

## Effective metal-free electrooxidative thiocyanation of anilines

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### Experimental

$^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{DMSO-}d_6$  on a Bruker Avance 300 instrument (300.13 MHz for  $^1\text{H}$ ). HRMS spectra were recorded on a Bruker micrOTOF II instrument. Reagents, solvents and silica gel 0.035–0.070 mm, 60 Å for column chromatography (Acros Organics) were used as purchased.

CV studies were carried out in a temperature-controlled (25 °C) cell ( $V = 10$  ml) using a P30JM potentiostat (Elins, scan rate  $0.1 \text{ V s}^{-1}$ ). A glassy carbon (GC) disk 3 mm in diameter in a Teflon casing was used as the working electrode. SCE separated from the solution by a salt bridge (filled with the supporting electrolyte (0.1M solution of  $\text{NaClO}_4$  in MeCN) was used as the reference electrode. A GC plate ( $S = 3 \text{ cm}^2$ ) was used as the counter electrode. The concentration of all studied compounds was 0.002 M.

Preparative electrolysis was carried out using the above-mentioned potentiostat and supporting electrolyte (85 ml) in a glass temperature-controlled (25 °C) divided cell equipped with a tracing-paper diaphragm, a glassy carbon (GC) anode ( $S = 10 \text{ cm}^2$ ) and GC cathode ( $S = 3 \text{ cm}^2$ ).

*General procedure:* A solution of  $\text{NH}_4\text{SCN}$  (4 mmol) and aniline **2a-e,4** (1 mmol) in the supporting electrolyte (70 ml) was placed into the anodic compartment, and the supporting electrolyte (15 ml) was placed into the cathodic compartment. The process was performed at  $E_{\text{anode}} = 0.60 \text{ V}$  (vs. SCE) by passing  $2F$ – $3F$  ( $Q = 194 - 298 \text{ C}$ ) of electricity (for a one-electron oxidation of thiocyanate ion or for a two-electron oxidation of initial arene). After the solvent was distilled off *in vacuo*, the residue was diluted in  $\text{H}_2\text{O}$  (15 ml) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $4 \times 20 \text{ ml}$ ). The combined extracts were dried with anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. Column chromatography on  $\text{SiO}_2$  using  $\text{CH}_2\text{Cl}_2$  as the eluent gave pure products **3a-e,6**, which were identified using  $^1\text{H}$  NMR spectroscopy and HRMS according to the reported<sup>S1-S3</sup> characteristics.

*4-Thiocyanatoaniline 3a*: yellow crystals, mp 54–56 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.78 (br s, 2 H, NH<sub>2</sub>), 6.65 (d, 2 H, C<sup>2</sup>H, C<sup>6</sup>H, *J*<sub>2(3),6(5)</sub> 8.1 Hz), 7.33 (d, 2 H, C<sup>3</sup>H, C<sup>5</sup>H, *J*<sub>3(2),5(6)</sub> 8.1 Hz). HRMS (ESI), *m/z*: 151.0323 (calc. for C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>S, *m/z*: 151.0324 [M + H]<sup>+</sup>).

*N-Methyl-4-thiocyanatoaniline 3b*: yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.84 (s, 3 H, Me), 4.09 (br s, 1 H, NH), 6.56 (d, 2 H, C<sup>2</sup>H, C<sup>6</sup>H, *J*<sub>2(3),6(5)</sub> 8.6 Hz), 7.36 (d, 2H, C<sup>3</sup>H, C<sup>5</sup>H, *J*<sub>3(2),5(6)</sub> 8.6 Hz). HRMS (ESI), *m/z*: 165.0477 (calc. for C<sub>8</sub>H<sub>9</sub>N<sub>2</sub>S, *m/z*: 165.0481 [M + H]<sup>+</sup>).

*N-Phenyl-4-thiocyanatoaniline 3c*: brownish crystals, mp 61–63 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 6.95 (t, 1 H, N-Ph, C<sup>4</sup>H, *J*<sub>4',3'(5')</sub> 7.3 Hz), 7.08–7.19 (m, 4H, Ph, N-Ph, C<sup>2</sup>H, C<sup>6</sup>H, C<sup>2'</sup>H, C<sup>6'</sup>H), 7.29 (dd, 2 H, C<sup>3</sup>H, C<sup>5</sup>H, *J*<sub>3'(5'),4'</sub> 7.3 Hz, *J*<sub>3'(5'),2'(6')</sub> 8.4 Hz), 7.5 (d, 2 H, Ph, C<sup>3</sup>H, C<sup>5</sup>H, *J*<sub>3(5),2(6)</sub> 8.7 Hz), 8.65 (br s, 1 H, NH). HRMS (ESI), *m/z*: 227.0642 (calc. for C<sub>13</sub>H<sub>11</sub>N<sub>2</sub>S, *m/z*: 227.0637 [M + H]<sup>+</sup>).

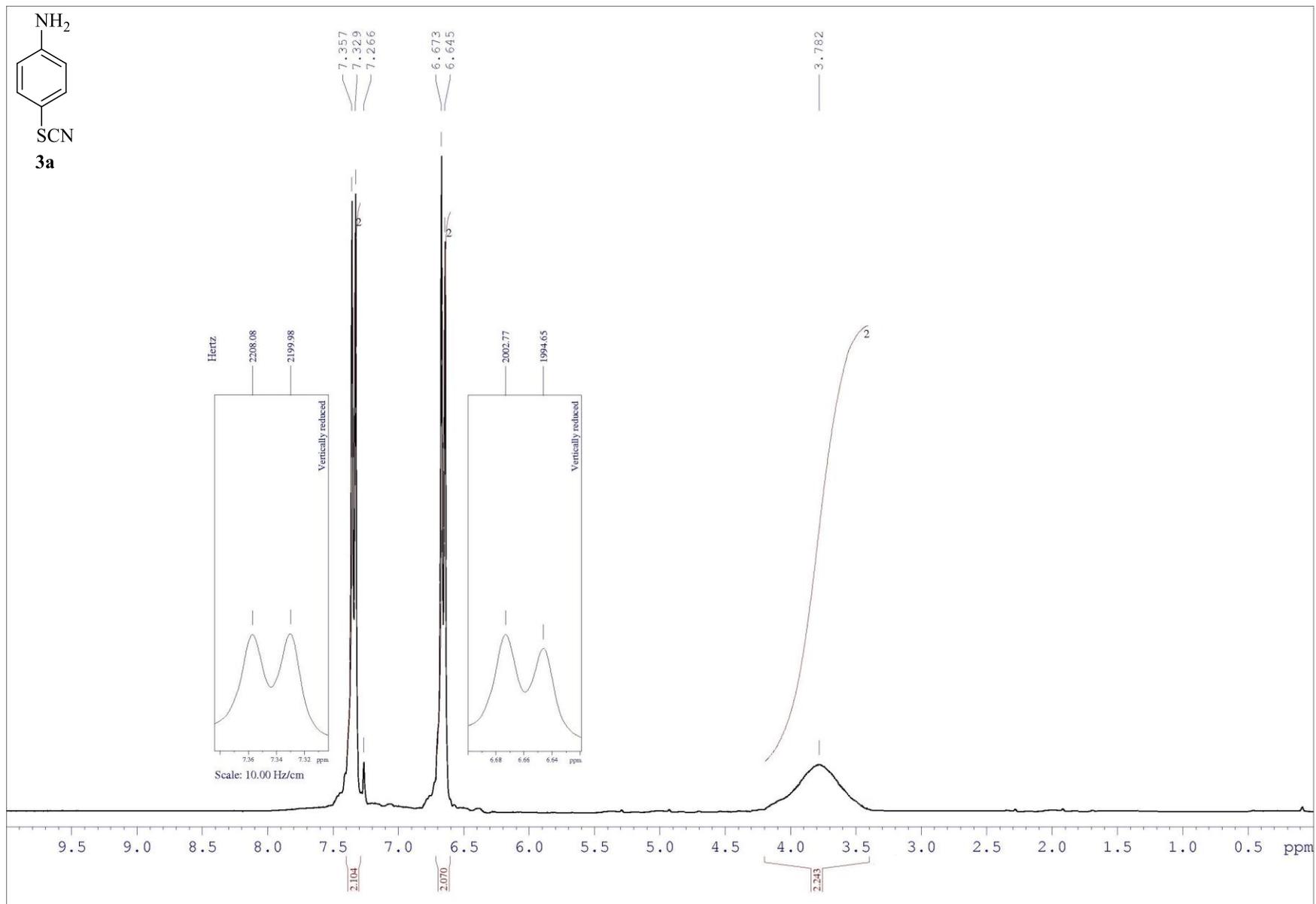
*N,N-Dimethyl-4-thiocyanatoaniline 3d*: yellow crystals, mp 70–72 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.00 (s, 6 H, Me), 6.66 (d, 2 H, C<sup>2</sup>H, C<sup>6</sup>H, *J*<sub>2(3),6(5)</sub> 8.8 Hz), 7.40 (d, 2 H, C<sup>3</sup>H, C<sup>5</sup>H, *J*<sub>3(2),5(6)</sub> 8.8 Hz). HRMS (ESI), *m/z*: 179.0642 (calc. for C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>S, *m/z*: 179.0637 [M + H]<sup>+</sup>).

*N,N-Diethyl-4-thiocyanatoaniline 3e*: yellow oil. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 1.05 (t, 6 H, Me, <sup>3</sup>*J* 7.0 Hz), 1.05 (q, 4 H, CH<sub>2</sub>, <sup>3</sup>*J* 7.0 Hz), 6.73 (d, 2H, C<sup>2</sup>H, C<sup>6</sup>H, *J*<sub>2(3),6(5)</sub> 9.0 Hz), 7.42 (d, 2H, C<sup>3</sup>H, C<sup>5</sup>H, *J*<sub>3(2),5(6)</sub> 9.0 Hz). HRMS (ESI), *m/z*: 207.0956 (calc. for C<sub>11</sub>H<sub>15</sub>N<sub>2</sub>S, *m/z*: 207.0950 [M + H]<sup>+</sup>).

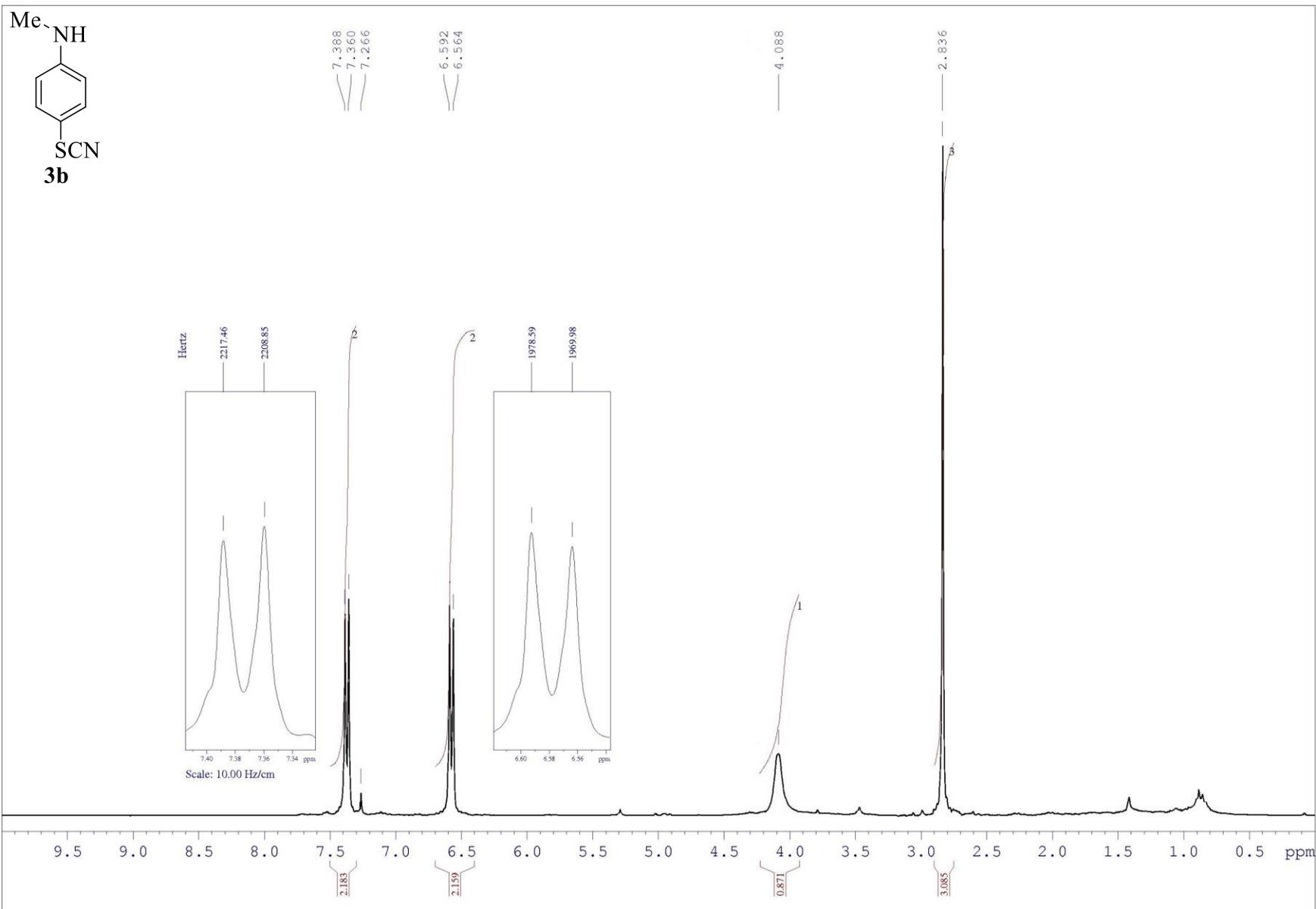
*6-Methoxybenzo[d]thiazol-2-amine 6*: brown crystals, mp 158–160 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 3.64 (br s, 2 H, NH<sub>2</sub>), 3.72 (s, 3 H, OMe), 6.83 (dd, 1 H, Ph, C<sup>7</sup>H, *J*<sub>7,8</sub> 8.7 Hz, *J*<sub>7,5</sub> 2.1 Hz), 7.25 (d, 1 H, Ph, C<sup>7</sup>H, *J*<sub>8,7</sub> 8.7 Hz), 7.33 (d, 1 H, Ph, C<sup>5</sup>H, *J*<sub>5,7</sub> 2.1 Hz). HRMS (ESI), *m/z*: 181.0435 (calc. for C<sub>8</sub>H<sub>9</sub>N<sub>2</sub>OS, *m/z*: 181.0430 [M + H]<sup>+</sup>).

## References

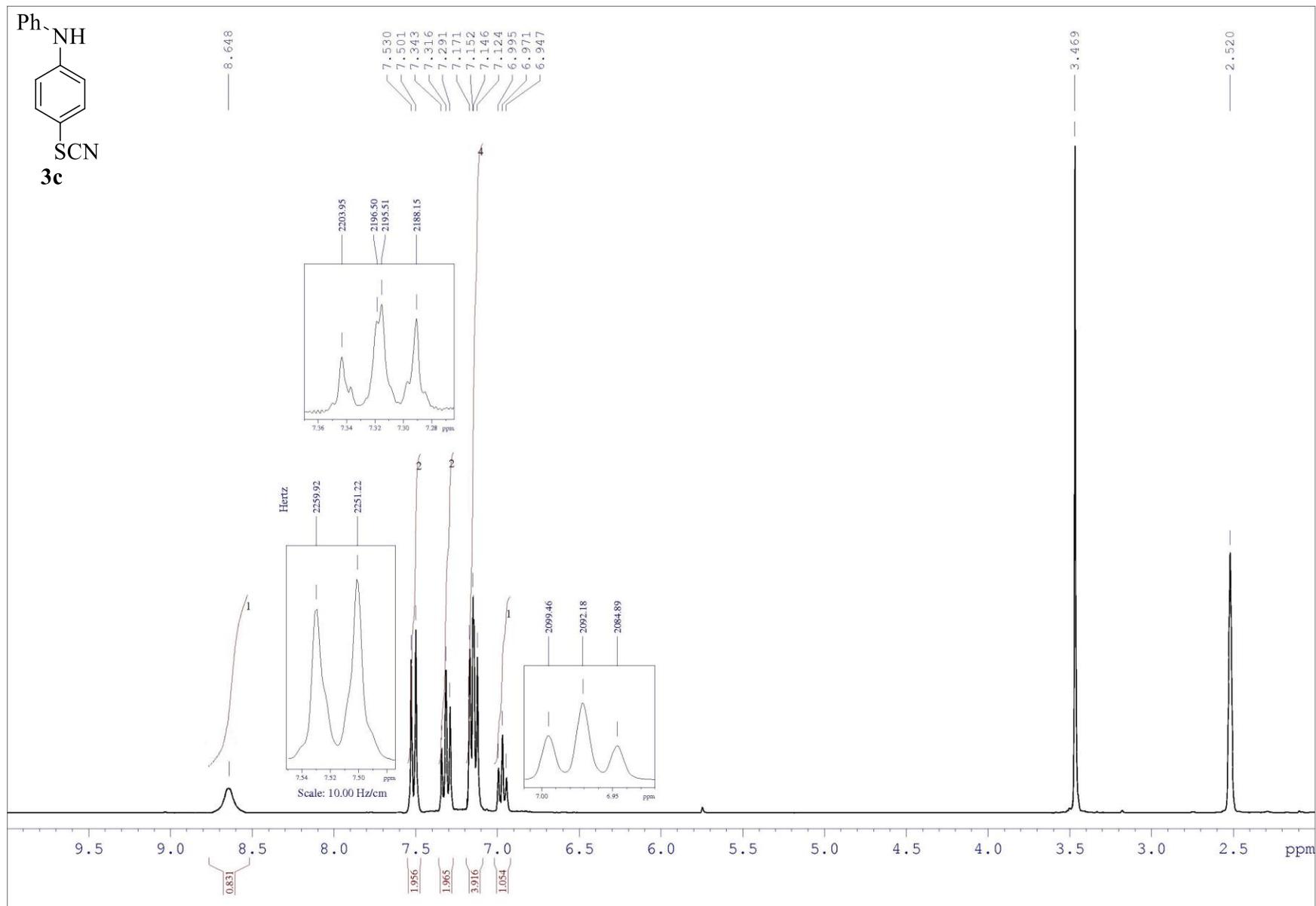
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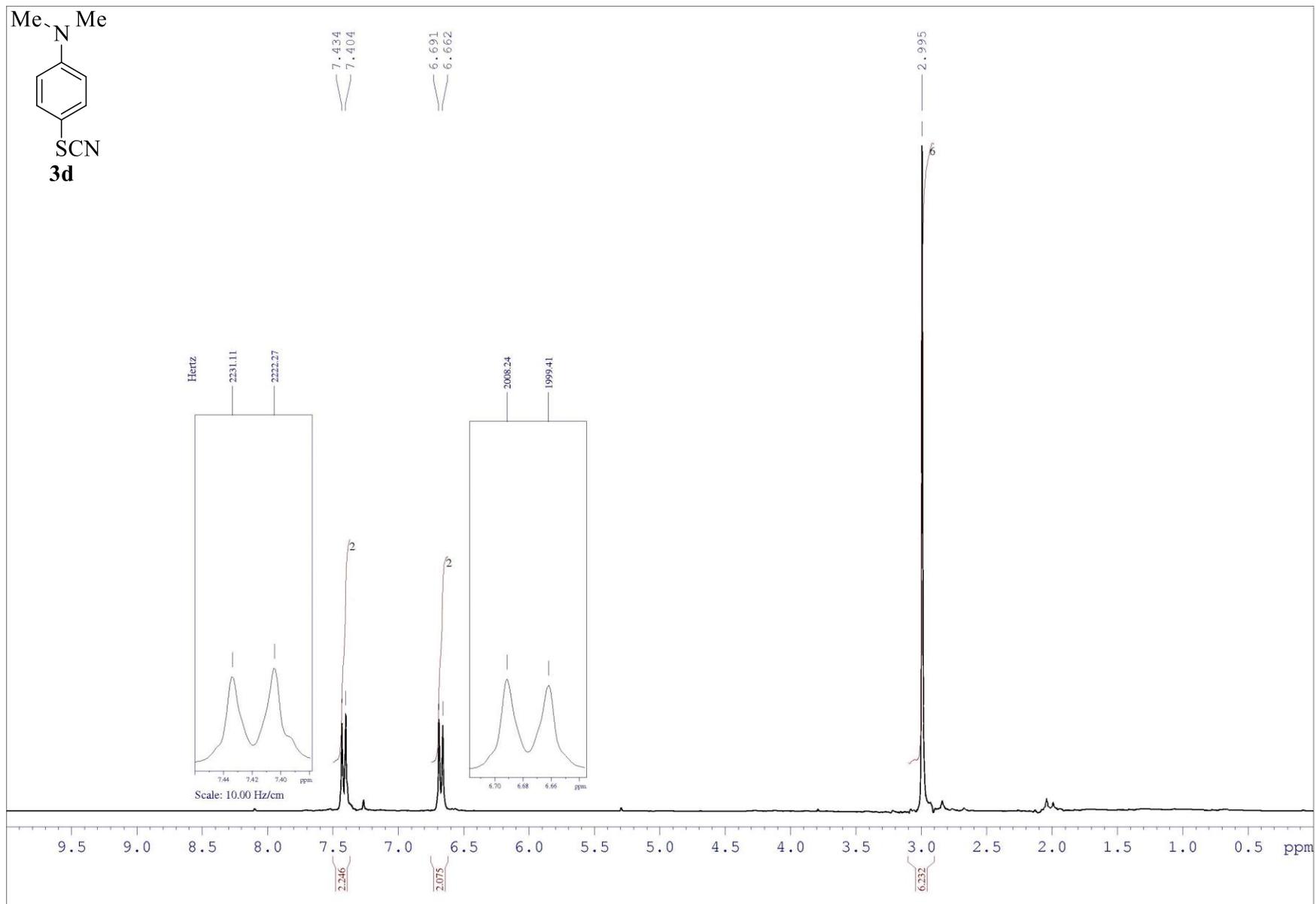
**Figure S1**  $^1\text{H}$  NMR spectrum of compound **3a** in  $\text{CDCl}_3$



**Figure S2**  $^1\text{H}$  NMR spectrum of compound **3b** in  $\text{CDCl}_3$



**Figure S3** <sup>1</sup>H NMR spectrum of compound **3c** in DMSO-*d*<sub>6</sub>



**Figure S4**  $^1\text{H}$  NMR spectrum of compound **3d** in  $\text{CDCl}_3$

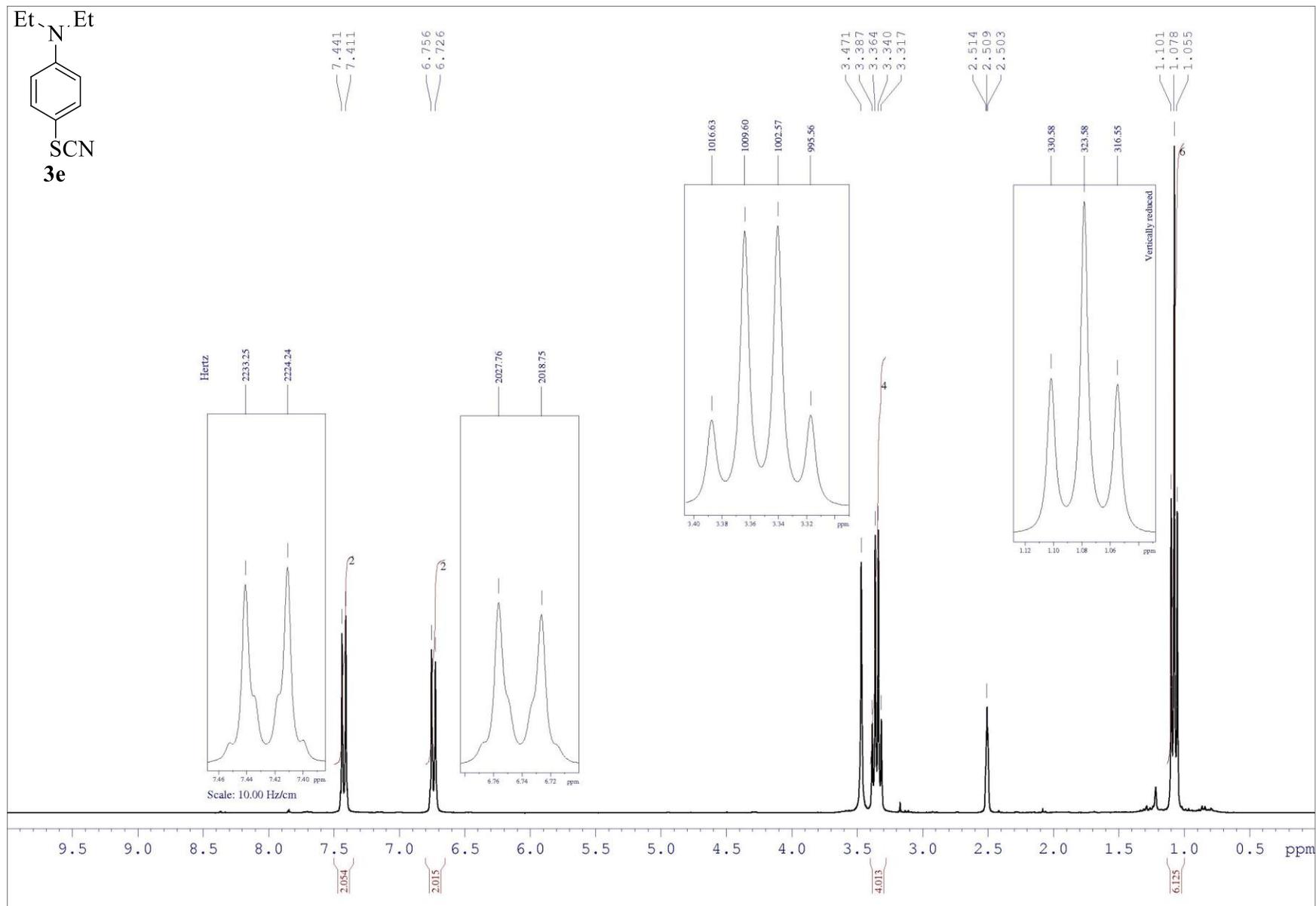
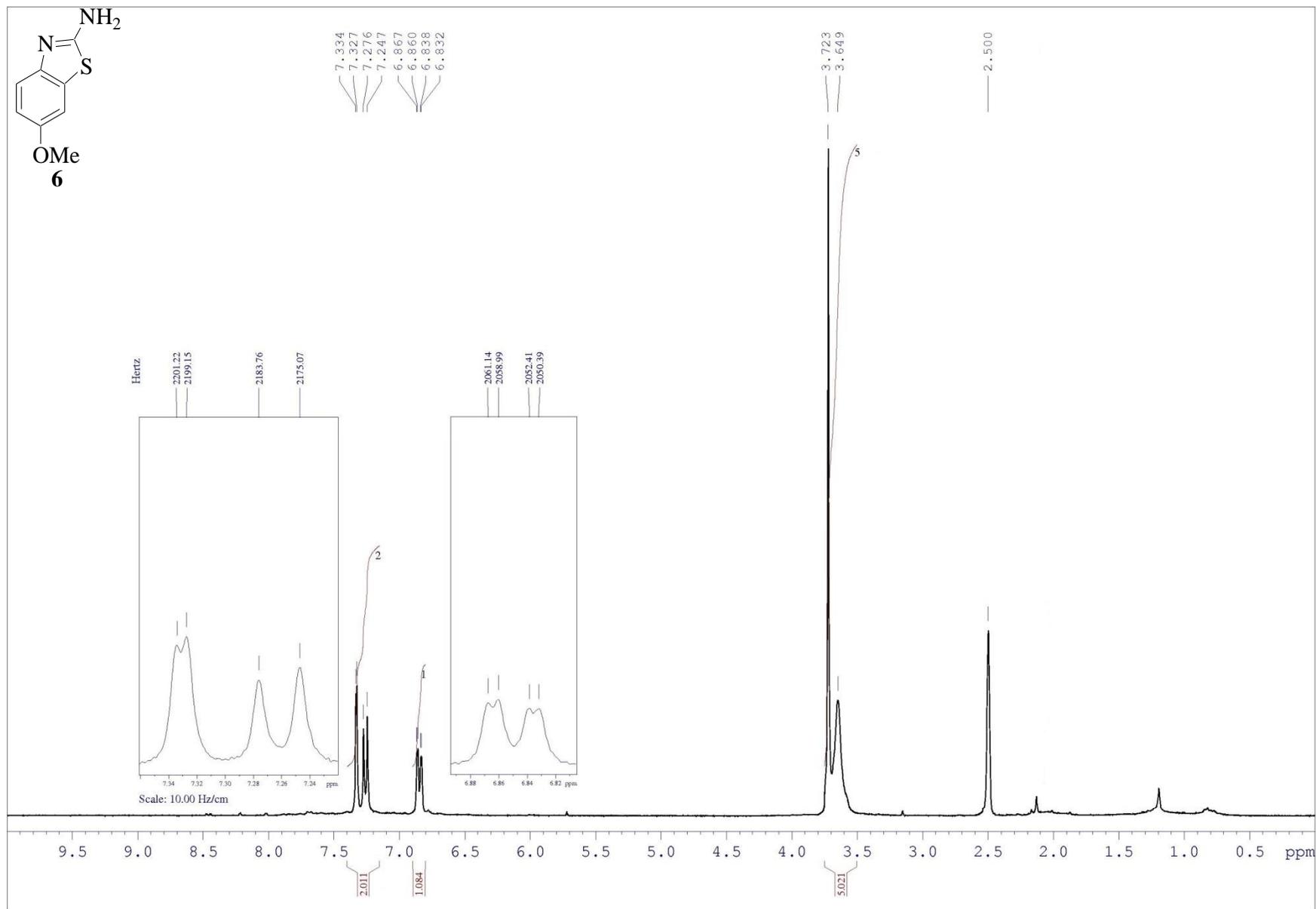


Figure S5  $^1\text{H}$  NMR spectrum of compound **3e** in  $\text{DMSO-}d_6$



**Figure S6**  $^1\text{H}$  NMR spectrum of compound **6** in  $\text{DMSO-}d_6$