Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Table salt as catalyst for oxidation of aromatic alcohols and amines to acids and imines in aqueous medium: Effectively carrying out oxidation reactions in sea water

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Contents

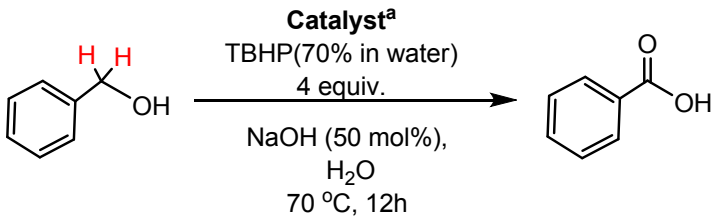
General Information

Unless otherwise stated, all reactions were performed under open atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Spectrospin DPX-300 and Bruker Ascend 400 NMR spectrometer at 300 and 75.47 MHz, respectively. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are related to residual solvent peaks [$CDCl_3$: 7.26 (^{1}H), 77.16 (^{13}C); DMSO-d_6: 2.50 (^{1}H), 39.52 (^{13}C)]. All primary alcohols and amines were purchased from commercial sources and secondary alcohols were prepared according to literature procedure.[1] Deionised water, TBHP (70% in water), TBHP in decane, NaCl,$Et_4N^+Cl^-$and NaOH were used as received.Sea water was collected from Kanyakumari (The southern-most tip of India where Indian Ocean, Arabian Sea and Bay of Bengal meets). The collected sea water was analyzed at Central Salt and Marine Chemicals Research Institute (CSMCRI), Gujarat, India by ICP-OES, Perkin Elmer, Optima 2000 DV and IC, Thermo Scientific, Dionex ICS 5000, Column: AS 11HC and AG 11HC with auto suppression mode using conductivity detector.

Experimental Section:

1. Optimization of reaction conditions for oxidation of alcohols

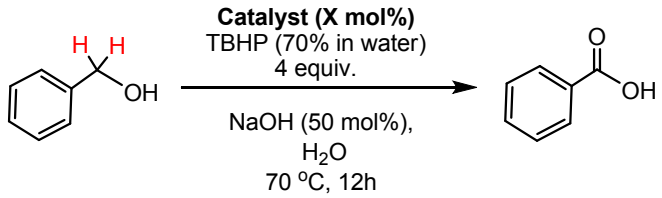
Table S1: Effect of catalysts for oxidation of alcohol.



Entry No.	Catalyst	% of yield (isolated)
1	—	—
2	NaCl	92
3	KCl	88
4	NCS	74
5	$Et_4N^+Cl^-$	70
6	NaBr	91
7[b]	Sea water	81

[a] All the reactions were carried out using 20 mol% catalyst and 5 mmol of benzyl alcohol.[b] Reaction was carried out using 80 mol% NaOH.

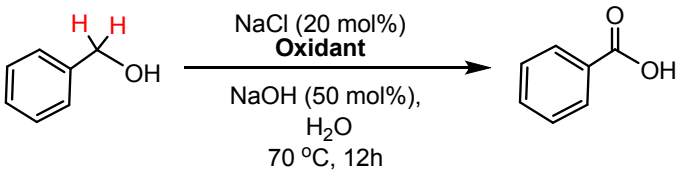
Table S2: Effect of amount of catalyst loading for the oxidation reaction.



Entry No.	Amount of NaCl (X mol%)	% of yield (isolated)
1	—	—
2	2	5
3	4	15
4	5	28
5	10	55
6	15	80
7	**20**	**92**
8	25	92
9[b]	Sea Water	81

[b] Reaction was carried out using 80 mol% NaOH.

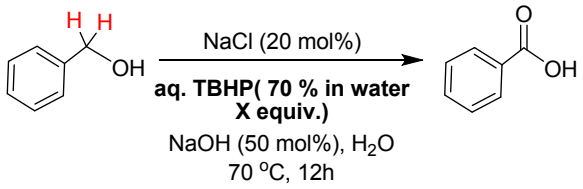
Table S3: Effect of oxidants used for the reaction.



Entry No.	**Oxidant**	% of yield (isolated)
1	-	**-**
2	**aq. TBHP**	**92**
3	**6M TBHP in decane**	**90**
4	O_2	0
5	H_2O_2	5
6	DTBP	0
7	$K_2S_2O_8$	0
8	NMO	0
9[c]	Oxone	0

[c] Under the reaction condition we obtained corresponding ester (benzyl benzoate) in 20% yield

Table S4: Effect of amount of oxidant used for oxidation reaction

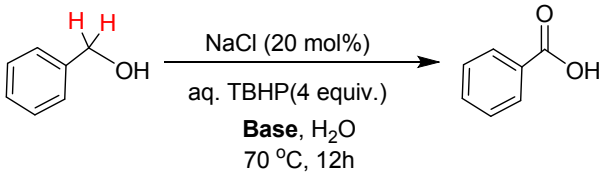


Entry No.	**aq. TBHP (x equiv.)**	% of yield (isolated)
1	-	**-**
2	1	12
3	2	32
4	3	63
5	**4**	**92**
6	5	92

Table 5: Effect of temperature in amine oxidation.

Entry No.	**Temperature (°C)**	% of yield (isolated)
1	25	0
2	40	20
3	50	32
4	60	75
5	**70**	**92**
6	80	92
7	90	90

Table S6: Effect of base and solvent used for the reaction



Entry No.	Base (20mol%)	Solvent	% ofyield (isolated)
1	—	—	0
2	**NaOH**	**H_2O**	**92**
3	**NaOH**	—	**92***
4	KOH	H_2O	87
5	Na_2CO_3	H_2O	88
6	K_2CO_3	H_2O	83
7	NaOAc	H_2O	76
8	KOAc	H_2O	75

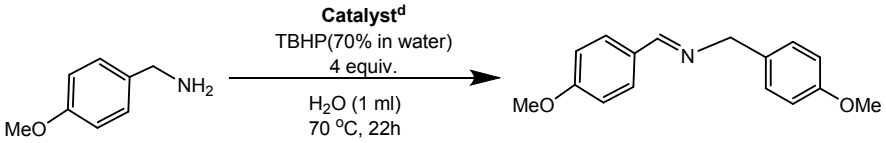
*Water from aqueous TBHP is present

Table S7: Effect of amount of base used for the reaction

Entry No.	NaOH (X mol%)	% of yield (isolated)
1	—	0
2	10	30
3	20	46
4	30	62
5	40	88
6	**50**	**92**
7	55	92
8	60	92

2. Optimization of reaction conditions for oxidation of primary amines

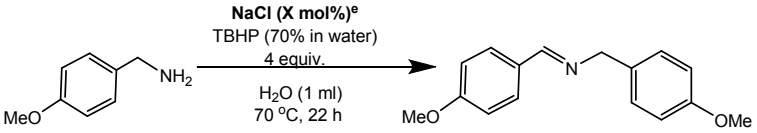
Table S8: Effect of catalysts on the oxidation of alcohol.



Entry No.	**Catalyst**	% of yield (isolated)
1	—	35
2	**NaCl**	**90**
3	KCl	85
4	NCS	50
5	$Et_4N^+Cl^-$	62
6	NaBr	65
7	**Sea water**	**93**

[d]All the reactions were carried out using 20 mol% catalysts and 0.5gm of 4-methoxy benzylamines.

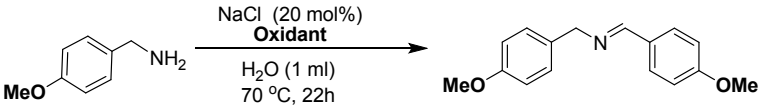
Table S9: Effect of amount of catalyst loading for the oxidation reaction.



Entry No.	Amount of NaCl (X mol%)	% of yield (isolated)
1	-	30
2	5	54
3	10	72
4	15	81
5	**20**	**90**
6	25	90
7	30	90
8	40	90
9	**Sea Water 1 mL**	**93**

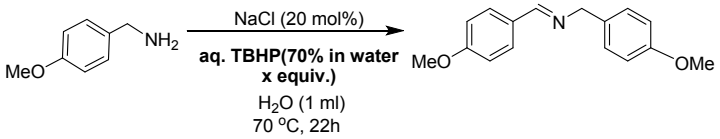
[e]All the reactions were carried out using 0.5gm of 4-methoxy benzylamine.

Table 10: Effect of oxidant used for the reaction.



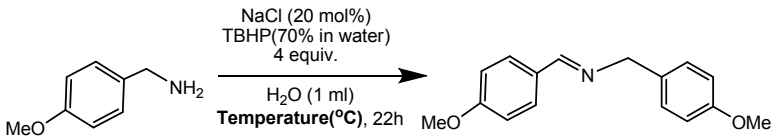
Entry No.	**Oxidant**	% of yield (isolated)
1	-	-
2	**aq. TBHP**	**90**
3	O_2	0
4	H_2O_2	40
5	DTBP	5
6	Oxone	0

Table 11: Effect of amount of oxidant used for oxidation reaction



Entry No.	**aq. TBHP (x equiv.)**	% of yield (isolated)
1	-	-
2	1	24
3	2	40
4	3	65
5	**4**	**90**
6	5	90

Table 12: Effect of temperature in amine oxidation.



Entry No.	**Temperature (°C)**	% of yield (isolated)
1	25	8
2	40	56
3	50	64
4	60	78
5	**70**	**90**
6	80	82
7	90	71
8	100	65

3. General procedure for oxidation of alcohols using NaCl

A 15 ml screw capped vial was charged with a magnetic bead, 5 mmol of alcohol, 1 mmol (20 mol%) of NaCl and 20 mmol (4 equiv.) of aq. TBHP (70% in H_2O). Afterwards,2.5 mmol (50mol%) of NaOH with additional 0.5 mL of deionized water were added to the reaction mixture and it was heated at 70 ^oC for 10-18 h. Afterwards, the reaction mixture was neutralized by aq. HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and after evaporation of the solvent analytically pure carboxylic acids or ketones were obtained.[2,3]

4. General procedure for oxidation of alcohols using sea water

A 15 ml screw capped vial was charged with a magnetic bead, 1gm of alcohol, 1.5 mL of filtered sea water and (4 equiv.) of aq. TBHP (70% in H_2O). Afterwards, 50 mol% of NaOH with additional was added to the reaction mixture and it was heated at 70 ^oC for 15 h. Afterwards, the reaction mixture was neutralized by aq. HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and after evaporation of the solvent analytically pure carboxylic acids or ketones were obtained.[2, 3]

5. General procedure for oxidation of primary amines for synthesis of symmetrical imines using NaCl

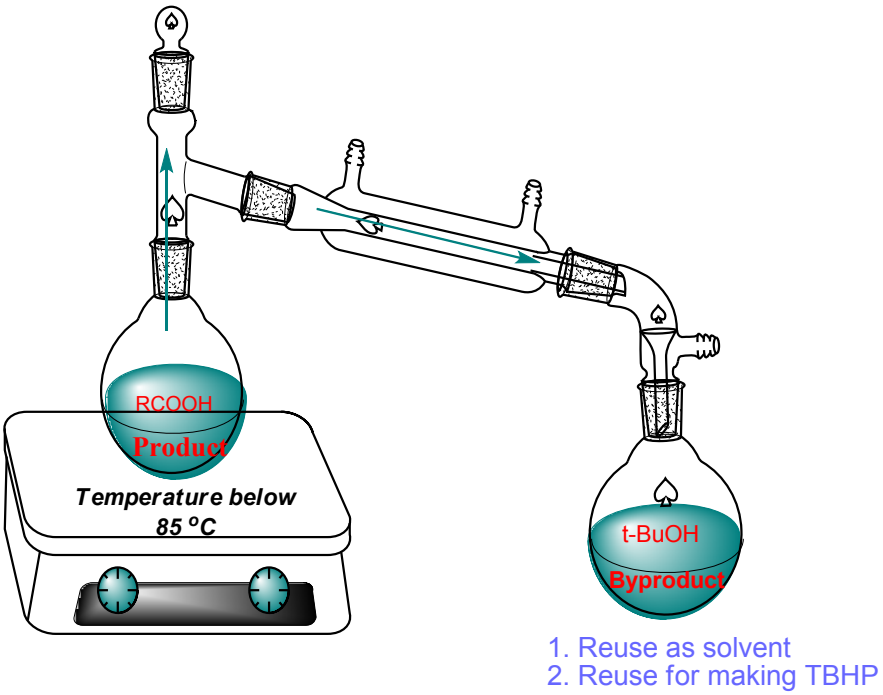
A 25 ml single necked round bottom flask was charged with a magnetic bead, 5 mmol of amines, 1 mmol (20 mol%) of NaCl, 20 mmol (4 equiv.) of aq. TBHP in 1 mL of deionised H_2O and it was heated at 70 ^oC for 15-22 h. Afterwards, the reaction mixture was extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and after evaporation of the solvent analytically pure imines was obtained.[4]However, in some cases the imine was purified through base (Et_3N) neutralized silica gel column chromatography using hexane and ethyl acetate (90:10) as eluent.[4]

6. General procedure for oxidation of primary amines for synthesis of symmetrical imines using sea water

A 25 ml single necked round bottom flask was charged with a magnetic bead, 1 gm of amines, 2 mL of filtered sea water (4 equiv.) of aq. TBHP and it was heated at 70 ^{o}C for 22 h. Afterwards, the reaction mixture was extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and after evaporation of the solvent analytically pure imines was obtained.[4]

7. Gram scale synthesis of benzoic acid using NaCl as catalysts and extracting of side product t-BuOH

A 250 ml of round bottom flask was charged with a magnetic bead, 0.277 mol (30 gm) of benzylalcohol, 0.055 mol (20 mol%) of NaCl and 1.108 mol (4 equiv.) of aq. TBHP. Afterwards, 0.138mol (50 mol%) of NaOH was added to the reaction mixture and it was fitted with a distillation assembly and heated around 80 ^{o}C making sure that the flask does not go to dryness and most of the t-BuOH distils out. Afterwards, the wet mixture was neutralized by aq. HCl and the benzoic acid got precipitated out. The solid benzoic acid was filtered off and washed with cold water (3 times). After drying using a vacuum pump 31.20 gm (92% yield) of benzoic acid was obtained as a white crystalline solid. The reaction was performed in a fume hood and adequate care was taken for handling TBHP.



8. Gram scale synthesis of benzylimine from benzylamines using NaCl as catalyst

A 250 ml of round bottom flask was charged with a magnetic bead, 0.280 mol (30 gm) of benzyl amine, 0.056 mol (20 mol%) of NaCl and 1.121 mol (4 equiv.) of aq. TBHP and heated at 70 °C for 40 h. Afterwards, EtOAc was added to the reaction mixture. The organic layer was dried over anhydrous Na_2SO_4 and after evaporation of the solvent benzylimine was obtained in 89% yield (24.3 gm).

9. Gram scale synthesis of benzoic acid using sea water

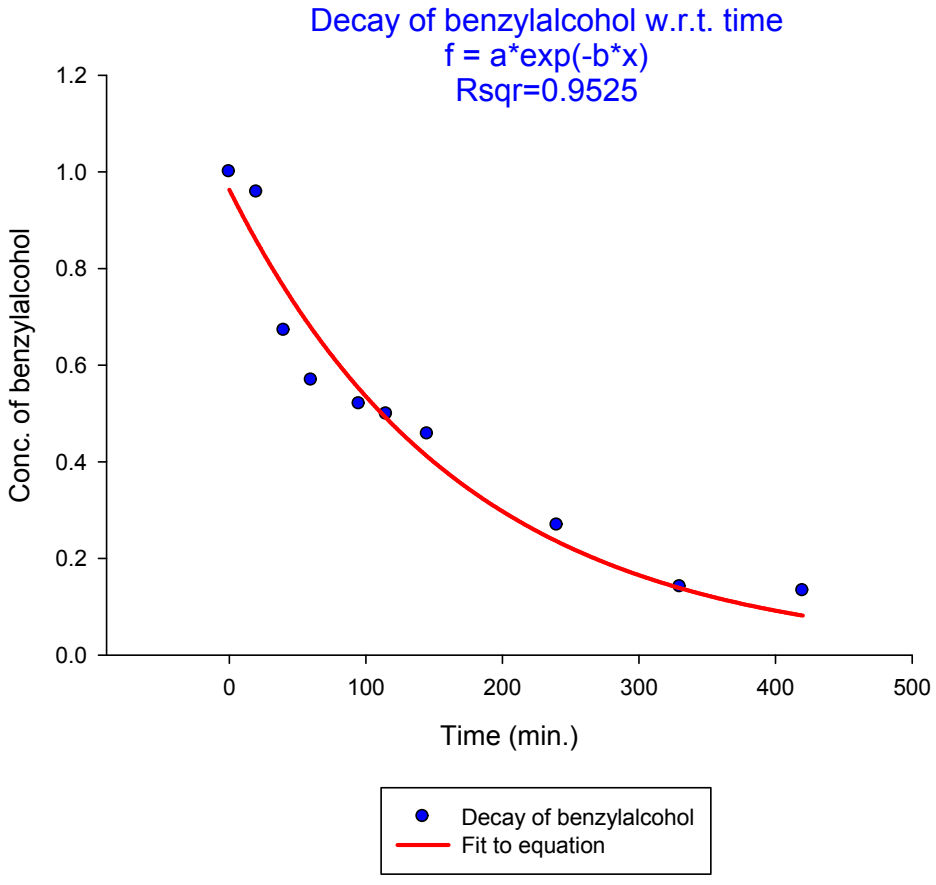
A 250 ml of beaker was charged with a magnetic bead, 15 gm (0.138 mol) of benzyl alcohol, 4.45 gm of NaOH (0.11 mol, 80 mol%), 50 gm of aq. TBHP (0.55 mol, 4 equiv.) and 22.5 mL filtered sea water and heated at 70 °C for 15 h. Afterwards, the wet reaction mixture was neutralized by aq. HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and after evaporation of the solvent and drying using a vacuum pump 13.30 gm (79% yield) of benzoic acid was obtained as a white crystalline solid. The reaction was performed in a fume hood and adequate care was taken for handling TBHP.

10. Gram scale synthesis of benzylimine from benzylamines using sea water

A 250 ml of round bottom flask was charged with a magnetic bead, 15 gm (0.14 mol) of benzyl amine, 50.5 gm of aq. TBHP (0.56 mol, 4 equiv.), 30 mL filtered sea water and heated at 70 ^{o}C for 40 h. Afterwards, EtOAc was added to the reaction mixture. The organic layer was dried over anhydrous Na_2SO_4 and after evaporation of the solvent benzylimine was obtained in 84% yield (11.6 gm).

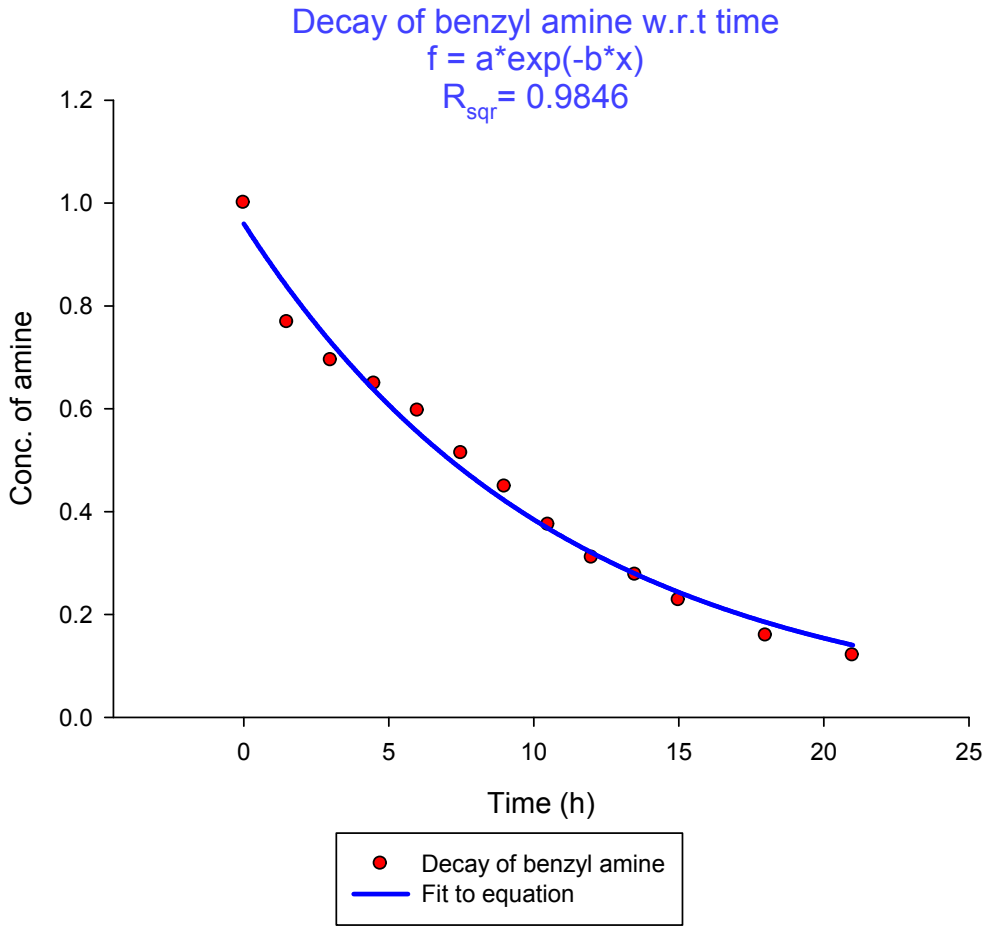
11. Determination of order and rate of reaction w.r.t benzyl alcohol

The order of the reaction w.r.t to alcohol was determined by time dependent ^{1}H-NMR studies. We monitored the change in concentration of benzyl alcohol w. r. t time, using $CDCl_3$as solvent and toluene as internal standard for 10h. The result is fitted for the decay of benzylalcohol with the equation y=a*[1-exp(-b*x)] which indicates a first order reaction.



12. Determination of order and rate of reaction w.r.t benzyl amine

The order of the reaction w.r.t to amine was determined by time dependent ^{1}H-NMR studies. We monitored the change in concentration of benzylamine w. r. t time, using $CDCl_3$as solvent and toluene as internal standard for 21h. The result is fitted for the decay of benzylamine with the equation y=a*[1-exp(-b*x)] which indicates a first order reaction.



13. Determination of chloride ion concentration by titration (Mohr's Method)[5]

Sea water sample was prepared according to reported procedure. 10 mL diluted sea water was titrated with standard $AgNO_3$ solution (C= 0.1 mol/L) using K_2CrO_4 (C= 0.25 mol/L) as indicator.

Entry	Voloume of sea water (mL)	Volume of $AgNO_3$ (mL)
1	10	66.8
2	10	66.9
3	10	66.7
4	10	66.8

Avg. Vol. of $AgNO_3$ = 66.8

Calculation:

C_{AgNO3} = 0.1 mol/L

Vol. of $AgNO_3$ used = 66.8 mL

Vol. of sea water = 10 mL.

Total no. of moles of $AgNO_3$ used for 10 mL sea water = (0.1 * 66.8)/1000

= 0.0068 moles

$$Ag^+ (aq) + Cl^- (aq) \longrightarrow AgCl (s)..... 1$$

According to the eqn 1, one mole Ag^+ ions consume one mol of Cl^- ions.

Total no. of moles of Cl^- ion in 1L of sea water = (0.0068*100) moles = 0.68 moles

Total amount of NaCl in 1L of sea water = (0.68*58.44) gm/L = 39.73 gm/L

14. Analysis of sea water by inductively coupled plasma -optical emission spectrometry (ICP-OES) and ion chromatography (IC)

Analysis: A solid sample (powdered form) was submitted for ICP-OES analysis of sodium, potassium, calcium and magnesium in it. 50 ml solution was prepared by dissolving 100 mg of the given sample (as such). This solution was used for analysis of element of interest by

ICP-OES instrument. To fall the readings in working range (i.e. 0.3-10 ppm), appropriate dilution of the solution was done wherever needed. Results taking account of sample weight and volume are given in the table below.

Element	Dilution factor	ICP-OES instrument reading (ppm)	Reading (ppm) including dilution	Calculated concentration (ppm)	Calculated concentration (%)
Ca	10	1.881	18.81	9405.00	0.9405
K	10	2.266	22.66	11330.00	1.133
Mg	10	7.218	72.18	36090.00	3.609
Na	100	5.377	537.7	268850.00	26.885

IC analysis of sea water

Cl^- content in %	SO_4^{2-} content in %	Br^- content in ppm
43.19	5.26	1508

15. References:

1.Reduction of Aldehydes and Ketones using $NaBH_4$ or $LiAlH_4$. https://home.cc.umanitoba.ca/~hultin/chem2220/Support/Reduction_of_Carbonyl_Compounds_using_$NaBH_4$_or_$LiAlH_4$.pdf

2.Hazra, S., Deb, M. & Elias, A. J.Iodine catalyzed oxidation of alcohols and aldehydes to carboxylic acids in water: a metal-free route to the synthesis of furandicarboxylic acid and terephthalic acid. *Green Chem.***19**, 5548-5552 (2017).

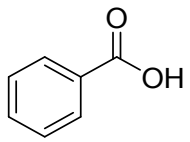
3.Sarbajna, A., Dutta, I., Daw, P., Dinda, S., Rahaman, S. M. W., Sarkar, A.& Bera, J. K. Catalytic conversion of alcohols to carboxylic acid salts and hydrogen with alkaline water. *ACS Catal.***7**, 2786-2790 (2017).

4.Hazra, S., Pilania, P., Deb, M., Kushawaha, A. K. & Elias, A. J. Aerobic oxidation of primary amines to imines in water using a cobalt complex as recyclable catalyst under mild conditions. *Chem. Eur. J.***24**, 15766-15771 (2018).

5. Mendhan. J., Denney. R. C., Baraes. J. D. & Thomas. M. J. K. Vogel's text book of quantitative chemical analysis, 6th edition, Pearson, pp 401, 2002.

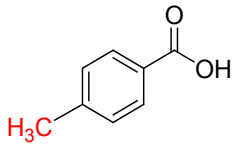
16. Identification of products (carboxylic acids and ketones):

Compound 1a



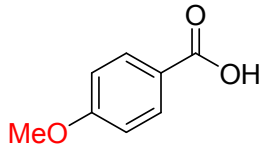
1a, white crystalline solid; (^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 12.98 (br, 1H), 7.97-7.95 (d, J= 6Hz), 7.62-7.45 (m, 3H); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 167.80, 133.26, 131.23, 129.73, 128.97.

Compound 1b



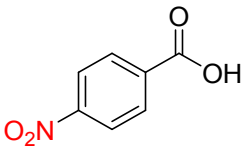
1b, white solid; ^{1}H-NMR (DMSO-d_6, 400 MHz, ppm): 12.81 (s, 1H), 7.85-7.83 (d, J=8Hz, 2H), 7.31-7.29 (d, J= 8Hz, 2H), 2.37 (s, 3H);^{13}C-NMR (DMSO-d_6, 100 MHz, ppm): 167.76, 143.48, 129.79, 129.58, 128.49, 21.58.

Compound 1c



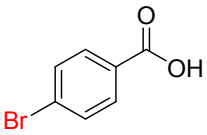
1c, white solid; ^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 12.65 (br, 1H), 7.91-7.89 (d, J= 6Hz, 2H), 7.01-6.99 (d, J= 6Hz, 2H), 3.80 (s, 3H); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 167.51, 163.27, 131.80, 123.40, 114.19, 55.76.

Compound 1d



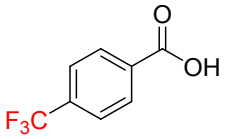
1d, yellow solid; ^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 13.64 (br, 1H), 8.26-8.23 (d, J= 9Hz, 2H), 8.12-8.09 (d, J=9Hz, 2H); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 166.19, 150.36, 136.75, 131.05, 124.03.

Compound 1e



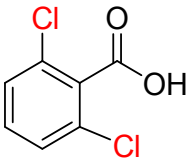
1e, white solid; ^{1}H-NMR (DMSO-d_6, 400 MHz, ppm): 13.19 (s, 1H), 7.87-7.85 (d, J=8Hz, 2H), 7.72-7.70 (d, J= 8Hz, 2H);^{13}C-NMR (DMSO-d_6, 100 MHz, ppm): 167.07, 132.17, 131.75, 130.48, 127.34.

Compound 1f



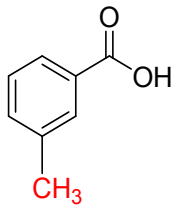
^{1}H-NMR (DMSO-d_6, 400 MHz, ppm): 13.47 (br, 1H), 8.12-8.14 (d, J= 9Hz, 2H), 7.84-7.86 (d, J= Hz, 2H); ^{13}C-NMR (DMSO-d_6, 100 MHz, ppm): 166.64, 135.05, 130.52, 125.99, 79.60.

Compound 1g



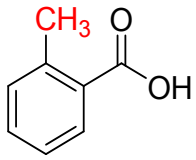
1g, yellowish solid; ^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 7.97-7.95(d, J= 6Hz, 1H), 7.62-7.45 (m, 2H); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 167.80, 133.26, 131.22, 129.72, 128.97.

Compound 1h



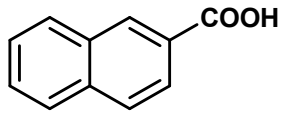
1h, white solid; ^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 12.89 (br, 1H), 7.77 (m, 2H), 7.40-7.34 (m, 2H), 2.33 (s, 3H); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 167.90, 138.29, 133.84, 131.17, 130.19, 128.82, 126.90, 21.20.

Compound 1i



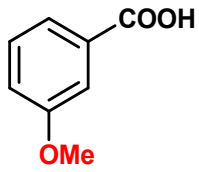
1i, white solid; ^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 12.81 (br, 1H), 7.84.7.81 (d, J= 9Hz, 1H), 7.41-7.39 (t, 1H), 7.28-7.26 (d, J=6Hz, 2H), 2.52 (s, 3H); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 169.14, 139.48, 132.12, 131.93, 130.87, 130.65, 126.24, 21.70.

Compound 1j



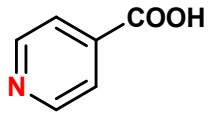
1j, white solid; ^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 13.12 (br, 1H), 8.62 (s, 1H), 8.12-7.97 (m, 4H), 7.66-7.56 (m, 2H); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 167.93, 135.38, 132.60, 131.00, 129.74, 128.77, 128.62, 128.52, 128.11, 127.25, 125.63.

Compound 1k



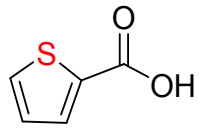
1k, white solid; ^{1}H-NMR (DMSO-d_6, 400 MHz, ppm): 13.03 (br, 1H), 7.15-7.56 (3H),3.79 (s, 3H); ^{13}C-NMR (DMSO-d_6, 100 MHz, ppm): 167.60, 159.67, 132.68, 130.06, 122.00, 119.21, 114.20, 55.60.

Compound 1l



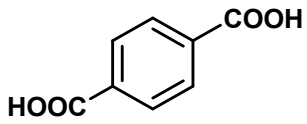
^{1}H-NMR (DMSO-d6, 300 MHz, ppm): 13.68 (br, 1H), 8.76-8.68 (d, J= 9Hz, 2H), 7.80-7.82 (d, 2H); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 166.60, 151.30, 138.54, 123.20.

Compound 1m



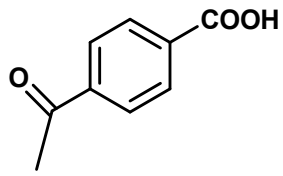
1m, white solid; ^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 13.08(br, 1H), 7.87-7.84 (d, J=5Hz, 1Hz, 1H), 7.73-7.72 (dd, J=4Hz, 1Hz, 1H), 7.18-7.15 (dd, J=4.92Hz, 3.75Hz, 1H); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 163.39, 135.12, 133.67, 128.66.

Compound 1n



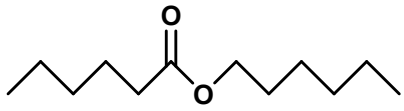
1n, white solid; ^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 7.30 (s, 2H), ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): 159.40, 147.53, 118.77.

Compound 1o



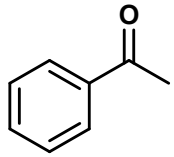
1o, white solid; ^{1}H-NMR (DMSO-d_6, 400 MHz, ppm): 13.34 (s, 1H), 8.05 (s, 4H), 2.63 (s, 3H);^{13}C-NMR (DMSO-d_6, 100 MHz, ppm): 198.21, 167.11, 140.30, 134.98, 130.01, 128.79, 27.48.

Compound 1p



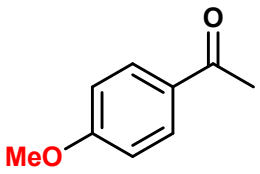
1p, colourless liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 3.57-3.52 (t, 2H), 2.23 (t, 2H), 1.50-1.48 (m, 4H), 1.24-1.22(m, 7H), 1.17(m, 2H), 0.82-0.79(m, 7H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 178.35, 80.58, 62.67, 34.00, 32.33, 31.19, 26.37, 25.98, 24.43 22.56, 22.25, 13.92 .

Compound 1q



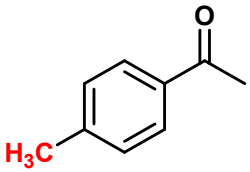
1q, colourless liquid; ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): 7.96-7.93 (d, J= 12 Hz, 2H), 7.55 (t, 1H), 7.47-7.45 (t, 3H), 2.59 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 198.20, 137.10, 133.11, 128.56, 128.30, 26.57.

Compound 1r



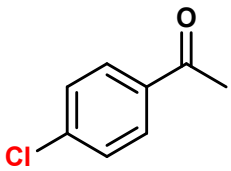
1r, yellow liquid; ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): 7.91-7.89 (d, J= 12 Hz, 2H), 6.91-6.89 (d, J=12Hz, 2H), 3.82 (s, 3H), 2.52 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 196.66, 163.44, 130.51, 130.25, 113.62, 55.36, 26.22.

Compound 1s



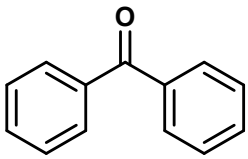
1s, yellow liquid; ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): 7.82-7.80 (d, J= 8 Hz, 2H), 7.20-7.18 (d, J=8Hz, 2H), 2.51 (s, 3H), 2.35 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 197.57, 143.73, 134.64, 129.16, 128.36, 26.35, 21.48.

Compound 1t



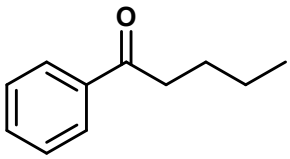
1t, yellow liquid; ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): 7.87-7.85 (d, J= 8 Hz, 2H), 7.40-7.38 (d, J=8Hz, 2H), 2.56 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 196.65, 139.42, 135.38, 129.67, 128.79, 26.45.

Compound 1u



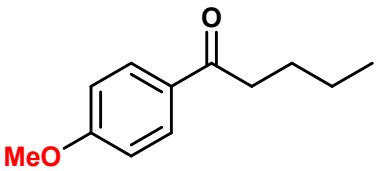
1u, white solid; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 7.82-7.78 (m, 4H), 7.58-7.75 (m, 2H), 7.50-7.45 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 196.76, 137.60, 132.45, 130.08, 128.31.

Compound 1v



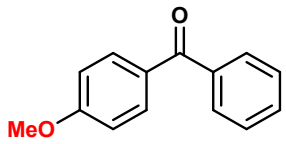
1v, colourless liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 7.97-7.93 (d, J= 9 Hz, 2H), 7.56-7.51 (t, 1H), 7.46-7.41 (t, 2H), 2.93-2.93 (t, 2H), 1.76-1.69 (m, 2H), 1.44-1.36 (m, 2H), 0.97-0.92 (t, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 200.50, 137.06, 132.85, 128.53, 128.03, 38.30, 26.46, 22.48, 13.95.

Compound 1w



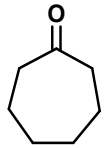
1w, yellow liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 7.95-7.93 (d, J= 6 Hz, 2H), 6.94-6.91 (d, J=9Hz, 2H), 3.86 (s, 3H), 2.93-2.88 (t, 2H), 1.73-1.68 (m, 2H), 1.44-1.36 (m, 2H), 0.97-0.92 (t, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 199.28, 163.30, 132.29, 130.31, 113.71, 55.42, 38.00, 26.75, 22.53, 13.94.

Compound 1x



1x, yellow liquid;^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 7.83-7.73 (dd, 4H), 7.48-7.45 (dt, 3H), 6.96-6.93 (d, J= 9Hz, 2H), 3.86 (s, 3H);^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 195.59, 163.94, 138.28, 132.57, 131.91, 130.13, 129.73,128.76, 113.73, 55.49.

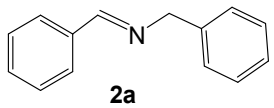
Compound 1y



1y, colourless liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 2.44-2.40 (t, 4H), 1.65-1.61 (m, 8H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 214.97, 43.64, 30.25, 24.16.

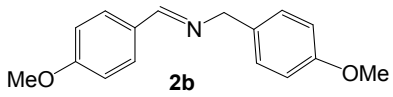
Identification of products (Imines)

Compound 2a



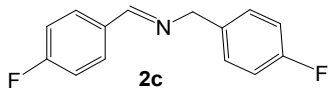
Imine**2a**: yellow oil; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.32 (s, 1H), 7.74-7.76(d, 2H), 7.30-7.36 (m, 8H), 4.77 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 162.05, 139.45, 136.29, 130.87, 128.72, 128.62, 128.40, 128.09, 127.10, 65.14.

Compound 2b



Imine **2b**: yellow oil; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.15 (s, 1H), 7.58-7.60(d, 2H), 7.11-7.14 (d, 2H), 6.74-6.80 (m, 4H), 4.59 (s, 2H), 3.67(s, 3H), 3.64 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 161.70, 160.93, 158.67, 131.72, 129.84, 129.22, 129.19, 113.99, 113.92, 64.42, 55.33, 55.27.

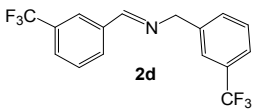
Compound 2c



2c

Imine **2c**: yellow oil; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.14 (s, 1H), 7.58-7.62 (m, 2H), 7.10-7.15 (m, 2H), 6.82-6.95 (m, 4H), 4.58 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 166.08, 163.63, 162.75, 160.53, 160.39, 135.10, 135.06, 132.44, 132.40, 130.28, 130.16, 129.57, 115.87, 115.17, 64.11; ^{19}F-NMR ($CDCl_3$): -115.76 (s, 1F), -109.04 (s, 1F).

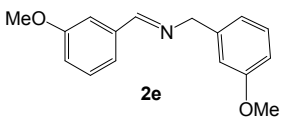
Compound 2d



2d

Imine **2d**: yellow oil; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.46 (s, 1H), 7.98 (1H), 8.07 (s, 1H), 7.50-7.68 (m, 6H), 4.89 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 160.97, 139.91, 131.46, 131.31, 129.21, 129.01, 130.66, 129.21, 129.01, 125.68, 124.63, 124.03, 64.41;; ^{19}F-NMR ($CDCl_3$): -62.56 (s, 1F), -62.77 (s, 1F).

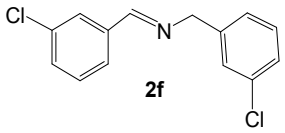
Compound 2e



2e

Imine **2e**: yellow oil; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.23 (s, 1H), 7.13-7.30 (m, 4H), 6.69-6.89 (m, 4H), 4.69 (s, 2H), 3.72(s, 3H), 3.69 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 162.05, 159.95, 159.83, 140.87, 137.62, 129.59, 129.52, 120.36, 117.59, 113.70, 64.89, 55.39, 55.21.

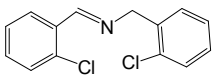
Compound 2f



2f

Imine **2f**: yellow oil; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.27 (s, 1H), 7.74 (s, 1H), 7.55 (d, 1H), 7.16-7.34 (m, 6H), 4.71 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 160.92, 141.00, 137.66, 134.86, 134.38, 130.90, 129.89, 129.77, 128.01, 127.95, 127.25, 126.03, 64.25.

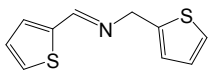
Compound 2g



2g

Imine **2g**: colorless oil; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.87 (s, 1H), 8.20 (d, 1H), 7.23-7.45 (m, 7H), 4.94 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 159.71, 136.84, 135.30, 133.42, 133.12, 131.73, 129.82, 129.67, 129.34, 128.47, 128.31, 127.02, 126.92, 62.18.

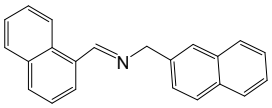
Compound 2h



2h

Imine **2h:** yellow oil; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.30 (s, 1H), 7.30 (d, 1H), 7.28 (d, 1H), 7.22 (d, 1H), 6.95 (d, 1H), 6.87-6.89 (m, 2H), 4.83 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 155.43, 142.128, 131.08, 129.35, 127.41, 126.90, 125.29, 124.84, 58.52.

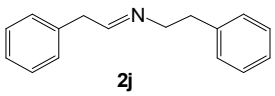
Compound 2i



2i

Imine **2i**: colorless oil; ^{1}H-NMR ($CDCl_3$,300 MHz, ppm): 9.08 (s, 1H), 8.96 (d, 1H, J = 9 Hz), 8.24 (d, 1H), 7.80-7.95 (m, 5H), 7.47-7.60 (m, 7H), 5.41 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) 161.95, 133.86, 131.13, 129.15, 128.69, 128.60, 127.81, 127.19, 126.12, 126.03, 125.87, 125.69, 125.62, 125.22, 124.44, 123.96,63.25.

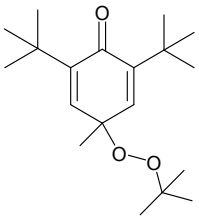
Compound 2j



2j

Imine **2j**: colorless oil; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.21 (s, 1H), 7.75-7.77 (m, 2H), 7.44-7.47 (m, 3H), 7.27-7.34 (m, 5H), 3.91 (t, 2H), 3.07-3.09(m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 161.53, 139.93, 136.20, 130.60, 129.04, 128.85, 128.60, 128.36, 128.07, 126.13, 63.20, 37.54.

Compound peroxide 6

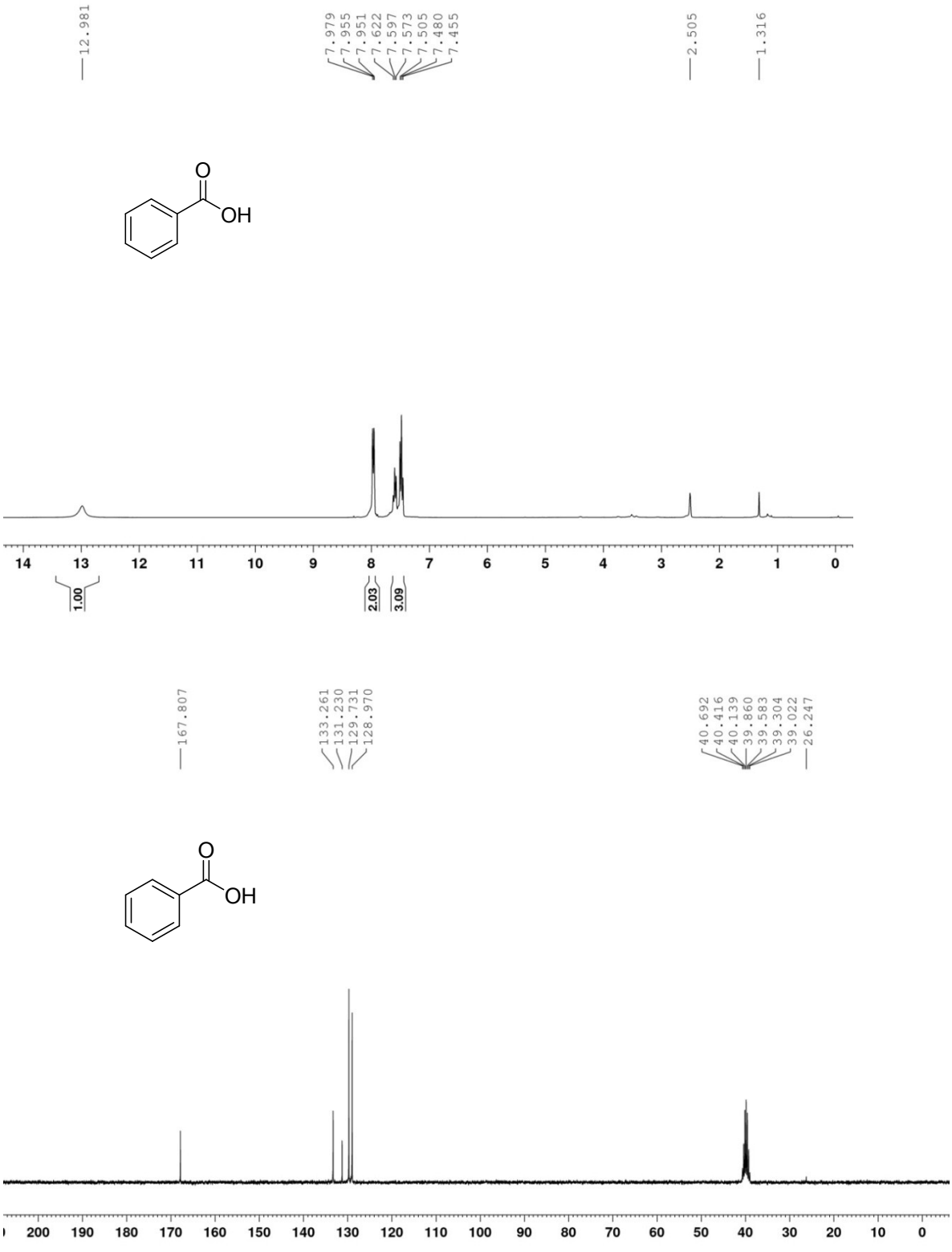


peroxide 6

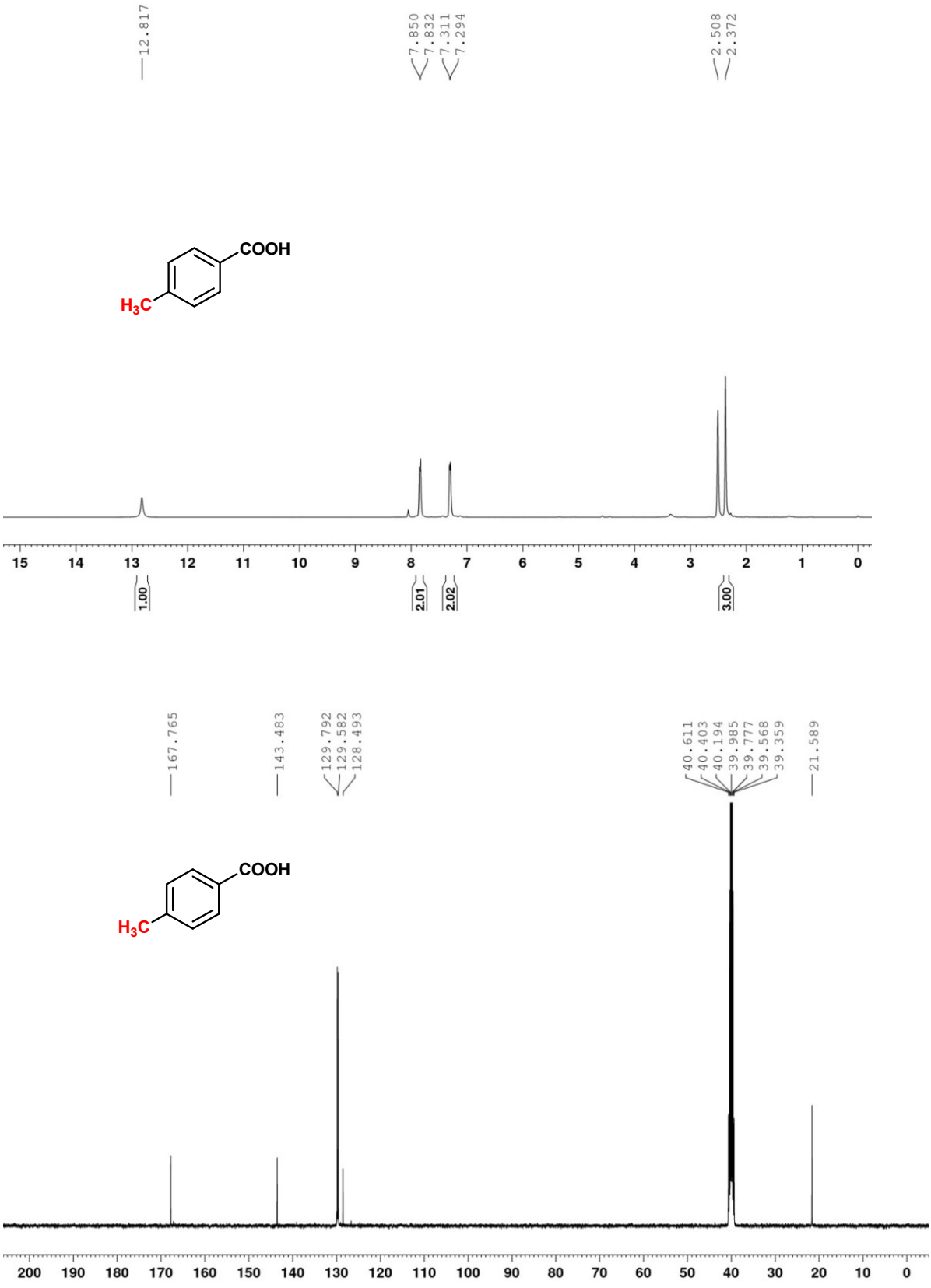
Peroxide **6**: yellow orange solid; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 6.56 (s, 2H), 1.19-1.44 (m,30H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 186.71, 146.61, 141.84, 34.72, 30.38, 29.46, 26.49, 24.25. HRMS; m/z = 331.2246, calcd for $C_{19}H_{32}O_3Na$ [M+Na]= 331.2244.

^{1}H and $^{13}C\{^{1}H\}$ NMR data

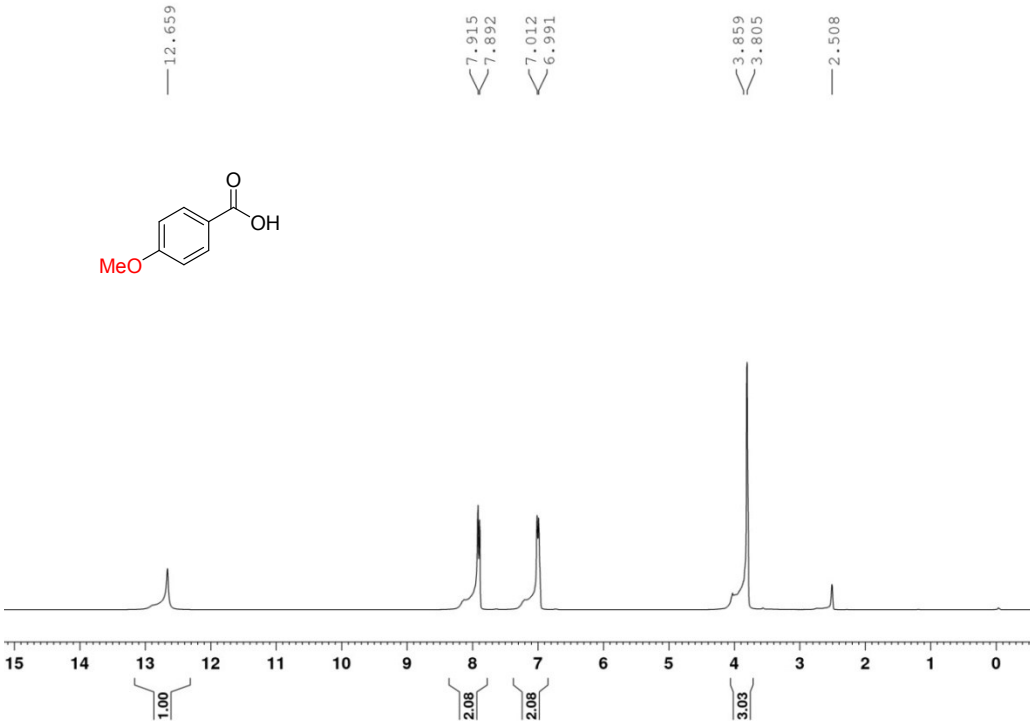
^{1}H-NMR &^{13}C $\{^{1}H\}$ (in DMSO-d_6) spectra of compound **1a**

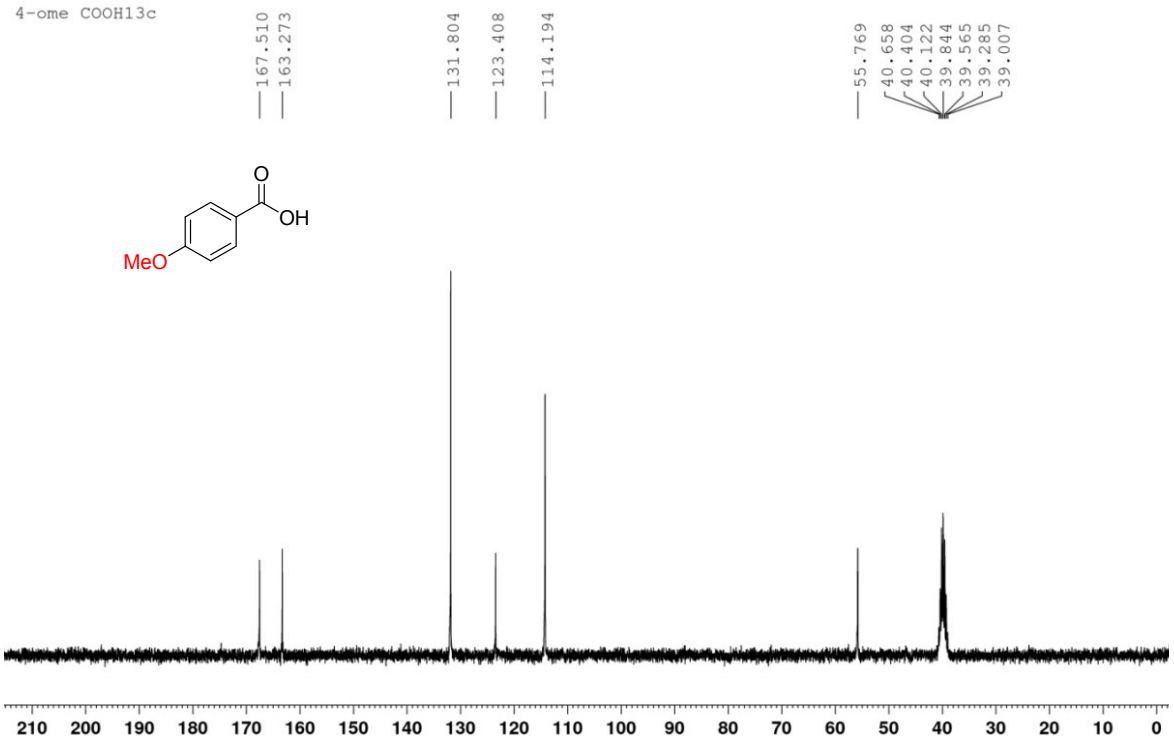


^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1b**

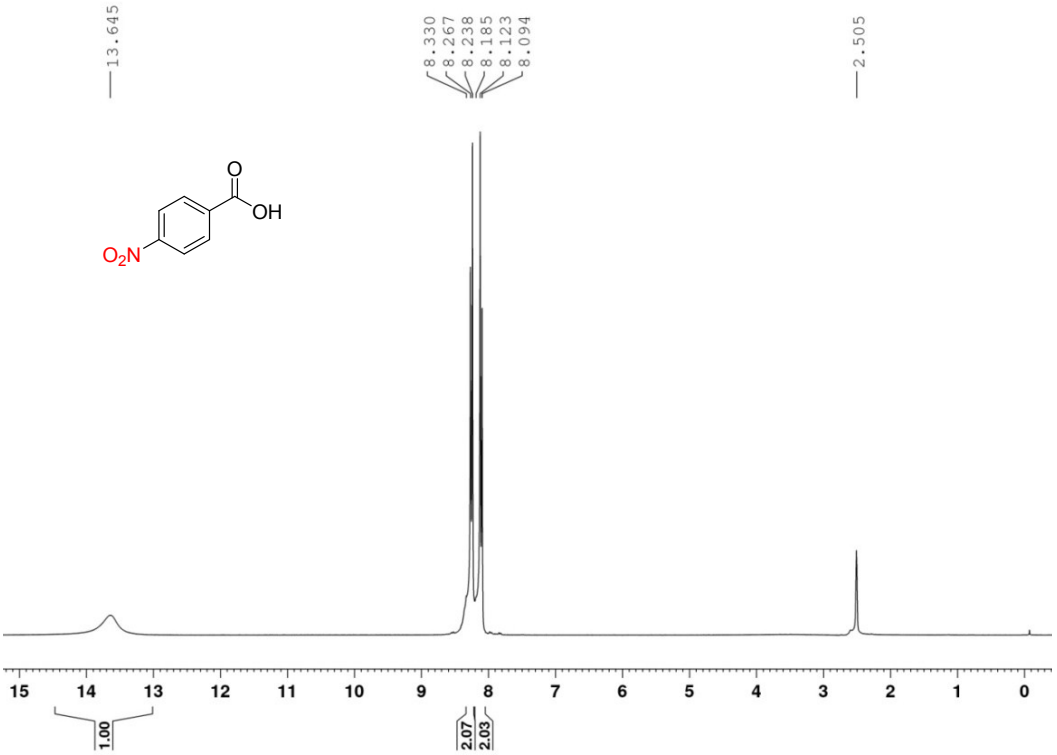


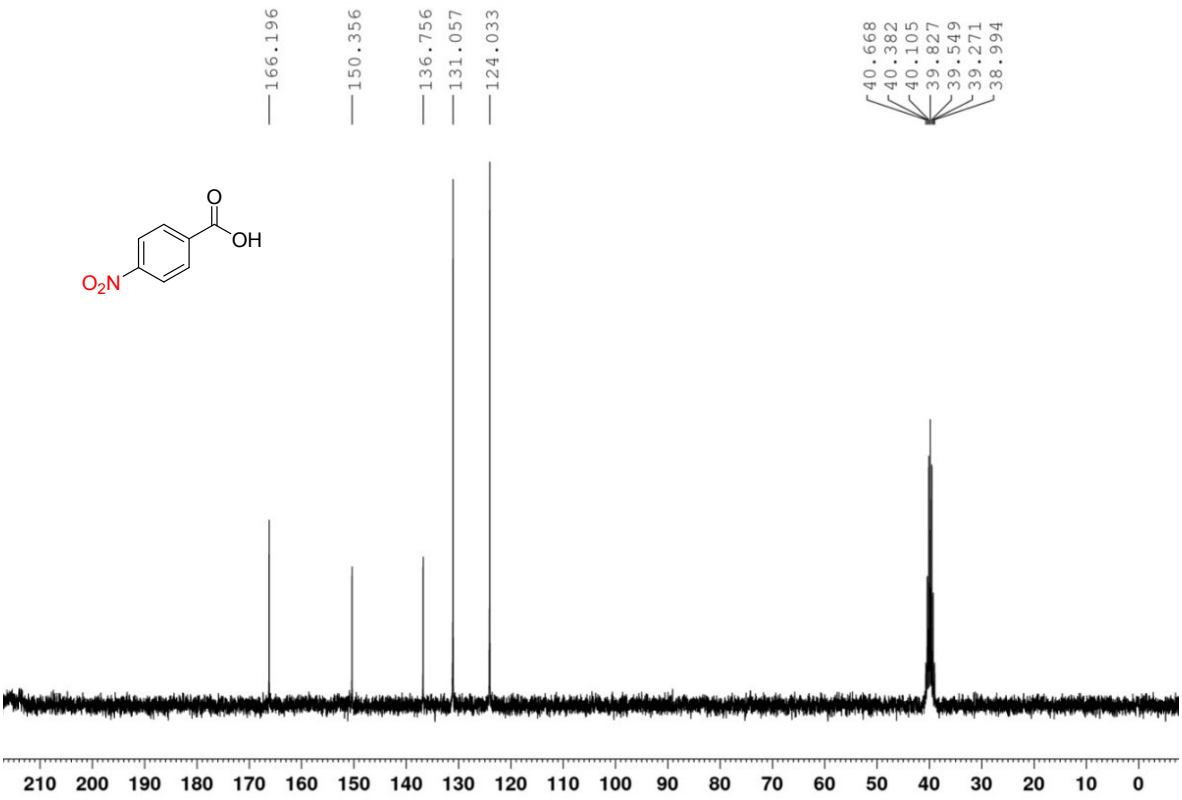
^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1c**



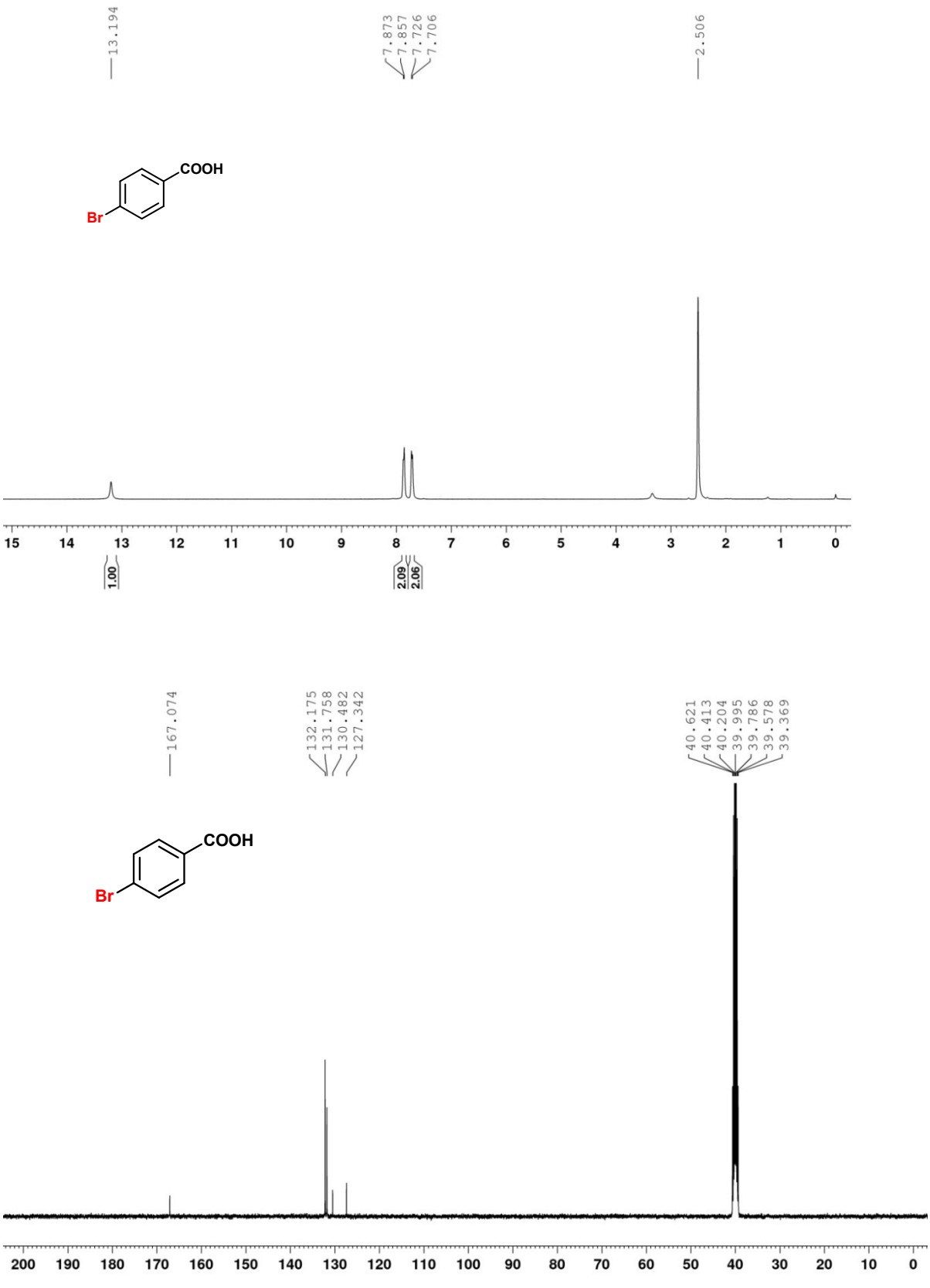


^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1d**

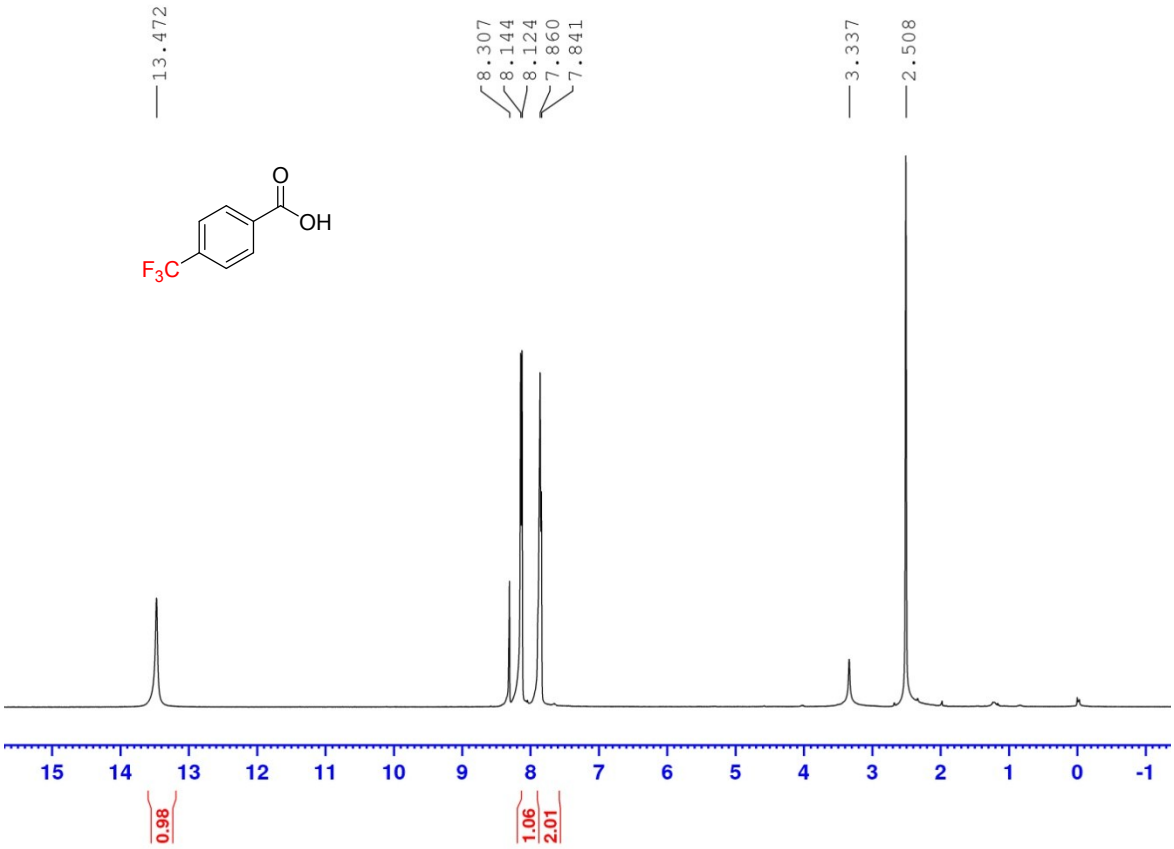


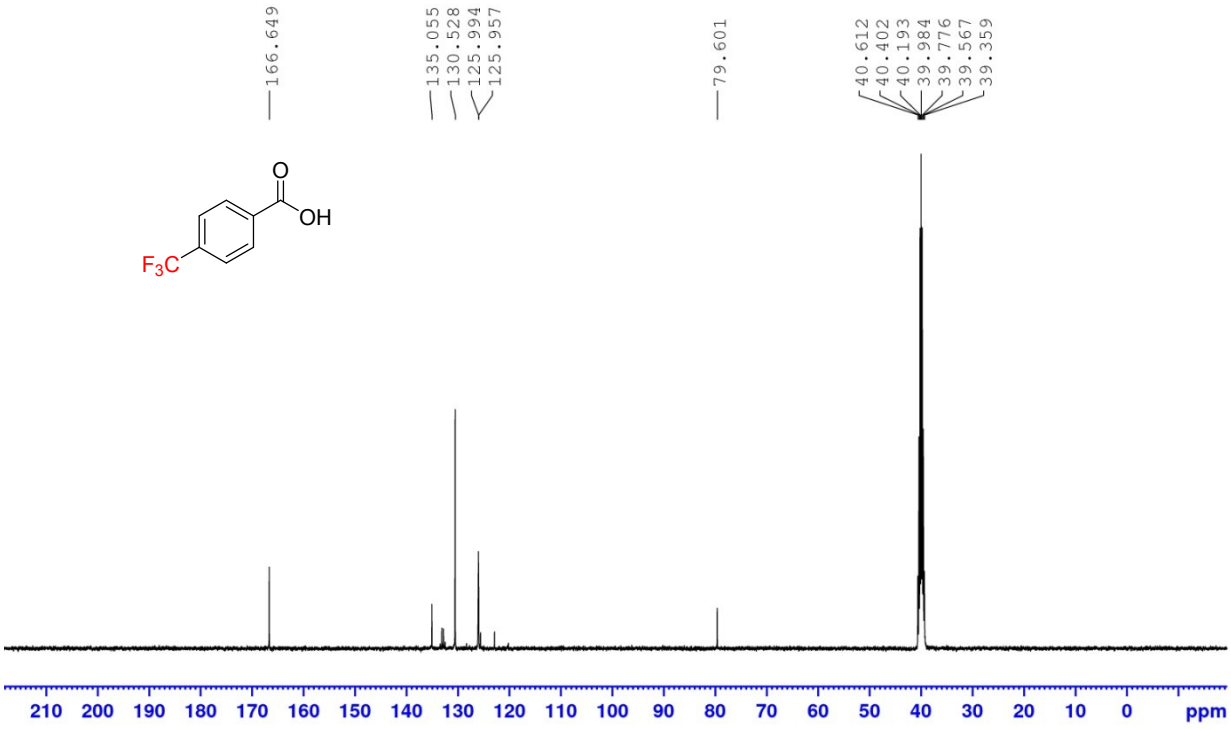


^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1e**

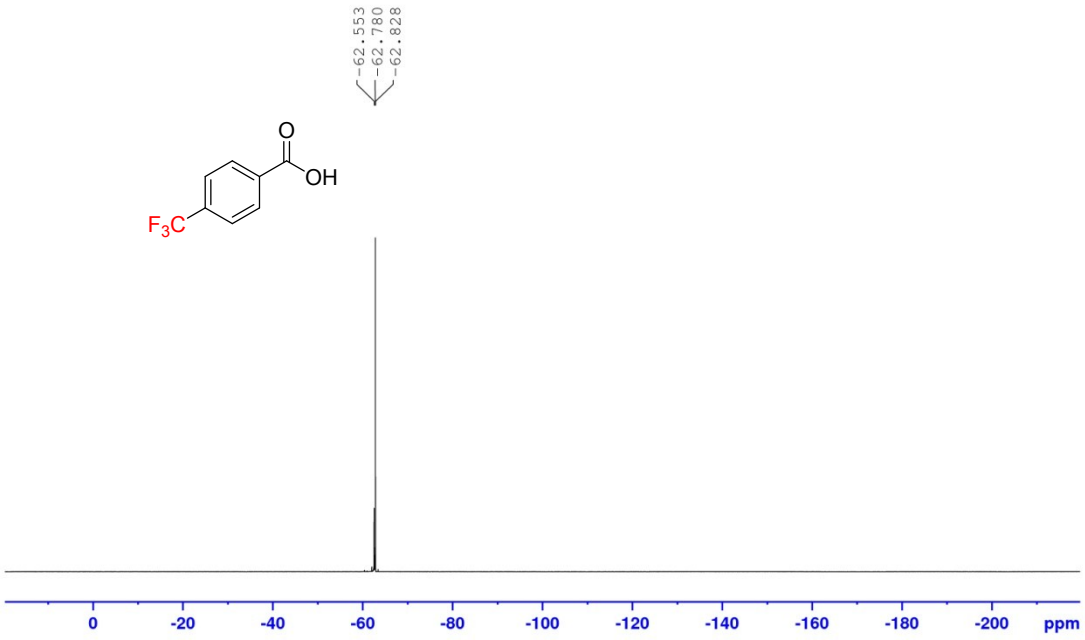


^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1f**

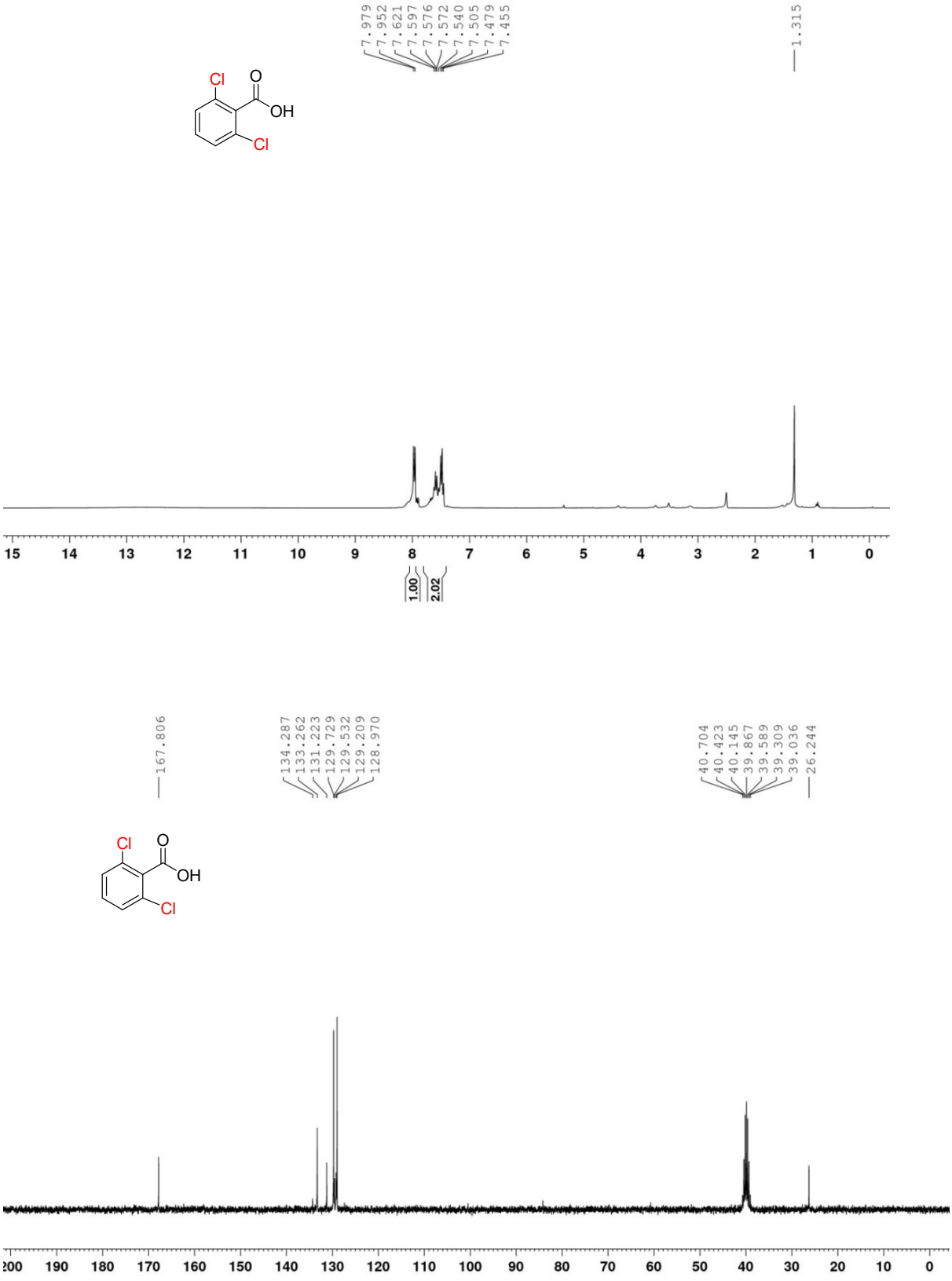




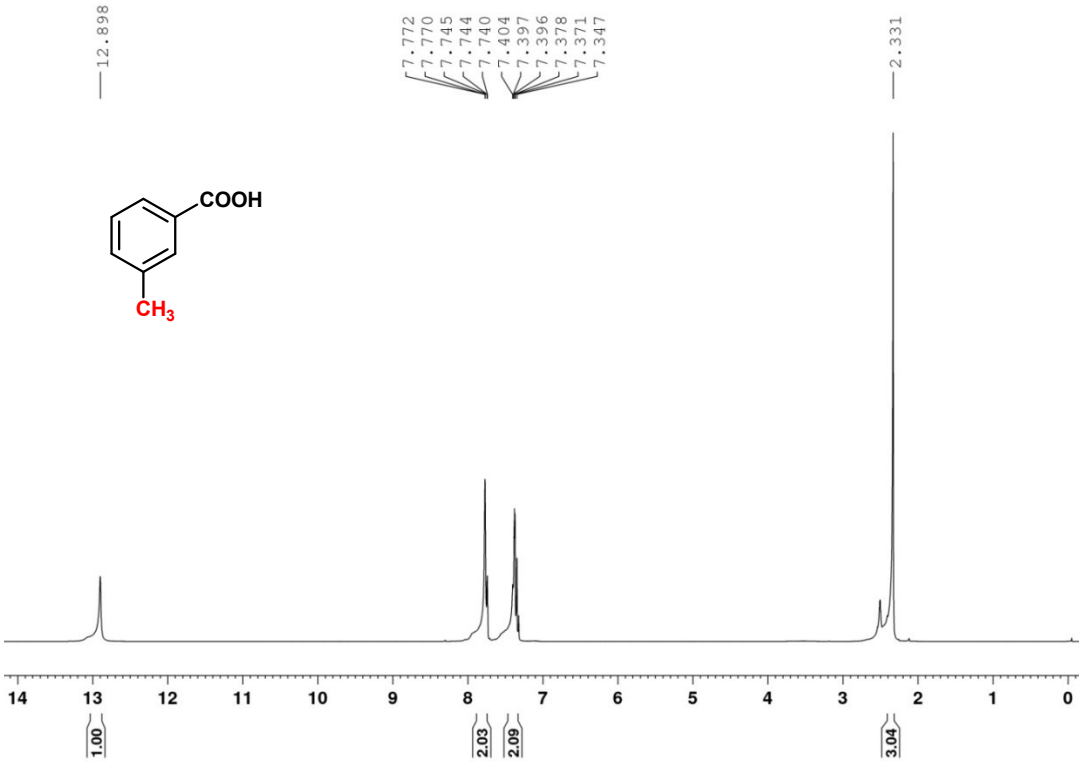
^{19}F NMR (in DMSO-d_6) spectra of compound **1f**

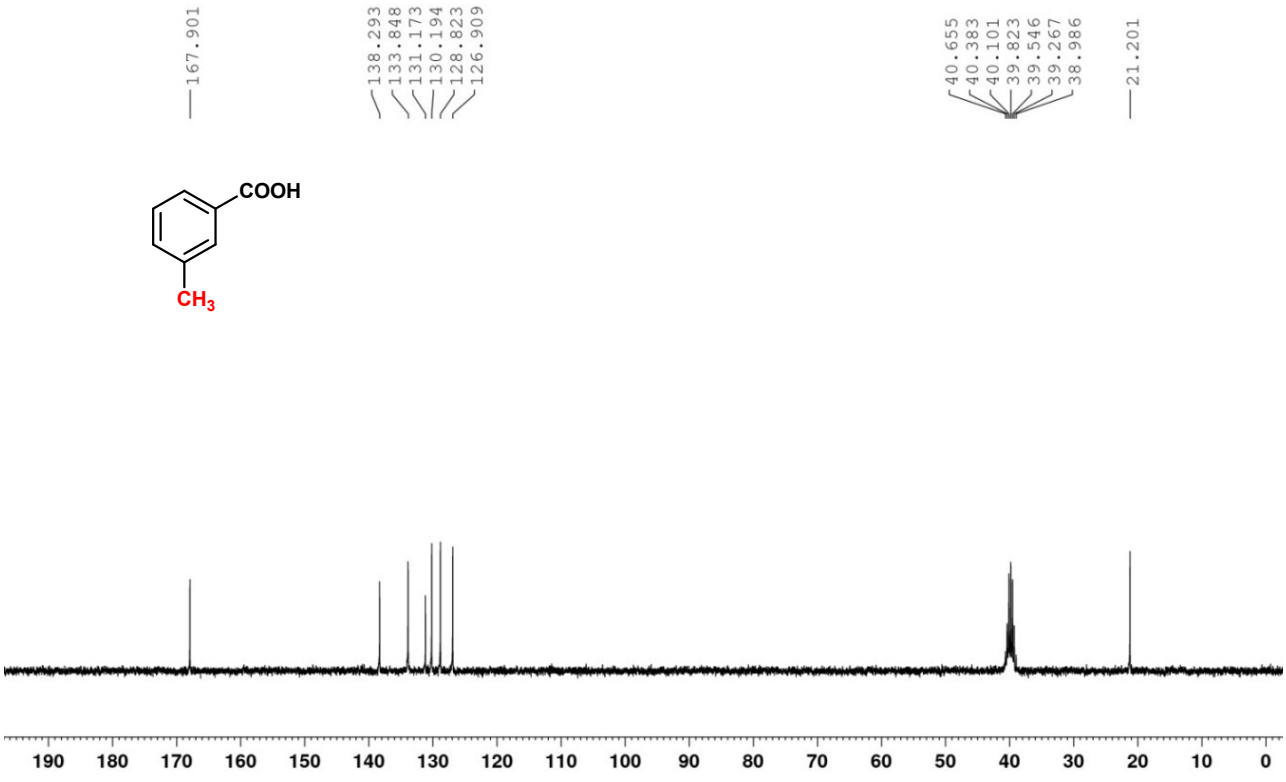


^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1g**

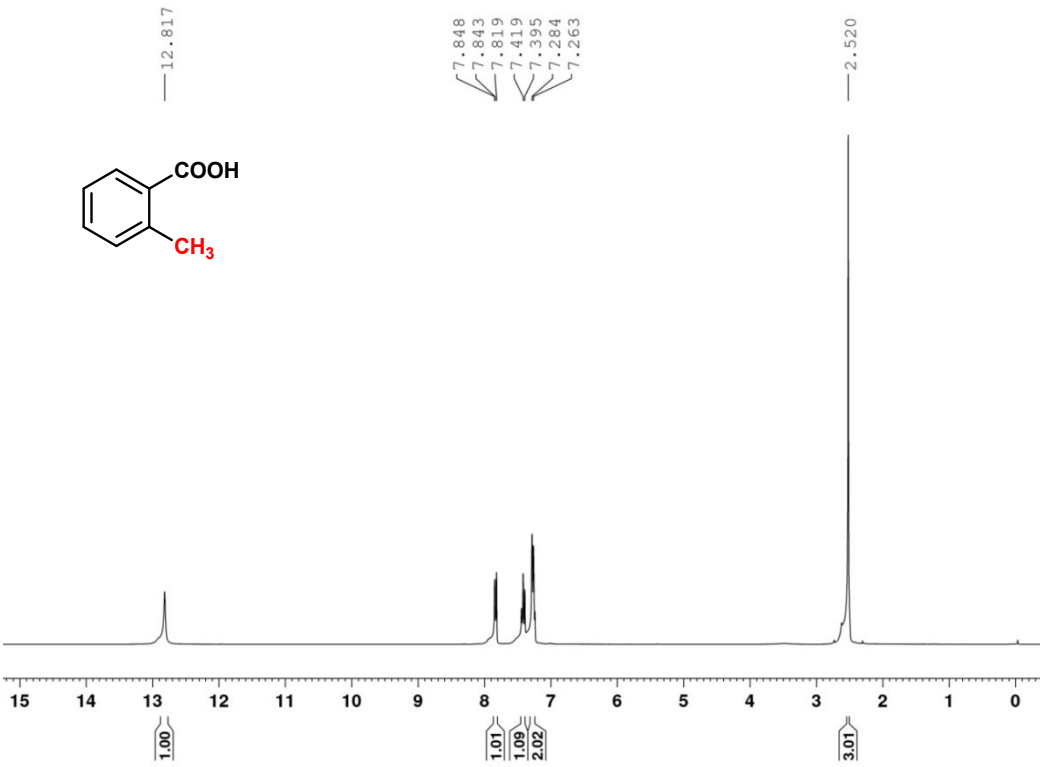


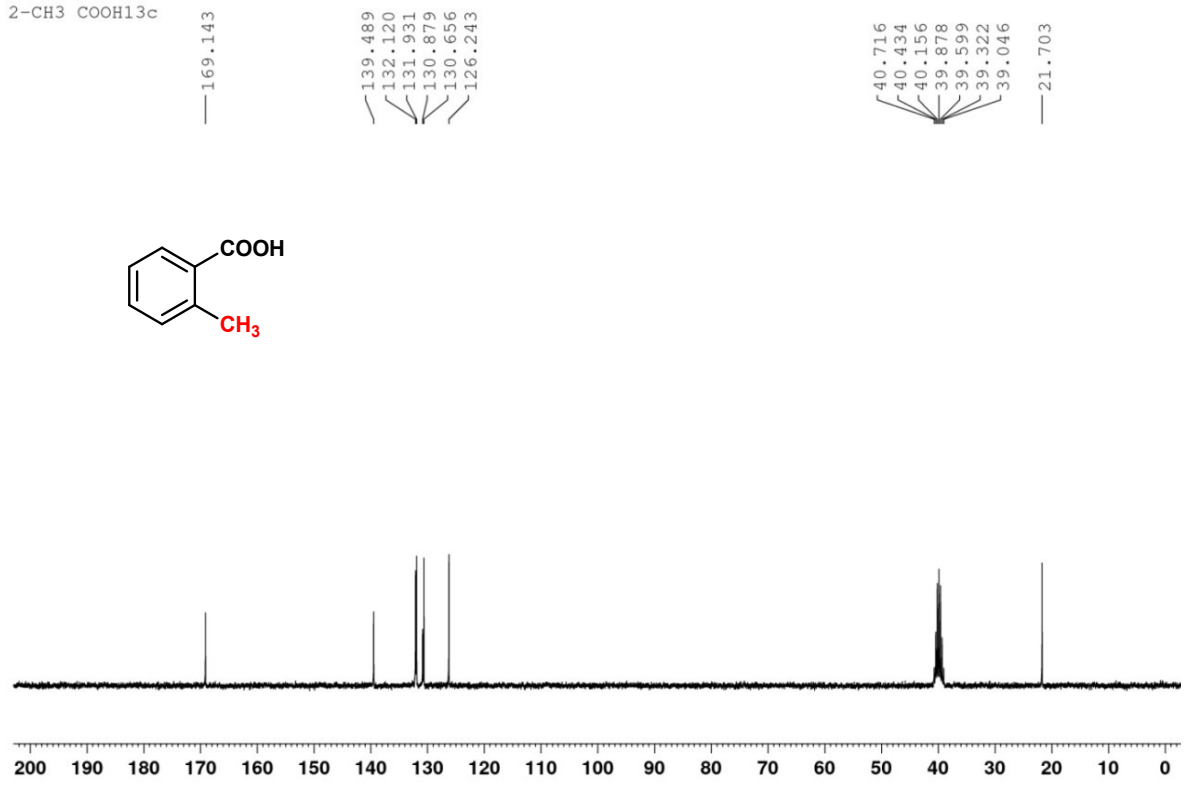
^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1h**



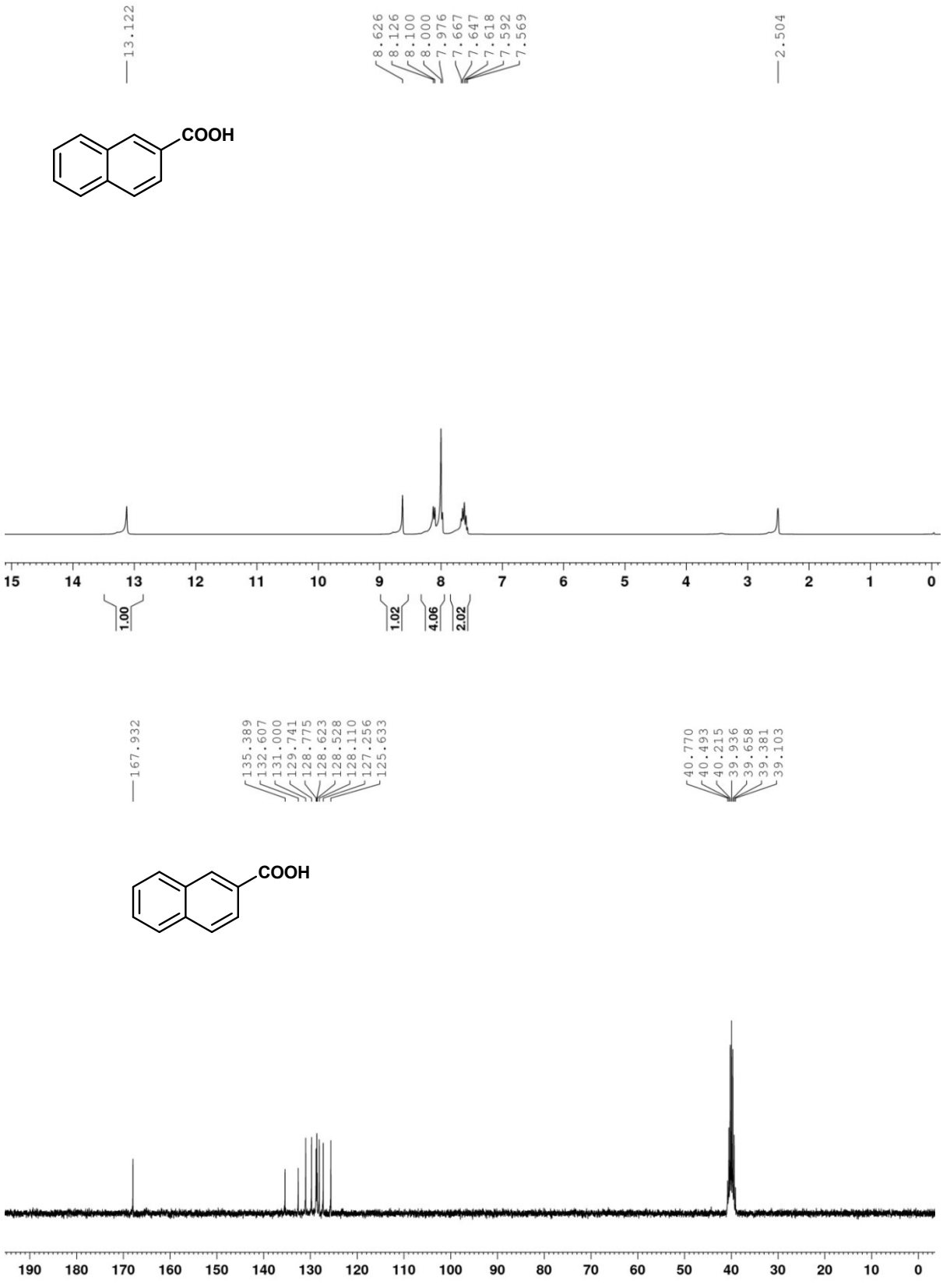


^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1i**

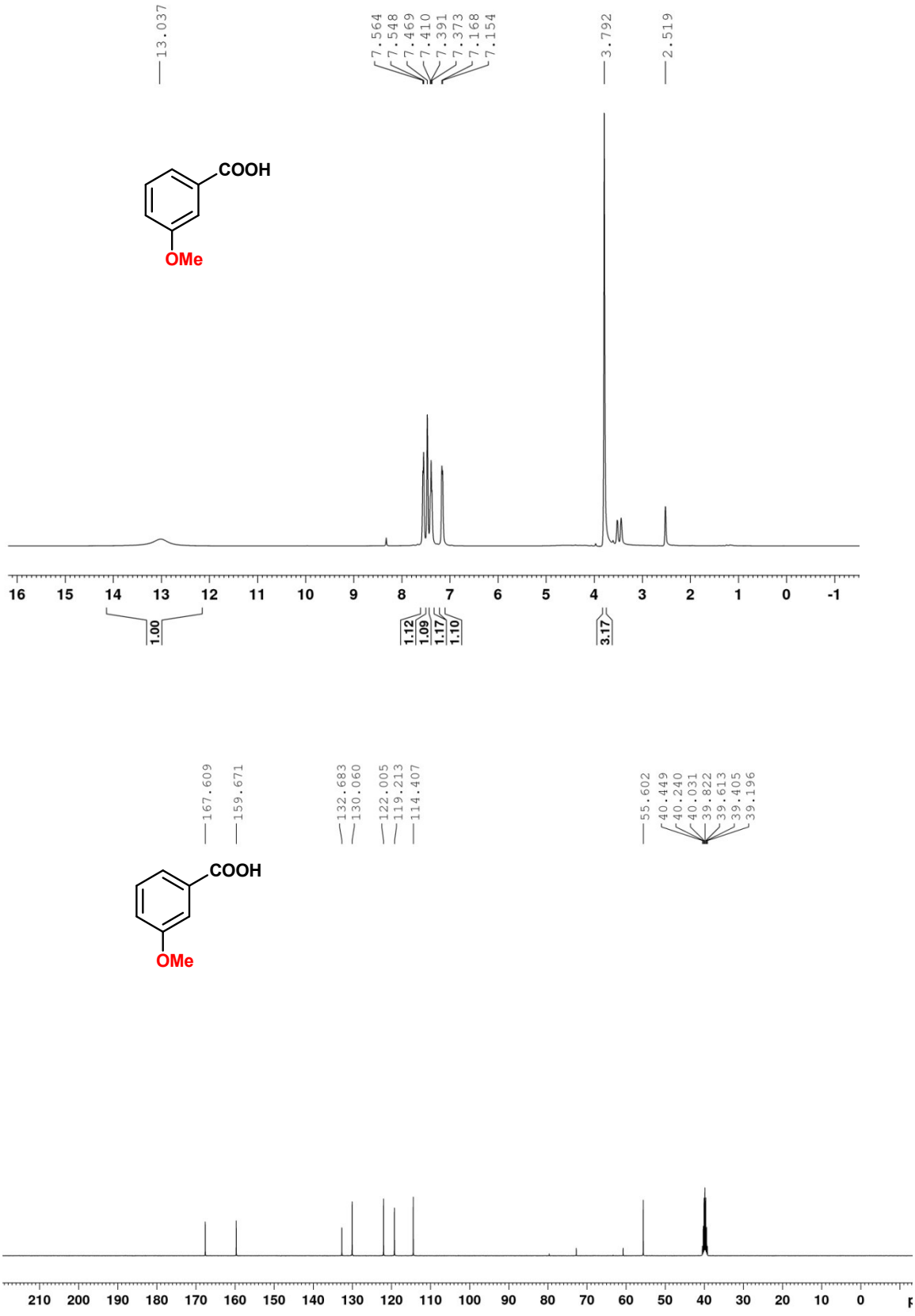




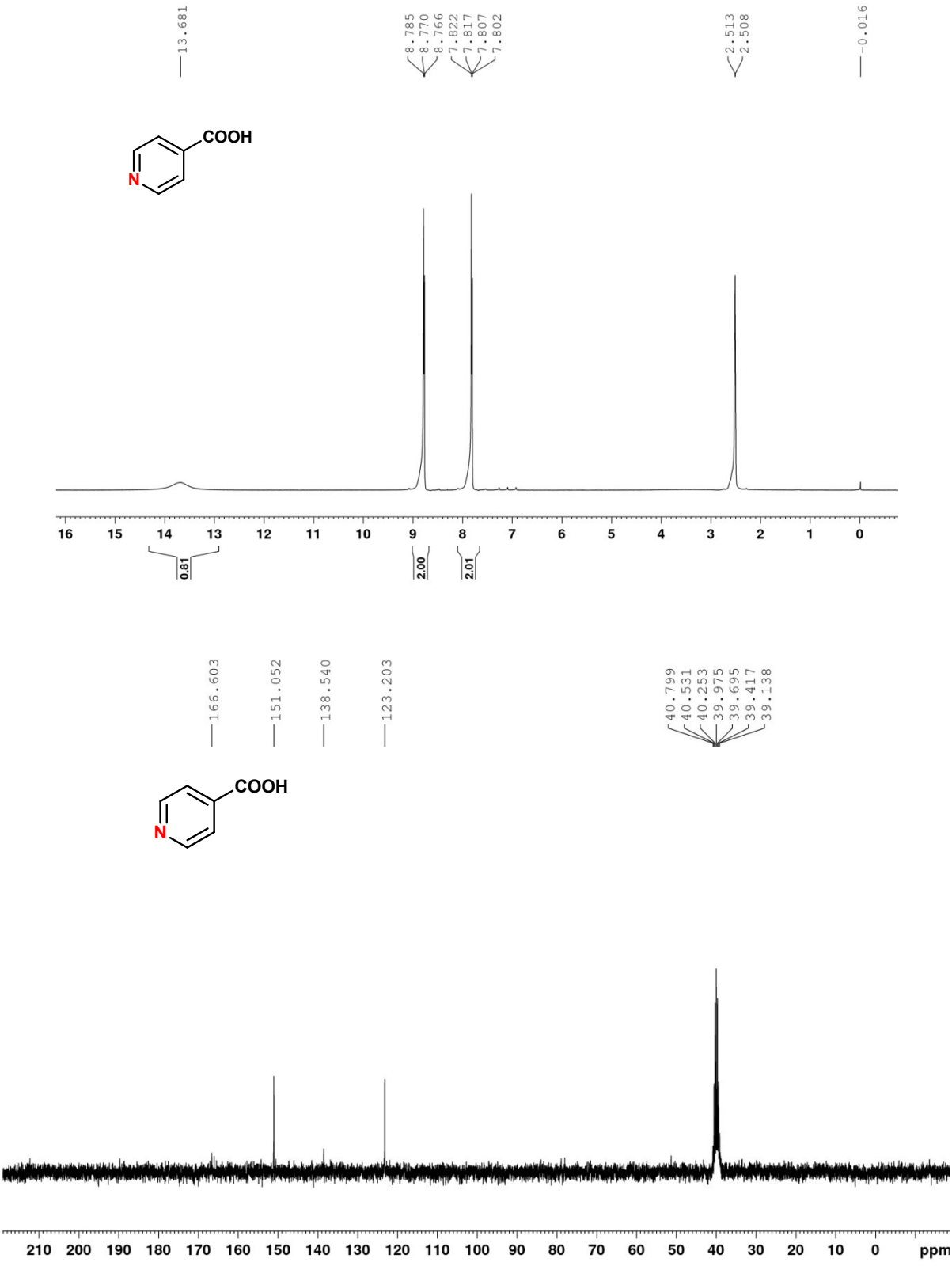
^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1j**



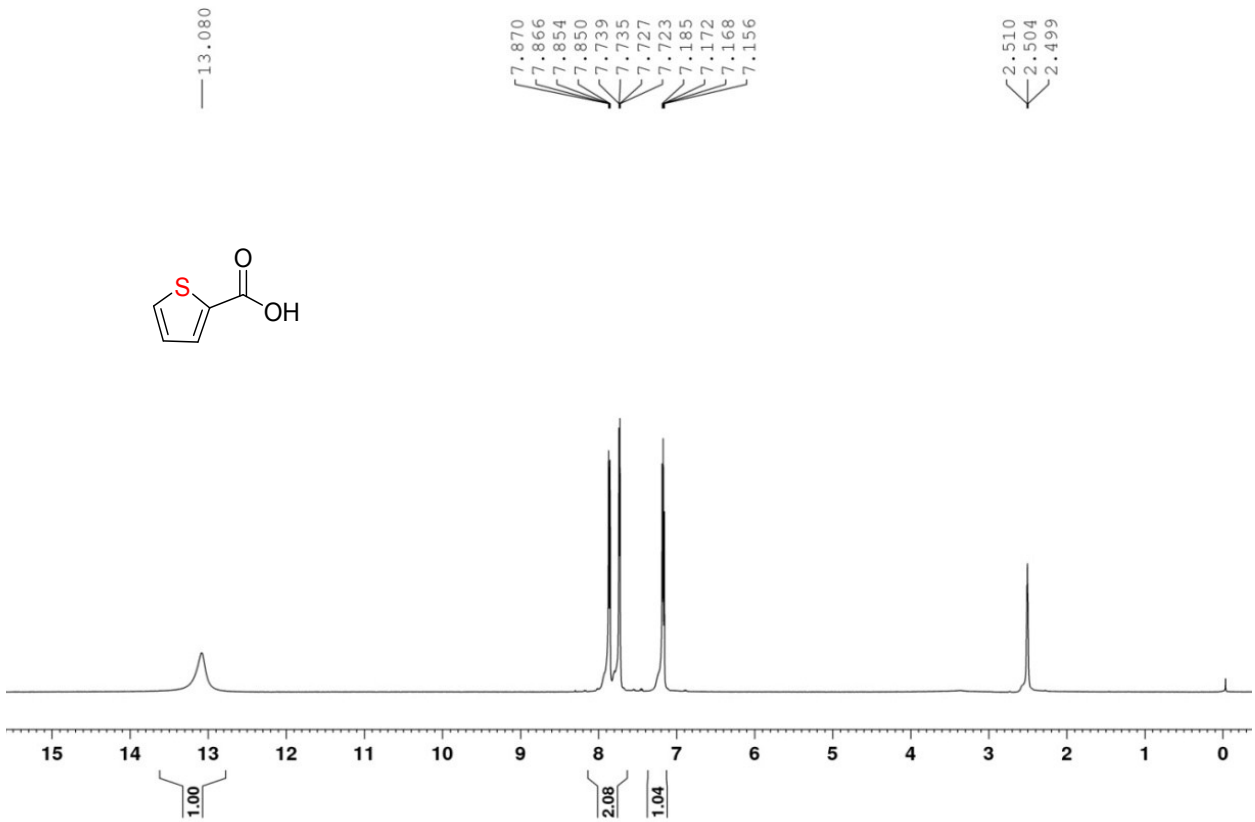
^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1k**

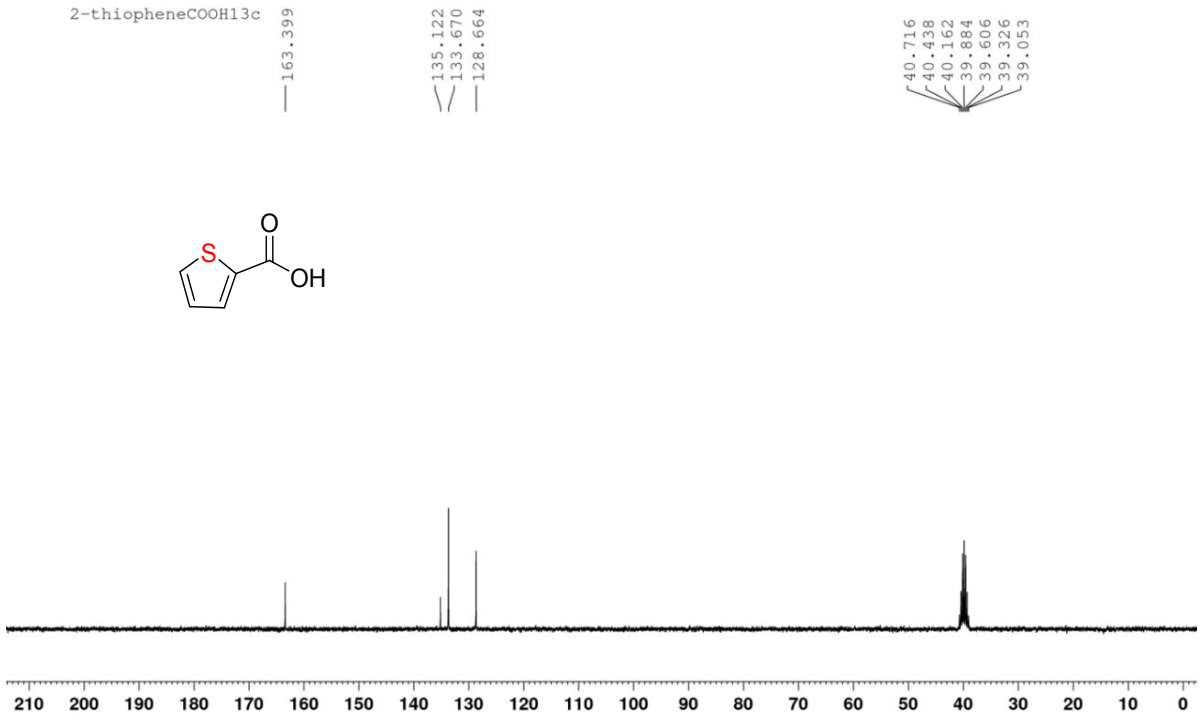


^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1l**

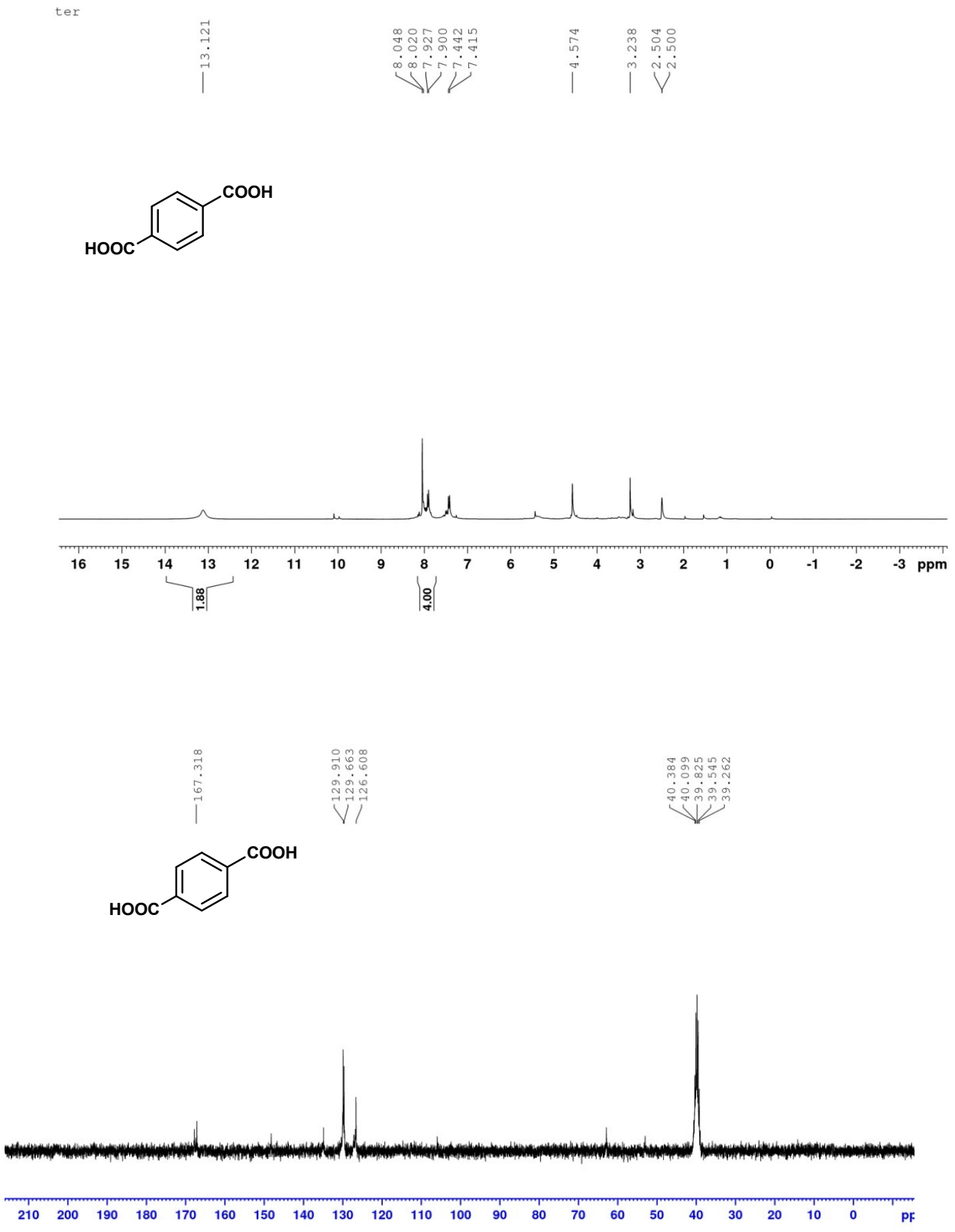


^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d$_6$) spectra of compound **1m**

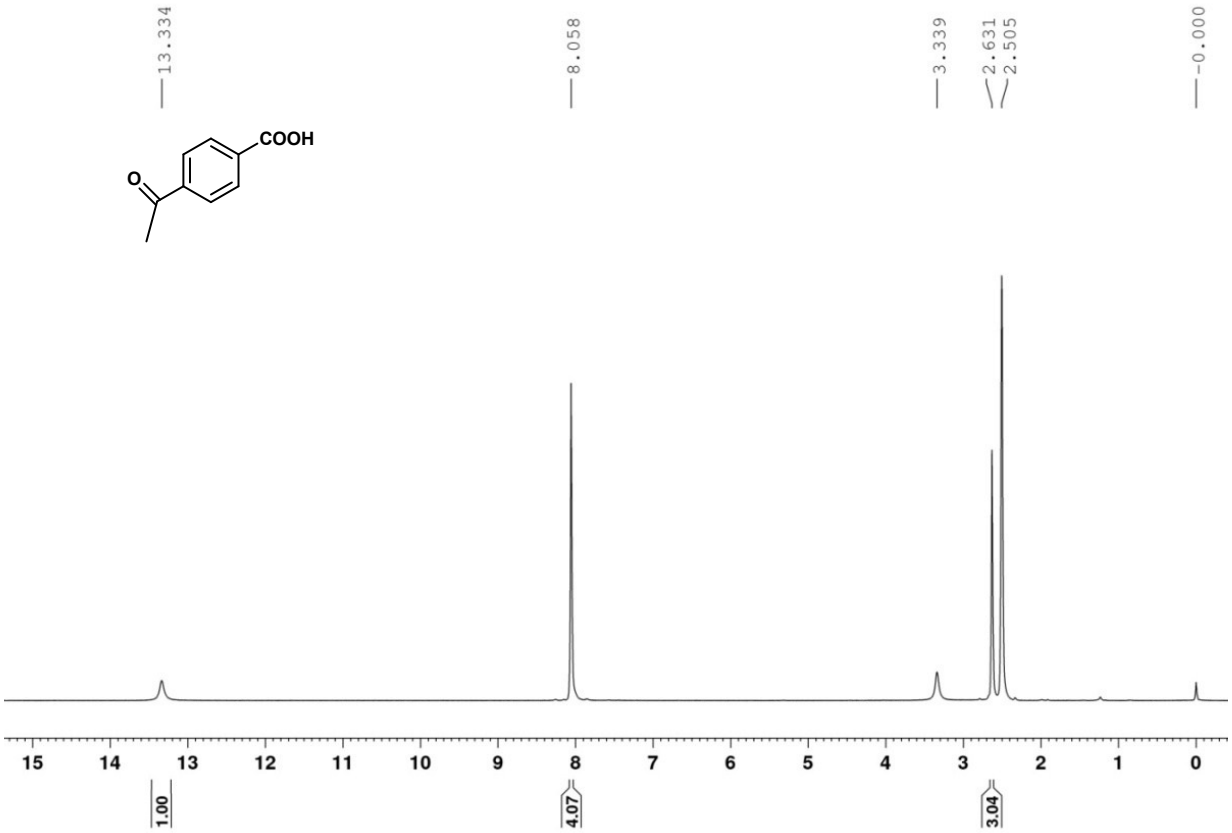


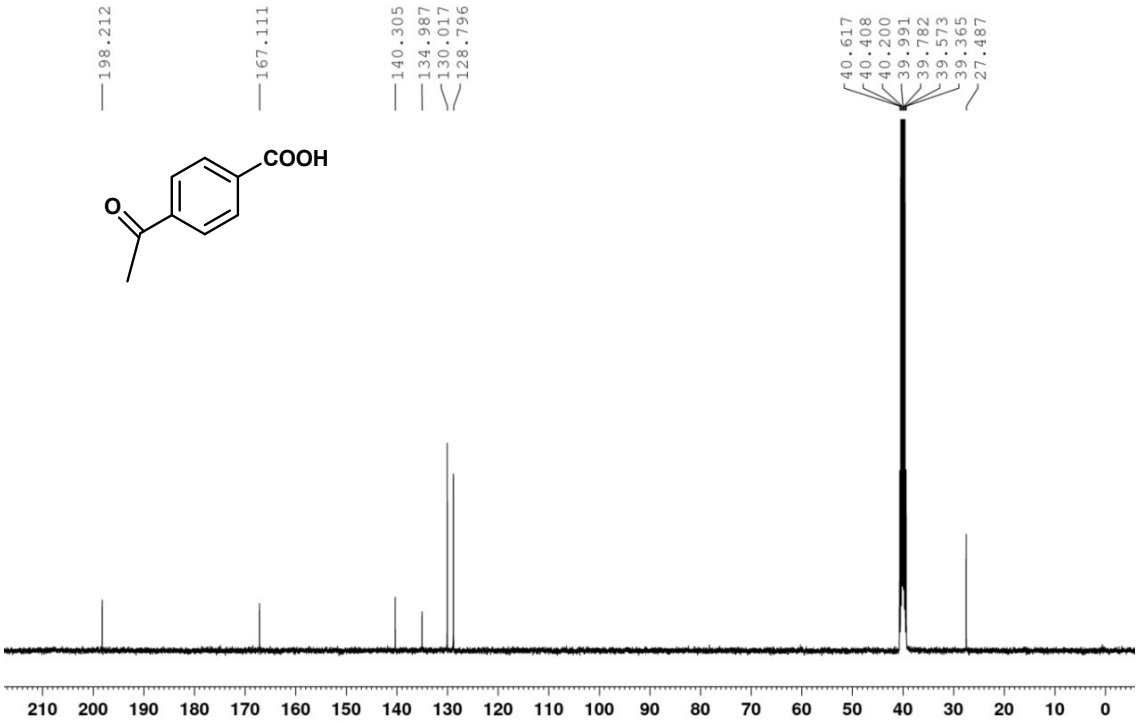


^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1n**

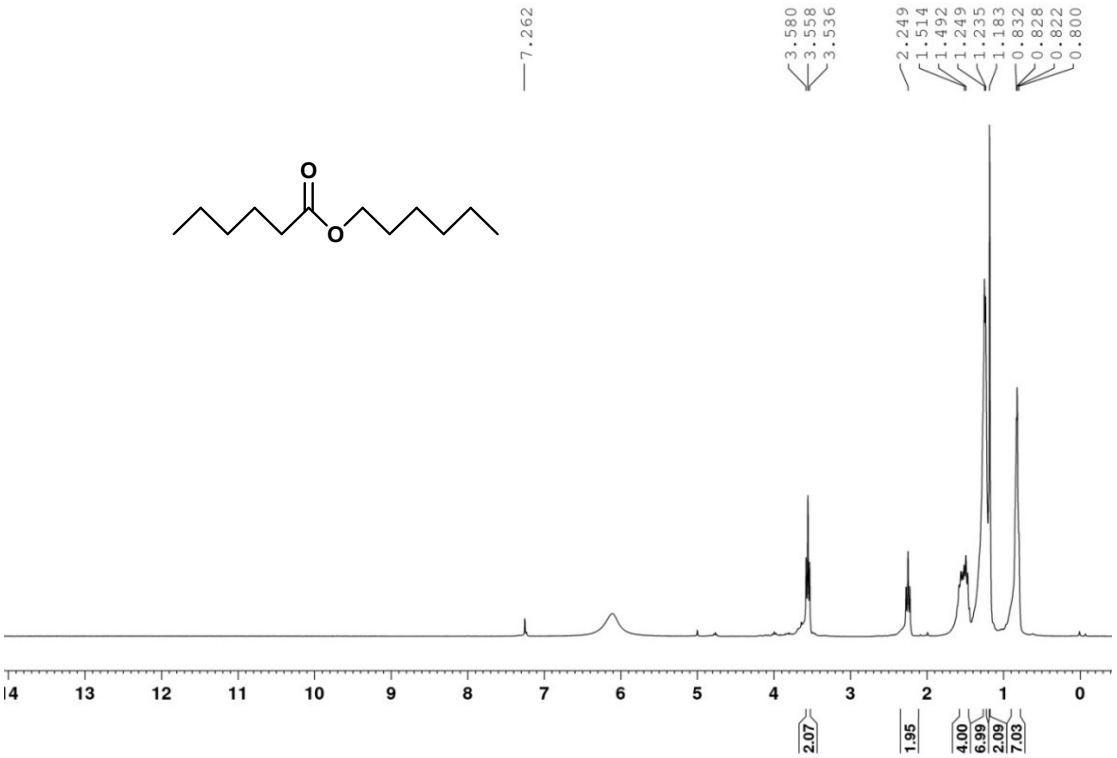


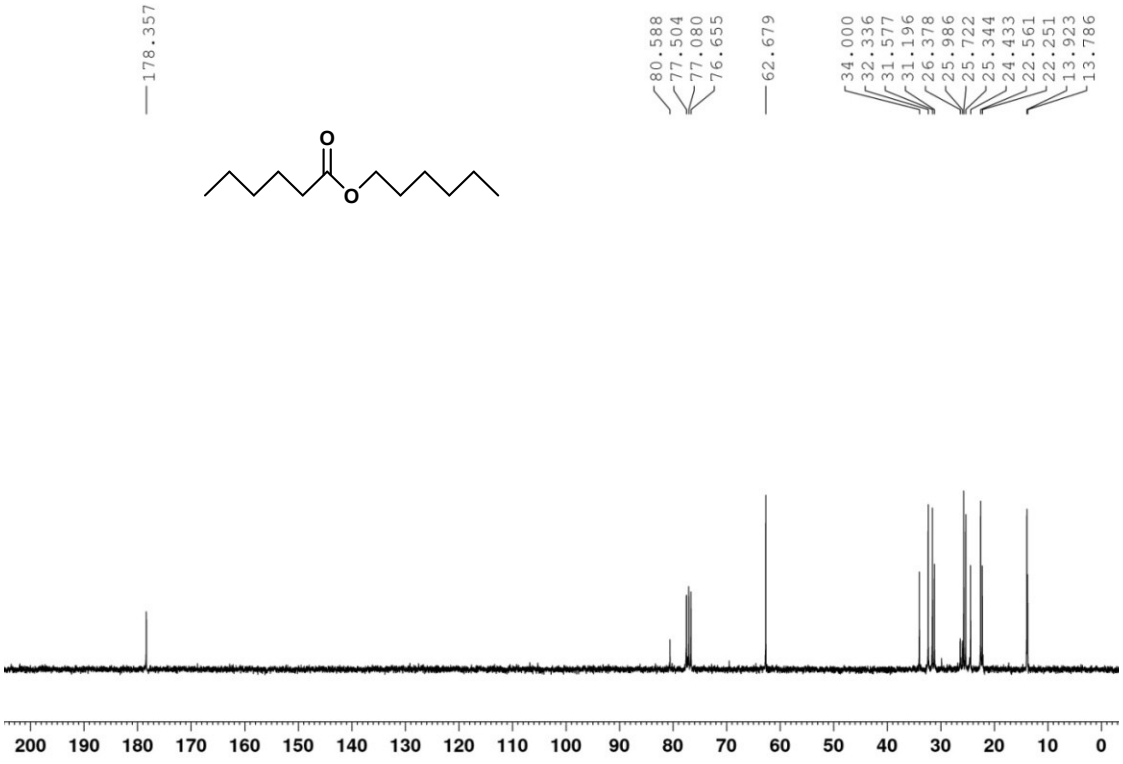
^{1}H-NMR &^{13}C {^{1}H} (in DMSO-d_6) spectra of compound **1o**



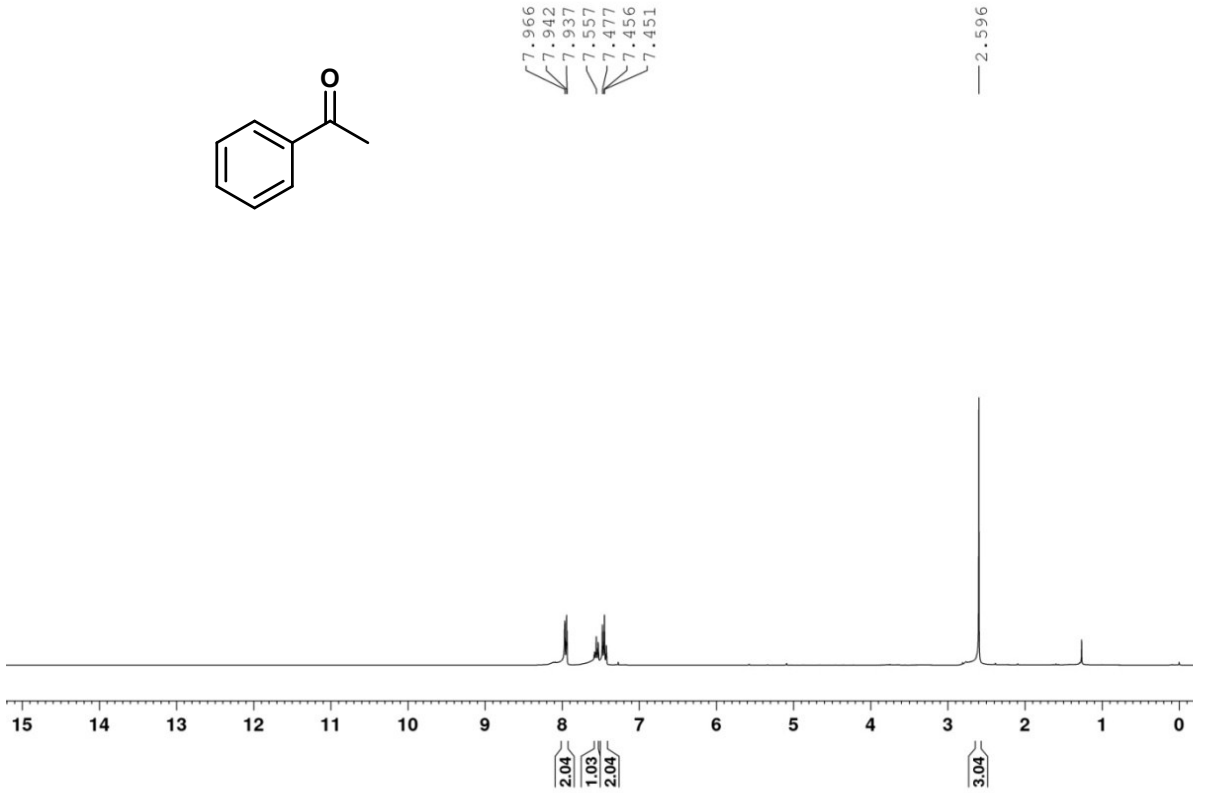


^{1}H-NMR &^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1p**

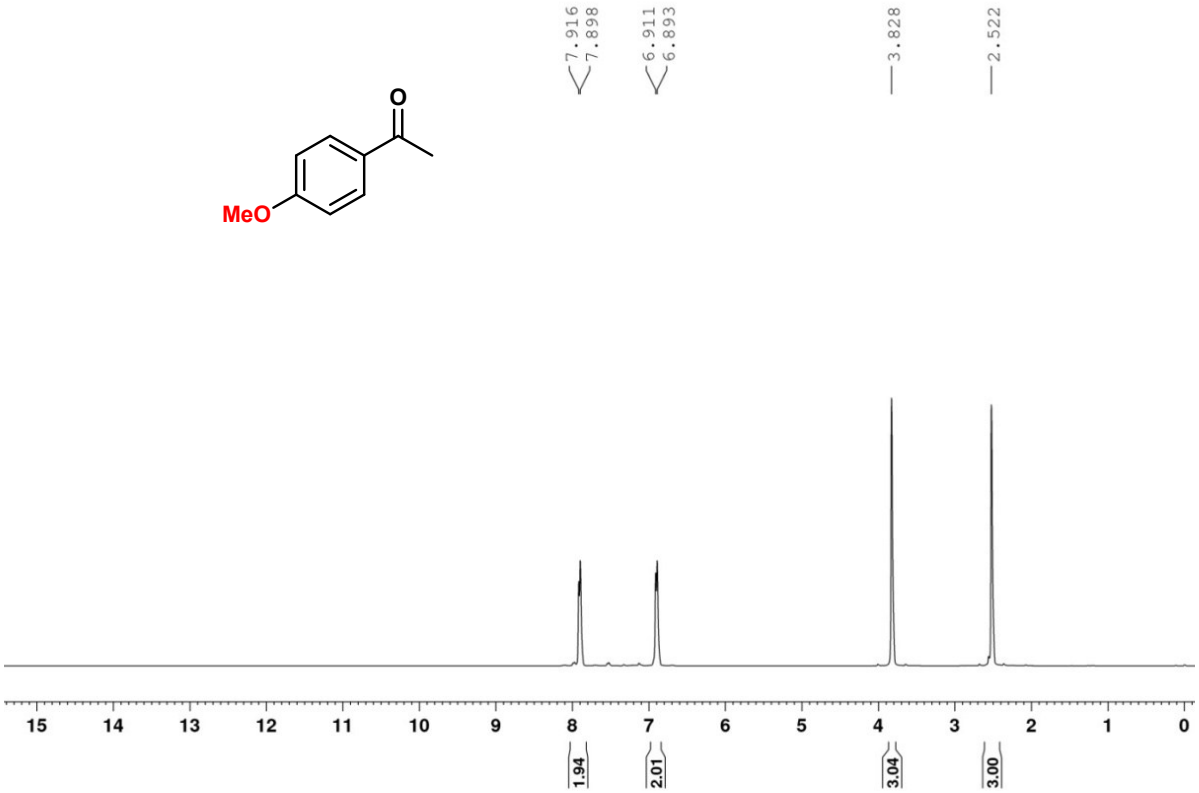


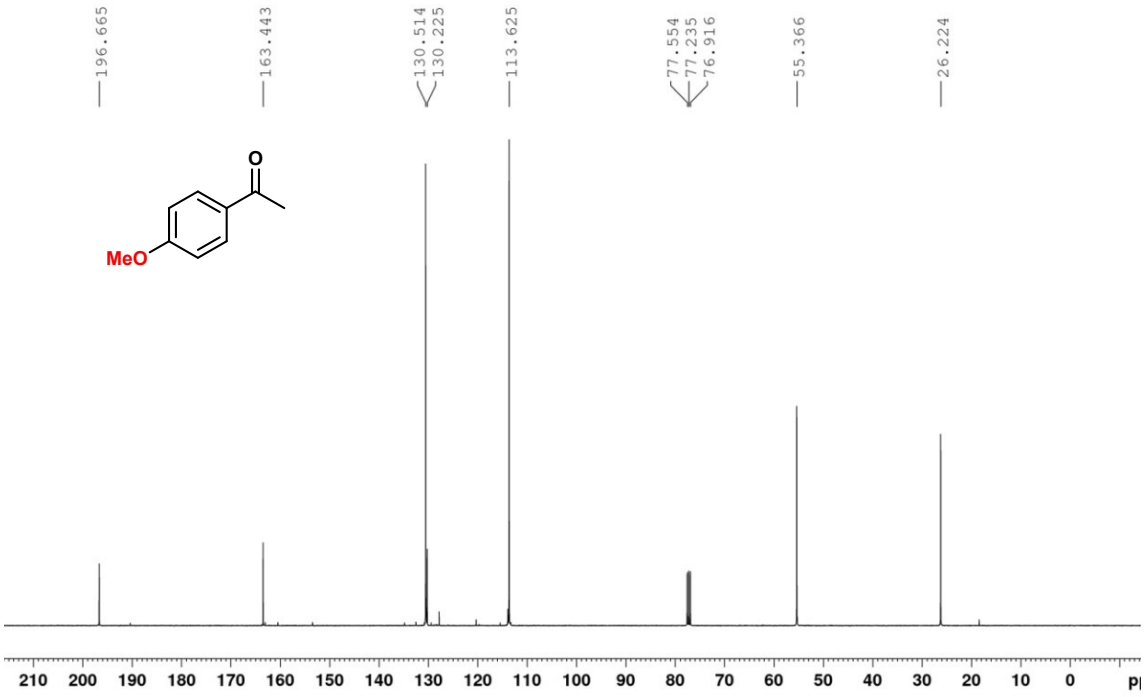


^{1}H-NMR &^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1q**

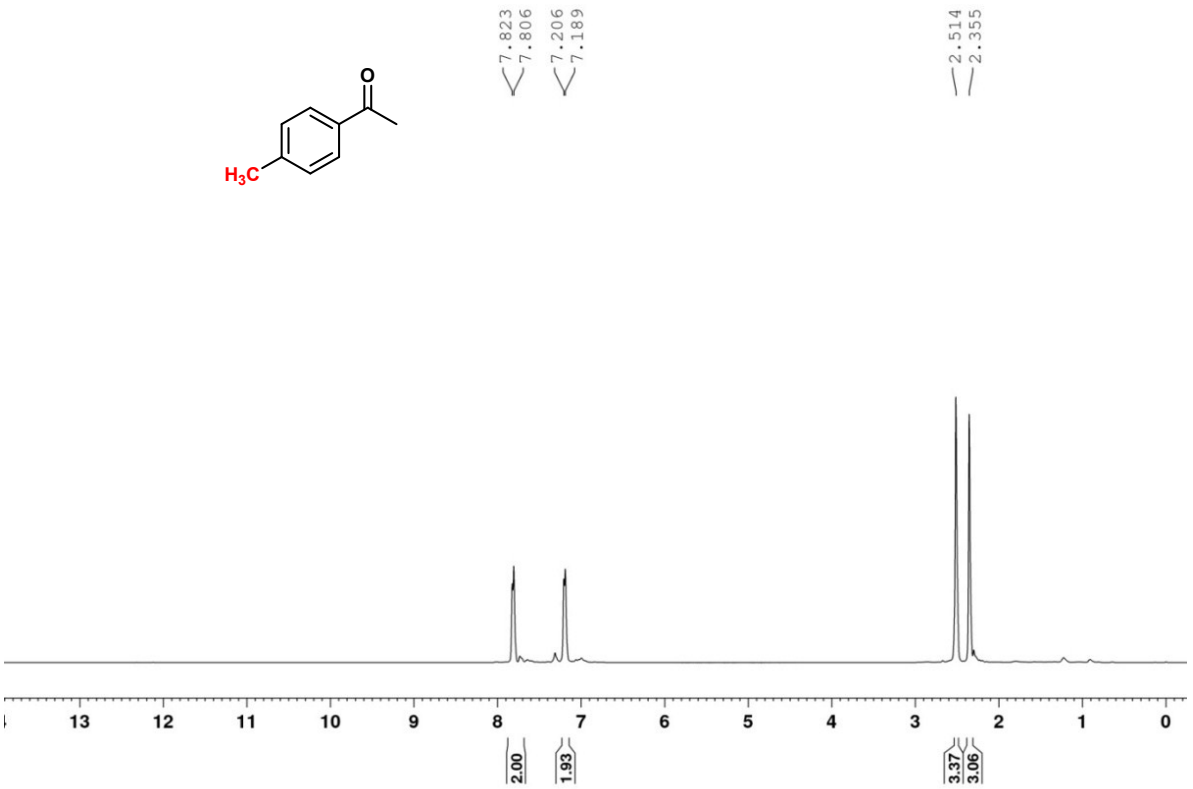


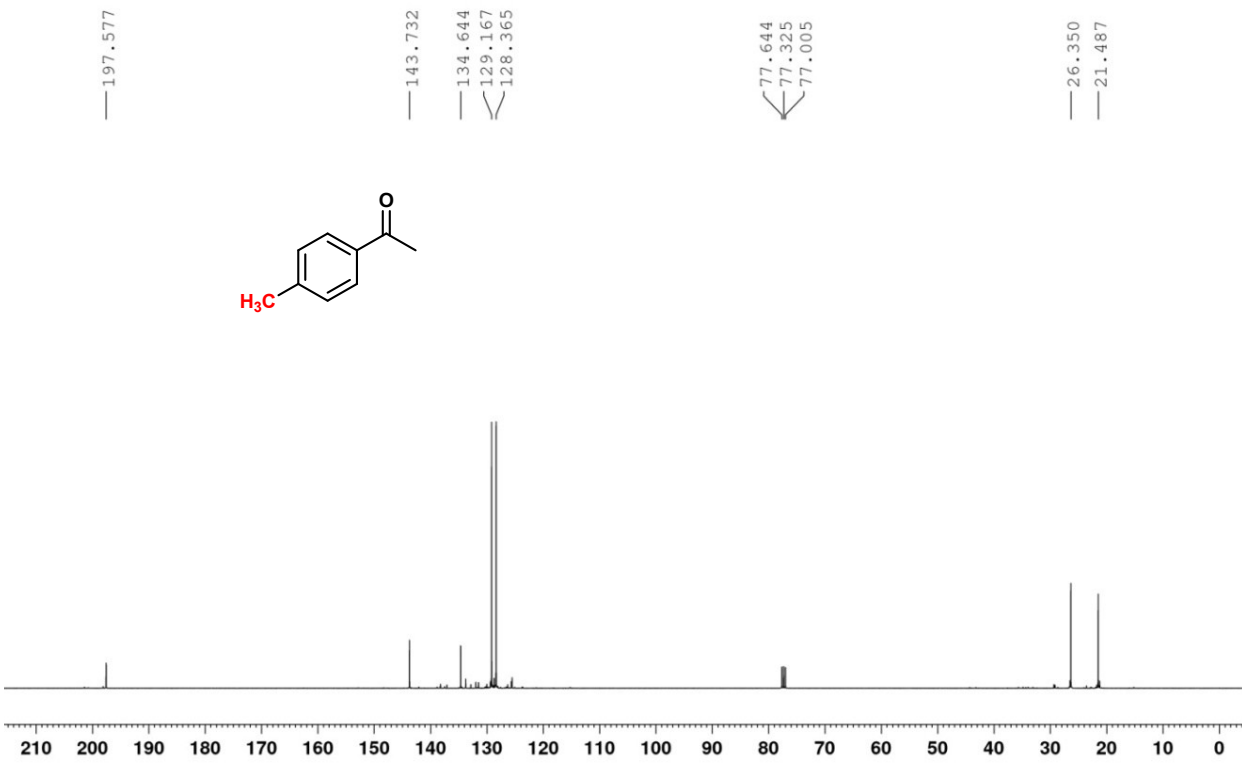
^{1}H-NMR &^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1r**



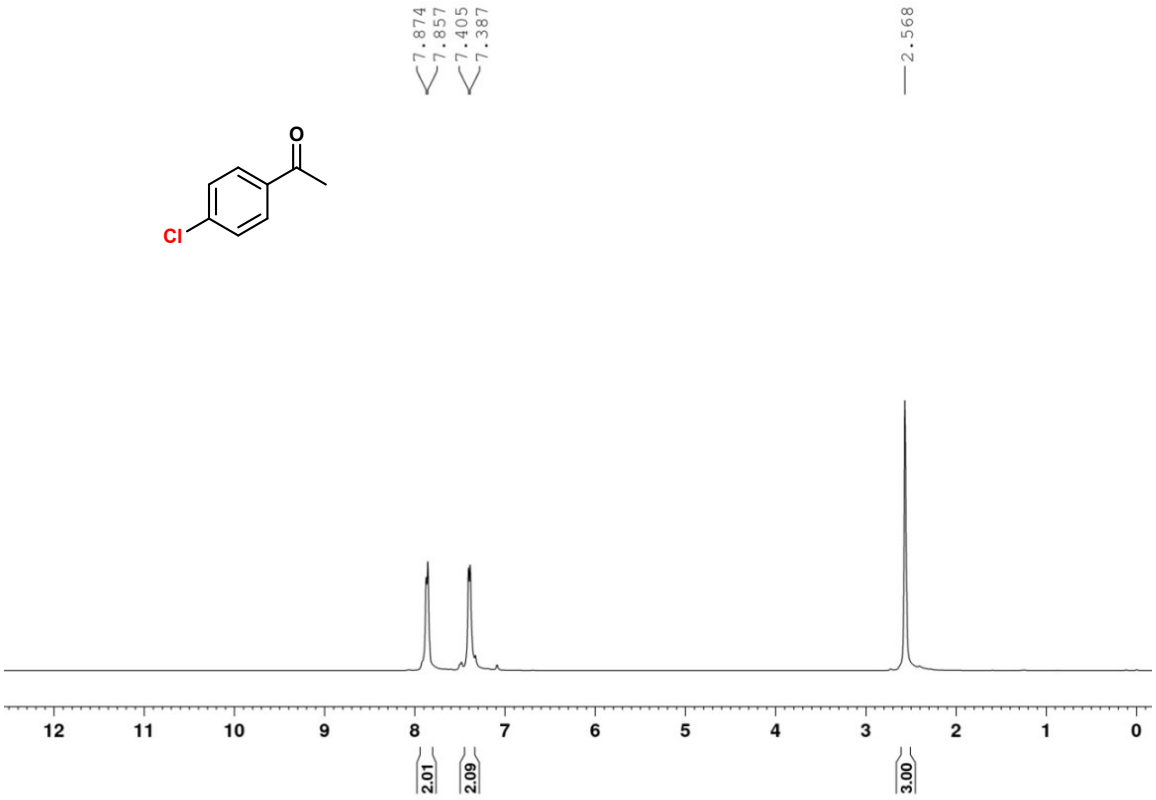


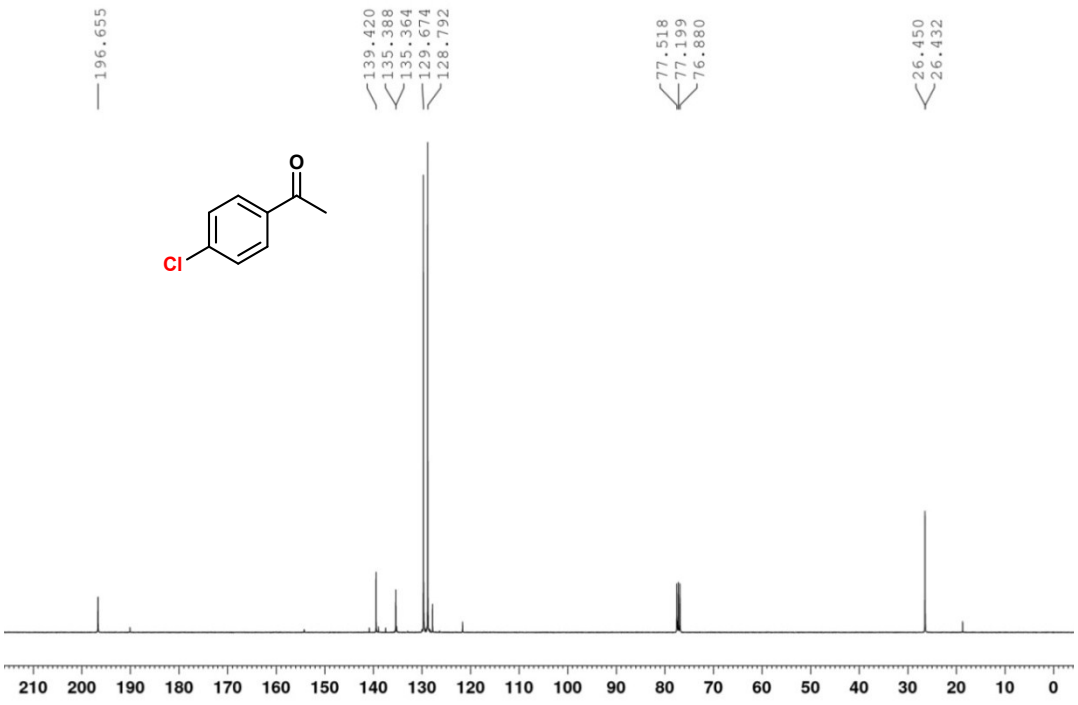
^{1}H-NMR &^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1s**



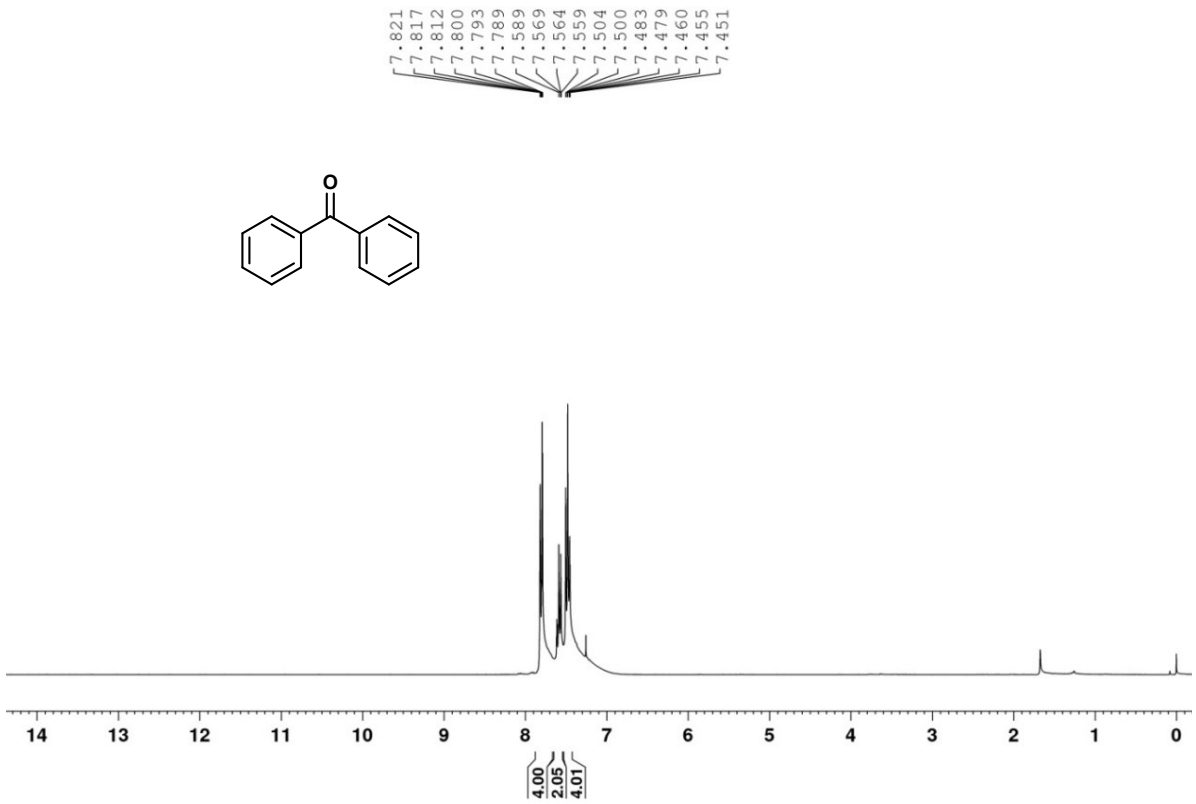


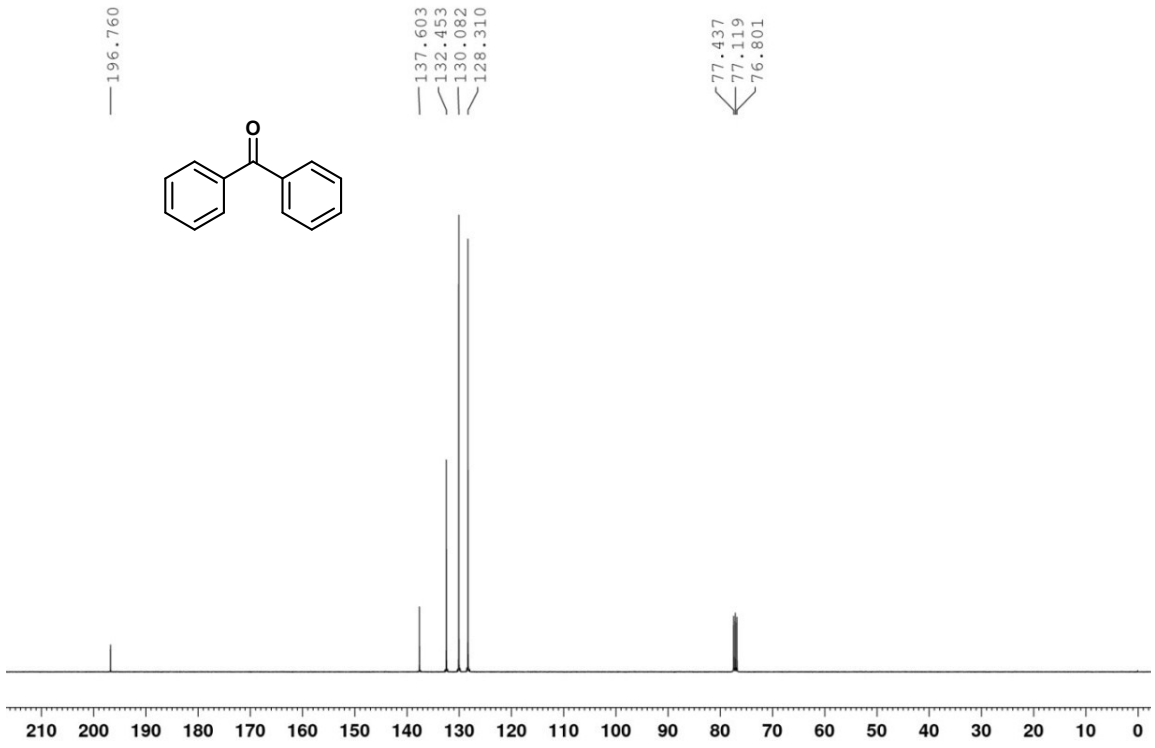
^{1}H-NMR &^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1t**



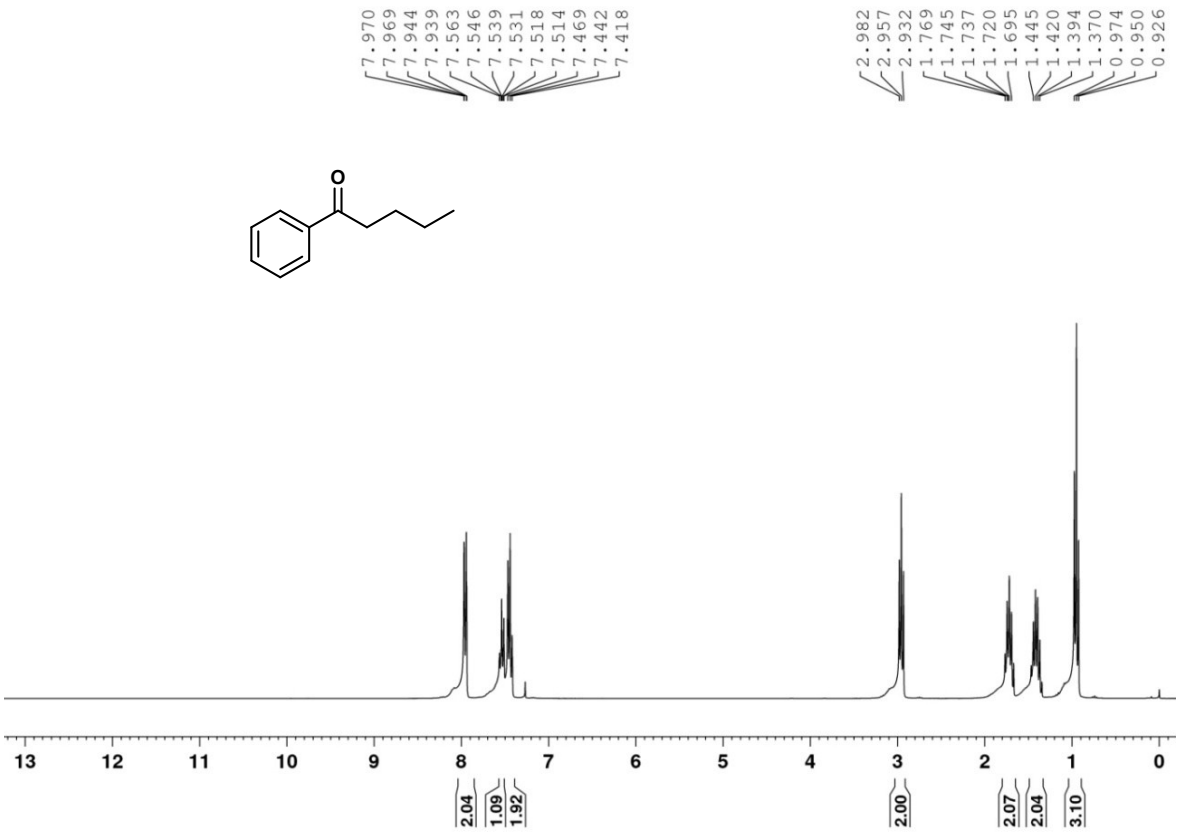


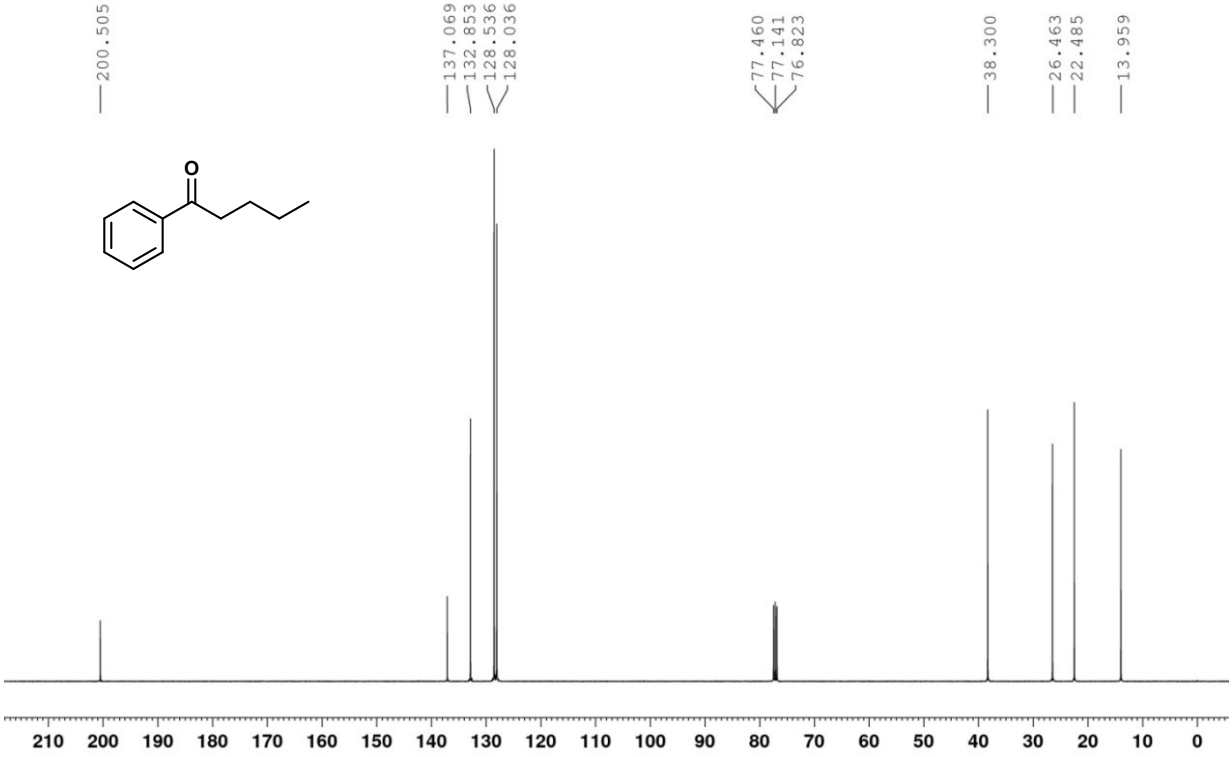
^{1}H-NMR &^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1u**



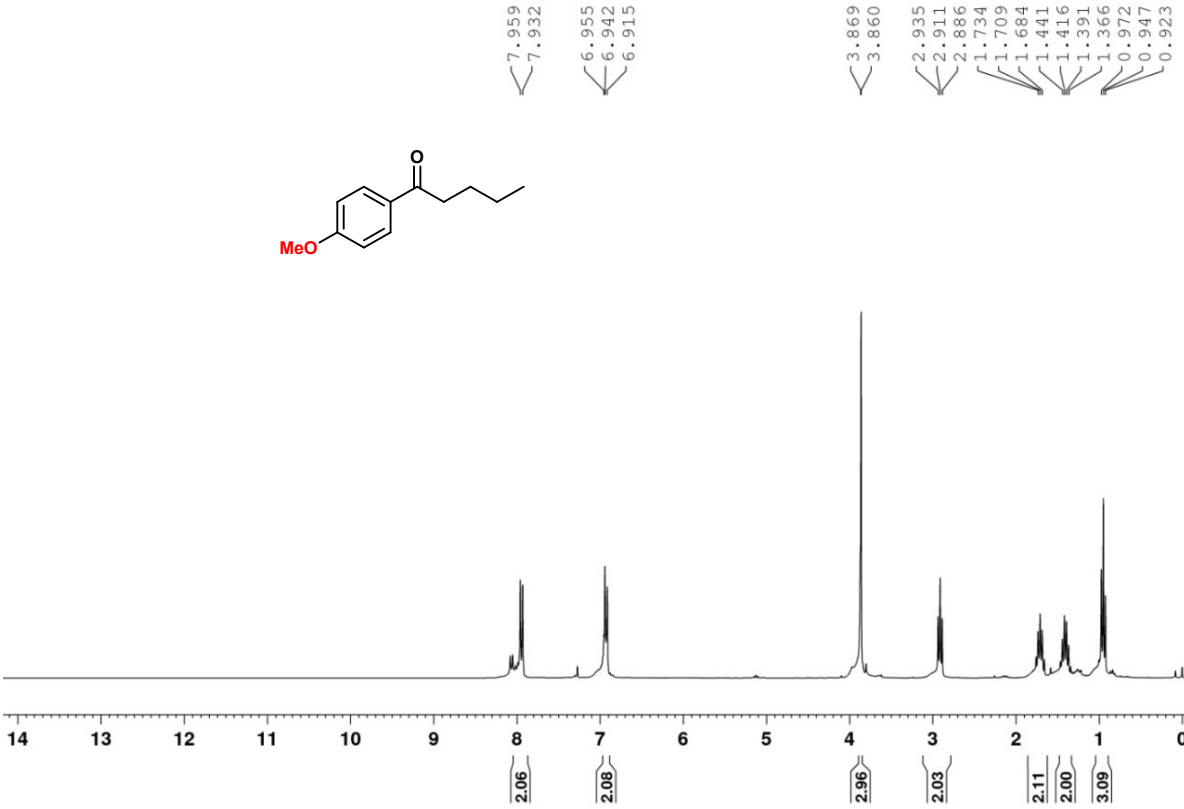


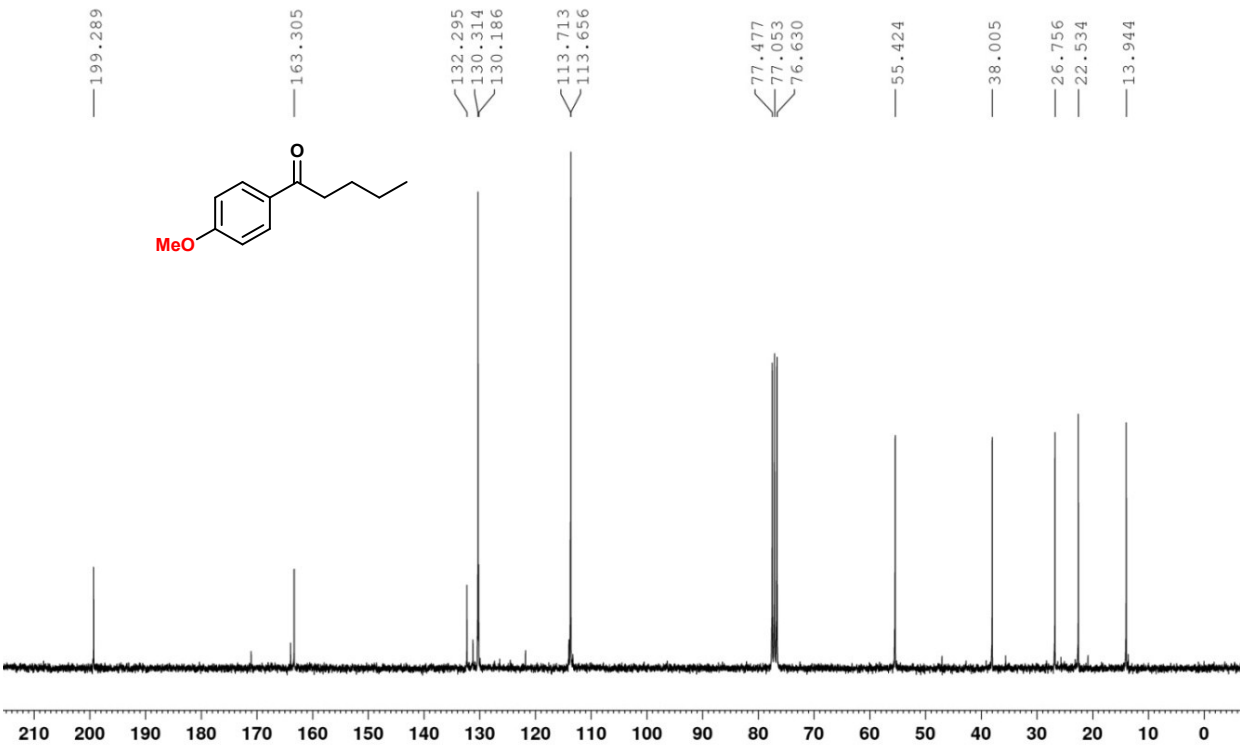
^{1}H-NMR &^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1v**



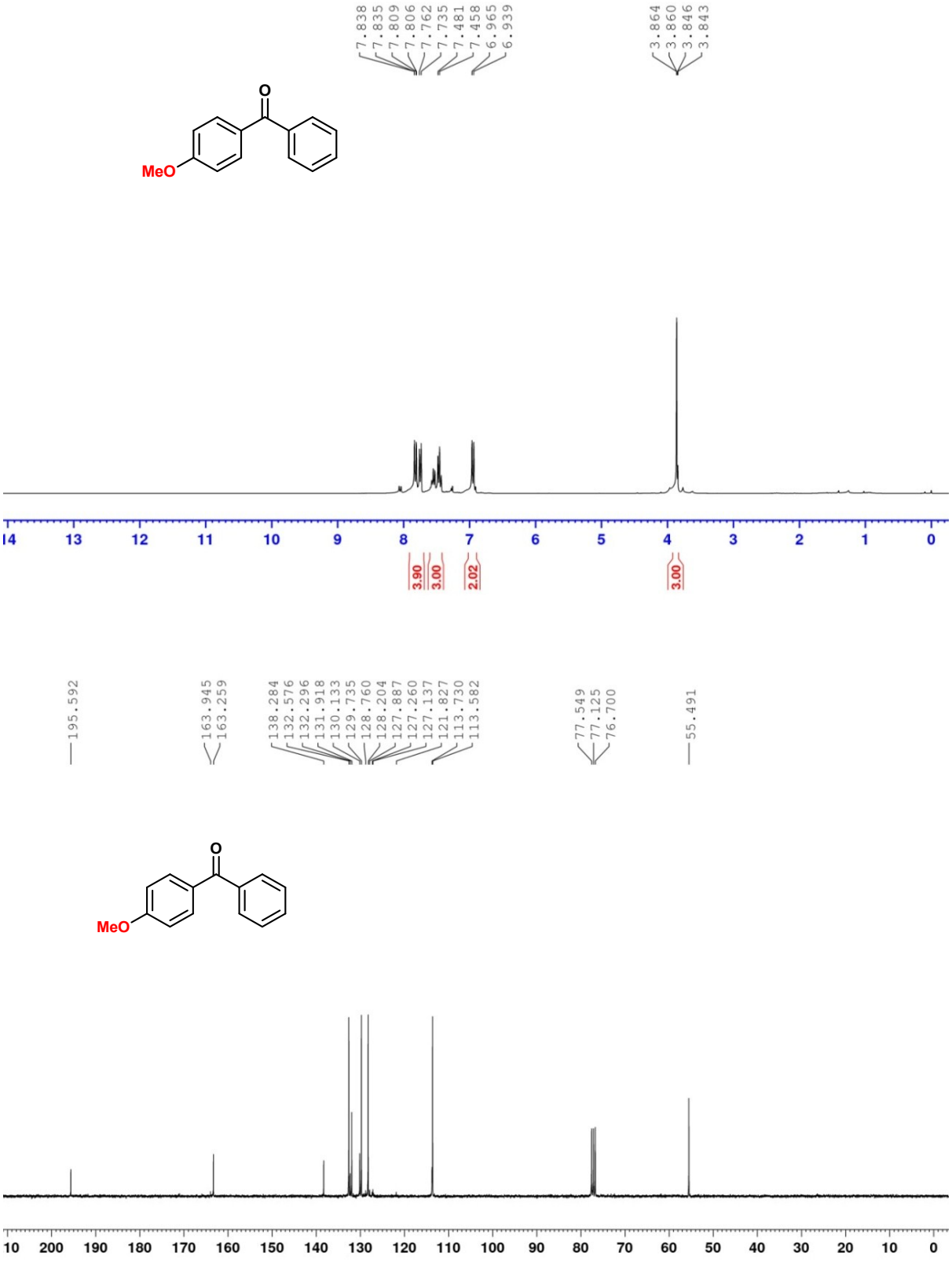


^{1}H-NMR &^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1w**

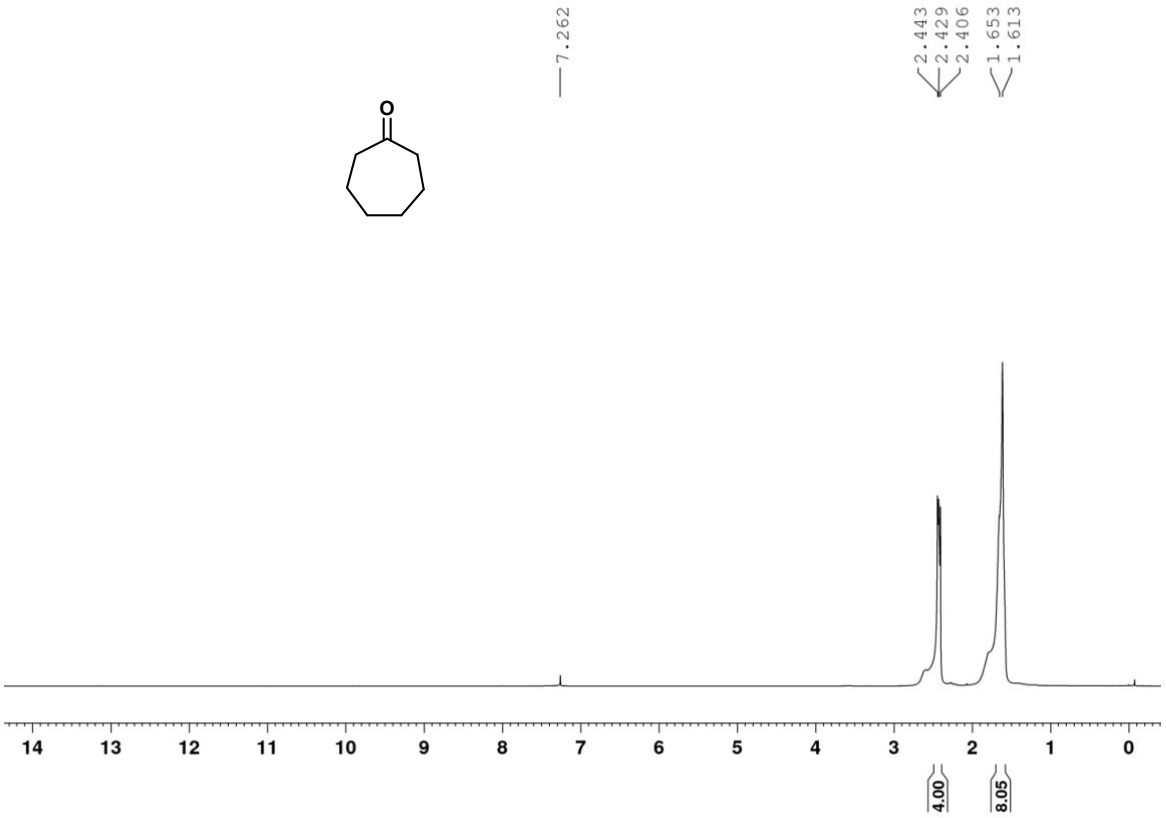


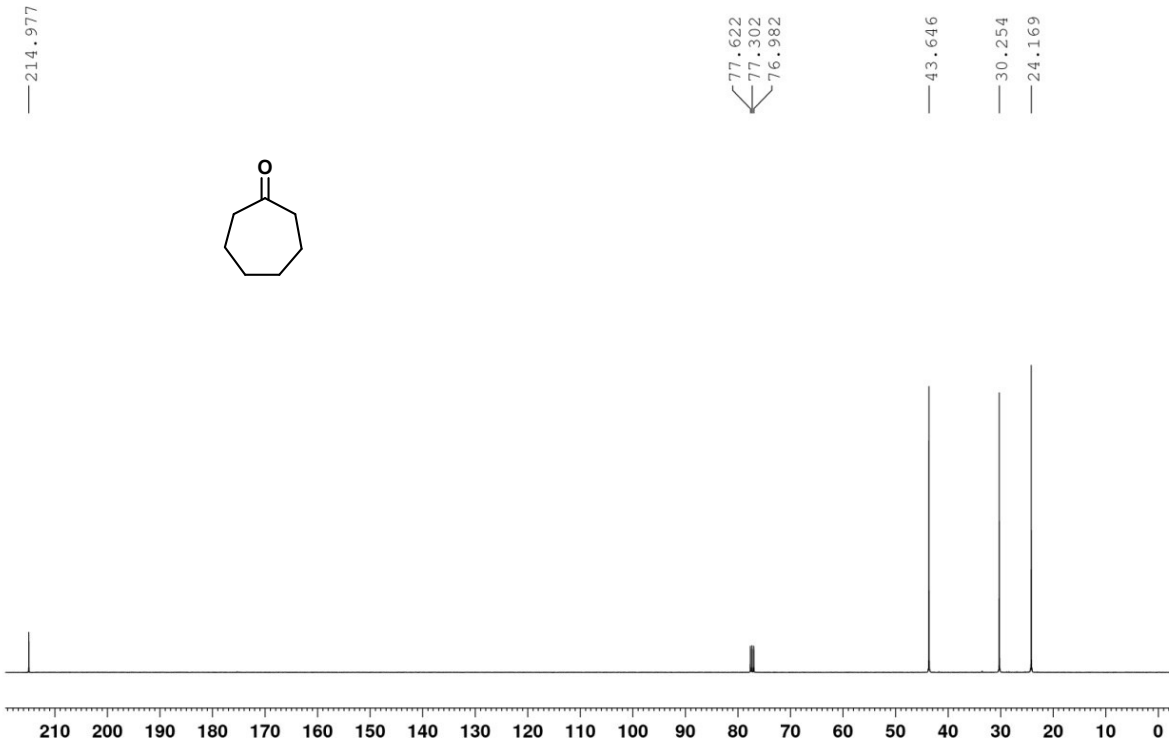


^{1}H-NMR &^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1x**

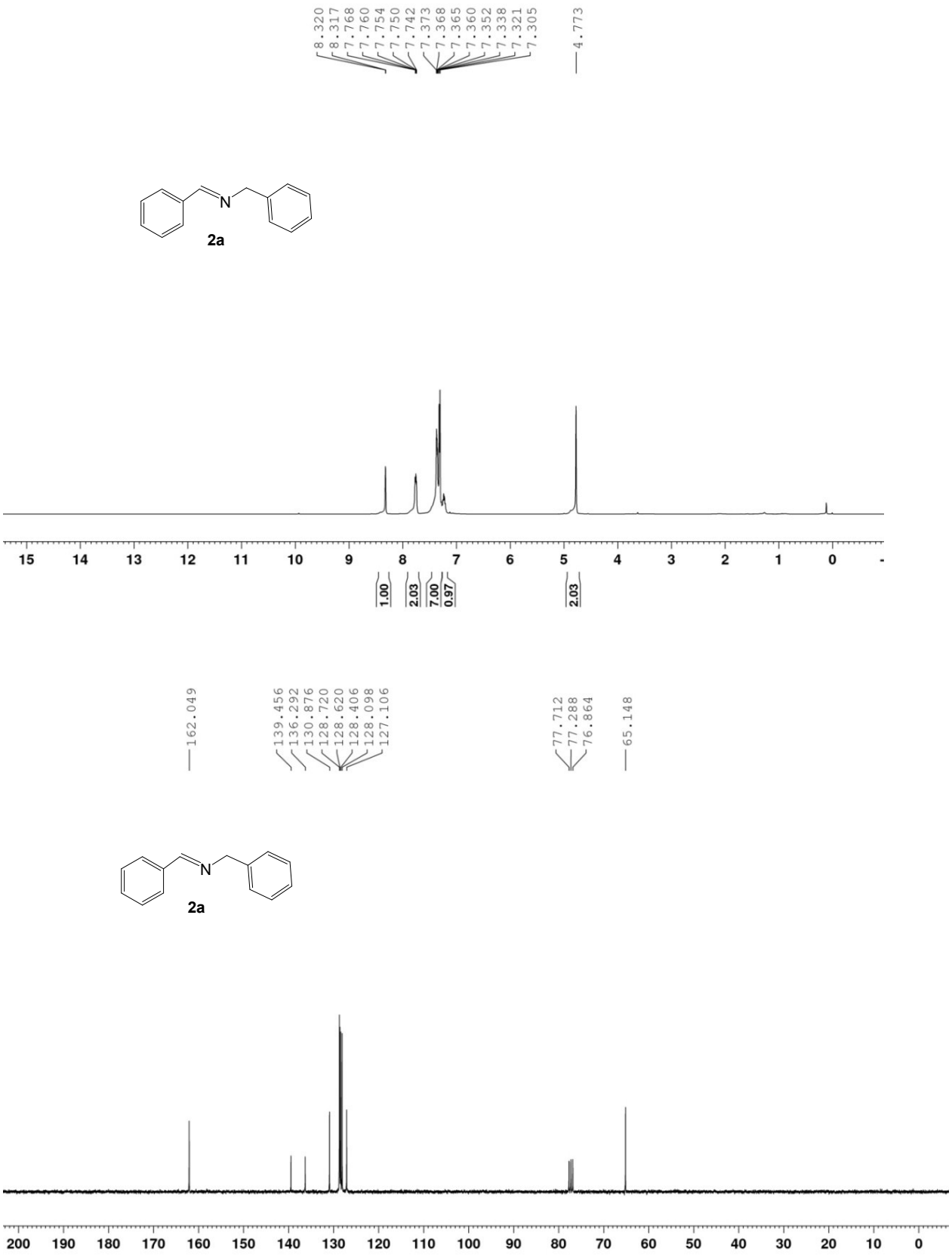


^{1}H-NMR & ^{13}C {^{1}H} (in $CDCl_3$) spectra of compound **1y**

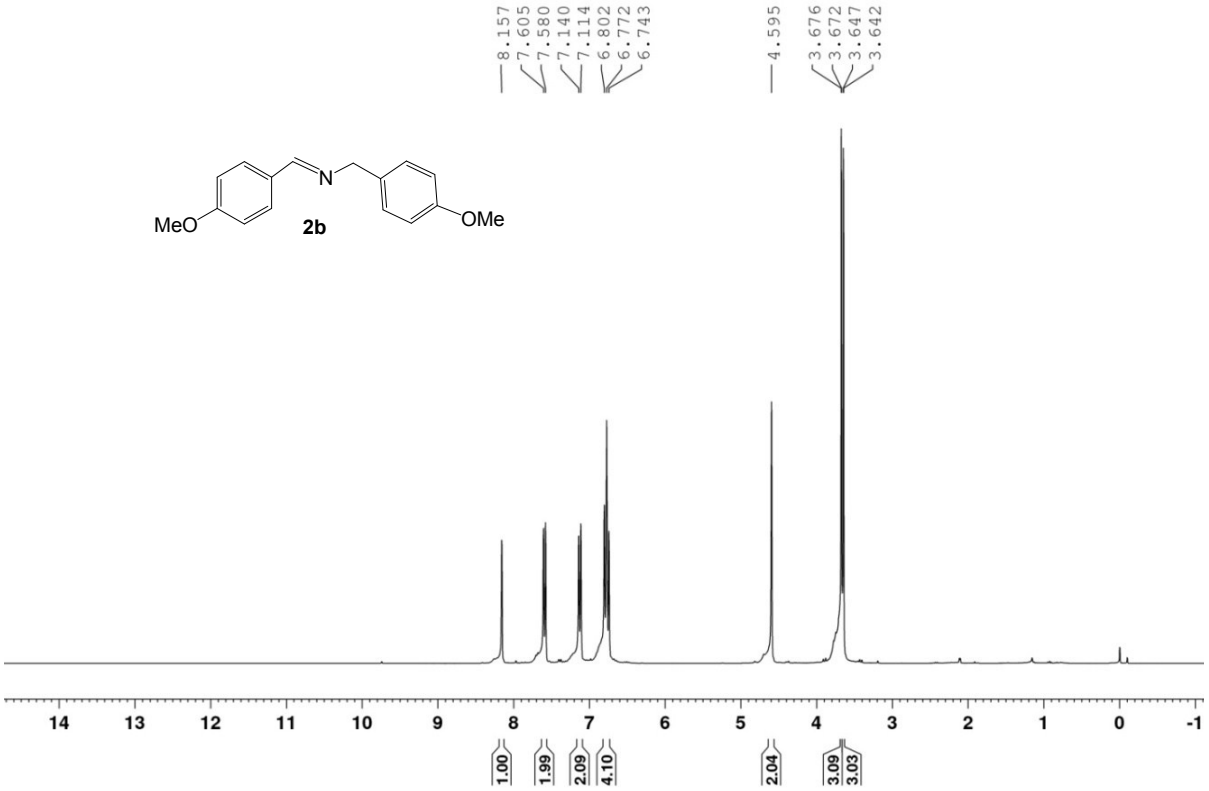


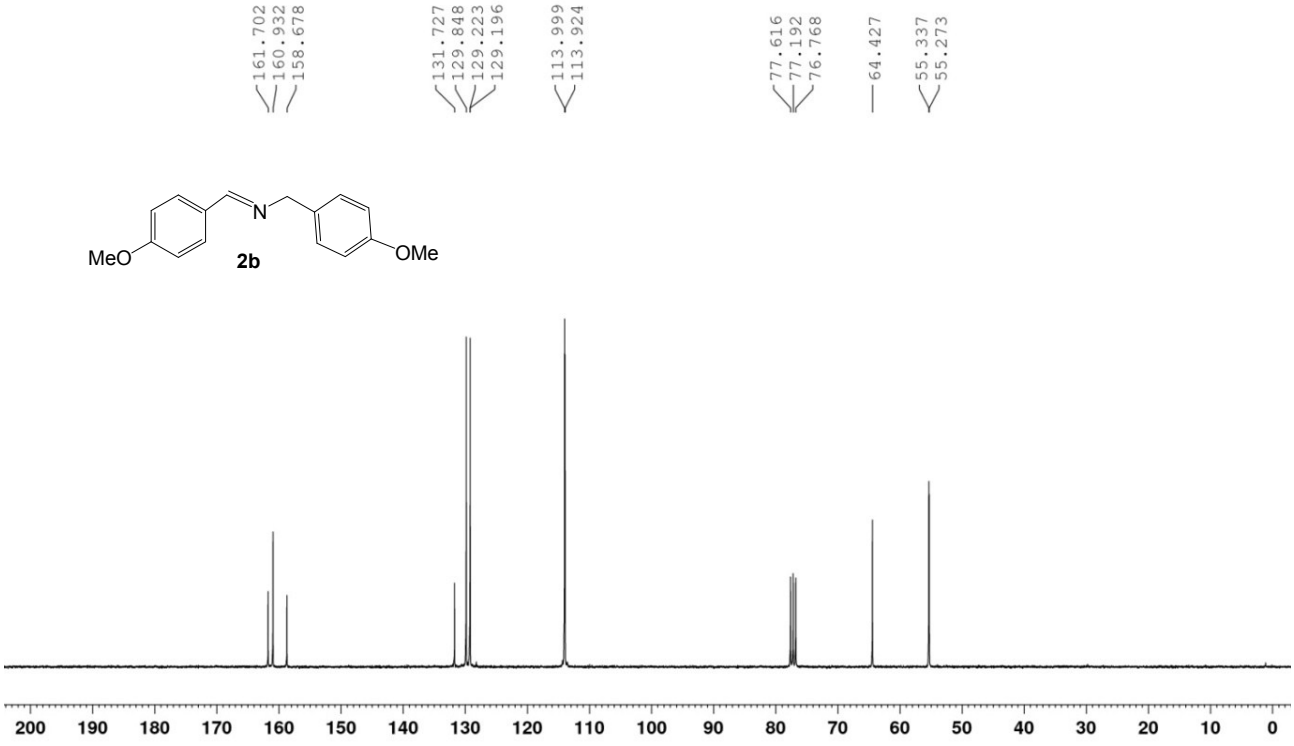


^{1}H & $^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2a

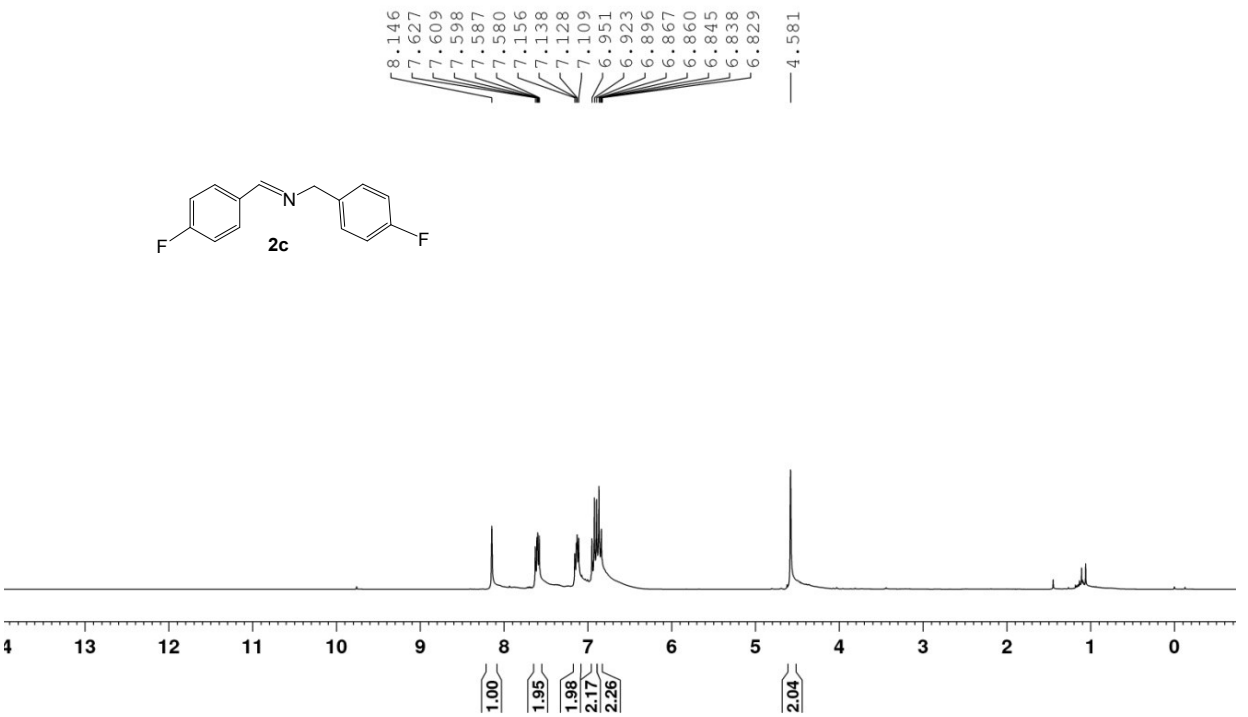


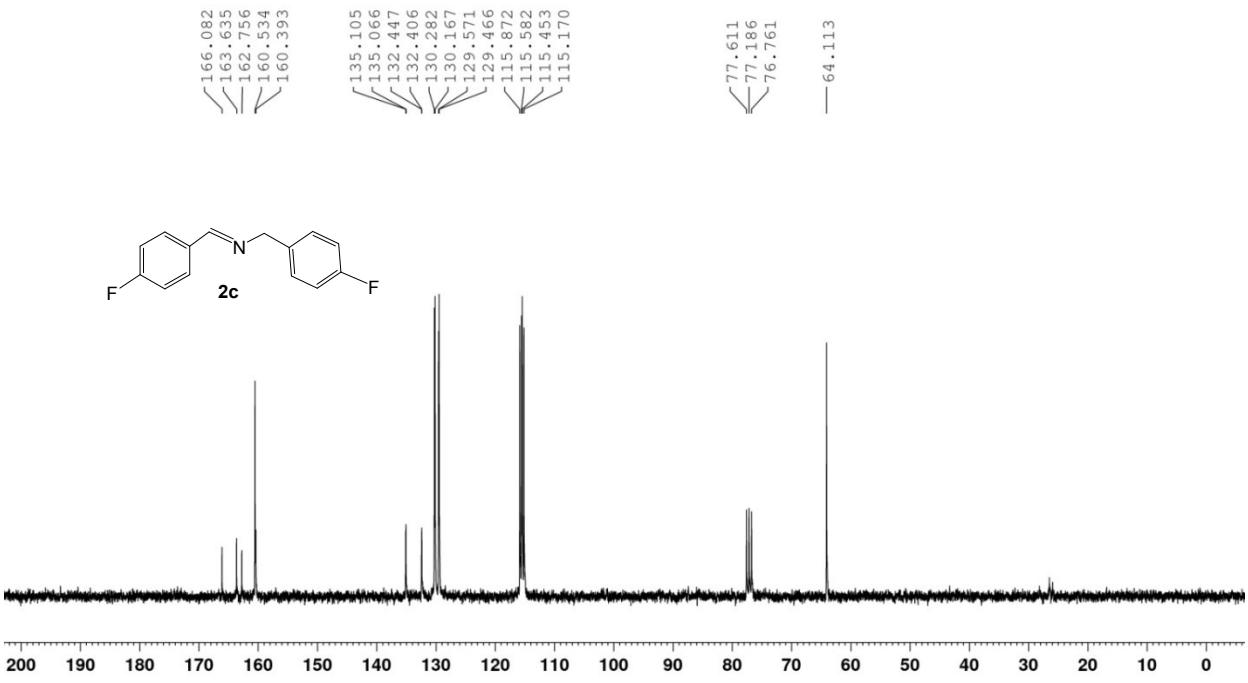
^{1}H & $^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2b



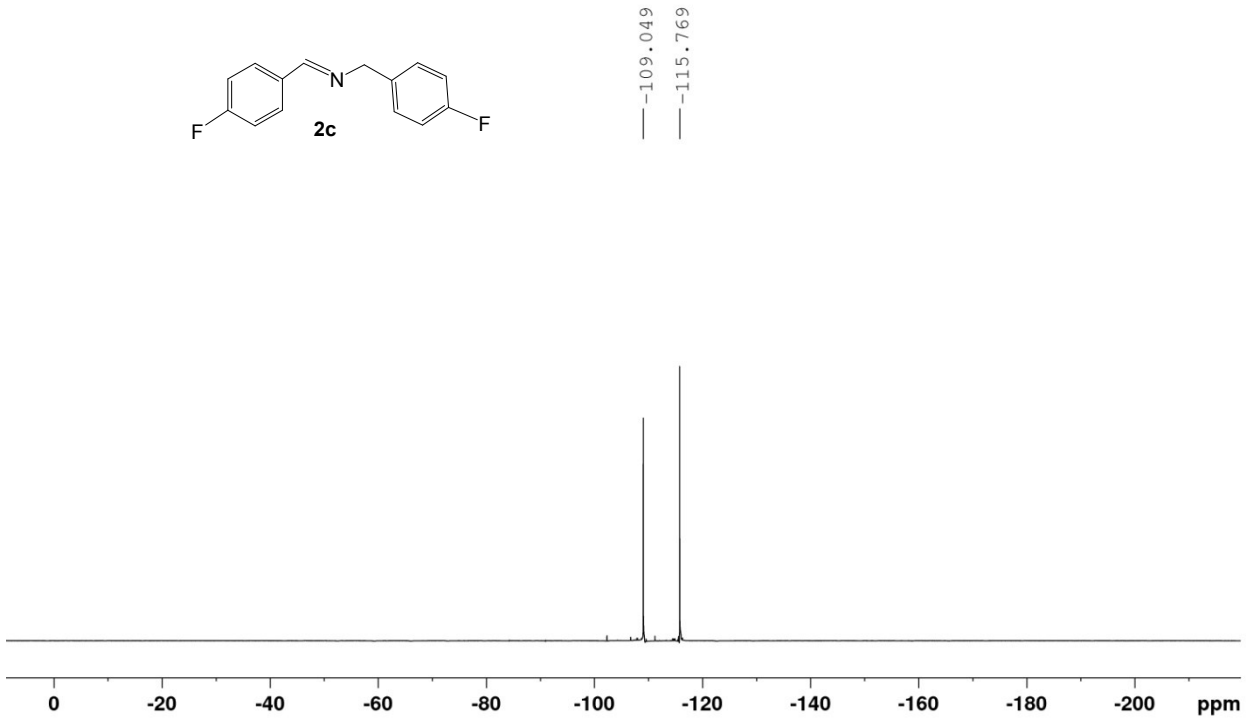


^{1}H & $^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2c

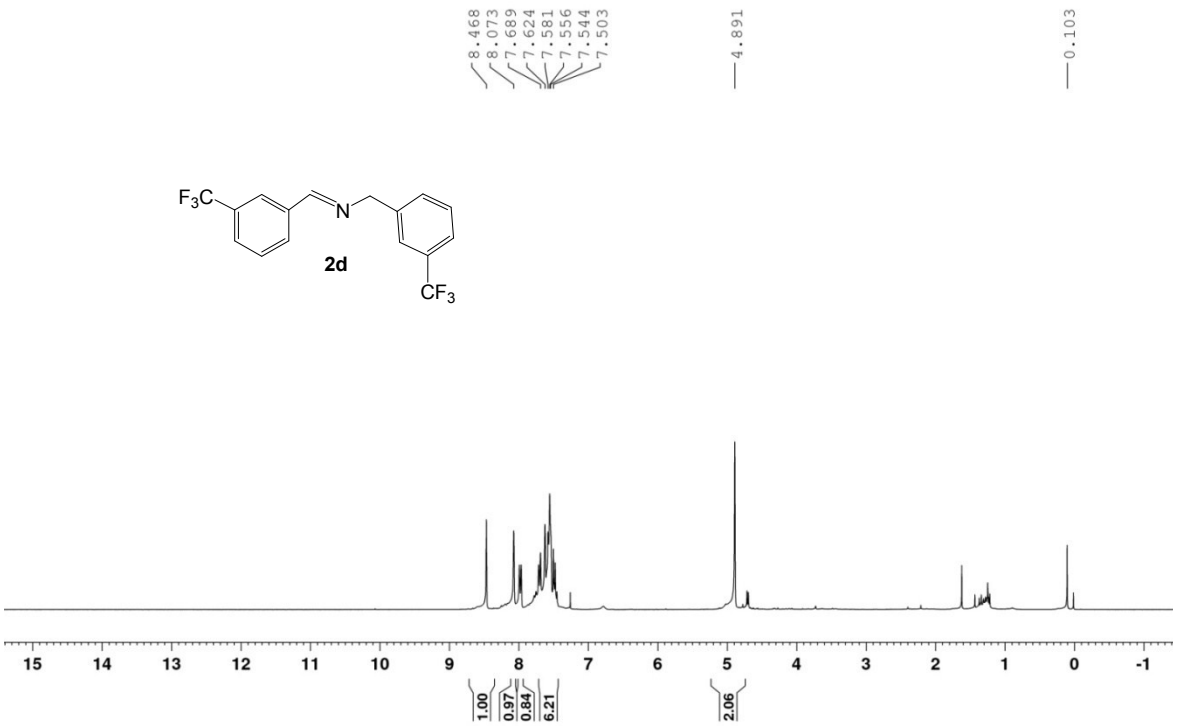


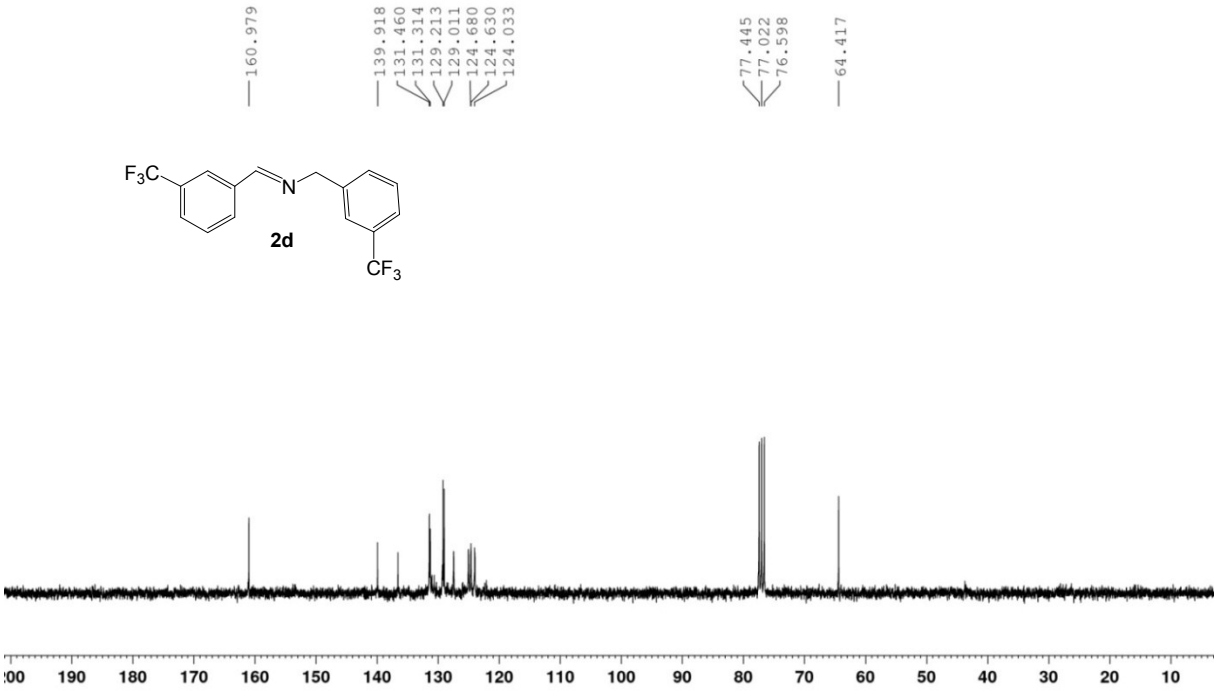


^{19}F-NMR (in $CDCl_3$) spectra of compound 2c

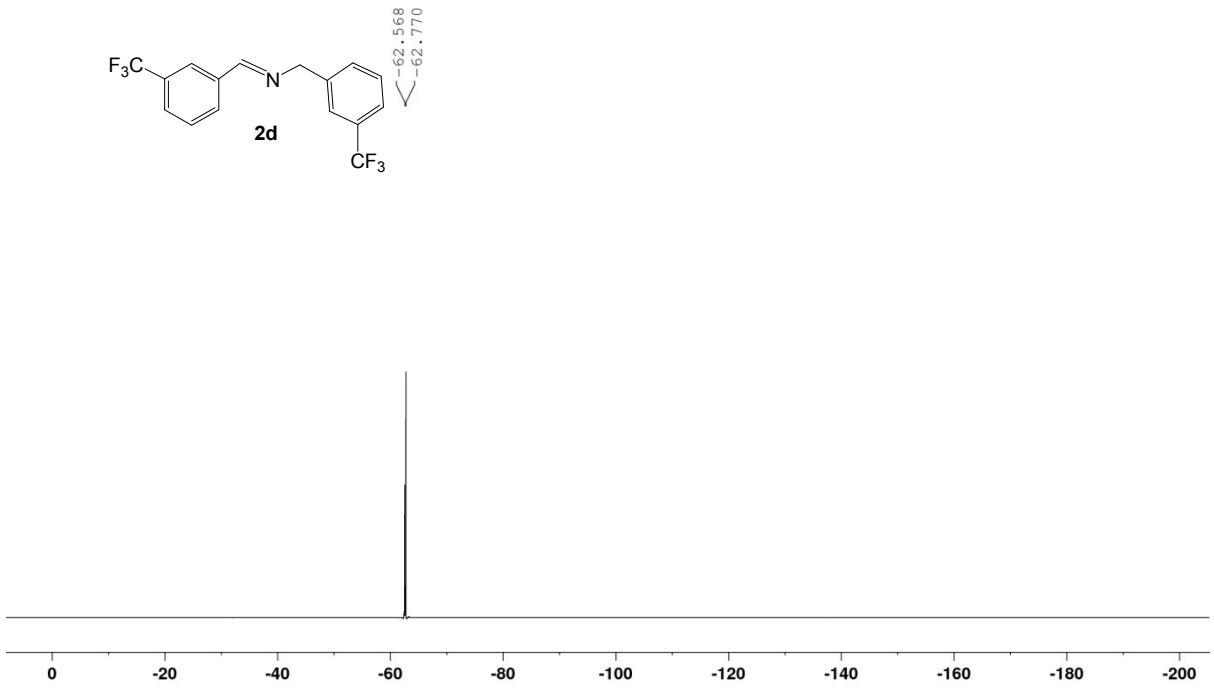


^{1}H & $^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2d

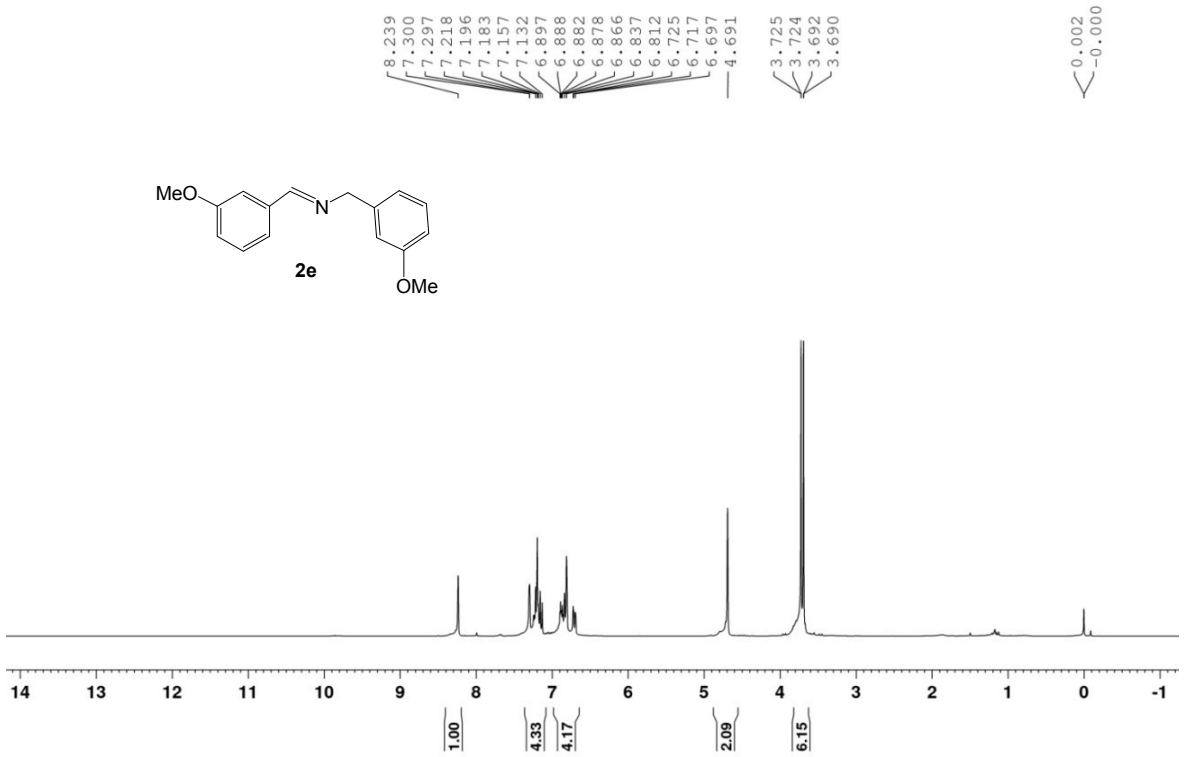


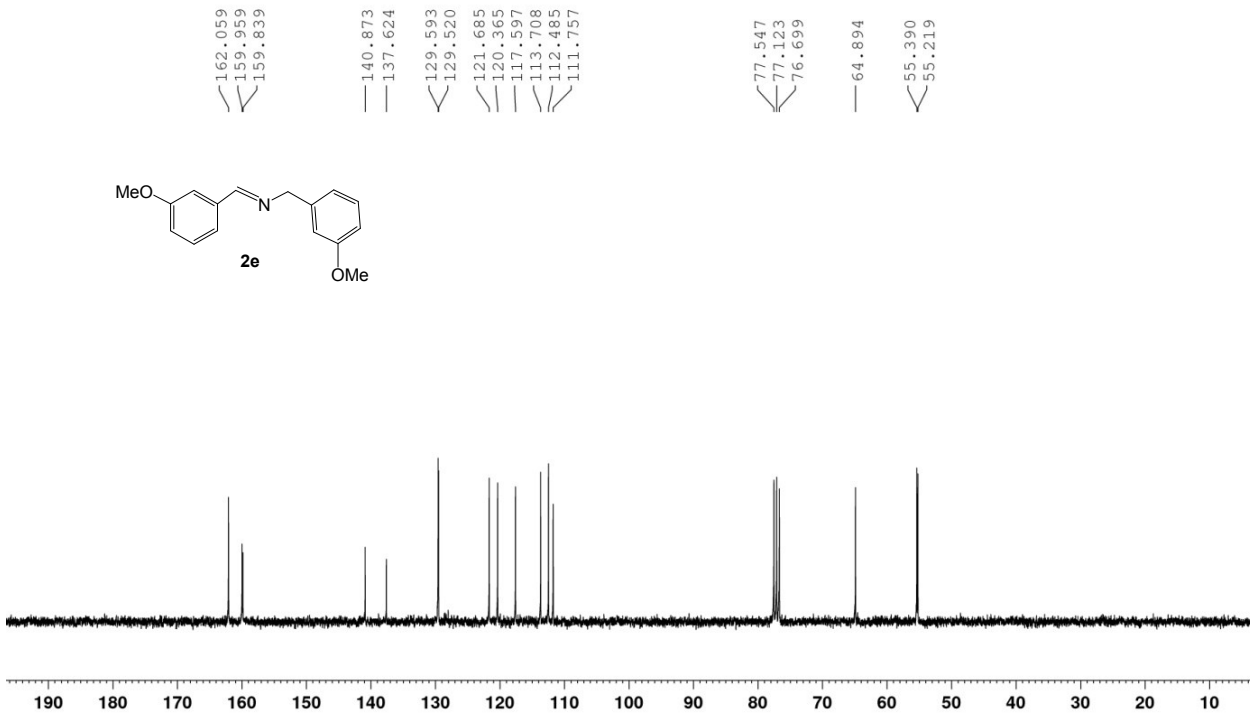


^{19}F-NMR (in $CDCl_3$) spectra of compound 2d

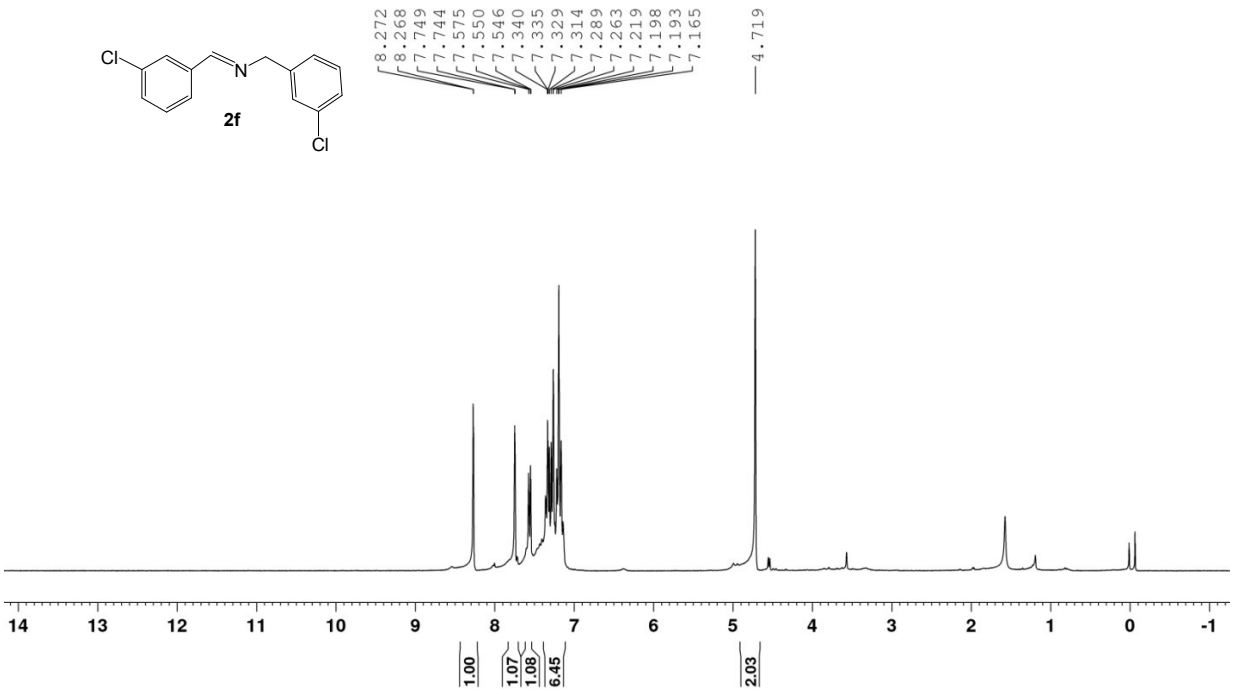


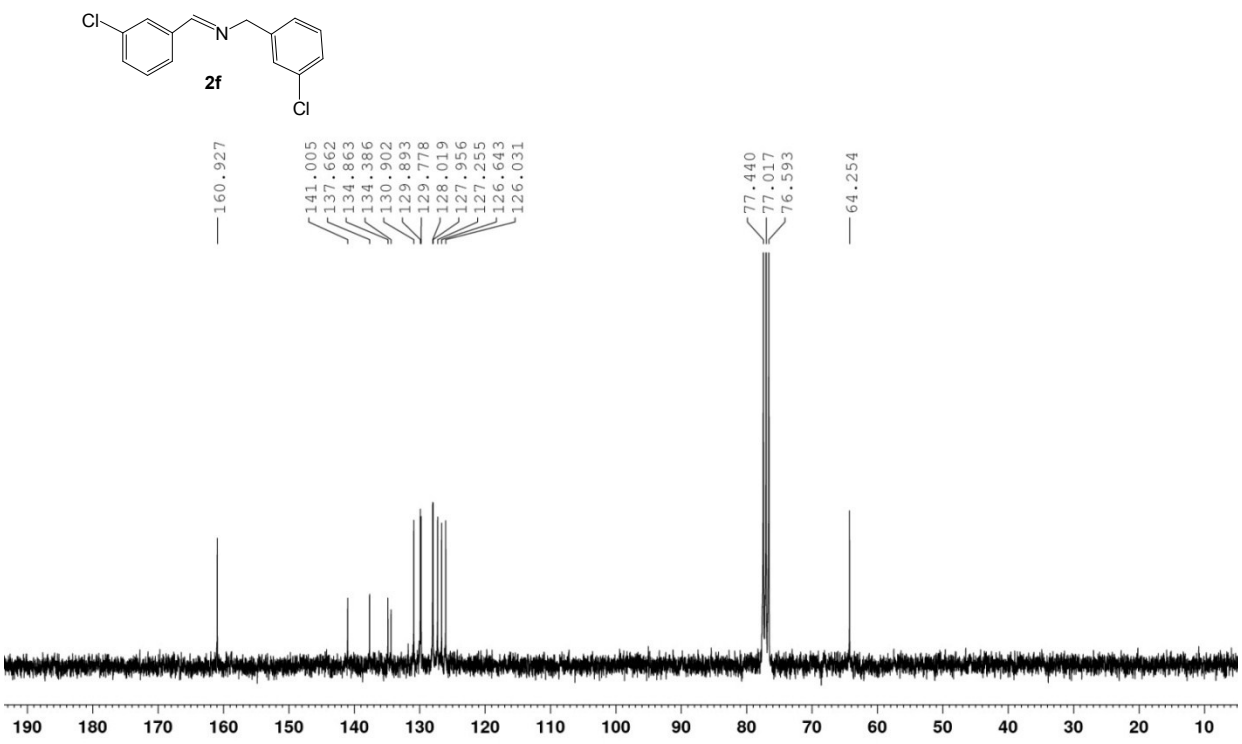
^{1}H & $^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2e



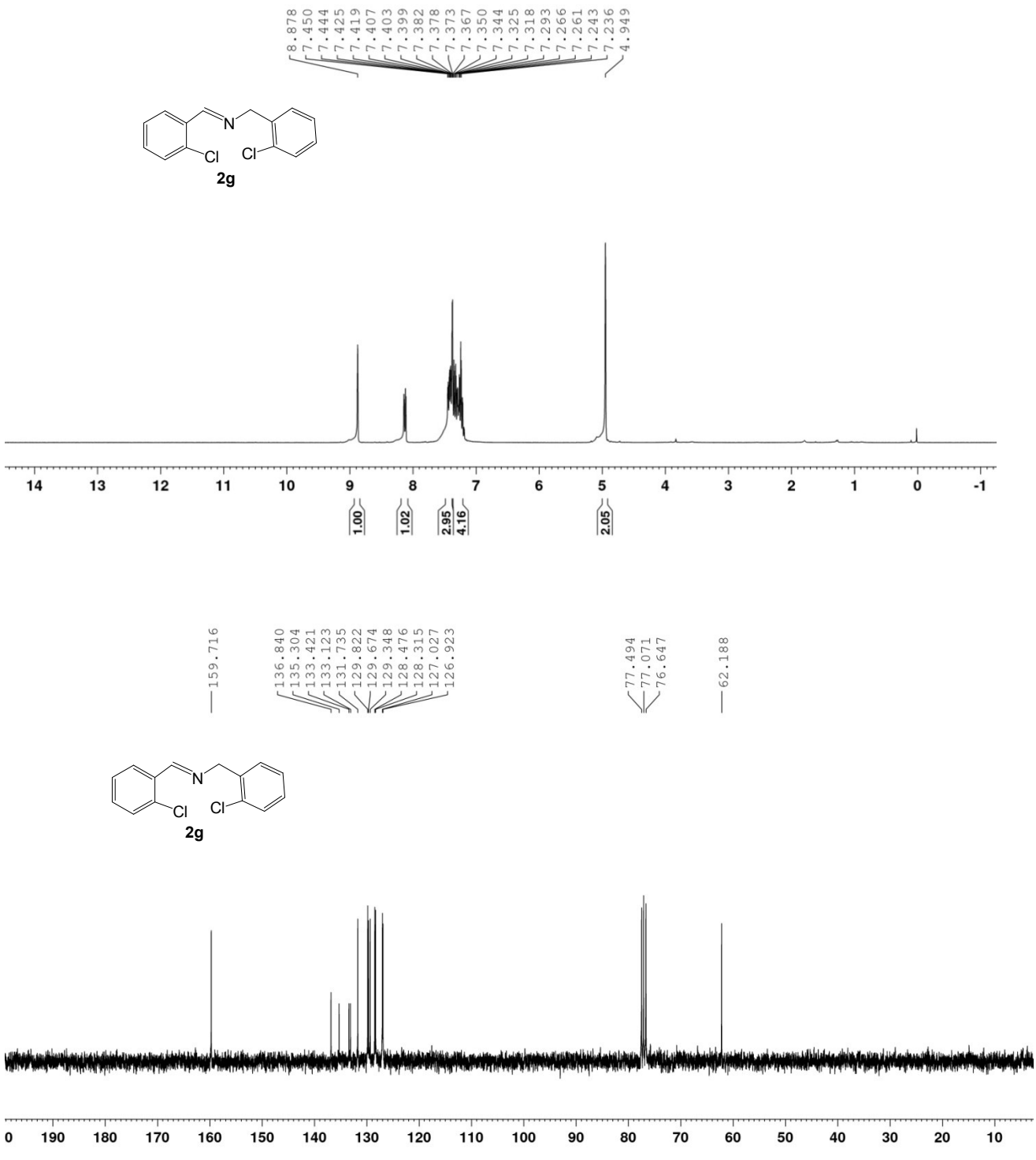


^{1}H & $^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2f

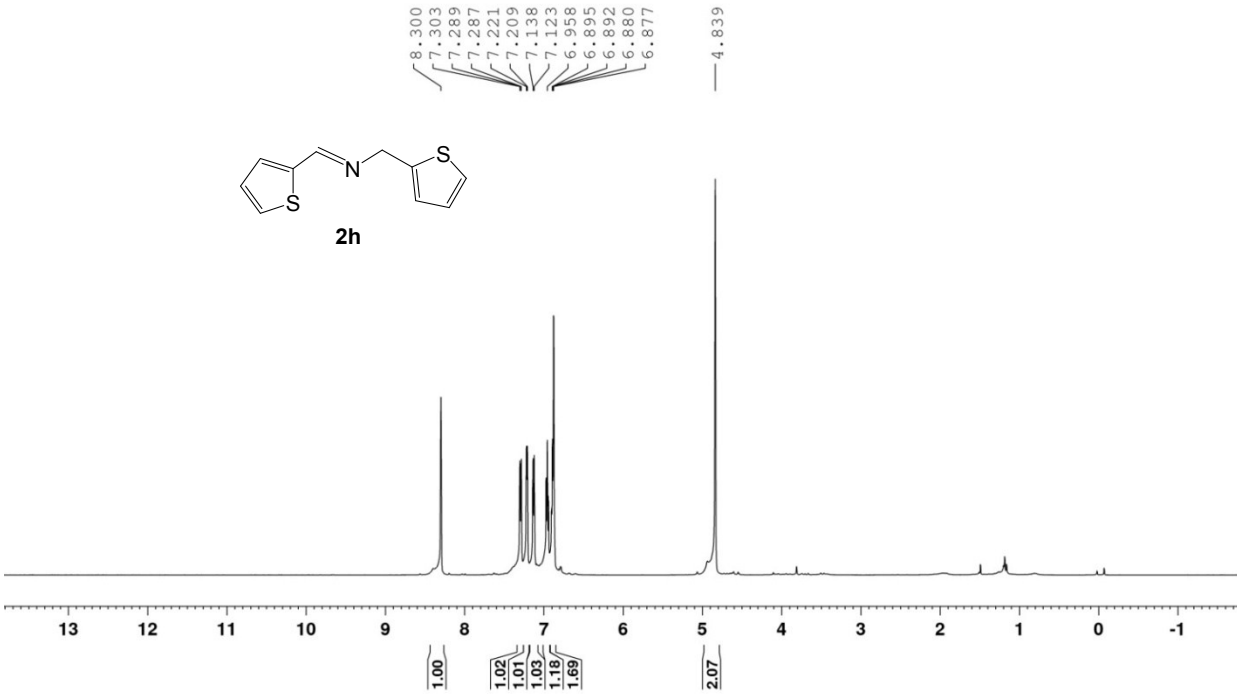


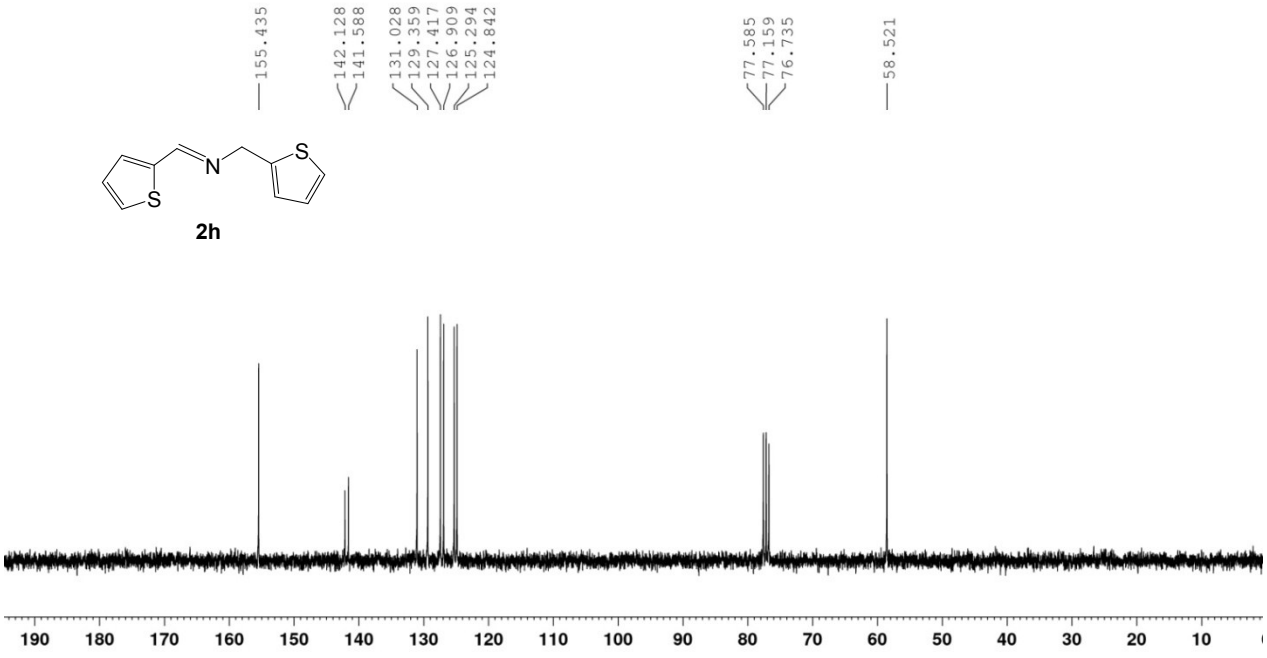


^{1}H & $^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2g

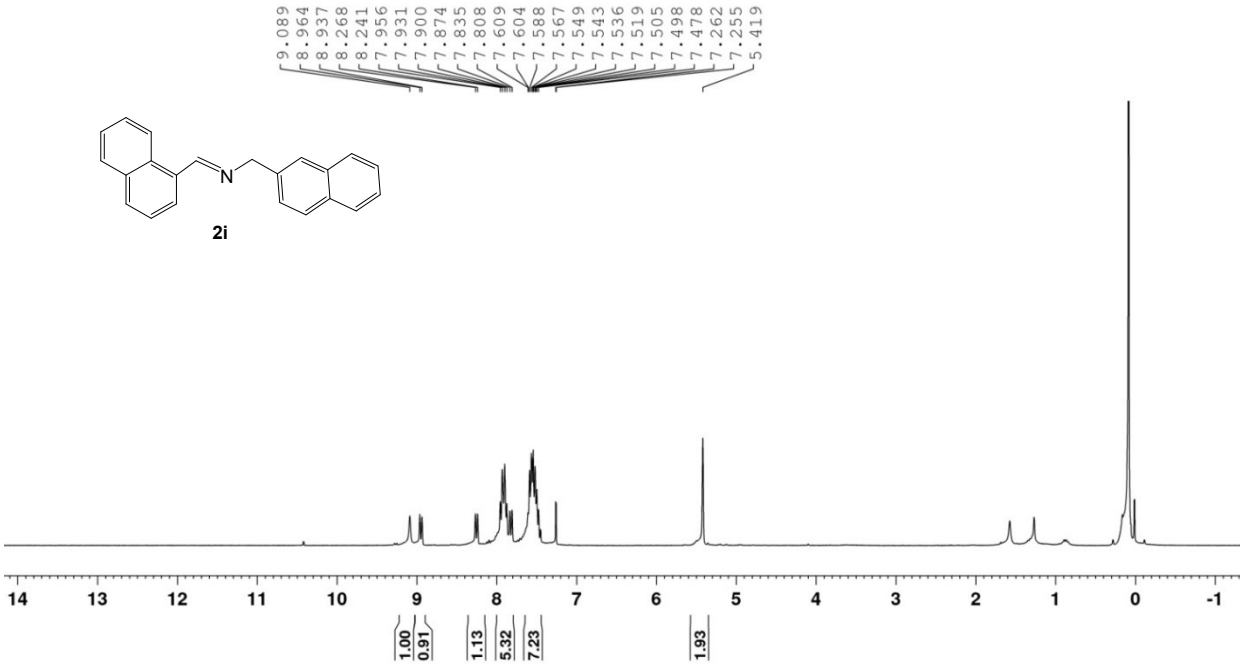


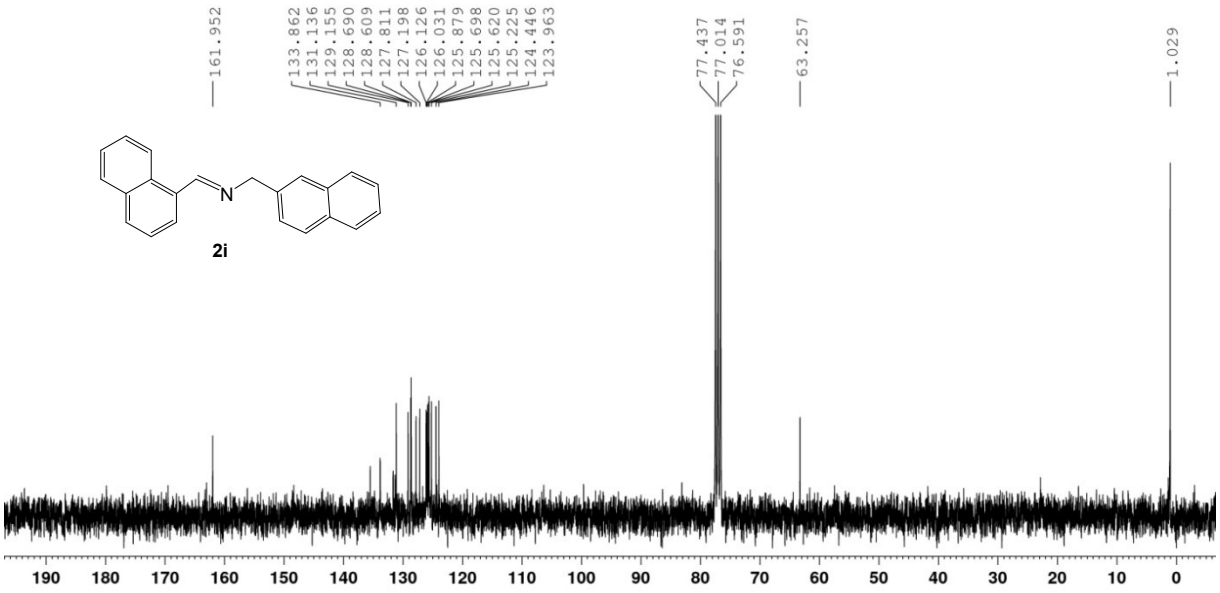
^{1}H &$^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2h



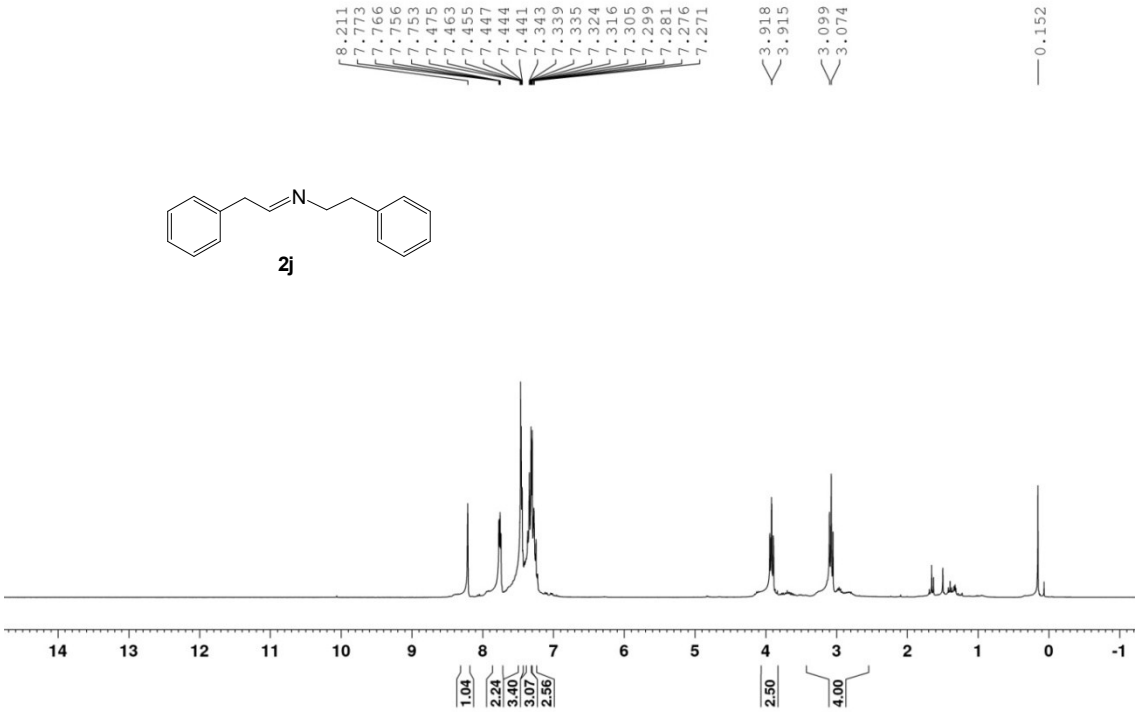


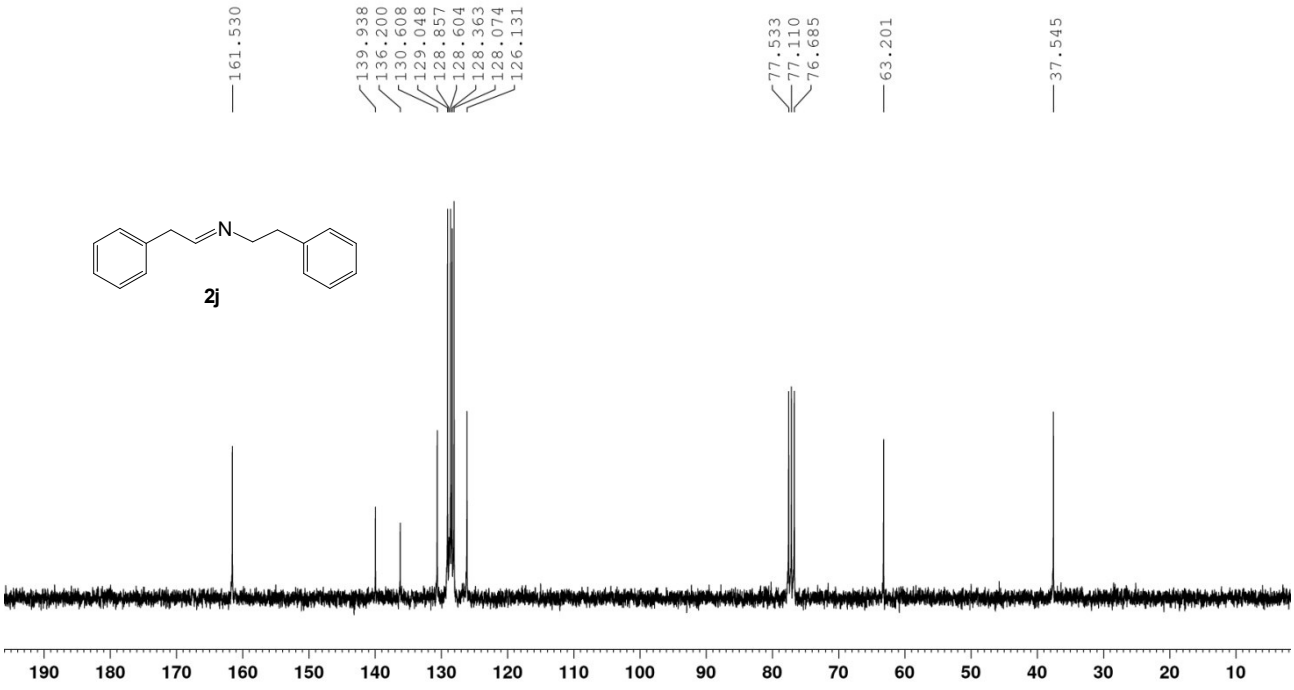
^{1}H &$^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2i





^{1}H &$^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of compound 2j





^{1}H &$^{13}C\{^{1}H\}$-NMR (in $CDCl_3$) spectra of peroxide 6