Selective photochemical synthesis of primary arylamines and symmetric diarylamines via amination of aryl bromides using Ni(NH$_3$)$_6$Cl$_2$ as a nitrogen source and catalyst

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1. General information

Unless otherwise specified, the chemicals were obtained commercially and used
without further purification. All reactions were carried out under argon atmosphere with
dry solvents under anhydrous conditions. Analytical thin-layer chromatography (TLC)
was conducted with TLC plates (Silica gel 60 F254, Qingdao Haiyang) and
visualization on TLC was achieved by UV light and the use of ninhydrin and iodine
color developer to assist. Flash column chromatography was performed on silica gel
200-300 mesh.

$^1$H NMR spectra, $^{13}$C{$^1$H} NMR spectra and $^{19}$F NMR spectra were recorded on a
Bruker Advance 400 MHz spectrometer. $^1$H NMR spectra was reported in units of parts
per million (ppm) relative to tetramethylsilane ($\delta$ 0 ppm), CDCl$_3$ ($\delta$ 7.26 ppm) or
DMSO-d$_6$ ($\delta$ 2.50 ppm). Multiplicities are given as: br (broad), s (singlet), d (doublet),
t (triplet), q (quartet), dd (doublets of doublet), dt (doublets of triplet) or m (multiplet).
$^{13}$C{$^1$H} NMR spectra was reported in ppm relative to tetramethylsilane ($\delta$ 0 ppm),
CDCl$_3$ ($\delta$ 77.16 ppm) or DMSO-d$_6$ ($\delta$ 39.52 ppm). HRMS (ESI) were performed on
fourier transform ion cyclotron resonance mass spectrometer.

The purple LED lamp used in the experiments was assembled by ourselves (Figure
S1). Each of lamp include: 9 W purple LED (390-395 nm, 3 LED lamp beads in series),
aluminium radiator with fan, electric driver (XC-8W600-OS). The optical power up to
200 ± 10 mw at 1 cm axis distance detected by Thorlabs’ Optical Power Meter
(PM100D, S120VC). The LED beads were purchased from Zhuhai UV Optoelectronics
Co., Ltd. (THUV395T3WL-3535-60).

Figure S1. Pictures of photo device and reaction tube
2. Optimization of reaction conditions

2.1 The reaction conditions for preparation of primary arylamines

Table S1. The screening of solvents

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent (2.0 mL)</th>
<th>diarylamine</th>
<th>arylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO</td>
<td>13%</td>
<td>59%</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>16%</td>
<td>51%</td>
</tr>
<tr>
<td>3</td>
<td>DMAc</td>
<td>13%</td>
<td>42%</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>N.D.</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>1,4-Dioxane</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>6</td>
<td>CH$_3$CN</td>
<td>N.D.</td>
<td>7%</td>
</tr>
<tr>
<td>7</td>
<td>2-MeTHF</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>8</td>
<td>DMSO:THF=5:1</td>
<td>5%</td>
<td>35%</td>
</tr>
<tr>
<td>9</td>
<td>DMSO:THF=9:1</td>
<td>5%</td>
<td>16%</td>
</tr>
</tbody>
</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), d-Me bpy (5 mol%), DBU (1.5 equiv), solvent (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by $^1$H NMR using 1,3-benzodioxole as an internal standard.

Table S2. The screening of bases

<table>
<thead>
<tr>
<th>entry</th>
<th>base (1.5 equiv)</th>
<th>diarylamine</th>
<th>arylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DBU</td>
<td>13%</td>
<td>59%</td>
</tr>
<tr>
<td>2</td>
<td>DBN</td>
<td>7%</td>
<td>31%</td>
</tr>
<tr>
<td>3</td>
<td>TBD</td>
<td>23%</td>
<td>40%</td>
</tr>
<tr>
<td>4</td>
<td>MTBD</td>
<td>trace</td>
<td>98%</td>
</tr>
<tr>
<td>5</td>
<td>DMTHPM</td>
<td>18%</td>
<td>61%</td>
</tr>
<tr>
<td>6</td>
<td>DABCO</td>
<td>5%</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>TMG</td>
<td>6%</td>
<td>41%</td>
</tr>
<tr>
<td>8</td>
<td>t-BuTMG</td>
<td>trace</td>
<td>86%</td>
</tr>
<tr>
<td>9</td>
<td>DIPEA</td>
<td>trace</td>
<td>N.D.</td>
</tr>
<tr>
<td>10</td>
<td>Et$_3$N</td>
<td>5%</td>
<td>trace</td>
</tr>
</tbody>
</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), d-Me bpy (5 mol%), base (1.5 equiv), DMSO (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by $^1$H NMR using 1,3-benzodioxole as an internal standard.
Table S3. The screening of ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>76%</td>
</tr>
<tr>
<td>b</td>
<td>83%</td>
</tr>
<tr>
<td>c</td>
<td>81%</td>
</tr>
<tr>
<td>d</td>
<td>N.D.</td>
</tr>
<tr>
<td>e</td>
<td>61%</td>
</tr>
<tr>
<td>f</td>
<td>80%</td>
</tr>
<tr>
<td>g</td>
<td>4%</td>
</tr>
<tr>
<td>h</td>
<td>39%</td>
</tr>
<tr>
<td>i</td>
<td>51%</td>
</tr>
<tr>
<td>j</td>
<td>53%</td>
</tr>
<tr>
<td>k</td>
<td>34%</td>
</tr>
</tbody>
</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), ligand (5 mol%), t-BuTMG (1.5 equiv), DMSO (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. The yields of arylamines were determined by $^1$H NMR using 1,3-benzodioxole as an internal standard.

Table S4. The screening of the amount of DMSO

<table>
<thead>
<tr>
<th>Entry</th>
<th>DMSO (x mL)</th>
<th>Diarylamine</th>
<th>Arylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0 mL</td>
<td>5%</td>
<td>70%</td>
</tr>
<tr>
<td>2</td>
<td>1.5 mL</td>
<td>trace</td>
<td>77%</td>
</tr>
<tr>
<td>3</td>
<td>2.0 mL</td>
<td>trace</td>
<td>80%</td>
</tr>
<tr>
<td>4</td>
<td>2.5 mL</td>
<td>trace</td>
<td>76%</td>
</tr>
<tr>
<td>5</td>
<td>3.0 mL</td>
<td>trace</td>
<td>65%</td>
</tr>
</tbody>
</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), d-Meppy (5 mol%), t-BuTMG (1.5 equiv), DMSO (x mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by $^1$H NMR using 1,3-benzodioxole as an internal standard.
Table S5. The screening of Ni(NH$_3$)$_6$X$_2$ (x mol%) for diarylation

<table>
<thead>
<tr>
<th>entry</th>
<th>[Ni]-NH$_3$ (x mol%)</th>
<th>diaryamine</th>
<th>arylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(NH$_3$)$_6$Br$_2$ (35 mol%)</td>
<td>5%</td>
<td>62%</td>
</tr>
<tr>
<td>2</td>
<td>Ni(NH$_3$)$_6$I$_2$ (35 mol%)</td>
<td>trace</td>
<td>40%</td>
</tr>
<tr>
<td>3</td>
<td>Ni(NH$_3$)$_6$Cl$_2$ (17 mol%)</td>
<td>trace</td>
<td>75%</td>
</tr>
<tr>
<td>4</td>
<td>Ni(NH$_3$)$_6$Cl$_2$ (20 mol%)</td>
<td>trace</td>
<td>74%</td>
</tr>
<tr>
<td>5</td>
<td>Ni(NH$_3$)$_6$Cl$_2$ (25 mol%)</td>
<td>trace</td>
<td>79%</td>
</tr>
<tr>
<td>6</td>
<td>Ni(NH$_3$)$_6$Cl$_2$ (30 mol%)</td>
<td>trace</td>
<td>79%</td>
</tr>
<tr>
<td>7</td>
<td>Ni(NH$_3$)$_6$Cl$_2$ (35 mol%)</td>
<td>trace</td>
<td>83%</td>
</tr>
<tr>
<td>8</td>
<td>Ni(NH$_3$)$_6$Cl$_2$ (40 mol%)</td>
<td>trace</td>
<td>80%</td>
</tr>
</tbody>
</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$X$_2$ (x mol%), d-MeCy (5 mol%), t-BuTMG (1.5 equiv), DMSO (x mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by $^1$H NMR using 1,3-benzodioxole as an internal standard.

Table S6. Control experiments

<table>
<thead>
<tr>
<th>entry</th>
<th>reaction conditions</th>
<th>diaryamine</th>
<th>arylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standard conditions</td>
<td>trace</td>
<td>98%</td>
</tr>
<tr>
<td>2</td>
<td>No Ni(NH$_3$)$_6$Cl$_2$</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>3</td>
<td>No ligand</td>
<td>N.D.</td>
<td>11%</td>
</tr>
<tr>
<td>4</td>
<td>No base</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>5</td>
<td>No light, 70 °C</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>6</td>
<td>Air instead of Ar</td>
<td>N.D.</td>
<td>31%</td>
</tr>
</tbody>
</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), d-MeCy (5 mol%), MTBD (1.5 equiv), DMSO (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by $^1$H NMR using 1,3-benzodioxole as an internal standard.
2.2 The reaction conditions for preparation of symmetric diarylamines

Table S7. The screening of photosensitizers

<table>
<thead>
<tr>
<th>entry</th>
<th>PS (2.0 mol%)</th>
<th>diaryamine</th>
<th>arylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>—</td>
<td>10%</td>
<td>48%</td>
</tr>
<tr>
<td>2</td>
<td>BP (5.0 mol%)</td>
<td>23%</td>
<td>49%</td>
</tr>
<tr>
<td>3</td>
<td>[Ir(dtbbpy)(ppy)$_2$][PF$_6$] (2.0 mol%)</td>
<td>45%</td>
<td>45%</td>
</tr>
<tr>
<td>4</td>
<td>[Ir(dF(CF$_3$)$_2$ppy)$_2$(dtbbpy)][PF$_6$] (2.0 mol%)</td>
<td>22%</td>
<td>8%</td>
</tr>
<tr>
<td>5</td>
<td>Ru(2,2'-bpy)$_2$Cl$_2$·6H$_2$O (2.0 mol%)</td>
<td>10%</td>
<td>36%</td>
</tr>
</tbody>
</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), d-Mebpy (5 mol%), PS (2.0 mol% / 5.0 mol%), DBU (1.5 equiv), DMSO:THF=1:1 (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S8. The screening of bases

<table>
<thead>
<tr>
<th>entry</th>
<th>base (1.5 equiv)</th>
<th>diaryamine</th>
<th>arylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DBU</td>
<td>46%</td>
<td>45%</td>
</tr>
<tr>
<td>2</td>
<td>DBN</td>
<td>42%</td>
<td>24%</td>
</tr>
<tr>
<td>3</td>
<td>TBD</td>
<td>trace</td>
<td>14%</td>
</tr>
<tr>
<td>4</td>
<td>MTBD</td>
<td>5%</td>
<td>6%</td>
</tr>
<tr>
<td>5</td>
<td>DMTHPM</td>
<td>31%</td>
<td>46%</td>
</tr>
<tr>
<td>6</td>
<td>DABCO</td>
<td>trace</td>
<td>6%</td>
</tr>
<tr>
<td>7</td>
<td>TMG</td>
<td>29%</td>
<td>30%</td>
</tr>
<tr>
<td>8</td>
<td>t-BuTMG</td>
<td>38%</td>
<td>58%</td>
</tr>
<tr>
<td>9</td>
<td>DIPEA</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>DIPA</td>
<td>31%</td>
<td>12%</td>
</tr>
<tr>
<td>11</td>
<td>Et$_3$N</td>
<td>trace</td>
<td>7%</td>
</tr>
</tbody>
</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), d-Mebpy (5 mol%), [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (2.0 mol%), base (1.5 equiv), DMSO:THF=1:1 (2.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard.
Table S9. The screening of solvents, light sources and additives

![Reaction conditions diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent (2.0 mL)</th>
<th>light source</th>
<th>additive (1.0 equiv)</th>
<th>diarylamine</th>
<th>aryamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO:THF=1:1</td>
<td>390-395 nm</td>
<td>—</td>
<td>45%</td>
<td>45%</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>390-395 nm</td>
<td>—</td>
<td>20%</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>1,4-Dioxane</td>
<td>390-395 nm</td>
<td>—</td>
<td>23%</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>CH$_3$CN</td>
<td>390-395 nm</td>
<td>—</td>
<td>21%</td>
<td>60%</td>
</tr>
<tr>
<td>5</td>
<td>2-MeTHF</td>
<td>390-395 nm</td>
<td>—</td>
<td>17%</td>
<td>8%</td>
</tr>
<tr>
<td>6</td>
<td>Toluene</td>
<td>390-395 nm</td>
<td>—</td>
<td>15%</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>390-395 nm</td>
<td>—</td>
<td>46%</td>
<td>46%</td>
</tr>
<tr>
<td>8</td>
<td>DMAc</td>
<td>390-395 nm</td>
<td>—</td>
<td>45%</td>
<td>18%</td>
</tr>
<tr>
<td>9</td>
<td>DMF</td>
<td>390-395 nm</td>
<td>—</td>
<td>50%</td>
<td>17%</td>
</tr>
<tr>
<td>10</td>
<td>DMF</td>
<td>365-370 nm</td>
<td>—</td>
<td>21%</td>
<td>35%</td>
</tr>
<tr>
<td>11</td>
<td>DMF</td>
<td>460-465 nm</td>
<td>—</td>
<td>35%</td>
<td>45%</td>
</tr>
<tr>
<td>12</td>
<td>DMF</td>
<td>490-495 nm</td>
<td>—</td>
<td>32%</td>
<td>57%</td>
</tr>
<tr>
<td>13</td>
<td>DMF</td>
<td>520-530 nm</td>
<td>—</td>
<td>26%</td>
<td>54%</td>
</tr>
<tr>
<td>14</td>
<td>DMF</td>
<td>390-395 nm</td>
<td>TBAC</td>
<td>32%</td>
<td>29%</td>
</tr>
<tr>
<td>15</td>
<td>DMF</td>
<td>390-395 nm</td>
<td>TBAB</td>
<td>39%</td>
<td>18%</td>
</tr>
<tr>
<td>16</td>
<td>DMF</td>
<td>390-395 nm</td>
<td>TBAI</td>
<td>9%</td>
<td>63%</td>
</tr>
<tr>
<td>17</td>
<td>DMF</td>
<td>390-395 nm</td>
<td>NaCl</td>
<td>44%</td>
<td>24%</td>
</tr>
<tr>
<td>18</td>
<td>DMF</td>
<td>390-395 nm</td>
<td>NaBr</td>
<td>38%</td>
<td>27%</td>
</tr>
<tr>
<td>19</td>
<td>DMF</td>
<td>390-395 nm</td>
<td>KBr</td>
<td>45%</td>
<td>27%</td>
</tr>
<tr>
<td>20</td>
<td>DMF</td>
<td>390-395 nm</td>
<td>KI</td>
<td>8%</td>
<td>74%</td>
</tr>
</tbody>
</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), d-Me bpy (5 mol%), [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (2.0 mol%), DBU (1.5 equiv), additive (1.0 equiv), solvent (2.0 mL), light source, 65-70 °C, Ar, 24 h. Yields determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard.
Table S10. The screening of the amount of DBU, DMSO and [Ir(dtbbpy)(ppy)2][PF6]

<table>
<thead>
<tr>
<th>entry</th>
<th>DBU (y equiv)</th>
<th>DMSO (z mL)</th>
<th>[Ir] (x mol%)</th>
<th>diarylamine</th>
<th>arylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>2.0 mL</td>
<td>2.0 mol%</td>
<td>32%</td>
<td>11%</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>2.0 mL</td>
<td>2.0 mol%</td>
<td>61%</td>
<td>21%</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>2.0 mL</td>
<td>2.0 mol%</td>
<td>47%</td>
<td>38%</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>2.0 mL</td>
<td>2.0 mol%</td>
<td>48%</td>
<td>39%</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>2.0 mL</td>
<td>2.0 mol%</td>
<td>42%</td>
<td>46%</td>
</tr>
<tr>
<td>6</td>
<td>3.0</td>
<td>2.0 mL</td>
<td>2.0 mol%</td>
<td>39%</td>
<td>48%</td>
</tr>
<tr>
<td>7</td>
<td>3.5</td>
<td>2.0 mL</td>
<td>2.0 mol%</td>
<td>36%</td>
<td>51%</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>1.0 mL</td>
<td>2.0 mol%</td>
<td>63%</td>
<td>11%</td>
</tr>
<tr>
<td>9</td>
<td>1.0</td>
<td>1.5 mL</td>
<td>2.0 mol%</td>
<td>59%</td>
<td>17%</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>2.5 mL</td>
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<td>1.5 mol%</td>
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<td>4.0 mol%</td>
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Reaction conditions: aryl bromide (0.2 mmol), Ni(NH3)6Cl2 (35 mol%), d-Meppy (5 mol%), [Ir(dtbbpy)(ppy)2][PF6] (x mol%), DBU (y equiv), DMSO (z mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S11. The screening of Ni(NH3)6X2

<table>
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<tr>
<th>entry</th>
<th>[Ni]-NH3 (35 mol%)</th>
<th>diarylamine</th>
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<tr>
<td>1</td>
<td>Ni(NH3)6Cl2</td>
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<tr>
<td>2</td>
<td>Ni(NH3)6Br2</td>
<td>61%</td>
<td>8%</td>
</tr>
<tr>
<td>3</td>
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<td>8%</td>
<td>79%</td>
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Reaction conditions: aryl bromide (0.2 mmol), Ni(NH3)6X2 (35 mol%), d-Meppy (5 mol%), [Ir(dtbbpy)(ppy)2][PF6] (3.5 mol%), DBU (1.0 equiv), DMSO (1.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard.
Table S12. The screening of ligands

Ni(NH$_3$)$_6$Cl$_2$ (35 mol%) & ligand (5 mol%) & [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (3.5 mol%)

DBU (1.0 equiv) & DMSO (1.0 mL) & 390-395 nm, 65-70 °C, 24 h

<table>
<thead>
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<th>Ligand</th>
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<td>72%</td>
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<td></td>
<td>50%</td>
<td>66%</td>
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Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), ligand (5 mol%), [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (3.5 mol%), DBU (1.0 equiv), DMSO (1.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. The yields of diarylamines were determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S13. Control experiments

Ni(NH$_3$)$_6$Cl$_2$ (35 mol%) & d-MeBpy (5 mol%) & [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (3.5 mol%)

DBU (1.0 equiv) & DMSO (1.0 mL) & 390-395 nm, 65-70 °C, 24 h

<table>
<thead>
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<th>Entry</th>
<th>Reaction conditions</th>
<th>Diarylamine</th>
<th>Arylamine</th>
</tr>
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<td>Standard conditions</td>
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<td>No dMeBpy</td>
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<tr>
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<td>trace</td>
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<tr>
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<tr>
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<td>Air instead of Ar</td>
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<td>33%</td>
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<tr>
<td>8</td>
<td>390-395 nm, R.T.</td>
<td>19%</td>
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</table>

Reaction conditions: aryl bromide (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), d-MeBpy (5 mol%), [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (3.5 mol%), DBU (1.0 equiv), DMSO (1.0 mL), purple LEDs (390-395 nm), 65-70 °C, Ar, 24 h. Yields determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard.
3. General procedure for reactions

3.1 Synthesis of [(NH₃)₆Ni]X₂[2]

\[
\text{NiX}_2 + \text{NH}_4\text{X}, \text{excessive NH}_3\text{H}_2\text{O} \xrightarrow{\text{ice bath}} [(\text{NH}_3)_{6}\text{Ni}]\text{X}_2
\]

In an ice bath, a magnetic stir bar, NiX₂, NH₄X and excessive ammonia water, were placed into an oven-dried 25 mL dried round-bottomed flask. The reaction mixture for 2-12 h when the reaction is completed. The resulting purplish solution was rinsed with ammonia water and ethanol. The precipitate was filtered collected on a frit, rinsed with ethanol and residual solvent was removed under vacuum to give the compound. The compound was used without further purification.

3.2 Standard procedure for exploration of the scope of arylamines

\[
\begin{align*}
\text{Ni(NH}_3)_6\text{Cl}_2 (35 \text{ mol}) & \quad \text{d-Mebpy (5 mol\%)} \\
& \quad \text{t-BuTMG (1.5 equiv)} \\
& \quad \text{DMSO (2.0 mL)} \\
\text{R} & \quad \text{Br} & \quad \text{R} & \quad \text{NH}_2
\end{align*}
\]

To an oven-dried 10 mL of storage tube were added solid aryl bromides (0.2 mmol) (liquid aryl bromides were added via syringe after purged and evacuated), Ni(NH₃)₆Cl₂ (35 mol%), d-Mebpy (4,4’-dimethyl-2,2’-bipyridine) (5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then t-BuTMG (1.5 equiv) or MTBD (1.5 equiv) and DMSO (2.0 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with 9 W purple LEDs (390-395 nm, 1 cm away from the tube, optical power: 200 ± 10 mw/cm²) at 65-70 °C for 24 hours. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine or saturated NH₄Cl (3×10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.

3.3 Standard procedure for exploration of the scope of symmetric diarylamines

\[
\begin{align*}
\text{Ni(NH}_3)_6\text{Cl}_2 (35 \text{ mol}) & \quad \text{d-Mebpy (5 mol\%)} \\
& \quad \text{[Ir(dibppy)(ppy)]PF}_6 (3.5 \text{ mol\%}) \\
& \quad \text{DBU (1.0 equiv)} \\
& \quad \text{DMSO (1.0 mL)} \\
\text{R} & \quad \text{Br} & \quad \text{R} & \quad \text{R}
\end{align*}
\]

S10
To an oven-dried 10 mL of storage tube were added solid aryl bromides (0.2 mmol) (liquid aryl bromides were added via syringe after purged and evacuated), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), $d$-Mebpy (4,4'-dimethyl-2,2'-bipyridine) (5 mol%), [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (3.5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then DBU (1.0 equiv) and DMSO (1.0 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with 9 W purple LEDs (390-395 nm, 1 cm away from the tube, optical power: 200 ± 10 mw/cm$^2$) at 65-70 °C for 24 hours. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine or saturated NH$_4$Cl (3×10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.

3.5 Preparation of antioxidant at gram scale

To an oven-dried 200 mL of storage tube were added solid aryl bromides (0.2 mmol), Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), $d$-Mebpy (4,4'-dimethyl-2,2'-bipyridine) (5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then ethyl 4-bromobenzoate (10 mmol), $t$-BuTMG (1.5 equiv) and DMSO (100 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with purple LEDs (390-395 nm, 1 cm away from the tube) at 65-70 °C for 24 hours. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine or saturated NH$_4$Cl, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.
To an oven-dried 100 mL of storage tube were added Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), $d$-Mebpy (4,4'-dimethyl-2,2'-bipyridine) (5 mol%), [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (3.5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then 1-bromo-4-octylbenzene (5 mmol), DBU (1.0 equiv) and DMSO (25 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with purple LEDs (390-395 nm, 1 cm away from the tube) at 65-70 °C for 48 hours. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine or saturated NH$_4$Cl, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.

### 3.6 Preparation of bis(4-methoxyphenyl)amine

To an oven-dried 10 mL of storage tube were added Ni(NH$_3$)$_6$Cl$_2$ (35 mol%), $d$-Mebpy (4,4'-dimethyl-2,2'-bipyridine) (5 mol%), [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (3.5 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then 4-bromoanisole (2 mmol), DBU (1.0 equiv) and DMSO (4 mL) were added. The tube was sealed with a Teflon screw valve. The reaction mixture was then irradiated with purple LEDs (390-395 nm, 1 cm away from the tube) at 65-70 °C for 24 hours. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine or saturated NH$_4$Cl, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.
3.7 Preparation of organic hole-transporting material Spiro-OMeTAD

According to literature, Spiro-OMeTAD was synthesized.\textsuperscript{[22]} To an oven-dried 10 mL of storage tube were added 2,2',7,7'-tetraiodo-9,9'-spirobi[9H-fluorene] (0.2 mmol), 4,4'-dimethoxydiphenylamine (0.9 mmol), sodium tert-butoxide (6.0 equiv), tris(dibenzylideneacetone)dipalladium(0) (5 mol%), tri-tert-butylphosphine (10 mol%) and a magnetic stir bar under argon atmosphere. The mixture was evacuated and backfilled with argon for at least three times. Then toluene (2 mL) was added. The tube was sealed with a Teflon screw valve. The reaction mixture was heated at 110 °C for 16 h. After the reaction was completed, the mixture was diluted with ethyl acetate after cooling to room temperature. The organic phases were washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel to give the desired product.

4. Analytical data of products

\textbf{Aniline (4):} light yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.19 (t, J = 7.6 Hz, 2H), 6.79 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 8.0 Hz, 2H), 3.61 (br, 2H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}) δ 146.5, 129.4, 118.6, 115.2. Spectral datas obtained for the compound are in good agreement with the reported datas.\textsuperscript{[1]}

\textbf{4-(Methylsulfonyl)aniline (5):} yellow solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.67 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 4.24 (br, 2H), 2.99 (s, 3H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}) δ 151.5, 129.6, 128.9, 114.2, 45.1. Spectral datas obtained for the compound are in good agreement with the reported datas.\textsuperscript{[2]}
4-Aminobenzenesulfonamide (6): yellow solid; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.50 (d, $J = 8.7$ Hz, 2H), 6.93 (s, 2H), 6.64 (d, $J = 8.7$ Hz, 2H), 5.82 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 151.9, 130.1, 127.5, 112.5. Spectral data obtained for the compound are in good agreement with the reported data.$^{[3]}$

4-(Trifluoromethyl)aniline (7): light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 8.3$ Hz, 1H), 6.69 (d, $J = 8.3$ Hz, 1H), 3.94 (br, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 149.5, 126.8 (q, $J = 4.0$ Hz), 125.0 (q, $J = 269.0$ Hz), 120.3 (q, $J = 32.0$ Hz), 114.3. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -61.25. Spectral data obtained for the compound are in good agreement with the reported data.$^{[2]}$

4-Aminobenzonitrile (8): white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 8.4$ Hz, 2H), 6.64 (d, $J = 8.4$ Hz, 2H), 4.17 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 150.6, 133.9, 120.3, 114.5, 100.2. Spectral data obtained for the compound are in good agreement with the reported data.$^{[2]}$

Methyl 4-aminobenzoate (9): white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 8.7$ Hz, 2H), 6.63 (d, $J = 8.7$ Hz, 2H), 4.08 (br, 2H), 3.85 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 150.9, 131.7, 119.9, 113.9, 51.7. Spectral data obtained for the compound are in good agreement with the reported data.$^{[2]}$

1-(4-Aminophenyl)ethan-1-one (10): light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.6$ Hz, 2H), 6.64 (d, $J = 8.6$ Hz, 2H), 4.13 (br, 2H), 2.50 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 196.6, 151.2, 130.9, 128.1, 113.9, 26.2. Spectral data obtained for the compound are in good agreement with the reported data.$^{[2]}$
N-(4-Aminophenyl)acetamide (11): yellow solid; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.60 (s, 1H), 7.23 (d, $J = 8.6$ Hz, 2H), 6.52 (d, $J = 8.6$ Hz, 2H), 4.84 (br, 2H), 1.99 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) δ 167.8, 145.0, 129.1, 121.3, 114.3, 24.1. Spectral data obtained for the compound are in good agreement with the reported data.\textsuperscript{[2]}

4-Vinylaniline (12): yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 (d, $J = 8.3$ Hz, 2H), 6.60 (d, $J = 8.3$ Hz, 2H), 6.58 – 6.56 (m, 1H), 5.52 (d, $J = 17.6$ Hz, 1H), 5.01 (d, $J = 10.9$ Hz, 1H), 3.66 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 146.3, 136.7, 128.5, 127.5, 115.1, 110.1. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ -126.85. Spectral data obtained for the compound are in good agreement with the reported data.\textsuperscript{[2]}

4-Fluoroaniline (13): light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.86 (t, $J = 8.7$ Hz, 1H), 6.63 – 6.60 (m, 1H), 3.53 (br, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 156.6 (d, $J = 235.0$ Hz) 142.5, 116.2 (d, $J = 7.0$ Hz), 115.8 (d, $J = 23.0$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -126.85. Spectral data obtained for the compound are in good agreement with the reported data.\textsuperscript{[2]}

4-Chloroaniline (14): light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.10 (d, $J = 8.5$ Hz, 2H), 6.60 (d, $J = 8.5$ Hz, 2H), 3.63 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 145.1, 129.2, 123.2, 116.3. Spectral data obtained for the compound are in good agreement with the reported data.\textsuperscript{[2]}

4-Bromoaniline (15): yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 (d, $J = 8.8$ Hz, 2H), 6.56 (d, $J = 8.8$ Hz, 2H), 3.66 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 145.5, 132.1, 116.8, 110.3. Spectral data obtained for the compound are in good agreement with the reported data.\textsuperscript{[2]}
[1,1'-Biphenyl]-4-amine (16): white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J$ = 7.3 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.30 – 7.26 (m, 1H), 6.77 (d, $J$ = 8.5 Hz, 2H), 3.72 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 146.0, 141.3, 131.7, 128.8, 128.2, 126.5, 126.4, 115.5. Spectral data obtained for the compound are in good agreement with the reported data.[2]

$p$-Toluidine (17): white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.98 (d, $J$ = 7.7 Hz, 2H), 6.62 (d, $J$ = 7.7 Hz, 2H), 3.44 (br, 2H), 2.25 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 143.8, 129.9, 128.0, 115.4, 20.6. Spectral data obtained for the compound are in good agreement with the reported data.[7]

4-Isopropylaniline (18): light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (d, $J$ = 8.2 Hz, 2H), 6.66 (d, $J$ = 8.2 Hz, 2H), 3.47 (br, 2H), 2.85 (hept, $J$ = 6.9 Hz, 1H), 1.24 (d, $J$ = 6.9 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 144.3, 139.3, 127.2, 115.3, 33.3, 24.3. Spectral data obtained for the compound are in good agreement with the reported data.[2]

4-Octylaniline (19): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.9 (d, $J$ = 8.3 Hz, 2H), 6.63 (d, $J$ = 8.3 Hz, 2H), 3.48 (br, 2H), 2.50 (t, $J$ = 7.6 Hz, 2H), 1.56 (p, $J$ = 7.2 Hz, 2H), 1.31 – 1.27 (m, 10H), 0.89 (t, $J$ = 6.7 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 144.1, 133.3, 129.3, 115.4, 35.2, 32.0, 32.0, 29.6, 29.4, 29.4, 22.8, 14.2. Spectral data obtained for the compound are in good agreement with the reported data.[4]

4-Cyclopropylaniline (20): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.91 (d, $J$ = 8.1 Hz, 2H), 6.62 (d, $J$ = 8.1 Hz, 2H), 3.27 (br, 2H), 1.85 – 1.78 (m, 1H), 0.86 (q, $J$ = 5.1 Hz, 2H), 0.59 (q, $J$ = 5.1 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 144.1, 134.0, 126.9, 115.4, 14.7, 8.4. Spectral data obtained for the compound are in good agreement
with the reported data.

**4-(Trifluoromethoxy)aniline (21):** yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.01 (d, $J = 8.8$ Hz, 2H), 6.64 (d, $J = 8.8$ Hz, 2H), 3.68 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 145.4, 141.5, 122.5, 120.8 (d, $J = 256.5$ Hz), 115.6. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -58.48. Spectral data obtained for the compound are in good agreement with the reported data.

**4-Methoxyaniline (22):** black solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.75 (d, $J = 8.8$ Hz, 2H), 6.65 (d, $J = 8.8$ Hz, 2H), 3.75 (s, 3H), 3.32 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 153.3, 140.5, 116.9, 115.3, 56.3. Spectral data obtained for the compound are in good agreement with the reported data.

**3,5-Dimethylaniline (2):** yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.43 (s, 1H), 6.35 (s, 2H), 3.45 (br, 2H), 2.23 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 146.3, 139.1, 120.7, 113.2, 21.4. Spectral data obtained for the compound are in good agreement with the reported data.

**o-Toluidine (23):** light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11 – 7.07 (m, 2H), 6.76 (t, $J = 7.3$ Hz, 1H), 6.71 (d, $J = 7.8$ Hz, 1H), 3.59 (s, 2H), 2.21 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 144.7, 130.5, 127.0, 122.4, 118.7, 115.0, 17.4. Spectral data obtained for the compound are in good agreement with the reported data.

**2-Isopropylaniline (24):** yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.04 (td, $J = 7.7$, 1.5 Hz, 1H), 6.80 (td, $J = 7.9$, 1.1 Hz, 1H), 6.69 (dd, $J = 7.9$, 1.1 Hz, 1H), 3.65 (s, 2H), 2.92 (hept, $J = 6.8$ Hz, 1H), 1.28 (d, $J = 6.8$ Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 143.4, 132.8, 126.6, 125.5, 119.2, 116.0, 27.8, 22.4. Spectral data obtained for the compound are in good agreement with the reported data.
3-Fluoroaniline (25): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.12 – 7.06 (m, 1H), 6.47 – 6.36 (m, 3H), 3.71 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 164.0 (d, $J = 244.4$ Hz), 148.4 (d, $J = 11.1$ Hz), 130.6 (d, $J = 10.1$ Hz), 110.8 (d, $J = 2.0$ Hz), 105.2 (d, $J = 21.2$ Hz), 102.1 (d, $J = 25.3$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -113.20. Spectral data obtained for the compound are in good agreement with the reported data.$^{[10]}$

3-Chloroaniline (26): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.07 (t, $J = 8.0$ Hz, 1H), 6.73 (dd, $J = 8.0$, 1.0 Hz, 1H), 6.67 (t, $J = 2.0$ Hz, 1H), 6.54 (dd, $J = 8.0$, 1.5 Hz, 1H), 3.67 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 147.8, 134.9, 130.4, 118.5, 115.0, 113.3. Spectral data obtained for the compound are in good agreement with the reported data.$^{[6]}$

3-(Difluoromethoxy)aniline (27): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.12 (t, $J = 8.0$ Hz, 1H), 6.66 – 6.29 (m, 4H), 3.63 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 151.7, 147.2, 129.6, 115.2 (t, $J = 259.6$ Hz), 111.1, 107.8, 105.0. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -80.24 (d, $J = 71.4$ Hz). Spectral data obtained for the compound are in good agreement with the reported data.$^{[12]}$

Naphthalen-2-amine (28): white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 – 7.68 (m, 2H), 7.63 (d, $J = 8.5$ Hz, 1H), 7.41 (t, $J = 7.1$ Hz, 1H), 7.27 (t, $J = 9.1$ Hz, 1H), 7.00 – 6.96 (m, 2H), 3.86 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 144.2, 135.1, 129.3, 128.1, 127.8, 126.5, 125.9, 122.6, 118.4, 108.7. Spectral data obtained for the compound are in good agreement with the reported data.$^{[8]}$

Pyridin-2-amine (29): light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 4.9$
Hz, 1H), 7.36 (td, J = 8.3, 1.8 Hz, 1H), 6.58 (td, J = 4.9, 1.8 Hz, 1H), 6.44 (d, J = 8.3 Hz, 1H), 4.57 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 158.6, 148.1, 137.7, 113.9, 108.6. Spectral data obtained for the compound are in good agreement with the reported data.

**Pyridin-3-amine (30):** light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, J = 2.7 Hz, 1H), 7.95 (d, J = 4.7 Hz, 1H), 7.00 (dd, J = 8.1, 4.7 Hz, 1H), 6.91 (dd, J = 8.1, 2.7 Hz, 1H), 3.82 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 142.8, 139.8, 137.4, 123.7, 121.4. Spectral data obtained for the compound are in good agreement with the reported data.

**4-(Trifluoromethyl)pyridin-2-amine (31):** brown oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (d, J = 5.5 Hz, 1H), 6.86 (d, J = 1.8 Hz, 1H), 6.62 (dd, J = 5.5, 1.8 Hz, 1H), 4.65 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 154.0, 150.4, 149.0 (q, J = 34.0 Hz), 121.8 (q, J = 272.0 Hz), 111.2, 106.4 (q, J = 2.0 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -68.54. Spectral data obtained for the compound are in good agreement with the reported data.

**3-Methylpyridin-2-amine (32):** yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, J = 6.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 6.54 (dd, J = 8.0, 6.0 Hz, 1H), 4.56 (br, 2H), 2.05 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 157.3, 145.6, 137.6, 116.5, 114.2, 17.1. Spectral data obtained for the compound are in good agreement with the reported data.

**6-Methoxypyridin-3-amine (33):** brown oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, J = 2.9 Hz, 1H), 7.01 (dd, J = 8.7, 2.9 Hz, 1H), 6.59 (d, J = 8.7 Hz, 1H), 3.85 (s, 3H), 3.16 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 158.2, 136.8, 133.0, 127.8, 110.8, 53.4. Spectral data obtained for the compound are in good agreement with the reported
5-Chloro-2-methoxypyridin-3-amine (34): yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J = 2.2$ Hz, 1H), 6.84 (d, $J = 2.2$ Hz, 1H), 3.95 (s, 3H), 3.60 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 151.5, 132.7, 131.8, 124.4, 119.6, 53.7. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[9]}$

Dibenzo[b,d]furan-3-amine (35): light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 7.3$ Hz, 1H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.47 (d, $J = 7.9$ Hz, 1H), 7.33 – 7.25 (m, 2H), 6.84 (s, 1H), 6.68 (d, $J = 8.0$ Hz, 1H), 3.36 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 158.1, 156.1, 146.9, 125.3, 125.0, 122.7, 121.4, 119.5, 115.8, 111.4, 111.3, 97.6. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[11]}$

1H-Indol-5-amine (36): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (br, 1H), 7.19 (d, $J = 8.5$ Hz, 1H), 7.12 (s, 1H), 6.95 (s, 1H), 6.67 (d, $J = 8.5$ Hz, 1H), 6.38 (s, 1H), 3.50 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 139.7, 130.9, 129.0, 124.8, 113.1, 111.6, 105.7, 101.7. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[2]}$

Benzo[b]thiophen-3-amine (37): yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 8.5$ Hz, 1H), 7.38 (d, $J = 5.4$ Hz, 1H), 7.15 (d, $J = 5.4$ Hz, 1H), 7.10 (d, $J = 1.8$ Hz, 1H), 6.78 (dd, $J = 8.5$, 1.8 Hz, 1H), 3.58 (br, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 143.7, 141.0, 130.6, 127.2, 123.2, 123.1, 115.0, 108.4. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[2]}$
2,3-Dihydrobenzo[b][1,4]dioxin-6-amine (38): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.67 (d, $J = 8.5$ Hz, 1H), 6.24 (d, $J = 2.6$ Hz, 1H), 6.20 (dd, $J = 8.5$, 2.6 Hz, 1H), 4.22 – 4.20 (m, 2H), 4.18 – 4.16 (m, 2H), 3.28 (br, 2H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 144.0, 140.9, 136.5, 117.7, 108.8, 104.3, 64.8, 64.3. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[2]}$

5-Aminoisobenzofuran-1(3H)-one (39): yellow solid; $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 7.48 (d, $J = 8.4$ Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 6.62 (s, 1H), 6.28 (s, 2H), 5.19 (s, 2H). $^{13}$C {$^1$H} NMR (100 MHz, DMSO-d$_6$) $\delta$ 170.8, 154.7, 150.2, 126.2, 114.8, 111.1, 104.5, 68.7. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[2]}$

Quinolin-2-amine (40): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.55 (td, $J = 7.0$, 1.3 Hz, 1H), 7.25 (t, $J = 7.0$ Hz, 1H), 6.71 (d, $J = 8.8$ Hz, 1H), 4.96 (br, 2H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 157.2, 147.8, 138.2, 129.9, 127.6, 126.1, 123.7, 122.8, 111.8. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[9]}$

Isoquinolin-3-amine (41): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.93 (s, 1H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.55 – 7.49 (m, 2H), 7.26 (t, $J = 8.2$ Hz, 1H), 6.77 (s, 1H), 4.52 (br, 2H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 154.7, 151.8, 139.0, 130.5, 127.9, 124.8, 124.2, 123.2, 99.7. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[9]}$

4-(9H-Carbazol-9-yl)aniline (42): yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J = 7.7$ Hz, 2H), 7.45 – 7.42 (m, 2H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.33 – 7.28 (m, 4H), 6.86 (d, $J = 8.5$ Hz, 2H), 3.80 (br, 2H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 146.1,
Ethyl 4-aminobenzoate (76): yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J$ = 8.7 Hz, 2H), 6.63 (d, $J$ = 8.7 Hz, 2H), 4.31 (q, $J$ = 7.1 Hz, 2H), 4.05 (br, 2H), 1.36 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, Chloroform-d) $\delta$ 166.83, 150.84, 131.69, 120.31, 113.92, 76.84, 60.43, 14.56. Spectral datas obtained for the compound are in good agreement with the reported datas.[2]

Diphenylamine (45): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (t, $J$ = 7.7 Hz, 4H), 7.12 (d, $J$ = 8.1 Hz, 4H), 6.99 (t, $J$ = 7.3 Hz, 2H), 5.72 (br, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 143.3, 129.5, 121.2, 118.0. Spectral datas obtained for the compound are in good agreement with the reported datas.[13]

Di-p-tolylamine (46): white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.07 (d, $J$ = 8.2 Hz, 4H), 6.95 (d, $J$ = 8.2 Hz, 4H), 5.51 (br, 1H), 2.30 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 141.3, 130.3, 130.0, 118.1, 20.8. Spectral datas obtained for the compound are in good agreement with the reported datas.[13]

Bis(4-octylphenyl)amine (47): brown oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (d, $J$ = 8.4 Hz, 4H), 6.97 (d, $J$ = 8.4 Hz, 4H), 2.54 (t, $J$ =7.6 Hz, 4H), 1.59 (p, $J$ = 7.4 Hz, 4H), 1.34 – 1.26 (m, 20H), 0.88 (t, $J$ = 6.8 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 141.4, 135.6, 129.3, 118.0, 35.4, 32.1, 31.9, 29.7, 29.5, 29.4, 22.8, 14.3. Spectral datas obtained for the compound are in good agreement with the reported datas.[15]

Bis(4-decylphenyl)amine (48): black solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.07 (d, $J$ = 8.4 Hz, 4H), 6.98 (d, $J$ = 8.4 Hz, 4H), 2.55 (t, $J$ =7.6 Hz, 4H), 1.60 (p, $J$ = 7.2 Hz,
$^{1}$H NMR (100 MHz, CDCl$_3$) δ 141.4, 135.6, 129.3, 118.0, 35.4, 32.1, 31.9, 29.9, 29.8, 29.7, 29.5, 22.8, 14.3. HRMS (ESI) m/z calc. for C$_{32}$H$_{52}$N [M+H]$^+$: 450.4094, found: 450.4089.

Bis(4-dodecylphenyl)amine (49): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.06 (d, $J = 8.3$ Hz, 4H), 6.97 (d, $J = 8.3$ Hz, 4H), 5.56 (br, 1H), 2.62–2.47 (m, 4H), 1.65–1.53 (m, 6H), 1.27 (s, 34H), 0.89 (t, $J = 6.7$ Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 141.4, 135.6, 129.3, 118.0, 35.4, 32.1, 31.9, 29.8, 29.7, 29.5, 22.9, 14.3. HRMS (ESI) m/z calc. for C$_{36}$H$_{60}$N [M+H]$^+$: 506.4720, found: 334.2529.

Bis(4-cyclohexylphenyl)amine (50): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.10 (d, $J = 8.4$ Hz, 4H), 6.98 (d, $J = 8.4$ Hz, 4H), 2.52–2.39 (m, 2H), 1.94–1.67 (m, 11H), 1.39 (p, $J = 12.0$ Hz, 9H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 141.4, 140.7, 127.5, 43.82, 34.8 27.0, 26.21. HRMS (ESI) m/z calc. for C$_{24}$H$_{32}$N [M+H]$^+$: 334.2529, found: 334.2529.

N-(Bicyclo[4.2.0]octa-1,3,5-trien-3-yl)bicyclo[4.2.0]octa-1(6),2,4-trien-3-amine (51): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.92 (d, $J = 7.8$ Hz, 2H), 6.84 (d, $J = 7.8$ Hz, 2H), 6.81 (s, 2H), 3.12 (s, 8H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 146.6, 143.3, 138.2, 123.5, 117.6, 113.2, 29.3, 29.1. HRMS (ESI) m/z calc. for C$_{16}$H$_{16}$N [M+H]$^+$: 222.1277, found: 222.1275.

Bis(4-phenoxyphenyl)amine (52): gray solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36–7.29 (m, 4H), 7.11–6.92 (m, 14H), 5.55 (br, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 158.4, 150.9, 139.8, 129.8, 122.7, 120.8, 119.5, 118.0. HRMS (ESI) m/z calc. for C$_{24}$H$_{20}$NO$_2$ [M+H]$^+$: 354.1489, found: 354.1488.
**Bis(4-methoxyphenyl)amine (53):** black solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.94 (d, $J = 8.7$ Hz, 4H), 6.83 (d, $J = 8.7$ Hz, 4H), 5.30 (br, 1H), 3.78 (s, 6H). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$) δ 154.4, 138.1, 119.7, 114.8, 55.8. Spectral datas obtained for the compound are in good agreement with the reported datas.[15]

![Bis(4-methoxyphenyl)amine](image)

**Bis(4-(methylthio)phenyl)amine (54):** black solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.14 (d, $J = 7.0$ Hz, 4H), 6.89 (d, $J = 7.4$ Hz, 4H), 5.56 (br, 1H), 2.36 (s, 6H). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$) δ 141.4, 130.0, 129.4, 118.7, 18.0. Spectral datas obtained for the compound are in good agreement with the reported datas.[16]

![Bis(4-(methylthio)phenyl)amine](image)

**Bis(4-(trimethylsilyl)phenyl)amine (55):** brown oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, $J = 8.4$ Hz, 4H), 7.11 (d, $J = 8.4$ Hz, 4H), 5.80 (br, 1H), 0.28 (s, 18H). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$) δ 143.5, 134.7, 131.9, 117.2, -0.3. HRMS (ESI) m/z calc. for C$_{15}$H$_{28}$NSi$_2$ [M+H]$^+$: 314.1760, found: 314.1757.

![Bis(4-(trimethylsilyl)phenyl)amine](image)

**Bis(4-fluorophenyl)amine (56):** brown oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.96 (m, 8H), 5.48 (br, 1H). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$) δ 157.8 (d, $J = 240.4$ Hz), 139.8 (d, $J = 2.0$ Hz), 119.4 (d, $J = 8.1$ Hz), 116.0 (d, $J = 22.2$ Hz) $^{19}$F NMR (376 MHz, CDCl$_3$) δ -122.63. Spectral datas obtained for the compound are in good agreement with the reported datas.[13]

![Bis(4-fluorophenyl)amine](image)

**Bis(4-(trifluoromethyl)phenyl)amine (57):** brown oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, $J = 8.5$ Hz, 4H), 7.16 (d, $J = 8.5$ Hz, 4H), 6.11 (br, 1H). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$) δ 145.1, 124.6 (d, $J = 271.7$ Hz), 127.1 (d, $J = 3.0$ Hz), 123.9 (d, $J = 32.3$ Hz), 116.0 (d, $J = 22.2$ Hz), 119.4 (d, $J = 8.1$ Hz), 116.0 (d, $J = 22.2$ Hz) $^{19}$F NMR (376 MHz, CDCl$_3$) δ -122.63. Spectral datas obtained for the compound are in good agreement with the reported datas.[13]

![Bis(4-(trifluoromethyl)phenyl)amine](image)
Hz), 117.7. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -61.78. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[13]}$

1,1'-(Azanediylbis(4,1-phenylene))bis(ethan-1-one) (58): black solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, $J = 8.8$ Hz, 4H), 7.15 (d, $J = 8.8$ Hz, 4H), 2.56 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 196.6, 146.1, 131.0, 130.6, 117.1, 26.4. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[18]}$

Dimethyl 4,4'-azanediyl dibenzoate (44): yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, $J = 8.6$ Hz, 4H), 7.12 (d, $J = 8.6$ Hz, 4H), 6.61 (br, 1H), 3.88 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 166.8, 146.0, 131.6, 123.3, 117.1, 52.0. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[18]}$

4,4'-Azanediyl dibenzonitrile (59): brown solid; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.51 (br, 1H), 7.74 (d, $J = 7.4$ Hz, 4H), 7.30 (d, $J = 7.4$ Hz, 4H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) δ 145.7, 133.7, 119.4, 117.3, 102.1. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[19]}$

Bis(4-chlorophenyl)amine (60): brown oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.22 (d, $J = 8.7$ Hz, 4H), 6.96 (d, $J = 8.7$ Hz, 4H), 5.64 (br, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 141.4, 129.4, 126.1, 112.0. Spectral datas obtained for the compound are in good agreement with the reported datas.$^{[13]}$

Di-o-tolylamine (61): white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.21 (d, $J = 7.4$ Hz, 2H), 7.13 (t, $J = 7.6$ Hz, 2H), 7.00 (d, $J = 7.9$ Hz, 2H), 6.92 (t, $J = 7.4$ Hz, 2H), 5.16 (br, 1H), 2.28 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 142.1, 131.0, 127.1, 126.9, 121.5,
118.4, 17.9. Spectral data obtained for the compound are in good agreement with the reported data.[14]

Bis(2-methoxyphenyl)amine (62): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 7.6$ Hz, 2H), 6.95 – 6.84 (m, 6H), 6.52 (br, 1H), 3.91 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 149.2, 132.7, 120.9, 120.3, 115.7, 110.8, 55.8. HRMS (ESI) m/z calc. for C$_{14}$H$_{15}$NNaO$_2$ [M+Na]$^+$: 252.1000, found: 252.0990.

Bis(2-isopropylphenyl)amine (63): colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 7.6$ Hz, 2H), 7.10 (t, $J = 7.6$ Hz, 2H), 7.02 – 6.94 (m, 4H), 5.33 (br, 1H), 3.12 (hept, $J = 6.8$ Hz, 2H), 1.30 (d, $J = 6.8$ Hz, 12H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 141.4, 138.2, 126.5, 125.8, 121.8, 119.4, 27.8, 22.8. Spectral data obtained for the compound are in good agreement with the reported data.[14]

Bis(2-isopropoxyphenyl)amine (64): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 7.8$ Hz, 2H), 6.90 (t, $J = 7.7$ Hz, 4H), 6.81 (m, 2H), 4.55 (hept, $J = 5.7$ Hz, 2H), 1.39 (d, $J = 6.0$ Hz, 12H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 146.9, 134.1, 121.1, 119.7, 115.0, 114.3, 71.4, 22.5. HRMS (ESI) m/z calc. for C$_{18}$H$_{23}$NNaO$_2$ [M+Na]$^+$: 308.1626, found: 308.1621.

Bis(3-fluoro-4-methoxyphenyl)amine (65): black solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.88 (t, $J = 9.0$ Hz, 2H), 6.79 (dd, $J = 12.8$, 2.7 Hz, 2H), 6.68 – 6.71 (m, 2H), 3.86 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 153.2 (d, $J = 246.4$ Hz), 142.5 (d, $J = 11.11$ Hz), 137.9 (d, $J = 9.1$ Hz), 115.3 (d, $J = 3.0$ Hz), 113.9 (d, $J = 4.0$ Hz), 107.3 (d, $J = 21.2$ Hz), 57.2. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -132.92. HRMS (ESI) m/z calc. for C$_{14}$H$_{13}$F$_2$NNaO$_2$ [M+Na]$^+$: 288.0807, found: 288.0807.
Bis(3,5-difluoro-4-methoxyphenyl)amine (66): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.65 – 6.49 (m, 4H), 5.58 (br, 1H), 3.93 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 156.8 (dd, $J = 248.5$, 8.1 Hz), 138.0 (t, $J = 12.1$ Hz), 131.3 (t, $J = 15.2$ Hz), (102.5, 102.4, 102.3, 102.2), 62.3 (t, $J = 3.0$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -127.30. HRMS (ESI) m/z calc. for C$_{14}$H$_{11}$F$_4$NNaO$_2$ [M+Na]$^+$: 324.0618, found: 324.0622.

Di(thiophen-2-yl)amine (67): brown solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.30 (m, 2H), 7.21 (dd, $J = 3.5$, 1.2 Hz, 2H), 7.00 – 6.92 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 135.7, 132.9, 129.8, 127.6. Spectral data obtained for the compound are in good agreement with the reported data.

Bis(6-methoxypyridin-3-yl)amine (68): brown oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, $J = 2.9$ Hz, 2H), 7.27 (dd, $J = 8.8$, 2.9 Hz, 2H), 6.67 (d, $J = 8.8$ Hz, 2H), 5.21 (br, 1H), 3.89 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 159.8, 137.0, 134.7, 130.5, 111.2, 53.6. HRMS (ESI) m/z calc. for C$_{12}$H$_{14}$N$_3$O$_2$ [M+H]$^+$: 232.1081, found: 232.1078.

Bis(6-methylpyridin-2-yl)amine (69): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (t, $J = 7.8$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.28 (br, 1H), 6.69 (d, $J = 7.3$ Hz, 2H), 2.46 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 156.8, 153.6, 138.1, 115.6, 108.4, 24.4. Spectral data obtained for the compound are in good agreement with the reported data.

Bis(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)amine (70): black solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.75 (d, $J = 8.6$ Hz, 2H), 6.56 (s, 2H), 6.50 (s, 2H), 4.30 – 4.14 (m, 8H).
$^{13}$C-$^1$H NMR (100 MHz, CDCl$_3$) $\delta$ 144.0, 138.5, 138.2, 117.7, 111.9, 107.3, 64.7, 64.4. HRMS (ESI) m/z calc. for C$_{16}$H$_{16}$NO$_4$ [M+H]$^+$: 286.1074, found: 286.1074.

Bis(4-(9H-carbazol-9-yl)phenyl)amine (71): black oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (d, $J$ = 7.8 Hz, 4H), 7.63 – 7.45 (m, 13H), 7.37 – 7.34 (m, $J$ = 7.9, 4.0 Hz, 7H). $^{13}$C-$^1$H NMR (100 MHz, CDCl$_3$) $\delta$ 142.6, 141.4, 130.9, 128.5, 126.0, 123.3, 120.4, 119.9, 118.9, 109.9. Spectral data obtained for the compound are in good agreement with the reported data.$^{[21]}$

N$_2$N$_2$N$_2'$N$_2'$,N$_7$N$_7$,N$_7'$N$_7'$-Octakis(4-methoxyphenyl)-9,9'-spirobi[fluorene]-2,2',7,7'-tetraamine (74): yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J$ = 8.2 Hz, 4H), 6.92 (d, $J$ = 8.9 Hz, 16H), 6.81 – 6.75 (m, 20H), 6.56 (d, $J$ = 1.7 Hz, 4H), 3.77 (s, 24H). $^{13}$C-$^1$H NMR (100 MHz, CDCl$_3$) $\delta$ 155.2, 150.2, 147.3, 141.7, 135.7, 125.2, 122.9, 119.9, 118.3, 114.6, 65.7, 55.6. Spectral data obtained for the compound are in good agreement with the reported data.$^{[22]}$

5. References


6. Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of products

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 4

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 4
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 5
\(^1\)H NMR (400 MHz, DMSO-\textit{d}_6) spectrum of compound 6

\[^{13}\text{C}\{^1\text{H}\}\] NMR (100 MHz, DMSO-\textit{d}_6) spectrum of compound 6
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 7

$^{13}$C$_{(1)}$H NMR (100 MHz, CDCl$_3$) spectrum of compound 7
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 7

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 8
$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 8

$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum of compound 9
$^{13}$C {\text{\textsuperscript{1}H}}$ NMR (100 MHz, CDCl$_3$) spectrum of compound 9

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 10
$^{13}$C{\(^{1}H\)} NMR (100 MHz, CDCl$_3$) spectrum of compound 10

$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of compound 11
$^{13}$C($^1$H) NMR (100 MHz, DMSO-$d_6$) spectrum of compound 11

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 12
$^{13}$C{\(^1\)H} NMR (100 MHz, CDCl\(_3\)) spectrum of compound 12

$^1$H NMR (400 MHz, CDCl\(_3\)) spectrum of compound 13
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl$_3$) spectrum of compound 13

$^{19}\text{F}$ NMR (376 MHz, CDCl$_3$) spectrum of compound 13
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 14

$^{13}$C{${^1}$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 14
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 15

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 15
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 16

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 16
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 17

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 17
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 18

$^{13}$C{${^1}$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 18
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 19

$^{13}$C\{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 19
$^1\text{H NMR}$ (400 MHz, CDCl$_3$) spectrum of compound 20

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl$_3$) spectrum of compound 20
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 21

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 21
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 21

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 22
$^{13}$C\{$^{1}$H\} NMR (100 MHz, CDCl$_3$) spectrum of compound 22

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2
\textbf{13C\{^1H\} NMR (100 MHz, CDCl\textsubscript{3}) spectrum of compound 2}

\textbf{1H NMR (400 MHz, CDCl\textsubscript{3}) spectrum of compound 23}
$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 23

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 24
$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 24

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 25
$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 25

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 25
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 26

$^{13}$C{$_^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 26
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 27

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 27
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 27

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 28
$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 28

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 29
$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 29

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 30
$^{13}$C\{(1H) NMR (100 MHz, CDCl$_3$) spectrum of compound 30

\begin{center}
\includegraphics[width=\textwidth]{c_nmr.png}
\end{center}

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 31

\begin{center}
\includegraphics[width=\textwidth]{h_nmr.png}
\end{center}
$^{13}$C$\{^1\text{H}\}$ NMR (100 MHz, CDCl$_3$) spectrum of compound 31

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 31
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 32

$^{13}$C{${}^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 32
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 33

$^{13}$C{$_1^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 33
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 34

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 34
$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum of compound 35

$^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 35
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 36

$^{13}$C{H} NMR (100 MHz, CDCl$_3$) spectrum of compound 36
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 37

$^{13}$C\{$^1$H\} NMR (100 MHz, CDCl$_3$) spectrum of compound 37
$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum of compound 38

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 38
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of compound 39

$^{13}$C($^1$H) NMR (100 MHz, DMSO-$d_6$) spectrum of compound 39
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 40

$^{13}$C-{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 40
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 41

$^{13}$C{'^1}$H NMR (100 MHz, CDCl$_3$) spectrum of compound 41
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 42

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 42
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 76

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 76
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 45

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 45
$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum of compound 46

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 46
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 47

$^{13}$C-$^1$H NMR (100 MHz, CDCl$_3$) spectrum of compound 47
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 48

$^{13}$C-$^1$H NMR (100 MHz, CDCl$_3$) spectrum of compound 48
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 49

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 49
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 50

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 50
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 51

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 51
$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum of compound 52

$^{13}$C-$^1$H NMR (100 MHz, CDCl$_3$) spectrum of compound 52
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 53

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 53
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 54

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 54
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 55

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 55
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 56

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 56
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 56

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 57
$^{13}\text{C}^{1}{\text{H}}$ NMR (100 MHz, CDCl$_3$) spectrum of compound 57

$^{19}\text{F}$ NMR (376 MHz, CDCl$_3$) spectrum of compound 57
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 58

$^{13}$C\{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 58
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 44

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) spectrum of compound 44
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of compound 59

$^{13}$C\{$^1$H\} NMR (100 MHz, DMSO-$d_6$) spectrum of compound 59
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 60

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 60
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 61

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 61
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 62

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 62
$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum of compound 63

$^{13}$C $^{1}$H NMR (100 MHz, CDCl$_3$) spectrum of compound 63
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 64

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 64
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 65

$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 65
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 65

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 66
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 67

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 67
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 68

$^{13}$C\{$^1$H\} NMR (100 MHz, CDCl$_3$) spectrum of compound 68
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 69

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 69
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 70

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 70
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 71

$^{13}$C-{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of compound 71
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 74

$^{13}$C$^{'^1}$H NMR (100 MHz, CDCl$_3$) spectrum of compound 74