Electronic Supplementary Information

Highly Efficient and Practical Aerobic Oxidation of Alcohols with by Inorganic-ligand Supported Copper Catalysis

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I. General information

The catalysts was prepared according to published literature methods.[1,2] 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 and Bruker AVANCE III 400MHz (400MHz for proton, 100MHz for carbon) with tetra-methylsilane as the internal reference using $CDCl_3$ or DMSO-d_6 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. ESI-MS was performed on Analysis Center of Shanghai Institute of Technology. GC mass spectra were recorded on Shimadzu GCMS-QP2010 with RTX-5MS column (0.25 mm× 30 m). Column chromatography was performed using 300-400 mesh silica gel.

II. Preparation of inorganic-ligand supported copper-catalyst

$(NH_4)_4[CuMo_6O_{18}(OH)_6]\cdot 5H_2O$ was synthesized according to a published procedure[1,2] with modification: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (5.3g) was dissolved in water (80 ml) and then heated to 100°C. $CuSO_4\cdot 5H_2O$ (0.99g) was dissolved in water (20ml), which was slowly added into the above solution under stirring. The mixture solution was kept stirring for 1h after $CuSO_4$ being completely added. On cooling, the mixture solution was filtered to remove any insoluble precipitate produced, and the filtrate was allowed to stand at room temperature for crystalization without disturbance. Light blue-green crystalline aim product (3.1g) was deposited and collected within a week. (Figure. S1) IR: 1631.65 (δ OH m), 1400.56 (δ NH, s), 931.62(ν Mo=O, vs), 897.66(ν Mo=O, vs), 640.18 (ν Mo-O-Mo, vs), 577.68 (ν M-O-Mo, w) cm^{-1}.

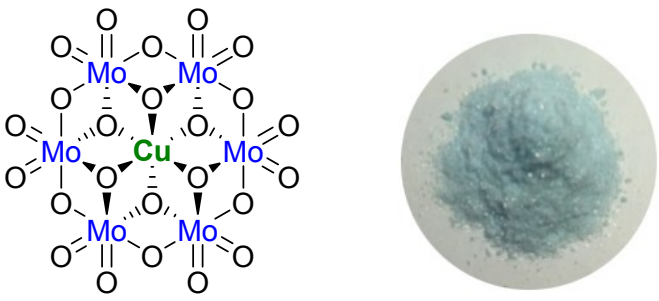


Figure. S1 Appearance of $(NH_4)_4[CuMo_6O_{18}(OH)_6]\cdot 5H_2O$

III. FT-IR spectra of catalysts 1

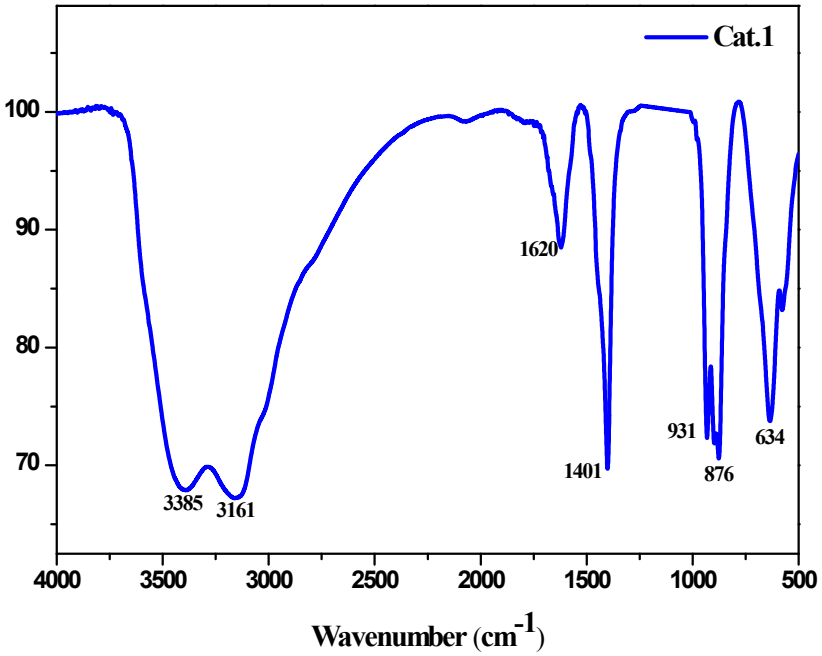


Figure S2. FT-IR spectra of catalyst **1**

IV. XRD spectra of catalyst 1

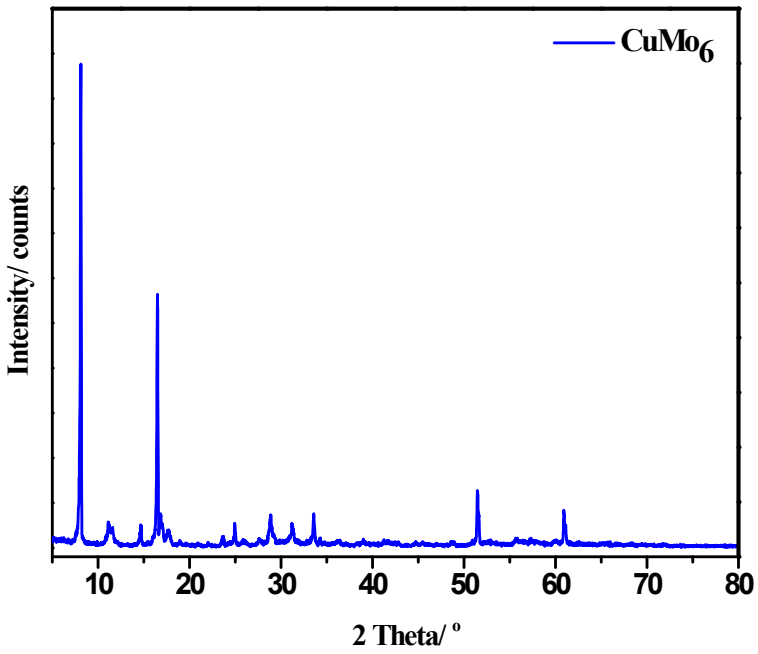


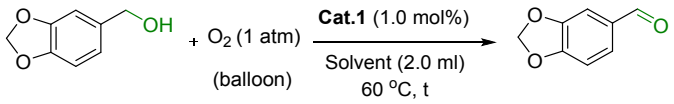
Figure S3. XRD spectra of catalyst **1**

V. General procedure for catalytic oxidation of alcohol

Aerobic oxidation reactions of alcohols were carried out in 2 ml aqueous solution containing 1 mmol alcohols and 10 mol% NaCl, together with 1.0 mol% cat. **1.** in test tubes. Meanwhile, oxygen gas balloonswere utilized to fulfill the reaction tubes with oxygen, and the reactions were kept at 60 °C for 6-24 hours. The reaction yield was determined *via* gas chromatography-mass spectrometry (GC-MS). When the reaction finished, a small amount of ethyl acetate was added into the reaction mixture and the solution was quickly filtered. The filtered solid was washed with ether, dried and redispersed for recyclability tests. Finally, the solvent was removed in vacuum, and the corresponding aldehydes were purified by washing through silica gel column. (EA:PE=1:6 or 1:10)

VI. Optimization of reaction conditions

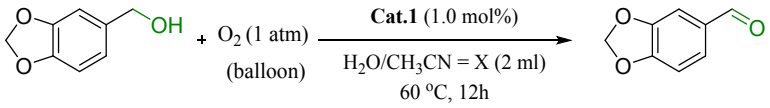
Table S1. The effect of solvent.[a]



Entry	Solvent	Time (h)	Sel. (%)[†]	Yield (%)
1	H_2O	24	99	72
2	CH_3CN	16	99	66
3	DCM	12	99	60
4	Dioxane	15	93	32
5	DMF	20	90	30
6	DMSO	20	86	<10
7	H_2O/CH_3CN	12	99	90
8	H_2O/DCM	10	99	81
9	H_2O/Dioxane	14	95	52
10	H_2O/DMF	16	99	46
11	H_2O/DMSO	18	99	17

[a] Reaction conditions: Cat. 1(1.0 mol%), alcohol (2.0 mmol), O_2 (1 atm), and solvent (2 mL) at 60°C, Volume ratio: v/v=1/1, unless otherwise noted. [b], [c] Selectivity and yields were calculated by GC and confirmed by GC-MS.

Table S2. The effect of water. [a]



Entry	H_2O/CH_3CN (v : v)	Sel.(%)[b]	Yield (%)[c]
1	0.5:1	97	83
2	1:1	>99	90
3	2:1	99	87
4	3:1	99	87
5	4:1	95	85
6	5:1	92	83

[a] Reaction conditions: Cat. 1(1.0 mol%), alcohol (2.0 mmol), O_2 (1 atm), and solvent (2 mL) at 60°C, Volume ratio: v/v=1/1, unless otherwise noted. [b], [c] Selectivity and yields were calculated by GC and confirmed by GC-MS.

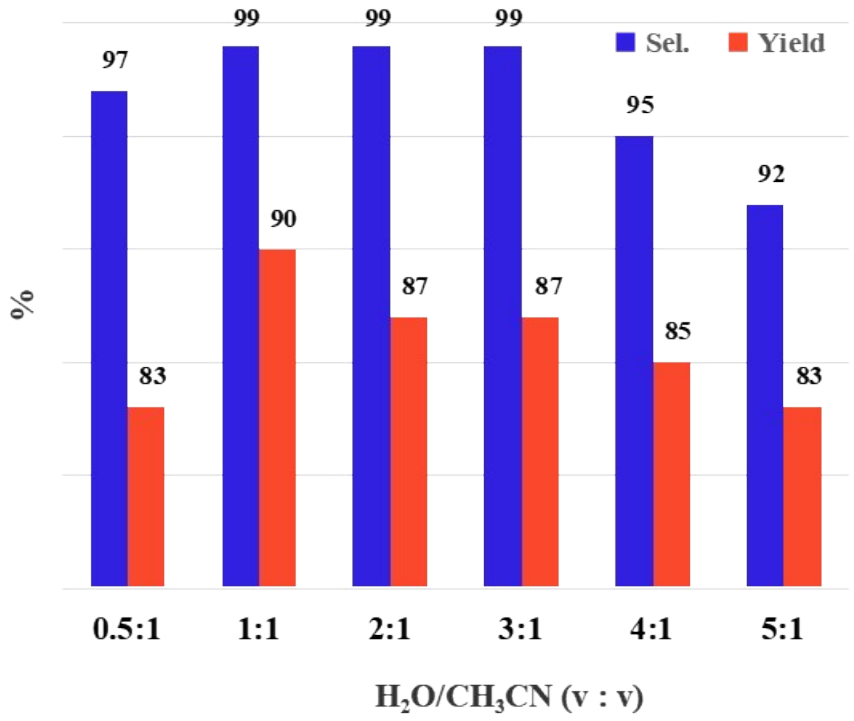
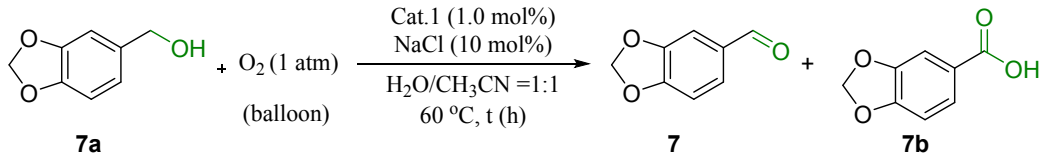


Figure S4. The effect of solvent

Table S3. Monitoring the reaction of piperitol with NaCl and 18-Crown-6 [a]



7a 7 7b

Time (h)	Recovery of	piperinic aldehyde	piperinic acid (%)[d]
2	97	-	-
4	95	3	-
6	95	4	-
8	94	4	-
10	93	5	-
12	92	5	-
14	90	7	-
16	89	7	-
18	88	8	-
20	86	10	-
22	85	12	-
24	82	13	-

[a] The reaction was carried out on a 10 mmol scale of piperitol in 40 mL of H_2O/CH_3CN (1:1). The reaction mixtures were calculated by GC and confirmed by GC-MS once per hour. [b],[c],[d] Yields were calculated from GC-Ms.

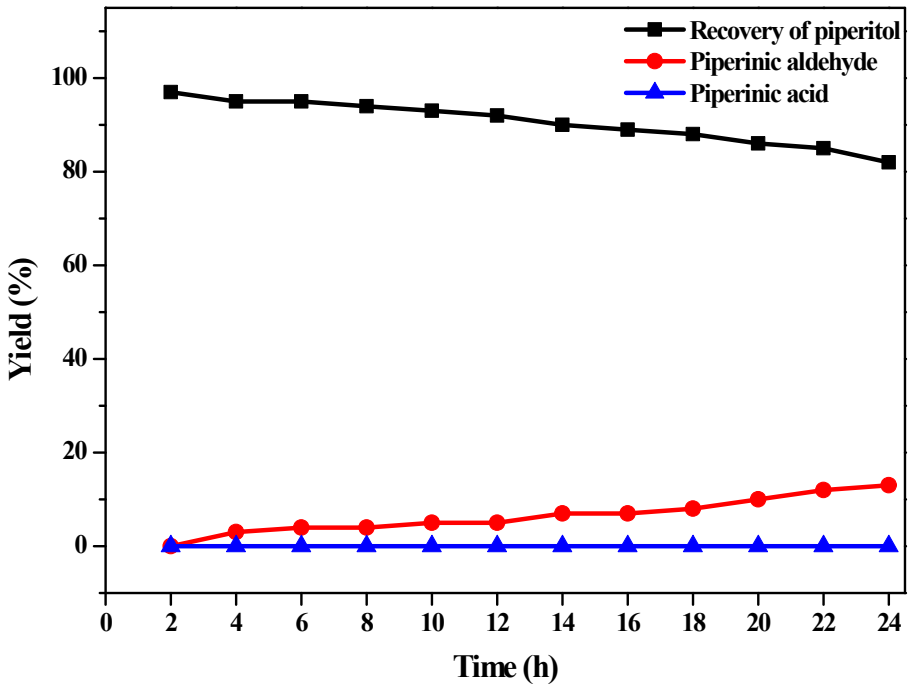
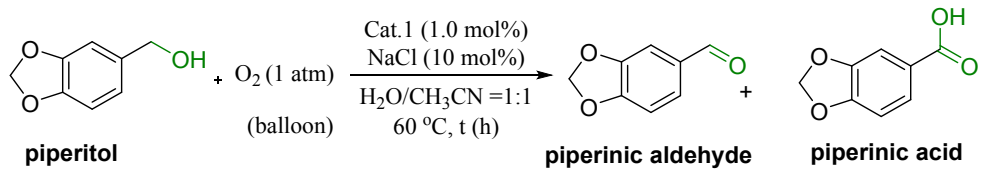


Figure S5. Monitoring the reaction of piperitol with NaCl and 18-Crown-6

Table S4. Monitoring the reaction of piperitol with NaCl [a]



Time (h)	piperitol (%) [b]	piperinic aldehyde [c]	piperinic acid [d]
2	92	8	-
4	85	14.5	-
6	78.5	21	-
8	70.5	28.5	-
10	62	33	-
12	58.5	39.5	-
14	50.5	48.5	-
16	46	53	-
18	42.5	57	-
20	37.5	62.5	-
22	33.5	65.5	-
24	31	69	-

[a] The reaction was carried out on a 10 mmol scale of piperitol in 40 mL of H_2O/CH_3CN (1:1). Every one hour, the reaction mixtures were calculated by GC and confirmed by GC-MS. [b,c,d] Yields were calculated from GC-MS.

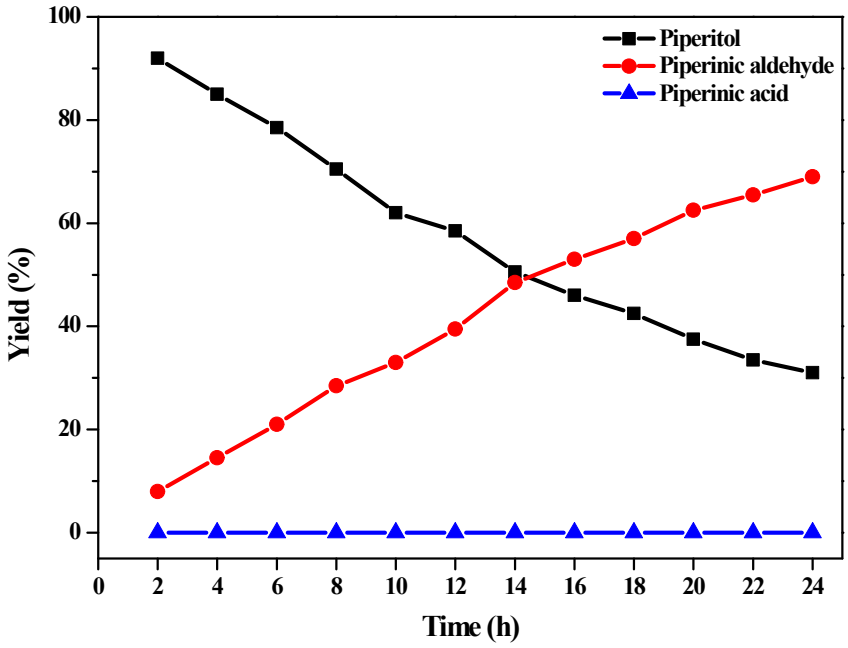
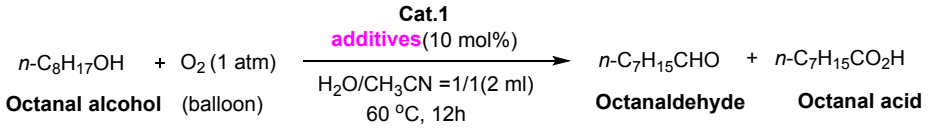


Figure S6. Monitoring the reaction of piperitol with NaCl

Table S5. Optimization of reaction conditions [a]



Entry	Additive	Sel. (%) [b]	Yield of aldehyde (%) [c]	Yield of acid (%) [d]
1	Na_2CO_3	72	12	53
2	Na_2SO_4	85	15	68
3	$NaSO_3$	99	95	0
4	$NaClO_4$	99	4	93
5	$NaHSO_4$	92	33	60
6	NaF	76	20	51
7	NaCl	99	27	75
8	NaBr	92	21	73
9	NaI	91	16	69
10	K_2SO_3	95	14	70
11	$MgSO_3$	15	<5	<5
12	$CaSO_3$	18	5	11
13[e]	$NaSO_3$	72	34	13
14[f]	$NaSO_3$	92	85	5
15[g]	$NaSO_3$	96	88	-
16[h]	$NaSO_3$	-	<5	-

[a] Reaction conditions: Cat. **1** (1.0 mol%), alcohols (1.0 mmol), O_2 (1 atm), additive (10 mol%) and CH_3CN / H_2O=1/1 (2 mL) at 60°C. Unless otherwise noted. [b], [c], [d] Selectivity were determined by GC and confirmed by GC-MS. [c] Yields were calculated from ^1H NMR spectra. [e] At 25 °C. [f] At 70 °C. [g] Reactions were carried out under atmospheric air, 24 h. [h] Reactions were carried out under nitrogen atmosphere.

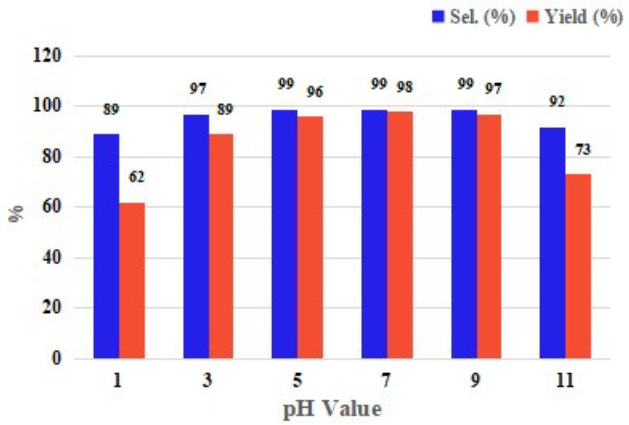
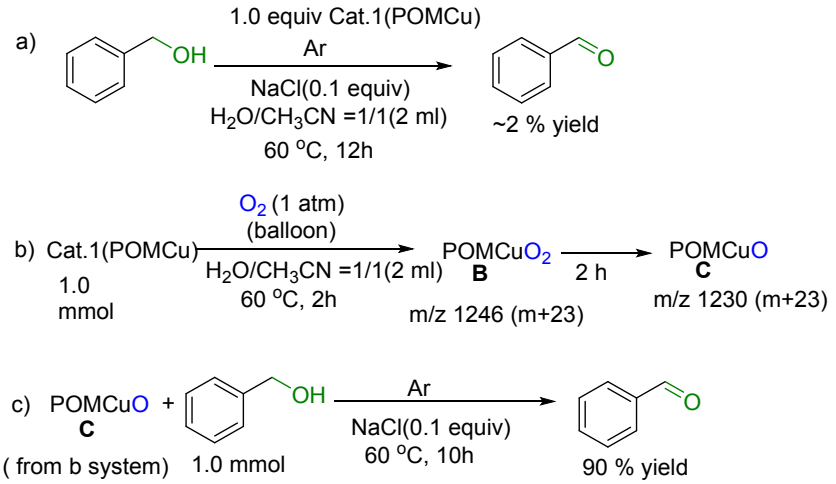


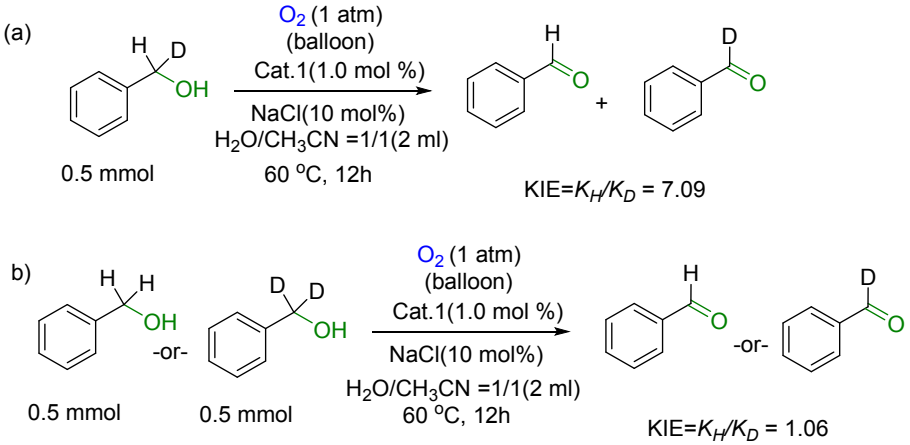
Figure S7. Screening of pH on the catalytic oxidation of piperonyl alcohol. Reaction conditions: Cat. 1 (1.0 mol%), Piperonyl alcohol (1.0 mmol), O_2 (1 atm), NaCl (10 mol%) and MeCN/H_2O=1/1 (2 mL) at

60°C. Unless otherwise noted, Selectivity were determined by GC and confirmed by GC-MS. Yields were calculated from ^{1}H NMR spectra.

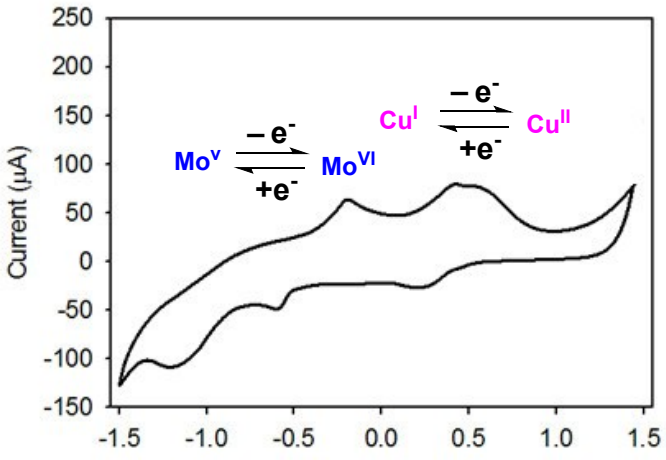
A: Control experiments



B: Kinetic Isotopic Effect experiments

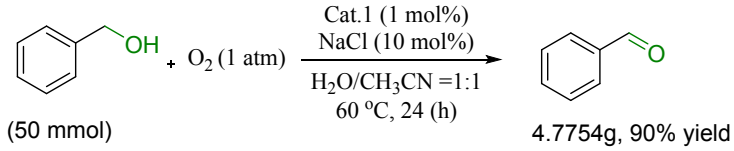


C: Cyclic voltammograms of catalyst 1/NaCl(1:10)



Potentiol Vs. Fc/Fc$^+$(V)

Figure S8. Experimental studies providing insight into the mechanism of the copper-catalyzed oxidation of alcohols. These include (A) control experiments, (B) kinetic isotope effects, (C) cyclic voltammograms of catalyst **1**/NaCl (1:10).



Schem S1. Gram-scale oxidation of benzyl alcohol to benzaldehyde

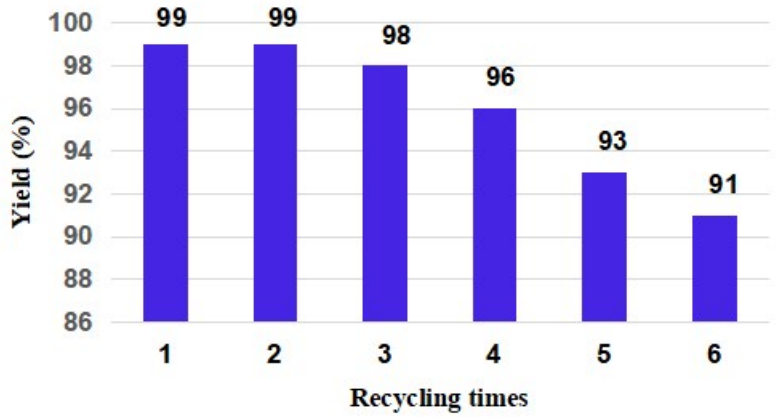


Figure S9. Recycling experiments of the Catalyst 1

VII. Recycling experiments of catalyst for oxidative reaction

The copper catalyst was precipitated after the oxidative reaction experiments, and then recovered for reuse. The recovered catalyst was characterized by FT-IR and XRD (Figure. S9 and S10.). The infrared image contains a blue line of fresh catalyst and a red line of the catalyst recycled five times.

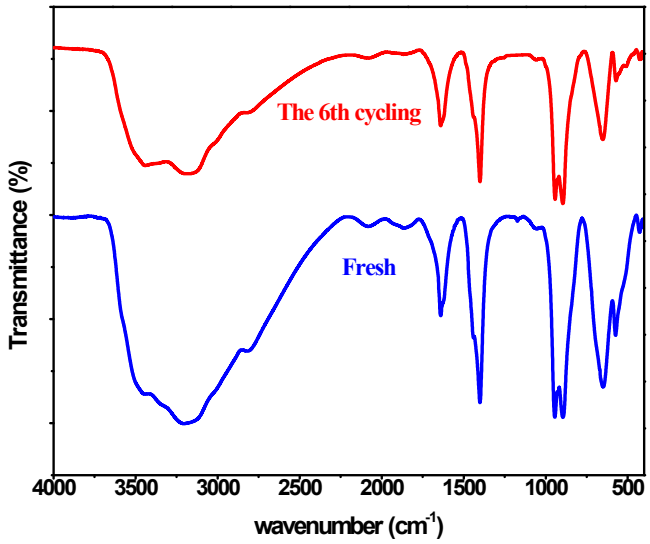


Figure S10. FT-IR spectra of the Catalyst 1 before and after reaction

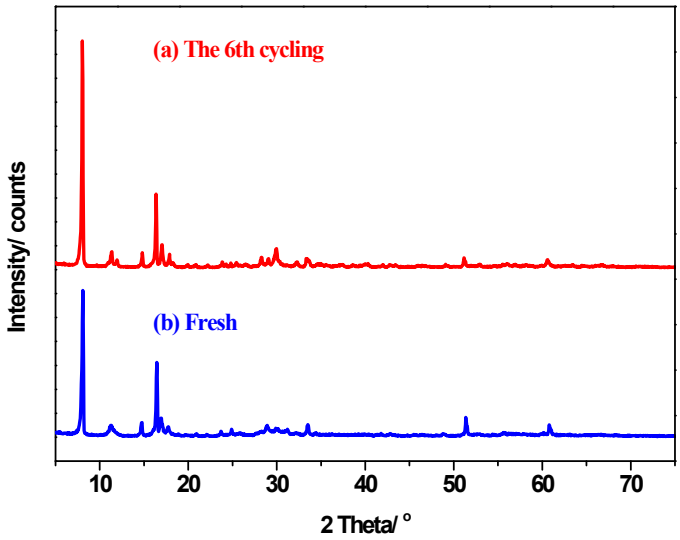


Figure S11. XRD of recycled Catalyst 1

VIII. ESI-Ms spectra of cat. 1 intermediate

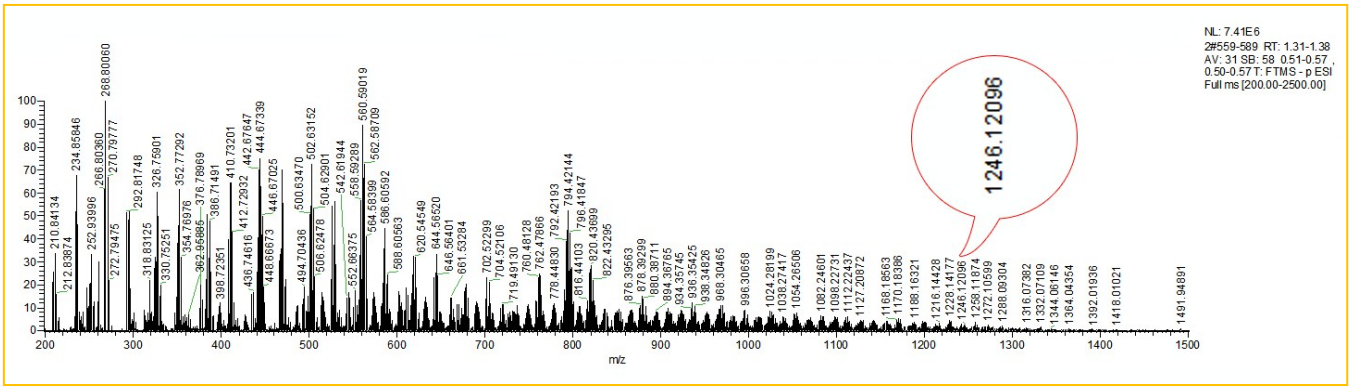


Figure S12. ESI-Ms of B

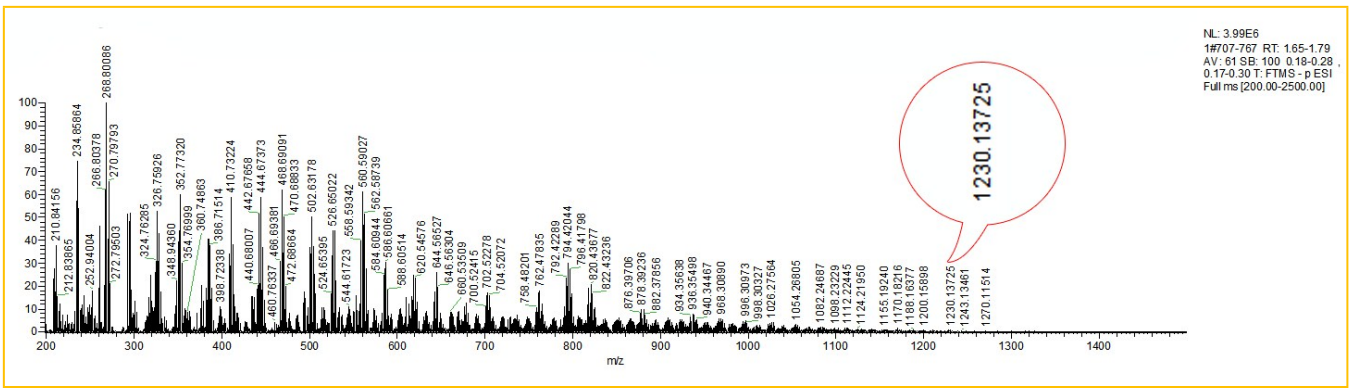


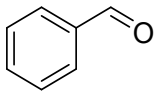
Figure S13. ESI-Ms of C

IX. References

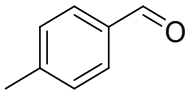
[1]. Nomiya, K.; Takahashi, T.; Shirai, T.; Miwa, M. *Polyhedron.* **1987**, *6*, 213.

[2]. Blazevic, A.; Al-Sayed, E.; Roller, A.; Giester, G.; Rompel, A. *Chemistry.* **2015**, *21*, 4762.

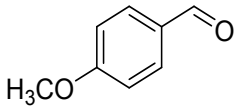
X. NMR data of products



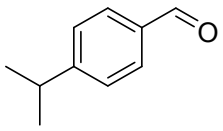
Benzaldehyde (2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.06 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.81 (ddd, *J* = 7.4, 4.1, 1.3 Hz, 1H), 7.71 (dd, *J* = 10.7, 4.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4 (s), 136.4 (s), 134.5 (s), 129.8 (s), 129.0 (s).



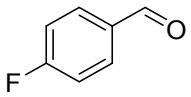
p-Tolualdehyde (3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.93 (d, *J* = 2.9 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 2.40 (d, *J* = 2.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9 (s), 145.5 (s), 134.2 (s), 129.8 (d, *J* = 15.0 Hz), 21.8 (s).



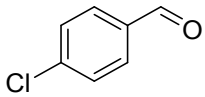
4-Methoxylbenzaldehyde (4): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (d, *J* = 2.5 Hz, 1H), 7.84 – 7.69 (m, 2H), 7.01 – 6.86 (m, 2H), 3.81 (dd, *J* = 4.3, 3.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.9 (s), 164.6 (s), 132.0 (s), 129.9 (s), 114.3 (s), 55.6 (s).



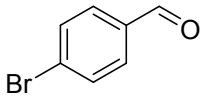
4-Isopropylbenzaldehyde (5): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.91 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.21 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1 (s), 156.3 (s), 134.6 (s), 130.4 (s), 130.0 (s), 127.2 (s), 125.6 (s), 34.5 (s), 23.7 (s).



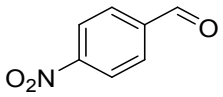
4-Fluorobenzaldehyde (6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.91 (dd, J = 8.5, 5.5 Hz, 2H), 7.21 (t, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5 (s), 167.5 (s), 133.0 (s), 132.2 (s), 116.4 (s).



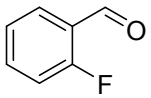
4-Chlorobenzaldehyde (7): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.9 (s), 141.0 (s), 134.8 (s), 130.9 (s), 129.5 (s).



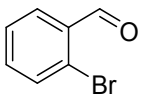
4-Bromobenzaldehyde (8): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.1 (s), 135.1 (s), 132.5 (s), 131.0 (s), 129.8 (s).



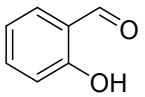
4-Nitrobenzaldehyde (9): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.55 (d, *J* = 8.6 Hz, 2H), 8.25 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4 (s), 151.1 (s), 140.1 (s), 130.5 (s), 124.3 (s).



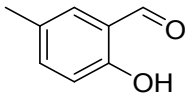
2-Fluorobenzaldehyde (10): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.05 (dd, *J* = 10.4, 4.2 Hz, 1H), 7.84 – 7.71 (m, 1H), 7.45 (dd, *J* = 9.6, 5.5 Hz, 1H), 7.40 - 7.29 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.3 (s), 165.8 (s), 163.7 (s), 136.4 (s), 128.7 (s), 124.7 (s), 116.6 (s).



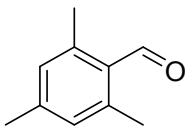
2-Bromoaldehyde (11): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.94 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.51 – 7.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0 (s), 135.4 (s), 133.9 (s), 133.5 (s), 129.9 (s), 128.0 (s), 100.0 (s).



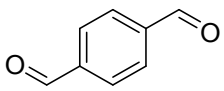
Salicylaldehyde (12): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.04 (s, 1H), 9.90 (s, 1H), 7.66 – 7.47 (m, 2H), 7.13 – 6.95 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6 (s), 161.6 (s), 137.0 (s), 133.7 (s), 120.7 (s), 119.8 (s), 117.6 (s).



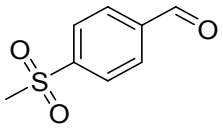
5-Methylsalicylaldehyde (13): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.85 (s, 1H), 9.87 (s, 1H), 7.36 (d, *J* = 6.3 Hz, 2H), 6.91 (d, *J* = 9.1 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6 (s), 159.6 (s), 138.1 (s), 133.4 (s), 129.2 (s), 120.4 (s), 117.4 (s), 20.2 (s).



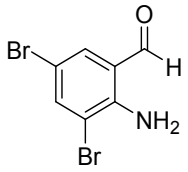
2,4,6-Trimethylbenzaldehyde (14): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.57 (s, 1H), 6.91 (s, 2H), 2.59 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0 (s), 143.8 (s), 141.5 (s), 130.5 (s), 130.0 (s), 21.5 (s), 20.5 (s).



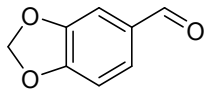
Terephthalaldehyde (15): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.30 (s, 2H), 8.22 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6 (s), 140.0 (s), 130.2 (s).



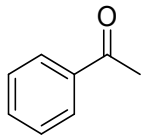
4-Methylsulphonylbenzaldehyde (16): ^{1}H NMR (400 MHz, DMSO) δ 9.94 (d, *J* = 5.3 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.40 – 7.35 (m, 2H), 2.37 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 193.2 (s), 145.9 (s), 1 34.7 (s), 130.3 (d, *J* = 11.5 Hz), 22.0 (s).



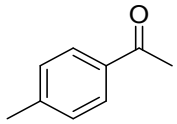
3,5-Bibromo-2-aminobenzaldehyde (17): ^{1}H NMR (500 MHz, DMSO) δ 9.81 (s, 1H), 7.90 (d, *J* = 2.3 Hz, 2H), 3.34 (s, 2H); ^{13}C NMR (125 MHz, DMSO) δ 193.8 (s), 146.7 (s), 139.9 (s), 137.9 (s), 120.4 (s), 110.3 (s), 105.7 (s).



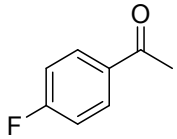
Piperonal (18): ^{1}H NMR (500 MHz, DMSO) δ 9.87 – 9.67 (m, 1H), 7.55 (d, *J* = 4.0 Hz, 1H), 7.25 (d, *J* = 83.4 Hz, 1H), 7.15 (d, *J* = 5.6 Hz, 1H), 6.24 – 6.03 (m, 2H); ^{13}C NMR (125 MHz, DMSO) δ 191.4 (s), 158.0 (s), 153.2 (s), 129.0 (s), 125.7 (s), 109.1 (s), 106.8 (s), 102.8 (s).



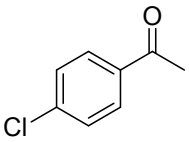
Acetophenone (19): ^{1}H NMR (400 MHz, DMSO) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.75 – 7.58 (m, 1H), 7.58 – 7.45 (m, 2H), 2.57 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 198.5 (s), 137.5 (s), 133.8 (s), 128.8 (s), 27.3 (s).



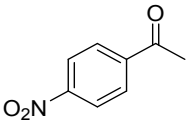
4-Methylaldehyde (20): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 2H), 2.60 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0 (s), 171.0 (s), 143.9 (s), 134.7 (s), 129.3 (s), 128.5 (s), 26.6 (s), 21.7 (s).



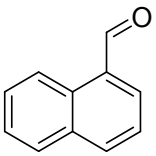
4-Fluoroacetophenone (21): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (ddd, *J* = 6.7, 5.4, 2.1 Hz, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.5 (s), 166.7 (s), 133.6 (s), 130.9 (s), 115.5 (s), 26.5 (s).



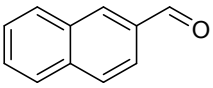
4-Chloroacetophenone (22): ^{1}H NMR (500 MHz, DMSO) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 197.4 (s), 138.6 (s), 135.9 (s), 130.5 (s), 129.2 (s), 27.15 (s).



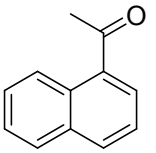
4-Nitroacetophenone (23): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.6 Hz, 2H), 8.13 (d, *J* = 8.6 Hz, 2H), 2.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4 (s), 150.4 (s), 141.4 (s), 129.3 (s), 123.9 (s), 27.0 (s).



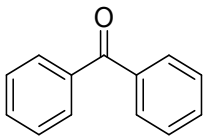
1-Naphthaldehyde (24): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 9.28 (d, *J* = 8.6 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.68 -7.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6 (s), 139.0 (s), 136.7 (s), 135.3 (s), 133.8 (s), 131.4 (s), 130.6 (s), 129.1 (s), 128.5 (s), 126.0 (s), 124.9 (s).



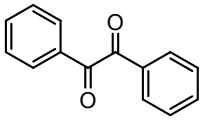
2-Naphthaldehyde (25): ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.38 (s, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 8.01 – 7.92 (m, 3H), 7.70 – 7.60 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6 (s), 136.7 (s), 135.3 (s), 133.8 (s), 131.4 (s), 130.6(s), 129.1 (s), 128.5 (s), 127.0 (s), 124.9 (s).



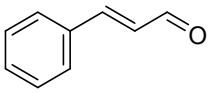
Acetonaphthone (26): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.7 Hz, 1H), 7.91 (ddd, *J* = 21.4, 19.0, 8.2 Hz, 3H), 7.55 (dddd, *J* = 28.0, 15.4, 7.4, 4.4 Hz, 3H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8 (s), 135.4 (s), 134.0 (s), 133.1 (s), 130.2 (s), 128.8 (s), 128.5 (s), 128.1 (s), 125.5 (s), 125.1 (s), 124.3 (s), 30.0 (s).



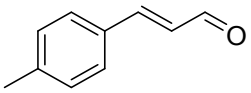
Benzophenone (27): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.3 Hz, 4H), 7.62 (t, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6 (s), 134.9 (s), 133.0 (s), 129.9 (s), 129.0 (s).



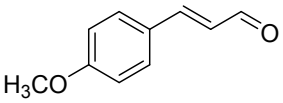
Benzil (28): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 4H), 7.64 (t, J = 7.4 Hz, 2H), 7.50 (t, J = 7.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.69 (s), 135.01 (s), 133.06 (s), 130.0 (s), 129.1 (s).



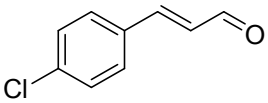
Cinnamaldehyde (29): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.51 (m, 2H), 7.51 – 7.33 (m, 4H), 6.72 (dd, *J* = 16.0, 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7 (s), 152.8 (s), 134.0 (s), 131.3 (s), 129.1 (s), 128.6 (d, *J* = 7.6 Hz).



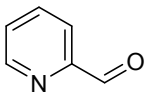
4-Methylcinnamaldehyde (30): ^{1}H NMR (500 MHz, DMSO) δ 9.65 (d, *J* = 7.8 Hz, 1H), 7.68 (dd, *J* = 27.5, 11.9 Hz, 3H), 7.29 (d, *J* = 7.8 Hz, 2H), 6.82 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 194.9 (s), 153.8 (s), 141.9 (s), 131.9 (s), 130.2 (s), 129.3 (s), 128.1 (s), 21.6 (s).



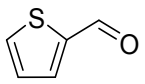
4-Methoxylcinnamaldehyde (31): ^{1}H NMR (500 MHz, DMSO) δ 9.61 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 15.8 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.75 (dd, *J* = 15.8, 7.8 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 194.6 (s), 162.2 (s), 153.7 (s), 131.2 (s), 127.2 (s), 125.8 (s), 115.0 (s), 55.9 (s).



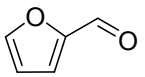
4-Chlorocinnamaldehyde (32): ^{1}H NMR (500 MHz, DMSO) δ 9.68 (d, *J* = 7.7 Hz, 1H), 7.77 (dd, *J* = 23.9, 12.2 Hz, 3H), 7.55 (d, *J* = 8.4 Hz, 2H), 6.90 (dd, *J* = 15.9, 7.7 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 194.9 (s), 152.1 (s), 136.2 (s), 133.5 (s), 130.9 (s), 129.6 (d, *J* = 5.4 Hz).



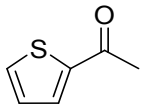
2-Pyridinecarboxaldehyde (33): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (dd, *J* = 3.9, 0.7 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.03 (td, *J* = 7.8, 1.6 Hz, 1H), 6.38 (ddd, *J* = 7.4, 4.8, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 194.1 (s), 152.8 (s), 150.6 (s), 138.0 (s), 128.8 (s), 122.0 (s).



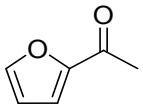
2-Thenaldehyde (34): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.75 (d, *J* = 3.3 Hz, 1H), 7.72 (d, *J* = 4.8 Hz, 1H), 7.22 - 7.12 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.1 (s), 144.0 (s), 136.6 (s), 135.2 (s), 128.4 (s).



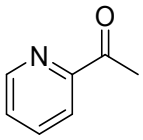
Furfural (35): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.71 (s, 1H), 7.27 (d, *J* = 3.5 Hz, 1H), 6.62 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.9 (s), 153.0 (s), 148.1 (s), 121.1 (s), 112.6 (s).



2-Acetylthiophene (36): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.49 (s, 1H), 6.97 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6 (s), 144.4 (s), 133.8 (s), 132.6 (s), 128.2 (s), 26.7 (s).

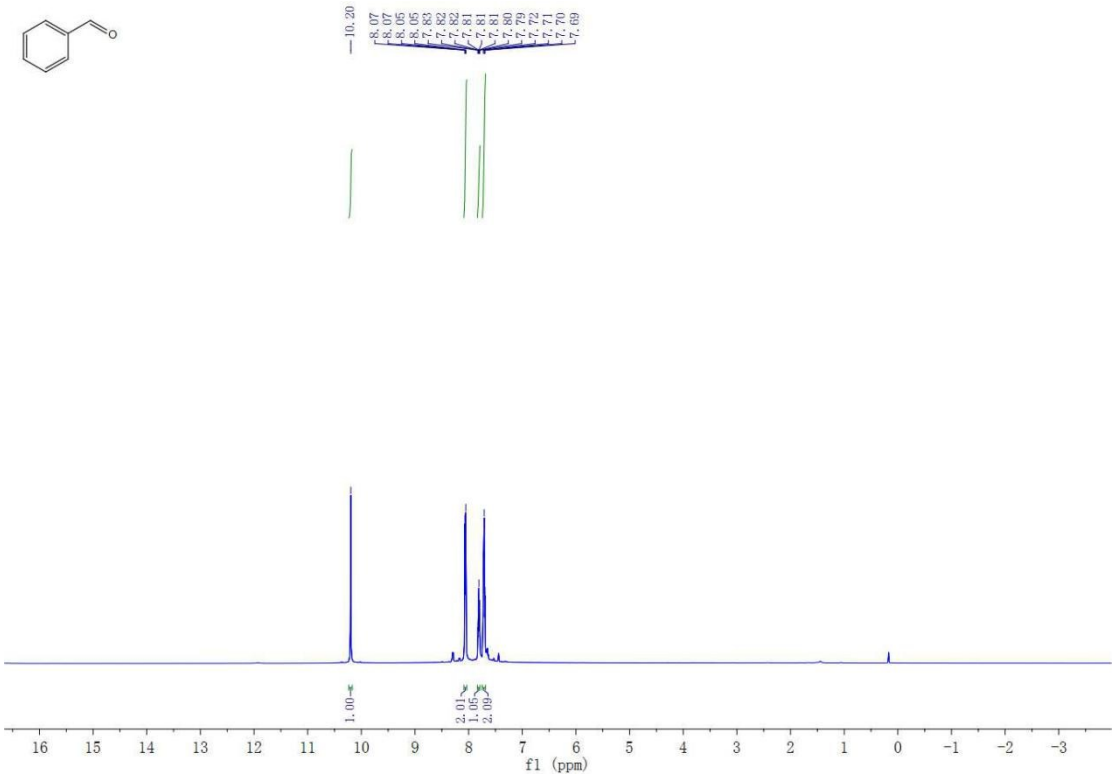


2-Acetylfuran (37): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.20 (d, *J* = 3.5 Hz, 1H), 6.59 – 6.50 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9 (s), 146.5 (s), 117.3 (s), 112.3 (s), 26.0 (s).

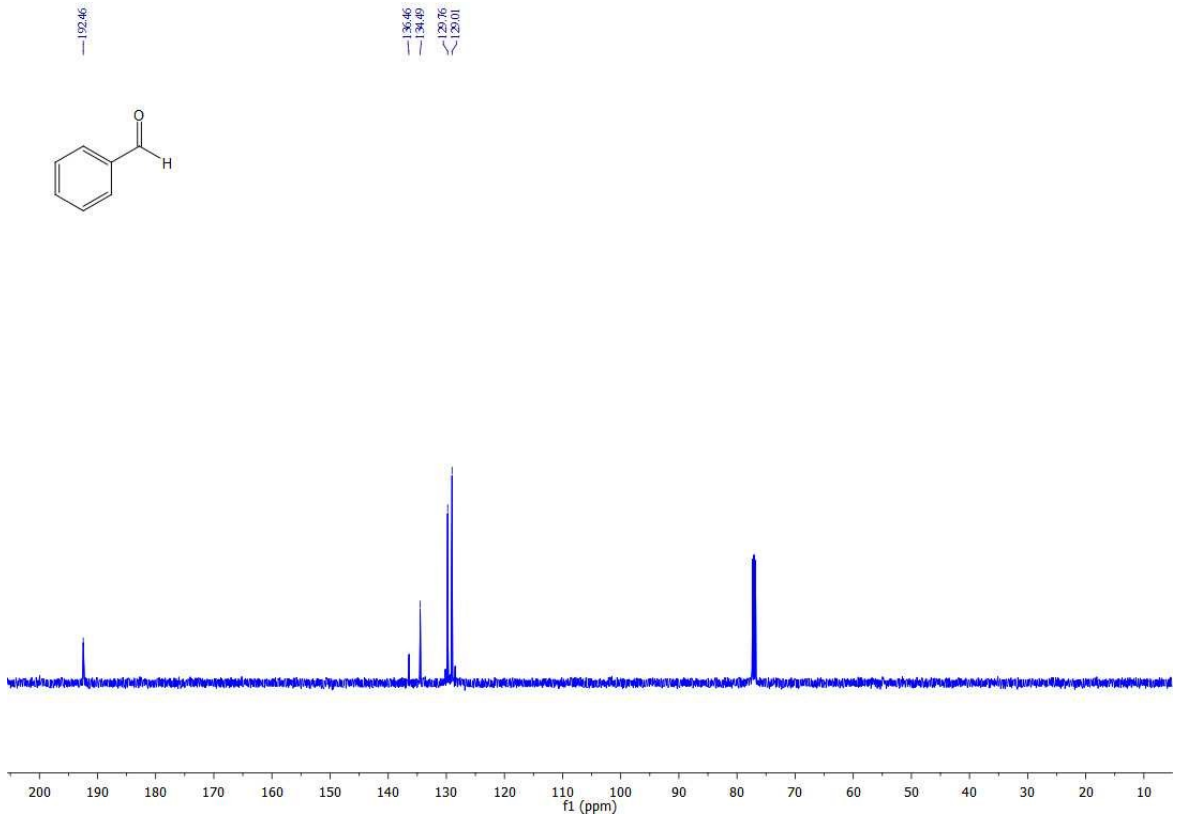


2-acetylpyridine (38): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 3.9, 0.7 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.70 (td, *J* = 7.8, 1.6 Hz, 1H), 7.34 (ddd, *J* = 7.4, 4.8, 1.1 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.8 (s), 153.4 (s), 148.9 (s), 136.7 (s), 126.0 (s), 121.4 (s), 25.6 (s).

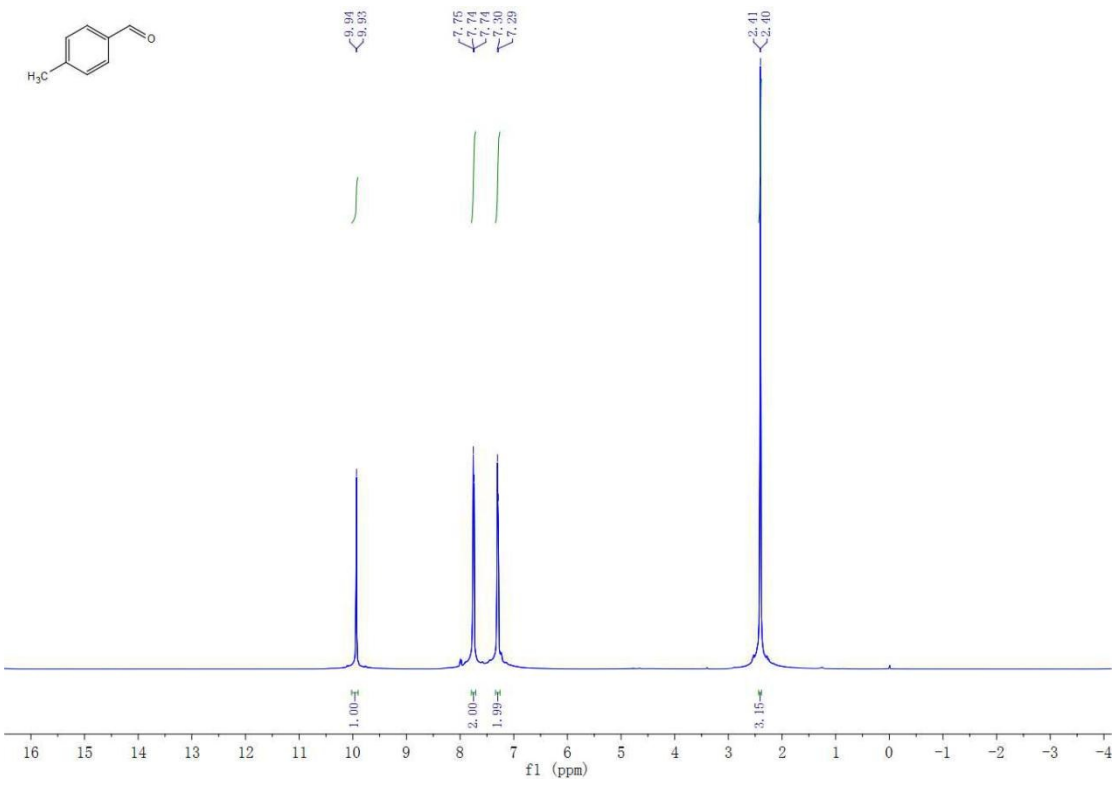
XI. NMR spectra



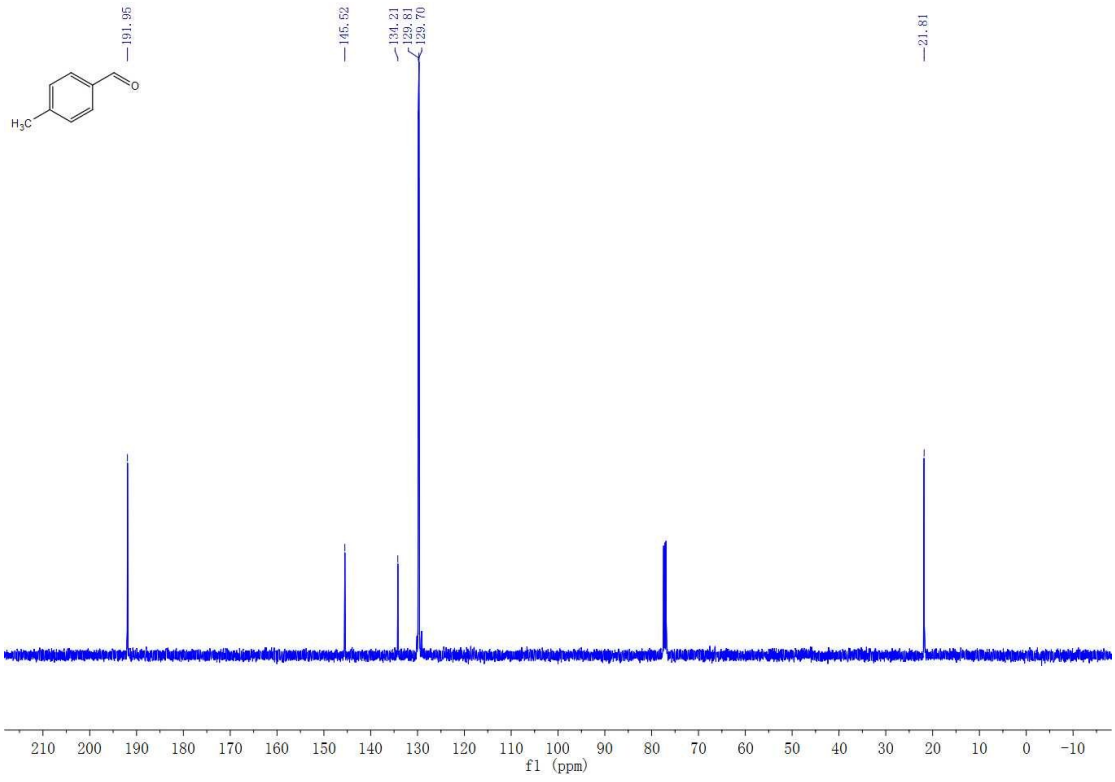
^{1}H NMR spectra of **2** (500 MHz, $CDCl_3$)



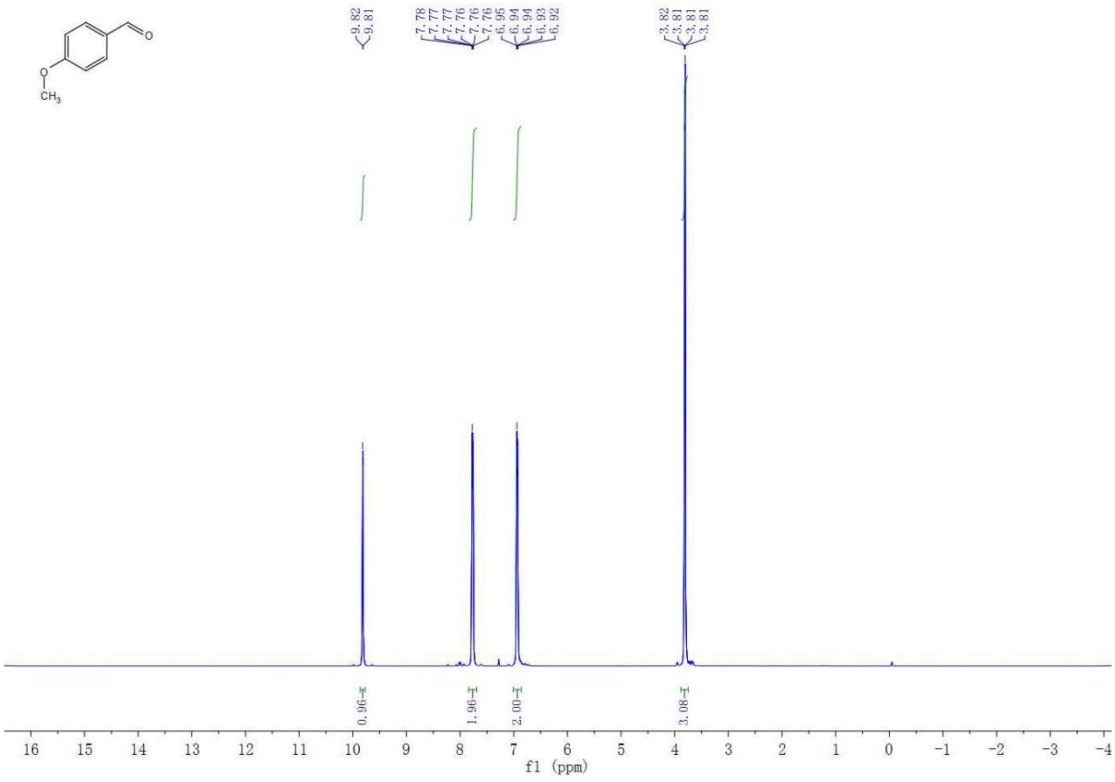
^{13}C NMR spectra of **2** (125 MHz, $CDCl_3$)



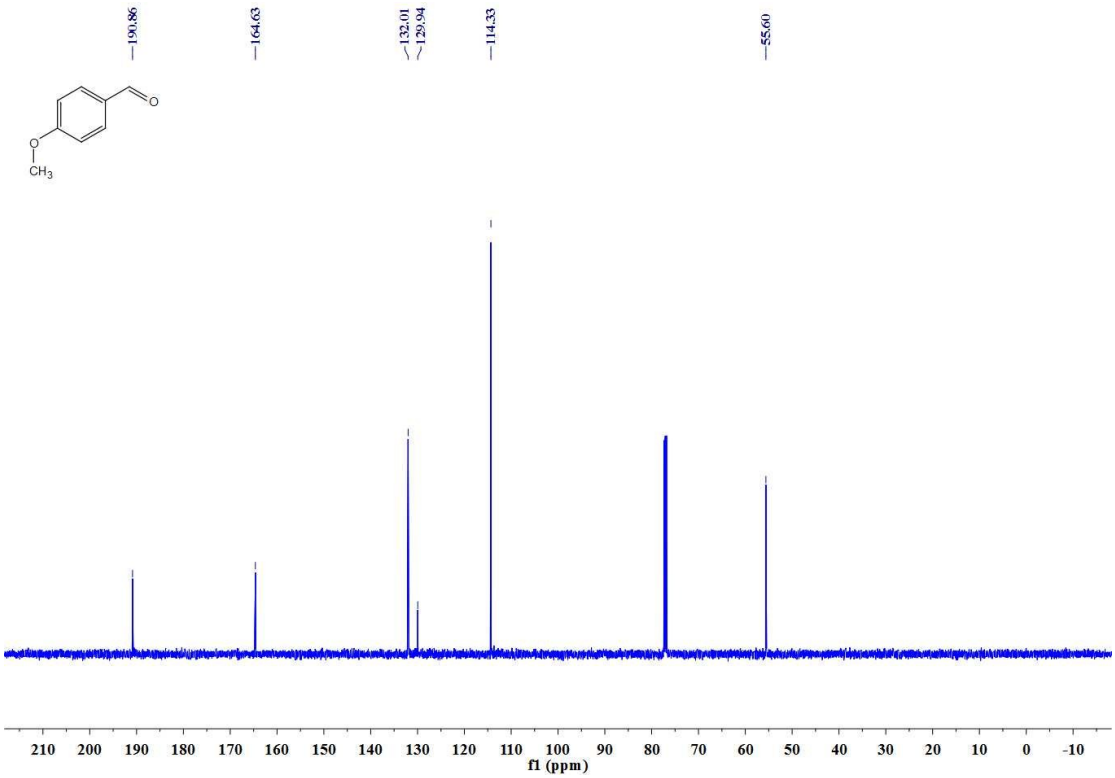
^{1}H NMR spectra of **3** (500 MHz, $CDCl_3$)



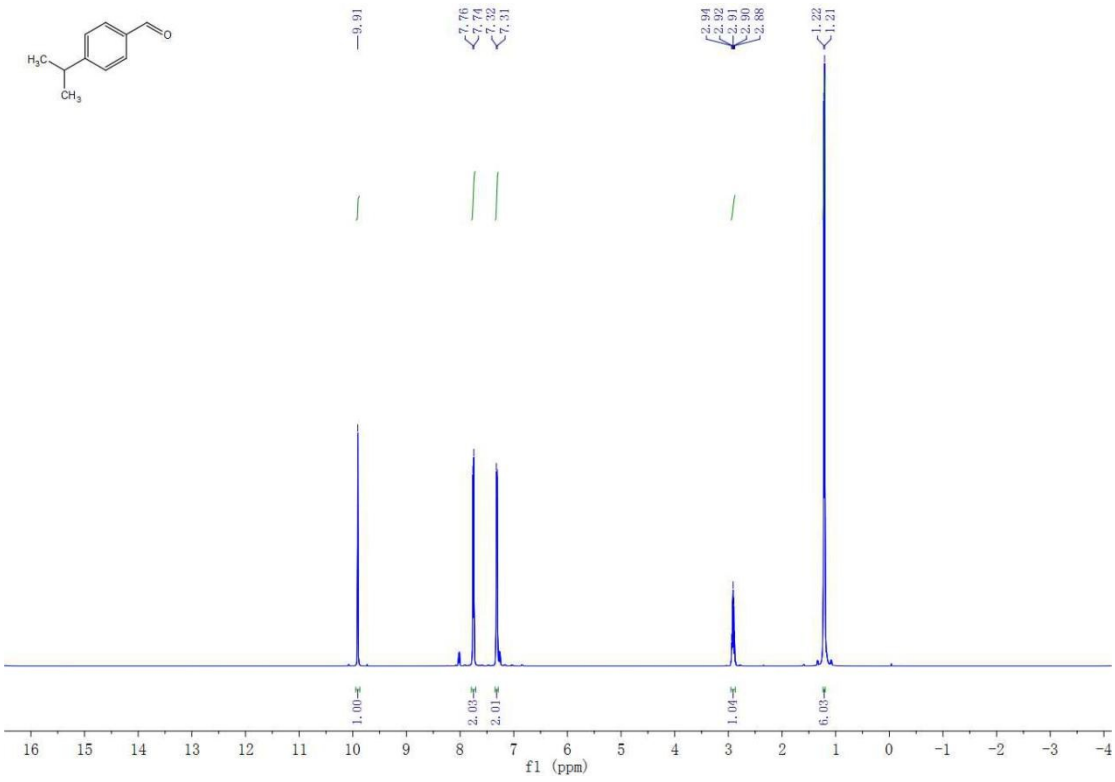
^{13}C NMR spectra of **3** (125 MHz, $CDCl_3$)



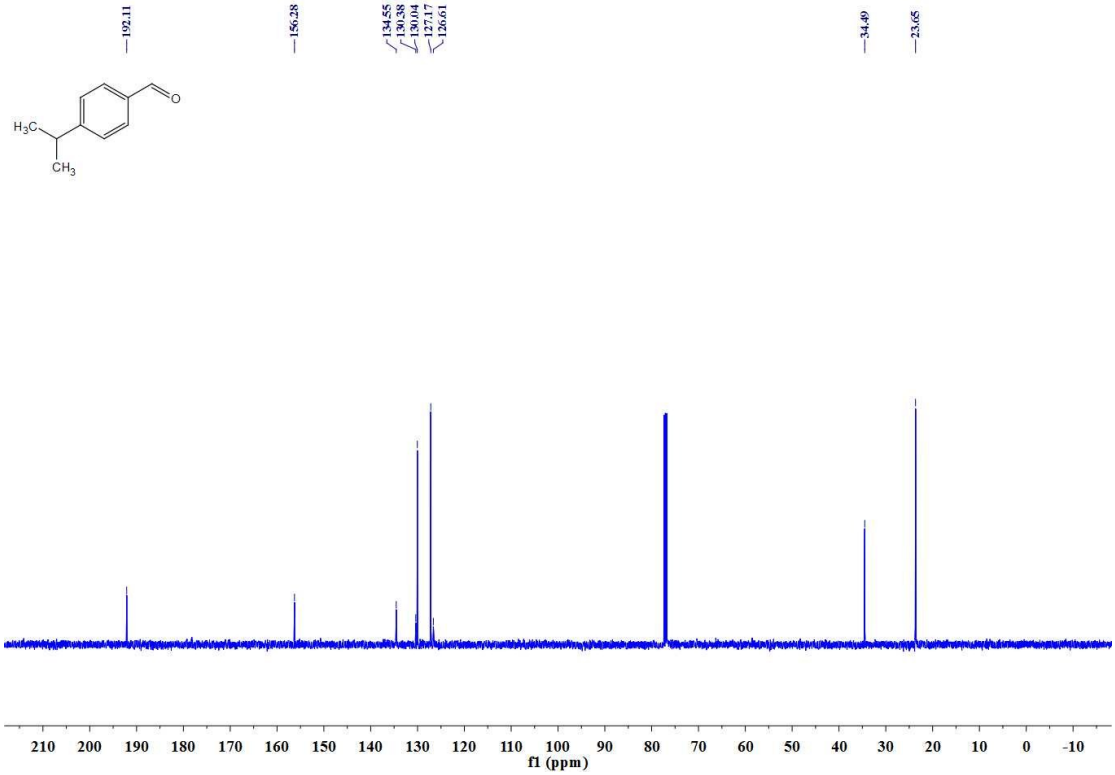
^{1}H NMR spectra of **4** (500 MHz, $CDCl_3$)



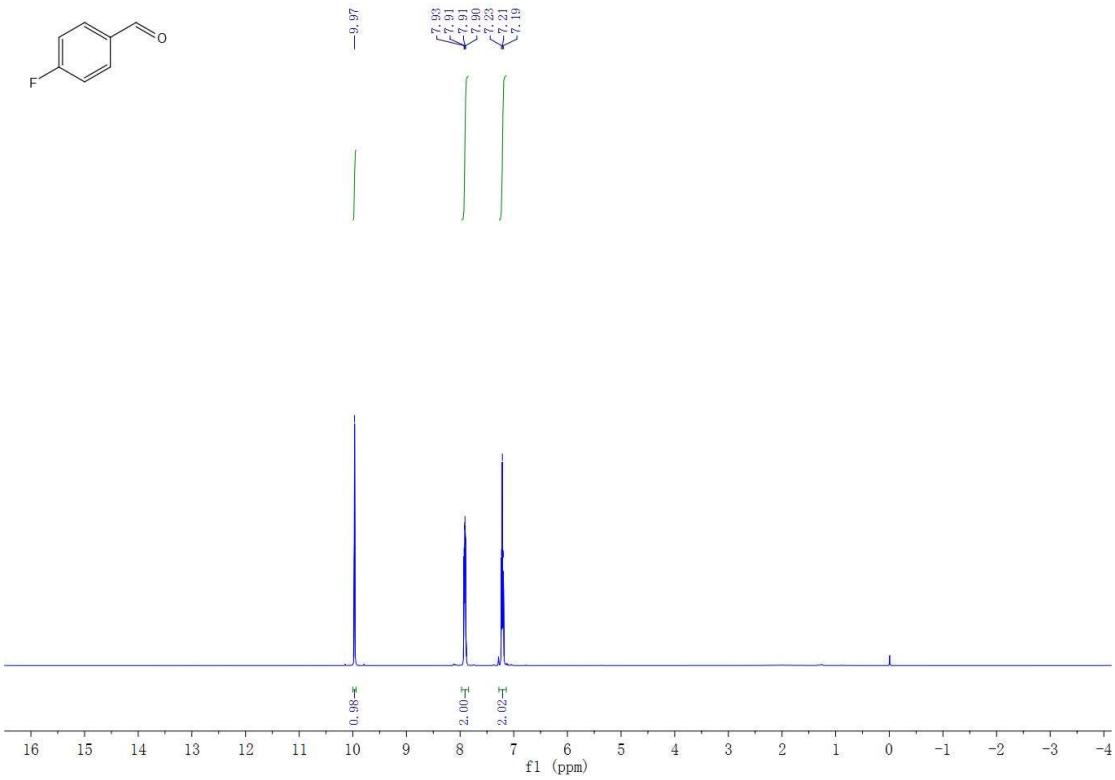
^{13}C NMR spectra of **4** (125 MHz, $CDCl_3$)



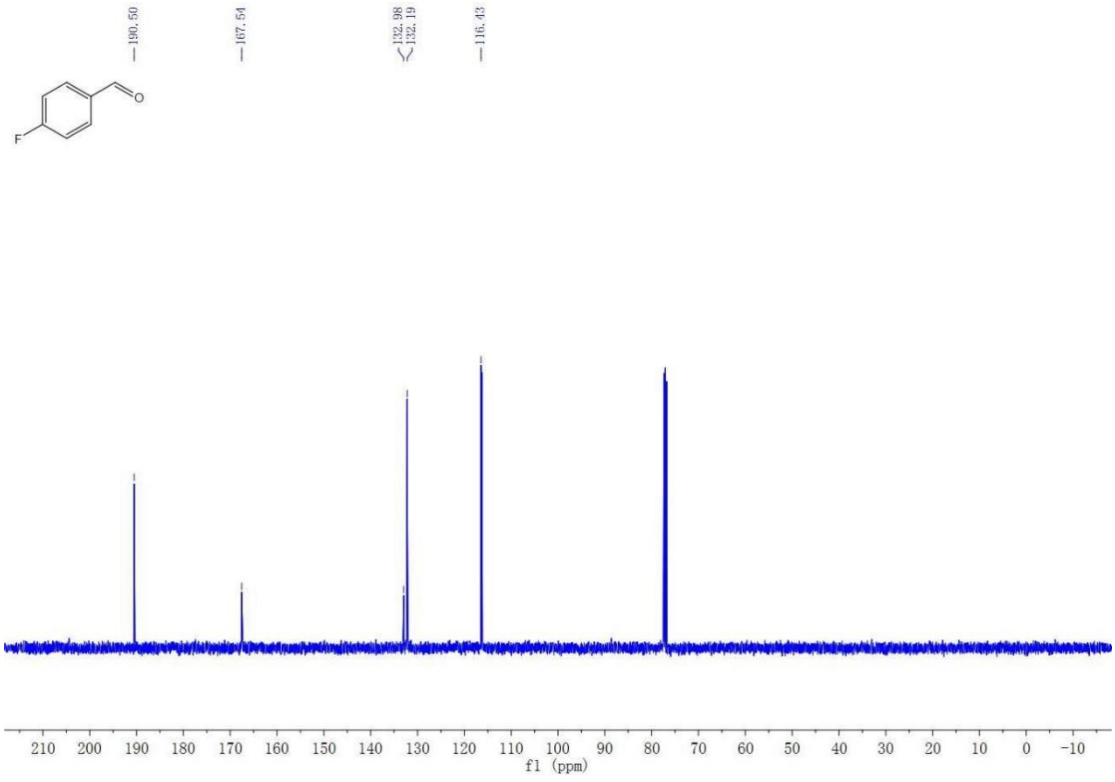
^{1}H NMR spectra of **5** (500 MHz, $CDCl_3$)



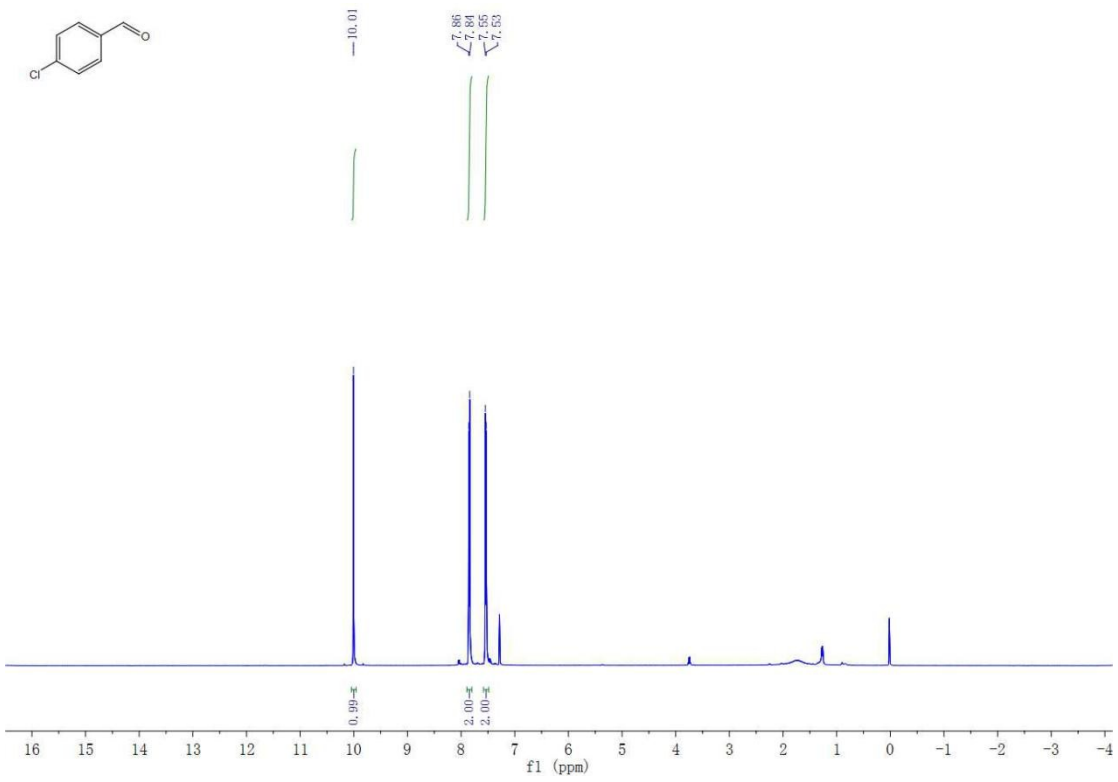
^{13}C NMR spectra of **5** (125 MHz, $CDCl_3$)



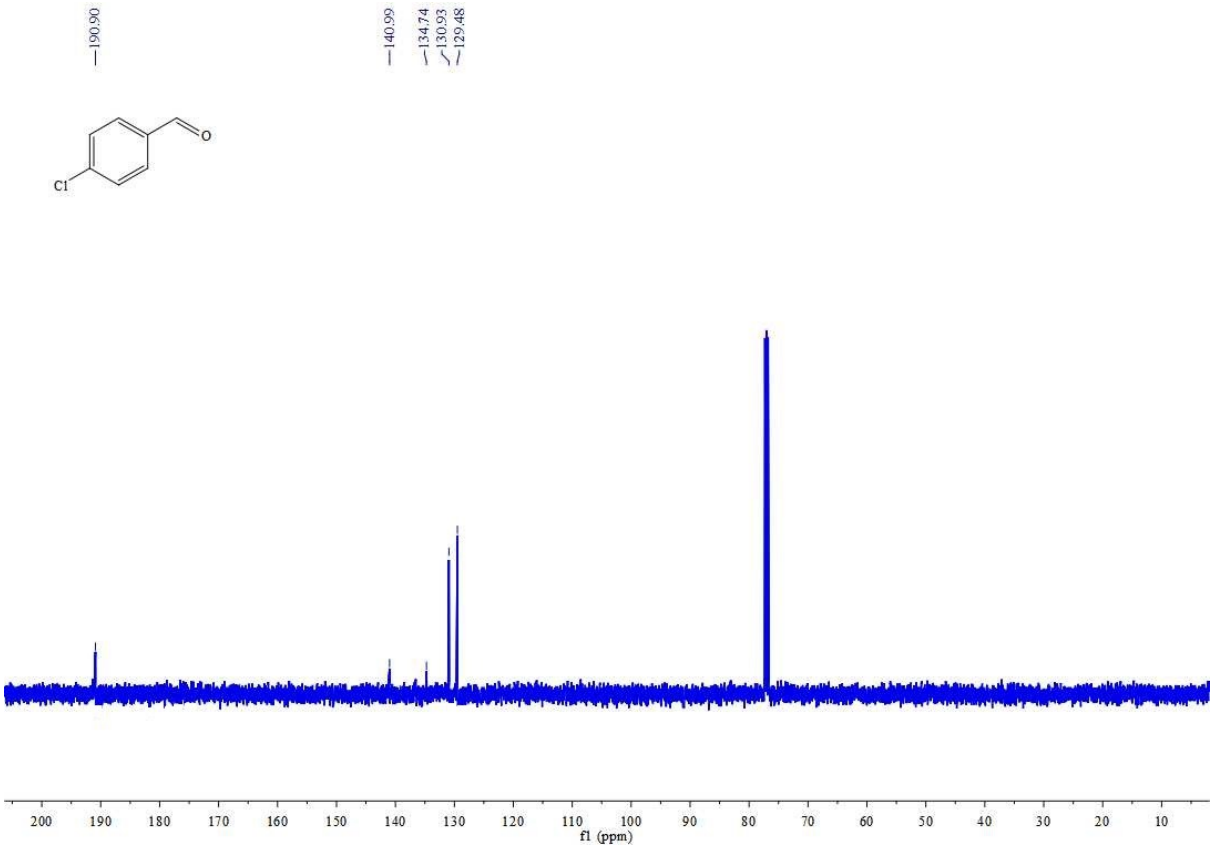
^{1}H NMR spectra of **6** (500 MHz, $CDCl_3$)



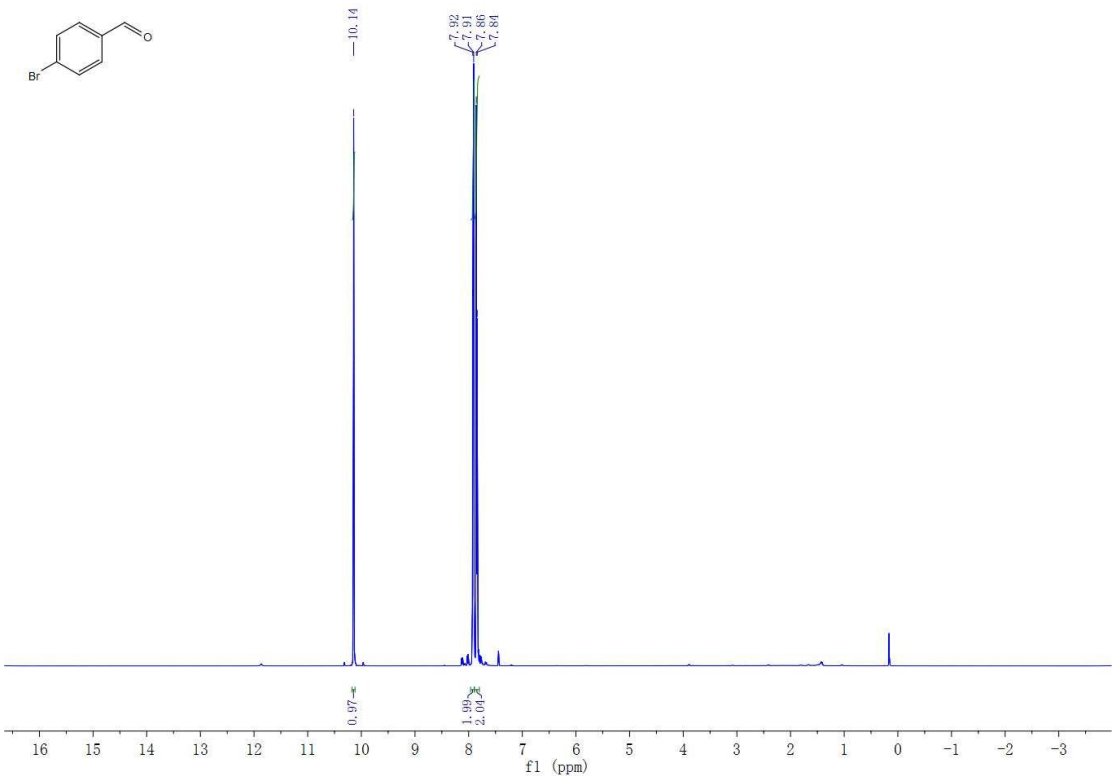
^{13}C NMR spectra of **6** (125 MHz, $CDCl_3$)



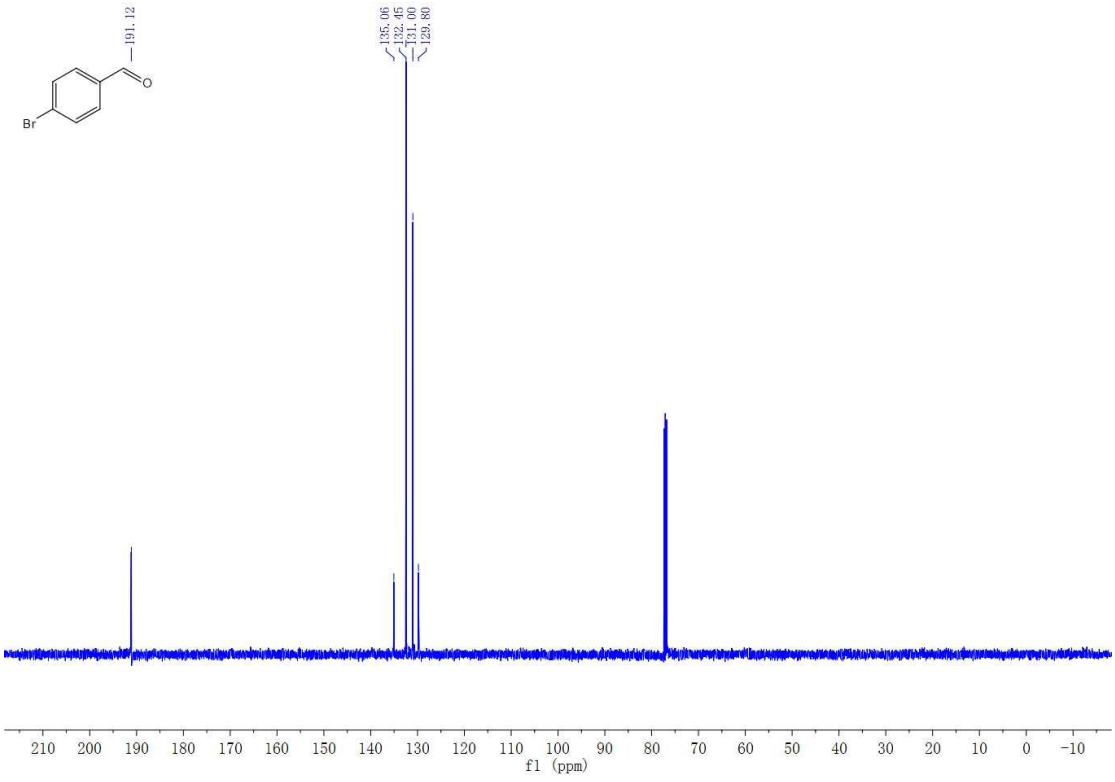
^{1}H NMR spectra of **7** (500 MHz, $CDCl_3$)



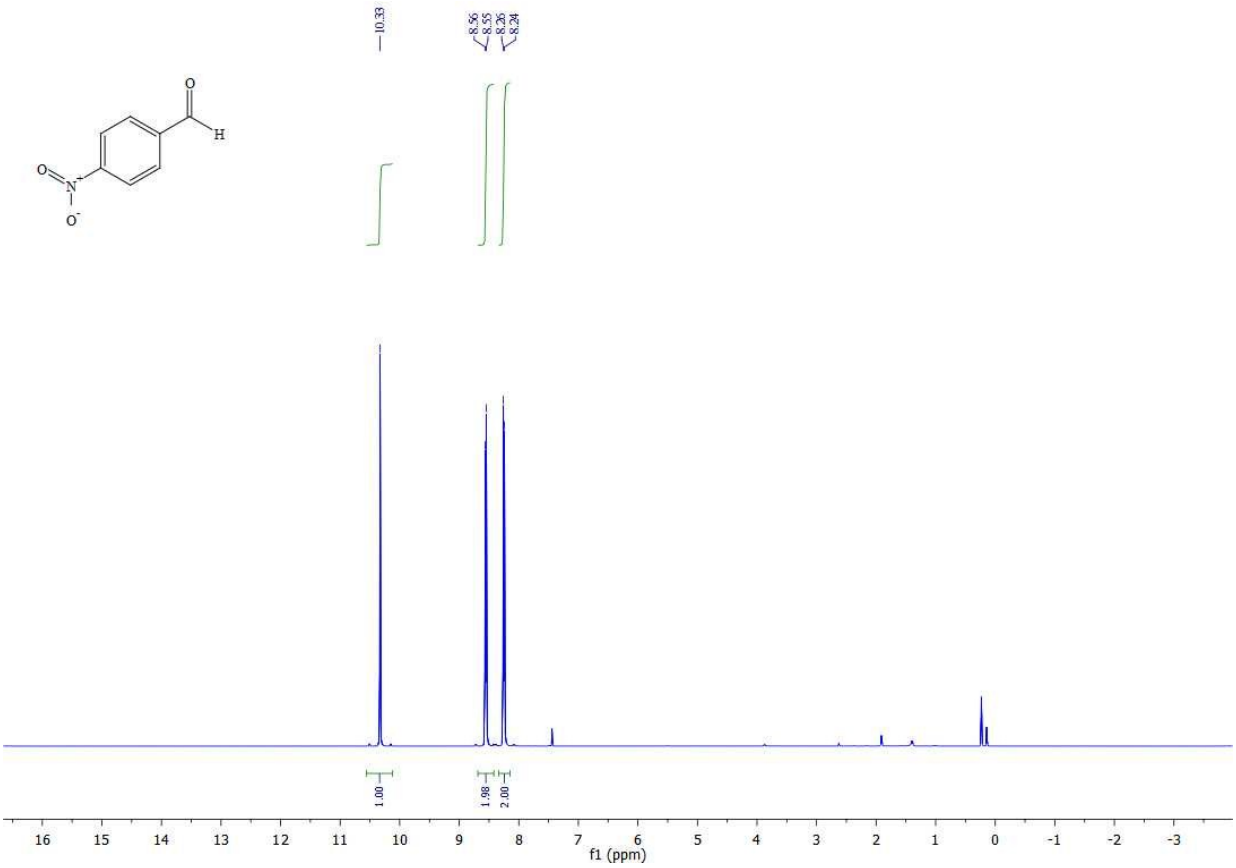
^{13}C NMR spectra of **7** (125 MHz, $CDCl_3$)



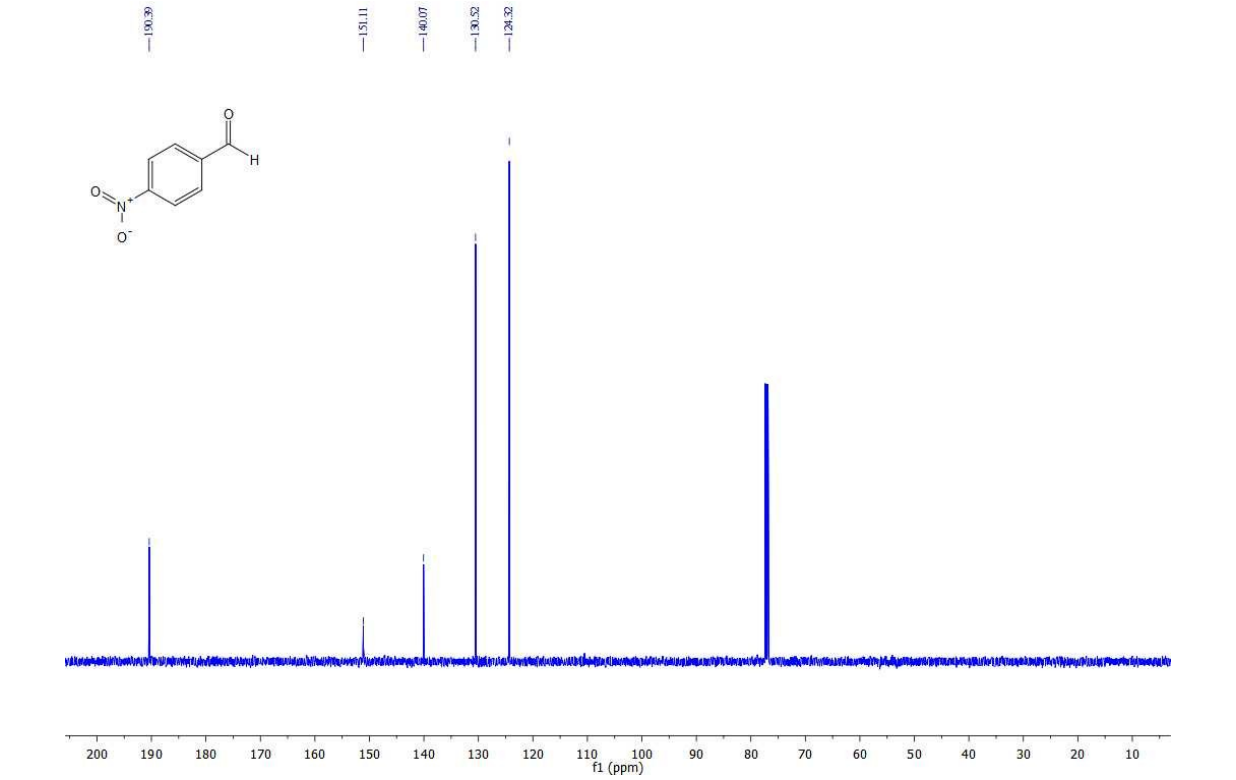
^{1}H NMR spectra of **8** (500 MHz, $CDCl_3$)



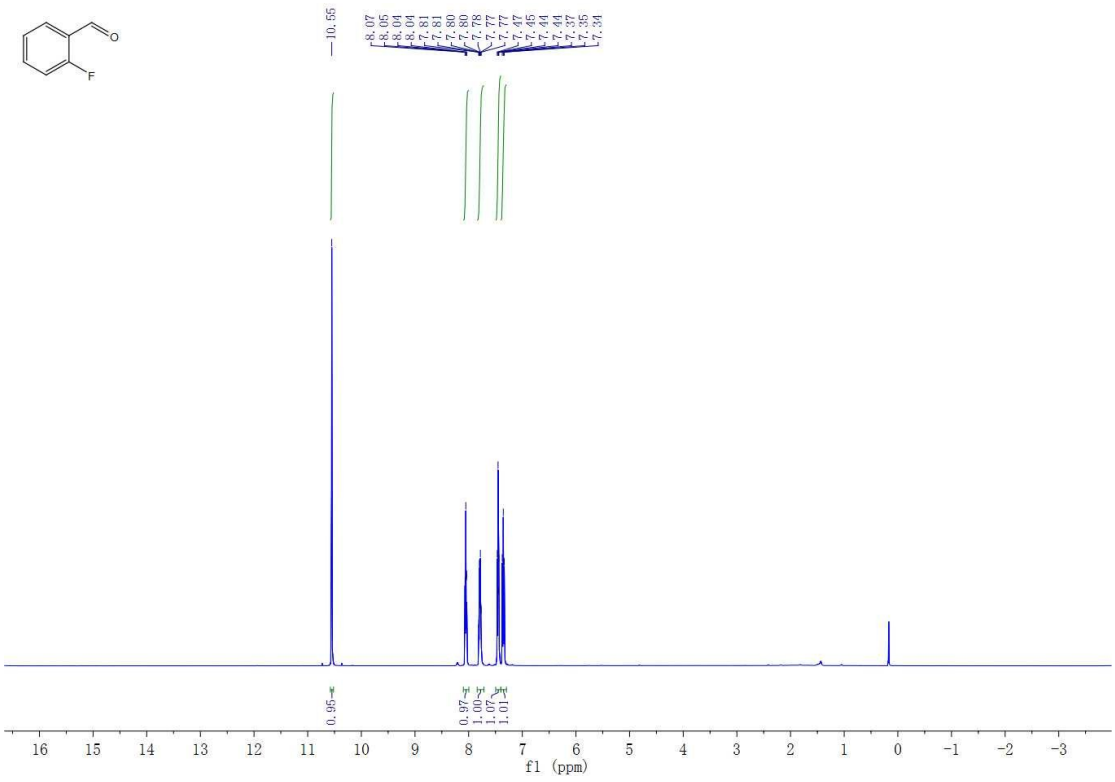
^{13}C NMR spectra of **8** (125 MHz, $CDCl_3$)



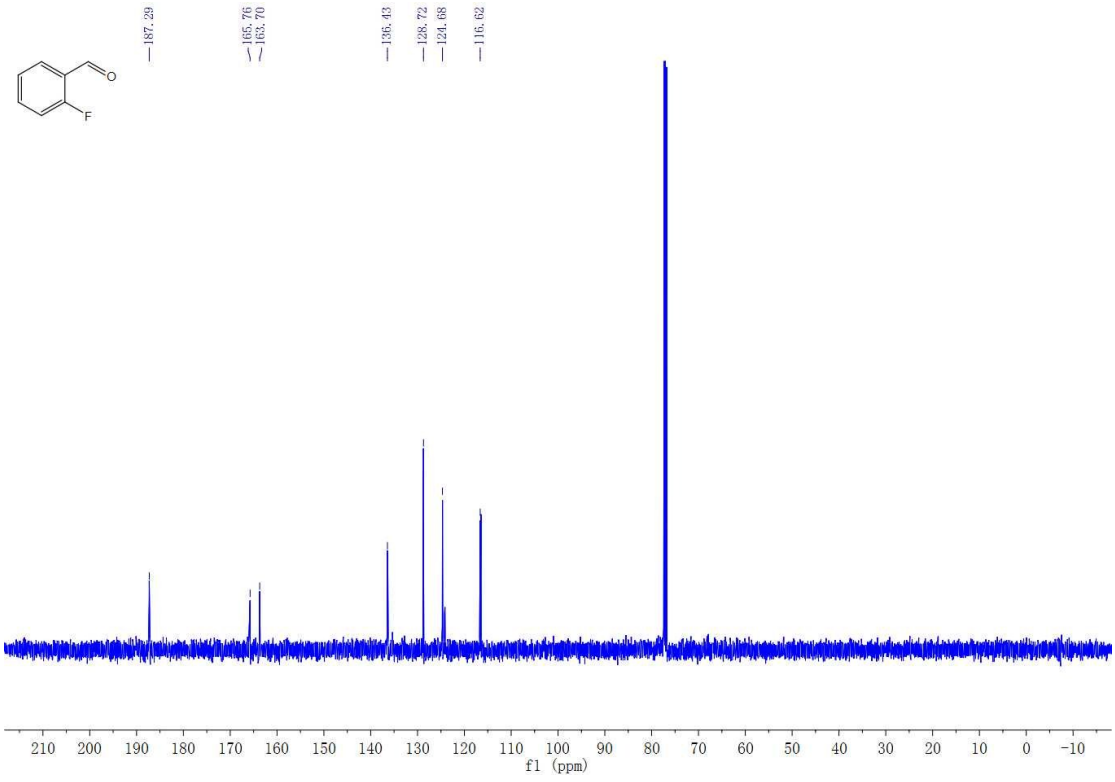
^{1}H NMR spectra of **9** (500 MHz, $CDCl_3$)



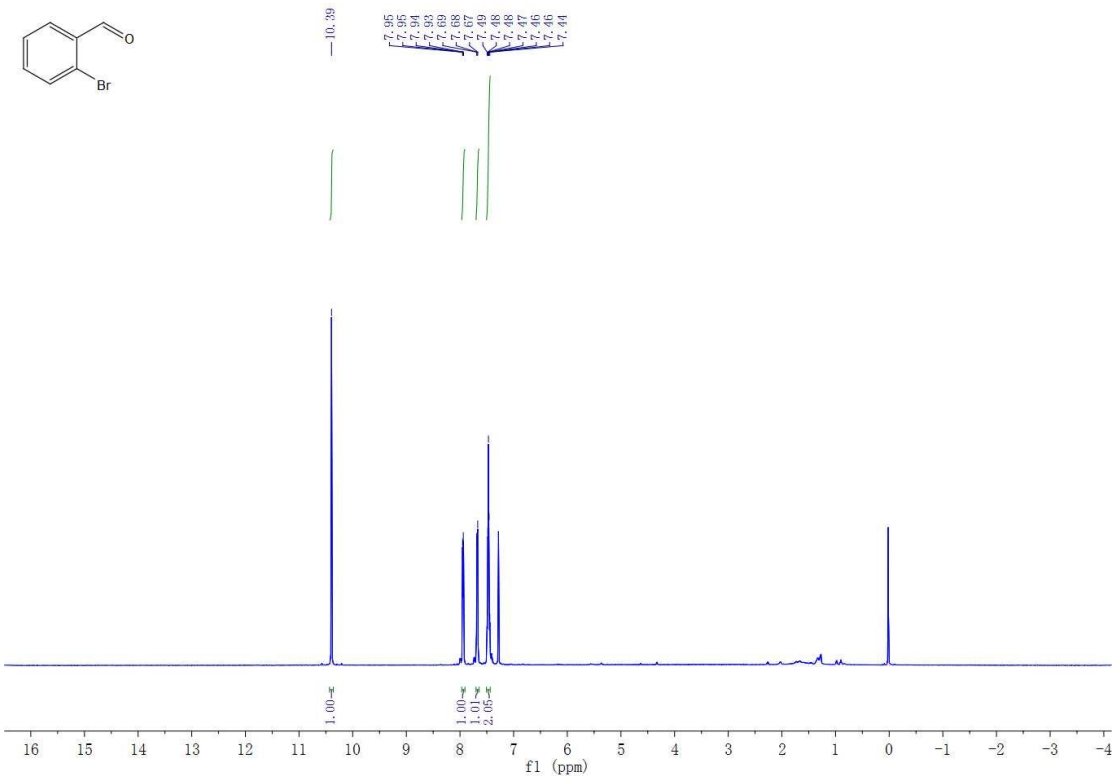
^{13}C NMR spectra of **9** (125 MHz, $CDCl_3$)



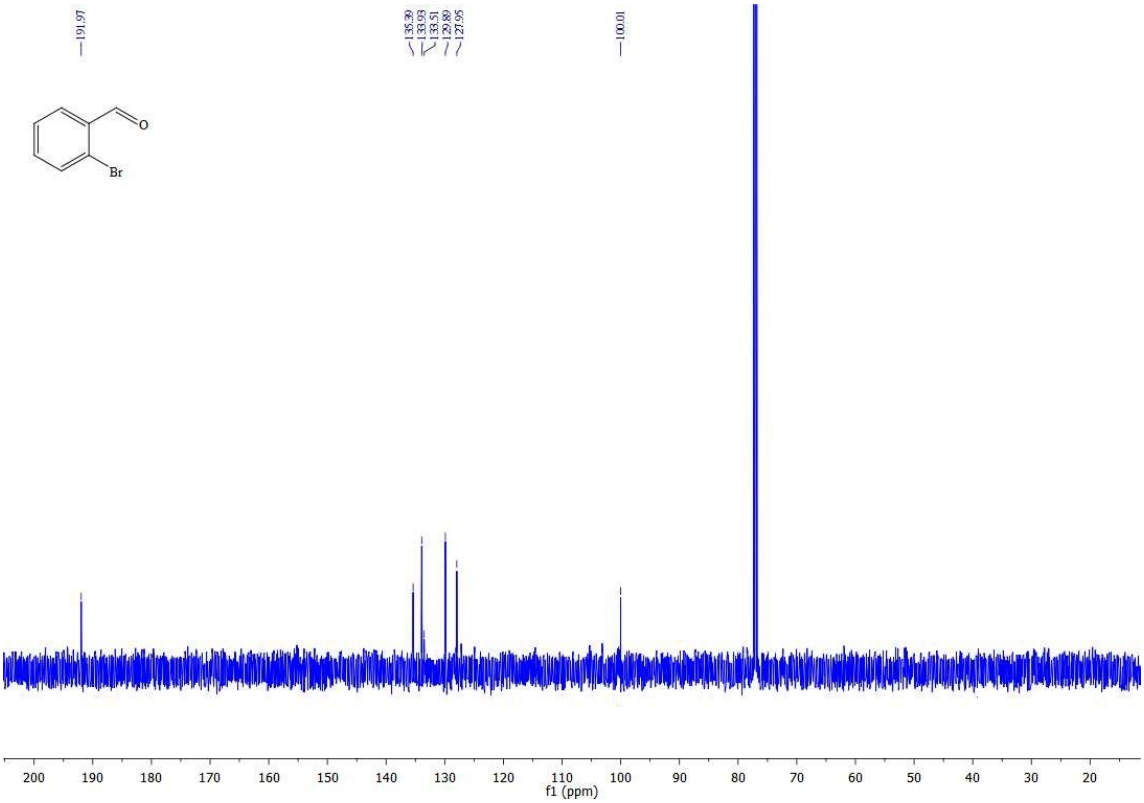
^{1}H NMR spectra of **10** (500 MHz, $CDCl_3$)



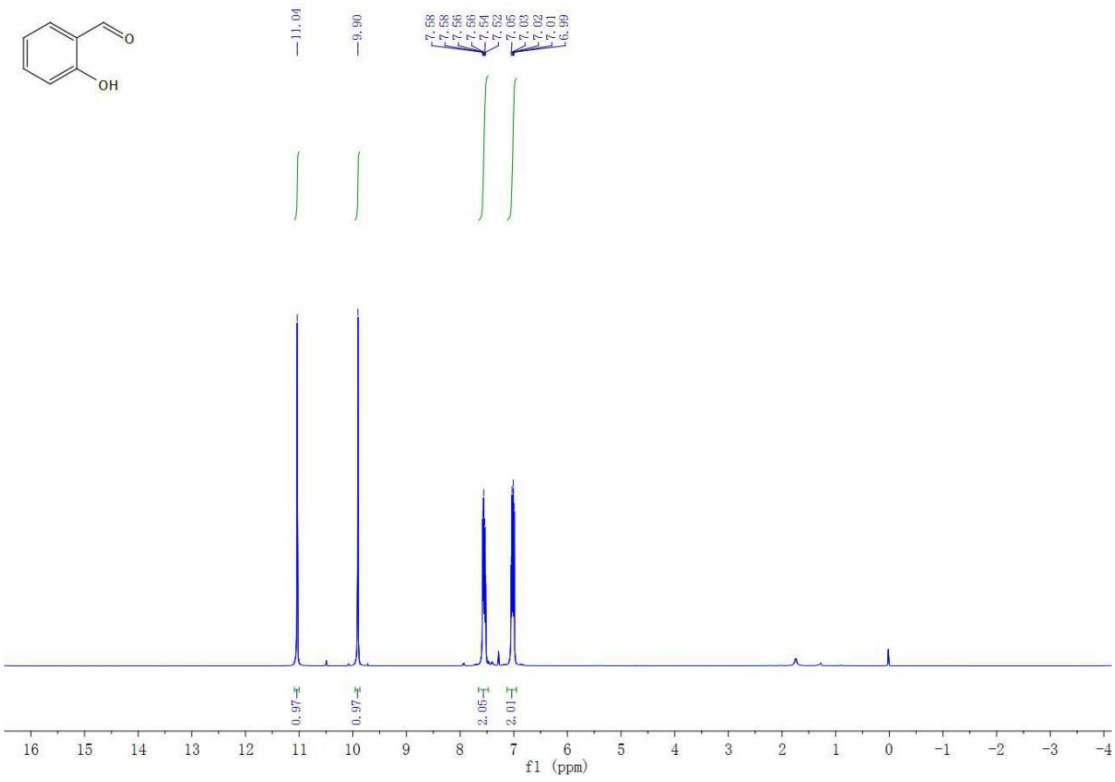
^{13}C NMR spectra of **10** (125 MHz, $CDCl_3$)



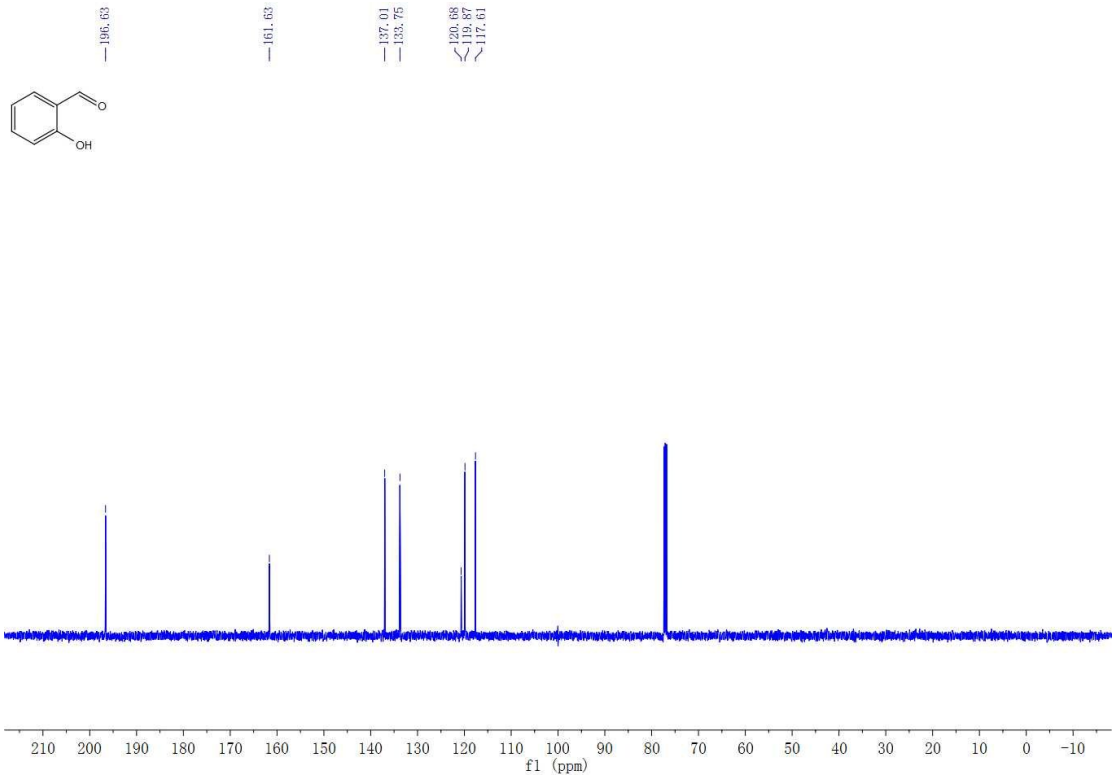
^{1}H NMR spectra of **11** (500 MHz, $CDCl_3$)



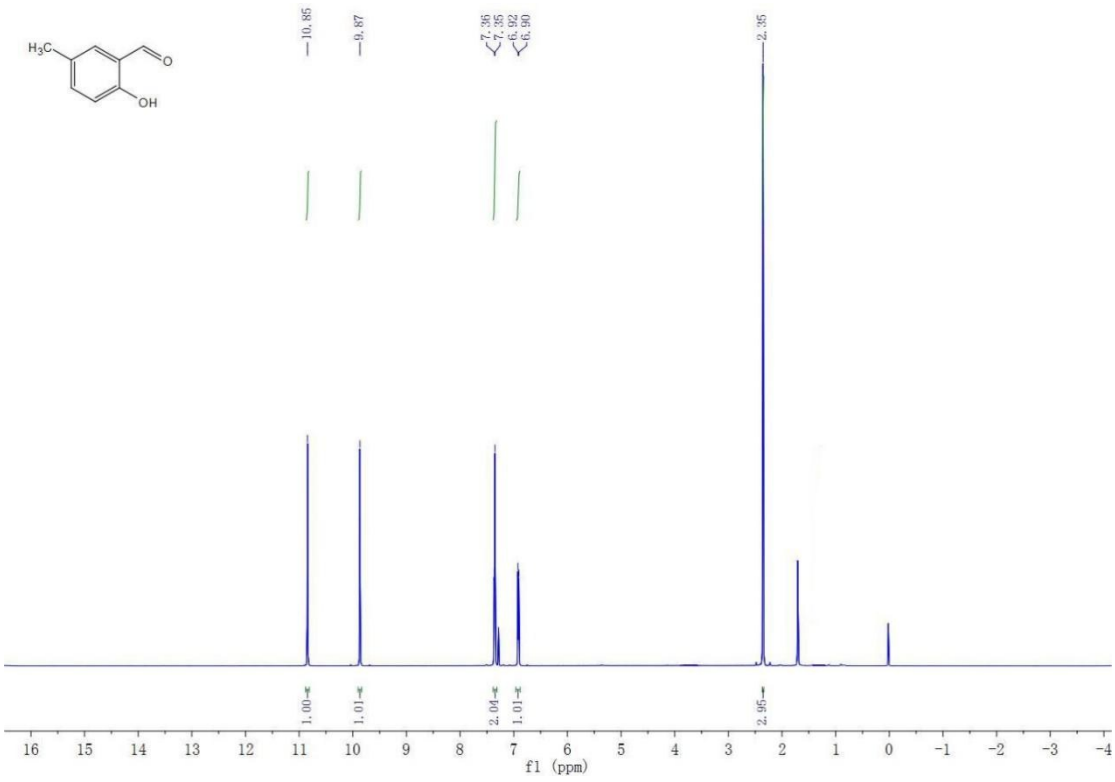
^{13}C NMR spectra of **11** (125 MHz, $CDCl_3$)



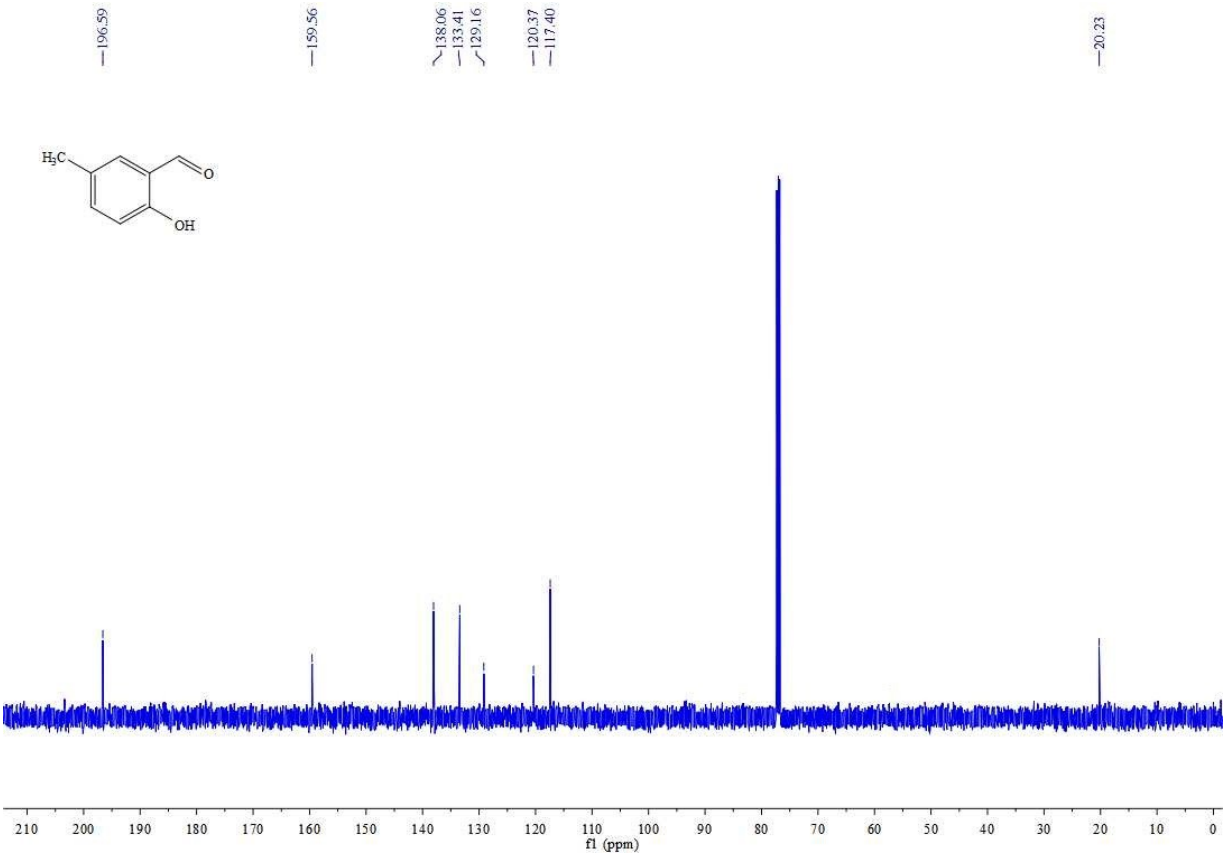
^{1}H NMR spectra of **12** (500 MHz, $CDCl_3$)



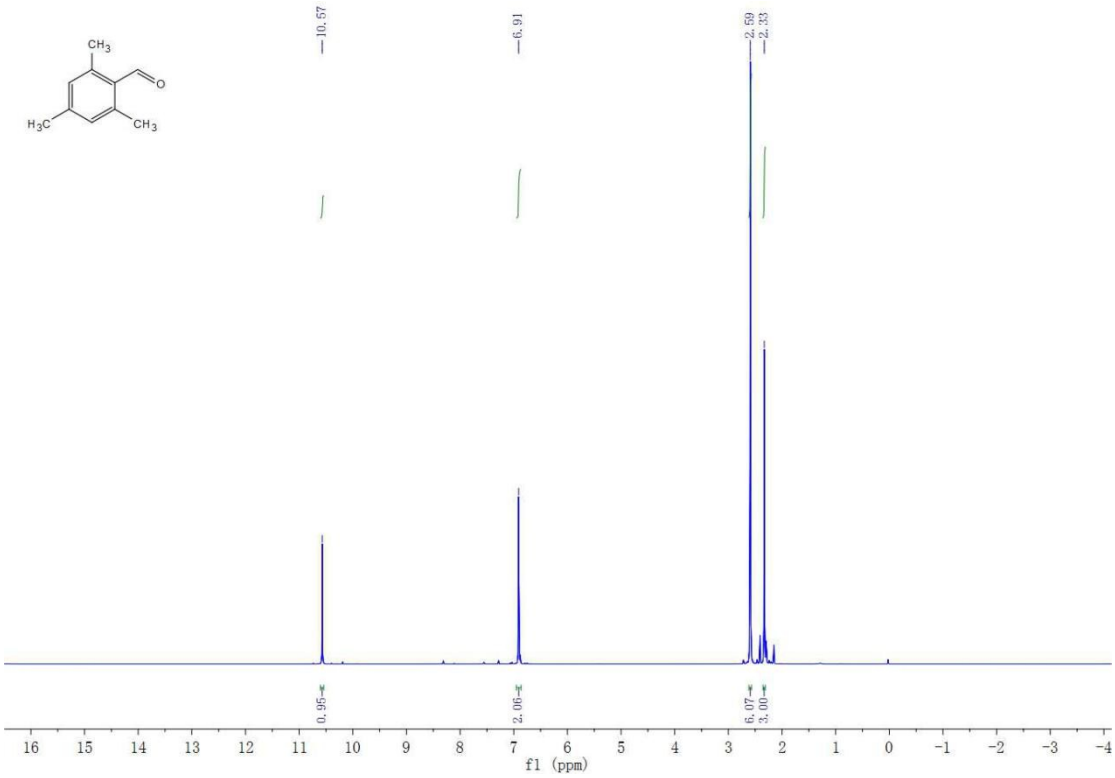
^{13}C NMR spectra of **12** (125 MHz, $CDCl_3$)



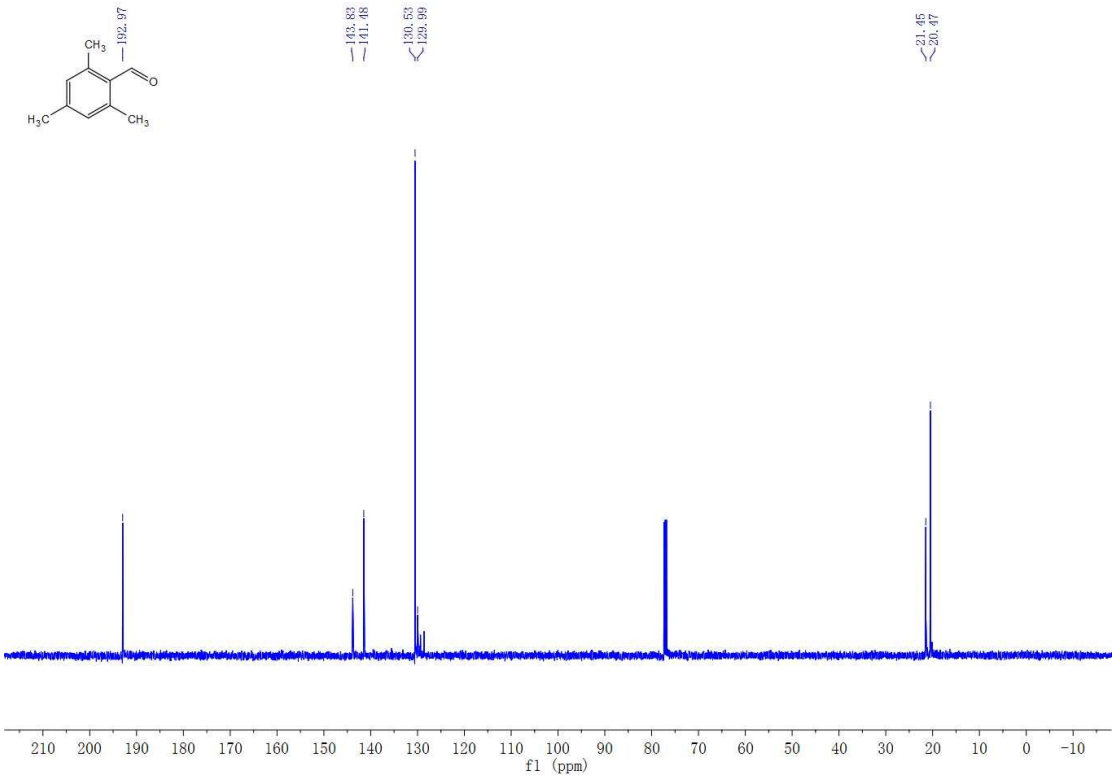
^{1}H NMR spectra of **13** (500 MHz, $CDCl_3$)



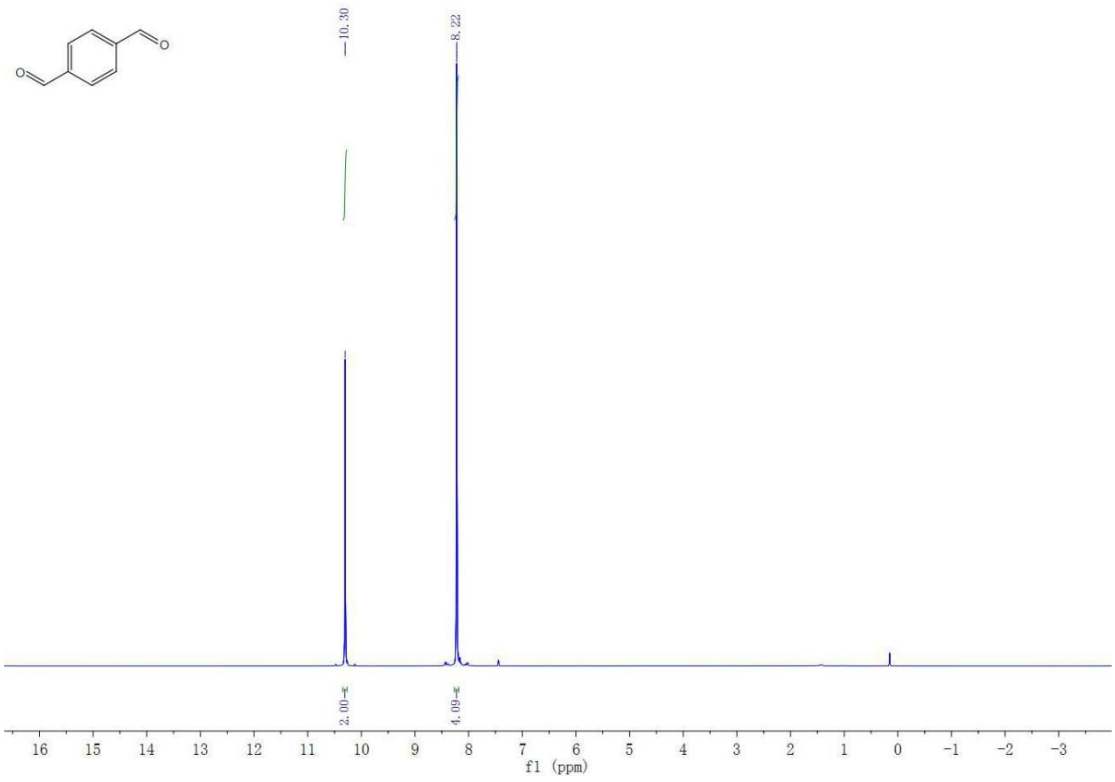
^{13}C NMR spectra of **13** (125 MHz, $CDCl_3$)



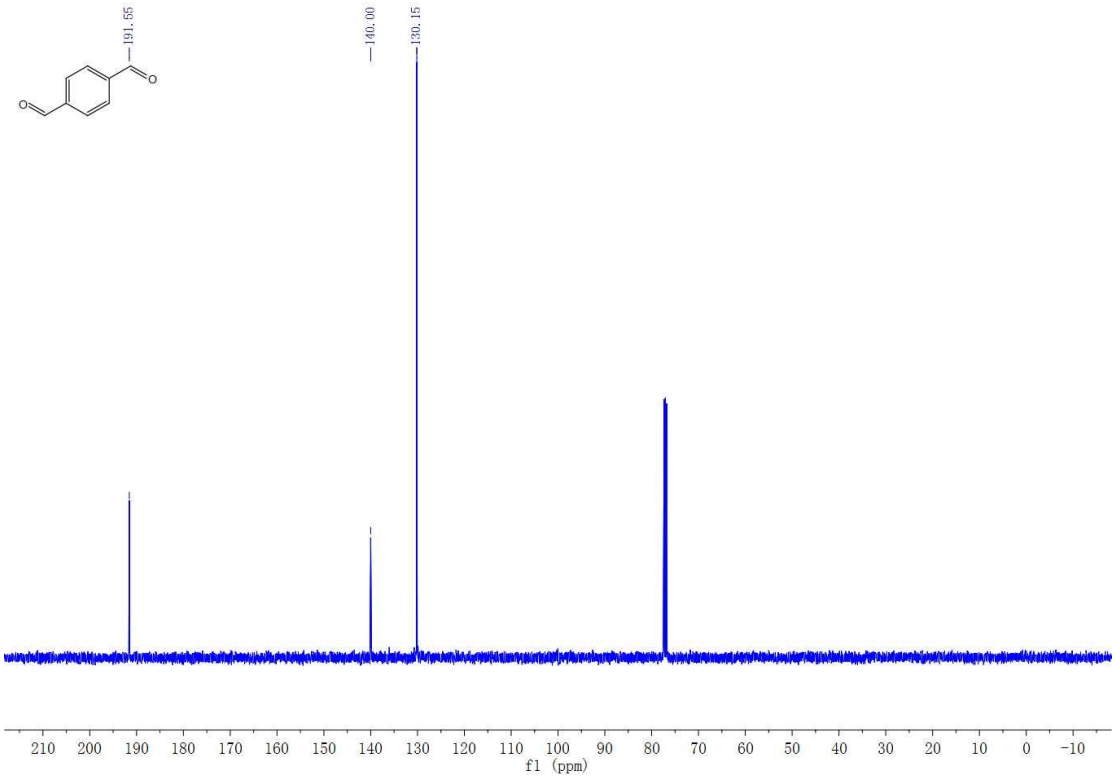
^{1}H NMR spectra of **14** (500 MHz, $CDCl_3$)



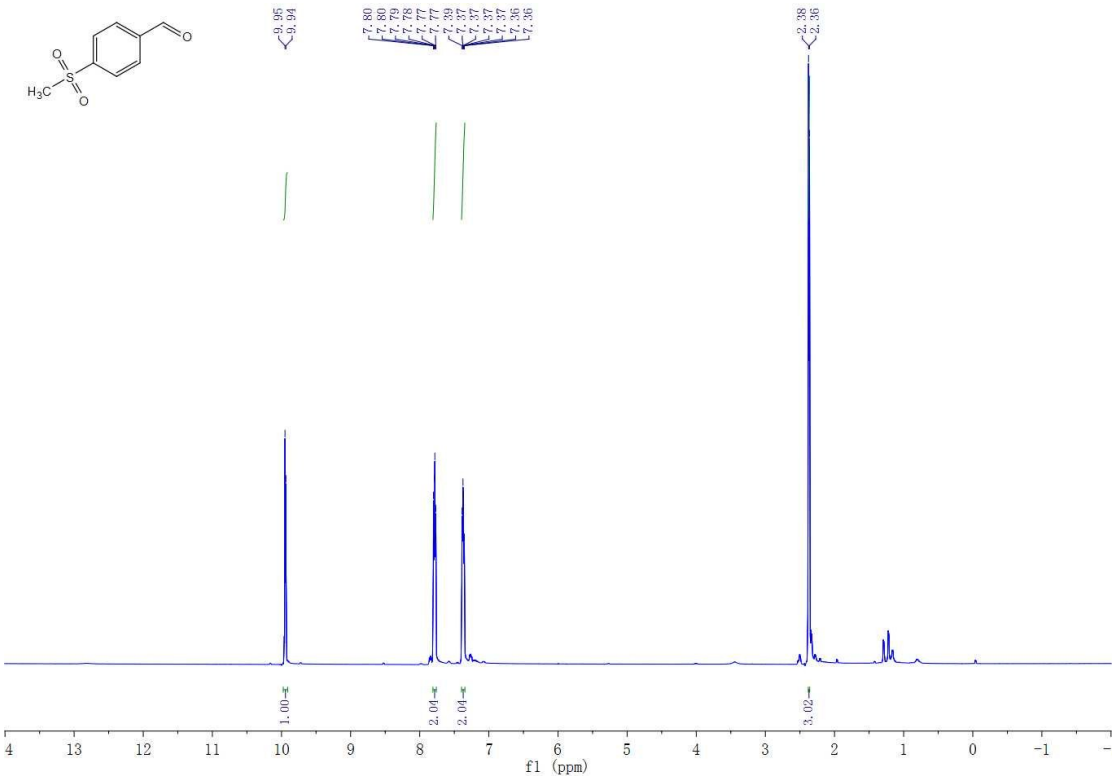
^{13}C NMR spectra of **14** (125 MHz, $CDCl_3$)



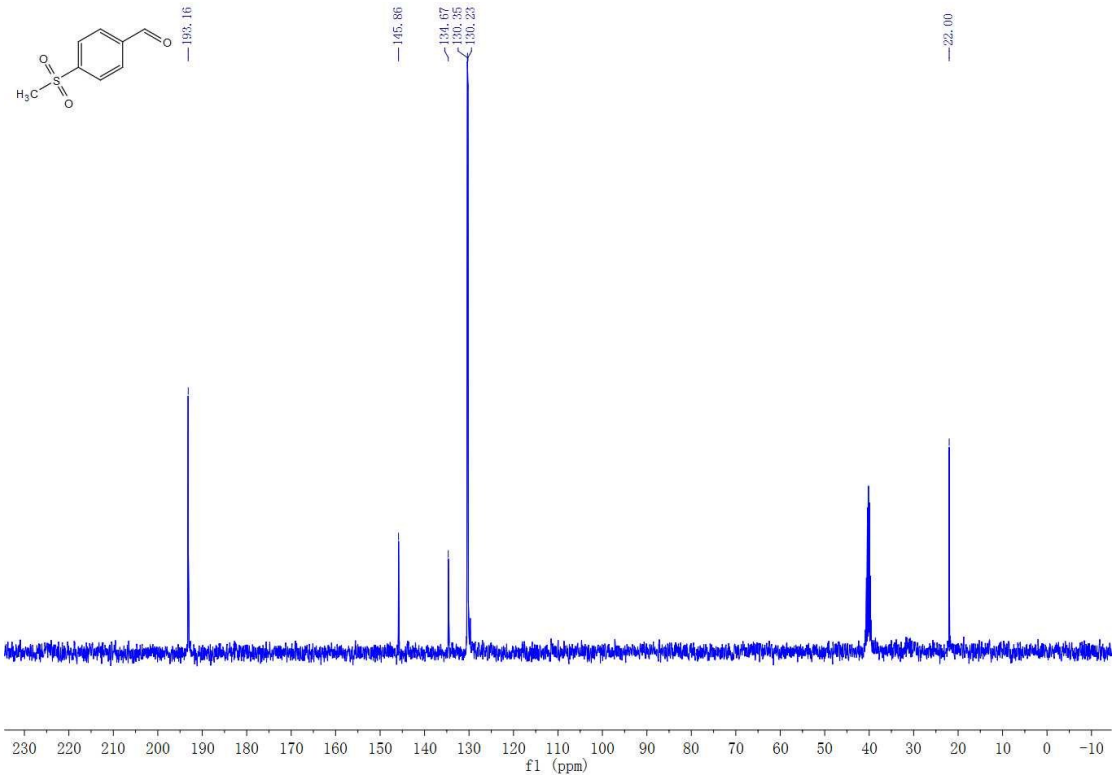
^{1}H NMR spectra of **15** (500 MHz, $CDCl_3$)



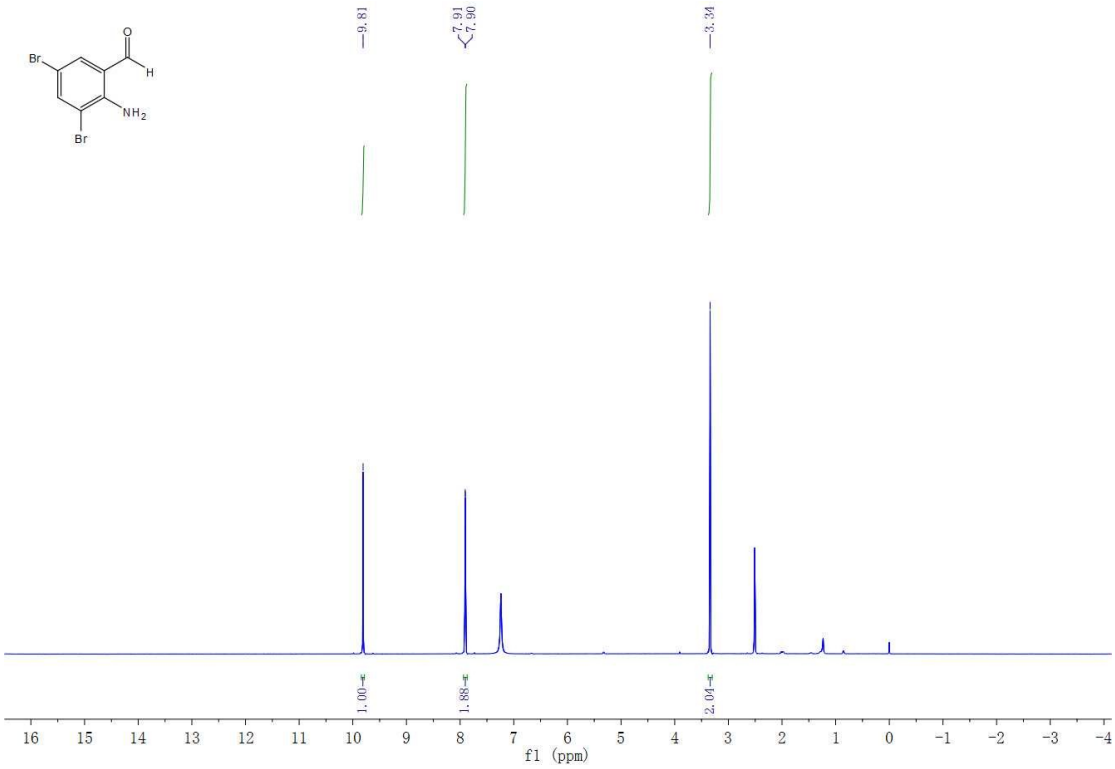
^{13}C NMR spectra of **15** (125 MHz, $CDCl_3$)



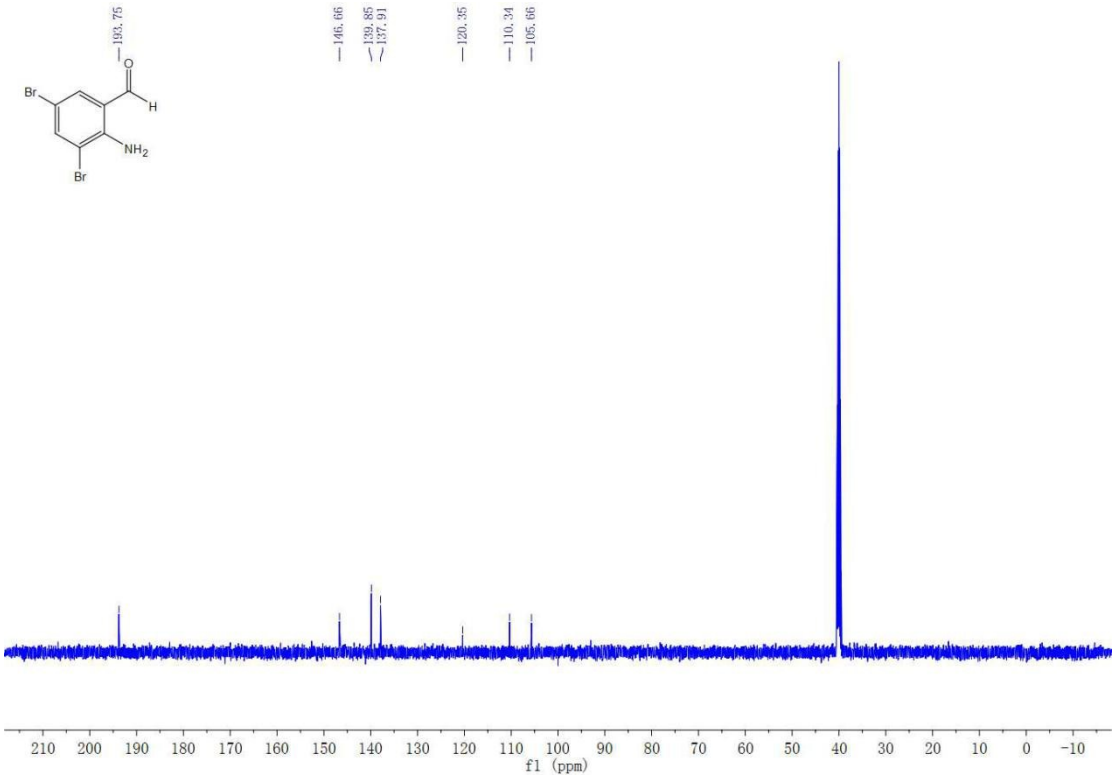
^{1}H NMR spectra of **16** (500 MHz, DMSO)



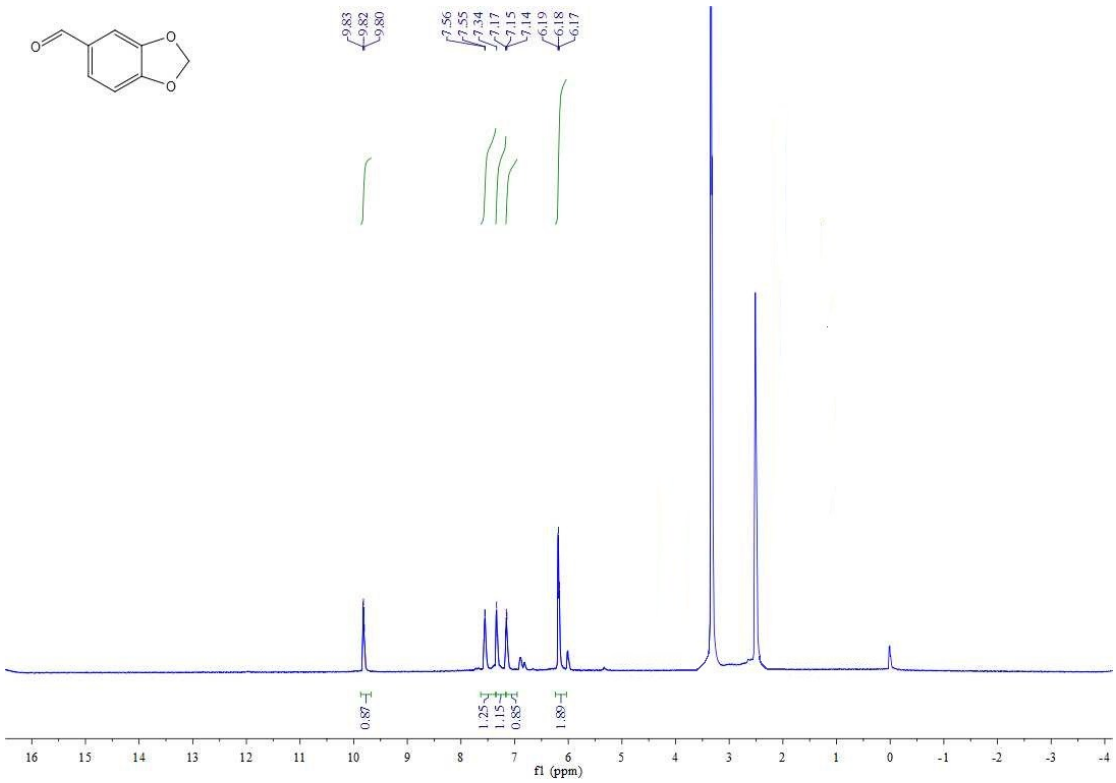
^{13}C NMR spectra of **16** (125 MHz, DMSO)



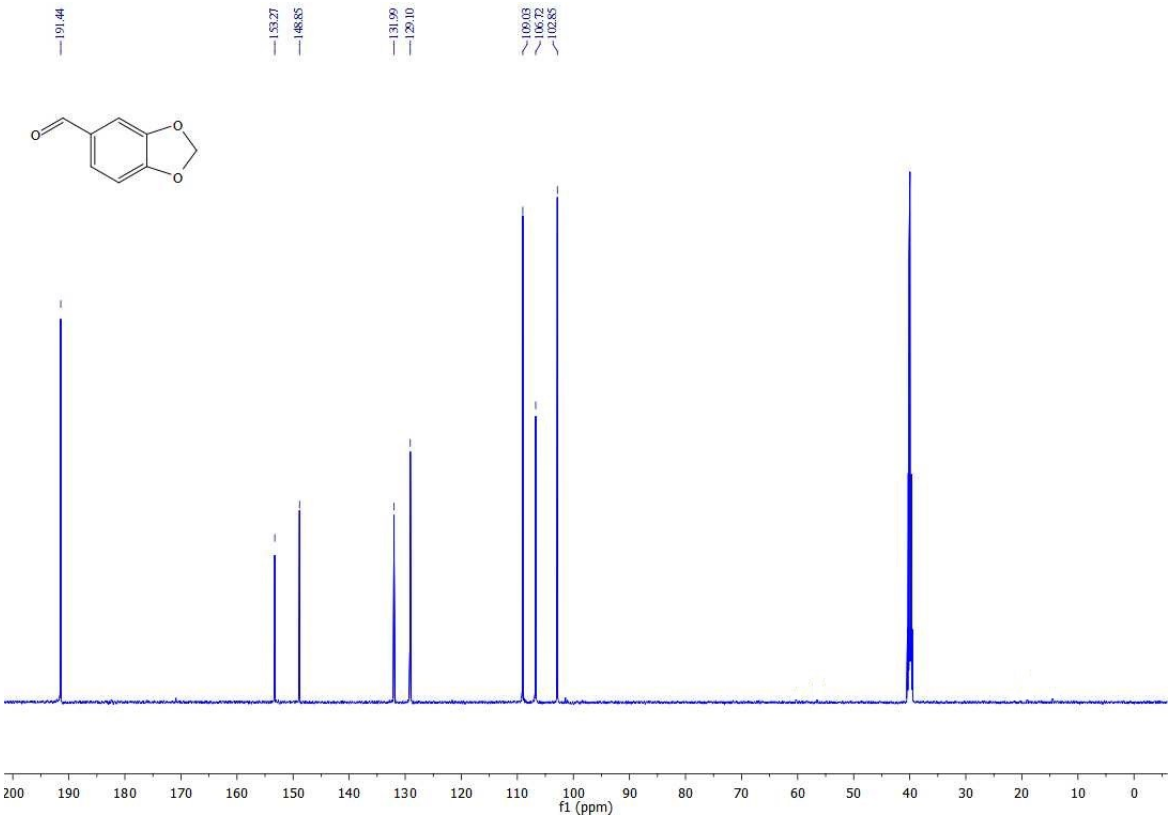
^{1}H NMR spectra of **17** (500 MHz, DMSO)



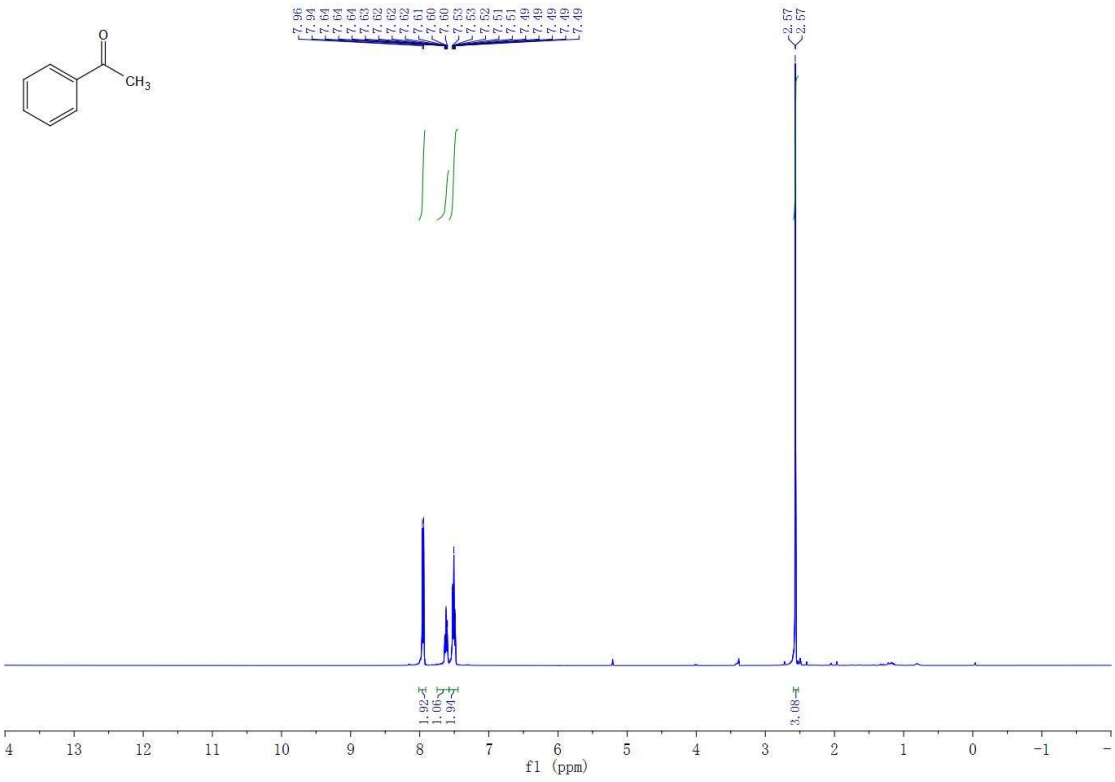
^{13}C NMR spectra of **17** (125 MHz, DMSO)



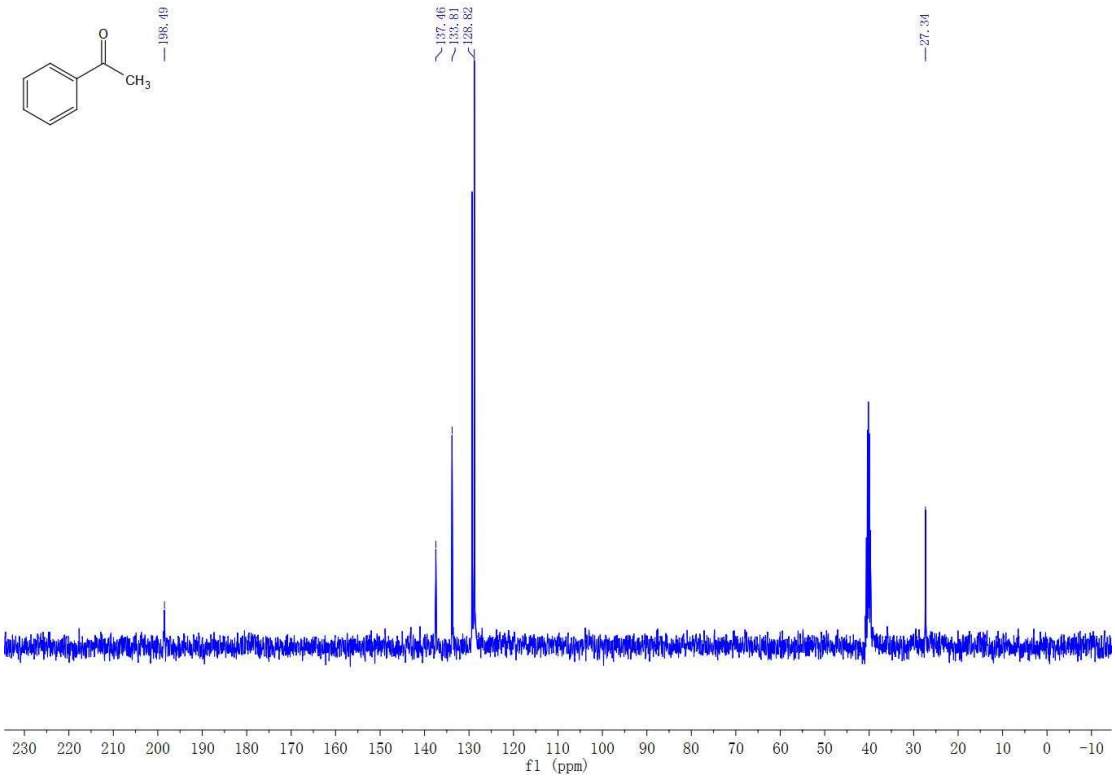
^{1}H NMR spectra of **18** (500 MHz, DMSO)



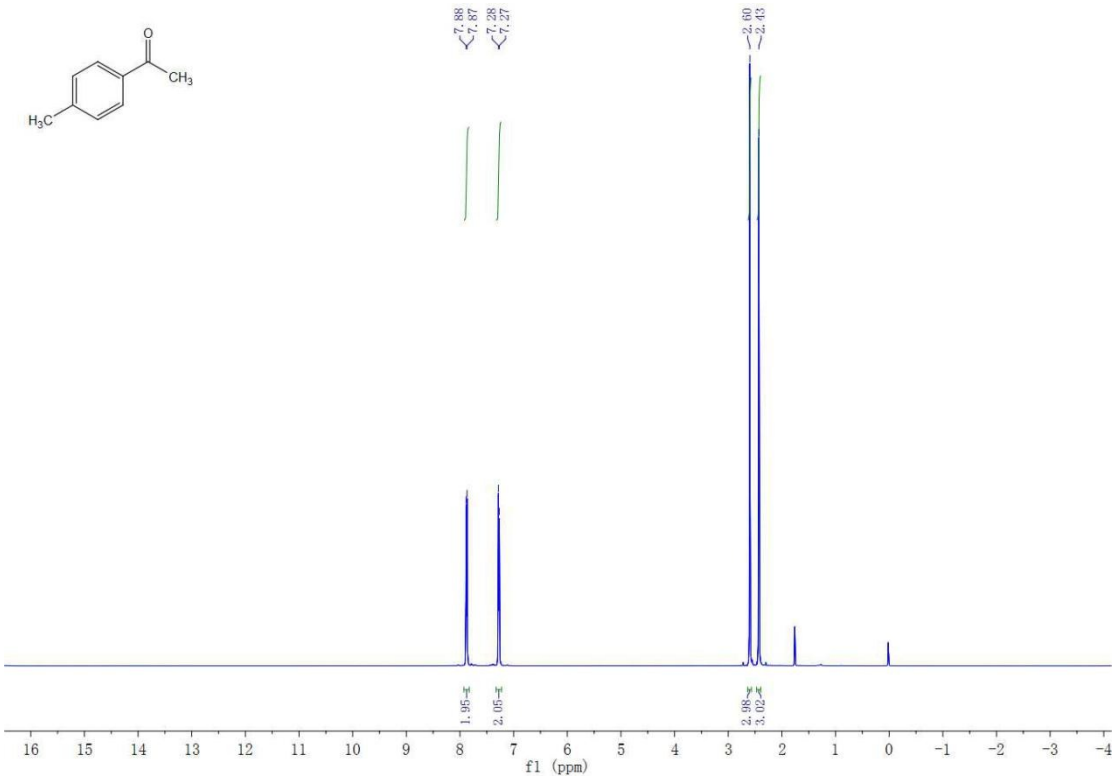
^{13}C NMR spectra of **18** (125 MHz, DMSO)



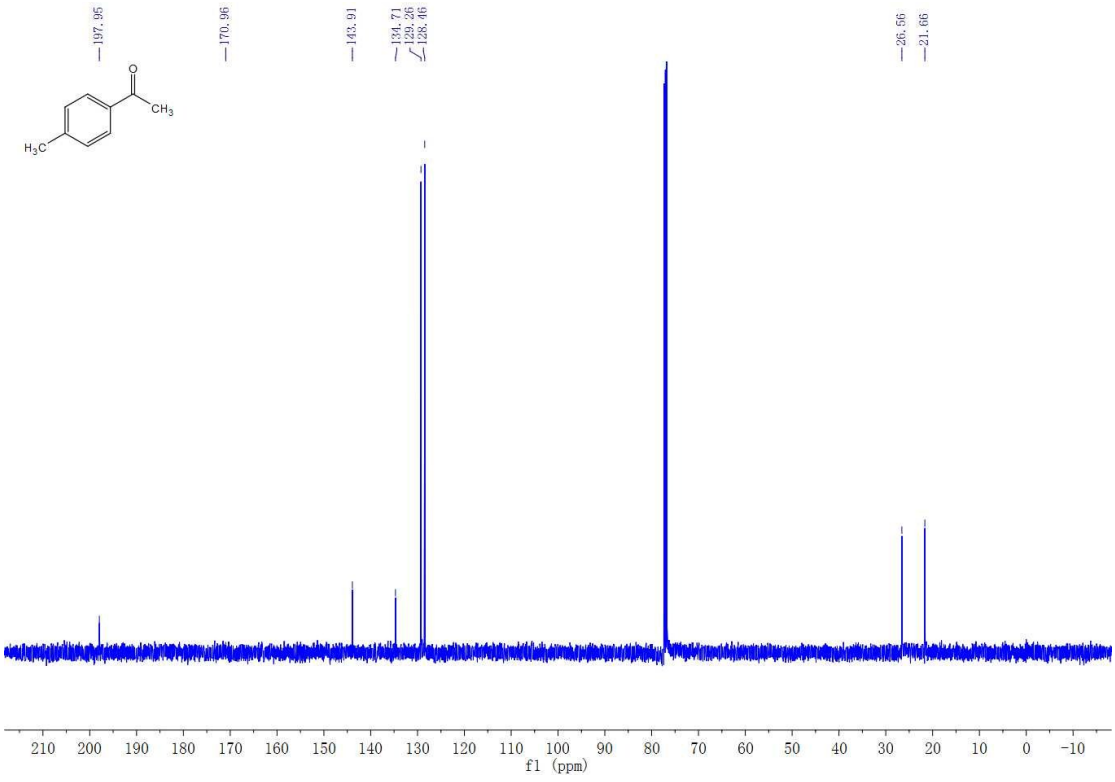
^{1}H NMR spectra of **19** (500 MHz, DMSO)



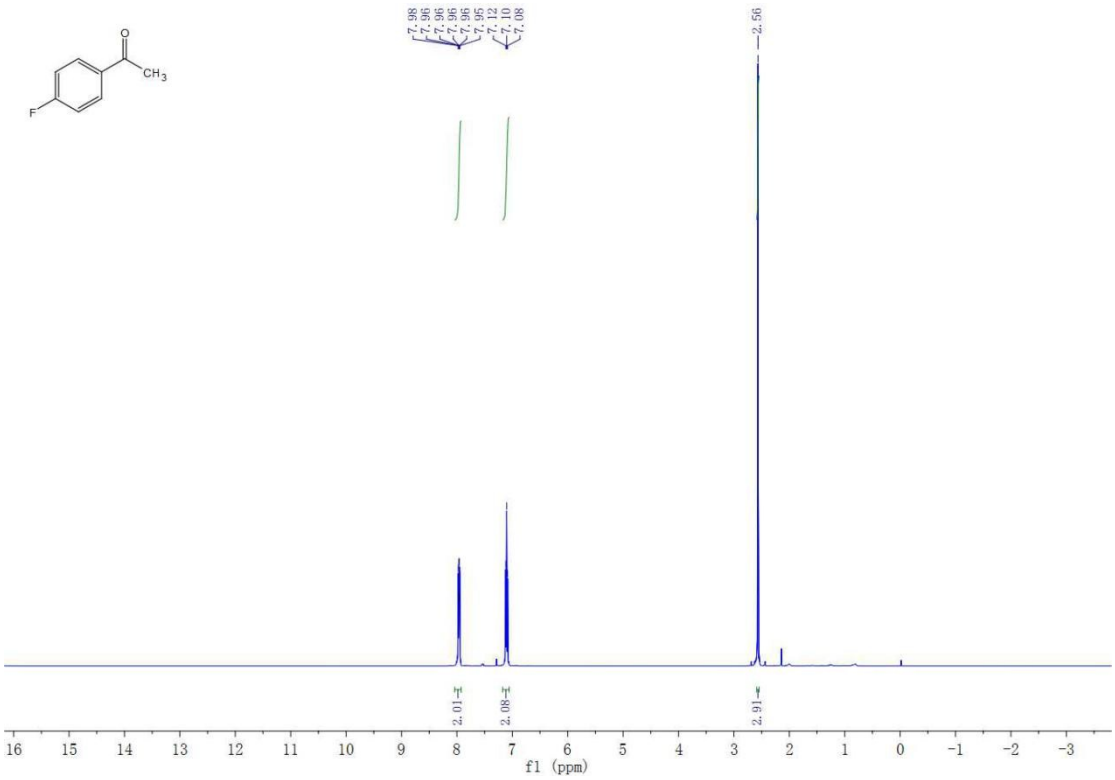
^{13}C NMR spectra of **19** (125 MHz, DMSO)



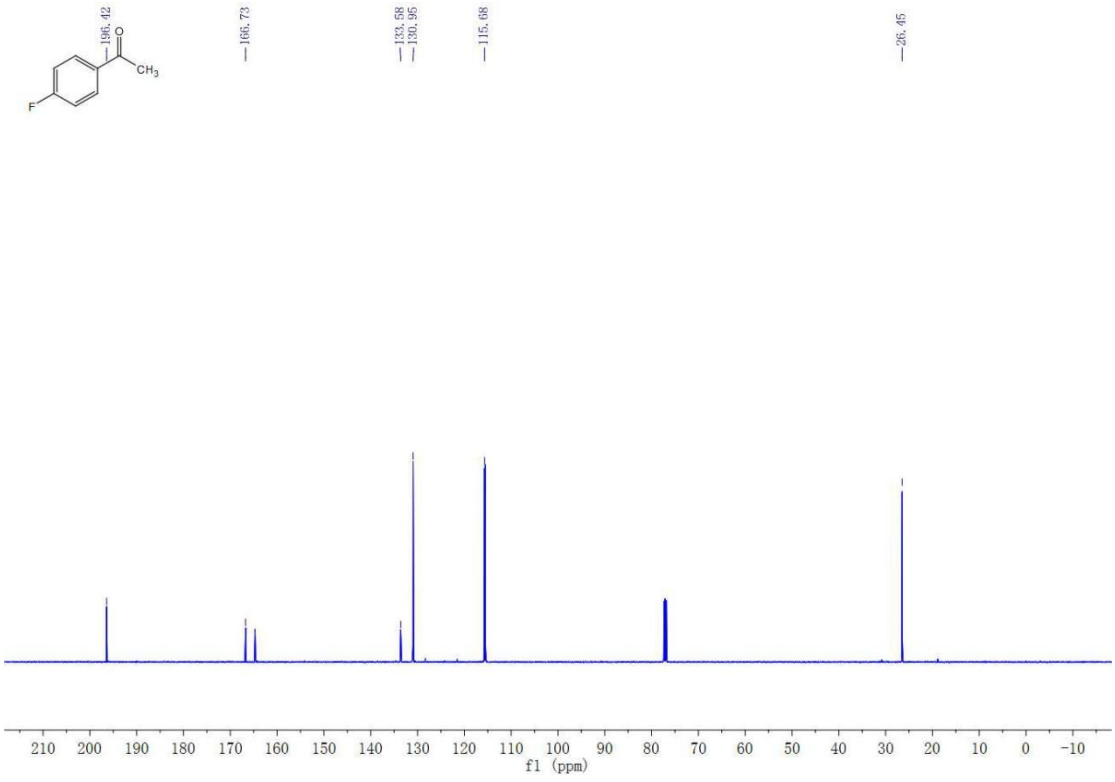
^{1}H NMR spectra of **20** (500 MHz, $CDCl_3$)



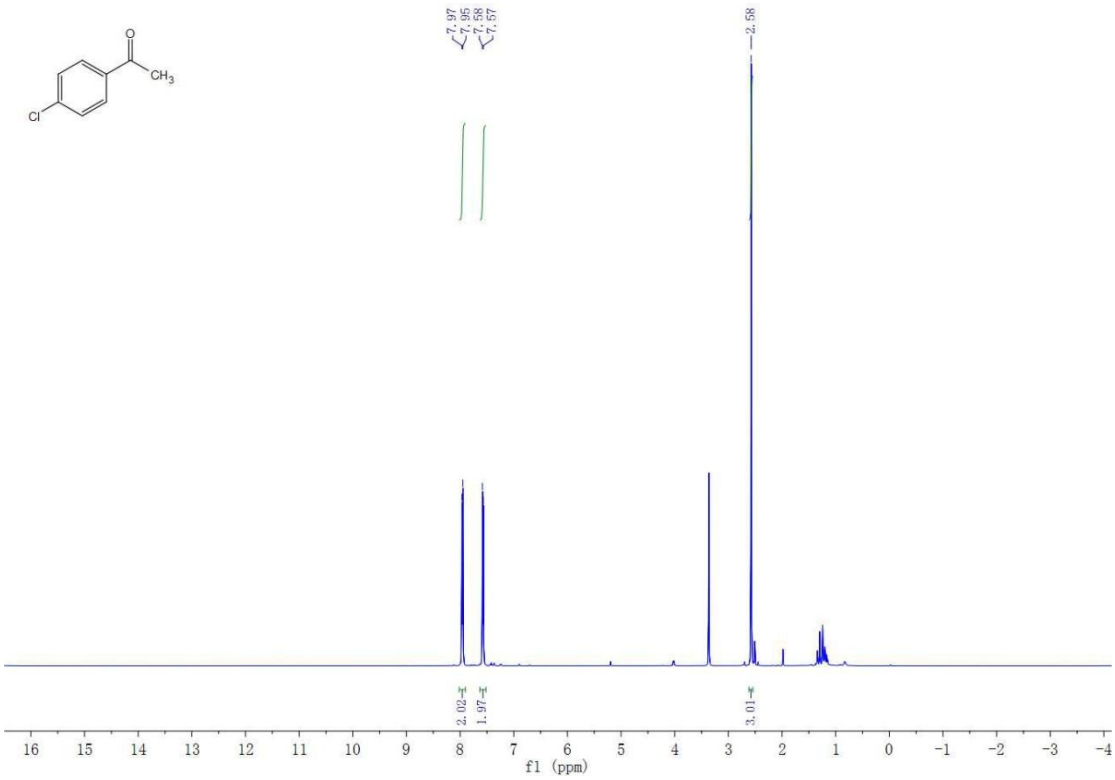
^{13}C NMR spectra of **20** (125 MHz, $CDCl_3$)



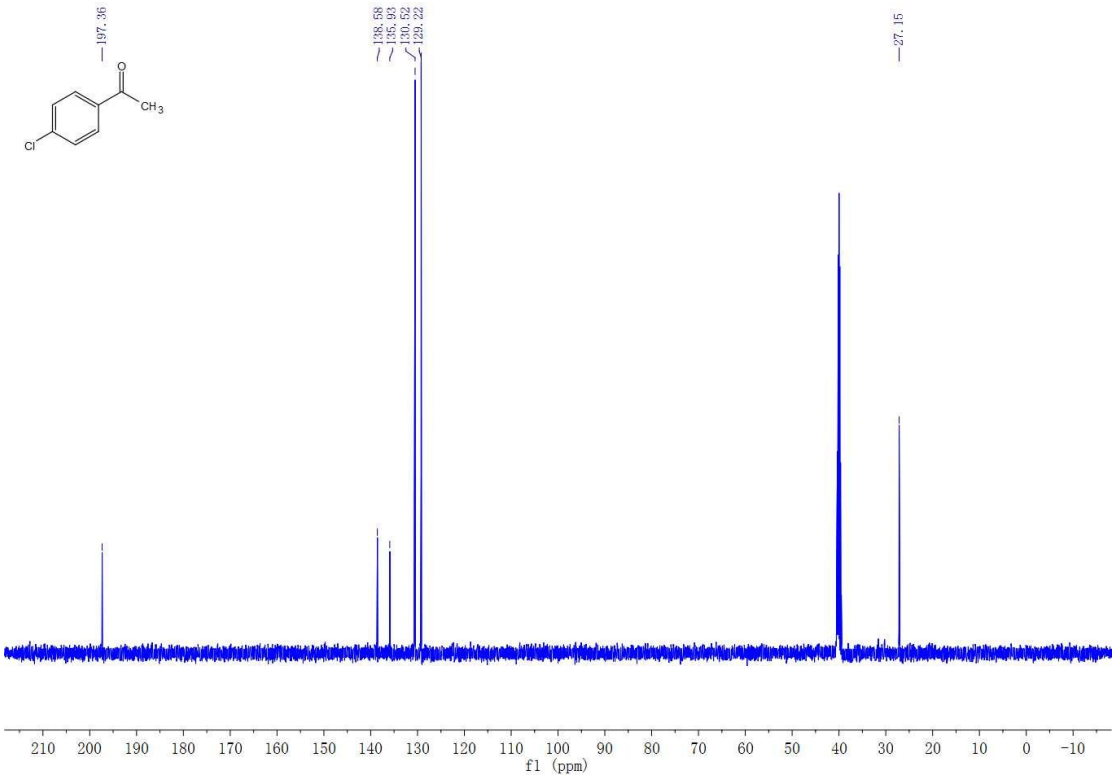
^{1}H NMR spectra of **21** (500 MHz, $CDCl_3$)



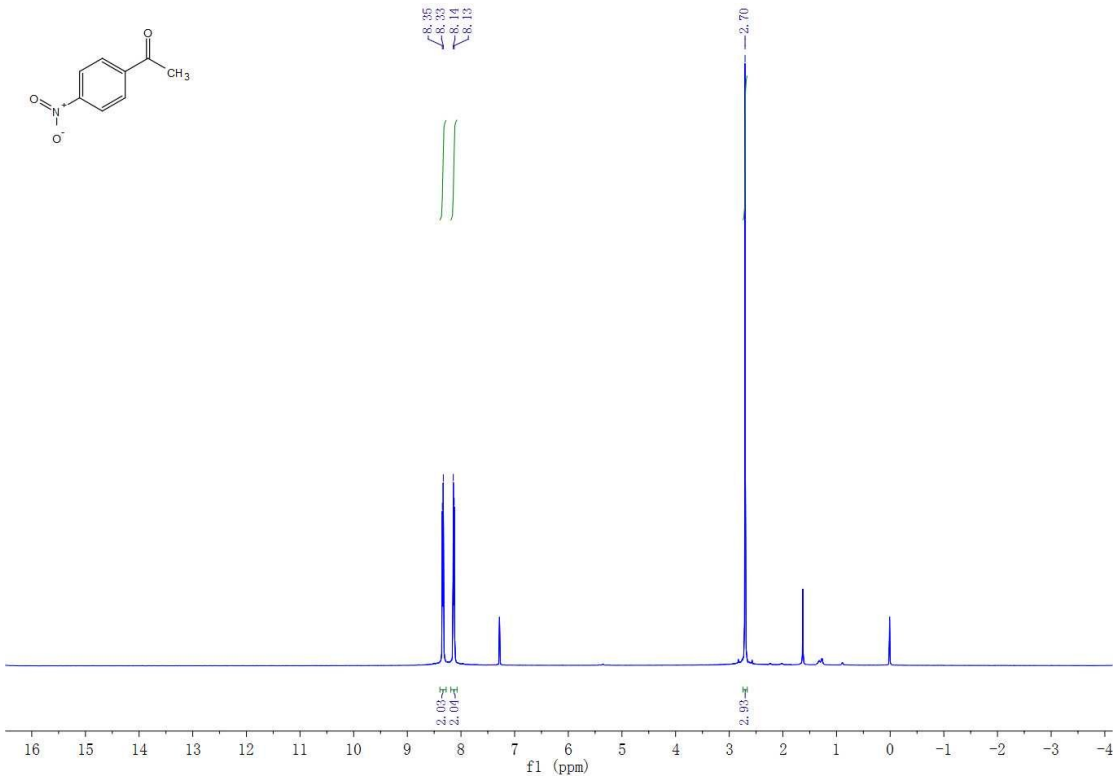
^{13}C NMR spectra of **21** (125 MHz, $CDCl_3$)



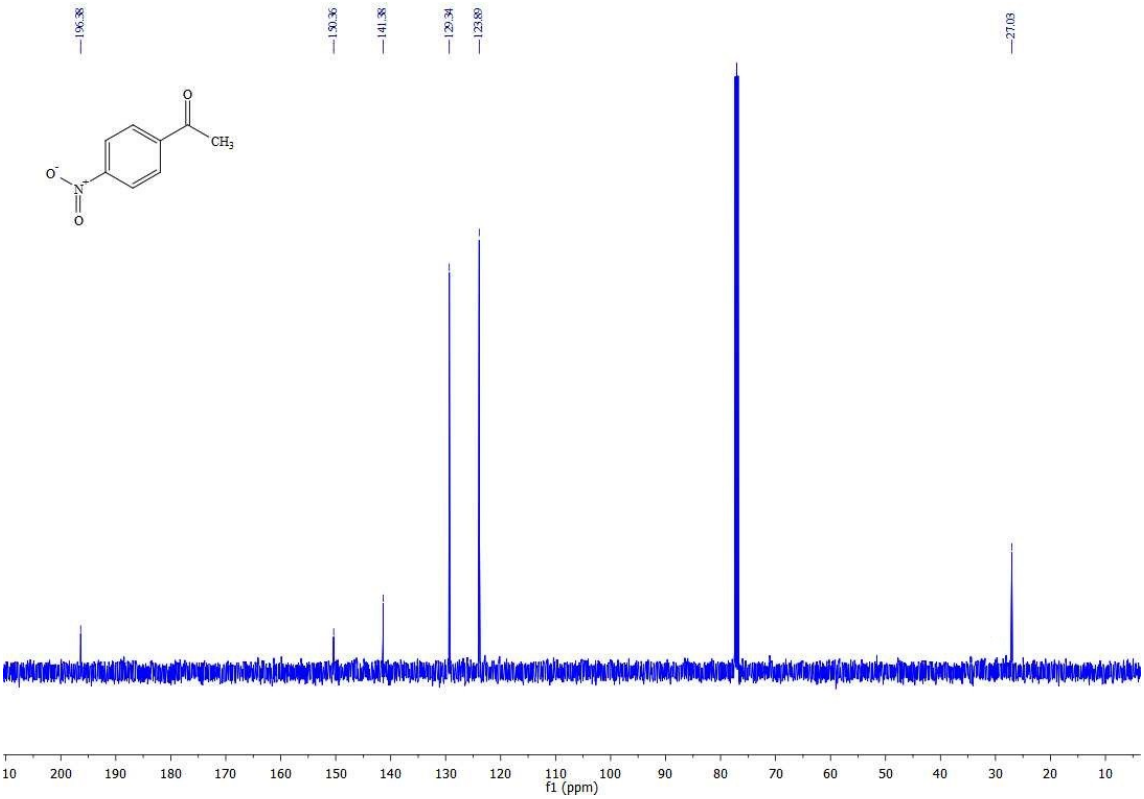
^{1}H NMR spectra of **22** (500 MHz, DMSO)



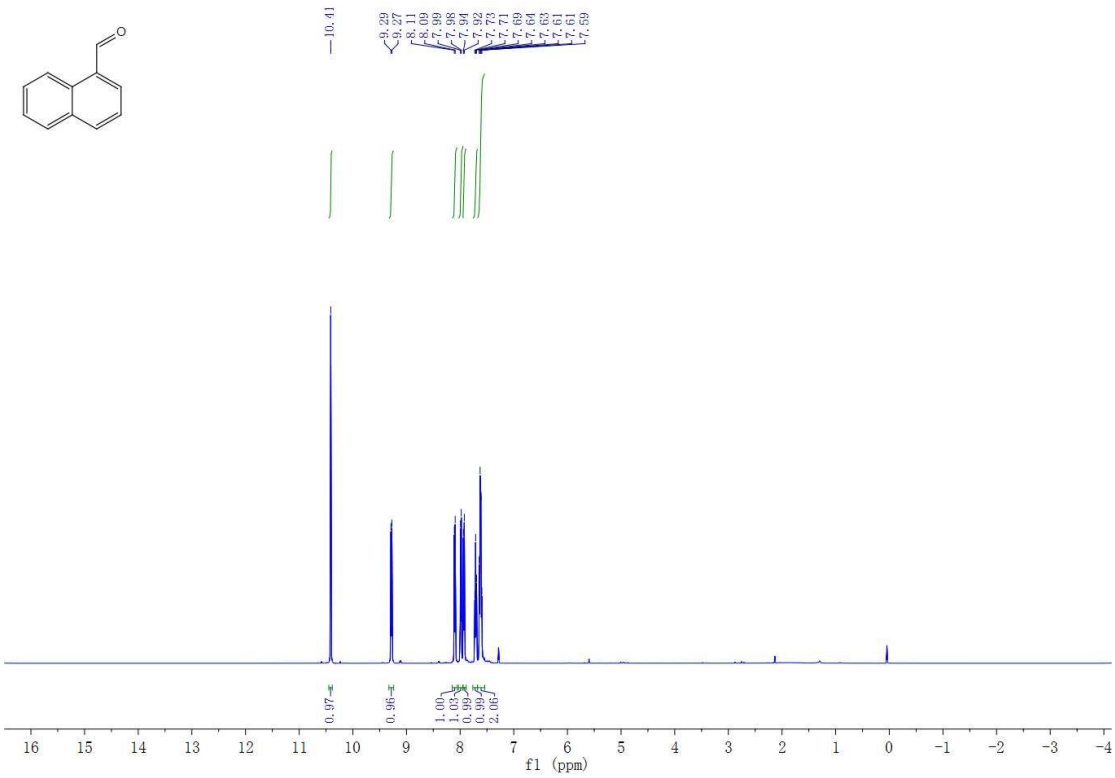
^{13}C NMR spectra of **22** (125 MHz, DMSO)



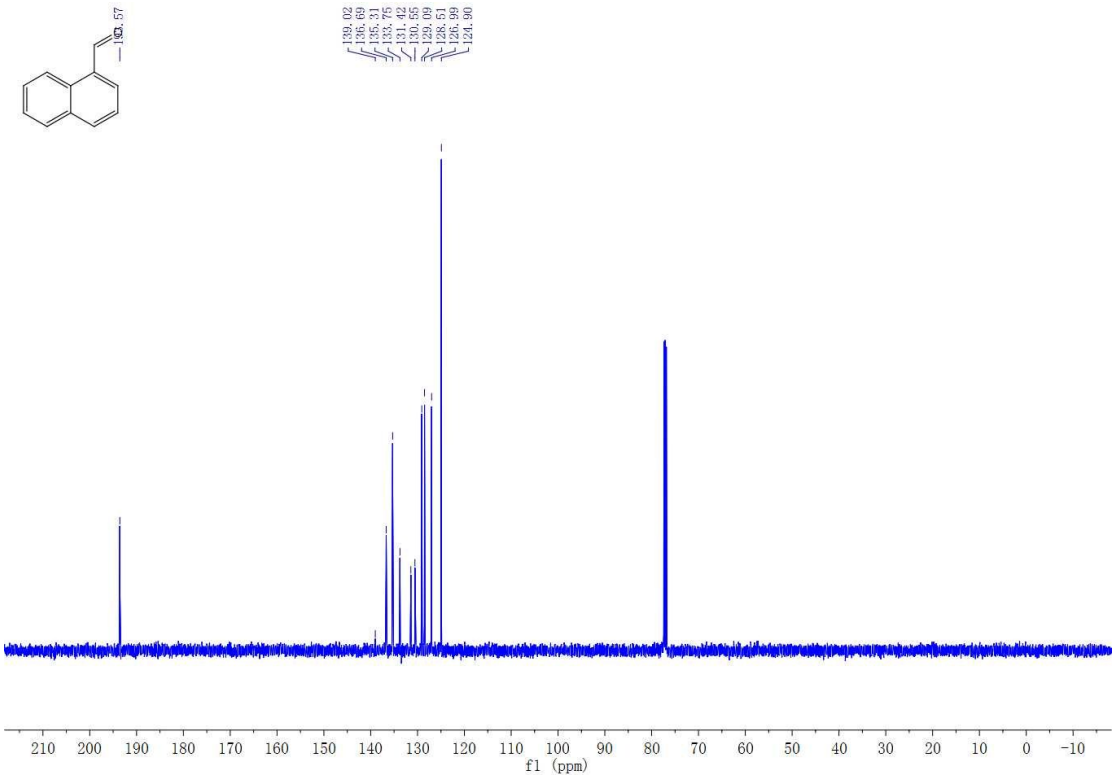
^{1}H NMR spectra of **23** (500 MHz, $CDCl_3$)



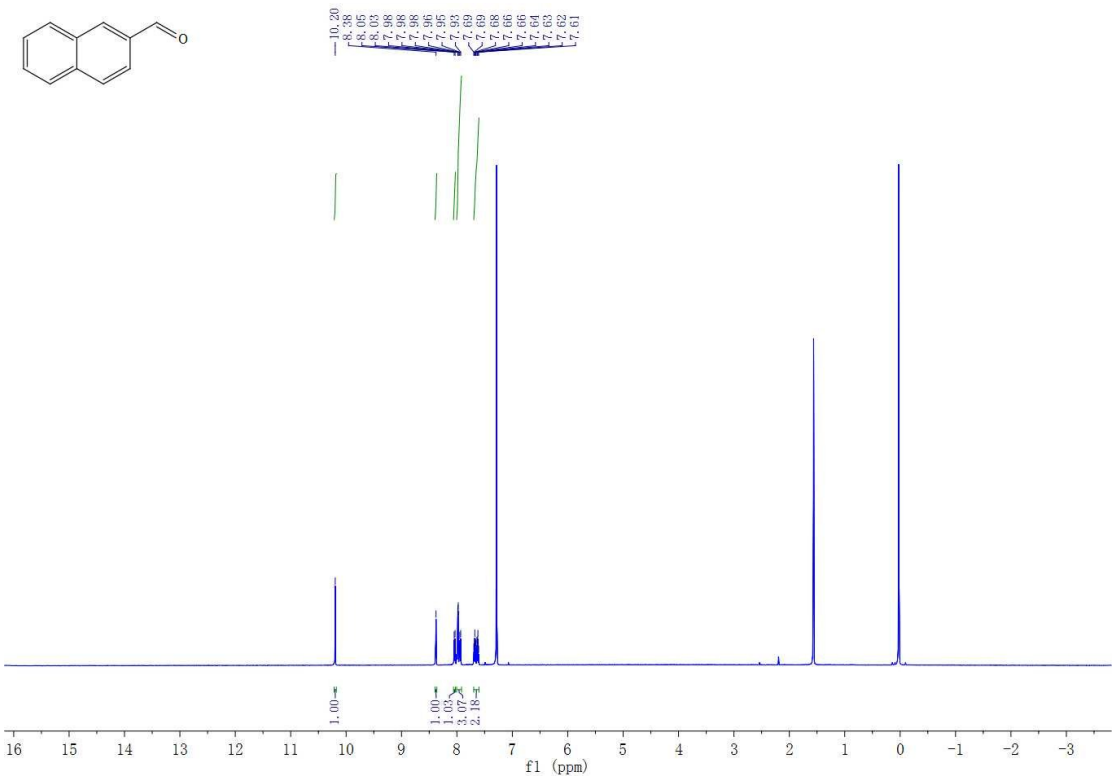
^{13}C NMR spectra of **23** (125 MHz, $CDCl_3$)



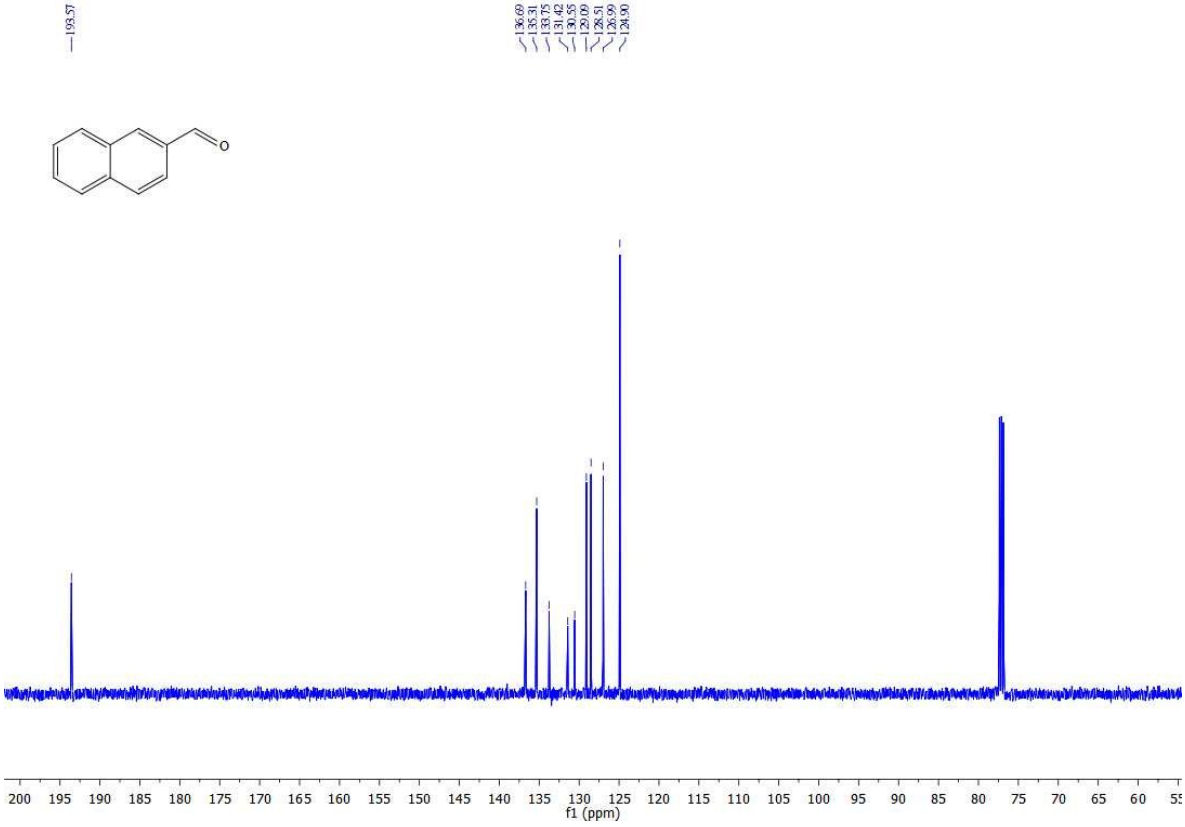
^{1}H NMR spectra of **24** (500 MHz, $CDCl_3$)



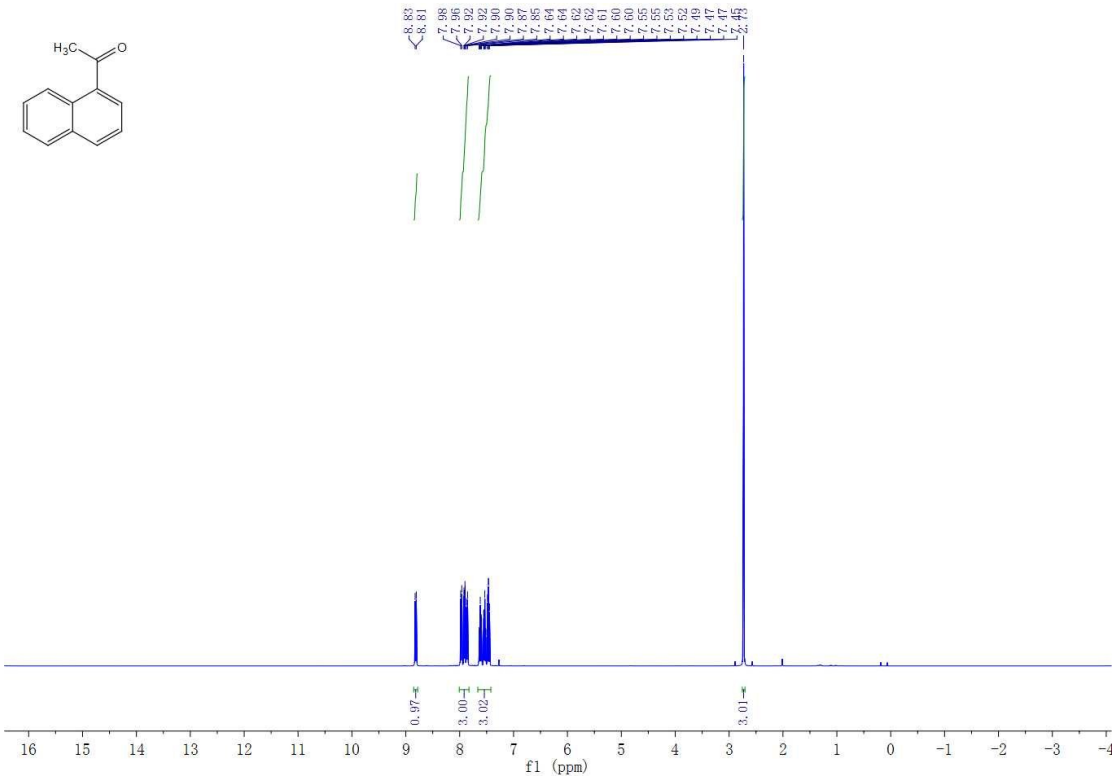
^{13}C NMR spectra of **24** (125 MHz, $CDCl_3$)



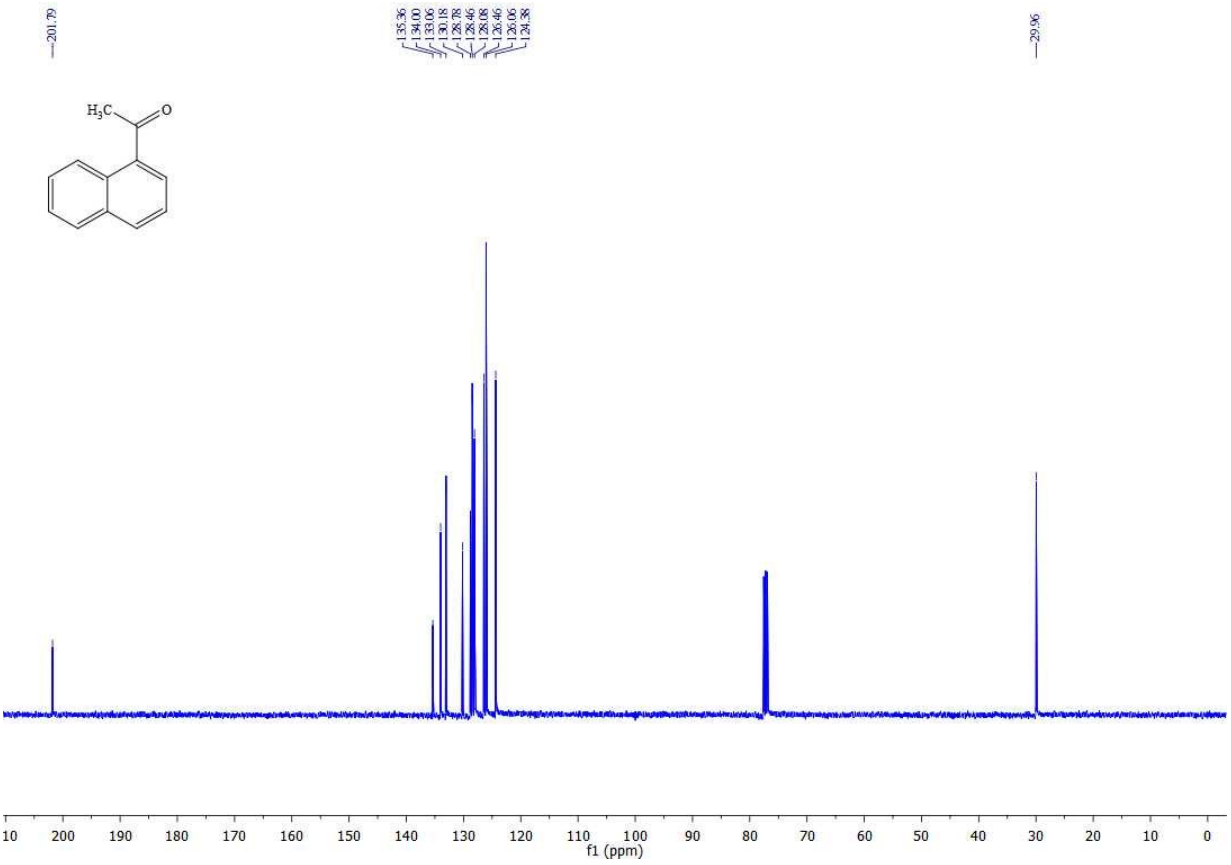
^{1}H NMR spectra of **25** (500 MHz, $CDCl_3$)



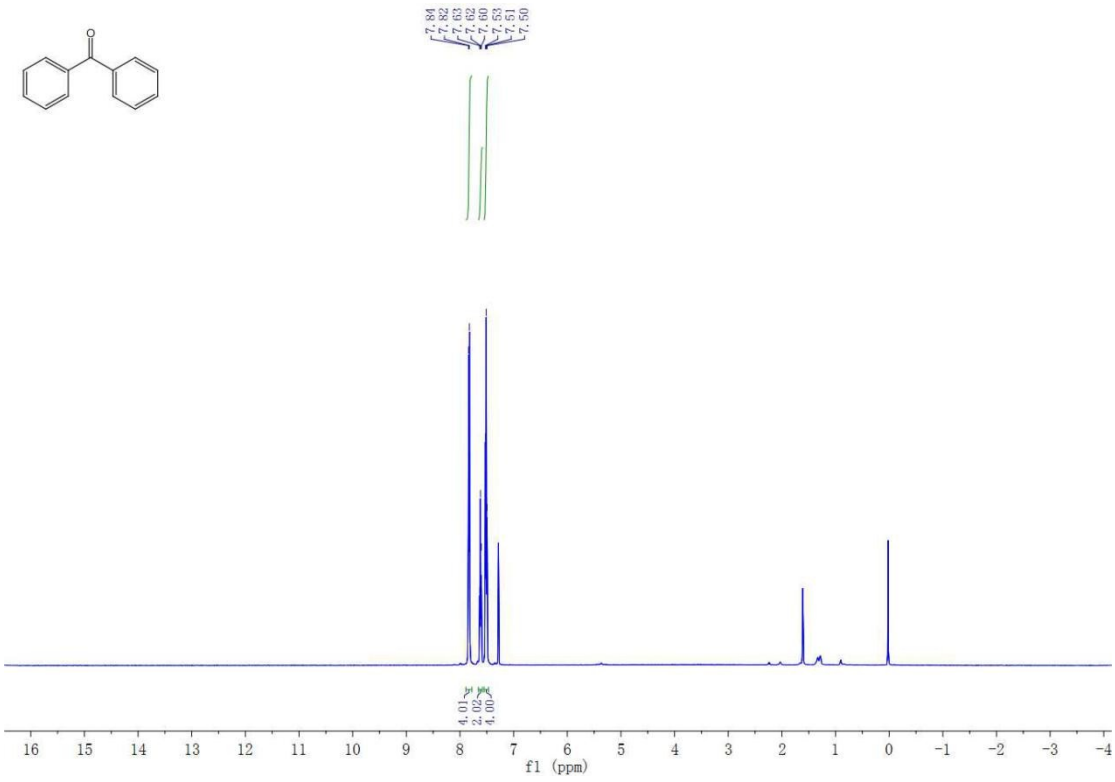
^{13}C NMR spectra of **25** (125 MHz, $CDCl_3$)



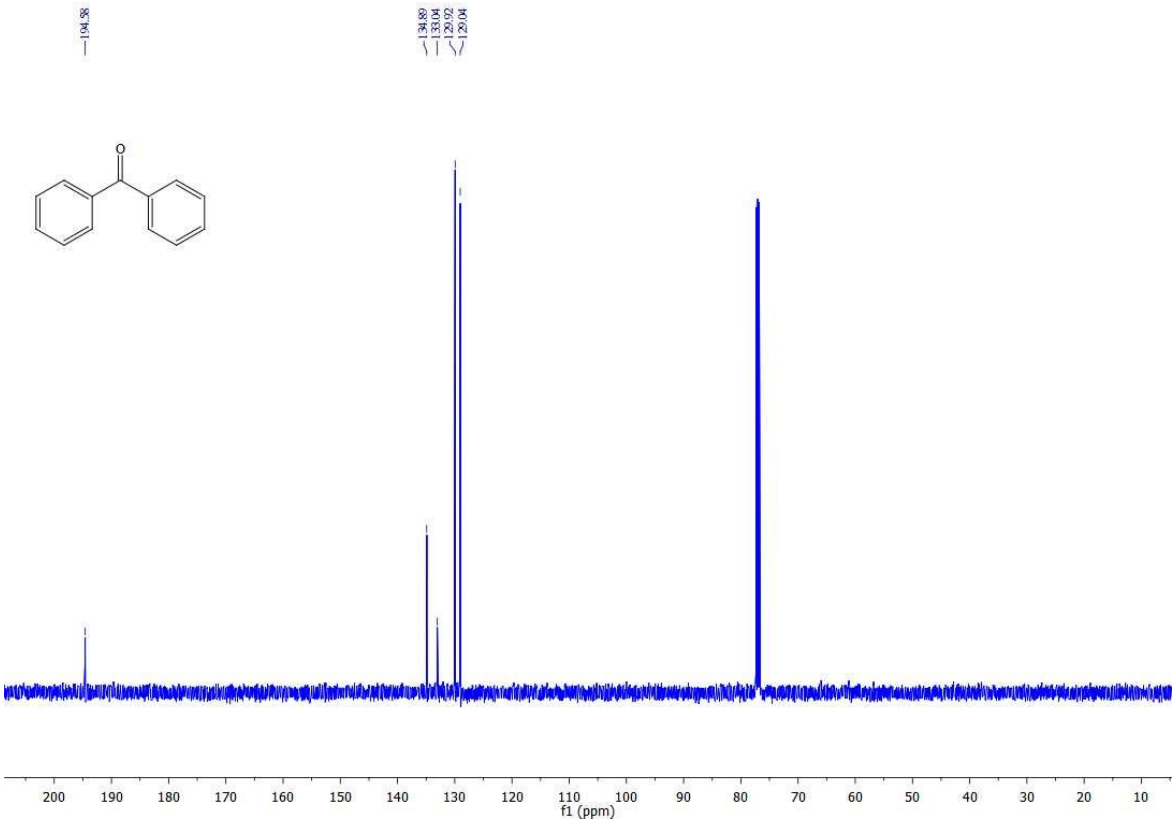
^{1}H NMR spectra of **26** (500 MHz, $CDCl_3$)



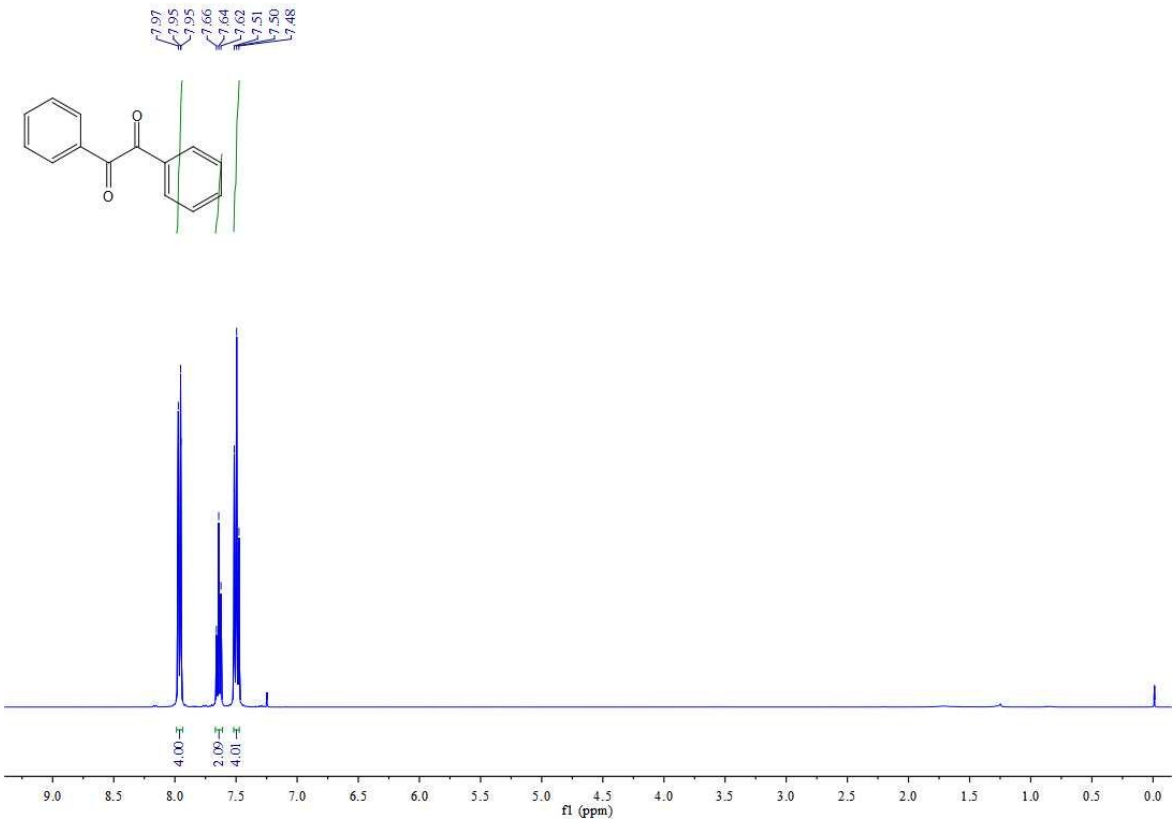
^{13}C NMR spectra of **26** (125 MHz, $CDCl_3$)



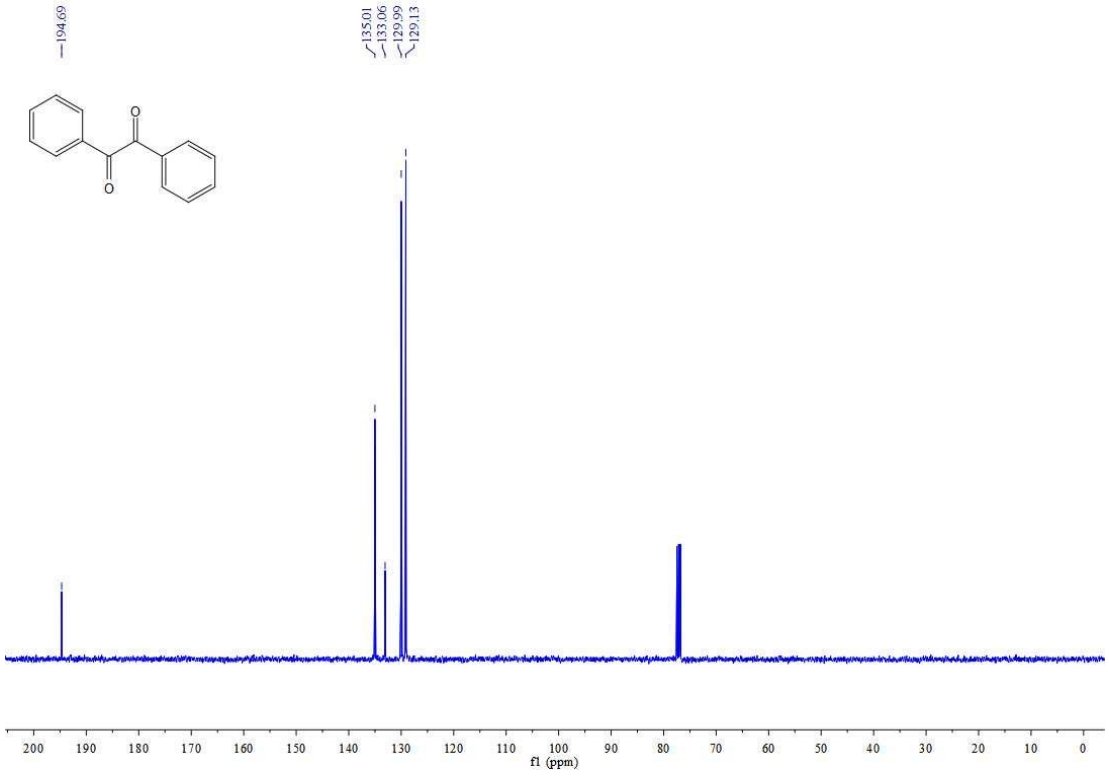
^{1}H NMR spectra of **27** (500 MHz, $CDCl_3$)



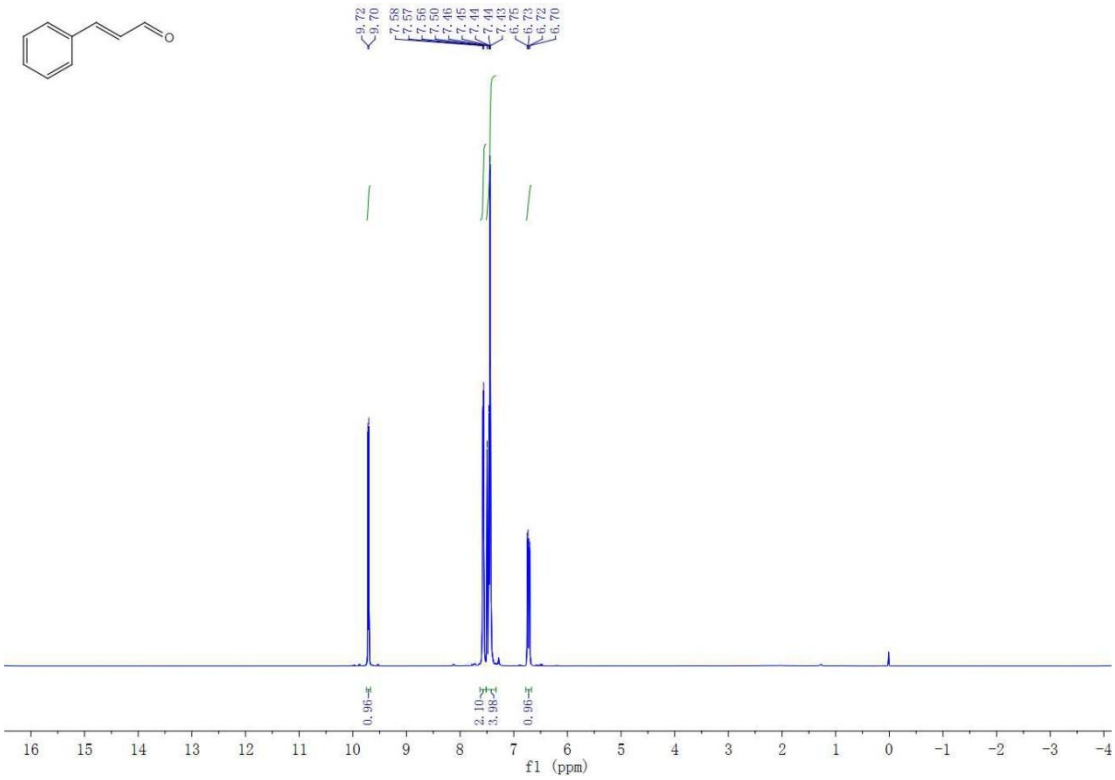
^{13}C NMR spectra of **27** (125 MHz, $CDCl_3$)



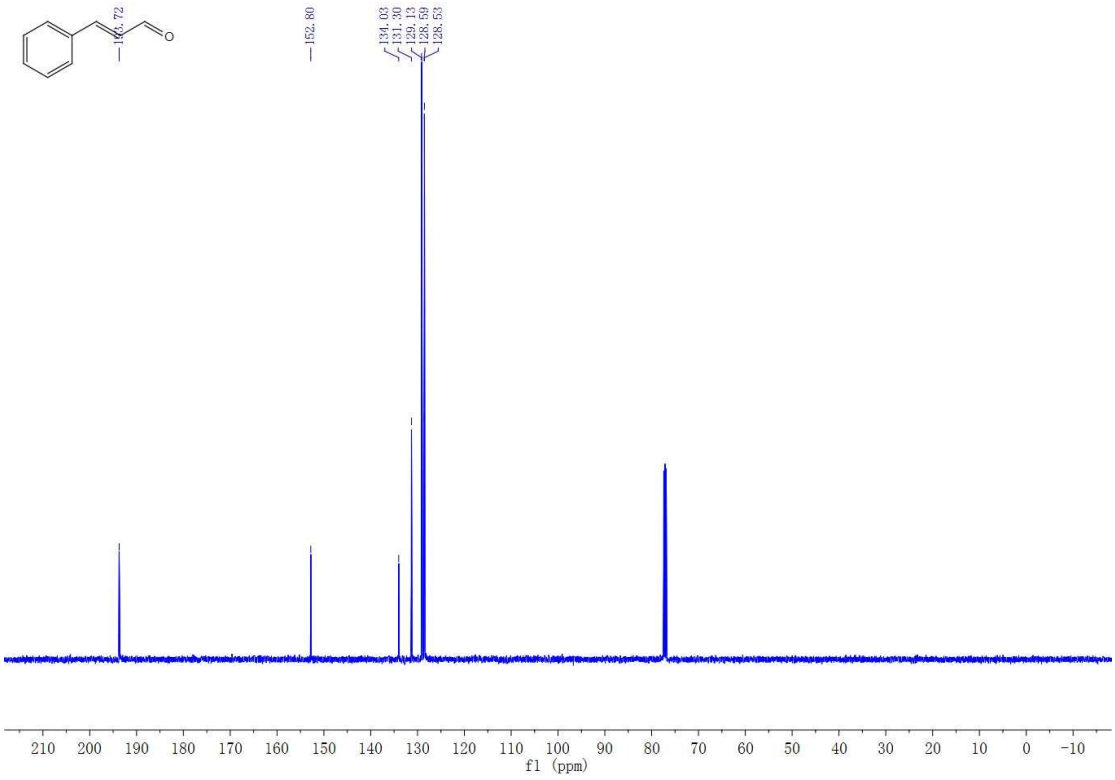
^{1}H NMR spectra of **28** (500 MHz, $CDCl_3$)



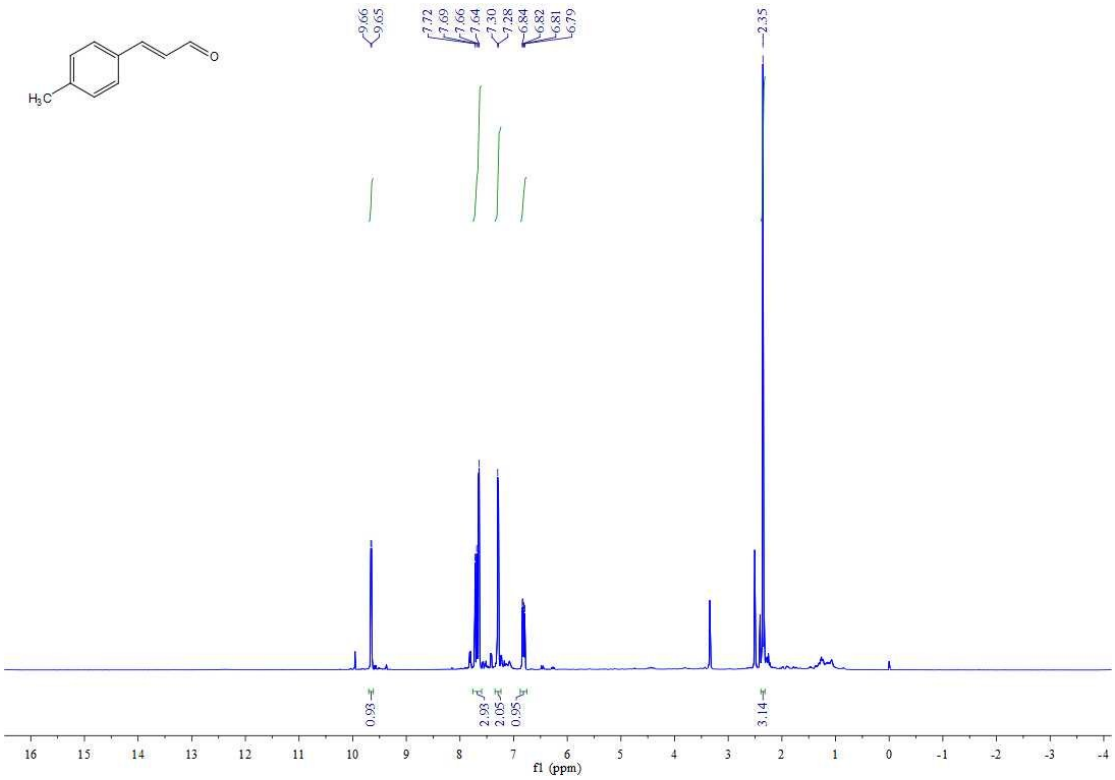
^{13}C NMR spectra of **28** (125 MHz, $CDCl_3$)



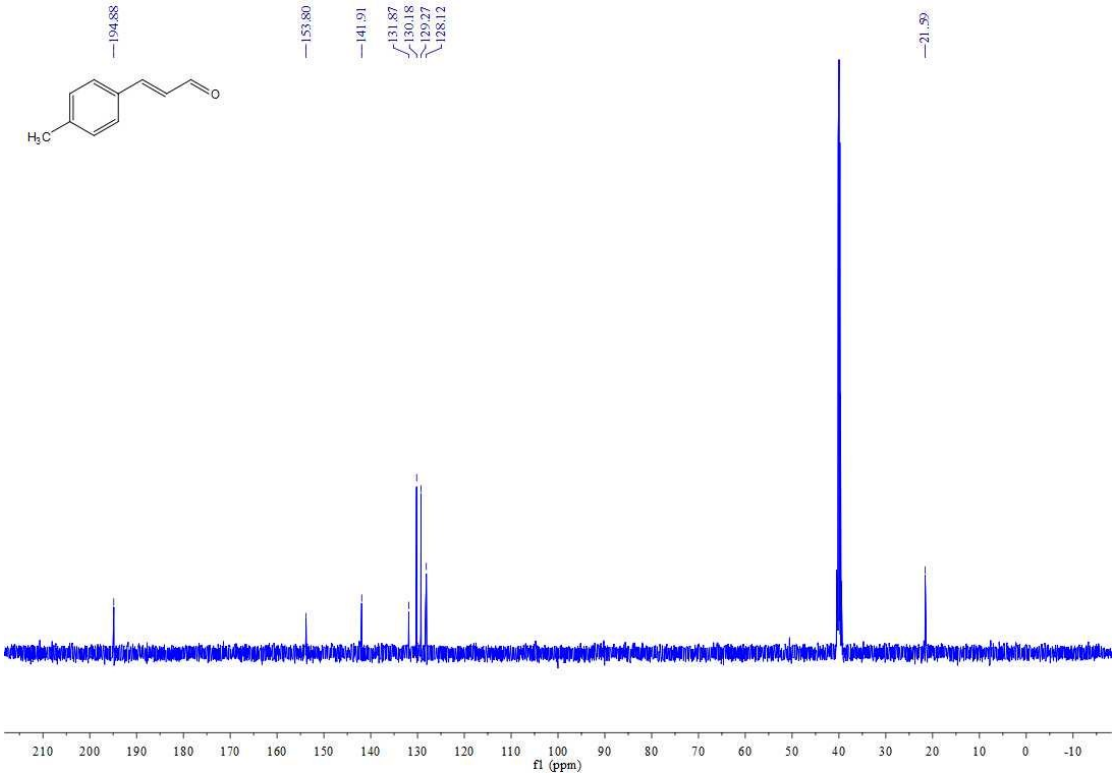
^{1}H NMR spectra of **29** (500 MHz, $CDCl_3$)



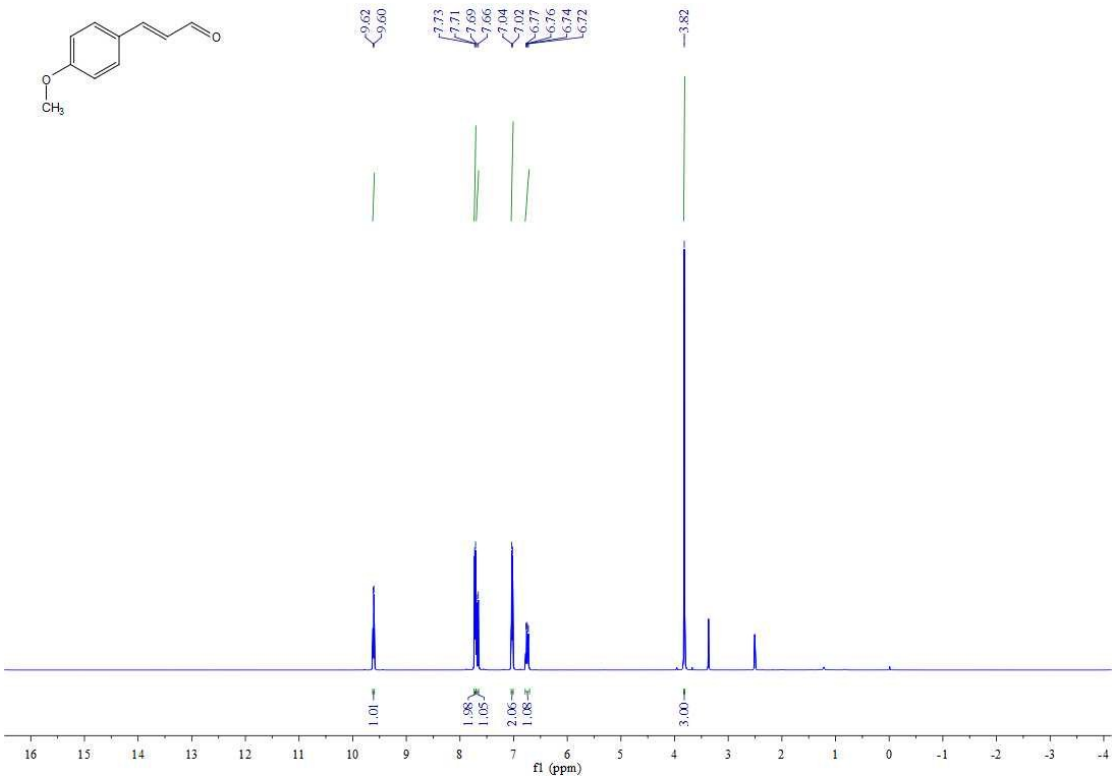
^{13}C NMR spectra of **29** (125 MHz, $CDCl_3$)



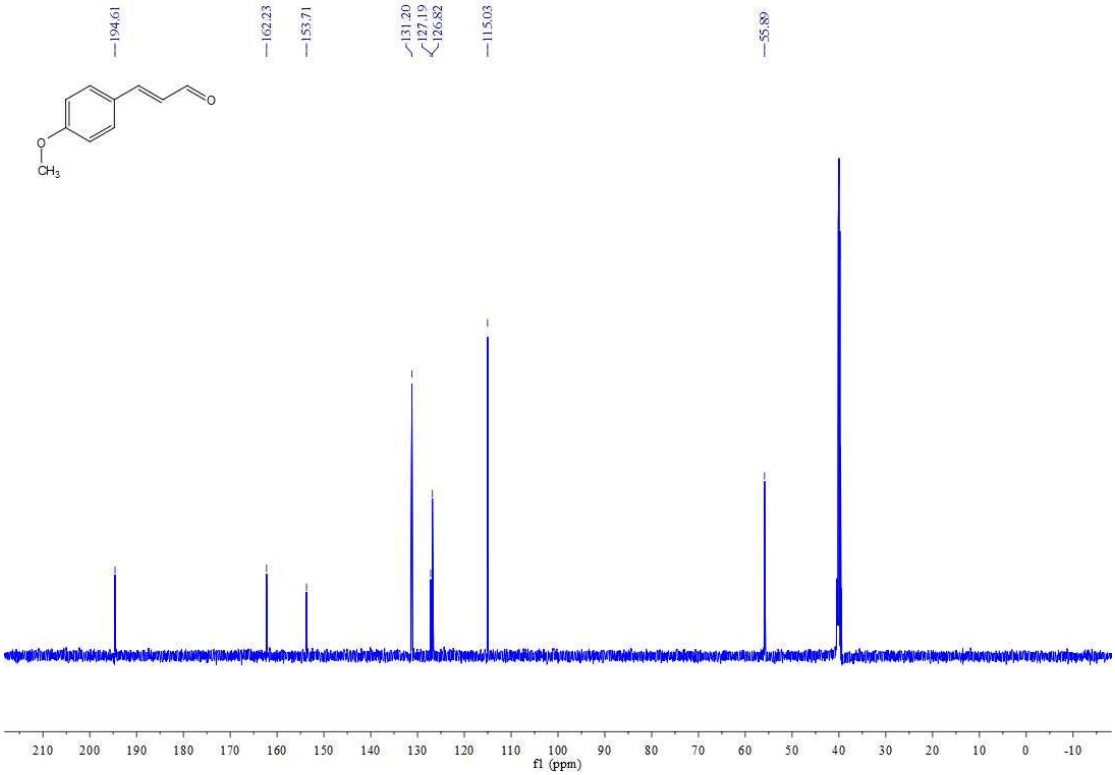
^{1}H NMR spectra of **30** (500 MHz, DMSO)



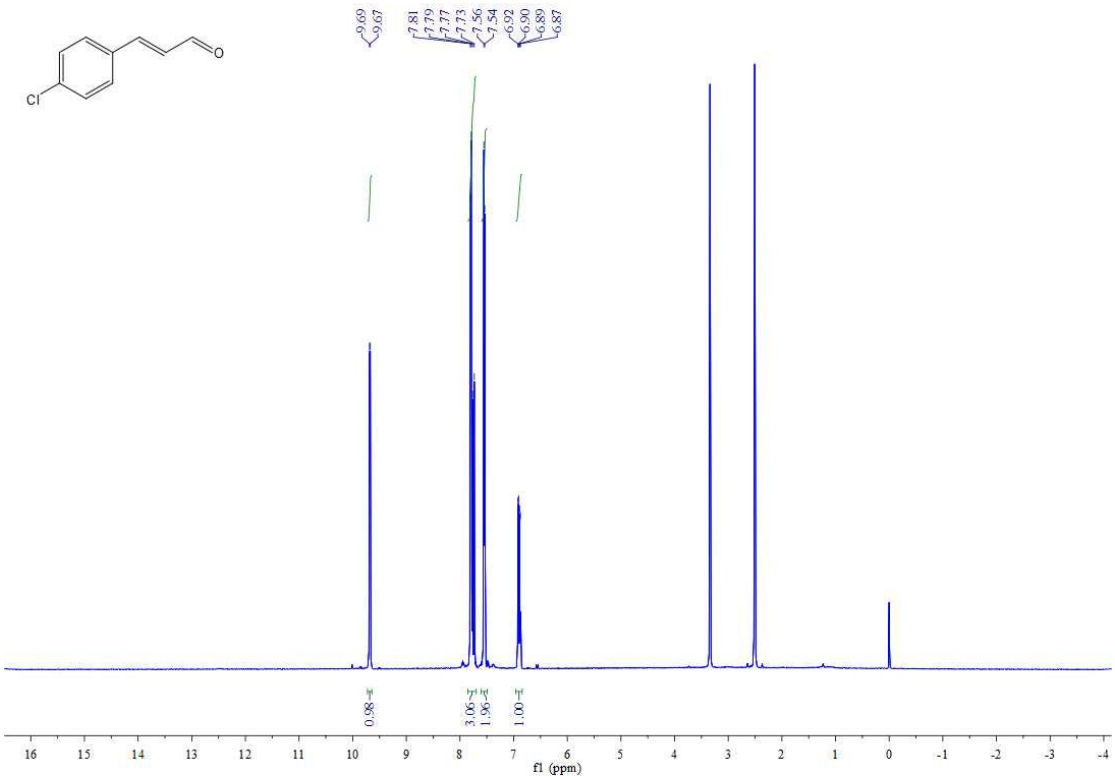
^{13}C NMR spectra of **30** (125 MHz, DMSO)



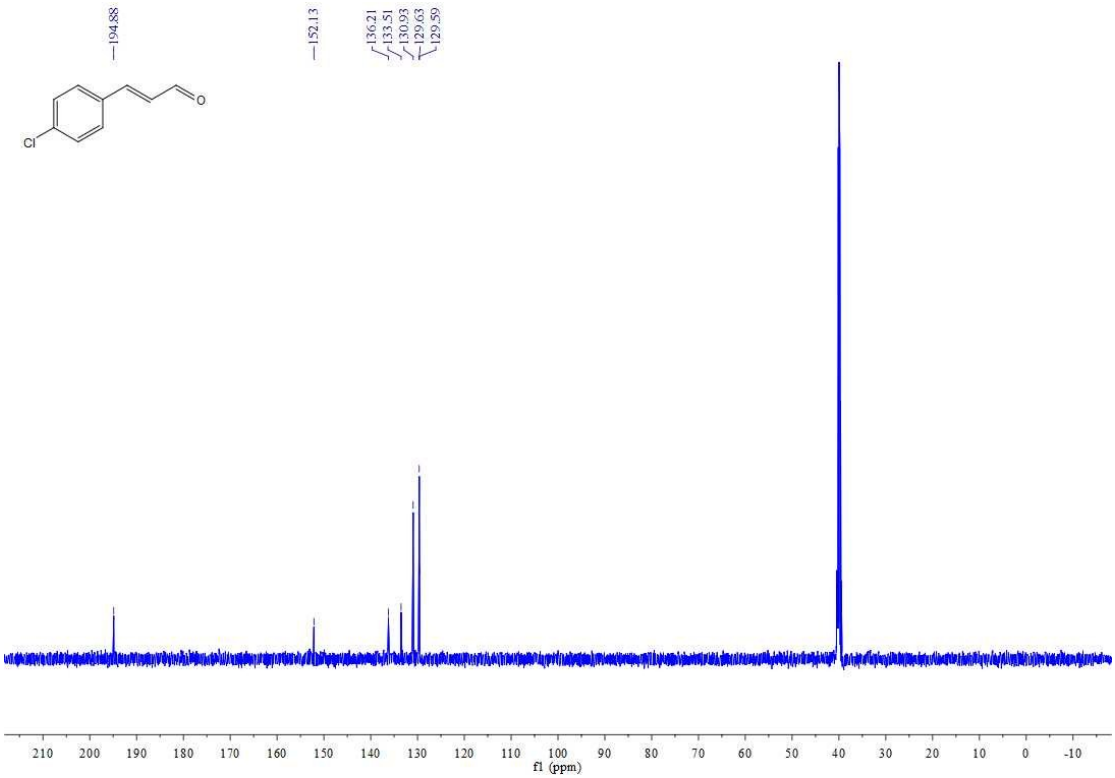
^{1}H NMR spectra of **31** (500 MHz, DMSO)



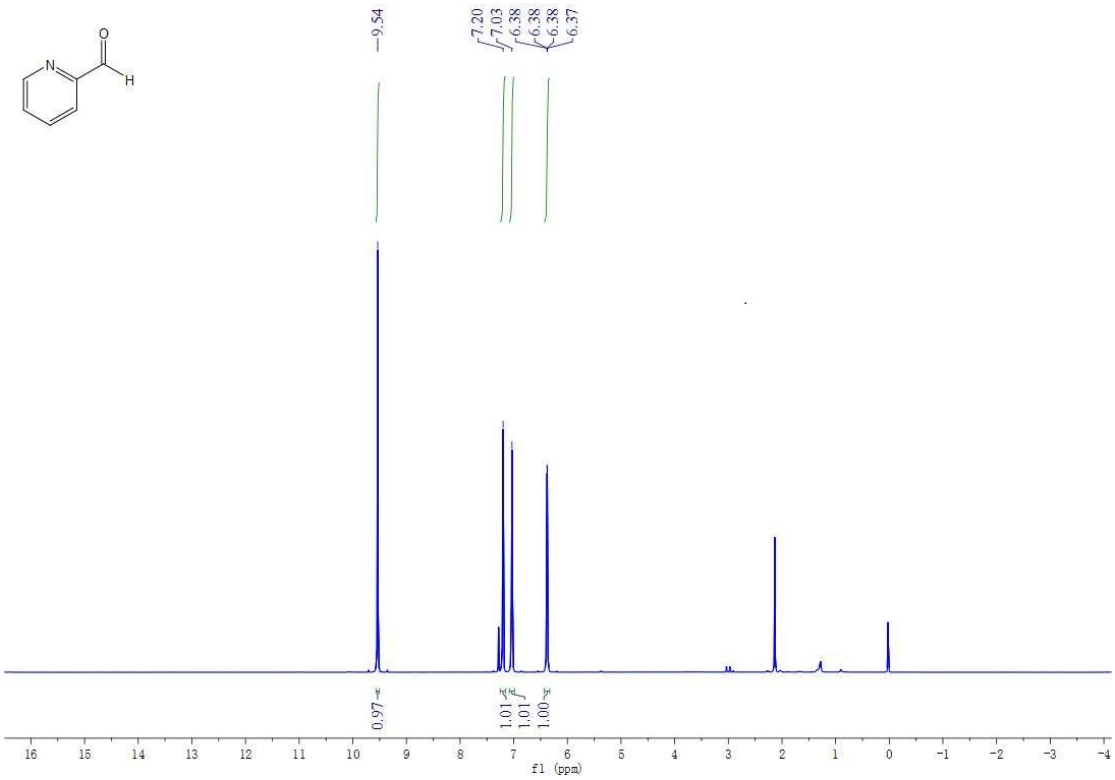
^{13}C NMR spectra of **31** (125 MHz, DMSO)



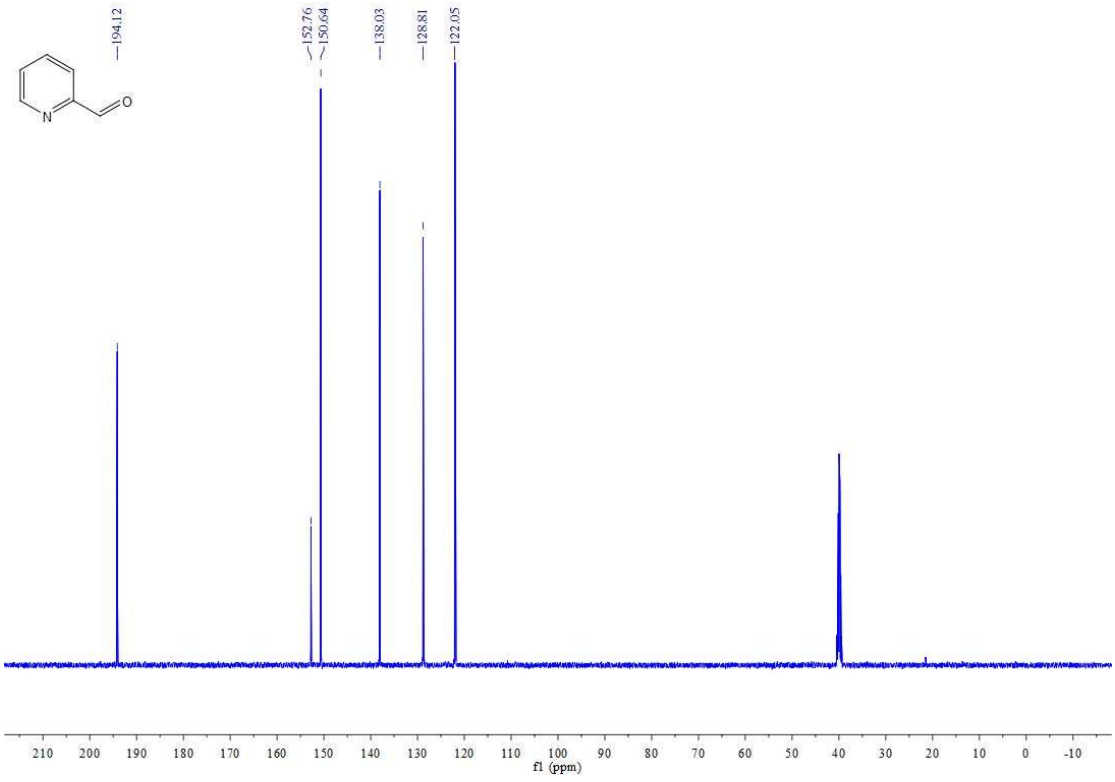
^{1}H NMR spectra of **32** (500 MHz, DMSO)



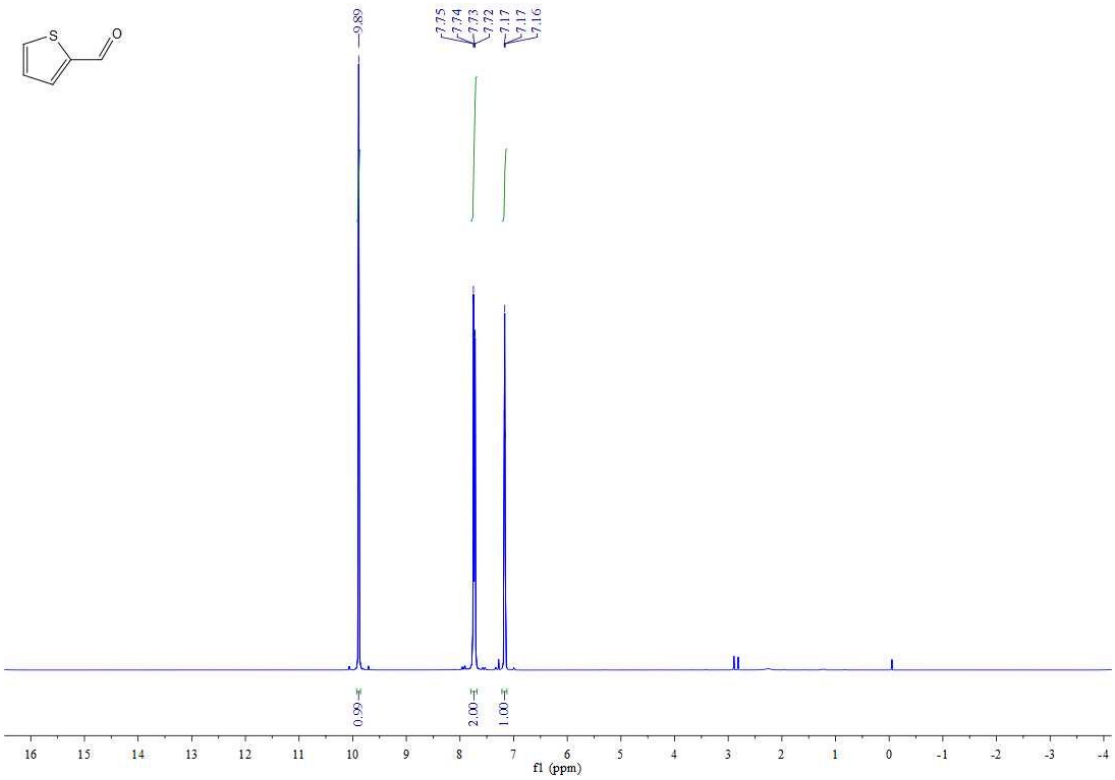
^{13}C NMR spectra of **32** (125 MHz, DMSO)



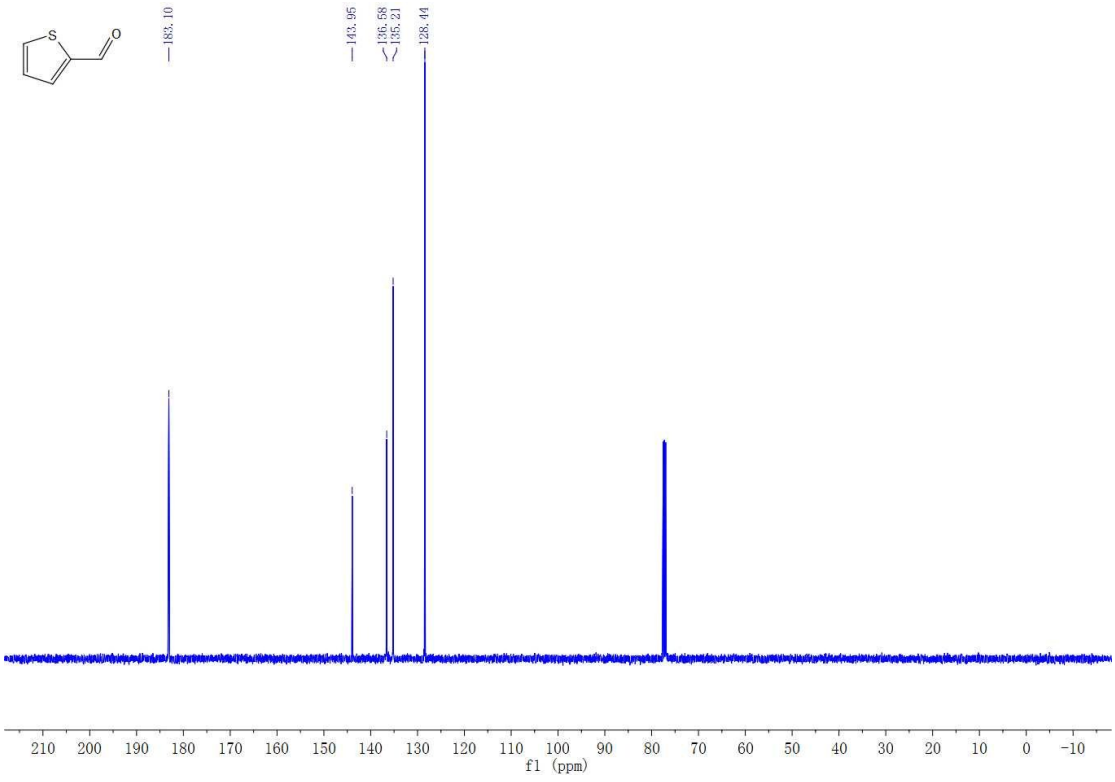
^{1}H NMR spectra of **33** (500 MHz, $CDCl_3$)



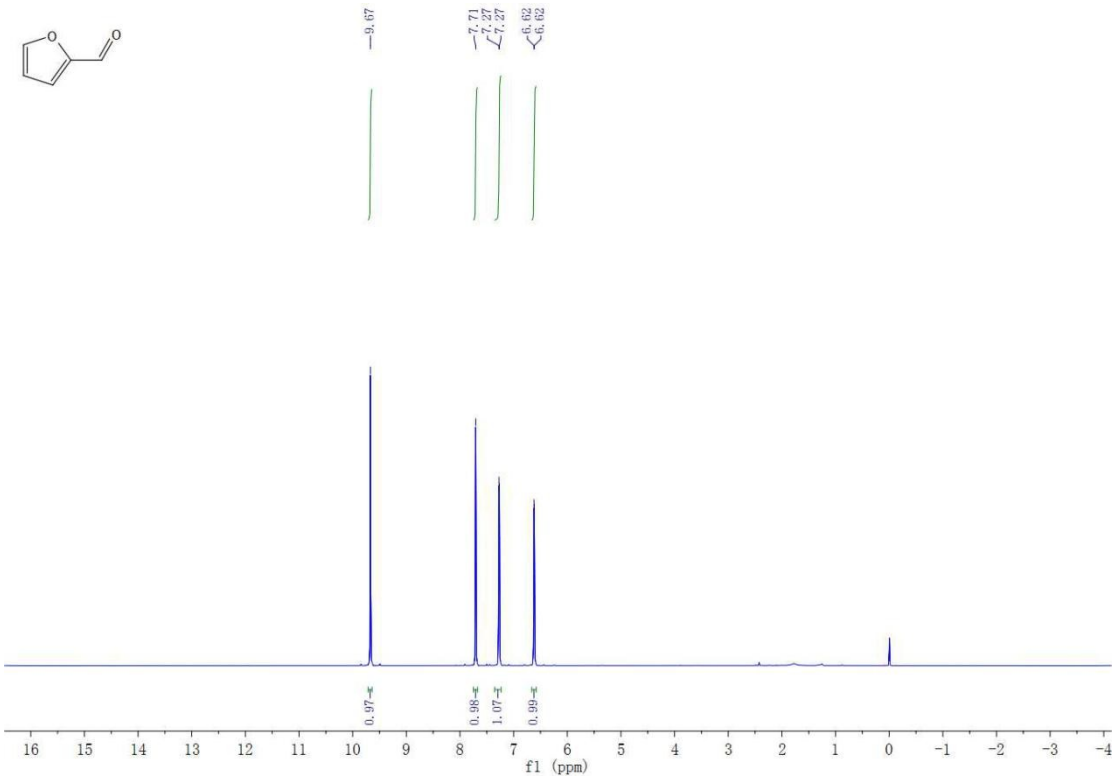
^{13}C NMR spectra of **33** (125 MHz, $CDCl_3$)



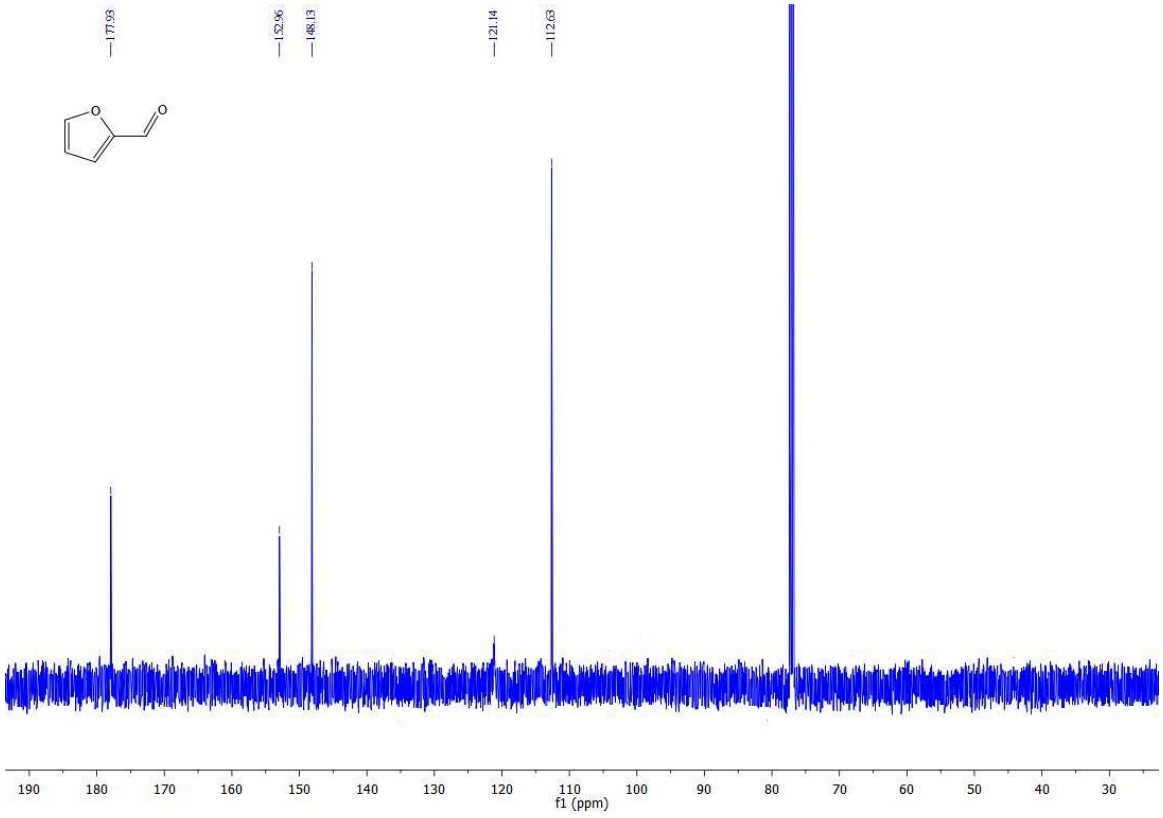
^{1}H NMR spectra of **34** (500 MHz, $CDCl_3$)



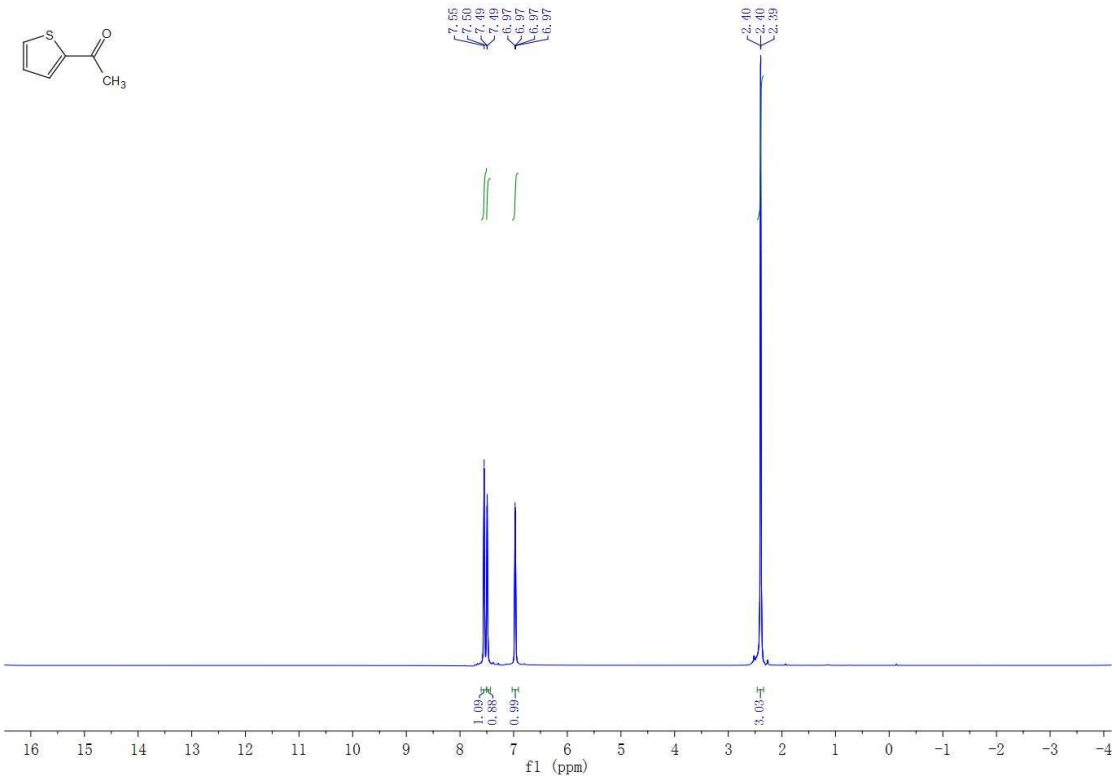
^{13}C NMR spectra of **34** (125 MHz, $CDCl_3$)



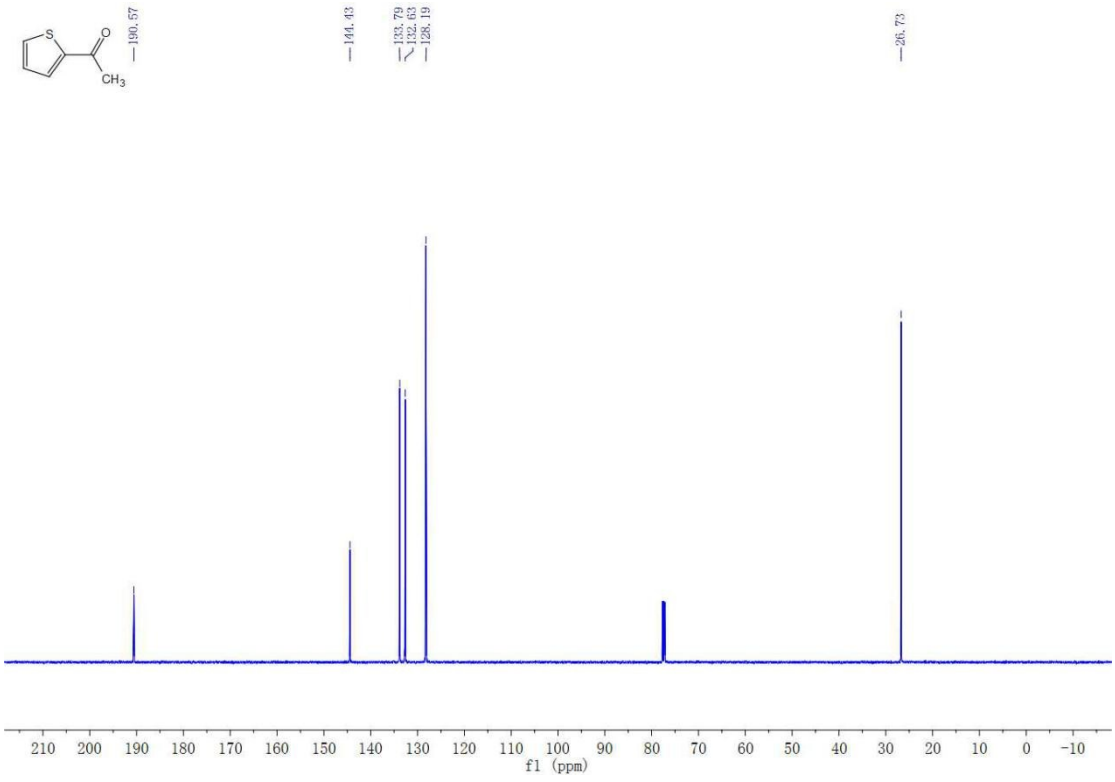
^{1}H NMR spectra of **35** (500 MHz, $CDCl_3$)



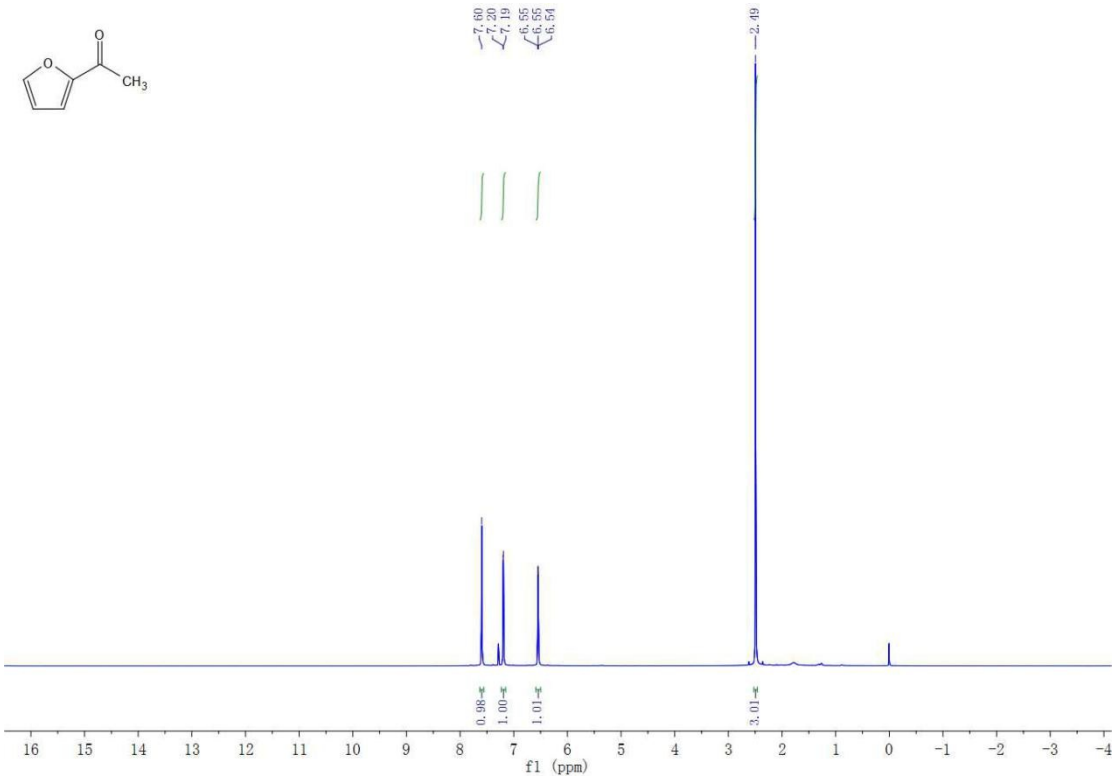
^{13}C NMR spectra of **35** (125 MHz, $CDCl_3$)



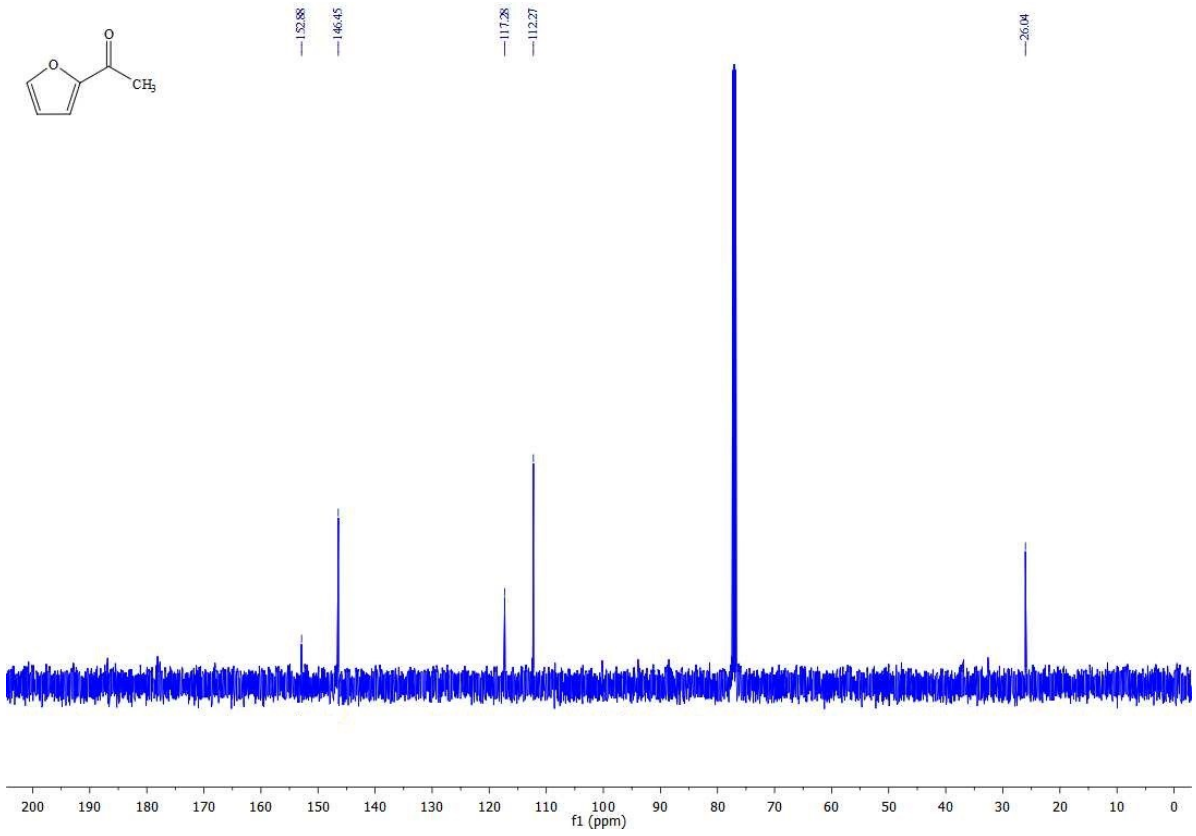
^{1}H NMR spectra of **36** (500 MHz, $CDCl_3$)



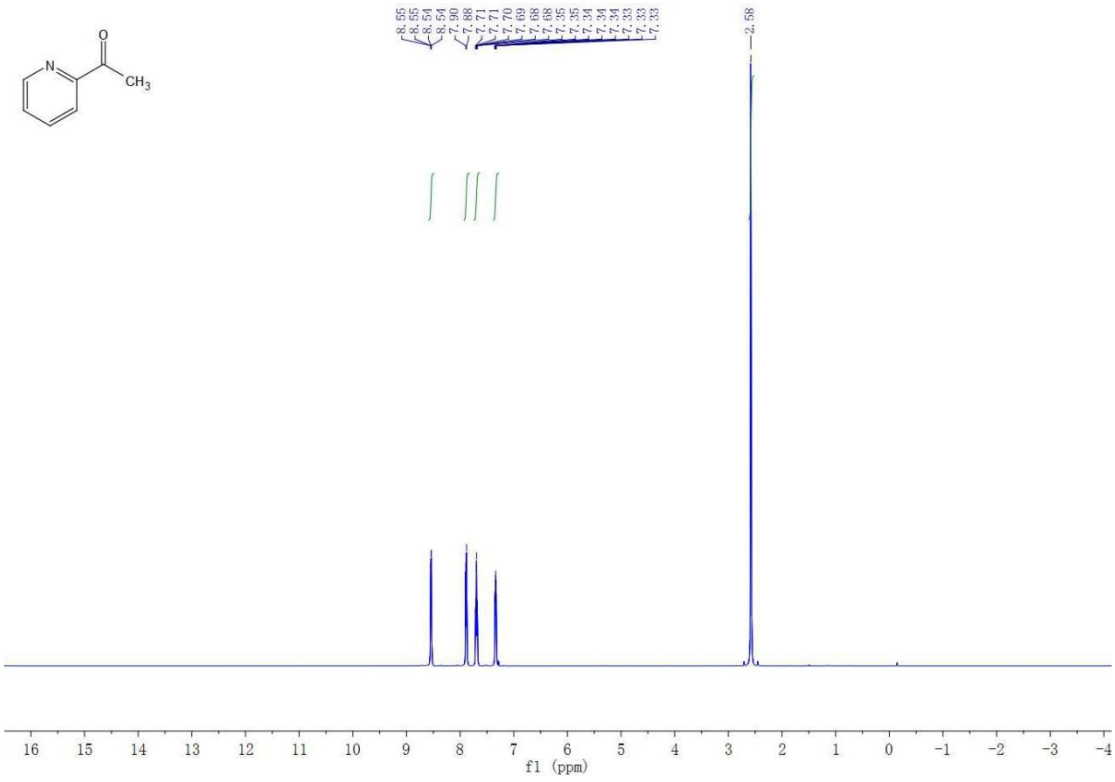
^{13}C NMR spectra of **36** (125 MHz, $CDCl_3$)



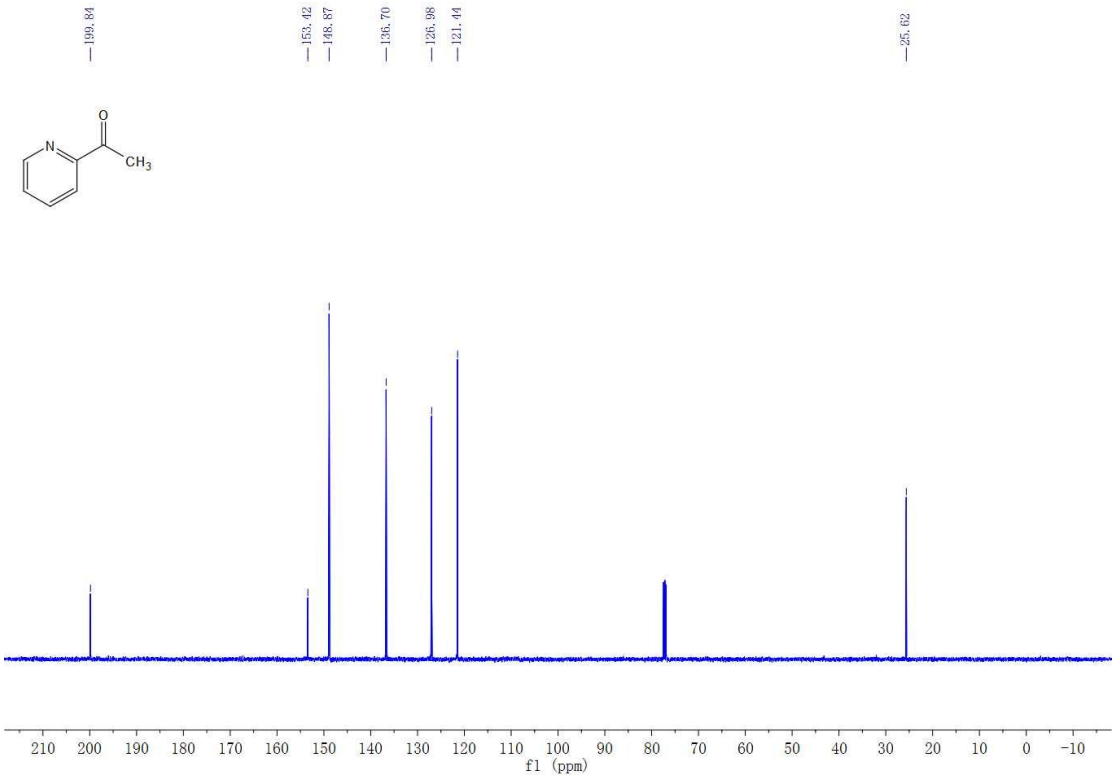
^{1}H NMR spectra of **37** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of **37** (125 MHz, $CDCl_3$)



^{1}H NMR spectra of **38** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of **38** (125 MHz, $CDCl_3$)