

*Supporting Information For*

**Brønsted Acid Catalysed Aerobic Photo-Oxygenation of Benzylic C–H**

**Bonds**

Jieqing Wu,<sup>†</sup> Jiwei Chen,<sup>†</sup> Lei Wang, Hongjun Zhu, Rui Liu, Guangliang Song, Chao Feng,<sup>\*</sup> and  
Yufeng Li<sup>\*</sup>

<sup>a</sup>*School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing, 211816, China*

**Contents:**

1. General information.....	S2
2. Conditions exploration .....	S3-S5
3. General procedure for the oxygenation .....	S5-S6
4. Gram scale synthesis of benzoic acid and catalyst reusability .....	S6-S7
5. UV-vis experiments.....	S7-S8
6. EPR experiments.....	S8
7. Determination of the kinetic isotope effect (KIE) .....	S9-S11
8. TEMPO quenching experiments.....	S12
9. Trapping of <sup>1</sup> O <sub>2</sub> with DPA.....	S13-S14
10. Spectral data of <b>3</b> and <b>5</b> .....	S15-S24
11. NMR spectra of <b>3</b> and <b>5</b> .....	S25-S69
12. References.....	S70-S71

## 1. General information

General: The light reaction experiment adopts the parallel light reaction instrument of Sustainable Safe Sun, the model is SSSTECH-LAL1CV1.0 (Figure S1). NMR spectra were recorded on a Bruker WM 400 spectrometer (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$  and 376 MHz for  $^{19}\text{F}$ ) at 298 K unless otherwise indicated. Chemical shifts  $\delta$  are given in ppm, using residual solvent as an internal standard. Coupling constants  $J$  are reported in Hz. Agilent 1200 HPLC system was used for quantitative measurements of benzoic acid (Santa Clara, USA), equipped with a pump (model G1312A), an auto sampler (ALS) (model G1329A), and a Hypersil Gold Thermo Scientific C18 (250 cm  $\times$  4.6 mm) 5  $\mu\text{m}$  column (Paisley, UK), and the detector consisted of UV/VIS operated at 230 nm. Agilent 7890A GC system was used for determination of the kinetic isotope effect (KIE). High-resolution mass spectra were obtained on Acquity UPLC/XEVO G2-XS QTOF, equipped with a linear ion trap and orbitrap analyzers. The EPR measurements were performed on a Bruker Model A200 spectrometer (Bruker Instrument, Germany) equipped with a Bruker ER4112SHQ X-band resonator. UV/Vis spectra were recorded on TU-1900 UV-Vis spectrophotometer. The progress of the reactions was monitored by thin-layer chromatography using TLC plates and visualized by shortwave ultraviolet light. Flash chromatography was performed with Qingdao Haiyang flash silica gel (200-300 mesh). Melting points were measured on a WRS-1C Melt-Temp apparatus and were uncorrected.

Starting materials and reagents were purchased from Sigma-Aldrich, Acros, Innochem, Energy Chemical, TCI China or Alfa Aesar, and used without further purification.

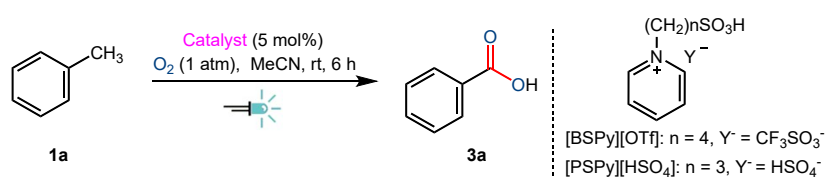


Figure S1. The photocatalytic reactor

## 2. Conditions exploration

All reactions were performed in quartz tubes equipped with O<sub>2</sub> balloon on 1 mmol scale with 5 mol% catalysts in 2 mL solvent under UV irradiation (365 nm, 8 W) at room temperature (20 °C), unless otherwise noted. Yield of **3a** was determined on HPLC instrument with a detection wavelength of 230 nm by external standard method using Na<sub>2</sub>HPO<sub>4</sub> (0.05 M) : H<sub>2</sub>O = 1 : 1 as the eluent. The operating temperature of the column was set at 30°C. The injection volume was 10 μL, and the flow rate was maintained at 1.0 mL/min.

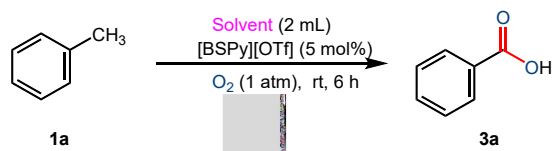
**Table S1.** Catalyst screening experiments.



Entry	Catalyst	Solvent	Wave length (nm)	Yield (%) <sup>b</sup>
1	–	MeCN	365	trace
2	H <sub>2</sub> SO <sub>4</sub> (40% w)	MeCN	365	86
3	HCl (6 M)	MeCN	365	54
4	HF <sub>4</sub> (70% w)	MeCN	365	92
5	CH <sub>3</sub> SO <sub>3</sub> H (98% w)	MeCN	365	92
6	<i>p</i> -TsOH	MeCN	365	93
7	CF <sub>3</sub> SO <sub>3</sub> H	MeCN	365	91
8	[BSPy][OTf]	MeCN	365	96
9	[PSPy][HSO <sub>4</sub> ]	MeCN	365	90
10	H <sub>3</sub> PO <sub>4</sub> (85% w)	MeCN	365	trace
11	KHSO <sub>4</sub> (30% w)	MeCN	365	17
12	HOAc	MeCN	365	trace
13 <sup>a</sup>	[BSPy][OTf]	MeCN	365	trace
14	HNO <sub>3</sub> (65%)	MeCN	365	63
15	HNO <sub>3</sub> (33%)	MeCN	365	54

<sup>a</sup>Under 1 atm O<sub>2</sub> atmosphere. <sup>b</sup>Yields were determined with HPLC. [BSPy][OTf]: *N*-butylsulfonate pyridinium trifluoromethanesulfonate. [PSPy][HSO<sub>4</sub>]: *N*-propylsulfonate pyridinium bisulfate.

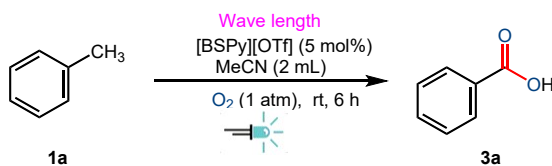
**Table S2.** Influence of solvents on the reaction.



Entry	Catalyst	Solvent	Wave length (nm)	Yield (%) <sup>a</sup>
1	[BSPy][OTf]	EA	365	trace
2	[BSPy][OTf]	C <sub>6</sub> H <sub>6</sub>	365	17
3	[BSPy][OTf]	CH <sub>2</sub> Cl <sub>2</sub>	365	52
4	[BSPy][OTf]	DMF	365	26
5	[BSPy][OTf]	DMSO	365	35
6	[BSPy][OTf]	NMP	365	41
7	[BSPy][OTf]	EtOH	365	Trace
8	[BSPy][OTf]	THF	365	38
9	[BSPy][OTf]	MeCN	365	96

<sup>a</sup>Yields were determined with HPLC. EA: ethyl acetate. DMF: *N,N*-dimethyl formamide. DMSO: dimethyl sulfoxide. NMP: *N*-methyl-2-pyrrolidone. THF: tetrahydrofuran.

**Table S3.** Effect of light wavelength on the reaction.

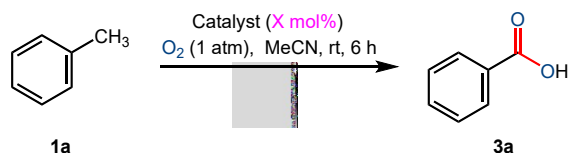


Entry	Catalyst	Solvent	Wave length (nm)	Yield (%) <sup>b</sup>
1	[BSPy][OTf]	MeCN	–	NR
2	[BSPy][OTf]	MeCN	365	96
3	[BSPy][OTf]	MeCN	400	32
4	[BSPy][OTf]	MeCN	460	Trace

5 [BSPy][OTf] MeCN 520 NR

<sup>a</sup>Yields were determined with HPLC. NR: no reaction.

**Table S4.** Influence of catalyst loadings on the reaction.

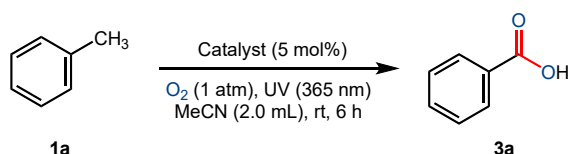


Entry	Catalyst	Catalyst loadings(X mol%)	Solvent	Wave length (nm)	Yield (%) <sup>b</sup>
1	[BSPy][OTf]	–	MeCN	365	NR
2	[BSPy][OTf]	1	MeCN	365	50
3	[BSPy][OTf]	5	MeCN	365	96
4	[BSPy][OTf]	10	MeCN	365	95
5	[BSPy][OTf]	20	MeCN	365	97

<sup>a</sup>Yields were determined with HPLC.

### 3. General procedure for the oxygenation.

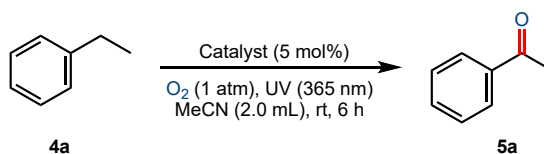
#### 3.1 General procedure A for the oxygenation of methyl aromatics



Toluene (92.1 mg, 1 mmol), [BSPy][OTf] (18.25 mg, 5 mol%) and MeCN (2 mL) were added into a 25 mL quartz tube, which was then vacuumed and purged with oxygen via an oxygen balloon for three times. The reaction mixture was then stirred vigorously for 6 h under UV irradiation (365 nm, 8 W) at room temperature (20 °C). At the end of the reaction, 10 mL EA was added thereto, and the resulted mixture was washed with water (5 mL × 2). The oil layer was dried anhydrous Na<sub>2</sub>SO<sub>4</sub> and then evaporated under vacuum. The solid residue was purified over a column of silica gel (eluant: EA: PE: H<sub>2</sub>O = 1:10:1) to afford the desired benzoic acid (**3a**) with 91% yield (111 mg).

Compounds **3b**~**3x** were synthesized according to this procedure.

### 3.2 General Procedure B for the oxygenation of nonmethyl aromatics :

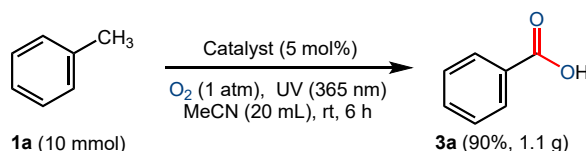


Ethylbenzene (106.2 mg, 1 mmol), [BSPy][OTf] (18.25 mg, 5 mol%) and MeCN (2 mL) were added into a 25 mL quartz tube, which was then vacuumed and purged with oxygen via an oxygen balloon for three times. The reaction mixture was stirred vigorously for 6 h under UV irradiation (365 nm, 8 W) at room temperature (20 °C). At the end of the reaction, the reaction mixture was evaporated with rotary evaporator to give a residue, which was dispersed with 5 mL dichloromethane. The mixture was filtered to recover the catalyst and the liquid phase was evaporated with rotary evaporator to give a residue, which was purified over a column of silica gel (eluent: EA: PE= 1:20) to obtain acetophenone (**5a**) with 92% yield (110 mg).

Compounds **5a**~**5q** were synthesized in light of this procedure.

## 4. Gram scale synthesis of benzoic acid and catalyst reusability

### 4.1 Gram scale synthesis of benzoic acid (**3a**)



Toluene (0.92 g, 10 mmol), [BSPy][OTf] (182.5 mg, 5 mol%) and MeCN (20 mL) were reacted in accordance with General Procedure A. At the end of the reaction, 50 mL chloroform was added thereto, and the resulted mixture was washed with water (10 mL × 4). The organic layer was dried anhydrous Na<sub>2</sub>SO<sub>4</sub> and then evaporated under vacuum to give the crude product, which was purified over a column of silica gel (eluent: EA: PE: H<sub>2</sub>O = 1:10:1) to afford the desired benzoic acid (**3a**) with 90% yield (1.1 g).

### 4.2 Catalyst recover and reuse

During the foregoing gram scale process, water washing (10 mL × 4) led to a combined water phase containing [BSPy][OTf], which was evaporated under vacuum to give the recovered ionic liquid. The recovered [BSPy][OTf] was then reused along the foregoing procedure for gram scale

synthesis of **3a**.

## 5. UV-vis experiments

**UV-vis spectrum of toluene:** Toluene (9.2 mg, 0.1 mmol) and MeCN (10 mL) were added into an oven dried Schlenk tube, which was then vacuumed and purged with Ar for three times. Then, the mixture was stirred at room temperature in dark for 15 min. The solution was subsequently used for UV-vis analysis.

**UV-vis spectrum of *p*-TsOH·H<sub>2</sub>O:** *p*TsOH·H<sub>2</sub>O (19.0 mg, 0.1 mmol) was added into an oven dried Schlenk tube, which was then vacuumed and purged with Ar for three times. MeCN (10 mL) was injected through a syringe. Then, the mixture was stirred at room temperature in dark for 15 min. The solution was subsequently used for UV-vis analysis.

**UV-vis spectrum of [BSPy][OTf]:** [BSPy][OTf] (36.5 mg, 0.1 mmol) was added into an oven dried Schlenk tube, which was then vacuumed and purged with Ar for three times. MeCN (10 mL) was injected through a syringe. Then, the mixture was stirred at room temperature in dark for 15 min. The solution was subsequently used for UV-vis analysis.

**UV-vis spectrum of the mixture of toluene and H<sub>2</sub>SO<sub>4</sub>:** Toluene (9.2 mg, 1 mmol), H<sub>2</sub>O (14.7 mg), H<sub>2</sub>SO<sub>4</sub> (9.8 mg, 0.1 mmol), and MeCN (10 mL) were added into an oven dried Schlenk tube, which was then vacuumed and purged with Ar for three times. Then, the mixture was stirred at room temperature in dark for 15 min. The solution was subsequently used for UV-vis analysis.

**UV-vis spectrum of the mixture of toluene and *p*TsOH:** Toluene (9.2 mg, 0.1 mmol), *p*TsOH·H<sub>2</sub>O (19.0 mg, 0.1 mmol), and MeCN (10 mL) were added into an oven dried Schlenk tube, which was then vacuumed and purged with Ar for three times. Then, the mixture was stirred at room temperature in dark for 15 min. The solution was subsequently used for UV-vis analysis.

**UV-vis spectrum of the mixture of toluene and MsOH:** Toluene (9.2 mg, 0.1 mmol), MsOH (9.6 mg, 0.1 mmol), and MeCN (10 mL) were added into an oven dried Schlenk tube, which was then vacuumed and purged with Ar for three times. Then, the mixture was stirred at room temperature in dark for 15 min. The solution was subsequently used for UV-vis analysis.

**UV-vis spectrum of the mixture of toluene and [BSPy][OTf]:** Toluene (9.2 mg, 0.1 mmol), [BSPy][OTf] (36.5 mg, 0.1 mmol), and MeCN (10 mL) were added into an oven dried Schlenk tube, which was then vacuumed and purged with Ar for three times. Then, the mixture was stirred at

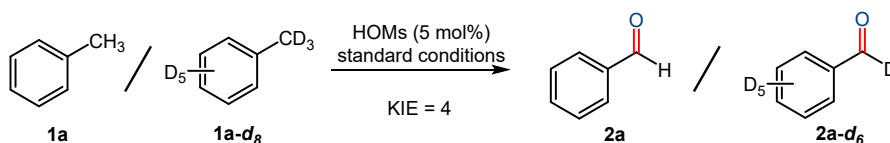
room temperature in dark for 15 min. The solution was subsequently used for UV-vis analysis.

## 6. EPR experiments

All samples were prepared in MeCN solvent under oxygen (1 atm) conditions unless otherwise stated. TEMP and DMPO were used as trapping agents to monitor HO· and <sup>1</sup>O<sub>2</sub>·. The relative concentrations of *p*-chlorotoluene: acid catalyst: TEMP for spin trapping experiments were 10 : 0.5 : 1 (1 M : 50 mM : 100 mM). *In situ* light irradiation of each sample was maintained at 365 nm for 5 min after the addition of trapping agents. Samples were then transferred into 1.3 mm outer diameter (1 mm inner diameter) silica capillary EPR tubes (80 mm height; Wilmad LabGlass) and inserted into a 4 mm outer diameter (3 mm inner diameter) quartz tube. All EPR samples were measured at room temperature on a Bruker Model A200 spectrometer (Bruker Instrument, Germany) equipped with a Bruker ER4112SHQ X-band resonator.



## 7. Determination of the kinetic isotope effect (KIE)



Described below is experiments performed for **1a** and **1a-d<sub>8</sub>** Parallel KIE measurements using chlorobenzene as the internal standard substance. The value of KIE was derived by comparing the conversion rate of toluene-*h<sub>8</sub>* and toluene-*d<sub>8</sub>*.

Toluene-*h<sub>8</sub>* oxidation:

Toluene (92.1 mg, 1 mmol), chlorobenzene (56.3 mg, 0.5 mmol), CH<sub>3</sub>SO<sub>3</sub>H (98% w) (4.8 mg, 5 mol%) and MeCN (2 mL) were added into a 25 mL quartz tube, which was then vacuumed and purged with oxygen via an oxygen balloon for three times. Three parallel reactions were performed under UV irradiation (365 nm, 8 W) at room temperature (20 °C). The reactions were worked up separately for GC measurements at intervals of 0.5, 1, and 1.5 h.

Toluene-*d<sub>8</sub>* oxidation:

Toluene-*d<sub>8</sub>* (100.1 mg, 1 mmol), chlorobenzene (56.3 mg, 0.5 mmol), CH<sub>3</sub>SO<sub>3</sub>H (98% w) (4.8 mg, 5 mol%) and MeCN (2 mL) were added into a 25 mL quartz tube, which was then vacuumed and purged with oxygen via an oxygen balloon for three times. Three parallel reactions were performed under UV irradiation (365 nm, 8 W) at room temperature (20 °C). The reactions were worked up separately for GC measurements at intervals of 0.5, 1, and 1.5 h.

**Table S5:** Determination of the kinetic isotope effect.

Entry	Time (h)	Conversion Rate (%)	
		Toluene- <i>h<sub>8</sub></i>	Toluene- <i>d<sub>8</sub></i>
1	0.5	10.566	2.403
2	1.0	25.753	6.414
3	1.5	40.628	10.370

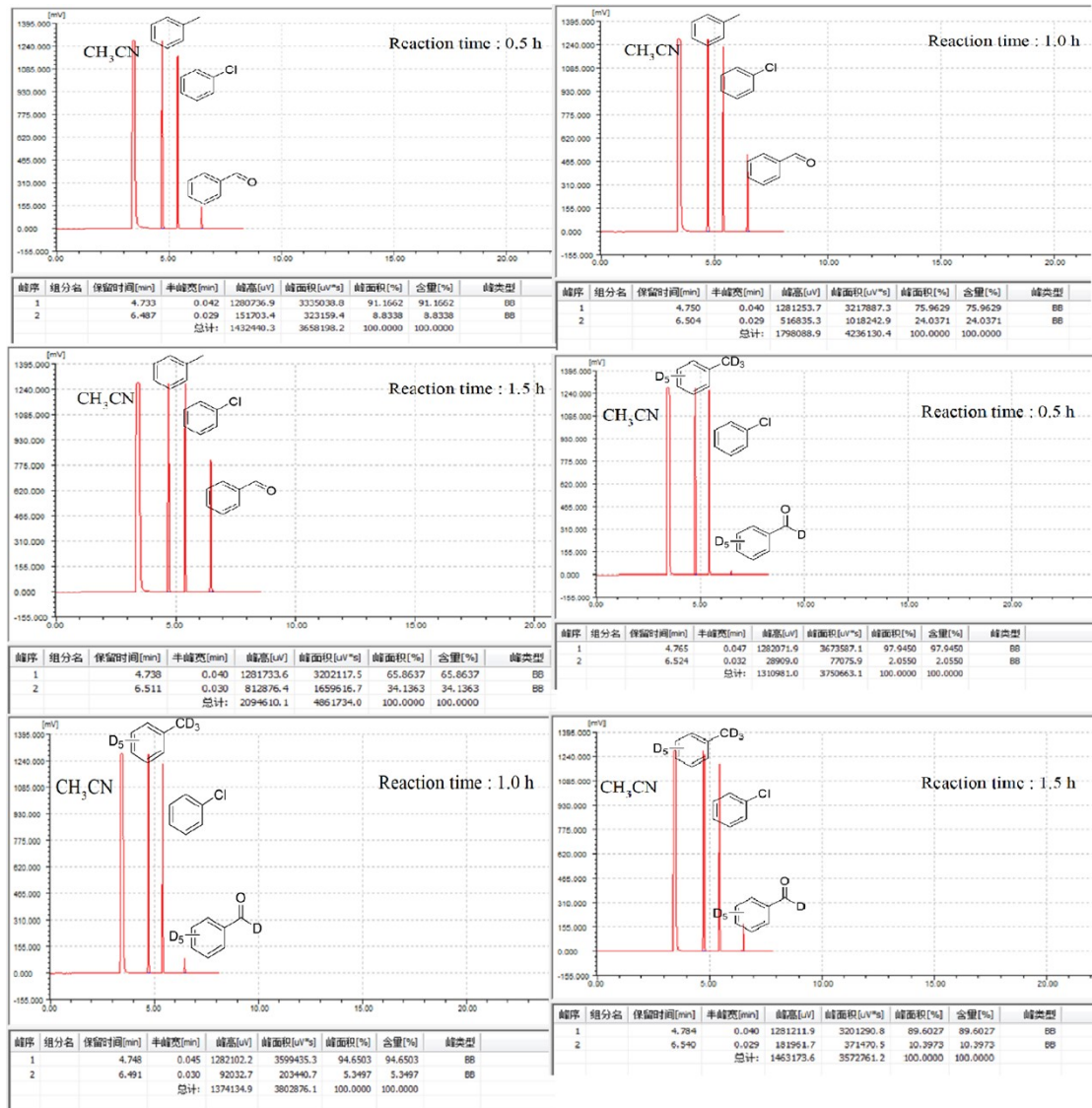
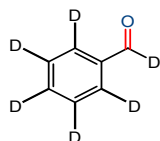


Figure S2. GC analytical results of parallel reactions of 2a and 2a-d<sub>6</sub> using PhCl as the internal standard

### Benzaldehyde- $D_6$ (2a- $d_6$ )



A colorless liquid.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 192.06 (t,  $J=26.53$ , 1C), 136.26-136.11 (m, 1C), 133.96 (t,  $J=24.53$ , 1C), 129.32(t,  $J=24.63$ , 2C), 128.49(t,  $J=24.53$ , 2C).

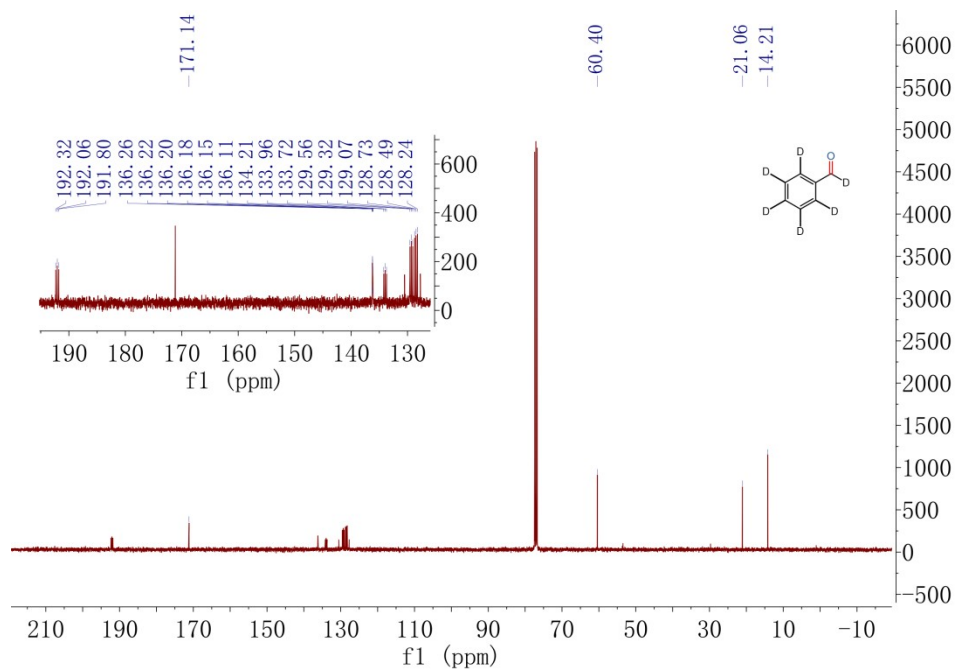
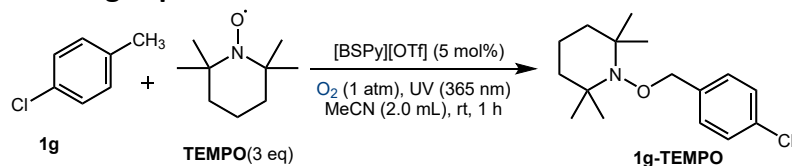


Figure S3.  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of 2a- $d_6$  in  $\text{CDCl}_3$

## 8. TEMPO quenching experiments



4-chlorotoluene (126 mg, 1 mmol), [BSPy][OTf] (18.25 mg, 5 mol%) and MeCN (2 mL) were added into a 25 mL quartz tube, which was then vacuumed and purged with oxygen via an oxygen balloon for three times. The reactor was connected to a balloon of O<sub>2</sub> through a T joint and was illuminated under UV irradiation (365 nm, 8 W) at room temperature (20 °C) for 1 h. After that, the reactor was turned on and TEMPO (2,2,6, 6-tetramethylpiperidine oxide, 468 mg, 3 mmol, 3 equiv.) was added thereto. After repeating the oxygen replacement, the mixture was further illuminated for 10 min, samples were filtered for HRMS.

The reaction was inhibited by the submission of TEMPO, indicating that the reaction occurred along a radical pathway. The molecular ion peak of TEMPO- benzylic radical adduct was found in HRMS, Figure S2.

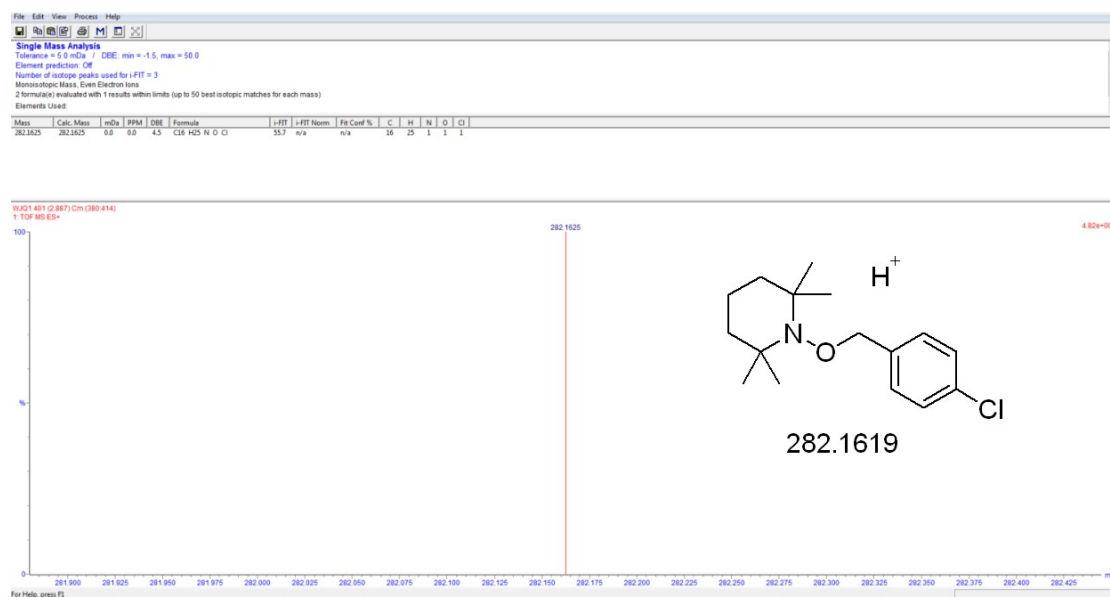
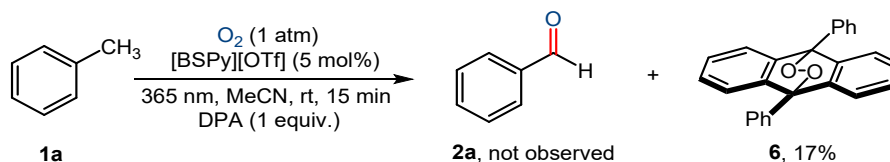


Figure S4: Observed intermediates by HRMS.

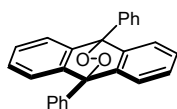
## 9. Trapping of $^1\text{O}_2$ with DPA.

Experiments trying to verify the presence of photoexcited singlet oxygen was performed using 9,10-diphenylanthracene, affording 9,10-diphenyl-9,10-dihydro-9,10-epidioxyanthracene (**6**) in 17% yield.<sup>[32]</sup>



Toluene (126 mg, 1 mmol), [BSPy][OTf] (18.25 mg, 5 mol%) and MeCN (2 mL) were added into a 25 mL quartz tube, which was then vacuumed and purged with oxygen via an oxygen balloon for three times. Then the tube was placed into the reactor and the reaction mixture was stirred vigorously under UV irradiation (365 nm) for 1 h. After that, the reactor was turned on and DPA (9,10-diphenylanthracene, 330 mg, 1 mmol, 1 equiv.) was added thereto. Oxygen replacement was conducted, and the reaction mixture was further illuminated for 10 min. At the end of the reaction, 10 mL EA was added thereto, and the resulted mixture was washed with water (5 mL  $\times$  2). The oil layer was dried anhydrous  $\text{Na}_2\text{SO}_4$  and then evaporated under vacuum. The solid residue was purified over a column of silica gel (eluant: EA : PE = 1 : 10) to afford the desired product (**6**) with 17% yield (61 mg).

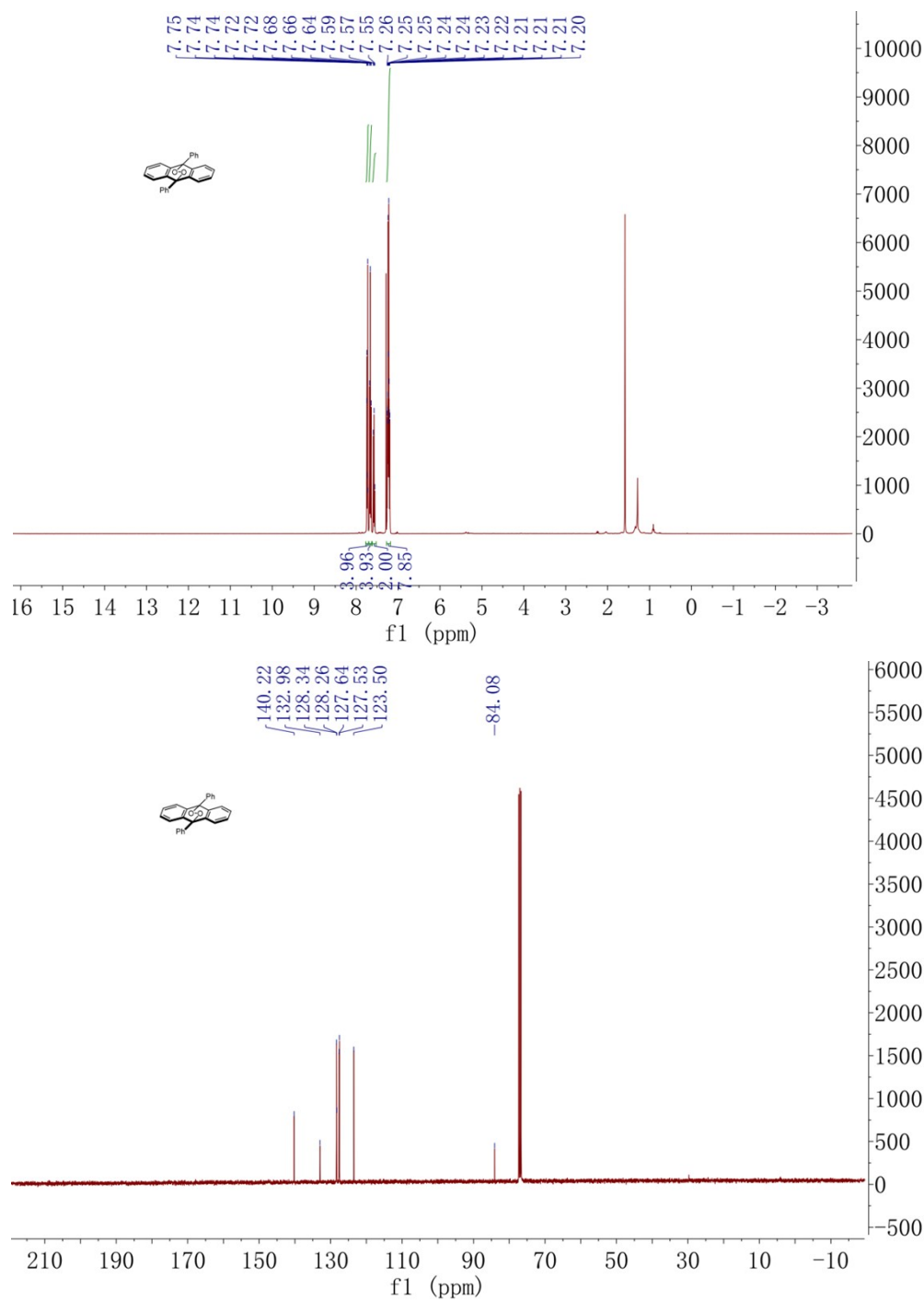
**9,10-diphenyl-9,10-dihydro-9,10-epidioxyanthracene (6)**



A light white powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77-7.70 (m, 4H), 7.66 (t,  $J =$

7.6 Hz, 4H), 7.57 (t,  $J = 7.3$  Hz, 2H), 7.27-7.18 (m, 8H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

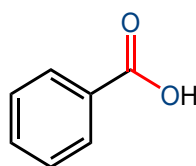
$\delta$  140.22, 132.98, 128.34, 128.26, 127.64, 127.53, 123.50, 84.08. The spectroscopic data for this product match the literature data<sup>[32]</sup>.



**Figure S5.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}}$  (101 MHz) NMR spectra of 6 in  $\text{CDCl}_3$**

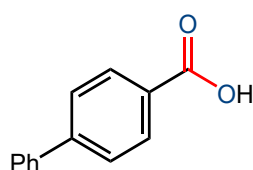
## 10. Spectral data of 3 and 5

### Benzoic acid (3a)



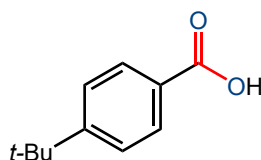
The reaction was performed following the General Procedure A with toluene (1a, 92 mg, 1 mmol) for 6 h. The crude product was purified over a column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (111 mg, 91% yield) as a white solid, mp 121-123 °C (lit<sup>[17]</sup> 121-122 °C). The spectroscopic data for this product match the literature data<sup>[1]</sup>.

### Biphenyl-4-carboxylic acid (3b)



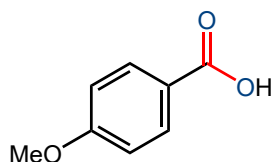
The reaction was performed following the General Procedure A with 4-phenyltoluene (1b, 168 mg, 1 mmol) for 6 h. The crude product was purified over a column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (184 mg, 93% yield) as a white solid, mp 223-224 °C (lit<sup>[18]</sup> 224-225 °C). The spectroscopic data for this product match the literature data<sup>[6]</sup>.

### 4-tert-Butylbenzoic acid (3c)



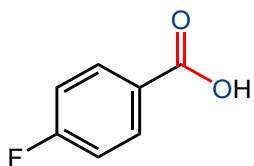
The reaction was performed following the General Procedure A with 4-tert-butyltoluene (1c, 148 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 0.8) to give the product (158 mg, 89% yield) as a white solid, mp 162-163 °C (lit<sup>[19]</sup> 163-164 °C). The spectroscopic data for this product match the literature data<sup>[8]</sup>.

### 4-Methoxybenzoic acid (3d)



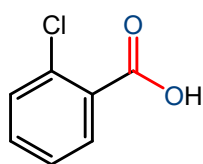
The reaction was performed following the General Procedure A with 4-methoxytoluene (1d, 122 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 0.5) to give the product (132 mg, 87% yield) as a white solid, mp 184-185 °C (lit<sup>[18]</sup> 183-184 °C). The spectroscopic data for this product match the literature data<sup>[2]</sup>.

#### 4-Fluorobenzoic acid (3e)



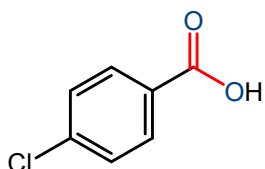
The reaction was performed following the General Procedure A with 4-fluorotoluene (**1e**, 110 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : H<sub>2</sub>O = 1 : 10 : 1) to give the product (132 mg, 94% yield) as a white solid, mp 182-183 °C (lit<sup>[18]</sup>183-184°C). The spectroscopic data for this product match the literature data<sup>[2]</sup>.

#### 2-Chlorobenzoic acid (3f)



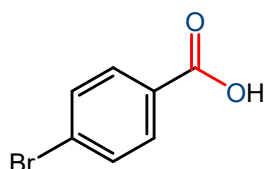
The reaction was performed following the General Procedure A with 2-chlorotoluene (**1f**, 126 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : H<sub>2</sub>O = 1 : 10 : 1) to give the product (140 mg, 90% yield) as a white solid, mp 140-141 °C (lit<sup>[20]</sup>141-142°C). The spectroscopic data for this product match the literature data<sup>[5]</sup>.

#### 4-Chlorobenzoic acid (3g)



The reaction was performed following the General Procedure A with 4-chlorotoluene (**1g**, 126 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : H<sub>2</sub>O = 1 : 10 : 1) to give the product (148 mg, 95% yield) as a white solid, mp 239-240 °C (lit<sup>[18]</sup>238-240°C). The spectroscopic data for this product match the literature data<sup>[6]</sup>.

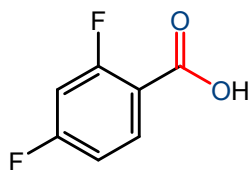
#### 4-Bromobenzoic acid (3h)



The reaction was performed following the General Procedure A with 4-bromotoluene (**1h**, 170 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : H<sub>2</sub>O = 1 : 10 : 1) to give the product (186 mg, 93% yield) as a white solid, mp 253-254 °C (lit<sup>[21]</sup>252-254°C). The spectroscopic data for this product match the literature data<sup>[6]</sup>.

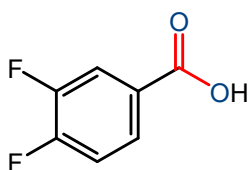


### **2,4-Difluorobenzoic acid (3i)**



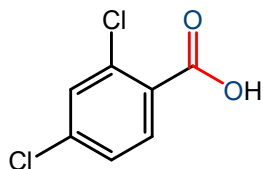
The reaction was performed following the General Procedure A with 2,4-difluorotoluene (**1i**, 128 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 20 : 1) to give the product (131 mg, 83% yield) as a white solid, mp 188-189 °C (lit<sup>[21]</sup>188-190°C). The spectroscopic data for this product match the literature data<sup>[10]</sup>.

### **3,4-Difluorobenzoic acid (3j)**



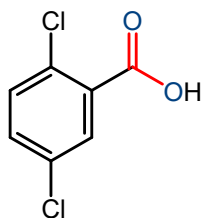
The reaction was performed following the General Procedure A with 3,4-difluorotoluene (**1j**, 128 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (137 mg, 87% yield) as a white solid, mp 118-119 °C (lit<sup>[22]</sup>119-120°C). The spectroscopic data for this product match the literature data<sup>[7]</sup>.

### **2,4-Dichlorobenzoic acid (3k)**



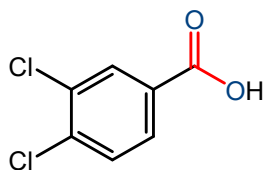
The reaction was performed following the General Procedure A with 2,4-dichlorotoluene (**1k**, 160 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (156 mg, 82% yield) as a white solid, mp 160-161 °C (lit<sup>[21]</sup>157-160°C). The spectroscopic data for this product match the literature data<sup>[9]</sup>.

### **2,5-Dichlorobenzoic acid (3l)**



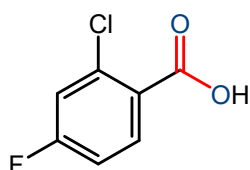
The reaction was performed following the General Procedure A with 2,5-dichlorotoluene (**1l**, 160 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (152 mg, 80% yield) as a white solid, mp 154-155 °C (lit<sup>[23]</sup>153-155°C). The spectroscopic data for this product match the literature data<sup>[11]</sup>.

### 3,4-Dichlorobenzoic acid (3m)



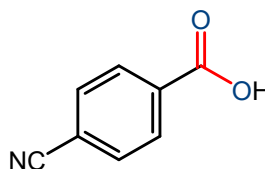
The reaction was performed following the General Procedure A with 3,4-dichlorotoluene (**1m**, 160 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (175 mg, 92% yield) as a white solid, mp 204-205 °C (lit<sup>[24]</sup>204-206°C). The spectroscopic data for this product match the literature data<sup>[5]</sup>.

### 2-Chloro-4-fluorobenzoic acid (3n)



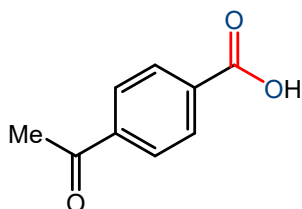
The reaction was performed following the General Procedure A with 2-chloro-4-fluorotoluene (**1n**, 144 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (157 mg, 90% yield) as a white solid, mp 184-185 °C (lit<sup>[23]</sup>185-186 °C). The spectroscopic data for this product match the literature data<sup>[6]</sup>.

### 4-Cyanobenzoic acid (3o)



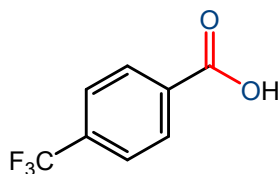
The reaction was performed following the General Procedure A with p-tolunitrile (**1o**, 117 mg, 1 mmol) for 18 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (124 mg, 84% yield) as a white solid, mp 219-220 °C (lit<sup>[21]</sup>220-222°C). The spectroscopic data for this product match the literature data<sup>[6]</sup>.

### 4-Acetylbenzoic acid (3p)



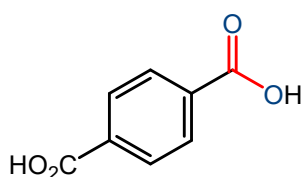
The reaction was performed following the General Procedure A with 4-methylacetophenone (**1p**, 134 mg, 1 mmol) for 18 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (154 mg, 94% yield) as a white solid, mp 209-210 °C (lit<sup>[18]</sup>208-209°C). The spectroscopic data for this product match the literature data<sup>[6]</sup>.

#### 4-(Trifluoromethyl)benzoic acid (3q)



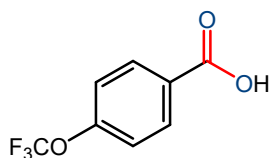
The reaction was performed following the General Procedure A with 4-trifluoromethyltoluene (**1q**, 160 mg, 1 mmol) for 18 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME = 1 : 10 : 1) to give the product (171 mg, 90% yield) as a white solid, mp 219-220 °C (lit<sup>[18]</sup>218-220°C). The spectroscopic data for this product match the literature data<sup>[2]</sup>.

#### Terephthalic acid (3r)



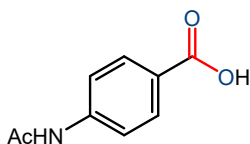
The reaction was performed following the General Procedure A from 4-methylbenzoic acid (**1r**, 136 mg, 1 mmol) for or p-xylene (**1v**, 106 mg, 1mmol) both for 18 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME : HOAc = 1 : 10 : 0.5 : 0.5) to give the product with 82% (136 mg) and 80% (133 mg) yields, respectively. White solid, mp 285-300 °C (lit<sup>[26]</sup>280-300°C). The spectroscopic data for this product match the literature data<sup>[1]</sup>.

#### 4-(Trifluoromethoxy)benzoic acid (3s)



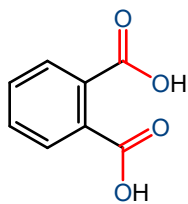
The reaction was performed following the General Procedure A with 4-(trifluoromethoxy)toluene (**1s**, 176 mg, 1 mmol) for 18 h. The crude product was purified over a flash column of silica gel (eluant: EA :PE : HOME : HOAc = 1 : 10 : 0.5 : 0.5) to give the product (177 mg, 86% yield) as a white solid, mp 151-152 °C (lit<sup>[27]</sup>152-153°C). The spectroscopic data for this product match the literature data<sup>[5]</sup>.

#### 4-Acetamido benzoic acid (3t)



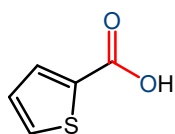
The reaction was performed following the General Procedure A with p-acetotoluidide (**1t**, 149 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : HOME : HOAc = 1 : 10 : 0.5 : 0.5) to give the product (149 mg, 83% yield) as a white solid, mp 257-258 °C (lit<sup>[28]</sup>257-259°C). The spectroscopic data for this product match the literature data<sup>[12]</sup>.

### **Phthalic acid (3u)**



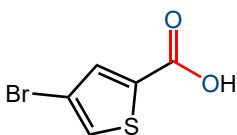
The reaction was performed following the General Procedure A with o-xylene (**1u**, 106 mg, 1 mmol) for 18 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : H<sub>2</sub>O : HOAc = 1 : 10 : 0.5 : 0.25) to give the product (139 mg, 84% yield) as a white solid, mp 207-208 °C (lit<sup>[29]</sup>208-209°C). The spectroscopic data for this product match the literature data<sup>[1]</sup>.

### **2-Thiophenic acid (3w)**



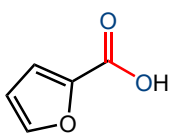
The reaction was performed following the General Procedure A with 2-methylthiophene (**1w**, 98 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : H<sub>2</sub>O = 1 : 10 : 1) to give the product (113 mg, 88% yield) as a white solid, mp 204-205 °C (lit<sup>[24]</sup>204-206°C). The spectroscopic data for this product match the literature data<sup>[2]</sup>.

### **4-Bromo-2-thiophenecarboxylic acid (3x)**



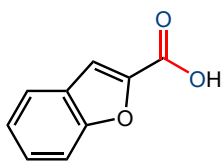
The reaction was performed following the General Procedure A with 4-bromo-2-methylthiophene (**1x**, 177 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : H<sub>2</sub>O = 1 : 10 : 1) to give the product (152 mg, 74% yield) as a white solid, mp 113-115 °C (lit<sup>[25]</sup>110-118°C). The spectroscopic data for this product match the literature data<sup>[13]</sup>.

### **Furan-2-carboxylic acid (3y)**



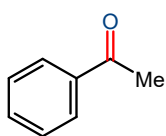
The reaction was performed following the General Procedure A with 2-methylfuran (**1y**, 82 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : H<sub>2</sub>O = 1 : 10 : 1) to give the product (64 mg, 57% yield) as a white solid, mp 130-131 °C (lit<sup>[33]</sup>129-131°C). The spectroscopic data for this product match the literature data<sup>[33]</sup>.

### ***Benzofuran-2-carboxylic Acid (3z)***



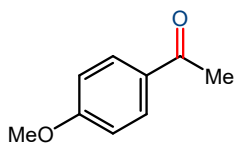
The reaction was performed following the General Procedure A with 2-methylcumaronone (**1z**, 132 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE : H<sub>2</sub>O = 1 : 10 : 1) to give the product (120 mg, 74% yield) as a white solid, mp 192-193 °C (lit<sup>[34]</sup>193-194°C). The spectroscopic data for this product match the literature data<sup>[34]</sup>.

### ***Acetophenone (5a)***



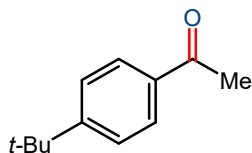
The reaction was performed following the General Procedure B with ethylbenzene (**4a**, 106 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) give the product (110 mg, 92% yield) as a colorless oil. The spectroscopic data for this product match the literature data<sup>[1]</sup>.

### ***1-(4-Methoxyphenyl)ethan-1-one (5b)***



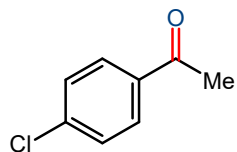
The reaction was performed following the General Procedure B with *p*-ethyl anisole (**4b**, 136 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (129 mg, 86% yield) as a colorless oil. The spectroscopic data for this product match the literature data<sup>[8]</sup>.

### ***1-(4-*t*-Butylphenyl)ethan-1-one (5c)***



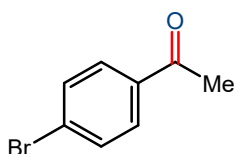
The reaction was performed following the General Procedure B with 4-ethyl-1-*tert*-butylbenzene (**4c**, 162 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (155 mg, 88% yield) as a colorless oil. The spectroscopic data for this product match the literature data<sup>[3]</sup>.

#### **1-(4-Chlorophenyl)ethan-1-one (5d)**



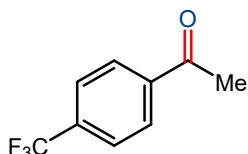
The reaction was performed following the General Procedure B with 4-chloroethylbenzene (**4d**, 141 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (143 mg, 93% yield) as a colorless oil. The spectroscopic data for this product match the literature data<sup>[3]</sup>.

#### **1-(4-Bromophenyl)ethan-1-one (5e)**



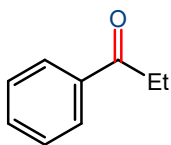
The reaction was performed following the General Procedure B with 4-bromoethylbenzene (**4e**, 185 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA : PE= 1 : 15) to give the product (182 mg, 92% yield) as a white solid, mp 108-109 °C (lit<sup>[24]</sup>107-108°C). The spectroscopic data for this product match the literature data<sup>[3]</sup>.

#### **1-(4-(Trifluoromethyl)phenyl)ethan-1-one (5f)**



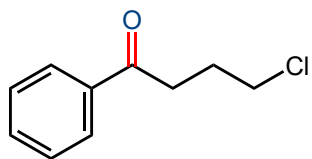
The reaction was performed following the General Procedure B with 4-trifluoromethyl-1-ethylbenzene (**4f**, 174 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (164 mg, 87% yield) as a colorless liquid. The spectroscopic data for this product match the literature data<sup>[4]</sup>.

#### **Propiophenone (5g)**



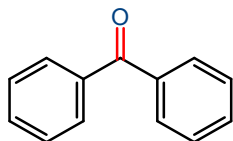
The reaction was performed following the General Procedure B with n-propylbenzene (**4g**, 120 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (121 mg, 90% yield) as a colorless liquid. The spectroscopic data for this product match the literature data<sup>[3]</sup>.

#### **4-Chloro-1-phenylbutan-1-one (5h)**



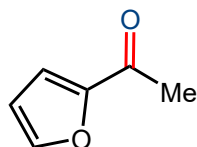
The reaction was performed following the General Procedure B with 1-chloro-4-phenylbutane (**4h**, 168 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (149 mg, 82% yield) as a colorless liquid. The spectroscopic data for this product match the literature data<sup>[14]</sup>.

#### **Benzophenone (5i)**



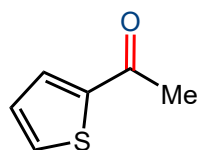
The reaction was performed following the General Procedure B with diphenylmethane (**4i**, 168 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (171mg, 94% yield) as a colorless solid, mp 49-50 °C (lit<sup>[24]</sup>49-51°C). The spectroscopic data for this product match the literature data<sup>[4]</sup>.

#### **2-Acetylfuran (5n)**



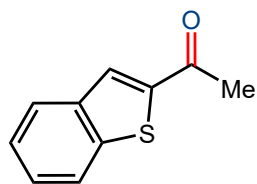
The reaction was performed following the General Procedure B with 2-ethylfuran (**4n**, 96mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (73 mg, 66% yield) as a brown liquid. The spectroscopic data for this product match the literature data<sup>[15]</sup>.

#### **2-Acetylthiophene(5o)**



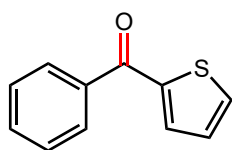
The reaction was performed following the General Procedure B with 2-ethylthiophene (**4o**, 112 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (91 mg, 72% yield) as a light brown liquid. The spectroscopic data for this product match the literature data<sup>[15]</sup>.

### 2-Acetylbenzothiophene (5p)



The reaction was performed following the General Procedure B with 2-ethyl-1-benzothiophene (**4p**, 162 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (144 mg, 82% yield) as a light brown solid, mp 85-86°C (lit<sup>[30]</sup>86-87°C). The spectroscopic data for this product match the literature data<sup>[16]</sup>.

### 2-Benzoylthiophene (5q)



The reaction was performed following the General Procedure B with 2-benzylthiophene (**4q**, 174 mg, 1 mmol) for 6 h. The crude product was purified over a flash column of silica gel (eluant: EA: PE = 1 : 20) to give the product (171 mg, 91% yield) as a colorless solid, mp 56-57°C (lit<sup>[31]</sup>54-55°C). The spectroscopic data for this product match the literature data<sup>[16]</sup>.



## 11. NMR spectra of 3 and 5

### Benzoic acid (3a)

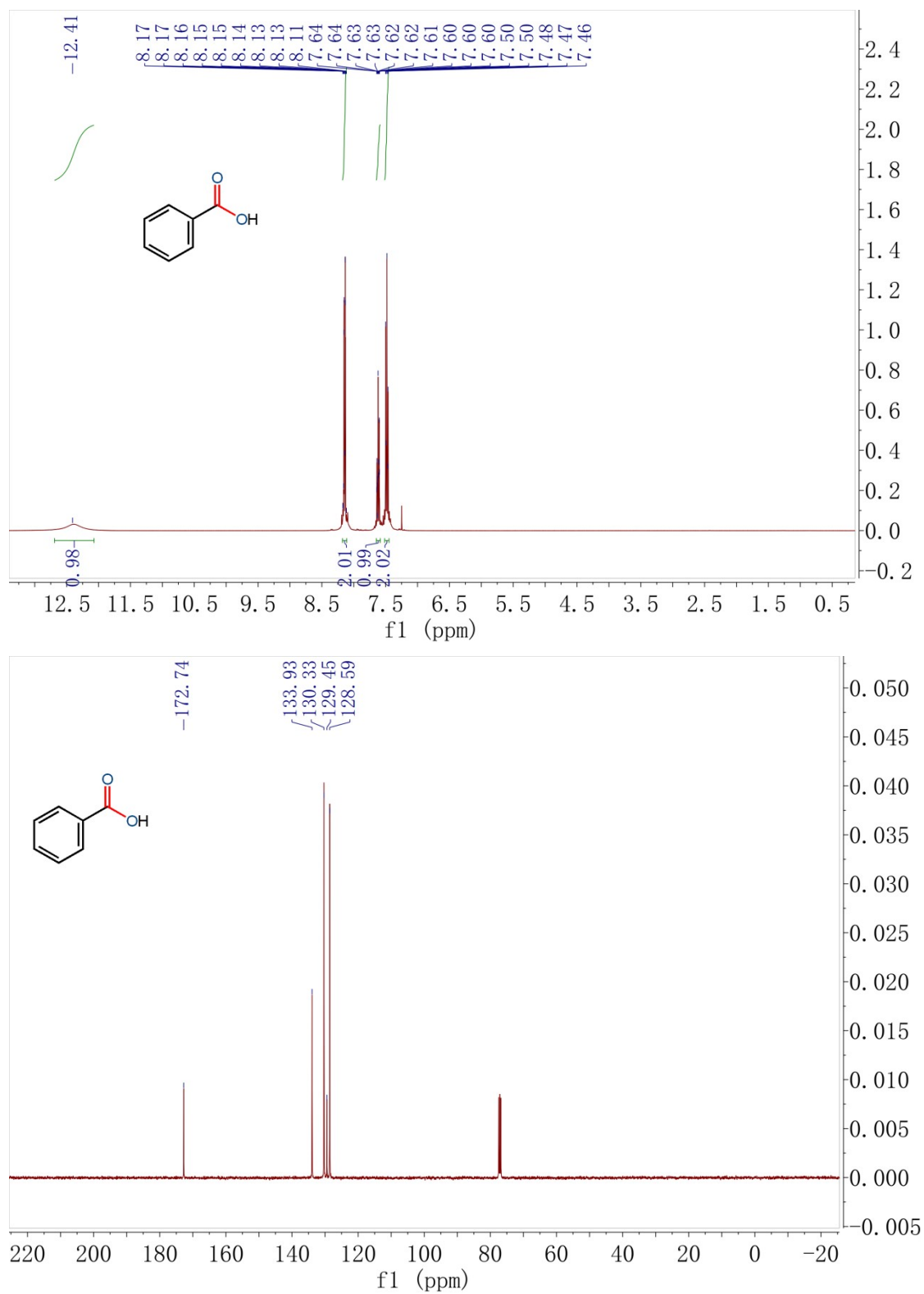
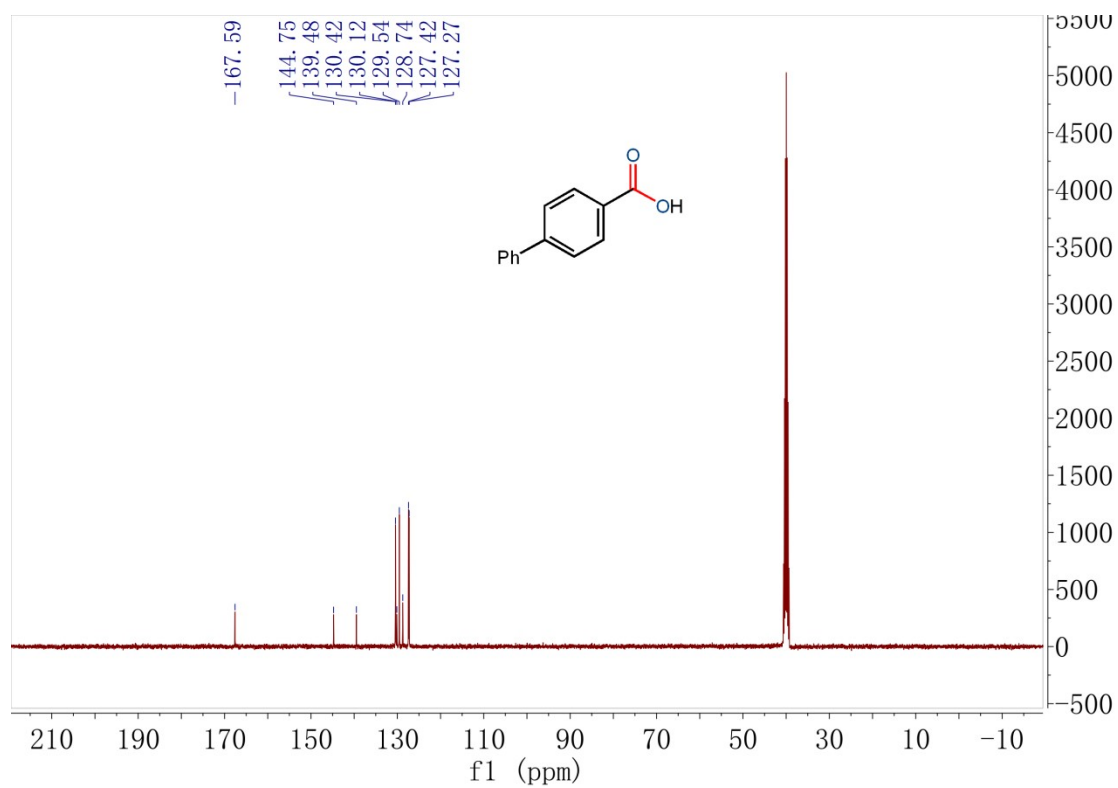
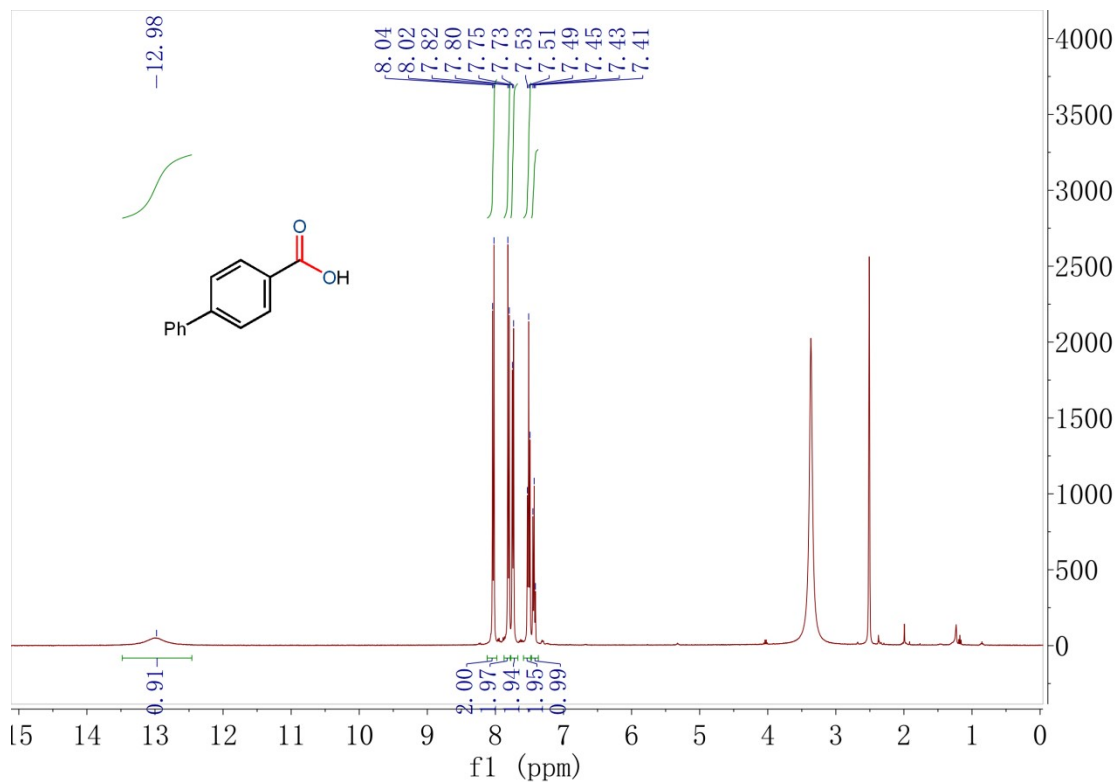


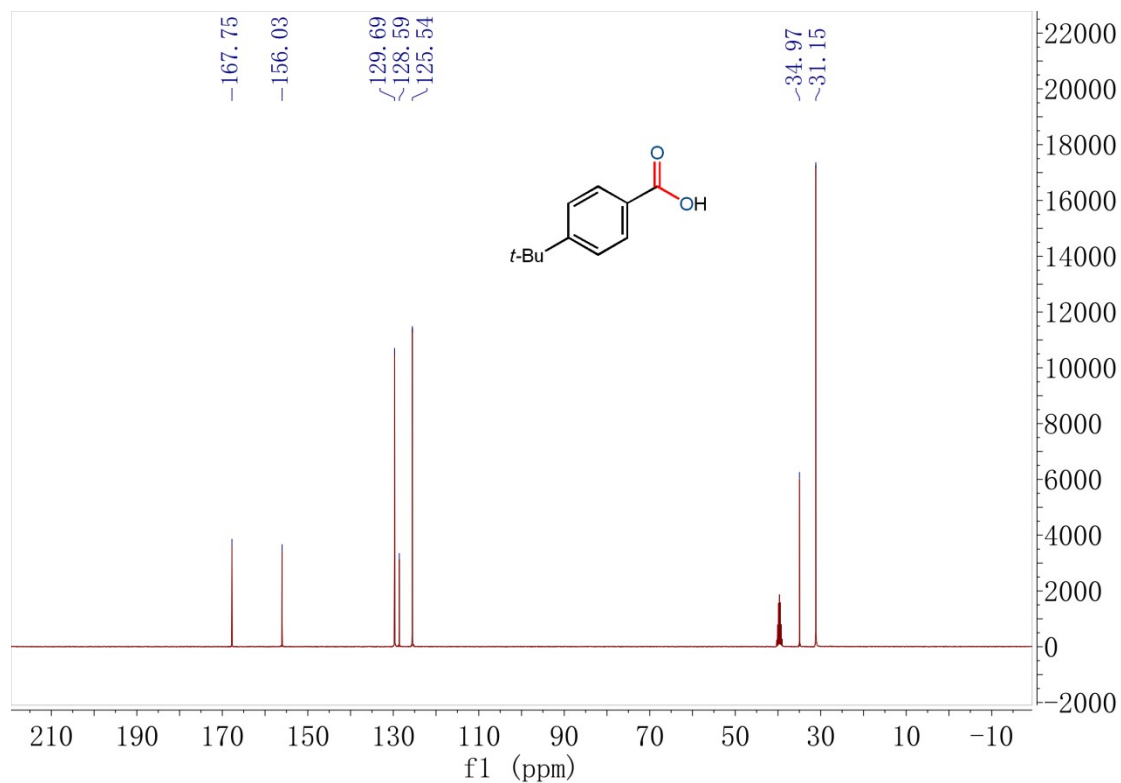
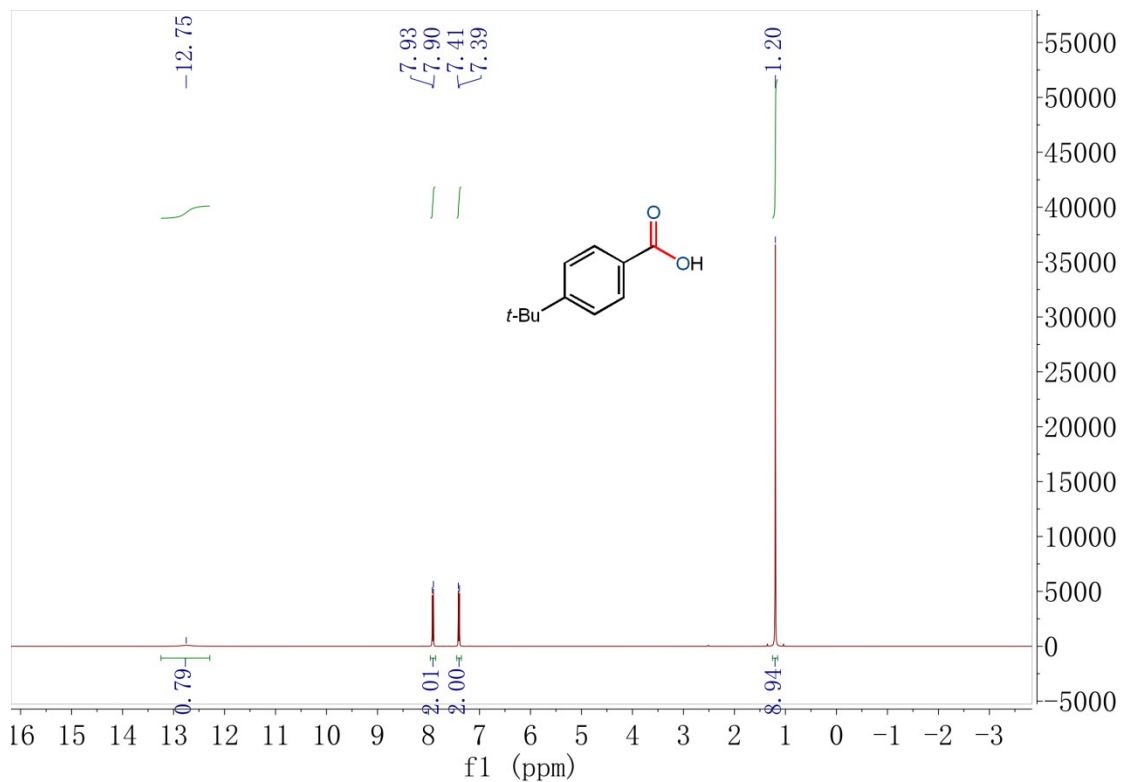
Figure S6. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 3a in CDCl<sub>3</sub>

**Biphenyl-4-carboxylic acid (3b)**



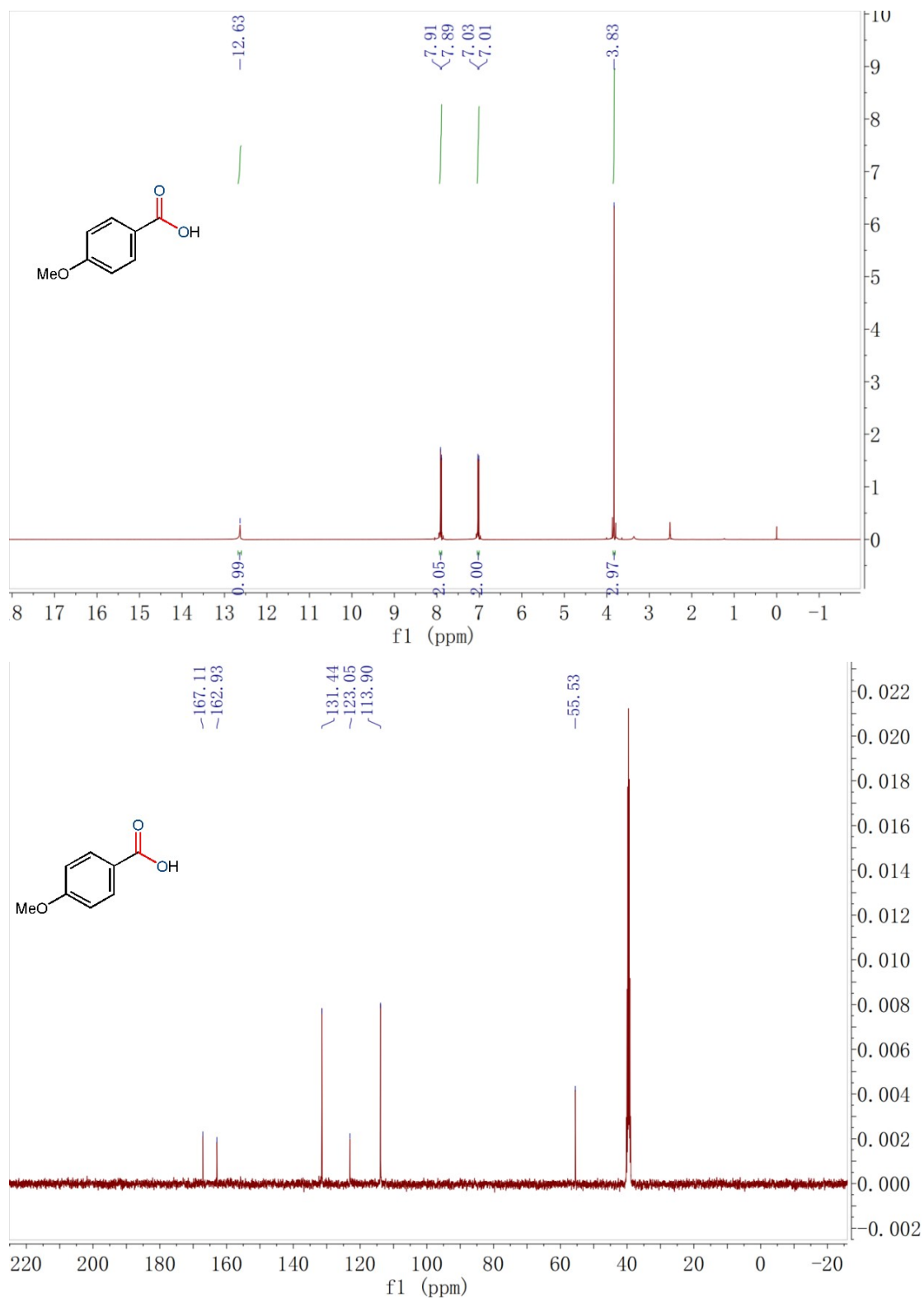
**Figure S7. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 3b in DMSO-*d*<sub>6</sub>**

**4-tert-Butylbenzoic acid (3c)**



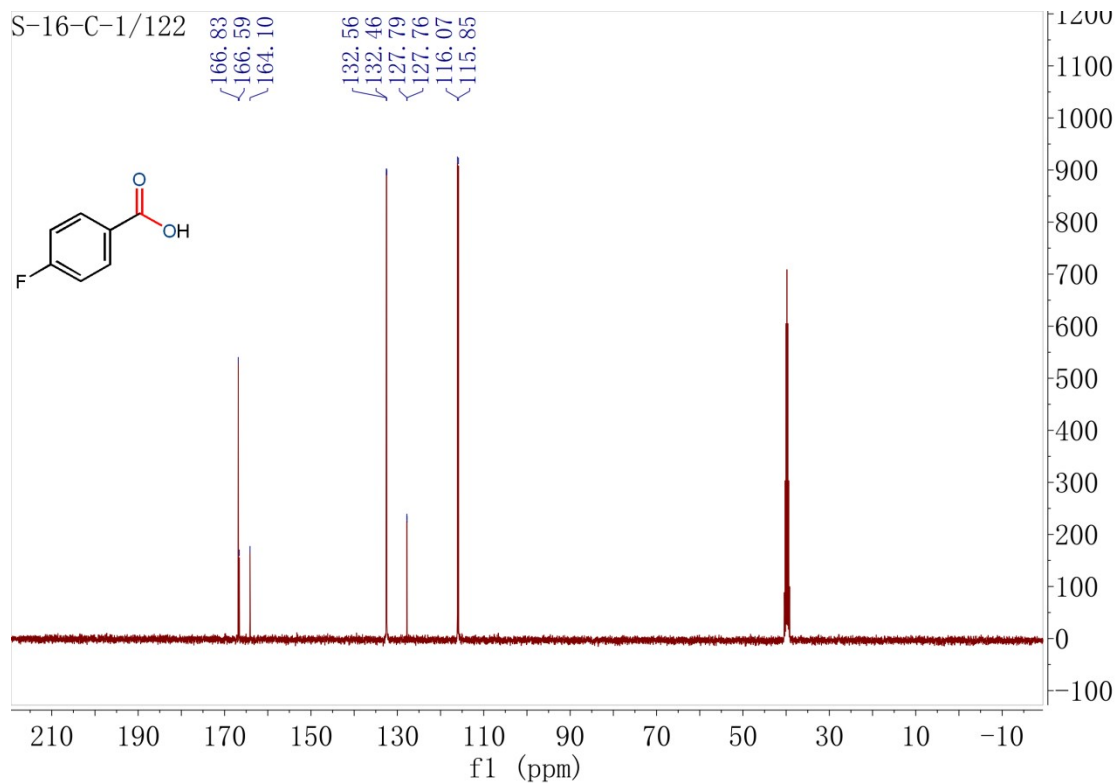
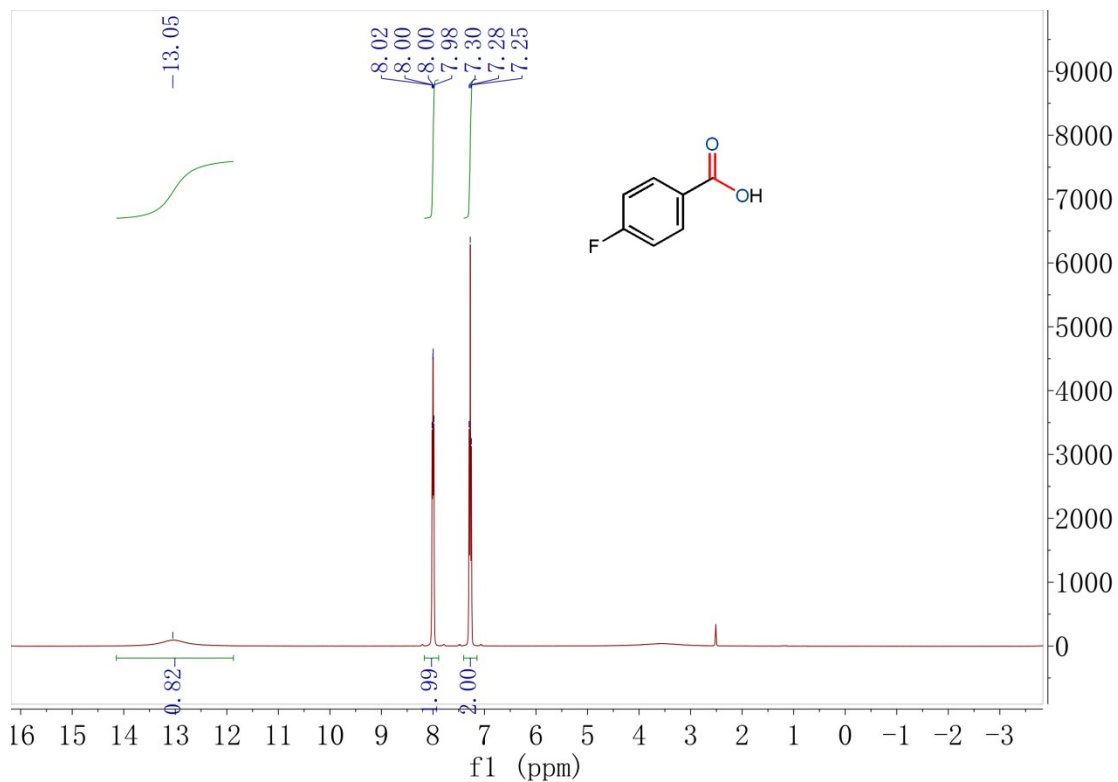
**Figure S8. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 3c in DMSO-*d*<sub>6</sub>**

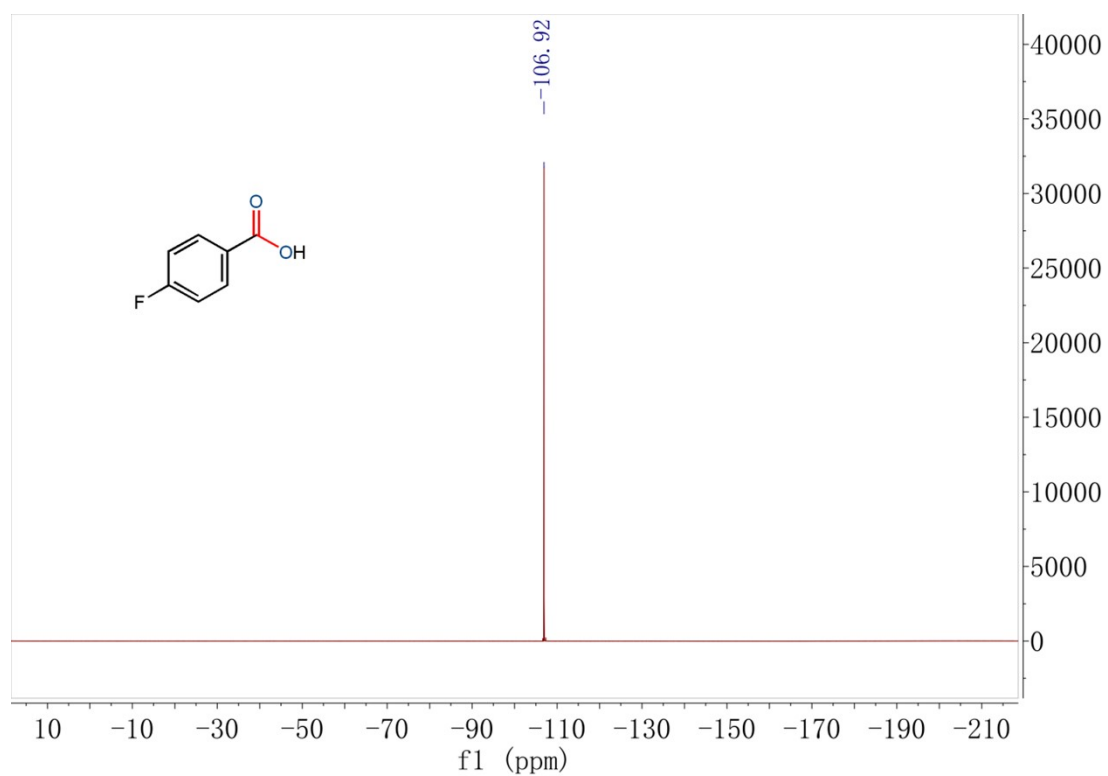
**4-Methoxybenzoic acid (3d)**



**Figure S9. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 3d in DMSO-d<sub>6</sub>**

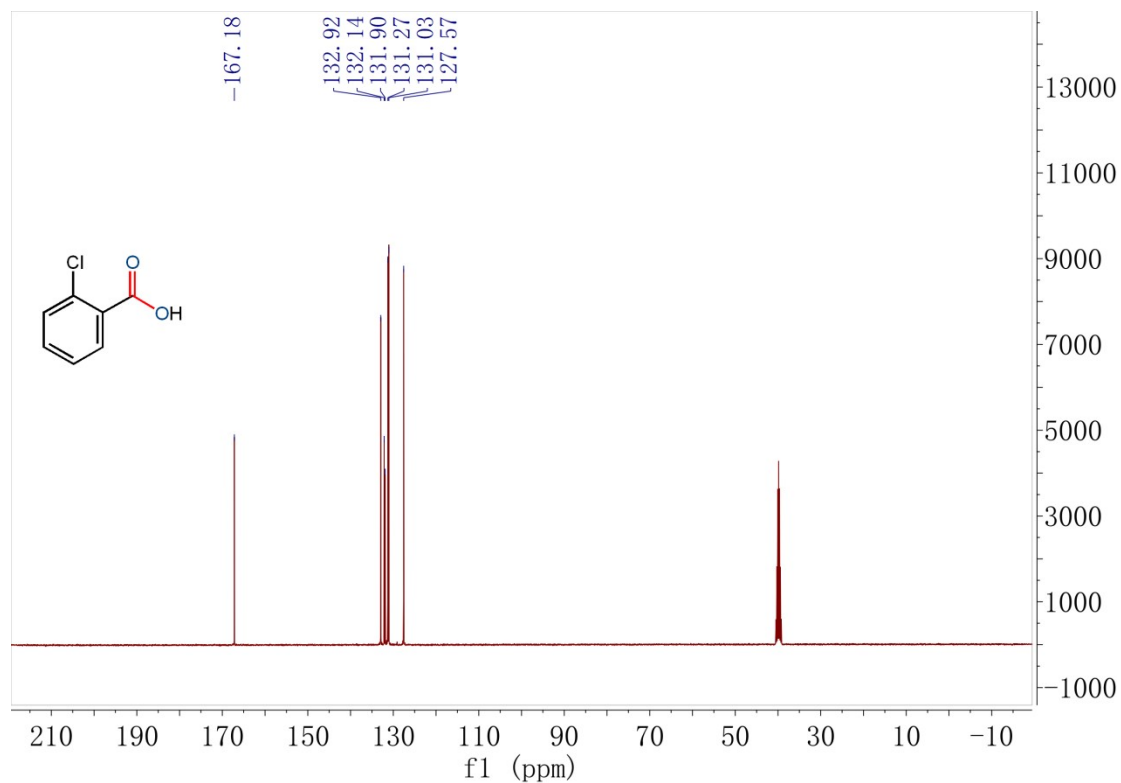
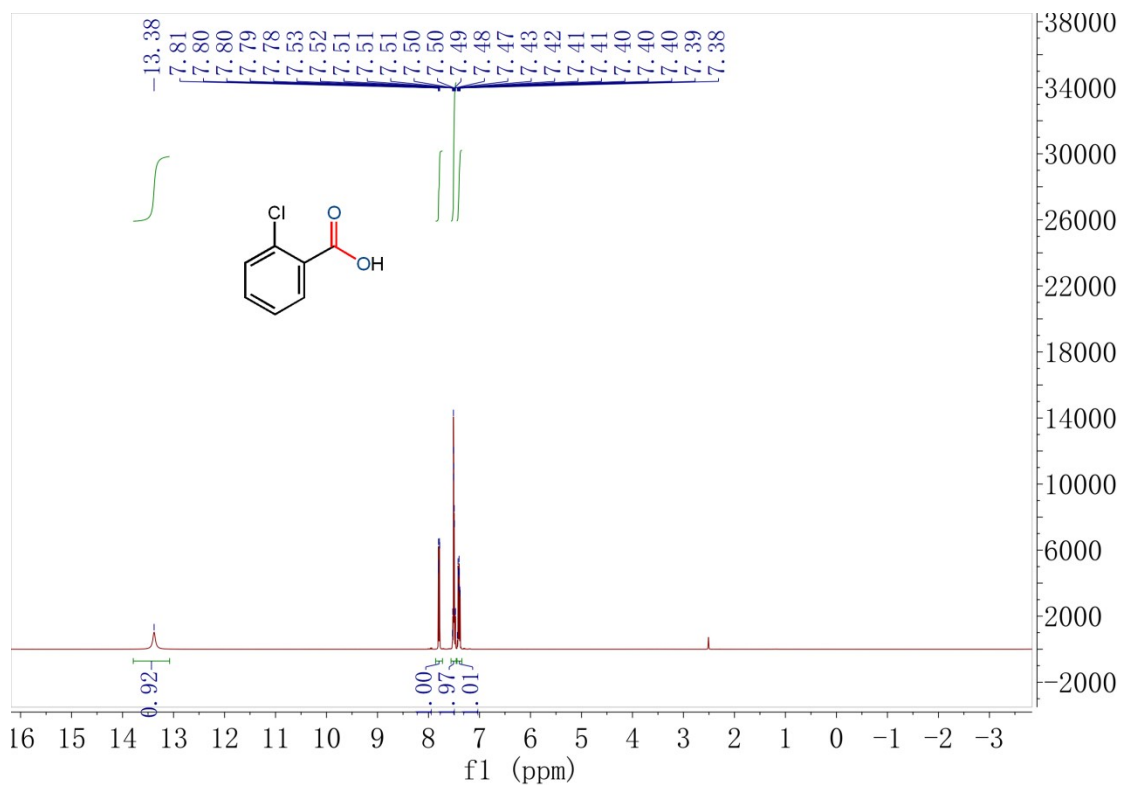
**4-Fluorobenzoic acid (3e)**





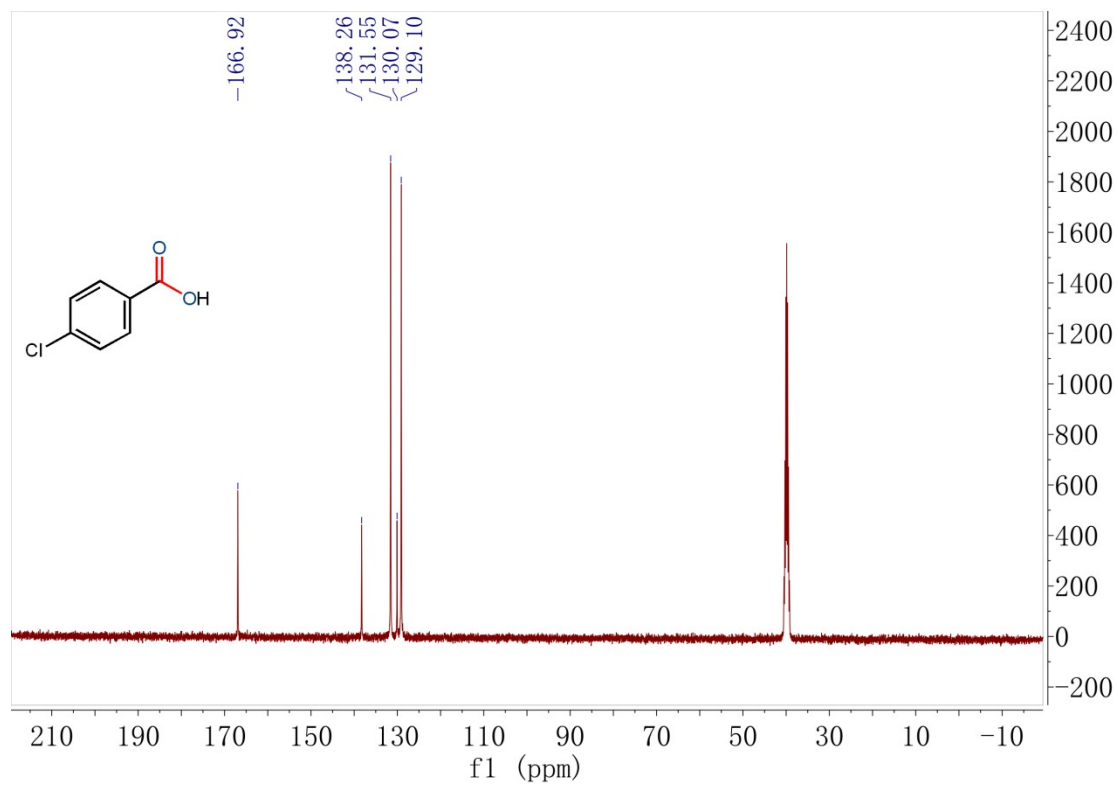
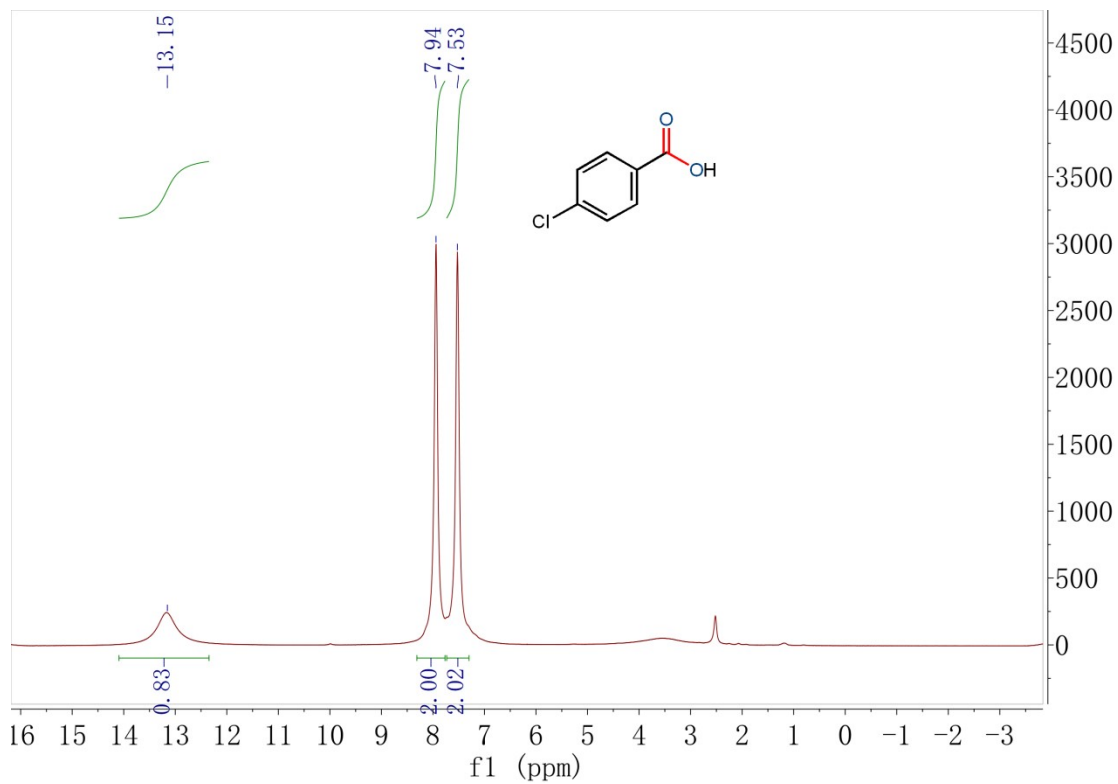
**Figure S10.**  $^1\text{H}$  (400 MHz)、 $^{13}\text{C}$  {1H} (101 MHz) and  $^{19}\text{F}$  {1H} (376 MHz) NMR spectra of 3e in  $\text{DMSO-}d_6$

**2-Chlorobenzoic acid (3f)**



**Figure S11. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 3f in DMSO-*d*<sub>6</sub>**

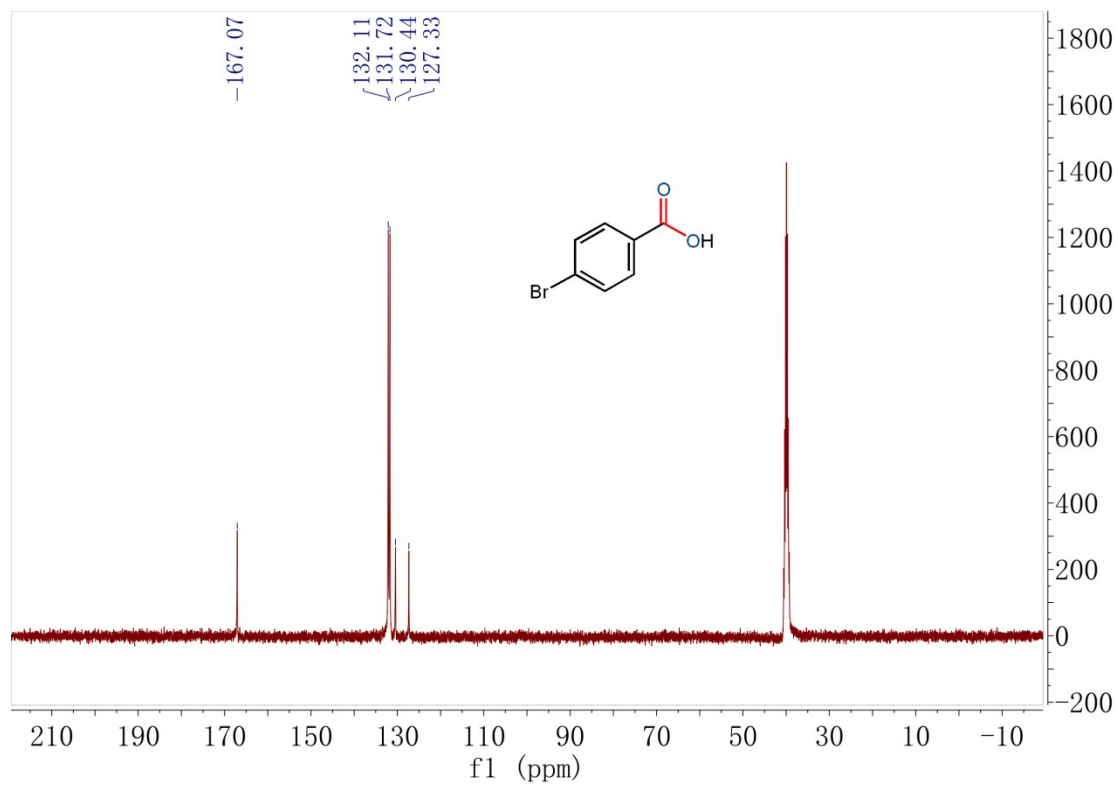
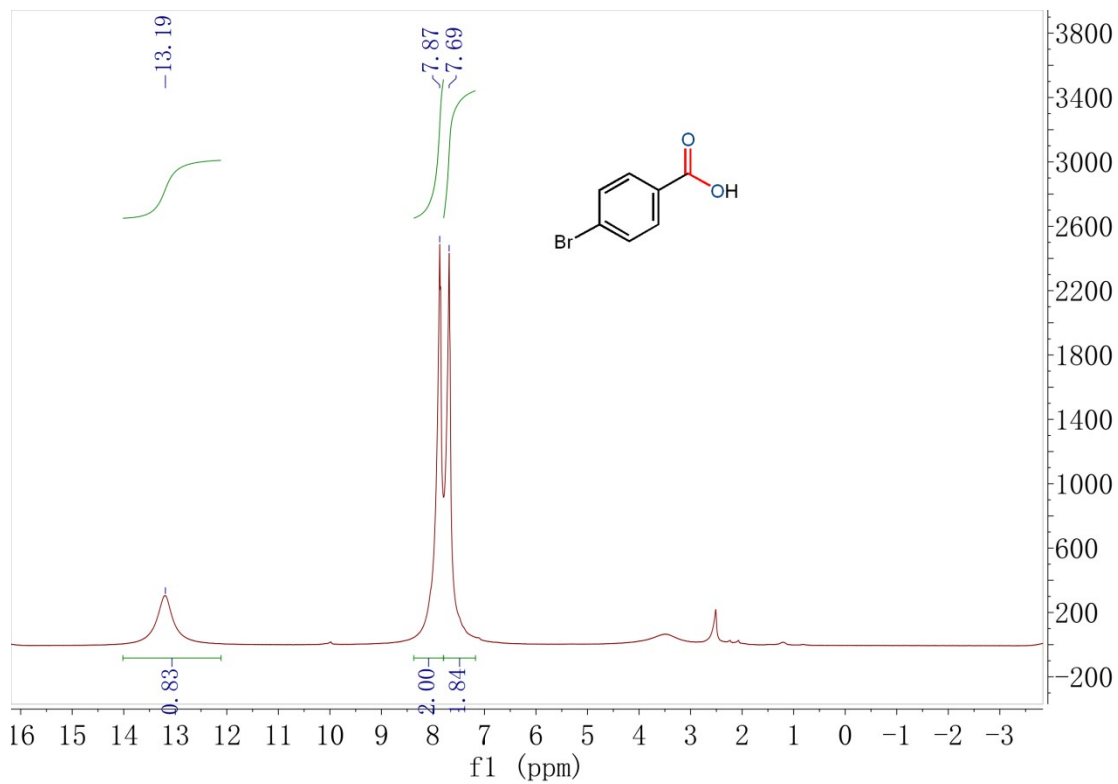
**4-Chlorobenzoic acid (3g)**



**Figure S12.**  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of **3g** in  $\text{DMSO-}d_6$

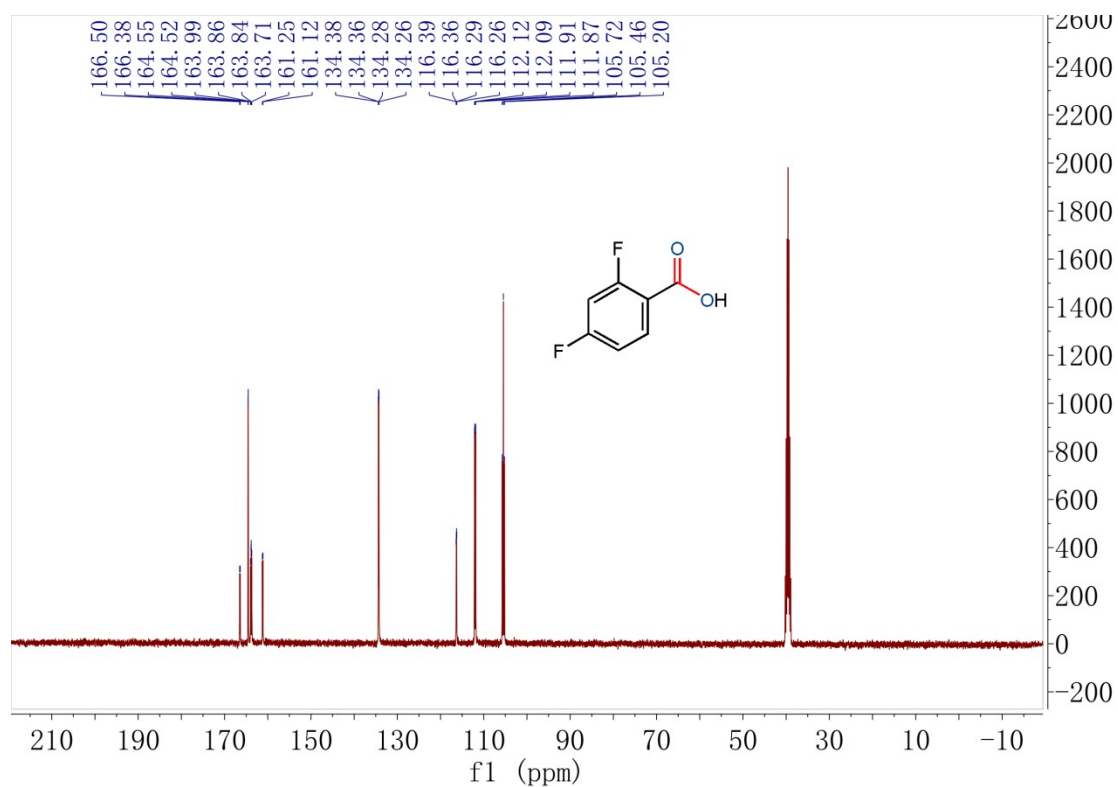
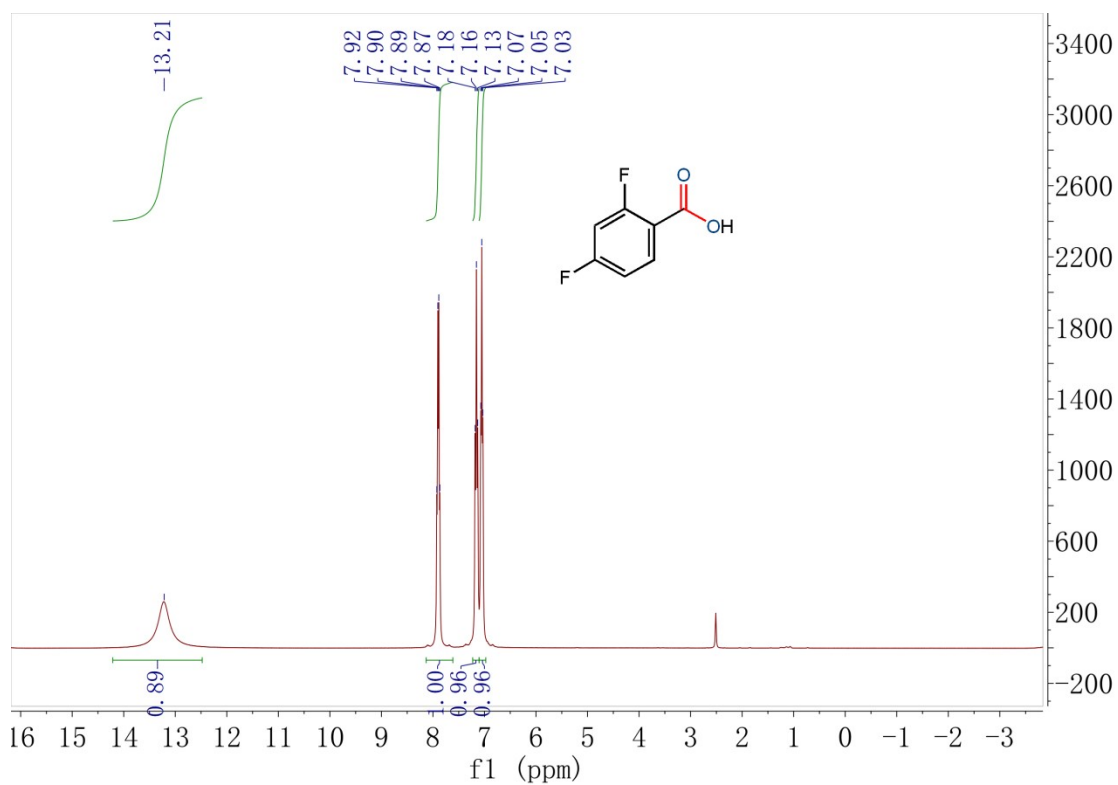


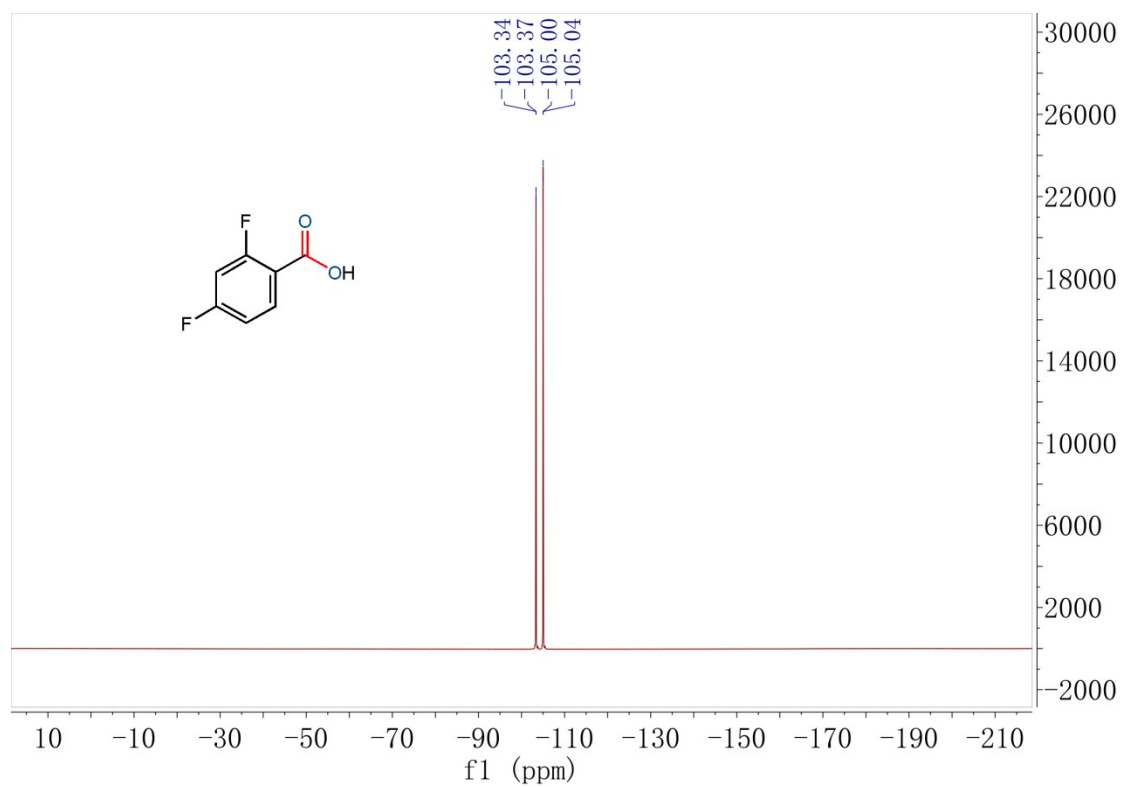
**4-Bromobenzoic acid (3h)**



**Figure S13.** <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 3h in DMSO-*d*<sub>6</sub>

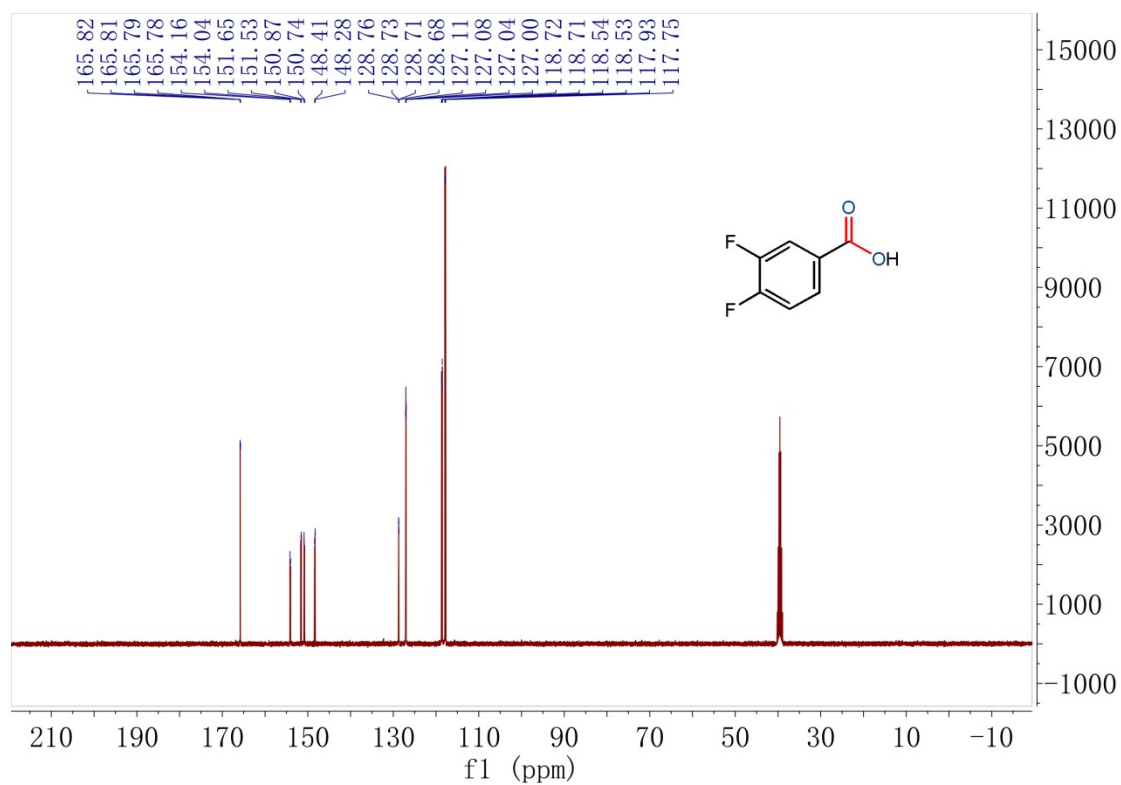
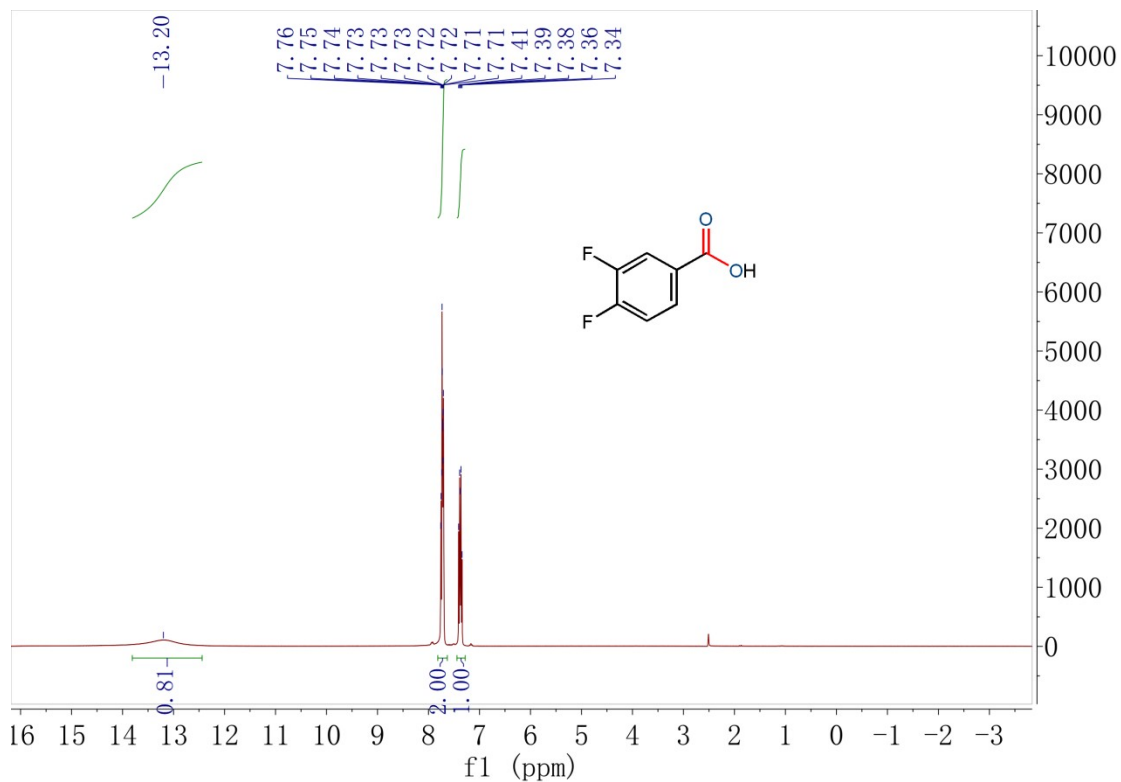
**2,4-Difluorobenzoic acid (3i)**





**Figure S14.**  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}\{^1\text{H}\}$  (376 MHz) NMR spectra of **3i** in  $\text{DMSO-}d_6$

**3,4-Difluorobenzoic acid (3j)**



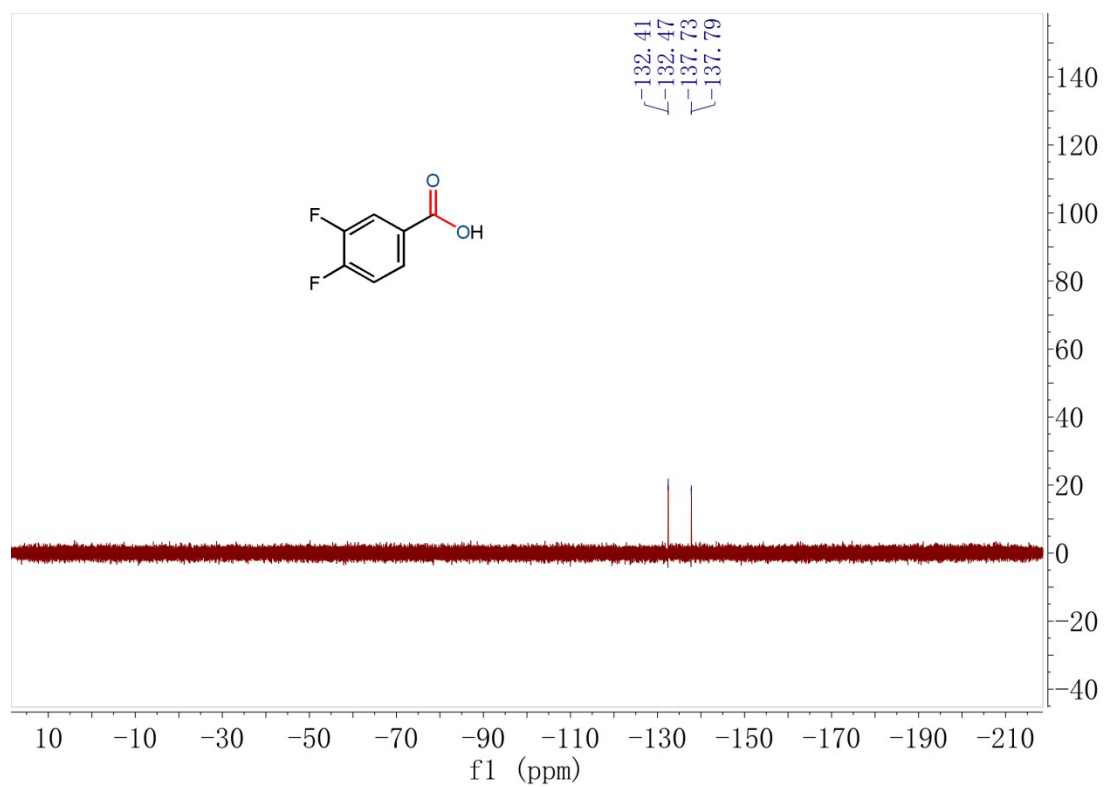
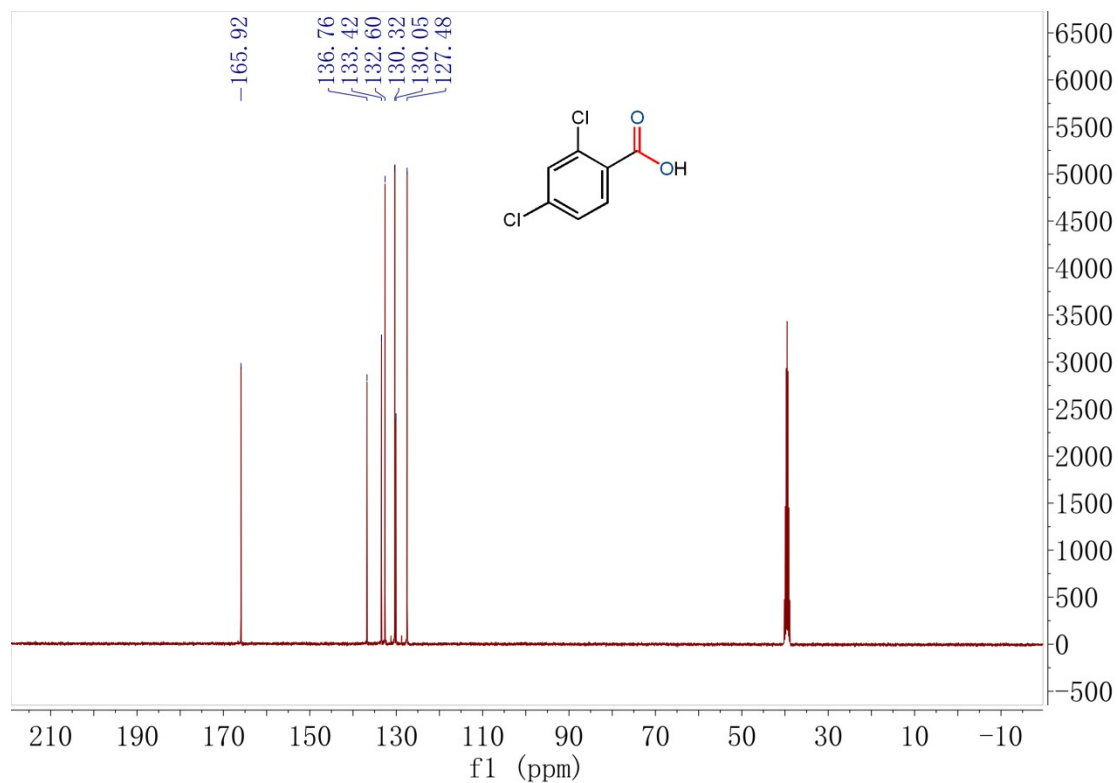
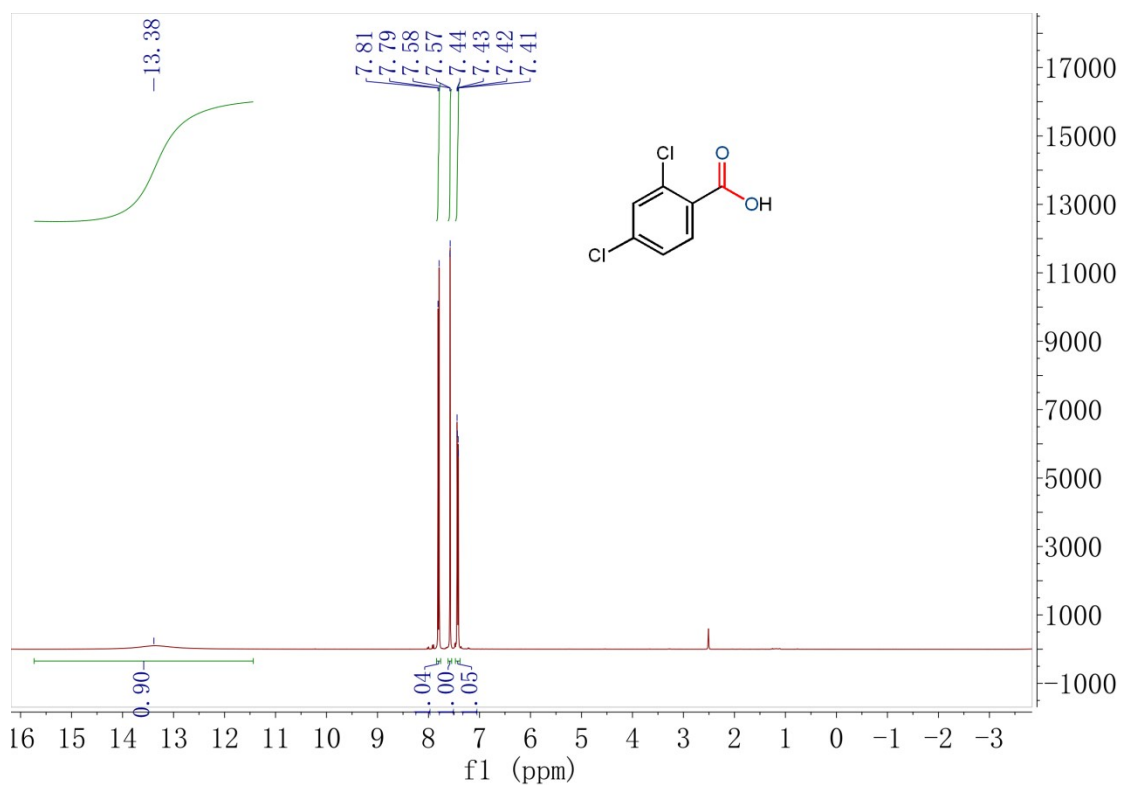


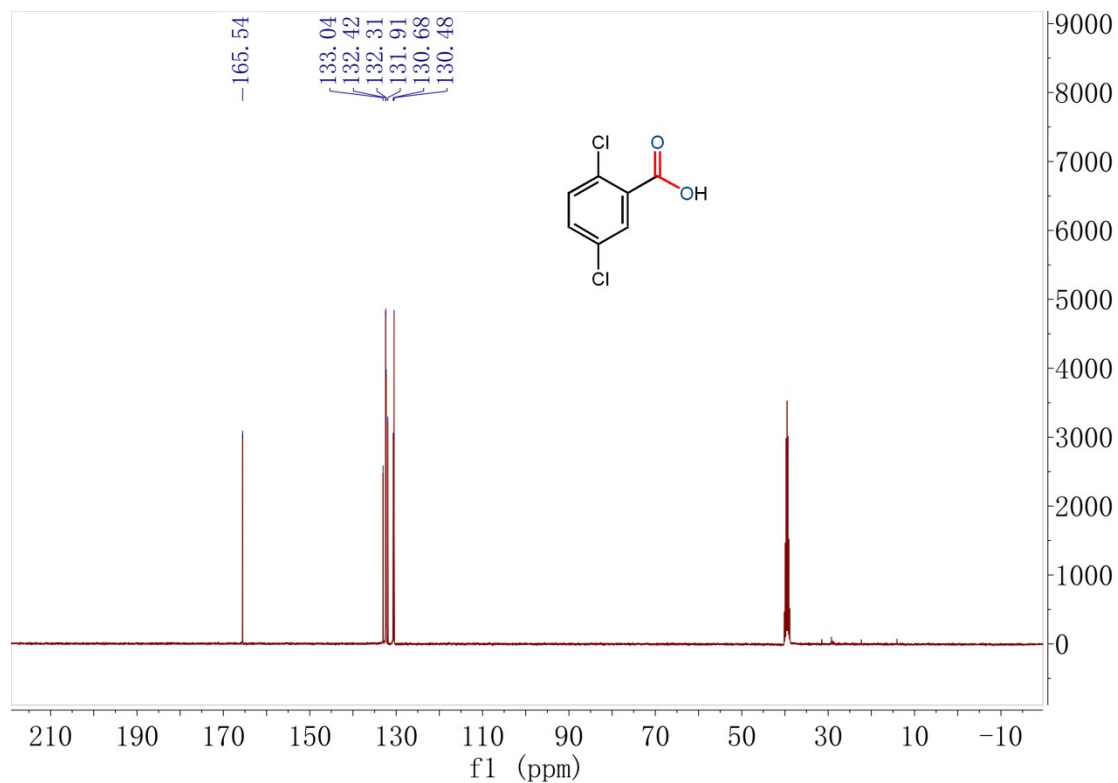
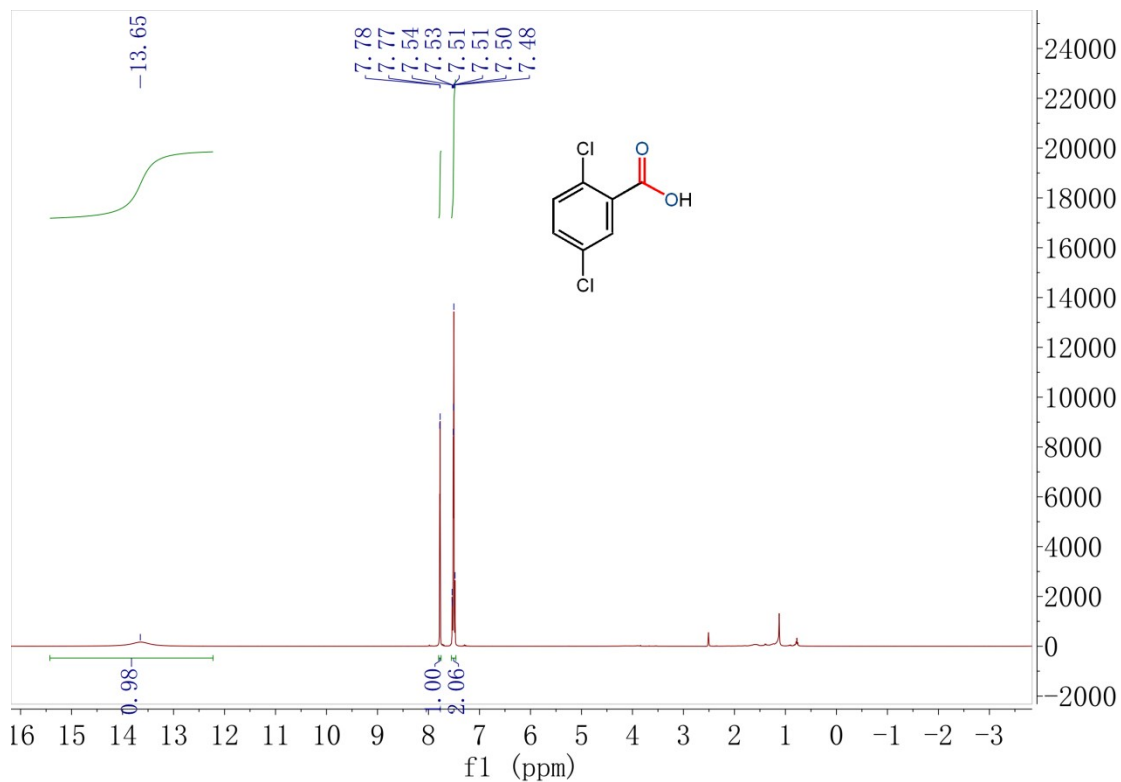
Figure S15.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  {1H} (101 MHz) and  $^{19}\text{F}$  {1H} (376 MHz) NMR spectra of 3j in  $\text{DMSO-}d_6$

**2,4-Dichlorobenzoic acid (3k)**



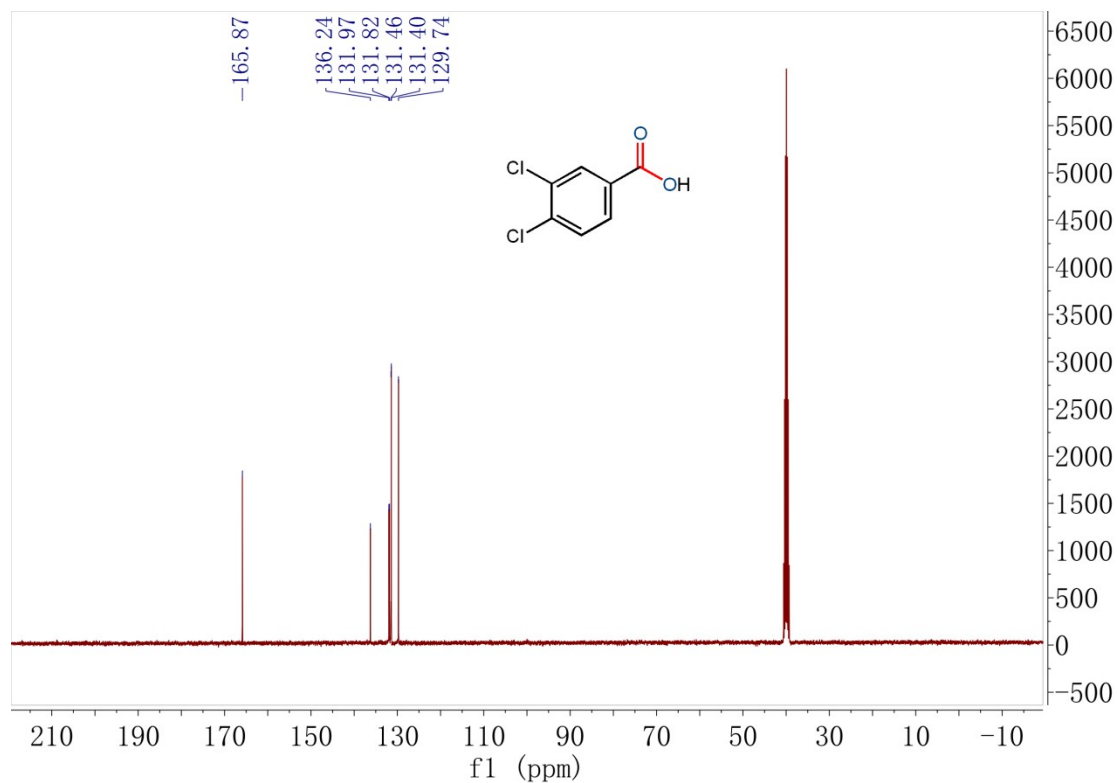
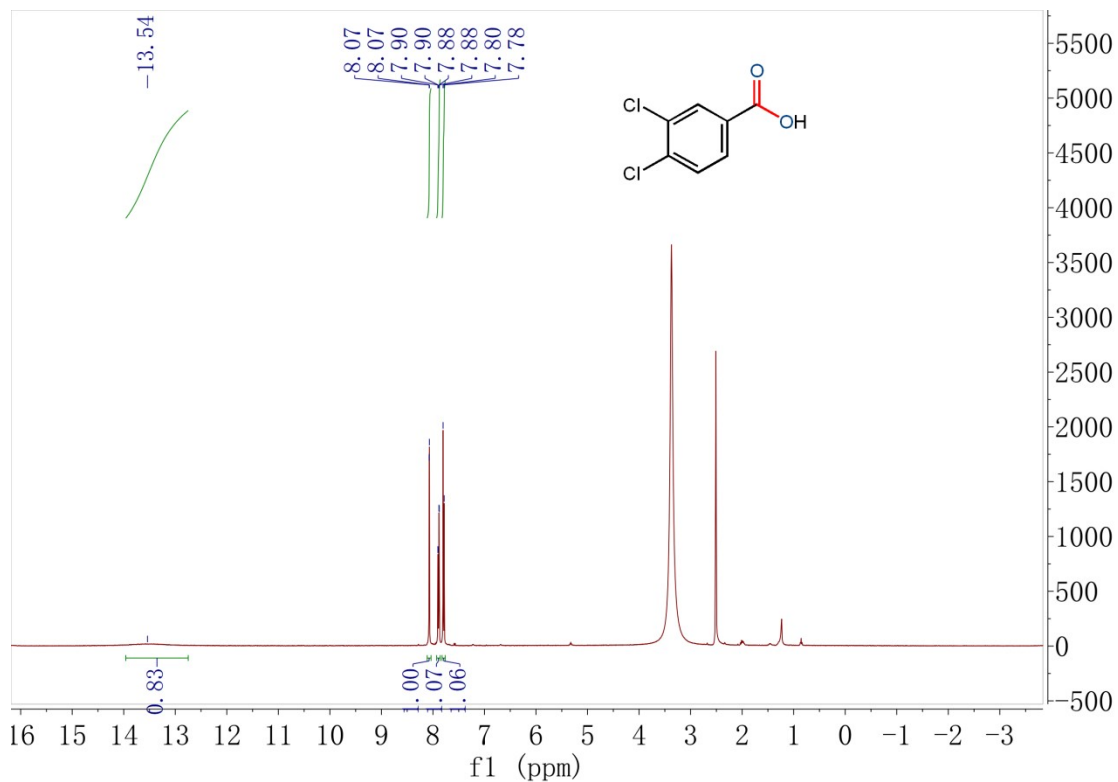
**Figure S16.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of 3k in  $\text{DMSO-}d_6$**

**2,5-Dichlorobenzoic acid (3I)**



**Figure S17. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 3I in DMSO-*d*<sub>6</sub>**

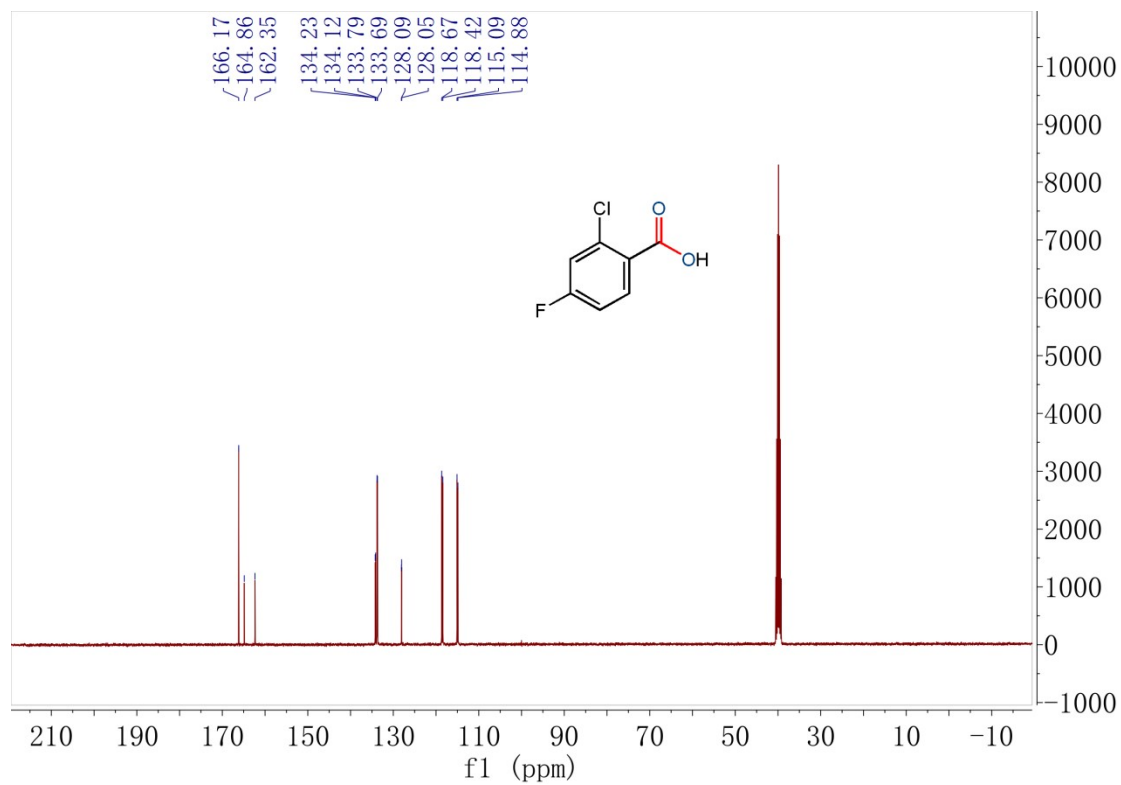
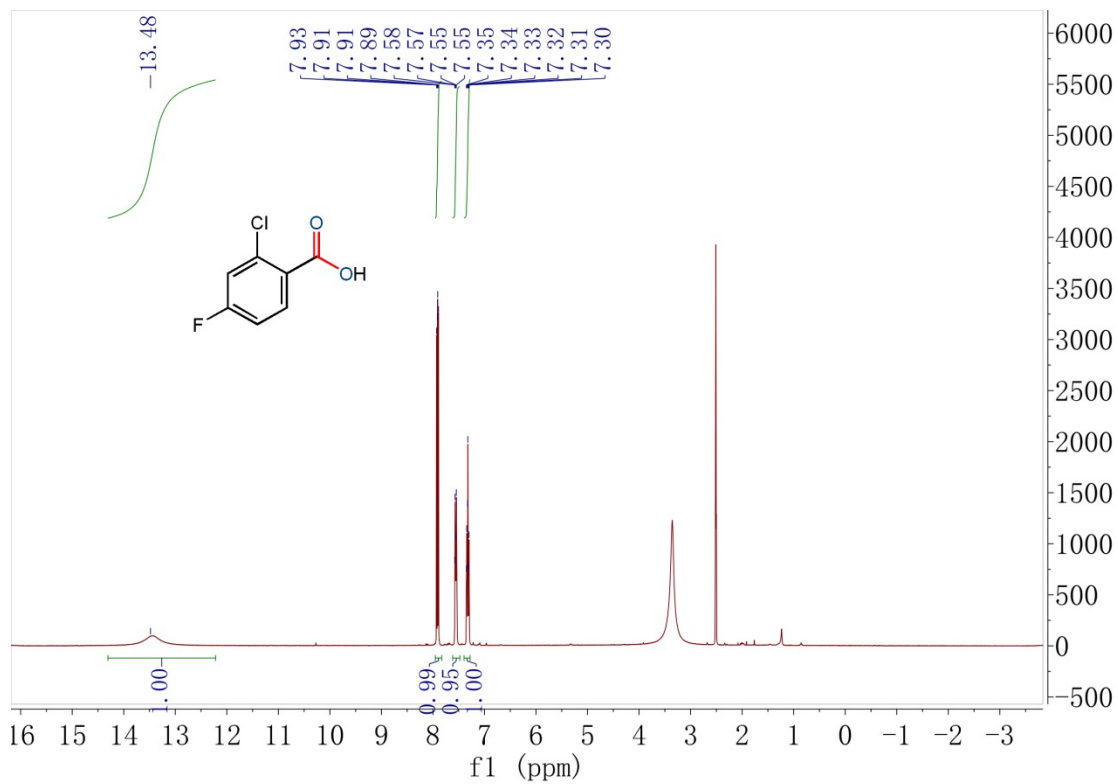
**3,4-Dichlorobenzoic acid (3m)**

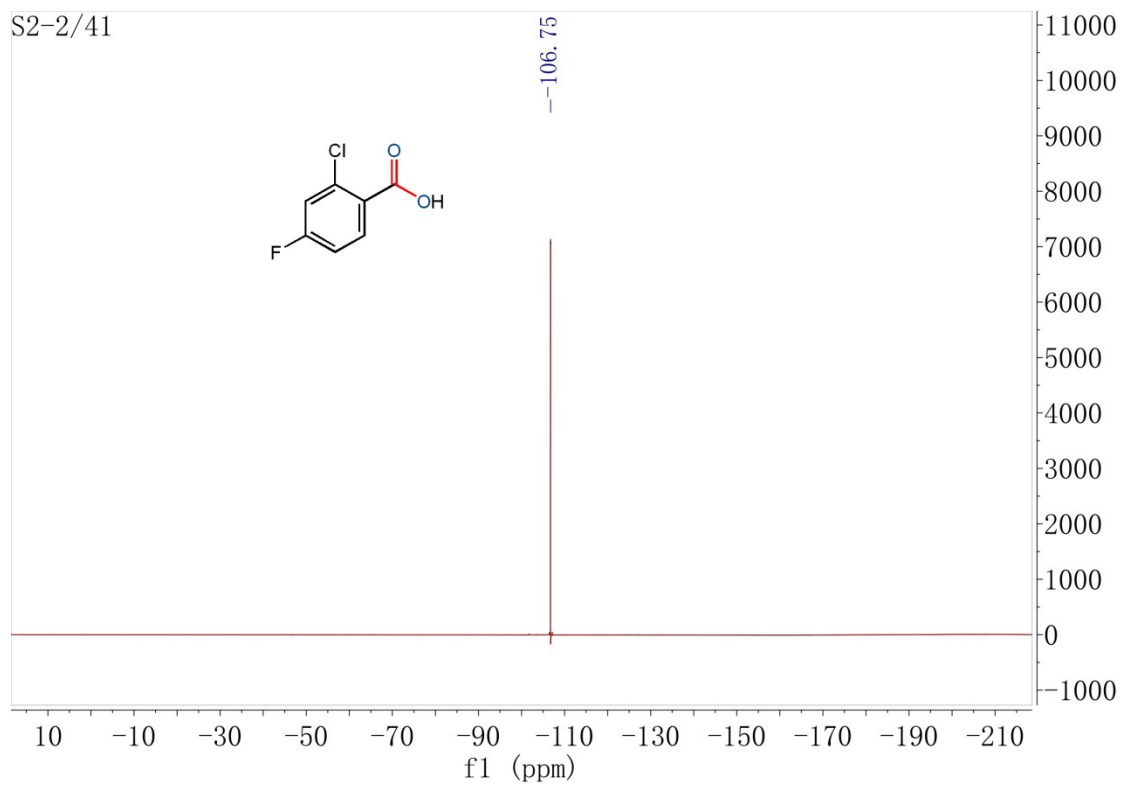


**Figure S18.**  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of 3m in  $\text{DMSO-}d_6$



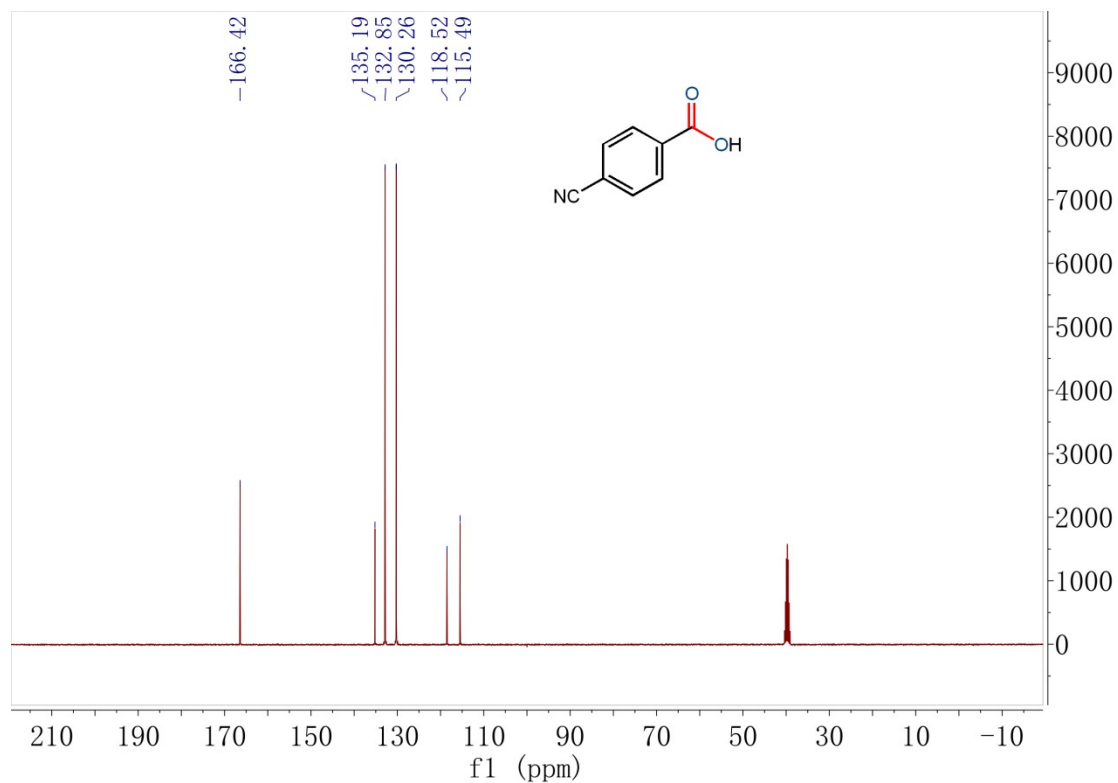
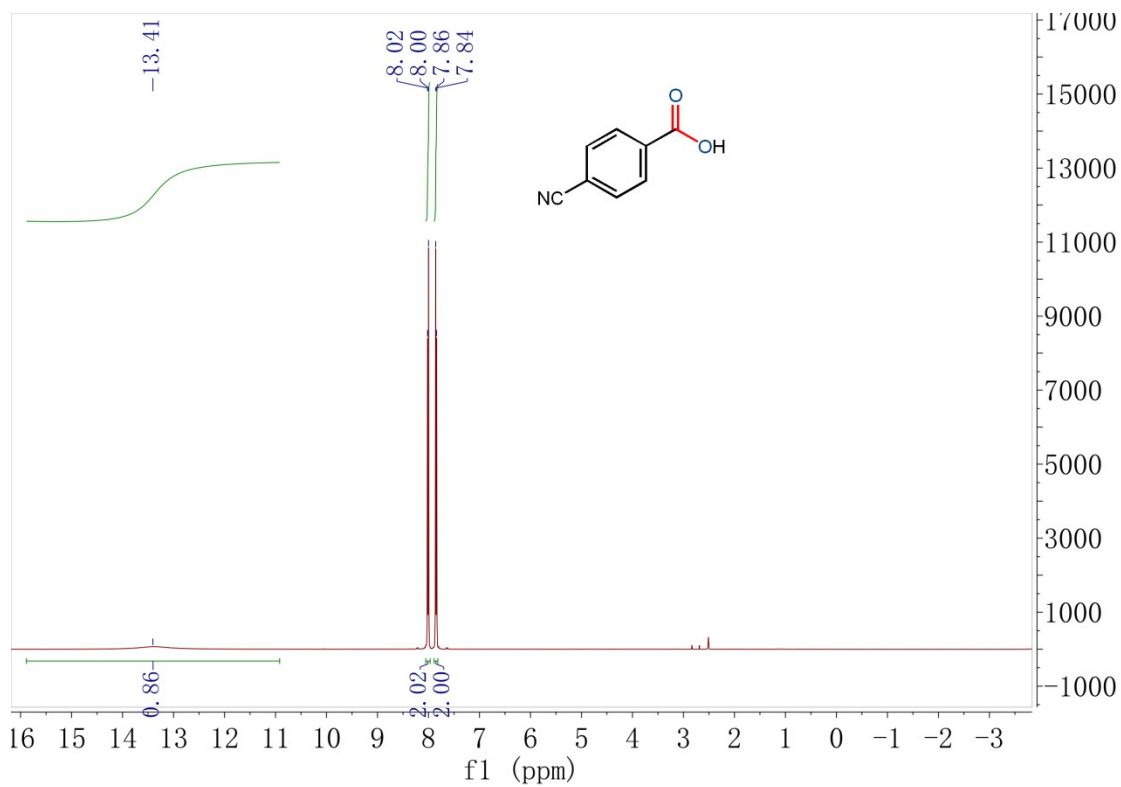
**2-Chloro-4-fluorobenzoic acid (3n)**





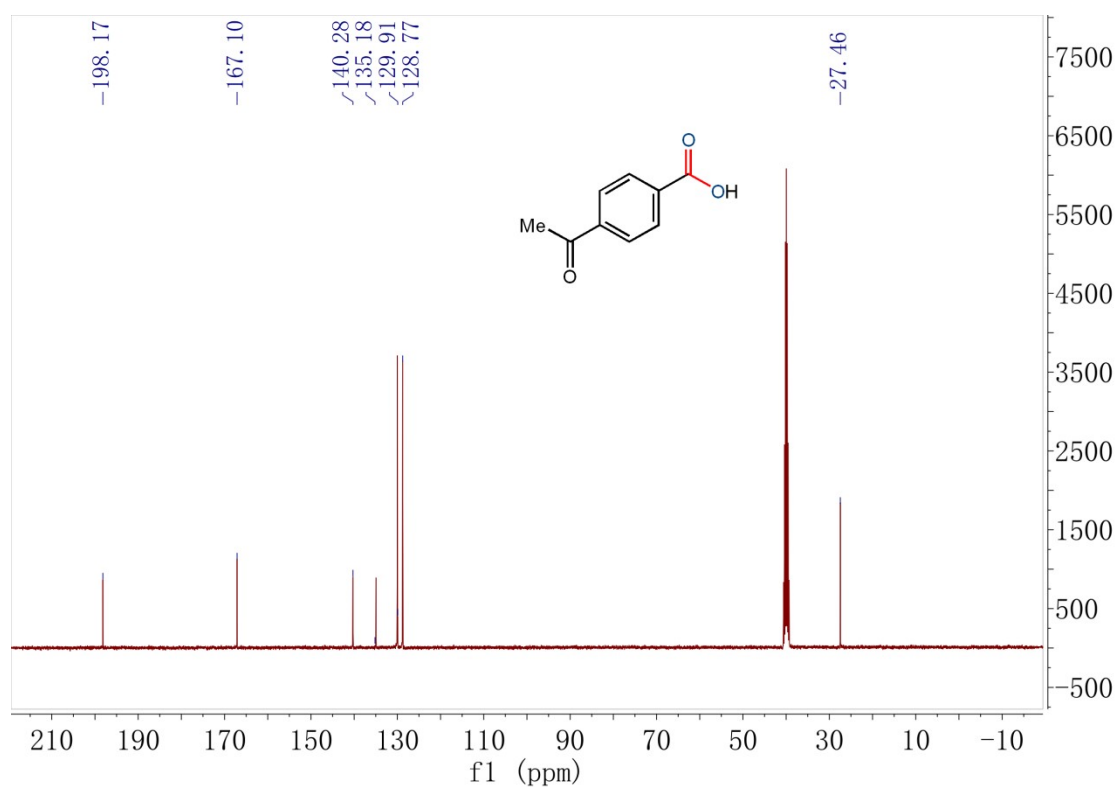
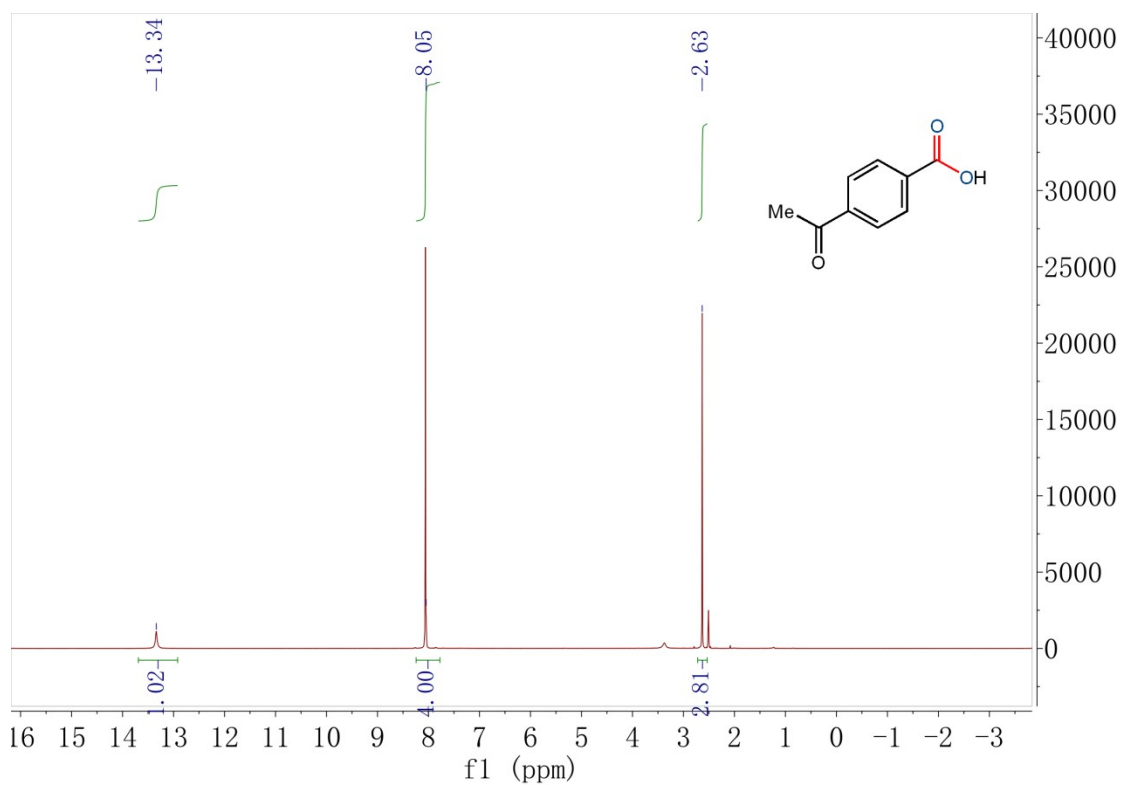
**Figure S19.**  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  {1H} (101 MHz) and  $^{19}\text{F}$  {1H} (376 MHz) NMR spectra of **3n** in  $\text{DMSO-}d_6$

**4-Cyanobenzoic acid (3o)**



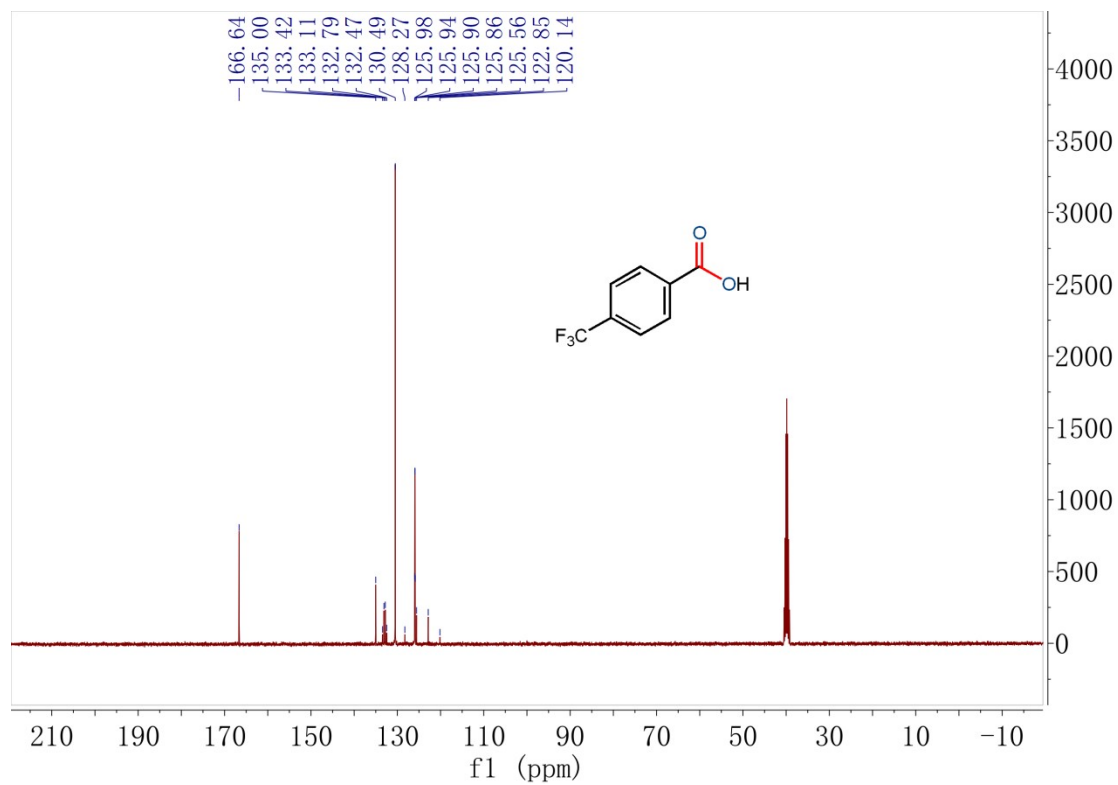
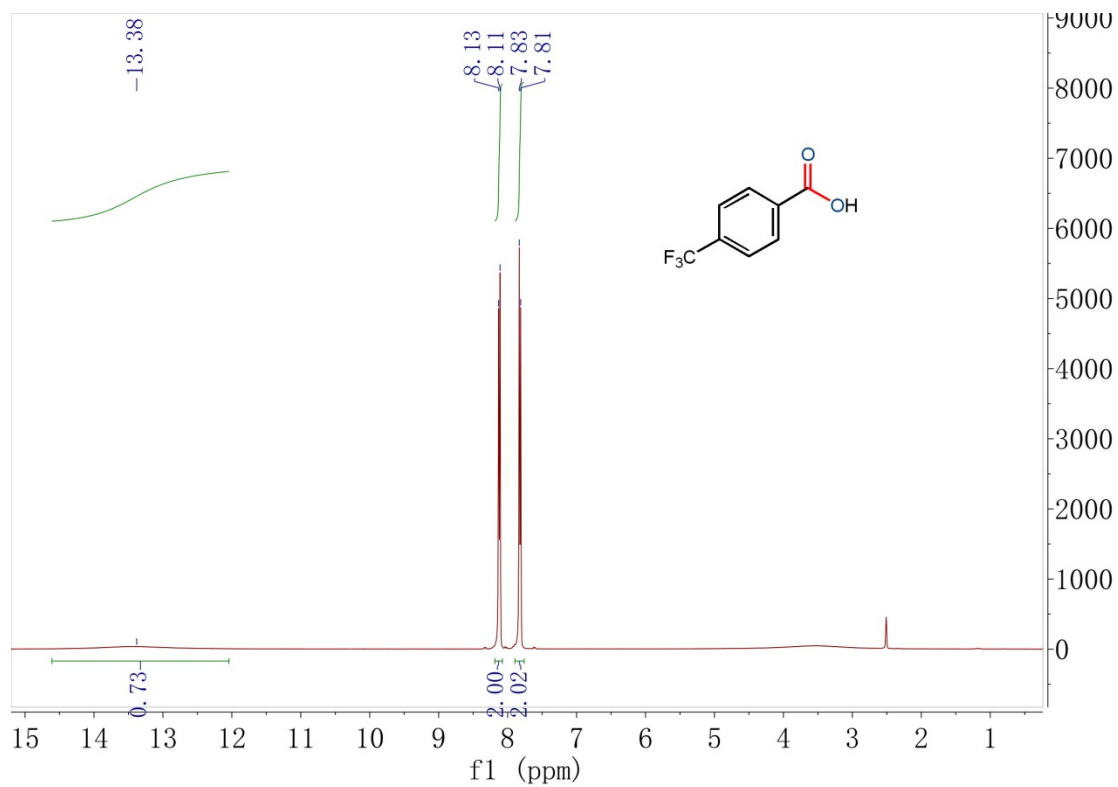
**Figure S20.**  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of **3o** in  $\text{DMSO-}d_6$

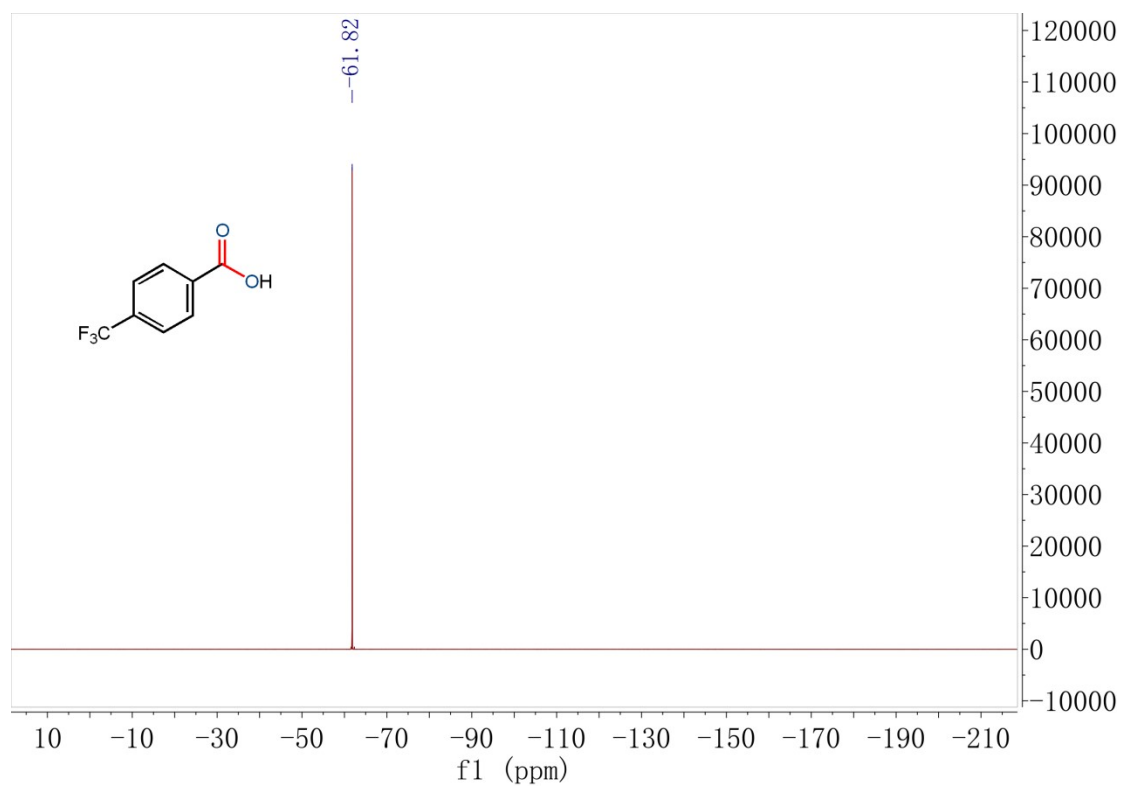
**Acetylbenzoic acid (3p)**



**Figure S21. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 3p in DMSO-*d*<sub>6</sub>**

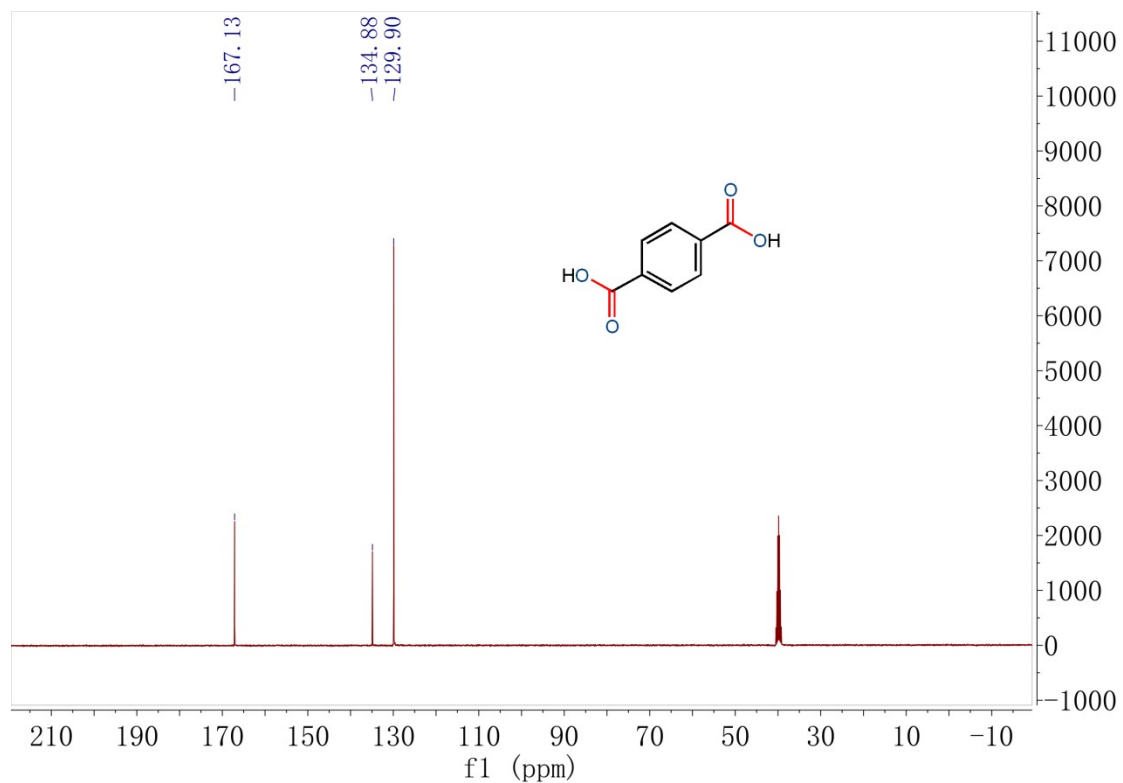
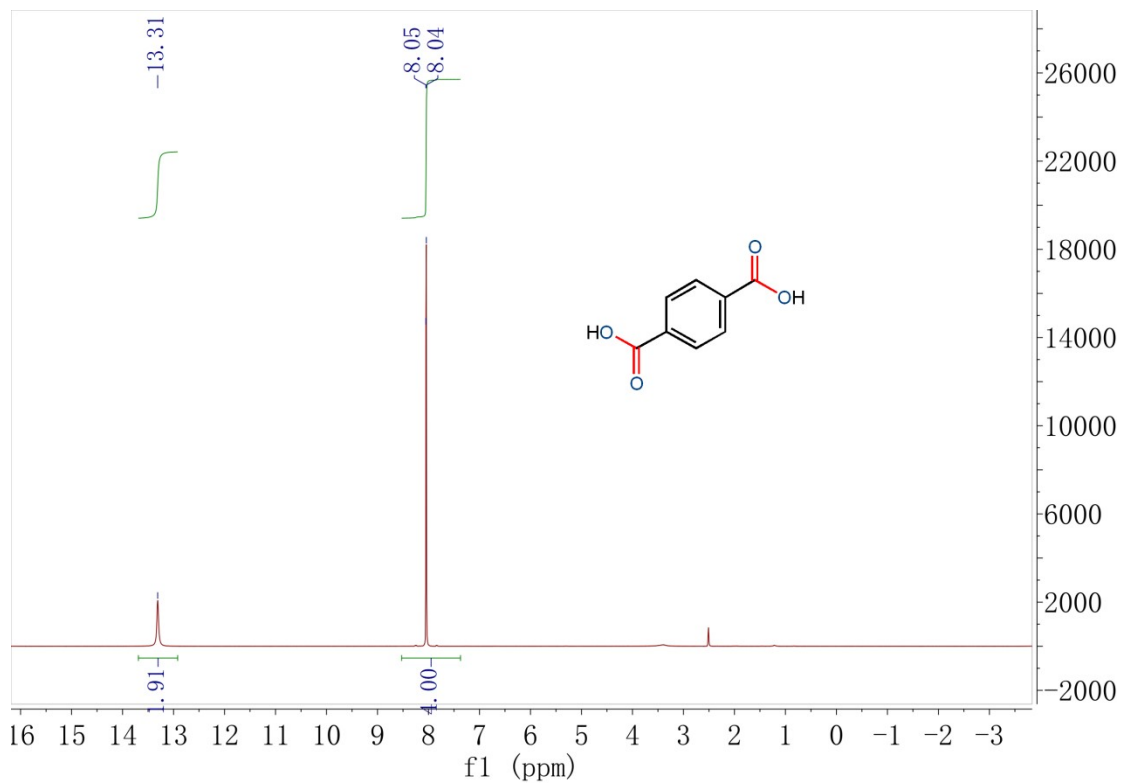
**4-(Trifluoromethyl)benzoic acid (3q)**





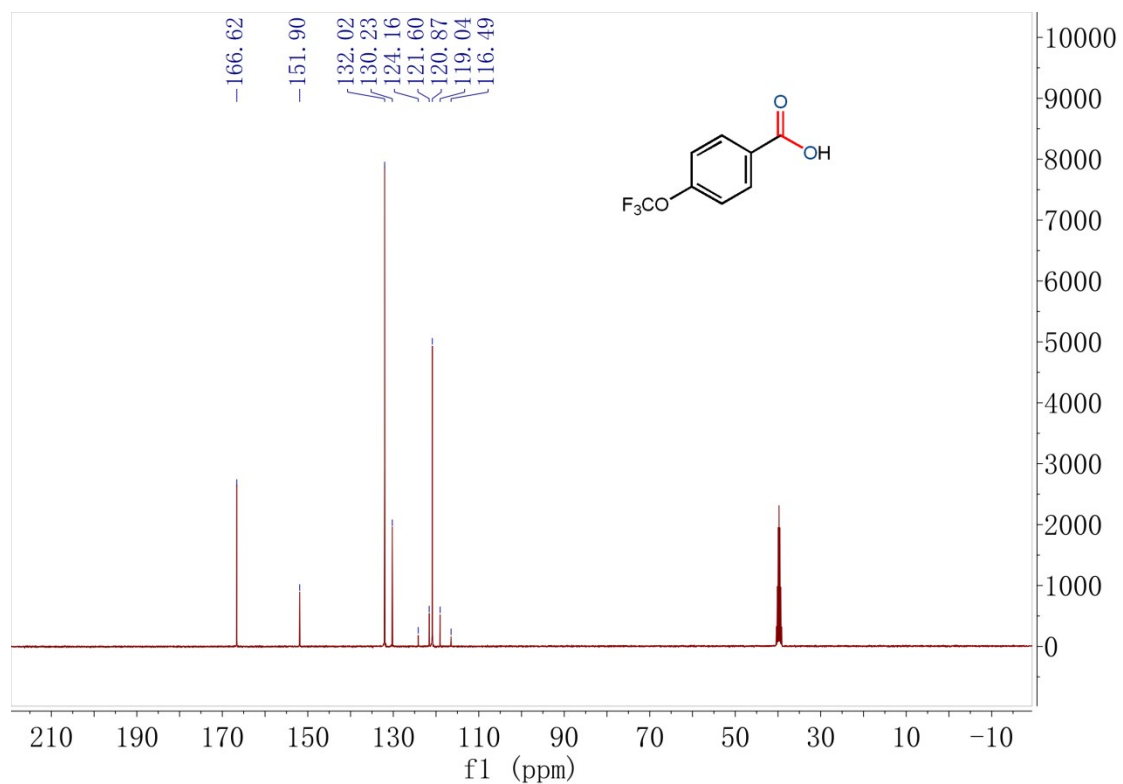
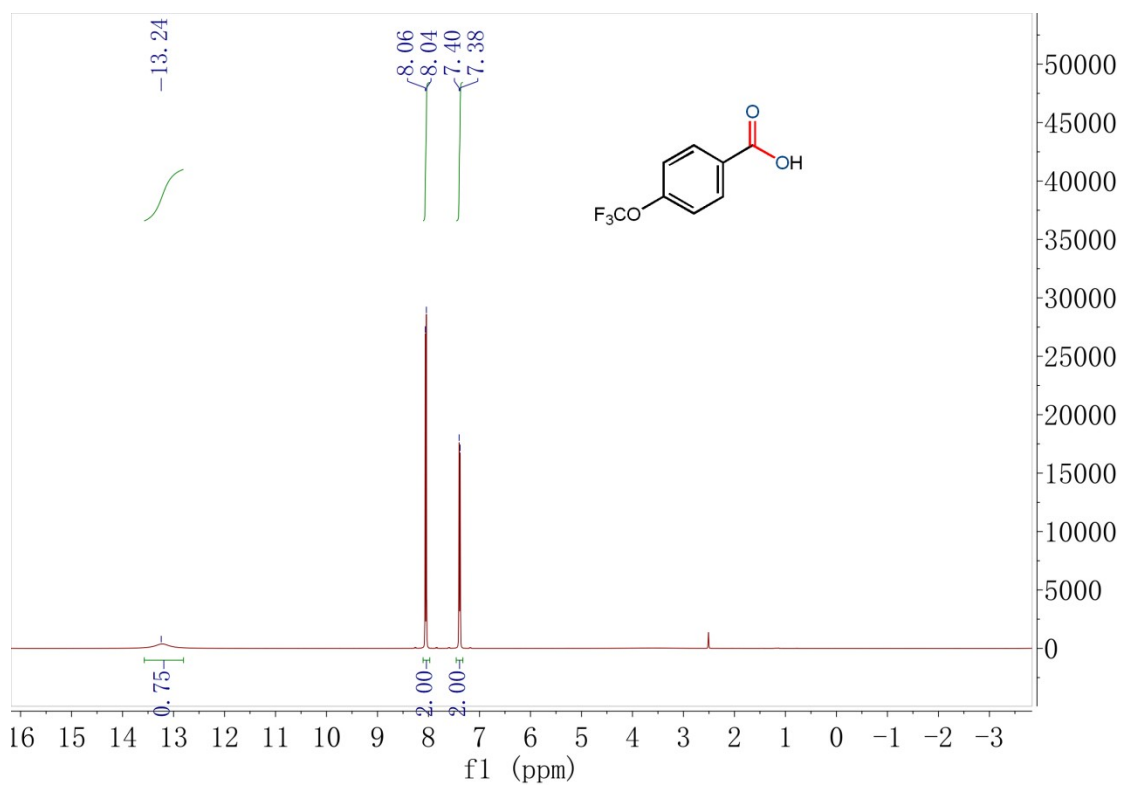
**Figure S22.**  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  {1H} (101 MHz) and  $^{19}\text{F}$  {1H} (376 MHz) NMR spectra of 3q in  $\text{DMSO-}d_6$

**Terephthalic acid (3r)**

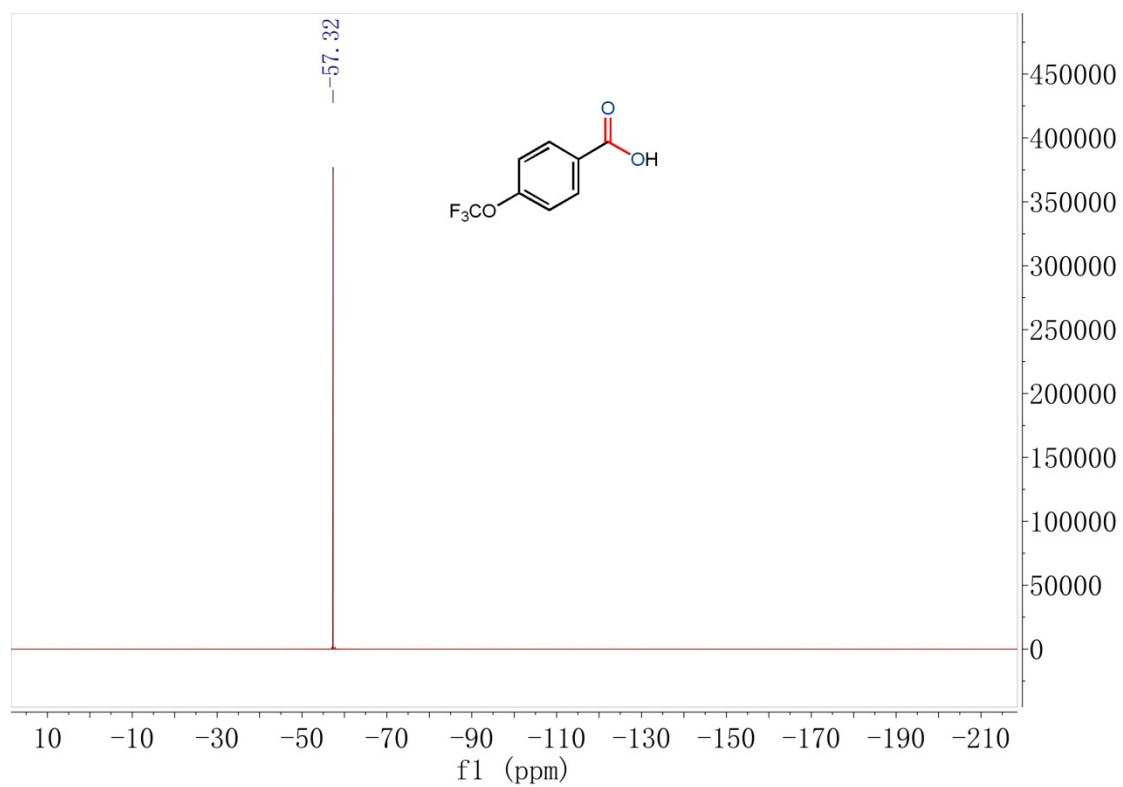


**Figure S23.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of 3r in  $\text{DMSO-}d_6$**

**4-(Trifluoromethoxy)benzoic acid (3s)**

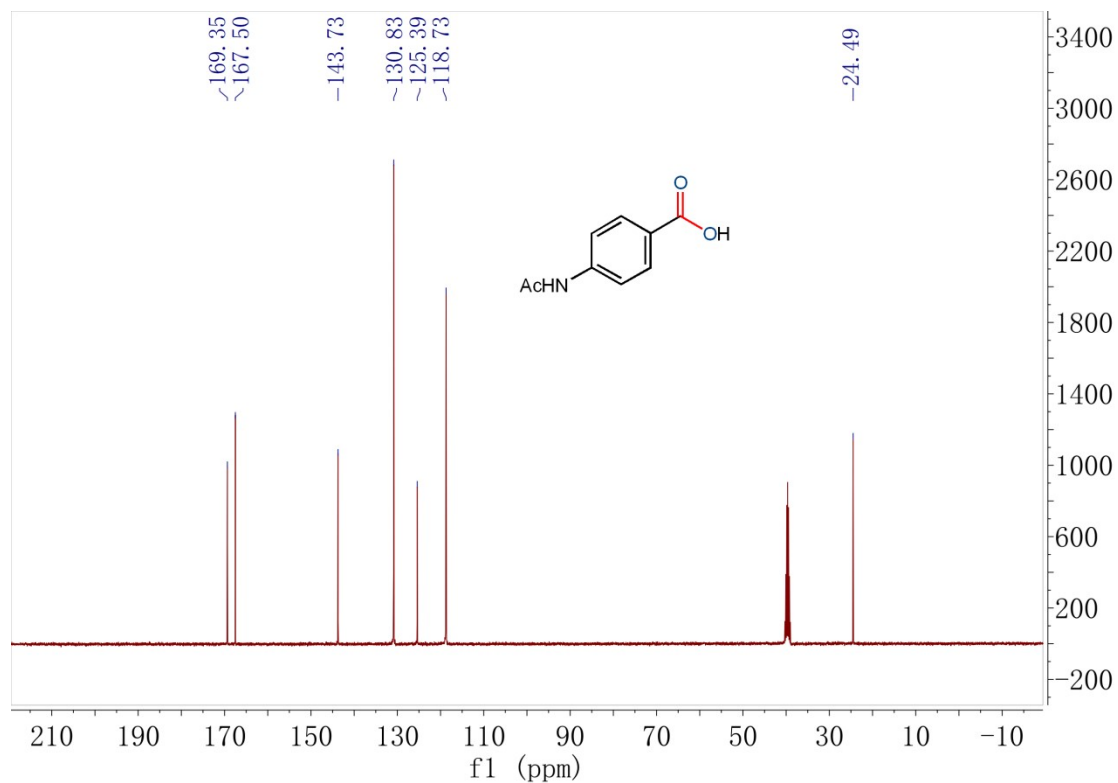
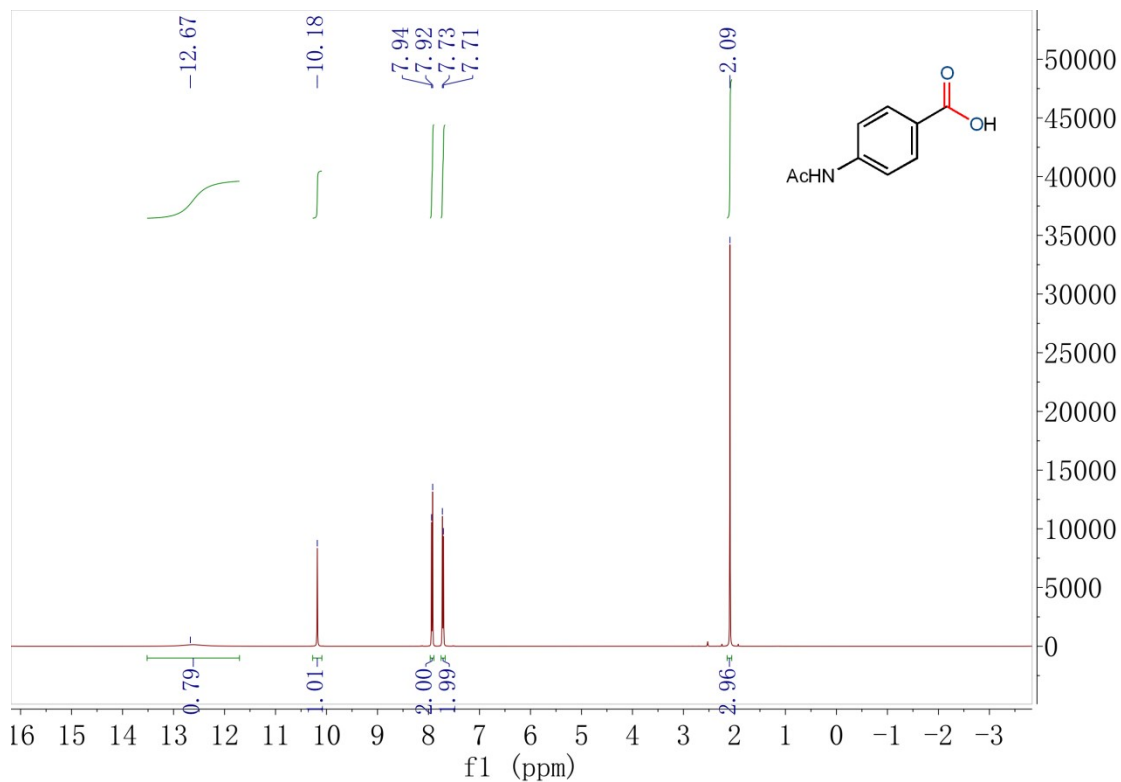






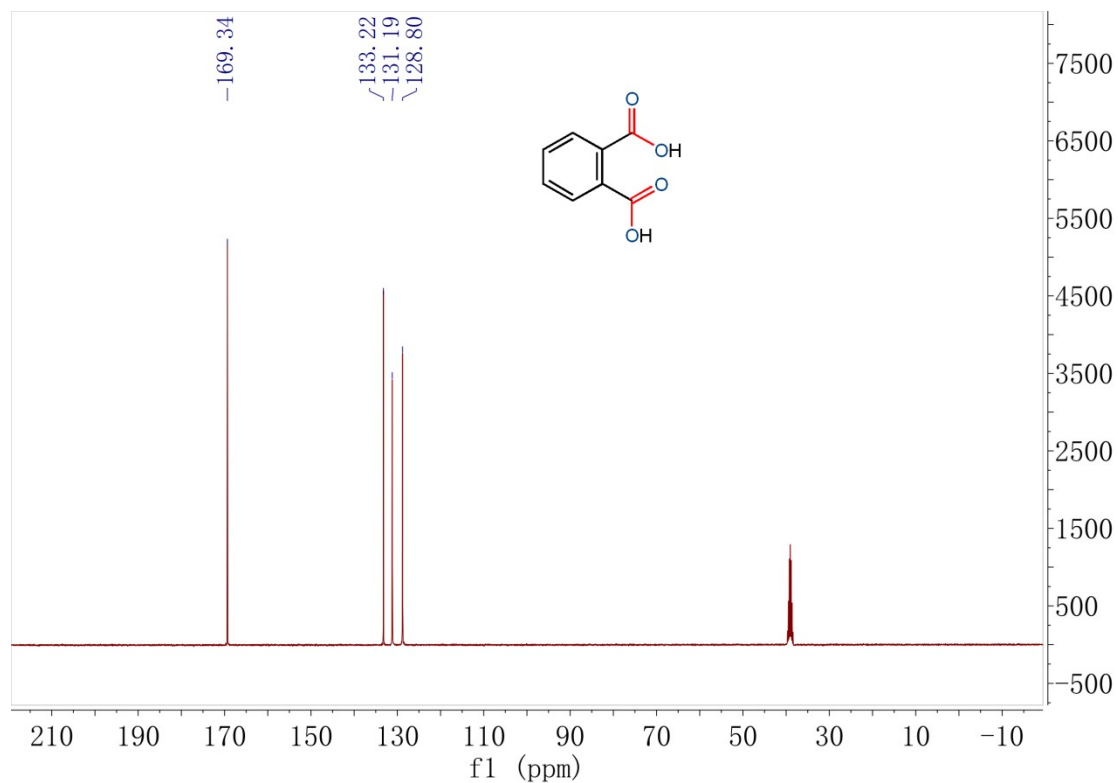
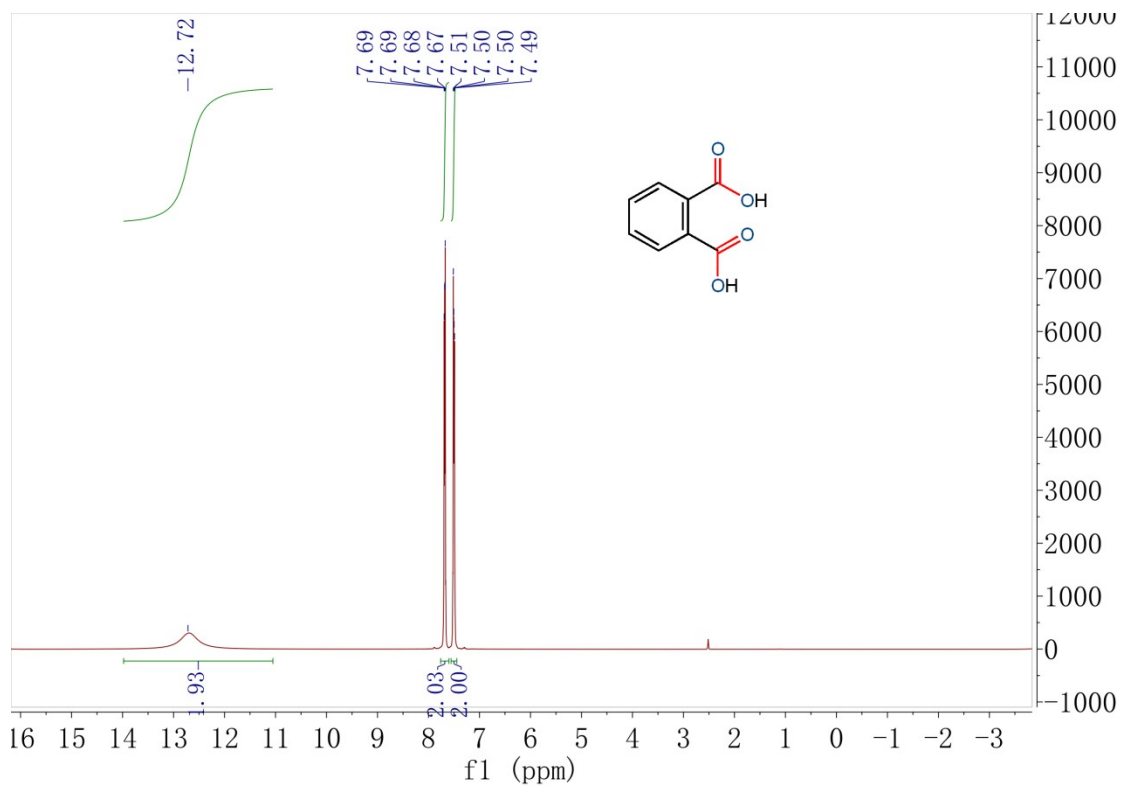
**Figure S24.**  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) and  $^{19}\text{F}$  { $^1\text{H}$ } (376 MHz) NMR spectra of 3s in  $\text{DMSO-}d_6$

**4-Acetamido benzoic acid (3t)**



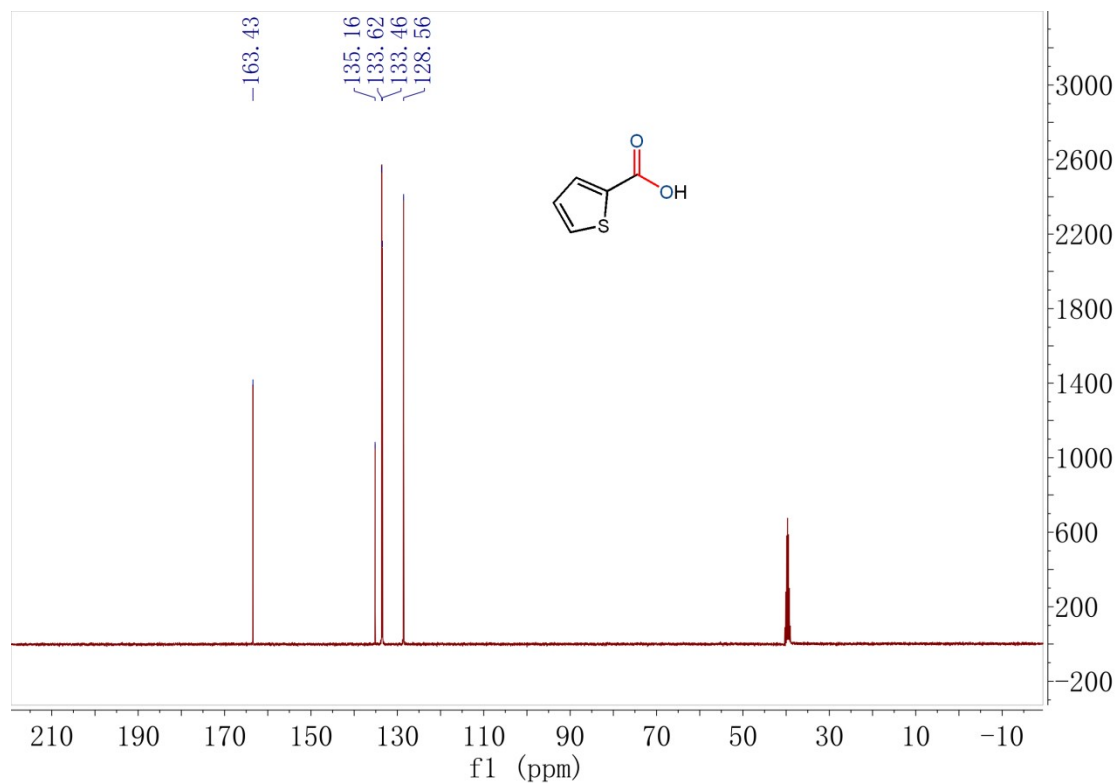
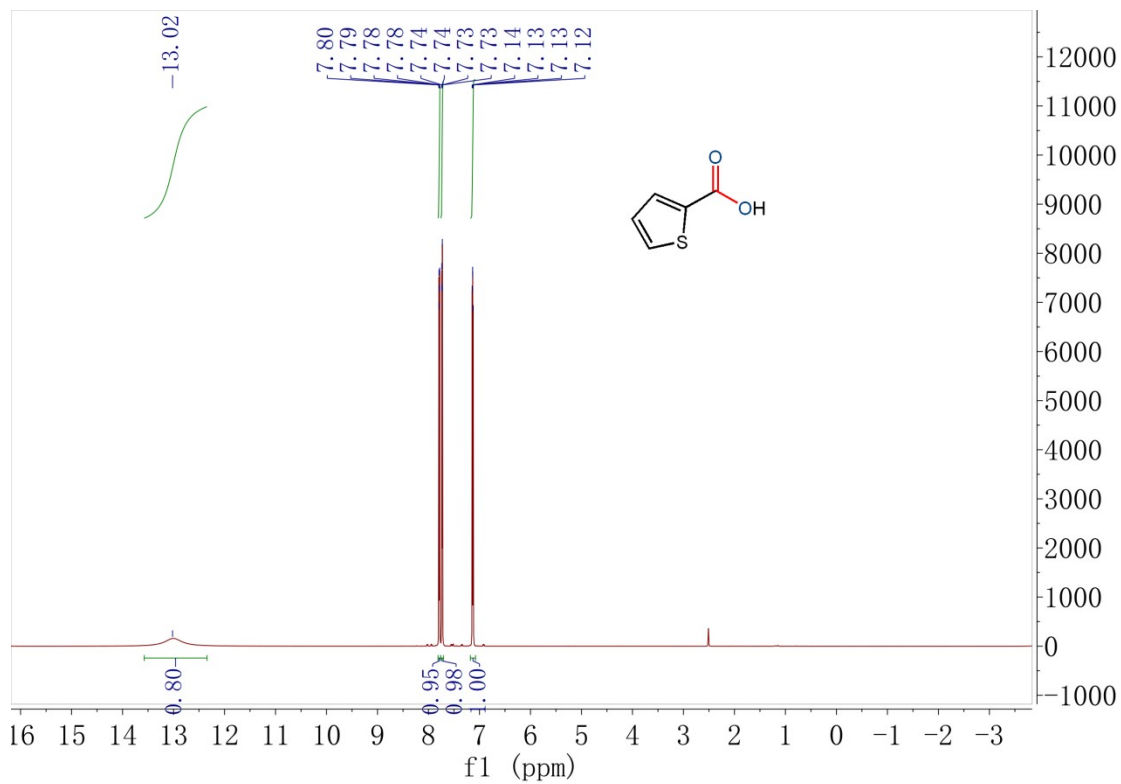
**Figure S25.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of 3t in  $\text{DMSO-}d_6$**

**Phthalic acid (3u)**



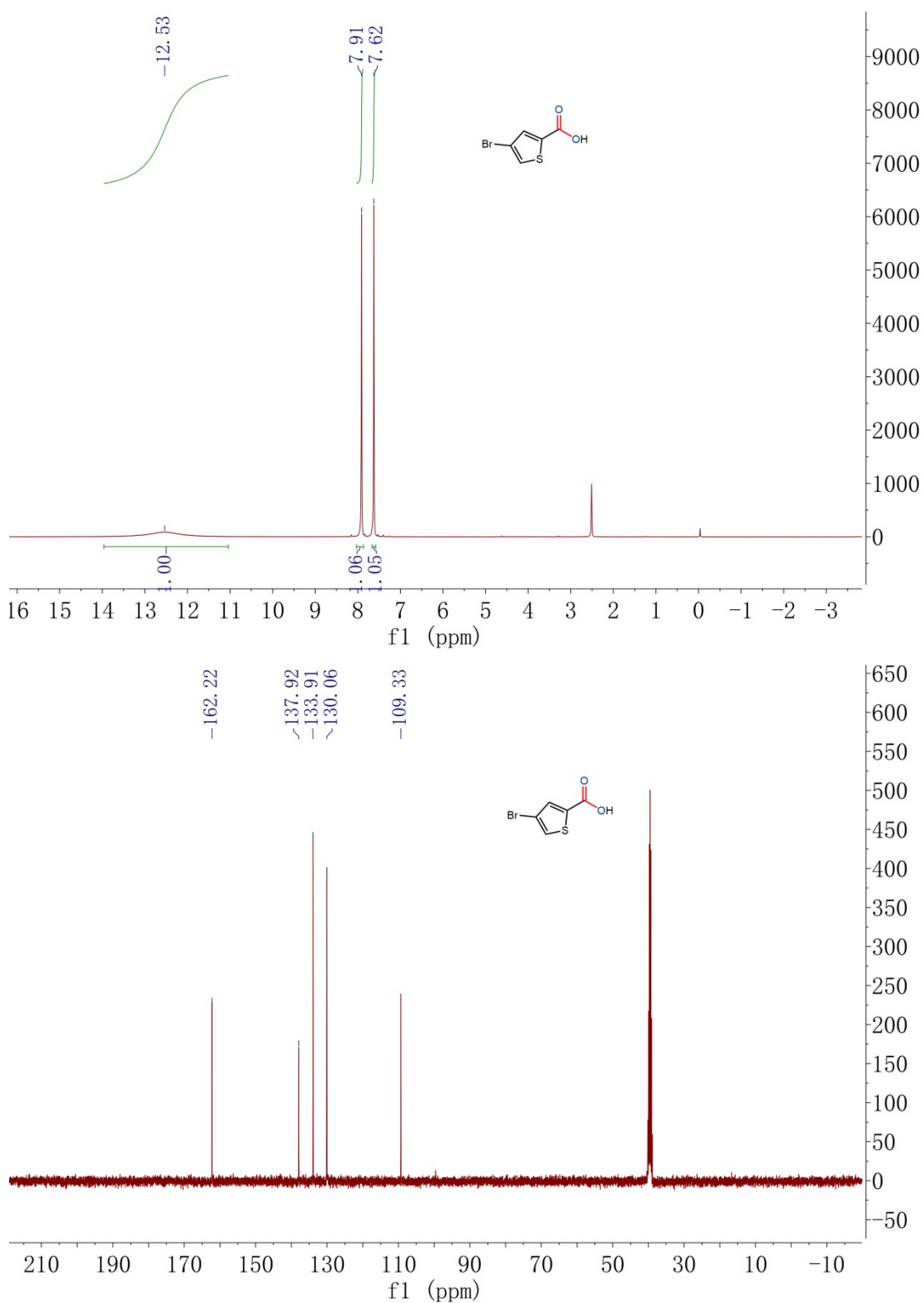
**Figure S26. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 3u in DMSO-*d*<sub>6</sub>**

**2-Thiophenic acid (3w)**



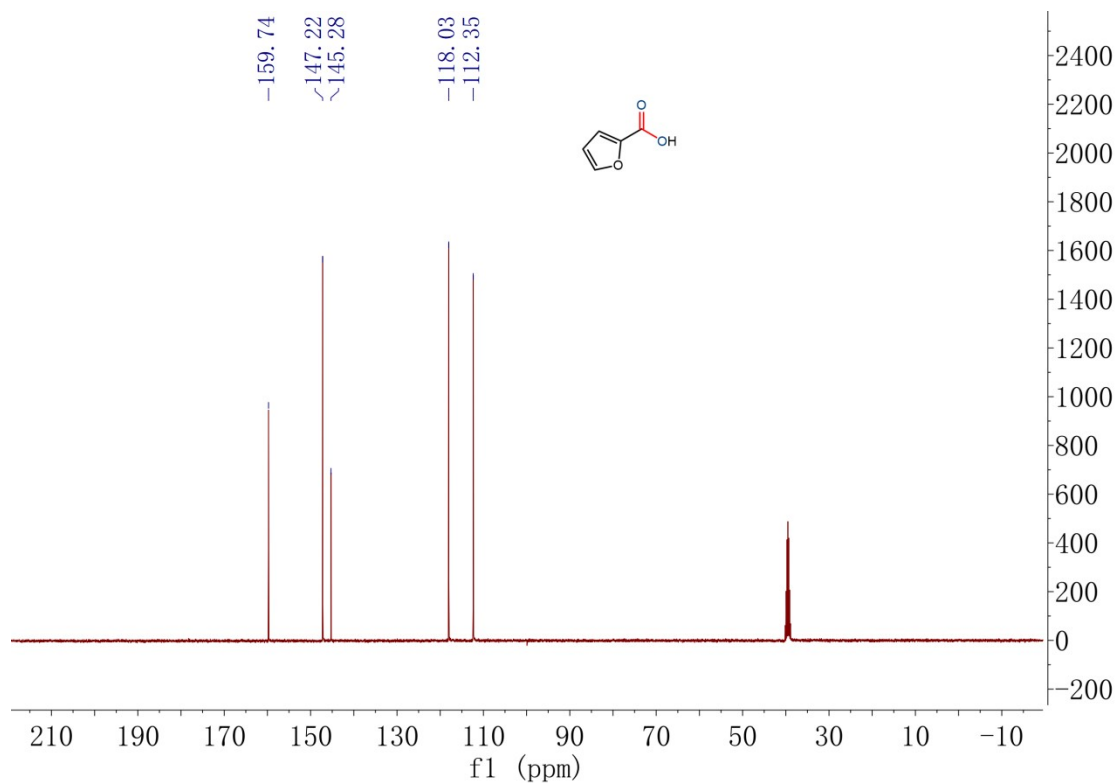
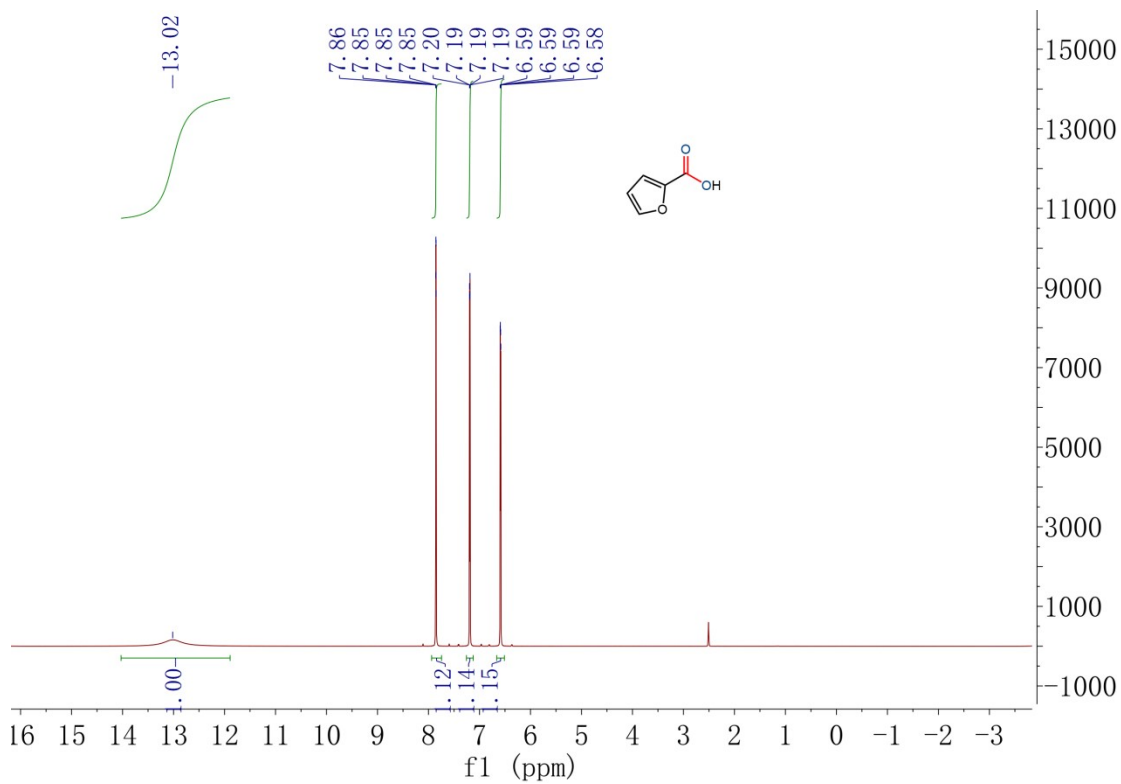
**Figure S27. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR Spectra of 3w in DMSO-*d*<sub>6</sub>**

**4-Bromo-2-thiophenecarboxylic acid (3x)**



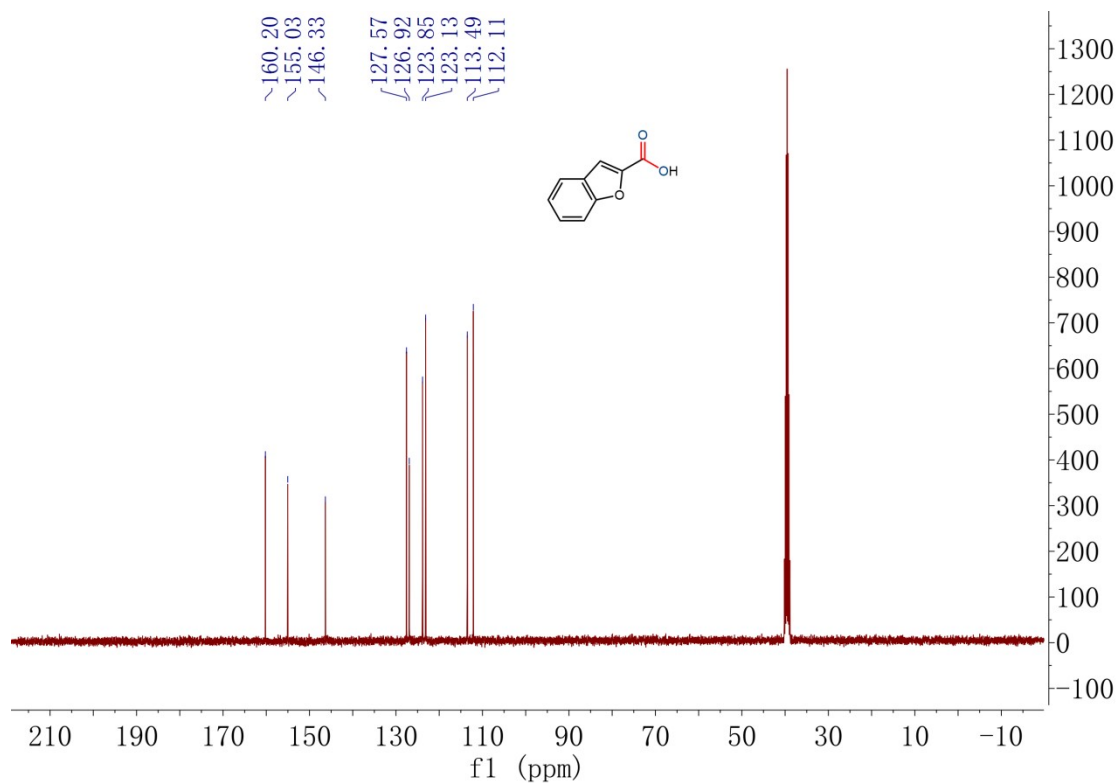
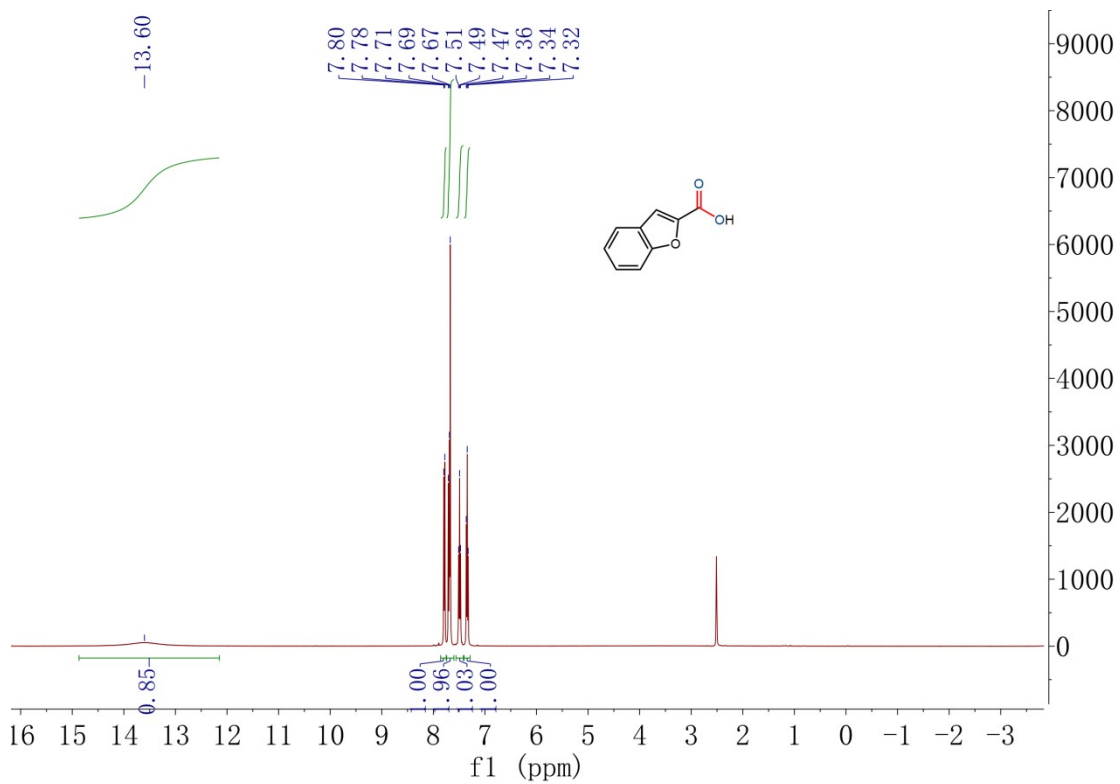
**Figure S28. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR Spectra of 3x in DMSO-d<sub>6</sub>**

**Furan-2-carboxylic acid (3y)**



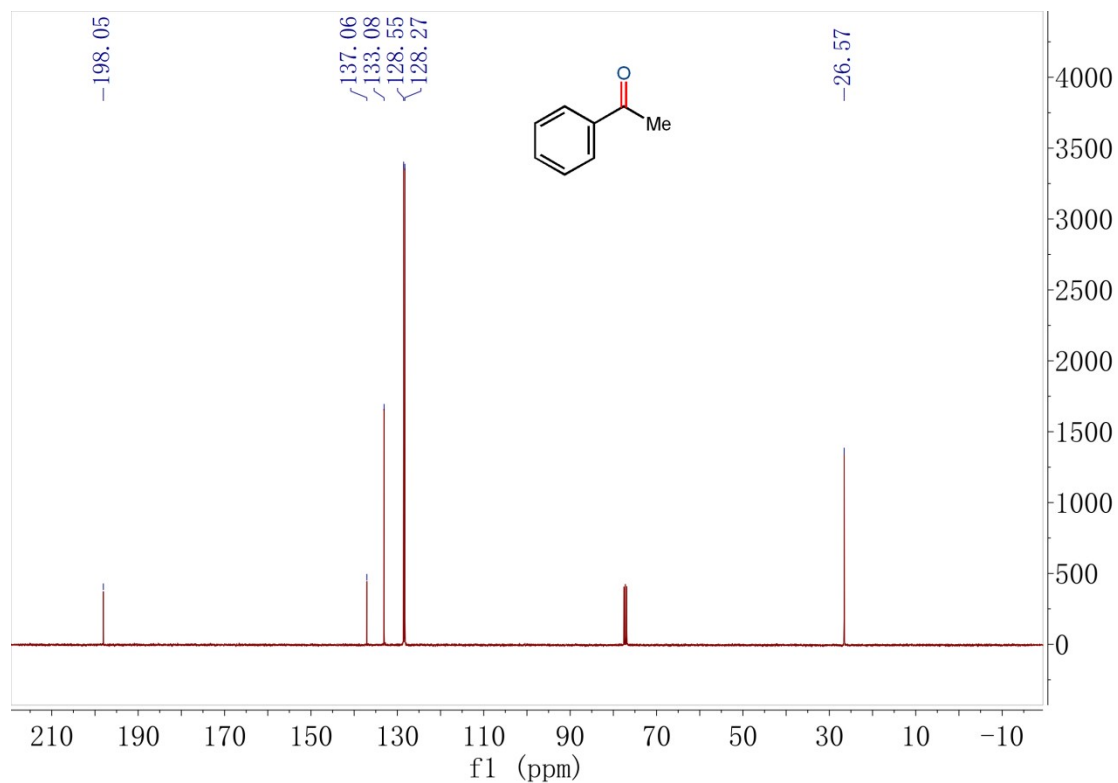
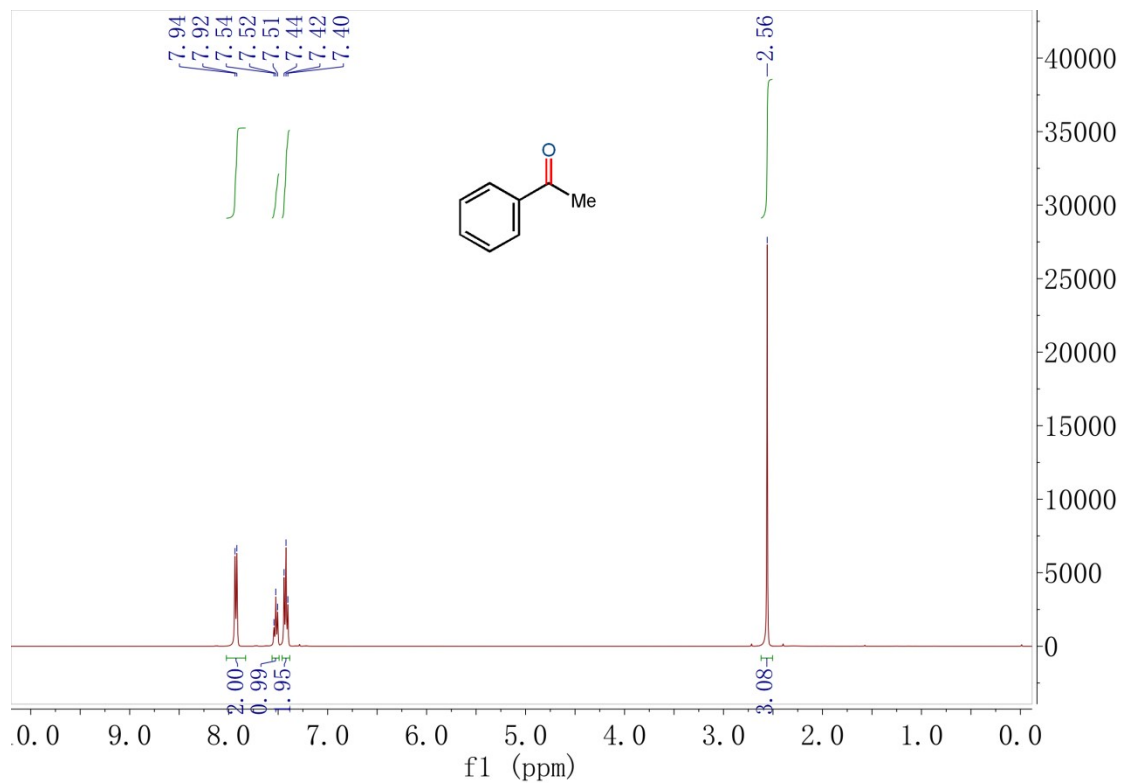
**Figure S29. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR Spectra of 3y in DMSO-*d*<sub>6</sub>**

**Benzofuran-2-carboxylic Acid (3z)**



**Figure S30.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR Spectra of 3z in  $\text{DMSO-}d_6$**

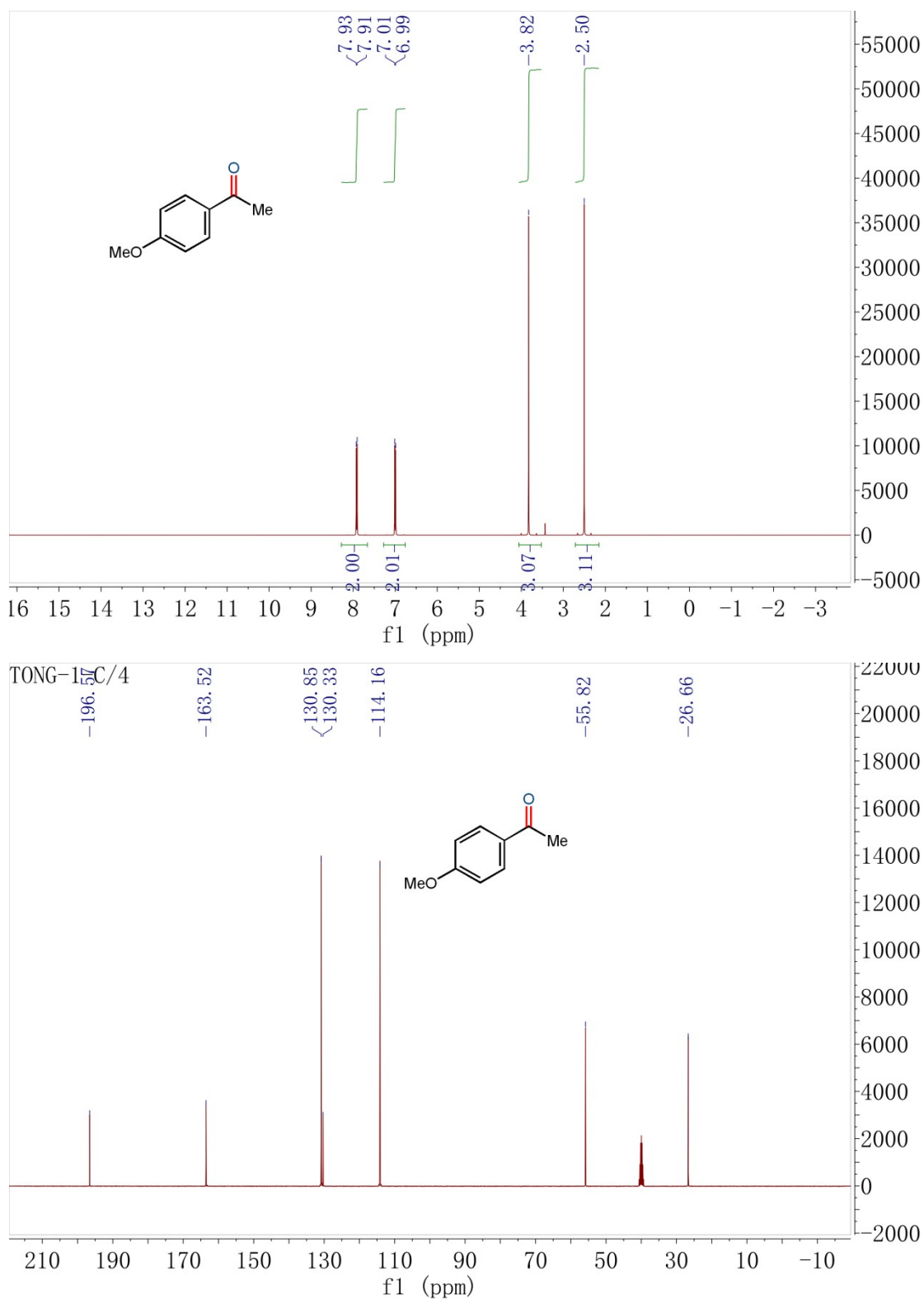
**Acetophenone (5a)**



**Figure S31. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 5a in CDCl<sub>3</sub>**

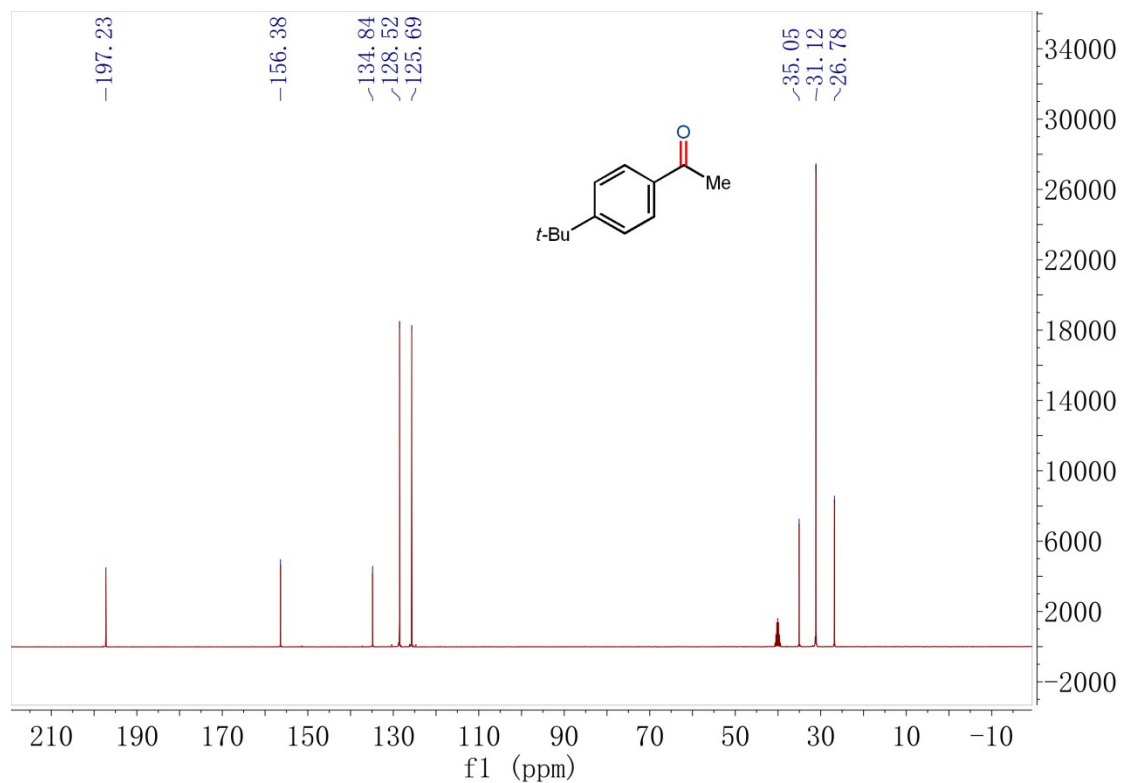
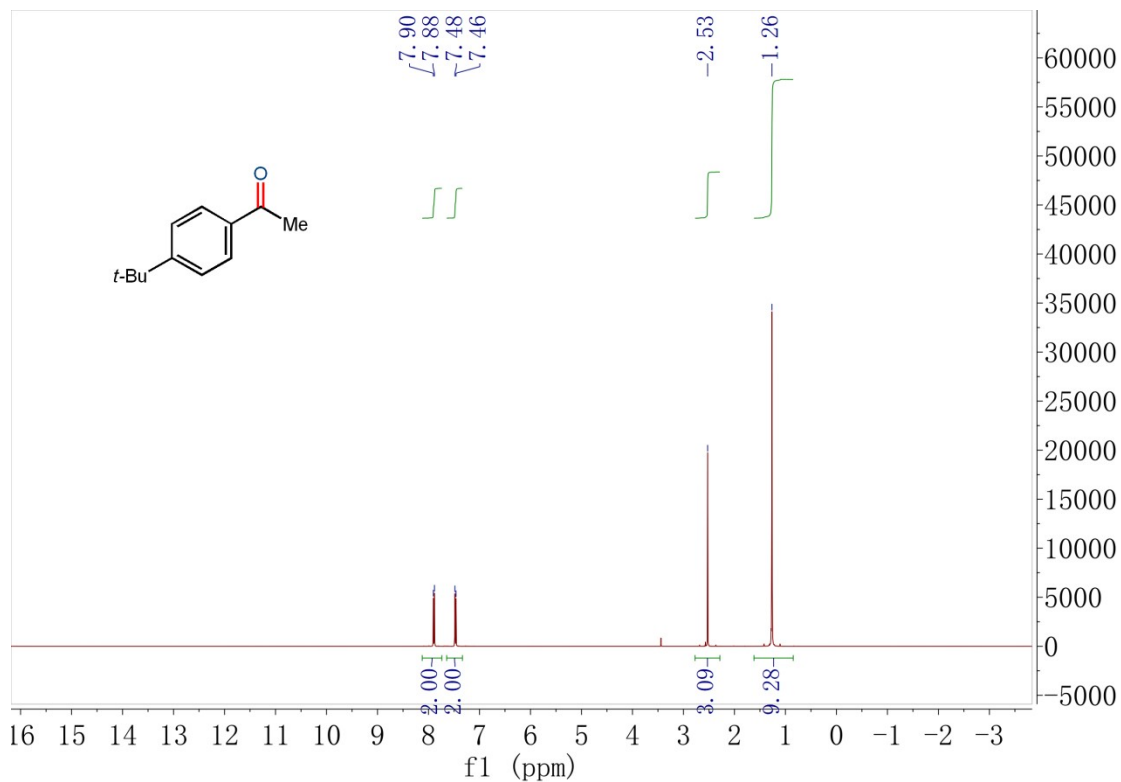


**1-(4-methoxyphenyl)ethan-1-one (5b)**



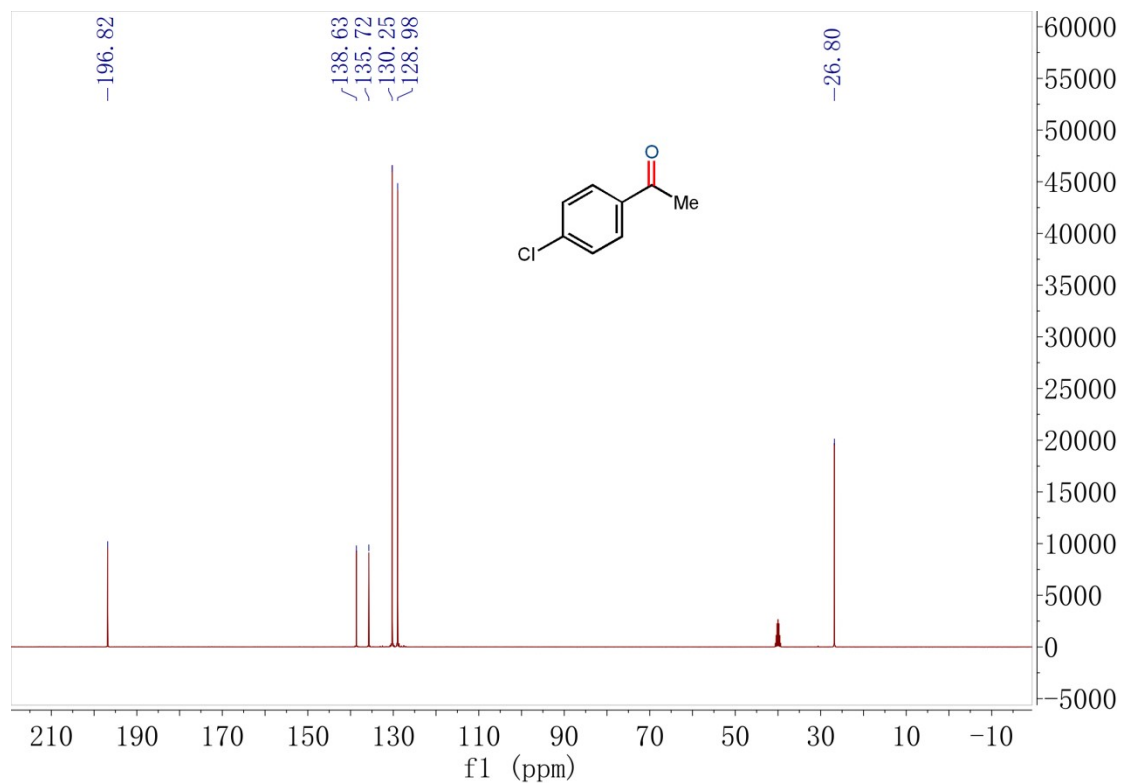
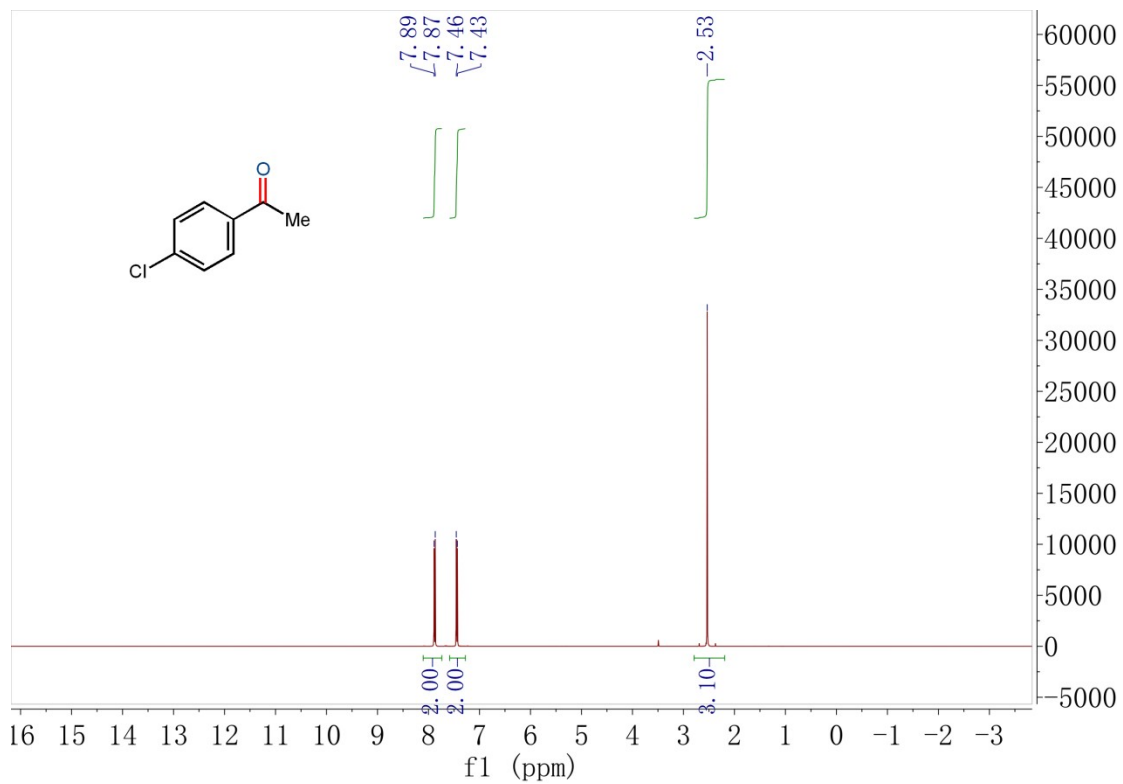
**Figure S32. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 5b in DMSO-*d*<sub>6</sub>**

**1-(4-tert-butylphenyl)ethan-1-one (5c)**



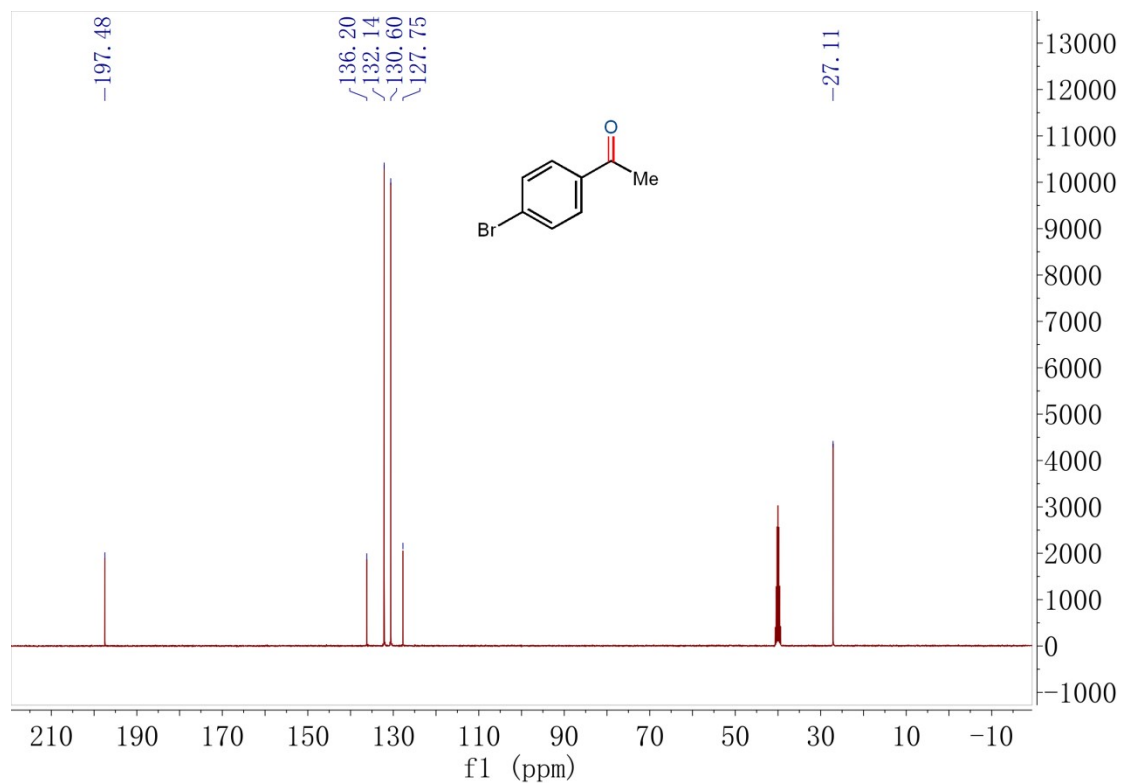
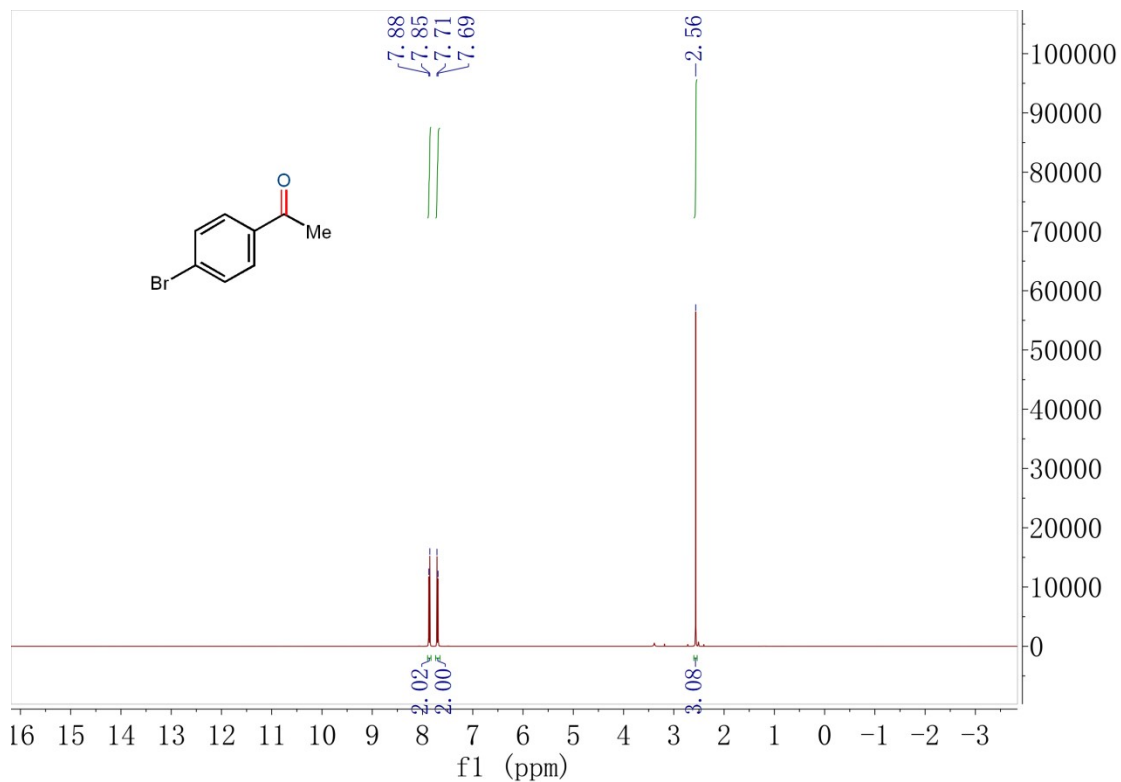
**Figure S33. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR Spectra of 5c in DMSO-*d*<sub>6</sub>**

**1-(4-Chlorophenyl)ethan-1-one (5d)**



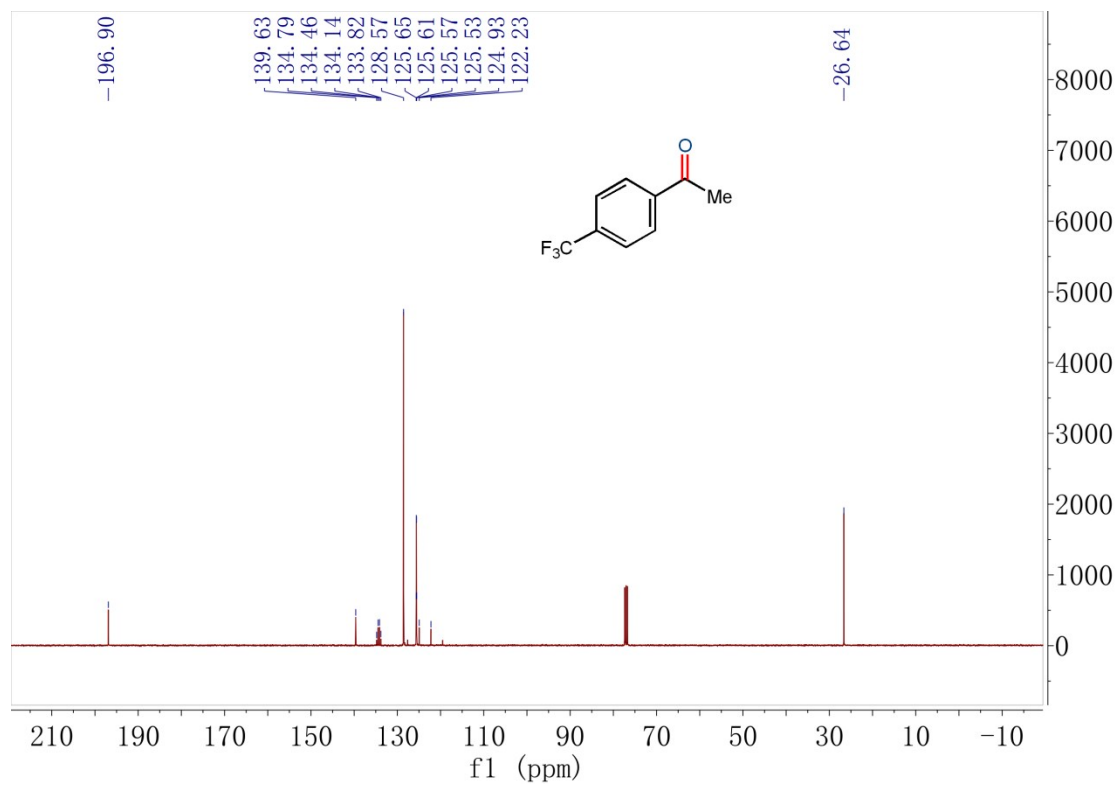
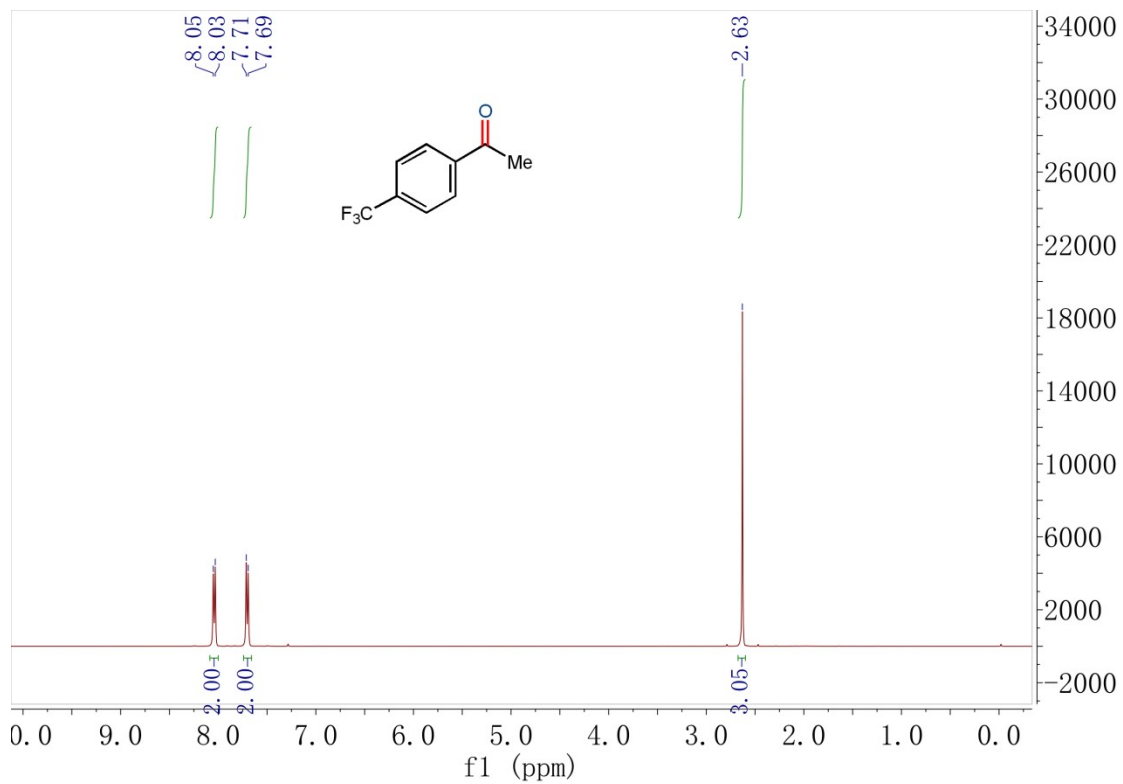
**Figure S34. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 5d in DMSO-*d*<sub>6</sub>**

**1-(4-Bromophenyl)ethan-1-one (5e)**



**Figure S35. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 5e in DMSO-*d*<sub>6</sub>**

**1-(4-Trifluoromethylphenyl)ethan-1-one (5f)**



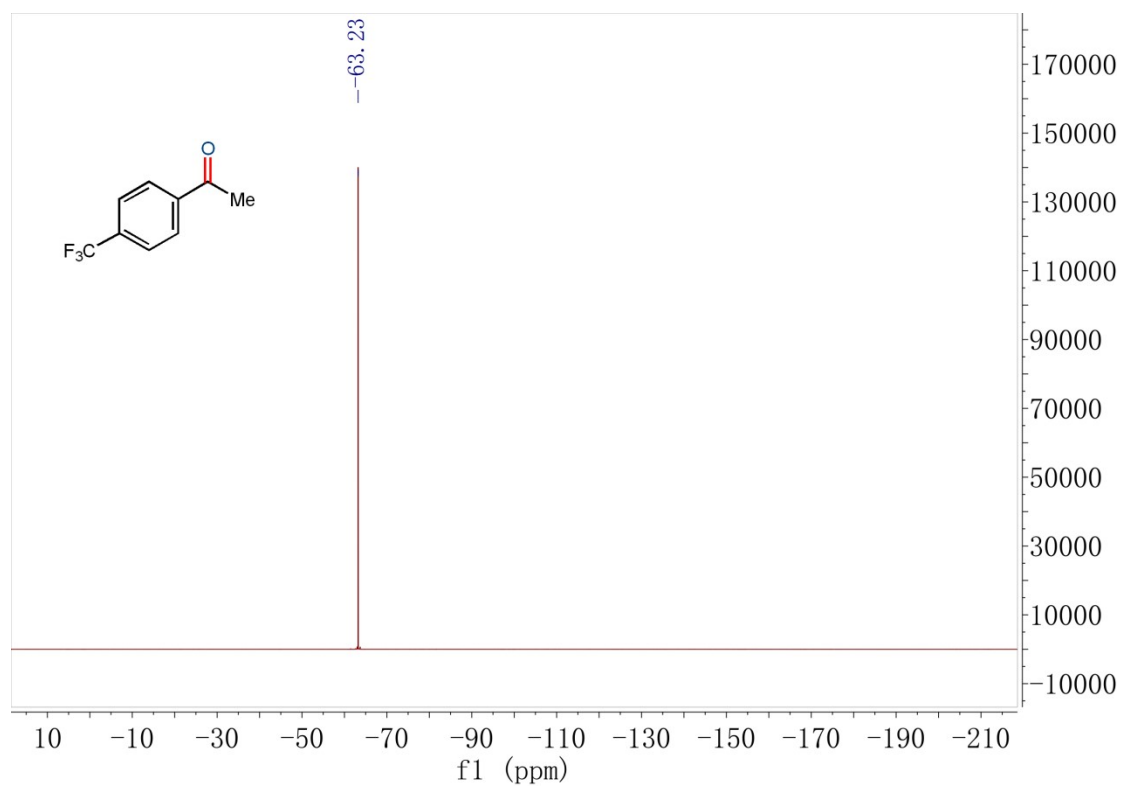
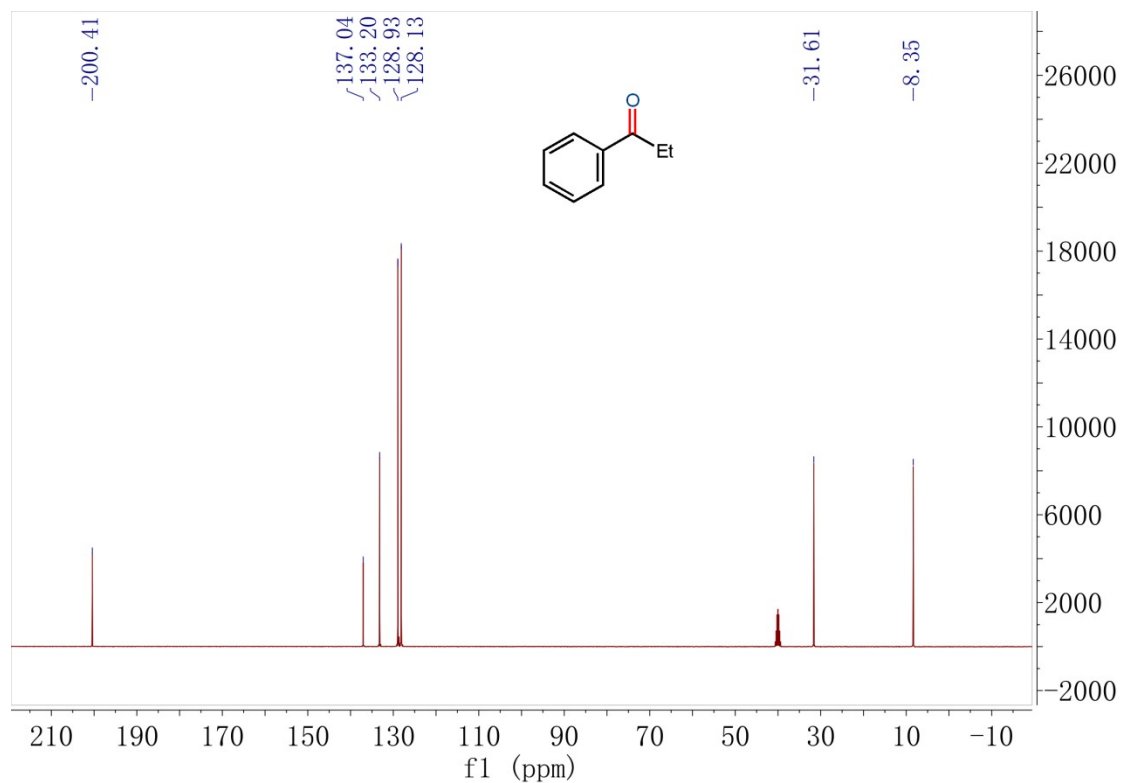
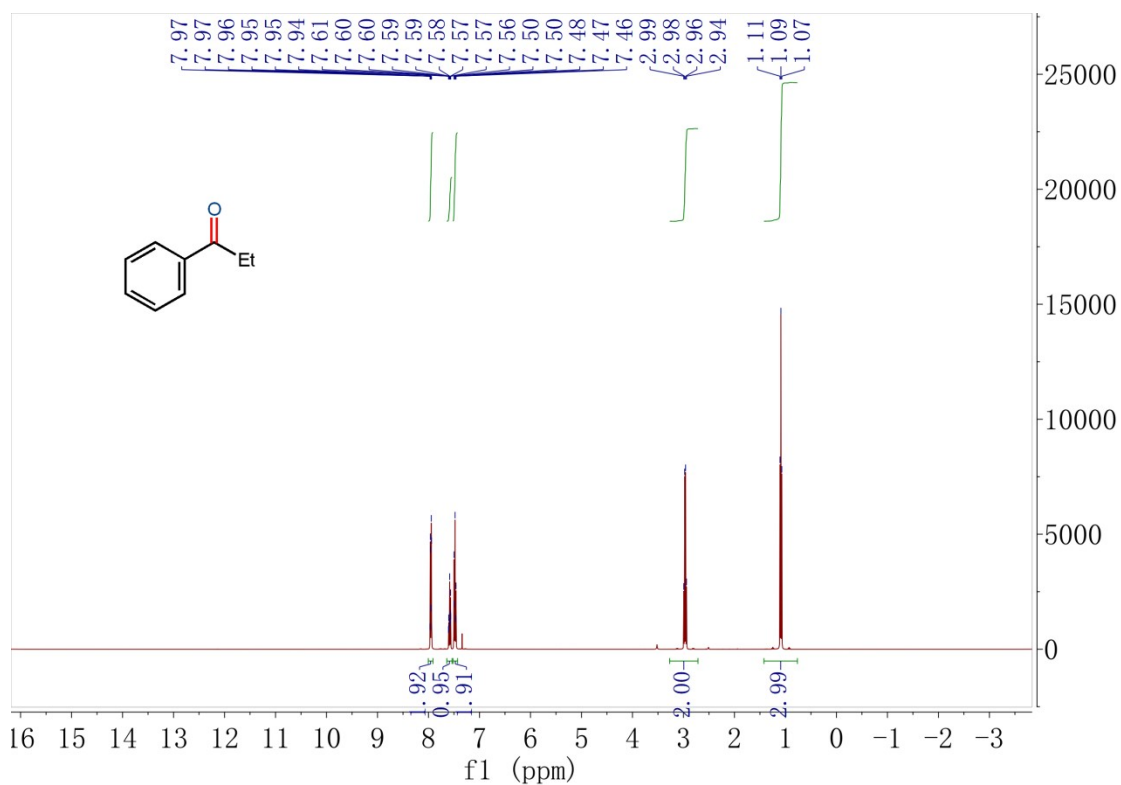


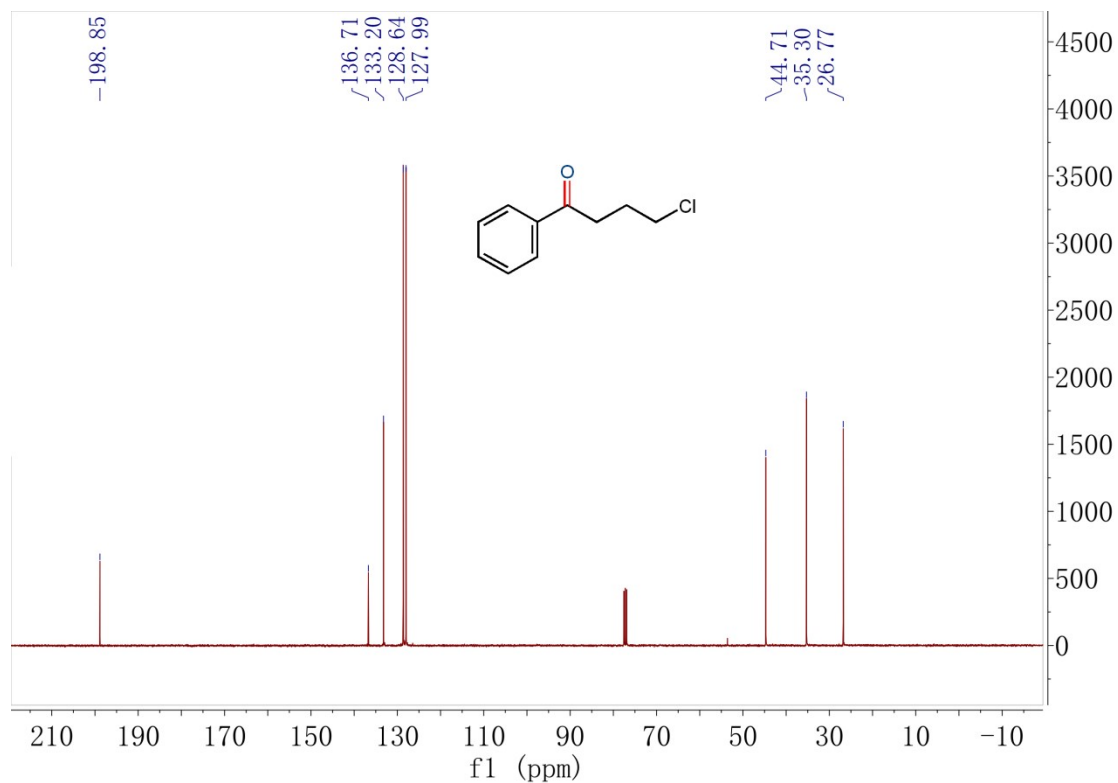
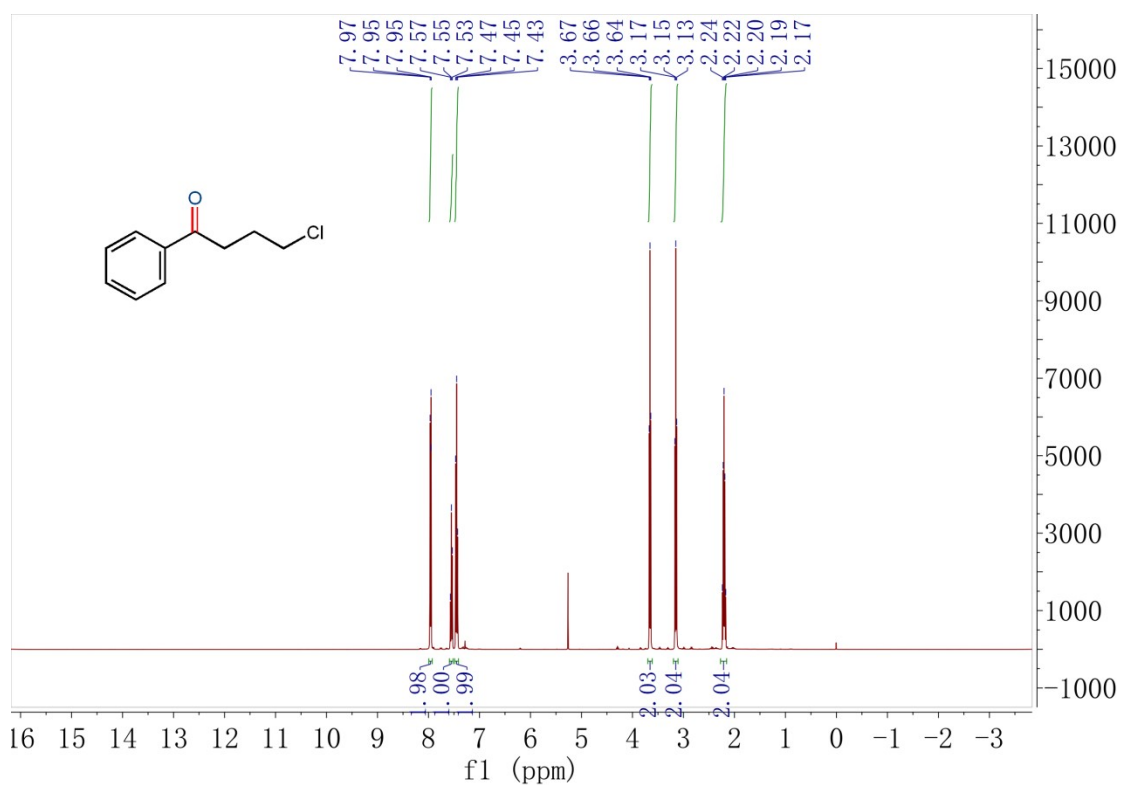
Figure S36.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  {1H} (101 MHz) and  $^{19}\text{F}$  {1H} (376 MHz) NMR spectra of 5f in  $\text{CDCl}_3$

**Propiophenone (5g)**



**Figure S37.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of 5g in  $\text{DMSO-}d_6$**

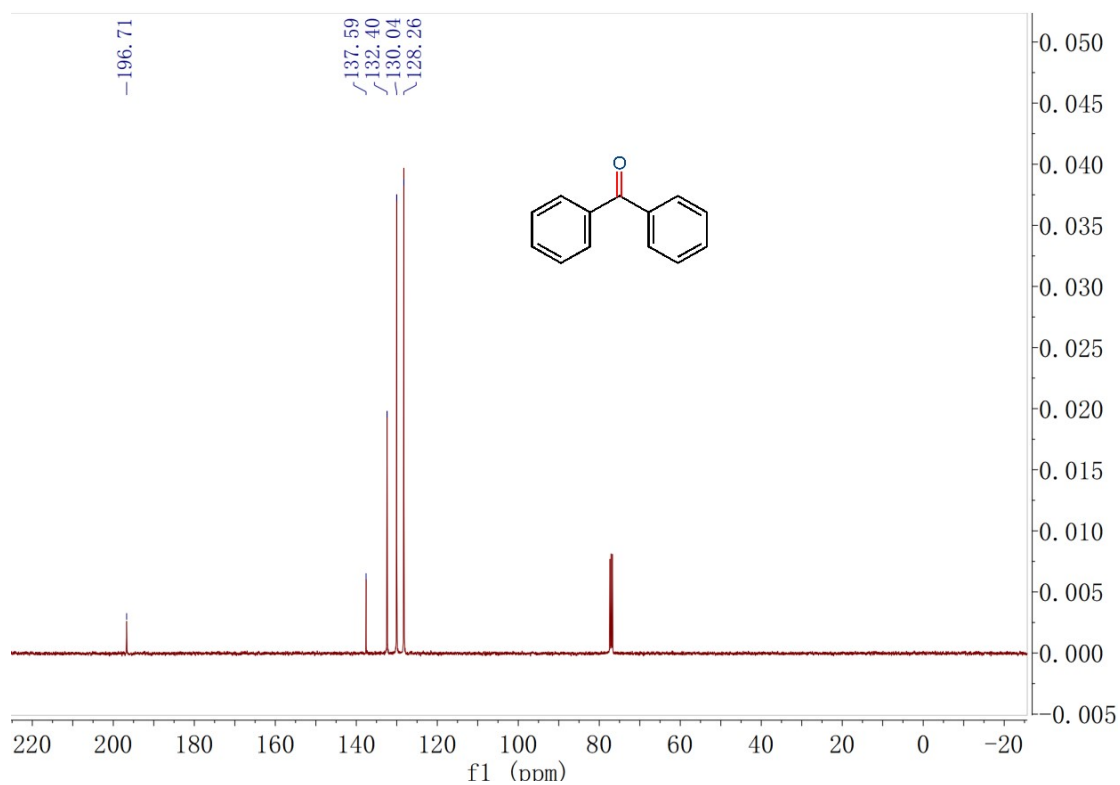
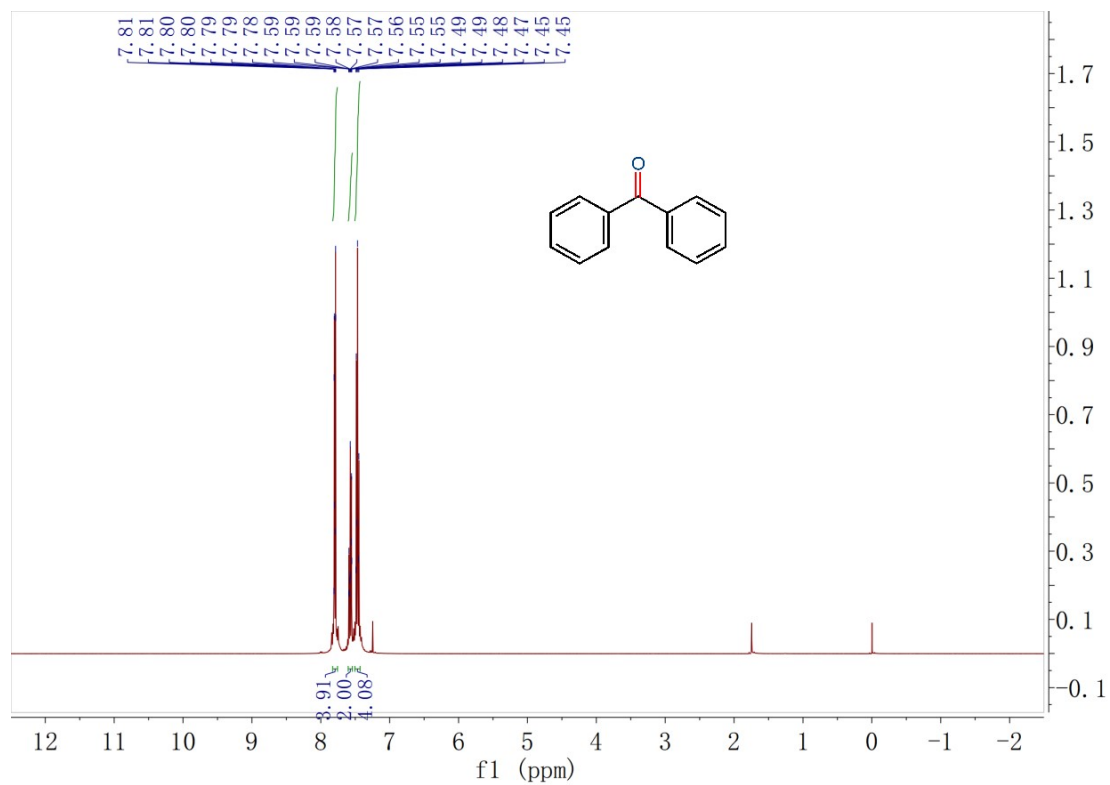
**4-Chloro-1-phenylbutan-1-one (5h)**



**Figure S38.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of 5h in  $\text{CDCl}_3$**

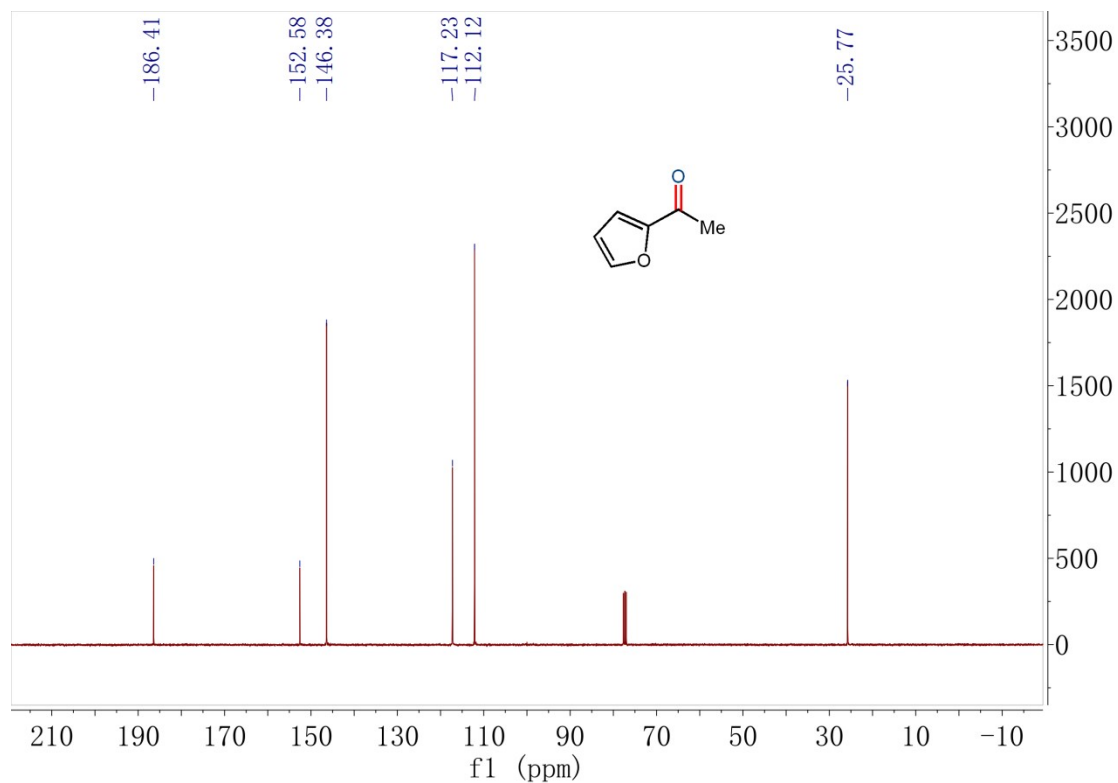
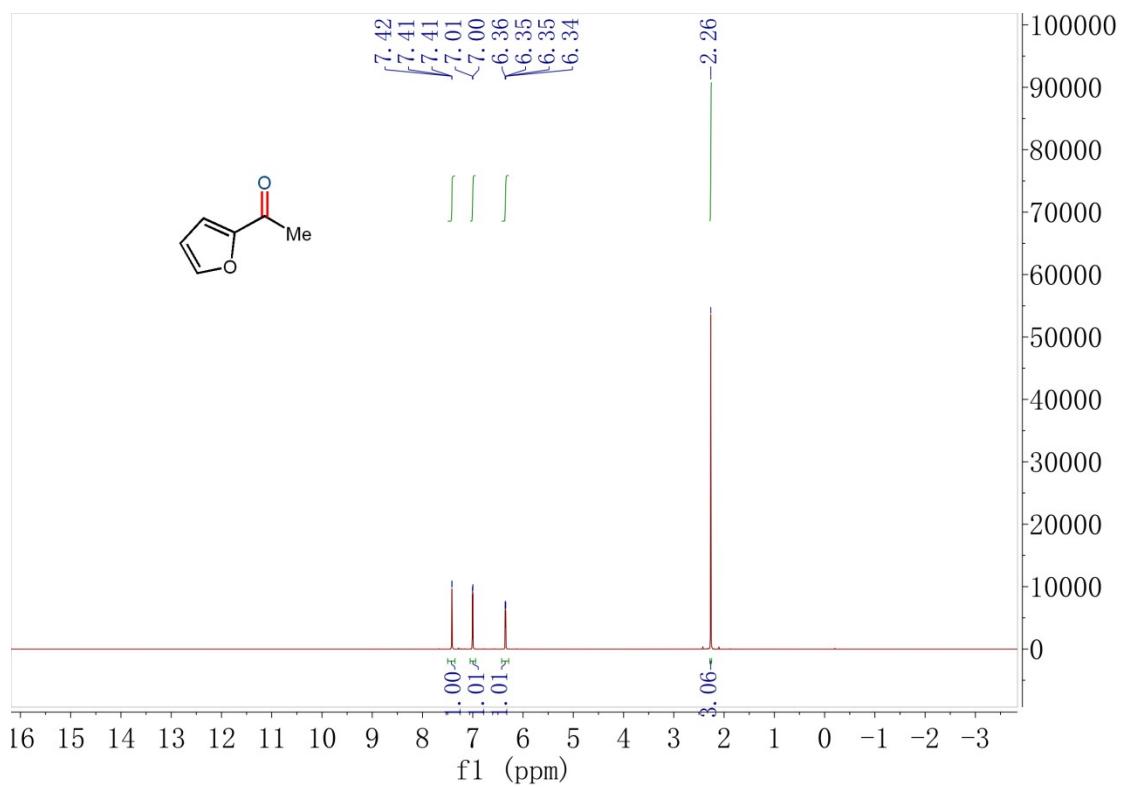


**Benzophenone (5i)**



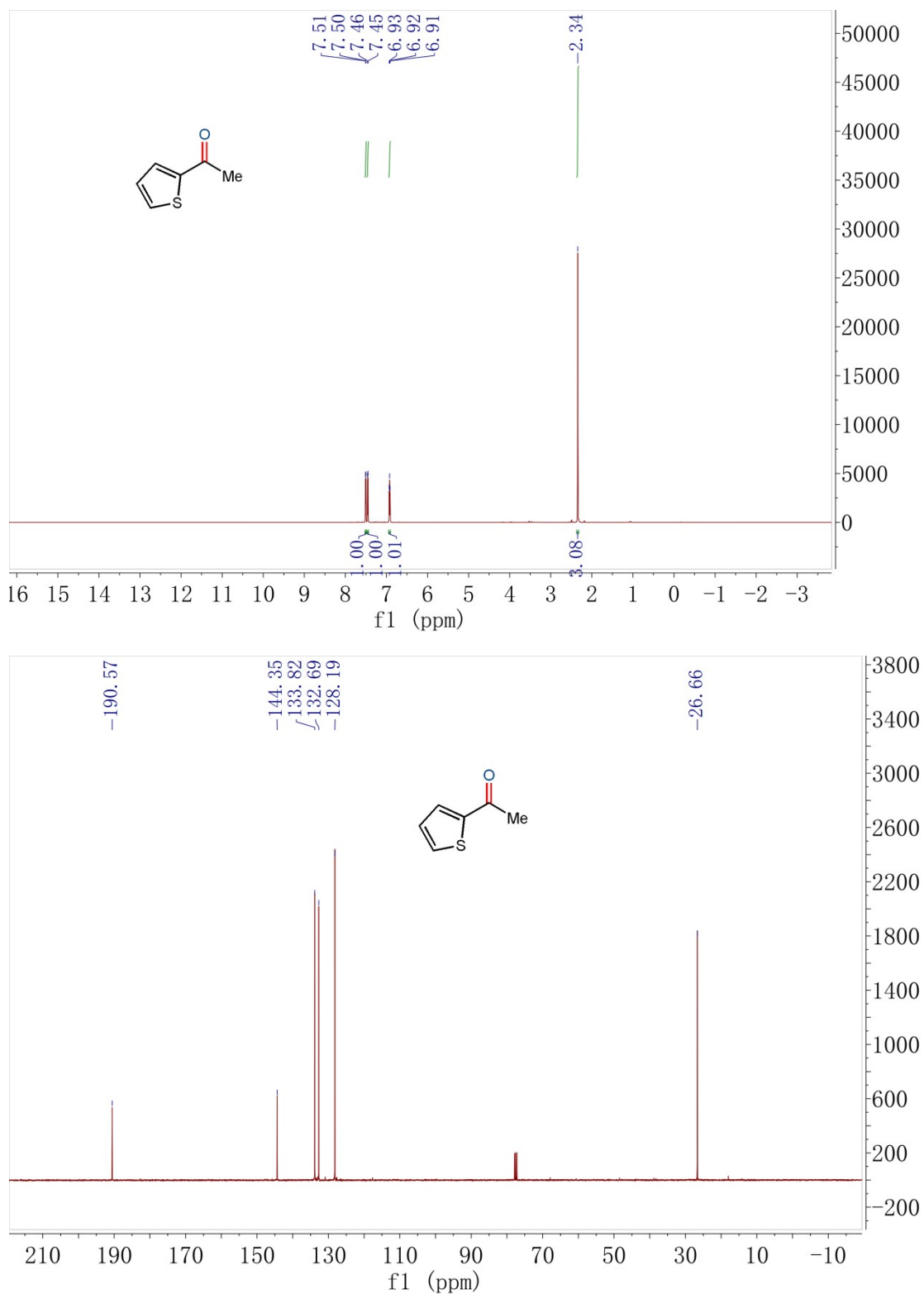
**Figure S39.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of 5i in  $\text{CDCl}_3$**

**2-Acetylfuran (5n)**



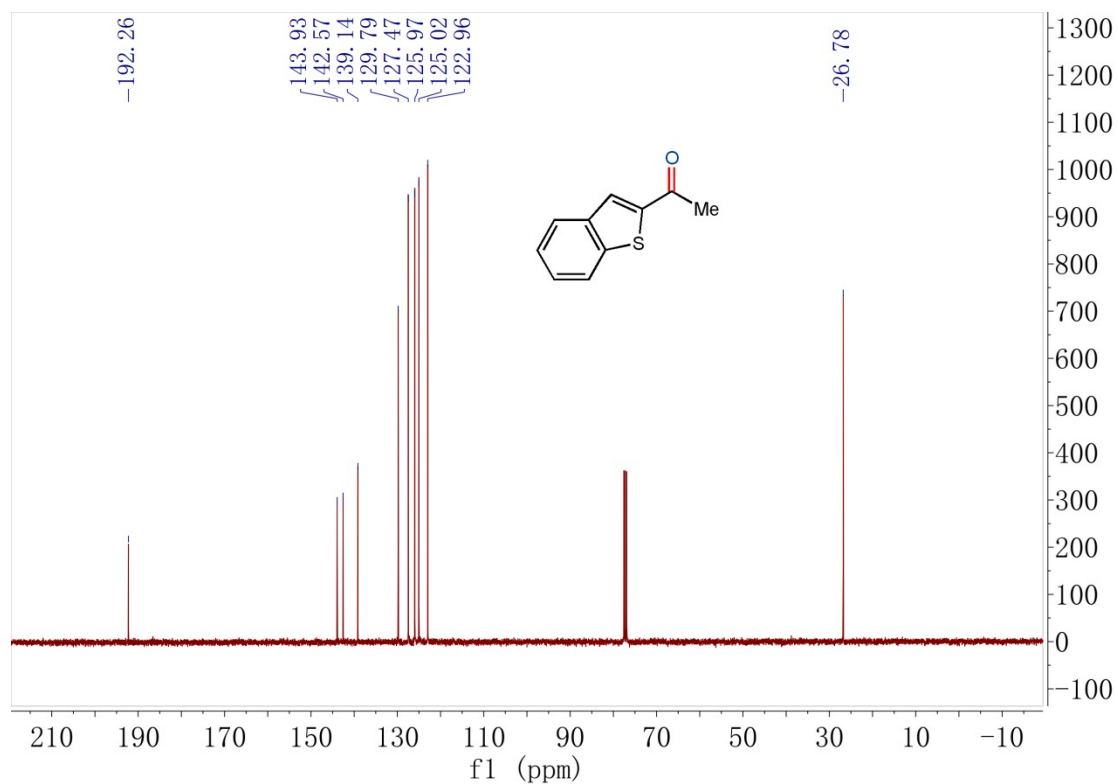
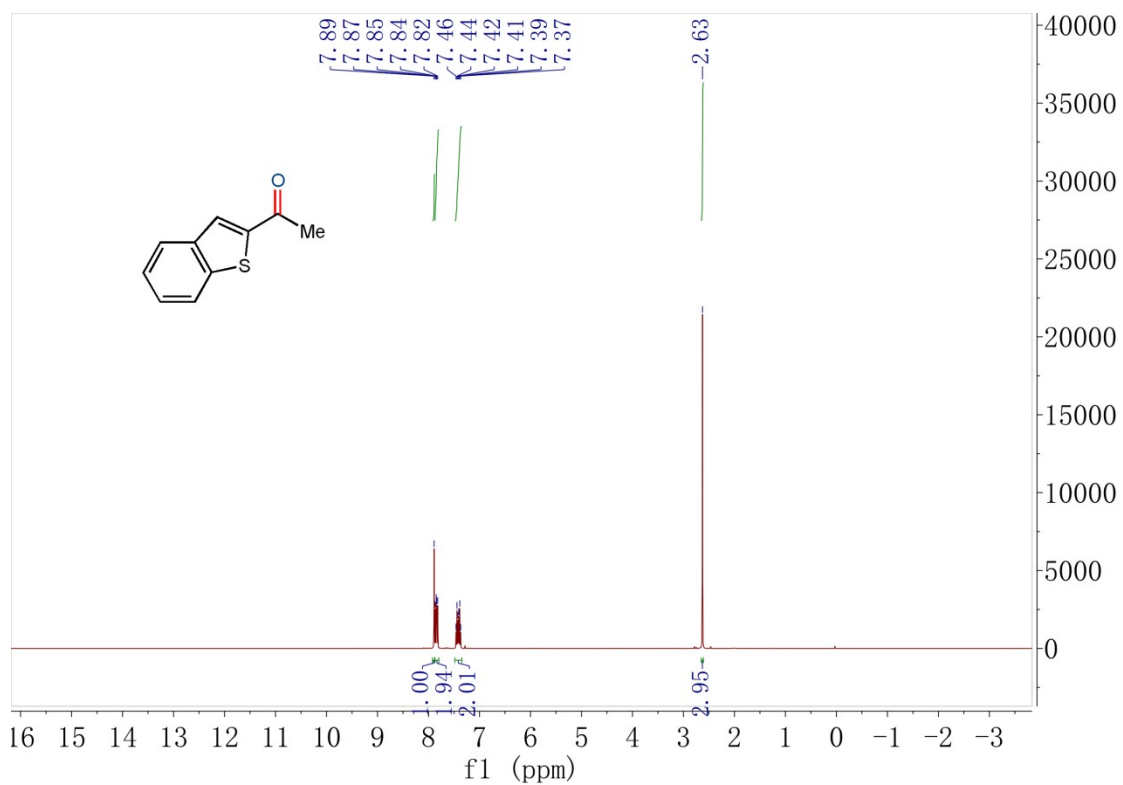
**Figure S40. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 5n in CDCl<sub>3</sub>**

**2-Acetylthiophene (5o)**



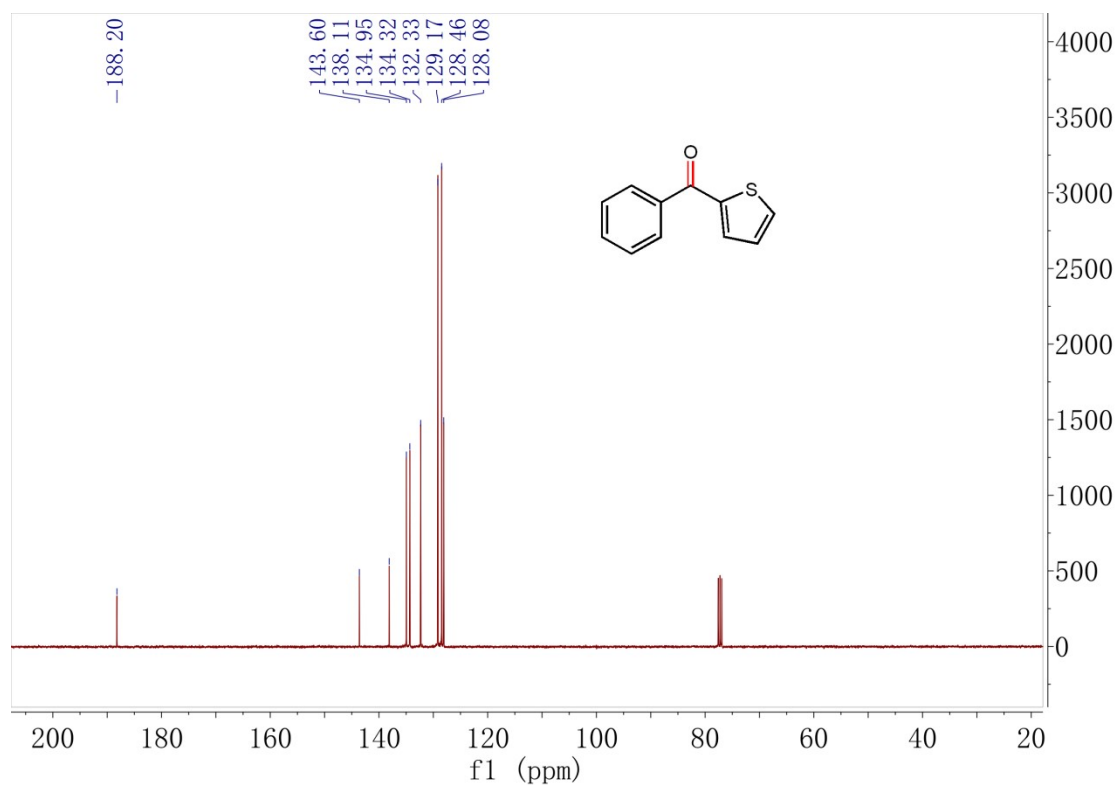
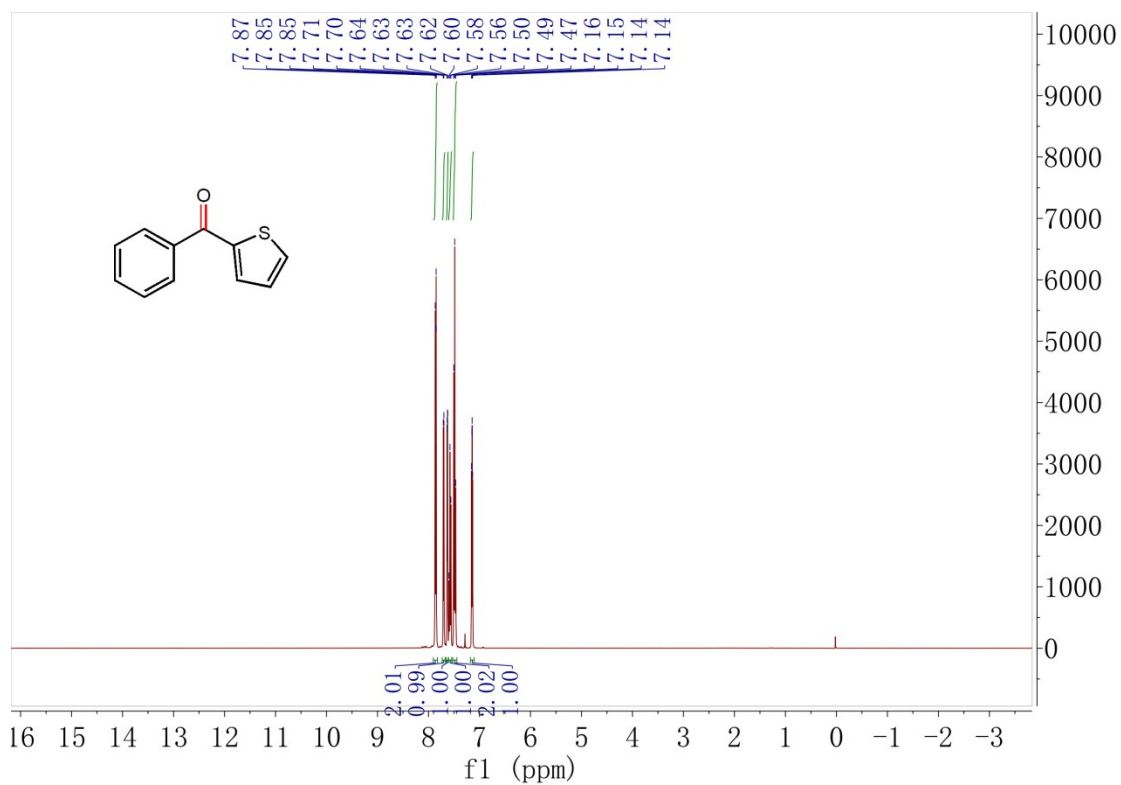
**Figure S41. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 5o in CDCl<sub>3</sub>**

**2-Acetylbenzothiophene (5p)**



**Figure S42.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  { $^1\text{H}$ } (101 MHz) NMR spectra of 5p in  $\text{CDCl}_3$**

**2-Benzoylthiophene (5q)**



**Figure S43. <sup>1</sup>H (400 MHz) and <sup>13</sup>C {<sup>1</sup>H} (101 MHz) NMR spectra of 5q in CDCl<sub>3</sub>**

## 12. References.

- [1] K. C. Hwang, A. Sagadevan, P. Kundu, *Green Chem.*, 2019, 21, 6082-6088.
- [2] W. Han, F. Jin, Q. Zhou, *Synthesis* 2015, 47, 1861–1868.
- [3] G. Oss, J. Ho, T. V. Nguyen, *Eur. J. Org. Chem.* 2018,29, 3974-3981.
- [4] X. Zhu, C. Liu, Y. Liu, H. Yang, H. Fu, *Chem. Commun.*, 2020, 56, 12443-12446.
- [5] J. Ou, H. Tan, S. He, W. Wang, B. Hu, G. Yu, K. Liu, *J. Org. Chem.* 2021, 86, 14974–14982.
- [6] De. Hu, X. Jiang, *Green Chem.*, 2022, 24, 124–129.
- [7] T. V. Q. Nguyen, W. Yoo, S. Kobayashi, *Asian J. Org. Chem.*, 2018, 7 ,116-118.
- [8] L. Cui, K. Liu, C. Zhang, *Org. Biomol. Chem.*, 2011, 9, 2258-2265.
- [9] M. Horvata, J. Iskra, *Green Chem.*, 2022, 24, 2073-2081.
- [10] S. Kumar, S. K. Dixit, S. K. Awasthi, *Tetrahedron Lett.* 2014, 55, 3802-3804.
- [11] C. J. Mallia, G. C. Walter, I. R. Baxendale, *Beilstein J. Org. Chem.* 2016, 12, 1503-1511.
- [12] H. Lu, Z. Geng, J. Li, D. Zou, Y. Wu, Y. Wu, *Org. Lett.*, 2016, 18, 2774-2776.
- [13] Y. Yamamoto, M. Ota, S. Kodama, K. Michimoto, A. Nomoto, A. Ogawa, M. Furuya, K. Kawakami, *ACS Omega.* 2021, 6, 2239–2247.
- [14] B. D. W. Allen, M. D. Hareram, A. C. Seastram, T. McBride, T. Wirth, D. L. Browne, L. C. Morrill, *Org. Lett.* 2019, 21, 9241-9246.
- [15] P. Thiruvengadam, D. K. Chand, *J. Org. Chem.* 2022, 87, 4061-4077.
- [16] B. Xiong, X. Zeng, S. Geng, S. Chen, Y. He, Z. Feng, *Green Chem.*, 2018, 20, 4521-4527.
- [17] R. M. Roberts, S. G. Brandenberger, *J. Am. Chem. Soc.* 1957, 79, 5484-5488.
- [18] B. Philippe, B. Alla, C. J. Claude, M. Sylviane, *Synthesis* 2006, 18, 3106-3110.
- [19] S. T. M. Ali, E. Lourdasamy, S. Arumugam, *J. Org. Chem.* 2006, 71, 5043-5046.
- [20] G. V. Baelen, B. U. W. Maes, *Tetrahedron.* 2008, 64, 5604-5619.
- [21] G. W. Ebert, W. L. Juda, R. H. Kosakowski, B. Ma, L. Dong, K. E. Cummings, M. V. B. Phelps, A. E. Mostafa, J. Luo, *J. Org. Chem.* 2005, 70, 4314-4317.
- [22] J. T. Minor, C. A. Vanderwerf, *J. Org. Chem.* 1952, 17, 1425-1430.
- [23] C. J. Mallia, G. C. Walter, I. R. Baxendale, *Beilstein J. Org. Chem.* 2016, 12, 1503-1511.
- [24] X. Zhu, Y. Liu, C. Liu, H. Yang, H. Fu, *Green Chem.*, 2020, 22, 4357-4363.
- [25] D. L. Ladd, P. B. Harrsch, L. I. Krusef, *J. Org. Chem.* 1988, 53, 417-420.

- [26] D. Yang, H. Yang, H. Fu, *Chem. Commun.*, 2011, 47, 2348-2350.
- [27] M. Jakubczyk, S. Mkrtchyan, M. Shkooor, S. Lanka, Š. Budzák, M. Iliáš, M. Skoršepa, V. O. Iaroshenko, *J. Am. Chem. Soc.* 2022, 144, 10438–10445.
- [28] C. K. Lee, Y. M. Ahn, *J. Org. Chem.* 1989, 54, 3744-3747.
- [29] M. T. Nunez, V. S. Martin, *J. Org. Chem.* 1990, 55, 1928-1932.
- [30] Y. Yokoyama, T. Shiozawa, Y. Tani, T. Ubukata, *Angew. Chem. Int. Ed.*, 2009, 48, 4521-4523.
- [31] M. Cai, G. Zheng, L. Zha, J. Peng, *Eur. J. Org. Chem.* 2009, 10, 1585-1591.
- [32] K. Wei, K. Luo, F. Liu, L. Wu, L. Wu, *Org. Lett.* 2019, 21, 1994-1998.
- [33] V. Nair, V. Varghese, R. R. Paul, A. Jose, C. R. Sinu, R. S. Menon, *Org. Lett.* 2010, 12, 2653-2655.
- [34] Q. Mo, N. Sun, L. Jin, B. Hu, Z. Shen, X. Hu, *J. Org. Chem.*, 2020, 85, 11490-11500.