Supporting Information

Highly chemoselective and fast practical visible photoreduction of nitroaromatic compounds to aromatic amines and amides using a self-assembled triad TiO_2-TEOA-NC (LMCT/EDA) complex system

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1. Meterials and Apparatuses

TiO_2 (Degussa P25) was provided from Degussa Corporation. All reagents were used without further purification. Triethanolamine (TEOA, $C_6H_{15}NO_3$), *tert*-Butanol anhydrous (*t*-BuOH, $(CH_3)_3COH$), Triethyl orthoformate ($HC(OC_2H_5)_3$), Acetic anhydride (Ac_2O, $(CH_3CO)_2O$) , Benzoic anhydride ($(C_6H_5CO)_2O$), Nitro compounds (NC), Sodium bicarbonate ($NaHCO_3$), Sodium chloride (NaCl), Chloroform ($CHCl_3$), *n*-Hexane (C_6H_{14}), Ethyl acetate (EtOAc, $C_4H_8O_2$), were purchased from Sigma-Aldrich and Merck Company.

FTIR was measured using a Perkin Elmer spectrometer with KBr pellets. N_2 adsorption–desorption isotherms were measured using BELSORP max apparatus (77 K). Before investigating the surface areas of the materials, samples were degassed firstly at 200°C. UV-Visible diffusive reflectance spectra (DRS) were monitored by using a Cary 100 UV-Vis spectrophotometer with a diffuse reflectance accessory, samples were mixed in $BaSO_4$ (1:20 sample $BaSO_4$) and pressed into a tablet, a $BaSO_4$ tablet made under the same conditions was used as a reference. The photoluminescence (PL) spectra were obtained at 25°C with a fluorospectrophotometer (Varian) using a Xe lamp as an excitation source. Photocatalytic reduction reaction was also carried out under violet LED irradiation (LED Epistar, 50 W, 20- 30 LM 700 mA h light bulb). Thermogravimetric analysis (TGA) was done using a Diamond TG/DTA (Perkin Elmer, USA) instrument. The Dynamic Light Scattering (DLS) technique for particle size measurement was carried out using a Malvern instrument (ZEN3600).

2. Synthesis of chemically absorbed TiO_2-TEOA complex

The chemically absorbed TiO_2-TEOA surface complex was synthesized using visible light irradiation. 50 mg of TiO_2-P25 was suspended in 10 mL of deionized water. To the above suspension, required amount (2 ml) of triethanolamine (TEOA) was added drop by drop under continuous stirring. The resulting suspension was irradiated under stirring by a violet LED (400 nm, 1×50 w) as a light source for 3h at room temperature. The LED was placed about 1 cm from the down middle of the flask. Then after 20 minutes, the color of the reaction mixture was changed from white to a turquoise blue, which indicating the formation of TiO_2-TEOA

surface complex. Finally, the product was collected by centrifugation and washed several times with deionized water to remove residual organic moiety and dried at 70 ˚C for 24 h.

3. General procedure for the photoreduction of nitro compounds

TiO_2-P25 (10 mg), triethanolamine (7.5 mmol), H_2O (3 ml) and t-BuOH (0.3 ml) was transferred into a round-bottom Pyrex flask (5 mL). Then nitro compounds (1 mmol) were added to this solution and was sonicated for 10-15 min. The flask was irradiated under stirring by a violet LED (50 w) according to the data in Table 1. To avoid the photo-heating effect, during the reaction, a cooling fan was used to cool down the reaction flask to assure that the reaction was done at room temperature. After the completion of the reaction according to GC monitoring, the organic material was extracted with $CHCl_3$ (3×15 mL). The organic layer was washed with 5% $NaHCO_3$ aqueous solution (3×15 mL) and saturated NaCl solution (3×15 mL), dried with anhydrous sodium sulfate, filtered and the remaining organic phase after concentration in vacuom was analyzed using thin-layered chromatography (TLC) and pure products were extracted by plate chromatography using n-hexane/EtOAc as an eluent (n-Hexane, EtOAc 5:1). Assignments of the products were done by ^1H NMR and ^{13}C NMR spectroscopy.

4. Scale-up test for the photoreduction of nitro compounds

TiO_2-P25 (10 mg), triethanolamine (7.5 mmol), H_2O (3 ml) and t-BuOH (0.3 ml) was transferred into a round-bottom Pyrex flask (5 mL). Then nitro compounds (1 mmol) were added to this solution and was sonicated for 10 min. The flask was irradiated under stirring by a violet LED (50 w) and after the completion of the reaction according to GC monitoring, another 1 mmol of the nitro compound was added to the same flask and after 10 minutes sonicate was irradiated with the same LED lamp. After the completion of the reaction, the third mmol with 0.5 ml (3.79 mmol) of TEOA was added, and after sonicate was irradiated with the same LED. This method continued until 5 mmol of the substrate and after the completion of the reaction according to GC monitoring, the organic material was extracted with $CHCl_3$ (3×15 mL). The organic layer was washed with 5% $NaHCO_3$ aqueous solution (3×15 mL) and saturated NaCl solution (3×15 mL), dried with anhydrous sodium sulfate, filtered and the remaining organic phase after concentration in vacuum was analyzed using thin-layered chromatography (TLC) and pure products were extracted by plate chromatography using n-hexane/EtOAc as an eluent (n-Hexane, EtOAc 5:1). Assignments of the products were done by ^1H NMR and ^{13}C NMR spectroscopy.

5. General procedure for one-pot synthesis of amides from nitro compounds

TiO_2-P25 (10 mg), triethanolamine (6 mmol), H_2O (3 ml) and t-BuOH (0.3 ml) was transferred into a round-bottom Pyrex flask (5 mL) then nitro compounds (1 mmol) and triethyl orthoformate (1.2 mmol) for formylation or anhydride (acetic anhydride or benzoic anhydride) (1.2 mmol) were added to this solution and

was sonicated for 15 min. The flask was irradiated under stirring by a violet LED (50 w) according to the data in Table 5. After the completion of the reaction according to GC monitoring, the organic material was extracted with $CHCl_3$ (3×15 mL). The organic layer was washed with 5% $NaHCO_3$ aqueous solution (3×15 mL) and saturated NaCl solution (3×15 mL), dried with anhydrous sodium sulfate, filtered and the remaining organic phase after concentration in vacuom was analyzed using thin-layered chromatography (TLC) and pure products were extracted by plate chromatography using n-hexane/EtOAc as an eluent (n-Hexane, EtOAc 4:1). Assignments of the products were done by ^{1}H NMR and ^{13}C NMR spectroscopy

6. Testing with iodine solution

Iodine solution was used as an indicator to identify H_2 to check for the possibility of H_2 release during the reaction (if H_2 is present in the solution, HI is produced, which changes the colour of the iodine solution). The contents of the reaction flask were transferred to a round-bottomed Pyrex flask, which was then connected to a balloon containing iodine solution in ethanol (at a concentration of 5%) with a tube tied to a needle at the other end. No colour change was observed at the start of the reaction and at the time of LED irradiation, but it was observed that 10 minutes after the start of the reaction, the iodine solution flowed out of the tube into the reaction balloon (Fig. S6). This observation indicated that in the presence of triethanolamine during the reaction, oxygen is absorbed by the solution, causing the iodine solution to rise towards the reaction vessel. The results of this experiment which are proof of the consumption of dissolved oxygen by the triethanolamine were completely consistent with the previous results obtained in this research as well as other recent research. [1] Also, according to the lack of colour change of the iodine solution and the absence of bubbles during the reaction, it can be concluded that H_2 is not produced during the process.

7. Optimization of TiO_2-P25 and TEOA amounts

Table *S1*: The optimization of TiO_2-P25 and TEOA amounts in water solvent and violet LED irradiation [a]

Entry	reductant (mmol)	TiO_2-P25 (mg)	Time (h)	Yield [b] (%)
1	TEOA	7	1.5	100
2	TEOA	10	0.75	100
3	TEOA	15	1	98
4	TEOA	20	3.5	98
5	TEOA	30	3	95
6	TEOA	40	1	90
7	TEOA	10	3	100 [c]
8	TEOA	10	8	100 [d]

[a] Nitrobenzene (1 mmol), TiO_2- P25 (10 mg), TEOA (7.5 mmol), H_2O (3 ml), *t*-BuOH (0.3 ml), Air atmosphere conditions, LED 50 w (λ =400 nm) and room temperature.
[b] Isolated yield.
[c] TEOA: 5 mmol
[d] TEOA: 3 mmol

8. The photograph of the solutions containing photocatalyst before and after the light irradiation

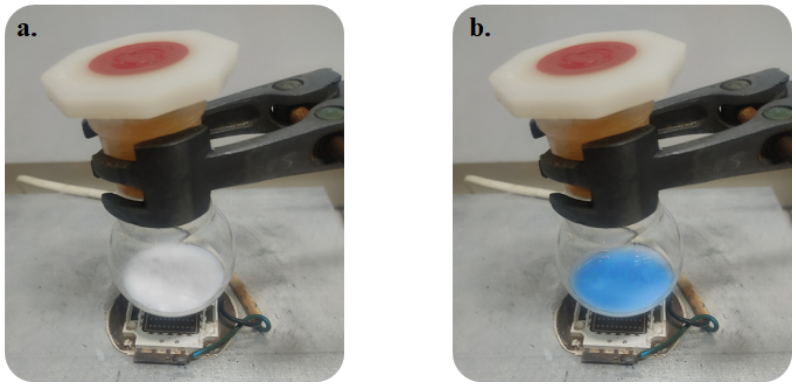


Fig *S*1 The photograph of the solutions containing photocatalyst before and after the light irradiation: a) A water solution containing TiO_2-P25 and TEOA before light irradiation. b) A water solution containing TiO_2-P25 and TEOA after the light irradiation for 0.5 h with purple LED. Conditions: TiO_2-P25 (15 mg), TEOA (7.5 mmol) and H_2O (3 ml). A purple LED lamp (50 w) was used as the light source. As shown in these photographs, the color of the TiO_2 solution changed from white to blue after the formation of the TiO_2-TEOA (in situ) under light irradiation.

9. TG/DTG analysis of TiO_2-TEOA

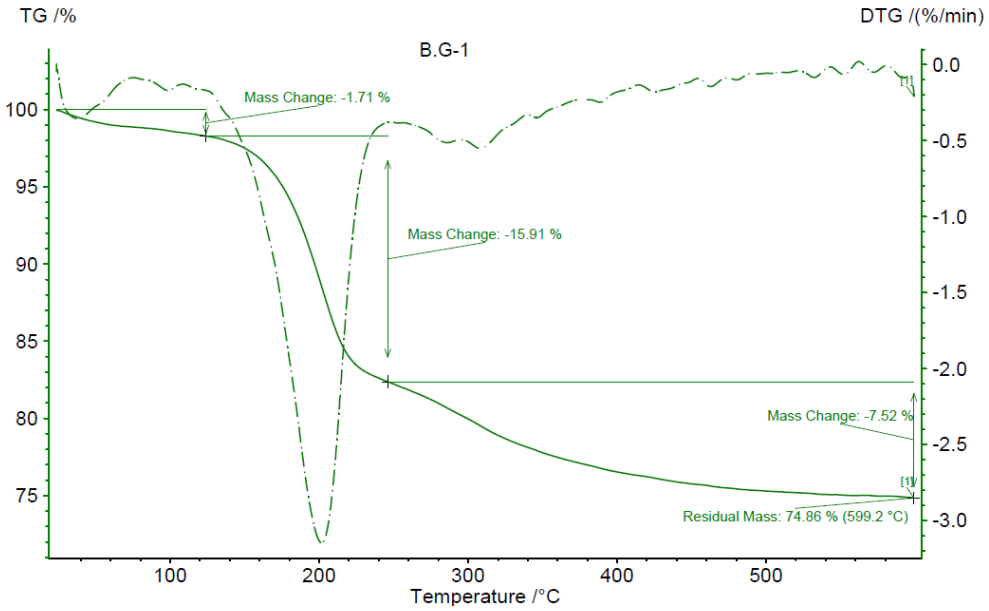


Fig *S*2. TG/DTG analysis of TiO_2-TEOA

10. TG/DTG analysis of recycled TiO_2-TEOA

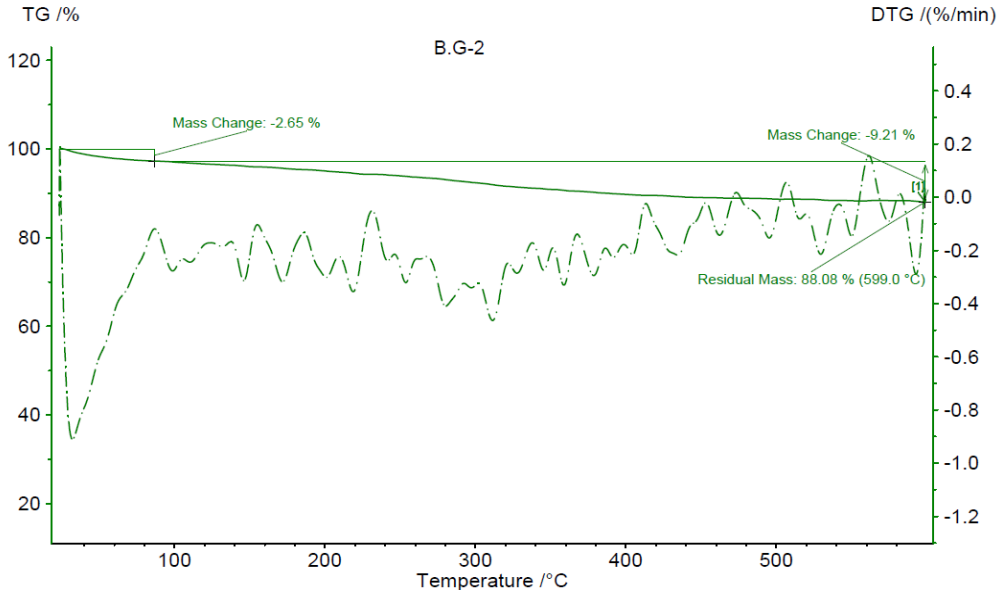


Fig *S*3. TG/DTG analysis of recycled TiO_2-TEOA obtained from the nitrobenzene reduction in the presence of triethylamine (without triethanolamine as the reducing agent)

11. Photographs related to the amount of dispersion of TiO_2-P25 and TiO_2-TEOA powders

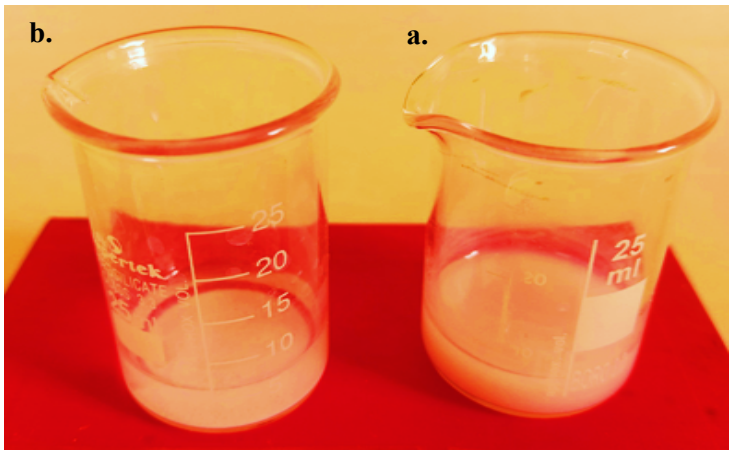


Fig *S*4. Image of aqueous solutions (immediately, after 5 minutes of dispersion in an ultrasonic device) (a) TiO_2- P25, (b) TiO_2-TEOA

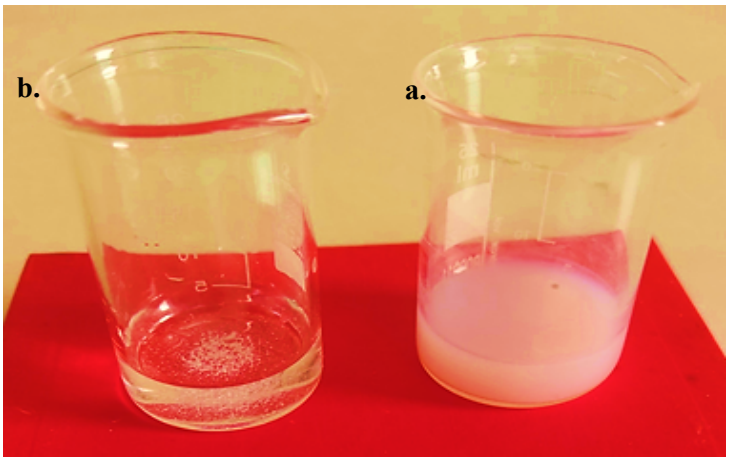


Fig *S*5. Image of aqueous solutions (after 10 minutes of stillness) (a) TiO_2- P25, (b) TiO_2-TEOA

12. The photograph of testing with iodine solution

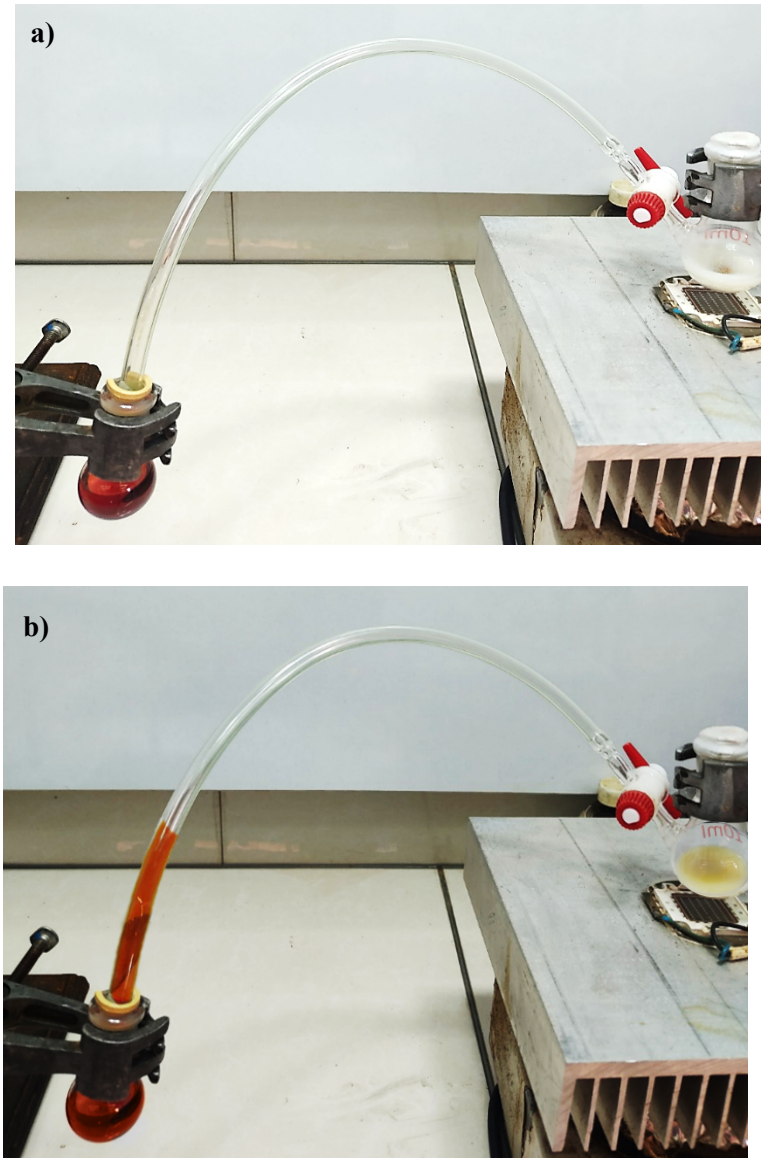
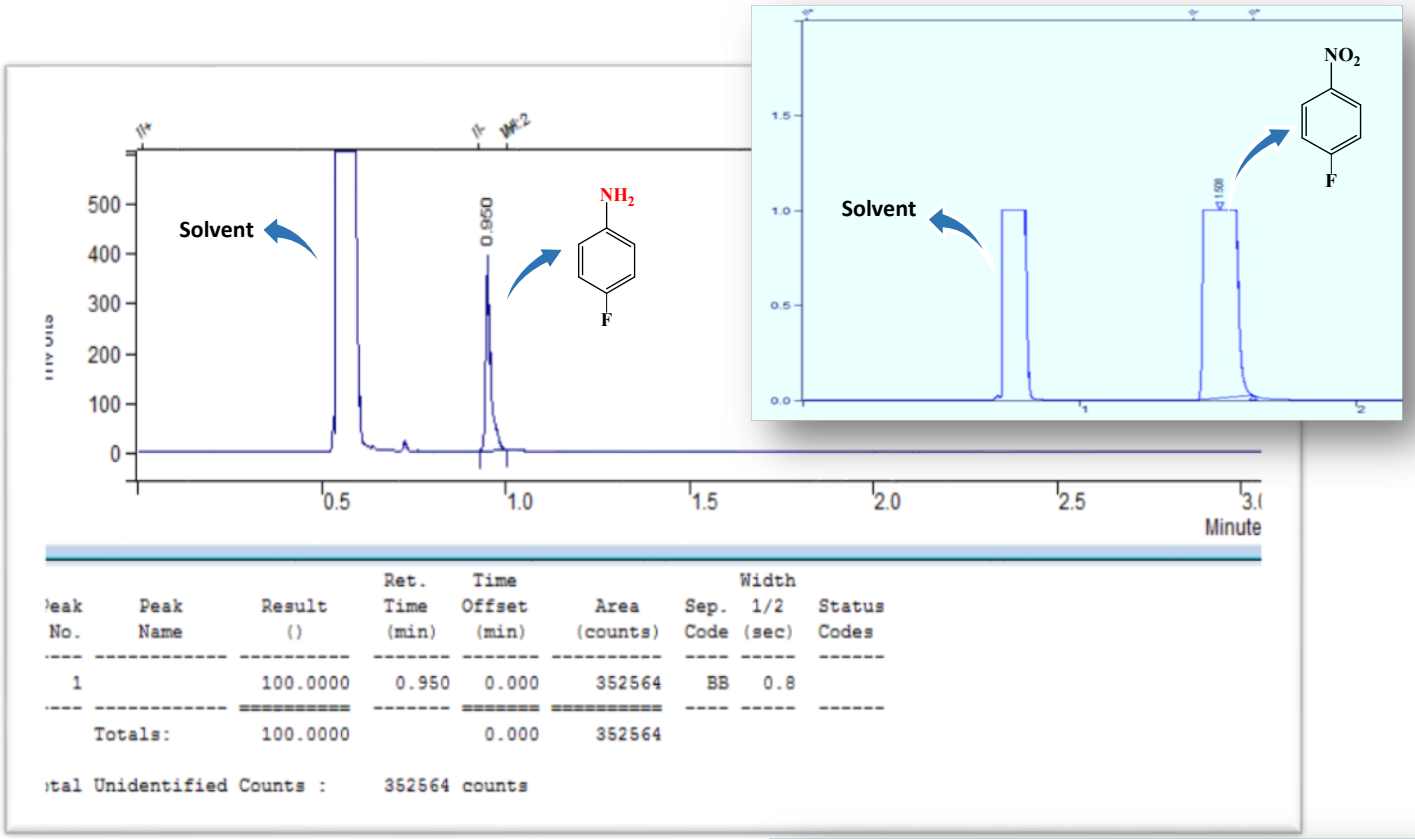


Fig *S*6. Testing with iodine solution. **a)** Before the start of the reaction, **b)** After 10 minutes from the start of the reaction, the reaction solution has absorbed oxygen from the air, so that the iodine solution then flows into the reaction vessel.

13. Column specifications

Test conditions	Parameter
CP-Sil 8 CB (25 m × 0.32 mm × 1.2 um (Column Flow = 2 and Split Ratio = 1/20) Condition: Temperature: 180˚ C Rate: 10 Hz Flow: 10 psi Injector: 1041, T (˚C) : 230 ˚C Carrier gas: N_2	Non-alcoholic column
Rtx-BAC2 (30 m × 0.53 mm × 2 um Condition: Temperature: 180˚ C Rate:10 psi Flow: 10 psi Injector: 1079, T (˚C) : 230 ˚C Carrier gas: N_2	Alcoholic column
220˚ C – Flame Ionization detector (FID)	Detector temperature

14. GC results of a number of products



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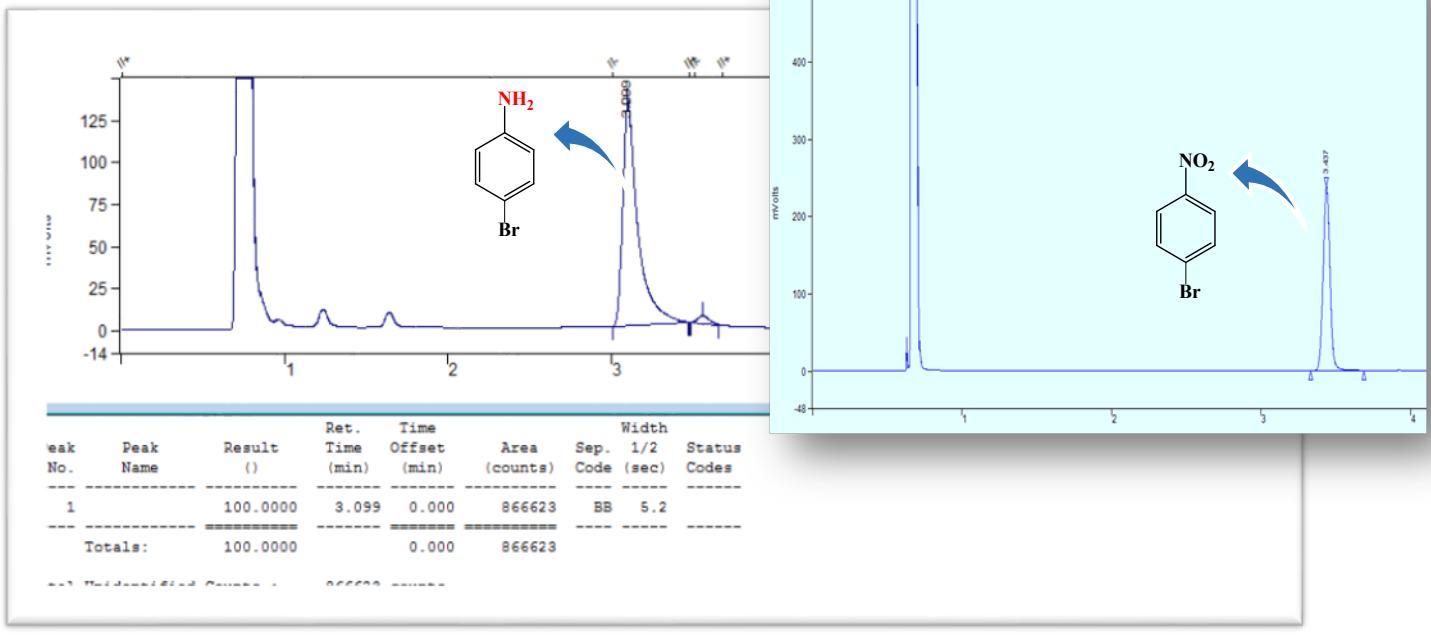
tal Unidentified Counts : 352564 counts



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1		100.0000	3.099	0.000	866623	BB	5.2	
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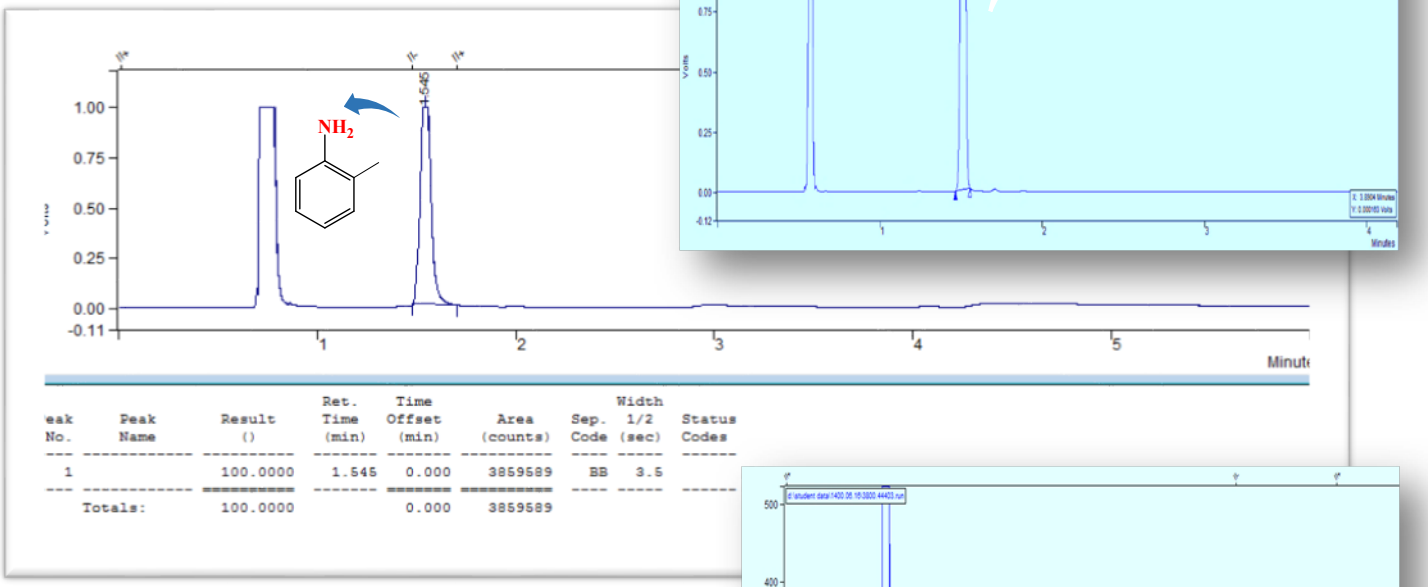

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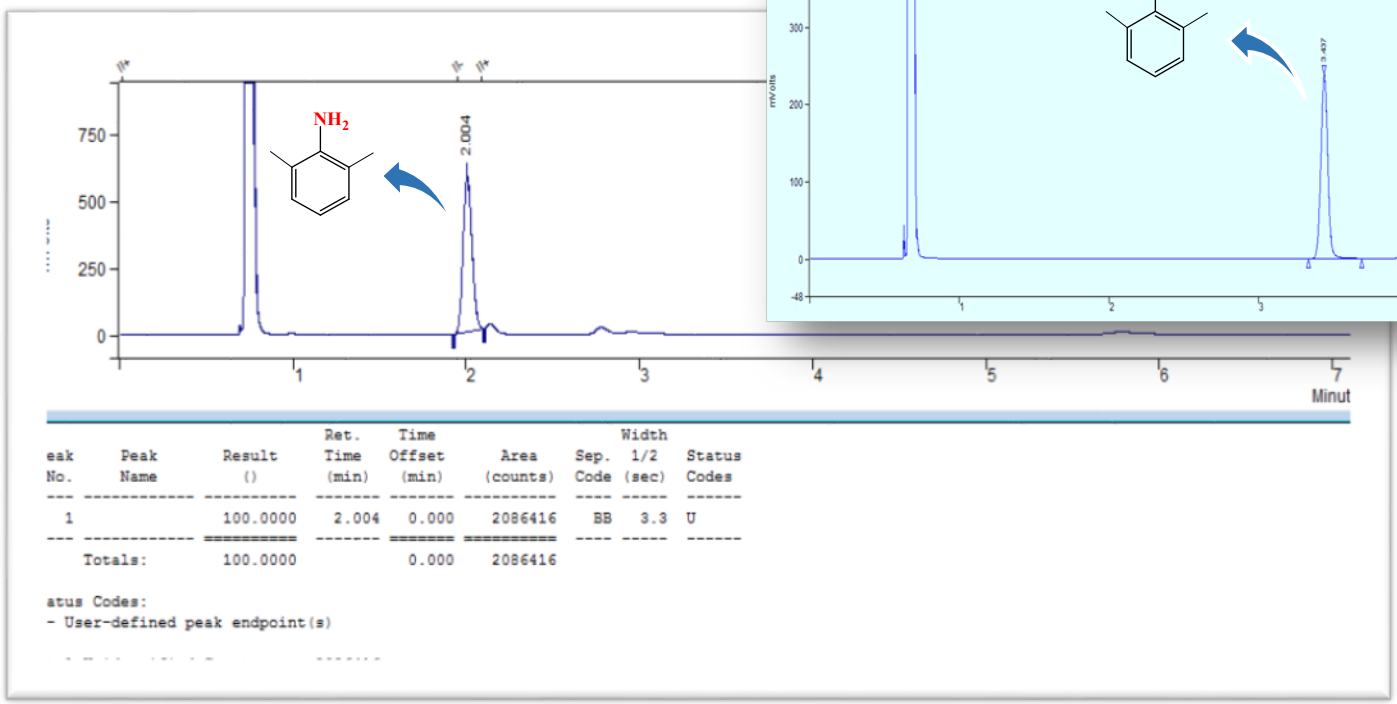
1		100.0000	1.545	0.000	3859589	BB	3.5	
Totals:		100.0000		0.000	3859589			



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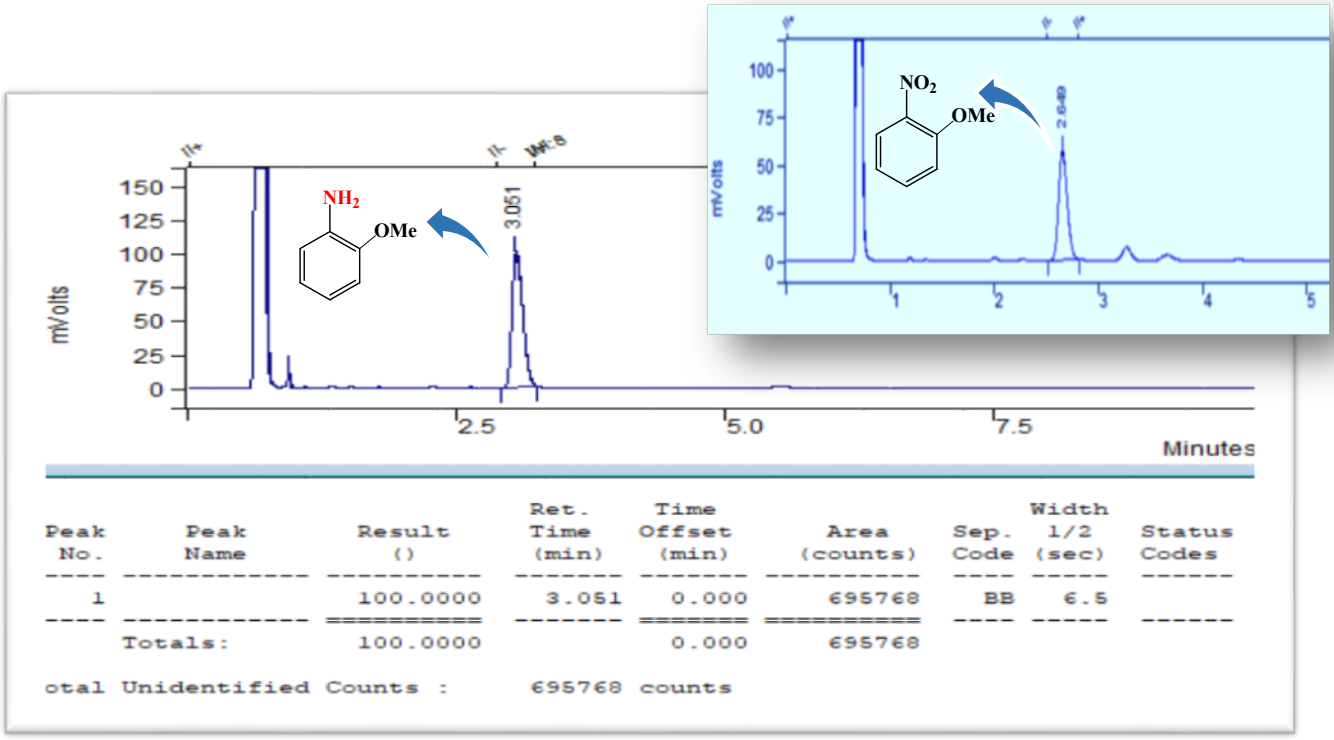
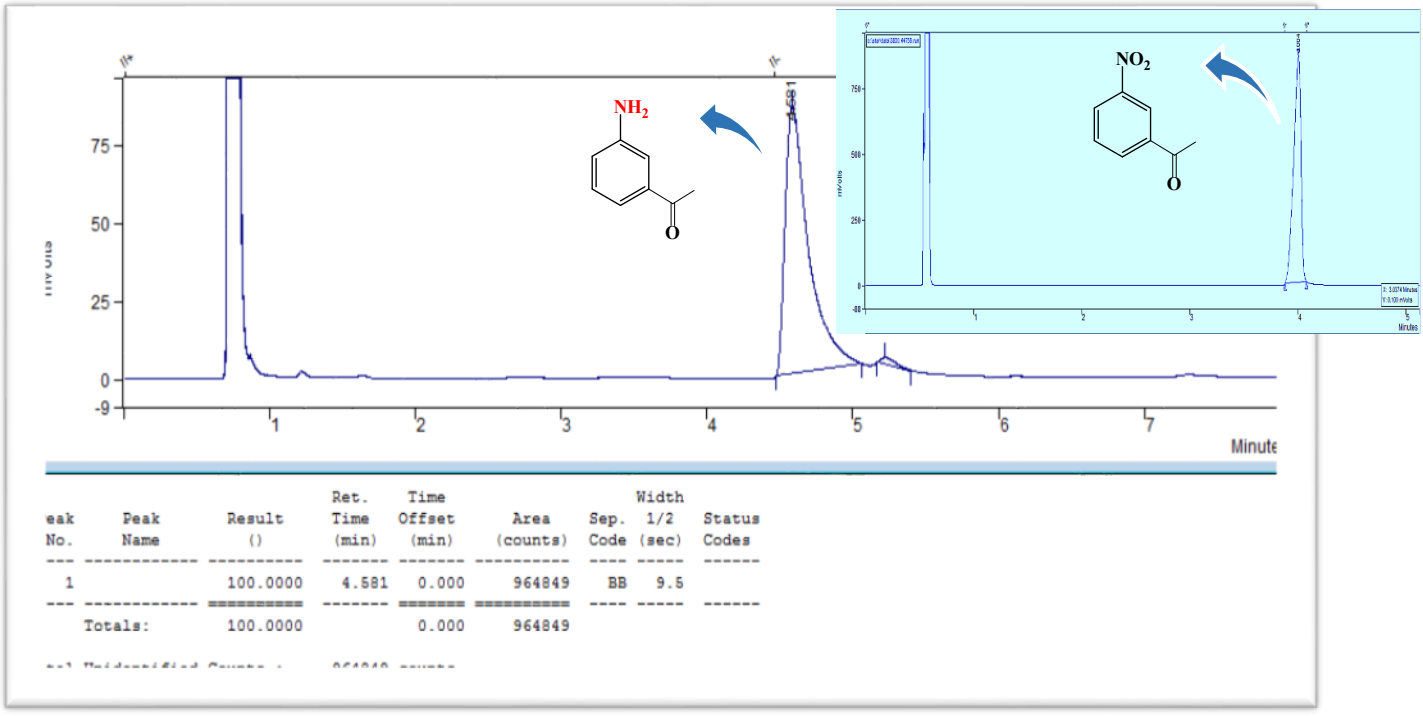
1		100.0000	2.004	0.000	2086416	BB	3.3	U
Totals:		100.0000		0.000	2086416			

atus Codes:
- User-defined peak endpoint(s)



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	3.051	0.000	695768	BB	6.5	
	Totals:	100.0000		0.000	695768			

otal Unidentified Counts : 695768 counts



eak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	4.581	0.000	964849	BB	9.5	
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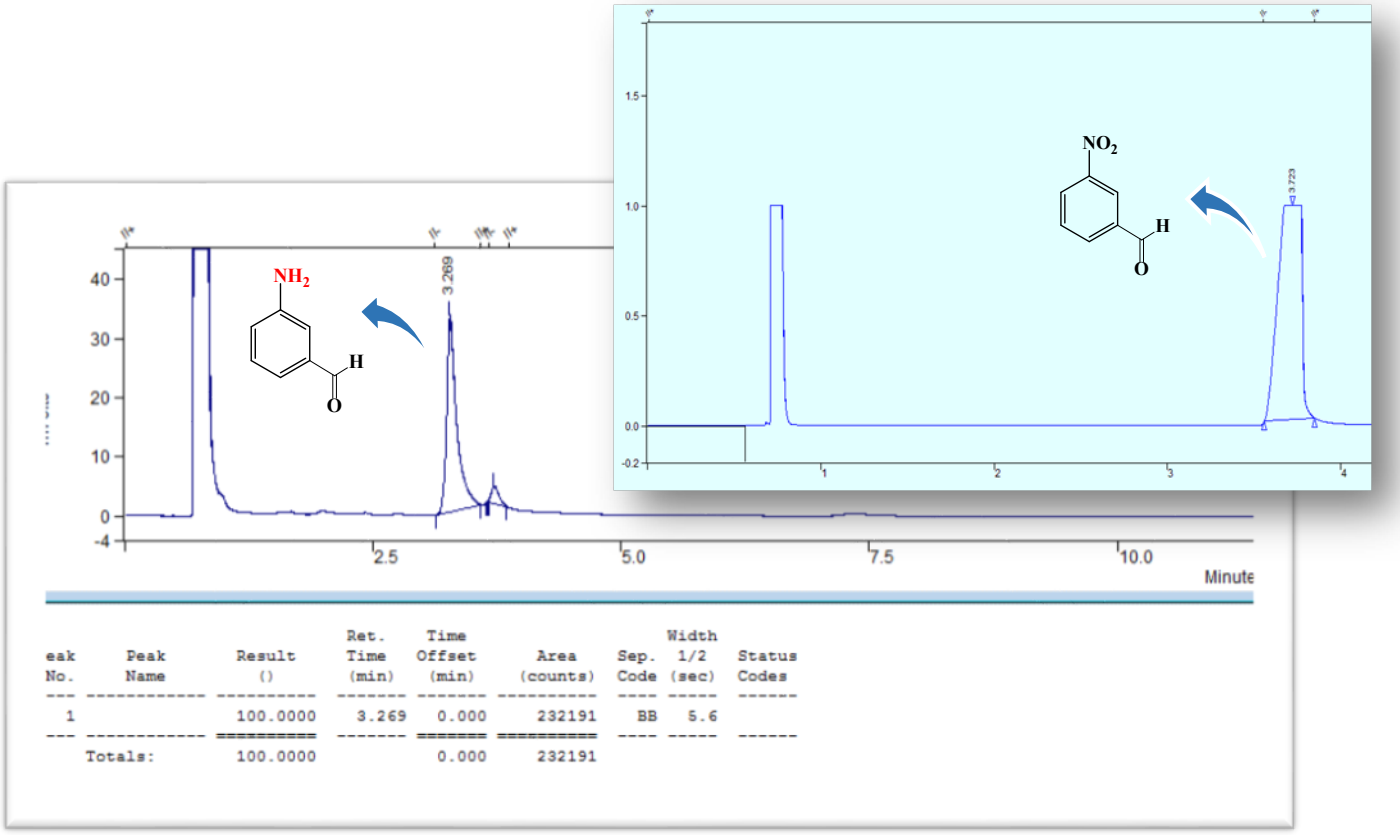

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
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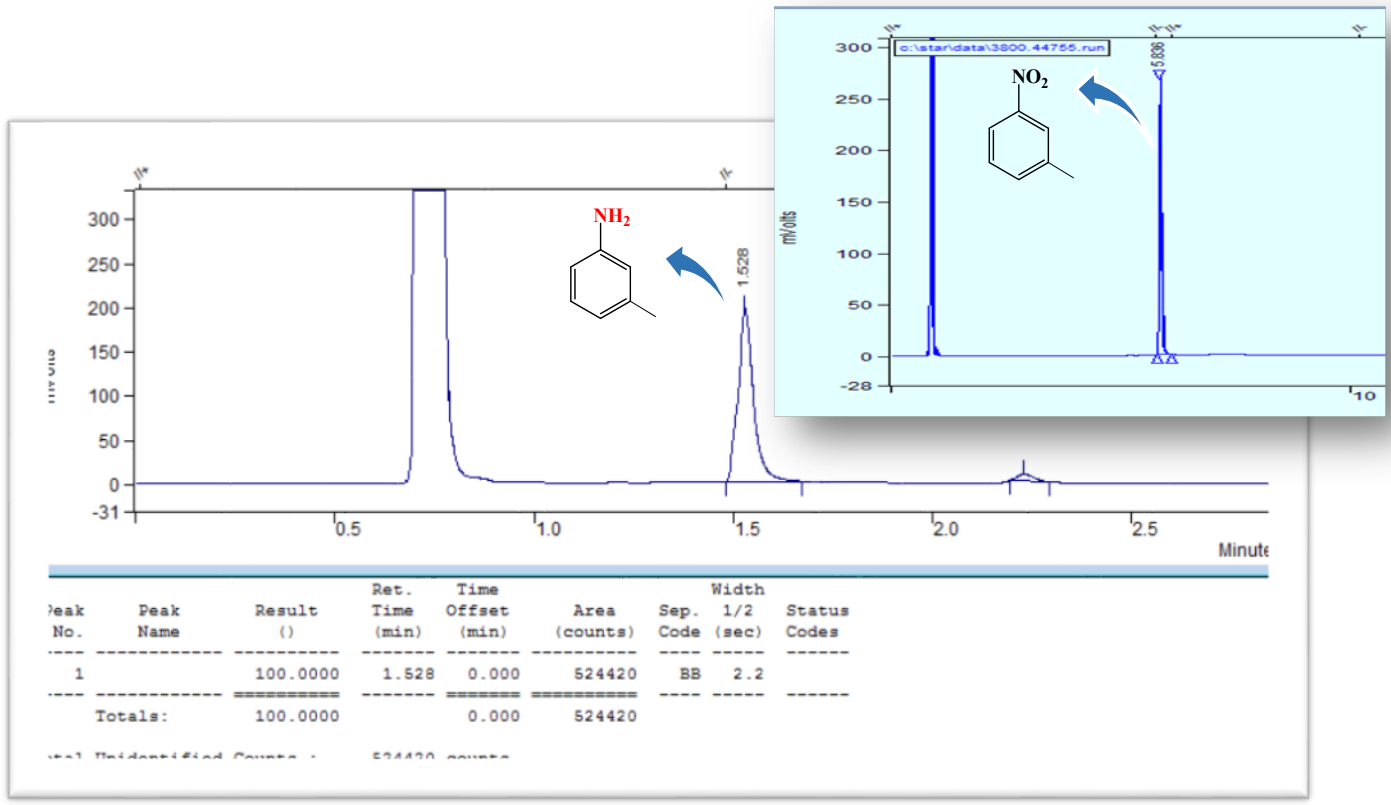

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
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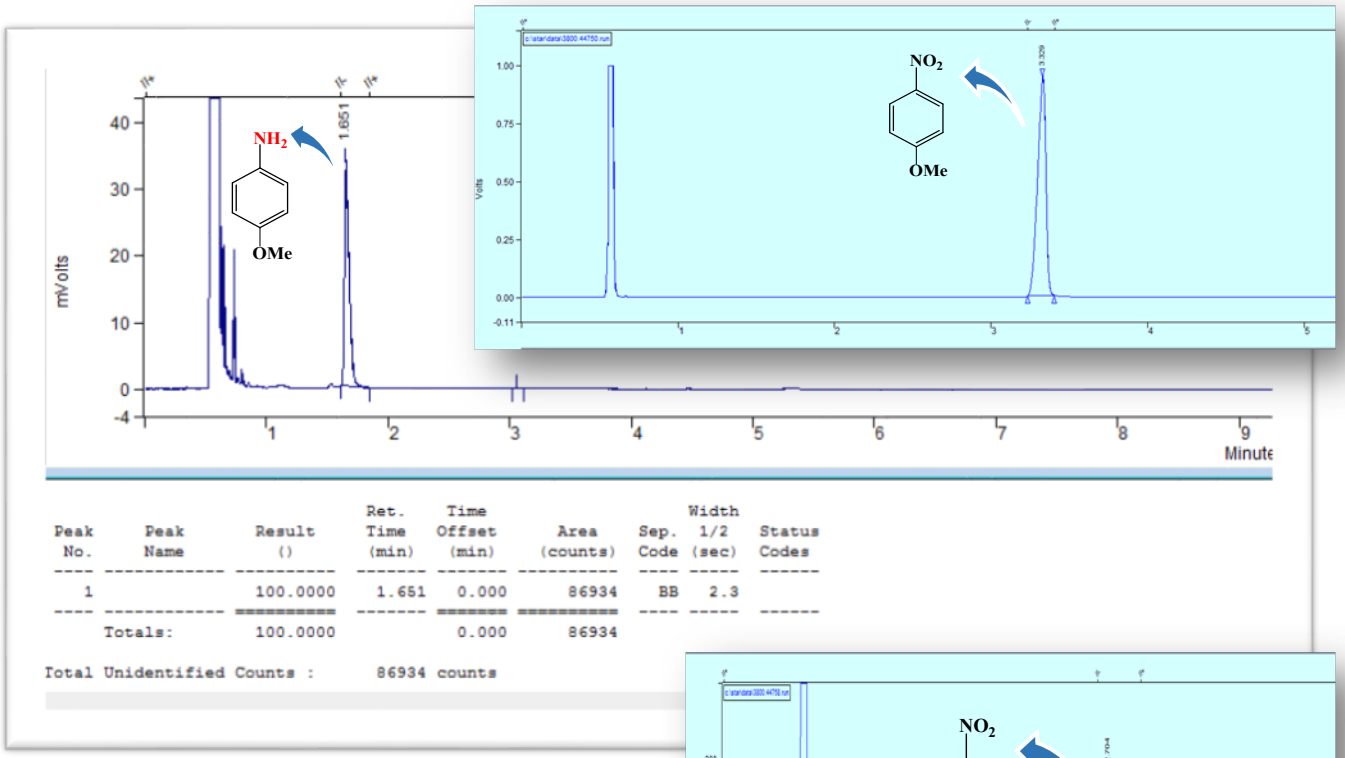
Totals:		100.0000		0.000	524420			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	1.651	0.000	86934	BB	2.3	
	Totals:	100.0000		0.000	86934			

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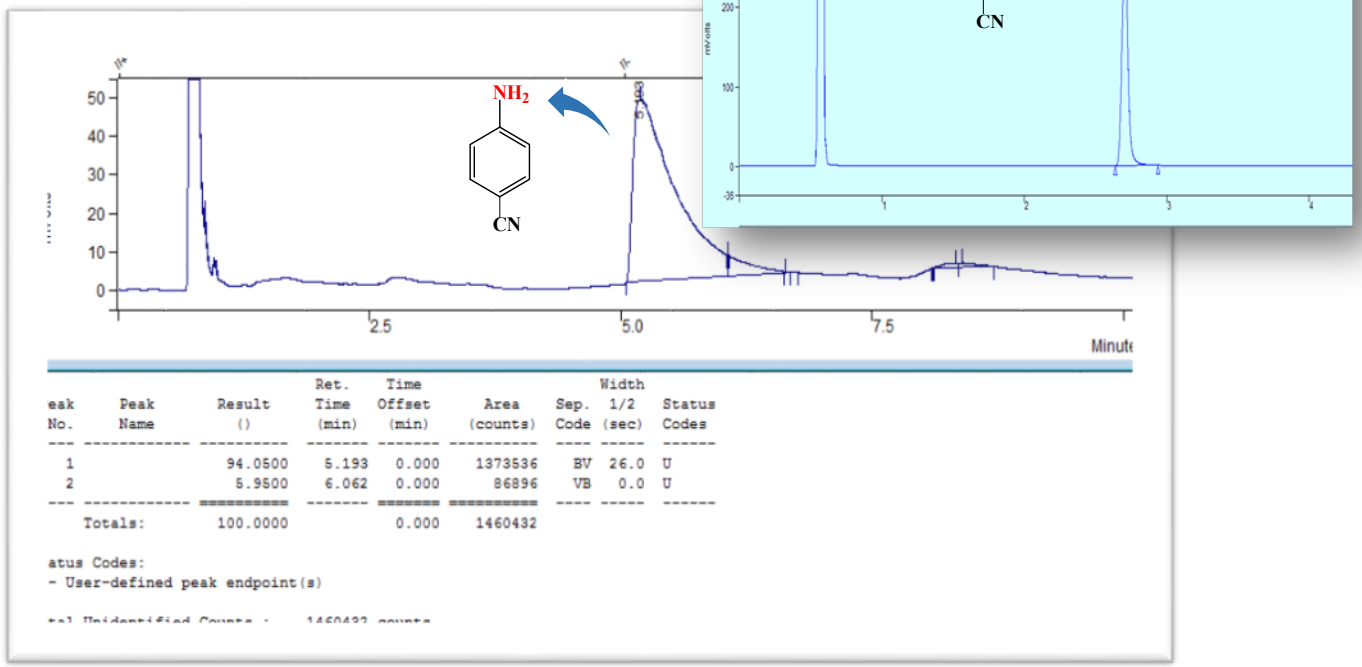

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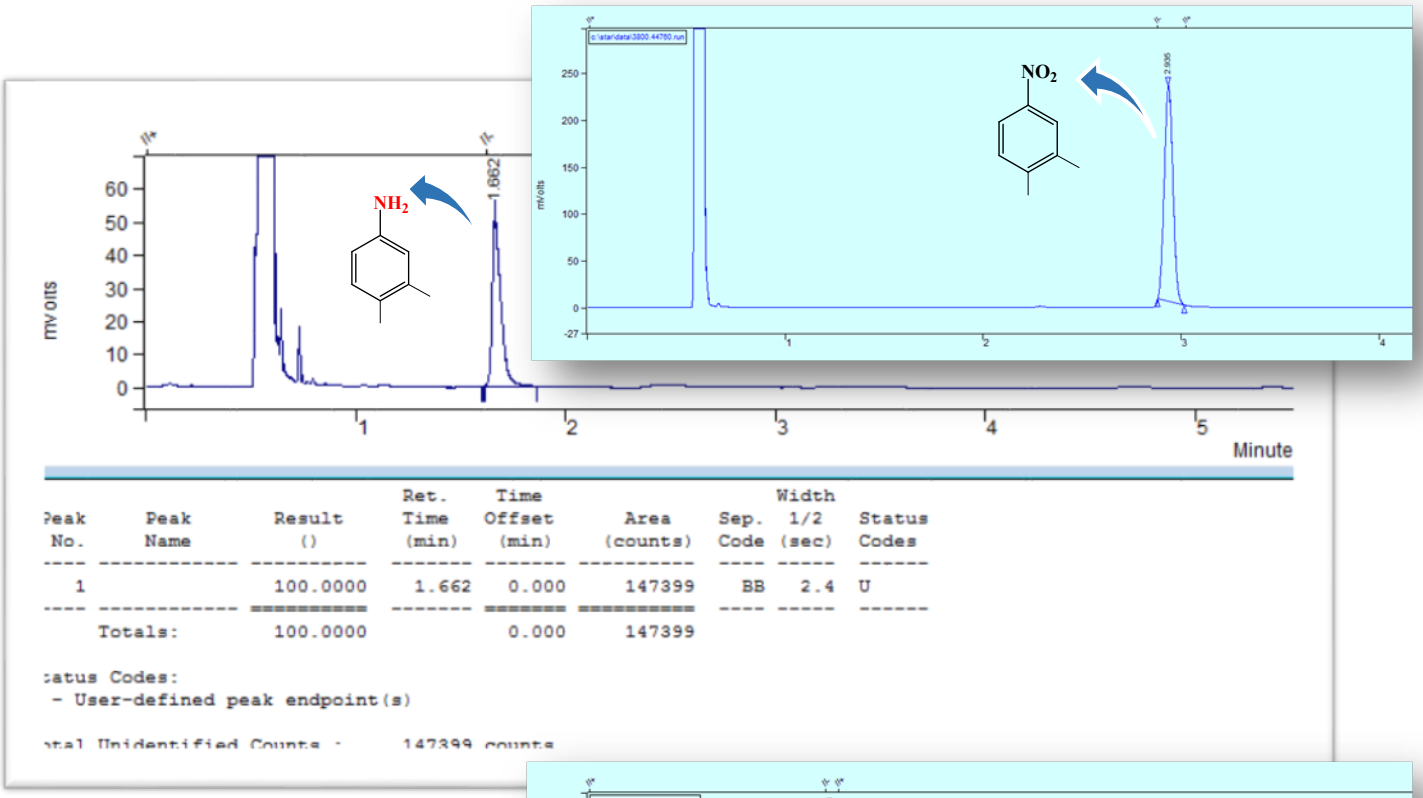
1		94.0500	5.193	0.000	1373536	BV	26.0	U
2		5.9500	6.062	0.000	86896	VB	0.0	U
	Totals:	100.0000		0.000	1460432			

atus Codes:
- User-defined peak endpoint(s)

tal Unidentified Counts : 1460432 counts



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	1.662	0.000	147399	BB	2.4	U
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Status Codes:
- User-defined peak endpoint(s)

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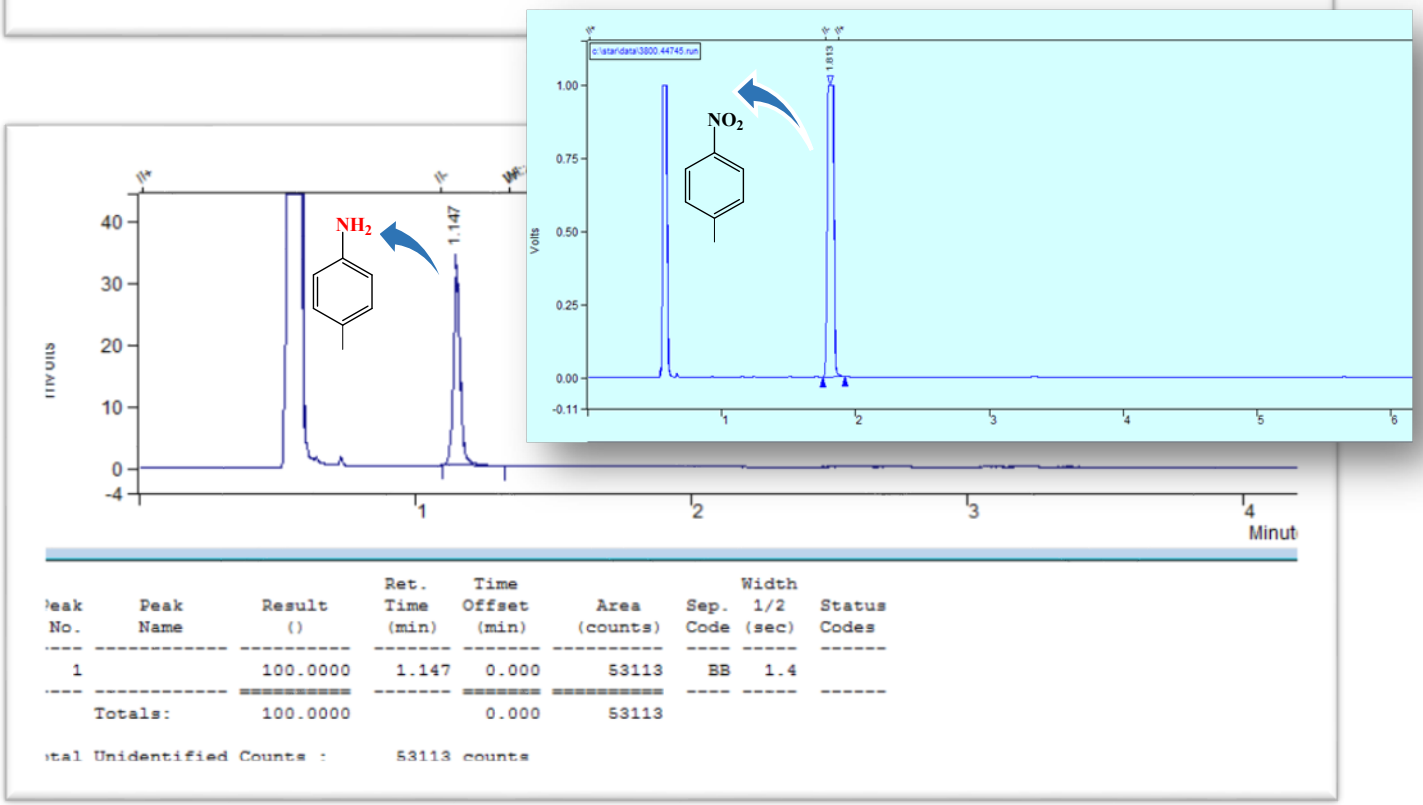

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	1.147	0.000	53113	BB	1.4	
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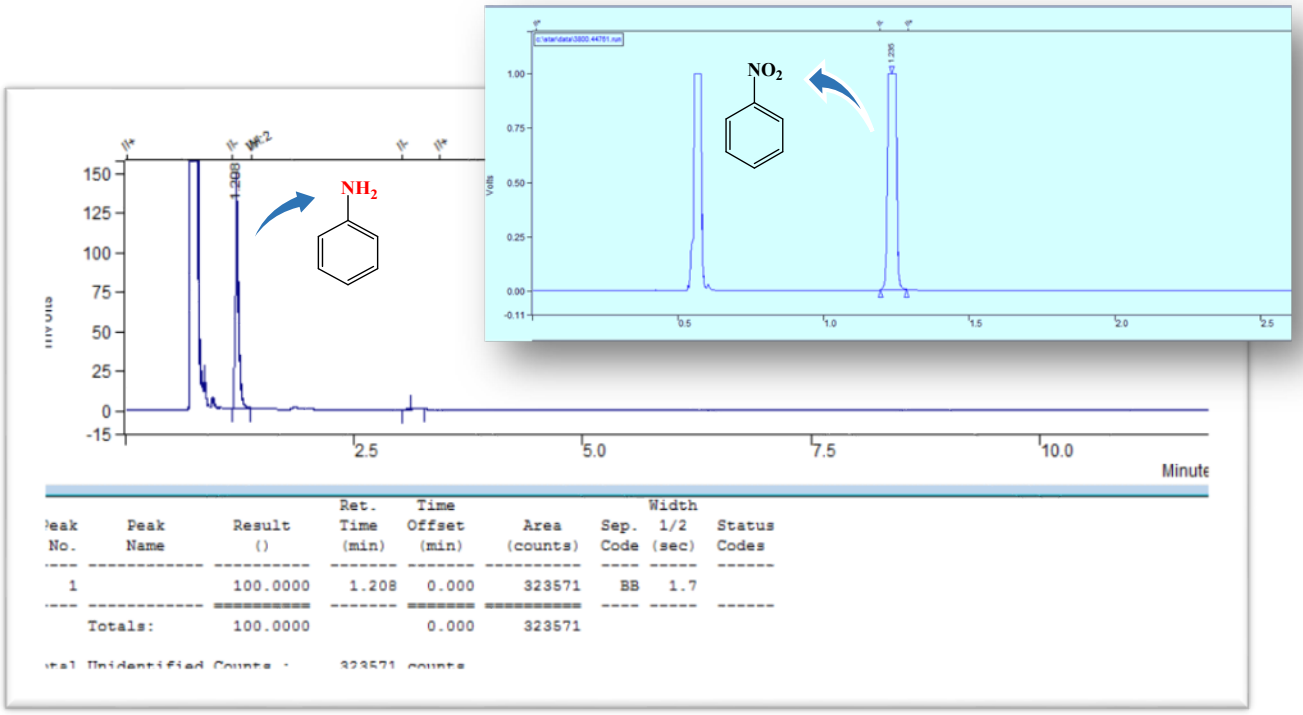
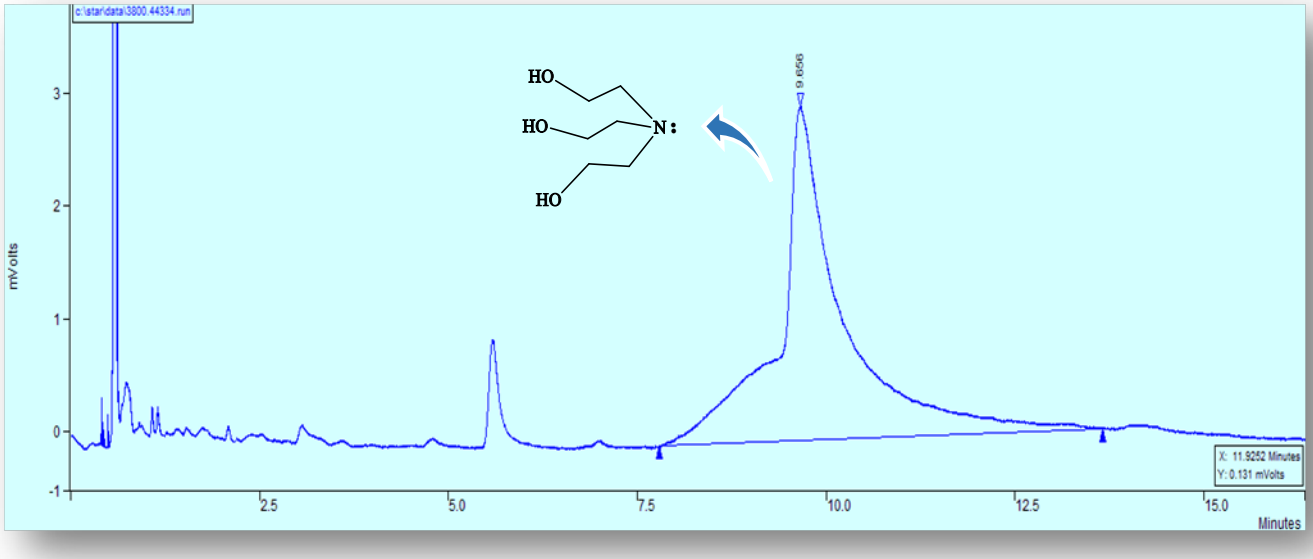

NH2
NO2
1.208
1.235
Minute
Peak No. | Peak Name | Result () | Ret. Time (min) | Time Offset (min) | Area (counts) | Sep. Code | Width 1/2 (sec) | Status Codes
1 | | 100.0000 | 1.208 | 0.000 | 323571 | BB | 1.7 |
Totals: | | 100.0000 | | 0.000 | 323571 |


HO
HO
HO
N:
9.656
mVolts
Minutes
X: 11.9252 Minutes
Y: 0.131 mVolts

15. Photocurrent measurements for TiO_2-P25 at different light wavelengths

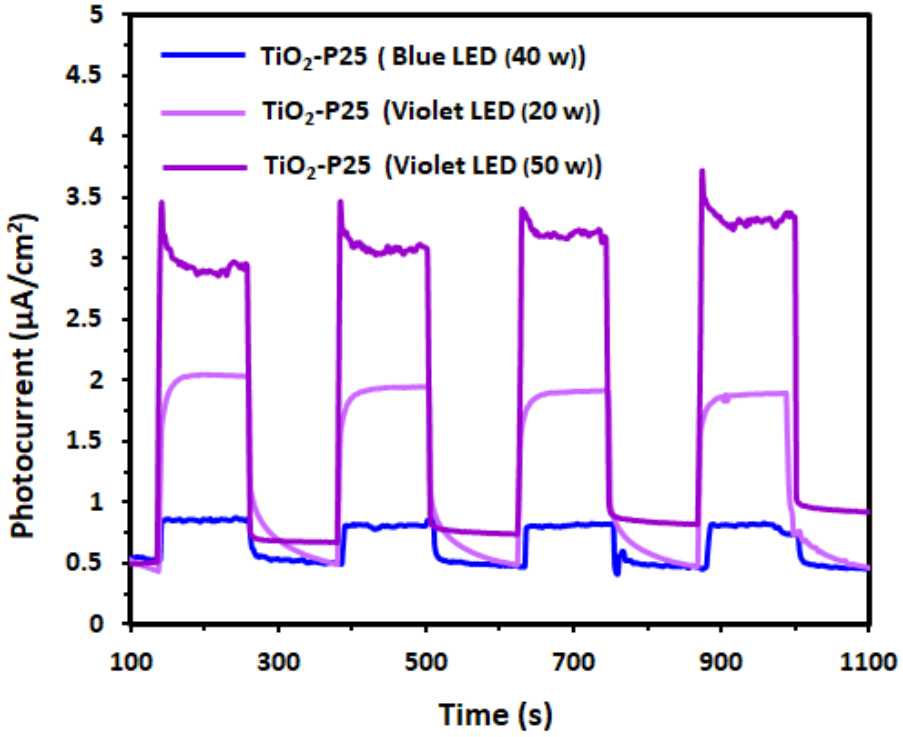
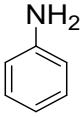


Fig S7. Photocurrent measurements for TiO_2-P25 under blue LED (460 nm, 40 w), violet LED (400 nm, 20 w) and violet LED (400 nm, 50 w) irradiation

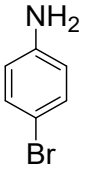
16. NMR data of the amine and amide products

Aniline [2]



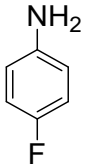
Light yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (t, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.78 (s, br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 147.02, 129.63, 118.63, 115.43.

4-Bromoaniline [3]



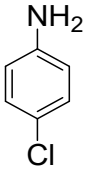
White powder, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.15 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 5.27 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 148.52, 131.82, 116.27, 106.58.

4-Fluoroaniline [4]



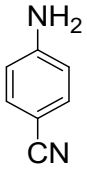
Light-colored oily liquid, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 6.85 (t, *J* = 8.9 Hz, 2H), 6.55 (dd, *J* = 8.8, 4.7 Hz, 2H), 4.94 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 155.81, 153.5, 145.65, 115.66, 115.44, 115.01.

4-Chloroaniline [4]



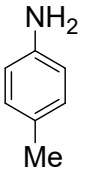
Beige crystals, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.02 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 5.26 (s, br, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 148.25, 128.97, 119.20, 115.63.

4-Aminobenzonitrile [5]



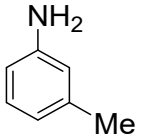
Off-white crystalline powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 4.44 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 151.10, 133.76, 120.64, 114.44, 99.15.

***p*-Toluidine [6]**



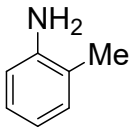
Beige crystals, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 6.83 (d, *J* = 8.9 Hz, 2H), 6.48 (d, *J* = 7.9 Hz, 2H), 4.79 (s, br, 2H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 146.54, 129.69, 124.35, 114.48, 20.60.

***m*-Toluidine [7]**



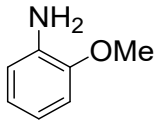
Yellow to brown liquid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.94 (t, *J* = 7.6 Hz, 1H), 6.47 – 6.40 (m, 2H), 6.38 (d, *J* = 7.4 Hz, 1H), 4.93 (s, 2H), 2.20 (s, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 148.96, 138.25, 129.19, 117.19, 115.15, 111.75, 21.70.

***o*-Toluidine [6]**



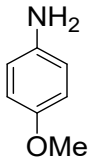
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32 – 7.24 (m, 3H), 6.76 (d, *J* = 8.0 Hz, 1H), 3.64 (s, br, 2H), 2.27 (s, 3H).). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 148.55, 129.24, 126.67, 123.53, 119.13, 114.01, 17.09.

***o*-Anisidine [8]**



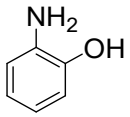
Yellow liquid, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 6.80 (d, J = 7.9 Hz, 1H), 6.75 – 6.59 (m, 2H), 6.55 (t, J = 7.4 Hz, 1H), 4.67 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 146.84, 138.05, 121.32, 116.67, 114.30, 111.01, 55.64.

***p*-Anisidine [9]**



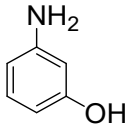
Gray crystals, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 6.66 (d, J = 7.5 Hz, 2H), 6.53 (d, J = 7.6 Hz, 2H), 4.60 (s, br, 2H), 3.64 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 151.06, 142.71, 115.42, 114.97, 55.75.

2-Aminophenol [9]



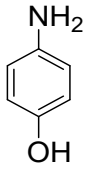
White gray powder, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.98 (s, br, 1H), 6.67 (dd, J = 7.7, 1.2 Hz, 1H), 6.62 – 6.54 (m, J = 8.9, 7.7, 1.5 Hz, 2H), 6.42 (td, J = 7.5, 1.8 Hz, 1H), 4.49 (s, br, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 144.46, 136.99, 120.00, 116.93, 114.92, 114.84.

3-Aminophenol [4]



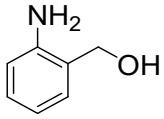
White powder, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.89 (s, 1H), 6.81 (t, J = 7.8 Hz, 1H), 6.20 – 5.86 (m, 3H), 4.90 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 158.53, 150.27, 129.98, 105.95, 103.84, 101.45.

4-Aminophenol [4]



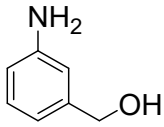
Light brown powder, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.36 (s, 1H), 6.41-6.49 (m, *J* = 25.1, 8.5 Hz, 4H), 4.39 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 148.66, 141.15, 115.99, 115.68.

2-Aminobenzyl alcohol [4]



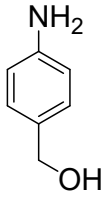
White powder, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.07 (d, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.54 (t, *J* = 7.3 Hz, 1H), 5.00 (t, *J* = 5.4 Hz, 1H), 4.91 (s, 2H), 4.40 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 146.82, 128.17, 128.11, 125.83, 116.27, 115.01, 61.65.

3-Aminobenzyl alcohol [10]



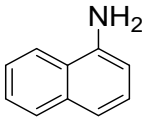
White powder, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 6.96 (t, *J* = 7.6 Hz, 1H), 6.56 (s, 1H), 6.52 – 6.38 (m, 2H), 5.06 – 4.91 (m, 3H), 4.36 (d, *J* = 5.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 148.91, 143.60, 128.94, 114.49, 112.81, 112.57, 63.70.

4-Aminobenzyl alcohol [6]



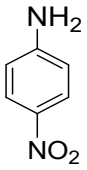
Light yellow crystal, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.01 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 8.3 Hz, 2H), 4.94 (s, br, 3H), 4.33 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 147.89, 130.12, 128.47, 114.13, 63.65.

1-Amino-naphthalene [9]



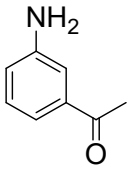
Light purple solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.08 (d, *J* = 8.2 Hz, 1H), 7.74 (m, 1H), 7.44 – 7.34 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.70 (dd, *J* = 7.4, 0.7 Hz, 1H), 5.73 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 145.19, 134.67, 128.29, 127.22, 125.96, 124.09, 123.16, 122.82, 115.82, 107.88.

4-Nitroaniline [6]



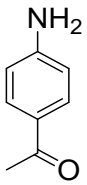
Yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.96 (d, *J* = 9.2 Hz, 2H), 6.75 (s, 2H), 6.62 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 156.18, 136.09, 126.88, 112.84.

3-Aminoacetophenone [11]



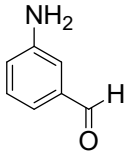
Yellow to light brown crystalline, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.20 – 7.10 (m, 3H), 6.82 (d, *J* = 7.3 Hz, 1H), 5.35 (s, 2H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 198.71, 149.47, 138.13, 129.52, 118.95, 116.41, 113.18, 27.16.

4-Aminoacetophenone [7]



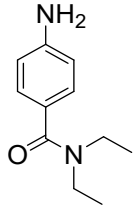
Light yellow to brown powder, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.69 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 6.06 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 195.44, 154.10, 131.06, 125.33, 112.95, 26.32.

3-Aminobenzaldehyde [12]



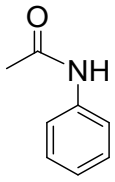
Pale yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 9.29 (s, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 7.0 Hz, 2H), 6.38 (dd, *J* = 7.1, 1.4 Hz, 1H), 5.30 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 196.65, 149.64, 132.13, 129.69, 118.79, 117.45, 115.24.

4-amino-*N*, *N*-diethylbenzamide [13]



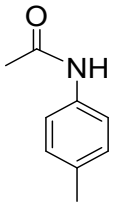
Colorless solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.07 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.5 Hz, 2H), 5.43 (s, 2H), 3.32 (t, J = 14.3, 7.3 Hz, 4H), 1.10 (t, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 171.16, 150.33, 128.54, 124.17, 113.24, 13.95.

***N*-phenylacetamide [14]**



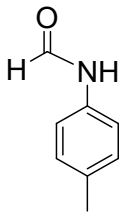
White crystal, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.83 (s, br, 1H), 7.57 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.15 – 7.08 (m, 1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 169.80, 138.15, 128.89, 124.40, 120.50, 24.22.

***N*-(p-tolyl) acetamide [14]**



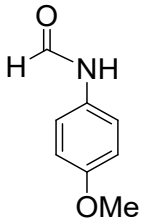
White crystal, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.33 (s, br, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.32 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 169.36, 135.46, 133.96, 129.38, 120.43, 24.18, 20.87.

_N_-(p-tolyl) formamide [15]



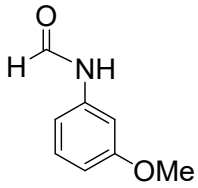
White crystal, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.66 (d, *J* = 11.2 Hz, 0.5H), 8.39 (s, 0.5H), 7.90 (s, br, 0.5H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.29 (s, 0.5H), 7.18 (t, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 1H), 2.36 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 163.41, 159.21, 136.33, 135.82, 135.62, 135.02, 127.34, 127.15, 122.16, 119.79, 14.68, 14.62.

_N_-(4-methoxyphenyl) formamide [16]



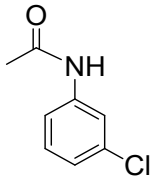
White crystal, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.67 (s, 1H), 8.54 (d, *J* = 11.2 Hz, 1H), 8.30 (s, 1H), 8.17 (d, *J* = 34.1 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.90-6.84 (dd, *J* = 16.9, 8.5 Hz, 4H), 3.80 (d, *J* = 8.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 163.39, 159.34, 157.56, 156.63, 130.18, 129.73, 121.88, 121.51, 114.88, 114.18, 55.56, 55.48.

_N_-(3-methoxyphenyl) formamide [17]



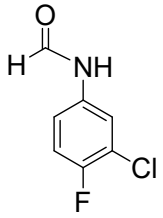
Brown oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.92 (s, 1H), 8.72 (d, *J* = 11.3 Hz, 1H), 8.36 (d, *J* = 1.7 Hz, 1H), 8.19 (s, 1H), 7.38 – 7.17 (m, 3H), 7.12 – 7.01 (d, 1H), 6.82 – 6.59 (m, 4H), 3.81 (d, *J* = 9.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 163.01, 160.67, 160.11, 159.60, 138.26, 138.09, 130.60, 129.80, 112.25, 110.89, 110.45, 106.02, 104.88, 55.40, 55.32.

_N_-(3-chlorophenyl) acetamide [18]



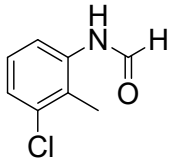
White crystal, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.25 (s, 1H), 7.71 (t, *J* = 2.0 Hz, 1H), 7.36 (d, *J* = 8.2, 1.0 Hz, 1H), 7.18 (t, *J* = 8.1 Hz, 1H), 7.10 – 7.02 (d, 1H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 170.32, 139.30, 134.34, 129.92, 124.38, 120.54, 118.47, 24.17.

_N_-(3-chloro-4-fluorophenyl) formamide [16]



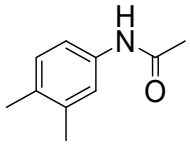
White crystal, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.63 (d, *J* = 11.2 Hz, 1H), 8.52 (s, 0.6H), 8.39 (s, 1.4H), 7.76 (dd, *J* = 6.5, 2.6 Hz, 1H), 7.64 (s, 1H), 7.39 (ddd, *J* = 8.8, 3.9, 2.7 Hz, 1.4H), 7.26 – 7.07 (m, 3H), 7.02 (ddd, *J* = 8.8, 3.8, 2.8 Hz, 0.6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.61 (s), 159.05 (s), 157.14 (s), 156.31 (s), 154.68 (s), 153.85 (s), 133.40 (d, *J* = 3.1 Hz), 122.31 (s), 121.46 (d, *J* = 8.8 Hz), 121.23 (s), 119.67 (d, *J* = 7.1 Hz), 118.99 (d, *J* = 6.8 Hz), 117.60 (d, *J* = 22.7 Hz), 116.80 (d, *J* = 22.0 Hz).

_N_-(3-chloro-2-methylphenyl) formamide [19]



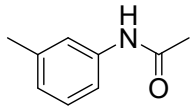
Pink crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.50 (dd, *J* = 21.6, 6.3 Hz, 2H), 8.22 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.23 (m, 3H), 7.18 (td, *J* = 8.0, 5.4 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 1H), 2.38 (d, *J* = 15.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 163.41, 159.21, 136.33, 135.82, 135.62, 135.02, 128.65, 127.80, 127.34, 127.15, 127.10, 126.71, 122.16, 119.79, 14.68, 14.62.

_N_-(3, 4-dimethylphenyl) acetamide [20]



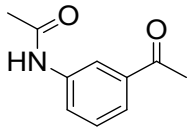
Crystal-Powder, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (s, 1H), 7.33 – 7.28 (m, 1H), 7.24 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 2.24-2.19 (m, 6H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 168.80, 137.09, 135.78, 132.58, 129.88, 121.56, 117.72, 24.39, 19.90, 19.21.

_N_-(3-Methylphenyl) acetamide [14]



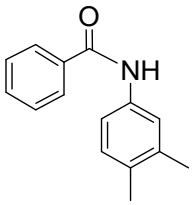
Light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.26 (s, br, 1H), 7.39 (s, 1H), 7.36 – 7.28 (m, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 2.31 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 169.10, 138.77, 138.06, 128.72, 125.07, 120.83, 117.26, 24.42, 21.48.

_N_-(3-acetylphenyl) acetamide [21]



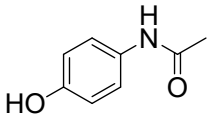
White solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 10.21 (s, 1H), 8.17 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 2.57 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 198.18, 169.13, 140.15, 137.73, 129.60, 123.94, 123.58, 118.57, 27.21, 24.48.

_N_-(3, 4-dimethylphenyl) benzamide [22]



White solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 10.07 (s, 1H), 7.96 – 7.89 (m, 2H), 7.61 – 7.63-7.41 (m, 5H), 7.08 (d, *J* = 8.1 Hz, 1H), 2.21 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 165.25, 136.89, 136.06, 135.19, 131.37, 131.31, 129.43, 128.29, 127.54, 121.80, 118.09, 19.53, 18.72.

N-(4-hydroxyphenyl) acetamide [23]



White crystalline powder, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 9.66 (s, 1H), 9.15 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 6.70 (d, *J* = 7.5 Hz, 2H), 2.00 (s, 3H). ^{13}C NMR (ppm) (101 MHz, DMSO-d_6) δ (ppm) 167.99, 153.60, 131.50, 121.30, 115.47, 24.20.

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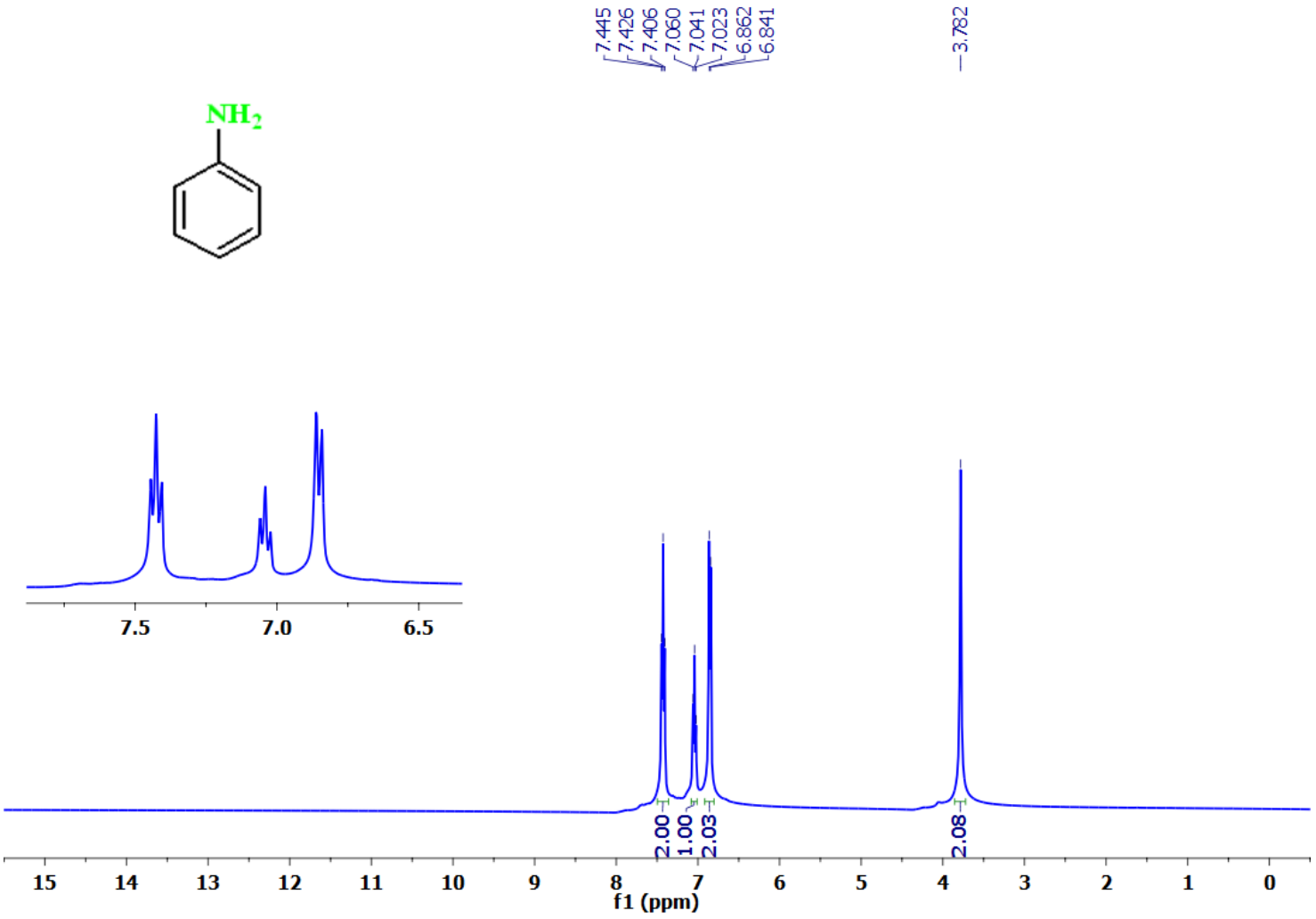
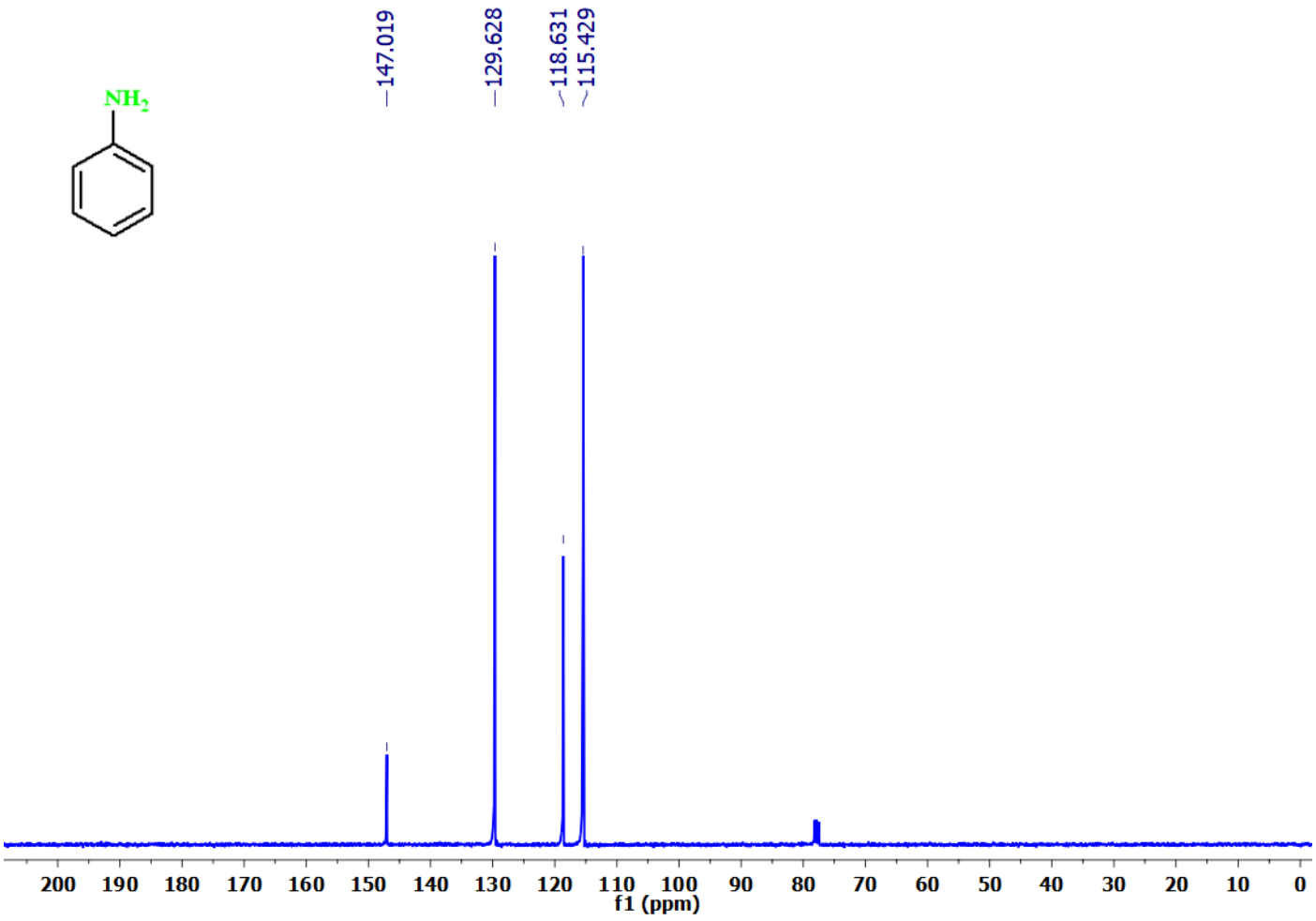
18. Copy of Original ^{1}H NMR and ^{13}C NMR spectra



^{1}H NMR of Aniline



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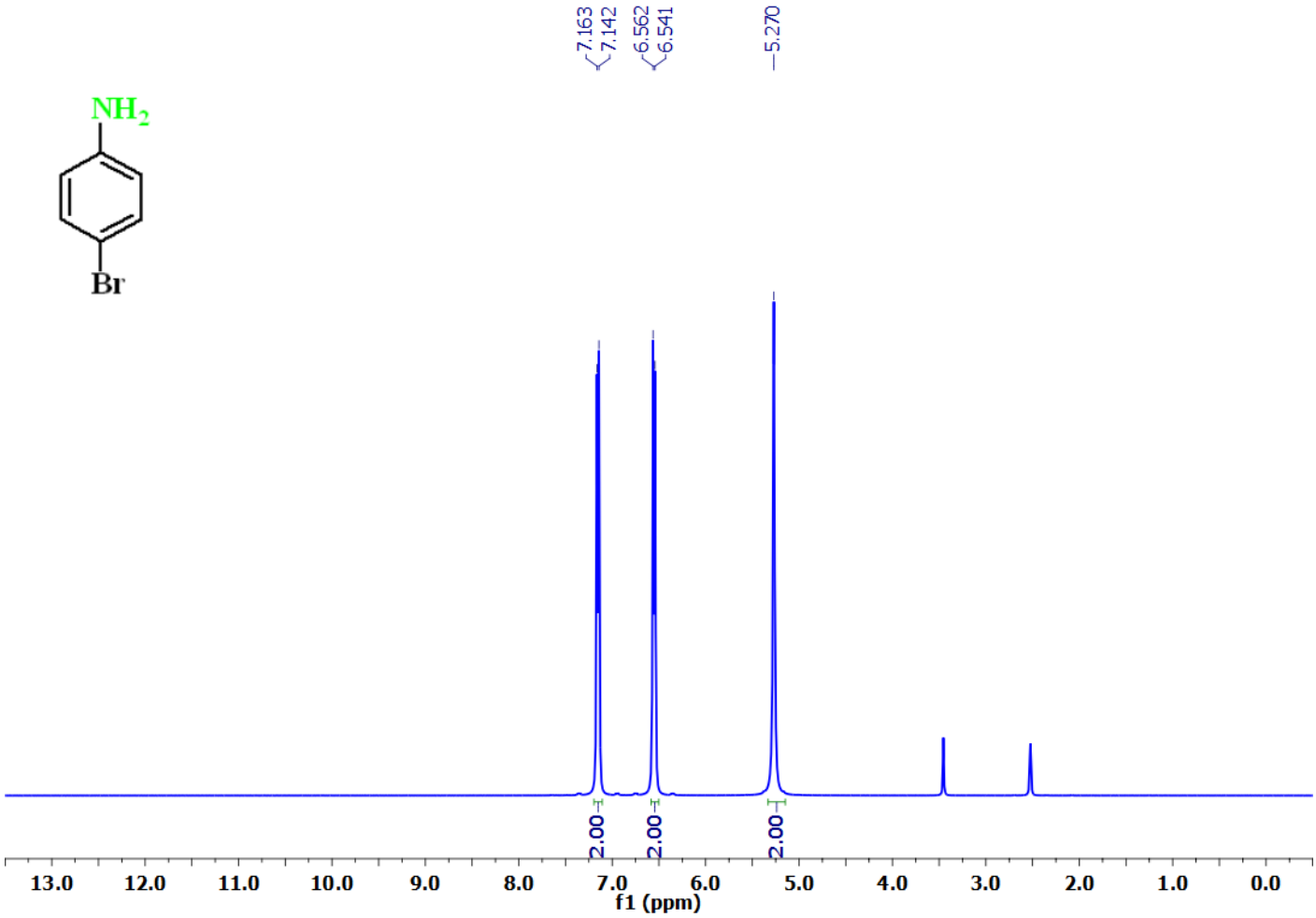
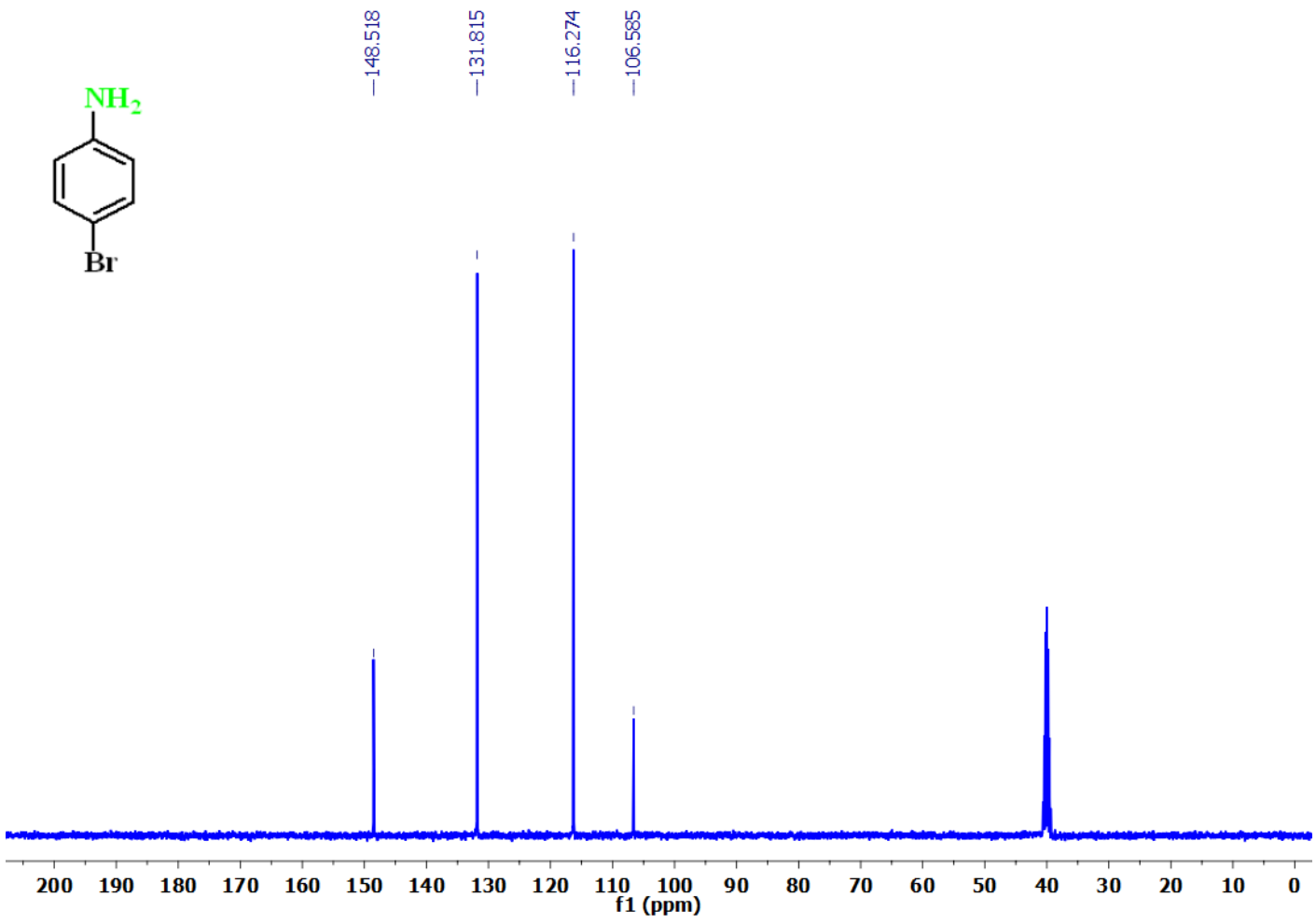


[1] H NMR of 4-Bromoaniline



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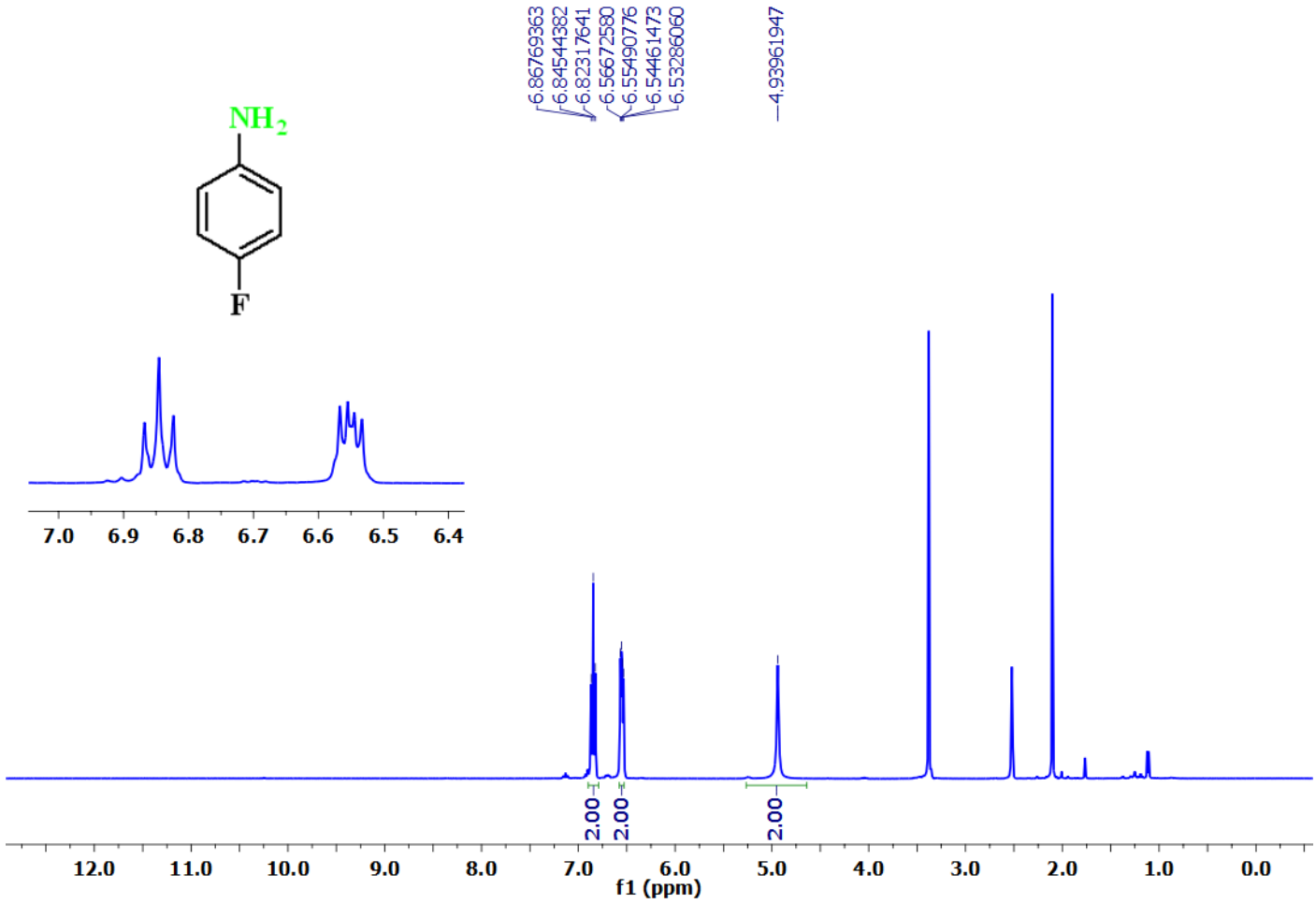

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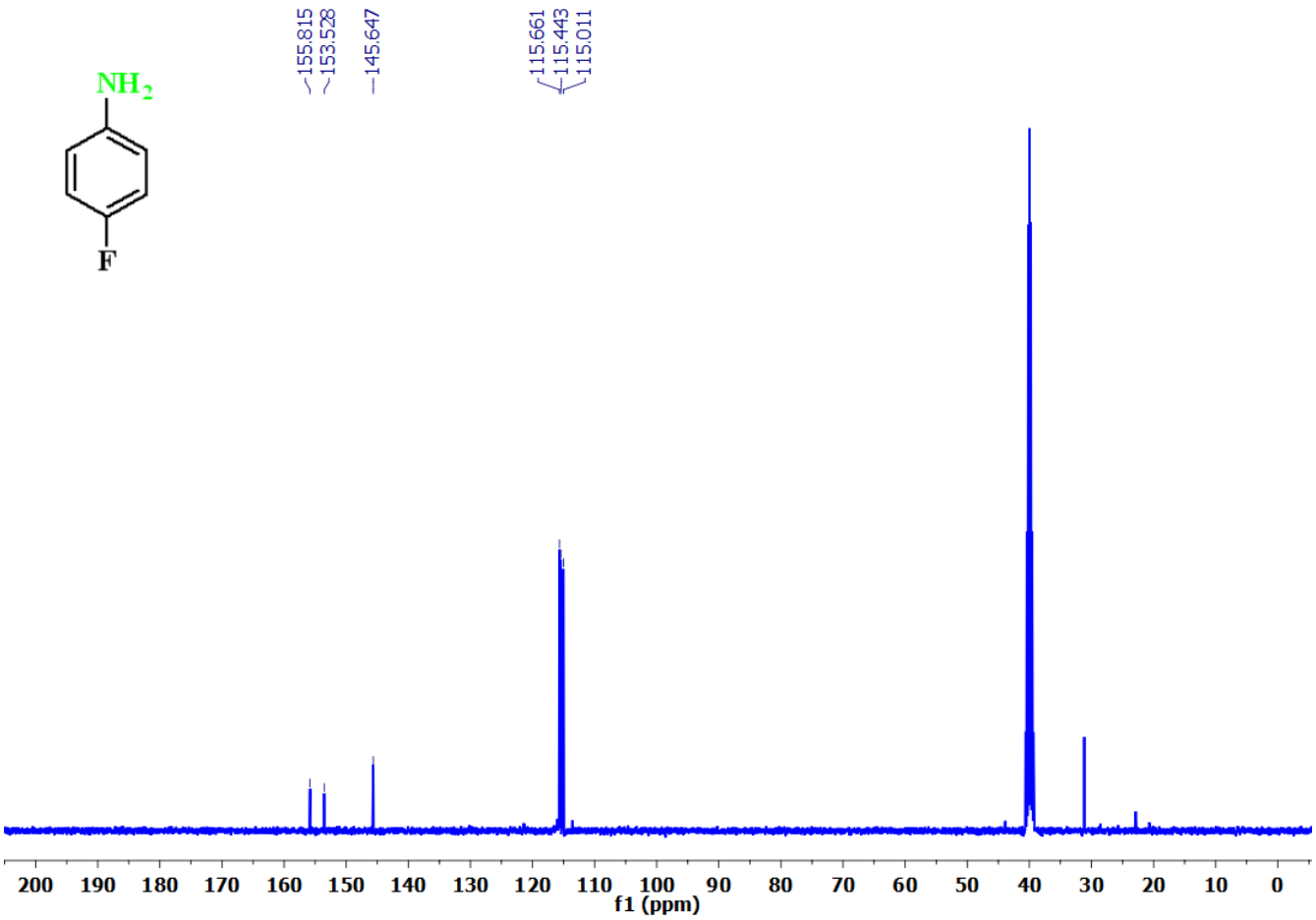
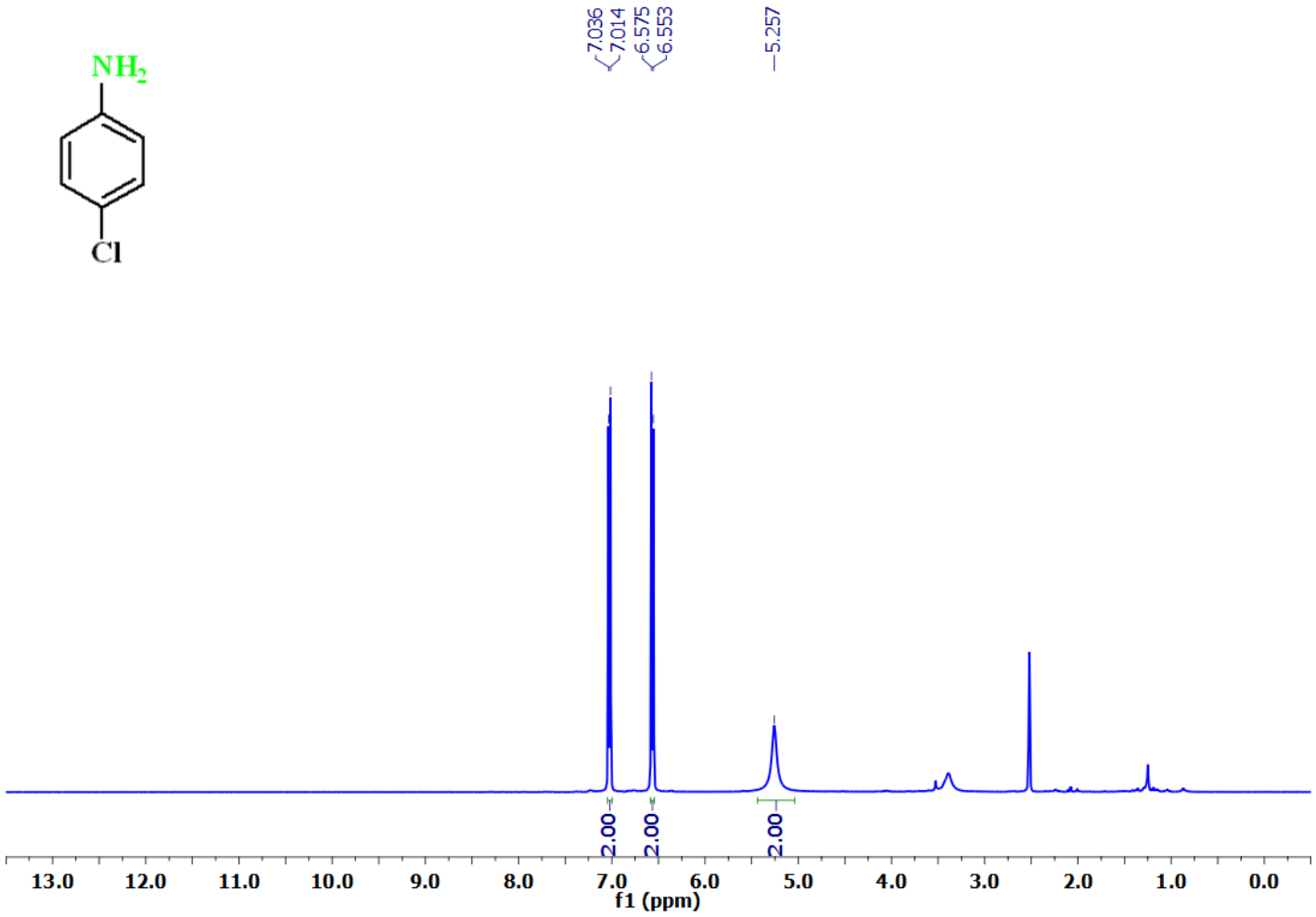
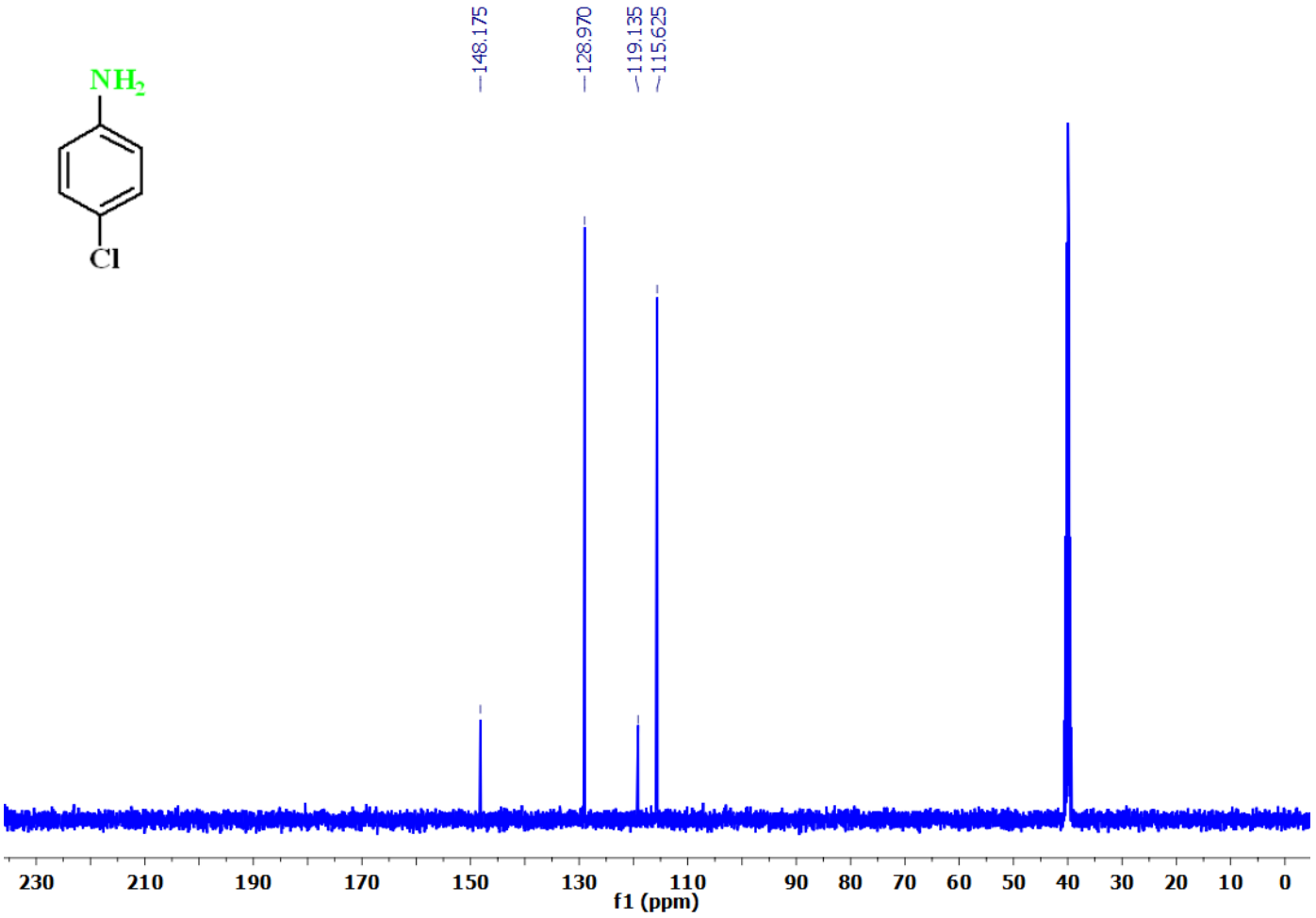


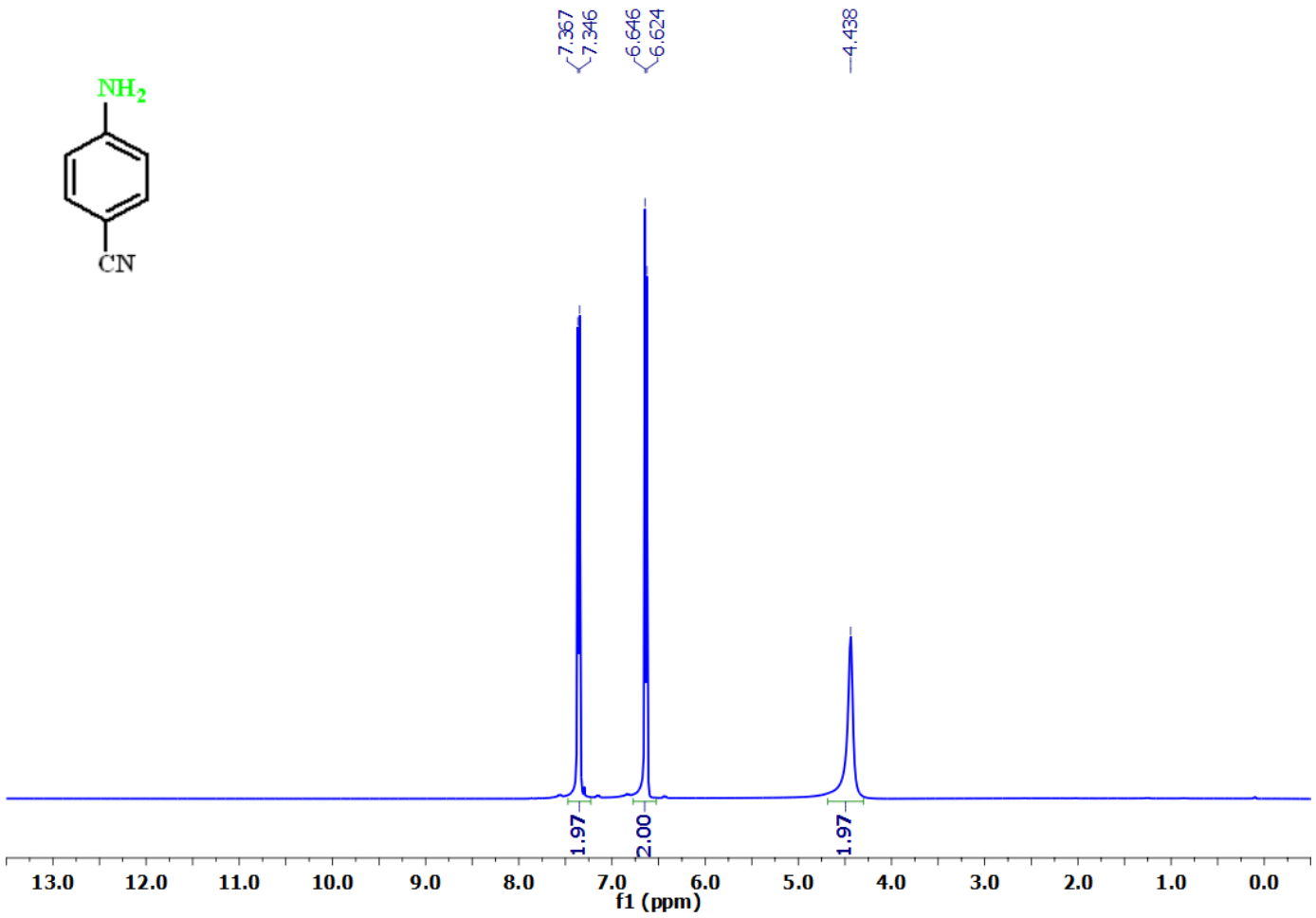
^{13} C NMR of 4-Fluoroaniline



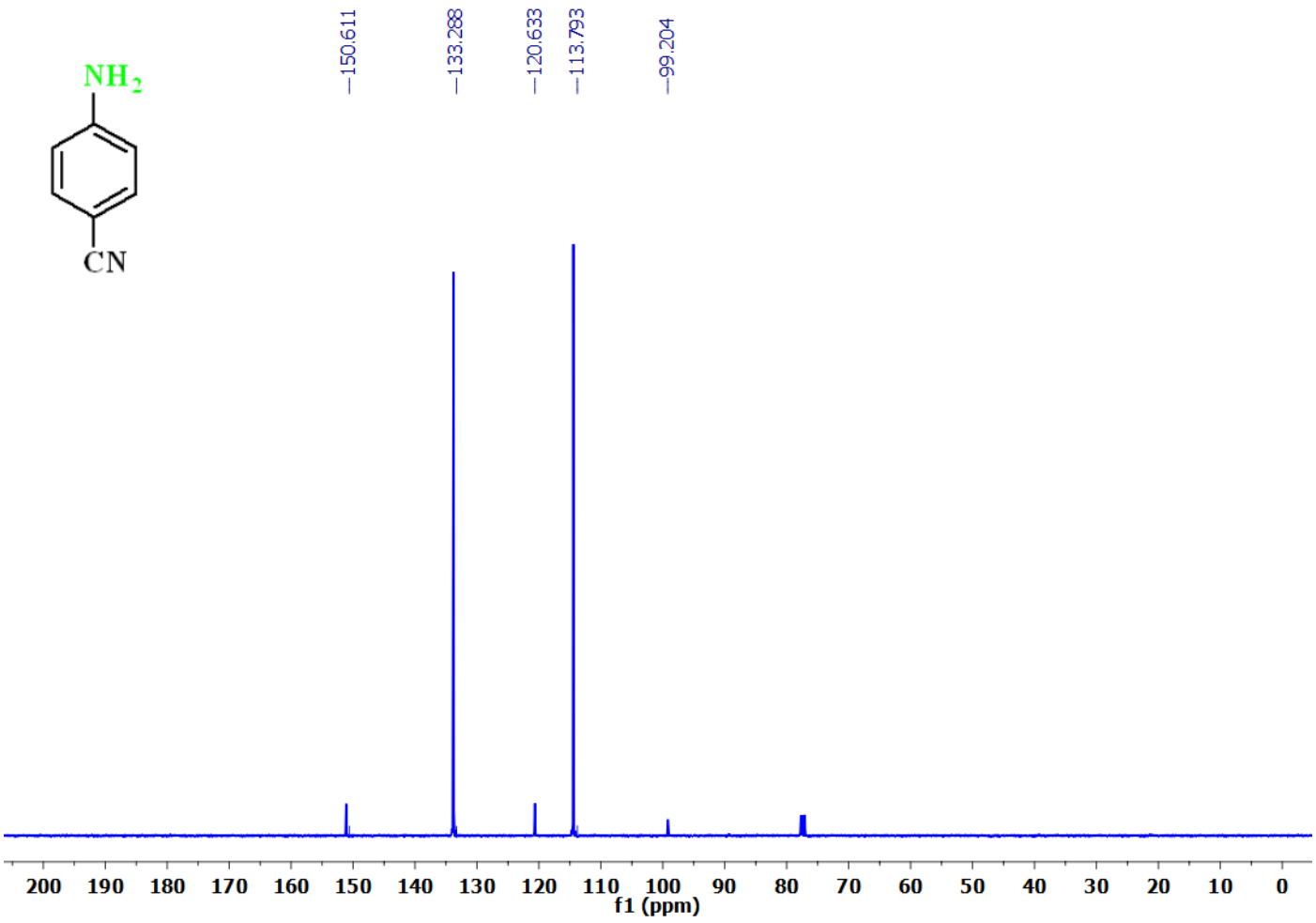
[1] H NMR of 4-Chloroaniline



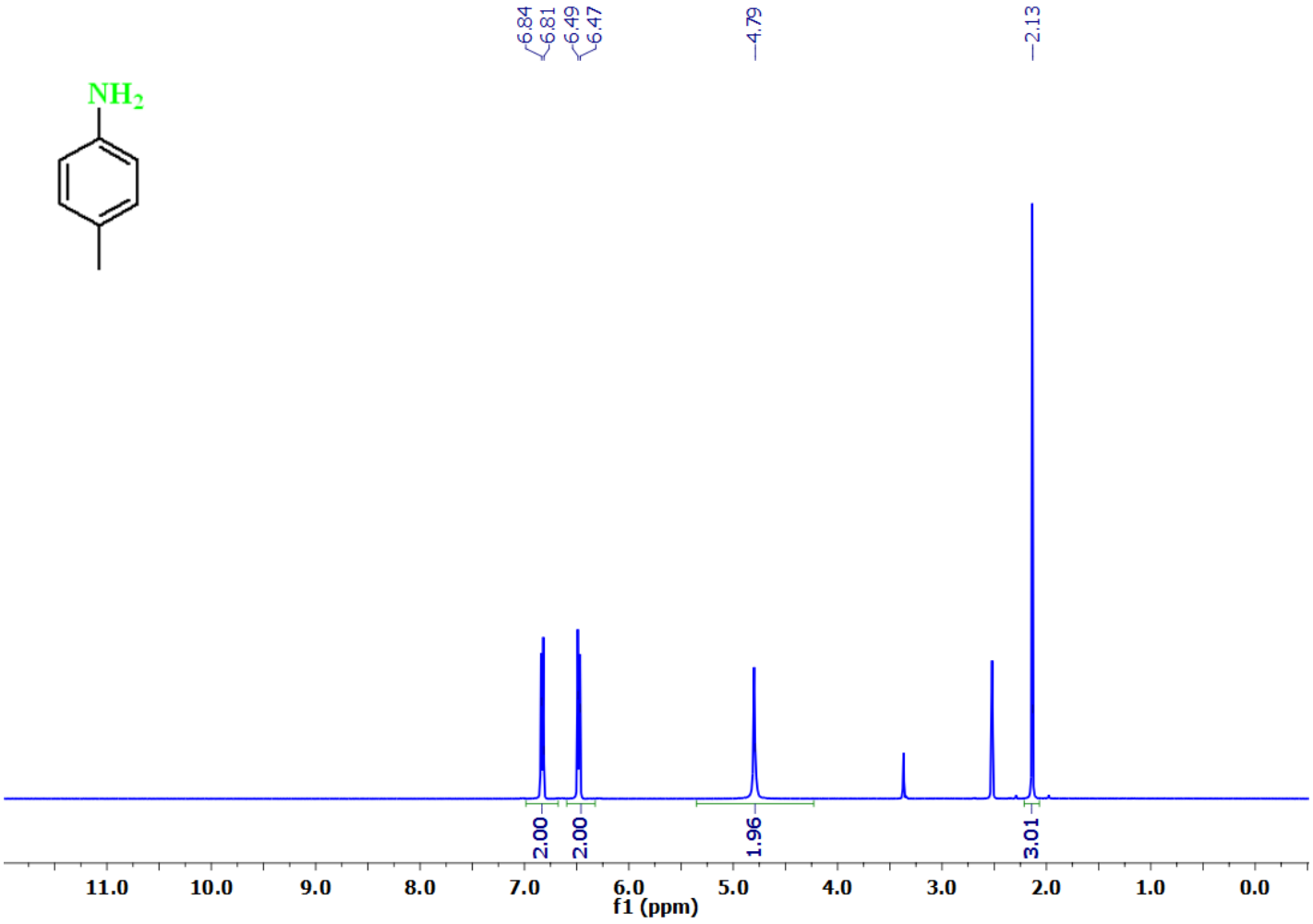
^{13} C NMR of 4-Chloroaniline



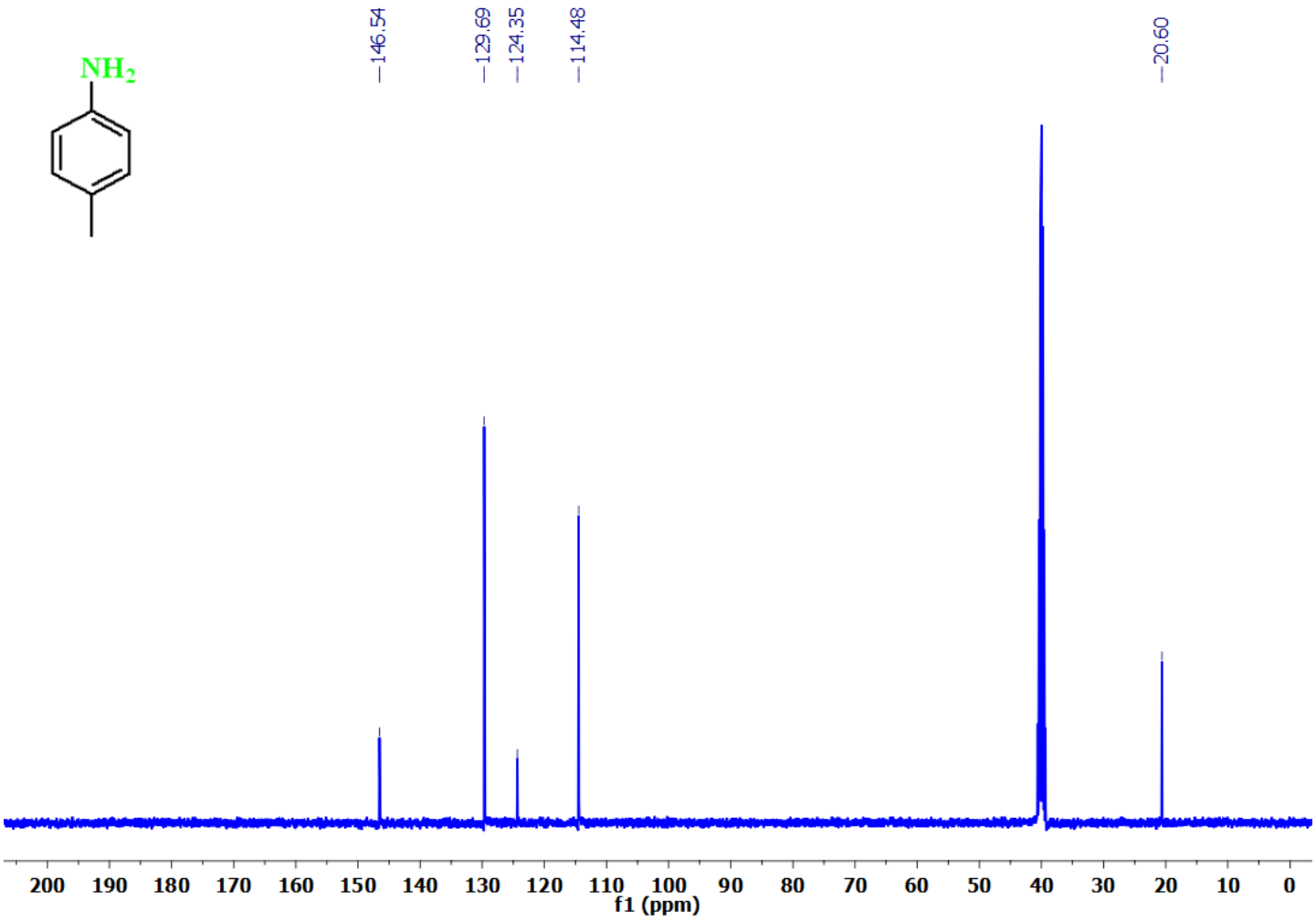
^{1}H NMR of 4-Aminobenzonitrile



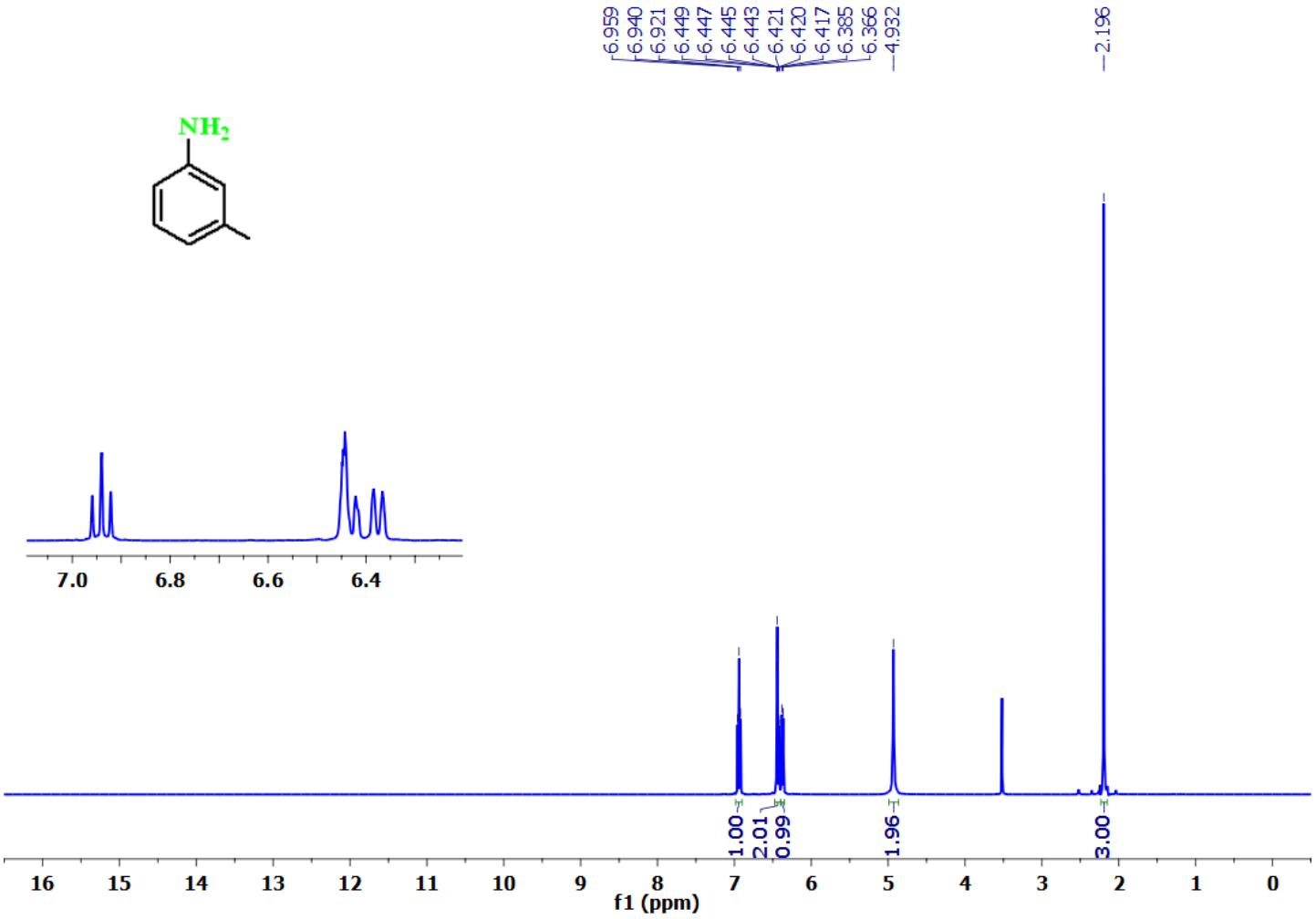
^{13}C NMR of 4-Aminobenzonitrile



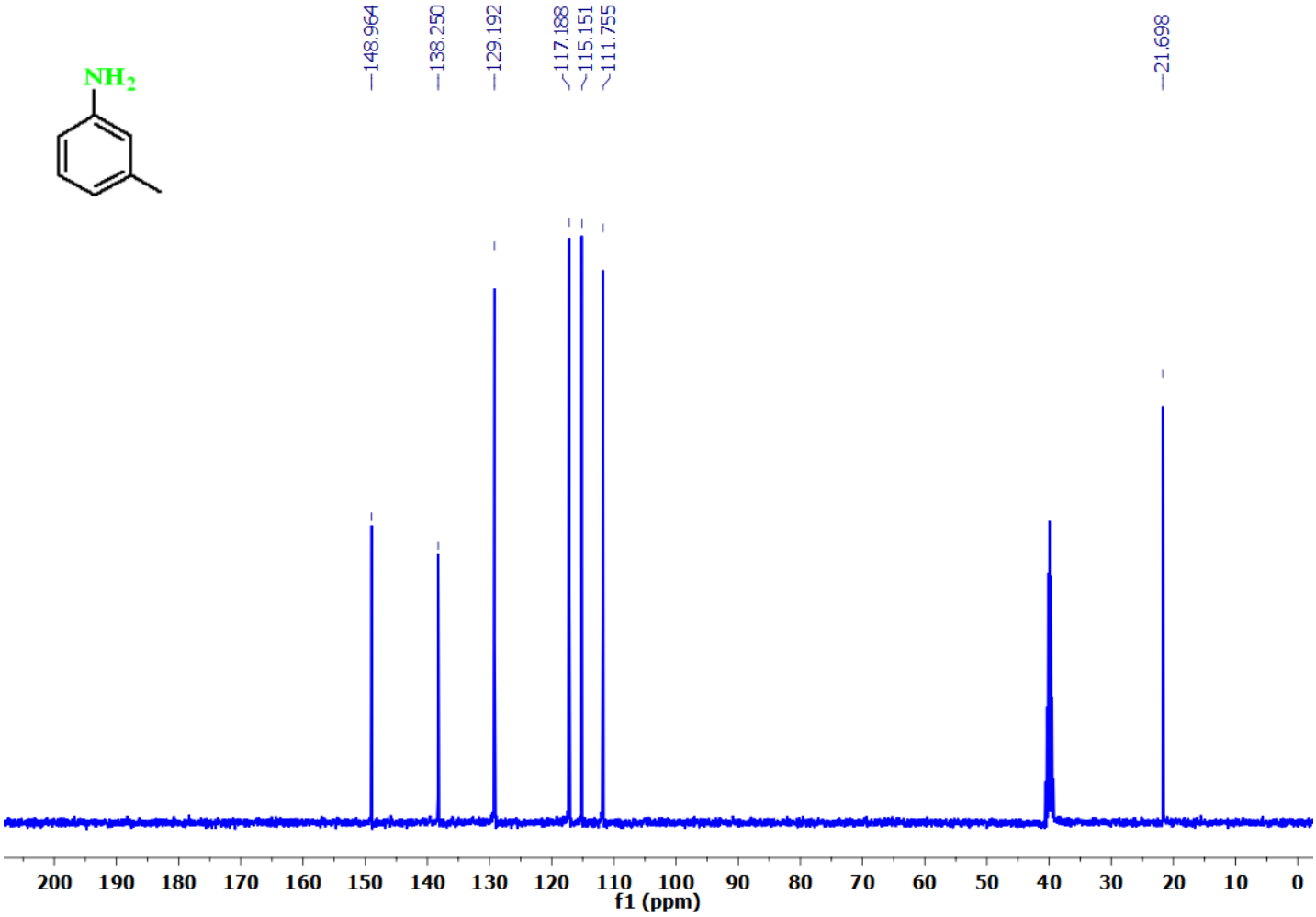
^{1}H NMR of *p*-Toluidine



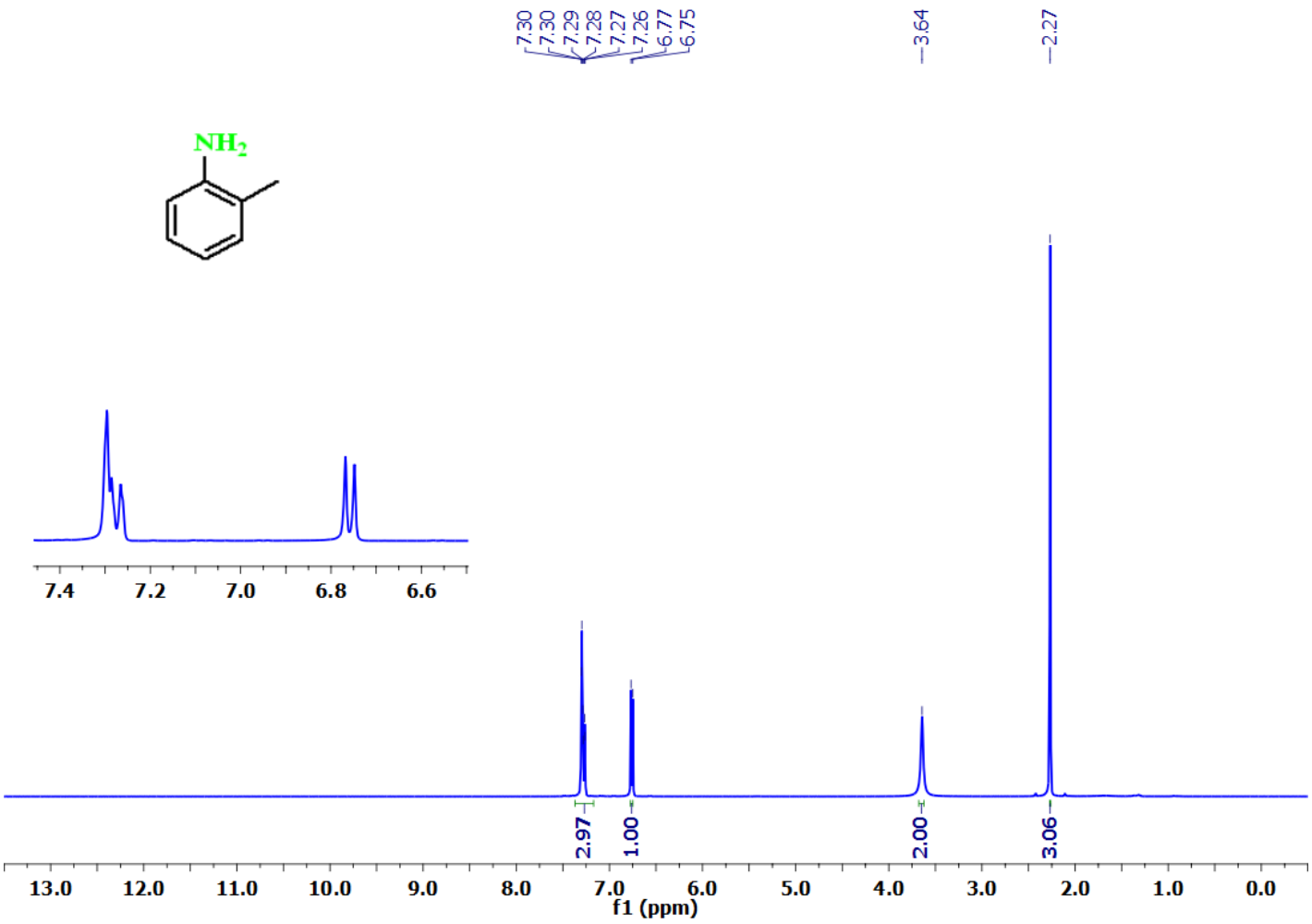
^{13}C NMR of *p*-Toluidine



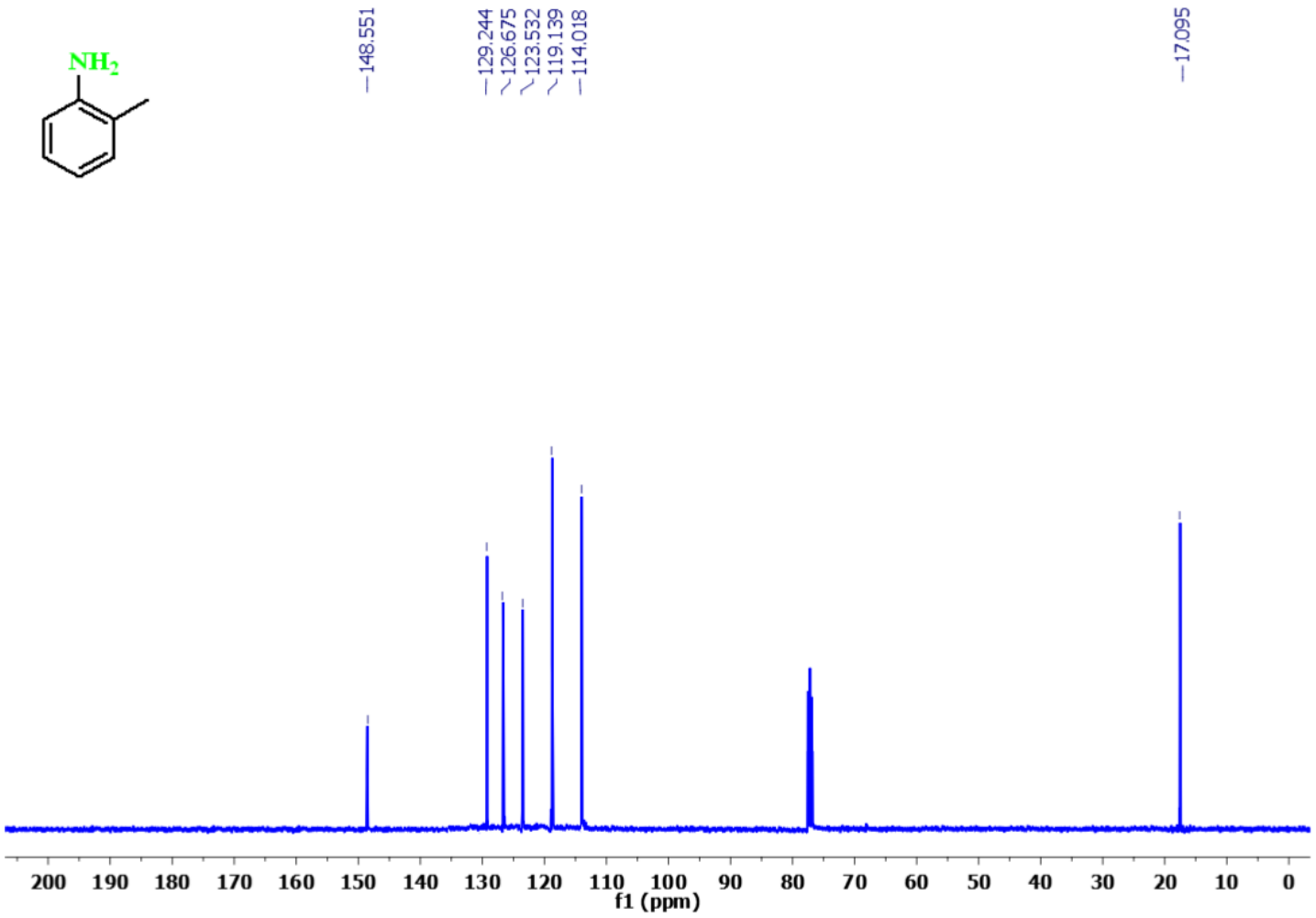
[1] H NMR of *m*-Toluidine



^{13}C NMR of *m*-Toluidine



^{1}H NMR of *o*-Toluidine



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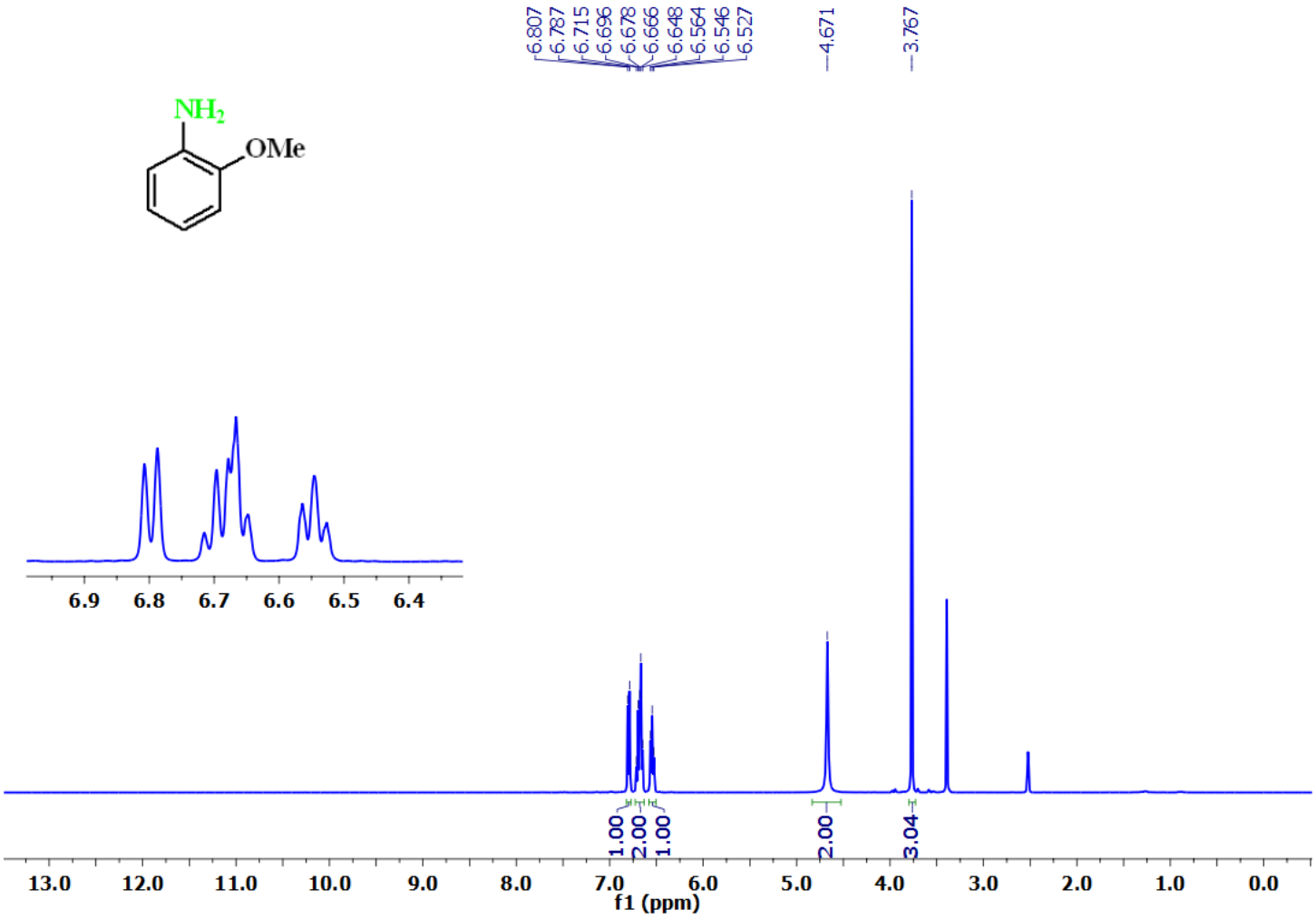
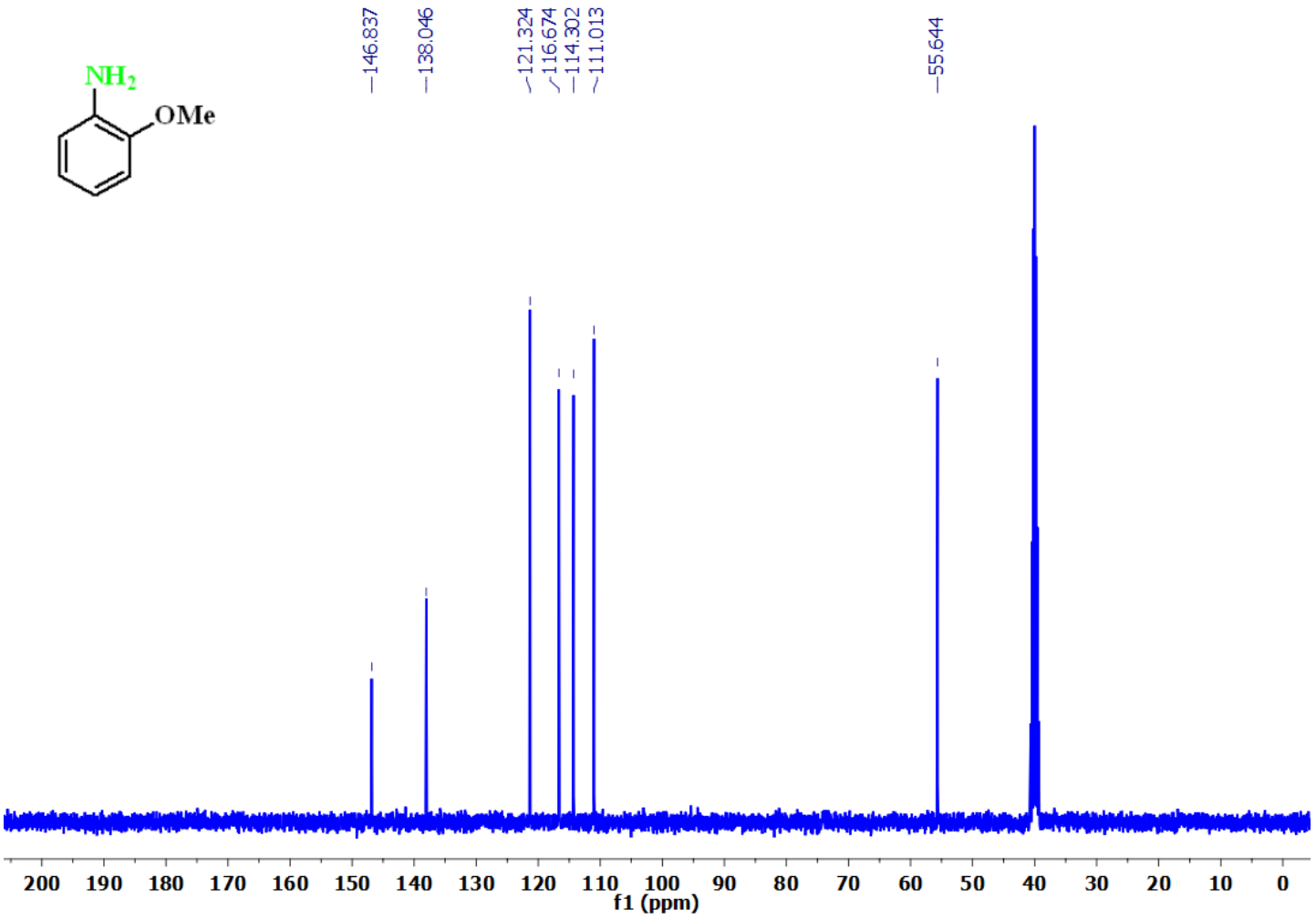


[1] H NMR of *o*-Anisidine



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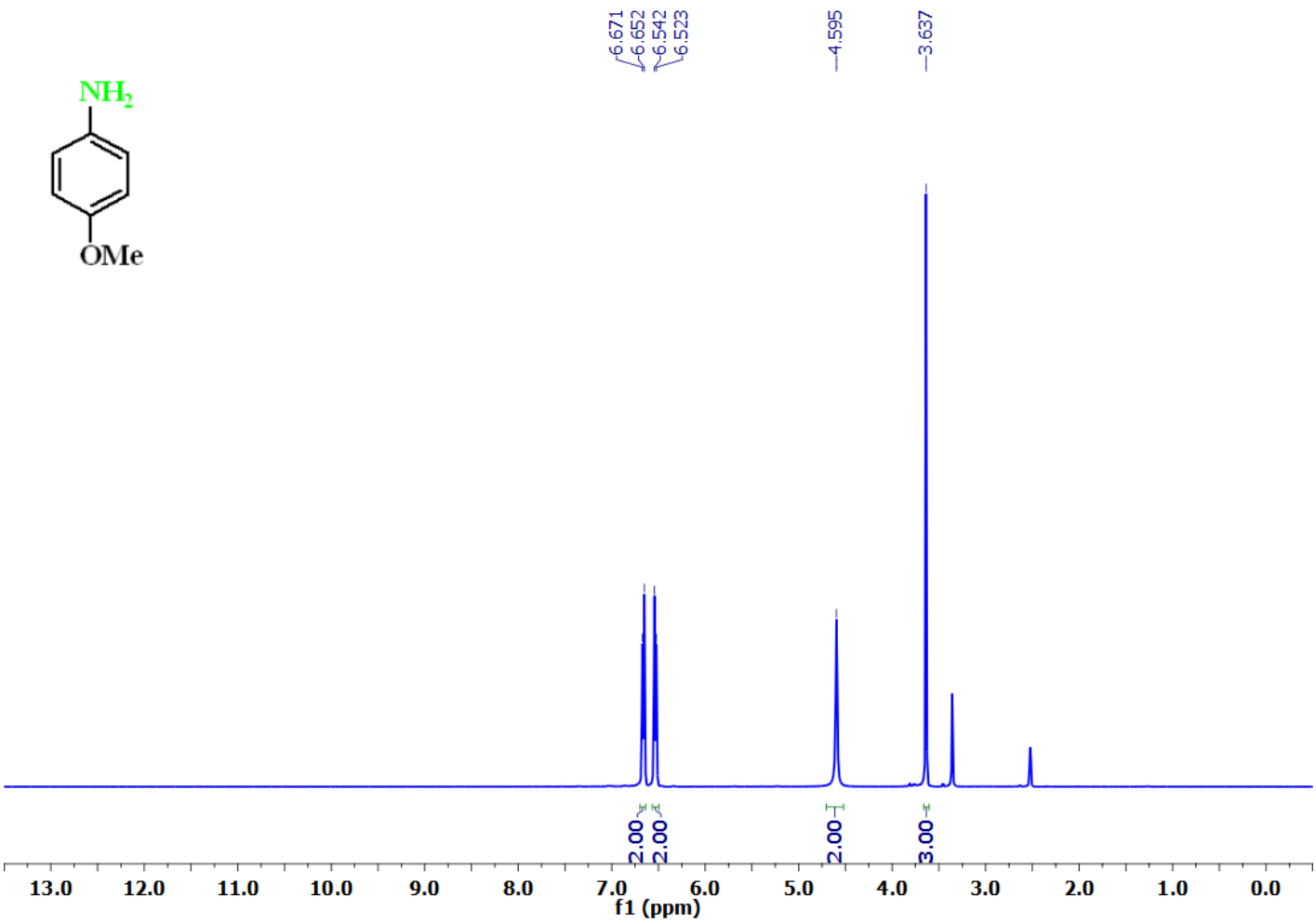
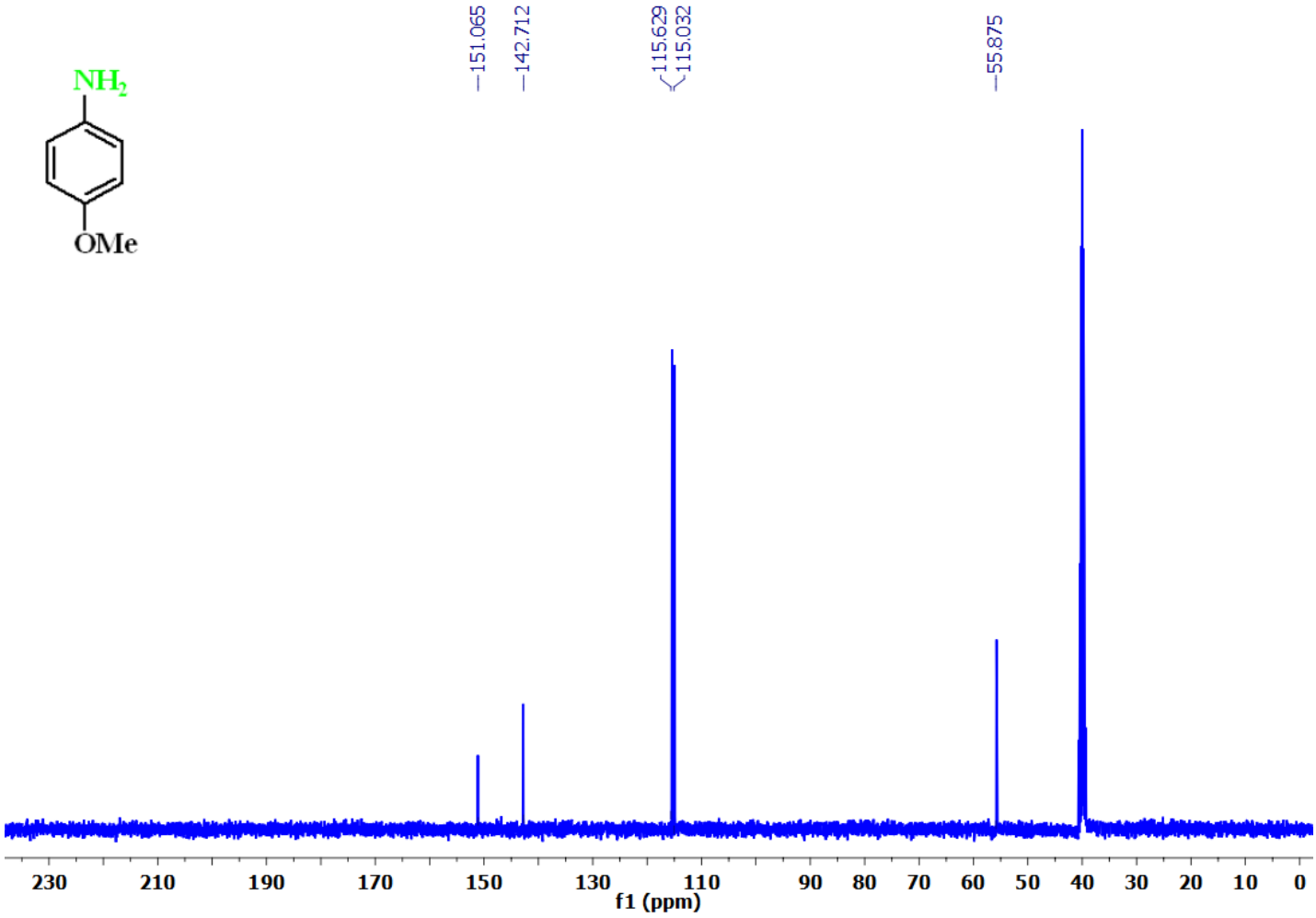


[1] H NMR of *p*-Anisidine



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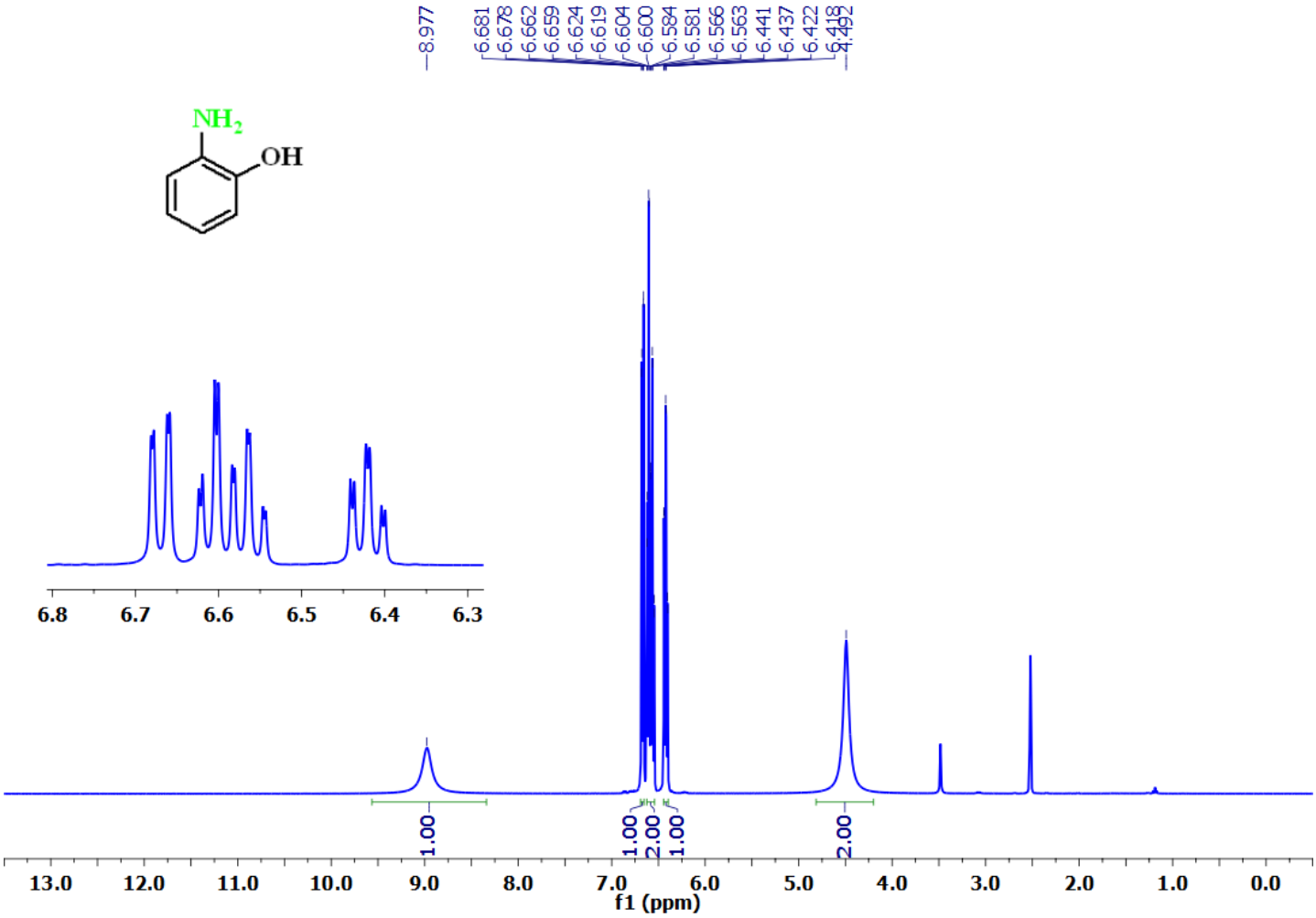
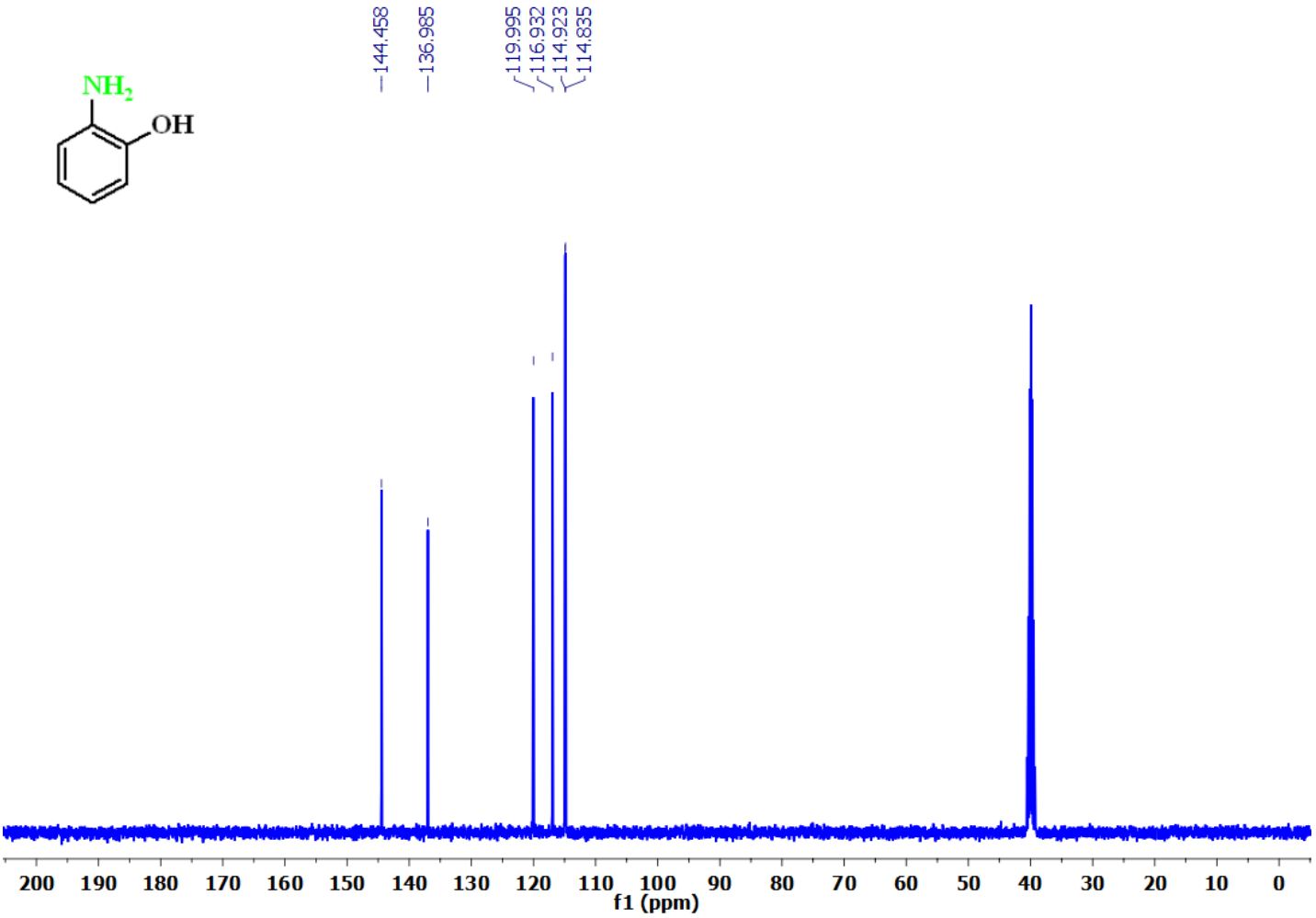
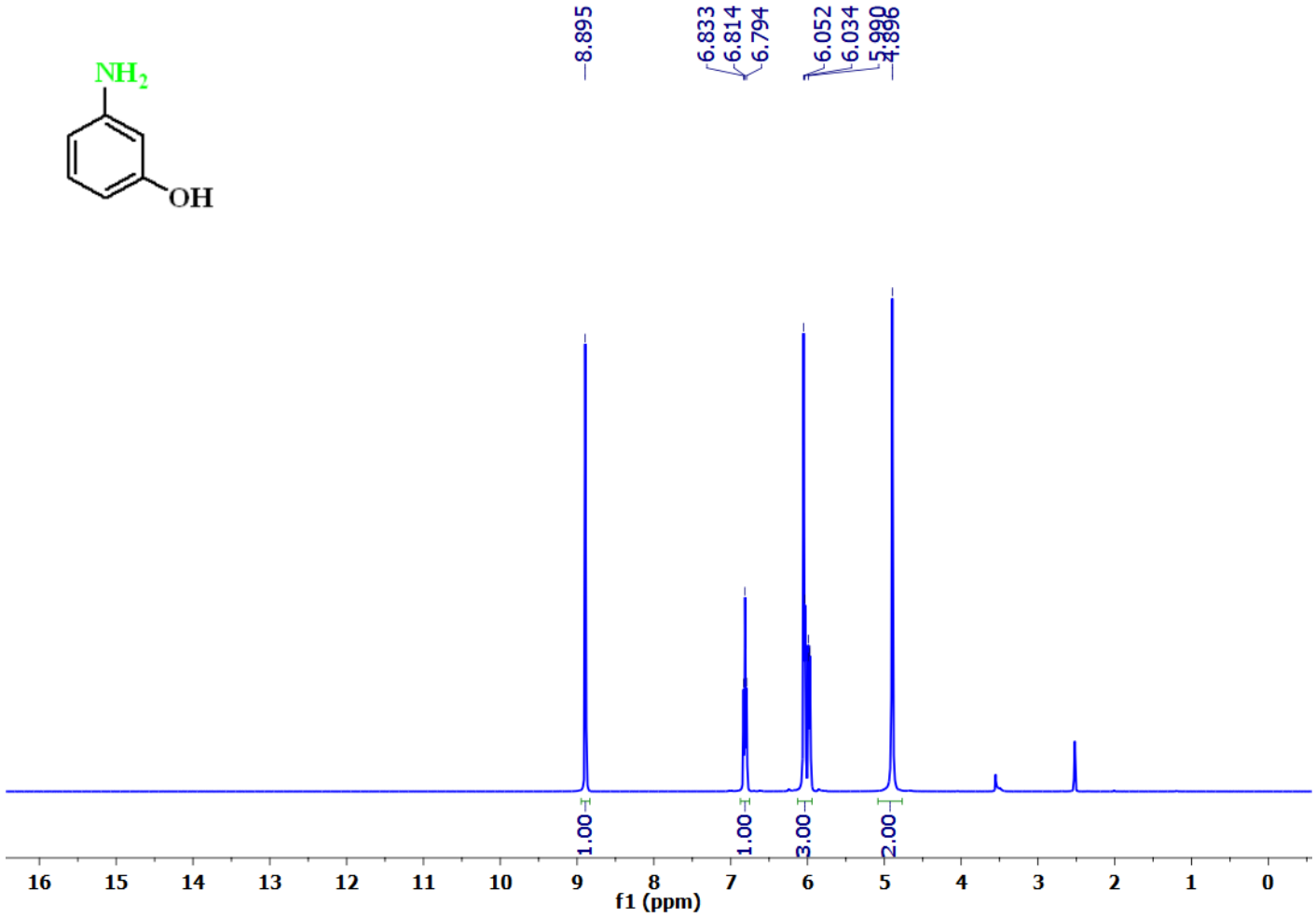


[1] H NMR of 2-Aminophenol



^{13}C NMR of 2-Aminophenol



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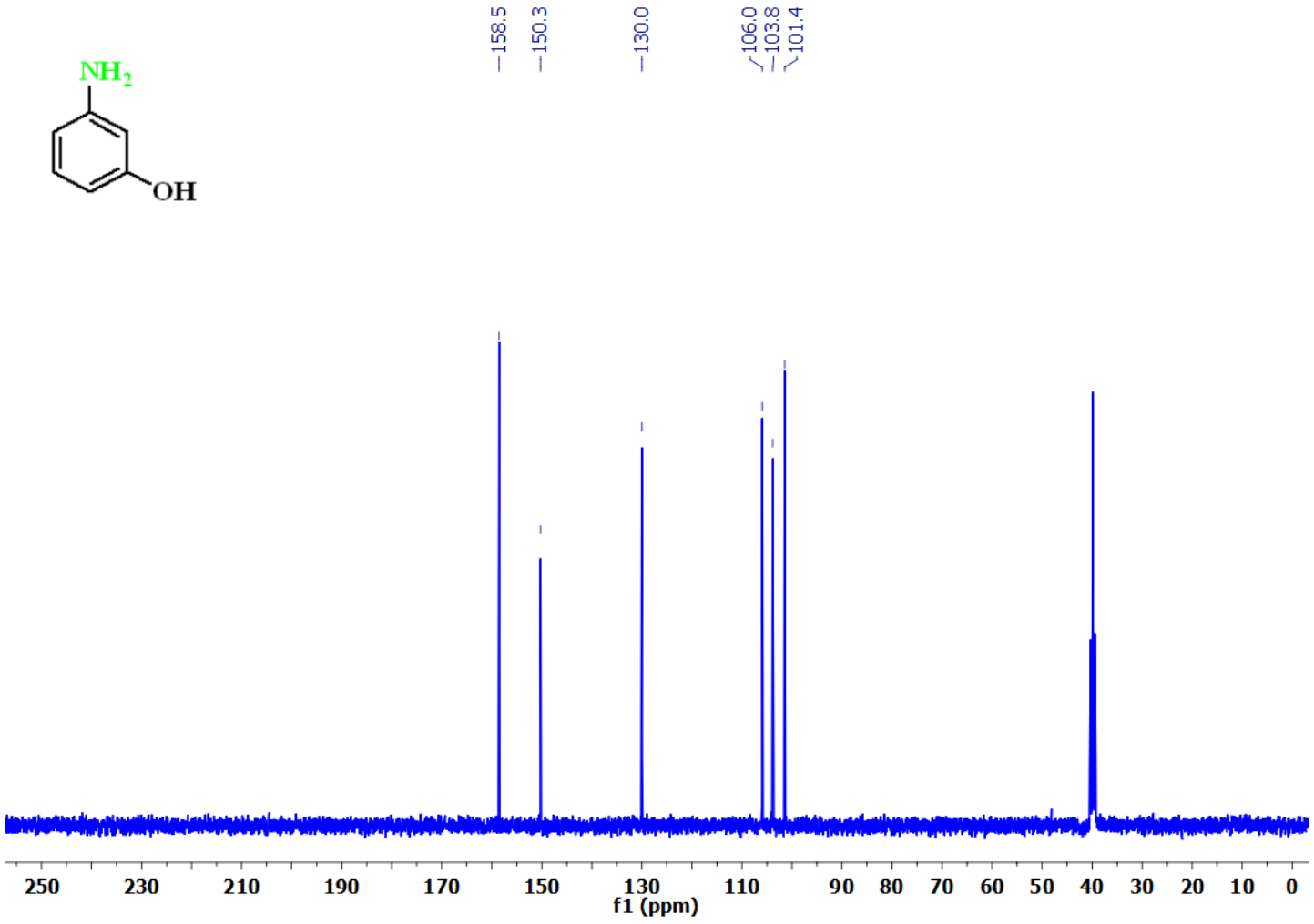
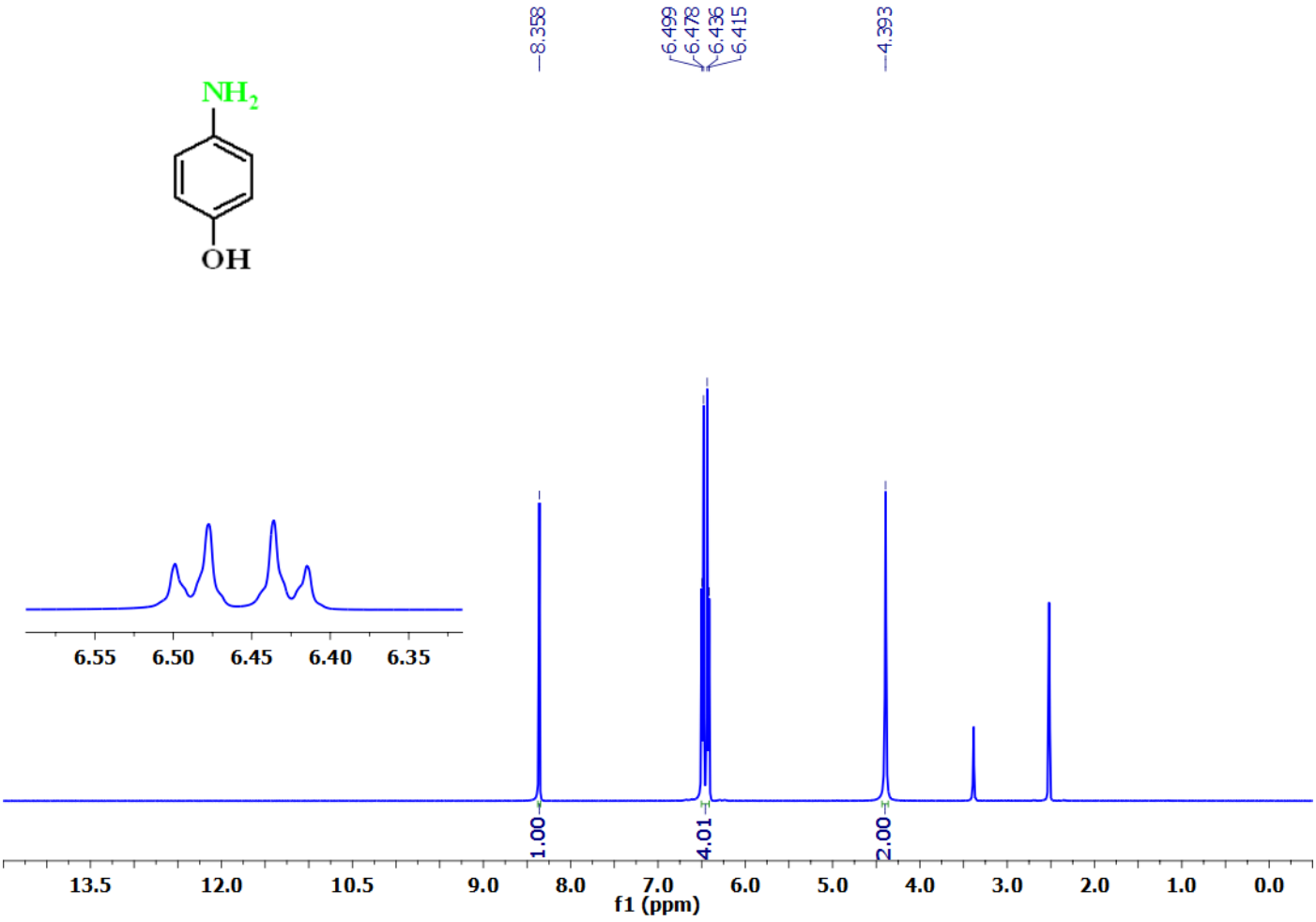
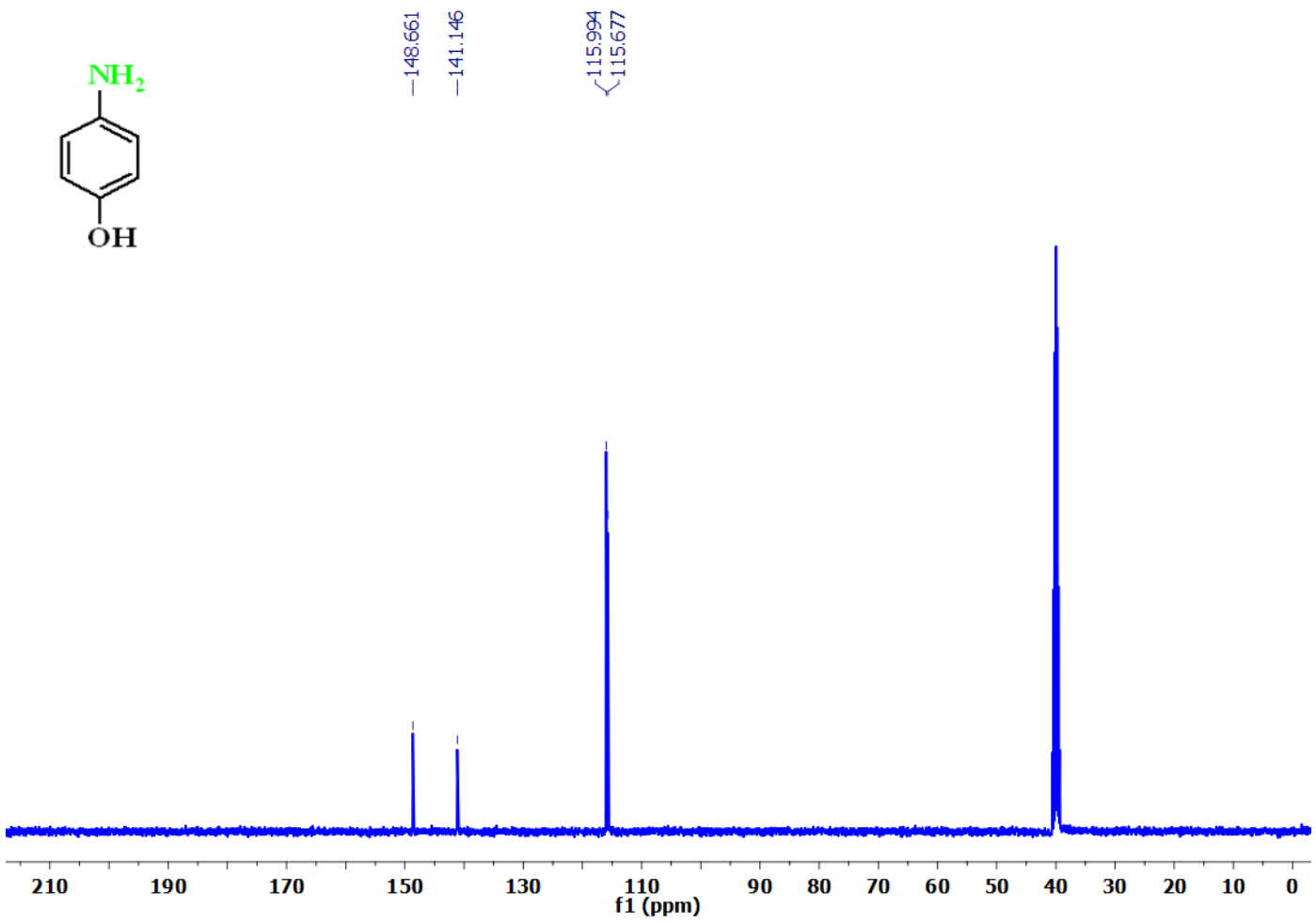


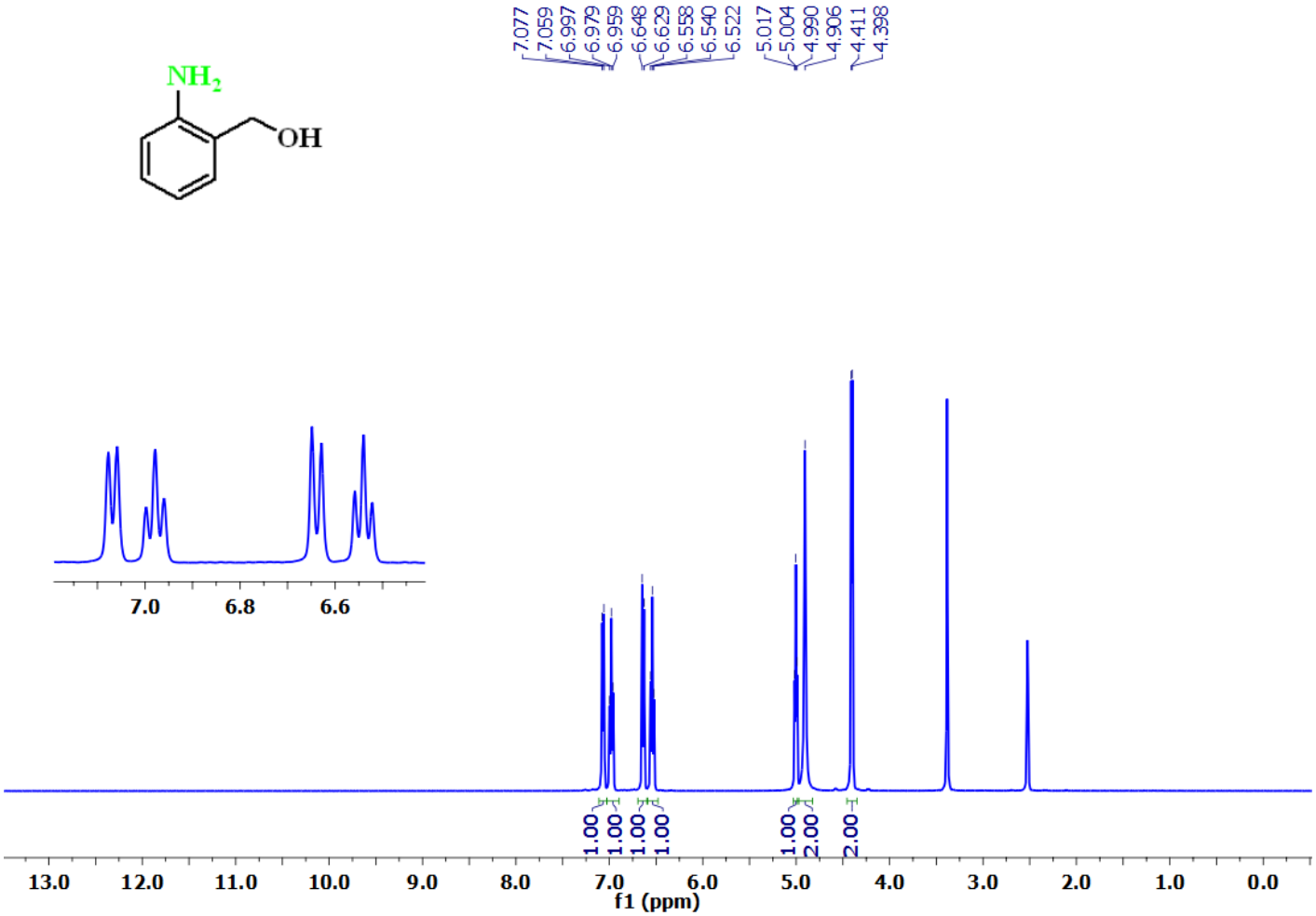
^{13}C NMR of 3-Aminophenol



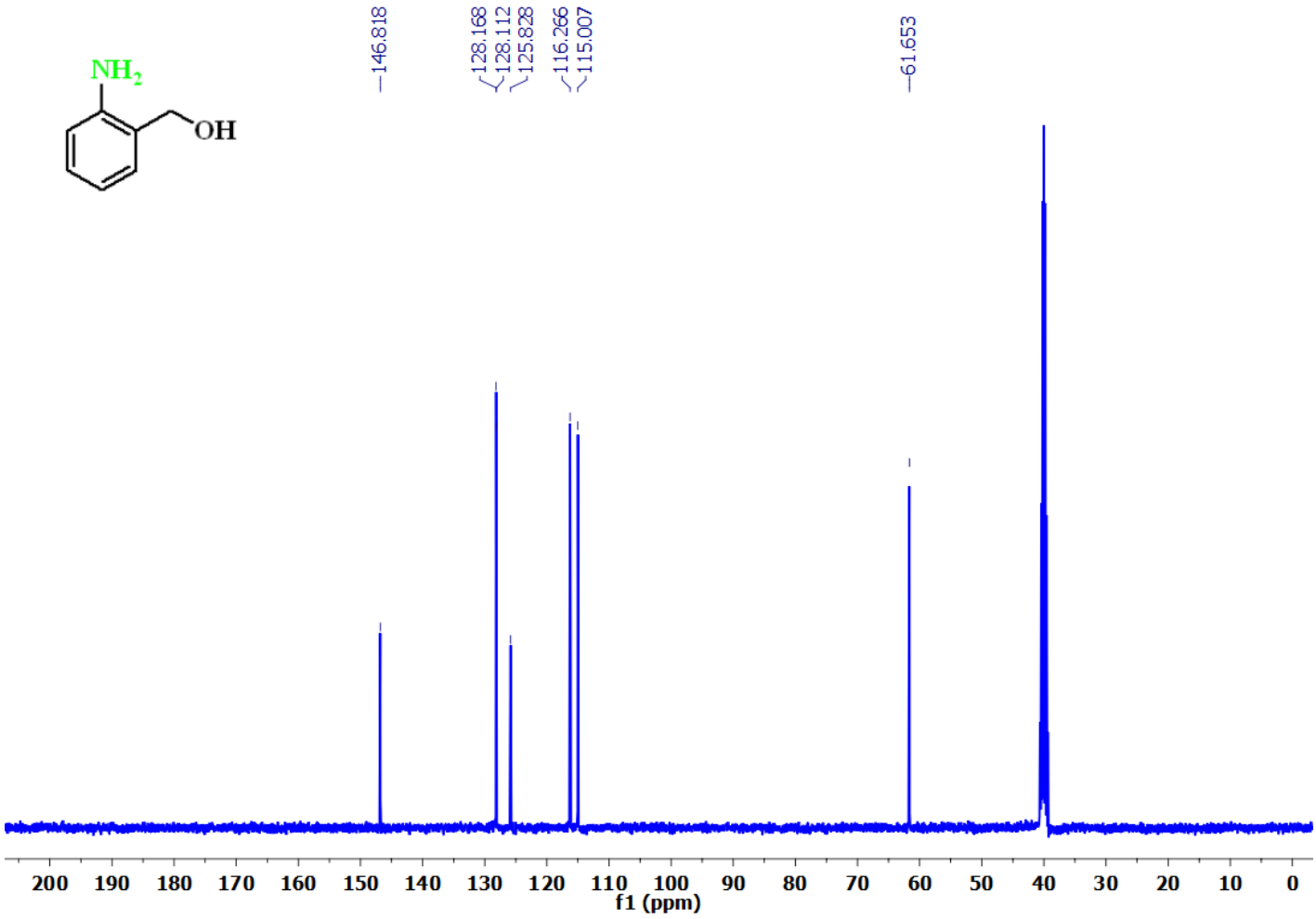
^{1}H NMR of 4-Aminophenol



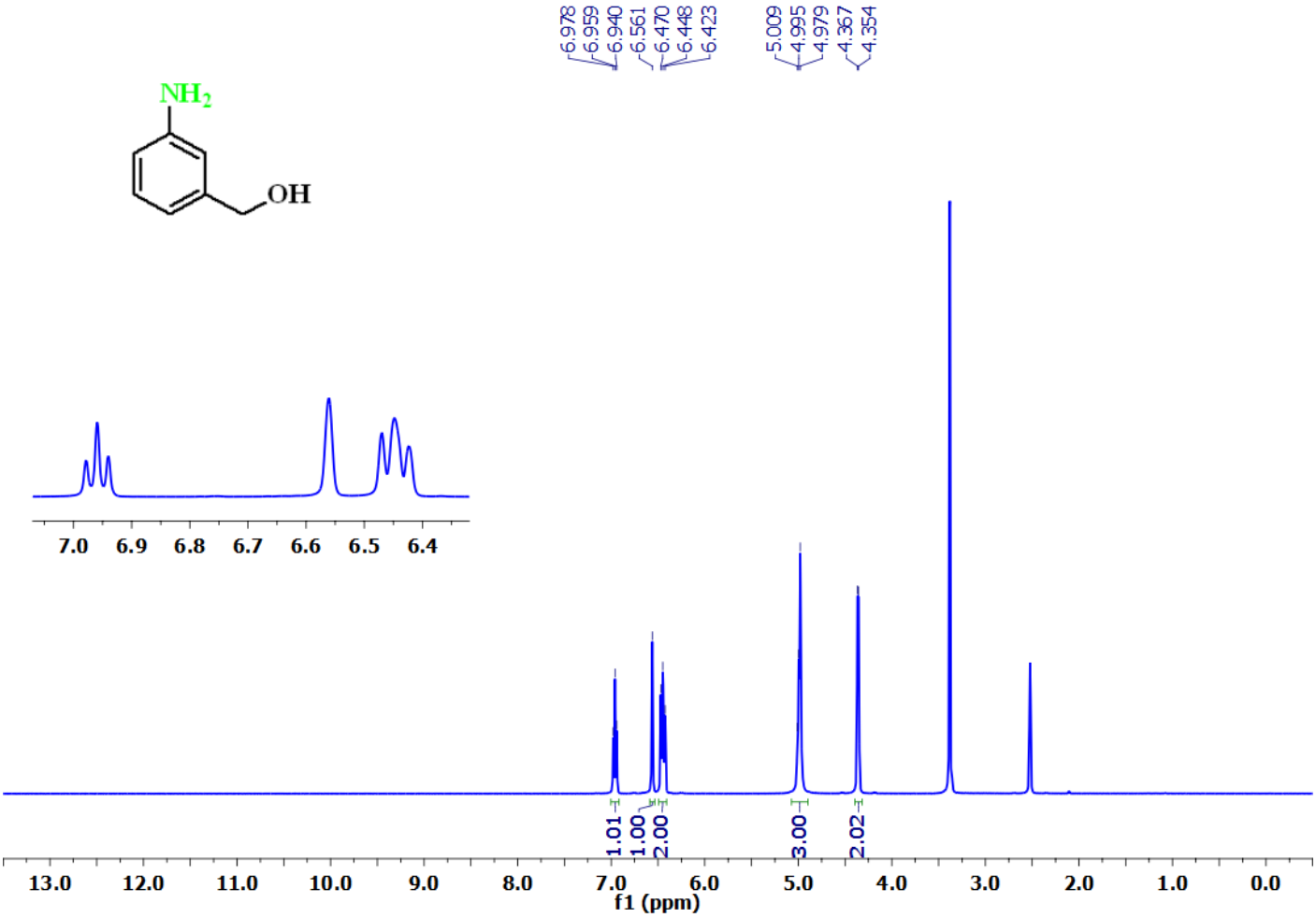
^{13}C NMR of 4-Aminophenol



[1] H NMR of 2-Aminobenzyl alcohol



^{13}C NMR of 2-Aminobenzyl alcohol



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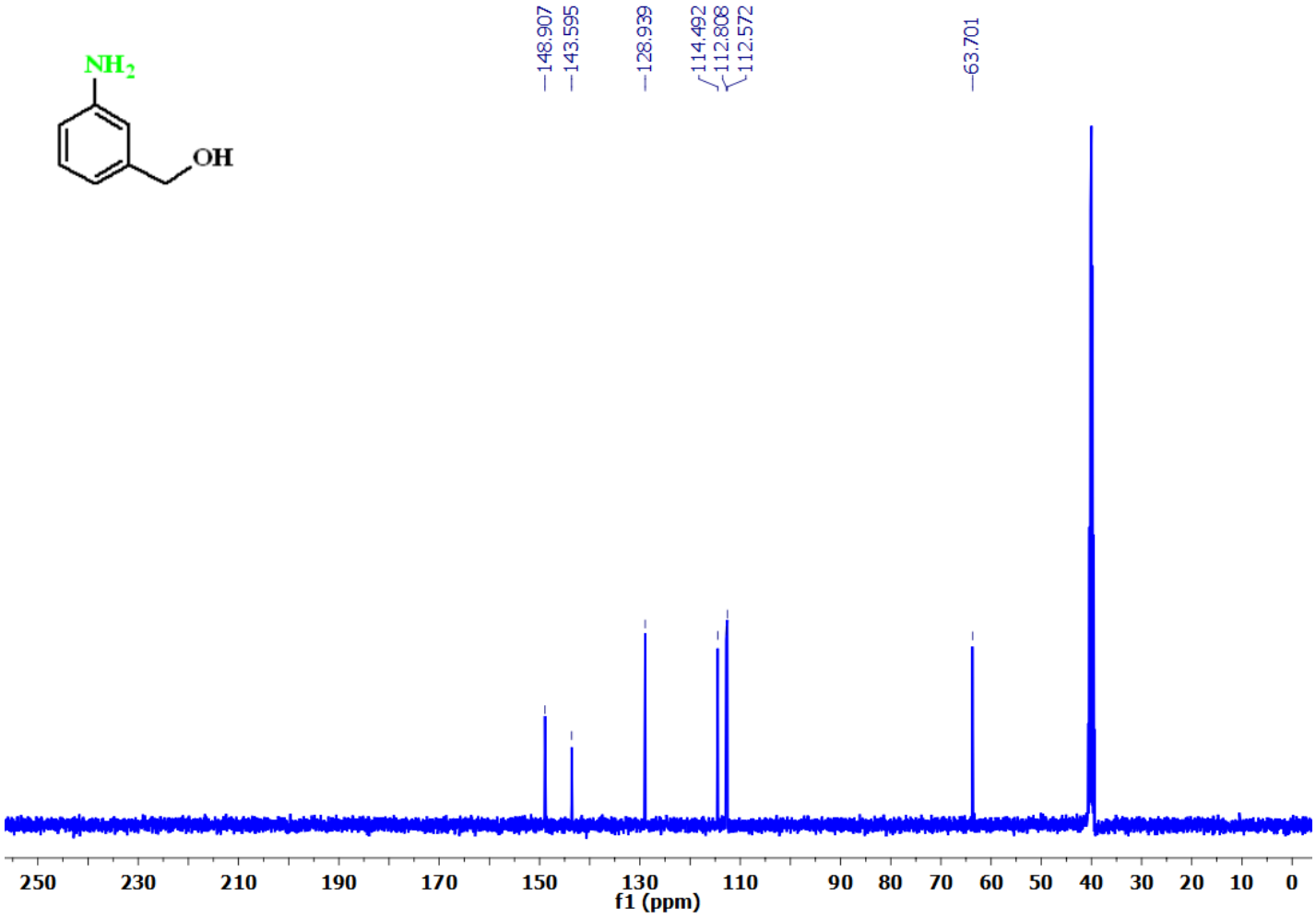
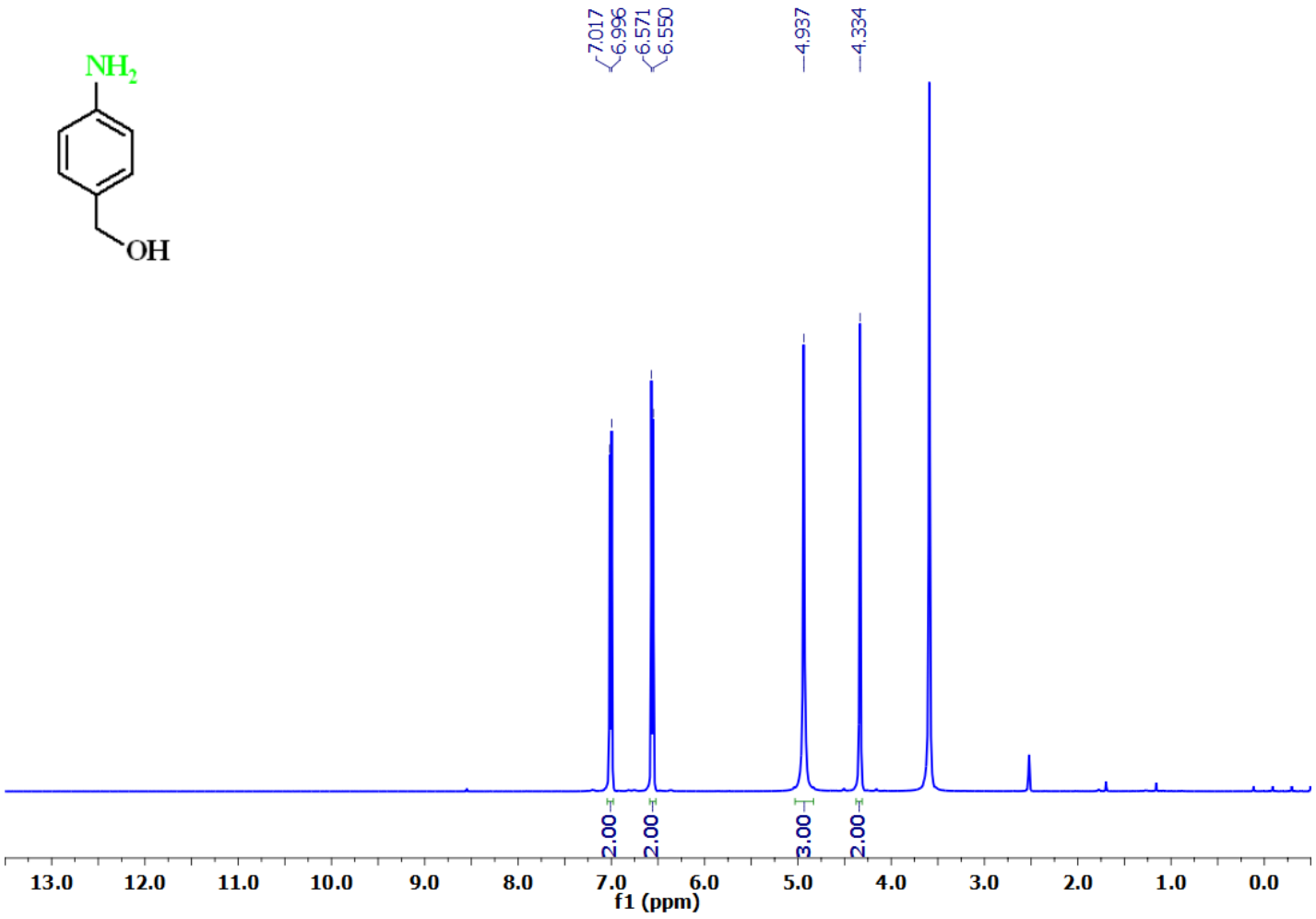
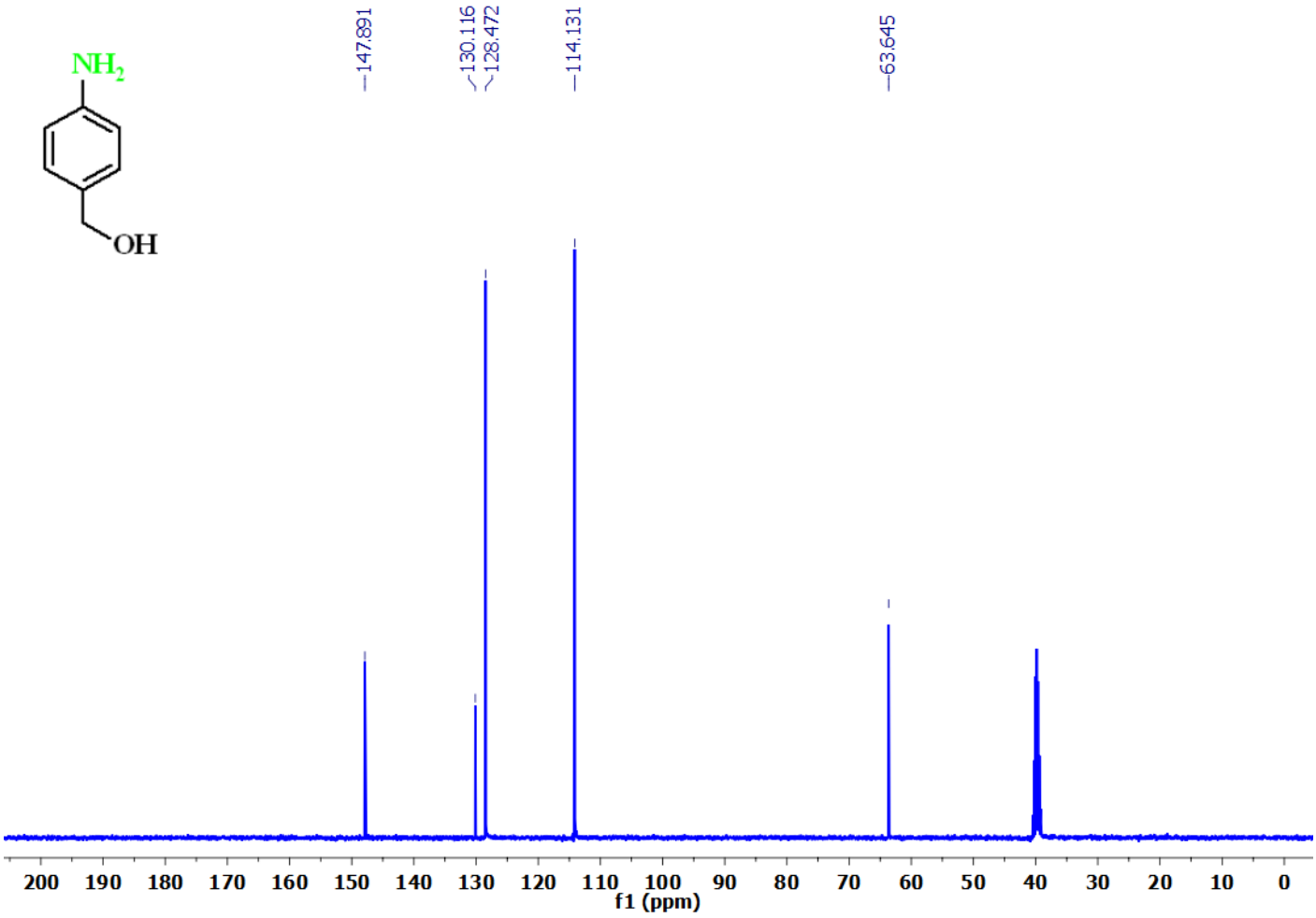


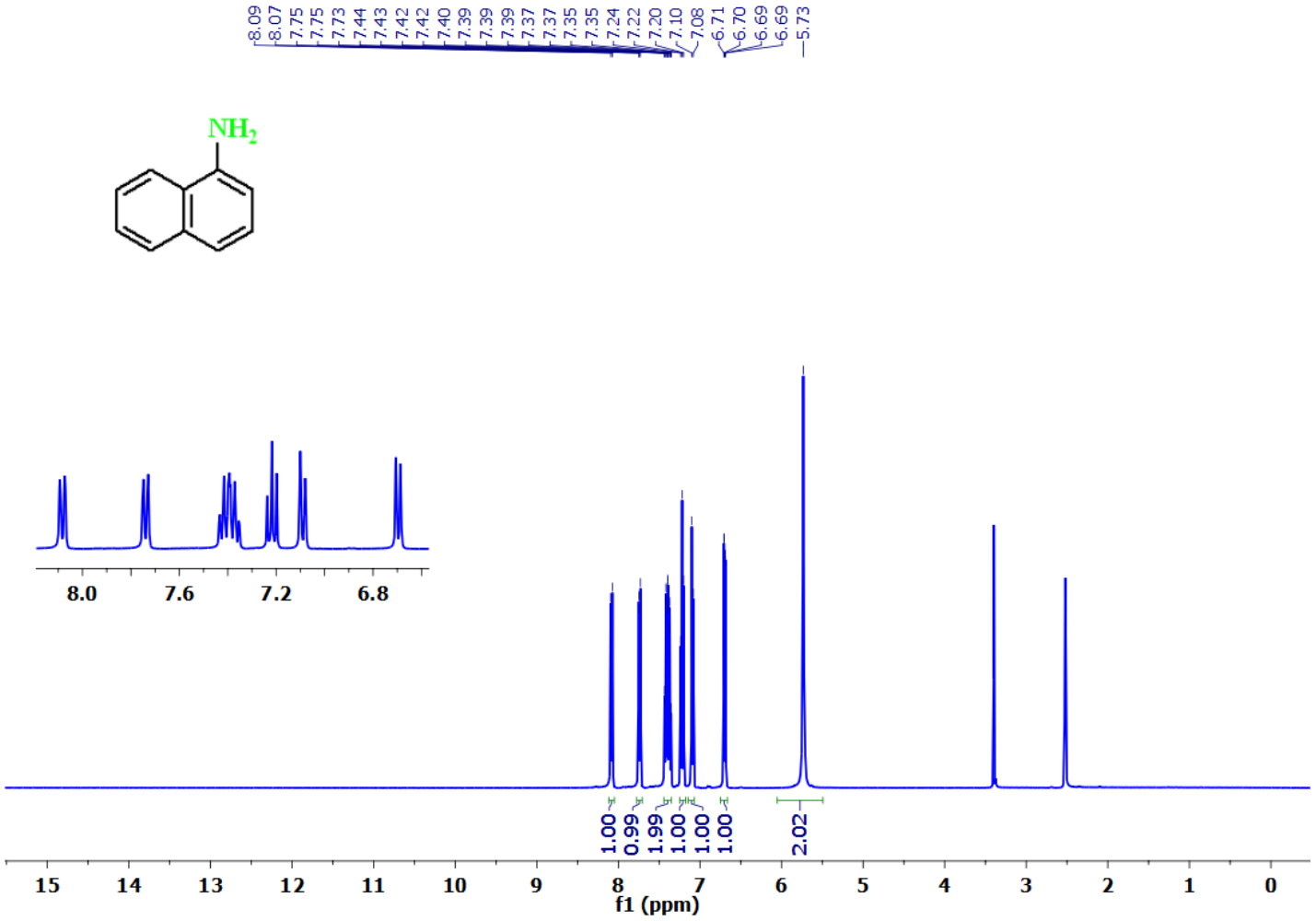
^{13}C NMR of 3-Aminobenzyl alcohol



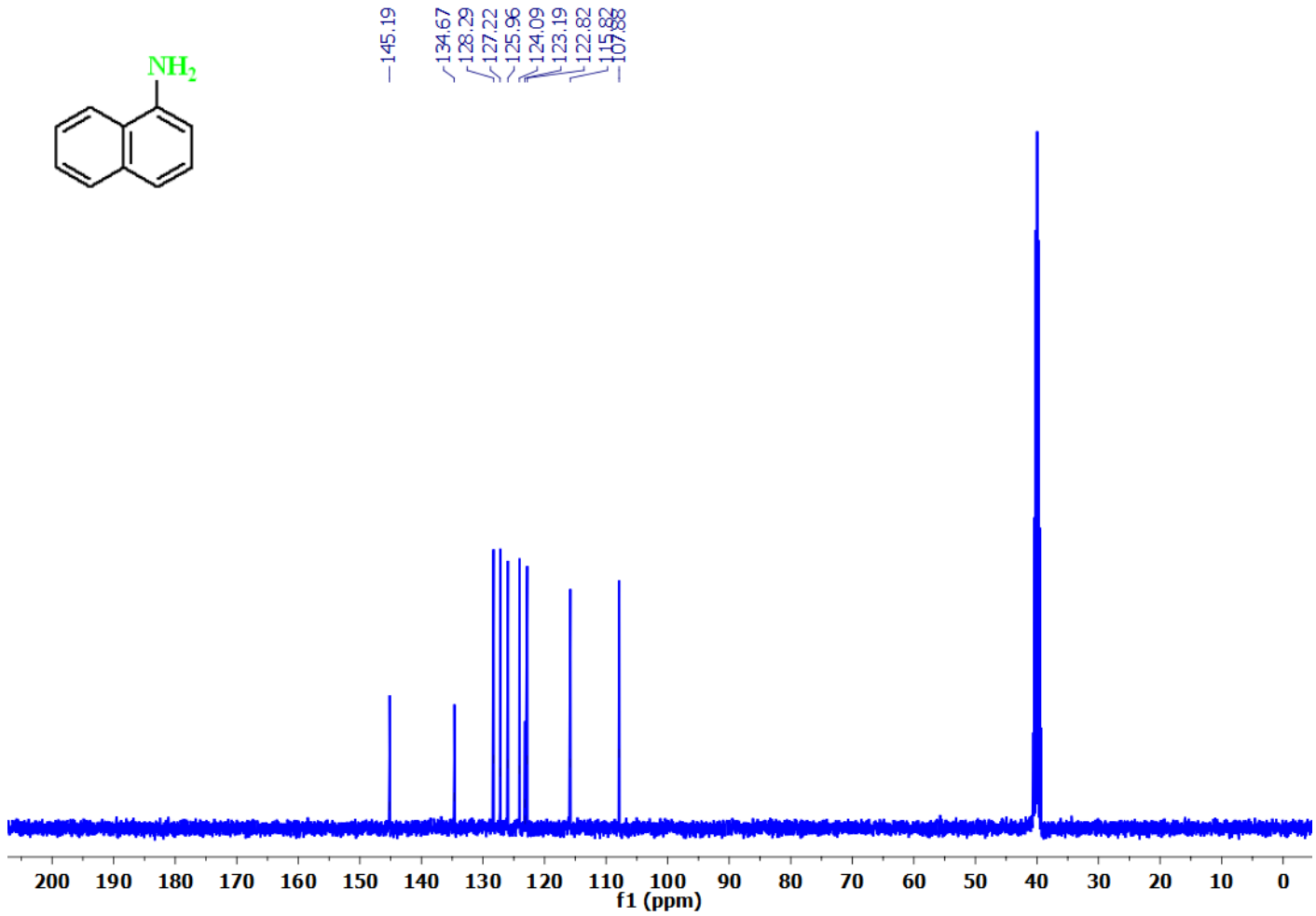
^{1}H NMR of 4-Aminobenzyl alcohol



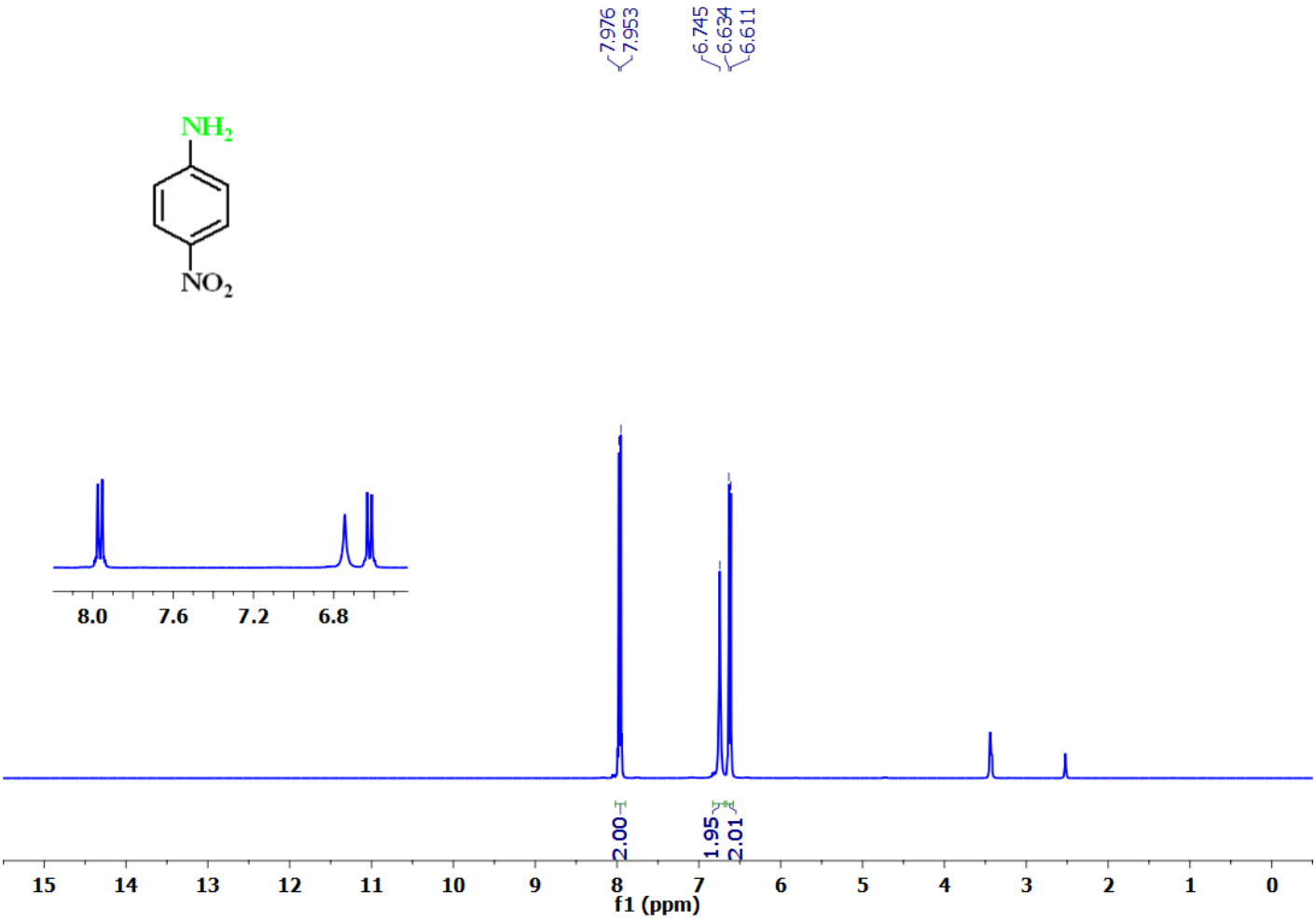
^{13}C NMR of 4-Aminobenzyl alcohol



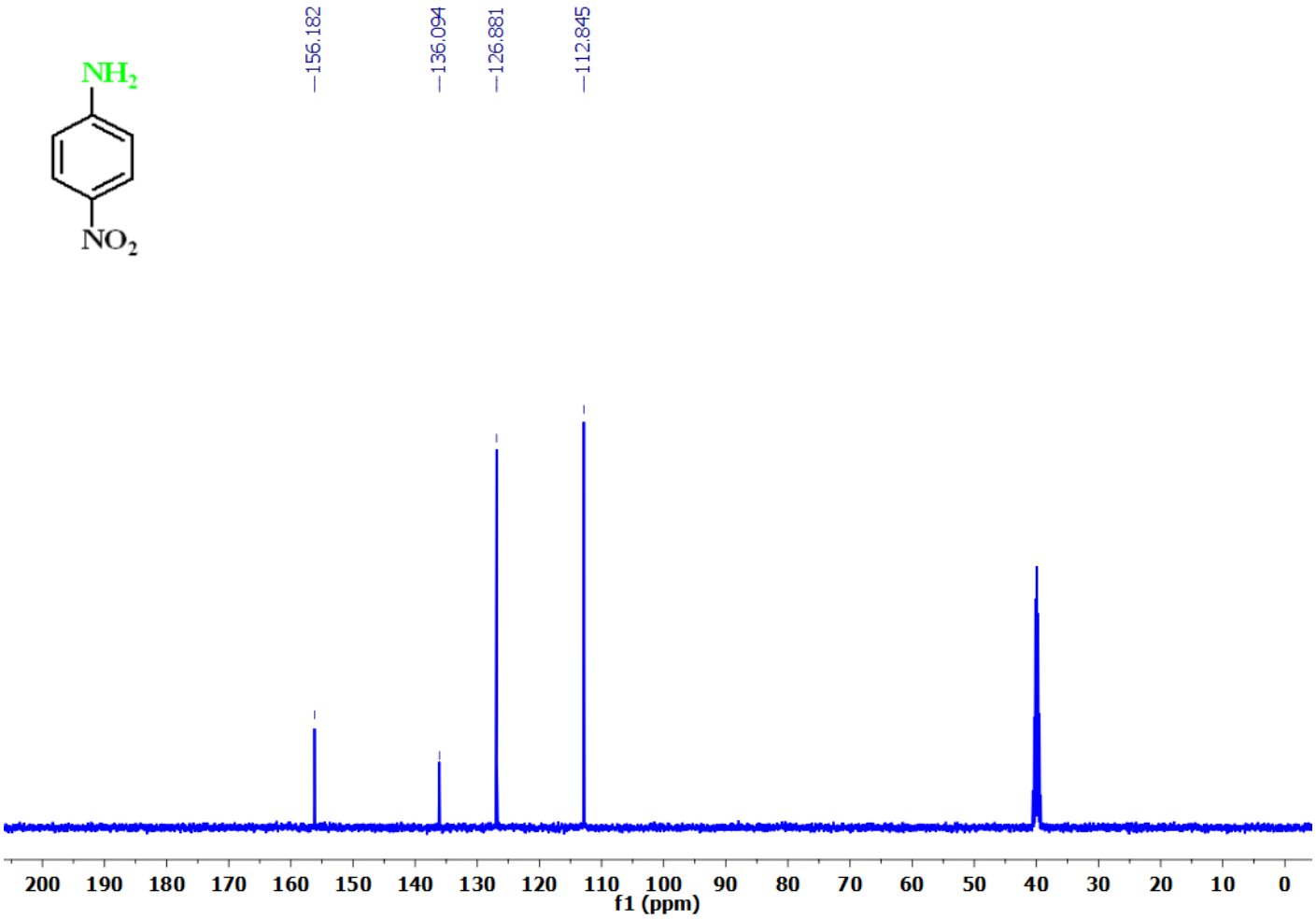
[1] H NMR of Naphthalen-1-amine



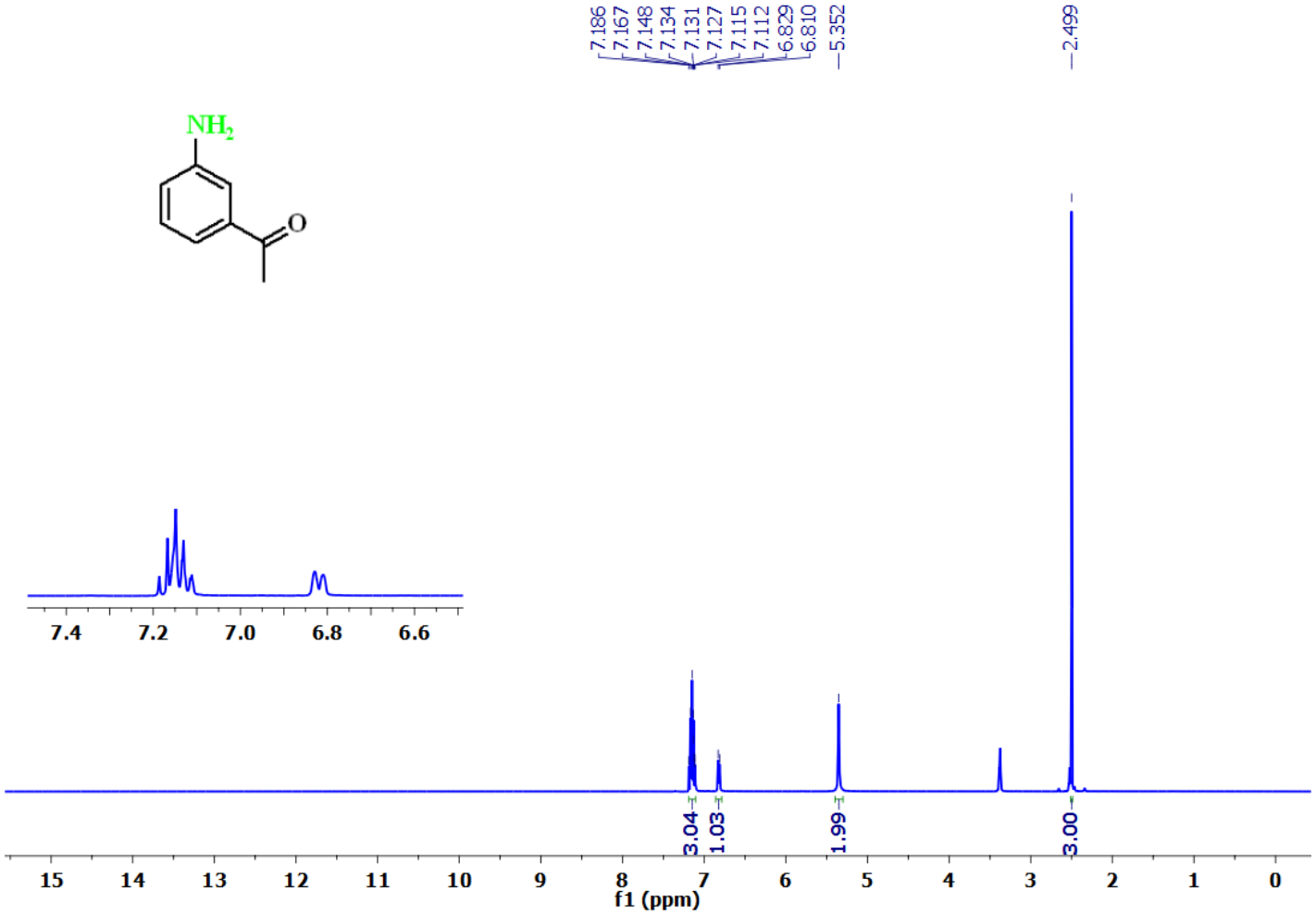
^{13}C NMR of Naphthalen-1-amine



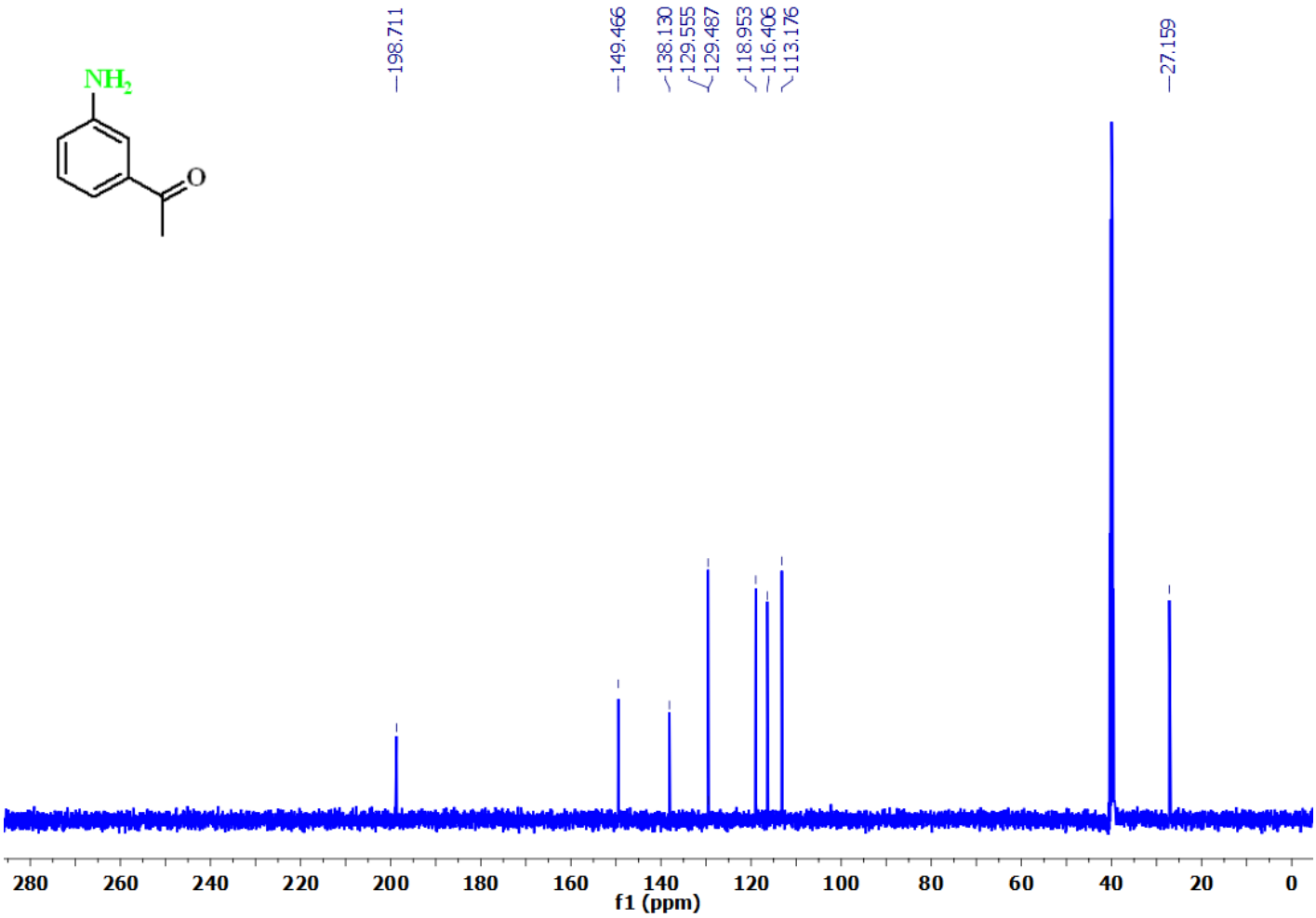
[1] H NMR of 4-Nitroaniline



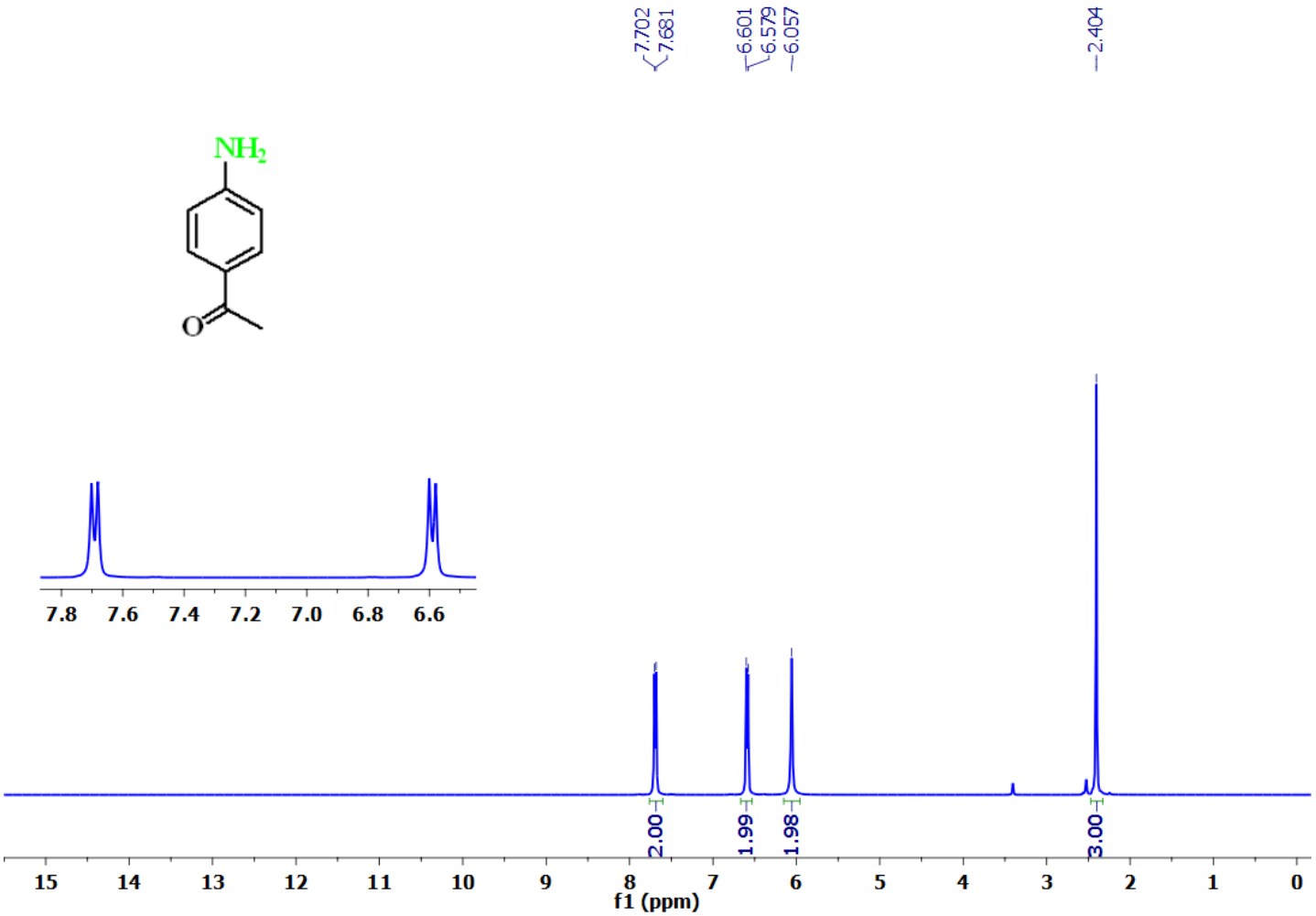
^{13}C NMR of 4-Nitroaniline



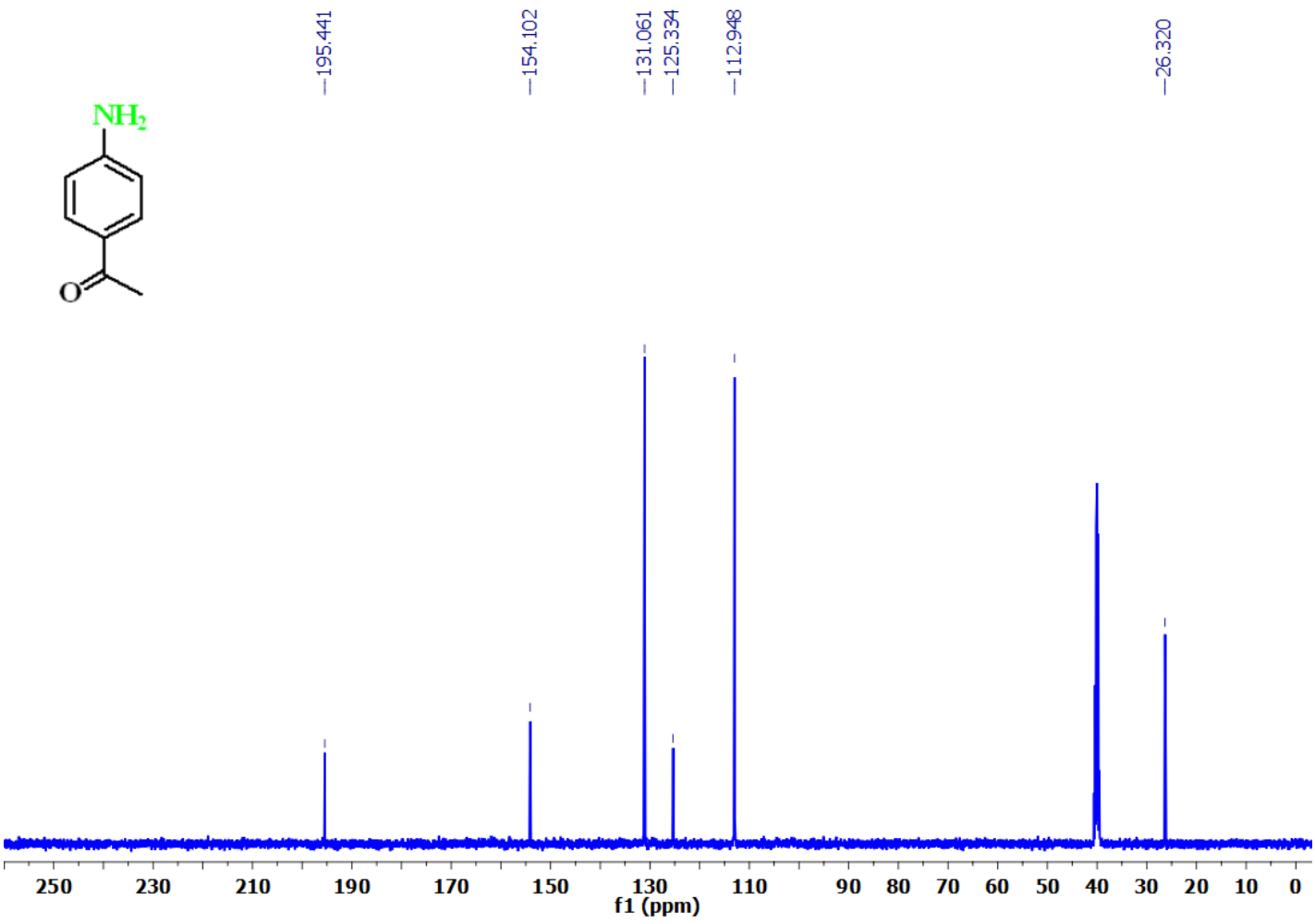
^{1}H NMR of 3-Aminoacetophenone



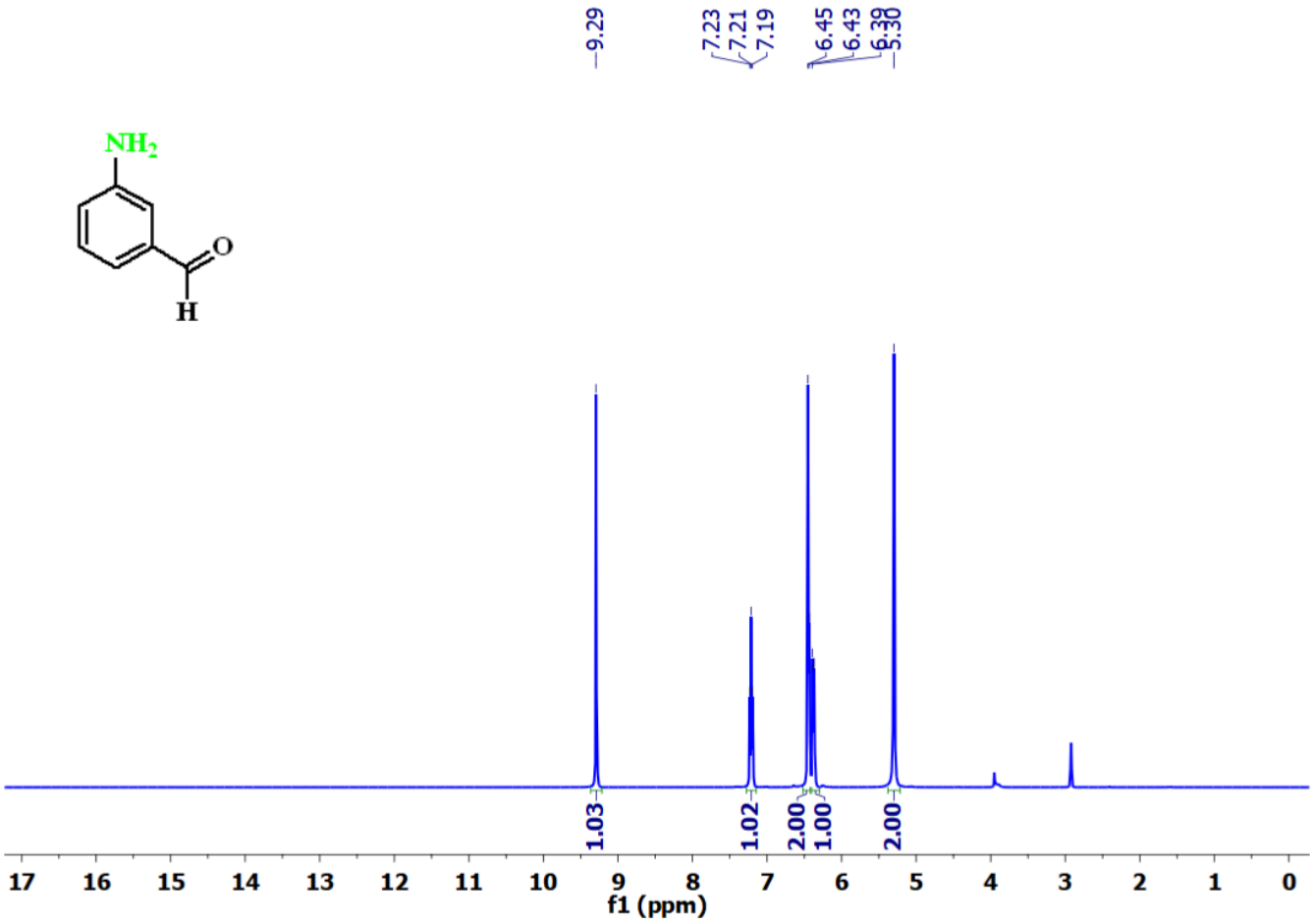
^{13}C NMR of 3-Aminoacetophenone



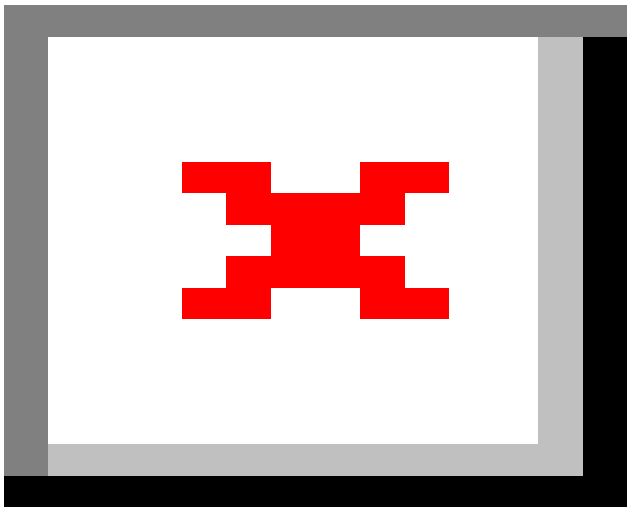
[1] H NMR of 4-Aminoacetophenone



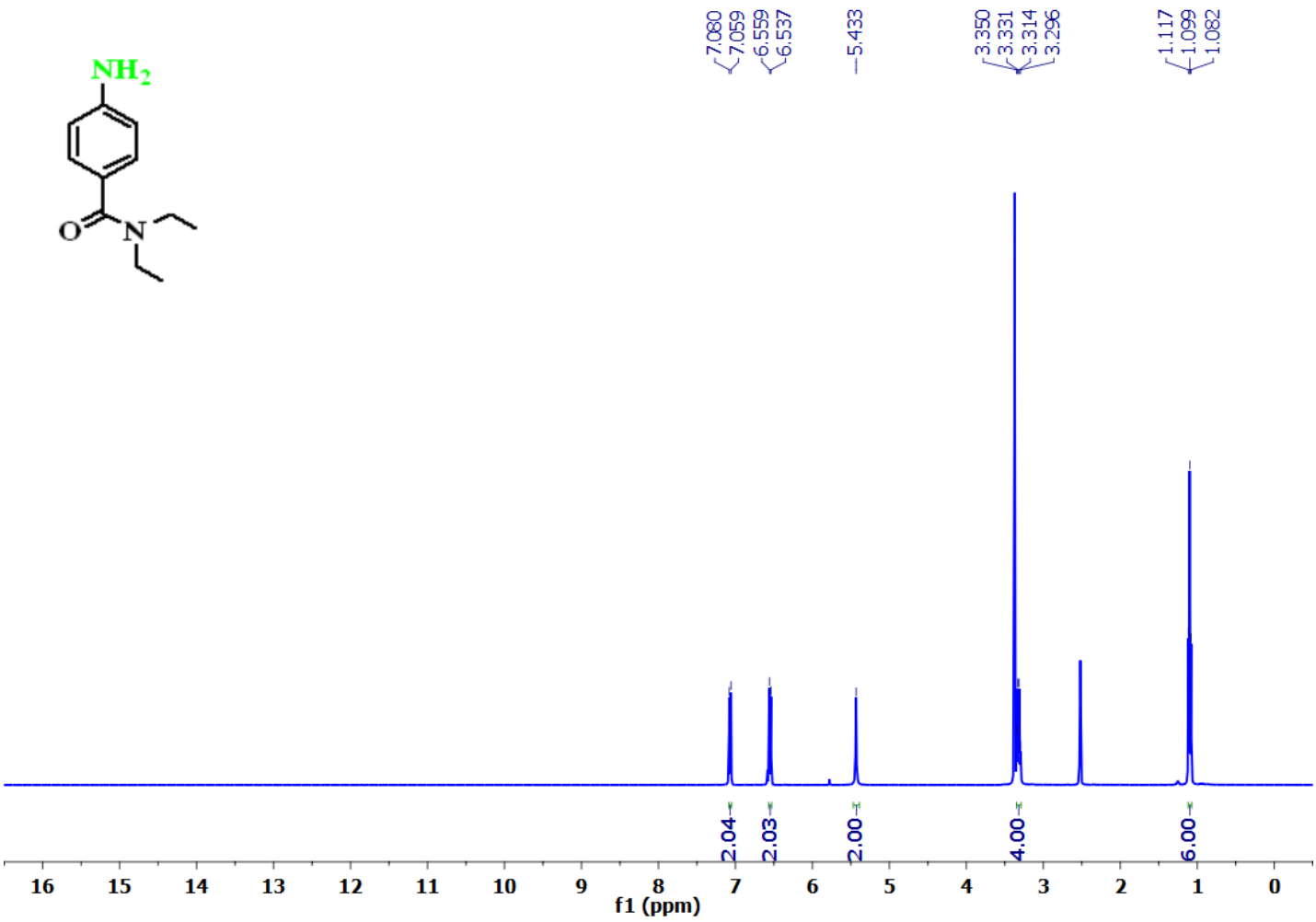
^{13}C NMR of 3-Aminoacetophenone



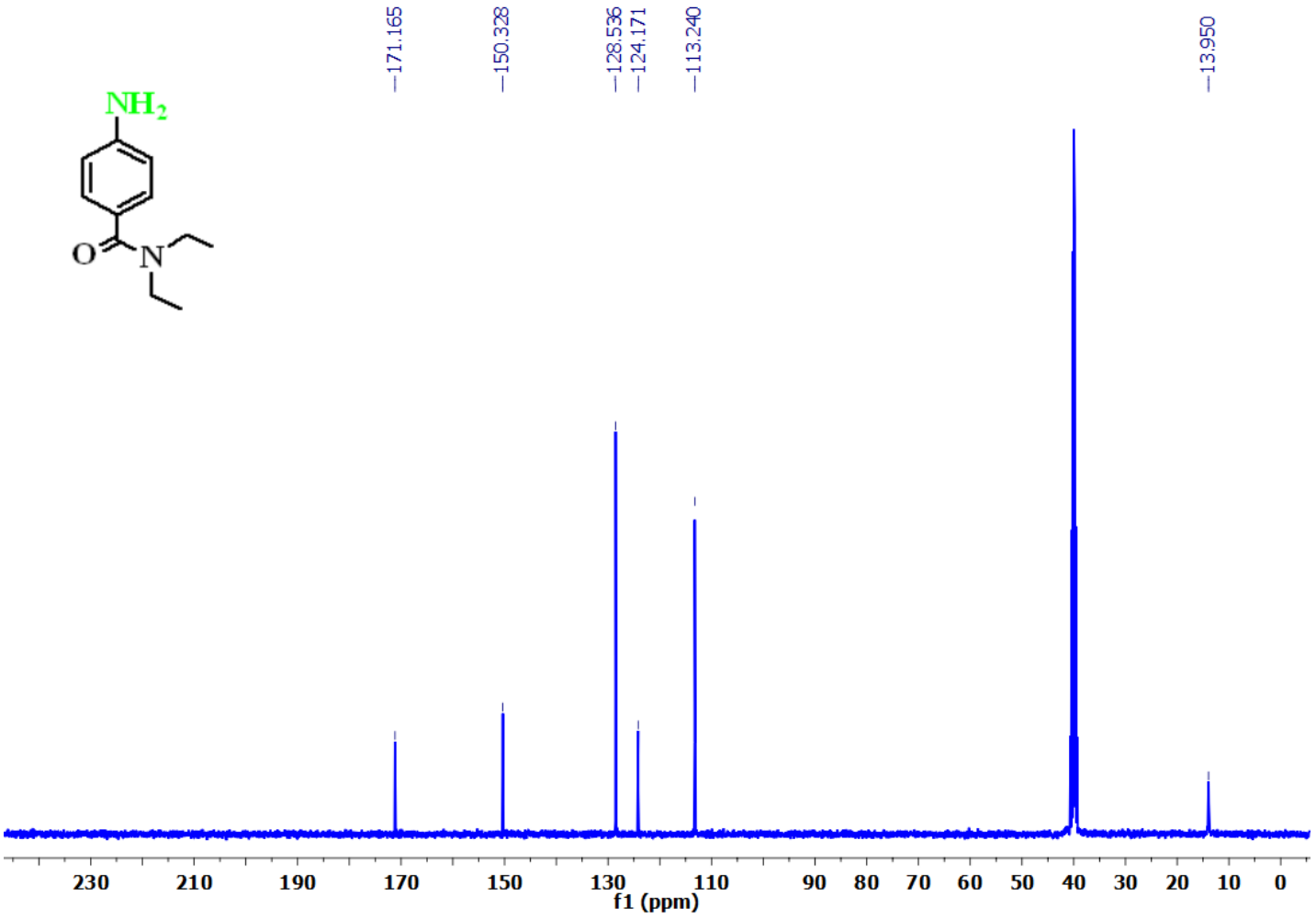
[1] H NMR of 3-Aminobenzaldehyde



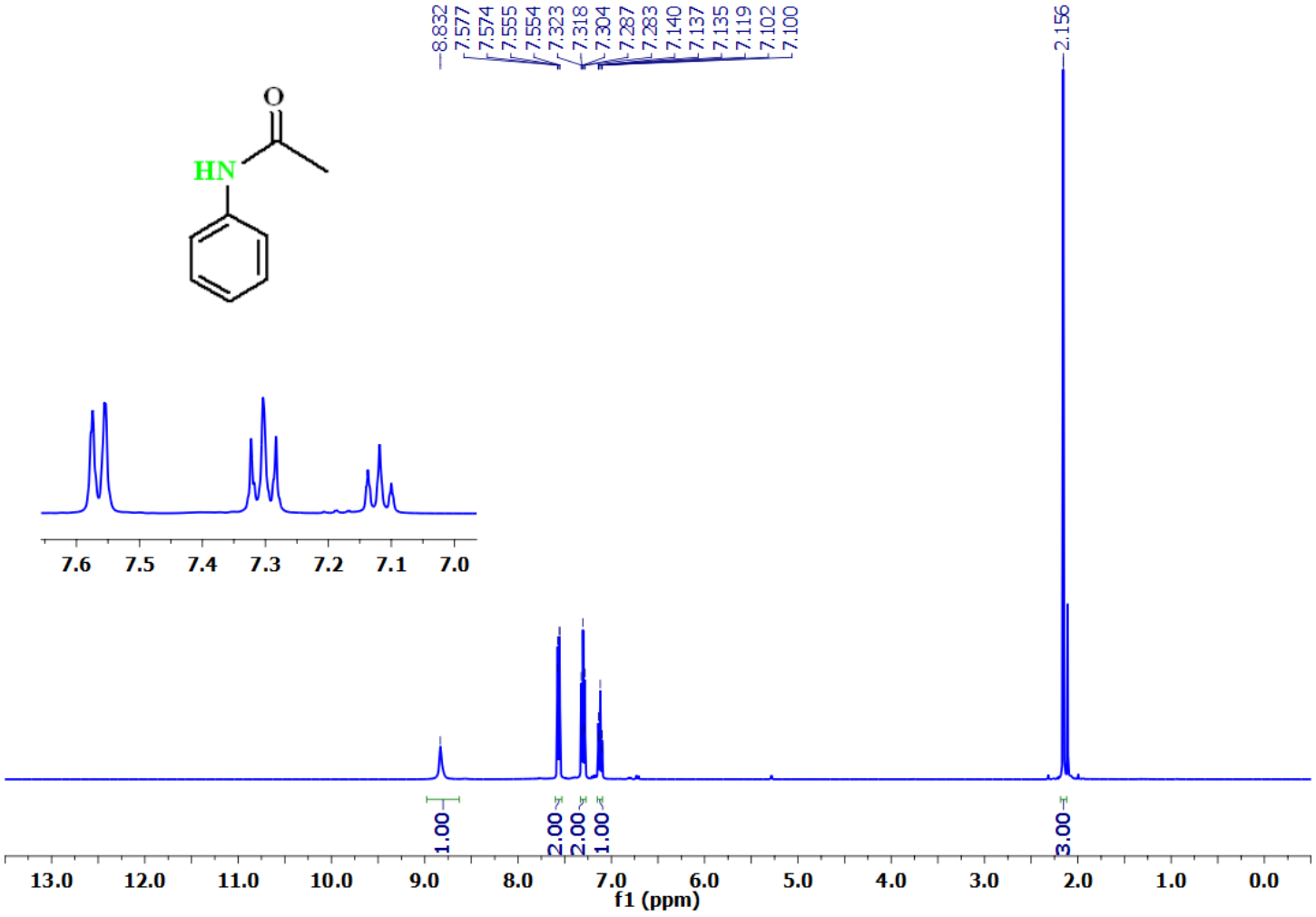
^{13}C NMR of 3-Aminobenzaldehyde



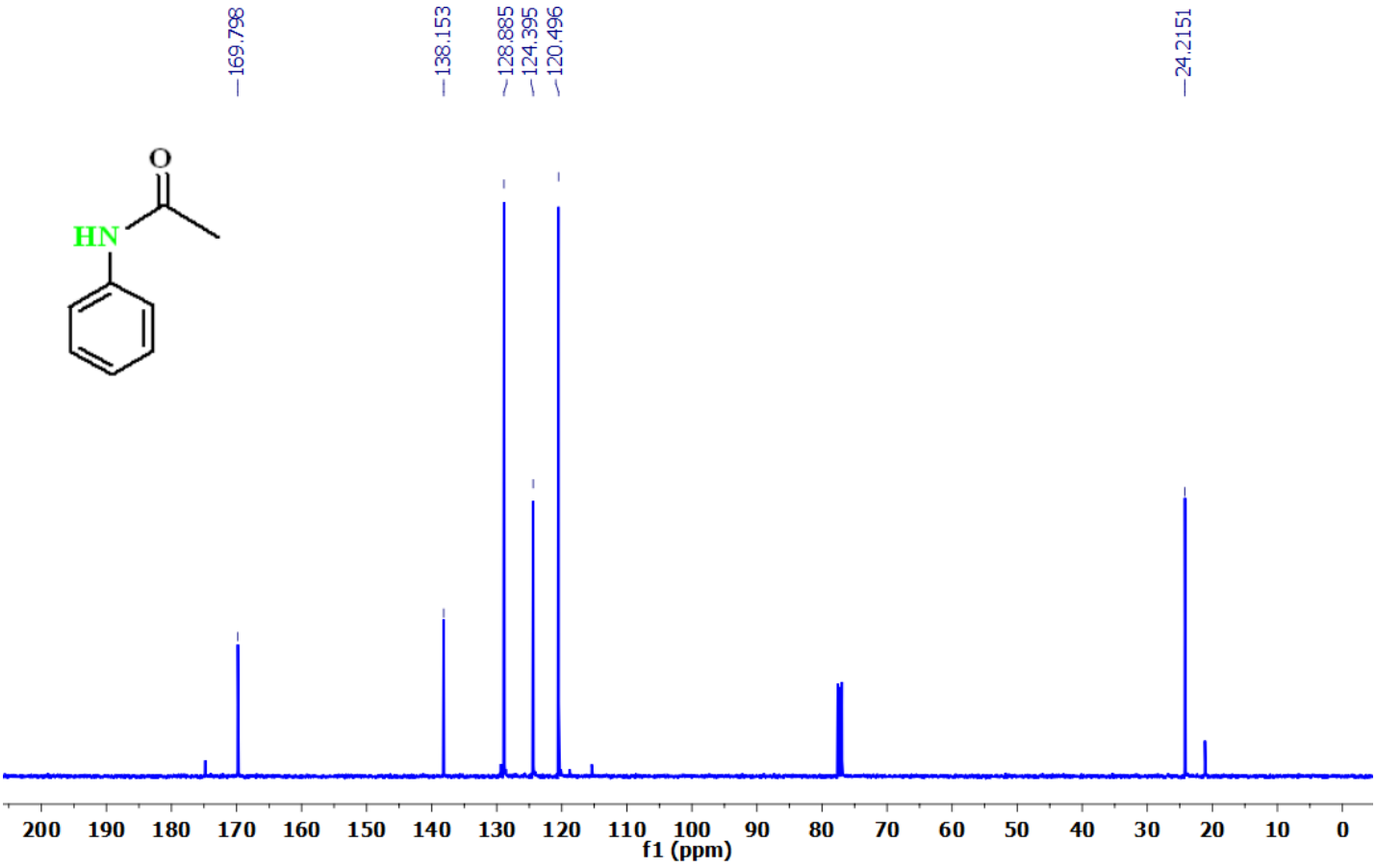
[1] H NMR of 4-Amino-*N*, *N*-diethylbenzamide



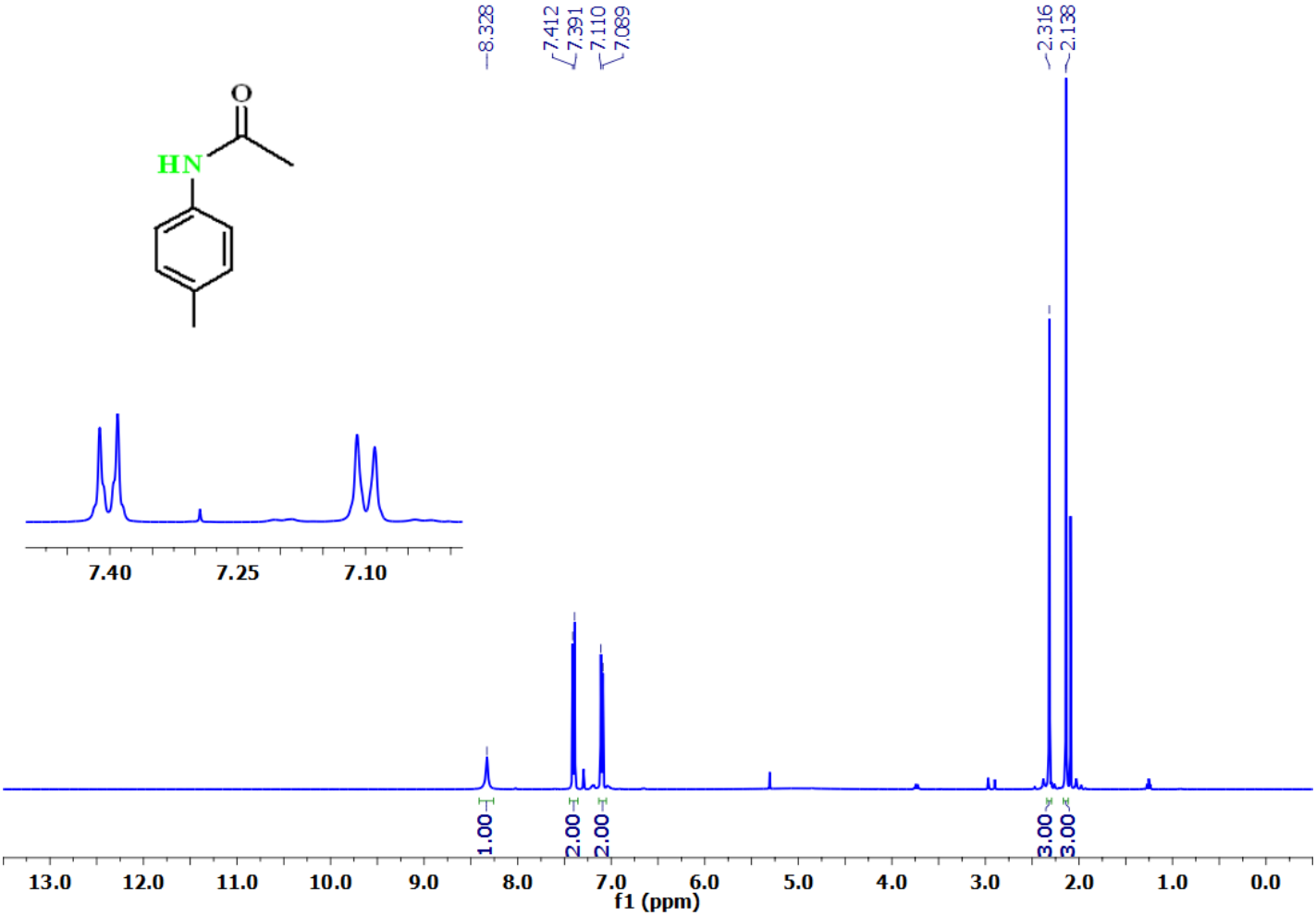
^{13}C NMR of 4-Amino-*N*, *N*-diethylbenzamide



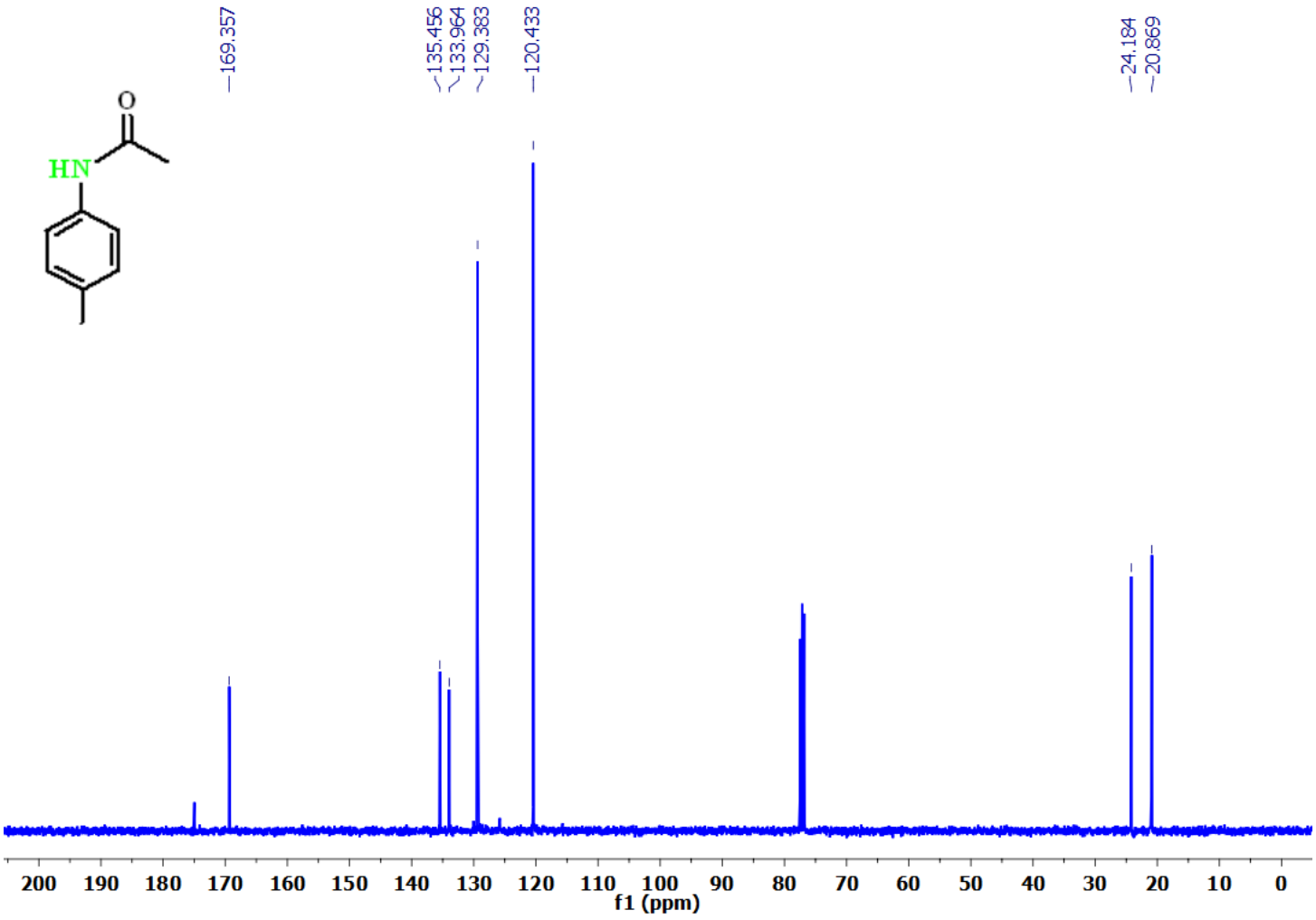
^{1}H NMR of *N*-phenylacetamide



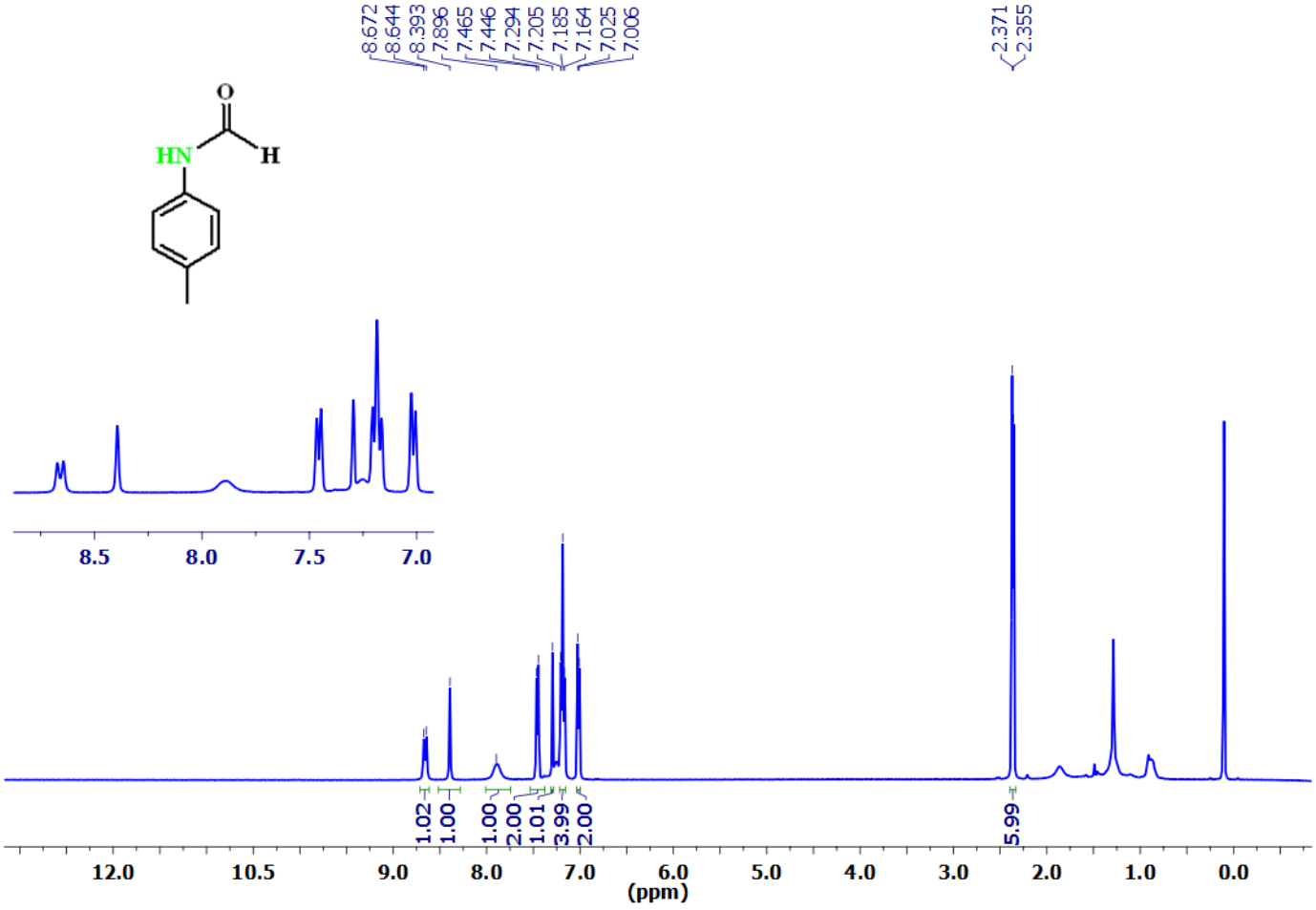
^{13}C NMR of *N*-phenylacetamide



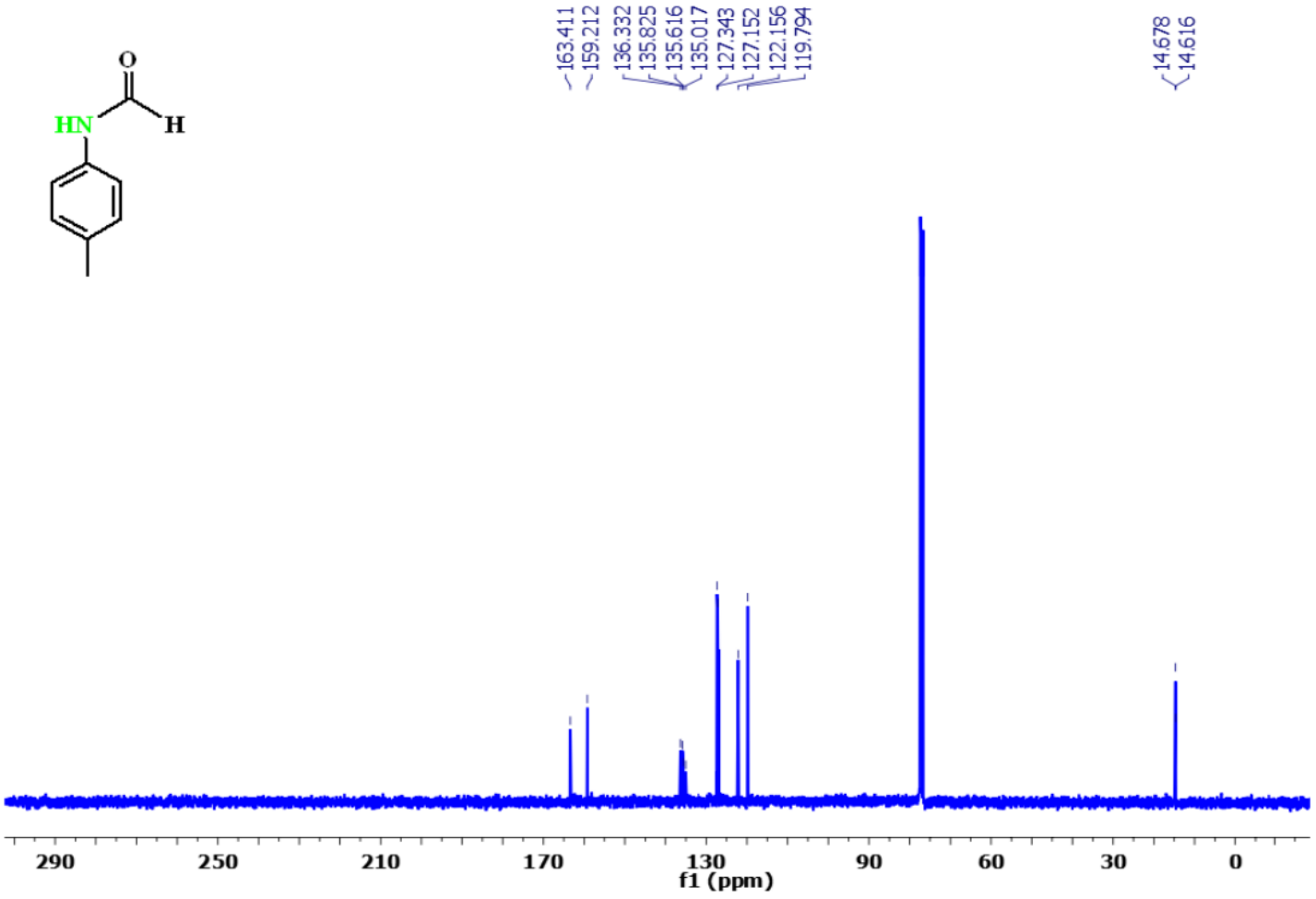
[1] H NMR of *N*-(p-tolyl) acetamide



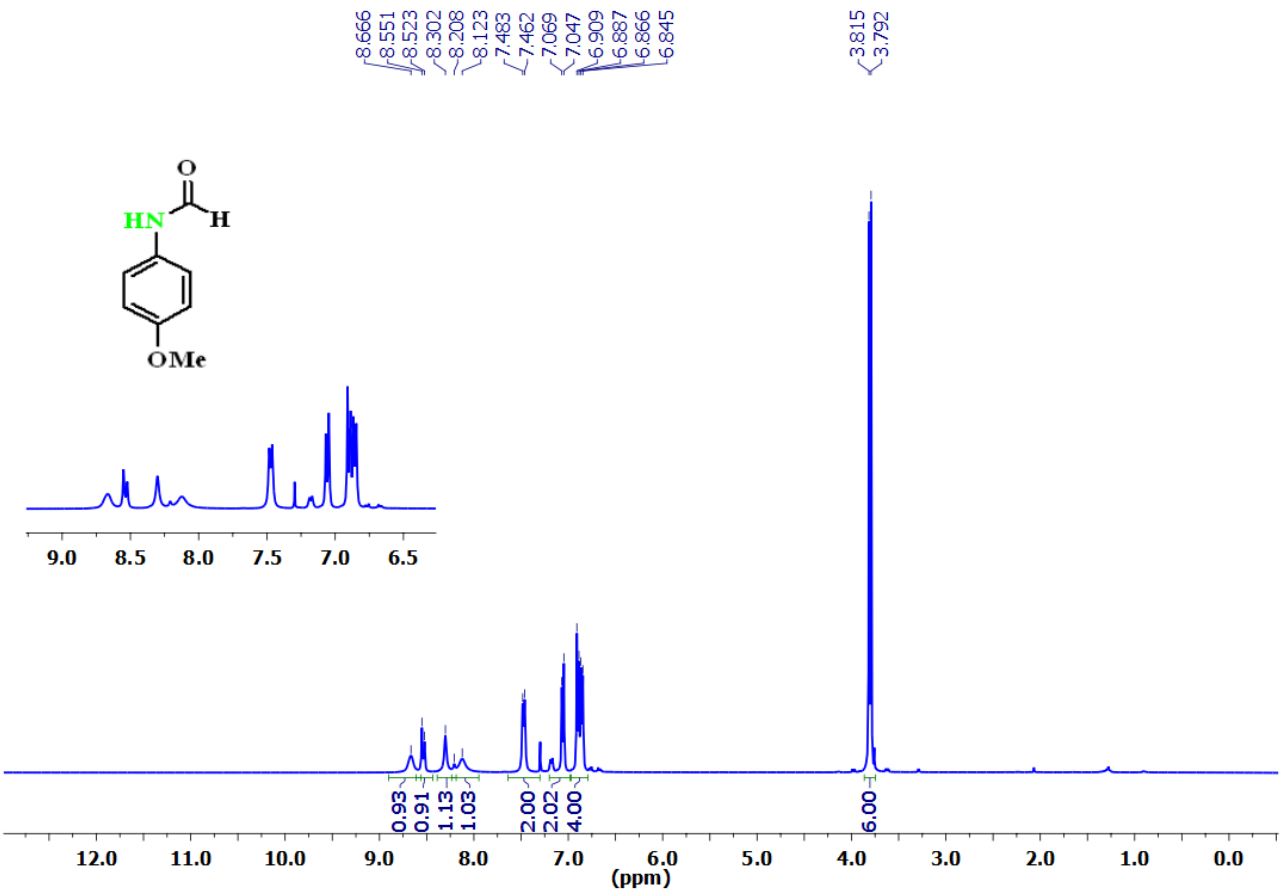
^{13}C NMR of *N*-(p-tolyl) acetamide



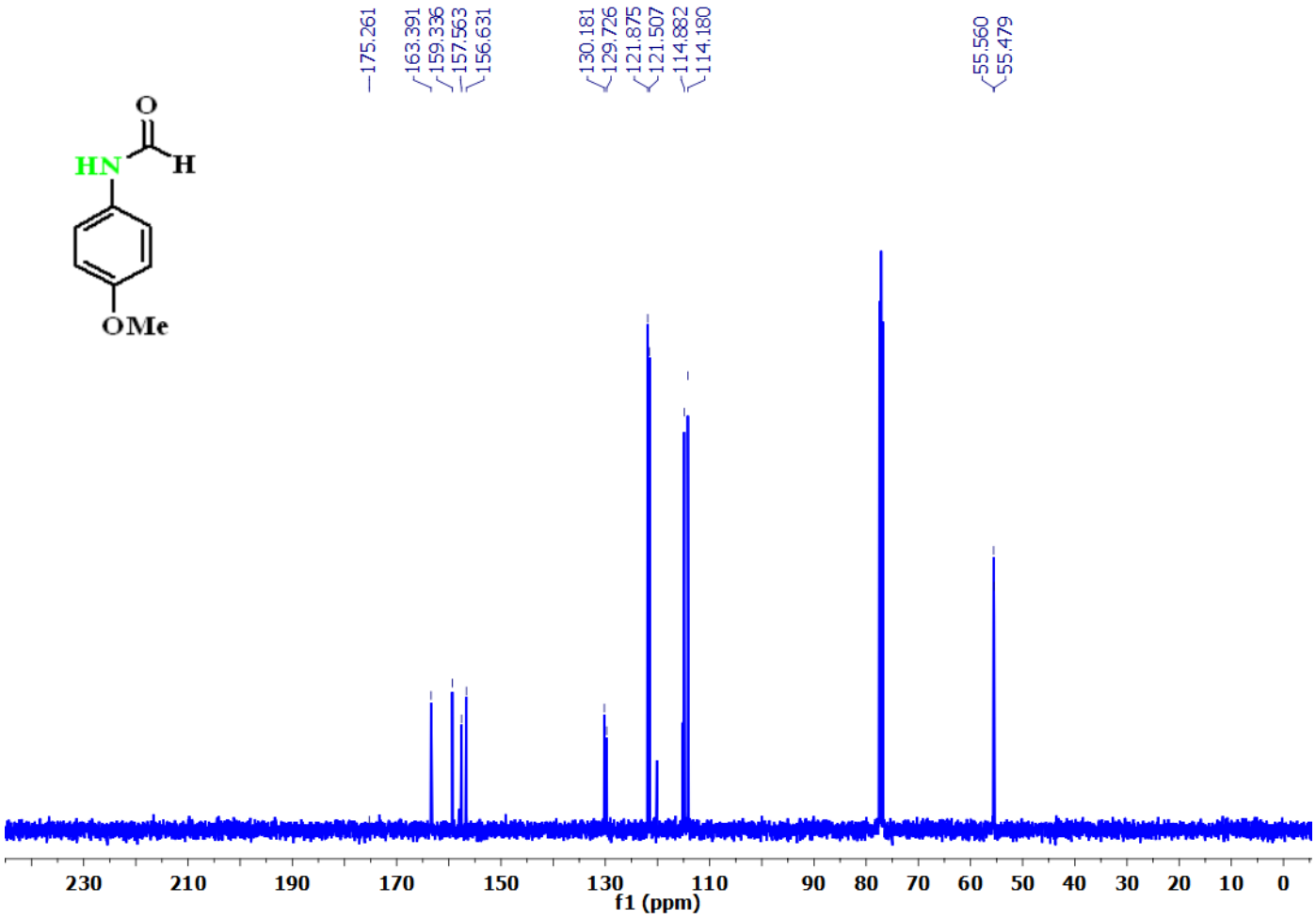
[1] H NMR of *N*-(p-tolyl) formamide



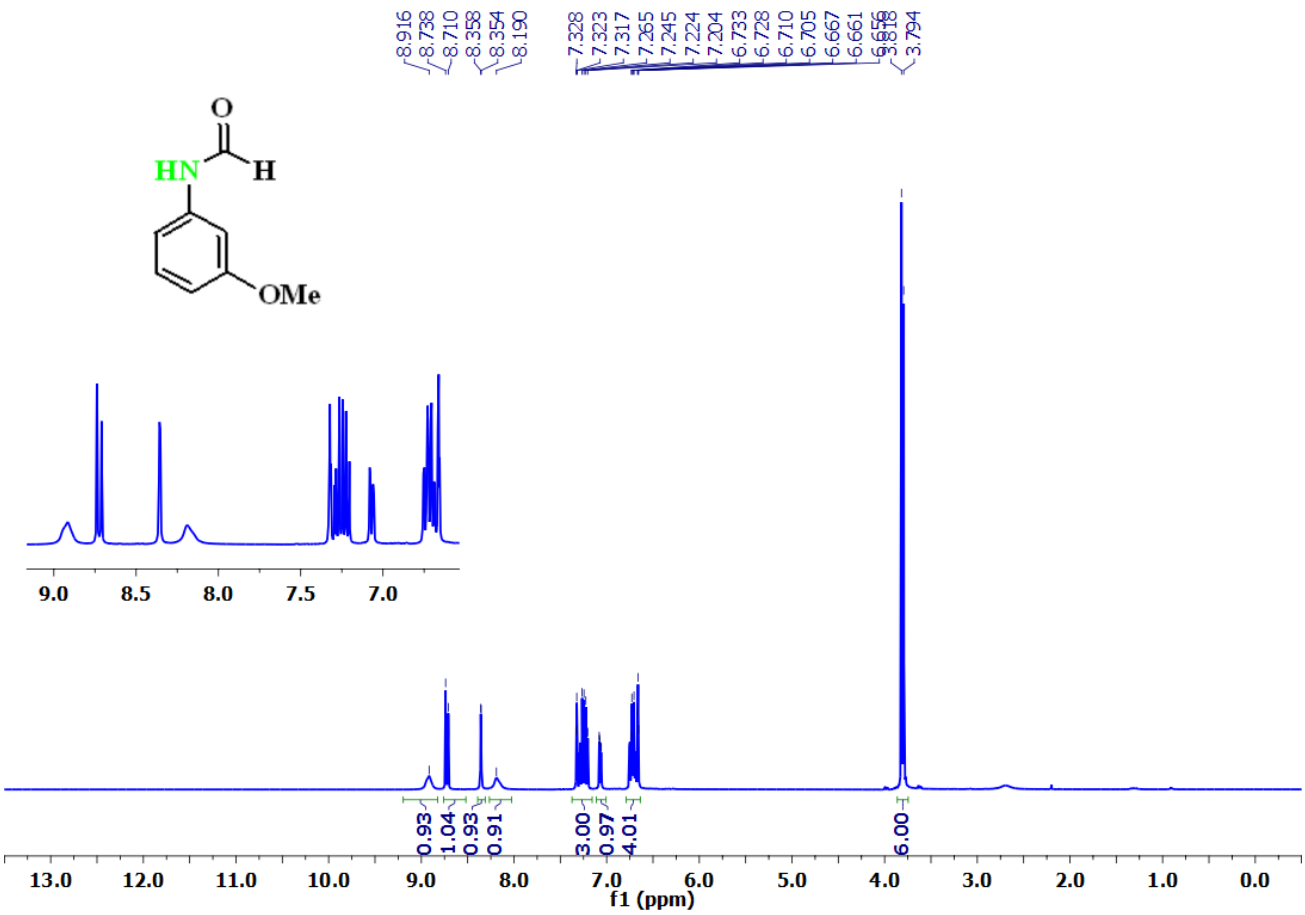
^{13}C NMR of *N*-(p-tolyl) formamide



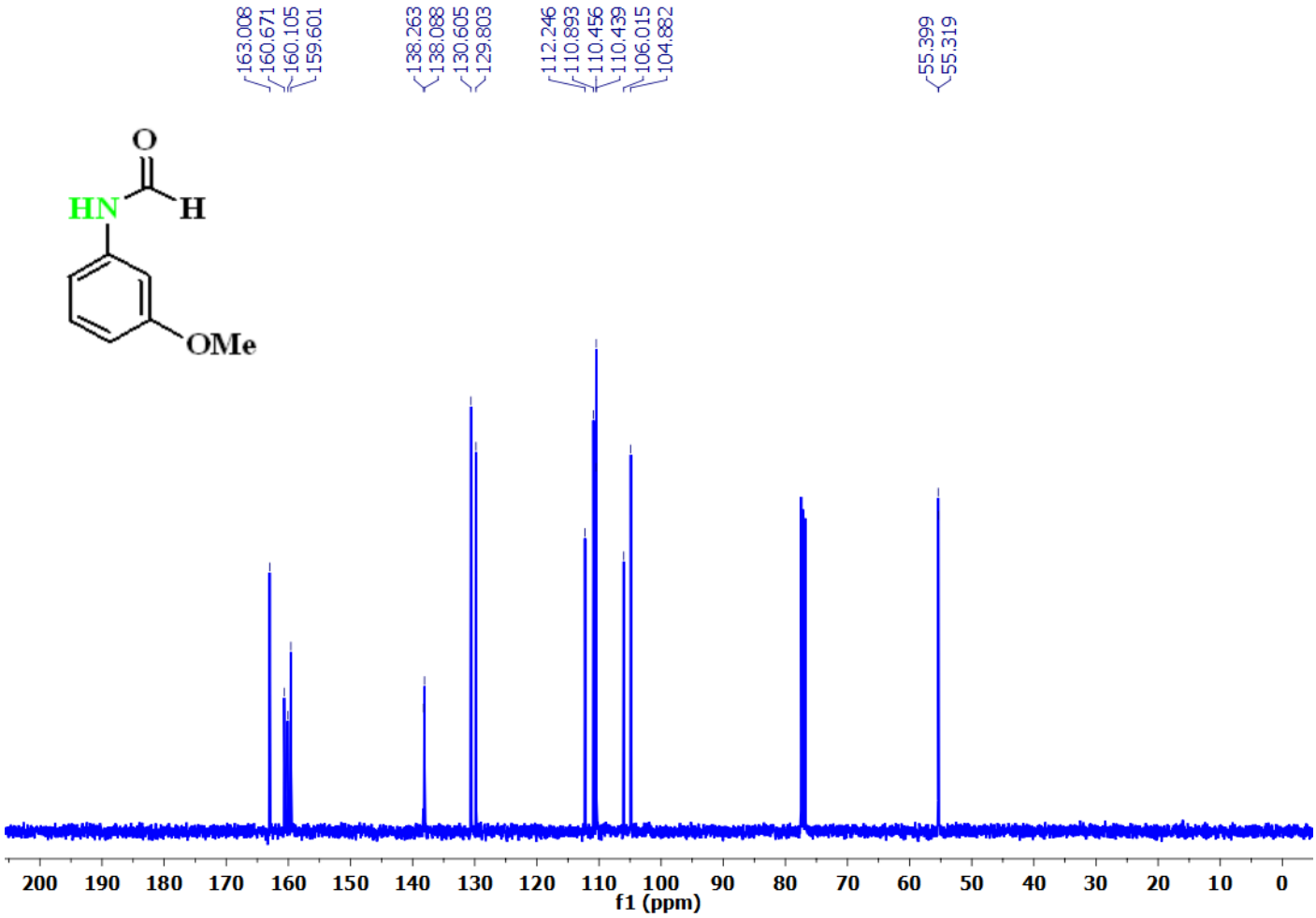
[1] H NMR of *N*-(4-methoxyphenyl) formamide



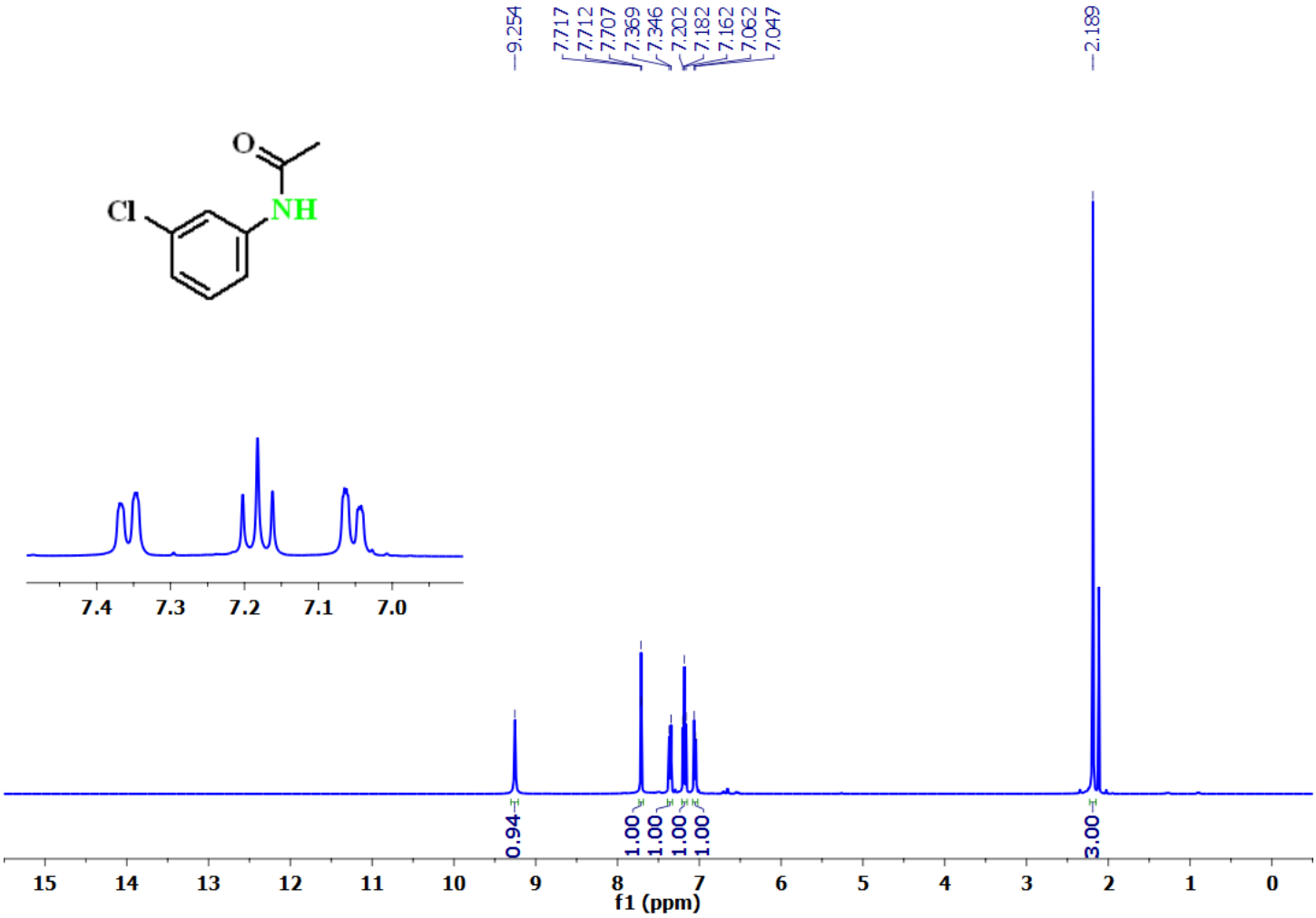
^{13}C NMR of *N*-(4-methoxyphenyl) formamide



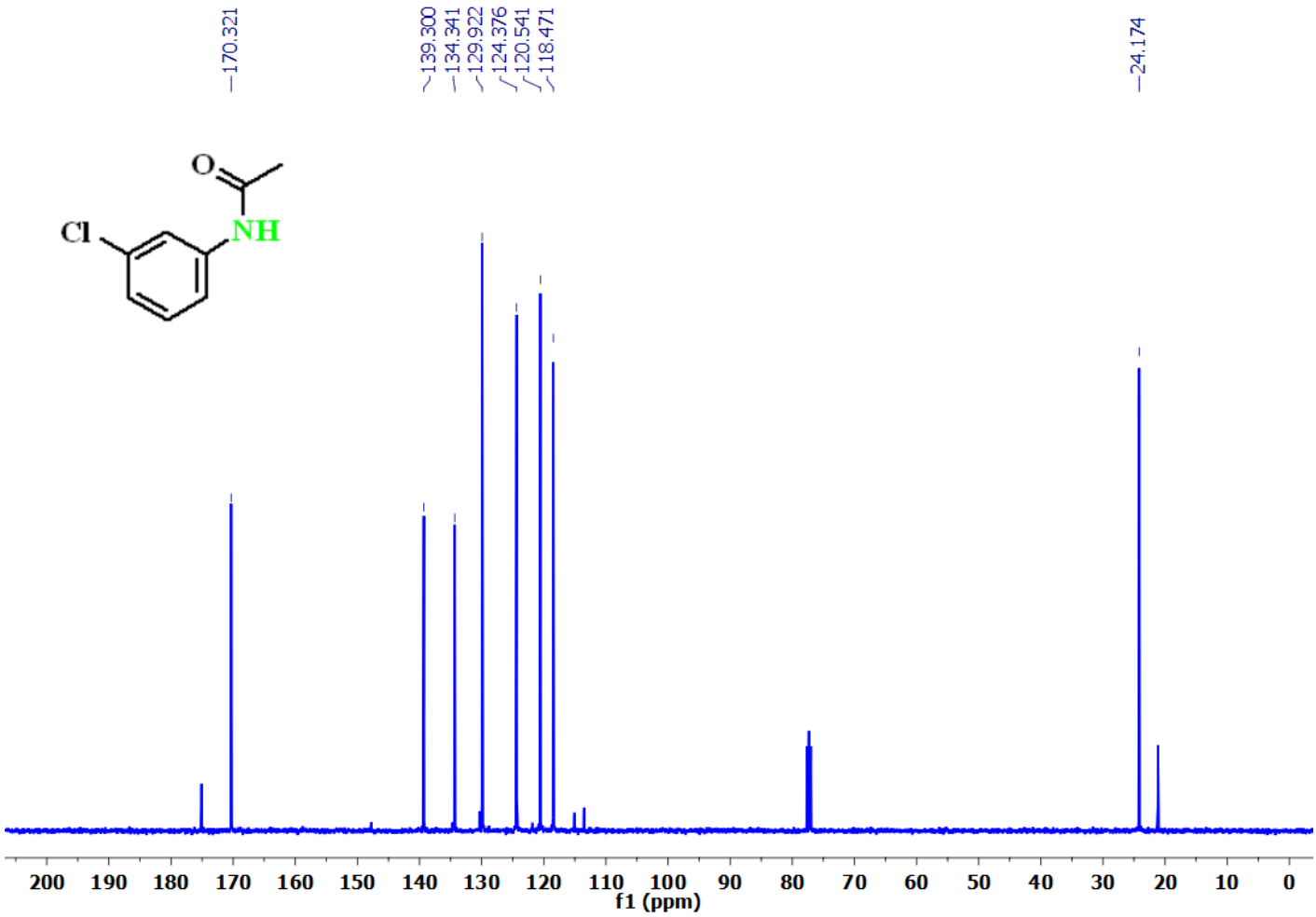
[1] H NMR of *N*-(3-methoxyphenyl) formamide



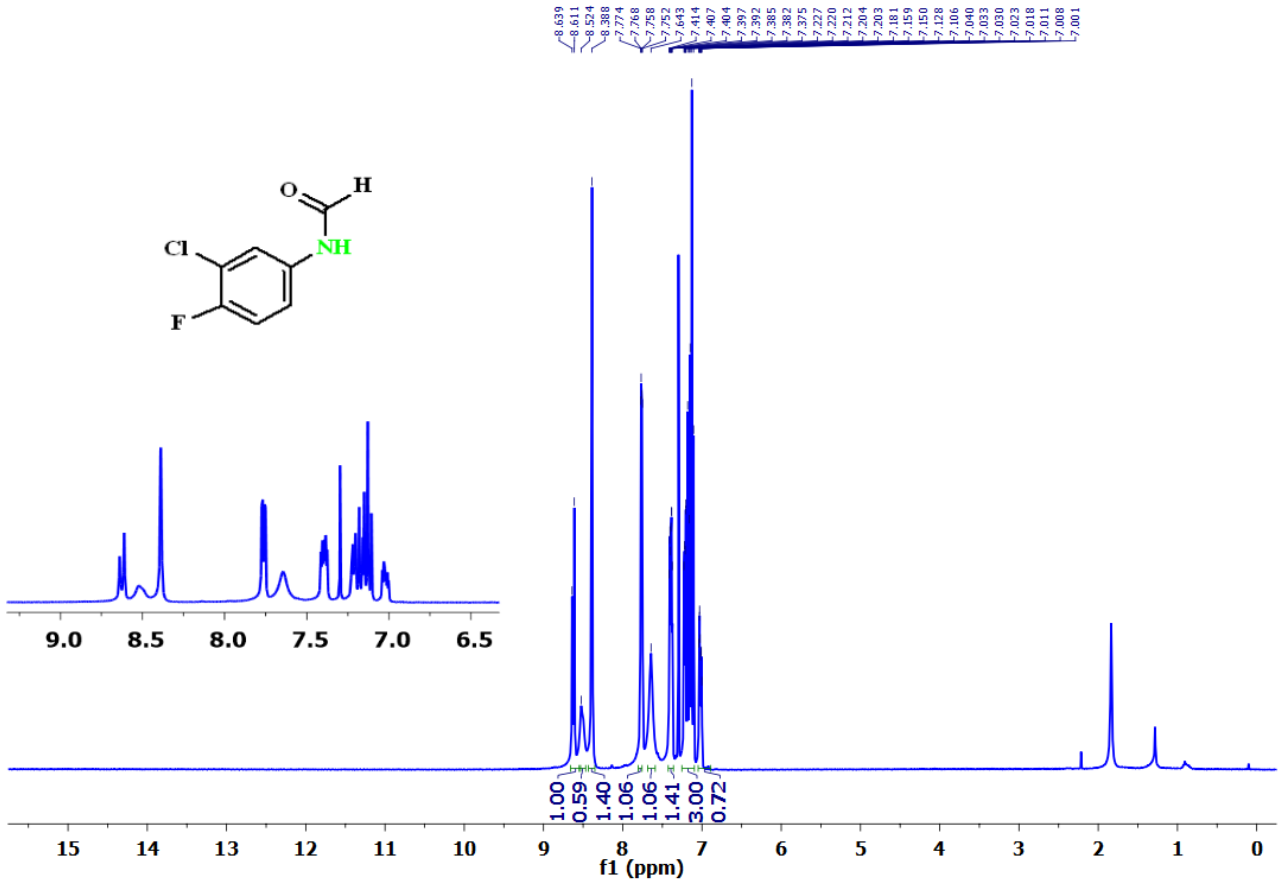
^{13}C NMR of *N*-(3-methoxyphenyl) formamide



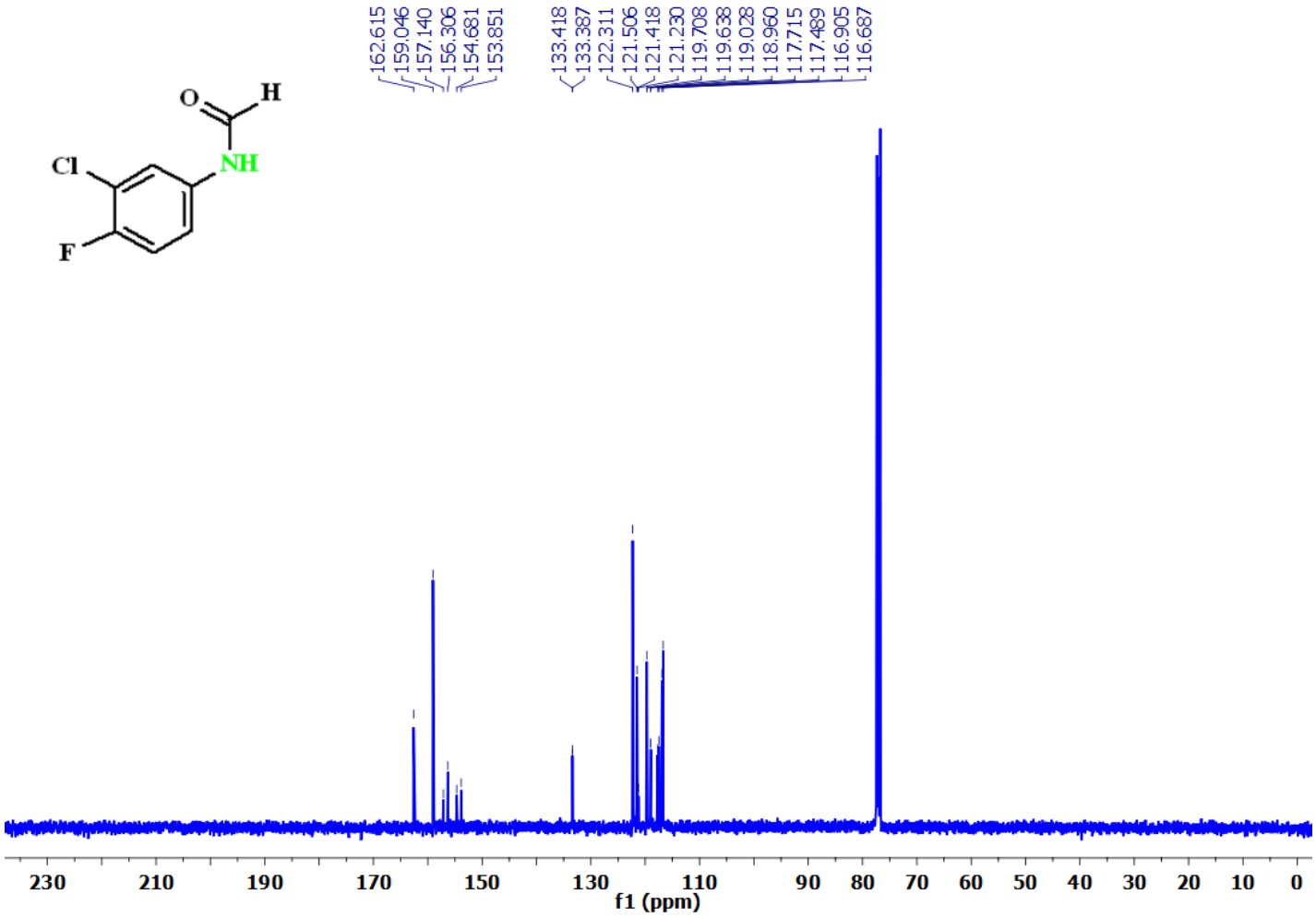
[1] H NMR of *N*-(3-chlorophenyl) acetamide



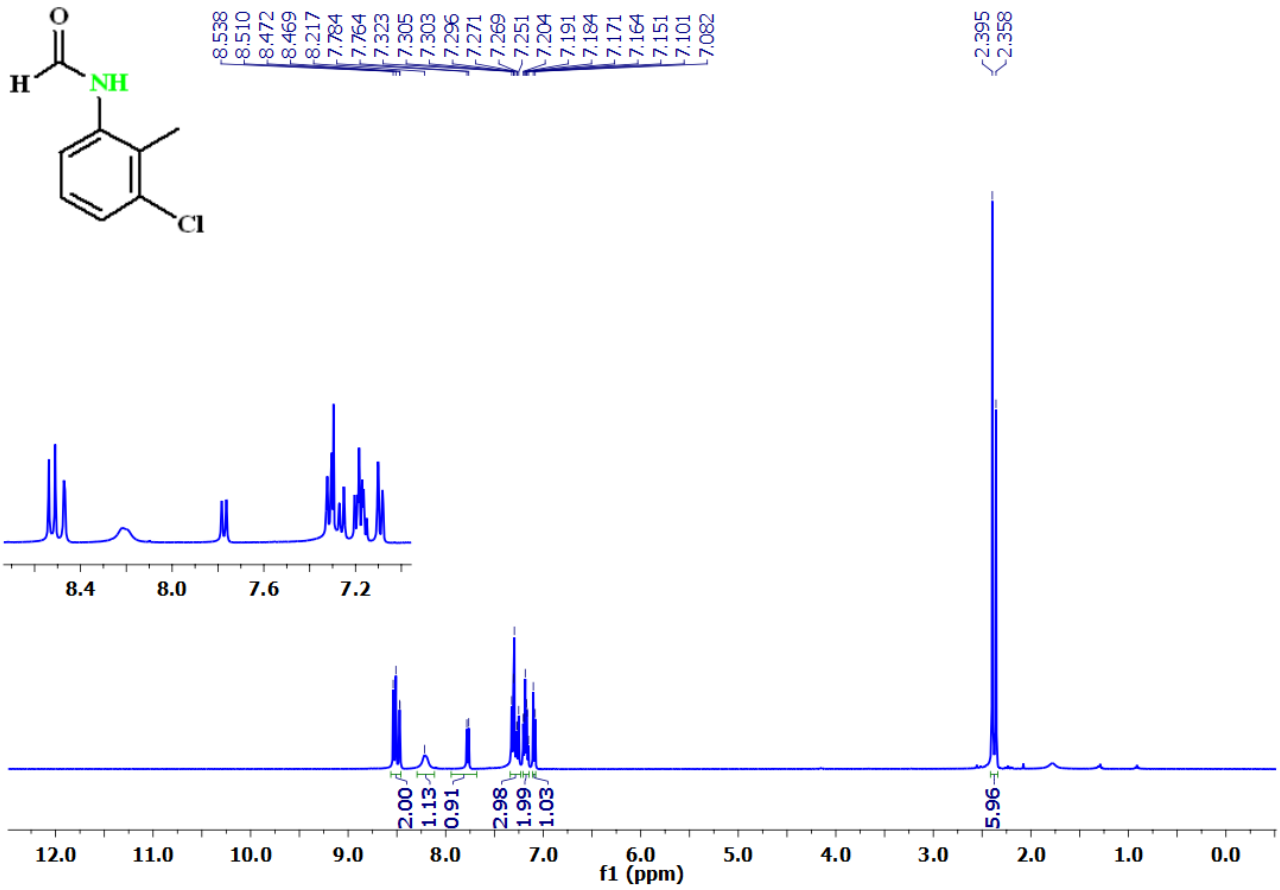
^{13}C NMR of *N*-(3-chlorophenyl) acetamide



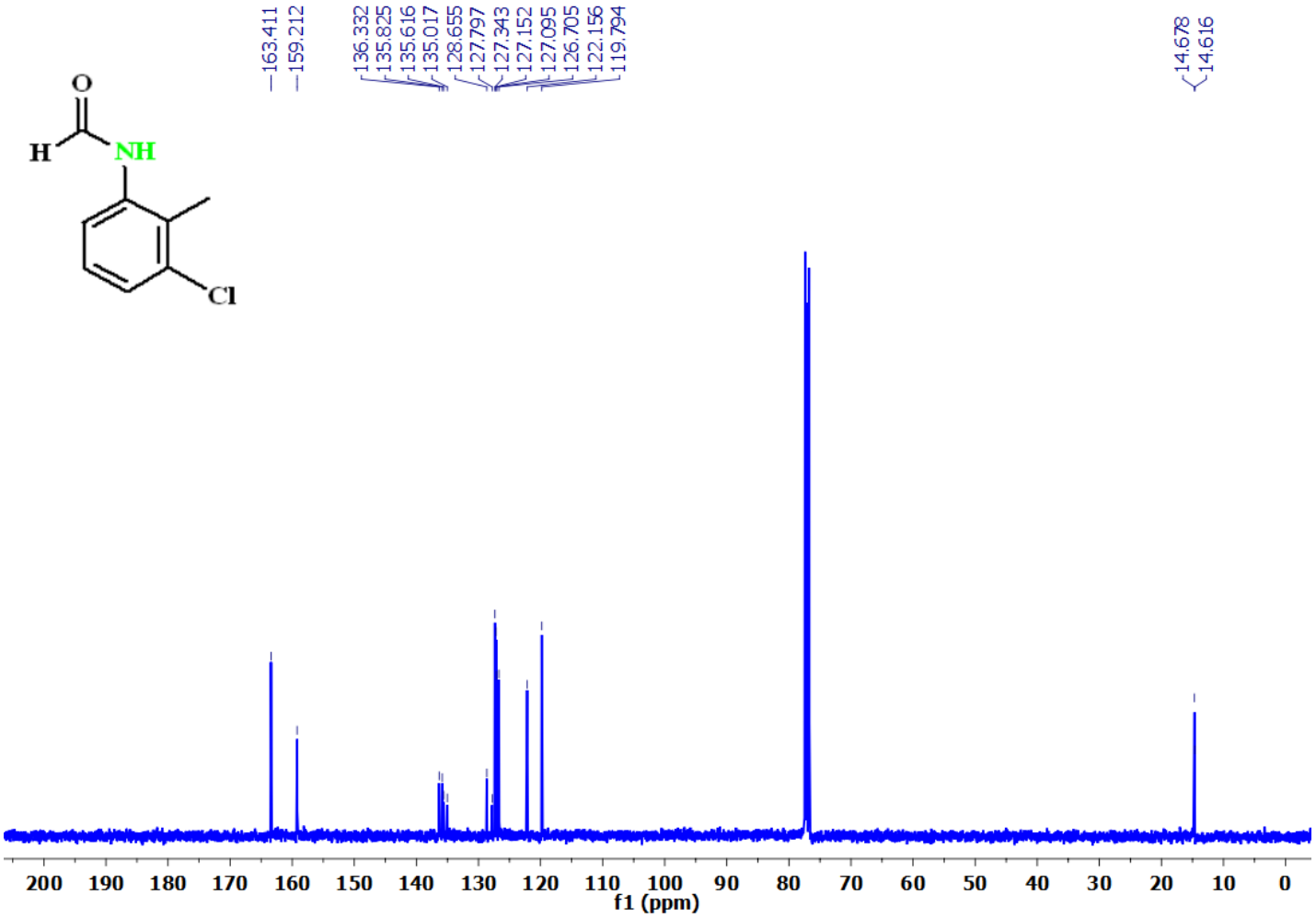
[1] H NMR of *N*-(3-chloro-4-fluorophenyl) formamide



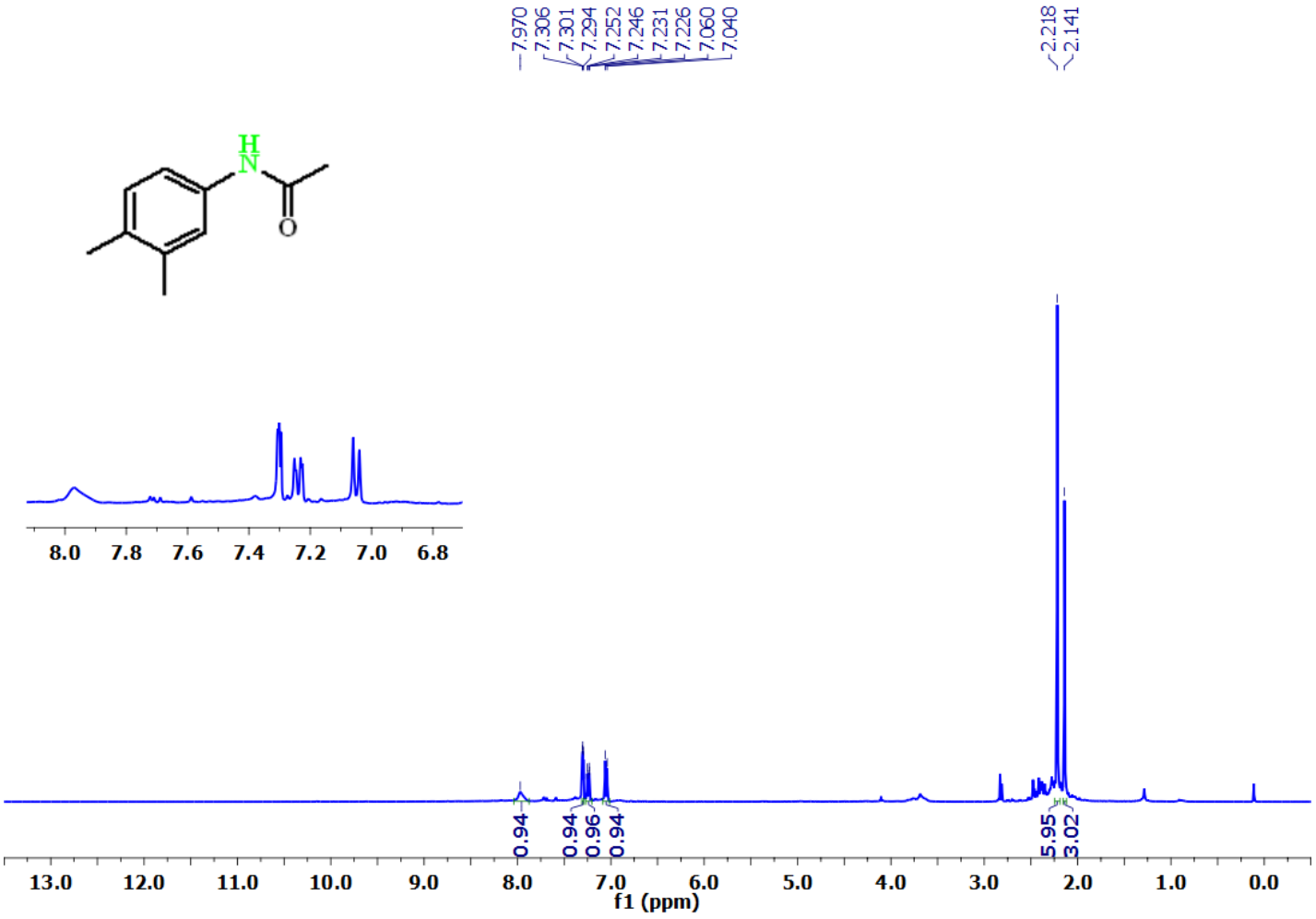
^{13}C NMR of *N*-(3-chloro-4-fluorophenyl) formamide



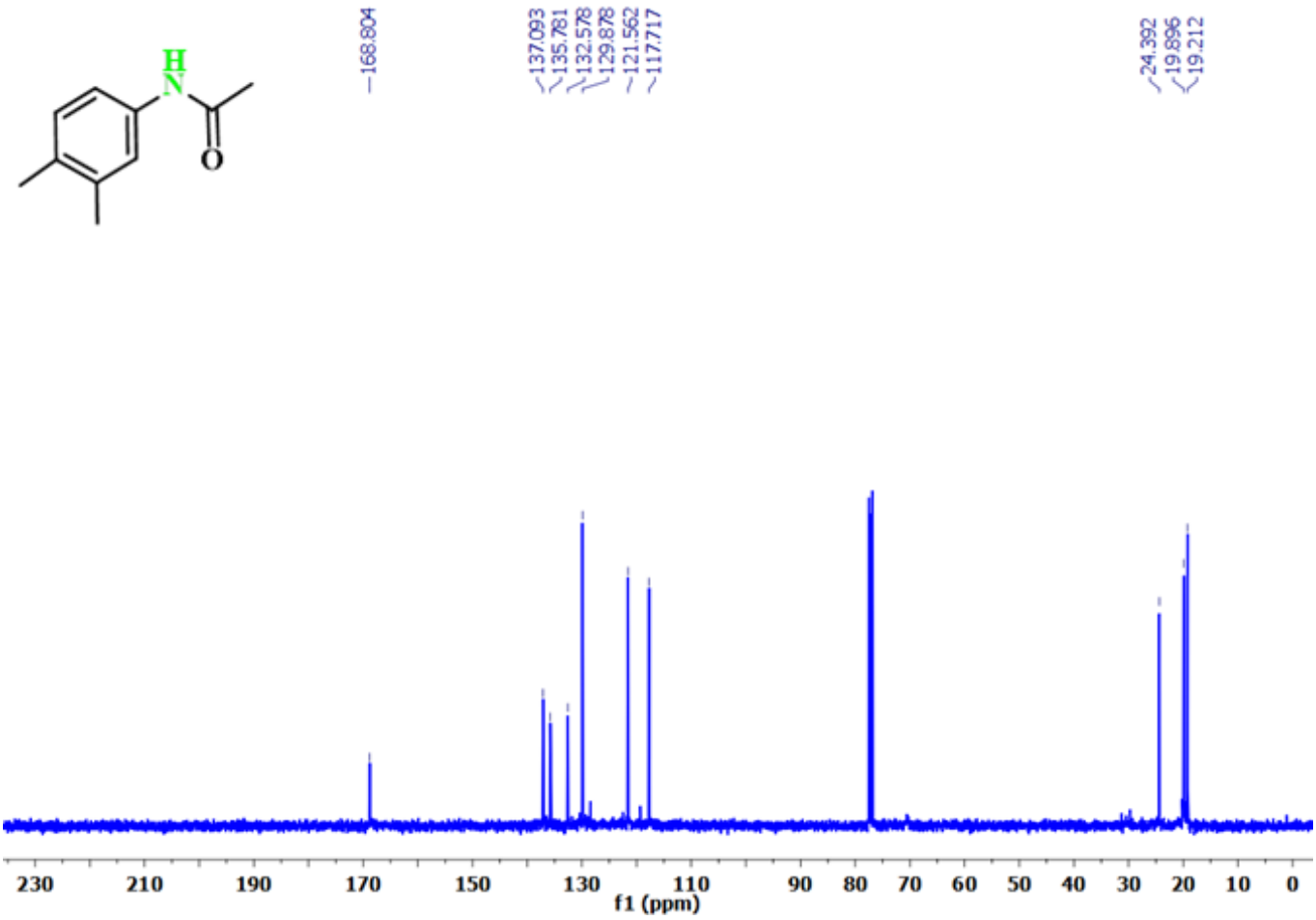
[1] H NMR of *N*-(3-chloro-2-methylphenyl) formamide



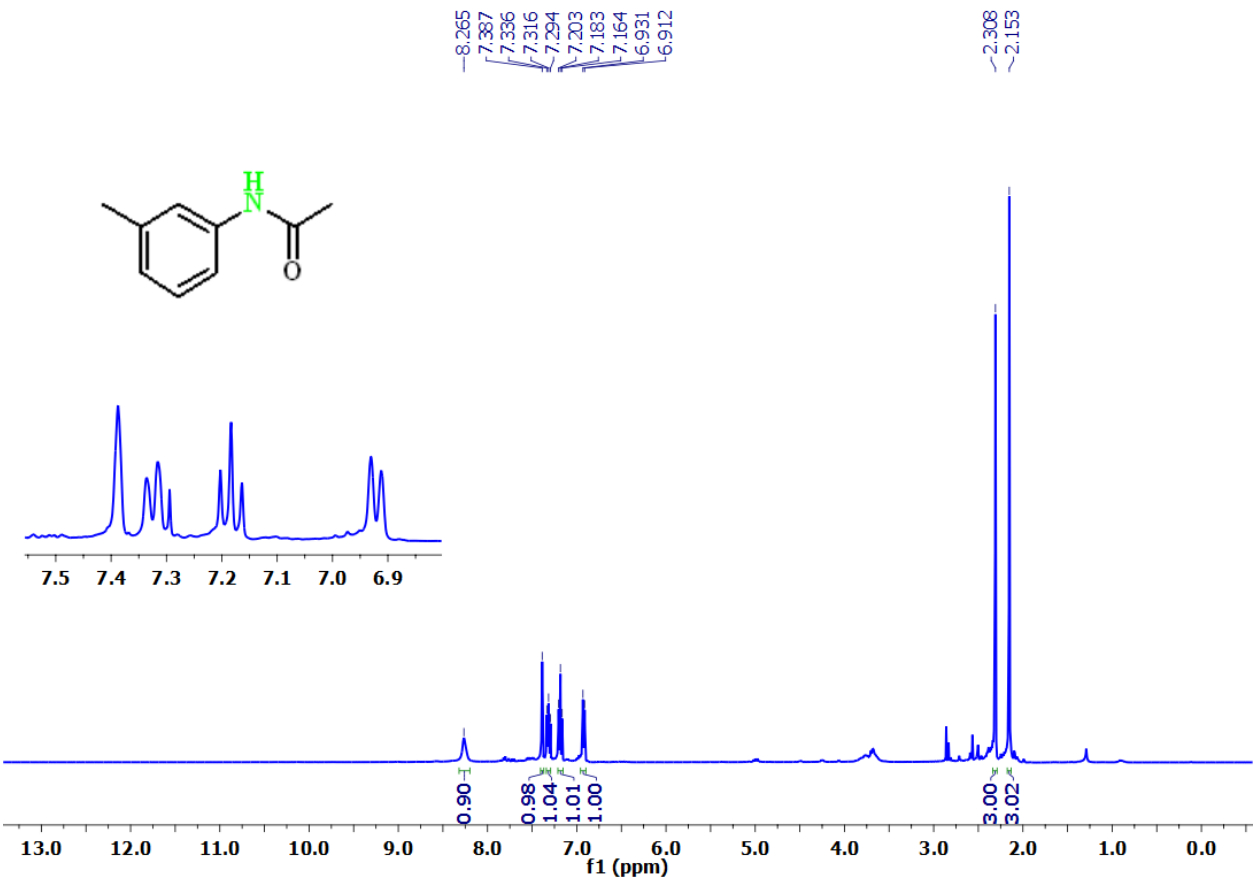
^{13}C NMR of *N*-(3-chloro-2-methylphenyl) formamide



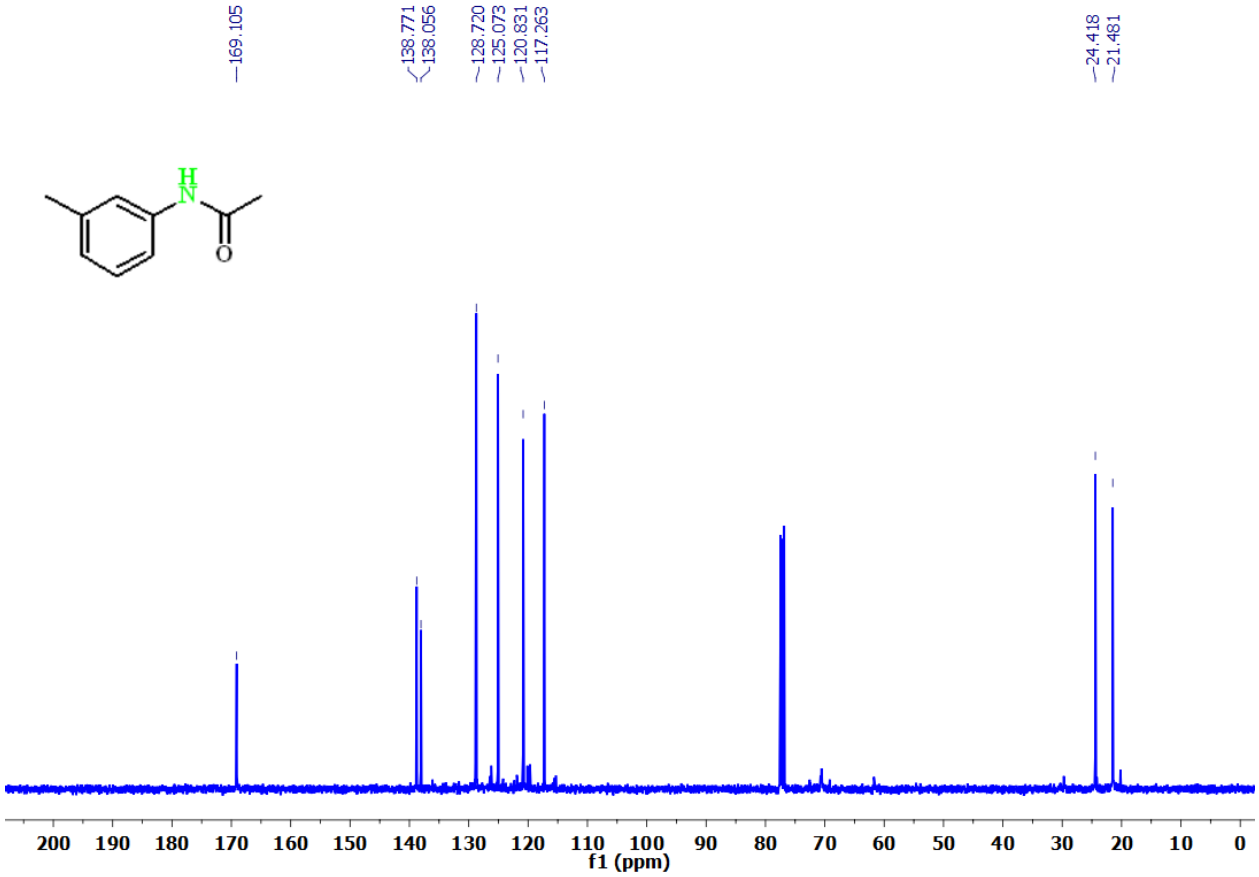
[1] H NMR of *N*-(3,4-dimethylphenyl) acetamide



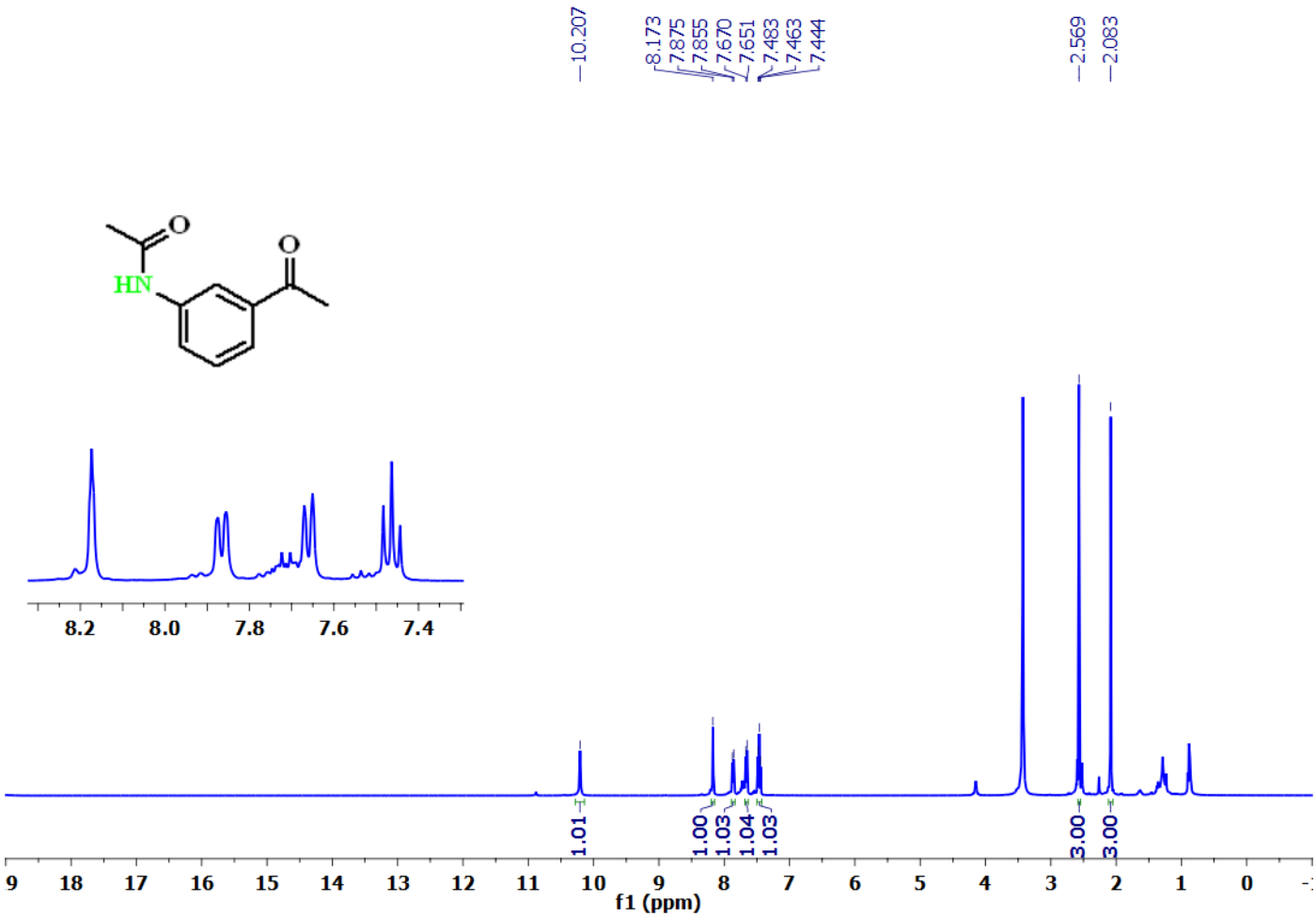
^{13}C NMR of *N*-(3,4-dimethylphenyl) acetamide



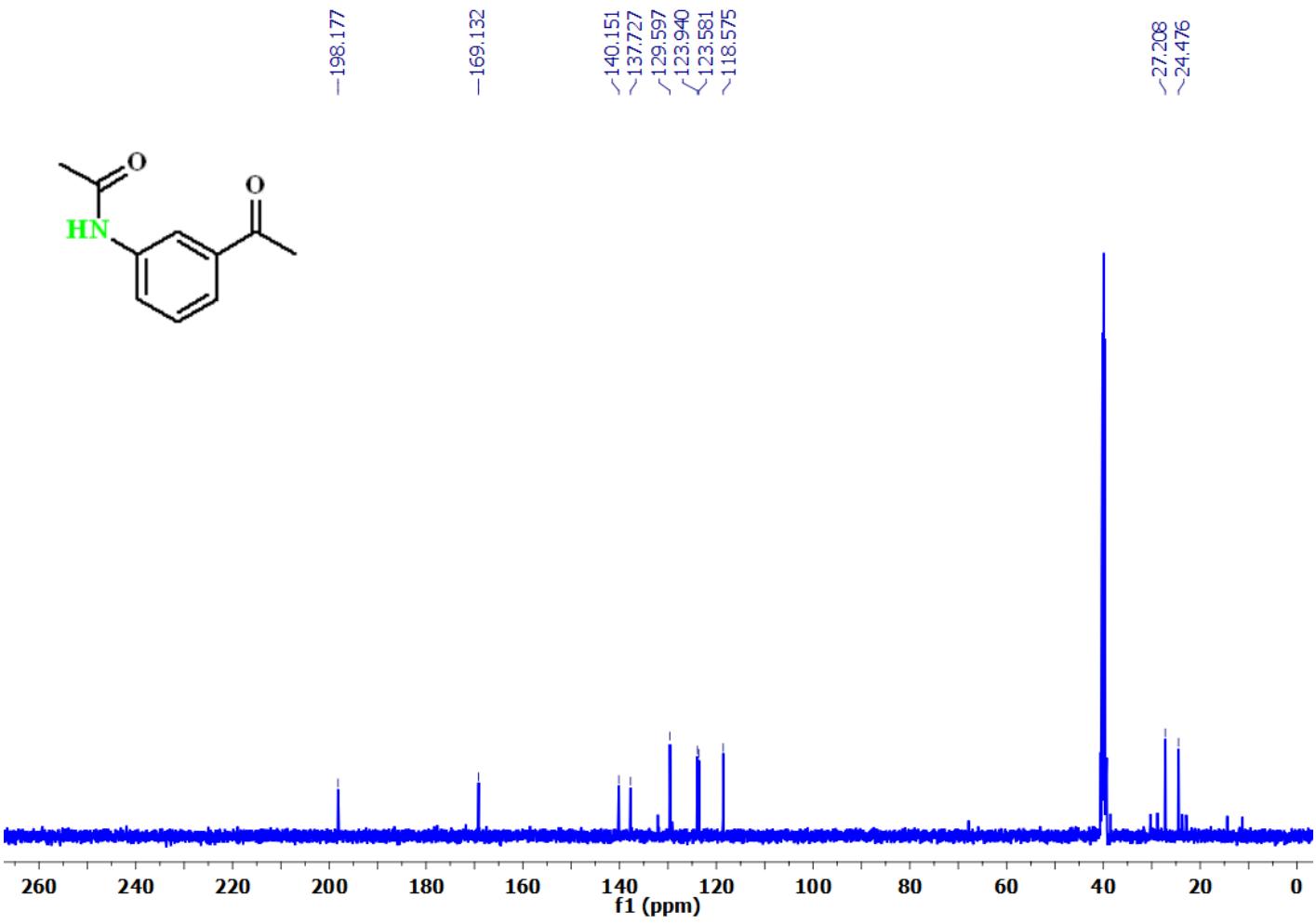
[1] H NMR of *N*-(3-Methylphenyl) acetamide



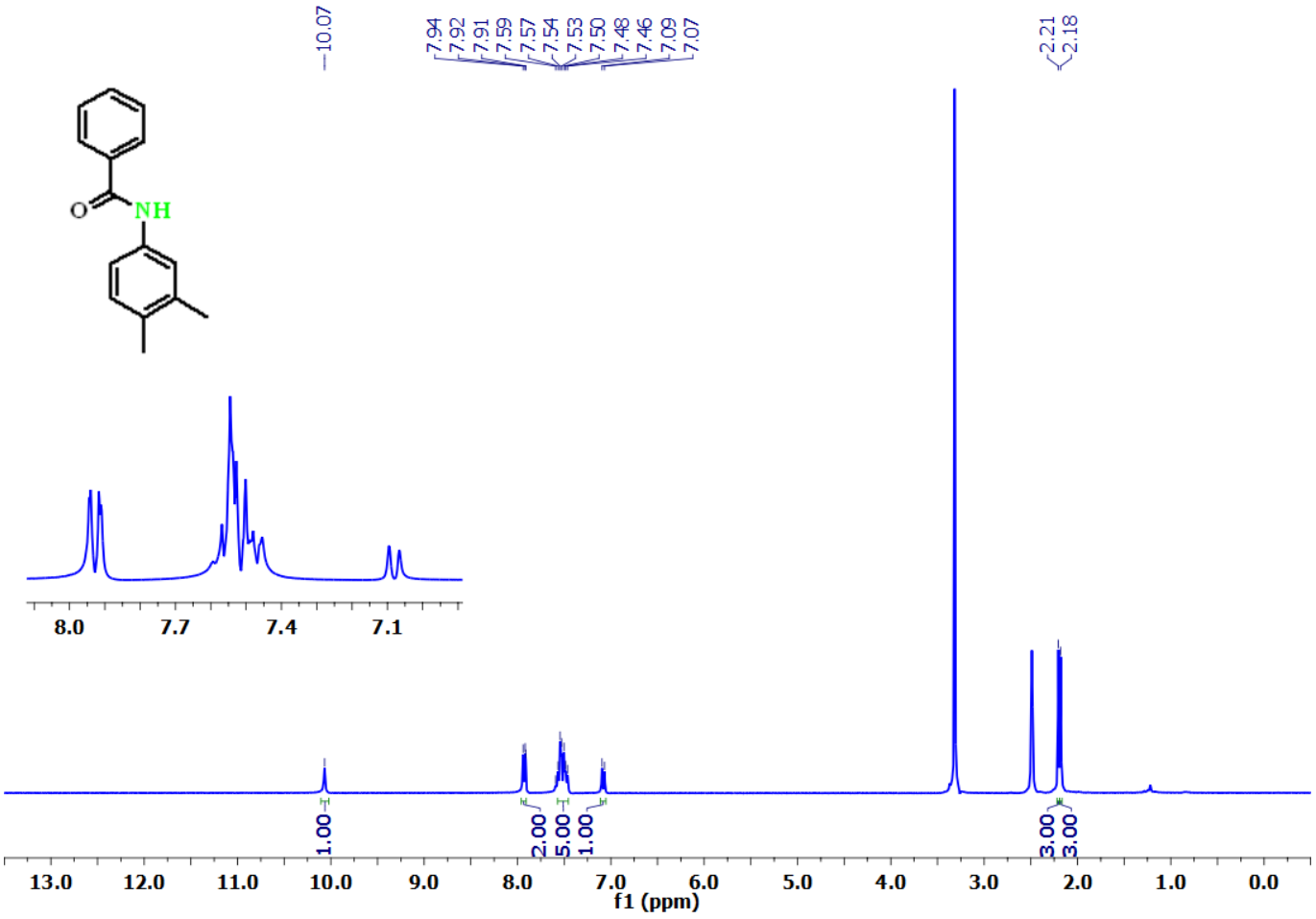
^{13}C NMR of *N*-(3-Methylphenyl) acetamide



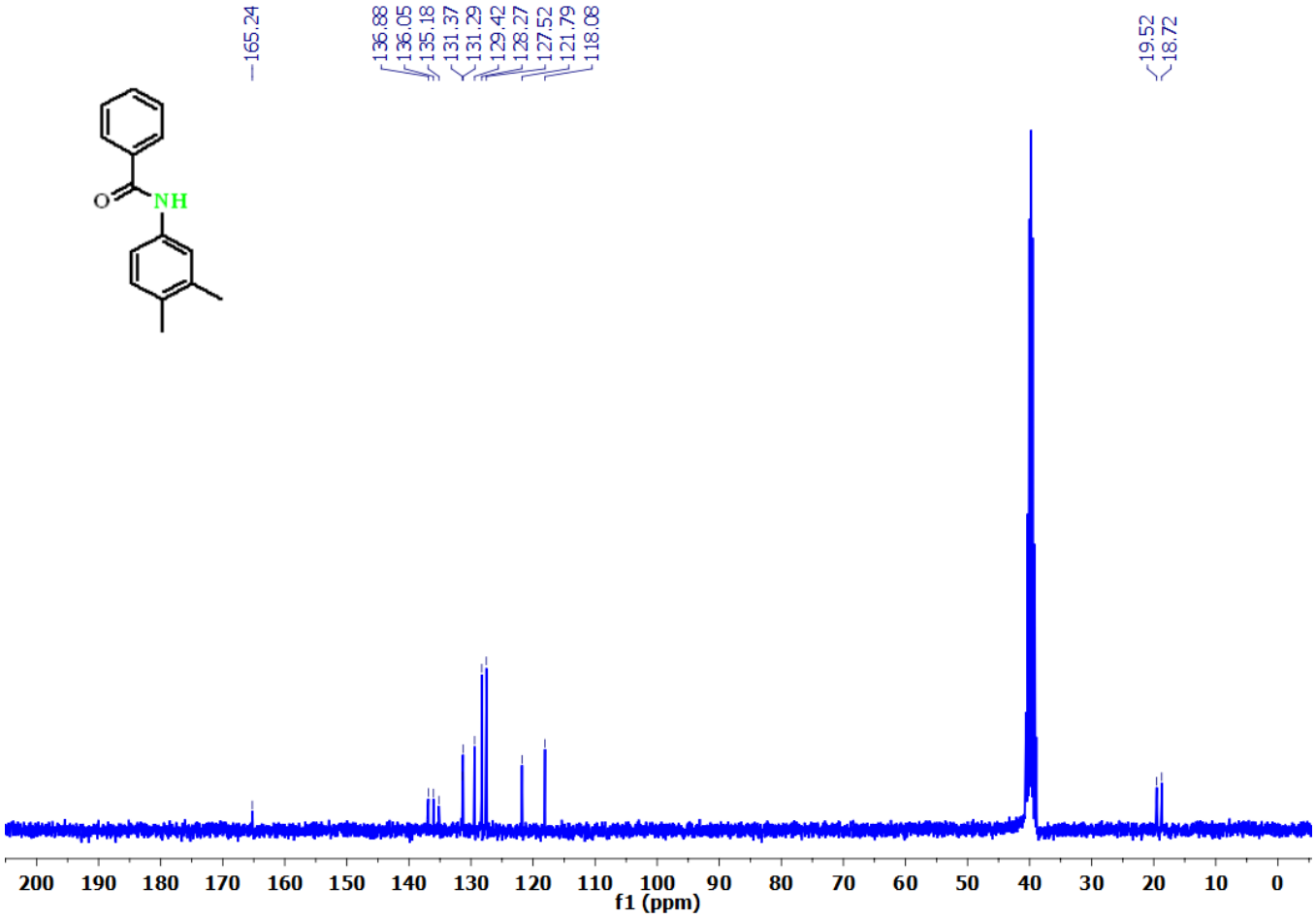
[1] H NMR of *N*-(3-acetylphenyl) acetamide



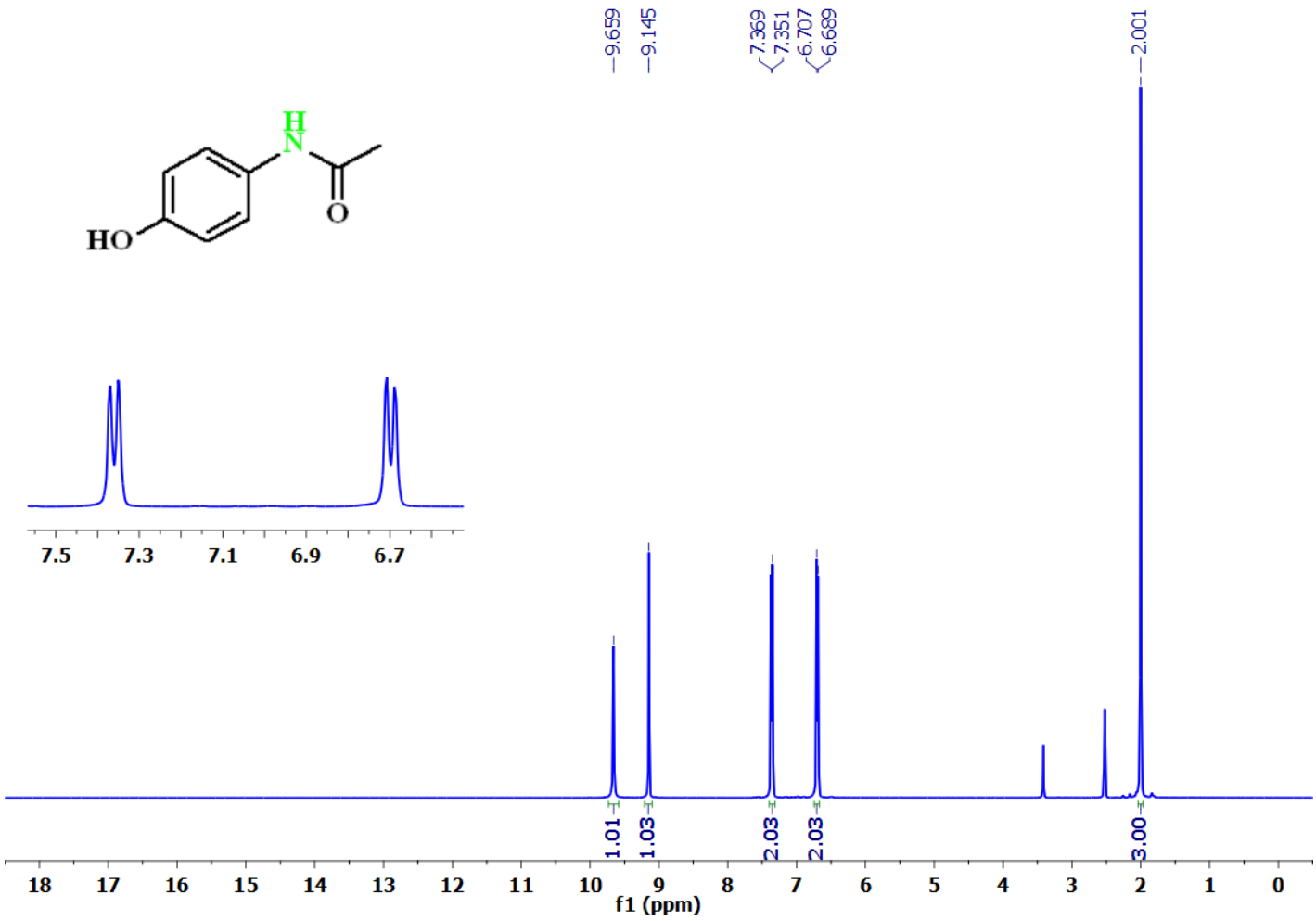
^{13}C NMR of *N*-(3-acetylphenyl) acetamide



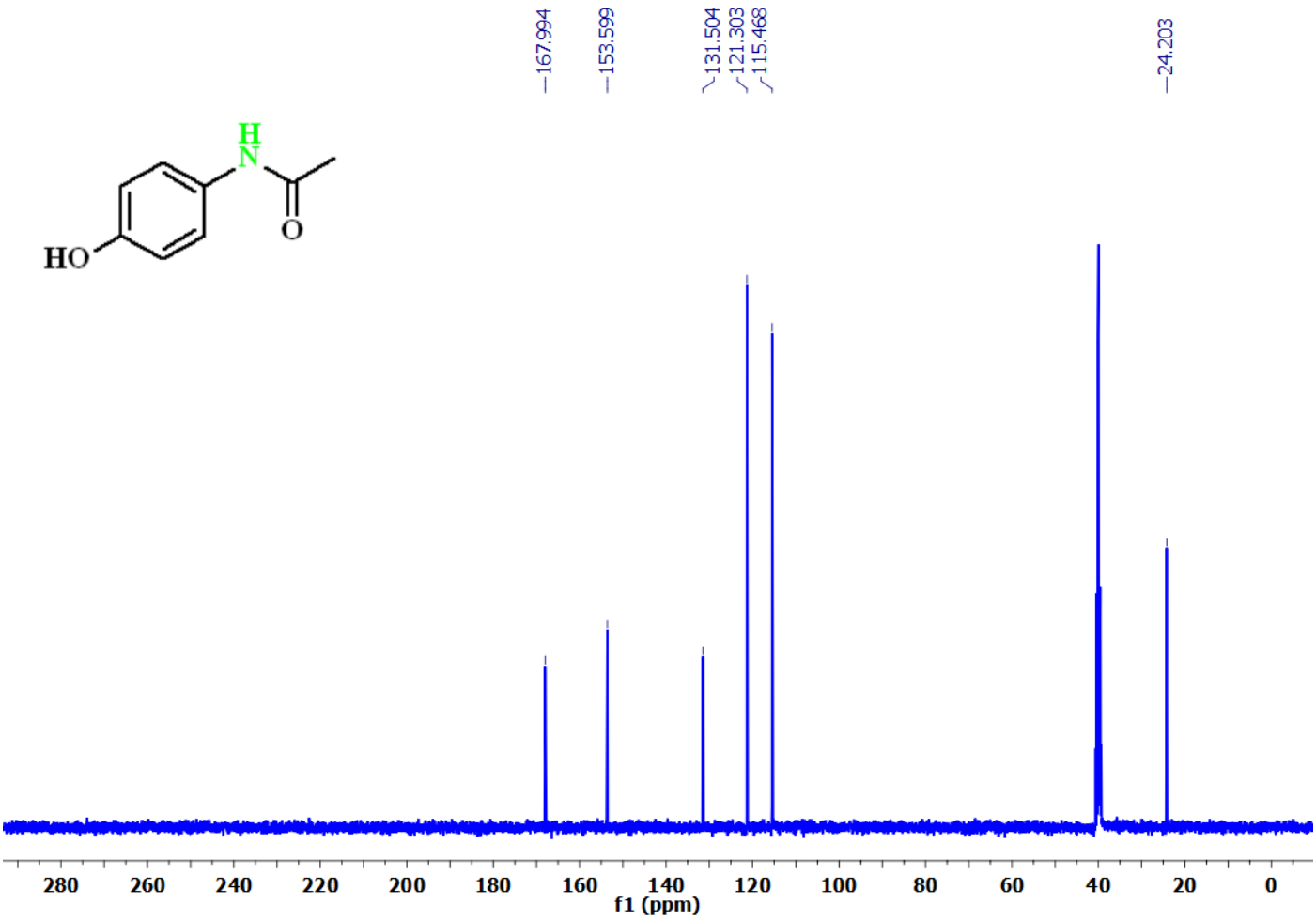
[1] H NMR of *N*-(3,4-dimethylphenyl) benzamide



^{13}C NMR of *N*-(3,4-dimethylphenyl) benzamide



[1] H NMR of *N*-(4-hydroxyphenyl) acetamide



^{13}C NMR of *N*-(4-hydroxyphenyl) acetamide