Supplementary Information

Cyclotrimetaphosphate-Assisted Ruthenium Catalyst for the Hydration of Nitriles and Oxidation of Primary Amines to Amides Under Aerobic Conditions in Water

Kishor Kumar Chouhan,[a] Deep Chowdhury,[a] and Arup Mukherjee[a,]*

[a]*Department of Chemistry, Indian Institute of Technology Bhilai, GEC Campus, Sejbahar, Raipur, Chhattisgarh 492015, India.*

E-mail: arup@iitbhilai.ac.in

Table of Contents

(1) General consideration.

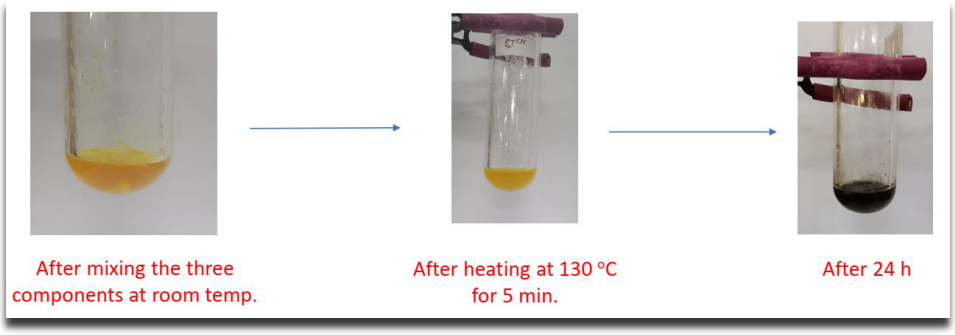
Unless otherwise mentioned, all reactions were performed without any precautions under aerobic conditions. All the chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, Merck, Avra, Loba Chemie, and TCI and were used without any further purifications. Deuterated solvents were procured from Sigma-Aldrich. Merck precoated 0.25 mm silica gel plates (60 F_{254}) were used to perform the analytical thin-layer chromatography (TLC). Visualization was achieved with short-wave UV light. Column chromatography purifications were performed using silica gel 100–200

mesh size. UV studies were carried out on a Shimadzu UV-2600 instrument. NMR spectroscopy was measured on Bruker Avance 400 MHz spectrometers using DMSO-d_6 and $CDCl_3$ solvent. GC-MS analyses were carried out on a Thermo Scientific Trace 1310 equipped with a TG-17MS column (30 m x 0.25 mm x 0.25 µm). High-resolution mass analysis was carried out on Agilent 6545XT Advance Bio LC/Q-TOF.

(2) General procedure.

2.1. General procedure for the hydration of nitriles to amides:

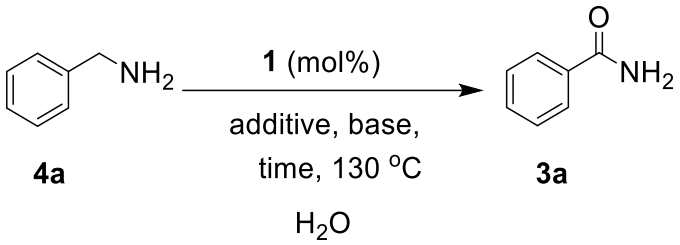
In a 15 mL oven-dried thick-walled pressure tube, nitrile (1 mmol), **1** (0.02 mmol), $Na_3P_3O_9$ (1 equiv.), and H_2O (3 mL) were taken. The pressure tube was sealed tightly and kept in a pre-heated oil bath at 130 ^oC for 24 h. After the specific time, the pressure tube was cooled down to room temperature, and water (10 mL) was added. The reaction mixture was extracted with dichloromethane (3 x 10 mL), and the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure. The crude product was purified through column chromatography using hexane and ethyl acetate as an eluent to get the pure product.



2.2. General procedure for the oxidation of primary amines to amides:

In a 15 mL oven-dried thick-walled pressure tube, amine (1 mmol), **1** (0.05 mmol), $Na_3P_3O_9$ (1 equiv.), KO^tBu (2 equiv.), and H_2O (3 mL) were taken. The pressure tube was sealed tightly and kept in a pre-heated oil bath at 130 ^oC for 24 h. After the specific time, the pressure tube was cooled down to room temperature and water (10 mL) was added. The reaction mixture was extracted with dichloromethane (3 x 10 mL) and the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure. The crude product was purified through column chromatography using hexane and ethyl acetate as an eluent to get the pure product.

Table S1. Optimization of primary amine oxidation in water with Ru-catalyst.[a]



Entry	1 (mol%)	$Na_3P_3O_9$ (equiv.)	Base (equiv.)	Time (h)	Yield (%)[b]
1	**1** (2)	1	–	24	20
2	**1** (2)	1	KO^{t}Bu (1)	24	26
3	**1** (2)	1	KO^{t}Bu (2)	24	30
4	**1** (2)	1	NaO^{t}Bu (2)	24	trace
5	**1** (2)	1	KOH (2)	24	trace
6	**1** (2)	1	NaOH (2)	24	trace
7	**1** (5)	1	KO^{t}Bu (2)	24	35
8	**1** (7.5)	1	KO^{t}Bu (2)	24	37
9	**1** (5)	1	KO^{t}Bu (2)	36	36
10	**1** (5)	2	KO^{t}Bu (2)	24	30
11	**1** (5)	0.5	KO^{t}Bu (2)	24	23
12	–	1	KO^{t}Bu (2)	24	trace
13	**1** (5)	–	KO^{t}Bu (2)	24	trace
14	–	–	KO^{t}Bu (2)	24	trace

[a]Reaction Conditions: Ru-Cat. (**1**), **4a** (1 mmol), $Na_3P_3O_9$, base, and water (3 mL) were heated at 130 °C in a thick-walled sealed tube under air; [b]Yields of the isolated products.

(3) Spectroscopic study.

3.1. UV-Vis absorption study of 1 and $Na_3P_3O_9$:

For studying the interaction between **1** and $Na_3P_3O_9$ through UV-Vis spectroscopy, 0.02 mmol of **1**, 0.02 mmol of $Na_3P_3O_9$ were prepared in water and taken in a cuvette for recording the absorbance spectra individually. Thereafter a mixture of **1** (0.02 mmol) and $Na_3P_3O_9$ (0.02 mmol) was taken in a cuvette and recorded the absorption spectra. **1** exhibits bands at 256, 313, and 403 nm in the water, while that for $Na_3P_3O_9$ was found at 290 nm. Notably, a prominent spectral change was observed in the mixture and the bands were shifted to 260, 325, and 415 nm.

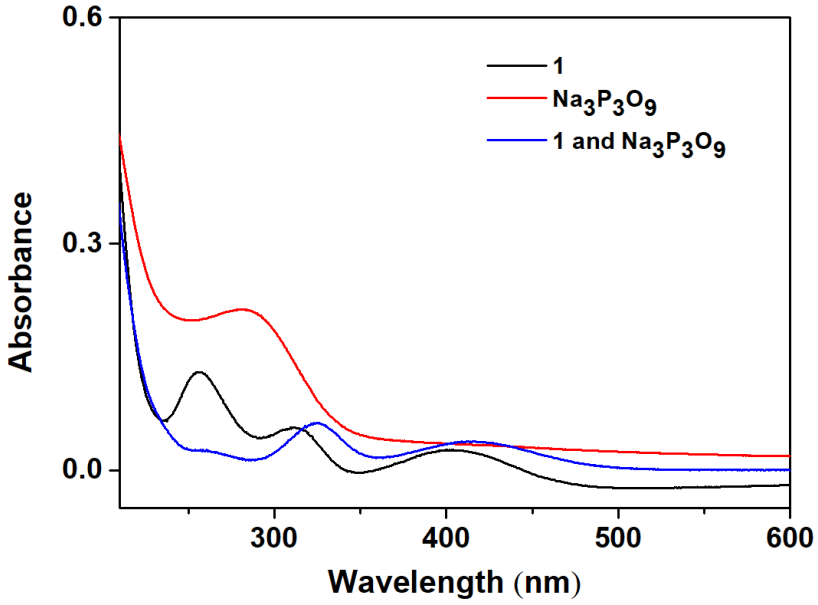
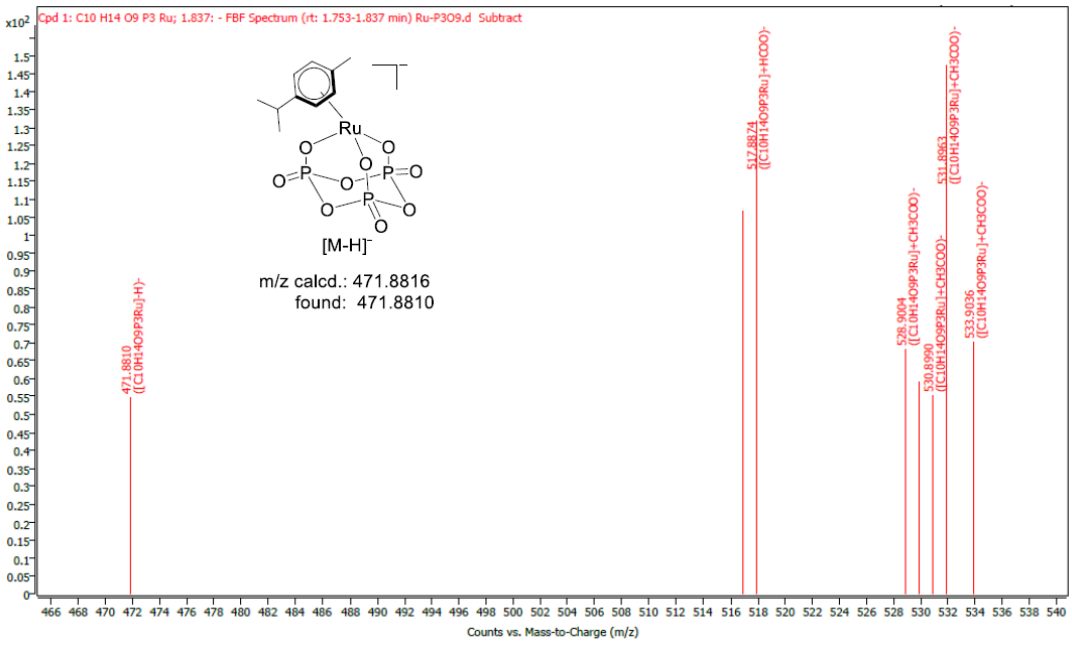


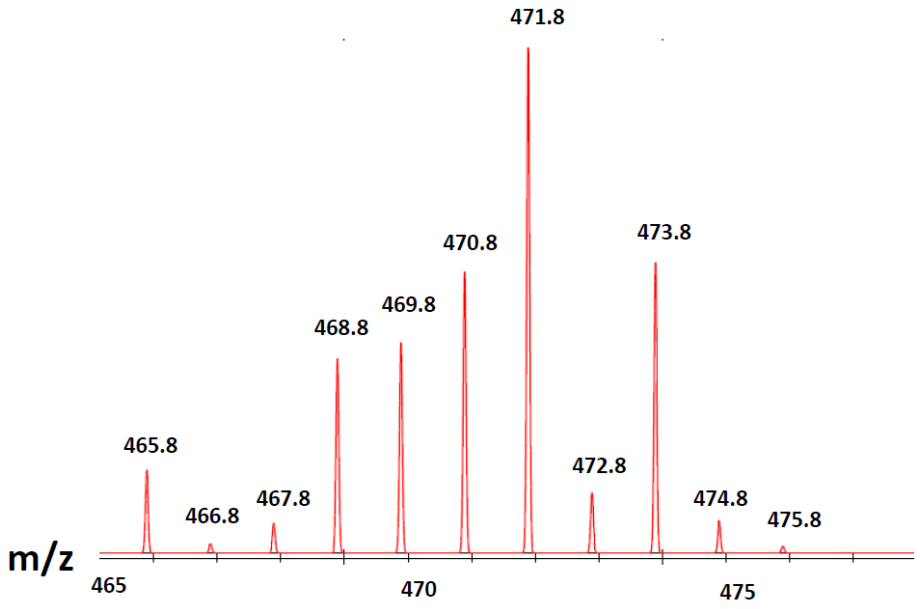
Figure S1. UV-Vis absorption spectra of **1**, $Na_3P_3O_9$, and the mixture of **1** and $Na_3P_3O_9$.

3.2. ESI-MS data of the reaction mixture:

(i)



(ii)



(iii)

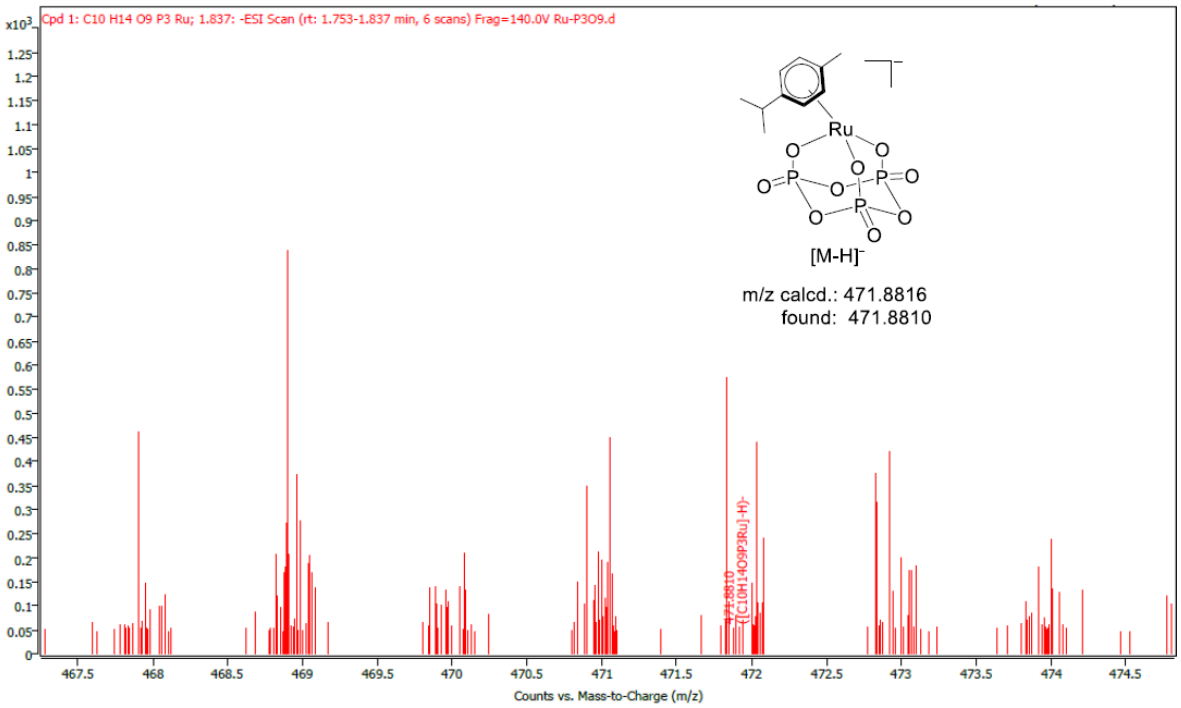
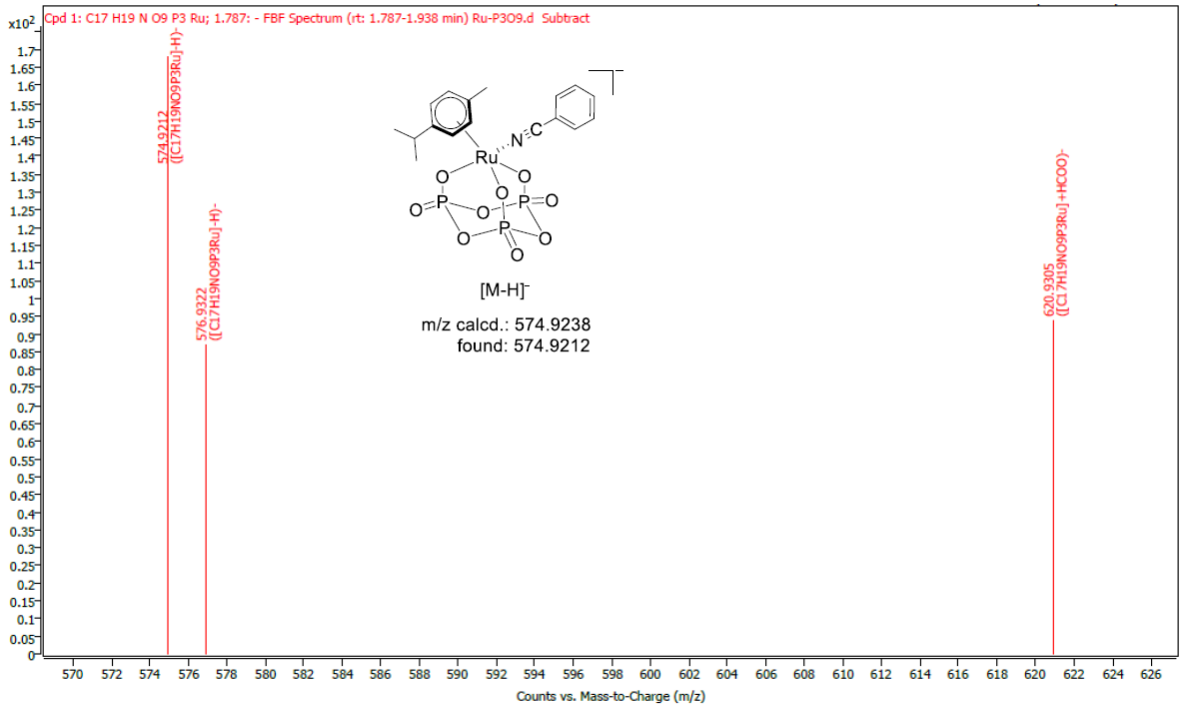
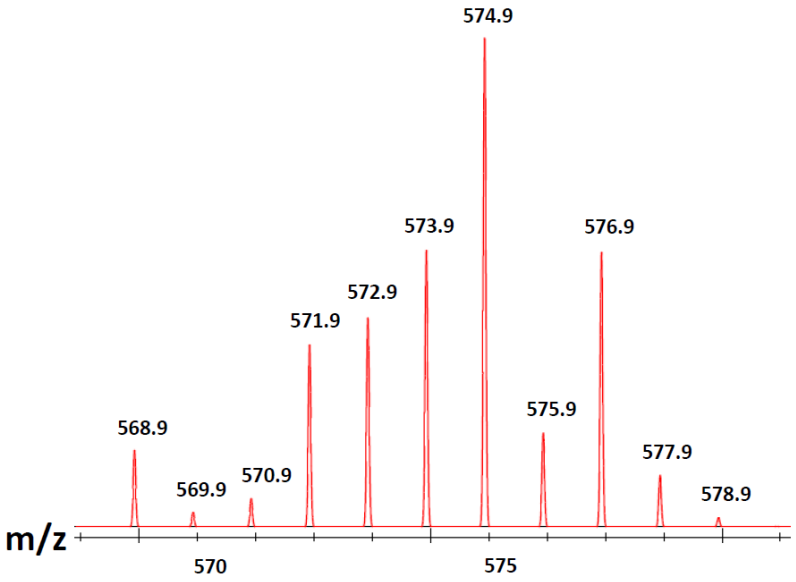


Figure S2. (i) ESI-MS data of the selected region of the desired mass of [(η^6-*p*-cymene)Ru(κ^3–P_3O_9)–H]$^-$ complex; (ii) Simulated isotope distribution patterns of [(η^6-*p*-cymene)Ru(κ^3–P_3O_9) –H]$^-$ complex; (iii) ESI-MS data of [(η^6-*p*-cymene)Ru(κ^3–P_3O_9) –H]$^-$ complex: m/z [M–H]$^-$ found: 471.8810, calcd.:471.8816.

(iv)



(v)



(vi)

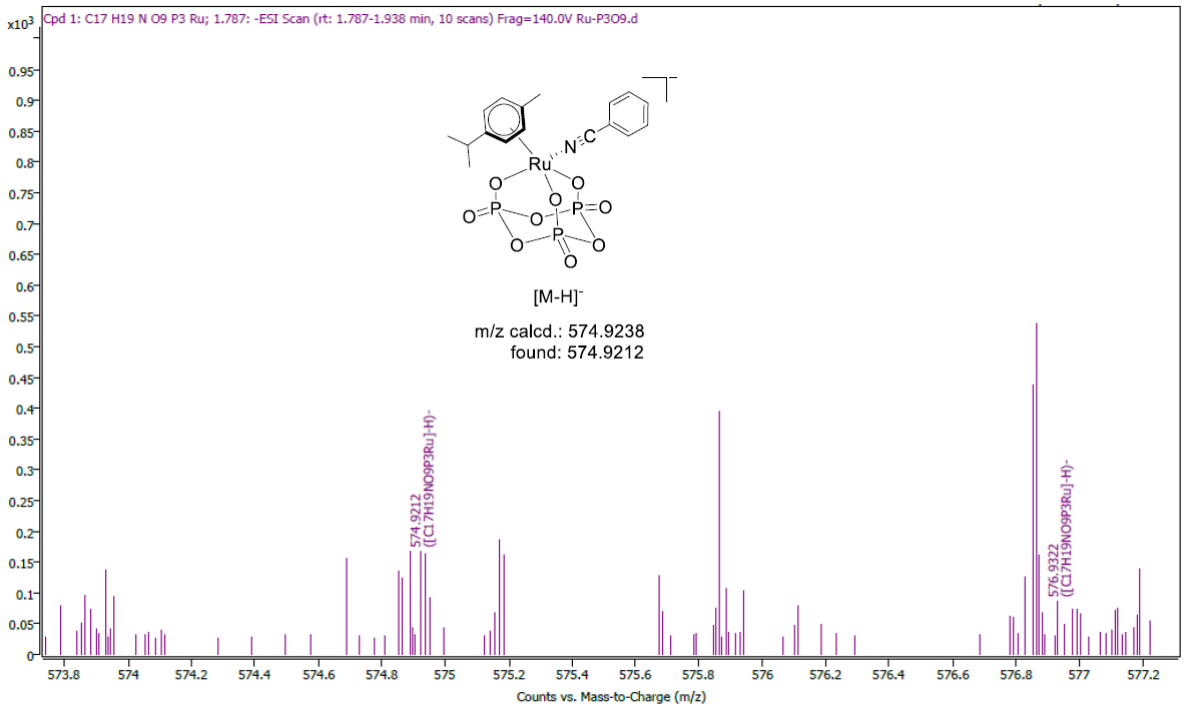
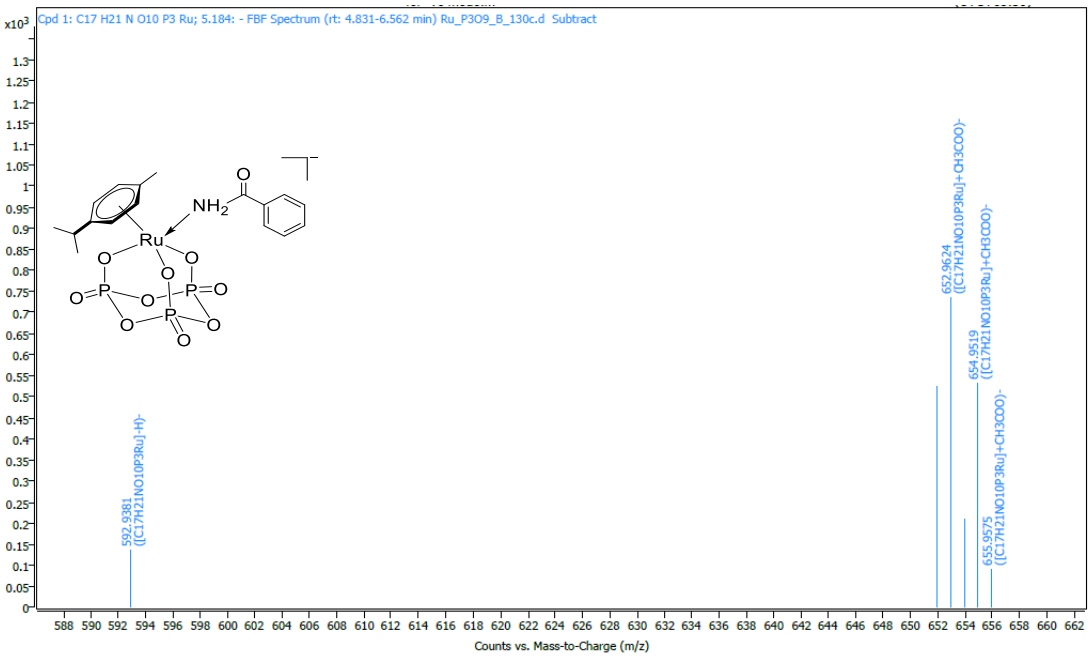
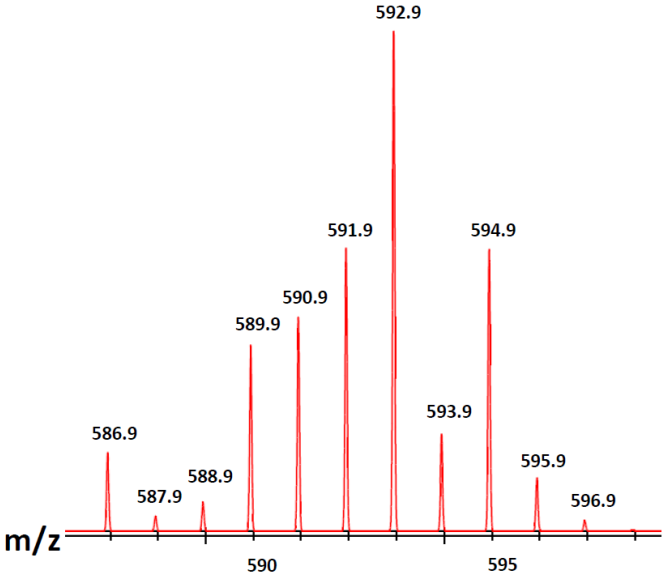


Figure S3. (iv) ESI-MS data of the selected region of the desired mass of [(η^6-*p*-cymene)Ru(κ^3–P_3O_9)(PhCN)–H]$^-$ complex; (v) Simulated isotope distribution patterns of [(η^6-*p*-cymene)Ru(κ^3–P_3O_9)(PhCN)–H]$^-$ complex; (vi) ESI-MS data of [(η^6-*p*-cymene)Ru(κ^3–P_3O_9)(PhCN)–H]$^-$ complex: m/z [M-H]$^-$ found: 574.9212, calcd.: 574.9238.

(vii)


Cpd 1: C17 H21 N O10 P3 Ru; 5.184: - FBF Spectrum (rt: 4.831-6.562 min) Ru_P3O9_B_130c.d Subtract
x10^3
NH2
Ru
592.9381
([C17H21NO10P3Ru]-H)-
652.9624
([C17H21NO10P3Ru]+CH3COO)-
654.9519
([C17H21NO10P3Ru]+CH3COO)-
655.9575
([C17H21NO10P3Ru]+CH3COO)-
Counts vs. Mass-to-Charge (m/z)

(viii)


592.9
591.9
594.9
590.9
589.9
593.9
586.9
595.9
588.9
587.9
596.9
m/z
590
595

(ix)

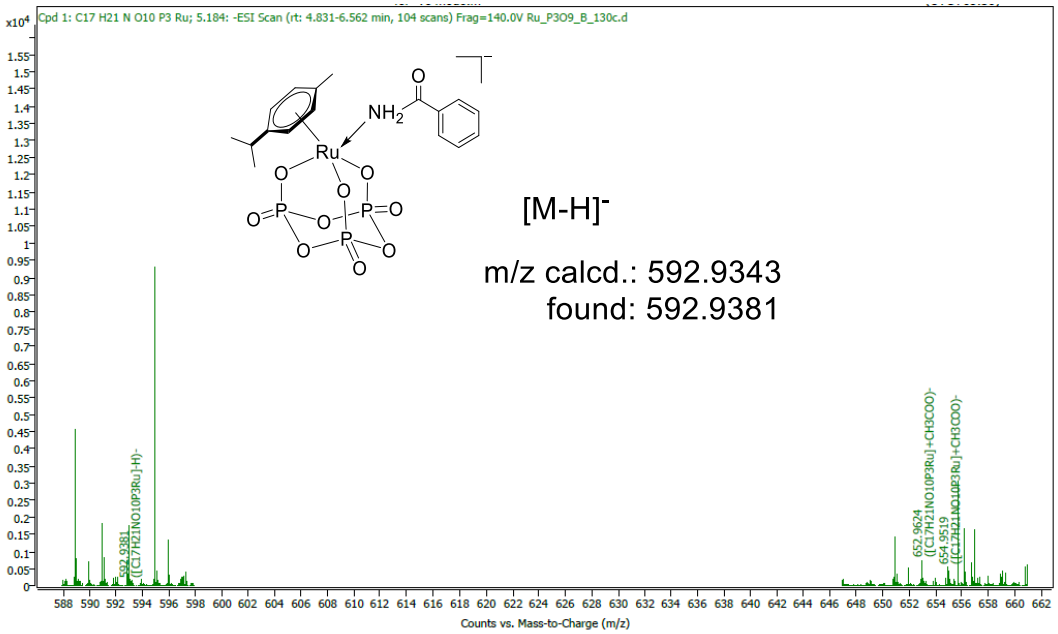
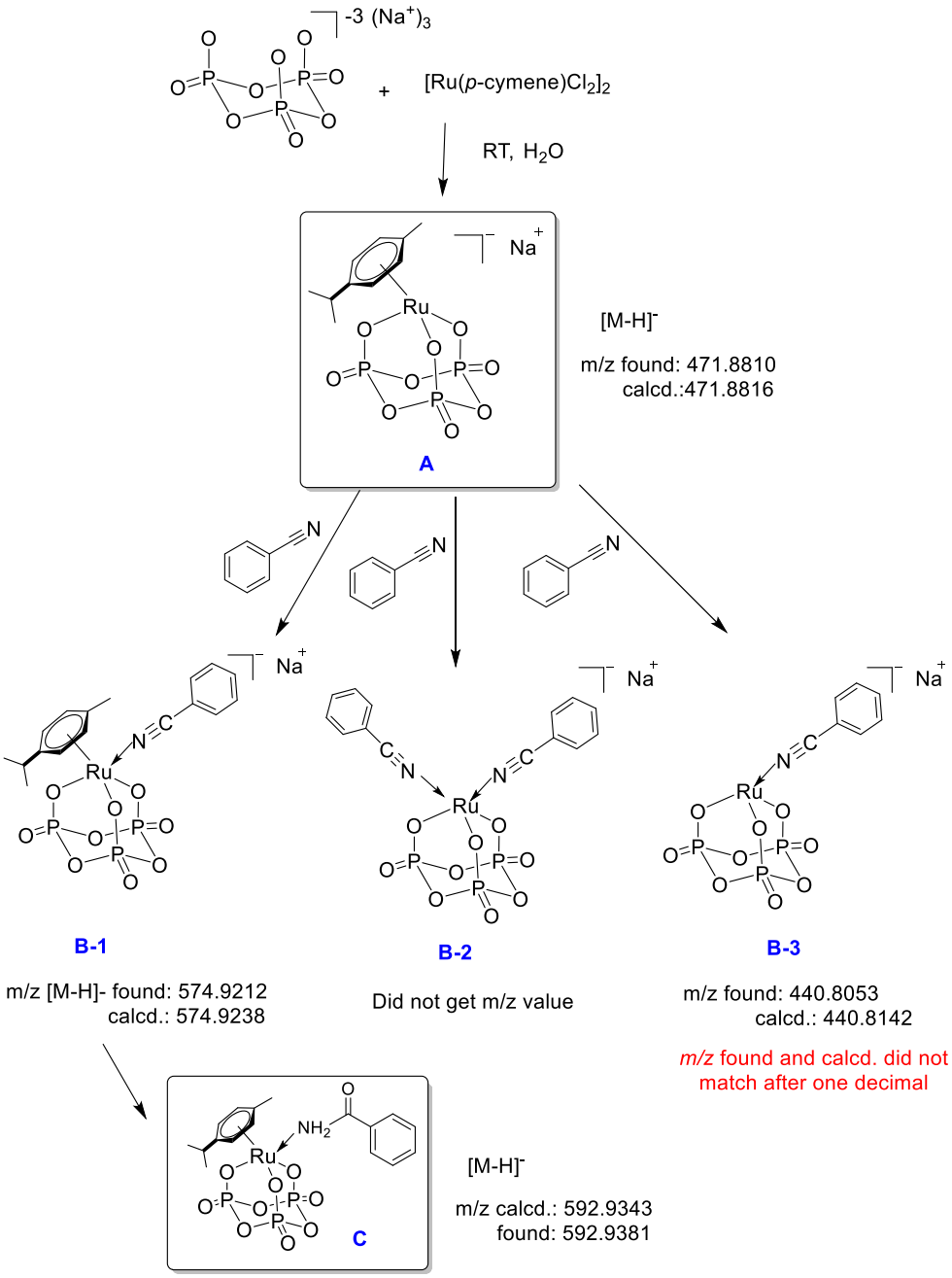
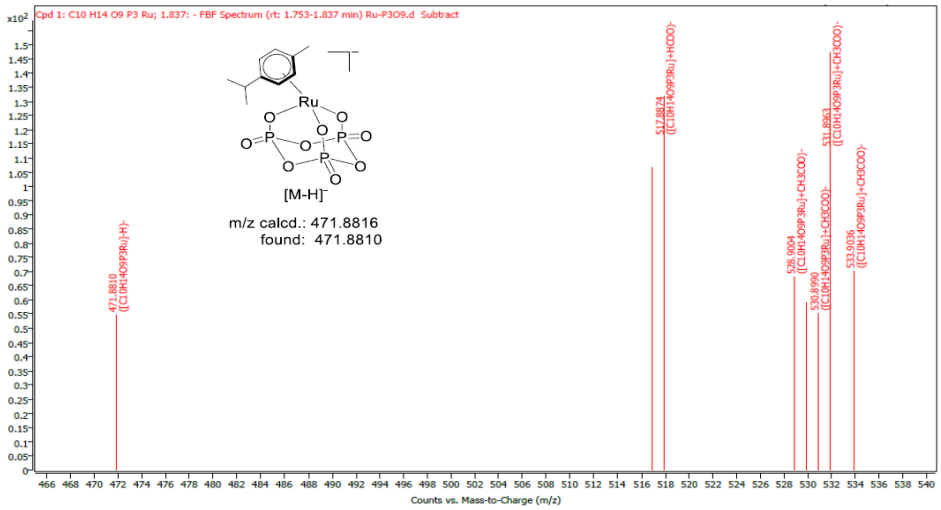
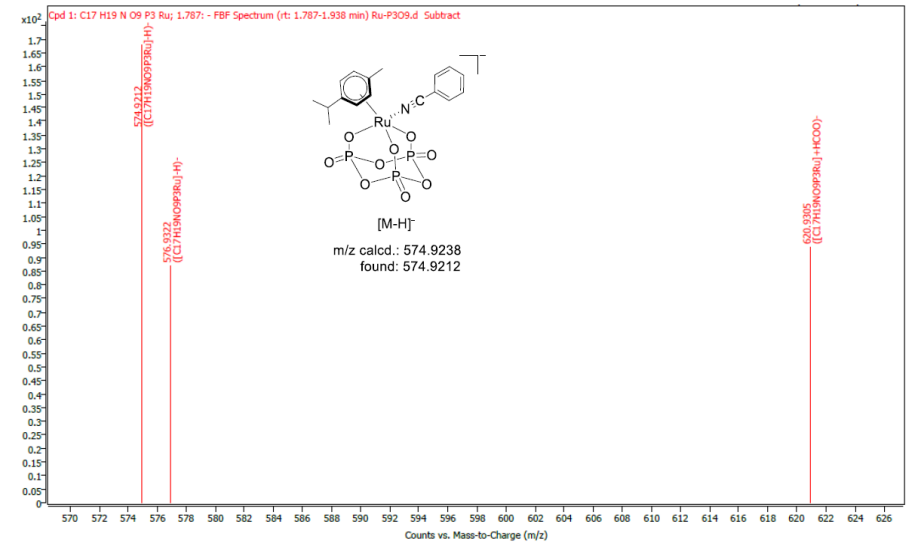

Cpd 1: C17 H21 N O10 P3 Ru; 5.184: -ESI Scan (rt: 4.831-6.562 min, 104 scans) Frag=140.0V Ru_P3O9_B_130c.d
x10^4
NH2
Ru
[M-H]-
m/z calcd.: 592.9343
found: 592.9381
592.9381
([C17H21NO10P3Ru]-H)-
652.9624
([C17H21NO10P3Ru]+CH3COO)-
654.9519
([C17H21NO10P3Ru]+CH3COO)-
Counts vs. Mass-to-Charge (m/z)

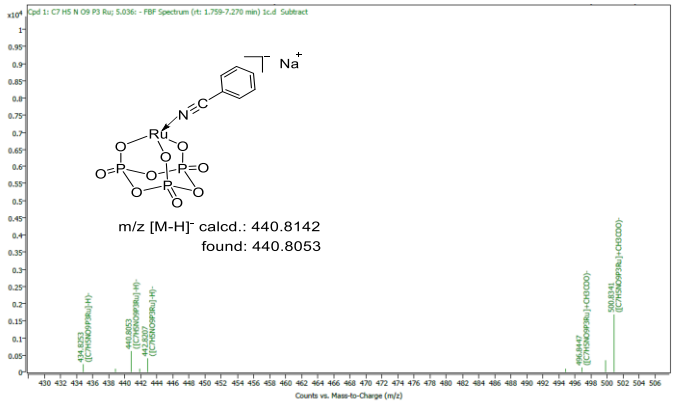
Figure S4. (vii) ESI-MS data of the selected region of the desired mass of [(η^6-*p*-cymene)Ru(κ^3–P_3O_9)($PhCONH_2$)–H]$^-$ complex; (viii) Simulated isotope distribution patterns of [(η^6-*p*-cymene)Ru(κ^3–P_3O_9)($PhCONH_2$)–H]$^-$ complex; (ix) ESI-MS data of [(η^6-*p*-cymene)Ru(κ^3–P_3O_9)($PhCONH_2$)–H]$^-$ complex: m/z [M-H]$^-$ found: 592.9381, calcd.: 592.9343.

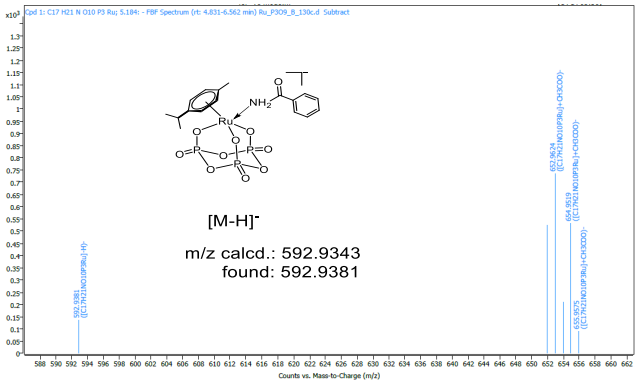
(i) Analysis of the reaction mixture with benzonitrile under the standard conditions:



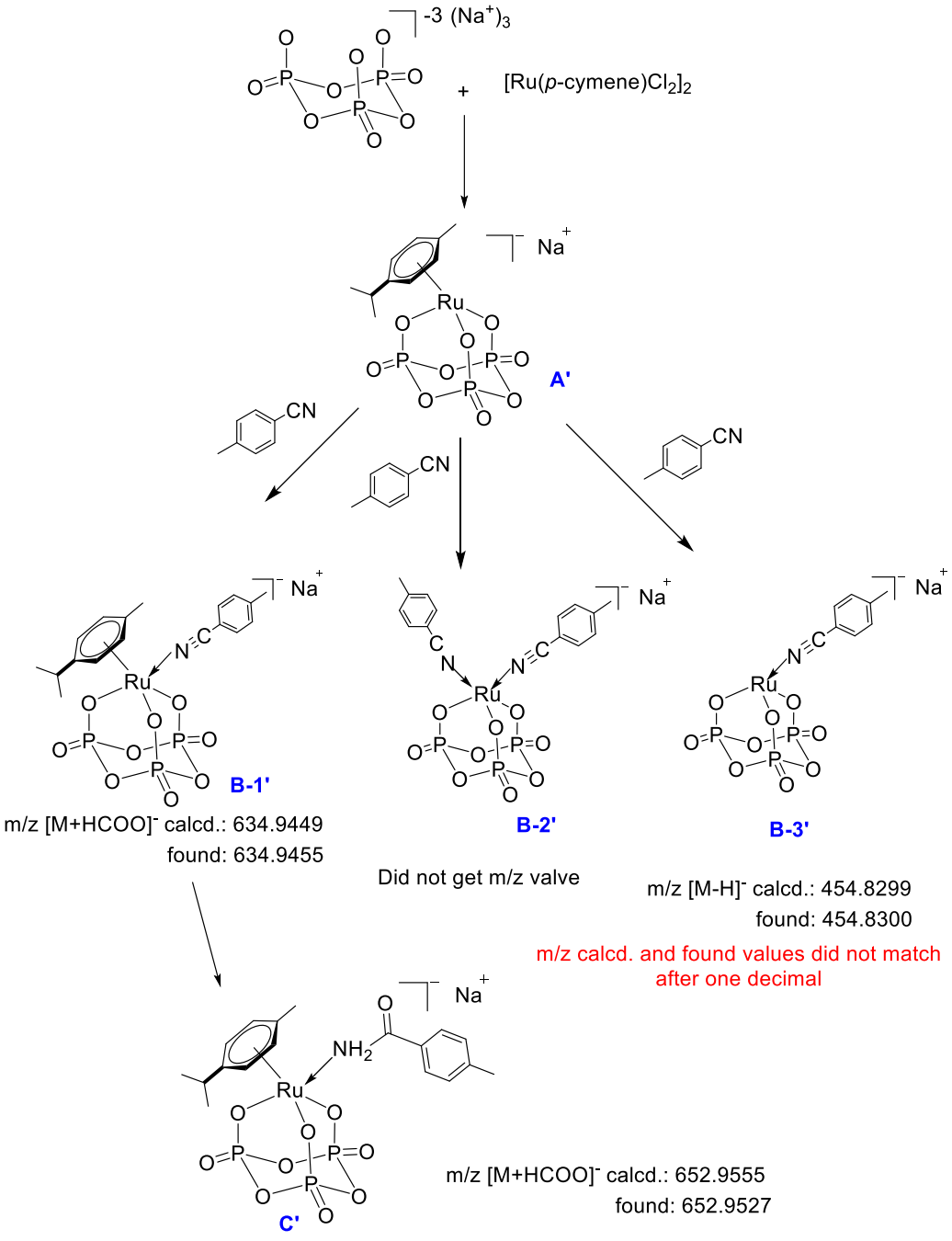

Cpd 1: C10 H14 O9 P3 Ru; 1.837: - FBF Spectrum (rt: 1.753-1.837 min) Ru-P3O9.d Subtract
[M-H]⁻
m/z calcd.: 471.8816
found: 471.8810
Counts vs. Mass-to-Charge (m/z)

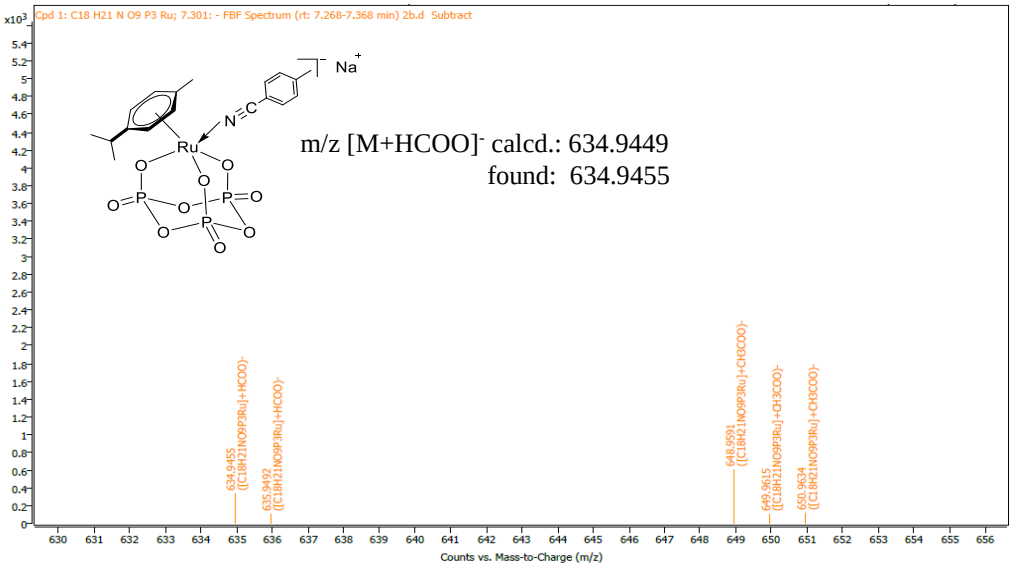

Cpd 1: C17 H19 N O9 P3 Ru; 1.787: - FBF Spectrum (rt: 1.787-1.938 min) Ru-P3O9.d Subtract
[M-H]⁻
m/z calcd.: 574.9238
found: 574.9212
Counts vs. Mass-to-Charge (m/z)

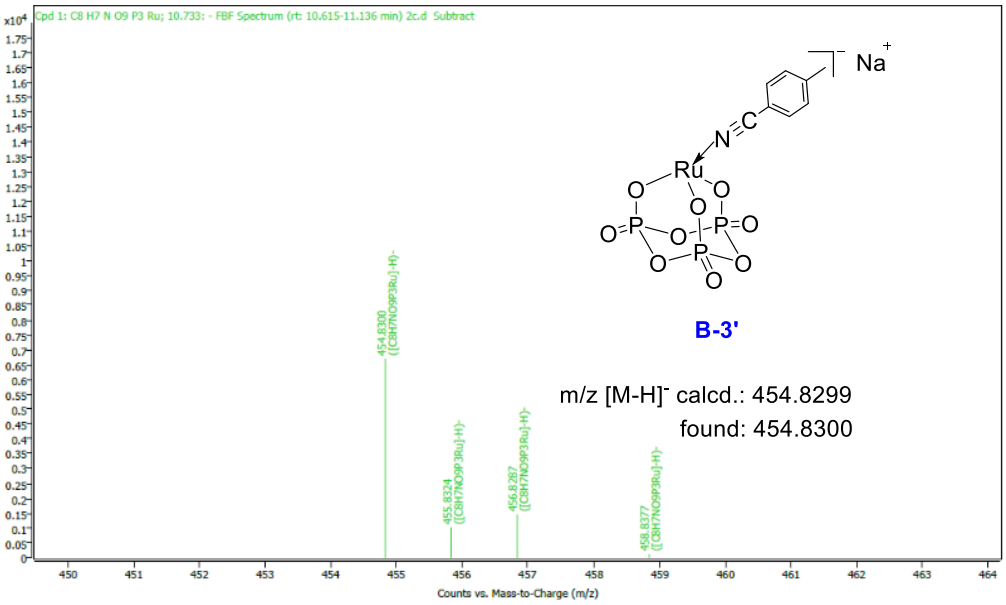

Na⁺
m/z [M-H]⁻ calcd.: 440.8142
found: 440.8053
Counts vs. Mass-to-Charge (m/z)

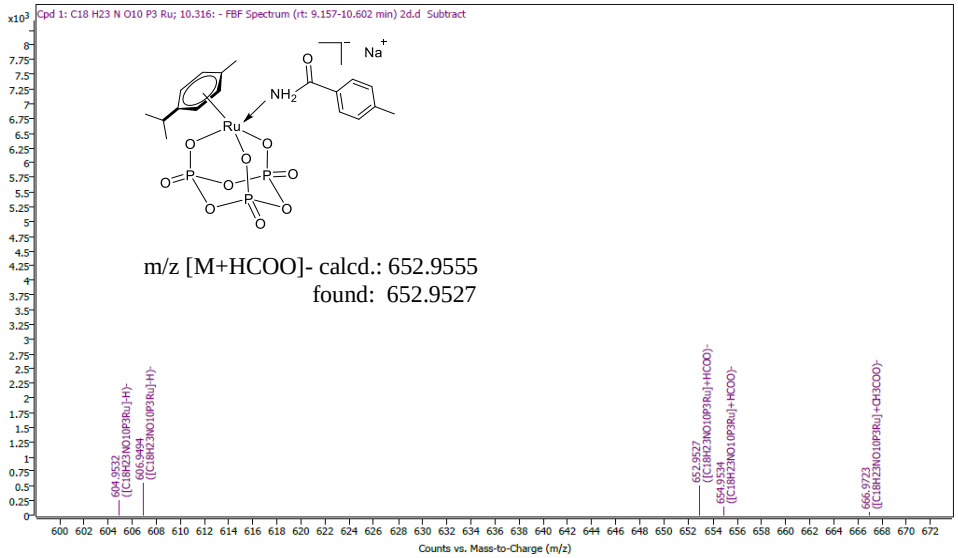

[M-H]⁻
m/z calcd.: 592.9343
found: 592.9381
Counts vs. Mass-to-Charge (m/z)

(ii) Analysis of the reaction mixture with 4-methylbenzonitrile under the standard conditions:

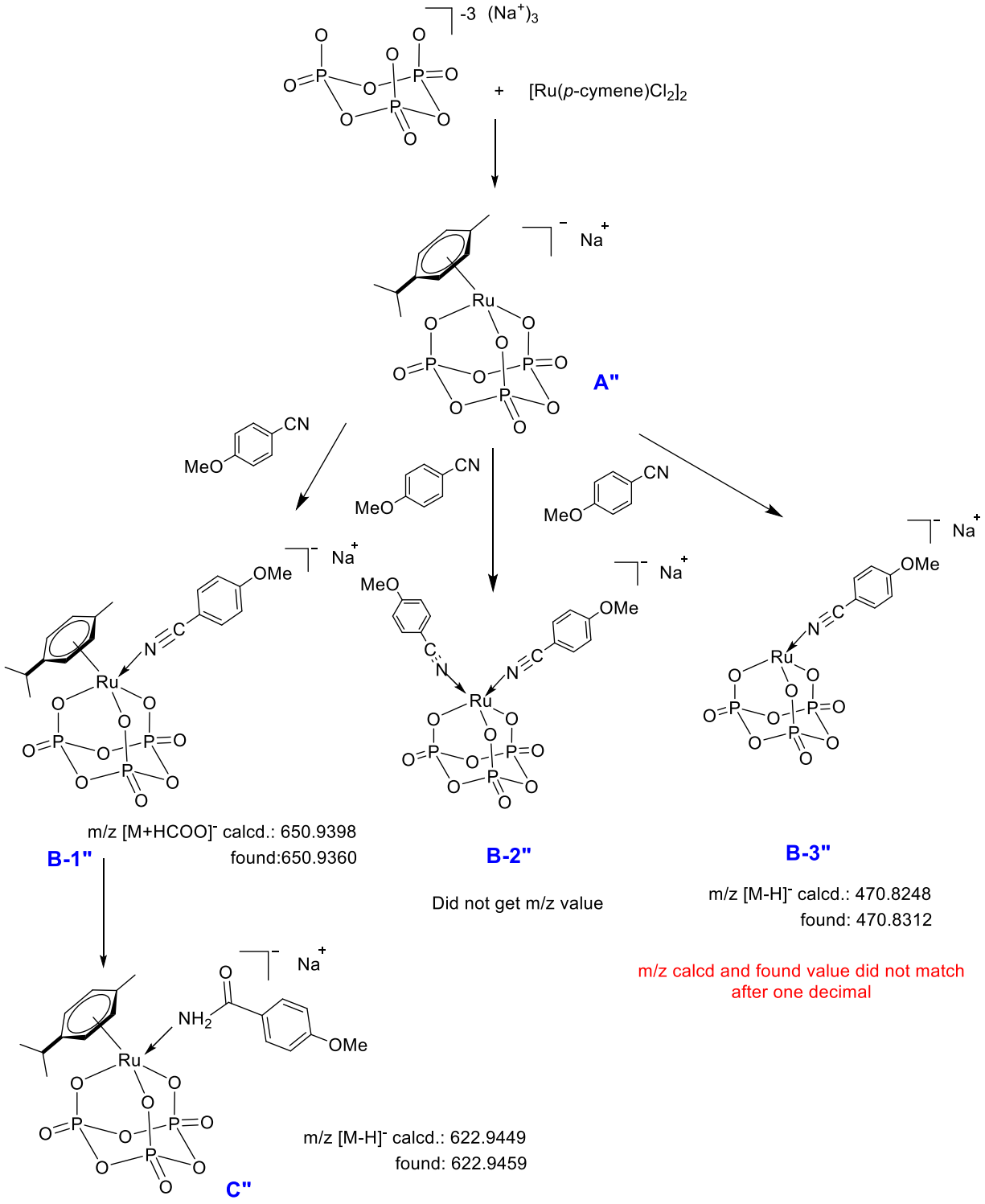


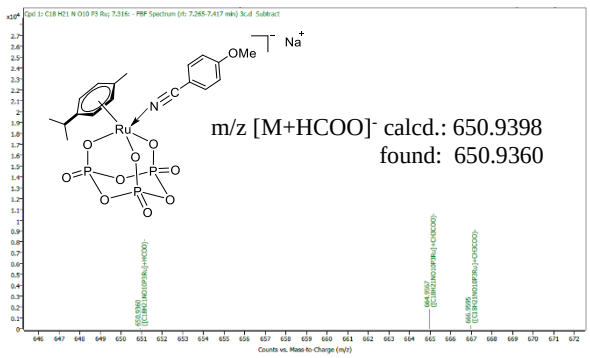

Cpd 1: C18 H21 N O9 P3 Ru; 7.301: - FBF Spectrum (rt: 7.268-7.368 min) 2b.d Subtract
m/z [M+HCOO]- calcd.: 634.9449
found: 634.9455
Counts vs. Mass-to-Charge (m/z)

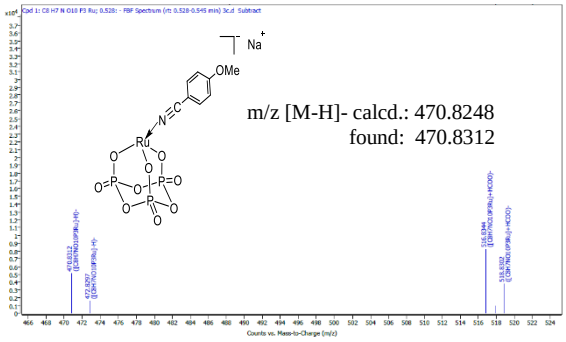

Cpd 1: C8 H7 N O9 P3 Ru; 10.733: - FBF Spectrum (rt: 10.615-11.136 min) 2c.d Subtract
B-3'
m/z [M-H]- calcd.: 454.8299
found: 454.8300
Counts vs. Mass-to-Charge (m/z)

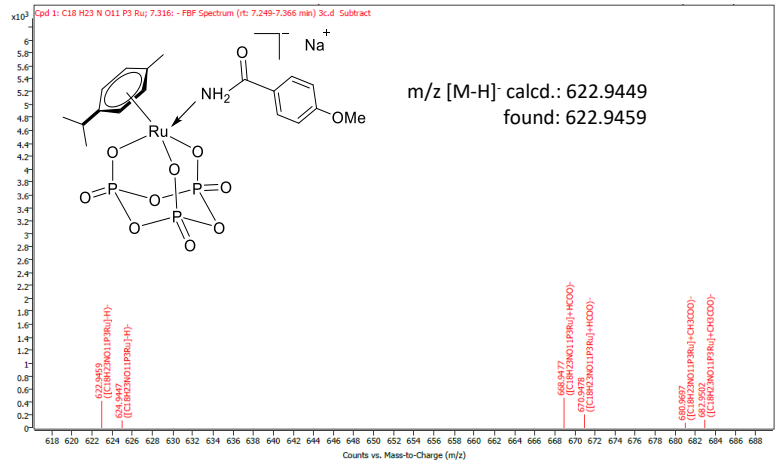

Cpd 1: C18 H23 N O10 P3 Ru; 10.316: - FBF Spectrum (rt: 9.157-10.602 min) 2d.d Subtract
m/z [M+HCOO]- calcd.: 652.9555
found: 652.9527
Counts vs. Mass-to-Charge (m/z)

(iii) Analysis of the reaction mixture with 4-methoxylbenzonitrile under the standard conditions:



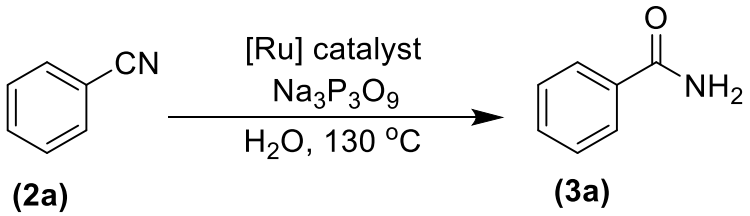






(4) Kinetic Studies of the ruthenium-catalyzed hydration reaction of benzonitrile:

In an oven-dried thick-walled reaction tube, benzonitrile (**2a**) was taken under aerobic conditions. To this, an appropriate amount of $Na_3P_3O_9$ and [Ru] catalyst were added. The reaction vessel was sealed and placed in a preheated oil bath at 130 ^{0}C. After a certain time, interval, a small amount of aliquot was collected, and the yield of benzamide (**2a**) was determined by GC-MS.



(A) Determination of reaction order with respect to benzonitrile concentration (2a):

To determine the order of the reaction with respect to **2a**, the catalytic reaction was carried out in three different concentrations of benzonitrile (0.167–0.417 M), keeping the concentration of the catalyst (0.0067 M) and $Na_3P_3O_9$ (0.33 M) constant.

Entry	Benzonitrile (mmol)	Concentration of benzonitrile (M)	Concentration of catalyst (M)	Concentration of $Na_3P_3O_9$ (M)
1	0.5	0.167	0.0067	0.33
2	0.75	0.25	0.0067	0.33
3	1	0.33	0.0067	0.33
4	1.25	0.417	0.0067	0.33

For each reaction, after a certain time interval, a small amount of aliquot was taken from the reaction mixture, and yields were determined using GC-MS. For each reaction, the concentration of the product formed was plotted against time where for every case a linear equation was obtained, and the slope corresponds to the rate constant (K_{obs}). Subsequently, $-\ln K_{obs}$ was plotted against –ln[Benzonitrile] which results in a slope of 1.17 suggesting the order with respect to the benzonitrile is approximately 1.

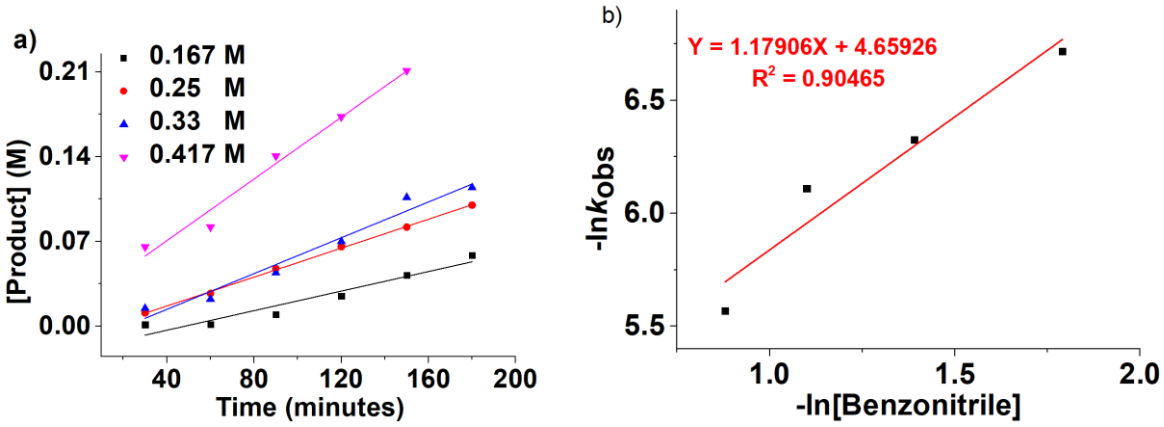


Figure S5: Kinetic studies of catalytic hydration of benzonitrile to benzamide*:* a) plot of concentration of product formed vs time and b) plot of $-\ln K_{obs}$ vs –ln[Benzonitrile].

(B) Determination of reaction order with respect to Ru-catalyst concentration:

To determine the order of the reaction with respect to the Ru-catalyst, the catalytic reaction was carried out in different Ru-catalyst loading (1.5–2.25 mol%), keeping concentration of benzonitrile (0.33 M taken for each) and concentration of $Na_3P_3O_9$ (0.33 M taken for each) constant.

Entry	Concentration of benzonitrile (M)	Catalyst (mmol)	Concentration of catalyst (M)	Concentration of $Na_3P_3O_9$ (M)
1	0.33	0.0225	0.0075	0.33
2	0.33	0.02	0.0067	0.33
3	0.33	0.0175	0.0058	0.33
4	0.33	0.015	0.005	0.33

For each reaction, after a specific time interval, a small amount of aliquot was taken from the reaction mixture, and yields were determined using GC-MS. For each reaction, the concentration of the product formed was plotted against time, where for every case, a linear equation was obtained, and the slope corresponds to the rate constant (K_{obs}). Subsequently, $-\ln K_{obs}$ was plotted against –ln[Catalyst], which results in a slope of 1.2, suggesting the order with respect to the Ru-catalyst is approximately 1.

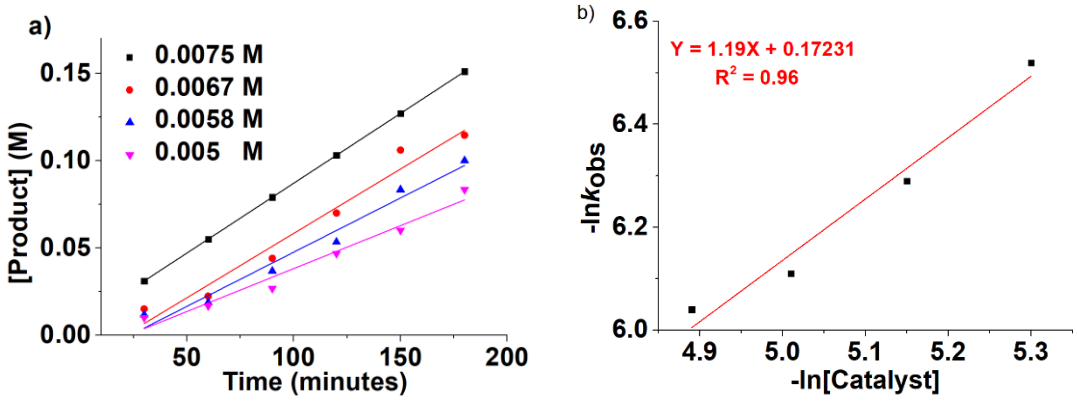


Figure S6: Kinetic studies of catalytic hydration of benzonitrile to benzamide*:* a) plot of concentration of product formed vs time and b) plot of $-\ln K_{obs}$ vs –ln[Catalyst].

(C) Determination of reaction order with respect to $Na_3P_3O_9$:

To determine the order of the reaction with respect to $Na_3P_3O_9$, the catalytic reaction was carried out in three different concentrations of $Na_3P_3O_9$ (0.167–0.417 M), keeping the concentration of benzonitrile (0.33 M taken for each) and catalyst loading (0.0067 M taken for each) constant.

Entry	Concentration of benzonitrile (M)	Concentration of catalyst (M)	$Na_3P_3O_9$ (mmol)	Concentration of $Na_3P_3O_9$ (M)
1	0.33	0.0067	0.5	0.167
2	0.33	0.0067	0.75	0.25
3	0.33	0.0067	1	0.33
4	0.33	0.0067	1.25	0.417

For each reaction, after a certain time interval, a small amount of aliquot was taken from the reaction mixture, and yields were determined using GC-MS. For each reaction, the concentration of the product formed was plotted against time where for every case a linear equation was obtained, and the slope corresponds to the rate constant (K_{obs}). Subsequently, $-\ln K_{obs}$ was plotted against $-\ln[Na_3P_3O_9]$ which results in a slope of 0.08 suggesting the order with respect to the benzonitrile is zero.

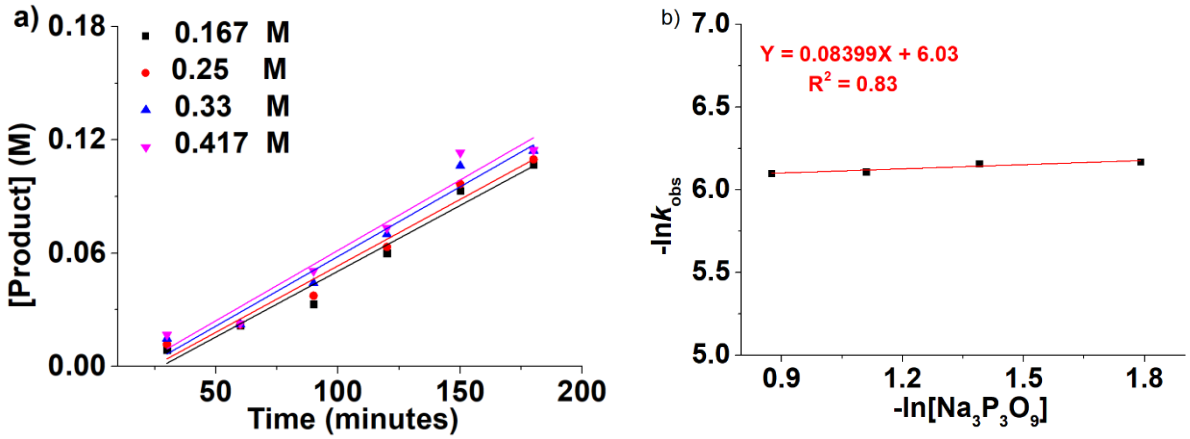


Figure S7: Kinetic studies of catalytic hydration of benzonitrile to benzamide*:* a) plot of concentration of product formed vs time and b) plot of $-\ln K_{obs}$ vs $-\ln[Na_3P_3O_9]$.

(D) Experimental Procedure for determining Kinetic Isotope Effect:

Two parallel reactions were carried out for the hydration of benzonitrile with D_2O and H_2O under similar reaction conditions. An oven-dried thick-walled reaction tube was charged with benzonitrile (1 mmol), [Ru] catalyst (0.0043 mmol), and $Na_3P_3O_9$ (1 mmol) in 3 mL H_2O. Similarly, another oven-dried thick-walled reaction tube was charged with benzonitrile (1 mmol), [Ru] catalyst (0.0043 mmol), and $Na_3P_3O_9$ (1 mmol) in 3 mL D_2O. Both tubes were placed in a pre-heated (130 ºC) oil bath with stirring under ambient conditions. After stipulated time intervals, a small amount of aliquots was taken out and worked up with DCM. The DCM samples were injected in GC–MS, and product formation was monitored. The following plot was used to analysis the KIE value for deuterated D_2O and non-deuterated H_2O. For H_2O / D_2O, the KIE value was found to be almost 0.91, which can be approximated to 1.

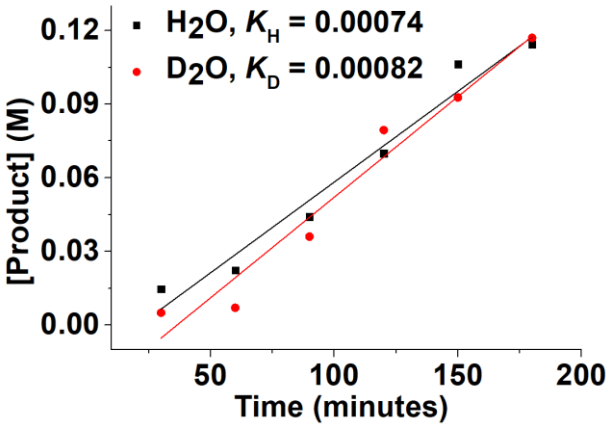


Figure S8. KIE studies for the nitrile hydration in H_2O and D_2O.

(E) Hammett Studies:

In an oven-dried thick-walled reaction tube, benzonitrile derivative (**1a**) was taken under aerobic conditions. An appropriate amount of $Na_3P_3O_9$ and [Ru] catalyst were added. The reaction vessel was sealed and placed in a preheated oil bath at 130 ^{0}C. After a specific time interval, a small amount of aliquot was collected, and the yield GC-MS monitored the yield of benzamide (**2a**). Reactivity for this reaction follows the following order *p*-F > *p*-H > *p*-Me > *p*-OMe (Figure S9). For this particular reaction, ρ value was obtained as +2.05 (Figure S10).

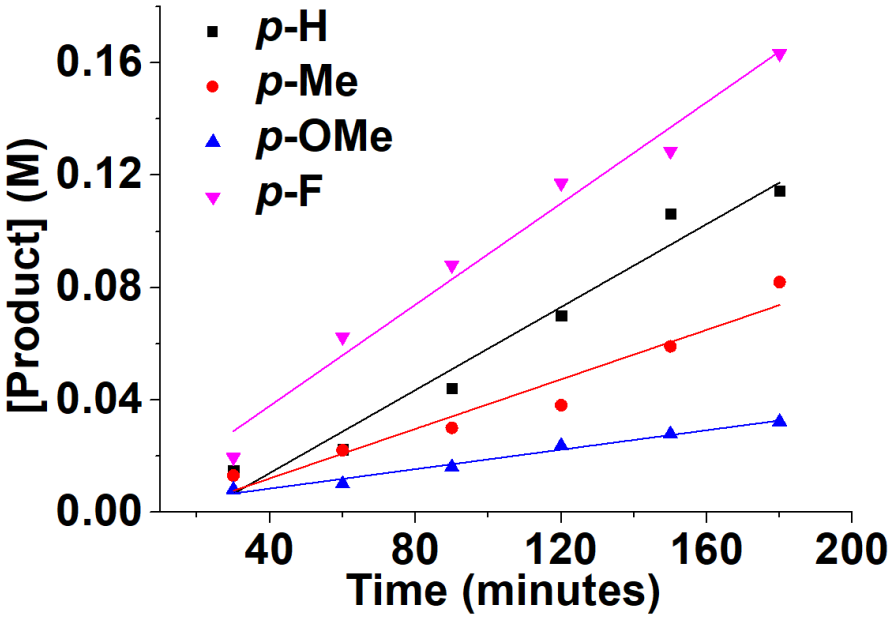


Figure S9. Kinetic data for the hydration of benzonitrile and its *para*-substituted derivatives.

Hammett Plot kinetic Study Data			
Substrate	**Slope**	**log(K_X/K_H)**	**σ_p**
p-OMe	0.00017	-0.639	-0.268
p-Me	0.00044	-0.226	-0.17
p-H	0.00074	0	0
p-F	0.0009	0.085	0.062
ρ = 2.05			

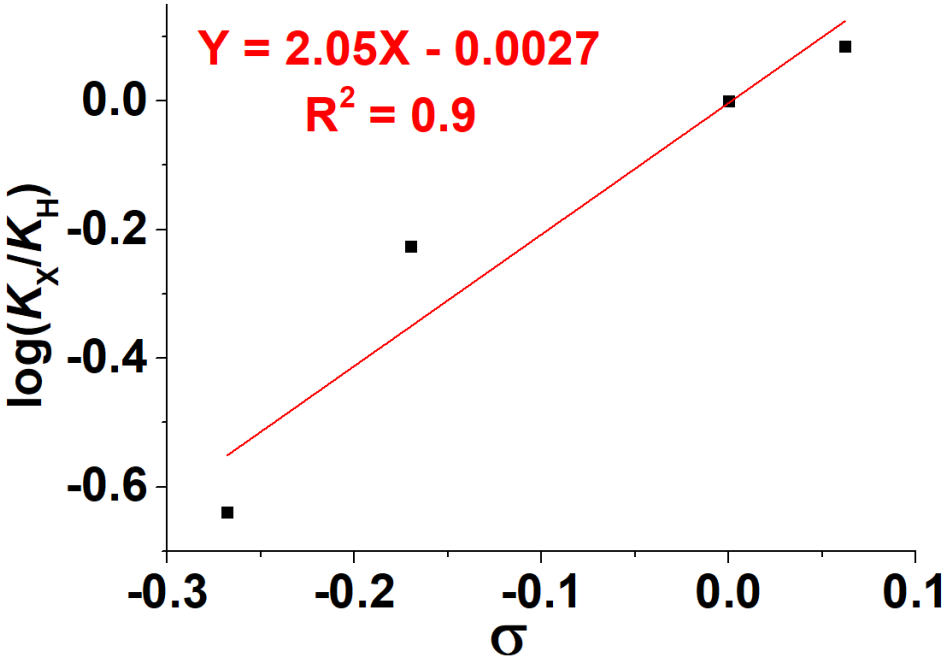
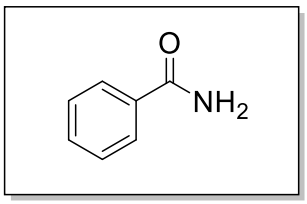


Figure S10. Hammett plot for the hydration of substituted benzonitriles.

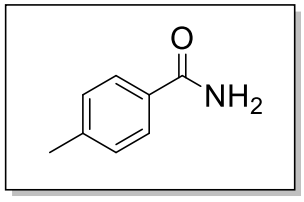
(5) Analytical data of the isolated compounds.

Benzamide (3a)[1]. Reaction scale: Benzonitrile (103.04 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



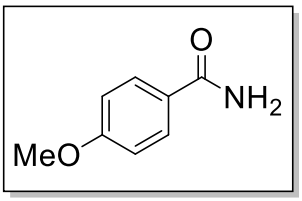
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 80% (97 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 6.31 (br s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.75, 133.43, 131.99, 128.62, 127.36 ppm.

***p*-Toluamide (3b)**[1]**.** Reaction scale: *p*-Tolunitrile (117.15 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



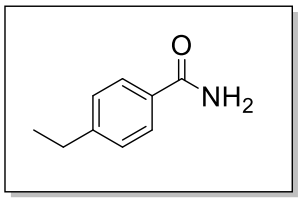
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 65% (71 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.13 (m, 2H), 5.94 (d, *J* = 51.5 Hz, 0.27 H), 2.33 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.42, 142.53, 130.51, 129.29, 127.38, 21.49 ppm.

***p*-Methoxybenzamide (3c)**[1]**.** Reaction scale: 4-Methoxybenzonitrile (133.15 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



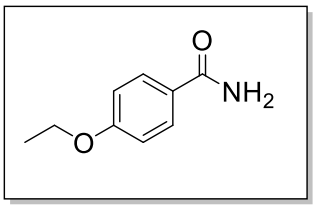
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 65% (98 mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.88 (d, *J* = 49.5 Hz, 0.17 H), 3.88 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.88, 162.61, 129.29, 125.58, 113.81, 55.44 ppm.

4-Ethylbenzamide (3d)[2]. Reaction scale: 4-Ethylbenzonitrile (131.17 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



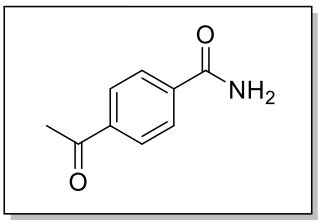
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 60% (90 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.87 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.34–7.08 (m, 3H), 2.59 (q, *J* = 14.9 Hz, 2H), 1.13 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 168.36, 147.74, 132.28, 128.11, 128.08, 28.54, 15.89 ppm.

4-Ethoxybenzamide (3e)[3]. Reaction scale: 4-Ethoxybenzonitrile (147.17 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



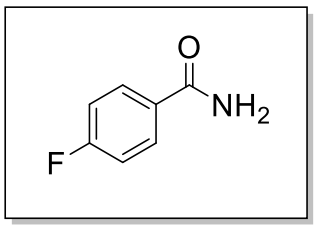
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 67% (111 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.82–7.75 (m, 3H), 7.14 (s, 1H), 6.93–6.86 (m, 2H), 4.02 (q, *J* = 6.9 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.98, 161.39, 129.87, 126.85, 114.27, 63.76, 15.06 ppm.

4-acetylbenzamide (3f)[4]. Reaction scale: 4-Acetylbenzonitrile (145.16 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



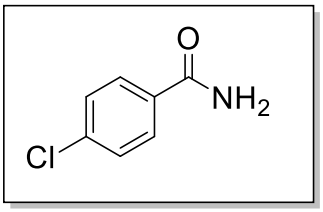
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 68% (111 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12 (br. s, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.55 (br. s, 1H), 2.57 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 198.25, 167.65, 139.16, 138.61, 128.60, 128.28, 27.45 ppm.

4-Fluorobenzamide (3g)[5]. Reaction scale: 4-Fluorobenzonitrile (121.11 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



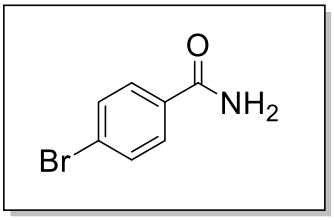
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 78% (108 mg); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97 (br. s, 1H), 7.94 – 7.84 (m, 2H), 7.38 (br s, 1H), 7.28 – 7.14 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.31, 164.44 (d, $J_{C\text{-}F}$ = 248.4 Hz), 131.23, 130.63 (d, $J_{C\text{-}F}$ = 9.1 Hz), 115.62 (d, $J_{C\text{-}F}$ = 21.7 Hz) ppm.

4-Chlorobenzamide (3h)[1]. Reaction scale: 4-Chlorobenzonitrile (137.57mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



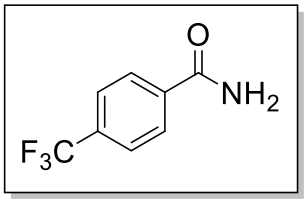
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 66% (102 mg).^{1}H NMR (400 MHz, DMSO-d_6): δ 8.14 (br. s, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.49 (br. s, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.35, 136.61, 133.54, 129.92, 128.81 ppm.

4-Bromobenzamide (3i)[5]. Reaction scale: 4-Bromobenzonitrile (182.02 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



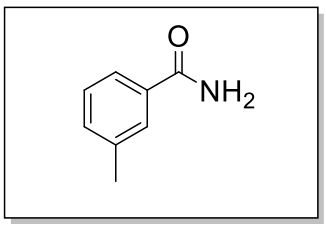
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 51% (102 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.01 (br. s, 1H), 7.81 – 7.73 (m, 2H), 7.66 – 7.58 (m, 2H), 7.43 (br. s, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.47, 133.89, 131.77, 130.13, 125.56 ppm.

4-(Trifluoromethyl)benzamide (3j)[6]. Reaction scale: 4-(Trifluoromethyl) benzonitrile (171.12 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89, 1 equiv.), H_2O (3 mL).



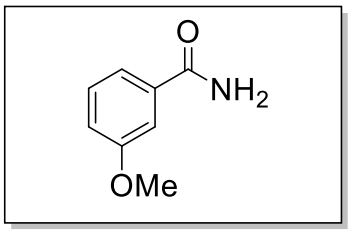
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 76% (144 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.28 (br. s, 1H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.66 (br. s, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.66, 138.33, 131.74 (d, *J* = 32.2 Hz),128.77, 125.78 (d, *J* = 2.9 Hz), 123.00 ppm.

***m*-Toluamide (3k)[5].** Reaction scale: *m*-Tolunitrile (117.15 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



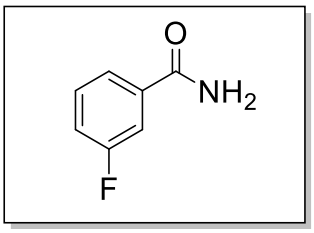
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 76% (103 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.88 (br. s, 1H), 7.65 (s, 1H), 7.64 – 7.58 (m, 1H), 7.28 (d, *J* = 4.9 Hz, 2H), 7.24 (br. s, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 168.60, 137.94, 134.75, 132.29, 128.60, 125.10, 21.47 ppm.

3-Methoxybenzamide (3l)[6]. Reaction scale: 3-Methoxybenzonitrile (133.15 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (1 equiv.), H_2O (3 mL).



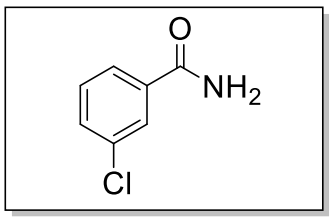
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 77% (116 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.93 (br. s, 1H), 7.40 (dd, *J* = 11.8, 4.7 Hz, 2H), 7.34 (br., s 1H), 7.34 – 7.27 (m, 1H), 7.03 (dd, *J* = 7.9, 2.3 Hz, 1H), 3.75 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 168.20, 159.65, 136.23, 129.84, 120.20, 117.57, 113.15, 55.72 ppm.

3-Fluorobenzamide (3m)[7]. Reaction scale: 3-Fluorobenzonitrile (121.11 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



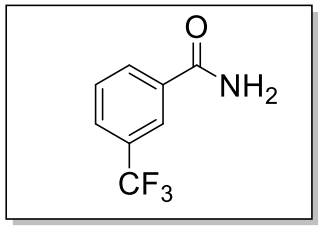
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 78% (108 mg); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.03 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.50 (s, 1H), 7.50 – 7.40 (m, 1H), 7.33 (td, *J* = 8.5, 2.3 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.18, 162.49 (d, *J* = 244.0 Hz), 137.22 (d, *J* = 6.4 Hz), 130.86, 124.11, 118.62 (d, *J* = 21.1 Hz), 114.75 (d, *J* = 22.5 Hz) ppm.

3-Chlorobenzamide (3n)[4]. Reaction scale: 3-Chlorobenzonitrile (137.57 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



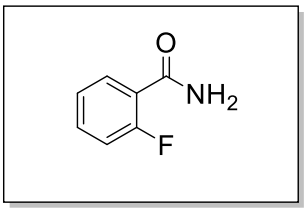
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 54% (84 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.23 (br. s, 1H), 7.92 (d, *J* = 1.5 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.67–7.61 (m, 1H), 7.57 (br. s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO- d_6): δ 167.59, 136.31, 133.70, 131.79, 130.87, 127.69, 126.56 ppm.

3-(Trifluoromethyl)benzamide (3o)[6]. Reaction scale: 3-(Trifluoromethyl)benzonitrile (171.12 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



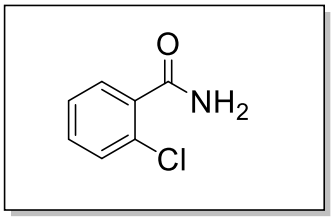
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 79% (149 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.21 (s, 1H), 8.18 – 8.10 (m, 2H), 7.84 (s, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.60 (s, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 166.91, 135.66, 131.98, 129.98, 128.25, 125.83, 124.60, 123.12 ppm.

2-Fluorobenzamide (3p)[7]. Reaction scale: 2-Fluorobenzonitrile (121.11 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



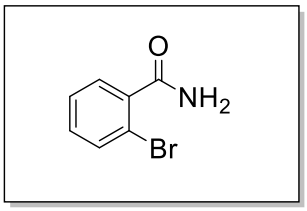
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 65% (90 mg).^{1}H NMR (400 MHz, DMSO-d_6): δ 7.78 (br. s, 1H), 7.71 (td, *J* = 7.8, 1.8 Hz, 1H), 7.67 (br. s, 1H), 7.62–7.54 (m, 1H), 7.36–7.28 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 165.93, 160.98, 158.50, 133.10 (d, *J* = 8.6 Hz), 130.66 (d, *J* = 2.8 Hz), 124.94 (d, *J* = 3.5 Hz), 116.57 (d, *J* = 22.7 Hz) ppm.

2-Chlorobenzamide (3q)[4]. Reaction scale: 2-Chlorobenzonitrile (137.57 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



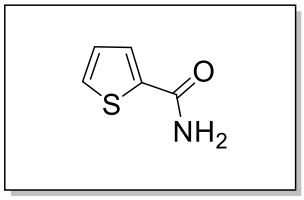
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 29% (45 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85 (s, 1H), 7.57 (s, 1H), 7.50–7.17 (m, 4H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 168.71, 137.67, 131.08, 130.12, 129.18, 128.60, 127.54 ppm.

2-Brombenzamide (3r)[8]. Reaction scale: 2-bromobenzonitrile (182.02 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



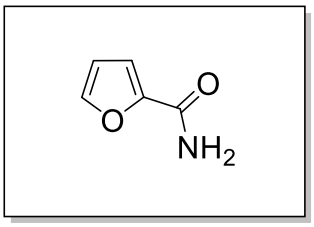
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 22% (44 mg)**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.82 (br. s, 1H), 7.61–7.57 (m, 1H), 7.52 (br. s, 1H), 7.40–7.34 (m, 2H), 7.29 (ddd, *J* = 7.8, 6.3, 2.8 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 169.61, 139.85, 133.22, 131.17, 129.07, 128.01, 119.12 ppm.

Thiophene-2-Carboxamide (3s)[5]. Reaction scale: Thiophene -2-carbonitrile (109 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



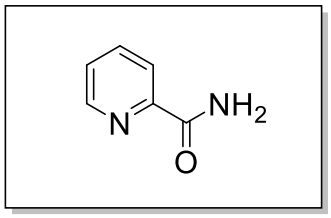
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 91% (116 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.06 (s, 1H), 7.78 (d, *J* = 3.3 Hz, 2H), 7.40 (s, 1H), 7.19 (d, *J* = 3.5 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO- d_6): δ 163.65, 140.30, 131.59, 129.33, 128.45 ppm.

Furan-2-carboxamide (3t)[6]. Reaction scale: 2-Furonitrile (93.09, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



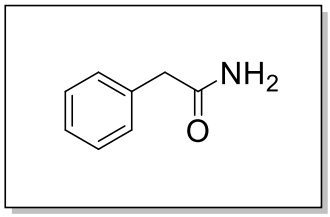
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 84% (93 mg)**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.76 (s, 1H), 7.73 (s, 1H), 7.33 (s, 1H), 7.05 (d, *J* = 3.2 Hz, 1H), 6.55 (dd, *J* = 3.5, 1.7 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO- d_6): δ 159.98, 148.55, 145.52, 114.15, 112.29 ppm.

Picolinamide (3u)[5]. Reaction scale: 2-Pyridincarbonitrile (104.11 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



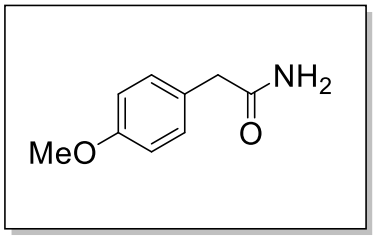
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 57% (70 mg)**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68 (d, *J* = 4.7 Hz, 1H), 8.25 (s, 1H), 8.11 – 8.00 (m, 2H), 7.68 – 7.60 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 166.95, 150.23, 149.04, 138.26, 127.16, 122.44 ppm.

2-Phenylacetamide (3v)[9]. Reaction scale: Phenylacetonitrile (117.15, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



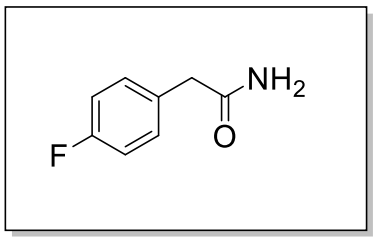
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 29% (39 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 (br. s, 1H), 7.32 –7.08 (m, 5H), 6.84 (br. s, 1H), 3.32 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.78, 137.01, 129.57, 128.67, 126.78, 42.78 ppm.

2-(4-methoxyphenyl)acetamide (3w)[4]. Reaction scale: 4-methoxyphenylacetonitrile (147.17, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



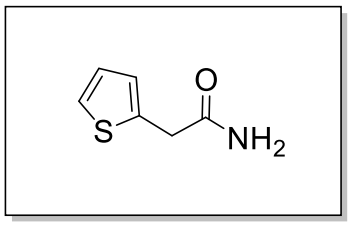
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 30% (49 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.36 (br. s, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.82 (br. s, 1H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.68 (s, 3H), 3.24 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 173.16, 158.36, 130.54, 128.94, 114.10, 55.52, 41.86 ppm.

2-(4-Fluorophenyl)acetamide (3x)[9]. Reaction scale: 4-Fluorophenylacetonitrile (135.14, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



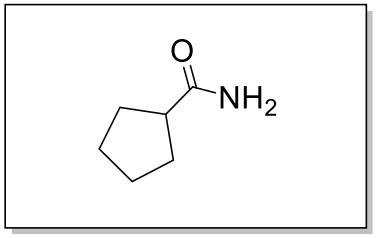
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 29% (45 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 (br. s, 1H), 7.27–7.20 (m, 2H), 7.12 – 7.00 (m, 2H), 6.85 (br. s, 1H), 3.31 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.71, 161.50 (d, *J* = 241.7 Hz)., 133.15 (d, *J* = 2.4 Hz), 131.38 (d, *J* = 8.1 Hz), 115.33 (d, *J* = 21.1 Hz), 41.73 ppm.

2-(Thiophen-2-yl)acetamide (3y)[10]. Reaction scale: 2-Thiopheneacetonitrile (123.18, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



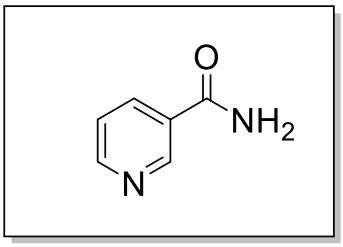
The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 20% (28 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47 (br. 1H), 7.30 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.93 (br. s, 1H), 6.90 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.87 – 6.81 (m, 1H), 3.55 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.70, 138.25, 127.03, 126.54, 125.25, 36.85 ppm.

Cyclopentanecarboxamide (3ab)[11]. Reaction scale: cyclopentanecarbonitrile (95.14, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).



The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 27% (31 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.18 (s, 1H), 6.63 (s, 1H), 1.75–1.61 (m, 2H), 1.60–1.49 (m, 4H), 1.43 (t, *J* = 7.1 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.93, 44.56, 30.39, 26.08 ppm.

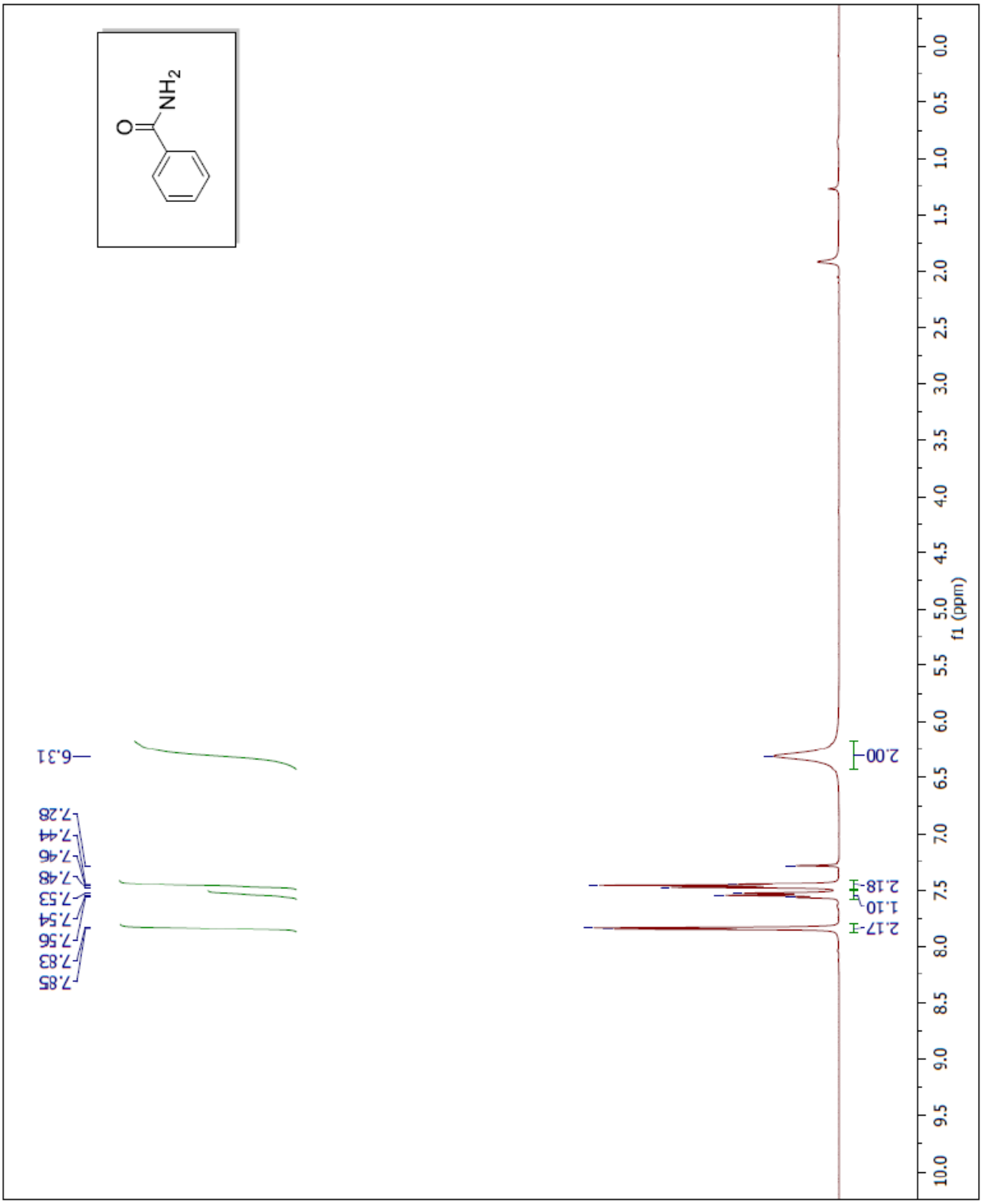
Nicotinamide[6]. Reaction scale: 3-Pyridincarbonitrile (104.11 mg, 1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.02 mmol), $Na_3P_3O_9$ (305.89 mg, 1 equiv.), H_2O (3 mL).

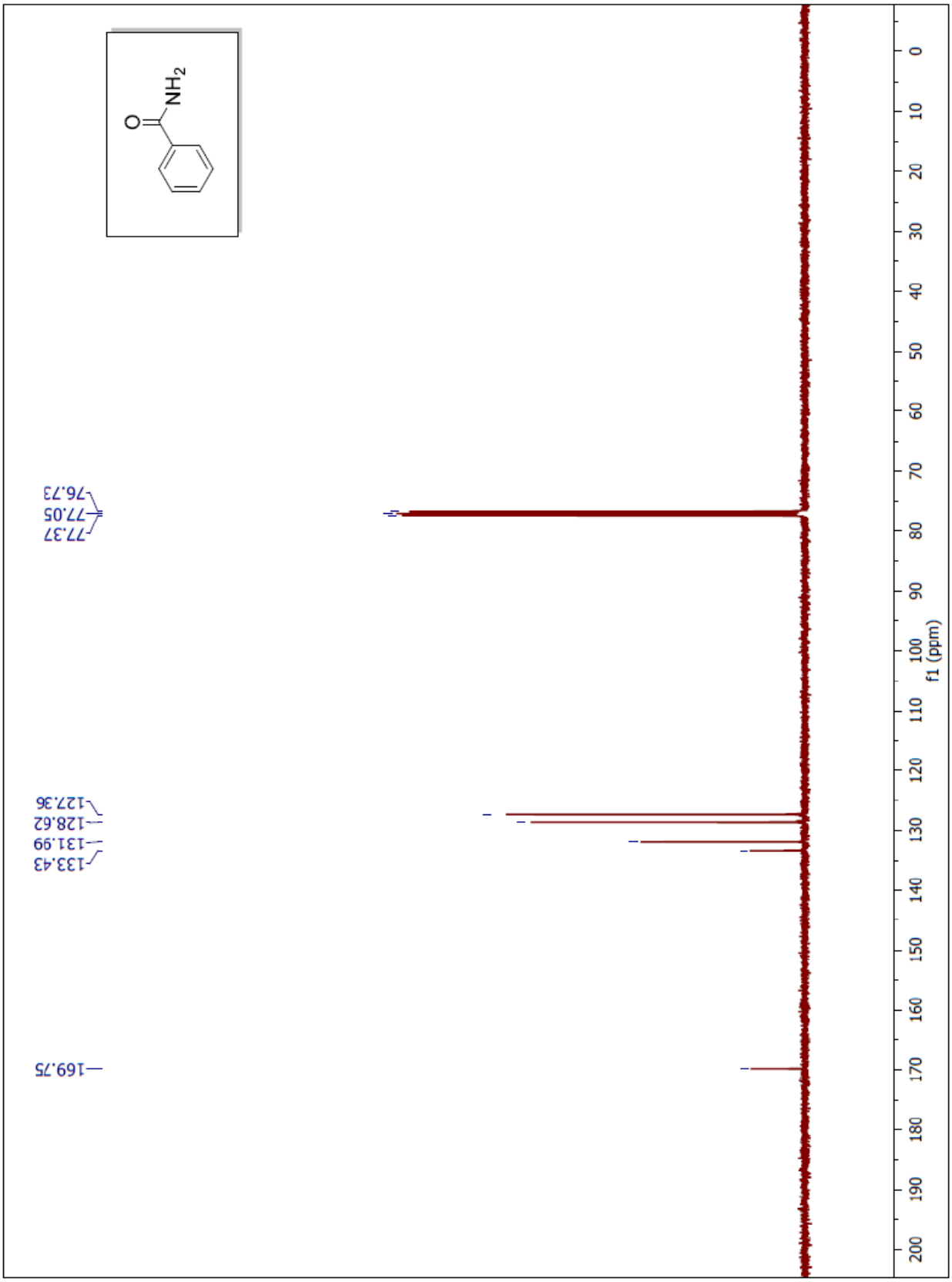


The title compound was synthesized according to general procedure and isolated through column chromatography. The isolated yield is 93% (113 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.99 (d, *J* = 1.8 Hz, 1H), 8.66 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.19 – 8.15 (m, 1H), 8.14 (s, 1H), 7.58 (s, 1H), 7.45 (dd, *J* = 7.8, 4.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.03, 152.41, 149.22, 135.68, 130.17, 123.92 ppm.

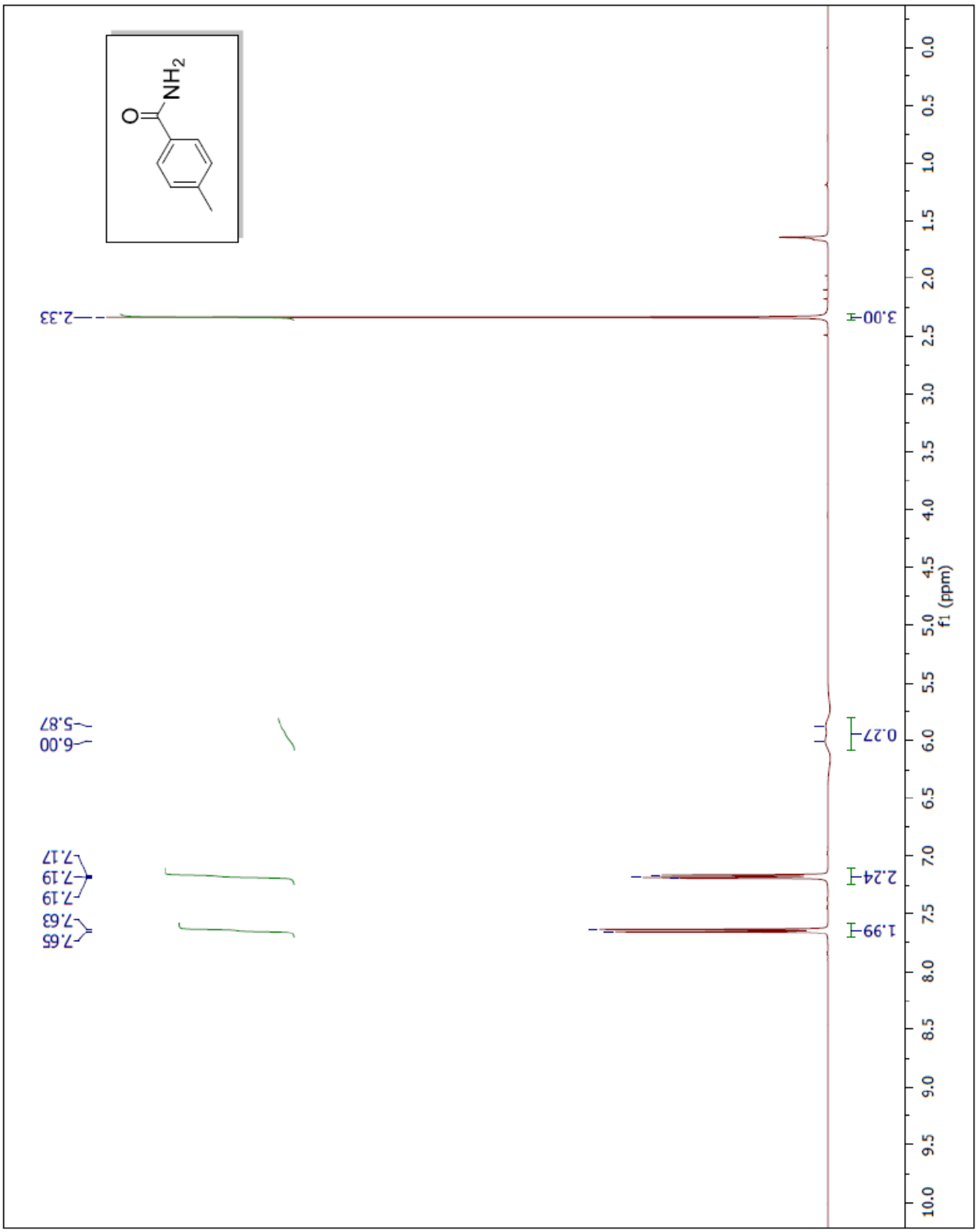
(6) ^{1}H and ^{13}C NMR spectra of all the isolated compounds

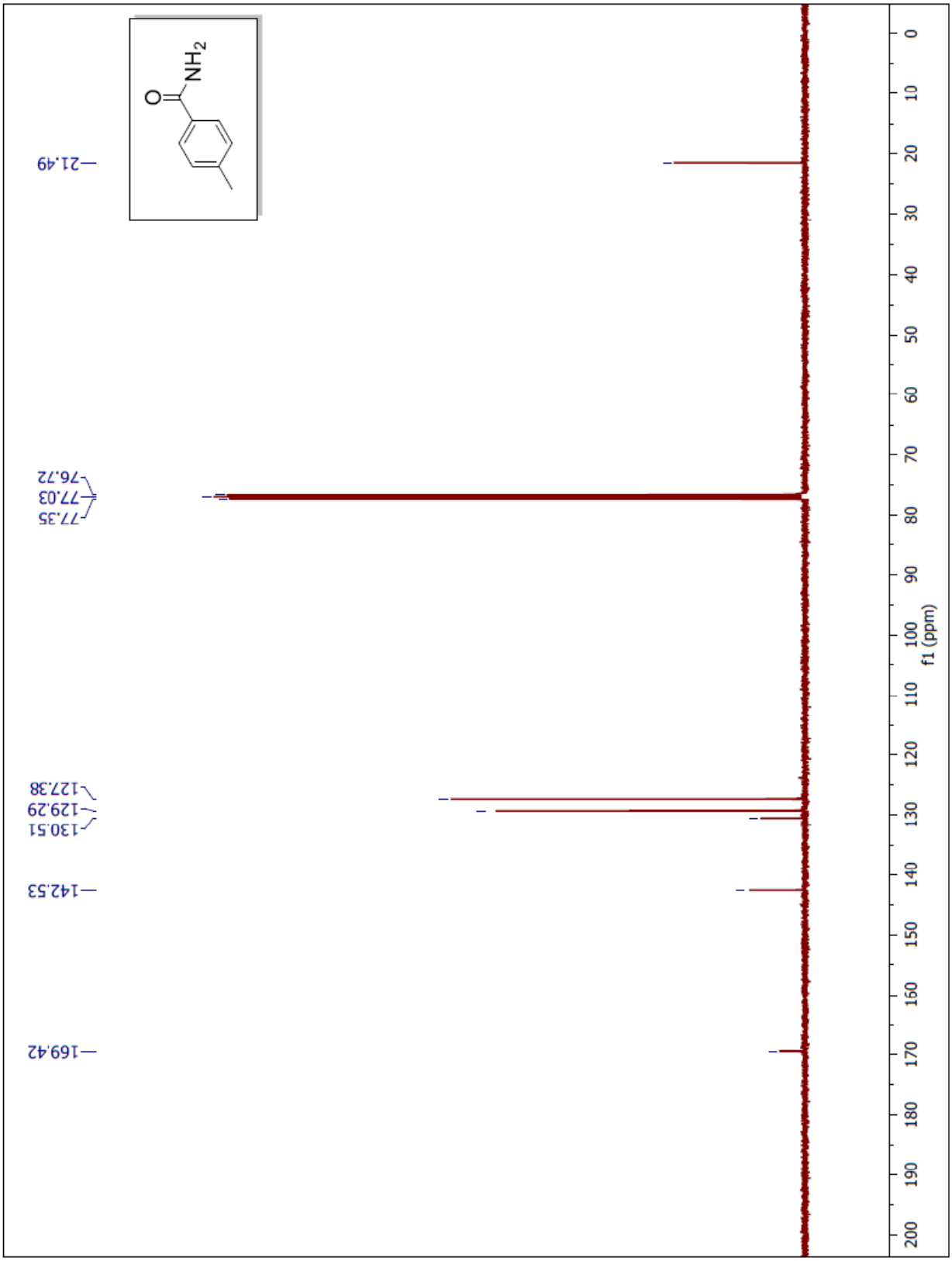
^{1}H and ^{13}C NMR spectra of compound 3a:



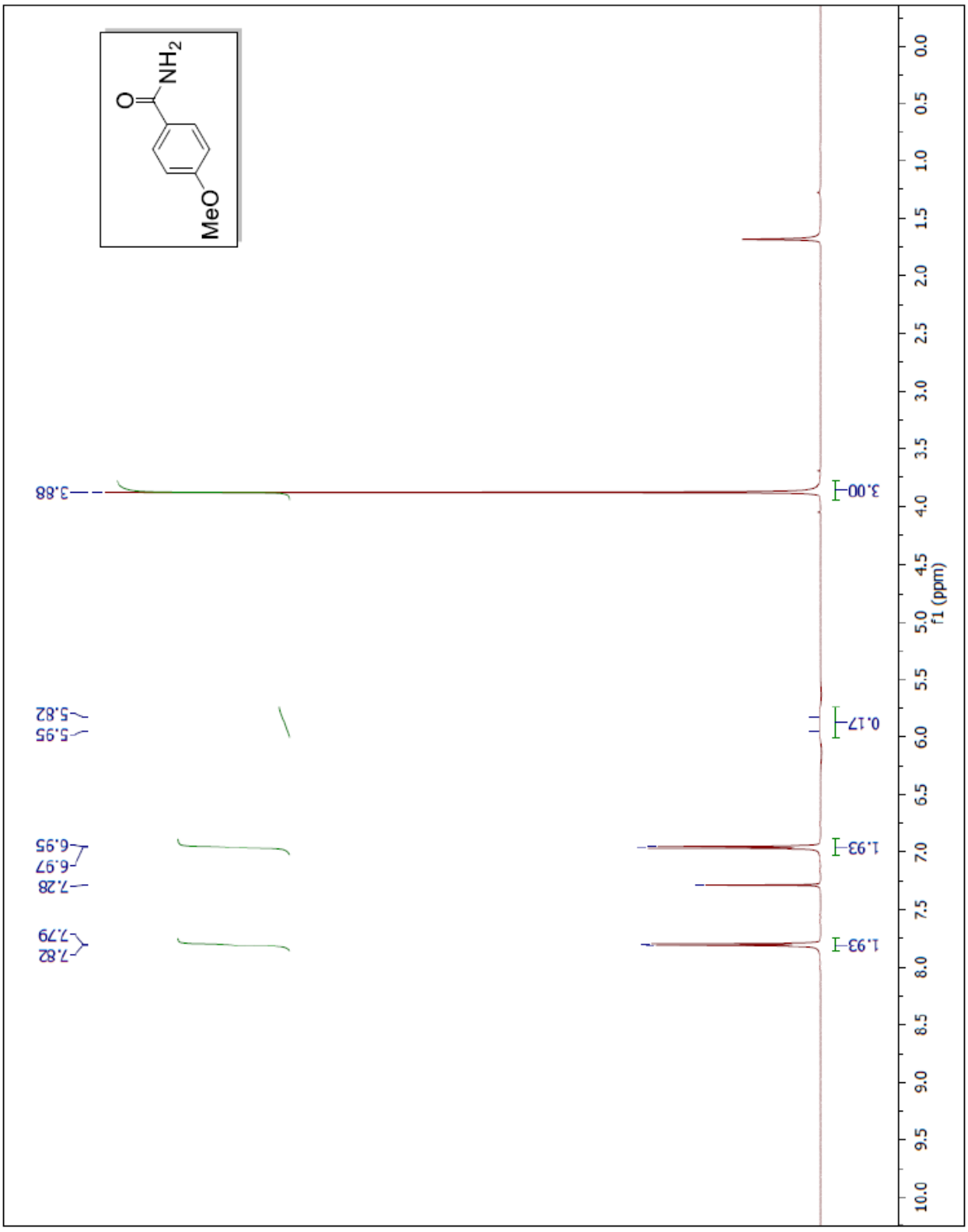

NH2
O
169.75
133.43
131.99
128.62
127.36
77.37
77.05
76.73
f1 (ppm)

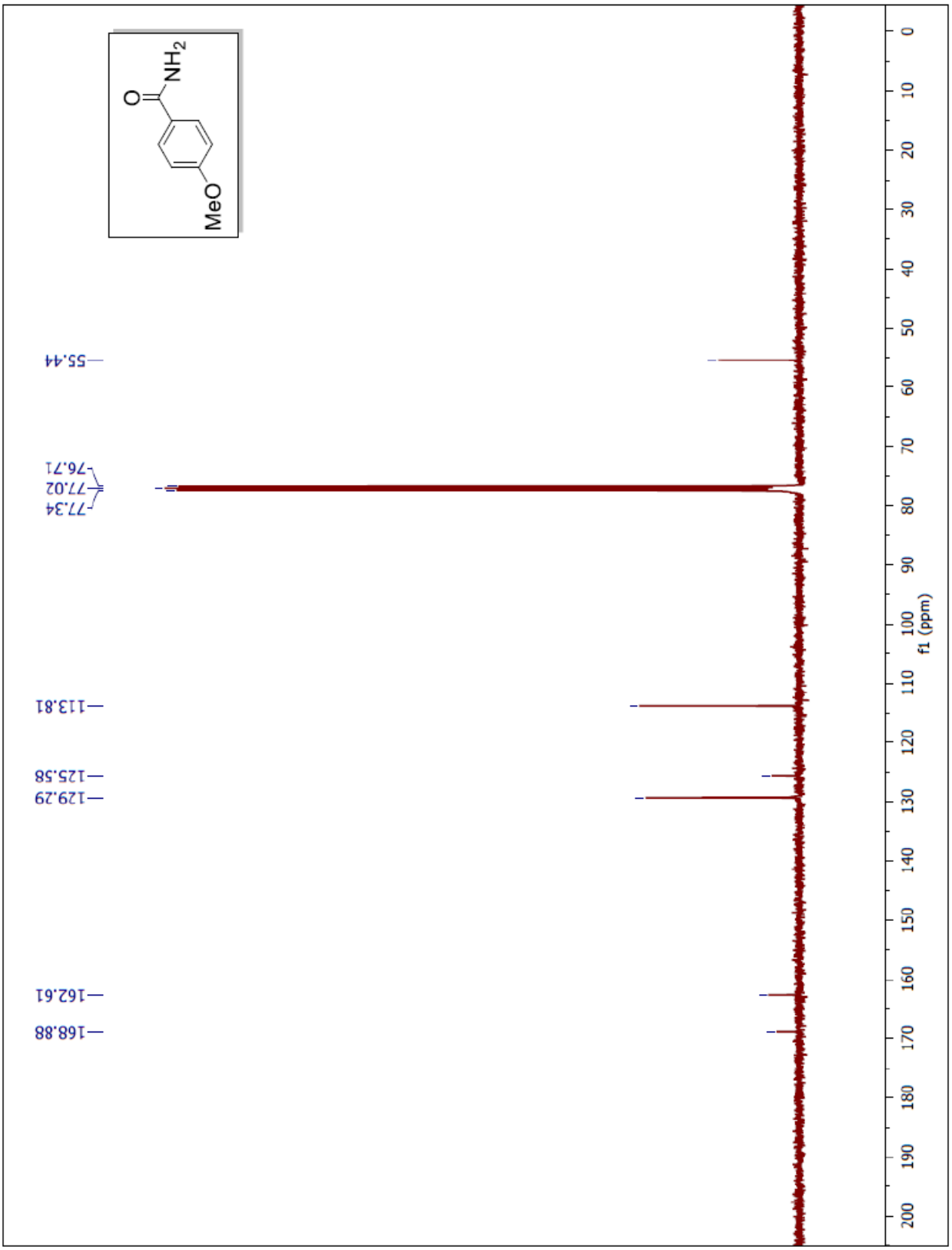
^{1}H and ^{13}C NMR spectra of compound 3b:



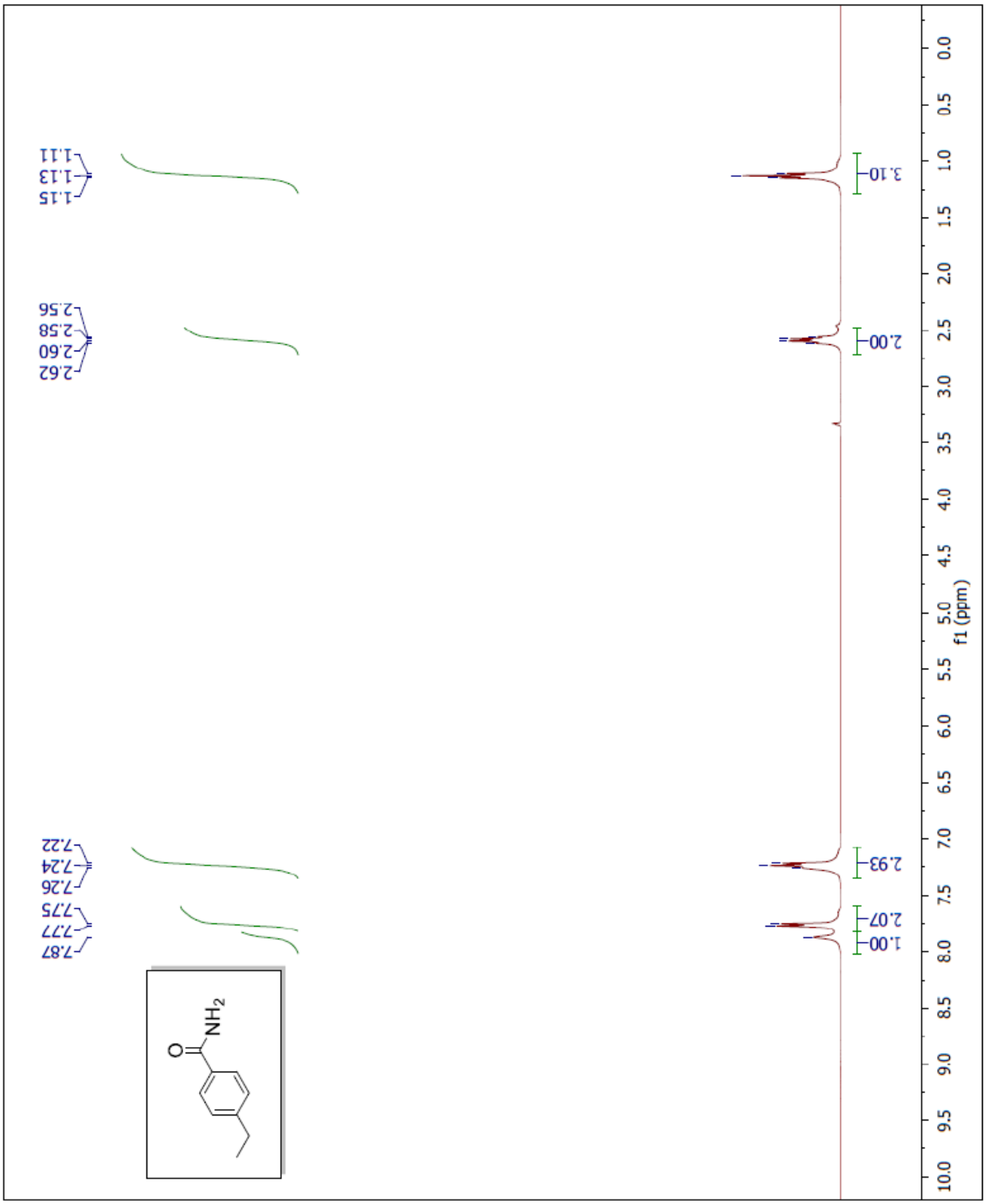

NH2
O
21.49
76.72
77.03
77.35
127.38
129.29
130.51
142.53
169.42
f1 (ppm)

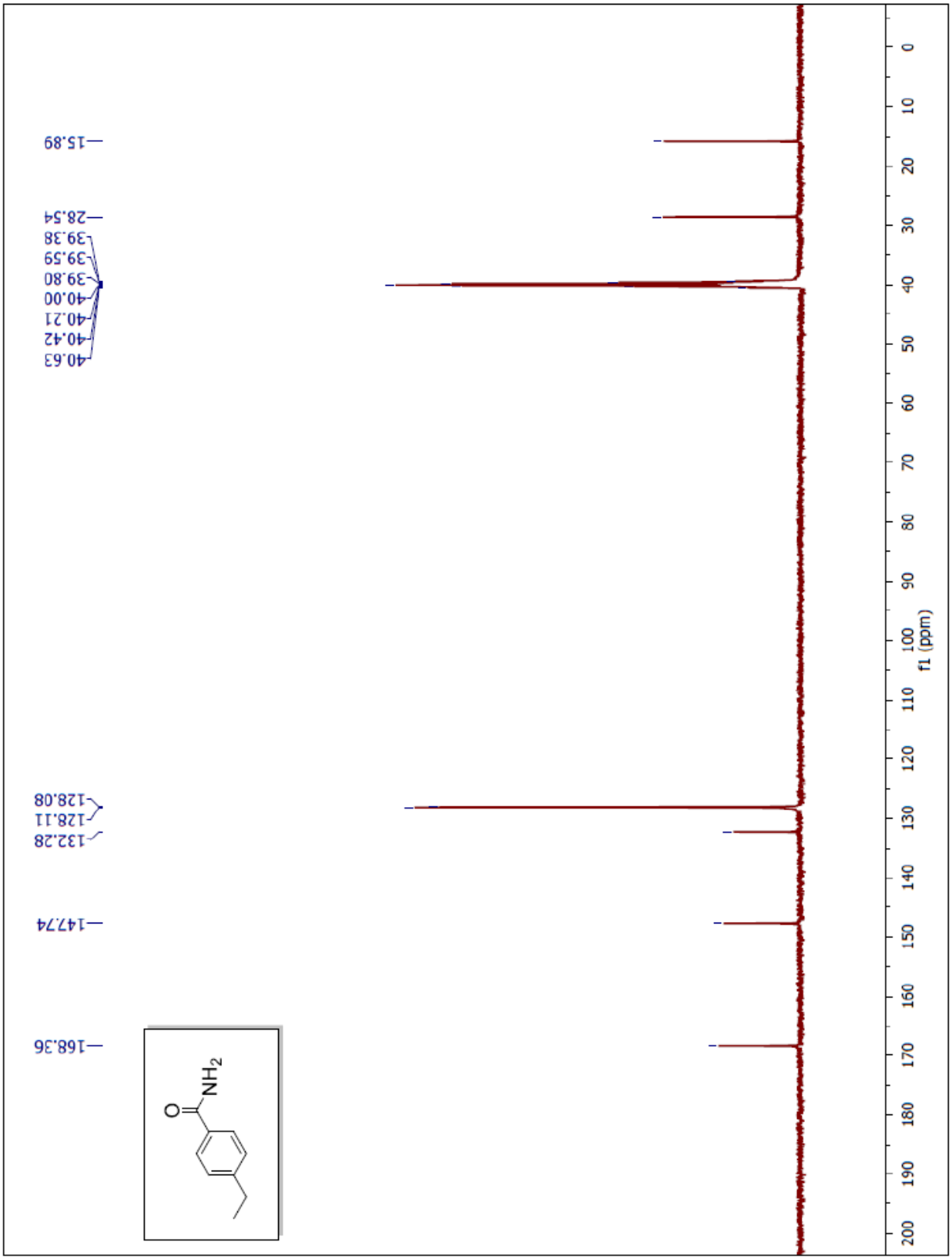
^{1}H and ^{13}C NMR spectra of compound 3c:



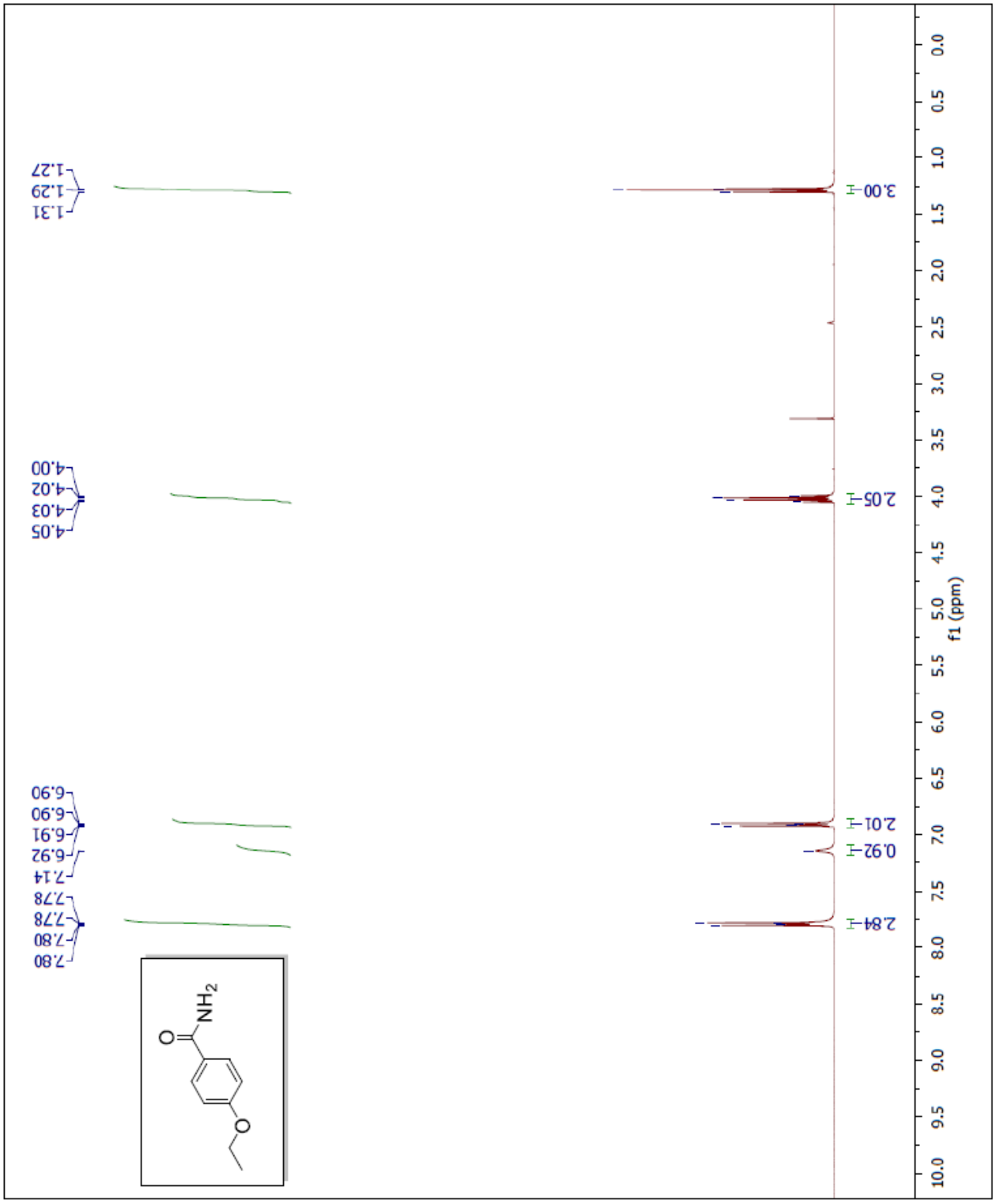

NH2
O
MeO
55.44
76.71
77.02
77.34
113.81
125.58
129.29
162.61
168.88
f1 (ppm)

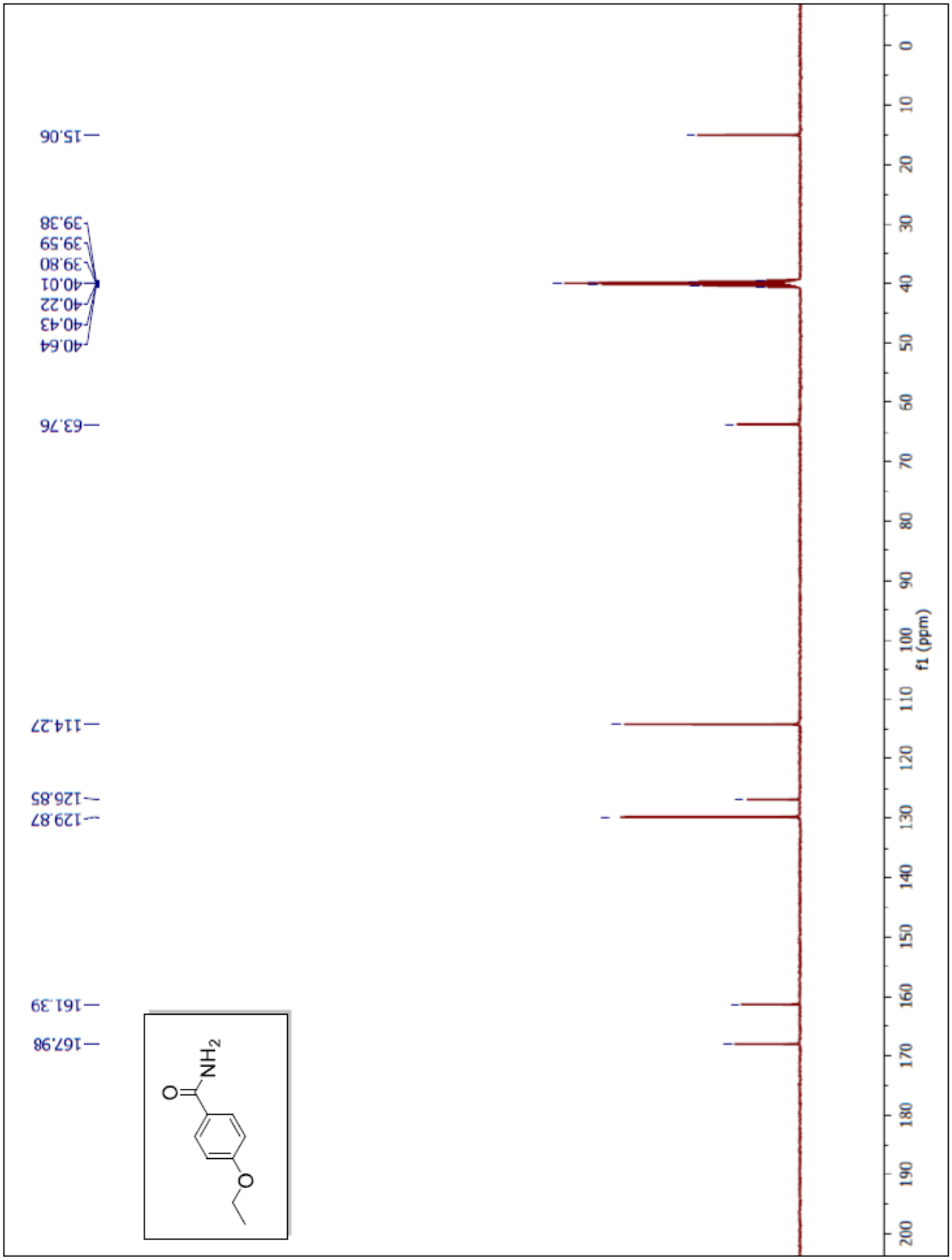
^{1}H and ^{13}C NMR spectra of compound 3d:



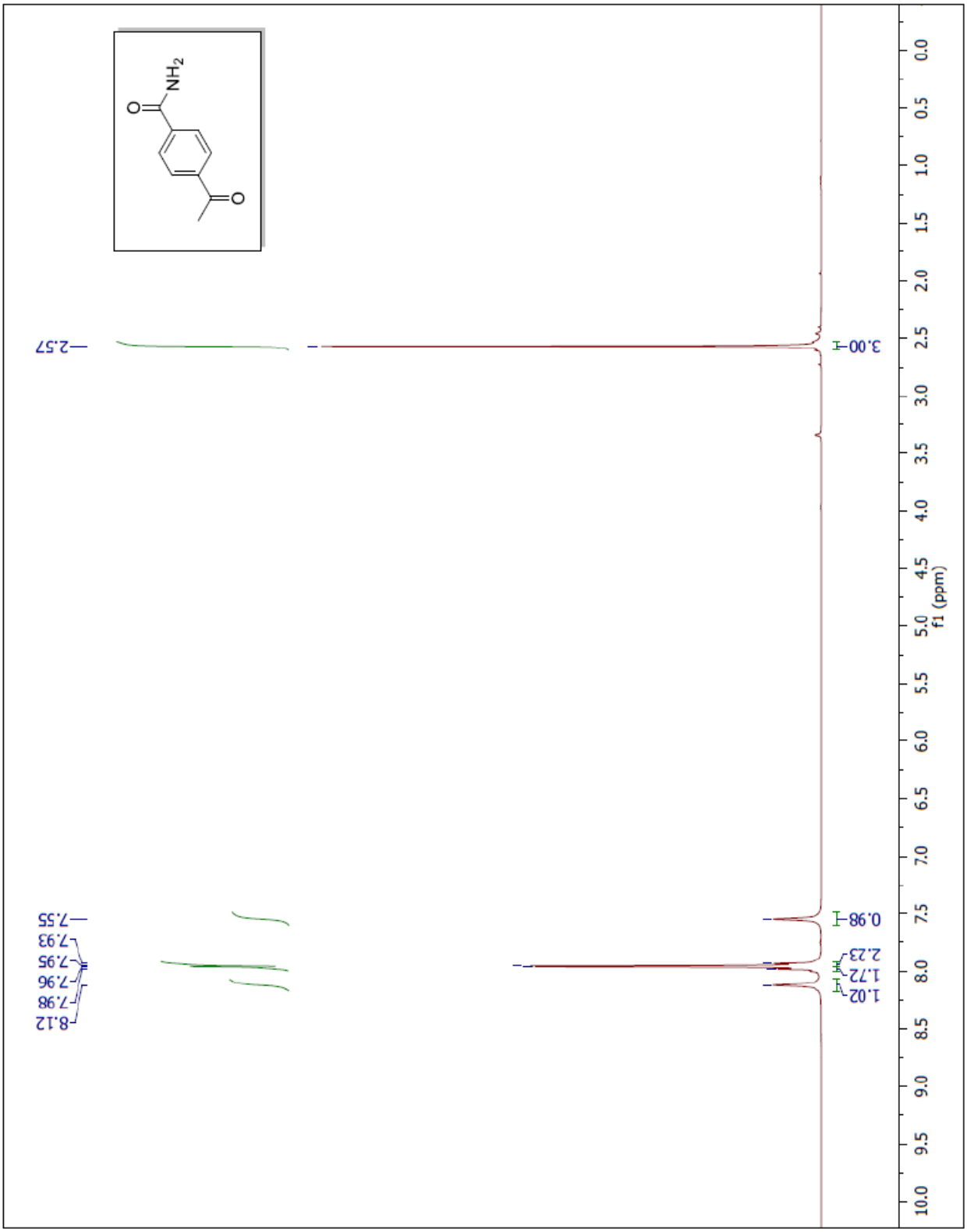

15.89
28.54
39.38
39.59
39.80
40.00
40.21
40.42
40.63
128.08
128.11
132.28
147.74
168.36
NH2
O
f1 (ppm)

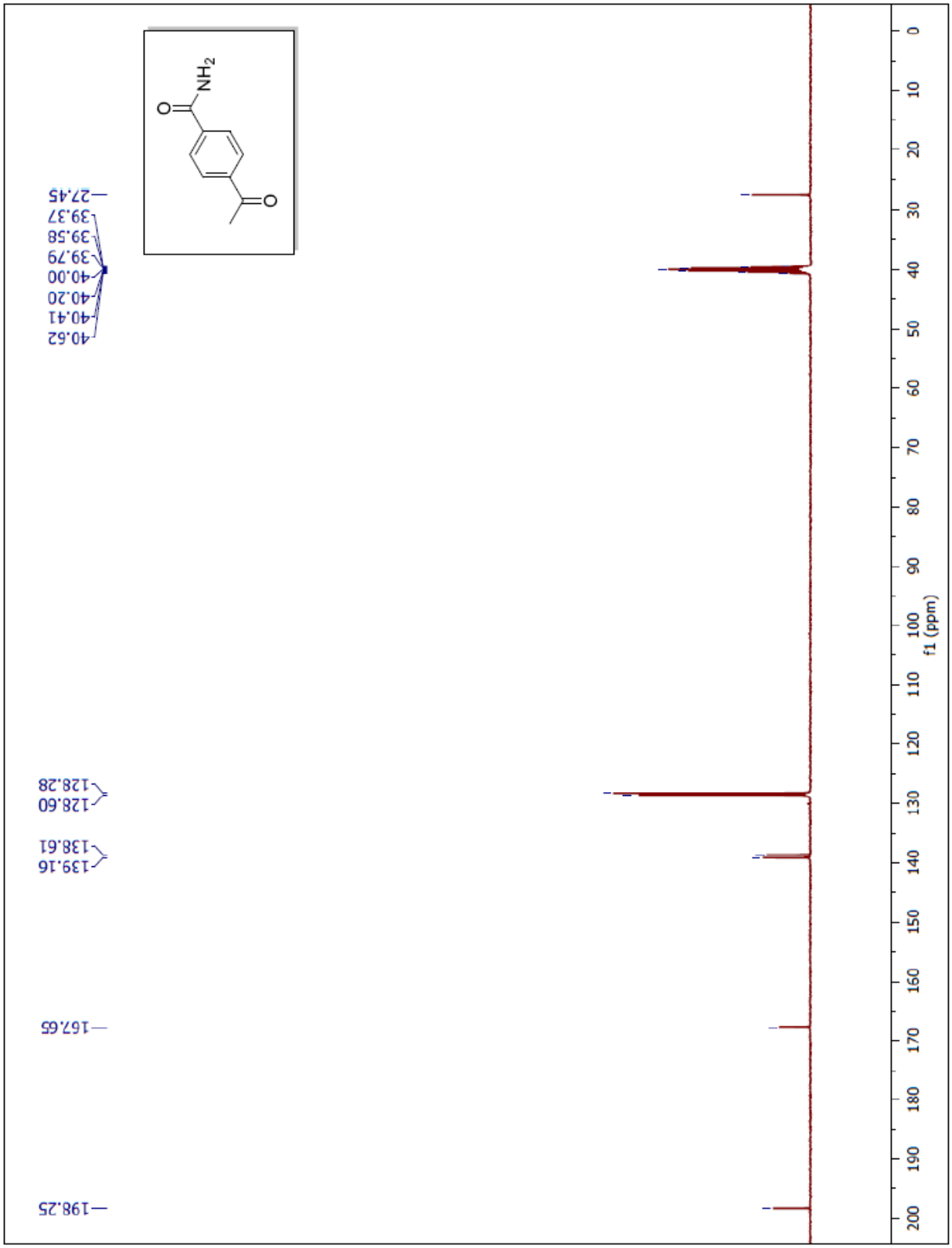
^{1}H and ^{13}C NMR spectra of compound 3e:



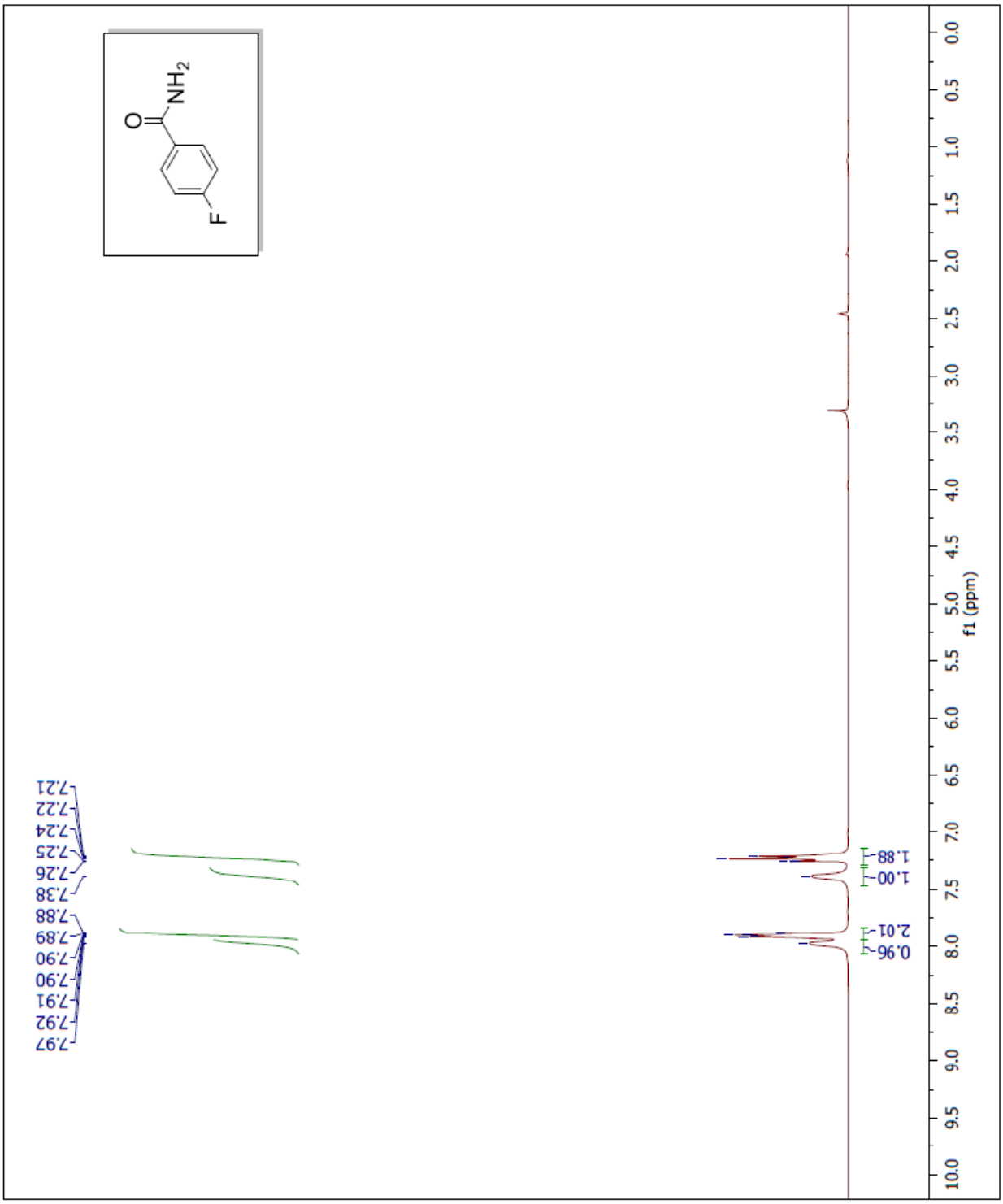

15.06
39.38
39.59
39.80
40.01
40.22
40.43
40.64
63.76
114.27
126.85
129.87
161.39
167.98
NH2
O
O
f1 (ppm)

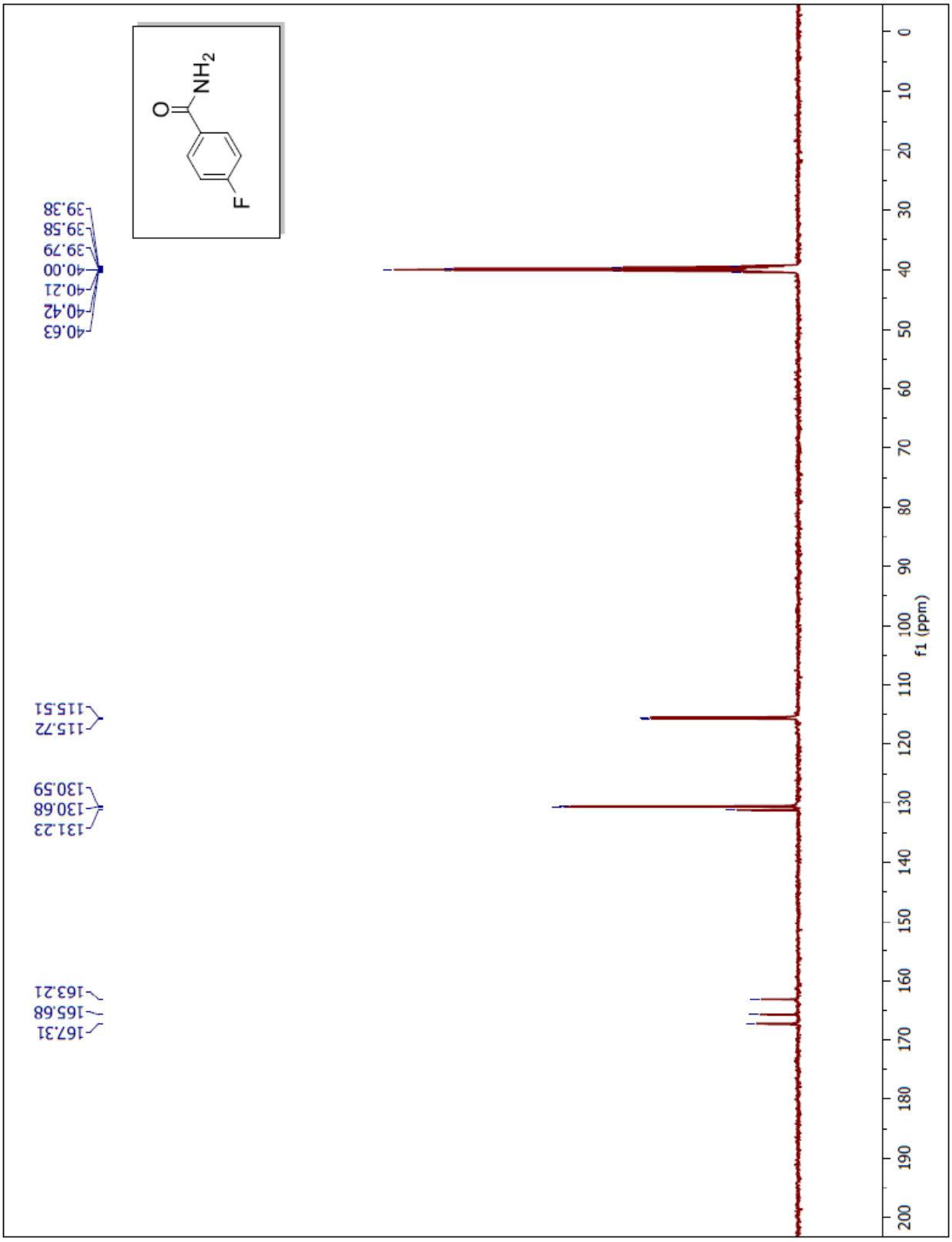
^{1}H and ^{13}C NMR spectra of compound 3f:



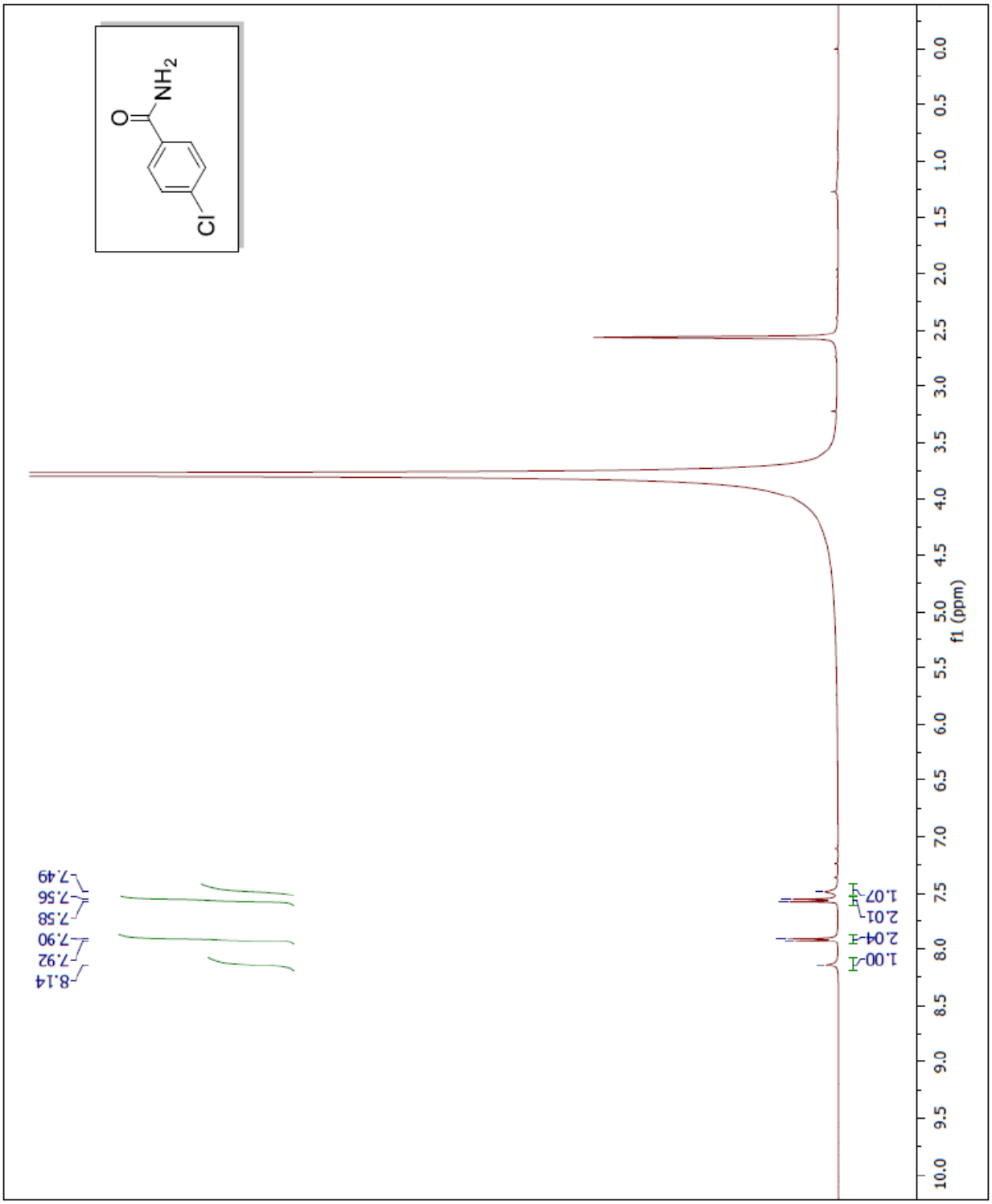

198.25
167.65
139.16
138.61
128.60
128.28
40.52
40.41
40.20
40.00
39.79
39.58
39.37
27.45
NH2
O
O
f1 (ppm)

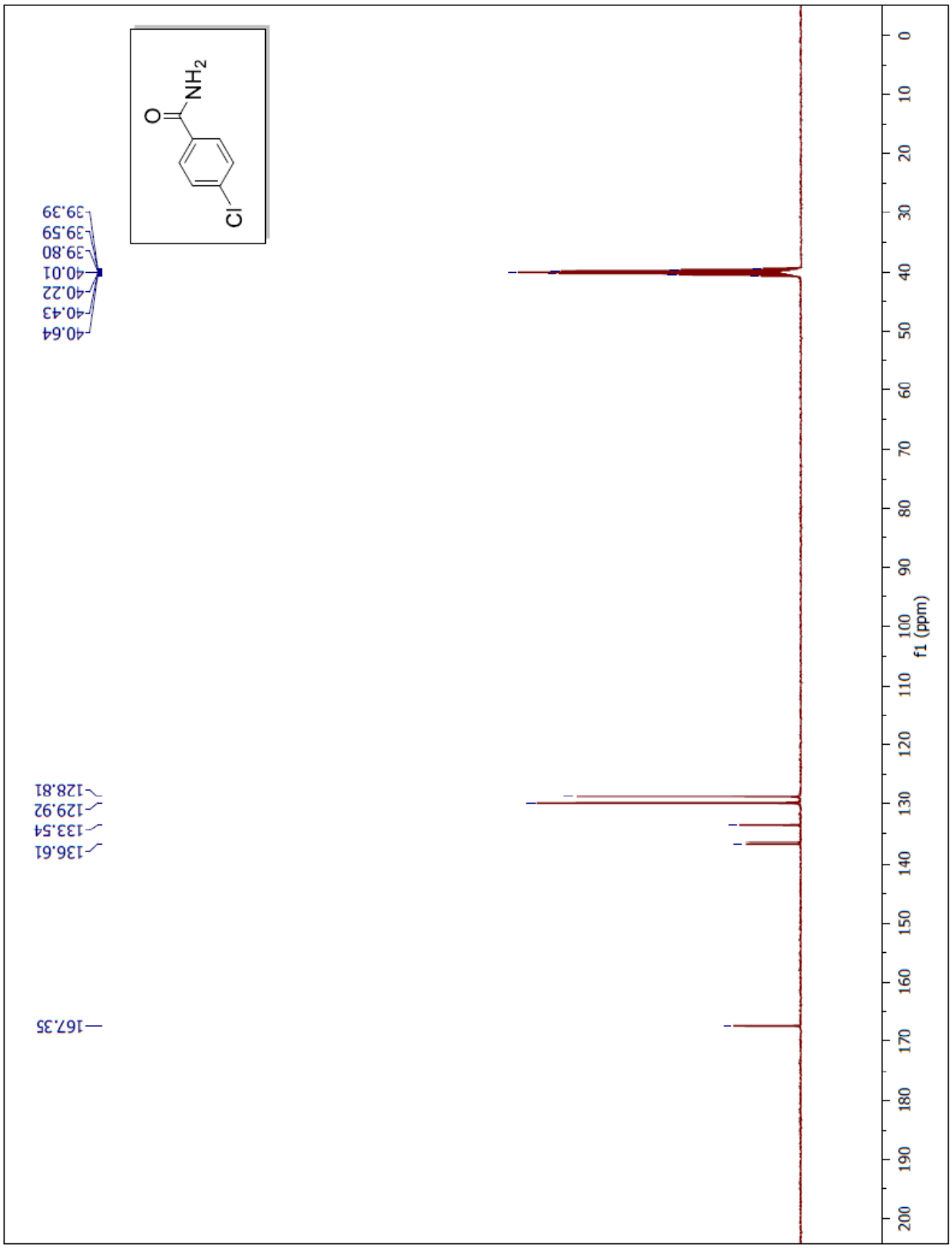
^{1}H and ^{13}C NMR spectra of compound 3g:



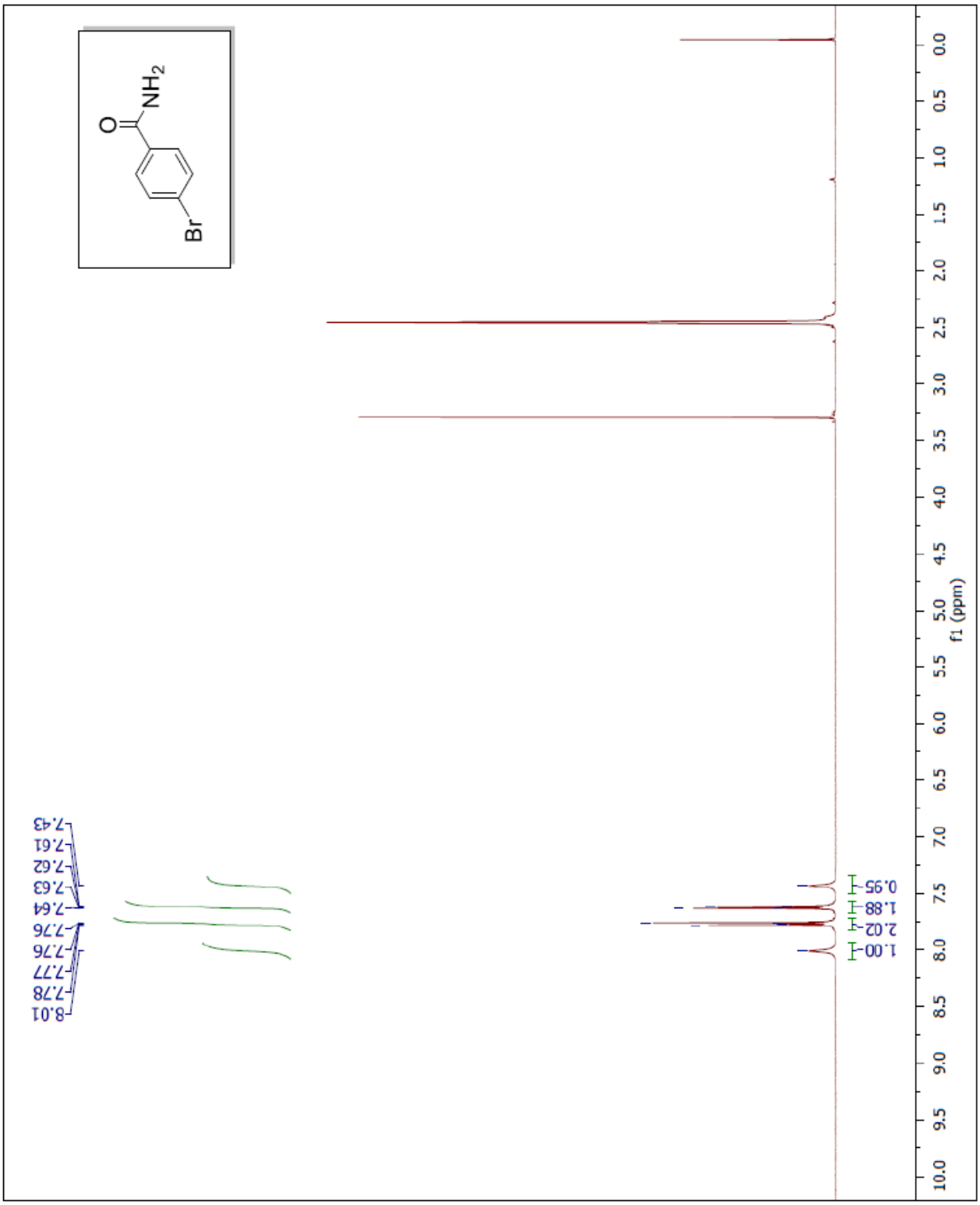

O
NH2
F
39.38
39.58
39.79
40.00
40.21
40.42
40.63
115.51
115.72
130.59
130.68
131.23
163.21
165.68
167.31
f1 (ppm)

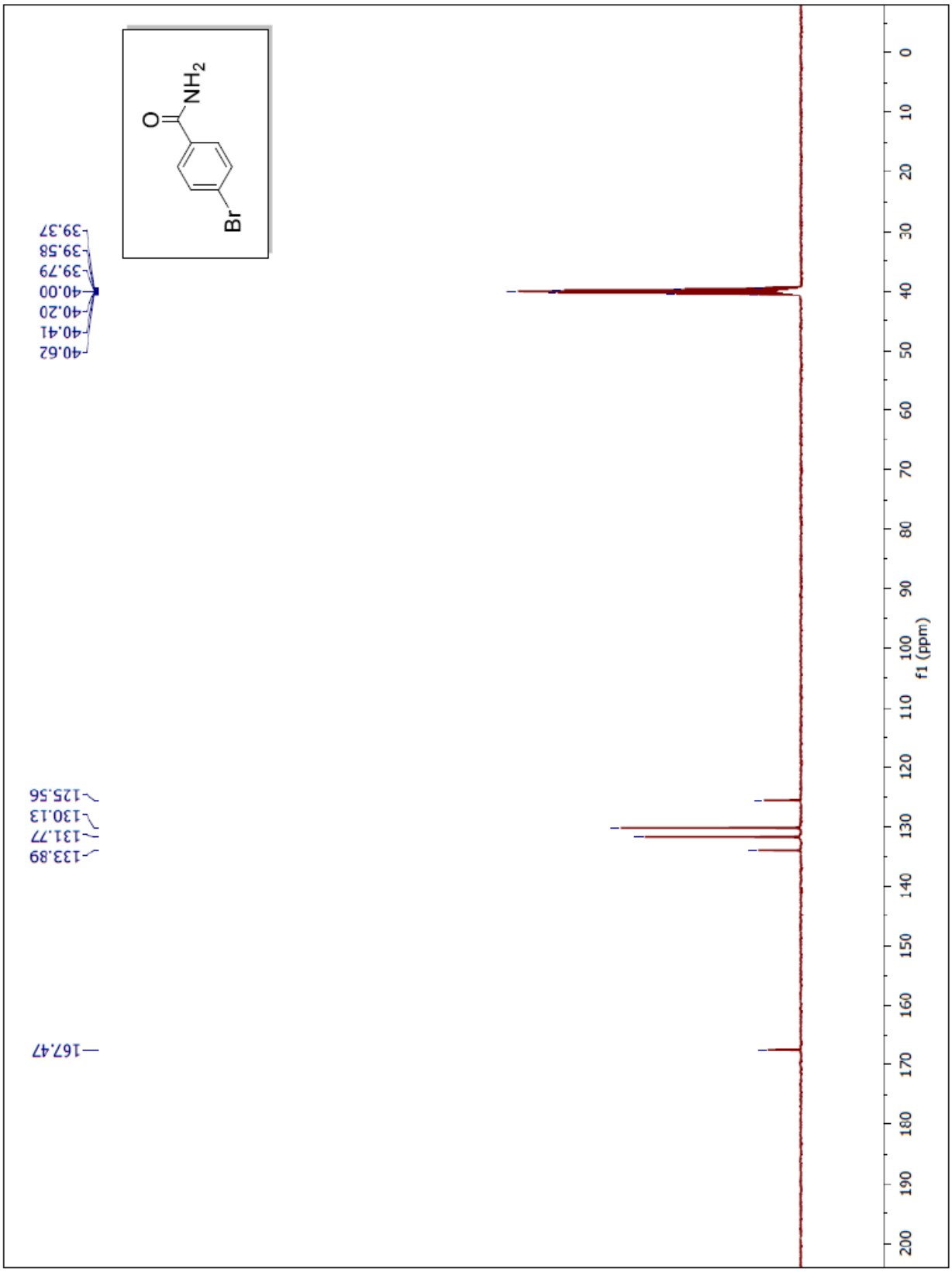
^{1}H and ^{13}C NMR spectra of compound 3h:



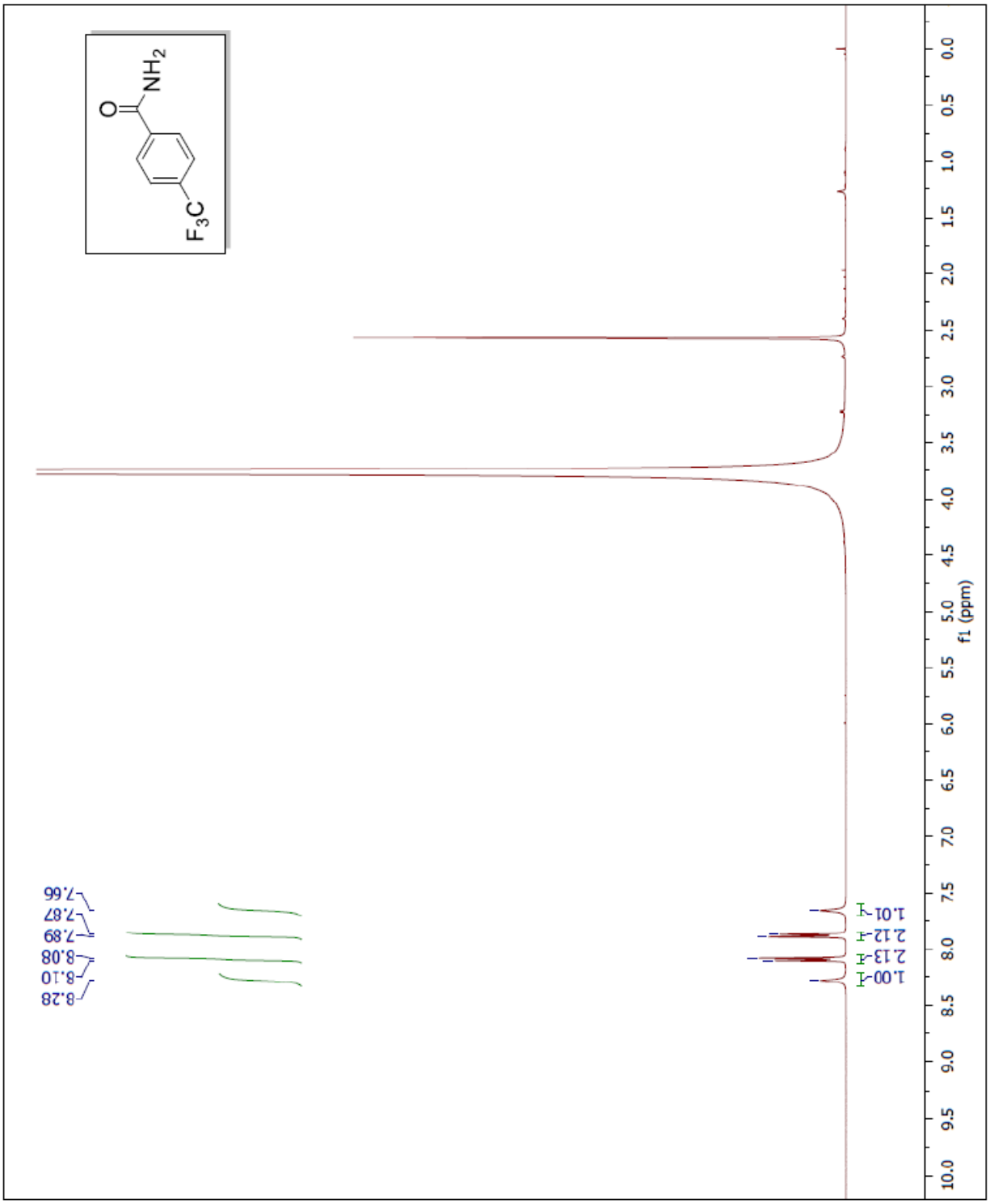

O
NH2
Cl
167.35
136.61
133.54
129.92
128.81
40.64
40.43
40.22
40.01
39.80
39.59
39.39
f1 (ppm)

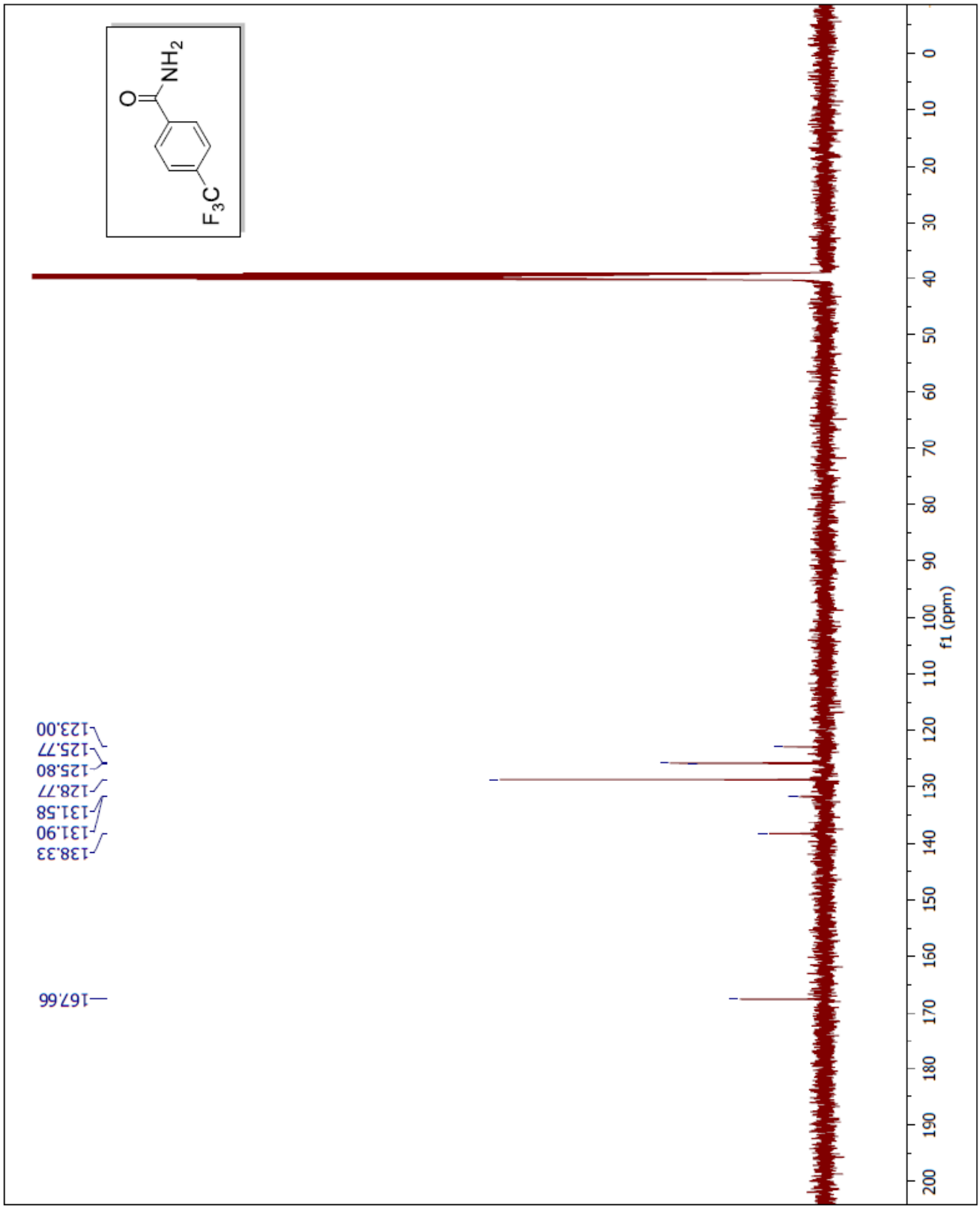
^{1}H and ^{13}C NMR spectra of compound 3i:



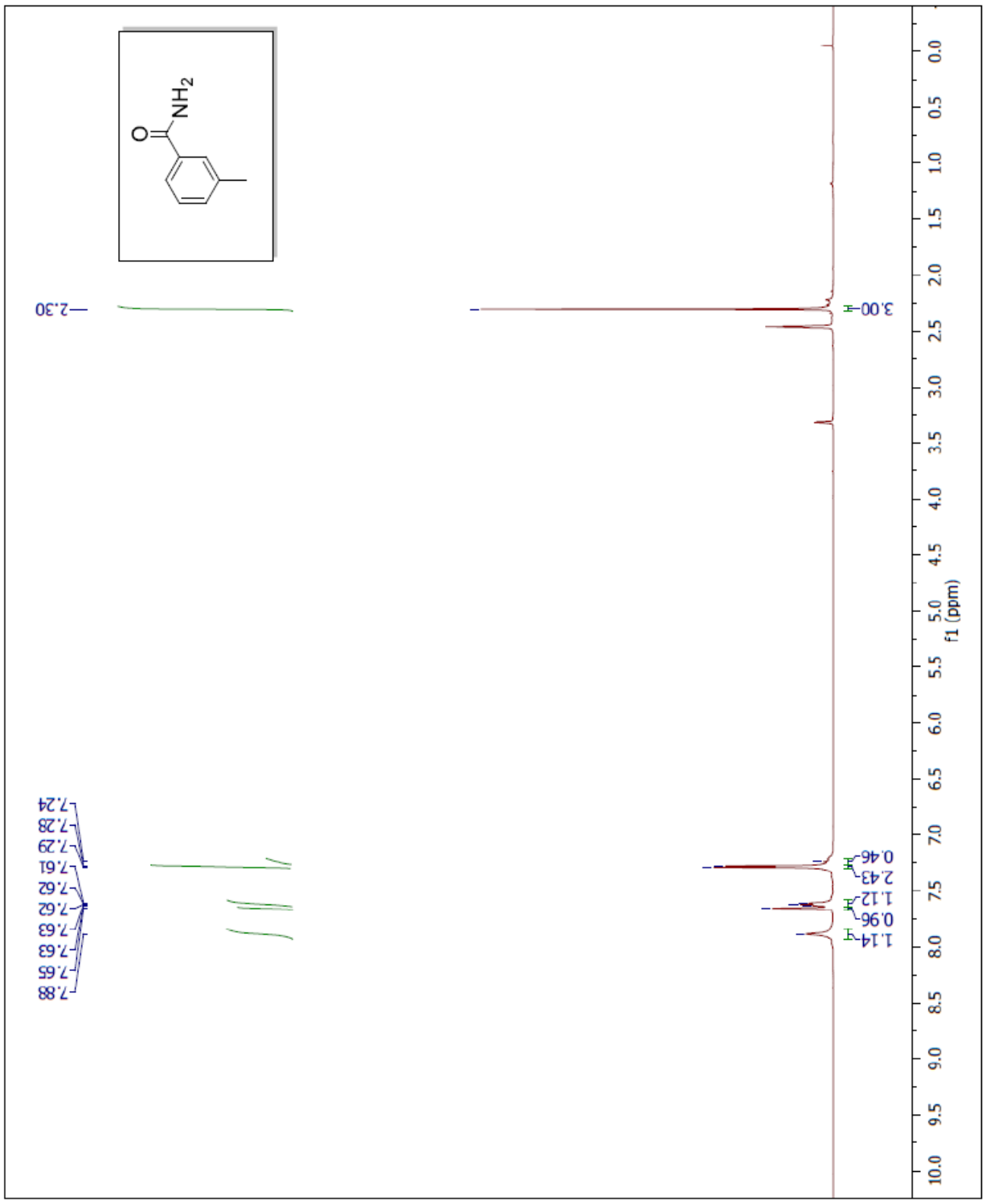

NH2
O
Br
167.47
133.89
131.77
130.13
125.56
40.62
40.41
40.20
40.00
39.79
39.58
39.37
f1 (ppm)

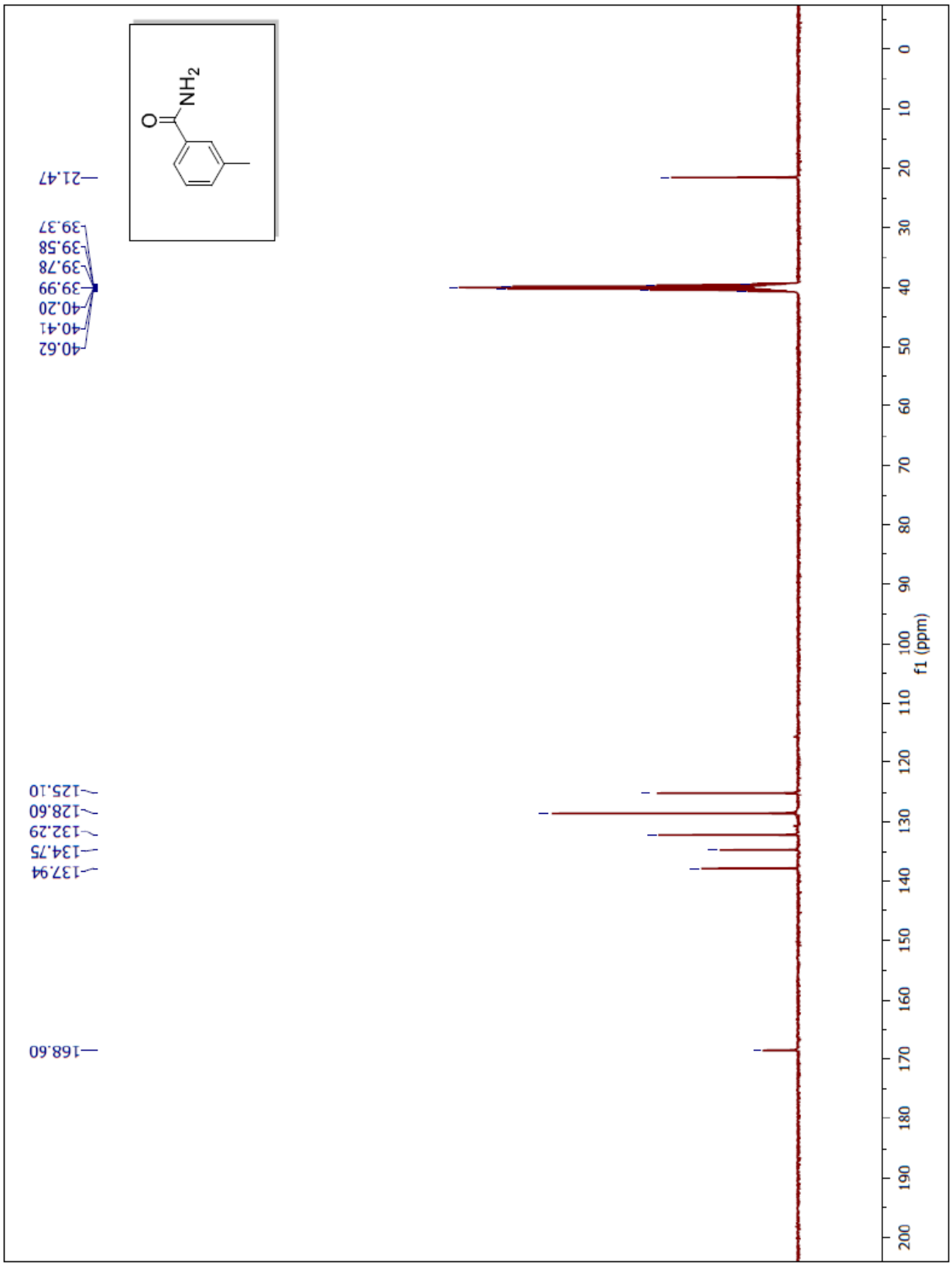
^{1}H and ^{13}C NMR spectra of compound 3j:



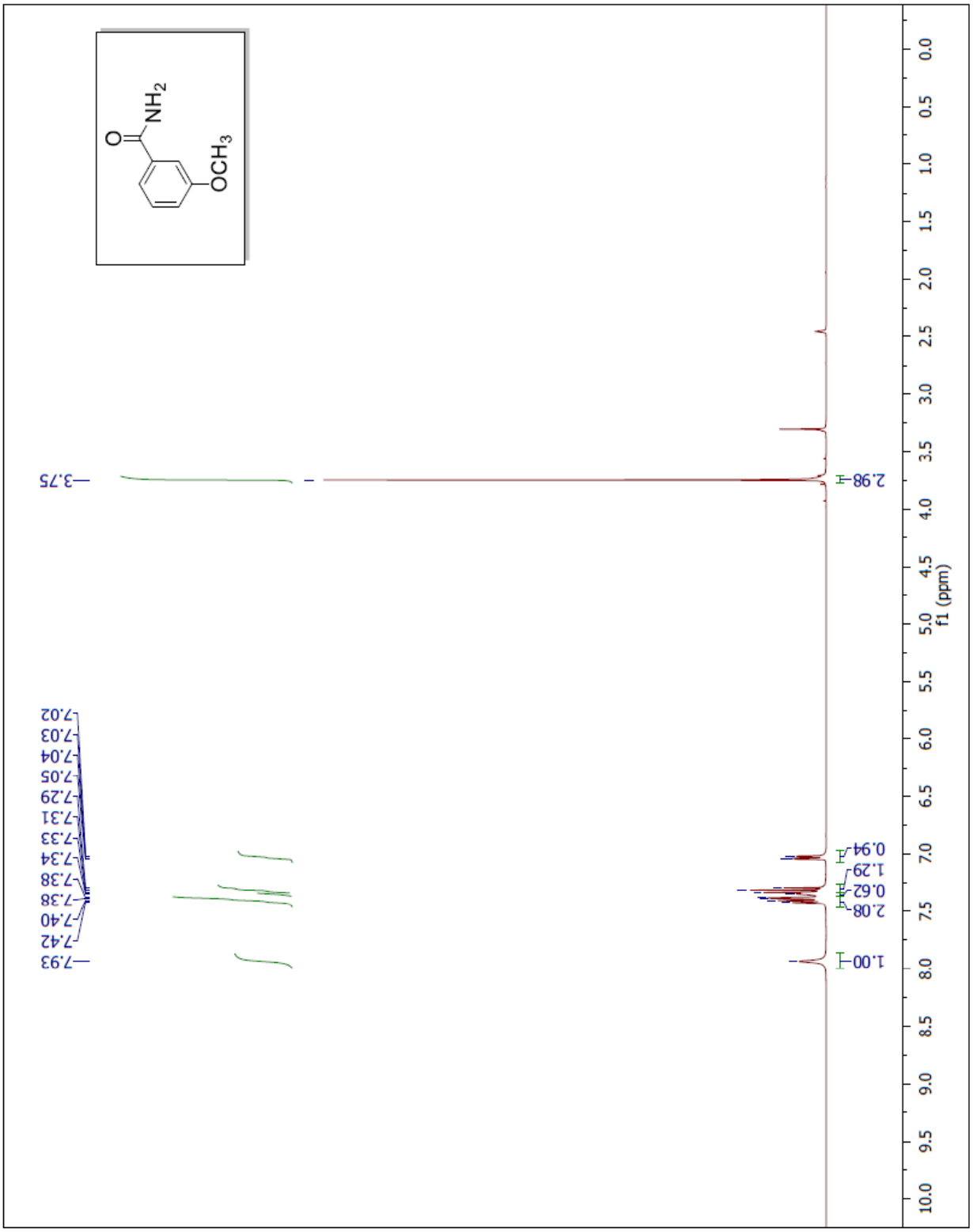

O
NH2
F3C
167.66
138.33
131.90
131.58
128.77
125.80
125.77
123.00
f1 (ppm)

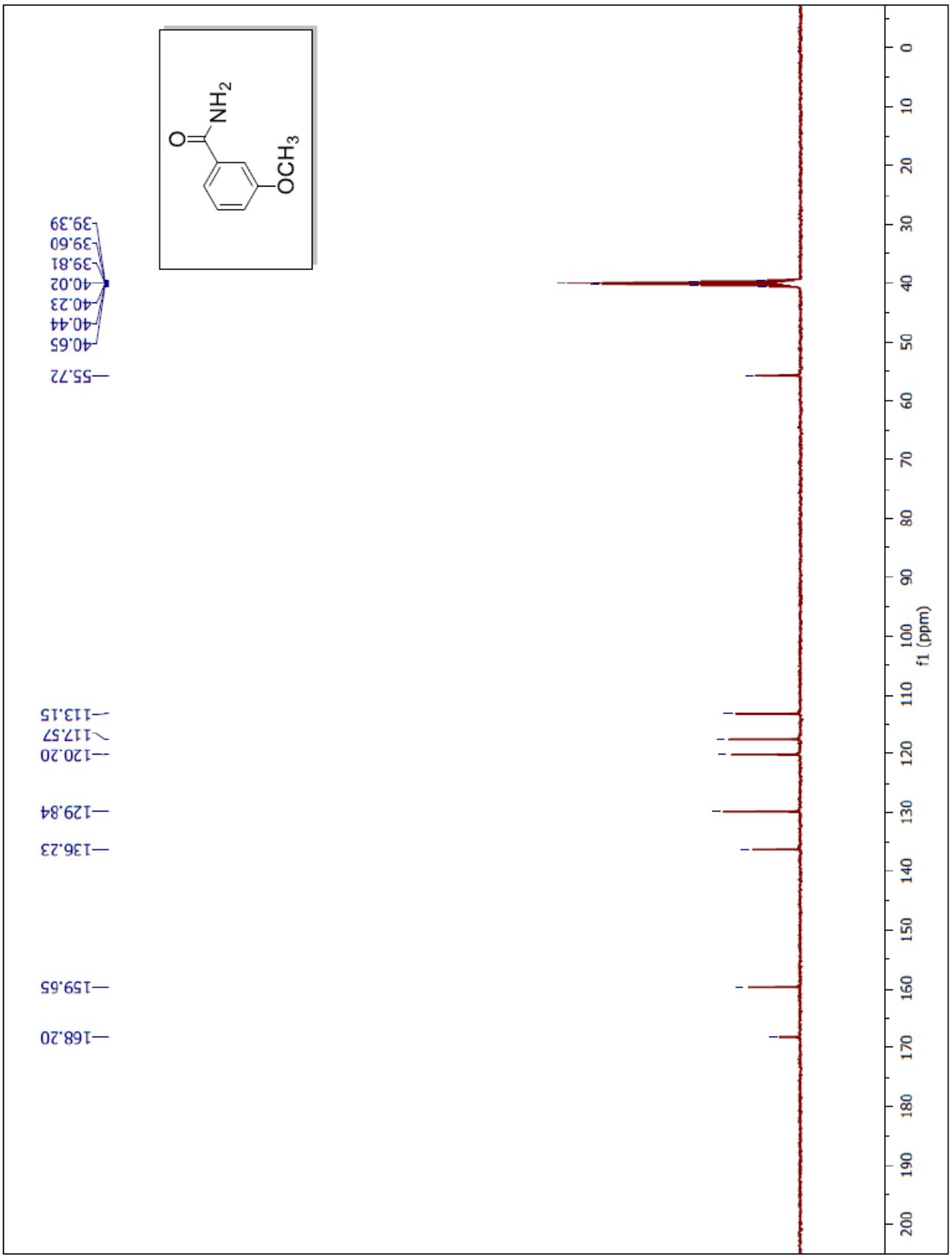
^{1}H and ^{13}C NMR spectra of compound 3k:



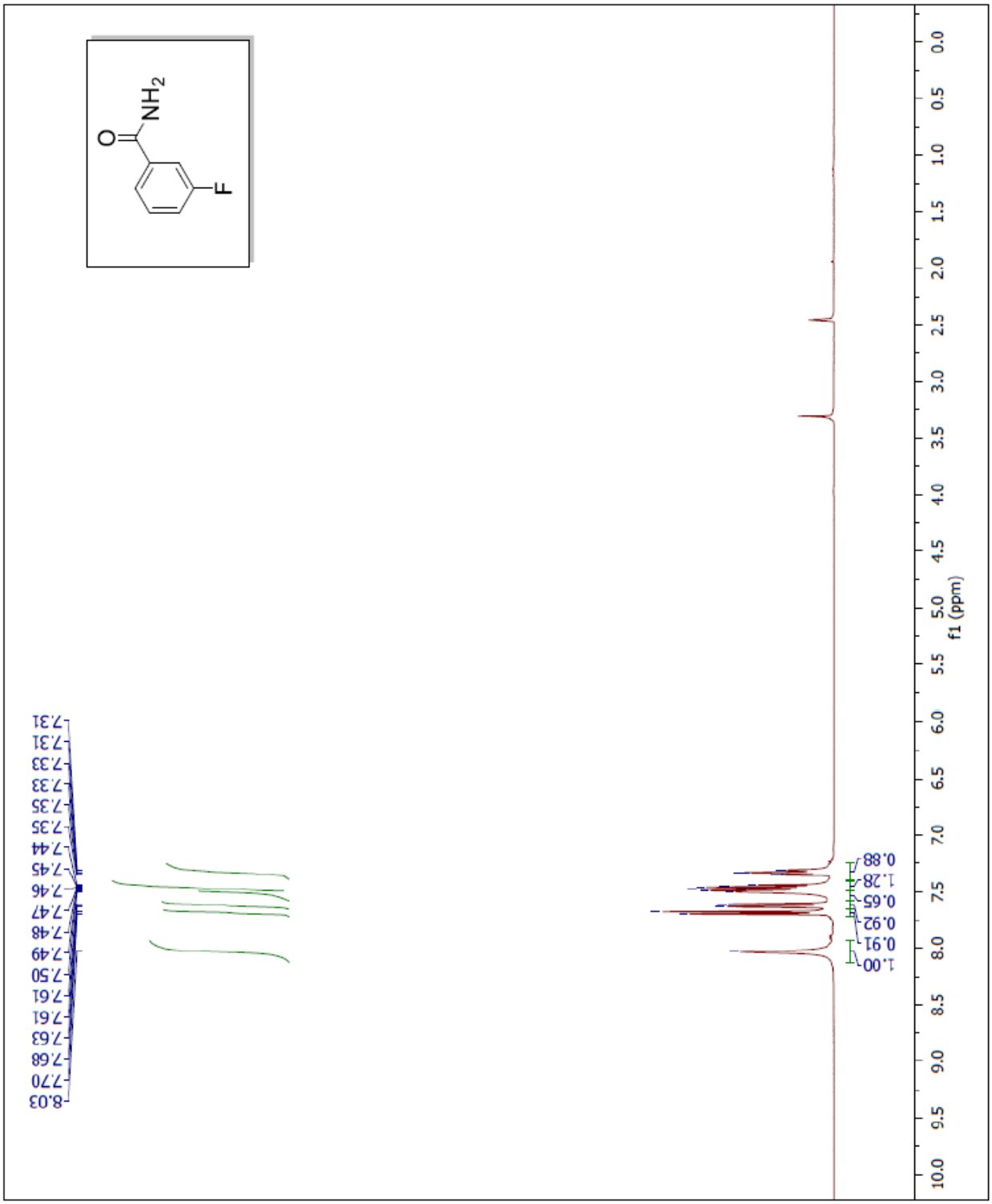

NH2
O
21.47
39.37
39.58
39.78
39.99
40.20
40.41
40.62
125.10
128.60
132.29
134.75
137.94
168.60
f1 (ppm)

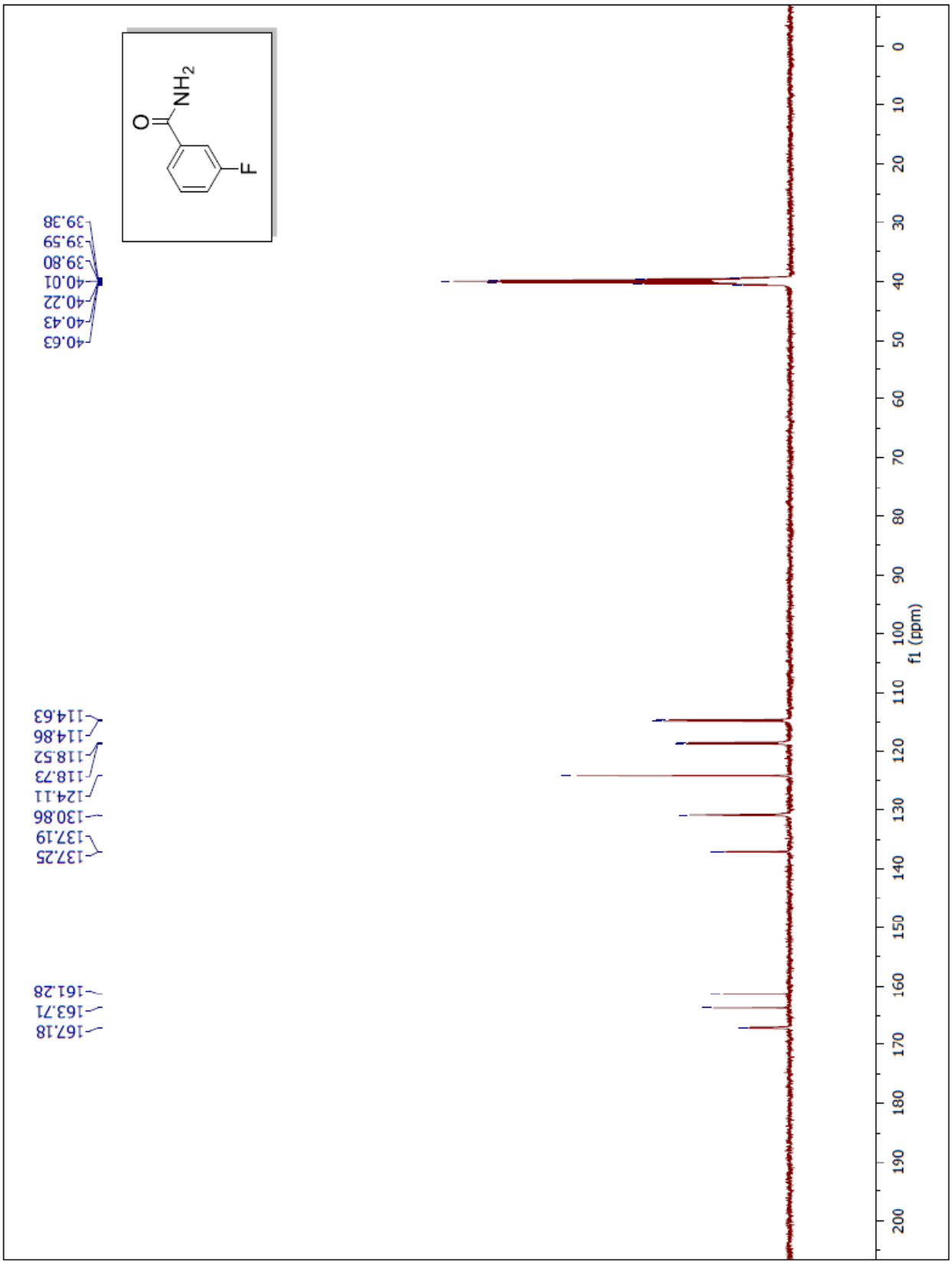
^{1}H and ^{13}C NMR spectra of compound 3l:



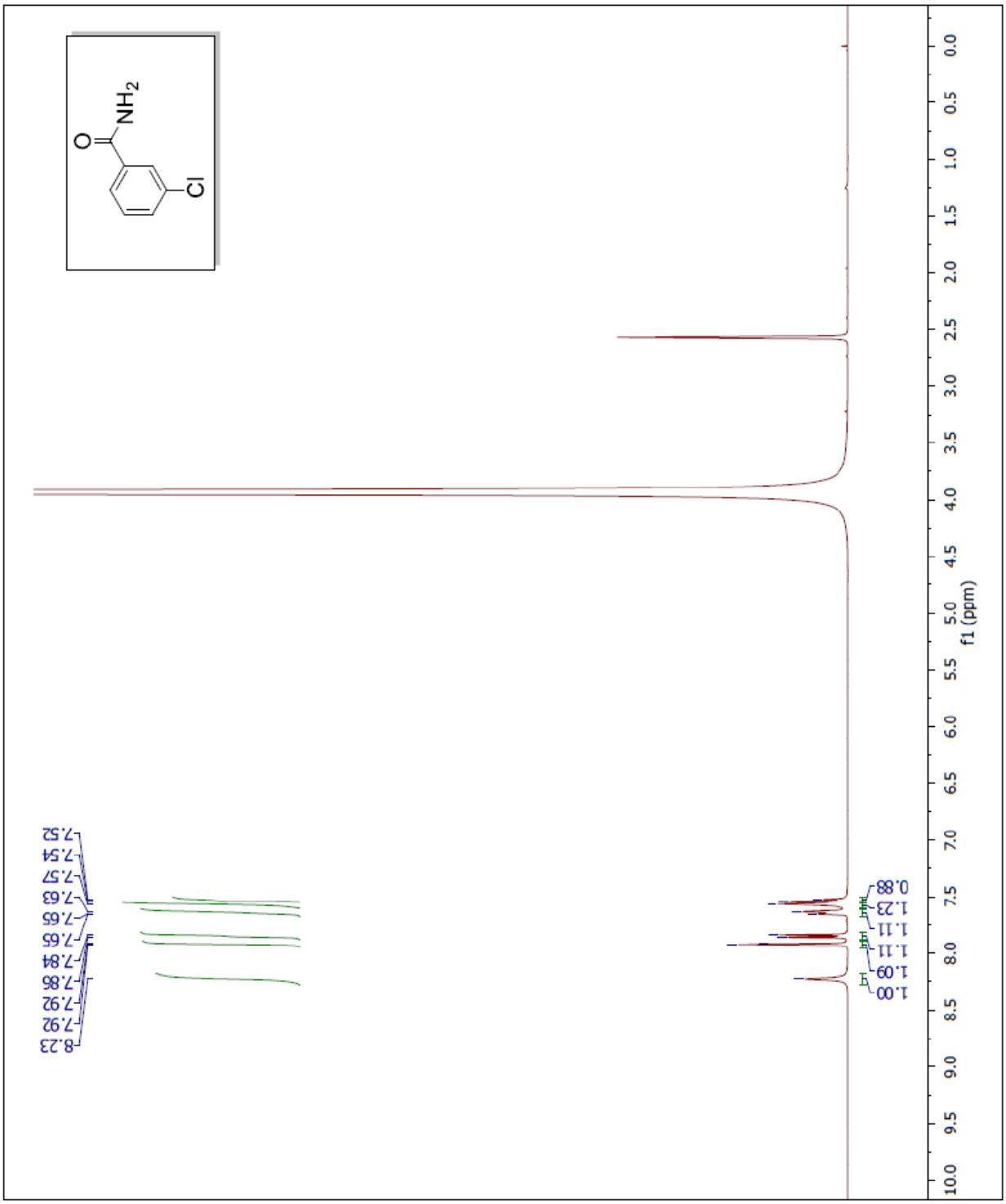

NH2
O
OCH3
39.39
39.60
39.81
40.02
40.23
40.44
40.65
55.72
113.15
117.57
120.20
129.84
136.23
159.65
168.20
f1 (ppm)

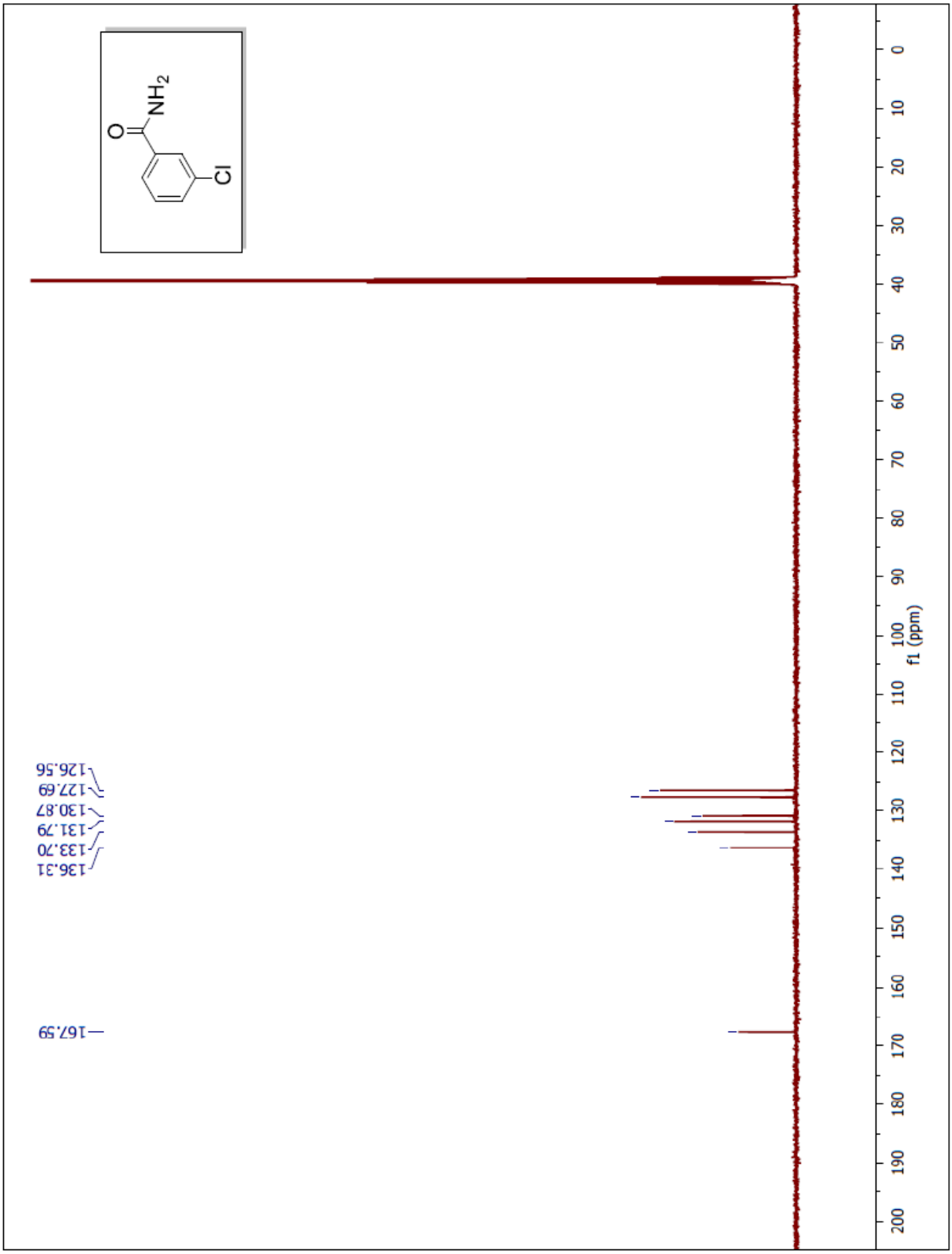
^{1}H and ^{13}C NMR spectra of compound 3m:



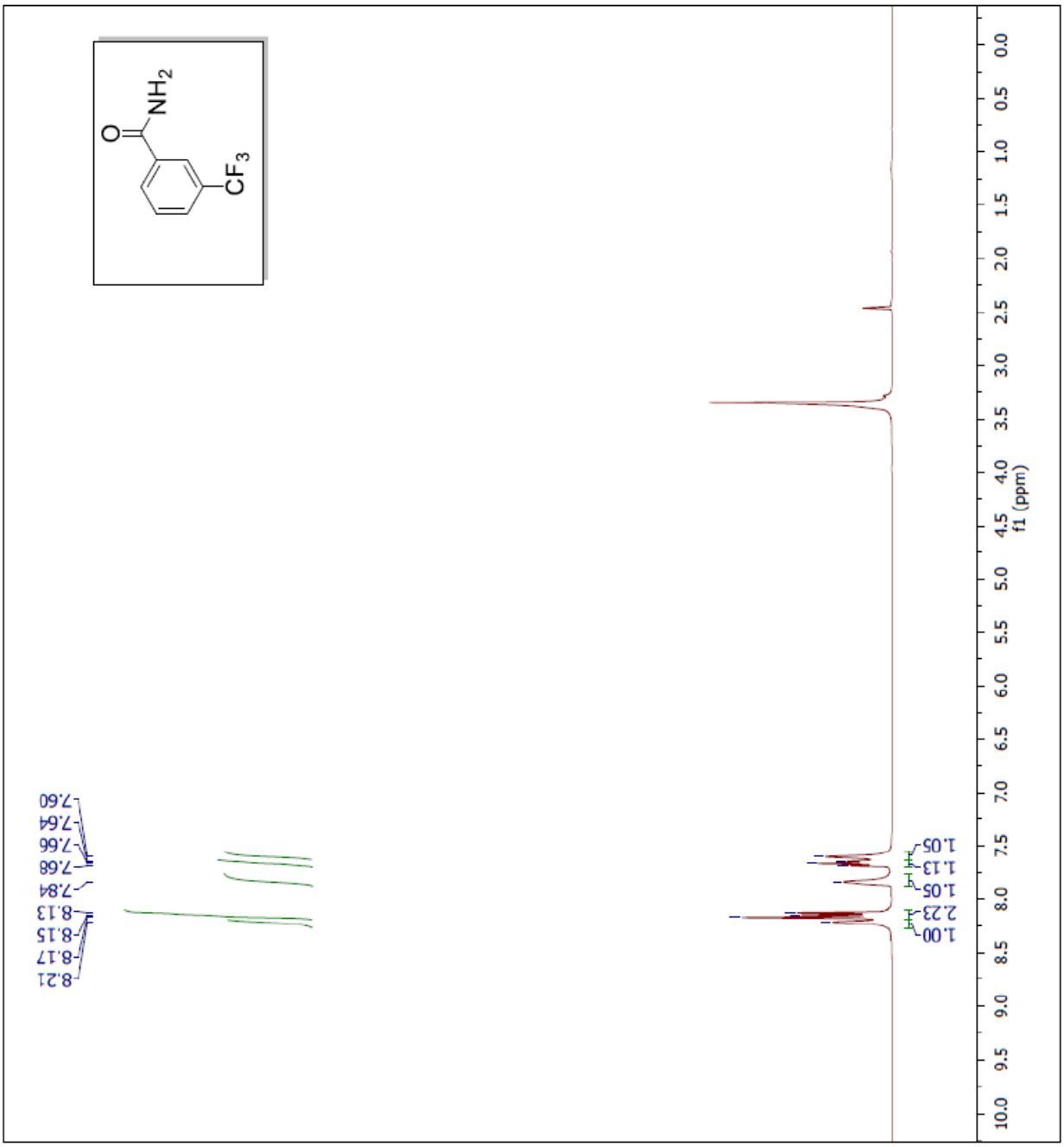

NH2
O
F
39.38
39.59
39.80
40.01
40.22
40.43
40.63
114.63
114.86
118.52
118.73
124.11
130.86
137.19
137.25
161.28
163.71
167.18
f1 (ppm)

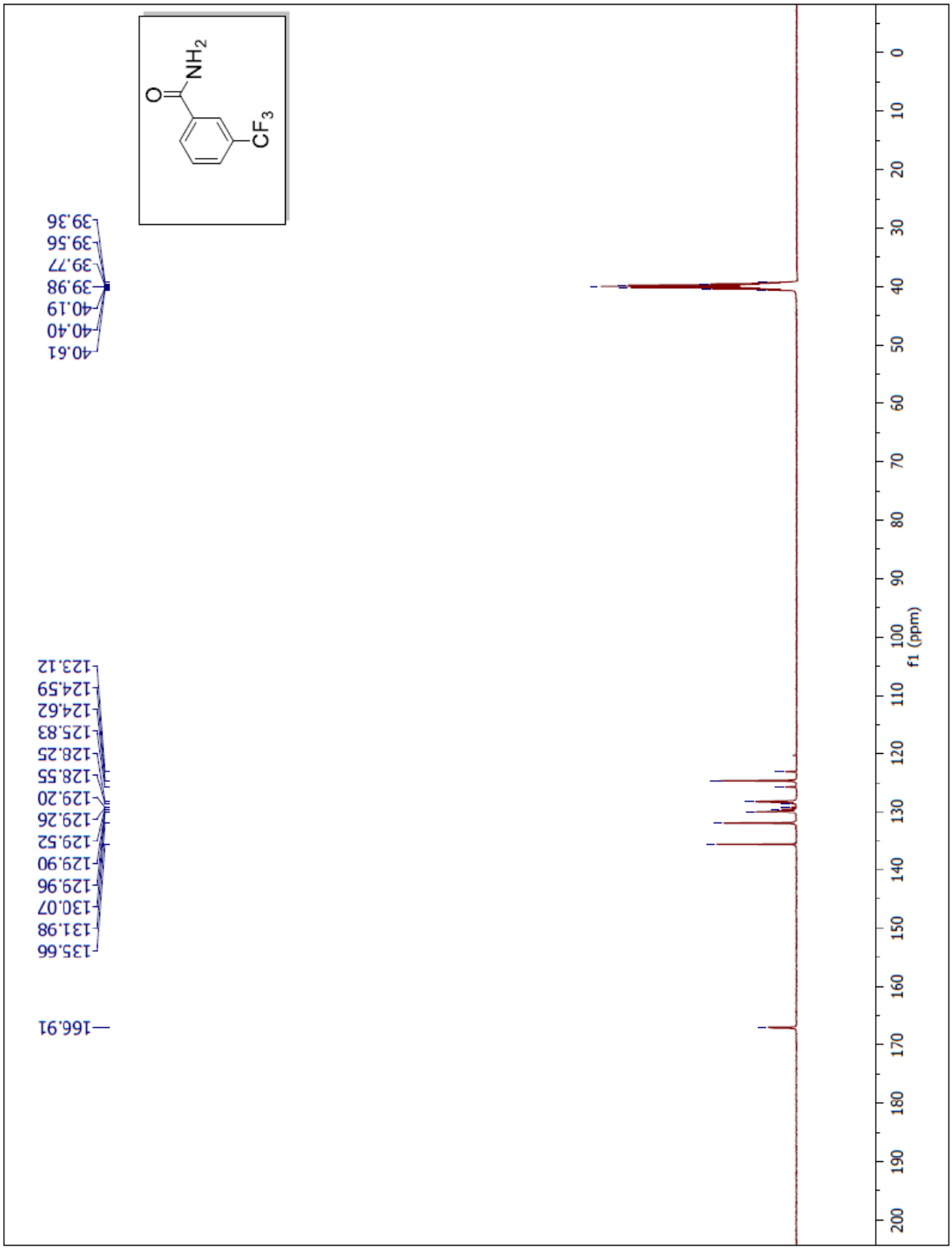
^{1}H and ^{13}C NMR spectra of compound 3n:



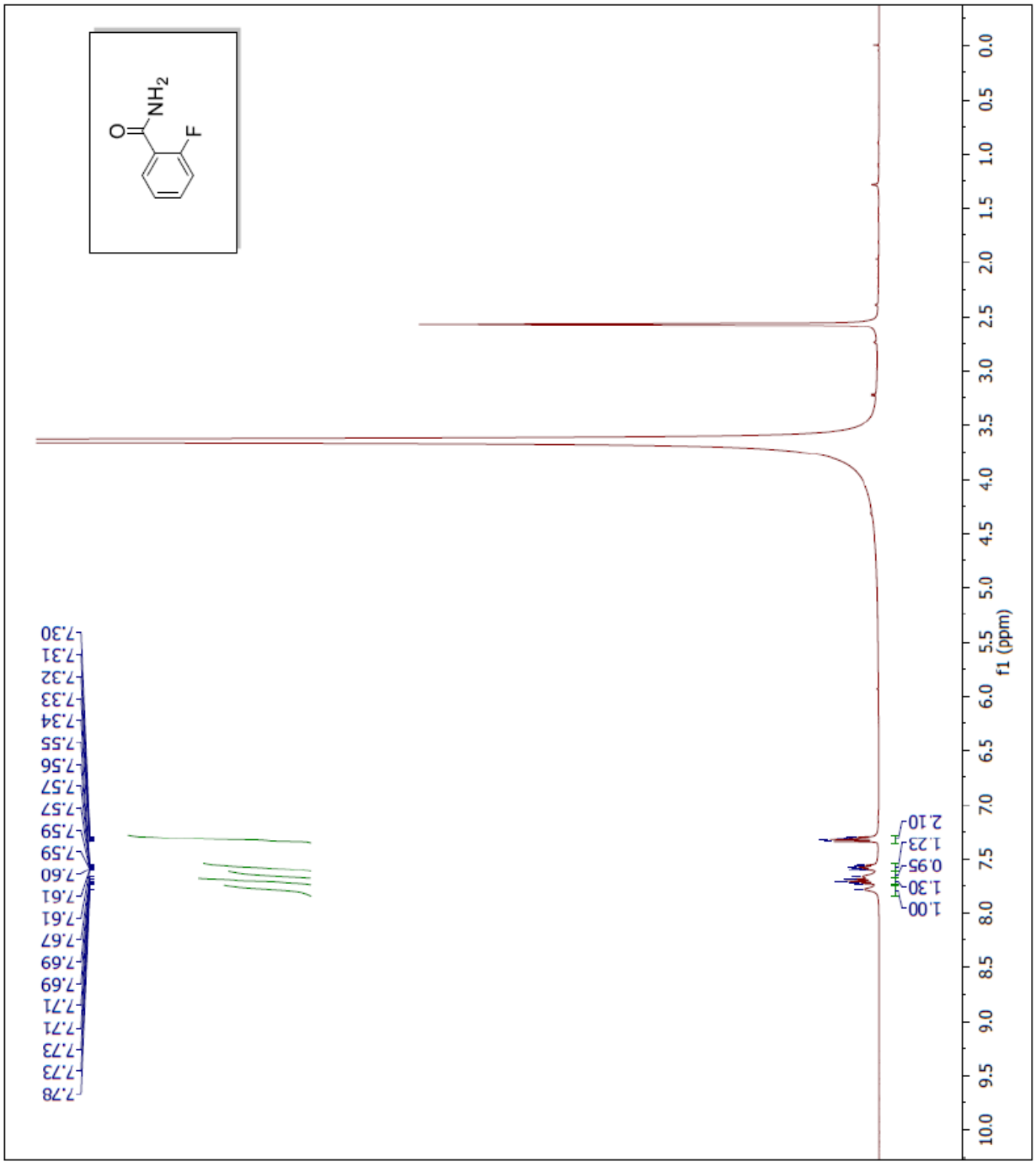

O
NH2
Cl
167.59
136.31
133.70
131.79
130.87
127.69
126.56
f1 (ppm)

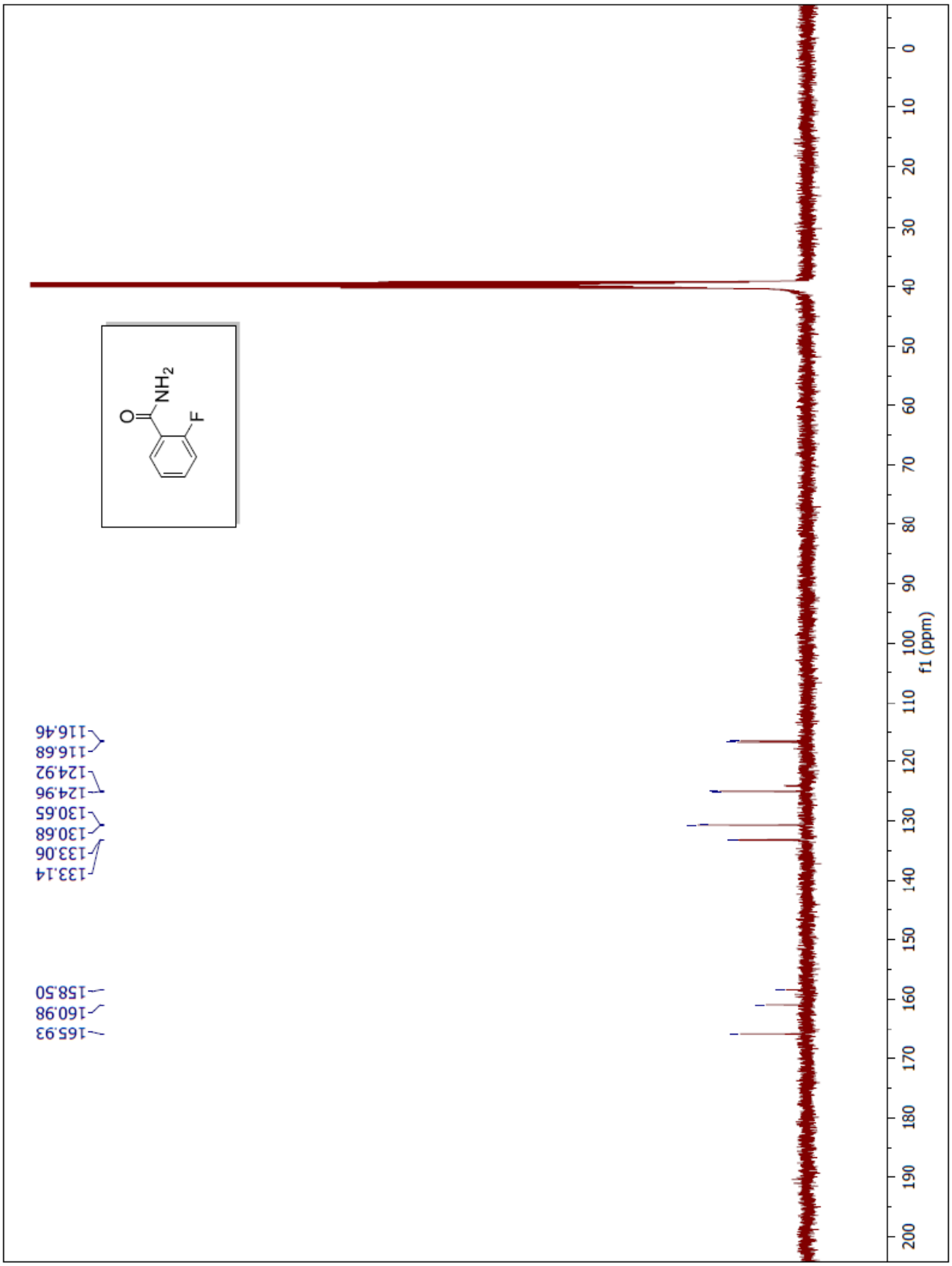
^{1}H and ^{13}C NMR spectra of compound 3o:



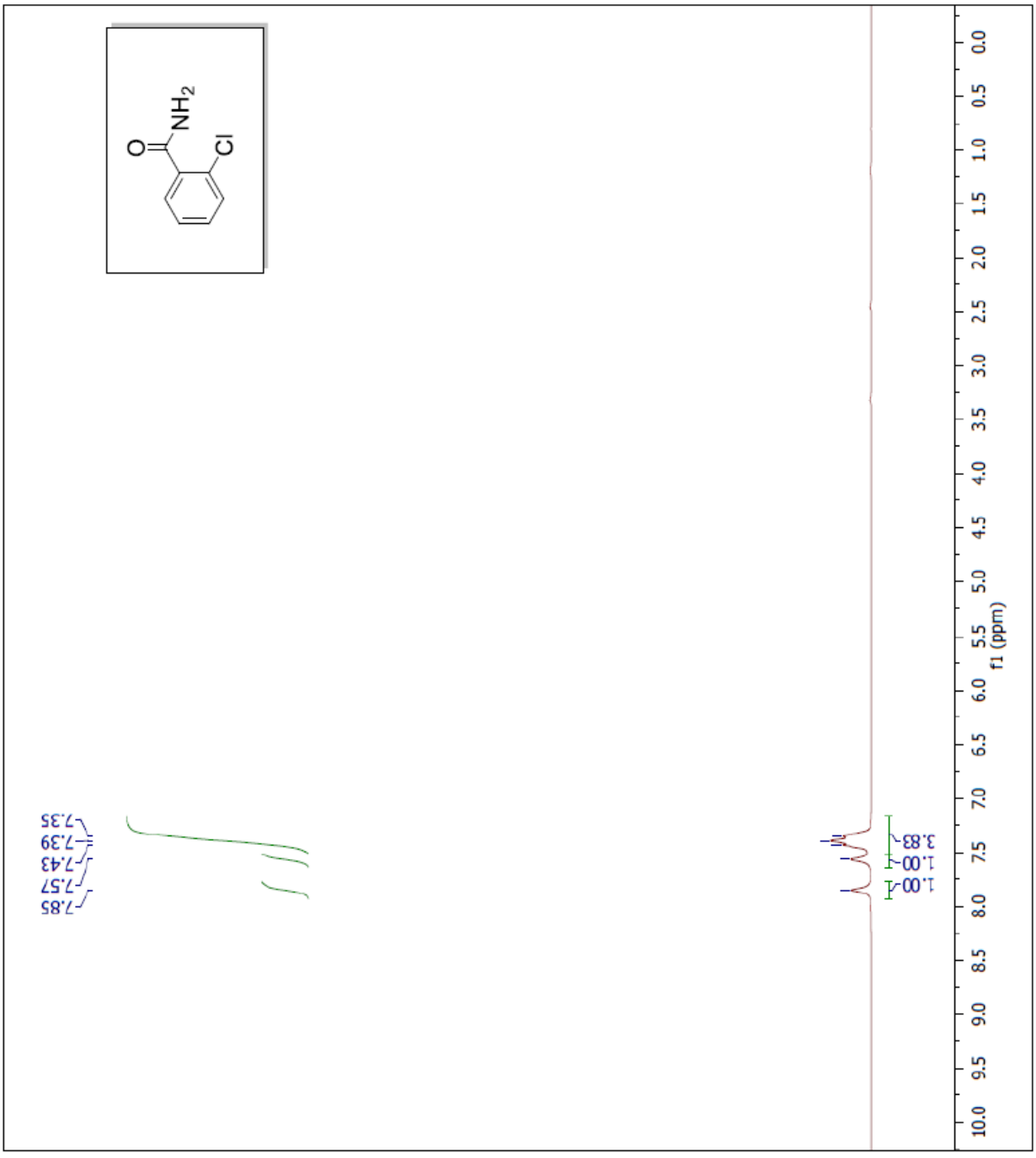

NH2
O
CF3
39.36
39.56
39.77
39.98
40.19
40.40
40.61
123.12
124.59
124.62
125.83
128.25
128.55
129.20
129.26
129.52
129.90
129.96
130.07
131.98
135.66
166.91
f1 (ppm)

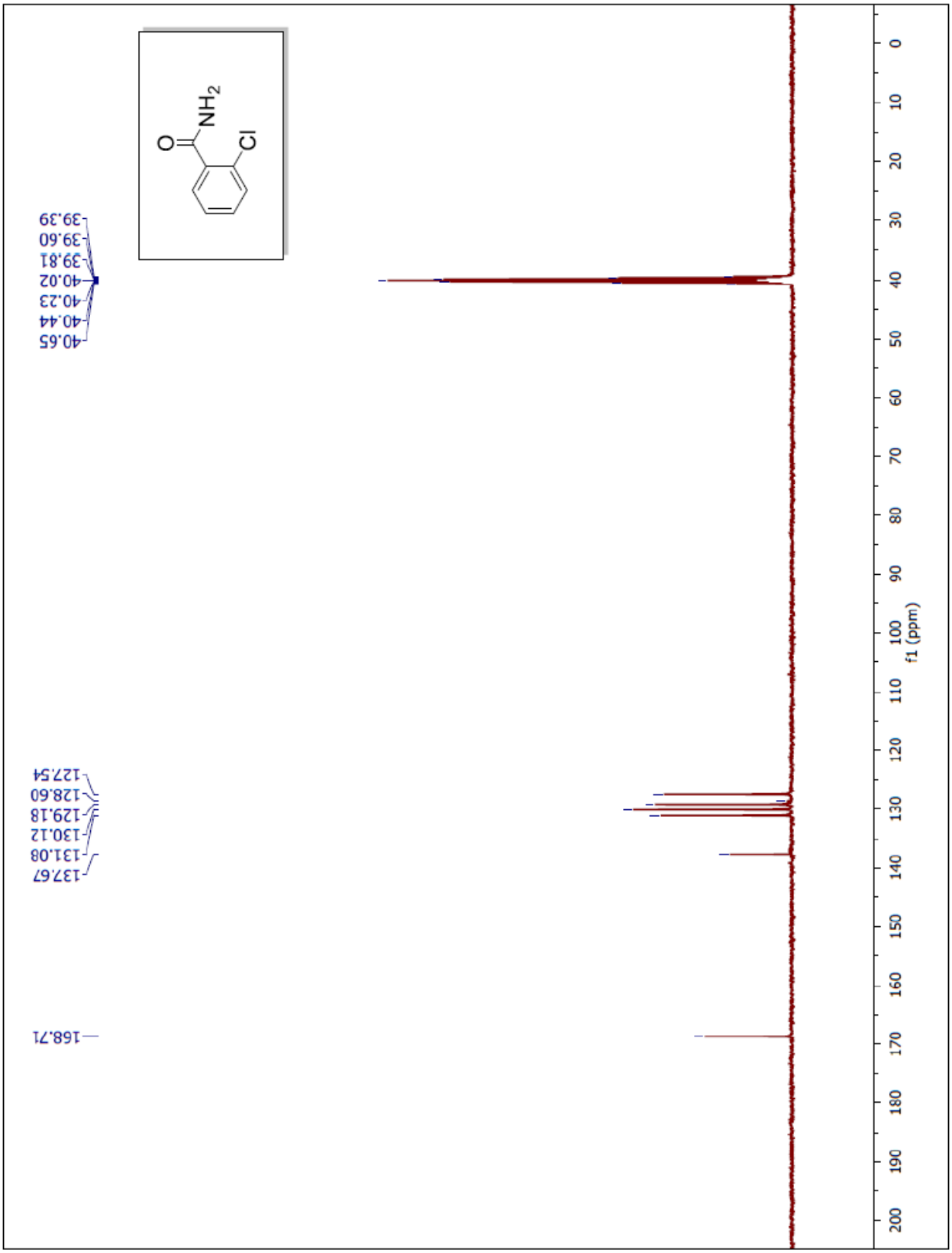
^{1}H and ^{13}C NMR spectra of compound 3p:



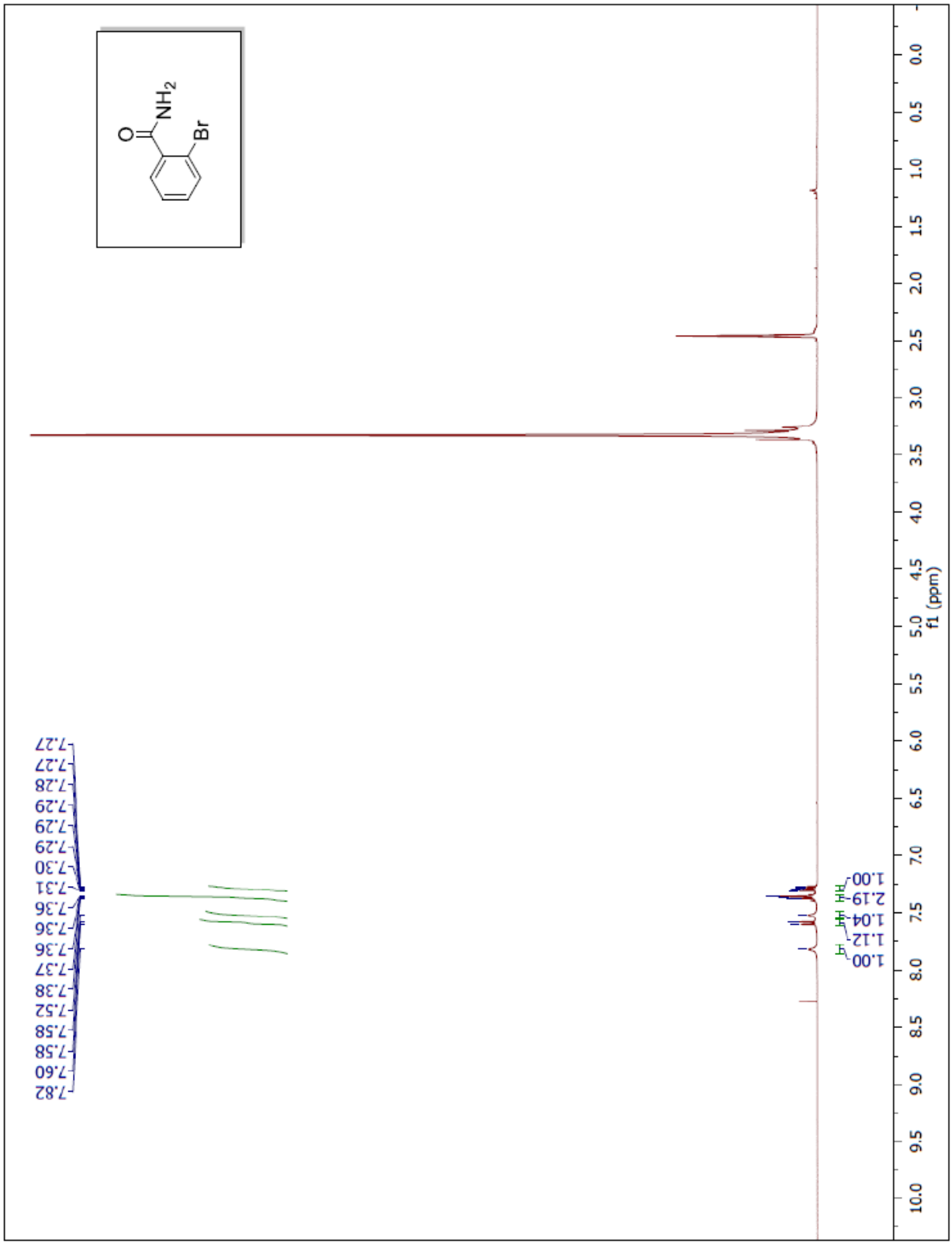

O
NH2
F
165.93
160.98
158.50
133.14
133.06
130.68
130.65
124.96
124.92
116.68
116.46
f1 (ppm)

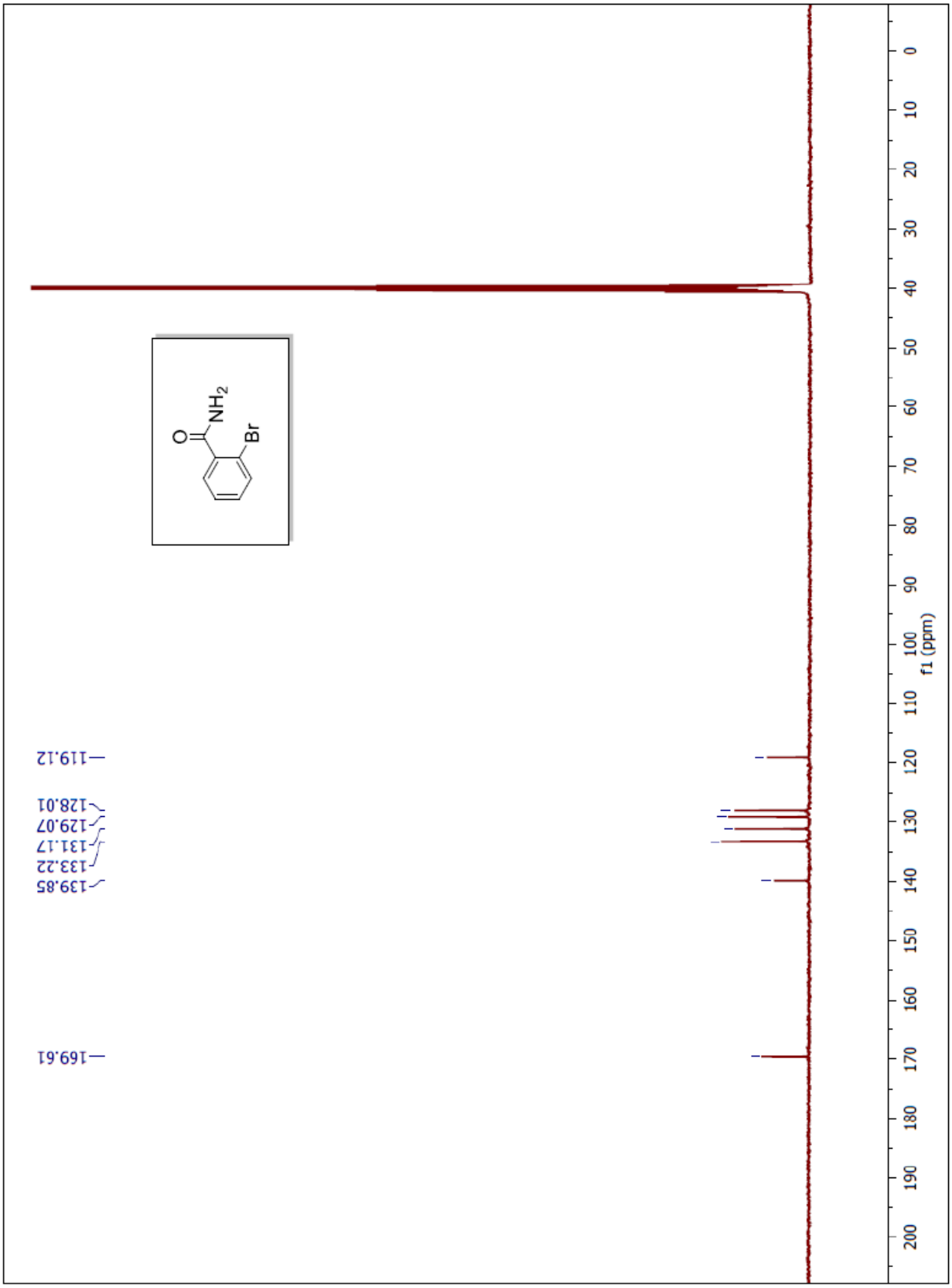
^{1}H and ^{13}C NMR spectra of compound 3q:



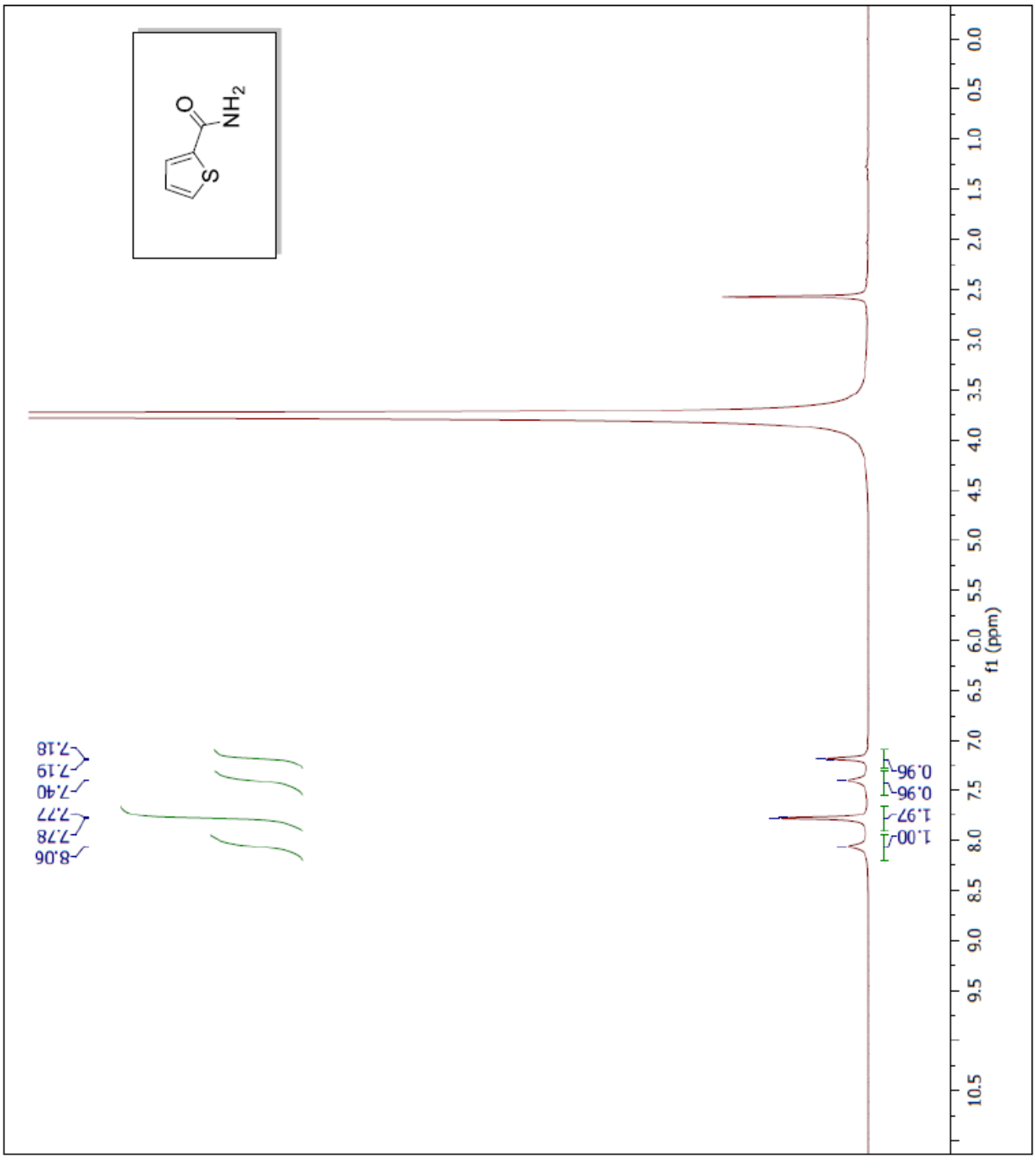

O
NH2
Cl
168.71
137.67
131.08
130.12
129.18
128.60
127.54
40.65
40.44
40.23
40.02
39.81
39.60
39.39
f1 (ppm)

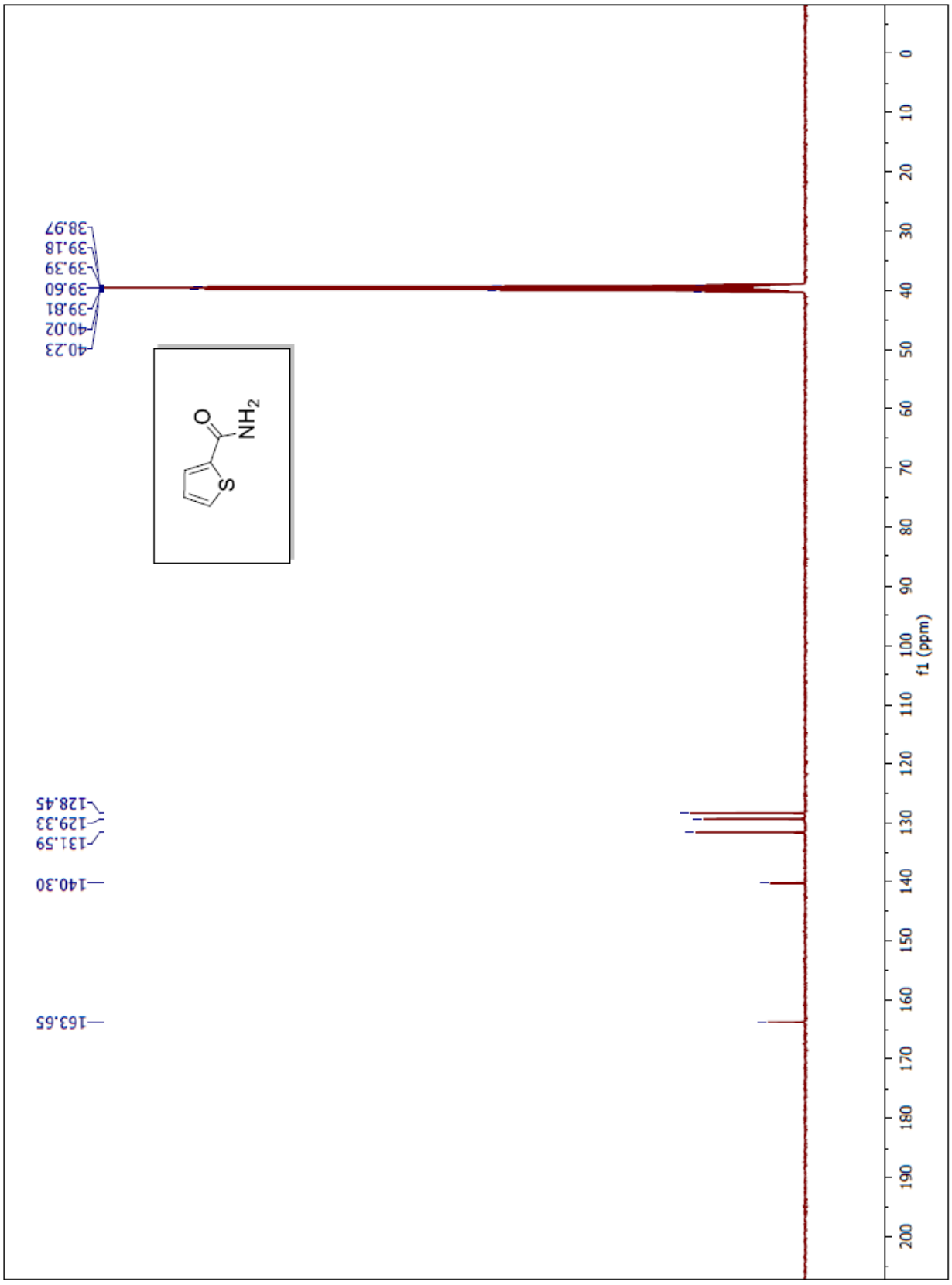
^{1}H and ^{13}C NMR spectra of compound 3r:



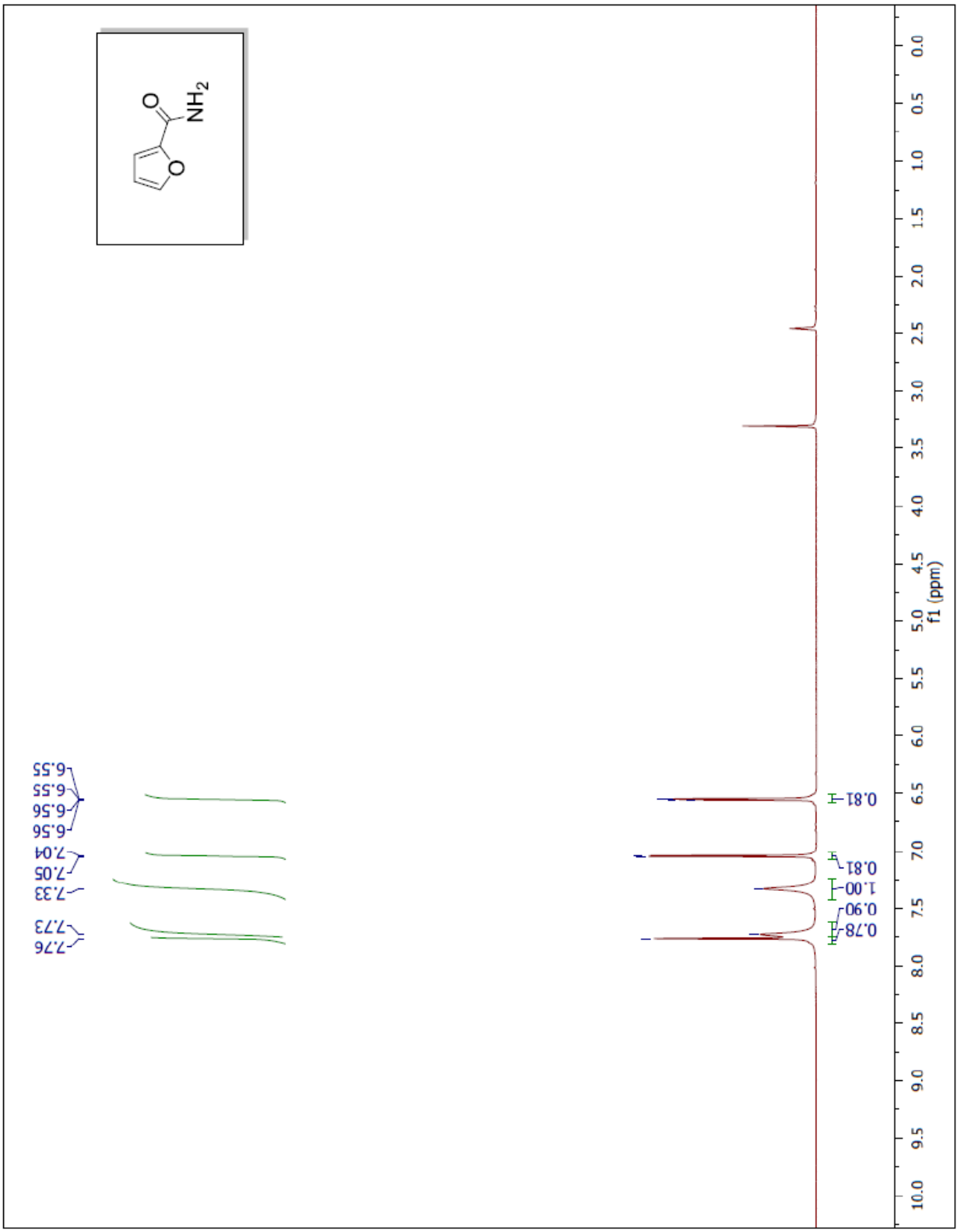

O
NH2
Br
169.61
139.85
133.22
131.17
129.07
128.01
119.12
f1 (ppm)

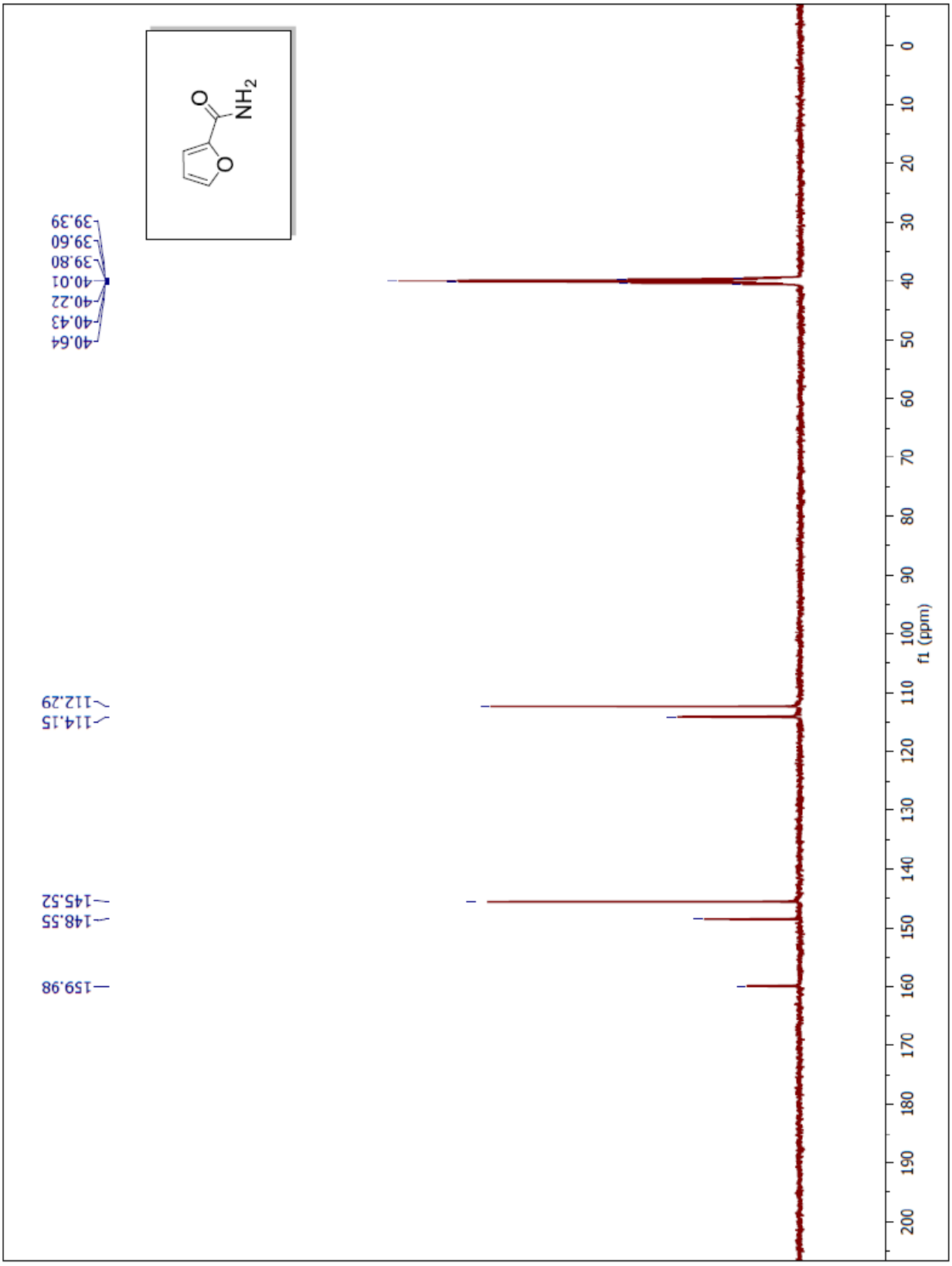
^{1}H and ^{13}C NMR spectra of compound 3s:



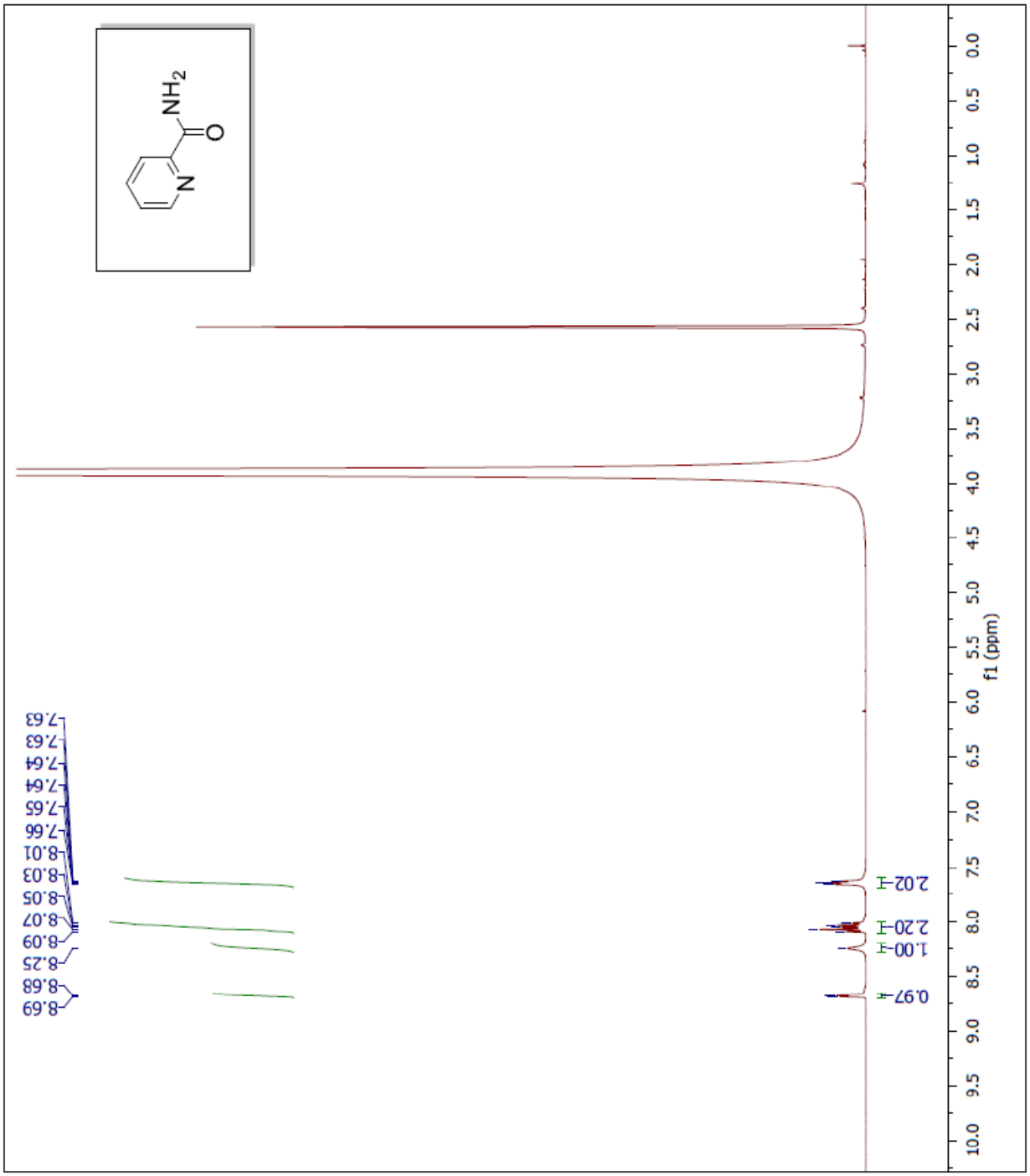

163.65
140.30
131.59
129.33
128.45
40.23
40.02
39.81
39.60
39.39
39.18
38.97
O
NH2
S
f1 (ppm)

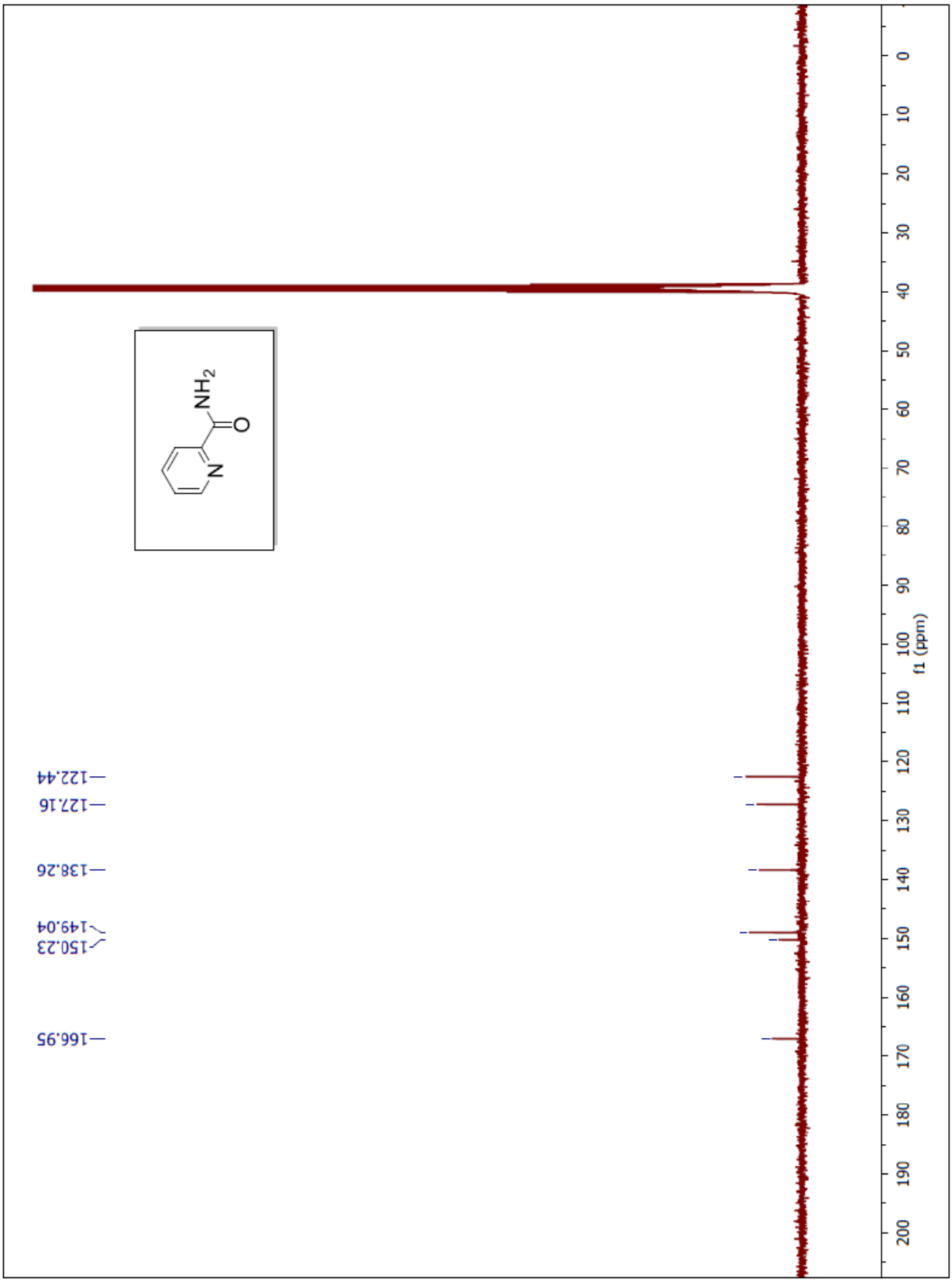
^{1}H and ^{13}C NMR spectra of compound 3t:



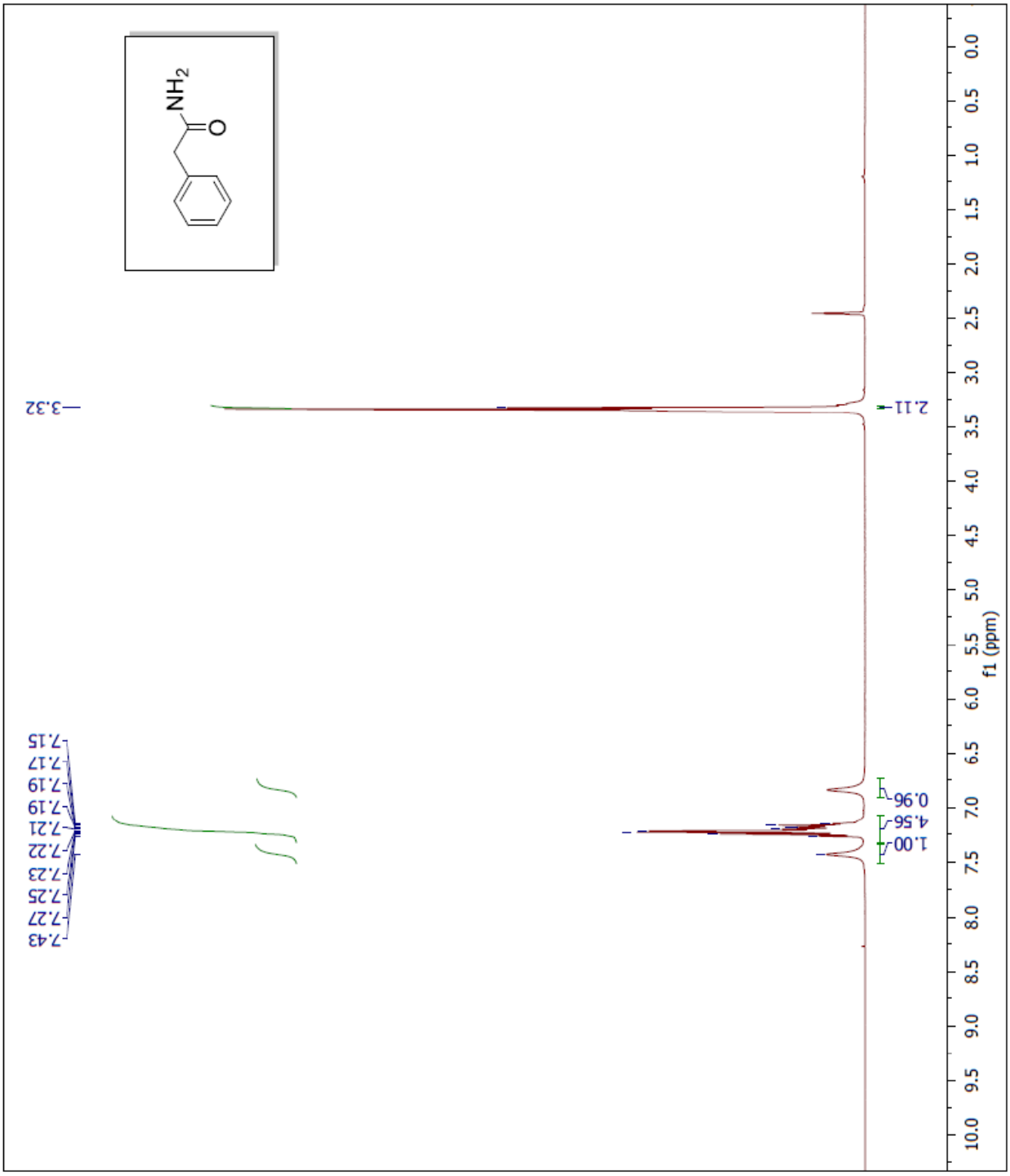

O
NH2
O
159.98
148.55
145.52
114.15
112.29
40.64
40.43
40.22
40.01
39.80
39.60
39.39
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

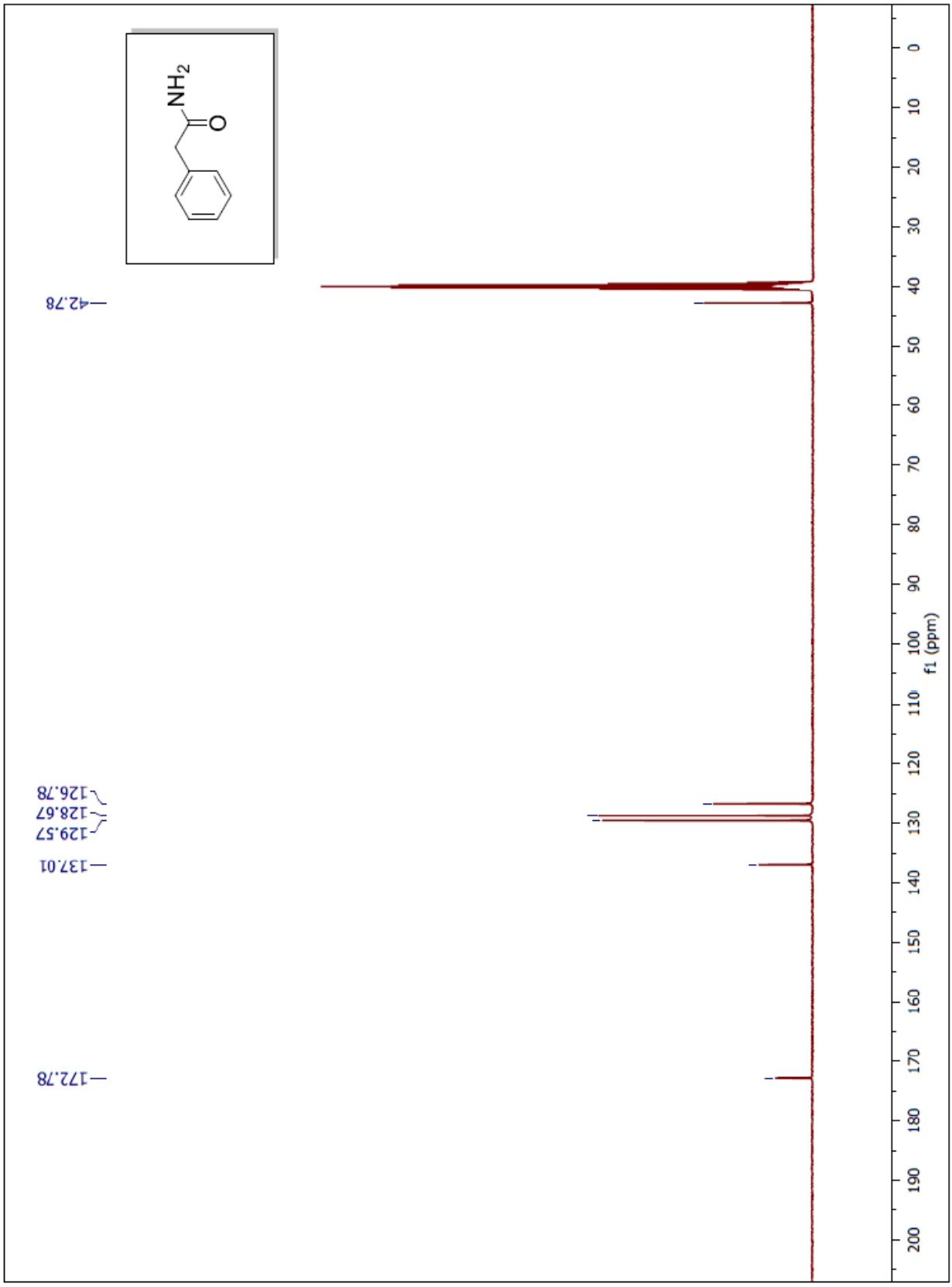
^{1}H and ^{13}C NMR spectra of compound 3u:



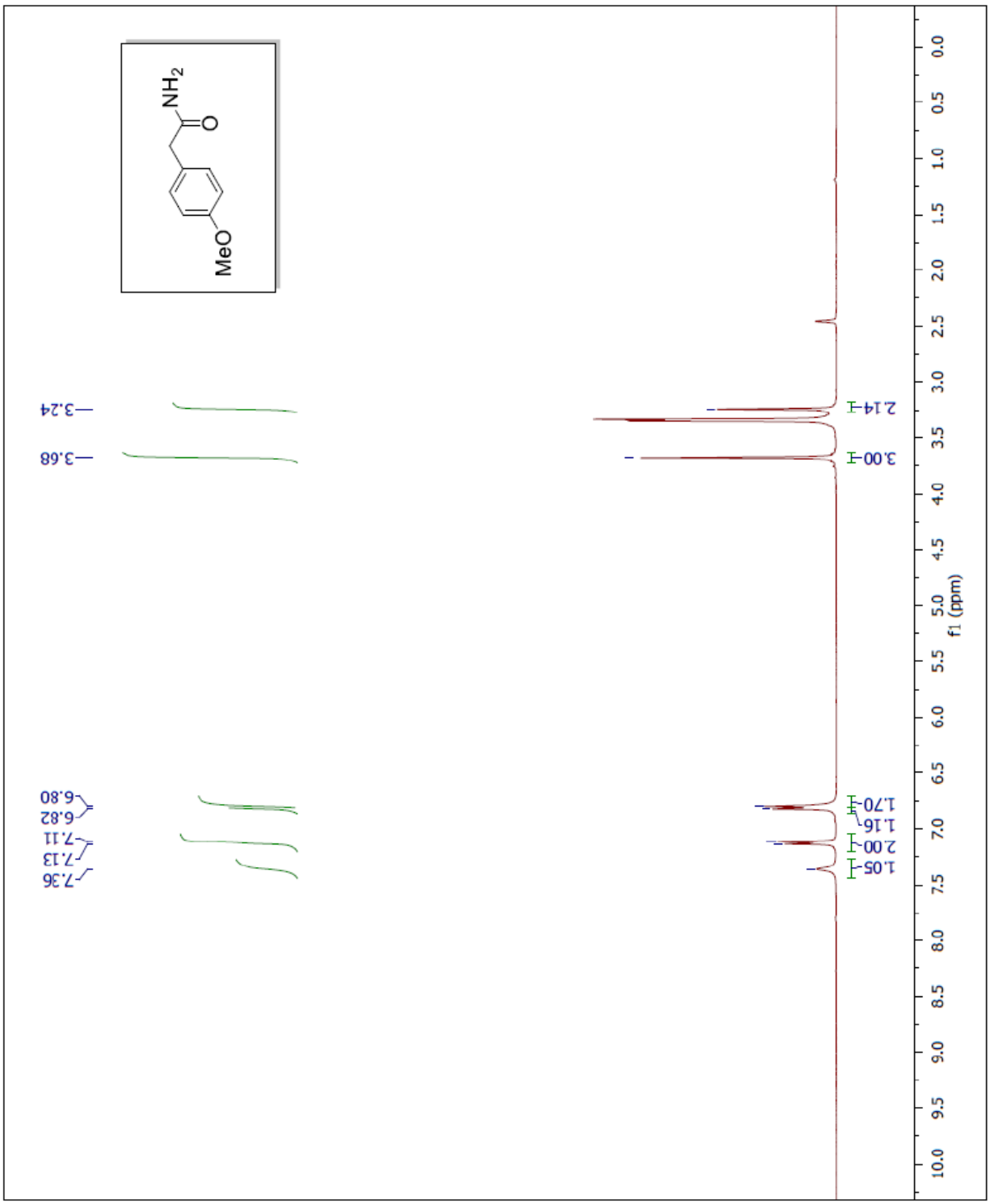

166.95
150.23
149.04
138.26
127.16
122.44
f1 (ppm)

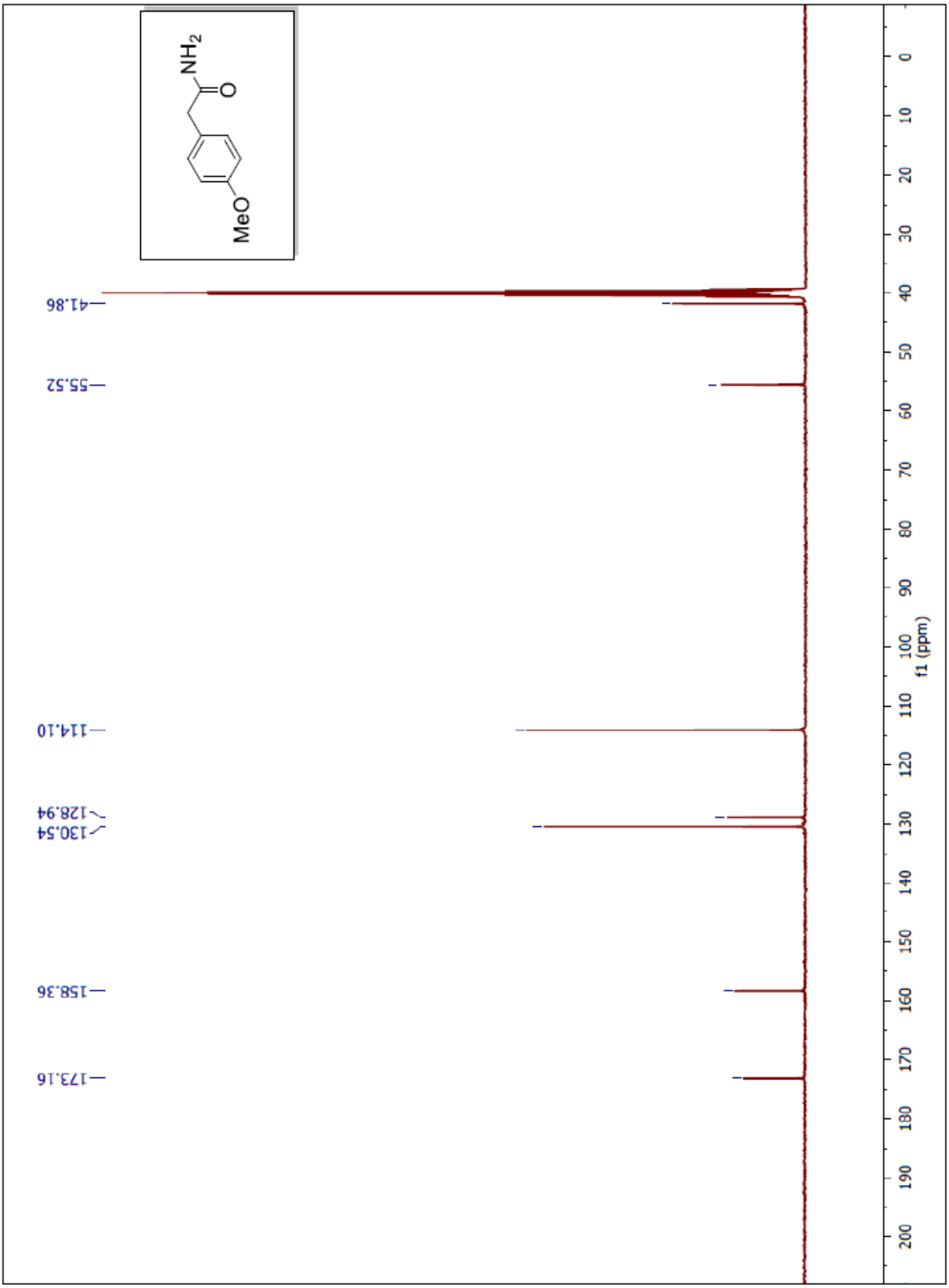
^{1}H and ^{13}C NMR spectra of compound 3v:



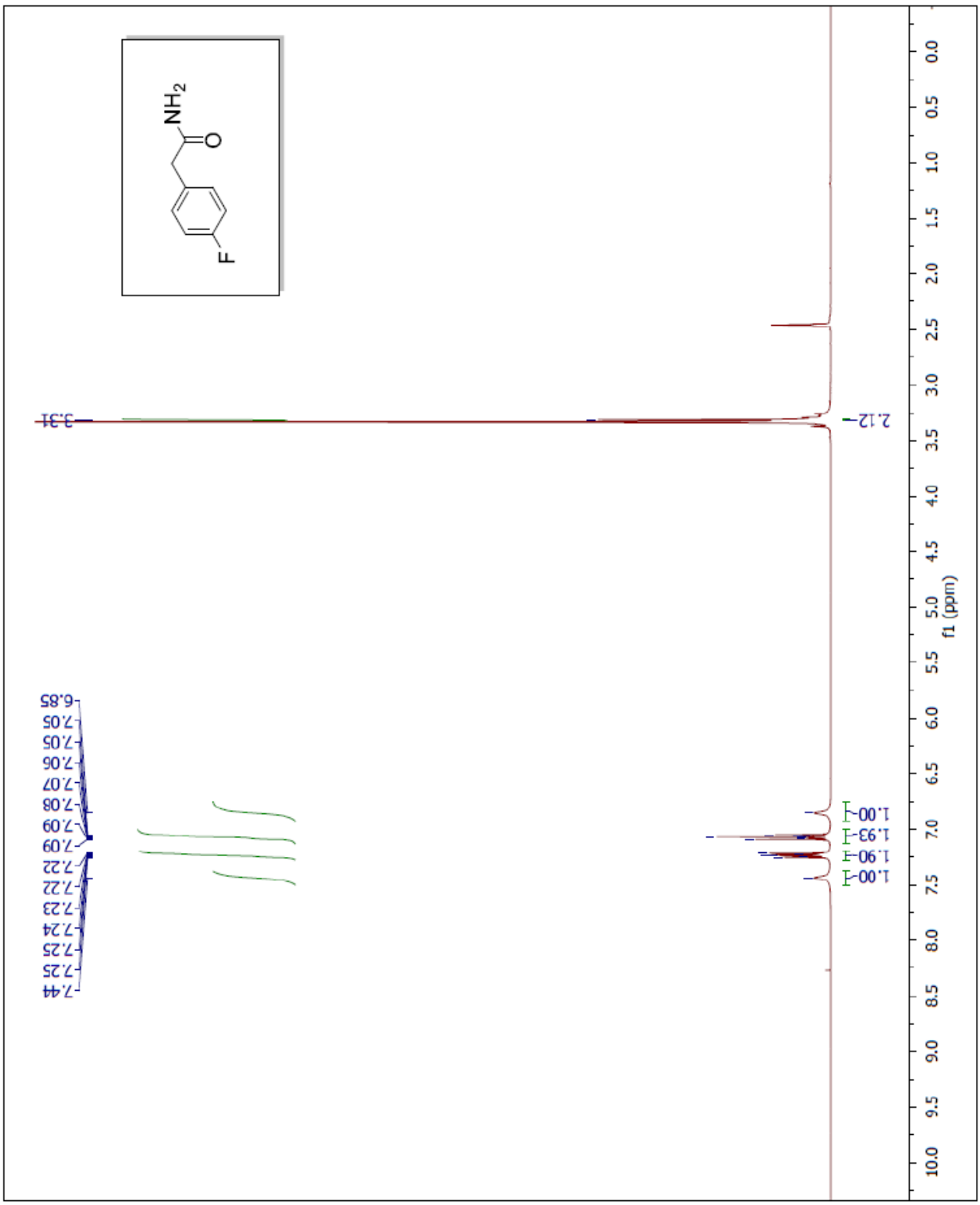

NH2
O
42.78
126.78
128.67
129.57
137.01
172.78
f1 (ppm)

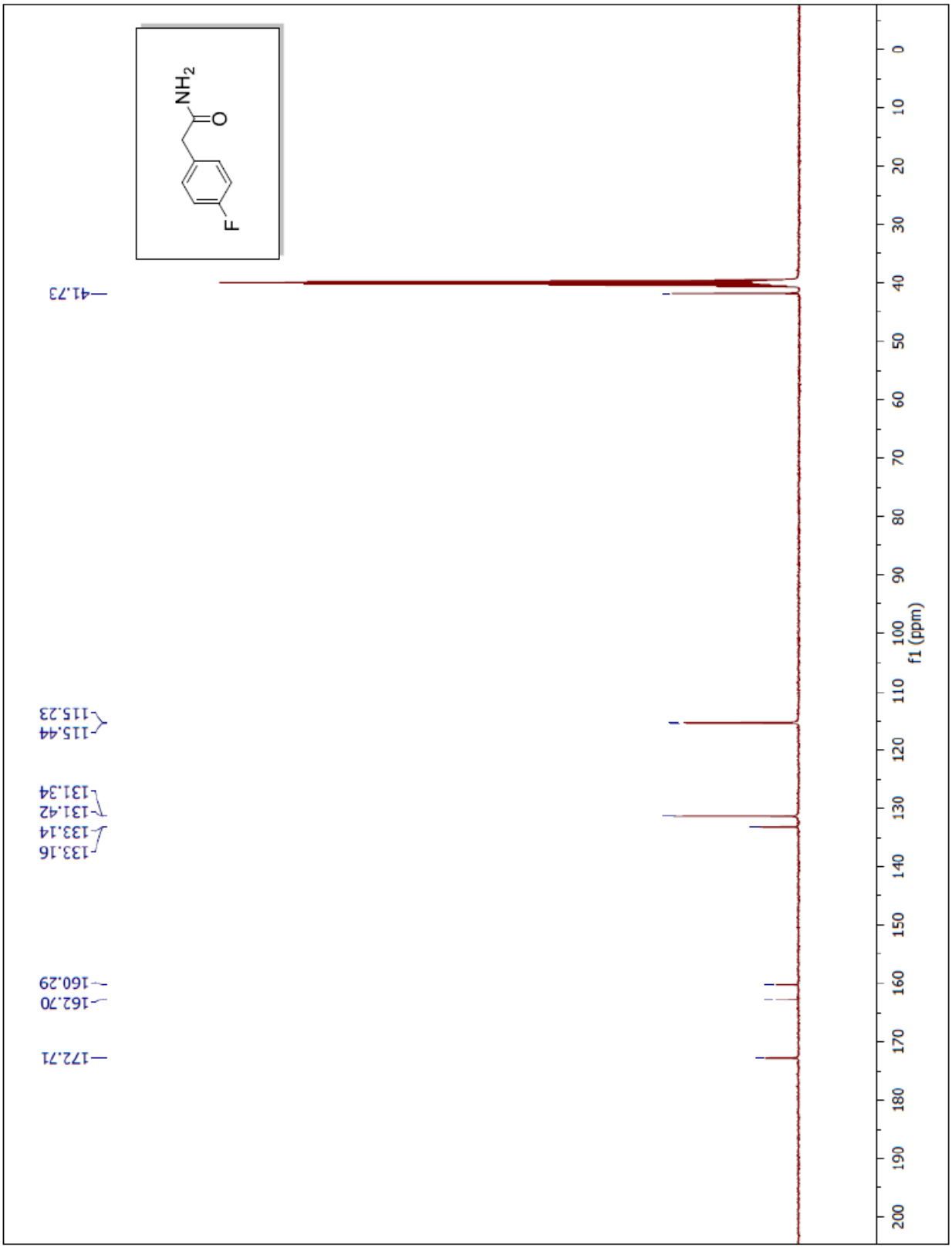
^{1}H and ^{13}C NMR spectra of compound 3w:



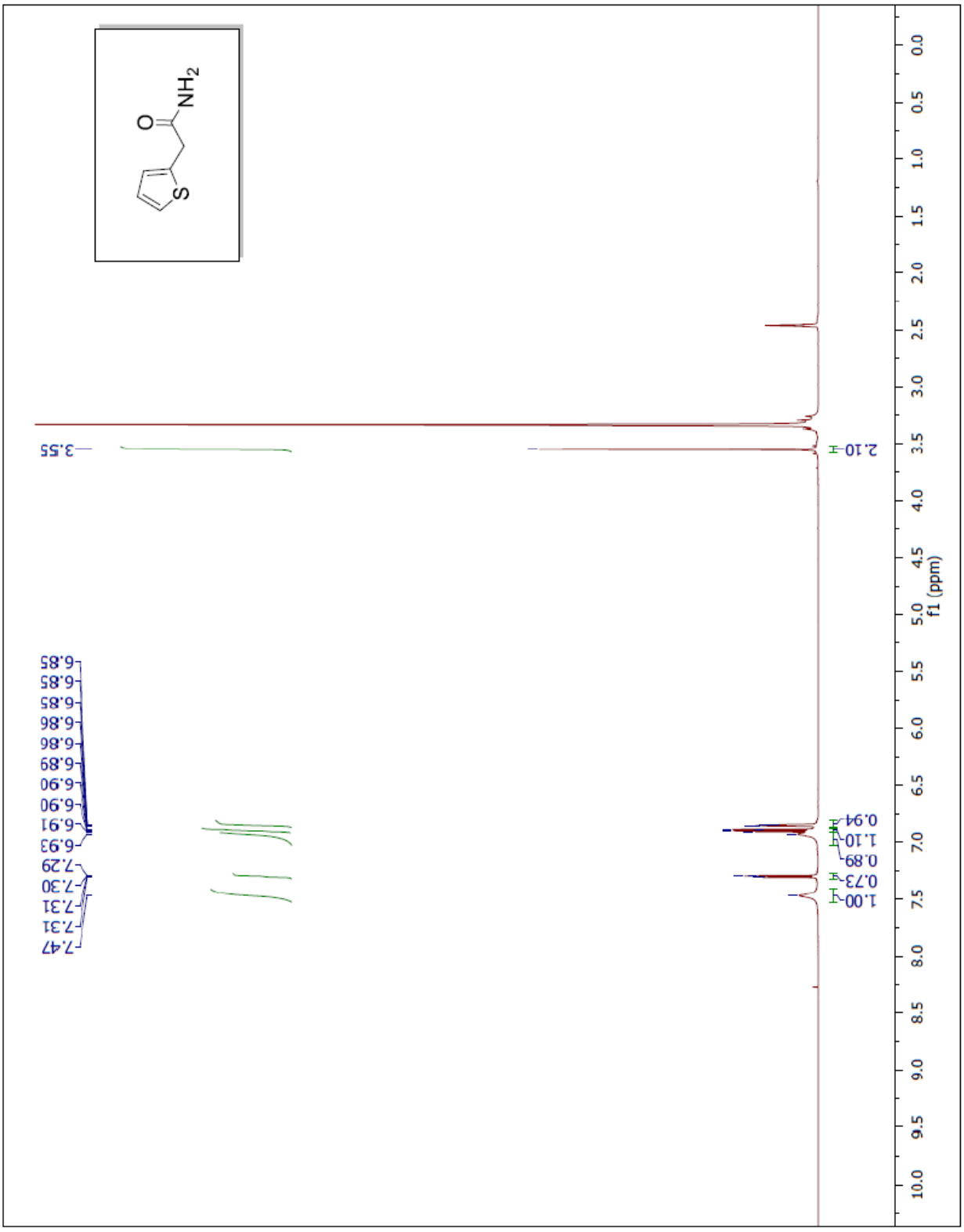

NH2
O
MeO
41.86
55.52
114.10
128.94
130.54
158.36
173.16
f1 (ppm)

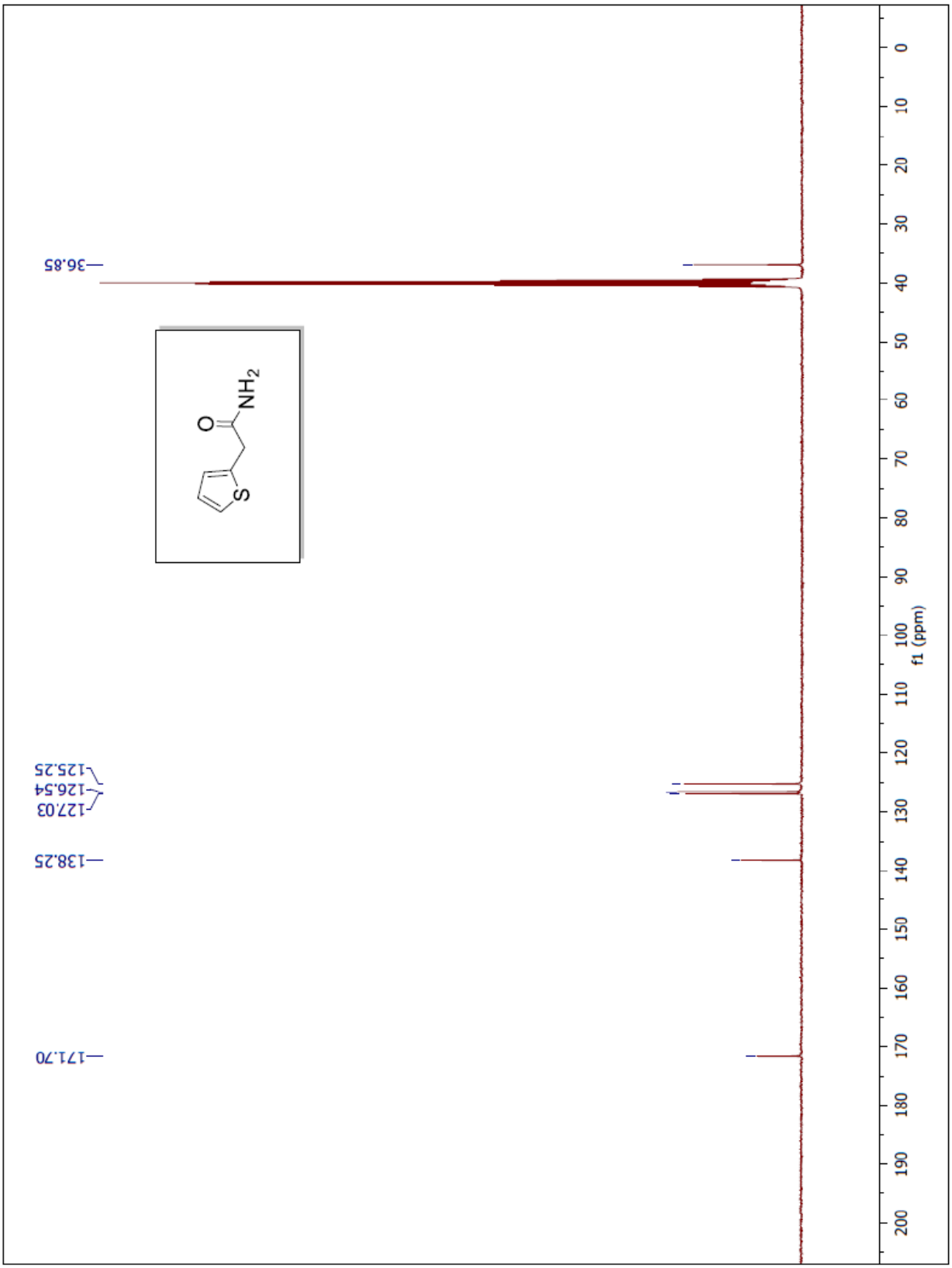
^{1}H and ^{13}C NMR spectra of compound 3x:



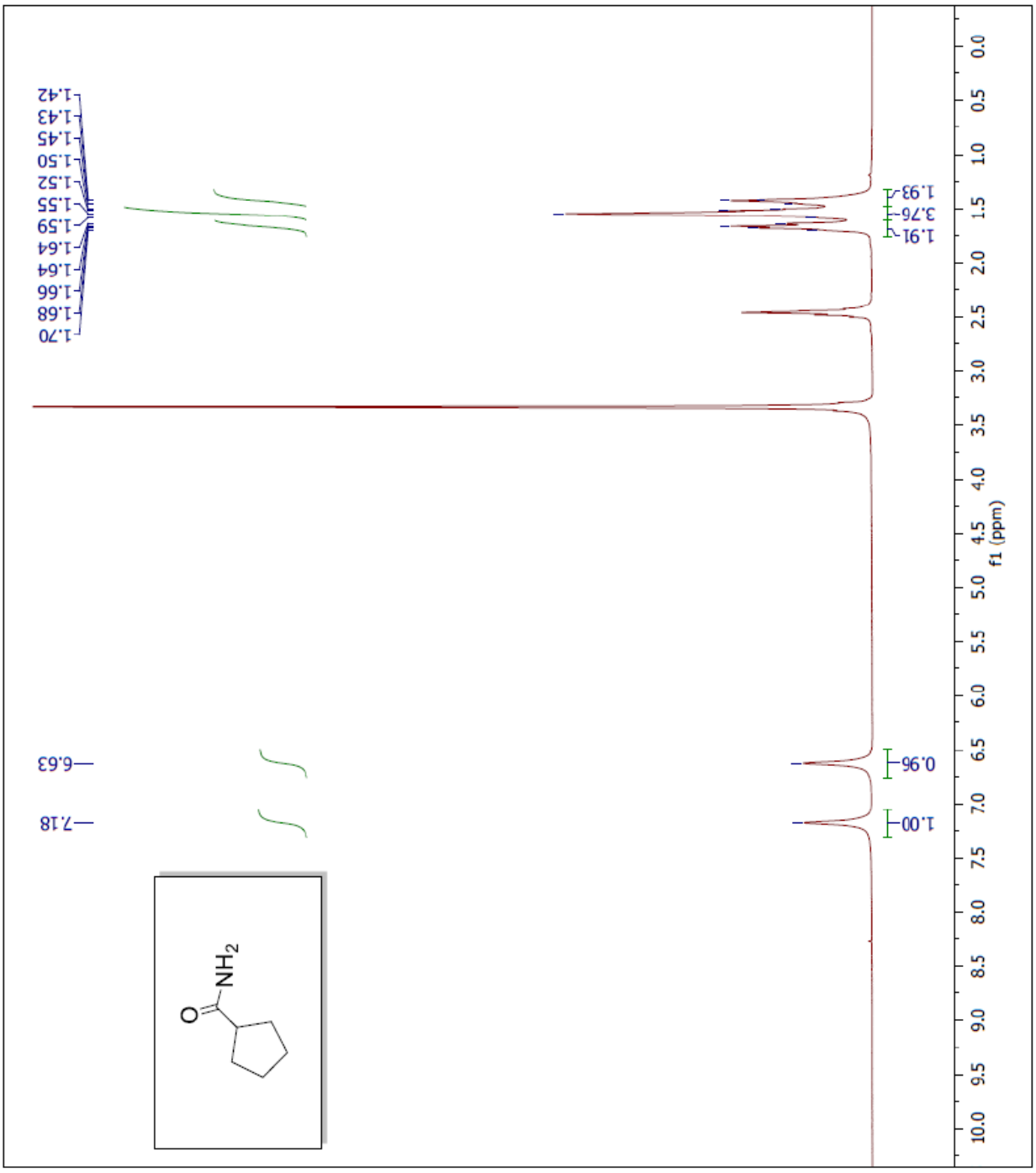

NH2
O
F
41.73
115.44
115.23
131.34
131.42
133.14
133.16
160.29
162.70
172.71
f1 (ppm)

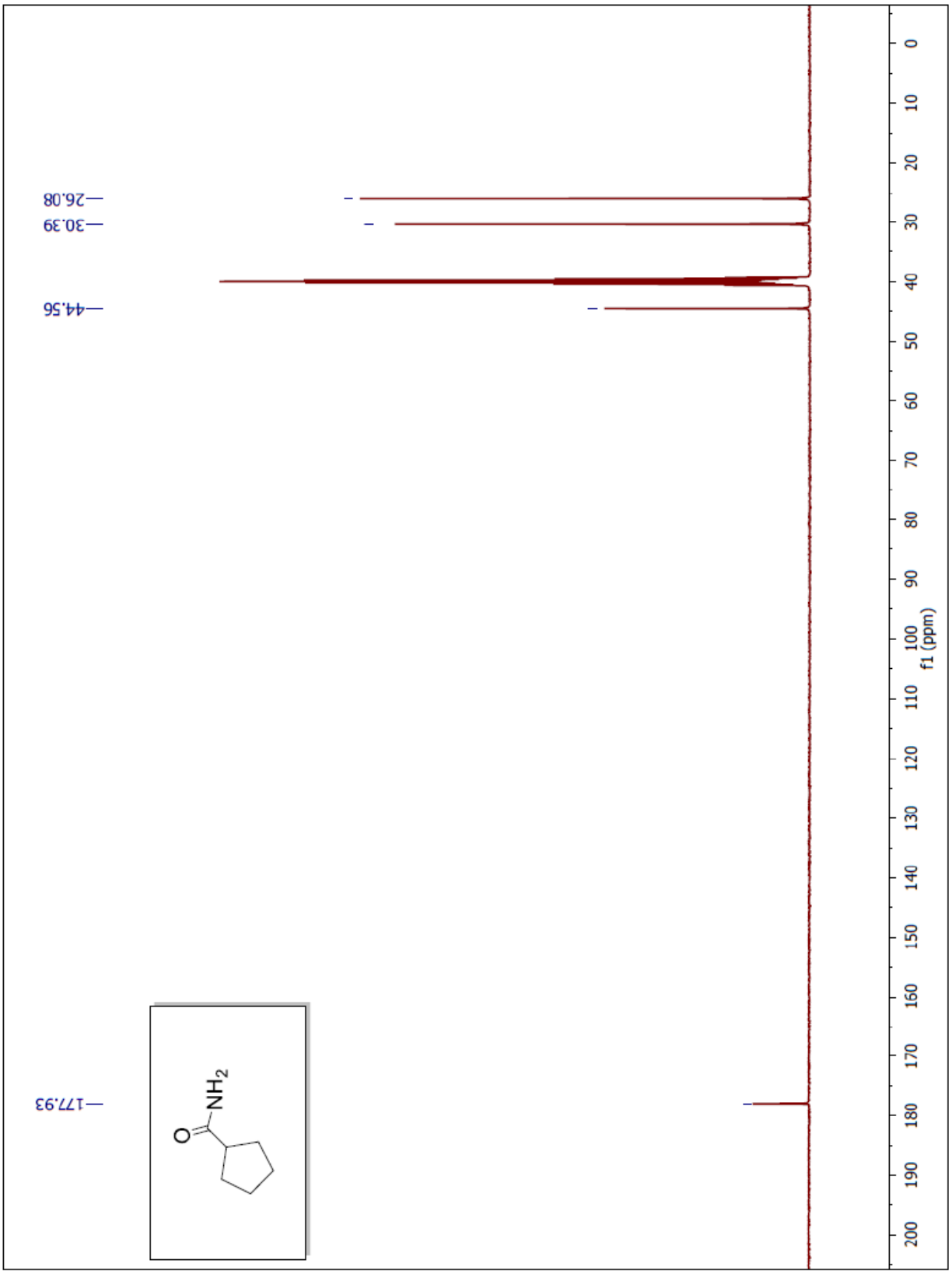
^{1}H and ^{13}C NMR spectra of compound 3y:



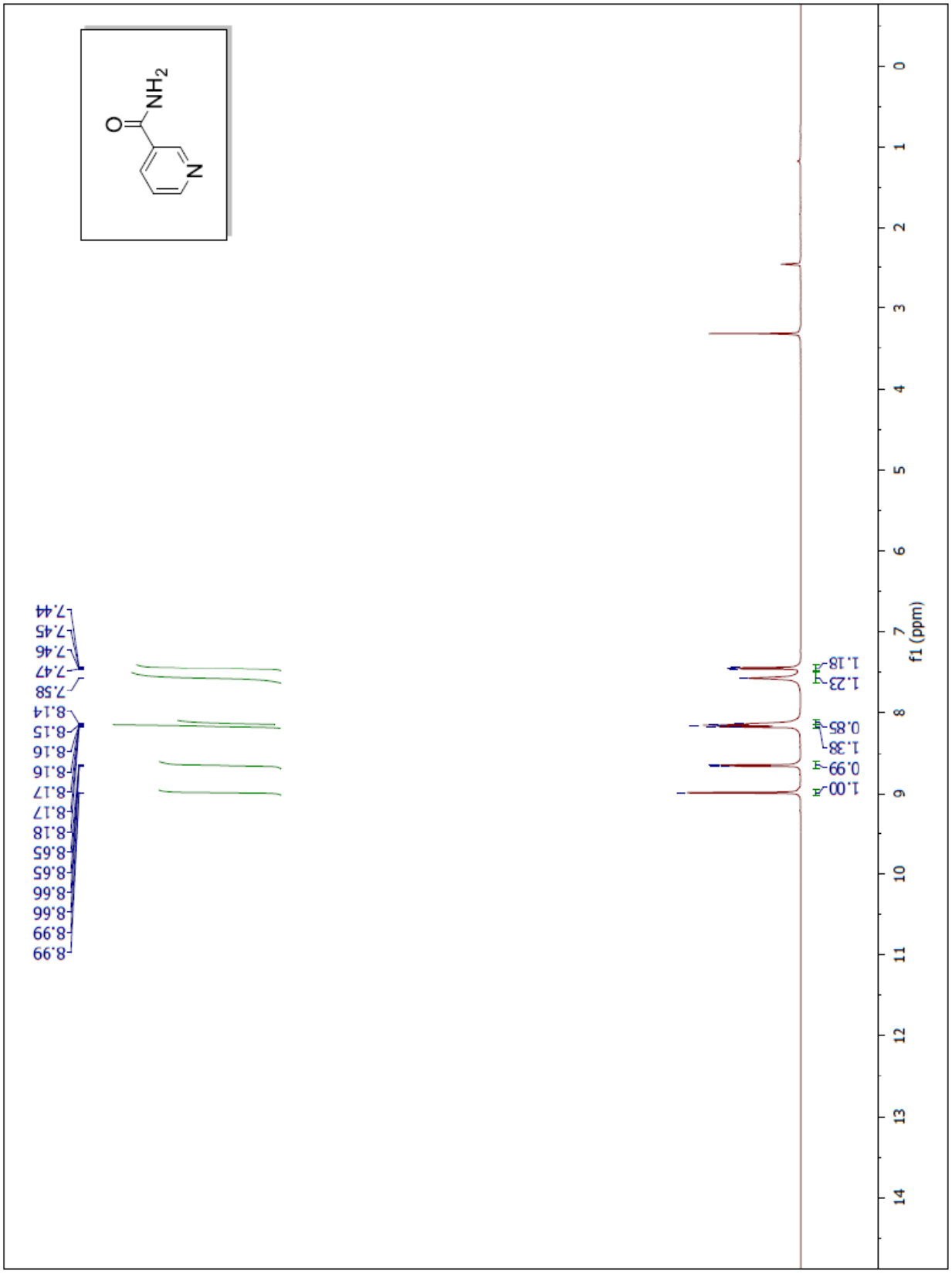

36.85
125.25
126.54
127.03
138.25
171.70
O
NH2
S
f1 (ppm)

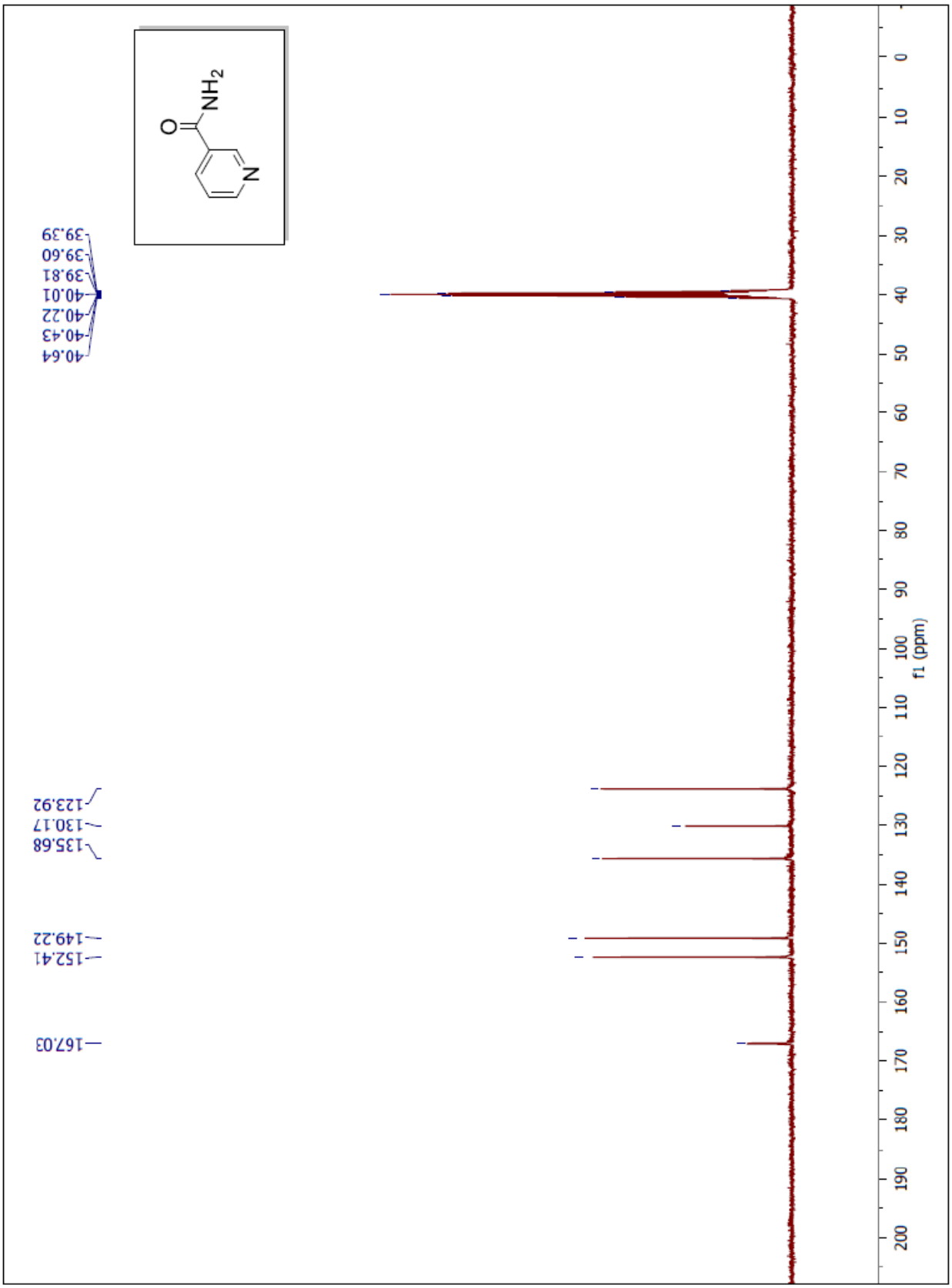
^{1}H and ^{13}C NMR spectra of compound 3ab:




177.93
44.56
30.39
26.08
O
NH2
f1 (ppm)

^{1}H and ^{13}C NMR spectra of Nicotinamide:




NH2
O
N
167.03
152.41
149.22
135.68
130.17
123.92
40.64
40.43
40.22
40.01
39.81
39.60
39.39
f1 (ppm)

(7) References.

(1) S. Yadav, N. U. D. Reshi, S. Pal and J. K. Bera, *Catal. Sci. Technol*. 2021, **11**, 7018-7028.

(2) M. Sharif, J. Chen, P. Langer, M. Beller and X. F. Wu, *Org. Biomol. Chem*. 2014, **12**, 6359-6362.

(3) L. Cao, J. Ding, M. Gao, Z. Wang, J. Li and A. Wu, *Org. Lett.* 2009, **11**, 3810-3813.

(4) H. Chen, W. Dai, Y. Chen, Q. Xu, J. Chen, L. Yu, Y. Zhao, M Ye and Y Pan, *Green Chem.* 2014, **16**, 2136-2141.

(5) Y. Li, H. Chen, J. Liu, X. Wan and Q. Xu, *Green Chem.* 2016, **18**, 4865-4870.

(6) R. Ray, A. S. Hazari, S. Chandra, D. Maiti and G. K. Lahiri, *Chem. Eur. J.* 2018, **24**, 1067-1071.

(7) G. C. Midya, A. Kapat, S. Maiti and J. Dash, *J. Org. Chem*. 2015, **80**, 4148-4151.

(8) T. E. Schmid, A. Gómez-Herrera, O. Songis, D. Sneddon, A. Révolte, F. Nahra and C. S. Cazin, *Catal. Sci. Technol*. 2015, **5**, 2865-2868.

(9) S. S. Choudhury, S. Mahapatra and H. S. Biswal, *Green Chem.* 2022, **24**, 4981-4990

(10) M. Tang, F. Zhang, Y. Zhao, Y. Wang, Z. Ke, R. Li, W. Zeng, B. Han and Z. Liu, *Green Chem.* 2021, **23**, 9870-9875.

(11) R. S. Ramon, N. Marion and S. P. Nolan, *Chem. Eur. J.* 2009, **15**, 8695-8697.