Solvent-free aerobic photocatalytic oxidation of C(sp^3)–H and C(sp^3)–OH to C=O bonds

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1. EXPERIMENT

The conversion of ethyl benzene (Conv.), the yield of acetophenone (Y) and the selectivity of acetophenone (Sel.) were calculated as follows:

$$\text{Conversion}_{\text{(ethyl benzene)}} = \left(1 - \frac{n_{remaining\ ethylbenzene}}{n_{initial\ ethylbenzene}}\right) \times 100\%$$

$$\text{Yield}_{\text{(acetophenone)}} = \frac{n_{acetophenone}}{n_{n_{initial\ ethylbenzene}}} \times 100\%$$

$$\text{Selectivity}_{\text{(acetophenone)}} = \frac{Yield_{acetophenone}}{Conversion_{ethyl\ benzene}} \times 100\%$$

2. TABLES

Table S1 Photocatalytic oxidation of ethylbenzene to acetophenone over different catalysts.

Entry	Catalyst	Substrate	Reaction conditions	Solvent	Conv. (%)	Fr (μmol·g-1·h-1)[a]	Ref.
1	4CD/BiMO	Ethylbenzene	Catalyst (20 mg), 10 W white LED, λ>420 nm, 1 atm O_2, RT, 16 h.	acetonitrile (8 mL)	38	416	[1]
2	VO@g-C_3N_4	Ethylbenzene	Catalyst (25 mg), 40 W domestic bulb, H_2O_2 (1.5 mmol), RT, 12 h.	acetonitrile (2 mL)	99	3330	[2]
3	BiVO$_4$/Ag/C_3N_4	Ethylbenzene	Catalyst (50 mg), visible light irradiation (λ >400 nm), O_2 flow rate (3 mL· min^{-1}), RT, 3 h.	acetonitrile (5 mL)	>99	140	[3]
4	α-Fe_2O_3	Ethylbenzene	Catalyst (10 mg), NHPI (4 mg), HY zeolite (3 mg), O_2 (1 atm), blue LED light (455 nm, 3 W), RT, 8 h.	acetonitrile (1 mL)	98	58.4	[3]
5	FePW/g-C_3N_4	Ethylbenzene	Catalyst (10 mg), tBuOOH (2.5 mmol), purple LED lamp (15 W, 425 nm, 13.4 mW· cm^{-2}), RT, 15 h.	acetonitrile (10 mL)	99	6600	[4]
6	BiOBr$_{0.85}$I$_{0.15}$	Ethylbenzene	Catalyst (10 mg), NHSI 3 mg, 1 atm O_2, purple LED lamp (15 W, 425 nm, 13.4 mW·cm^{-2}), RT, 15 h.	acetonitrile (10 mL)	98	614	[5]
7	TCNS-5	Ethylbenzene	Catalyst (20 mg), 1 atm O_2, solar light, 35 ℃, 6 h.	acetonitrile (10 mL)	56.1	1561	[6]
8	p-BiOBr	Ethylbenzene	Catalyst (20 mg), 1 atm O_2, H_2O:TBA=2:2, 300 W xenon lamp λ>320 nm, RT, 10 h.	acetonitrile (10 mL)	80	680	[7]
9	W10/C8 -AP-SBA	Ethylbenzene	Catalyst (60 mg), O_2 (3 mL·min^{-1}), H_2O:TBA=2:2, λ>320 nm, 6~10 ℃, 6 h.	acetonitrile/water =1:1 (4 mL)	97	4443	[8]
10	SACo@g-C_3N_4	Ethylbenzene	Catalyst (5 mg), 0.5 mmol PMS, λ>320 nm, 60 ℃, 15 h.	acetonitrile/water =1:1 (4 mL)	97.5	1242	[9]
11	C, N-TiO_2 nanosheet	Ethylbenzene	Catalyst (10 mg), 1 atm O_2, 100 W Xe lamp (350 < λ < 780 nm), RT, 6 h.	methanol (5 mL)	100	1563	[10]
12	CdS nanocrystals	Ethylbenzene	Catalyst (5 mg), 1 atm O_2, 40 W CFL lamp, RT, 2 h.	benzotrifluoride (5 mL)	50	2250	[11]
13	Nb_2O_5	Ethylbenzene	Catalyst (100 mg), O_2 flow, 2 mL·min^{-1}, 40 W CFL lamp, RT, 24 h.		0.35	112	[12]

	Catalyst	Substrate	Reaction conditions		Conversion (%)	Fr[a]	Ref.
14	5wt%Pd/CeO$_2$	Ethylbenzene	Catalyst (20 mg), 1 mmol TBHP, visible light, 80 °C, 4 h.	-	99.8	9855	[13]
15	Ag/AgBr/TiO$_2$	Ethylbenzene	Catalyst (30 mg), 1 atm Air, CFL White 15 W, RT, 4 h.	-	90	2160	[14]
16	Ce-BTC MOF	Ethylbenzene	Catalyst (70 mg), O$_2$ 5.5 mL·min^{-1}, LED λ=450 nm, 160 °C, 20 h.		85	23681	[15]
17	1%Pd/H$_2$Ti$_3$O$_7$	Benzyl alcohol	Catalyst (100 mg), 1 atm O$_2$, Halogen lamp (150 W), 90 °C, 6h.		89	98318.0	[16]
18	Ir/TiO$_2$-p	Benzyl alcohol	Catalyst (300 mg), 1 atm O$_2$, Halogen lamp (315-420 nm), 80 °C, 6 h.		11	17203	[17]
19	Pd/TiO$_2$ (B)	Benzyl alcohol	Catalyst (100 mg), 1 atm O$_2$, Halogen lamp (150 W), 90 °C, 4 h.		82	2016.0	[18]
20	Cu/Nb$_2$O$_5$	Benzyl alcohol	Catalyst (100 mg), 1 atm O$_2$, Halogen lamp (150 W), RT, 24 h.		36	14285.7	[19]
21	Pt-TiO$_2$	Benzyl alcohol	Catalyst (50 mg), 1 atm O$_2$, λ=366 nm, RT, 1 h.		71	440	[20]
22	ZnO/C$_3$N$_4$	Benzyl alcohol	Catalyst (100 mg), EDTA-2Na (1 mmol), 1 atm O$_2$, light source (blue LED light, 10 W, λ=400-405 nm), RT, 12 h.		99.8	16633.3	[21]
23	0.27% PdO/C-Nb$_2$O$_5$	Ethylbenzene	Catalyst (100 mg), 1 atm O$_2$, light source (blue LED light, 10 W, λ=400-405 nm), RT, 12 h.		67.4	10997	This work
24	0.27% PdO/C-Nb$_2$O$_5$	Ethylbenzene	Catalyst (100 mg), 1 atm O$_2$, light source (blue LED light, 10 W, λ=400-405 nm), RT, 24 h.		80.4	6776	This work
25	0.27% PdO/C-Nb$_2$O$_5$	Ethylbenzene	Catalyst (100 mg), 1 atm O$_2$, light source (blue LED light, 10 W, λ=400-405 nm), RT, 48 h.		87.4	3665	This work
26	0.27% PdO/C-Nb$_2$O$_5$	Benzyl alcohol	Catalyst (100 mg), 1 atm O$_2$, light source (blue LED light, 10 W, λ=400-405 nm), RT, 12 h.		99.0	16500	This work

[a] Formation rate (Fr) = $\mu mol_{acetophenone} \cdot g_{catalyst}^{-1} \cdot h_{reaction\ time}^{-1}$.

Table S2 Photocatalytic oxidation of benzene to phenol over different catalysts.

Entry	Catalyst	Oxidation	Reaction conditions	Conv. (%)	Sel. (%)	Ref.
1	BCW-4	O_2 (3 mL/min),	benzene (0.5mmol), photocatalyst (50 mg), acetonitrile (3 mL), H_2O (100 μL), light irradiation (λ ≥ 400nm), RT, 3 h.	5.8%	>99%	22
2	ZnTi-LDH	1 atm air	Benzene (0.2 mmol), 20 mL H_2O, 20 mg catalyst, 300 W Xe lamp, 3 h, and 48 °C.	5.7%	81.12%	23
3	Pt/TiO$_2$-P	1 atm O_2	Benzene (18.8 μmol), H_2O 7.5 mL, 300 W Xe lamp, RT, 12 h.	26.6	83.8%	24
4	C16 Qu-PW	1 atm air	benzene (1.28 mmol), photocatalyst (50 mg), acetonitrile 10 mL, water 1 mL, atmospheric air, RT, 10 h.	20.9	>99%	25
5	$W_{10}O_{32}$	1 atm O_2	benzene (0.5mmol), photocatalyst (20 mg), Water/aceticacid (5/1), 300 W xenon lamp; 10 °C, 1 h.	21.0	81	26
6	$(C_{16}$-Quin$)_2V_6$	1 atm O_2	benzene (0.5mmol), photocatalyst (50 mg), (H_2O/CH_3CN, 3:17 =v:v), light irradiation (λ ≥ 400nm), RT, 12 h.	22.5	99%	27
7	MIL-100(Fe)	H_2O_2 (2 mmol)	benzene (0.5 mmol), photocatalyst (10 mg), $CH_3CN/H2O$, 1:1=4 mL, light irradiation (λ ≥ 420 nm), 8 h.	22.5%	92%	28
8	0.2 NCWCN	H_2O_2 (2 mmol)	benzene (1 mL, 11.3 mmol), catalyst (20 mg), RT, 15 min, sunlight.	98.5	82.7	29
9	$FeVO_4$	H_2O_2 (25 mmol)	Benzene (10 mmol), acetonitrile (6 mL), catalyst (50 mg), 300 W Xe lamp, RT, 4 h.	30.4	100	30
10	CuO@CN	H_2O_2 (25 mmol)	Benzene (1 mmol), MeCN (6 mL), catalyst (40 mg), RT, 12 h and AM 1.5 illumination.	99.9%	99.9%	31
12	PdO/C-Nb$_2$O$_5$	1 atm O_2	Benzene (1 mmol), acetonitrile (2 mL), catalyst (100 mg), blue LED lamp (10 W, 400-405 nm), RT, 48 h.	7.6%	100	This work
13	PdO/C-Nb$_2$O$_5$	1 atm O_2	Benzene (1 mmol), acetonitrile (2 mL), catalyst (150 mg), blue LED lamp (10 W, 400-405 nm), RT, 72 h.	8.03%	100	This work

Table S3 Texture properties of prepared materials.

Entry	Samples	BET surface area (m^2/g)	BJH adsorption average pore diameter (nm)	BJH pore cumulative volume ($\times 10^{-3}$ cm^3/g)
1	Nb_2O_5-P	31	16.1881	0.128706
2	C-Nb_2O_5	233	5.4603	0.229425
3	0.27% PdO/C-Nb_2O_5	205	5.1025	0.231228

Table S4 X-ray photoelectron spectra of C, Pd, Nb, and O element on the samples surface.

Entry	Catalysts	C (at. %)	Pd (at. %)	Nb (at. %)	O (at. %)
1	Nb_2O_5-P	8.32	-	57.52	34.16
2	C-Nb_2O_5	30.24	-	14.56	55.2
3	0.27% PdO/C-Nb_2O_5	17.39	0.10	20.61	61.9

Table S5 The ICP results of 0.27% PdO/C-Nb_2O_5

Entry	Sample	ICP content (Pd wt.%)	Theoretical content (Pd wt.%)
1	Fresh PdO/C-Nb_2O_5	0.274	0.267
2	Used PdO/C-Nb_2O_5	0.257	0.267

Table S6 Photocatalytic oxidation reactions over PdO/Nb_2O_5 and PdO/C-Nb_2O_5

Entry	Catalyst	Substrate	Conversion (%)	Selectivity (%)
1	PdO/Nb_2O_5	ethylbenzene	23.3	87.5
2	PdO/Nb_2O_5	1-phenylethanol	43.4	88.9
3	PdO/C-Nb_2O_5	ethylbenzene	67.4	97.7
4	PdO/C-Nb_2O_5	1-phenylethanol	91.2	98.9

Reaction conditions: substrate 20 mmol, catalyst 100 mg, oxygen pressure 0.1 atm, 25 °C, blue LED light (10 W, λ = 400–405 nm), and a stirring speed of 1500 rpm.

3. FIGURES
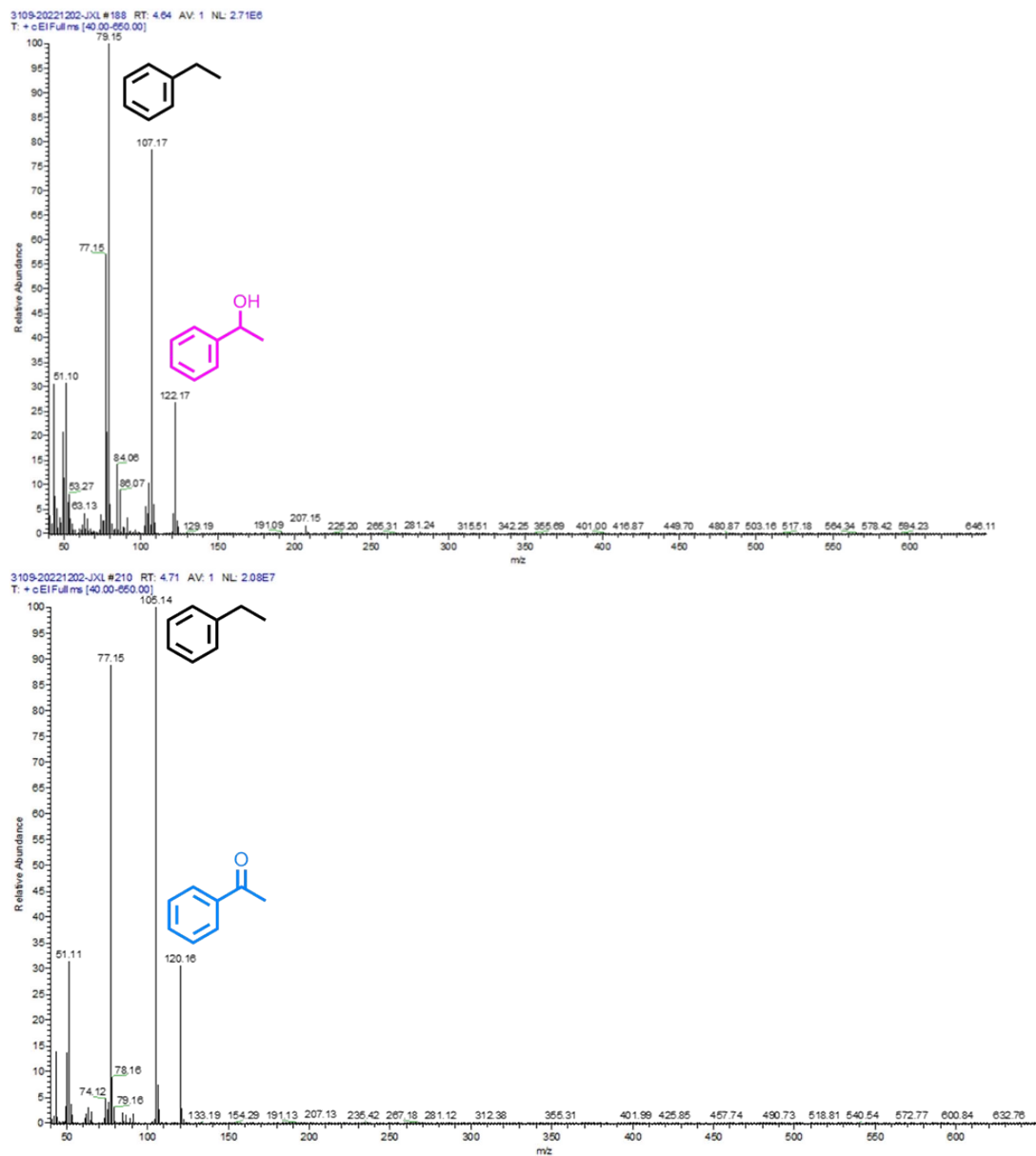
Figure S1 The MS of acetophenone and 1-phenylethanol products.

Figure S2 ^{1}H and ^{13}C NMR spectra of acetophenone
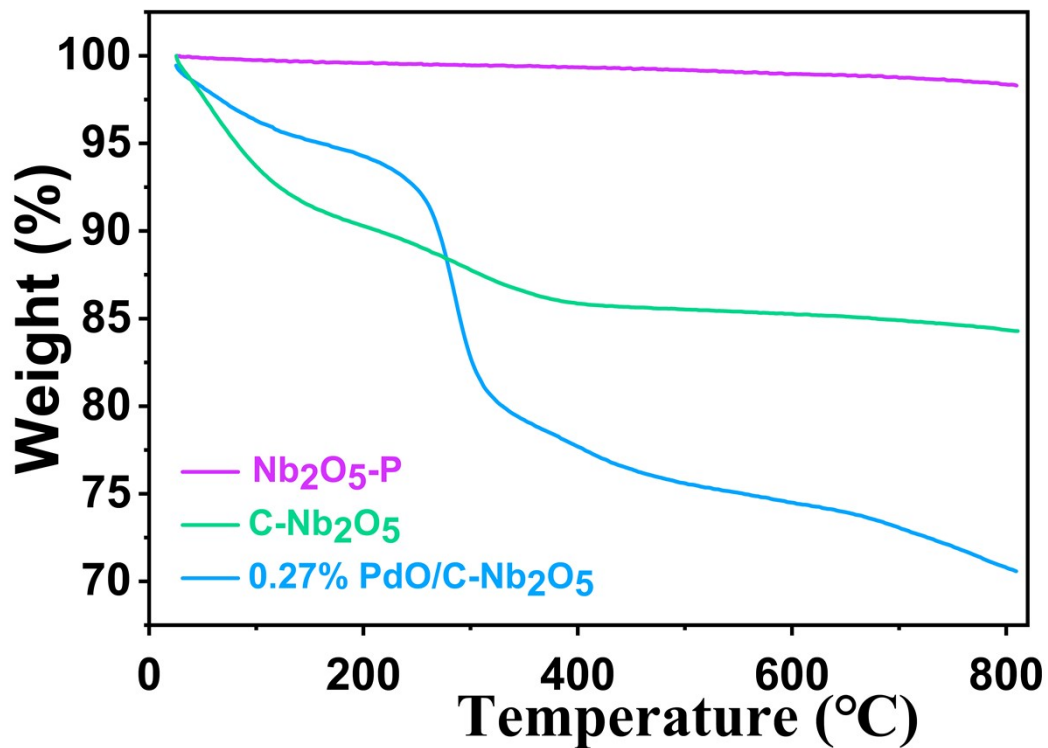
Figure S3 The TG curves of various catalysts
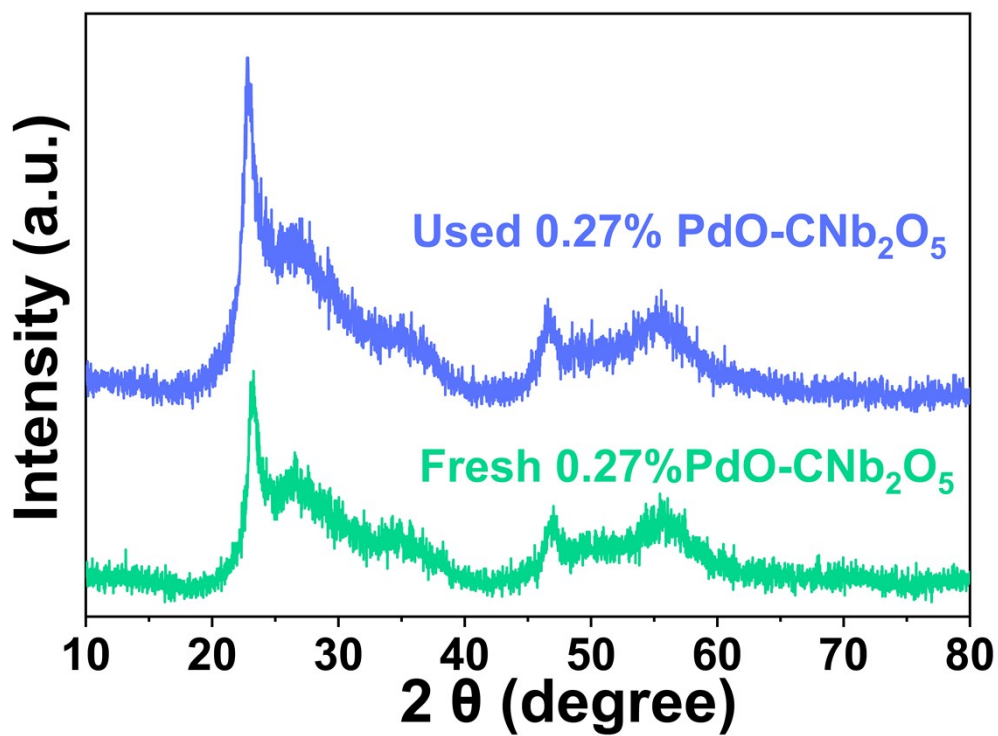
Figure S4 XRD patterns of fresh and used PdO/C-Nb$_2$O$_5$.
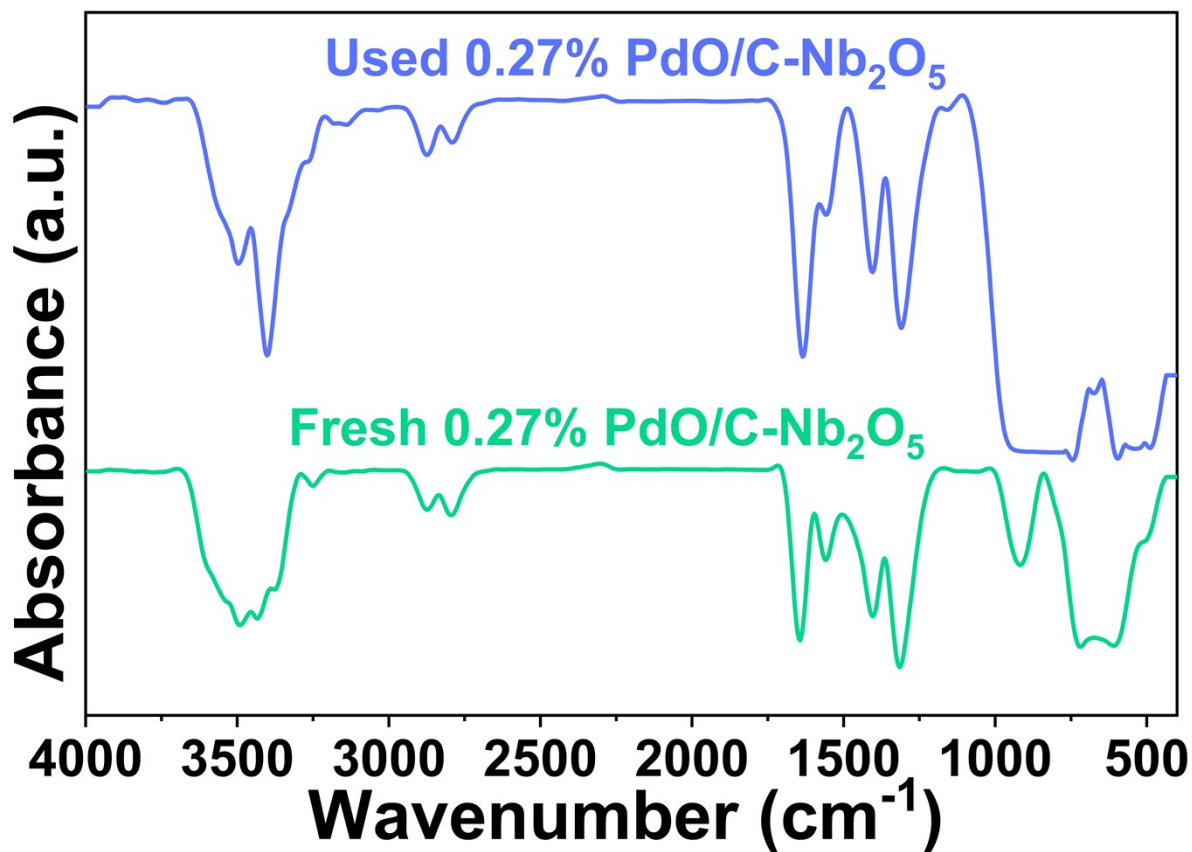
Figure S5 FT-IR spectra of fresh and used PdO/C-Nb$_2$O$_5$.
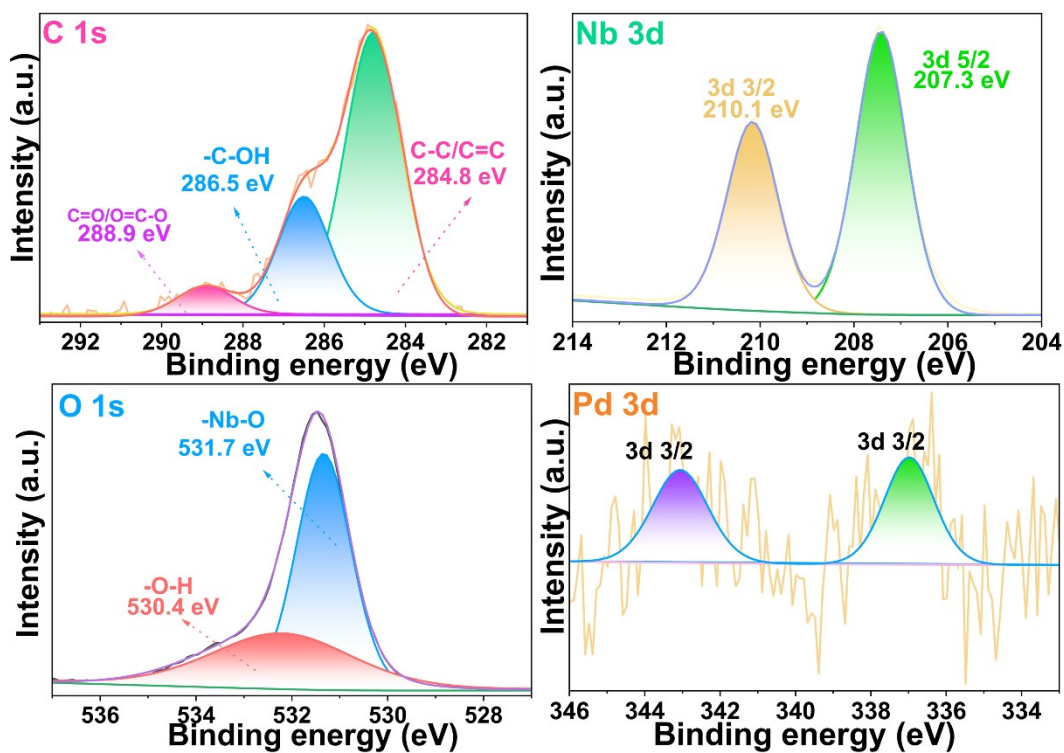
Figure S6 XPS spectra of used PdO/C-Nb$_2$O$_5$.
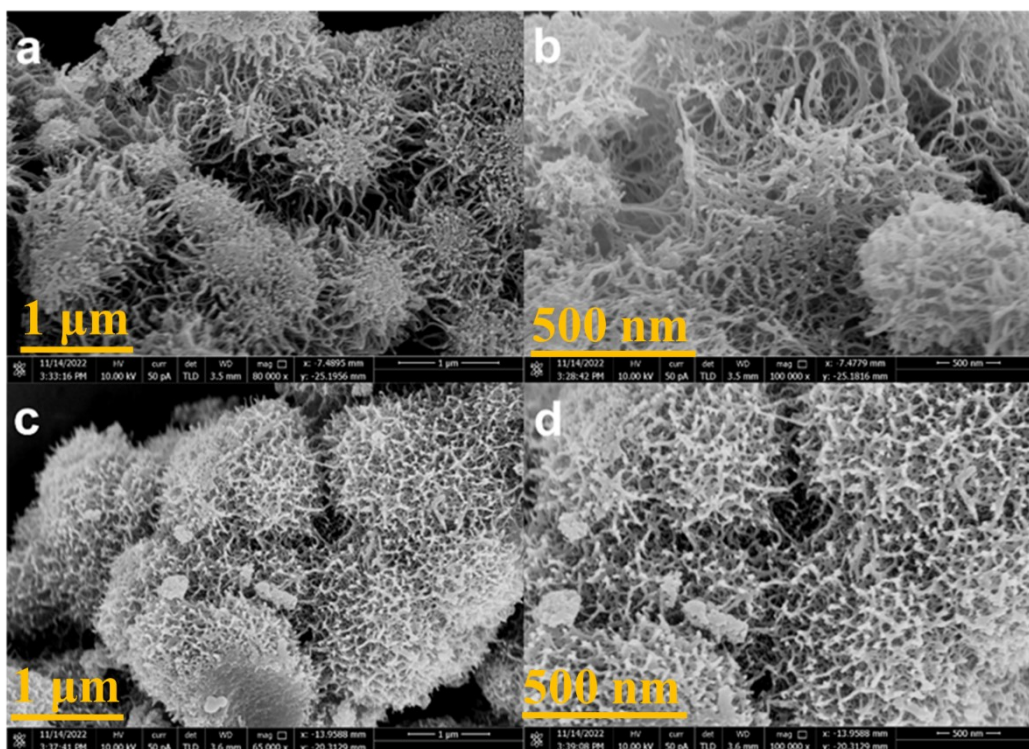
Figure S7 TEM images of the fresh (a, b) and used (c, d) 0.27% PdO/C-Nb$_2$O$_5$.
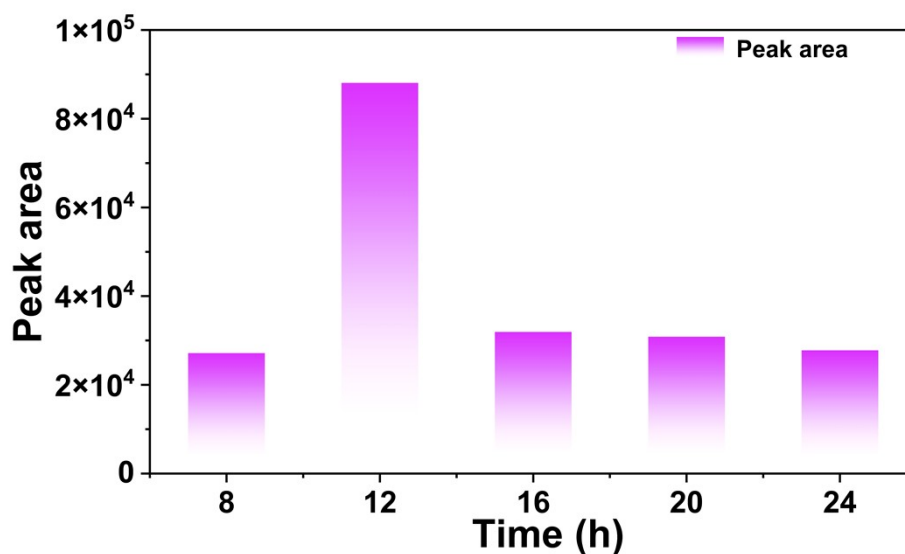
Figure S8 1-Phenylethanol peak area change diagram against time during the reaction. Reaction conditions: substrate (20 mmol), 100 mg of catalyst, 1 atm of oxygen, 10 W blue LED lamp λ=400-405 nm, room temperature.

The conclusion of consecutive reaction was based on the fact that the 1-phenylethanol was detected and the amount of 1-phenylethanol was determined. The amount of the 1-phenylethanol was roughly determined by the peak area of HPLC due to the content was too low. As shown in Fig. S8, it can be found that the amount of 1-phenylethanol was first increase and the decrease with the reaction undergoing, which was the typical characteristic of reaction intermediate compound in the consecutive reaction. Therefore, we postulated the reaction was a consecutive reaction and the 1-phenylethanol was the intermediate.
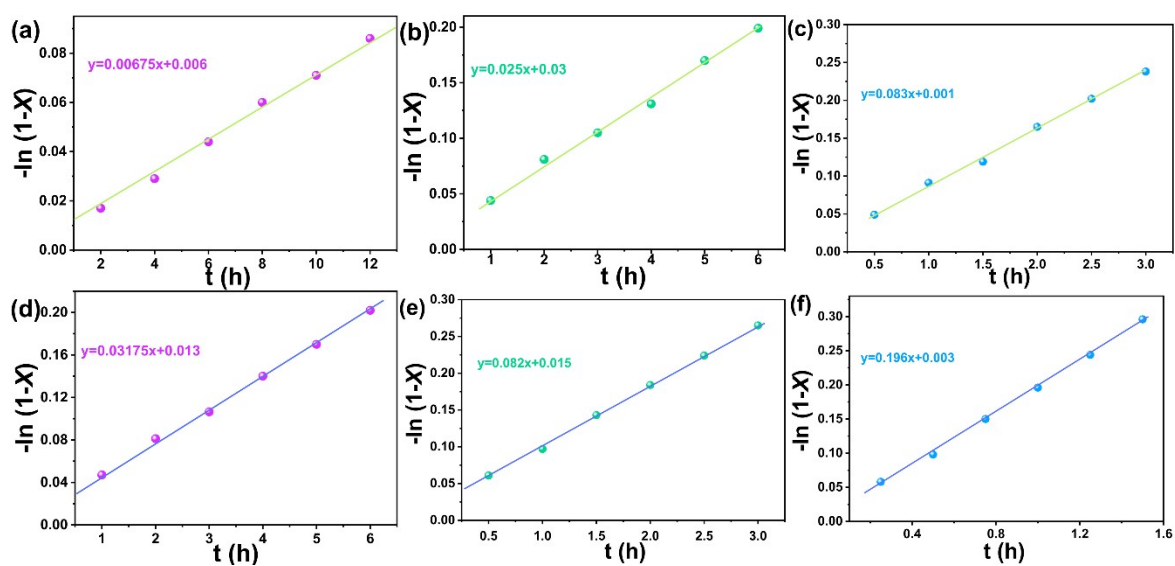
Figure S9 Kinetic study for the conversion of (a-c) ethyl benzene, and (d-f) 1-phenylethanol over Nb_2O_5-P (a, d), C-Nb_2O_5 (b, e), and 0.27% PdO/C-Nb_2O_5 (c, f). Reaction conditions: substrate (20 mmol), 100 mg of catalyst, 1 atm of oxygen, 10 W blue LED lamp λ=400-405 nm, room temperature.
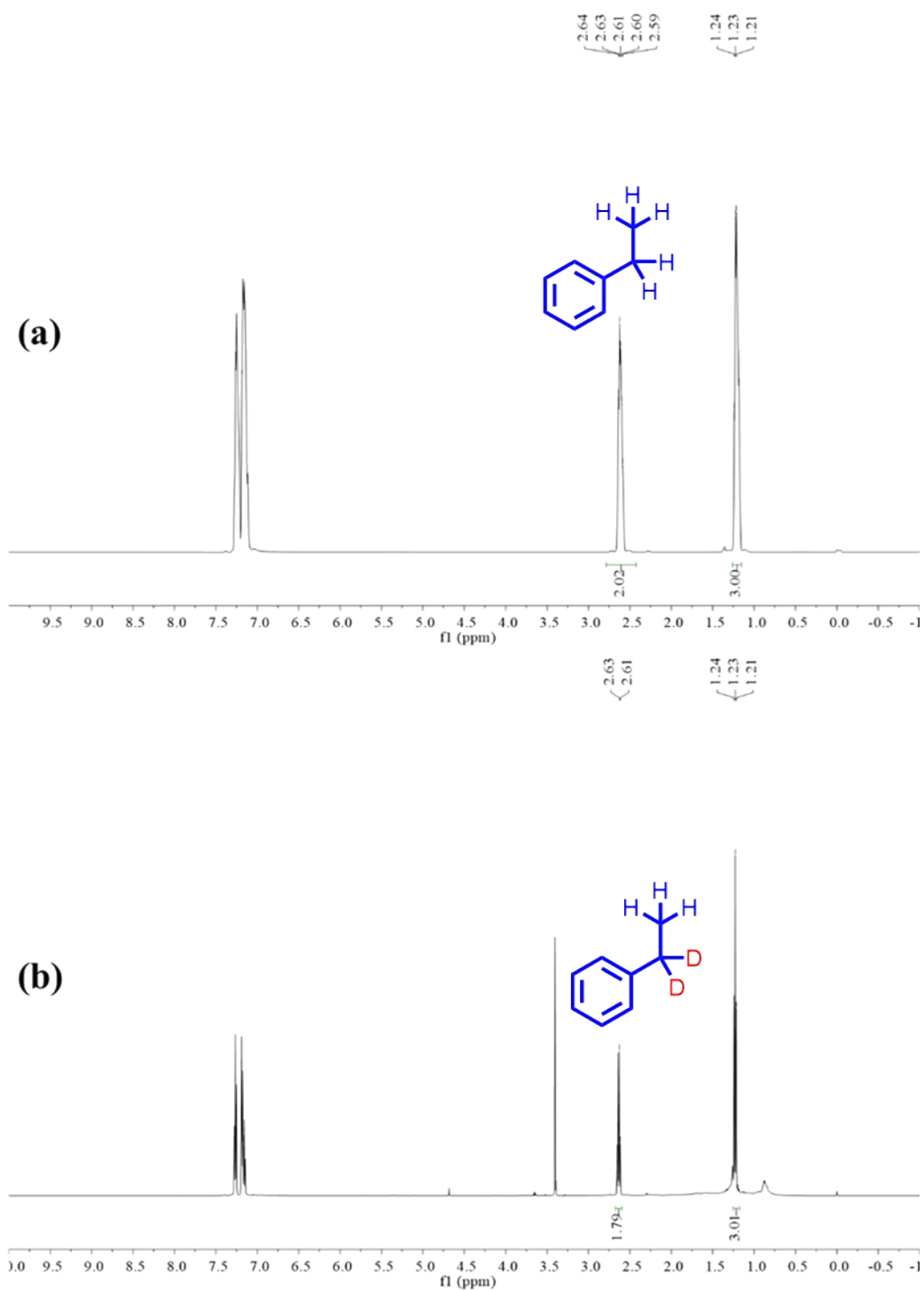
Figure S10 1H NMR spectra of the pure ethylbenzene (a) and ethylbenzene exchanged by H and D (b) Reaction conditions: ethylbenzene 5 mmol, catalyst 100 mg, 2 mL CD₃OD, 0.1 atm N², 25 °C, blue LED light (10 W, λ = 400–405 nm), and a stirring speed of 1500 rpm. The deuterated solvent is CDCl₃, 600 MHz NMR spectrometer.
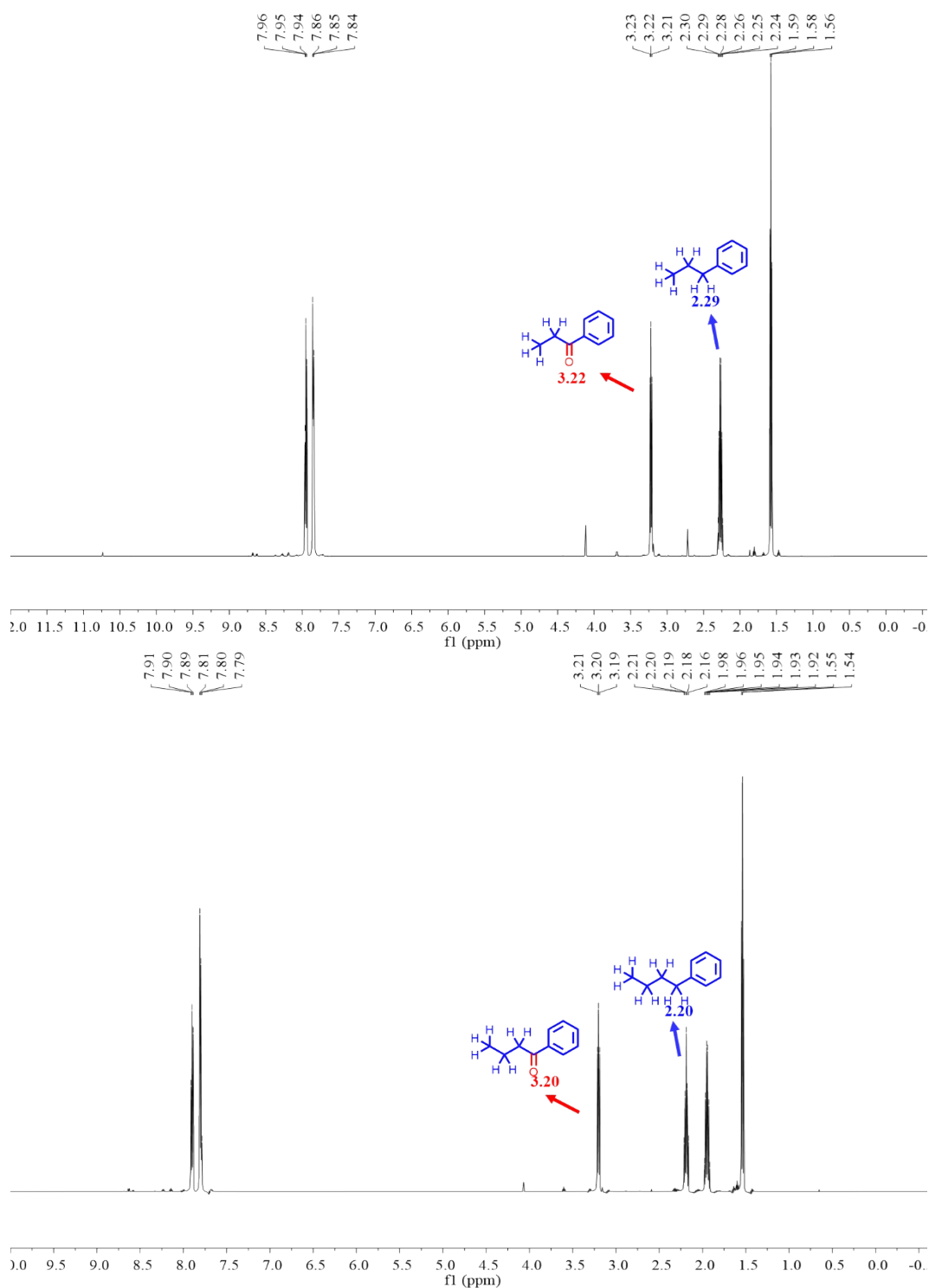
Figure S11 ^{1}H NMR spectra of the propylene and butylbenzene product mixtures

Reaction conditions: substrate 20 mmol, catalyst 100 mg, oxygen pressure 0.1 atm, 25 °C, blue LED light (10 W, λ = 400–405 nm), and a stirring speed of 1500 rpm. The deuterated solvent is DMSO-*d*, 600 MHz NMR spectrometer.
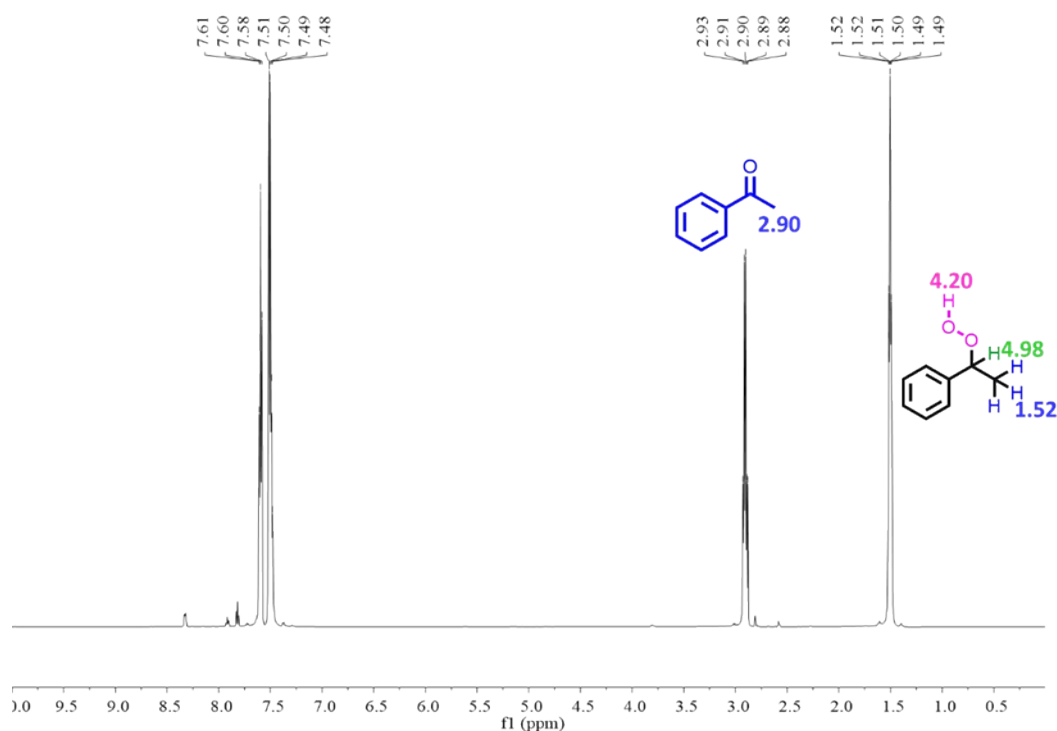
Figure S12 ^{1}H NMR spectra of the product mixtures

Reaction conditions: substrate 20 mmol, catalyst 100 mg, oxygen pressure 0.1 atm, 25 °C, blue LED light (10 W, λ = 400–405 nm), and a stirring speed of 1500 rpm. The deuterated solvent is DMSO-*d*, 600 MHz NMR spectrometer.

The reacted mixture obtained under standard conditions was detected by ^{1}H NMR using DMSO-d$_6$ as solvent. The ^{1}H NMR spectrum was shown in Fig. S12. The H in the peroxide was expected to be located at 4.20 ppm, H on the benzyl group was expected to be at 4.98 ppm, and H on the methyl was expected to be at 1.52 ppm. However, the H peak in the peroxide position was not detected in the ^{1}H NMR spectrum (Fig. S12), which may be because the peroxide was unstable and difficult to exist stably.
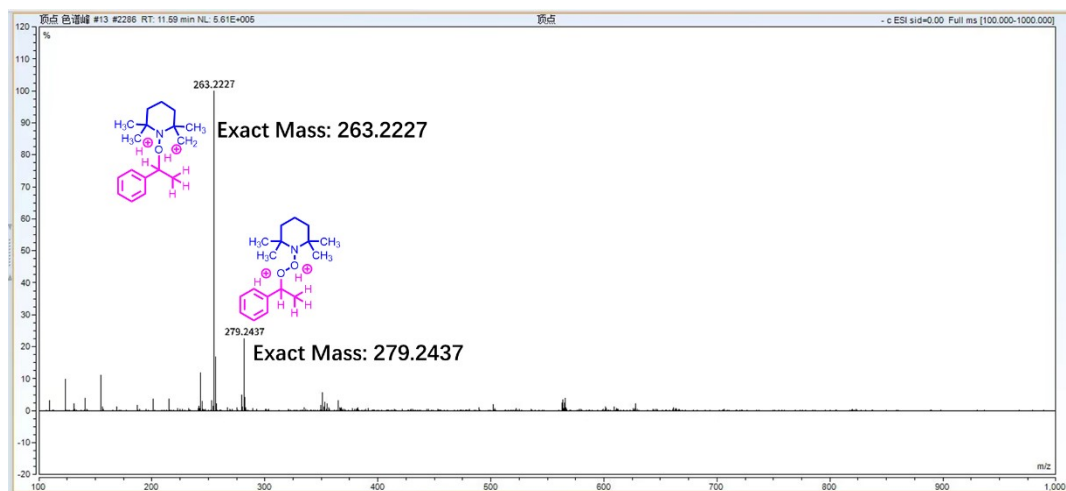
Figure S13 Mechanistic experiments

Reaction conditions: substrate 20 mmol, catalyst 100 mg, TEMPO 1 mmol, oxygen pressure 0.1 atm, 25 °C, blue LED light (10 W, λ = 400–405 nm), and a stirring speed of 1500 rpm. HPLC-MS determination.

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5. NMR DATA

Acetophenone

¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 198.01, 137.20, 133.04, 128.41 (d, *J* = 26.9 Hz), 26.51.
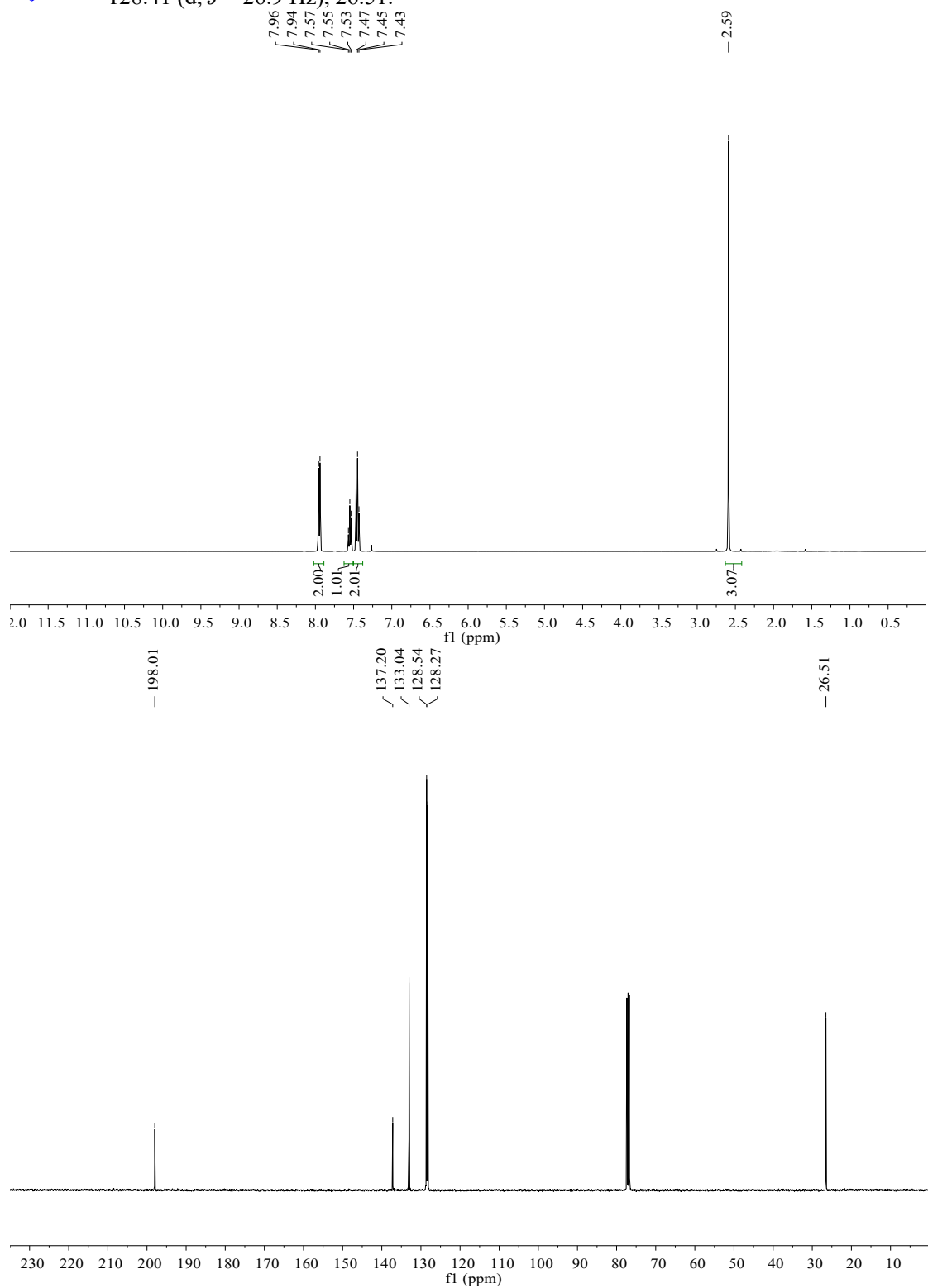
Figure S14 ¹H and ¹³C NMR spectrogram of acetophenone

2-Methylacetophenone
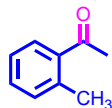
¹H NMR (600 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.30 – 7.16 (m, 2H), 2.57 (s, 3H), 2.53 (s, 3H). **¹³C NMR (151 MHz, Chloroform-d)** δ 201.70, 138.39, 137.66, 132.04, 131.51, 129.36, 125.70, 29.52, 21.57.
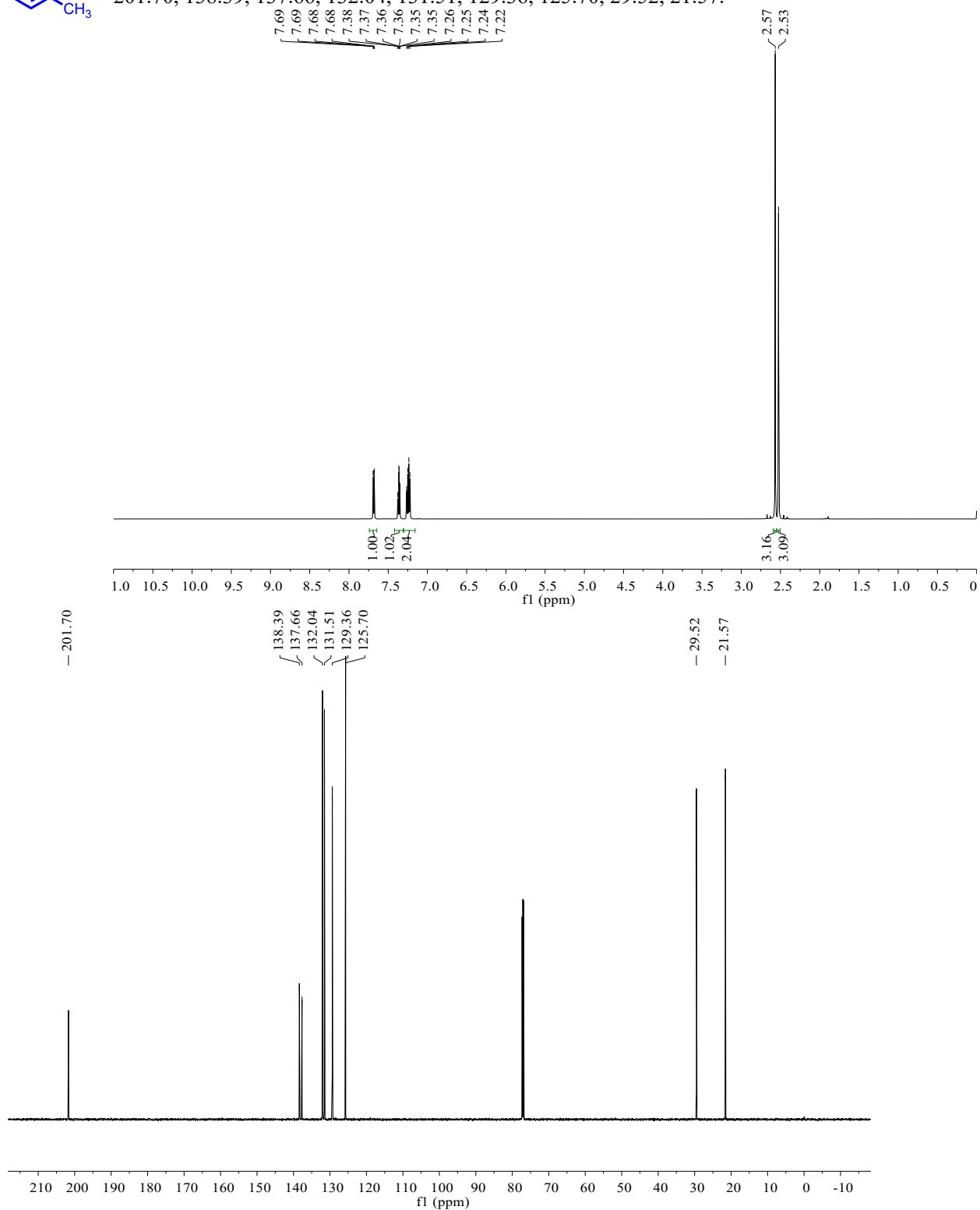
Figure S15 ¹H and ¹³C NMR spectrogram of 2-methylacetophenone

3-Methylacetophenone
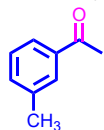
¹H NMR (600 MHz, Chloroform-*d*) δ 8.00 – 7.61 (m, 2H), 7.35 (dt, *J* = 15.0, 7.5 Hz, 2H), 2.58 (s, 3H), 2.40 (s, 3H). **¹³C NMR (151 MHz, Chloroform-d)** δ 198.36, 138.34, 137.18, 133.85, 128.78, 128.44, 125.58, 26.64, 21.31.
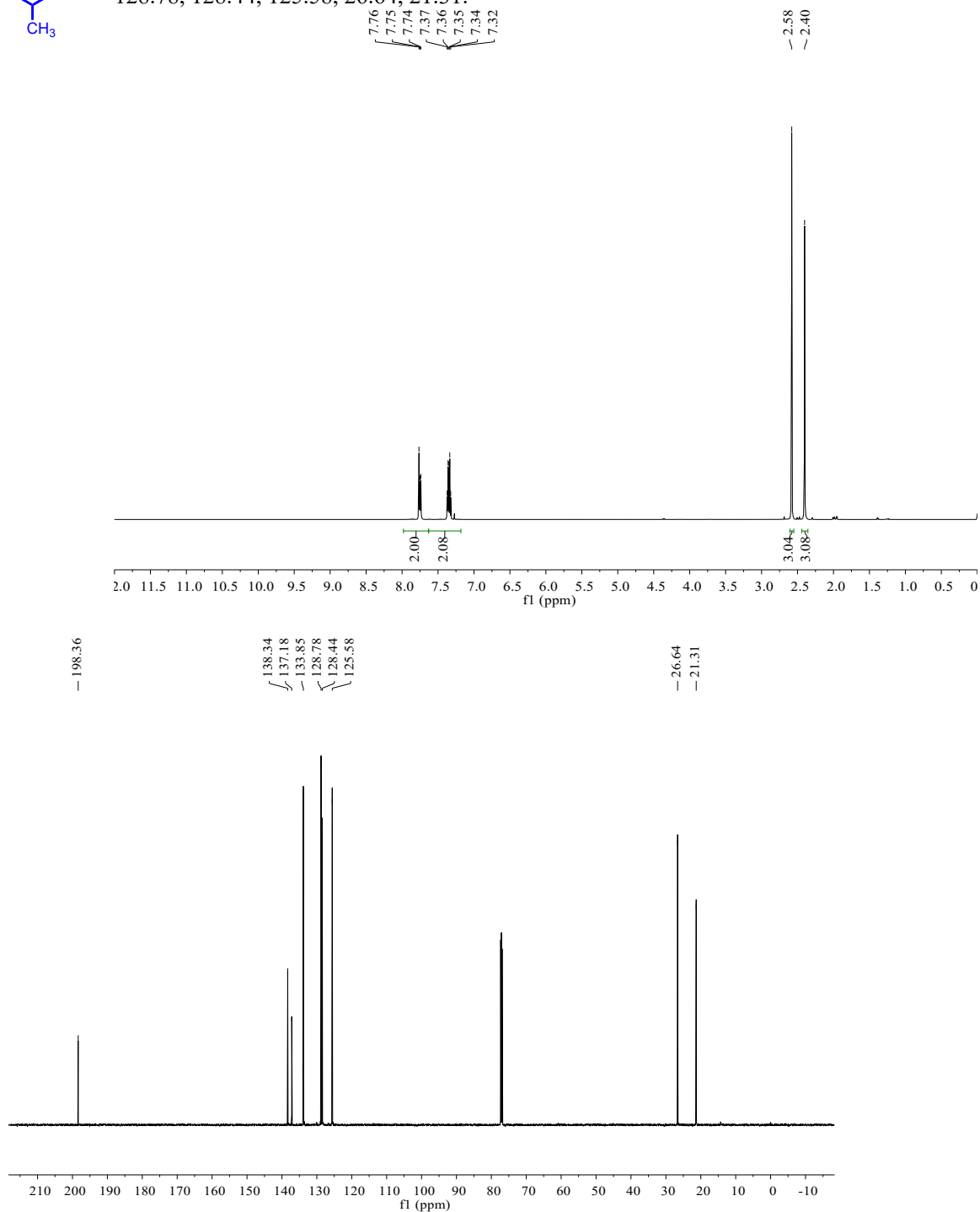
Figure S16 ¹H and ¹³C NMR spectrogram of 3-methylacetophenone

4-Methylacetophenone
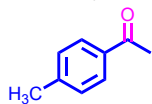
¹H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.56 (s, 3H), 2.40 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 196.75, 163.49, 130.46 (d, *J* = 35.2 Hz), 113.68, 55.45, 26.30.
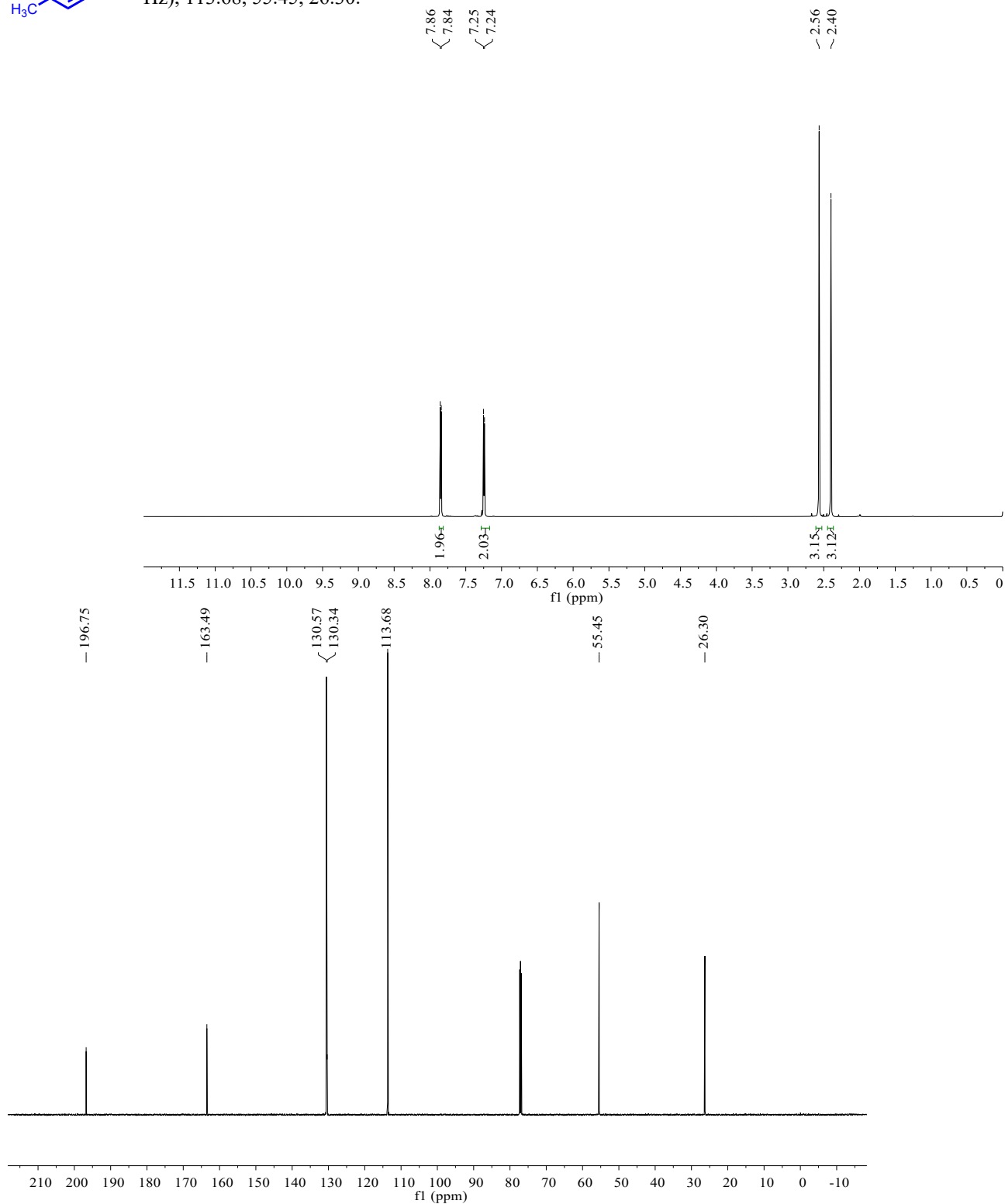
Figure S17 ¹H and ¹³C NMR spectrogram of 4-methylacetophenone

4-Methoxy-acetophenone
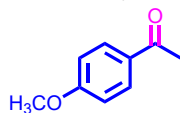
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.9 Hz, 2H), 7.08 (d, J = 8.9 Hz, 2H), 4.01 (s, 3H), 2.70 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 196.75, 163.49, 130.57, 130.34, 113.68, 55.45, 26.30.
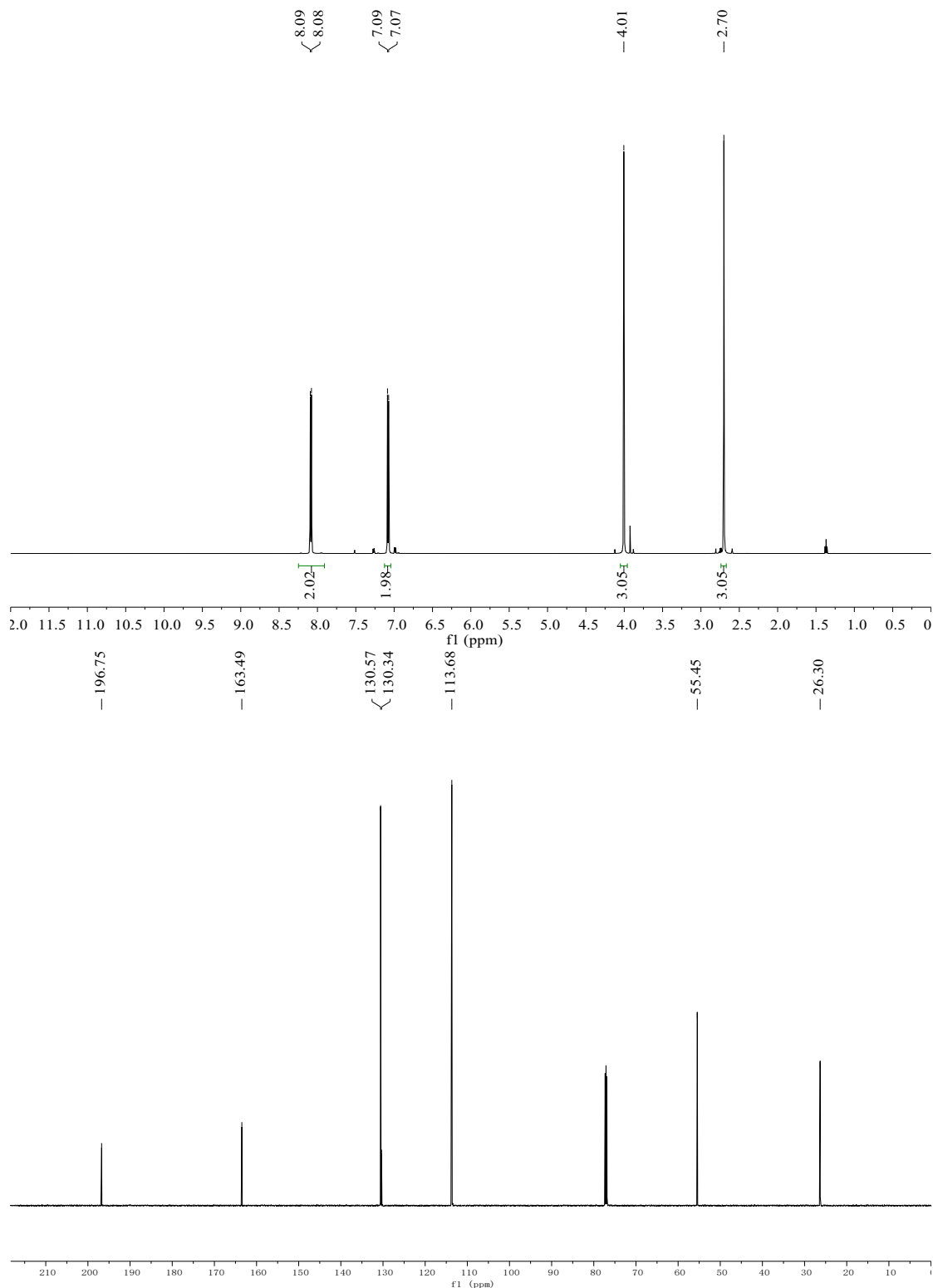
Figure S18 ^{1}H and ^{13}C NMR spectrogram of 4-methoxy-acetophenone

4-Hydroxyacetophenone
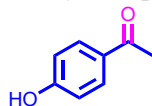
¹H NMR (600 MHz, DMSO-d_6) δ 10.33 (s, 1H), 7.84 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 2.48 (s, 3H). **¹³C NMR (151 MHz, DMSO-d_6)** δ 194.01, 159.97, 128.69, 126.56, 113.12, 24.23.
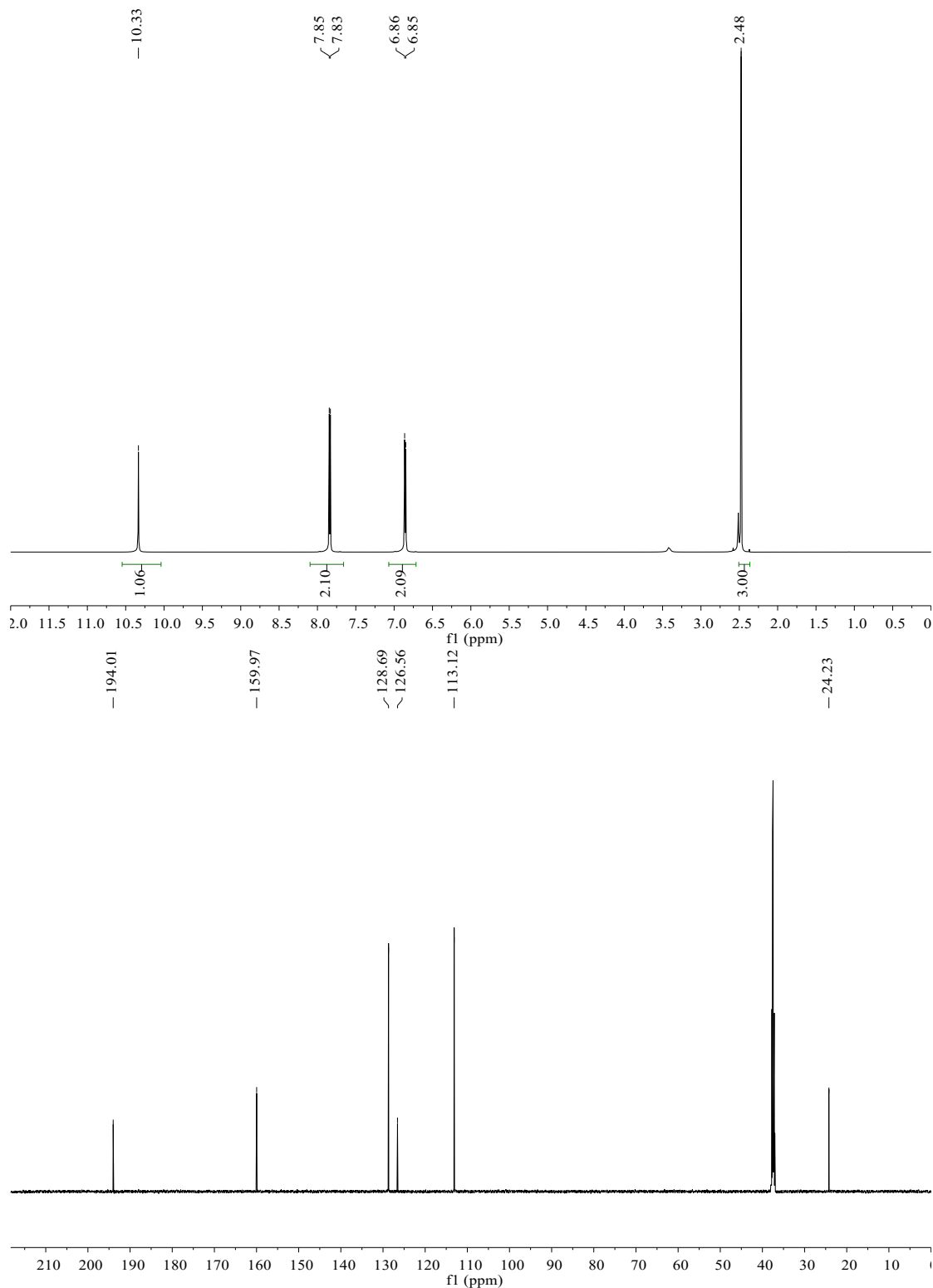
Figure S19 ¹H and ¹³C NMR spectrogram of 4-hydroxyacetophenone

2-Hydroxyacetophenone
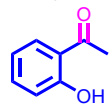
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.99 (s, 1H), 7.88 (dd, J = 8.1, 1.5 Hz, 1H), 7.65 – 7.39 (m, 1H), 7.15 – 6.83 (m, 2H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 202.59, 158.79, 134.26, 129.41, 117.15, 115.54, 25.55.
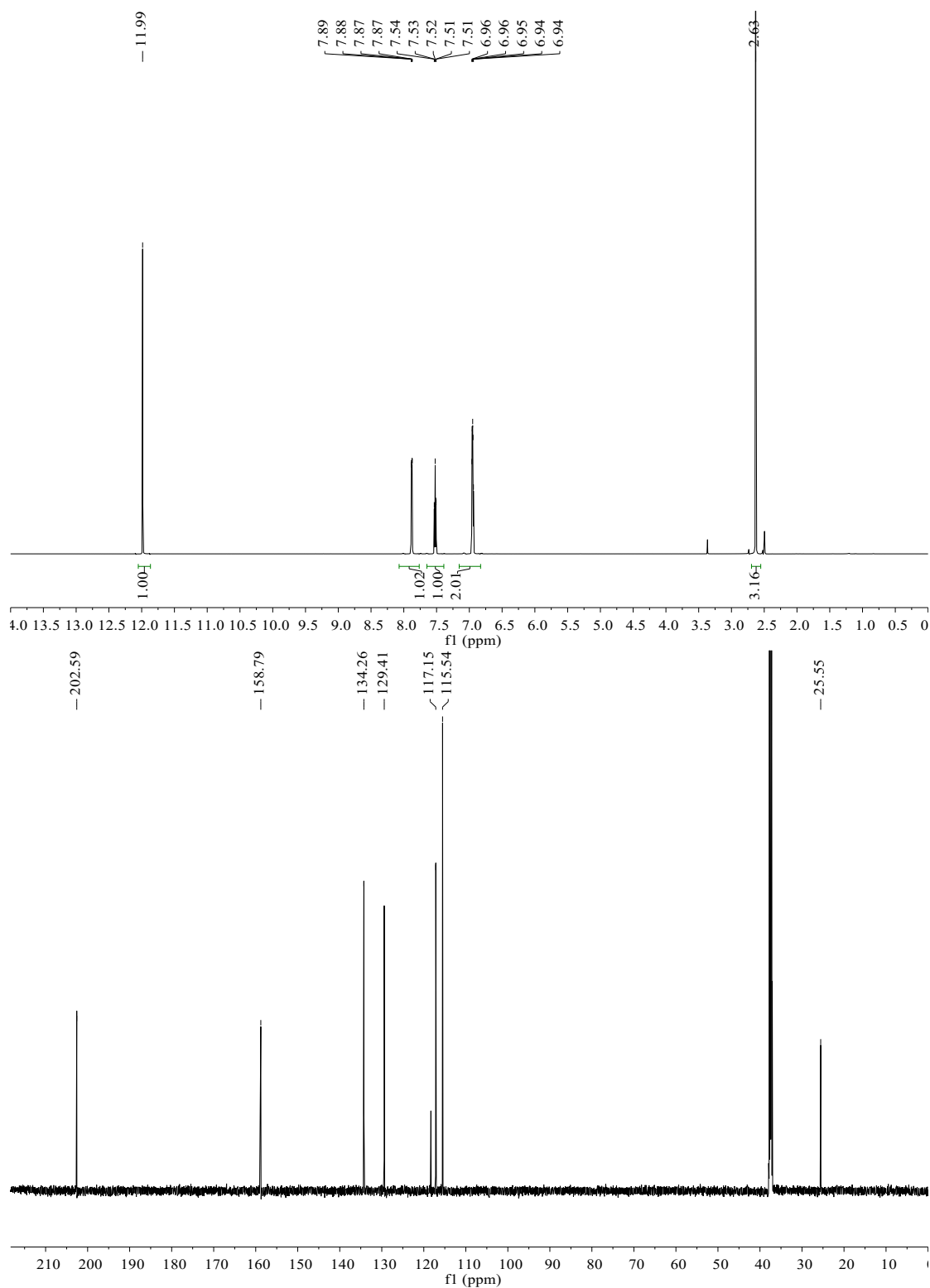
Figure S20 ^{1}H and ^{13}C NMR spectrogram of 2-hydroxyacetophenone

2-Bromophenone

¹H NMR (600 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.29 (td, *J* = 7.9, 1.7 Hz, 1H), 2.63 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 201.34, 141.45, 133.84, 131.81, 128.92, 127.46, 118.88, 30.31.
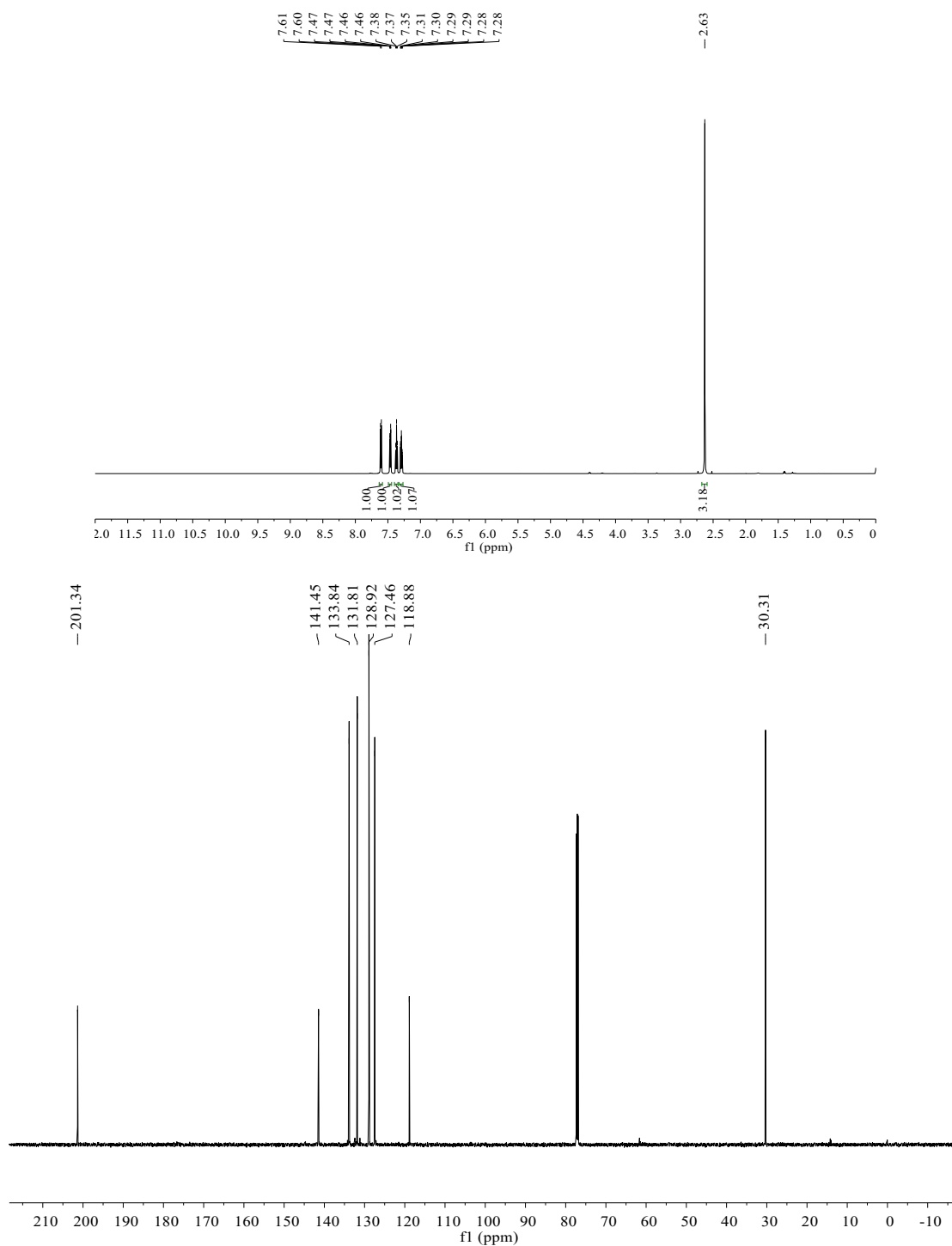
Figure S21 ¹H and ¹³C NMR spectrogram of 2-bromophenone

4-Bromoacetophenone
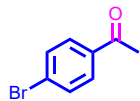
¹H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 2.58 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 196.94, 135.78, 131.83, 129.79, 128.24, 26.47.
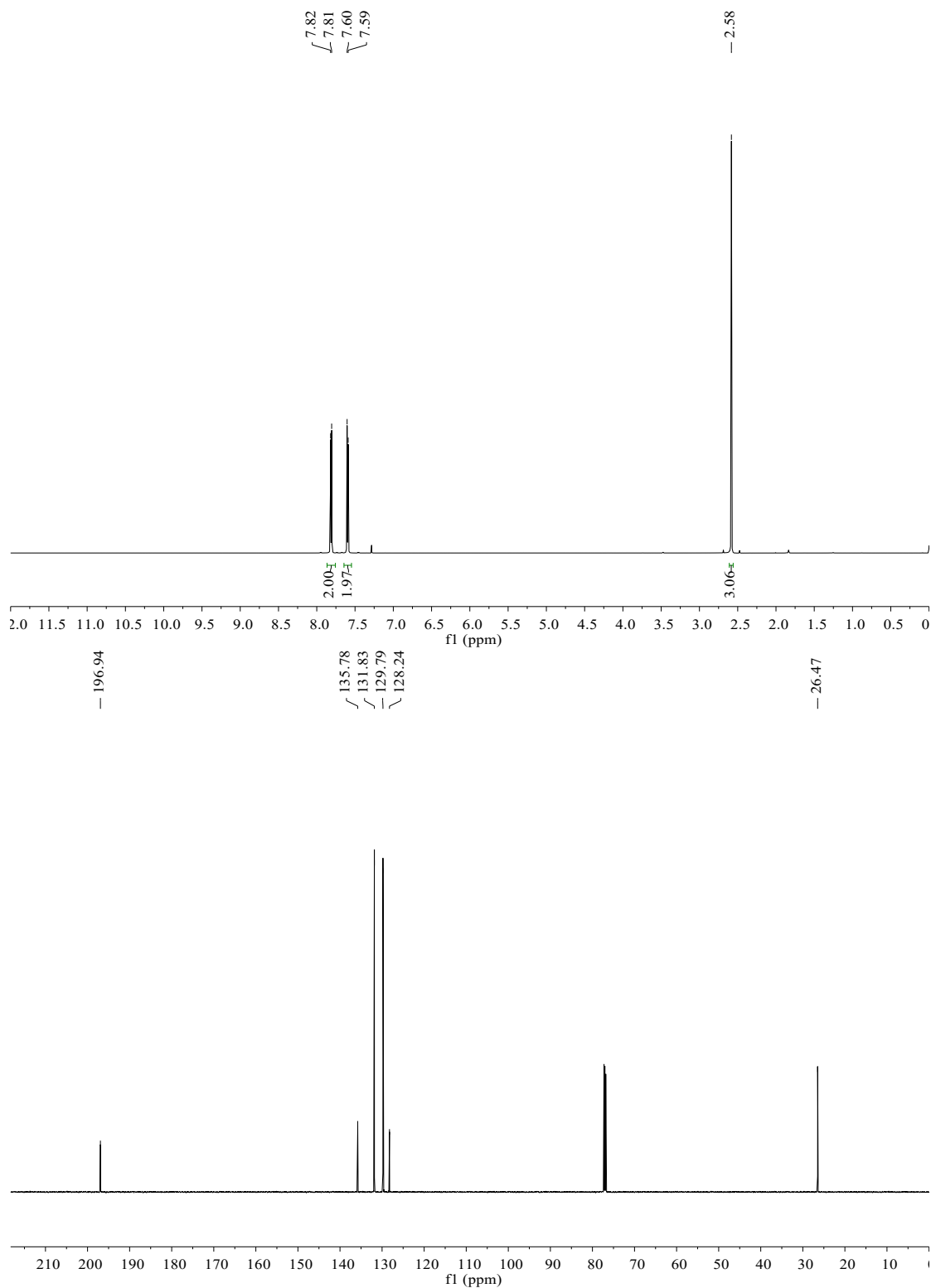
Figure S22 ¹H and ¹³C NMR spectrogram of 4-bromophenone

4-Iodophenone
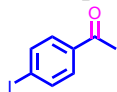
 ¹H NMR (600 MHz, Chloroform-*d*) δ 7.83 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 2.58 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 197.38, 137.92, 136.34, 129.75, 101.16, 26.53.
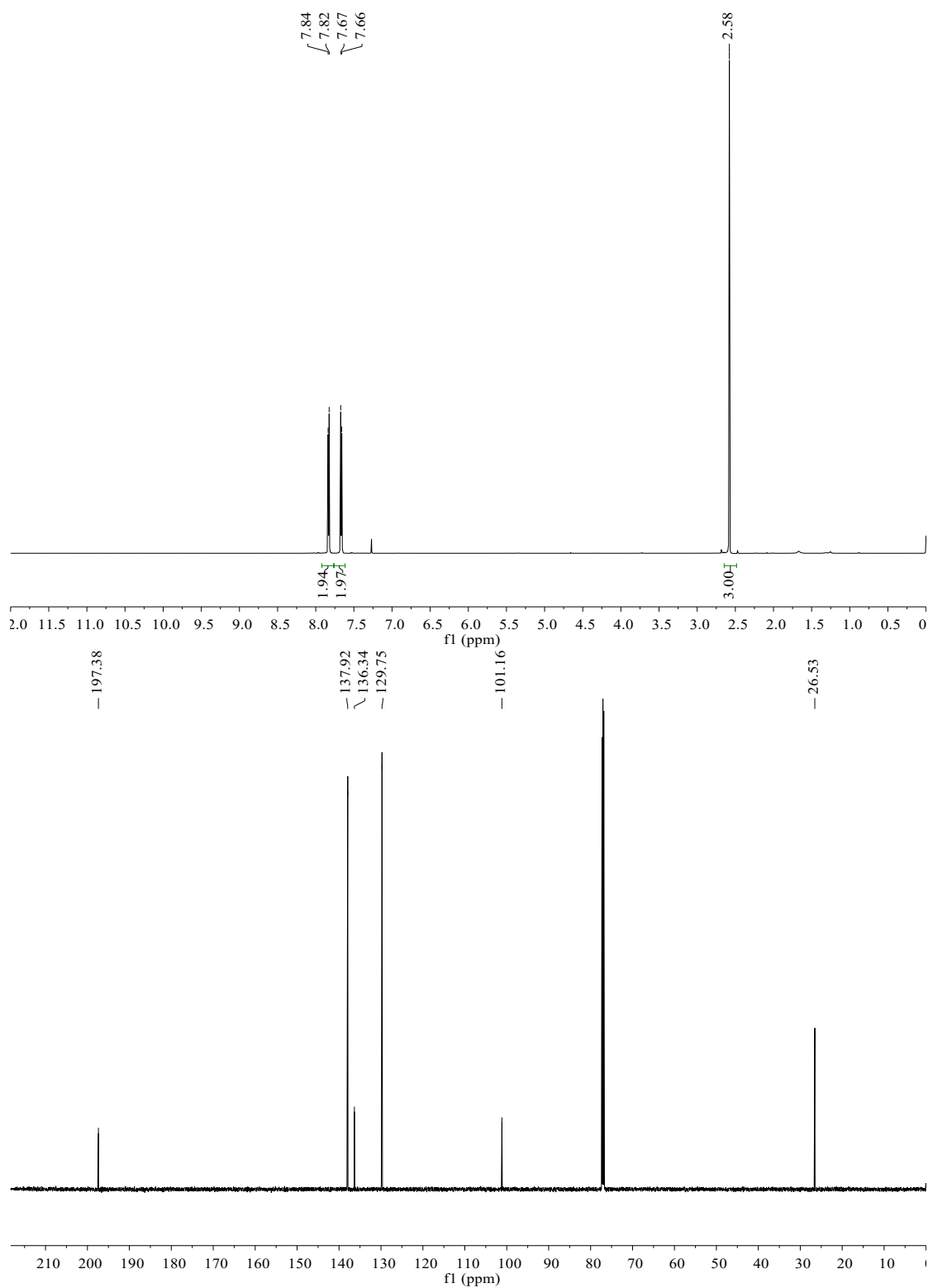
Figure S23 ¹H and ¹³C NMR spectrogram of 4-iodophenone

4-Aminoacetophenone
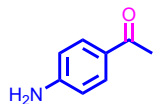
¹H NMR (600 MHz, DMSO-*d₆*) δ 7.67 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.04 (s, 2H), 2.39 (s, 3H). **¹³C NMR (151 MHz, DMSO-*d₆*)** δ 195.44, 154.12, 131.07, 125.35, 112.96, 26.35.
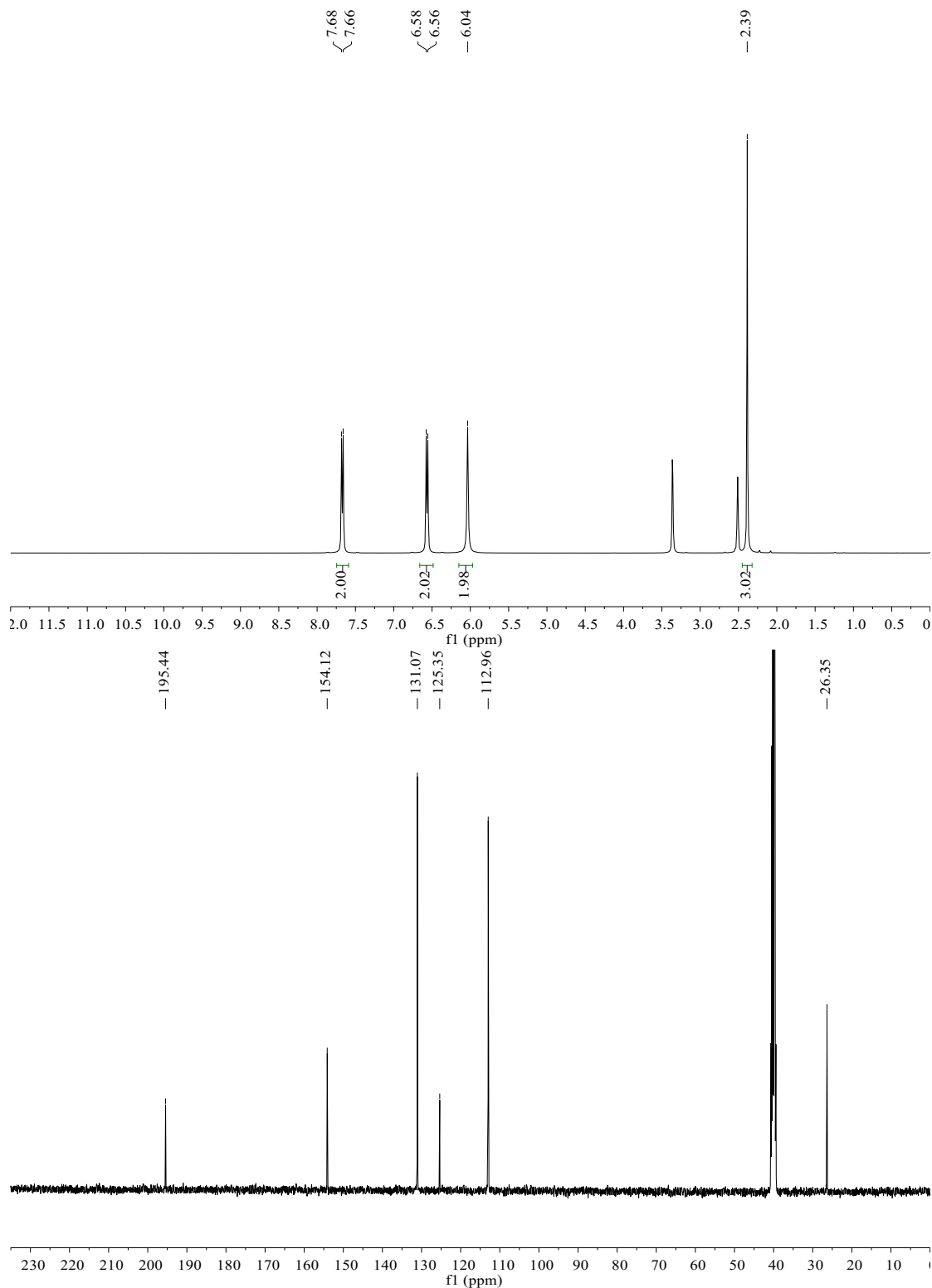
Figure S24 ¹H and ¹³C NMR spectrogram of 4-aminoacetophenone

4-Nitrophenone
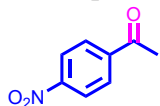
¹H NMR (600 MHz, Chloroform-*d*) δ 8.31 (td, *J* = 5.8, 4.7, 2.3 Hz, 2H), 8.21 – 8.08 (m, 2H), 2.75 – 2.68 (m, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 196.42, 150.28, 141.37, 129.32, 123.81, 26.96.
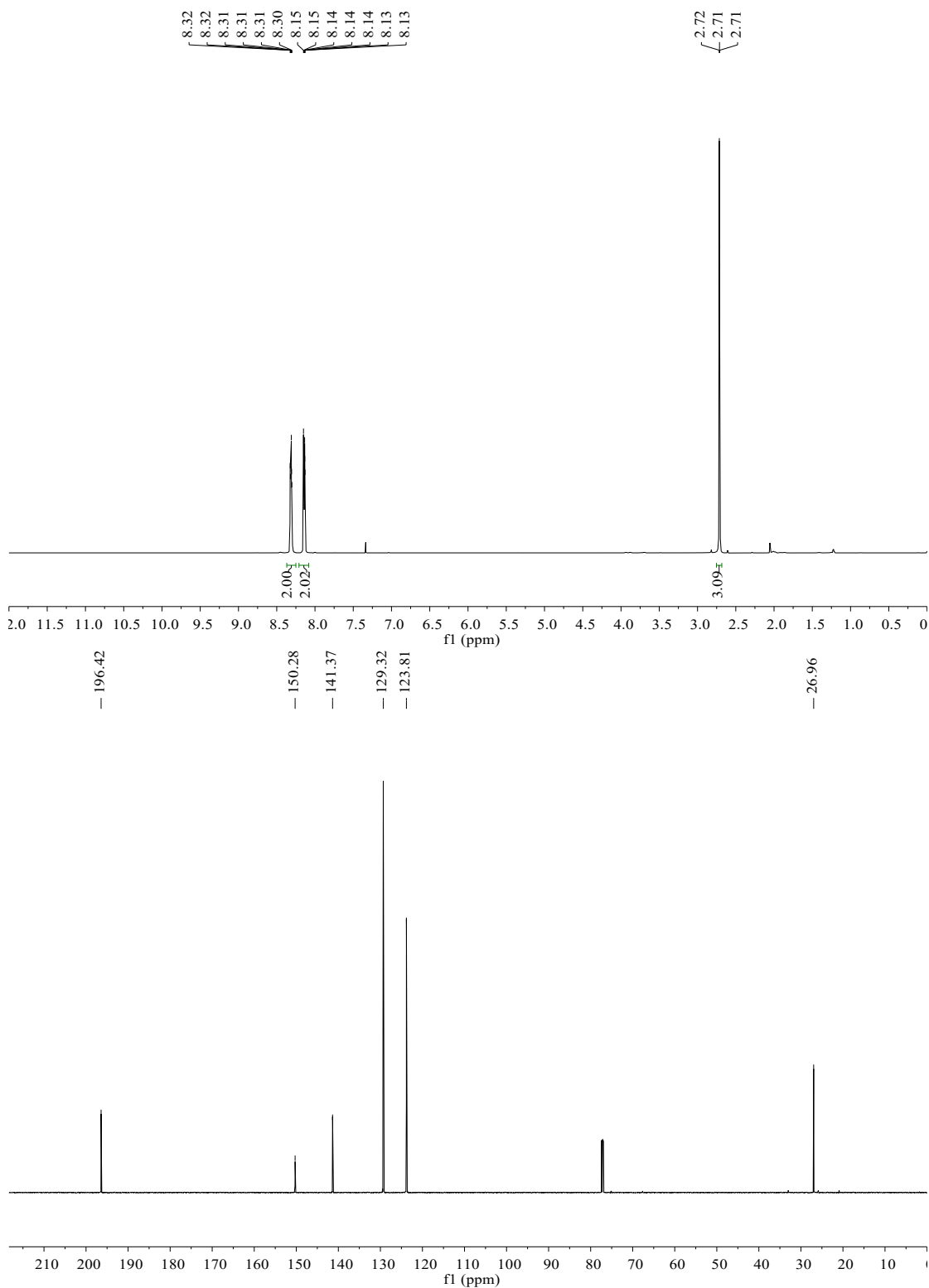
Figure S25 ¹H and ¹³C NMR spectrogram of 4-nitrophenone

Benzophenone
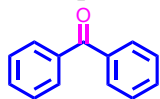
¹H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.9 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 4H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 196.80, 137.61, 132.46, 130.09, 128.31.
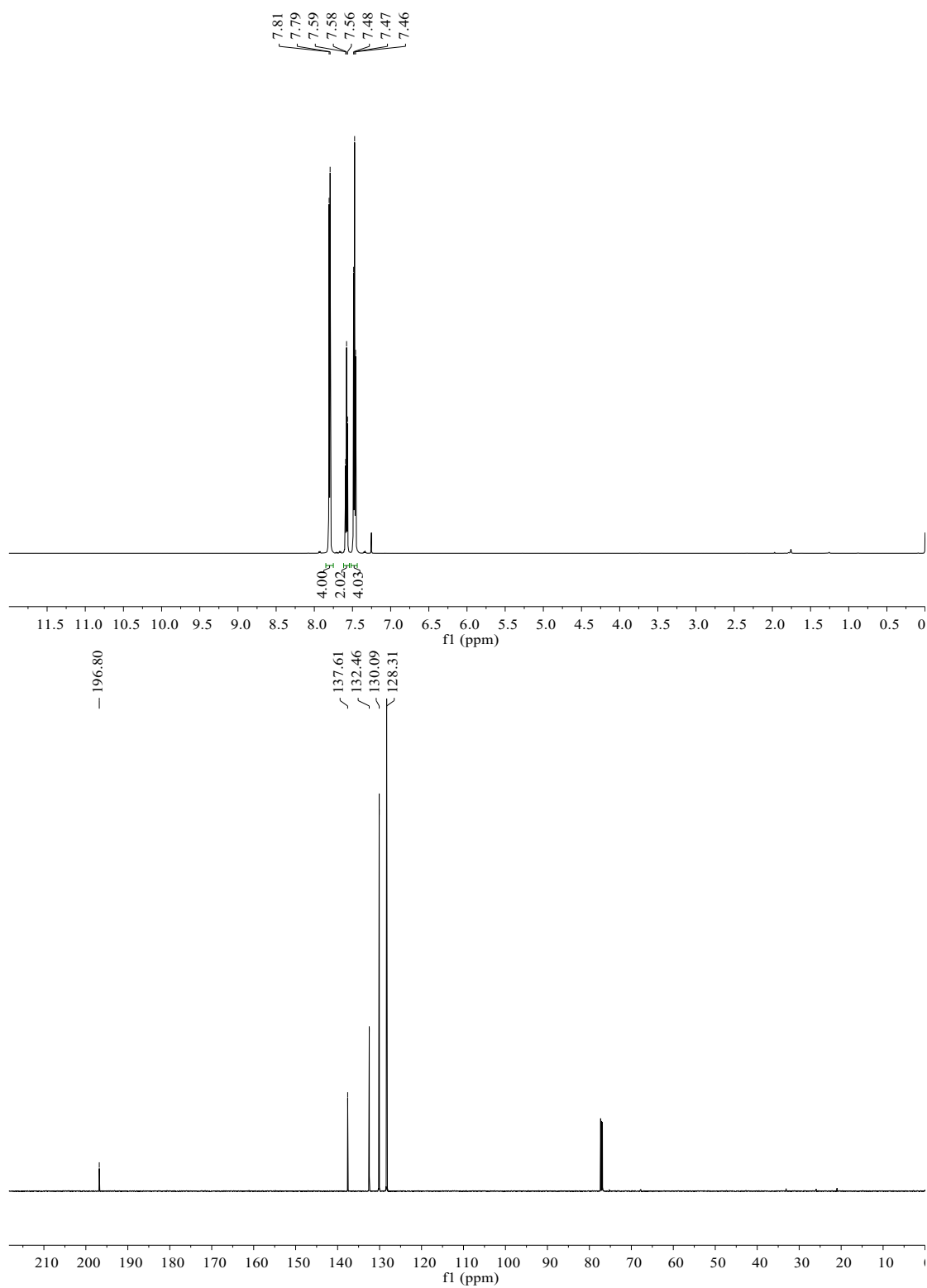
Figure S26 ¹H and ¹³C NMR spectrogram of benzophenone

4, 4-Dihydroxy-benzophenon
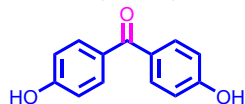
¹H NMR (600 MHz, DMSO-*d₆*) δ 10.30 (s, 2H), 7.62 (d, *J* = 8.7 Hz, 4H), 6.90 (d, *J* = 8.7 Hz, 4H). **¹³C NMR (151 MHz, DMSO-*d₆*)** δ 193.56, 161.74, 132.54, 129.30, 115.52.
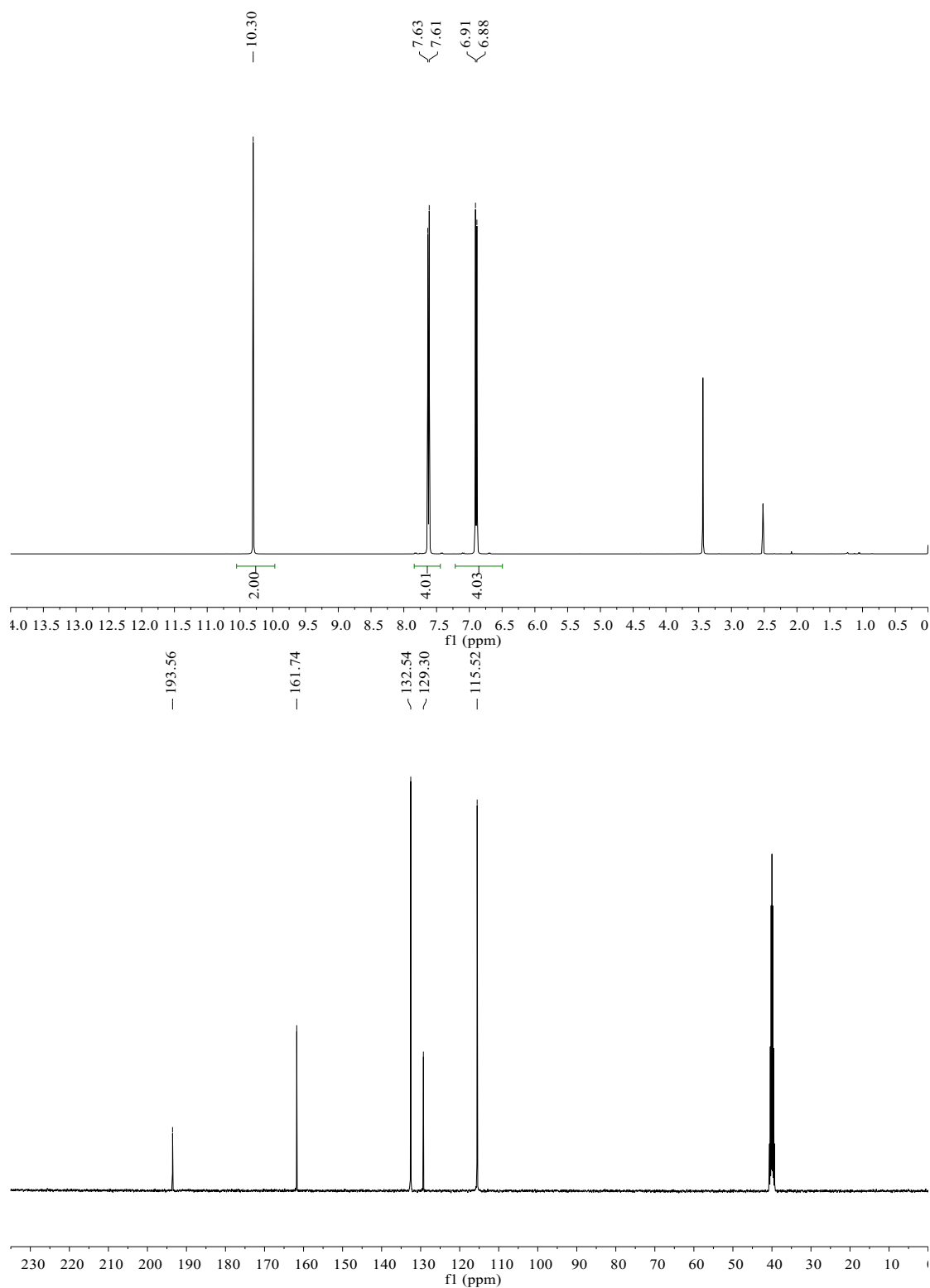
Figure S27 ¹H and ¹³C NMR spectrogram of 4, 4-dihydroxy-benzophenon

4, 4-Diaminobenzophenone
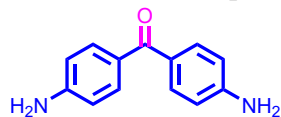
¹H NMR (600 MHz, DMSO-*d₆*) δ 7.47 (d, *J* = 8.4 Hz, 4H), 6.61 (d, *J* = 8.4 Hz, 4H), 5.93 (s, 4H). **¹³C NMR (151 MHz, DMSO-*d₆*)** δ 150.44, 129.78, 123.45, 110.37.
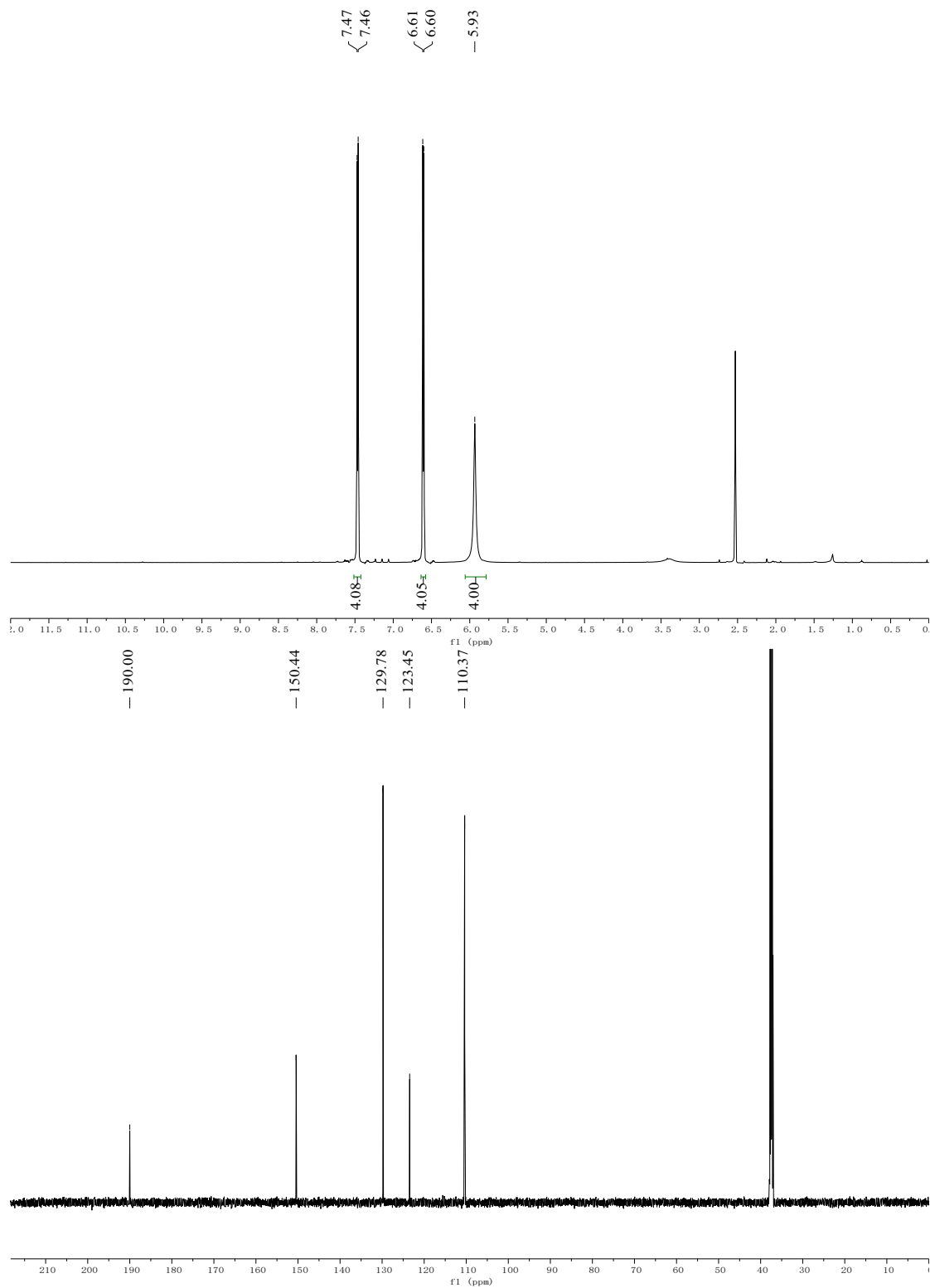
Figure S28 ¹H and ¹³C NMR spectrogram of 4, 4-diaminobenzophenon

Xanthone
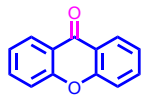
¹H NMR (600 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 7.9 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 137.30, 132.27, 129.89, 129.27, 126.31, 125.99.
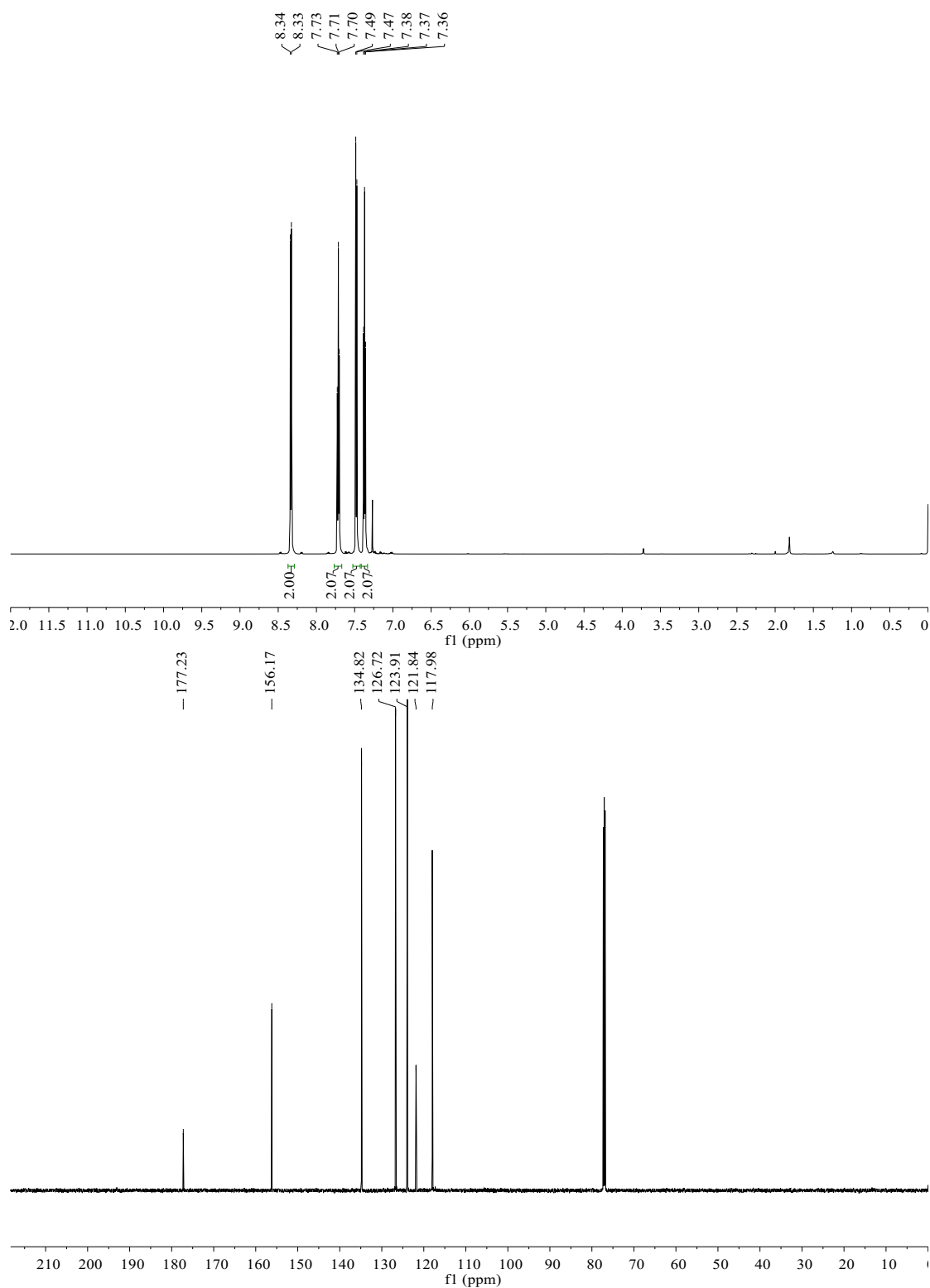
Figure S29 ¹H and ¹³C NMR spectrogram of xanthone

Thioxanthen-9-one
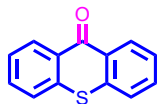
¹H NMR (600 MHz, Chloroform-*d*) δ 8.63 (s, 2H), 7.55 (d, *J* = 80.1 Hz, 6H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 179.98, 137.30, 132.27, 129.89, 126.31, 125.99.
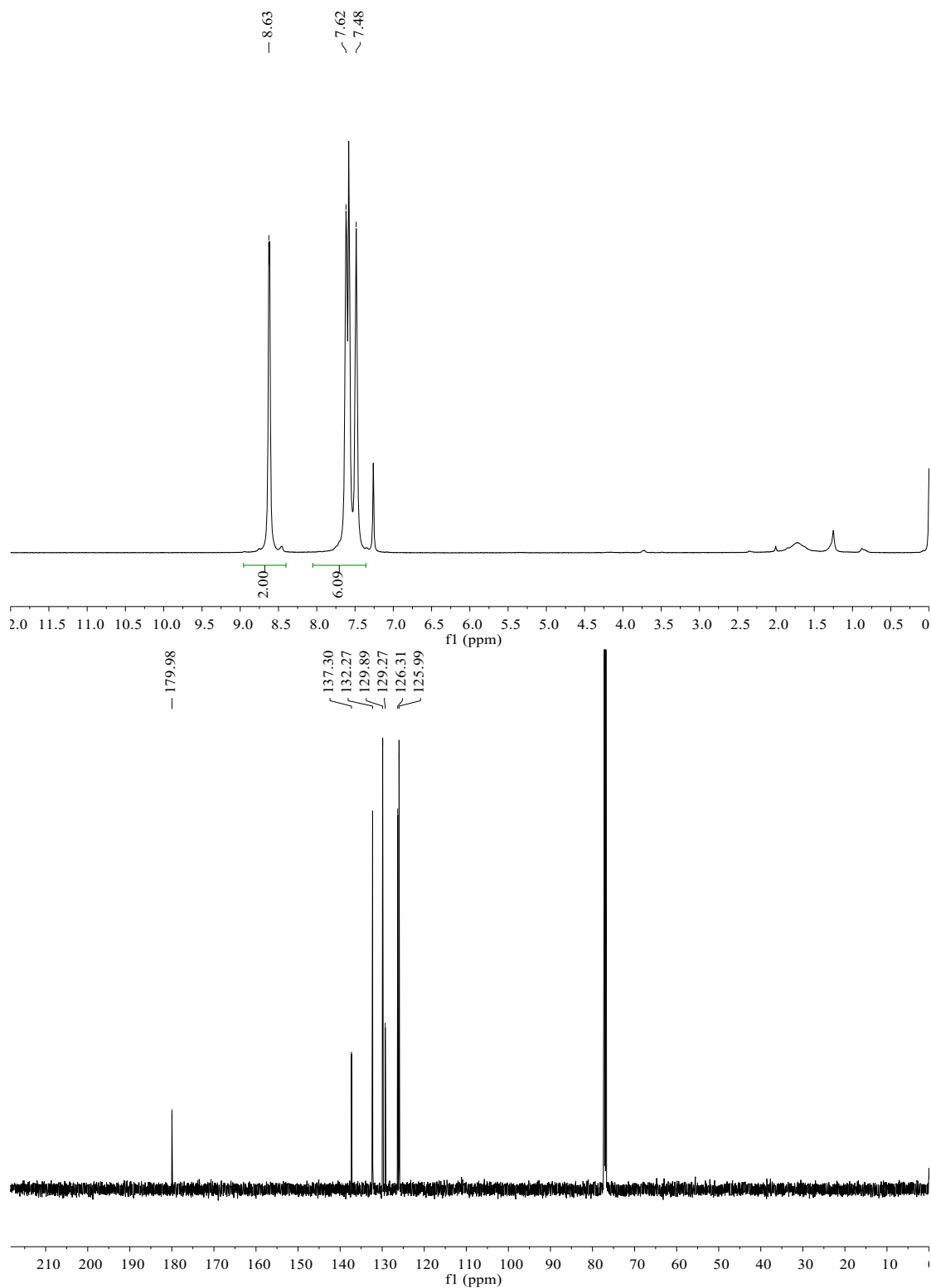
Figure S30 ¹H and ¹³C NMR spectrogram of thioxanthen-9-one

Benzaldehyde
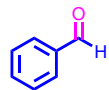
¹H NMR (600 MHz, Chloroform-*d*) δ 10.02 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.62 (q, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 179.98, 137.30, 129.89, 129.27, 126.31, 125.99.
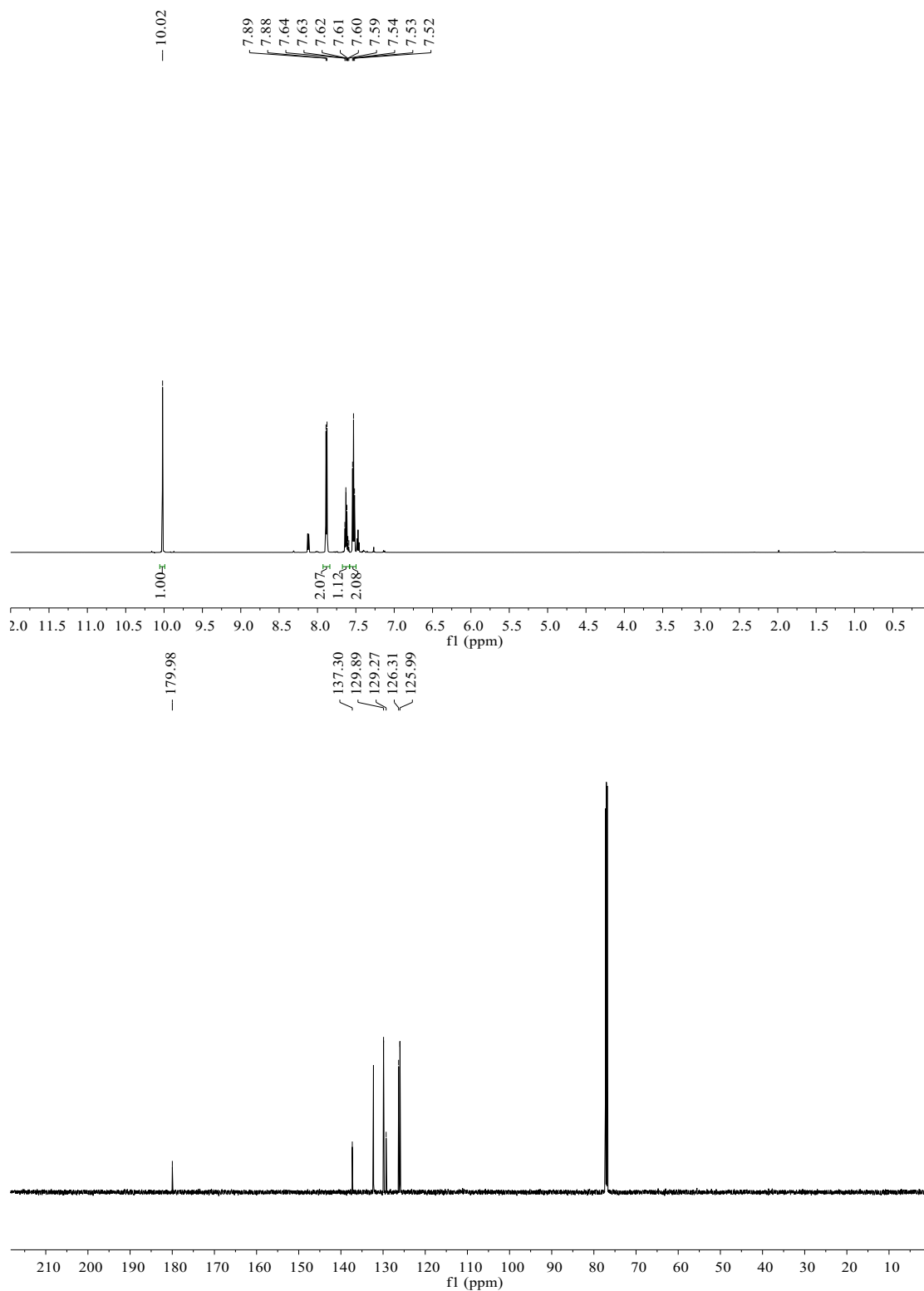
Figure S31 ¹H and ¹³C NMR spectrogram of benzaldehyde

Cyclohexanone

¹H NMR (600 MHz, Chloroform-*d*) δ 9.70 (d, *J* = 7.7 Hz, 1H), 7.56 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.52 − 7.33 (m, 4H), 6.72 (dd, *J* = 15.9, 7.7 Hz, 1H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 211.98, 41.88, 26.93, 24.90.
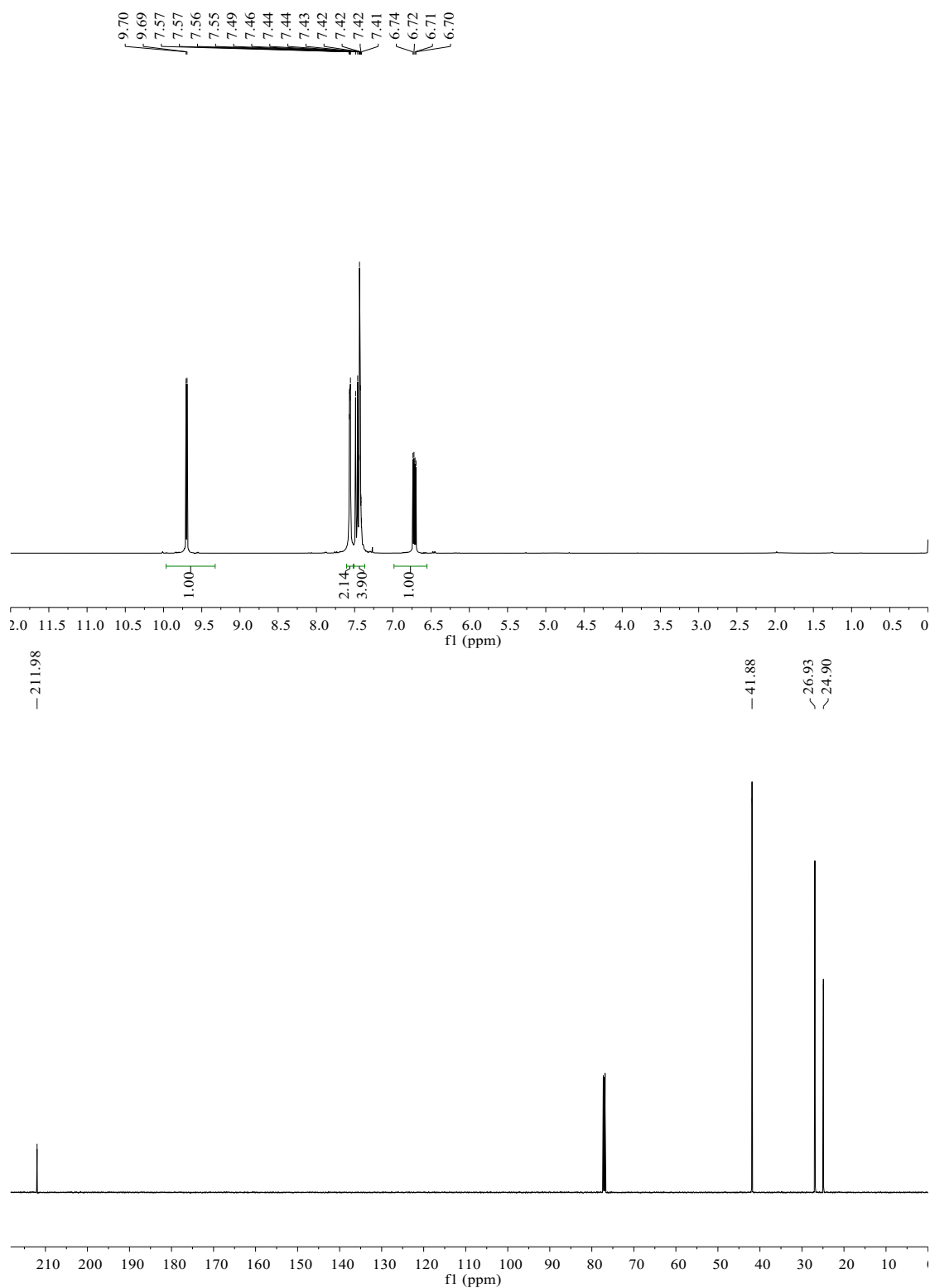
Figure S32 ¹H and ¹³C NMR spectrogram of cyclohexanone

Phenol

¹H NMR (400 MHz, DMSO-*d₆*) δ 9.35 (s, 1H), 7.20 – 7.16 (m, 2H), 6.80-6.76 (d, *J* = 8.4 Hz, 3H).
¹³C NMR (101 MHz, DMSO-*d₆*) δ 157.82, 129.87, 119.30, 115.72.
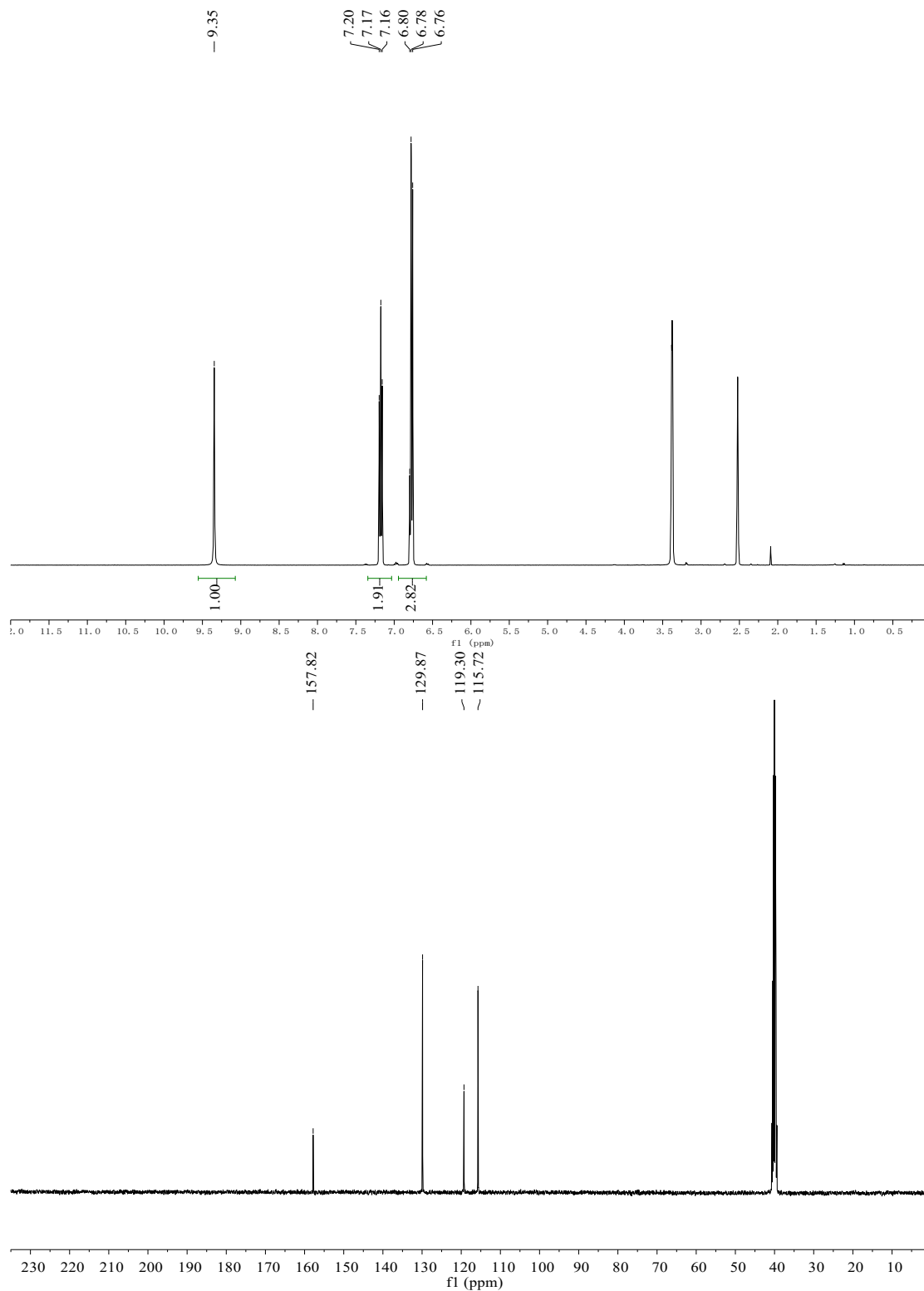
Figure S33 ¹H and ¹³C NMR spectrogram of phenol
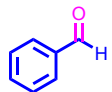
Benzaldehyde

¹H NMR (600 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 192.46, 136.41, 134.50, 129.77, 129.02.
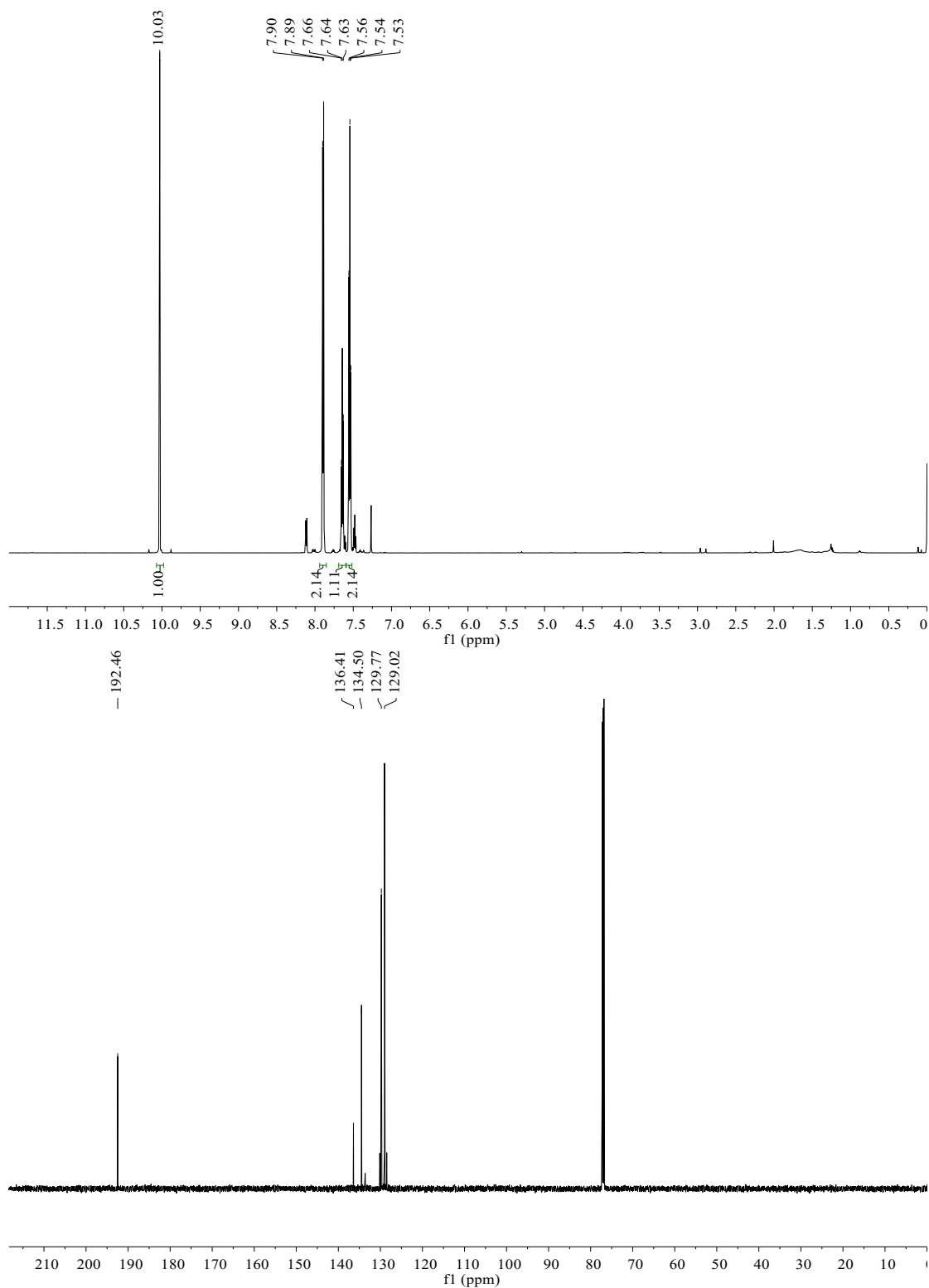
Figure S34 ¹H and ¹³C NMR spectrogram of benzaldehyde

Phenylacetaldehyde
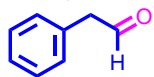
¹H NMR (600 MHz, Chloroform-*d*) δ 9.64 (s, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 3.58 (s, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 199.50, 131.90, 129.66, 129.04, 127.45, 50.60.
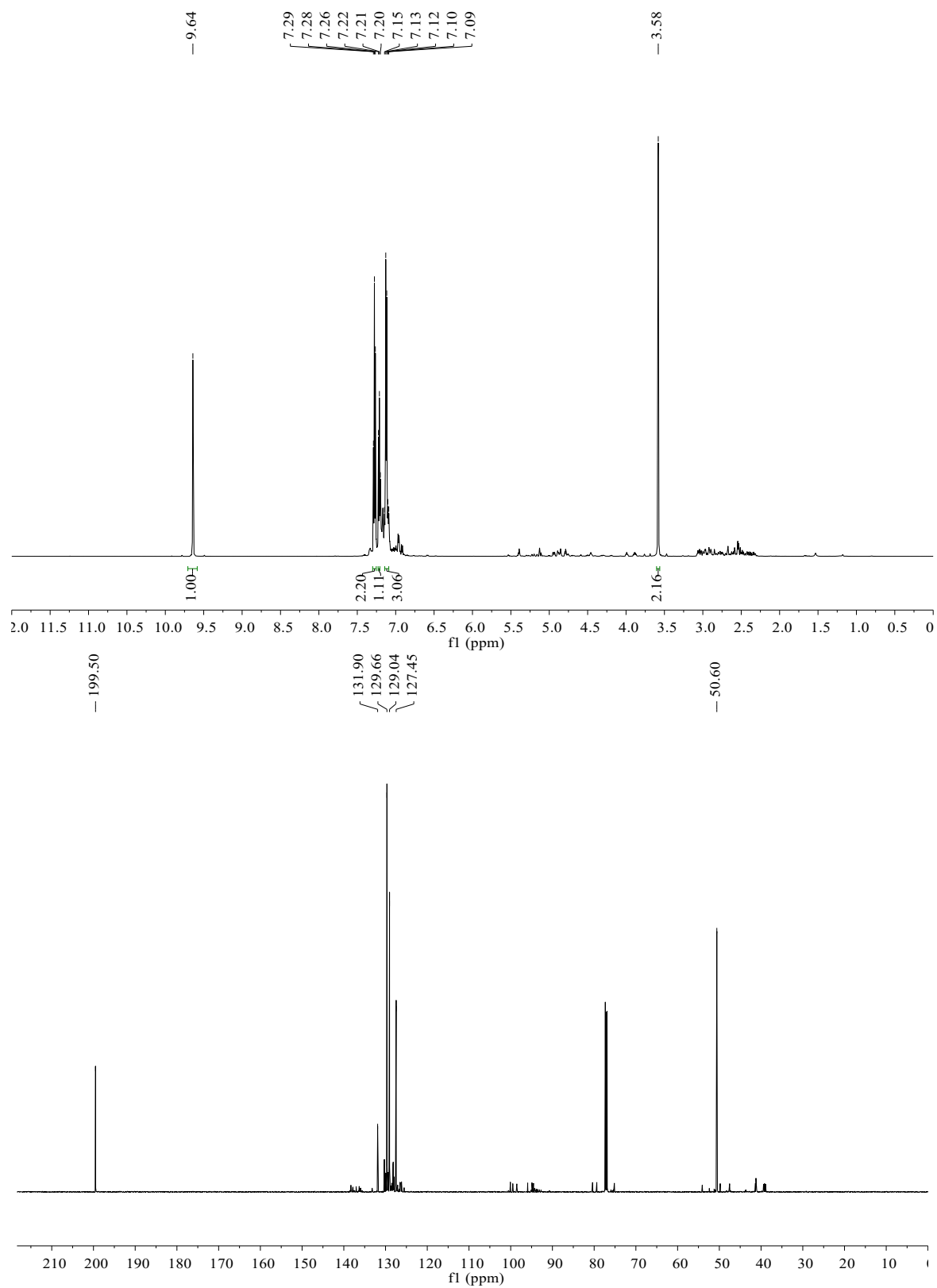
Figure S35 ¹H and ¹³C NMR spectrogram of phenylacetaldehyde

4-pyridinaldehyde
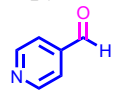
¹H NMR (600 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 8.90 (d, *J* = 5.8 Hz, 2H), 7.74 (d, *J* = 5.9 Hz, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 191.48, 151.27, 141.43, 122.13.
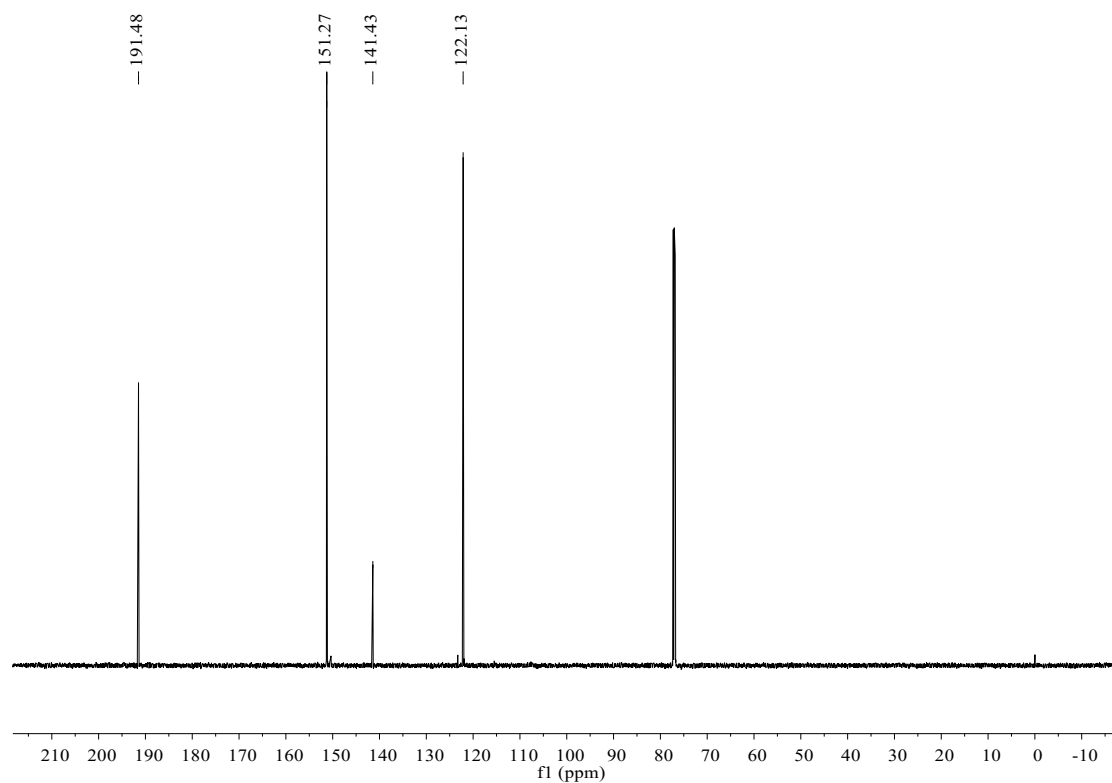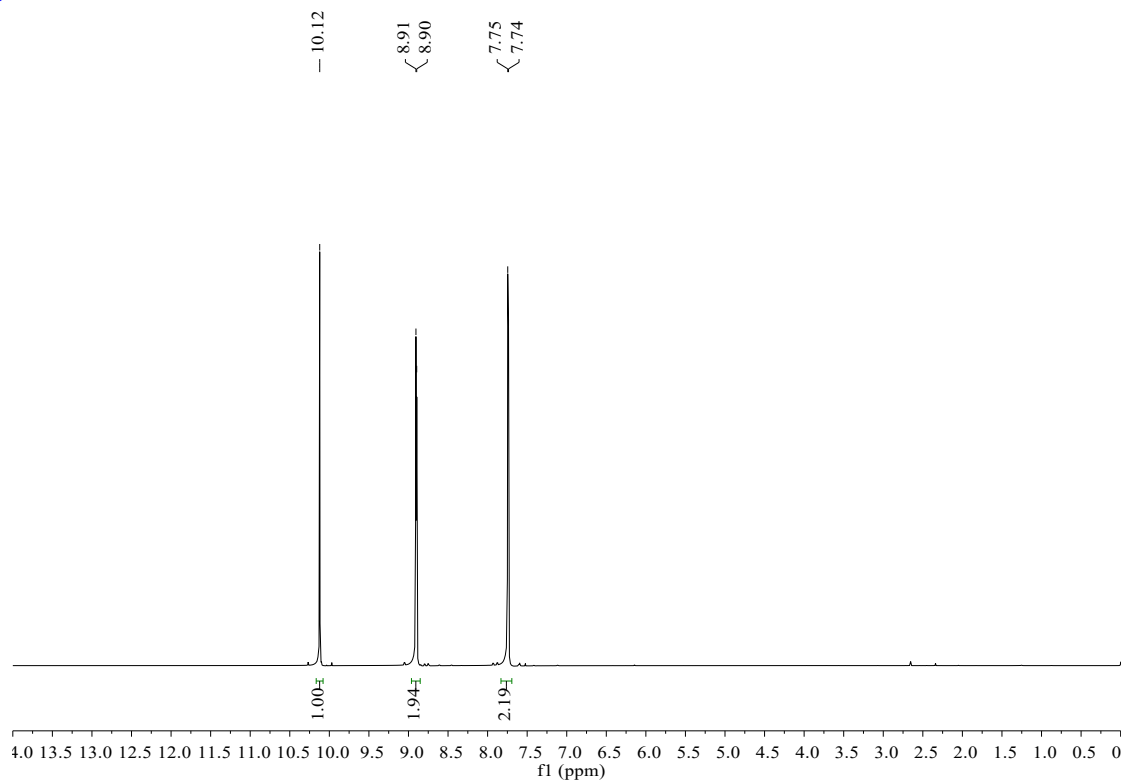
Figure S36 ¹H and ¹³C NMR spectrogram of 4-pyridinaldehyde

Cinnamaldehyde
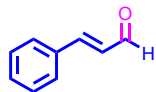
^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.70 (s, 1H), 7.56 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.51 – 7.39 (m, 4H), 6.72 (dd, *J* = 15.9, 7.7 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 193.80, 152.88, 134.01, 131.32, 129.14, 128.57 (d, *J* = 9.7 Hz).
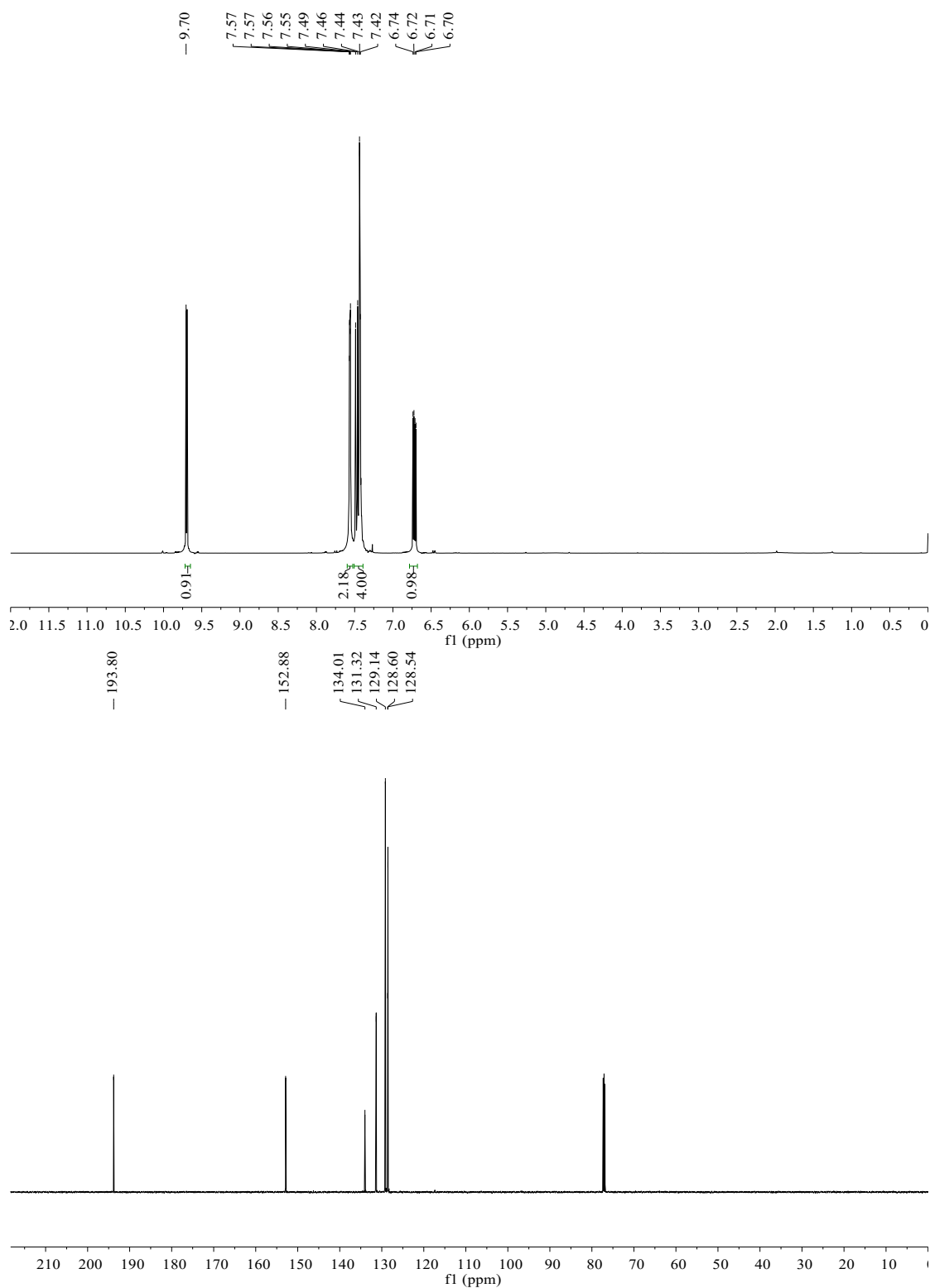
Figure S37 ^{1}H and ^{13}C NMR spectrogram of cinnamaldehyde
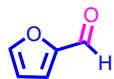
Furfural

¹H NMR (600 MHz, Chloroform-d) δ 9.67 (s, 1H), 7.71 (s, 1H), 6.62 (s, 1H). **¹³C NMR (151 MHz, Chloroform-d)** δ 177.90, 153.01, 148.08, 121.01, 112.59.
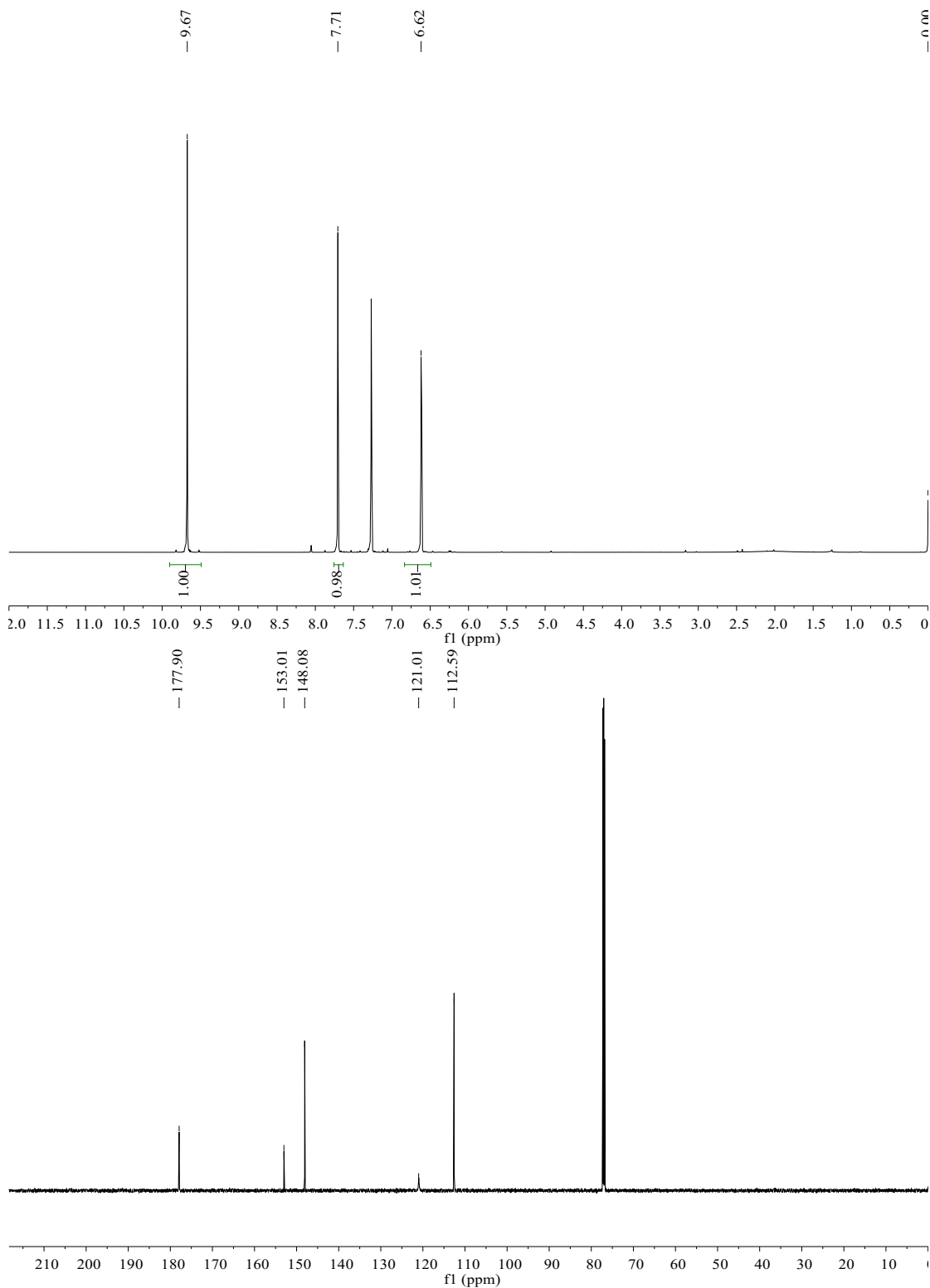
Figure S38 ¹H and ¹³C NMR spectrogram of furfural
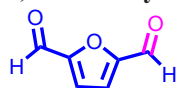
2, 5-Diformylfuran

¹H NMR (600 MHz, Chloroform-*d*) δ 9.87 (s, 2H), 7.35 (s, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 179.25, 154.22, 119.26.
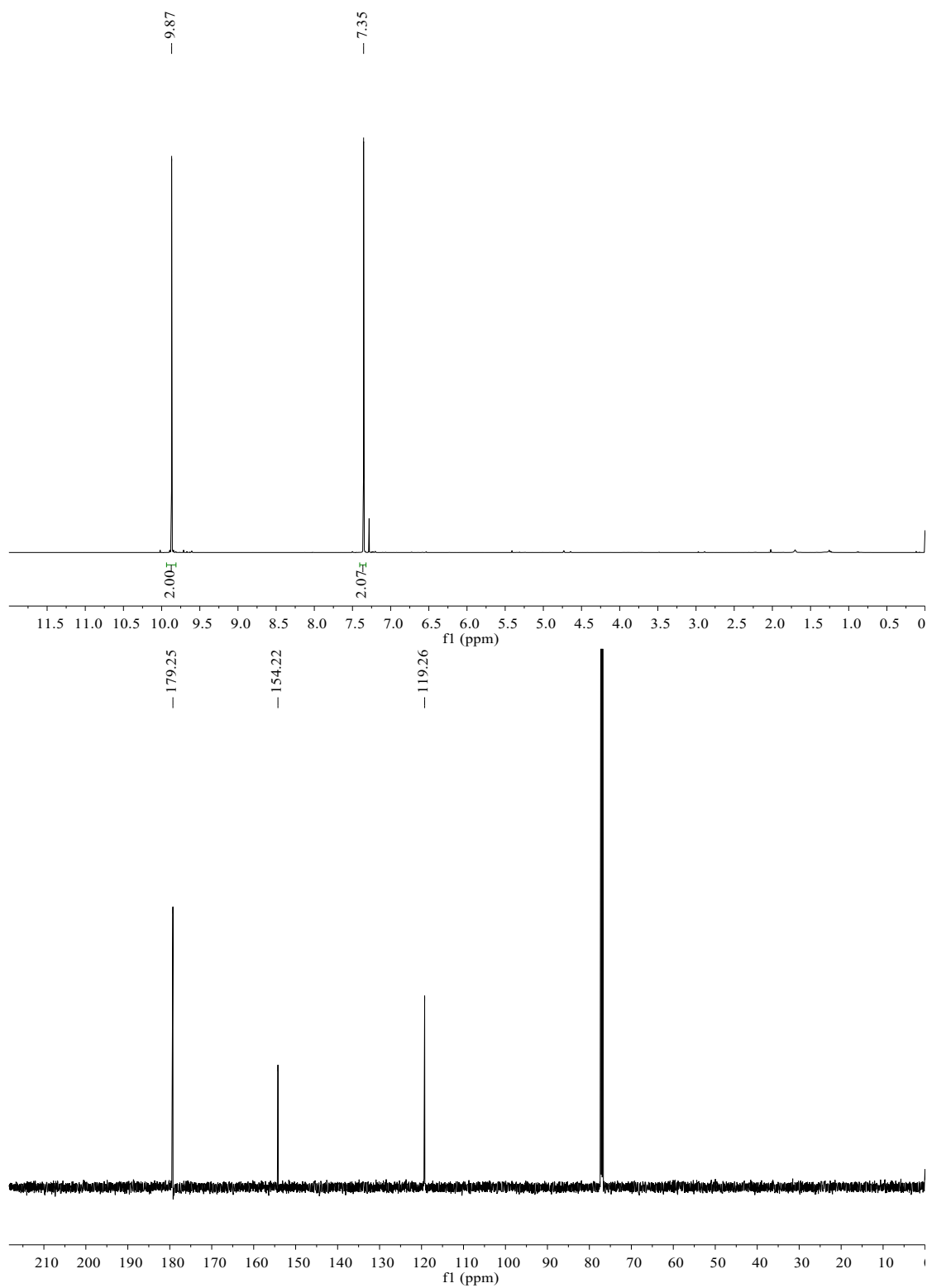
Figure S39 ¹H and ¹³C NMR spectrogram of 2, 5-diformylfuran
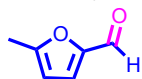
5-Methyl furfural

¹H NMR (600 MHz, Chloroform-*d*) δ 9.51 (s, 1H), 7.17 (d, *J* = 3.5 Hz, 1H), 6.24 (d, *J* = 3.4 Hz, 1H), 2.43 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 176.92, 159.86, 151.92, 109.50, 14.11.
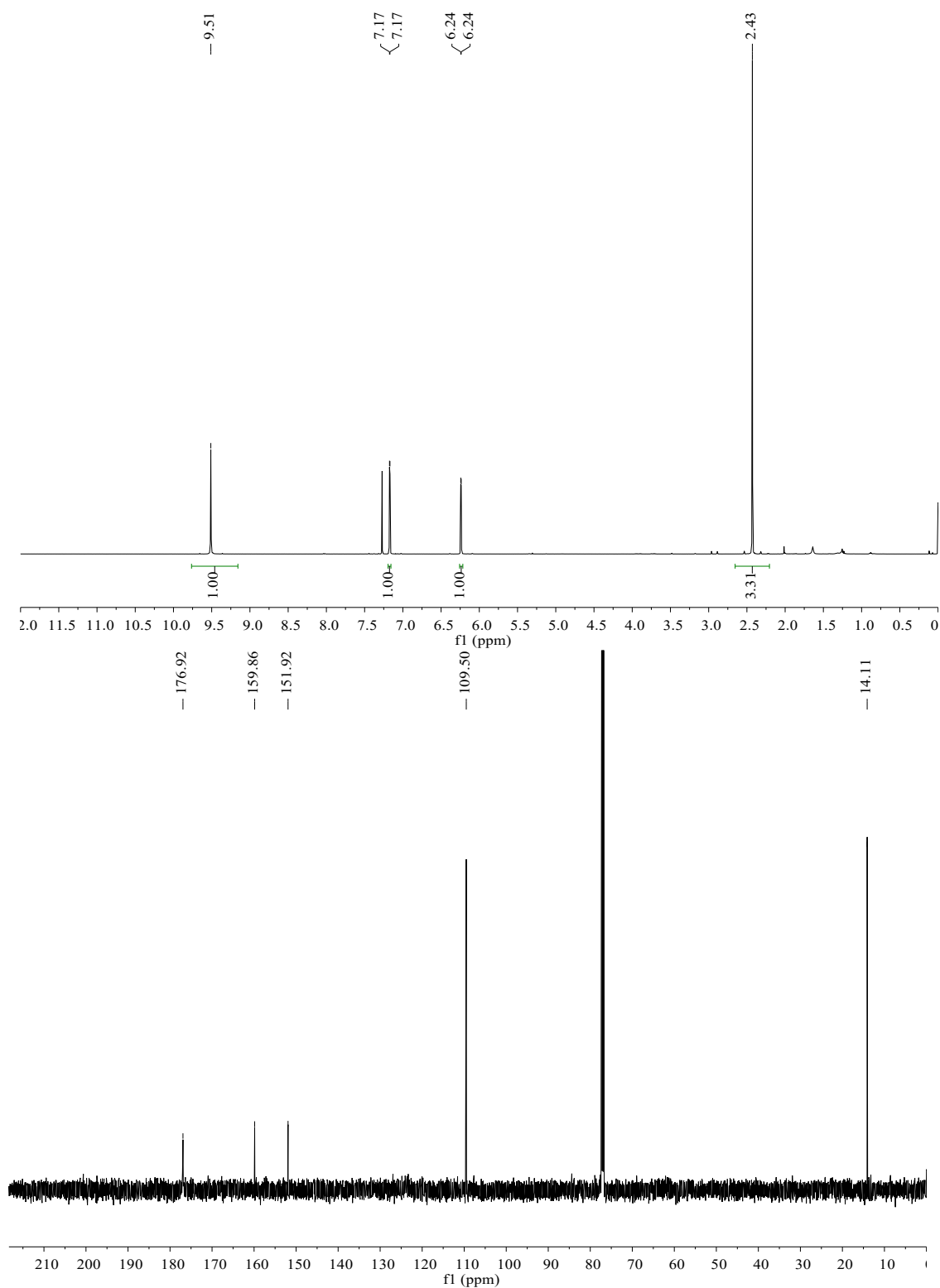
Figure S40 ¹H and ¹³C NMR spectrogram of 5-methyl furfural

5-Carboxy-2-formylfuran
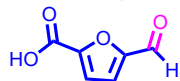
¹H NMR (600 MHz, DMSO-*d₆*) δ 9.74 (s, 1H), 7.61 (s, 1H), 7.40 (s, 1H). 13C NMR **(151 MHz, DMSO-*d₆*)** δ 180.38, 159.47, 153.73, 148.61, 122.74, 119.03.
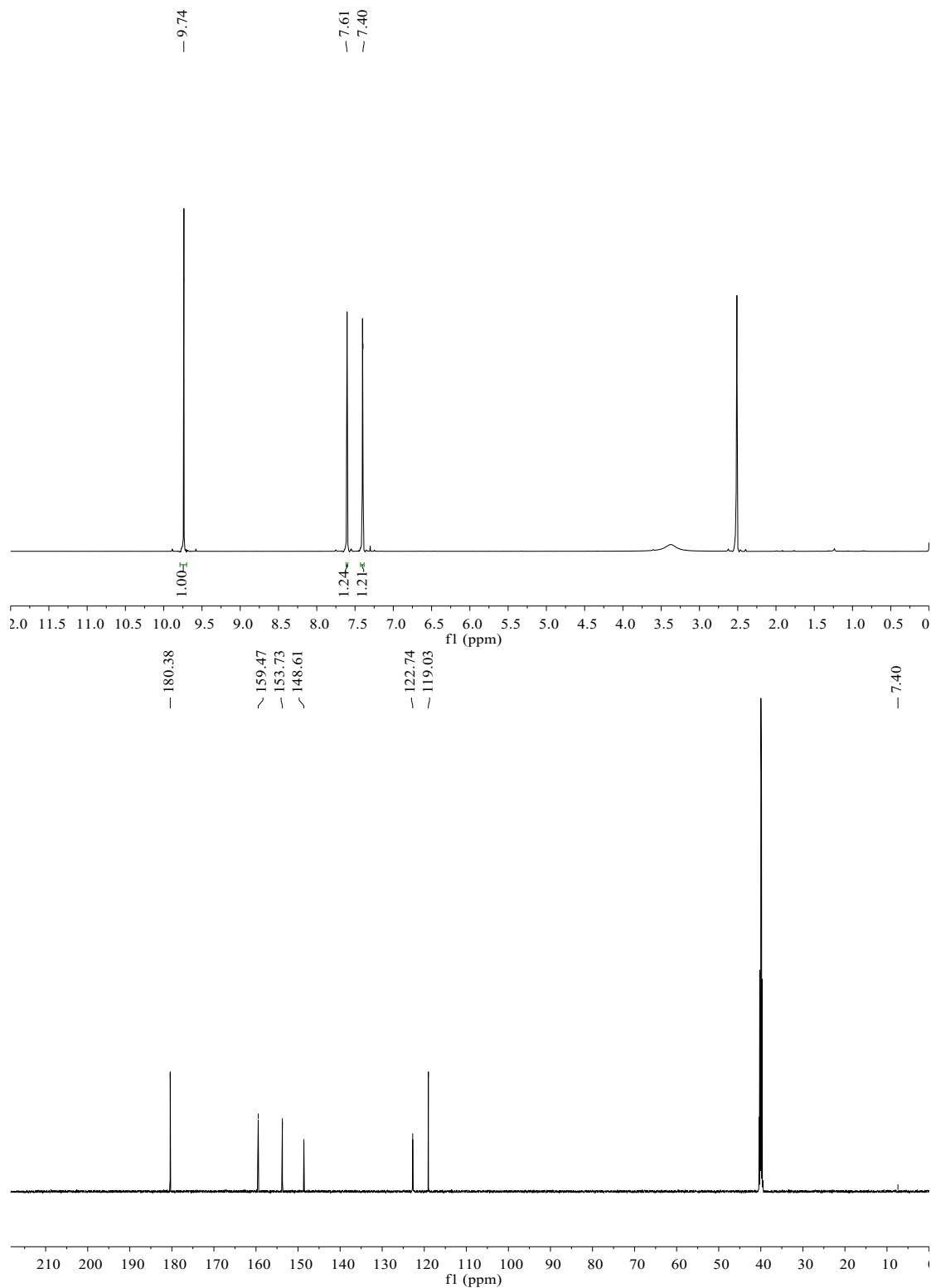
Figure S41 ¹H and ¹³C NMR spectrogram of 5-carboxy-2-formylfuran

2-Thiophene formaldehyde
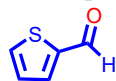
¹H NMR (600 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 8.00 – 7.59 (m, 2H), 7.22 (t, *J* = 4.3 Hz, 2H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 183.01, 144.06, 136.33, 135.14, 128.34.
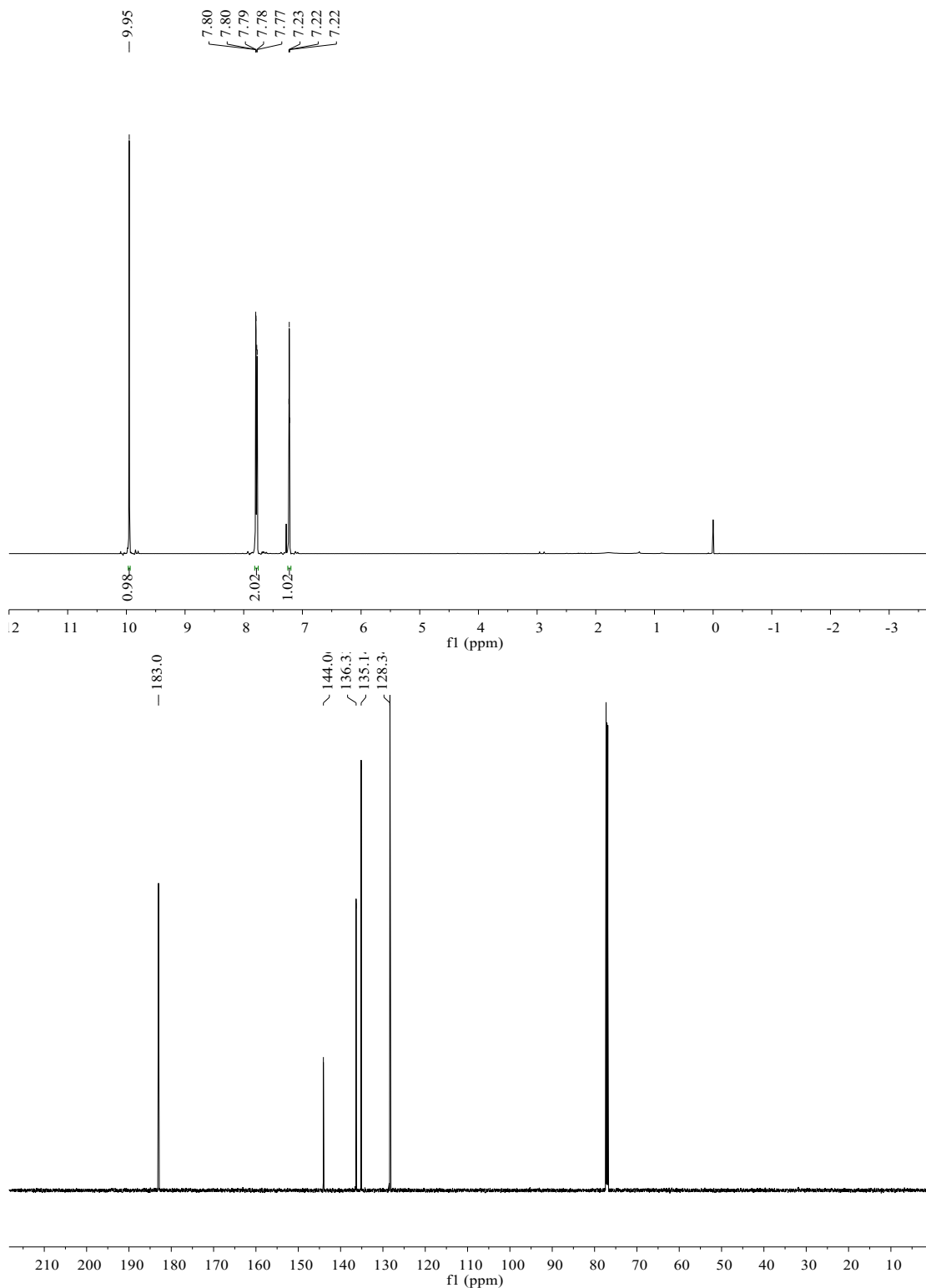
Figure S42 ¹H and ¹³C NMR spectrogram of 2-thiophene formaldehyde

4-Quinolinecarboxaldehyde
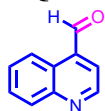
¹H NMR (600 MHz, Chloroform-*d*) δ 10.53 (s, 1H), 9.22 (d, J = 4.2 Hz, 1H), 9.04 (d, J = 9.2 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.89 – 7.69 (m, 3H), 7.26 (s, 1H).**¹³C NMR (151 MHz, Chloroform-*d*)** δ 192.88, 150.46, 149.28, 136.78, 130.21, 130.05, 129.41, 125.82, 124.44, 123.89.
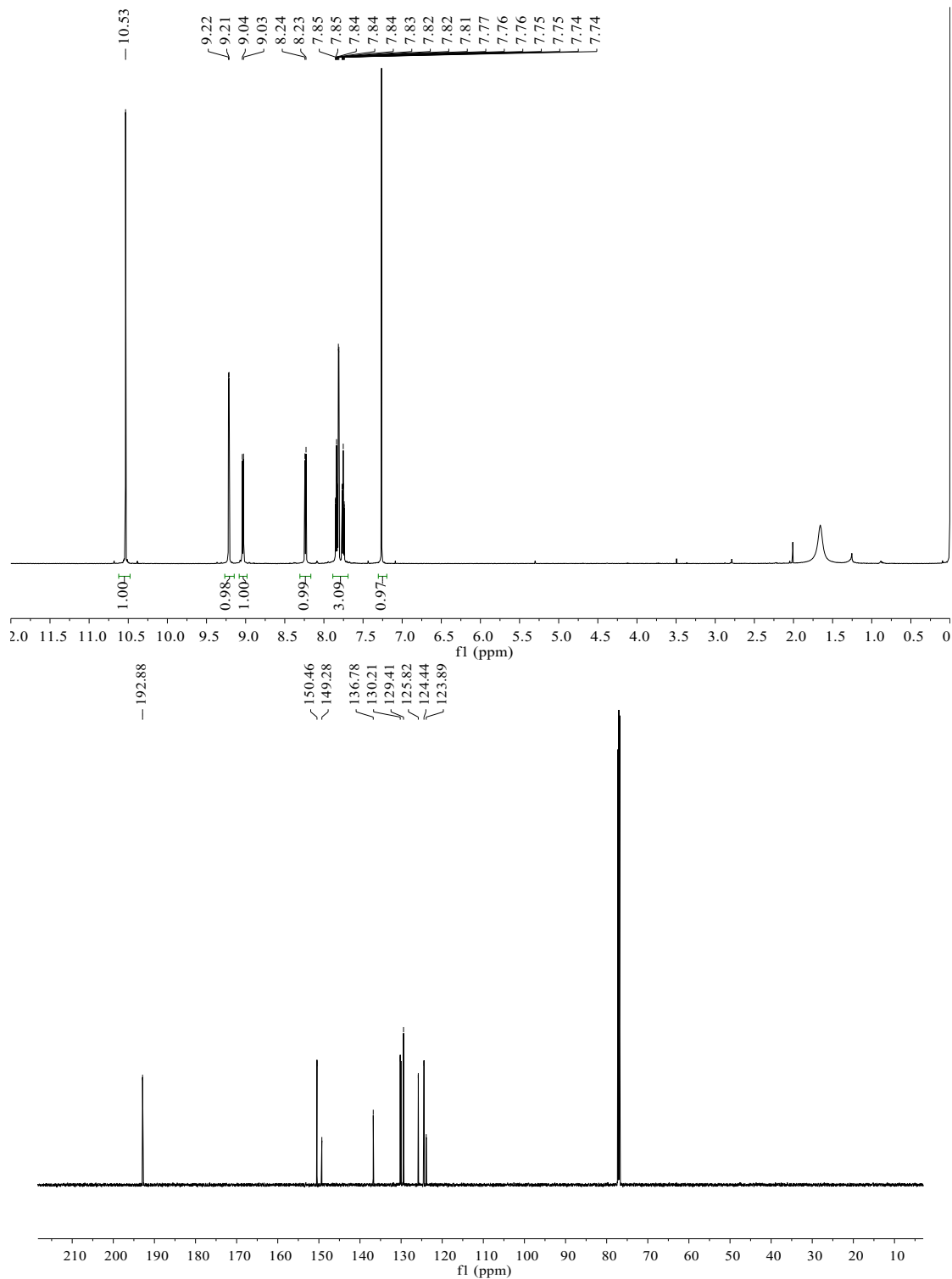
Figure S43 ¹H and ¹³C NMR spectrogram of 4-quinolinecarboxaldehyde

Indole-3-carboxaldehyde
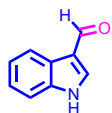
¹H NMR (600 MHz, Chloroform-*d*) δ 10.08 (s, 1H), 8.73 (s, 1H), 8.33 (d, J = 8.6 Hz, 1H), 7.94 -7.71 (m, 1H), 7.45 (s, 1H), 7.36 - 7.30 (m, 2H).**¹³C NMR (151 MHz, DMSO-*d₆*)** δ 185.42, 138.92, 137.55, 124.61, 123.92, 122.58, 121.30, 118.65, 112.89.
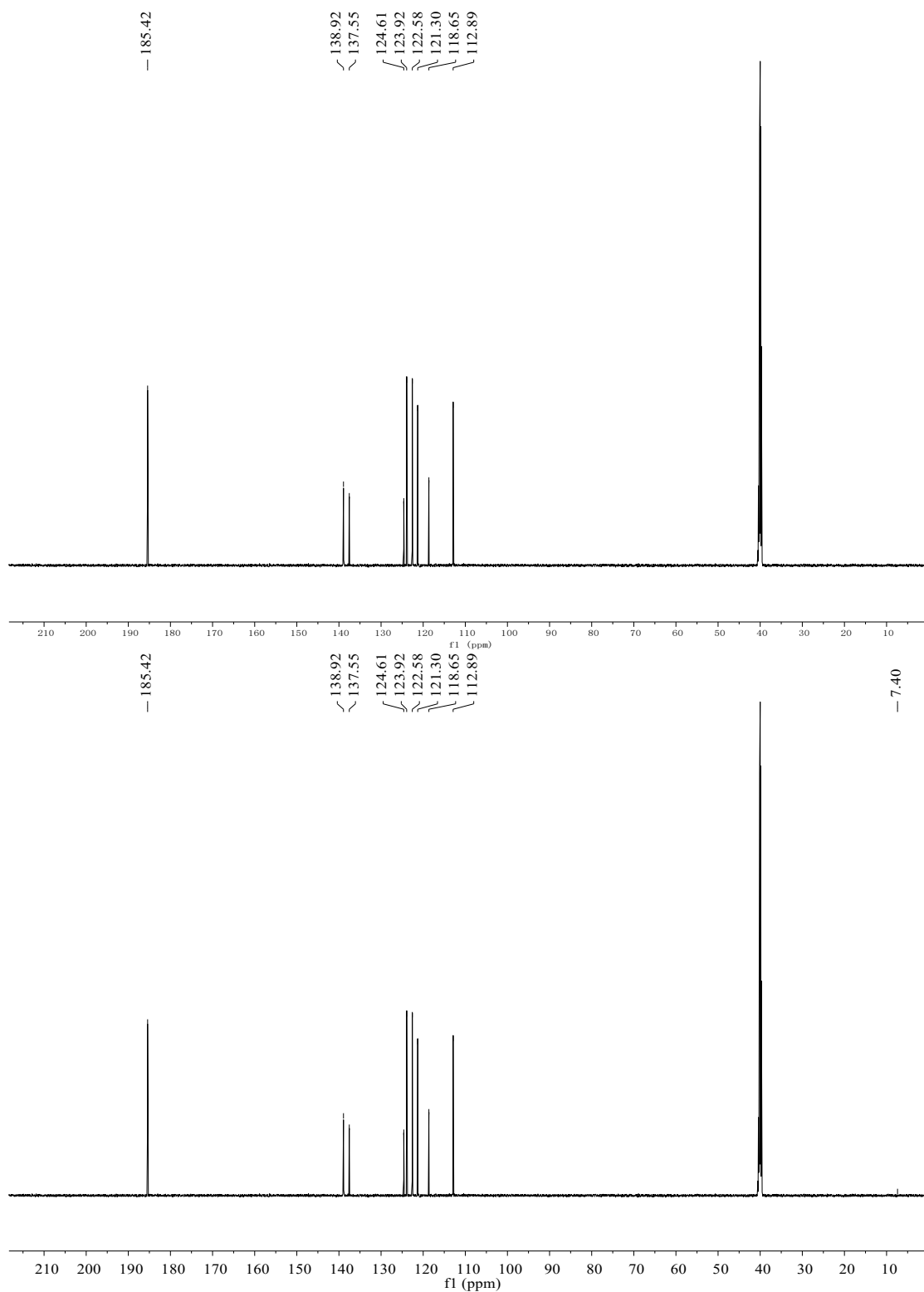
Figure S44 ¹H and ¹³C NMR spectrogram of indole-3-carboxaldehyde

Cyclohexanone

¹H NMR (600 MHz, Chloroform-*d*) δ 2.34 (t, *J* = 6.7 Hz, 2H), 1.87 (p, *J* = 6.2 Hz, 2H), 1.75 – 1.69 (m, 1H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 212.03, 41.92, 26.98, 24.95.
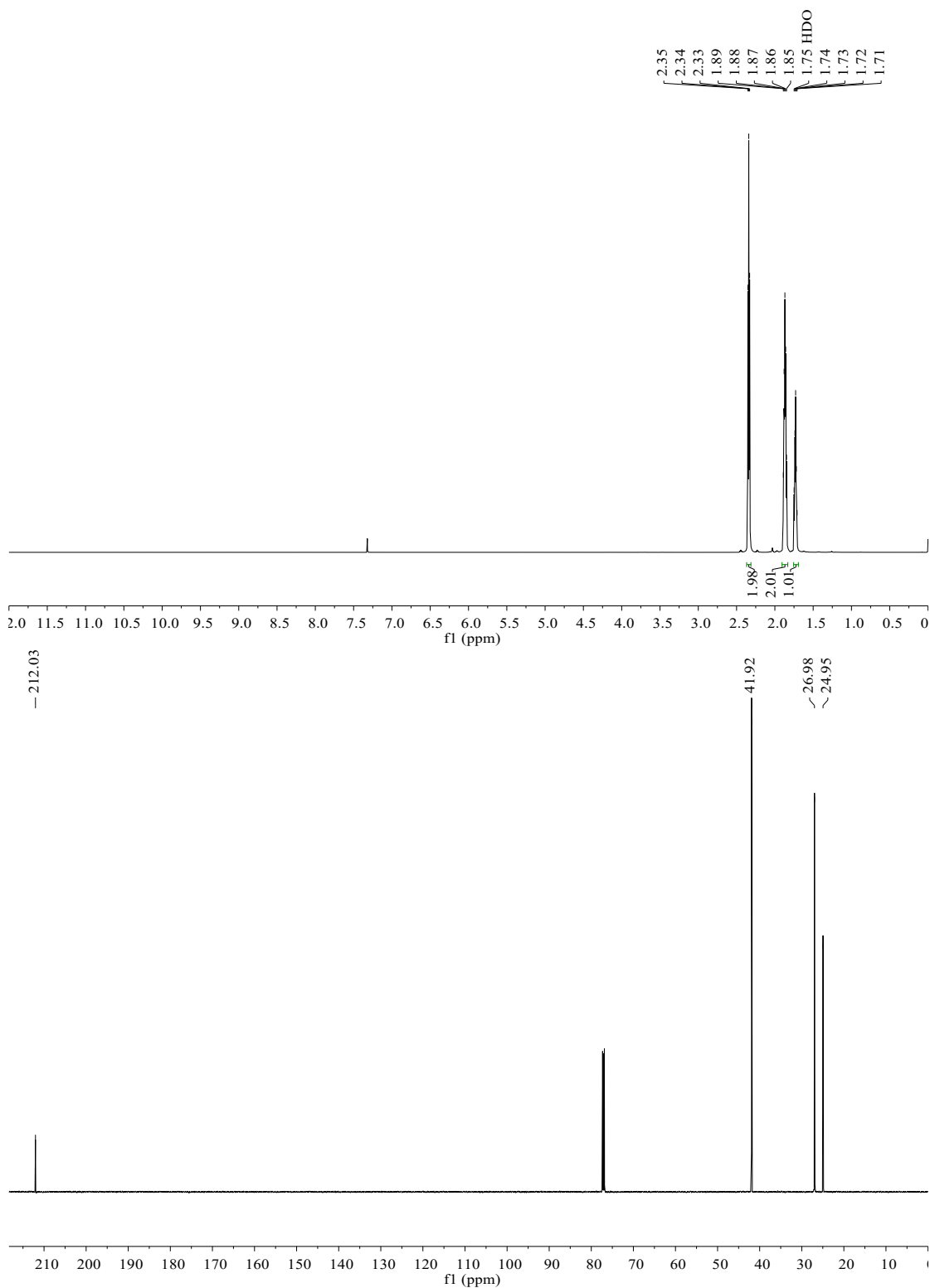
Figure S45 ¹H and ¹³C NMR spectrogram of cyclohexanone

n-Propionaldehyde

¹H NMR (600 MHz, Chloroform-*d*) δ 9.80 (t, J = 1.3 Hz, 1H), 2.48 (qd, J = 7.4, 1.4 Hz, 2H), 1.11 (t, J = 7.4 Hz, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 203.06, 37.25, 6.01.
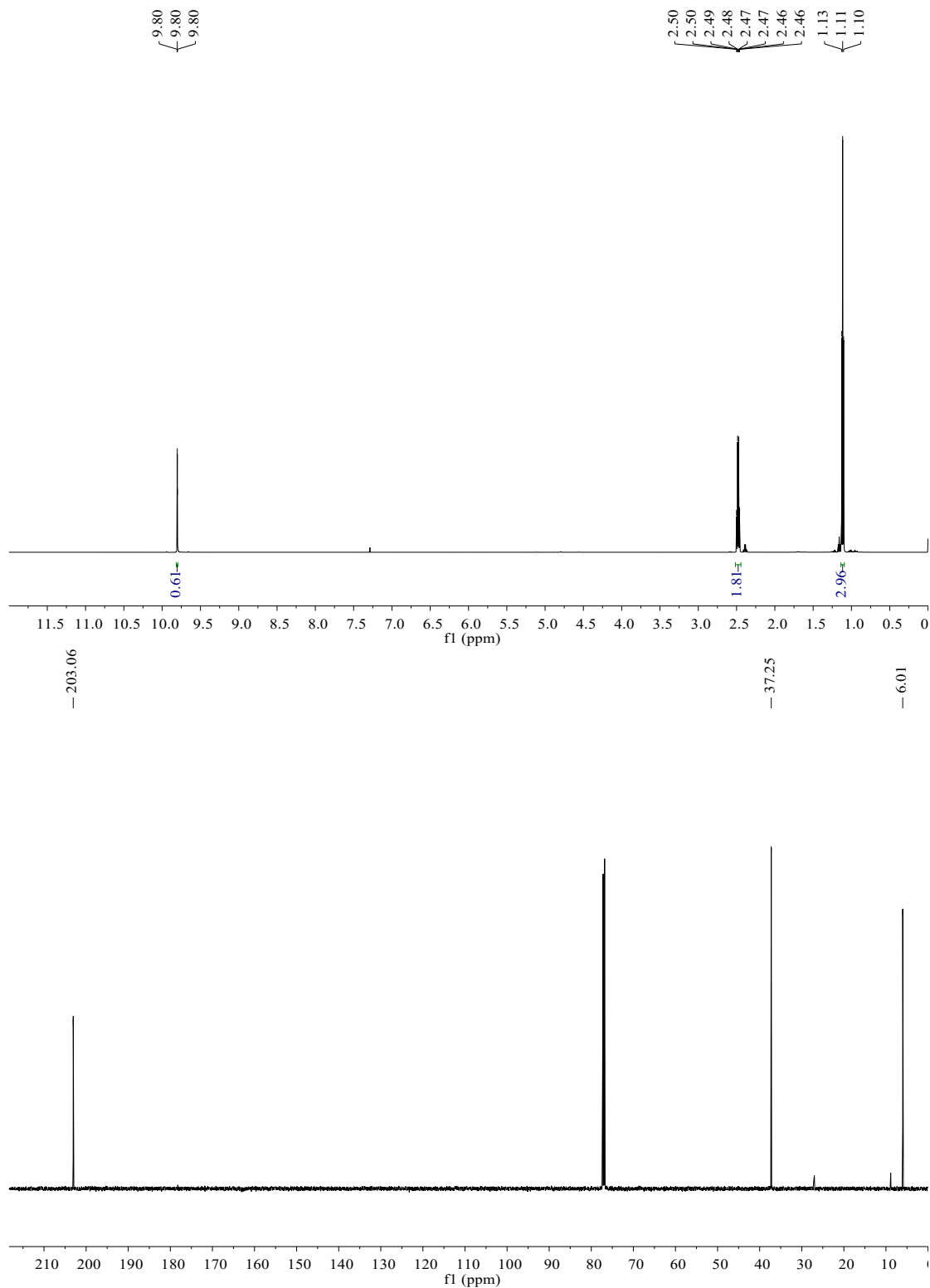
Figure S46 ¹H and ¹³C NMR spectrogram of n-propionaldehyde
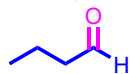
n-Butylaldehyde

[1H] NMR (600 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 2.42 (tdd, J = 7.3, 1.8, 0.8 Hz, 2H), 1.69 – 1.64 (m, 2H), 0.96 (dd, J = 7.4, 0.8 Hz, 3H). **[13C] NMR (151 MHz, Chloroform-*d*)** δ 202.89, 45.71, 15.58, 13.64.
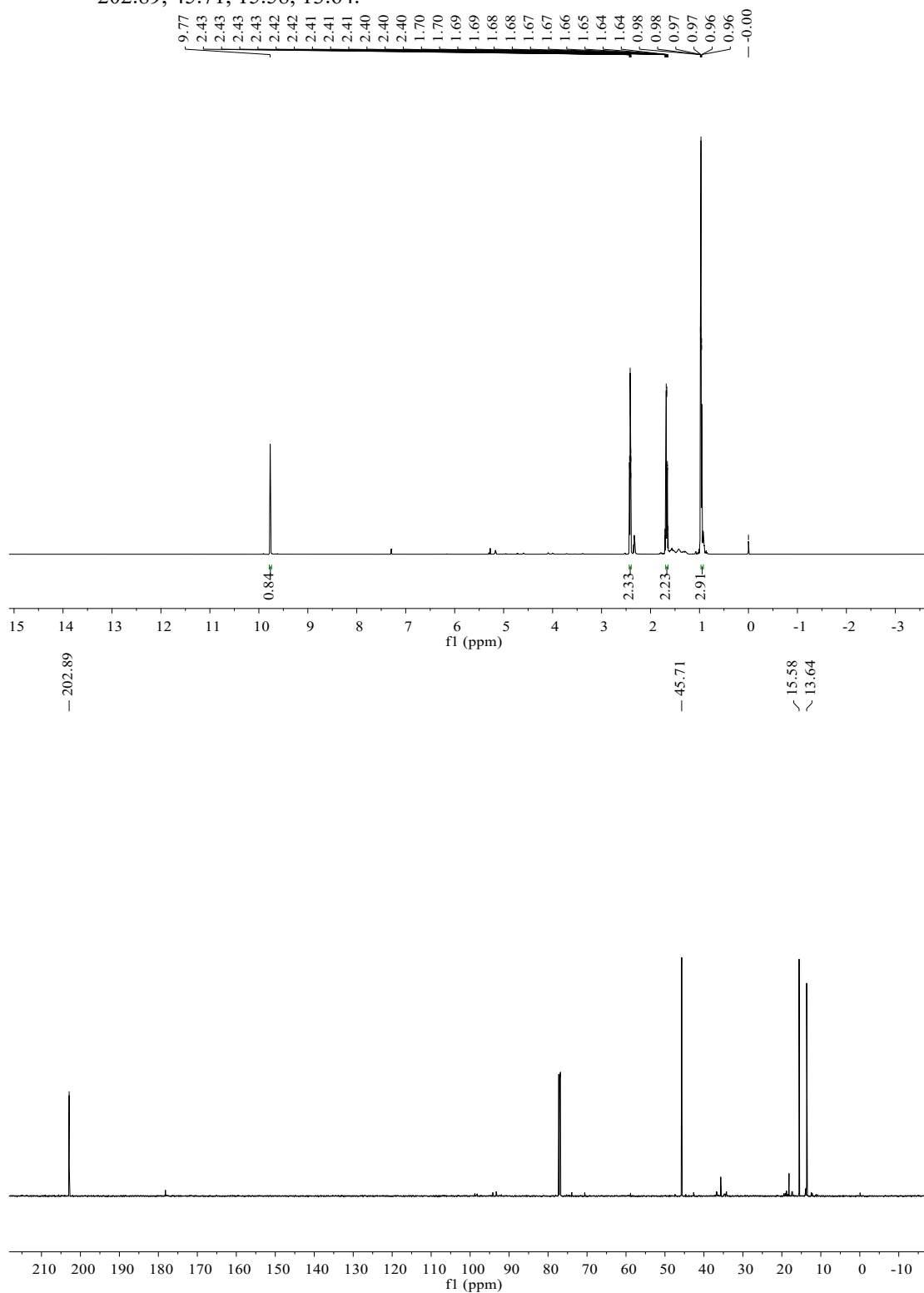
Figure S47 [1H] and [13C] NMR spectrogram of n-butylaldehyde
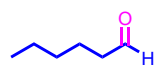
n-Hexanal

¹H NMR (600 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 2.42 (dt, J = 7.5, 4.6 Hz, 2H), 1.64 (p, J = 7.4 Hz, 2H), 1.33 (td, J = 8.1, 7.0, 4.7 Hz, 4H), 0.92 (s, 3H). **¹³C NMR (151 MHz, Chloroform-*d*)** δ 203.02, 43.88, 31.30, 22.40, 21.75, 13.86.
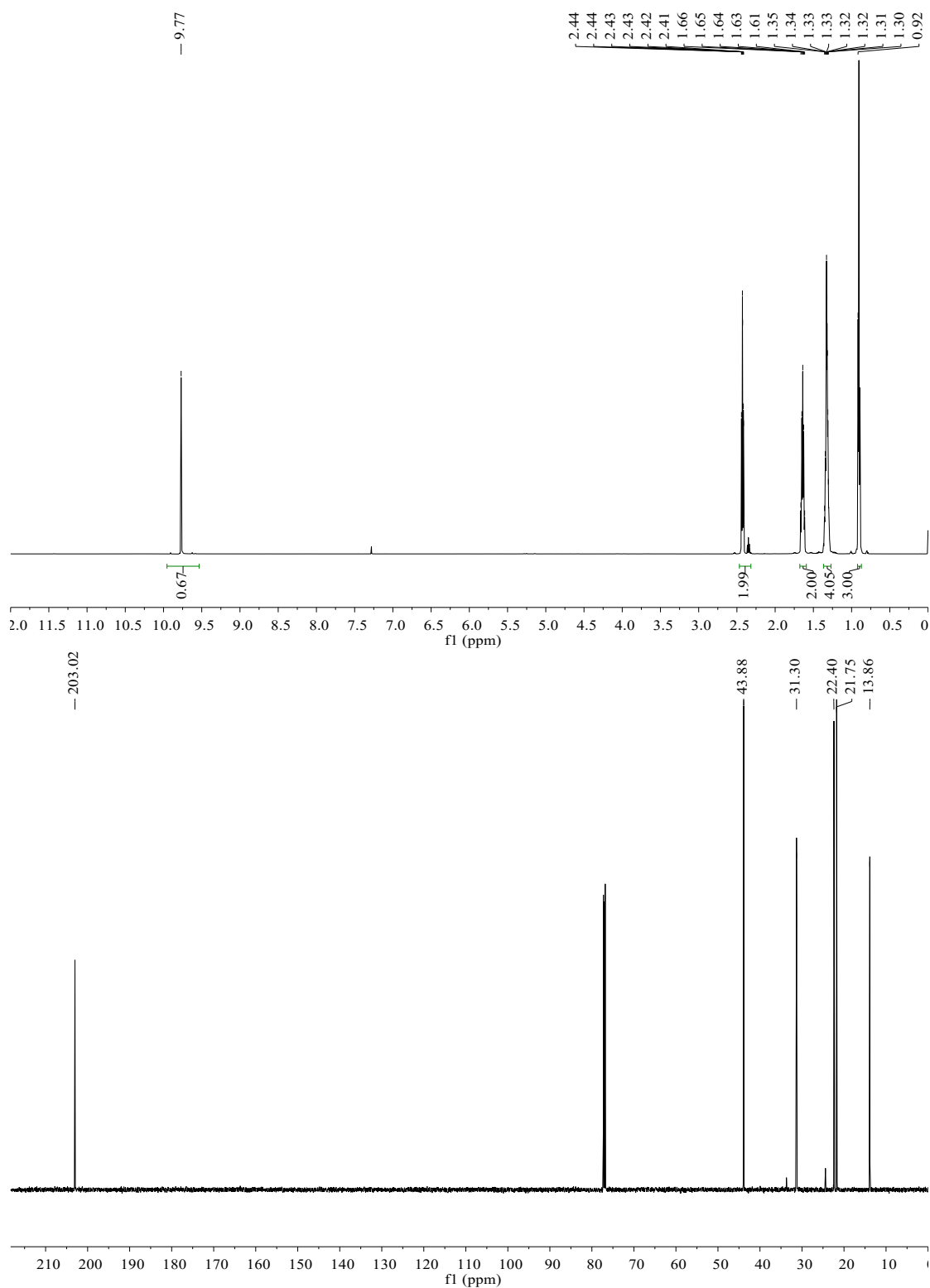
Figure S48 ¹H and ¹³C NMR spectrogram of n-hexanal
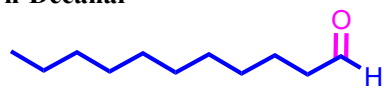
n-Decanal

1H NMR (600 MHz, Chloroform-*d*) δ 9.76 (t, J = 1.9 Hz, 1H), 2.42 (td, J = 7.4, 1.9 Hz, 2H), 1.63 (p, J = 7.3 Hz, 2H), 1.29 (dd, J = 20.3, 5.4 Hz, 12H), 0.88 (t, J = 7.0 Hz, 3H). **13C NMR (151 MHz, Chloroform-*d*)** δ 203.05, 43.94, 31.88 (d, *J* = 6.3 Hz), 29.37, 22.69, 22.09, 14.11.
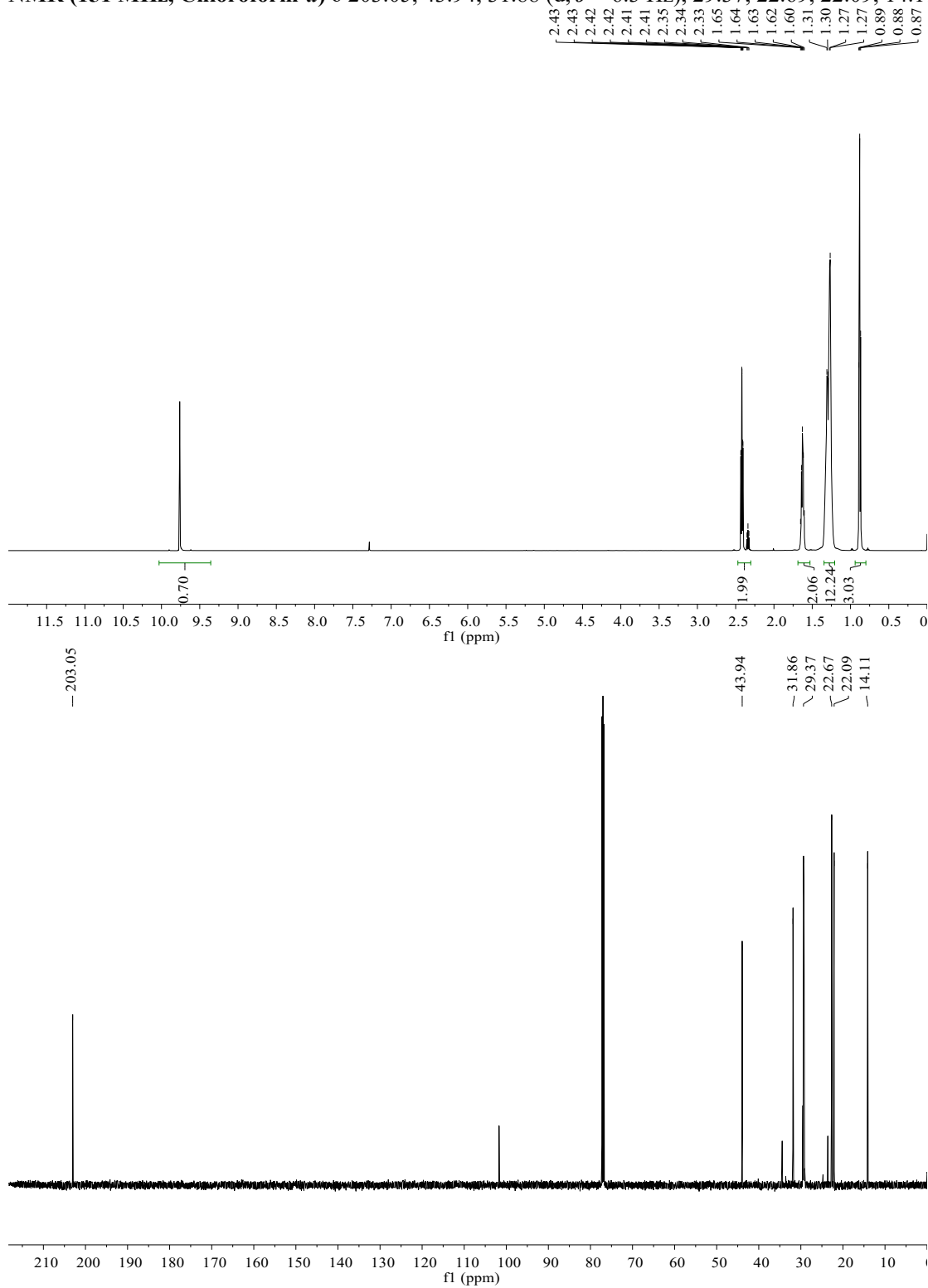
Figure S49 1H and 13C NMR spectrogram of n-decanal

6. HPLC/GC, GC-MS/HPLC-MS, AND ¹H NMR DATA

Acetophenone

HPLC, GC-MS, and ¹H NMR spectrogram of acetophenone

2-Methylacetophenone

HPLC, GC-MS, and ^{1}H NMR spectrogram of 2-methylacetophenone

3-Methylacetophenone

HPLC, GC-MS, and ¹H NMR spectrogram of 3-methylacetophenone

4-Methylacetophenone

HPLC, GC-MS, and ¹H NMR spectrogram of 4-methylacetophenone

4-Methoxy-acetophenone

HPLC, GC-MS, and ¹H NMR spectrogram of 4-methoxy-acetophenone

4-Hydroxyacetophenone

HPLC, GC-MS, and ¹H NMR spectrogram of 4-hydroxyacetophenone

2-Hydroxyacetophenone

HPLC, GC-MS, and ¹H NMR spectrogram of 2-hydroxyacetophenone

2-Bromoacetophenone
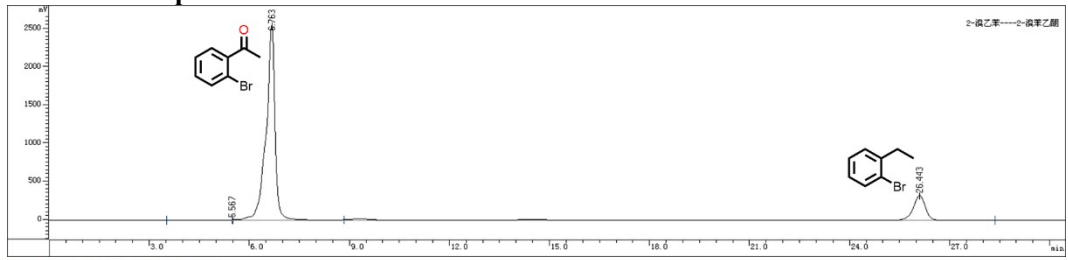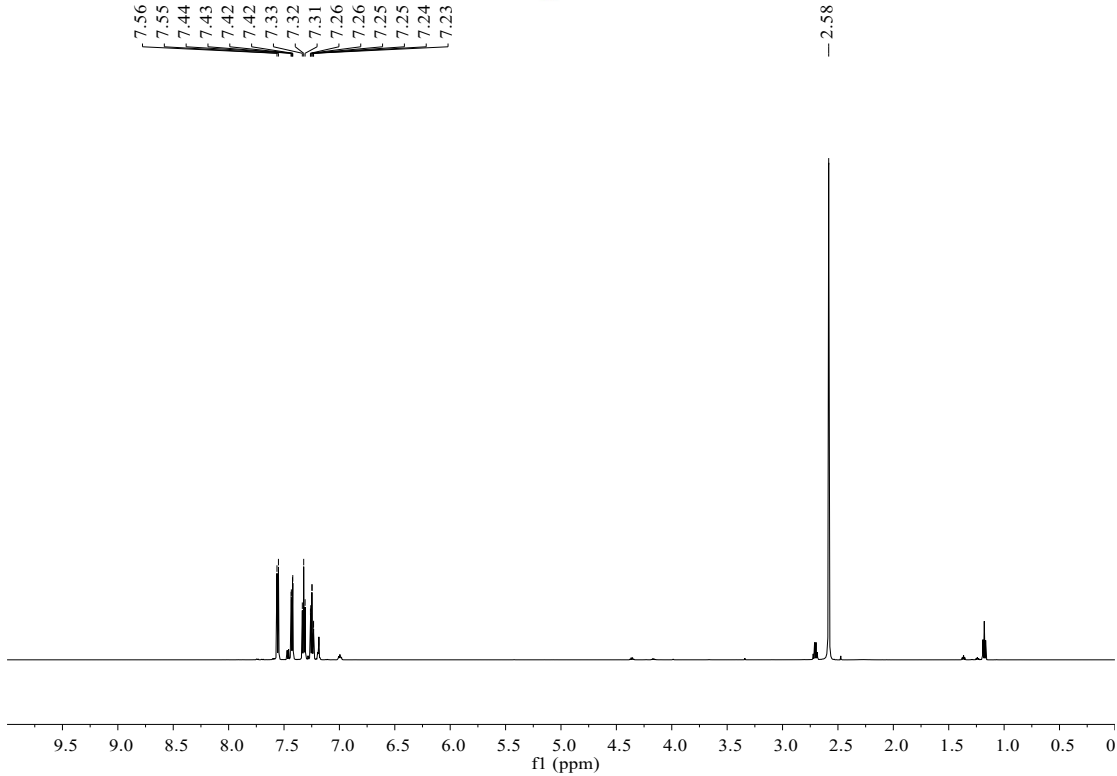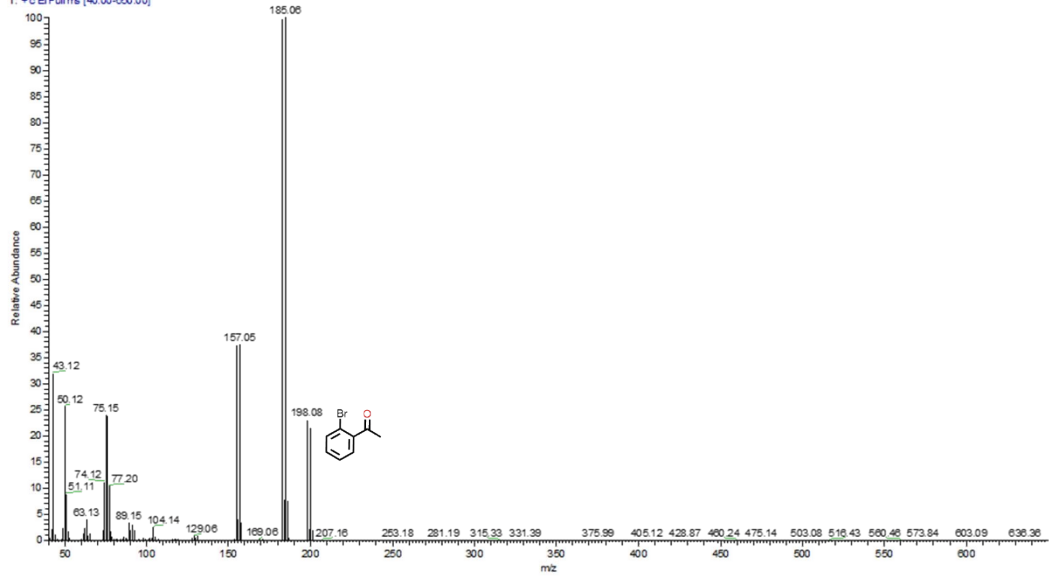
HPLC, GC-MS, and ¹H NMR spectrogram of 2-bromoacetophenone

4-Bromoacetophenone
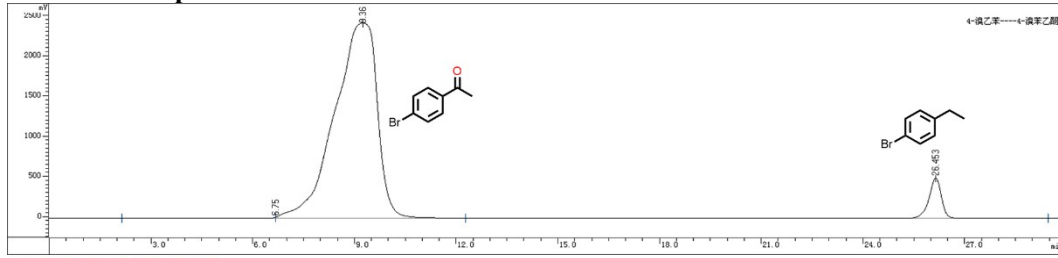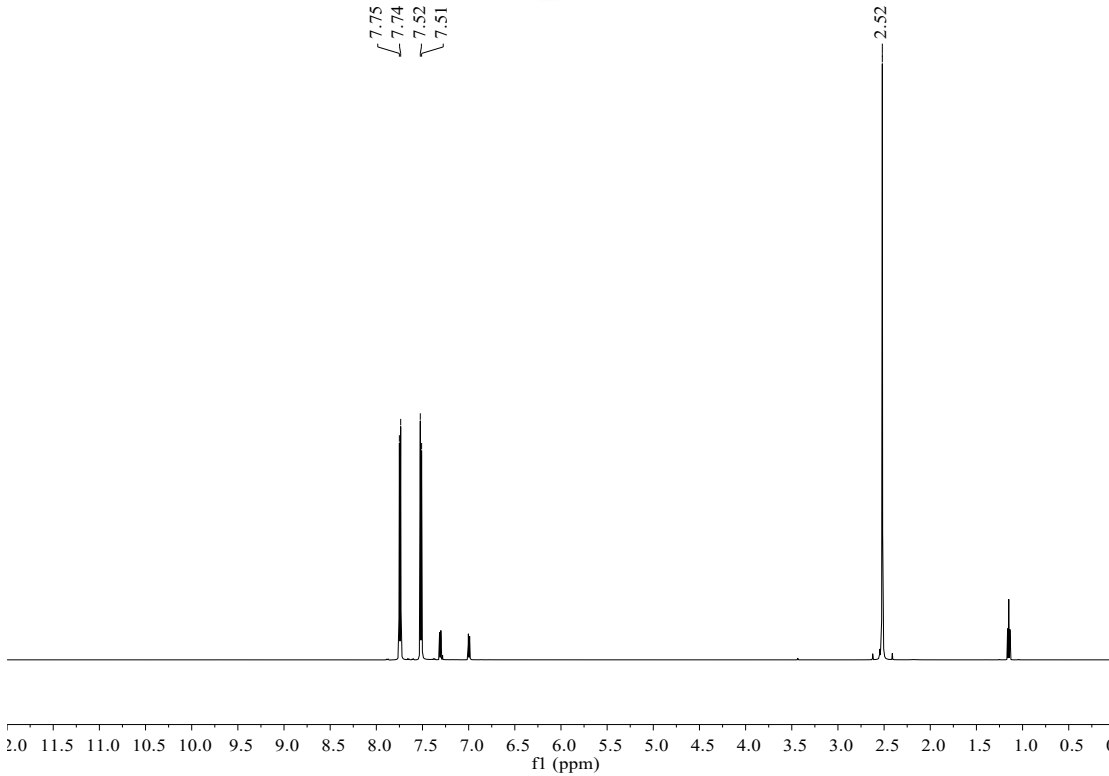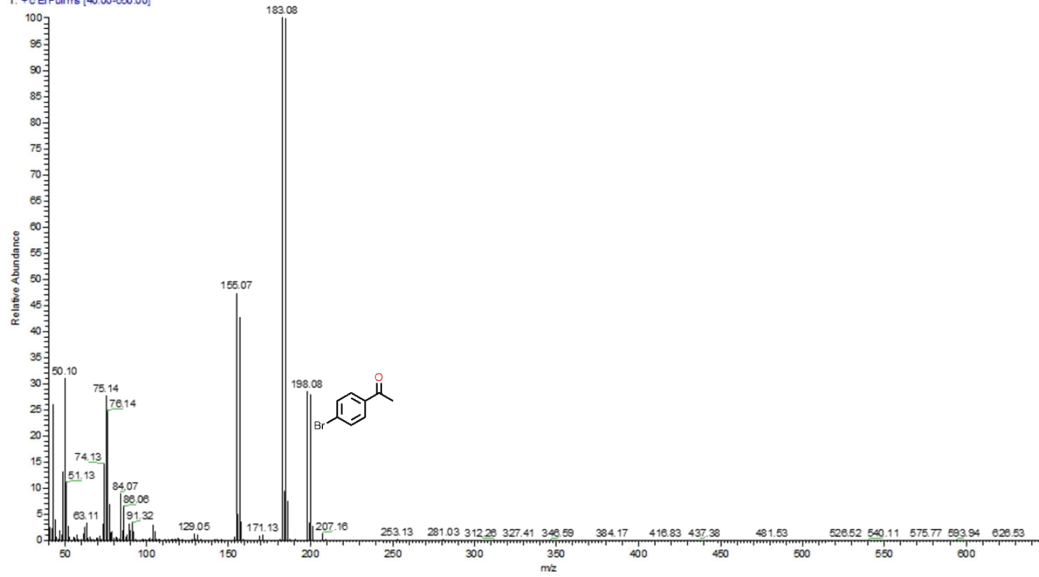
HPLC, GC-MS, and ¹H NMR spectrogram of 4-bromoacetophenone

4-Iodoacetophenone
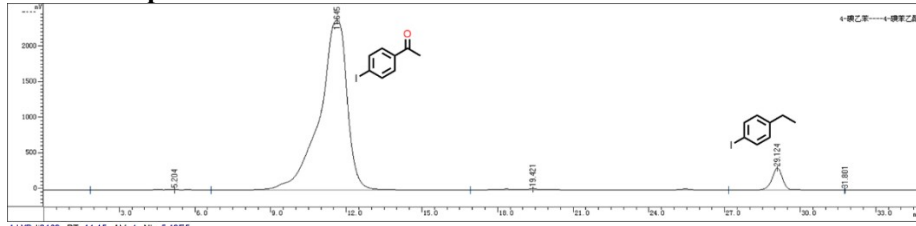
HPLC, GC-MS, and ^{1}H NMR spectrogram of 4-Iodoacetophenone

4-Aminoacetophenone
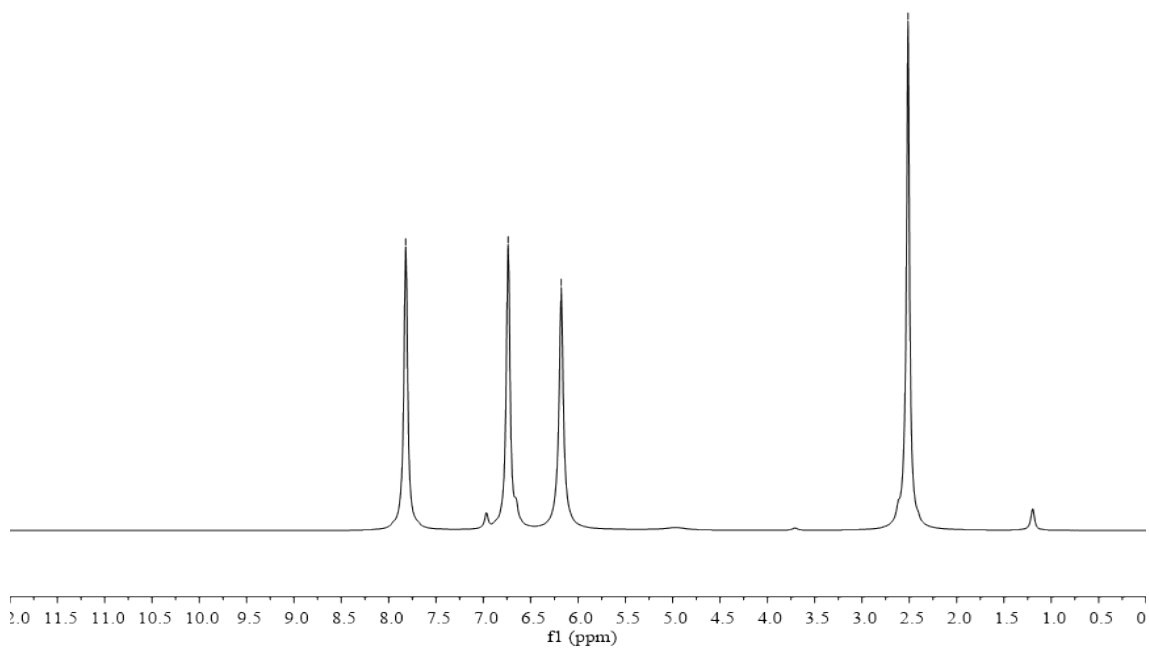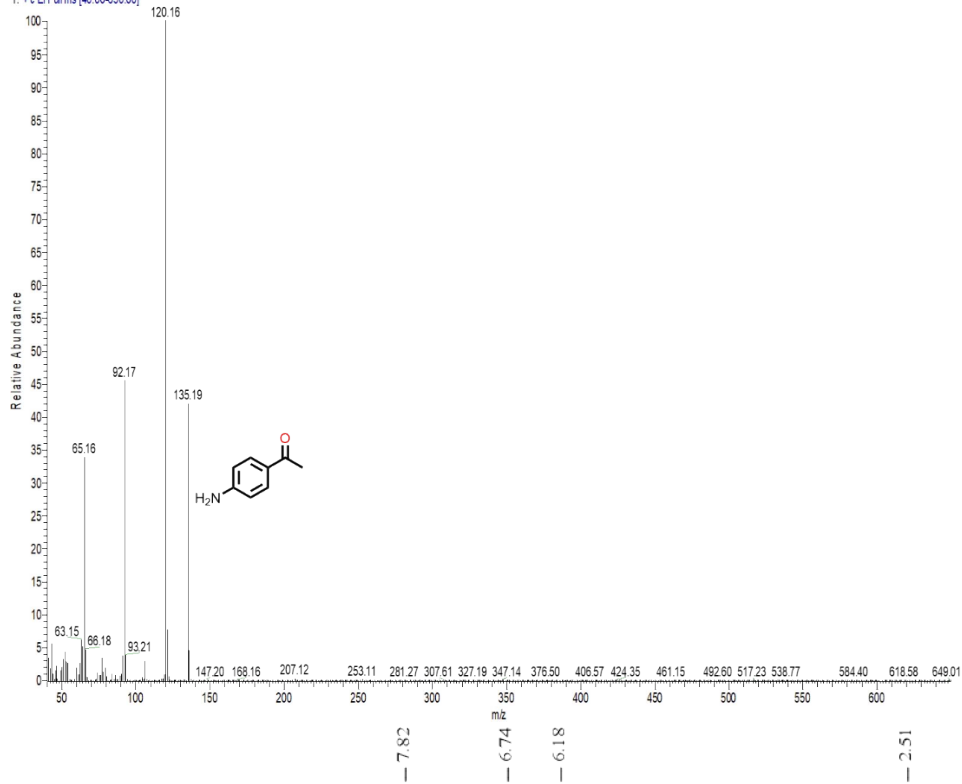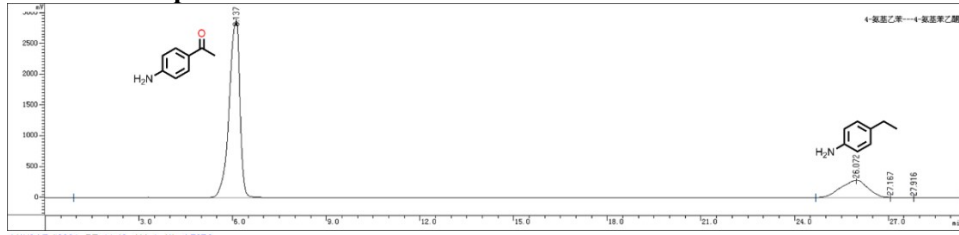
HPLC, GC-MS, and ¹H NMR spectrogram of 4-aminoacetophenone

4-Nitroacetophenone
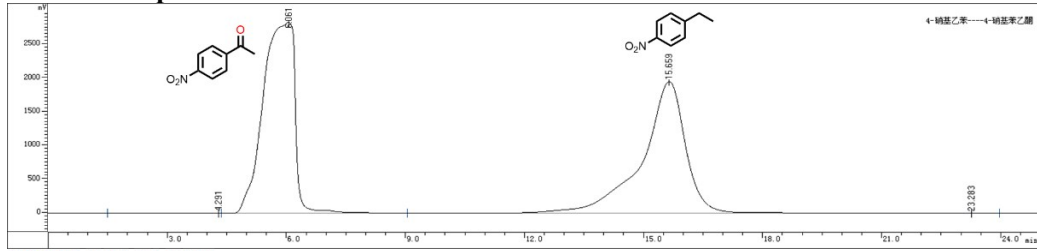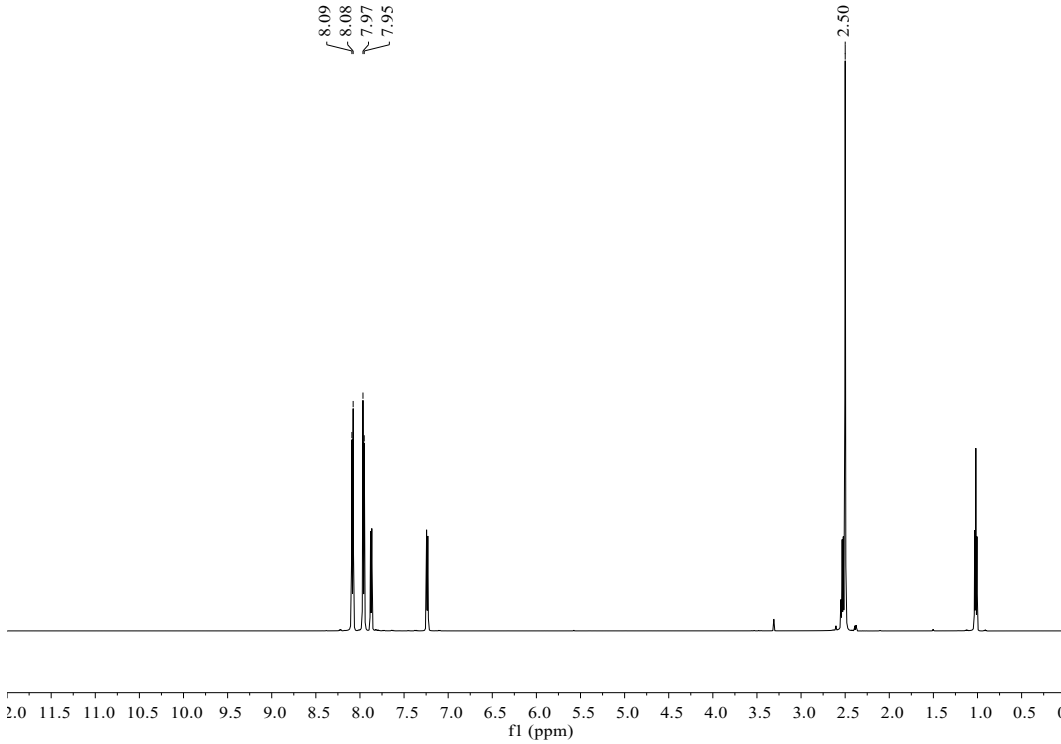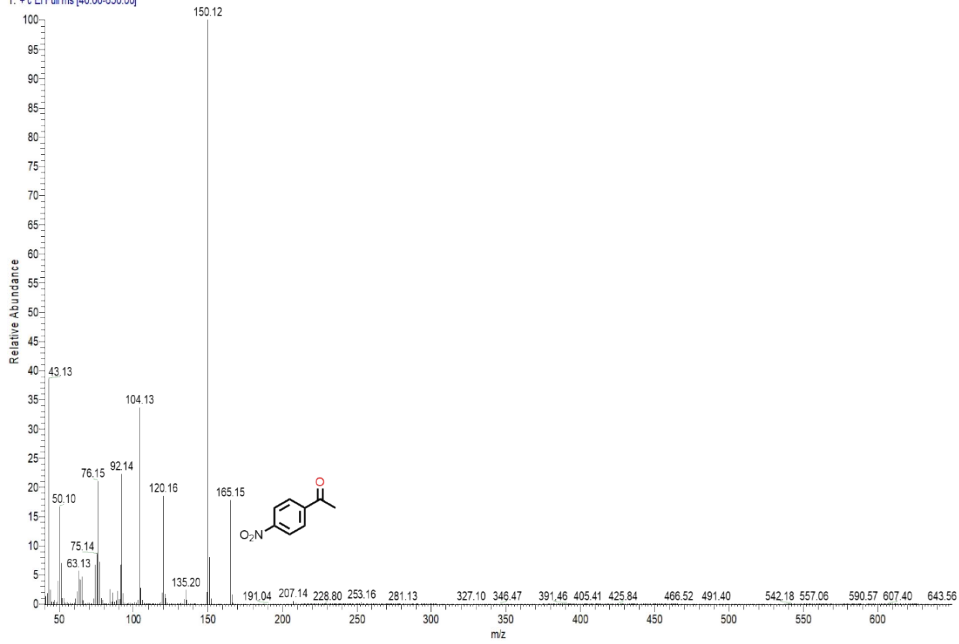
HPLC, GC-MS, and ^{1}H NMR spectrogram of 4-nitroacetophenone

Benzophenone
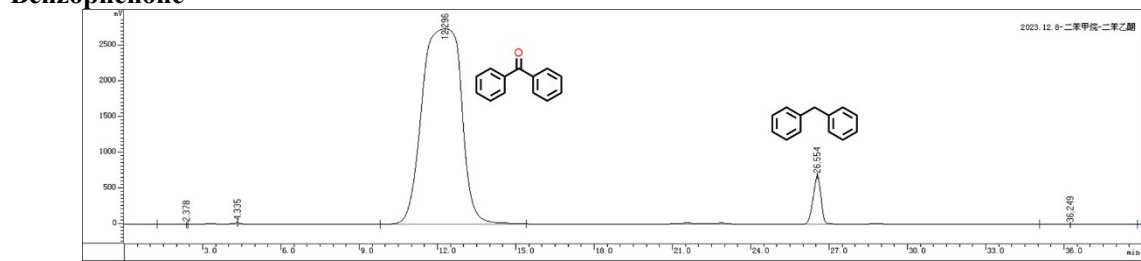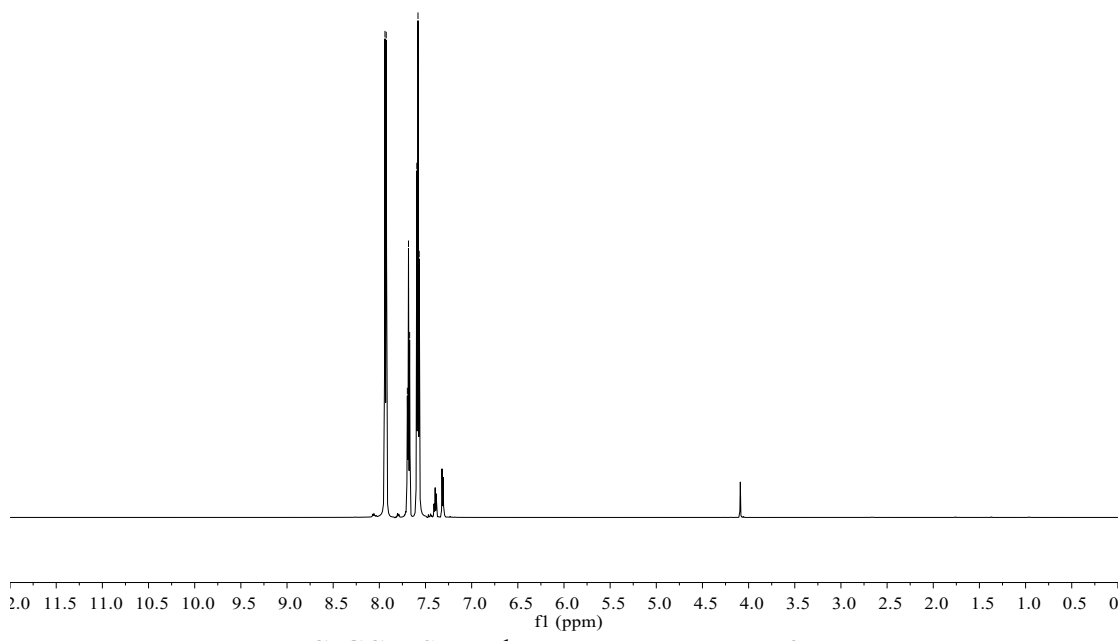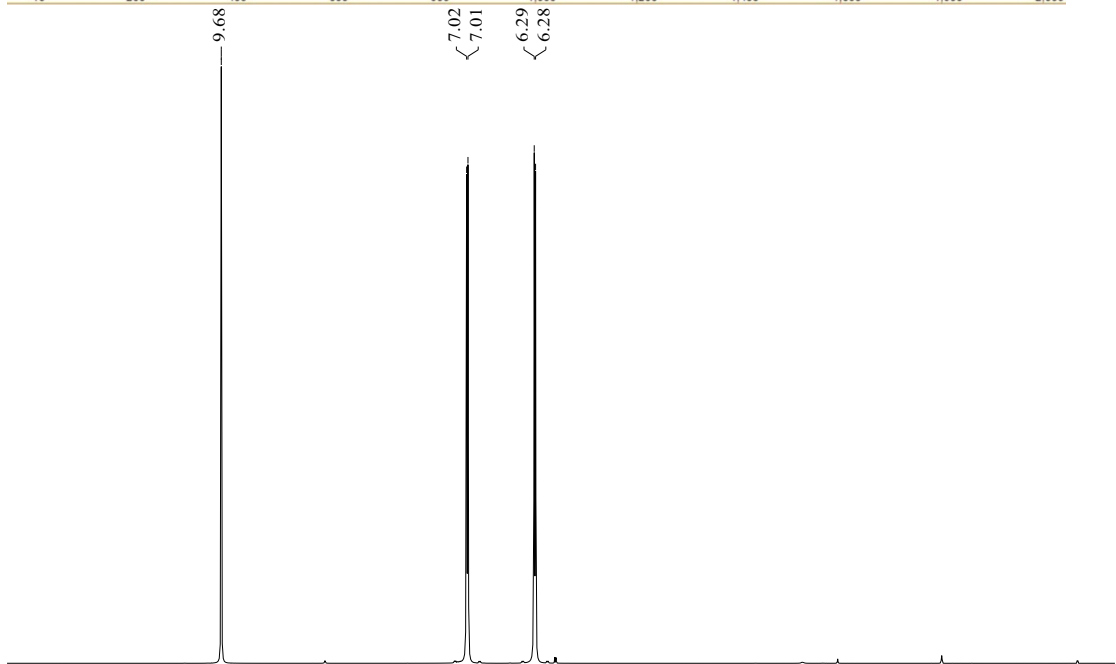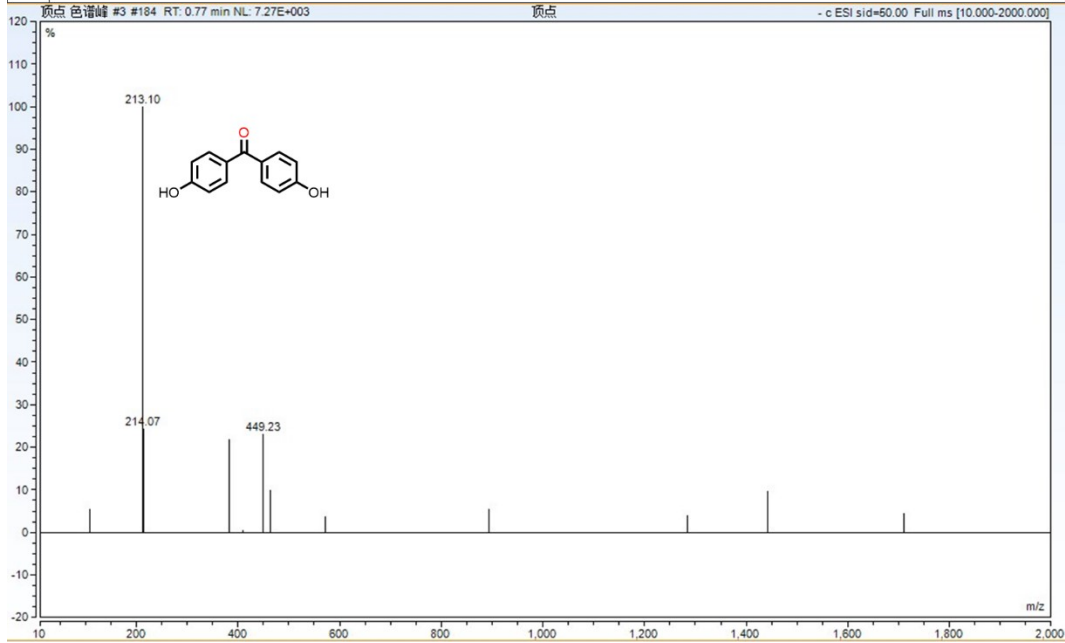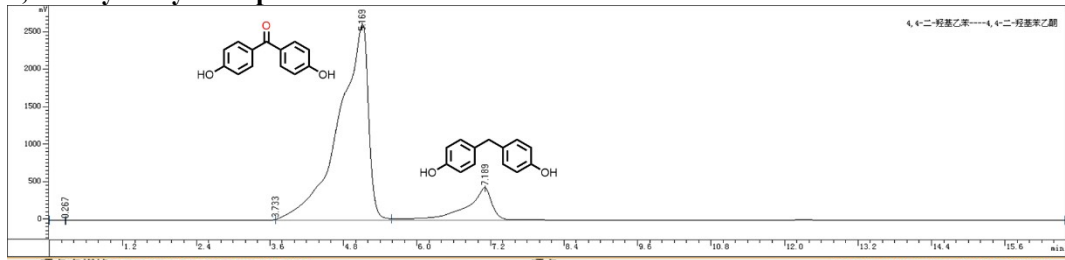
HPLC, GC-MS, and ¹H NMR spectrogram of benzophenone

4, 4-Dihydroxybenzophenone

HPLC, HPLC-MS, and ¹H NMR spectrogram of 4, 4-dihydroxybenzophenone

4, 4-Diaminobenzophenone
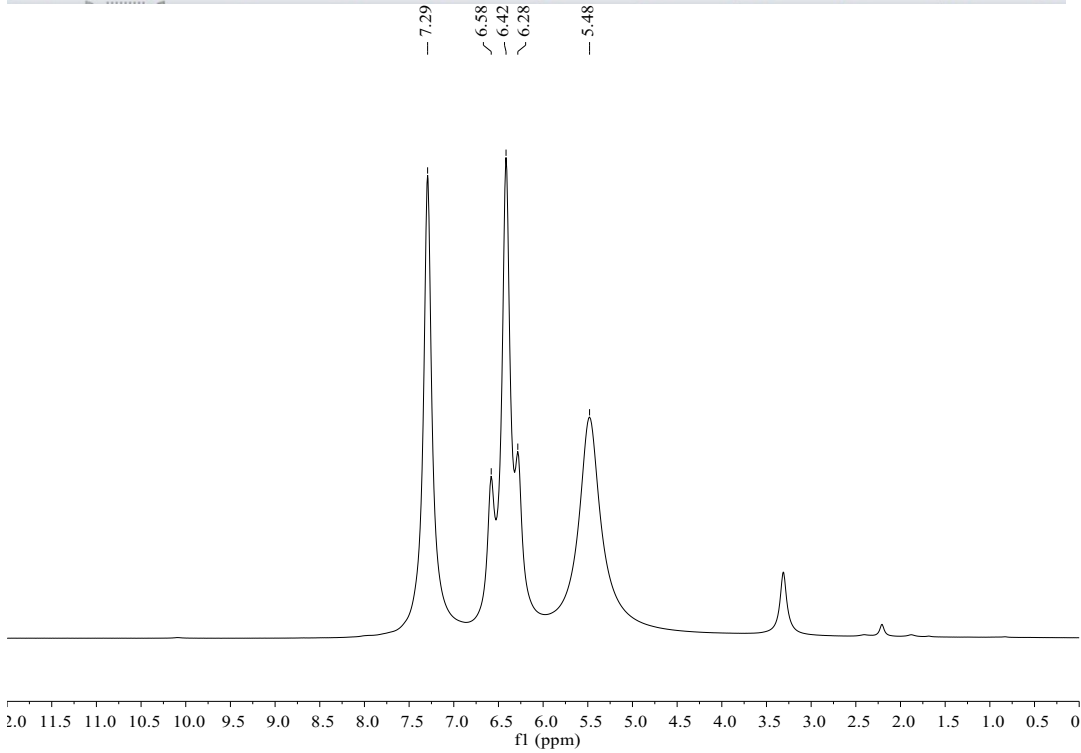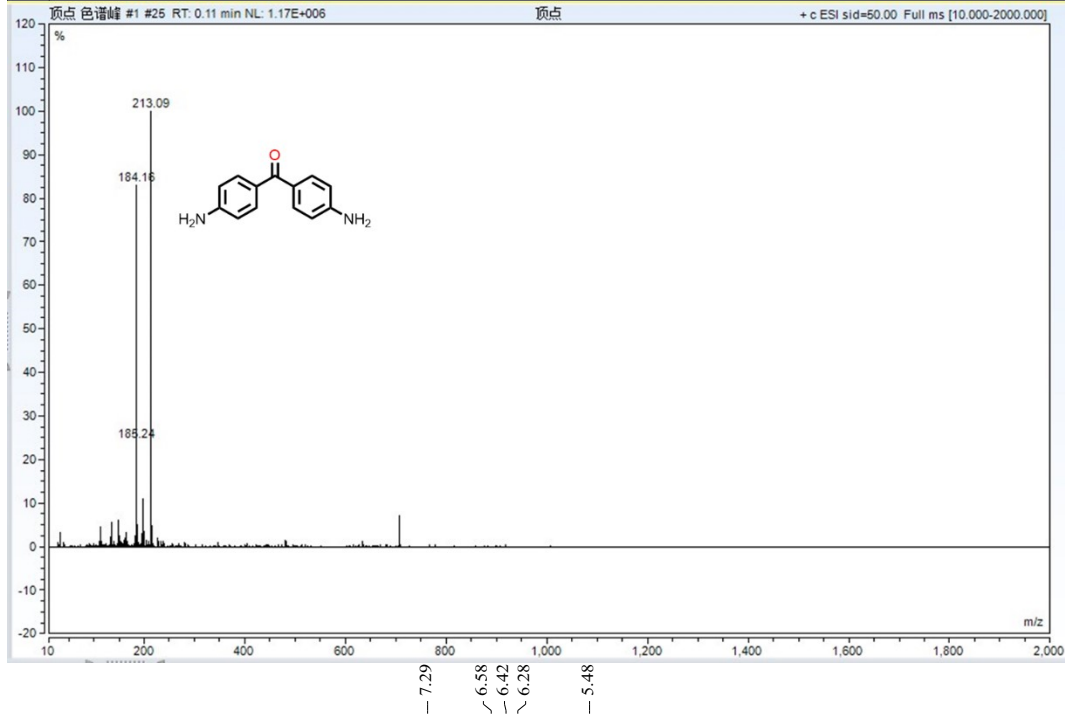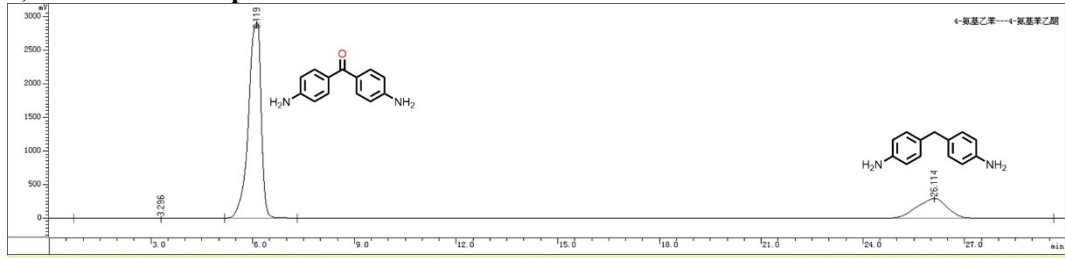
HPLC, HPLC-MS, and ¹H NMR spectrogram of 4, 4-diaminobenzophenone

Xanthone
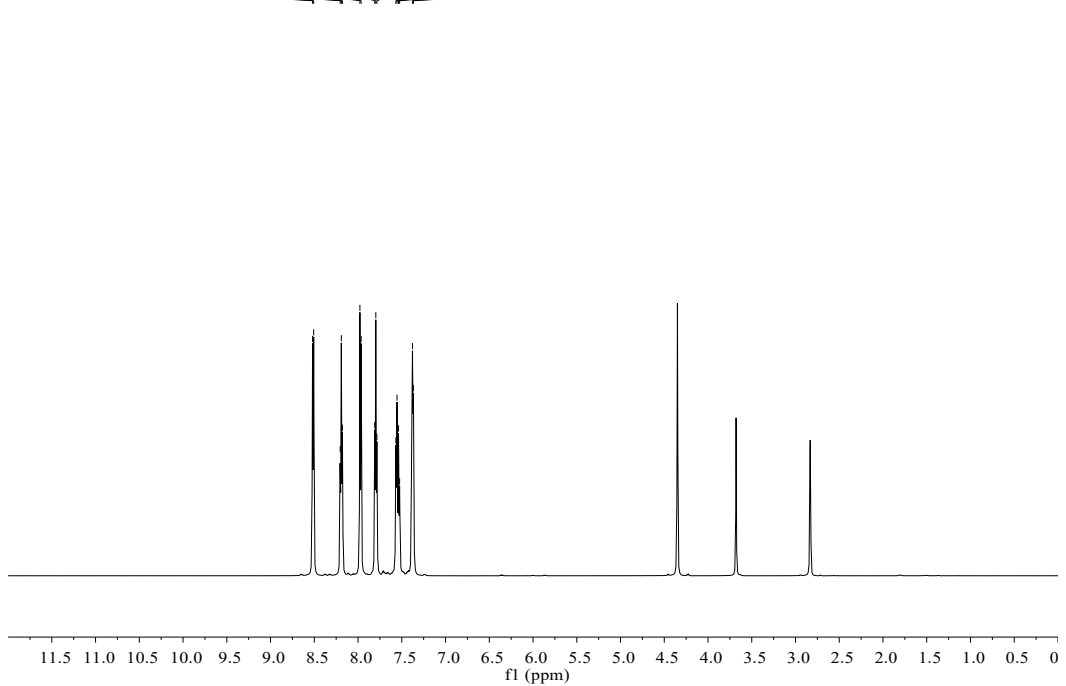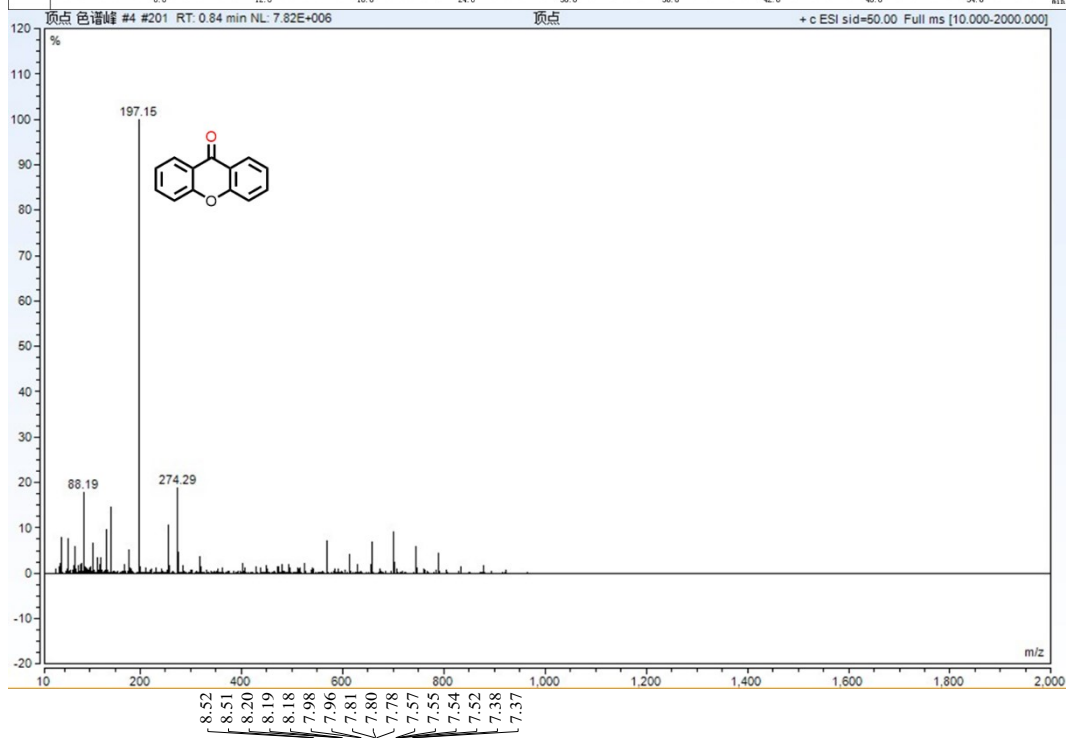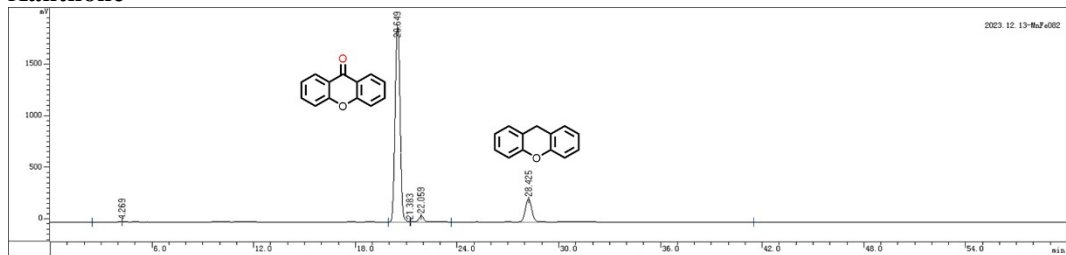
HPLC, HPLC-MS, and ¹H NMR spectrogram of xanthone

9-Thioxanthone
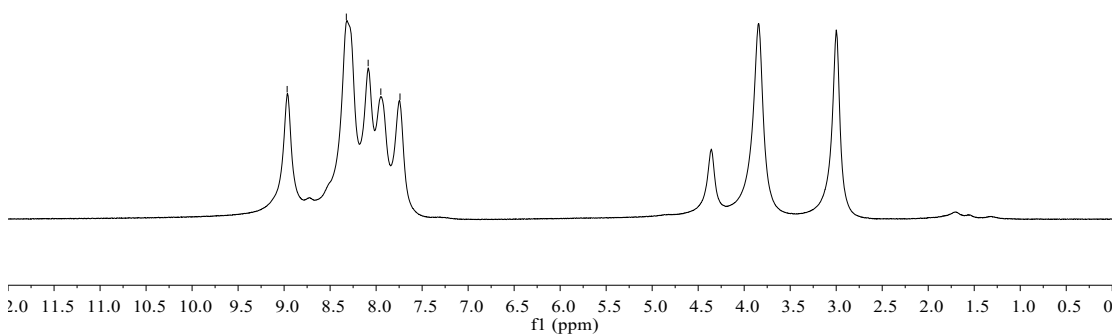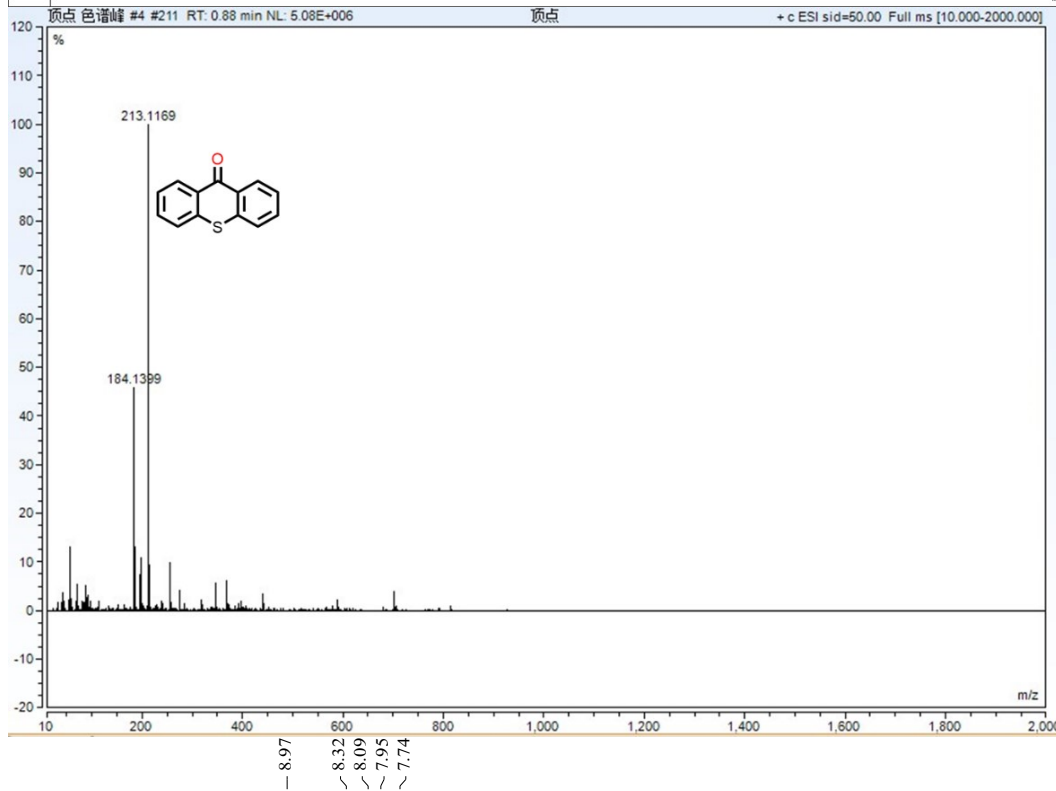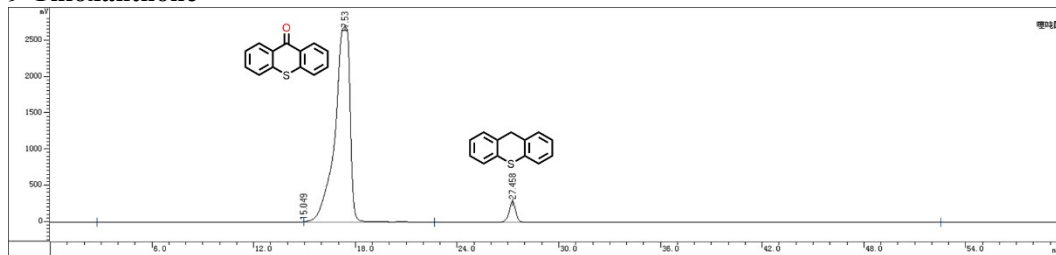
HPLC, HPLC-MS, and ¹H NMR spectrogram of 9-thioxanthone

Benzaldehyde
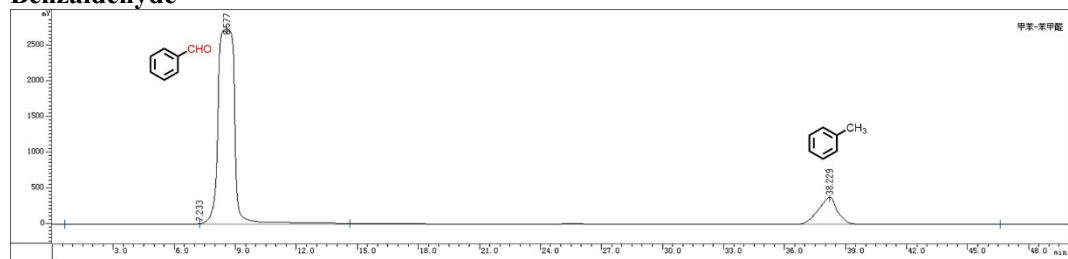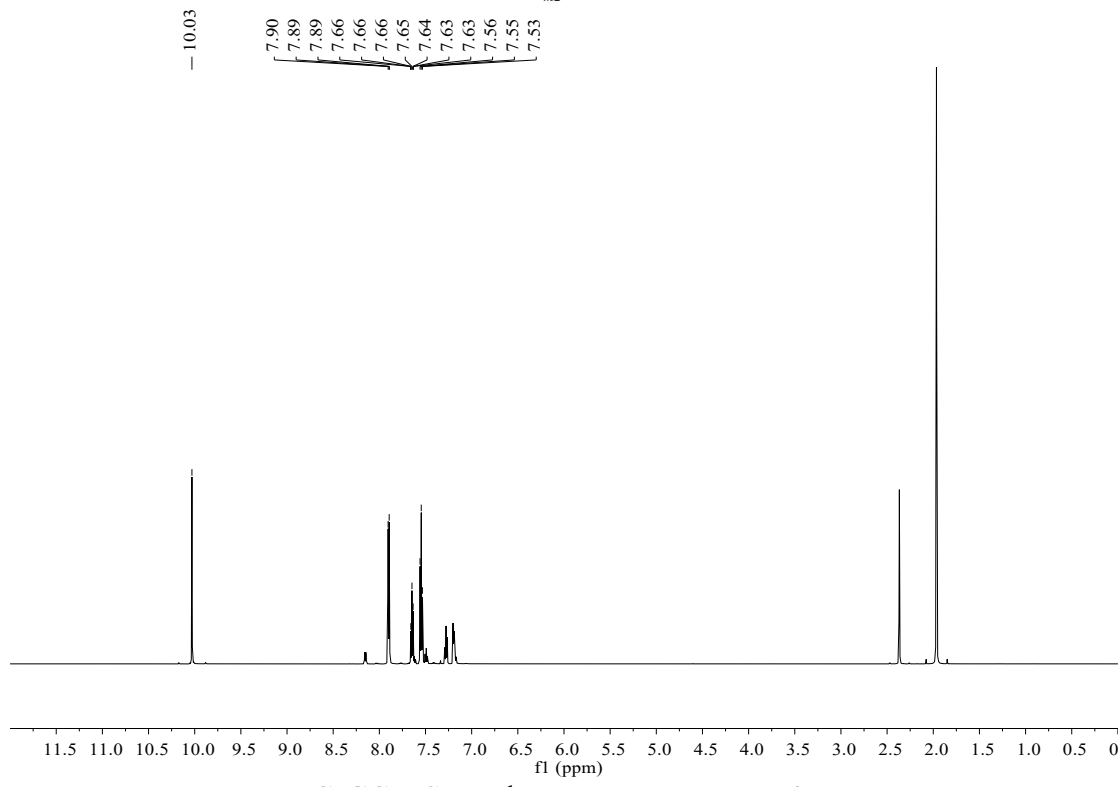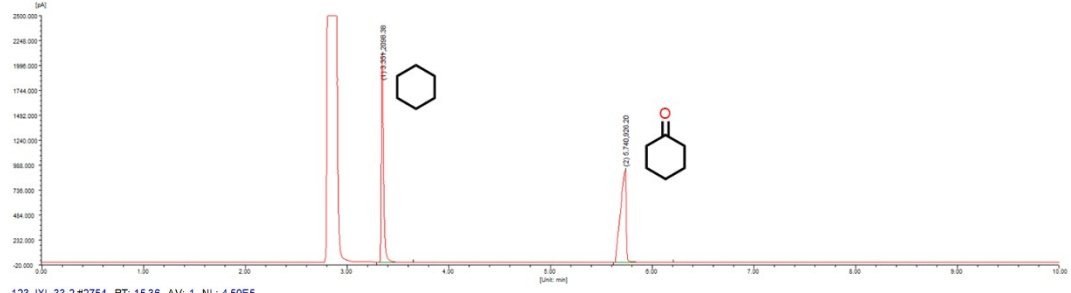
HPLC, GC-MS, and ^{1}H NMR spectrogram of benzaldehyde
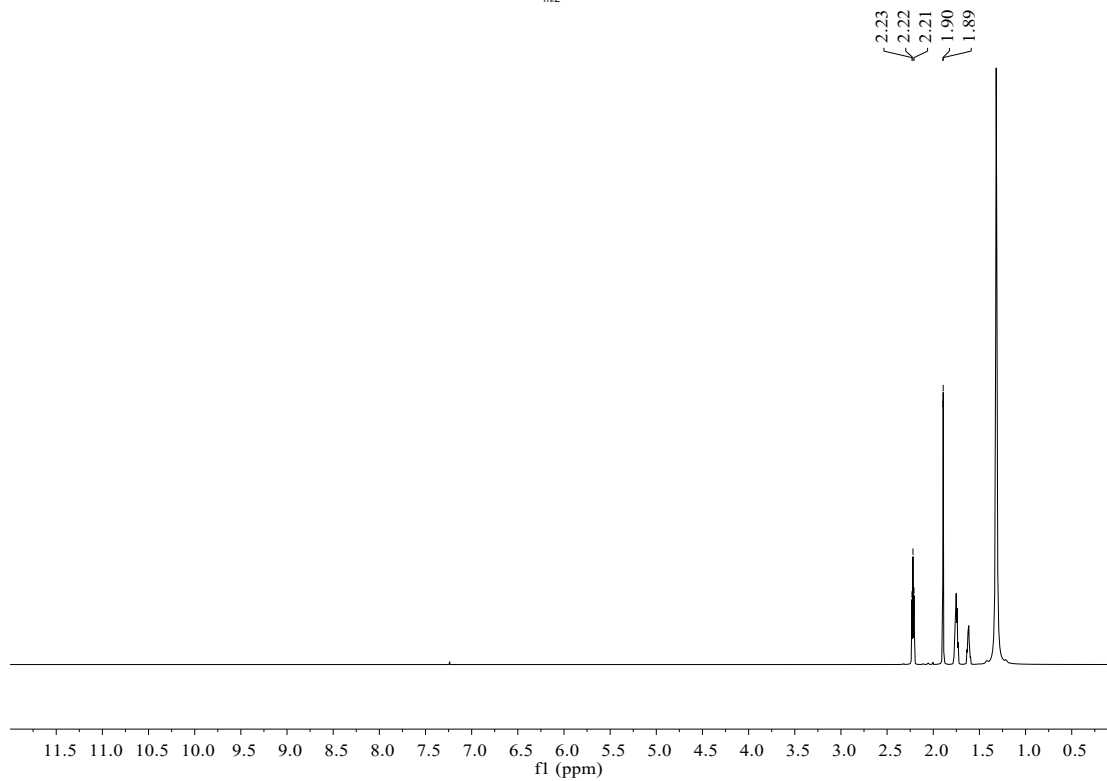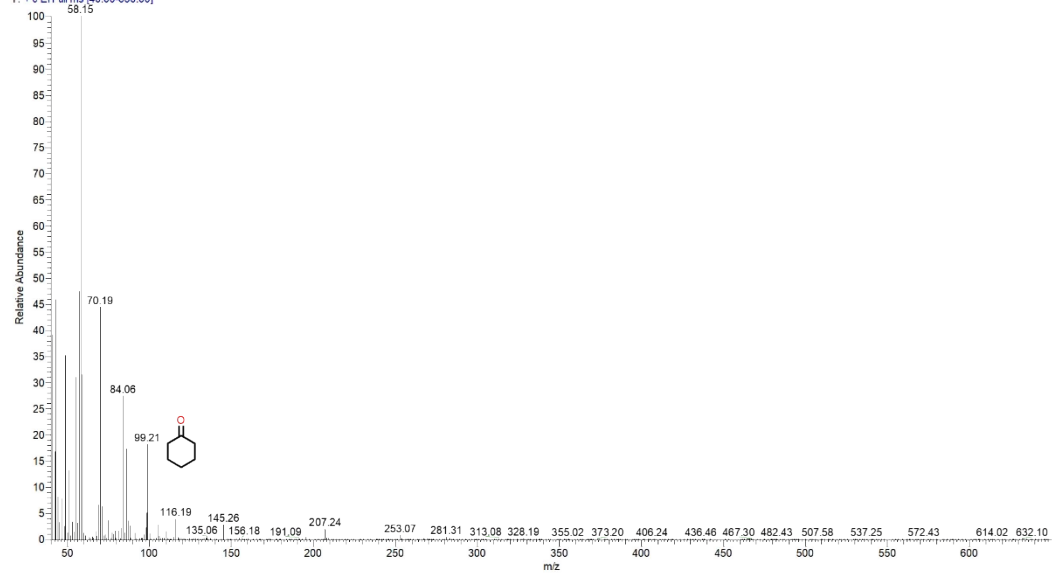
Cyclohexanone

GC, GC-MS, and ¹H NMR spectrogram of cyclohexanone
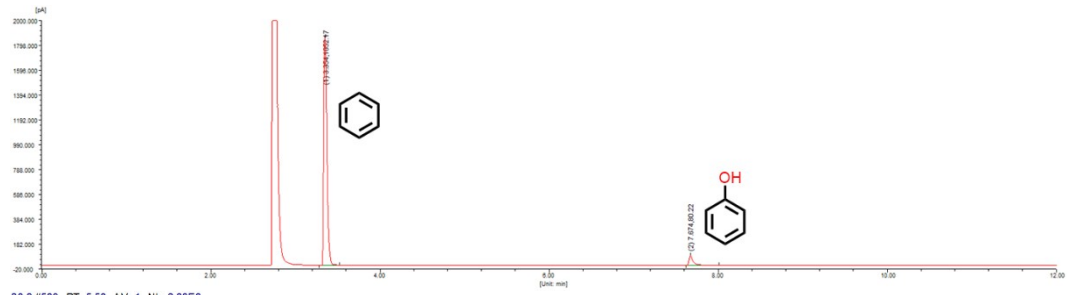
Phenol

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T: + c EI Full ms [40.00-650.00]
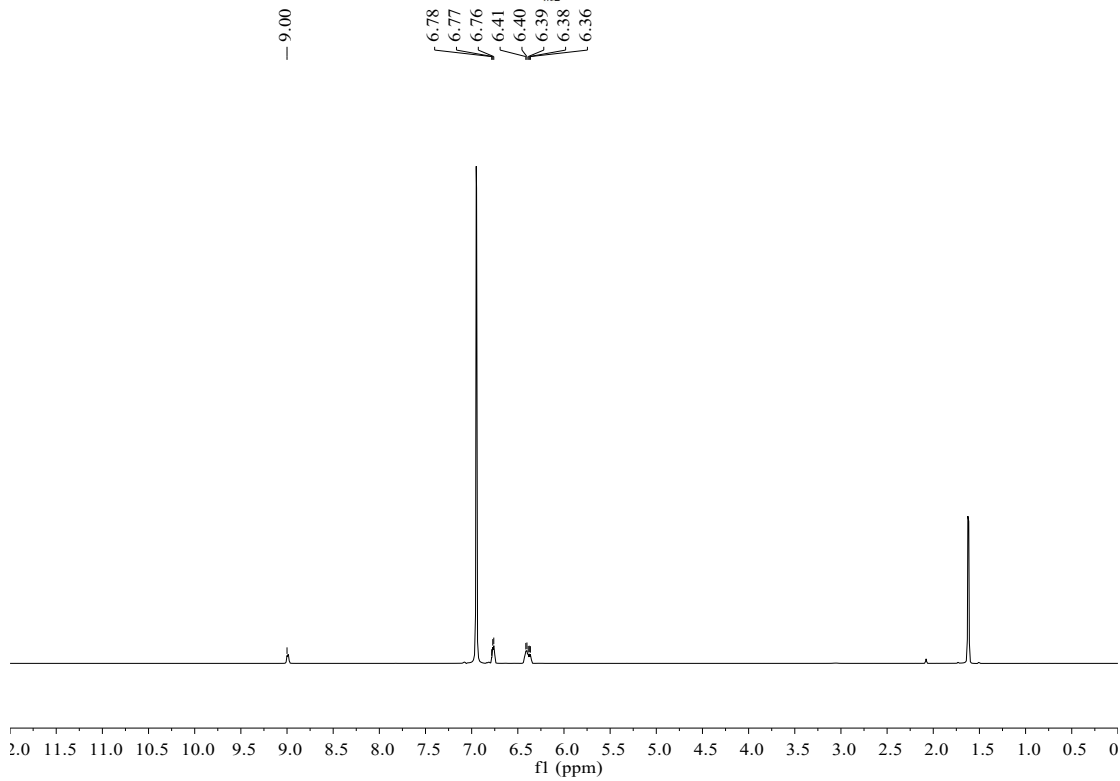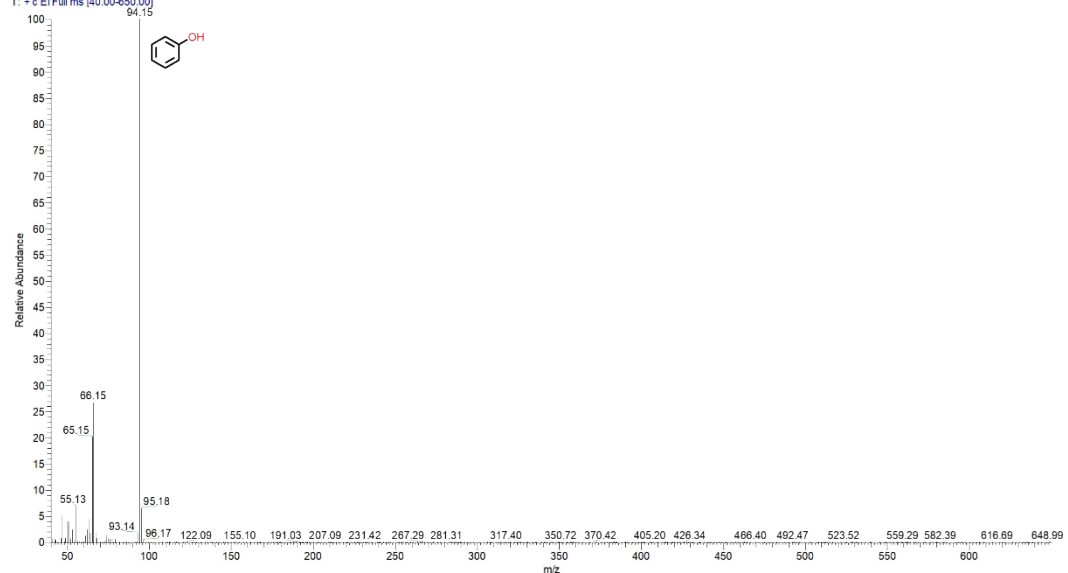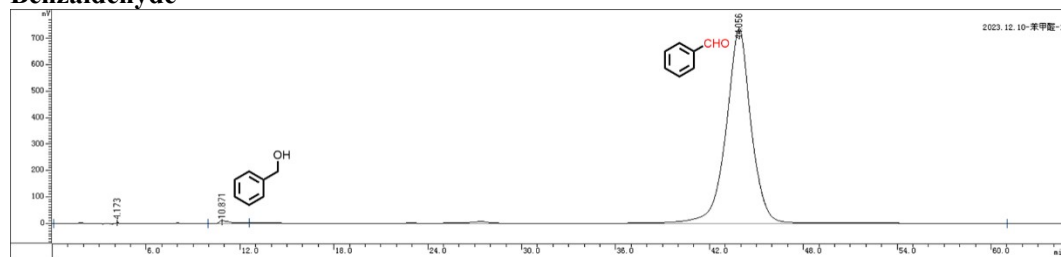
GC, GC-MS, and ¹H NMR spectrogram of phenol
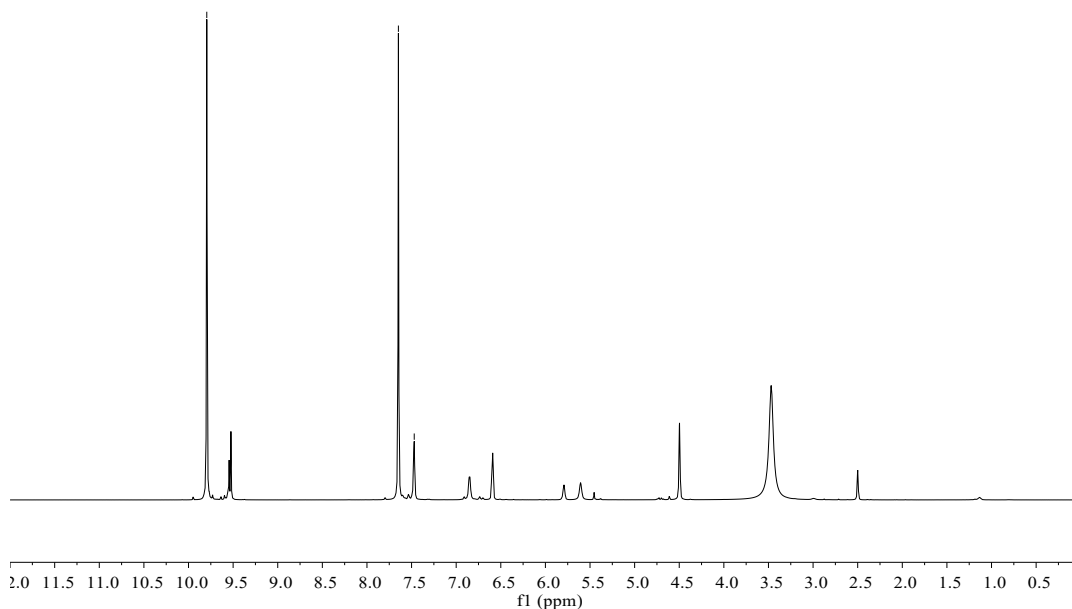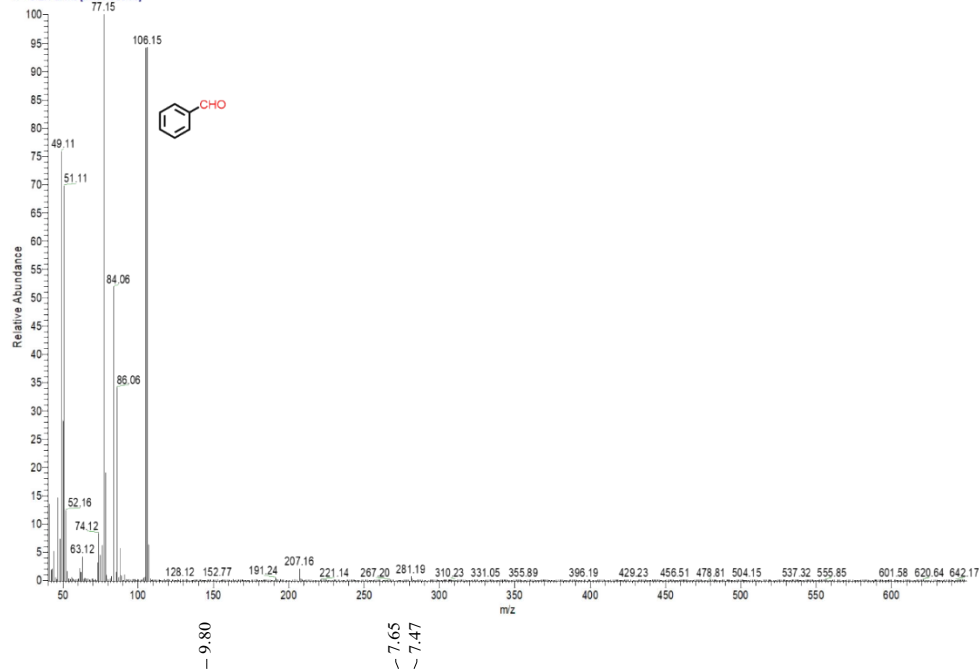
Benzaldehyde

HPLC, GC-MS, and ¹H NMR spectrogram of benzaldehyde

Phenyl acetaldehyde
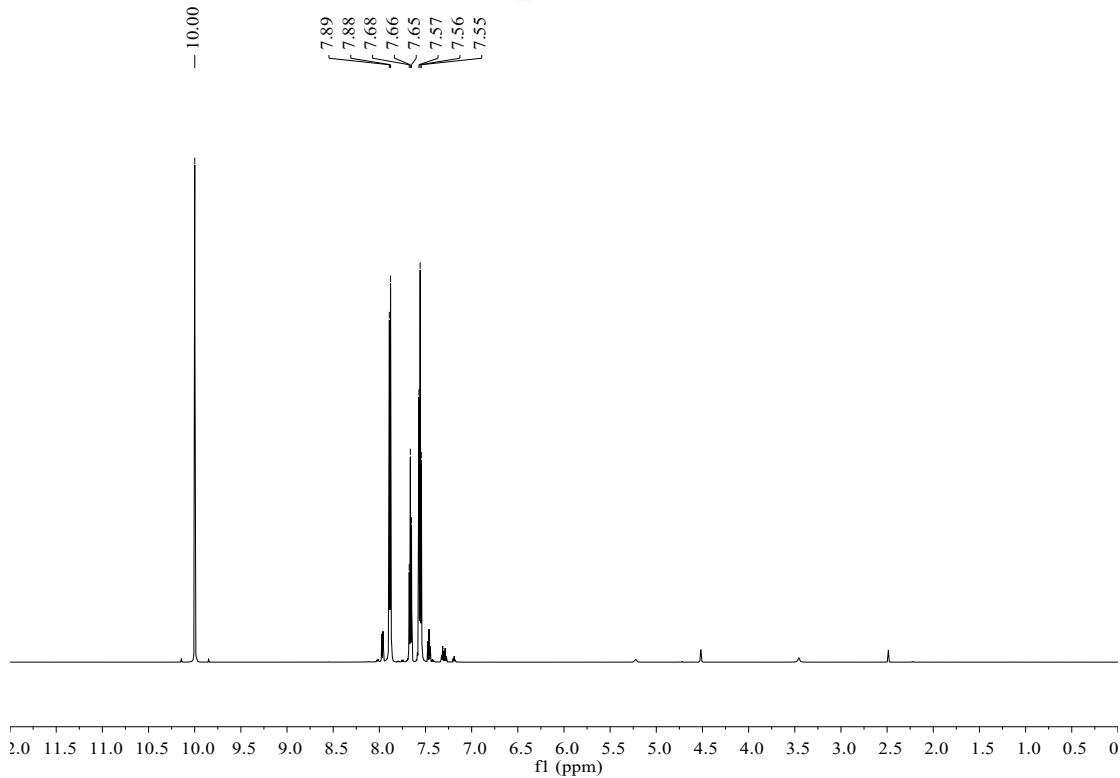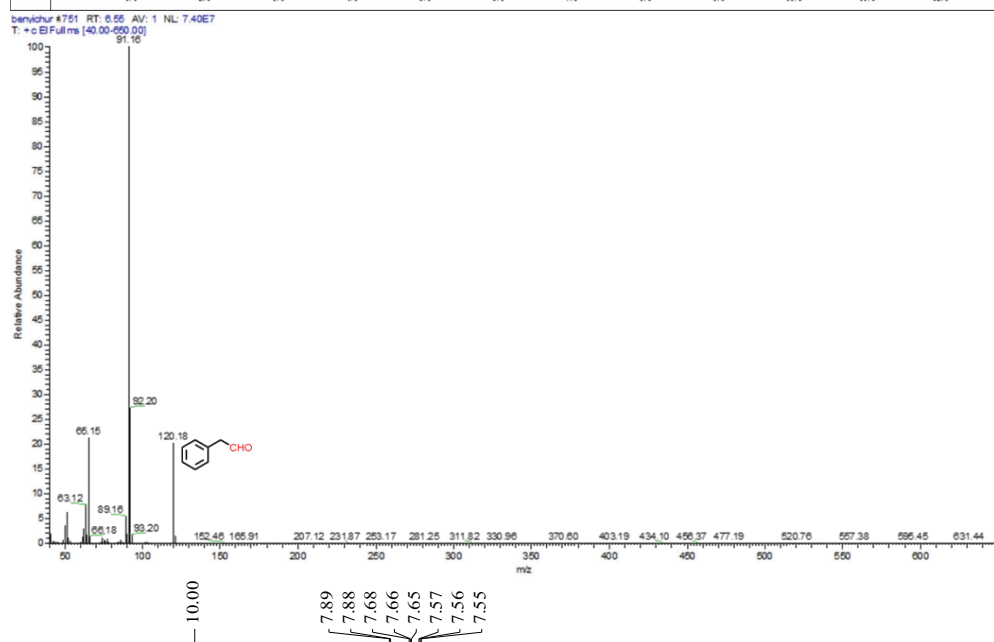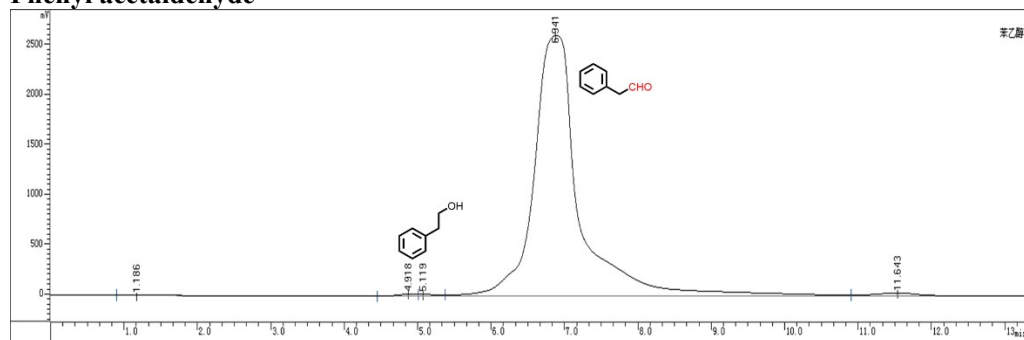
HPLC, GC-MS, and ¹H NMR spectrogram of phenyl acetaldehyde

4-Formylpyridine
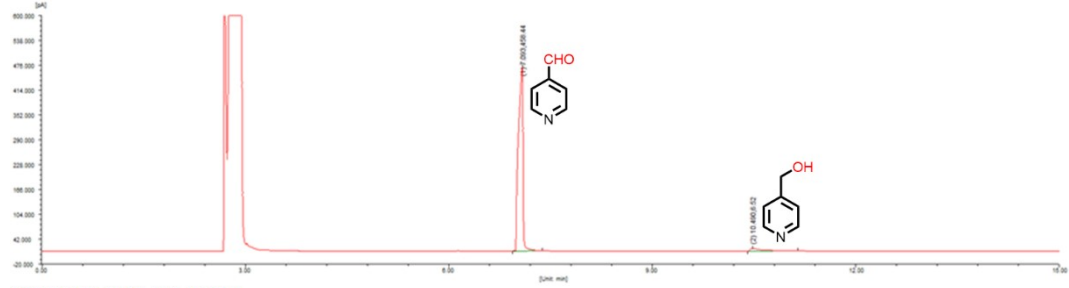
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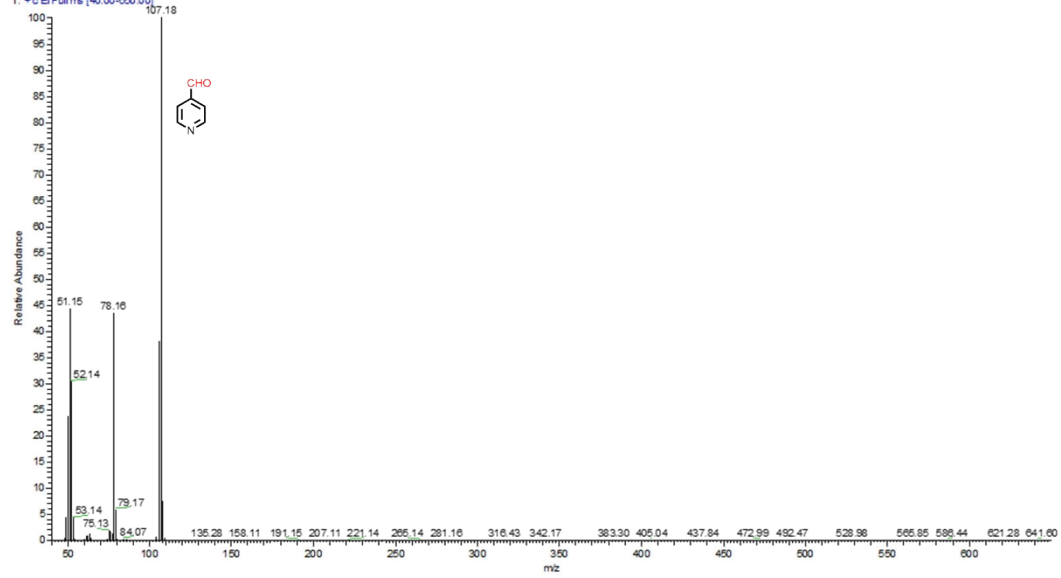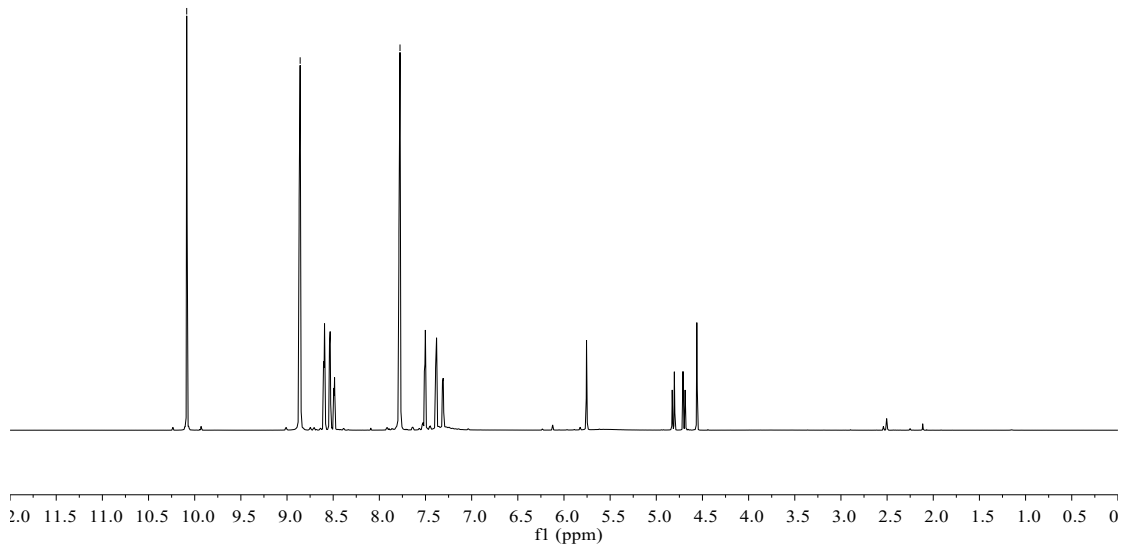
GC, GC-MS, and ^{1}H NMR spectrogram of 4-formylpyridine

Cinnamaldehyde
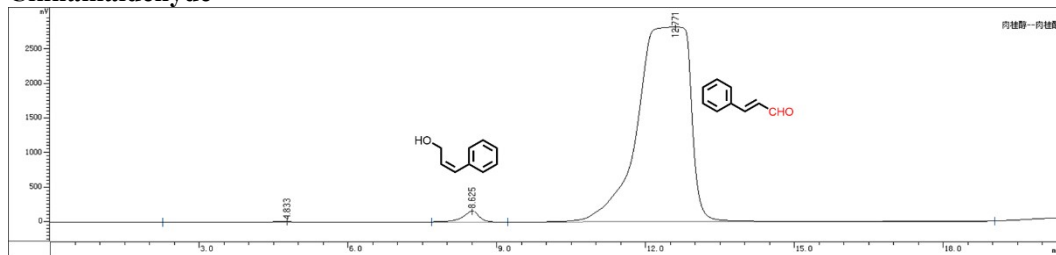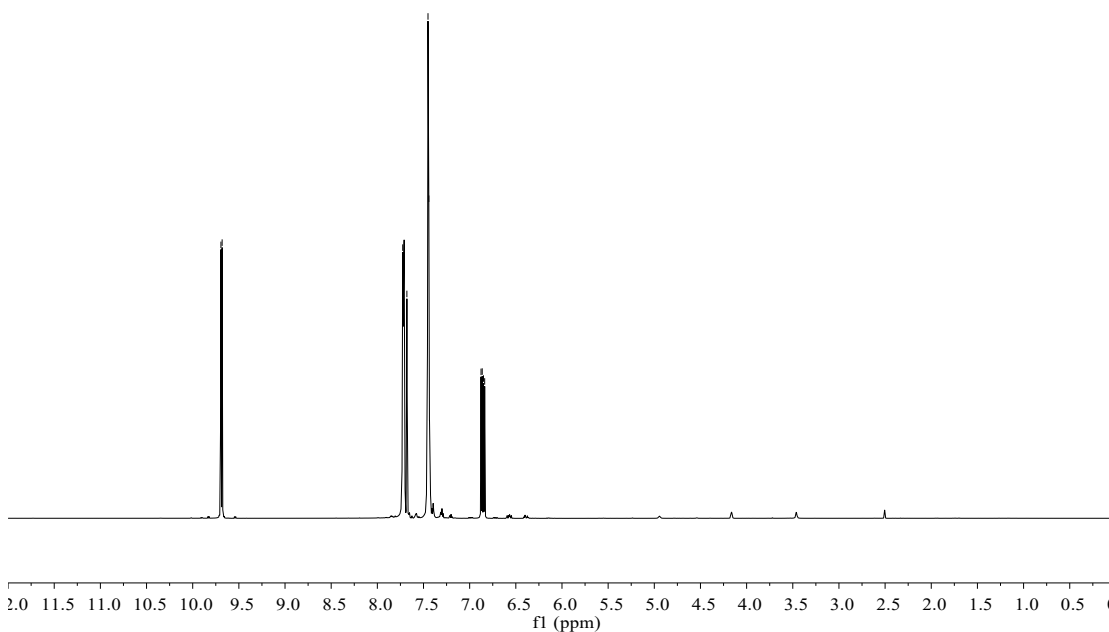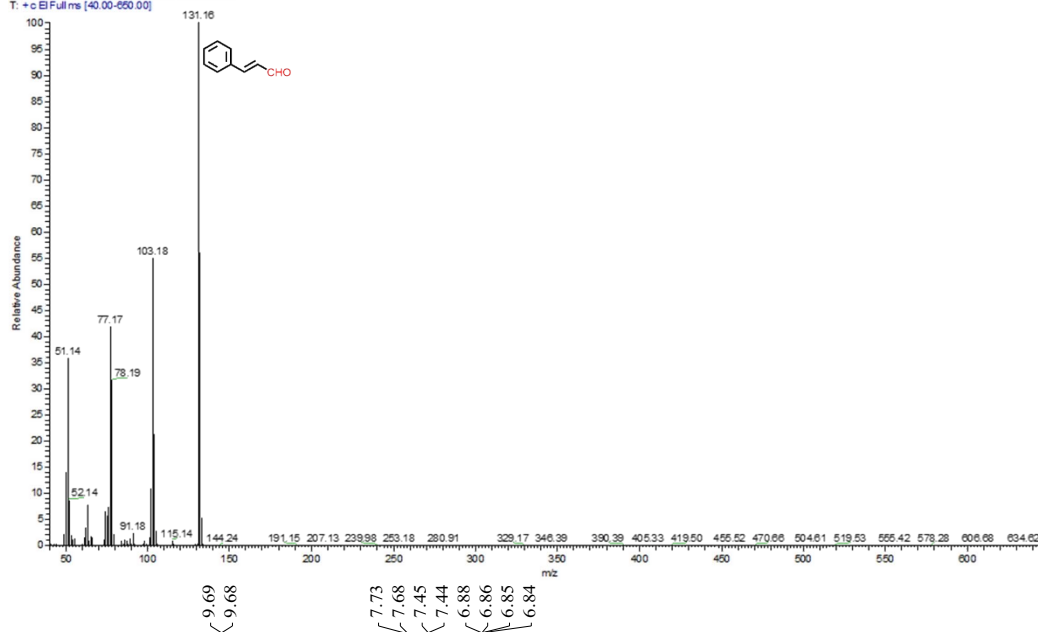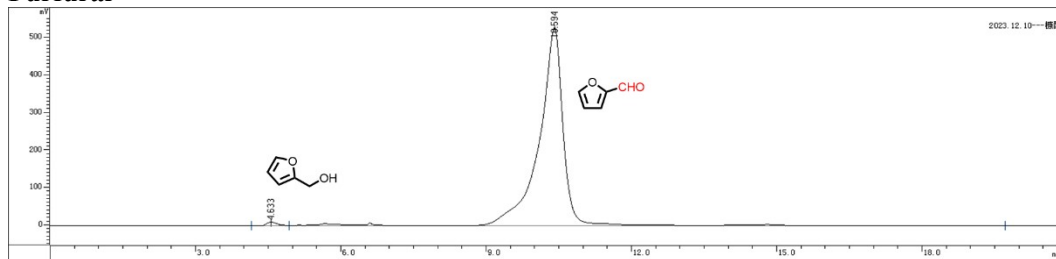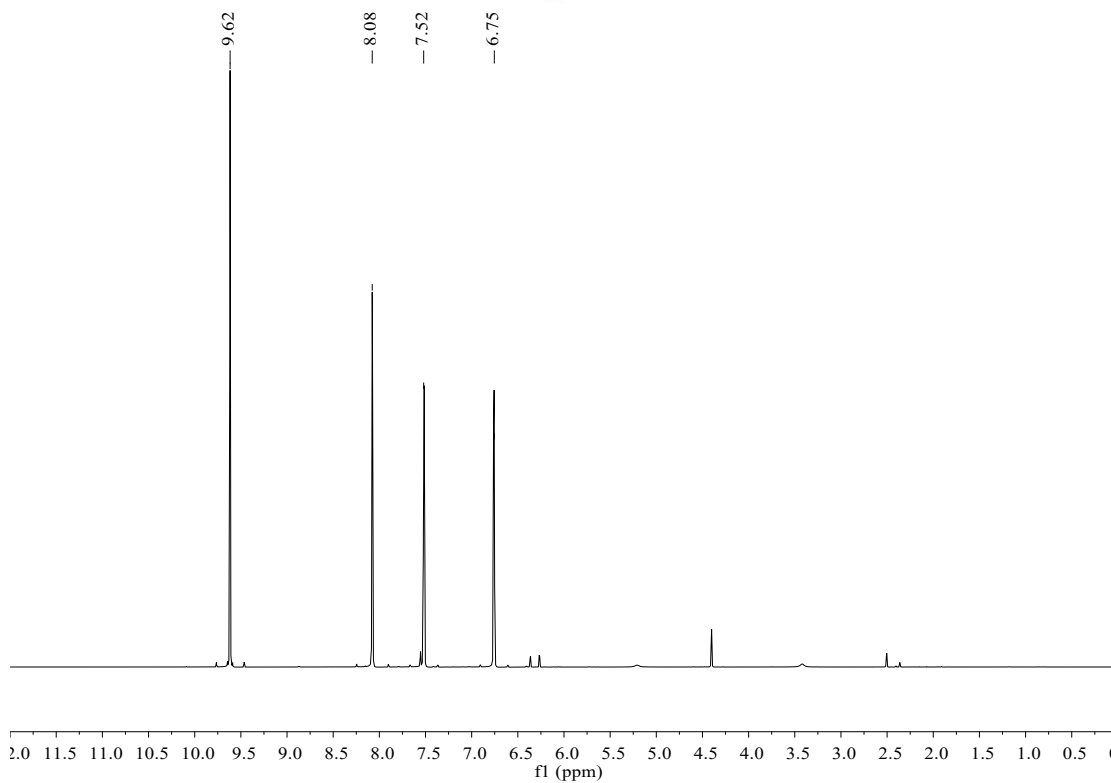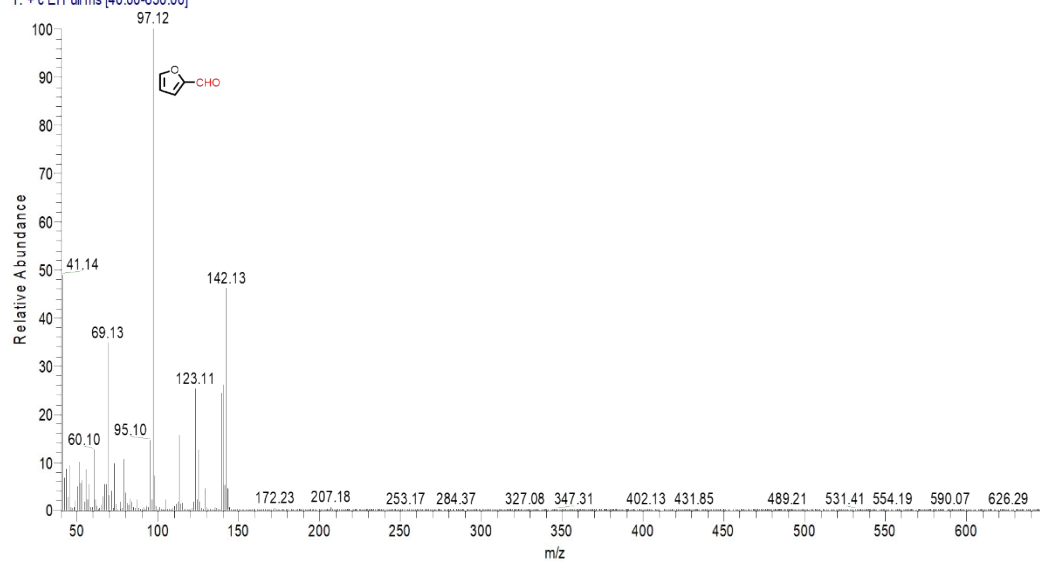
HPLC, GC-MS, and ^{1}H NMR spectrogram of cinnamaldehyde

Furfural
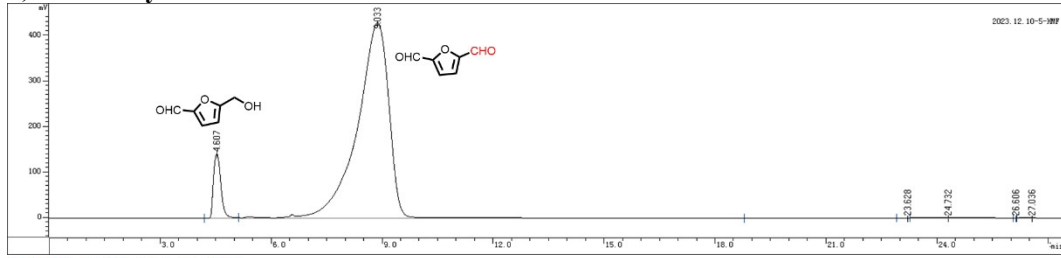
HPLC, GC-MS, and ^{1}H NMR spectrogram of furfural
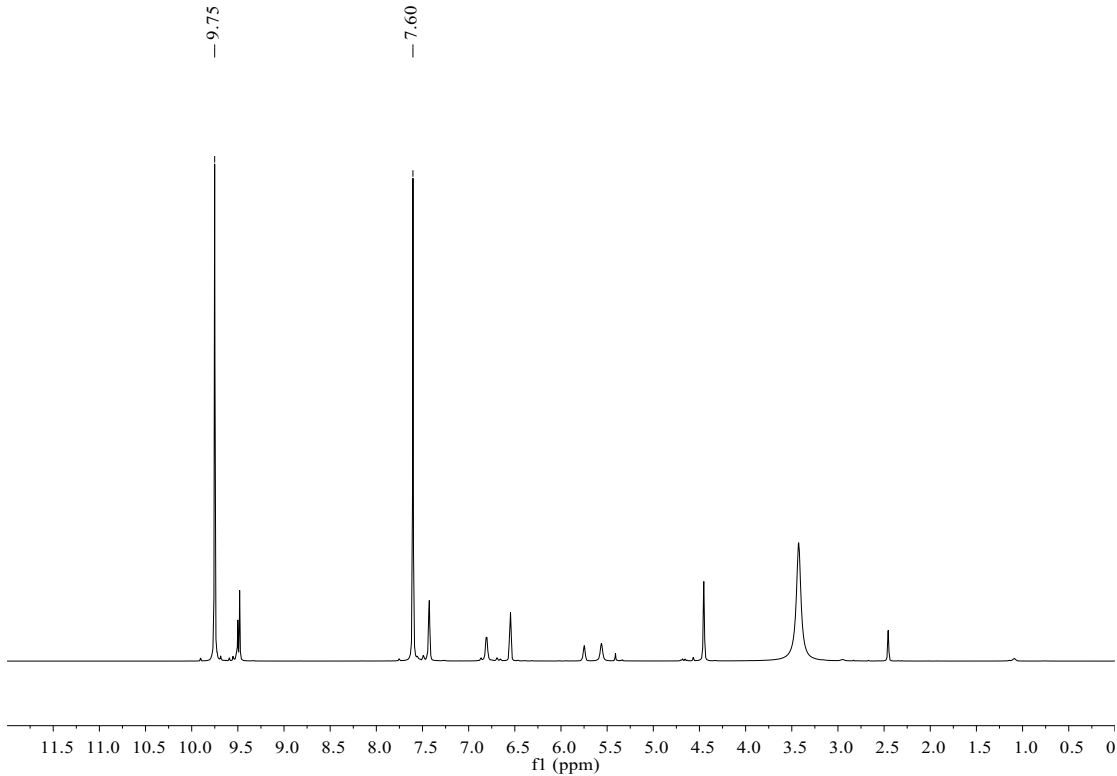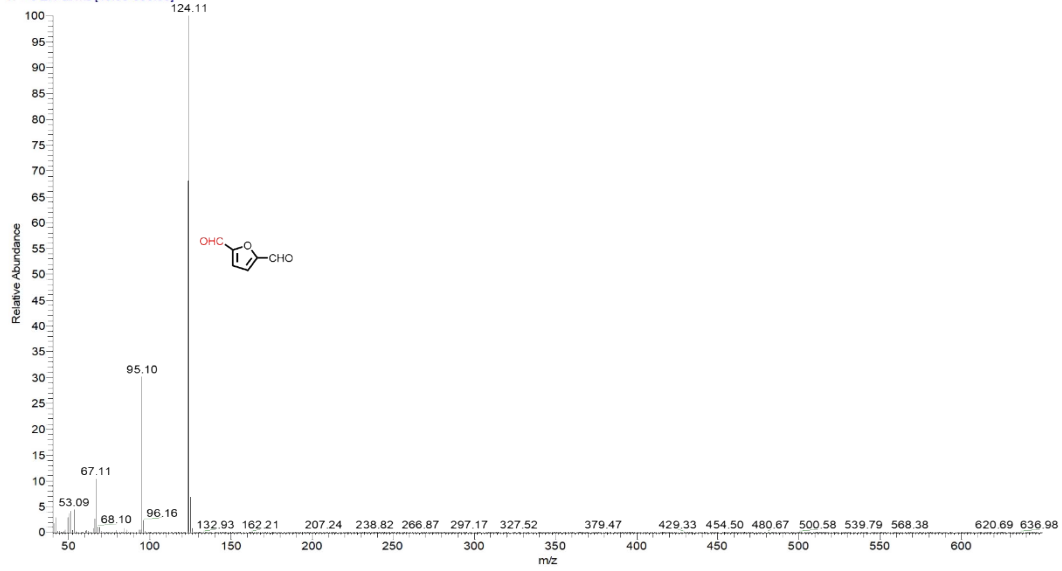
2, 5-Diformylfuran

HPLC, GC-MS, and ^{1}H NMR spectrogram of 2, 5-diformylfuran
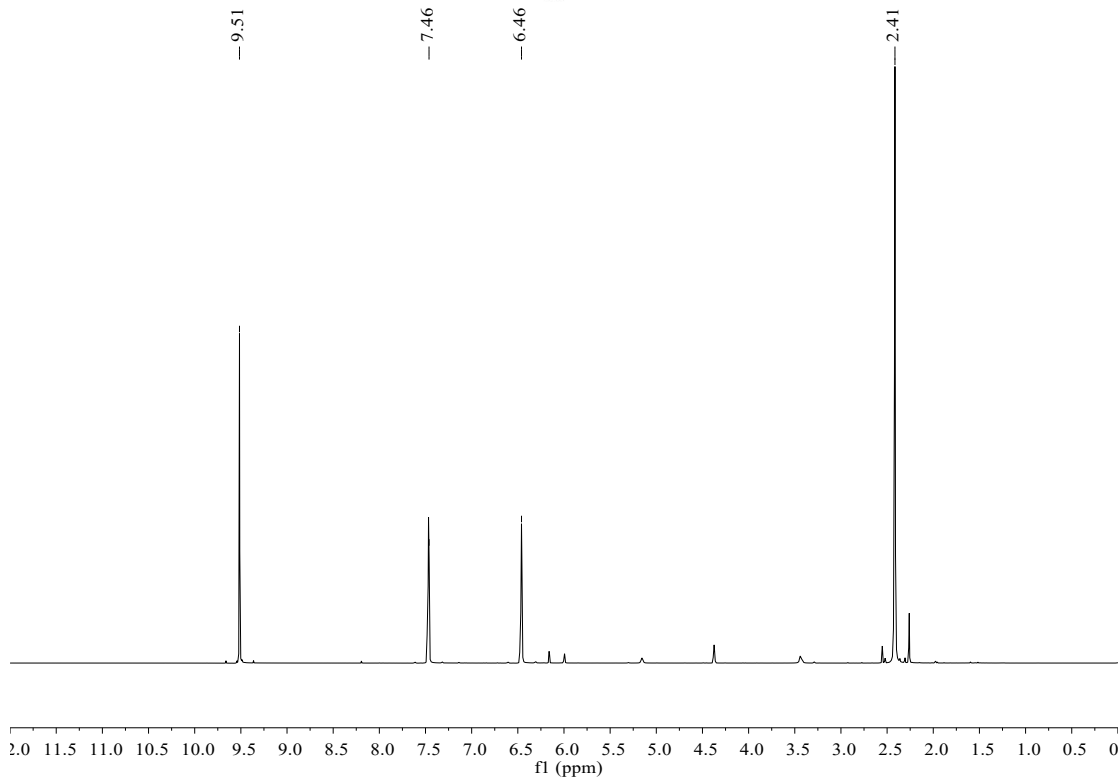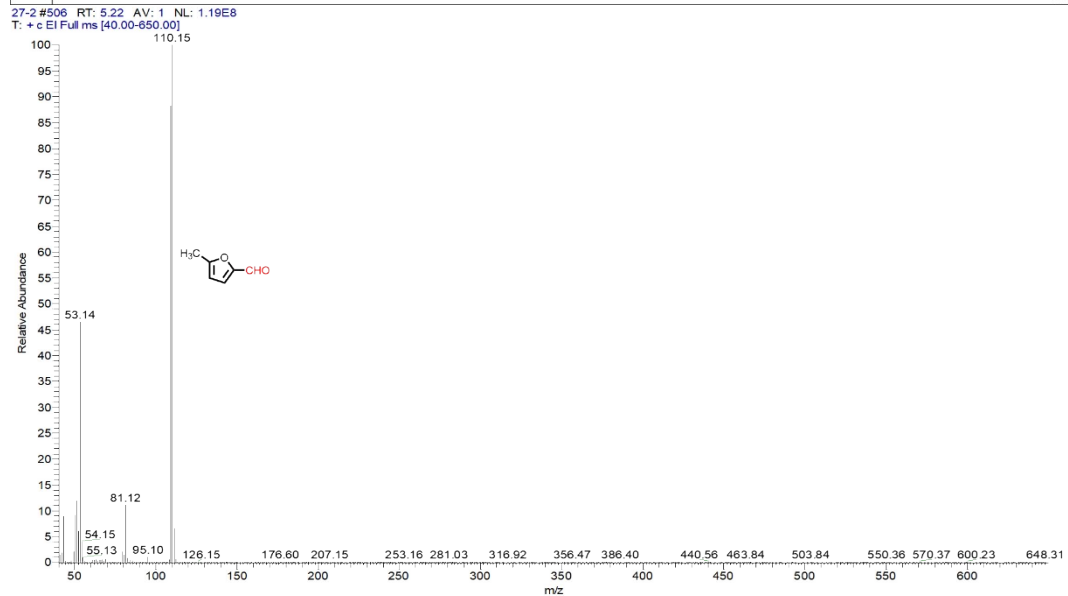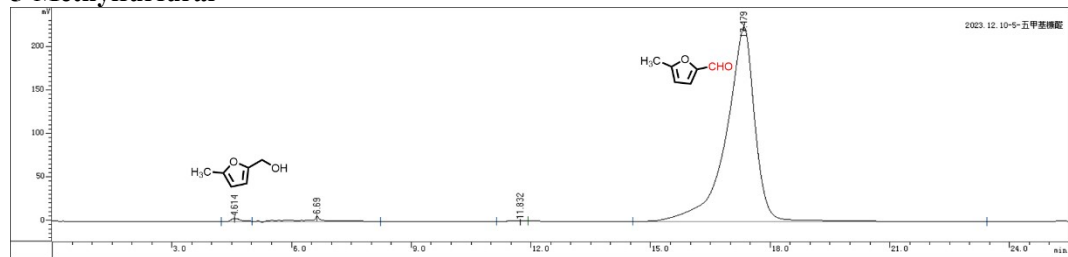
5-Methylfurfural

HPLC, GC-MS, and ¹H NMR spectrogram of 5-methylfurfural

5-Formyl-2-Furoic Acid
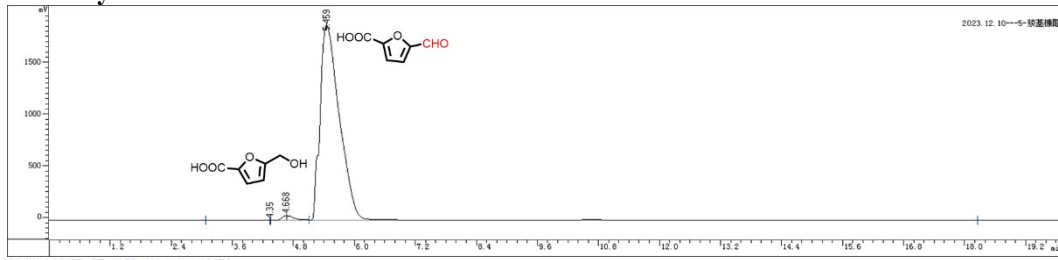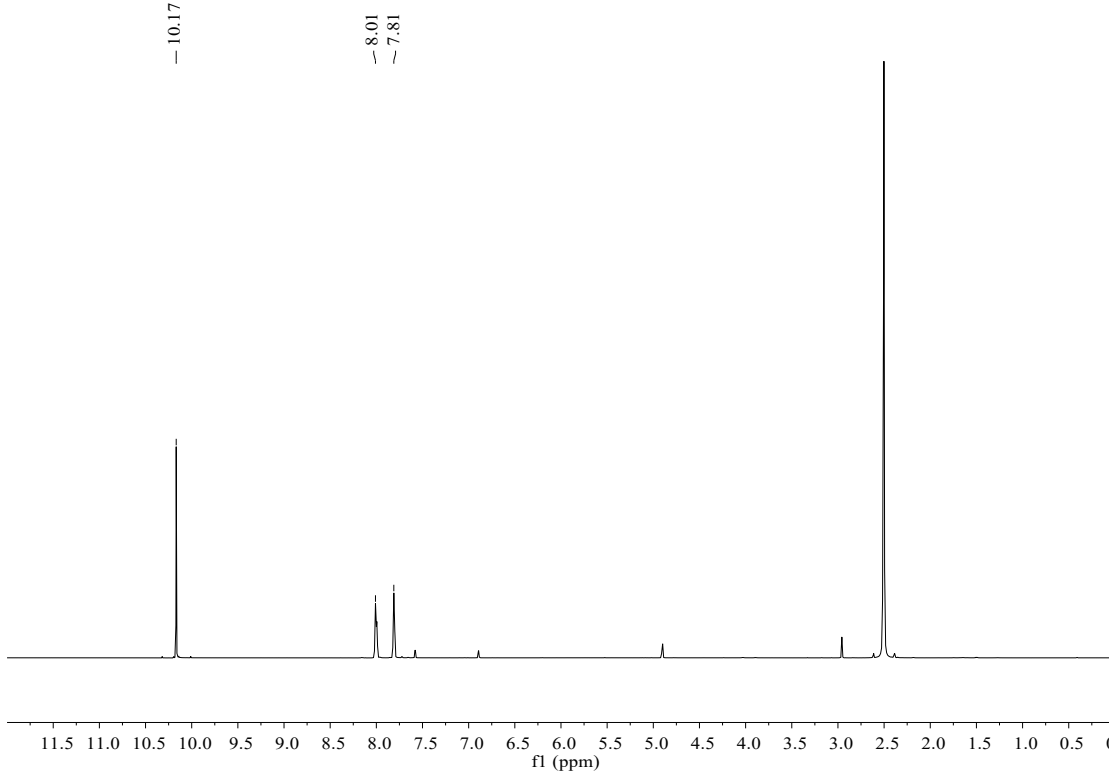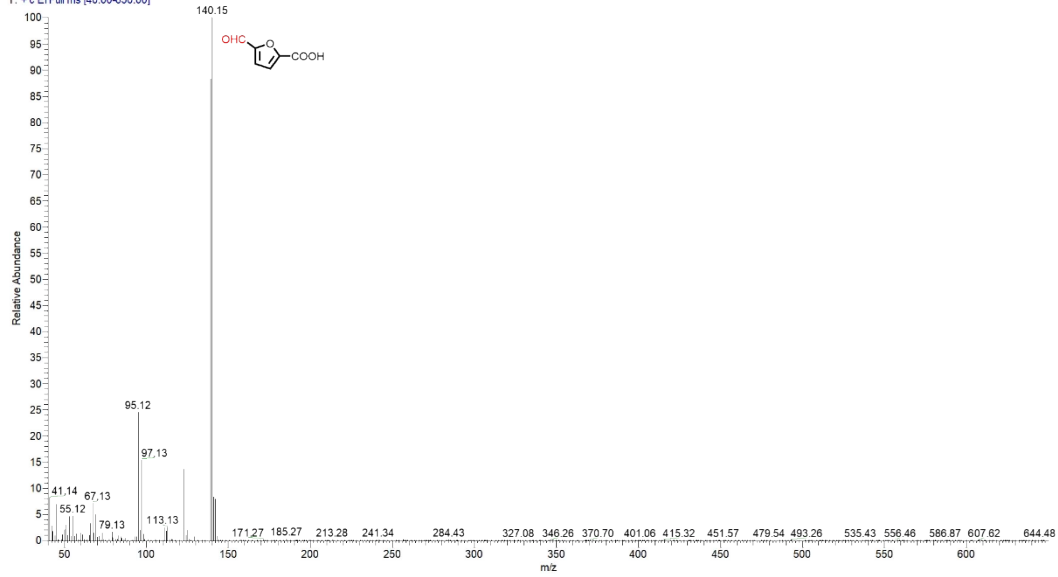
HPLC, GC-MS, and ¹H NMR spectrogram of 5-formylfuran-2-carboxylicacid

2-Thiophene formaldehyde
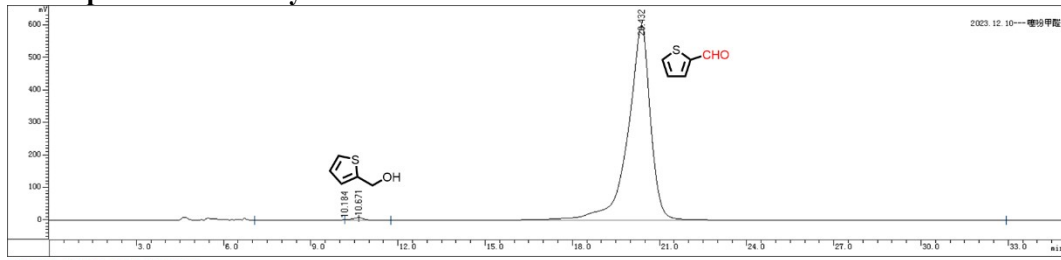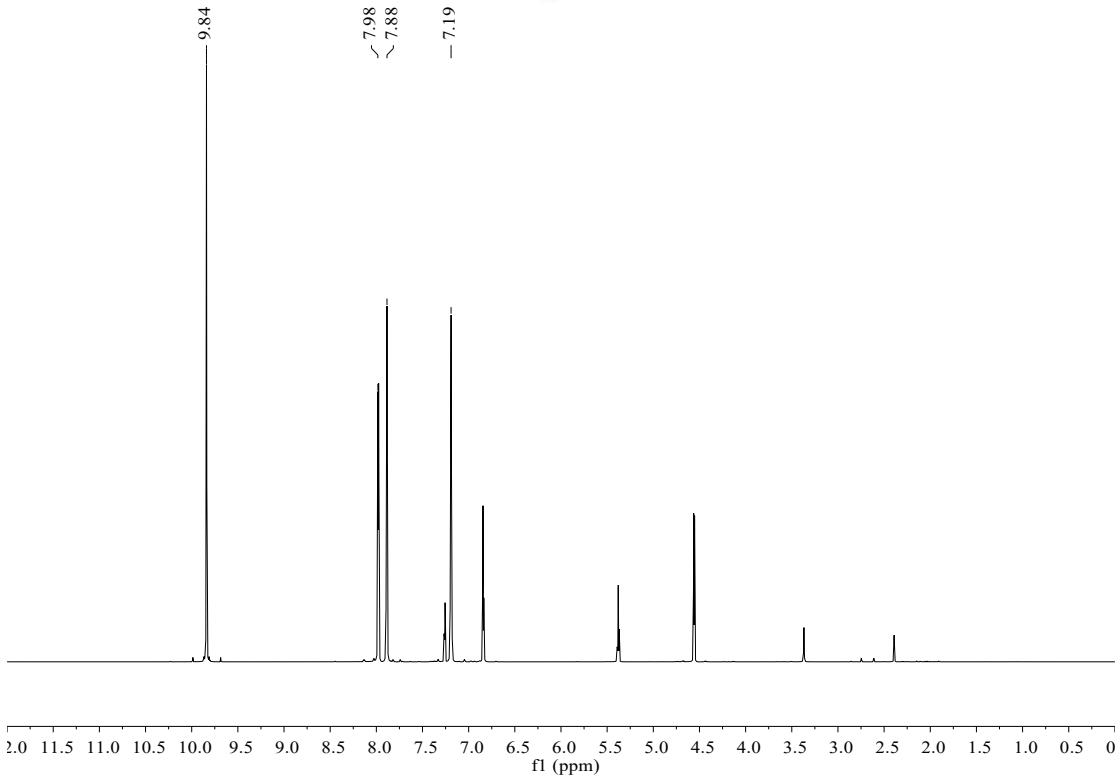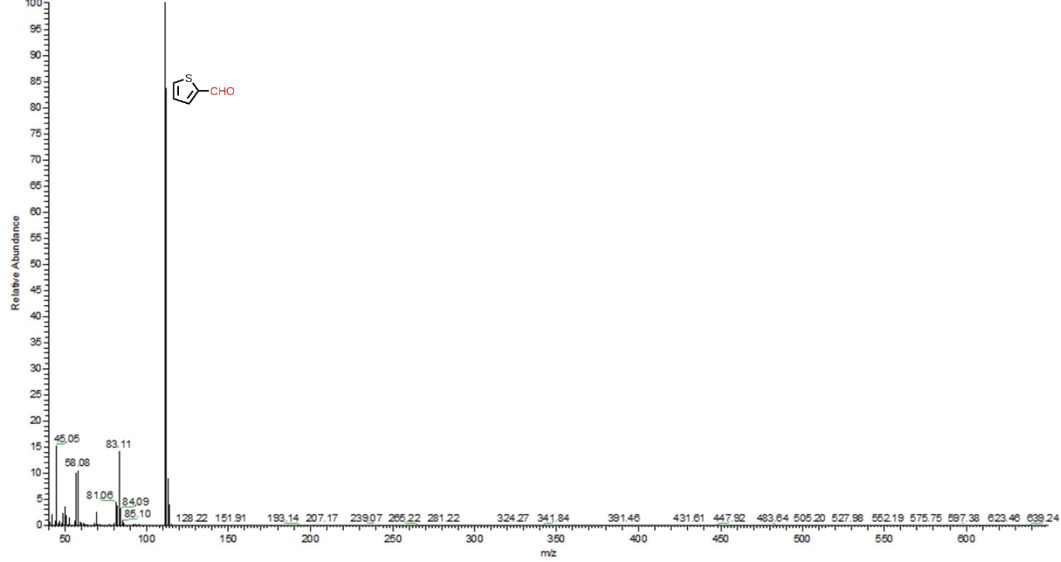
HPLC, GC-MS, and ¹H NMR spectrogram of 2-thiophene formaldehyde

4-Quinoline formaldehyde
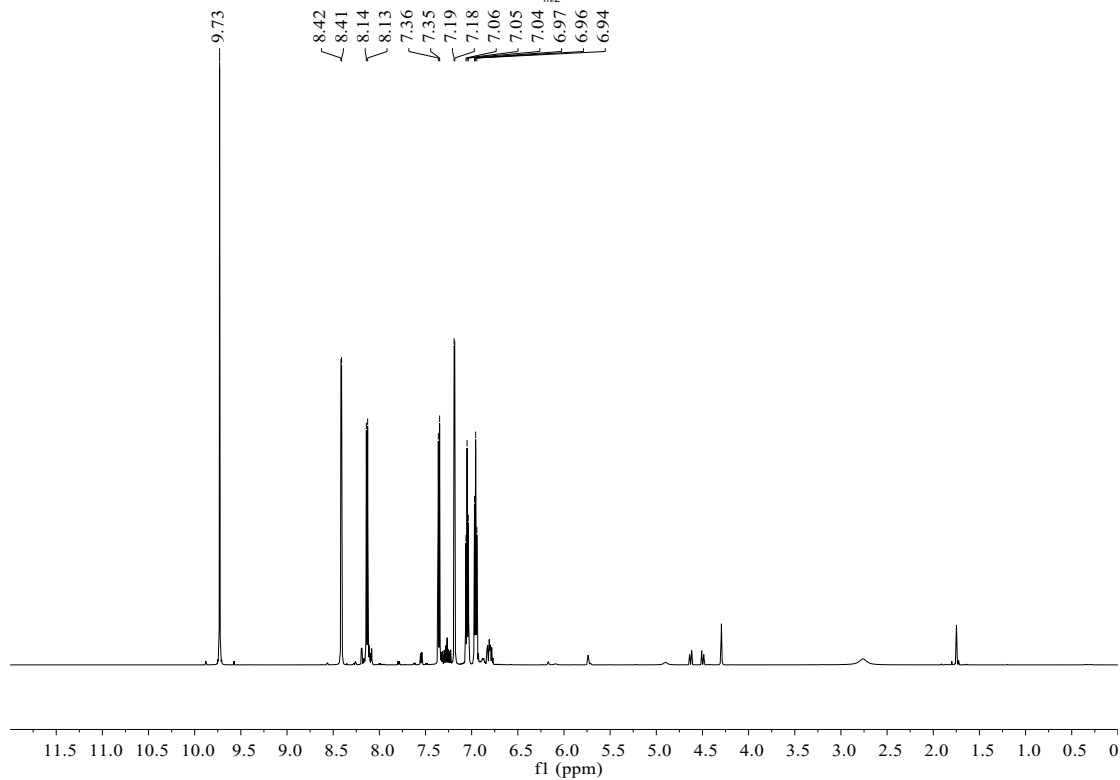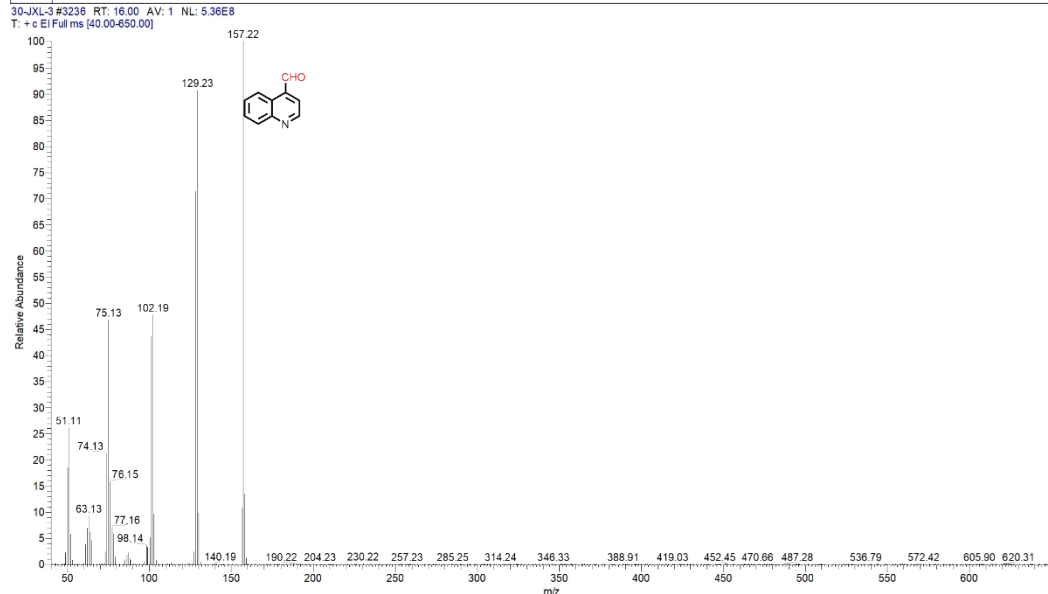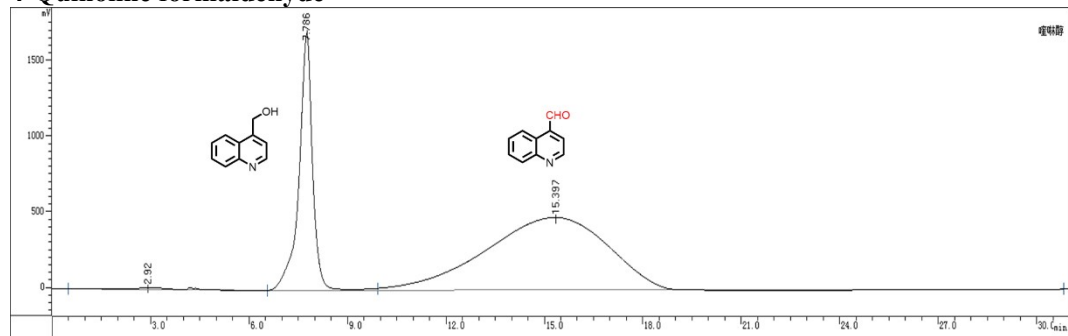
HPLC, GC-MS, and ¹H NMR spectrogram of 4-quinoline formaldehyde

3-Indolecarboxaldehyde
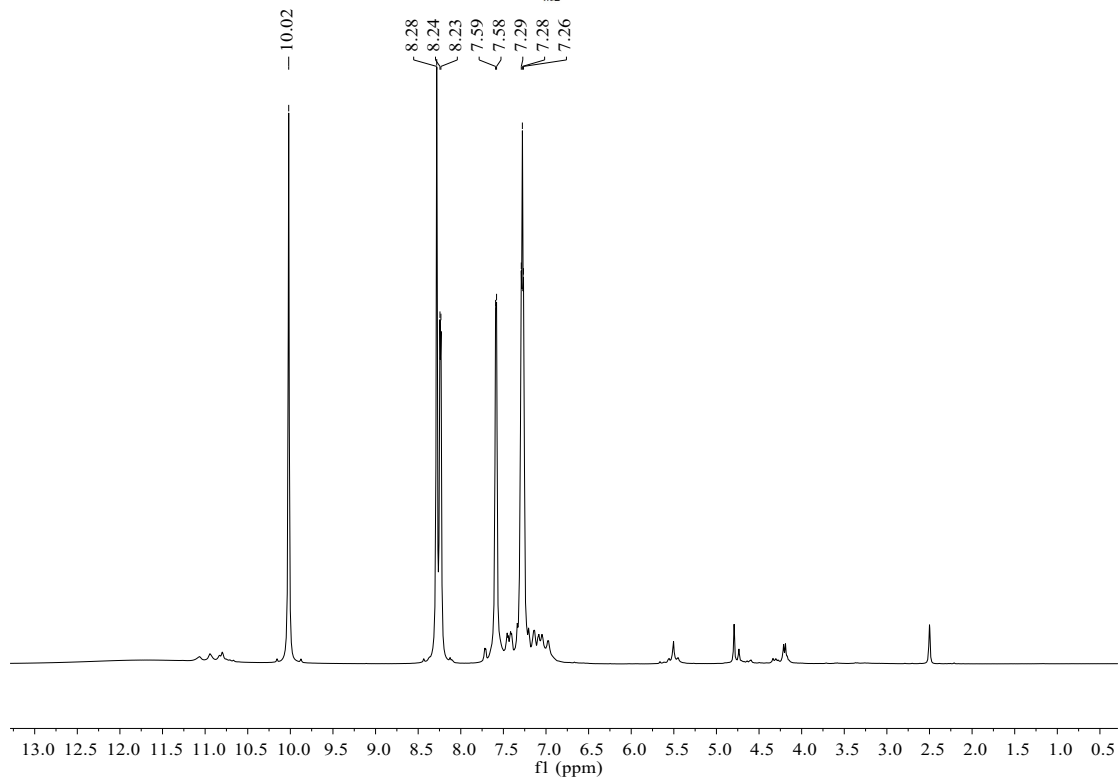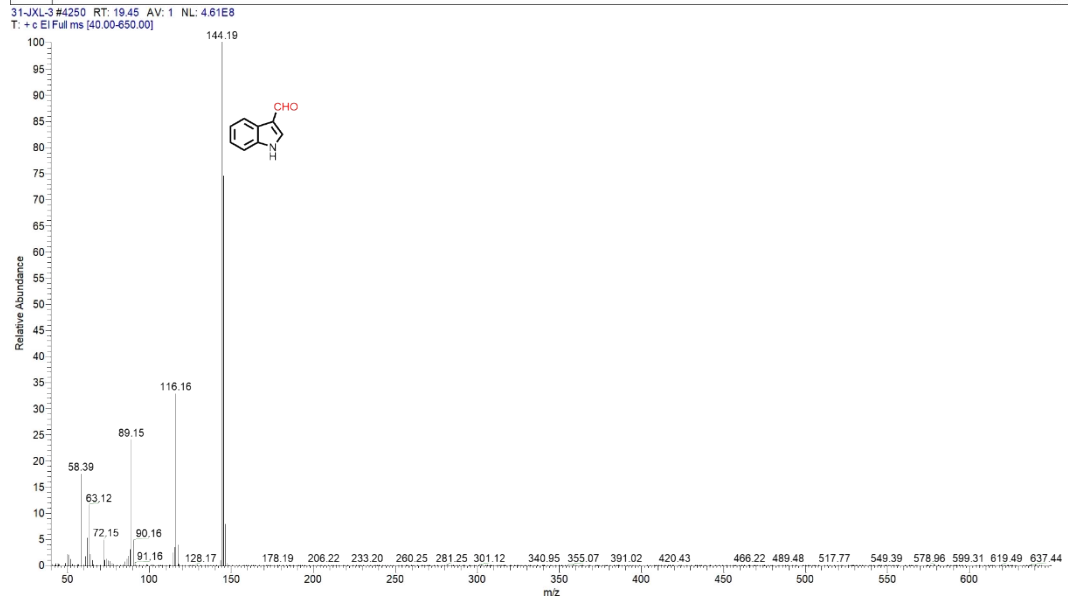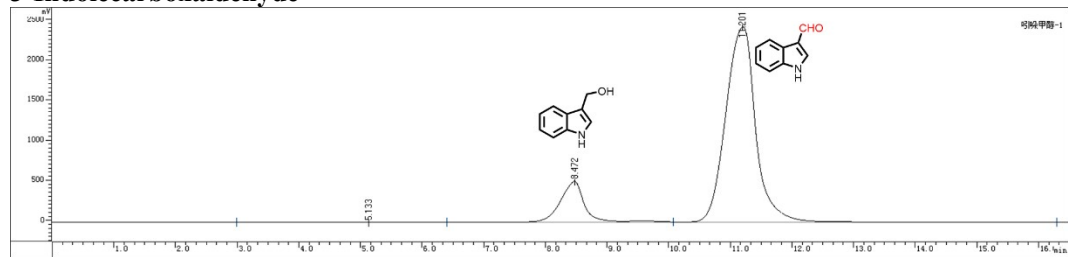
HPLC, GC-MS, and ^{1}H NMR spectrogram of 3-indolecarboxaldehyde

Cyclohexanone

GC, GC-MS, and ¹H NMR spectrogram of cyclohexanone

n- Propionaldehyde

GC, GC-MS, and ¹H NMR spectrogram of n-propionaldehyde

n-Butylaldehyde

GC, GC-MS, and ^{1}H NMR spectrogram of n-butylaldehyde

n- Hexanal

GC, GC-MS, and ¹H NMR spectrogram of n- hexanal

n-Decanal

GC, GC-MS, and ¹H NMR spectrogram of n-decanal