Supporting Information

Anderson-Type Polyoxometalate-based Metal-Organic Framework as An Efficient Heterogeneous Catalyst for Selective Oxidation of Benzylic C-H Bonds

Hong-Ru Tan,[a] Xiang Zhou,[b] Tengfei Gong[c], Hanqi You,[a] Qi Zheng,[b] Sheng-Yin Zhao,[*a] Weimin Xuan[*a]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials & College of Chemistry and Chemical Engineering, Donghua University, Shanghai 201620, P. R. China. E-mail: syzhao8@dhu.edu.cn, weiminxuan@dhu.edu.cn

[b] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials & College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China. E-mail: qi.zheng@dhu.edu.cn

[c] Jiaxing Jiayuan Inspection Technology Service Co., Ltd, Building 2, No. 1403， Hongbo Road, Economic and Technological Development Zone, Jiaxing City, Zhejiang Province.

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1. General information

Materials

Unless otherwise noted, all the materials were purchased from commercial suppliers and used without further purification.

Instruments and measurements

NMR (^{1}H and ^{13}C) spectra were recorded using a Bruker AV 400 & 600 MHz spectrometer in DMSO-d_6 and $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were recorded in ppm.

SCXRD (Single crystal X-ray diffraction): Crystal was coated with Paratone Oil on a Cryloop pin were mounted on a Bruker D8 VENTURE Apex II single-crystal x-ray diffractometer equipped with a CCD area detector at 1500 W power (50 kV, 30 mA) to generate Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods with SHELXS-2014 and refined with SHELXL-2014 using OLEX 2.13.[1] All the non-hydrogen atoms except guest molecules were refined by full-matrix least-squares techniques with anisotropic displacement parameters. [1] Crystallographic data for the structures reported in this paper has been deposited in the Cambridge Crystallographic Data Center with CCDC number of 2300360.

Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku D/Max-2550 PC (Japan) diffractometer, using Cu-Kα radiation (λ = 1.541 Å) at 40 kV, 30 mA over the angular range 2θ 3°-50° at a scan rate of 2° min^{-1}.

IR spectra ATR-FTIR spectra were taken on a Nicolet iS□□
(Thermo Fisher Scientific) spectrometer with a diamond ATR crystal as
the window material.
ATR-FTIR spectra were taken on a Nicolet iS□□

(Thermo Fisher Scientific) spectrometer with a diamond ATR crystal as the window material.
ATR-FTIR spectra were taken on a Nicolet iS□□
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ATR-FTIR spectra were taken on a Nicolet iS□□
(Thermo Fisher Scientific) spectrometer with a diamond ATR crystal as the window material.

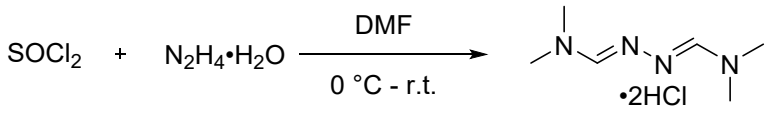
ATR-FTIR spectra were taken on a Nicolet iS50 (Thermo Fisher Scientific) spectrometer with a diamond ATR crystal as the window material in 400-4000cm^{-1}.

Thermogravimetric analysis (TGA) was conducted under a nitrogen atmosphere with a heating rate of 10 °C min^{-1} on a TG 209 F1 Libra® up to 800 °C.

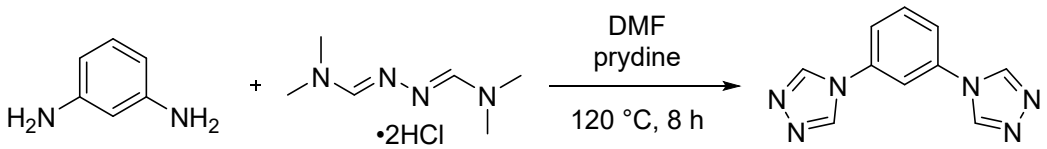
GCMS analysis was carried out on an Agilent 8860 GC system and 5977B GC/MSD system with EI mode.

Elemental analysis (C, H and N) was performed on a VarioEL III elemental analyzer. Cu, Cr and Mo were analyzed using a Prodigy-ICP atomic emission spectrometer.

2. Experimental procedures



N,N-Dimethylformamide Azine Dihydrochloride was synthesized according to the literature.[2] $SOCl_2$ (28.6 mL, 0.4 mol) was added with stirring to freshly distilled DMF (150 mL) in ice bath. After 24 h, the mixture of 85 % hydrazine solution (5 mL, 0.1 mol) and DMF (20 mL) were added into the reaction in ice bath. The mixture was then stirred at r.t. for 2 days and the white precipitate was collected by filtration and washed with DMF and Et_2O. Yield: 17.5g (82%).^{1}H NMR (400 MHz, DMSO-d_6) δ 6.30 (s, 2H), 1.19 (br, 12H).



1,3-di-(1,2,4-triazol-4-yl)benzene (**L**) was synthesized according to the literature.[3] A mixture of 2.5 g m-phenylenediamine (23.1 mmol), 10.4 g N,N-dimethylformamide azine (73.1 mmol) in DMF (25 mL) and pyridine (25 mL) was heated at 120 ℃ for 8 h. The reaction mixture was cooled to room temperature and the white precipitate was collected by filtration and washed with CH_3CN. Yield: 3.43 g (71%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.25 (s, 4H), 8.17 (s, 1H), 7.82 - 7.80 (m, 2H), 7.78 - 7.74 (m, 1H).

$Na_3[CrMo_6O_{18}(OH)_6]$ (Na_3**CrMo$_6$**) was synthesized according to the literature method.[4] The pH of a solution containing 145 g $Na_2MoO_4{\cdot}2H_2O$ (0.6 mol) in 300 mL of water was adjusted to 4.5 with concentrated HNO_3. A second solution was made by dissolving 40.0 g $Cr(NO_3)_3{\cdot}9H_2O$ (0.1 mol) in 40 mL water. Half of each solution was mixed together, and the mixture was boiled for 1 min and filtered while hot. The filtrate was set aside in a 1500 mL beaker for 2 weeks before the precipitate was filtered off and washed several times with cold water. The pink crystal was dried in the air. Yield: 38.5 g (32.2% based on Cr). FI-IR (cm^{-1}): 3460, 3125, 1647, 1617, 963, 927, 886, 814, 740, 630.

Synthesis of **POMOF-1** $H_2[Cu_4(OH)_2(H_2O)_7\mathbf{L}_2\{CrMo_6\}_2]{\cdot}6H_2O$. $CuCl_2{\cdot}2H_2O$ (5.38 mg, 0.04 mmol), **L** (4.24mg, 0.02 mmol) and $Na_3[CrMo_6O_{18}(OH)_6]$ (17.96 mg, 0.015 mmol) were added into 5 mL H_2O. The solution was stirred and adjust pH = 3.6 by 1 M HCl. Then the mixture was heated in a Teflon-lined stainless steel reactor at 140 ºC for 3 days. After cooling to room temperature, green bulk crystals were obtained by filtration and washed with DMSO, H_2O, EtOH and Et_2O. Yield: 14.3 mg. 32.4% based on Cr. Elemental analysis for **POMOF-1**: C 8.16%, H 1.56%, N 5.71%, Cr 3.54%, Mo 39.16%, Cu 8.65%; found: C 8.01%, H 1.77%, N 5.62%, Cr 3.56%, Mo 39.03%, Cu 8.77%. FT-IR (cm^{-1}): 3369, 2960, 2872, 1637, 1479, 1381, 1116, 1026, 935, 911, 894, 638, 563.

3. Crystallographic data and structure refinements

Table S1 Crystallographic data

Name	**POMOF-1**

Empirical formula	C20 H52.78 Cr2 Cu4 Mo12 N12 O61.39
Formula weight	2951.18
Temperature (K)	150
Wave length (Å)	0.71073
Crystal system	Triclinic
Space group	P1
a (Å)	10.2257(9)
b (Å)	14.3320(16)
c (Å)	14.3731(14)
α (deg)	106.760(4)°
β (deg)	110.599(4)°
γ (deg)	105.352(4)°
Volume ($Å^3$)	1723.2(3)
Z, Dcalc (Mg/m^3)	1, 2.844
Absorption coefficient (mm^{-1})	3.736
F (000)	1414
θ range (deg)	2.148 to 25.462
index range (deg)	-12<=h<=12, -17<=k<=17, -17<=l<=17
Data completeness	99.8 %
Reflections collected / unique	44837/12055 [R(int) = 0.1220]
Data / restraints / parameters	12055 / 5285 / 1010
Goodness-of-fit on F^2	1.022
R_1, wR_2 ($I > 2\sigma(I)$)	0.0506, 0.1169
R_1, wR_2 (all data)	0.0587, 0.1251
Largest diff. peak and hole (e $Å^{-3}$)	1.279 and -1.570

$R_1 = \Sigma||Fo|-|Fc||/\ \Sigma|Fo|$. $wR_2 = [\Sigma[\ w\ (Fo^2-Fc^{\ 2})^2] / \Sigma[\ w\ (Fo^{\ 2})^2]]^{1/2}$

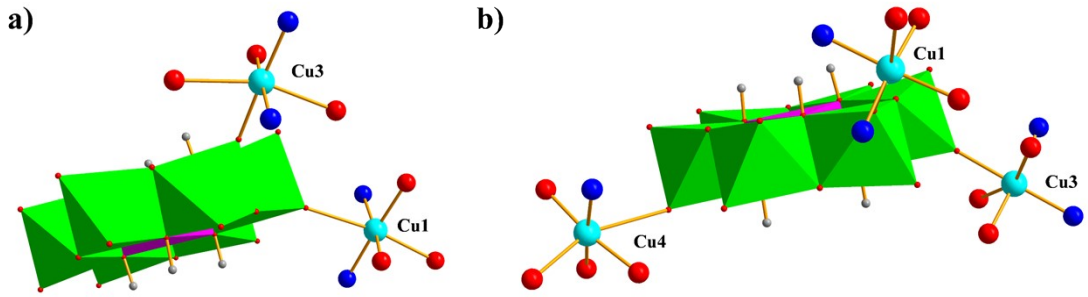


Figure S1. Connection modes of two kinds of $\{CrMo_6\}$ clusters in **POMOF-1**

4. Characterization of POMOF-1

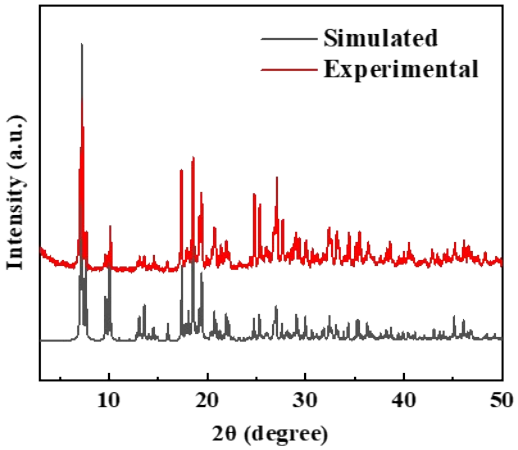


Figure S2. PXRD pattern of **POMOF-1**

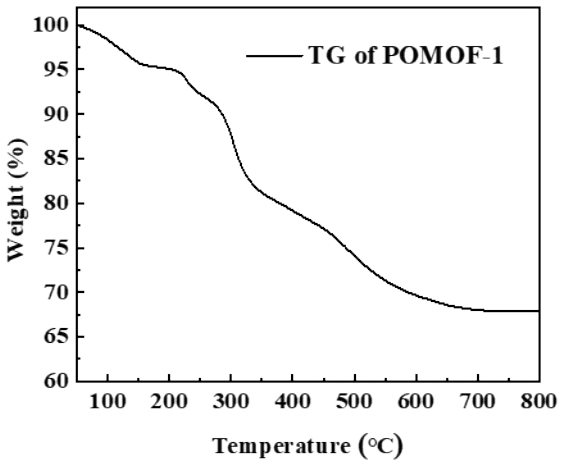


Figure S3. The TGA Curve of **POMOF-1**

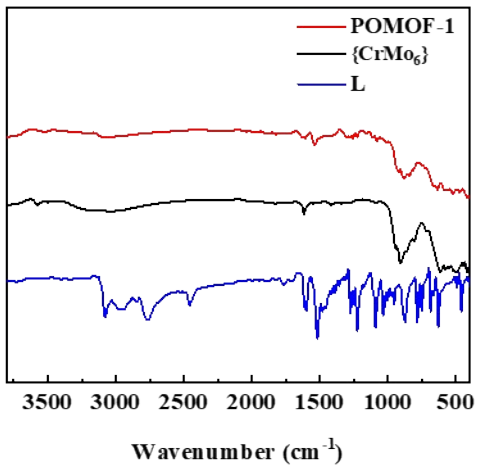
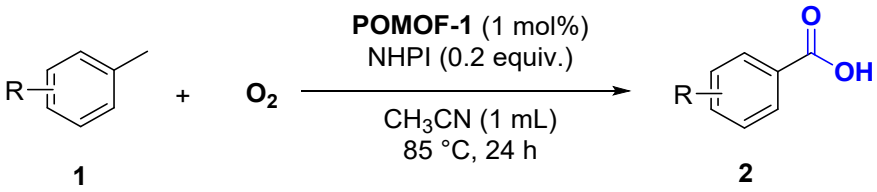


Figure S4. The FT-IR spectra of **L**, {$CrMo_6$} and **POMOF-1**

5. Catalytic performance of POMOF-1

General methods for oxidation reaction of methylarenes.

POMOF-1 (0.1 mol%), NHPI (0.04 mmol), methylarenes **1** (0.2 mmol) and CH_3CN (1 mL) were added into seal tube, which was subsequently charged with 1 atm O_2. Then the reaction was heated at 85 °C and kept stirring for 24 h. The reactor was cooled to room temperature, the catalyst was centrifuged and the supernatant was diluted with ethyl acetate. The conversion of methylarenes **1** and yields of product aromatic acid **2** were determined by gas chromatography-mass spectrometry (GC-MS) with hexadecane as internal standard. Then, the reaction was quenched with H_2O and extracted with ethyl acetate. Filtering out the insoluble substances, the organic phases were washed with H_2O, and dried over anhydrous Na_2SO_4. The organic phases were filtered and concentrated under reduced pressure and the crude products were purified by silica gel column chromatography (eluent: ethyl acetate-petroleum ether, 1: 10-5: 1) to yield the pure products. The products were characterized by ^1H NMR, ^{13}C NMR analyses.



General methods for oxidation reaction of alkylarenes.

POMOF-1 (0.1 mol%), alkylarenes **4** (0.2 mmol)and CH_3CN (1 mL) were added into seal tube, which was subsequently charged with 1 atm O_2. Then the reaction was heated at 85 °C and kept stirring for 24 h. The reactor was cooled to room temperature, the catalyst was centrifuged and the supernatant was diluted with ethyl acetate. The conversion of alkylarenes **4** and yields of product aromatic ketones **5** were determined by gas chromatography-mass spectrometry (GC-MS) with hexadecane as internal standard. Then, the reaction was quenched with H_2O and extracted with ethyl acetate. Filtering out the insoluble substances, the organic phases were washed with H_2O, and dried over anhydrous Na_2SO_4. The organic phases were filtered and concentrated under reduced pressure and the crude products were purified by silica gel column chromatography (eluent: ethyl acetate-petroleum ether, 1:100-500) to yield the pure products. The products were characterized by ^1H NMR, ^{13}C NMR analyses.

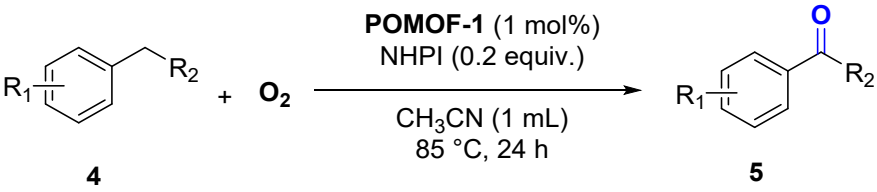
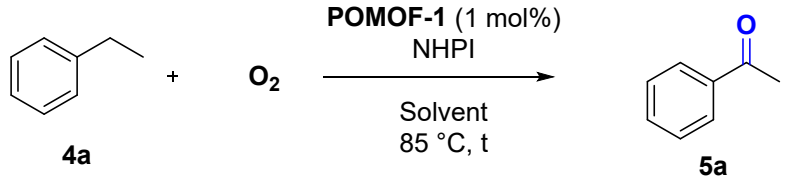


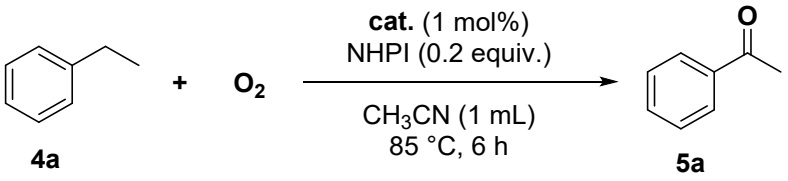
Table S2. Oxidation reaction of ethylbenzene (**4a**) with **POMOF-1**



Entry	NHPI	t/h	Solvent	Yields%
1	0.2 equiv.	24	CH_3CN	91
2	0.2 equiv.	12	CH_3CN	92
3	0.2 equiv.	6	CH_3CN	90
4	0.1 equiv.	6	CH_3CN	58
5[a]	0.2 equiv.	6	CH_3CN	70
6	0.2 equiv.	6	EtOH	20
7	0.2 equiv.	6	Acetone	42
8	0.2 equiv.	6	THF	trace
9	0.2 equiv.	6	DCM	27
10	0.2 equiv.	6	DMF	19
11	0.2 equiv.	6	DMSO	28

Reaction condition: **POMOF-1** (1 mol%), NHPI, Solvent (1 mL), ethylbenzene **4a** (0.2 mmol) in O_2 atmosphere (1 atm) at 85 °C. Yields were determined by GC-MS and hexadecane as internal standard. [a]Reaction temperature: 65 °C.

Table S3. Control experiments for oxidation reaction of ethylbenzene (**4a**)



Entry	Cat.	**5** yield%
1	**POMOF-1**	90
2	none	46
3	$CuCl_2$	65
4	$\{CrMo_6\}$	50
5	**L**	39
6	$CuCl_2$ + **L**	70
7	$CuCl_2$ + $\{CrMo_6\}$	67
8	$\{CrMo_6\}$ + **L**	47
9	$CuCl_2$ + **L** + $\{CrMo_6\}$	69

Reaction condition: Cat. (1 mol%), NHPI (0.2 equiv.), ethylbenzene **4a** (0.2 mmol) and CH_3CN (1 mL) in O_2 (1 atm) at 85 °C for 6 h. Yields were determined by GC-MS and hexadecane as internal standard.

6. Recycling experiment of POMOF-1.

The reusability of the catalyst **POMOF-1** was tested using toluene (**1a**) and ethylbenzene (**4a**) as the substrates. After the completion of the catalytic reaction, the catalyst was recovered by filtration and then washed with CH_3OH and Acetone. The recovered **POMOF-1** was dried under vacuum and reused for the next run under the same conditions.

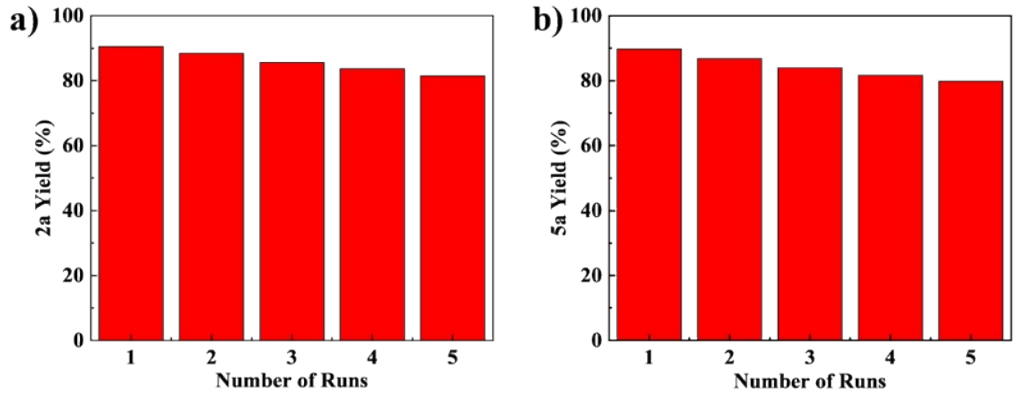


Figure S5. Recyclability of **POMOF-1** for **a)** oxidation reaction of toluene and **b)** oxidation reaction of ethylbenzene

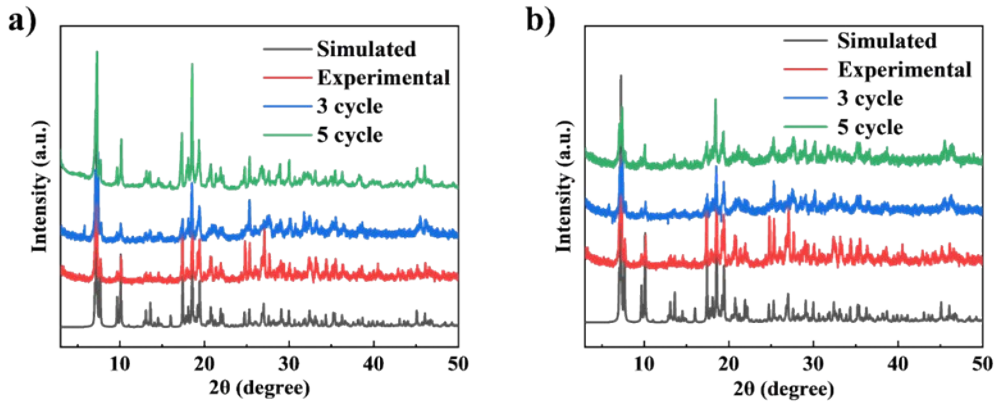


Figure S6. PXRD patterns of the recovered catalyst **POMOF-1** after 3 and 5 cycles in **a)** oxidation reaction of toluene and **b)** oxidation reaction of ethylbenzene.

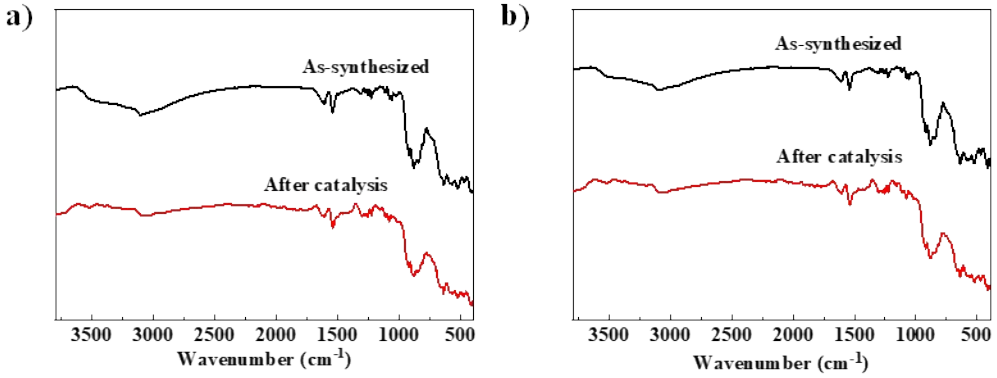


Figure S7. FT-IR spectra of the recovered catalyst **POMOF-1** after 5 cycles in **a)** oxidation reaction of toluene and **b)** oxidation reaction of ethylbenzene.

Table S4. ICP Analysis of **POMOF-1** and filtrate after catalysis.

Analytes	Cu (%)	Cr (%)	Mo (%)
Calculated values for **POMOF-1**	8.65	3.54	39.16
Experimental values for **POMOF-1**	8.77	3.56	39.03
POMOF-1 recovered after oxidation of toluene	8.58	3.39	38.72
POMOF-1 recovered after oxidation of ethylbenzene	8.63	3.45	38.78
Filtrate after oxidation of toluene	< 0.01	< 0.01	< 0.01
Filtrate after oxidation of ethylbenzene	< 0.01	< 0.01	< 0.01

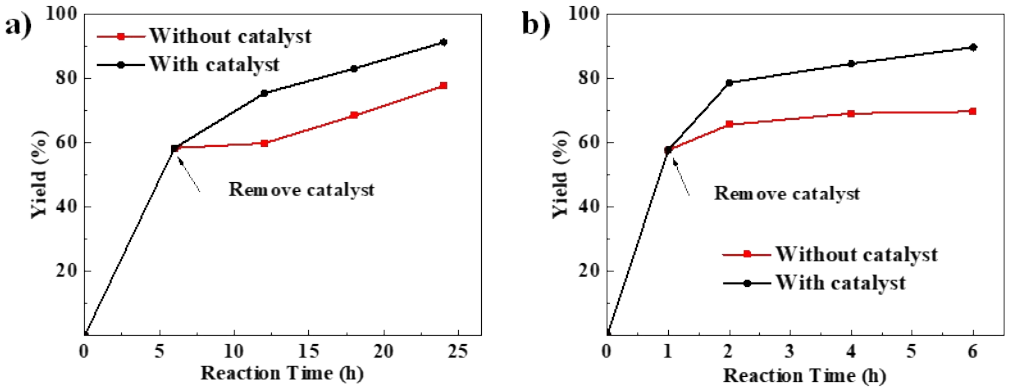


Figure S8. Hot filtration test for **a)** oxidation reaction of toluene and **b)** oxidation reaction of ethylbenzene. black: **POMOF-1** as the catalyst during the reaction, red: the catalyst was filtered out during the reaction.

7. Mechanism study

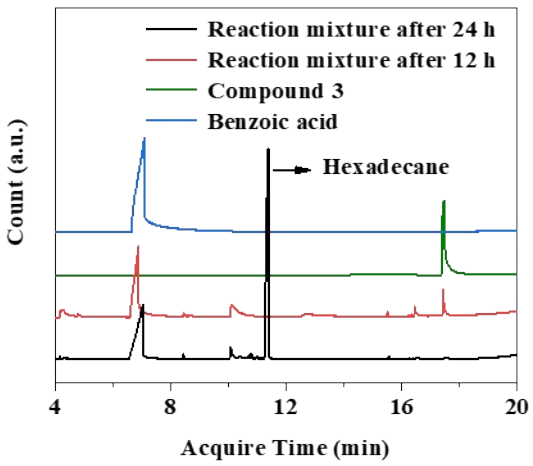
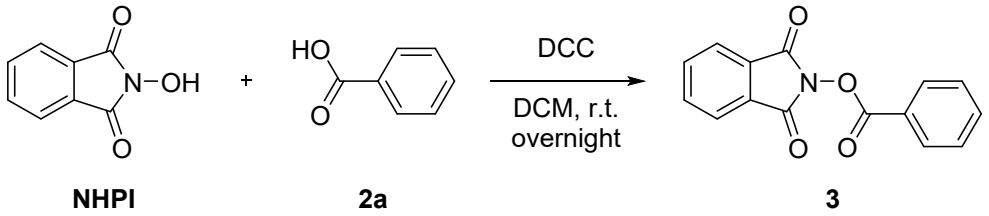


Figure S9. GC spectra of reaction mixture of oxidation of toluene after 24 h (black) and 12 h (red), **3** (green) and benzoic acid (blue).

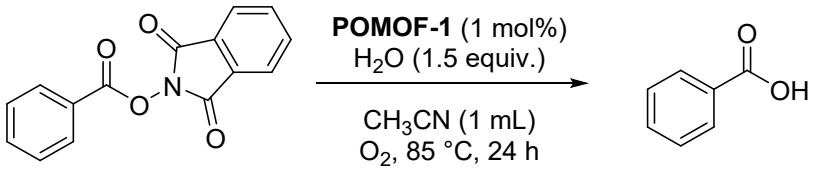
7.1 Synthesis of 1,3-dioxoisoindolin-2-yl benzoate (3).



NHPI **2a** **3**

According to the literature,[5] 152 mg dicyclohexylcarbodiimide (0.736 mmol) was added into a suspension of 100 mg NHPI (0.613 mmol) and 82.3 mg benzoic acid (0.674 mmol) in dichloromethane (5 mL). The mixture was stirred overnight under ambient temperature. After the reaction was complete, the mixture was filtered by Kieselguhr and washed by dichloromethane. After removing the dichloromethane under reduced pressure, the crude products were purified by silica gel column chromatography (eluent: ethyl acetate-petroleum ether, 1:5) to yield the pure products **3** as white solid. Yield: 122.9 mg (75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 - 8.17 (m, 2H), 7.93 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.82 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 - 7.68 (m, 1H), 7.57 - 7.51 (m, 2H).

7.2 Catalytic hydrolysis of 1,3-dioxoisoindolin-2-yl benzoate (3) by POMOF-1



3 **2a, 95%**

POMOF-1 (1 mol%), 1,3-dioxoisoindolin-2-yl benzoate (**3**, 0.2 mmol), H_2O (1.5 equiv.) and CH_3CN (1 mL) were added into seal tube,which was subsequently charged with 1 atm O_2. Then the reaction was heated at 85 ^{o}C and stirring for 24 h. The reactor was cooled to room temperature, the catalyst was centrifuged and the supernatant was diluted with ethyl acetate. The conversion of **3** and yields of product benzoic acid **2a** were determined by gas chromatography-mass spectrometry (GC-MS) with hexadecane as internal standard. Then, the reaction was quenched with H_2O and extracted with ethyl acetate. Filtering out the insoluble substances, the organic phases were washed with H_2O, and dried over anhydrous Na_2SO_4. The organic phases were filtered and concentrated under reduced pressure and the crude products were purified by silica gel column chromatography (eluent: ethyl acetate-petroleum ether, 1:5) to yield the pure products. The products were characterized by ^{1}H NMR. **2a** was obtained as a white solid, Yield: 22.1 mg (91%).

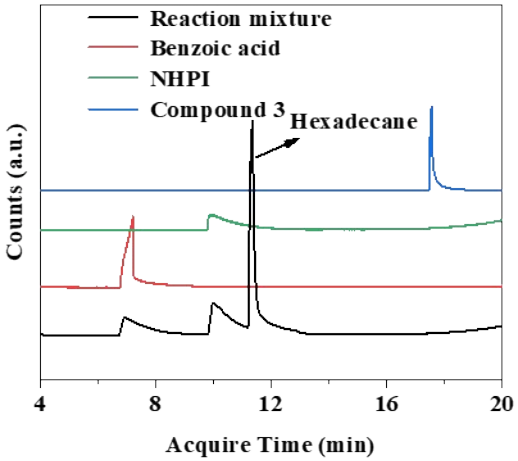


Figure S10. GC spectra of reaction mixture of hydrolysis reaction of **3** after 24 h (black), benzoic acid (red), NHPI (green) and **3** (blue).

Table S5. Different rate constant with various substituted methylarenes.

Substrate	σ	kx	log(kx/kH)
4-H	0	3.40352E-4	0
4-OCH_3	-0.27	5.03853E-4	0.17038
4-Br	0.23	1.9108E-4	-0.25071
4-CN	0.66	1.04898E-4	-0.51116
4-NO2	0.78	4.72073E-5	-0.85792

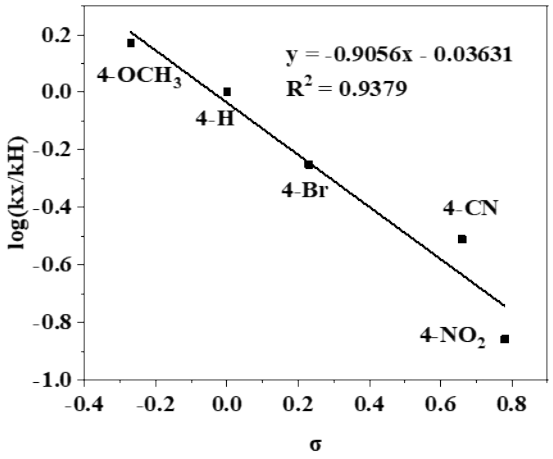
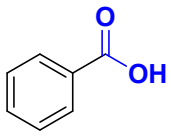
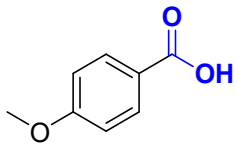


Figure S11. Hammett plot based on the reactions using various para-substituted methylarenes with ρ = -0.90.

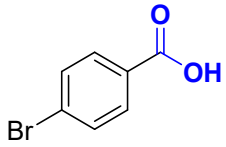
8. Characterization of products



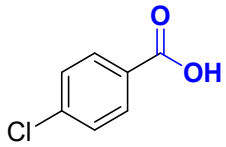
Benzoic acid (**2a**).[6] White solid, Yield: 21.4 mg (88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.50, 133.86, 130.24, 129.33, 128.51.



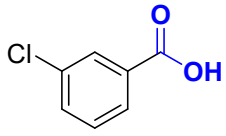
4-Methoxybenzoic acid (2b).[7] White solid. Yield: 25.3 mg (83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.57, 164.05, 132.37, 121.62, 113.76, 55.50.



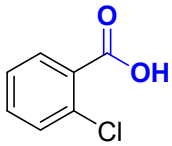
4-Bromobenzoic acid (2c).[6] White solid. Yield: 26.1 mg (65%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.89 - 7.85 (m, 2H), 7.73 - 7.70 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.02, 132.17, 131.75, 130.39, 127.37.



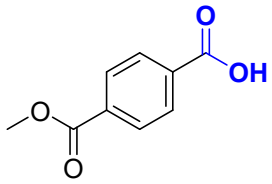
4-Chlorobenzoic acid (2d).[8] White solid. Yield: 25.4 mg (81%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.20 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.93, 138.25, 131.61, 130.08, 129.21.



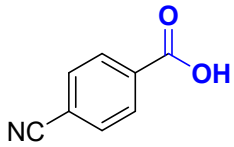
3-Chlorobenzoic acid (2e).[8] White solid. Yield: 23.8 mg (76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (t, *J* = 1.9 Hz, 1H), 8.04 - 8.02 (m, 1H), 7.63 - 7.61 (m, 1H), 7.46 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.02, 134.73, 133.94, 130.95, 130.28, 129.87, 128.34.



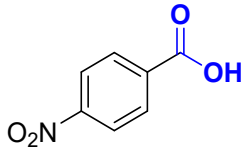
2-Chlorobenzoic acid (2f).[7] White solid. Yield: 22.5 mg (72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 - 7.49 (m, 2H), 7.41 - 7.38 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.79, 134.80, 133.63, 132.52, 131.53, 128.37, 126.72.



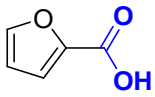
4-(Methoxycarbonyl)benzoic acid (2g).[9] White solid. Yield: 26.7 mg (74%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.44 (s, 1H), 8.07 (s, 4H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.01, 166.07, 135.28, 133.61, 130.06, 129.82, 52.95.



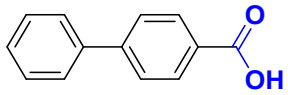
4-Cyanobenzoic acid (2h).[7] White Solid. Yield: 18.2 mg (62%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.47, 135.23, 133.16, 130.39, 118.65, 115.55.



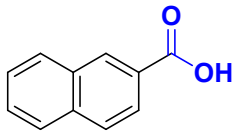
4-Nitrobenzoic acid (2i).[6] Light yellow solid. Yield: 7.4 mg (22%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.34 - 8.31 (m, 2H), 8.18 - 8.15 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.21, 150.48, 136.74, 131.16, 124.18.



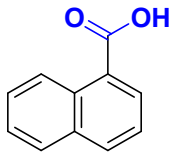
Furan-2-carboxylic acid (2j).[9] White solid. Yield: 12.1 mg (54%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.36 (dd, *J* = 3.6, 0.9 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.42, 147.46, 143.78, 120.18, 112.31.



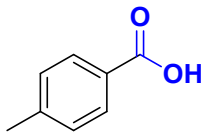
[1,1'-Biphenyl]-4-carboxylic acid (2k).[8] White solid. Yield: 28.1 mg (71%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.03 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.7 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.56, 144.79, 139.47, 130.42, 130.01, 129.55, 128.76, 127.43, 127.29.



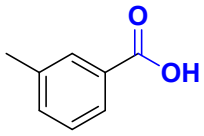
2-Naphthoic acid (2l).[9] White solid. Yield: 23.4 mg (68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.16 (dd, J = 8.5, 1.7 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.95 (dd, J = 11.1, 8.5 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.11, 135.98, 132.45, 132.19, 129.57, 128.70, 128.36, 127.84, 126.81, 126.49, 125.40.



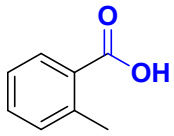
1-Naphthoic acid (2m).[8] White solid. Yield: 13.1 mg (38%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.18 (s, 1H), 8.87 (d, J = 8.6 Hz, 1H), 8.16 (t, J = 7.8 Hz, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.67 - 7.59 (m, 1H), 7.60 (t, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 169.16, 133.93, 133.40, 131.16, 130.35, 129.07, 128.17, 128.03, 126.65, 125.97, 125.34.



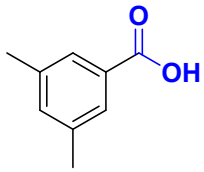
4-Methylbenzoic acid (2n).[7] White solid. Yield: 22.1 mg (81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.46, 144.70, 130.30, 129.25, 126.61, 21.82.



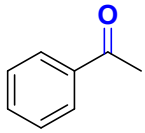
3-Methylbenzoic acid (2o).[8] White solid. Yield: 20.7 mg (76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 - 7.94 (m, 2H), 7.45 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.50, 138.35, 134.65, 130.75, 129.28, 128.43, 127.42, 21.31.



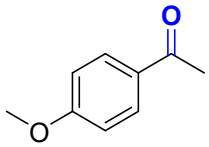
2-Methylbenzoic acid (2p).[10] White solid. Yield: 17.8 mg (66%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.44 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.50 - 7.47 (m, 1H), 7.34 - 7.29 (m, 2H) 2.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.15, 141.42, 133.01, 131.98, 131.63, 128.32, 125.91, 22.18.



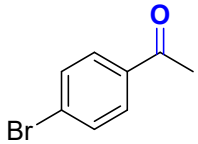
3,5-Dimethylbenzoic acid (2q).[11] White solid. Yield: 19.5 mg (65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.27 (s, 1H), 2.41 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.55, 138.18, 135.51, 129.15, 127.92, 21.17.



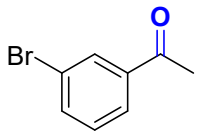
Acetophenone (**5a**).[12] Light yellow liquid. Yield: 20.4 mg (85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.19, 137.12, 133.12, 128.58, 128.32, 26.65.



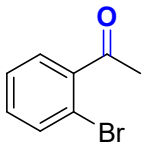
1-(4-Methoxyphenyl)ethan-1-one (5b).[7] White solid. Yield: 26.4 mg (88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 - 7.94 (m, 2H), 6.96 - 6.93 (m, 2H), 3.89 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.80, 163.47, 130.59, 130.33, 113.68, 55.48, 26.37.



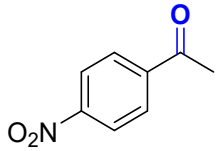
1-(4-Bromophenyl)ethan-1-one (5c).[9] Light yellow solid. Yield: 33.8 mg (85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.02, 135.81, 131.90, 129.85, 128.31, 26.57.



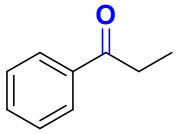
1-(3-Bromophenyl)ethan-1-one (5d).[9] Yellow liquid. Yield: 34.2 mg (86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (t, *J* = 1.8 Hz, 1H), 7.90 - 7.89 (m, 1H), 7.72 - 7.70 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.65, 138.78, 135.97, 131.38, 130.21, 126.86, 122.96, 26.65.



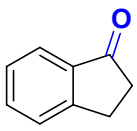
1-(2-Bromophenyl)ethan-1-one (5e).[7] Light yellow liquid. Yield: 32.2 mg (81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.41 - 7.38 (m, 1H), 7.33 - 7.30 (m, 1H), 2.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.41, 141.47, 133.85, 131.81, 128.93, 127.45, 118.92, 30.36.



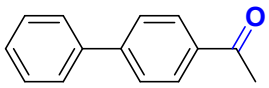
1-(4-Nitrophenyl)ethan-1-one (5f).[7] Brownish yellow solid. Yield: 26.42 mg (80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 2H), 8.16 - 8.11 (m, 2H), 2.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.31, 150.36, 141.37, 129.32, 123.88, 27.02.



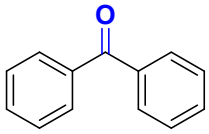
Propiophenone (5g).[9] Yellow liquid. Yield: 20.9 mg (78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 3.03 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.86, 136.91, 132.89, 128.56, 127.98, 31.80, 8.26.



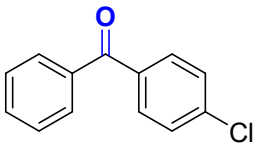
2,3-Dihydro-1H-inden-1-one (5h).[7] White solid. Yield: 17.2 mg (65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 3.19 - 3.15 (m, 2H), 2.72 - 2.71 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.12, 155.18, 137.10, 134.61, 127.30, 126.71, 123.74, 36.24, 25.83.



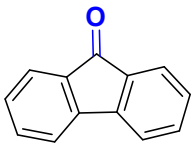
1-([1,1'-Biphenyl]-4-yl)ethan-1-one (5i).[9] White solid. Yield: 31.8 mg (81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.66 (dd, J = 8.2, 1.2 Hz, 2H), 7.52 - 7.49 (m, 2H), 7.45 - 7.42 (m, 1H), 2.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.78, 145.80, 139.88, 135.85, 128.97, 128.25, 127.24, 26.70.



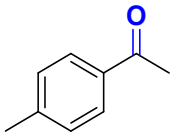
Benzophenone (5j).[7] White solid. Yield: 30.6 mg (84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 - 7.81 (m, 4H), 7.62 (t, J = 7.4 Hz, 2H), 7.51 (t, J = 7.7 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.78, 137.60, 132.44, 130.08, 128.29.



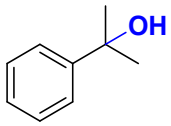
(4-Chlorophenyl)(phenyl)methanone (5k).[13] White solid. Yield: 22.1 mg (51%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 - 7.77 (m, 4H), 7.64 - 7.61 (m, 1H), 7.53 - 7.47 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.51, 138.91, 137.24, 135.87, 132.66, 131.48, 129.94, 128.65, 128.41.



9H-fluoren-9-one (5l).[7] Yellow solid. Yield: 33.9 mg (94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 - 7.61 (m, 1H), 7.55 - 7.45 (m, 2H), 7.34 - 7.27 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.90, 144.41, 134.70, 134.12, 129.07, 124.28, 120.32.

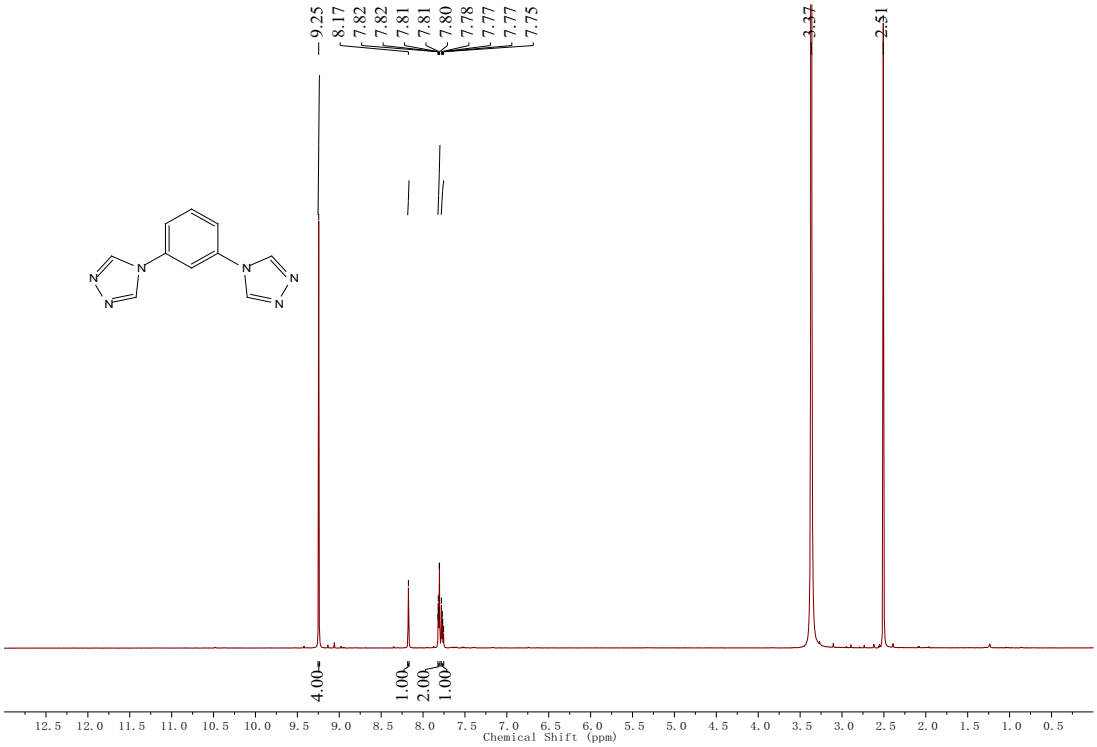


1-(p-Tolyl)ethan-1-one (5m).[14] White liquid. Yield: 24.4 mg (91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.60 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.88, 143.89, 134.71, 129.25, 128.45, 26.56, 21.66.

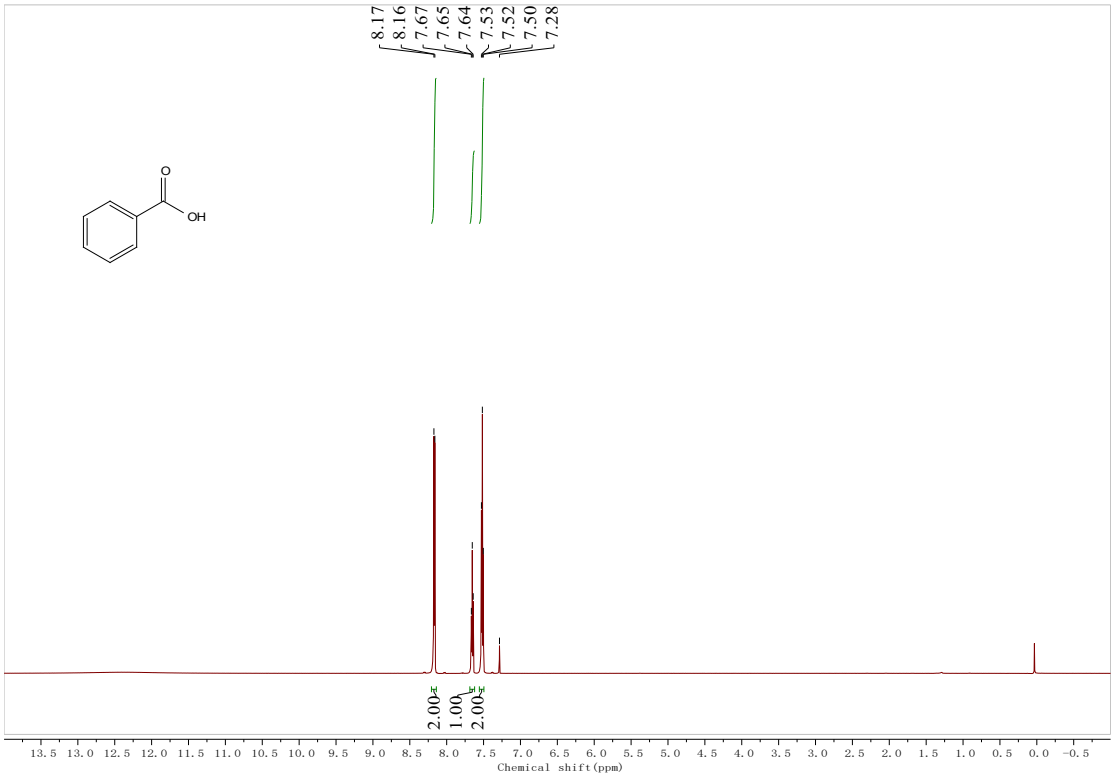


2-Phenylpropan-2-ol (5n).[15] Light yellow liquid. Yield: 24.8 mg (91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 - 7.51 (m, 2H), 7.40 - 7.36 (m, 2H), 7.29 - 7.26 (m, 1H), 1.62 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.11, 128.24, 126.71, 124.38, 72.56, 31.76.

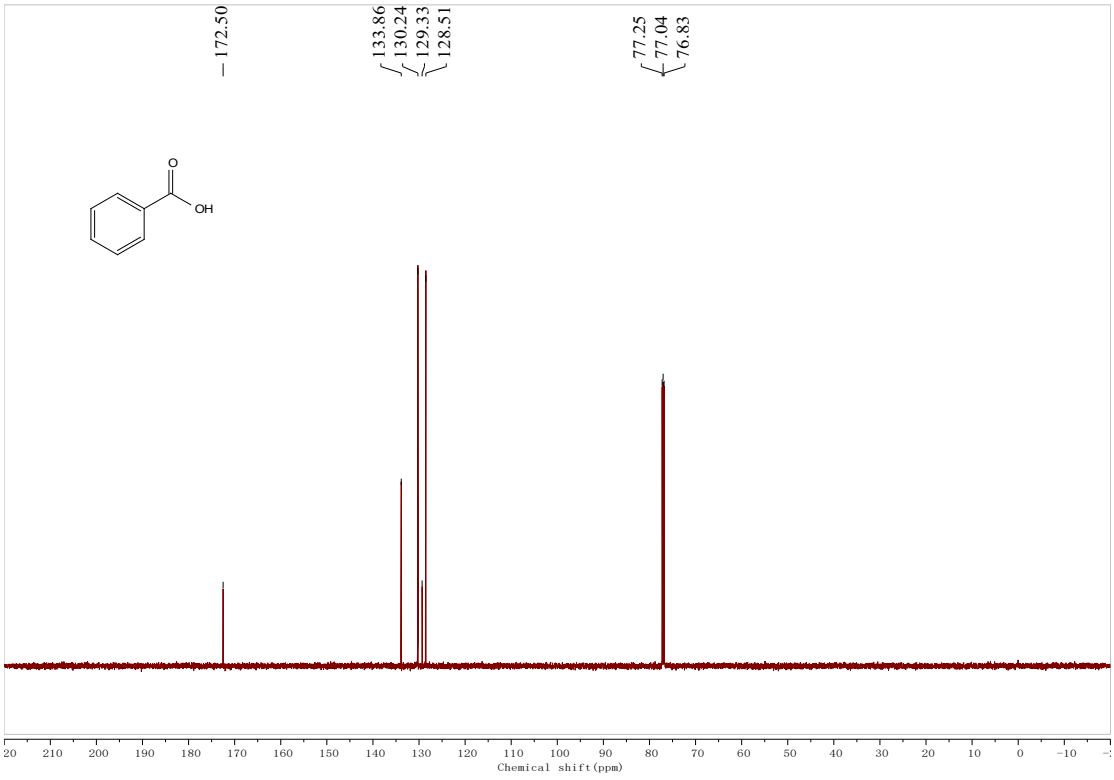
9. NMR spectra



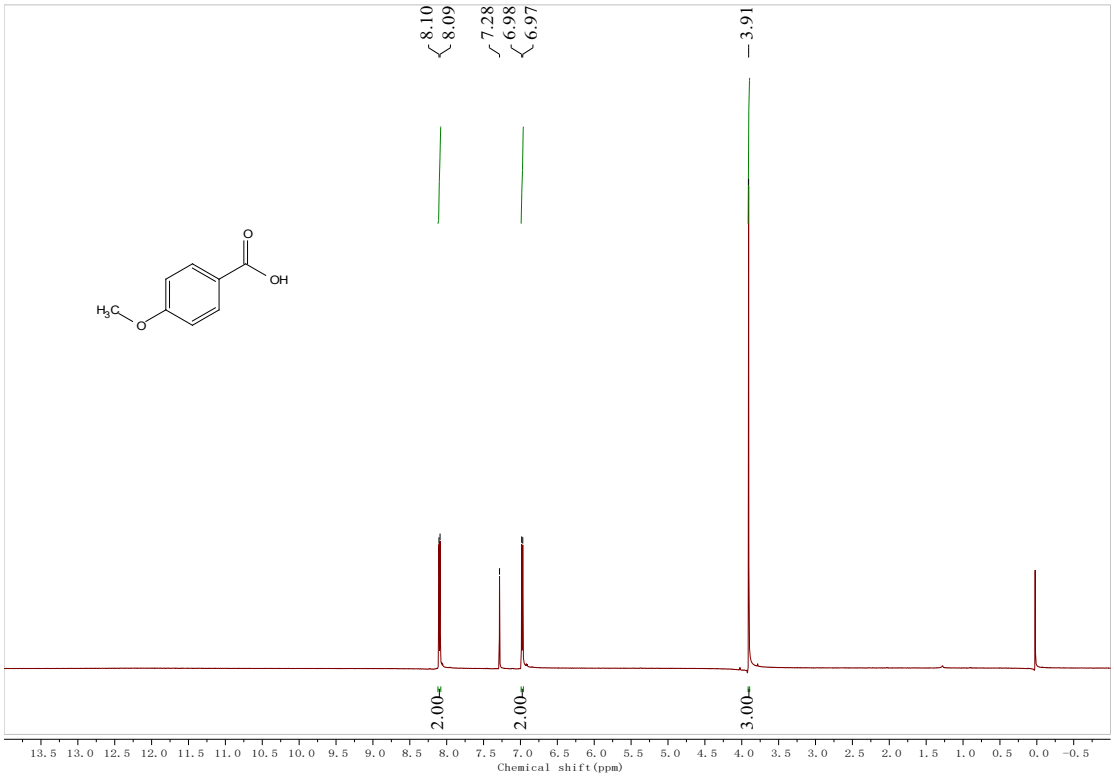
^{1}H NMR spectrum of **L**



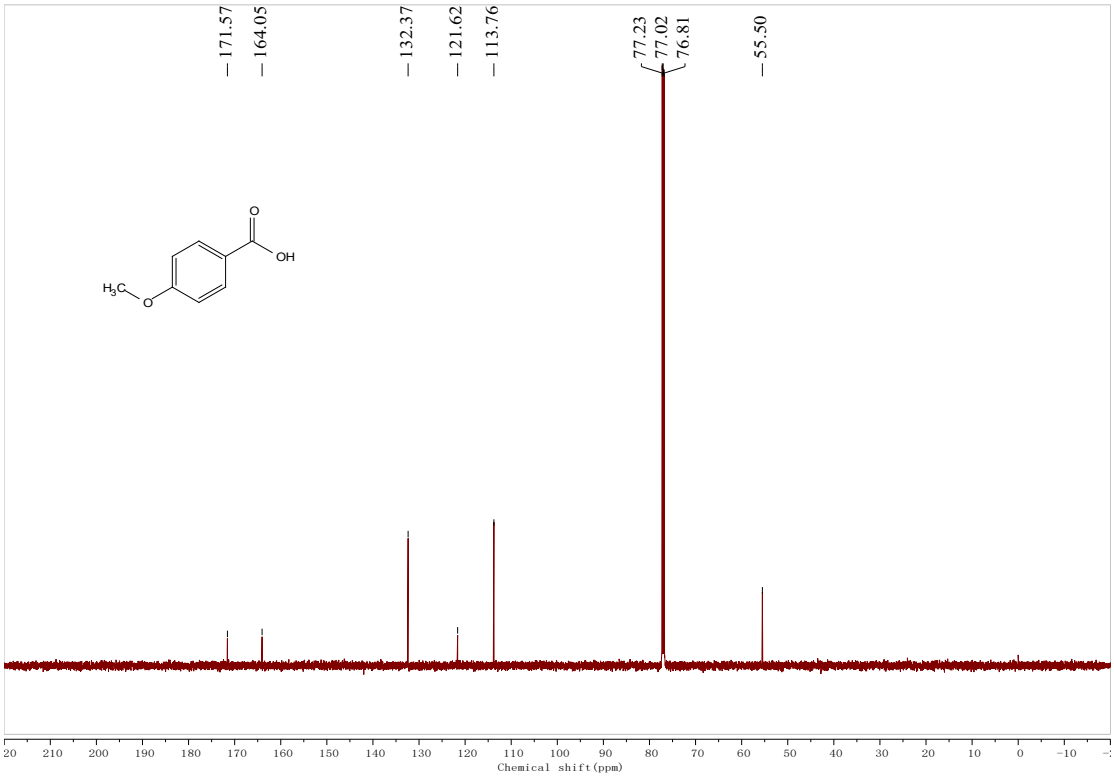
^{1}H NMR spectra of **2a**



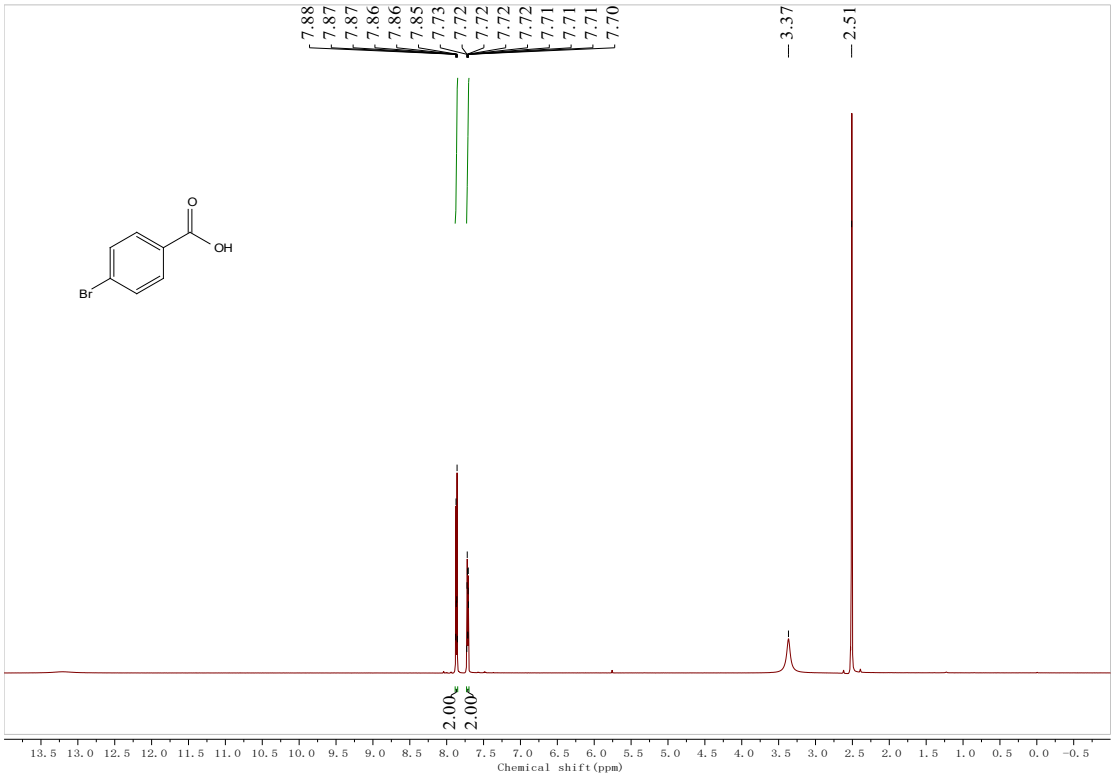
^{13}C NMR spectra of **2a**



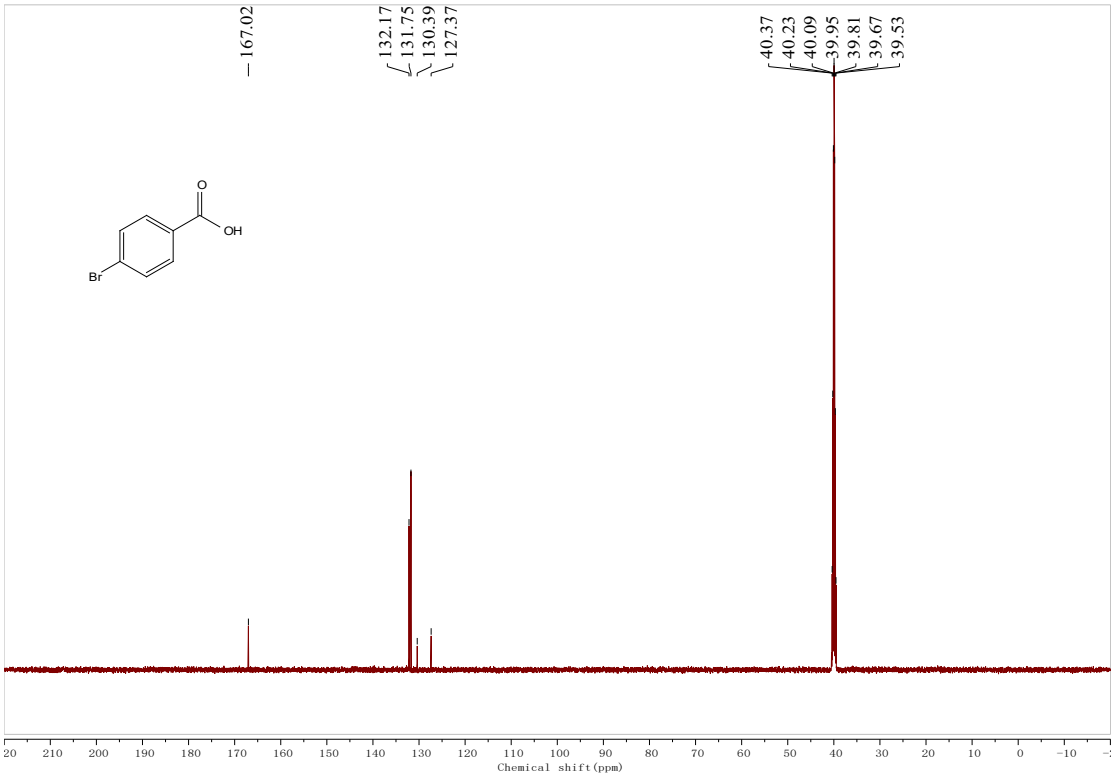
^{1}H NMR spectra of **2b**



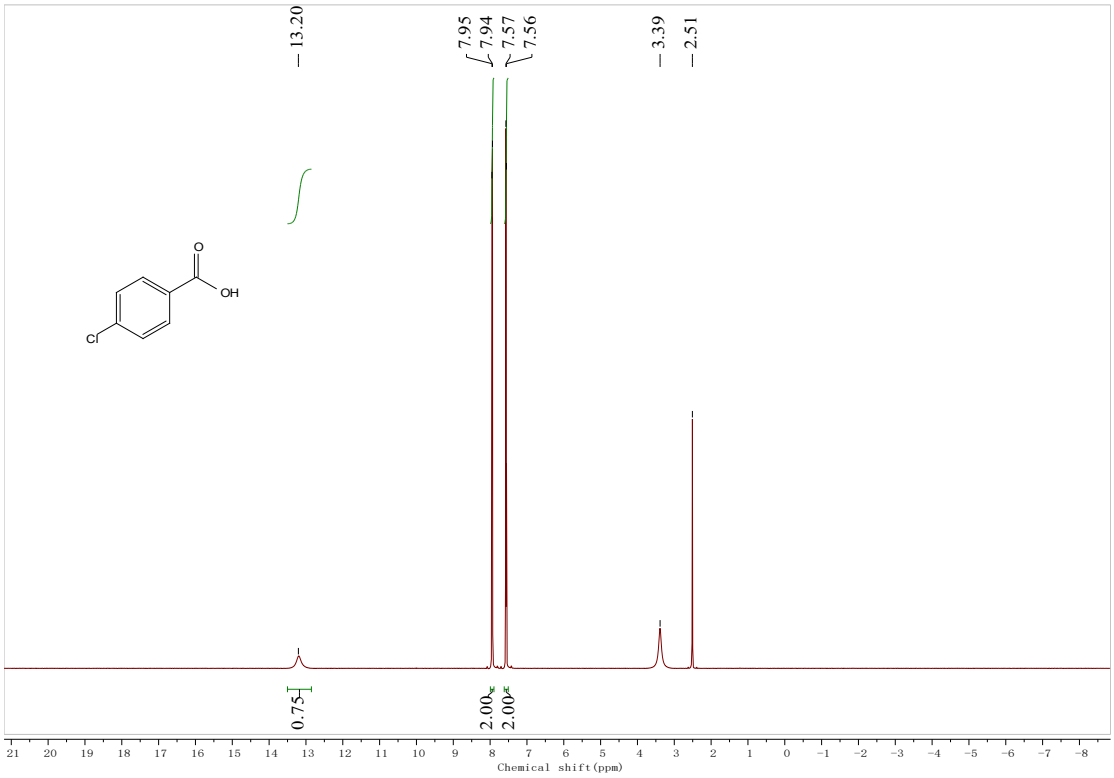
^{13}C NMR spectra of **2b**



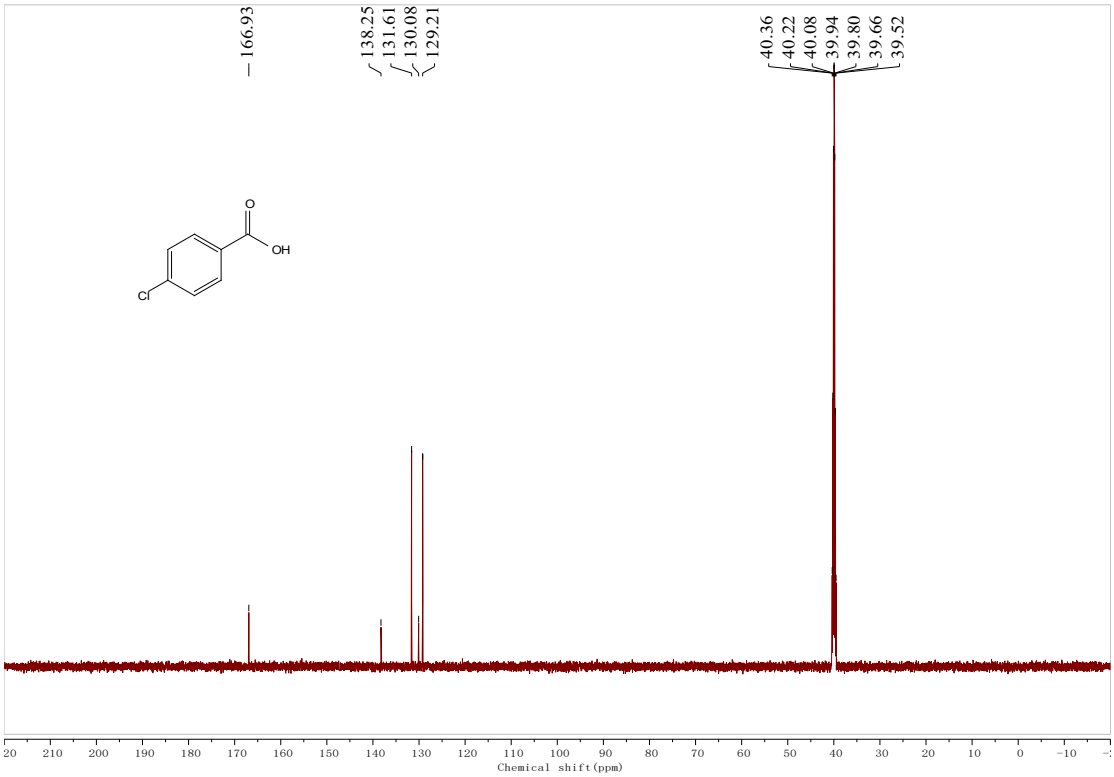
^{1}H NMR spectra of **2c**



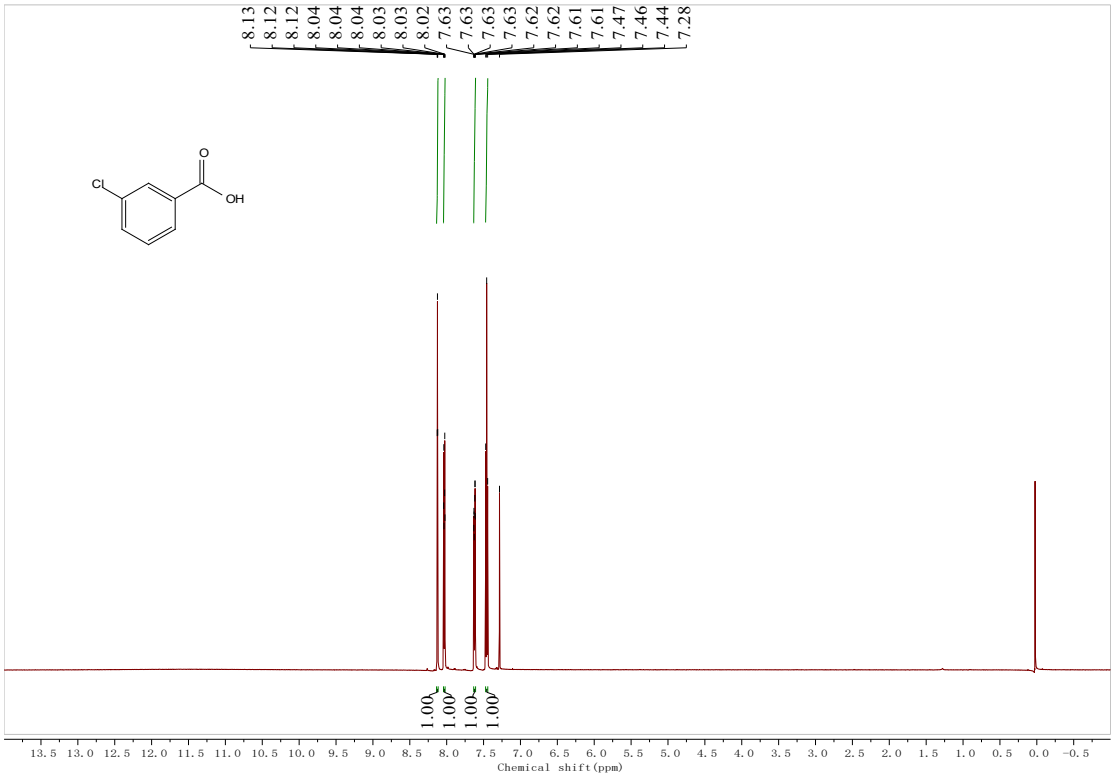
^{13}C NMR spectra of **2c**



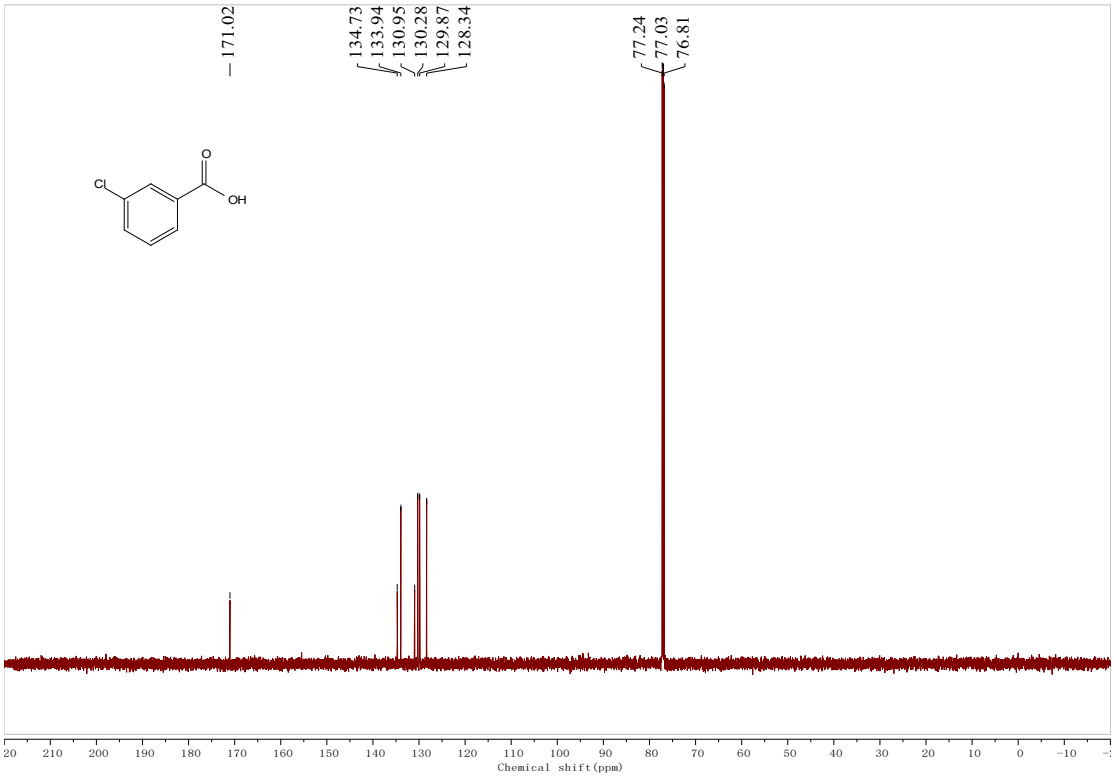
^{1}H NMR spectra of **2d**



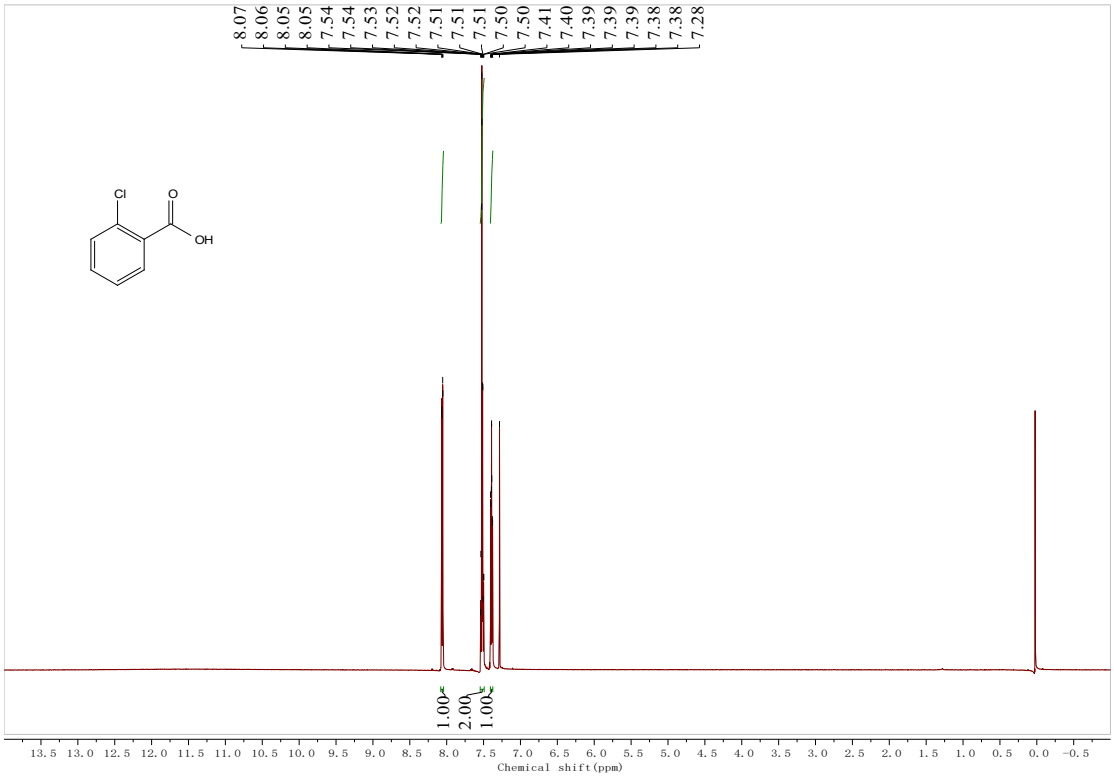
^{13}C NMR spectra of **2d**



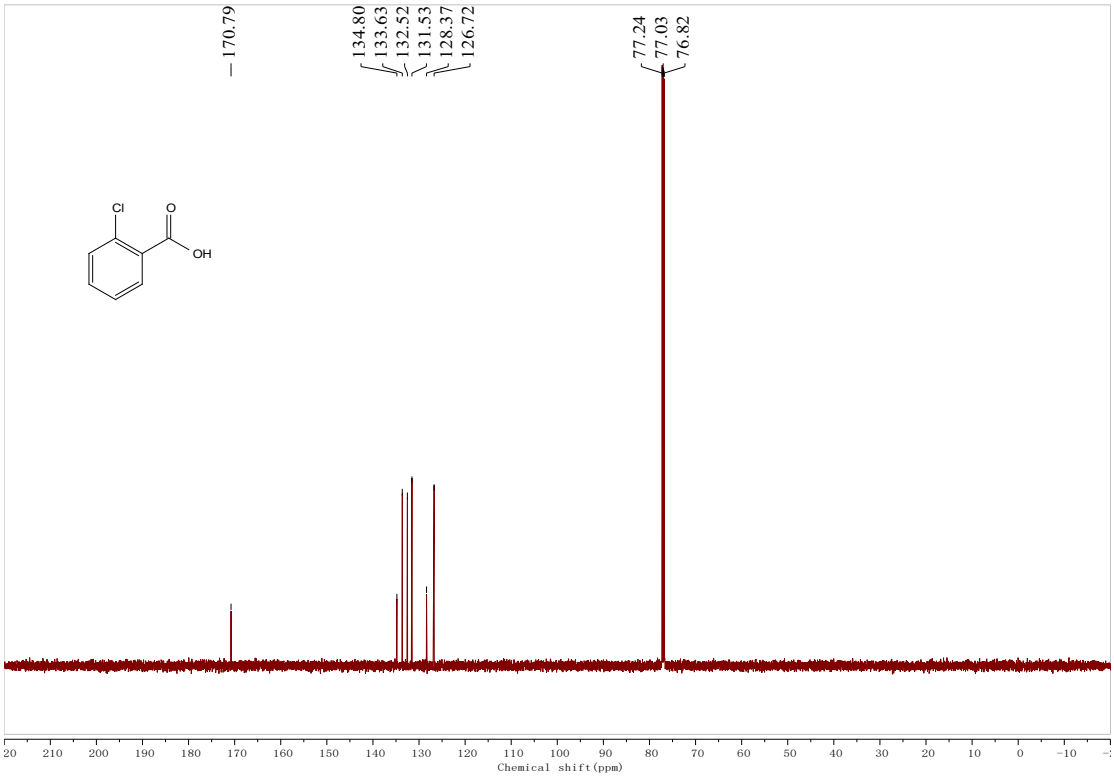
^{1}H NMR spectra of **2e**



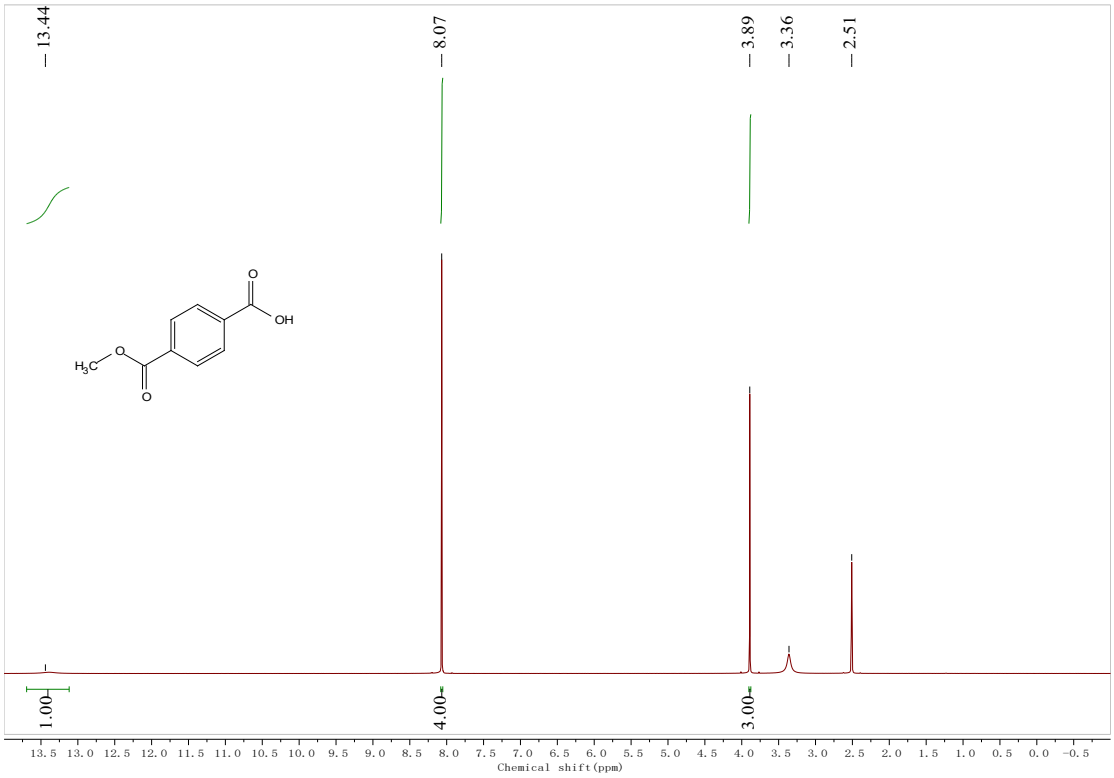
^{13}C NMR spectra of **2e**



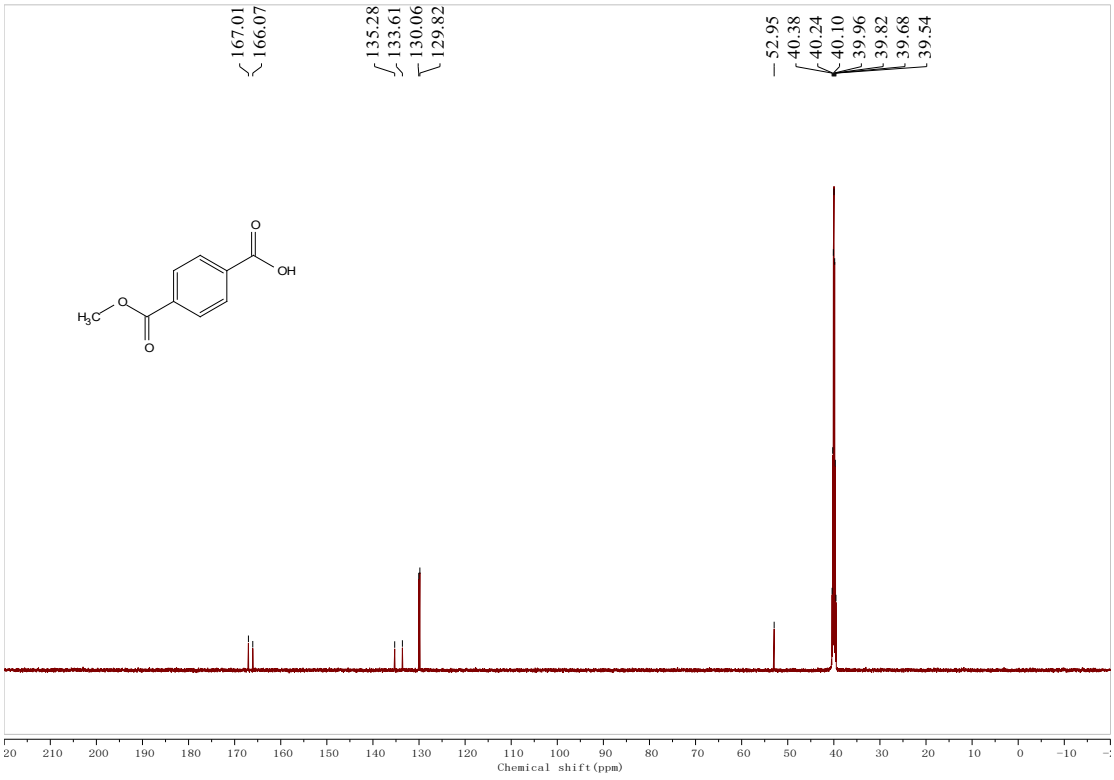
^{1}H NMR spectra of **2f**



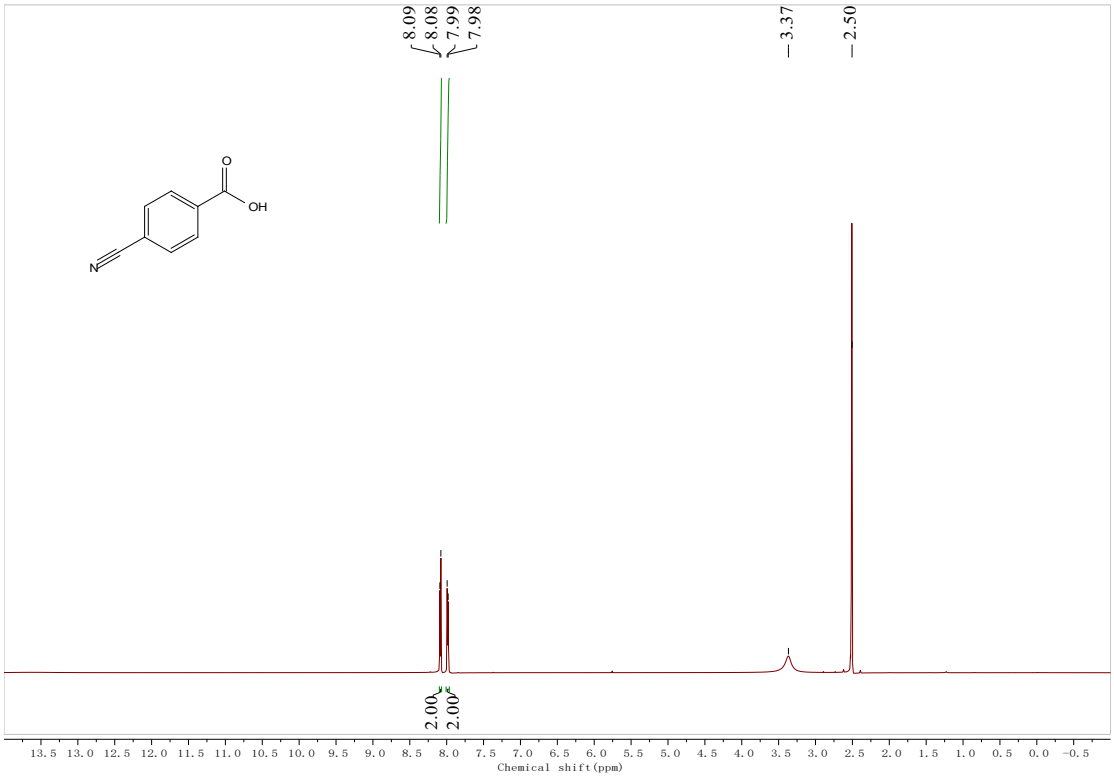
^{13}C NMR spectra of **2f**



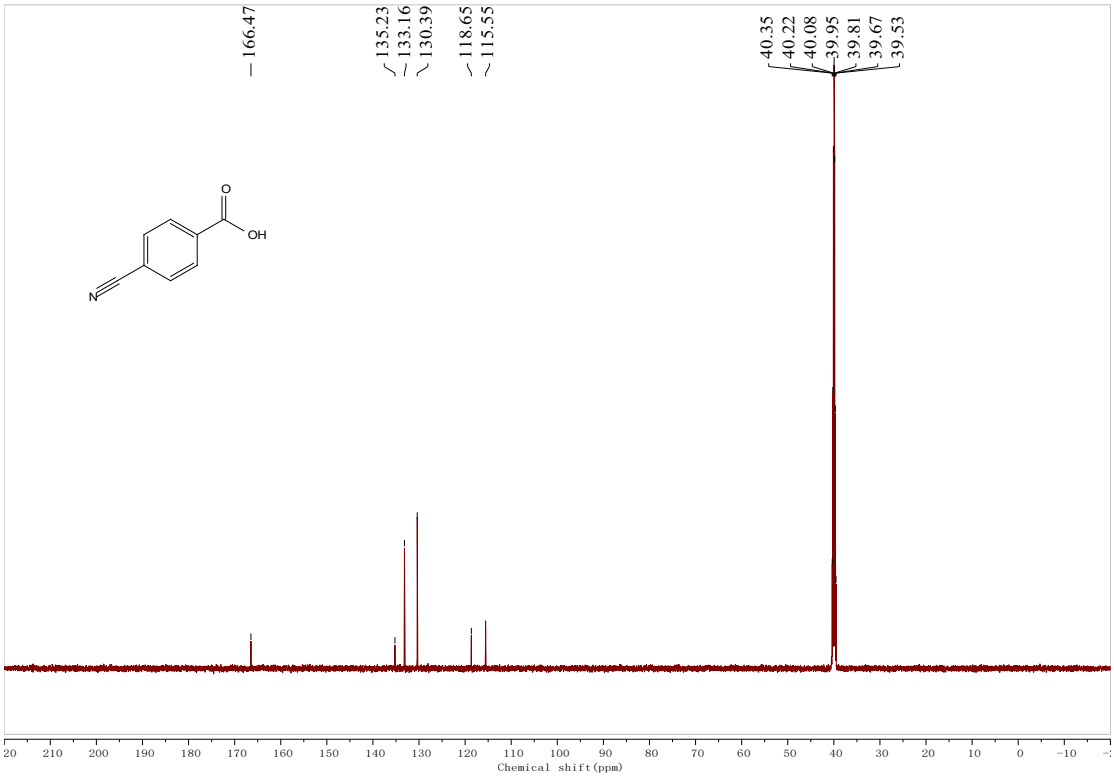
^{1}H NMR spectra of **2g**



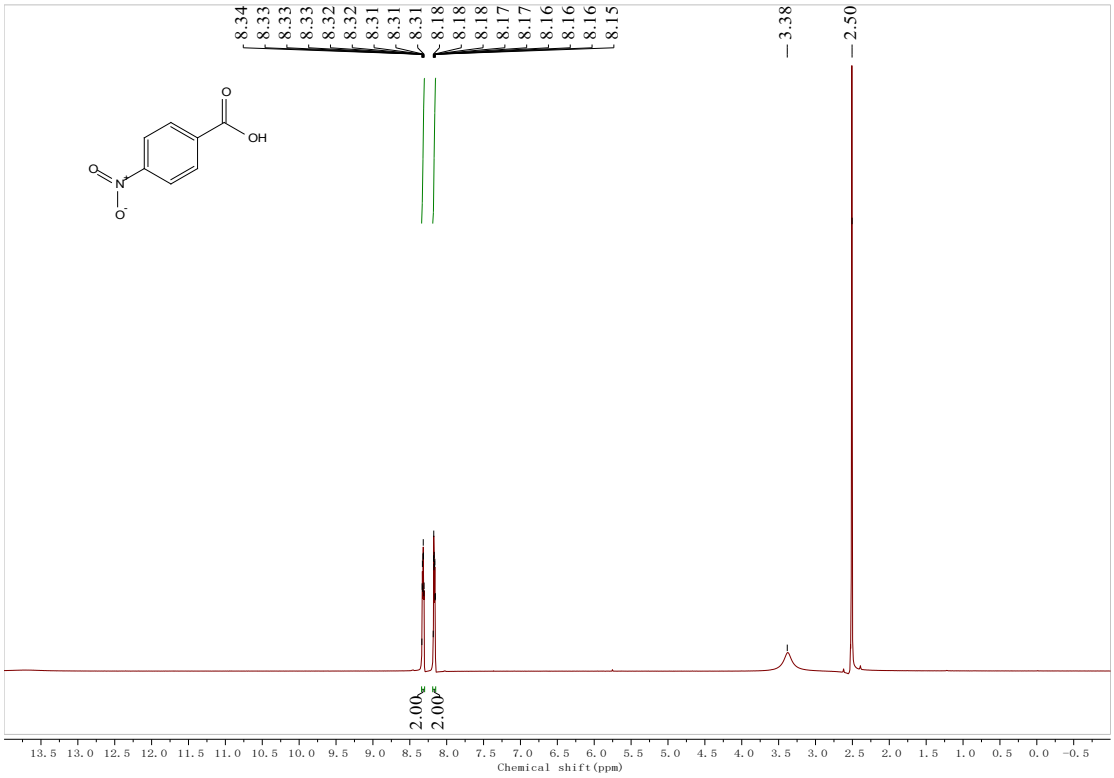
^{13}C NMR spectra of **2g**



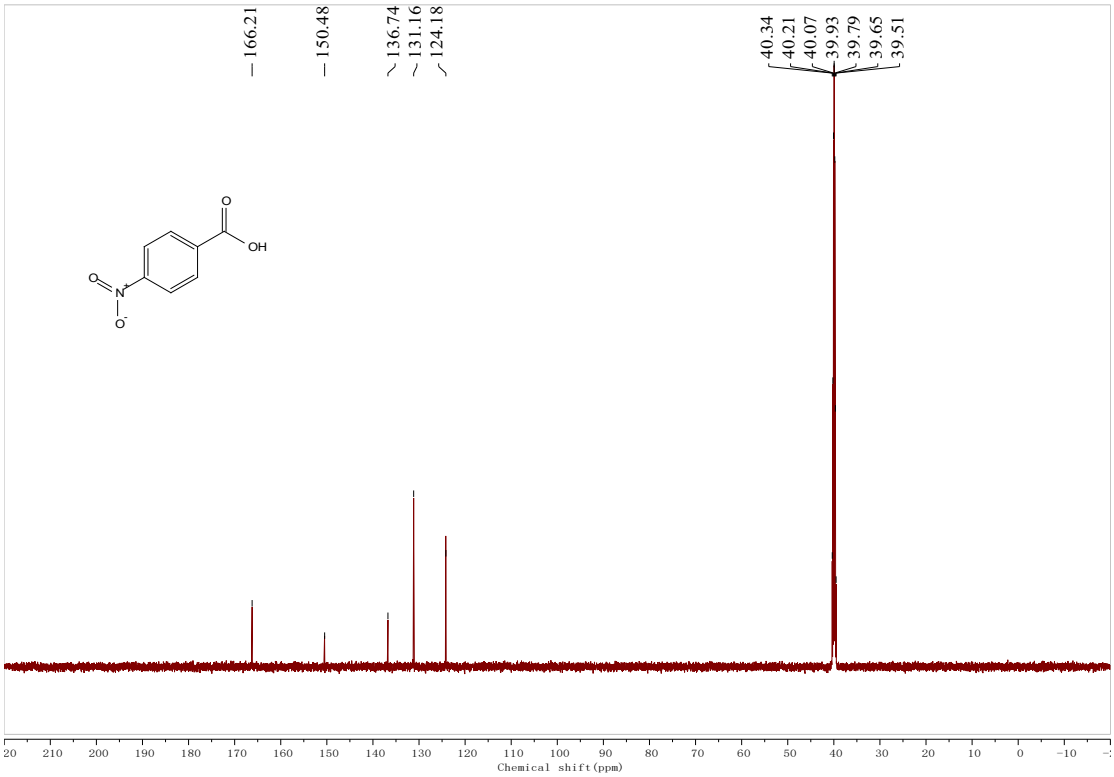
^{1}H NMR spectra of **2h**



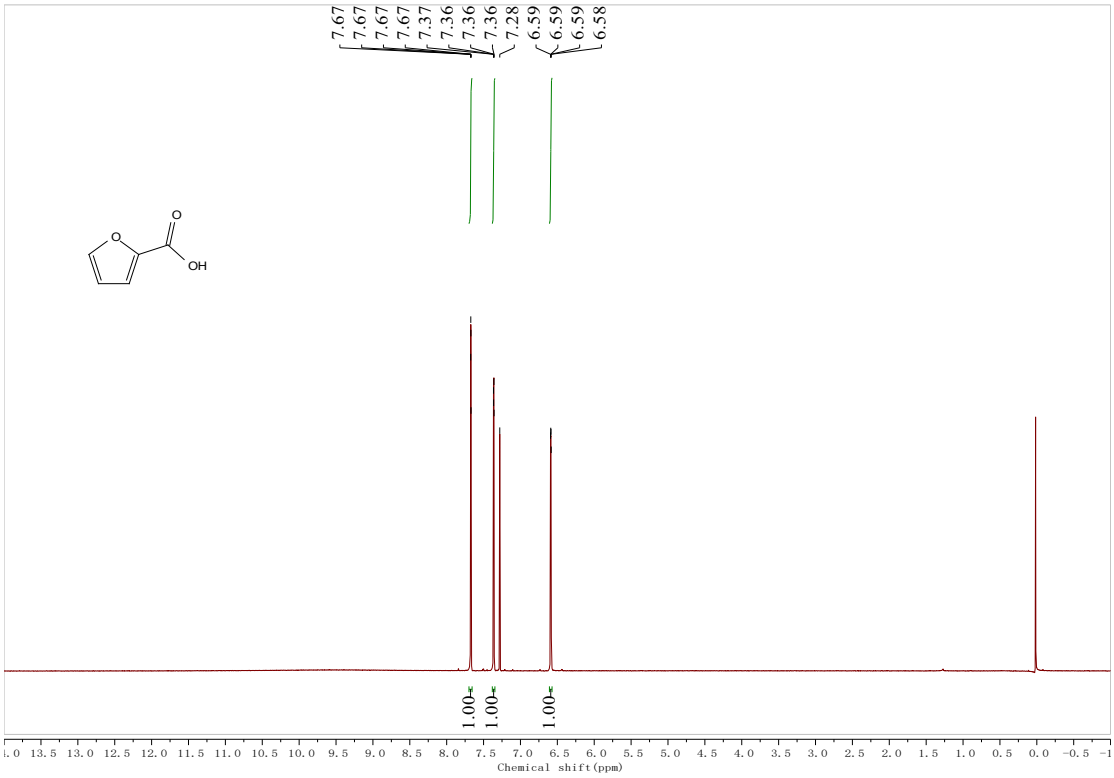
^{13}C NMR spectra of **2h**



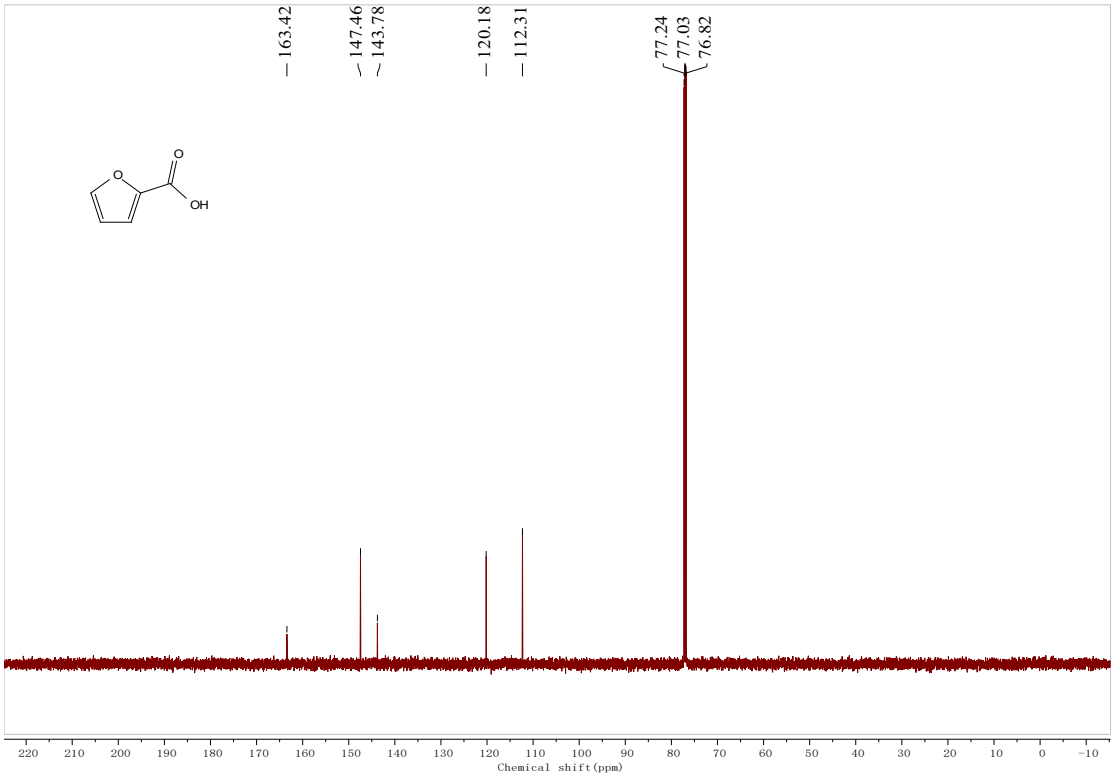
^{1}H NMR spectra of **2i**



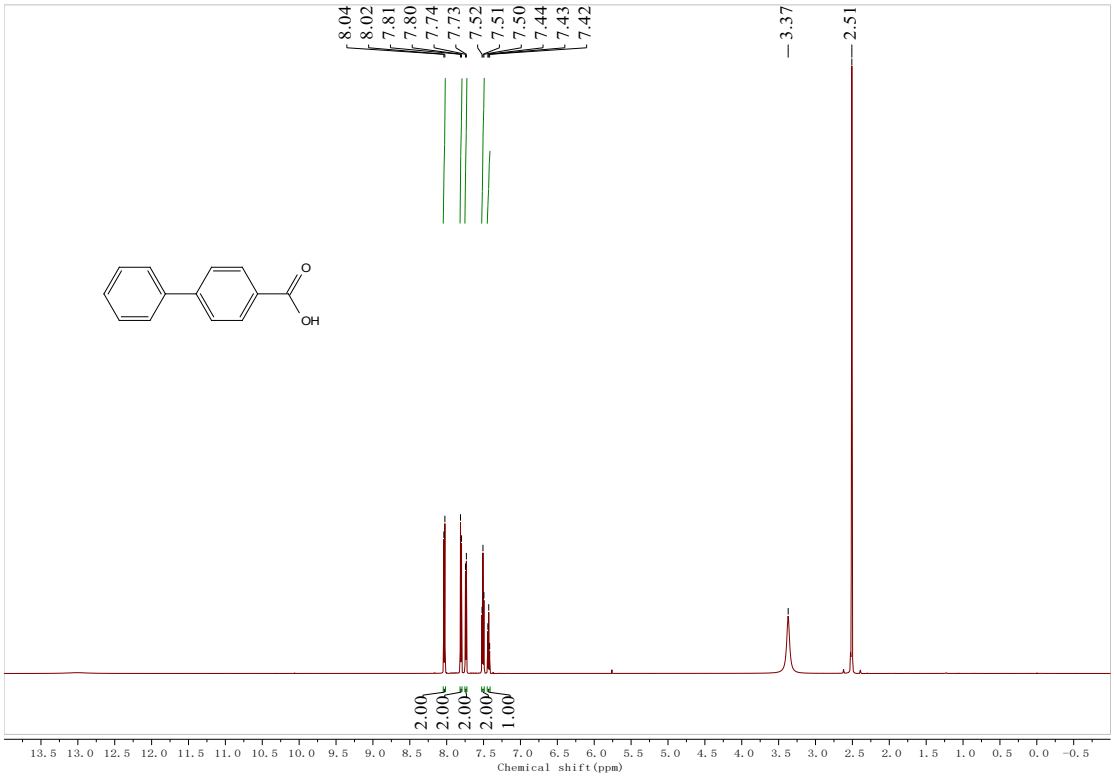
^{13}C NMR spectra of **2i**



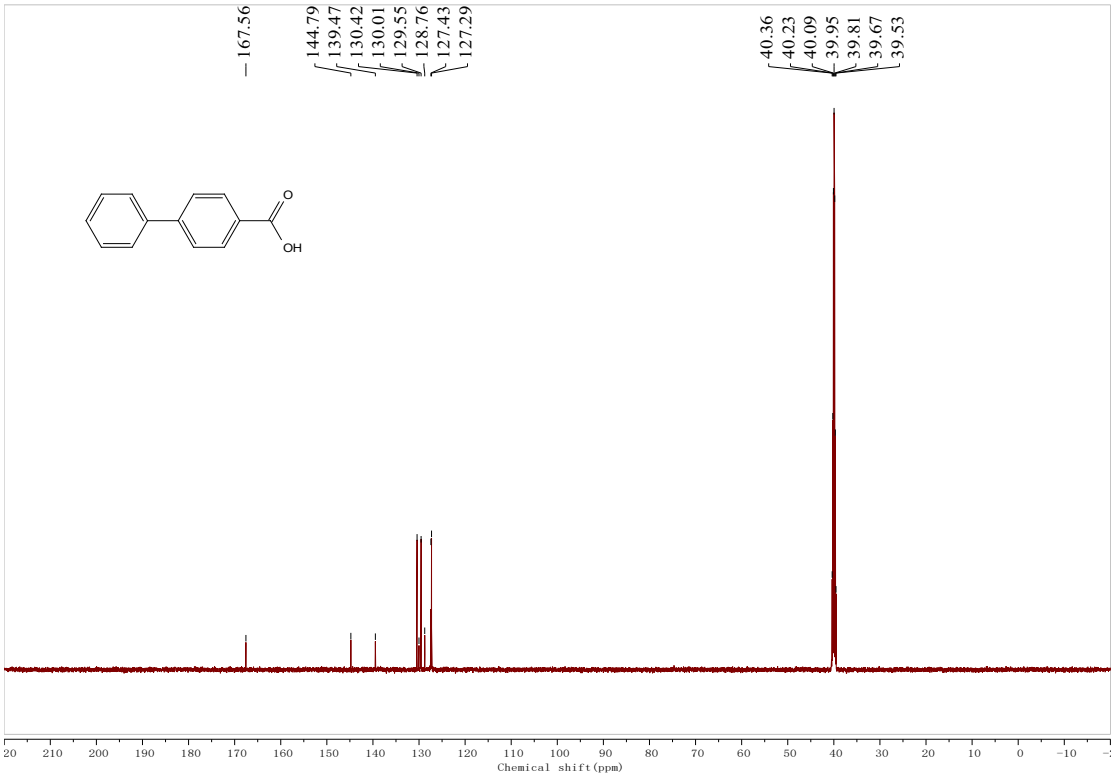
^{1}H NMR spectra of **2j**



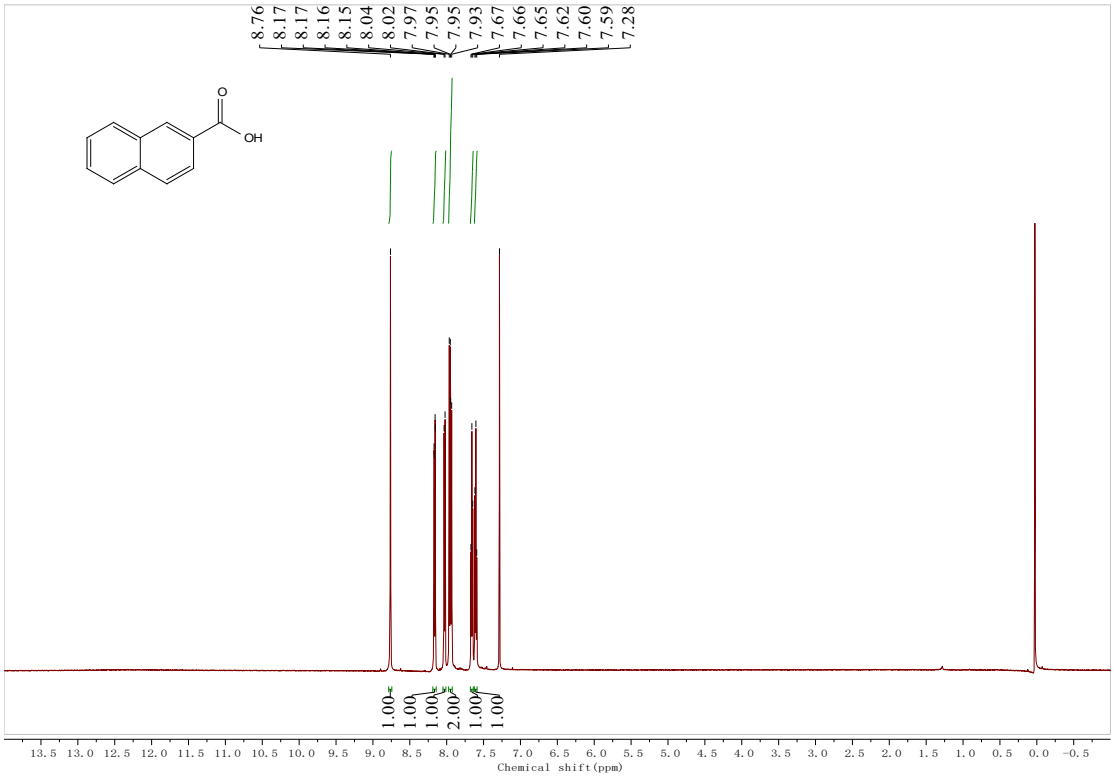
^{13}C NMR spectra of **2j**



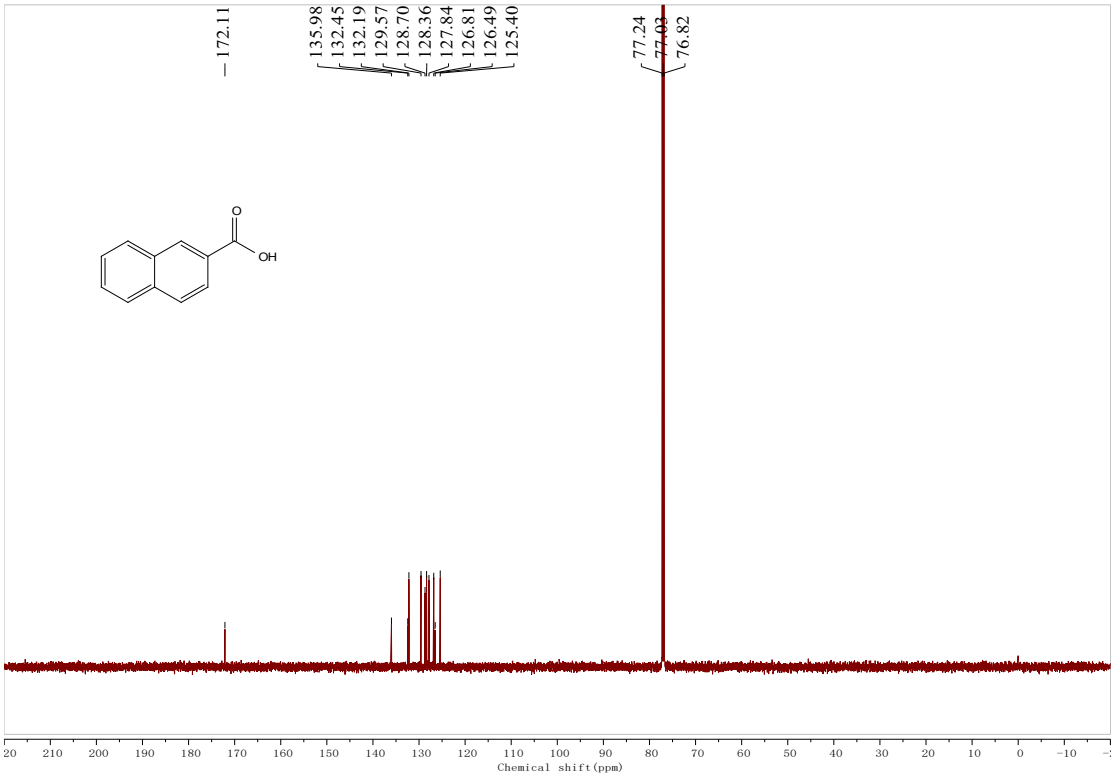
^{1}H NMR spectra of **2k**



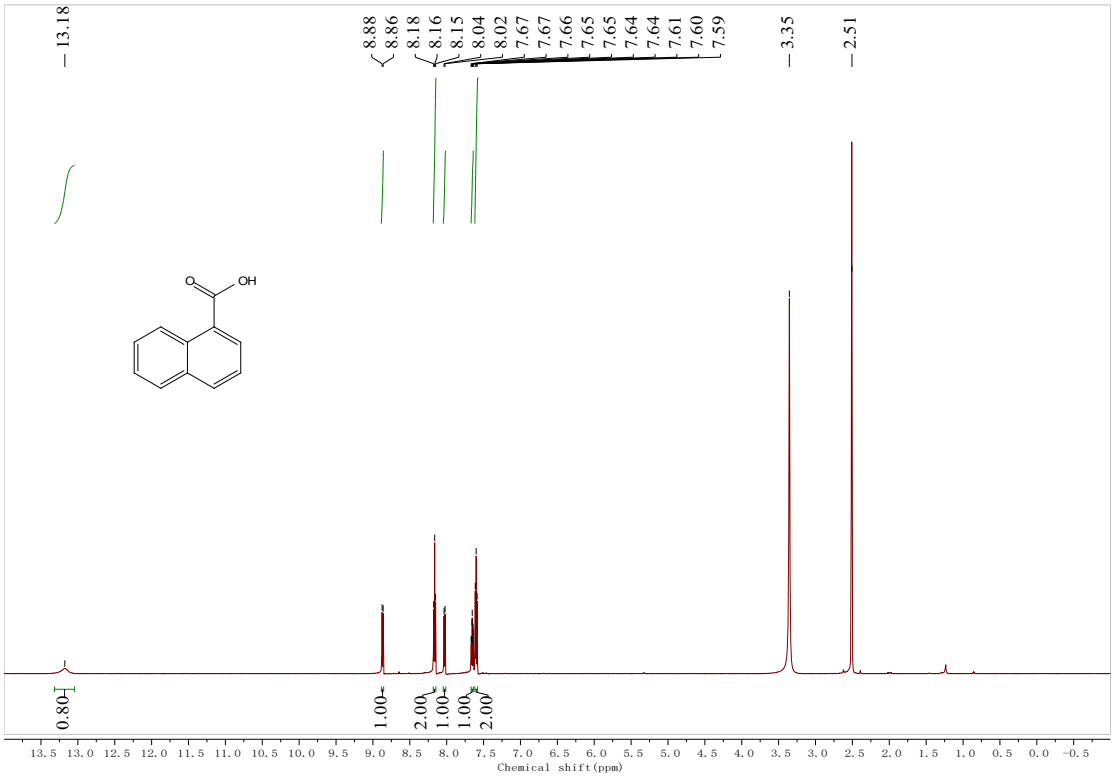
^{13}C NMR spectra of **2k**



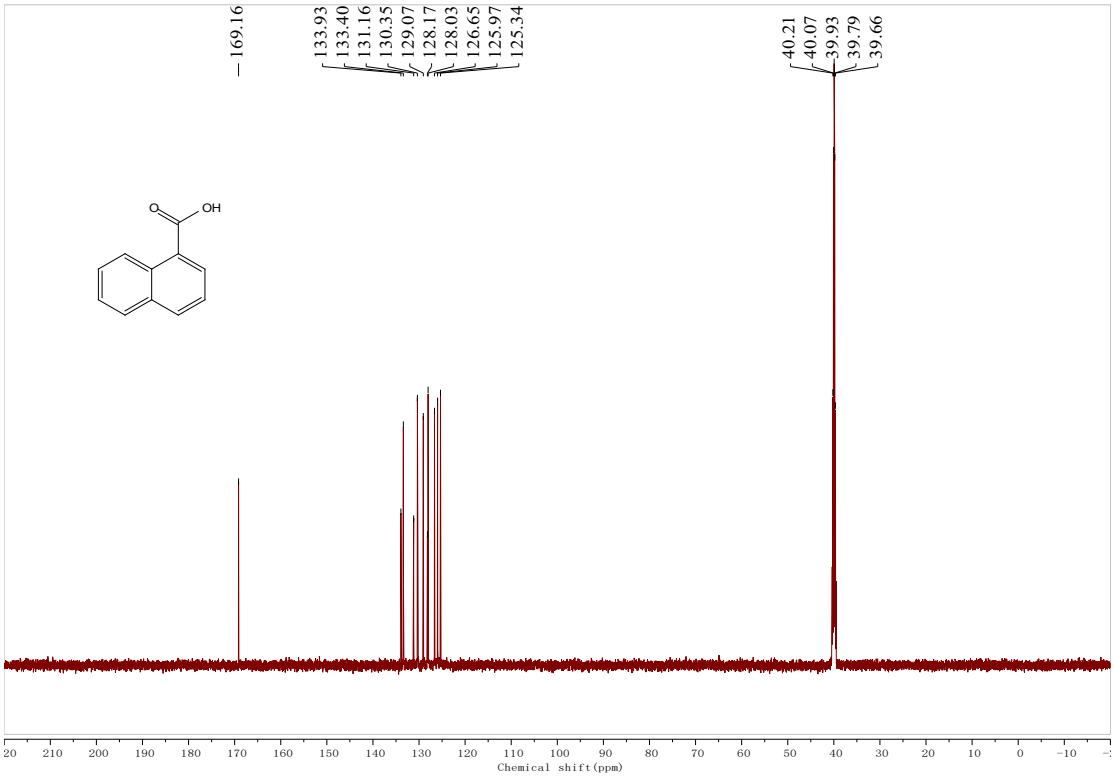
^{1}H NMR spectra of **2l**



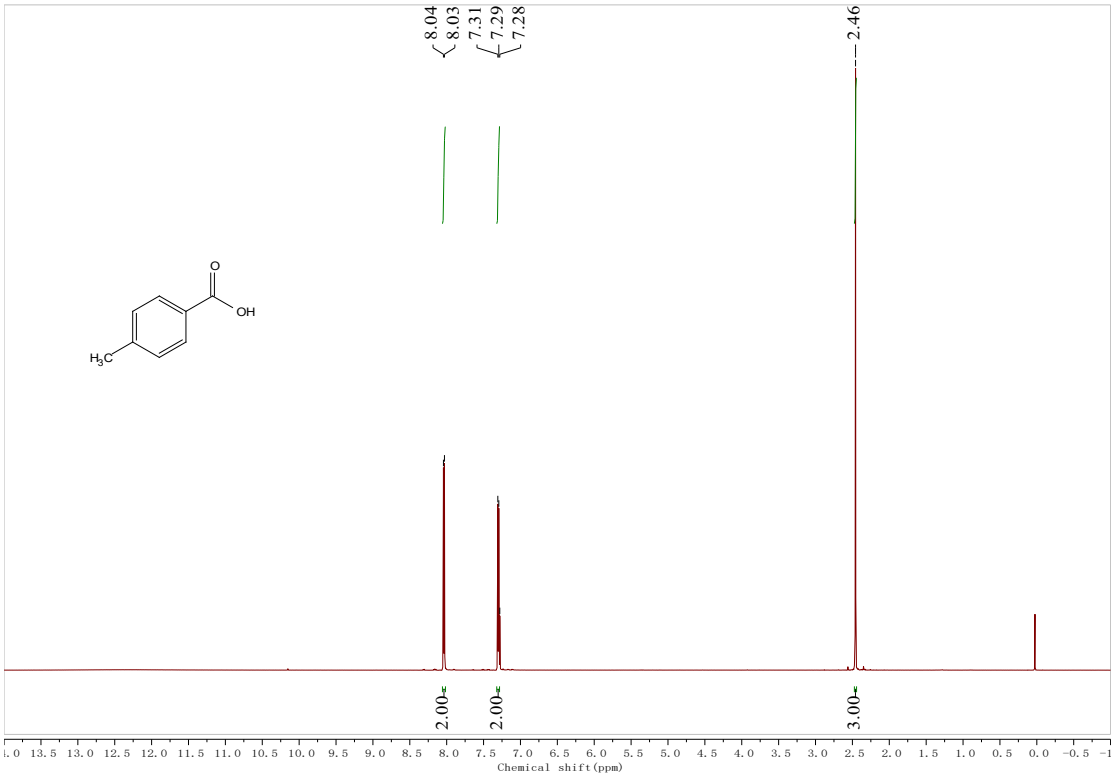
^{13}C NMR spectra of **2l**



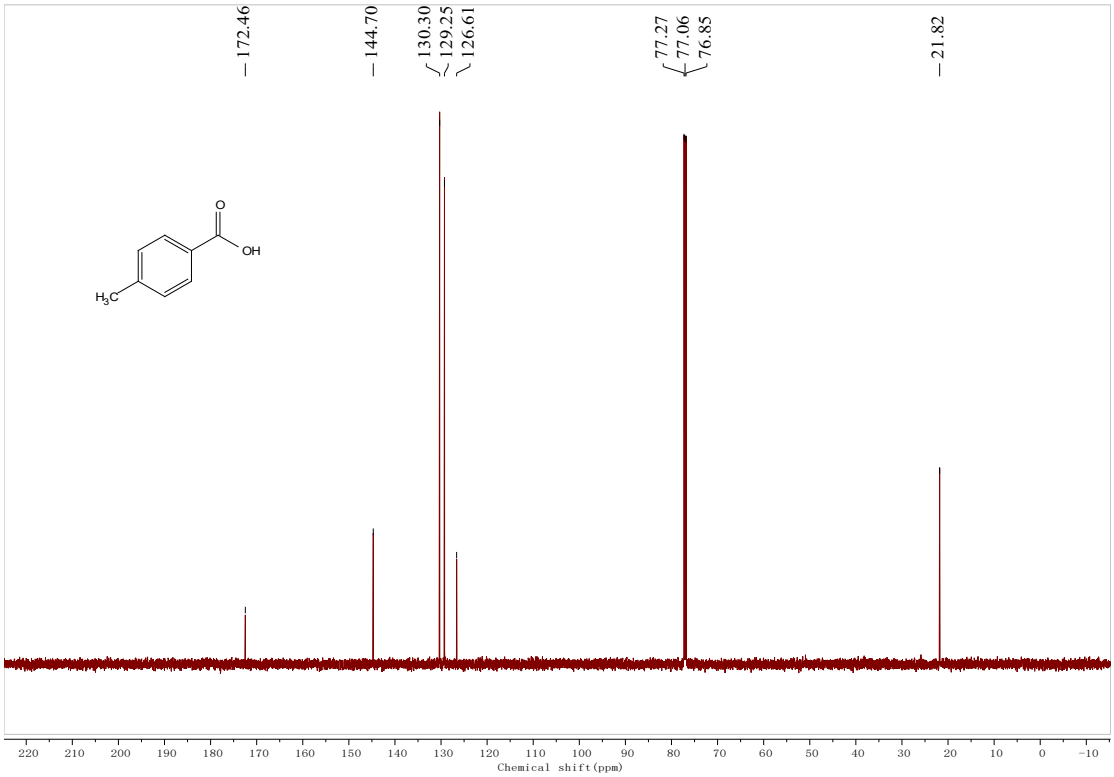
^{1}H NMR spectra of **2m**



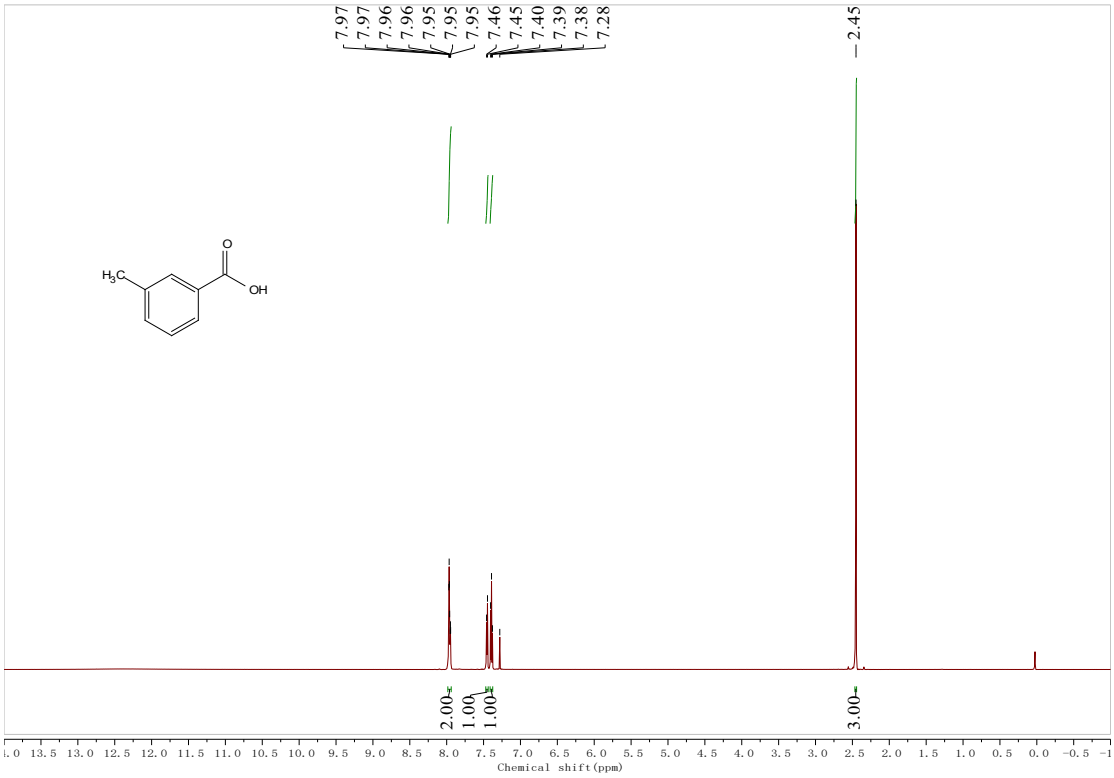
^{13}C NMR spectra of **2m**



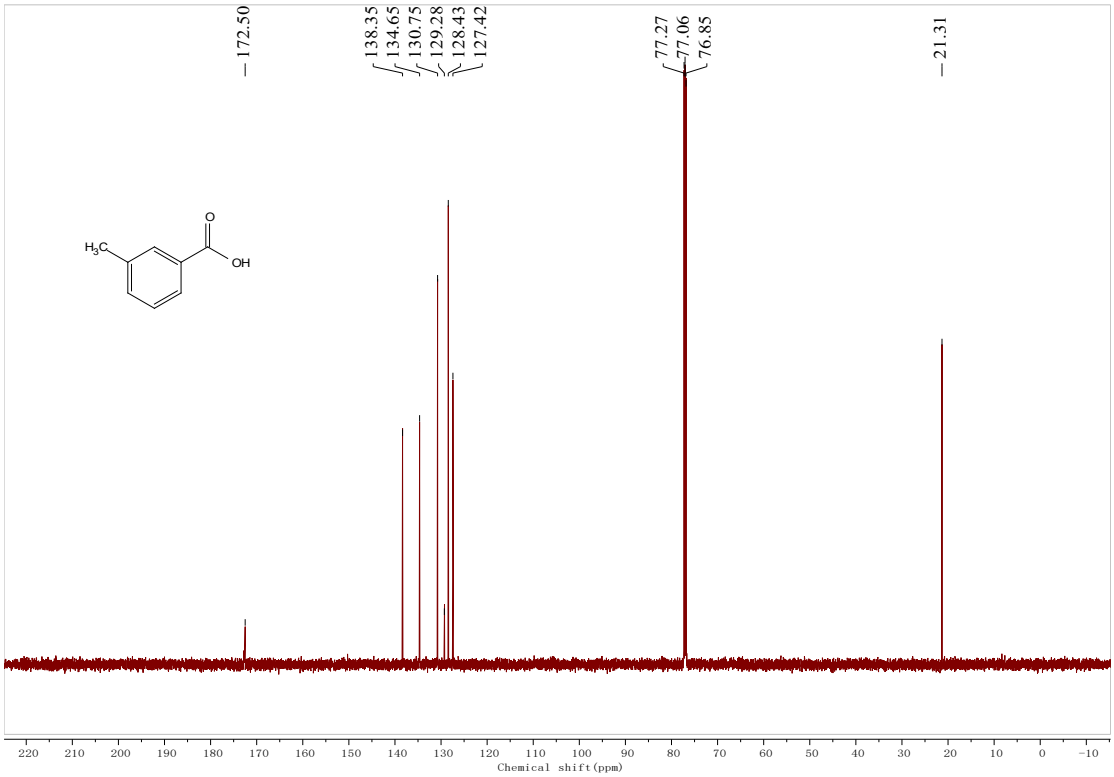
^{1}H NMR spectra of **2n**



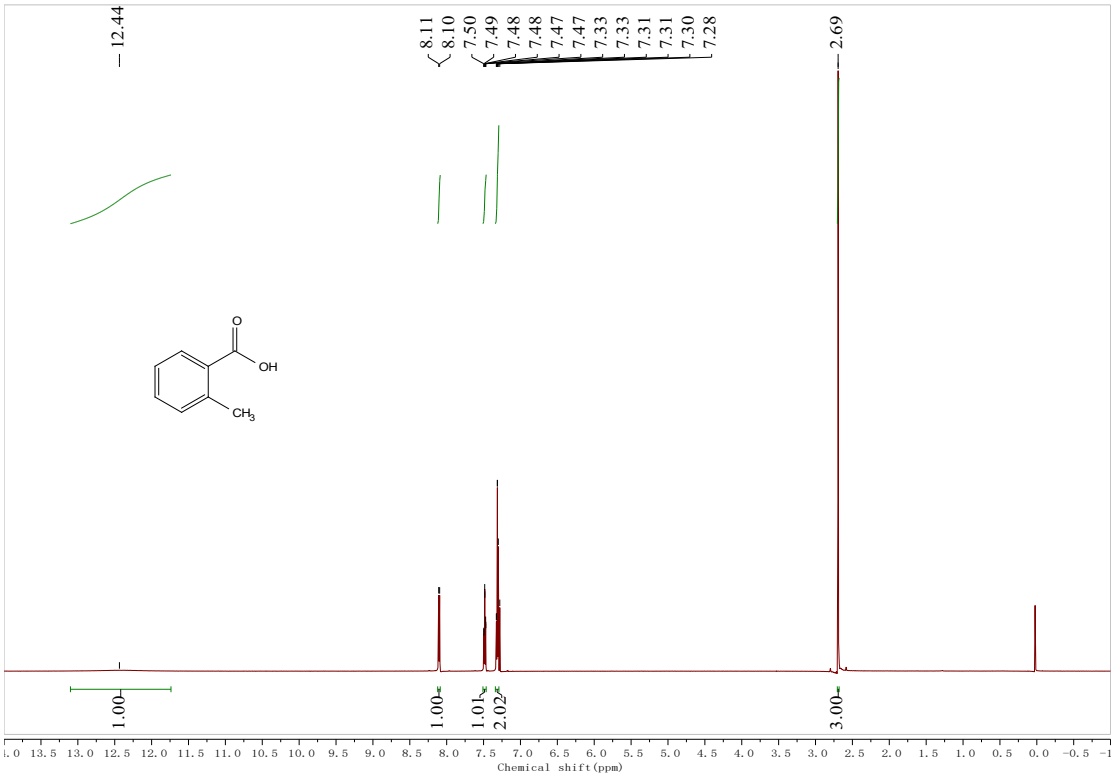
^{13}C NMR spectra of **2n**



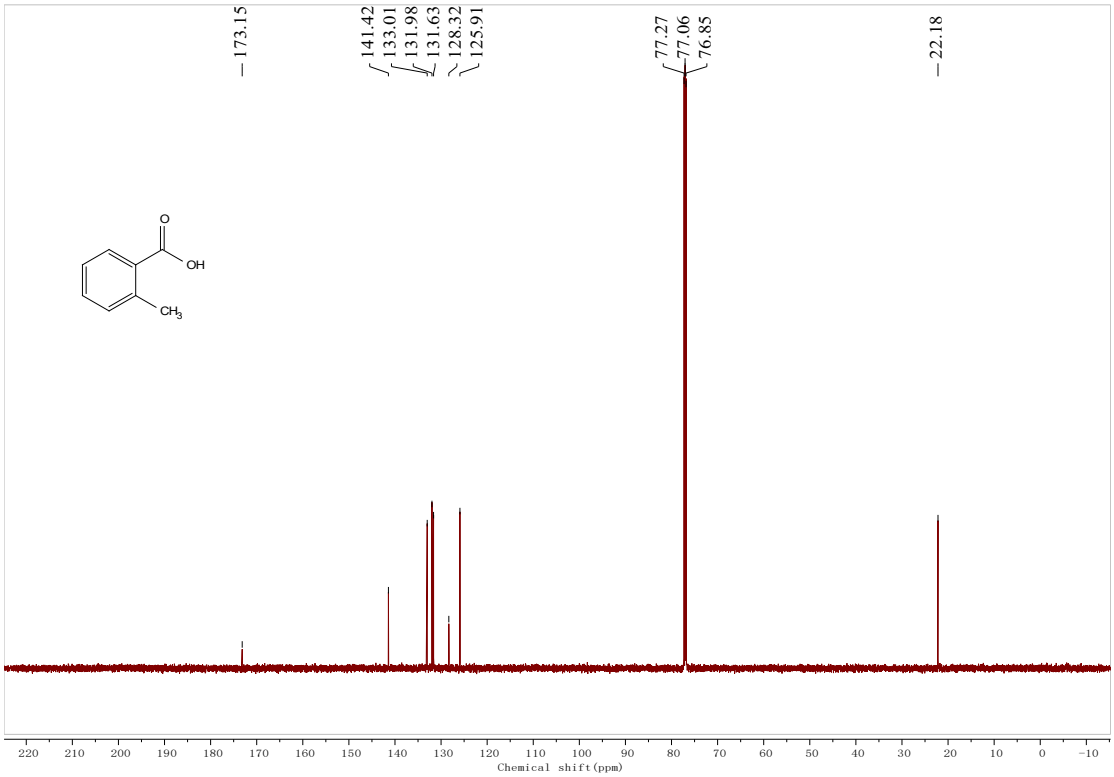
^{1}H NMR spectra of **2o**



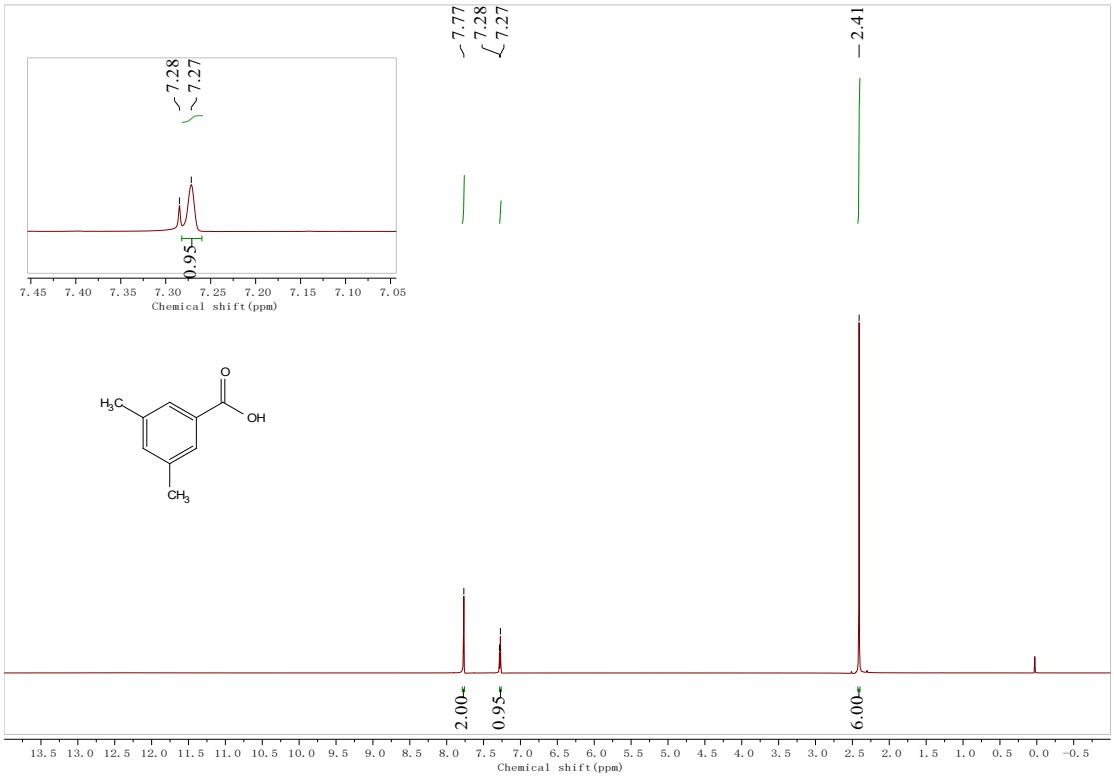
^{13}C NMR spectra of **2o**



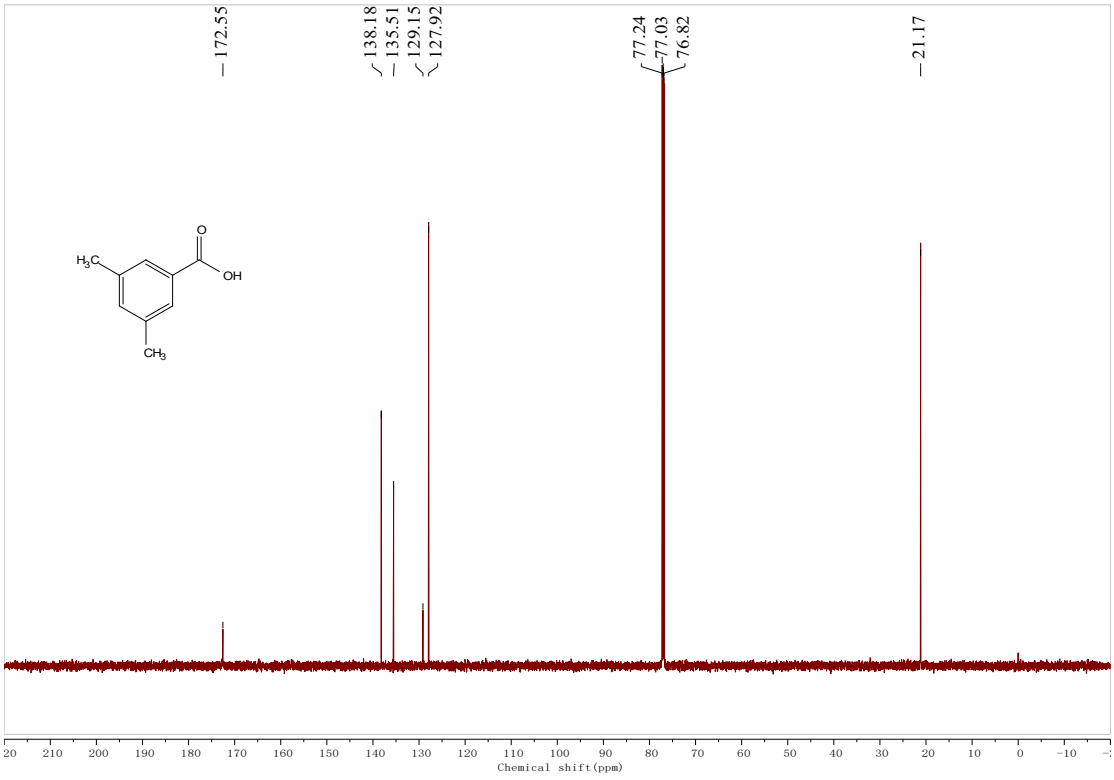
^{1}H NMR spectra of **2p**



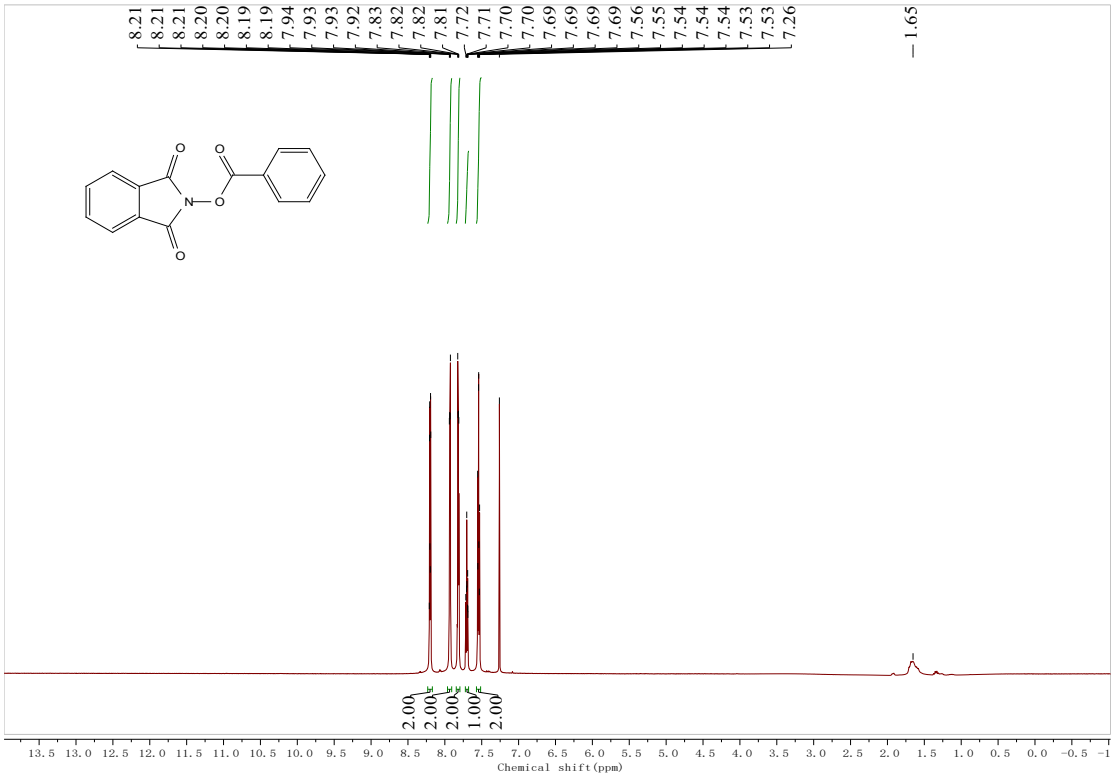
^{13}C NMR spectra of **2p**



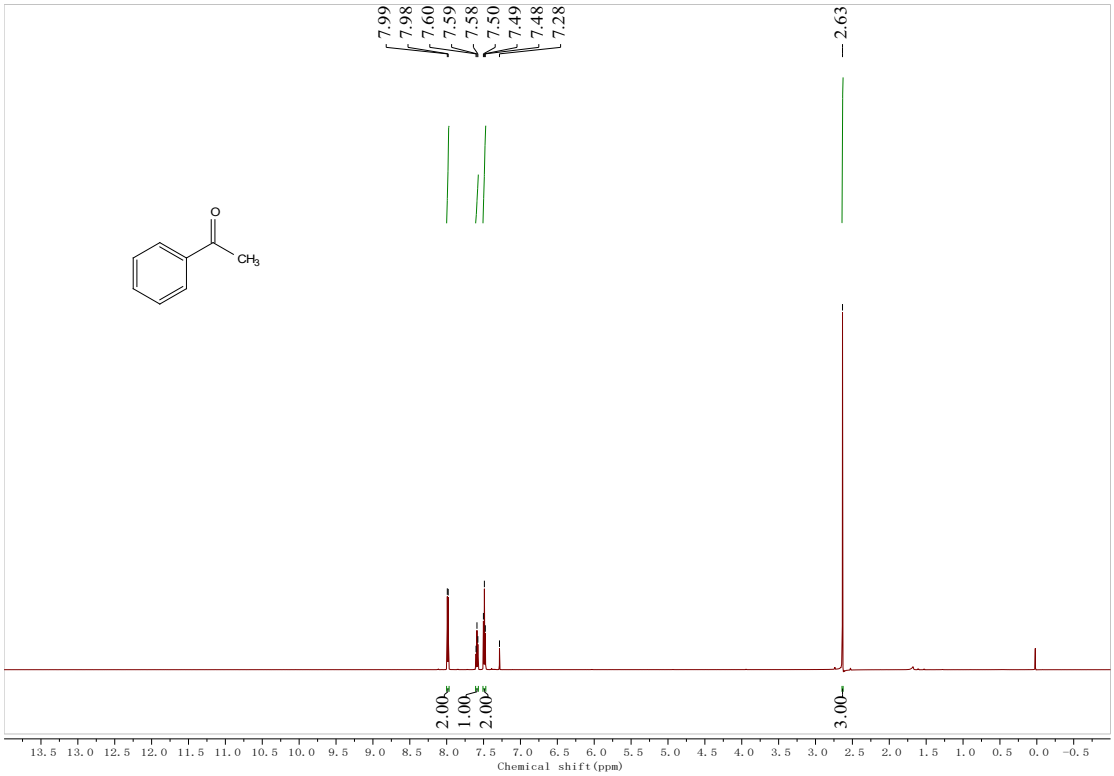
^{1}H NMR spectra of **2q**



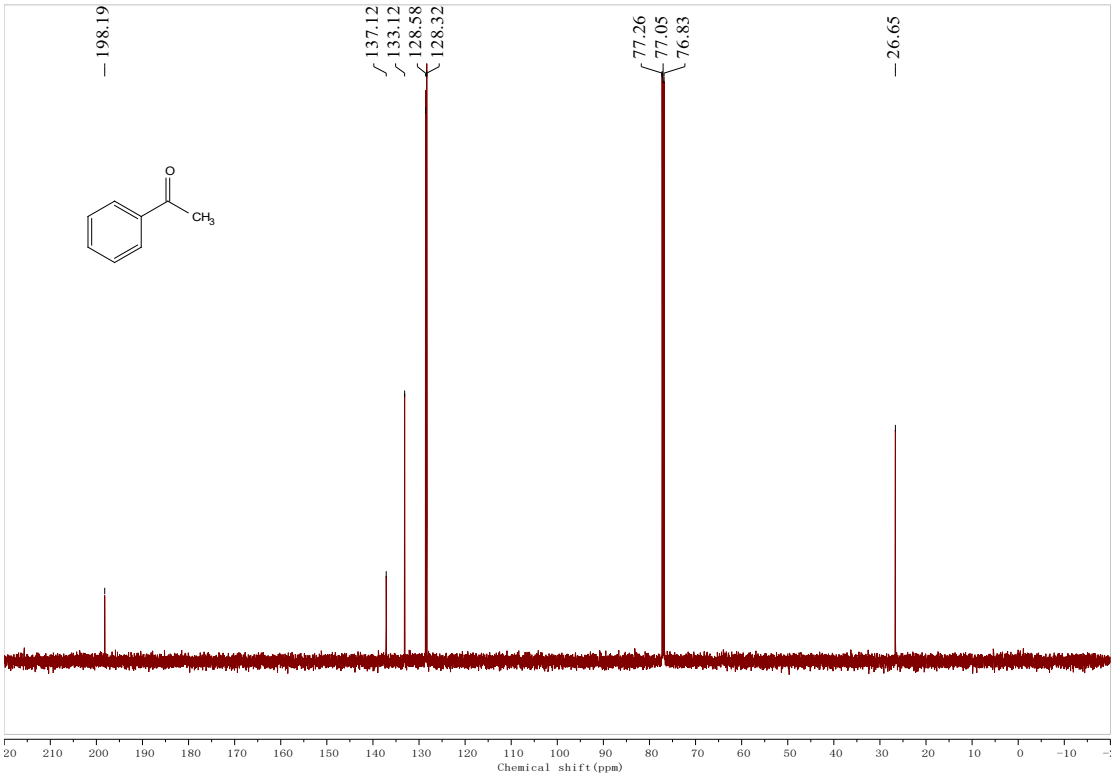
^{13}C NMR spectra of **2q**



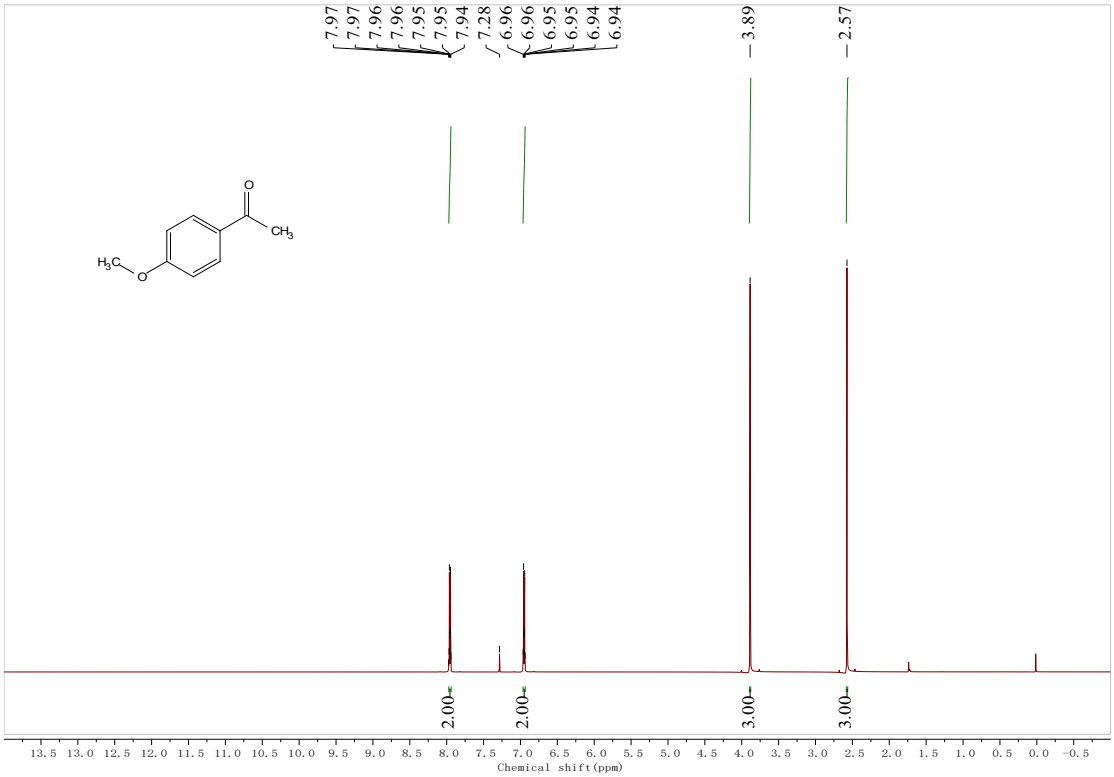
^{1}H NMR spectra of **3**



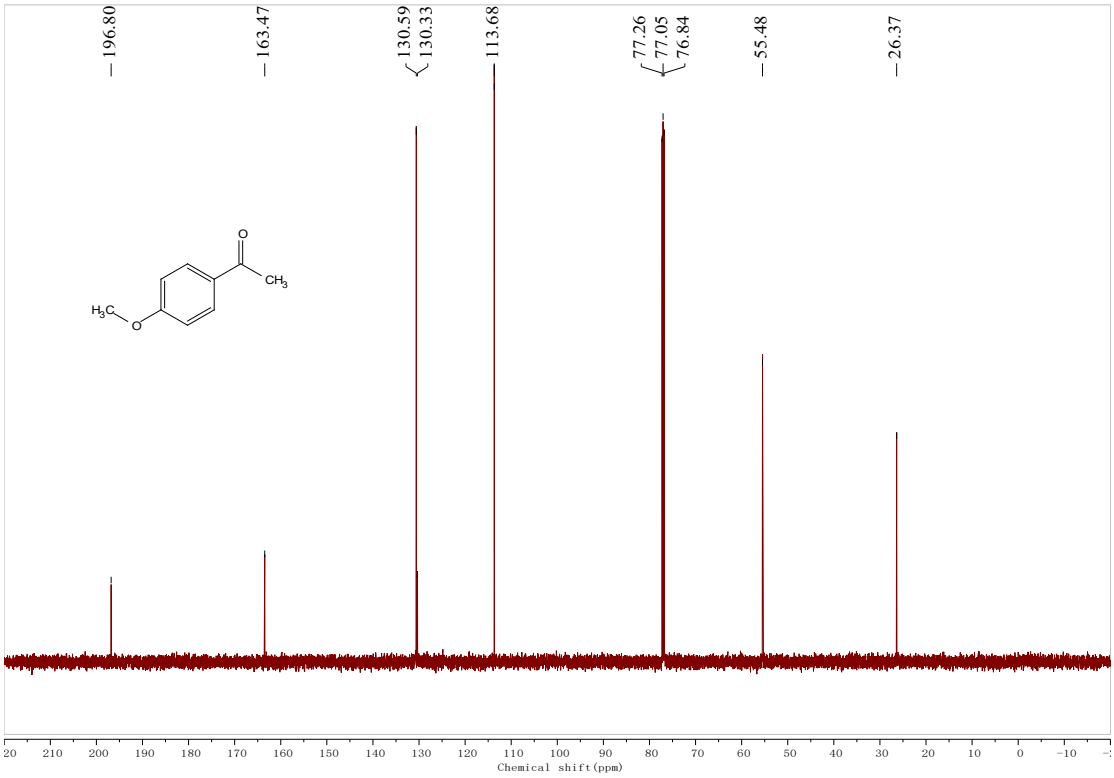
^{1}H NMR spectra of **5a**



^{13}C NMR spectra of **5a**

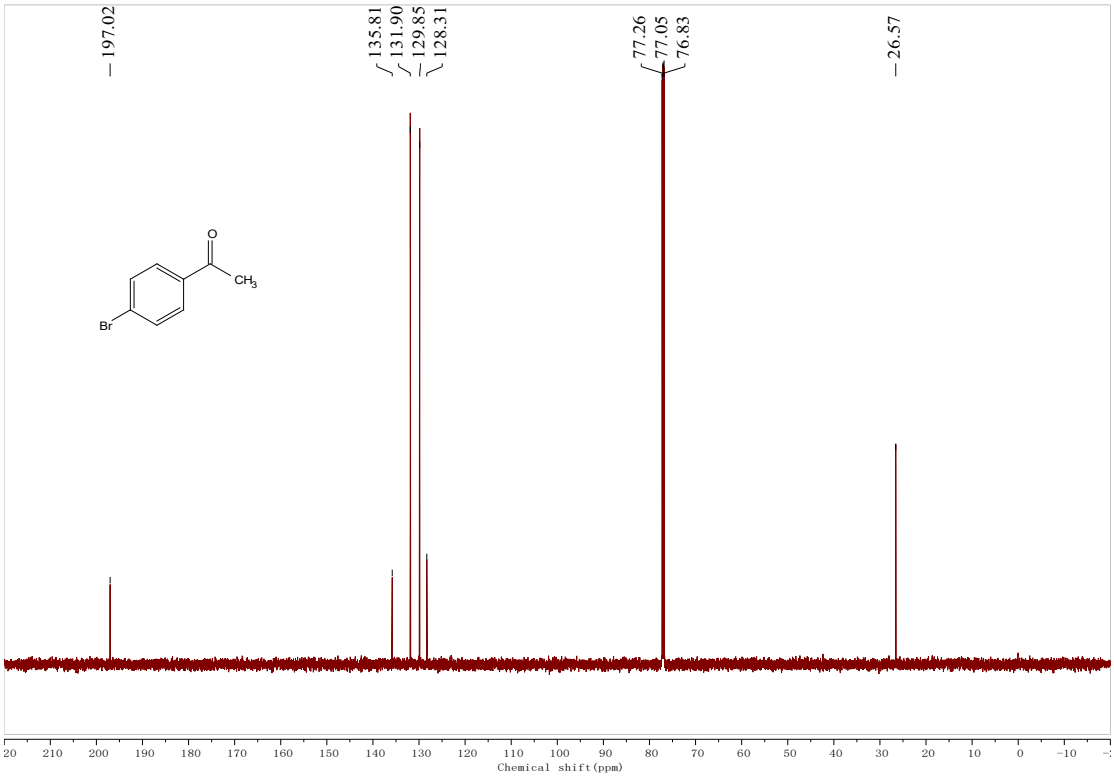


^{1}H NMR spectra of **5b**

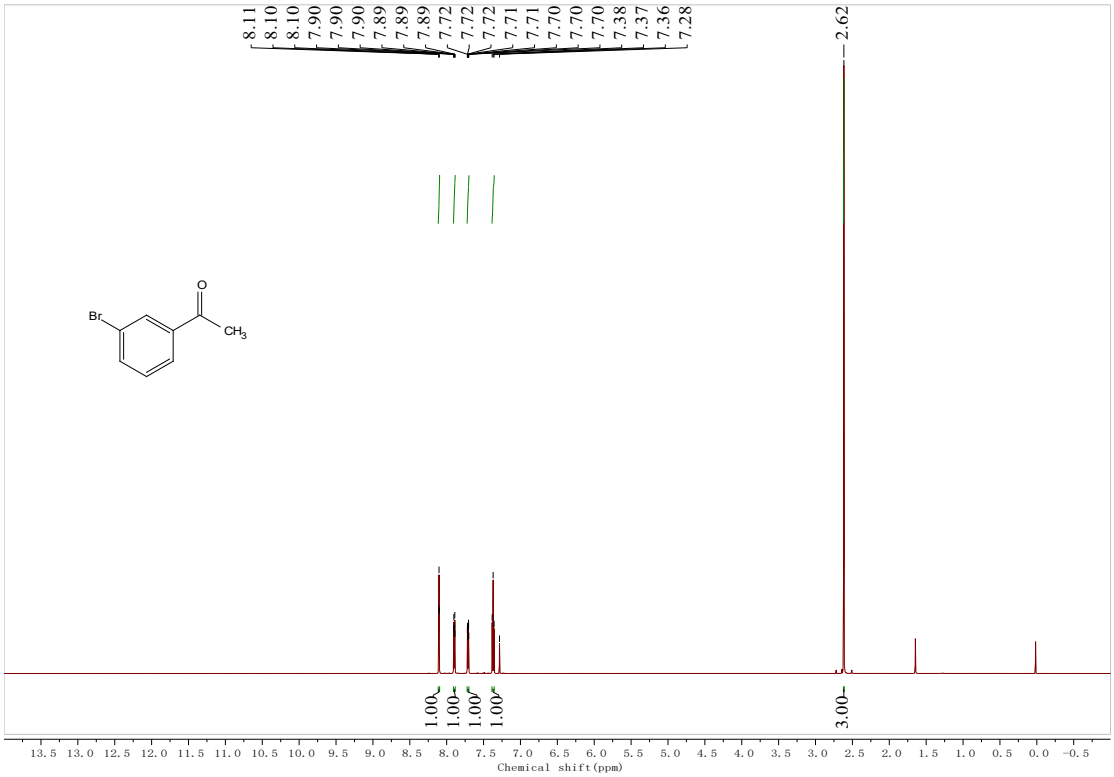


^{13}C NMR spectra of **5b**

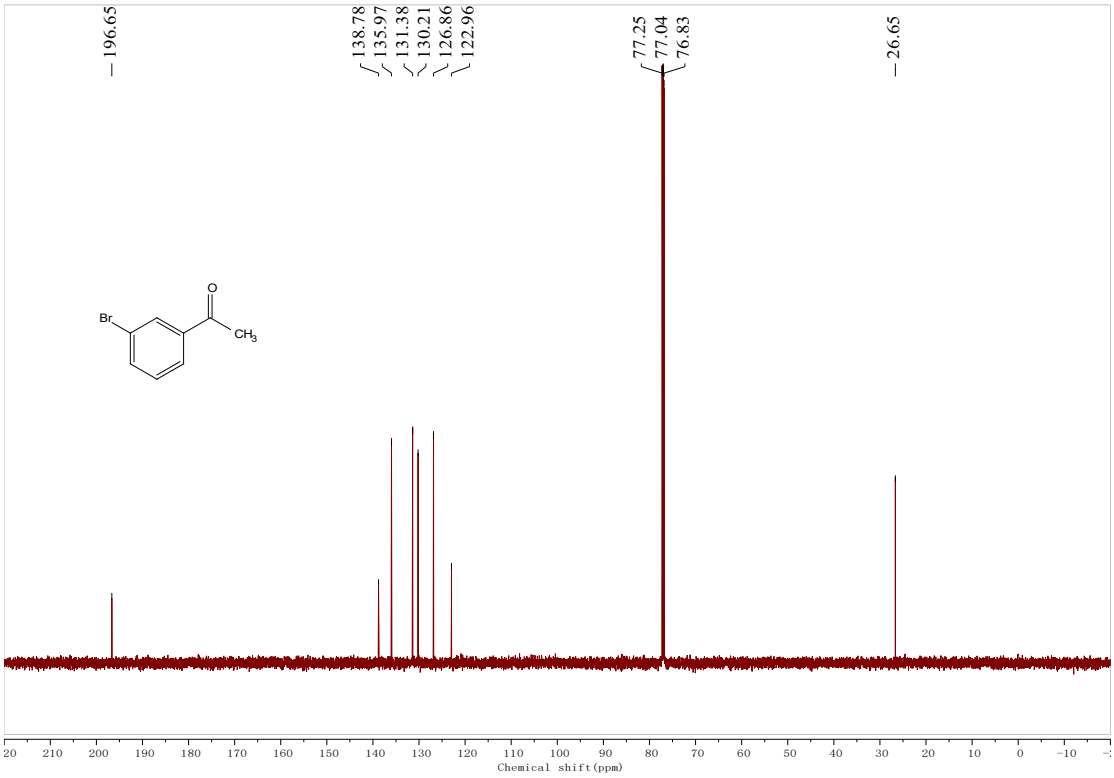
^{1}H NMR spectra of **5c**



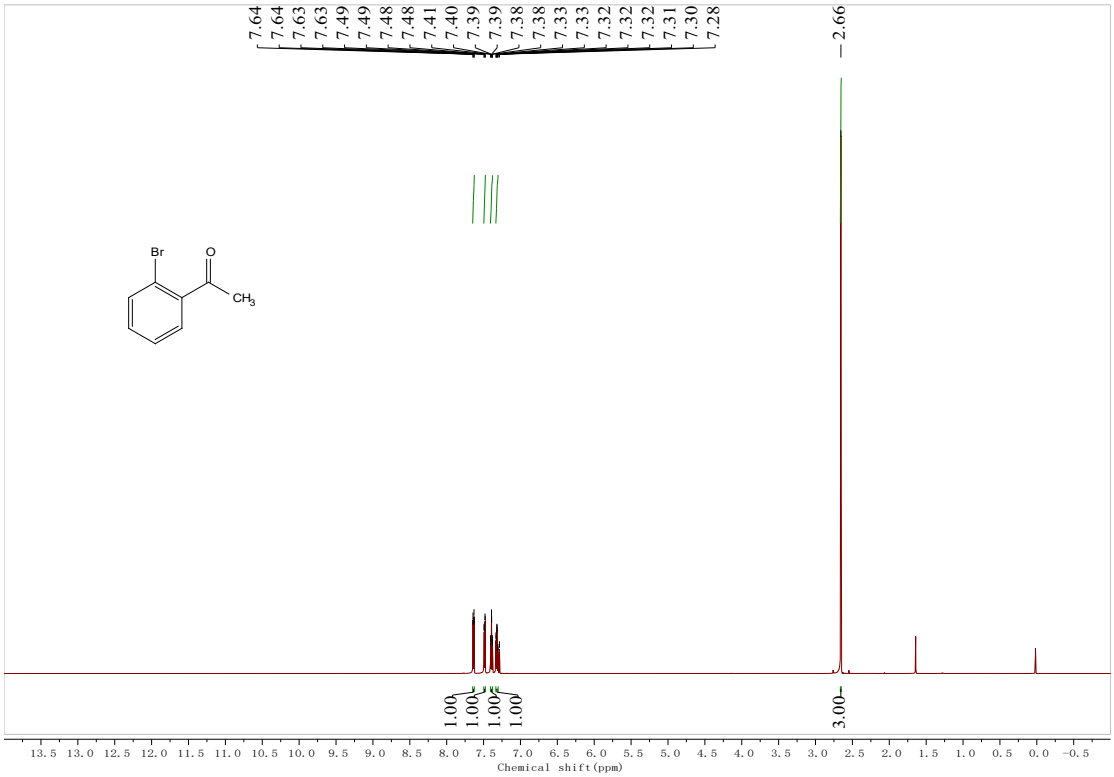
^{13}C NMR spectra of **5c**



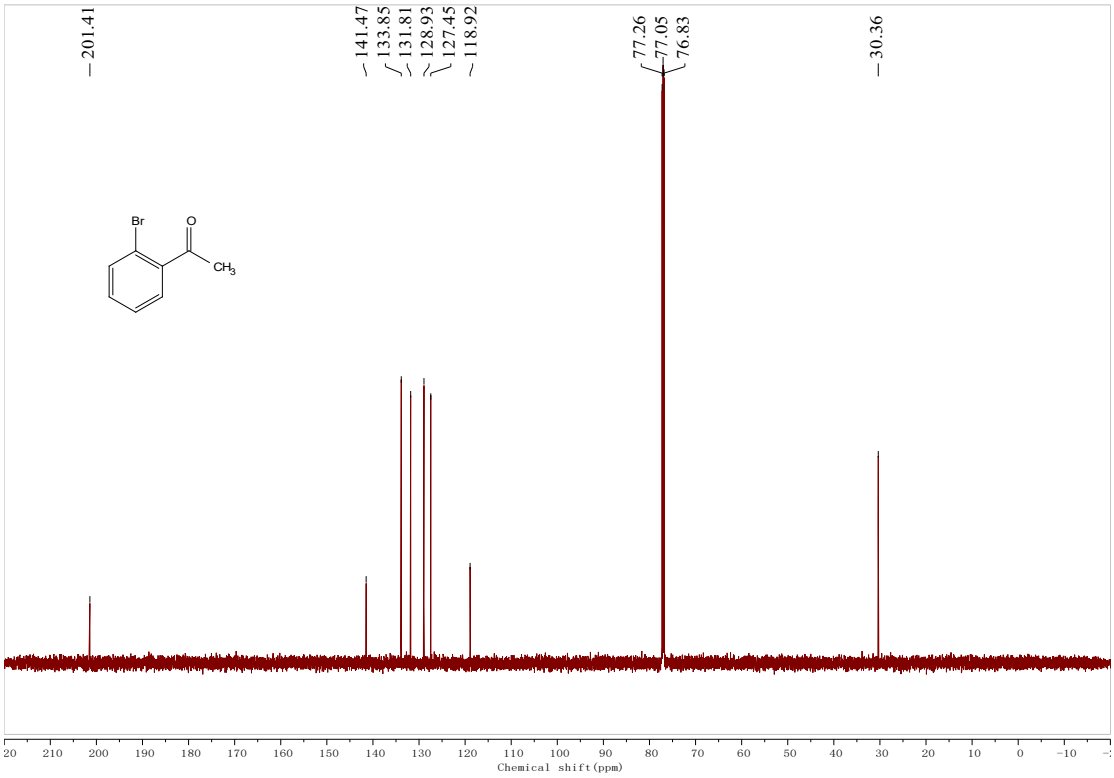
^{1}H NMR spectra of **5d**



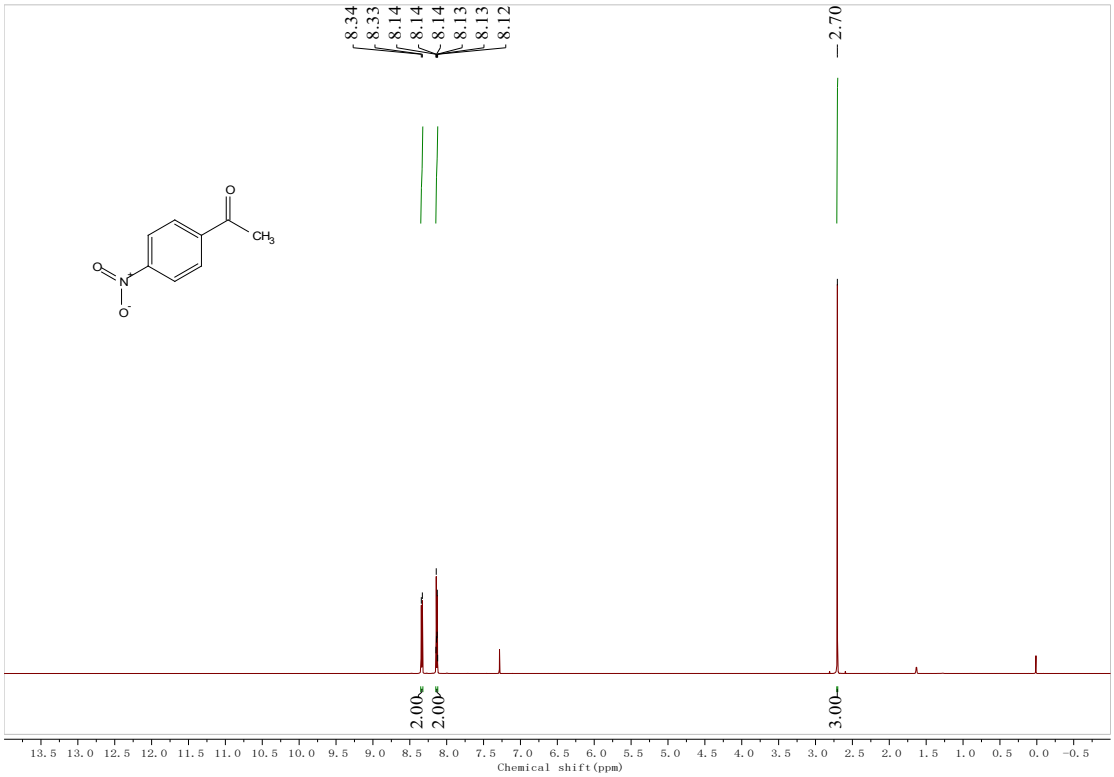
^{13}C NMR spectra of **5d**



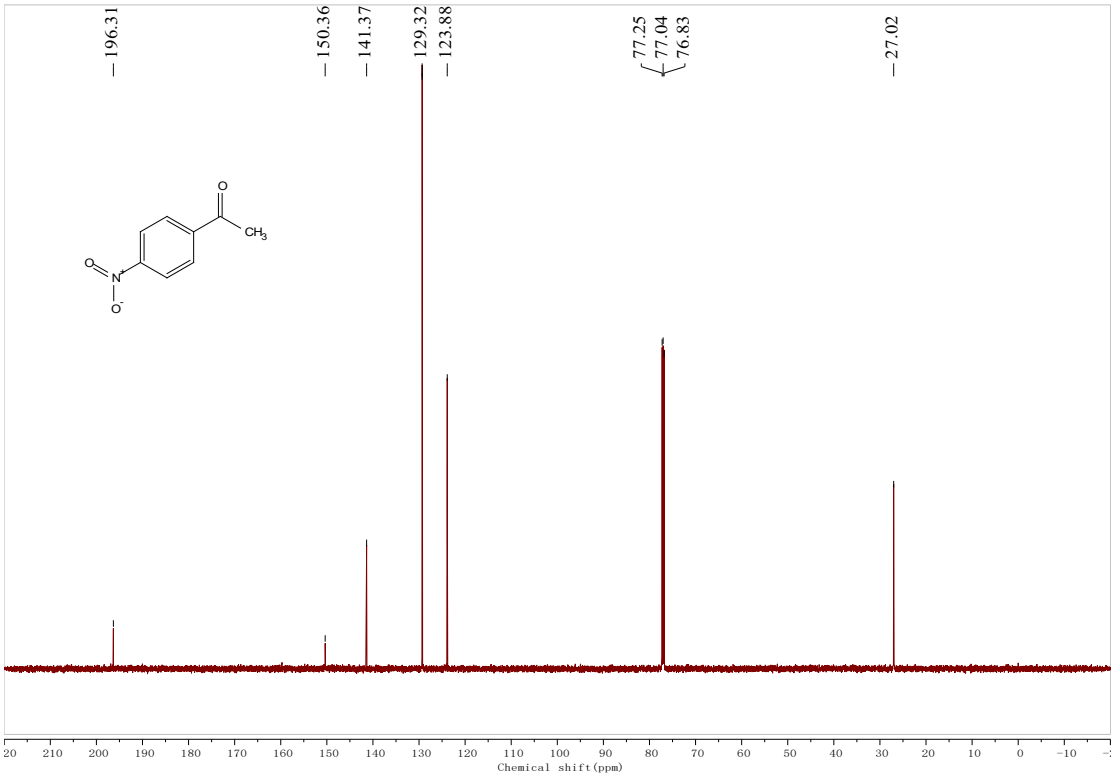
^{1}H NMR spectra of **5e**



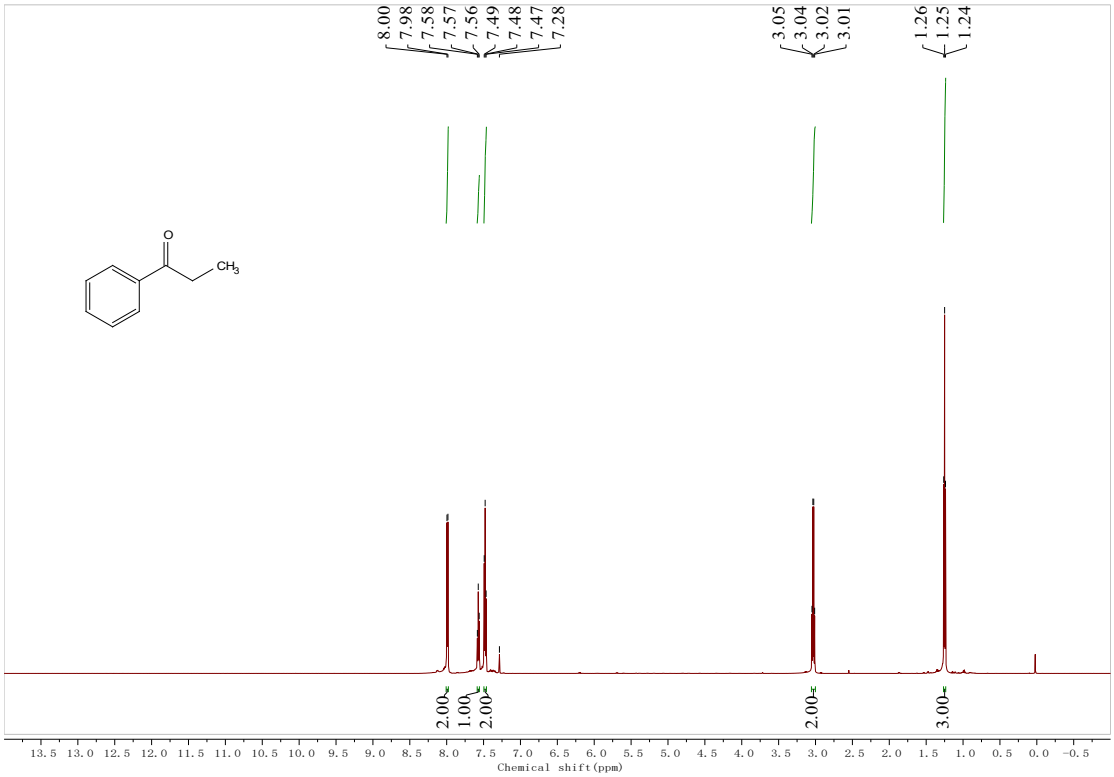
^{13}C NMR spectra of **5e**



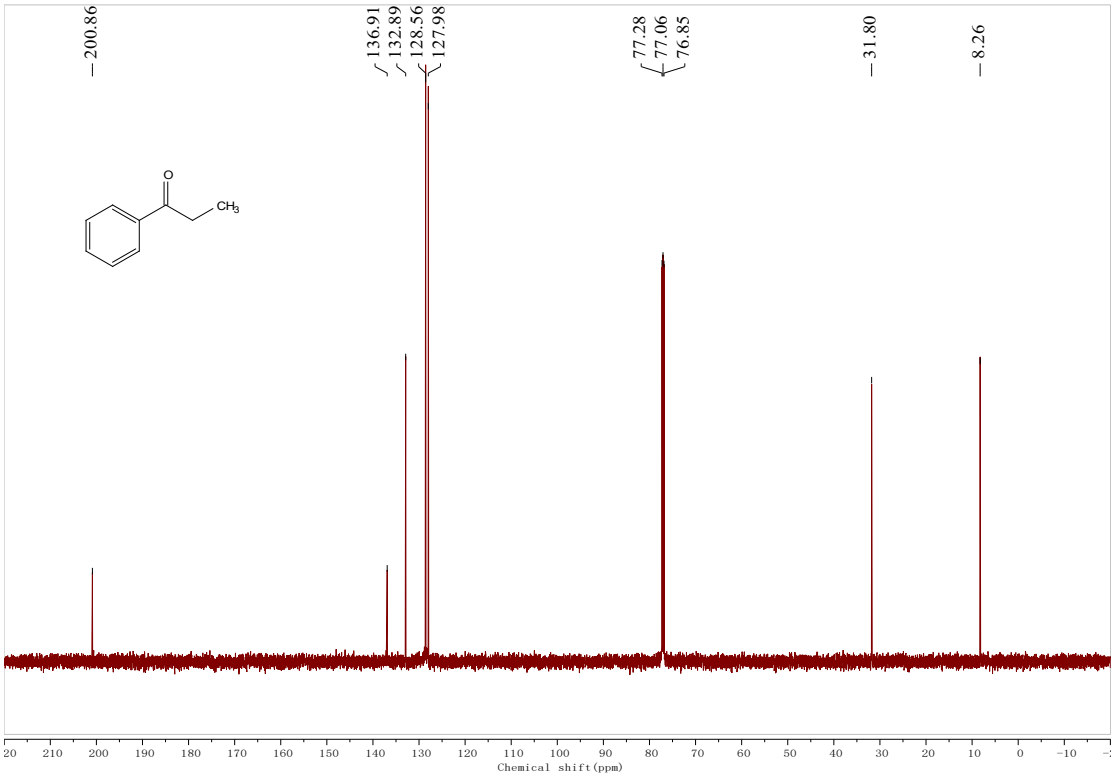
^{1}H NMR spectra of **5f**



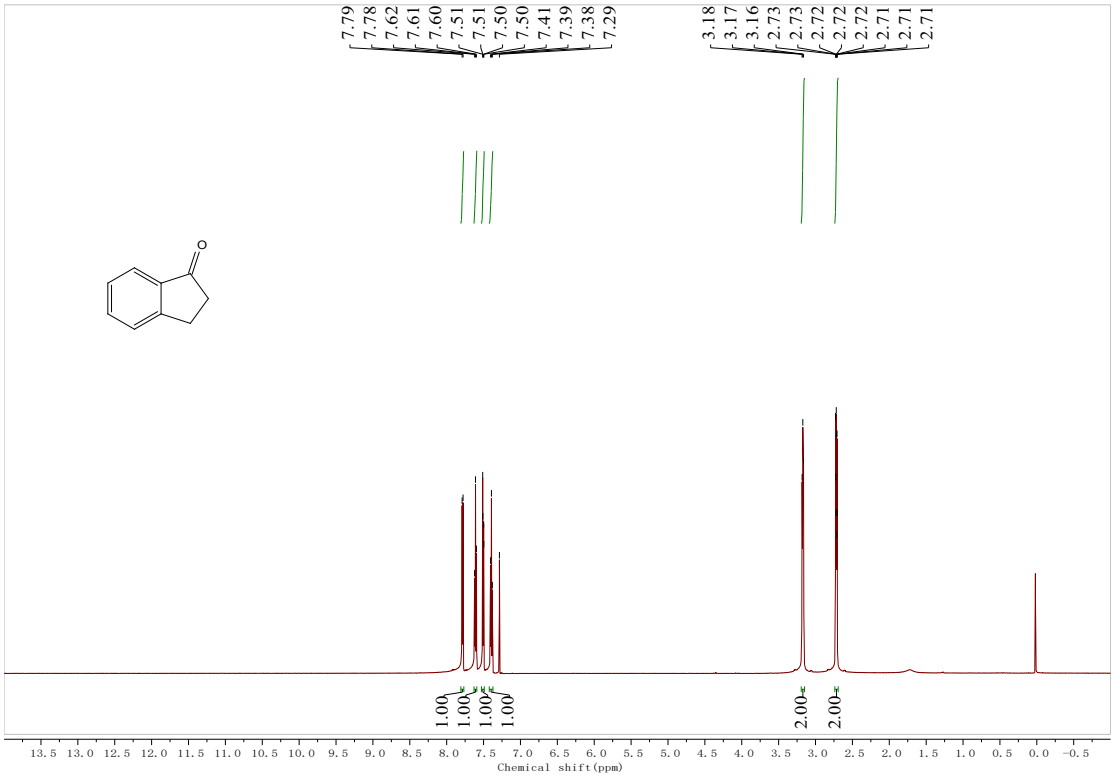
^{13}C NMR spectra of **5f**



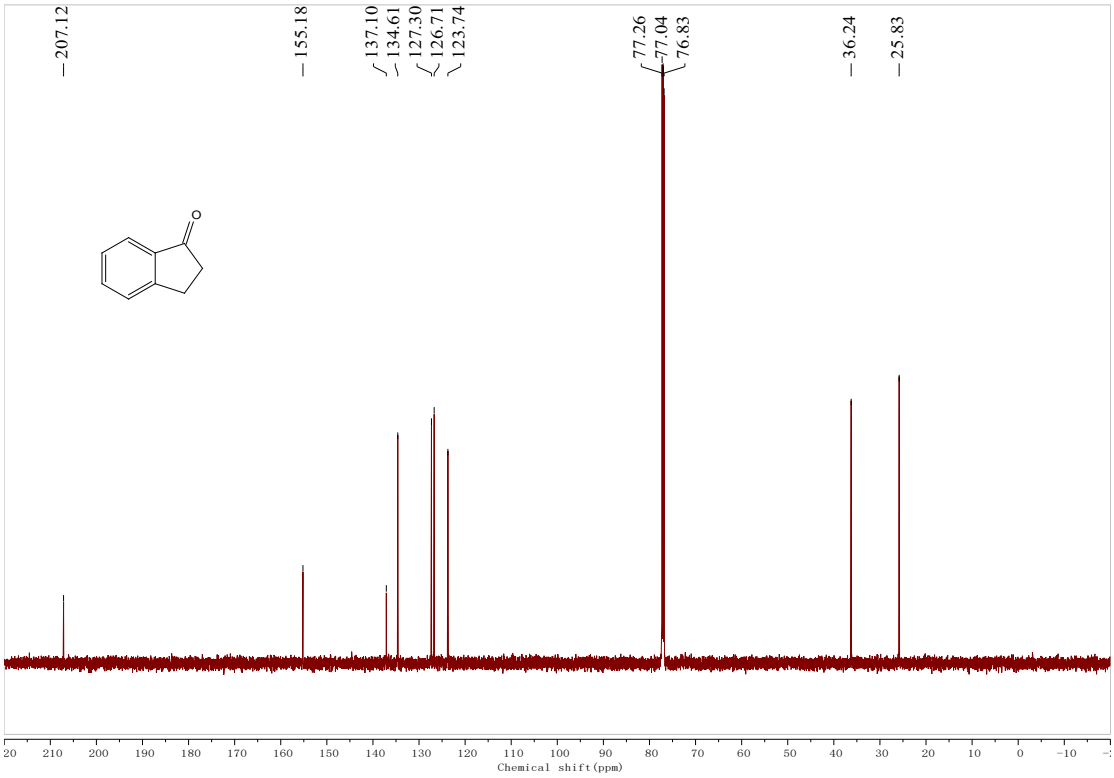
^{1}H NMR spectra of **5g**



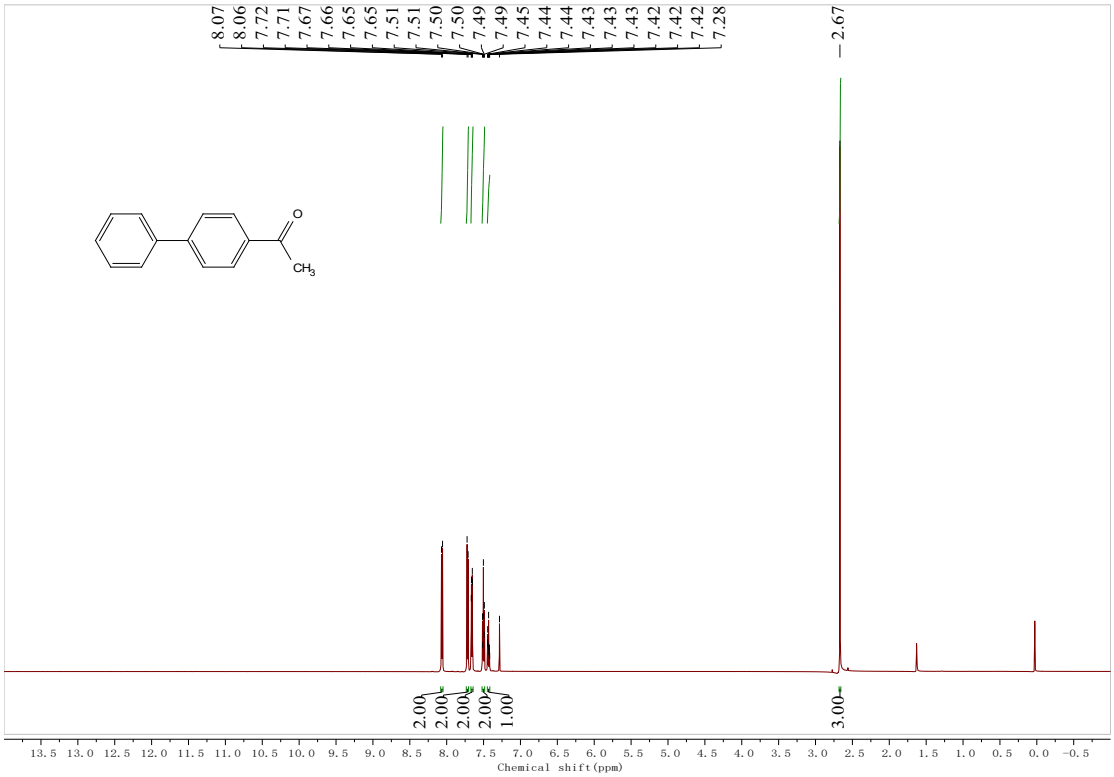
^{13}C NMR spectra of **5g**



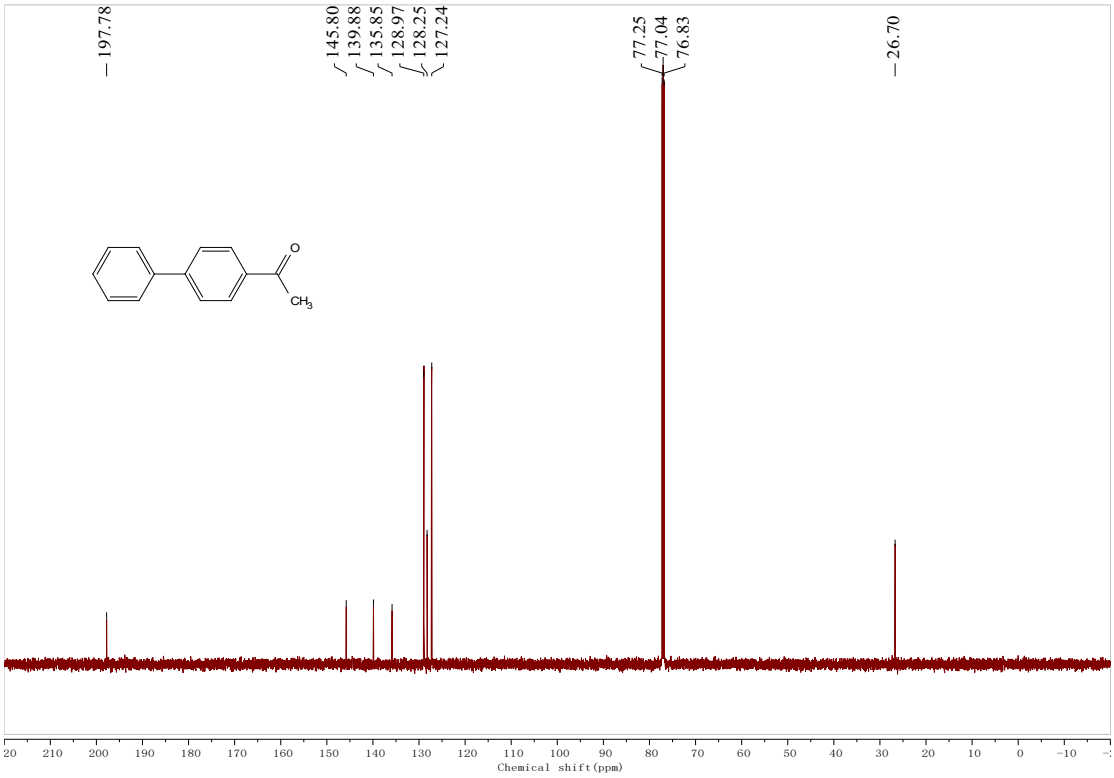
^{1}H NMR spectra of **5h**



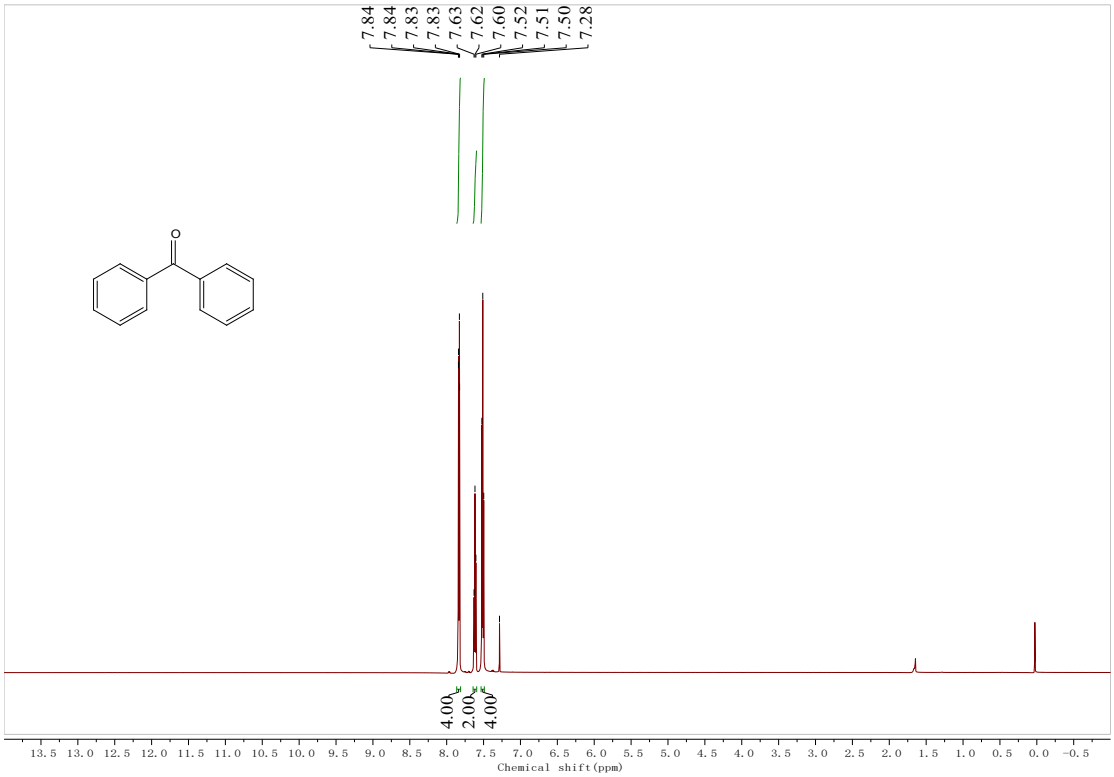
^{13}C NMR spectra of **5h**



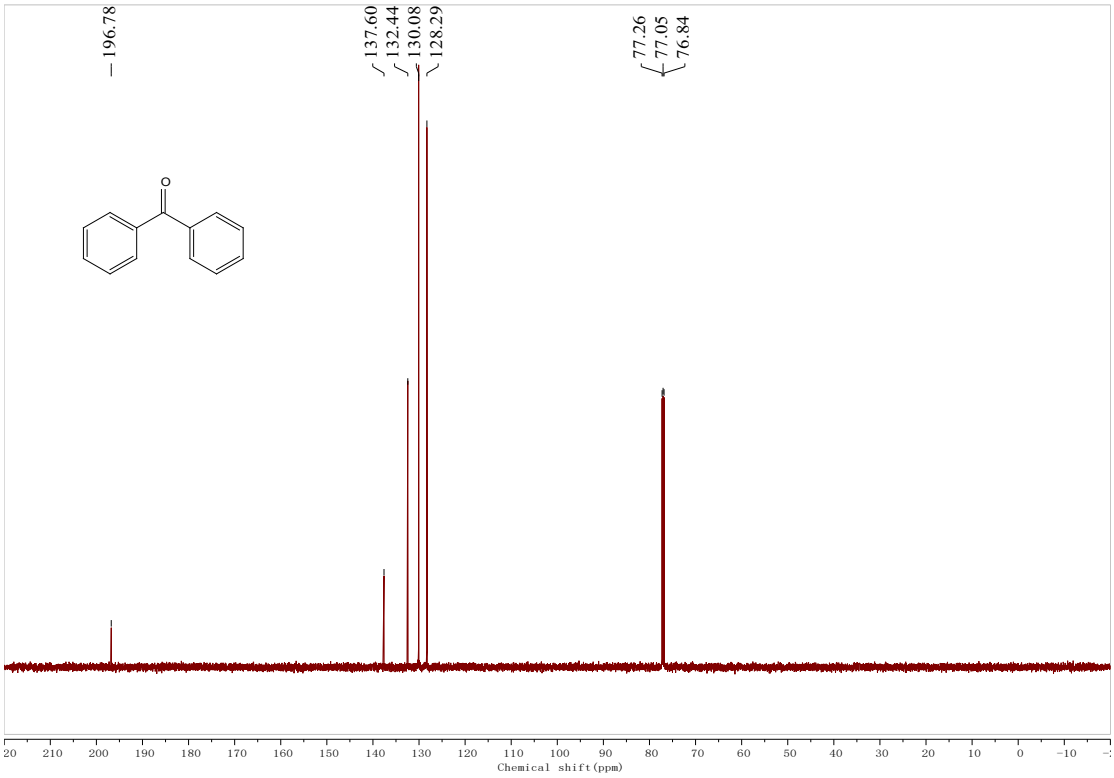
^{1}H NMR spectra of **5i**



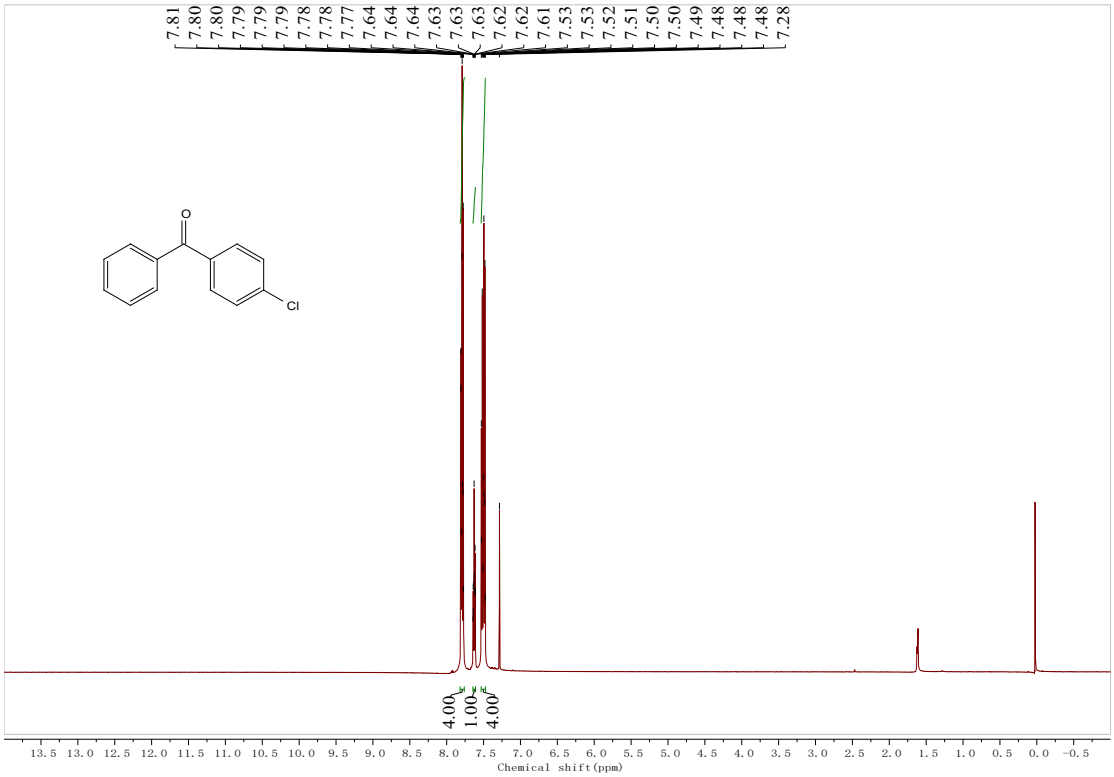
^{13}C NMR spectra of **5i**



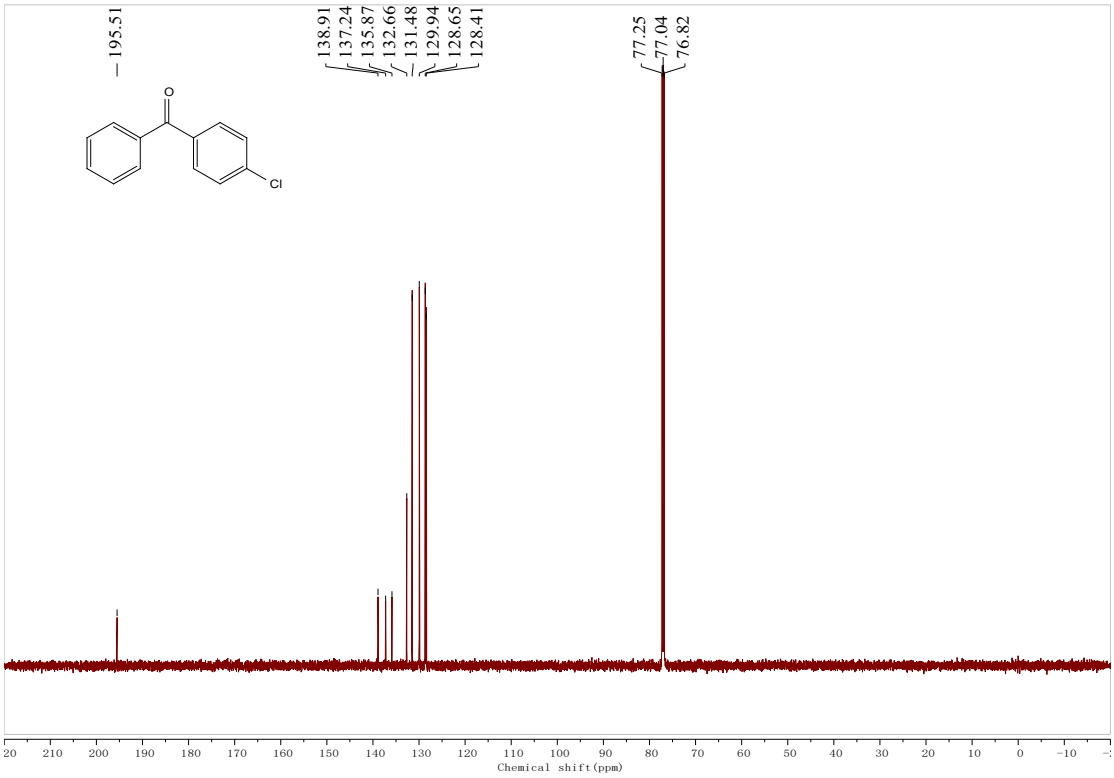
^{1}H NMR spectra of **5j**



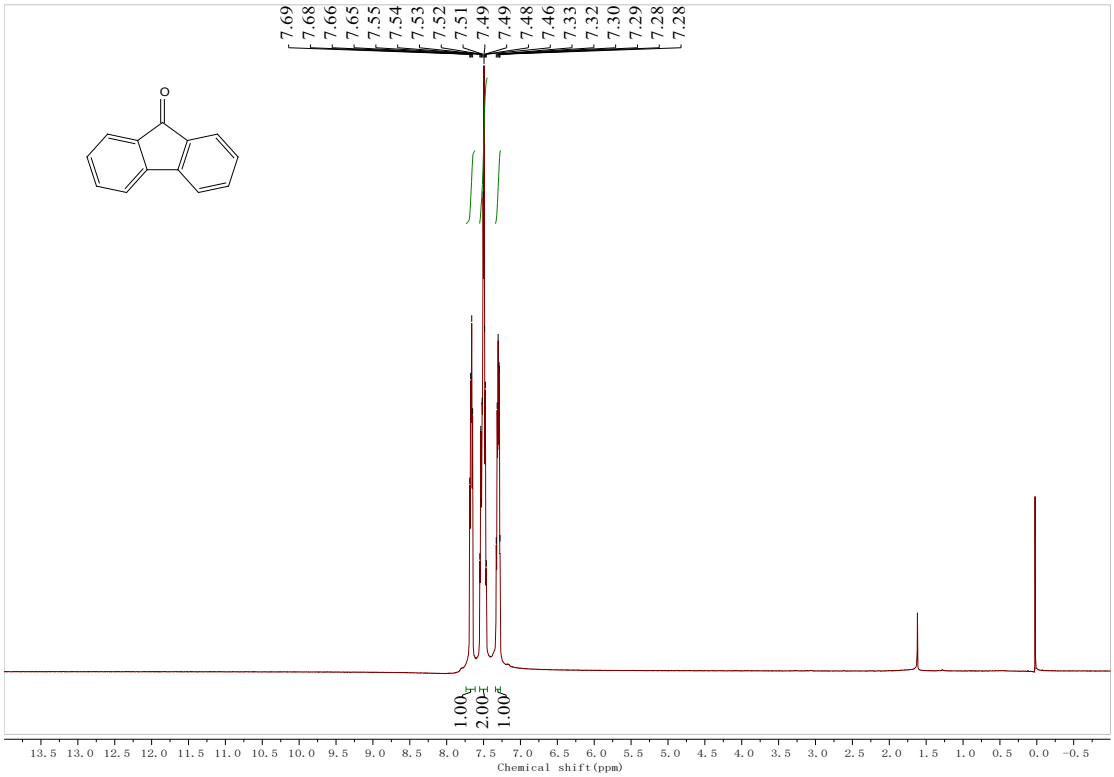
^{13}C NMR spectra of **5j**



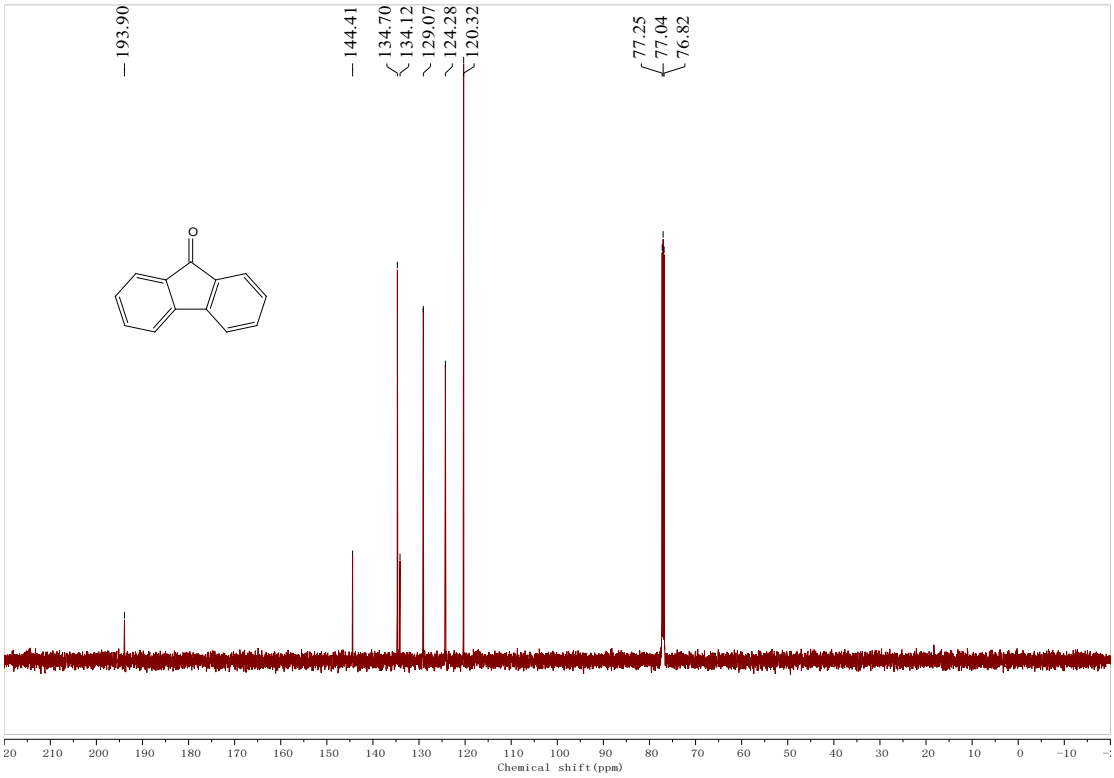
^{1}H NMR spectra of **5k**



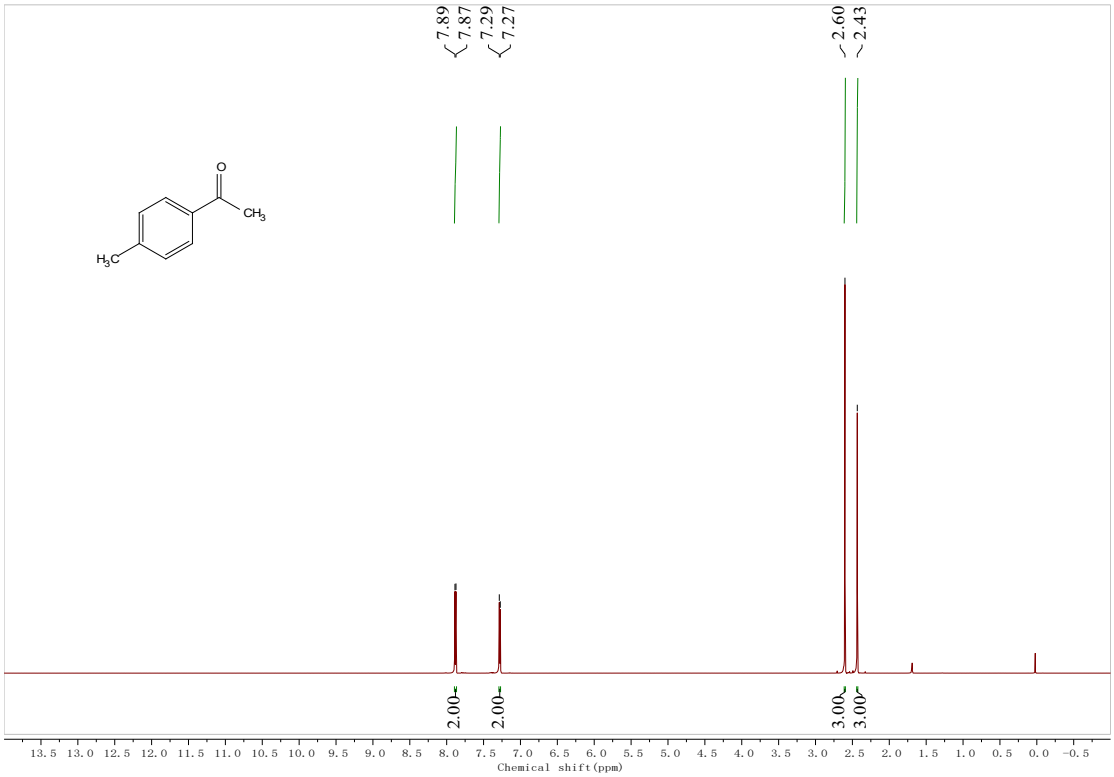
^{13}C NMR spectra of **5k**



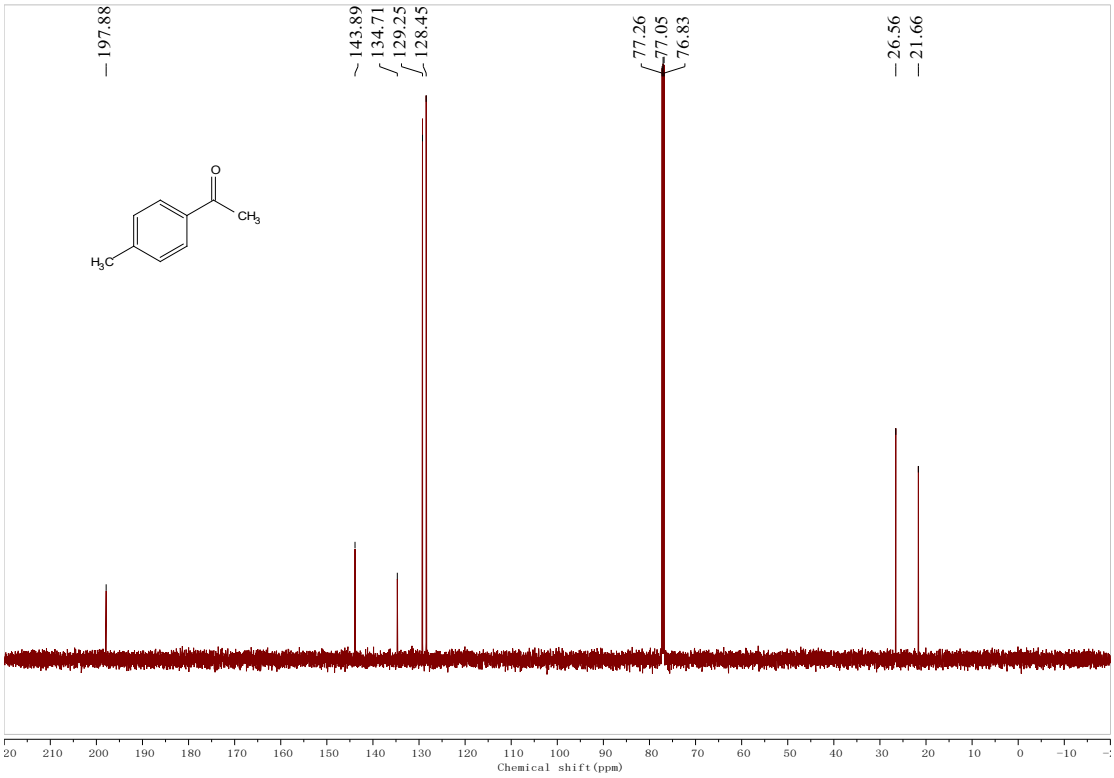
^{1}H NMR spectra of **5l**



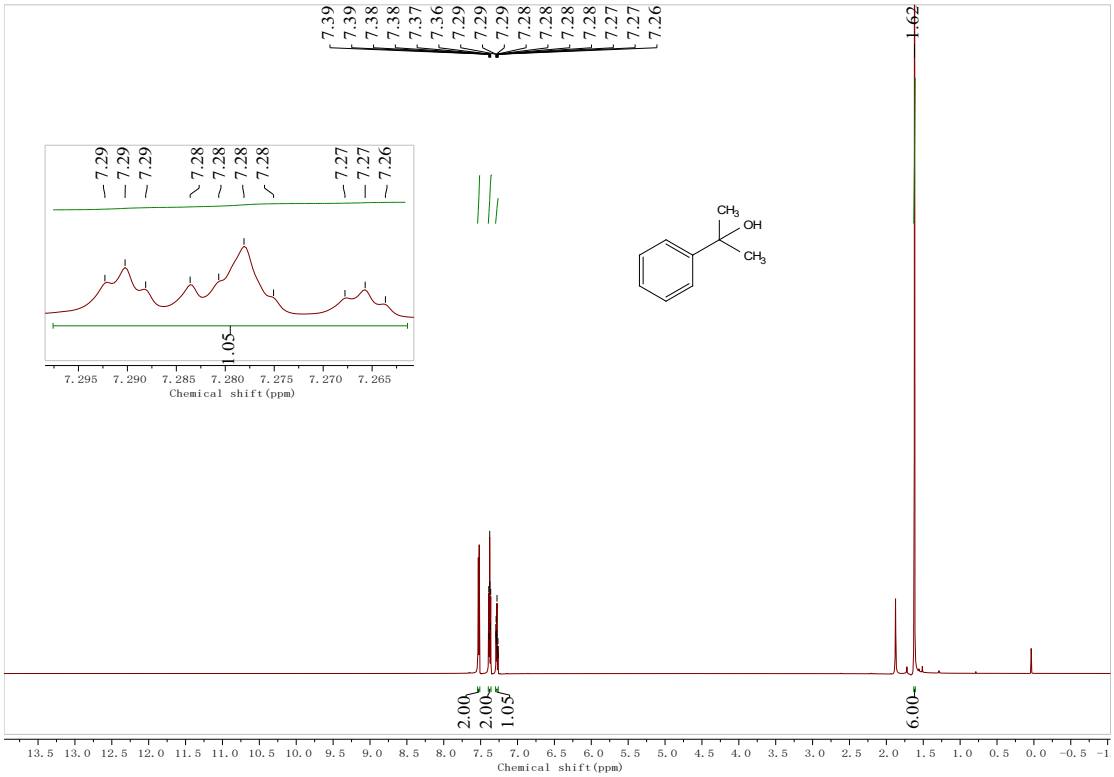
^{13}C NMR spectra of **5l**



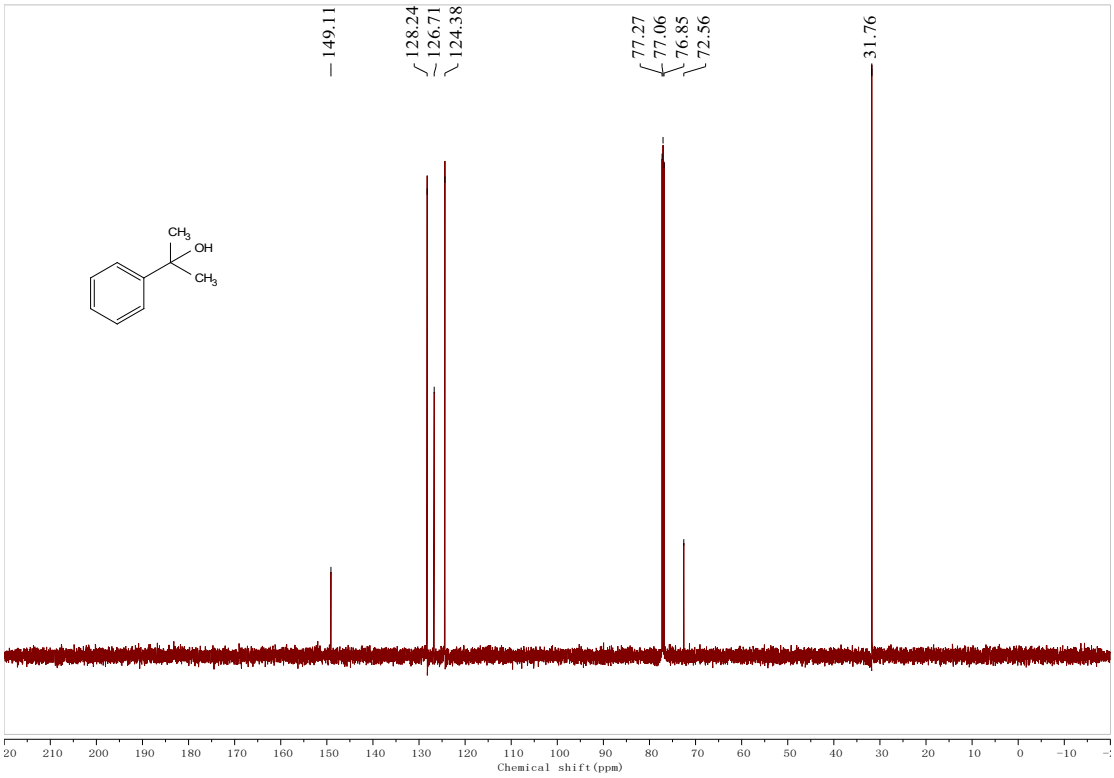
^{1}H NMR spectra of **5m**



^{13}C NMR spectra of **5m**



^{1}H NMR spectra of **5n**



^{1}H NMR spectra of **5n**

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