

Heterogeneous photocatalysis of azides: extending nitrenes photochemistry to longer wavelengths

Ignacio Lemir^{a,b}, Juan Argüello^b, Anabel E. Lanterna^{*a} and Juan C. Scaiano^{*a}

[a] Department of Chemistry and Biomolecular Science and Centre for Advanced Materials Research (CAMaR), University of Ottawa, 10 Marie Curie, Ottawa, ON K1N 6N5, Canada.

[b] Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Haya de la Torrey esq. Medina Allende, Córdoba, 5000, Argentina.

Table of Content

Materials and instrumentation.....	3
Synthesis of Pd@TiO ₂ catalyst	3
Synthesis of reagents.....	3
Scheme S1. Synthesis of azides from the corresponding amine. ^[2]	3
Table S1. Reaction conditions screening. ^a	4
Figure S1. Absorption spectra of different reagents [phenyl azide (black), 4-methoxy phenyl azide (blue), and 4-trifluoromethyl phenyl azide (red)] versus emission spectrum (2% ND filter) of the LED used (purple).....	5
Scheme S2. General reaction pathway for nitrene intermediates. ^[5] As RK and RAZ are the trappable reactive intermediates, one would expect formation of RK-X or RAZ-X depending on the conditions and the nature of X nucleophiles. ^[6]	5
Scheme S3. Curtius rearrangement of carbonyl azides.....	5
Photocatalytic reduction of azides	6
Scheme S4. General reaction scheme for the photocatalytic reduction of azides using Pd@TiO ₂ catalyst.	6
Reusability test.....	9
MS characterization	11
NMR characterisation	15
Other products characterization	54

Figure S2. ^1H NMR spectrum of deuterated aniline obtained from the reaction of phenylazide in deuterated water.	54
Figure S3. ^{13}C NMR spectrum of deuterated aniline obtained from the reaction of phenylazide in deuterated water.	55
Figure S4. Mass spectra of azobenzene (left) obtained from the reaction run in acetonitrile, and 1,2-diphenylhydrazine (right) obtained from the reaction of azobenzene in water (Scheme 3).	55
Figure S5. ^1H NMR spectrum of 1,2-diphenylhydrazine obtained from the reaction of azobenzene in water (Scheme 3).	56
Figure S6. ^{13}C NMR spectrum of 1,2-diphenylhydrazine obtained from the reaction of azobenzene in water (Scheme 3).	57
Figure S7. Mass spectrum of the product of the nucleophilic substitution of aziridines.	57
Figure S8. ^1H NMR spectrum of the product of the nucleophilic substitution of aziridines.	58
Figure S9. ^{13}C NMR spectrum of the product of the nucleophilic substitution of aziridines.	59
References	60

Materials and instrumentation

Unless otherwise stated, all reagents were purchased from Sigma Aldrich and used as received. P25 TiO₂ was purchased from Univar Canada.

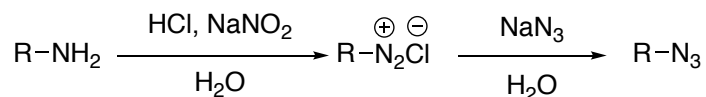
Light-emitting diodes (LEDs) of 10 W from LedEngin were used for the photocatalytic reduction of azides under UV irradiation (centred at 368 nm) working at 0.06 W/cm². All ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer expressing the chemical shifts in ppm relative to the residual H(or C)-signal of the corresponding solvent (CHCl₃: δ_H = 7.26 ppm, δ_C = 77 ppm; DMSO: δ_H = 2.5 ppm, δ_C = 39.5 ppm; D₂O: δ_H = 4.79 ppm). The detection of the aniline products was performed in a Perkin Elmer Claurus Gas Chromatographer coupled to a flame ionization detector (FID) and a DB-5 column (30 m length, 0.320 mm diameter, 0.25 μm film) using Helium as carrier gas. Characterization of the compounds was performed by mass spectrometry in an Agilent 6890-N Gas Chromatograph with an Agilent 5973 mass selective detector calibrated with acetophenone.

Synthesis of Pd@TiO₂ catalyst

The Pd@TiO₂ photocatalysts was synthesised following a reported protocol^[1] to yield *ca.* 2wt% Pd loading, with particle size *ca.* 1.5 nm diameter. Briefly, TiO₂-P25 was mixed together with PdCl₂ in deionized water and exposed to UVA irradiation under continuous stirring for 8 h. The slurry was centrifuged and washed with water (3x) and dried overnight in a desiccator.

Synthesis of reagents

Aryl and alkyl azides were synthesised following a reported protocol^[2] as described in Scheme S1. Briefly, 1 equiv. of HCl (37 % w/w) and 1 equiv. of NaNO₂ are added to an aqueous solution of the amine precursor (1 mmol in 3 ml of water) using an ice bath and constant magnetic stirring. After 30 min, 1.2 equiv. of NaN₃ are added to the mixture and after 12 h of reaction at room temperature between 50 to 99 % yields of the corresponding azides were recovered. The products were separated by chromatographic column (silica gel 60, hexane:ethyl acetate (90:10)) and characterized by mass spectroscopy.



Scheme S1. Synthesis of azides from the corresponding amine.^[2]

Two different protocols were used for the synthesis of 4-(trifluoromethyl)azide^[3] and benzoyl azide^[4].

Synthesis of 4-(trifluoromethyl)azide. Aryl boronic acid (1 mmol), NaN₃ (1.2 mmol), and anhydrous CuSO₄ (10 mmol%) in MeOH (3 mL) were mixed under vigorous stirring at room temperature for 24 h. The reaction mixture was extracted with ethyl acetate (AcOEt). The organic layers were combined, dried (Na₂SO₄), and purified by column chromatography (silica gel 60, AcOEt:hexane (20:80)) to give the desired product.

Synthesis of benzoyl azide. A solution of sodium azide (7.5 mmol) in water (10 mL) was added dropwise (1 hour) into a solution of benzoyl chloride (5 mmol) in acetone (15 mL) at 0 °C. The reaction mixture was warmed up to room temperature and stirred overnight. After completion, the reaction mixture was extracted with AcOEt. The combined organic layers were dried over Na₂SO₄ and solvent was removed under reduced pressure. The residue was purified using silica gel column chromatography (AcOEt:hexane (20:80)) to give the corresponding acyl azide.

Table S1. Reaction conditions screening.^a

Entry	Change of conditions	Conversion (%) ^b
1	None	100
2	5 h	100
3	3.5 h	75
4	Dark, RT	N.R.
5	Dark, 44 °C	N.R.
6	Dark, 66 °C, THF or H ₂ O	N.R.
7	No catalyst	N.R.
8	465 nm LED	N.R.
9	TiO ₂ as catalyst	N.R.
10	10 mol% PdCl ₂ as catalyst	<5
11 ^c	No catalyst, UVC, 8h	Traces

^aReaction conditions: 0.2 mmol phenyl azide, 8 mg of Pd@TiO₂, 2 ml of H₂O, Ar atmosphere, UVA irradiation (368 nm LED working at 0.06 W/cm²), 18 h. ^b Conversion determined by GC-MS analysis. ^cConversion followed by thin layer chromatography.

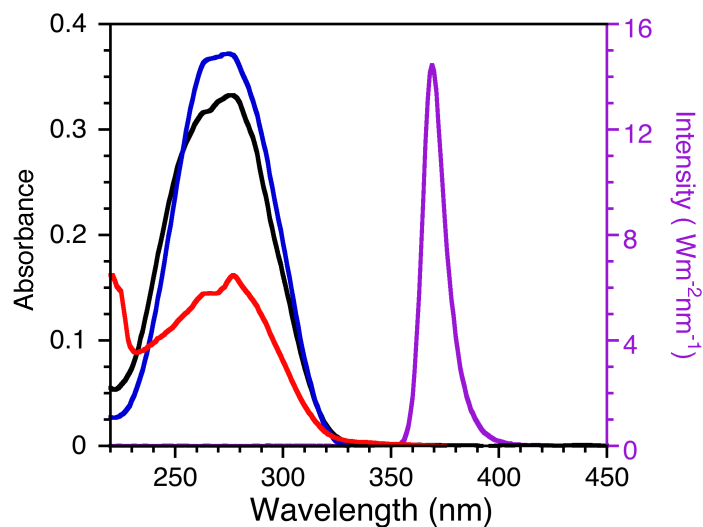
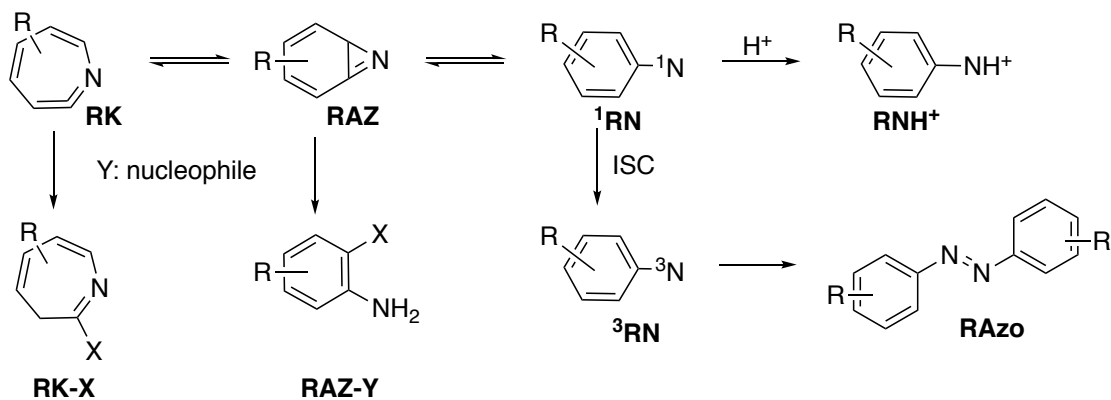
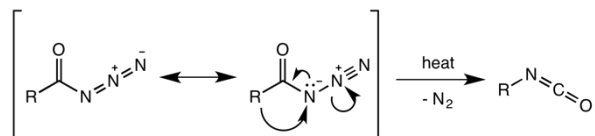


Figure S1. Absorption spectra of different reagents [phenyl azide (black), 4-methoxy phenyl azide (blue), and 4-trifluoromethyl phenyl azide (red)] versus emission spectrum (2% ND filter) of the LED used (purple).



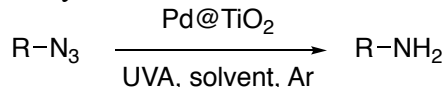
Scheme S2. General reaction pathway for nitrene intermediates.^[5] As RK and RAZ are the trappable reactive intermediates, one would expect formation of RK-X or RAZ-X depending on the conditions and the nature of X nucleophiles.^[6]



Scheme S3. Curtius rearrangement of carbonyl azides.

Photocatalytic reduction of azides

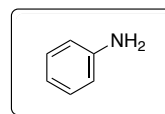
Photocatalytic reduction of azides was carried out in the presence of Pd@TiO₂ catalyst in one step as shown in Scheme S4. Briefly, 8 mg of catalyst are dispersed in 2 ml of water together with 0.2 mmol of the corresponding azide. The reaction vessel is sealed and the suspension is purged with Ar and irradiated with UVA light under vigorous stirring for 5h. The reaction generates N₂ as by-product which can be visually detected by the formation of bubbles. After reaction is complete, the catalyst is separated by centrifugation and the products isolated. For that, the reaction products are extracted in ethyl acetate, separated by chromatographic column (silica gel 60, hexane/ethyl acetate (90:10)) and characterized by ¹H and ¹³C NMR and Mass spectroscopies.



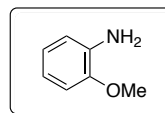
Scheme S4. General reaction scheme for the photocatalytic reduction of azides using Pd@TiO₂ catalyst.

The synthesis methods of each product are described in the following paragraphs:

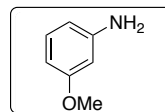
Aniline. Following the general procedure for the reaction in one step, phenylazide (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a pale-yellow oil (17.1 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.33 (m, 2H), 7.14 (ddt, *J* = 7.7 Hz, 1H), 7.06 – 7.01 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 186.70, 129.91, 125.03, 119.17.



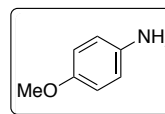
2-methoxyaniline. Following the general procedure for the reaction in one step, 1-azido-2-methoxybenzene (29.2 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a brown oil (16.2 mg, 66% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.07 (t, *J* = 8.0 Hz, 1H), 6.32 (dddd, *J* = 14.9, 7.9, 2.3, 0.8 Hz, 2H), 6.25 (t, *J* = 2.3 Hz, 1H), 3.77 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 160.85, 147.90, 130.21, 108.01, 104.03, 101.16, 55.17.



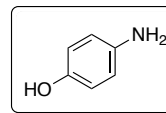
3-methoxyaniline. Following the general procedure for the reaction in one step, 1-azido-3-methoxybenzene (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a brown oil (21.6 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.07 (t, *J* = 8.0 Hz, 1H), 6.40 – 6.29 (m, 2H), 6.25 (t, *J* = 2.3 Hz, 1H), 3.67 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 160.85, 147.90, 130.21, 108.01, 104.03, 101.16, 55.17.



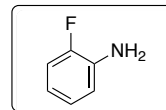
4-methoxyaniline. Following the general procedure for the reaction in one step, 1-azido-4-methoxybenzene (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a brown solid (23.8 mg, 97% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.79 – 6.72 (m, 2H), 6.68 – 6.62 (m, 2H), 3.75 (s, 3H), 3.42 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 153.03, 139.90, 116.63, 114.96, 55.89.



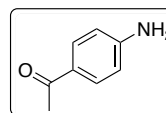
4-hidroxyaniline. Following the general procedure for the reaction in one step, 4-azidophenol (27 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a brown oil (17.6 mg, 81% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.21 (dd, J = 4.7, 1.5 Hz, 2H), 6.51 (dd, J = 4.7, 1.6 Hz, 2H), 4.12 (s, 2H), 1.82 (d, J = 13.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 152.70, 150.50, 109.76.



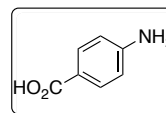
2-fluoroaniline. Following the general procedure for the reaction in one step, 4-fluorophenylazide (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording an orange oil (12.4 mg, 56% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.06 – 6.90 (m, 2H), 6.84 – 6.76 (m, 1H), 6.74 – 6.66 (m, 1H), 3.71 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 153.02, 150.65, 134.66, 134.54, 124.56, 124.53, 118.78, 118.71, 117.06, 117.03, 115.42, 115.24, 77.16.



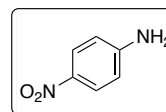
1-(4-aminophenyl)ethan-1-one. Following the general procedure for the reaction in one step, 1-(4-azidophenyl)ethan-1-one (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a pale-yellow solid (18.9 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.77 (m, 2H), 6.72 – 6.59 (m, 2H), 4.11 (s, 2H), 2.51 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.59, 151.16, 130.95, 113.88, 77.16, 26.24.



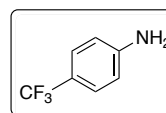
4-aminobenzoic acid. Following the general procedure for the reaction in one step, 4-azidobenzoic acid (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a white solid (19.2 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.8 Hz, 1H), 6.74 – 6.61 (m, 1H), 5.30 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 151.78, 132.54, 118.29, 113.93, 101.85.



4-nitroaniline. Following the general procedure for the reaction in one step, 1-azido-4-nitrobenzene (32.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording 79% as a yellow solid (25.4 mg, 79% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.00 (m, 2H), 6.69 – 6.57 (m, 2H), 4.35 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 152.58, 144.17, 126.51, 113.53.

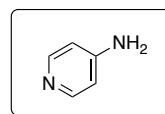


4-(trifluoromethyl)aniline. Following the general procedure for the reaction in one step, 1-azido-4-(trifluoromethyl)benzene (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a yellow solid (25.4 mg, 79% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.22 (m, 2H), 7.21 – 7.14 (m, 2H),

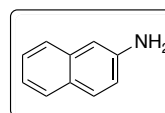


7.08 – 6.98 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.27, 137.24, 133.90, 131.38, 129.58, 128.83, 128.26, 127.67, 125.06, 118.88.

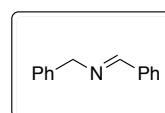
Pyridin-4-amine. Following the general procedure for the reaction in one step, 4-azidopyridine (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO_2 were placed in a glass tube with 2 mL of water. The reaction was carried under Argon Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a white solid (8.3 mg, 44% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 7.97 (m, 2H), 7.14 – 7.03 (m, 2H), 5.30 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.15, 132.24, 119.13.



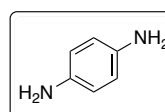
Naphthalen-2-amine. Following the general procedure for the reaction in one step, 2-azidonaphthalene (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO_2 were placed in a glass tube with 2 mL of water. The reaction was carried under Argon Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a brown solid (13.7 mg, 48% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.77 (m, 2H), 7.52 – 7.43 (m, 2H), 7.36 – 7.28 (m, 2H), 6.79 (dd, $J = 6.8, 1.6$ Hz, 1H), 4.15 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.07, 134.53, 128.69, 126.46, 125.99, 125.03, 123.82, 120.92, 119.21, 109.91.



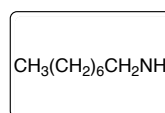
N-benzyl-1-phenylmethanimine. Following the general procedure for the reaction in one step, (azidomethyl)benzene (26.6 mg, 0.2 mmol) and 8 mg of Pd@TiO_2 were placed in a glass tube with 2 mL of water. The reaction was carried under Argon Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Conversion verified by CG-MS.



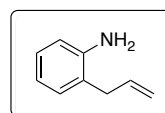
Benzene-1,4-diamine. Following the general procedure for the reaction in one step, 1,4-diazidobenzene (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO_2 were placed in a glass tube with 2 mL of water. The reaction was carried under Argon Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a pale-yellow solid (20 mg, 92% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.57 (s, 1H), 3.33 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.74, 116.86, 77.16.



Octan-1-amine. Following the general procedure for the reaction in one step, 1-azidooctane (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO_2 were placed in a glass tube with 2 mL of water. The reaction was carried under Argon Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording 28% as a colorless oil (7.2 mg, 28% yield). ^1H NMR (400 MHz, CDCl_3) δ 3.05 (d, $J = 13.3$ Hz, 1H), 2.20 (s, 9H), 1.82 (s, 2H), 1.29 (d, $J = 8.7$ Hz, 5H), 0.90 (t, $J = 6.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 31.65, 30.95, 30.95, 29.05, 29.02, 27.62, 26.44, 22.61, 14.09.

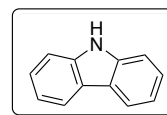


2-allylaniline. Following the general procedure for the reaction in one step, 1-allyl-2-azidobenzene (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO_2 were placed in a glass tube with 2 mL of water. The reaction was carried under Argon Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a yellow oil (26 mg, 98% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.09 – 7.02 (m, 4H), 6.00 – 5.86 (m, 1H), 5.18 – 5.01 (m, 4H, overlap = CH_2 &

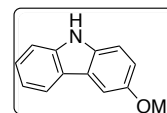


NH₂ signals), 3.33 (ddd, $J = 11.4, 6.6, 3.9$ Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 153.39, 126.28, 126.21, 125.37, 125.33, 121.51, 117.29, 117.10, 30.17.

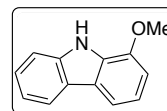
9H-carbazole. Following the general procedure for the reaction in one step, 2-azido-1,1'-biphenyl (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a colorless solid (32.8 mg, 99% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.04 (m, 4H), 7.48 – 7.37 (m, 4H), 7.25 – 7.22 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 139.64, 125.98, 123.05, 120.48, 119.59, 110.71.



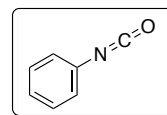
3-methoxy-9H-carbazole. Following the general procedure for the reaction in one step, 2-azido-4-methoxy-1,1'-biphenyl (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a pale-yellow solid (17 mg, 43% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.31 (m, 3H), 7.30 – 7.17 (m, 1H), 7.12 – 6.72 (m, 2H), 6.93 (ddd, $J = 8.3, 2.6, 0.9$ Hz, 1H), 3.85 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.40, 139.62, 137.24, 133.72, 131.30, 129.24, 128.90, 125.00, 122.01, 118.88, 115.36, 113.10, 55.39.



1-methoxy-9H-carbazole. Following the general procedure for the reaction in one step 2-azido-4-methoxy-1,1'-biphenyl (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a pale-yellow solid (20.5 mg, 52% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.08 – 8.00 (m, 1H), 7.91 (s, 1H), 7.57 (d, $J = 2.5$ Hz, 1H), 7.44 – 7.38 (m, 2H), 7.33 (d, $J = 8.7$ Hz, 1H), 7.24 – 7.19 (m, 1H), 7.08 (dd, $J = 8.8, 2.5$ Hz, 1H), 3.94 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 154.03, 140.41, 134.50, 129.98, 125.94, 123.91, 123.48, 120.38, 119.18, 115.20, 111.43, 110.88, 103.30, 56.22.



Isocyanatobenzene. Following the general procedure for the reaction in one step, 2-azidobenzoyl chloride (23.8 mg, 0.2 mmol) and 8 mg of Pd@TiO₂ were placed in a glass tube with 2 mL of water. The reaction was carried under Argon. Then, the mixture was irradiated with UV-A LED (365 nm), stirring for 5 h. Purification was performed by flash column chromatography affording a pale-yellow oil (22.6 mg, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, $J = 8.4, 1.3$ Hz, 2H), 7.67 – 7.55 (m, 1H), 7.50 – 7.38 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 147.03, 126.50, 125.79, 119.55, 113.54.

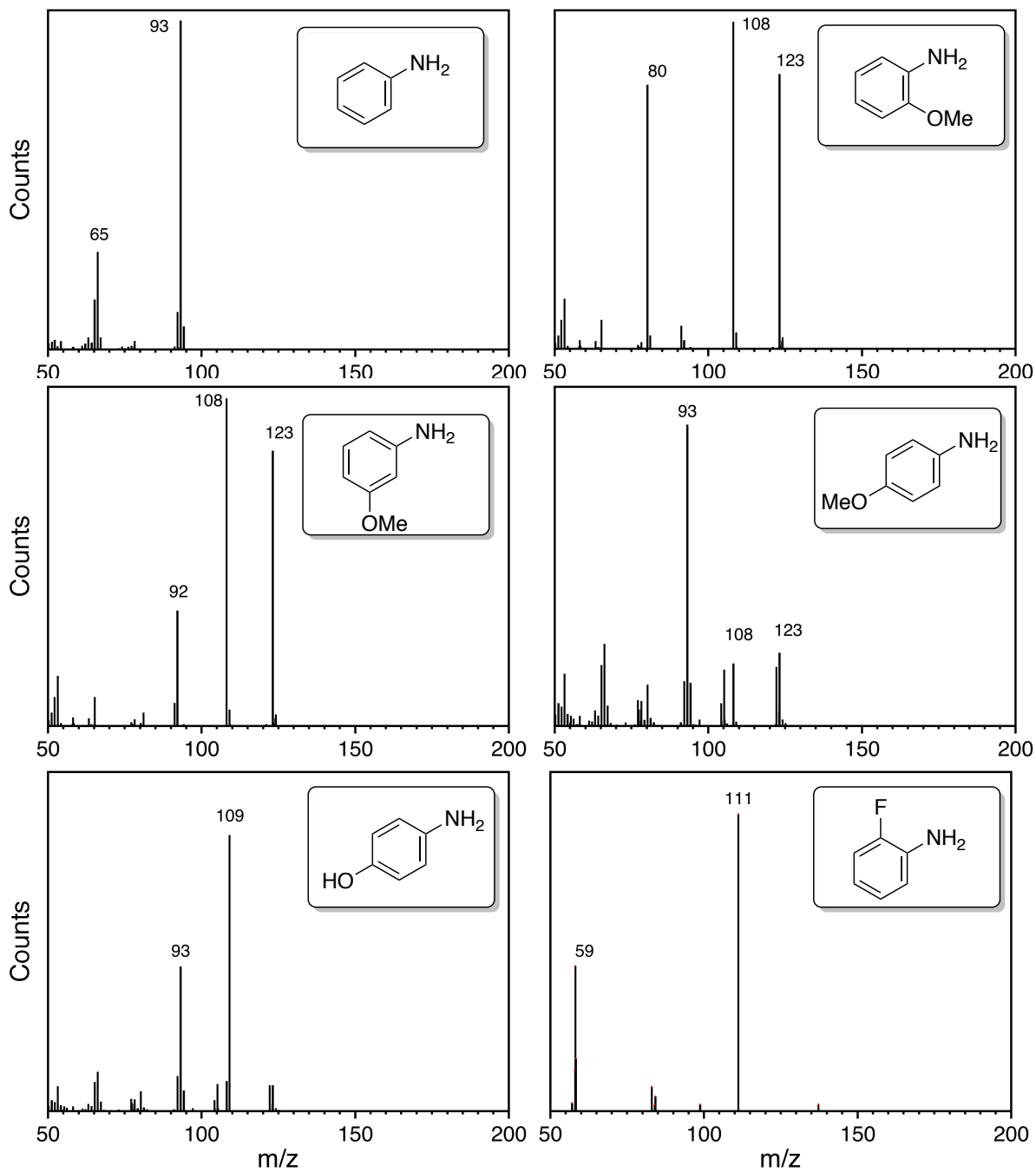


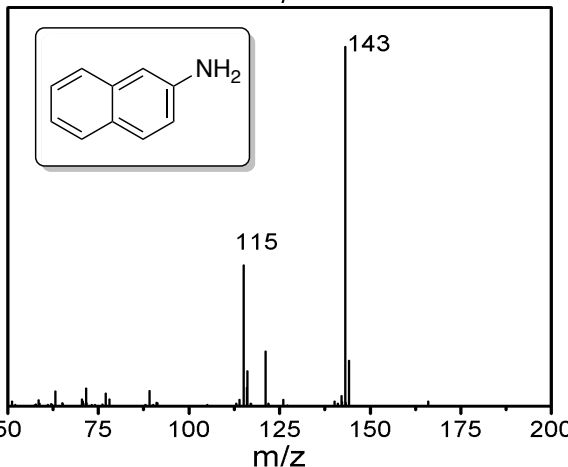
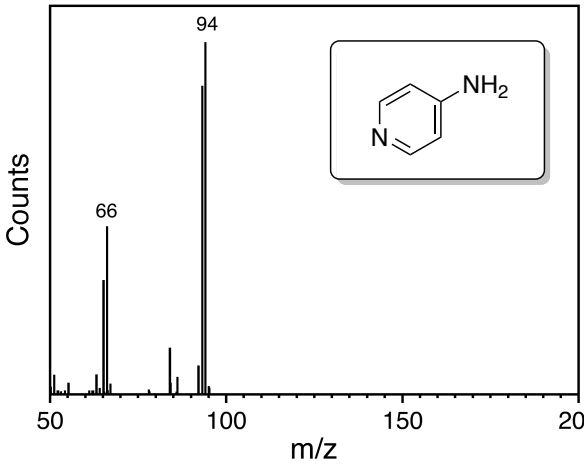
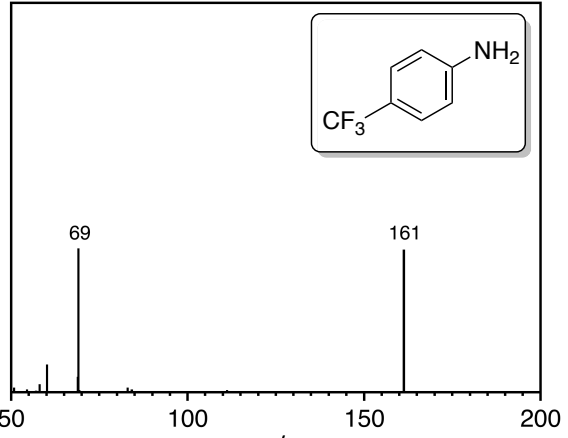
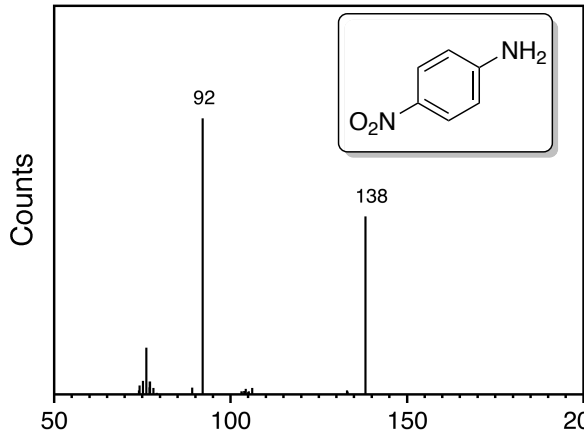
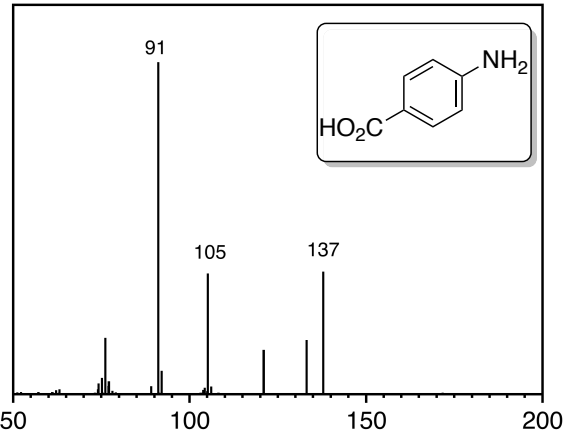
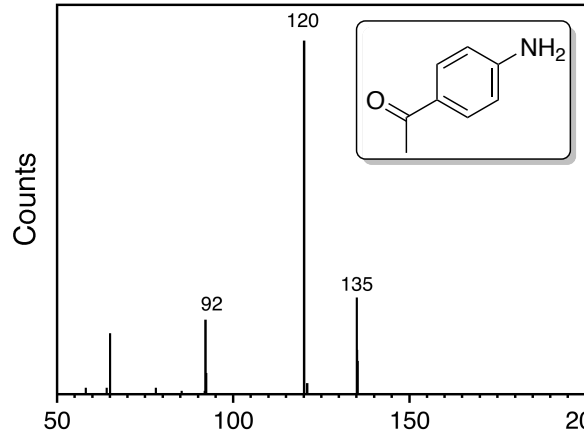
Reusability test

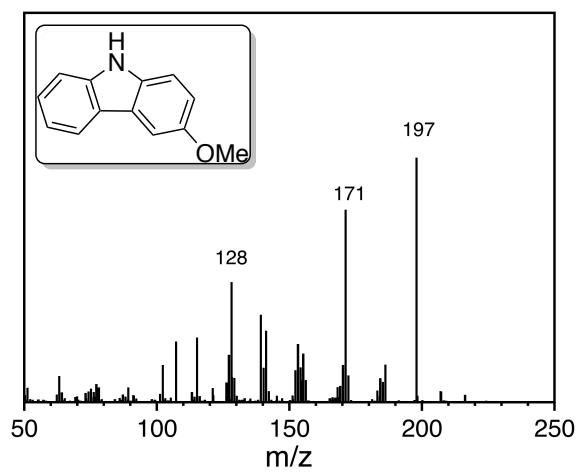
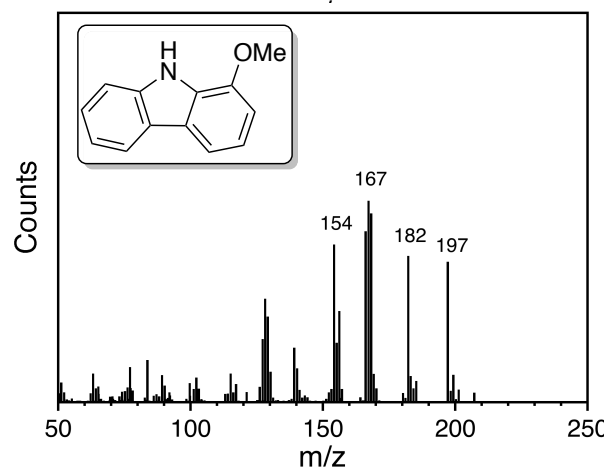
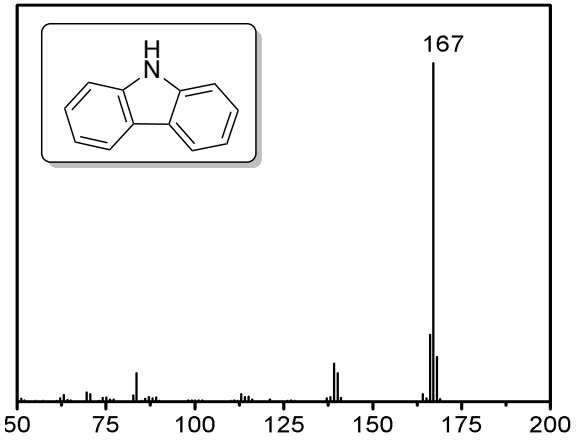
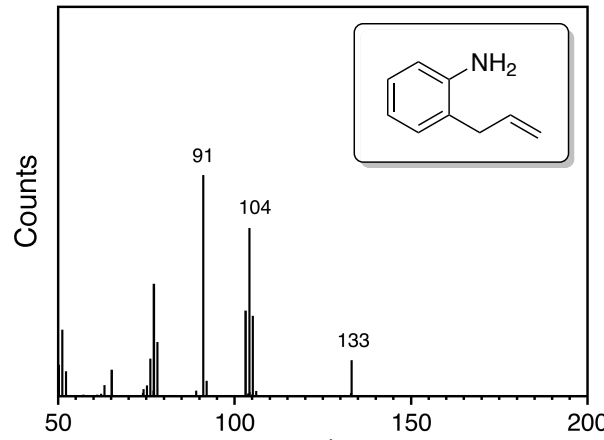
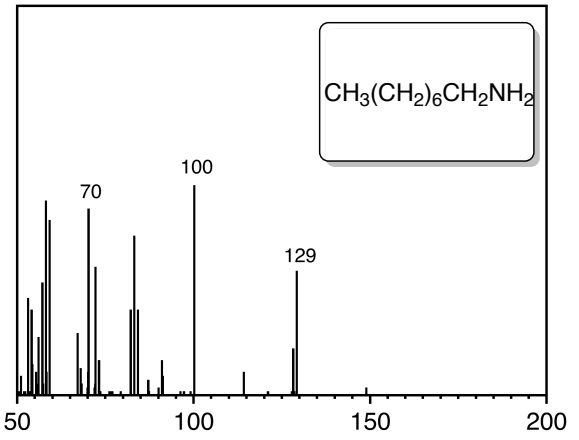
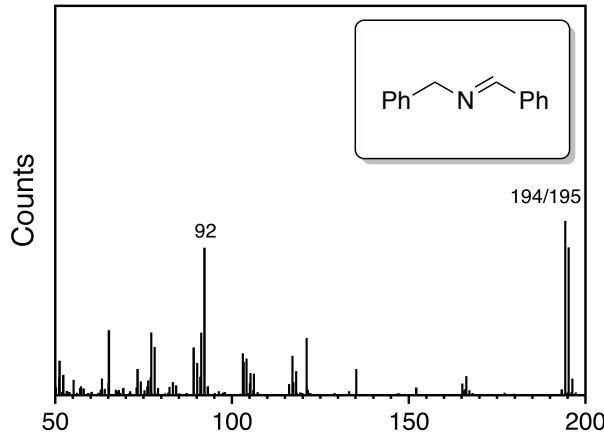
Method I: Sequential addition of reagent. The reaction mixture (phenylazide and Pd@TiO₂ catalyst in water) was irradiated under Ar atmosphere for 18h. After reaction completion, the same initial amount of substrate was added (0.2 mmol of phenylazide) to the reaction mixture and irradiated for another 18h. This procedure was repeated for 5 cycles, without removing neither light irradiation nor inert atmosphere. The conversions were measured by GC-MS.

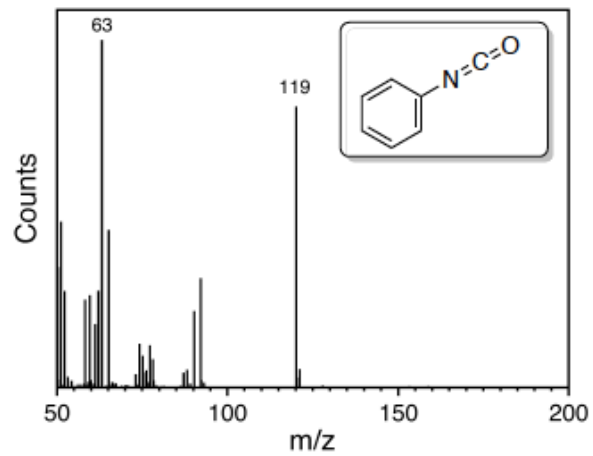
Method II: Separation of catalyst. The reaction mixture (phenylazide and Pd@TiO₂ catalyst in water) was irradiated under Ar atmosphere for 18h. After reaction completion, Pd@TiO₂ catalyst was recovered by centrifugation (5 min at 8000 rpm) and washing 3x with water, dichloromethane and acetone, respectively. Finally, the material was dried in an oven overnight. Another reaction mixture was prepared with the catalyst recovered and the photocatalytic activity was evaluated for second time. This same procedure was repeated five times to verify the reusability of the material.

MS characterization

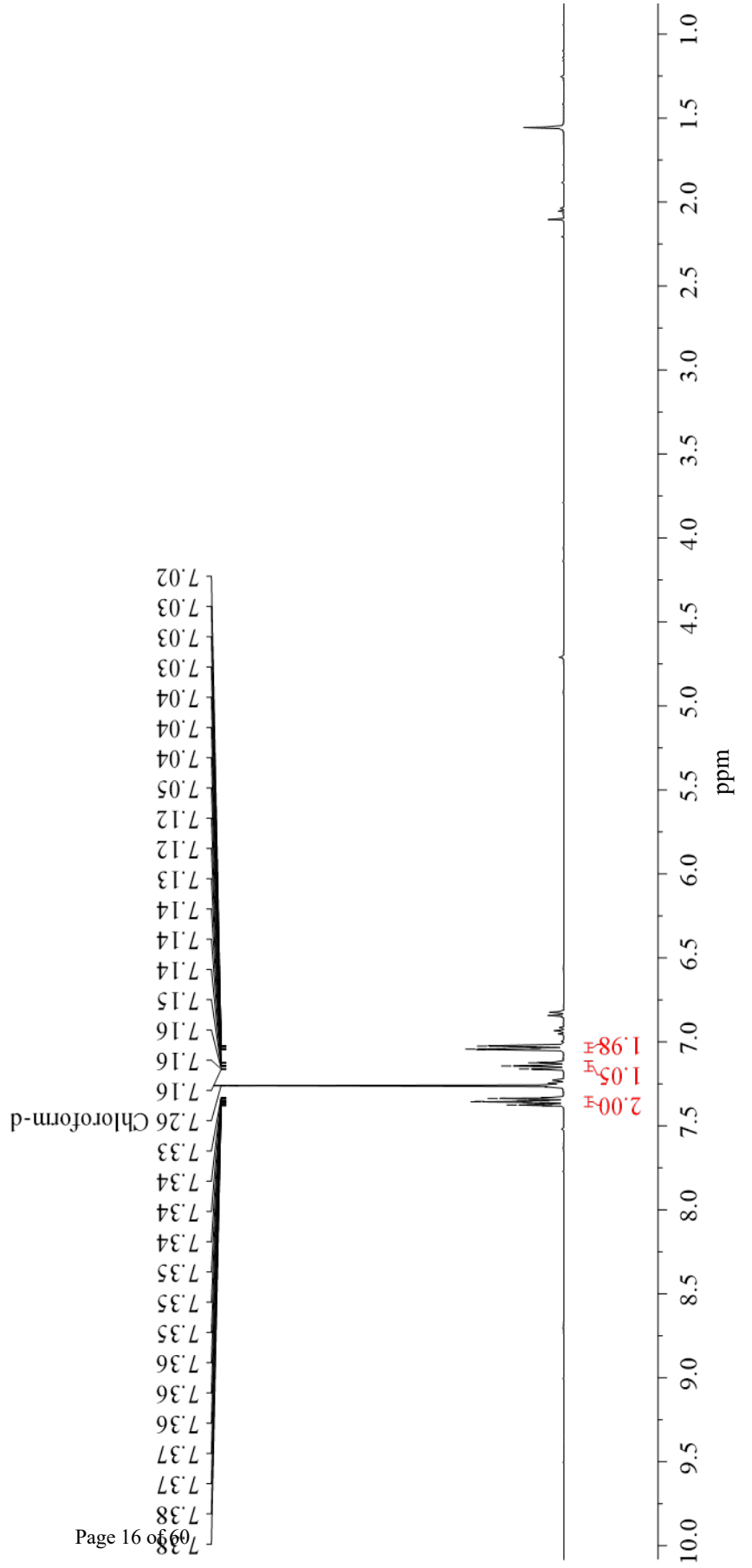
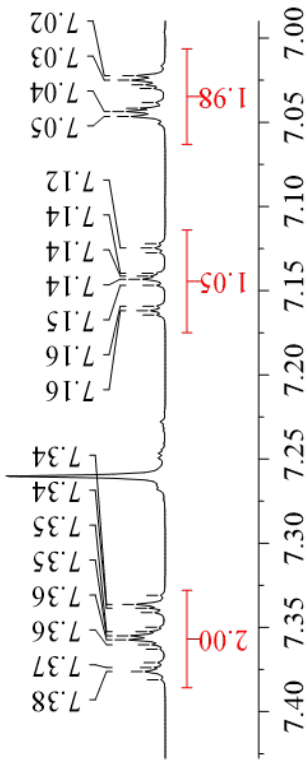
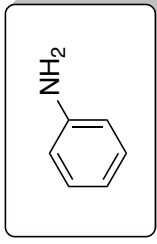


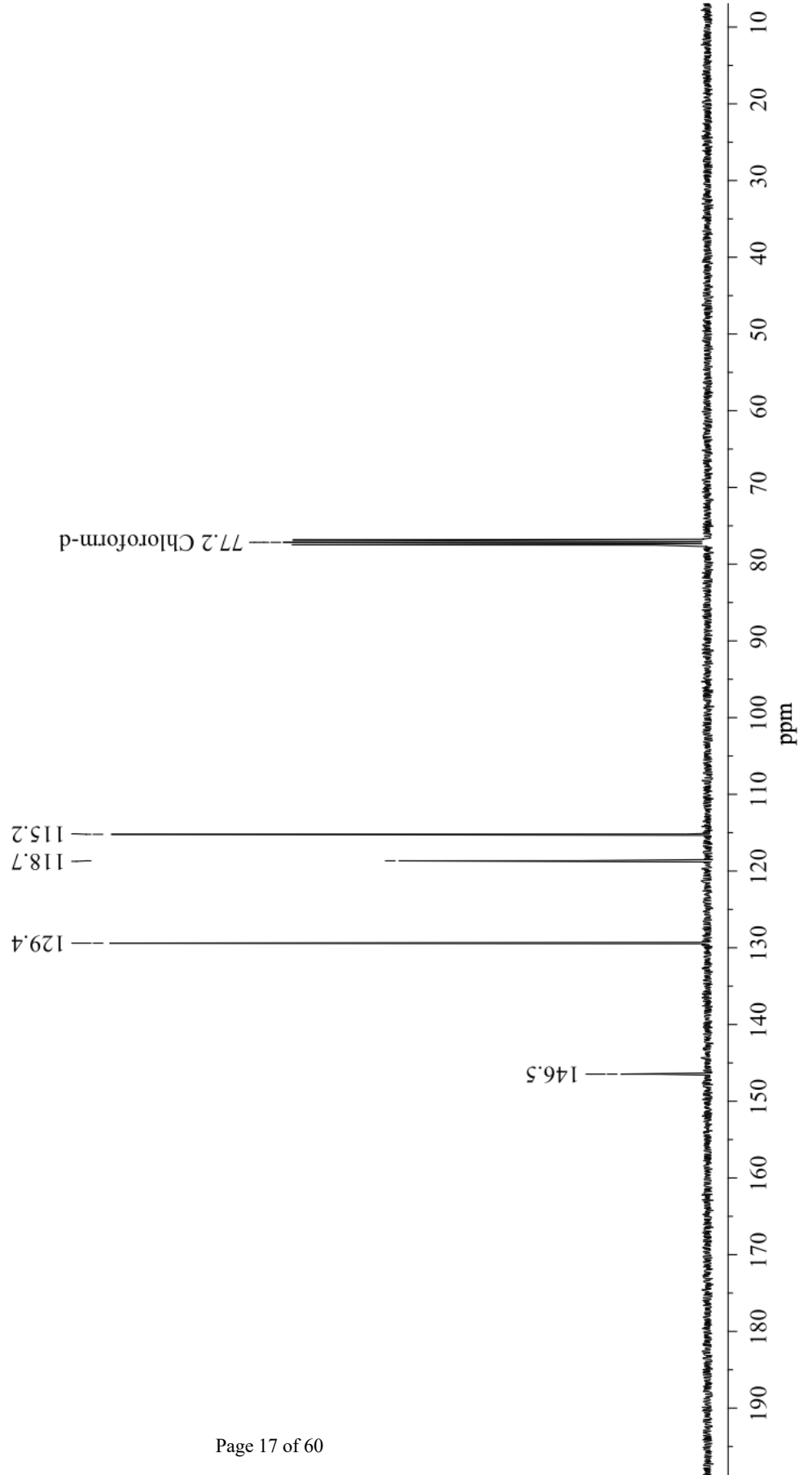
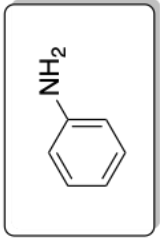


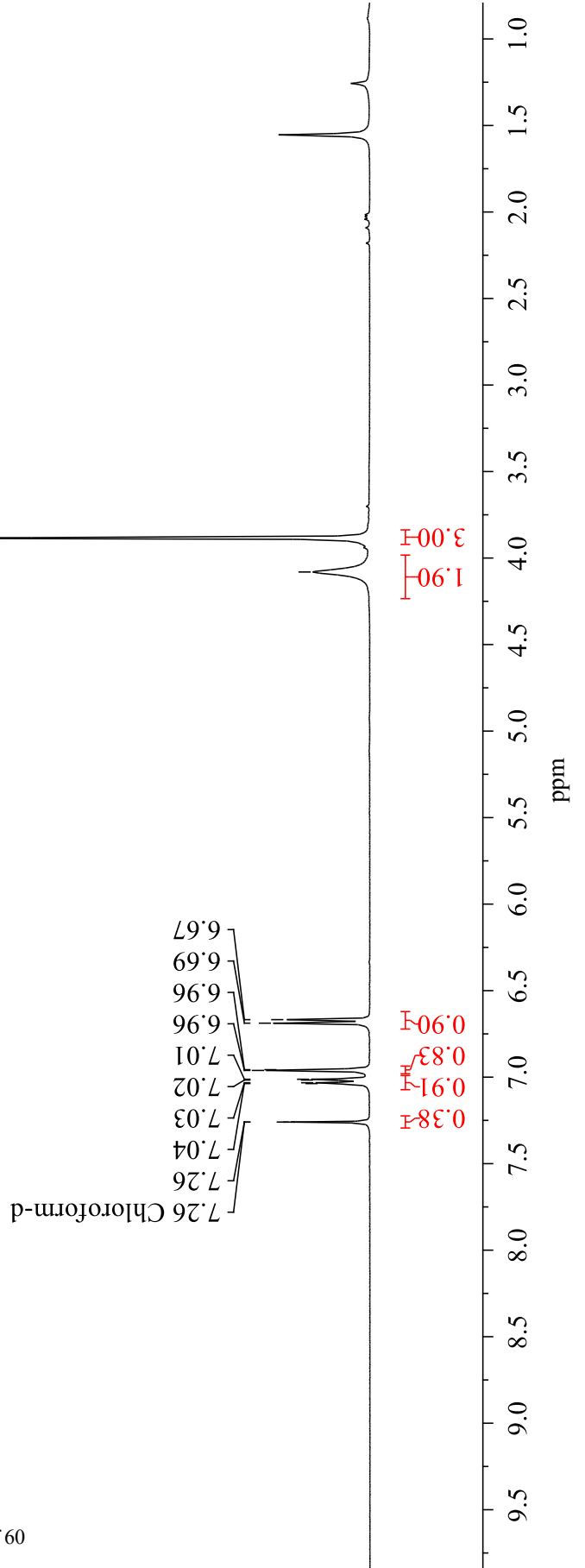
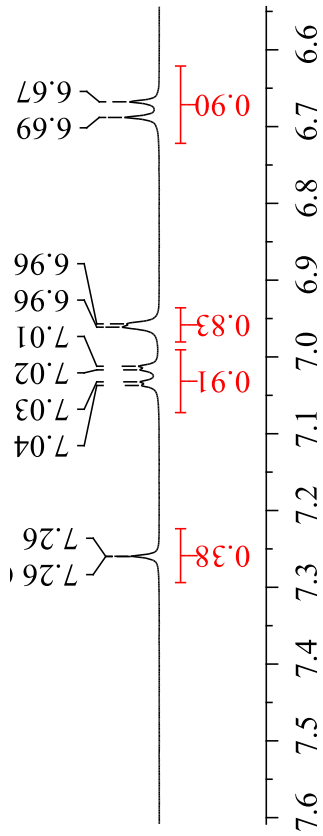
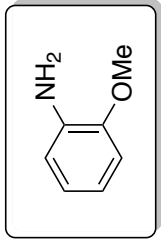


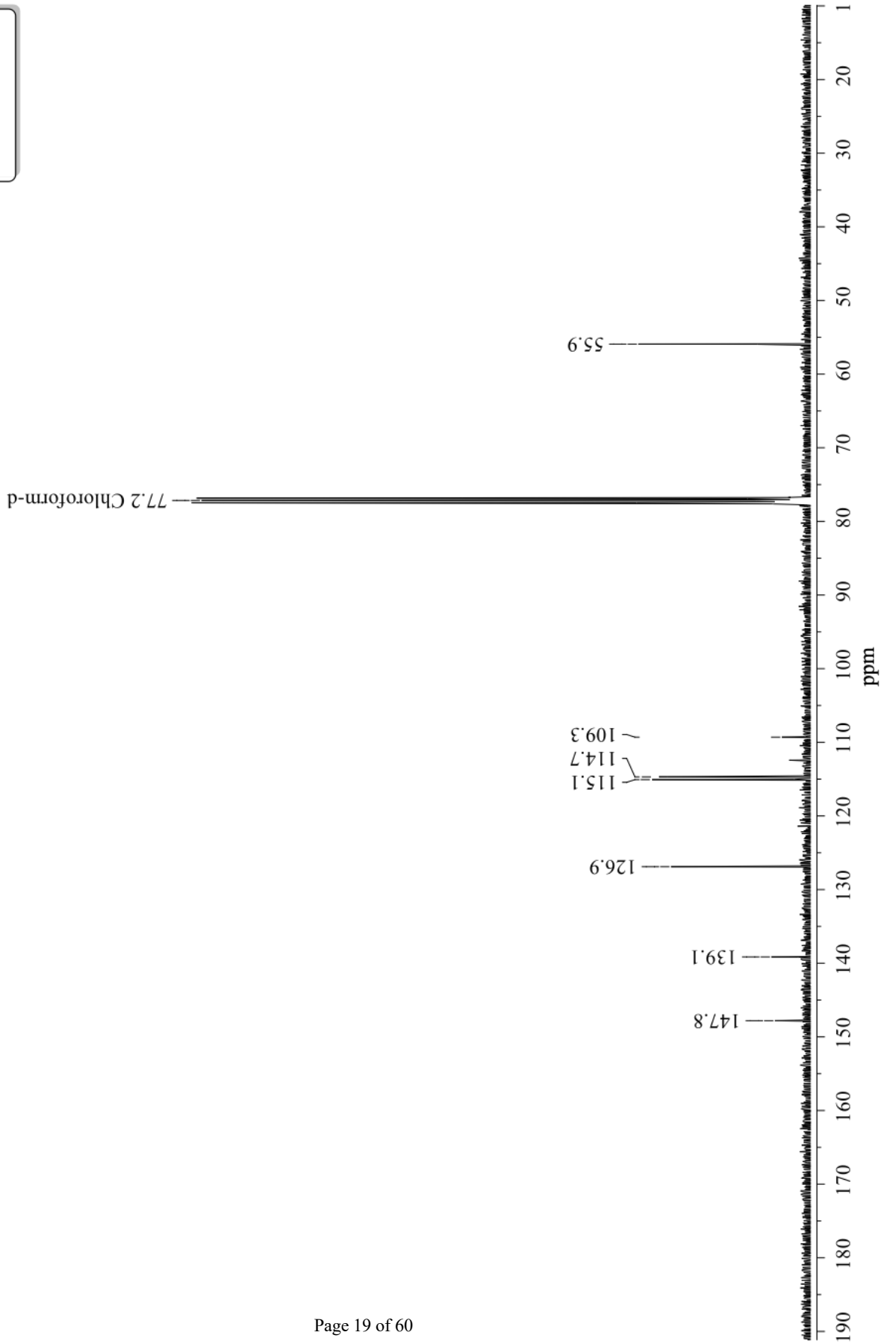
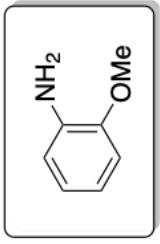


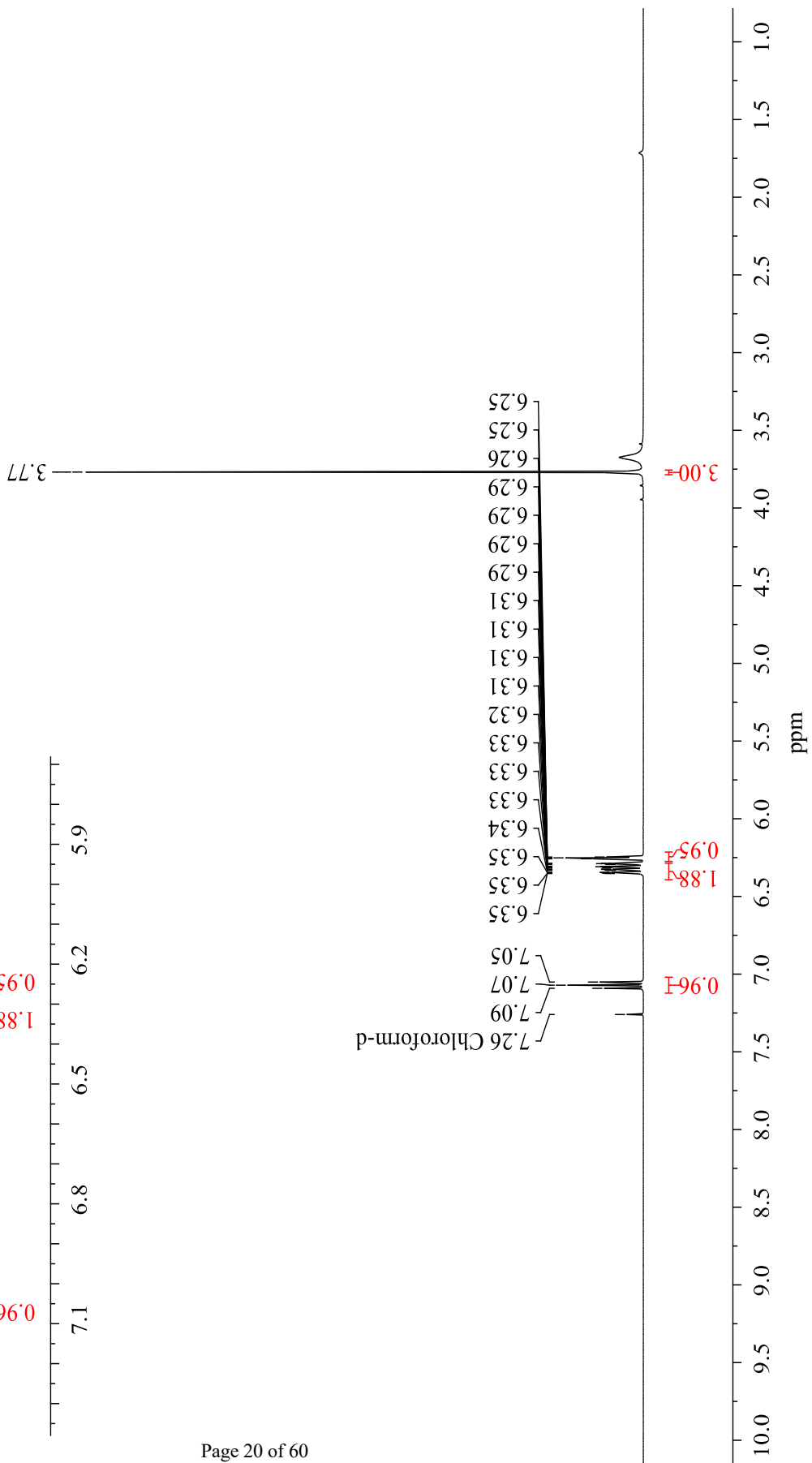
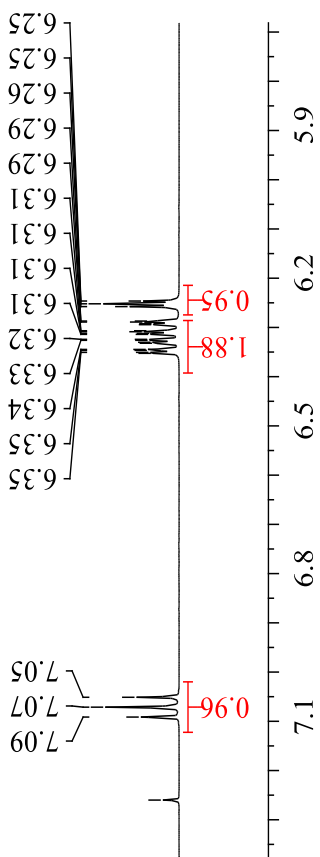
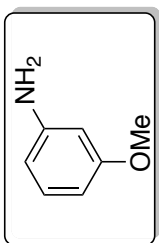
NMR characterisation

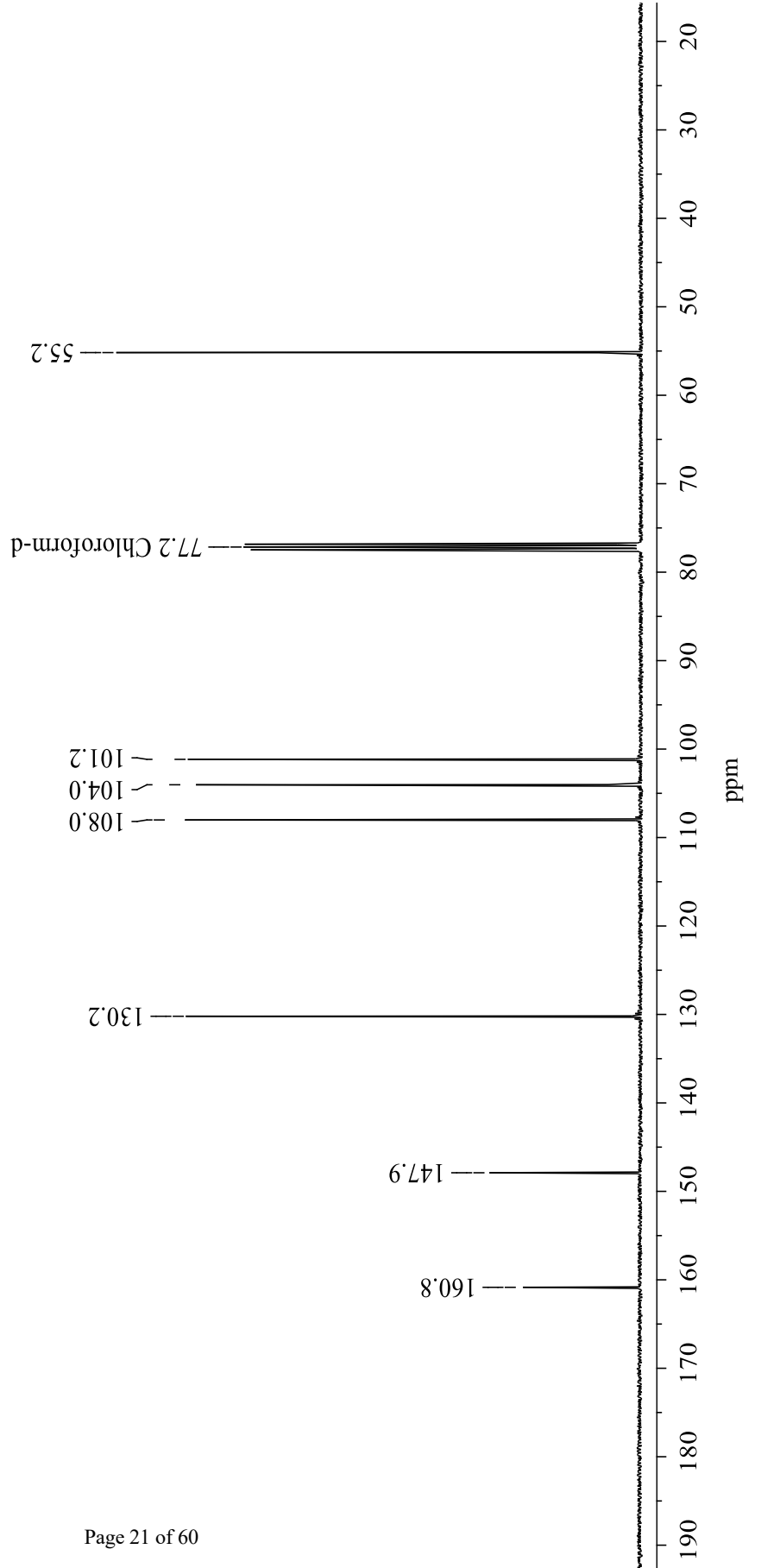
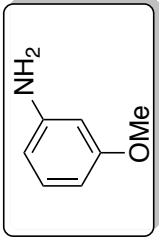


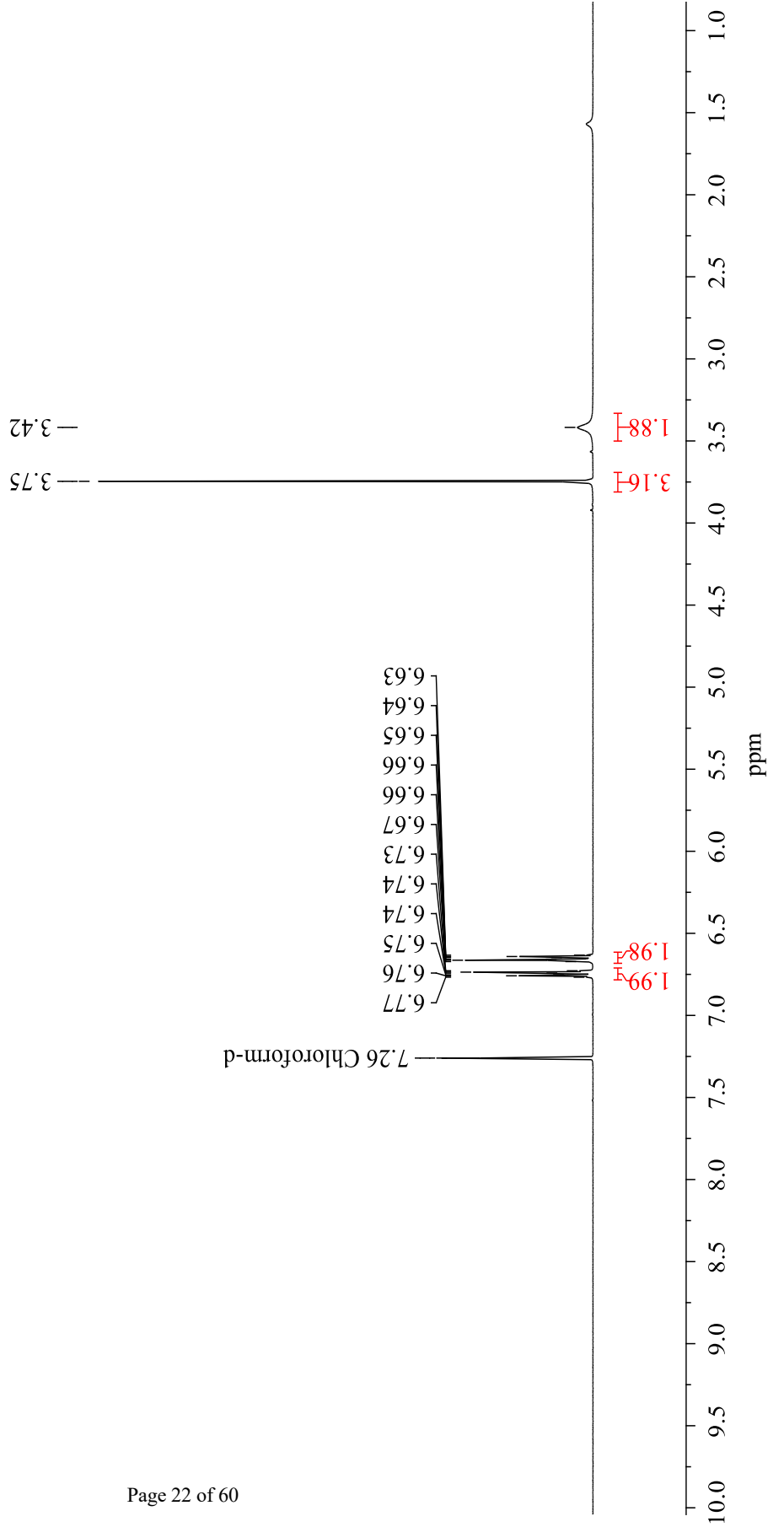
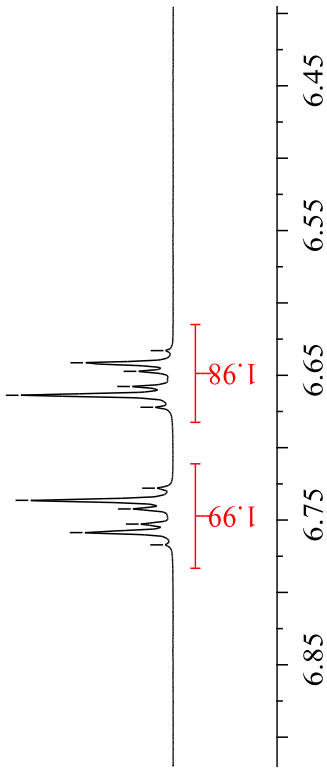
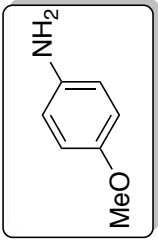


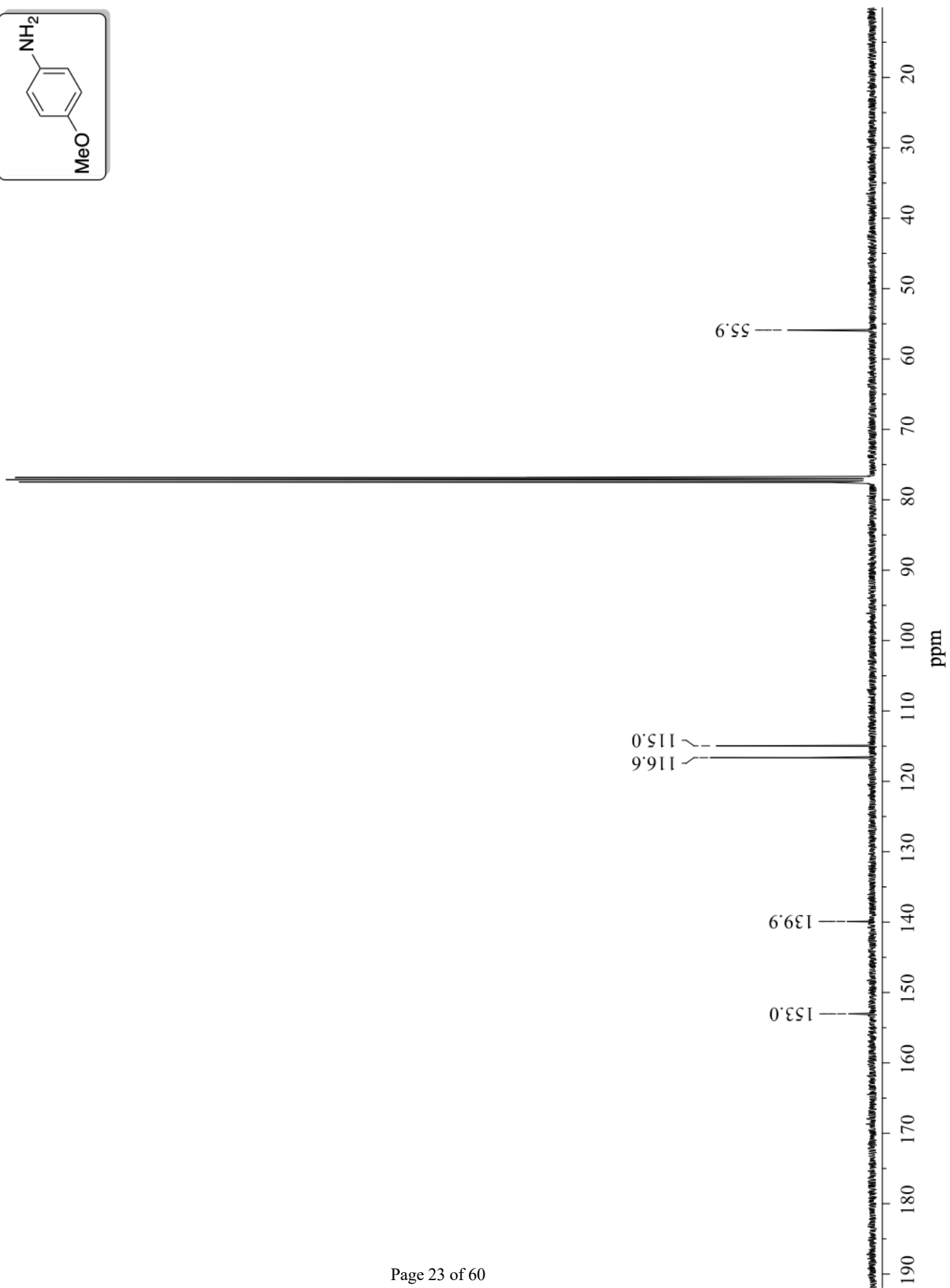
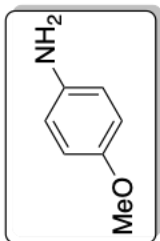


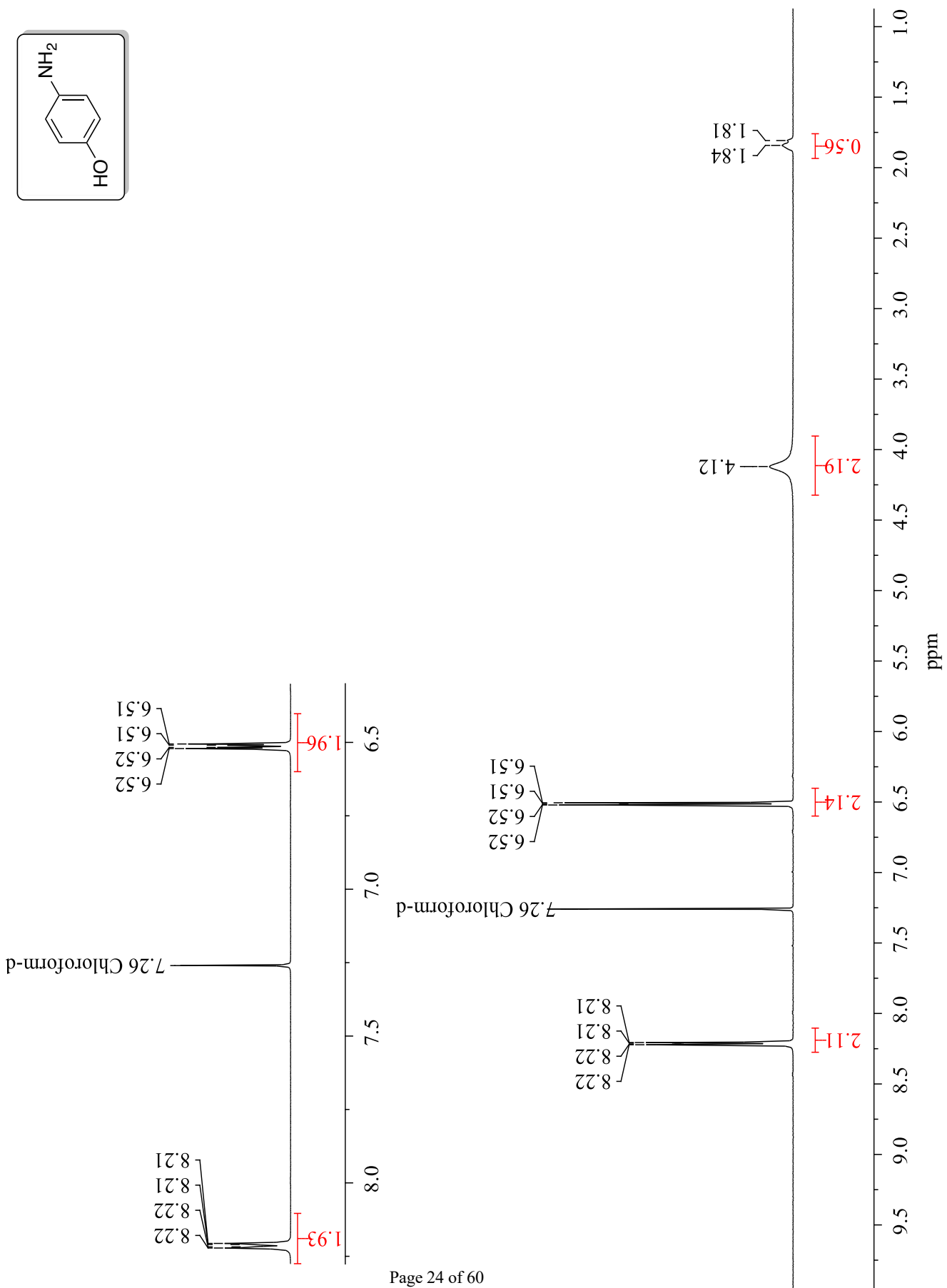
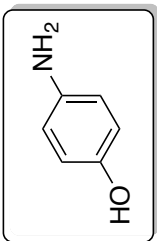


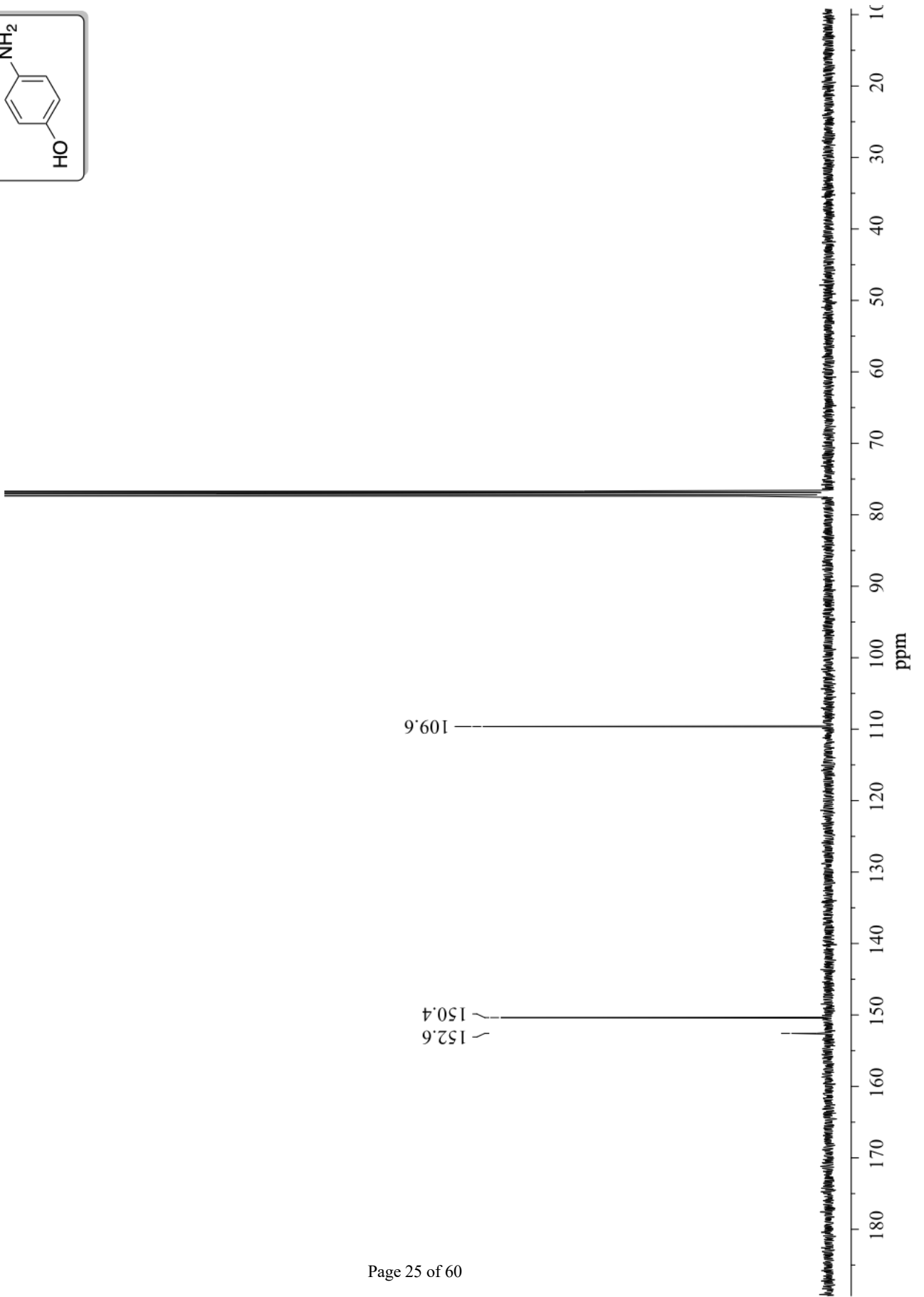
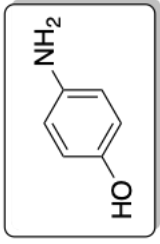


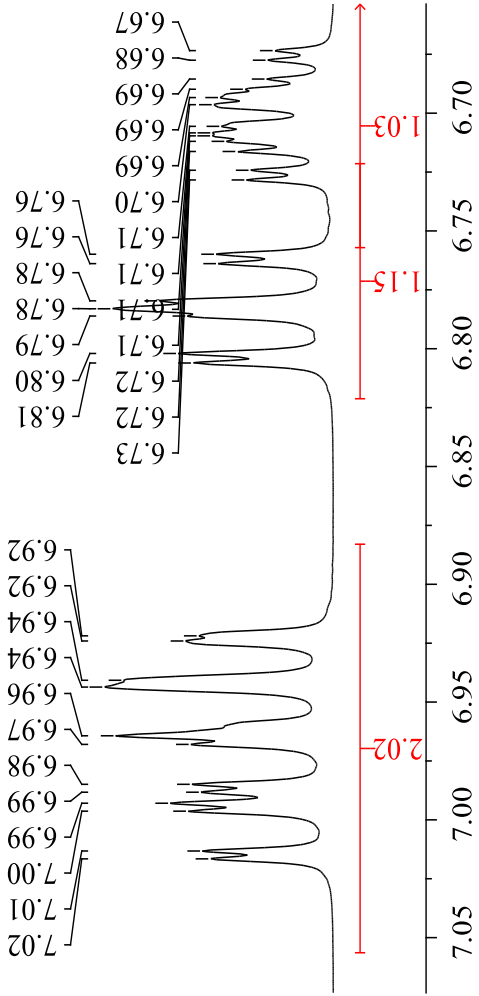
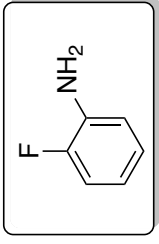




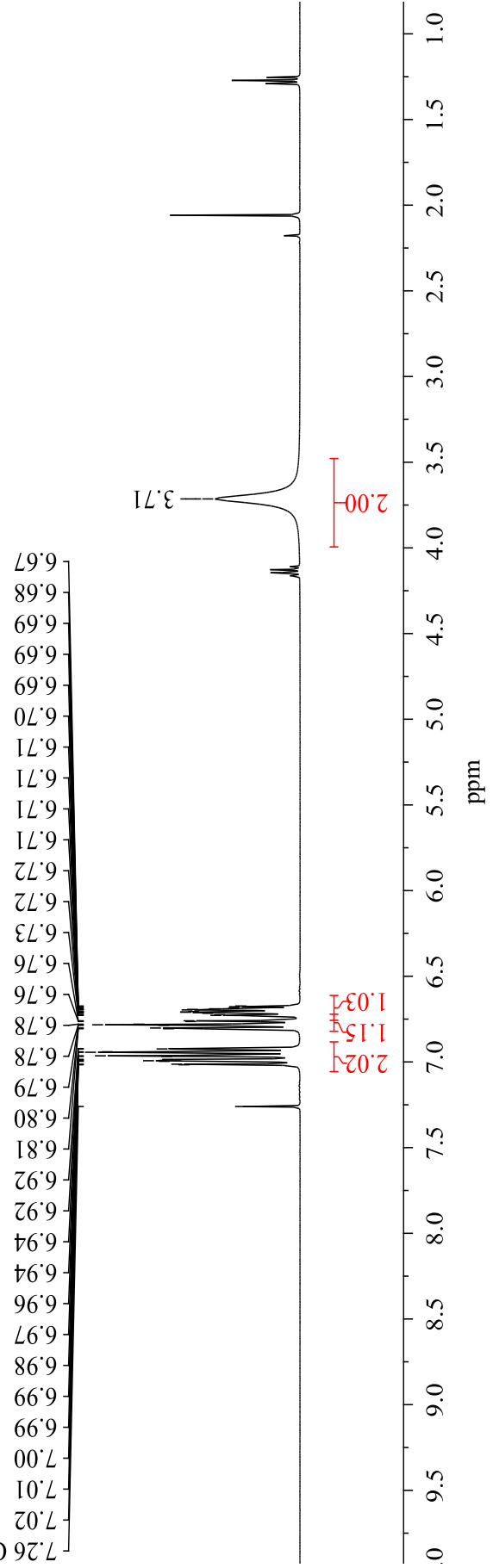


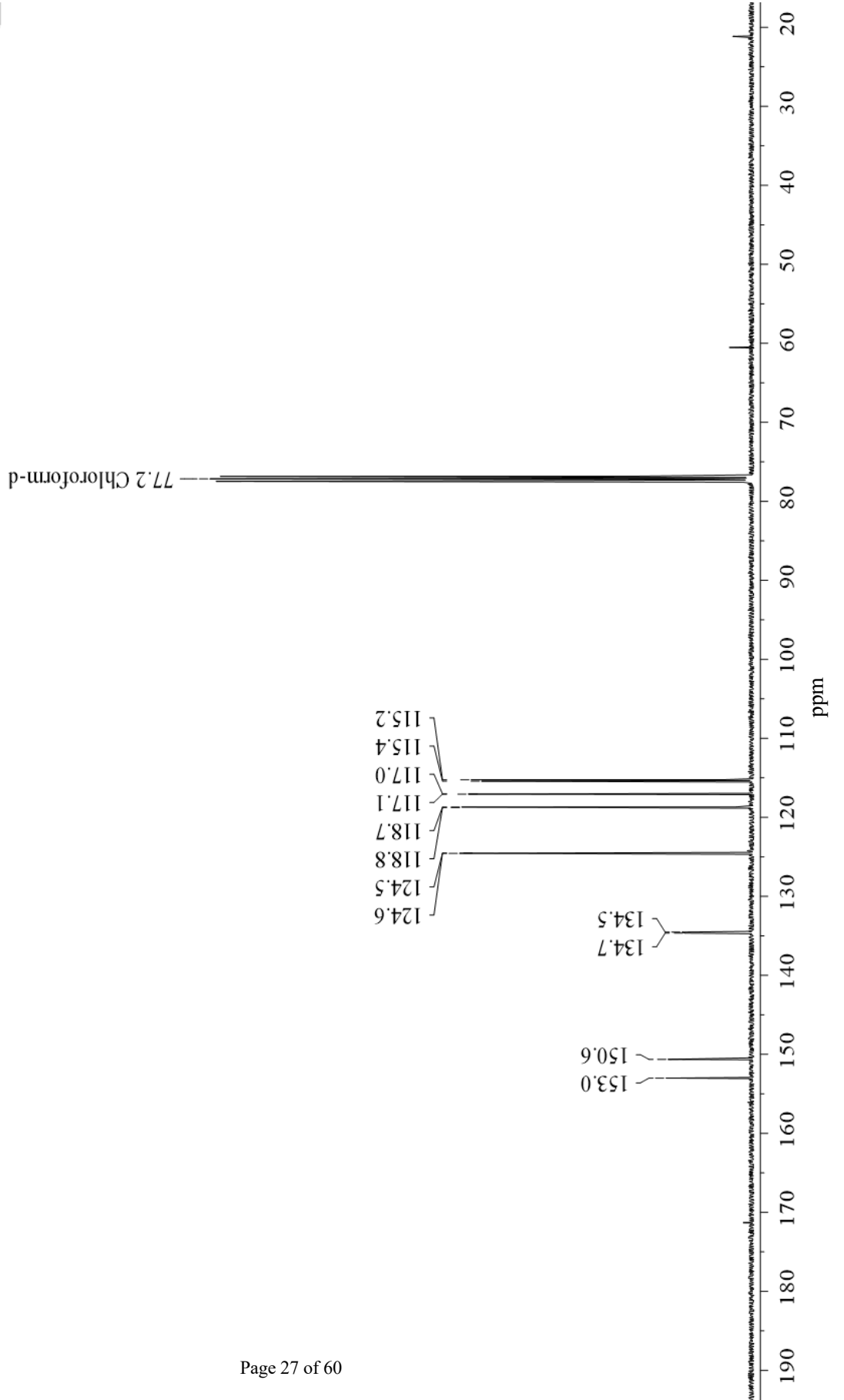
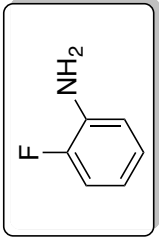


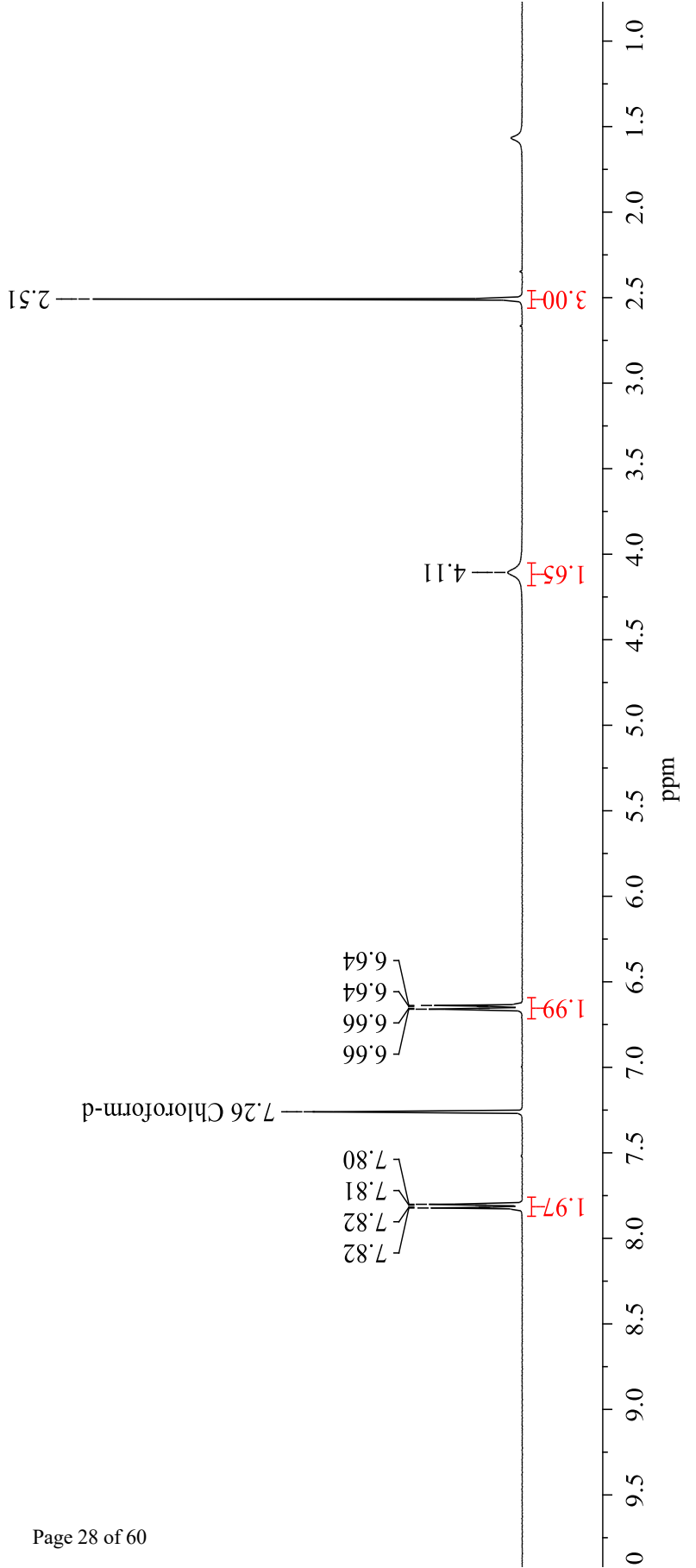
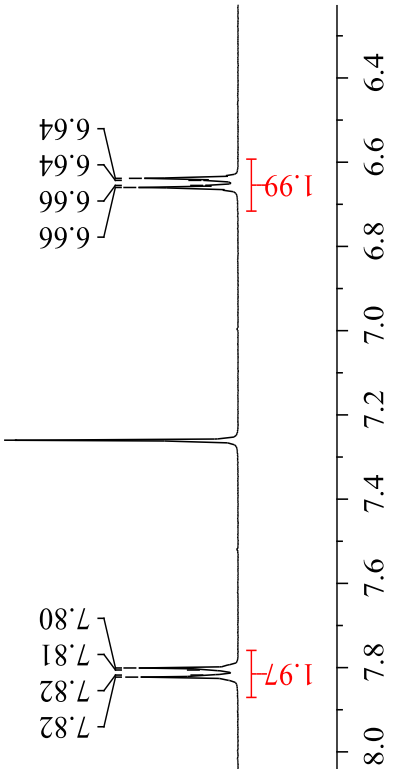
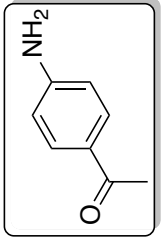


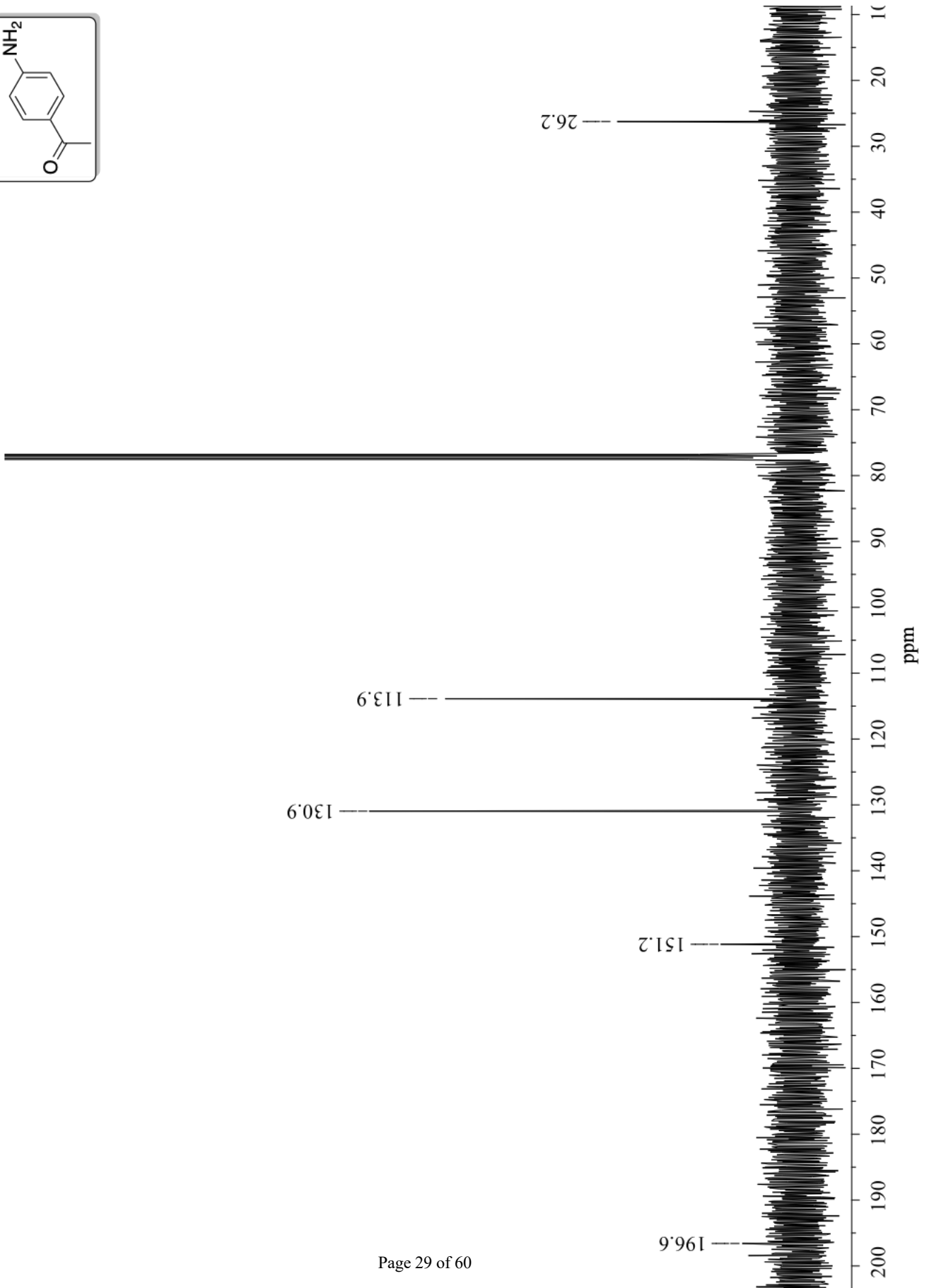
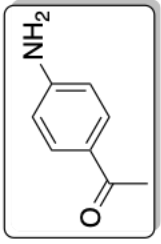


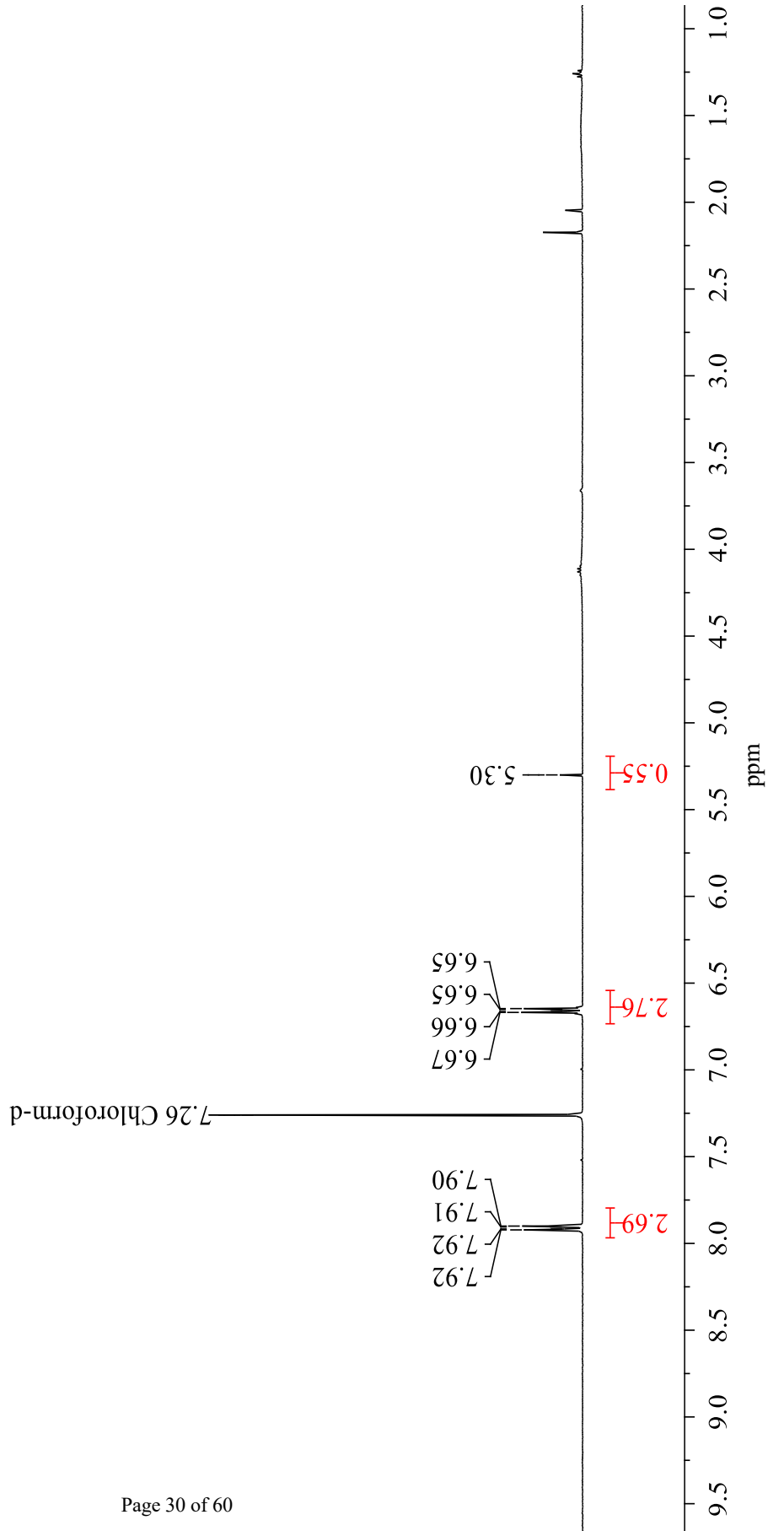
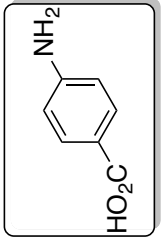
Chloroform-d
09 26 of 69 Page

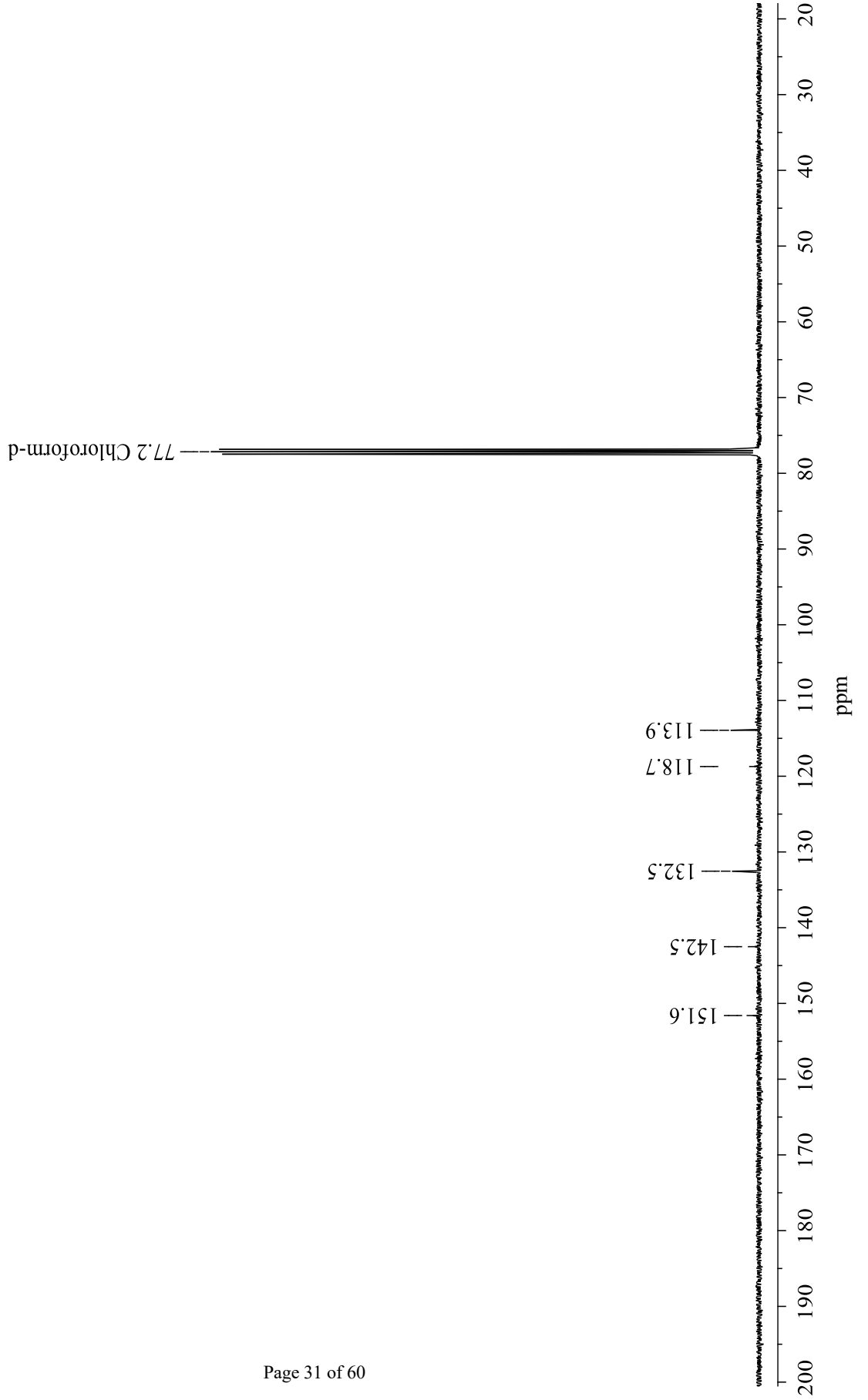
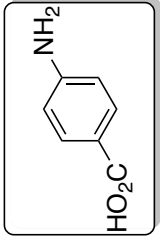


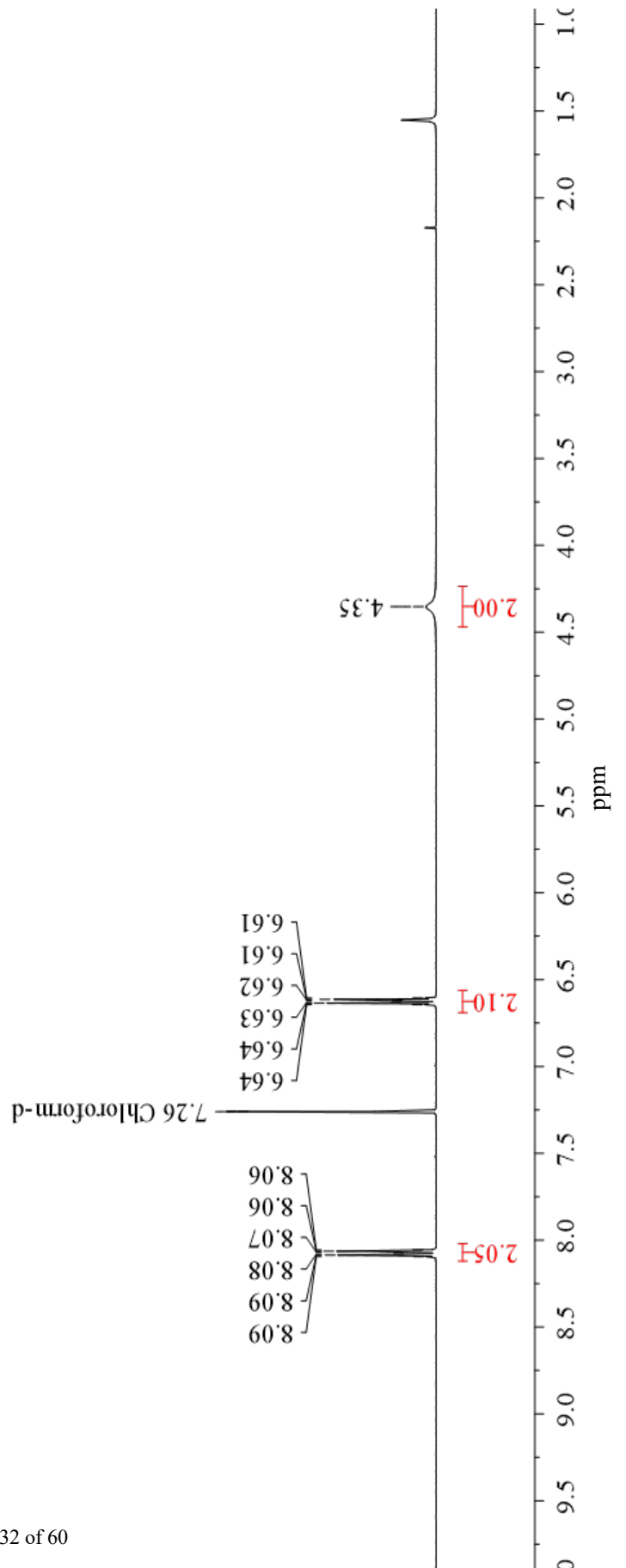
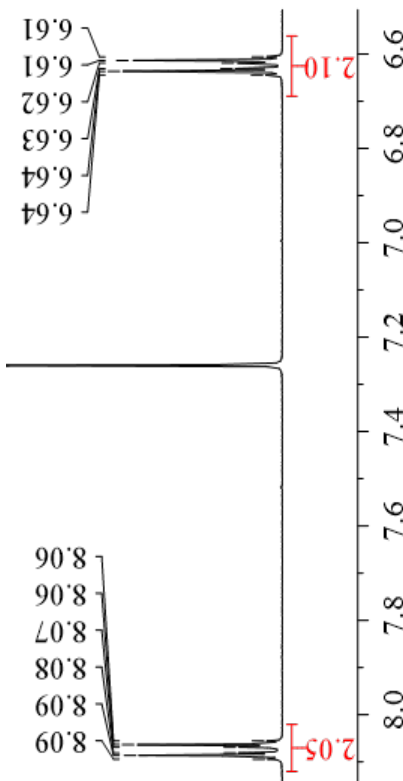
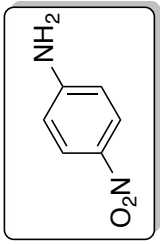


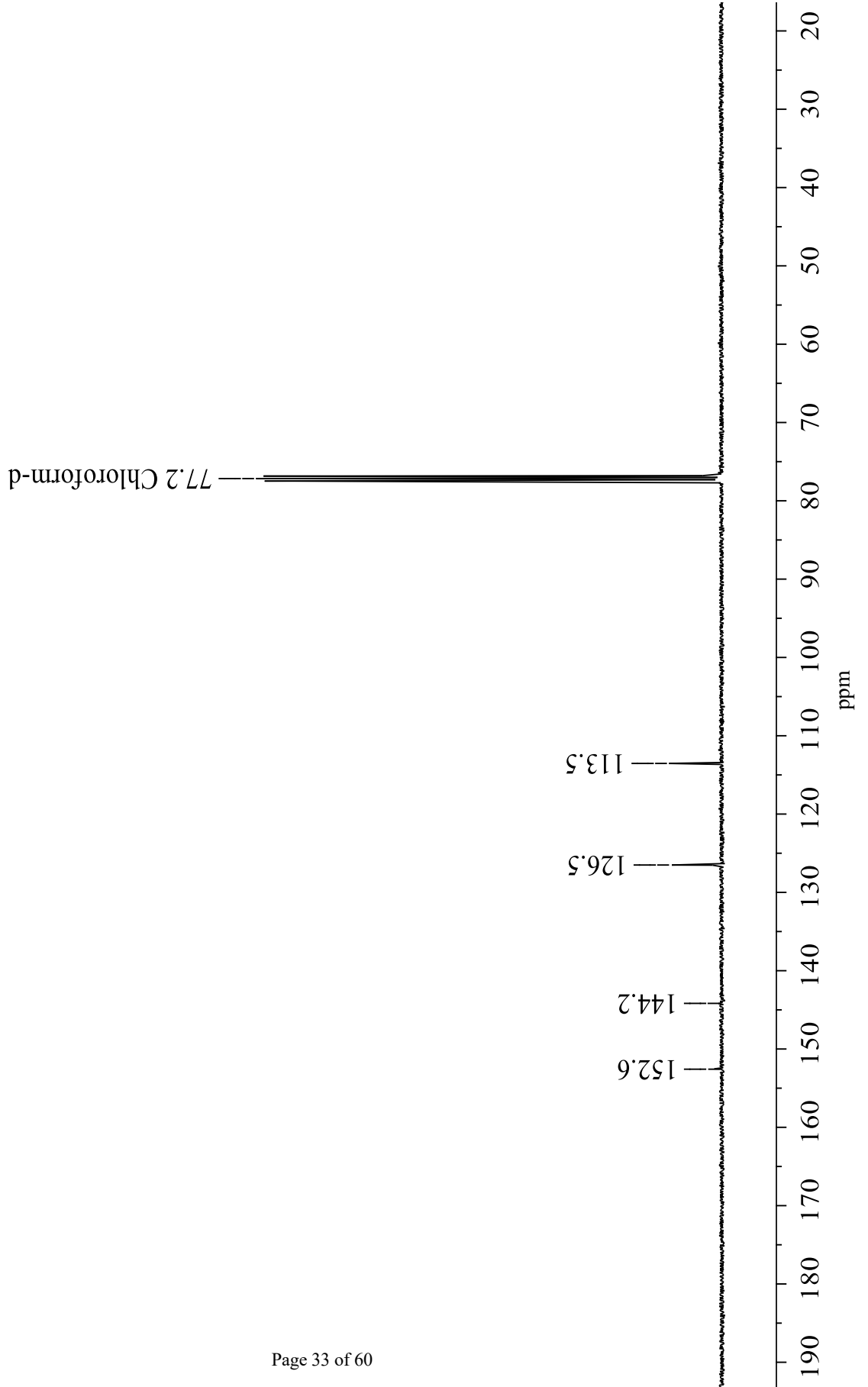
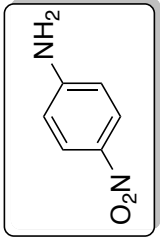


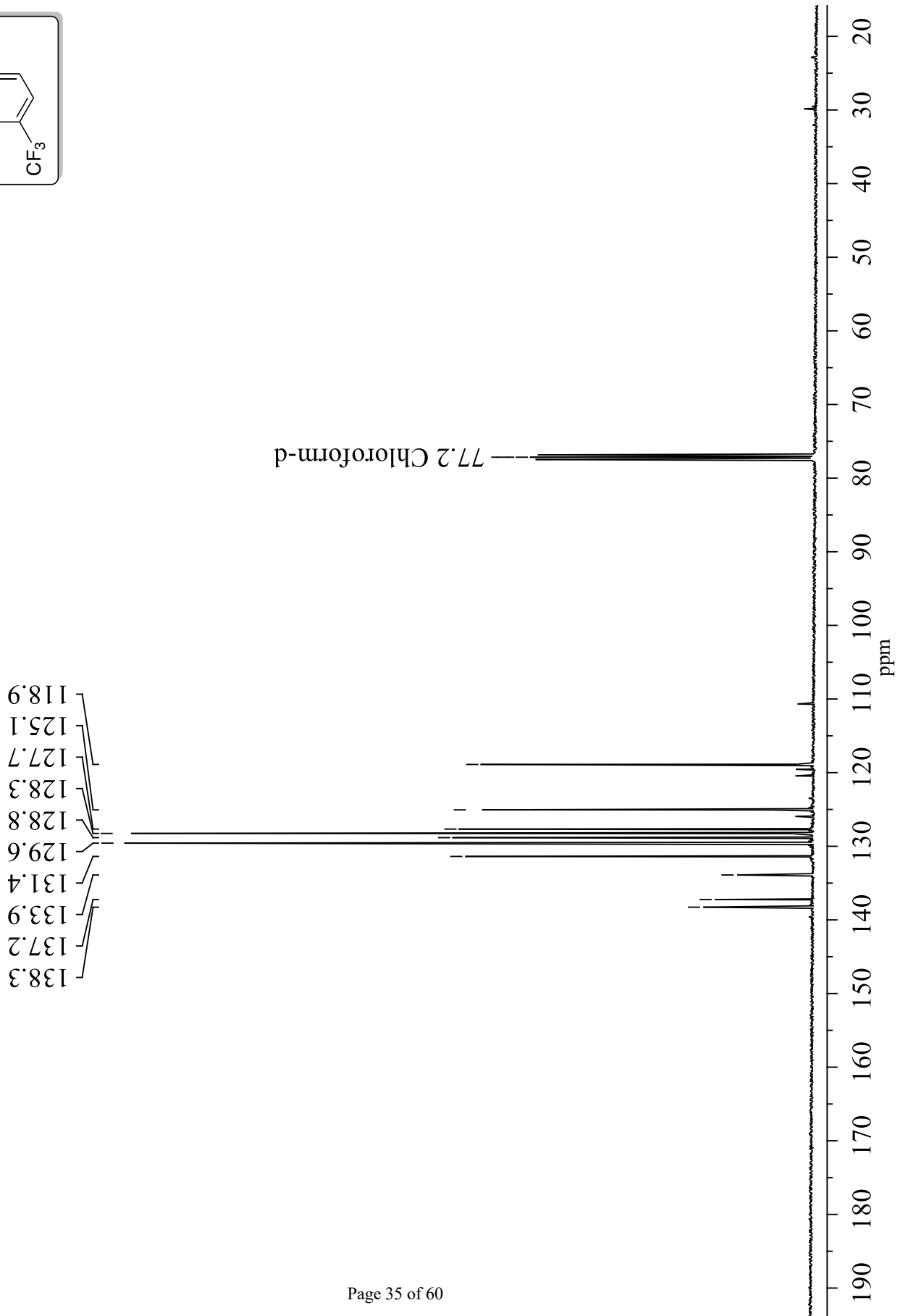
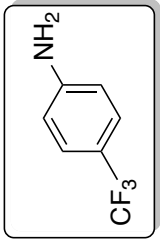


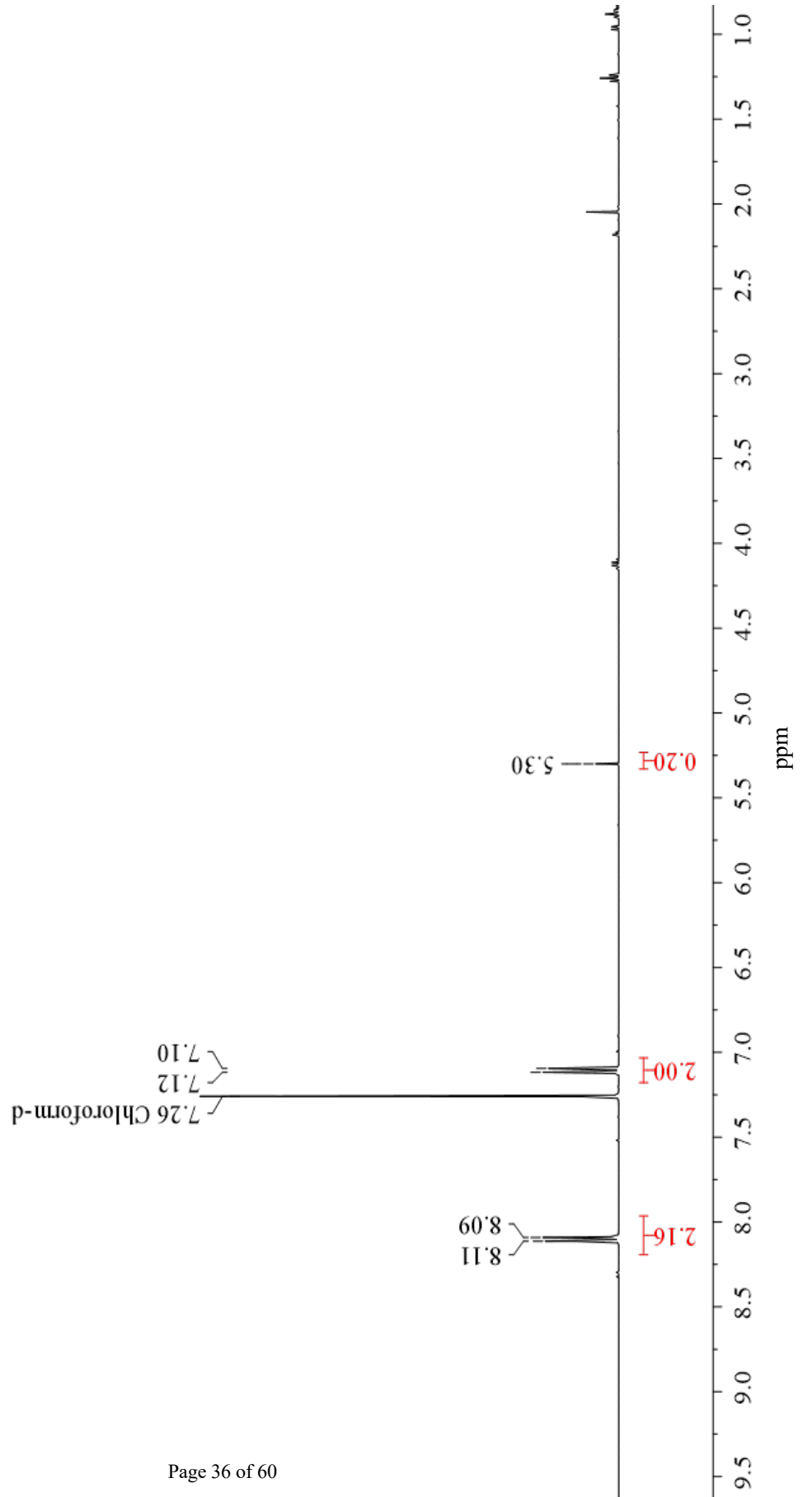
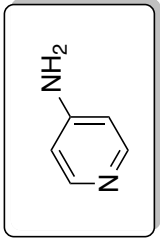


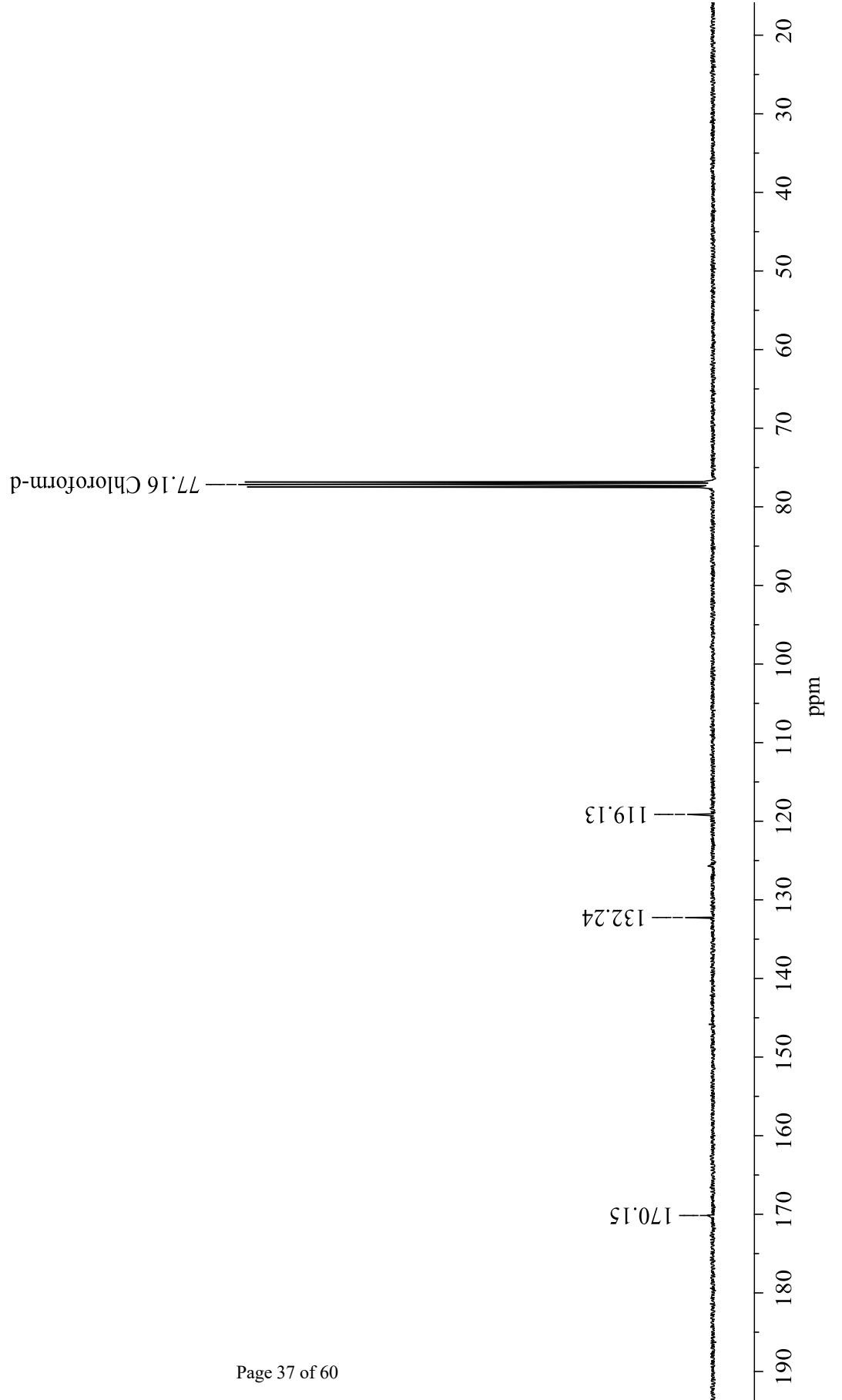
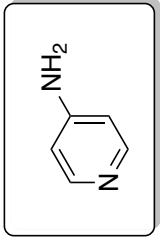


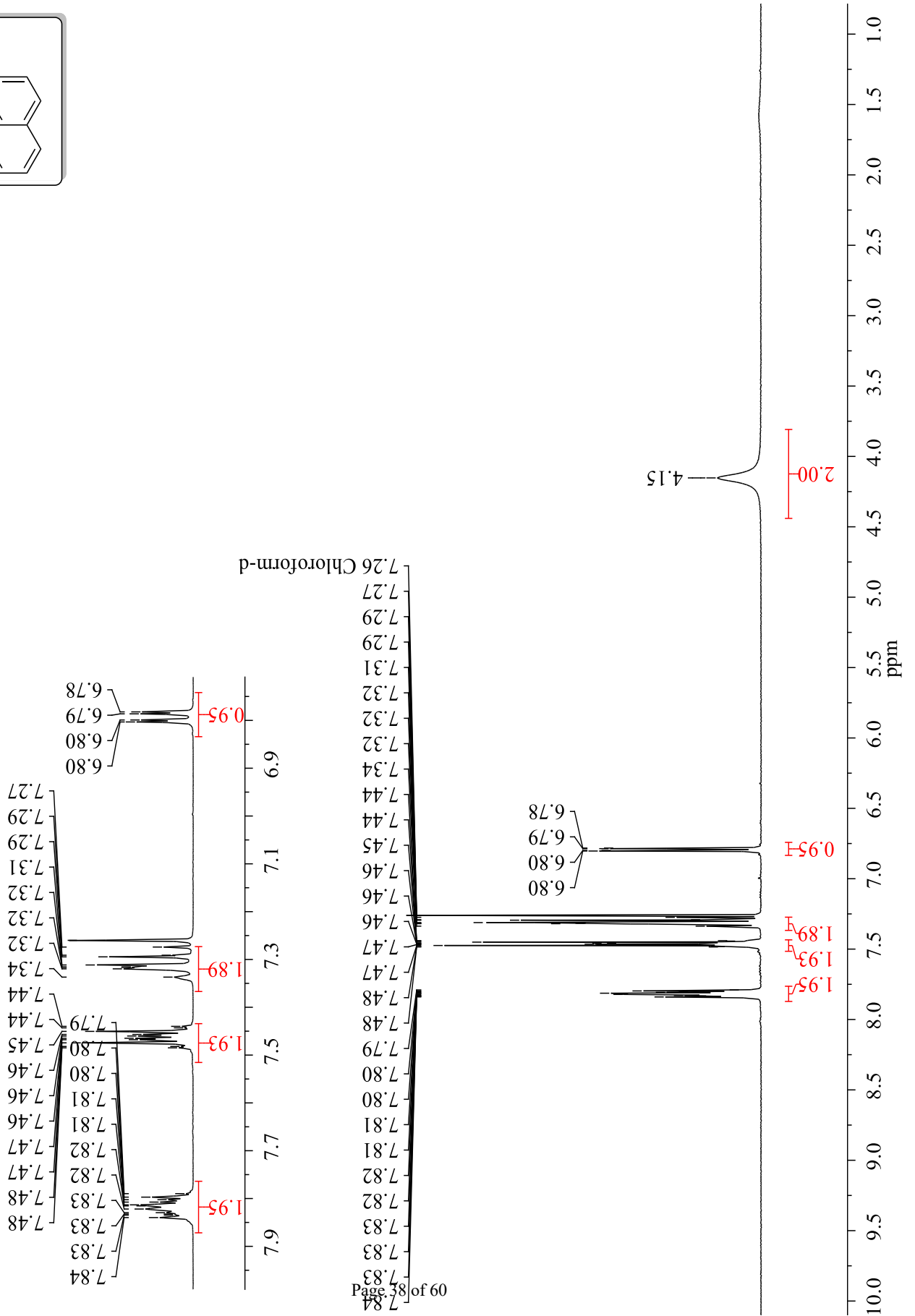
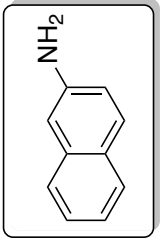


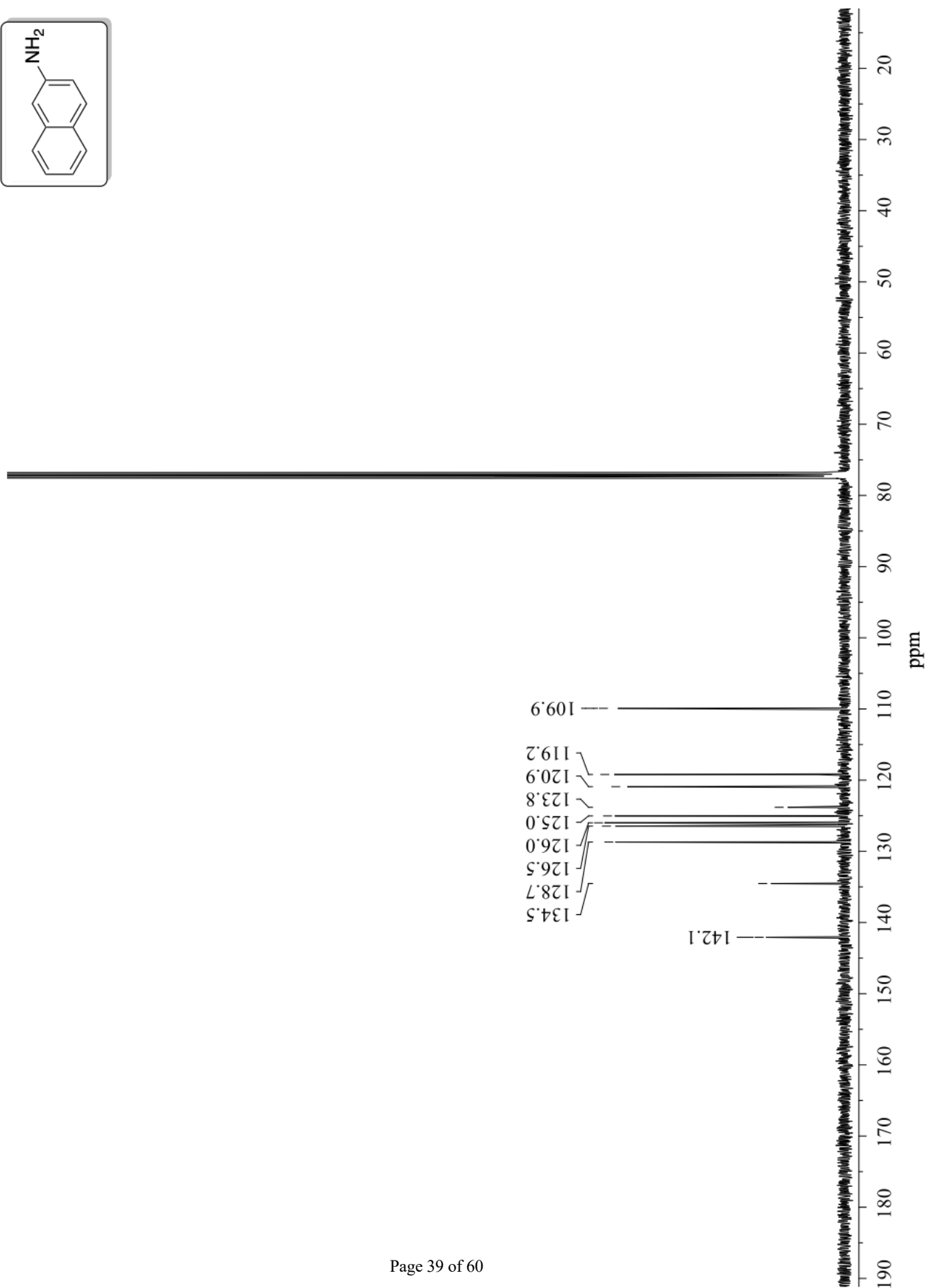
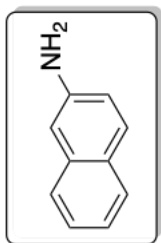


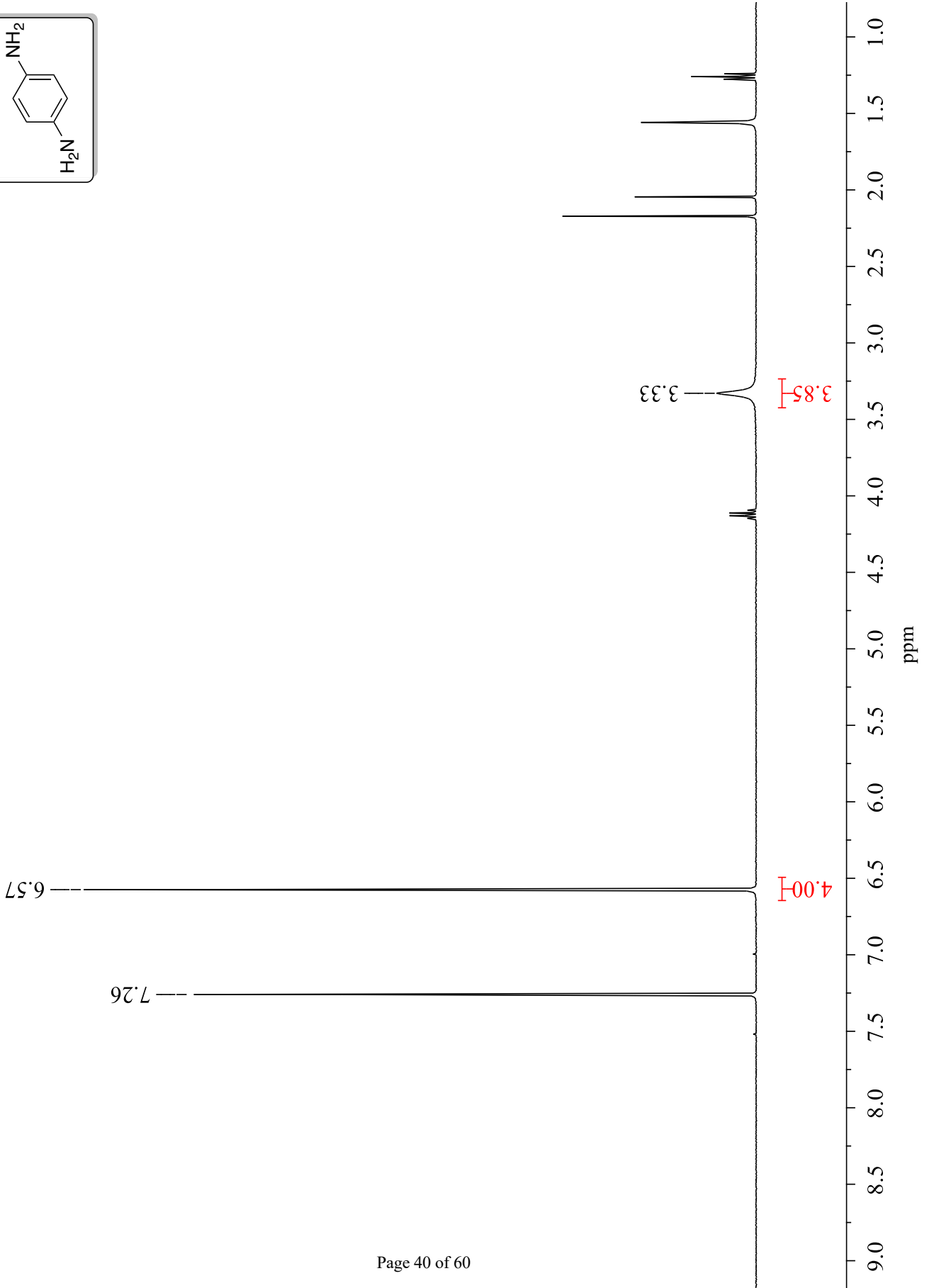
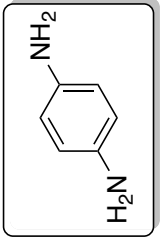


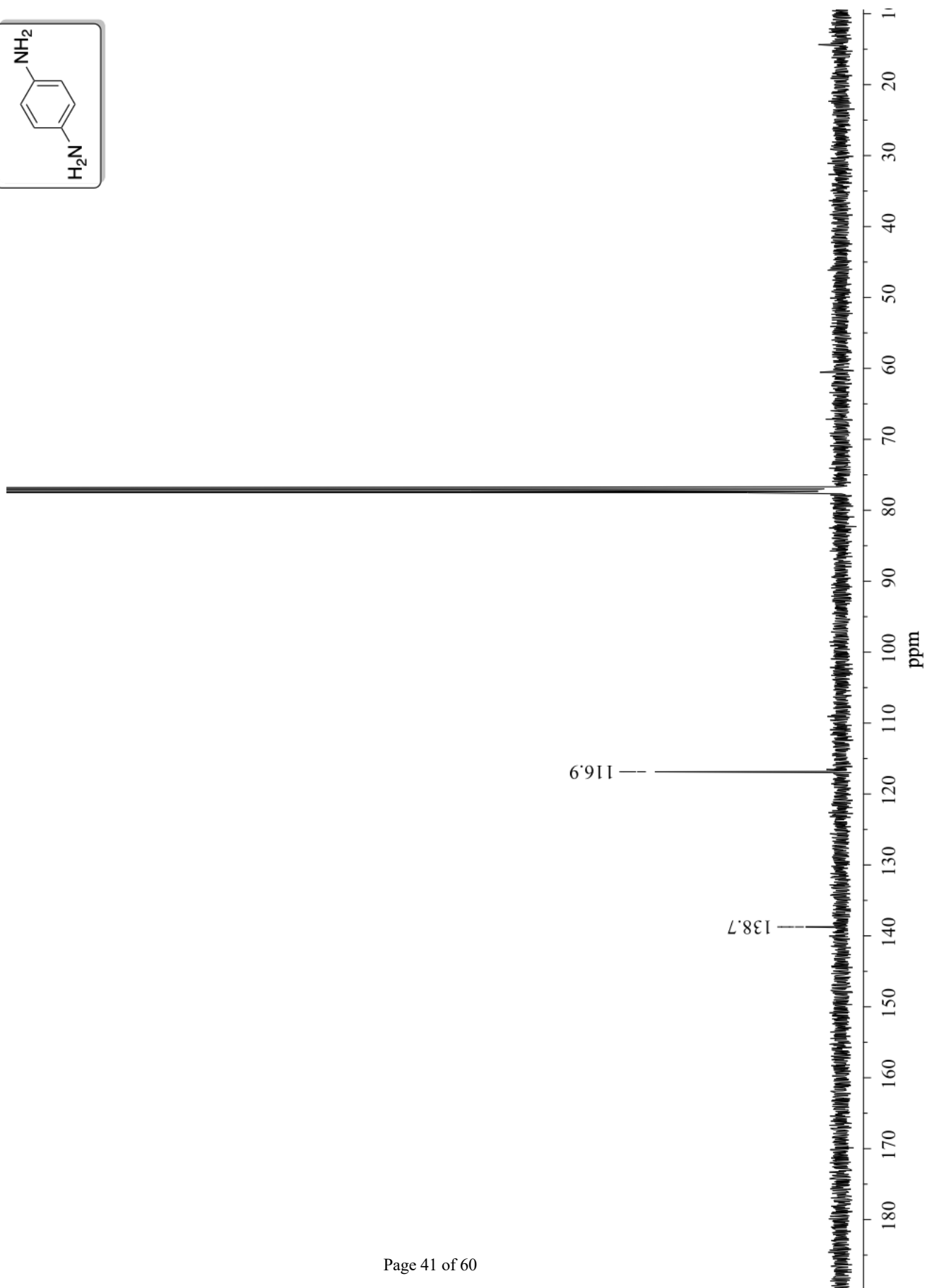
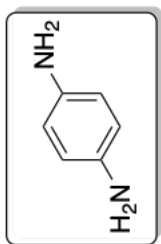


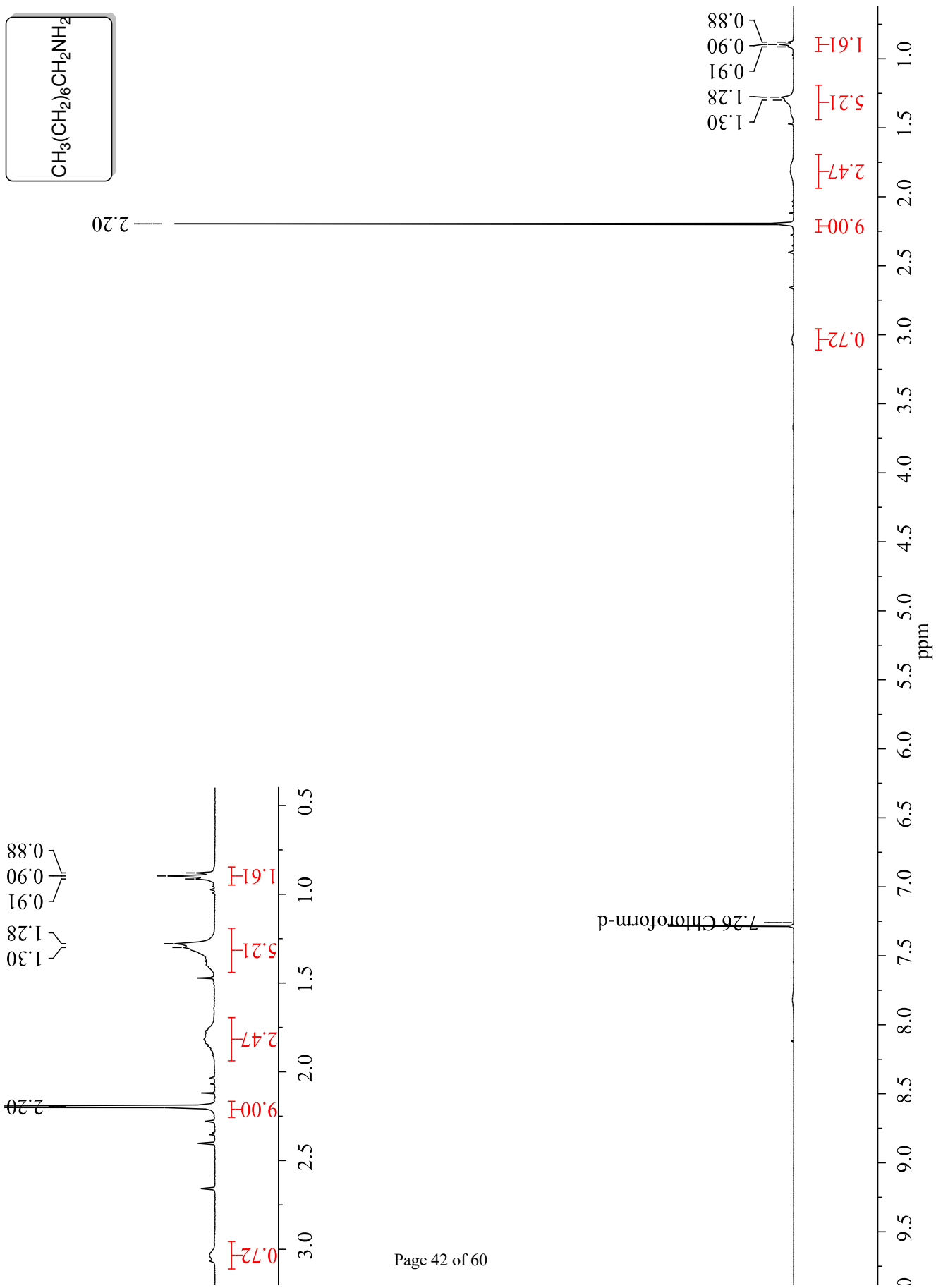
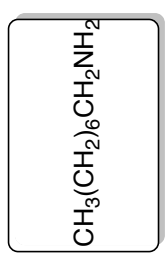


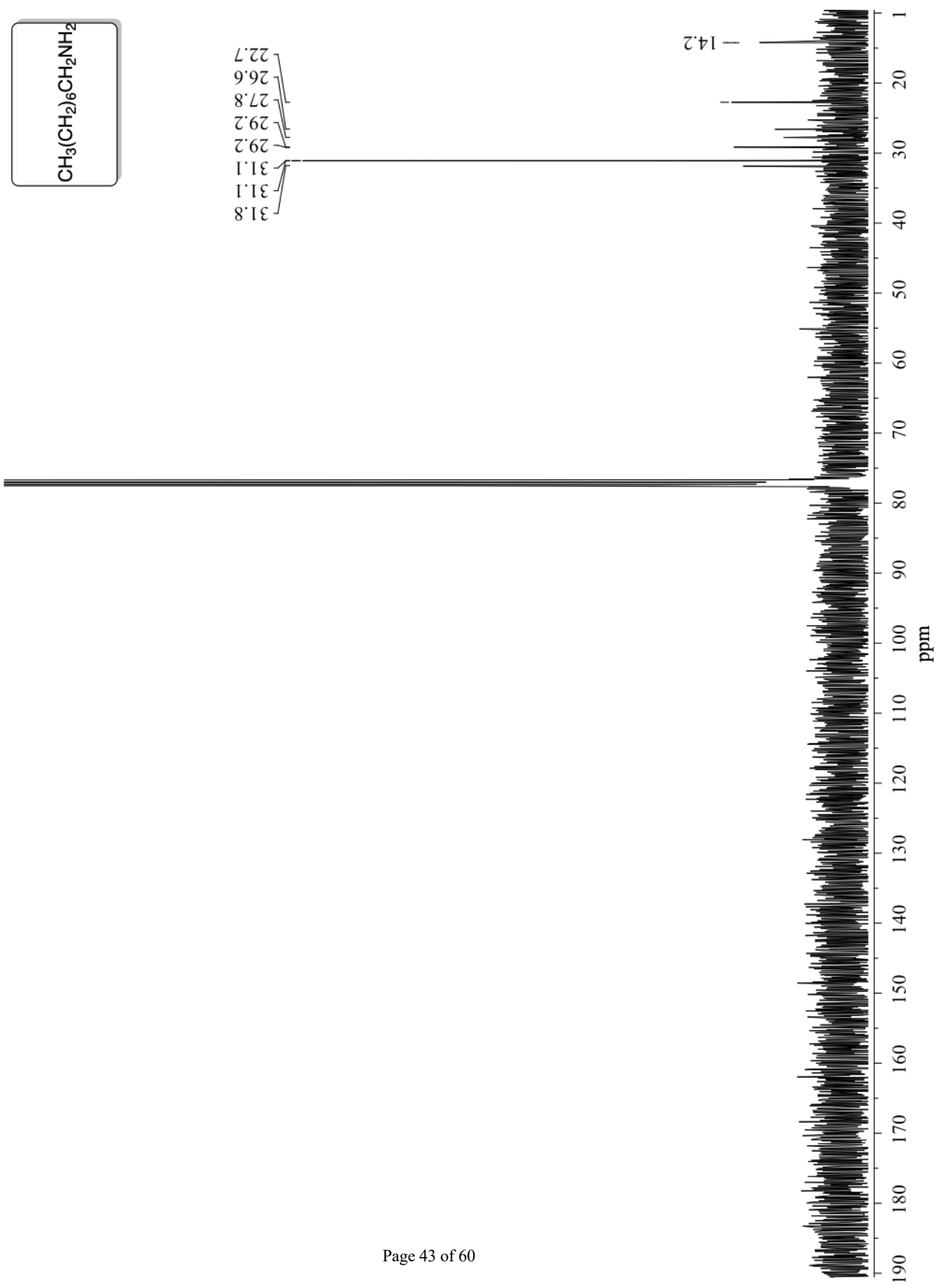


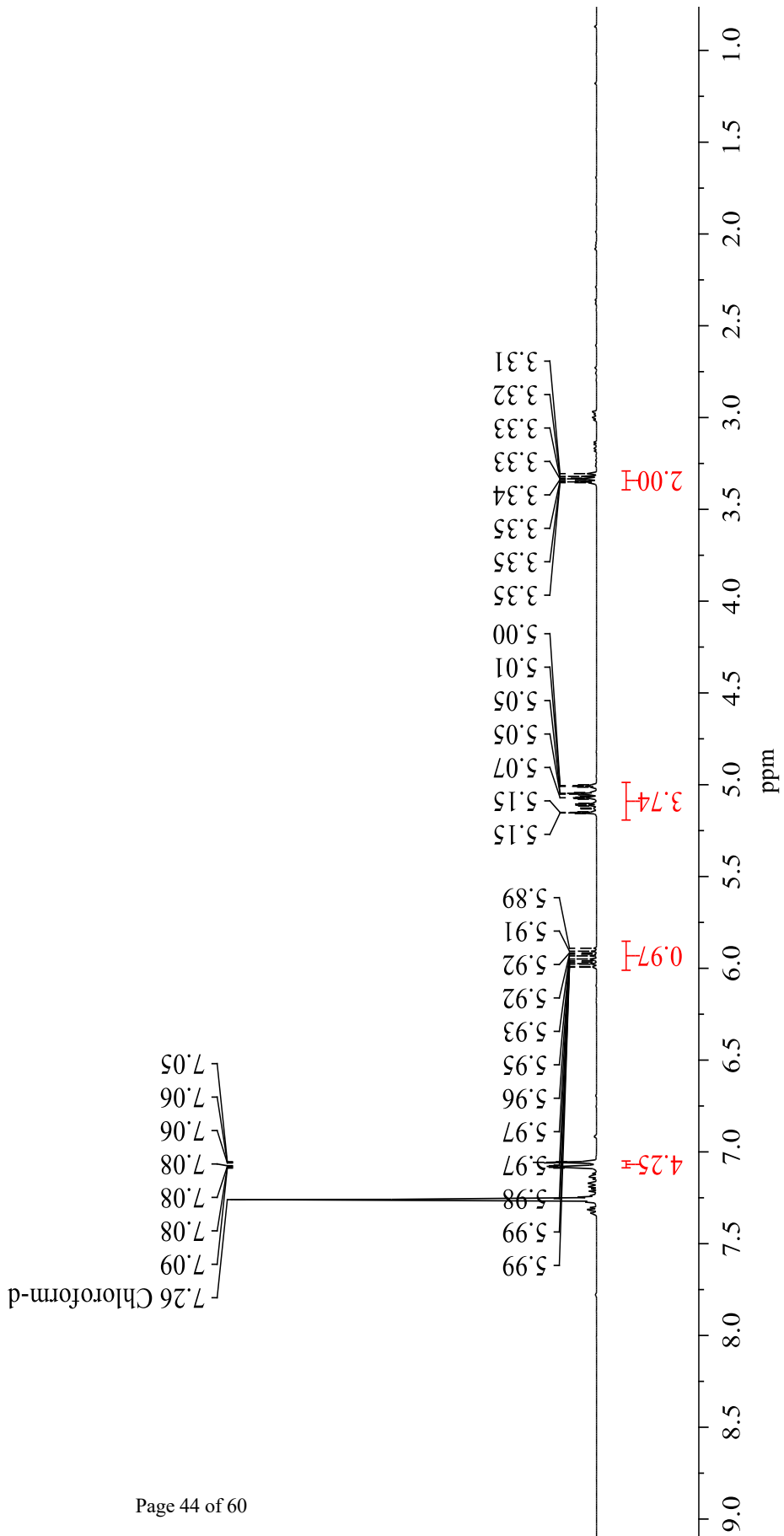
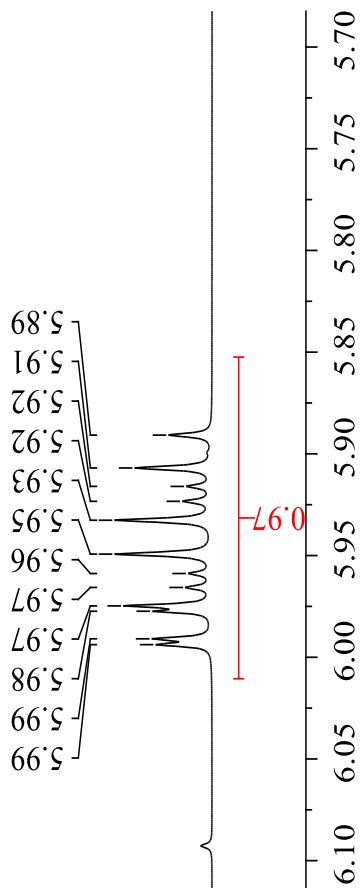
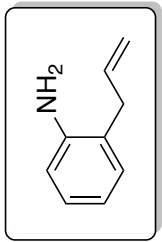


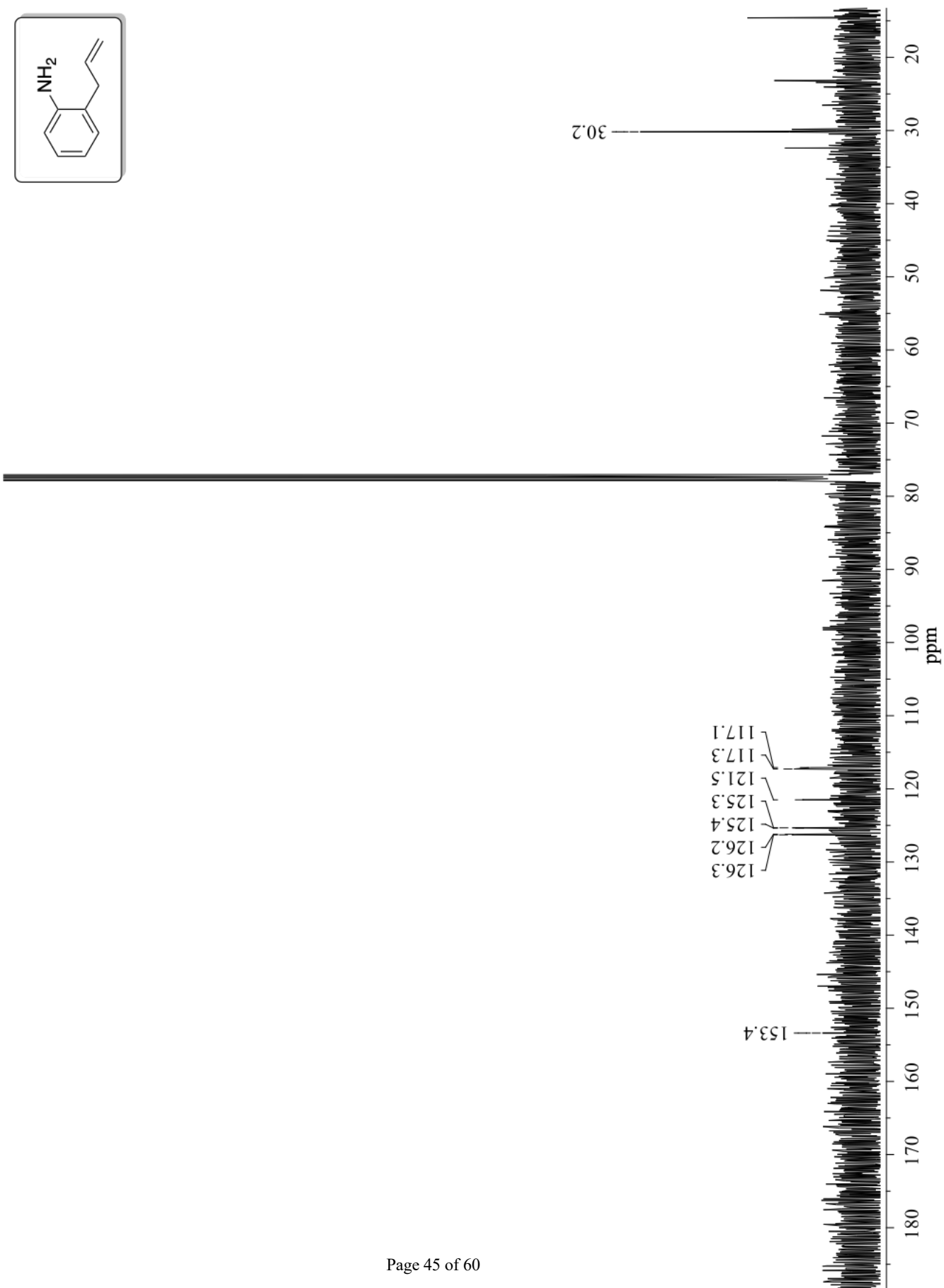
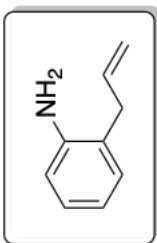


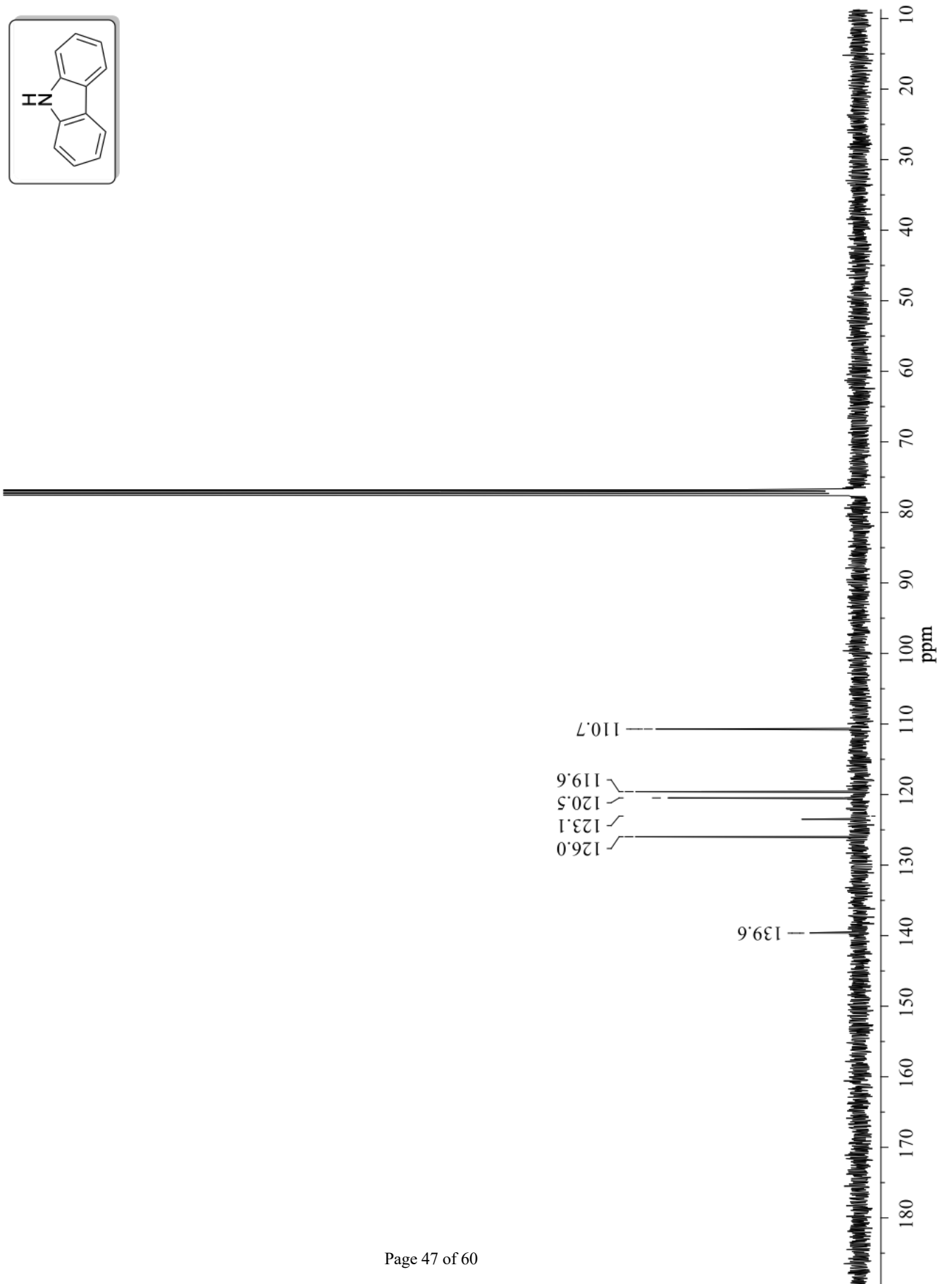
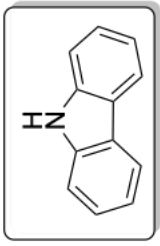


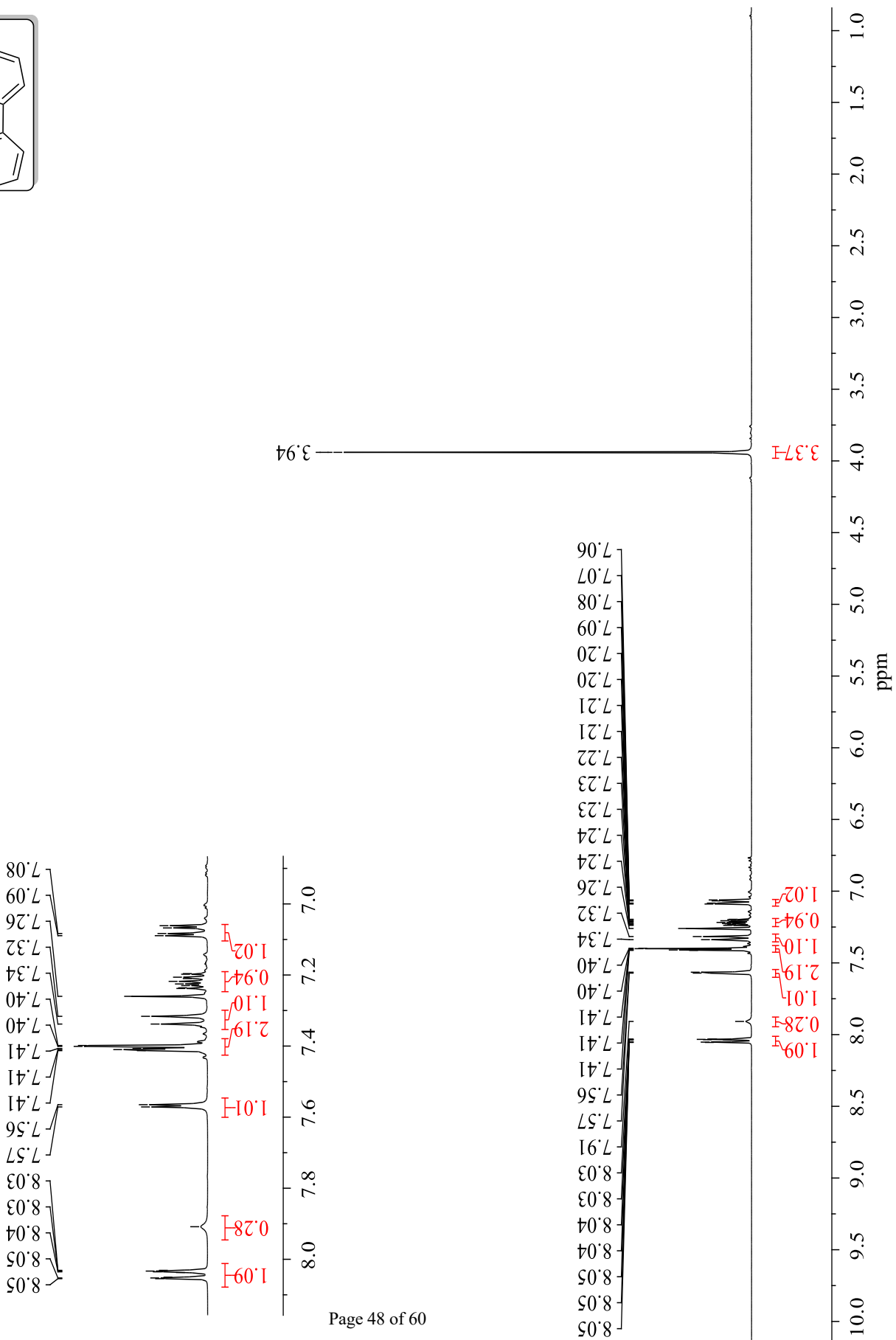
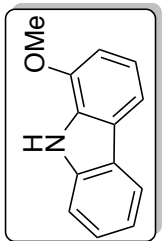


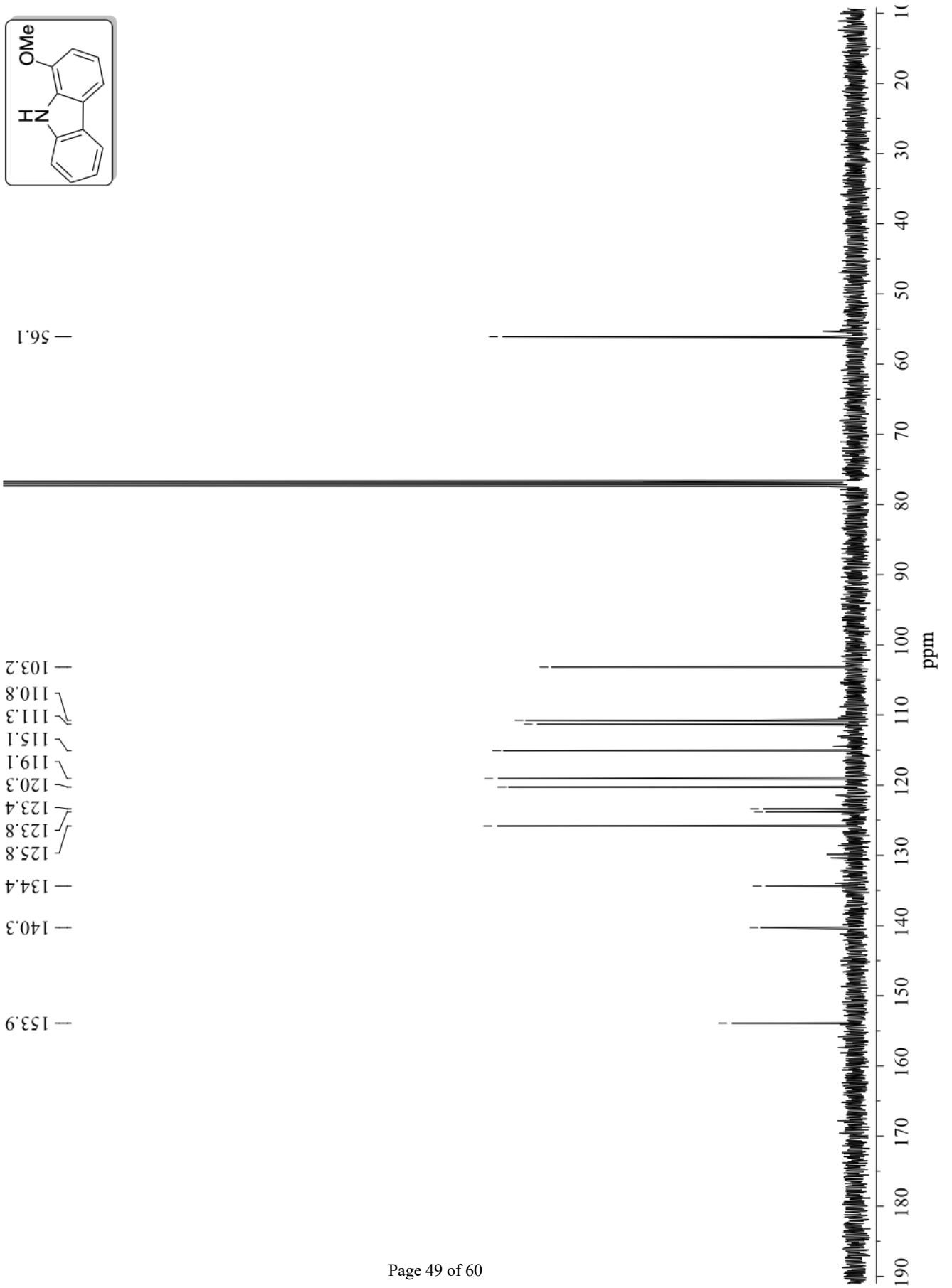
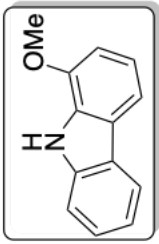


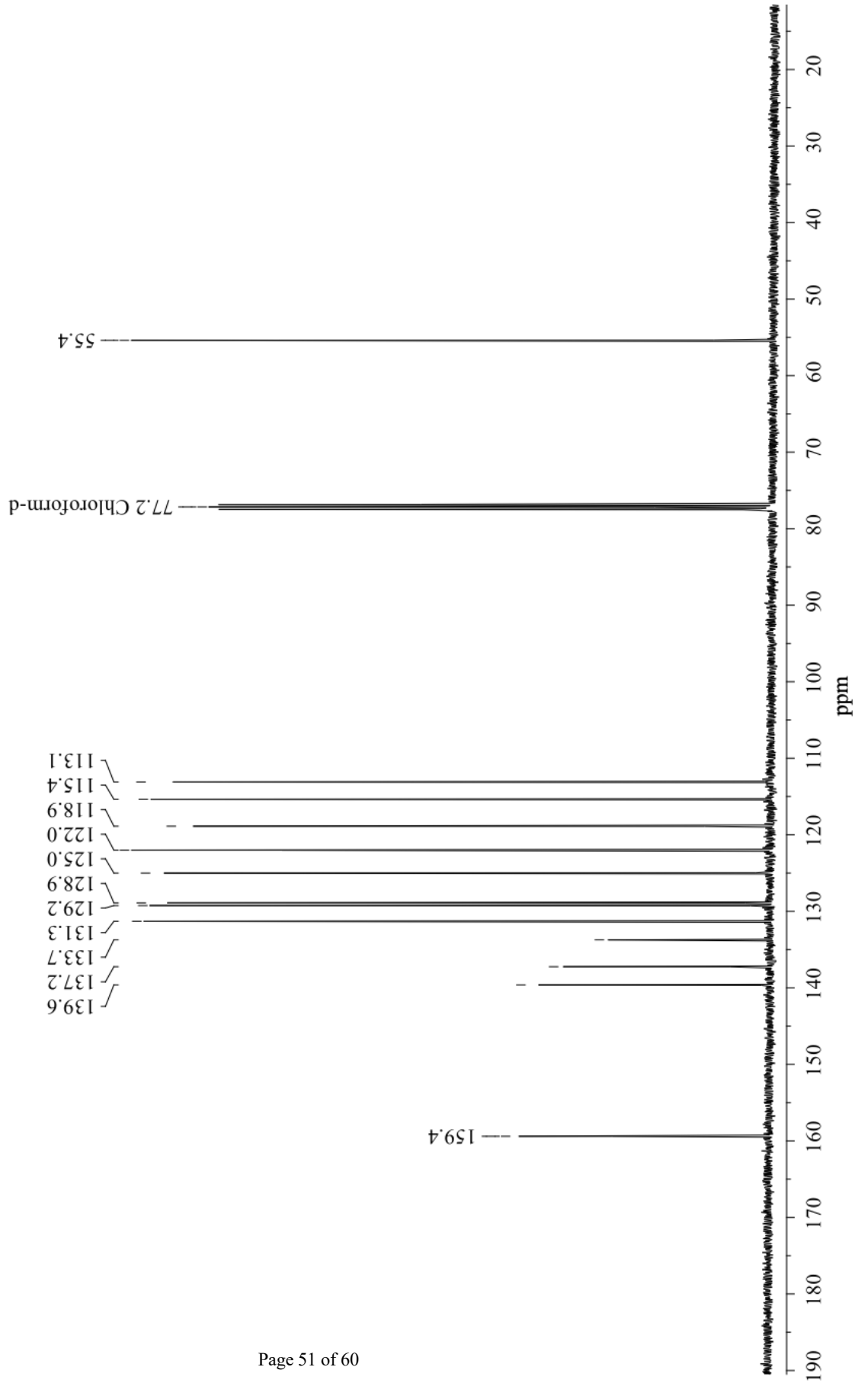
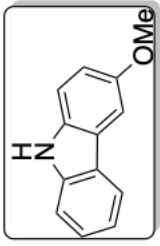


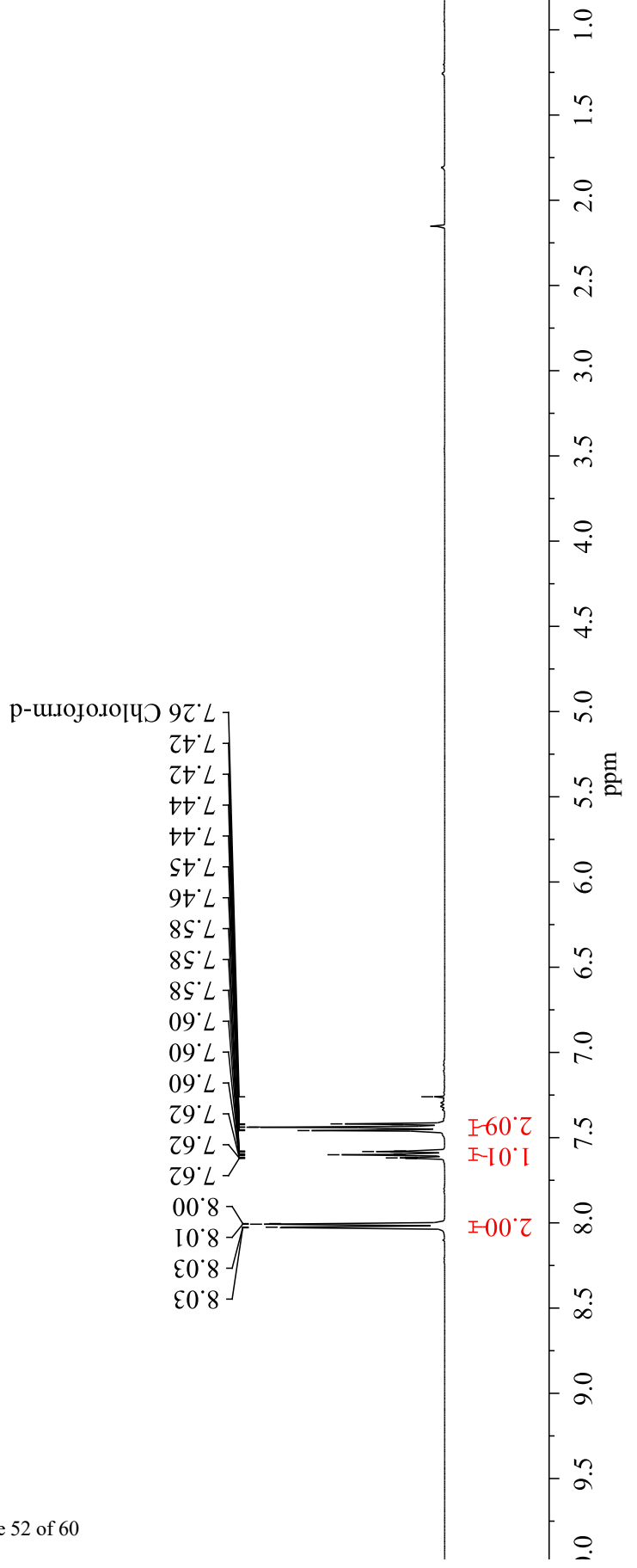
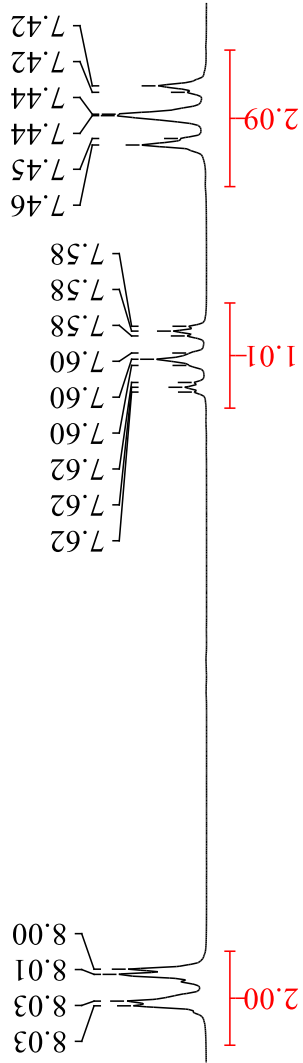
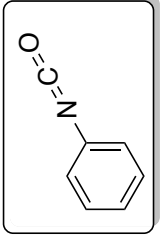


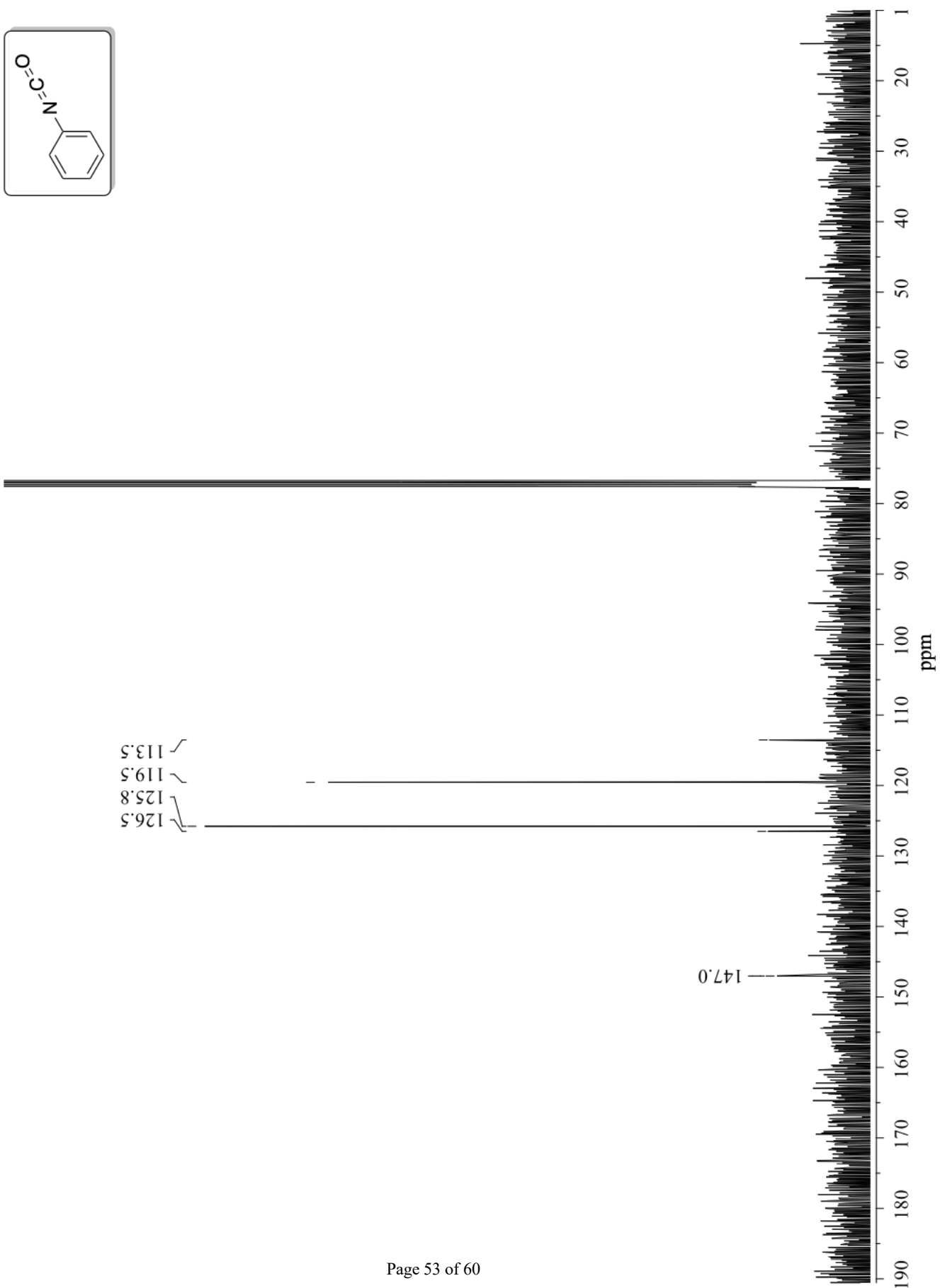
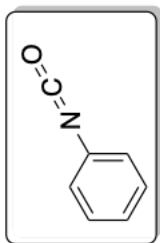












Other products characterization

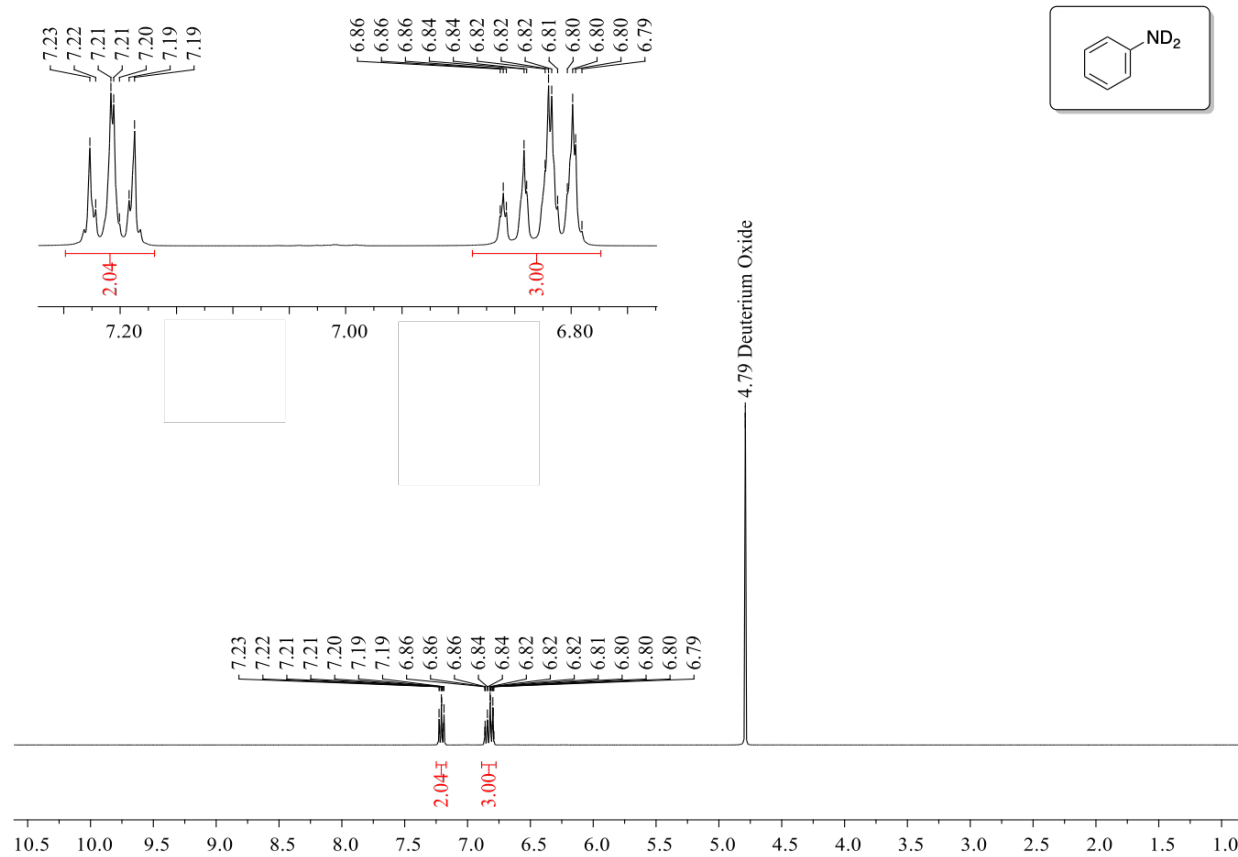


Figure S2. ^1H NMR spectrum of deuterated aniline obtained from the reaction of phenylazide in deuterated water.

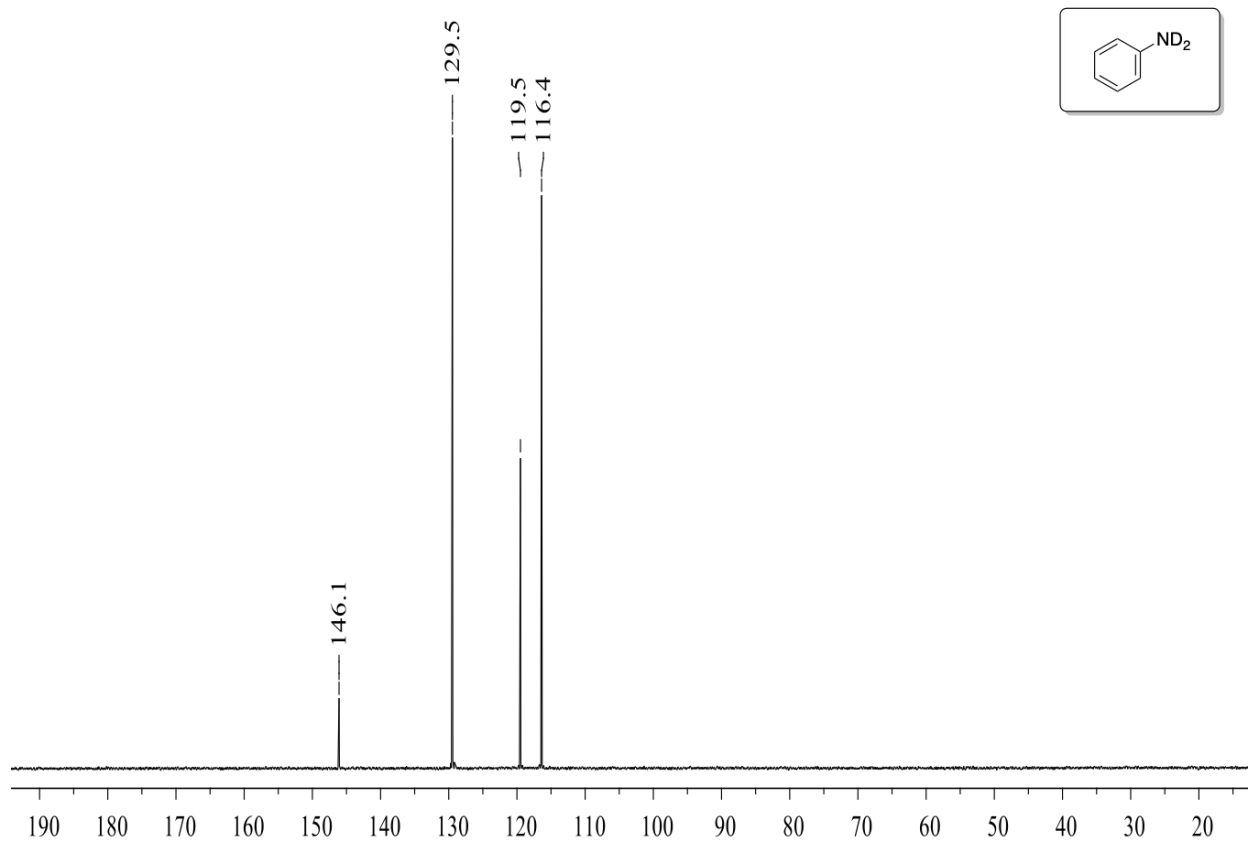


Figure S3. ¹³C NMR spectrum of deuterated aniline obtained from the reaction of phenylazide in deuterated water.

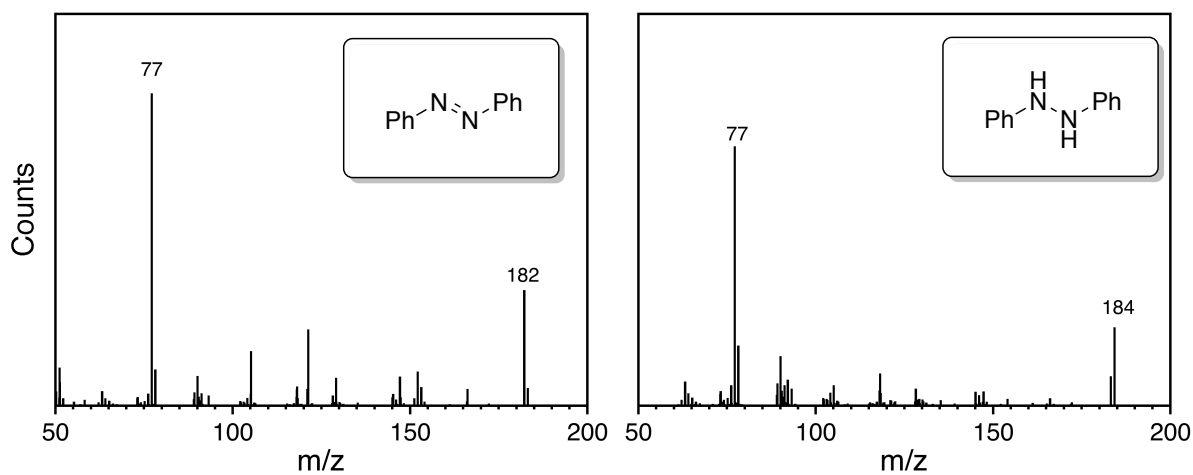


Figure S4. Mass spectra of azobenzene (left) obtained from the reaction run in acetonitrile, and 1,2-diphenylhydrazine (right) obtained from the reaction of azobenzene in water (Scheme 3).

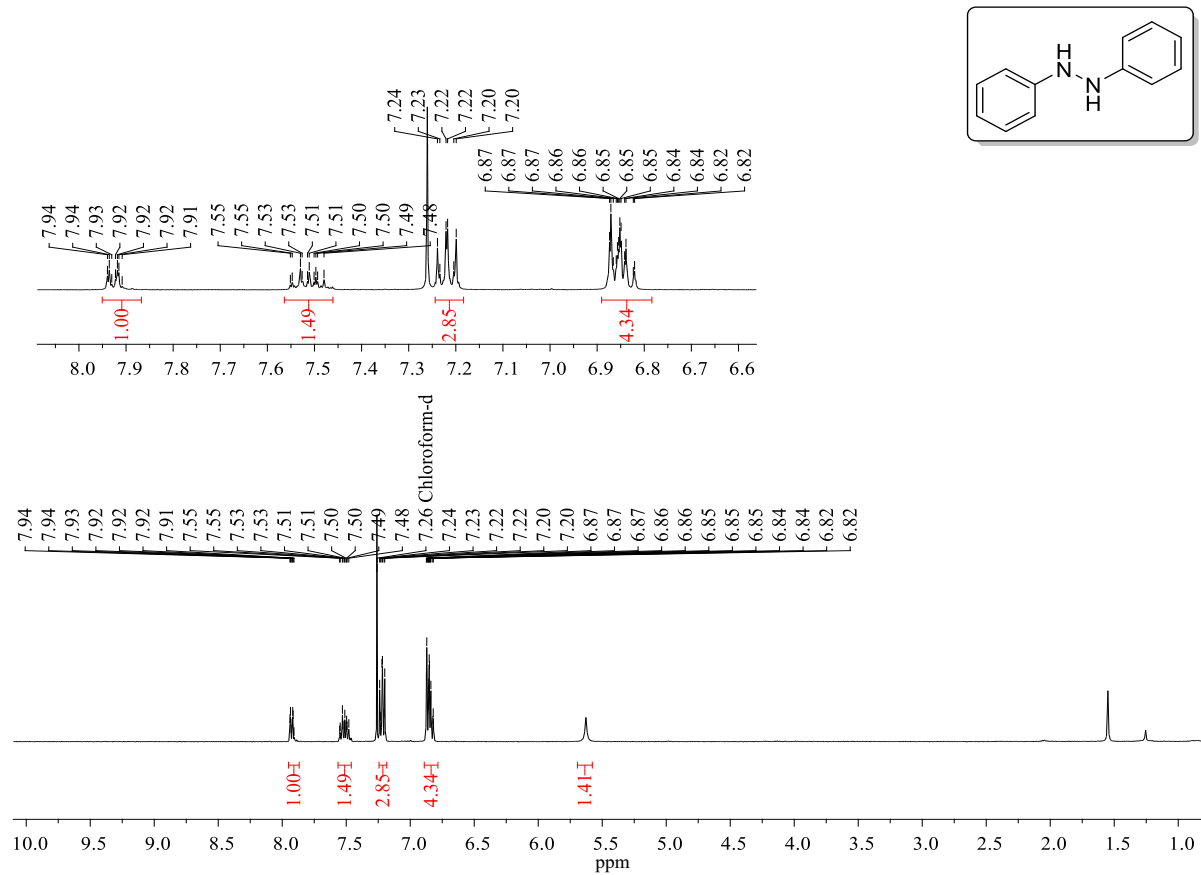


Figure S5. ¹H NMR spectrum of 1,2-diphenylhydrazine obtained from the reaction of azobenzene in water (Scheme 3).

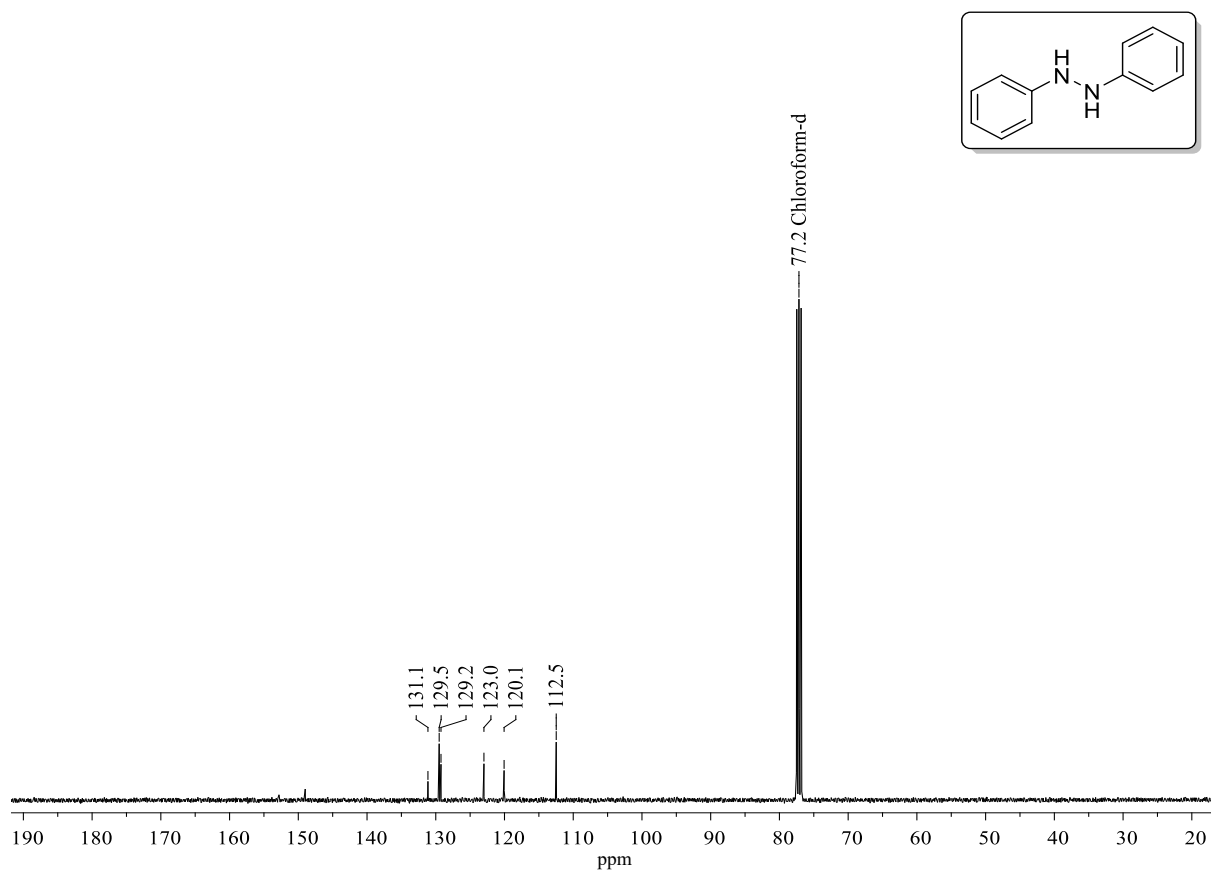


Figure S6. ^{13}C NMR spectrum of 1,2-diphenylhydrazine obtained from the reaction of azobenzene in water (Scheme 3).

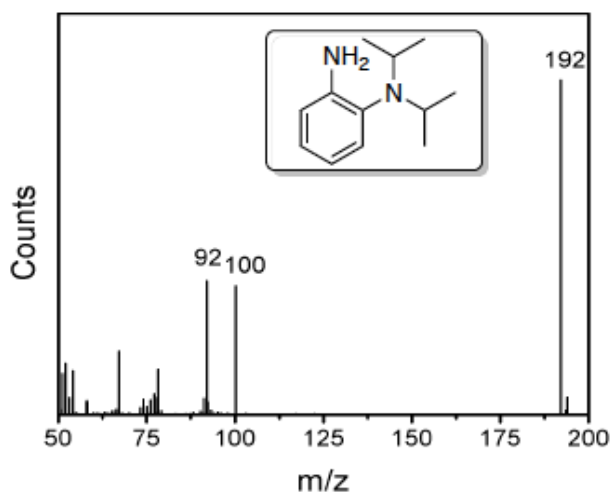


Figure S7. Mass spectrum of the product of the nucleophilic substitution of aziridines.

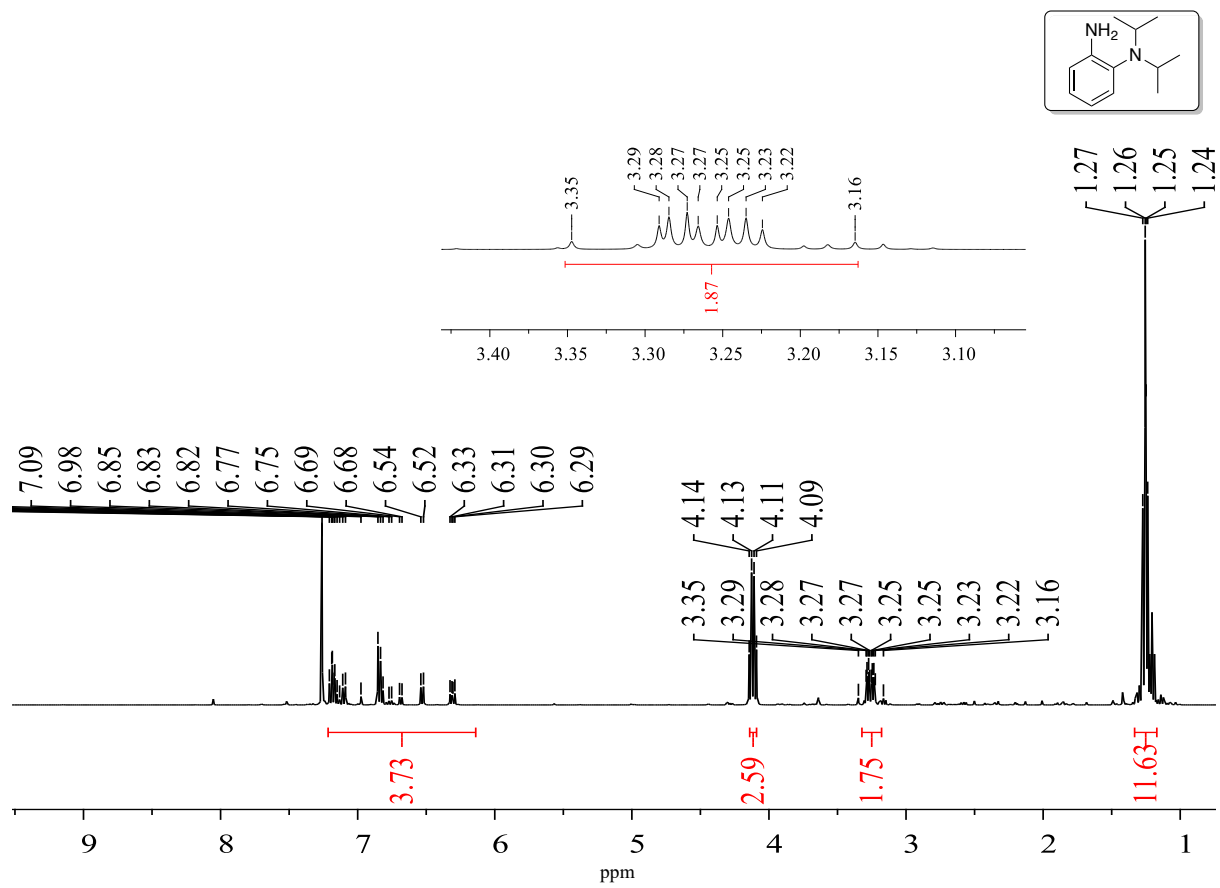


Figure S8. ¹H NMR spectrum of the product of the nucleophilic substitution of aziridines.

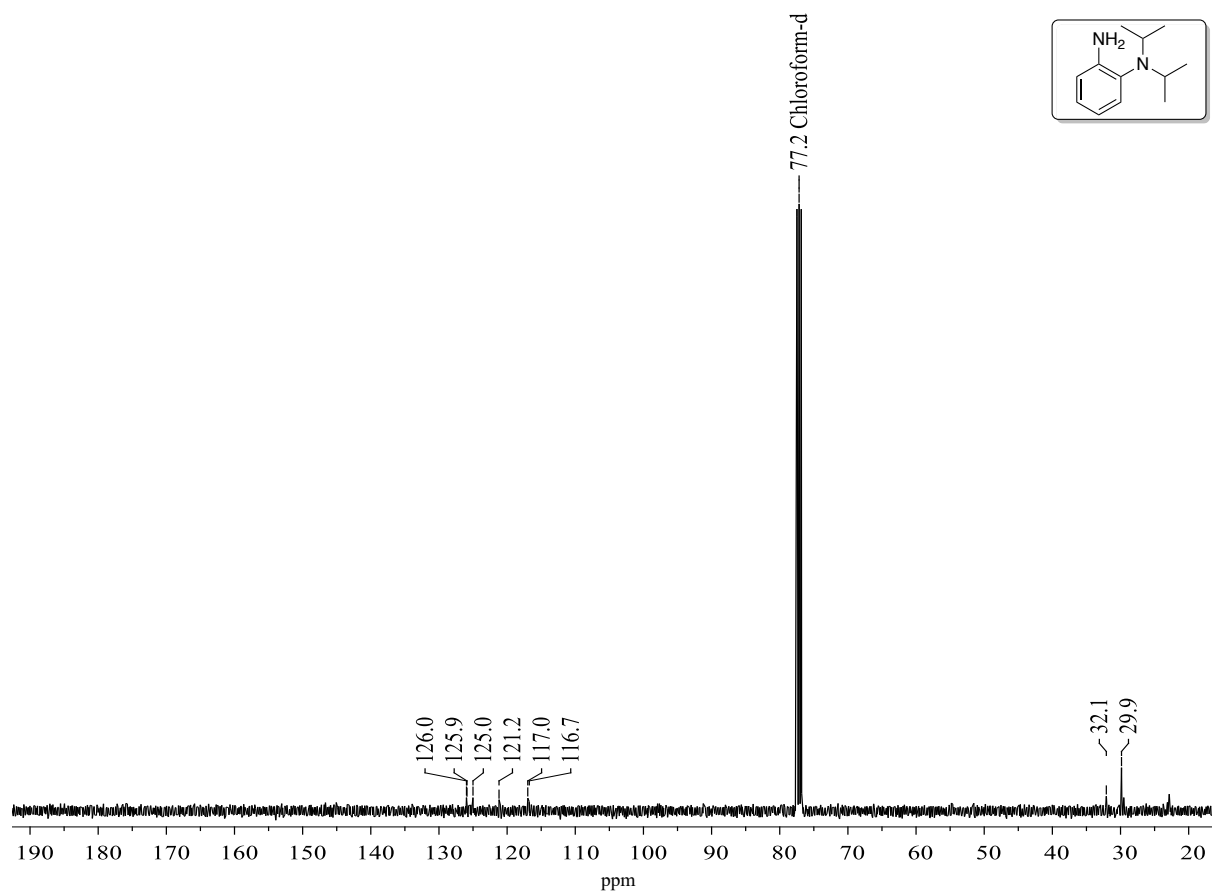


Figure S9. ^{13}C NMR spectrum of the product of the nucleophilic substitution of aziridines.

References

- [1] A. Elhage, A. E. Lanterna, J. C. Scaiano, *ACS Catal.* **2017**, *7*, 250-255.
- [2] M. Kurumi, K. Sasaki, H. Takata, T. Nakayama, *Heterocycles* **2000**, *53*, 2809-+.
- [3] C.-Z. Tao, X. Cui, J. Li, A.-X. Liu, L. Liu, Q.-X. Guo, *Tetrahedron Lett.* **2007**, *48*, 3525-3529.
- [4] D. B. Bagal, S.-W. Park, H.-J. Song, S. Chang, *Chem. Commun.* **2017**, *53*, 8798-8801.
- [5] D. E. Falvey, A. D. Gudmundsdottir, *Nitrenes and Nitrenium Ions*, Wiley, Hoboken, New Jersey, **2013**.
- [6] M. Jones, Jr., R. A. Moss, M. Platz, M. Jones, *Reactive Intermediate Chemistry*, Wiley-Interscience, Hoboken, N.J., **2004**.