Highly Selective Direct Reductive Amidation of Nitroarenes with Carboxylic Acids using Cobalt(II) Phthalocyanine/PMHS

Vishal Kumar, Manoranjan Kumar, Sushila Sharma and Neeraj Kumar*

Natural Plant Products Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh 176 061, India

neerajnpp@rediffmail.com; neeraj@ihbt.res.in

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General experimental

Metal salts used were purchased from Merck, Germany. Metal phthalocyanines were synthesized by a reported procedure with some modification and characterized by FTIR and UV-VIS spectroscopy. Silica gel (60-120 mesh) used for column chromatography was purchased from Sisco Research Laboratories Pvt. Ltd. India and all other chemicals were purchased from Spectrochem, India, Merck, Germany, and Sigma-Aldrich, USA and were used without further purification. NMR spectra were recorded on Bruker Avance-300/600 spectrometers. Mass spectra were recorded on QTOF-Micro of Waters Micromass and Maxis-Bruker. The GC-MS analysis was carried out on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan), AOC-20i auto-sampler coupled, and a DB-5MS capillary column, (30 m x 0.25 mm i.d., 0.25µm). The initial temperature of column was 70 °C held for 4 min. and was programmed to 230 °C at 4°C/min., then held for 15 min. at 230 °C; the sample injection volume was 2 µL in GC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 ml min⁻¹ on split mode (1: 50).

Procedure for synthesis of metal phthalocyanines

Metal phthalocyanines were synthesized by using a reported method with some modification.

Synthesis of Cobalt (II) phthalocyanine

A mixture of phthalimide (26.28 g, 0.18 mol), urea (55.2 g, 0.92 mol), CoCl₂.6H₂O (11.85 g, 0.05 mol) and ammonium molybdate (4.69 g, 0.0038 mol) was heated under microwave irradiation for 3 min. The reaction mixture was cooled to room temperature and in sequence washed with 5% NaOH, distilled water and 2% HCl and finally with distilled water again. After that the resulting solid was dissolved in minimum quantity of concentrated H₂SO₄ and poured in distilled water to precipitate the desired cobalt (II) phthalocyanine, which were then filtered to give 9.5 g (48.5% yield) of cobalt (II) phthalocyanine.

Synthesis of Iron, Nickel and Copper(II) phthalocyanines

Iron, Nickel and Copper(II) phthalocyanines were prepared from FeSO₄.7H₂O, NiCl₂ and CuSO₄.7H₂O respectively using same procedure as described above.

General experimental procedure for reductive amidation of nitroarenes with carboxylic acids

To a stirred suspension of CoPc (0.01 mmol) in carboxylic acid (2 mL) were added nitroarene (1.0 mmol) and PMHS (4.0 H equiv.) at room temperature and then the temperature was raised to 100 °C. On completion of the reaction (as monitored by TLC), reaction mixture was dried under vacuum and the
crude product was analyzed directly by GC-MS. For the purification of desired product column chromatography was carried out (n-hexane: ethyl acetate).

**Procedure for recyclability of the catalyst**

To a stirred suspension of CoPc (0.01 mmol) in acetic acid (2 mL) were added nitrobenzene (1.0 mmol) and PMHS (4.0 H equiv.) at room temperature and then the temperature was raised to 100 °C. After 12 h, the reaction mixture was analyzed by GC and GC-MS. Further, nitrobenzene (1.0 mmol) and PMHS (4.0 H equiv.) were added to the reaction mixture and stirred at 100 °C for 12 h. The same procedure was repeated for further cycles and excellent yield of product was observed up to three cycles, whereas in forth cycle the yield was reduced.

**Table S1.** Reductive amidation of nitrobenzene in different solvents using stoichiometric amount of carboxylic acids

<table>
<thead>
<tr>
<th>entry</th>
<th>carboxylic acid</th>
<th>solvent</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AcOH</td>
<td>EtOH</td>
<td>nr</td>
</tr>
<tr>
<td>2</td>
<td>AcOH</td>
<td>MeOH</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>AcOH</td>
<td>MeCN</td>
<td>nr</td>
</tr>
<tr>
<td>4</td>
<td>AcOH</td>
<td>DMSO</td>
<td>nr</td>
</tr>
<tr>
<td>5</td>
<td>AcOH</td>
<td>DMF</td>
<td>nr</td>
</tr>
<tr>
<td>6</td>
<td>AcOH</td>
<td>Toluene</td>
<td>nr</td>
</tr>
<tr>
<td>7</td>
<td>AcOH</td>
<td>PEG-400</td>
<td>nr</td>
</tr>
<tr>
<td>8</td>
<td>AcOH</td>
<td>EG</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>AcOH</td>
<td>DCE</td>
<td>nr</td>
</tr>
<tr>
<td>10</td>
<td>PhCO₂H</td>
<td>EG</td>
<td>nr</td>
</tr>
<tr>
<td>11</td>
<td>Cinnamic acid</td>
<td>EG</td>
<td>nr</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: nitrobenzene (1.0 mmol), carboxylic acid (5.0 mmol), CoPc (1 mol%), PMHS (4.0 H equiv.), <sup>b</sup>GC yield. DMSO = dimethylsulfoxide, DMF = dimethylformamide, PEG = polyethylene glycol, EG = ethylene glycol, DCE = dichloroethane.
**Table S2** Reductive amidation of nitrobenzene in different solvents in the presence of mineral acids using stoichiometric amount of carboxylic acids\(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>yield (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtOH</td>
<td>nr</td>
</tr>
<tr>
<td>2</td>
<td>MeOH</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>MeCN</td>
<td>nr</td>
</tr>
<tr>
<td>4</td>
<td>DMSO</td>
<td>nr</td>
</tr>
<tr>
<td>5</td>
<td>DMF</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>Toluene</td>
<td>nr</td>
</tr>
<tr>
<td>7</td>
<td>PEG-400</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>EG</td>
<td>22</td>
</tr>
<tr>
<td>9</td>
<td>DCE</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>EG</td>
<td>20(^c)</td>
</tr>
<tr>
<td>11</td>
<td>EG</td>
<td>12(^d)</td>
</tr>
<tr>
<td>12</td>
<td>EG</td>
<td>24(^e)</td>
</tr>
<tr>
<td>13</td>
<td>EG</td>
<td>7(^f)</td>
</tr>
<tr>
<td>14</td>
<td>EG</td>
<td>20(^g)</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: nitrobenzene (1.0 mmol), AcOH (3.0 mmol), CoPc (1 mol%), PMHS (4.0 H equiv.), 1M HCl in solvent (2 mL) at 100 °C for 12h. \(^b\)Isolated yield. \(^c\)1M HBr was used instead of HCl. \(^d\)2.0 mmol AcOH was used. \(^e\)5.0 mmol AcOH was used. \(^f\)0.5M HCl was used. \(^g\)2.0M HCl was used. nr = no reaction, DMSO = dimethylsulfoxide, DMF = dimethylformamide, PEG = polyethylene glycol, EG = ethylene glycol, DCE = dichloroethane.
Spectral data of isolated compounds

1. N-Acetylaniline (Table 2, entry 1)
   \[
   \begin{array}{c}
   \text{H} \quad \text{N} \quad \text{O} \\
   \end{array}
   \]
   
   \[\begin{array}{c}
   \text{H NMR (CDCl}_3, \text{ 300 MHz)} \delta 2.15 (s, 3H), 7.10 (t, 1H, J = 7.3 Hz), 7.28-7.33 (m, 2H), 7.52 (d, 2H, J = 7.7 Hz), 8.01 (brs, 1H); \text{ } \text{^{13}C NMR (CDCl}_3, \text{ 75 MHz)} \delta 24.8, 120.5, 124.6, 129.3, 138.4, 169.3; \text{ } \text{HRESIMS calcd for C}_8\text{H}_{10}\text{NO} [M+H]^+ 136.0762, \text{ found 136.0734.}\n   \end{array}\]

2. N-Acetyl-4-fluoroaniline (Table 2, entry 2)
   \[
   \begin{array}{c}
   \text{F} \quad \text{H} \quad \text{N} \quad \text{O} \\
   \end{array}
   \]
   
   \[\begin{array}{c}
   \text{H NMR (CD}_3\text{OD, 300 MHz)} \delta 2.11 (s, 3H), 7.00-7.06 (m, 2H), 7.50-7.55 (m, 2H); \text{ } \text{^{13}C NMR (CD}_3\text{OD, 75 MHz)} \delta 22.6, 115.0, 115.3, 121.9, 122.0, 135.0, 158.0, 161.2, 170.5; \text{ } \text{HRESIMS calcd for C}_8\text{H}_8\text{N}_3\text{OS} [M+H]^+ 154.0668, \text{ found 154.0631.}\n   \end{array}\]

3. N-Acetyl-4-chloroaniline (Table 2, entry 3)
   \[
   \begin{array}{c}
   \text{Cl} \quad \text{H} \quad \text{N} \quad \text{O} \\
   \end{array}
   \]
   
   \[\begin{array}{c}
   \text{H NMR (CD}_3\text{OD, 300 MHz)} \delta 2.09 (s, 3H), 7.20 (d, 2H, J = 8.8 Hz), 7.46 (d, 2H, J = 8.8 Hz); \text{ } \text{^{13}C NMR (CD}_3\text{OD, 75 MHz)} \delta 23.8, 121.6, 129.0, 129.2, 137.3, 170.4; \text{ } \text{HRESIMS calcd for C}_8\text{H}_9\text{ClNO} [M+H]^+ 170.0373, \text{ found 169.0348.}\n   \end{array}\]

4. N-Acetyl-4-bromoaniline (Table 2, entry 4)
   \[
   \begin{array}{c}
   \text{Br} \quad \text{H} \quad \text{O} \\
   \end{array}
   \]
   
   \[\begin{array}{c}
   \text{H NMR (CD}_3\text{OD, 300 MHz)} \delta 2.04 (s, 3H), 7.29-7.38 (m, 4H); \text{ } \text{^{13}C NMR (CD}_3\text{OD, 75 MHz)} \delta 23.6, 116.5, 121.5, 131.6, 137.4, 169.8; \text{ } \text{HRESIMS calcd for C}_9\text{H}_9\text{N}_2\text{O} [M+H]^+ 213.9868, \text{ found 213.9811.}\n   \end{array}\]

5. 4-(N-Acetylamino)toluene (Table 2, entry 5)
1H NMR (CD$_3$OD, 300 MHz) $\delta$ 2.15 (s, 3H), 2.31 (s, 3H), 7.10 (d, 2H, $J = 8.1$ Hz), 7.38 (d, 2H, $J = 8.1$ Hz), 7.69 (brs, 1H); $^{13}$C NMR (CD$_3$OD, 75 MHz) $\delta$ 21.2, 24.7, 120.5, 129.8, 134.2, 135.8, 168.9; HRESIMS calcd for C$_9$H$_{12}$NO [M+H]$^+$ 150.0919, found 150.0950.

6. 4-(N-Acetylamino)phenol (Table 2, entry 6)$^5$

1H NMR (CD$_3$OD, 300 MHz) $\delta$ 2.09 (s, 3H), 6.71-6.76 (m, 2H), 7.28-7.32 (m, 2H); $^{13}$C NMR (CD$_3$OD, 75 MHz) $\delta$ 24.2, 116.9, 124.1, 132.4, 156.1, 172.1; HRESIMS calcd for C$_8$H$_{10}$NO$_2$ [M+H]$^+$ 152.0712, found 152.0729.

7. Methyl-3-(N-acetylamino)benzoate (Table 2, entry 7)$^6$

1H NMR (CD$_3$OD, 300 MHz) $\delta$ 2.14 (s, 3H), 3.89 (s, 3H), 7.37-7.42 (m, 1H), 7.72-7.73 (m, 1H), 7.77-7.81 (m, 1H), 8.21 (s, 1H); $^{13}$C NMR (CD$_3$OD, 75 MHz) $\delta$ 22.8, 51.6, 120.8, 124.4, 124.8, 128.9, 130.9, 139.3, 167.2, 170.7; HRESIMS calcd for C$_{10}$H$_{12}$NO$_3$ [M+H]$^+$ 194.0817, found 194.0809.

8. 3-(N-Acetylamino)benzonitrile (Table 2, entry 8)$^1$

1H NMR (CDCl$_3$, 600 MHz) $\delta$ 2.20 (s, 3H), 7.38-7.41 (m, 2H), 7.72 (d, 1H, $J = 6.6$ Hz), 7.89 (s, 1H), 7.93 (s, 1H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 24.5, 112.8, 118.5, 122.8, 123.9, 127.6, 129.9, 138.8, 168.9; HRESIMS calcd for C$_9$H$_{10}$N$_2$O [M+H]$^+$ 161.0715, found 161.0704.

9. 4-(N-Acetylamino)acetophenone (Table 2, entry 9)$^7$
1H NMR (CD$_3$OD, 300 MHz) δ 2.16 (s, 3H), 2.56 (s, 3H), 7.68-7.71 (m, 2H), 7.94-7.97 (m, 2H); 13C NMR (CD$_3$OD, 75 MHz) δ 23.0, 25.4, 119.0, 129.6, 132.6 143.7, 170.9, 198.4; HRESIMS calcd for C$_8$H$_8$N$_3$OS [M+H]$^+$ 178.0868, found 178.0851.

10. 1,4-Di-(N-acetylamino)benzene (Table 2, entry 10)$^5$

1H NMR (DMSO-d$_6$, 600 MHz) δ 1.99 (s, 6H), 7.45 (s, 4H), 9.83 (s, 2H); 13C NMR (DMSO-d$_6$, 150 MHz) δ 24.3, 119.8, 135.0, 168.4; HRESIMS calcd for C$_{10}$H$_{13}$N$_2$O$_2$ [M+H]$^+$ 193.0977, found 193.0942.

11. 3-(N-Acetylamino)styrene (Table 2, entry 11)$^8$

1H NMR (CD$_3$OD, 300 MHz) δ 2.13 (s, 3H), 5.24 (d, 1H, $J = 11.0$ Hz), 5.76 (d, 1H, $J = 17.5$ Hz), 6.66-6.75 (m, 1H), 7.16 (d, 1H, $J = 7.6$ Hz), 7.26 (m, 1H), 7.43 (d, 1H, $J = 8.0$ Hz), 7.65 (s, 1H); 13C NMR (CD$_3$OD, 75 MHz) δ 24.3, 114.8, 119.2, 121.0, 123.5, 130.4, 138.4, 140.1, 140.6, 172.1; HRESIMS calcd for C$_{10}$H$_{12}$NO [M+H]$^+$ 162.0919, found 162.0933.

12. N-Acetyl-3-nitroaniline (Table 2, entry 12)$^9$

1H NMR (CD$_3$OD, 600 MHz) δ 2.15 (s, 3H), 7.50 (s, 1H), 7.82 (d, 1H, $J = 6.0$ Hz), 7.90 (d, 1H, $J = 6.0$ Hz), 8.57 (s, 1H); 13C NMR (CD$_3$OD, 150 MHz) δ 24.2, 115.6, 119.6, 126.6, 131.1, 141.6, 150.2, 172.3; HRESIMS calcd for C$_8$H$_9$N$_2$O$_3$ [M+H]$^+$ 181.0613, found 181.0637.

13. 1,4-Di-(N-acetylamino)benzene (Table 2, entry 13)$^5$
$^1$H NMR (DMSO-d$_6$, 300 MHz) $\delta$ 2.00 (s, 6H), 7.46 (s, 4H), 9.85 (s, 2H); $^{13}$C NMR (DMSO-d$_6$, 75 MHz) $\delta$ 24.1, 119.6, 134.8, 168.2; HRESIMS calcd for C$_{10}$H$_{13}$N$_2$O$_2$ [M+H]$^+$ 193.0977, found 193.0934.

14. 2-(N-Acetylamino)fluorine (Table 2, entry 14)$^{10}$

$^1$H NMR (CD$_3$OD, 300 MHz) $\delta$ 2.14 (s, 3H), 3.82 (s, 2H), 7.21-7.26 (m, 1H), 7.29-7.34 (m, 1H), 7.45-7.50 (m, 2H), 7.68-7.73 (m, 2H), 7.80 (s, 1H); $^{13}$C NMR (CD$_3$OD, 75 MHz) $\delta$ 24.0, 37.8, 118.2, 120.2, 120.5, 121.0, 126.1, 127.5, 127.9, 138.9, 139.3, 142.7, 144.6, 145.4, 171.7; HRESIMS calcd for C$_{15}$H$_{14}$NO [M+H]$^+$ 224.1075, found 224.1021.

15. 4-(N-Acetylamino)phthalide (Table 2, entry 15)$^{11}$

$^1$H NMR (DMSO-d$_6$, 600 MHz) $\delta$ 2.06 (s, 3H), 5.32 (s, 2H), 7.56 (d, 1H, J = 6.0 Hz), 7.75 (d, 1H, J = 6.0 Hz), 8.17 (s, 1H), 10.28 (s, 1H); $^{13}$C NMR (DMSO-d$_6$, 150 MHz) $\delta$ 24.1, 69.8, 114.0, 123.3, 125.2, 125.5, 140.1, 141.6, 168.9, 170.7; HRESIMS calcd for C$_{10}$H$_{10}$NO$_3$ [M+H]$^+$ 192.0661, found 192.0637.

16. 6-(N-Acetylamino)benzothiazole (Table 2, entry 16)$^{12}$

$^1$H NMR (CD$_3$OD, 300 MHz) $\delta$ 2.17 (s, 3H), 7.52 (dd, 1H, J = 1.8, 8.8 Hz), 7.95 (d, 1H, J = 8.8 Hz), 8.47 (d, 1H, J = 1.8 Hz), 9.11 (s, 1H); $^{13}$C NMR (CD$_3$OD, 75 MHz) $\delta$ 22.9, 112.5, 119.5, 122.7, 134.6, 137.0, 149.4, 154.9, 170.8; HRESIMS calcd for C$_9$H$_8$N$_2$OS [M+H]$^+$ 193.0436, found 193.0411.

17. 4-(N-Acetylamino)-2,1,3-benzothiadiazole (Table 2, entry 17)$^{13}$
1H NMR (CD$_3$OD, 300 MHz) δ 2.31 (s, 3H), 7.58-7.63 (m, 1H), 7.68-7.71 (m, 1H), 8.32 (d, 1H, J = 7.1 Hz); 13C NMR (CD$_3$OD, 75 MHz) δ 24.4, 117.6, 118.3, 132.0, 132.2, 149.9, 156.8, 172.7; HRESIMS calcd for C$_8$H$_8$N$_3$OS [M+H]$^+$ 194.0388, found 194.0345.

18. 5-(N-Acetylamino)isoquinoline (Table 2, entry 18)$^{14}$

1H NMR (CD$_3$OD, 300 MHz) δ 2.31 (s, 3H), 7.67-7.31 (m, 1H), 7.93-8.01 (m, 3H), 8.48 (d, 1H, J = 6.0 Hz), 9.26 (s, 1H); 13C NMR (CD$_3$OD, 75 MHz) δ 23.5, 117.5, 127.1, 128.2, 128.9, 130.8, 132.7, 134.0, 143.1, 153.6, 172.9; HRESIMS calcd for C$_{11}$H$_{11}$N$_2$O [M+H]$^+$ 187.0871, found 187.0886.

19. 4-(N-acetylamino)phthalimide (Table 2, entry 19)

1H NMR (DMSO-d$_6$, 300 MHz) δ 2.11 (s, 3H), 7.73 (d, 1H, J = 8.1 Hz), 7.80-7.84 (m, 1H), 8.12-8.13 (m, 1H), 10.52 (s, 1H), 11.56 (brs, 1H); 13C NMR (DMSO-d$_6$, 75 MHz) δ 24.1, 112.3, 123.0, 123.9, 126.2, 134.0, 144.6, 168.7, 168.9, 169.1.

20. 6-(N-Acetylamino)chromone (Table 2, entry 20)$^{15}$

1H NMR (DMSO-d$_6$, 300 MHz) δ 2.07 (s, 3H), 6.30 (d, 1H, J = 6.0 Hz), 7.58 (d, 1H, J = 9.0 Hz), 7.88-7.92 (m, 1H), 8.24 (d, 1H, J = 6.0 Hz), 8.30 (s, 1H), 10.25 (s, 1H); 13C NMR (DMSO-d$_6$, 75 MHz) δ 24.8, 112.5, 114.0, 119.8, 125.2, 126.4, 137.4, 152.6, 157.5, 169.4, 171.1; HRESIMS calcd for C$_{11}$H$_{10}$NO$_3$ [M+H]$^+$ 204.0661, found 204.0643.
21. 4-(N-Acetylamino)chalcone (Table 2, entry 21)\textsuperscript{16}

![Structural formula]

\(^1\)H NMR (CD\textsubscript{3}OD, 600 MHz) \(\delta\) 2.13 (s, 1H), 7.53 (d, 2H, \(J = 6.0\) Hz), 7.61-7.75 (m, 7H), 8.05 (d, 2H, \(J = 6.0\) Hz); \(^{13}\)C NMR (CD\textsubscript{3}OD, 150 MHz) \(\delta\) 23.9, 120.8, 121.5, 129.5, 129.6, 130.5, 131.6, 134.0, 139.4, 142.3, 145.8, 171.7, 192.2; HRESIMS calcd for C\textsubscript{10}H\textsubscript{12}NO\textsubscript{3} [M+H]\textsuperscript{+} 266.1181, found 266.1169.

22. N-Phenylpropanamide (Table 3, entry 3)\textsuperscript{5}

![Structural formula]

\(^1\)H NMR (CD\textsubscript{3}OD, 300 MHz) \(\delta\) 1.20 (t, 3H, \(J = 7.5\) Hz), 2.39 (q, 2H, \(J = 7.5\) Hz), 7.08 (t, 1H, \(J = 7.4\) Hz), 7.27-7.32 (m, 2H), 7.54 (d, 2H, \(J = 7.7\) Hz); \(^{13}\)C NMR (CD\textsubscript{3}OD, 75 MHz) \(\delta\) 9.2, 30.0, 120.2, 124.0, 128.7, 138.9, 174.4; HRESIMS calcd for C\textsubscript{9}H\textsubscript{12}NO [M+H]\textsuperscript{+} 150.0919, found 150.0922.

23. N-Phenylbutanamide (Table 3, entry 4)\textsuperscript{17}

![Structural formula]

\(^1\)H NMR (CD\textsubscript{3}OD, 600 MHz) \(\delta\) 0.99-1.00 (m, 3H), 1.71-1.72 (m, 2H), 2.33 (s, 2H), 7.07 (s, 1H), 7.28 (s, 2H), 7.53 (m, 2H); \(^{13}\)C NMR (CD\textsubscript{3}OD, 150 MHz) \(\delta\) 13.8, 20.1, 39.7, 121.1, 124.9, 129.6, 139.7, 174.4; HRESIMS calcd for C\textsubscript{10}H\textsubscript{14}NO [M+H]\textsuperscript{+} 164.1075, found 164.1054.
$^1$H and $^{13}$C NMR spectra of isolated compounds

In $^1$H NMR spectra, peaks at $\delta$ 3.31 and 4.90 correspond to trace amount of protonated solvent in CD$_3$OD and peaks at $\delta$ 2.50 and 3.34 correspond to trace amount of protonated solvent in DMSO-d$_6$.

1. N-Acetylaniline in CDCl$_3$ (Table 2, entry 1)

$^1$H NMR

$^{13}$C NMR
2. *N*-Acetyl-4-fluoroaniline in CD$_3$OD (Table 2, entry 2)

\[
\begin{align*}
\text{H NMR} \\
\end{align*}
\]

\[
\begin{align*}
\text{C NMR} \\
\end{align*}
\]
3. \(N\)-Acetyl-4-chloroaniline in CD\(_3\)OD (Table 2, entry 3)

\[
\begin{align*}
\text{\(N\)-Acetyl-4-chloroaniline} \\
\end{align*}
\]

\(^1\)H NMR

\[
\begin{align*}
\text{\(^1\)H NMR} \\
\end{align*}
\]

\(^{13}\)C NMR

\[
\begin{align*}
\text{\(^{13}\)C NMR} \\
\end{align*}
\]
4. *N*-Acetyl-4-bromoaniline in CD$_3$OD (Table 2, entry 4)

\[
\begin{array}{c}
\text{Br} \\
\text{H NMR}
\end{array}
\]

$^1$H NMR

\[
\begin{array}{c}
\text{C NMR}
\end{array}
\]

$^{13}$C NMR
5. 4-(N-Acetylamino)toluene in CD$_3$OD (Table 2, entry 5)

\[
\begin{align*}
\text{H NMR} \\
\text{C NMR}
\end{align*}
\]
6. 4-(N-Acetylamino)phenol in CD$_3$OD (Table 2, entry 6)

\[
\text{HO}
\]
\[
\text{\textbullet}
\]
\[
\text{\textbullet}
\]

$^1$H NMR

$^1$C NMR
7. Methyl-3-(N-acetylamino)benzoate in CD$_3$OD (Table 2, entry 7)

![Chemical Structure Image]

$^1$H NMR

$^1$C NMR
8. 3-(N-Acetylamino)benzonitrile in CD$_3$OD (Table 2, entry 8)

$\text{H NMR}$

$\text{C NMR}$
9. 4-(N-Acetylamino)acetophenone in CD$_3$OD (Table 2, entry 9)

![Chemical structure of 4-(N-Acetylamino)acetophenone]

$^1$H NMR

$^1$C NMR
10. 1,4-Di-(N-acetylamino)benzene in DMSO-d$_6$ (Table 2, entry 10)

\[
\begin{align*}
\text{H NMR} & \\
\text{C NMR}
\end{align*}
\]
11. 3-(N-Acetylamino)styrene in CD$_3$OD (Table 2, entry 11)

$\text{HN}$

$\text{C}$

$\text{H NMR}$

$\text{13C NMR}$
12. \(N\)-Acetyl-3-nitroaniline in CD\(_3\)OD (Table 2, entry 12)

\[
\text{H NMR}
\]

\[
\text{C NMR}
\]
13. 1,4-Di-(N-acetylamino)benzene in DMSO-d$_6$ (Table 2, entry 13)

\[
\begin{align*}
\text{1H NMR} \\
\end{align*}
\]

\[
\begin{align*}
\text{13C NMR} \\
\end{align*}
\]
14. 2-(N-Acetylamino)fluorine in CD$_3$OD (Table 2, entry 14)

$\text{\includegraphics[width=0.5\textwidth]{an_image.png}}$

$^1$H NMR

$^1$C NMR
15. 4-(N-Acylamino)phthalide in DMSO-d$_6$ (Table 2, entry 15)

$^1$H NMR

$^{13}$C NMR
16. 6-(N-Acetylamino)benzothiazole in CD$_3$OD (Table 2, entry 16)

^1^H NMR

^1^C NMR
17. 4-(N-Acetylamo)-2,1,3-benzothiadiazole in CD$_3$OD (Table 2, entry 17)

$^{1}H$ NMR

$^{13}C$ NMR
18. 5-(N-Acetylamino)isoquinoline in CD$_3$OD (Table 2, entry 18)

\[
\begin{align*}
\text{H NMR} & \\
\text{C NMR} &
\end{align*}
\]
19. 4-(N-acetylamino)phthalimide in DMSO-d$_6$ (Table 2, entry 19)

$^1$H NMR

$^1$C NMR
20. 6-(N-Acetylamino)chromone in DMSO-d$_6$ (Table 2, entry 20)

\[
\begin{align*}
\text{H NMR} \\
\end{align*}
\]

\[
\begin{align*}
\text{C NMR} \\
\end{align*}
\]
21. 4-(N-Acetylamino)chalcone in CD$_3$OD (Table 2, entry 21)

\[ \text{Chemical structure image} \]

$^1$H NMR

$^1$C NMR
22. *N*-Phenylpropanamide in CD$_3$OD (Table 3, entry 3)

\[
\text{\begin{tikzpicture}
\draw[thick] (0,0) .. controls (1,1) and (2,1) .. (3,0);
\end{tikzpicture}}
\]

$^1$H NMR

\begin{center}
\includegraphics{h_nmr}
\end{center}

$^1$C NMR

\begin{center}
\includegraphics{c_nmr}
\end{center}
23. *N*-Phenylbutanamide in CD$_3$OD (Table 3, entry 4)

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

$^1$H NMR

$^1$C NMR
HRMS (ESI) of isolated compounds

1. N-Acetylaniline (Table 2, entry 1)

\[
\text{\includegraphics{image.png}}
\]
2. *N*-Acetyl-4-fluoroaniline (Table 2, entry 2)
3. *N*-Acetyl-4-chloroaniline (Table 2, entry 3)
4. *N*-Acetyl-4-bromoaniline (Table 2, entry 4)
5.  4-(N-Acetylamino)toluene (Table 2, entry 5)
6. 4-(N-Acetylamino)phenol (Table 2, entry 6)
7. 3-(N-Acetylamino)benzonitrile (Table 2, entry 8)
8. 4-(N-Acetylamino)acetophenone (Table 2, entry 9)
9. 1,4-Di-(N-acetylamino)benzene (Table 2, entry 10)
10. N-Acetyl-3-nitroaniline (Table 2, entry 12)
11. 1,4-Di-(N-acetylamino)benzene (Table 2, entry 13)
12. 2-\((N\text{-Acetylamino})\text{fluorine}\) (Table 2, entry 14)
13. 4-(N-Actylamino)phthalide (Table 2, entry 15)
14. 6-(N-Acetylamino)benzothiazole (Table 2, entry 16)
15. 4-(N-Acetylamino)-2,1,3-benzothiadiazole (Table 2, entry 17)
16. 6-(N-Acetylamino)chromone (Table 2, entry 20)
17. 4-(N-Acetylamino)chalcone (Table 2, entry 21)
18. N-Phenylpropanamide (Table 3, entry 3)
19. N-Phenylbutanamide (Table 3, entry 4)
Mechanistic study

Experimental procedure for reaction of PMHS with AcOH

PMHS (4.0 mmol) was treated with AcOH (2.0 mL) at 100 °C for 12 h. The solvent was evaporated under reduced pressure and resultant product was dissolved in CDCl$_3$ for NMR analysis.

Experimental procedure for reaction of PMHS with CoPc

PMHS (4.0 mmol) was treated with CoPc (1.0 mol%) at 100 °C for 12 h under solvent free conditions. The resultant product was dissolved in CDCl$_3$ for NMR analysis.

$^1$HNMR spectrum of PMHS in CDCl$_3$
$^1$HNMR spectrum of PMHS + AcOH reaction (600 MHz, CDCl$_3$)

$^1$HNMR spectrum of PMHS + CoPc reaction (600 MHz, CDCl$_3$)
References