Electronic Supplementary Material (ESI) for Green Chemistry.

Acceptorless dehydrogenation and aerobic oxidation of alcohols with a reusable binuclear rhodium(II) catalyst in water

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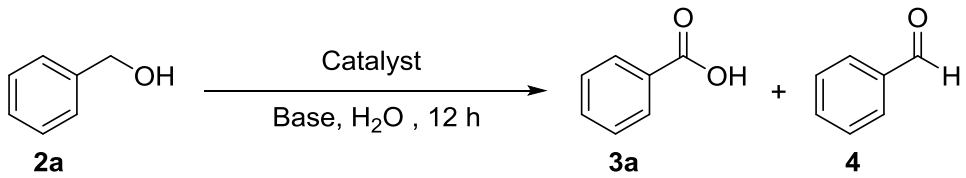
1. General information

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with TMS as the internal standard. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates and visualization on TLC was achieved by UV light (254 nm). Gas chromatography (GC) analysis was performed on a SHIMADZU GC-2014 gas chromatograph with a HP-5 MS column (quartz capillary column, 30 m x 0.25 mm x 0.25 μm). The GC trace of hydrogen gas was recorded on a SHIMADZU GC-2014 instrument with a 5 Å molecular sieves column (3 m x 4 mm) and a TCD detector. GC-MS analysis was carried out on an Agilent 7890A GC-MS with a HP-5 MS column (quartz capillary column, 30 m x 0.25 mm x 0.25 μm) and an Agilent 5975C mass-selective detector (58 psi helium gas, 58 psi hydrogen gas, injector temperature 250 ℃, FID detector temperature 300 ℃ for GC, EI detector for Mass). ICP-MS analysis was carried out on an Agilent 7700s. HRMS data were recorded on Bruker Apex IV FTMS with ESI source.

2. Optimisation of reaction conditions for Rh catalysed alcohol oxidation

Table S1. Rhodium catalysed oxidation of benzylalcohol.



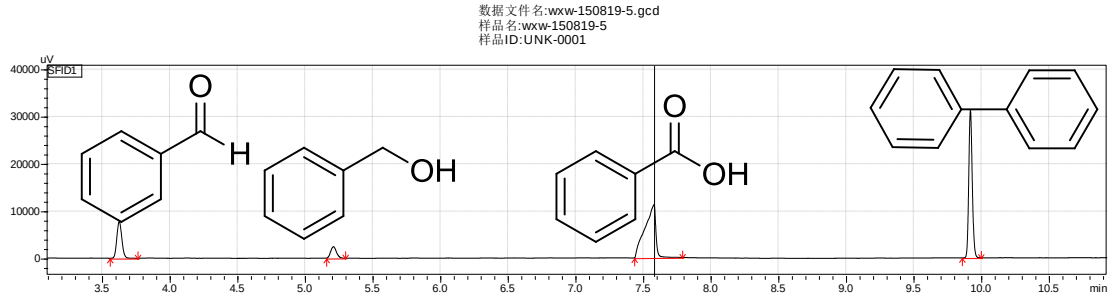
2a **3a** **4**

Entry[a]	Catalyst	Base	T (^{o}C)	Yield of **3a** (%) [b]	Yield of **4 (%)**[b]
1	**1**	NaOAc	100	18	53
2	**1**	K_2CO_3	100	44	19
3	**1**	Na_2CO_3	100	68	23
4	**1**	$NaHCO_3$	100	50	18
5	**1**	K_3PO_4	100	75	15
6	**1**	NaOH	100	86	<5
7	**1**	KOH	100	83	<5
8	**1**	NaOH	25	36	<5
9	**1**	NaOH	60	68	<5
10	**1**	NaOH	80	75	<5
11[c]	**1**	NaOH	100	20	<5
12[d]	**1**	NaOH	100	38	<5
13[e]	**1**	NaOH	100	94	<5
14[f]	**1**	none	100	0	22
15[g]	**1**	NaOH	100	0	<5
16[e]	$RhCl_3•3H_2O$	NaOH	100	0 (0)	12 (5)
17[e]	$[Rh(OAc)_2]_2$	NaOH	100	32 (48)	23 (20)
18[e]	$[Cp^*RhCl_2]_2$	NaOH	100	13 (27)	7 (3)

[a] Reaction conditions: **2a** (0.5 mmol), catalyst **1** (0.0025 mmol), base (0.5 mmol), H_2O (2 mL), 100 ^{o}C, 12 h, under argon. [b] The yields were determined by GC with diphenyl as internal standard. [c] 0.25 equivalent of NaOH. [d] 0.5 equivalent of NaOH. [e] The numbers in brackets refer to yields under air. [f] Without base under air. [g] Without catalyst under air.

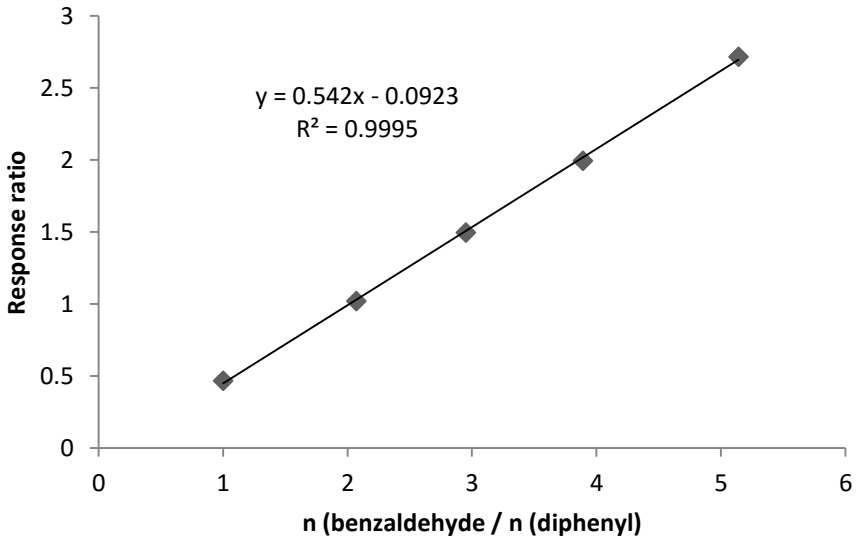
The yields in Table S1 were measured by GC with diphenyl as internal standard. GC parameters: injector temperature 230 ℃, FID detector, temperature 250 ℃. Column temperature program: 80 ℃ was maintained for 5 minutes, then 80 ℃ followed by a ramp at 20 ℃/min to 200 ℃. benzaldehyde (t_R = 3.629 min), benzylalcohol (t_R = 5.212 min), benzoic acid (t_R = 7.581 min), biphenyl (t_R = 9.922 min).

The GC trace for an example of oxidation of benzylalcohol with diphenyl as internal standard is given below.

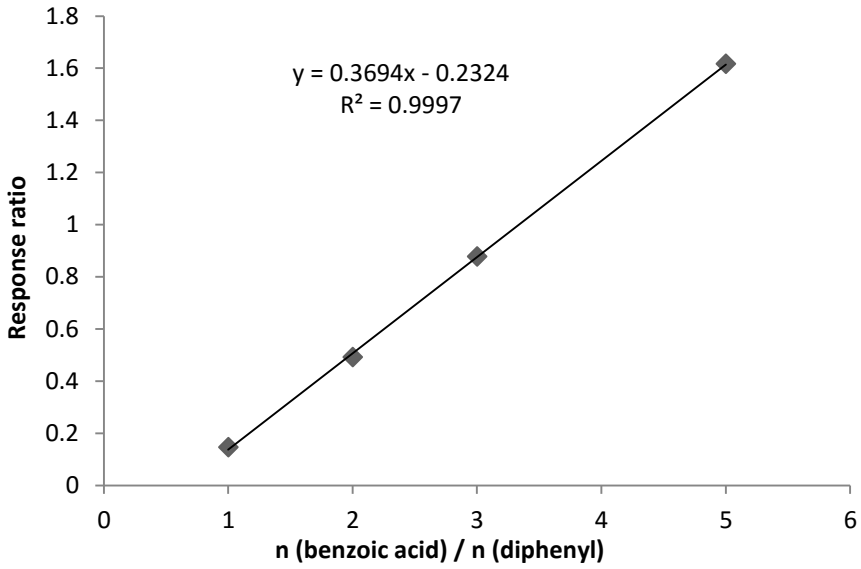


Peak#	R.Time	Area	Height	Area%
1	3.629	19991	7744	0.009
2	5.212	7338	2433	0.003
3	7.581	62925	11211	0.028
4	9.922	56035	30666	0.025

A standard curve of benzaldehyde with diphenyl as internal standard is shown below.



A standard curve of benzoic acid with diphenyl as internal standard is shown below.



3. Procedure for the preparation of the binuclear rhodium(II) complex 1

3.1 Synthesis of complex $[Rh(OCOCH_3)_2]_2$[1]

$RhCl_3 \cdot 3H_2O$ (0.5 g, 1.86 mmol) and CH_3COONa (1.0 g. 12.20 mmol) in glacial acetic acid (10 mL) and ethanol (10 mL) were gently refluxed under nitrogen for an hour. The initial red solution rapidly became green, and the precipitation of green solids was observed. After cooling to room temperature the green solids were collected by filtration. The crude product was dissolved in boiling methanol (ca. 60 mL) and filtered; after concentration to about 10 mL, the solution was kept in a refrigerator overnight, Green crystals were formed. The crystals were collected by filtration and dried *in vacuo* at 45 ^{o}C for 20 hours to yield emerald-green crystals of $[Rh(OCOCH_3)_2]_2$ (288 mg, 0.65 mmol, 70% yield).

3.2 Synthesis of complex 1[2]

Complex **1** was prepared according to the literature.[2] $[Rh(OCOCH_3)_2]_2$ (88.4 mg, 0.2 mmol), terpyridine (93.2 mg, 0.4 mmol), NaCl (117 mg, 2 mmol) and ethanol (5 mL) were mixed, degassed with Ar and stirred at 80 ^{o}C for 6 h. The red solids formed were filtered off and recrystallised from water. Yield: 116 mg, 0.11 mmol, 55%; ^{1}H NMR (D_2O, 400 MHz) δ (ppm) 8.14 (d, *J* = 5.6 Hz, 4H), 7.85-8.02 (m, 14H), 7.44 (t, *J* = 6.6 Hz, 4H), 2.72 (s, 3H); ^{13}C NMR (D_2O, 100 MHz) δ (ppm) 192.3, 155.2, 154.7, 151.5,

140.2, 139.2, 129.1, 124.6, 123.8, 24.5; HRMS (ESI) for $C_{32}H_{25}Cl_2N_6O_2Rh_2$ $[M]^+$: calc.: 800.9526; found: 800.9530.

4. General procedure for oxidation of alcohols

4.1 General procedure for oxidation of primary alcohols to carboxylic acids in water under air

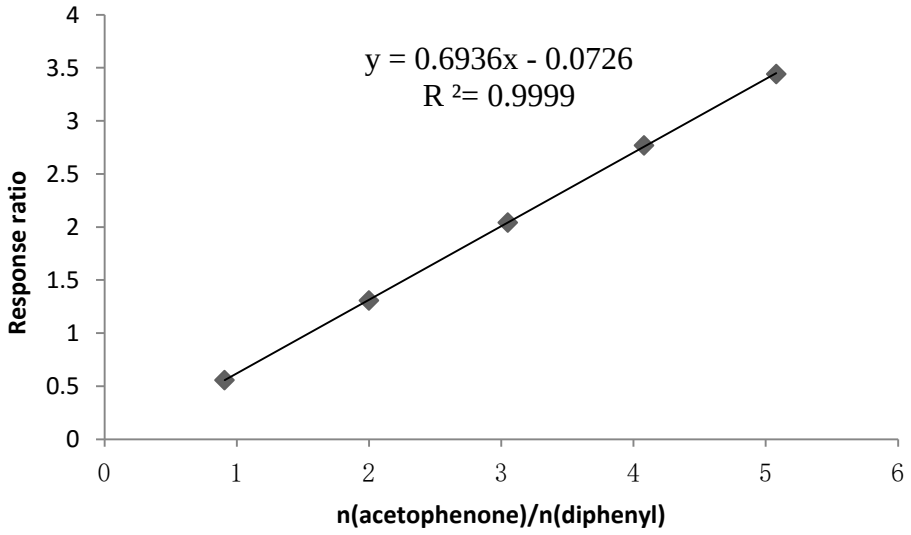
A primary alcohol (0.5 mmol), catalyst **1** (0.5-1 mol%), NaOH (0.5-1.0 mmol), water (2 mL) and a magnetic stir bar were placed in a Radleys Carousel tube. The tube was then sealed and connected to an empty balloon. The mixture was stirred at 100 ^oC under air for 12-20 h. After cooling to room temperature, the aqueous solution was washed with diethyl ether to remove unreacted alcohol substrate. HCl solution (1 M) was used to acidify the aqueous solution to pH < 3, which was then extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was then removed under reduced pressure to obtain the carboxylic acid product without further purification.

4.2 General procedure for acceptorless dehydrogenation of primary alcohols to carboxylic acids in water

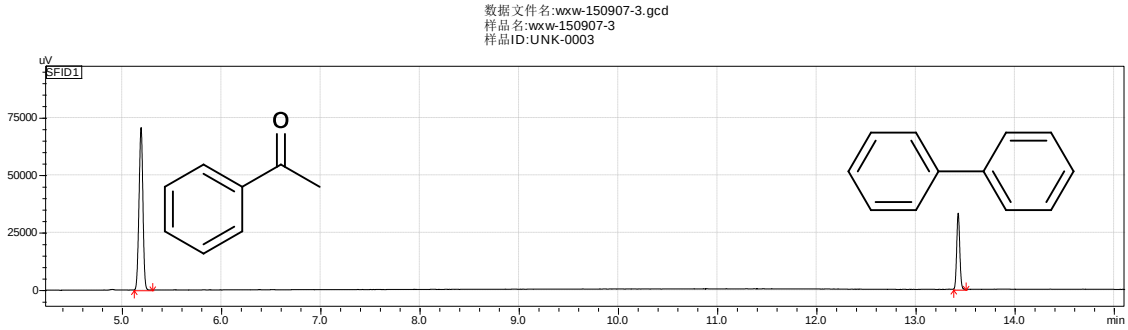
A primary alcohol (0.5 mmol), catalyst **1** (0.5-1 mol%), NaOH (0.5-1.0 mmol), water (2 mL) and a magnetic stir bar were placed in a Radleys Carousel tube. The mixture was bubbled with argon for 15 min and the tube was sealed and connected to an empty balloon. The mixture was then stirred at 100 ^oC for 12-20 h. After cooling to room temperature, the aqueous solution was washed with diethyl ether to remove unreacted alcohol substrate. HCl solution (1 M) was used to acidify the aqueous solution to pH < 3, which was then extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was then removed under reduced pressure to obtain the carboxylic acid product without further purification.

4.3 General procedure for the oxidation of secondary alcohols to ketones in water under air

A secondary alcohol (0.5 mmol), catalyst **1** (0.5 mol%), NaOH (0.005-0.5 mmol), water (2 mL) and a magnetic stir bar were placed in a Radleys Carousel tube. The tube was then sealed and connected to an empty balloon. The mixture was stirred at 100 ^{o}C under air for 8-16 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3 x 10 mL). The organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the product was purified by flash chromatography using petroleum ether and ethyl acetate as eluent. The yield for acetophenone during reaction condition optimisation was determined by GC analysis. GC parameters: injector temperature 230 ℃; FID detector, temperature 250 ℃; column temperature program: 100 ℃ followed by a ramp at 1 ℃/min to 110 ℃, then 110 ℃ followed by a ramp at 20 ℃/min to 200 ℃. acetophenone (t_R = 5.196 min) , 1-phenylethanol (t_R = 5.019 min), biphenyl (t_R = 13.433 min). A standard curve of acetophenone with diphenyl as standard is shown below.



The GC trace for oxidation of 1-phenylethanol under optimised reaction conditions with diphenyl as internal standard is given below.



Peak#	R.Time	Area	Height	Area%
1	5.196	193737	70176	0.085
2	13.433	71509	32823	0.031

4.4 General procedure for acceptorless dehydrogenation of secondary alcohols to ketones in water

A secondary alcohol (0.5 mmol), catalyst **1** (0.5 mol%), NaOH (0.005 mmol), water (2 mL) and a magnetic stir bar were placed in a Radleys Carousel tube. The mixture was bubbled with argon for 15 min and the tube was sealed and connected to an empty balloon. The mixture was then heated at 100 ^{o}C for 8-16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3 x 10 mL). The organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the product was purified by flash chromatography using petroleum ether and ethyl acetate as eluent.

5. Procedures for large scale oxidation in water

5.1 Procedure for the large scale oxidation of 2f to 3f in water

Catalyst **1** (0.005 mol, 5.3 mg in small amount of water), NaOH (25 mmol, 1 g in 4 mL H_2O) and a magnetic stir bar were placed in a round-bottom flask and the mixture was stirred at room temperature under air until the solution became yellow. To the mixture was added **2f** (25 mmol, 3.45g). The resulting mixture was then stirred at 100 ^{o}C under air for 72 h. After cooling to room temperature, the aqueous solution was washed with diethyl ether to remove unreacted alcohol substrate. HCl solution (1 M) was used to acidify the aqueous solution to pH < 3, with white precipitate formed. The white precipitation was then collected by filtration and dried *in vacuo* at 45 ^{o}C for 20 hours to afford 2.62 g of **3f** (white solid, 69% yield). The product contained 9.8

ppb of rhodium by ICP-MS analysis. A picture of the amount of catalyst used and the product obtained is shown below.

5.2 Procedure for the large scale oxidation of 5e to 6e in water

Catalyst **1** (0.0025 mol, 2.6 mg in small amount of water), NaOH (0.125 mmol, 5 mg in 1 mL of H_2O) and a magnetic stir bar were placed in a round-bottom flask and the mixture was stirred at room temperature under air until the solution became yellow. To the mixture was added **5e** (12.5 mmol, 1.9 g). And the resulting mixture was stirred at 100 ^oC under air atmosphere for 48 h. After cooling to room temperature, the mixture was extracted with petroleum ether (2 x 100 mL). The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the resulting white solid was dried *in vacuo* to afford 1.76 g of **6e** (white solid, 93% yield). The product contained 4.7 ppb of rhodium by ICP-MS analysis. A picture of the amount of catalyst used and the product obtained is shown below.

6. Procedure for catalyst recycle experiments

5e (1 mmol), catalyst **1** (0.005 mmol), NaOH (0.01 mmol), water (4 mL) and a magnetic stir bar were placed in a Radleys Carousel tube under air. The mixture was

stirred at 100 ^{o}C for 8 h. After cooling to room temperature, the mixture was carefully transferred to a separation funnel and extracted with petroleum ether (30 mL). The aqueous layer was transferred to the Radleys Carousel tube again, which was added 50 μL of NaOH solution (0.4 mg of NaOH in 50 μL of water) and another portion of **5e** (1 mmol) for the next run. 1,3,5-Trimethoxybenzene (0.2 mmol) was added to the organic layer and the organic solvent was removed under reduced pressure. The yield of **6e** was determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

7. Procedure for the detection of hydrogen gas and consumption of oxygen gas

7.1 Procedure for the detection of hydrogen gas under argon

Under an atmosphere of argon, 1-phenylethanol (2 mmol), NaOH (0.02 mmol), catalyst **1** (0.005 mol), water (2 mL) and a stir bar were placed in a Radleys reaction tube. The mixture was bubbled with argon for 15 min and sealed. The mixture was then stirred at 100 ^{o}C for 20 h. The head gas was collected by a gas-tight syringe and analyzed by GC. Hydrogen gas was detected from the head gas (Figure S1).

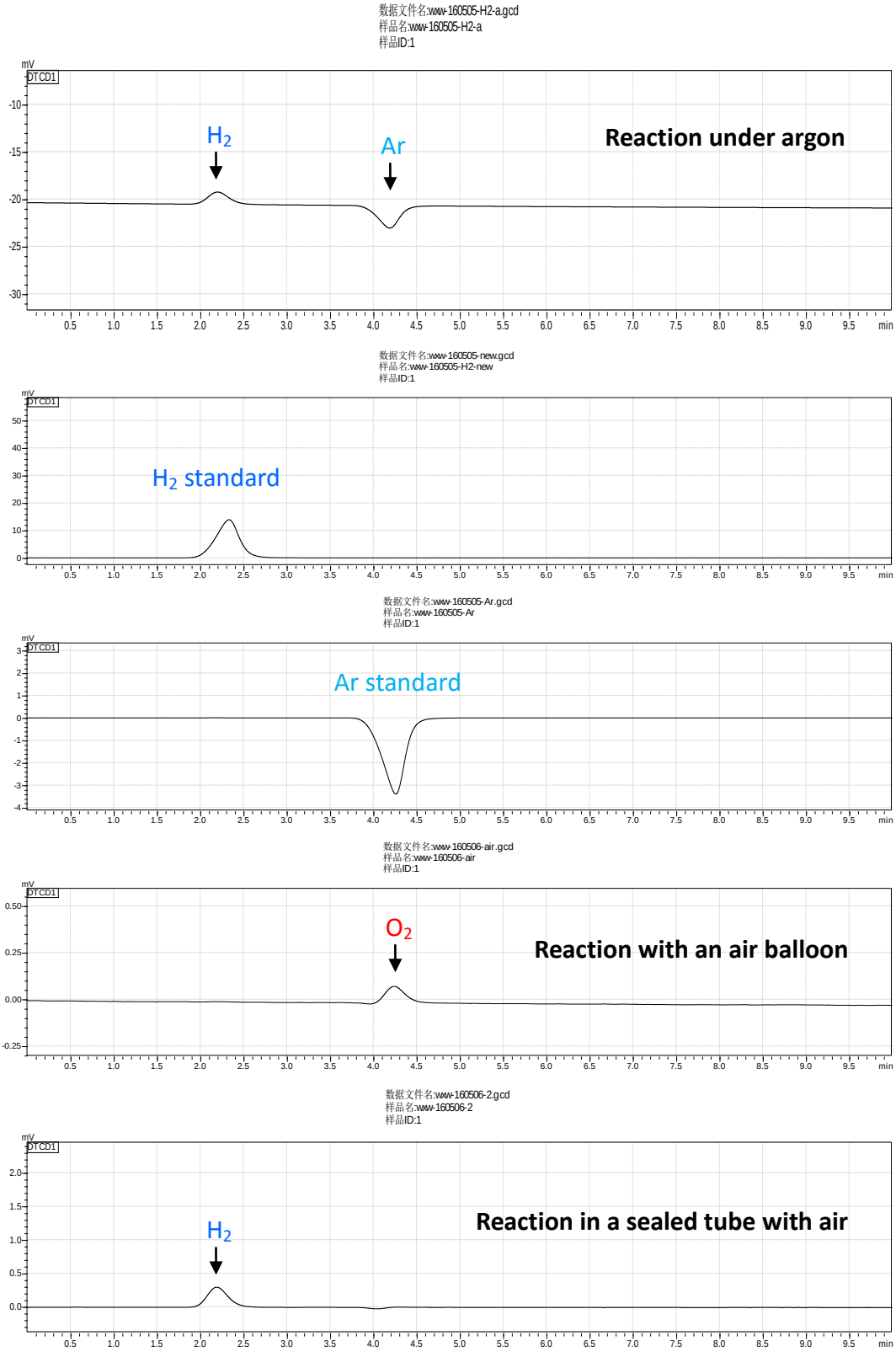
7.2 Procedure for the detection of hydrogen gas with an air balloon

Under an atmosphere of air, 1-phenylethanol (2 mmol), NaOH (0.02 mmol), catalyst **1** (0.005 mol), water (2 mL) and a stir bar were placed in a 25 ml two neck round-bottom flask. One neck of the flask was connected with an air balloon, which was extended into the reaction mixture via a needle; the other neck of the flask was equipped with a condenser, sealed and connected to an empty balloon. The mixture was then stirred at 100 ^{o}C for 12 h. The head gas was collected by a gas-tight syringe and analyzed by GC. No hydrogen gas was detected from the head gas (Figure S1).

7.3 Procedure for measuring the comsumption of O_2

Under an atmosphere of air, 1-phenylethanol (2 mmol), NaOH (0.02 mmol), catalyst **1** (0.005 mol), water (2 mL) and a stir bar were placed in a Radleys reaction tube and the tube was sealed. The mixture was then stirred at 100 ^{o}C for 20 h. The head gas was collected by a gas-tight syringe and analyzed by GC. The peak corresponding to oxygen disappeared and hydrogen gas was detected. A blank experiment of stirring 2

mL of water in a sealed Radleys tube for 20 h was done. GC analysis of its head gas showed the presence of oxygen gas (Figure S1).



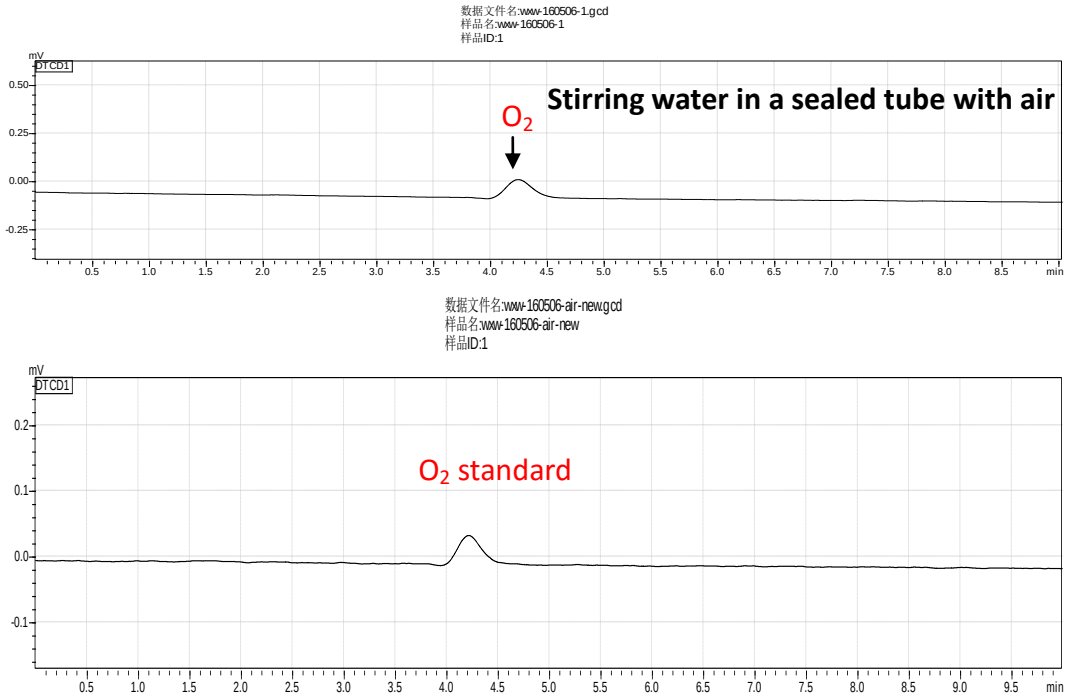


Figure S1. Detection of hydrogen gas with GC. GC parameters: injection temperature = 120 ^{o}C, column temperature = 70 ^{o}C, detector temperature = 120 ^{o}C. 5 Å molecular sieves column was used, and the carrier gas was N_2. The retention time for H_2, Ar and O_2 are 2.19 min, 4.23 min and 4.22 min respectively.

7.4 Quantitative measurement of hydrogen gas released

Procedure for calibration: A reaction tube equipped with a stir bar and charged with 2 mL of water was bubbled with nitrogen gas for 30 min and sealed with a new rubber septum. 3 mL of hydrogen gas was injected to the tube through the septum with a gas syringe. The tube was then shaked and gas mixture sample (250 μL) was taken from the tube (at 24 ^{o}C) with a gas-tight syringe and injected into the GC spectrometer. The same procedure was repeated for the complete by subsequent addition of hydrogen gas (3 mL each) into the same reaction tube.

H_2 volumne[a] (mL)	**GC Area**
0	0
3	15612
6	31440
9	45518
12	57857
15	67464
18	80211

[a] The volume of H_2 added into the reaction tube at 24 ^{o}C

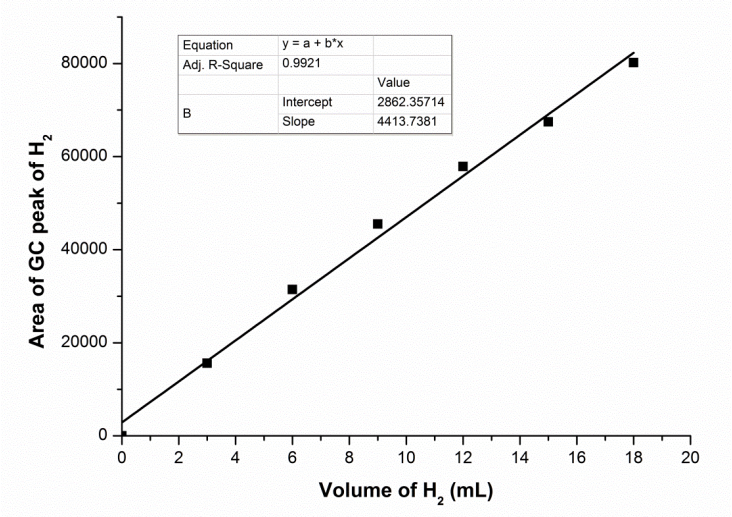


Figure S2. Calibration curve for the quantitative measurement of hydrogen gas

Procedure for measurement of hydrogen gas released: 1-Phenylethanol (2 mmol), NaOH (0.02 mmol), catalyst **1** (0.005 mol), water (2 mL) and a stir bar were placed in a reaction tube (same sizes of stir bar and reaction tube as that for calibration of hydrogen gas). The mixture was bubbled with nitrogen gas for 30 min and sealed with a new rubber septum. The mixture was then stirred at 100 ^{o}C for 20 h. After cooling to room temperature and shaking, the head gas (250 μL) was collected by a gas-tight syringe and analyzed by GC. GC area reading for hydrogen gas is 21067. Thus, according to the calibration curve obtained above, the volume of hydrogen gas should be 4.12 mL (24 ^{o}C, 1 atm). And according to the Van der Waals equation shown below:

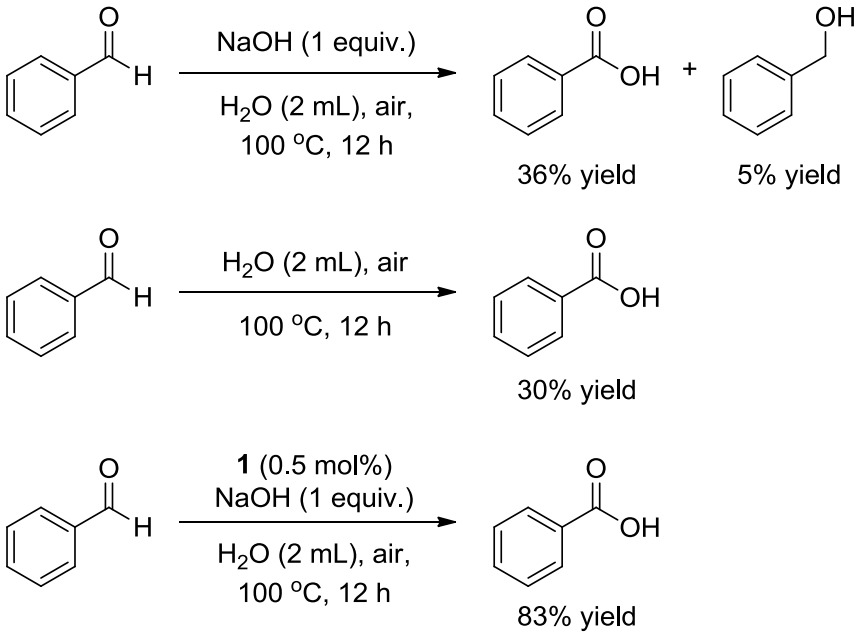
$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Where: R = 9.3145 m^3 Pa mol^{-1} K^{-1}, T = 297.15 K, p = 101325 Pa, a (H_2) = 0.002476 m^6 Pa mol^{-2}, b (H_2) = 0.02661 x 10^{-3} m^3 mol^{-1}

the amount of hydrogen gas released should be 0.17 mmol, corresponding to a yield of 9% based on alcohol. The GC analysis of the aqueous phase of the reaction showed that the yield of acetophenone is 12% with diphenyl as internal standard. *This results indicate that 1 equivalent of hydrogen gas was released for the transformation of 1-phenylethanol to acetophenone under nitrogen atmosphere.* The yield of ketone in *a sealed tube* (12%) under argon or nitrogen is considerably lower than that *with a*

empty balloon (full conversion), possibly due to the reversibility of the dehydrogenation reaction.

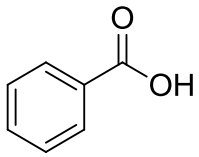
8. Mechanistic studies for the formation of carboxylic acid



Scheme S1. Oxidation of benzaldehyde under various conditions. Benzaldehyde (0.5 mmol), H_2O (2 mL), under air, 100 ^oC, 12 h.

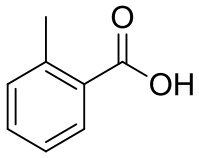
On stirring an equal molar amount of NaOH and benzaldehyde in water under air at 100 ^oC for 12 h without 1, 36% of benzoic acid and 5% of benzyl alcohol were detected by GC with an internal standard. Without NaOH, benzaldehyde was oxidised to benzoic acid with a GC yield of 30% under the same conditions, but without formation of benzyl alcohol. These experiments demonstrate that benzaldehyde could be oxidised to benzoic acid under air without 1 and the benzyl alcohol product results from the Cannizzaro reaction of benzaldehyde. However, the amount of benzyl alcohol formed is very small, suggesting that the base-promoted Cannizzaro reaction is very slow. On the other hand, in the presence of 0.5 mol% of **1** and 1 equivalent of NaOH, benzaldehyde was converted to benzoic acid in 83% GC yield under air for 12 h and no benzyl alcohol was observed. Taken together, these results suggest that the catalytic oxidation of alcohols to acids proceeds mainly via the pathway **a** in Scheme 4 in the text, where the catalyst catalyses both steps of the oxidation.

9. Analytical data of products



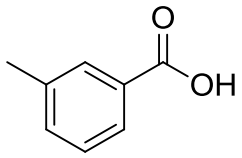
3a

Benzoic acid:[3] 56 mg; 92% isolated yield; white solid; m.p. = 120-122 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.13 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.64-7.60 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 172.3, 134.0, 130.4, 129.5, 128.6; MS (EI) for $C_7H_6O_2$ $[M]^+$: 122.



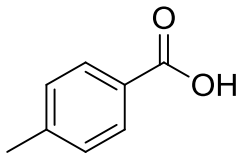
3b

2-Methylbenzoic acid:[3] 63 mg; 93% isolated yield; white solid; m.p. = 102-104 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.01 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.23-7.18 (m, 2H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 173.5, 141.5, 133.1, 132.1, 131.7, 128.4, 126.0, 22.3; MS (EI) for $C_8H_8O_2$ $[M]^+$: 136.



3c

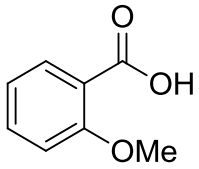
3-Methylbenzoic acid:[3] 39 mg; 57% isolated yield; pale yellow solid; m.p. = 109-111 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) 12.86 (brs, 1H), 7.76-7.73 (m, 2H), 7.42-7.36 (m, 2H) , 2.36 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 167.4, 137.9, 133.4, 130.7., 129.7, 128.4, 126.4, 20.8; MS (EI) for $C_8H_8O_2$ $[M]^+$: 136.



3d

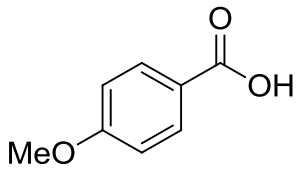
4-Methylbenzoic acid:[3-4] 59 mg; 87% isolated yield; white solid; m.p. = 181-182 ^{o}C;

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.03 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 172.3, 144.8, 130.4, 129.4, 126.8, 21.9; MS (EI) for $C_8H_8O_2$ $[M]^+$: 136.



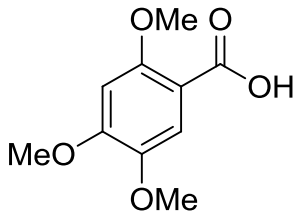
3e

2-Methoxybenzoic acid:[5] 68 mg; 89% isolated yield ; white solid; m.p. = 97-99 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) 12.57 (brs, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.52-7.48 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.01-6.97 (m, 1H), 3.81(s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 167.3, 158.0, 133.0, 130.6, 121.3, 120.0, 112.4, 55.7; MS (EI) for $C_8H_8O_3$ $[M]^+$: 152.



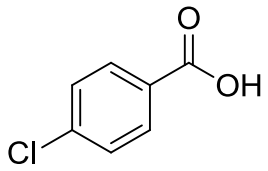
3f

4-Methoxybenzoic acid:[3] 70 mg; 92% isolated yield; white solid; m.p. = 180-183 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.07 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 171.6, 164.2, 132.5, 121.8, 113.9, 55.6; MS (EI) for $C_8H_8O_3$ $[M]^+$: 152.



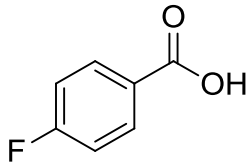
3g

2,4,5-Trimethoxybenzoic acid:[6] 102 mg; 96% isolated yield; white solid; m.p. = 141-144 ^{o}C; ^{1}H NMR（DMSO-d_6，400 MHz）12.19 (brs, 1H), 7.27 (s, 1H), 6.73(s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (DMSO-d6, 100 MHz) δ (ppm) 166.4, 154.8, 153.2, 142.1, 114.5, 110.7, 98.6, 56.7, 56.0, 55.8 ; MS (EI) for $C_{10}H_{12}O_5$ $[M]^+$: 212.



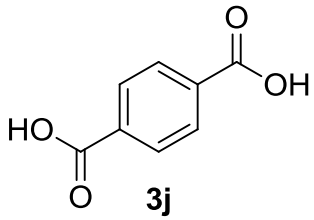
3h

4-Chlorobenzoic acid:[3] 74 mg; 95% isolated yield; white solid; m.p. = 236-238 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) 13.12 (brs, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 166.4, 137.8, 131.1, 129.6, 128.7; MS (EI) for $C_7H_5ClO_2$ $[M]^+$: 156.



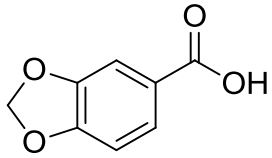
3i

4-Fluorobenzoic acid:[4] 63 mg; 90% isolated yield; white solid; m.p. = 184-186 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) 13.05 (brs, 1H), 8.02-7.98 (m, 2H), 7.31 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 171.2, 166.5 (d, $^{1}J_{CF}$ =253.7 Hz), 133.1 (d, $^{3}J_{CF}$ = 9.5 Hz), 125.7 (d, $^{4}J_{CF}$ =2.9 Hz), 115.9 (d, $^{2}J_{CF}$ =22 Hz); ^{19}F NMR (DMSO-d_6, 377 MHz) -106.9 (s). MS (EI) for $C_7H_5FO_2$ $[M]^+$: 140.



3j

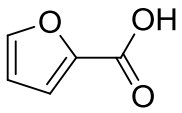
Terephthalic acid:[7] R = CN: 72 mg; 87% isolated yield; R = COOMe: 75 mg; 90% isolated yield; white solid; m.p. = 300 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) 13.30 (brs, 2H), 8.05 (s, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 166.7, 134.5, 129.5; MS (EI) for $C_8H_6O_4$ $[M]^+$: 166.



3k

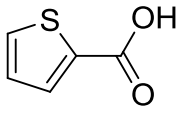
Benzo[d][1,3]dioxole-5-carboxylic acid:[8] 75 mg; 90% isolated yield; off-white solid;

m.p. = 228-229 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) 12.77 (brs, 1H), 7.54 (d, *J* = 6.4 Hz, 1H), 7.35 (s, 1H), 6.99 (d, *J* = 6.4 Hz, 1H), 6.12 (s, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 166.7, 151.2, 147.5, 125.0, 124.7, 108.9, 108.1, 102.0; MS (EI) for $C_8H_6O_4$ $[M]^+$: 166.



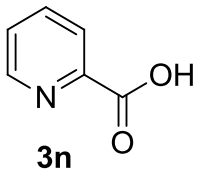
3l

Furan-2-carboxylic acid:[9] 48 mg; 86% isolated yield; off-white solid; m.p. = 128-132 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) 13.04 (brs, 1H), 7.91 (d, *J* = 0.8 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 6.66-6.64 (m, 1H) ; ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 159.3, 147.0, 144.9, 117.7, 112.1; MS (EI) for $C_5H_4O_3$ $[M]^+$: 112.



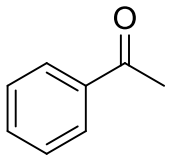
3m

Thiophene-2-carboxylic acid:[5] 60 mg; 94% isolated yield; pale yellow solid; m.p. = 133-135 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) 13.05 (brs, 1H), 7.89 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.74 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.20-7.18 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 162.9, 134.7, 133.3, 133.2,128.2; MS (EI) for $C_5H_4O_2S$ $[M]^+$: 128.



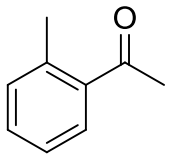
3n

2-Pyridinecarboxylic acid:[3] 55 mg; 89% isolated yield; off-white solid; m.p. = 135-137 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) 13.13 (brs, 1H), 8.71(d, *J* = 4.4 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.00-7.96 (m, 1H), 7.64-7.60 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 166.2, 149.5, 148.4, 137.6, 127.1, 124.7; MS (EI) for $C_6H_5NO_2$ $[M]^+$: 123.



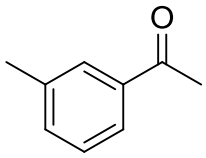
6a

Acetophenone:[10] 72% isolated yield in 8 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.92 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 198.2, 137.0, 133.1, 128.5, 128.3, 26.6; MS (EI) for C_8H_8O $[M]^+$: 120.



6b

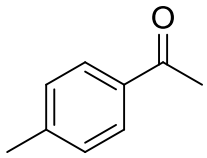
2-Methylacetophenone:[10] 14 mg; 21% isolated yield in 8 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.69 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.23-7.28 (m, 2H), 2.57 (s, 3H), 2.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 201.8, 138.5, 137.6, 132.1, 131.6, 129.5, 125.8, 29.6, 21.7; MS (EI) for $C_9H_{10}O$ $[M]^+$: 134.



6c

.

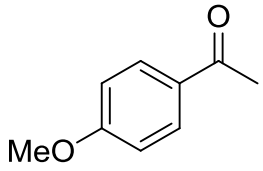
3-Methylacetophenone:[10] 60 mg; 90% isolated yield in 8 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.75 (d, *J* = 11.6 Hz, 2H), 7.32-7.38 (m, 2H), 2.58 (s, 3H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 198.5, 138.5, 137.3, 134.0, 128.9, 128.5, 125.7, 26.7, 21.4; MS (EI) for $C_9H_{10}O$ $[M]^+$: 134.



6d

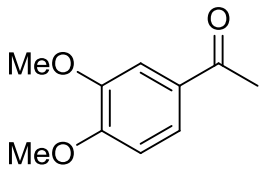
4-Methylacetophenone:[10] 57 mg; 85% isolated yield in 8 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.84 (d, *J* = 6.8 Hz, 2H), 7.24 (d, *J* = 6.8 Hz, 2H), 2.56 (s, 3H), 2.39 (s,

3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 198.0, 144.0, 134.8, 129.3, 128.5, 26.6, 21.7; MS (EI) for $C_9H_{10}O$ $[M]^+$: 134.



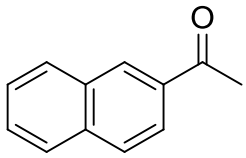
6e

4-Methoxylacetophenone:[10] 71 mg; 95% isolated yield in 8 h; m.p. = 36-38 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.94 (d, *J* = 9.2 Hz, 2H), 6.93 (d, *J* = 9.2 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 196.8, 163.5, 130.6, 130.4, 113.7, 55.5, 26.4; MS (EI) for $C_9H_{10}O_2$ $[M]^+$: 150.



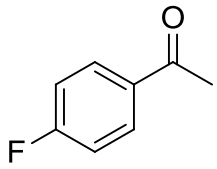
6f

3,4-Dimethoxylacetophenone:[11] 86 mg; 96% isolated yield in 8 h; m.p. = 48-52 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.53-7.56 (m, 1H), 7.49 (s, 1H), 6.84-6.87 (m, 1H), 3.90-3.91 (m, 6H), 2.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 196.9, 153.3, 149.0, 130.5, 123.3, 110.1, 110.0, 56.1, 56.0, 26.2; MS (EI) for $C_{10}H_{12}O_3[M]^+$: 180.



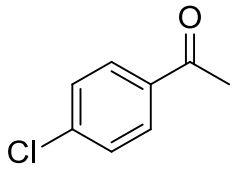
6g

2-Acetonaphthone:[12] 80 mg; 94% isolated yield in 8 h; m.p. = 51-53 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.45 (s, 1H), 8.03 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.85-7.89 (m, 2H), 7.52-7.57 (m, 2H), 2.71 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 198.1, 135.7, 134.6, 132.6, 130.3, 129.6, 128.5, 128.5, 127.9, 126.9, 124.0, 26.7; MS (EI) for $C_{12}H_{10}O$ $[M]^+$: 170.



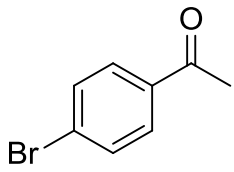
6h

4-Fluoroacetophenone:[13] 52 mg; 75% isolated yield in 16 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.95-7.98 (m, 2H), 7.11 (t, J = 8.8 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 196.6, 165.9 (d, $^{1}J_{C\text{-}F}$ = 253.3 Hz), 133.7 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 131.1 (d, $^{3}J_{C\text{-}F}$ = 9.7 Hz), 115.9 (d, $^{2}J_{C\text{-}F}$ = 21.4 Hz), 26.6; ^{19}F NMR ($CDCl_3$, 377 MHz) -105.3 (s); MS (EI) for C_8H_8FO $[M]^+$: 138.



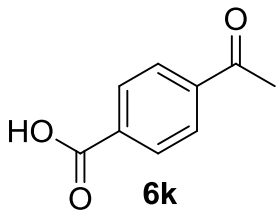
6i

4-Chloroacetophenone:[10] 65 mg; 86% isolated yield in 8 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.84 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 197.0, 139.7, 135.6, 129.9, 129.0, 26.7; MS (EI) for C_8H_8ClO $[M]^+$: 154.



6j

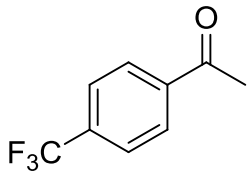
4-Bromoacetophenone:[10] 50 mg; 51% isolated yield in 16 h; m.p. = 50-52 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.79-7.82 (m, 2H), 7.58-7.60 (m, 2H), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 197.1, 135.9, 132.0, 130.0, 128.4, 26.7; MS (EI) for C_8H_8OBr $[M]^+$: 198.



6k

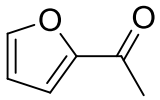
4-Acetylbenzoic acid:[5] 78 mg; 95% isolated yield in 16 h; m.p. = 208-209 ^{o}C; ^{1}H

NMR (DMSO-d_6, 400 MHz) δ (ppm) 13.32 (brs, 1H), 8.06 (s, 4H), 2.63 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 197.7, 166.7, 139.8, 134.5, 129.5, 128.3, 27.0; HRMS (ESI) for $C_9H_8O_3$ [M-H]$^-$: calc.: 163.0395; found: 163.0408.



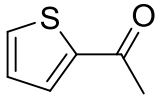
6l

4-(Trifluoromethyl)acetophenone:[14] 80 mg; 85% isolated yield in 16 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.07 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 2.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 197.1, 139.8, 134.5 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 128.7, 125.8 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.4 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 26.9; ^{19}F NMR ($CDCl_3$, 377 MHz) -62.7; MS (EI) for $C_9H_7F_3O$ [M]$^+$: 188.



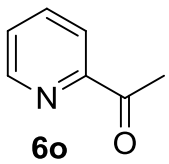
6m

2-Acetylfuran:[15] 45 mg; 82% isolated yield in 16 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.40-7.48 (m, 1H), 7.08 (d, J = 3.6 Hz, 1H), 6.42-6.43 (m, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 186.6, 152.7, 146.4, 117.2, 112.1, 25.8; MS (EI) for $C_6H_6O_2$ [M]$^+$: 110.



6n

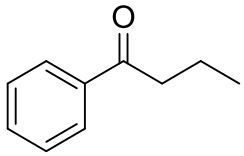
2-Acetylthiophene:[16] 48 mg; 76% isolated yield in 16 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):7.64-7.72 (m, 2H), 7.13-7.15 (m, 1H), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 190.7, 144.5, 133.8, 132.5, 128.1, 26.8; MS (EI) for C_6H_6OS [M]$^+$: 126.



6o

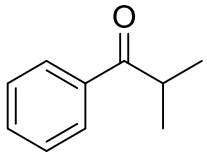
2-Acetylpyridine:[16] 50 mg; 83% isolated yield in 16 h; ^{1}H NMR ($CDCl_3$, 400 MHz)

δ (ppm) 8.58 (d, *J* = 4.8 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.71-7.75 (m, 1H), 7.37 (t, *J* = 5.6 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 200.0, 153.5, 149.0, 136.8, 127.1, 121.6, 25.7; MS (EI) for C_7H_7NO $[M]^+$: 121.



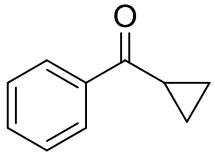
6p

1-Phenylbutan-1-one:[17] 70 mg; 95% isolated yield in 16 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.94-7.97 (m, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 1.74-1.80 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 200.3, 137.1, 132.8, 128.5, 128.0, 40.5, 17.7, 13.9; MS (EI) for $C_{10}H_{12}O$ $[M]^+$: 148.



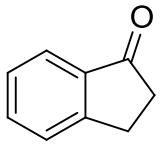
6q

2-Methyl-1-phenylpropan-1-one:[17] 64 mg; 86% isolated yield in 16 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.95 (d, *J* = 7.2 Hz, 2H), 7.52-7.56 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 3.52-3.59 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 204.6, 136.3, 132.9, 128.7, 128.4, 35.4, 19.2; MS (EI) for $C_{10}H_{12}O$ $[M]^+$: 148.



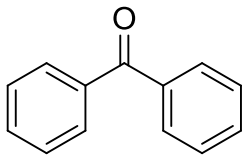
6r

Cyclopropyl(phenyl)methanone:[13] 64 mg; 86% isolated yield in 16 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.01 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 2.64-2.70 (m, 1H), 1.22-1.25 (m, 2H), 1.01-1.05 (m, 2H),; ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 200.7, 138.1, 132.8, 128.6, 128.1, 17.2, 11.7; MS (EI) for $C_{10}H_{10}O$ $[M]^+$: 146.



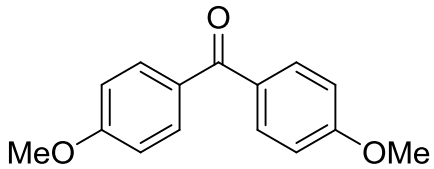
6s

1-Indanone:[18] 63 mg; 95% isolated yield in 16 h; m.p. = 37-39 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.76 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 3.14 (t, *J* = 5.6 Hz, 2H), 2.67-2.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 207.2, 155.3, 137.2, 134.7, 127.4, 126.8, 123.8, 36.3, 25.9; MS (EI) for C_9H_8O $[M]^+$: 132.



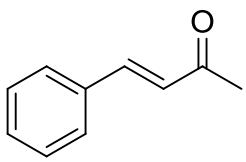
6t

Benzophenone:[12] 86 mg; 95% isolated yield in 16 h; m.p. = 47-48 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.81 (d, *J* = 7.2 Hz, 4H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 196.7, 137.7, 132.5, 130.2, 128.4; MS (EI) for $C_{13}H_{10}O$ $[M]^+$: 182.



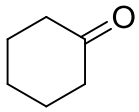
6u

4,4'-Dimethoxybenzophenone:[19] 116 mg; 96% isolated yield in 16 h; m.p. = 150-152 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.78 (d, *J* = 8.8 Hz, 4H), 6.95 (t, *J* = 8.4 Hz, 4H), 3.87 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 194.6, 162.9, 132.3, 130.9, 113.6, 55.6; MS (EI) for $C_{15}H_{14}O$ $[M]^+$: 242.



6v

(E)-4-Phenylbut-3-en-2-one:[20] 61 mg; 84% isolated yield in 16 h; m.p. = 39-41 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.48-7.52 (m, 3H), 7.37-7.38 (m, 3H), 6.70 (d, *J* = 16 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 198.4, 143.5, 134.5, 130.6, 129.0, 128.3, 127.2, 27.5; MS (EI) for $C_{10}H_{11}O$ $[M]^+$: 146.



6w

Cyclohexanone:[12] 90% GC yield in 16 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 2.29 (t, *J* = 6.4 Hz, 4H), 1.79-1.85 (m, 4H), 1.66-1.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 212.2, 42.0, 27.1, 25.0; MS (EI) for $C_6H_{10}O$ $[M]^+$: 98. GC parameters: injector temperature 230 ℃; FID detector, temperature 250 ℃; column temperature program: 50 ℃ followed by a ramp at 1 ℃/min to 60 ℃. cyclohexanone (t_R = 7.665 min), cyclohexanol (t_R = 7.272 min).

10. References

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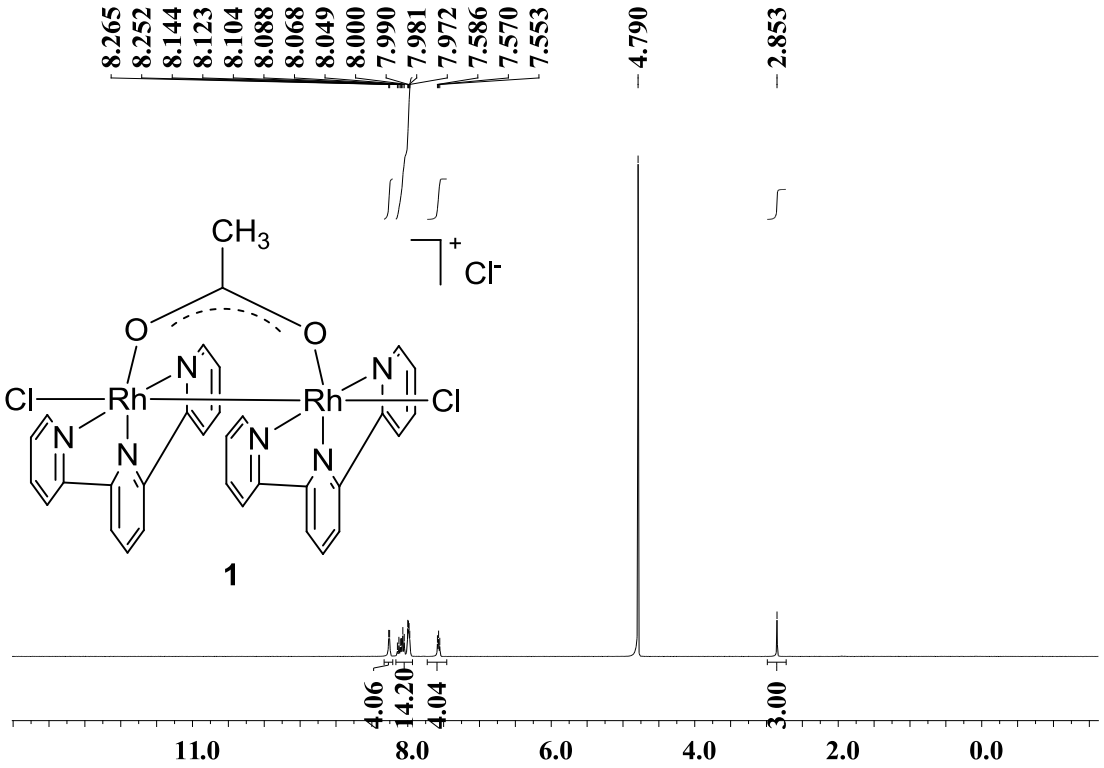
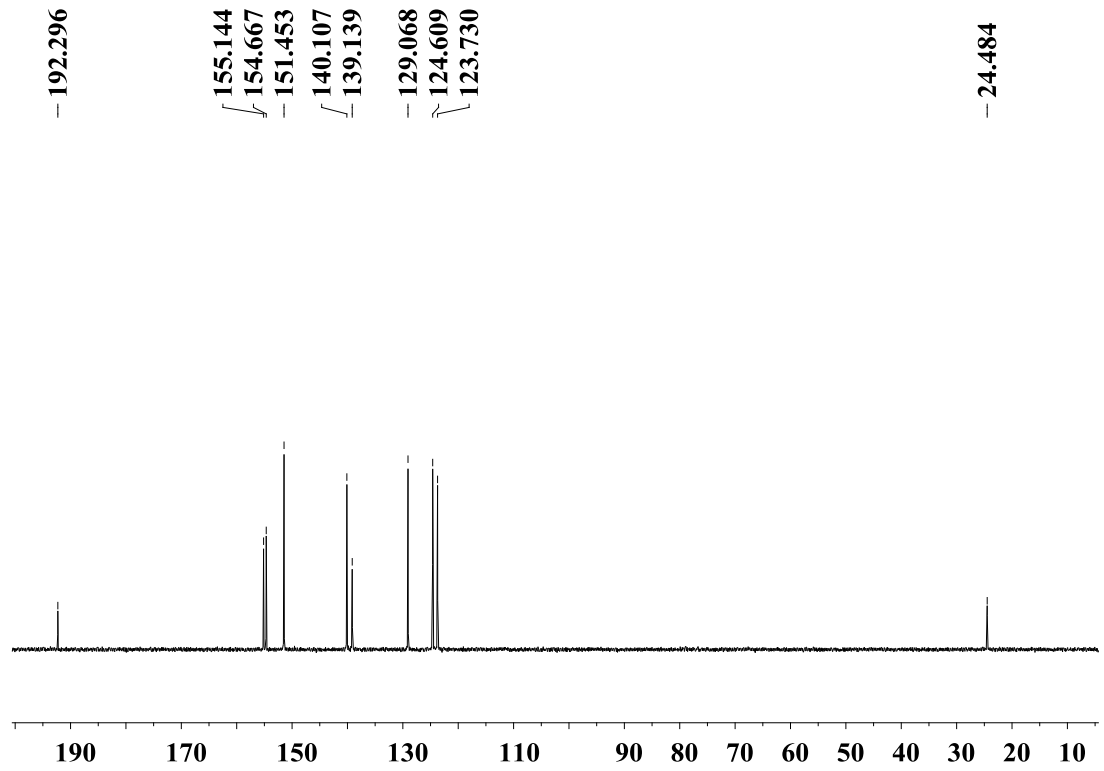
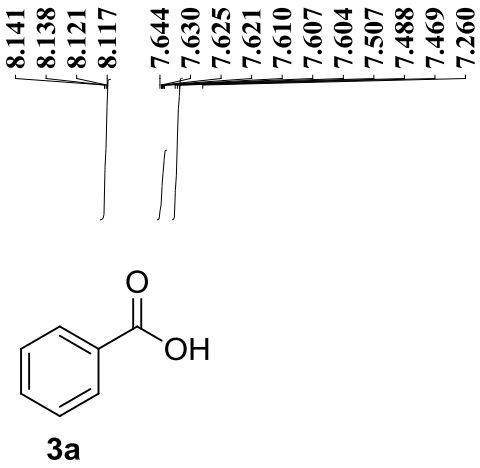
11. Traces of ^{1}H NMR and ^{13}C NMR spectra



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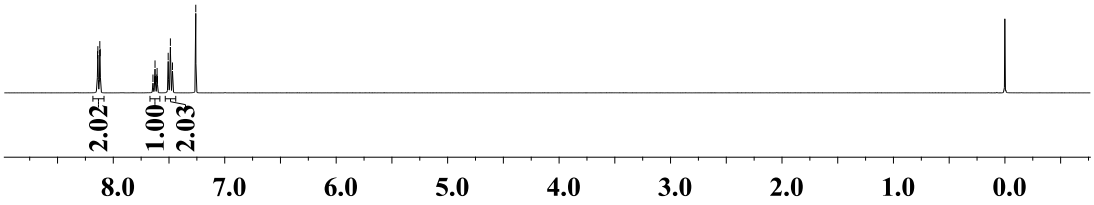
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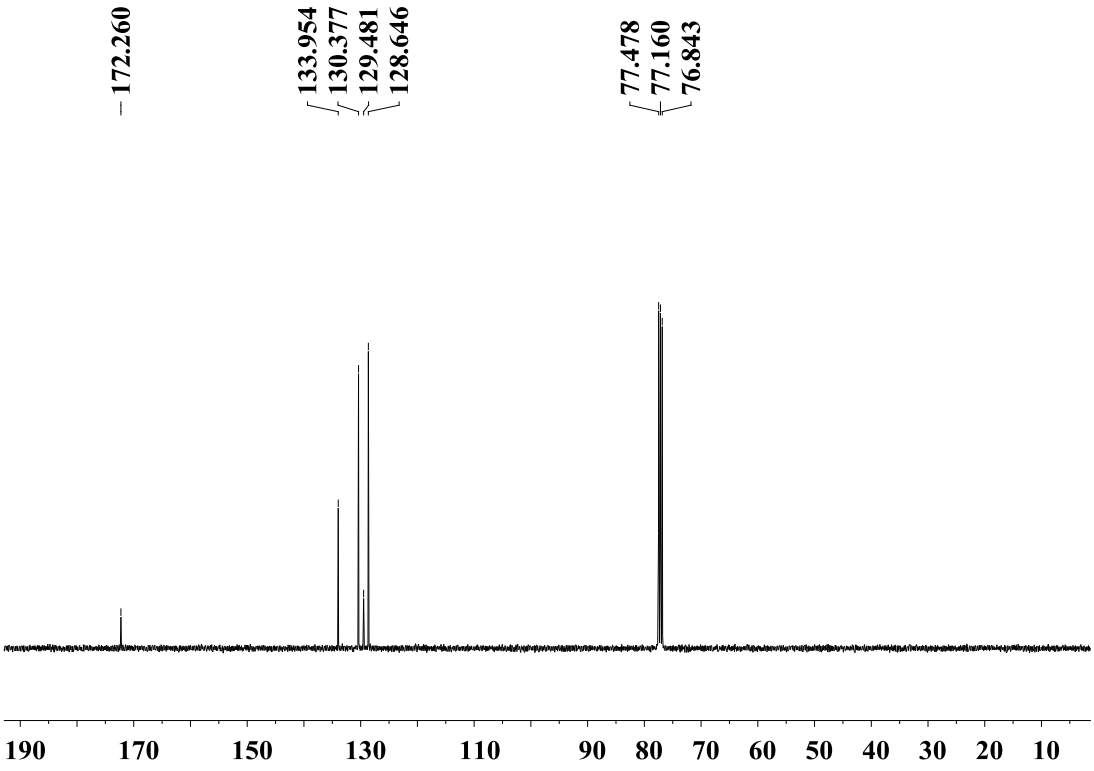
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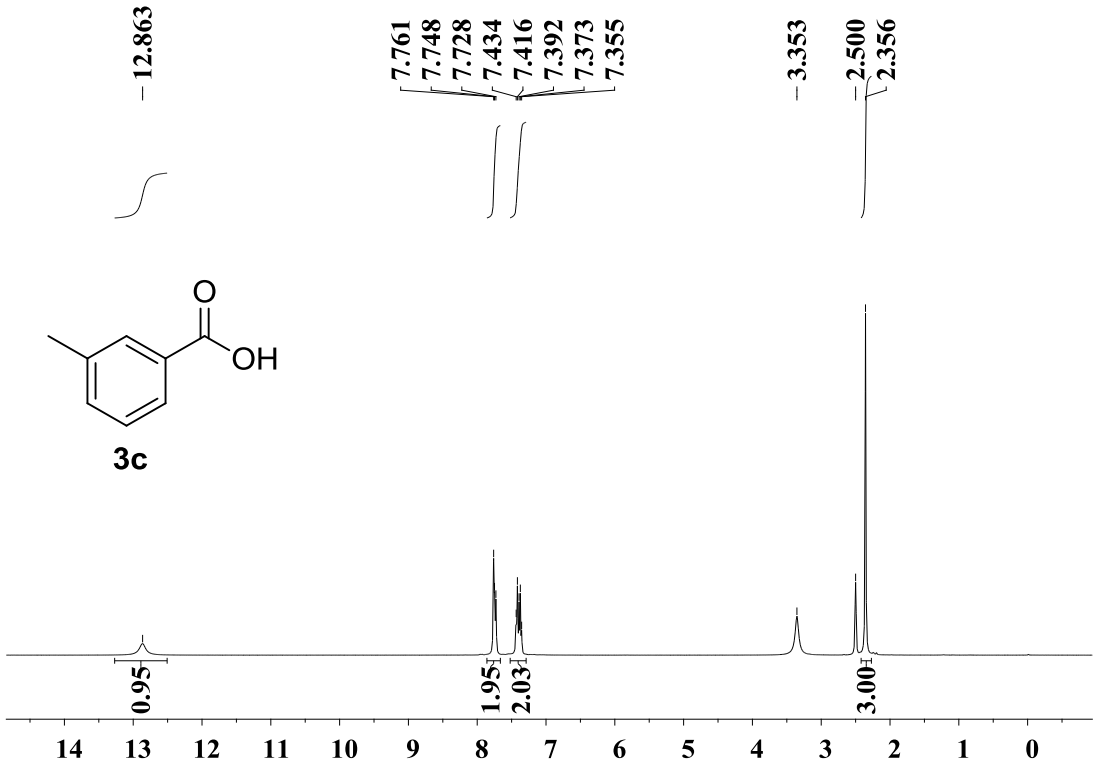
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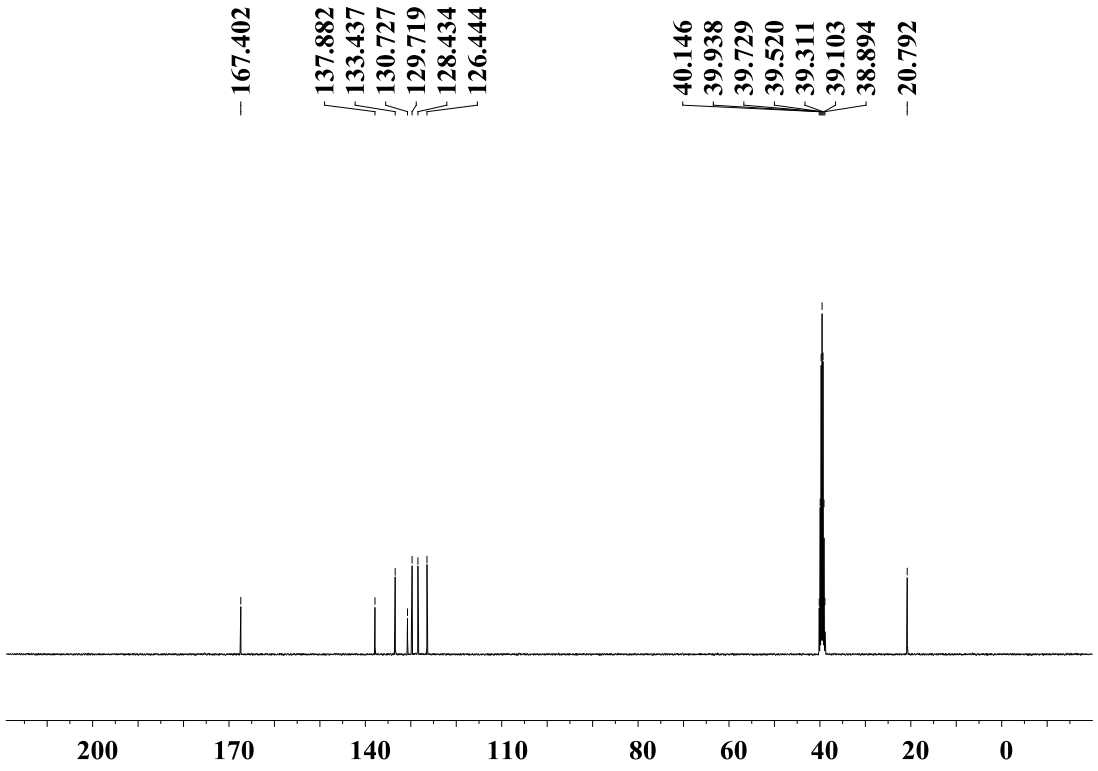
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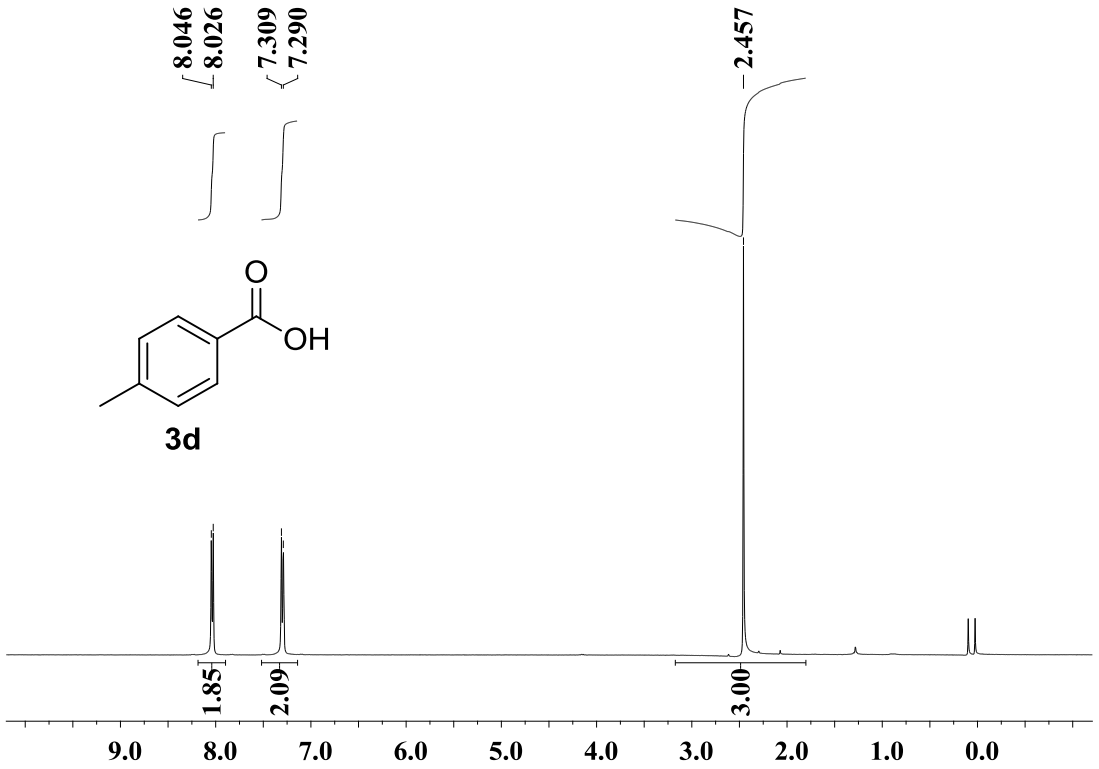
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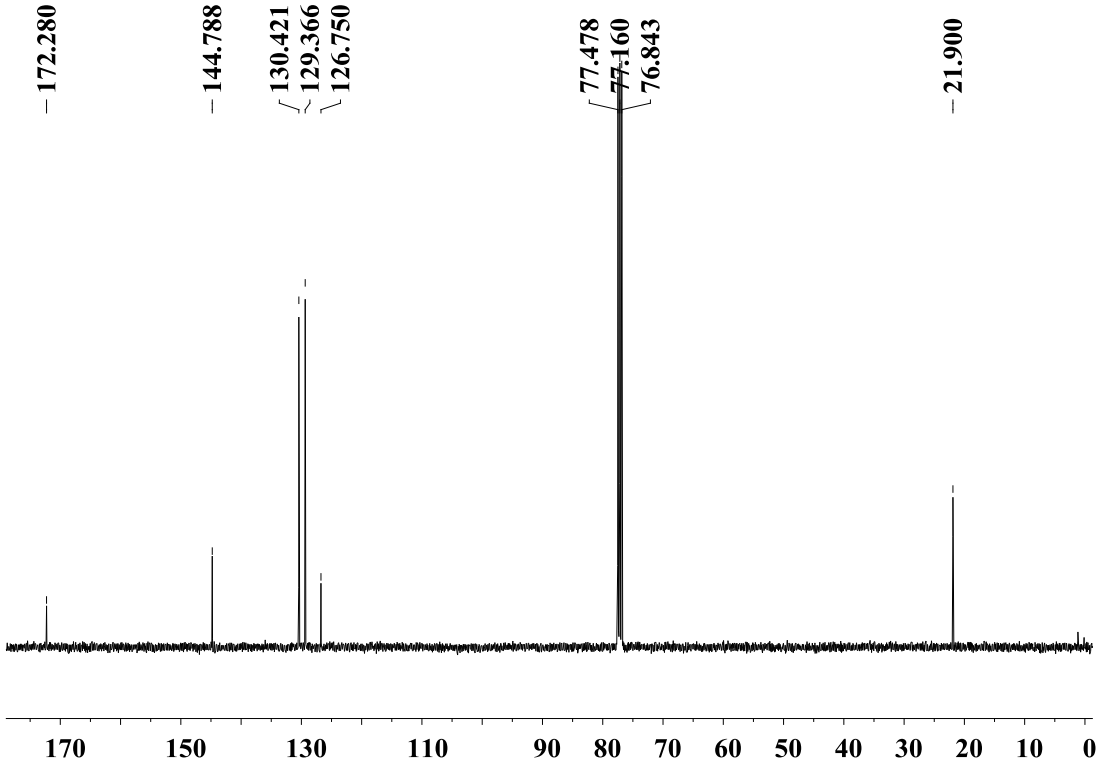
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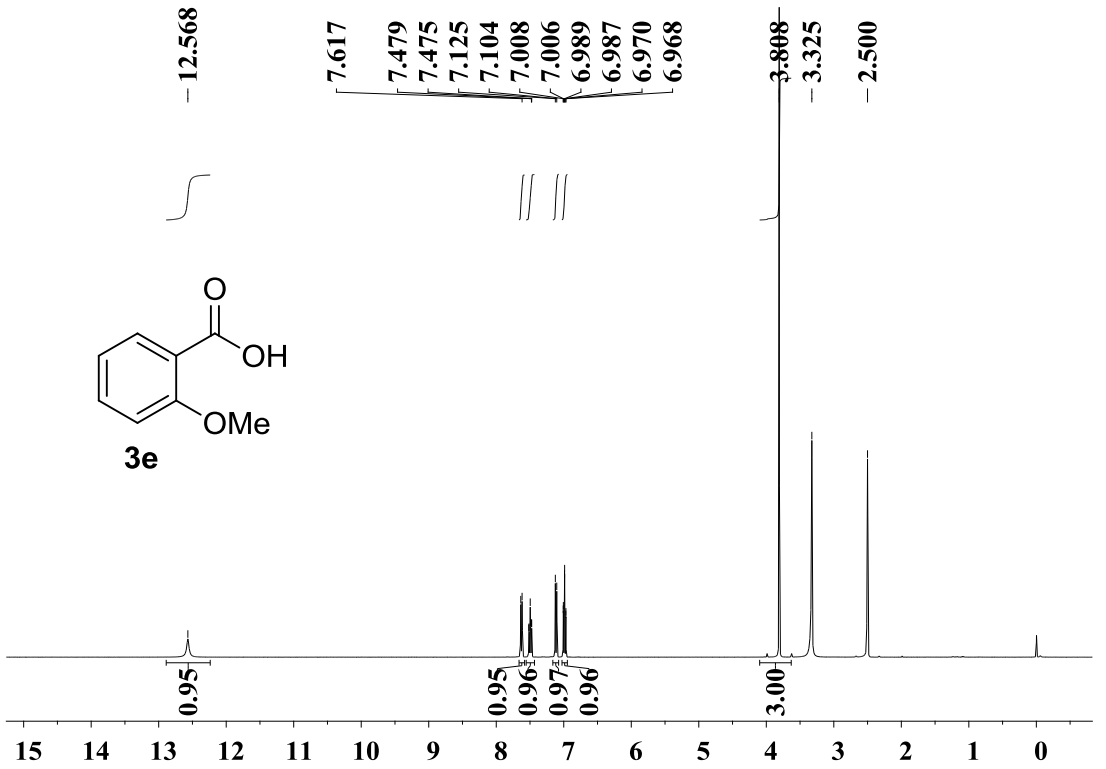
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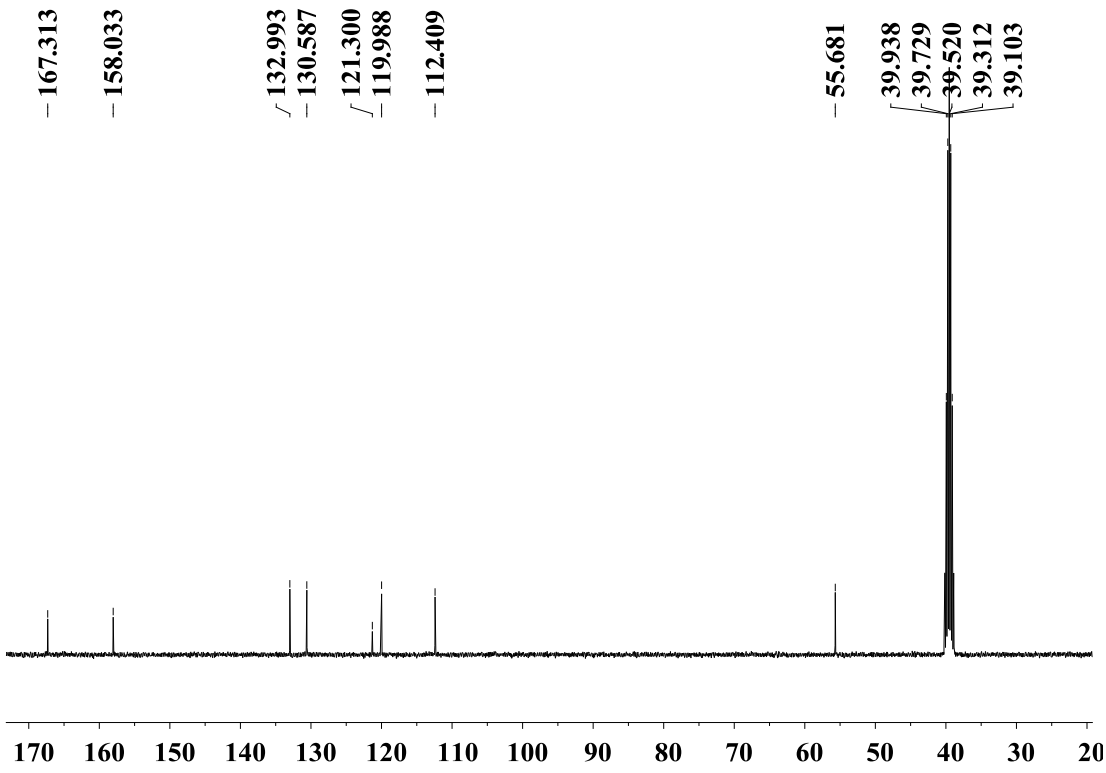
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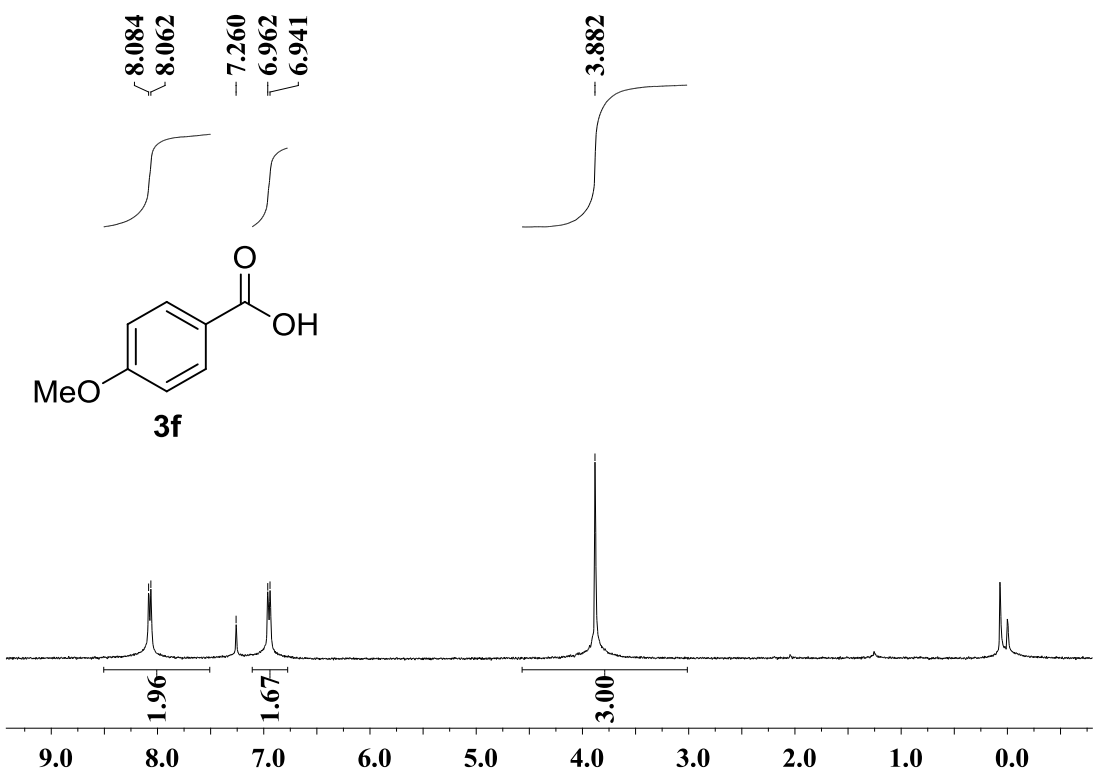
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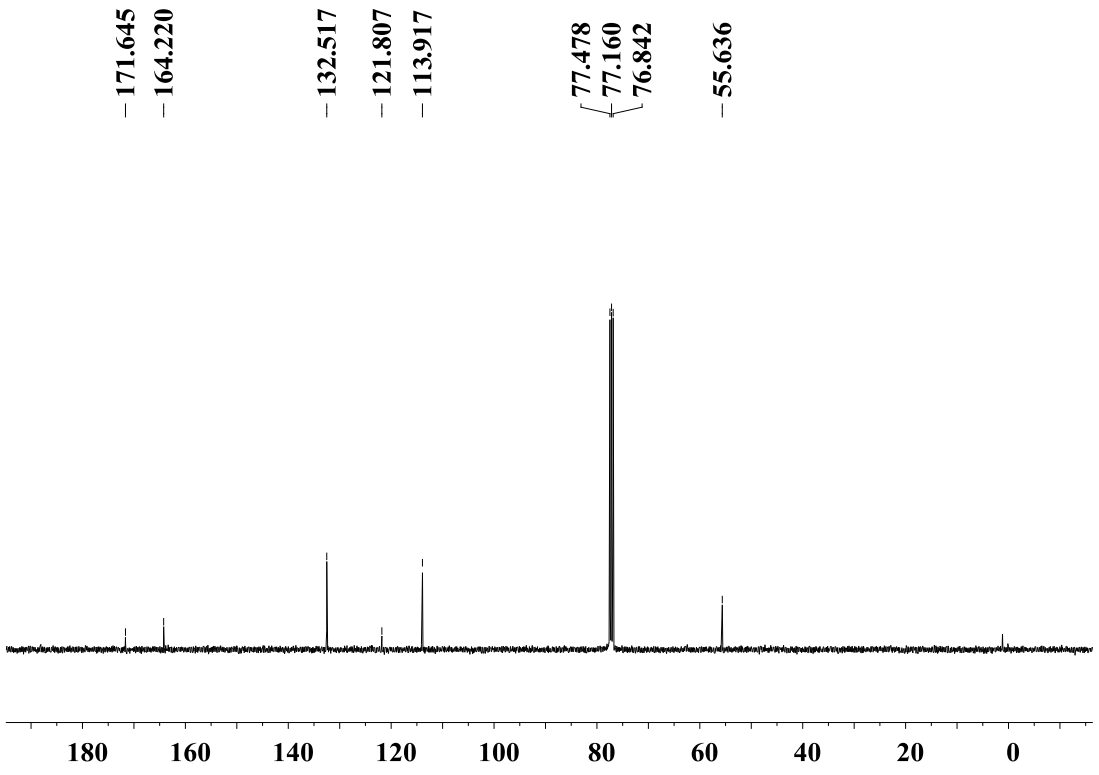
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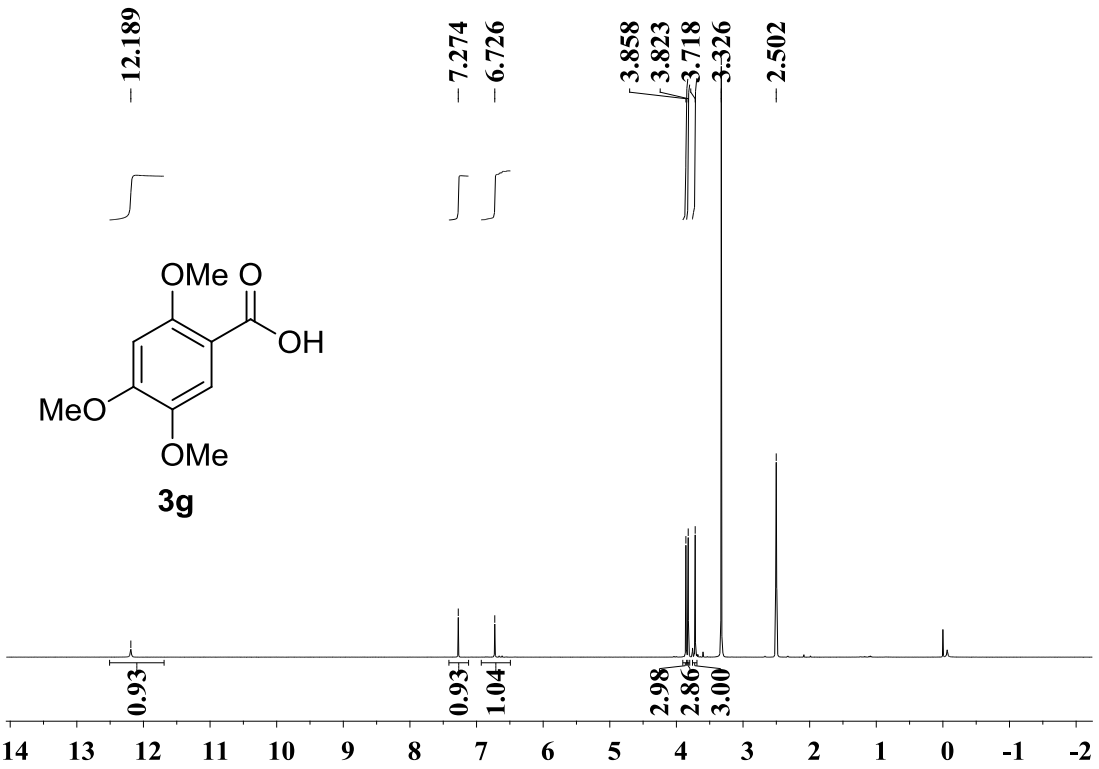
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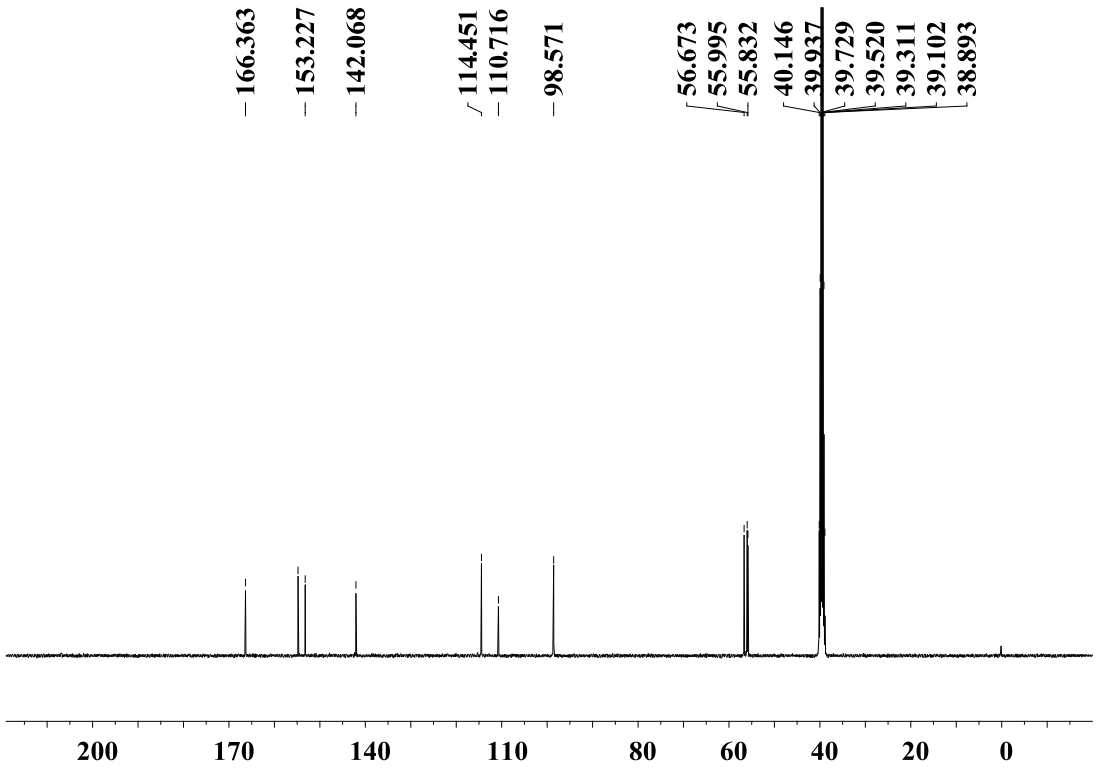
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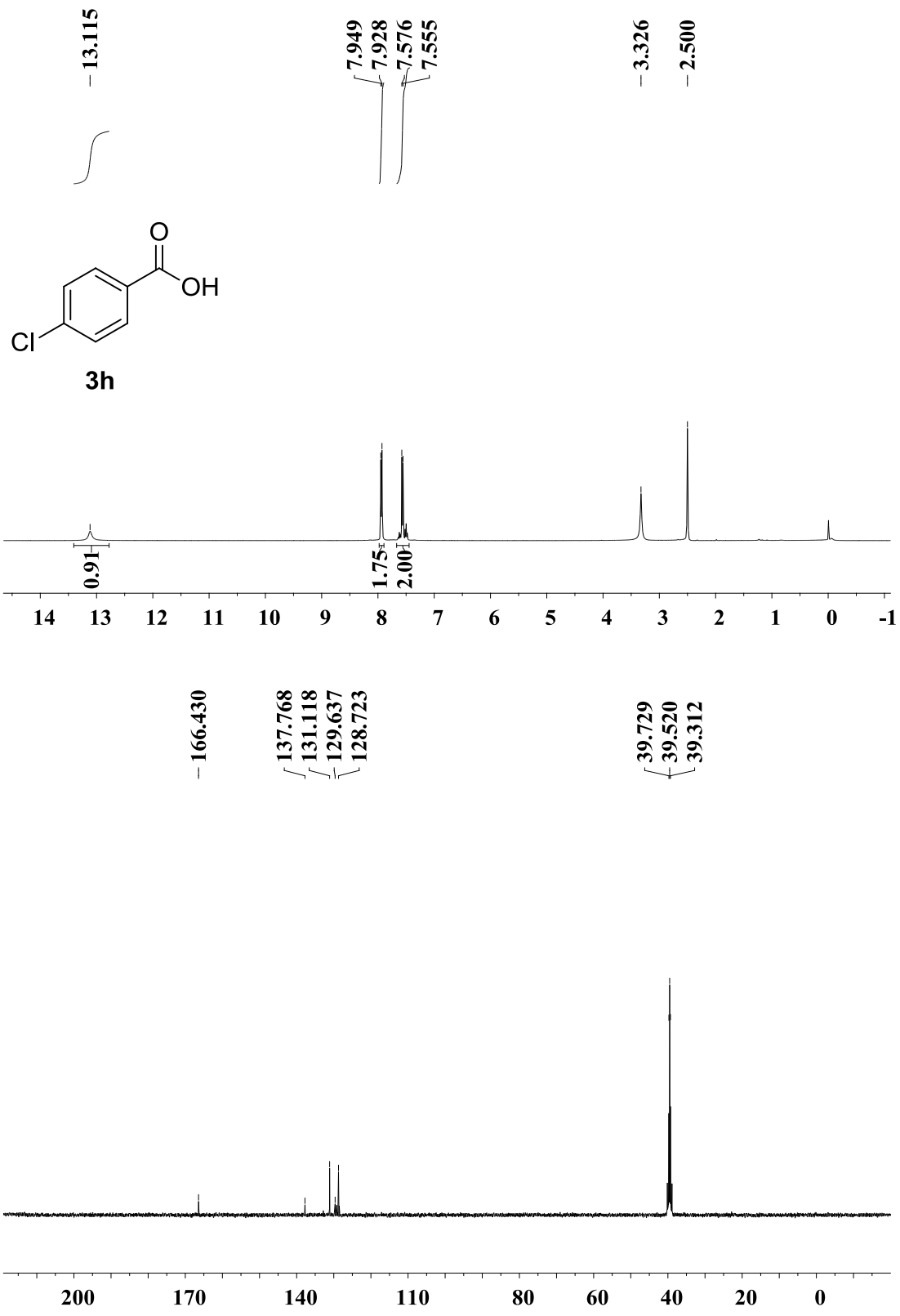
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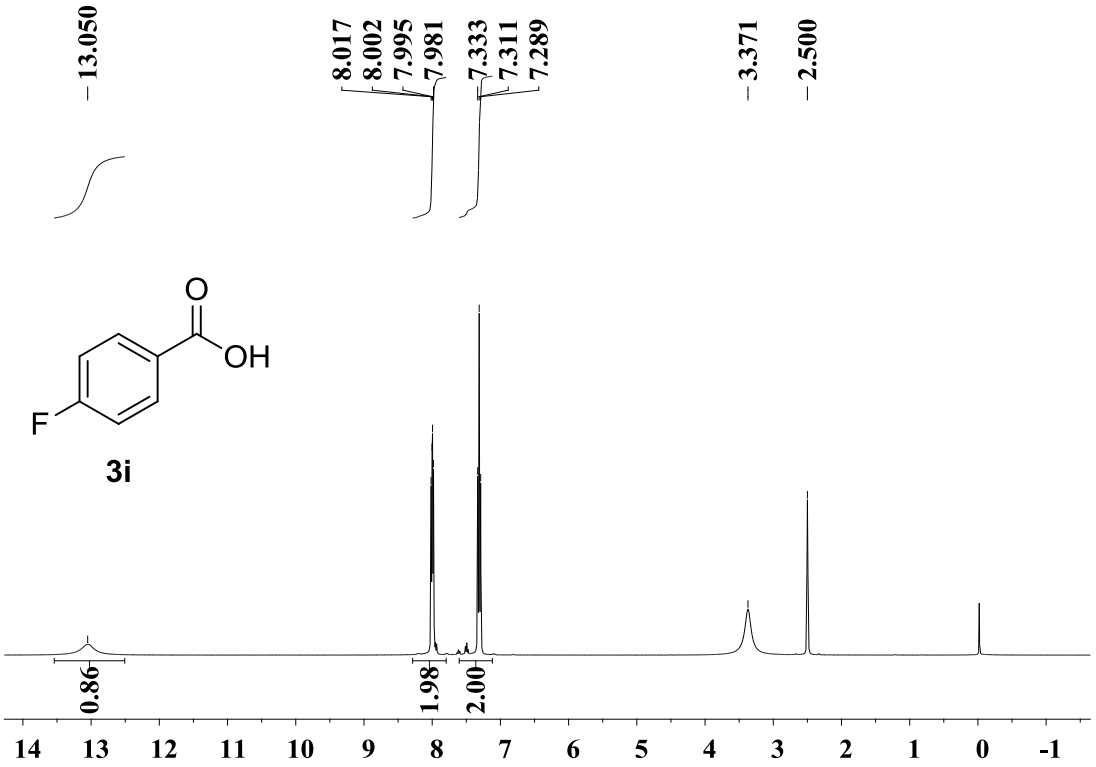
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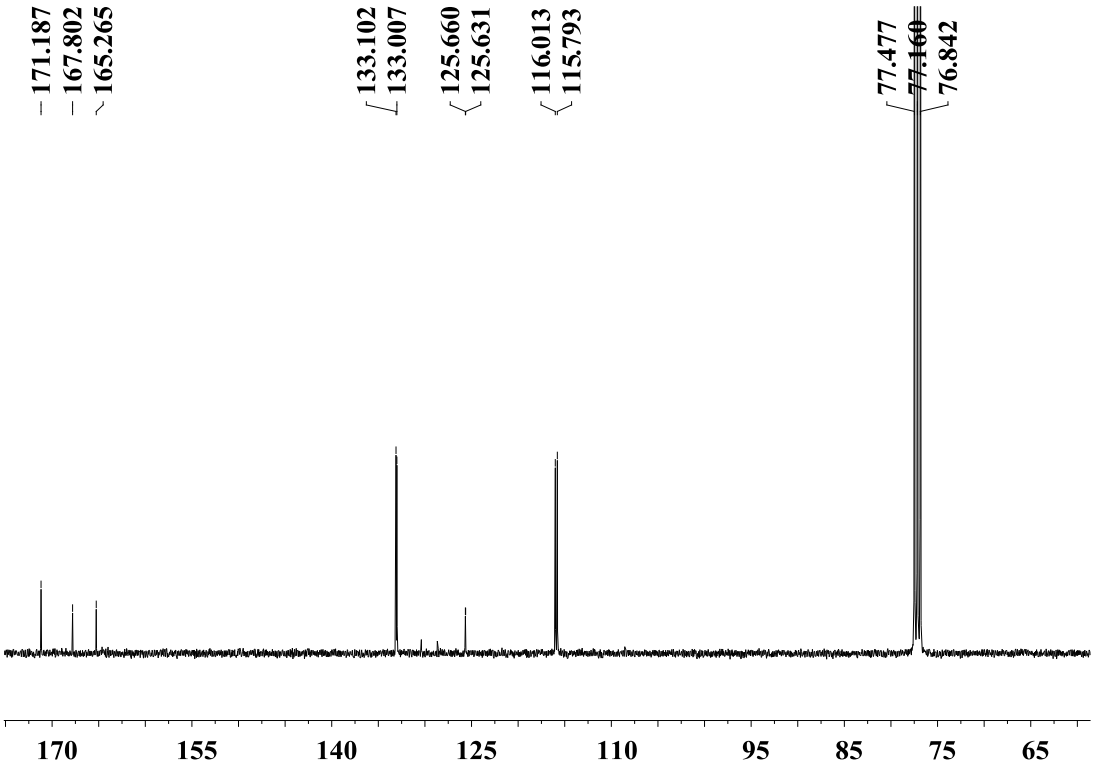
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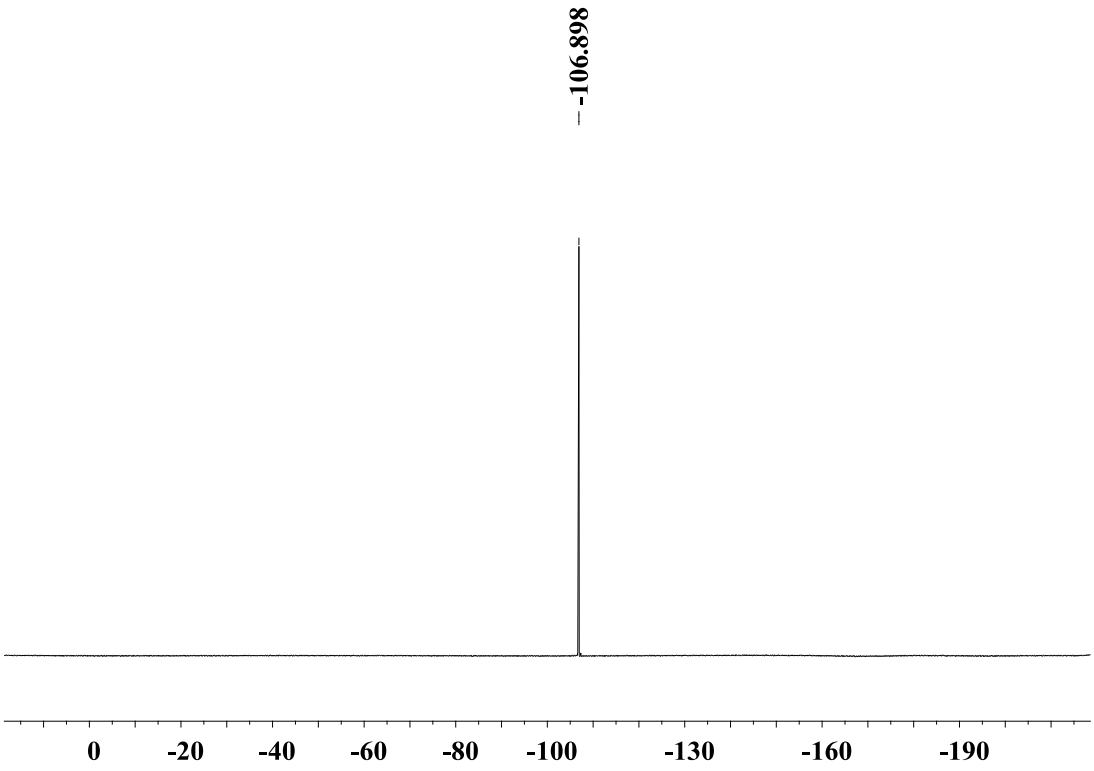
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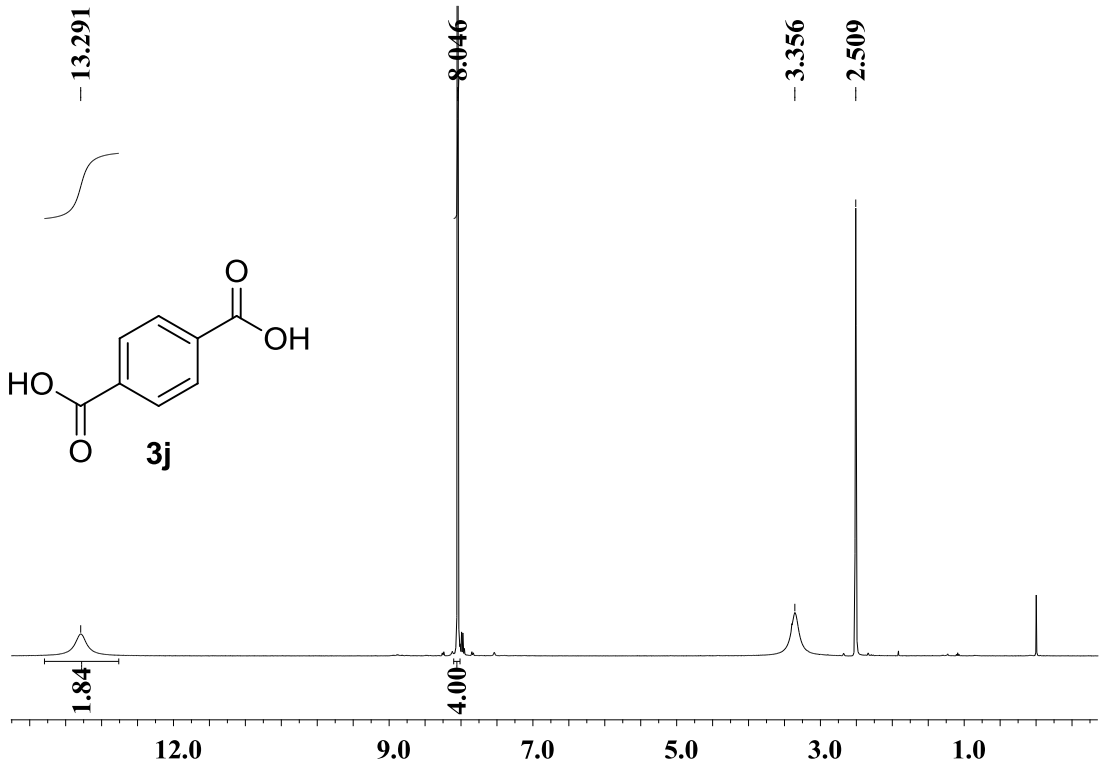
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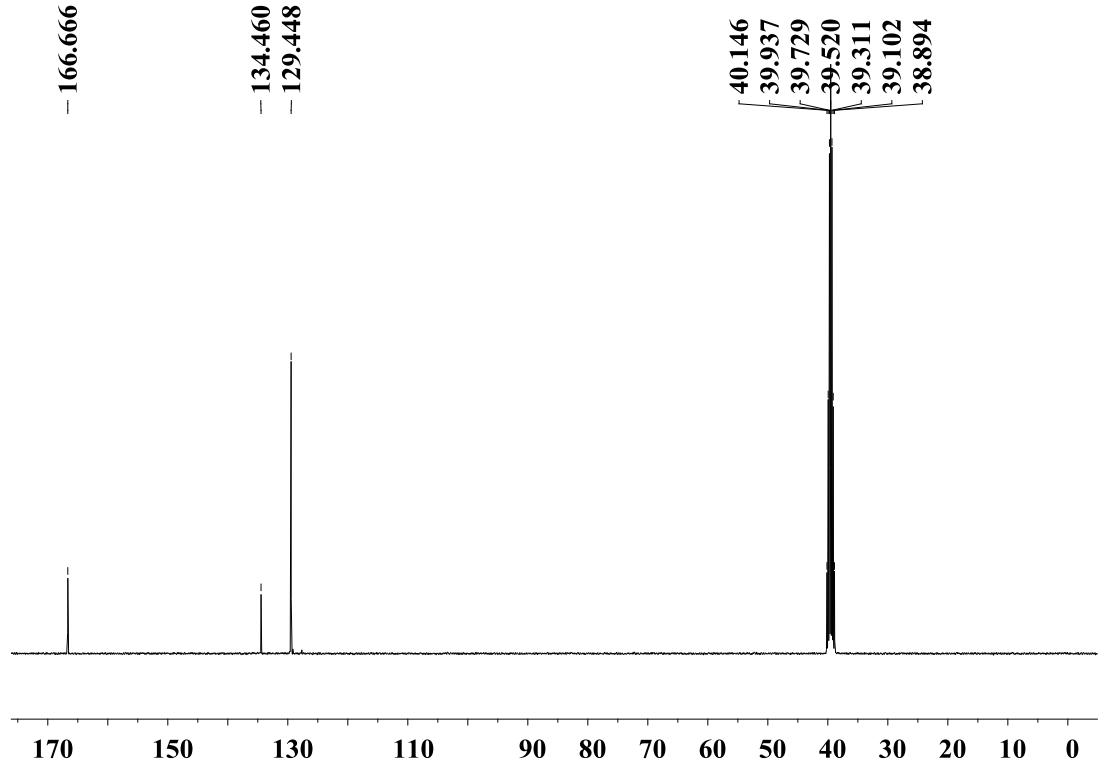
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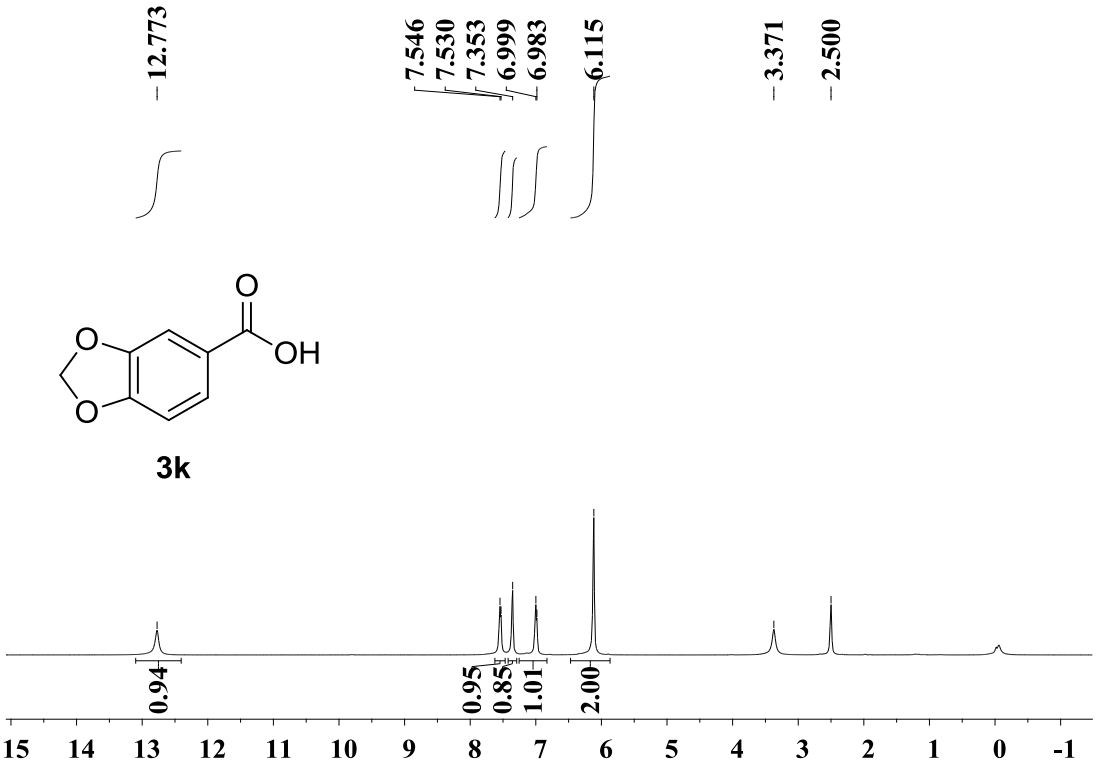
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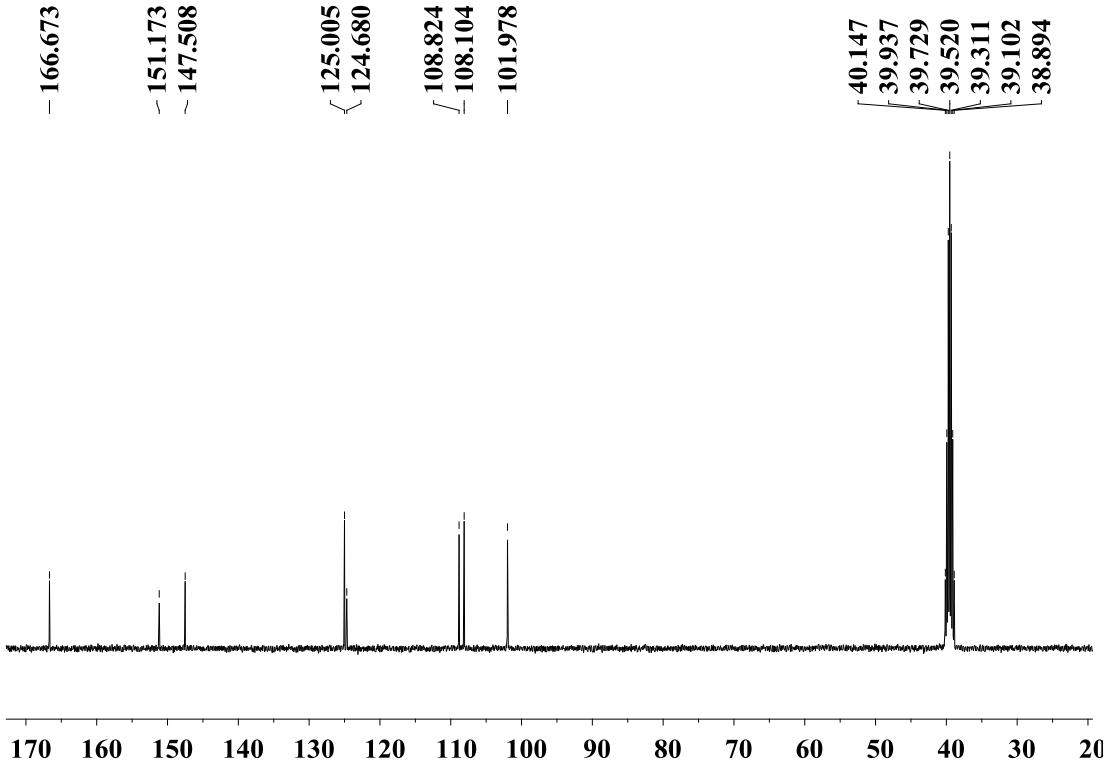
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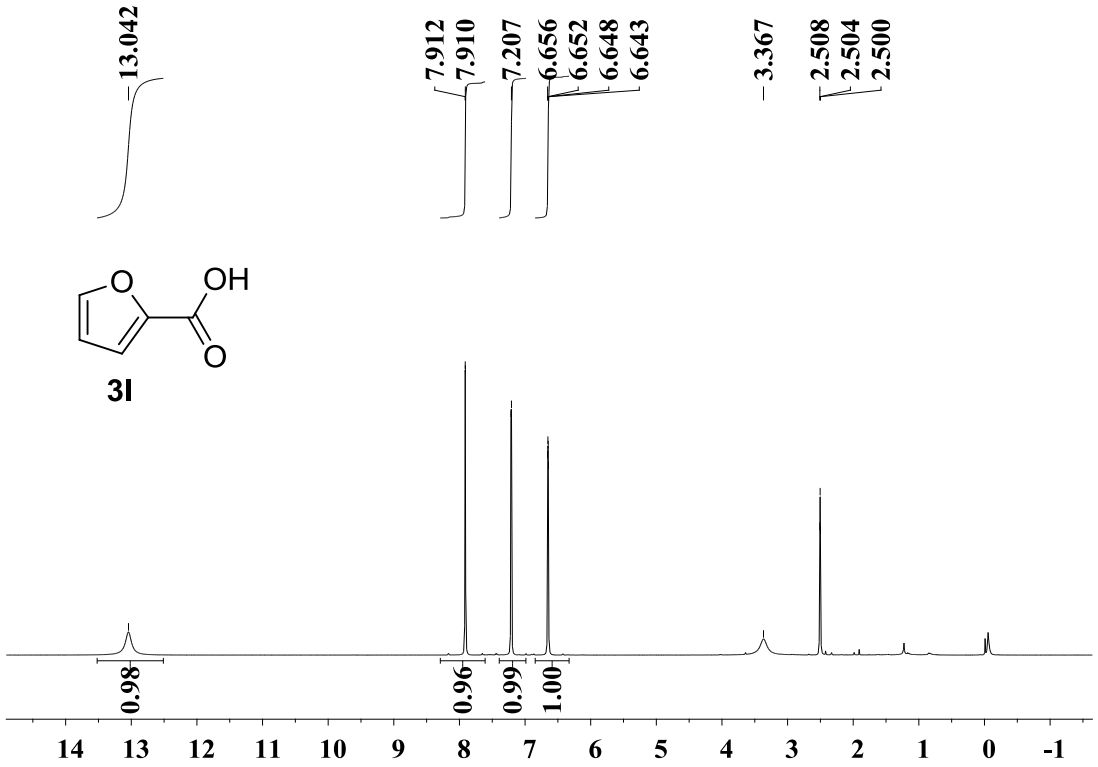
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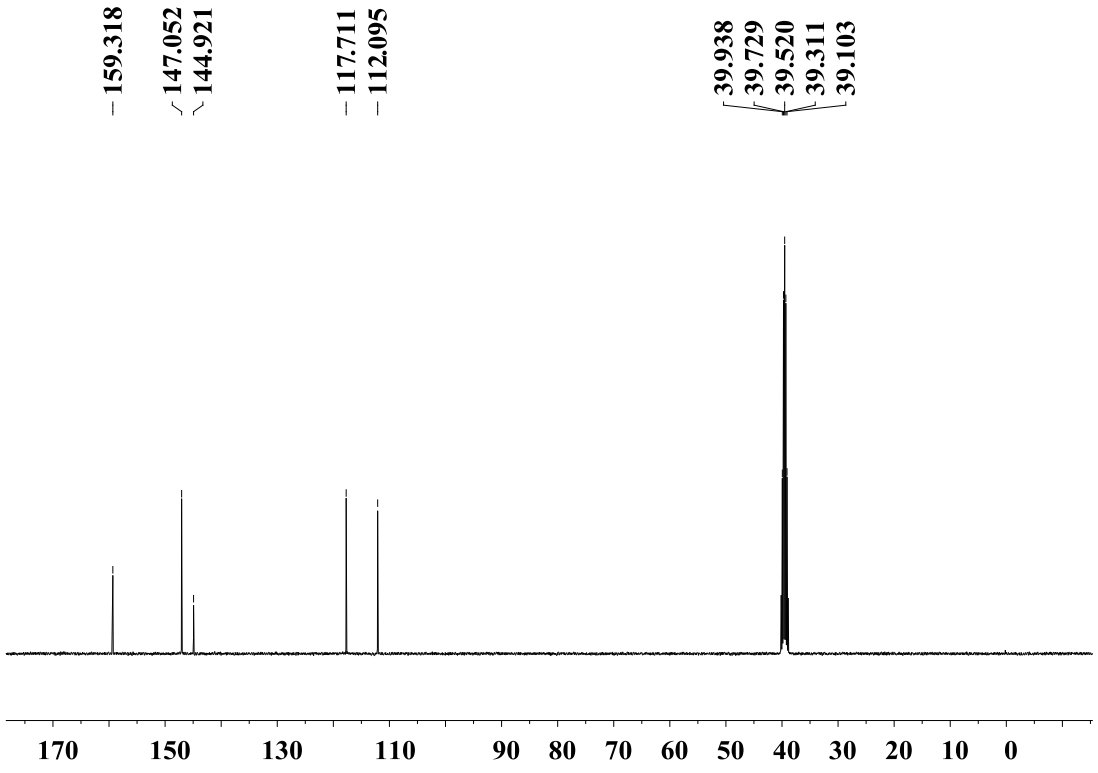
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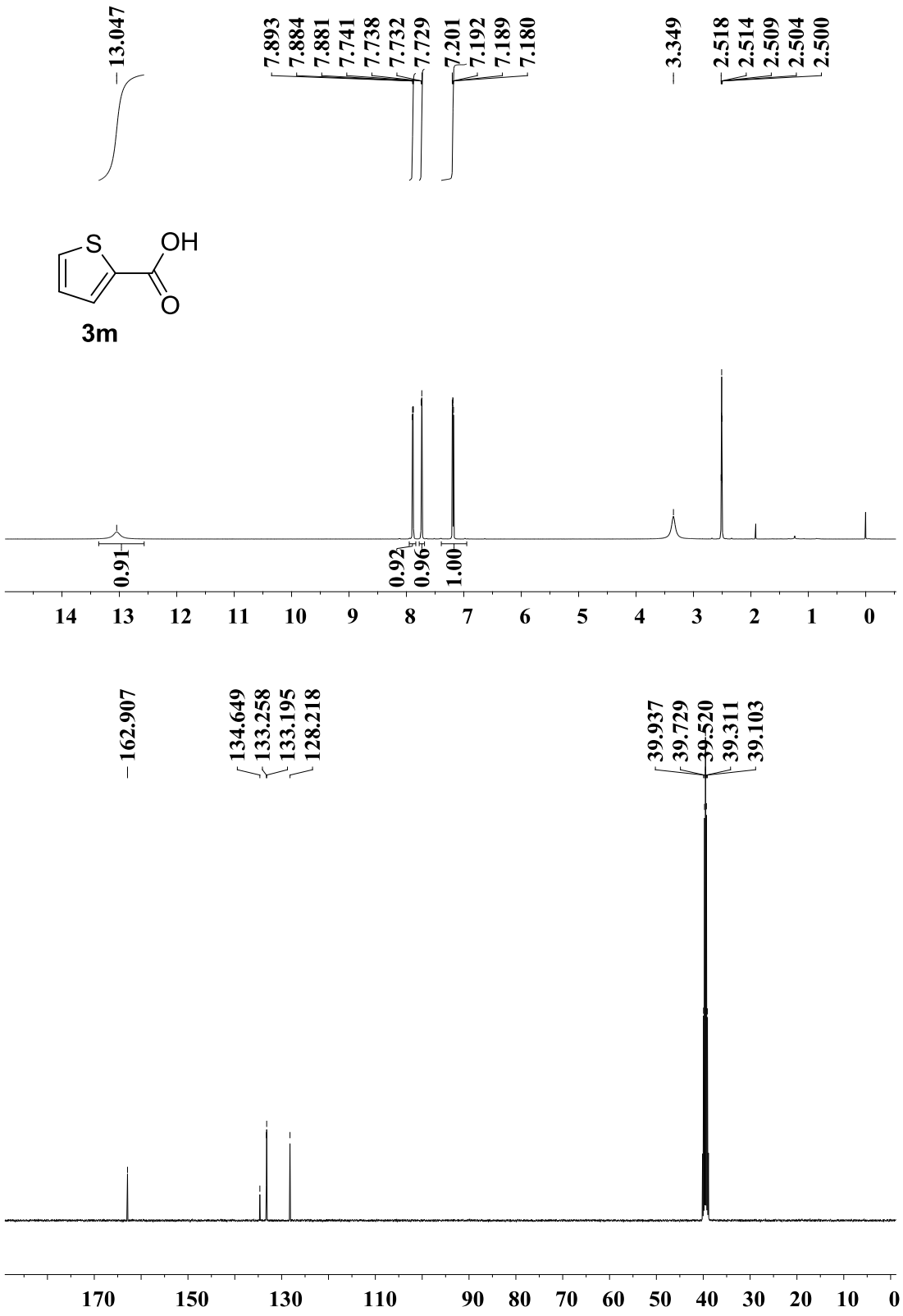
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2.514
2.509
2.504
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OH
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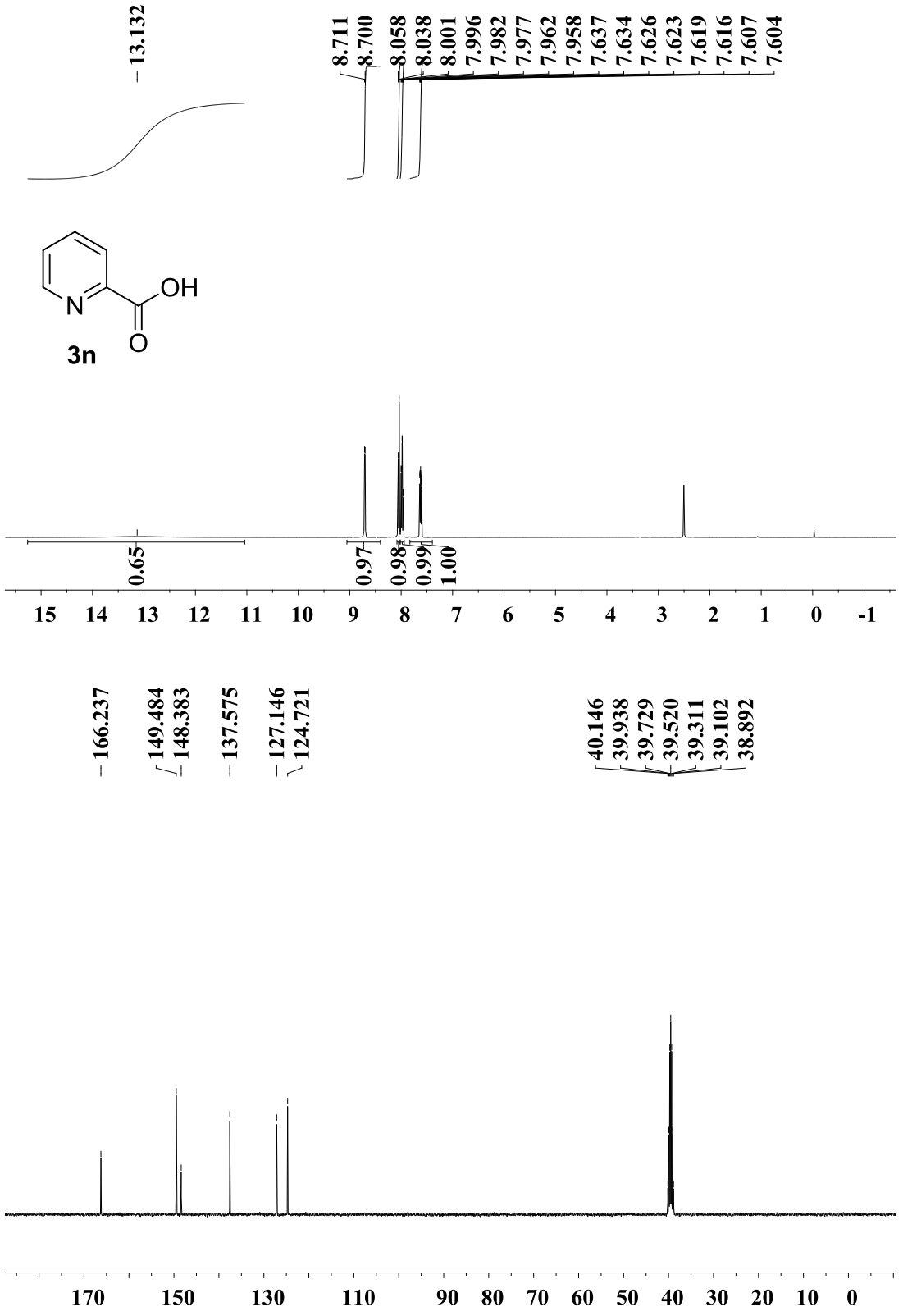
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7.623
7.619
7.616
7.607
7.604
OH
N
O
3n
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0.97
0.98
0.99
1.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
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148.383
137.575
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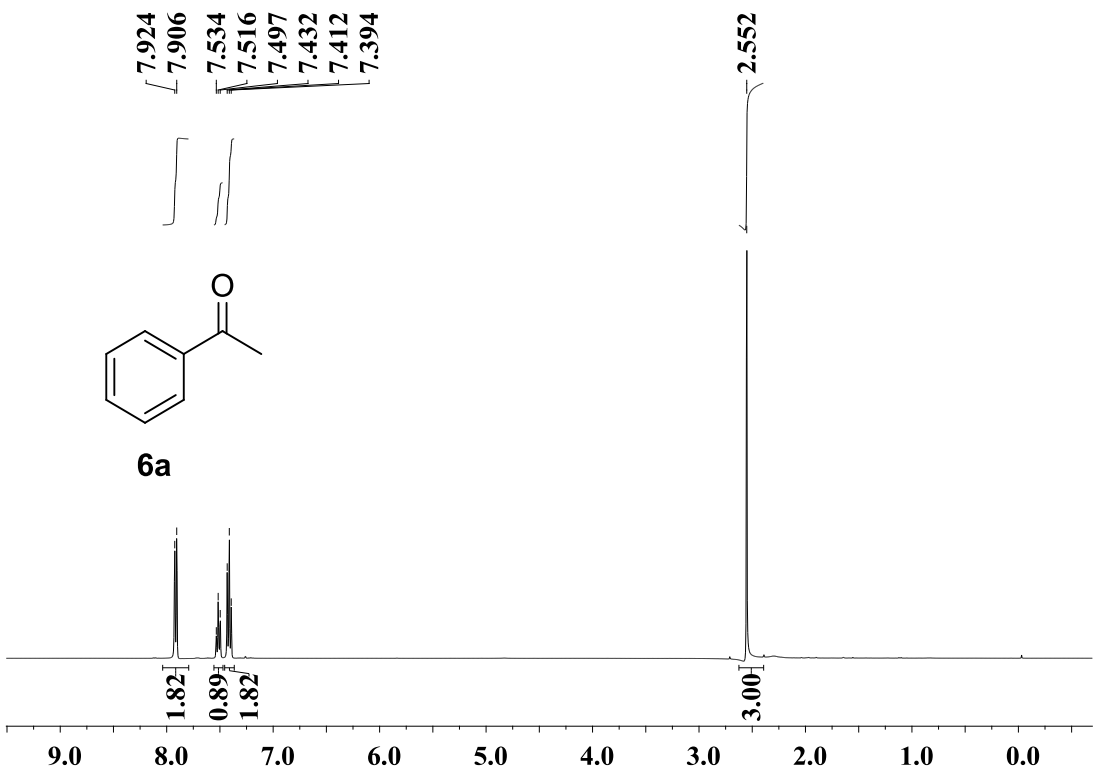
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7.394
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O
6a
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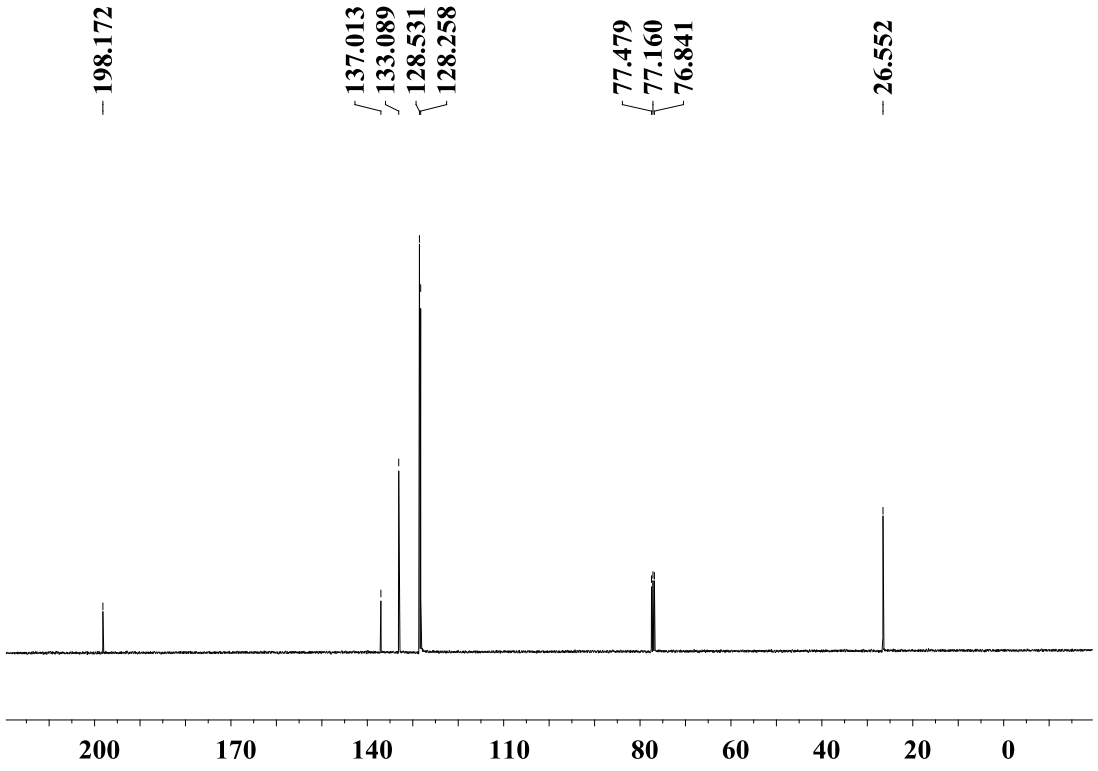
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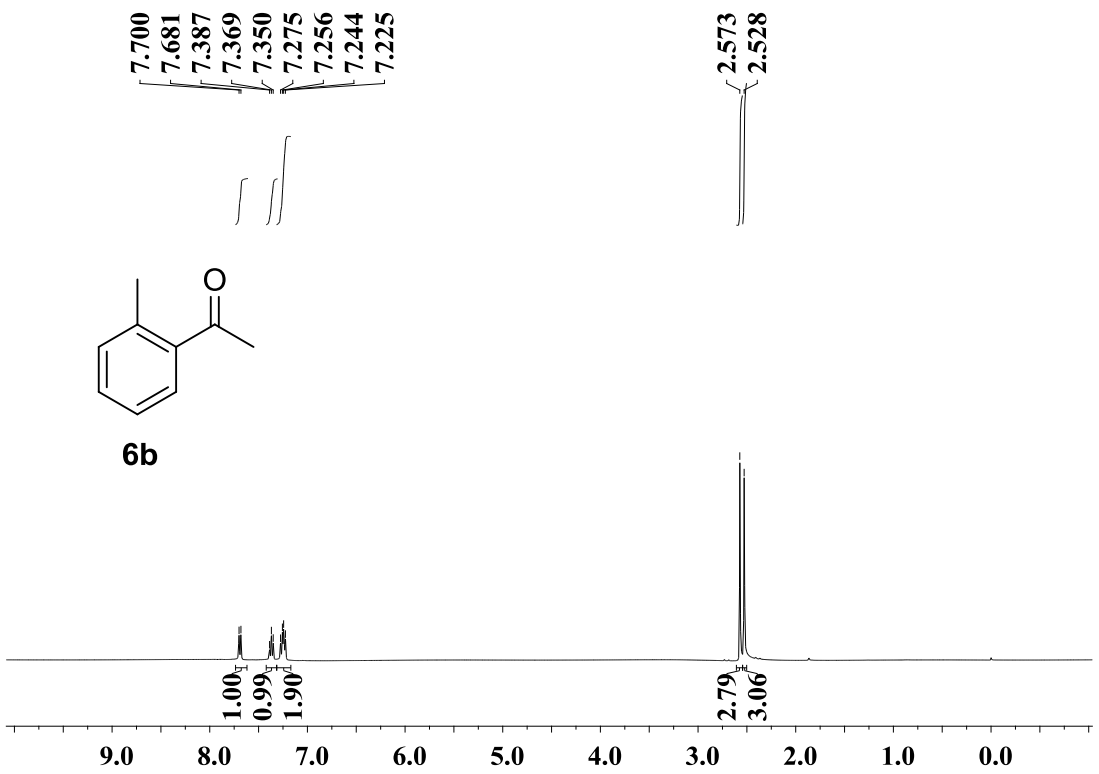
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7.244
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2.573
2.528
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0.99
1.90
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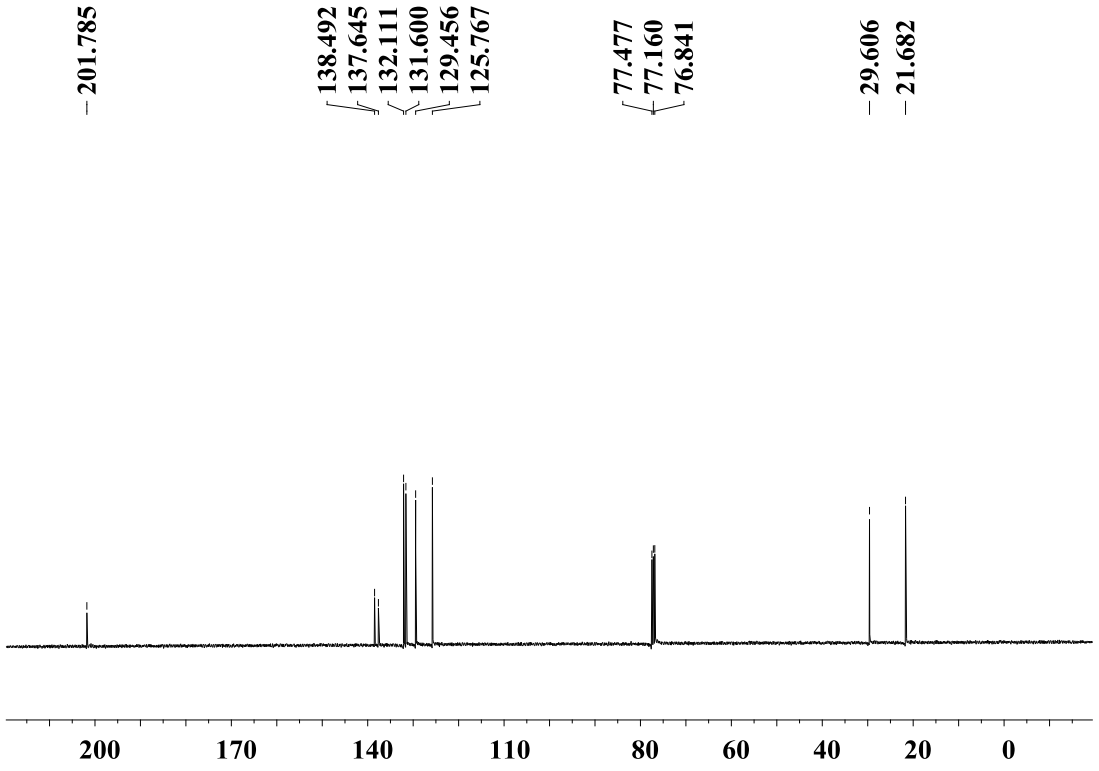
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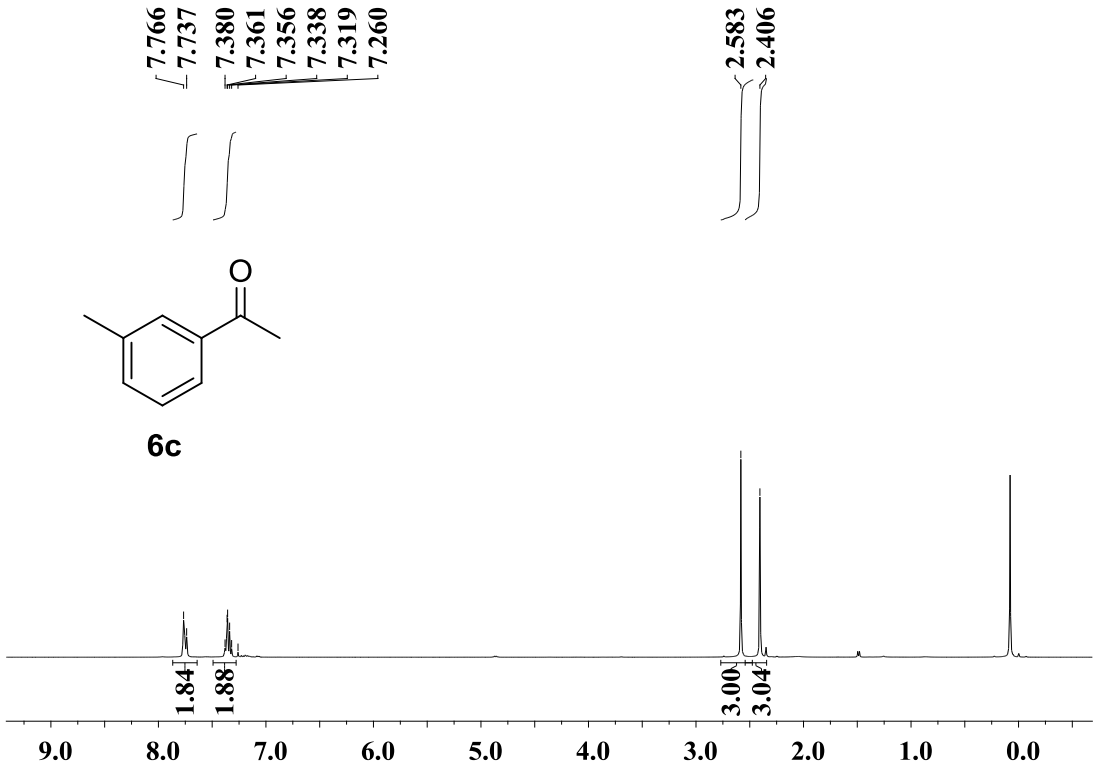
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6c
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1.88
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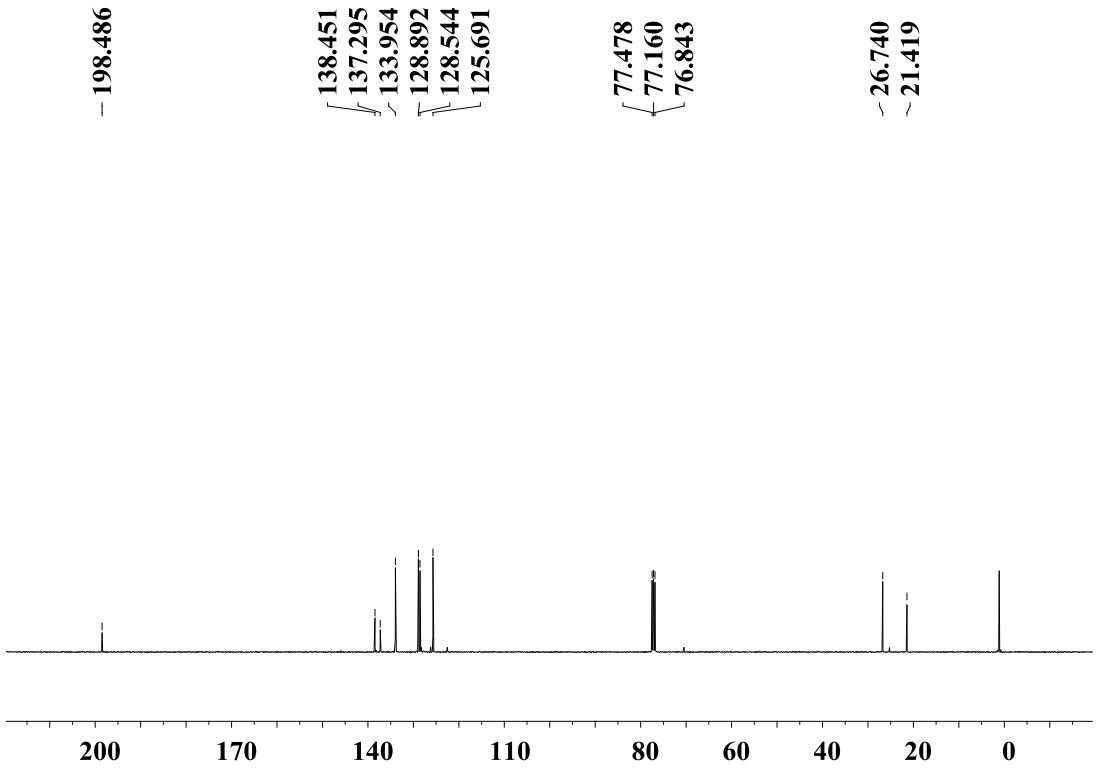
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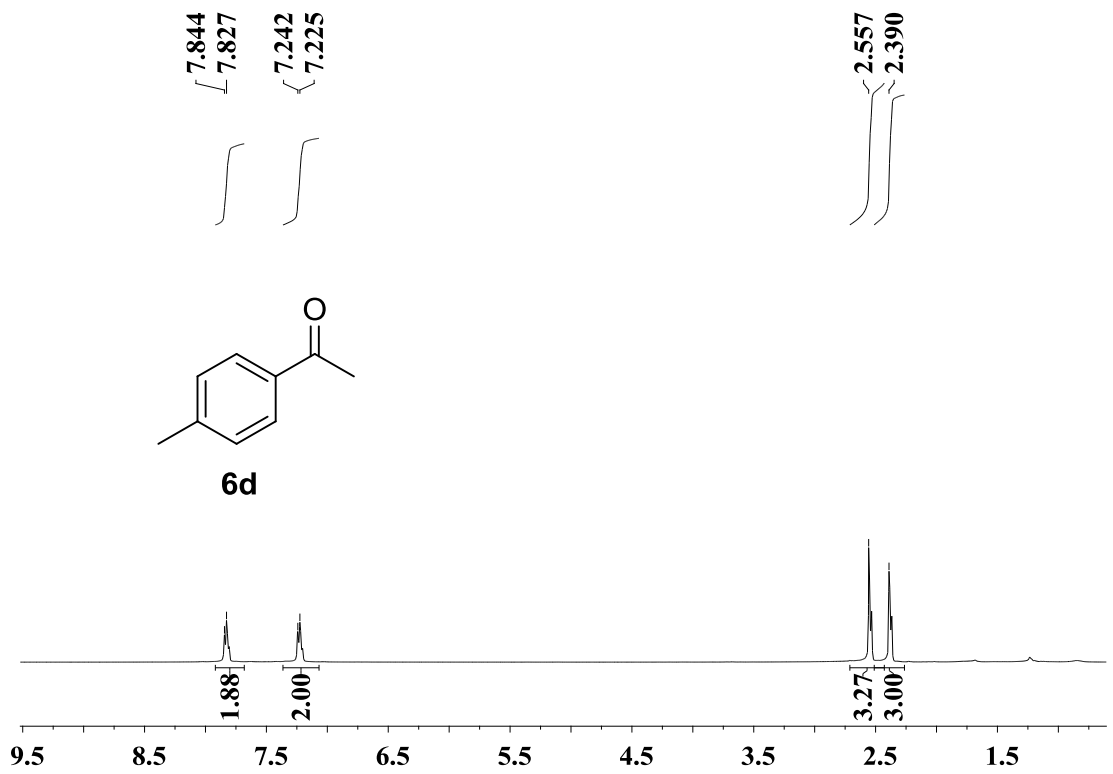
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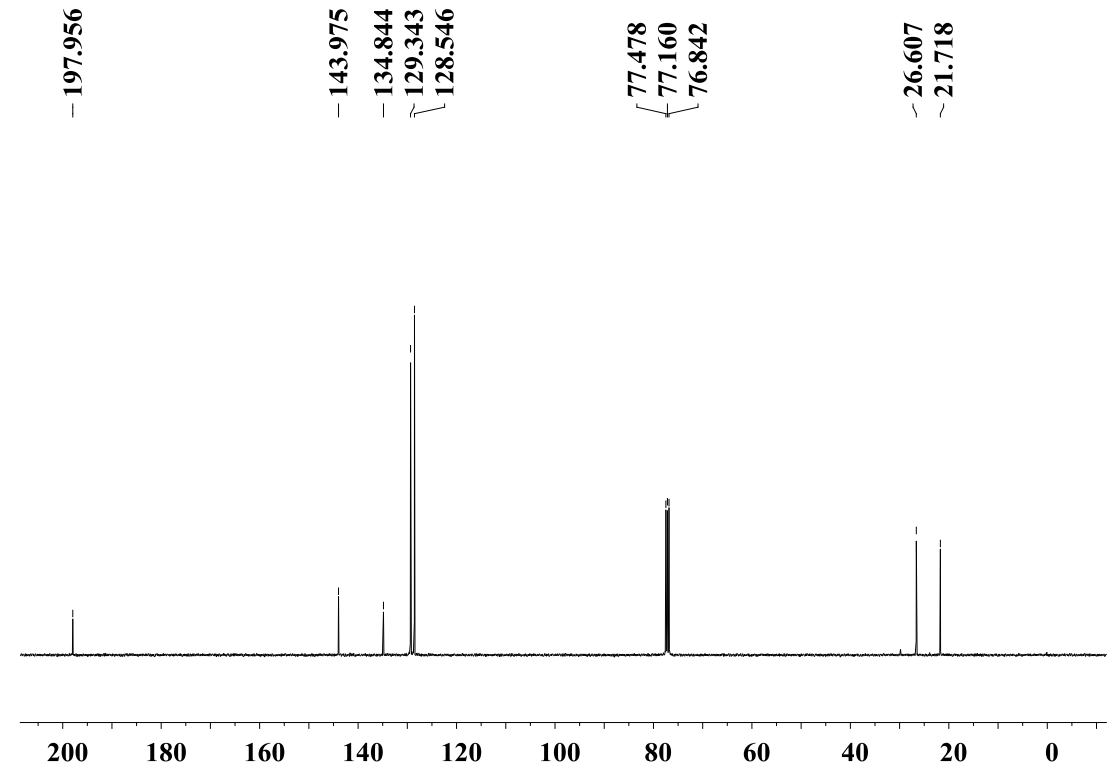
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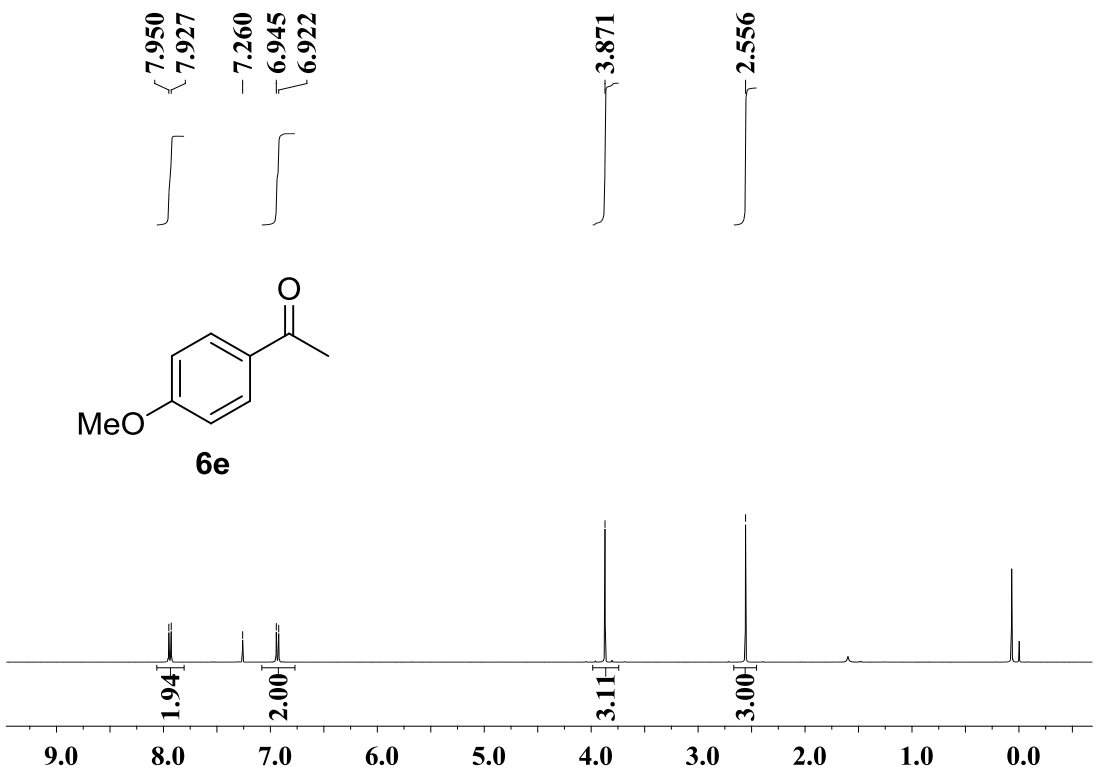
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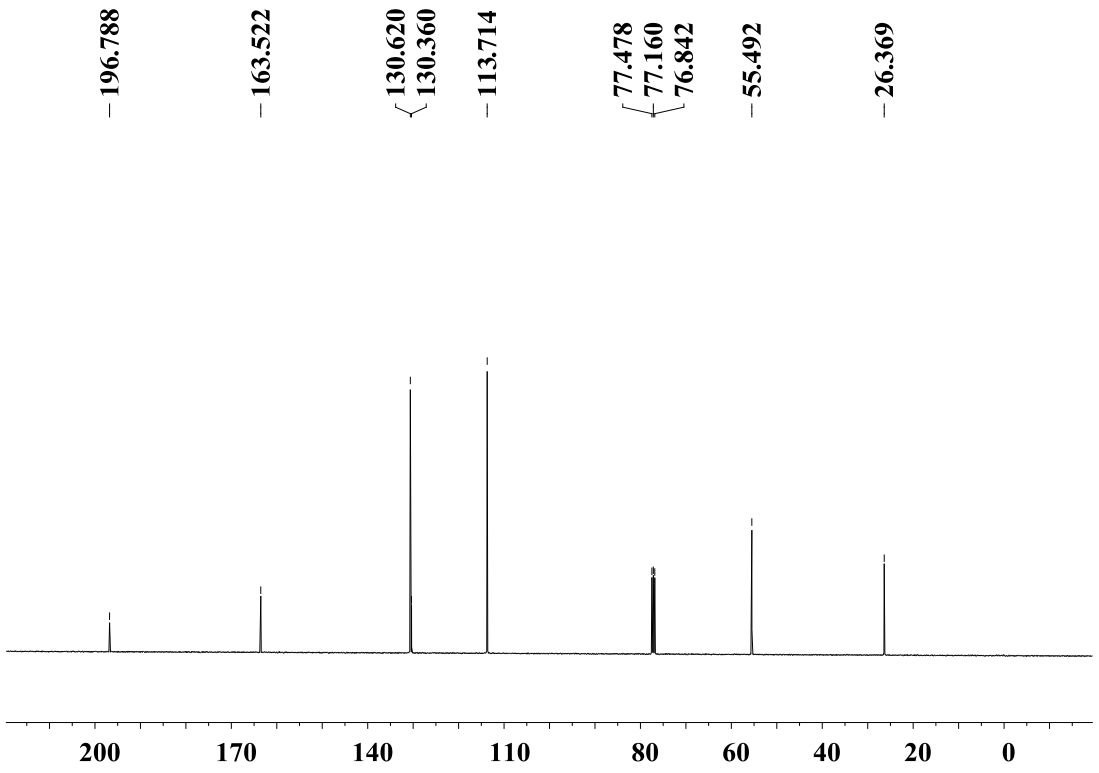
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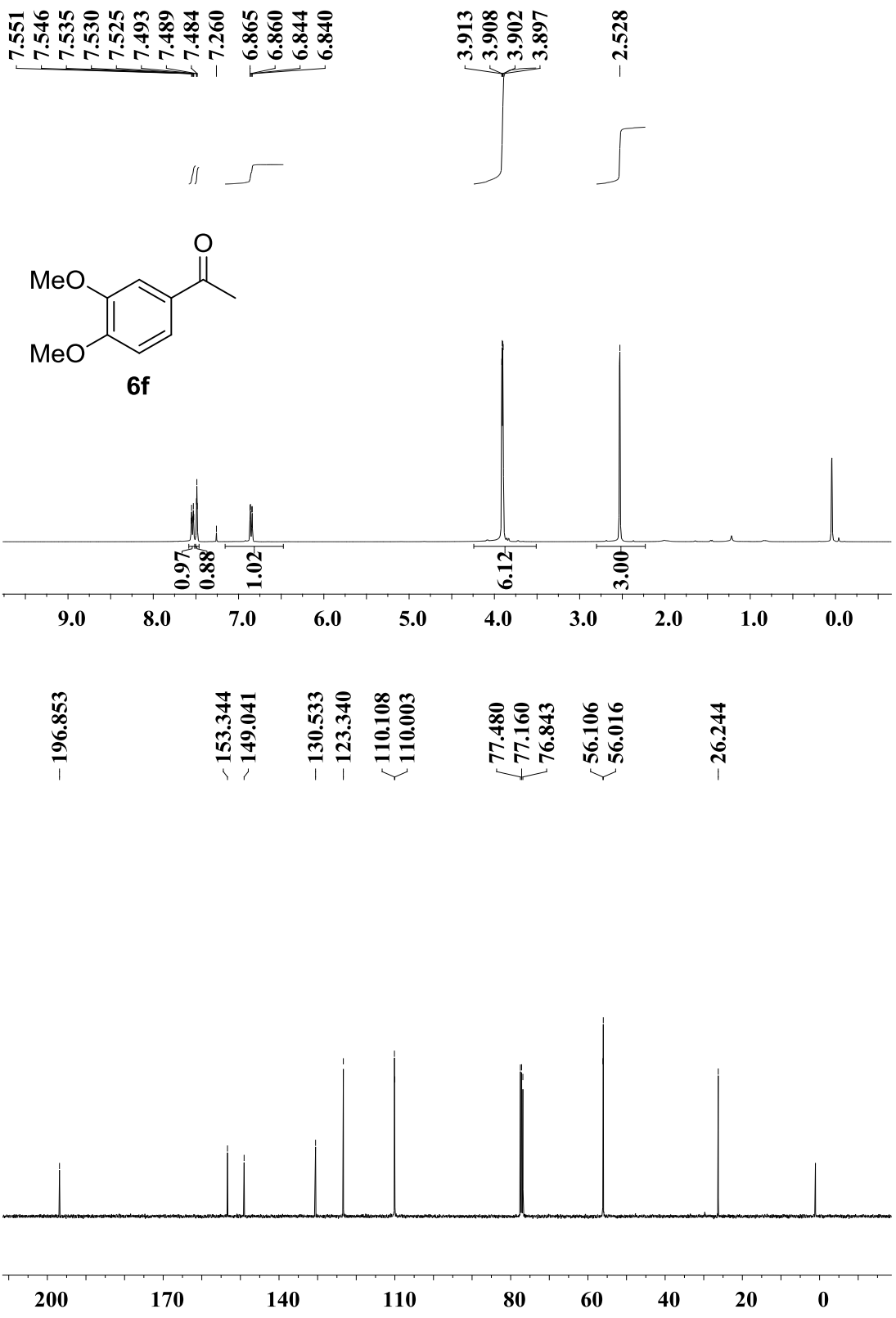
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MeO
MeO
6f
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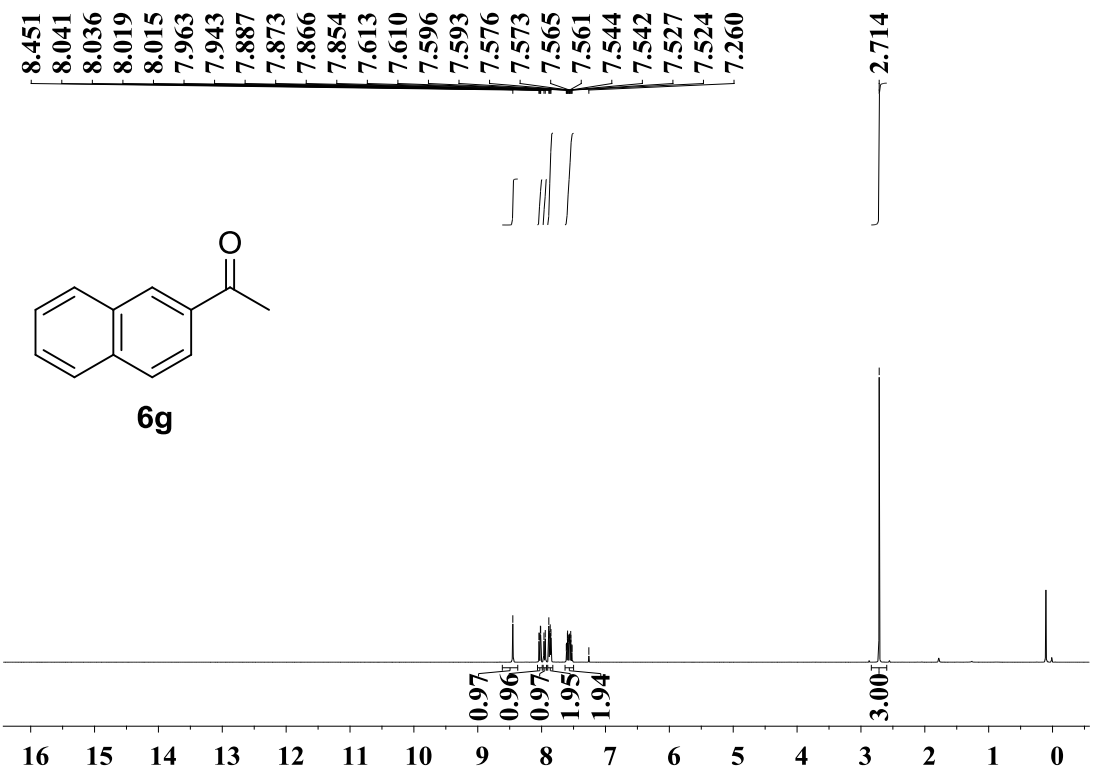
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7.524
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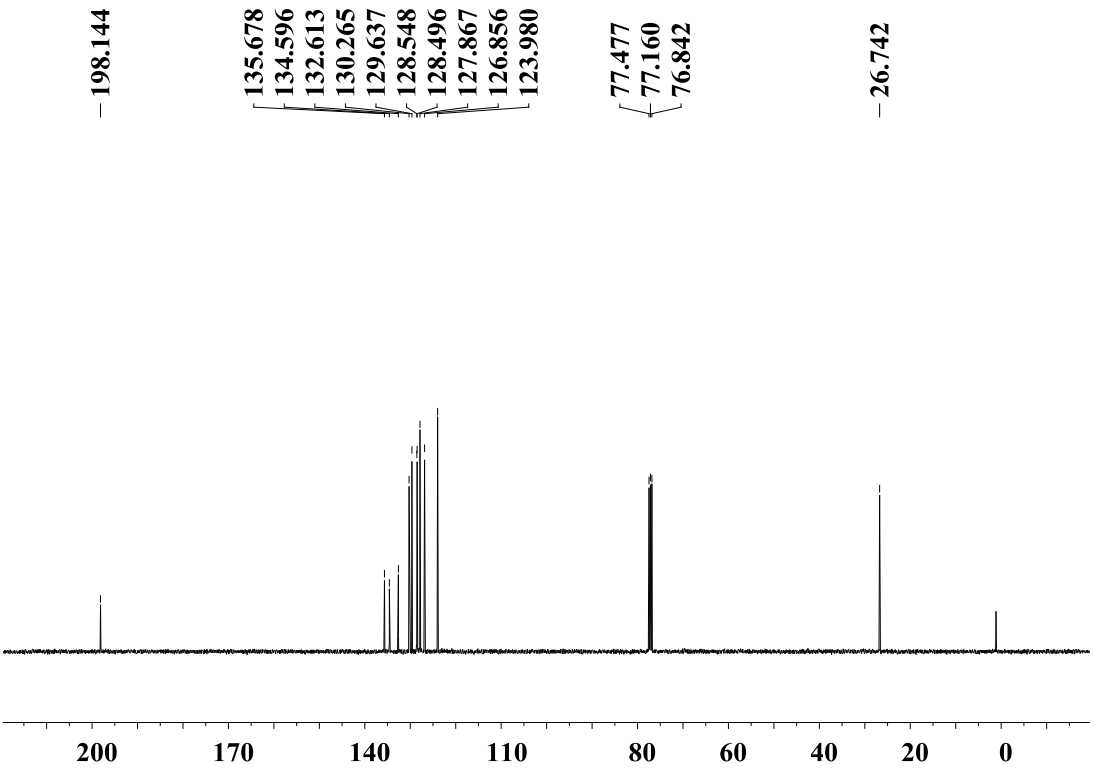
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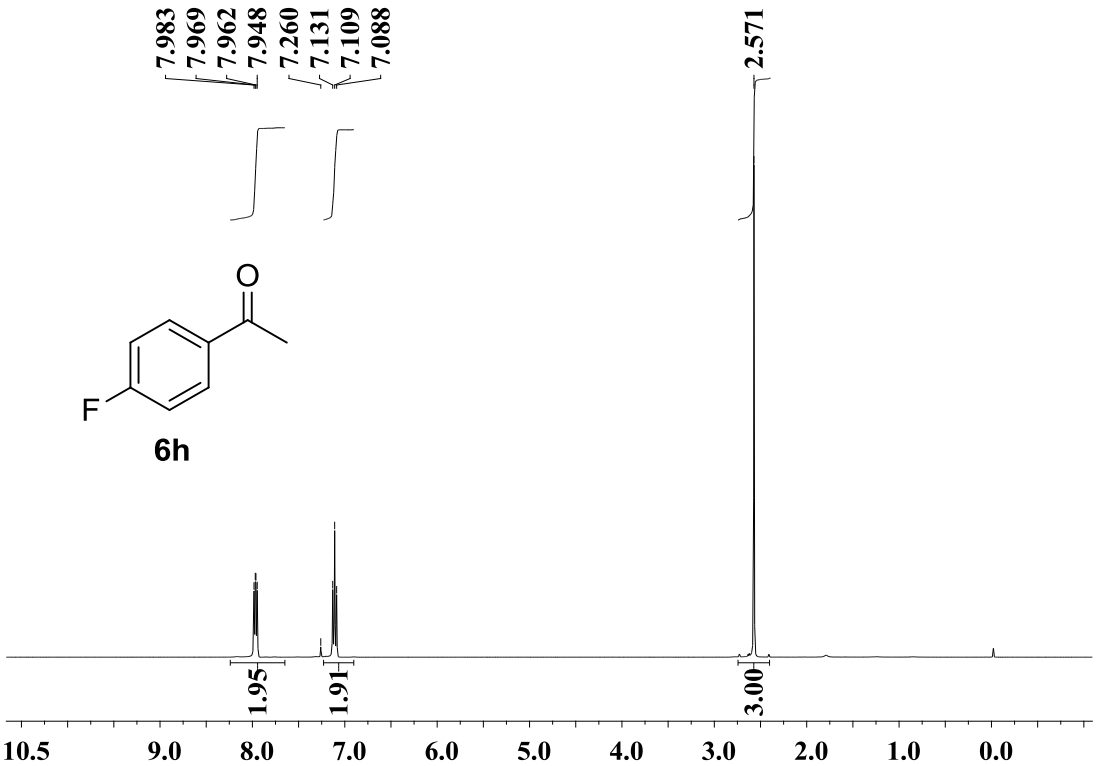
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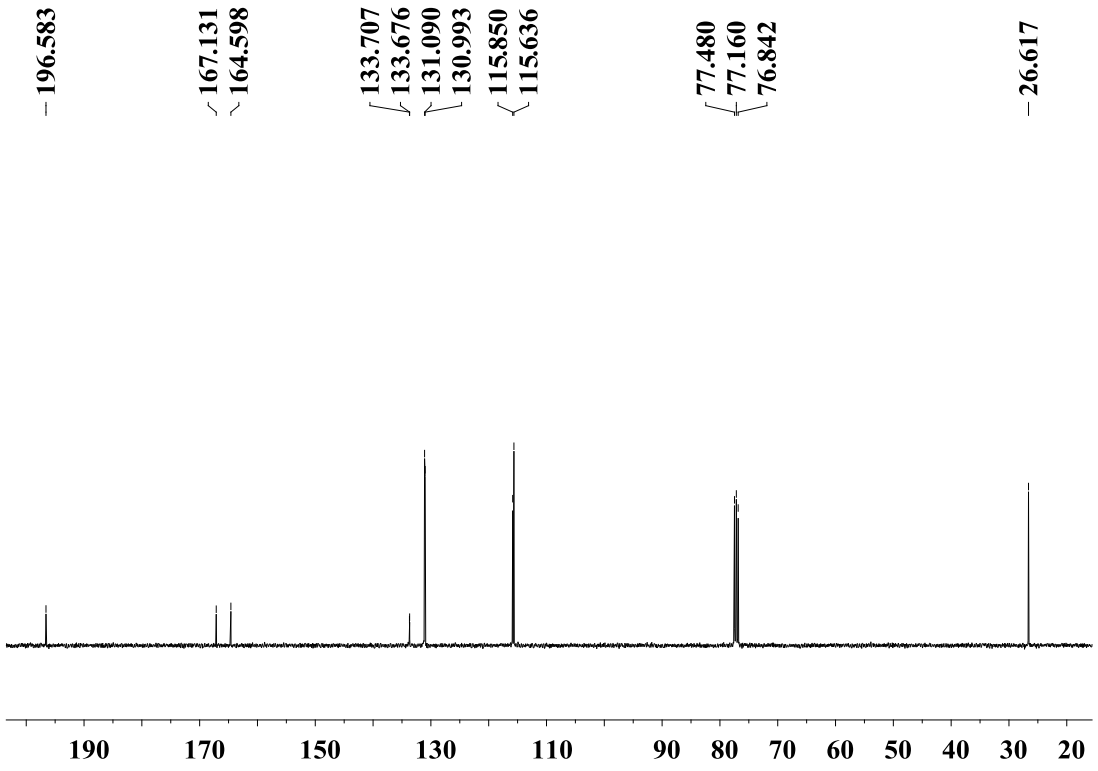
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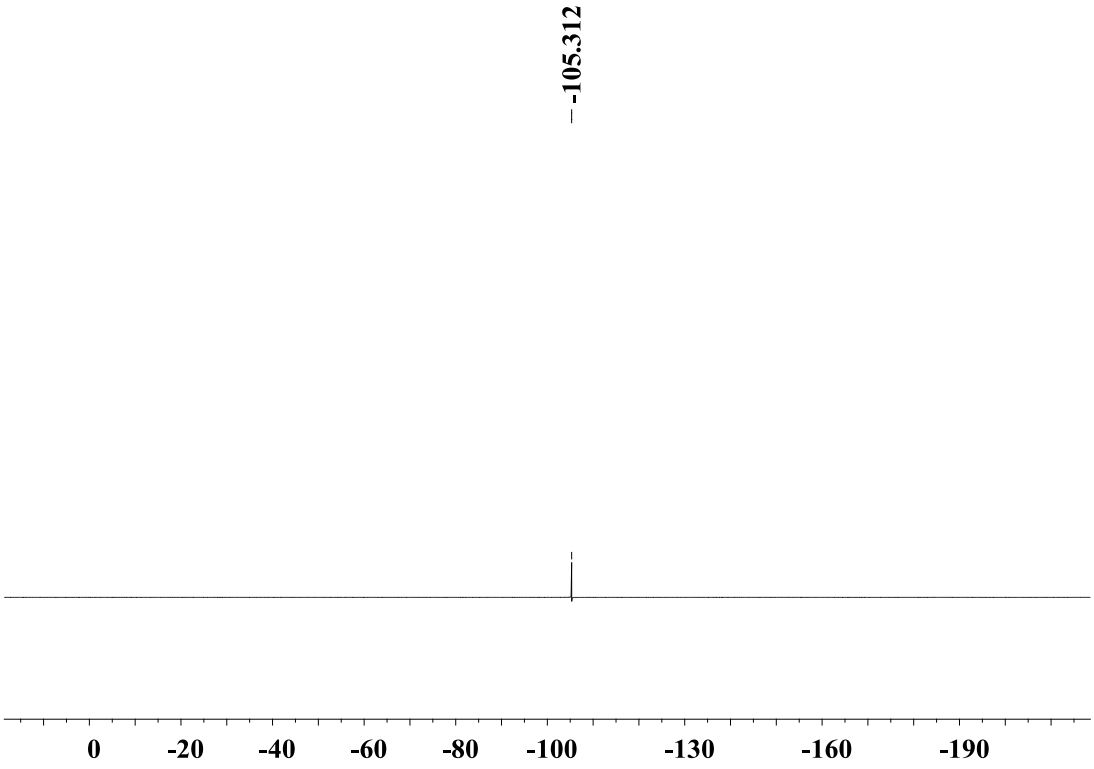
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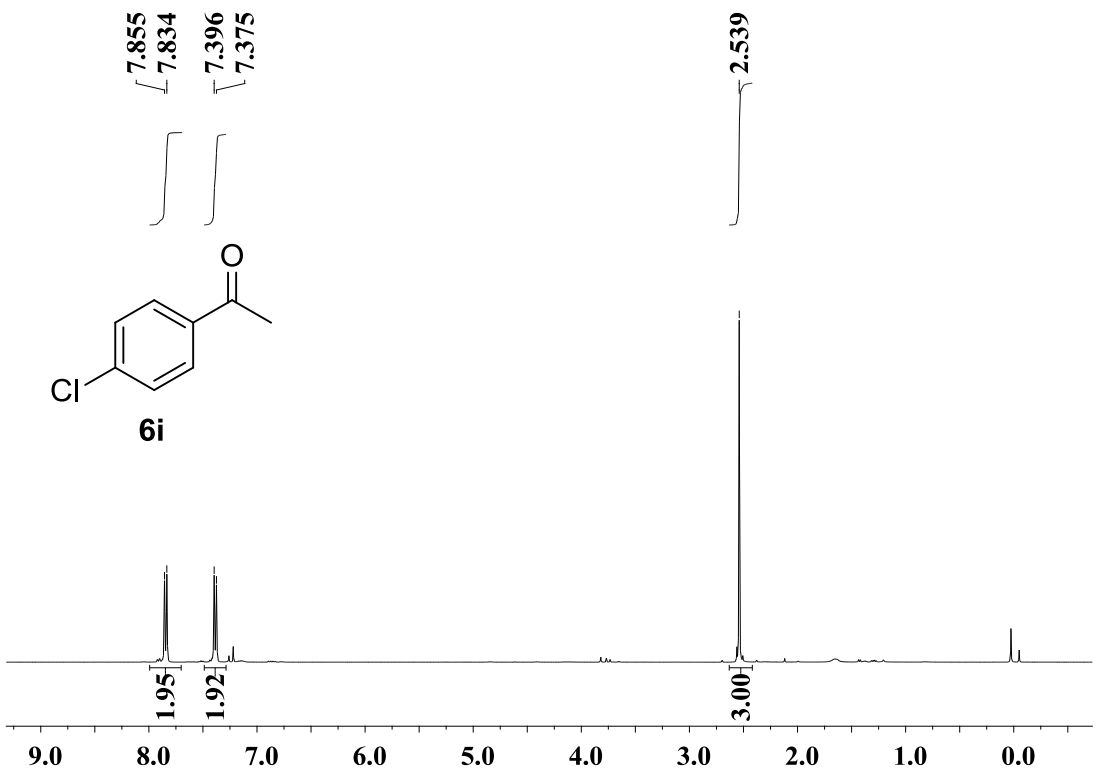
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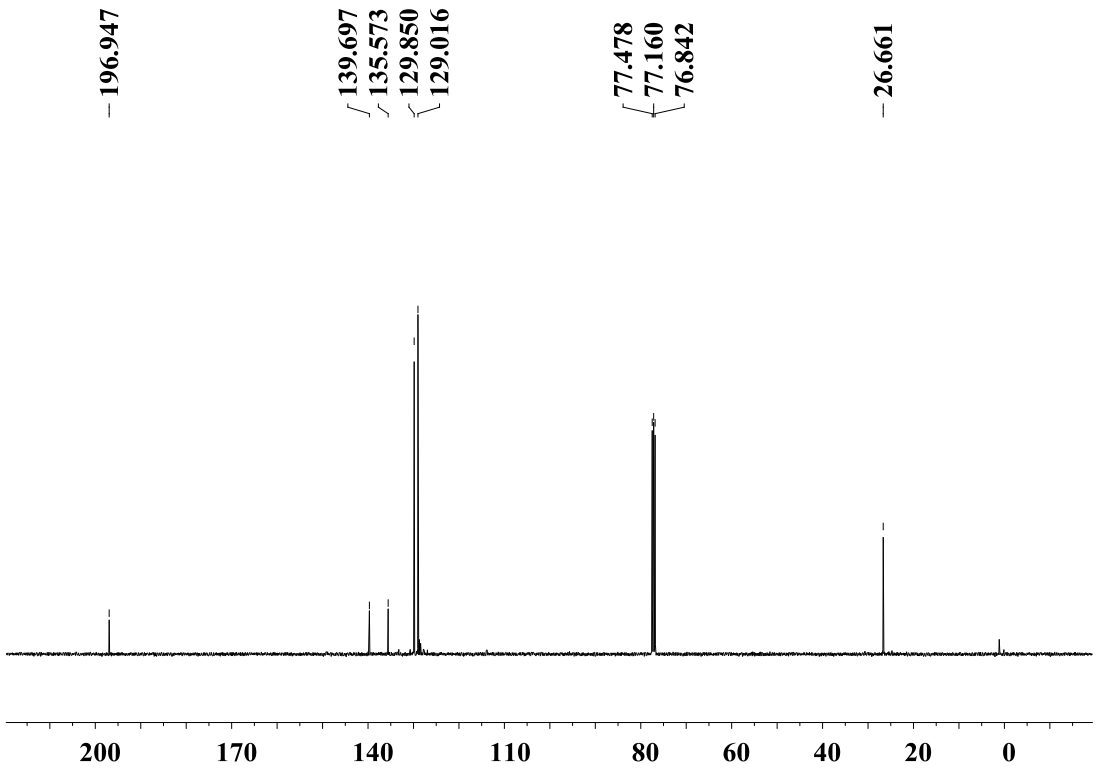
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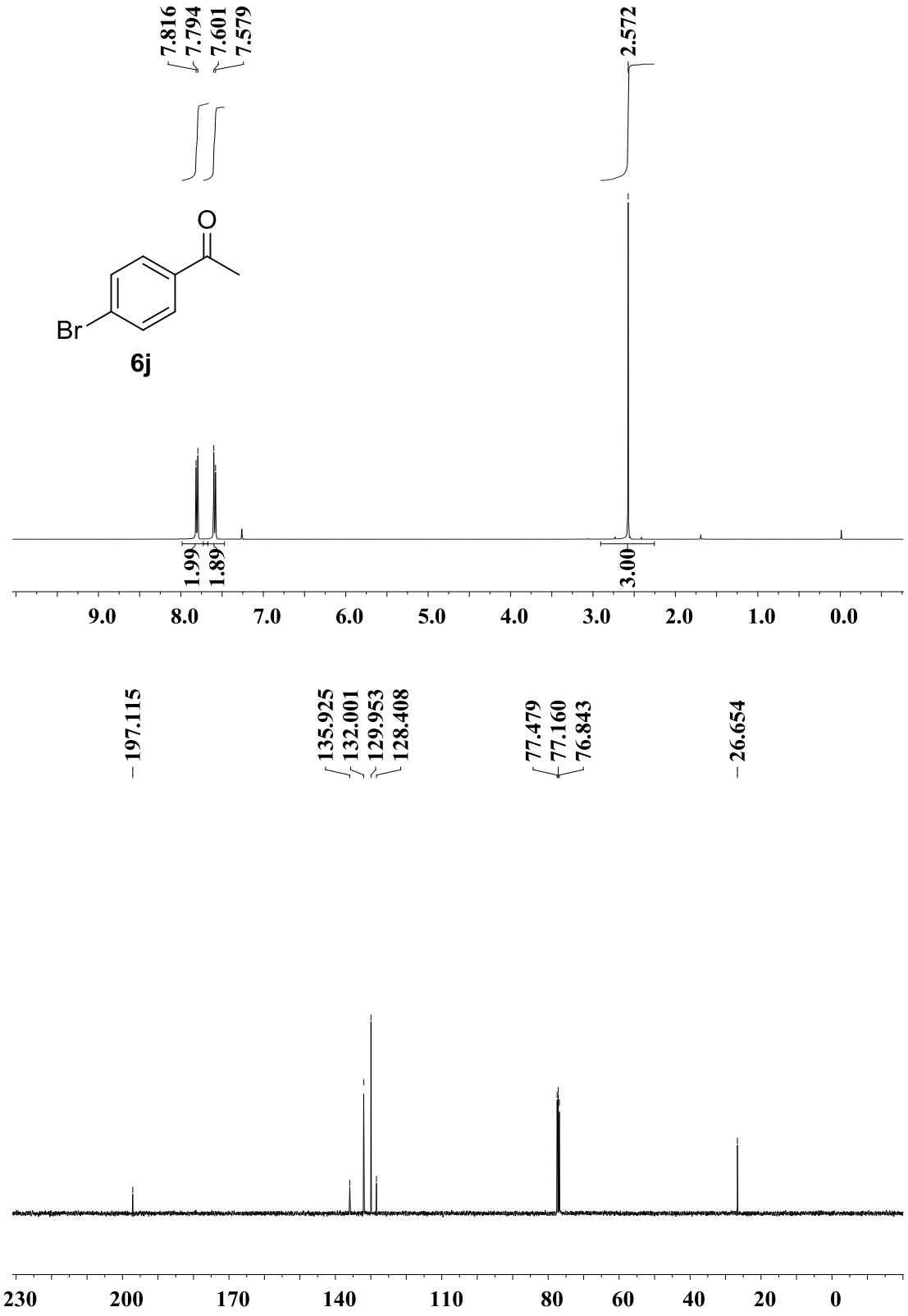
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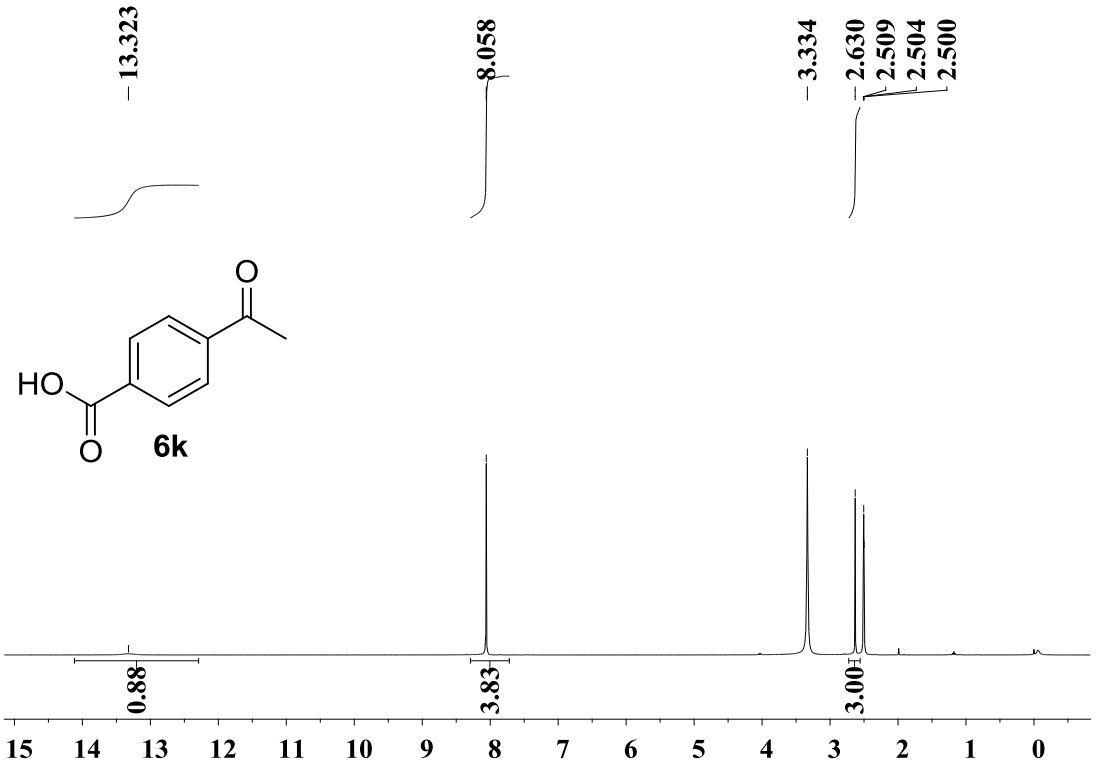
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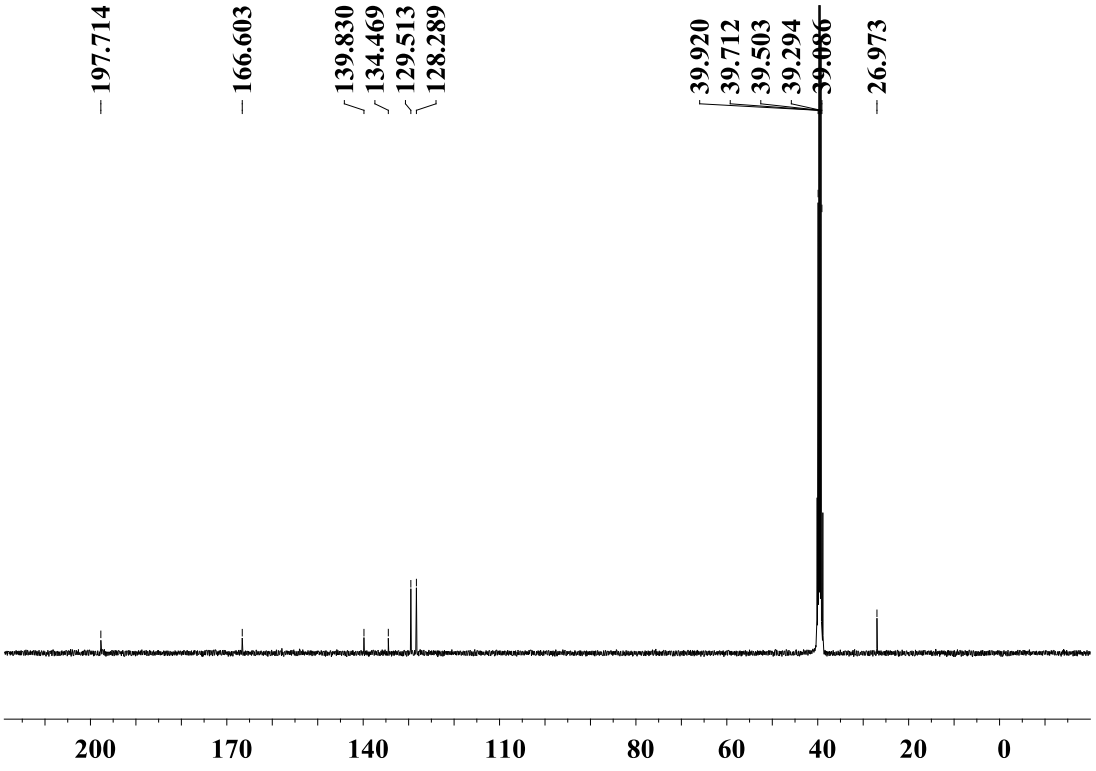
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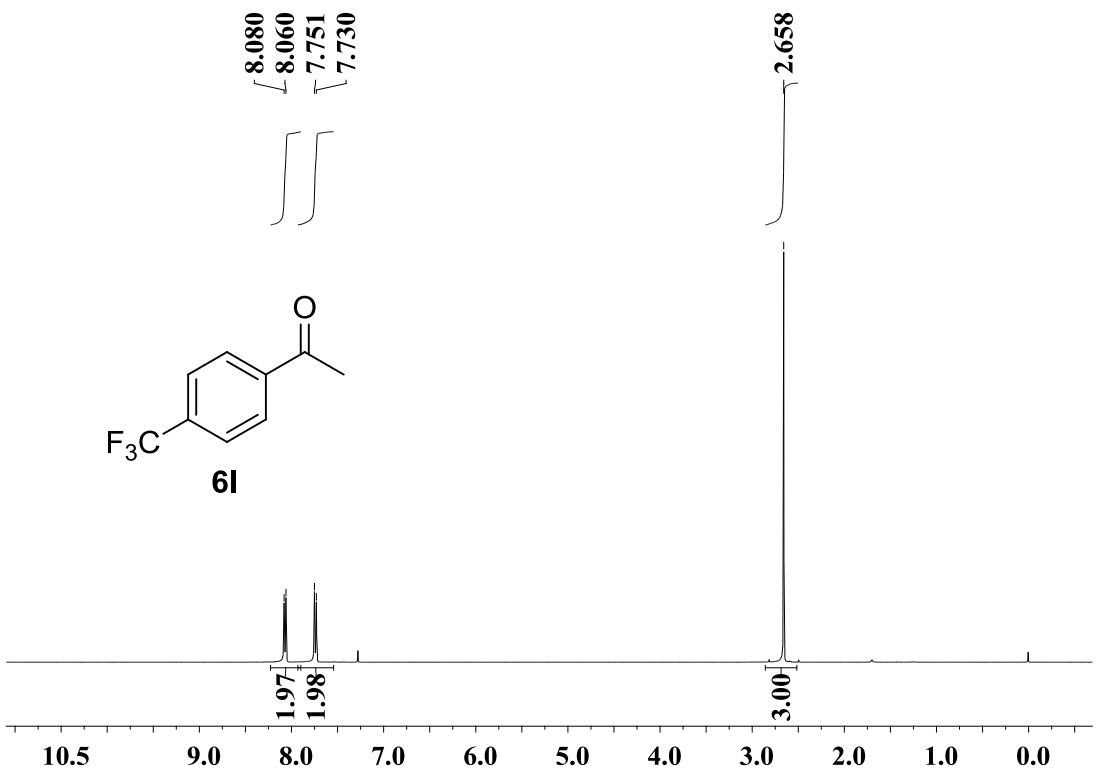
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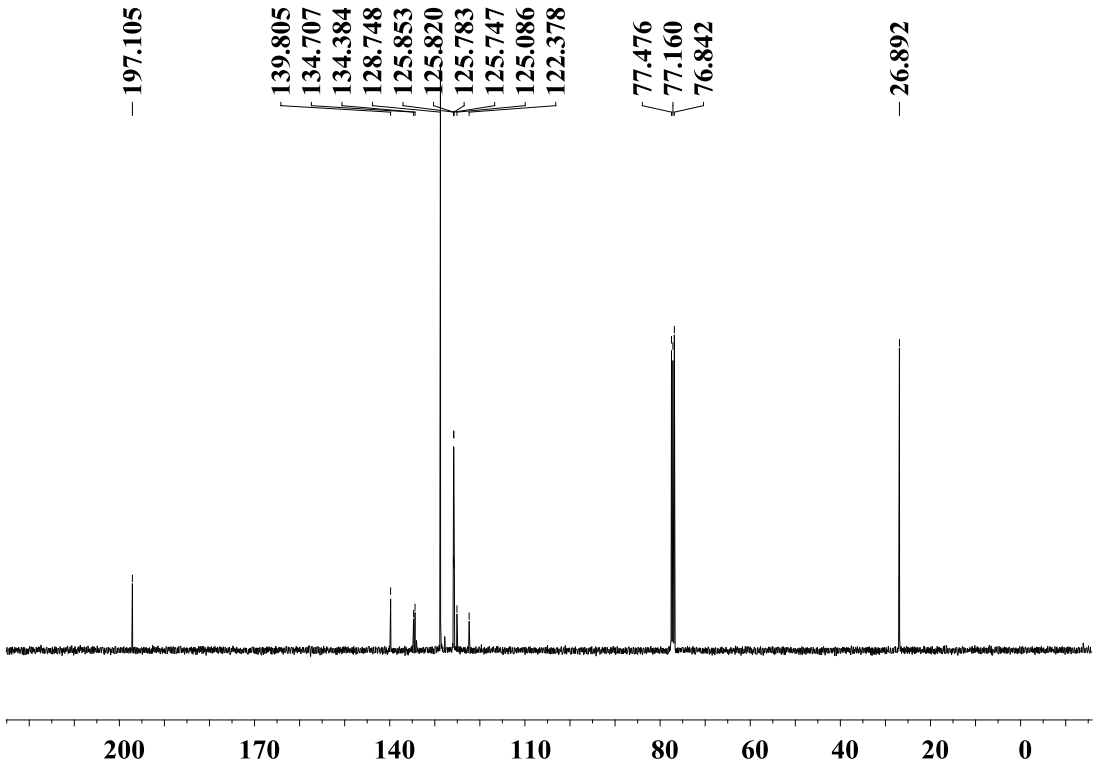
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200
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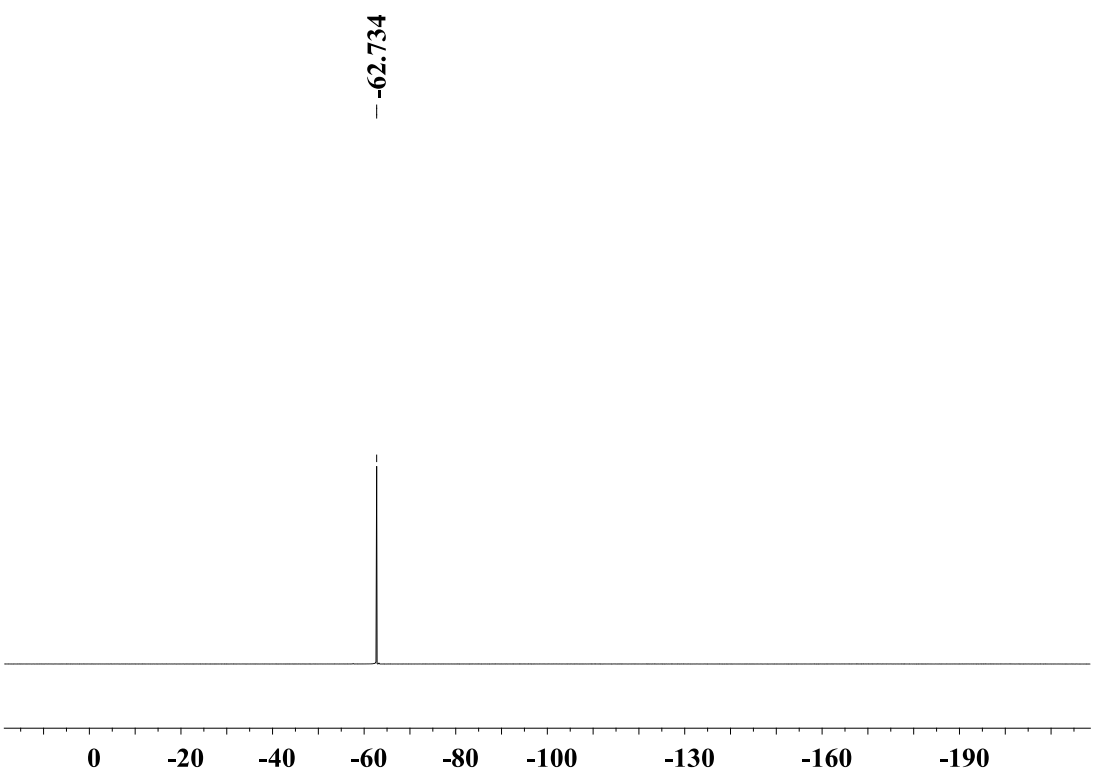
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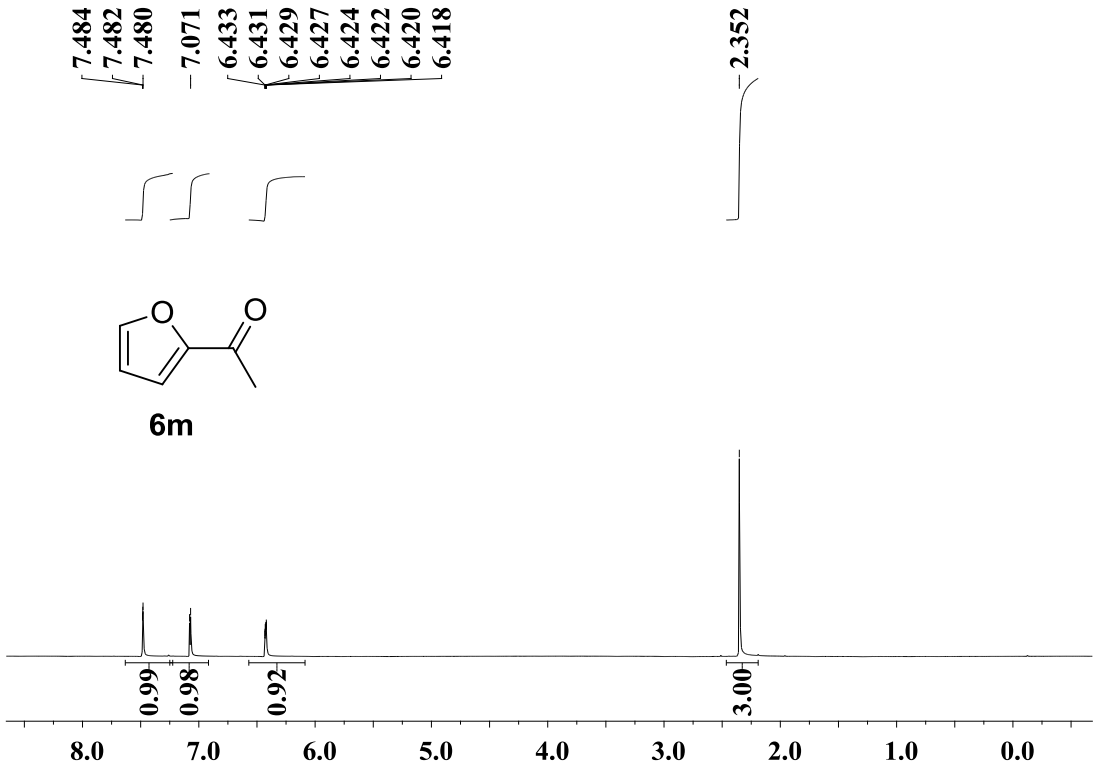
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O
O
6m
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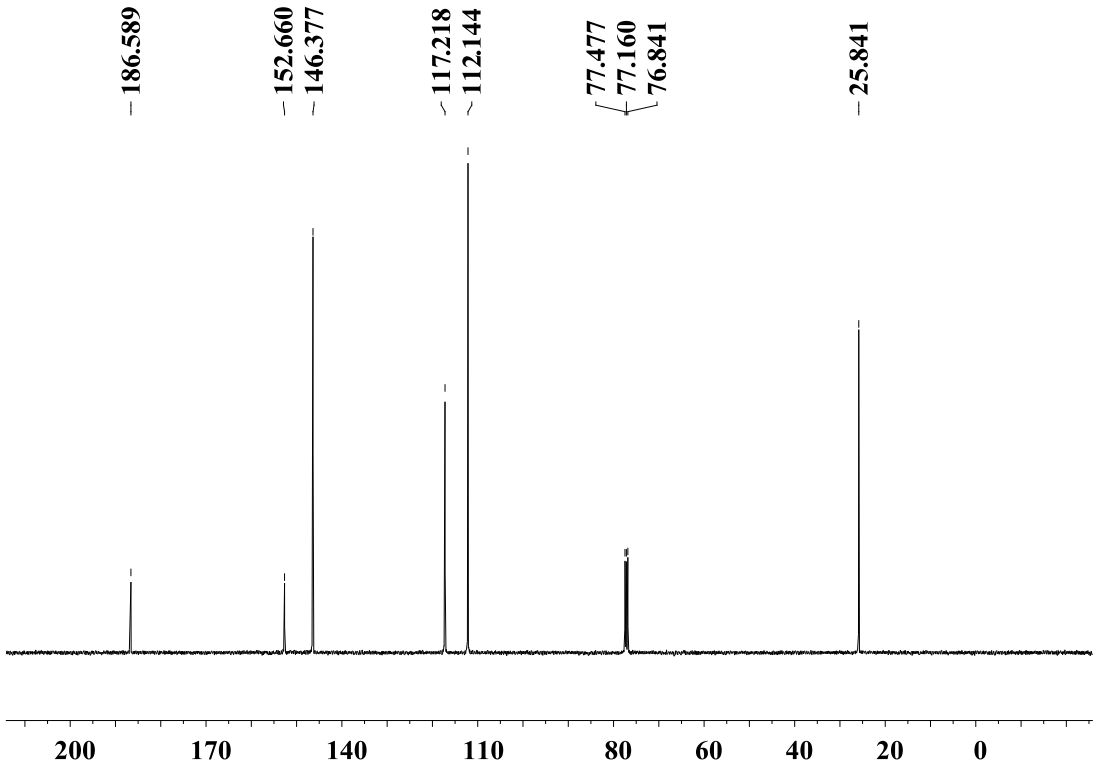
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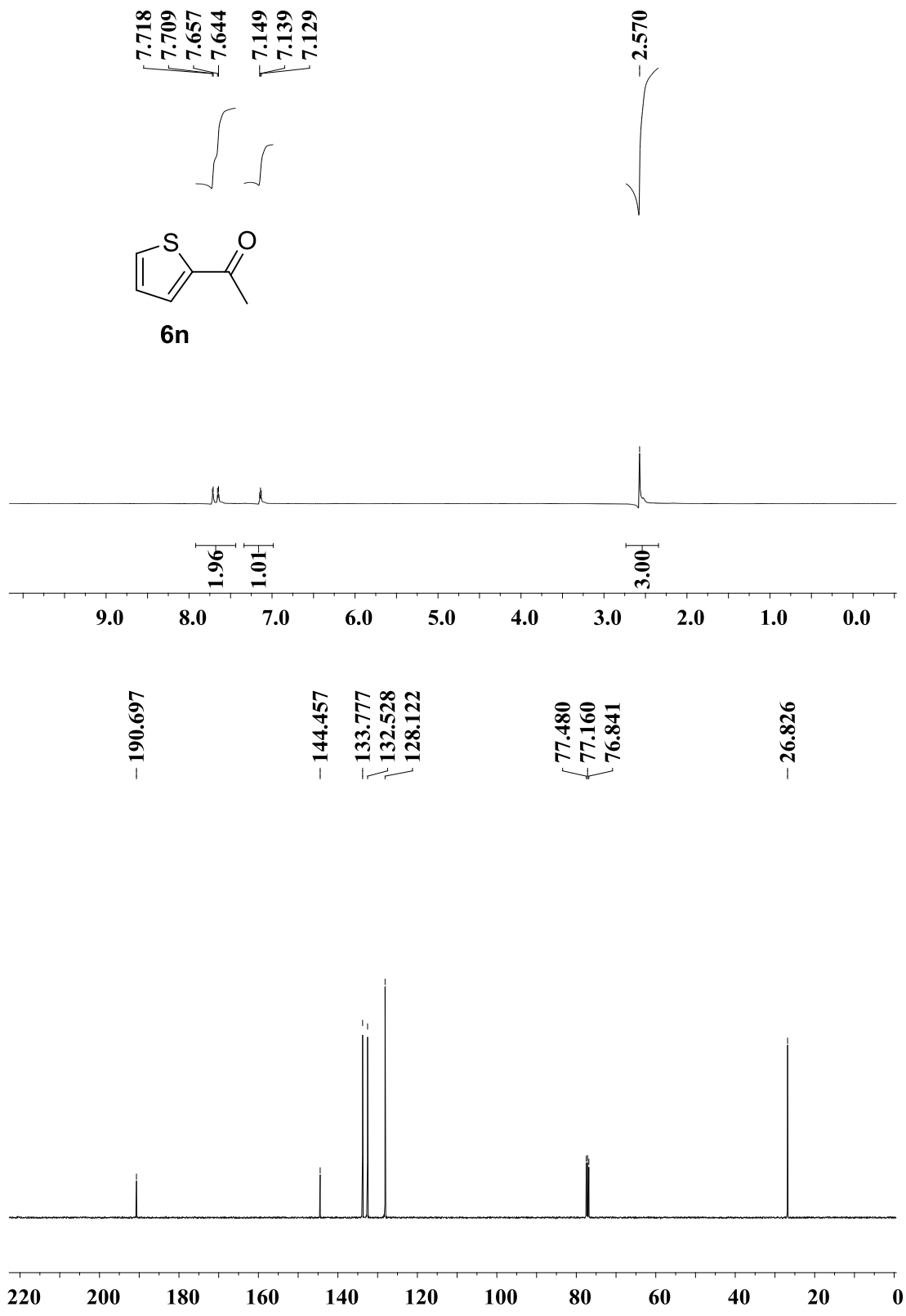
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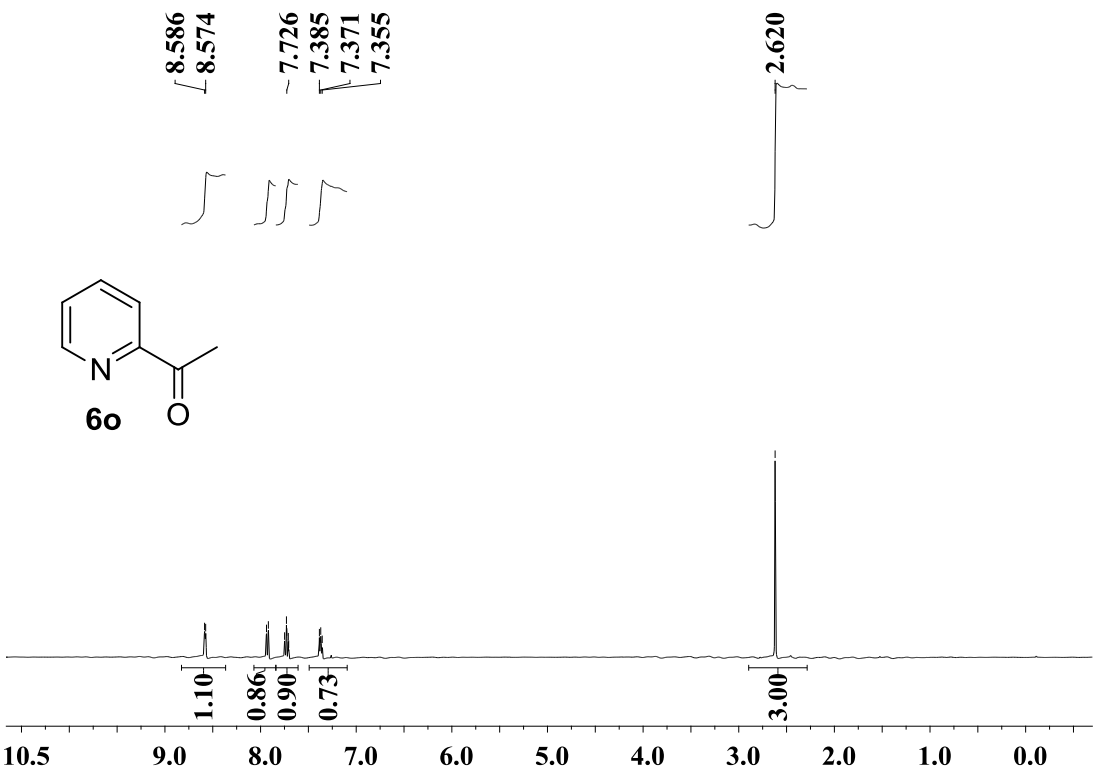
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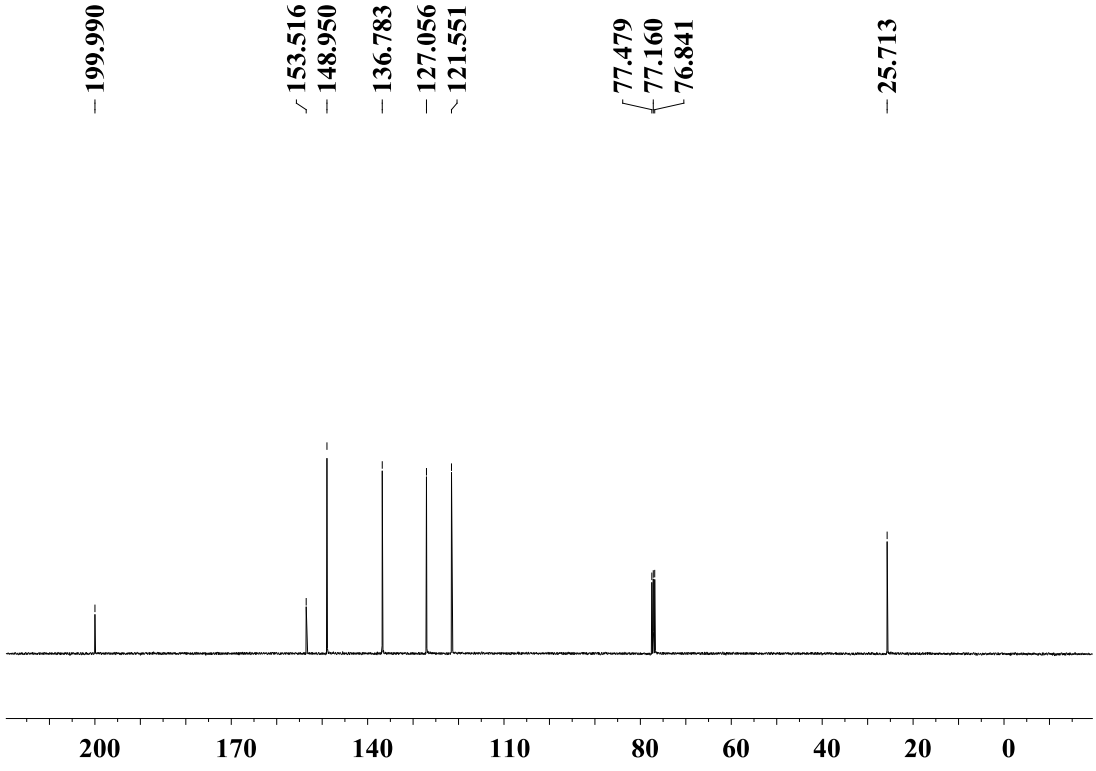
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200
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140
110
80
60
40
20
0


7.965
7.947
7.944
7.561
7.543
7.525
7.467
7.448
7.430
7.260
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6p
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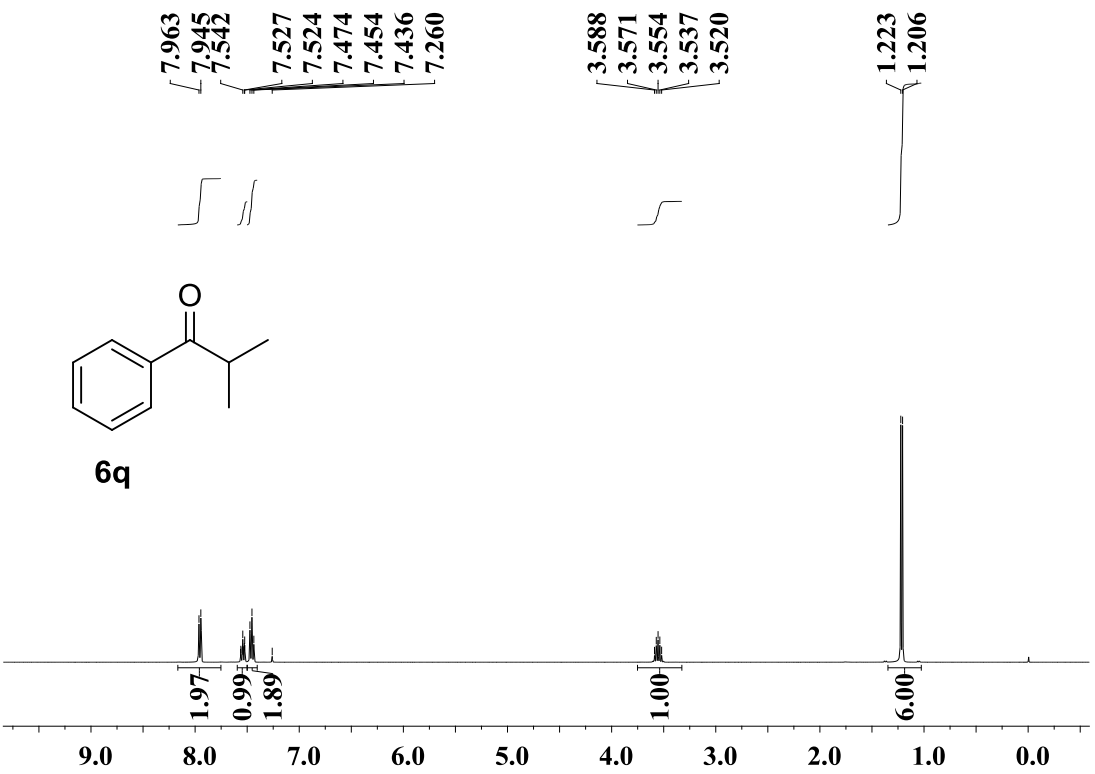
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3.537
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1.206
O
6q
1.97
0.99
1.89
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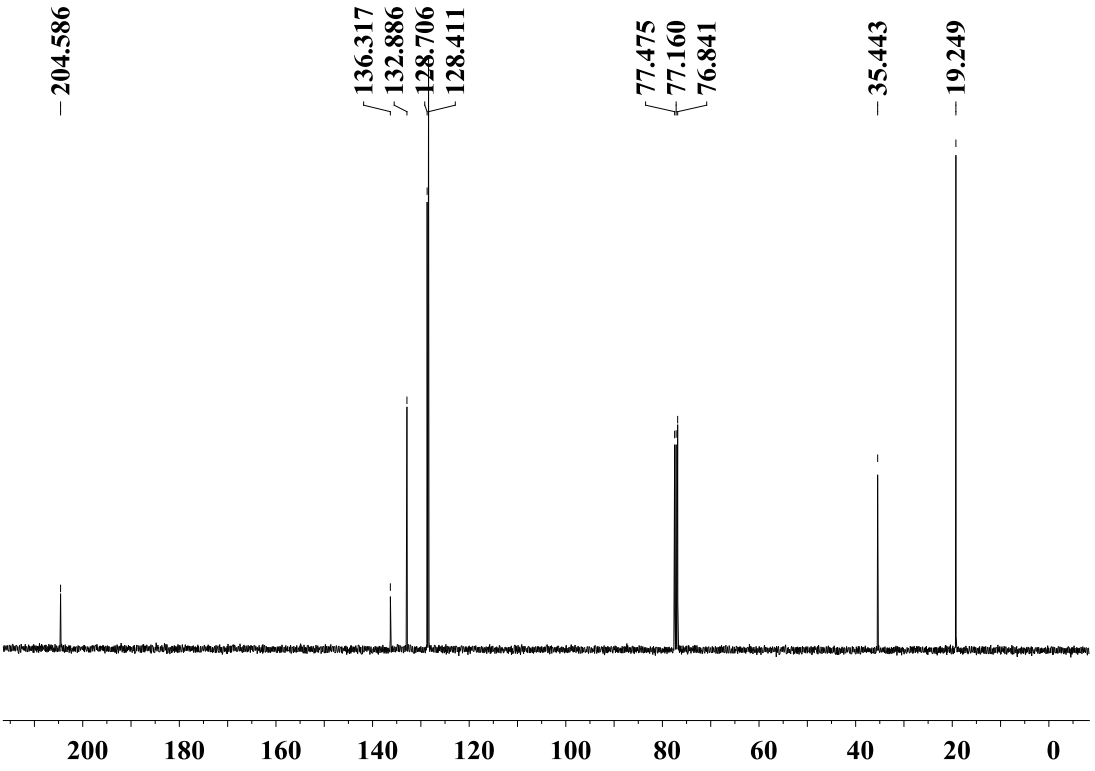
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140
120
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20
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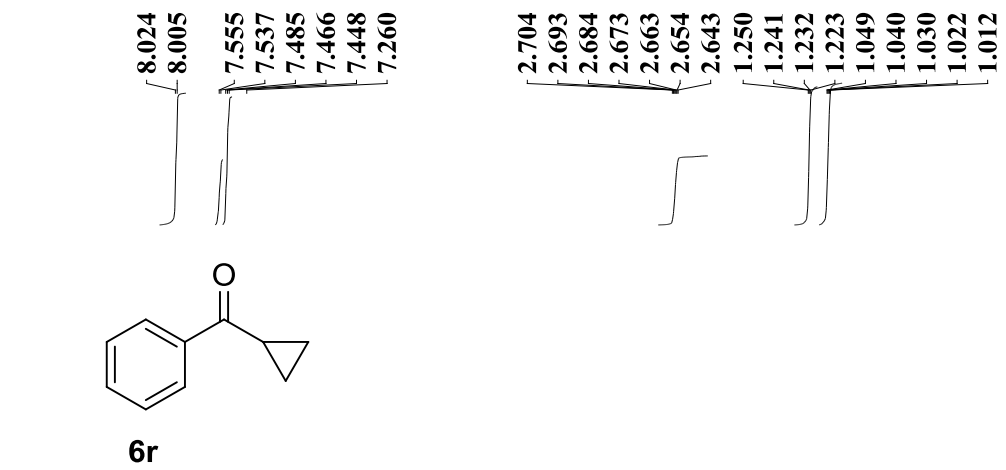
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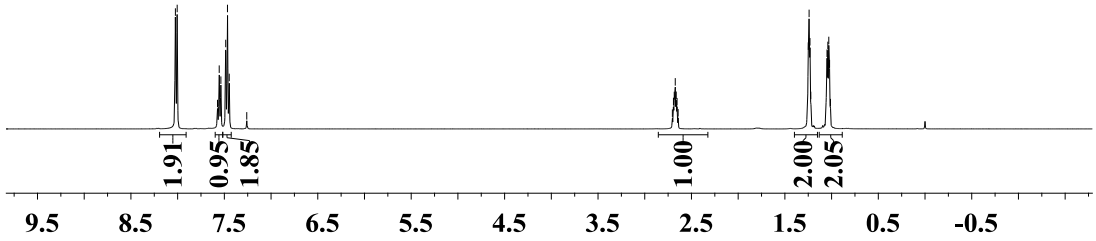
1.012
O

6r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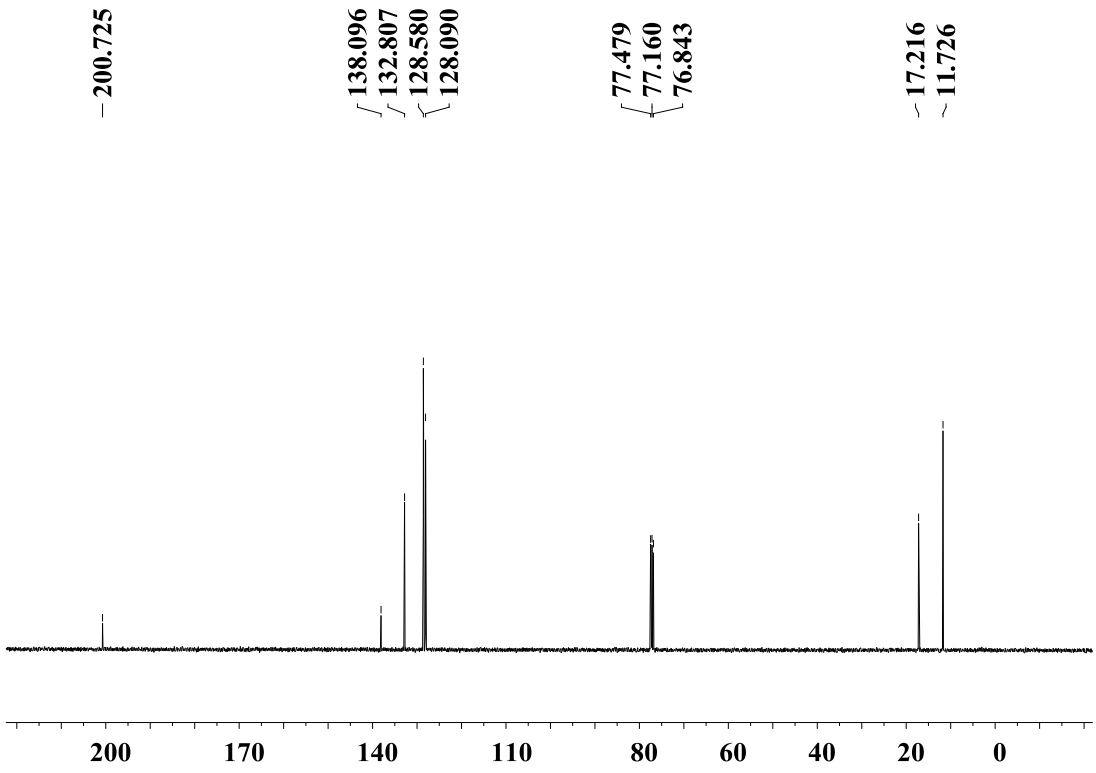
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20
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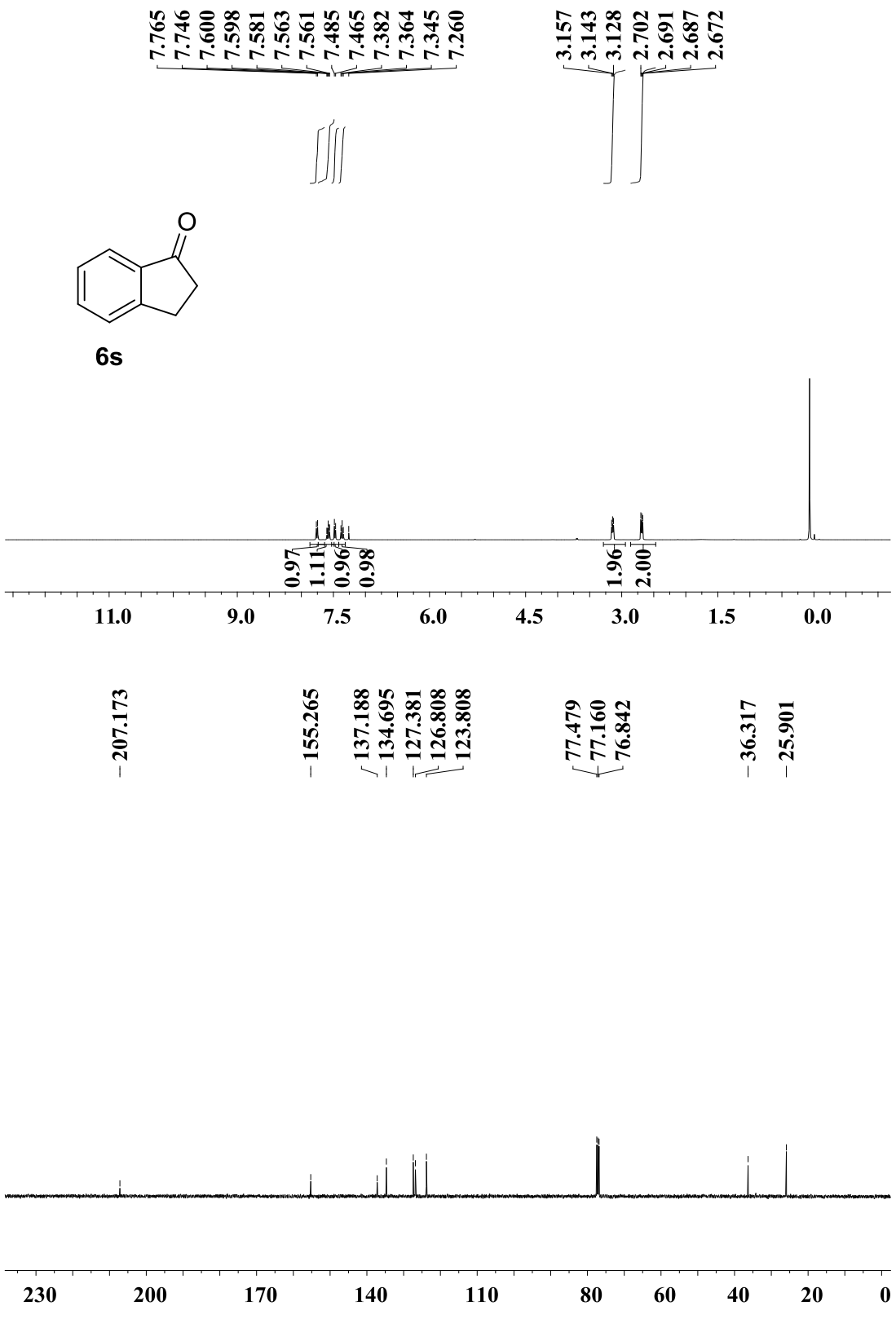
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7.260
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3.143
3.128
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2.691
2.687
2.672
O
6s
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0.96
0.98
1.96
2.00
11.0
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3.0
1.5
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126.808
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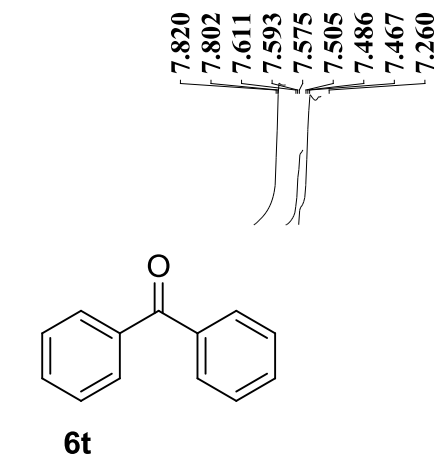
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7.260
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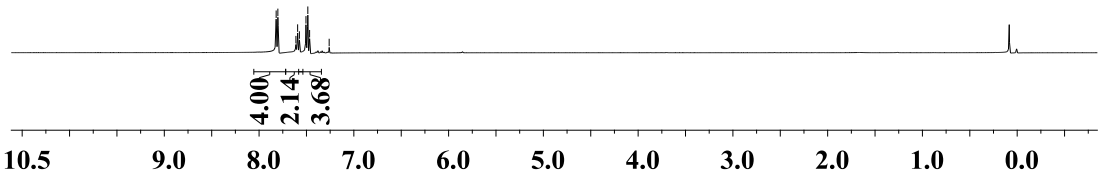
6t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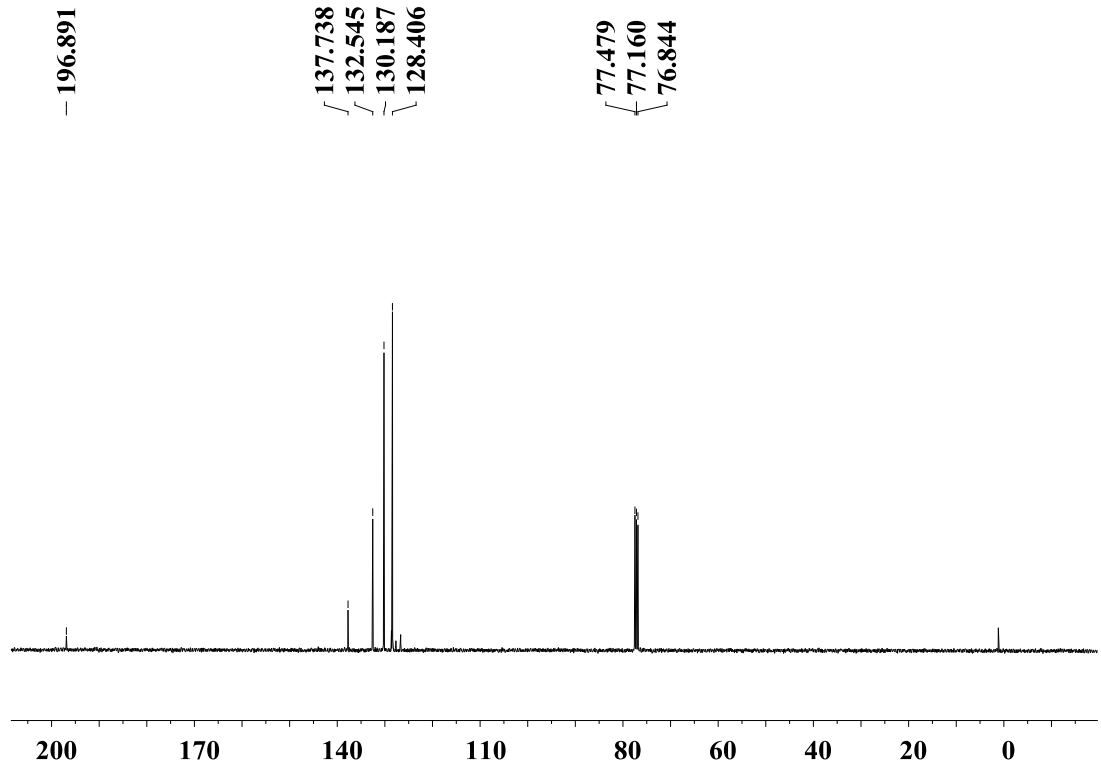
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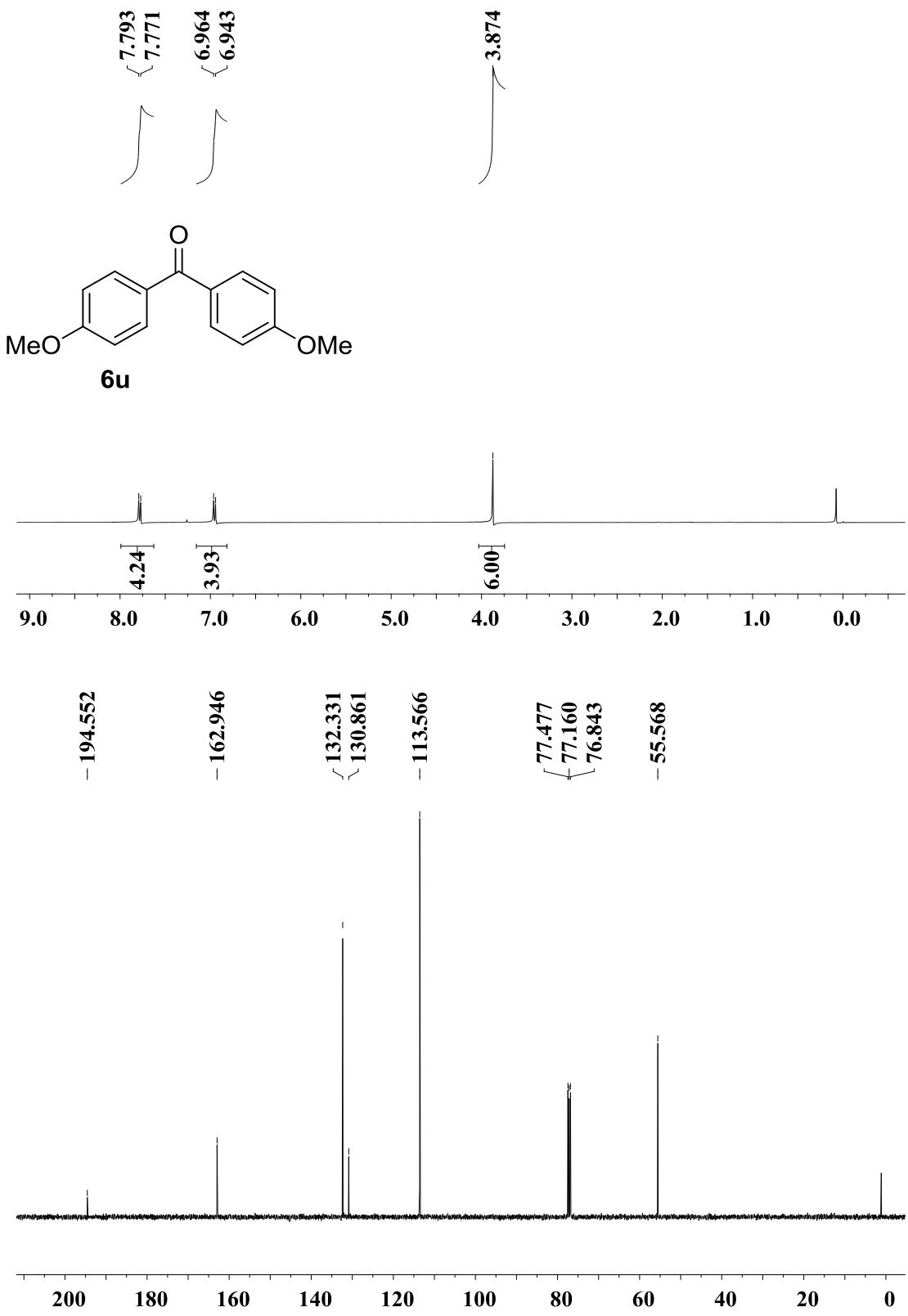
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OMe
6u
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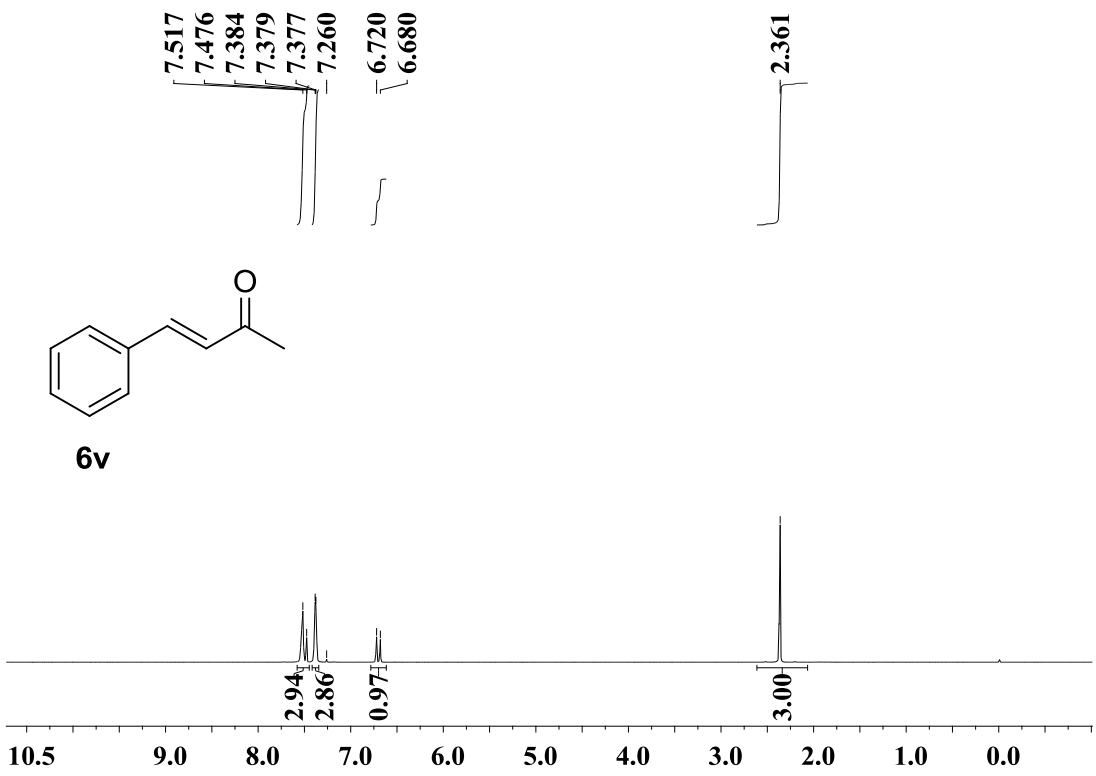
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6v
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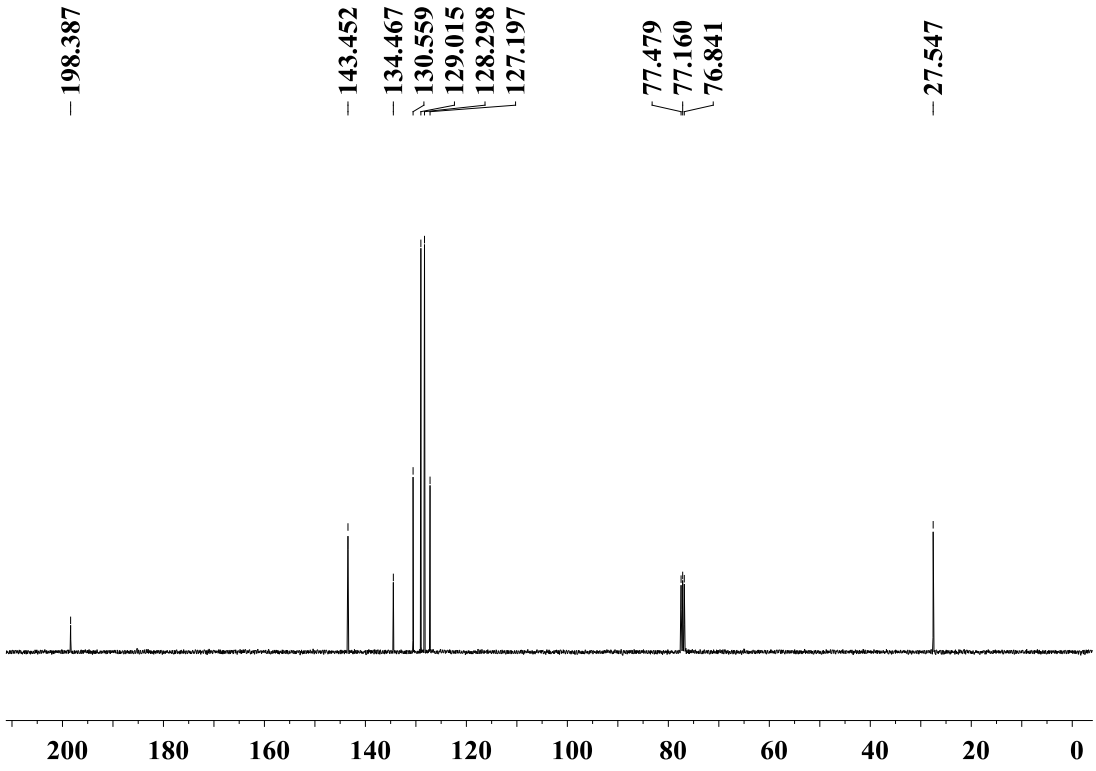
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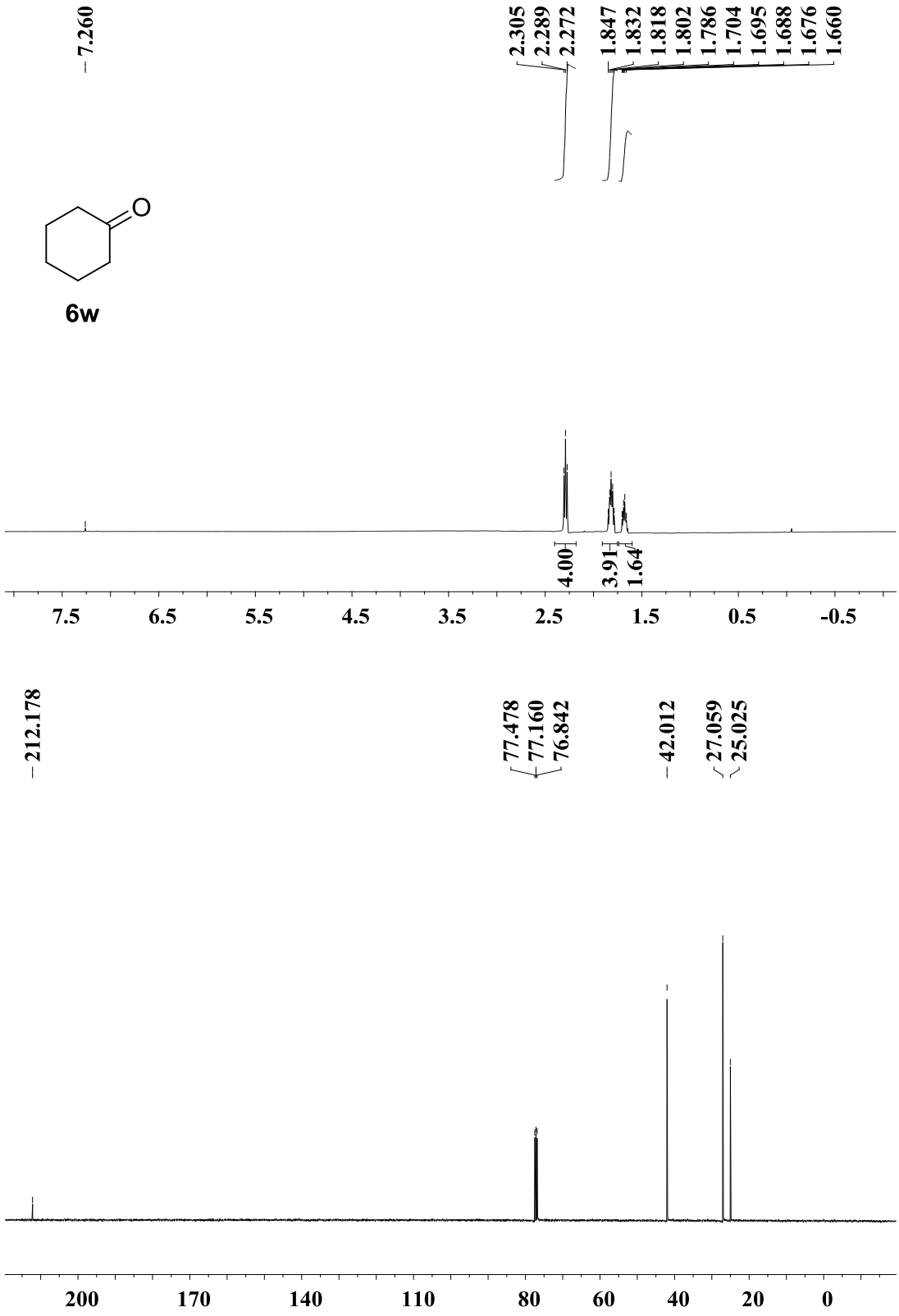
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