Electronic Supplementary Information

A Non-isothiocyanate Route to Synthesize Trisubstituted Thioureas of Arylamines using \textit{in situ} Generated Dithiocarbamates

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<table>
<thead>
<tr>
<th>Contents</th>
<th>Page Nos</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>General experimental</td>
</tr>
<tr>
<td>2</td>
<td>\textbf{ESI-Scheme 1}: Reaction of triethylammonium dithiocarbamate of aniline with piperidine</td>
</tr>
<tr>
<td>3</td>
<td>\textbf{Table 1} (Electronic Supporting Information): Screening studies</td>
</tr>
<tr>
<td>4</td>
<td>$^1$H, $^{13}$C NMR spectra</td>
</tr>
</tbody>
</table>
**General experimental:** NMR spectra were recorded on a BRUKER-AV400 spectrometer, using CDCl$_3$ and DMSO-d$_6$. Tetramethysilane (TMS; δ = 0.00 ppm; CDCl$_3$) and residual solvent signal (δ = 2.5 ppm; DMSO- d$_6$) served as internal standards for $^1$H NMR. The corresponding solvent signal (CDCl$_3$: δ = 77.00 ppm; DMSO: δ = 39.50 ppm ) was used as internal standards for $^{13}$C NMR. IR spectra were measured using a JASCO FT/IR-410 spectrometer, and Perkin-Elmer FT/IR Spectrum BX, GX. Mass spectra were measured with Micromass Q-Tof (ESI-HRMS). Melting points of the products were recorded using Buchi – M560. Column chromatography was performed on Silica gel 100-200 mesh. 3-Bromoaniline, 2-fluroaniline, 3,5-bis(trifluoromethyl)aniline, 4-aminobenzenesulfonamide, 4-aminobenzamide were purchased from Sigma-Aldrich Co., and 2,6-dimethylaniline was obtained from Alfa Aesar . All other chemicals were purchased from a chemical supplier and used as received.

**ESI-Scheme 1: Reaction of triethylammonium dithiocarbamate of aniline with piperidine**

![Chemical Structure](attachment:image.png)

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Product Yield</th>
<th>Isolated Yield</th>
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<tbody>
<tr>
<td>1 mmol H$_2$O, 10h</td>
<td>54 %</td>
<td>13 %</td>
</tr>
<tr>
<td>1 mmol H$_2$O, 10h</td>
<td>55 %</td>
<td>-</td>
</tr>
<tr>
<td>1 mmol H$_2$O, 18h</td>
<td>59 %</td>
<td>-</td>
</tr>
<tr>
<td>1 mmol CH$_3$CN, 6h</td>
<td>68 %</td>
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<tr>
<td>2 mmol CH$_3$CN, 6h</td>
<td>52 %</td>
<td>48 %</td>
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</table>

a Isolated yields. b NMR conversion
ESI- Table 1: (Electronic Supplementary Information): Screening studies

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>1a (mmol)</th>
<th>2</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>R = o-OMe</td>
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<td>66</td>
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<tr>
<td>2</td>
<td>1</td>
<td>R = o-OMe</td>
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<tr>
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<td>22</td>
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<td>76</td>
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<tr>
<td>24</td>
<td>2</td>
<td>R = H</td>
<td>6</td>
<td>96</td>
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</table>

a Conditions: 2 (1mmol), triethylamine (1.1 equiv with respect to 1a), CS$_2$ (1.2 equiv with respect to 1a), CH$_3$CN (3 mL). b Based on $^1$H NMR data. c The reaction did not go to completion even after 24 h. d Isolated yield. nd: not detected.
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$^1$H NMR (CDCl$_3$ 400 MHz)
$^{13}$C NMR (CDCl$_3$ 100 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
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$^{13}$C NMR (CDCl$_3$ 100 MHz)

![Chemical Structure](image)
13C NMR (CDCl3, 400 MHz)
$^1$H NMR (400 MHz, DMSO-d$_6$)
$^{13}$C NMR (400 MHz, DMSO-d$_6$)
The image contains an NMR spectrum with chemical shifts in ppm. The spectrum includes peaks at 7.7240, 7.1398, 7.0916, 7.0997, 7.0944, 6.8944, 6.8424, 7.0697, 7.0916, 7.1538, and 7.2740 ppm. There is also a structure labeled as 3af, indicating the chemical identity of the compound. The spectrum was recorded using CDCl₃ as a solvent at 400 MHz. The electronic supplementary material (ESI) for RSC Advances is referenced in the image.
$^{13}$C NMR (CDCl$_3$ 400 MHz)
$^1$H NMR (CDCl$_3$ 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
Electronic Supplementary Material (ESI) for RSC Advances
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$^1$H NMR (CDCl$_3$ 400 MHz)
$^{13}$C NMR (CDCl$_3$ 100 MHz)
$^1$H NMR (CDCl$_3$ 400 MHz)
$^{13}$C NMR (CDCl$_3$ 100 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)
\[\text{\^{13}}\text{C NMR (CDCl}_3\text{100 MHz)}\]
$^{1}$H NMR (DMSO-$d_6$, 400 MHz)
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$^{13}$C NMR (DMSO-$d_6$ 100 MHz)
$^{13}$C NMR (CDCl$_3$ 100 MHz)
$^1$H NMR (DMSO-d$_6$, 400 MHz)
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1H NMR (DMSO-d6, 400 MHz)
$^{13}$C NMR (DMSO-$d_6$ 100 MHz)
$^1$H NMR (CDCl$_3$ 400 MHz)
$^{13}$C NMR (CDCl$_3$ 100 MHz)

- 220
- 200
- 180
- 160
- 140
- 120
- 100
- 80
- 60
- 40
- 20
- 0 ppm
1H NMR (DMSO-d$_6$, 400 MHz)
$^{13}\text{C NMR (DMSO-d$_6$) 100 MHz}$
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$^1$H NMR (CDCl$_3$, 100 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^1$H NMR (DMSO-d$_6$ 100 MHz)
$^{13}$C NMR (DMSO-$d_6$, 100 MHz)
$^{1}H$ NMR (CDCl$_3$ 400 MHz)
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$^{13}$C NMR (CDCl$_3$ 100 MHz)
$^1$H NMR (DMSO-d$_6$ 400 MHz)
$^{13}$C NMR (DMSO-$d_6$, 100 MHz)
$^{13}$C NMR (DMSO-d$_6$, 100 MHz)
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$^{13}$C NMR (CDCl$_3$, 100 MHz)
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$^1$H NMR (CDCl$_3$ 400 MHz)


$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^1$H NMR (DMSO-$d_6$, 100 MHz)
^13C NMR (DMSO-d$_6$ 100 MHz)
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$^1$H NMR (CDCl$_3$, 400 MHz)
$^1$H NMR (CDCl$_3$ 400 MHz)
$^{13}$C NMR (CDCl$_3$ 100 MHz)
$^1$H NMR (CDCl$_3$, 100 MHz)
\[ 3gq \]

\[^{1}\text{H NMR (DMSO-}d_6\text{ 400 MHz)} \]
$^1$H NMR (DMSO-$d_6$ 400 MHz)
$^{13}$C NMR (DMSO-$d_6$, 100 MHz)