

# Green reusable Pd nanoparticles embedded in phytochemical resins for mild hydrogenations of nitroarenes

Mohamed Enneimy, Claude Le Drian, and Jean-Michel Becht\*

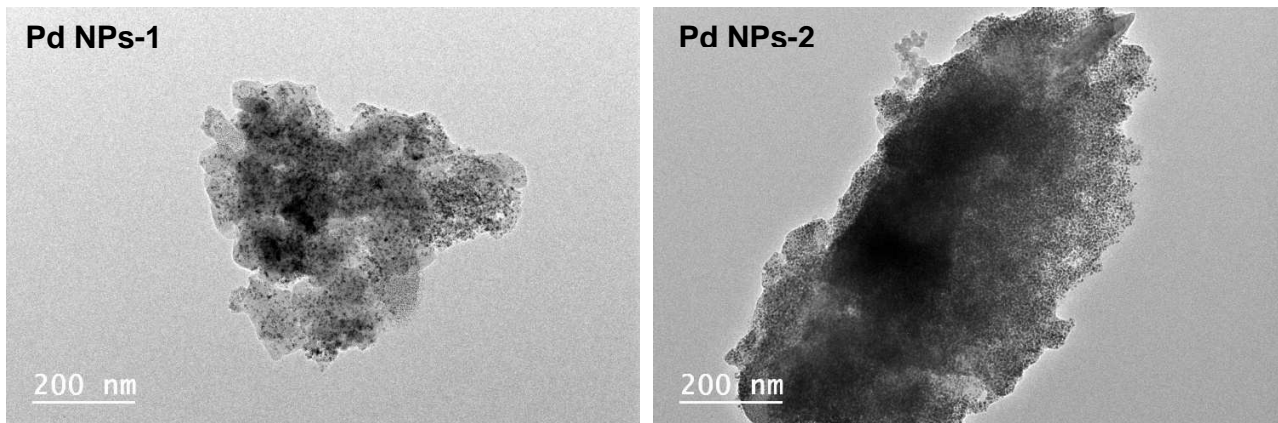
## ELECTRONIC SUPPORTING INFORMATION

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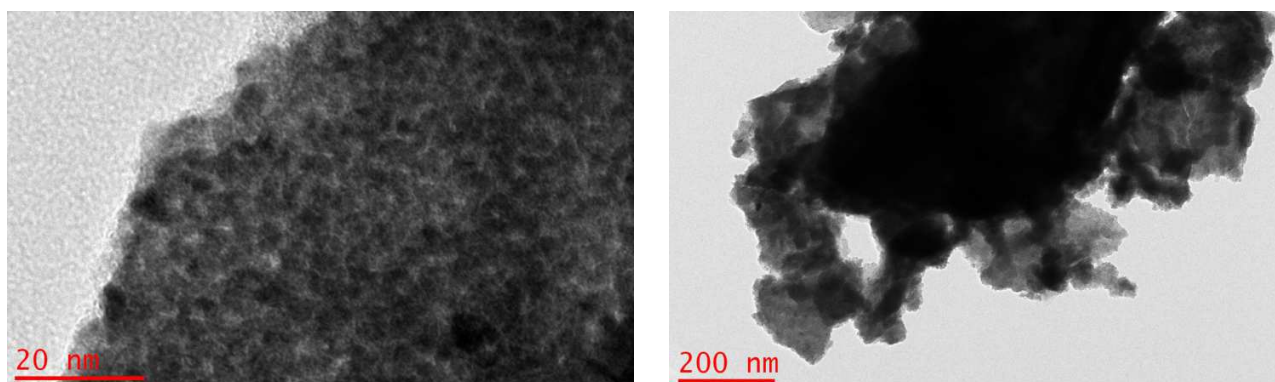
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**Figure S1:** TEM images of Pd NPs-1 and Pd NPs-2



**Figure S2:** TEM images of a phytochemical resin containing 10 % Pd

## **<sup>1</sup>H and <sup>13</sup>C-NMR Spectra of Aromatic Primary Amines 1a-k**

**4'-Aminoacetophenone (1a)**<sup>1</sup>: Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1a** as a white solid (297 mg, 99 % yield). <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>) : δ (ppm) = 7.60 (d, <sup>3</sup>J(H,H) = 9 Hz, 2H), 6.50 (d, <sup>3</sup>J(H,H) = 9 Hz, 2H), 5.95 (s, 2H), 2.32 (br. s, 3H). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) δ (ppm) = 197.8 , 154 , 130.79 , 125.5 , 112.8 , 24.5.<sup>1</sup>

**Ethyl 4-aminobenzoate (1b)** : Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1b** as an orange solid (327 mg, 99%). <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>) : δ (ppm) = 7.56 (d, <sup>3</sup>J(H,H) = 9 Hz, 2H), 6.50 (d, <sup>3</sup>J(H,H) = 9 Hz, 2H), 5.88 (br. s, 2H), 4.14 (q, <sup>3</sup>J(H,H) = 9 Hz, 2H), 1.20 (t, <sup>3</sup>J(H,H) = 9 Hz, 3H). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) : δ (ppm) = 167.5, 153.3, 131.0, 117.4, 112.9, 59.9, 13.3.<sup>2</sup>

**2-Aminobenzoic acid (1c)** : Elution with AcOEt / cyclohexane (40/60) as eluent afforded **1c** as a yellowish solid (269 mg, 98%). <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>) : δ (ppm) = 8.47 (br. s, 2H), 7.62 (dd, <sup>3</sup>J(H,H) = 9 Hz, <sup>4</sup>J(H,H) = 2 Hz, 1H), 7.15 (td, <sup>3</sup>J(H,H) = 9 Hz, <sup>4</sup>J(H,H) = 2 Hz, 1H), 6.67 (dd, <sup>3</sup>J(H,H) = 9 Hz, <sup>4</sup>J(H,H) = 2 Hz, 1H), 6.43 (td, <sup>3</sup>J(H,H) = 9 Hz, <sup>4</sup>J(H,H) = 2 Hz, 1H). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) : δ (ppm) = 170.2, 151.4, 133.6, 131.3, 116.3, 115.1, 110.3.<sup>3</sup>

**2-Aminoterephthalic acid (1d)**: Elution with AcOEt / cyclohexane (40/60) as eluent afforded **1d** as a yellow solid (333 mg, 92%). <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>) : δ (ppm) = 8.7 (br. s, 2H), 7.70 (d, <sup>3</sup>J(H,H) = 8 Hz, 1H), 7.31(d, <sup>4</sup>J(H,H) = 2 Hz, 1H), 6.95 (dd, <sup>3</sup>J(H,H) = 6 Hz, <sup>4</sup>J(H,H) = 2 Hz, 1H). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) : δ (ppm) = 169.5, 168.1, 151.2, 135.1, 131.4, 117.7, 115.2, 113.2.

**Aniline (1e)**: Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1e** as a colorless liquid (184 mg, 99%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) : δ (ppm) = 7.18 (def. t, <sup>3</sup>J(H,H) = 9 Hz, 2H), 6.78 (def. t, <sup>3</sup>J(H,H) = 9 Hz, 1H), 6.70 (def. d, <sup>3</sup>J(H,H) = 9 Hz, 2H), 3.65 (s, 2H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) : δ (ppm) = 147.1, 128.6, 117.9, 115.3.<sup>4</sup>

**4-Fluoroaniline (1f)**<sup>5</sup>: Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1f** as a brown liquid (219 mg, 99%) <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) : δ (ppm) = 6.83 (t, <sup>3</sup>J(H,H) = <sup>3</sup>J(H,F) = 9 Hz, 2H), 6.60 (dd, <sup>3</sup>J(H,H) = 9 Hz, <sup>4</sup>J(H,F) = 5 Hz, 2H), 3.48 (br. s, 2H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) : δ (ppm) = 157.4 (d, <sup>1</sup>J(C,F) = 235 Hz), 142.5 (d, <sup>4</sup>J(C,F) = 2.2 Hz), 116.1 (d, <sup>2</sup>J(C,F) = 7.4 Hz), 115.8 (d, <sup>3</sup>J(C,F) = 22.4 Hz). <sup>19</sup>F-NMR (470.5 MHz, CDCl<sub>3</sub>) δ (ppm) = -126.8.<sup>3</sup>

**1,2-Phenylenediamine (1g)**: Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1g** as a brown solid (214 mg, 99%). <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>) : δ (ppm) = 6.43 (m, 2H), 6.30 (m, 2H), 4.31 (br. s, 2H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) : δ (ppm) = 134.5, 119.4, 116.3.<sup>1</sup>

**2,4-Dimethylaniline (1h)**: Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1h** as a dark red liquid (240 mg, 99%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) : δ (ppm) = 6.85 (m, 2H), 6.60 (d, <sup>3</sup>J(H,H) = 9 Hz, 1H), 3.46 (br. s, 2H), 2.22 (s, 3H), 2.14 (s, 3H). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) : δ (ppm) = 141.4, 130.5, 128.0, 126.8, 123.3, 115.8, 19.2, 16.0.<sup>3</sup>

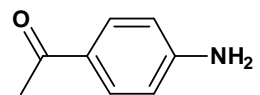
**1,4-Phenylenediamine (1i):** Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1i** as a brown solid (214 mg, 99%). <sup>1</sup>H-NMR (300 MHz, DMSO-d6) : δ (ppm) = 6.28 (s, 4H), 4.10 (br. s, 4H). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) : δ (ppm) = 138.8, 117.1.<sup>1</sup>

**4-Aminophenol (1j):** Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1j** as a yellowish solid (216 mg, 99%). <sup>1</sup>H-NMR (300 MHz, DMSO-d6) : δ (ppm) = 8.25 (s, 1H), 6.38 (AA'BB', <sup>3</sup>J(H,H) = 9 Hz, 4H), 4.30 (br. s, 2H). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) : δ (ppm) = 149.9, 138.9, 117.1, 115.3.<sup>4</sup>

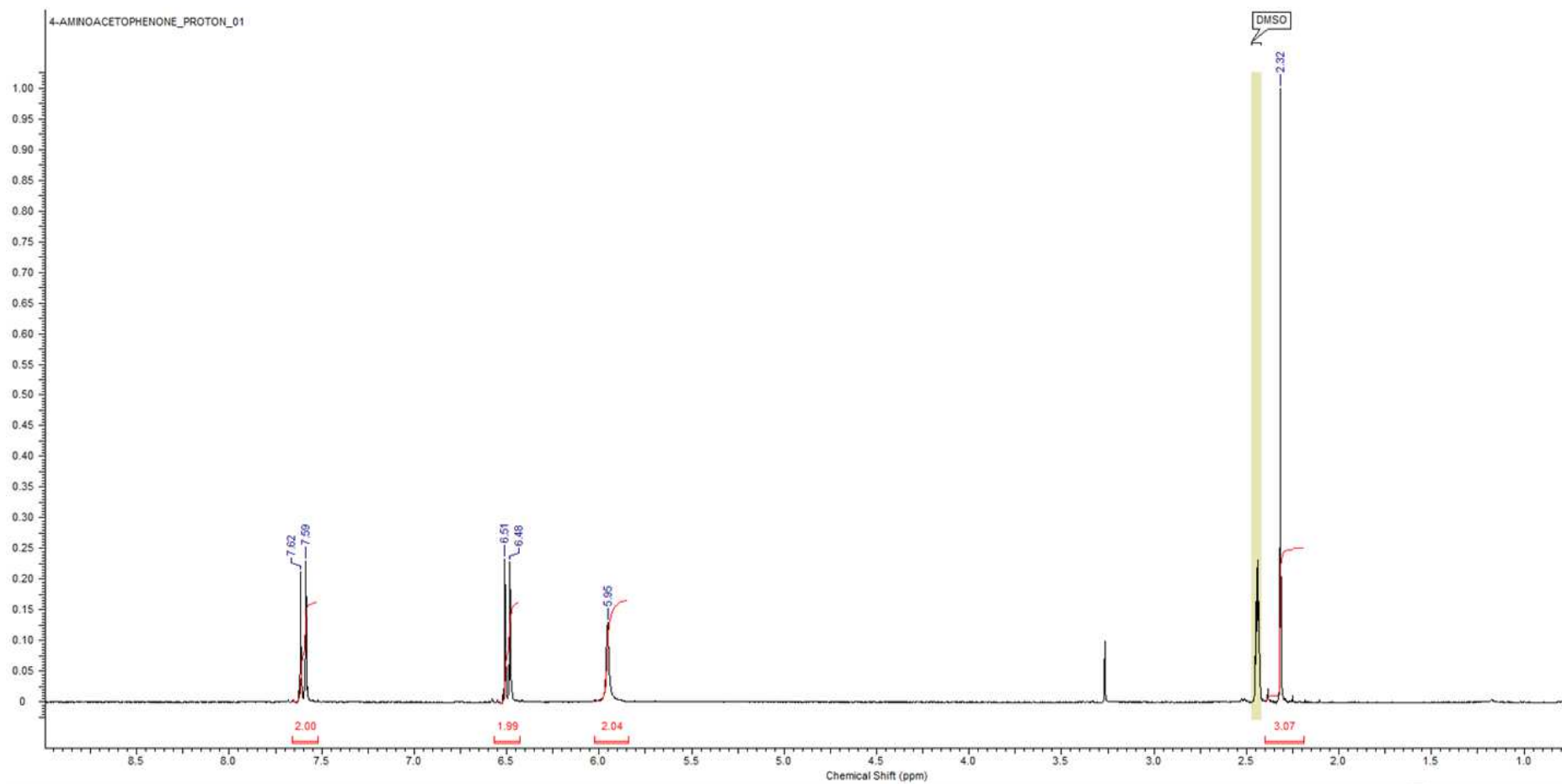
**3-aminopyridine (1k):** Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1k** as a brown solid (186 mg, 99%). <sup>1</sup>H-NMR (300 MHz, DMSO-d6) δ (ppm) = 7.86 (def. s, 1H), 7.66 (m, 1H), 6.94 (m, 1H), 6.83 (m, 1H), 5.18 (br. s, 2H). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) : δ (ppm) = 145.1, 136.9, 135.7, 124.0, 121.6.<sup>2</sup>

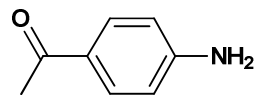
#### **Determinations of the Pd content of catalysts and of the Pd leached in the reaction medium**

The general procedures for the determinations of the Pd content of catalysts Pd NPs-1 and Pd NPs-2 and of the Pd leached in the reaction medium during the hydrogenation reaction have been described previously by our group.<sup>4</sup>



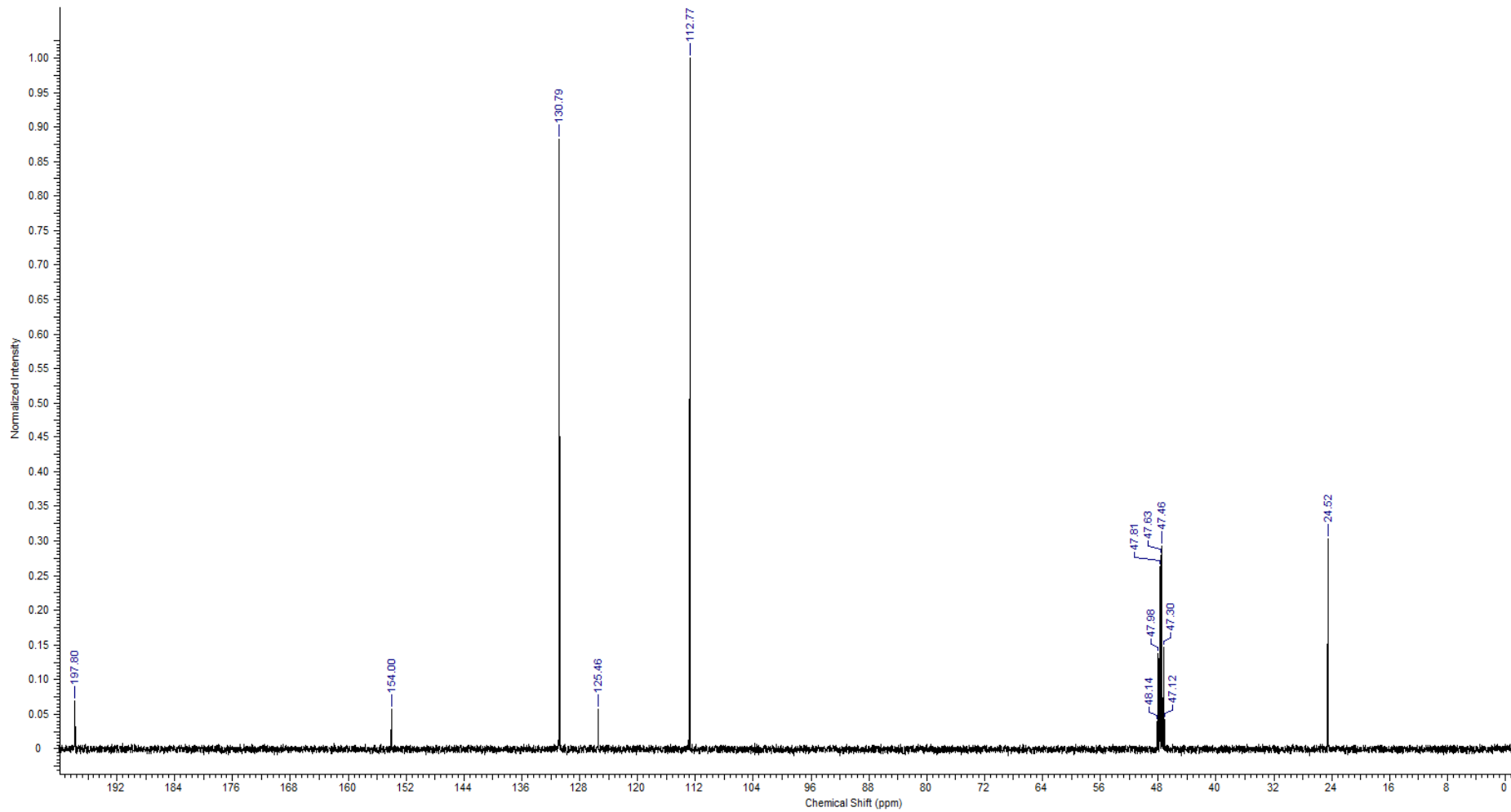
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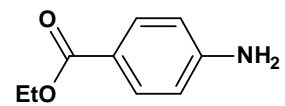




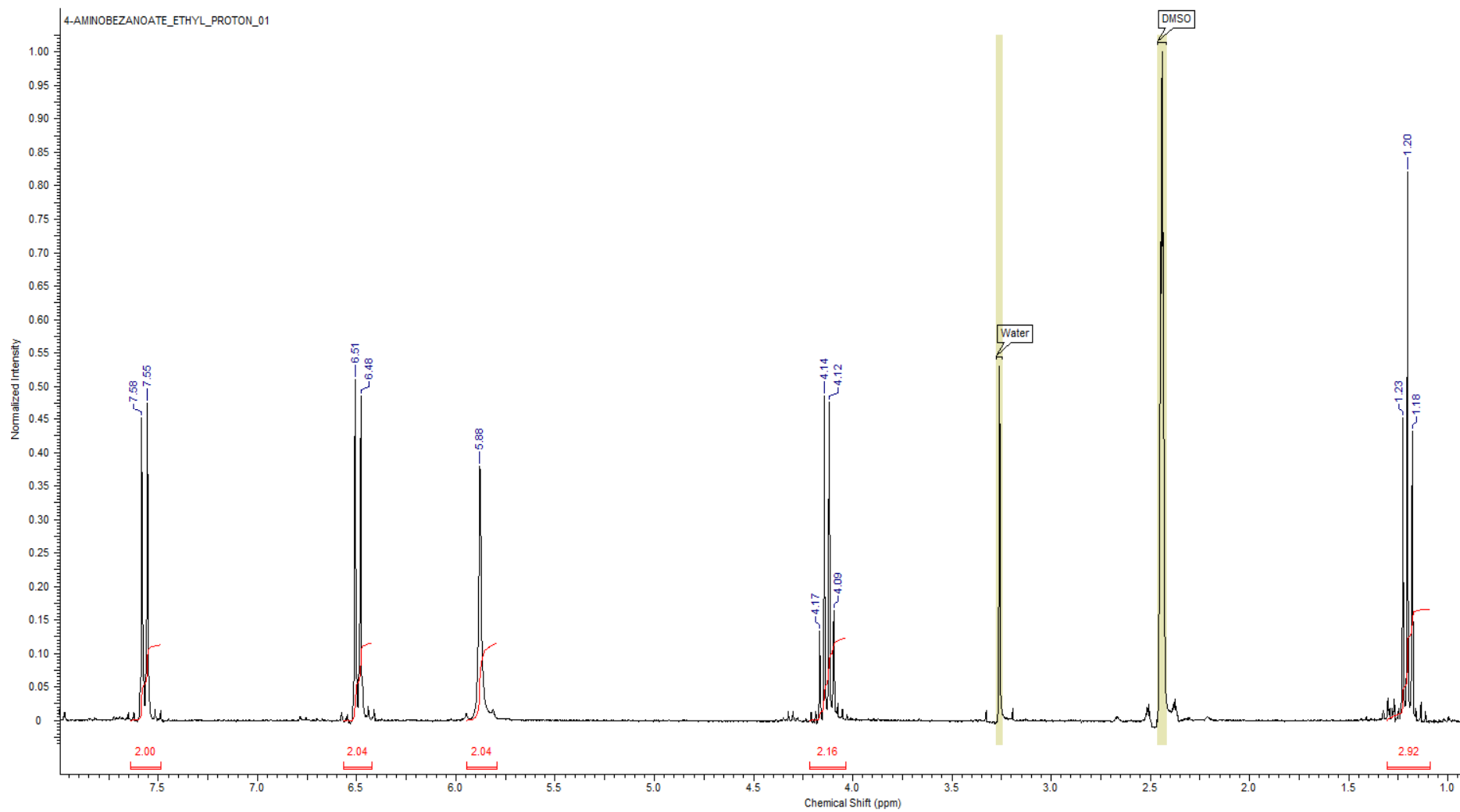
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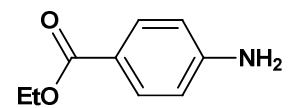
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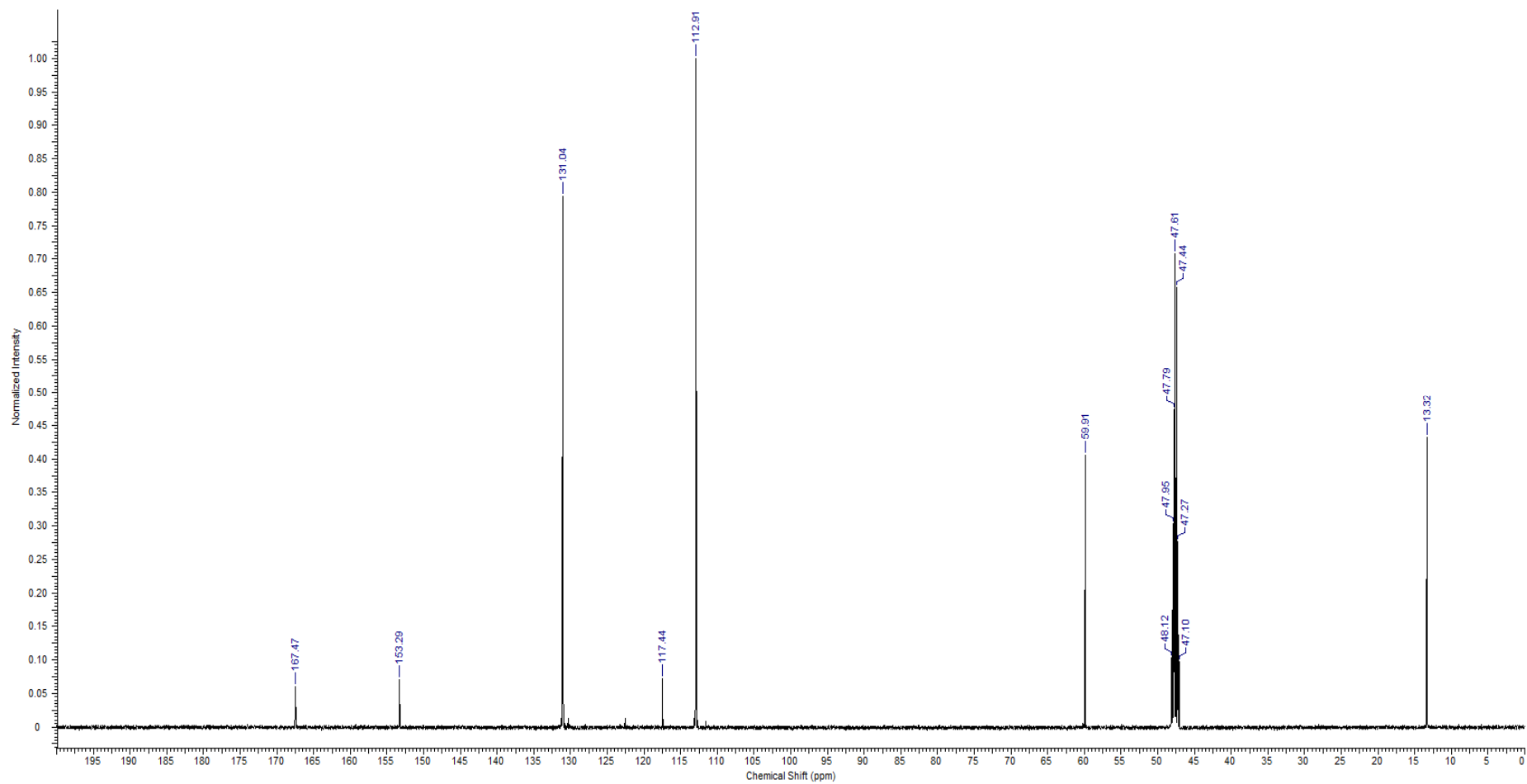


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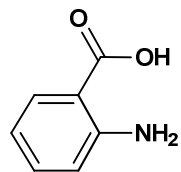




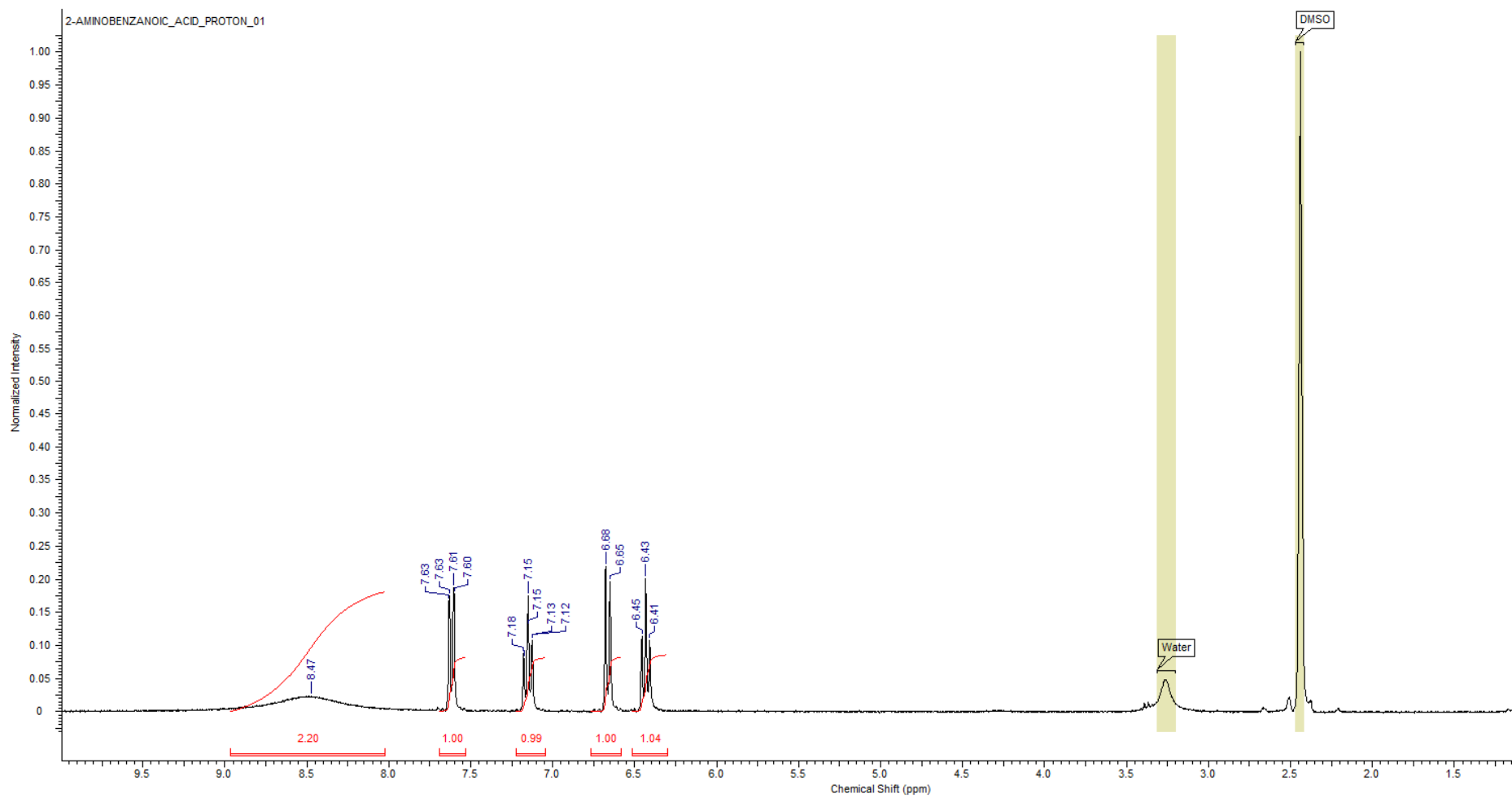
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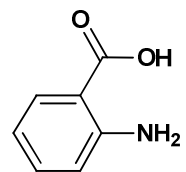




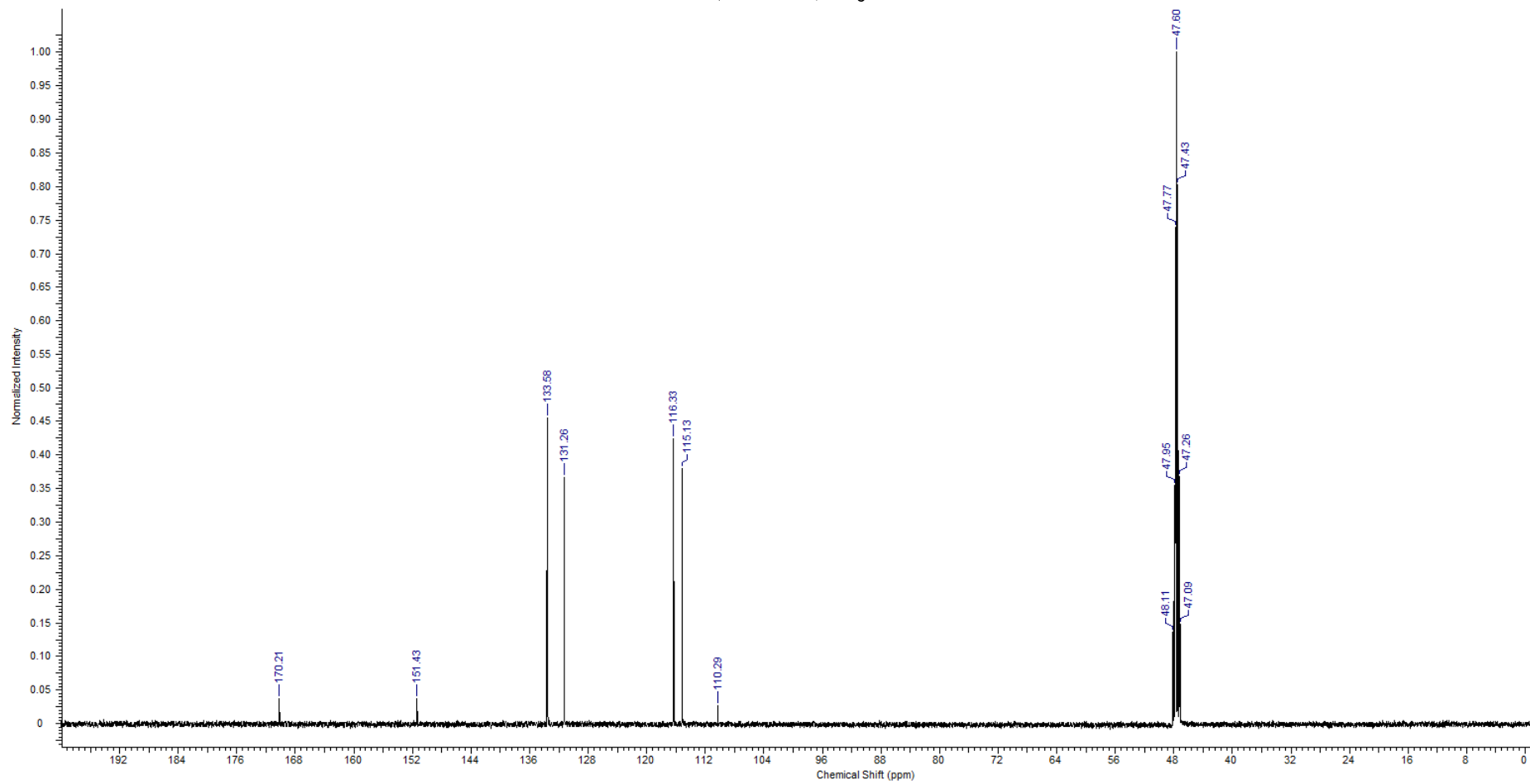


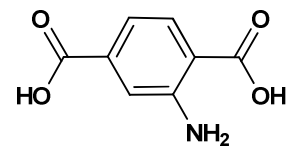
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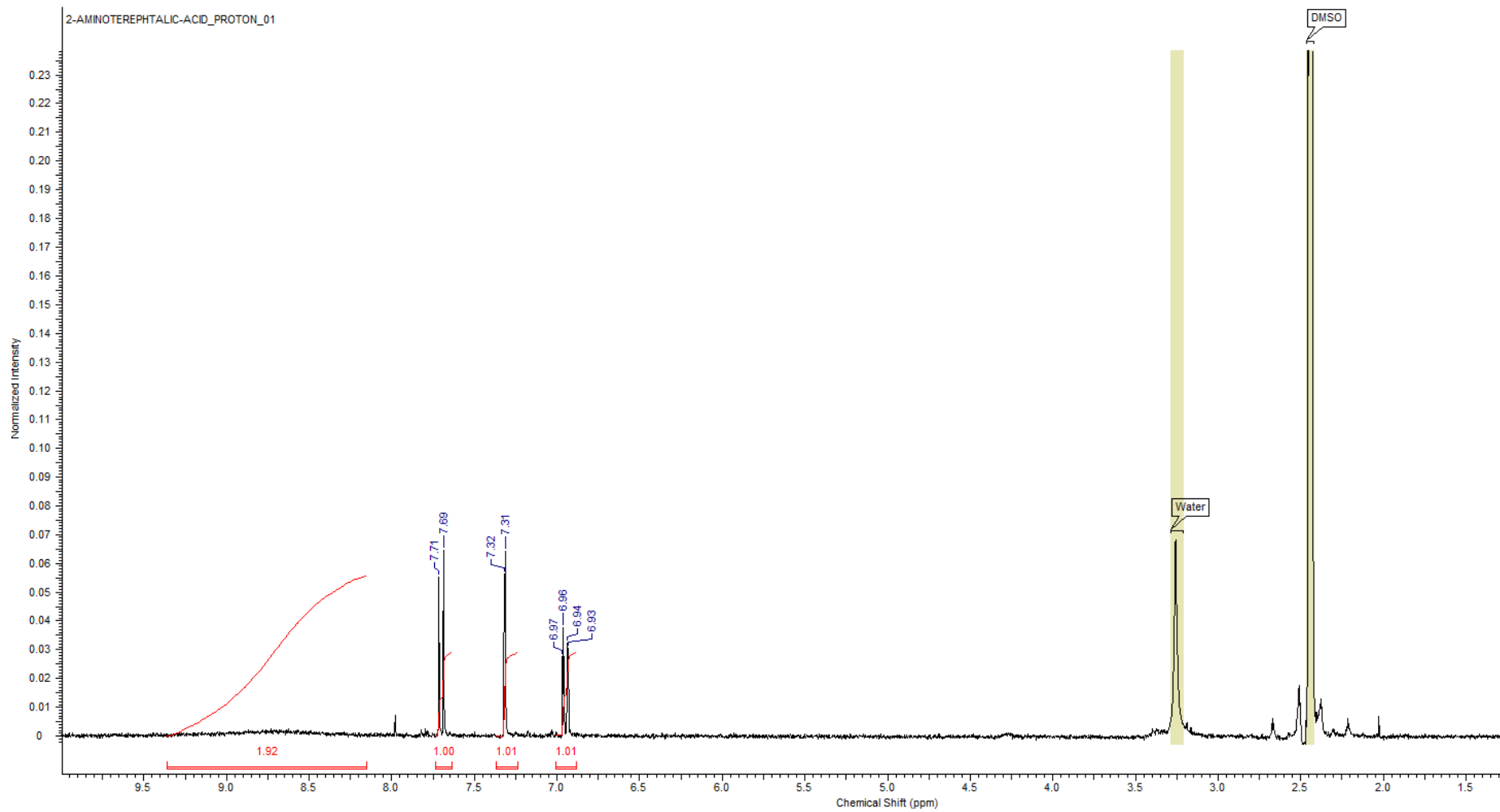
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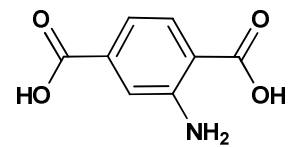




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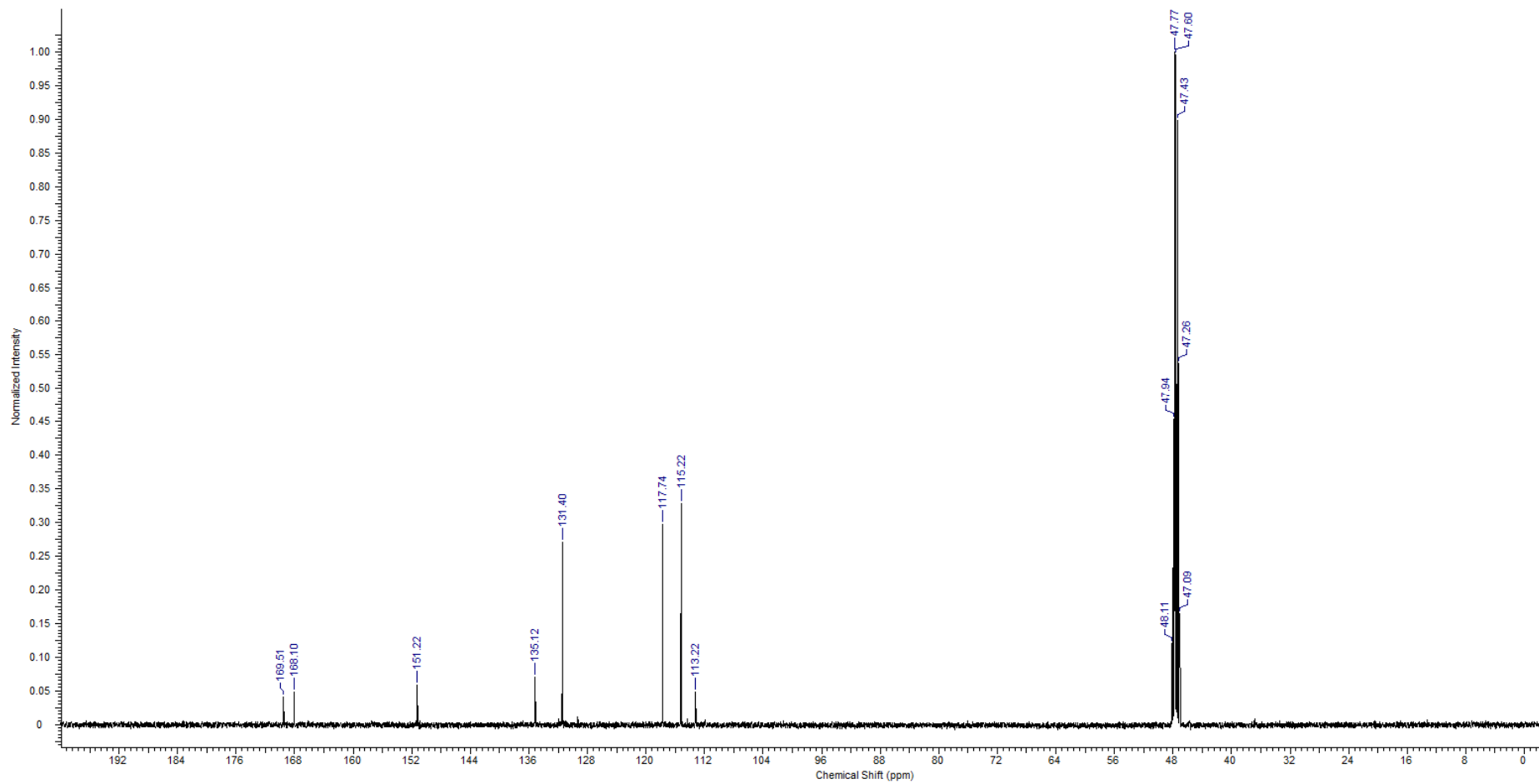
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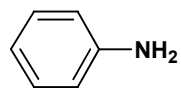




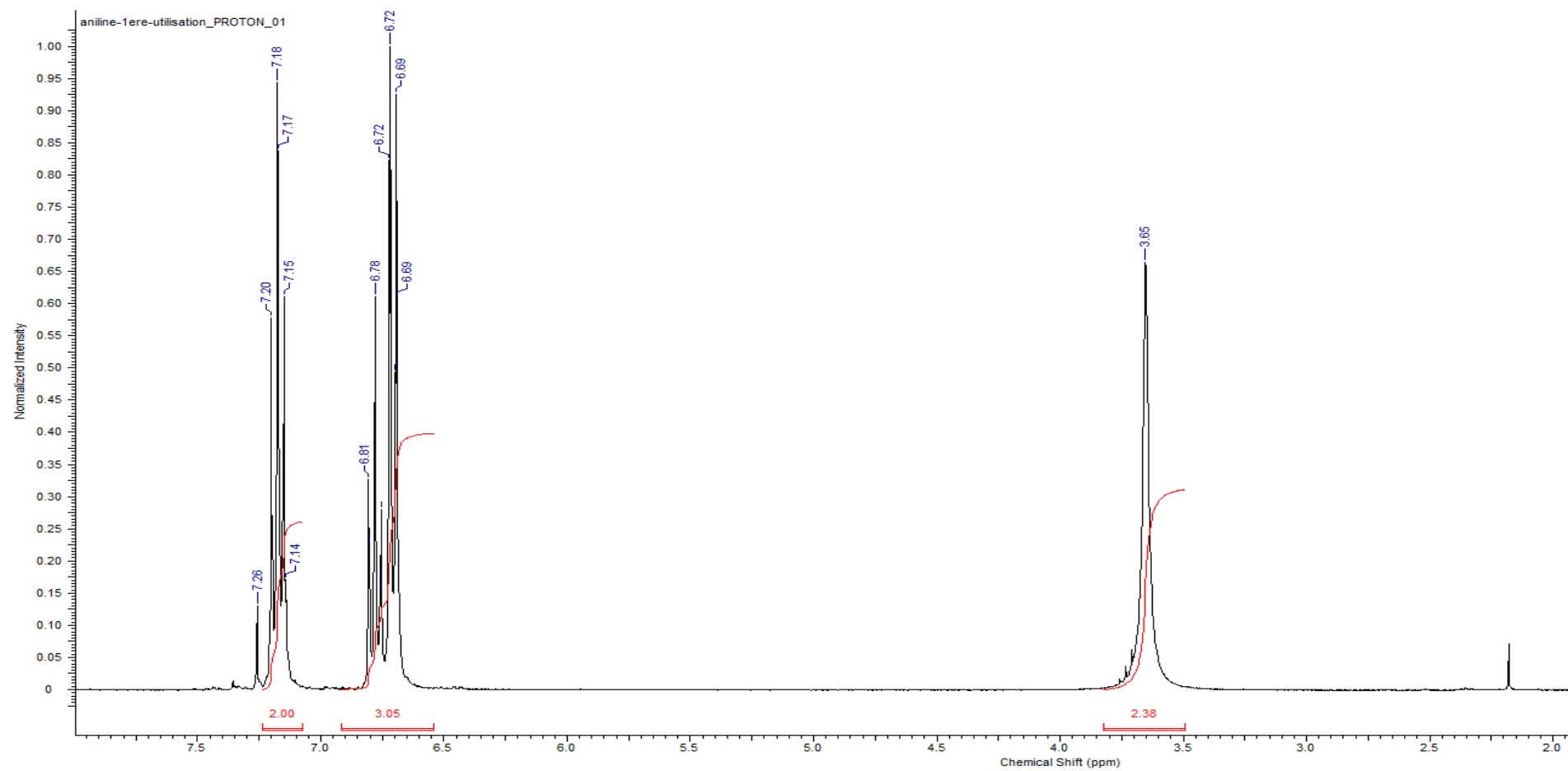
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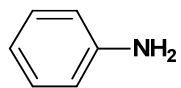
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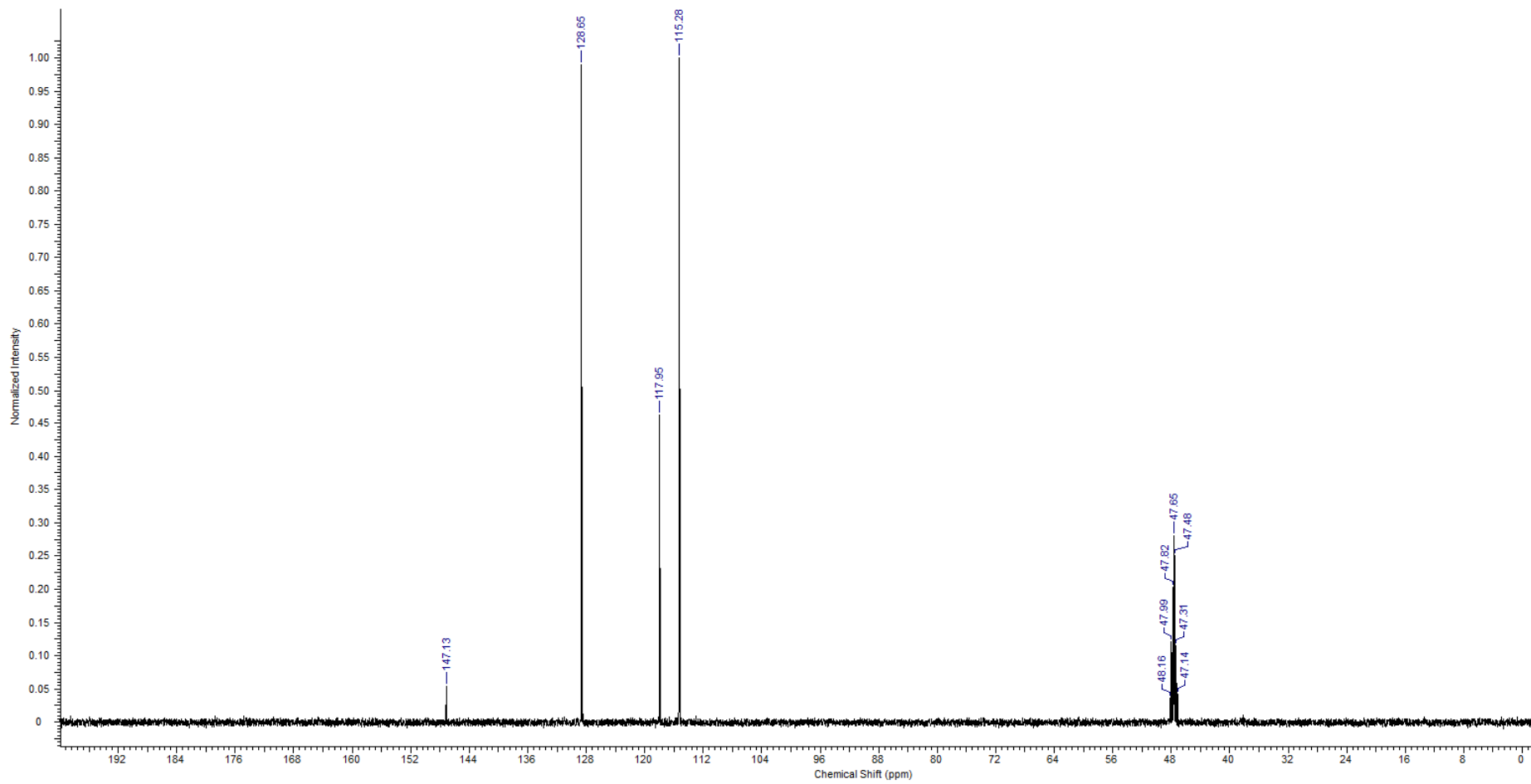
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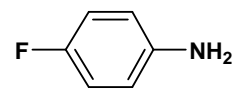




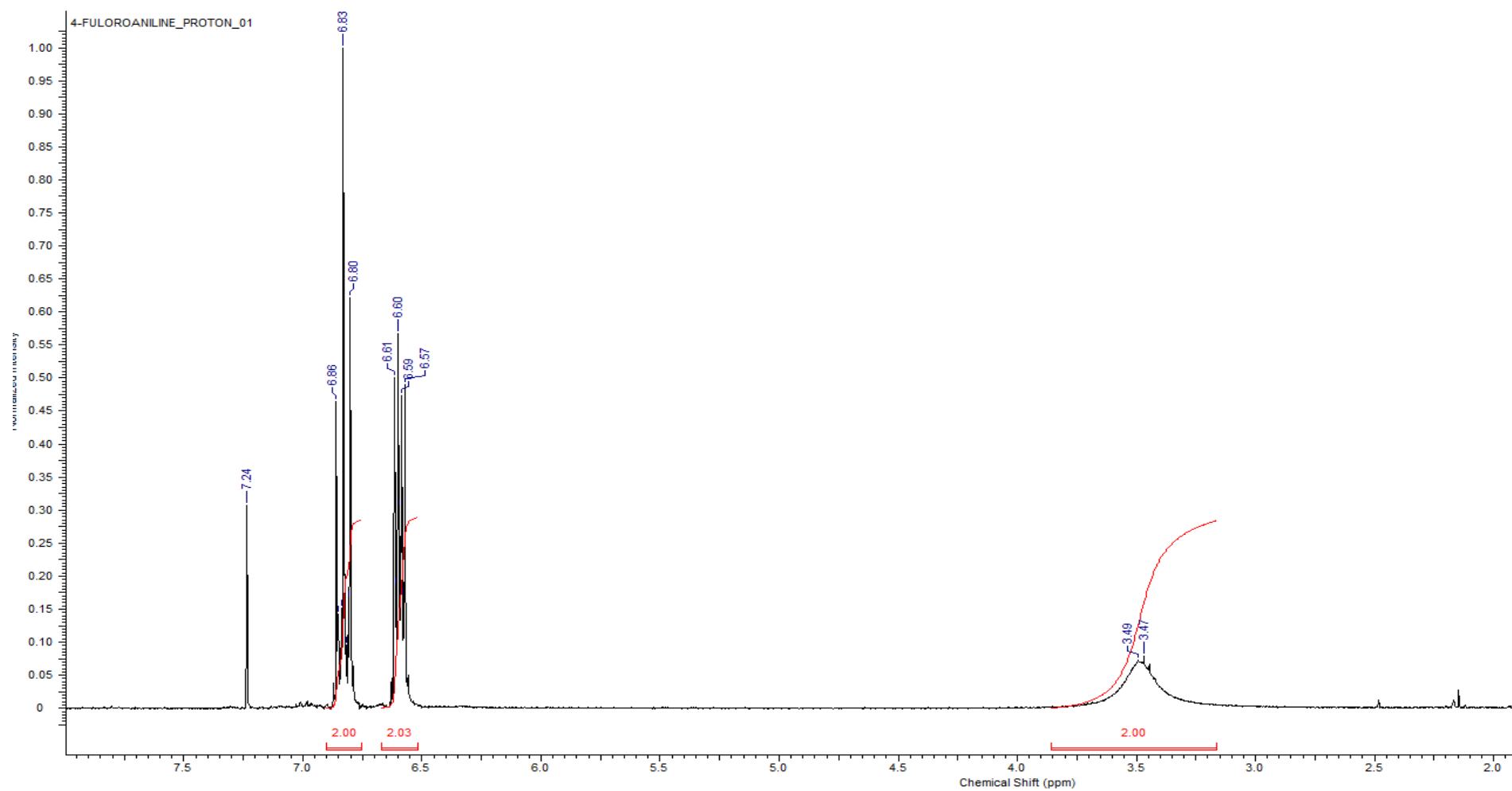
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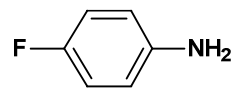
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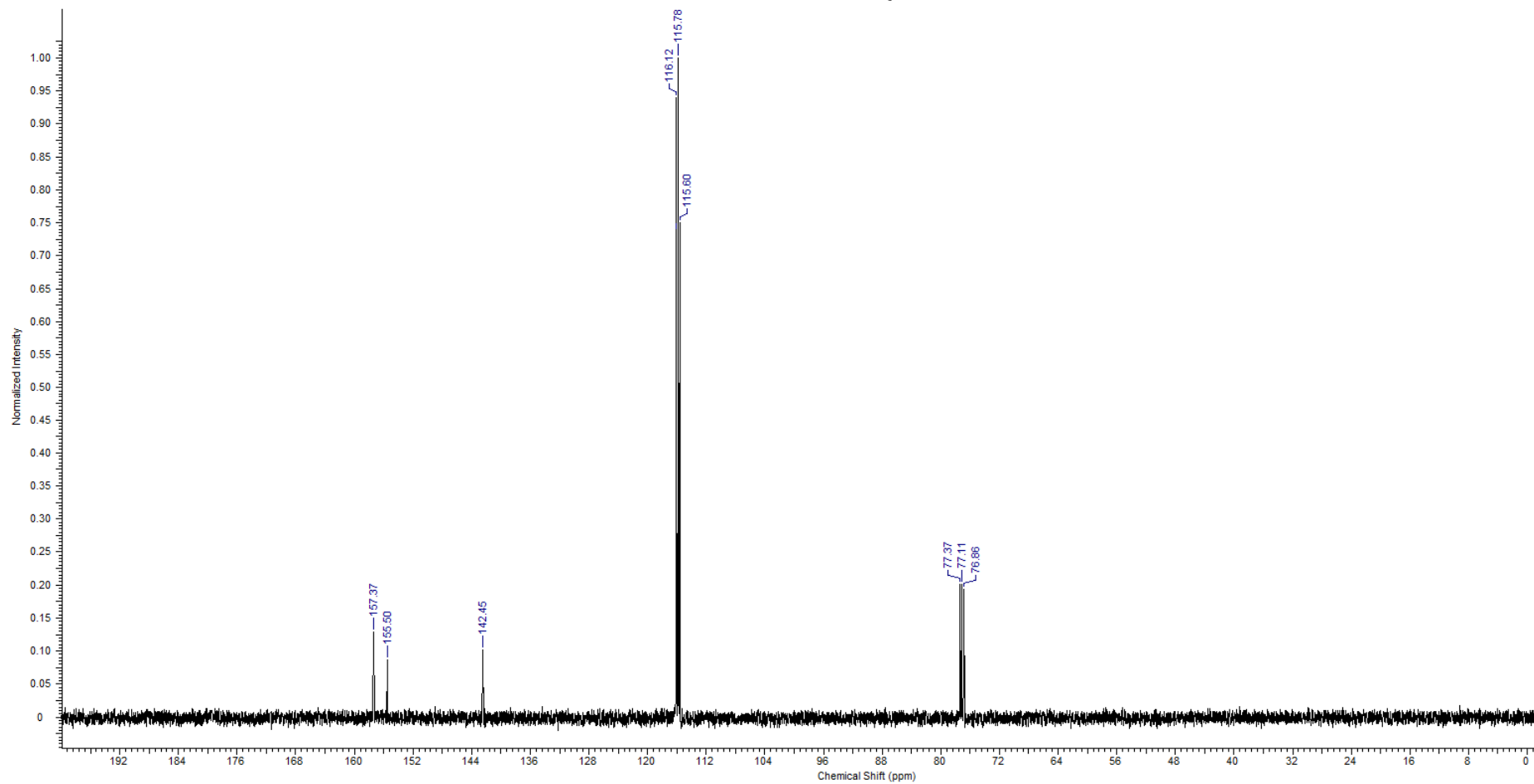
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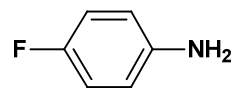


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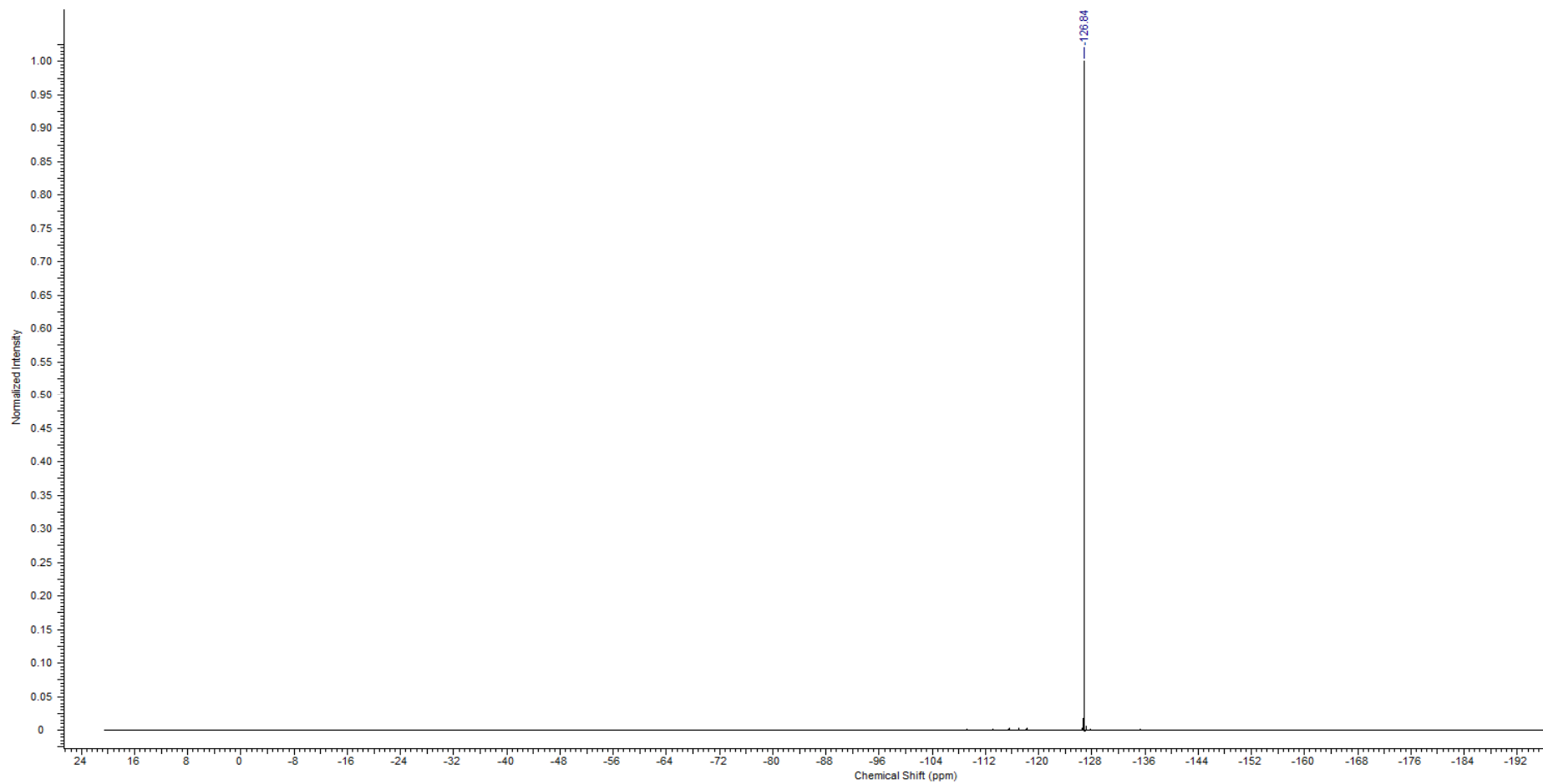
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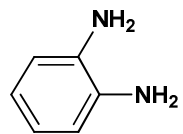




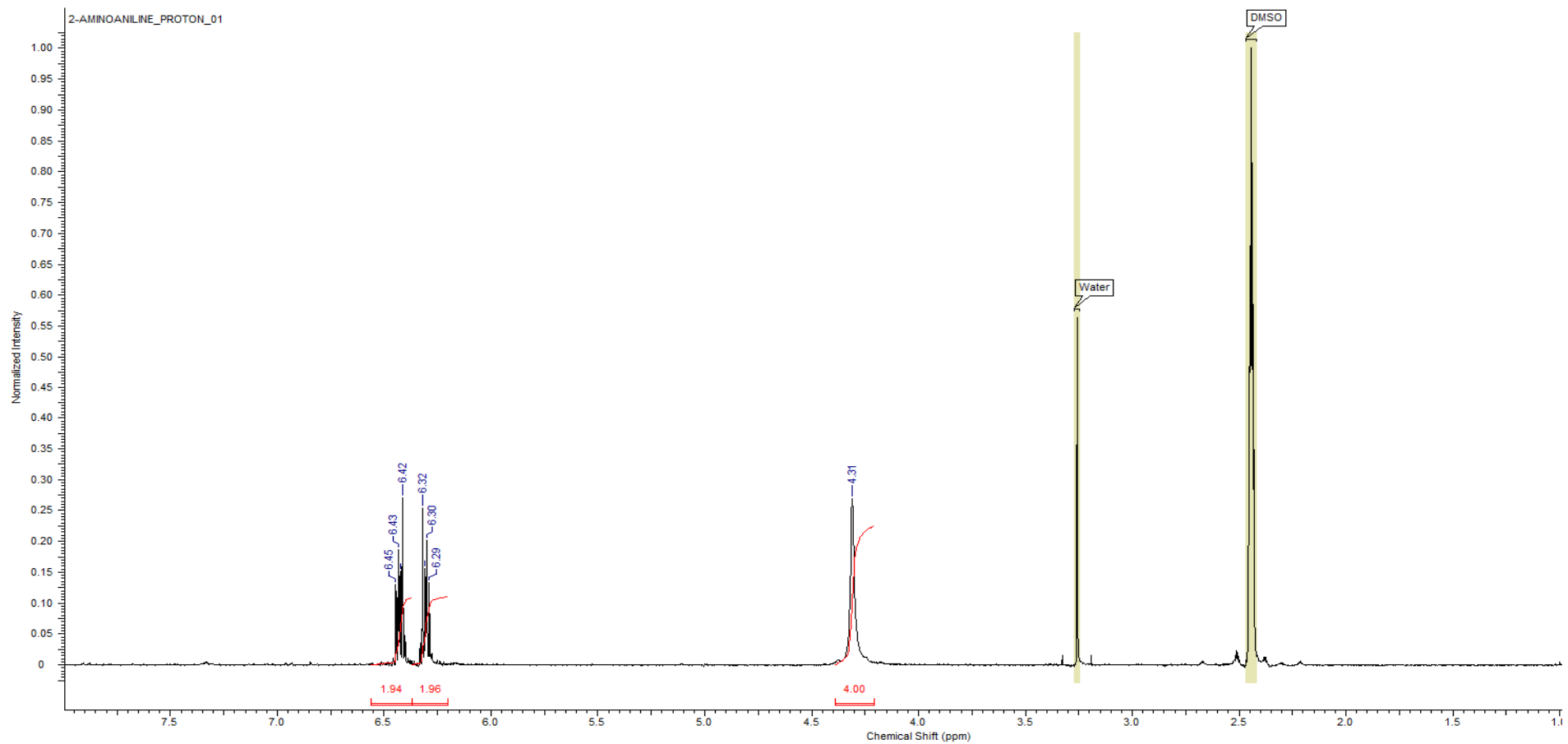


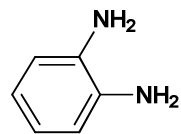
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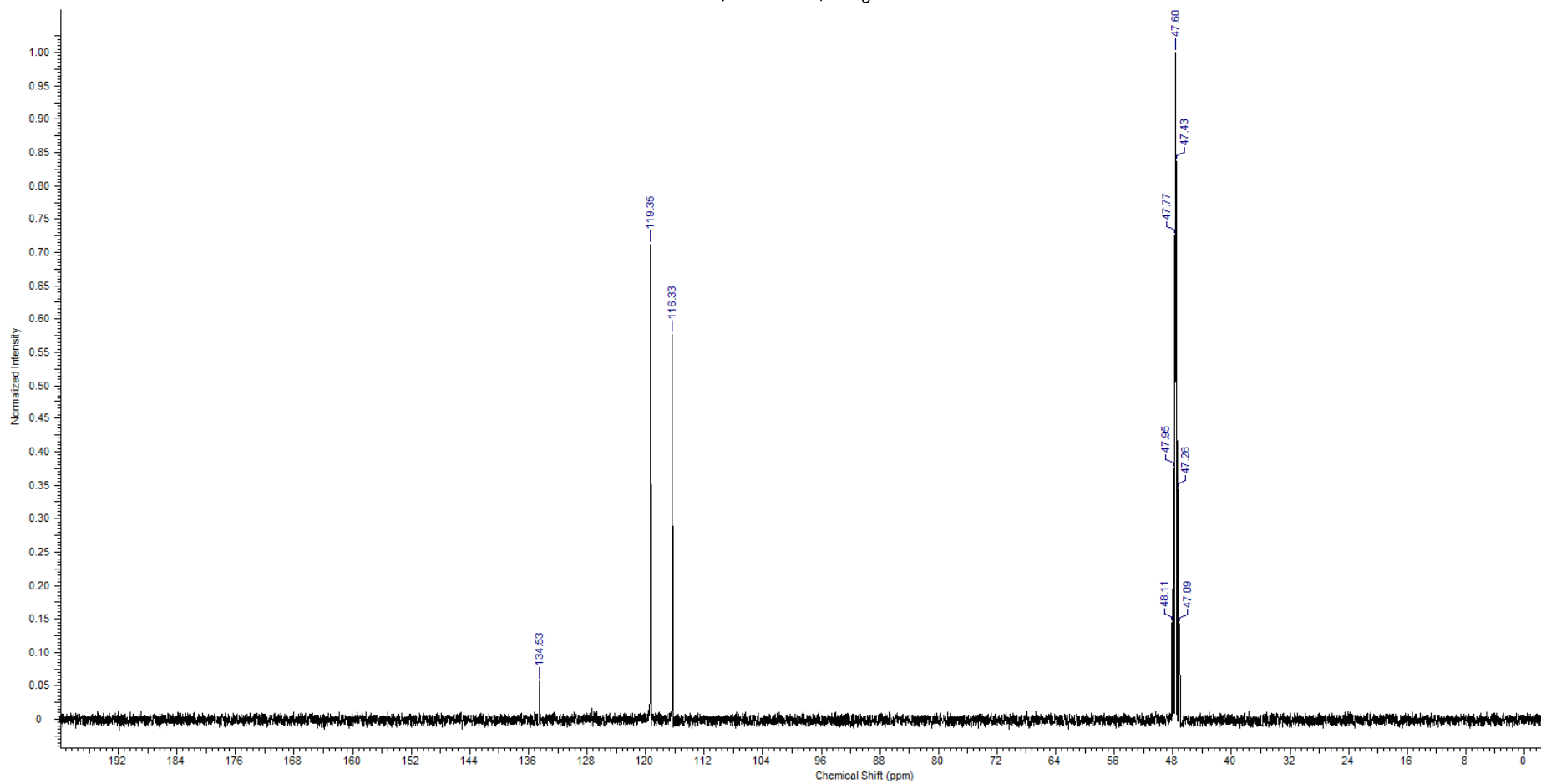


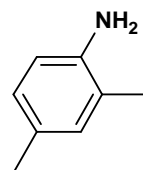
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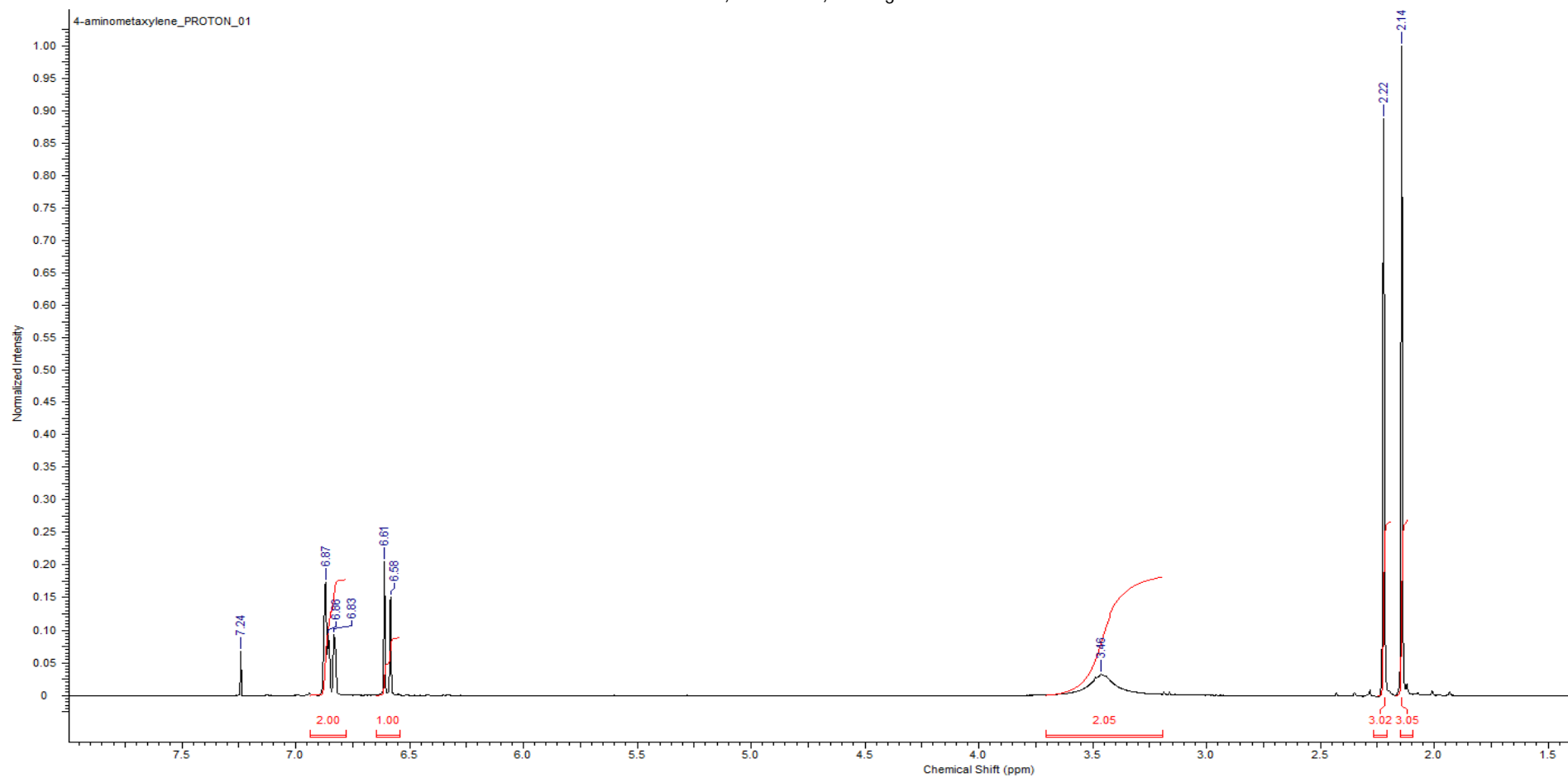


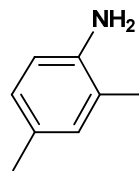
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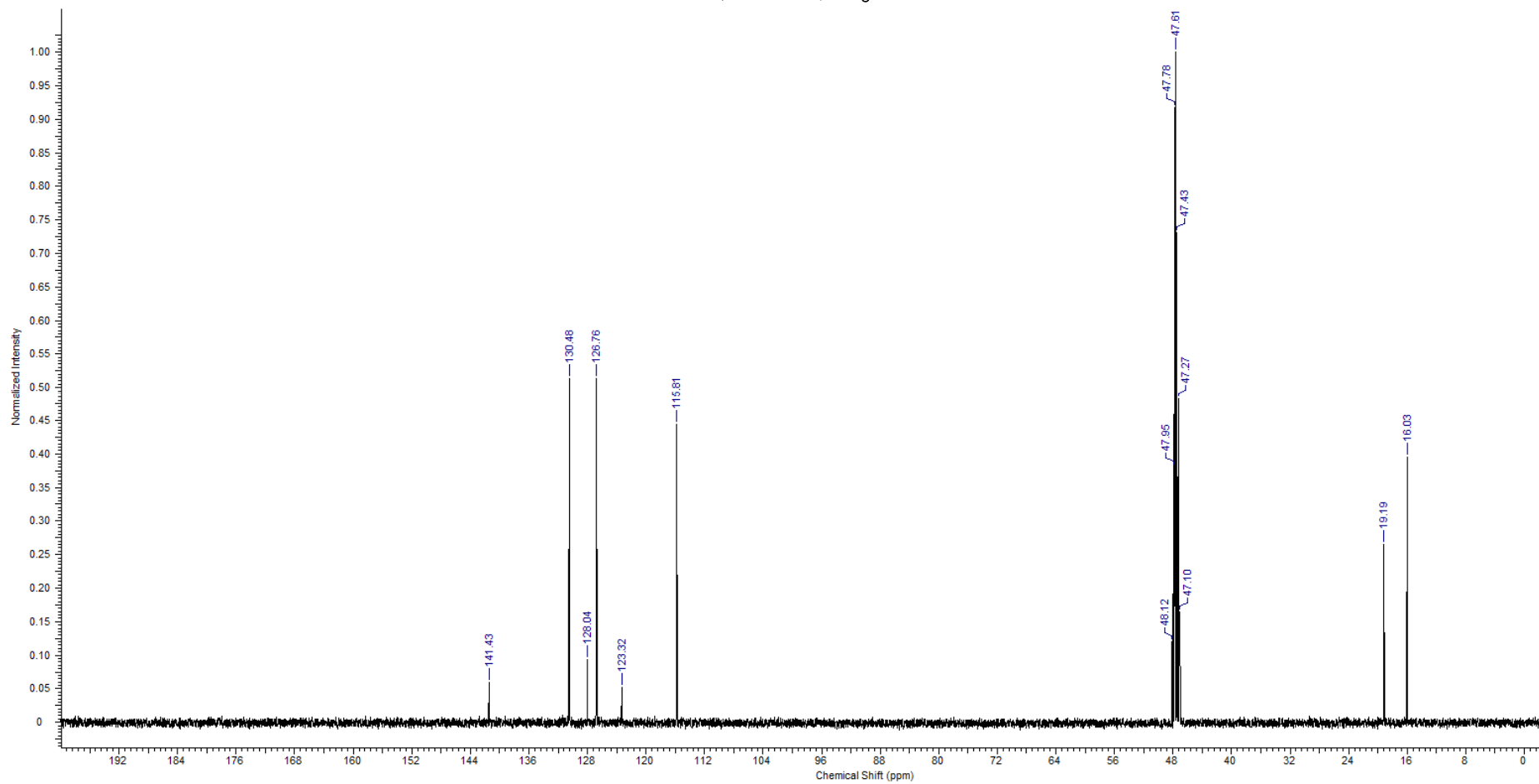


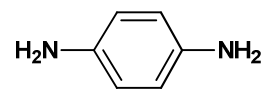
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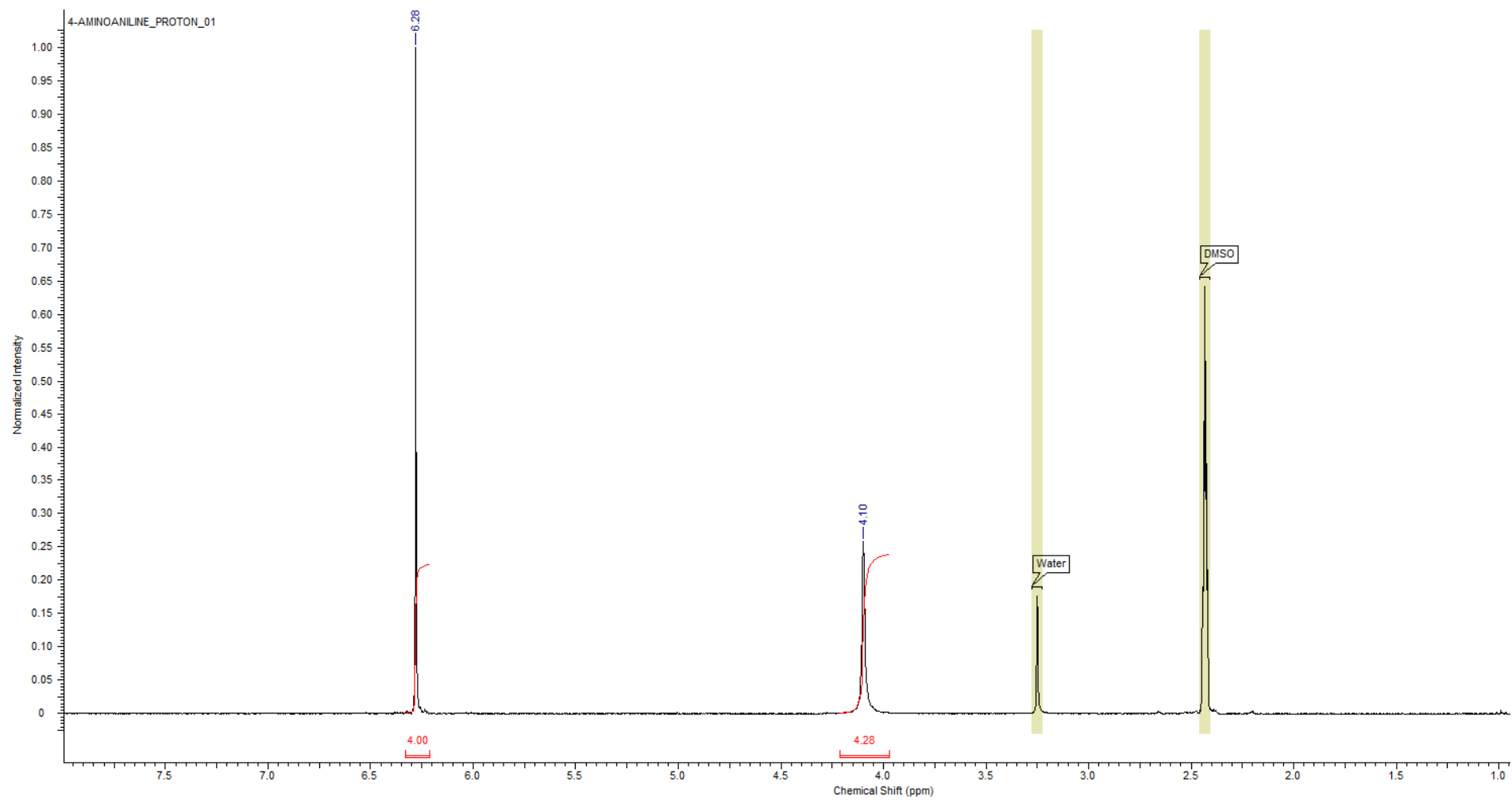


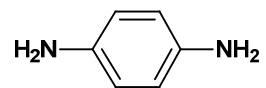
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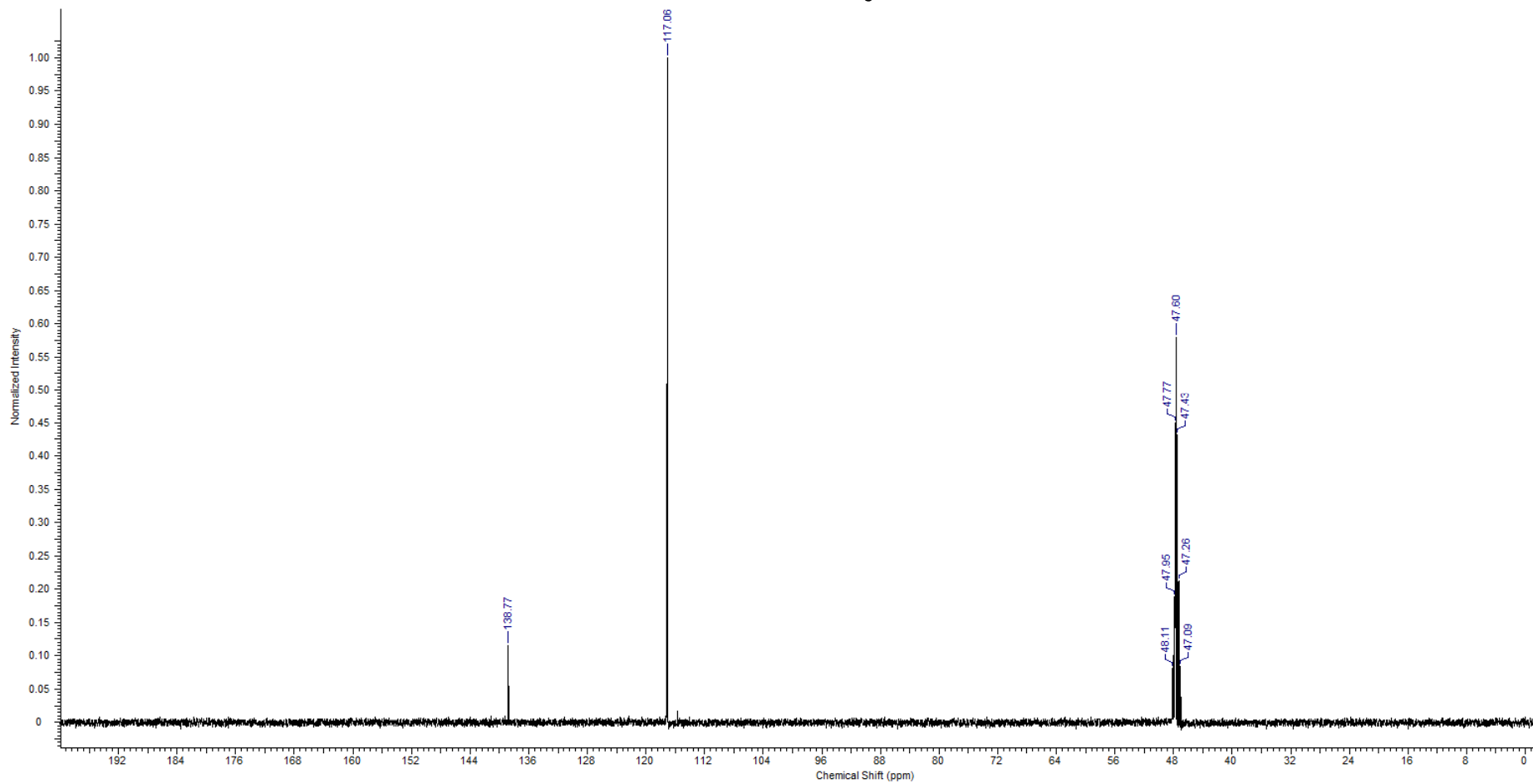
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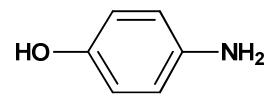




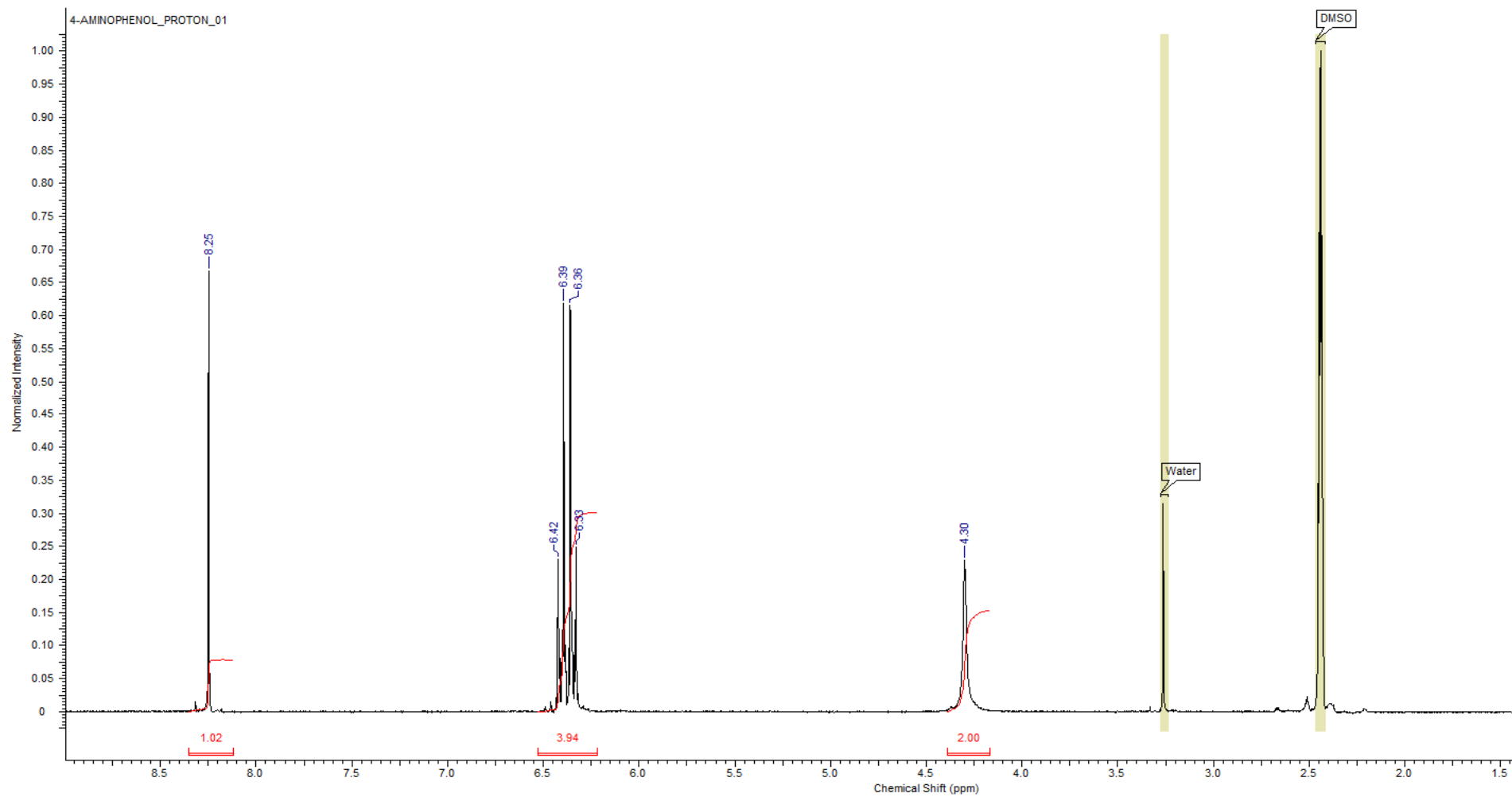
Compound 1i

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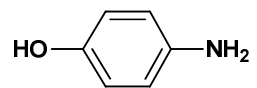




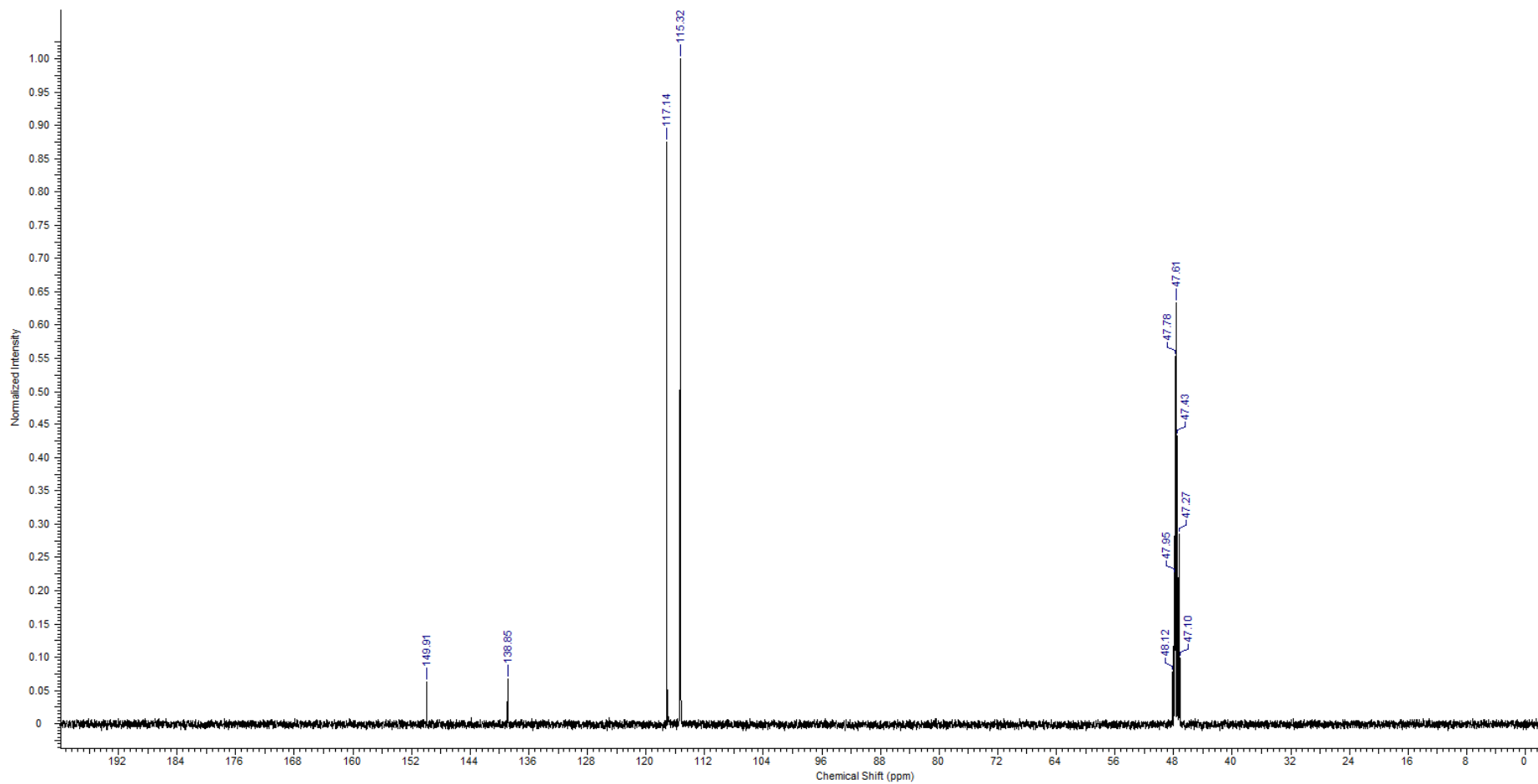
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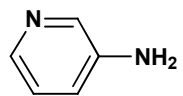




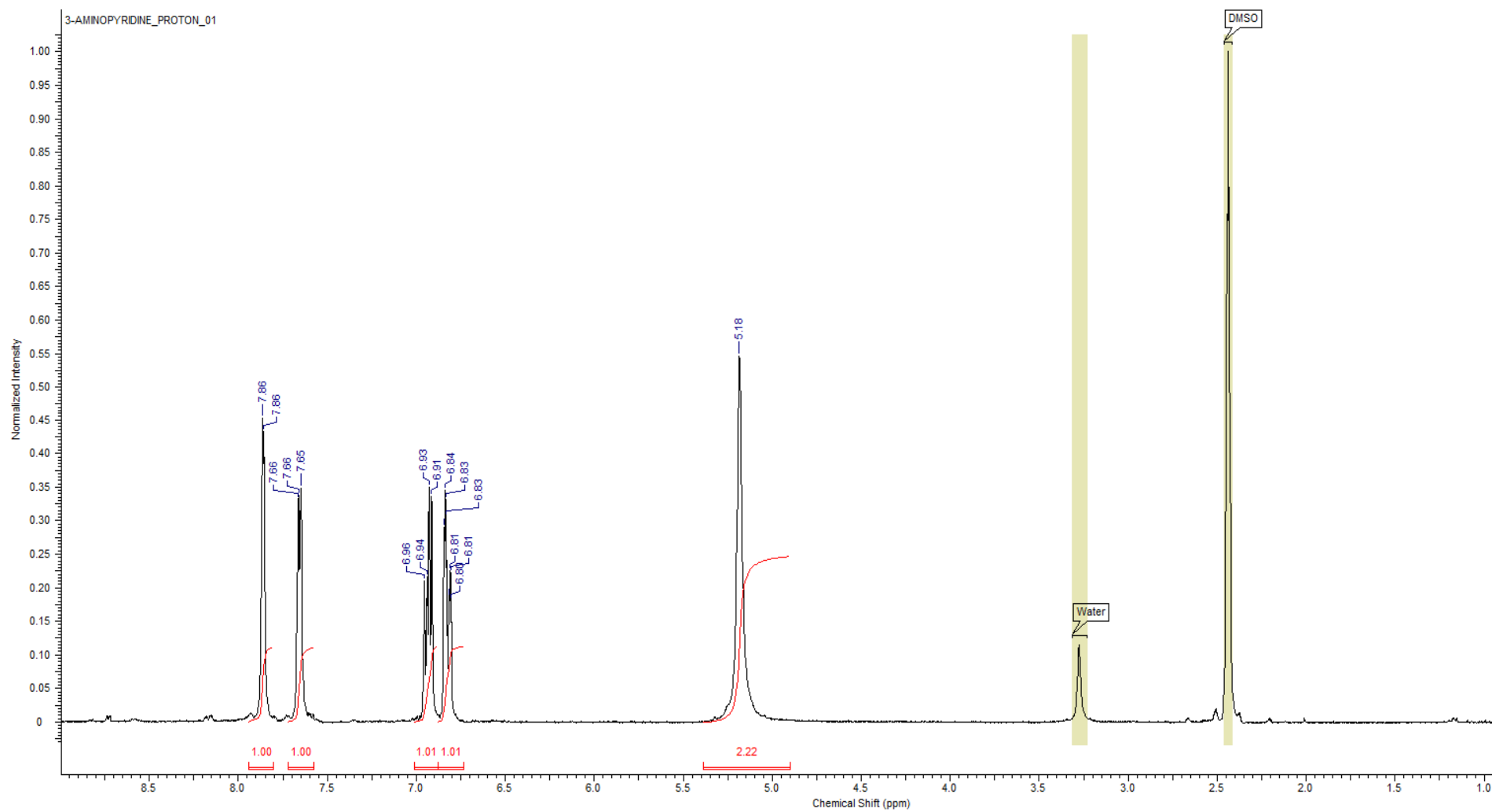


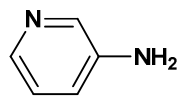
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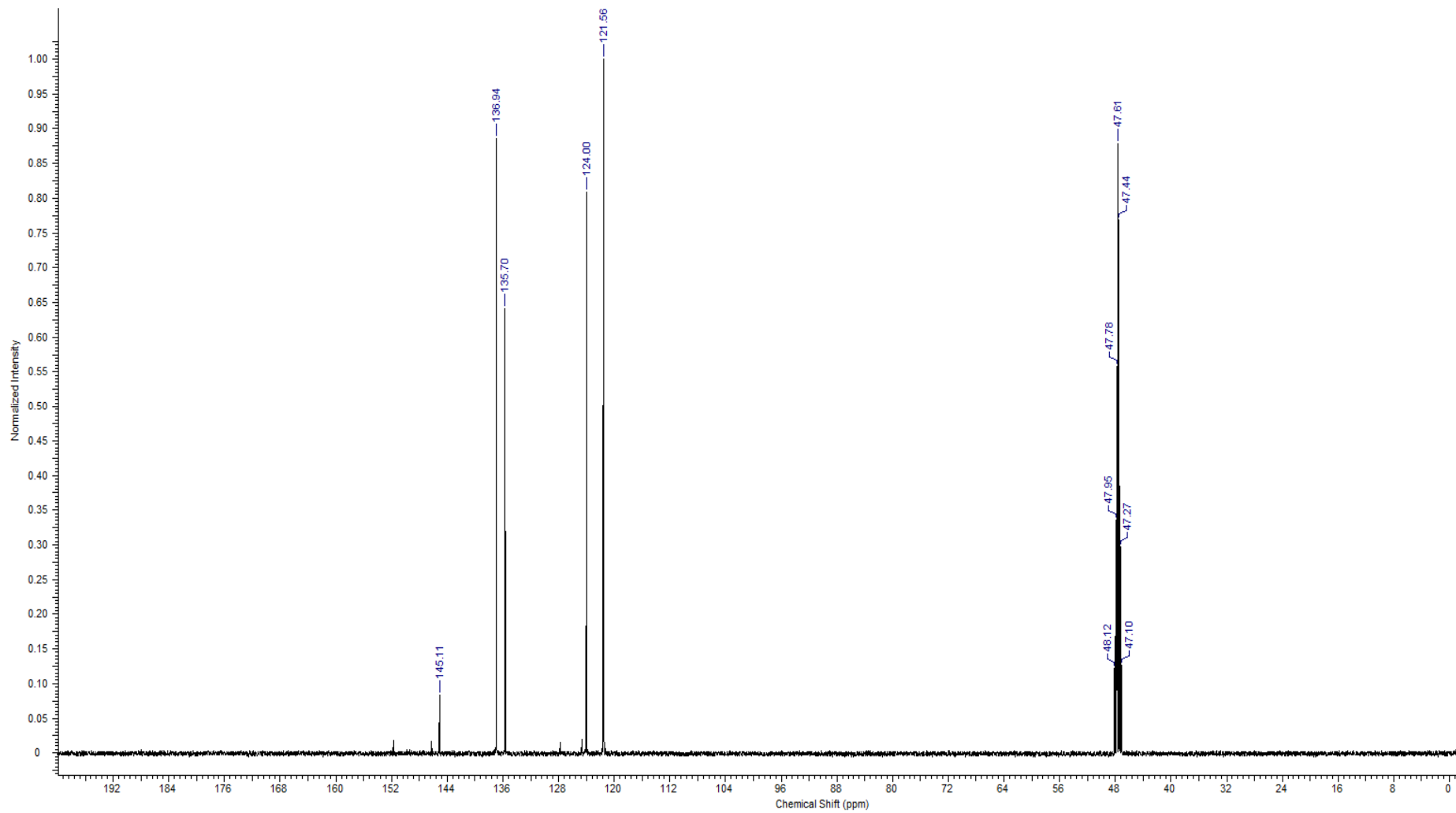
Compound 1k  
<sup>1</sup>H-NMR, 300 MHz, DMSO-d6





Compound **1k**

$^{13}\text{C}$ -NMR, 125 MHz,  $\text{CD}_3\text{OD}$



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- (3) H. Huang, X. Wang, M. Tan, C. Chen, X. Zou, W. Ding, X. Lu, *ChemCatChem* **2016**, *8* (8), 1485–1489.
- (4) O. Verho, K. P. J. Gustafson, A. Nagendiran, C.-W. Tai, J.-E. Bäckvall, *ChemCatChem* **2014**, *6* (11), 3153–3159.
- (5) M. Enneimy, C. Le Drian, C. Matei-Ghimbeu, J.-M. Becht, *RSC Adv.*, 2018, **8**, 17176.