Electronic Supplementary Information

Arylation of Benzyl Amines with Aromatic Nitriles

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1. General information

Unless stated otherwise, all reactions were carried out under an argon atmosphere. All chemicals obtained from the commercial suppliers, MTBE, DME were used without further purification, the other solvents were purified and dried by standard methods prior to use. Reactions were monitored by thin layer chromatography (TLC). Column chromatography purifications were carried out using silica gel GF254. ¹H NMR (300 MHz), ¹³C NMR (75 MHz or 101 MHz), and ¹⁹F NMR (282 MHz or 376 MHz) spectra were recorded on a Varian instrument spectrometer in CDCl₃ or DMSO, respectively. Data for ¹H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad, q = quartet, coupling constant(s) in Hz integration). Data for ¹³C NMR and ¹⁹F NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources.

2. Optimization of reaction conditions

a) Table S1. Screening of basic additives

<table>
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<th>Entry</th>
<th>Base</th>
<th>yield (%)</th>
<th>Entry</th>
<th>Base</th>
<th>yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>LiO^t^Bu</td>
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<td>8</td>
<td>TMEDA</td>
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<tr>
<td>2</td>
<td>NaO^t^Bu</td>
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<td>KHDMS</td>
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<tr>
<td>7</td>
<td>Et₃N</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Reaction conditions: Unless otherwise noted, reactions were conducted on a 0.2 mmol scale using 2 equiv of 1a, 3 equiv of base, and 1 mL solvent. Yields were determined by ¹H NMR spectroscopy of the reaction mixture using mesitylene as internal standard.*
b) Table S2. Screening of solvents

<table>
<thead>
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<th>Entry</th>
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<th>yield (%)</th>
<th>Entry</th>
<th>Solvent</th>
<th>yield (%)</th>
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</thead>
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<td>acetone</td>
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<td>6</td>
<td>DCE</td>
<td>0</td>
<td>12</td>
<td>EtOAc</td>
<td>0</td>
</tr>
</tbody>
</table>

*Reaction conditions: Unless otherwise noted, reactions were conducted on a 0.2 mmol scale using, 2 equiv of 1a and 1 mL solvent. NaHMDS 2M in THF was used. Yields were determined by ¹H NMR spectroscopy using mesitylene as internal standard.*

3. General procedure for the synthesis of ketimines and aromatic nitriles

Ketimines¹ and aromatic nitriles²,³ were prepared according to the literature procedures.

4. General procedure for the arylation reactions

To an oven-dried 10 mL glass vial with a magnetic stirring bar was added ketimines 1 (0.8 mmol) and 4-cyanopyridine 2 (0.4 mmol), sealed with a rubber septum. Then, the air was withdrawn and backfilled with argon (three times). NaHMDS (0.8 mmol, 2.0 mol/L in THF) and 2 mL of anhydrous DME were added to the reaction by syringes, respectively. The reaction was stirred at room temperature for 12 h, and then, quenched with two drops of H₂O, diluted with 10 mL of ethyl acetate, and filtered over a pad of MgSO₄ and silica. The pad was rinsed with an additional 20 mL of ethyl acetate (2 x 10 mL). The combined solutions were concentrated in vacuo and purified by a silica gel column chromatography (eluted with n-hexane/ethyl acetate 20:1:3:1) to afford the product.

5. Gram scale sequential one-pot ketimine synthesis and arylation procedure

An oven-dried 100 mL round bottom flask equipped with a stir bar was sealed with a rubber septum. The air was withdrawn and backfilled with argon (three times). DCM (10 mL) was added via syringe through the rubber septum. 2-furfurylamine (0.97 g, 10.0 mmol) and benzophenone imine (1.81 g, 10.0 mmol) were added under nitrogen via syringe through the rubber septum. The reaction was stirred at 23 ºC for 18 h. The solvent was completely
removed in vacuo and the flask was filled with argon. A solution of 4-cyanopyridine 2a (0.52 g, 5.0 mmol) in 25 mL anhydrous DME was added to the flask tube via syringe through the rubber septum. Next, NaHMDS (10 mmol, 2.0 mol/L in THF) was added by syringe through the rubber septum. The reaction mixture was stirred for 12 h at room temperature, then, quenched with 10 mL of H2O. The layers were separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were concentrated in vacuo. The crude material was purified by a silica gel column chromatography (eluted with n-hexane/ethyl acetate 20:1-3:1) to give the product (1.03 g, 61% yield) as a thick colorless oil.

6. Imine product hydrolysis

An oven-dried 10ml vial equipped with a stir bar was charged with 3s (40.7 mg 0.1 mmol). THF (1 mL) was added to the reaction vial via syringe and the reaction was cooled to 0 ºC. HCl (1 mL, 1 N) was added to the reaction vial via syringe. The solution was warmed to room temperature and monitored by TLC until 3s was totally consumed (reaction completed in 3 h). The reaction mixture was basified with 1 N NaOH until the pH reached 14. The the mixture was transferred to a 30 ml seperatory funnel and extracted with dichloromethane (3 x 2 mL). The combined organic layers were concentrated in vacuo and purified on a silica gel column chromatography (eluted with hexanes:ethyl acetate = 2:1) to give the amine product 4 as a yellow oil (23.3 mg, 96% yield).

7. References

8. Characterization of products

\[ \text{N-} \text{(diphenylmethylene)} \text{-1-phenyl-1-(pyridin-4-yl)methanamine (3a), 122.7 mg, yield: 88%. White solid, mp 117-119 °C.} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.50 (d, J = 6.0 \text{ Hz}, 2H), 7.75 (d, J = 6.7 \text{ Hz}, 2H), 7.49 - 7.43 (m, 3H), 7.43 - 7.35 (m, 3H), 7.35 - 7.27 (m, 7H), 7.09 - 7.00 (m, 2H), 5.50 (s, 1H).\)

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 168.27, 153.46, 149.79, 143.24, 139.36, 136.29, 130.41, 128.75, 128.72, 128.58, 128.54, 128.08, 127.61, 127.52, 127.26, 122.48, 68.92.\)


\[ \text{N-} \text{(diphenylmethylene)} \text{-1-(4-(tert-butyl)phenyl)-1-(pyridin-4-yl)methanamine (3b), 121.4 mg, yield: 75%. Thick colorless oil.} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.42 (d, J = 5.7 \text{ Hz}, 2H), 7.67 (d, J = 6.7 \text{ Hz}, 2H), 7.42 - 7.32 (m, 4H), 7.32 - 7.22 (m, 5H), 7.20 - 7.12 (m, 3H), 7.03 - 6.91 (m, 2H), 5.41 (s, 1H), 1.21 (s, 9H).\)

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 168.00, 153.81, 150.09, 149.53, 140.09, 139.40, 136.30, 130.35, 128.69, 128.52, 128.06, 127.58, 127.19, 125.48, 122.57, 68.68, 34.44, 31.35.\)

HRMS (ESI): C\(_{29}\)H\(_{28}\)N\(_2\) Calcd: 405.2325, Found: 405.2326.

\[ \text{N-} \text{(diphenylmethylene)} \text{-1-(4-methoxyphenyl)-1-(pyridin-4-yl)methanamine (3c), 116.6 mg, yield: 77%. White solid, mp 91-92 °C.} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.49 (d, J = 6.0 \text{ Hz}, 2H), 7.74 (d, J = 6.7 \text{ Hz}, 2H), 7.50 - 7.42 (m, 3H), 7.42 - 7.30 (m, 4H), 7.25 - 7.14 (m, 3H), 7.11 - 6.98 (m, 2H), 6.83 (d, J = 8.7 \text{ Hz}, 2H), 5.46 (s, 1H), 3.78 (s, 3H).\)

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 167.99, 158.79, 153.82, 149.81, 139.47, 136.41, 135.55, 130.40, 128.77, 128.73, 128.48, 128.12, 127.59, 122.46, 114.00, 68.33, 55.26.\)

N-(diphenylmethylene)-1-(4-phenoxyphenyl)-1-(pyridin-4-yl)methanamine (3d), 98.7 mg, yield: 56%. Thick colorless oil.

1H NMR (300 MHz, CDCl3) δ 8.51 (d, J = 6.0 Hz, 2H), 7.75 (d, J = 6.7 Hz, 2H), 7.51 – 7.36 (m, 6H), 7.36 – 7.27 (m, 5H), 7.15 – 6.85 (m, 8H), 5.48 (s, 1H).

13C NMR (75 MHz, CDCl3) δ 168.27, 156.97, 156.47, 153.54, 152.71, 149.74, 139.33, 138.03, 136.29, 130.47, 129.71, 128.94, 128.76, 128.59, 128.12, 127.51, 123.32, 122.43, 118.98, 118.78, 68.32.


N-(diphenylmethylene)-1-(4-fluorophenyl)-1-(pyridin-4-yl)methanamine (3e), 99.7 mg, yield: 68%. Thick colorless oil.

1H NMR (300 MHz, CDCl3) δ 8.51 (d, J = 4.4 Hz, 2H), 7.75 (d, J = 7.1 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.34 – 7.42 (m, 4H), 7.08 – 6.93 (m, 4H), 5.48 (s, 1H).

13C NMR (101 MHz, CDCl3) δ 168.49, 161.95 (d, J_{CF} = 247.5 Hz) 153.26, 149.86, 139.23, 139.03 (d, J_{CF} = 4.0 Hz) 136.22, 130.53, 129.19, 129.11, 128.81, 128.75, 128.61, 128.13, 127.44, 122.37, 115.44 (d, J_{CF} = 21.2 Hz) 68.13.

19F NMR (376 MHz, CDCl3) δ -115.12.


1-(4-chlorophenyl)-N-(diphenylmethylene)-1-(pyridin-4-yl)methanamine (3f), 108.7 mg, yield: 71%. Thick colorless oil.

1H NMR (300 MHz, CDCl3) δ 8.51 (d, J = 5.8 Hz, 2H), 7.74 (d, J = 7.0 Hz, 2H), 7.48 – 7.33 (m, 6H), 7.29 – 7.22 (m, 6H), 7.07 – 6.96 (m, 2H), 5.47 (s, 1H).

13C NMR (101 MHz, CDCl3) δ 168.73, 152.97, 149.91, 141.76, 139.18, 136.17, 133.09, 130.58, 128.94, 128.85, 128.76, 128.63, 128.15, 127.43, 122.38, 68.21.

N-(diphenylmethylene)-1-(pyridin-4-yl)-1-(m-tolyl)methanamine (3g), 114.5mg, yield: 79%.
Thick colorless oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.41 (d, \(J = 5.9\) Hz, 2H), 7.67 (dd, \(J = 8.1, 1.5\) Hz, 2H), 7.39 – 7.23 (m, 6H), 7.22 – 7.15 (m, 2H), 7.13 – 7.06 (m, 1H), 7.03 – 6.92 (m, 5H), 5.39 (s, 1H), 2.22 (s, 3H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 168.17, 153.65, 149.73, 149.60, 143.11, 139.37, 138.21, 136.28, 130.36, 128.69, 128.49, 128.41, 128.24, 128.04, 127.53, 124.64, 122.48, 68.95, 21.52.

HRMS (ESI): C\(_{26}\)H\(_{22}\)N\(_2\) + H\(^+\) Calcd: 363.1856, Found: 363.1860.

N-(diphenylmethylene)-1-(2-fluorophenyl)-1-(pyridin-4-yl)methanamine (3h), 98.2mg, yield: 67%.
Thick colorless oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.50 (d, \(J = 5.2\) Hz, 2H), 7.72 (dd, \(J = 17.8, 7.1\) Hz, 3H), 7.46 – 7.28 (m, 8H), 7.23 – 7.10 (m, 2H), 6.98 (dd, \(J = 18.1, 8.4\) Hz, 3H), 5.86 (s, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.33, 159.56 (d, \(J_{C\text{-}F} = 247.5\) Hz) 152.61, 149.85, 139.33, 136.16, 130.55, 129.33 (d, \(J_{C\text{-}F} = 4.0\) Hz) 128.81, 128.69, 128.74 (d, \(J_{C\text{-}F} = 9.0\) Hz), 128.13, 127.37, 124.50 (d, \(J_{C\text{-}F} = 4.0\) Hz) 115.34 (d, \(J_{C\text{-}F} = 22.2\) Hz) 61.48.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -118.18.


1-(2-chlorophenyl)-N-(diphenylmethylene)-1-(pyridin-4-yl)methanamine (3i), 107.2mg, yield: 70%.
Thick colorless oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.49 (d, \(J = 5.4\) Hz, 2H), 7.86 (d, \(J = 7.2\) Hz, 1H), 7.75 (d, \(J = 7.4\) Hz, 2H), 7.47 – 7.33 (m, 6H), 7.33 – 7.26 (m, 4H), 7.21 – 7.14 (m, 1H), 7.06 – 6.96 (m, 2H), 6.05 (s, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.35, 152.40, 149.79, 140.94, 139.30, 136.30, 132.46, 130.53, 130.15, 129.41, 128.82, 128.79, 128.60, 128.36, 128.11, 127.42, 127.31, 122.49, 64.48.

**3j**

\[ \text{N-(diphenylmethylene)-1-(pyridin-2-yl)-1-(pyridin-4-yl)methanamine} \]

Thick colorless oil.

\[ ^1H \text{NMR} (300 \text{ MHz, CDCl}_3) \delta 8.46 (d, J = 4.8 \text{ Hz, 1H}), 7.86 - 7.73 (m, 3H), 7.67 (td, J = 7.7, 1.7 \text{ Hz, 1H}), 7.43 - 7.35 (m, 7H), 7.35 - 7.27 (m, 2H), 7.23 - 7.15 (m, 1H), 7.14 - 7.08 (m, 1H), 7.08 - 6.99 (m, 2H), 5.75 (s, 1H). \]

\[ ^{13}C \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 167.99, 163.94, 148.93, 144.02, 139.89, 136.69, 136.41, 130.18, 128.83, 128.47, 128.40, 128.04, 127.78, 127.51, 126.86, 122.09, 121.83, 71.95. \]

HRMS (ESI): C_{23}H_{19}N_{2}O+H^+ Calcd: 339.1492, Found: 339.1500.

**3k**

\[ \text{N-(diphenylmethylene)-1-(furan-2-yl)-1-(pyridin-4-yl)methanamine} \]

White solid, mp 88-89°C.

\[ ^1H \text{NMR} (300 \text{ MHz, CDCl}_3) \delta 8.47 (d, J = 5.9 \text{ Hz, 2H}), 7.65 (d, J = 6.9 \text{ Hz, 2H}), 7.43 - 7.36 (m, 3H), 7.35 - 7.24 (m, 5H), 7.10 - 7.00 (m, 2H), 6.23 (dd, J = 3.1, 1.9 \text{ Hz, 1H}), 6.05 (d, J = 3.2 \text{ Hz, 1H}), 5.52 (s, 1H). \]

\[ ^{13}C \text{NMR} (75 MHz, CDCl}_3) \delta 169.95, 154.82, 150.35, 149.90, 149.78, 142.25, 139.20, 135.93, 130.61, 128.87, 128.62, 128.12, 127.61, 122.69, 110.31, 107.06, 63.35. \]

HRMS (ESI): C_{23}H_{19}N_{2}O+H^+ Calcd: 339.1492, Found: 339.1500.

**3l**

\[ \text{N-(diphenylmethylene)-1-(pyridin-4-yl)-1-(thiophen-2-yl)methanamine} \]

White solid, mp 110-111°C.

\[ ^1H \text{NMR} (300 \text{ MHz, CDCl}_3) \delta 8.45 (d, J = 5.2 \text{ Hz, 2H}), 7.68 (d, J = 6.8 \text{ Hz, 2H}), 7.41 - 7.35 (m, 3H), 7.35 - 7.22 (m, 5H), 7.19 - 7.11 (m, 1H), 7.04 - 6.94 (m, 2H), 6.84 (dd, J = 4.9, 3.6 Hz, 1H), 6.71 (d, J = 3.4 Hz, 1H), 5.68 (s, 1H). \]

\[ ^{13}C \text{NMR} (75 MHz, CDCl}_3) \delta 168.98, 152.97, 149.64, 146.82, 139.04, 135.78, 130.64, 130.03, 128.89, 128.61, 128.13, 127.48, 126.52, 125.09, 123.77, 122.31, 64.85. \]

HRMS (ESI): C_{23}H_{18}N_{2}S+H^+ Calcd: 355.1263, Found: 355.1269.
N-(diphenylmethylene)-1-(2-fluoropyridin-4-yl)-1-phenylmethanamine (3m), 99.7mg, yield: 68%. White solid, mp 106-107°C.

\[
\begin{align*}
\text{NMR (300 MHz, CDCl}_3\text{)} & : \delta 8.09 (d, 1H), 7.75 (d, J = 7.3 Hz, 2H), 7.51 - 7.43 (m, 3H), 7.40 (dd, J = 12.1, 7.4 Hz, 3H), 7.34 - 7.24 (m, 5H), 7.13 (d, J = 4.7 Hz, 1H), 6.96-7.04 (m, 3H), 5.51 (s, 1H).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (75 MHz, CDCl}_3\text{)} & : \delta 168.77, 164.04 (d, J_{C-F} = 236.3 Hz) 159.65, 147.38 (d, J_{C-F} = 15.0 Hz) 142.70, 139.16, 136.12, 128.85, 128.78, 128.72, 128.62, 128.14, 127.58, 127.53, 127.46, 120.24, 107.95 (d, J_{C-F} = 38.3 Hz) 68.66.
\end{align*}
\]

\[
\begin{align*}
\text{F NMR (282 MHz, CDCl}_3\text{)} & : \delta -68.08.
\end{align*}
\]

\[
\begin{align*}
\text{HRMS (ESI)}: C_{25}H_{19}F_N_2^H + \text{Calcd: 367.1605, Found: 367.1612.}
\end{align*}
\]

1-(2-chloropyridin-4-yl)-N-(diphenylmethylene)-1-phenylmethanamine (3n), 107.2mg, yield: 70%. White solid, mp 117-118°C.

\[
\begin{align*}
\text{NMR (300 MHz, CDCl}_3\text{)} & : \delta 8.26 (d, J = 5.1 Hz, 1H), 7.75 (d, J = 6.9 Hz, 2H), 7.50 - 7.44 (m, 3H), 7.42 - 7.32 (m, 4H), 7.32 - 7.24 (m, 5H), 7.19 (d, J = 4.7 Hz, 1H), 7.07 - 6.99 (m, 2H), 5.48 (s, 1H).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (75 MHz, CDCl}_3\text{)} & : \delta 168.79, 156.94, 151.56, 149.61, 149.46, 142.58, 139.06, 136.01, 130.60, 128.74, 128.62, 128.13, 127.54, 127.40, 122.80, 122.74, 121.32, 68.56.
\end{align*}
\]

\[
\begin{align*}
\text{HRMS (ESI)}: C_{25}H_{19}ClN_2^H + \text{Calcd: 383.1310, Found: 383.1316.}
\end{align*}
\]

N-(diphenylmethylene)-1-phenyl-1-(2-phenylpyridin-4-yl)methanamine (3o), 134.2mg, yield: 79%. Thick colorless oil.

\[
\begin{align*}
\text{NMR (300 MHz, CDCl}_3\text{)} & : \delta 8.50 (d, J = 5.1 Hz, 1H), 7.84 (d, J = 6.9 Hz, 2H), 7.68 (dd, J = 7.9, 1.4 Hz, 2H), 7.61 (s, 1H), 7.40 - 7.33 (m, 4H), 7.33 - 7.21 (m, 8H), 7.19 - 7.10 (m, 3H), 7.03 - 6.93 (m, 2H), 5.49 (s, 1H).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (75 MHz, CDCl}_3\text{)} & : \delta 168.29, 157.50, 154.28, 149.73, 149.62, 143.29, 139.52, 139.36, 136.32, 130.40, 128.77, 128.60, 128.09, 127.56, 127.26, 127.01, 126.92, 121.11, 119.43, 119.34, 69.21.
\end{align*}
\]

\[
\begin{align*}
\text{HRMS (ESI)}: C_{31}H_{25}N_2^H + \text{Calcd: 425.2012, Found: 425.2027.}
\end{align*}
\]
N-(diphenylmethylene)-1-phenyl-1-(2-(4-(trifluoromethyl)phenyl)pyridin-4-yl)methanamine (3p), 159.6 mg, yield: 81%. Thick colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.53 (d, $J = 5.1$ Hz, 1H), 7.97 (d, $J = 8.1$ Hz, 2H), 7.71 – 7.59 (m, 5H), 7.43 – 7.36 (m, 3H), 7.36 – 7.26 (m, 4H), 7.25 – 7.13 (m, 5H), 7.03 – 6.94 (m, 2H), 5.51 (s, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 168.62, 156.03, 154.75, 149.99, 143.23, 142.91, 139.39, 136.38, 130.57 (q, $J_{C-F} = 32.3$ Hz), 130.57, 128.87, 128.84, 128.74, 128.66, 128.21, 127.64, 127.61, 127.45, 127.33, 126.62 (q, $J_{C-F} = 32.3$ Hz) 122.01, 119.76, 69.16.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -62.50.

HRMS (ESI): C$_{32}$H$_{23}$F$_3$N$_2$+H+ Calcd: 493.1886, Found: 493.1902.

N-(diphenylmethylene)-1-(2-(4-methoxyphenyl)pyridin-4-yl)-1-phenylethanamine (3q), 138.2 mg, yield: 76%. Thick colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.46 (d, $J = 5.0$ Hz, 1H), 7.81 (d, $J = 8.8$ Hz, 2H), 7.68 (d, $J = 6.6$ Hz, 2H), 7.55 (s, 1H), 7.40 – 7.33 (m, 3H), 7.31 – 7.18 (m, 7H), 7.16 – 7.09 (m, 2H), 7.03 – 6.95 (m, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.47 (s, 1H), 3.74 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 168.25, 156.03, 154.75, 149.99, 143.23, 142.91, 139.39, 136.38, 132.14, 130.39, 128.78, 128.73, 128.59, 128.55, 128.23, 128.10, 127.60, 127.24, 120.49, 118.63, 113.99, 69.21, 55.31.

HRMS (ESI): C$_{32}$H$_{26}$N$_2$O+H+ Calcd: 455.2118, Found: 455.2134.

4-(((diphenylmethylene)amino)(phenyl)methyl)benzonitrile (3r), 98.3 mg, yield: 66%. Thick colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 6.9$ Hz, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.49 – 7.44 (m, 5H), 7.39 – 7.35 (m, 2H), 7.34 – 7.27 (m, 5H), 7.08 – 6.99 (m, 2H), 5.57 (s, 1H).
13C NMR (75 MHz, CDCl3) δ 168.14, 150.20, 143.56, 139.32, 136.29, 132.22, 130.45, 128.75, 128.61, 128.56, 128.45, 128.19, 128.10, 127.49, 127.48, 127.23, 119.01, 110.44, 69.45. HRMS (ESI): C27H20N2+H+ Calcd: 373.1699, Found: 373.1696.

**3s**

4-((2-chlorophenyl)((diphenylmethylene)amino)methyl)benzonitrile (3s), 114.0mg, yield: 70%. Thick colorless oil.

1H NMR (300 MHz, CDCl3) δ 7.80 (dd, J = 8.0, 1.4 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.52 – 7.45 (m, 2H), 7.43 – 7.37 (m, 4H), 7.36 – 7.24 (m, 4H), 7.23 – 7.17 (m, 2H), 7.15 – 7.06 (m, 1H), 6.97 – 6.87 (m, 2H), 6.01 (s, 1H).


**3t**

1-(benzo[d]oxazol-2-yl)-1-(2-chlorophenyl)-N-(diphenylmethylene)methanamine (3t), 90.1mg, yield: 58%. Thick colorless oil.

1H NMR (300 MHz, CDCl3) δ 7.96 (dd, J = 7.8, 1.4 Hz, 1H), 7.71 – 7.60 (m, 3H), 7.43 – 7.36 (m, 4H), 7.35 – 7.28 (m, 3H), 7.27 – 7.19 (m, 5H), 7.13 – 7.04 (m, 2H), 6.31 (s, 1H).

13C NMR (75 MHz, CDCl3) δ 171.75, 165.29, 150.93, 141.20, 139.17, 137.39, 135.88, 132.95, 130.76, 130.53, 129.40, 129.17, 129.05, 129.02, 128.72, 128.10, 127.64, 127.25, 124.86, 124.14, 120.39, 110.74, 61.23. HRMS (ESI): C27H20ClN2O+H+ Calcd: 423.1259, Found: 423.1258.

**3u**

4-(((diphenylmethylene)amino)(4-methoxyphenyl)methyl)-2-fluorobenzonitrile (3u), 58.9 mg, yield: 35%. Thick colorless oil.
\[1^H \text{NMR} \ (300 \text{ MHz, CDCl}_3) \ \delta \ 7.74 \ (dd, J = 8.1, 1.5 \text{ Hz, 2H}), \ 7.46 \ (dd, J = 5.6, 2.4 \text{ Hz, 4H}), \ 7.42 - 7.28 \ (m, 5H), \ 7.26 - 7.21 \ (m, 2H), \ 7.11 - 6.90 \ (m, 9H), \ 5.52 \ (s, 1H), \ 3.88 \ (s, 3H).\]

\[1^C \text{NMR} \ (75 \text{ MHz, CDCl}_3) \ \delta \ 168.33, \ 163.25 \ (d, J_{C-F} = 256.9 \text{ Hz}), \ 158.88, \ 153.95 \ (d, J_{C-F} = 7.3 \text{ Hz}), \ 139.19, \ 136.18, \ 135.24, \ 133.24, \ 130.58, \ 128.84, \ 128.76, \ 128.63, \ 128.56, \ 128.16, \ 127.46, \ 115.23, \ 114.24, \ 114.11, \ 99.28 \ (d, J_{C-F} = 15.65 \text{ Hz}), \ 68.49, \ 55.26.\]

\[1^F \text{NMR} \ (282 \text{ MHz, CDCl}_3) \ -106.24\]

HRMS (ESI): \(C_{28}H_{21}F_2N_2O^+\) Calcd: 443.1530, Found: 443.1513.

4-(((diphenylmethylene)amino)(4-phenoxyphenyl)methyl)-2-methoxybenzonitrile (3v), 134.5mg, yield: 68%. Thick colorless oil.

\[1^H \text{NMR} \ (300 \text{ MHz, CDCl}_3) \ \delta \ 7.53 \ (d, J = 8.4 \text{ Hz, 2H}), \ 7.46 \ (dd, J = 5.6, 2.4 \text{ Hz, 4H}), \ 7.42 - 7.28 \ (m, 5H), \ 7.26 - 7.21 \ (m, 2H), \ 7.11 - 6.90 \ (m, 9H), \ 5.52 \ (s, 1H), \ 3.88 \ (s, 3H).\]

\[1^C \text{NMR} \ (75 \text{ MHz, CDCl}_3) \ \delta \ 168.18, \ 161.42, \ 156.99, \ 156.44, \ 152.24, \ 139.37, \ 138.36, \ 136.33, \ 133.69, \ 130.54, \ 130.09, \ 129.77, \ 128.85, \ 128.76, \ 08, \ 55.98.\]

HRMS (ESI): \(C_{34}H_{26}N_2O_2^+\) Calcd: 495.2067, Found: 495.2049.

4-(amino(2-chlorophenyl)methyl)benzonitrile (4), 23.3mg, yield: 96%. Thick colorless oil.

\[1^H \text{NMR} \ (300 \text{ MHz, CDCl}_3) \ \delta \ 7.53 \ (d, J = 8.4 \text{ Hz, 2H}), \ 7.46 \ (d, J = 8.2 \text{ Hz, 2H}), \ 7.39 \ (dd, J = 7.6, 1.8 \text{ Hz, 1H}), \ 7.29 \ (dd, J = 7.6, 1.6 \text{ Hz, 1H}), \ 7.22 \ (dd, J = 7.4, 1.6 \text{ Hz, 1H}), \ 7.19 - 7.11 \ (m, 1H), \ 5.61 \ (s, 1H), \ 1.93 \ (s, 2H).\]

\[1^C \text{NMR} \ (75 \text{ MHz, DMSO}) \ \delta \ 149.36, \ 141.25, \ 132.29, \ 131.88, \ 129.39, \ 128.92, \ 128.63, \ 128.29, \ 127.57, \ 118.82, \ 109.70, \ 55.19.\]

HRMS (ESI): \(C_{14}H_{11}ClN_2H^+\) Calcd: 243.0684, Found: 243.0682.
9. NMR spectra of new compounds
$^{3}C$ NMR (75 MHz, CDCl$_3$)

$^{1}H$ NMR (300 MHz, CDCl$_3$)
$^{13}C$ NMR (101 MHz, CDCl₃)

$^{19}F$ NMR (376 MHz, CDCl₃)
$^{13}$C NMR (75 MHz, CDCl$_3$)

$^{19}$F NMR (376 MHz, CDCl$_3$)
$^4\text{C} \text{NMR (75 MHz, DMSO)}$