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Electronic Supporting Information

Palladium Nanoparticles Embedded in Mesoporous Carbons as Efficient, Green and Reusable Catalysts for Mild Hydrogenations of Nitroarenes

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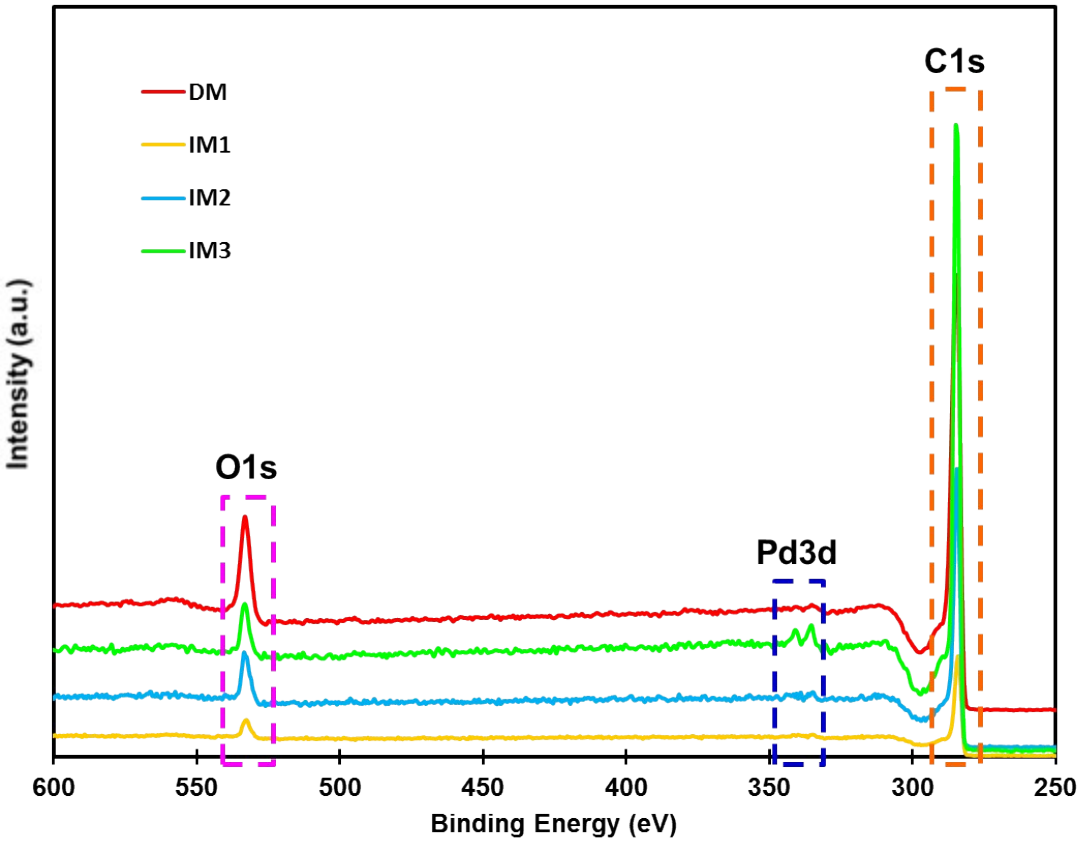


Figure S1: XPS wide scan of **IM1, IM2, IM3** and **DM**

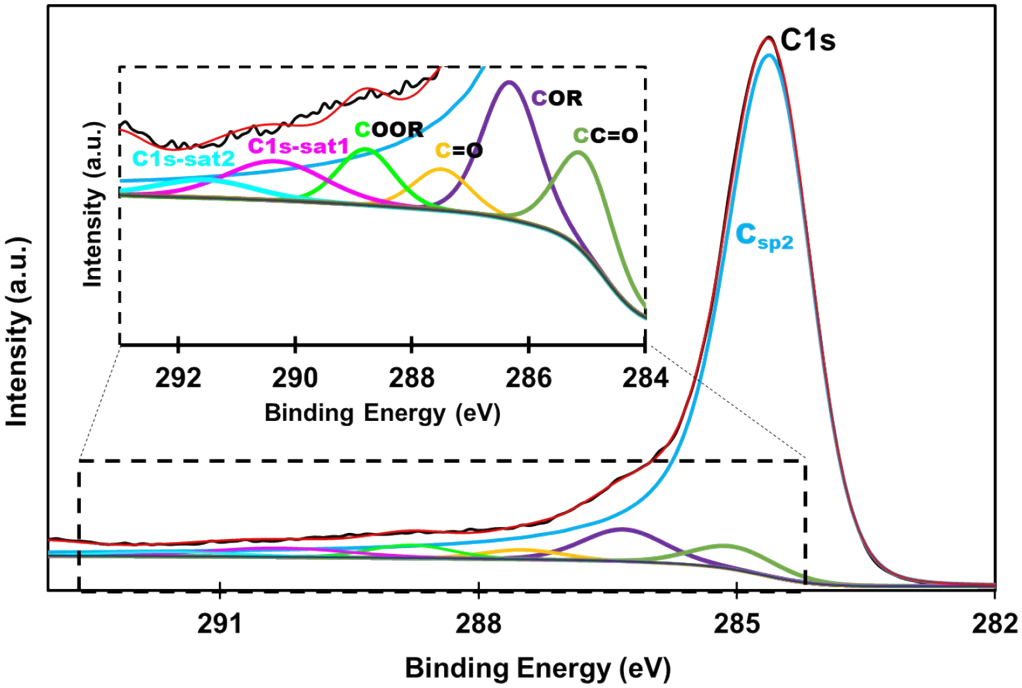


Figure S2: Deconvolution of XPS high resolution scan of C1*s* peak of mesoporous carbon support.

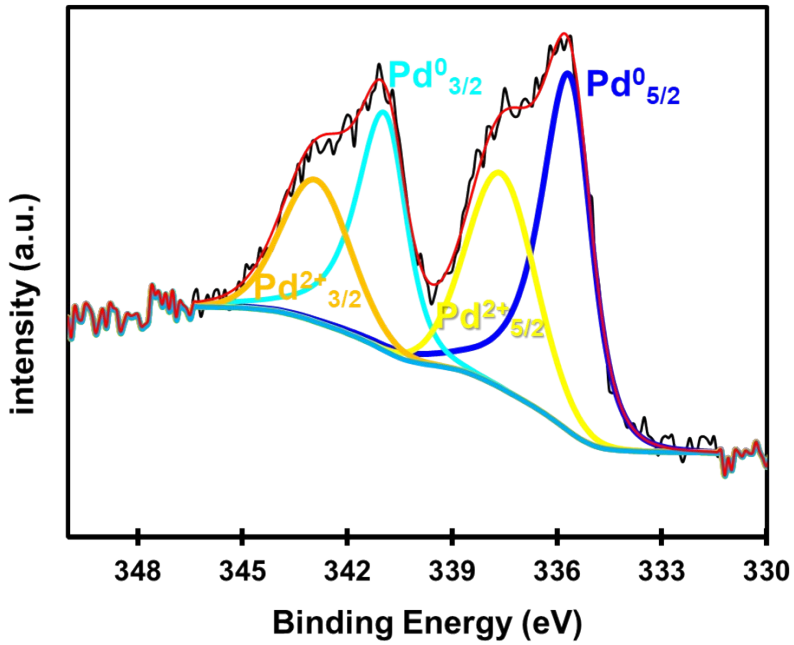


Figure S3: XPS high resolution deconvoluted spectra of **IM1** after the 4th use.

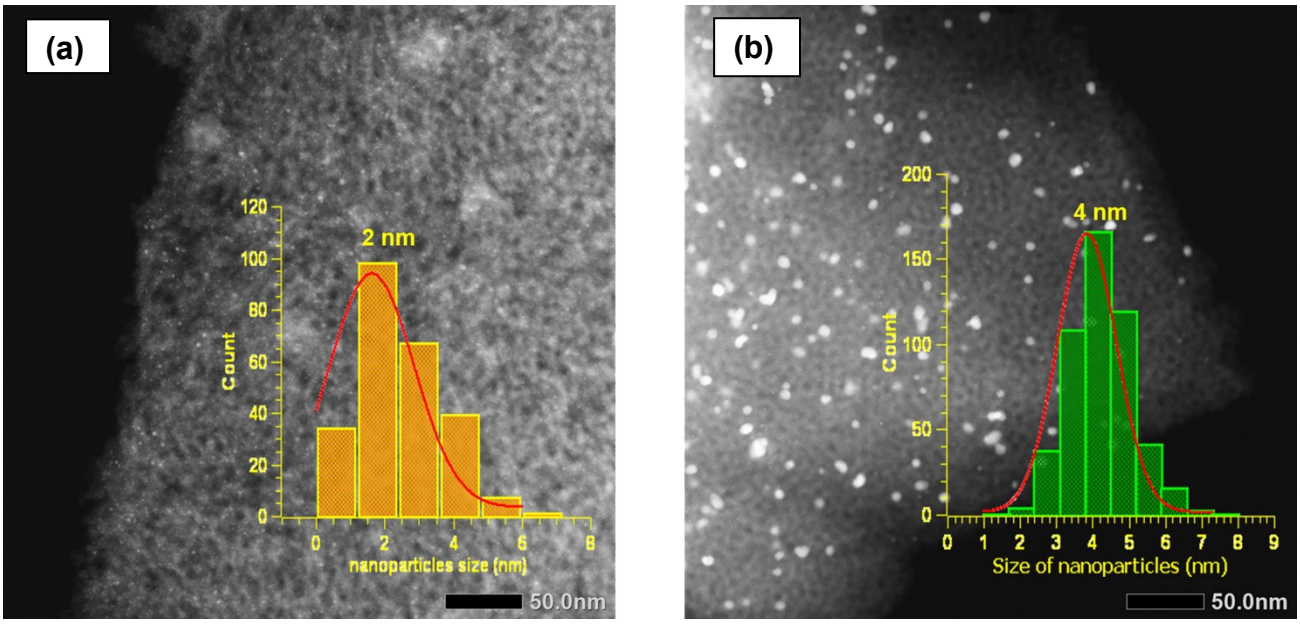


Figure S4: STEM image of **IM1** after the 4th use (a) and TEM image of **IM2** after the 7th use (b).

^{1}H and ^{13}C-NMR Spectra of Aromatic Primary Amines 1a-j[1]

4'-Aminoacetophenone (1a): Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1a** as a white solid (297 mg, 99 % yield). ^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 7.60 (d, ^{3}J(H,H) = 9 Hz, 2H), 6.50 (d, ^{3}J(H,H) = 9 Hz, 2H), 5.95 (br. s, 2H), 2.32 (s, 3H). ^{13}C-NMR (125 MHz, CD_3OD) δ (ppm) = 197.8 , 154 , 130.79 , 125.5 , 112.8 , 24.5.

Ethyl 4-aminobenzoate (**1b**): Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1b** as an orange solid (327 mg, 99 %). ^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 7.56 (d, ^{3}J(H,H) = 9 Hz, 2H), 6.50 (d, ^{3}J(H,H) = 9 Hz, 2H), 5.88 (br. s, 2H), 4.14 (q, ^{3}J(H,H) = 7 Hz, 2H), 1.20 (t, ^{3}J(H,H) = 7 Hz, 3H). ^{13}C-NMR (125 MHz, CD_3OD) : δ (ppm) = 167.5, 153.3, 131.0, 117.4, 112.9, 59.9, 13.3.

2-Aminobenzoic acid (1c): Elution with AcOEt / cyclohexane (40/60) as eluent afforded **1c** as a yellowish solid (269 mg, 98 %). ^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 12.1 (br. s, 1H), 8.47 (br. s, 2H), 7.62 (dd, ^{3}J(H,H) = 9 Hz, ^{4}J(H,H) = 2 Hz, 1H), 7.15 (td, ^{3}J(H,H) = 9 Hz, ^{4}J(H,H) = 2 Hz, 1H), 6.67 (dd, ^{3}J(H,H) = 9 Hz, ^{4}J(H,H) = 2 Hz, 1H)), 6.43 (td, ^{3}J(H,H) = 9 Hz, ^{4}J(H,H) = 2 Hz, 1H). ^{13}C-NMR (125 MHz, CD_3OD) : δ (ppm) = 170.2, 151.4, 133.6, 131.3, 116.3, 115.1, 110.3.

2-Aminoterephthalic acid (1d): Elution with AcOEt / cyclohexane (40/60) as eluent afforded **1d** as a yellow solid (333 mg, 92 %). ^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 12.2 (br. s, 2H), 8.7 (br. s, 2H), 7.70 (d, ^{3}J(H,H) = 8 Hz, 1H), 7.31(d, ^{4}J(H,H) = 2 Hz, 1H), 6.95 (dd, ^{3}J(H,H) = 8 Hz, ^{4}J(H,H) = 2 Hz, 1H). ^{13}C-NMR (125 MHz, CD_3OD): 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 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.18 (def. t, ^{3}J(H,H) = 9 Hz, 2H), 6.78 (def. t, ^{3}J(H,H) = 9 Hz, 1H), 6.70 (def. d, ^{3}J(H,H) = 9 Hz, 2H), 3.65 (br. s, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) : δ (ppm) = 147.1, 128.6, 117.9, 115.3.

4-Fluoroaniline (1f): Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1f** as a brown liquid (219 mg, 99 %) ^{1}H-NMR (300 MHz, $CDCl_3$) : δ (ppm) = 6.83 (t, ^{3}J(H,H) = ^{3}J(H,F) = 9 Hz, 2H), 6.60 (dd, ^{3}J(H,H) = 9 Hz, ^{4}J(H,F) = 5 Hz, 2H), 3.48 (br. s, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) =

157.4 (d, ^{1}J(C,F) = 235 Hz), 142.5 (d, ^{4}J(C,F) = 2.2 Hz), 116.1 (d, ^{2}J(C,F) = 7.4 Hz), 115.8 (d, ^{3}J(C,F) = 22.4 Hz). ^{19}F-NMR (470.5 MHz, $CDCl_3$) δ (ppm) = -126.8.

1,2-Phenylenediamine (1g): Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1g** as a brown solid (214 mg, 99 %). ^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 6.43 (m, 2H), 6.30 (m, 2H), 4,31 (br. s, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) : δ (ppm) = 134.5, 119.4, 116.3.

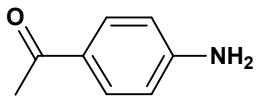
2,4-Dimethylaniline (1h): Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1h** as a dark red liquid (240 mg, 99 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.85 (m, 2H), 6.60 (d, ^{3}J(H,H) = 9 Hz, 1H), 3.46 (br. s, 2H), 2.22 (s, 3H), 2.14 (s, 3H). ^{13}C-NMR (125 MHz, CD_3OD) : δ (ppm) = 141.4, 130.5, 128.0, 126.8, 123.3, 115.8, 19.2, 16.0.

4-Aminophenol (1i): Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1j** as a yellowish solid (216 mg, 99 %). ^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 8.25 (s, 1H), 6.38 (AA'BB', ^{3}J(H,H) = 9 Hz, $\nu_o\delta$ = 16 Hz, 4H), 4.30 (br. s, 2H). ^{13}C-NMR (125 MHz, CD_3OD) : δ (ppm) = 149.9, 138.9, 117.1, 115.3.

3-aminopyridine (1j): Elution with AcOEt / cyclohexane (25/75) as eluent afforded **1k** as a brown solid (186 mg, 99 %). ^{1}H-NMR (300 MHz, DMSO-d6) δ (ppm) = 7.86 (def. s, 1H), 7.66 (dt, ^{3}J(H,H) = 4 Hz, ^{4}J(H,H) = 2 Hz, 1H), 6.94 ((ddd, ^{3}J(H,H) = 9 Hz, ^{3}J(H,H) = 4 Hz, ^{5}J(H,H) = 1 Hz, 1H), 6.83 (dt, ^{3}J(H,H) = 9 Hz, ^{4}J(H,H) = 2 Hz, 1H), 5.18 (br. s, 2H). ^{13}C-NMR (125 MHz, CD_3OD) : δ (ppm) = 145.1, 136.9, 135.7, 124.0, 121.6.

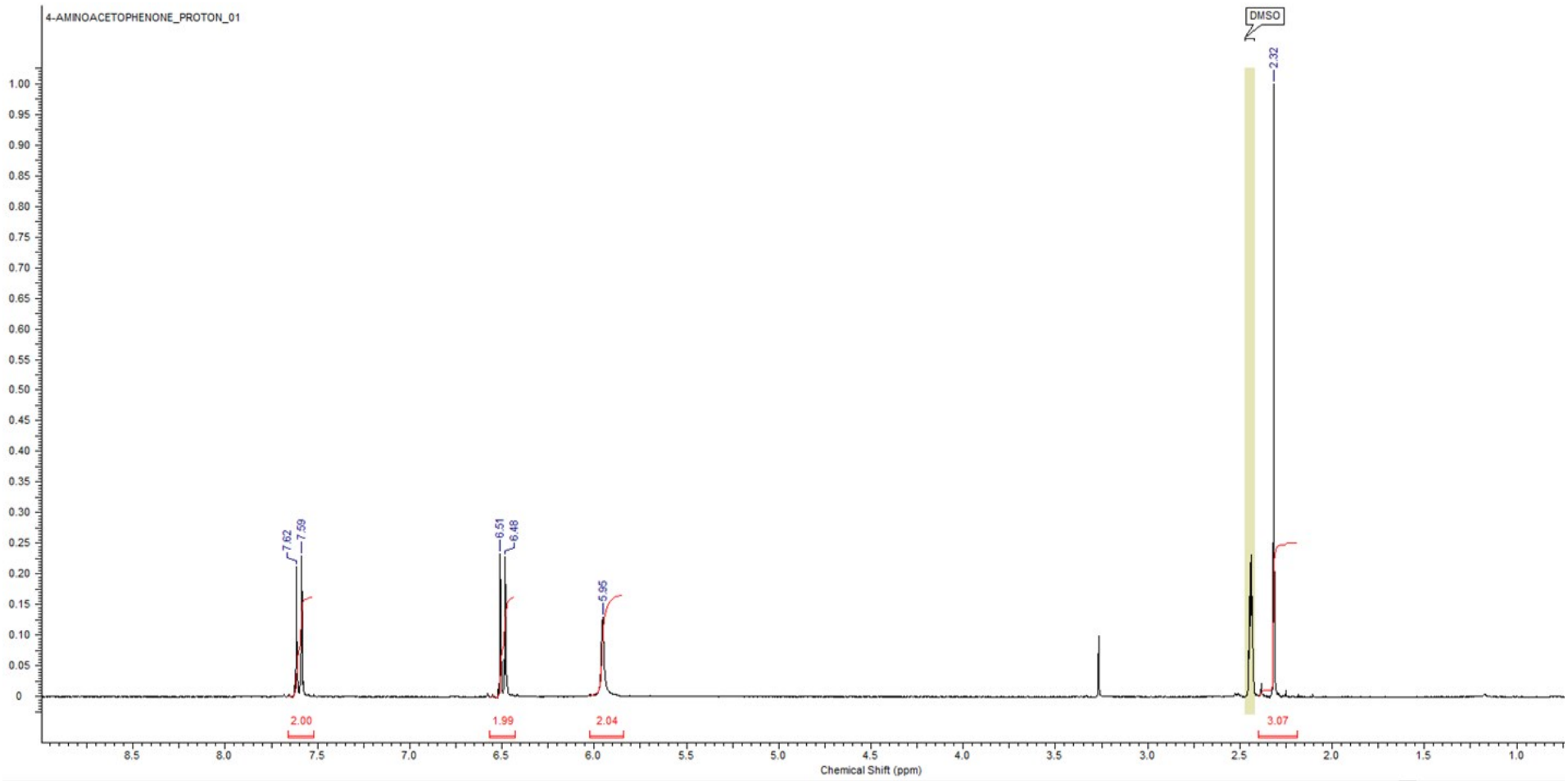
Determinations of the Pd content of catalysts and of the Pd leached in the reaction medium

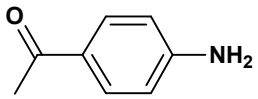
The general procedures for the determinations of the Pd content of catalysts **IM1-IM3** and **DM** and of the amount of Pd leached in the reaction medium during the hydrogenation reaction have been described previously by our group.[2]



Compound **1a**

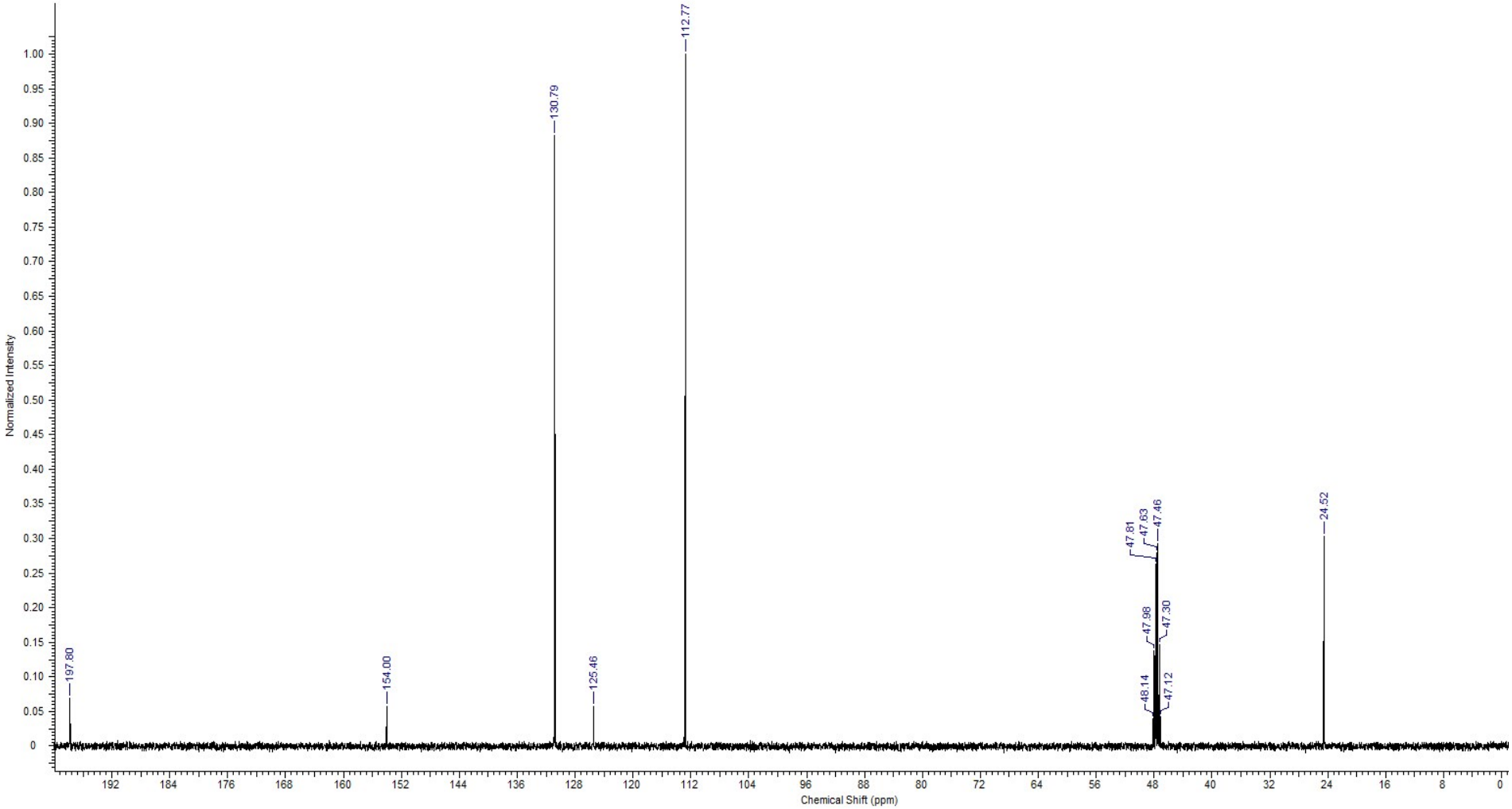
^{1}H-NMR, 300 MHz, DMSO-d6

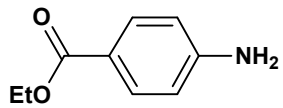




Compound **1a**

^{13}C-NMR, 125 MHz, CD_3OD





Compound **1b**

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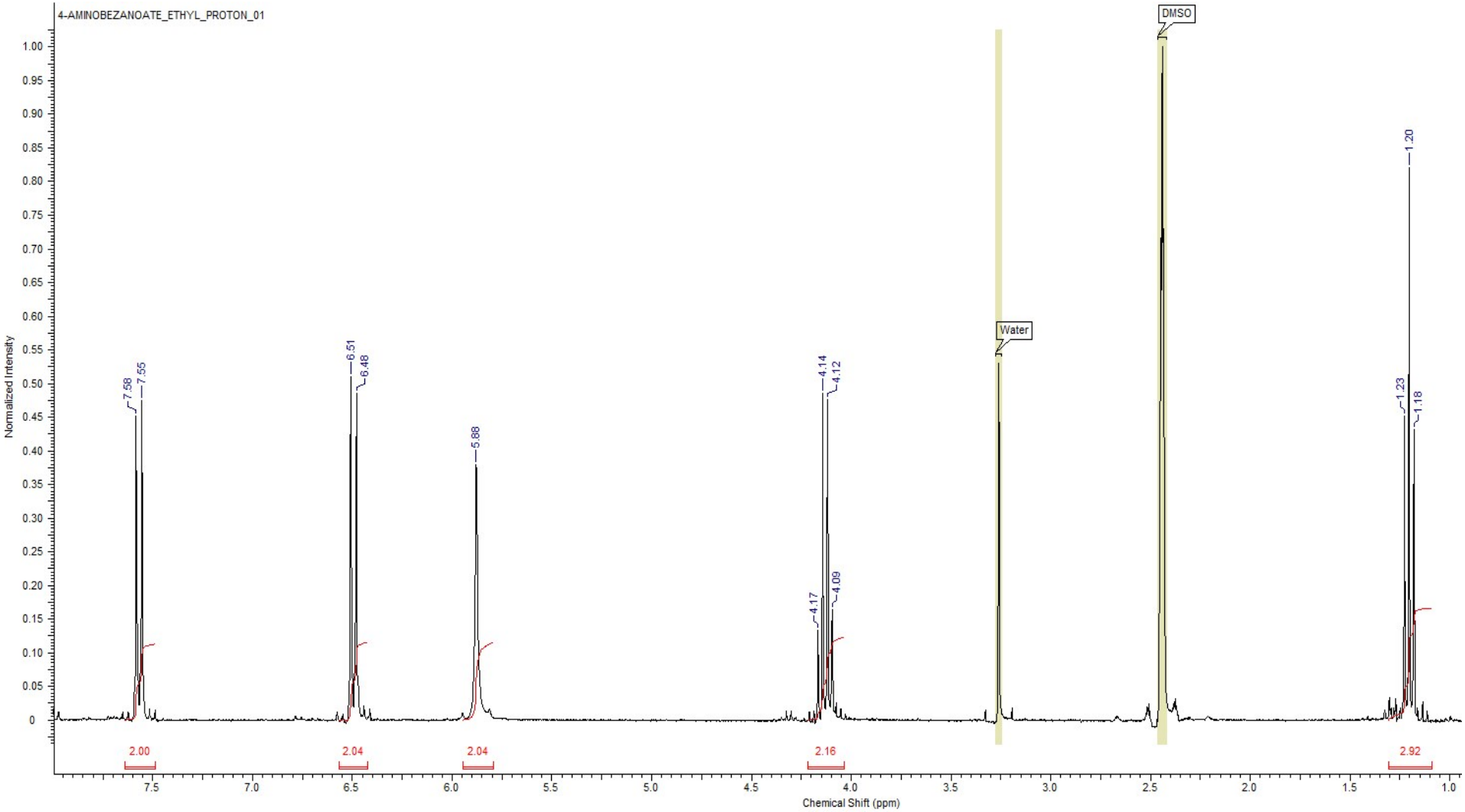
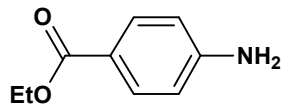
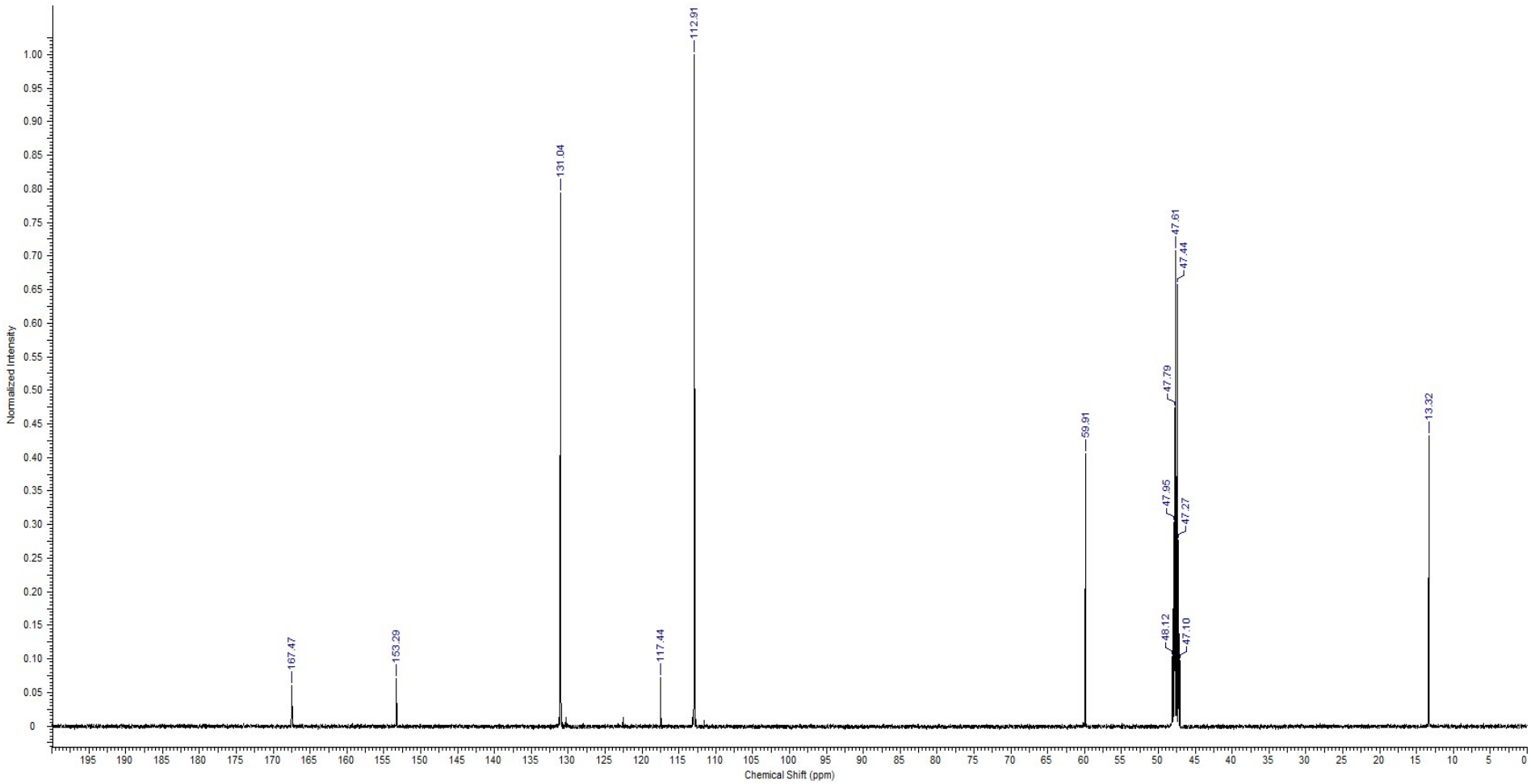
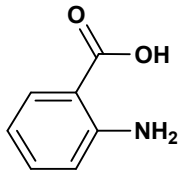




Compound **1b**

^{13}C-NMR, 125 MHz, CD_3OD





Compound **1c**

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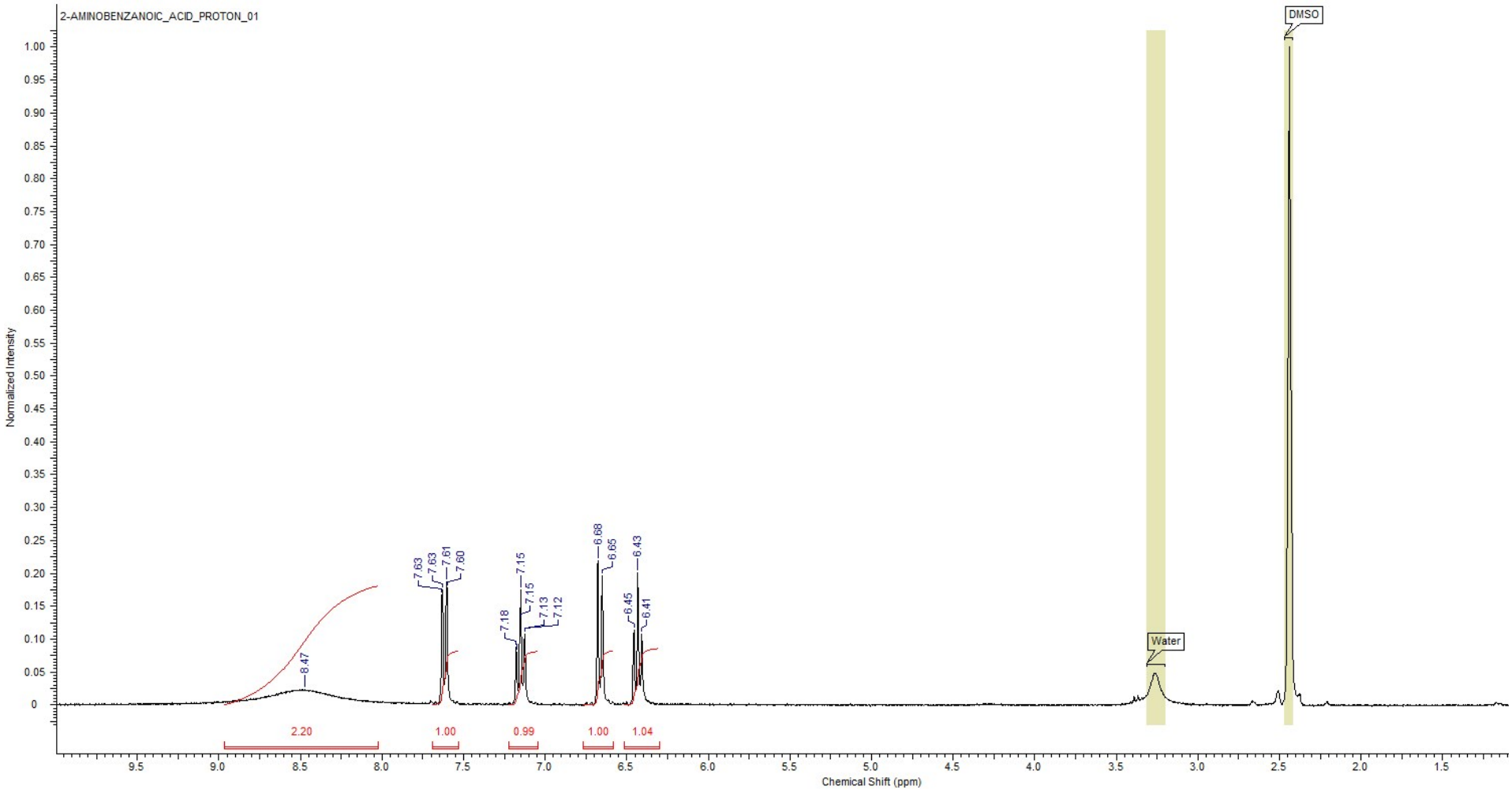
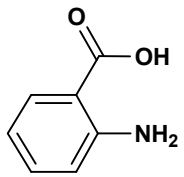
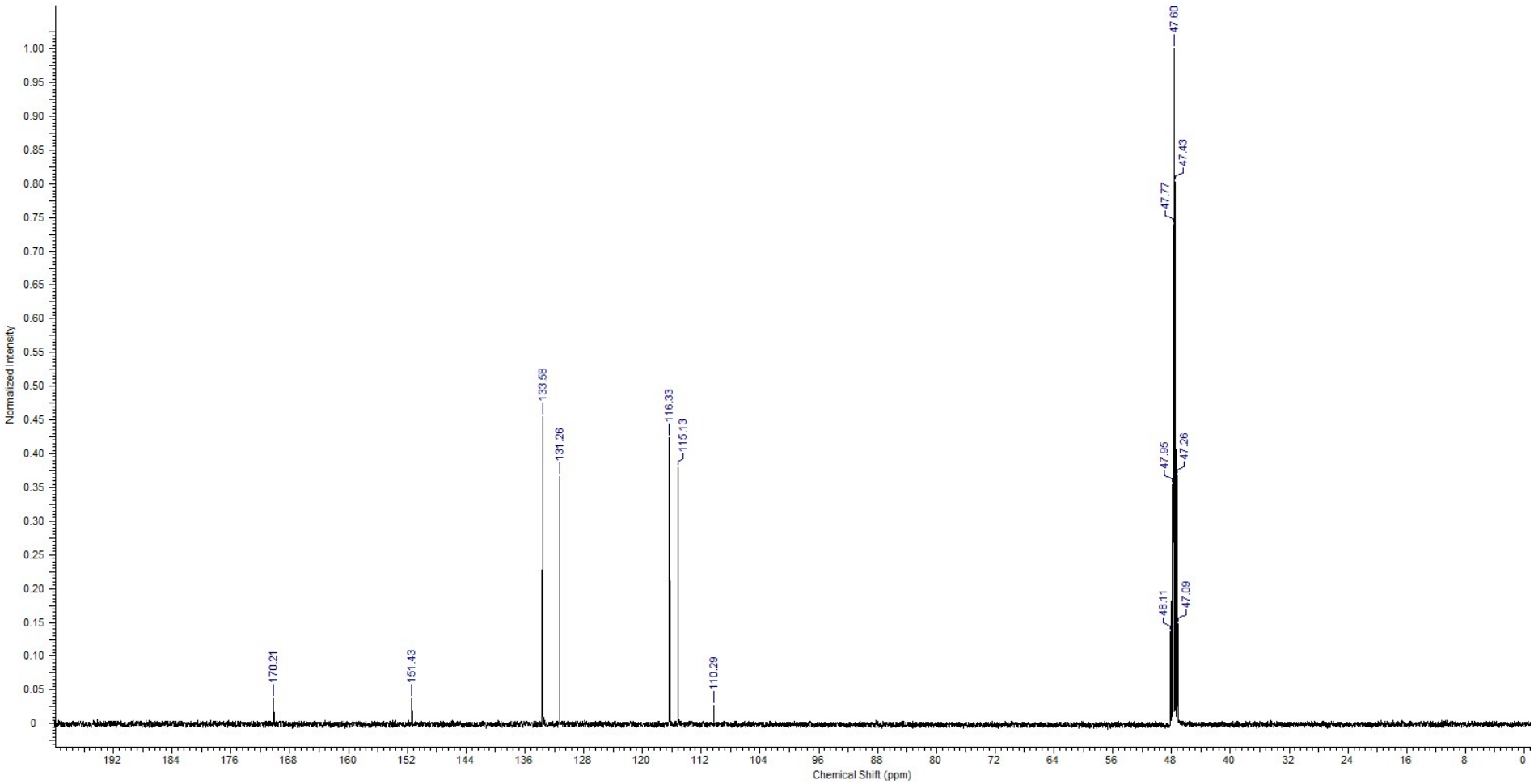
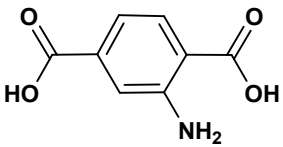




Compound **1c**

^{13}C-NMR, 125 MHz, CD_3OD





Compound **1d**

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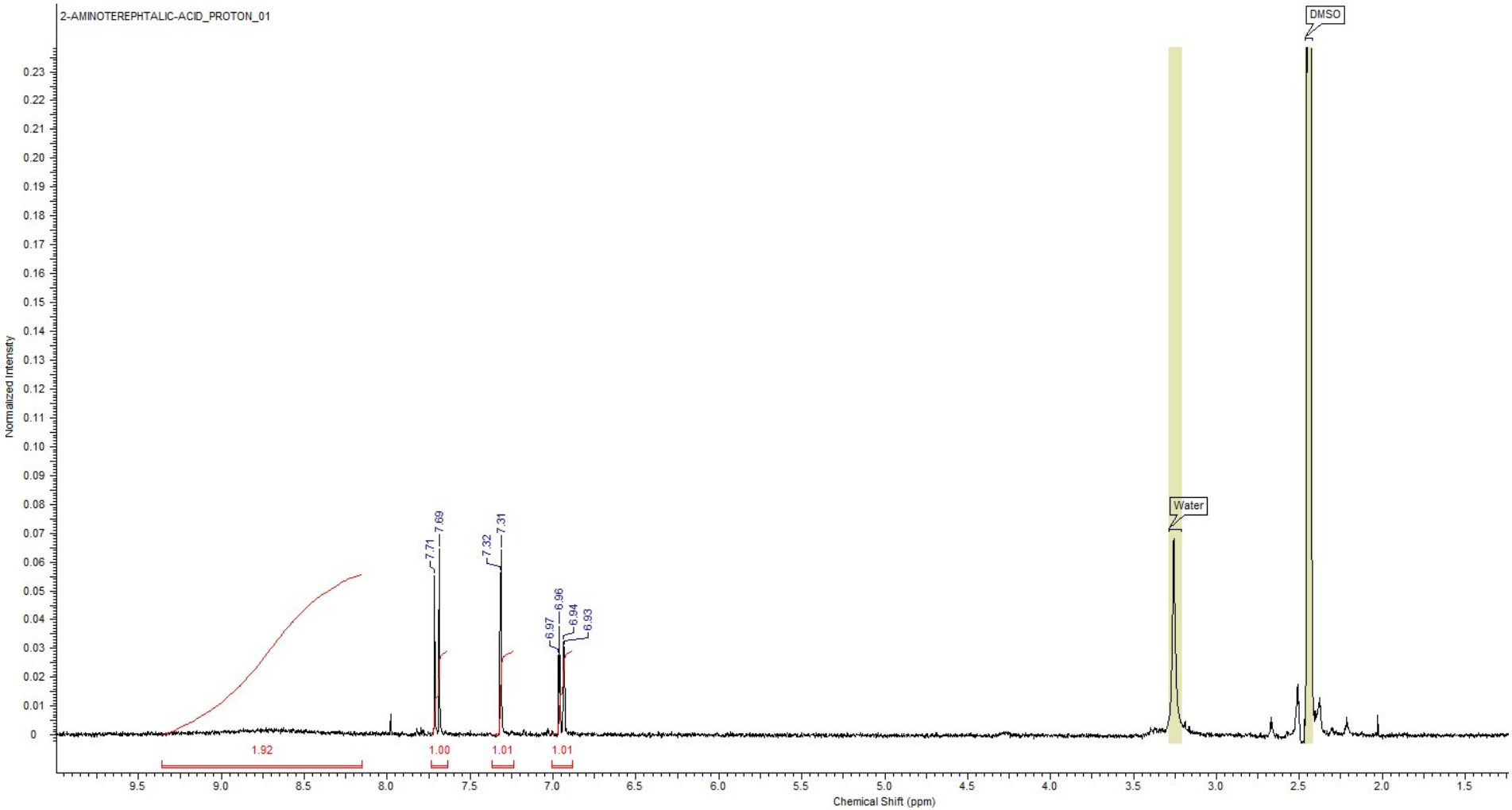
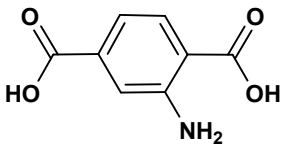
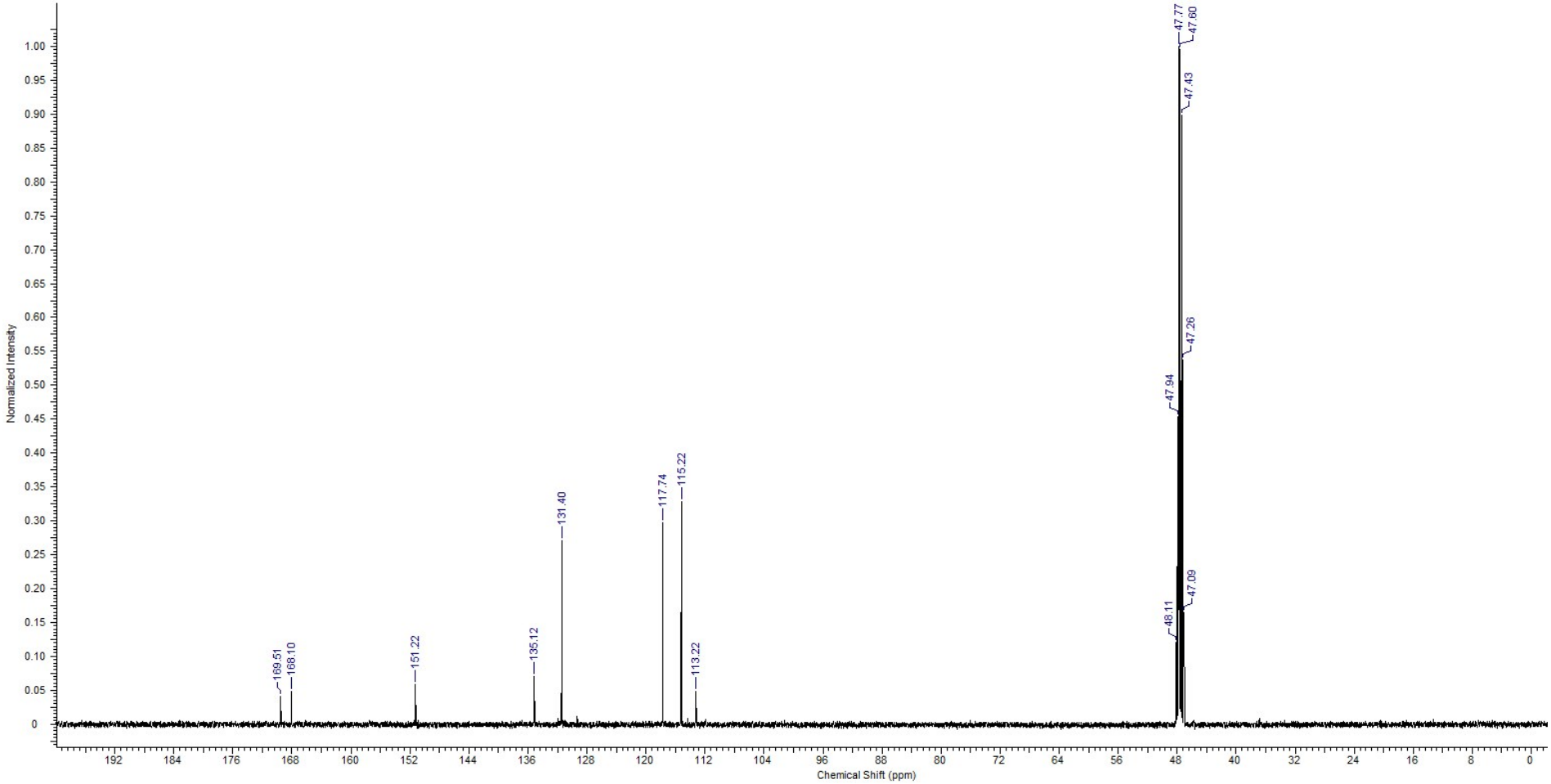
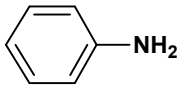




Compound **1d**

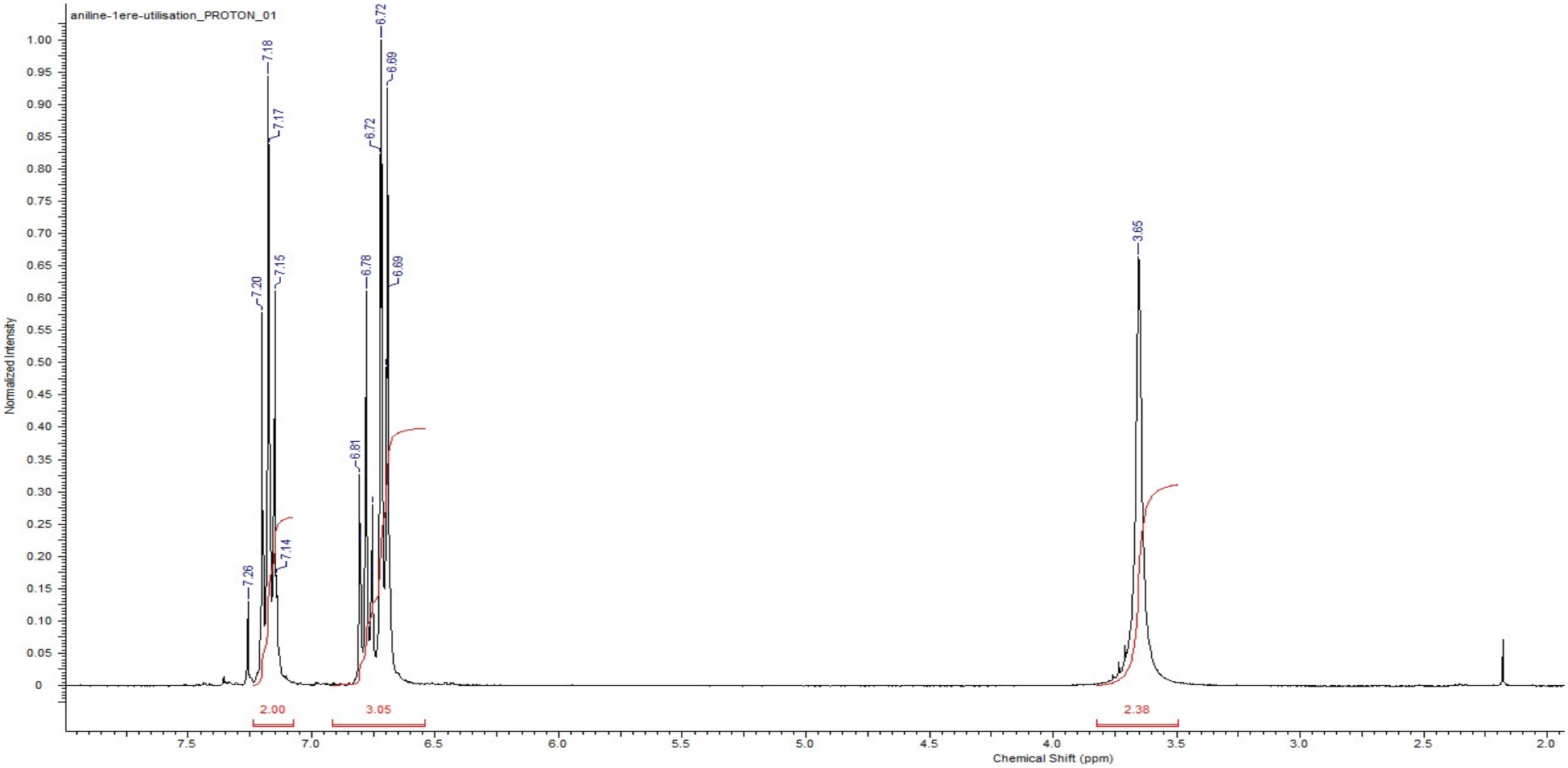
^{13}C-NMR, 125 MHz, CD_3OD

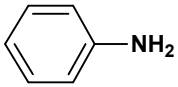




Compound **1e**

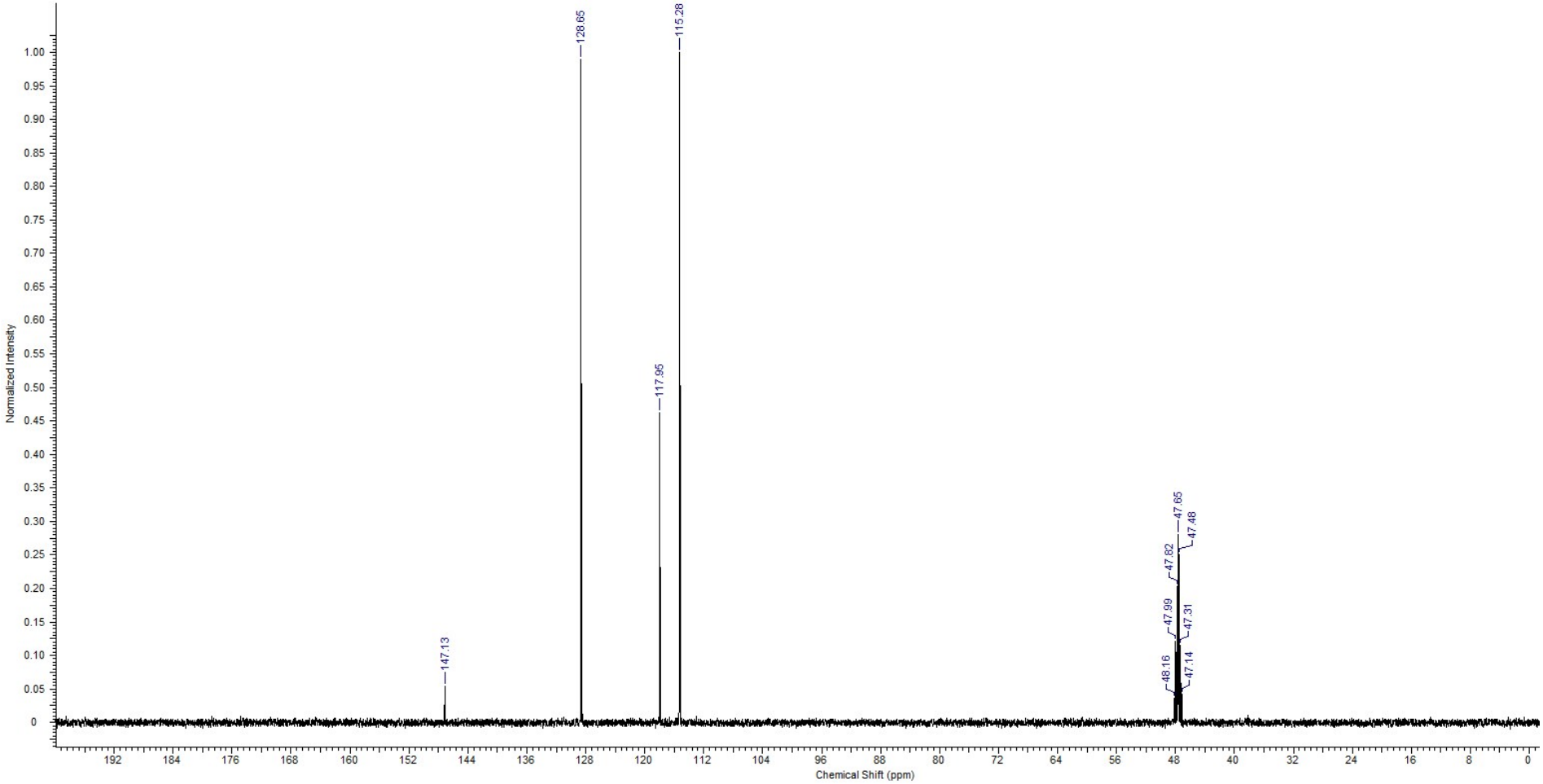
^{1}H-NMR, 300 MHz, $CDCl_3$

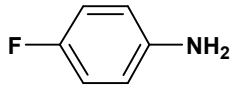




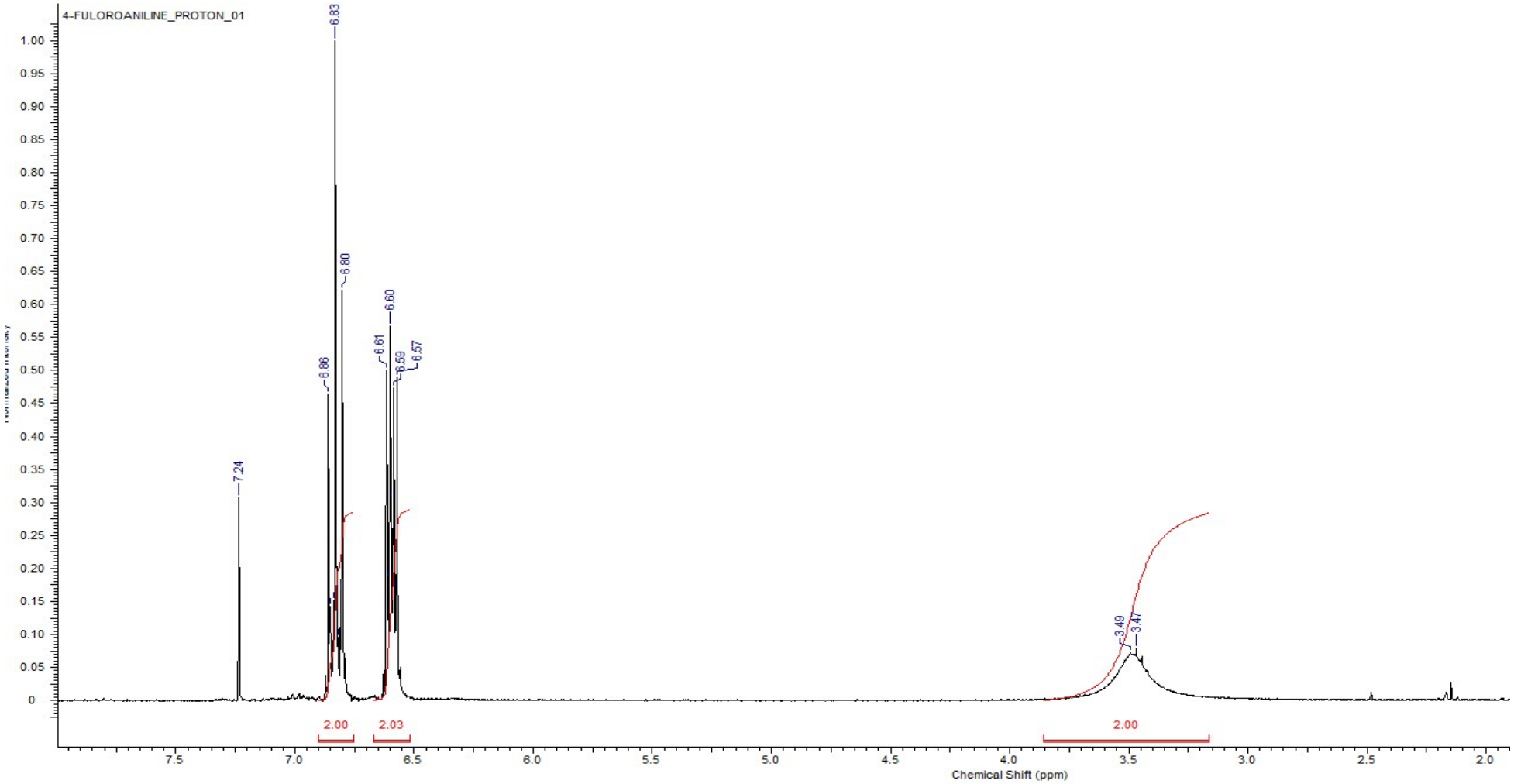
Compound **1e**

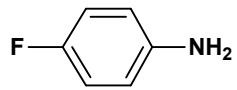
^{13}C-NMR, 125 MHz, $CDCl_3$





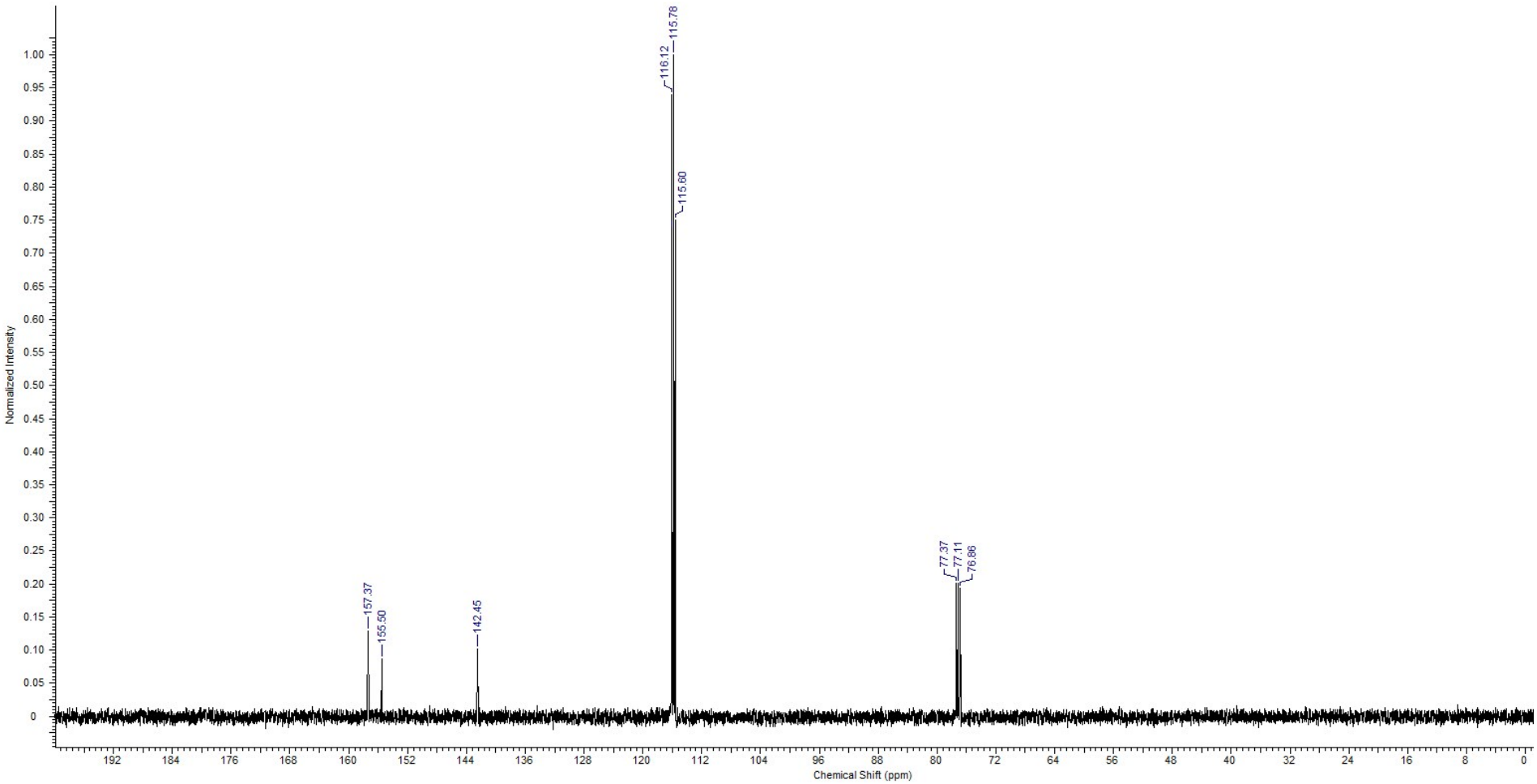
Compound **1f**
^{1}H-NMR, 300 MHz, $CDCl_3$

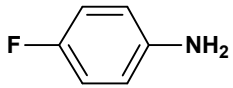




Compound **1f**

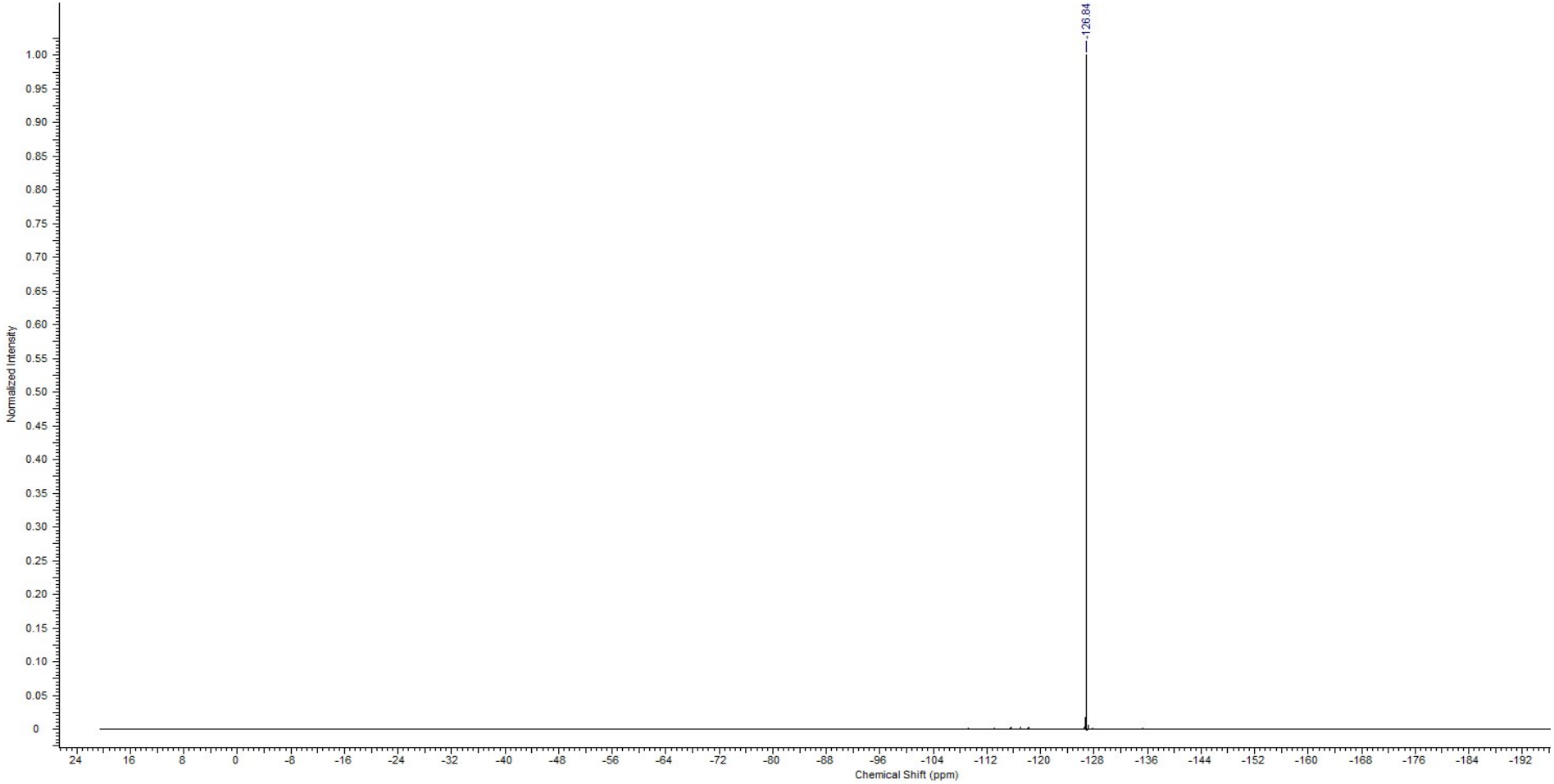
^{13}C-NMR, 125 MHz, $CDCl_3$

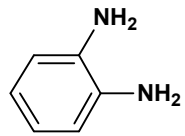




Compound **1f**

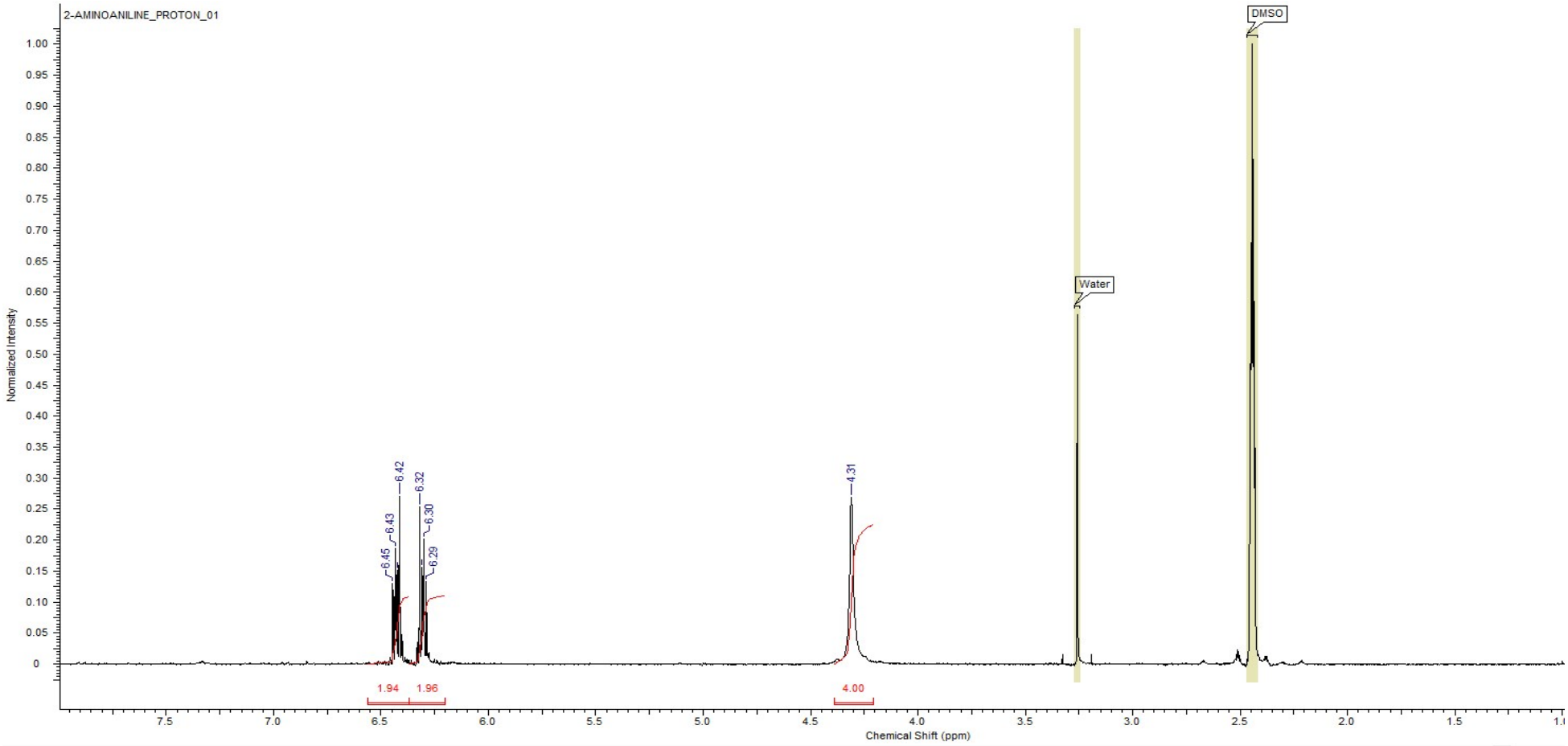
^{19}F-NMR, 470.5 MHz, $CDCl_3$

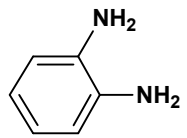




Compound **1g**

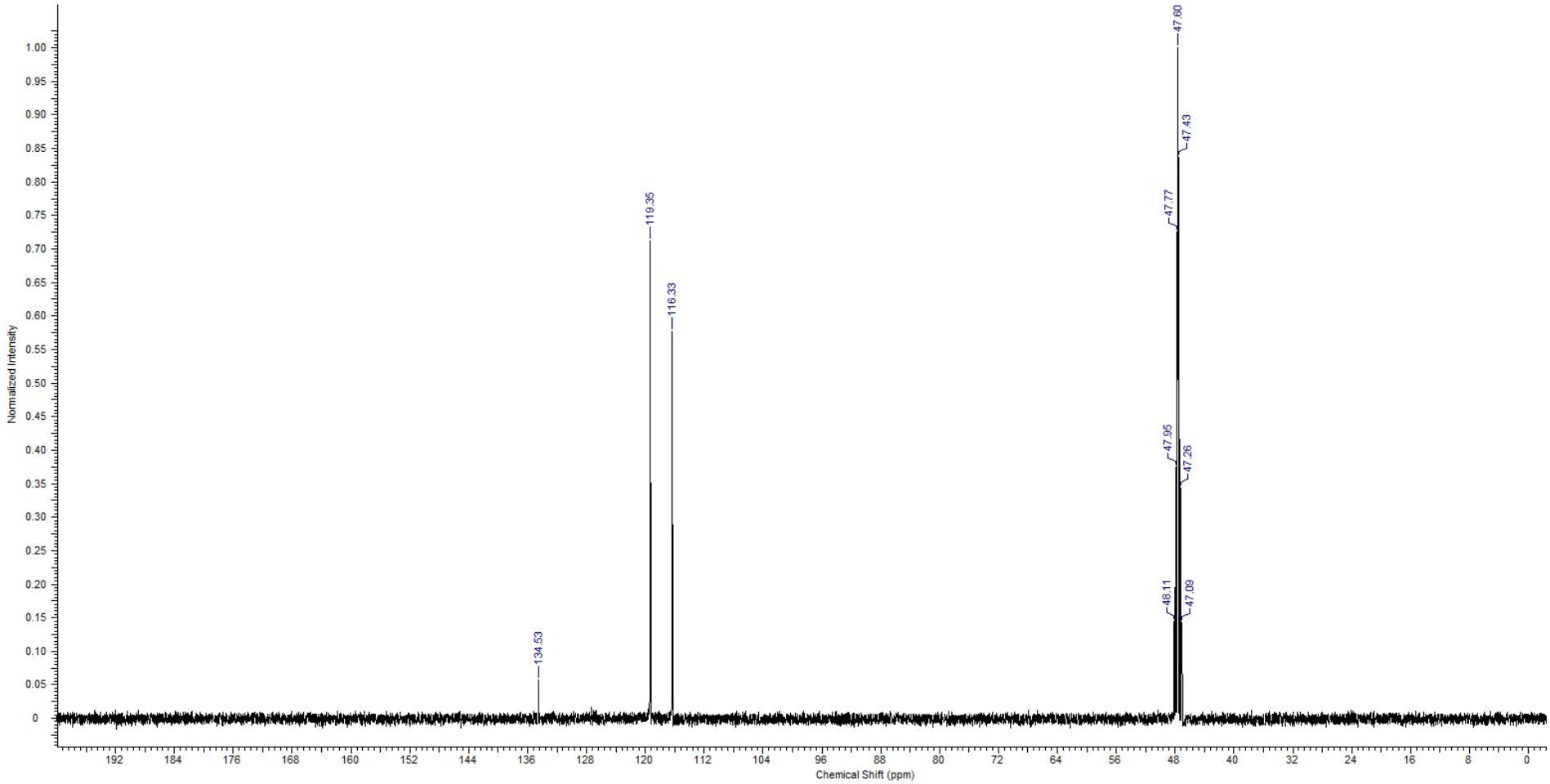
^{1}H-NMR, 300 MHz, DMSO-d6

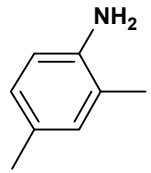




Compound **1g**

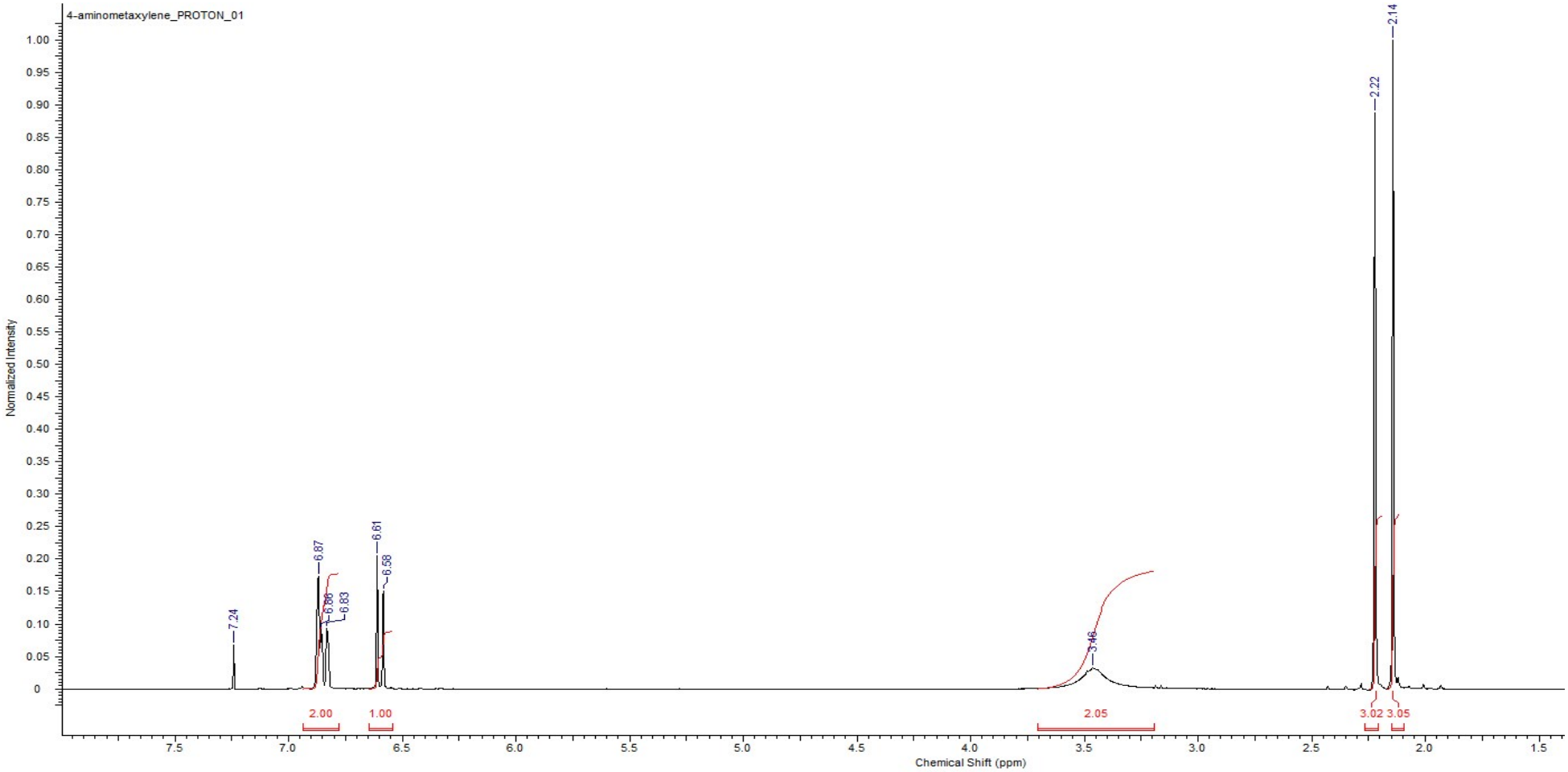
^{13}C-NMR, 125 MHz, CD_3OD

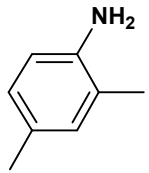




Compound **1h**

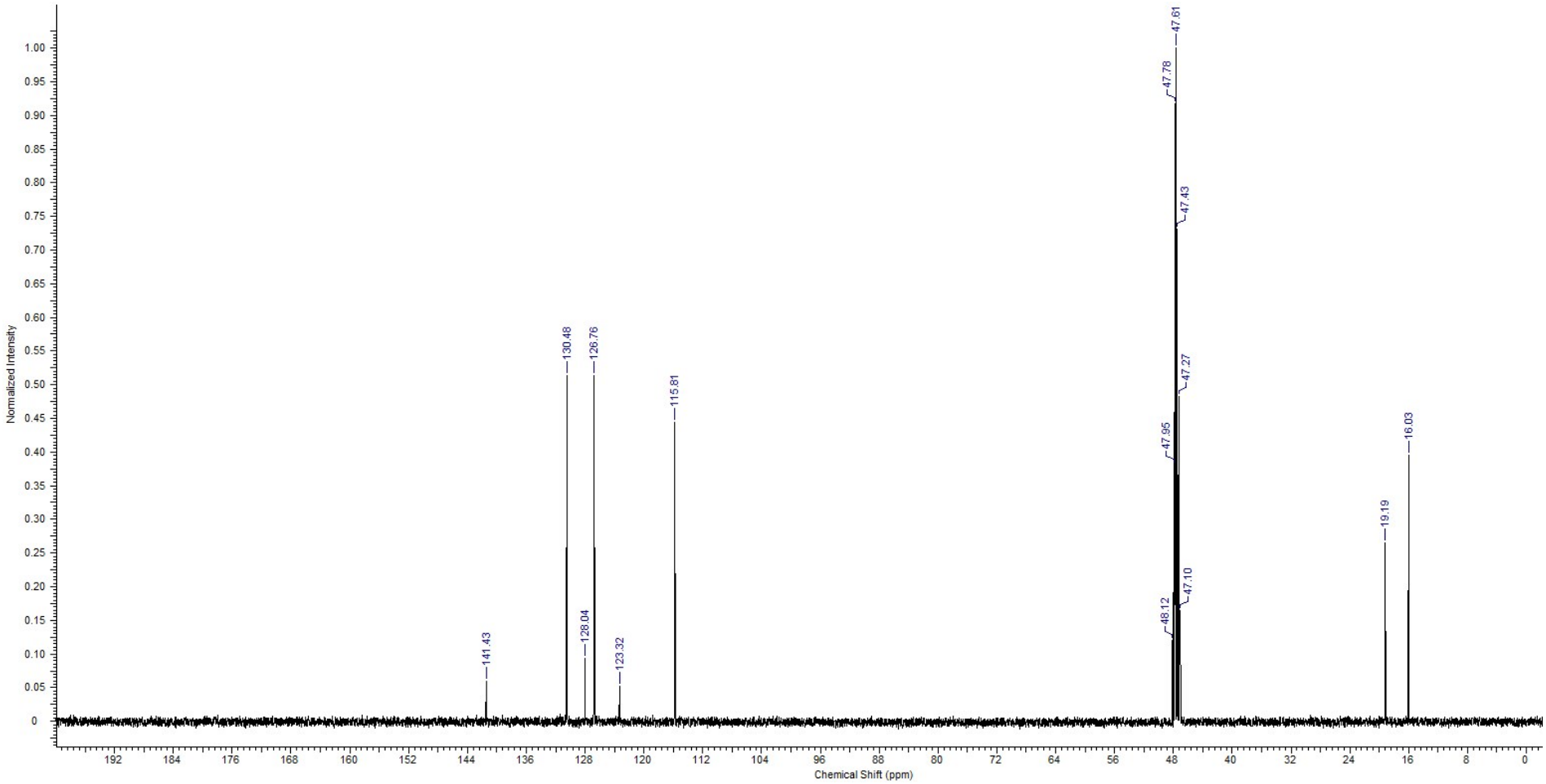
^{1}H-NMR, 300 MHz, $CDCl_3$

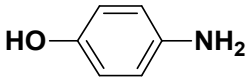




Compound **1h**

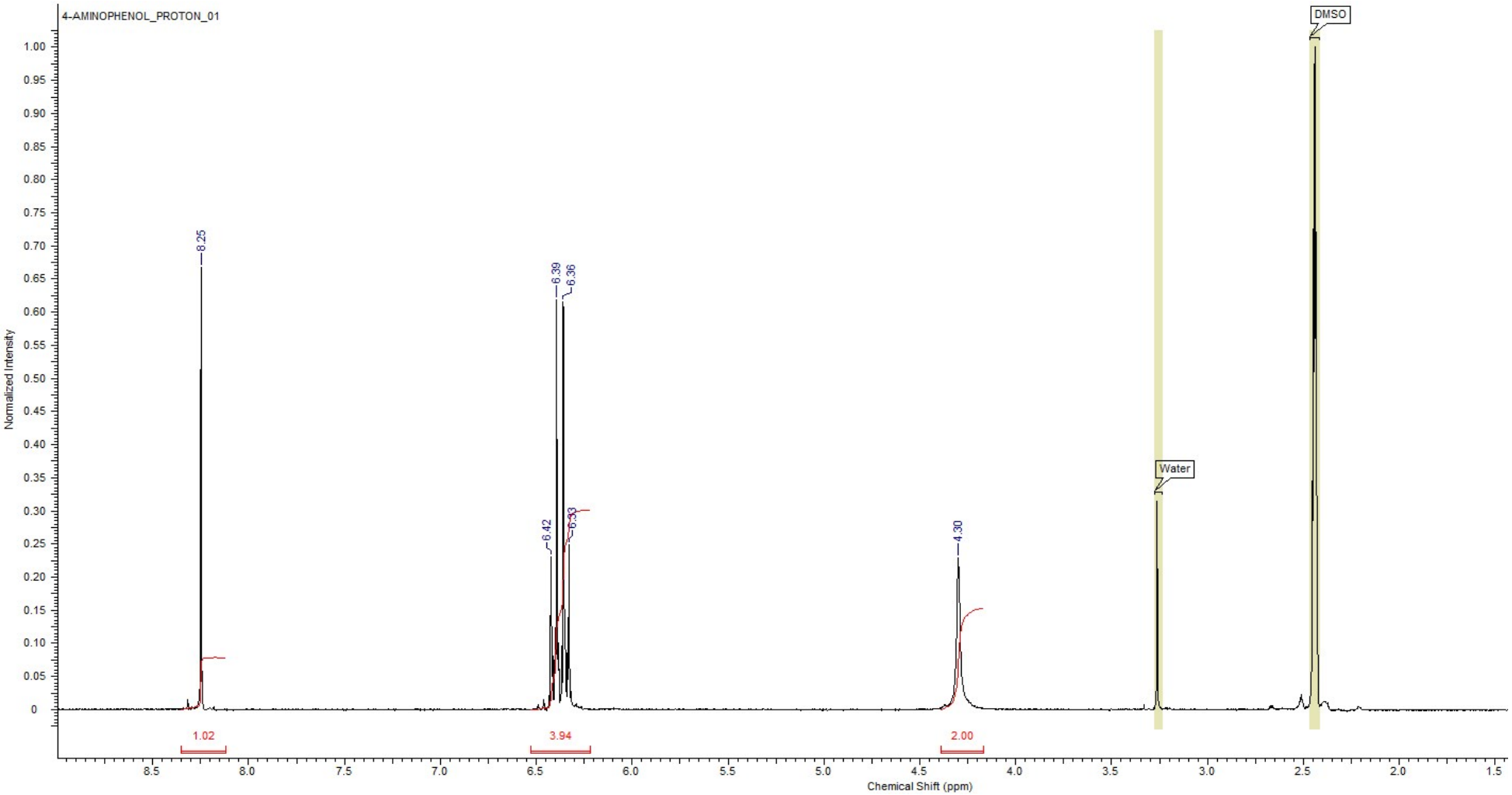
^{13}C-NMR, 125 MHz, CD_3OD

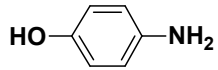




Compound **1i**

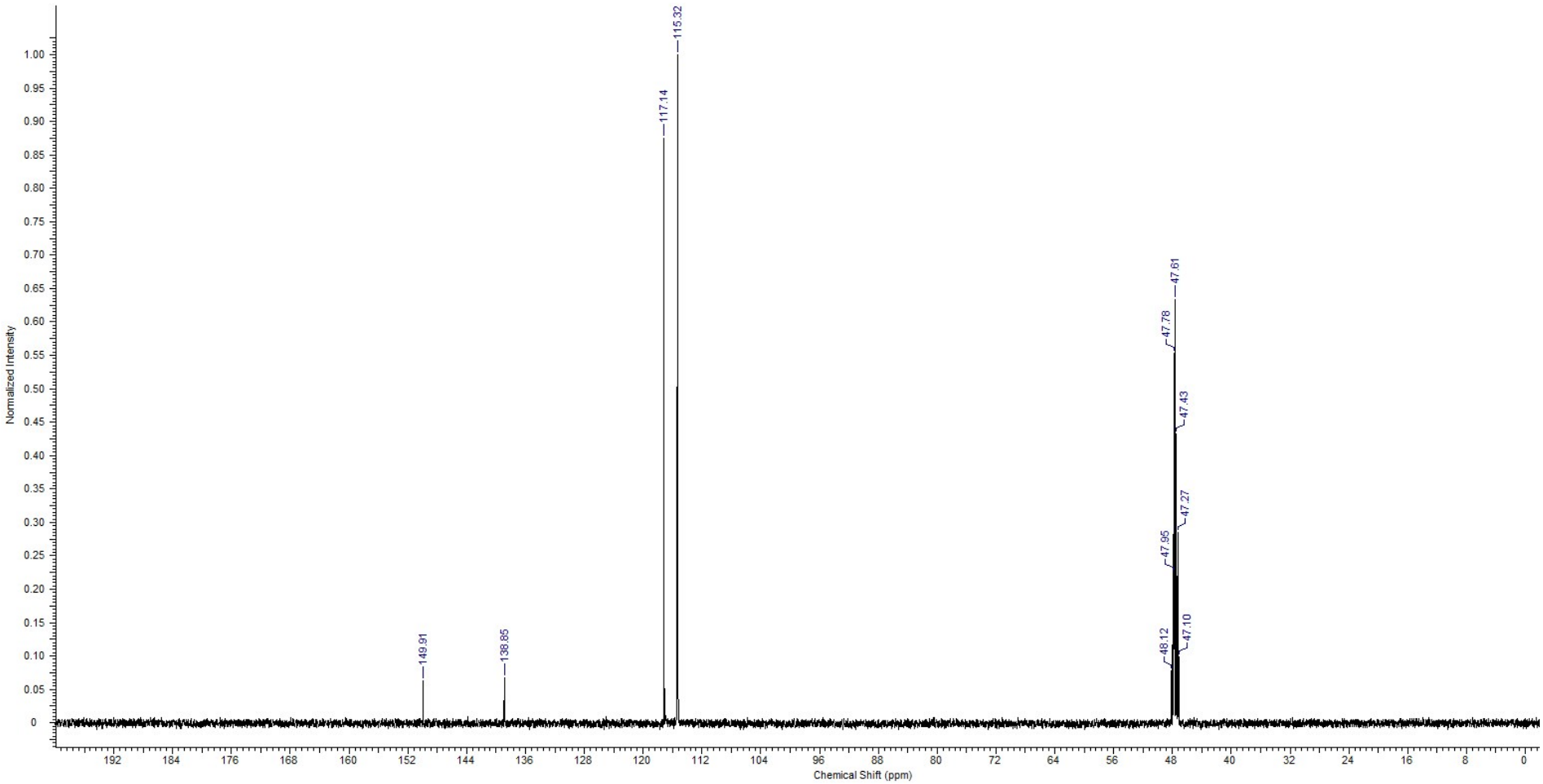
^{1}H-NMR, 300 MHz, DMSO-d6

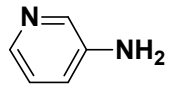




Compound **1i**

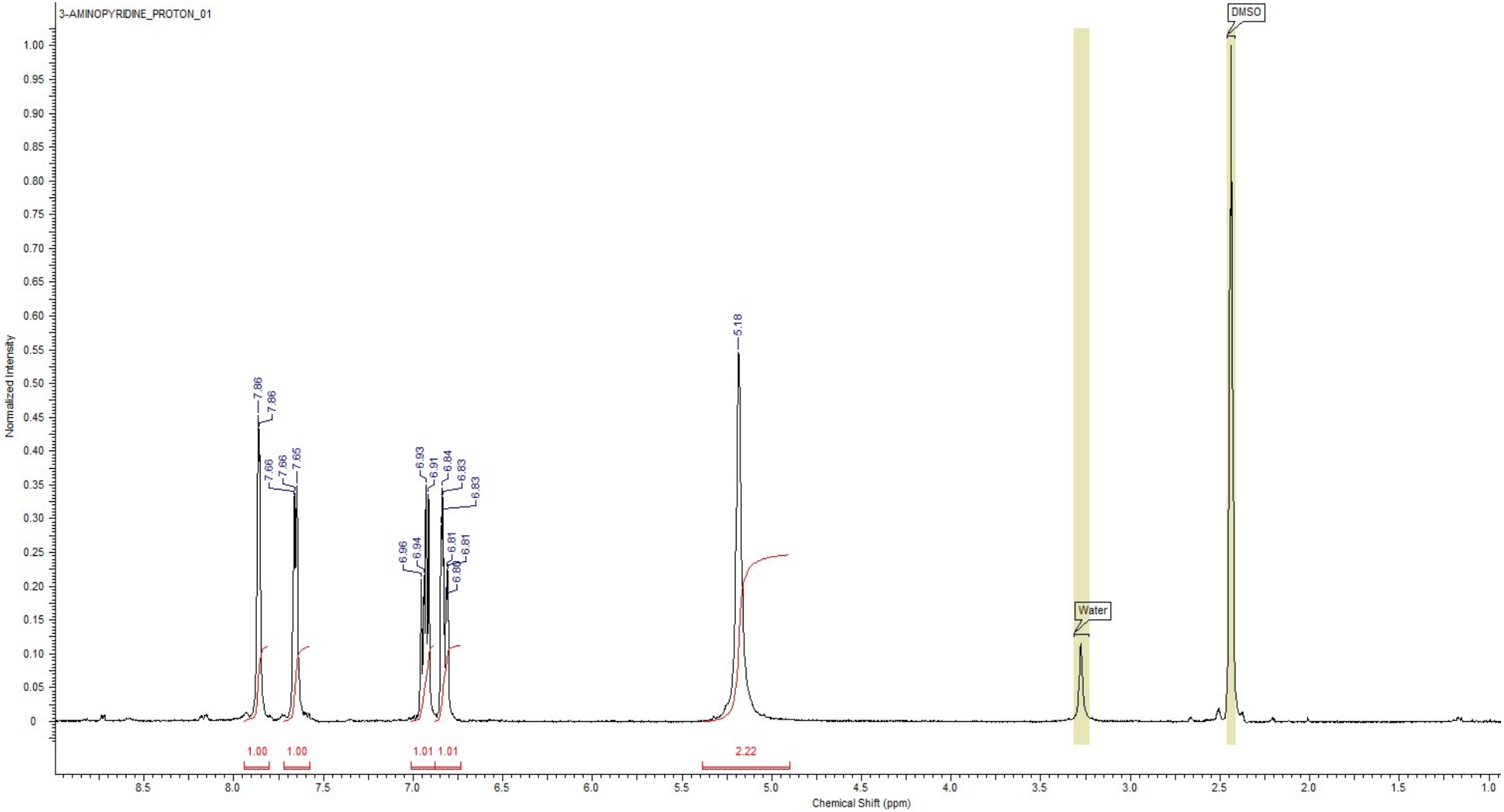
^{13}C-NMR, 125 MHz, CD_3OD

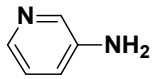




Compound **1j**

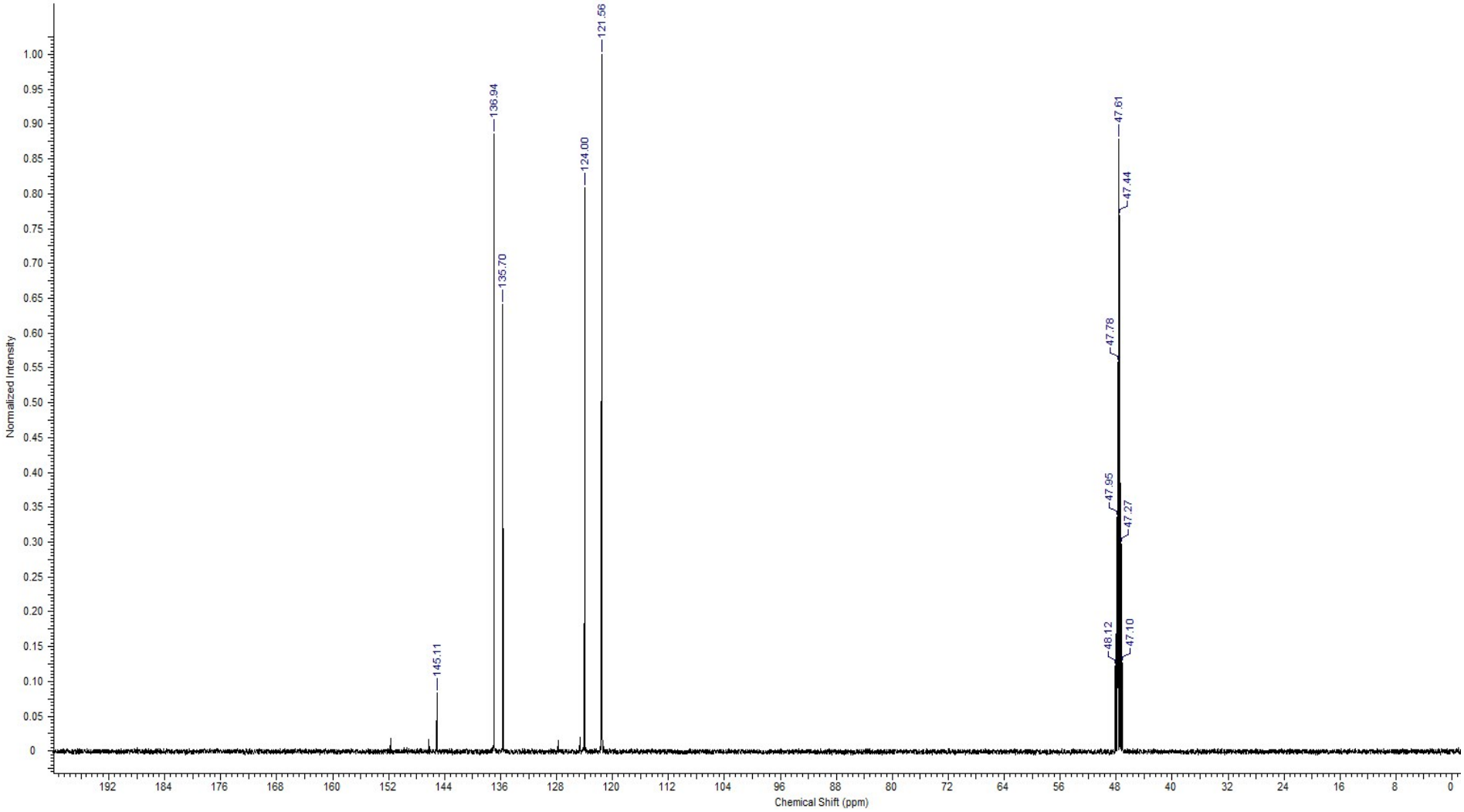
^{1}H-NMR, 300 MHz, DMSO-d6





Compound **1j**

^{13}C-NMR, 125 MHz, CD_3OD



References :

[1] ^{1}H- and ^{13}C-NMR spectra were in accordance with a previous literature report: M. Enneiymy, C. Le Drian, J.-M. Becht, *New J. Chem.* **2019**, *43*, 17383.

[2] A. Derible, C. Diebold, J. Dentzer, R. Gadiou, J.-M. Becht, C. Le Drian, *Eur. J. Org. Chem.* 2014, 7699 and Supporting Informations.