Supporting Information

Iron-Catalyzed Oxidative Functionalization of C(sp^3)–H Bonds under Bromide-synergized Mild Conditions

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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 and characterizations of catalyst

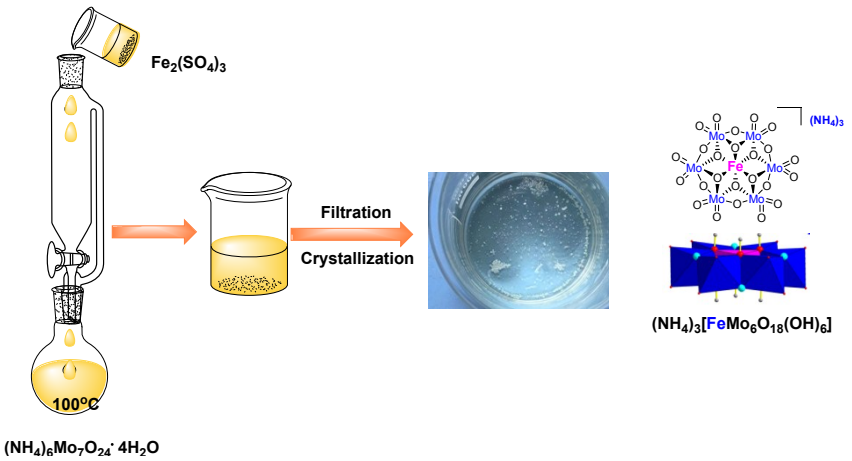


Figure S1. The process of catalyst preparation.

$(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$ was synthesized according to a published procedure[1] with suitable modification: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (15.9 g) was dissolved in water (250 mL) and then heated to 100 °C. $Fe_2(SO_4)_3$ (3.8 g) was dissolved in

water (60mL), which was slowly added in the solution with stirring. The pH value of mixed solution was kept to about 2.5~3.0. The mixture was still being stirred for 1h after complete adding, and then the crude ammonium salt filtrate obtained from the hot solution. The brown block crystals were filtered off after the filtrate stewed for 12h at room temperature. The colourless aim product (11.8 g) was collected after recrystallized in hot water (80 ^{o}C) for two times. IR: 3165 (ν_{as}NH, m), 1640.57 (δOH m), 1400.95 (δNH, s), 946.05(ν Mo=O, vs), 845.10(ν Mo=O, vs), 649.37 (ν Mo-O-Mo, vs), 574.83 (νM-O-Mo, w) cm^{-1}.

III. FT-IR and XRD spectra of catalysts 1

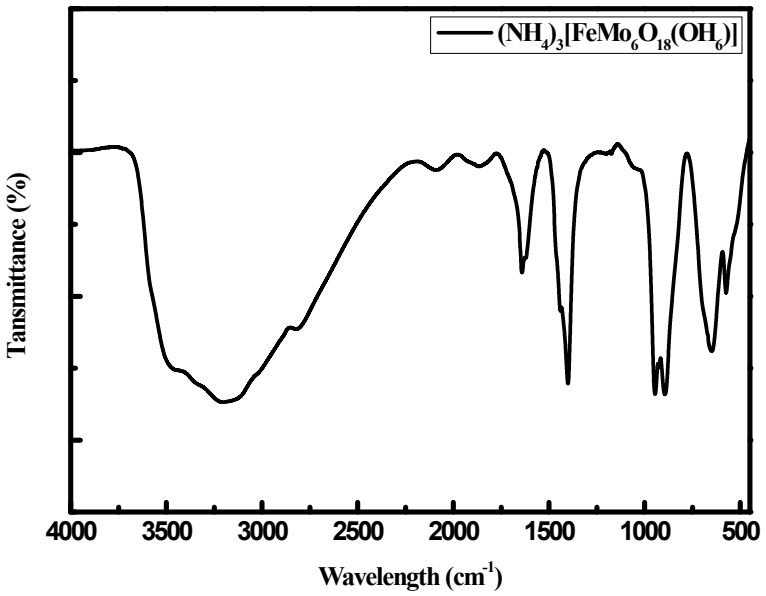


Figure S2. The FTIR spectra of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$.

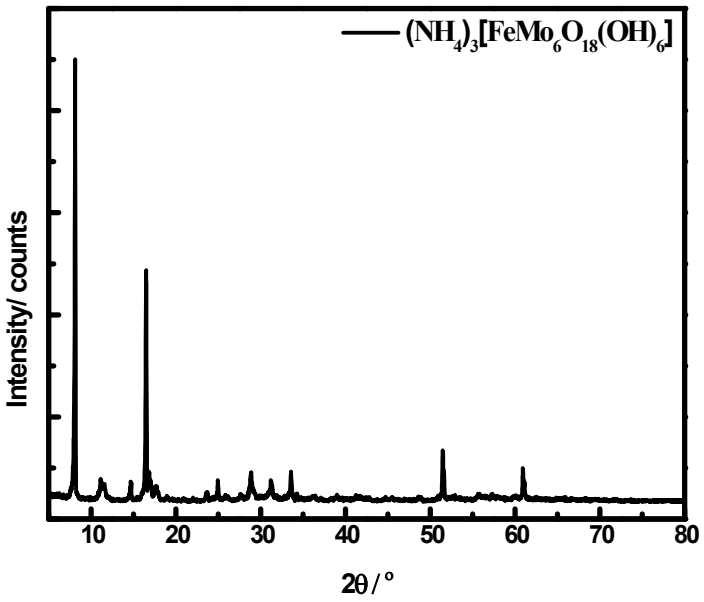


Figure S3. The XRD spectra of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$.

IV. General procedure for catalytic oxidative activation of C-H bonds

Methods Method A. The Cat. **1** (0.3 mol%), aromatic ethylbenzene (1.0 mmol), 30% H_2O_2 (3.5 equiv.) and TBAB (0.05 equiv.) were added into 0.6 mL 1,4-dioxane with stirring at 70 ^oC for 24 h in a tube. Afterwards, a small amount of ethyl acetate was added to the reaction mixture, which was then layered and removed from the water layer. The water layer was evaporated and the catalyst was recycled. Reaction mixture was analyzed by GC-MS analysis. Finally, the solvent was removed in vacuo, and the corresponding ketones was purified by washing through silica gel column. (Petroleum Ether: Ethyl acetate= 20: 1).

Methed B. The Cat. **1** (1.0 mol%)，*N*-heterocyclic 2-benzylpyridine (1.0 mmol), 30% H_2O_2 (4 equiv.) and $BrCH_2CO_2CH_2CH_3$ (0.05 equiv.) were added into 1.0 mL 1,4-dioxane with stirring at 85 ^oC for 24 h in a tube. Afterwards, a small amount of ethyl acetate was added to the reaction mixture, which was then layered and removed from the water layer. The water layer was evaporated and the catalyst was recycled. Reaction mixture was analyzed by GC-MS analysis. Finally, the solvent was removed in vacuo, and the corresponding ketones was purified by washing through silica gel column. (Petroleum Ether: Ethyl acetate= 2: 1).

Method C. The Cat. **1** (1.0 mol%)，aliphatic hexane (1.0 mmol)，50% H_2O_2 (4 equiv.) and TBAB (0.1 equiv.) were added into 1.0 mL 1,4-dioxane/1M HCl (2:1) with stirring at 85 ^oC for 24 h in a tube. Afterwards, a small amount of ethyl acetate was added to the reaction mixture, which was then layered and removed from the water layer. The water layer was evaporated and the catalyst was recycled. Reaction

mixture was analyzed by GC-MS analysis. Finally, the solvent was removed in vacuo, and the corresponding ketones was purified by washing through silica gel column. (Petroleum Ether: Ethyl acetate= 20: 1).

V. Control experiments of the catalytic C(sp^3)-H selective oxidation.

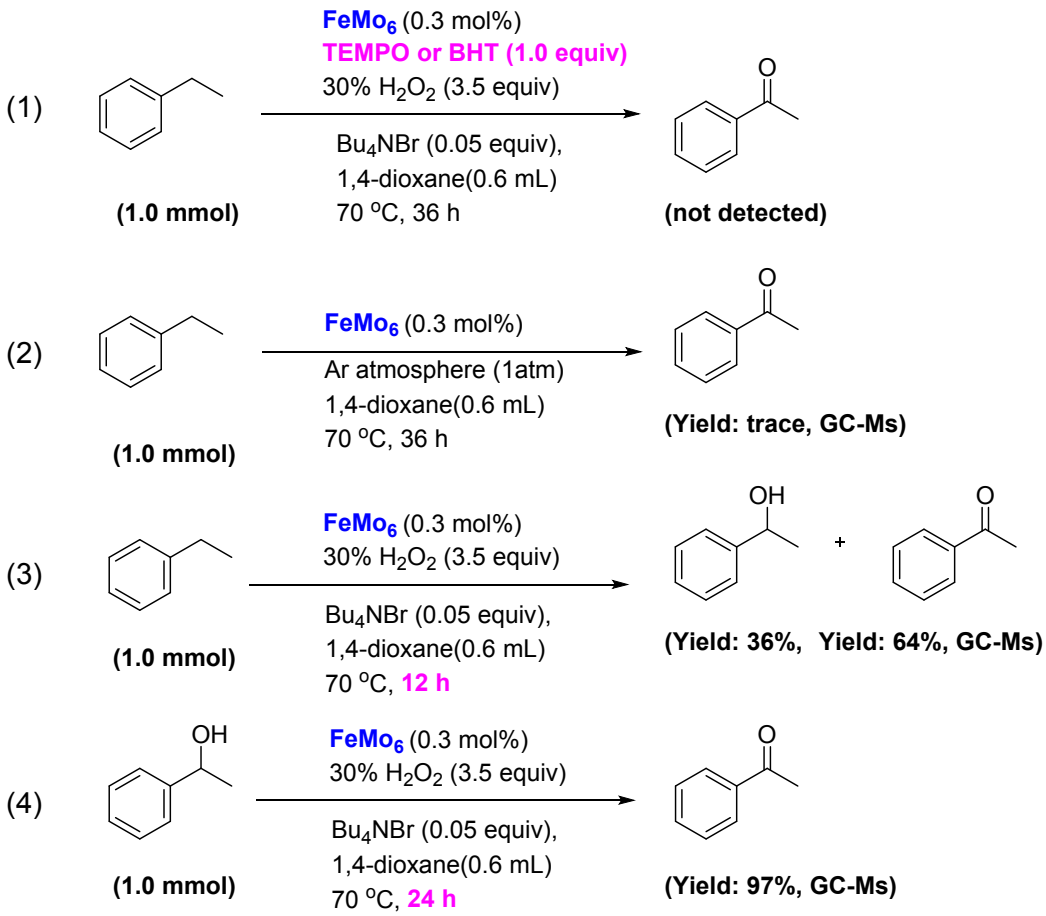


Figure S4. Control experiments using ethyl benzene as the model substrate were performed.

VI. Supplementary methods.

1.Cyclic voltammogram. Cyclic voltammograms obtained at the glassy carbon electrode and a 1.0 mM acetonitrile solution of the $FeMo_6$ in the presence of increasing amounts of TBAB at sweep rates of 100 mV s^{-1}.

2.Preparation of the crystals of $FeMo_6{\cdot}Br_2$. Single crystals of Bromide ion/ POM complex $FeMo_6{\cdot}Br_2$ were obtained by evaporation of an aquous solution of $[(C_4H_9)_4N]_3[FeMo_6O_{18}(OH)_6]$ (10.0 mmol) with stoichiometric ratio of $[(C_4H_9)_4N]Br$ (200.0 mmol) added.

3.X-ray Crystallography. Single-crystal X-ray diffraction analysis was performed on a Rigaku SuperNova diffractometer at 50 kV and 20 mA, using graphite

monochromatized Mo Kα radiation (λ = 0.71073 Å) at 100 K. Data collection, data reduction, cell refinement, and experimental absorption correction were performed with the software package of CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018). Structures were solved by direct methods and refined against F^2 by full matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically. All calculations were performed using the SHLEX97[6] in Olex2 program package[7]. (CCDC: 1882681) These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

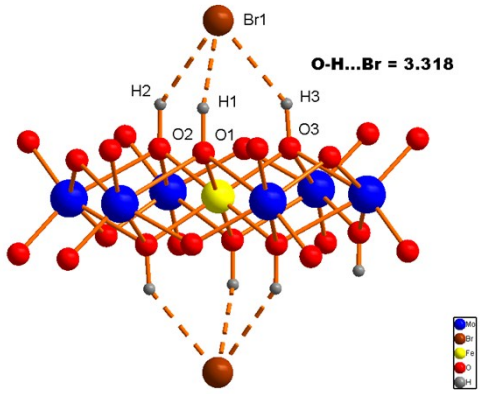


Figure S5. Cluster structure of the bromide ion binded cluster.

Red: O. Brown: Br. Yellow: Fe. Blue: Mo. Gray: H.

Table S1. Crystal data and structure refinement for $FeMo_6$·2Br

Identification code	$FeMo_6Br$
Empirical formula	$C_{64}H_{157}Br_2FeMo_6N_4O_{27}$
Formula weight	2206.24
Temperature/K	114.8(3)
Crystal system	monoclinic
Space group	*P*2/n
a/Å	22.2216(2)
b/Å	18.70299(17)
c/Å	22.4013(2)
α/°	90
β/°	92.7693(8)

γ/°	90
Volume/Å^3	9299.35(14)
Z	4
ρ_{calc}g/cm^3	1.576
μ/mm^{-1}	9.203
F(000)	4532.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.232 to 142.94
Index ranges	-27 ≤ h ≤ 24, -20 ≤ k ≤ 22, -23 ≤ l ≤ 27
Reflections collected	37817
Independent reflections	17662 [R_{int} = 0.0394, R_{sigma} = 0.0483]
Data/restraints/parameters	17662/69/1053
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0433, wR_2 = 0.1098
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1163
Largest diff. peak/hole / e Å^{-3}	1.24/-1.62

Table S2. Hydrogen bonds in $FeMo_6$·2Br.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O1-H1	0.980	2.460	142.55	3.292	Br1 [-x+1, -y, -z]
O13-H13	0.980	2.449	144.05	3.293	Br2
O15-H15	0.980	2.585	138.59	3.383	Br2
O3-H3	0.980	2.470	143.20	3.307	Br1
O2-H2	0.980	2.540	140.60	3.355	Br1 [-x+1, -y, -z]
O14-H14	0.980	2.440	142.95	3.276	Br2 [-x+1, -y+1, -z+1]
O25-H25C	0.850	2.506	172.00	3.349	Br2
O26-H26C	0.850	2.155	147.22	2.906	O23
O26-H26D	0.851	1.991	163.27	2.817	O25
O16-H16	0.850	1.848	177.14	2.697	O25
O6-H6_a	0.850	1.868	176.76	2.717	O28_a

4. Cyclic voltammograms.

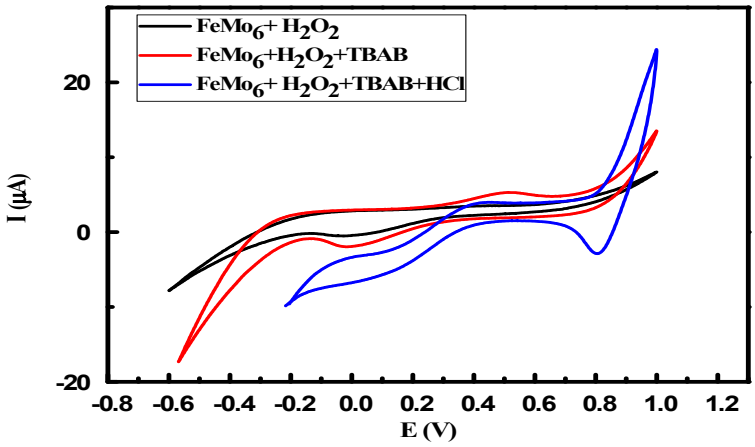


Figure S6. Control experiments.

Cyclic voltammograms (298 K, scan rate 100mV s^{-1}) of a 1.0 mM dioxane/H_2O_2 (2:1) solution of the $FeMo_6$ (black line), a 1.0 mM dioxane/H_2O_2/TBAB (2:1:0.05) solution of the $FeMo_6$ (red line), a 1.0 mM dioxane/H_2O_2/TBAB (2:1:0.05) solution of the $FeMo_6$ drip into the HCl (1M) (blue line).

5. Procedure for catalyst recycling:

The Cat. 1 was separated by centrifugation, washed in turn with water, acetone and ethyl acetate. Then, the dried catalyst was reused without any further purification. Finally, the recycled catalyst was characterized by FTIR (Figure 7) and XRD (Figure 8). The reaction conditions are the same as those of entry 30 in Table 1.

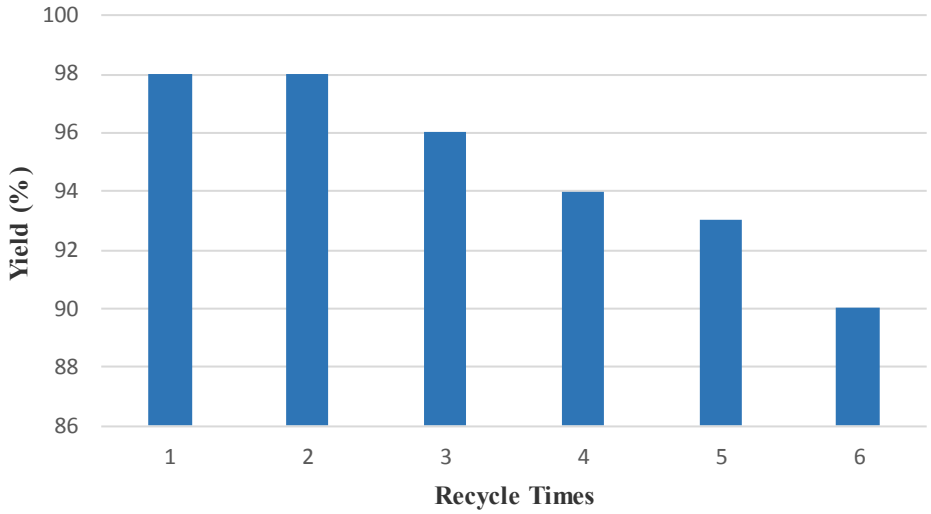


Figure S7. Recycling of iron catalyst for oxidative activation of C-H bonds.

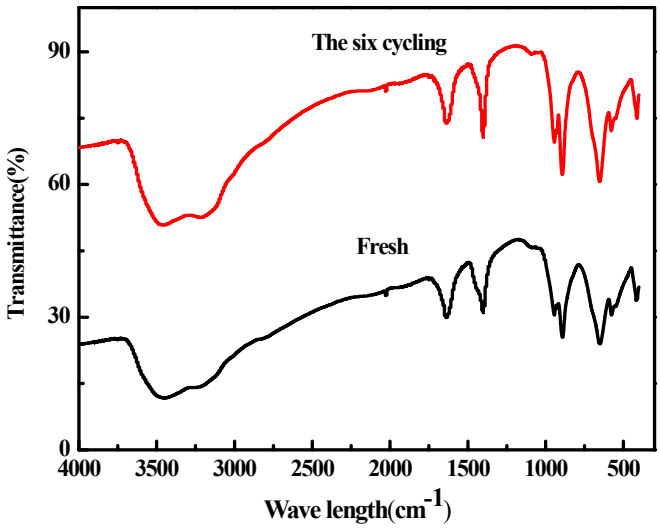


Figure S8. The FTIR spectra of the catalyst before and after the sixth reaction.

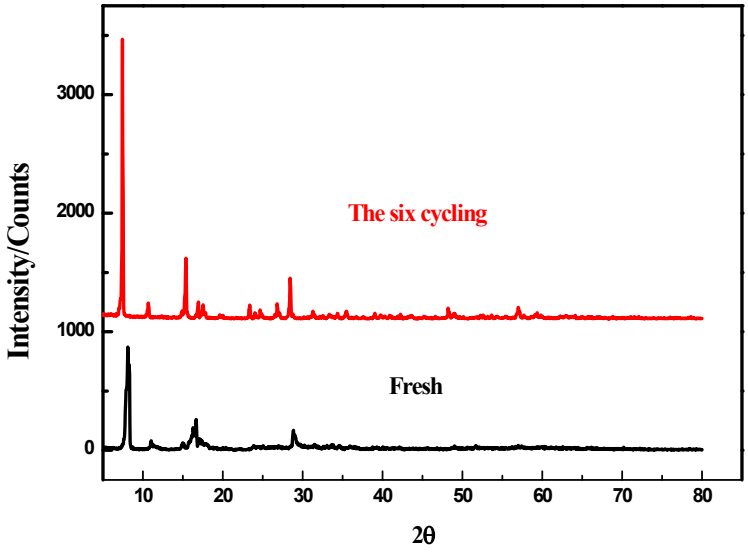
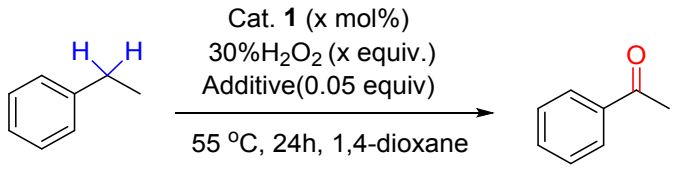


Figure S9. XRD of recycled Cat. 1

VII. Optimization of reaction conditions

Table S3. Reaction optimization of the C(sp3)-H oxidation of ethylbenzene with catalyst 1[a,b]

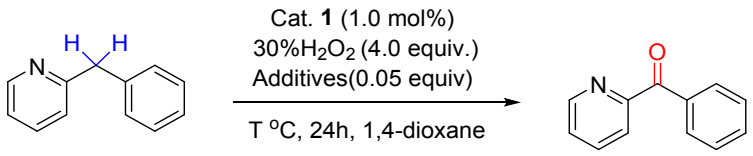


Entry	Catalyst (mol%)	Oxidant [equiv]	Additive [equiv]	Solvent (0.6 mL)	Yield[%]
1	0.3	H_2O_2(2.0)	-	1,4-dioxane	41
2	0.3	H_2O_2(2.0)	KCl	1,4-dioxane	43
3	0.3	H_2O_2(2.0)	$ZnCl_2$	1,4-dioxane	42
4	0.3	H_2O_2(2.0)	NH_4Cl	1,4-dioxane	41
5	0.3	H_2O_2(2.0)	NaCl	1,4-dioxane	44
6	0.3	H_2O_2(2.0)	NaBr	1,4-dioxane	50
7	0.3	H_2O_2(2.0)	NH_4Br	1,4-dioxane	51
8	0.3	H_2O_2(2.0)	KBr	1,4-dioxane	53
9	**0.3**	**H_2O_2(2.0)**	**TBAB**	**1,4-dioxane**	**69**
10	0.3	H_2O_2(2.0)	TBAB(1.0)	1,4-dioxane	55
11	0.3	H_2O_2(2.0)	TBAB(0.02)	1,4-dioxane	46
12	0.3	H_2O_2(2.0)	TBAB	THF	44
13	0.3	H_2O_2(2.0)	TBAB	acetone	40
14	0.3	H_2O_2(2.0)	TBAB	DMF	23
15	0.3	H_2O_2(2.0)	TBAB	DMSO	24
16	0.3	H_2O_2(2.0)	TBAB	CH_3CN	39
17	0.1	H_2O_2(2.0)	TBAB	1,4-dioxane	23

18	0.2	H_2O_2(2.0)	TBAB	1,4-dioxane	46
19	0.5	H_2O_2(2.0)	TBAB	1,4-dioxane	61
20	$NH_4Mo_7O_{24}{\cdot}4H_2O$ (0.3)	H_2O_2(2.0)	TBAB	1,4-dioxane	23
21	$Fe_2(SO_4)_3$ (0.3)	H_2O_2(2.0)	TBAB	1,4-dioxane	30
22[c]	0.3	H_2O_2(2.0)	TBAB	1,4-dioxane	59
23[d]	0.3	H_2O_2(2.0)	TBAB	1,4-dioxane	68
24	0.3	H_2O_2(1.5)	TBAB	1,4-dioxane	54
25	0.3	H_2O_2(2.5)	TBAB	1,4-dioxane	72
26	0.3	H_2O_2(3.5)	TBAB	1,4-dioxane	76
27	0.3	H_2O_2(4.0)	TBAB	1,4-dioxane	73
28[e]	0.3	H_2O_2(3.5)	TBAB	1,4-dioxane	82
29[f]	0.3	H_2O_2(3.5)	TBAB	1,4-dioxane	90
30[g]	**0.3**	H_2O_2(3.5)	**TBAB**	**1,4-dioxane**	**98**
31[h]	0.3	H_2O_2(3.5)	TBAB	1,4-dioxane	92
32	0.3	O_2(1.0bar)	TBAB	1,4-dioxane	23

[a]Reaction conditions: Cat. 1 (x mol%), substrate (1.0 mmol), 30%H_2O_2 (x equiv), 1,4-dioxane (0.6 mL), additive (0.05 equiv.) at 55 ^oC for 24h.[b]The yield was determined by GC-Ms analysis. TBAB = tetrabutylammonium bromide. [c]12 h. [d]30 h. [e]60 ^oC. [f]65 ^oC. [g]70 ^oC. [h]75 ^oC.

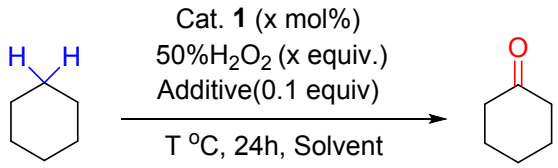
Table S4. Reaction optimization of the C(sp3)-H oxidation of 2-benzylpyridine with catalyst 1[a,b]



Entry	Catalyst (mol%)	Additive [equiv]	oxidant [equiv]	T [°C]	Yield [%]
1	0.3	TBAB	H_2O_2(4.0)	80	10
2	0.3	$ClCH_2CO_2CH_2CH_3$	H_2O_2(4.0)	80	22
3	0.3	$BrCH_2CO_2CH_2CH_3$	H_2O_2(4.0)	80	27
4	0.3	$BrCH_2CO_2CH_2CH_3$(0.1)	H_2O_2(4.0)	80	18
5	0.6	$BrCH_2CO_2CH_2CH_3$	H_2O_2(4.0)	80	40
6	1.0	$BrCH_2CO_2CH_2CH_3$	H_2O_2(4.0)	80	70
7	**1.0**	**$BrCH_2CO_2CH_2CH_3$**	**H_2O_2(4.0)**	**85**	**92**
8	1.0	$BrCH_2CO_2CH_2CH_3$	H_2O_2(3.0)	85	76
9	1.0	$BrCH_2CO_2CH_2CH_3$	H_2O_2(5.0)	85	80
9	1.0	$BrCH_2CO_2CH_2CH_3$	O_2(1.0 bar)	85	17

[a]Reaction conditions: Cat. **1** (x mol%), (1.0 mmol), 1,4-dioxane (1.0 mL), 30%H_2O_2 (x equiv), TBAB (0.05 equiv.) at T °C for 24h. [b]The yield was determined by GC-MS analysis. TBAB = tetrabutylammonium bromide.

Table S5. Reaction optimization of the C(sp3)-H oxidation of cyclohexane with catalyst 1[a,b]



Entry	Catalyst (mol%)	Additive [equiv]	Solvent (1.0mL)	oxidant [equiv]	T [°C]	Yield [%]
1	1.0	NaBr	1,4-dioxane	H_2O_2(4.0)	80	62
2	1.0	NH_4Br	1,4-dioxane	H_2O_2(4.0)	80	65
3	1.0	KBr	1,4-dioxane	H_2O_2(4.0)	80	61
4	1.0	TBAB	1,4-dioxane	H_2O_2(4.0)	80	68
5	0.5	TBAB	1,4-dioxane	H_2O_2(4.0)	80	47
6	1.5	TBAB	1,4-dioxane	H_2O_2(4.0)	80	67
7	**1.0**	TBAB	CH_3CN	H_2O_2(4.0)	80	35
8	1.0	TBAB	1,4-dioxane/1M HCl(1:1)	H_2O_2(4.0)	80	78
9	1.0	TBAB	1,4-dioxane/1M HCl(2:1)	H_2O_2(4.0)	80	82
10	**1.0**	**TBAB**	**1,4-dioxane/1M HCl(2:1)**	**H_2O_2(4.0)**	**85**	**85**
11	1.0	TBAB	1,4-dioxane/1M HCl(2:1)	H_2O_2(3.0)	85	77
12	1.0	TBAB	1,4-dioxane/1M HCl(2:1)	H_2O_2(5.0)	85	84
13	1.0	TBAB	1,4-dioxane/1M HCl(2:1)	O_2(1.0 bar)	85	10

[a]Reaction conditions: Cat. **1** (x mol%), cyclohexane (1.0 mmol), solvent (1.0 mL), 50%H_2O_2 (x equiv), TBAB (0.1 equiv.) for 24h. [b]The yield was determined by GC-Ms analysis. TBAB = tetrabutylammonium bromide.

VIII. References

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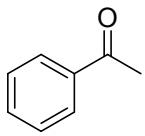
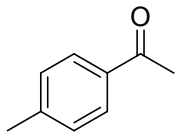
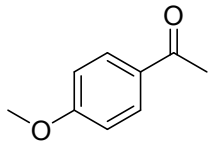
IX. NMR data of products



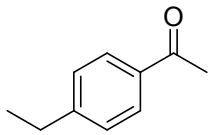
acetophenone(2)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.42 (s, 1H), 7.31 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.84, 137.00, 132.99, 128.20, 26.41.



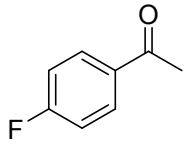
1-(p-tolyl)ethan-1-one(3)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.27 (s, 2H), 2.57 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.98, 143.90, 134.72, 129.25, 128.47, 26.45, 21.59.



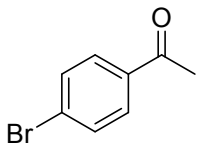
1-(4-methoxyphenyl)ethan-1-one(4)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.95 (s, 2H), 6.95 (s, 2H), 3.89 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.77, 163.52, 130.59, 130.41, 113.70, 55.46, 26.30.



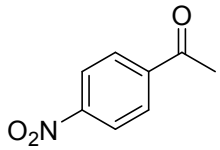
1-(4-ethylphenyl)ethan-1-one(5)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.29 (s, 2H), 2.71 (s, 2H), 2.57 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.87, 150.05, 134.92, 128.55, 128.06, 28.93, 26.51, 15.19.



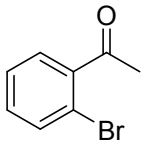
1-(4-fluorophenyl)ethan-1-one(6)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.00 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.25, 166.61, 133.49, 130.87, 115.54, 26.26.



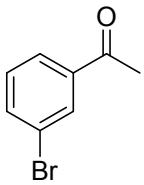
1-(4-bromophenyl)ethan-1-one(7)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.11, 135.81, 131.92, 129.87, 128.34, 26.60.



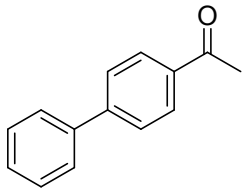
1-(4-nitrophenyl)ethan-1-one(8)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 2.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.38, 150.36, 141.38, 129.34, 123.89, 27.03.



1-(2-bromophenyl)ethan-1-one(9)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.48 (s, 1H), 7.39 (s, 1H), 7.32 (s, 1H), 2.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.33, 141.54, 133.86, 131.77, 128.91, 127.44, 118.92, 30.31.

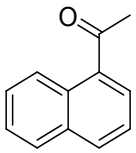


1-(3-bromophenyl)ethan-1-one(10)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.94 (s, 1H), 7.76 (s, 1H), 7.42 (s, 1H), 2.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.65, 138.89, 136.01, 131.45, 130.25, 126.90, 123.03, 26.63.

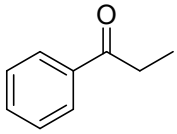


1-([1,1'-biphenyl]-4-yl)ethan-1-one(11)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.68 (d, *J* = 35.8 Hz, 4H), 7.46 (d, *J* = 34.7 Hz, 3H), 2.66 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.80, 145.80,

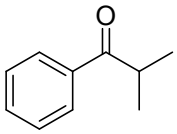
139.88, 135.87, 128.99, 128.27, 127.29, 26.68.



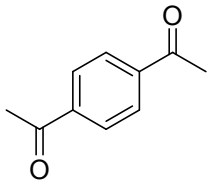
1-(naphthalen-1-yl)ethan-1-one (12)[3-5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81, 7.96, 7.90, 7.85, 7.62, 7.53, 7.47, 2.73. ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.79, 135.36, 134.00, 133.06, 130.18, 128.78, 128.46, 128.08, 126.46, 126.06, 124.38, 29.96.



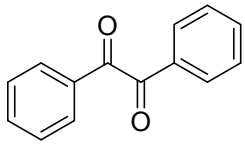
propiophenone(13)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.57 (s, 1H), 7.47 (s, 2H), 3.02 (s, 2H), 1.25 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.84, 136.97, 132.86, 128.55, 127.98, 31.78, 8.25.



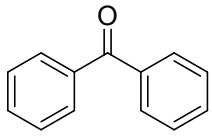
2-methyl-1-phenylpropan-1-one(14)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.57 (s, 1H), 7.48 (s, 2H), 3.58 (s, 1H), 1.23 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.56, 136.23, 132.80, 128.61, 35.37, 19.15.



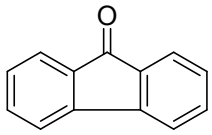
1,1'-(1,4-phenylene)bis(ethan-1-one)(15)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.04 (s, 3H), 2.66 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.62, 140.17, 128.52, 26.90.



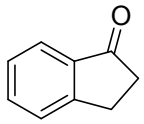
benzil(16)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.00 (d, J = 7.4 Hz, 4H), 7.68 (t, J = 7.4 Hz, 2H), 7.54 (t, J = 7.7 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.58, 134.89, 133.04, 129.92, 129.04.



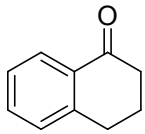
benzophenone(17)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 4H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.79, 137.62, 132.44, 130.08, 128.30.



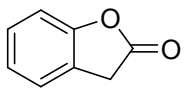
9H-fluoren-9-one(18)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.3 Hz, 2H), 7.49 (dt, *J* = 14.7, 7.2 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.98, 144.43, 134.72, 134.13, 129.09, 124.32, 120.34.



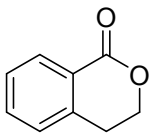
2,3-dihydro-1H-inden-1-one(19)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.61 (s, 1H), 7.51 (s, 1H), 7.39 (s, 1H), 3.17 (s, 2H), 2.73 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.09, 155.18, 137.07, 134.61, 126.71, 123.69, 36.21, 25.81.



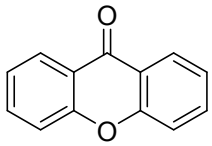
3,4-dihydronaphthalen-1(2H)-one(20)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.46 (s, 1H), 7.30 (s, 2H), 2.96 (s, 2H), 2.65 (s, 2H), 2.13 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.30, 144.49, 133.38, 132.63, 128.78, 127.14, 126.61, 39.16, 29.70, 23.29.



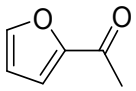
benzofuran-2(3H)-one(21)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.29 (s, 2H), 7.14 (s, 1H), 7.10 (s, 1H), 3.73 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.15, 154.70, 128.87, 124.67, 124.11, 123.13, 110.74, 32.96.



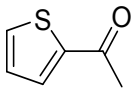
isochroman-1-one(22)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.40 (s, 1H), 7.26 (d, *J* = 20.7 Hz, 1H), 4.54 (s, 2H), 3.08 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.14, 139.68, 133.73, 130.30, 127.68, 127.36, 125.28, 67.38, 27.77.



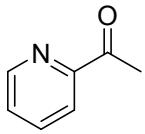
9H-xanthen-9-one(23)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.9 Hz, 2H), 7.71 (dd, *J* = 11.2, 4.2 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.16, 156.15, 134.78, 126.70, 123.89, 121.84, 117.96.



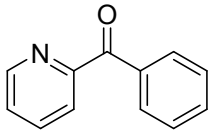
1-(furan-2-yl)ethan-1-one (24)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.60, 7.20, 7.19, 6.55, 6.55, 6.54, 2.49. ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.88, 146.45, 117.28, 112.27, 26.04.



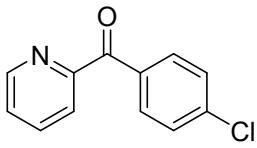
1-(thiophen-2-yl)ethan-1-one (25)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.55, 7.49, 6.97, 2.39. ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.57, 144.43, 133.79, 132.63, 128.19, 26.73.



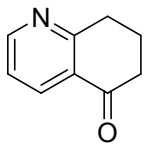
1-(pyridin-2-yl)ethan-1-one(26)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.00 (s, 1H), 7.81 (s, 1H), 7.44 (s, 1H), 2.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.09, 153.54, 148.96, 136.82, 127.08, 121.61, 25.75.



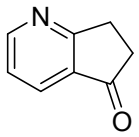
phenyl(pyridin-2-yl)methanone(27)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.07 (s, 3H), 7.92 (s, 1H), 7.61 (s, 1H), 7.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.90, 155.12, 148.57, 137.07, 136.29, 132.94, 131.00, 128.18, 126.18, 124.64.



(4-chlorophenyl)(pyridin-2-yl)methanone(28)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.07 (s, 3H), 7.91 (s, 1H), 7.49 (d, J = 16.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.42, 154.67, 148.52, 139.40, 137.22, 134.59, 132.51, 128.47, 126.44, 124.69.



7,8-dihydroquinolin-5(6H)-one(29)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.28 (s, 1H), 7.28 (s, 1H), 3.16 (s, 2H), 2.69 (s, 2H), 2.20 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.95, 163.65, 153.46, 135.05, 128.16, 122.26, 38.53, 32.49, 21.83.

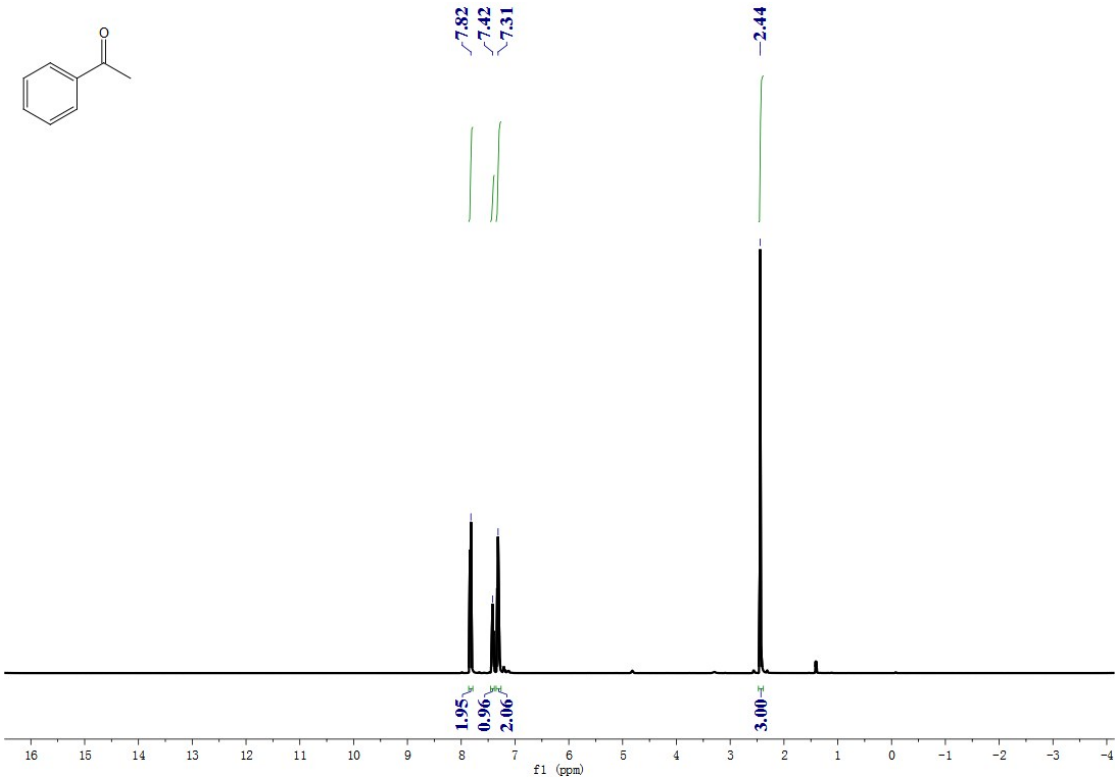


6,7-dihydro-5H-cyclopenta[b]pyridin-5-one(30)[3-5]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.00 (s, 1H), 7.32 (s, 1H), 3.27 (s, 2H), 2.78 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.98, 174.32, 155.67, 132.01, 130.35, 122.52, 35.76, 28.68.

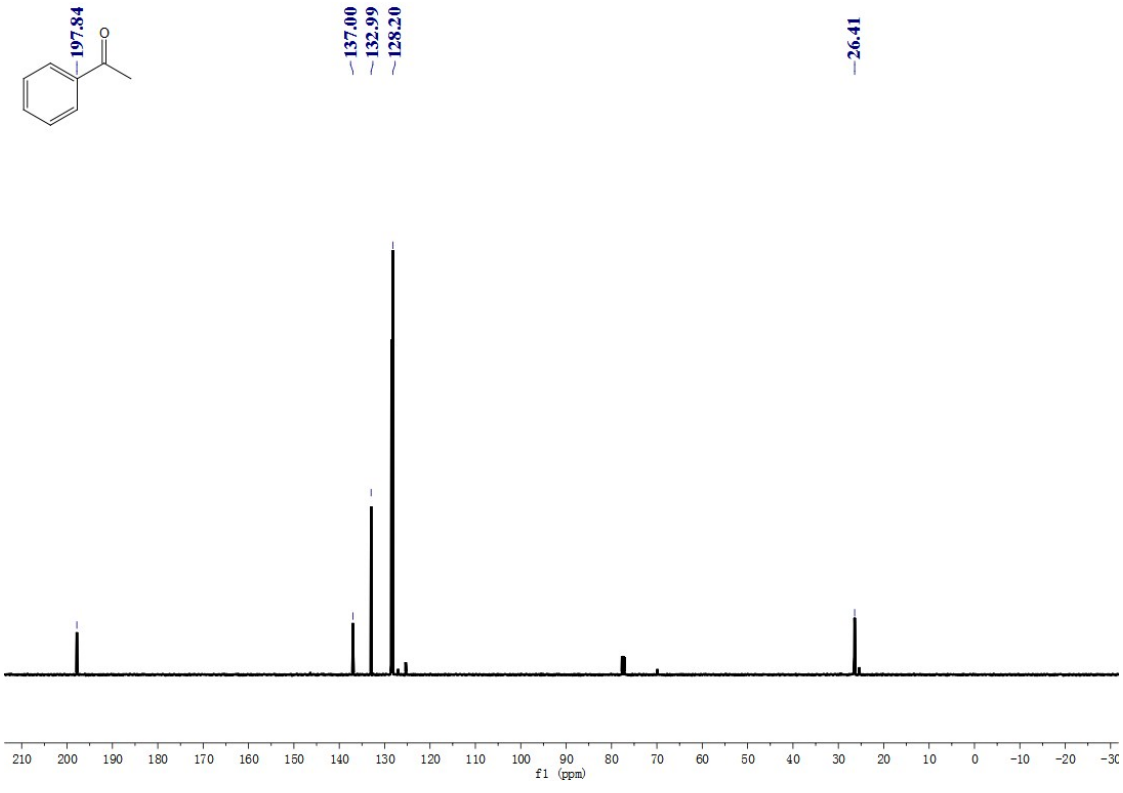
(5S,8aR,9aR)-3,5,8a-trimethyl-6,7,9,9a-tetrahydronaphtho[2,3-b]furan-2,8(5H,8aH)-dione(41)[3-5]:

(3S,5R,5aS,6R,9R,9aS,10R)-6-acetoxy-2,2,5a,9-tetramethyl-4,7-dioxooctahydro-2H-3,9a-methanobenzo[b]oxepine-5,10-diyl dibenzoate(42)[3-5]:

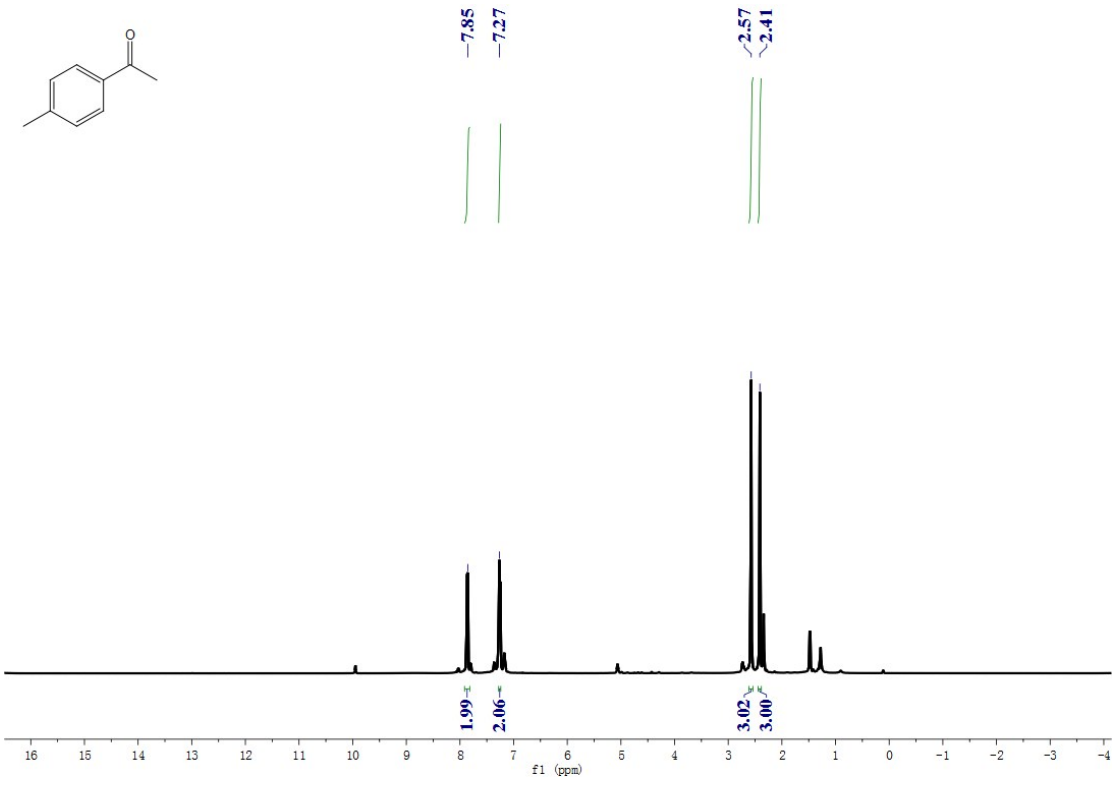
X. NMR spectra



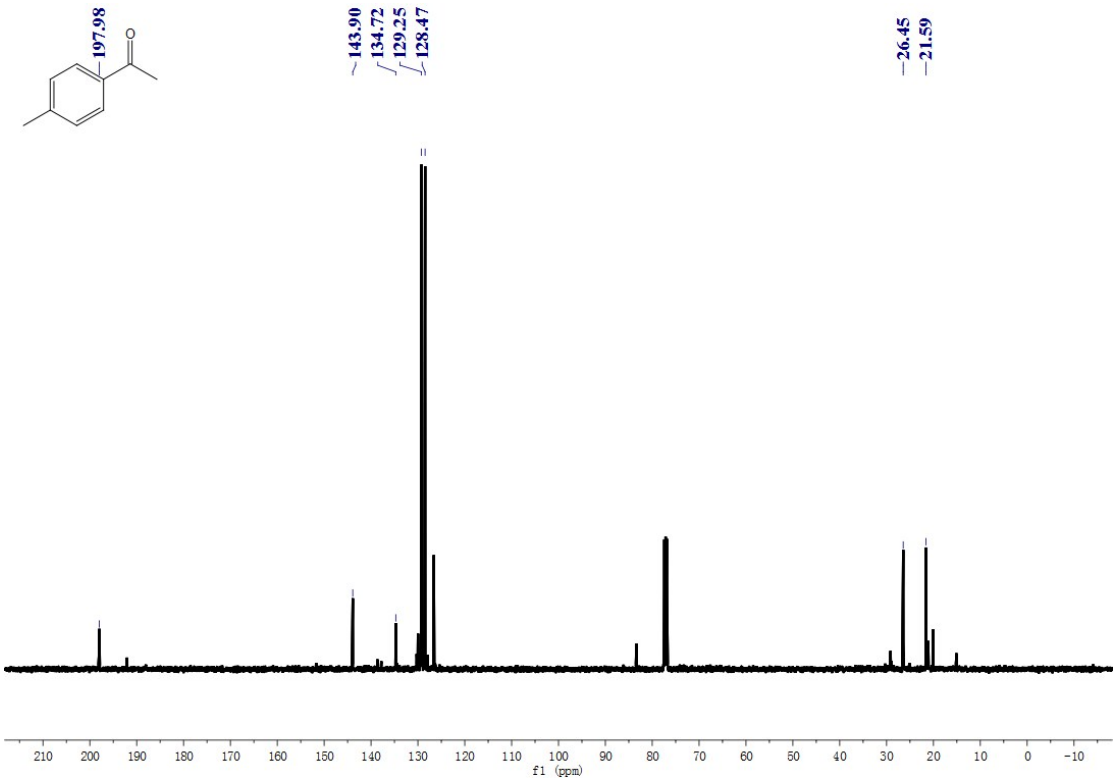
^{1}H NMR spectra of **2** (500 MHz, $CDCl_3$)



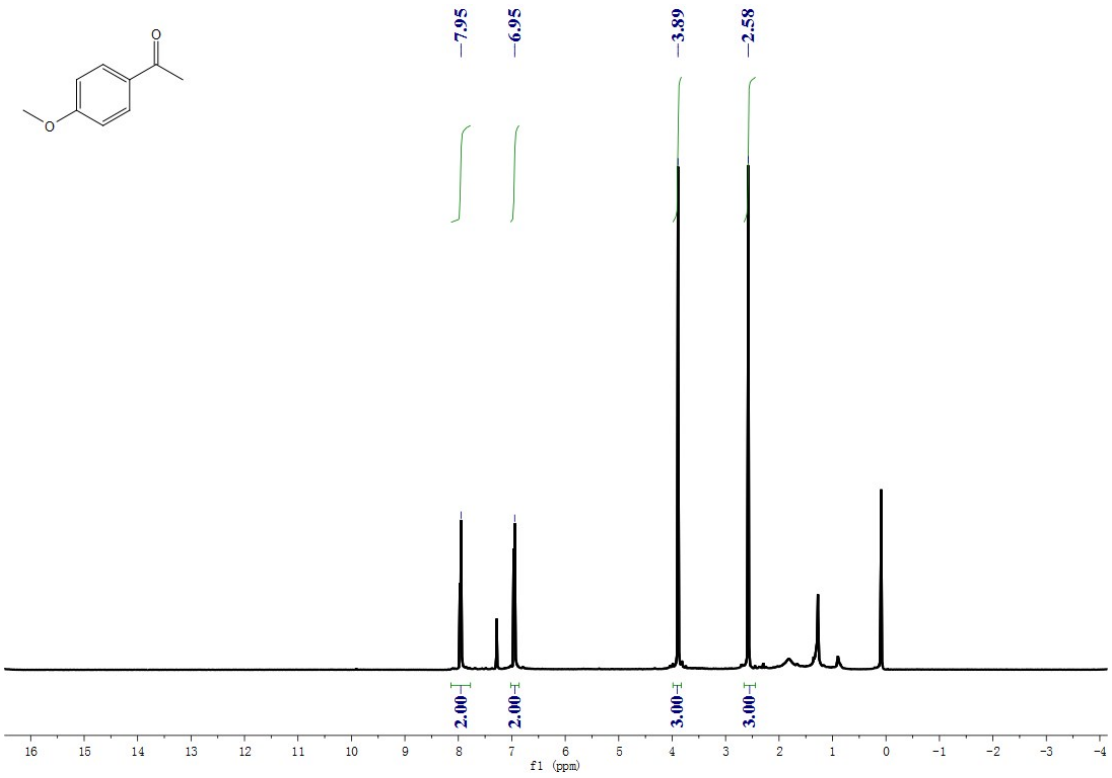
^{13}C NMR spectra of **2** (126 MHz, $CDCl_3$)



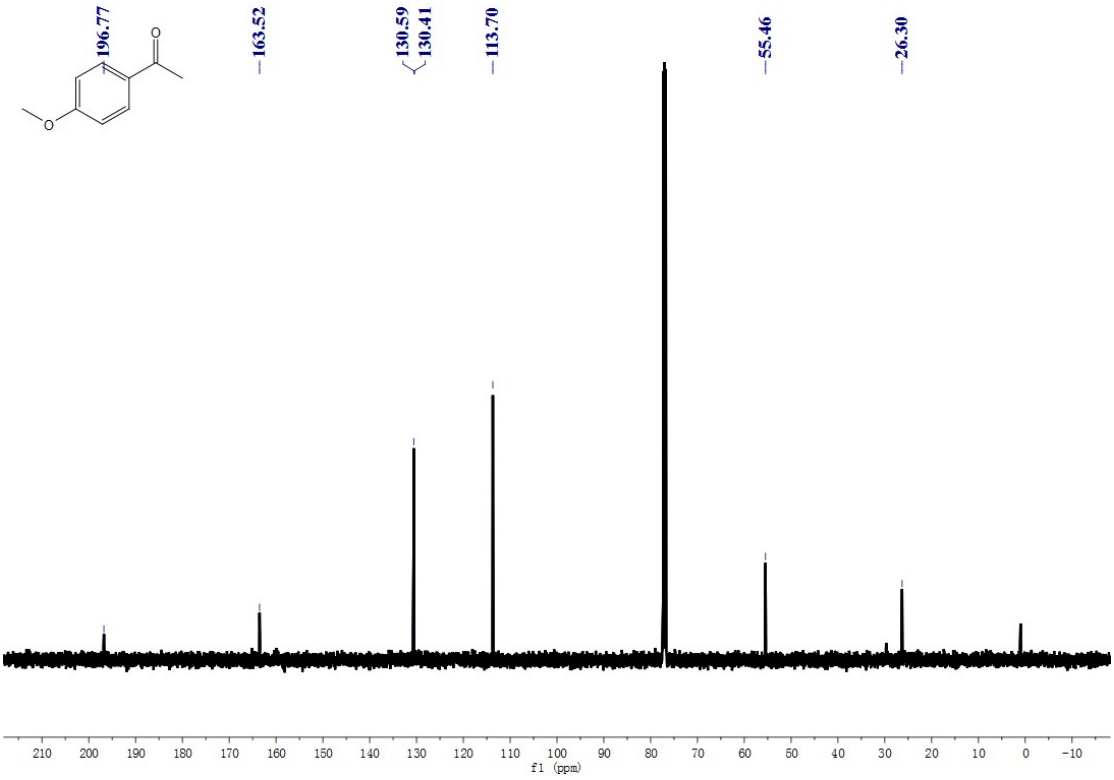
^{1}H NMR spectra of **3** (500 MHz, $CDCl_3$)



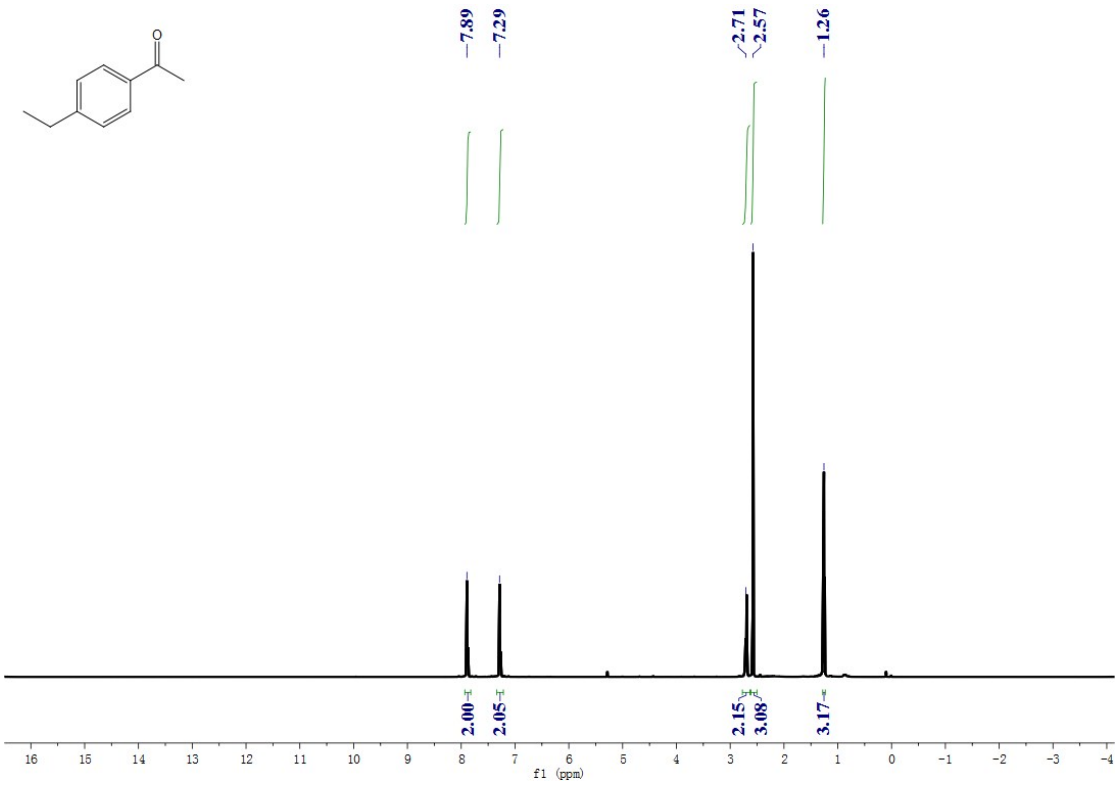
^{13}C NMR spectra of **3** (126 MHz, $CDCl_3$)



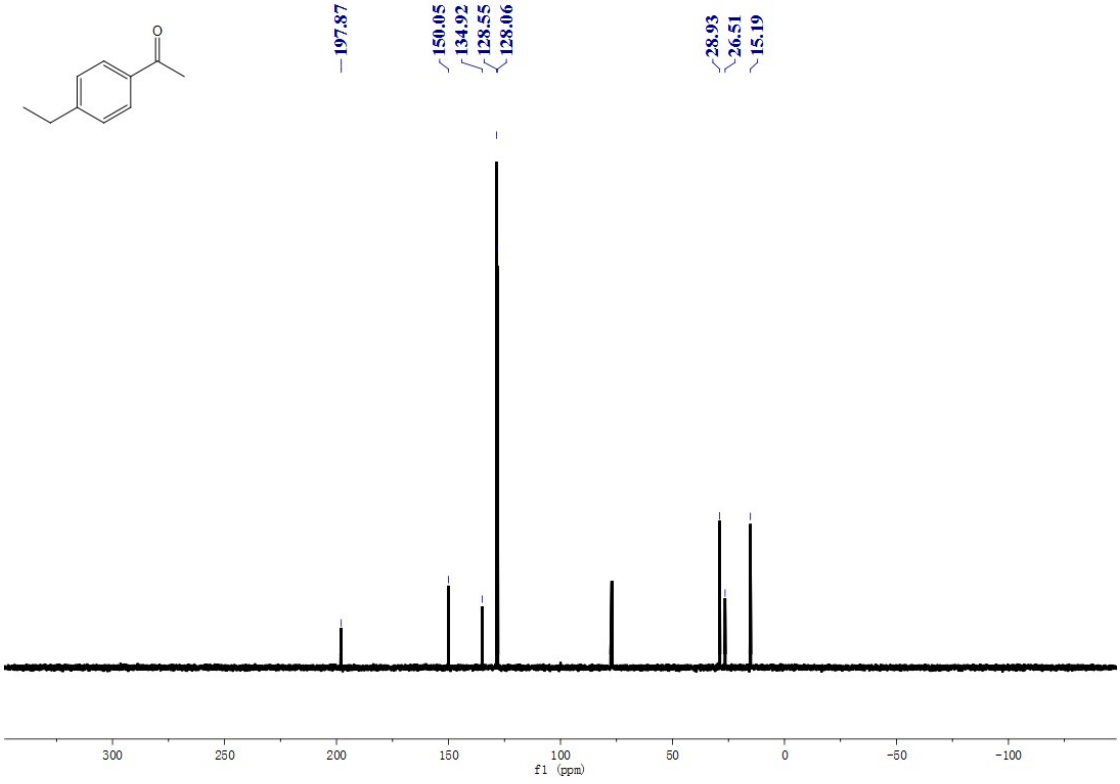
^{1}H NMR spectra of **4** (500 MHz, $CDCl_3$)



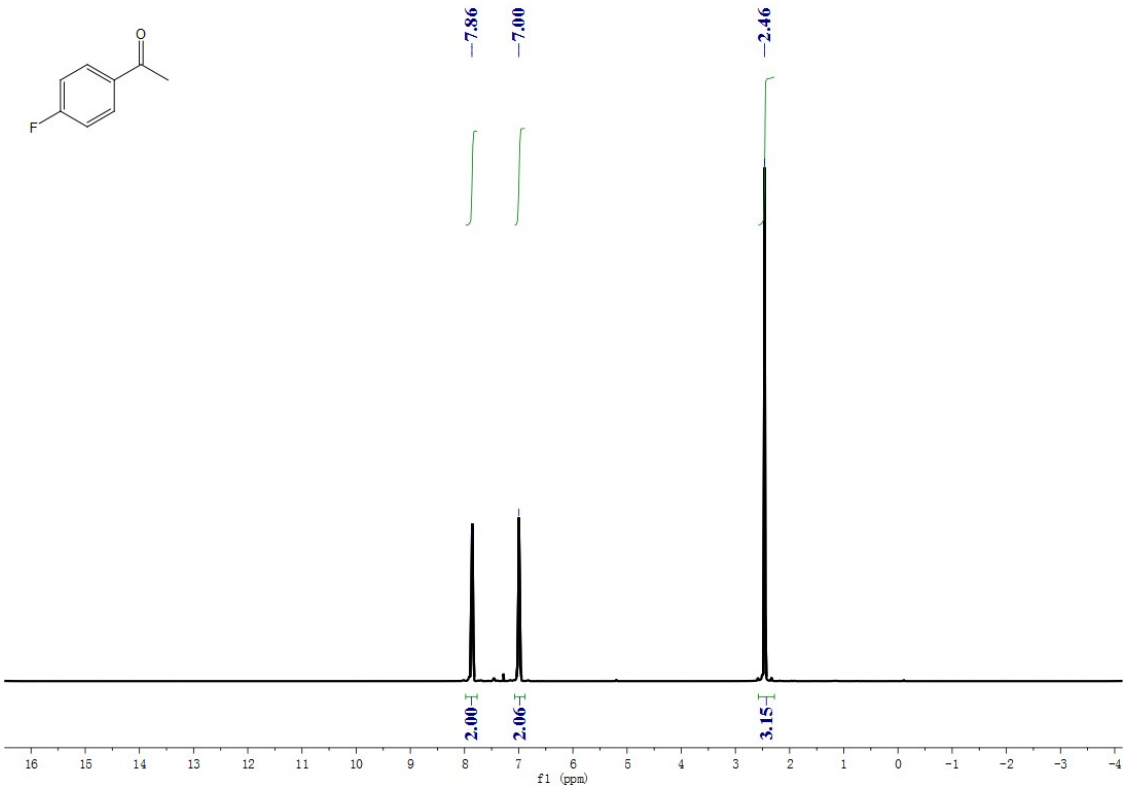
^{13}C NMR spectra of **4** (126 MHz, $CDCl_3$)



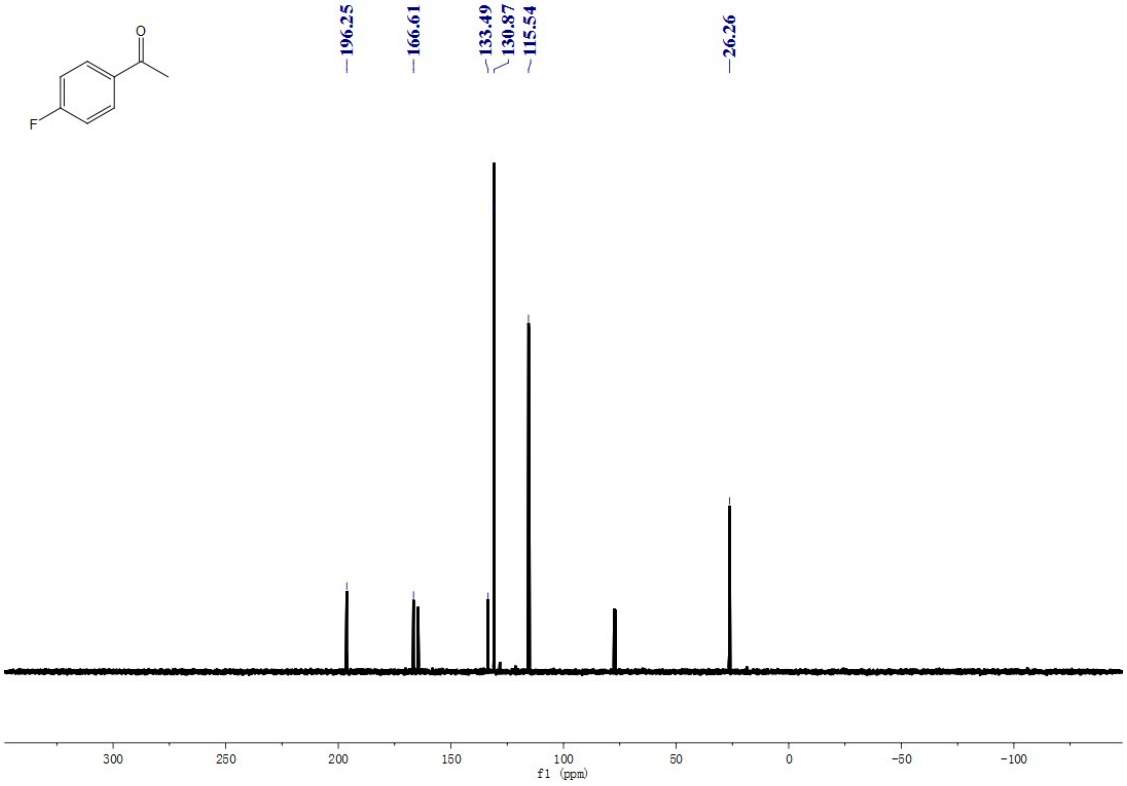
^{1}H NMR spectra of **5** (500 MHz, $CDCl_3$)



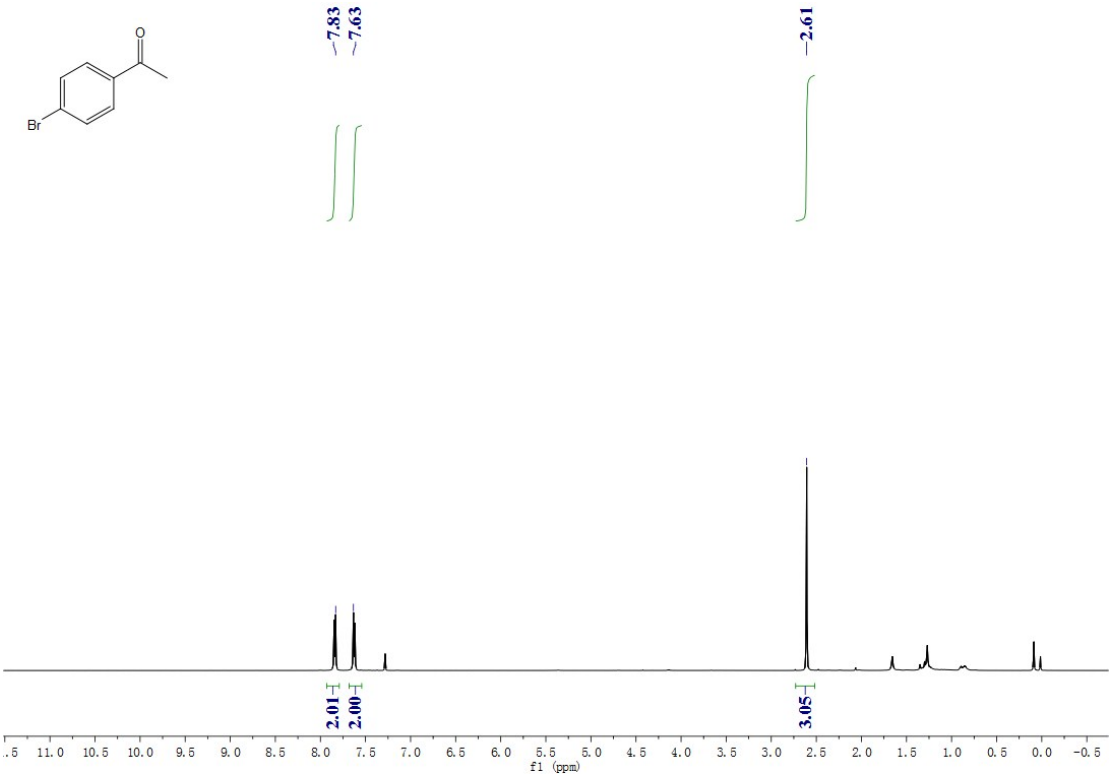
^{13}C NMR spectra of **5** (126 MHz, $CDCl_3$)



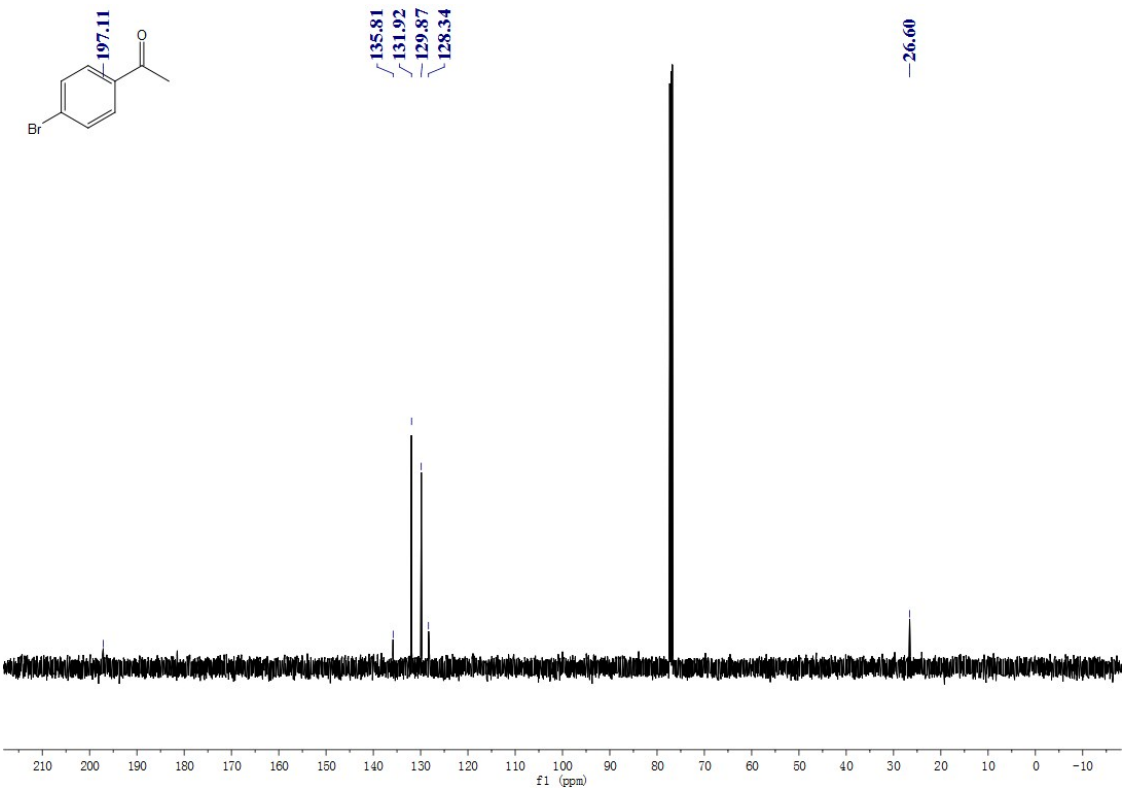
^{1}H NMR spectra of **6** (500 MHz, $CDCl_3$)



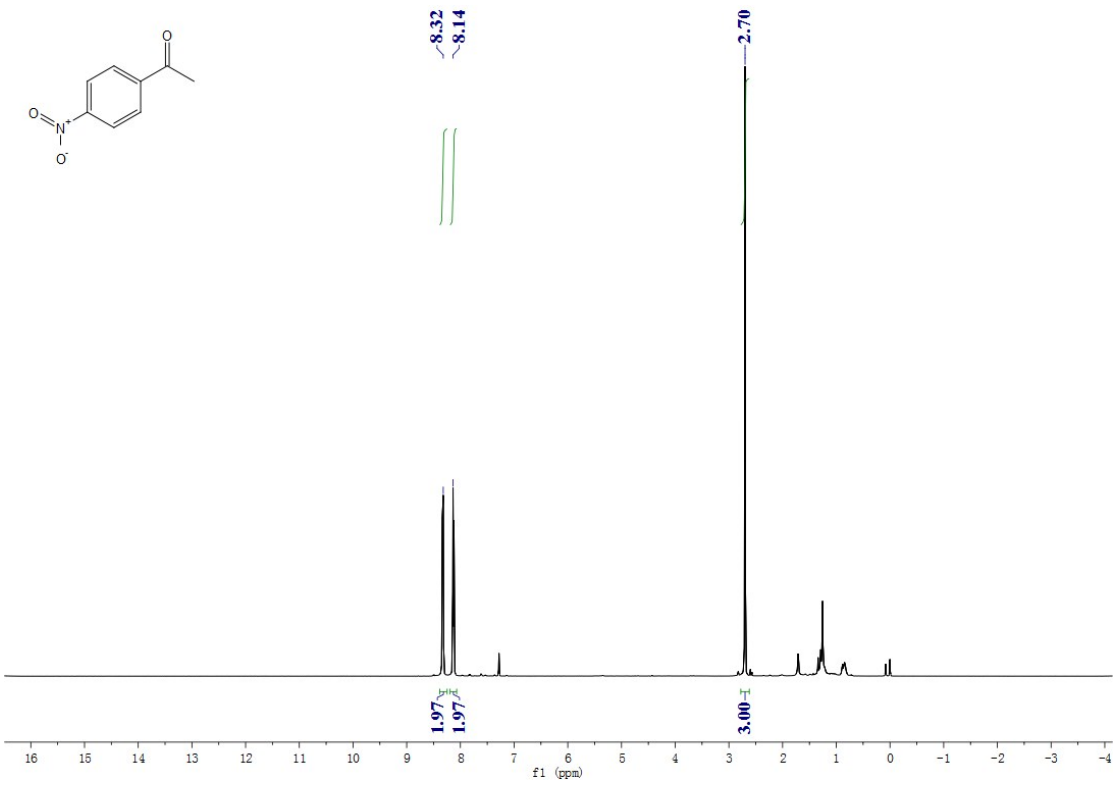
^{13}C NMR spectra of **6** (126 MHz, $CDCl_3$)



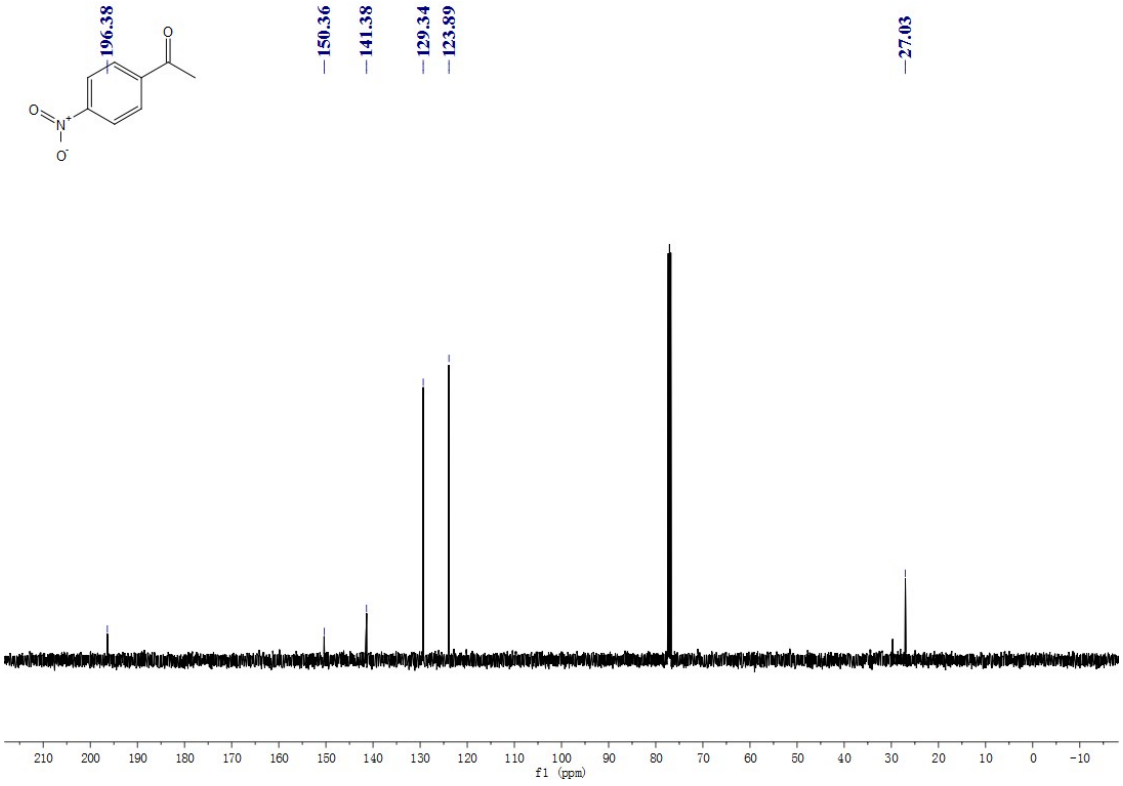
^{1}H NMR spectra of **7** (500 MHz, $CDCl_3$)



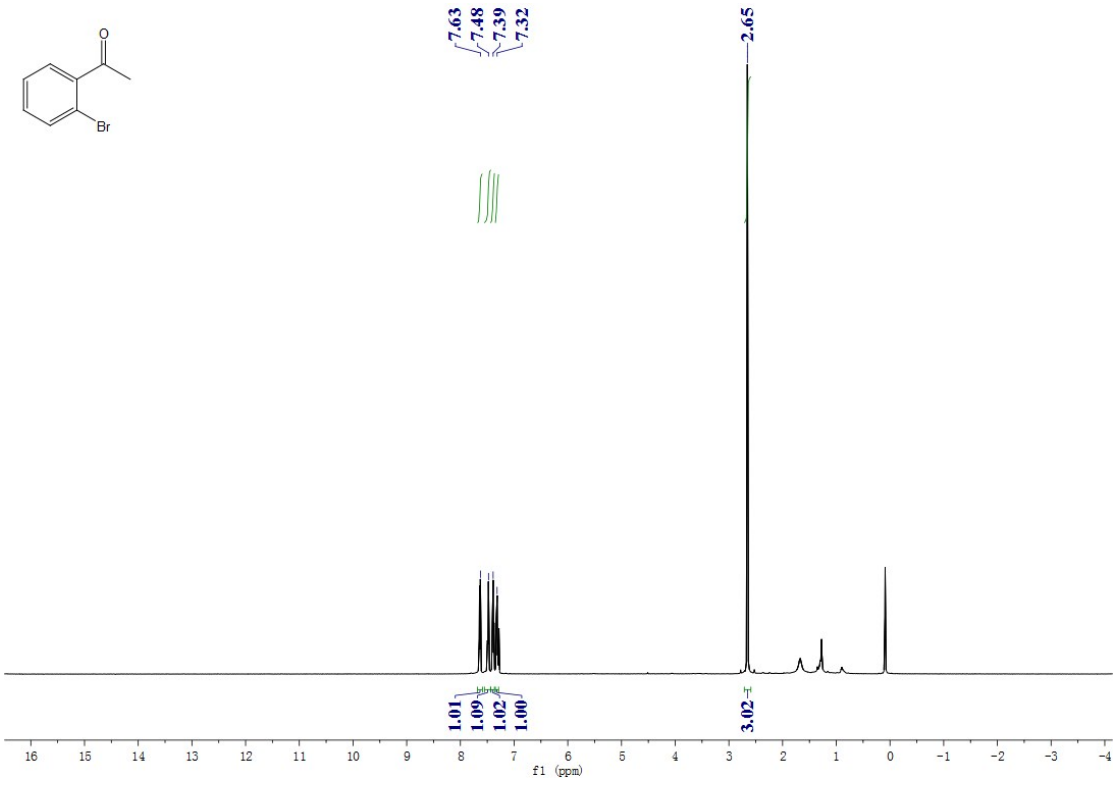
^{13}C NMR spectra of **7** (126 MHz, $CDCl_3$)



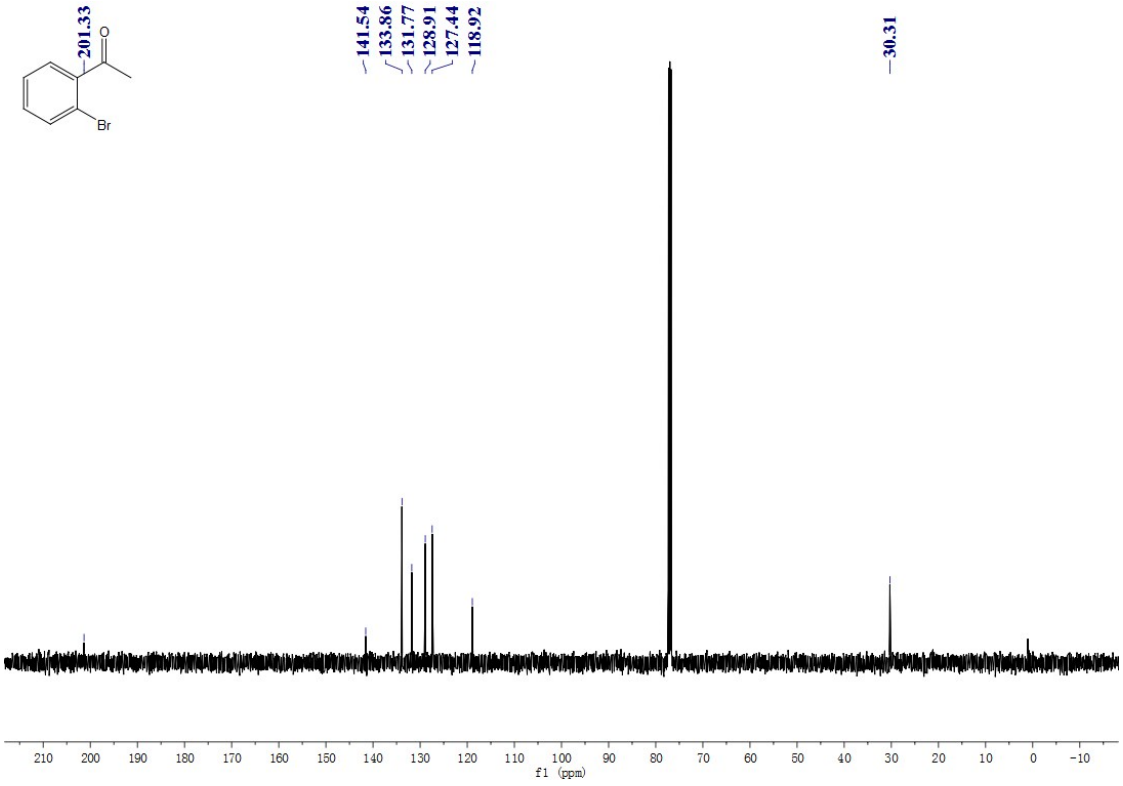
^{1}H NMR spectra of **8** (500 MHz, $CDCl_3$)



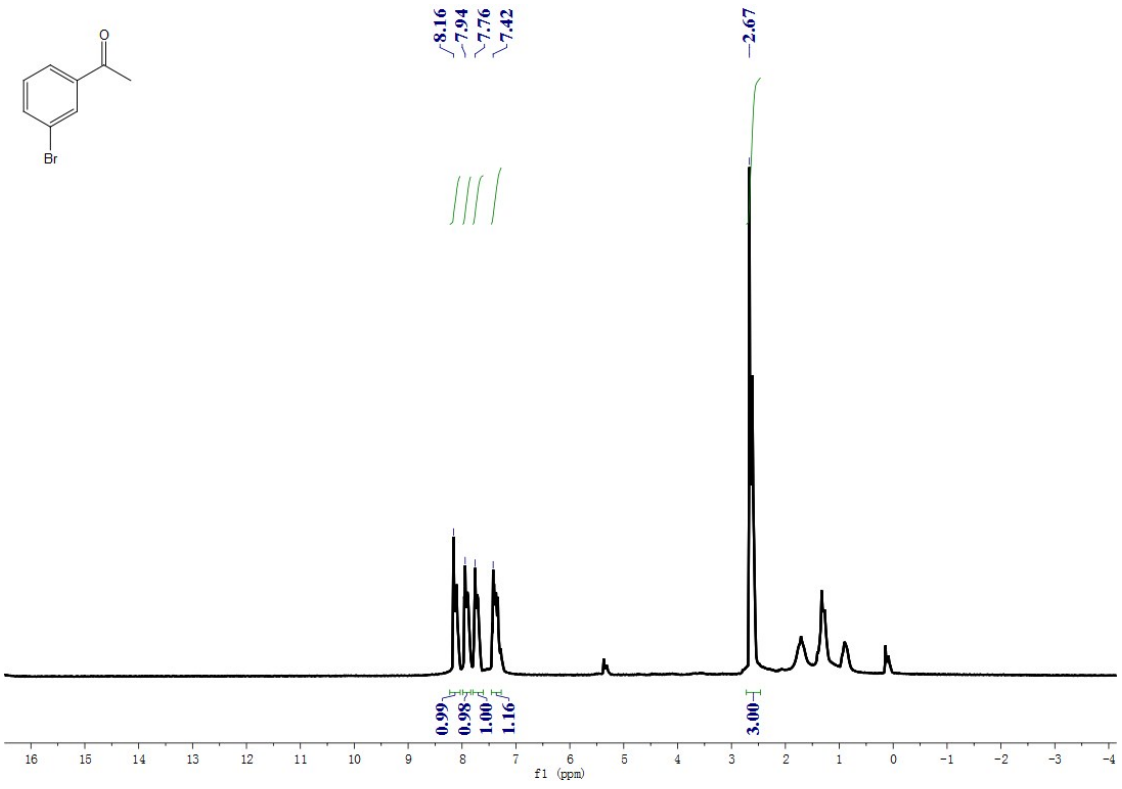
^{13}C NMR spectra of **8** (126 MHz, $CDCl_3$)



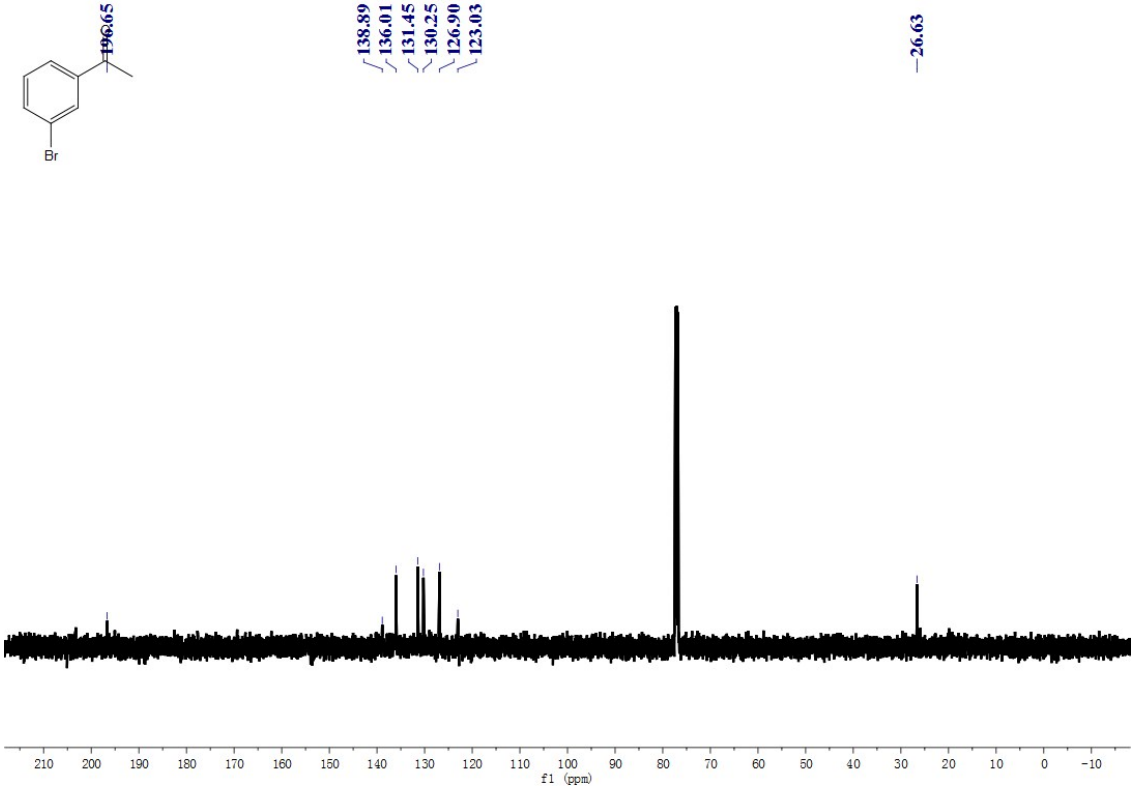
^{1}H NMR spectra of **9** (500 MHz, $CDCl_3$)



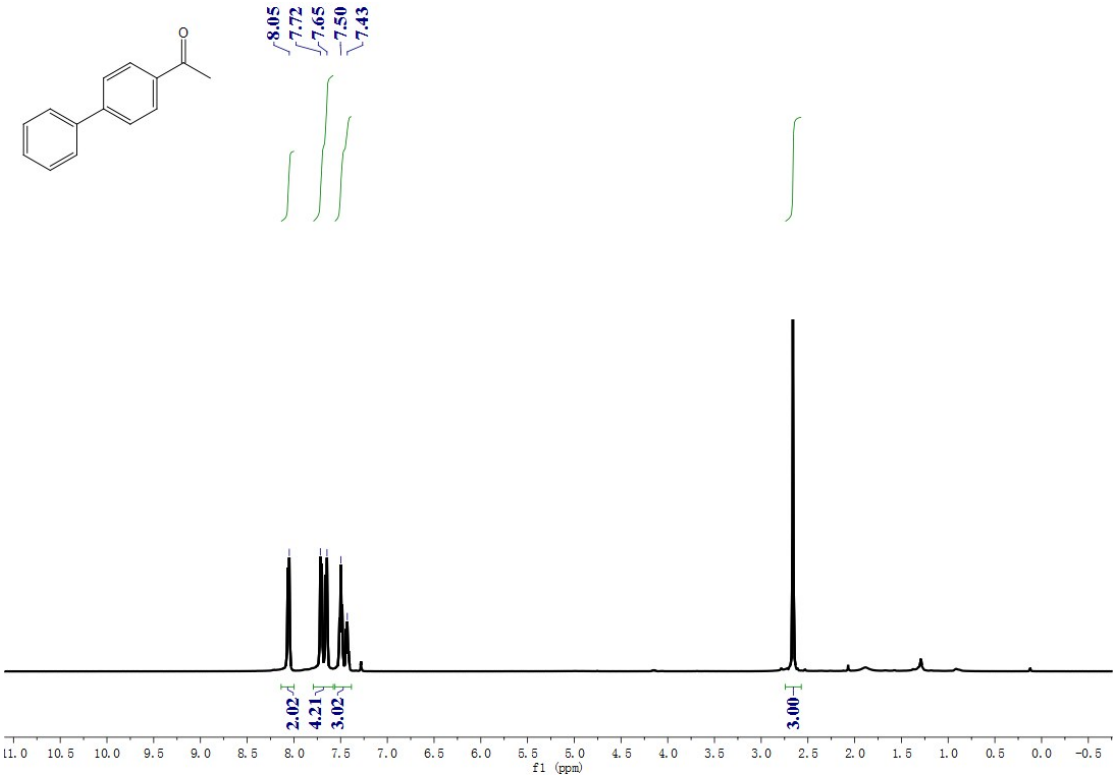
^{13}C NMR spectra of **9** (126 MHz, $CDCl_3$)



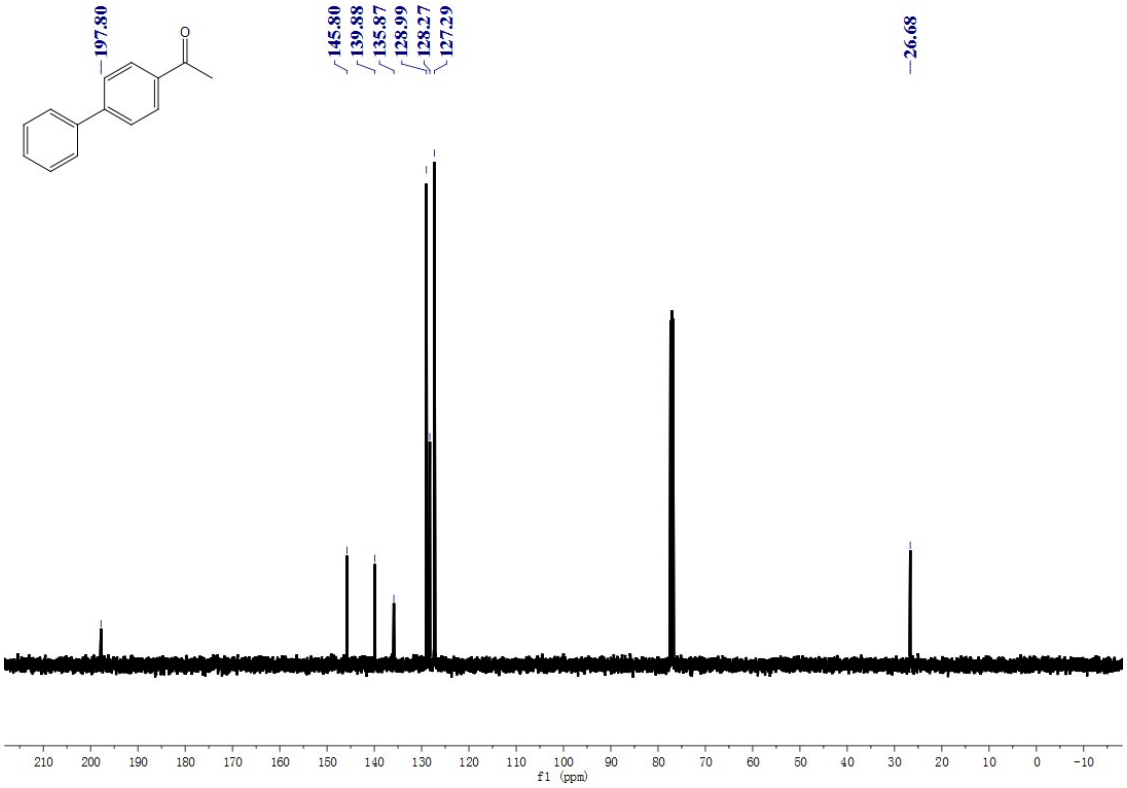
^{1}H NMR spectra of **10** (500 MHz, $CDCl_3$)



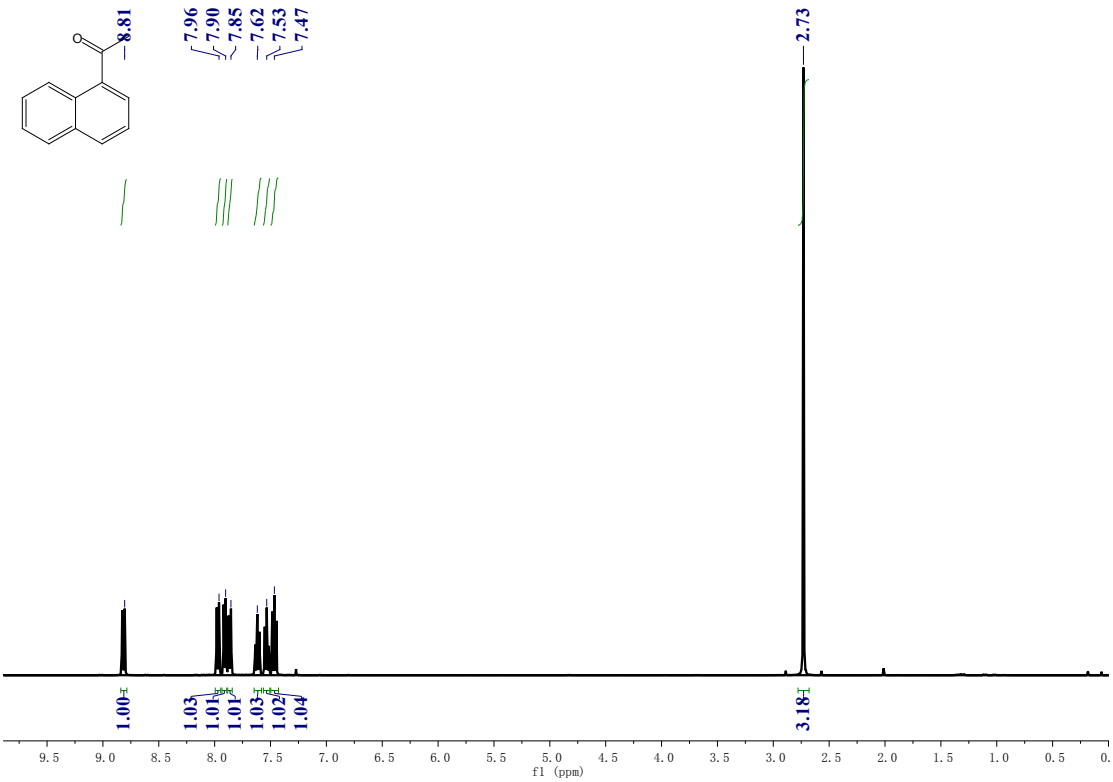
^{13}C NMR spectra of **10** (126 MHz, $CDCl_3$)



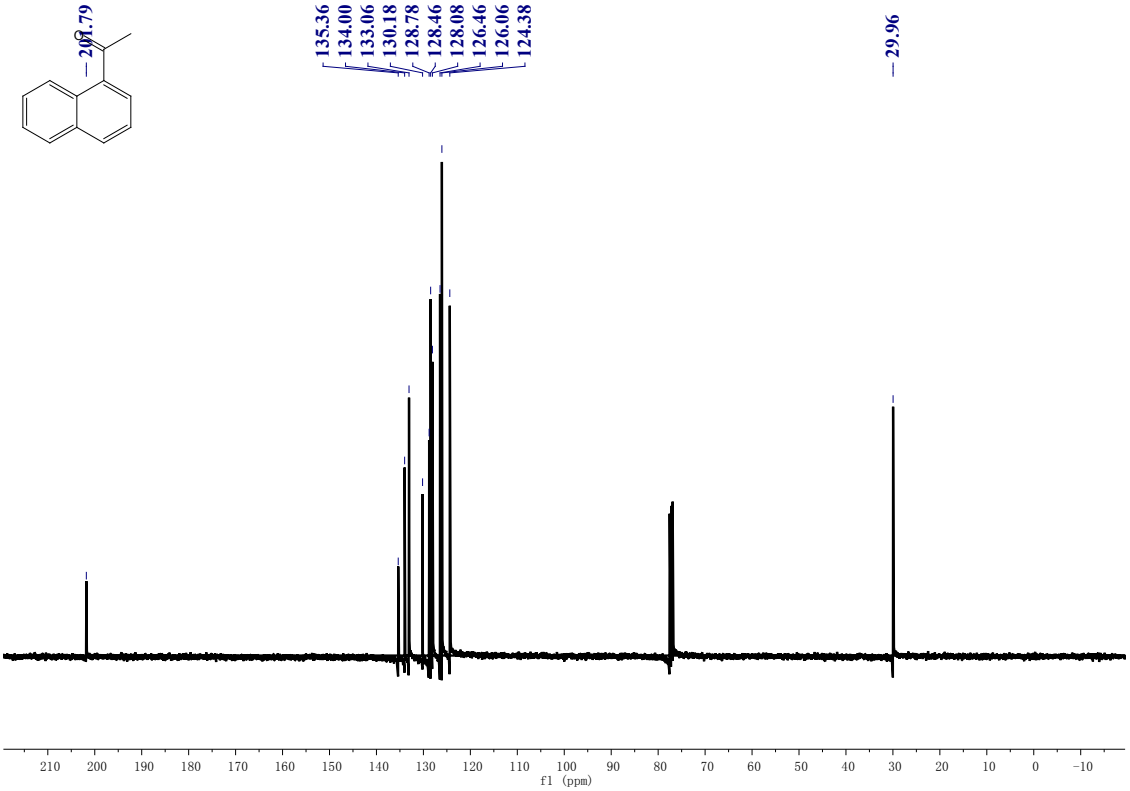
^{1}H NMR spectra of **11** (500 MHz, $CDCl_3$)



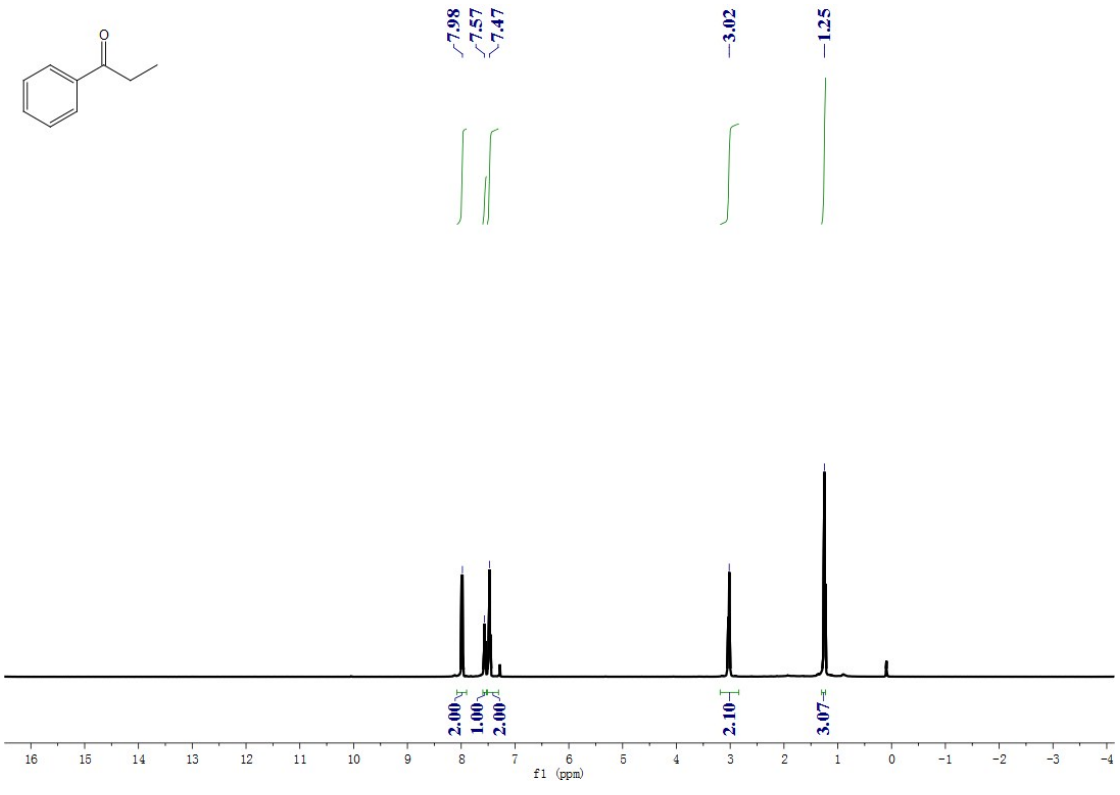
^{13}C NMR spectra of **11** (126 MHz, $CDCl_3$)



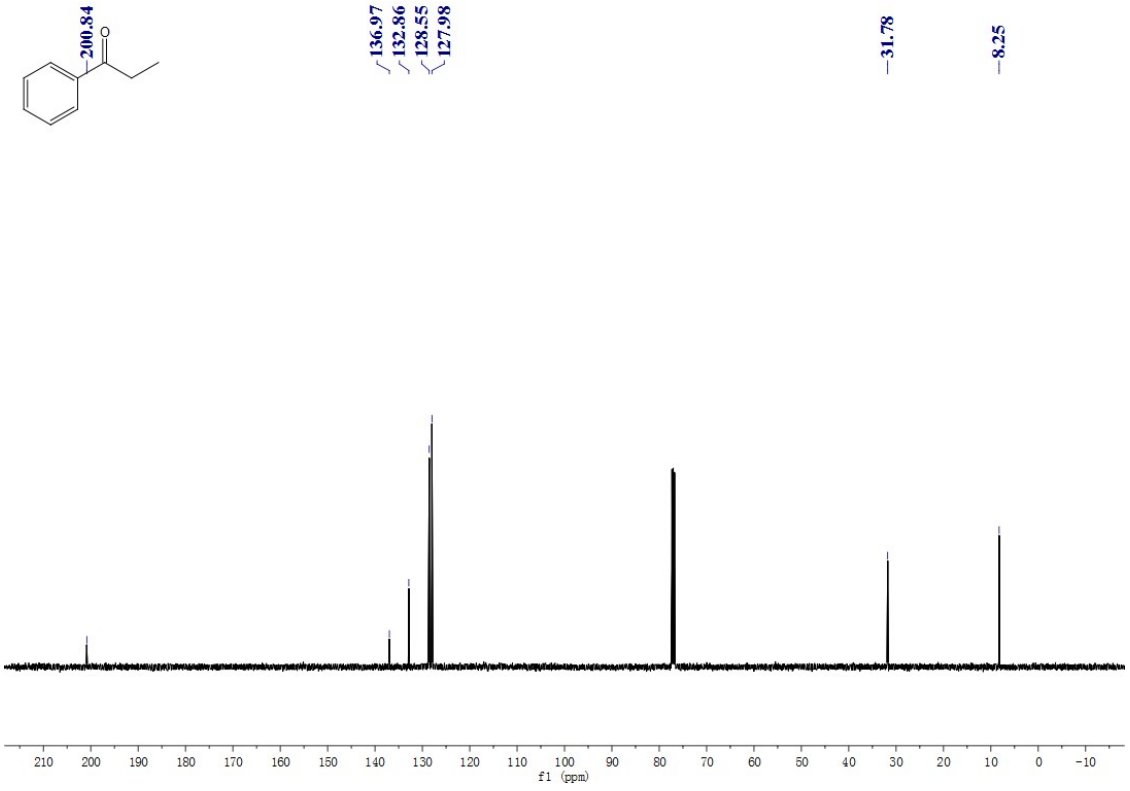
^{1}H NMR spectra of **12** (400 MHz, $CDCl_3$)



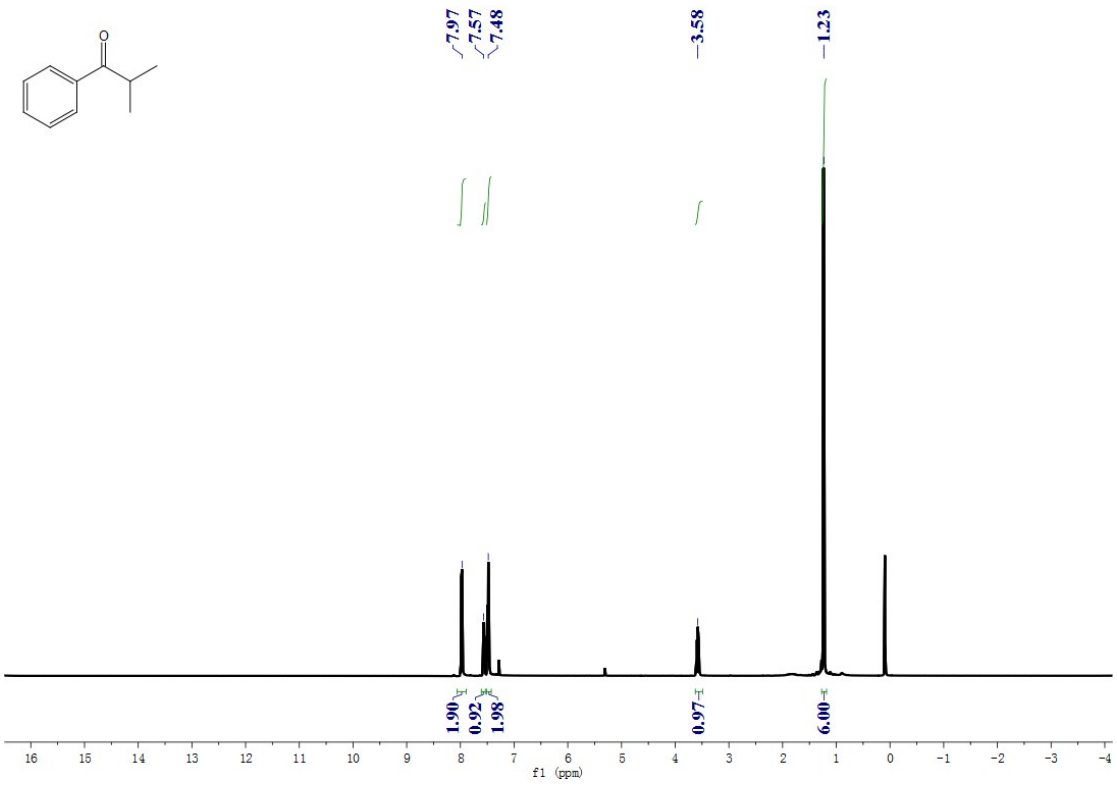
^{13}C NMR spectra of **12** (126 MHz, $CDCl_3$)



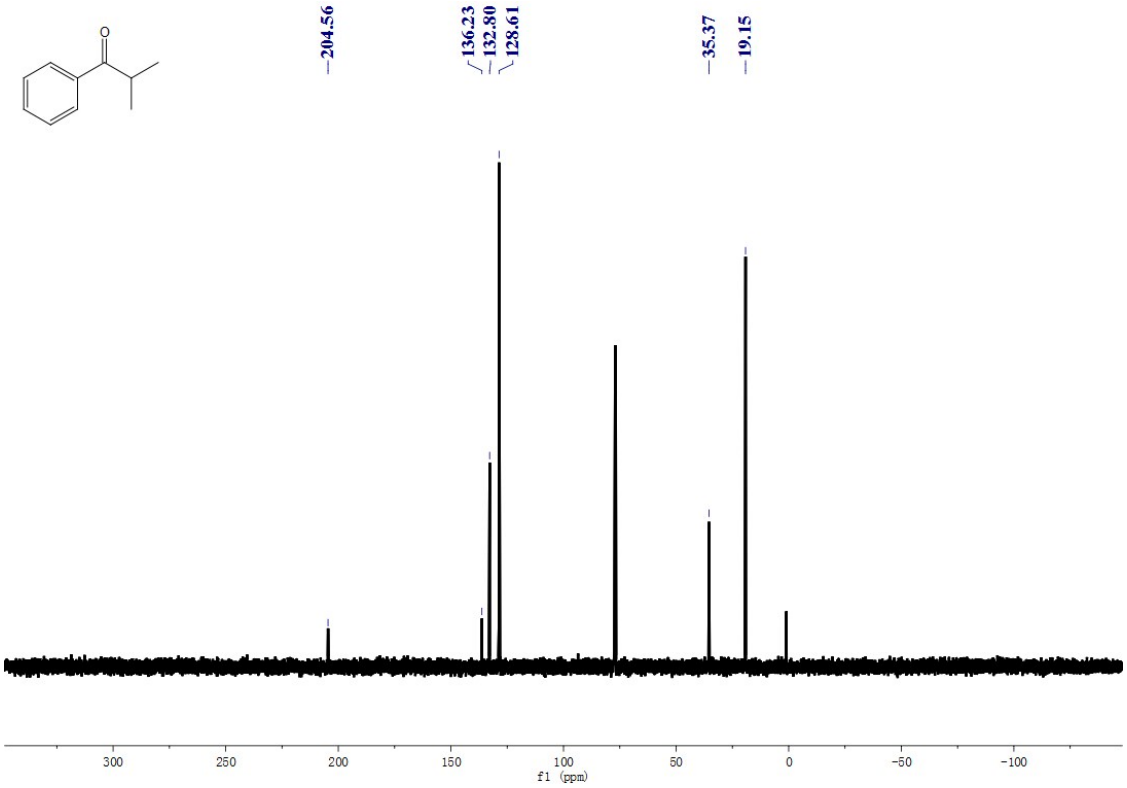
^{1}H NMR spectra of 1**3** (500 MHz, $CDCl_3$)



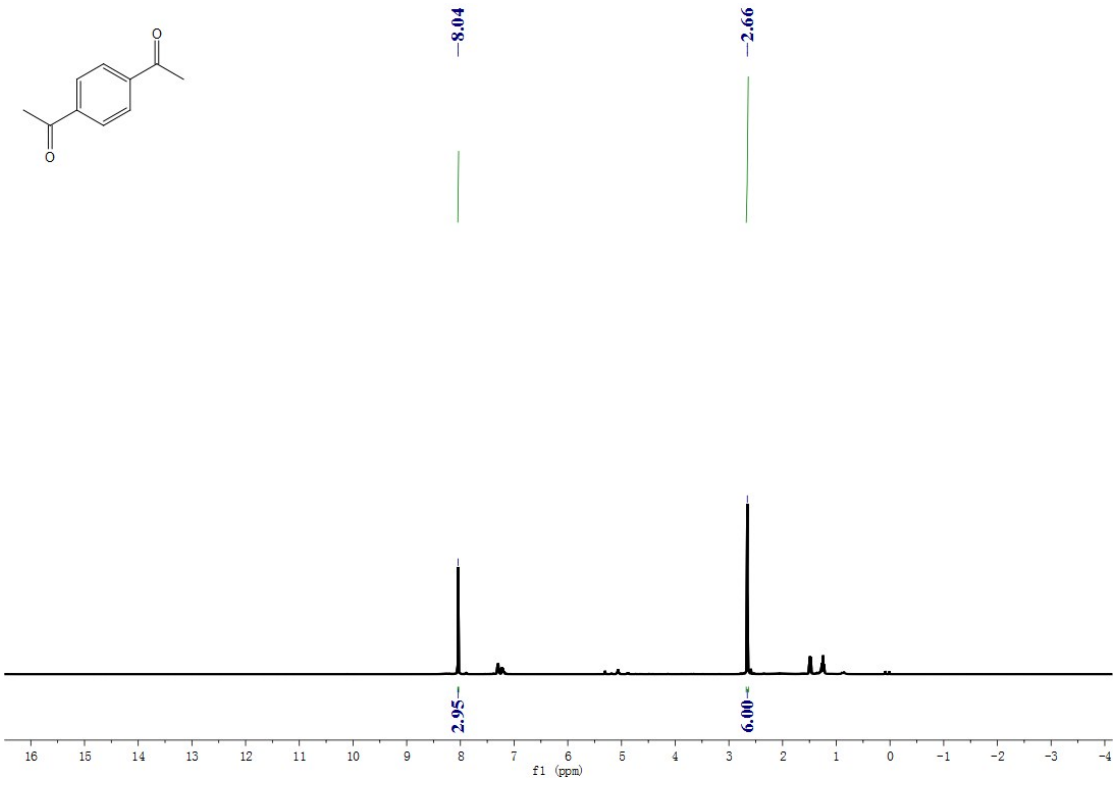
^{13}C NMR spectra of 1**3** (126 MHz, $CDCl_3$)



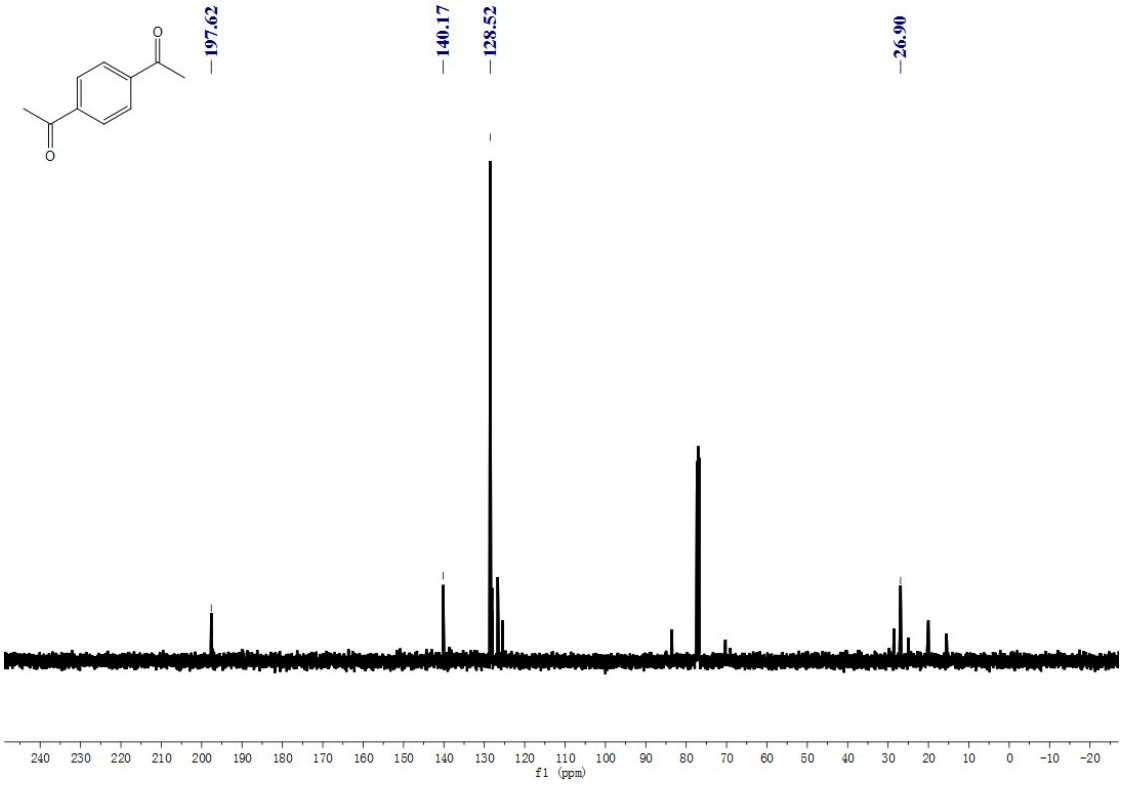
^{1}H NMR spectra of **14** (500 MHz, $CDCl_3$)



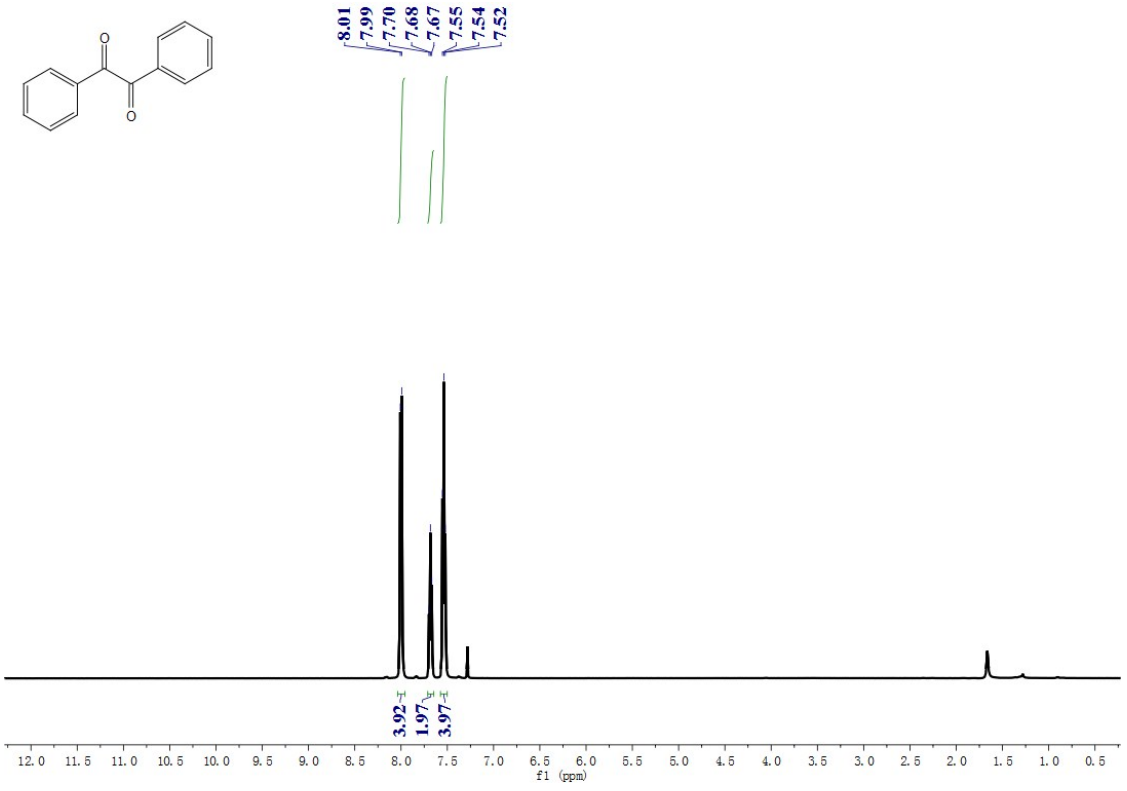
^{13}C NMR spectra of **14** (126 MHz, $CDCl_3$)



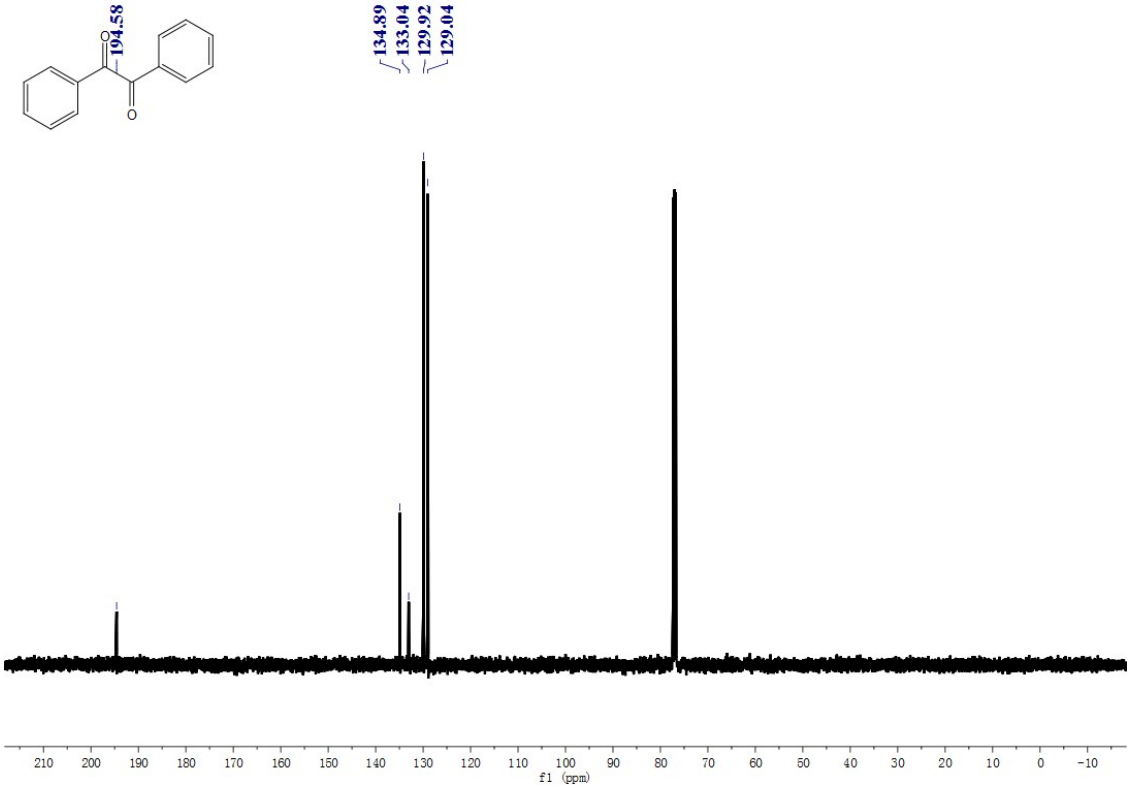
^{1}H NMR spectra of **15** (500 MHz, $CDCl_3$)



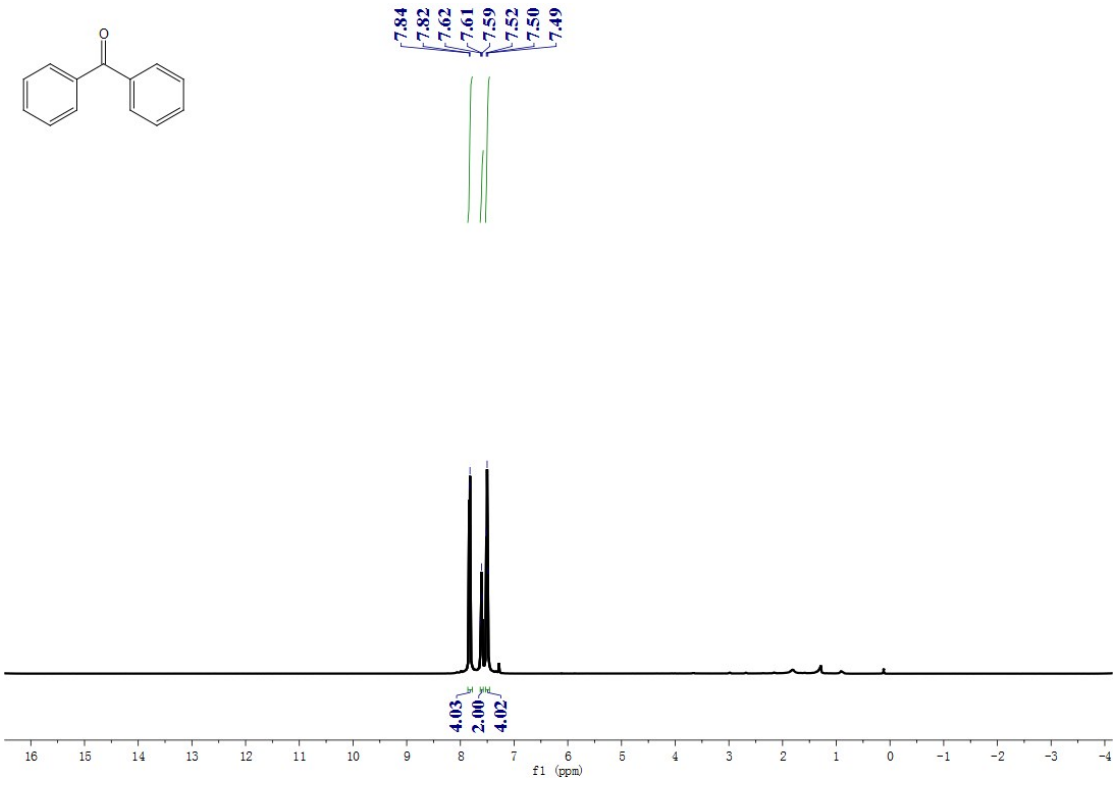
^{13}C NMR spectra of **15** (126 MHz, $CDCl_3$)



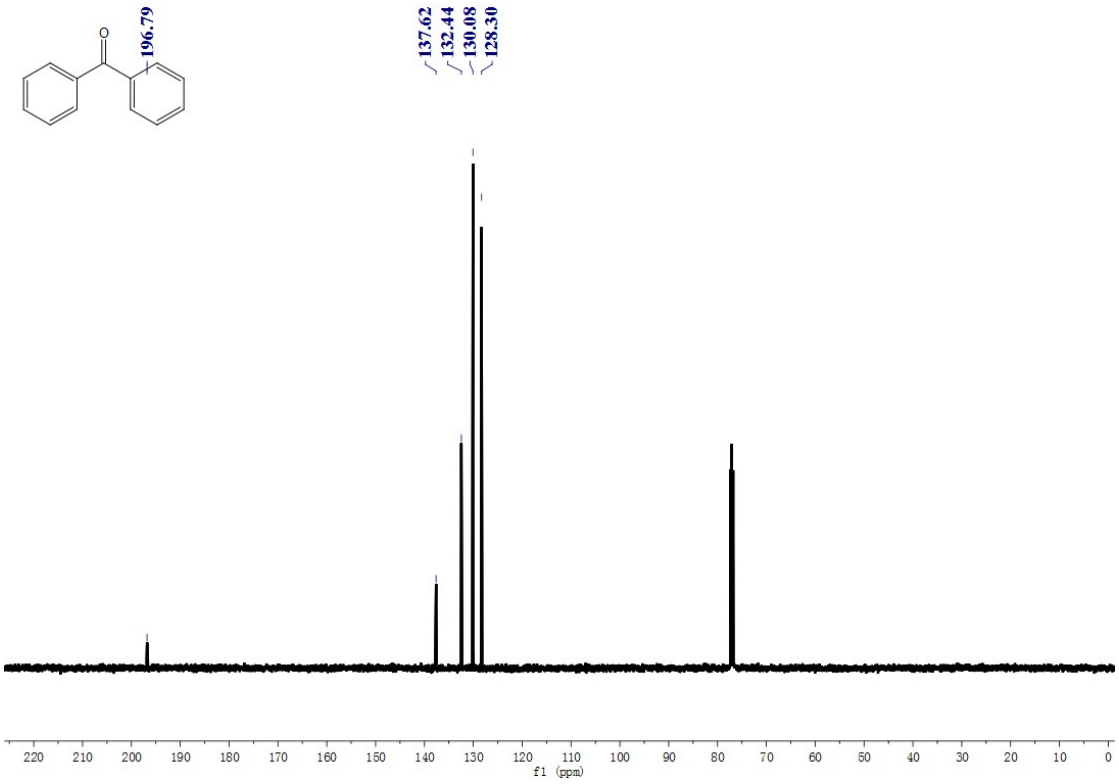
^{1}H NMR spectra of **16** (500 MHz, $CDCl_3$)



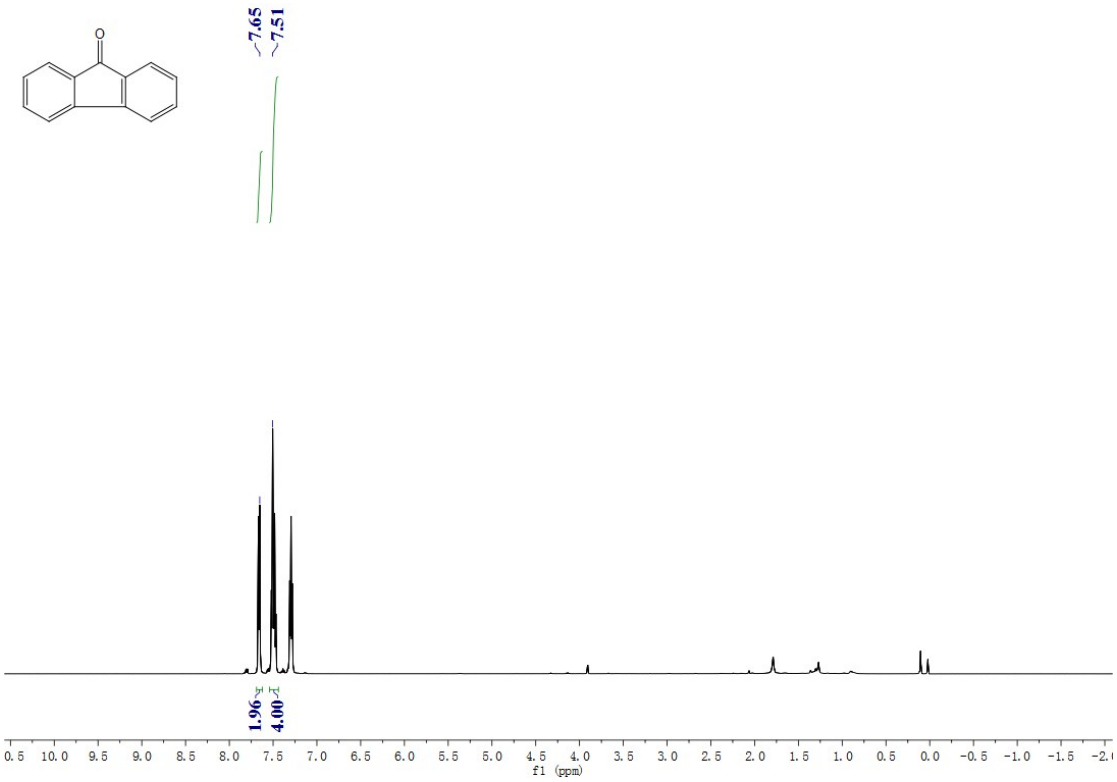
^{13}C NMR spectra of **16** (126 MHz, $CDCl_3$)



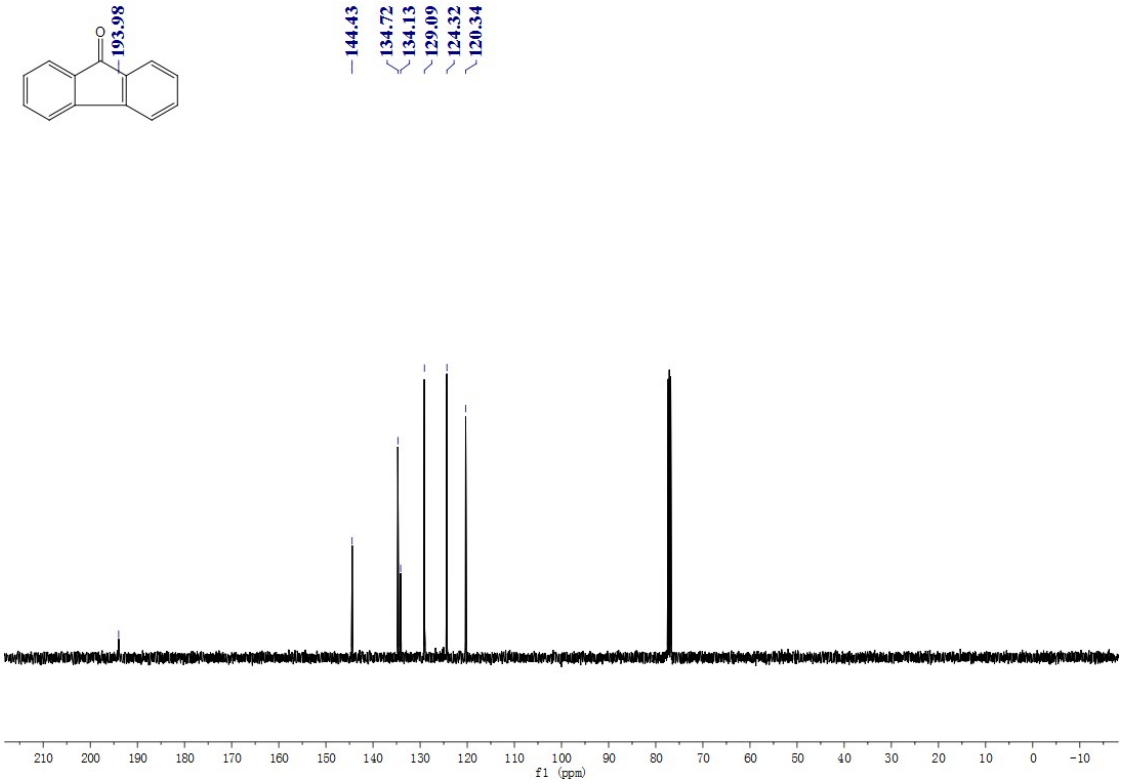
^{1}H NMR spectra of **17** (500 MHz, $CDCl_3$)



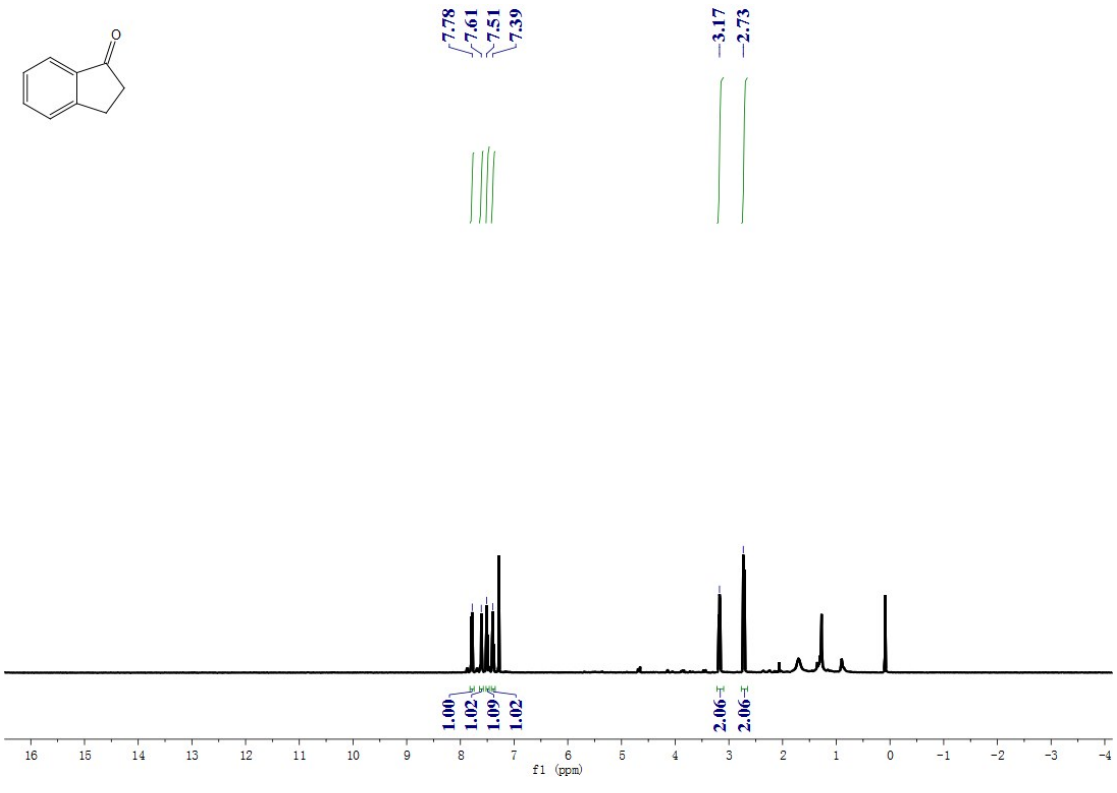
^{13}C NMR spectra of **17** (126 MHz, $CDCl_3$)



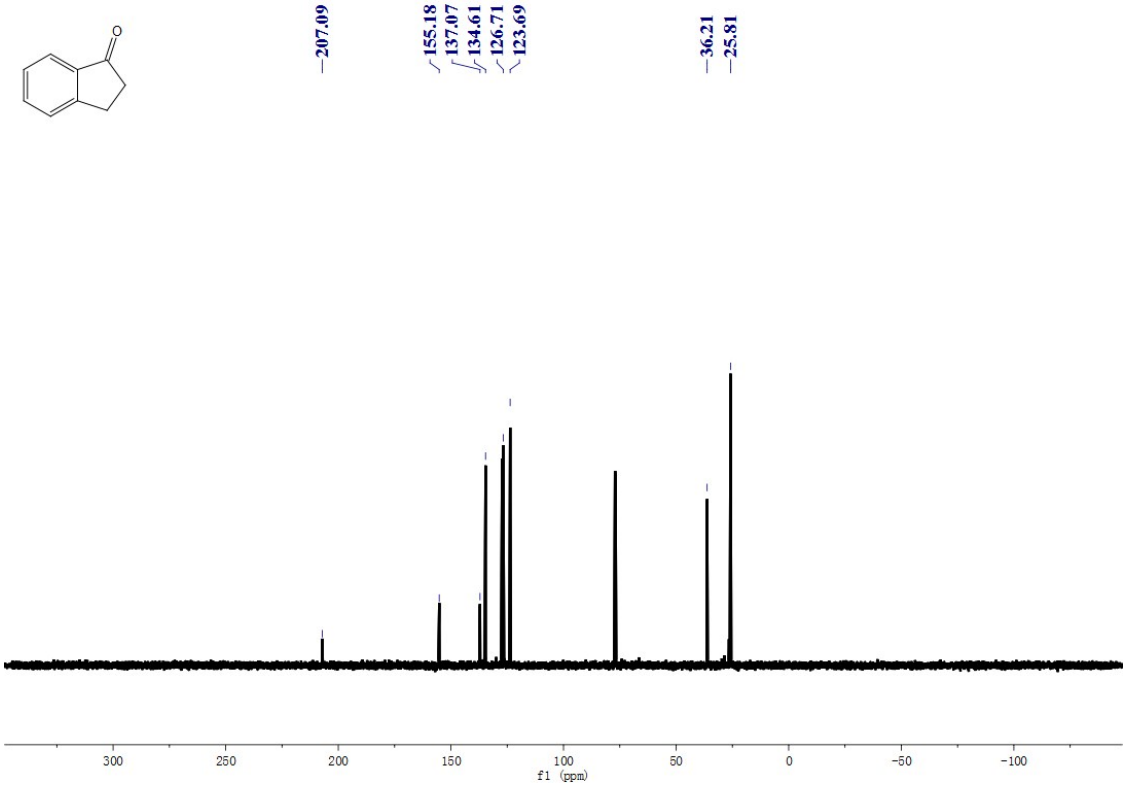
^{1}H NMR spectra of **18** (500 MHz, $CDCl_3$)



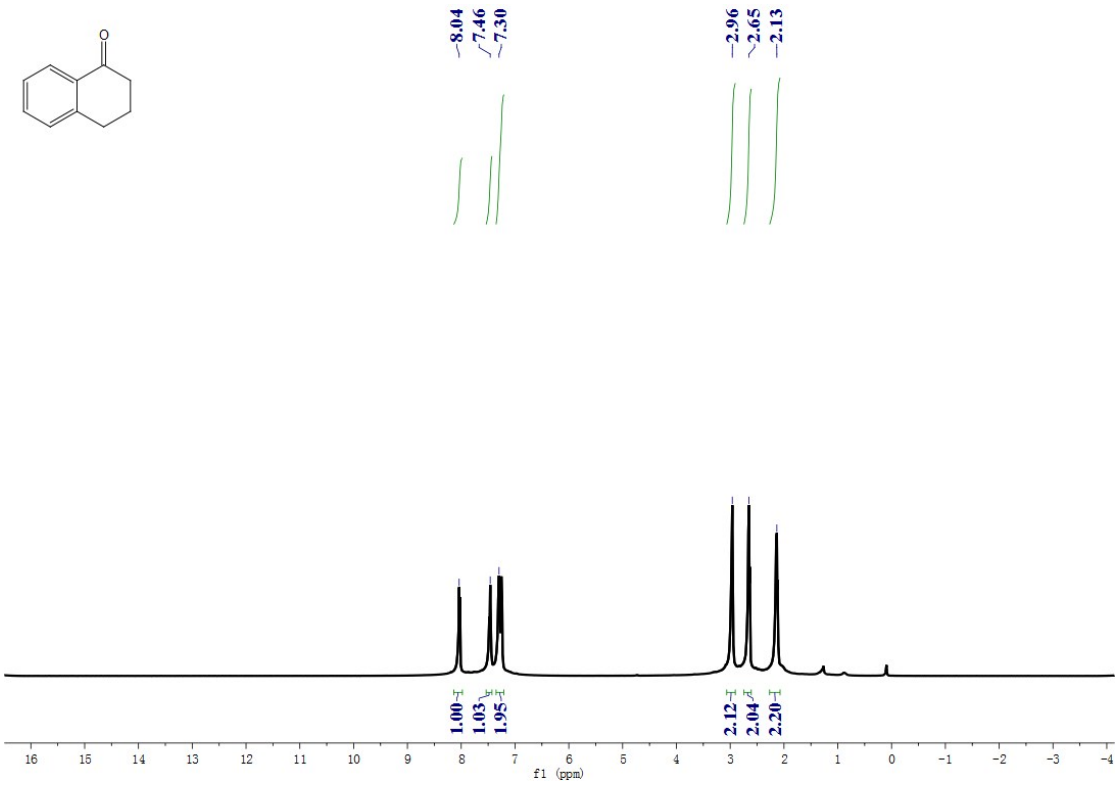
^{13}C NMR spectra of **18** (126 MHz, $CDCl_3$)



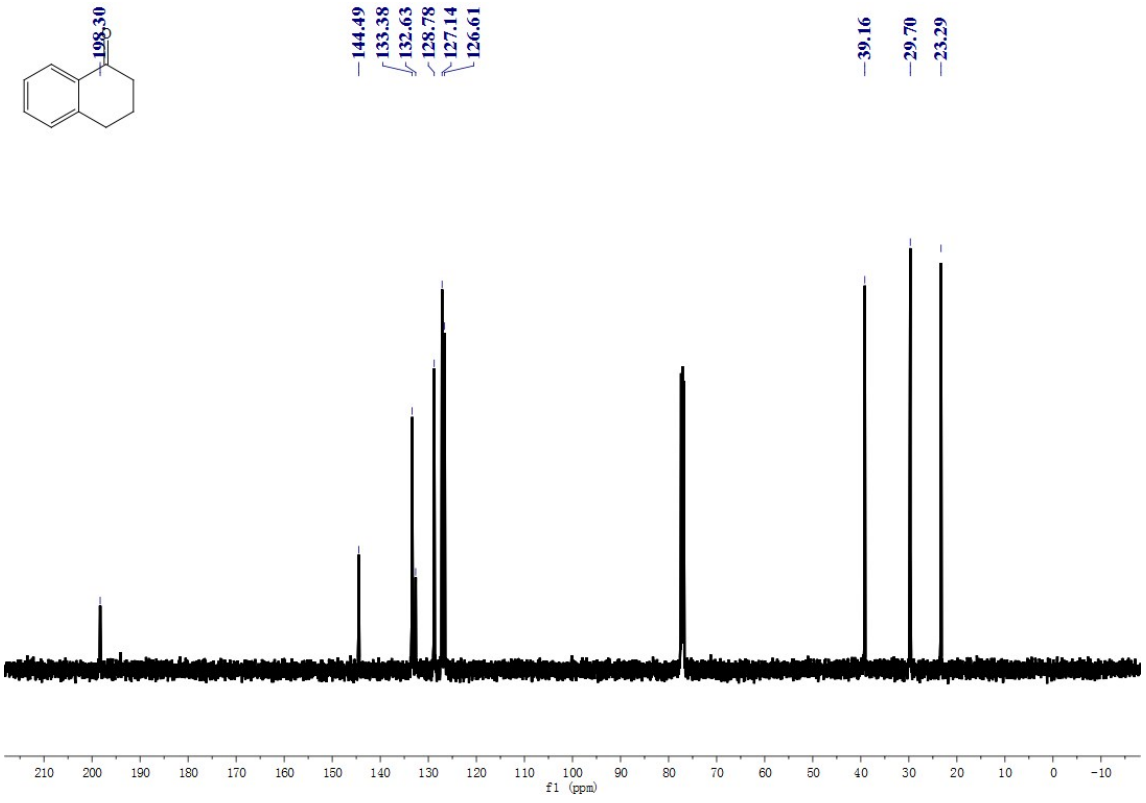
^{1}H NMR spectra of **19** (500 MHz, $CDCl_3$)



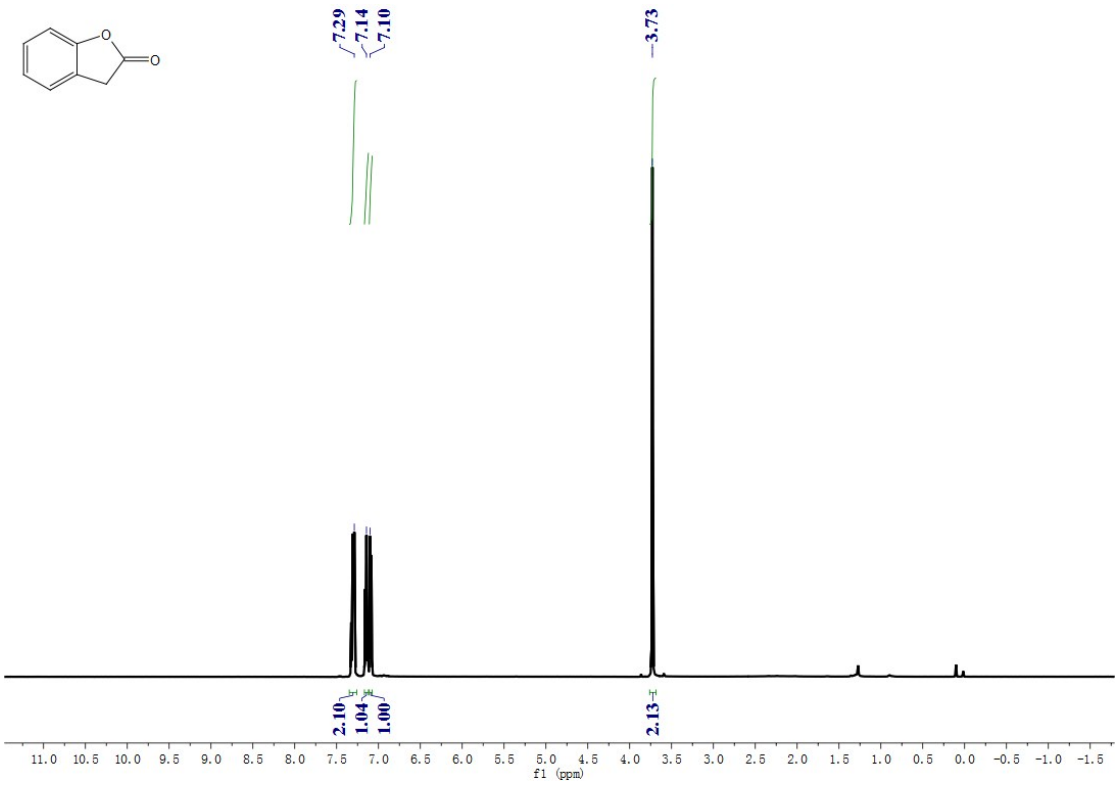
^{13}C NMR spectra of **19** (126 MHz, $CDCl_3$)



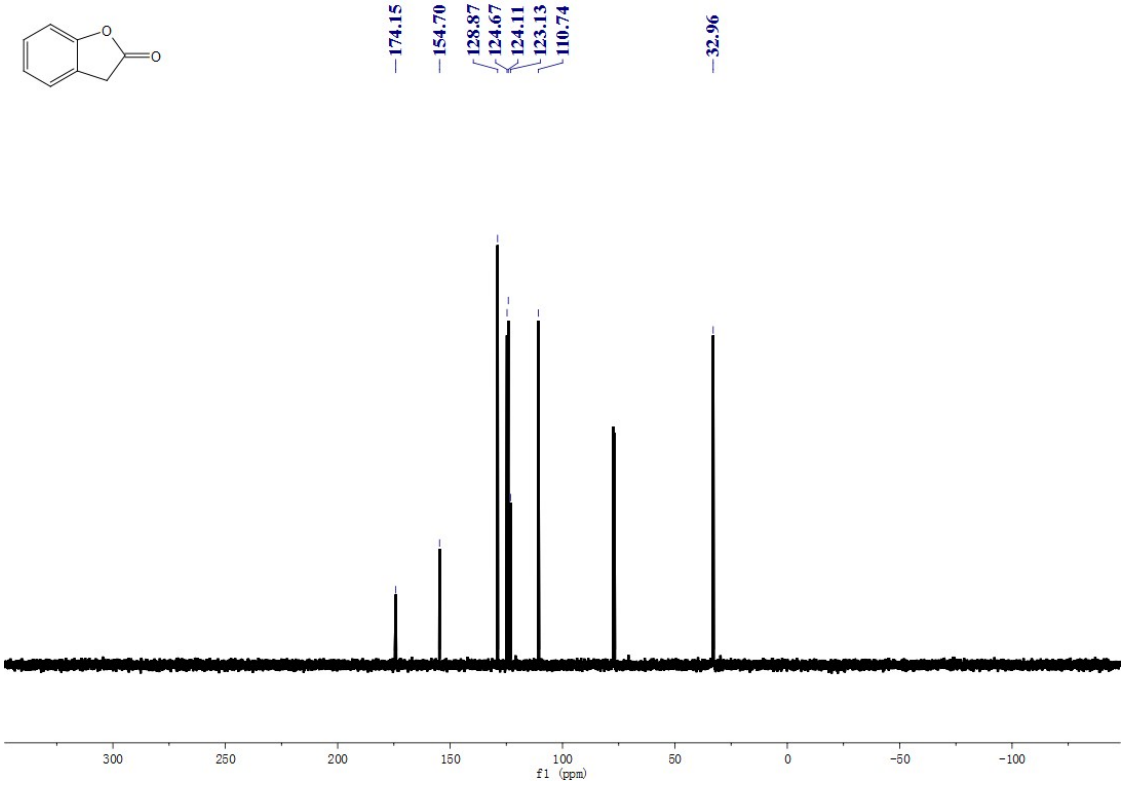
1H NMR spectra of **20** (500 MHz, $CDCl_3$)



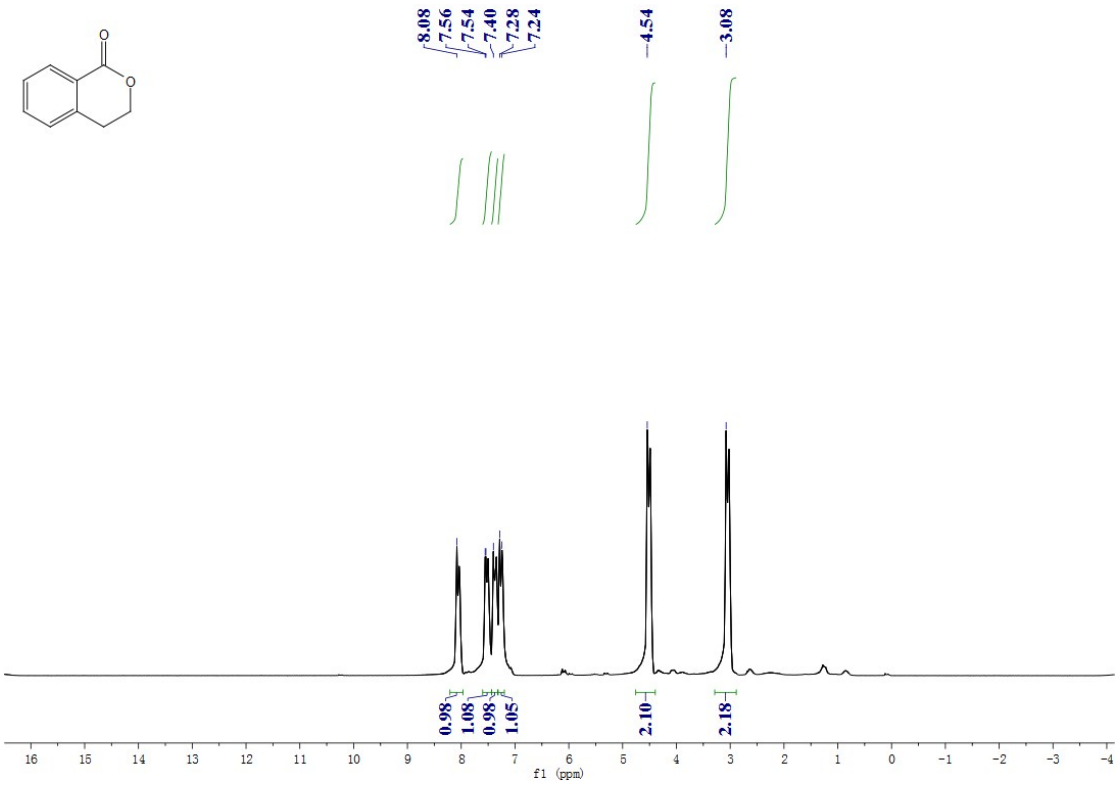
^{13}C NMR spectra of **20** (126 MHz, $CDCl_3$)



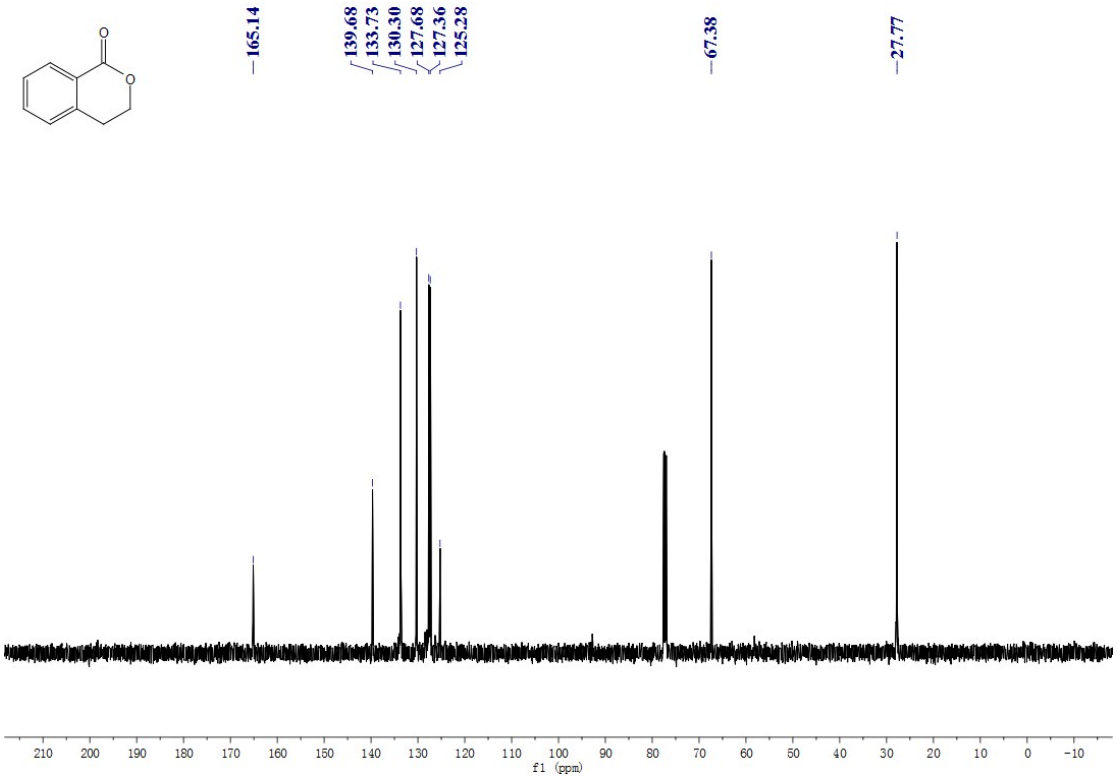
^{1}H NMR spectra of **21** (500 MHz, $CDCl_3$)



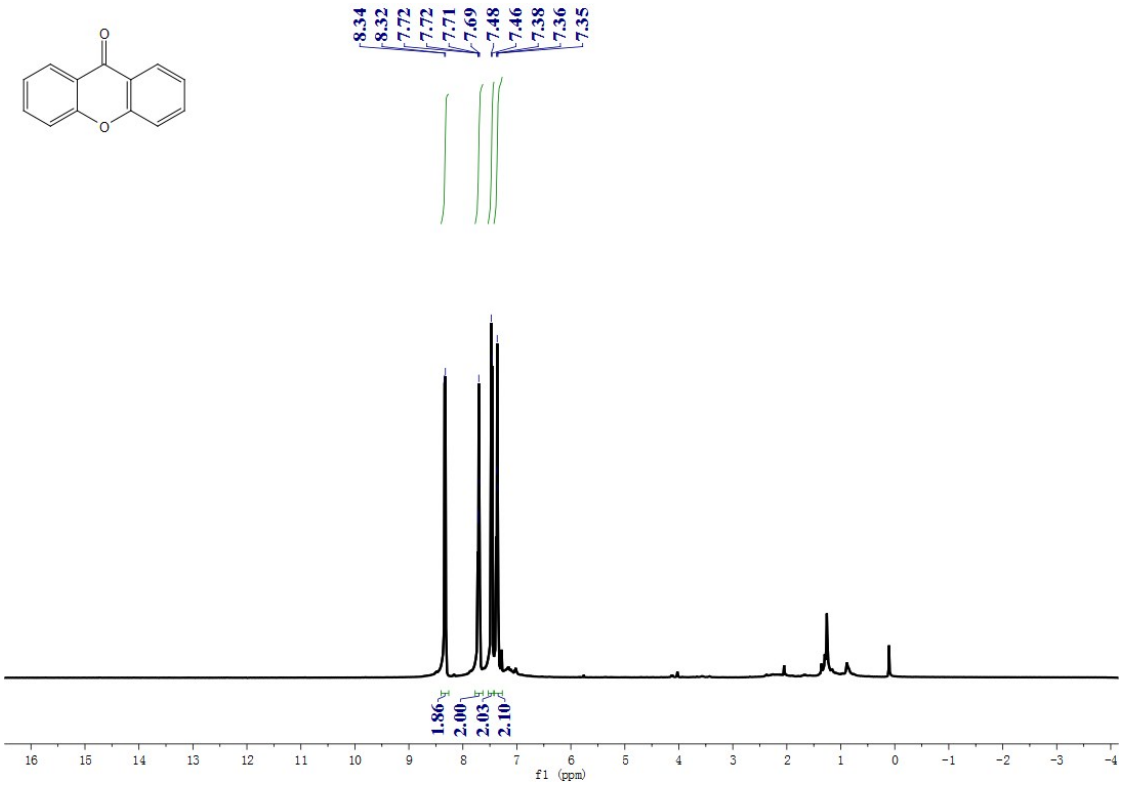
^{13}C NMR spectra of **21** (126 MHz, $CDCl_3$)



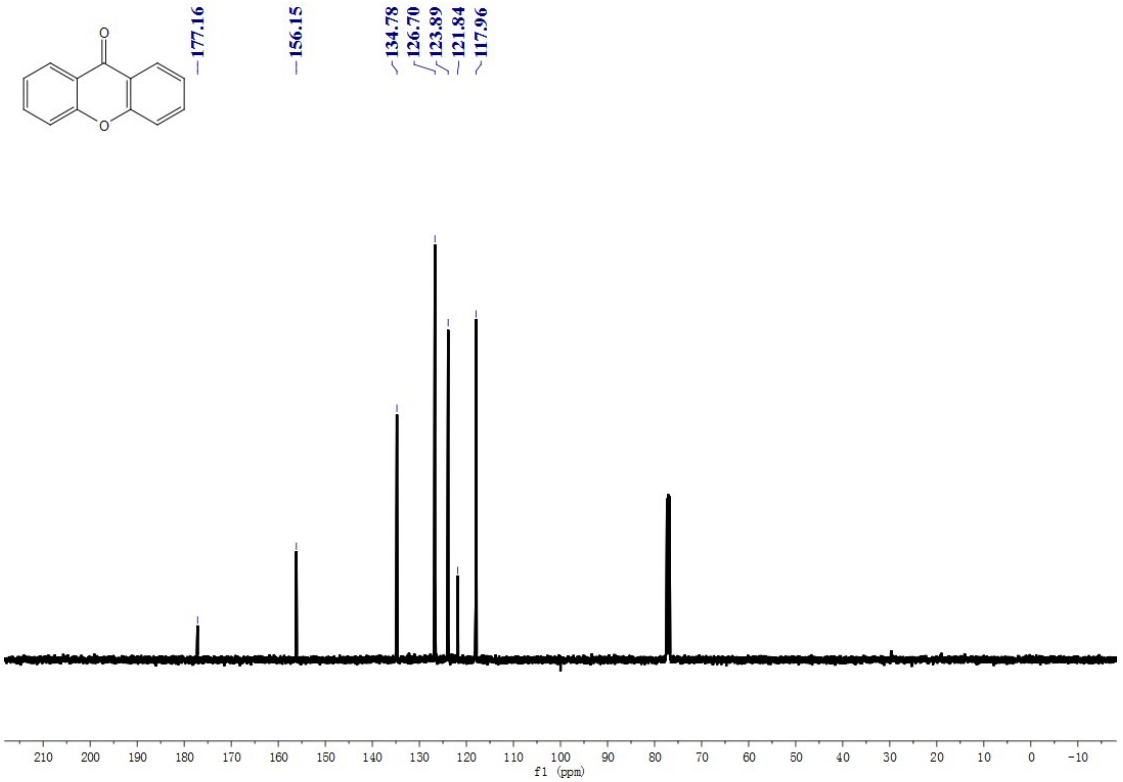
^{1}H NMR spectra of **22** (500 MHz, $CDCl_3$)



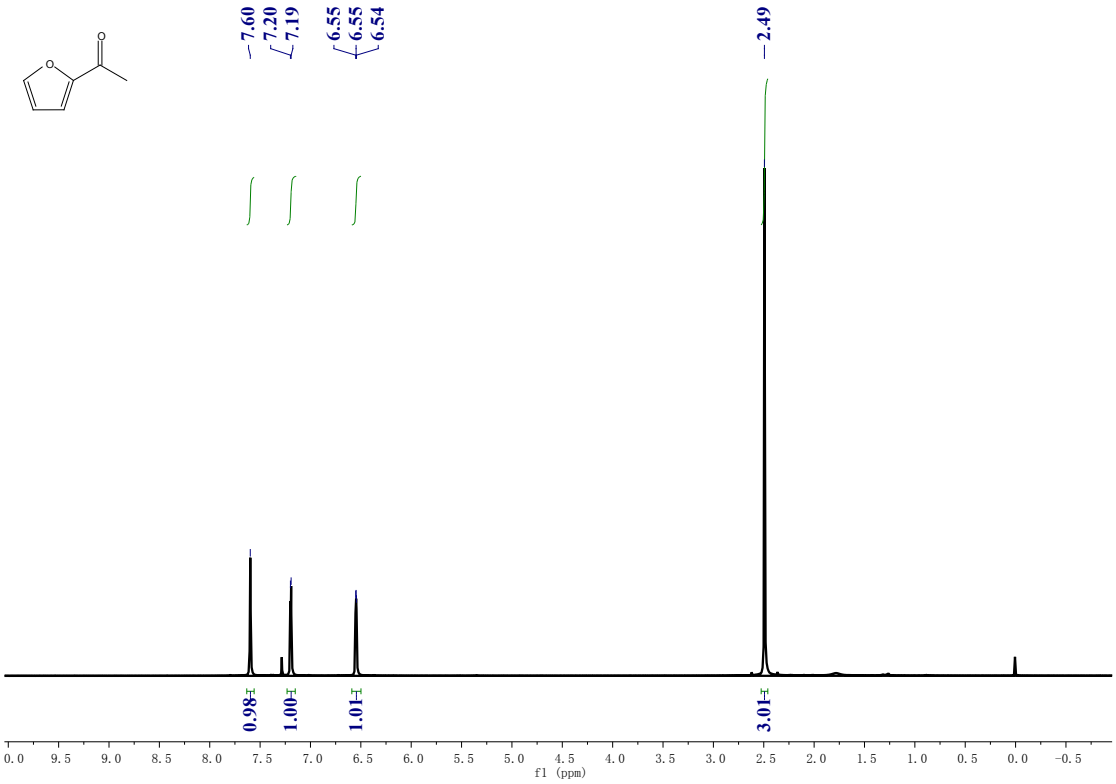
^{13}C NMR spectra of **22** (126 MHz, $CDCl_3$)



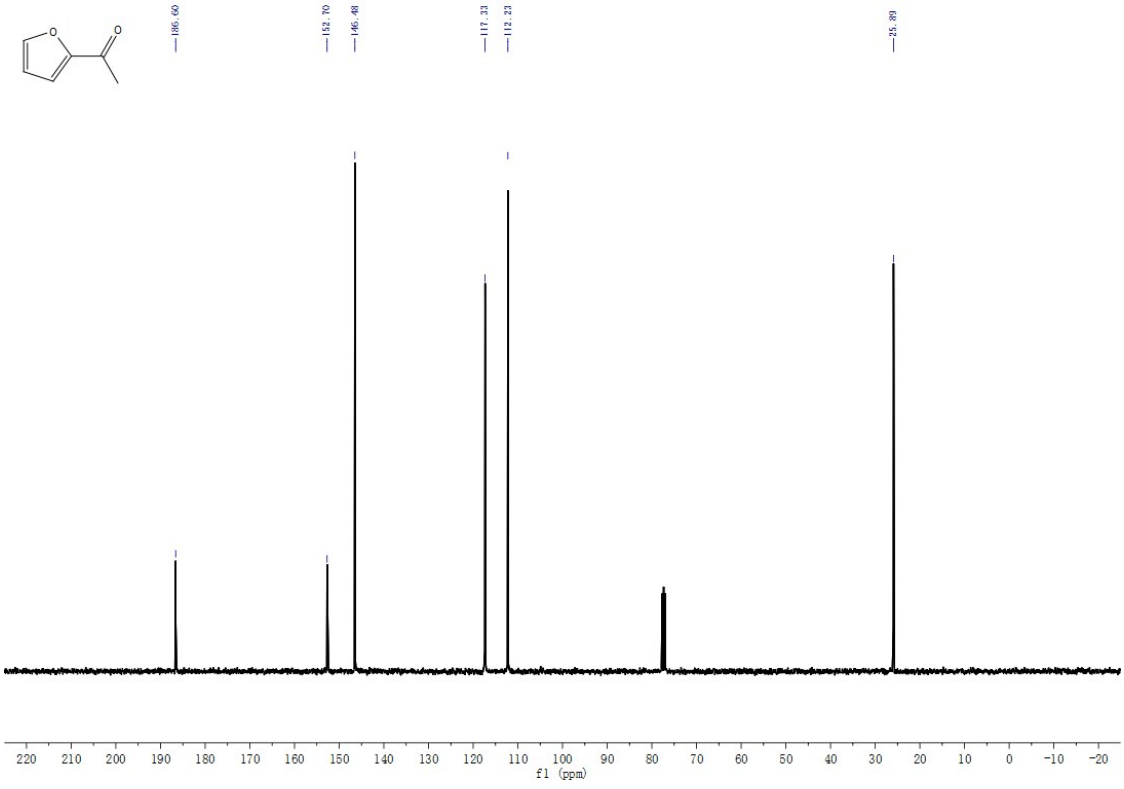
^{1}H NMR spectra of **23** (500 MHz, $CDCl_3$)



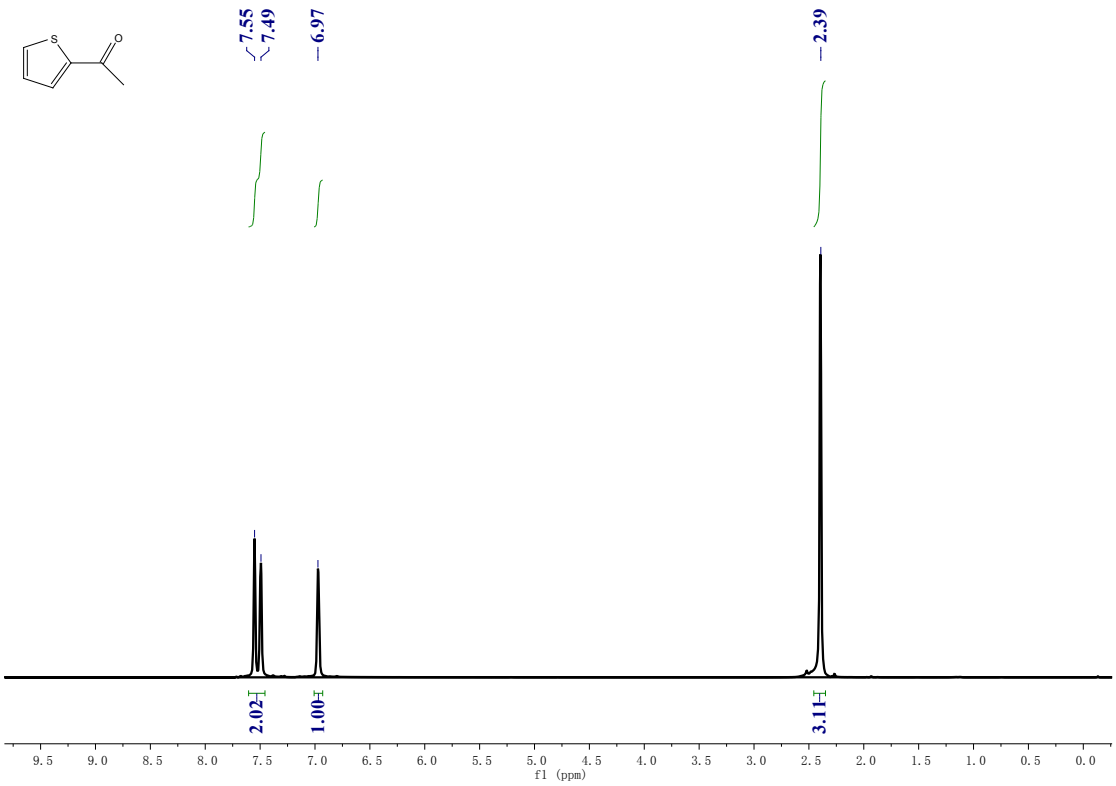
^{13}C NMR spectra of **23** (126 MHz, $CDCl_3$)



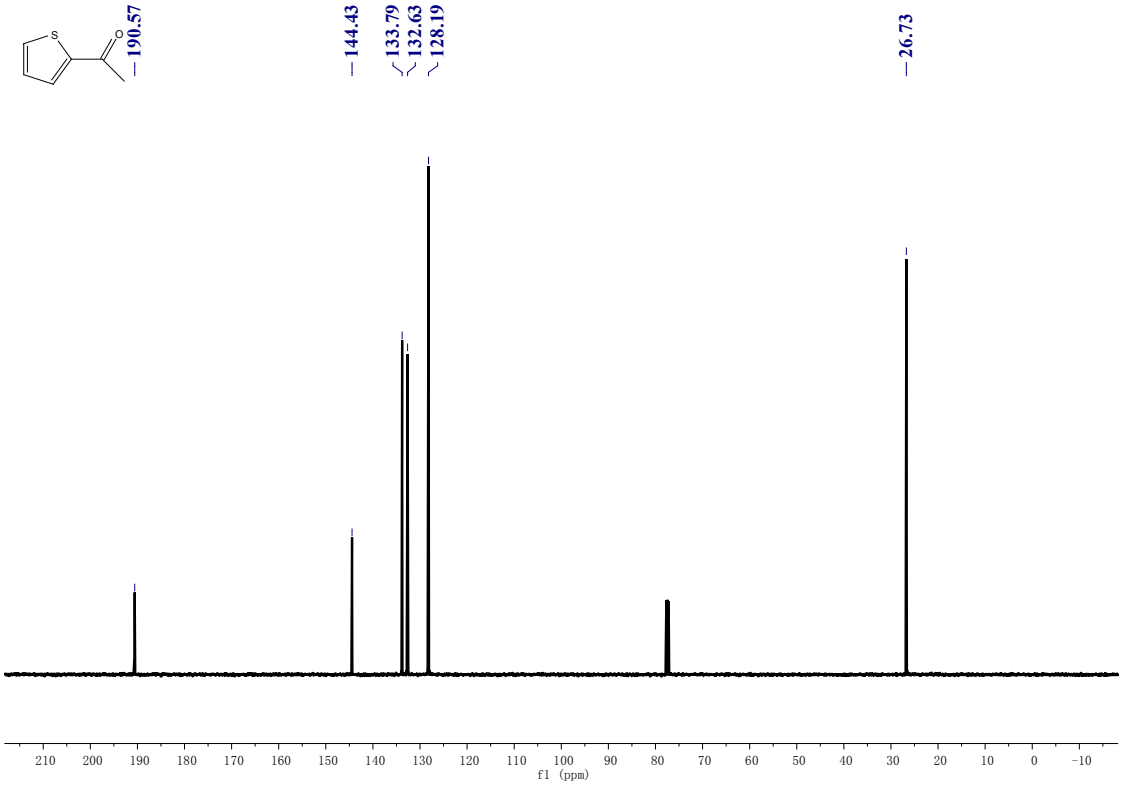
^{1}H NMR spectra of **24** (500 MHz, $CDCl_3$)



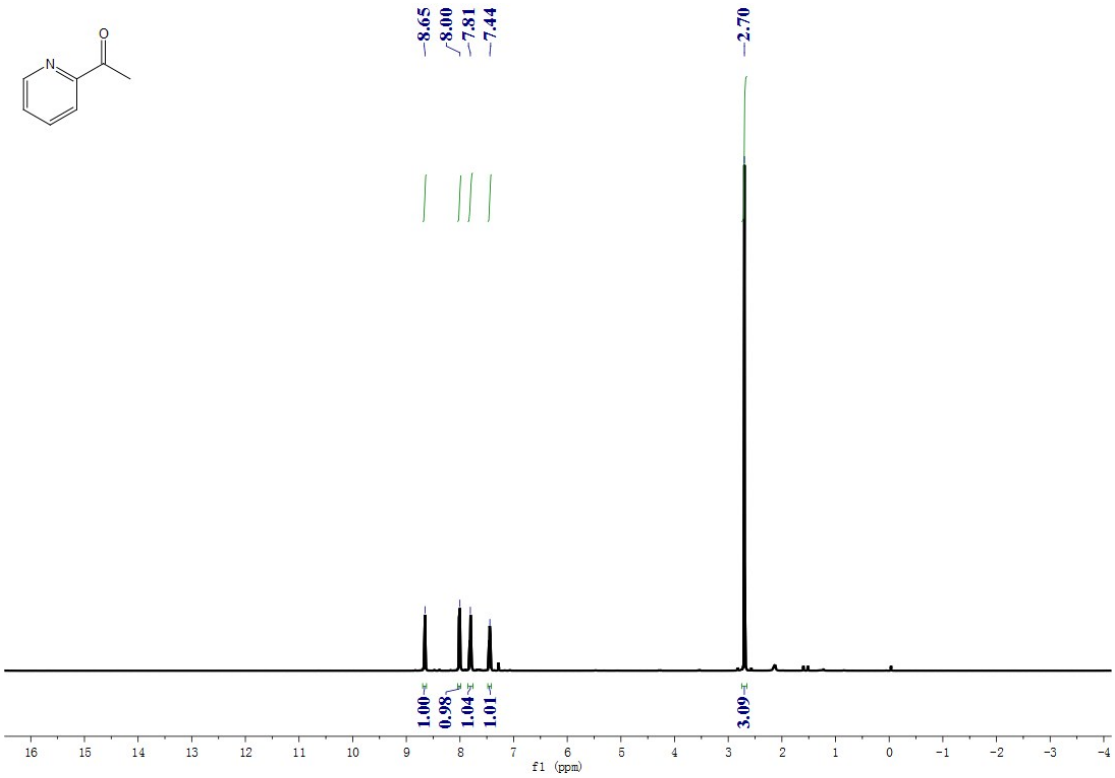
^{13}C NMR spectra of **24** (126 MHz, $CDCl_3$)



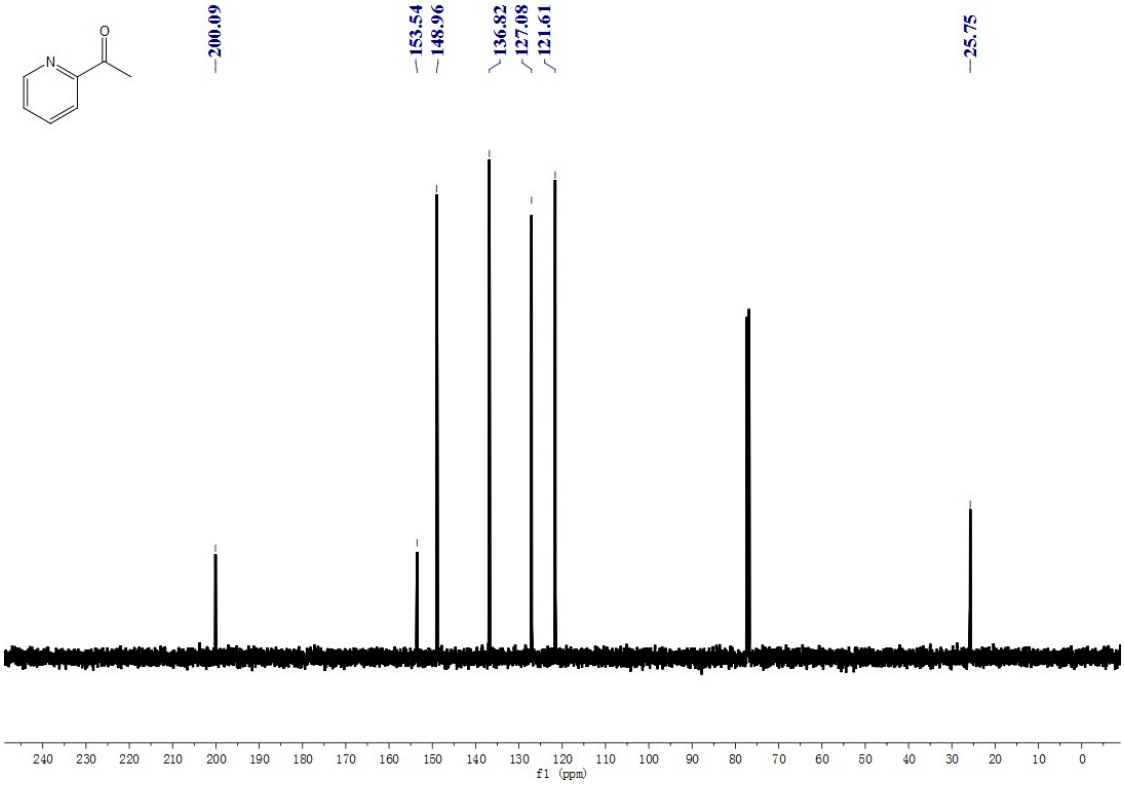
^{1}H NMR spectra of **25** (500 MHz, $CDCl_3$)



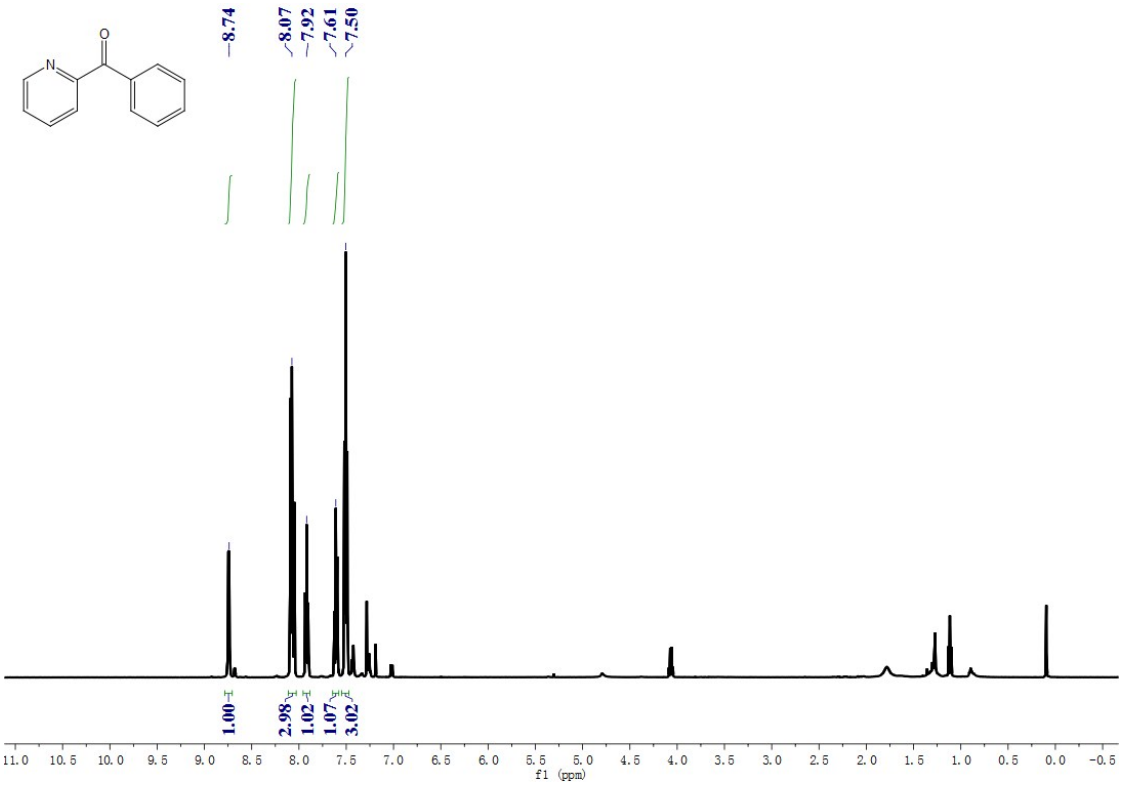
^{13}C NMR spectra of **25** (126 MHz, $CDCl_3$)



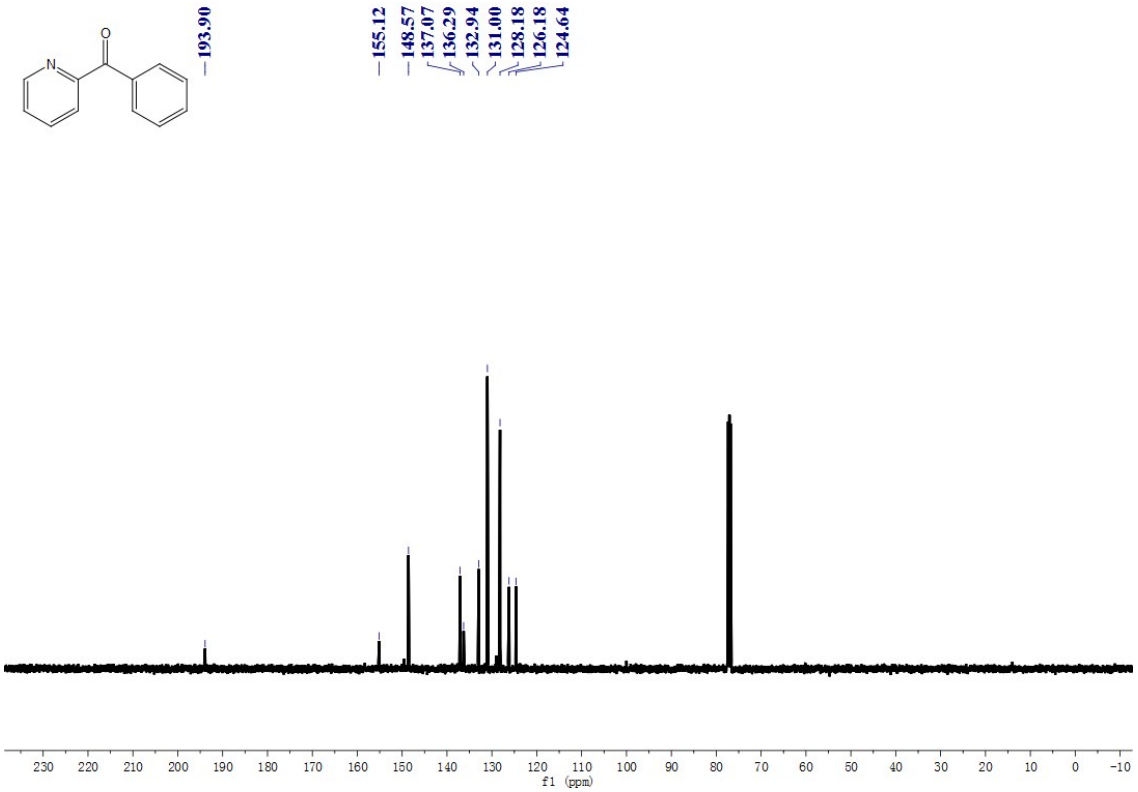
^{1}H NMR spectra of **26** (500 MHz, CDCl3)



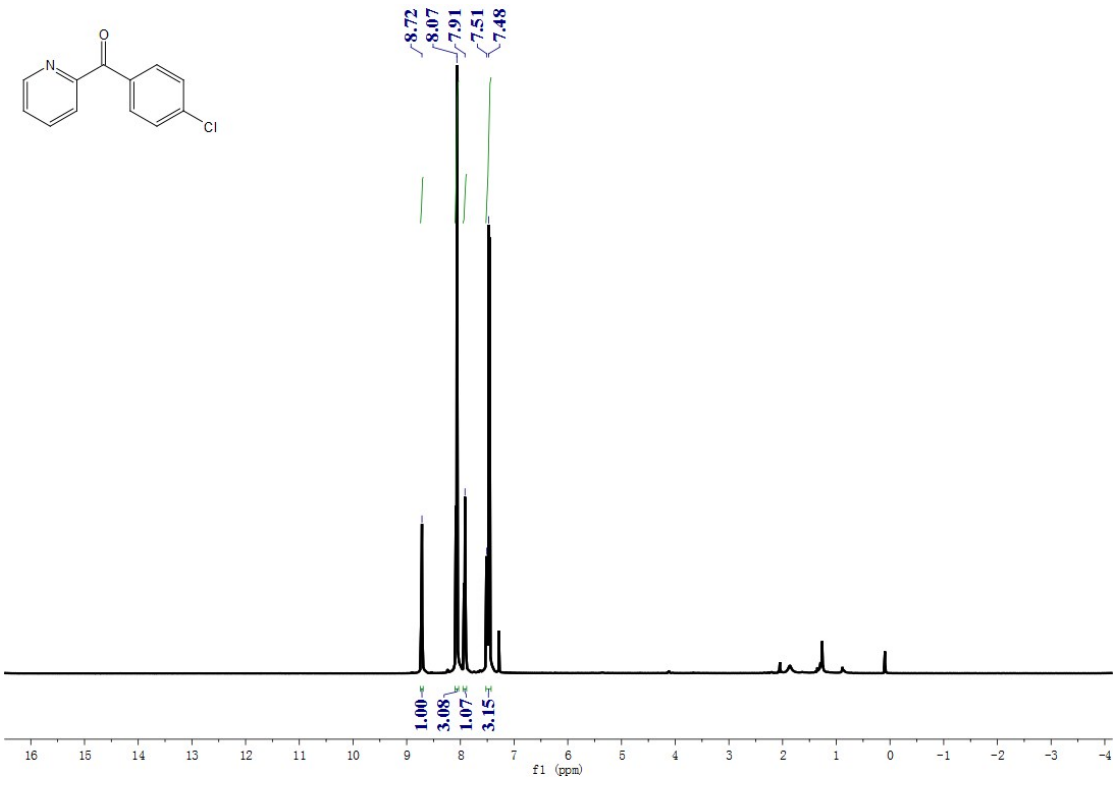
^{13}C NMR spectra of **26** (126 MHz, $CDCl_3$)



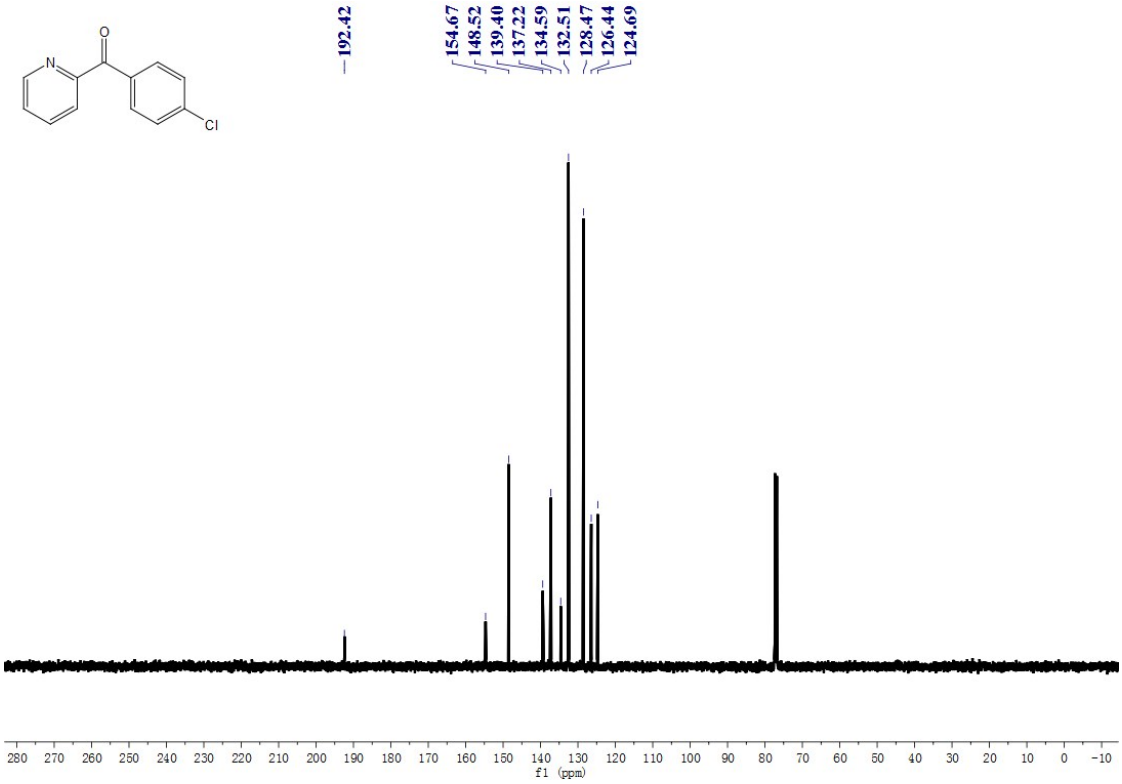
^{1}H NMR spectra of **27** (500 MHz, $CDCl_3$)



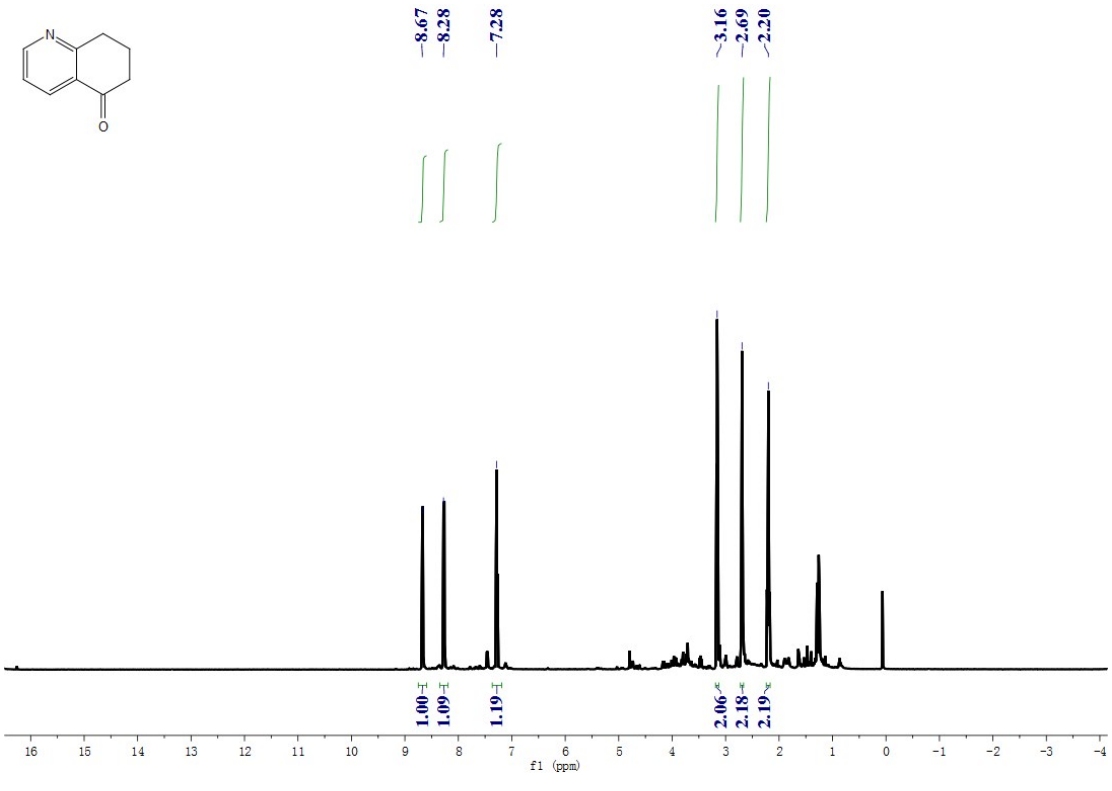
^{13}C NMR spectra of **27** (126 MHz, $CDCl_3$)



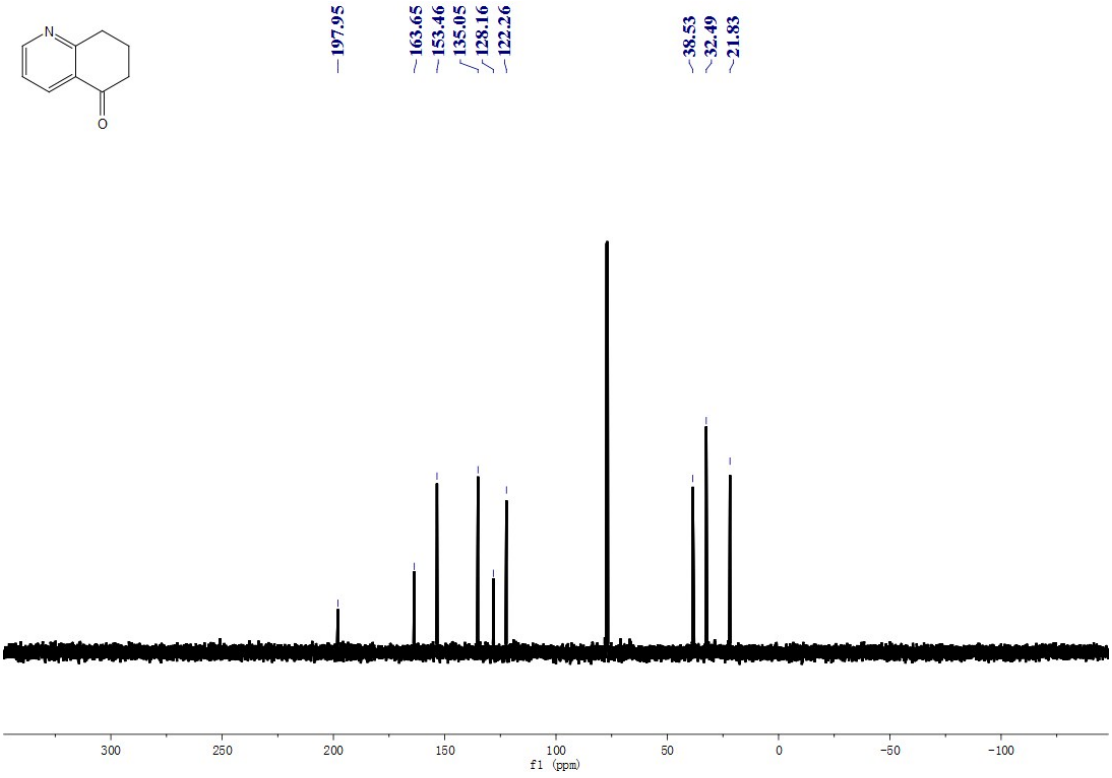
^{1}H NMR spectra of **28** (500 MHz, $CDCl_3$)



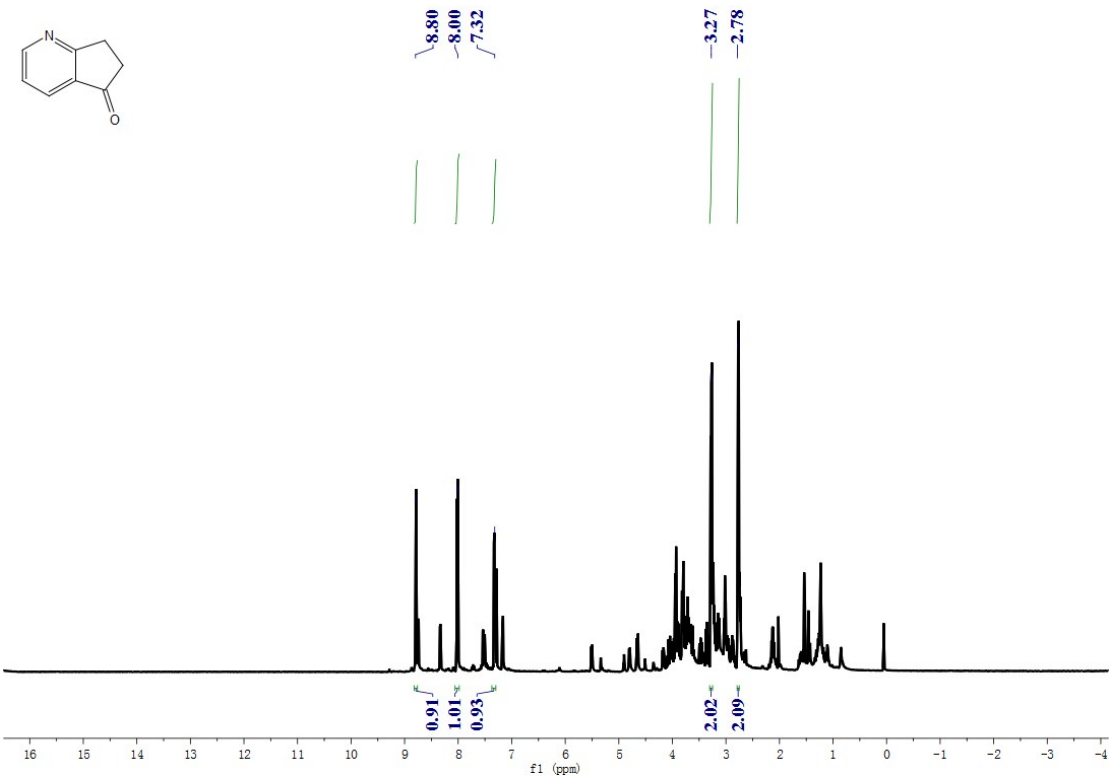
^{13}C NMR spectra of **28** (126 MHz, $CDCl_3$)



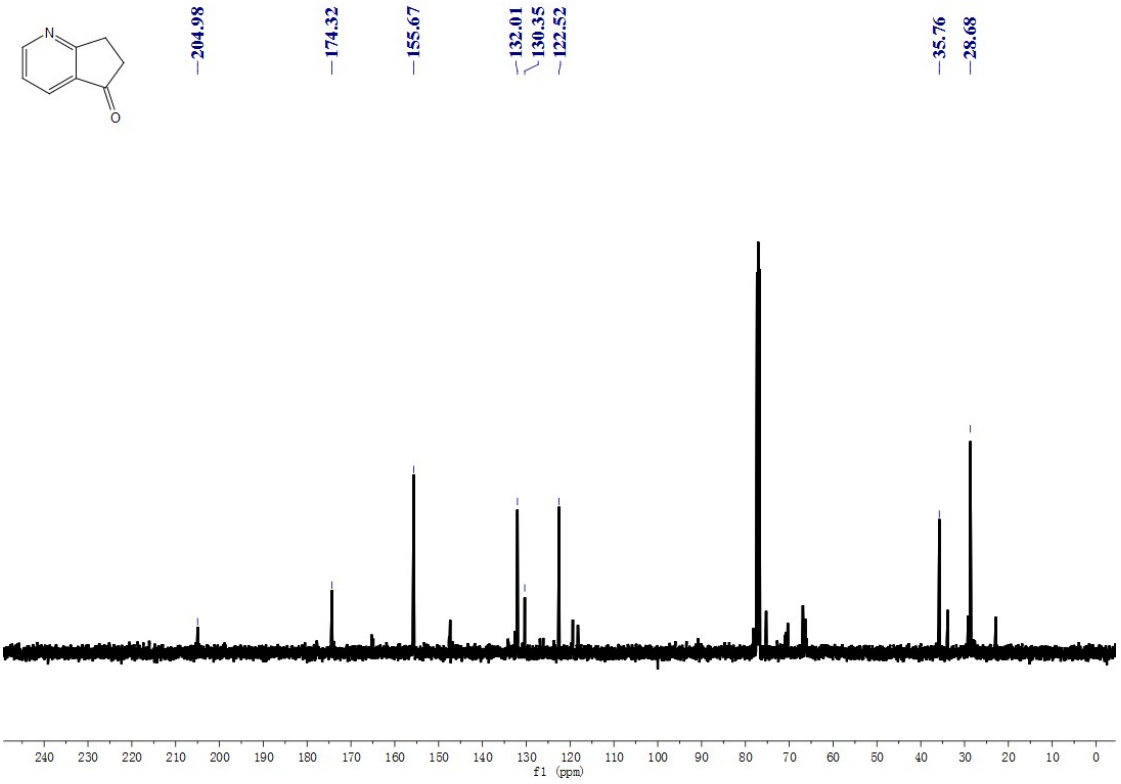
^{1}H NMR spectra of **29** (500 MHz, $CDCl_3$)



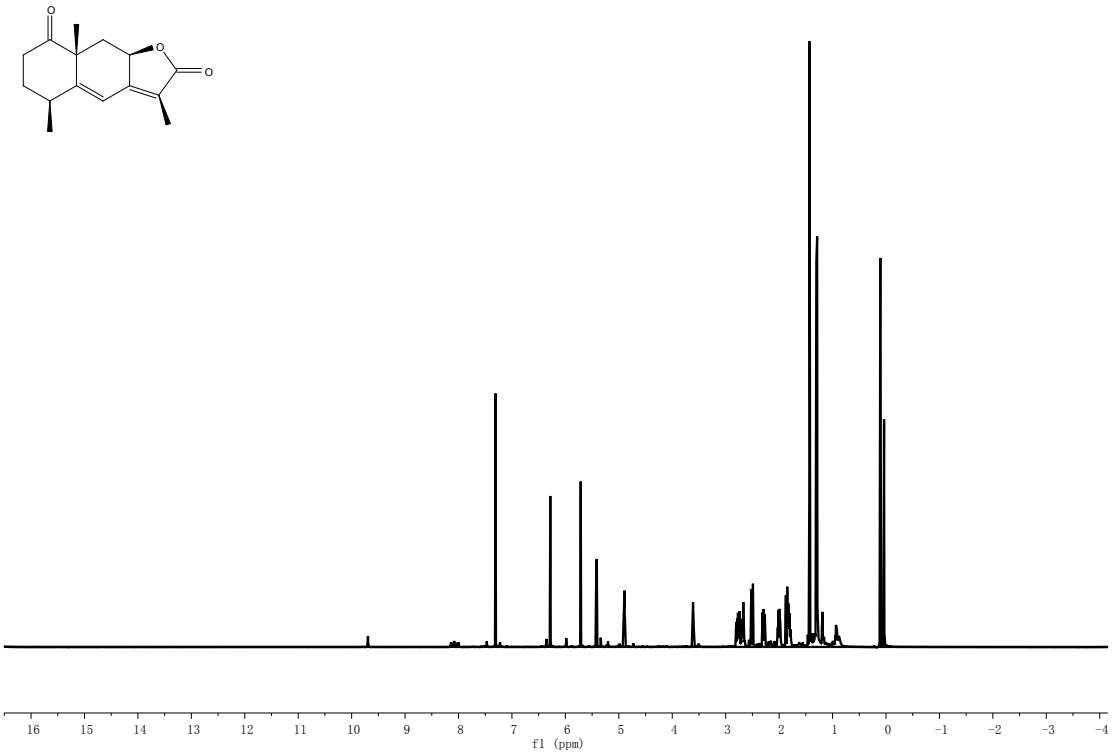
^{13}C NMR spectra of **29** (126 MHz, $CDCl_3$)



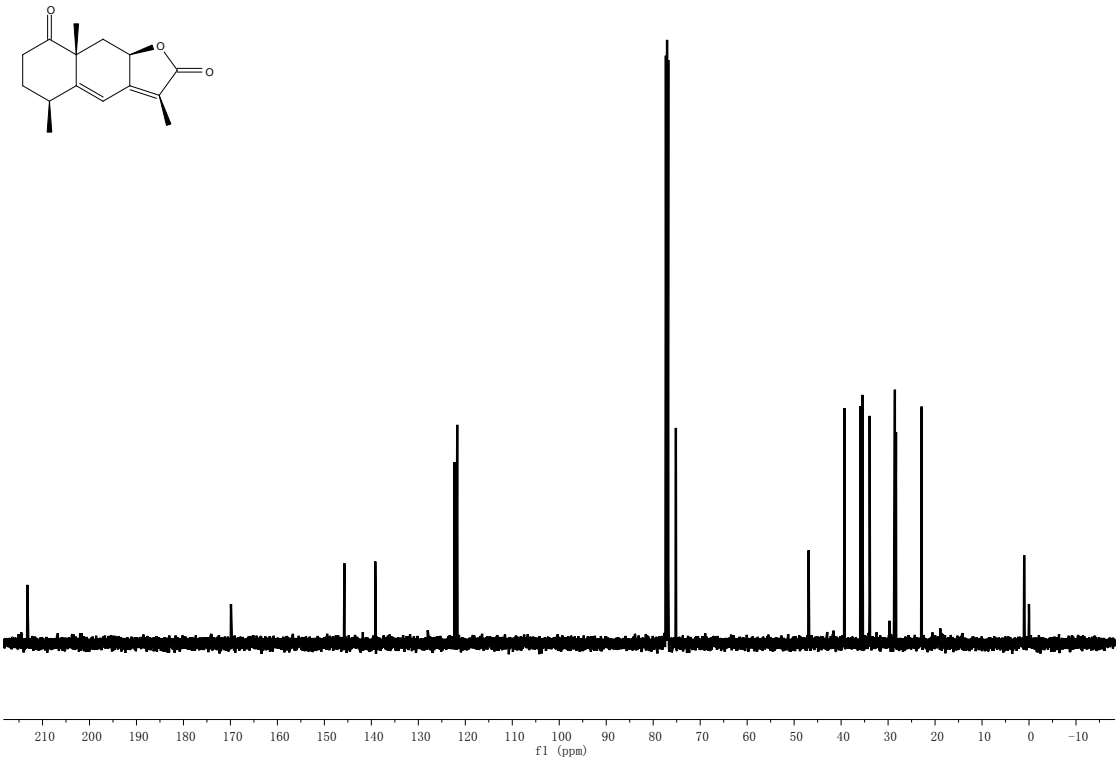
^{1}H NMR spectra of **30** (500 MHz, $CDCl_3$)



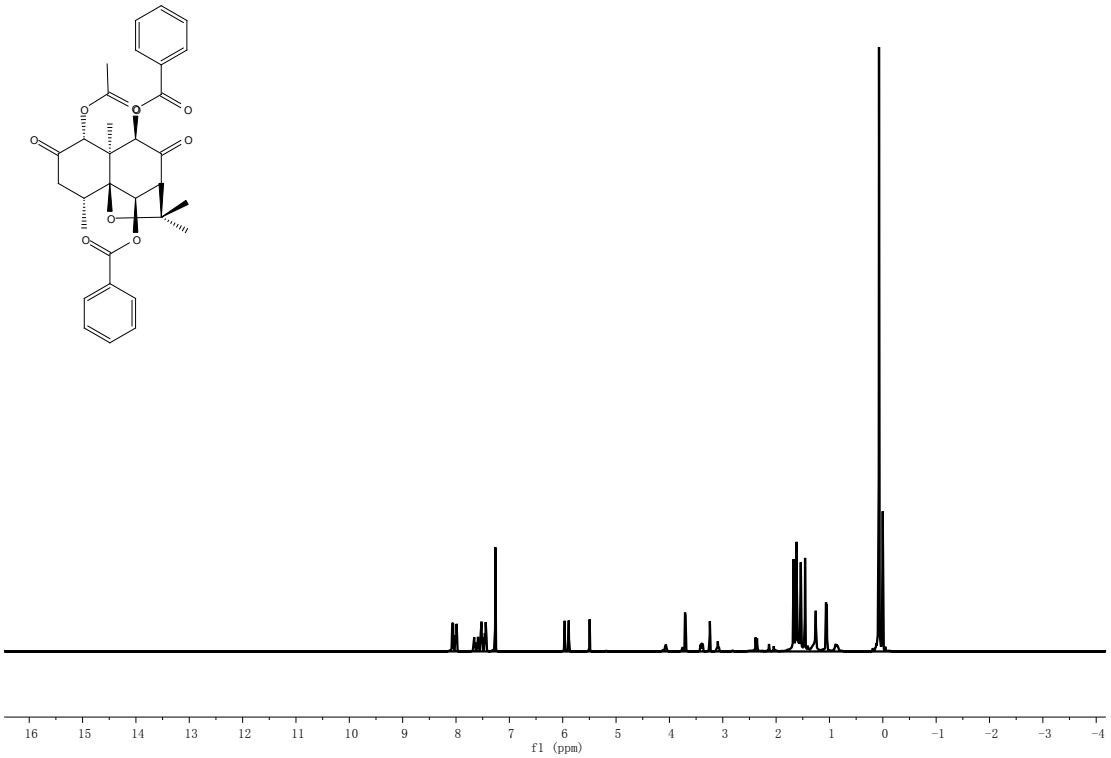
^{13}C NMR spectra of **30** (126 MHz, $CDCl_3$)



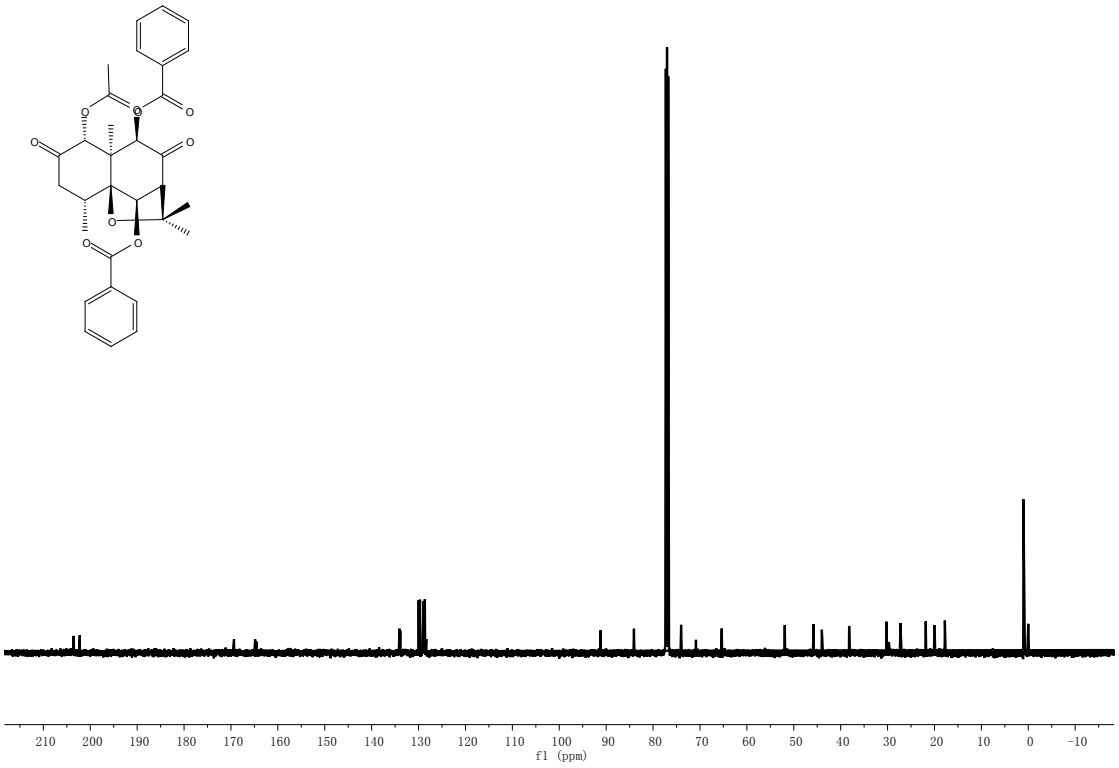
^{1}H NMR spectra of **41** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of **41** (126 MHz, $CDCl_3$)



^{1}H NMR spectra of **42** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of **42** (126 MHz, $CDCl_3$)