Electronic Supplementary Information

Highly Efficient Oxidation of Alcohols to Carboxylic Acids Using Polyoxometalate-supported Chromium(III) Catalyst and CO_2

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I. General information

The catalyst was prepared according to published literature methods.[1] All reagents were purchased from Sigma-Aldrich and Adamas-beta, which were used without further purification. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for proton, 125MHz for carbon) spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ as solvent in all cases, and chemical shifts were reported in parts per million (ppm, δ). FT-IR spectra were recorded on a Thermo Fisher Nicolet 6700. XRD were explored on D/max 2200PC of Japan. 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 Stabil wax capillary column (internal diameter = 0.25 mm, 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.

II. Preparation of chromium-catalyst

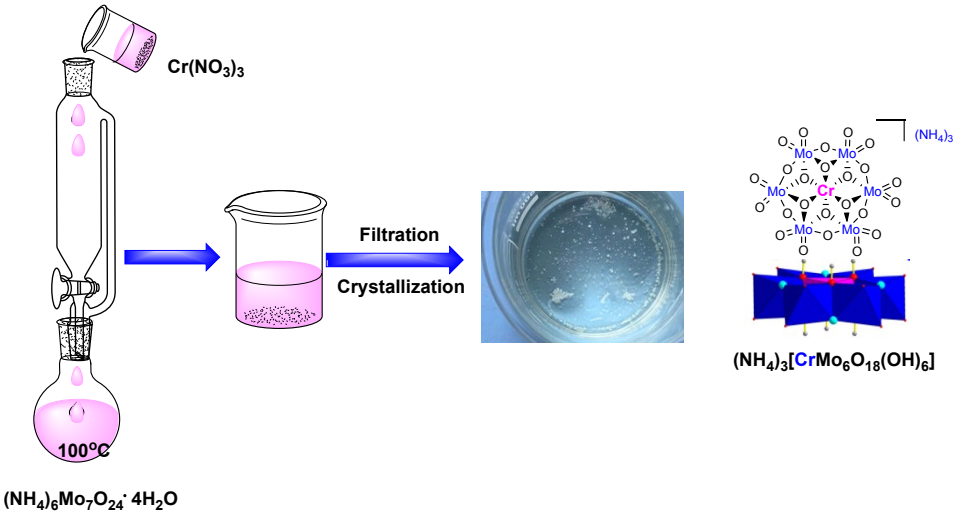


Figure S1. Preparation of $(NH_4)_3[CrMo_6O_{18}(OH)_6]$.

$(NH_4)_3[CrMo_6O_{18}(OH)_6]$ was synthesized according to the previously reported literature[1,2]: First of all, $(NH_4)_6Mo_7O_{24}\times 4H_2O$ (5.3 g, 4.2mmol) was dissolved in water (80ml) and the solution in a flask was put in an oil bath and heated to reflux. Then, $Cr(NO_3)_3$ (1.2 g, 3.0mmol) dissolved in 80ml of water was added dropwise into the above solution. The pH of the solution needed to be controlled at around 2.5 during this process. After the dropwise addition was completed, the mixed solution was further stirred at a constant temperature for 1 hour. Following by, the solution was filtered while hot. The obtained purple-red liquid was left at room temperature for 12 hours and precipitated the purple crystals. After recrystallized, filtered and vacuum dried, the purple crystals (4.9 g) was deposited and collected. IR: 3208.24 (vasNH, m), 1638.98 (δOH m), 1401.73 (δNH, s), 945.18(ν Mo=O, vs), 892.11 (ν Mo=O, vs), 648.03 (ν Mo-O-Mo, vs), 573.00 (ν M-O-Mo, w) cm^{-1}.

III. FT-IR and XRD spectra of catalyst

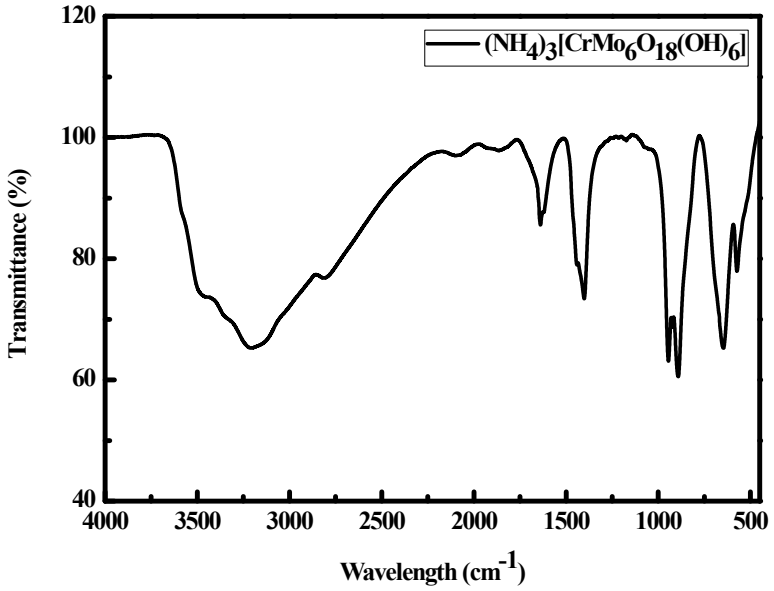


Figure S2. The FT-IR spectra of $(NH_4)_3[CrMo_6O_{18}(OH)_6]$.

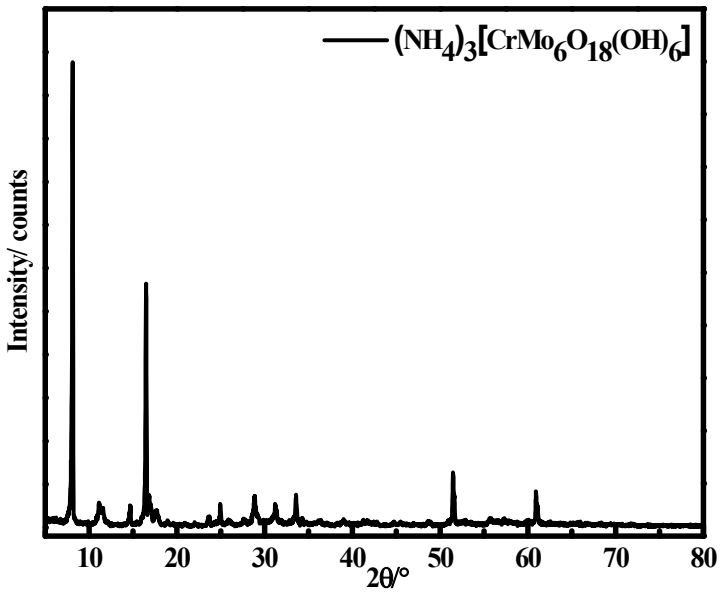
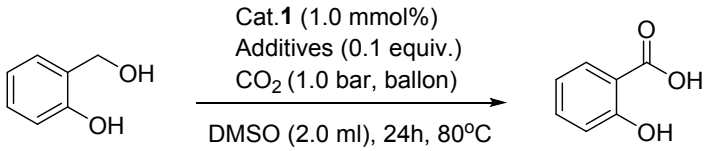


Figure S3. The XRD spectra of $(NH_4)_3[CrMo_6O_{18}(OH)_6]$.

IV. Optimization studies.

Table S1. The effects of conditions[ab]



Entry	Cat. (mol%)	Additives	Solvent	Time(h)	Conversion (%)[b]	Yield (%)[b]
1	1.0	-	DMSO	12	<5	Trace
2	1.0	Na_2SO_4	DMSO	12	21	12
3	1.0	NaF	DMSO	12	13	5
4	1.0	NaCl	DMSO	12	45	36
5	1.0	NaBr	DMSO	12	41	28
6	1.0	$NaNO_2$	DMSO	12	23	14
7	1.0	Na_2CO_3	DMSO	12	48	32
8	1.0	$CaCl_2$	DMSO	12	20	12
9	1.0	$MgCl_2$	DMSO	12	27	20
10	1.0	$ZnCl_2$	DMSO	12	15	4
11	1.0	LiCl	DMSO	12	17	9
12	1.0	KCl	DMSO	12	60	51
13	1.0	NH_4Cl	DMSO	12	12	7
14	1.0	K_3PO_4	DMSO	12	80	70
15	0.5	K_3PO_4	DMSO	12	74	61
16	2.0	K_3PO_4	DMSO	12	75	65
17	1.0	K_3PO_4	Dioxane/DMSO(1:1)	12	26	20
18	1.0	K_3PO_4	Toluene/DMSO(1:1)	12	17	10
19	1.0	K_3PO_4	DMF/DMSO(1:1)	12	13	8
20	1.0	K_3PO_4	MeOH/DMSO(1:1)	12	32	21
21	1.0	K_3PO_4	MeCN/DMSO(1:1)	12	21	15
22[c]	1.0	K_3PO_4	CH_2Cl_2/DMSO(1:1)	12	16	11
23[d]	1.0	K_3PO_4	THF/DMSO(1:1)	12	9	2
24[e]	1.0	K_3PO_4	Acetone/DMSO(1:1)	12	14	9
25	1.0	K_3PO_4	DMSO	18	84	77
26	**1.0**	**K_3PO_4**	**DMSO**	**24**	**99**	**85**
27	1.0	K_3PO_4	DMSO	30	99	81
28[f]	1.0	K_3PO_4	DMSO	24	90	78
29[g]	1.0	K_3PO_4	DMSO	24	96	80

[a] Reaction conditions: alcohols(1.0 mmol), DMSO (2.0 ml) with CO_2 balloon, [b] ^{1}H-NMR yield was determined using 1,3,5-mesitylene as an internal standard. [c]at 40°C, [d] at 60°C, [e]at 50°C, [f]at 70 °C, [g]at 90 °C. All reactions performed under air atmosphere.

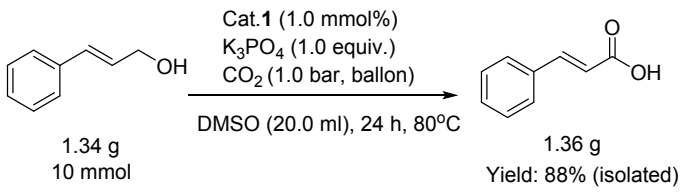


Figure S4. Gram-scale reaction of the catalyst.

Recycling experiments of the catalyst for alcohols to acids

The $Cr^{III}Mo_6$ 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.

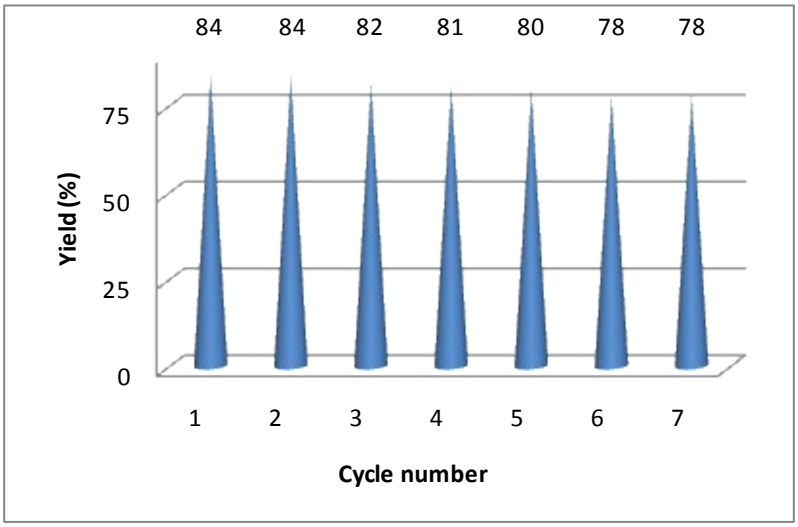


Figure S5. Recycling experiments of the catalyst. Conditions: Cat. 1 (1.0 mol%), alcohol (1.0 mmol), CO_2 (1.0 bar), K_3PO_4 (0.1 equiv.), and DMSO (2.0 ml) at 80°C for 24 h.

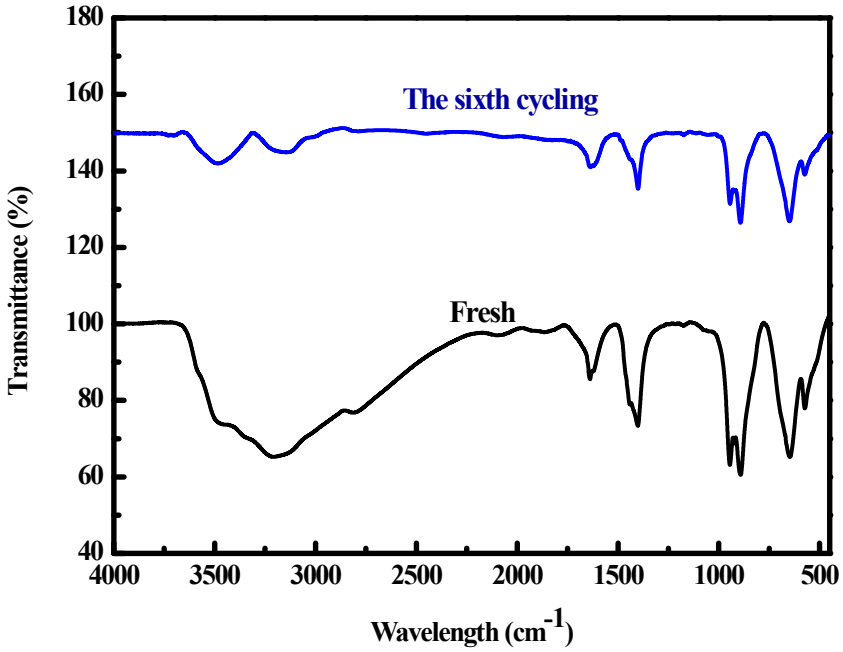


Figure S6. The FT-IR spectra of the catalyst before and after the reaction.

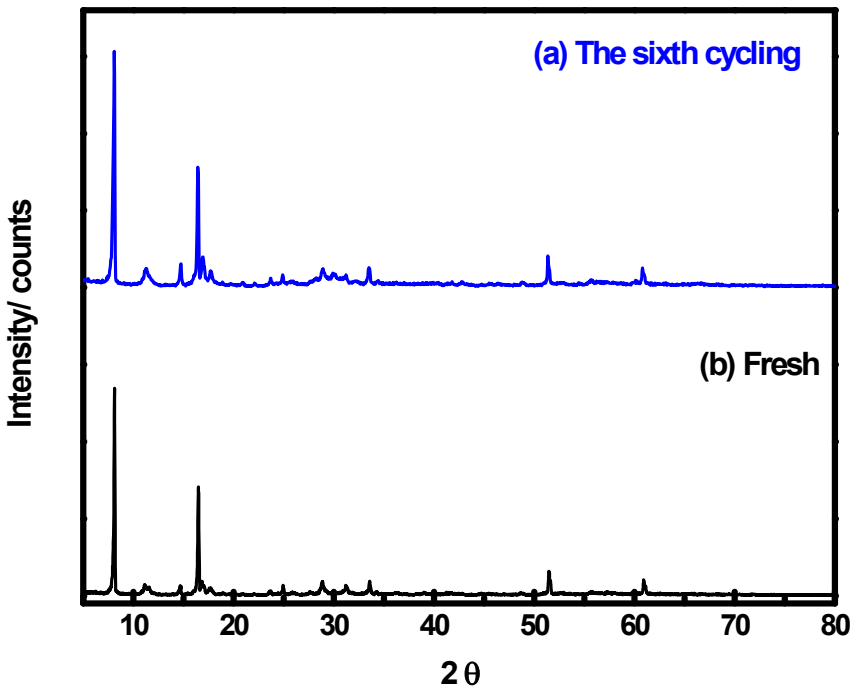


Figure S7. The XRD spectra of the catalyst before and after the reaction.

V. References

[1] Blazevic, A., Al-Sayed, E., Roller, A. *et al.* Tris-functionalized hybrid Anderson polyoxometalates: synthesis, characterization, hydrolytic stability and inversion of protein surface charge. *Chem. Eur. J.* **2015,** *21*, 4762-4771.

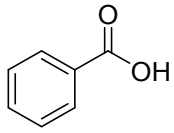
[2] Nomiya, K., Takahashi, T., Shirai, T., Miwa, M. Anderson-type heteropolyanions of molybdenum (VI) and tungsten (VI). *Polyhedron.* **1987**, *6*, 213-218.

[3] Liu, H., Eisen, M. S. Selective actinide-catalyzed tandem proton-transfer esterification of aldehydes with alcohols for the production of asymmetric esters. *Organometallics.* **2017**, *36*, 1461−1464.

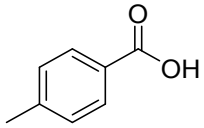
[4] Liu, H., Eisen, M. S. Facile Coupling of Aldehydes with Alcohols: An Evolved Tishchenko Process for the Preparation of Unsymmetrical Esters. *Eur. J. Org. Chem.* **2017**, *2017*, 4852–4858.

[5] Dong, S., Tang, J. J., Zhang, C. C. et al. Semisynthesis and in vitro cytotoxic evaluation of new analogues of 1-O-acetylbritannilactone, a sesquiterpene from Inula Britannica. *Eur. J. Med. Chem.* **2014**, *80*, 71-82.

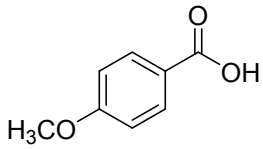
VI. NMR data of products



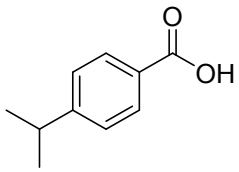
Benzoic acid (2)[3-5]: White solid. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.04 (d, J = 7.8 Hz, 2H), 9.57 (d, J = 3.1 Hz, 1H), 9.43 (d, J = 2.0 Hz, 2H).^{13}C NMR (101 MHz, CHLOROFORM-D) δ 173.90 (s), 135.88 (s), 132.07 (s), 131.23 (s), 130.54 (s).



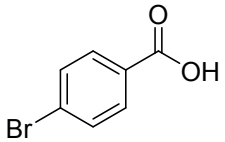
p-Toluic acid (3) [3-5]: White powder. ^{1}H NMR (400 MHz, DMSO-D6) δ 12.75 (s, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, DMSO-D6) δ 167.84 (s), 143.52 (s), 129.85 (s), 129.62 (s), 128.55 (s), 21.62 (s).



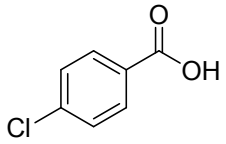
P-Methoxybenzoicacid (4) [3-5]: White powder. ^{1}H NMR (400 MHz, DMSO-D6) δ 12.59 (s, 1H), 7.85 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, DMSO-D6) δ 167.54 (s), 163.36 (s), 131.87 (s), 123.48 (s), 114.33 (s), 55.95 (s).



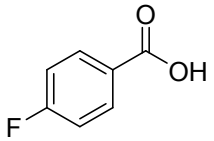
4-Isopropylbenzoic acid (5) [3-5]: White powder. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.04 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 2.98 (dt, J = 13.8, 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H).^{13}C NMR (101 MHz, CHLOROFORM-D) δ 172.51 (s), 155.48 (s), 130.50 (s), 126.72 (s), 125.65 (s), 34.44 (s), 23.77 (s).



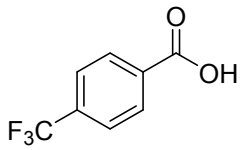
4-bromobenzoic acid (6) [3-5]**:** White powder. ^{1}H NMR (501 MHz, DMSO) δ 13.19 (s, 1H), 7.85 (s, 2H), 7.71 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 167.07 (s), 132.85 (s), 131.48 (s), 131.13 (s), 130.47 (s).



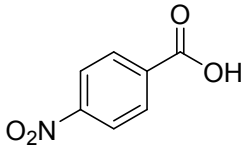
4-chlorobenzoic acid (7) [3-5]**:**White powder.^{1}H NMR (501 MHz, DMSO) δ 13.16 (s, 1H), 7.93 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 166.91 (s), 138.25 (s), 131.55 (s), 130.07 (s), 129.10 (s).



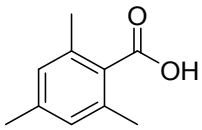
4-Fluorobenzoic acid (8) [3-5]**:**White powder. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.13 (dd, J = 8.9, 5.4 Hz, 2H), 7.14 (t, J = 8.6 Hz, 2H).^{13}C NMR (101 MHz, DMSO-D6) δ 166.89 (s), 132.63 (d, J = 9.5 Hz), 116.27 (s), 116.05 (s).



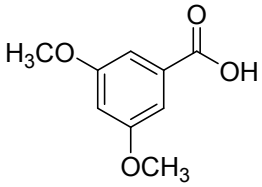
4-(trifluoromethyl)benzoic acid (9) [3-5]**:**White powder. ^{1}H NMR (501 MHz, DMSO) δ 13.49 (s, 1H), 8.14 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 166.65 (s), 135.05 (s), 132.81 (s), 130.55 (s), 126.05 (s), 125.34 (s).



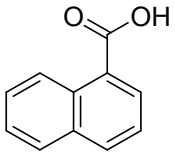
4-nitrobenzoic acid (10) [3-5]**:**Light yellow powder. ^{1}H NMR (400 MHz, DMSO-D6) δ 13.63 (s, 1H), 8.27 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-D6) δ 166.34 (s), 150.58 (s), 136.90 (s), 131.24 (s), 124.28 (s).



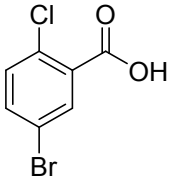
2,4,6-Trimethylbenzoic acid (11) [3-5]**:** White powder. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.83 (s, 2H), 4.31 (s, 6H), 4.22 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 176.29 (s), 142.14 (s), 137.89 (s), 131.31 (s), 130.65 (s), 22.86 (s), 21.94 (s).



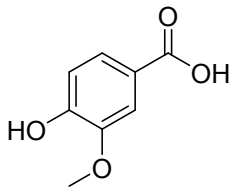
3,5-dimethoxybenzoic acid (12) [3-5]**:**White powder. ^{1}H NMR (501 MHz, DMSO) δ 12.94 (s, 1H), 6.97 (d, J = 2.3 Hz, 2H), 6.64 (t, J = 2.2 Hz, 1H), 3.69 (s, 6H). ^{13}C NMR (126 MHz, DMSO) δ 167.43 (s), 160.83 (s), 133.30 (s), 107.29 (s), 105.33 (s), 55.86 (s).



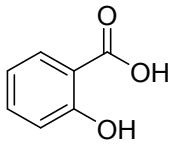
naphthoic acid (13) [3-5]**:**Light yellow powder. ^{1}H NMR (400 MHz, DMSO-D6) δ 13.05 (s, 1H), 8.58 (s, 1H), 8.10 – 7.93 (m, 4H), 7.64 – 7.52 (m, 2H). ^{13}C NMR (101 MHz, DMSO-D6) δ 167.98 (s), 135.46 (s), 132.67 (s), 131.05 (s), 129.80 (s), 128.71 (t, J = 12.7 Hz), 128.18 (s), 127.33 (s), 125.69 (s).



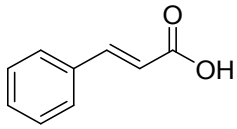
4-bromo-2-chlorobenzoic acid (14) [3-5]**:**White powder. ^{1}H NMR (501 MHz, DMSO) δ 13.73 (s, 1H), 7.94 (d, J = 2.3 Hz, 1H), 7.74 (dd, J = 8.6, 2.5 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 135.57 (s), 133.86 (s), 133.48 (s), 133.05 (s), 131.33 (s), 120.32 (s).



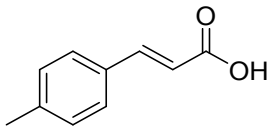
4-hydroxy-3-methoxybenzoic acid (15)[3-5]: liquid. ^{1}H NMR (400 MHz, DMSO-D6) δ 12.45 (s, 1H), 9.80 (s, 1H), 7.42 – 7.36 (m, 2H), 6.80 (d, J = 8.5 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, DMSO-D6) δ 167.73 (s), 151.60 (s), 147.72 (s), 123.98 (s), 122.10 (s), 115.53 (s), 113.19 (s), 56.03 (s).



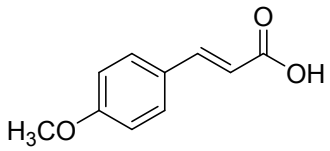
Salicylic acid (16) [3-5]**:**White solid.^{1}H NMR (400 MHz, DMSO-D6) δ 13.76 (s, 1H), 11.37 (s, 1H), 7.75 (dd, J = 7.9, 1.7 Hz, 1H), 7.48 – 7.44 (m, 1H), 6.92 – 6.85 (m, 2H). ^{13}C NMR (101 MHz, DMSO-D6) δ 172.48 (s), 161.68 (s), 136.17 (s), 130.79 (s), 119.69 (s), 117.61 (s), 113.40 (s).



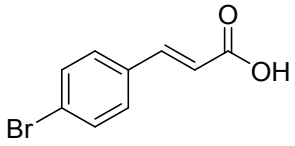
Cinnamic acid (17)[3-5]**:**White crystal.^{1}H NMR (400 MHz, DMSO-D6) δ 12.59 (s, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 16.1 Hz, 1H), 6.64 (d, J = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-D6) δ 167.73 (s), 142.60 (s), 138.81 (s), 130.18 (s), 129.35 (s), 126.22 (s), 122.69 (s).



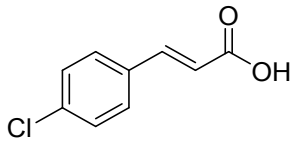
4-Methylcinnamic acid (18) [3-5]**:**White powder. ^{1}H NMR (400 MHz, DMSO-D6) δ 12.27 (s, 1H), 7.55 – 7.48 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 6.42 (d, J = 16.0 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, DMSO-D6) δ 168.20 (s), 144.45 (s), 140.66 (s), 132.03 (s), 130.03 (s), 128.71 (s), 118.62 (s), 21.53 (s).



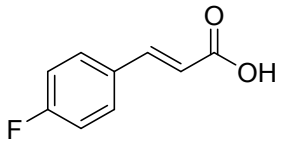
4-methoxycinnamic acid (19)[3-5]: white powder. ^{1}H NMR (400 MHz, DMSO-D6) δ 12.18 (s, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 16.0 Hz, 1H), 6.93 (d, J = 8.7 Hz, 2H), 6.34 (d, J = 16.0 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, DMSO-D6) δ 168.36 (s), 161.46 (s), 144.27 (s), 130.46 (s), 127.35 (s), 117.02 (s), 114.87 (s), 55.83 (s).



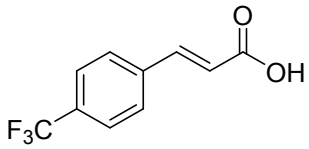
4-bromocinnamic acid (20) [3-5]**:** White crystal. ^{1}H NMR (400 MHz, DMSO-D6) δ 7.57 (dt, J = 19.6, 12.3 Hz, 5H), 6.53 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-D6) δ 167.94 (s), 143.13 (s), 134.07 (s), 132.38 (s), 130.68 (s), 124.05 (s), 120.67 (s).



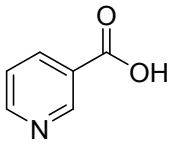
4-chlorocinnamic acid (21) [3-5]**:**Colorless crystal. ^{1}H NMR (400 MHz, DMSO-D6) δ 12.43 (s, 1H), 7.69 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 16.0 Hz, 1H), 7.43 (d, J = 8.5 Hz, 2H), 6.52 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-D6) δ 167.95 (s), 143.04 (s), 135.23 (s), 133.75 (s), 130.47 (s), 129.45 (s), 120.61 (s).



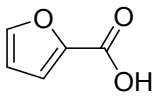
4-fluorocinnamic acid (22) [3-5]**:**White crystal. ^{1}H NMR (400 MHz, DMSO-D6) δ 12.35 (s, 1H), 7.72 (dd, J = 8.7, 5.6 Hz, 2H), 7.55 (d, J = 16.0 Hz, 1H), 7.20 (t, J = 8.8 Hz, 2H), 6.45 (d, J = 16.0 Hz, 1H).^{13}C NMR (101 MHz, DMSO-D6) δ 168.04 (s), 162.44 (s), 143.22 (s), 131.42 (s), 130.98 (s), 119.63 (s), 116.50 (s).



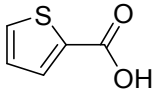
4-(trifluoromethyl)cinnamic acid (23)[3-5]: White powder. ^{1}H NMR (400 MHz, DMSO-D6) δ 12.61 (s, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 16.1 Hz, 1H), 6.64 (d, J = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-D6) δ 167.73 (s), 142.59 (s), 138.79 (s), 130.51 (s), 129.33 (s), 126.18 (d, J = 3.7 Hz), 122.68 (s).



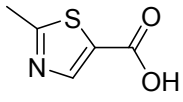
picolinic acid (24) [3-5]: White powder. ^{1}H NMR (400 MHz, DMSO-D6) δ 13.13 (s, 1H), 8.66 (d, J = 4.6 Hz, 1H), 8.01 – 7.92 (m, 2H), 7.58 (ddd, J = 7.5, 4.7, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-D6) δ 166.70 (s), 149.96 (s), 148.86 (s), 138.04 (s), 127.62 (s), 125.18 (s).



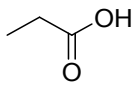
2-furoic acid (25) [3-5]: Off-white powder. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 11.32 (s, 1H), 7.66 – 7.61 (m, 1H), 7.35 – 7.30 (m, 1H), 6.55 (dd, J = 3.6, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 163.73 (s), 147.54 (s), 143.88 (s), 120.28 (s), 112.38 (s).



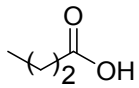
2-thiophenecarboxylic acid(26) [3-5]:solid. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.89 (dd, J = 3.7, 1.2 Hz, 1H), 7.64 (dd, J = 4.9, 1.1 Hz, 1H), 7.14 (dd, J = 4.9, 3.8 Hz, 1H).^{13}C NMR (101 MHz, CHLOROFORM-D) δ 167.74 (s), 135.13 (s), 134.13 (s), 132.92 (s), 128.17 (s).



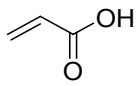
2-methl-1,3-thiazole-5-carboxylic acid (27) [3-5]**:**solid. ^{1}H NMR (501 MHz, DMSO) δ 13.29 (s, 1H), 8.07 (s, 1H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 172.21 (s), 162.54 (s), 147.99 (s), 130.50 (s), 19.78 (s).



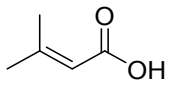
Propionic acid (28) [3-5]**:** Colorless liquid. ^{1}H NMR (501 MHz, CDCl3) δ 11.83 (s, 1H), 1.61 – 1.45 (m, 2H), 0.91 – 0.77 (m, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 180.15 (s), 17.88 (s), 13.11 – 12.95 (m).



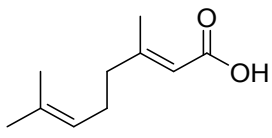
Valeric acid (29) [3-5]**:** Colorless liquid. ^{1}H NMR (501 MHz, CDCl3) δ 11.60 (s, 1H), 2.13 (td, J = 7.6, 2.4 Hz, 2H), 1.50 – 1.34 (m, 2H), 1.17 (pd, J = 7.5, 2.4 Hz, 2H), 0.72 (td, J = 7.4, 2.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 180.27 (s), 33.52 (s), 26.54 (s), 21.96 (s), 13.22 (s).



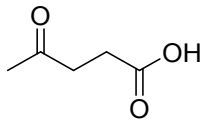
acrylic acid (30) [3-5]**:** Clear liquid. ^{1}H NMR (501 MHz, CDCl3) δ 11.63 (s, 1H), 6.26 (dd, J = 17.3, 1.2 Hz, 1H), 5.90 (dd, J = 17.3, 10.5 Hz, 1H), 5.71 (dd, J = 10.4, 1.2 Hz, 1H).^{13}C NMR (126 MHz, CDCl3) δ 171.34 (s), 132.70 (s), 127.80 (s).



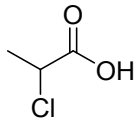
3,3-dimethylacrylic acid (31)[3-5]: white crystal. ^{1}H NMR (501 MHz, DMSO) δ 11.73 (s, 1H), 5.51 (s, 1H), 1.98 (s, 3H), 1.74 (s, 4H). ^{13}C NMR (126 MHz, DMSO) δ 167.75 (s), 155.83 (s), 116.93 (s), 27.22 (s), 20.08 (s).



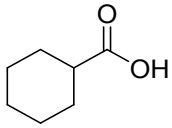
Geranic acid (32)[3-5]:solid. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 13.84 (s, 1H), 7.62 (d, J = 1.1 Hz, 1H), 7.08 – 6.97 (m, 1H), 4.15 – 4.09 (m, 6H), 3.86 (d, J = 1.3 Hz, 1H), 3.62 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 174.64 (s), 165.48 (s), 134.56 (s), 124.82 (s), 117.02 (s), 43.16 (s), 35.63 (s), 28.01 (s), 27.34 (s), 19.35 (s).



Levulinicacid(33) [3-5]**:**Clear yellow liquid. ^{1}H NMR (501 MHz, CDCl3) 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 (126 MHz, CDCl3) δ 208.31 (s), 176.96 (s), 37.26 (s), 28.97 (s), 27.32 (s).

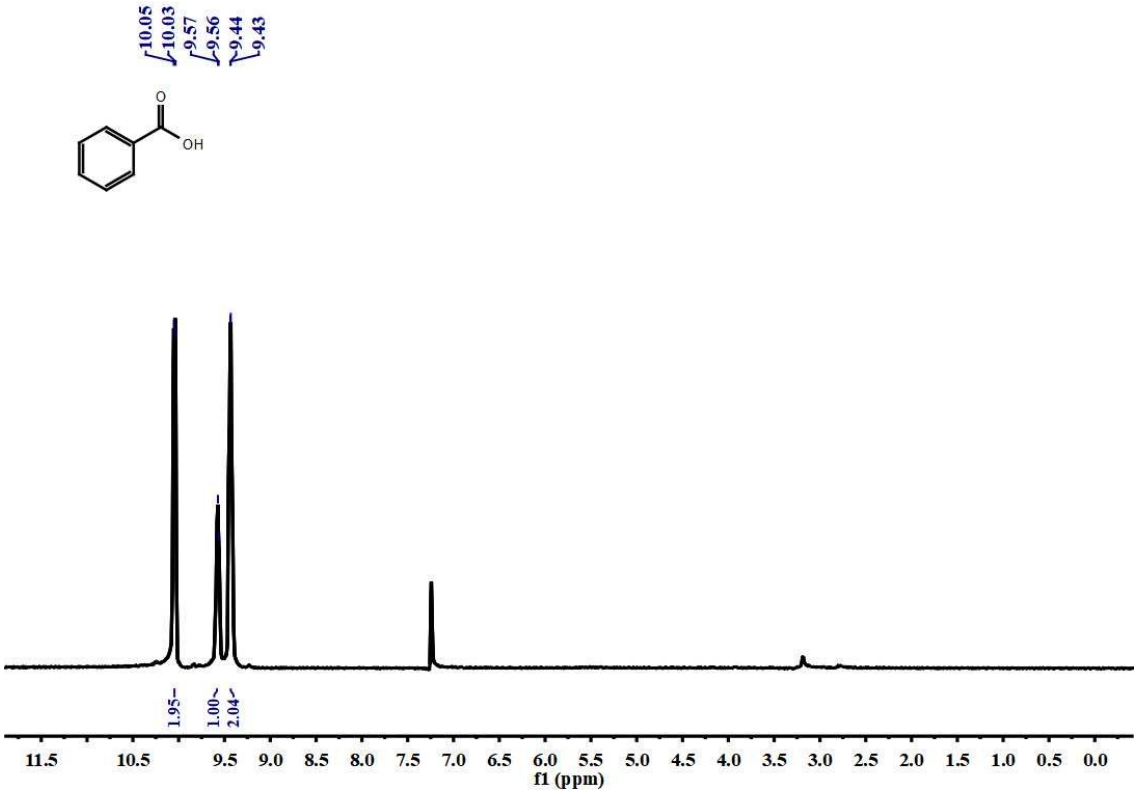


2-chloropropionic acid (34) [3-5]**:**Colourless liquid. ^{1}H NMR (501 MHz, CDCl3) δ 11.13 (s, 1H), 4.30 (q, J = 7.0 Hz, 1H), 1.52 (d, J = 7.1 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 176.03 (d, J = 1.3 Hz), 52.09 (s), 21.07 (s).

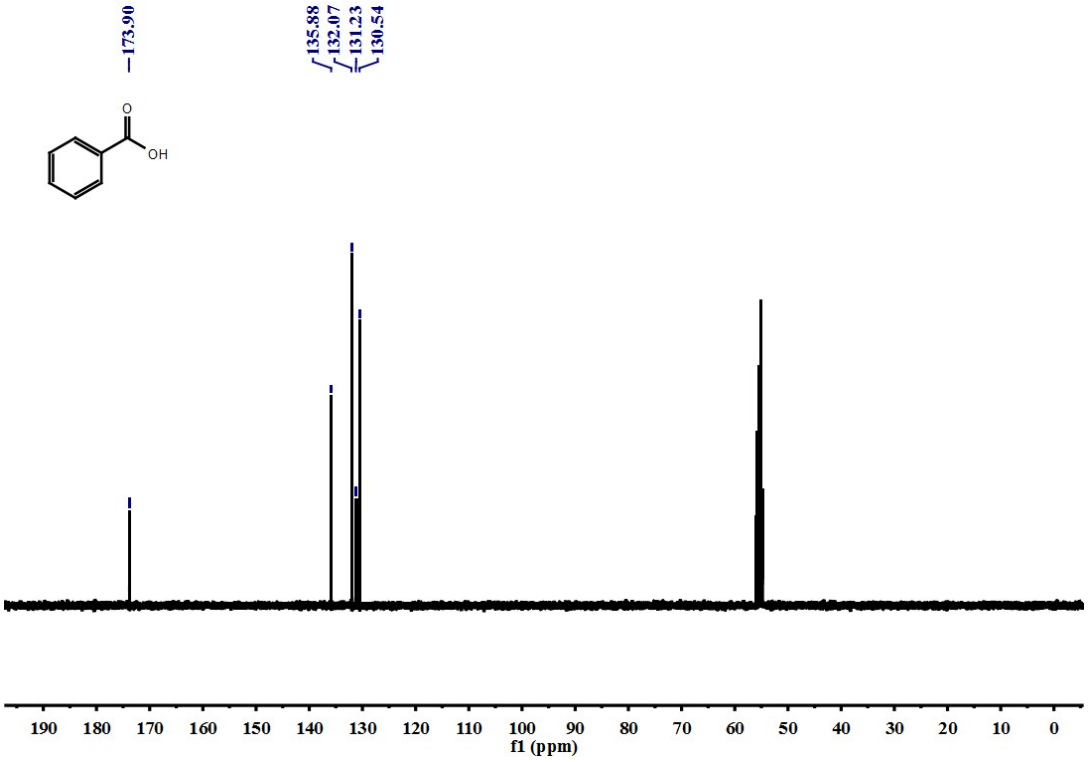


Cyclohexanecarboxylic acid (35)[3-5]**:** White solid.^{1}H NMR (501 MHz, CDCl3) δ 12.20 (s, 1H), 2.26 (d, J = 10.9 Hz, 1H), 1.87 (s, 2H), 1.70 (s, 2H), 1.58 (s, 1H), 1.40 (s, 2H), 1.31 – 1.09 (m, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 182.82 (s), 42.86 (s), 28.66 (s), 25.65 (s), 25.25 (s).

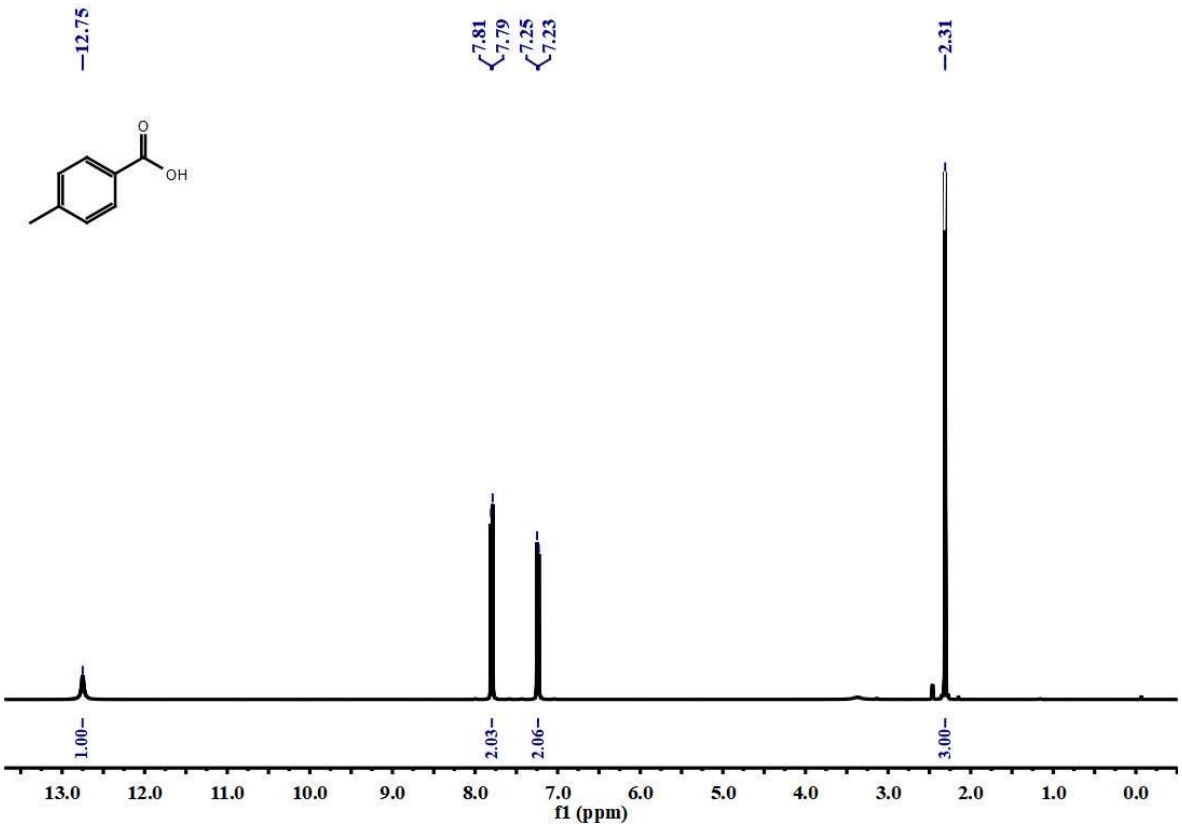
VII. NMR spectra



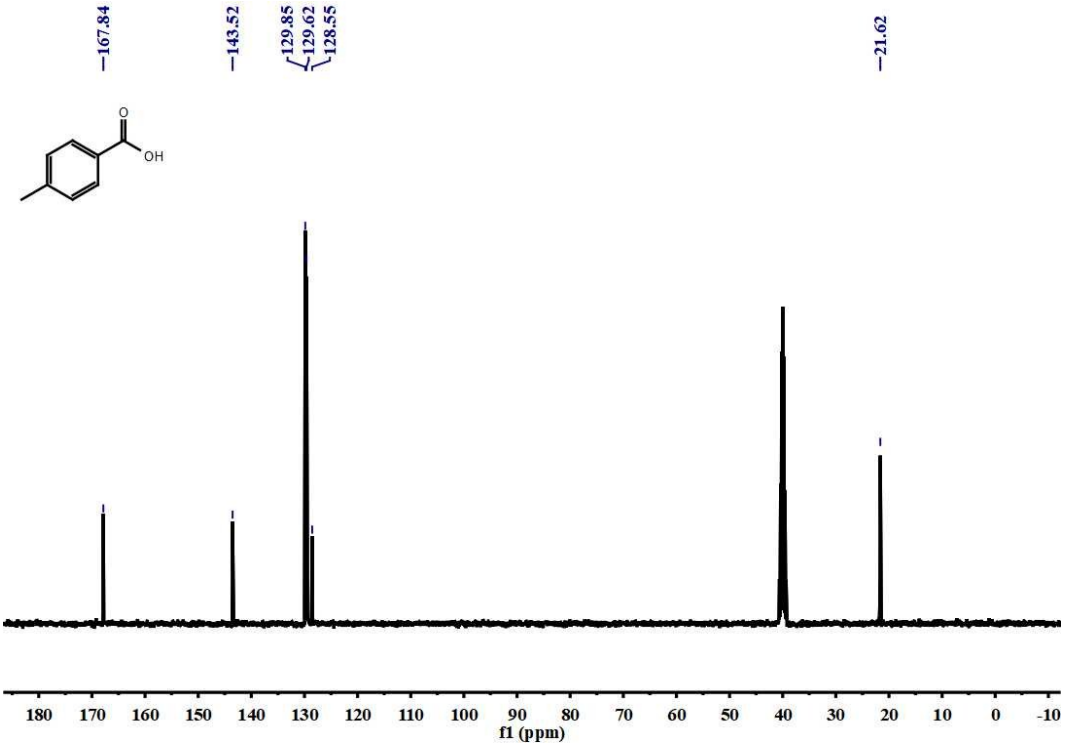
^{1}H NMR spectra of 2(500 MHz, $CDCl_3$)



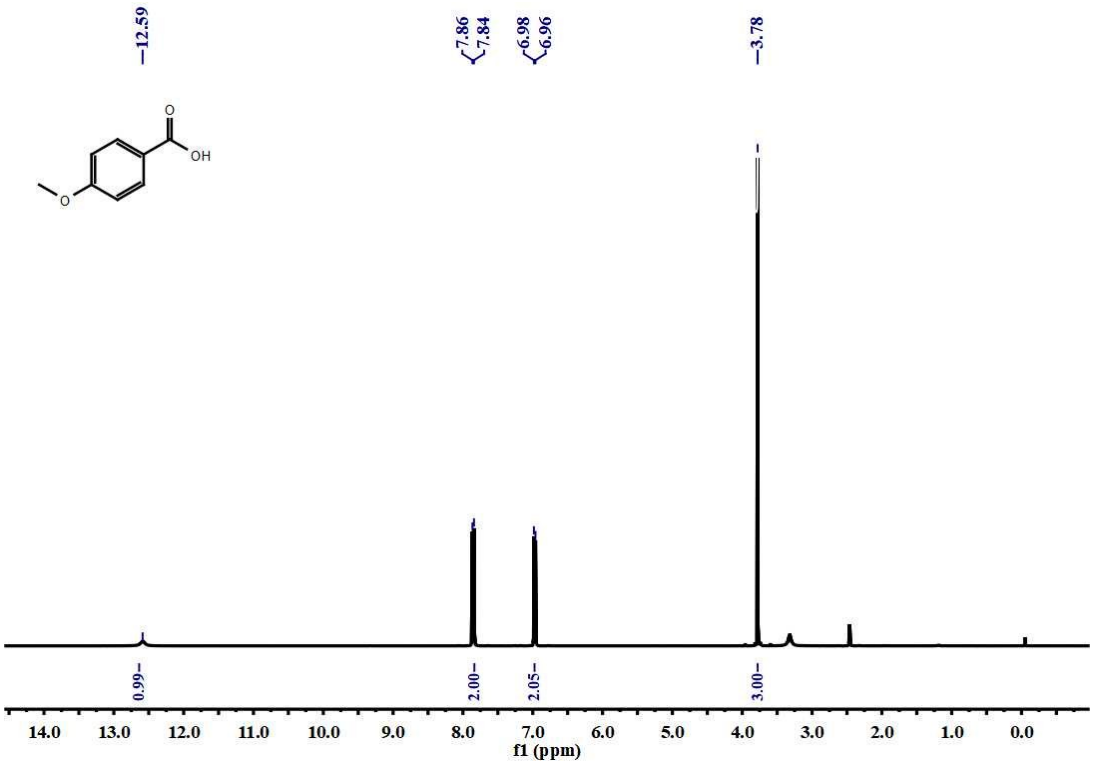
^{13}C NMR spectra of 2(125 MHz, CDCl3)



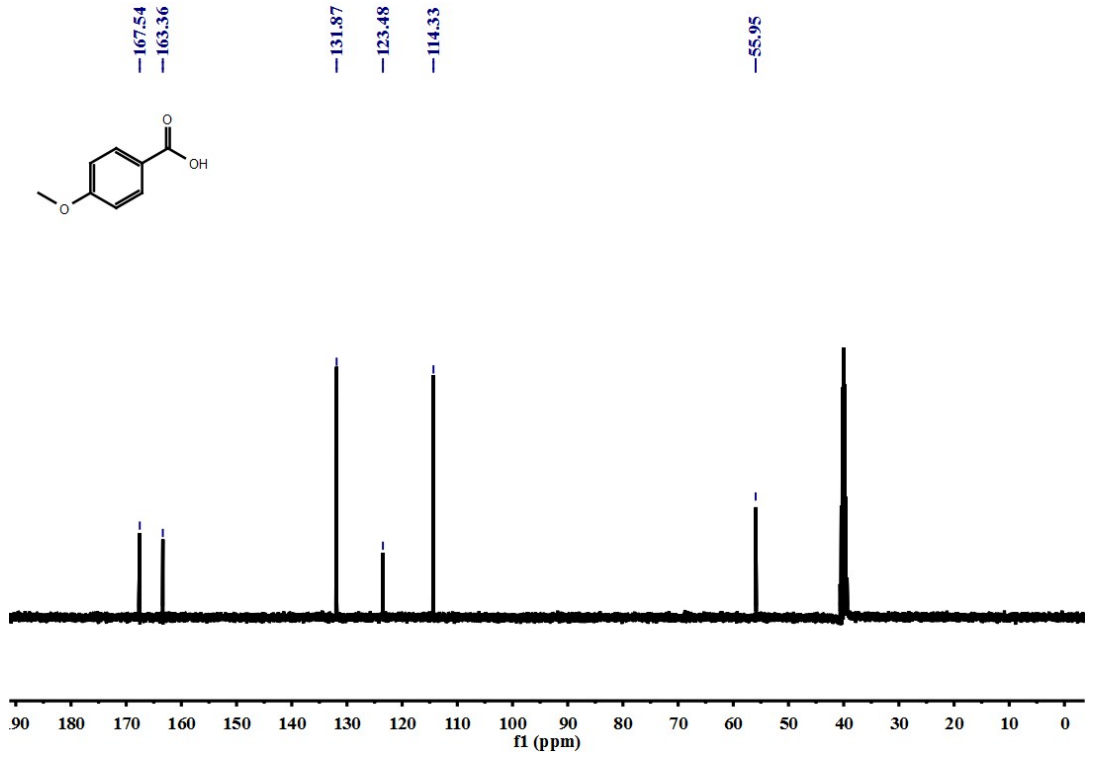
^{1}H NMR spectra of 3(500 MHz, DMSO)



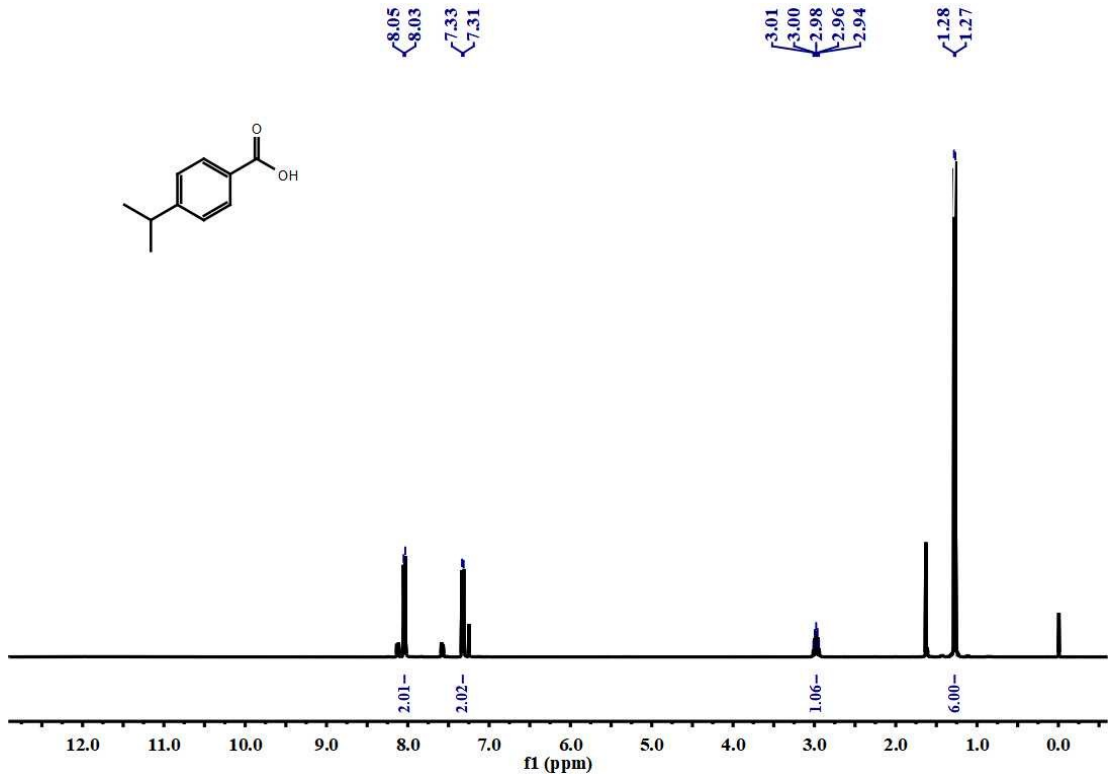
^{13}C NMR spectra of 3(125 MHz, DMSO)



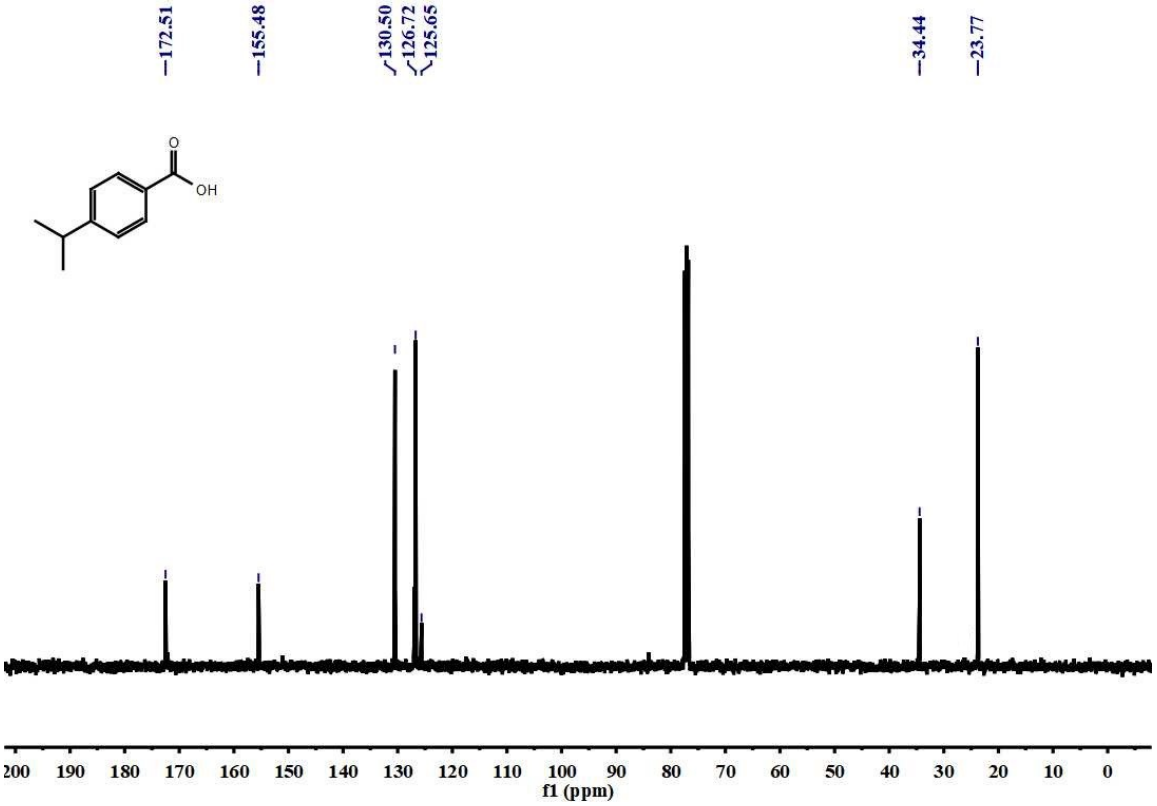
^{1}H NMR spectra of 4(500 MHz, DMSO)



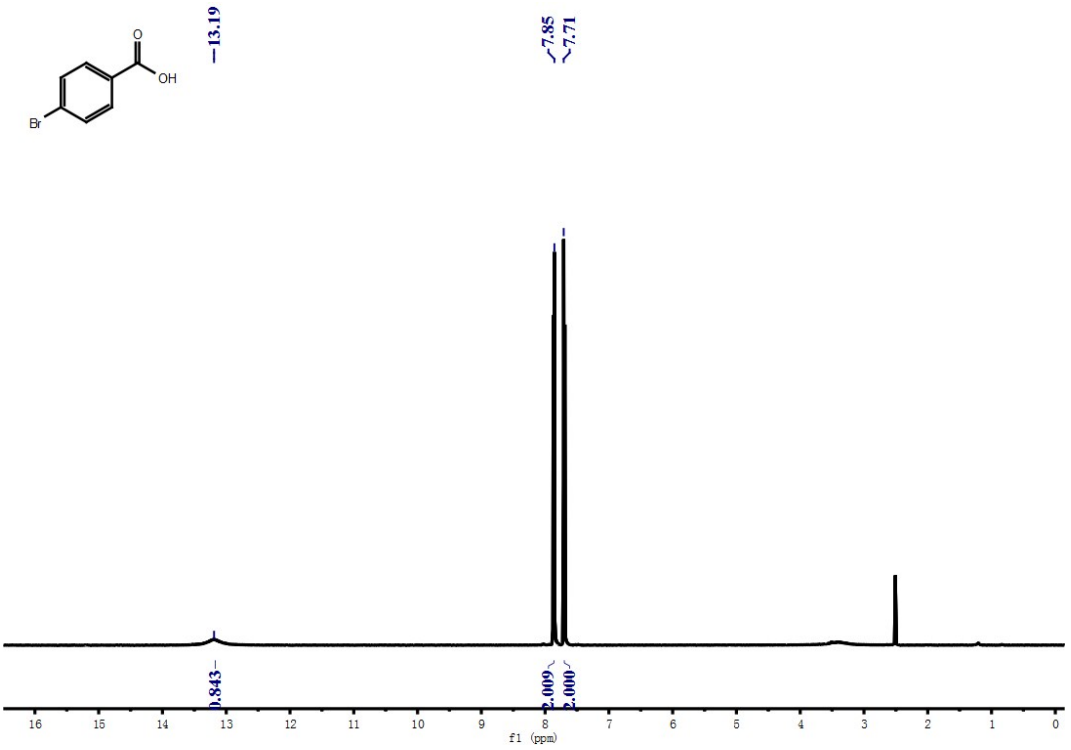
^{13}C NMR spectra of 4(125 MHz, DMSO)



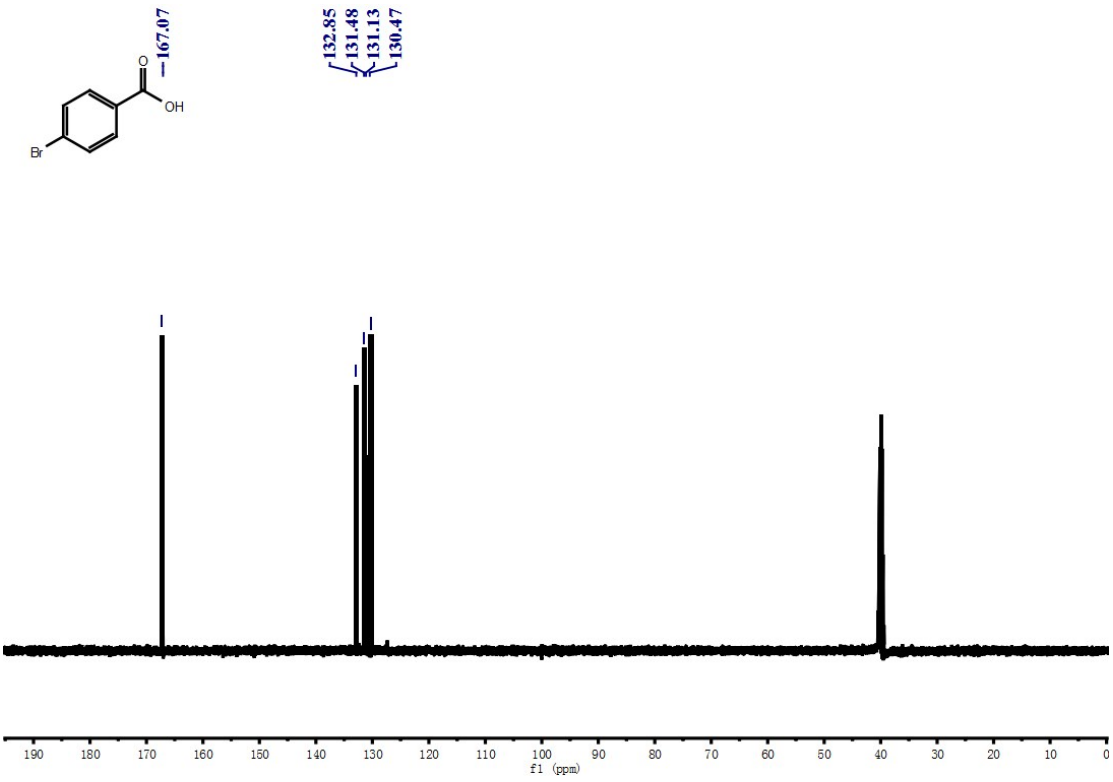
^{1}H NMR spectra of 5(500 MHz, CDCl3)



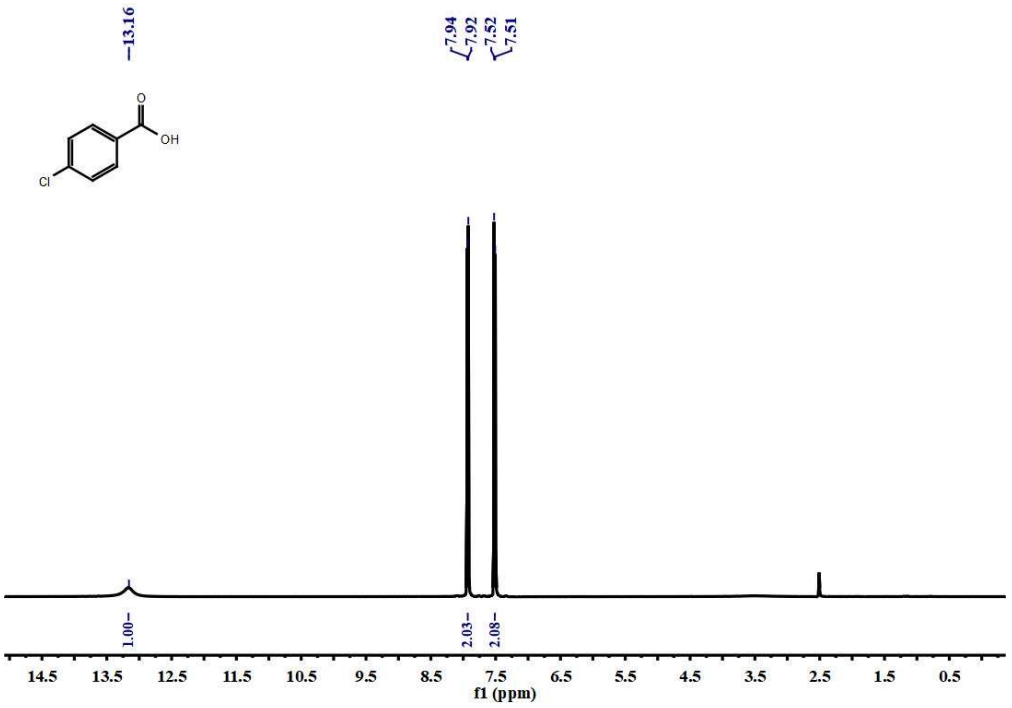
^{13}C NMR spectra of 5(125 MHz, CDCl3)



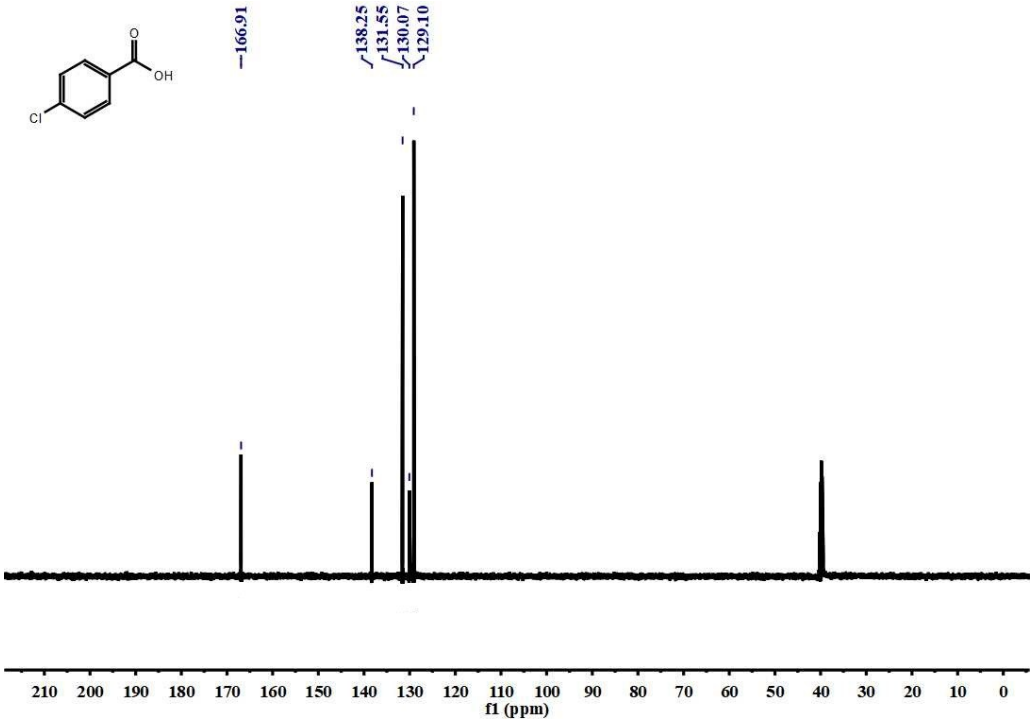
^{1}H NMR spectra of 6(500 MHz, DMSO)



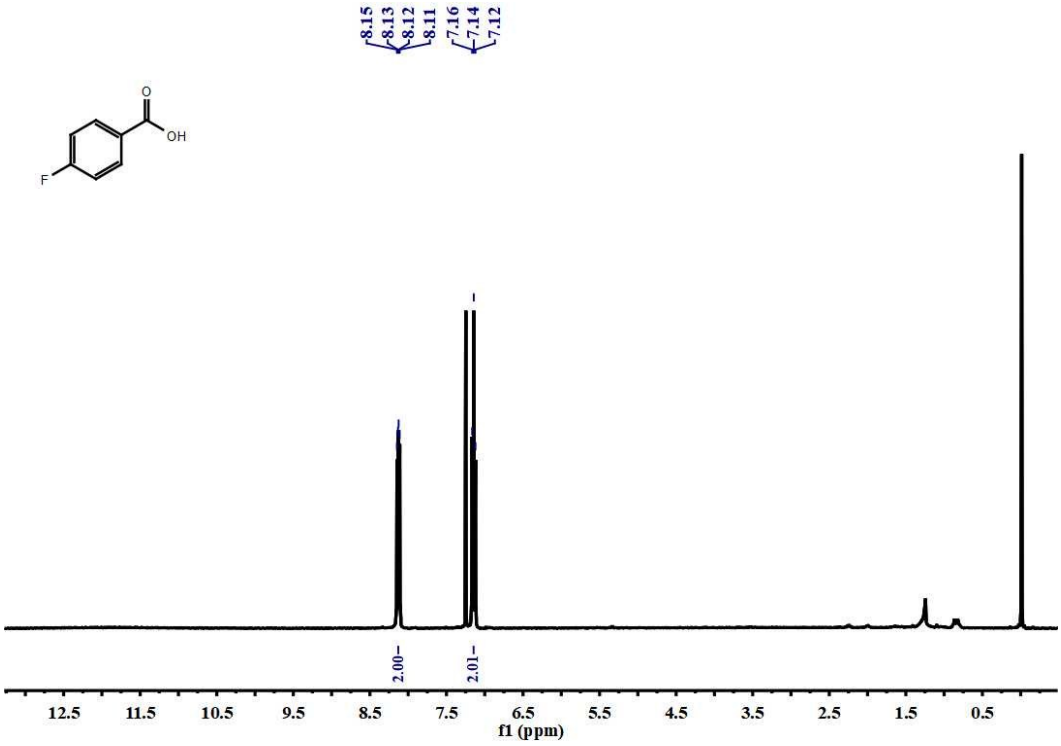
^{13}C NMR spectra of 6(125 MHz, DMSO)



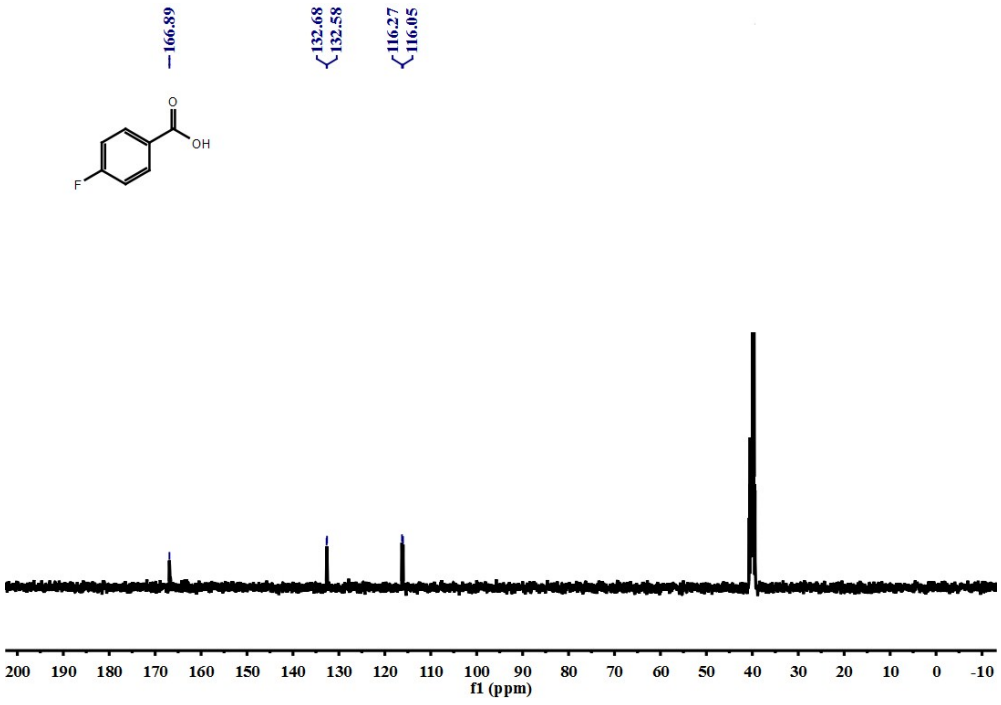
^{1}H NMR spectra of 7(500 MHz, DMSO)



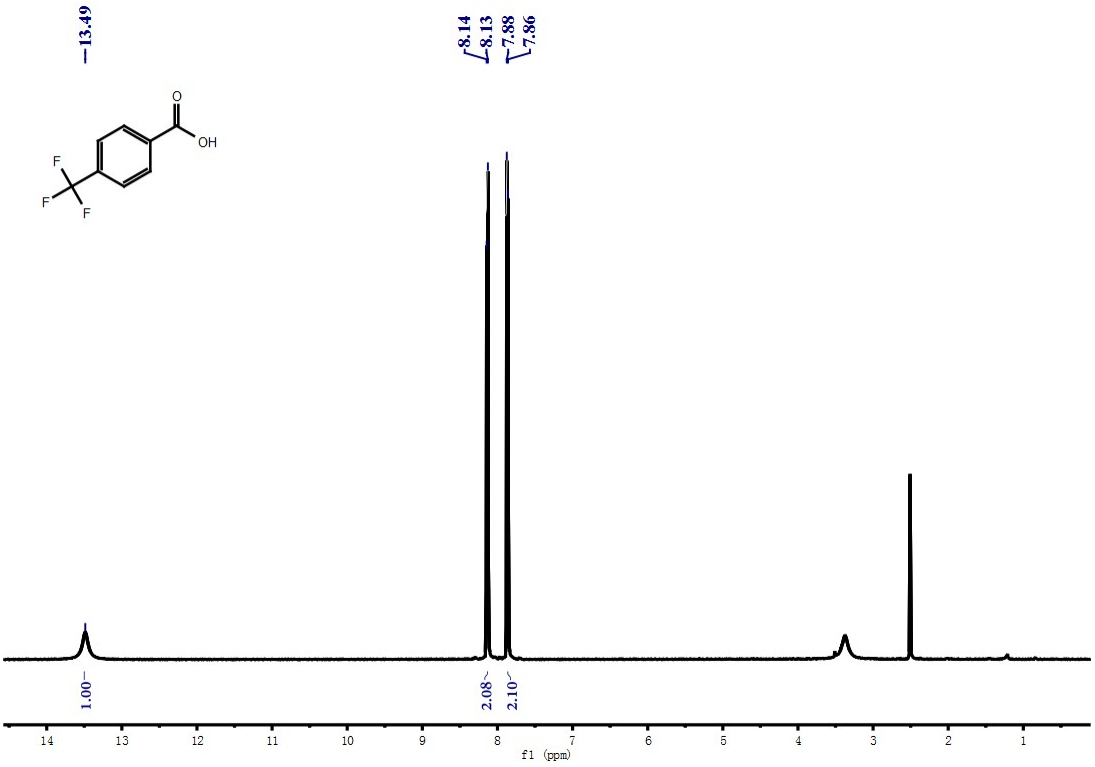
^{13}C NMR spectra of 7(125 MHz, DMSO)



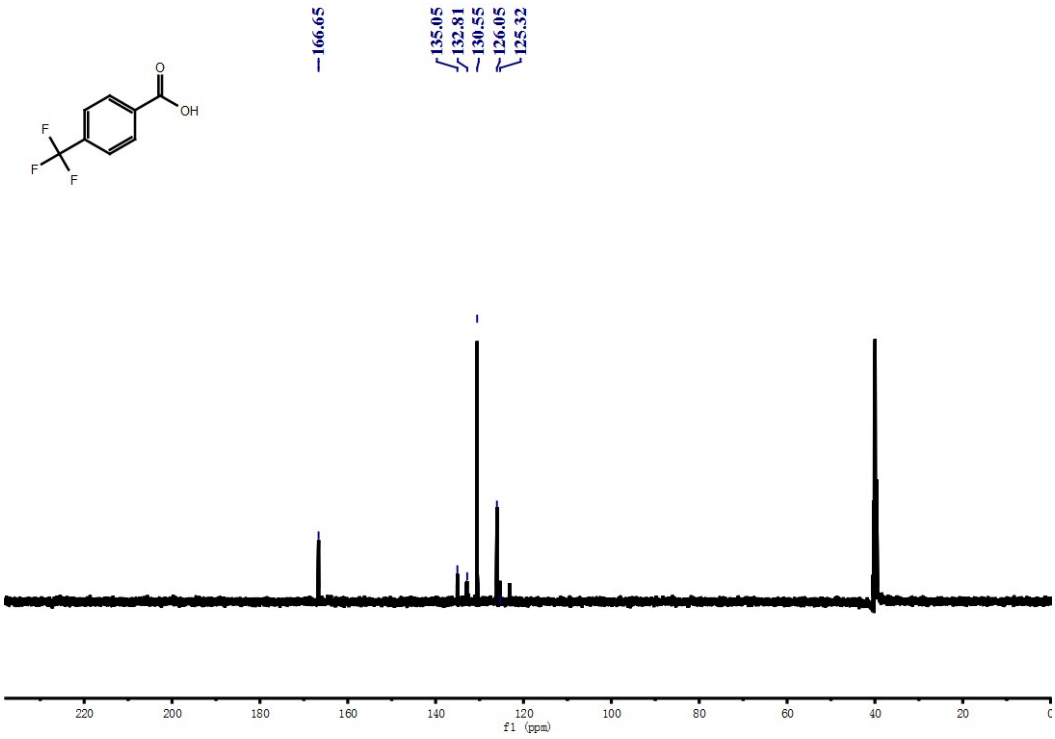
^{1}H NMR spectra of 8(500 MHz, $CDCl_3$)



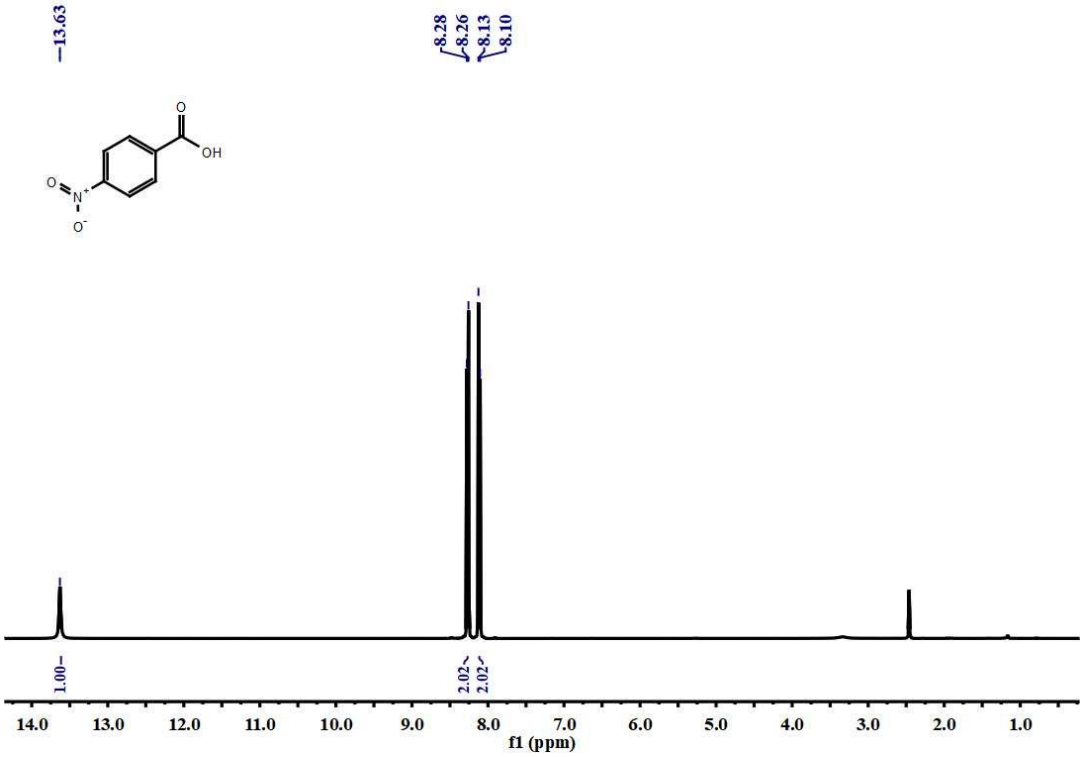
^{13}C NMR spectra of 8(125 MHz, CDCl3)



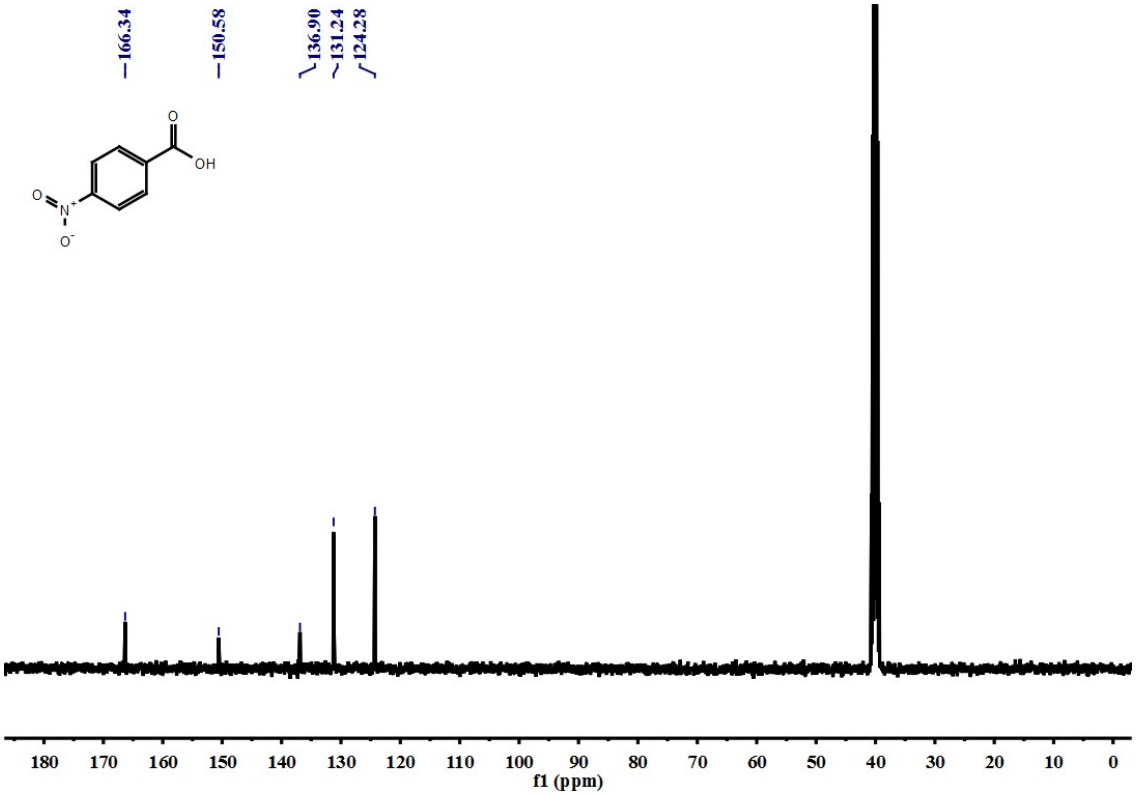
^{1}H NMR spectra of 9(500 MHz, DMSO)



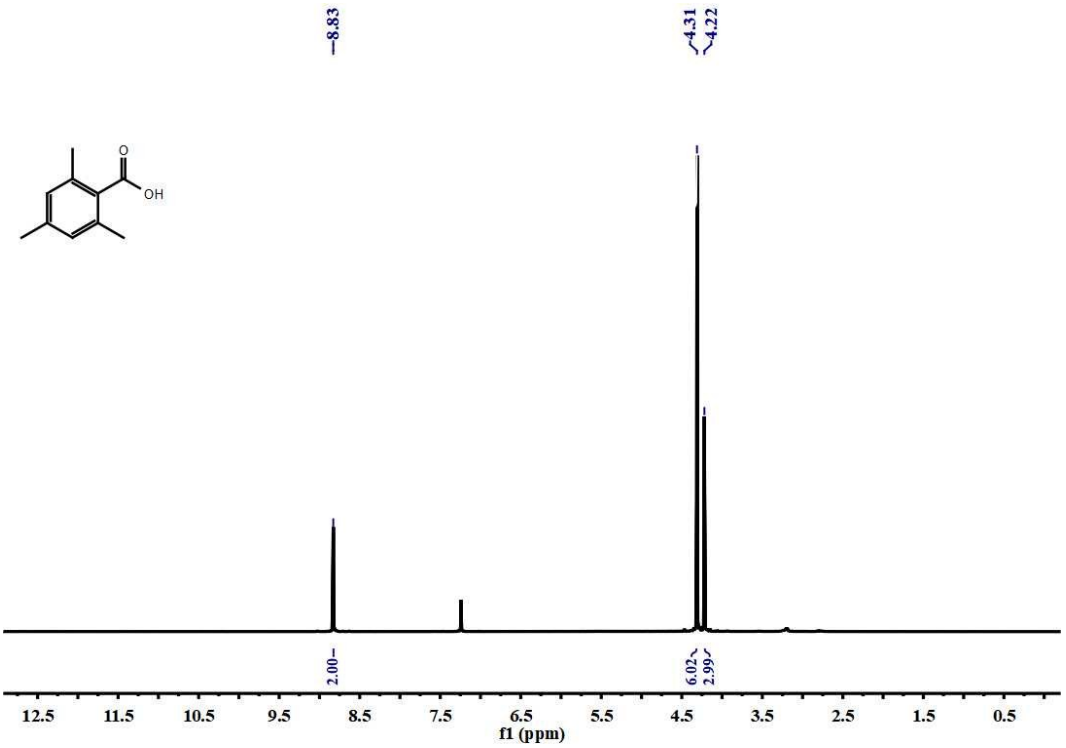
^{13}C NMR spectra of 9(125 MHz, DMSO)



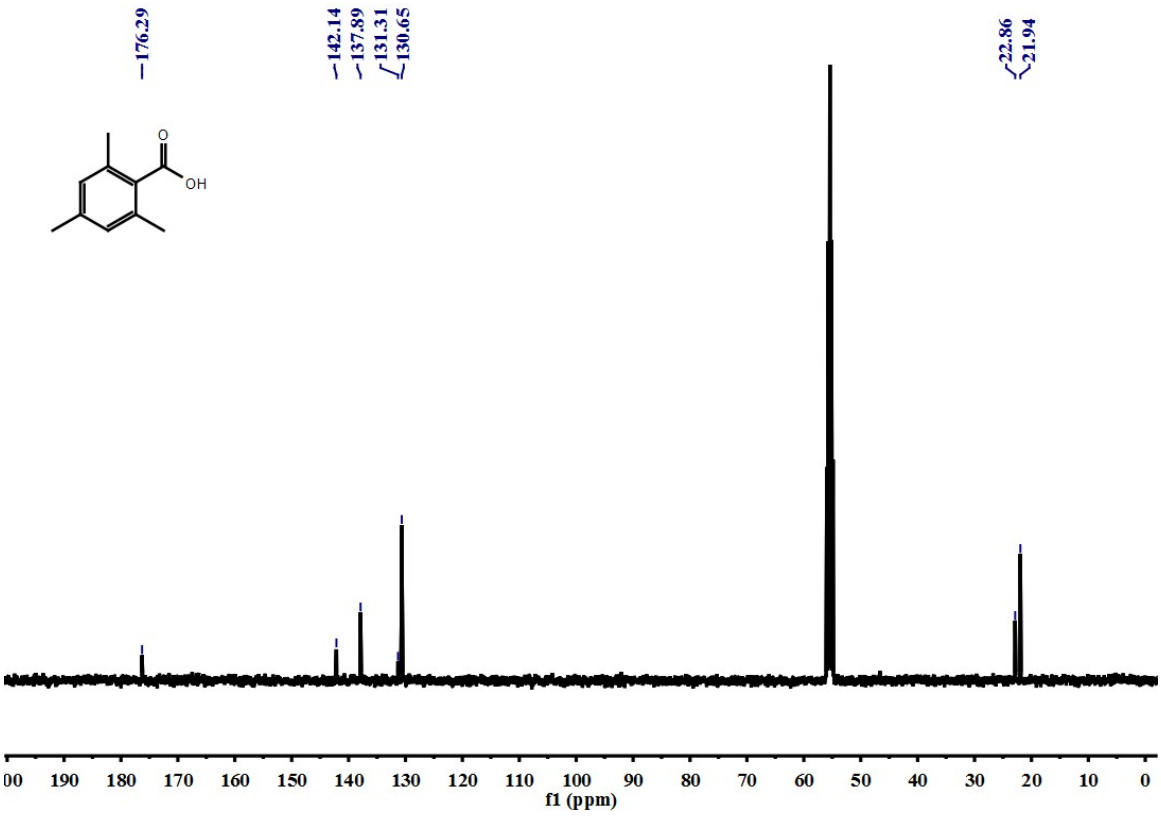
^{1}H NMR spectra of 10(500 MHz, DMSO)



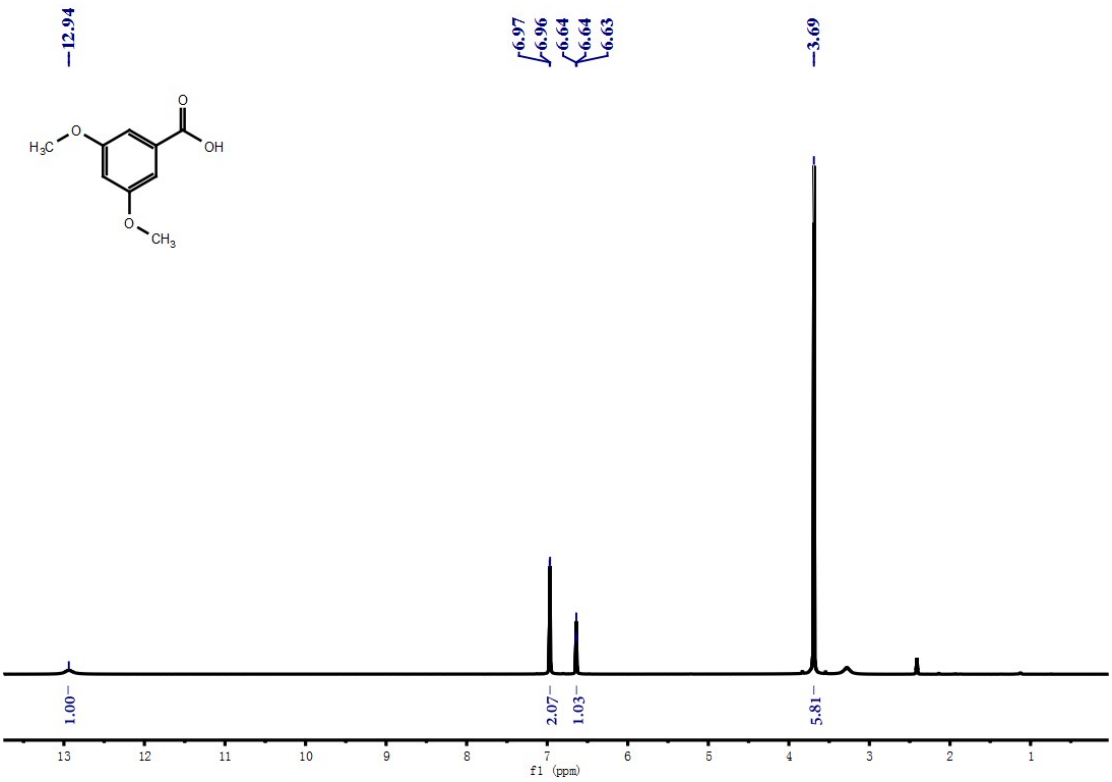
^{13}C NMR spectra of 10(125 MHz, DMSO)



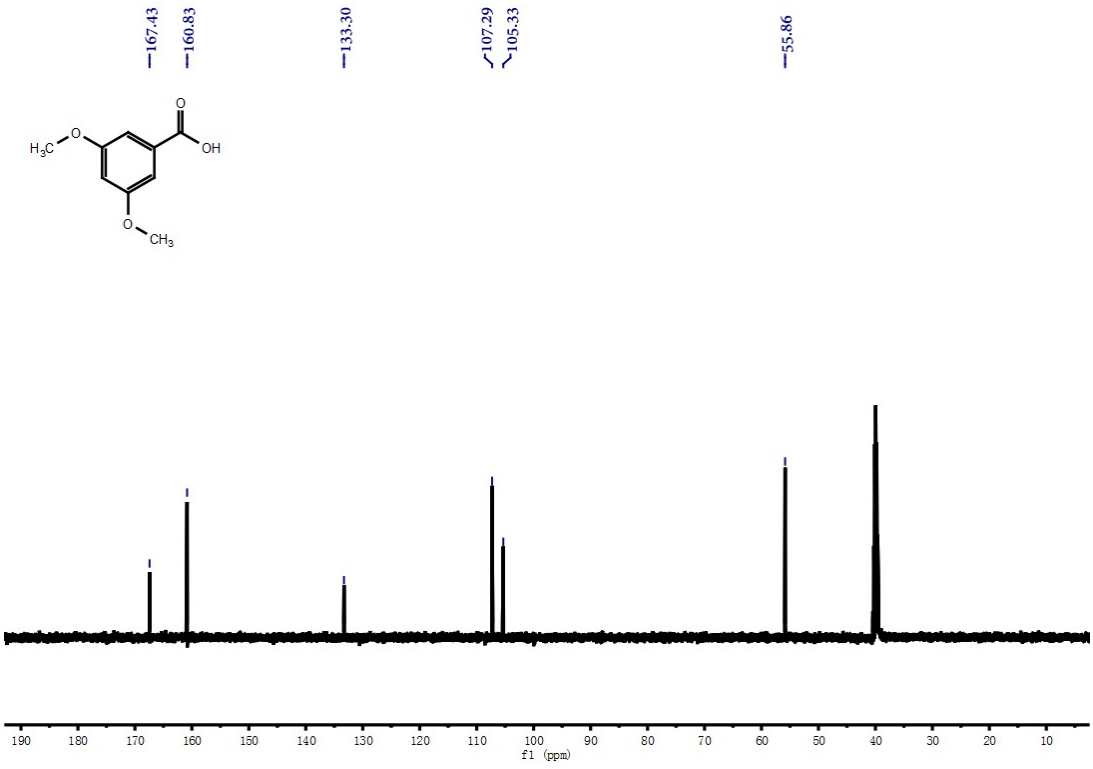
^{1}H NMR spectra of 11(500 MHz, CDCl3)



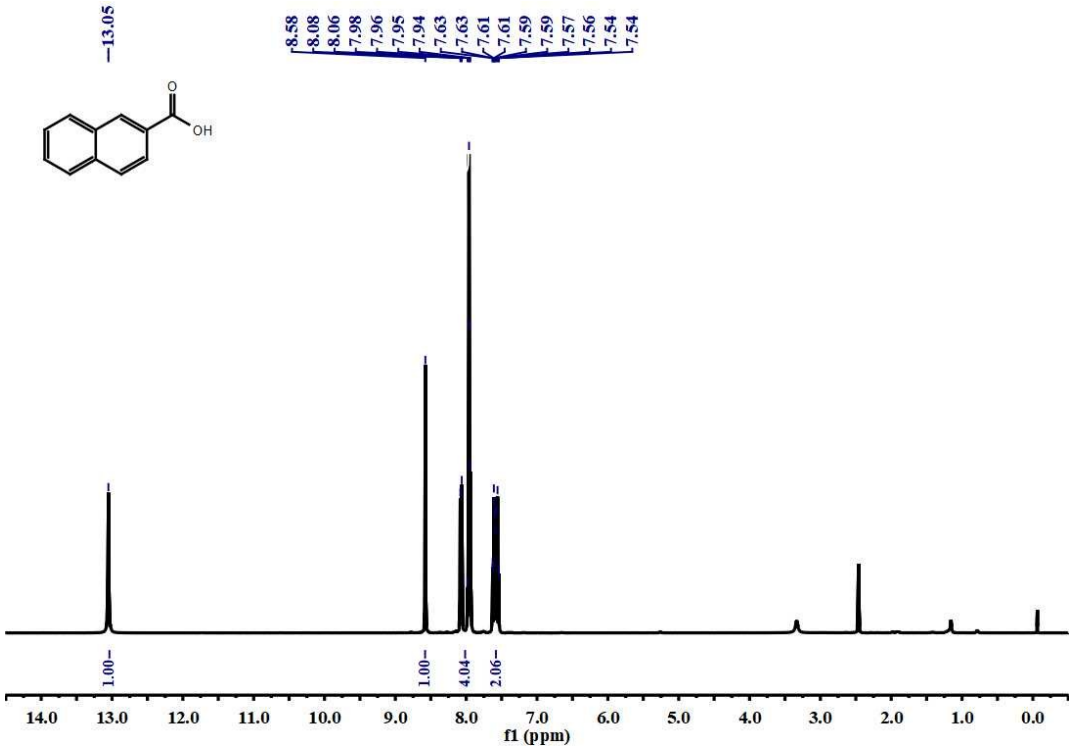
^{13}C NMR spectra of 11(125 MHz, CDCl3)



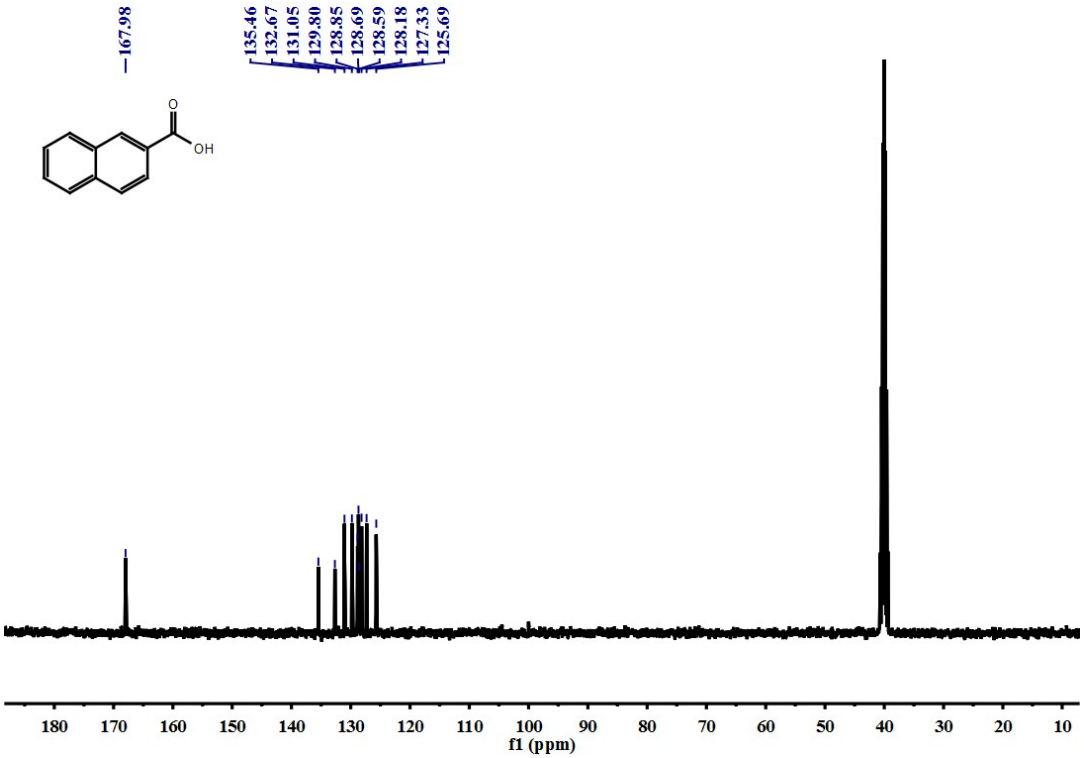
^{1}H NMR spectra of 12(500 MHz, DMSO)



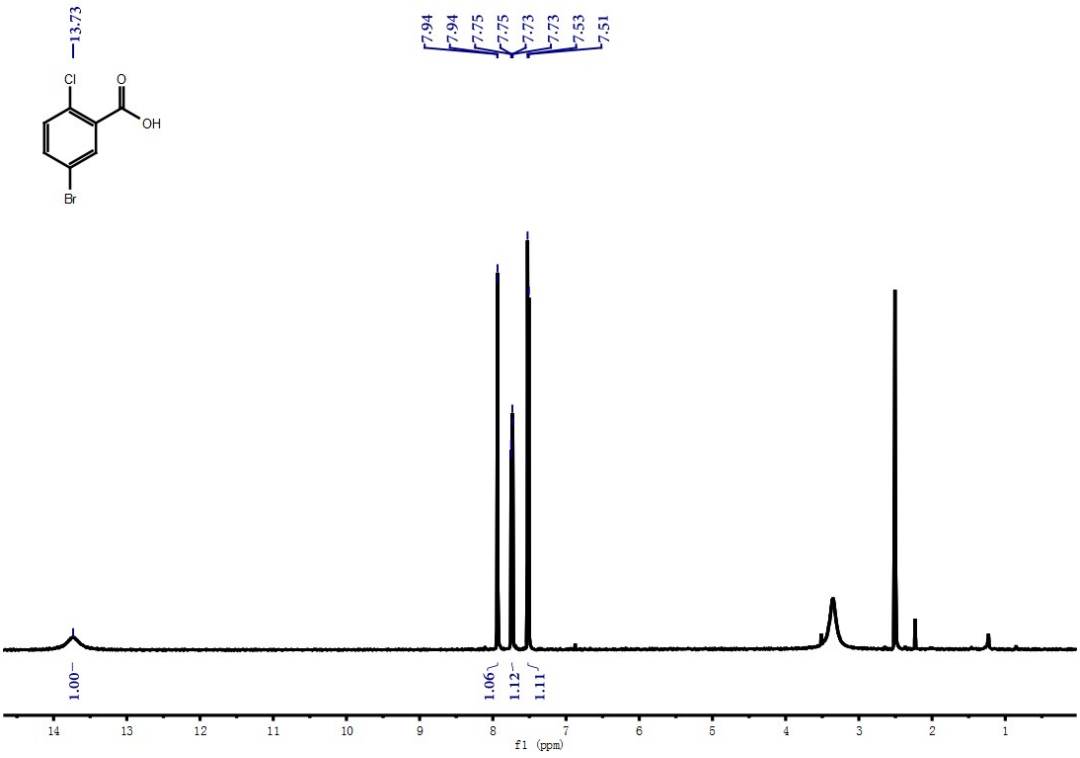
^{13}C NMR spectra of 12(125 MHz, DMSO)



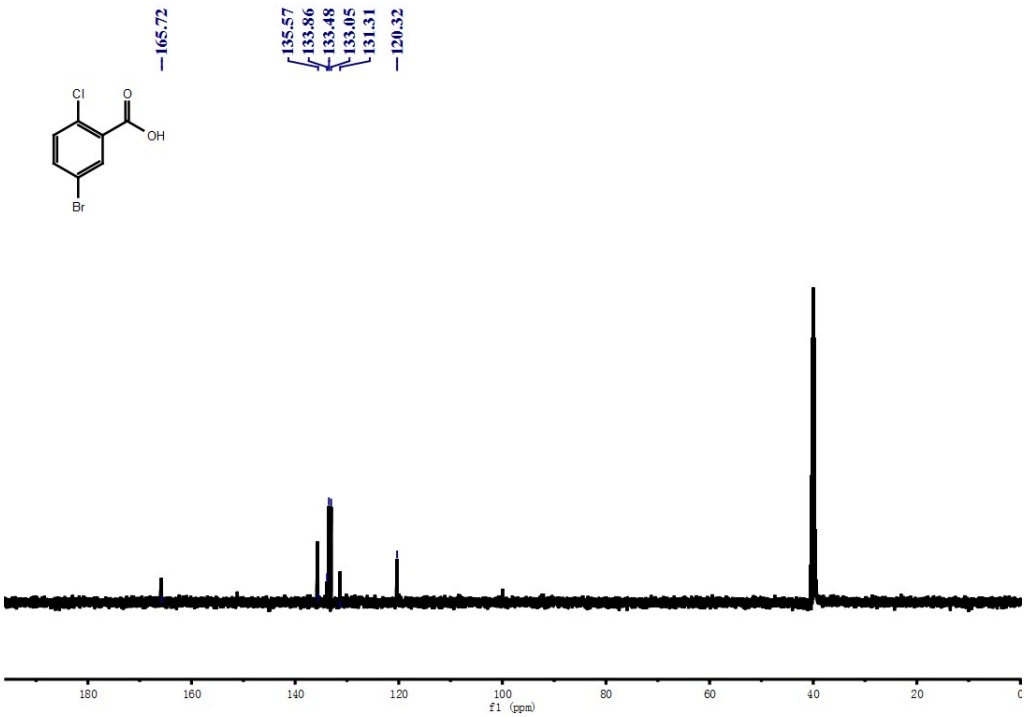
^{1}H NMR spectra of 13(500 MHz, DMSO)



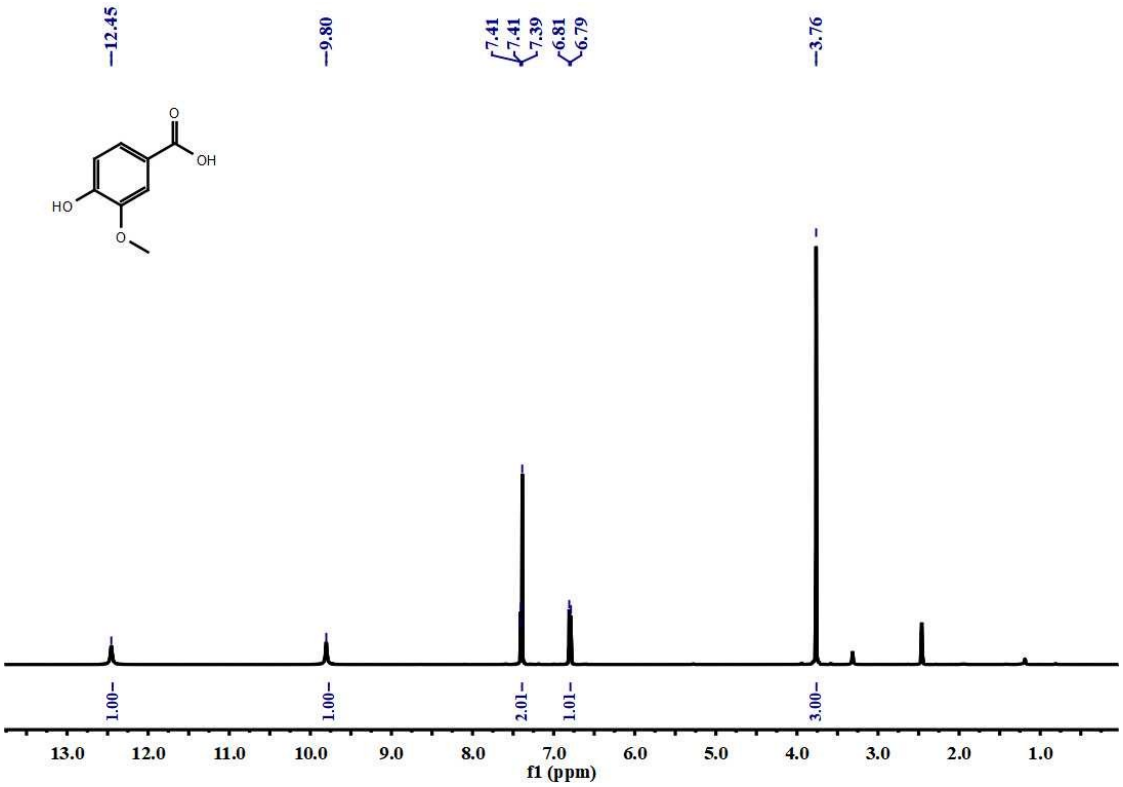
^{13}C NMR spectra of 13(125 MHz,DMSO)



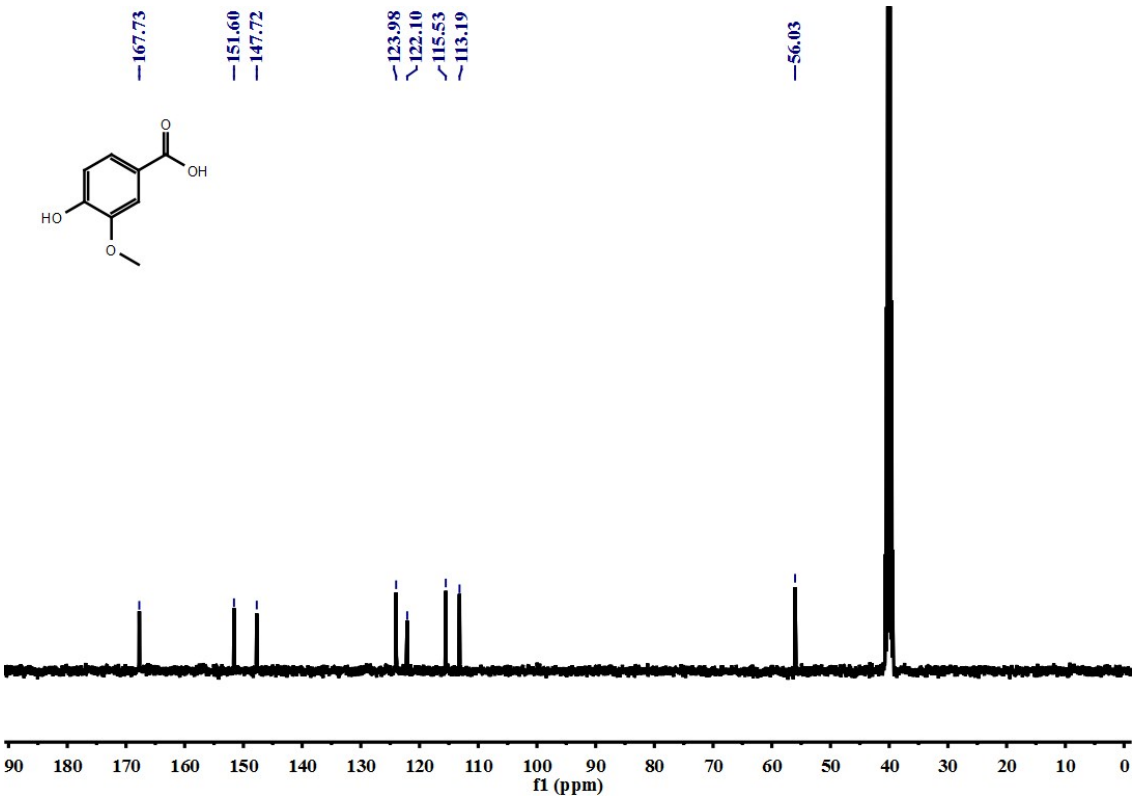
^{1}H NMR spectra of 14 (500 MHz, DMSO)



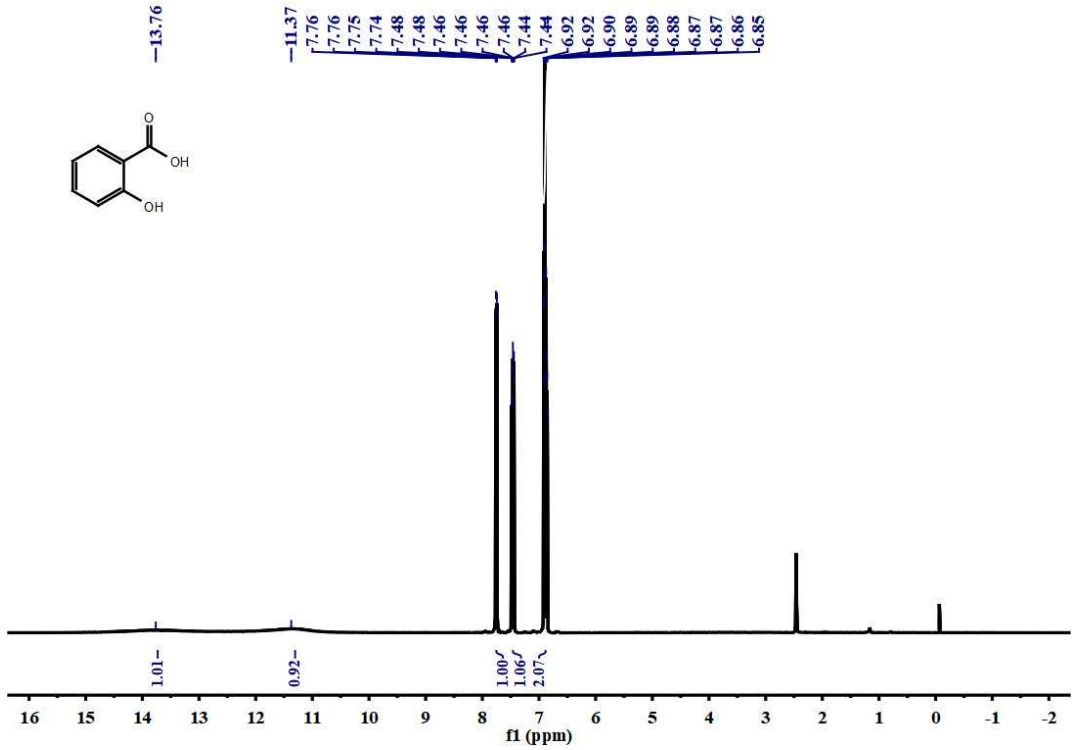
^{13}C NMR spectra of 14(125 MHz, DMSO)



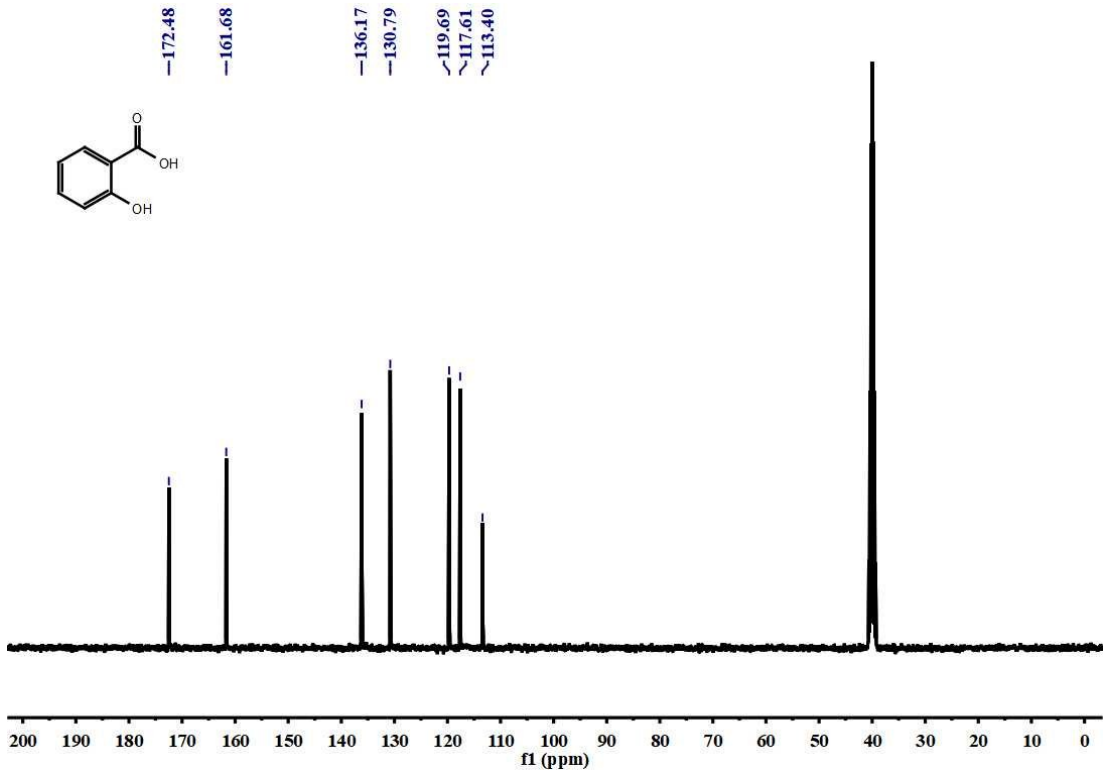
^{1}H NMR spectra of 15(500 MHz, DMSO)



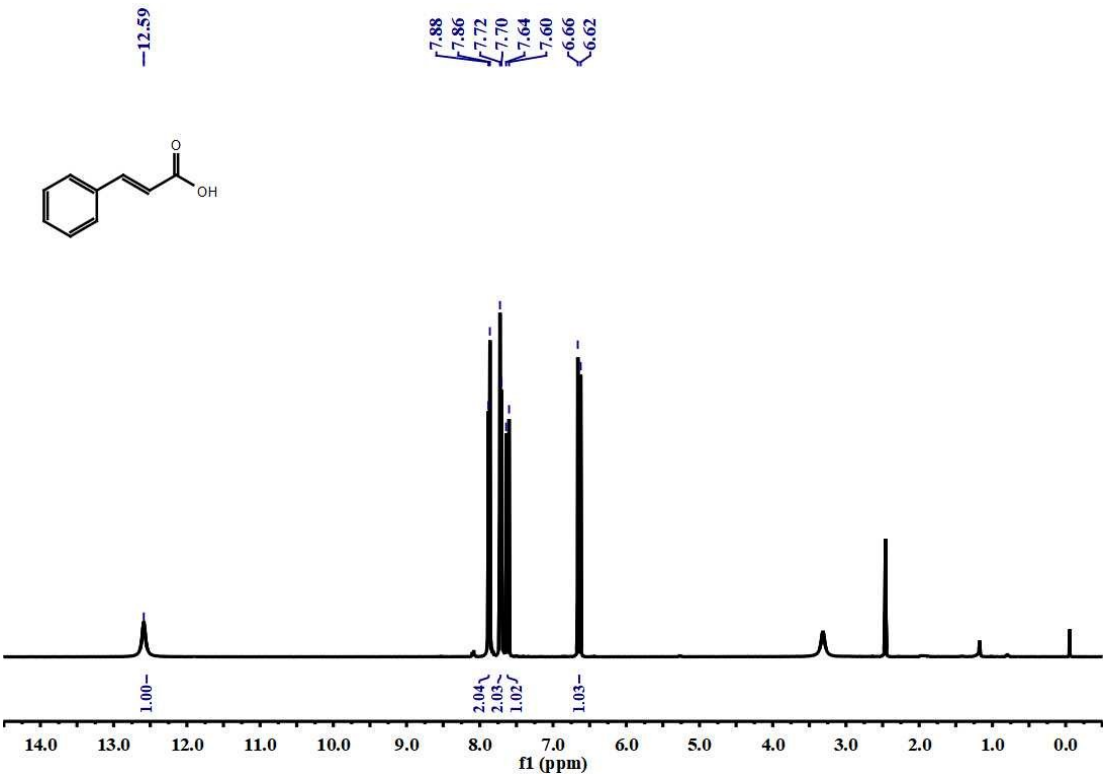
^{13}C NMR spectra of 15(125 MHz, DMSO)



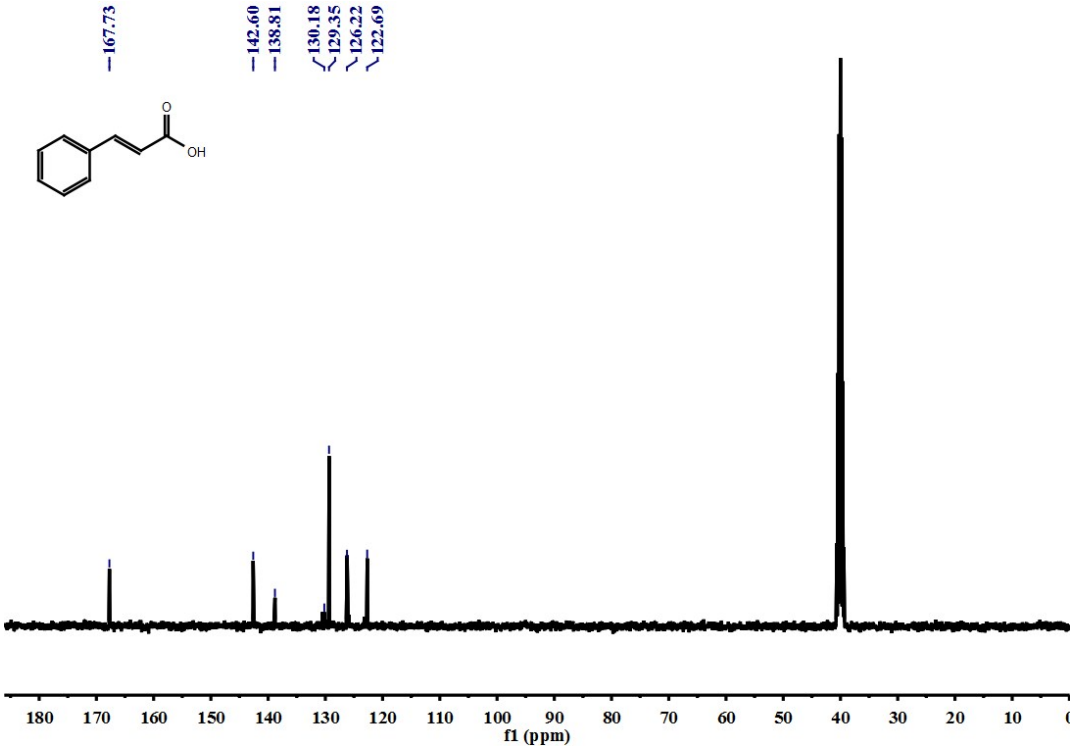
^{1}H NMR spectra of 16(500 MHz, DMSO)



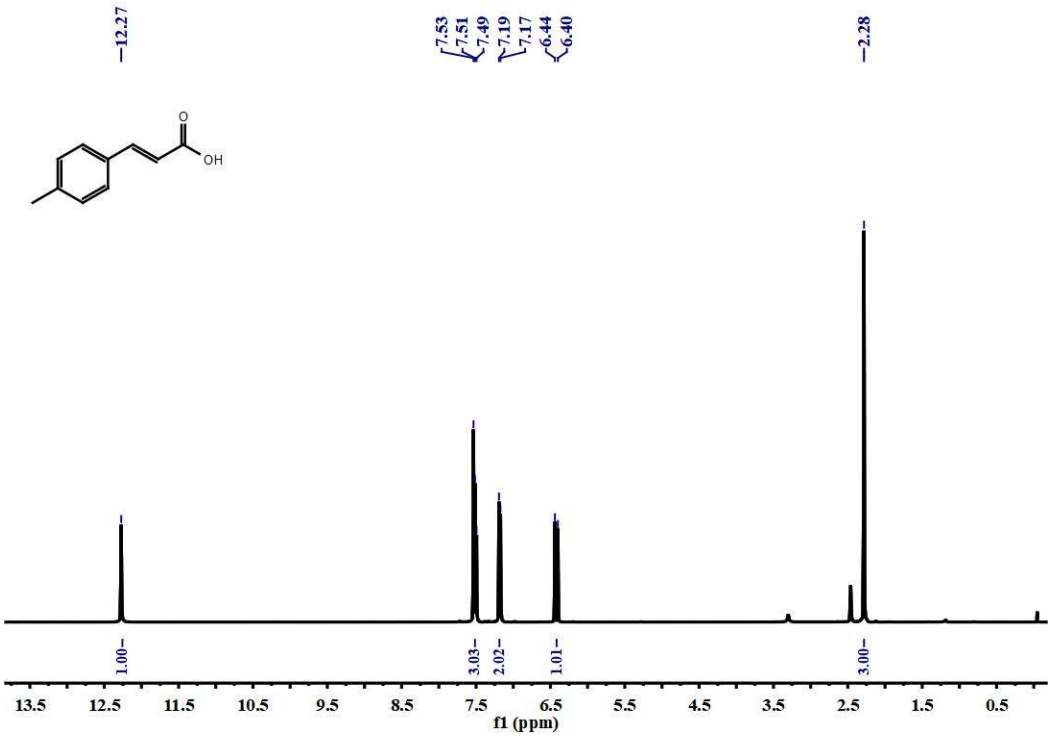
^{13}C NMR spectra of 16(125 MHz, DMSO)



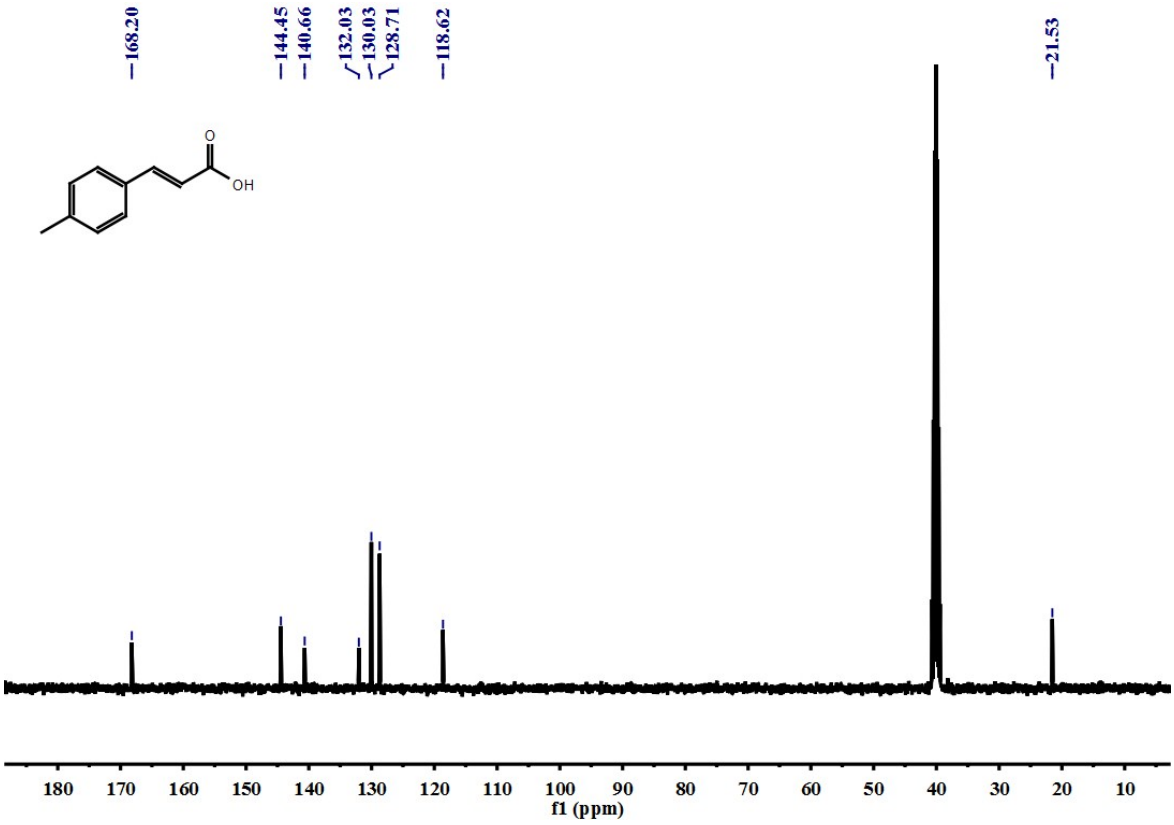
^{1}H NMR spectra of 17(500 MHz, DMSO)



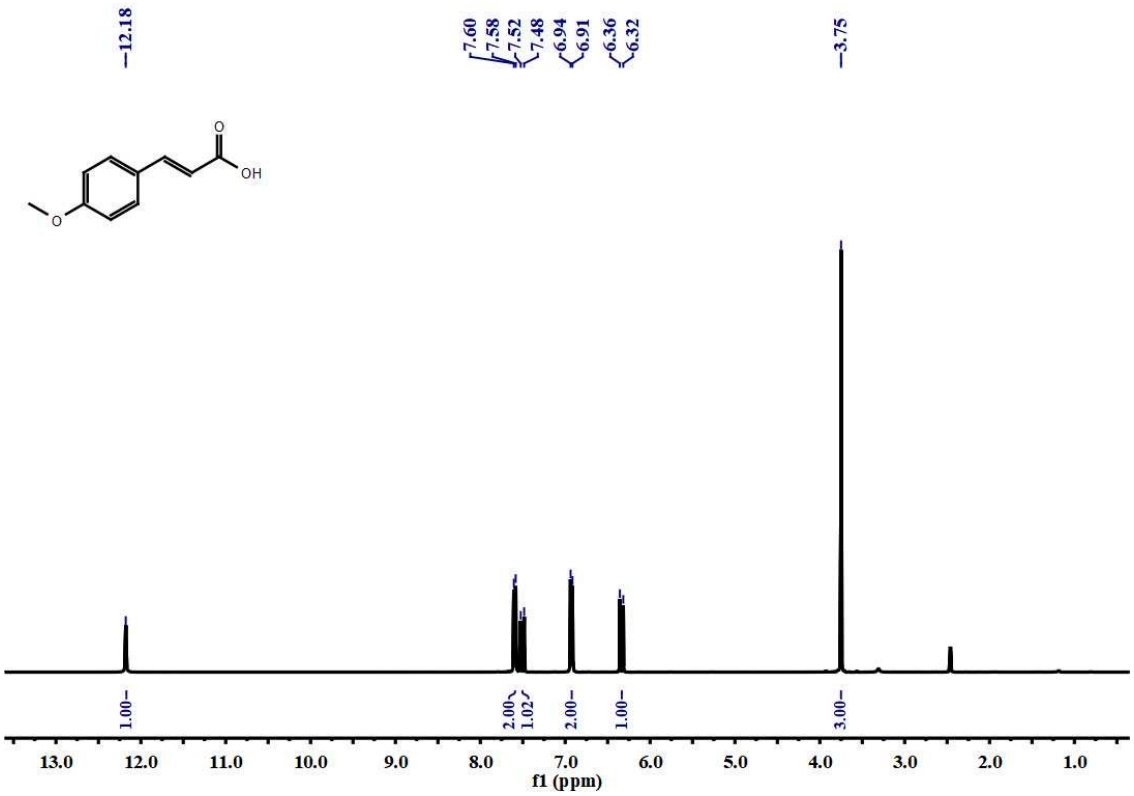
^{13}C NMR spectra of 17(125 MHz, DMSO)



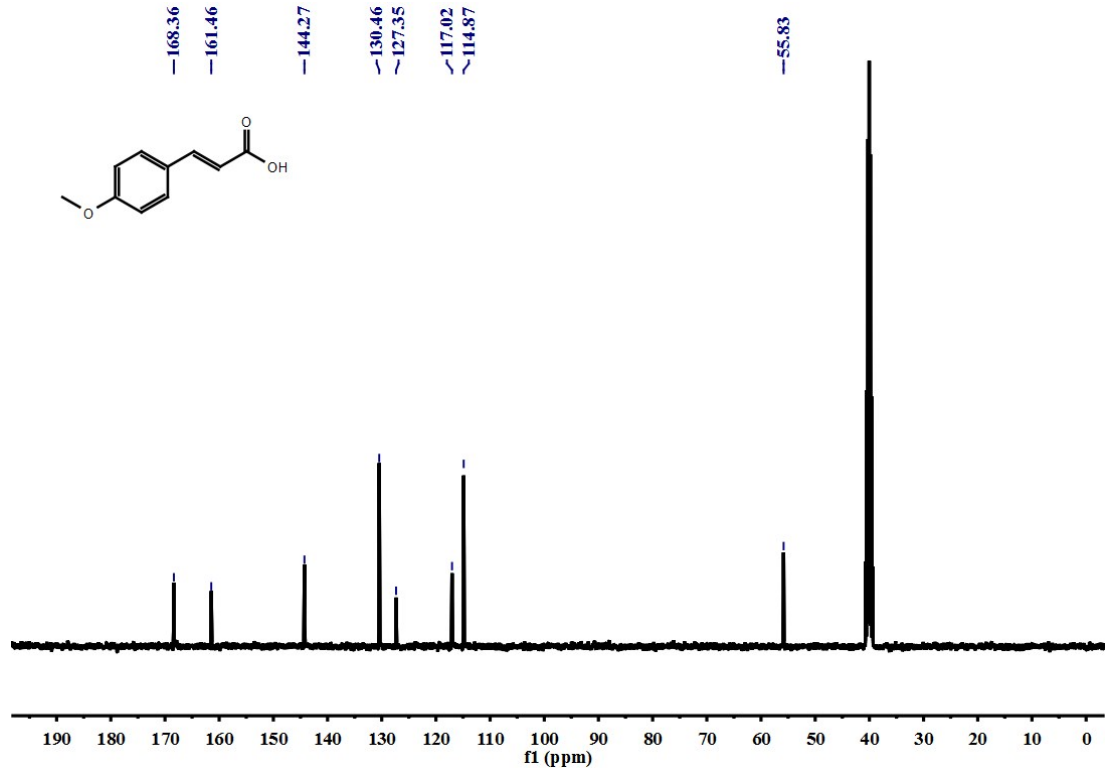
^{1}H NMR spectra of 18(500 MHz, DMSO)



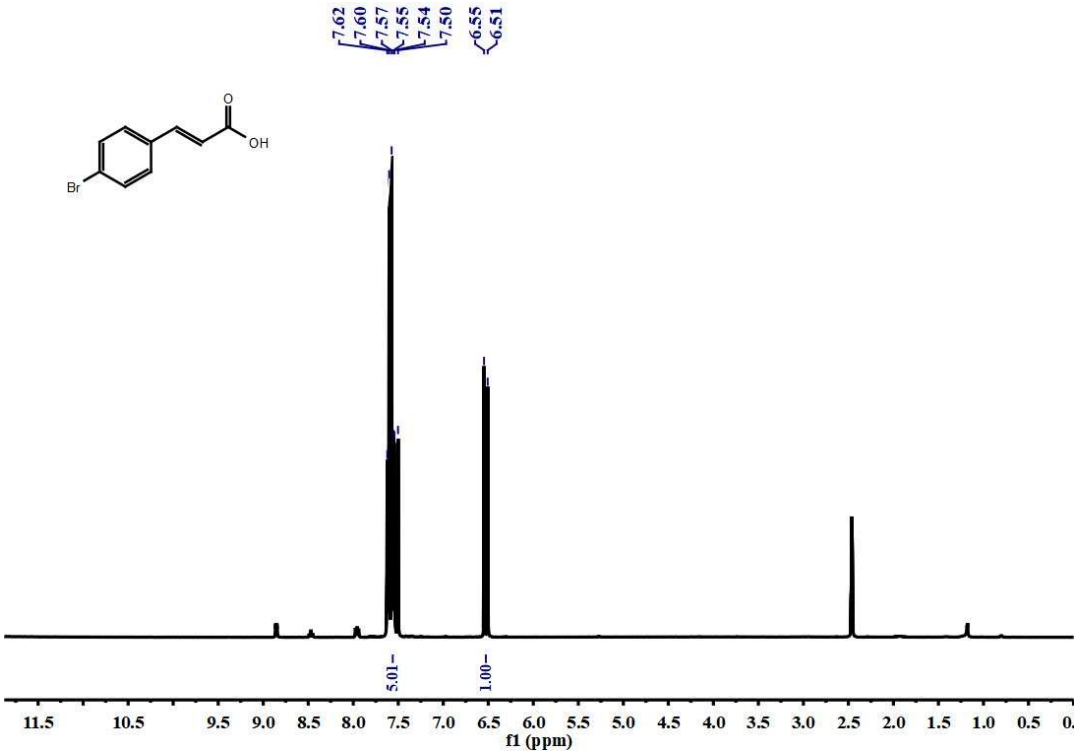
^{13}C NMR spectra of 18(125 MHz, DMSO)



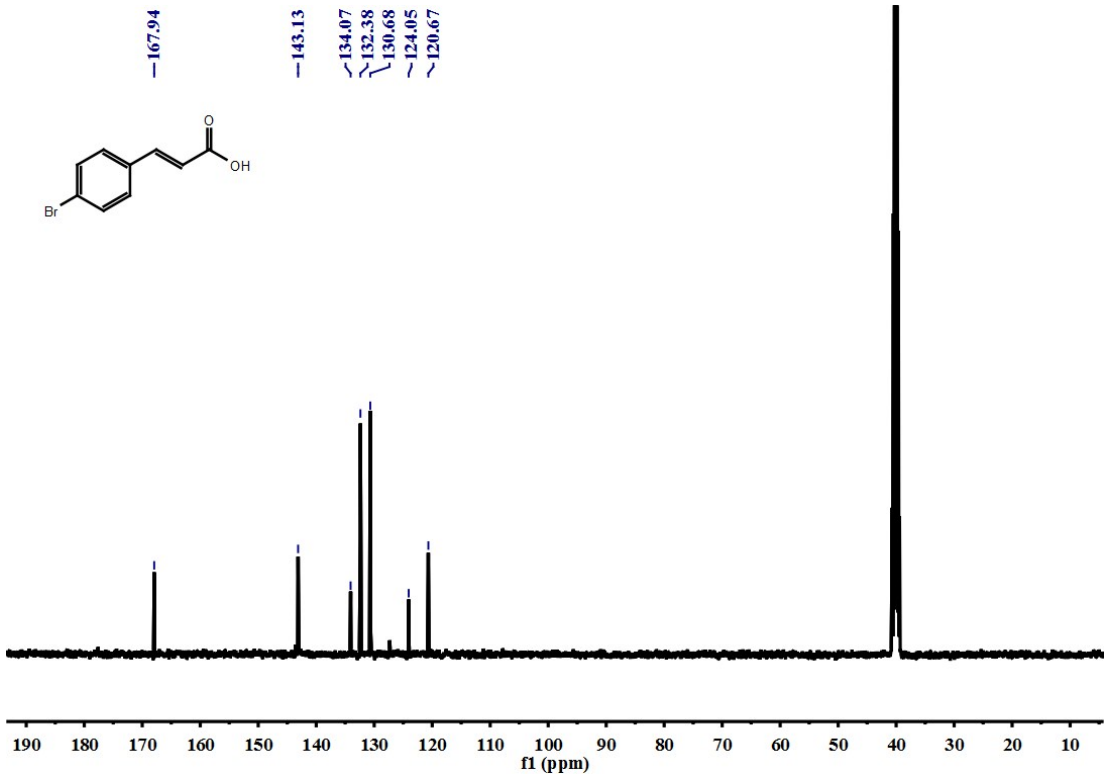
^{1}H NMR spectra of 19(500 MHz, DMSO)



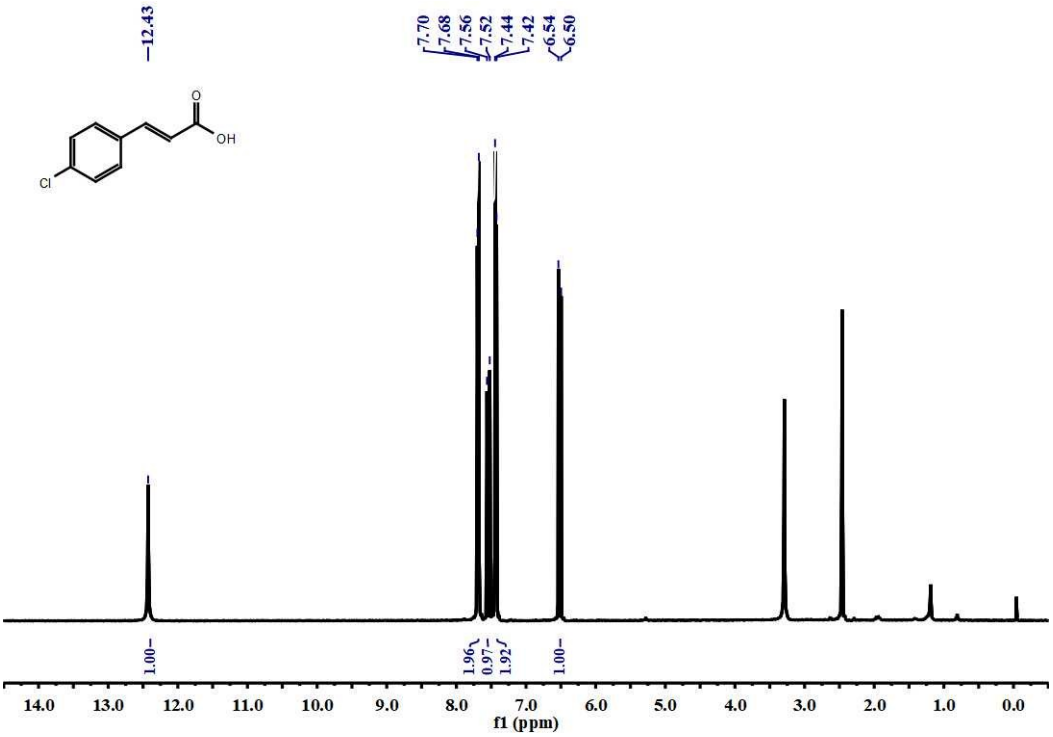
^{13}C NMR spectra of 19(125 MHz, DMSO)



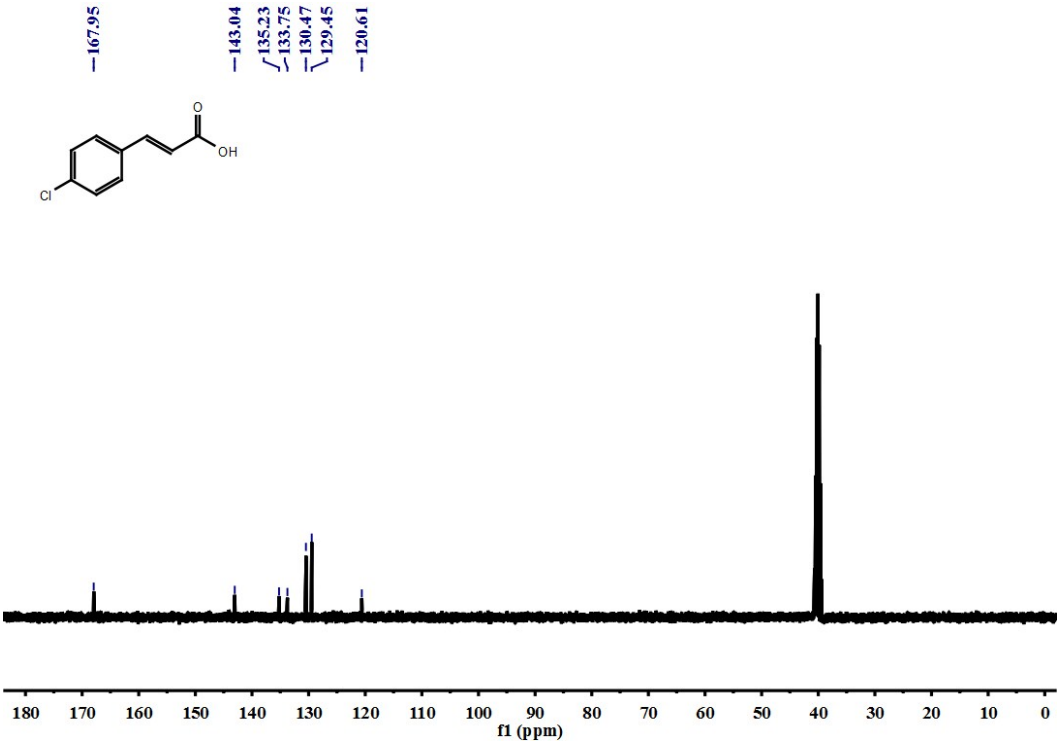
^{1}H NMR spectra of 20(500 MHz, DMSO)



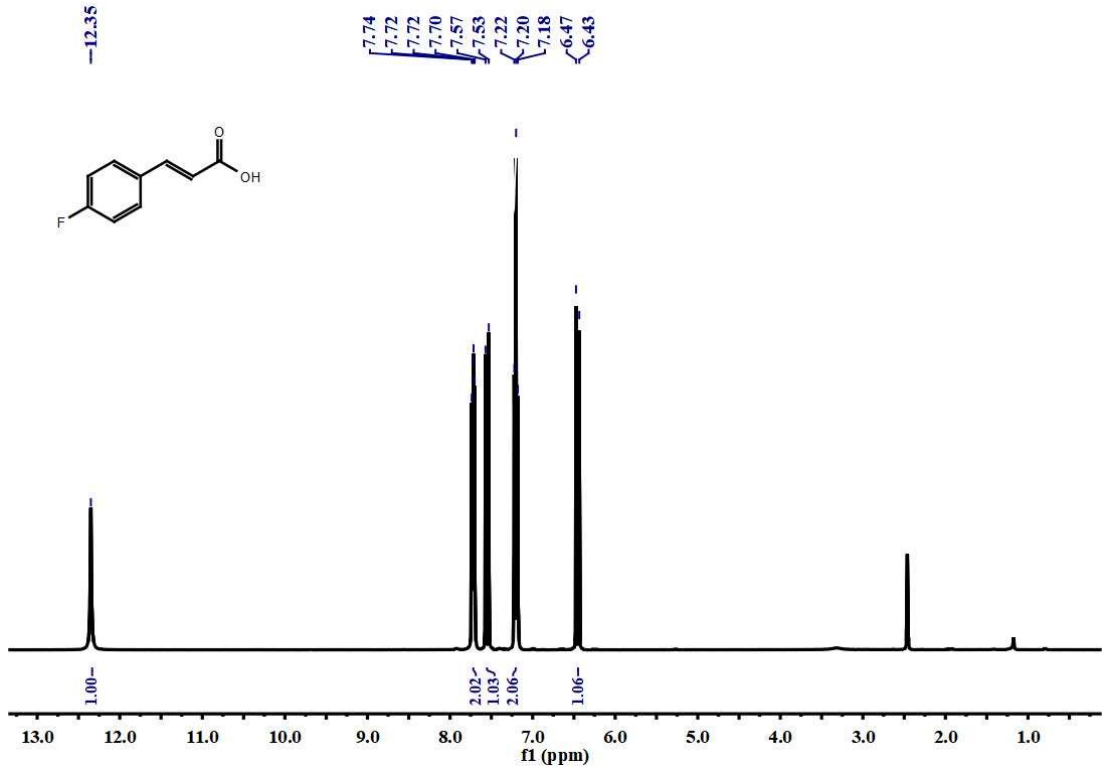
^{13}C NMR spectra of 20(125 MHz, DMSO)



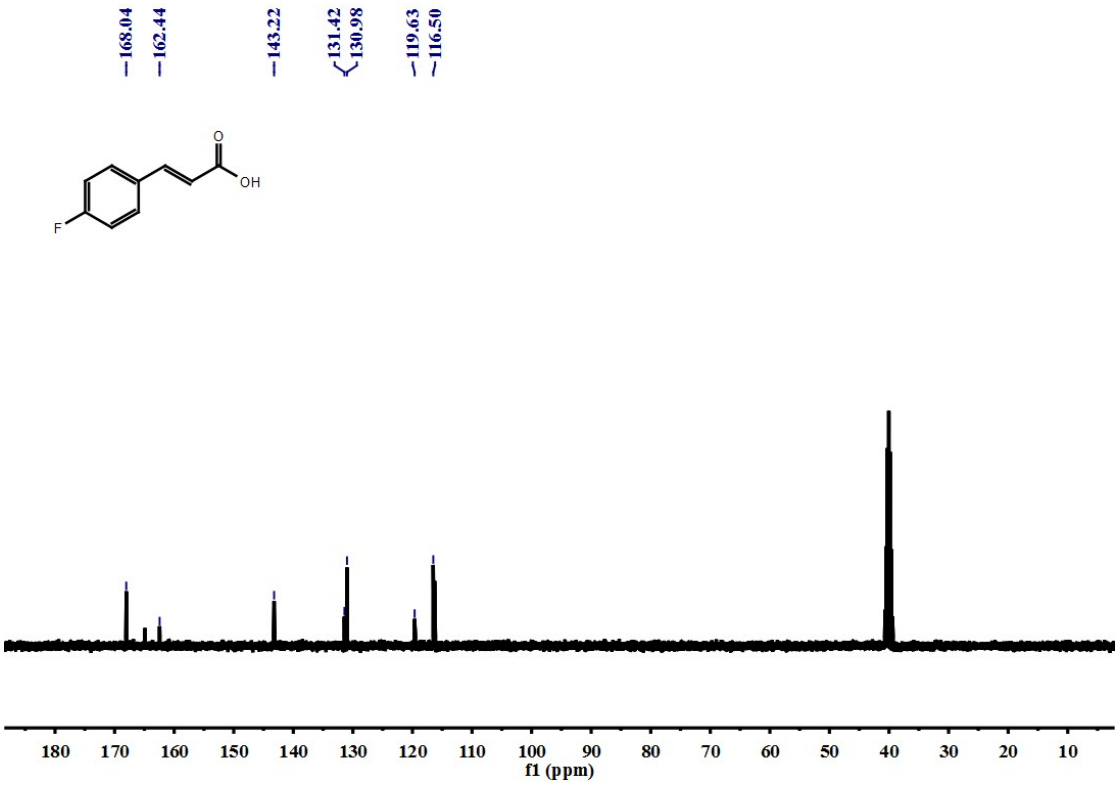
^{1}H NMR spectra of 21(500 MHz, DMSO)



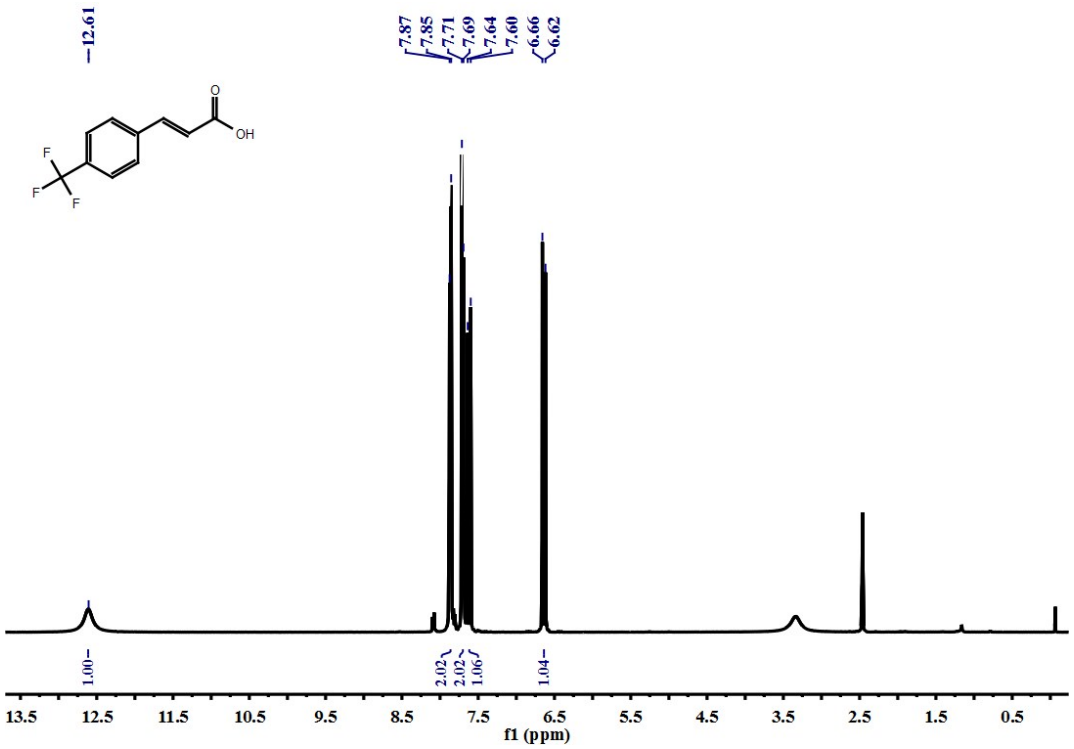
^{13}C NMR spectra of 21(125 MHz, DMSO)



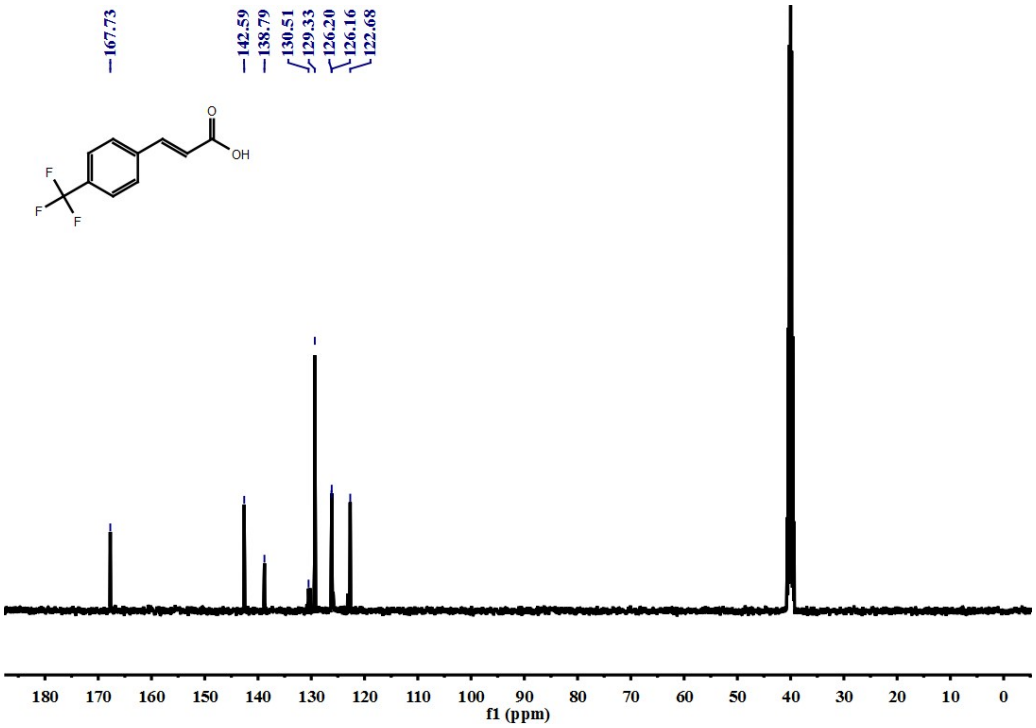
^{1}H NMR spectra of 22(500 MHz, DMSO)



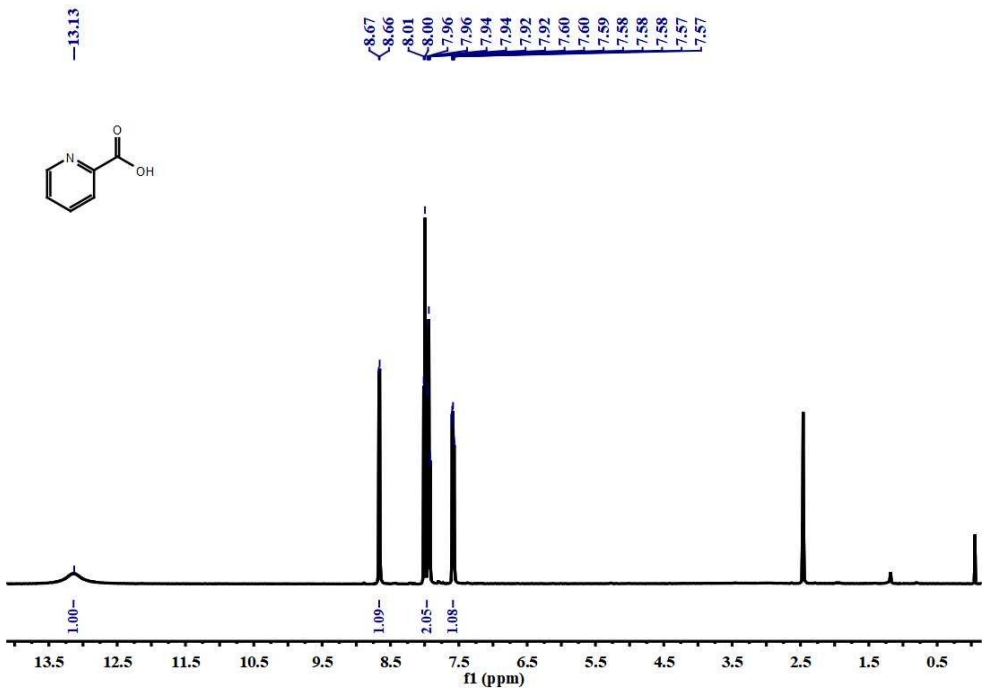
^{13}C NMR spectra of 22(125 MHz, DMSO)



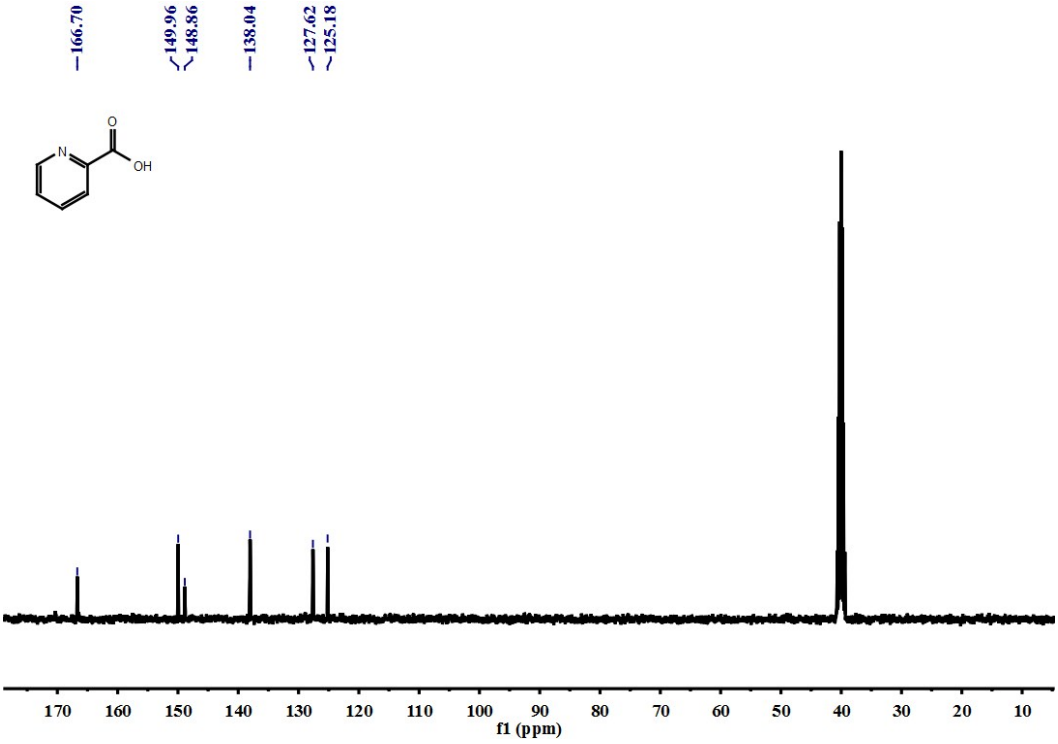
^{1}H NMR spectra of 23(500 MHz, DMSO)



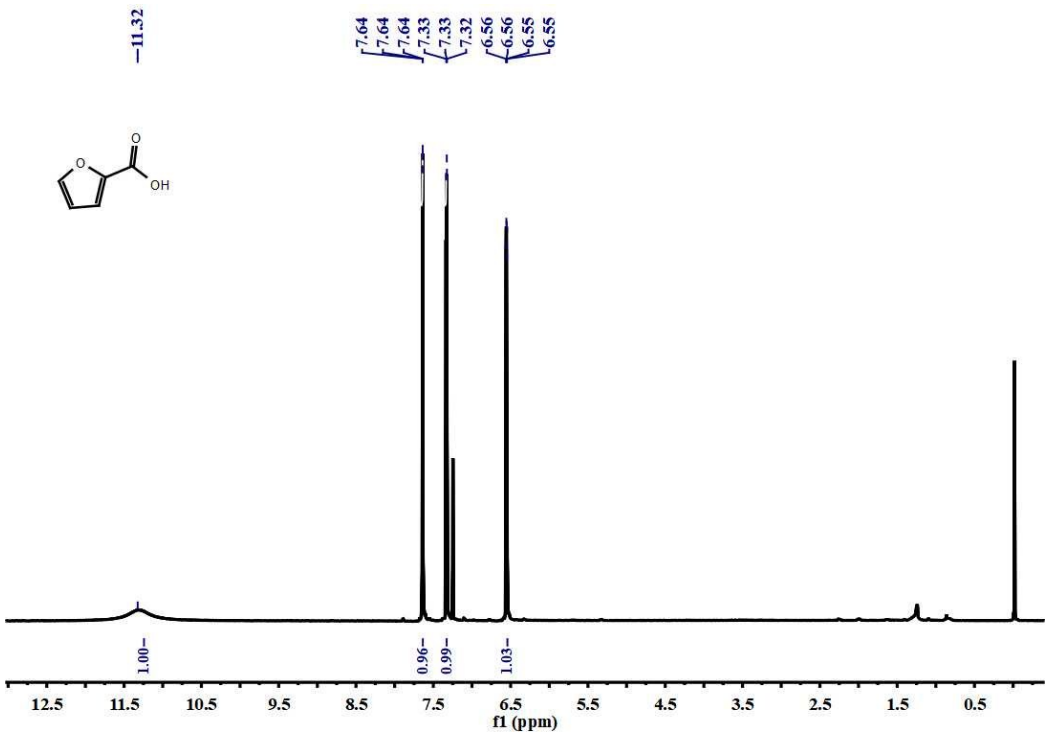
^{13}C NMR spectra of 23(125 MHz, DMSO)



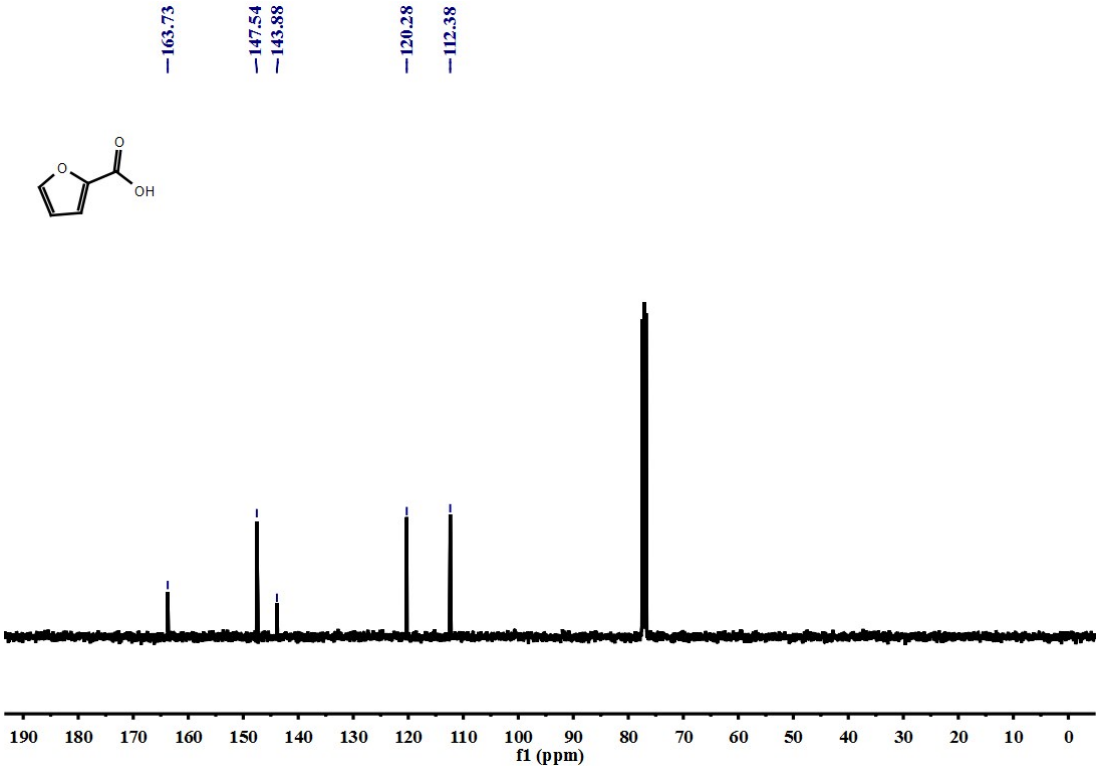
^{1}H NMR spectra of 24(500 MHz, DMSO)



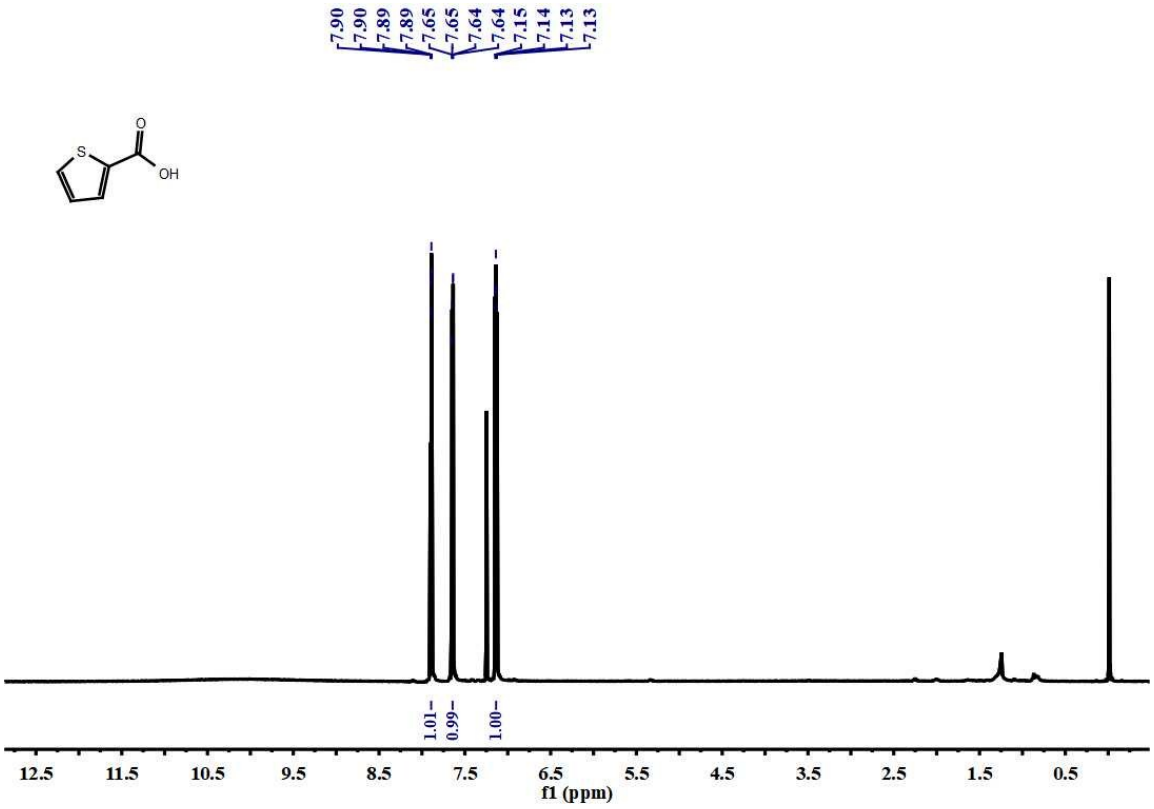
^{13}C NMR spectra of 24(125 MHz, DMSO)



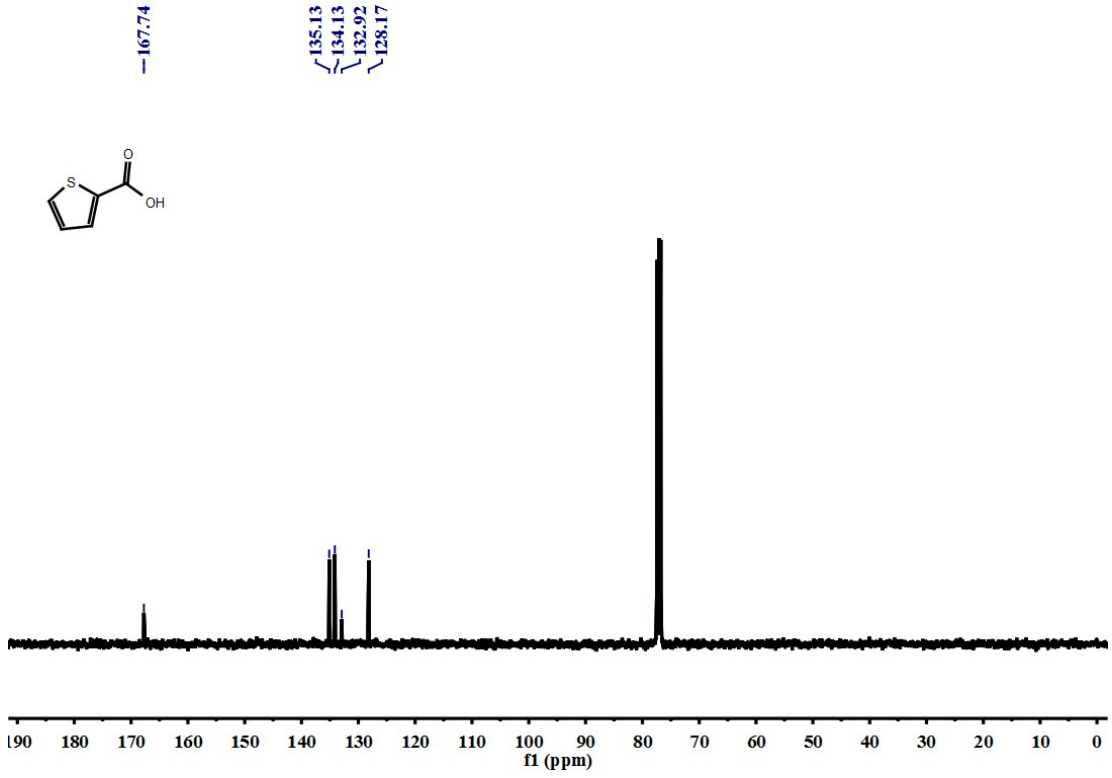
^{1}H NMR spectra of 25(500 MHz, CDCl3)



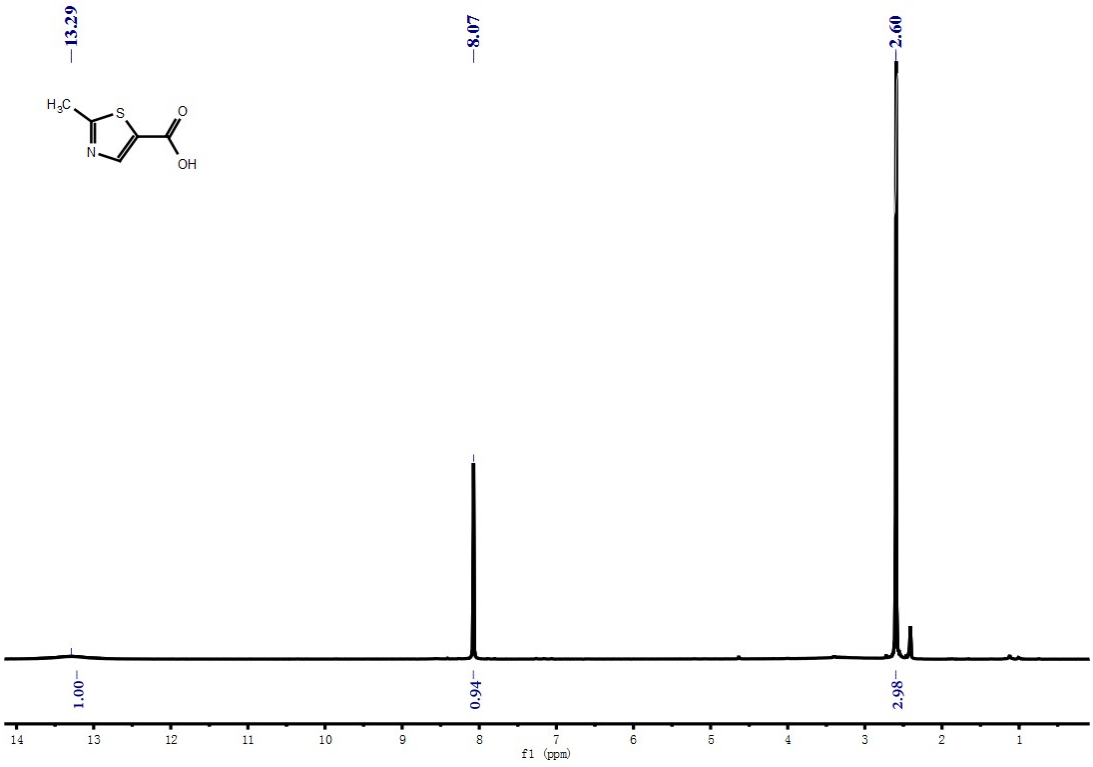
^{13}C NMR spectra of 25(125 MHz, $CDCl_3$)



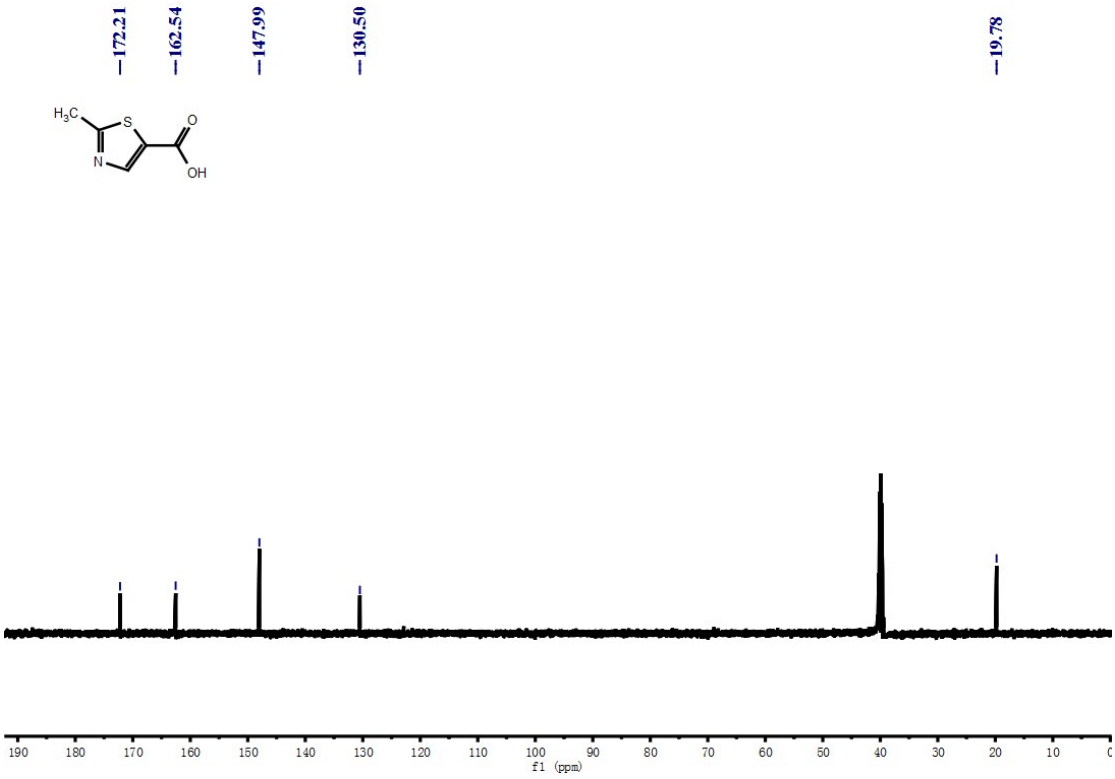
^{1}H NMR spectra of 26(500 MHz, $CDCl_3$)



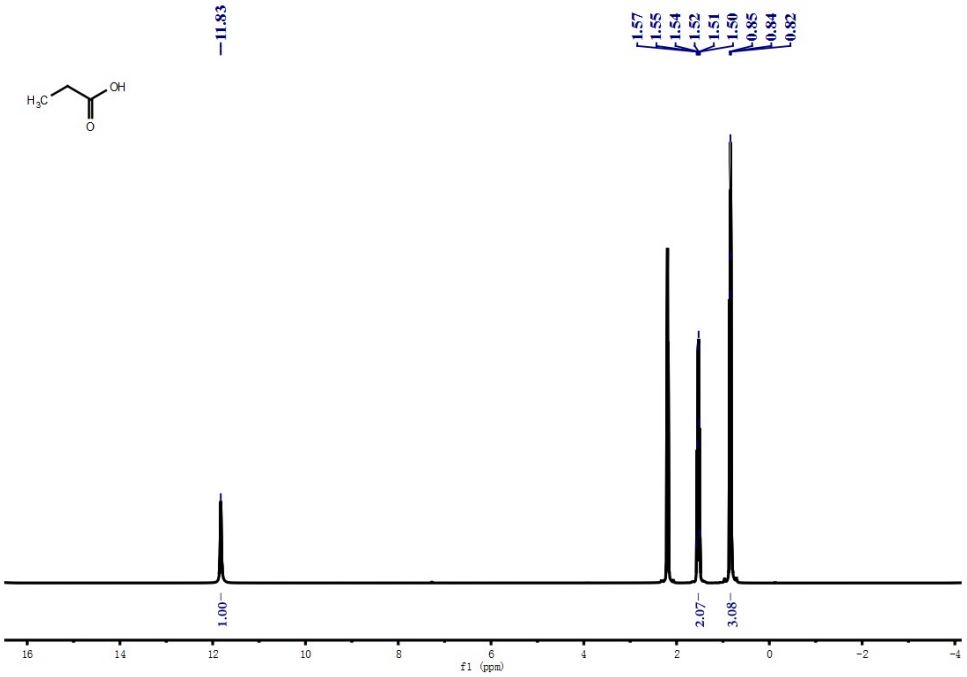
^{13}C NMR spectra of 26(125 MHz, $CDCl_3$)



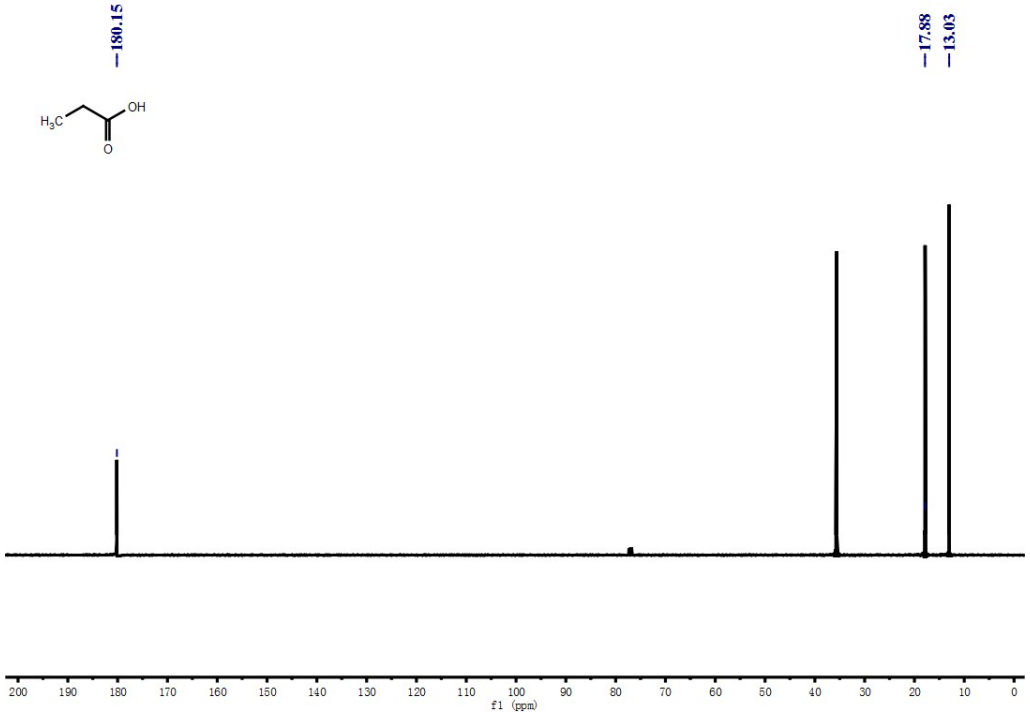
^{1}H NMR spectra of 27(500 MHz, DMSO)



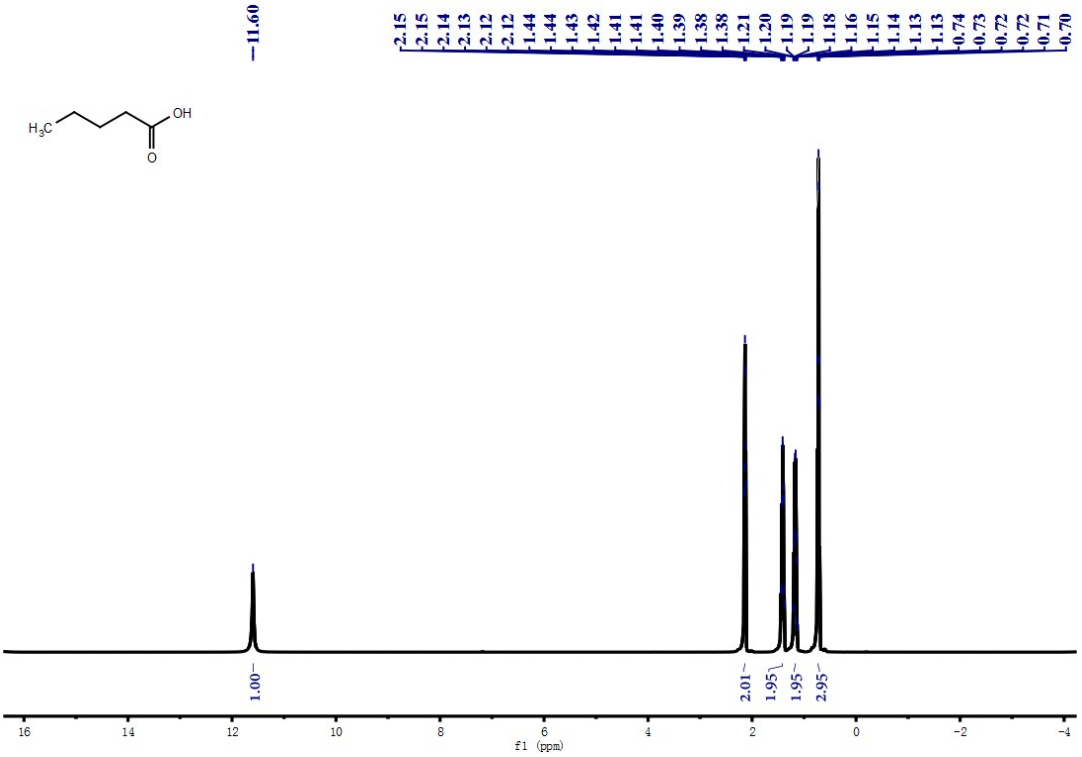
^{13}C NMR spectra of 27(125 MHz, DMSO)



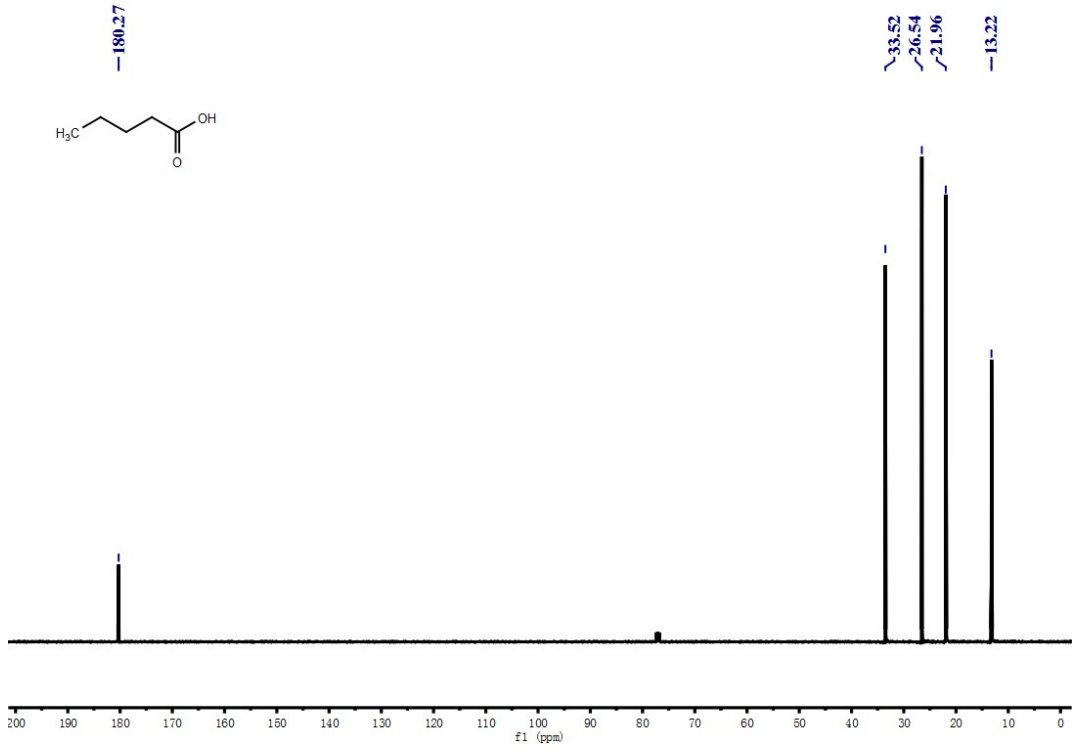
^{1}H NMR spectra of 28(500 MHz, $CDCl_3$)



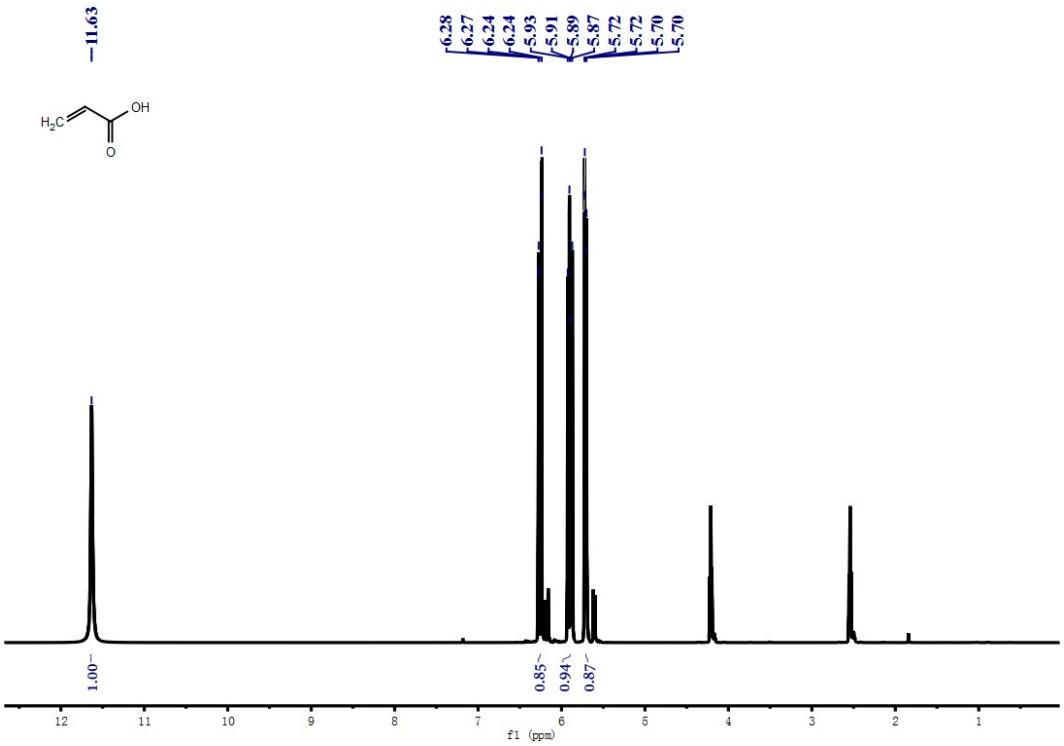
^{13}C NMR spectra of 28(125 MHz, CDCl3)



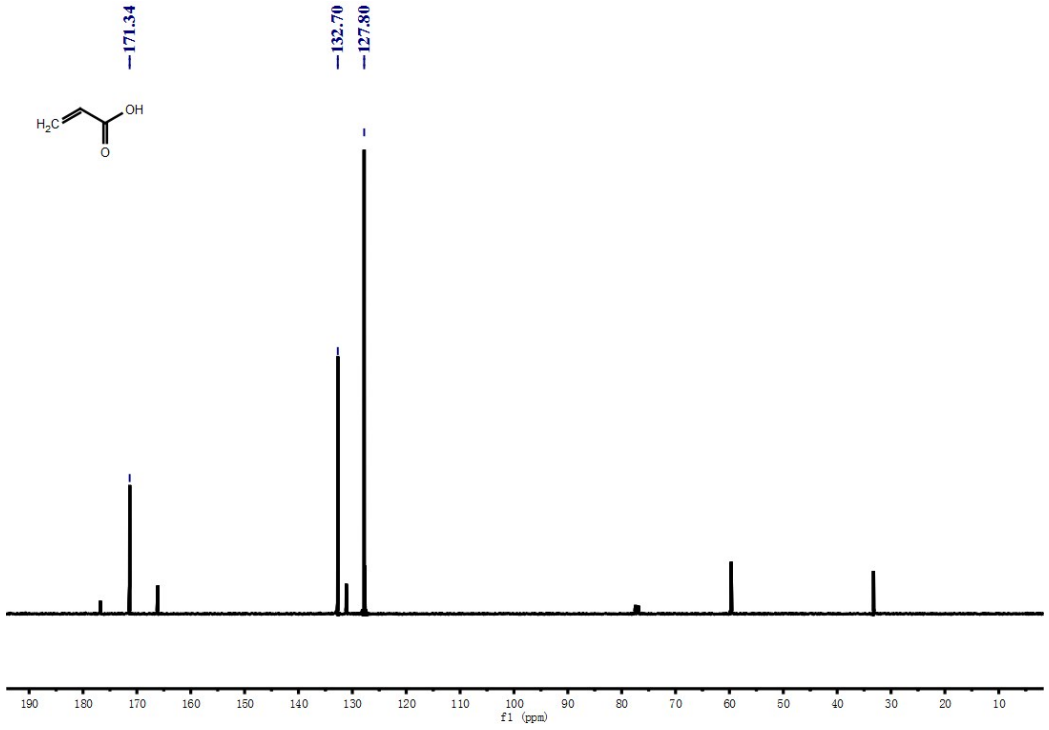
^{1}H NMR spectra of 29(500 MHz, CDCl3)



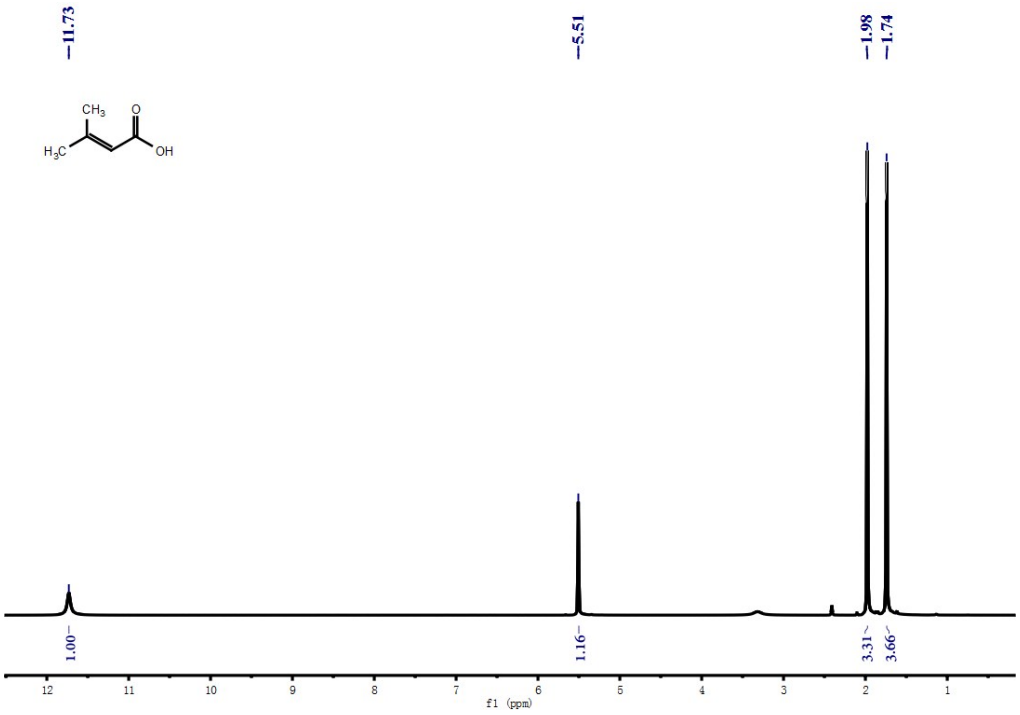
^{13}C NMR spectra of 29(125 MHz, CDCl3)



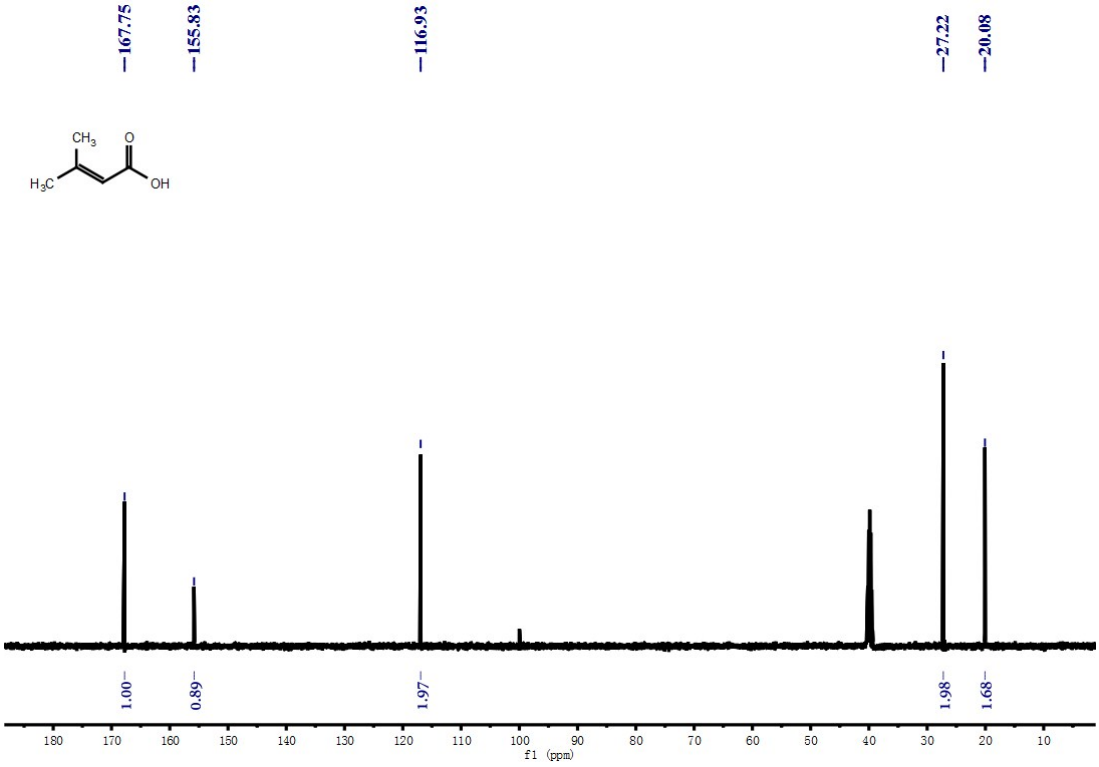
^{1}H NMR spectra of 30(500 MHz, CDCl3)



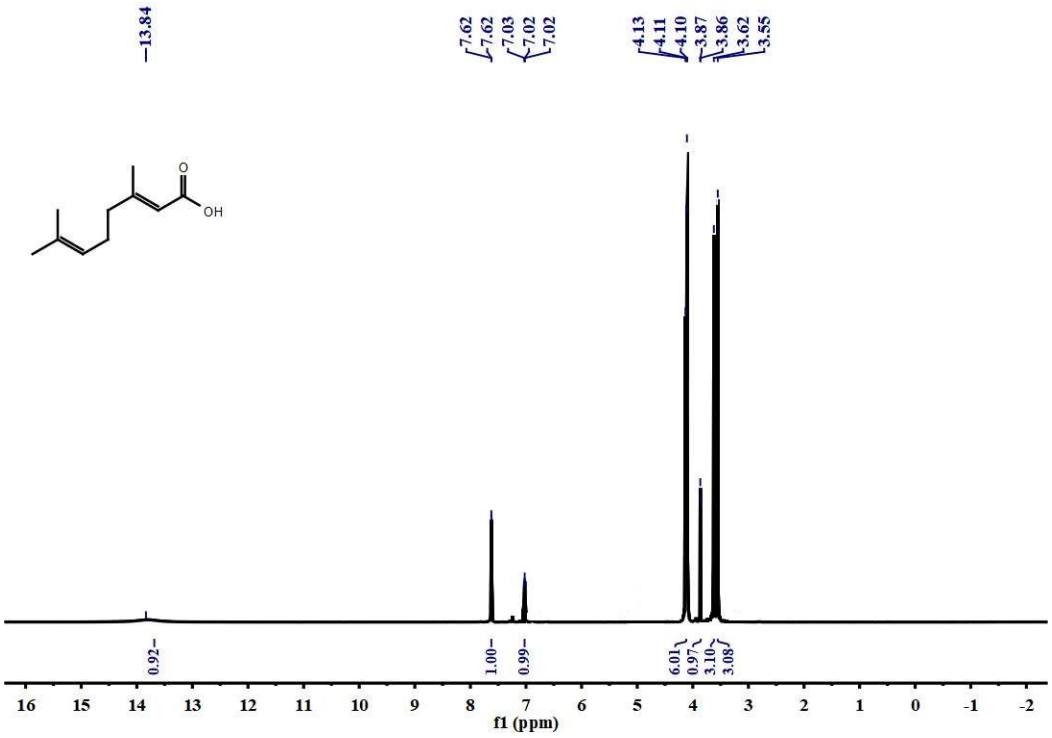
^{13}C NMR spectra of 30(125 MHz, CDCl3)



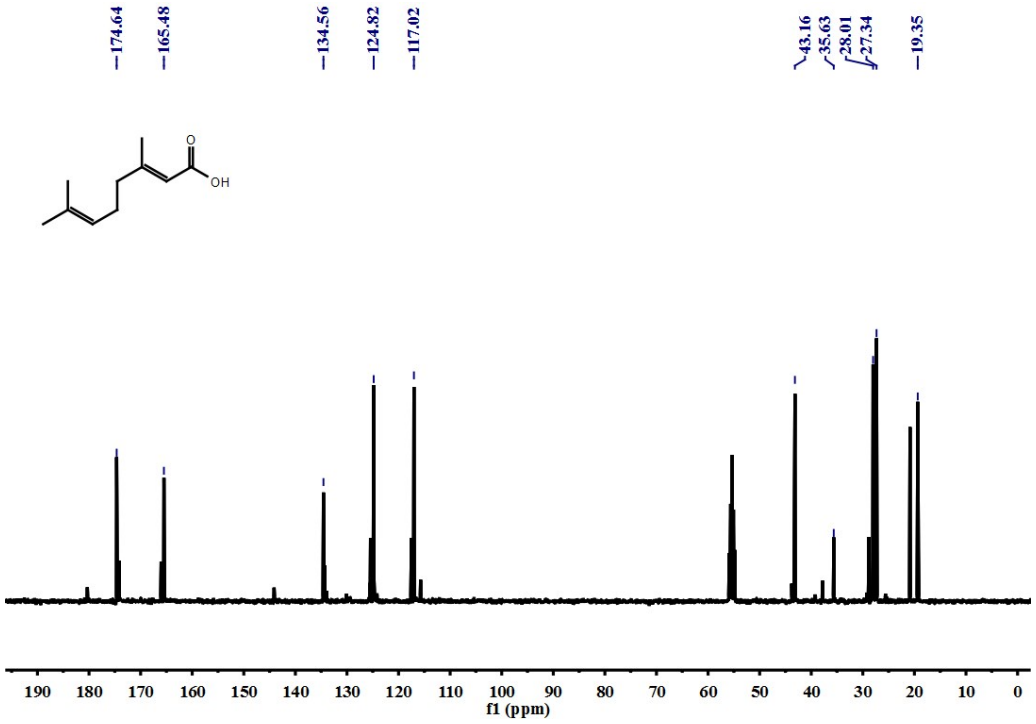
^{1}H NMR spectra of 31(500 MHz, DMSO)



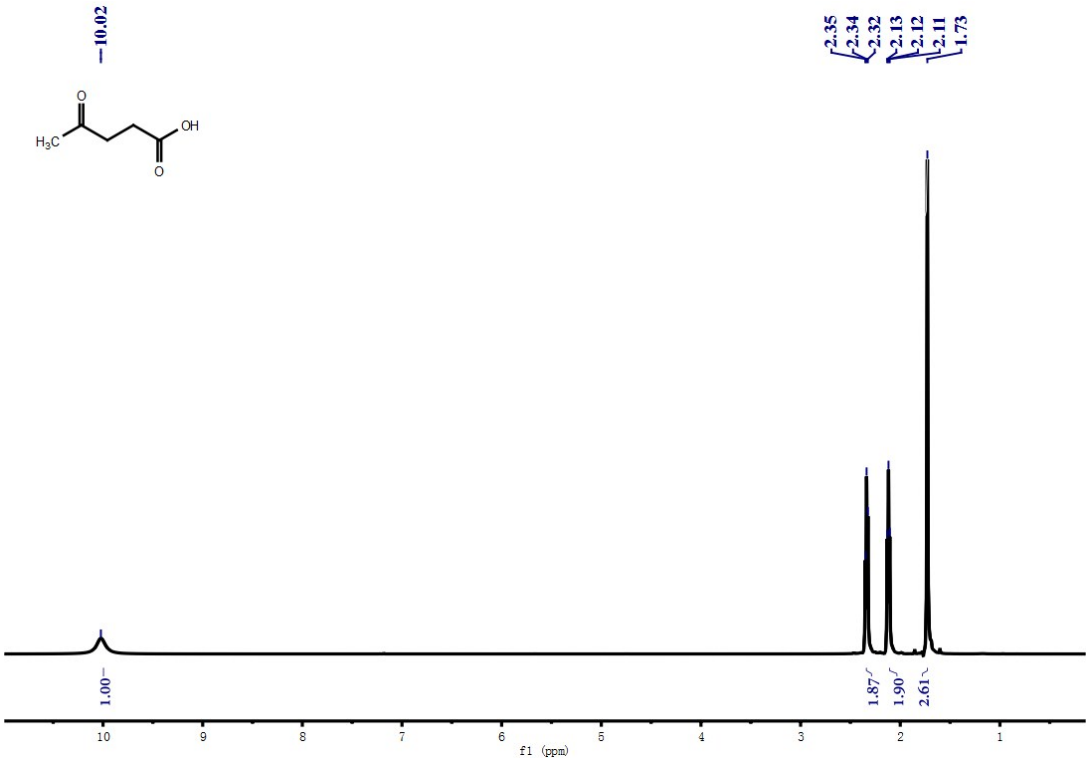
^{13}C NMR spectra of 31(125 MHz, DMSO)



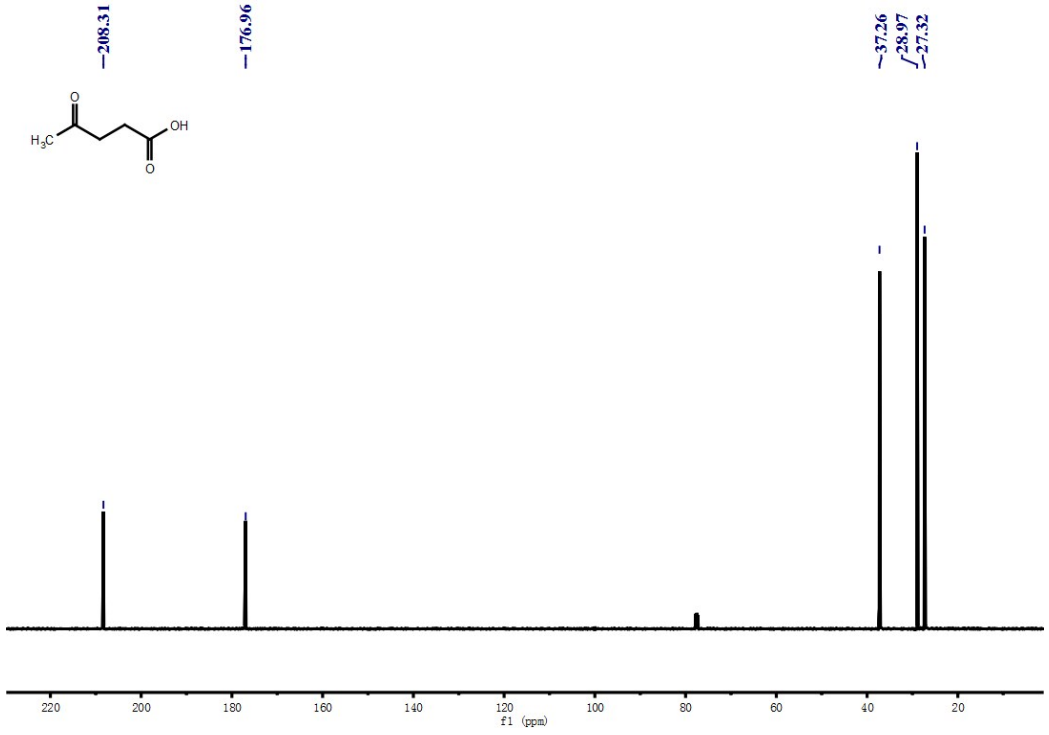
^{1}H NMR spectra of 32(500 MHz, CDCl3)



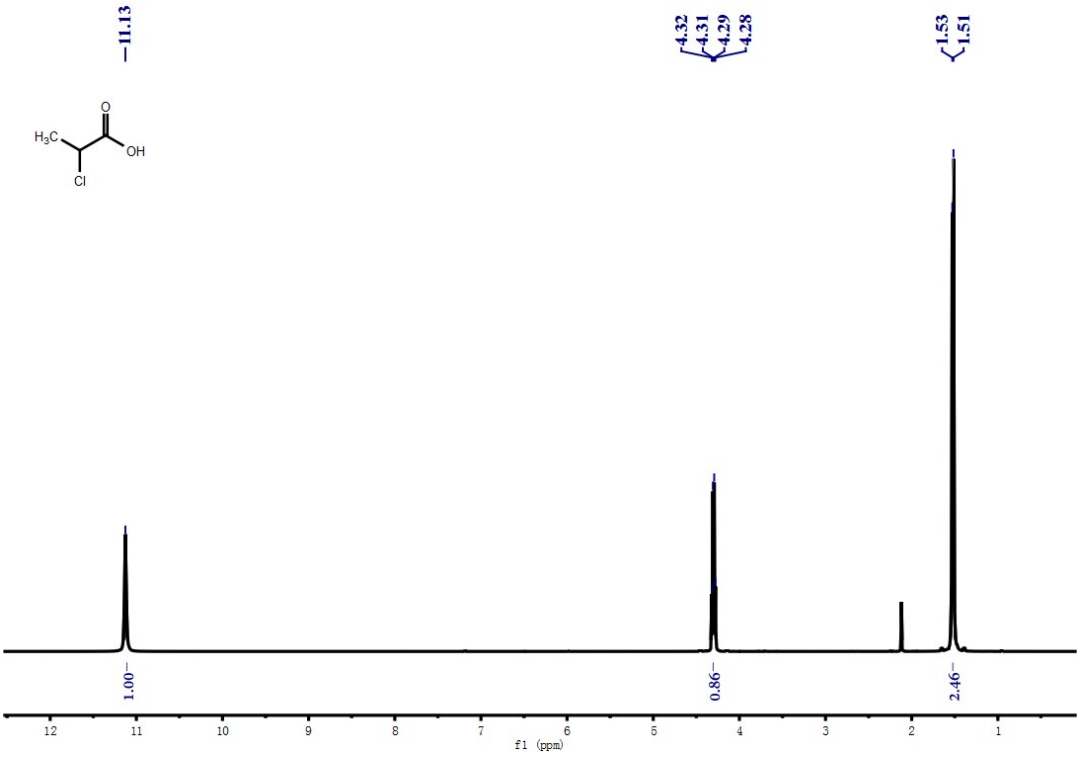
^{13}C NMR spectra of 32(125 MHz, CDCl3)



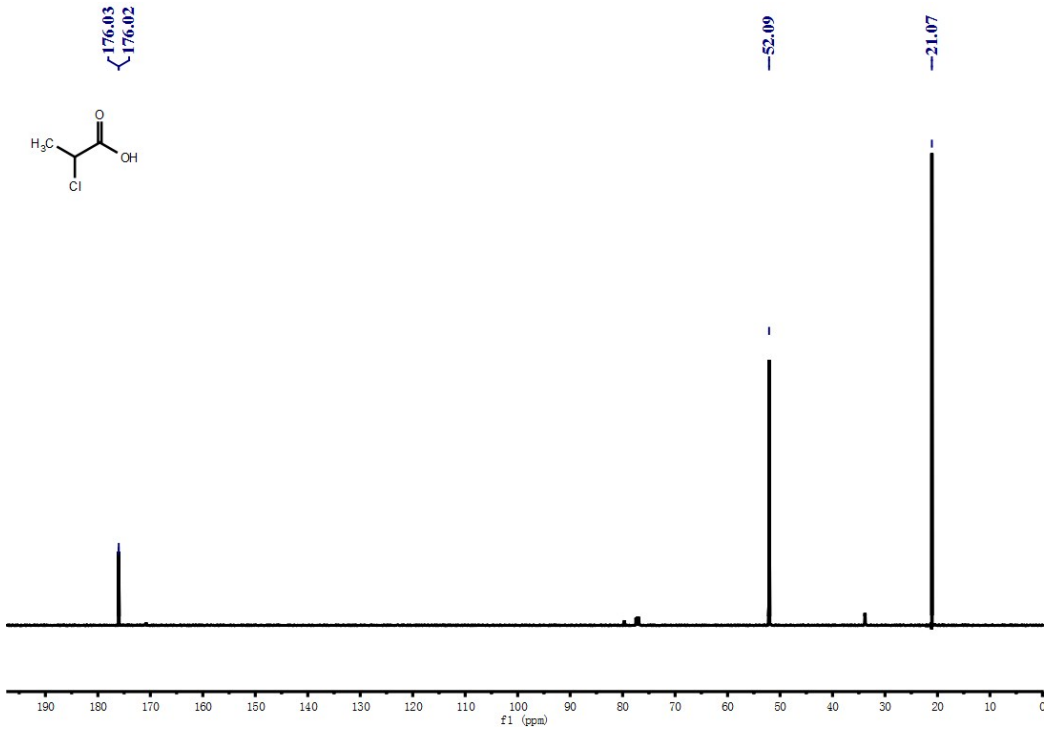
^{1}H NMR spectra of 33(500 MHz, CDCl3)



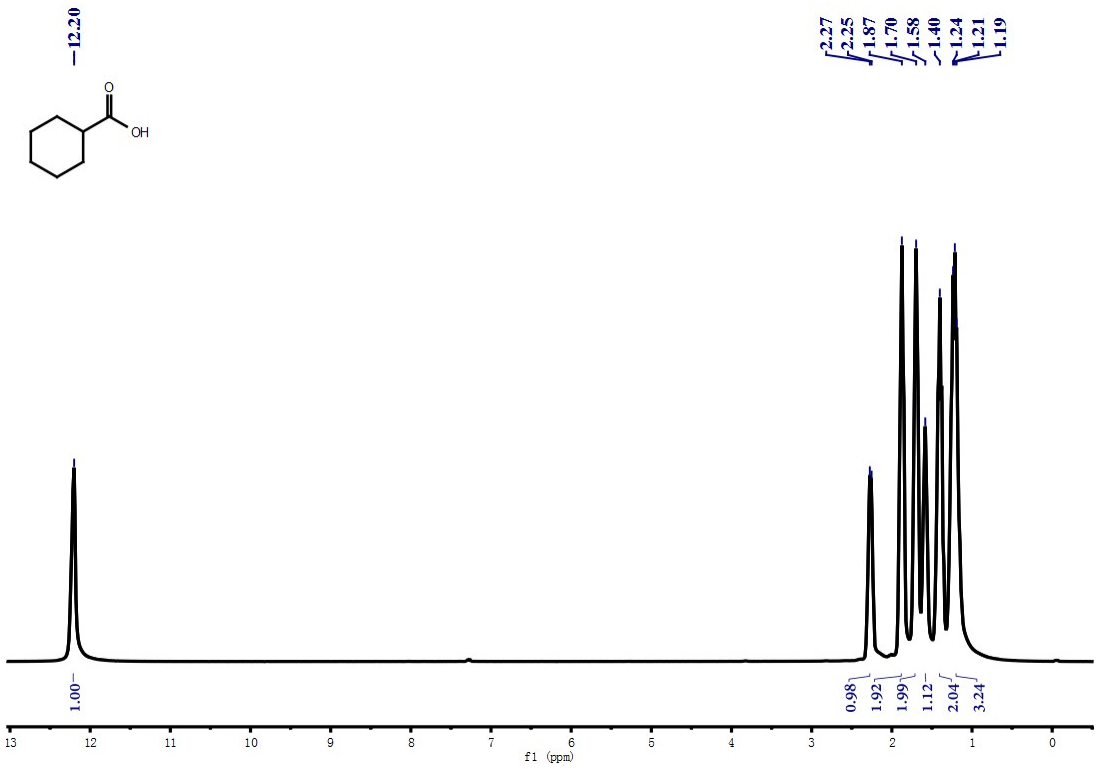
^{13}C NMR spectra of 33(125 MHz, CDCl3)



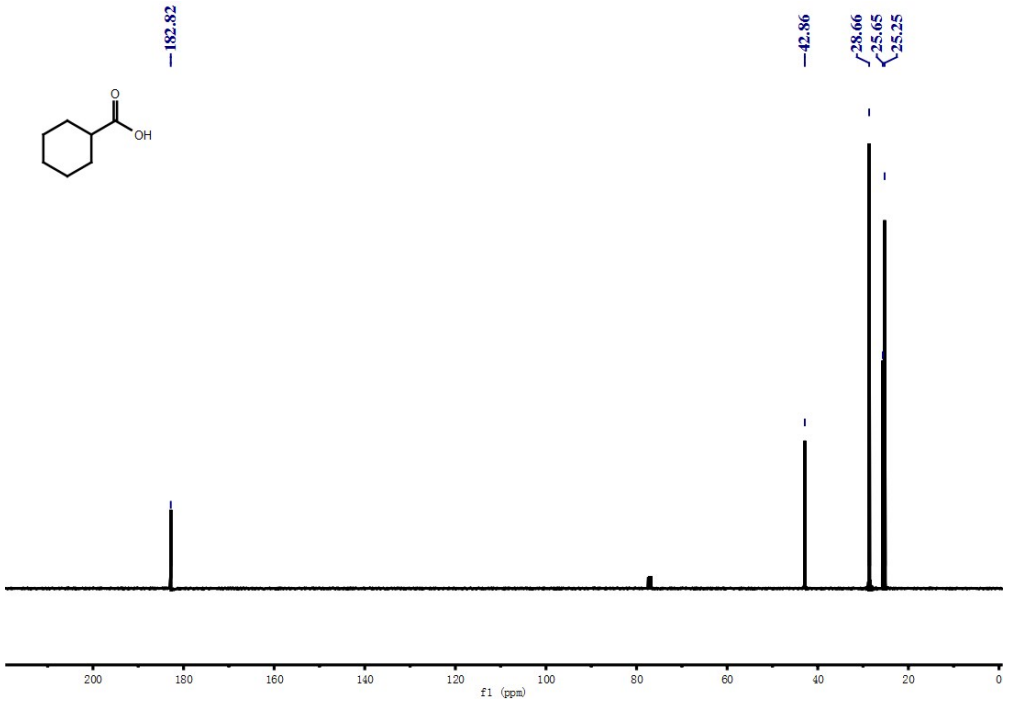
^{1}H NMR spectra of 34(500 MHz, CDCl3)



^{13}C NMR spectra of 34(125 MHz, CDCl3)



^{1}H NMR spectra of 35(500 MHz, CDCl3)



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