ = 149.5, 149.4, 136.6, 136.6, 131.2, 129.9, 129.2, 127.5, 124.7, 103.0, 102.7, 97.1, 77.3, 76.7, 48.1, 42.0, 37.0, 36.6, 30.4, 25.7, 25.4, 21.0, 19.5, 17.6. HRMS (EI): m/z Calcd for [M+H] C_{24}H_{35}N_2: 351.2795; Found: 351.2793.

5. References


6. Spectral data
Chemical Shift (ppm)

4.00 1.20 2.07 2.14

Chemical Shift (ppm)

4.00 1.20 2.07 2.14
Chemical Shift (ppm)

Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)

148.19  138.54  131.65  129.64  127.49  125.38  123.22  115.66  113.89  109.02

H N C F₃ 3d

Chemical Shift (ppm)
Chemical shift (ppm)
Chemical Shift (ppm)

3g

Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)
4g
Chemical Shift (ppm)

H N M e M e

4g

S63
Chemical Shift (ppm)
$6b$
Chemical Shift (ppm)

0.81 1.96 1.94 0.85 0.90 2.00 2.10 2.07 0.87
Chemical Shift (ppm)

Chemical Shift (ppm)
Chemical shift (ppm)

149.65  141.27  104.65  77.31
147.44  129.99  103.98  77.30
124.63  106.84  76.89

7d