Electronic Supplementary Information

Iron-Catalyzed Aerobic Oxidation of Alcohols in Water Selectively to Carboxylic Acids Mediated by Additives

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[†] Electronic Supplementary Information (ESI) available: experimental conditions, supplementary table and NMR spectra. See DOI: 10.1039/x0xx00000x

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1. General information

All commercially available materials and solvents were used directly without further purification unless otherwise noted. ^1H NMR and ^{13}C NMR data were recorded with a Bruker spectrometer (500 MHz) using TMS as internal standard and reported relative to residual solvent signals as follows: chemical shift (*δ* ppm), multiplicity, coupling constant (Hz), and integration. FT-IR spectra were recorded on a Thermo Fisher Nicolet 6700. XRD were explored on D/max 2200PC of Janpan. GC analyses were performed on Shimadzu GC-2014 with a flame ionization detector equipped with an Rtx-1 capillary column (internal diameter = 0.25 mm, length = 30 m) or a HP-INNOWAX (30*0.25*0.25, length = 30 m). GC mass spectra were recorded on Shimadzu GCMS-QP2010 with RTX-5MS column (0.25 mm× 30 m). Column chromatography was performed using 200-300 mesh silica gel.

CAUTION: The oxygen was used in the reaction, all ignition devices should be removed for that the oxygen can increase the intensity of any fire, including spark, stationary or flame sources, and so on. Pure oxygen inhalation should also be avoided. For more information, see: Cheremisinoff, N. P. *Handbook of Hazardous Chemical Properties*, Butterworth-Heinemann, Woburn, 1999.

2. Preparation of inorganic-ligand supported iron catalyst 1

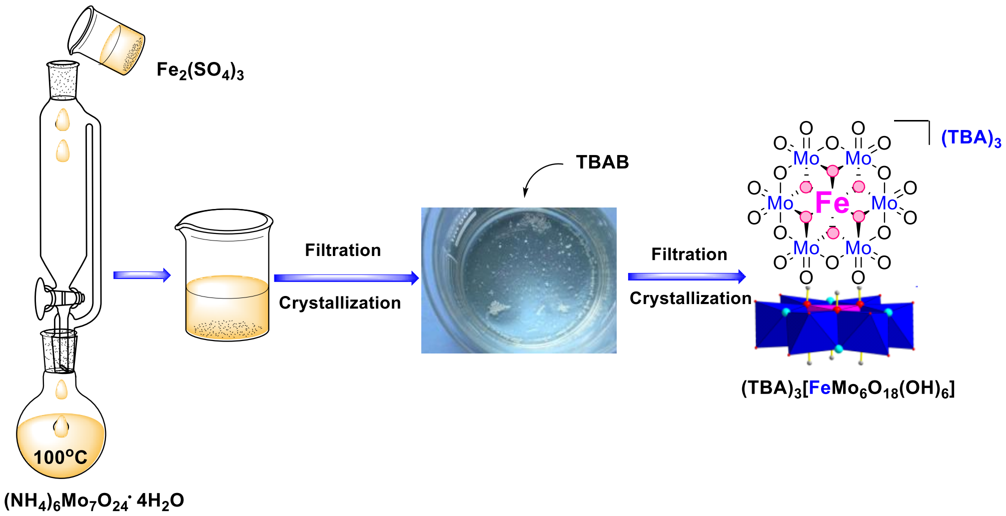


Figure S1. Preparation of $(TBA)_3[FeMo_6O_{18}(OH)_6]$.

$(NH_4)_3[FeMo_6O_{24}H_6]\cdot 7H_2O$ was synthesized according to a modified published procedure[1]: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$(15.9 g) was dissolved in water (250 mL) and then heated to 100 °C. $Fe_2(SO_4)_3$ (3.8 g) was dissolved in water (60 mL), which was slowly added in the solution with stirring. The pH value of the mixture was kept to about 2.5-3.0. The mixture was still stirring 1h after completely adding. Then the crude ammonium salt filtrate obtained from the refluxed solution by heat filtering. The brown block crystals were filtered off after the filtrate stewed for 12 h at room temperature. The light yellow aim product (11.8 g) was collected after recrystallized in hot water (100 °C) for two times.

Preparation of $(TBA)_3FeMo_6O_{18}(OH)_6$: Tetrabutylammonium bromide (TBAB, 2.9 g), $(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$ (2.4 g, 2.0 mmol) were added to 50 mL of H_2O, and heated to 100 °C with stirring for 30 min. Then, a large white solid (3.9 g) appeared by adding 50 mL of acetonitrile after cooling naturally to room temperature, the target product was obtained by suction filtration and drying.

IR: v～max=3401.29 (vas NH, w), 2953.21 (vCH, s), 2782.41 (v CH, s), 1609.32 (w), 1552.24 (δ CH, s), 1486.65 (δ CH, m), 1379.43(w), 959.55 (v Mo=O, s), 929.62 (v Mo=O, s), 857.03 (v Mo=O, s), 669.83 (v Mo-O-Mo, vs), 560.94 (w) cm-1. ^1H NMR (500 MHz, DMSO) δ 7.12 (s, 6H), δ 3.25 (d, 3H),δ 3.15 (t, 24H), 1.61 (m, 24H), 1.28 (m, 24H), 0.95 (t, 36H).

3. FT-IR and XRD spectra of the catalyst

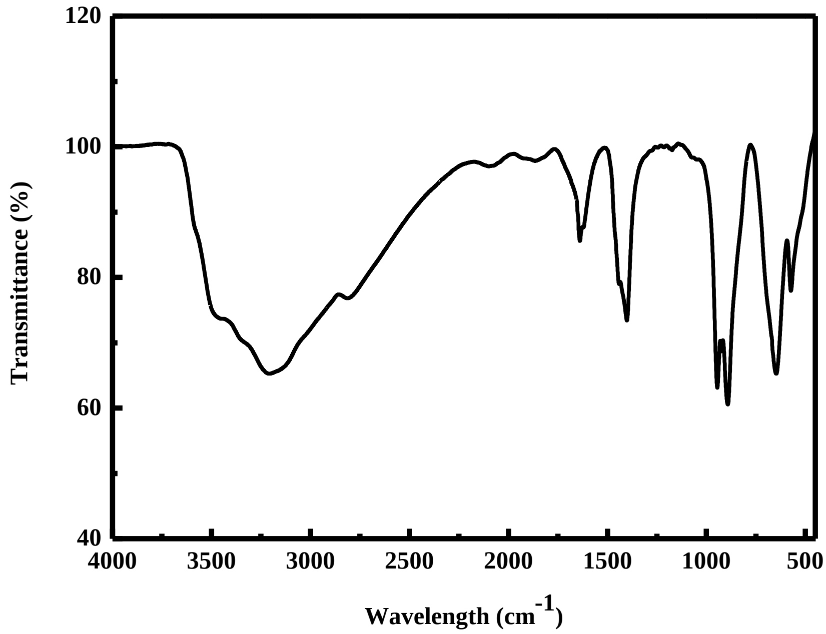


Figure S2. The FT-IR spectra of $(TBA)_3[FeMo_6O_{18}(OH)_6]$.

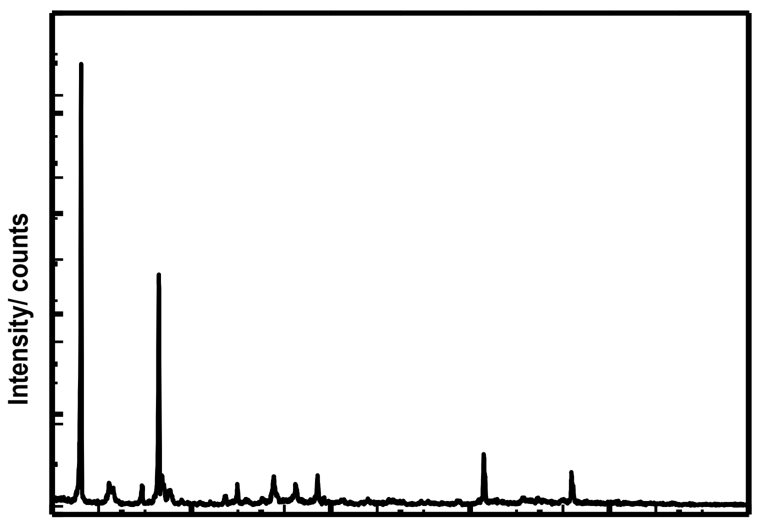


Figure S3. The XRD spectra of$(TBA)_3[FeMo_6O_{18}(OH)_6]$

4. Crystal data, structure refinement and hydrogen bonds for $FeMo_6{\cdot}Cl$

$FeMo_6{\cdot}Cl$ was synthesized according to a modified published procedure [3]: $(TBA)_3[FeMo_6O_{18}(OH)_6]$ (1.800 g, 1.0 mmol) and KCl (0.075 g, 1.0 mmol) was added into 20 mL H_2O and stirred for 30 minutes at 100 °C. Then the large white solid (1.223 g) appeared by adding 20 mL acetonitrile after cooling naturally to room temperature and filtered off.

Table S1. Crystal data and structure refinement for $FeMo_6{\cdot}Cl$

Identification code	$FeMo_6Cl$
CCDC number	1882680
Empirical formula	$C_{64}H_{172}ClFeMo_6N_4O_{35}$
Formula weight	2224.99
Temperature/K	100
Crystal system	orthorhombic
Space group	P*bca*
a/Å	48.6754(12)
b/Å	17.5864(3)
c/Å	23.1423(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	19810.4(7)
Z	8
ρ_{calc}g/cm^3	1.492
μ/mm^{-1}	0.978
F(000)	9272.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.67 to 59.276
Index ranges	-67 ≤ h ≤ 48, -24 ≤ k ≤ 23, -23 ≤ l ≤ 31
Reflections collected	83221
Independent reflections	23470 [R_{int} = 0.0708, R_{sigma} = 0.0827]
Data/restraints/parameters	23470/66/1105
Goodness-of-fit on F^2	1.177
Final R indexes [I>=2σ (I)]	R_1 = 0.0870, wR2 = 0.1479
Final R indexes [all data]	R1 = 0.1193, wR2 = 0.1592
Largest diff. peak/hole / e Å^{-3}	1.10/-1.81

Table S2. Hydrogen bonds for FeMo6·Cl.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O2-H2	0.980	2.313	141.83	3.143	Cl1
O6-H6	0.980	1.749	176.34	2.773	O5W
O1-H1	0.980	2.458	138.35	3.256	Cl1
O4-H4	0.980	2.601	129.67	3.314	O7W
O4-H4	0.980	2.345	129.70	3.065	O8W
O9W-H9WA	0.850	1.937	160.31	2.752	O10W
O9W-H9WB	0.850	1.907	152.77	2.691	O5W
O3-H3	0.980	2.273	143.51	3.116	Cl1
O5W-H5WA	0.849	1.871	176.34	2.719	O6W
O5W-H5WB	0.851	1.944	150.18	2.715	O4W
C50-H50B	0.970	2.539	152.17	3.427	O1W[-x+1/2, y-1/2, z]
O5-H5	0.980	1.776	168.21	2.742	O9W
C9-H9A	0.970	2.617	123.59	3.256	O14
C9-H9B	0.970	2.652	134.01	3.398	O8
O1W-H1WA	0.850	1.966	170.27	2.807	O12
O1W-H1WB	0.851	2.415	161.54	3.234	Cl1
O4W-H4WB	0.850	2.076	151.24	2.850	O23
O7W-H7WA	0.850	1.963	167.95	2.799	O8W
O7W-H1WB	0.850	2.495	121.53	3.028	O24
O7W-H7WB	0.850	2.454	137.72	3.135	O19
O3W-H3WA	0.851	2.570	146.10	3.331	Cl1
O3W-H3WB	0.850	1.915	178.22	2.765	O2W
O8W-H8WA	0.850	1.976	167.51	2.812	O9W
O10W-H10C	0.850	2.005	148.02	2.763	O11W
O10W-H10D	0.848	2.005	155.95	2.802	O21
O11W-H11C	0.850	2.064	168.74	2.903	O10W [-x, -y+1, -z+1]
O11W-H11D	0.850	2.038	161.31	2.856	O20 [-x, -y+1, -z+1]
O2W-H2WA	0.850	2.321	149.97	3.086	O1W
O2W-H2WB	0.850	2.328	161.69	3.146	O17
O2W-H2WB	0.850	2.519	113.23	2.959	O18
O6W-H6WA	0.850	1.941	166.57	2.775	O11

BET Report

BET surface area:	4.9402 ± 0.0802 m²/g
Slope:	0.877888 ± 0.014170 g/cm³ STP
Y-intercept:	0.003156 ± 0.001917 g/cm³ STP
C:	279.178060
Qm:	1.1350 cm³/g STP
Correlation coefficient:	0.9993493
Molecular cross-sectional area:	0.1620 nm²

Relative Pressure (P/Po)	Quantity Adsorbed (cm³/g STP)	1/[Q(Po/P - 1)]
0.056330459	1.0873	0.054902
0.075283944	1.1755	0.069258
0.100350420	1.2395	0.089992
0.125451405	1.2885	0.111330
0.150404865	1.3204	0.134075
0.175287077	1.3546	0.156899
0.200215694	1.3824	0.181095

Started:	2022/7/3 20:52:18	Analysis adsorptive:	N2
Completed:	2022/7/3 23:13:13	Analysis bath temp.:	77.300 K
Report time:	2022/7/4 11:14:23	Thermal correction:	No
Sample mass:	0.1238 g	Ambient free space:	16.7577 cm³ Measured
Analysis free space:	48.5383 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

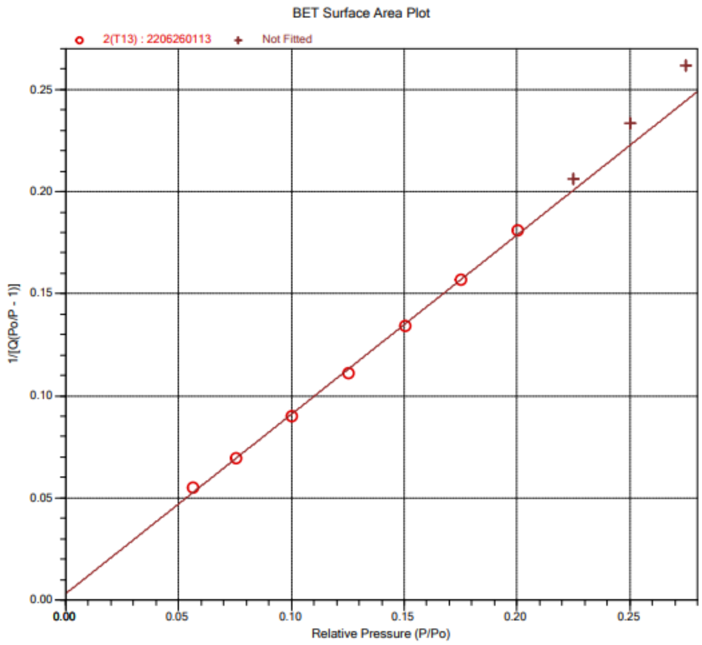


Figure S4 The BET report of $FeMo_6{\cdot}Cl$

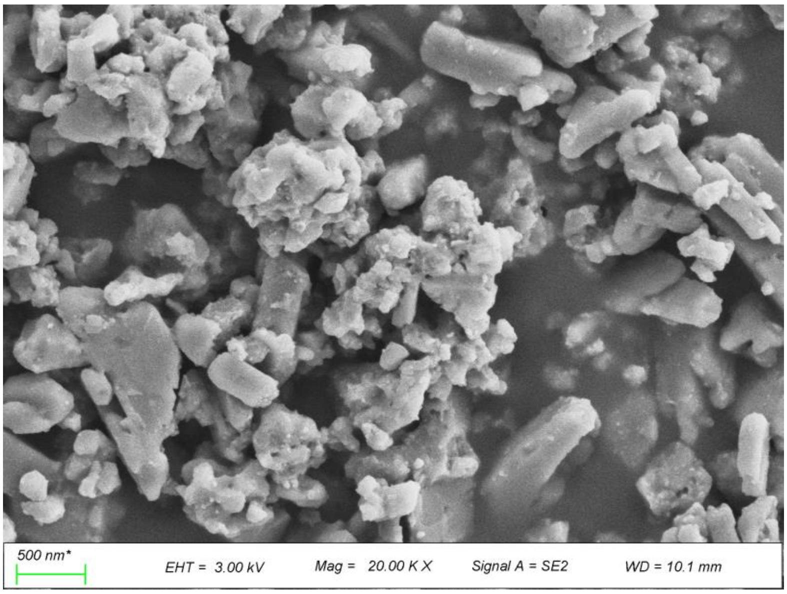


Figure S5 The SEM report of $FeMo_6 \cdot Cl$

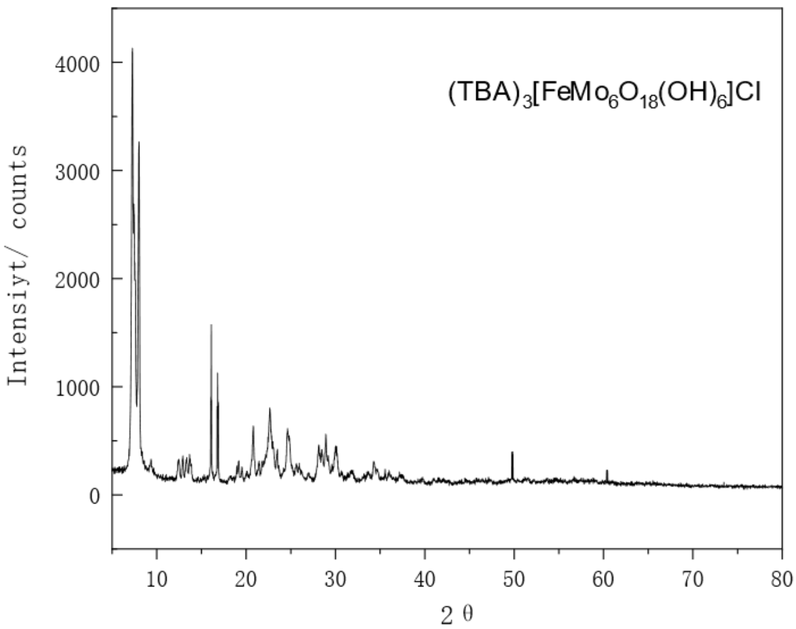


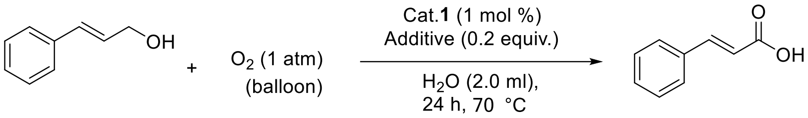
Figure S6 The XRD of $FeMo_6 \cdot Cl$

5. Condition Optimization

General procedure: To a Schlenk tube were added cinnamic alcohol (134.1 mg, 1.0 mmol), Cat. **1** (19.9 mg, 0.01mmol), KCl (14.9 mg, 0.2 mmol), and H_2O (2 mL) sequentially under the atmosphere of oxygen from a O_2 balloon. The Schlenk tube was then stirred at 70 °C until completion of the reaction as monitored by GC (24 h). The crude reaction mixture was extracted with ethyl acetate or ether (7.5 mL). After evaporation, the residue was purified by chromatography on silica gel to afford **2a** (136.3 mg, 92%) (eluent: petroleum ether/ethyl acetate) as a white crystal. The following starting materials **3-41** were conducted according to **General Procedure.**

Cyclic voltammogram: Cyclic voltammograms were obtained at the glassy carbon electrode and a 1.0 mM acetonitrile solution of the $FeMo_6$ in the presence of increasing respectively amounts of KCl, $MgCl_2$, RbCl, NH_4Cl, NaCl, LiCl, KF KBr, and KI at sweep rates of 100 mV s^{-1}.

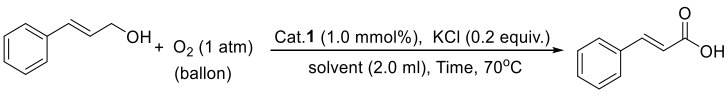
Table S3. The effects of catalyst and additives



Entry[a]	Cat. (mol%)	Additive	Conversion (%)	Yield (%)	Selectivity (%)
1	1	-	<5	n.t.	n.t.
2	1	Na_2SO_4	21	20	95
3[b]	1	Na_2SO_4	7	<3	n.t.
4	1	NaF	41	28	68
5	1	NaCl	33	32	98
6	1	NaBr	33	26	78
7	1	NaI	28	26	70
8	1	$NaNO_2$	0	20	0
9	1	$NaCO_2H$	0	0	0
10	1	Na_2CO_3	0	0	0
11	1	$NaHCO_3$	5	trace	n.t.
12	1	RbCl	17	9	n.t.
13	1	CsCl	27	13	n.t.
14	1	$CaCl_2$	12	7	n.t.
15	1	$MgCl_2$	0	0	0
16	1	$ZnCl_2$	6	trace	n.t.
17	1	LiCl	35	19	54
18	1	NH_4Cl	46	30	65
19	**1**	**KCl**	**>99**	**96**	**97**
20	0.5	KCl	93	88	95
21	2	KCl	>99	91	96
22[c]	1	KCl	96	80	92
23[d]	1	KCl	85	78	92
24	-	KCl	0	0	0
25	$Fe_2(SO_4)_3 \cdot 9H_2O$	KCl	0	0	0
26	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	KCl	0	0	0
27[e]	1	KCl	10	9	90
28	1	KF	66	48	72
29	1	KBr	59	40	68
30	1	KI	55	39	70

[a]Reaction conditions: cinnamic alcohol (1 mmol), **1** (1 mol%), additive (20 mol%), O_2 (1.0 atm, balloon), H_2O (2.0 mL), 70 °C, yields and selectivity were determined by GC and confirmed by GC-MS. [b]Reaction was carried out under atmospheric argon. [c]at 60 °C. [d]at 80 °C. [e]at 60 °C and air as oxidant.

Table S4. The effects of solvents and time



Entry[a]	Solvent	Time (h)	Selectivity (%)	Yield (%)
1	Dioxane	24	92	47
2	Toluene	24	95	61
3	DMF	24	97	55
4	MeOH	24	90	74
5	MeCN	24	94	69
6[b]	CH_2Cl_2	24	96	57
7[c]	THF	24	95	42
8[d]	Acetone	24	95	59
9	H_2O	24	99	96
10	MeOH	12	96	78
11	MeOH	30	97	82
12[e]	CH_2Cl_2	30	95	29

[a]Reaction conditions: cinnamic alcohol (1.0 mmol), **1** (1.0 mol%), KCl (0.2 equiv.), O_2 (1.0 atm), Solvent (2.0 mL), 70 °C, yields and selectivity were determined by GC and confirmed by GC-MS. [b]at 40 °C. [c]at 60 °C. [d]at 50 °C. [e]at 30 °C, air as oxidant.

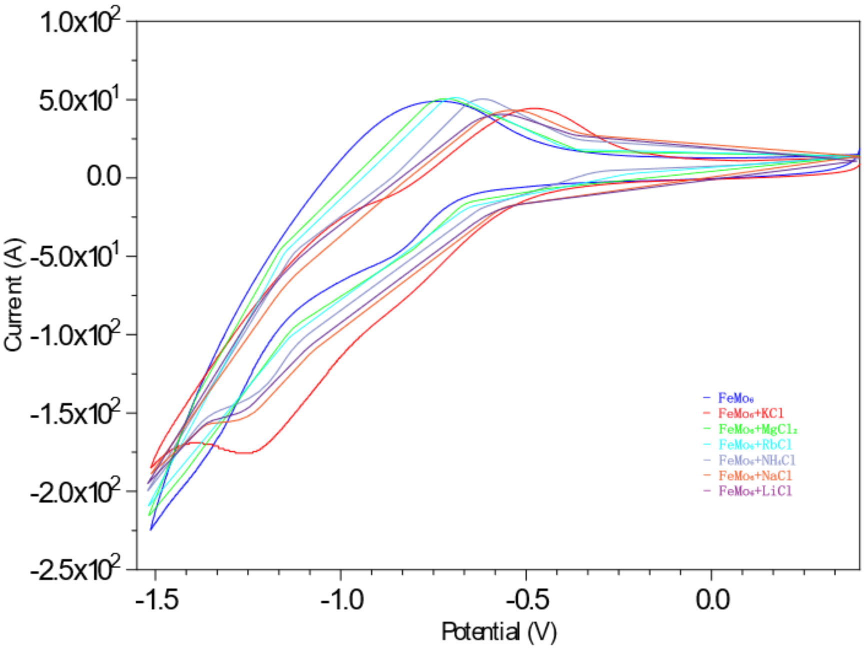


Figure S7. Cyclic voltammogram experiments. Cyclic voltammograms (298 K, scan rate 100mVs^{-1}) of a 1.0 mM acetonitrile solution of the $FeMo_6$ in the presence of KCl $MgCl_2$ RbCl NH_4Cl NaCl and LiCl.

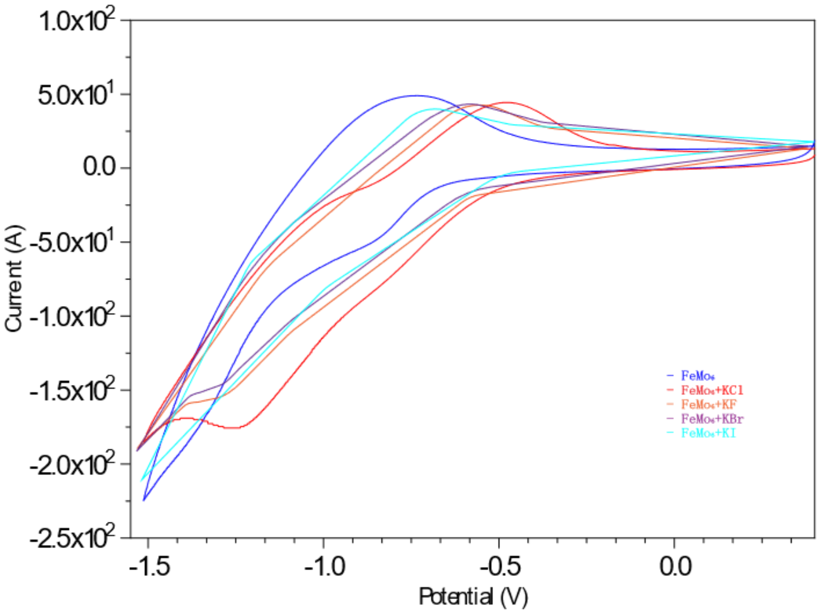


Figure S8. Cyclic voltammogram experiments. Cyclic voltammograms (298 K, scan rate 100mVs^{-1}) of a 1.0 mM acetonitrile solution of the $FeMo_6$ in the presence of KCl KF KBr and KI.

6. Gram-scale reaction

To a 50 mL three-necked bottle were added cinnamic alcohol (1.34 g, 0.01 mol), Cat.**1** (0.20 g, 0.0001mol), KCl (0.15 g, 0.002 mol), and H_2O (20 mL) sequentially under the atmosphere of O_2 from a gas bag with a valve. The three-necked bottle was then stirred at 70 °C until completion of the reaction as monitored by GC (24 h). The crude reaction mixture was extracted with ethyl acetate (3*20 mL). After evaporation, the residue was purified by recrystallization (water/ethanol = 3/1) to afford 2a (1.36 g, 92%) as a white crystal.

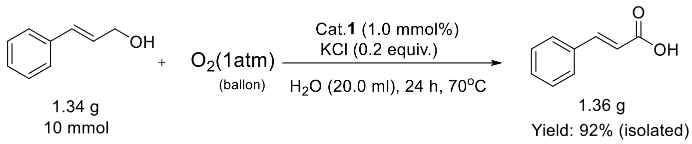


Figure S9. Gram-scale reaction of the catalyst.

7. Recycling experiments of the catalyst

The $Fe^{III}Mo_6$ catalyst was precipitated by adding ethyl acetate or anhydrous ether to the reaction system after the oxidative experiments, and then recovered for reuse. The recovered catalyst was characterized by FT-IR and XRD.

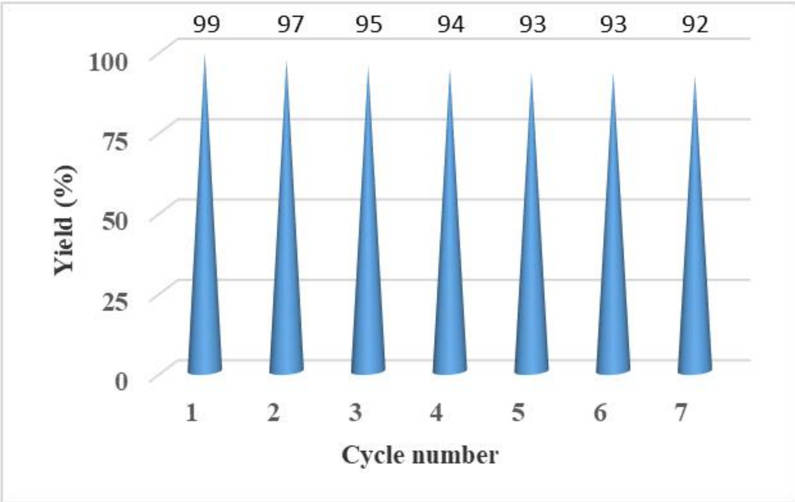


Figure S10. Recycling experiments of the catalyst.

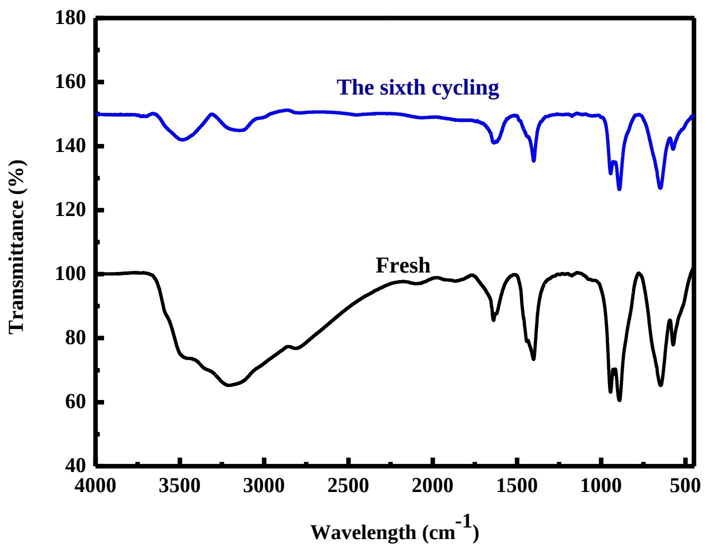


Figure S11. The FT-IR spectra of the catalyst before and after the reaction.

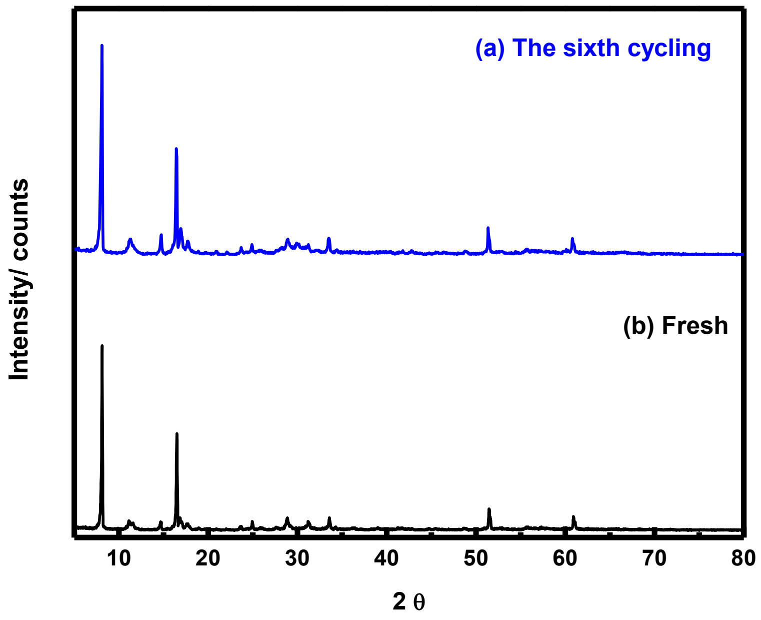


Figure S12. The XRD spectra of the catalyst before and after the reaction.

8. The [1]H NMR studies for tracking the oxidation process

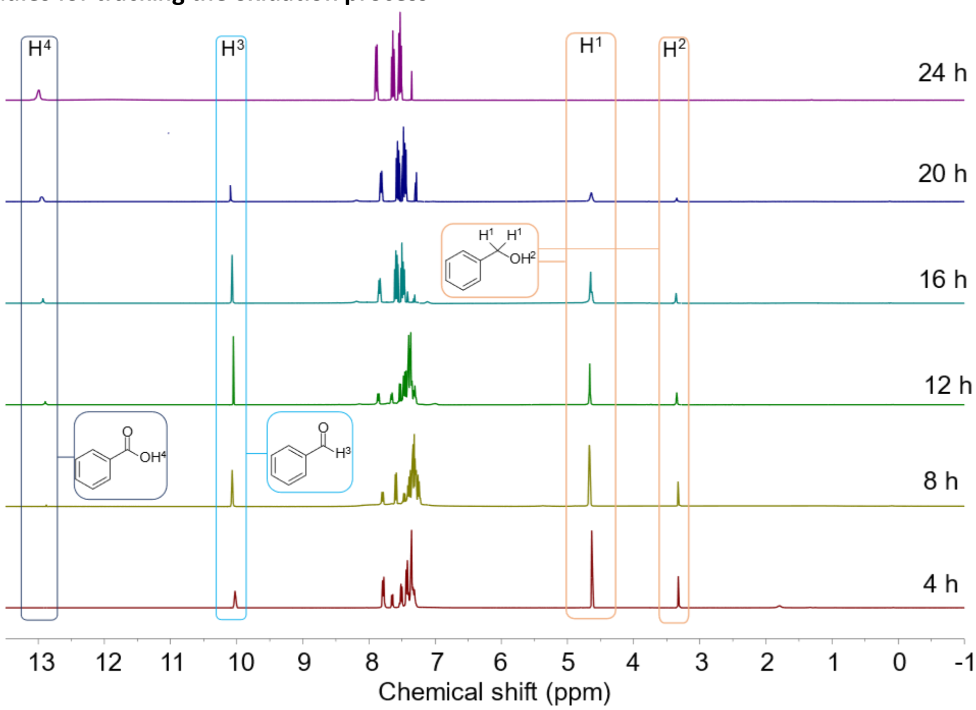


Figure S13. [1]H NMR spectra of the reaction mixture at different time points.

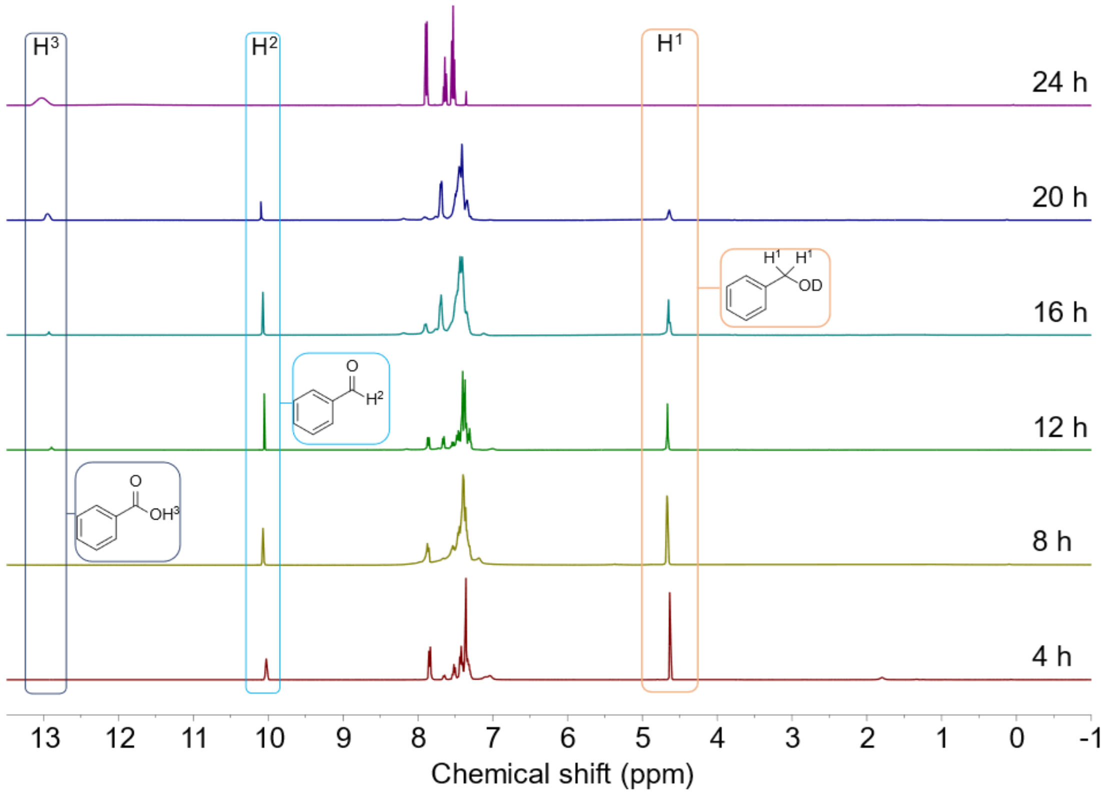


Figure S14. ^{1}H NMR Tracing of d_1-benzyl alcohol

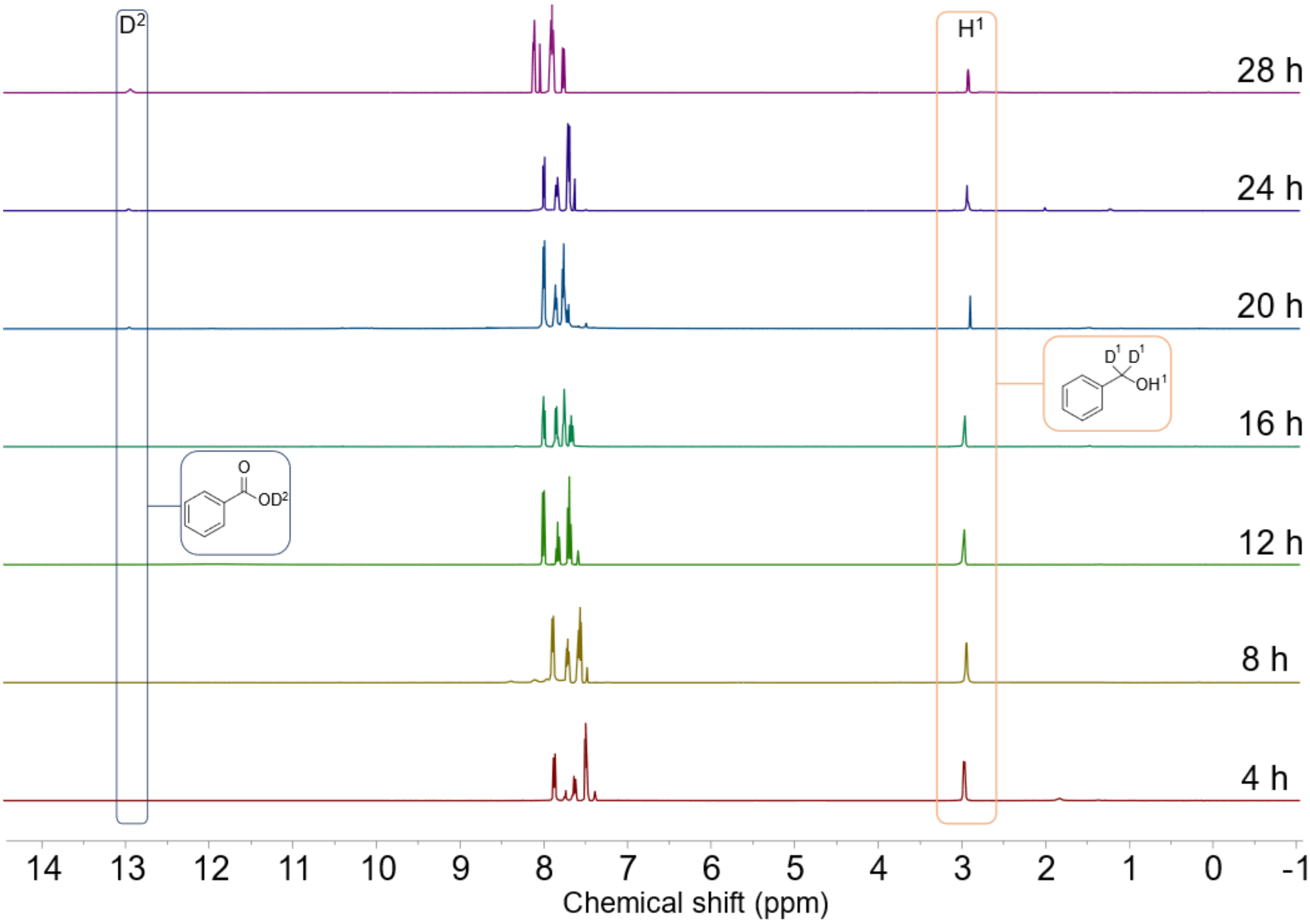


Figure S15. ^{1}H NMR tracing of d_2-benzyl alcohol (4-28 h)

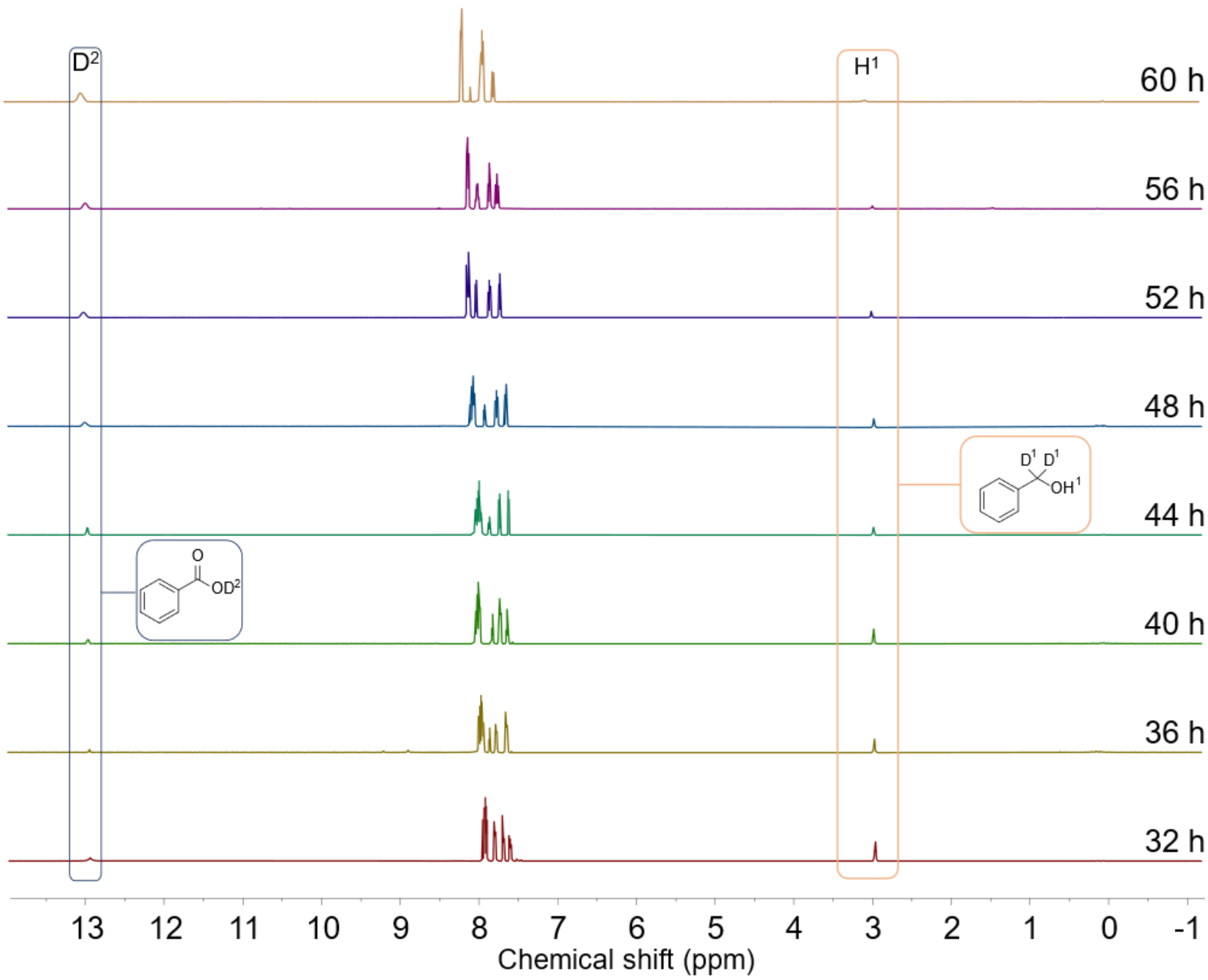


Figure S16. ^{1}H NMR tracing of d_2-benzyl alcohol (32-60 h)

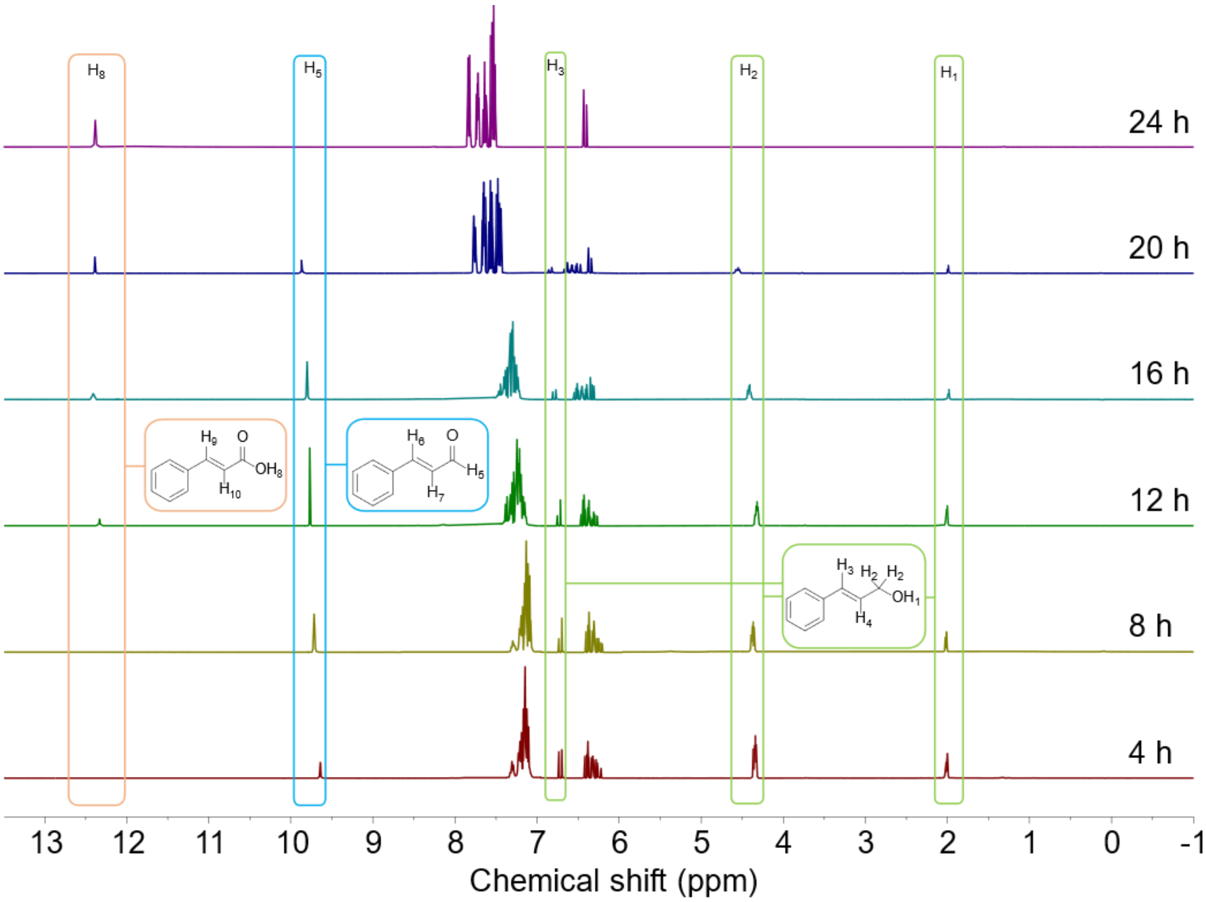


Figure S17. ^{1}H NMR tracing of cinnamyl alcohol

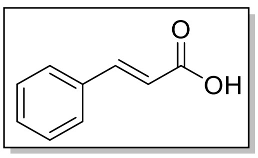
9. Computational details

All DFT calculations were performed by using B3LYP-D3 hybrid functional[4] in Gaussian 09 program package.[5] The solvent effect was modeled with the conductor-like polarizable continuum model (CPCM) in water.[6] The basis sets LANL2DZ[7] and 6-31G(d, p)[8] were applied for metal atoms (Fe, Mo) and non-metal atoms (H, C, O, Cl), respectively. On the basis of optimized structure, the single-point energy was obtained at B3LYP-D3/6-311+G(d,p)/SDD level.

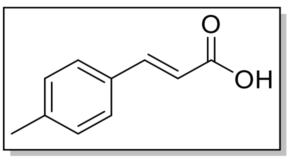
Table S5. The frontier molecular orbital energy levels of **I** (eV).

	LUMO	LUMO+1	LUMO+2
α spin	-2.19	-2.18	-2.06
β spin	-3.39	-3.29	-3.29

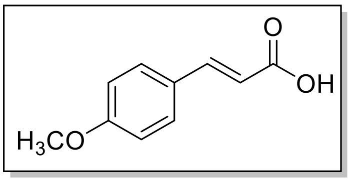
10. NMR data of products



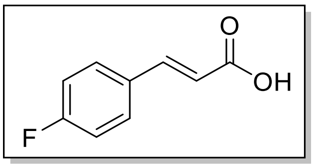
Cinnamic acid (2)[9]: White crystal. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.25 (s, 1H), δ 7.83 (d, *J* = 16.0 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.47 – 7.42 (m, 3H), 6.49 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.44 (s), 147.14 (s), 134.05 (s), 130.79 (s), 128.99 (s), 128.40 (s), 117.31 (s).



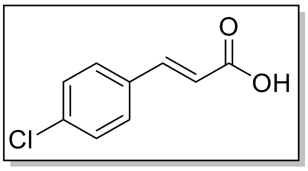
4-Methylcinnamic acid (3) [9]: White powder. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 12.27 (s, 1H), 7.55 – 7.48 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 6.42 (d, J = 16.0 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 168.20 (s), 144.45 (s), 140.66 (s), 132.03 (s), 130.03 (s), 128.71 (s), 118.62 (s), 21.53 (s).



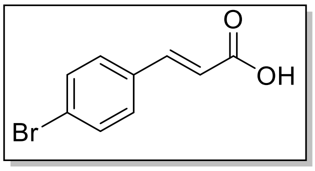
4-methoxycinnamic acid (4) [9]: White powder. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 12.18 (s, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 16.0 Hz, 1H), 6.93 (d, J = 8.7 Hz, 2H), 6.34 (d, J = 16.0 Hz, 1H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 168.36 (s), 161.46 (s), 144.27 (s), 130.46 (s), 127.35 (s), 117.02 (s), 114.87 (s), 55.83 (s).



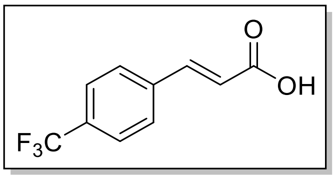
4-fluorocinnamic acid (5) [9]: White crystal. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 12.35 (s, 1H), 7.72 (dd, J = 8.7, 5.6 Hz, 2H), 7.55 (d, J = 16.0 Hz, 1H), 7.20 (t, J = 8.8 Hz, 2H), 6.45 (d, J = 16.0 Hz, 1H).**^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 168.04 (s), 162.44 (d, J = 246.98 Hz), 143.22 (s), 131.42 (s), 130.98 (s), 119.63 (s), 116.50 (s).



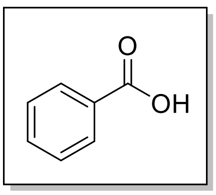
4-chlorocinnamic acid (6) [9]: Colorless crystal. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 12.43 (s, 1H), 7.69 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 16.0 Hz, 1H), 7.43 (d, J = 8.5 Hz, 2H), 6.52 (d, J = 16.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 167.95 (s), 143.04 (s), 135.23 (s), 133.75 (s), 130.47 (s), 129.45 (s), 120.61 (s).



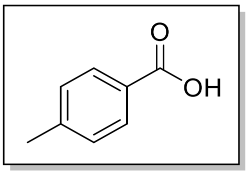
4-bromocinnamic acid (7) [9]: White crystal. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 7.57 (dt, J = 19.6, 12.3 Hz, 5H), 6.53 (d, J = 16.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 167.94 (s), 143.13 (s), 134.07 (s), 132.38 (s), 130.68 (s), 124.05 (s), 120.67 (s).



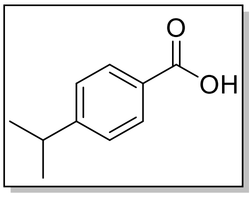
4-(trifluoromethyl)cinnamic acid (8) [9]: White powder. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 12.61 (s, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 16.1 Hz, 1H), 6.64 (d, J = 16.1 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 167.73 (s), 142.59 (s), 138.79 (s), 130.51 (s), 129.33 (s), 126.18 (d, J = 3.7 Hz), 122.68 (s).



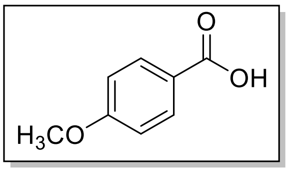
Benzoic acid (9) [9]: White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.04 (d, J = 7.8 Hz, 2H), 9.57 (d, J = 3.1 Hz, 1H), 9.43 (d, J = 2.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.90 (s), 135.88 (s), 132.07 (s), 131.23 (s), 130.54 (s).



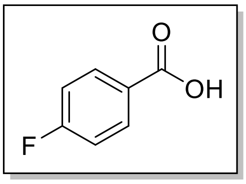
p-Toluic acid (10) [9]: White powder. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.75 (s, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.84 (s), 143.52 (s), 129.85 (s), 129.62 (s), 128.55 (s), 21.62 (s).



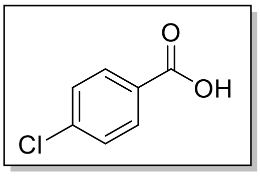
4-Isopropylbenzoic acid (11) [9]: White powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 2.98 (dt, J = 13.8, 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.51 (s), 155.48 (s), 130.50 (s), 126.72 (s), 125.65 (s), 34.44 (s), 23.77 (s).



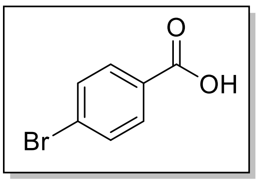
4-Methoxybenzoicacid (12) [9]: White powder. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.59 (s, 1H), 7.85 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.54 (s), 163.36 (s), 131.87 (s), 123.48 (s), 114.33 (s), 55.95 (s).



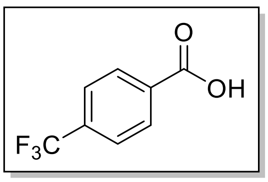
4-Fluorobenzoic acid (13) [9]: White powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 8.9, 5.4 Hz, 2H), 7.14 (t, J = 8.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.89 (d, J = 253.8 Hz), 132.63 (d, J = 9.5 Hz), 116.27 (s), 116.05 (s).



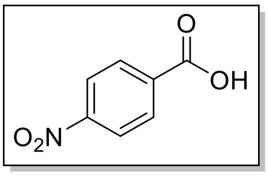
4-chlorobenzoic acid (14) [9]: White powder. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 13.16 (s, 1H), 7.93 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 166.91 (s), 138.25 (s), 131.55 (s), 130.07 (s), 129.10 (s).



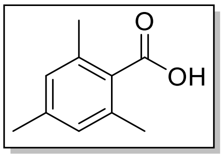
4-bromobenzoic acid (15) [9]: White powder. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 13.19 (s, 1H), 7.85 (s, 2H), 7.71 (s, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 167.07 (s), 132.85 (s), 131.48 (s), 131.13 (s), 130.47 (s).



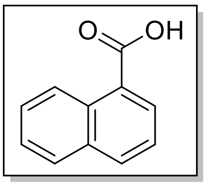
4-(trifluoromethyl)benzoic acid (16) [9]: White powder. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 13.49 (s, 1H), 8.14 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 166.65 (s), 135.05 (s), 132.81 (s), 130.55 (s), 126.05 (s), 125.34 (s).



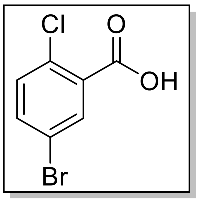
4-nitrobenzoic acid (17) [9]: Light yellow powder. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 13.63 (s, 1H), 8.27 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.34 (s), 150.58 (s), 136.90 (s), 131.24 (s), 124.28 (s).



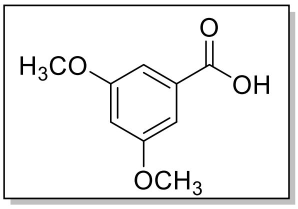
2,4,6-Trimethylbenzoic acid (18) [9]: White powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 (s, 2H), 4.31 (s, 6H), 4.22 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.29 (s), 142.14 (s), 137.89 (s), 131.31 (s), 130.65 (s), 22.86 (s), 21.94 (s).



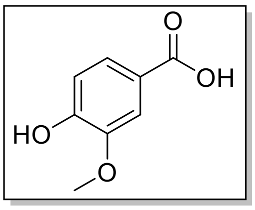
naphthoic acid (19) [9]: Light yellow powder. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 13.05 (s, 1H), 8.58 (s, 1H), 8.10 – 7.93 (m, 4H), 7.64 – 7.52 (m, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.98 (s), 135.46 (s), 132.67 (s), 131.05 (s), 129.80 (s), 128.71 (t, J = 12.7 Hz), 128.18 (s), 127.33 (s), 125.69 (s).



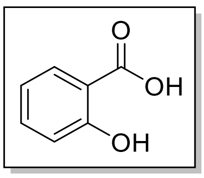
4-bromo-2-chlorobenzoic acid (20) [9]: White powder. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 13.73 (s, 1H), 7.94 (d, J = 2.3 Hz, 1H), 7.74 (dd, J = 8.6, 2.5 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 135.57 (s), 133.86 (s), 133.48 (s), 133.05 (s), 131.33 (s), 120.32 (s).



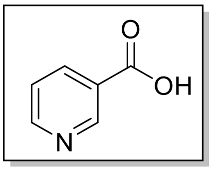
3,5-dimethoxybenzoic acid (21) [9]: White powder. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.94 (s, 1H), 6.97 (d, J = 2.3 Hz, 2H), 6.64 (t, J = 2.2 Hz, 1H), 3.69 (s, 6H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 167.43 (s), 160.83 (s), 133.30 (s), 107.29 (s), 105.33 (s), 55.86 (s).



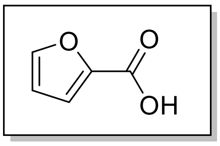
4-hydroxy-3-methoxybenzoic acid (22) [9]: liquid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.45 (s, 1H), 9.80 (s, 1H), 7.42 – 7.36 (m, 2H), 6.80 (d, J = 8.5 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.73 (s), 151.60 (s), 147.72 (s), 123.98 (s), 122.10 (s), 115.53 (s), 113.19 (s), 56.03 (s).



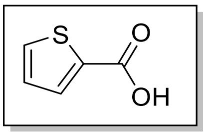
salicylic acid (23) [9]: White solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 13.76 (s, 1H), 11.37 (s, 1H), 7.75 (dd, J = 7.9, 1.7 Hz, 1H), 7.48 – 7.44 (m, 1H), 6.92 – 6.85 (m, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 172.48 (s), 161.68 (s), 136.17 (s), 130.79 (s), 119.69 (s), 117.61 (s), 113.40 (s).



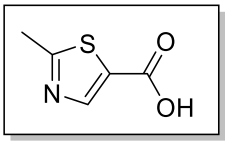
picolinic acid (24) [9]: White powder. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 13.13 (s, 1H), 8.66 (d, J = 4.6 Hz, 1H), 8.01 – 7.92 (m, 2H), 7.58 (ddd, J = 7.5, 4.7, 1.2 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.70 (s), 149.96 (s), 148.86 (s), 138.04 (s), 127.62 (s), 125.18 (s).



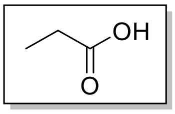
2-furoic acid (25) [9]: Off-white powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 7.66 – 7.61 (m, 1H), 7.35 – 7.30 (m, 1H), 6.55 (dd, J = 3.6, 1.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.73 (s), 147.54 (s), 143.88 (s), 120.28 (s), 112.38 (s).



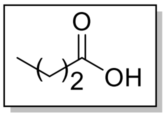
2-thiophenecarboxylic acid(26) [9]: Solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 3.7, 1.2 Hz, 1H), 7.64 (dd, J = 4.9, 1.1 Hz, 1H), 7.14 (dd, J = 4.9, 3.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.74 (s), 135.13 (s), 134.13 (s), 132.92 (s), 128.17 (s).



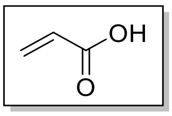
2-methyl-1,3-thiazole-5-carboxylic acid (27) [9]: Solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 13.29 (s, 1H), 8.07 (s, 1H), 2.60 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 172.21 (s), 162.54 (s), 147.99 (s), 130.50 (s), 19.78 (s).



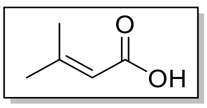
Propionic acid (28) [9]: Colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.83 (s, 1H), 1.61 – 1.45 (m, 2H), 0.91 – 0.77 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.15 (s), 17.88 (s), 13.11 – 12.95 (m).



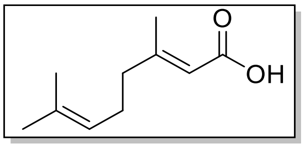
Valeric acid (29) [9]: Colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.60 (s, 1H), 2.13 (td, J = 7.6, 2.4 Hz, 2H), 1.50 – 1.34 (m, 2H), 1.17 (pd, J = 7.5, 2.4 Hz, 2H), 0.72 (td, J = 7.4, 2.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.27 (s), 33.52 (s), 26.54 (s), 21.96 (s), 13.22 (s).



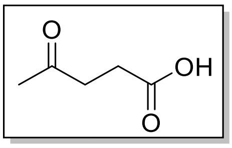
acrylic acid (30) [9]: Clear liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.63 (s, 1H), 6.26 (dd, J = 17.3, 1.2 Hz, 1H), 5.90 (dd, J = 17.3, 10.5 Hz, 1H), 5.71 (dd, J = 10.4, 1.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.34 (s), 132.70 (s), 127.80 (s).



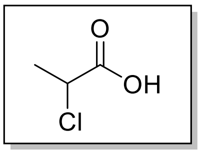
3,3-dimethylacrylic acid (31) [9]: White crystal. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.73 (s, 1H), 5.51 (s, 1H), 1.98 (s, 3H), 1.74 (s, 4H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 167.75 (s), 155.83 (s), 116.93 (s), 27.22 (s), 20.08 (s).



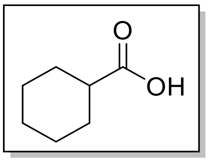
Geranic acid (32) [9]: Solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.84 (s, 1H), 7.62 (d, J = 1.1 Hz, 1H), 7.08 – 6.97 (m, 1H), 4.15 – 4.09 (m, 6H), 3.86 (d, J = 1.3 Hz, 1H), 3.62 (s, 3H), 3.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.64 (s), 165.48 (s), 134.56 (s), 124.82 (s), 117.02 (s), 43.16 (s), 35.63 (s), 28.01 (s), 27.34 (s), 19.35 (s).



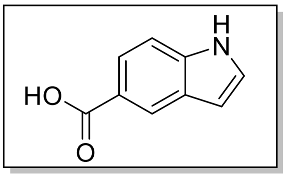
Levulinicacid (33) [9]: Clear yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 2.34 (t, J = 6.5 Hz, 2H), 2.12 (t, J = 6.5 Hz, 2H), 1.73 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.31 (s), 176.96 (s), 37.26 (s), 28.97 (s), 27.32 (s).



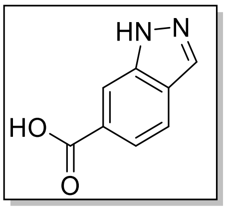
2-chloropropionic acid (34) [9]: Colourless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.13 (s, 1H), 4.30 (q, J = 7.0 Hz, 1H), 1.52 (d, J = 7.1 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.03 (d, J = 1.3 Hz), 52.09 (s), 21.07 (s).



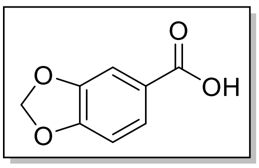
Cyclohexanecarboxylic acid (35) [9]: White solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.20 (s, 1H), 2.26 (d, J = 10.9 Hz, 1H), 1.87 (s, 2H), 1.70 (s, 2H), 1.58 (s, 1H), 1.40 (s, 2H), 1.31 – 1.09 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.82 (s), 42.86 (s), 28.66 (s), 25.65 (s), 25.25 (s).



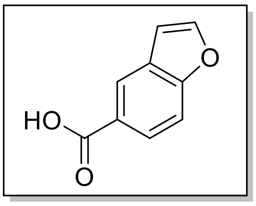
Indole-5-carboxylic acid (36) [9]: Light beige powder. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.38 (s, 1H), 11.43 (s, 1H), 8.24 (d, J = 0.6 Hz, 1H), 7.71 (dd, J = 8.5, 1.5 Hz, 1H), 7.49 – 7.41 (m, 2H), 6.61 – 6.55 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 168.88 (s), 138.78 (s), 127.64 (s), 127.37 (s), 123.26 (s), 122.66 (s), 121.85 (s), 111.55 (s), 102.94 (s).



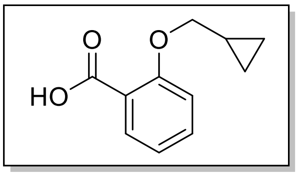
1h-indazole-6-carboxylic acid (37) [9]: White powder. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.38 (s, 1H), 11.43 (s, 1H), 8.24 (d, J = 0.6 Hz, 1H), 7.71 (dd, J = 8.5, 1.5 Hz, 1H), 7.49 – 7.41 (m, 2H), 6.61 – 6.55 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 168.88 (s), 138.78 (s), 127.64 (s), 127.37 (s), 123.26 (s), 122.66 (s), 121.85 (s), 111.55 (s), 102.94 (s).



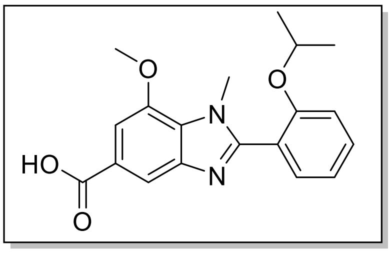
Piperonylic acid (38) [9]: Off-white powder. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.72 (s, 1H), 7.50 (dd, J = 8.1, 1.6 Hz, 1H), 7.32 (d, J = 1.6 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.08 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.15 (s), 151.65 (s), 147.99 (s), 125.48 (s), 109.31 (s), 108.58 (s), 102.46 (s).



1-benzofuran-5-carboxylic acid (39): Solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.78 (s, 1H), 8.21 (d, J = 0.8 Hz, 1H), 8.01 (d, J = 2.0 Hz, 1H), 7.83 (dd, J = 8.6, 1.3 Hz, 1H), 7.59 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 1.4 Hz, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 167.86 (s), 157.15 (s), 147.86 (s), 127.83 (s), 126.27 (d, J = 8.9 Hz), 123.88 (s), 111.74 (s), 107.77 (s).



2-(cyclopropylmethoxy)benzoic acid (40) [9]: Solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.54 (s, 1H), 7.63 (dd, J = 7.6, 1.7 Hz, 1H), 7.50 – 7.39 (m, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 3.89 (d, J = 6.6 Hz, 3H), 1.21 (s, 1H), 0.53 (dd, J = 8.1, 1.8 Hz, 3H), 0.35 (d, J = 6.2 Hz, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 167.91 (s), 157.80 (s), 133.25 (d, J = 3.1 Hz), 130.97 (s), 122.33 (s), 120.57 (s), 114.36 (s), 73.08 (s), 10.47 (s), 3.26 (s).



2-(2-isopropoxyphenyl)-7-methoxy-1-methyl-1H-benzo[d]imidazole-5-carboxylic acid (41) [9]: Solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.67 (s, 1H), 7.79 (s, 1H), 7.44 (t, J = 7.9 Hz, 2H), 7.36 (dd, J = 7.4, 1.2 Hz, 2H), 7.26 (s, 1H), 7.13 (d, J = 8.4 Hz, 1H), 6.99 (t, J = 7.4 Hz, 2H), 4.59 (dt, J = 12.0, 6.0 Hz, 2H), 3.89 (s, 5H), 3.70 (s, 5H), 1.10 (d, J = 6.0 Hz, 10H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 168.26 (s), 155.83 (s), 154.22 (s), 147.05 (s), 144.30 (s), 132.90 (s), 132.24 (s), 128.58 (s), 125.32 (s), 120.90 (s), 114.94 (s), 114.07 (s), 104.53 (s), 79.77 (s), 56.40 (s), 22.10 (s).

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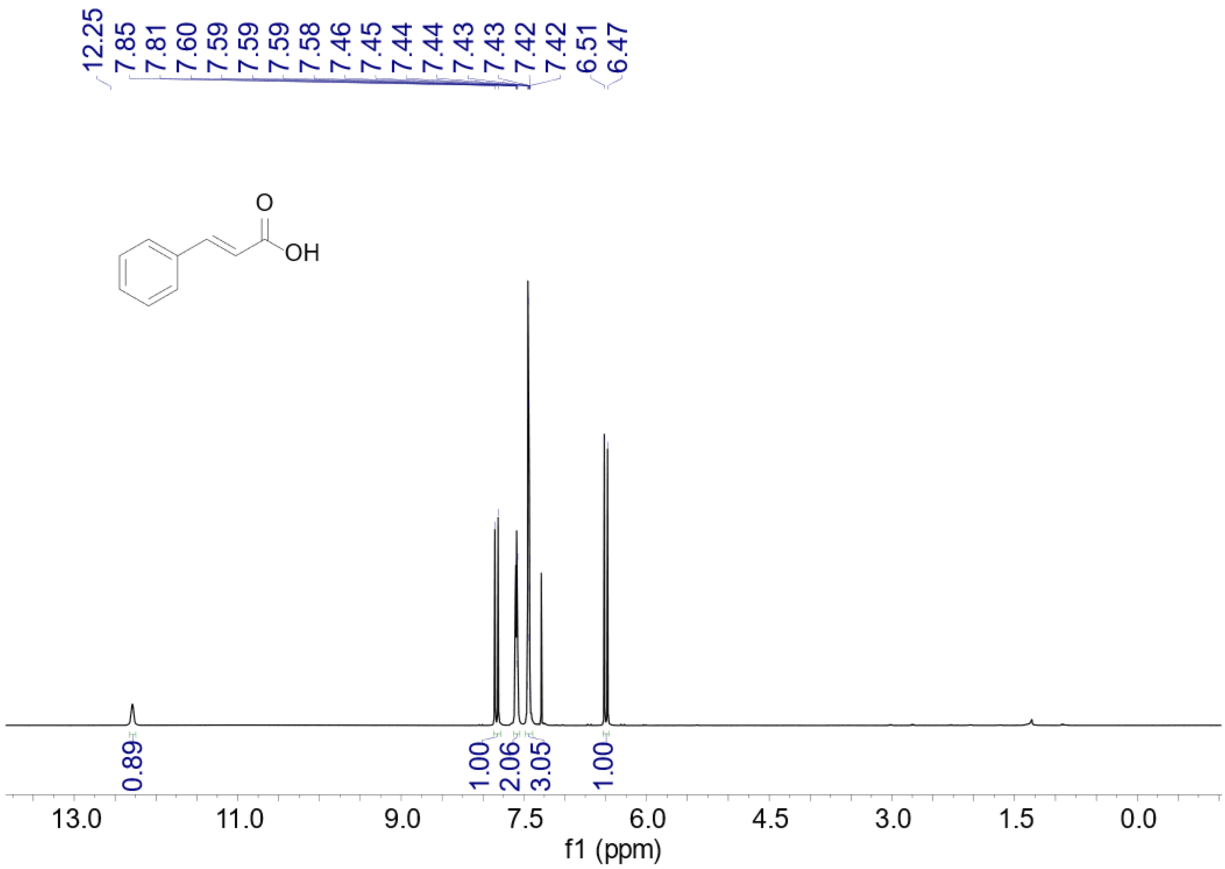
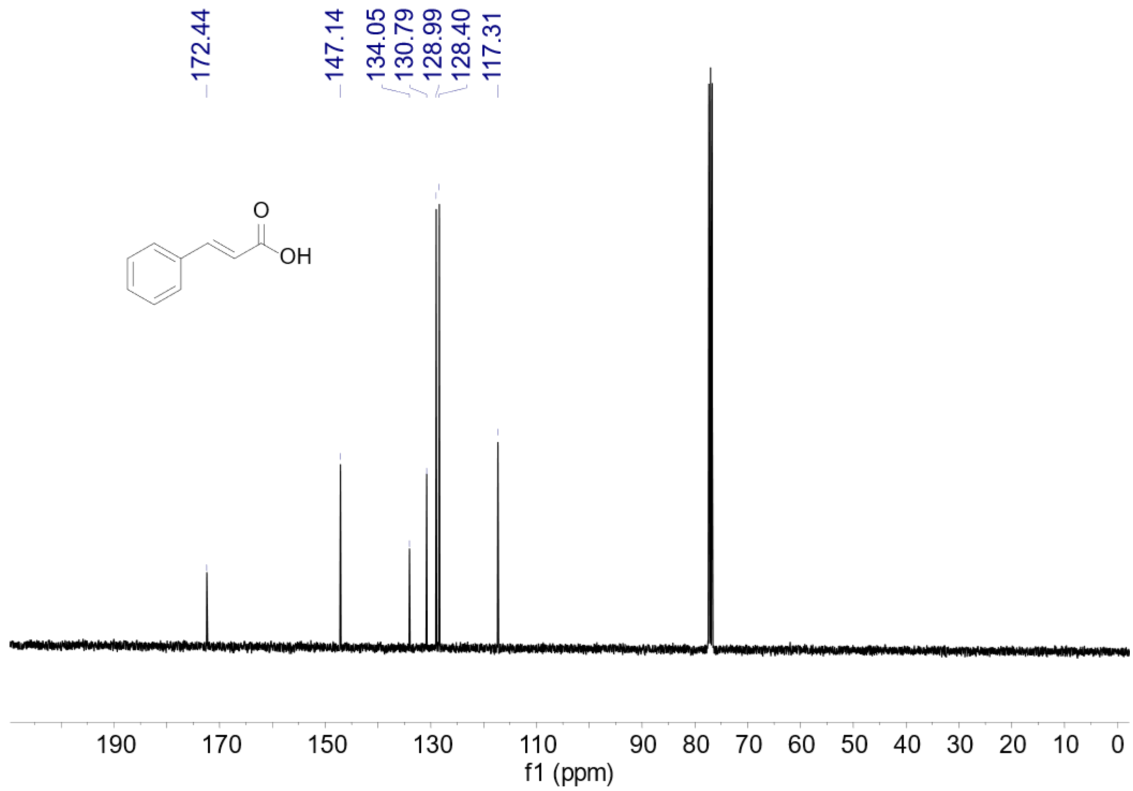
12. NMR Spectra



^{1}H NMR spectra of 2 (400 MHz, $CDCl_3$)



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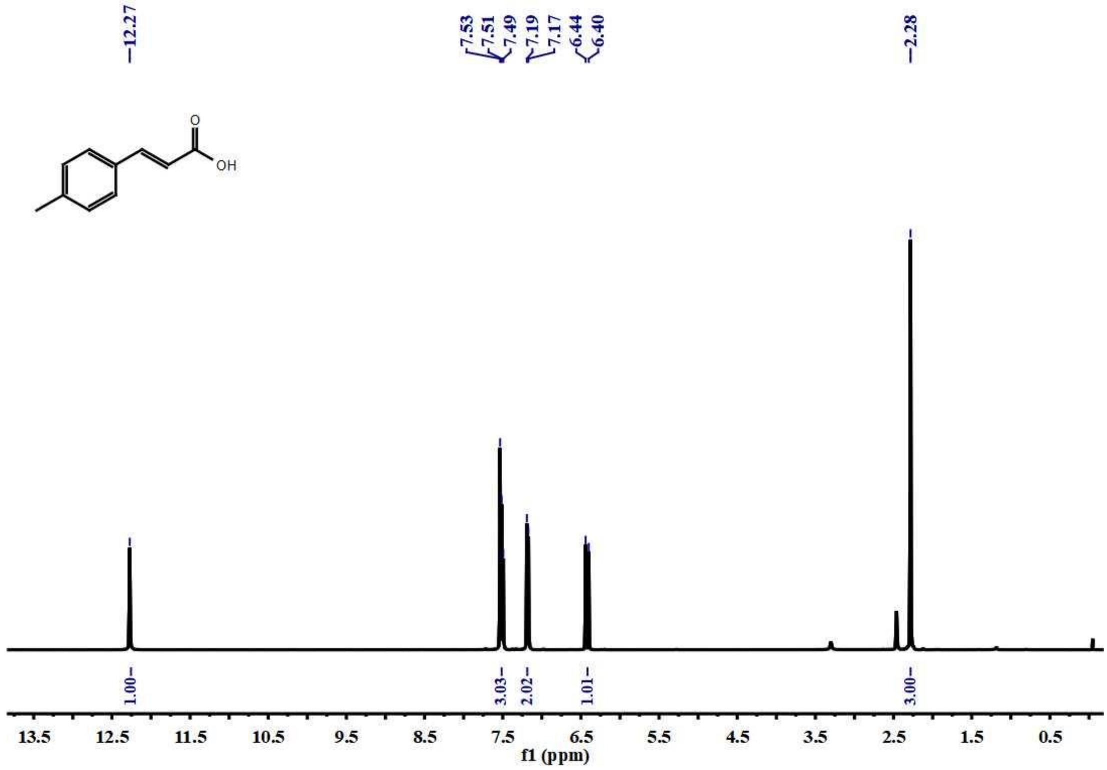

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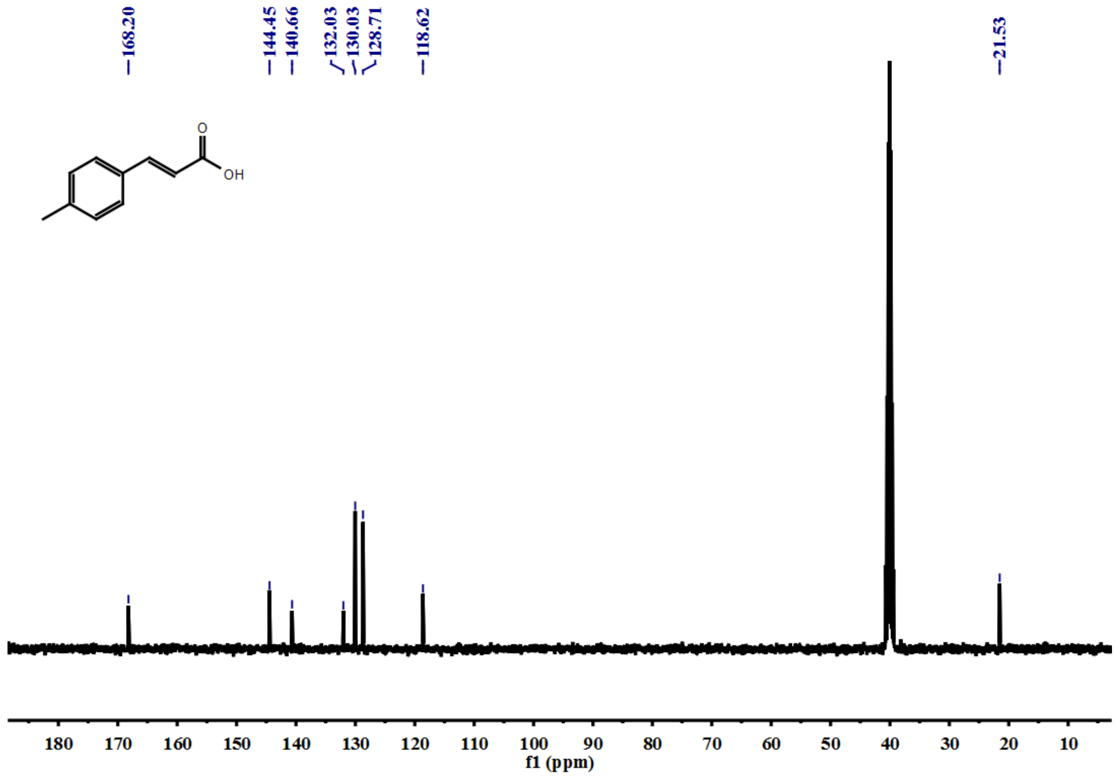

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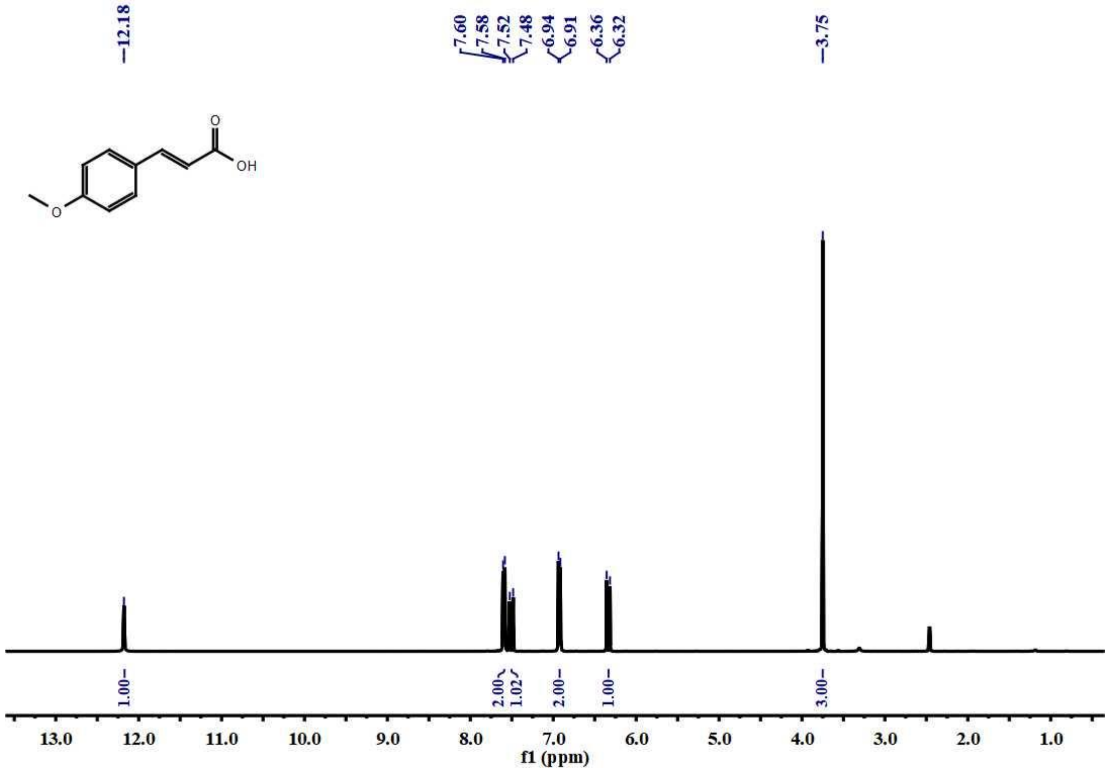

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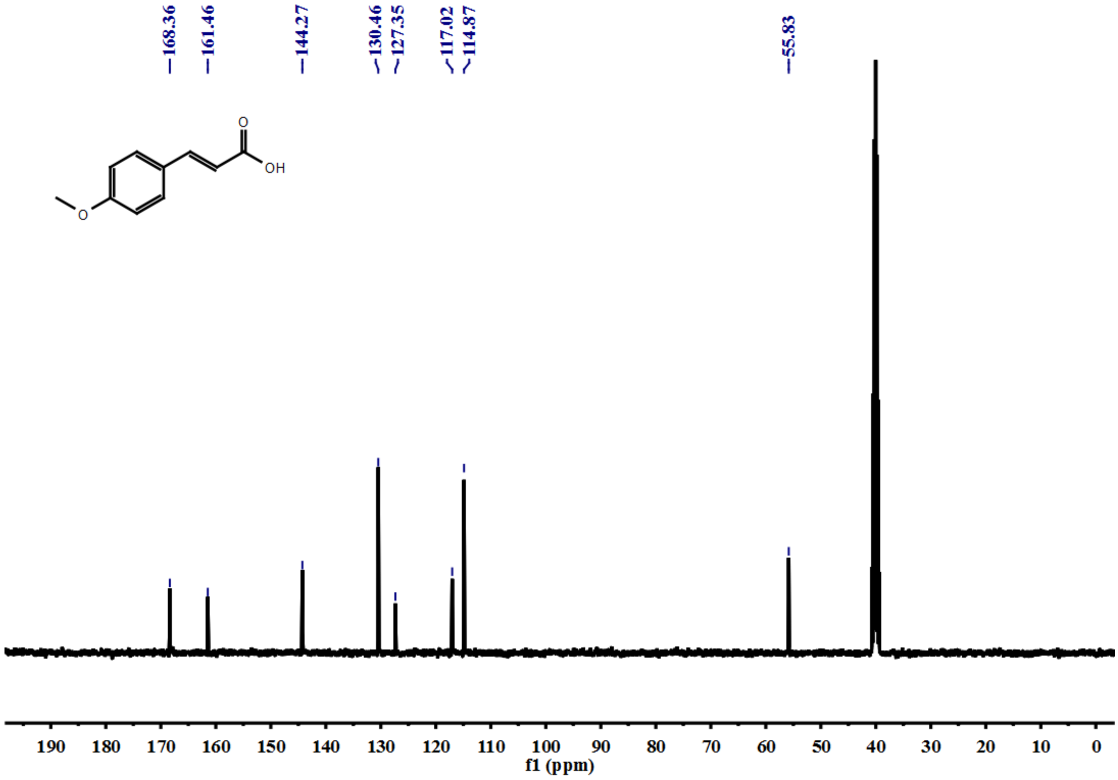

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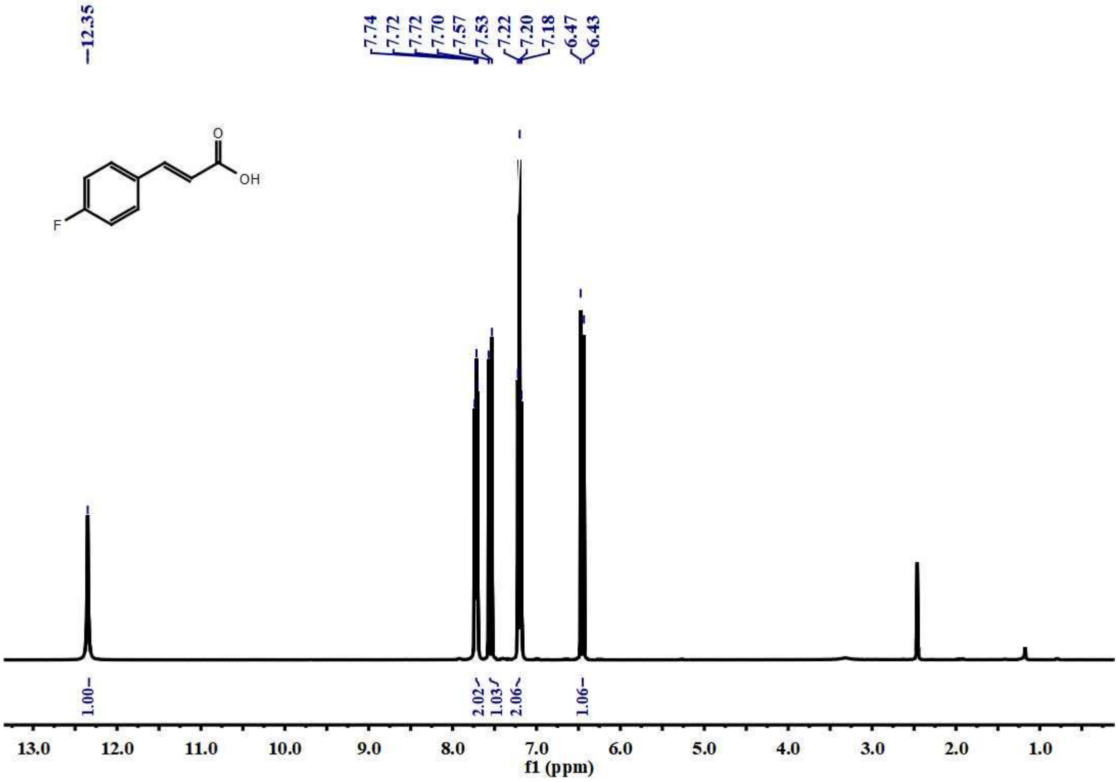

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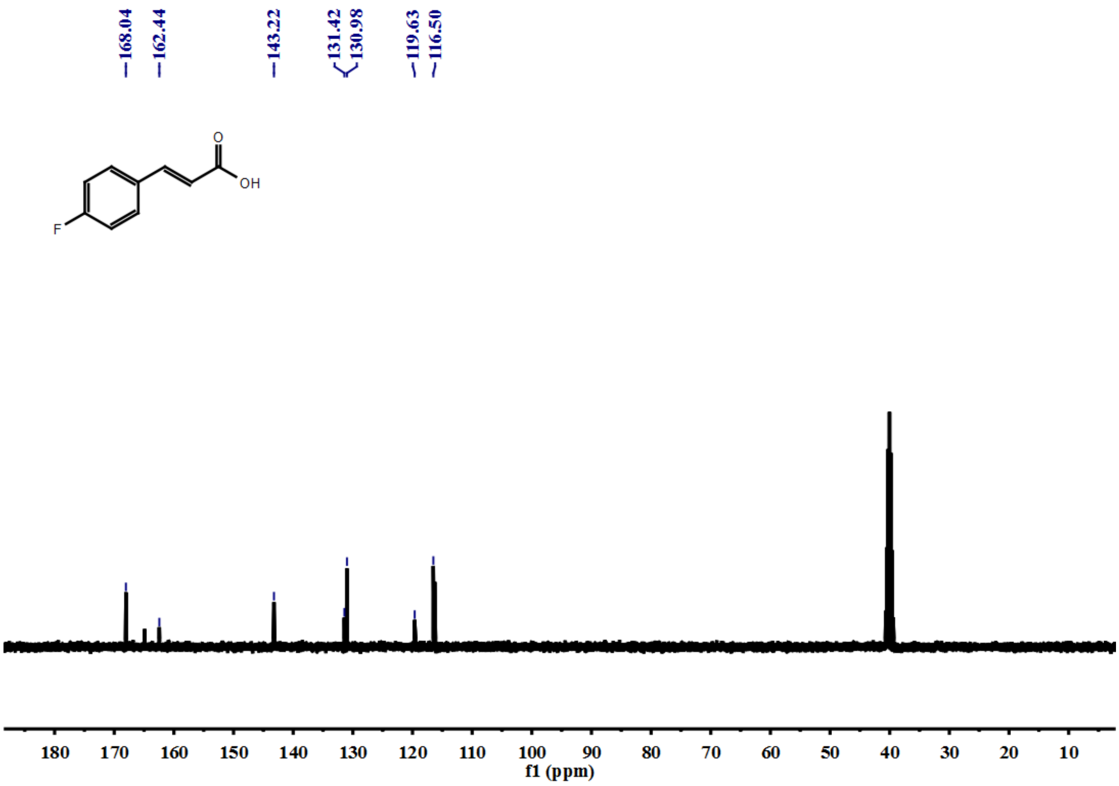

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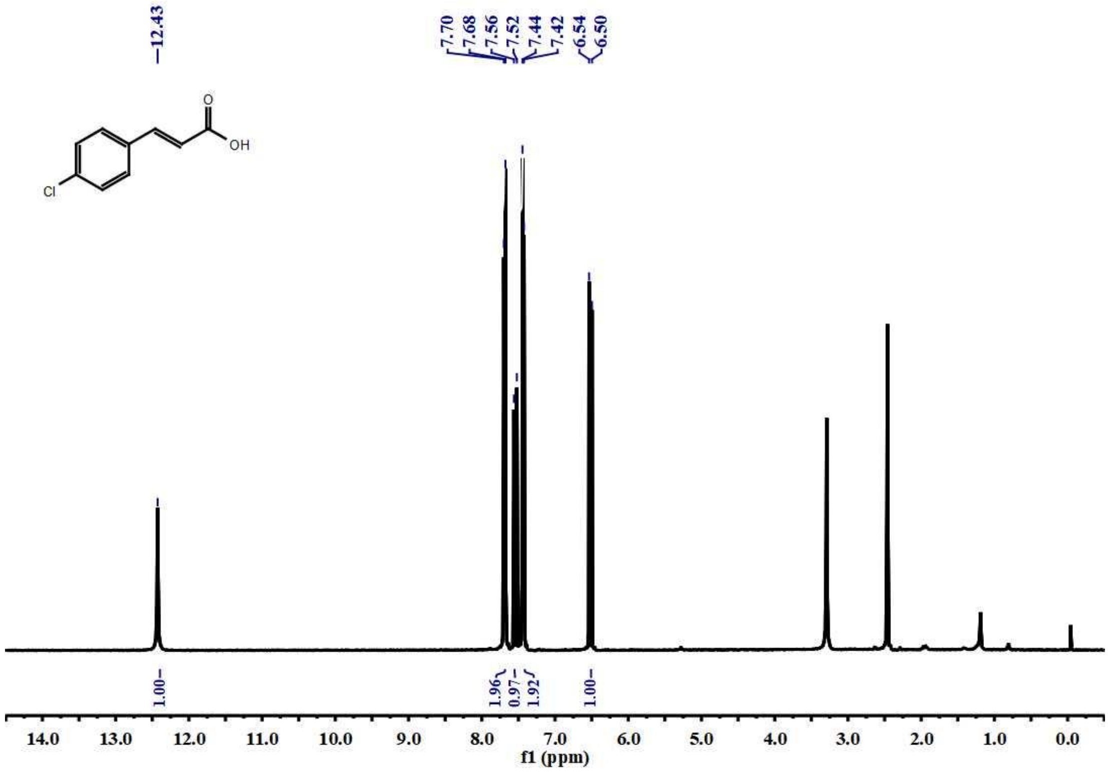
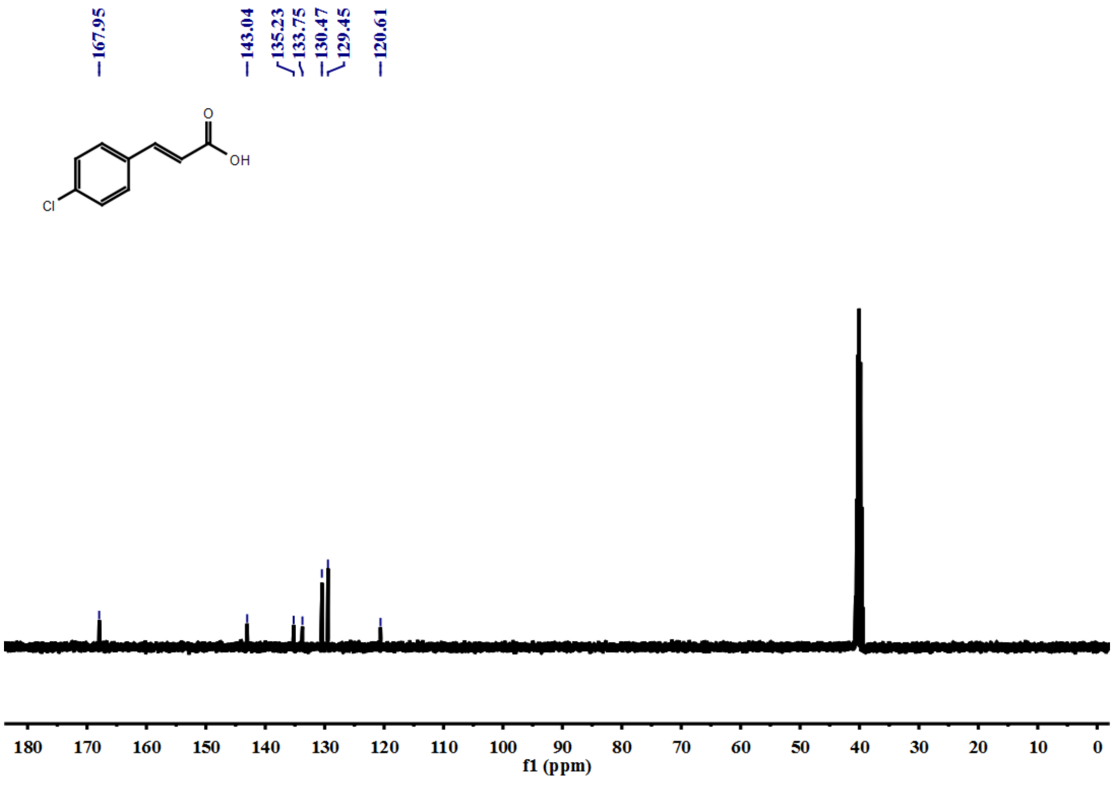
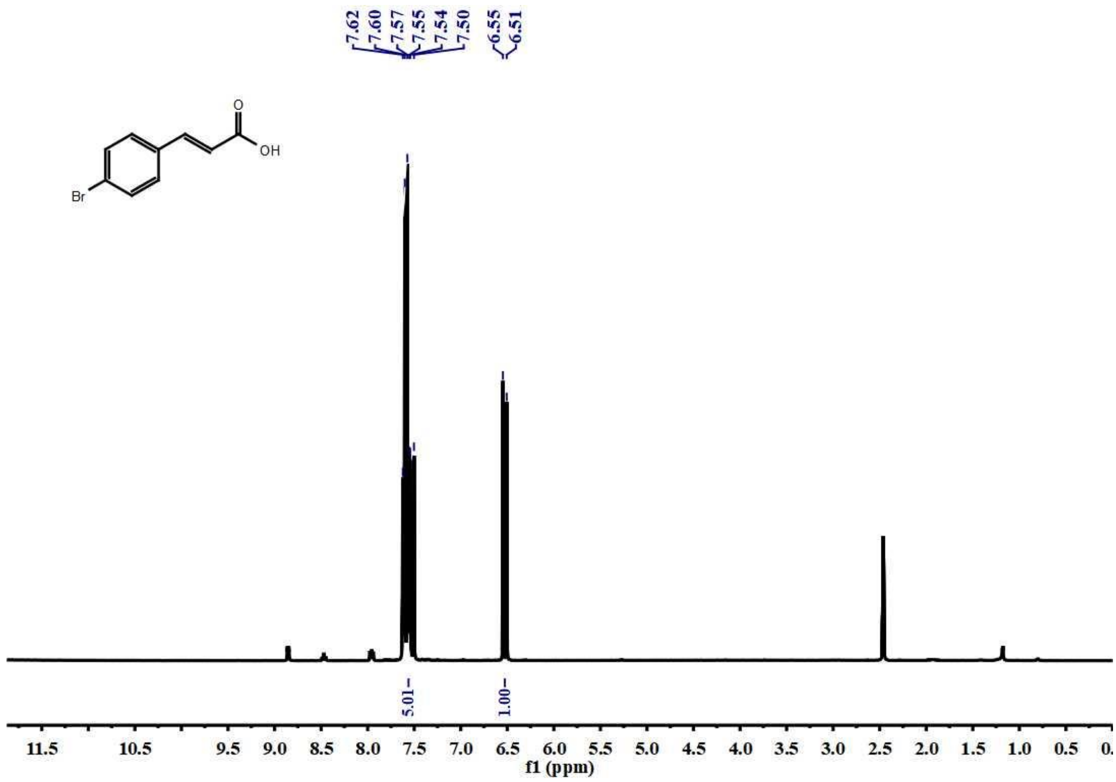


[1]H NMR spectra of 6 (500 MHz, DMSO-*d*$_6$)



[13]C NMR spectra of 6 (125 MHz, DMSO-*d*$_6$)

1.



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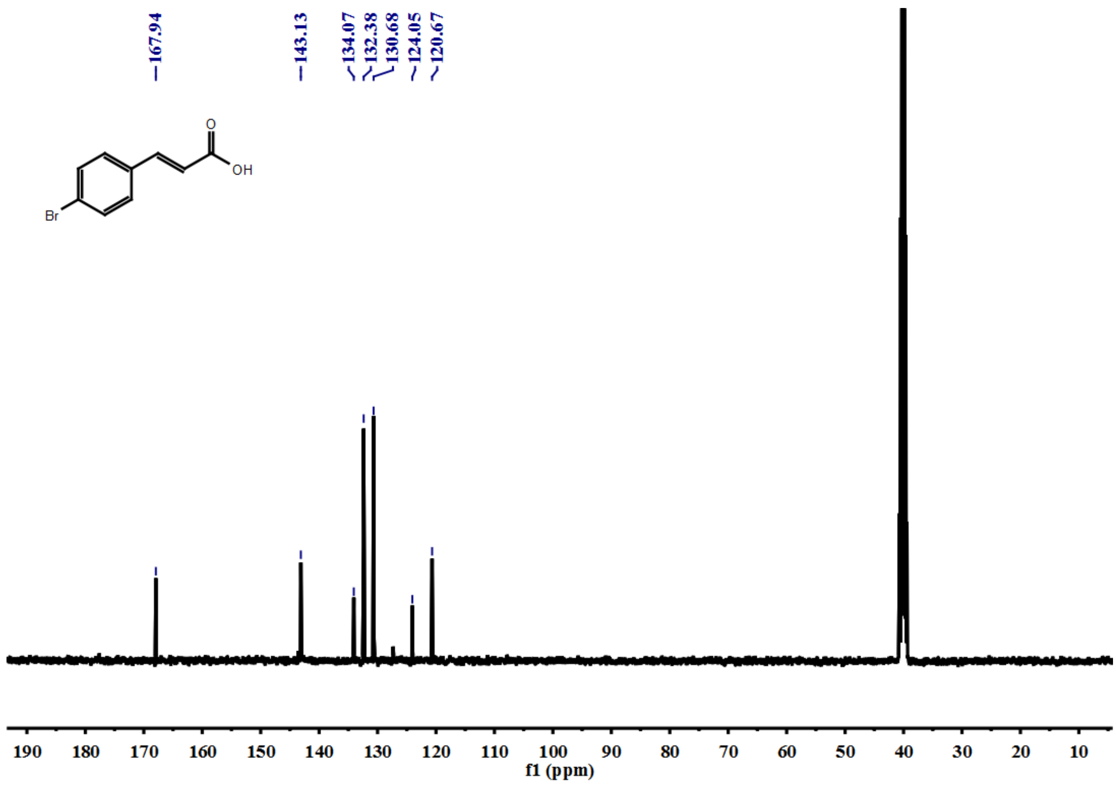

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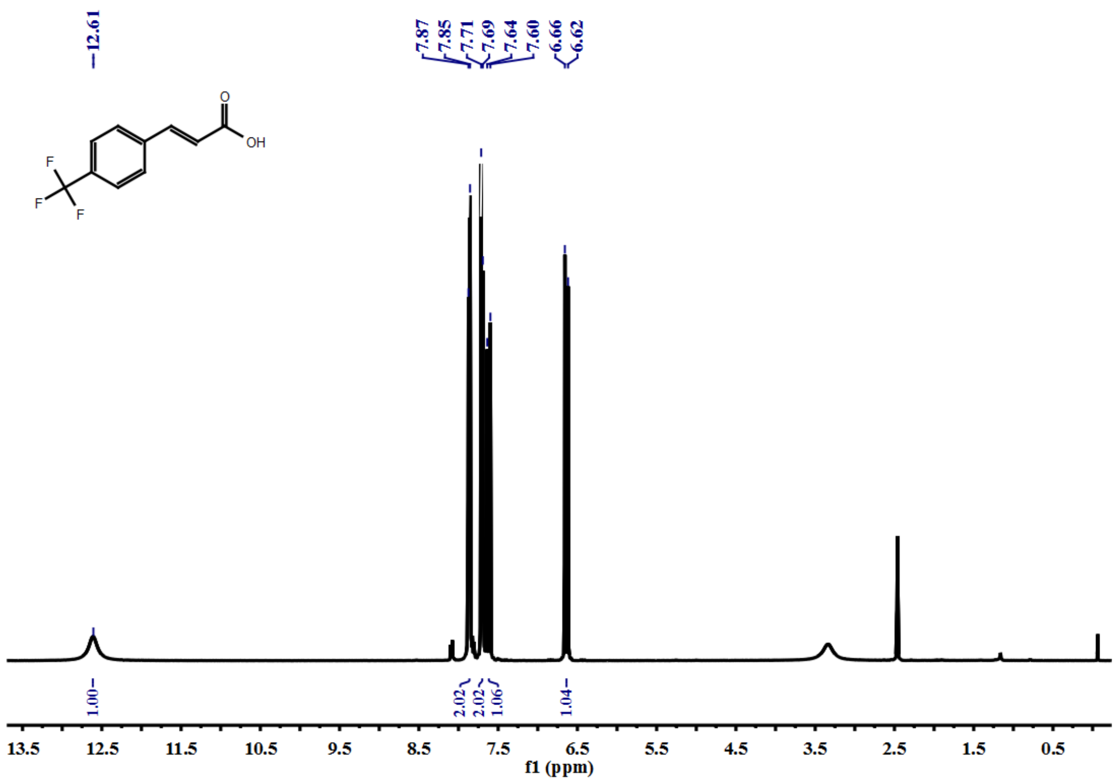

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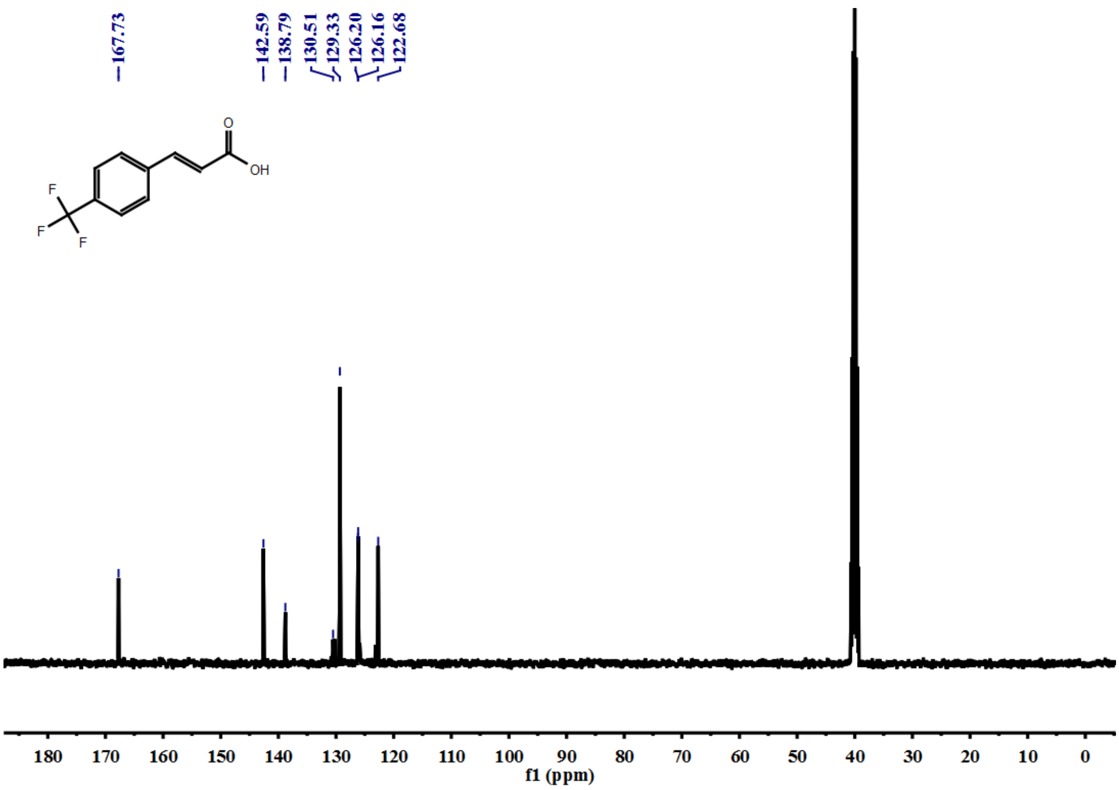

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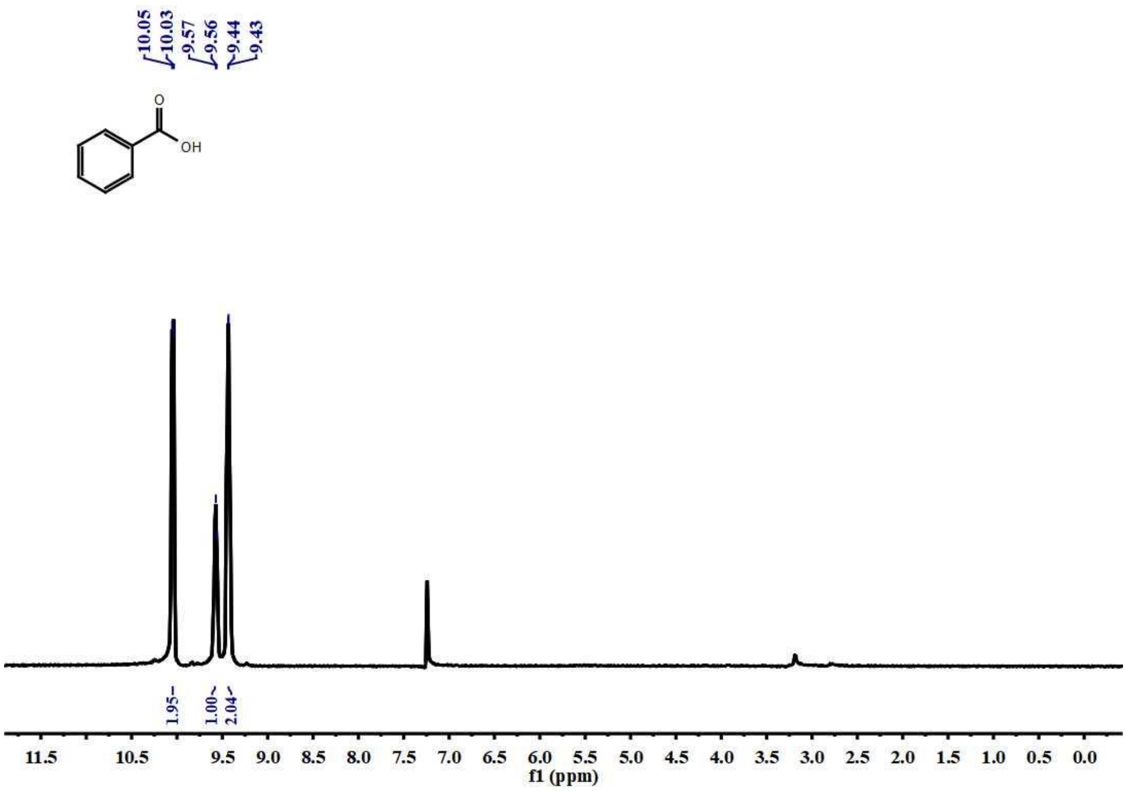
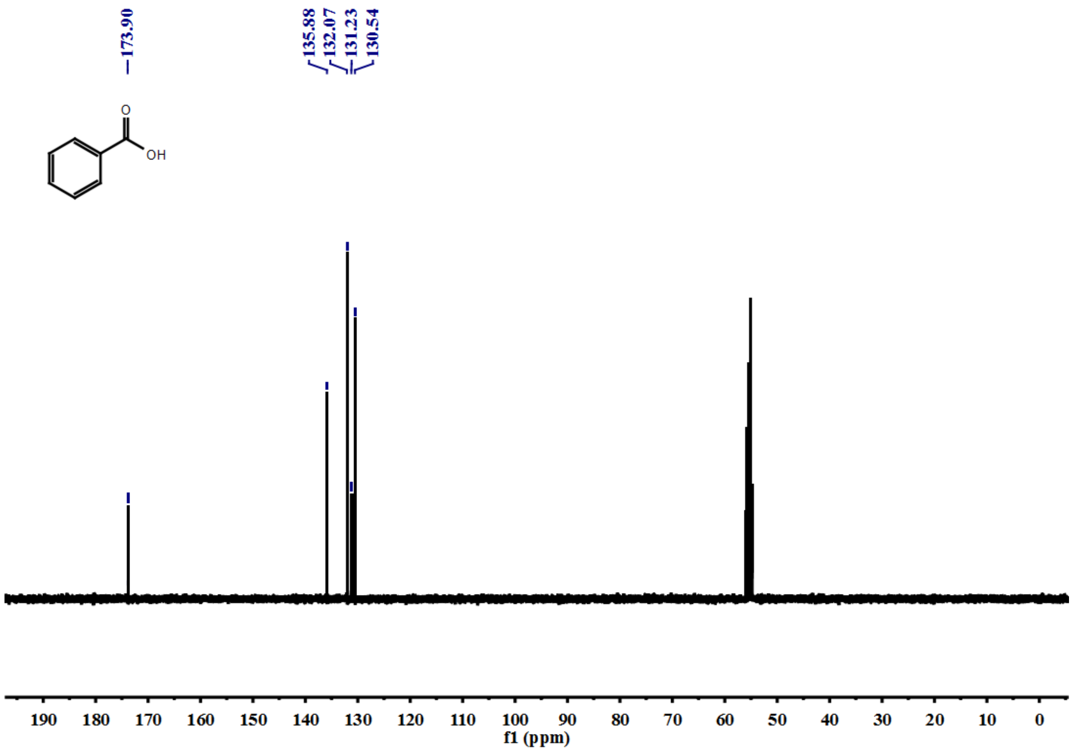


^{1}H NMR spectra of 9 (500 MHz, $CDCl_3$)



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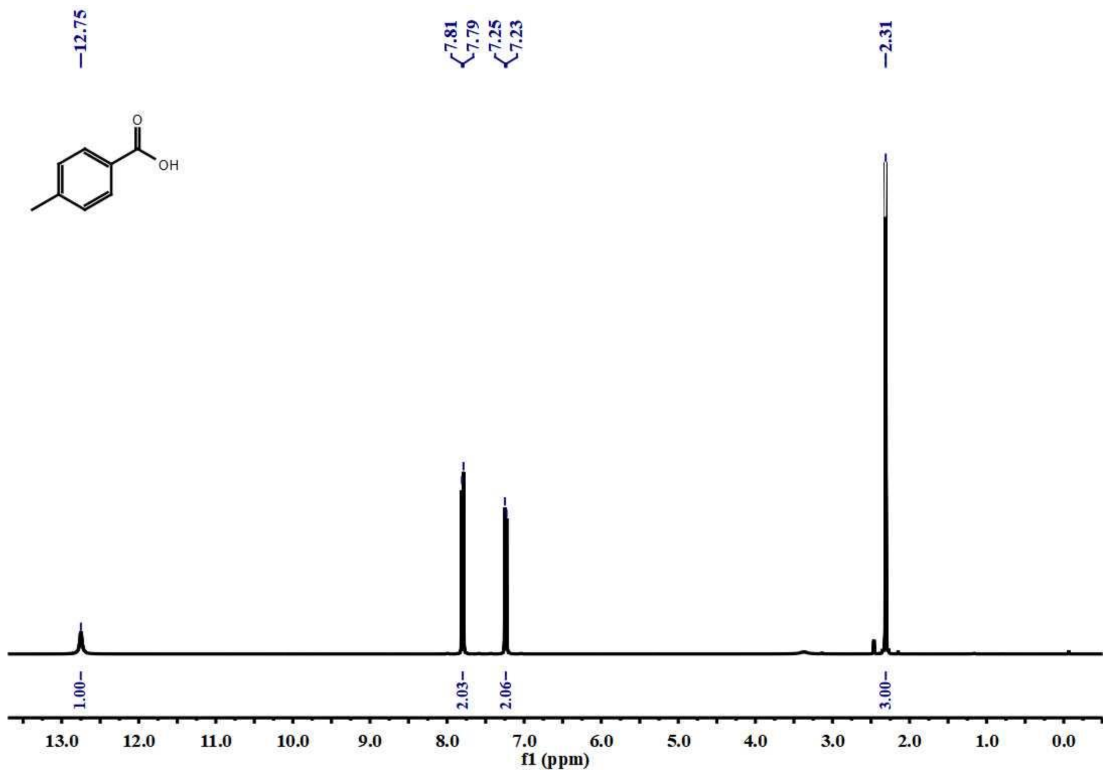

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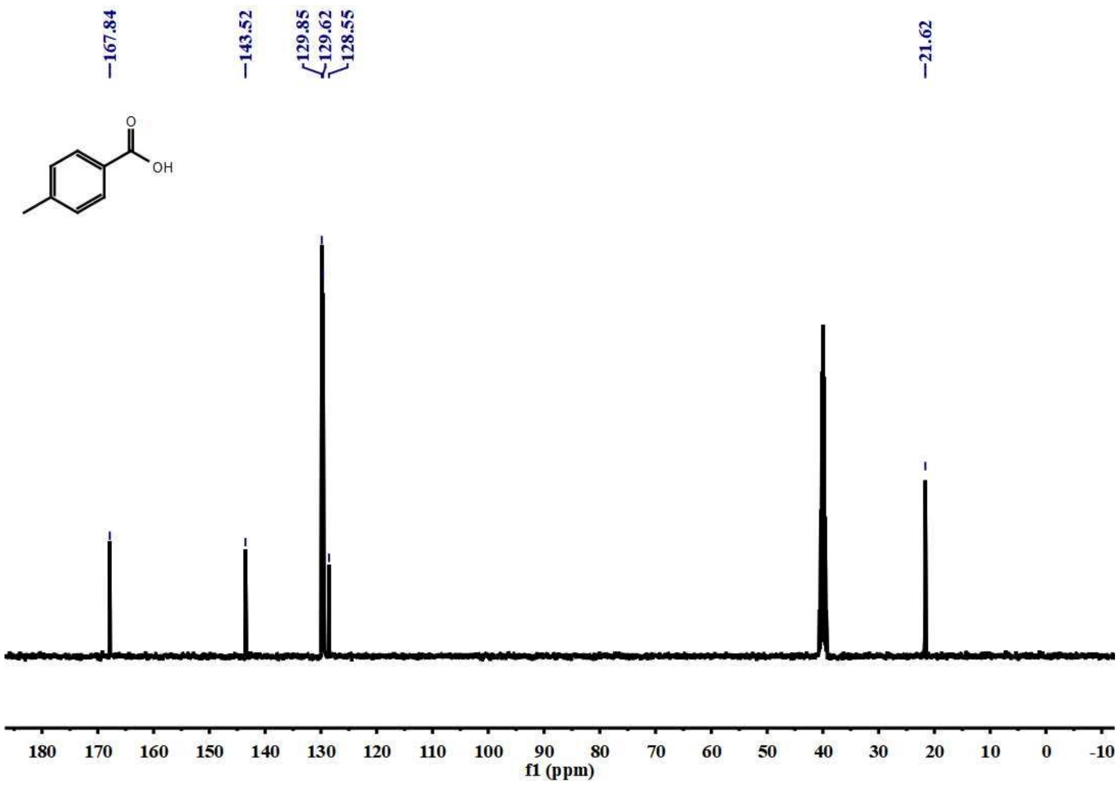

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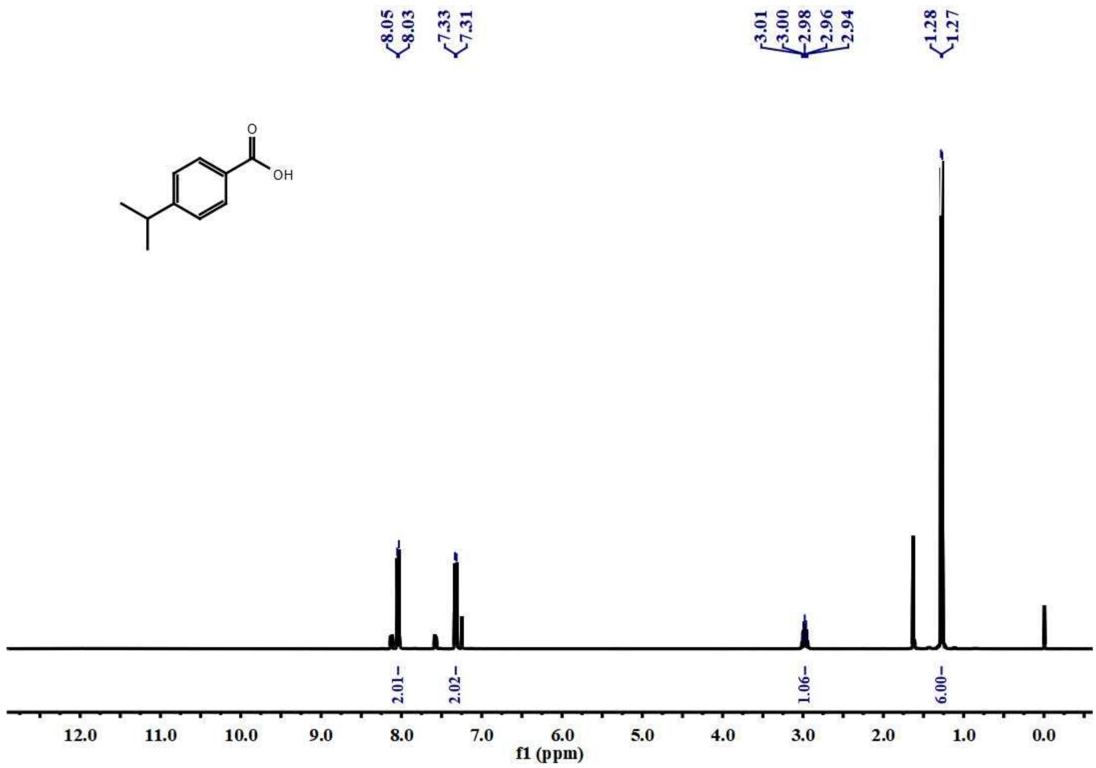

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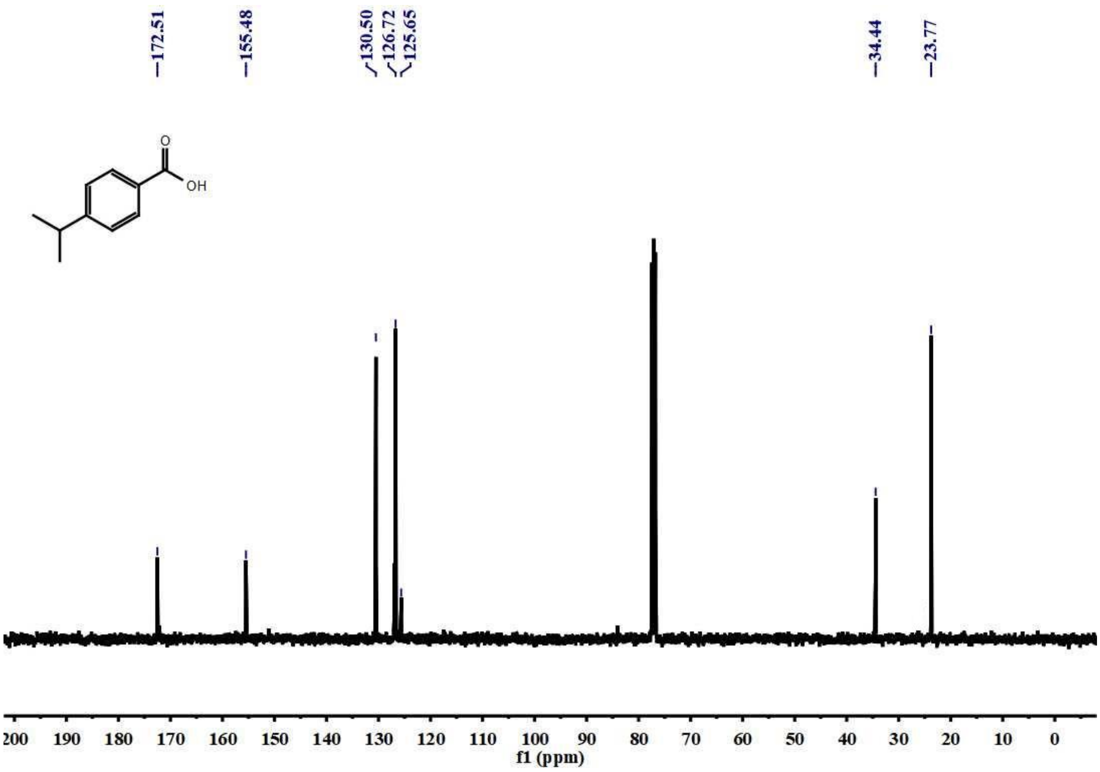

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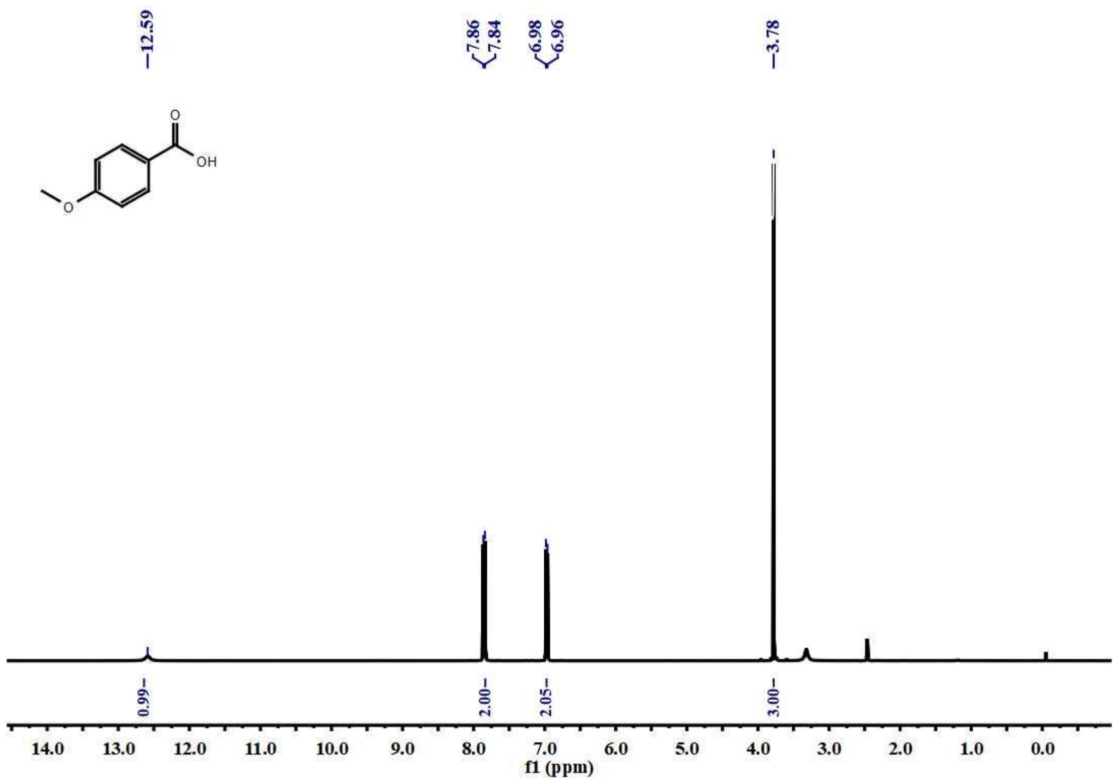

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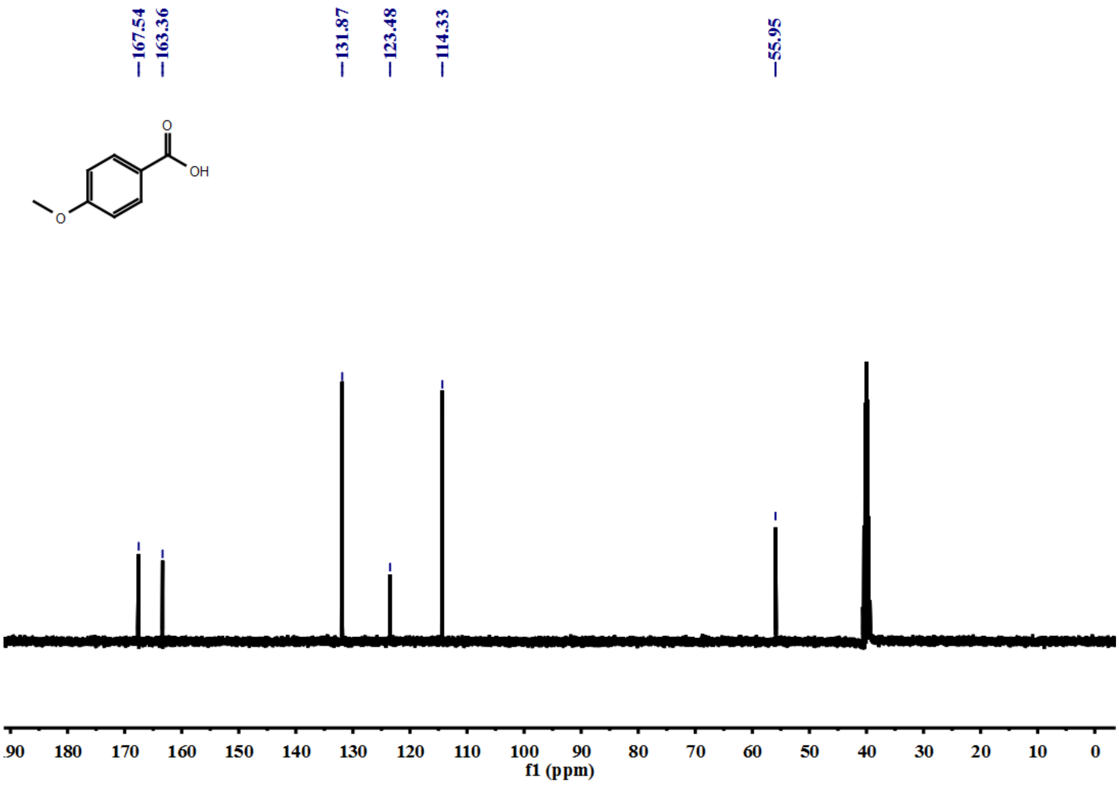

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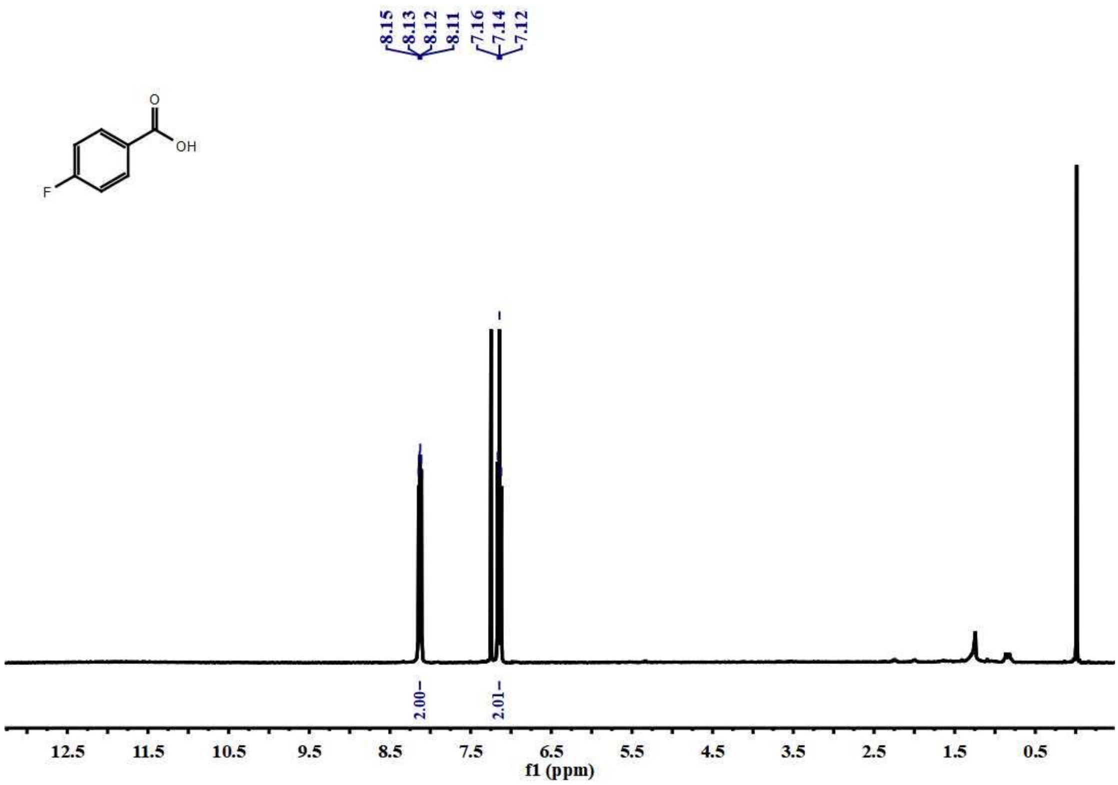

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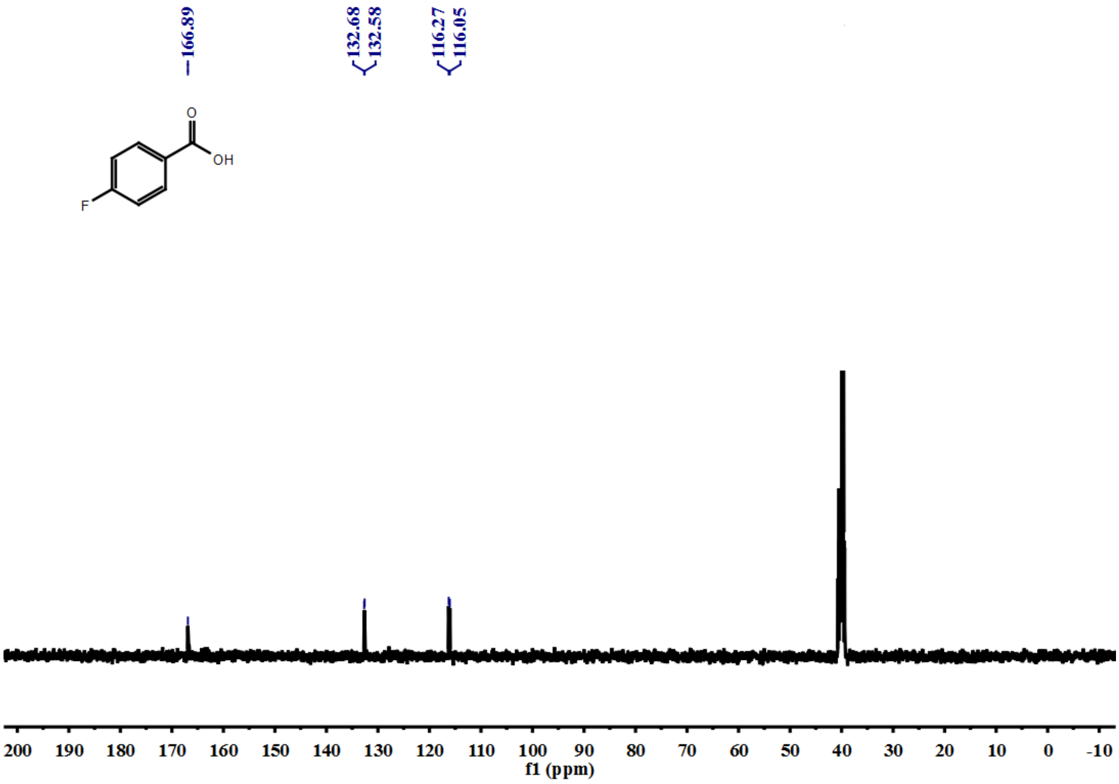

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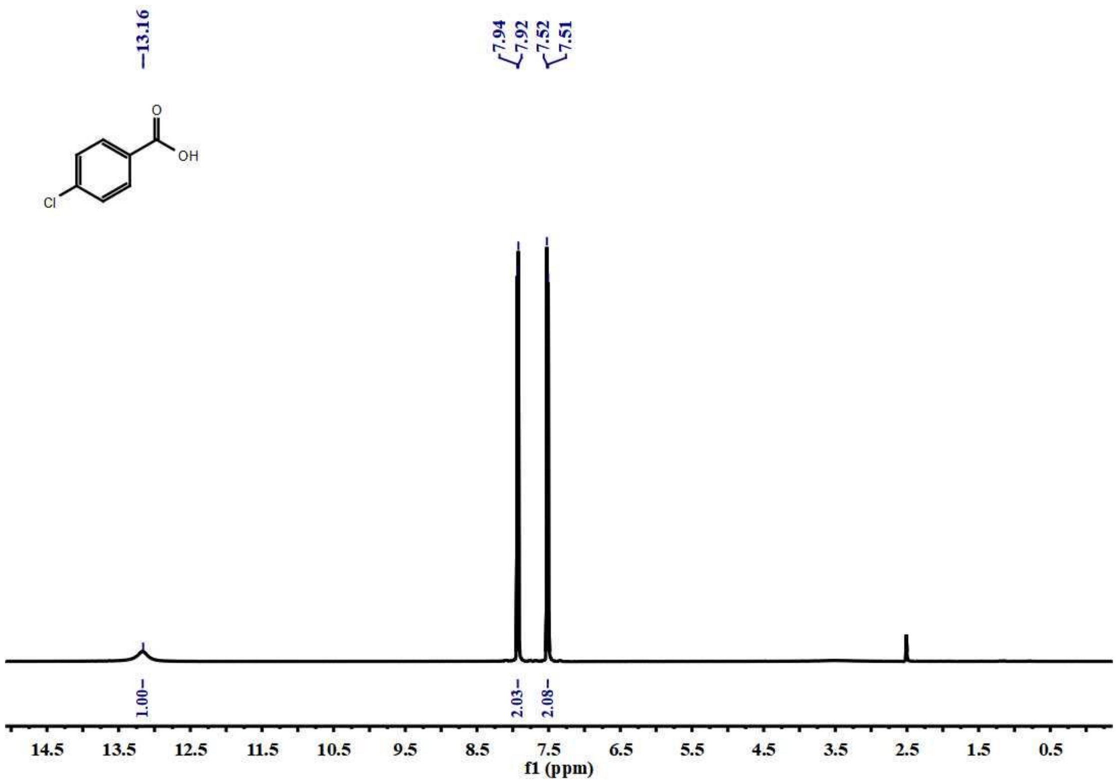

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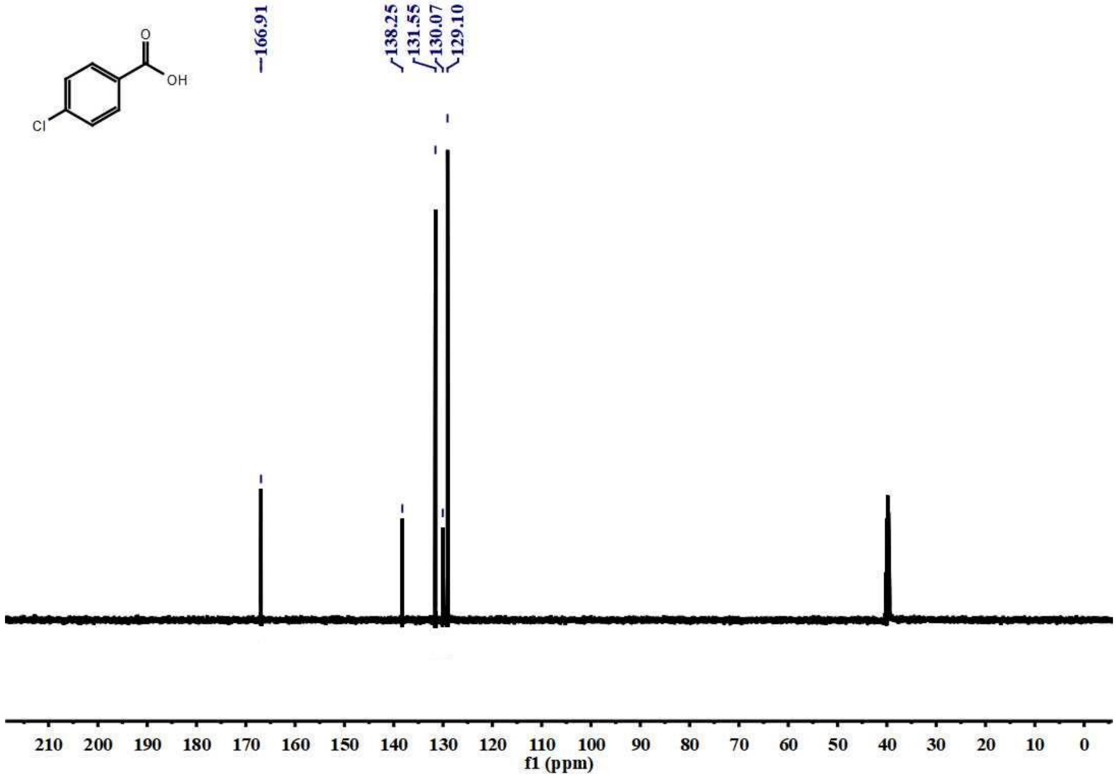

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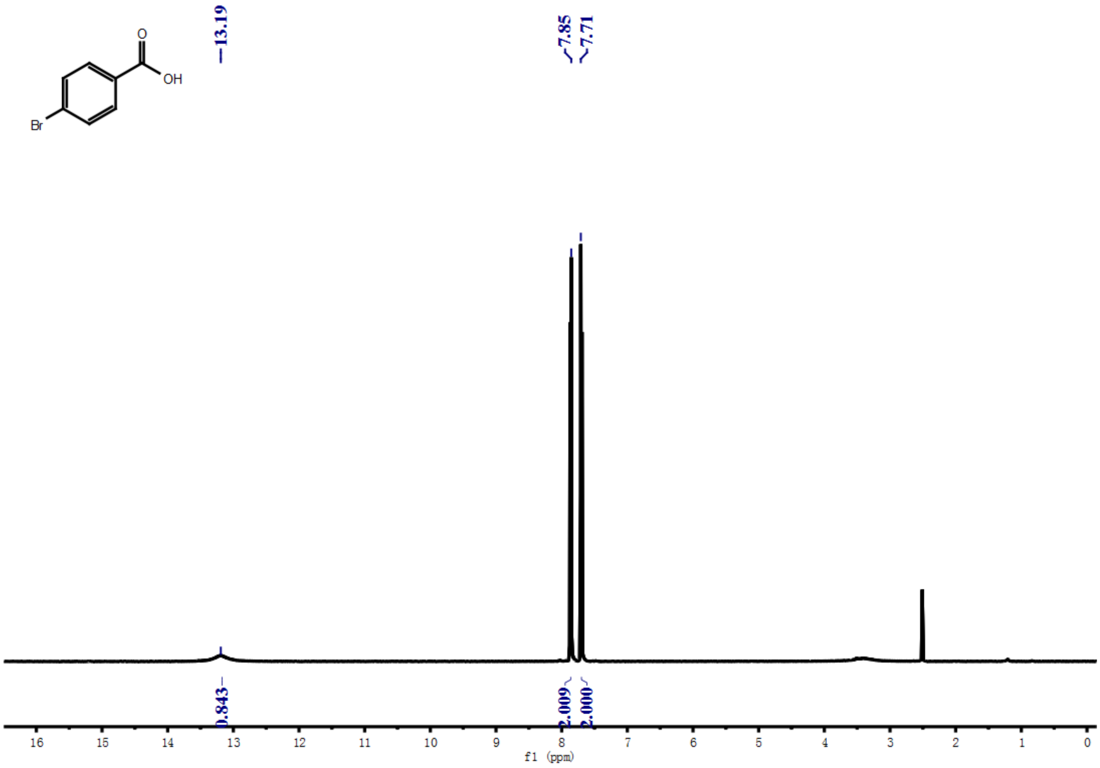

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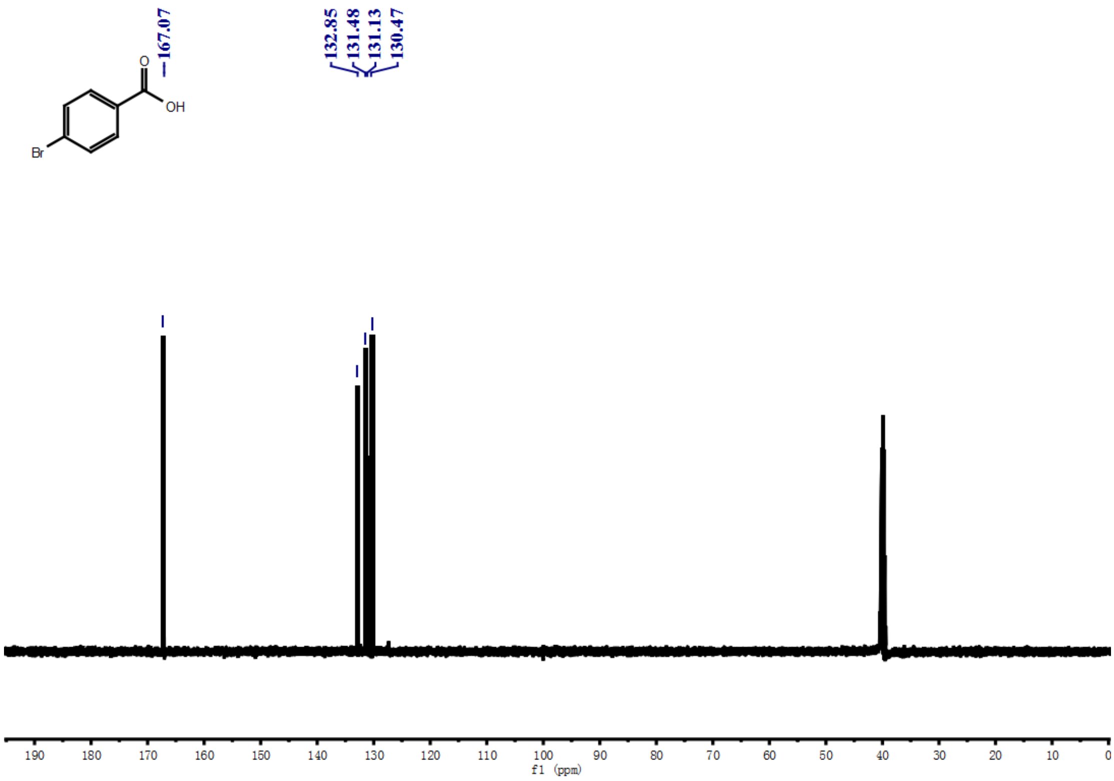
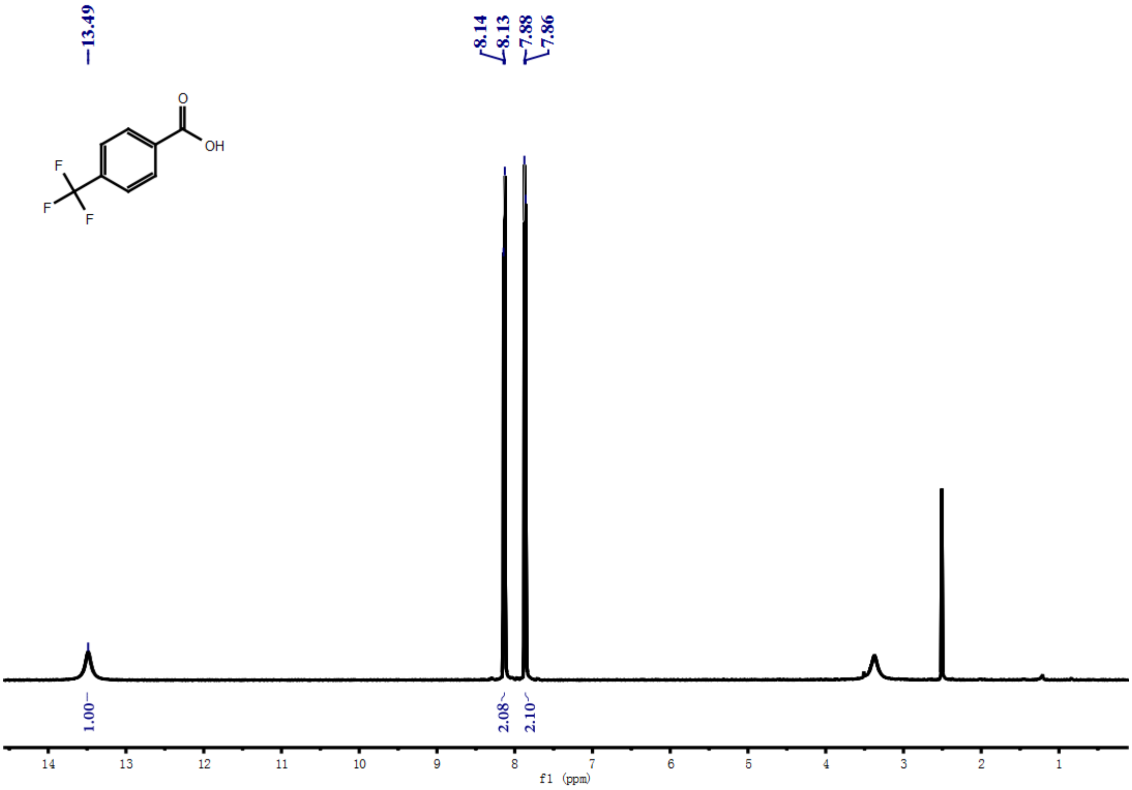


^{13}C NMR spectra of 15 (125 MHz, DMSO-d_6)



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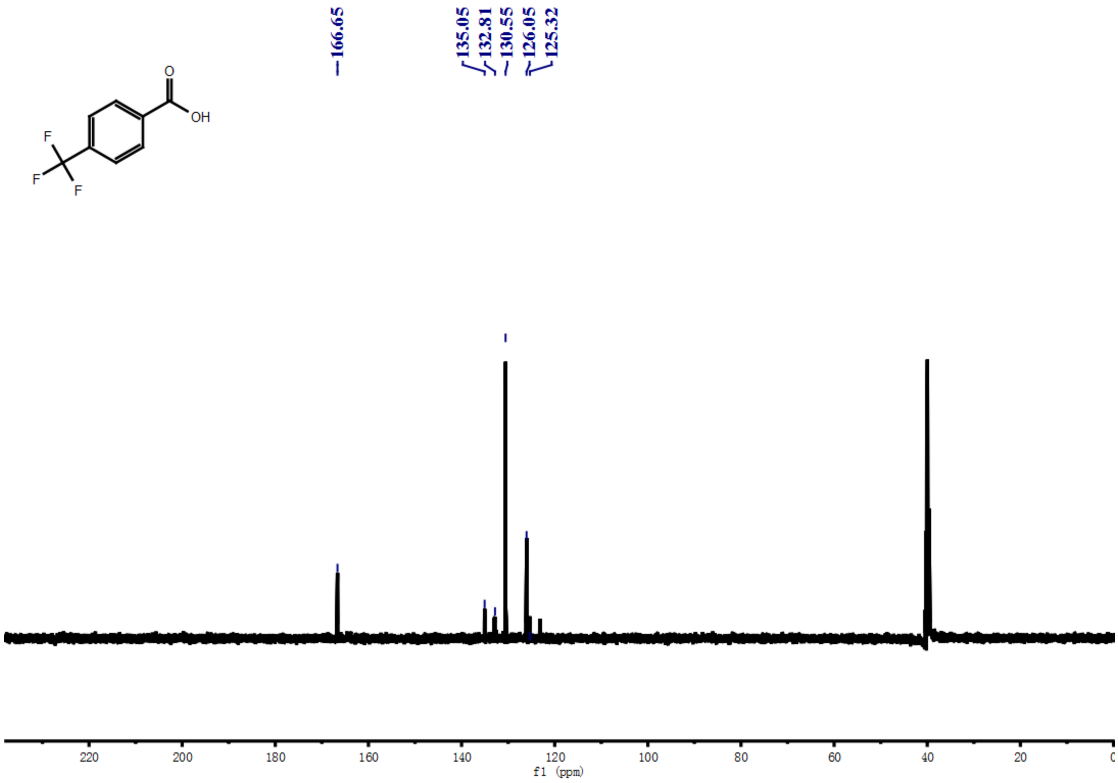

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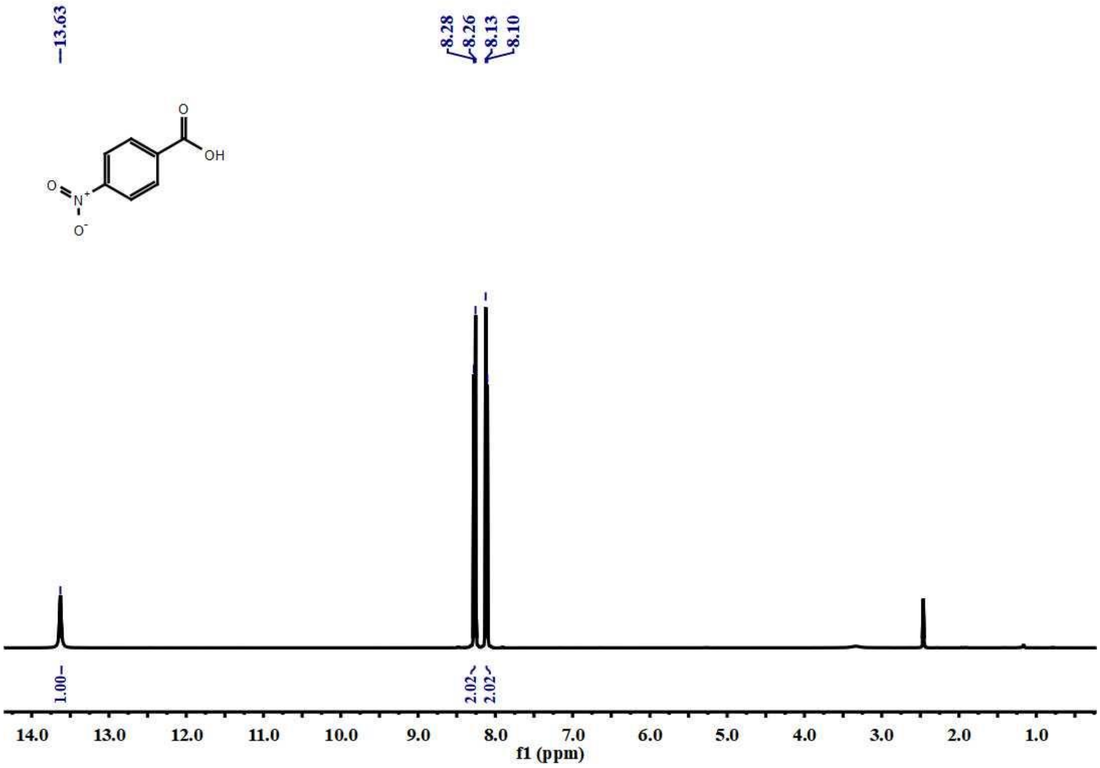

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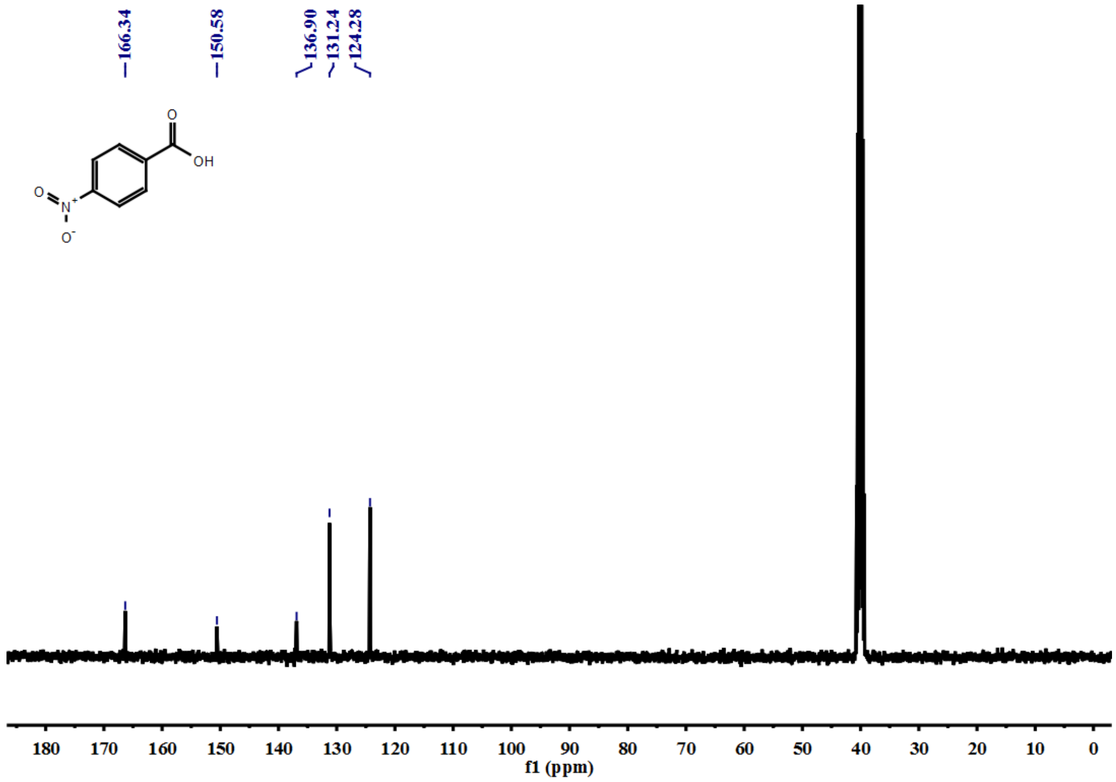

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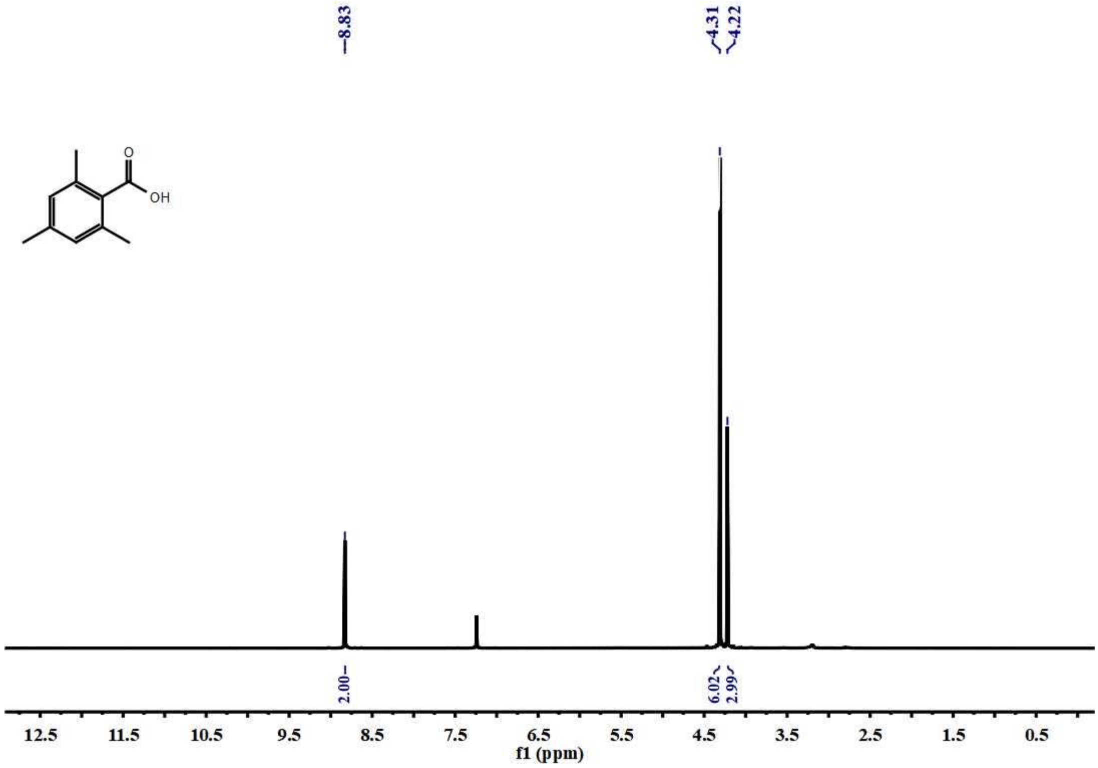
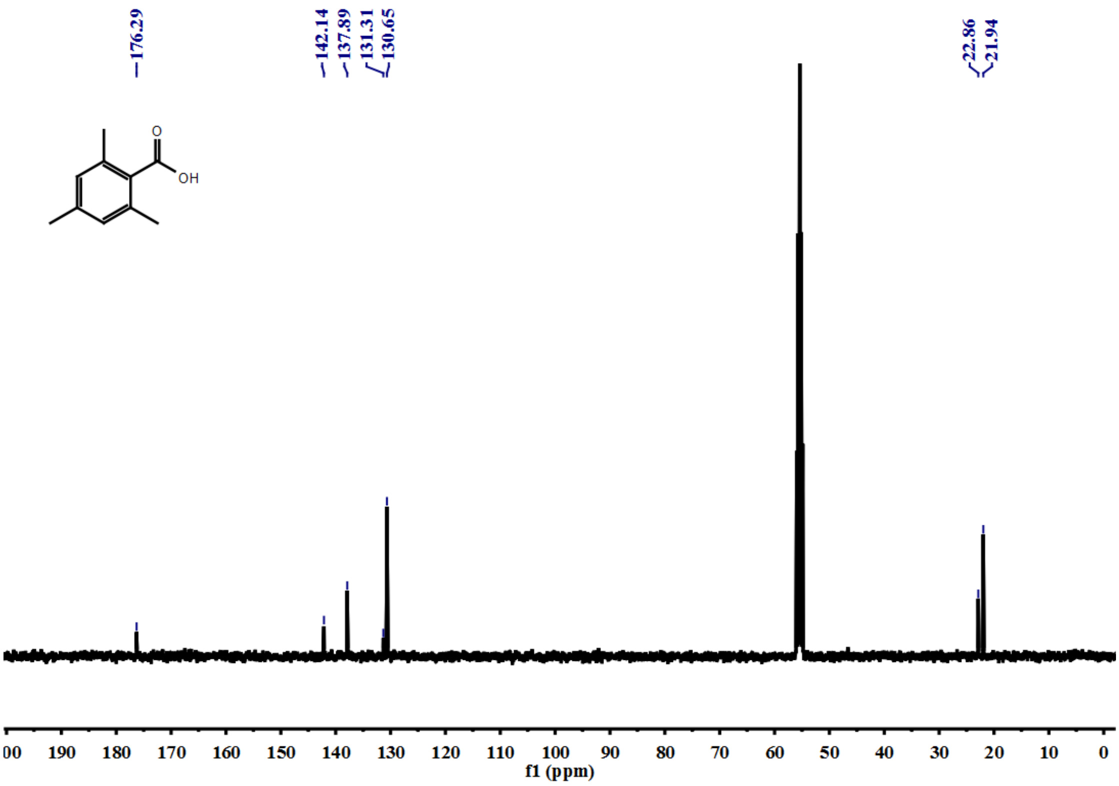
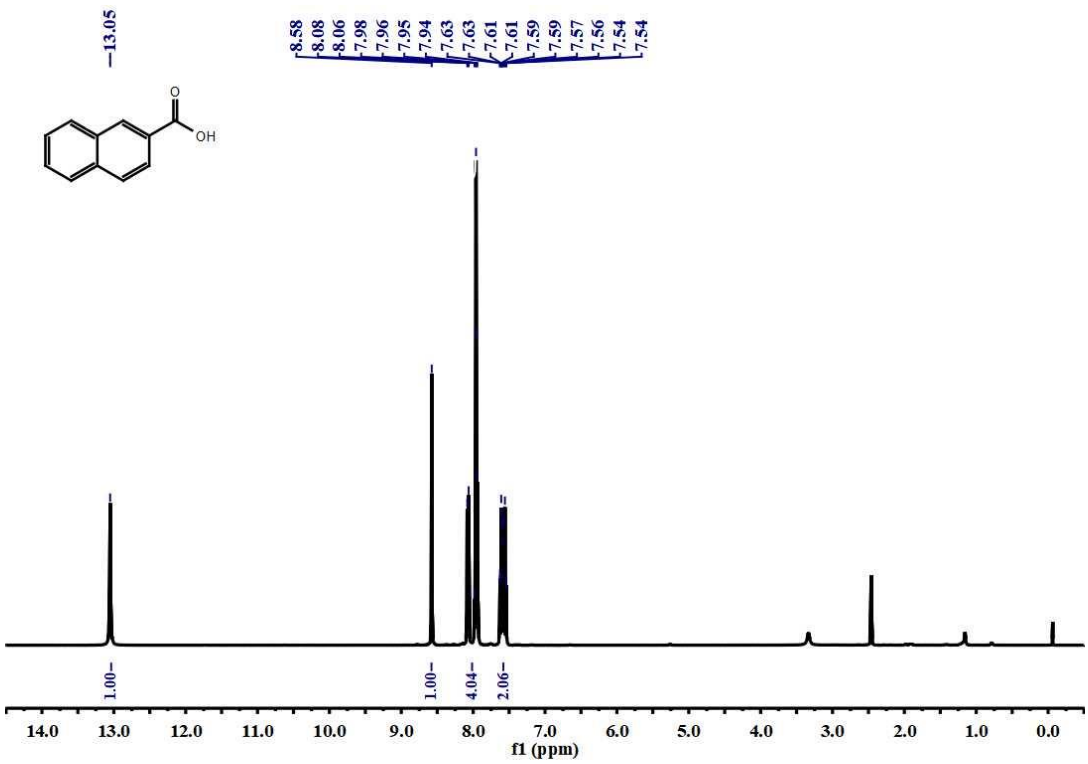


[1]H NMR spectra of 18 (500 MHz, $CDCl_3$)



[13]C NMR spectra of 18 (125 MHz, $CDCl_3$)



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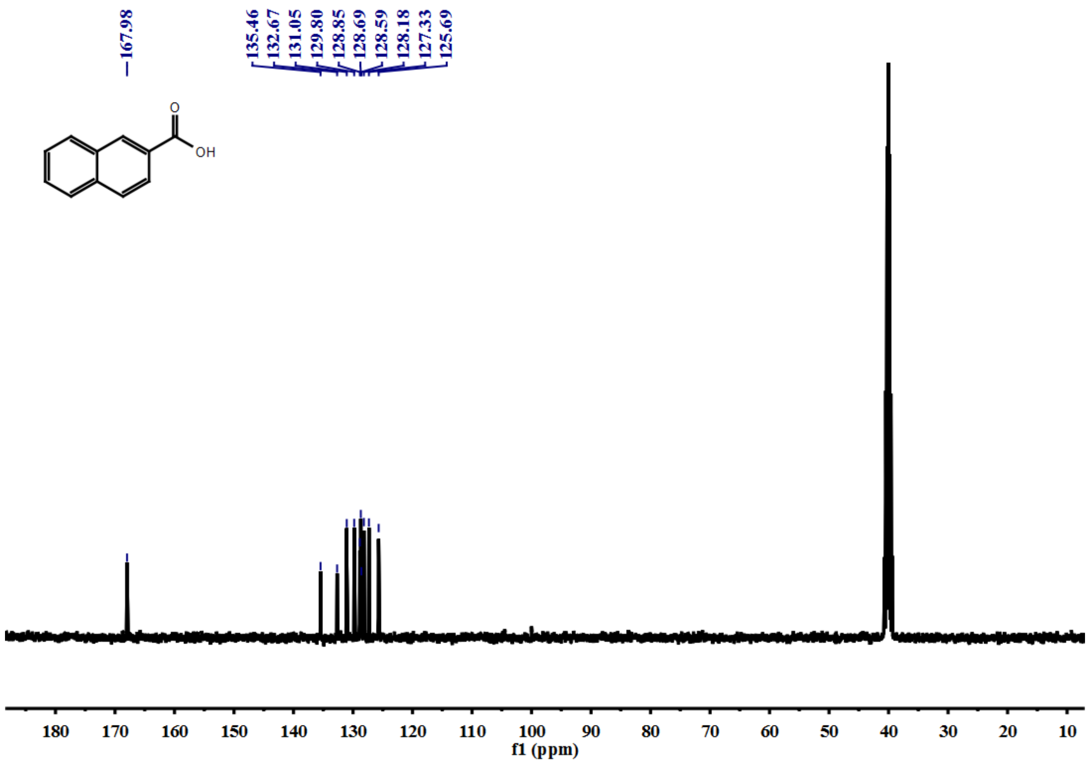

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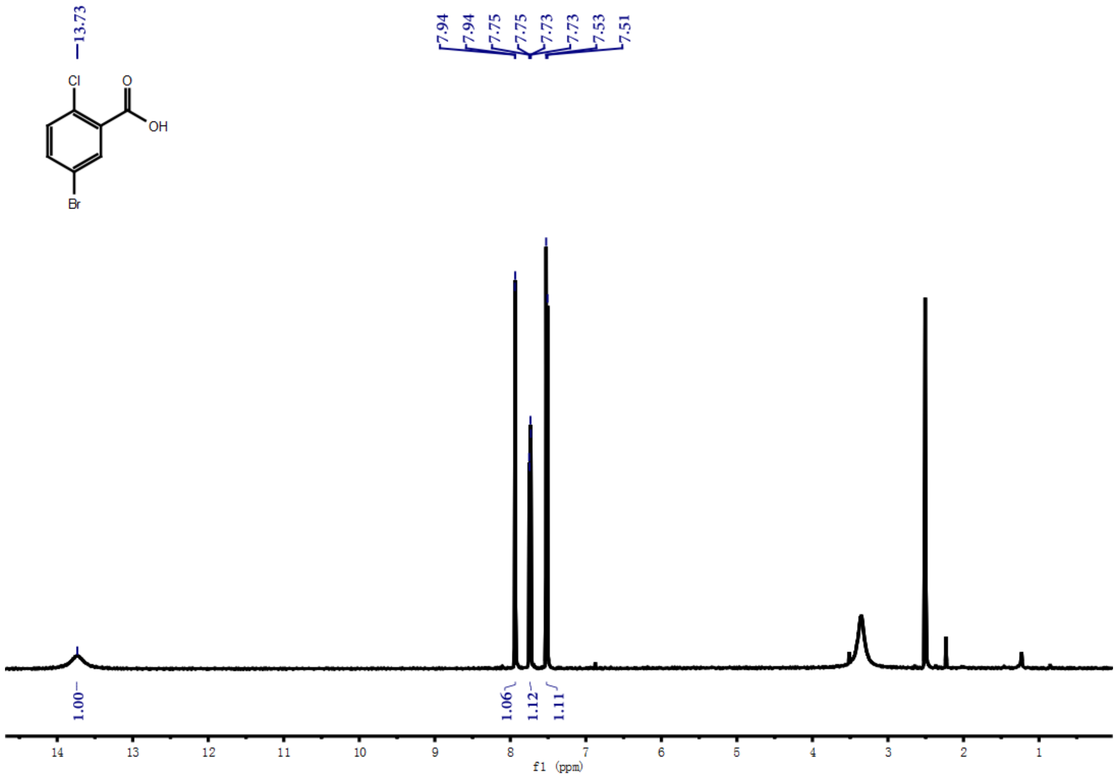
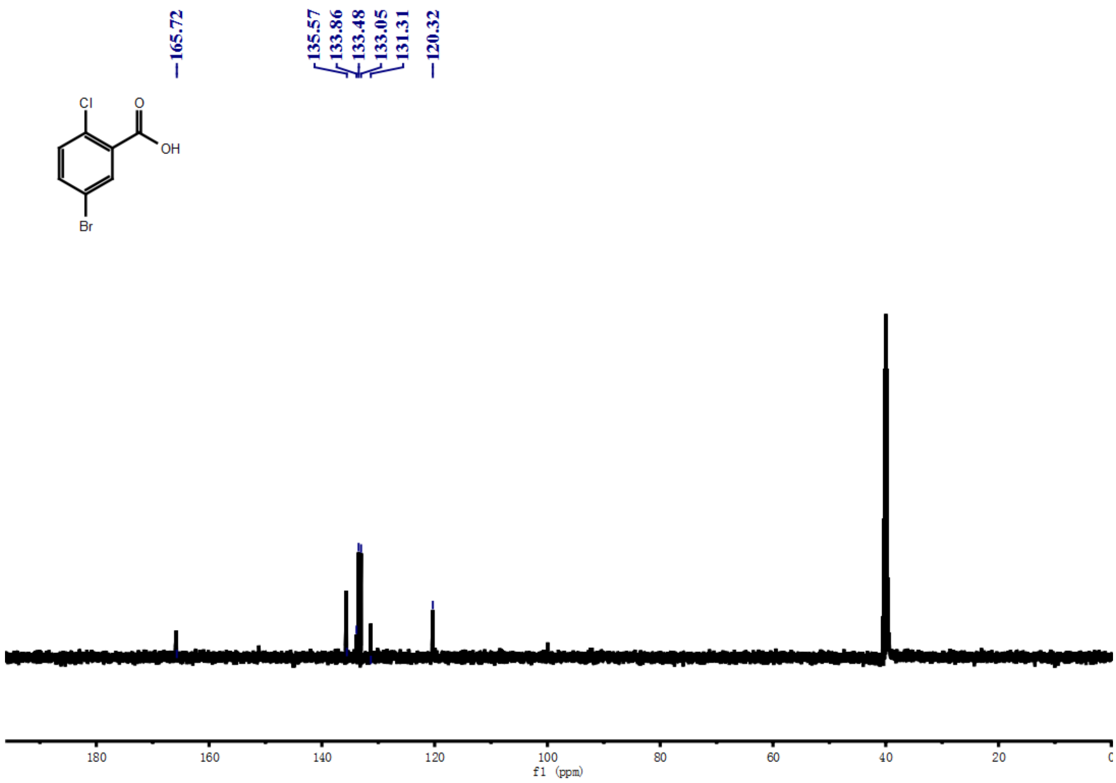
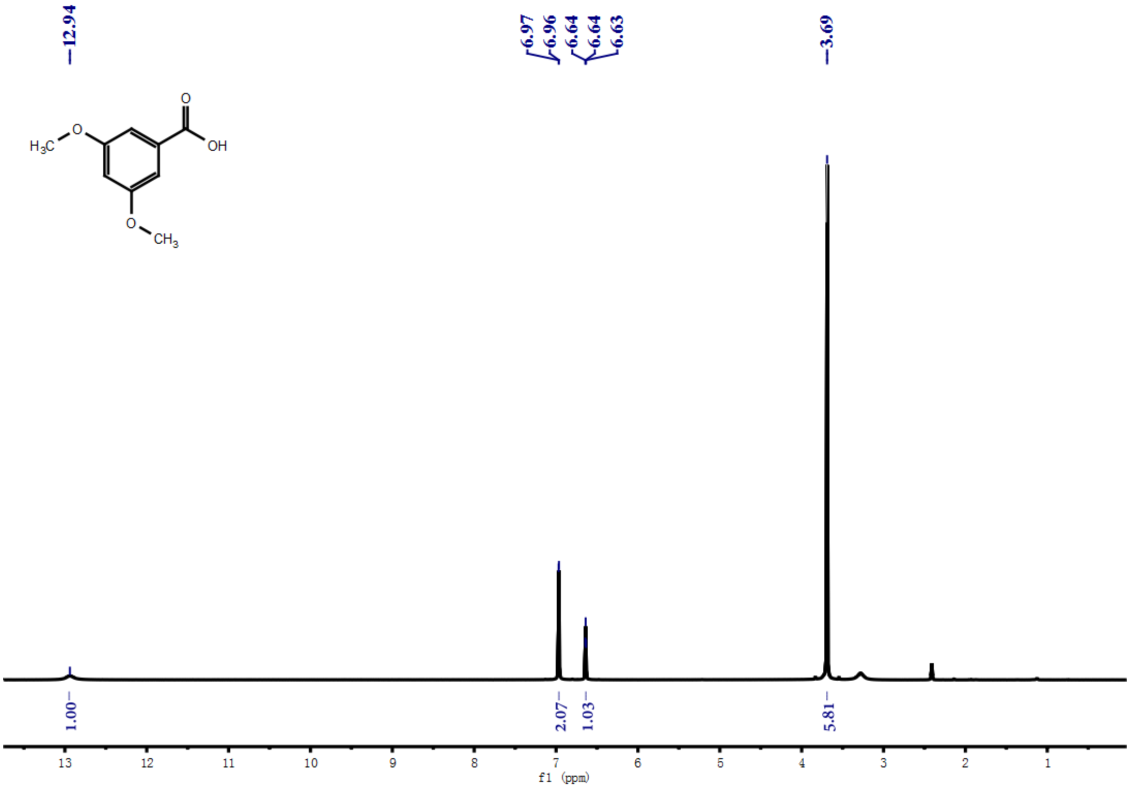


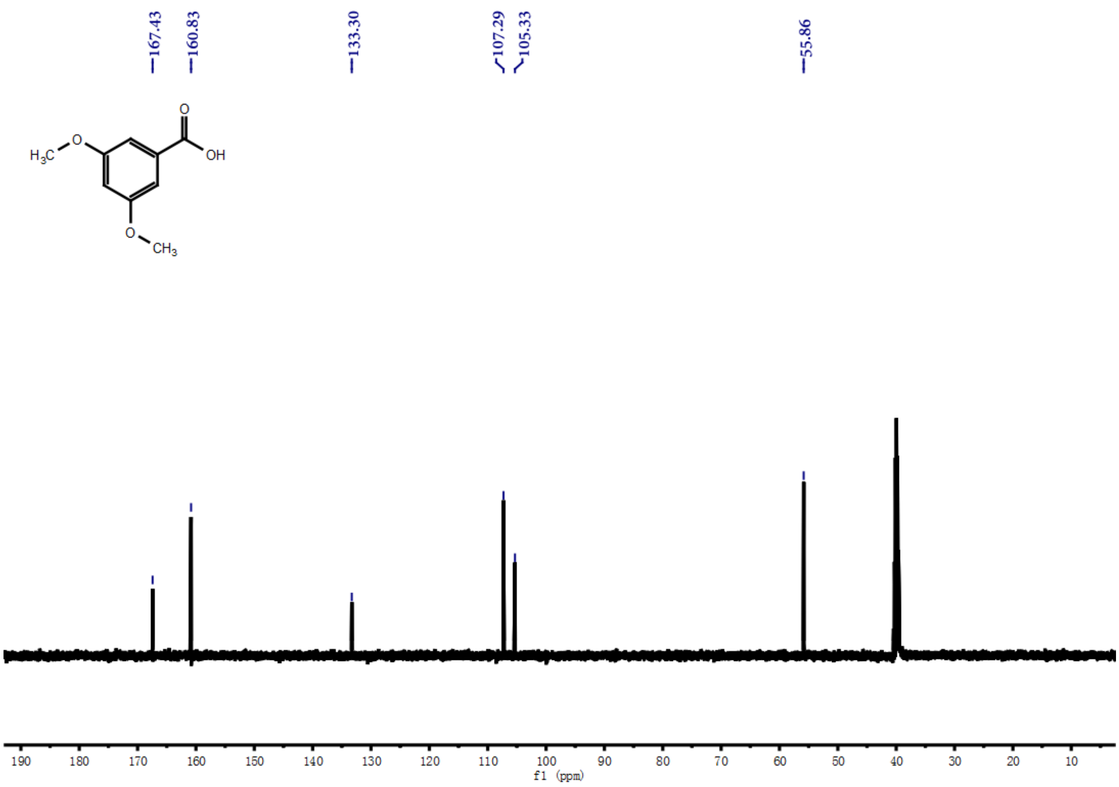
^{1}H NMR spectra of 20 (500 MHz, DMSO-d_6)



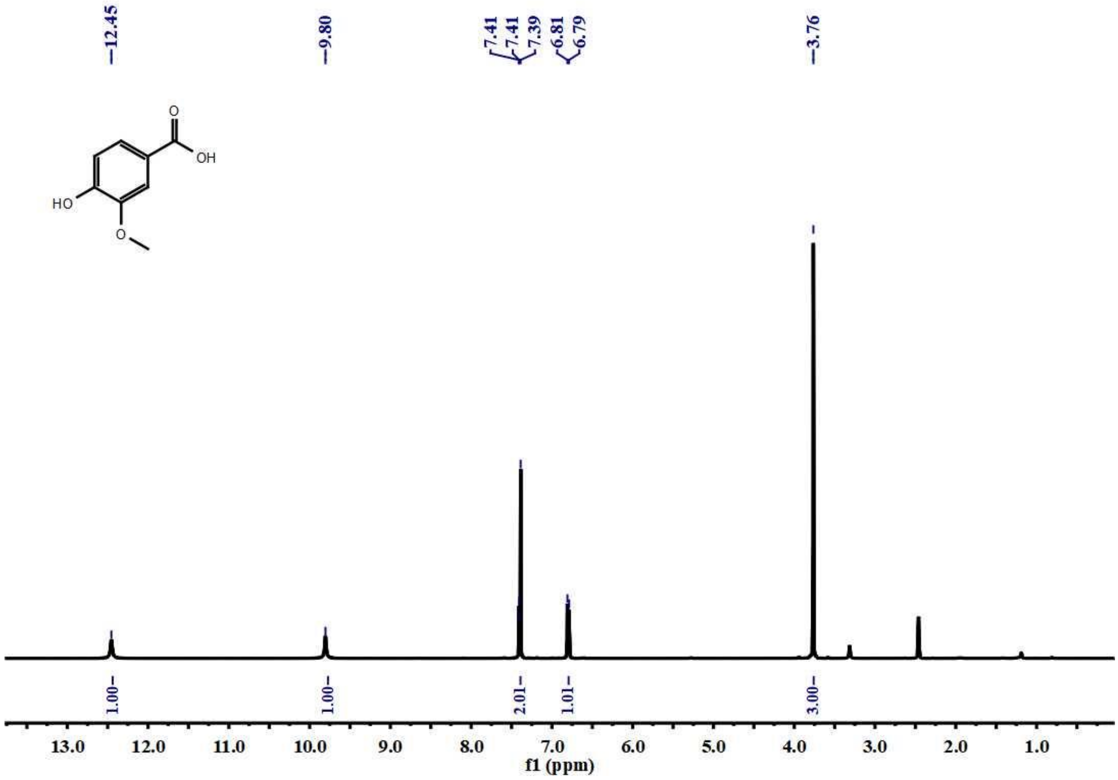
^{13}C NMR spectra of 20 (125 MHz, DMSO-d_6)



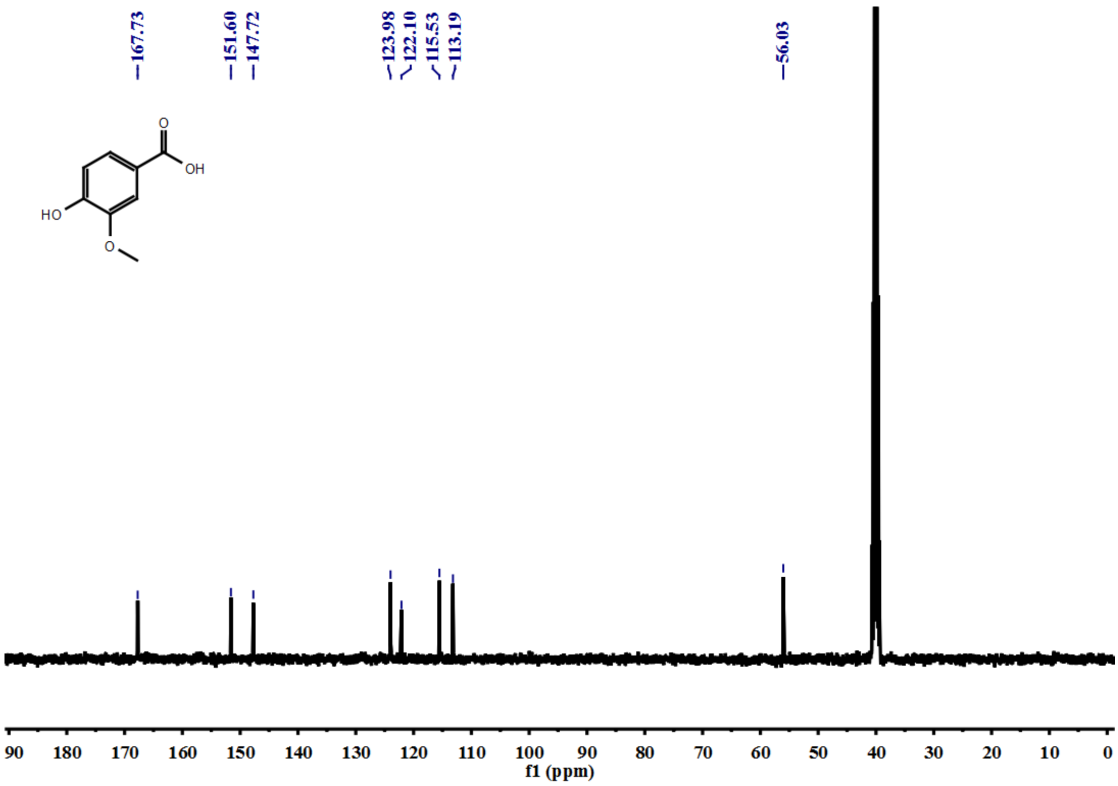
[1]H NMR spectra of 21 (500 MHz, DMSO-d_6)



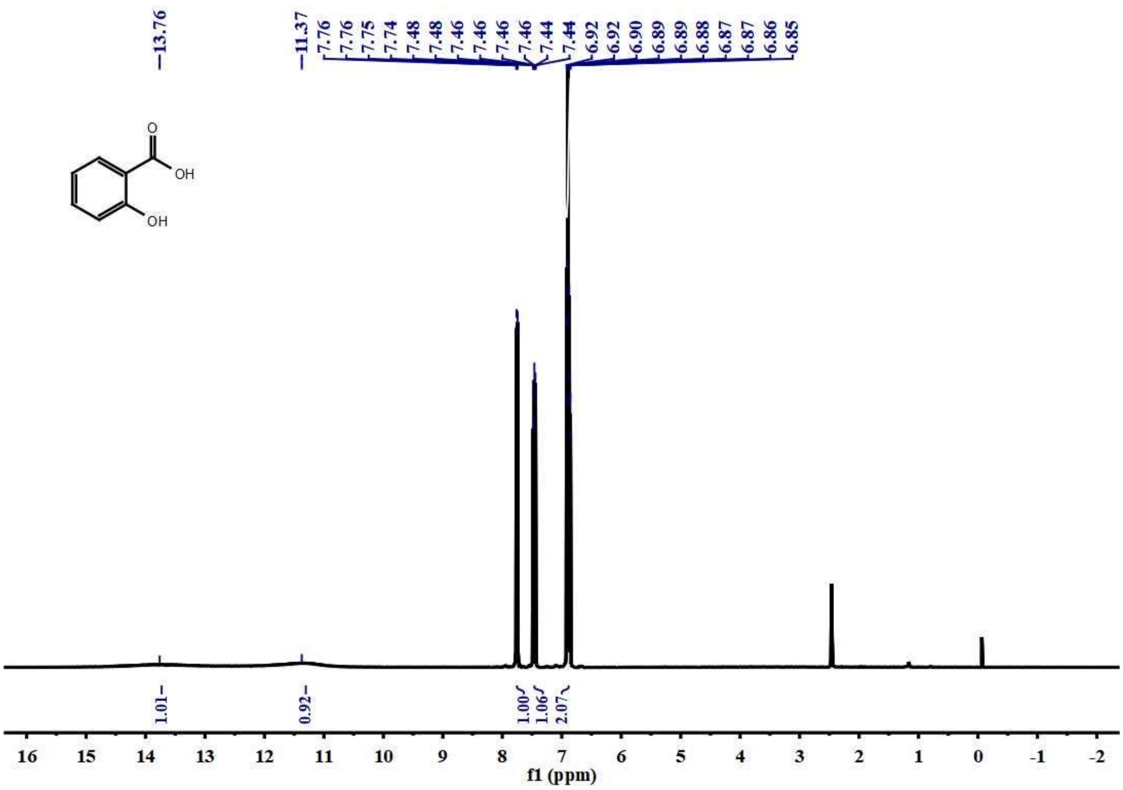
[13]C NMR spectra of 21 (125 MHz, DMSO-d_6)



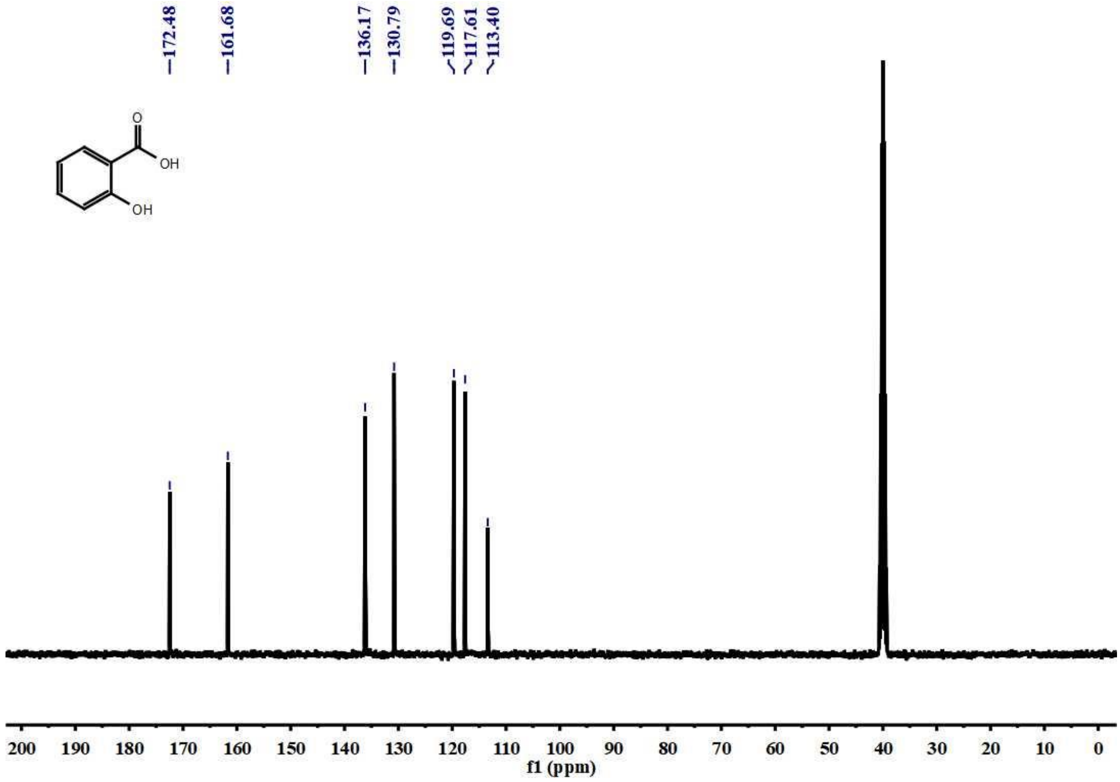
^1H NMR spectra of 22 (500 MHz, DMSO-d_6)



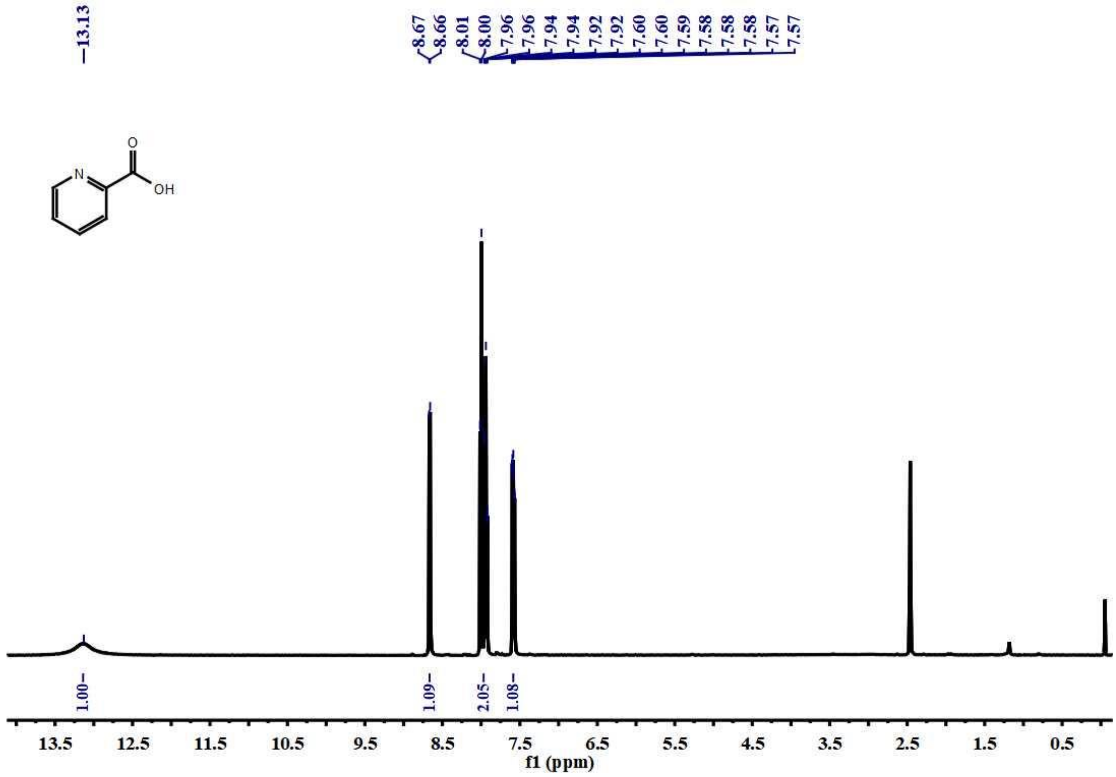
^{13}C NMR spectra of 22 (125 MHz, DMSO-d_6)



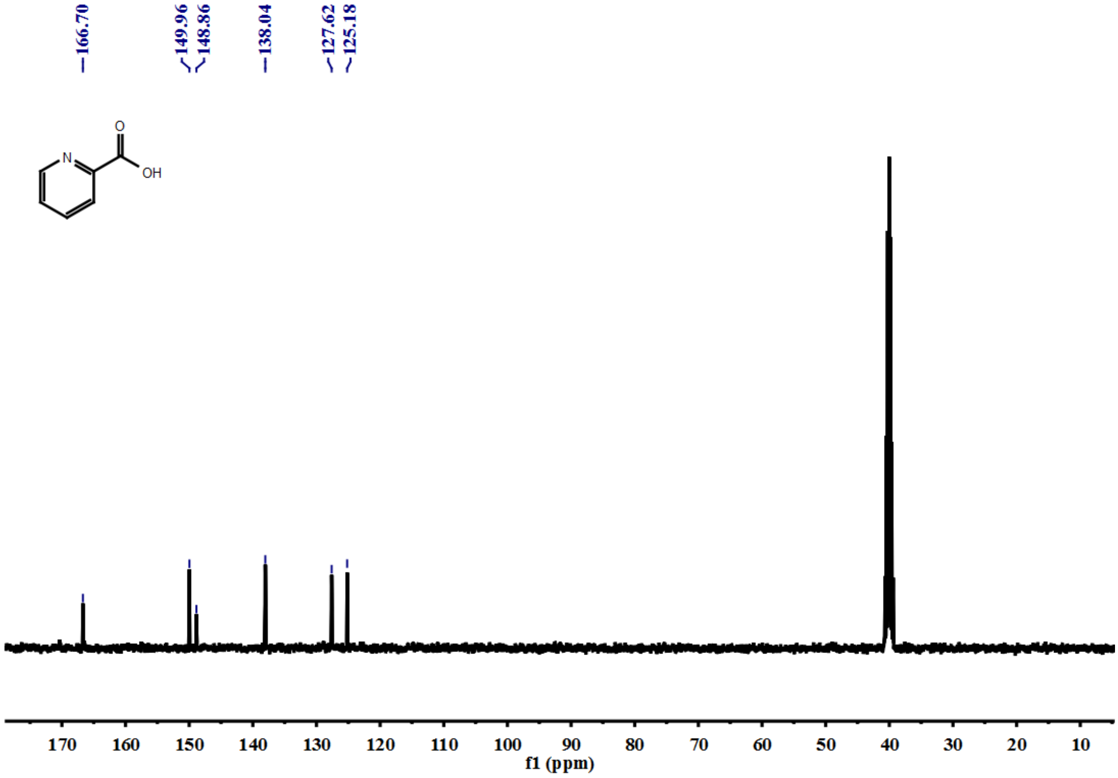
[1]H NMR spectra of 23 (500 MHz, DMSO-d_6)



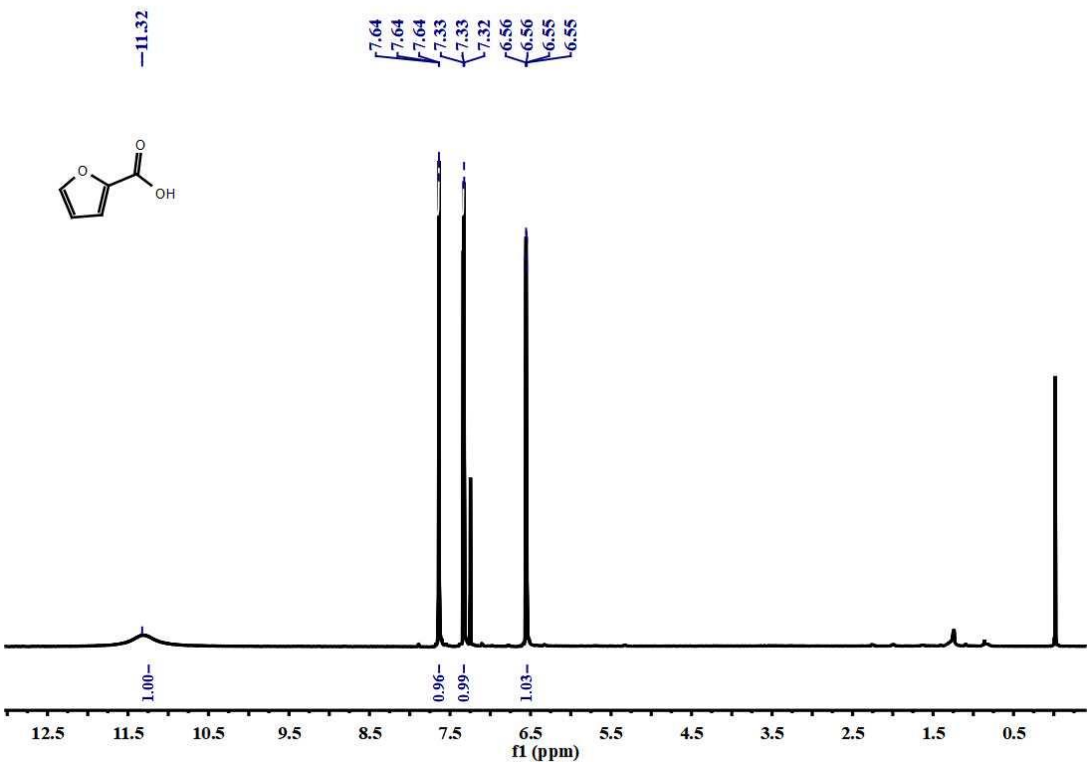
[13]C NMR spectra of 23 (125 MHz, DMSO-d_6)



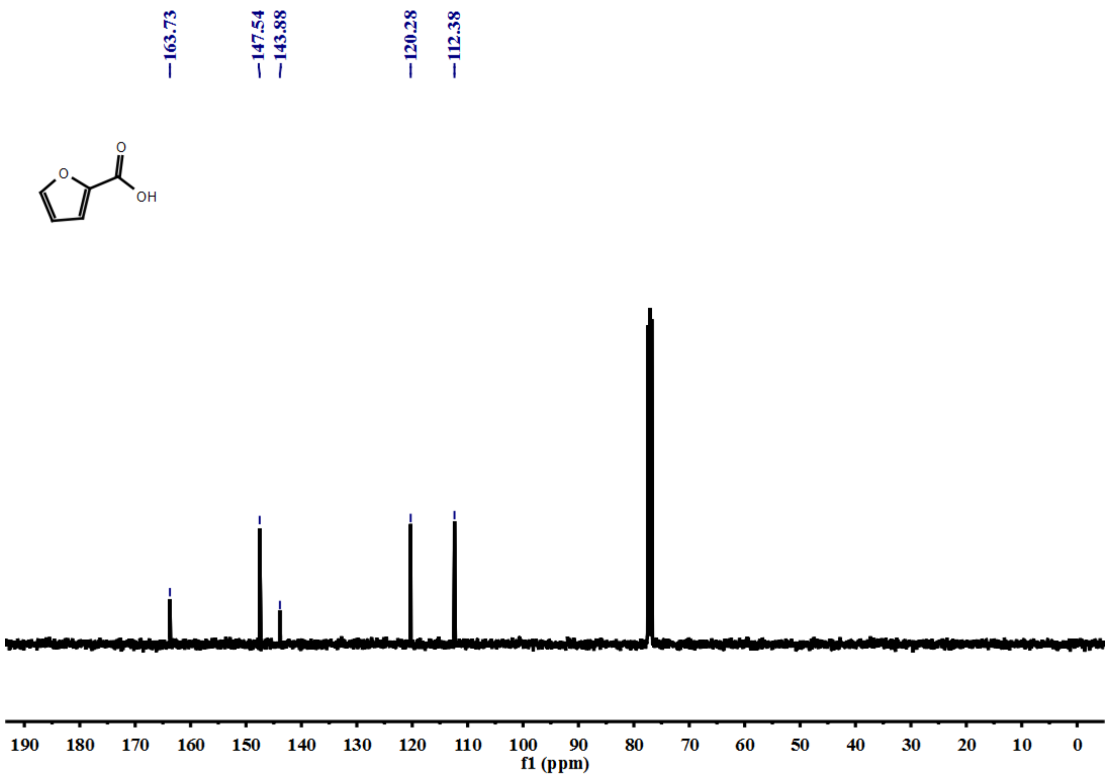
[1]H NMR spectra of 24 (500 MHz, DMSO-d_6)



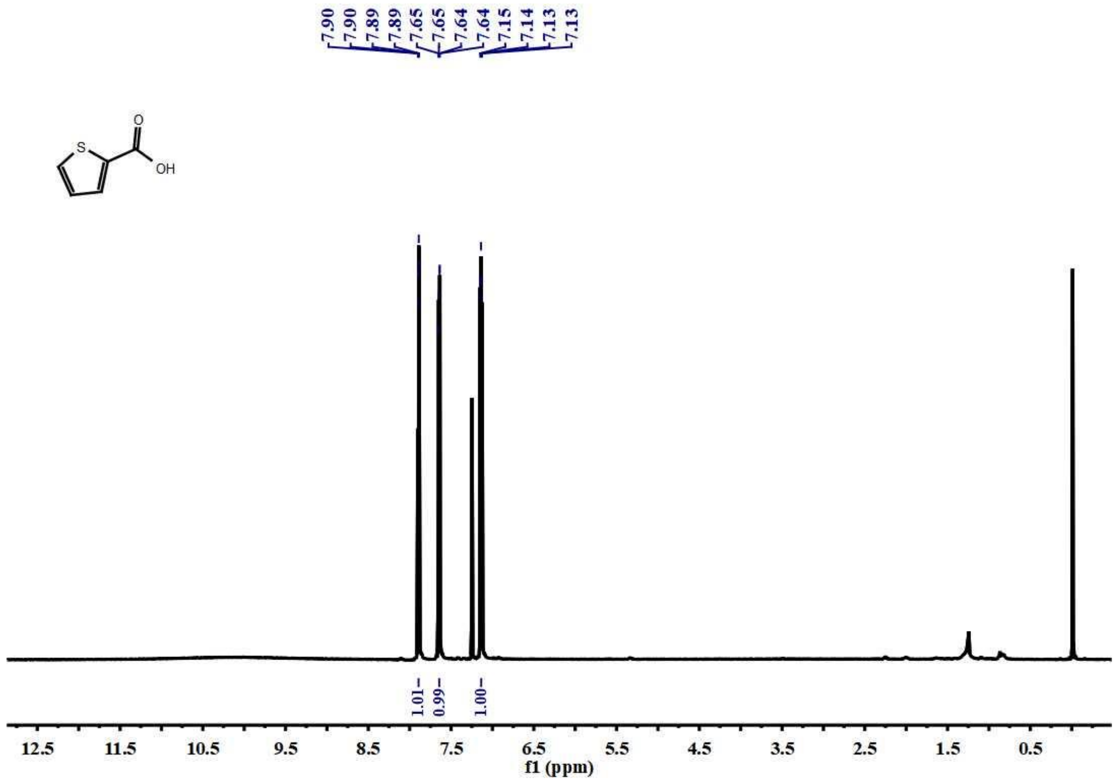
[13]C NMR spectra of 24 (125 MHz, DMSO-d_6)



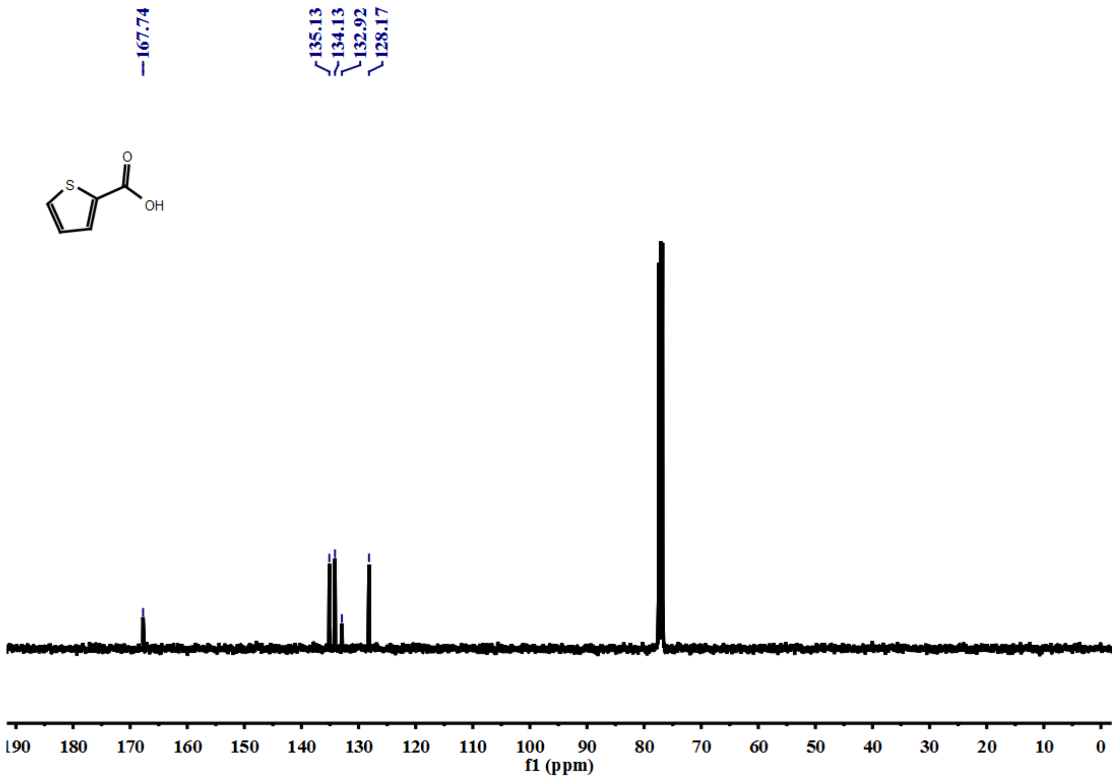
[1]H NMR spectra of 25 (500 MHz, $CDCl_3$)



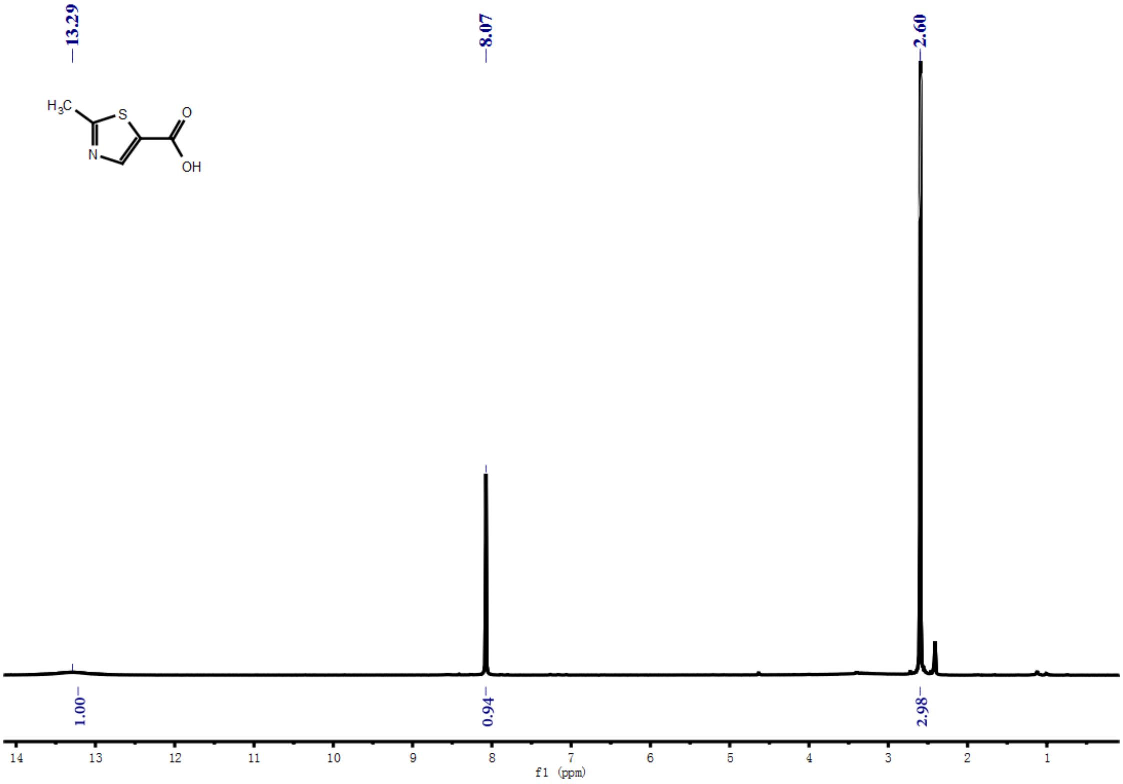
[13]C NMR spectra of 25 (125 MHz, $CDCl_3$)



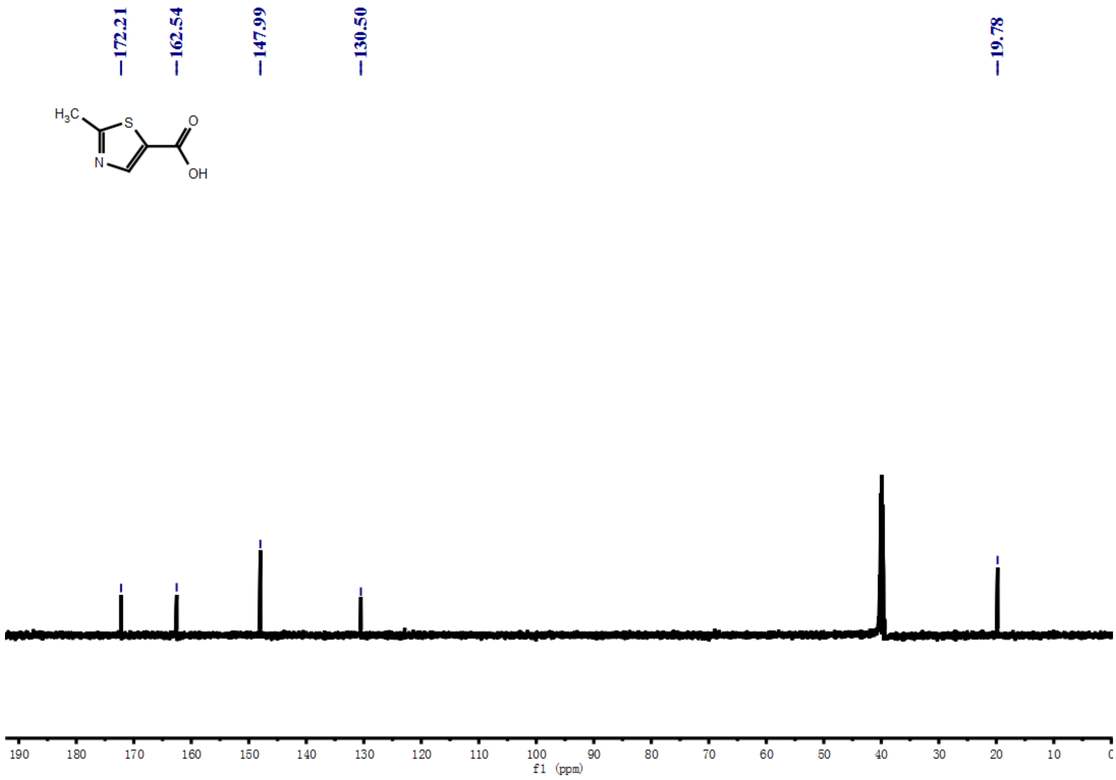
[1]H NMR spectra of 26 (500 MHz, $CDCl_3$)



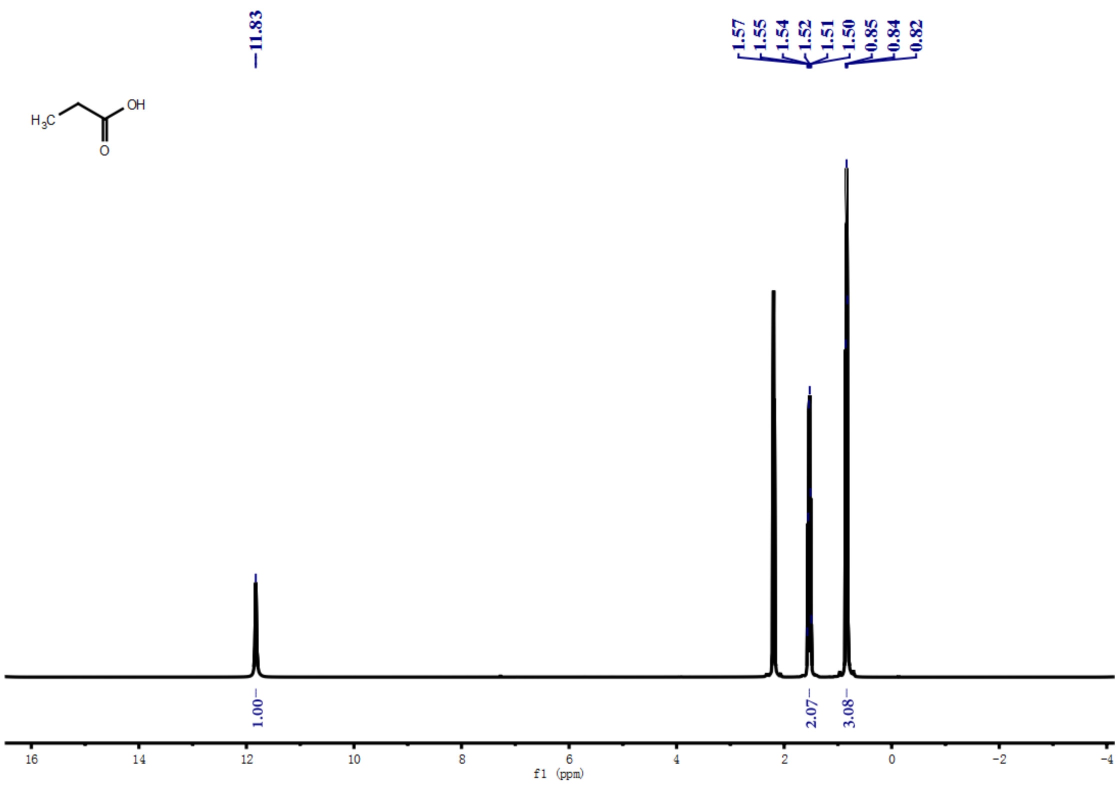
[13]C NMR spectra of 26 (125 MHz, $CDCl_3$)



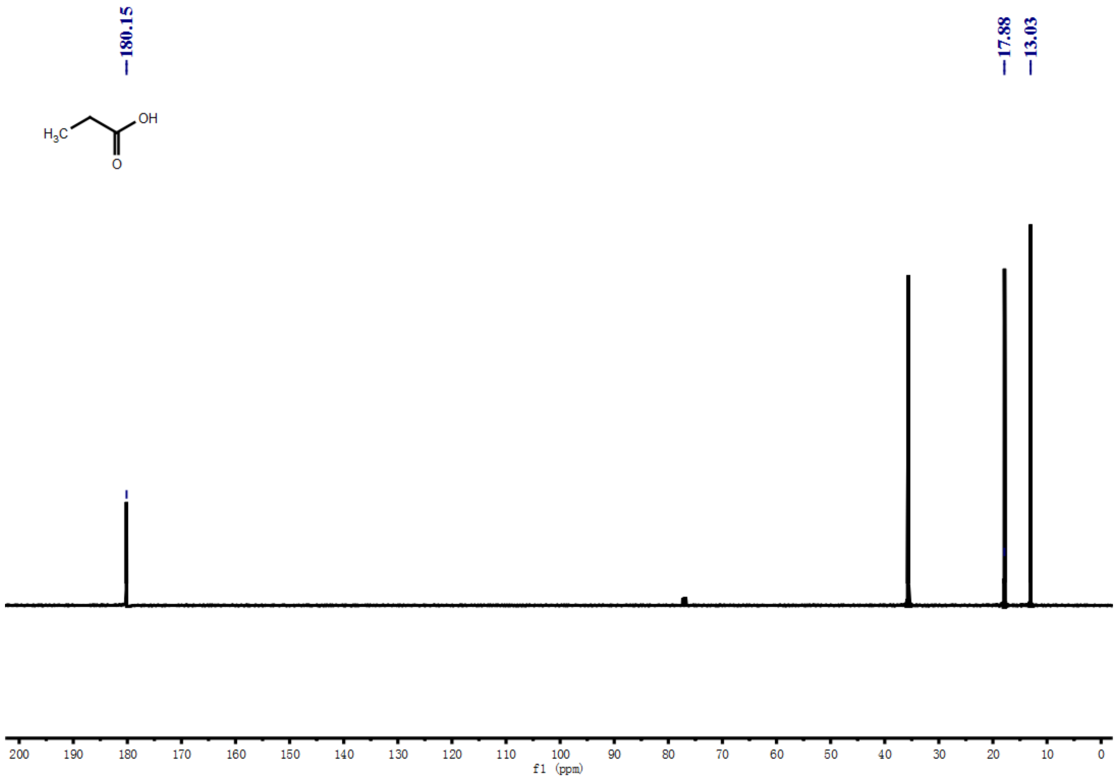
^{1}H NMR spectra of 27 (500 MHz, DMSO-d_6)



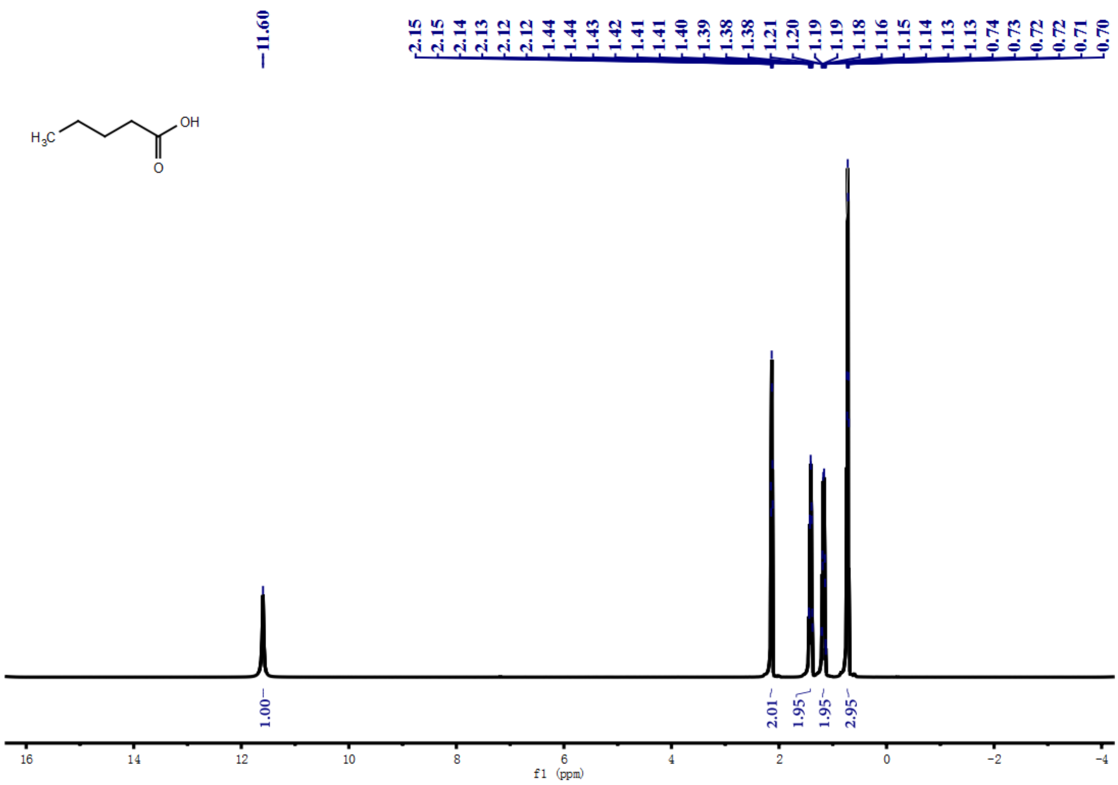
^{13}C NMR spectra of 27 (125 MHz, DMSO-d_6)



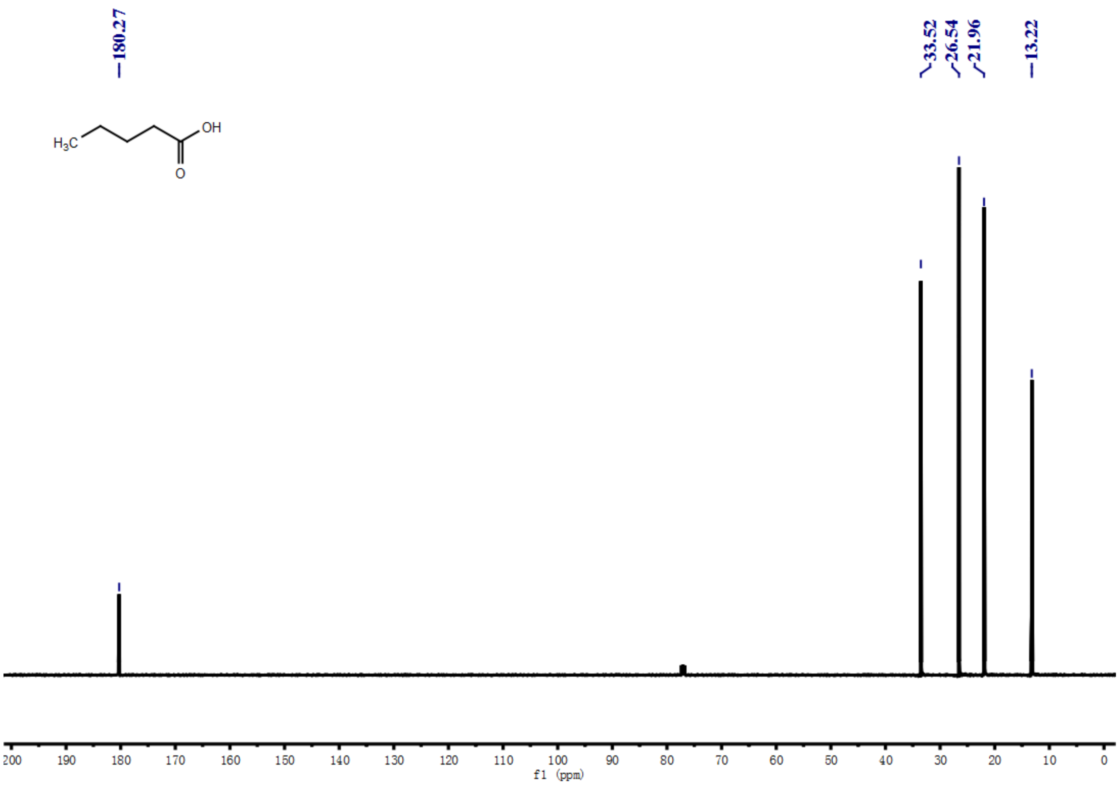
^1H NMR spectra of 28 (500 MHz, $CDCl_3$)



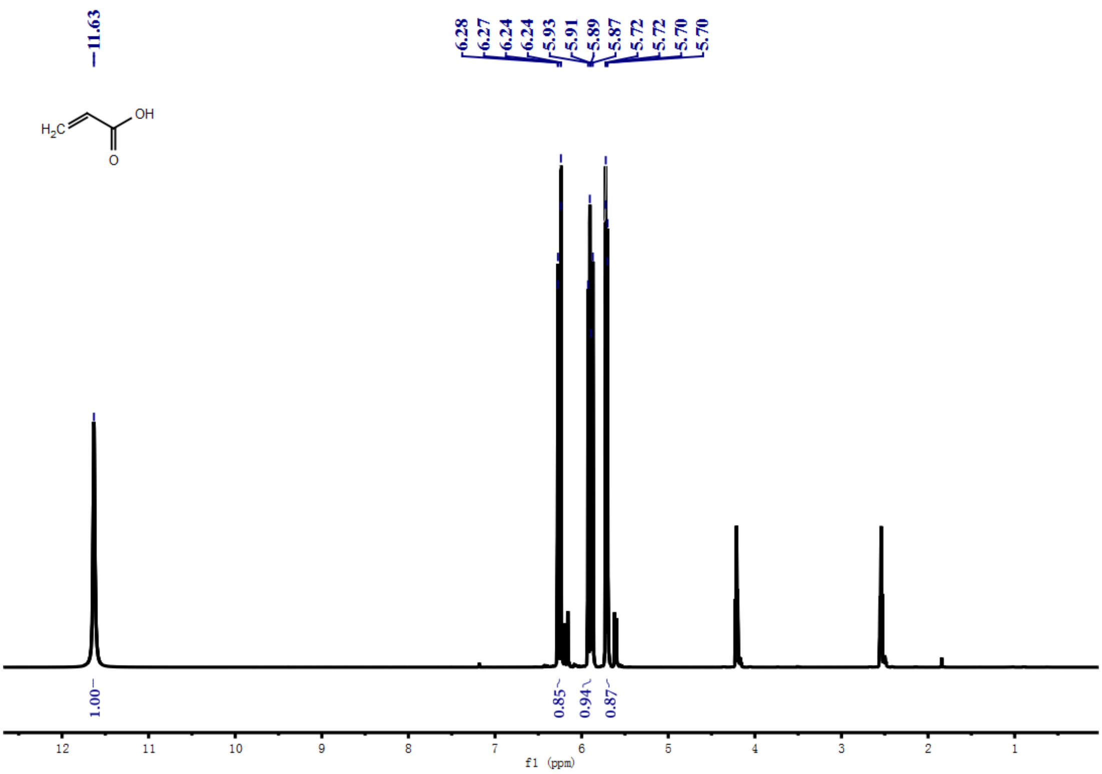
^{13}C NMR spectra of 28 (125 MHz, $CDCl_3$)



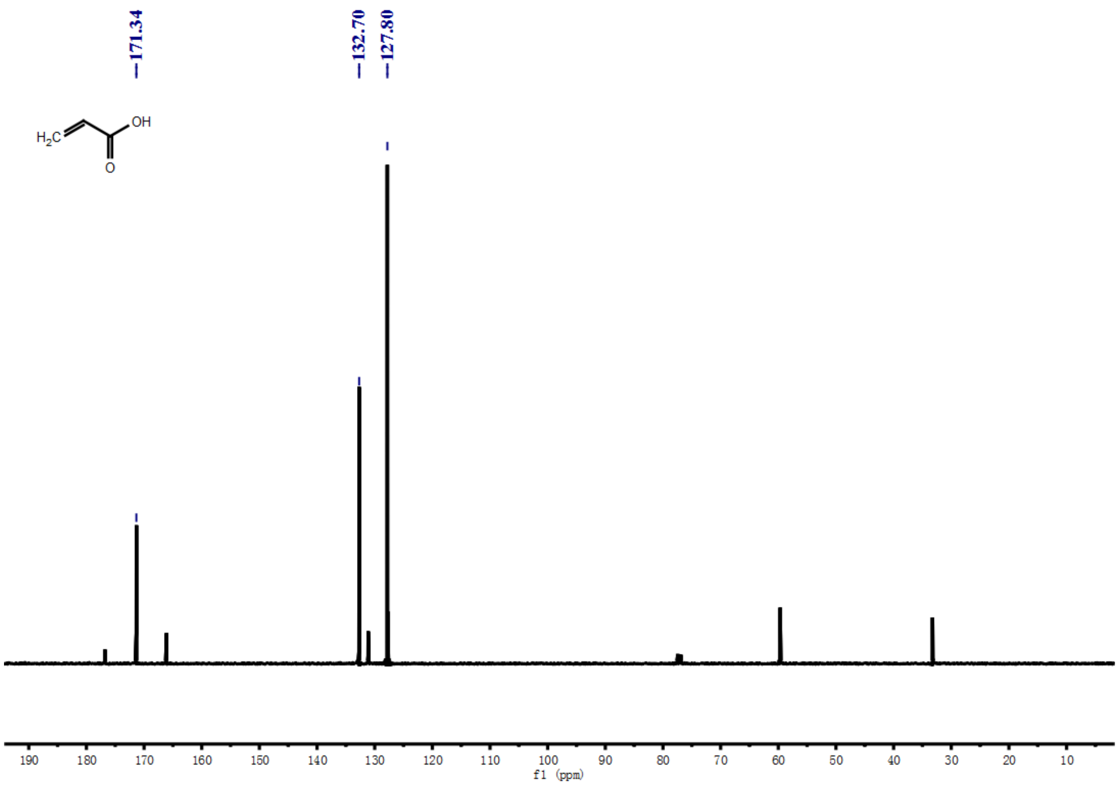
[1]H NMR spectra of 29 (500 MHz, $CDCl_3$)



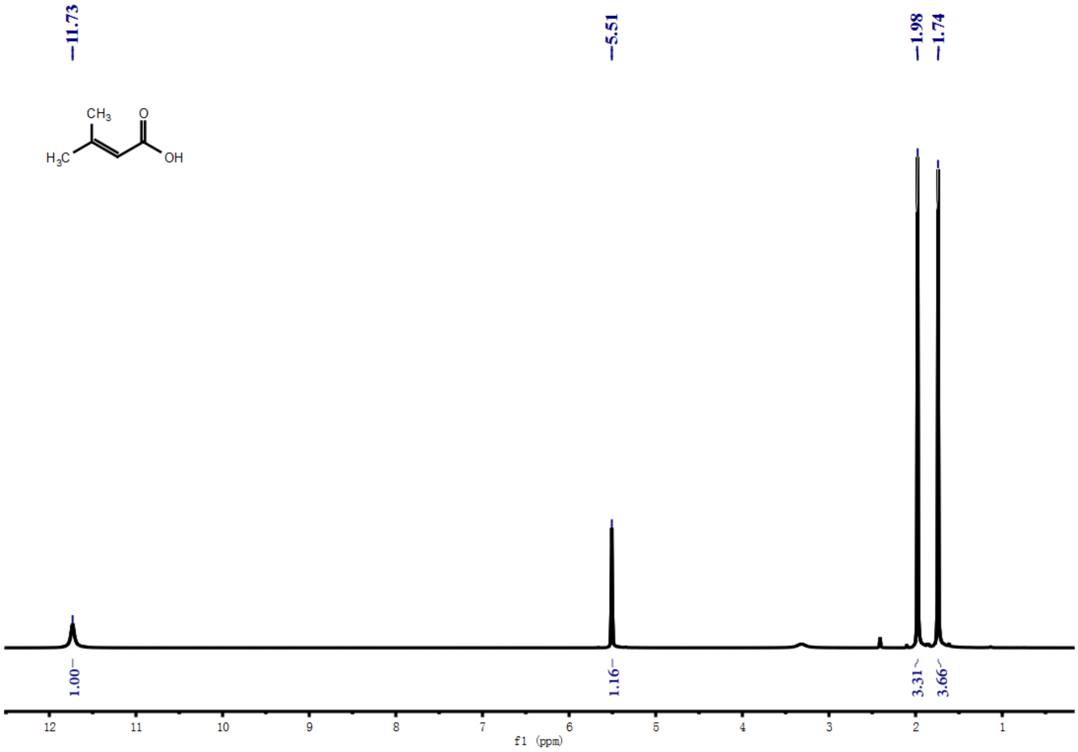
[13]C NMR spectra of 29 (125 MHz, $CDCl_3$)



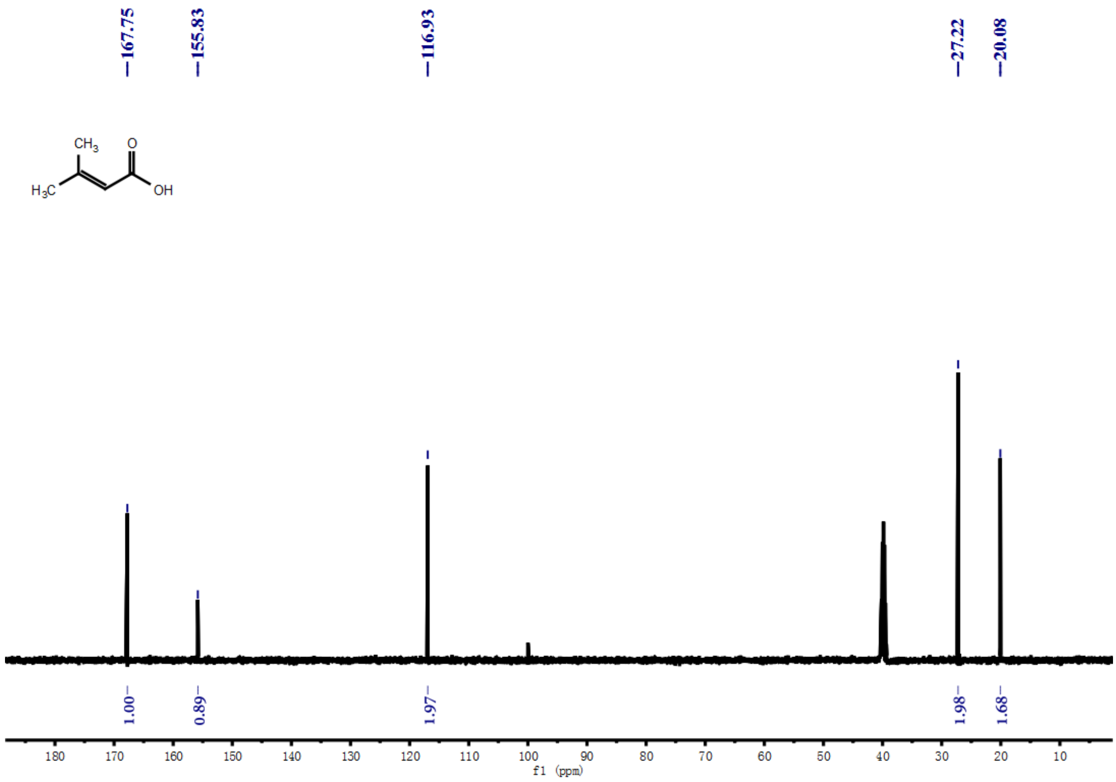
^{1}H NMR spectra of 30 (500 MHz, $CDCl_3$)



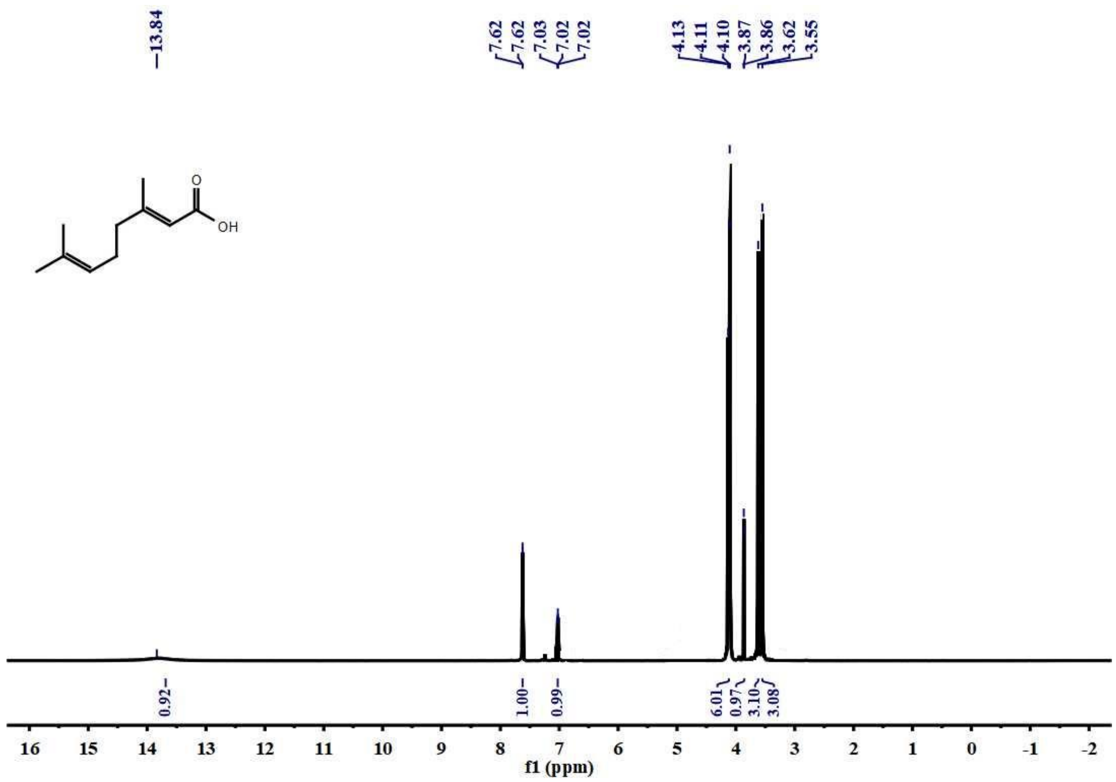
^{13}C NMR spectra of 30 (125 MHz, $CDCl_3$)



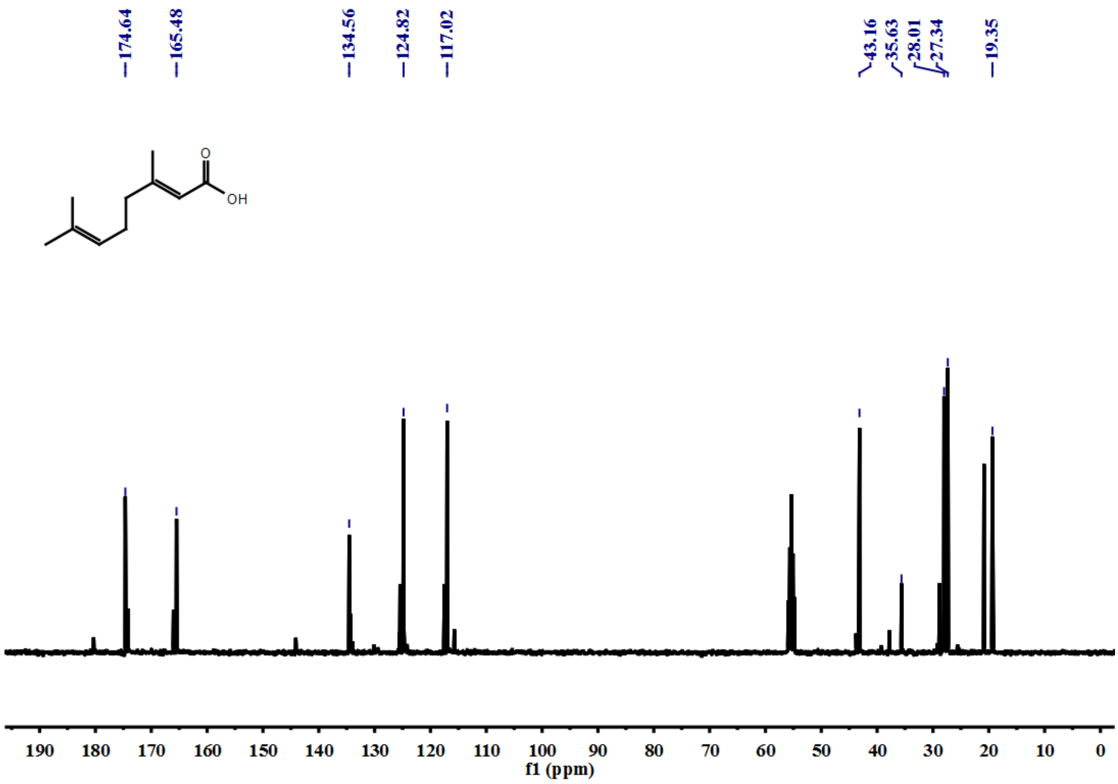
^{1}H NMR spectra of 31 (500 MHz, DMSO-d_6)



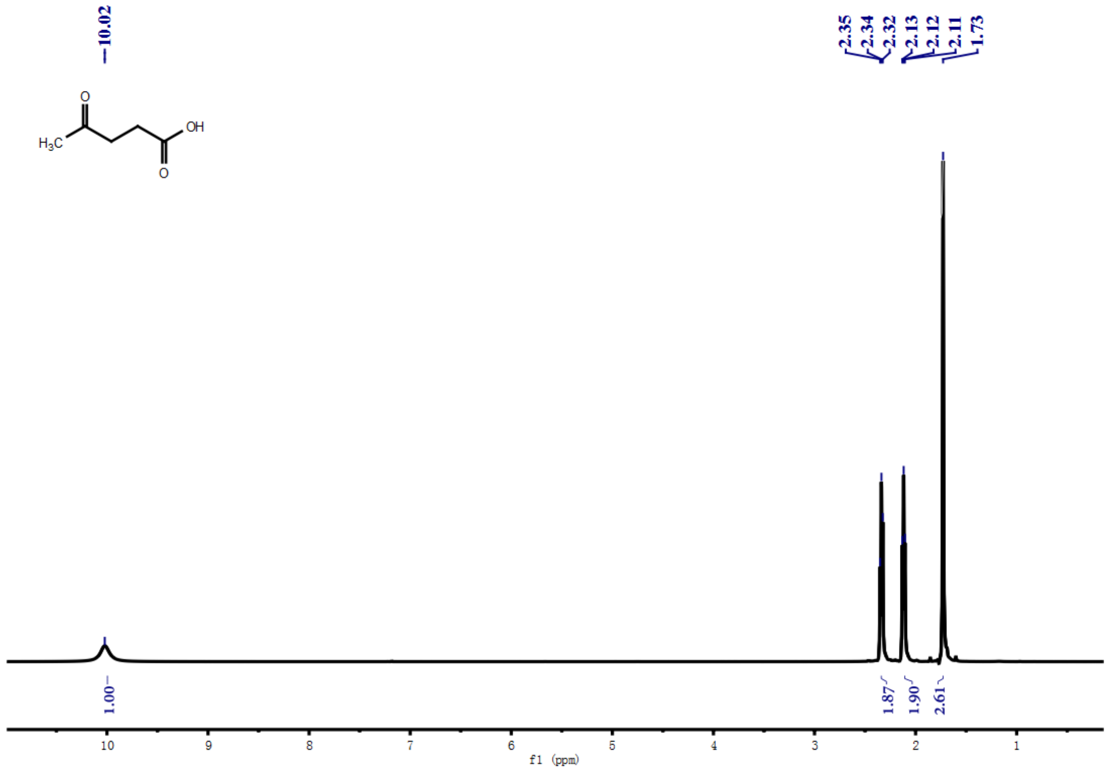
^{13}C NMR spectra of 31 (125 MHz, DMSO-d_6)



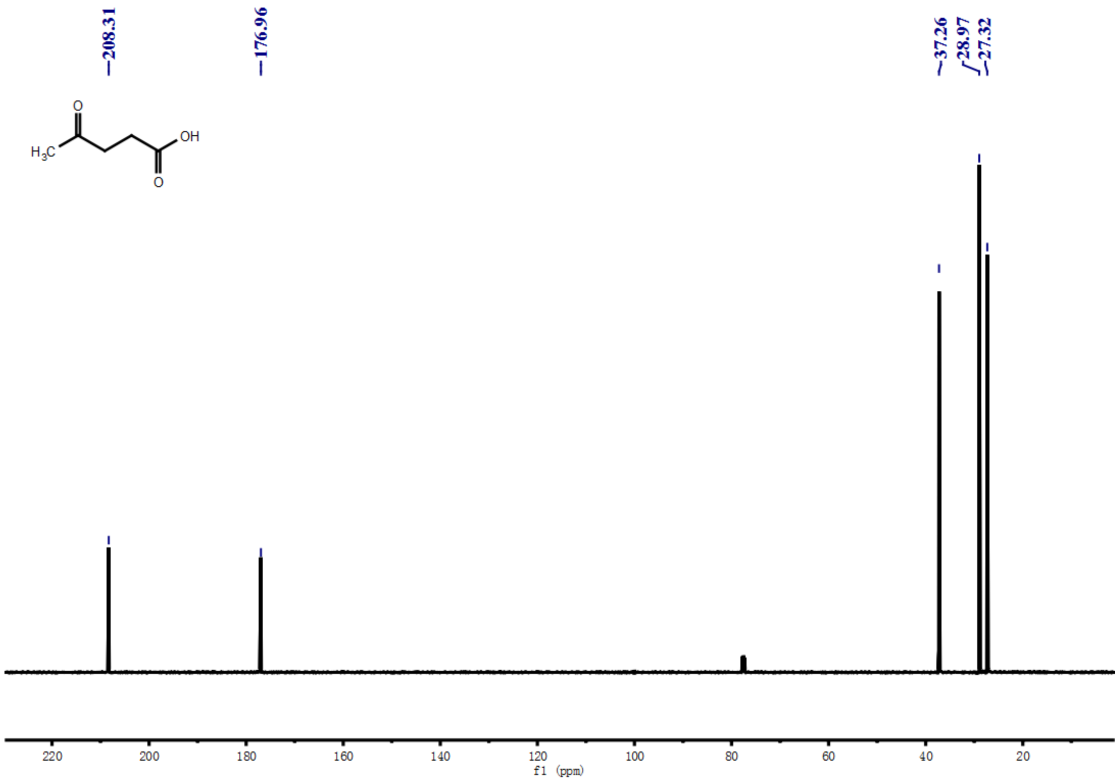
[1]H NMR spectra of 32 (500 MHz, $CDCl_3$)



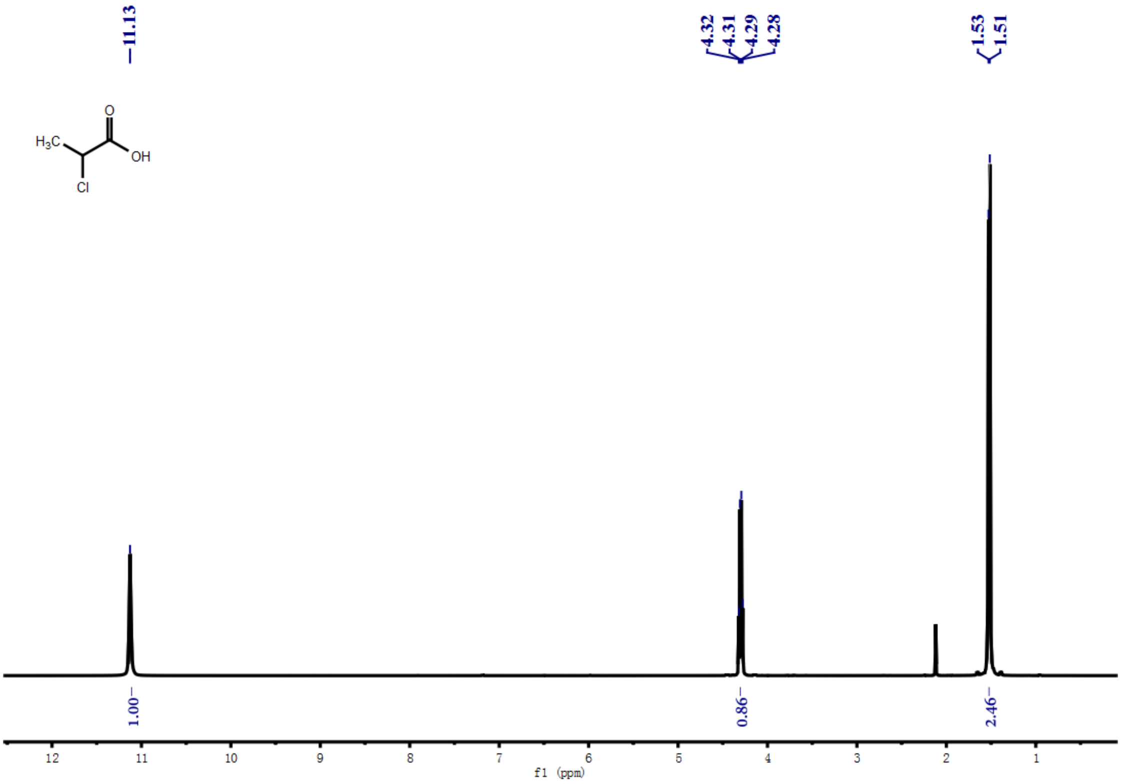
[13]C NMR spectra of 32 (125 MHz, $CDCl_3$)



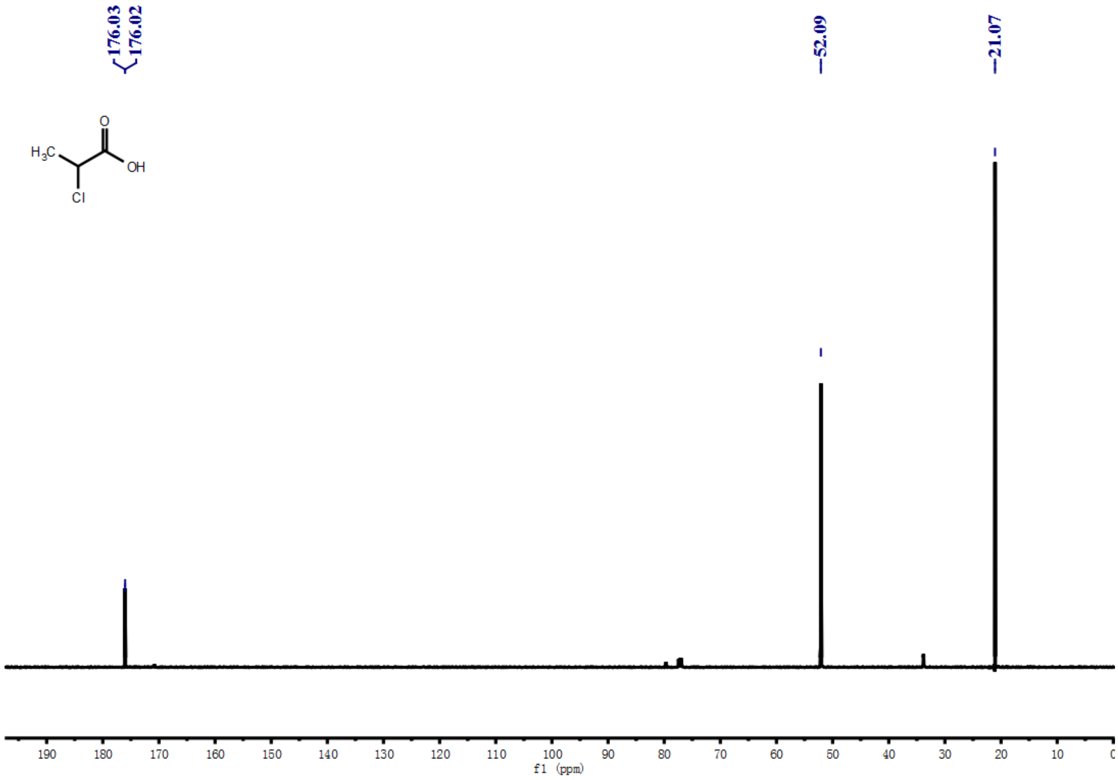
^{1}H NMR spectra of 33 (500 MHz, $CDCl_3$)



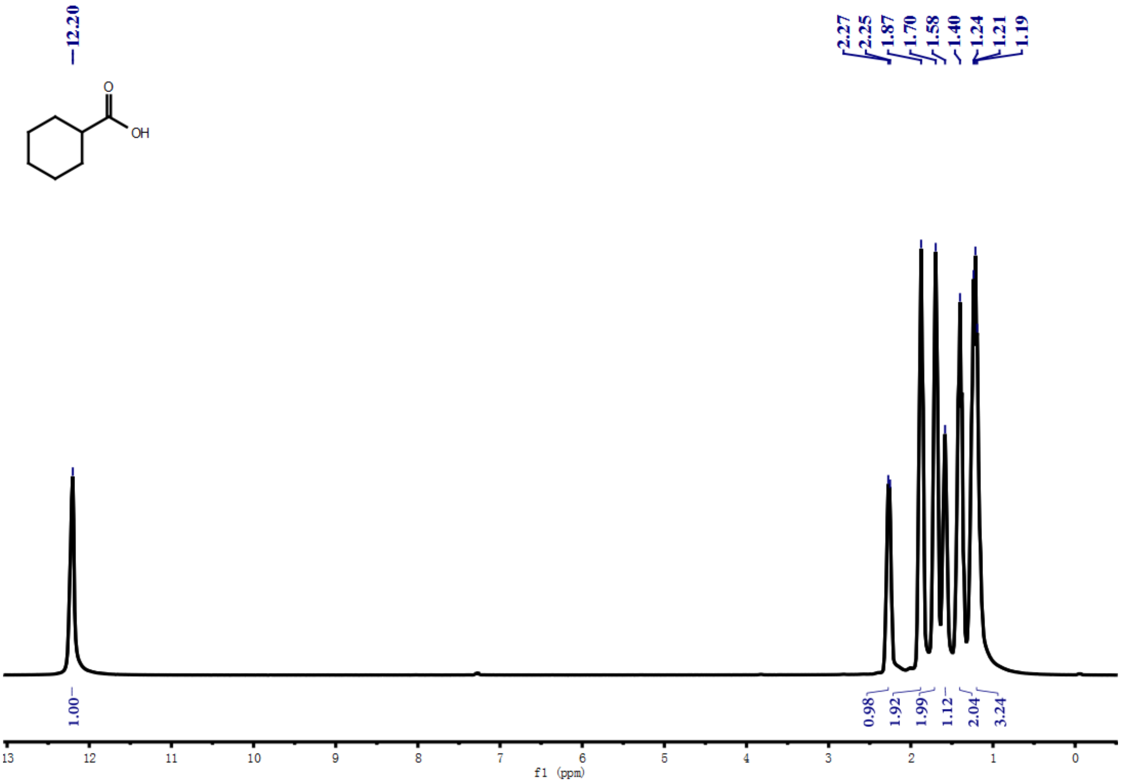
^{13}C NMR spectra of 33 (125 MHz, $CDCl_3$)



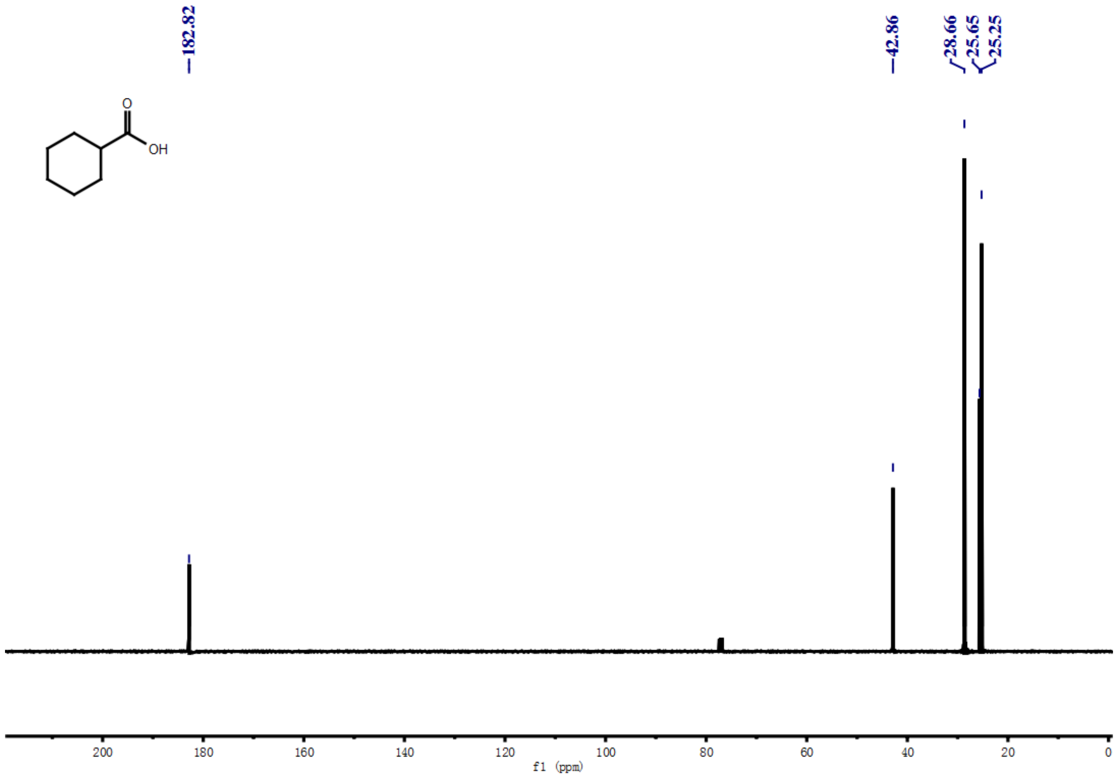
^1H NMR spectra of 34 (500 MHz, $CDCl_3$)



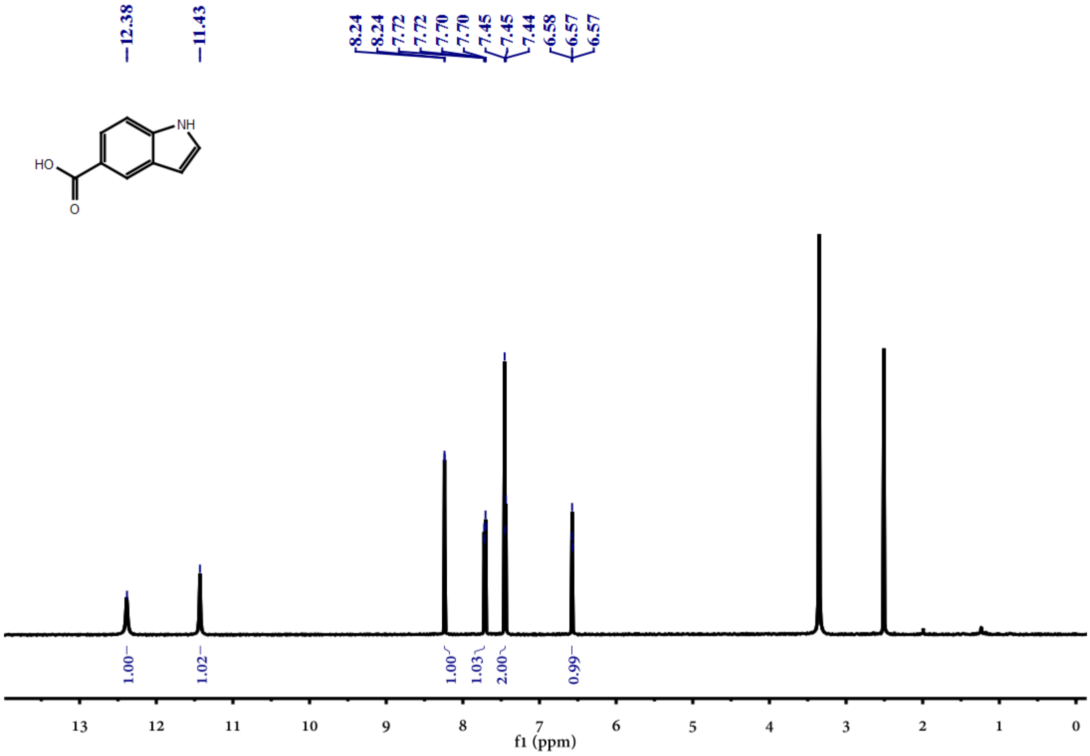
^{13}C NMR spectra of 34 (125 MHz, $CDCl_3$)



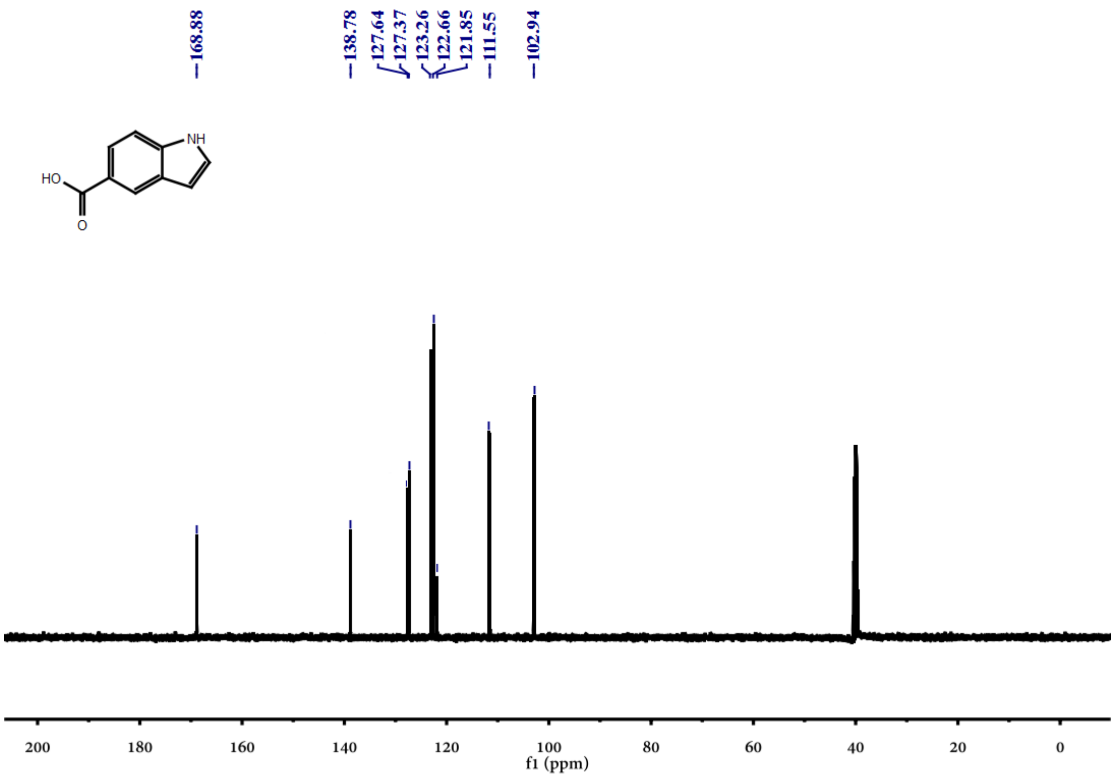
^{1}H NMR spectra of 35 (500 MHz, $CDCl_3$)



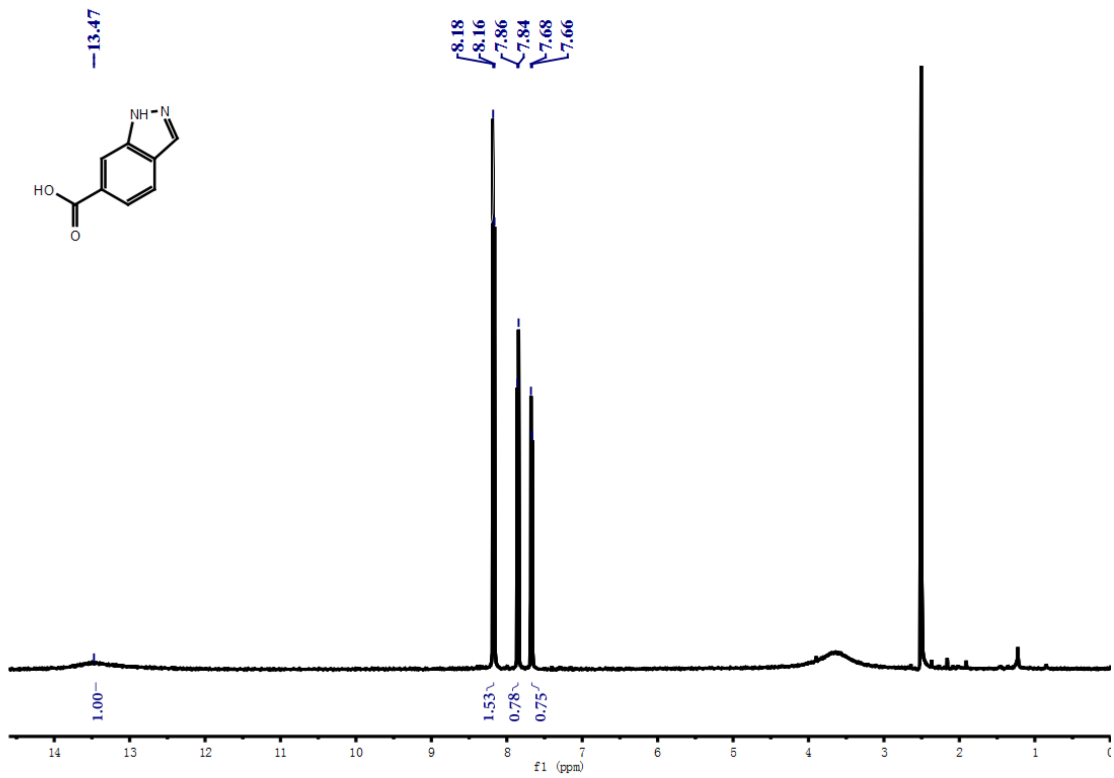
^{13}C NMR spectra of 35 (125 MHz, $CDCl_3$)



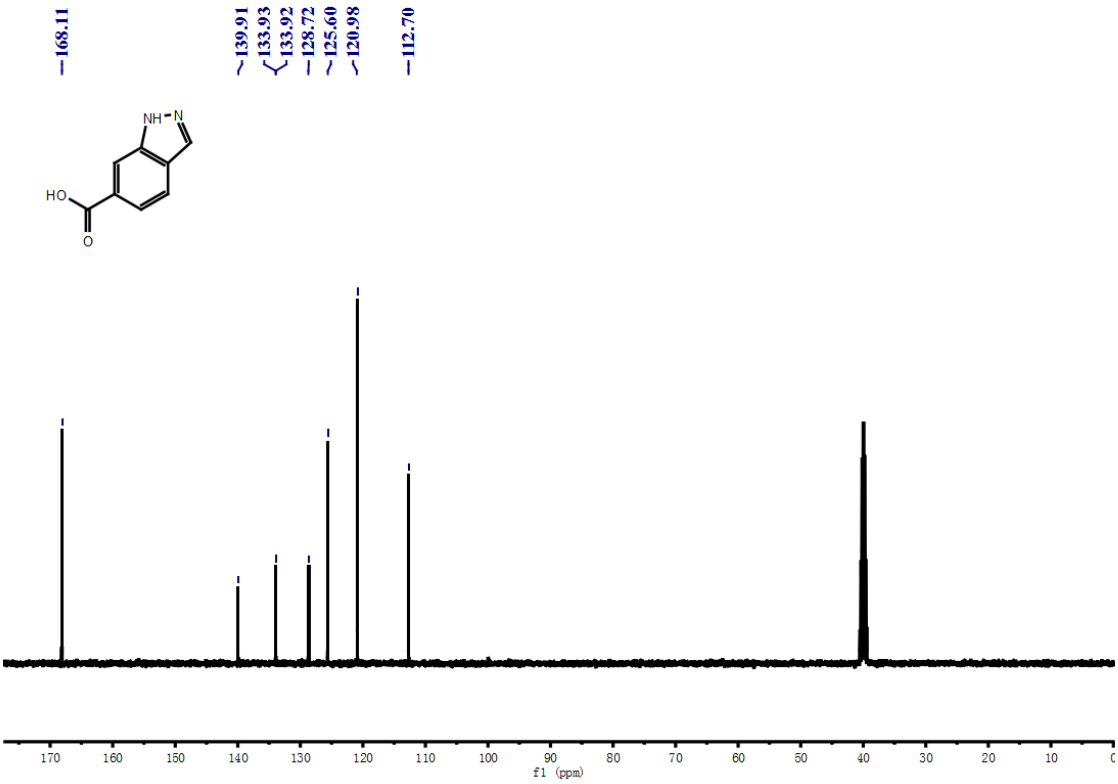
[1]H NMR spectra of 36 (500 MHz, DMSO-d_6)



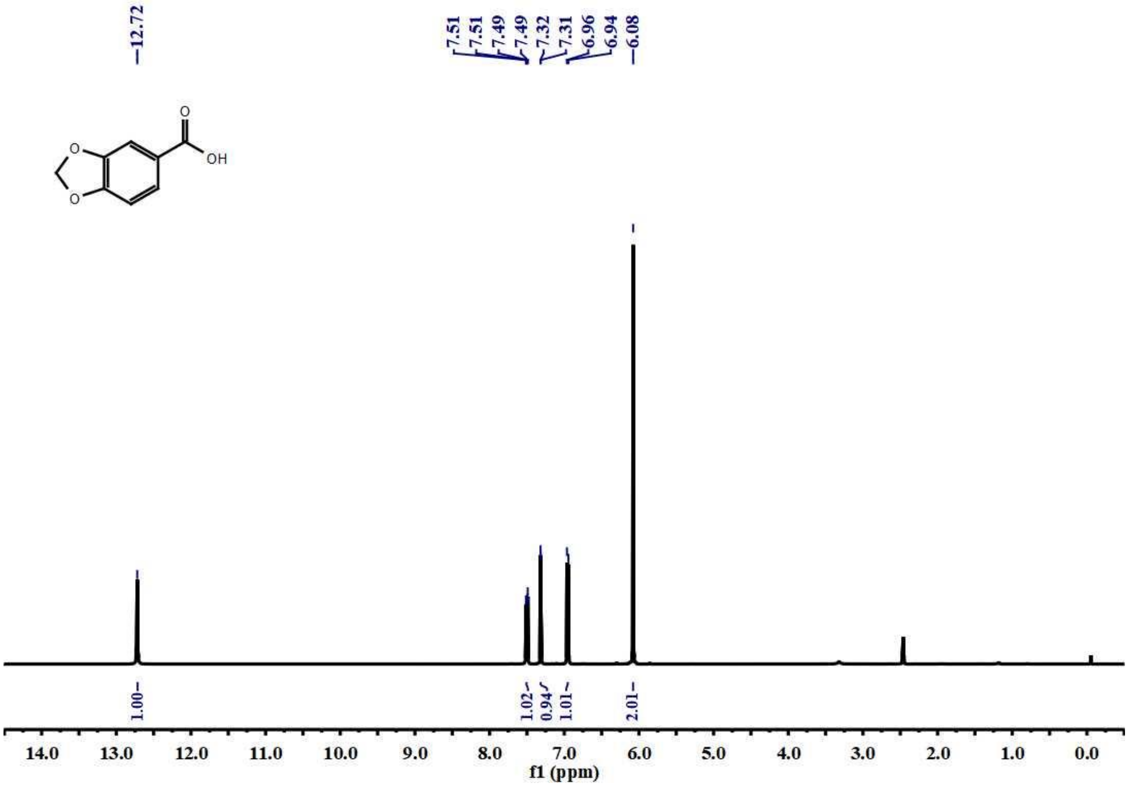
[13]C NMR spectra of 36 (125 MHz, DMSO-d_6)



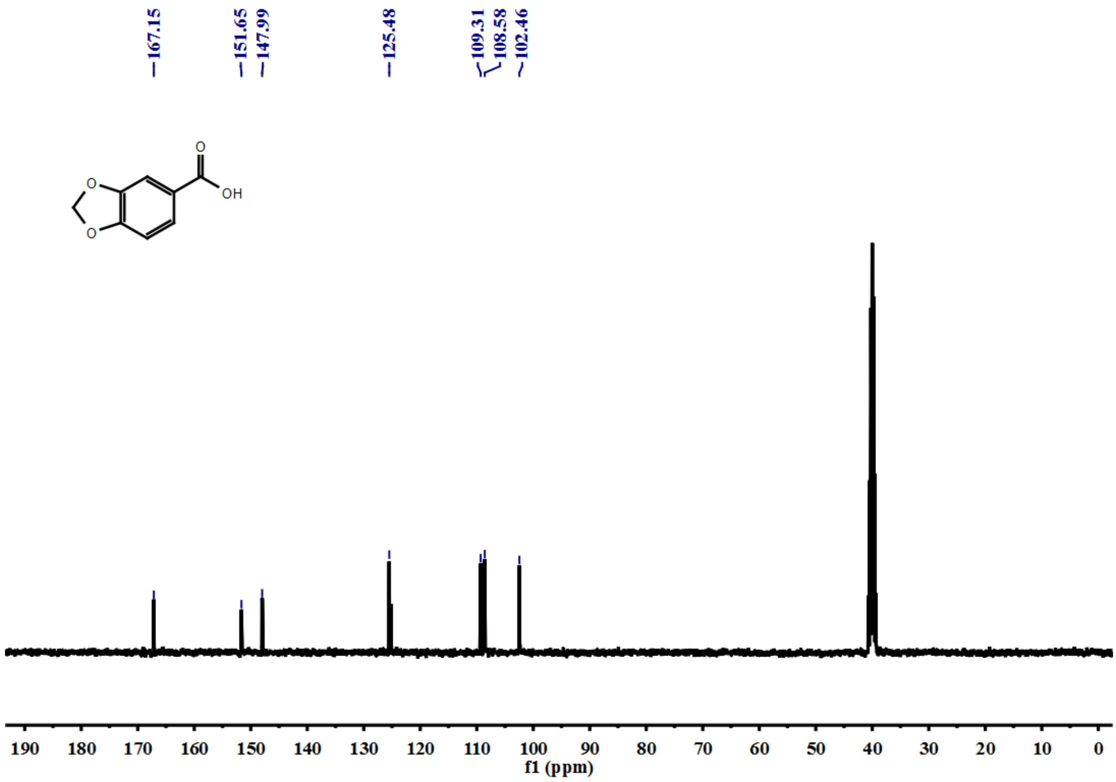
^{1}H NMR spectra of 37 (500 MHz, DMSO-d_6)



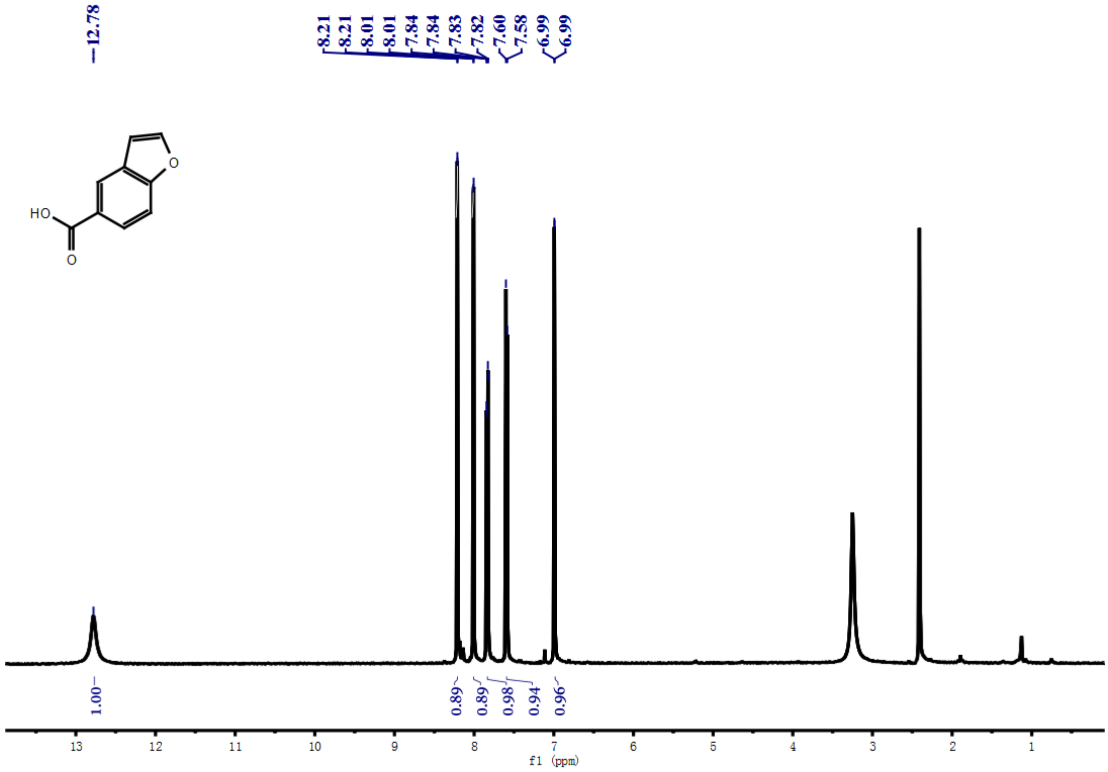
^{13}C NMR spectra of 37 (125 MHz, DMSO-d_6)



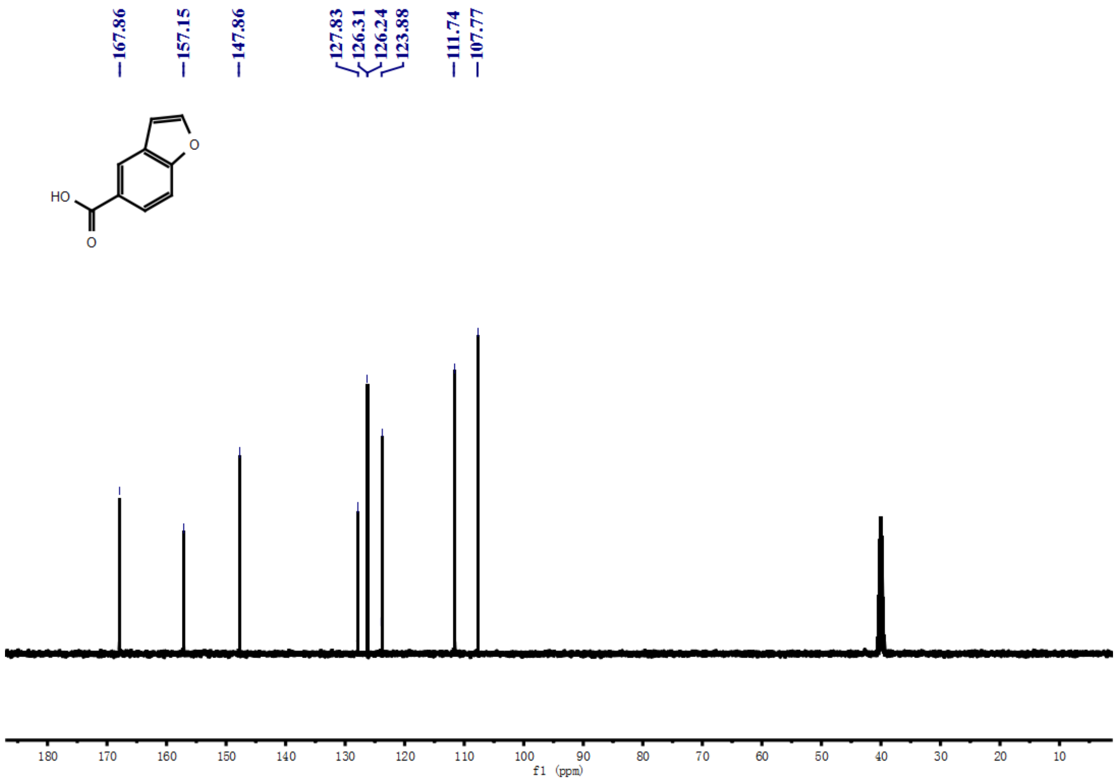
¹H NMR spectra of 38 (500 MHz, DMSO-d_6)



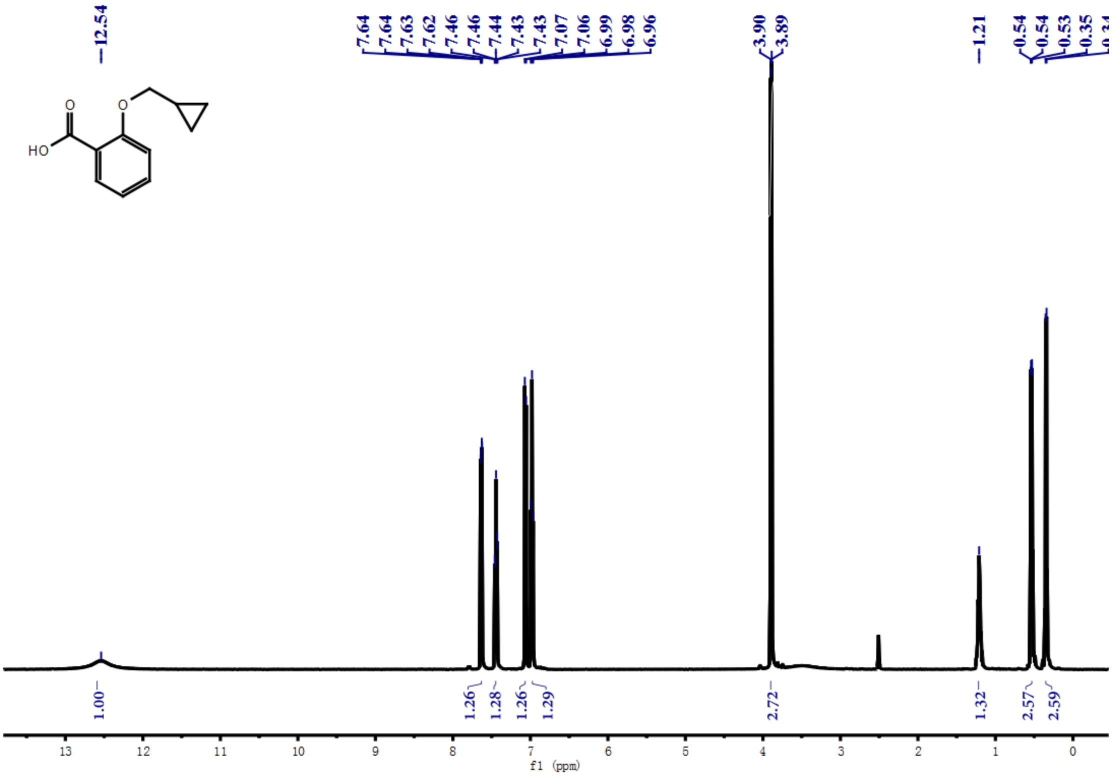
¹³C NMR spectra of 38 (125 MHz, DMSO-d_6)



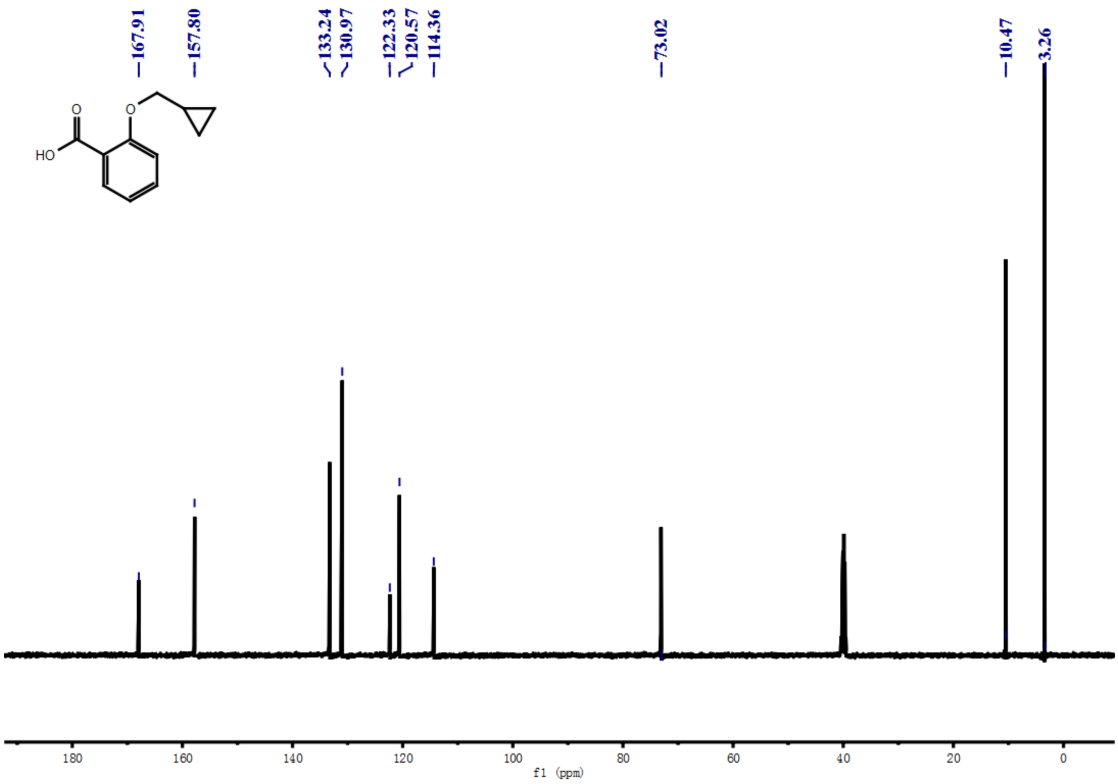
^{1}H NMR spectra of 39 (500 MHz, DMSO-d_6)



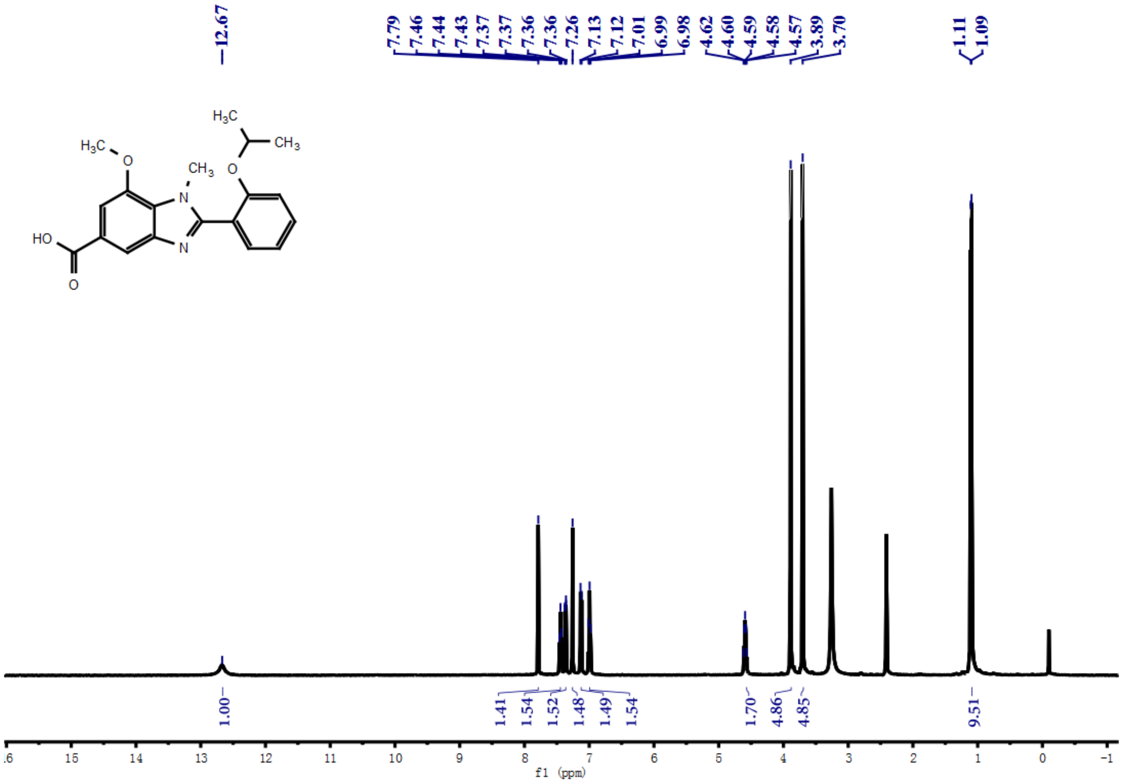
^{13}C NMR spectra of 39 (125 MHz, DMSO-d_6)



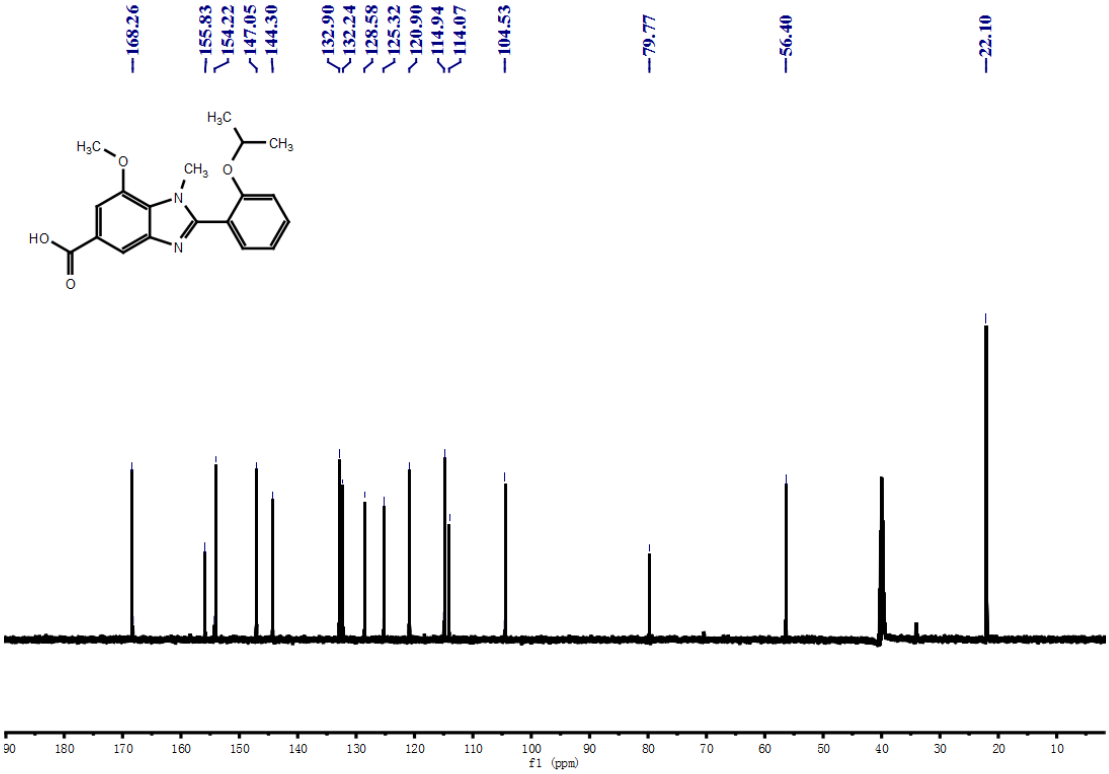
^{1}H NMR spectra of 40 (500 MHz, DMSO-d_6)



^{13}C NMR spectra of 40 (125 MHz, DMSO-d_6)



^{1}H NMR spectra of 41 (500 MHz, DMSO-d_6)



^{13}C NMR spectra of 41 (125 MHz, DMSO-d_6)