Supporting Information

Palladium-Catalyzed Cross-Coupling Reaction of Isocyanides with Azides: A General Route to Unsymmetric Carbodiimide

Zhen Zhang, Zongyang Li, Bin Fu and Zhenhua Zhang*
Department of Applied Chemistry, China Agricultural University, 2 West Yuanmingyuan Road, Beijing 100193 (China)
zhangzhh@cau.edu.cn

General All reactions were performed in a glass vial. Anhydrous solvents were distilled in small scale with CaH₂ or sodium and stored under N₂. The boiling point of petroleum ether is between 60 and 90°C. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ¹H and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz with Varian Mercury 400 spectrometer at ambient temperature. Chemical shifts are reported in ppm relative to chloroform (¹H, 7.26; ¹³C, 77.00) or DMSO (¹H, 2.50; ¹³C, 39.52). IR spectra were recorded with a Nicolet AVATAR 330 FT-IR spectrometer. Mass spectra were obtained on a Waters Auto Purification LC/MS system. HMRS were obtained on a Bruker Apex IV FTMS spectrometer, or Waters GCT Premier. All palladium catalysts were purchased from Sigma-Aldrich. All alkyl isocyanides and benzyl isocyanides are commercially available, unless stated otherwise.

General Procedures for the Preparation of Starting Materials

General Procedure for the Preparation of Azides
The aryl or heteroaryl azides 3a-c¹, 3d¹, 3e-f¹, 3g¹, 3h¹, 3i¹, 3j¹, 3k¹, 3l¹, 3m¹, 3n², 3o², 3p², 3q³, 3r³, 3t³, 3v⁴ were synthesized according to a standard procedure.¹

![Reaction Scheme 1](image1)

The aryl 3u⁴⁵, 3w⁴⁶ were synthesized according to a standard procedure.⁴⁷

![Reaction Scheme 2](image2)
The heteroaryl azides 3p, 3s were synthesized according to the literature.\(^\text{10}\)

A mixture of I (10 mmol), Fe (50 mmol), NH\(_4\)Cl (100 mmol), EtOH (32 ml) and water (8 ml) was refluxed under N\(_2\) protection for 4 hours. The mixture was cooled to rt and filtered. The filtrate was concentrated and dissolved in water. The mixture was basified with Na\(_2\)CO\(_3\) and extracted with EtOAc (20 ml x 2). The organic phases were combined, dried over Na\(_2\)SO\(_4\) and concentrated in vacuum. The colorless crude products were directly used for next step without further purification.

In a dried, 100 mL round-bottom flask, crude products II (740 mg, about 5 mmol) was dissolved in 70% AcOH (20 mL) and placed at 0 °C. After 10 min, NaNO\(_2\) (448 mg, 6.5 mmol) dissolved in H\(_2\)O (1 mL) was added dropwise, and the mixture was stirred for 10 min. NaN\(_3\) (420 mg, 6.48 mmol) was added in portions. After 45 min, the mixture was slowly poured into H\(_2\)O (25 mL) and saturated K\(_2\)CO\(_3\) (19 mL) to form a neutral pH. This was extracted with ethyl acetate (4 x 50 mL), washed with brine, dried with Na\(_2\)SO\(_4\), filtered, and concentrated. The crude product was purified by column chromatography on silica gel, yields 3s (611 mg, 65%).

III was prepared using the same procedure described for 3s.

To a suspended solution of NaH (6.00 g, 60% dispersion in mineral oil, 9 mmol) in THF (20 mL), III (474 mg, 3 mmol) dissolved in THF (3 mL) was added dropwise at 0 °C. The heterogeneous mixture was stirred at 0 °C for 30 min and 2 h at rt. The mixture was then cooled to 0 °C, treated with iodomethane (640 ml, 4.5 mmol), and allowed to warm to rt. After 30 min, the reaction mixture was cooled to 0 °C, quenched with saturated NH\(_4\)Cl (10 mL), and extracted with ethyl acetate (2 x 10 mL). The organic layers were combined, washed with brine, dried over anhydrous Na\(_2\)SO\(_4\) and concentrated in vacuum. The resulting oil was purified by column chromatography on silica gel to provide 3p (443 mg, 86%).

Benzyl azides 4a-b\(^\text{11}\), 4c\(^\text{16}\), 4d\(^\text{12}\), 4e\(^\text{13}\), 4f\(^\text{14}\), 4h\(^\text{12}\), 4g\(^\text{15}\), 4k\(^\text{12}\) were synthesized with method A. 4i\(^\text{14}\), 4j\(^\text{17}\) were synthesized with method B.

**Method A**\(^\text{18}\)

\[
\text{R-}^\text{Br} \xrightarrow{\text{NaN}_3, \text{H}_2\text{O : ACE = 1 : 1}} \text{R-}^\text{N}_3
\]

**Method B**\(^\text{17}\)
Alkyl azides \(7a^{19}, 7b^{19}, 7c^{21}, 7d^{20}, 7e^{19}, 7f^{22}\) were synthesized according to the literature.\(^{19}\)

![Reaction Scheme]

**General Procedure for the Preparation of Aryl isocyanides**

Aryl isocyanide \(2e-g^{2}\) were synthesized according to the literature.\(^{23}\)

![Reaction Scheme]

**Typical procedure for Pd(PPh\(_3\))\(_4\)-catalyzed reactions of Isocyanide with Aryl azides**

To a 10ml glass vial was added Pd(PPh\(_3\))\(_4\) (6 mg, 0.005 mmol), THF (2ml), azide (1a, 24 mg, 0.2 mmol). Then the vessel was sealed, evacuated and purged with N\(_2\). After 5 min, isocyanide (2a, 20 mg, 0.24 mmol) was added by syringe. The mixture was stirred for 5 h at room temperature. Then volatiles were evaporated under reduced pressure, the resulting residue was purified by flash column chromatography to give colorless oil 3aa, isolated yield 90%.

**Typical procedure for Pd(PPh\(_3\))\(_4\)-catalyzed reactions of Isocyanide with Benzyl azides and Alkyl azides**

To a 10ml glass vial was added Pd(PPh\(_3\))\(_4\) (12 mg, 0.01 mmol), THF (2 ml), azide (4a, 27 mg, 0.2 mmol). Then the vessel was sealed, evacuated and purged with N\(_2\). After 5 min, isocyanide (2a, 20 mg, 0.24 mmol) was added by syringe. The mixture was stirred for 10 h at 50 °C. Then volatiles were evaporated under reduced pressure, the resulting residue was purified by flash column chromatography to give colorless oil 5aa, isolated yield 79%.

**Table S1. Additional Experiments on the Conditions of Pd-Catalyzed Reaction of Isocyanide with Benzyl azide.\(^a\)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat. / L (mol%)</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>t [h]</th>
<th>Yield (%)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(PPh(_3))(_4) (5)</td>
<td>PhMe</td>
<td>60</td>
<td>18</td>
<td>63</td>
</tr>
<tr>
<td>Entry</td>
<td>Cat. / L (mol%)</td>
<td>Solvent</td>
<td>T [°C]</td>
<td>t [h]</td>
<td>Yield%&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>-------</td>
<td>----------------</td>
<td>---------</td>
<td>--------</td>
<td>-------</td>
<td>-------------------</td>
</tr>
<tr>
<td>2</td>
<td>Pd(PPh₃)₄(5)</td>
<td>THF</td>
<td>50</td>
<td>18</td>
<td>88 (79)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>Pd(PPh₃)₄(5)</td>
<td>DME</td>
<td>50</td>
<td>24</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>Pd(PPh₃)₄(5)</td>
<td>Dioxane</td>
<td>50</td>
<td>18</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>Pd(PPh₃)₄(5)</td>
<td>DCE</td>
<td>50</td>
<td>28</td>
<td>46</td>
</tr>
<tr>
<td>6</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>THF</td>
<td>50</td>
<td>18</td>
<td>&lt;5</td>
</tr>
<tr>
<td>7</td>
<td>Pd(PPh₃)₂Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>THF</td>
<td>50</td>
<td>18</td>
<td>&lt;5</td>
</tr>
<tr>
<td>8</td>
<td>Pd₂(dba)&lt;sub&gt;3&lt;/sub&gt;(2.5)</td>
<td>THF</td>
<td>50</td>
<td>18</td>
<td>37</td>
</tr>
<tr>
<td>9</td>
<td>Pd₂(dba)&lt;sub&gt;3&lt;/sub&gt;(2.5)/PPh₃(5)</td>
<td>THF</td>
<td>50</td>
<td>18</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>Pd₂(dba)&lt;sub&gt;3&lt;/sub&gt;(2.5)/PPh₃(10)</td>
<td>THF</td>
<td>50</td>
<td>18</td>
<td>43</td>
</tr>
<tr>
<td>11</td>
<td>Pd₂(dba)&lt;sub&gt;3&lt;/sub&gt;(2.5)/PPh₃(20)</td>
<td>THF</td>
<td>50</td>
<td>18</td>
<td>65</td>
</tr>
<tr>
<td>12</td>
<td>Pd₂(dba)&lt;sub&gt;3&lt;/sub&gt;(2.5)/PPh₃(25)</td>
<td>THF</td>
<td>50</td>
<td>18</td>
<td>71</td>
</tr>
<tr>
<td>13&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Pd(PPh₃)₄(5)</td>
<td>THF</td>
<td>50</td>
<td>18</td>
<td>73</td>
</tr>
<tr>
<td>14&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Pd(PPh₃)₄(10)</td>
<td>THF</td>
<td>50</td>
<td>15</td>
<td>72</td>
</tr>
</tbody>
</table>

[a] Determined by <sup>1</sup>H NMR using mesitylene as internal standard. [b] Isolated yield. [c] Na<sub>2</sub>SO₄ (20 mg) was added. [d] B (1.5 eq).

Table S2. Additional Experiments on the Conditions of Pd-Catalyzed Reaction of Isocyanide with Alkyl Azide.<sup>a</sup>

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat. / L (mol%)</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>t [h]</th>
<th>Yield%&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(PPh₃)₄(5)</td>
<td>THF</td>
<td>50</td>
<td>23</td>
<td>78 (65)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>Pd(PPh₃)₄(5)</td>
<td>THF</td>
<td>70</td>
<td>18</td>
<td>67</td>
</tr>
<tr>
<td>3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Pd(PPh₃)₄(10)</td>
<td>THF</td>
<td>50</td>
<td>15</td>
<td>74</td>
</tr>
<tr>
<td>4&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Pd(PPh₃)₄(5)</td>
<td>THF</td>
<td>50</td>
<td>23</td>
<td>70</td>
</tr>
</tbody>
</table>

[a] Determined by <sup>1</sup>H NMR using mesitylene as internal standard. [b] Isolated yield. [c] 4A MS (20 mg) was added. [d] Styrene (0.5 eq) was added as additive.
Mechanistic Discussion

Based on the literature reports[25], there are three possible pathways that may be considered. (Mechanism \textit{a, b, c})

**Mechanism a**

\[
\begin{align*}
&\text{PhN}_3 + \text{PPPh}_3 \\
&\text{1a} \quad \text{Pd(PPh}_3)_4 \\
&\text{THF, rt or 50 °C} \quad \text{R}^2\text{N}_3 + \text{R}^1\text{NC} \quad \overset{\text{std. cond.}}{\rightarrow} \text{R}^1\text{N} = \text{C}=\text{N} - \text{R}^2
\end{align*}
\]

In mechanism \textit{a}, the given intermediate \(N\)-(triphenylphosphoranylidene)-aniline (10) was speculated to be generated with triphenylphosphine and azide via aza-Wittig reaction. To elucidate this mechanism, 10 was prepared and isolated. When 10 was treated with 2a under the standard reaction conditions, desired product could not be detected. Moreover, no intermediate 10 can be detected in the model reaction of 1a with 2a in TLC or \(^{31}\)P NMR (Figure S1). These results indicated that 10 are not a key intermediate in this transformation and no free PPh\(_3\) are involved in the reaction of azides.

**Mechanism b**

In mechanism \textit{b}, firstly, palladium nitrene species \textit{A} is formed from \textit{1a} simultaneously with the release of N\(_2\). Subsequently, the insertion of isocyanide (2a) into palladium nitrene species \textit{A} occurred to give intermediate \textit{B}. The species \textit{B} subsequently undergoes reductive elimination to give final products 3aa.

**Mechanism c**

In mechanism \textit{c}, the first step of the reaction sequences involved a labile coordination of the organic azide and isocyanide to the metal, followed by the direct reaction of isocyanide with azide group to give species \textit{B} without palladium nitrene intermediate formation.

Compared with mechanism \textit{b} and mechanism \textit{c}, though mechanism \textit{c} may also provide a plausible explanation for the course of reaction, Besenyei[26] group have successfully
accomplished the preparation of stable palladium-nitrene intermediate \( \textbf{D} \) with azides and stoichiometric palladium complexes; subsequently, the species \( \textbf{D} \) can also react with CO (as a \( \sigma \)-donor/\( \pi \)-acceptor ligand as isocyanide) affording isocyanate. Thus, we consider the mechanism \( b \) is more plausible with the information currently available, although vigorous experiments are needed to unambiguously establish this mechanism.

\[
\begin{align*}
R-N_3 & \quad \xrightarrow{[\text{Pd}]} \quad Pd=NR \\
\textbf{D} & \quad \xrightarrow{CO} \quad R-\text{N}=\text{C}=\text{O}
\end{align*}
\]

Figure S1. \( ^{31} \text{P} \) NMR of different products or mixture
Spectra Data

5-azido-1-methyl-1H-indole (3p)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 – 7.25 (m, 2H), 7.06 (d, $J$ = 3.1 Hz, 1H), 6.89 (dd, $J$ = 8.6, 2.2 Hz, 1H), 6.42 (dd, $J$ = 3.1, 0.8 Hz, 1H), 3.77 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.47, 131.63, 130.19, 129.14, 113.52, 110.25, 100.54, 32.96. IR (neat, cm$^{-1}$): 2117, 1488, 1277, 720. HRMS m/z (EI) calcd for C$_9$H$_8$N$_4$ (M+) 172.0749, found 172.0751.

Ethyl 5-azidobenzofuran-2-carboxylate (3q)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 – 7.52 (m, 1H), 7.45 (s, 1H), 7.30 (d, $J$ = 2.3 Hz, 1H), 7.09 (dd, $J$ = 8.9, 2.3 Hz, 1H), 4.45 (q, $J$ = 7.1 Hz, 2H), 1.43 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.15, 152.96, 146.96, 136.11, 127.95, 119.33, 113.43, 113.06, 111.82, 61.64, 14.24. IR (neat, cm$^{-1}$): 2116, 1723, 1180. HRMS m/z (ES+) calcd for C$_{11}$H$_9$N$_3$NaO$_3$ ([M+Na$^+$]) 254.0536, found 254.0532.

6-azido-2-methylbenzo[d]oxazole (3s)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 8.5 Hz, 1H), 7.14 (d, $J$ = 2.1 Hz, 1H), 6.99 (dd, $J$ = 8.5, 2.1 Hz, 1H), 2.63 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.16, 151.55, 138.92, 137.01, 120.02, 115.53, 101.25, 14.49. IR (neat, cm$^{-1}$): 2113, 1478, 1305, 1228. HRMS m/z (EI) calcd for C$_8$H$_6$N$_4$O (M+) 174.0542, found 174.0542.

N-((tert-butylimino)methylene)aniline (3aa)
98% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.19 (m, 2H), 7.17 – 7.04 (m, 3H), 1.40 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.87, 136.28, 129.32, 124.56, 123.22, 57.39, 31.56.
**N-(tert-butylimino)methylene-4-methylaniline (3ba)** 28  
93% 1H NMR yield, colorless oil, 1H NMR (400 MHz, CDCl₃) δ 7.11 – 7.05 (m, 2H), 7.02 – 6.95 (m, 2H), 2.31 (s, 3H), 1.39 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 137.94, 136.88, 134.25, 129.90, 122.98, 57.25, 31.54, 20.87.

**N-(tert-butylimino)methylene-2-methylaniline (3ca)**  
92% 1H NMR yield, colorless oil, 1H NMR (400 MHz, CDCl₃) δ 7.16 – 7.09 (m, 3H), 7.04 – 6.97 (m, 1H), 2.29 (s, 3H), 1.40 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 139.22, 135.60, 132.04, 130.65, 126.65, 124.43, 123.36, 56.97, 31.55, 18.13. IR (neat, cm⁻¹): 2114, 1498, 1186, 757. HRMS m/z (EI) calcd for C₁₂H₁₆N₂ (M⁺) 188.1313, found 188.1319.

**N-(tert-butylimino)methylene-2,4,6-trimethylaniline (3da)** 27  
81% 1H NMR yield, colorless oil, 1H NMR (400 MHz, CDCl₃) δ 6.82 (d, J = 0.5 Hz, 2H), 2.31 (s, 6H), 2.24 (s, 3H), 1.35 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 134.13, 133.51, 132.75, 132.16, 128.72, 55.93, 31.29, 20.68, 18.98.

**N-(tert-butylimino)methylene-4-chloroaniline (3ea)** 29  
99% 1H NMR yield, colourless oil, 1H NMR (400 MHz, CDCl₃) δ 7.27 – 7.21 (m, 2H), 7.03 – 6.98 (m, 2H), 1.40 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 139.65, 135.62, 129.68, 129.35, 124.38, 57.65, 31.55.

**4-bromo-N-(tert-butylimino)methylene)aniline (3fa)** 30  
93% 1H NMR yield, colorless oil, 1H NMR (400 MHz, CDCl₃) δ 7.41 – 7.35 (m, 2H), 6.97 – 6.92 (m, 2H), 1.40 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 140.21, 135.47, 132.31, 124.81, 117.33, 57.68, 31.56.
**N-((tert-butylimino)methylene)-3-fluoroaniline (3ga)**

92\% HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 – 7.19 (m, 1H), 6.89 – 6.85 (m, 1H), 6.84 – 6.76 (m, 2H), 1.41 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.21 (d, $J_{CF}$ = 246.1 Hz), 142.92 (d, $J$ = 10.1 Hz), 135.23, 130.27 (d, $J$ = 9.4 Hz), 118.99 (d, $J$ = 2.9 Hz), 111.45 (d, $J$ = 21.3 Hz), 110.46 (d, $J$ = 23.2 Hz), 57.77, 31.56. IR (neat, cm$^{-1}$): 2118, 1609, 1180, 934. HRMS $m/z$ (EI) calcd for C$_{11}$H$_{13}$FN$_2$ (M+) 192.1063, found 192.1068.

**N-((tert-butylimino)methylene)-4-methoxyaniline (3ha)**

96\% HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.05 – 6.99 (m, 2H), 6.84 – 6.80 (m, 2H), 3.78 (s, 3H), 1.39 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.73, 137.25, 133.28, 124.04, 114.58, 57.17, 55.46 (d, $J$ = 2.3 Hz), 31.55.

**1-(3-((tert-butylimino)methylene)amino)phenyl)ethanone (3ia)**

95\% HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 – 7.63 (m, 2H), 7.38 (t, $J$ = 7.8 Hz, 1H), 7.30 – 7.25 (m, 1H), 2.59 (s, 3H), 1.43 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.48, 141.73, 138.26, 135.25, 129.51, 127.68, 124.35, 122.82, 57.73, 31.54, 26.66. IR (neat, cm$^{-1}$): 2123, 1687, 1256, 686. HRMS $m/z$ (ES+) calcd for C$_{13}$H$_{16}$N$_2$NaO ([M+Na]$^+$) 239.1155, found 239.1153.

**Ethyl 4-(((tert-butylimino)methylene)amino)benzoate (3ja)**

91\% HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (dd, $J$ = 8.4, 1.0 Hz, 2H), 7.11 (dd, $J$ = 8.4, 1.0 Hz, 2H), 4.36 (q, $J$ = 7.1 Hz, 2H), 1.42 (s, 9H), 1.38 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.07, 145.98, 134.41, 130.94, 126.41, 122.96, 60.80, 57.98, 31.56, 14.30.
4-(((tert-butylimino)methylene)amino)benzonitrile (3ka)
91% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.54 (m, 2H), 7.15 – 7.10 (m, 2H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 146.45, 133.41, 132.94, 123.85, 118.87, 107.39, 58.35, 31.54. IR (neat, cm⁻¹): 2130, 1601, 1190, 841. HRMS m/z (ES⁺) cale for C₁₂H₁₃N₃Na ([M+Na⁺]⁺) 222.1002, found 222.1001.

N-((tert-butylimino)methylene)-4-(trifluoromethyl)aniline (3la)
92% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 144.95, 134.42, 126.51 (q, J = 3.7 Hz), 126.22, 124.14 (q, J = 215.5 Hz), 123.32, 57.99, 31.54. IR (neat, cm⁻¹): 2128, 1322, 1123, 1065, 843. HRMS m/z (EI⁺) cale for C₁₂H₁₃F₃N₂ (M⁺) 242.1031, found 242.1038.

N-((tert-butylimino)methylene)naphthalen-1-amine (3ma)
90% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 8.33 – 8.27 (m, 1H), 7.82 – 7.77 (m, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.41 – 7.36 (m, 1H), 7.30 (dd, J = 7.3, 1.1 Hz, 1H), 1.44 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 141.60, 137.48, 135.82, 134.31, 128.76, 127.65, 126.35, 125.78, 124.43, 123.56, 119.08, 57.44, 31.66.

N-((tert-butylimino)methylene)quinolin-3-amine (3na)
93% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, J = 2.5 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.62 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.52 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 1.46 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 147.54, 145.42, 145.91, 134.66, 129.24, 128.43, 128.24, 127.16, 127.00, 126.65, 58.05, 31.57. IR (neat, cm⁻¹): 2119, 1182, 752. HRMS m/z (ES⁺) cale for C₁₄H₁₆N₃ ([M+H⁺]⁺) 226.1339, found 226.1336.
**N-((tert-butylimino)methylene)thiophen-3-amine (3oa)**

95% ^1^H NMR yield, colorless oil, ^1^H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (dd, $J = 5.1, 3.2$ Hz, 1H), 6.88 (dd, $J = 5.1, 1.4$ Hz, 1H), 6.80 (dd, $J = 3.2, 1.4$ Hz, 1H), 1.39 (s, 9H). ^13^C NMR (101 MHz, CDCl$_3$) $\delta$ 138.38, 137.62, 125.37, 123.68, 113.22, 57.33, 31.48. IR (neat, cm$^{-1}$): 2114, 1184, 772. HRMS m/z (ES$^+$) calcd for C$_9$H$_{13}$N$_2$S ([M+H]$^+$) 181.0794, found 181.0800.

**N-((tert-butylimino)methylene)-1-methyl-1H-indol-5-amine (3pa)**

75% ^1^H NMR yield, colorless oil, ^1^H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J = 2.1$ Hz, 1H), 7.21 (d, $J = 8.6$ Hz, 1H), 7.04 – 6.98 (m, 2H), 6.40 (dd, $J = 3.1, 0.8$ Hz, 1H), 3.74 (s, 3H), 1.41 (s, 9H). ^13^C NMR (101 MHz, CDCl$_3$) $\delta$ 137.91, 134.40, 132.24, 129.75, 128.95, 117.69, 114.56, 109.72, 100.56, 56.97, 32.91, 31.58. IR (neat, cm$^{-1}$): 2923, 2124, 1240, 720. HRMS m/z (ES$^+$) calcd for C$_{14}$H$_{18}$N$_3$ ([M+H]$^+$) 228.1495, found 228.1492.

**Ethyl 5-(((tert-butylimino)methylene)amino)benzofuran-2-carboxylate (3qa)**

90% ^1^H NMR yield, colorless oil, ^1^H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 – 7.47 (m, 1H), 7.46 (d, $J = 0.9$ Hz, 1H), 7.36 – 7.33 (m, 1H), 7.20 (dd, $J = 8.8, 2.2$ Hz, 1H), 4.44 (q, $J = 7.1$ Hz, 2H), 1.49 – 1.36 (m, 12H). ^13^C NMR (101 MHz, CDCl$_3$) $\delta$ 159.32, 153.28 – 152.14 (m), 146.50, 136.97, 136.12, 127.71, 123.50, 115.98, 113.38, 112.89, 61.51, 57.44, 31.54, 14.25. IR (neat, cm$^{-1}$): 2115, 1731, 1181, 764. HRMS m/z (ES$^+$) calcd for C$_{16}$H$_{20}$N$_2$O$_3$ ([M+Na]$^+$) 309.1210, found 309.1209.

**N-((tert-butylimino)methylene)benzo[d]thiazol-6-amine (3ra)**

94% ^1^H NMR yield, colorless oil, ^1^H NMR (400 MHz, CDCl$_3$) $\delta$ 8.90 (s, 1H), 8.03 (d, $J = 8.6$ Hz, 1H), 7.62 (d, $J = 2.1$ Hz, 1H), 7.27 (d, $J = 8.6, 2.2$ Hz, 1H), 1.44 (s, 9H). ^13^C NMR (101 MHz, CDCl$_3$) $\delta$ 153.04, 150.44, 139.04, 135.46, 134.81, 123.95, 122.35, 115.52, 57.72, 31.56. IR (neat, cm$^{-1}$): 2125, 1185, 828. HRMS m/z (ES$^+$) calcd for C$_{12}$H$_{13}$N$_3$S ([M+H]$^+$) 232.0909, found 232.0899.
N-((tert-butylimino)methylene)-2-methylbenzo[d]oxazol-6-amine (3sa)
81% 1H NMR yield, colorless oil, 1H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.4 Hz, 1H), 7.18 (dd, J = 2.0, 0.5 Hz, 1H), 7.06 (dd, J = 8.4, 2.0, 0.6 Hz, 1H), 2.61 (s, 3H), 1.42 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 163.78, 151.38, 138.54, 137.99, 135.93, 119.79, 119.38, 105.00, 57.61, 31.55, 14.46. IR (neat, cm⁻¹): 2116, 1619, 1184, 856. HRMS m/z (ES+) calcd for C₁₃H₁₆N₃O ([M+H]⁺) 230.1288, found 230.1284.

N-((tert-butylimino)methylene)pyridin-3-amine (3ta)
86% 1H NMR yield, colorless oil, 1H NMR (400 MHz, CDCl₃) δ 8.42 (d, J = 2.6 Hz, 1H), 8.33 (dd, J = 4.7, 1.5 Hz, 1H), 7.36 (ddd, J = 8.1, 2.6, 1.5 Hz, 1H), 7.22 (ddd, J = 8.1, 4.7, 0.7 Hz, 1H), 1.42 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 145.37, 144.98, 138.17, 134.58, 129.88, 123.79, 57.87, 31.54.

N¹-((tert-butylimino)methylene)benzene-1,3-diamine (3ua)
87% 1H NMR yield, white solid, 1H NMR (400 MHz, CDCl₃) δ 7.05 (t, J = 7.8 Hz, 1H), 6.56 – 6.47 (m, 1H), 6.46 – 6.35 (m, 1H), 3.67 (s, 2H), 1.39 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 147.41, 141.74, 136.43, 129.99, 113.45, 111.52, 109.79, 57.29, 31.55. IR (neat, cm⁻¹): 2114, 1600, 1181, 686. HRMS m/z (EI+) calcd for C₁₁H₁₅N₃ (M+) 189.1266, found 189.1268.

N-((tert-butylimino)methylene)-3-ethynylaniline (3va)
92% 1H NMR yield, colorless oil, 1H NMR (400 MHz, CDCl₃) δ 7.27 – 7.17 (m, 3H), 7.12 – 7.02 (m, 1H), 3.08 (s, 1H), 1.41 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 140.40, 136.15, 136.06, 126.63, 123.87, 123.12, 82.99, 77.49, 57.60, 31.54. IR (neat, cm⁻¹): 2135, 2116, 1598, 1179, 685. HRMS m/z (EI+) calcd for C₁₃H₁₄N₂ (M+) 198.1157, found 198.1157.

N-((tert-butylimino)methylene)-4-vinylaniline (3wa)
96% 1H NMR yield, colorless oil, 1H NMR (400 MHz, CDCl₃) δ 7.36 – 7.29 (m, 2H), 7.09 – 6.97 (m, 2H), 6.66 (dd, J = 17.6, 10.9 Hz, 1H), 5.67 (dd, J = 17.6, 0.7 Hz, 1H), 5.19 (dd, J = 10.9, 0.7 Hz, 1H), 1.40 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 140.40, 136.15, 136.06, 134.11, 127.19, 123.26, 112.96,
IR (neat, cm⁻¹): 2107, 1512, 1191, 841. HRMS m/z (El⁺) calcd for C₁₃H₁₆N₂ (M⁺) 200.1313, found 200.1314.

**N-((butylimino)methylene)aniline (3ab)**
95% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 2H), 7.13 – 7.05 (m, 3H), 3.41 (t, J = 6.8 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.51 – 1.40 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.71, 135.97, 129.30, 124.50, 123.41, 46.50, 33.37, 19.93, 13.56.

**N-((cyclohexylimino)methylene)aniline (3ac)**
90% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.23 (m, 2H), 7.15 – 7.04 (m, 3H), 3.47 (ddd, J = 13.5, 9.6, 3.8 Hz, 1H), 2.07 – 1.96 (m, 2H), 1.82 – 1.71 (m, 2H), 1.61 – 1.43 (m, 3H), 1.41 – 1.21 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.86, 136.16, 129.29, 124.46, 123.29, 56.60, 34.90, 25.29, 24.34.

**N-((benzylimino)methylene)aniline (3ad)**
93% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.28 (m, 5H), 7.27 – 7.21 (m, 2H), 7.11 – 7.05 (m, 1H), 7.02 – 6.95 (m, 2H), 4.55 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 139.90, 137.76, 137.24, 129.27, 128.75, 127.76, 127.34, 124.81, 123.59, 50.45.

**2,6-dimethyl-N-((phenylimino)methylene)aniline (3ae)**
82% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.28 (m, 2H), 7.20 – 7.10 (m, 3H), 7.07 – 6.96 (m, 3H), 2.39 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 139.83, 134.91, 132.84, 131.54, 129.46, 128.19, 125.15, 124.74, 123.67, 19.01.

**4-methoxy-N-((phenylimino)methylene)aniline (3af)**

---
73% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.28 (m, 2H), 7.20 – 7.14 (m, 3H), 7.13 – 7.08 (m, 2H), 6.88 – 6.82 (m, 2H), 3.79 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.44, 138.90, 135.80, 130.65, 129.44, 125.39, 125.14, 124.05, 114.69, 55.47.

![Structure 1](image1)

**Methyl 4-(((phenylimino)methylene)amino)benzoate (3ag)**

52% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 – 7.98 (m, 2H), 7.37 – 7.31 (m, 2H), 7.23 – 7.15 (m, 5H), 3.90 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.39, 143.39, 137.30, 134.07, 131.09, 129.58, 127.07, 126.02, 124.40, 124.01, 52.13. IR (neat, cm$^{-1}$): 2118, 1608, 1180, 934. HRMS m/z (ES$^+$) calcd for C$_{15}$H$_{13}$N$_2$O$_2$ ([M+H]$^+$) 253.0971, found 253.0968.

![Structure 2](image2)

**N-((benzylimino)methylene)-2-methylpropan-2-amine (5aa)**

88% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.25 (m, 5H), 4.32 (s, 2H), 1.13 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.71, 138.71, 128.49, 127.82, 127.44, 55.24, 50.80, 31.10.

![Structure 3](image3)

**2-methyl-N-(((4-(trifluoromethyl)benzyl)imino)methylene)propan-2-amine (5ba)**

82% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 8.2$ Hz, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 4.42 (s, 2H), 1.19 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.63, 140.10, 129.80, 129.48, 127.85, 125.45 (dd, $J = 7.5$, 3.7 Hz), 122.71, 55.51, 50.19, 31.15. IR (neat, cm$^{-1}$): 2126, 1326, 1127, 1067. HRMS m/z (ES$^+$) calcd for C$_{13}$H$_{13}$F$_3$N$_2$ ([M+H]$^+$) 257.1260, found 257.1257.

![Structure 4](image4)

**2-methyl-N-(((2-(trifluoromethyl)benzyl)imino)methylene)propan-2-amine (5ca)**

90% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 – 7.59 (m, 2H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.38 (t, $J = 7.6$ Hz, 1H), 4.56 (s, 2H), 1.17 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.07, 137.02, 132.10, 130.19, 127.81, 127.44, 125.76 (q, $J = 5.6$ Hz), 124.20 (q, $J_{CF} = 274.0$ Hz), 55.46, 47.09, 31.14. IR (neat, cm$^{-1}$): 2123, 1314, 1164, 1117, 768. HRMS m/z (EI) calcd for C$_{13}$H$_{13}$F$_3$N$_2$ (M+) 256.1187, found 256.1187.
2-methyl-\(N\)-((3-(trifluoromethyl)benzyl)imino)methylene)propan-2-amine (5da)
89% \(^1\)HNMR yield, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (s, 1H), 7.51 (m, 3H), 4.41 (s, 2H), 1.17 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.10, 139.68, 131.04, 130.72, 129.02, 124.45 (dd, \(J = 7.6, 3.8\) Hz), 124.26 (dd, \(J = 7.6, 3.7\) Hz), 123.99 (q, \(J_{CF} = 272.1\) Hz), 55.54, 50.26, 31.15. IR (neat, cm\(^{-1}\)): 2124, 1328, 1128, 1074. HRMS \(m/z\) (EI) calcd for C\(_{13}\)H\(_{15}\)F\(_3\)N\(_2\) (M\(^+\)) 256.1187, found 256.1192.

2-methyl-\(N\)-(((3-methylbenzyl)imino)methylene)propan-2-amine (5ea)
80% \(^1\)HNMR yield, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.23 (t, \(J = 7.6\) Hz, 1H), 7.11 (dd, \(J = 14.8, 7.2\) Hz, 3H), 4.29 (s, 2H), 2.35 (s, 3H), 1.14 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.72, 138.62, 138.10, 128.53, 128.38, 128.13, 124.83, 55.21, 50.76, 31.11, 21.32.

\(N\)-(((4-methoxybenzyl)imino)methylene)-2-methylpropan-2-amine (5fa)
72% \(^1\)HNMR yield, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.26 – 7.21 (m, 2H), 6.90 – 6.86 (m, 2H), 4.25 (s, 2H), 3.80 (s, 3H), 1.13 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.90, 140.94, 131.04, 129.14, 113.81, 55.22 (d, \(J = 2.1\) Hz), 55.17, 50.25, 31.10.

Methyl 4-(((tert-butylimino)methylene)amino)methylbenzoate (5ga)
84% \(^1\)HNMR yield, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 – 8.00 (m, 2H), 7.42 – 7.37 (m, 2H), 4.41 (s, 2H), 3.92 (s, 3H), 1.17 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.75, 143.72, 140.15, 129.82, 129.19, 127.54, 55.46, 52.04, 50.36, 31.18. IR (neat, cm\(^{-1}\)): 2118, 1724, 1278, 1106, 755. HRMS \(m/z\) (EI) calcd for C\(_{14}\)H\(_{18}\)N\(_2\)O\(_2\) (M\(^+\)) 246.1368, found 246.1372.

\(N\)-(((4-chlorobenzyl)imino)methylene)-2-methylpropan-2-amine (5ha)
70% \(^1\)HNMR yield, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.30 (m, 2H), 7.27 – 7.23 (m, 2H), 4.31 (s, 2H), 1.17 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.39, 137.19, 133.20, 129.10, 128.64, 55.44, 50.07, 31.19. IR (neat, cm\(^{-1}\)): 2122, 1492, 798. HRMS m/z (EI) calcd for \(\text{C}_{12}\text{H}_{15}\text{ClN}_{2}\) (M\(^+\)) 222.0924, found 222.0926.

\[\text{N}^-\text{Bu}_2\text{N}^-\text{C}^-\text{C}^-\text{N}^-\text{Bu}\]

\(2\)-methyl-\(\text{N}^-\text{((1-phenylethyl)imino)methylene}\)propan-2-amine (5ia)

56% \(^1\)HNMR yield, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 (d, \(J = 4.4\) Hz, 4H), 7.29 – 7.23 (m, 1H), 4.58 (q, \(J = 6.8\) Hz, 1H), 1.55 (d, \(J = 6.8\) Hz, 3H), 1.18 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.89, 139.91, 128.40, 127.26, 126.02, 56.65 (d, \(J = 1.6\) Hz), 55.21, 31.18, 24.44.

\[\text{O}^-\text{N}^-\text{C}^-\text{N}^-\text{Bu}_2\]

\(\text{N}^-\text{(((furan-2-ylmethyl)imino)methylene)-2-methylpropan-2-amine (5ja)}\)

72% \(^1\)HNMR yield, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 (dd, \(J = 1.9, 0.8\) Hz, 1H), 6.33 (dd, \(J = 3.2, 1.9\) Hz, 1H), 6.26 (dd, \(J = 3.2, 0.6\) Hz, 1H), 4.28 (s, 2H), 1.20 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 152.22, 142.21, 141.23, 110.31, 107.56, 55.46, 43.27, 31.04. IR (neat, cm\(^{-1}\)):

2925, 2129, 662. HRMS m/z (EI) calcd for \(\text{C}_{10}\text{H}_{14}\text{N}_{2}\text{O}\) (M\(^+\)) 178.1106, found 178.1108.

\[\text{S}^-\text{N}^-\text{C}^-\text{N}^-\text{Bu}_2\]

\(2\)-methyl-\(\text{N}^-\text{(((thiophen-2-ylmethyl)imino)methylene)propan-2-amine (5ka)}\)

88% \(^1\)HNMR yield, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.23 (dd, \(J = 4.9, 1.4\) Hz, 1H), 7.01 – 6.95 (m, 2H), 4.48 (s, 2H), 1.16 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 141.35, 140.83, 126.81, 125.84, 124.97, 55.53, 45.12, 31.10. IR (neat, cm\(^{-1}\)):

2120, 1186, 703. HRMS m/z (EI) calcd for \(\text{C}_{10}\text{H}_{14}\text{N}_{2}\text{S}\) (M\(^+\)) 194.0878, found 194.0880.

\[\text{N}^-\text{((benzylimino)methylene)butan-1-amine (5ab)}\]

73% \(^1\)HNMR yield, colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 – 7.25 (m, 5H), 4.35 (s, 2H), 3.14 (t, \(J = 6.8\) Hz, 2H), 1.47 – 1.39 (m, 2H), 1.33 – 1.23 (m, 2H), 0.86 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.74, 138.62, 128.50, 127.44, 127.36, 50.47, 46.18, 33.19, 19.77, 13.53.
N-((benzylimino)methylene)cyclohexanamine (5ac)
74% ^1^H NMR yield, colorless oil, ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.38 – 7.24 (m, 5H), 4.34 (s, 2H), 3.20 – 3.09 (m, 1H), 1.82 – 1.73 (m, 2H), 1.70 – 1.62 (m, 2H), 1.55 – 1.47 (m, 1H), 1.28 – 1.12 (m, 5H). ^1^C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 140.66, 138.65, 128.49, 127.62, 127.37, 55.62, 50.67, 34.63, 25.31, 24.42.

N,N'-methanediylidenebis(1-phenylmethanamine) (5ad)
40% ^1^H NMR yield, colorless oil, ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.34 – 7.24 (m, 6H), 7.22 – 7.14 (m, 4H), 4.30 (s, 4H). ^1^C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 141.27, 138.24, 128.57, 127.48, 127.45, 50.32.

N-((tert-butyldimethylsilyloxy)-N-((tert-butyldimethylsilyloxy)-3-phenylpropan-1-amine (7ca)
55% ^1^H NMR yield, colorless oil, ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 3.70 (t, \( J = 6.0 \) Hz, 2H), 3.32 (t, \( J = 6.0 \) Hz, 2H), 1.80 – 1.73 (m, 2H), 1.28 (s, 9H), 0.89 (s, 9H), 0.05 (s, 6H). ^1^C NMR (101 MHz,
CDCl$_3$ δ 139.96, 60.05, 55.00, 43.54, 34.37, 31.32, 25.89, 18.27, -5.37. IR (neat, cm$^{-1}$): 2126, 1101, 837, 776. HRMS m/z (ES+) calcd for $\text{C}_{14}\text{H}_{31}\text{N}_{2}\text{OSi}$ ([M+H]$^+$) 271.2220, found 271.2197.

$N$-(((2-(benzyloxy)ethyl)imino)methylene)-2-methylpropan-2-amine (7da)
74% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.25 (m, 5H), 4.56 (s, 2H), 3.59 (t, $J = 5.4$ Hz, 2H), 3.40 (t, $J = 5.4$ Hz, 2H), 1.26 (s, 9H). ¹³C NMR (101 MHz, CDCl$_3$) δ 140.14, 137.95, 128.30, 127.69, 127.59, 73.01, 69.94, 55.12, 46.70, 31.17. IR (neat, cm$^{-1}$): 2125, 1189, 698. HRMS m/z (ES+) calcd for $\text{C}_{14}\text{H}_{20}\text{N}_{2}$NaO ([M+Na]$^+$) 255.1468, found 255.1468.

2-methyl-$N$-((phenethylimino)methylene)propan-2-amine (7ea)
54% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 3.48 – 3.44 (m, 2H), 2.87 (t, $J = 7.3$ Hz, 2H), 1.19 (s, 9H). ¹³C NMR (101 MHz, CDCl$_3$) δ 139.75, 138.82, 128.73, 128.43, 126.39, 55.02, 48.14, 37.76, 31.14.

Ethyl 6-(((tert-butylimino)methylene)amino)hexanoate (7fa)
48% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl$_3$) δ 4.09 (q, $J = 7.1$ Hz, 2H), 3.18 (t, $J = 6.9$ Hz, 2H), 2.27 (t, $J = 7.5$ Hz, 2H), 1.66 – 1.51 (m, 4H), 1.42 – 1.32 (m, 2H), 1.24 (s, 9H), 1.23 – 1.19 (m, 3H). ¹³C NMR (101 MHz, CDCl$_3$) δ 173.48, 139.80, 60.15, 54.93, 46.64, 34.12, 31.26, 31.02, 26.35, 24.46, 14.16. IR (neat, cm$^{-1}$): 2122, 1736, 1186. HRMS m/z (ES+) calcd for $\text{C}_{13}\text{H}_{24}\text{N}_{2}$Na$_2$O$_2$ ([M+Na]$^+$) 263.1730, found 263.1731.

$N$-(((2-(benzyloxy)ethyl)imino)methylene)butan-1-amine (7db)
50% ¹H NMR yield, colorless oil, ¹H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.31 (m, 5H), 7.31 – 7.26 (m, 1H), 4.57 (s, 2H), 3.60 (t, $J = 5.3$ Hz, 2H), 3.39 (t, $J = 5.3$ Hz, 2H), 3.17 (t, $J = 6.9$ Hz, 2H), 1.57 – 1.48 (m, 2H), 1.40 – 1.29 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). ¹³C NMR (101 MHz, CDCl$_3$) δ 140.82, 137.95, 128.31, 127.62, 73.07, 69.88, 46.52, 46.28, 33.14, 19.88, 13.59. IR (neat, cm$^{-1}$): 2127, 697. HRMS m/z (ES+) calcd for $\text{C}_{14}\text{H}_{20}\text{N}_{2}$NaO ([M+Na]$^+$) 255.1468, found 255.1468.

$N$-(((2-(benzyloxy)ethyl)imino)methylene)cyclohexanamine (7dc)
67% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 4.56 (s, 2H), 3.60 (t, $J$ = 5.3 Hz, 2H), 3.39 (t, $J$ = 5.3 Hz, 2H), 3.25 – 3.14 (m, 1H), 1.92 – 1.83 (m, 2H), 1.73 – 1.65 (m, 2H), 1.56 – 1.47 (m, 1H), 1.35 – 1.12 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.43, 137.94, 128.27, 127.61, 127.56, 73.02, 69.94, 55.59, 46.60, 34.57, 25.31, 24.49. IR (neat, cm$^{-1}$): 2122, 1116, 697. HRMS m/z (ES+) calcd for C$_{16}$H$_{23}$N$_2$O ([M+H]$^+$) 259.1805, found 259.1804.

![1-(tert-butyl)-2-butyl-3-phenylguanidine (8a)](image)

67% yield, yellow oil, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.27 – 7.21 (m, 2H), 6.95 – 6.87 (m, 1H), 6.86 – 6.80 (m, 2H), 3.75 (br, 1H), 3.68 (br, 1H), 3.17 (t, $J$ = 6.8 Hz, 2H), 1.60 – 1.45 (m, 2H), 1.43 – 1.29 (m, 11H), 0.93 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.04, 150.38, 129.13, 123.29, 121.17, 50.60, 41.66, 31.86, 30.13, 20.19, 13.82. IR (neat, cm$^{-1}$): 1633, 1589, 1487, 699. HRMS m/z (ES+) calcd for C$_{15}$H$_{26}$N$_3$ ([M+H]$^+$) 248.2121, found 248.2121.

![2-benzyl-1-(2, 6-dimethylphenyl)-3-phenylguanidine (8b)](image)

60% yield, yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.16 (m, 7H), 7.12 – 6.83 (m, 6H), 5.34 (br, 1H), 4.55 (s, 2H), 3.85 (br, 1H), 2.20 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.14, 147.48, 147.11, 139.47, 129.88, 129.36, 128.63, 128.41, 128.26, 127.56, 127.39, 127.02, 45.40, 18.18. IR (neat, cm$^{-1}$): 1642, 1586, 1497, 752, 698. HRMS m/z (ES+) calcd for C$_{22}$H$_{24}$N$_3$ ([M+H]$^+$) 330.1965, found 330.1967.

![2-benzyl-1-(tert-butyl)-3-phenylguanidine (8c)](image)

73% yield, yellow oil, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.37 – 7.32 (m, 4H), 7.29 – 7.22 (m, 3H), 6.97 – 6.85 (m, 3H), 4.38 (s, 2H), 4.17 (br, 1H), 3.70 (br, 1H), 1.27 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.97, 149.62, 139.10, 129.26, 128.64, 127.42, 127.32, 123.23, 121.59, 50.90, 46.33, 30.08. IR (neat, cm$^{-1}$): 1635, 1588, 1486, 698. HRMS m/z (ES+) calcd for C$_{18}$H$_{26}$N$_3$ ([M+H]$^+$) 282.1965, found 282.1963.

![1-benzyl-2-butyl-3-phenylguanidine (8d)](image)

1-benzyl-2-butyl-3-phenylguanidine (8d)
70% yield, yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.23 (m, 7H), 7.00 – 6.93 (m, 1H), 6.93 – 6.89 (m, 2H), 4.38 (s, 2H), 4.21 (br, 1H), 3.76 (br, 1H), 3.11 (t, $J$ = 7.1 Hz, 2H), 1.49 – 1.37 (m, 2H), 1.25 (dq, $J$ = 14.3, 7.3 Hz, 2H), 0.87 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.18, 150.05, 139.04, 129.26, 128.69, 127.39, 127.32, 123.54, 121.52, 45.99, 41.62, 31.76, 19.94, 13.74.

![Diagram](image1.png)

1-(*tert*-butyl)-2-(4-methoxyphenyl)-3-phenylguanidine (8e)$^{40}$

51% yield, white solid, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (dd, $J$ = 10.0, 5.4 Hz, 2H), 7.03 – 6.90 (m, 4H), 6.87 – 6.73 (m, 3H), 5.70 (br, 1H), 3.96 (br, 1H), 3.76 (s, 3H), 1.41 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.05, 147.30, 129.30, 125.46, 123.74, 123.15, 121.90, 121.36, 114.62, 55.45, 51.06, 29.46.

![Diagram](image2.png)

2-butyl-1-(2, 6-dimethylphenyl)-3-phenylguanidine (8f)

68% yield, yellow oil, $^1$H NMR (400 MHz, DMSO) δ 7.48 – 7.10 (m, 4H), 7.00 – 6.66 (m, 4H), 5.01 (br, 1H), 3.13 – 2.98 (m, 2H), 2.08 (s, 6H), 1.43 (dt, $J$ = 14.6, 7.1 Hz, 2H), 1.25 (dq, $J$ = 14.5, 7.2 Hz, 2H), 0.85 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 152.79, 147.29, 146.36, 141.60, 128.98, 128.35, 127.49, 120.49, 119.30, 41.17, 31.80, 19.50, 18.33, 13.69. IR (neat, cm$^{-1}$): 1647, 1588, 1497, 653. HRMS $m/z$ (ES+) calcd for C$_{19}$H$_{26}$N$_3$ ([M+H]$^+$) 296.2121, found 296.2113.

![Diagram](image3.png)

1, 3-dibenzyl-2-phenylguanidine(8g)$^{41}$

65% yield, white solid, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.16 (m, 12H), 7.01 – 6.88 (m, 3H), 4.33 (br, 4H$_{\text{PhCH}_2}$, 2H$_{\text{NH}}$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.00, 149.40, 138.69, 129.32, 128.61, 127.30, 127.11, 123.46, 121.83, 45.87.
1-benzyl-2-(piperidin-1-yl)-1H-benzo[d]imidazole (9)\textsuperscript{42}
72% isolated yield, white solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textdelta 7.65 – 7.61 (m, 1H), 7.33 – 7.24 (m, 3H), 7.20 – 7.14 (m, 3H), 7.05 (td, \textit{J} = 7.7, 0.8 Hz, 1H), 7.00 – 6.95 (m, 1H), 5.19 (s, 2H), 3.23 – 3.16 (m, 4H), 1.70 – 1.56 (m, 6H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \textdelta 159.03, 141.66, 136.44, 135.35, 128.81, 127.44, 126.06, 121.69, 121.10, 117.89, 109.24, 51.86, 47.64, 25.67, 24.12.

References