SUPPORTING INFORMATION

CO-free, Aqueous Mediated, Instant and Selective Reduction of Nitrobenzene via Robustly Stable Chalcogen Stabilised Iron carbonyl Clusters (Fe₃E₂(CO)₉, E= S, Se, Te)

Charu Sharma, Avinash K. Srivastava, Aditi Soni, Sangeeta Kumari, Raj K. Joshi*

Department of Chemistry, Malaviya National Institute of Technology, Jaipur 302017, Rajasthan, India, Email: rkjoshi.chy@mnit.ac.in

Experimental Details: The ¹H, ¹³C {¹H} NMR spectra were recorded using JEOL ECS-400 spectrometer (operating at 400 MHz for ¹H and 100 MHz for ¹³C).

Chemicals and reagents: Reactants, reagents, chemicals and solvents available commercially within the country were used.

Experimental Section

In a clean reaction tube, take Fe₃Se₂(CO)₉ catalyst (3 mol%) and derivative of nitroarenes (1 mmol). To this added hydrazine hydrate (2 mmol) and water as a reaction medium. Above mixture is heated at 110°C for 15 min. Through TLC monitoring product formation was investigated. After that reaction mixture was cooled at room temperature, by adding water and EtOAc the organic layer was extracted. By using anhydrous Na₂SO₄ extracted layer was dried. Under reduced pressure solvent was evaporated to get the crude product. Finally, the product was purified through column chromatography.
### Characterisation Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>1H NMR (400MHz, CDCl₃)</th>
<th>13C NMR (100MHz, CDCl₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline¹</td>
<td></td>
<td>δ = 7.23-7.18 (m, 2H), 6.82-6.79 (t, 1H), 6.72-6.70 (t, 2H), 3.63 (s, 2H)</td>
<td>δ = 146.33, 129.42, 118.70, 115.03</td>
</tr>
<tr>
<td>4-Bromoaniline²</td>
<td></td>
<td>δ = 7.11-7.07 (m, 2H), 6.51-6.48 (m, 2H), 5.21 (s, 2H)</td>
<td>δ = 148.52, 131.85, 116.34, 106.68</td>
</tr>
<tr>
<td>4-Aminobenzonitrile³</td>
<td></td>
<td>δ = 7.38-7.34 (m, 2H), 6.63-6.60 (m, 2H), 4.25 (s, 2H)</td>
<td>δ = 150.76, 133.77, 113.97, 99.95</td>
</tr>
<tr>
<td>4-Iodoaniline⁴</td>
<td></td>
<td>δ = 7.41-7.37 (m, 2H), 6.51-6.44 (m, 2H), 3.53 (s, 2H)</td>
<td>δ = 145.56, 137.83, 117.25, 78.87</td>
</tr>
<tr>
<td>4-methoxyaniline⁵</td>
<td></td>
<td>δ = 6.76-6.72 (m, 2H), 6.65-6.61 (m, 2H), 3.73 (s, 3H), 3.42 (s, 2H)</td>
<td>δ = 152.88, 140.12, 116.51, 114.92, 55.33</td>
</tr>
<tr>
<td>2-Bromoaniline⁶</td>
<td></td>
<td>δ = 7.29-7.27 (m, 1H), 7.03-6.98 (m, 1H), 6.76-6.73 (m, 1H), 6.44-6.40 (m, 1H), 5.23 (s, 2H)</td>
<td>δ = 146.28, 132.62, 128.80, 117.85, 115.92, 107.95</td>
</tr>
<tr>
<td>Compound</td>
<td>1H NMR (400MHz, CDCl3)</td>
<td>13C NMR (100MHz, CDCl3)</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------------------------</td>
<td>-------------------------</td>
<td></td>
</tr>
<tr>
<td>Benzene-1,4-diamine(^7)</td>
<td>δ = 6.55 (s, 4H), 3.28 (s, 4H)</td>
<td>δ = 138.85, 116.42</td>
<td></td>
</tr>
<tr>
<td>4-Aminophenol(^8)</td>
<td>δ = 8.30 (s, 1H), 6.44-6.36 (m, 4H), 4.35 (s, 2H)</td>
<td>δ = 148.73, 141.16, 116.04, 115.74</td>
<td></td>
</tr>
<tr>
<td>4-Chloroaniline(^1)</td>
<td>δ = 7.10-7.08 (m, 2H), 6.60-6.57 (m, 2H), 3.65 (s, 2H)</td>
<td>δ = 144.50, 129.42, 123.16, 115.80</td>
<td></td>
</tr>
<tr>
<td>Benzene-1,2-diamine(^7)</td>
<td>δ = 6.73-6.68 (m, 4H), 3.32 (s, 4H)</td>
<td>δ = 134.82, 120.37, 116.84</td>
<td></td>
</tr>
<tr>
<td>o-Toluidine(^7)</td>
<td>δ = 7.05-7.01 (t, 2H), 6.72-6.66 (m, 2H), 3.59 (s, 1H), 2.14 (s, 3H)</td>
<td>δ = 144.12, 130.88, 126.82, 121.69, 119.09, 113.97, 18.09</td>
<td></td>
</tr>
<tr>
<td>4-Nitroaniline(^7)</td>
<td>δ = 8.07-8.05 (d, 2H), 6.63-6.59(m, 2H), 4.35 (s, 4H)</td>
<td>δ = 152.11, 139.15, 126.16, 113.18</td>
<td></td>
</tr>
<tr>
<td>Benzene-1,3-diamine(^7)</td>
<td>δ = 6.95-6.91 (t, 1H), 6.12-6.10 (m, 2H), 6.02-6.01 (d, 1H)</td>
<td>δ = 147.61, 130.29, 105.55, 102.27</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Structure</td>
<td>1H NMR (400MHz, CDCl₃)</td>
<td>13C NMR (100MHz, CDCl₃)</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-----------</td>
<td>------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>(4-Aminophenyl)methanol⁴</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>δ = 7.16-7.13 (d, 2H), 6.67-6.64 (m, 4H), 4.53 (s, 2H)</td>
<td>δ = 146.15, 131.49, 129.11, 114.66, 65.42</td>
</tr>
<tr>
<td>2,5-Dibromoaniline²</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>δ = 7.24-7.22 (d, 1H), 6.91-6.88 (t, 1H), 6.73-6.67 (m, 1H), 4.12 (s, 2H)</td>
<td>δ = 145.96, 144.49, 133.10, 121.98, 117.25, 108.07</td>
</tr>
<tr>
<td>p-Toluidine⁴</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>δ = 6.99-6.97 (d, 2H), 6.63-6.61 (d, 2H), 3.53 (s, 2H), 2.26 (s, 3H)</td>
<td>δ = 143.94, 129.42, 127.66, 115.37, 20.33</td>
</tr>
<tr>
<td>naphthalen-1-amine²</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>δ = 7.86-7.80 (m, 2H), 7.51-7.46 (m, 2H), 7.37-7.31 (m, 2H), 6.80-6.78 (d, 1H), 4.41 (s, 2H)</td>
<td>δ = 142.21, 134.51, 128.69, 126.56, 125.95, 125.00, 123.69, 120.96, 119.07, 109.73</td>
</tr>
<tr>
<td>1-(3-aminophenyl)ethan-1-one</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>δ = 7.31-7.29 (d, 2H), 7.24-7.19 (m, 2H), 6.86-6.84 (m, 1H), 3.82 (s, 2H), 2.54 (s, 3H)</td>
<td>δ = 198.81, 146.73, 137.84, 129.43, 119.47, 114.26, 99.56, 26.60</td>
</tr>
</tbody>
</table>
Figure s1: (a) FTIR spectrum of Unused Fe$_3$Se$_2$(CO)$_9$, (b) FTIR spectrum of Used Fe$_3$Se$_2$(CO)$_9$.
References


