

## Supporting Information

### **Aerobic conversion of benzylic $sp^3$ C–H in diphenylmethanes and benzyl ethers to C=O bonds under catalyst-, additive- and light-free condition**

Xinzhe Tian,<sup>a,c</sup> Xinqiang Cheng,<sup>c</sup> Xinzheng Yang,<sup>d</sup> Yun-Lai Ren,<sup>c,\*</sup> Kaisheng Yao,<sup>c</sup>  
Huiyong Wang,<sup>b</sup> and Jianji Wang<sup>b,\*</sup>

<sup>[a]</sup> College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, Gansu,  
P. R. China.

<sup>[b]</sup> School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan  
453007, P. R. China. E-mail address: jwang@htu.cn

<sup>[c]</sup> School of Chemical Engineering & Pharmaceutics, Henan University of Science and  
Technology, Luoyang, Henan 471003, P. R. China. E-mail address: renyunlai@126.com

<sup>[d]</sup> Beijing National Laboratory for Molecular Sciences, Chinese Academy of Sciences, Beijing  
100190, P. R. China. E-mail address: xyang@iccas.ac.cn

## Table of Contents

1. General.....	S1
1.1 Chemicals.....	S1
1.2 Instruments.....	S2
2. Experimental details.....	S2
2.1 Typical procedure for the aerobic oxidation of benzylic C–H bonds.....	S2
2.2 Experimental procedure for H <sub>2</sub> <sup>18</sup> O-labelling.....	S2
2.3 Experimental procedure for the effect of radical traps on the reaction.....	S3
2.4 Experimental procedure for the effect of metal ions on the reaction.....	S4
3. Computational details.....	S4
4. The spectroscopic data of the isolated products.....	S5
5. Reference.....	S12
6. <sup>1</sup> H NMR and <sup>13</sup> C NMR for the isolated products.....	S14

## 1. General

### 1.1 Chemicals

For the quality and suppliers of the chemicals, see Table S1 in the supporting information. Diphenylmethane derivatives were synthesized by a method described in the literatures.<sup>[1]</sup> Isochroman and xanthene derivatives were synthesized by a method described in the literatures.<sup>[2]</sup> Cyclohexane and other solvents were distilled under reduced pressure before use. All the other chemicals were obtained from commercial vendors and used without further purification.

**Table S1.** Quality and suppliers of chemicals used in this work

Entry	Compound	Purity	Supplier
1	cyclohexane	AR	Tianjin Fuyu Fine chemical Co., Ltd
2	cyclohexane (ACS/HPLC Certified)	99.7	J&K Scientific Ltd.
3	isochroman	98%	J&K Scientific Ltd.
4	xanthene	98%	J&K Scientific Ltd.
5	thioxanthene	98%	J&K Scientific Ltd.
6	fluorene	98%	J&K Scientific Ltd.
7	2-bromofluorene	95%	J&K Scientific Ltd.
8	2-acetylfluorene	98%	J&K Scientific Ltd.
9	<i>n</i> -hexane	99.5	Aladdin Chemistry Co., Ltd.
10	CCl <sub>4</sub>	99.5%	Aladdin Chemistry Co., Ltd.
11	toluene	AR	Tianjin Kermel Chemical Reagent Co., Ltd
12	tetrahydrofuran	99.5+%	Tianjin No.3 Chemical Reagent Co., Ltd
13	DMSO	AR	Aladdin Chemistry Co., Ltd.
14	methanol	AR	Tianjin Fuyu Fine chemical Co., Ltd
15	ethanol	AR	Shanxi Tongjie Chemical Reagent Co., Ltd
16	acetonitrile	≥99.8%	Aladdin Chemistry Co., Ltd.
17	<i>N,N</i> -dimethylformamide	>99.8%	Aladdin Chemistry Co., Ltd.

## 1.2 Instruments

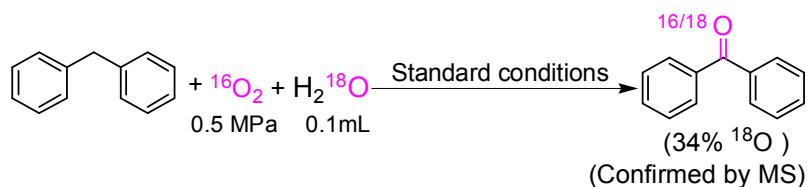
$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker 400 or 500 MHz instrument with chemical shifts reported in ppm relative to the internal standard tetramethylsilane. Gas chromatography analyses were performed on a Varian CP-3800 instrument with a FID detector and a CP-WAX 57CB FS capillary chromatographic column (25 m  $\times$  0.32 mm). GC-MS spectra were recorded on an Agilent 7890/5973N gas chromatography-mass spectrometry instrument. Data are reported as follows:  $m/z$ , % relative intensity, and possible fragment.

## 2. Experimental details

### 2.1 Typical procedure for the aerobic oxidation of benzylic C–H bonds

The selective oxidation of hydrocarbons was carried out in a 40 mL stainless steel autoclave lined with Teflon. Typically, 0.5 mmol substrate and 2 mL cyclohexane were added into the reactor and 0.5 MPa of oxygen was filled. Then, the reaction system was heated under magnetic stirring at 140°C for 20 h. Once the reaction time was reached, the mixture was cooled to room temperature. After that, 1 mL solution of diphenyl in cyclohexane (0.5 mmol/mL) was added as an internal standard into the reaction tube. GC analysis of the reaction mixture provided the GC yields of the products. In addition, the crude product from another parallel experiment was purified by column chromatography, and identified by  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR.

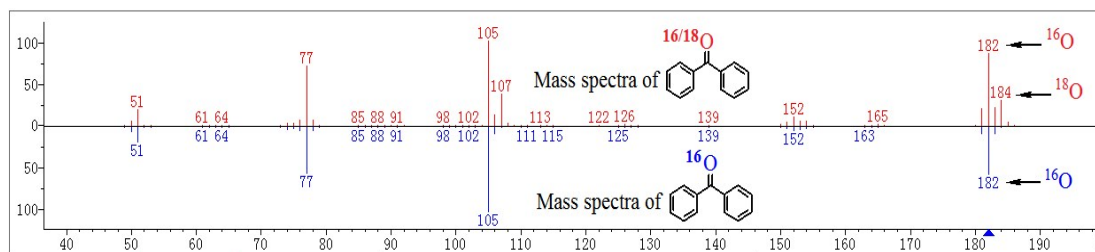
### 2.2 Experimental procedure for $\text{H}_2^{18}\text{O}$ -labelling



**Scheme S1.**  $\text{H}_2^{18}\text{O}$ -labelling experiment.

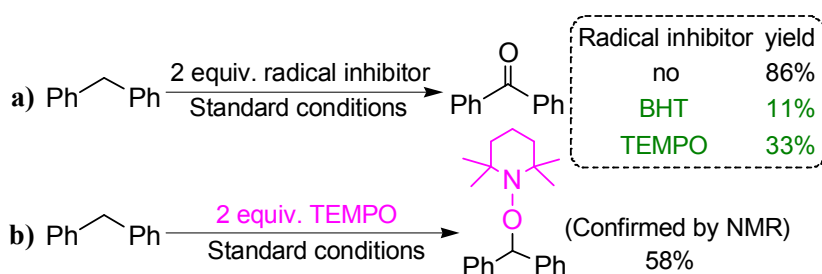
After 0.5 mmol diphenylmethane, 2 mL cyclohexane and 0.1 mL  $\text{H}_2^{18}\text{O}$  were added into the stainless steel autoclave, the reactor was filled with 0.5 MPa of oxygen. Then, the reaction system was heated under magnetic stirring at 140°C for 20 h. When the reaction time was reached, the reaction mixture was cooled to room temperature. The

products was elucidated via GC-MS.



**Figure S1.** Mass spectra from the  $\text{H}_2^{18}\text{O}$ -labelling experiment.

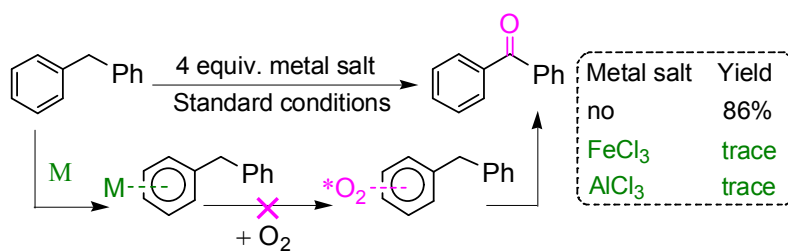
### 2.3 Experimental procedure for the effect of radical traps on the reaction



**Scheme S2.** Effect of a radical trap on the reaction.

After 0.5 mmol diphenylmethane, 2 mL cyclohexane and 1 mmol TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or BHT (2,6-di $t$ -butyl-4-methylphenol) were added into the stainless steel autoclave, the reactor was filled with 0.5 MPa of oxygen. Subsequently, the reaction system was heated under magnetic stirring at 140°C for 20 h. When the reaction time was reached, the reaction mixture was cooled to room temperature, then GC analysis of the mixture provided the GC yield of the product with diphenyl as the internal standard. The radical adduct was purified by silica gel column chromatography, and identified by  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ . The radical adduct<sup>[3]</sup>: white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.43 (d,  $J = 7.0$ , 4H), 7.32 (t,  $J = 7.0$  Hz, 4H), 7.21 (t,  $J = 7.5$  Hz, 2H), 5.70 (s, 1H), 1.48-1.49 (m, 4H), 1.32-1.35 (m, 2H), 1.22 (s, 6H), 0.80 (s, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 144.9, 128.2, 126.7, 126.6, 90.8, 59.9, 40.4, 34.0, 20.5, 17.2.

## 2.4 Experimental procedure for the effect of metal ions on the reaction



Scheme S3. Effect of metal ions on the reaction.

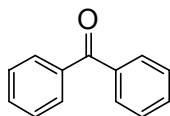
0.5 mmol diphenylmethane, 2 mmol metal salt and 2 mL cyclohexane were added into the reactor and 0.5 MPa of oxygen was filled. Then, the reaction system was heated under magnetic stirring at 140°C for 20 h. When the reaction time was reached, the reaction mixture was cooled to room temperature. GC analysis provided the GC yield of the product with diphenyl as the internal standard.

## 3. Computational details

All DFT calculations were performed using the Gaussian 09 suite of programs<sup>[4]</sup> for a hybrid meta-GGA level density functional M06<sup>[5]</sup> in conjugation with all-electron 6-31++G(d,p) basis set<sup>[6]</sup> for all atoms. An ultrafine grid (99,590) was used for numerical integrations. All structures were fully optimized in cyclohexane ( $\epsilon = 2.0165$ ) using the integral equation formalism polarizable continuum model (IEFPCM)<sup>[7]</sup> with the SMD radii<sup>[8]</sup> for solvent effect corrections. Thermal corrections were calculated within the harmonic potential approximation on optimized structures under  $T = 298.15$  K and 1 atm pressure. To be consistent with the experimental condition, a 10.0 atm pressure was used in the calculations of O<sub>2</sub>. Unless otherwise noted, the relative energies reported in the text are Gibbs free energies with the solvent effect corrections. The calculated structures were confirmed to have no imaginary vibrational mode for all equilibrium structures and only one imaginary vibrational mode for each transition state. Transition states were further characterized by intrinsic reaction coordinate (IRC) calculations to affirm that the stationary points were correctly connected.

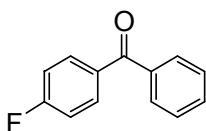
#### 4. The spectroscopic data of the isolated products

**Benzophenone** (Product from entry 1 in Table 2):



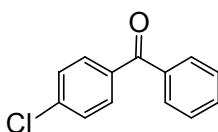
Known compound,<sup>[9]</sup> white solid, m.p. 46–48 °C (lit.<sup>[9]</sup> 47–48 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.84 (d, *J* = 7.0 Hz, 4H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 196.7, 137.6, 132.4, 130.1, 128.3.

**4-Fluorobenzophenone** (Product from entry 2 in Table 2):



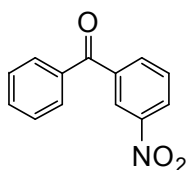
Known compound,<sup>[9]</sup> white solid, m.p. 47–48 °C (lit.<sup>[9]</sup> 48–49 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.83–7.86 (m, 2H), 7.76–7.78 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.14–7.18 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 195.3, 166.4, 164.4, 137.5, 133.8, 132.7, 132.65, 132.5, 129.9, 128.4, 115.6, 115.4.

**4-Chlorobenzophenone** (Product from entry 3 in Table 2):



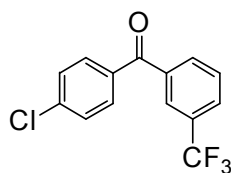
Known compound,<sup>[9]</sup> white solid, m.p. 74–75 °C (lit.<sup>[9]</sup> 73–74 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.74–7.78 (m, 4H), 7.59–7.62 (m, 1H), 7.45–7.51 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 195.5, 138.9, 137.3, 135.9, 132.7, 131.5, 129.9, 128.7, 128.4.

**3-Nitrobenzophenone** (Product from entry 4 in Table 2):



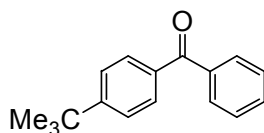
Known compound,<sup>[10]</sup> pale yellow solid, m.p. 92–93 °C (lit.<sup>[10]</sup> 92 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.65 (t, *J* = 1.8 Hz, 1H), 8.47 (td, *J*<sub>1</sub> = 8.2 Hz, *J*<sub>2</sub> = 1.3 Hz, 1H), 8.17 (d, *J* = 7.7 Hz, 1H), 7.82–7.84 (m, 2H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 194.2, 148.1, 139.1, 136.3, 135.5, 133.4, 130.0, 129.7, 128.8, 126.7, 124.7.

**(4-Chlorophenyl)(3-trifluoromethylphenyl)methanone** (Product from entry 5 in Table 2):



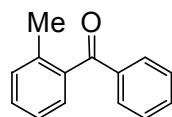
Known compound,<sup>[11]</sup> yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.06 (s, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 193.9, 139.6, 138.0, 135.1, 132.9, 131.4, 129.1, 129.0, 128.95, 126.6, 126.55.

**4-*t*-Butylbenzophenone** (Product from entry 6 in Table 2):



Known compound,<sup>[9]</sup> white solid, m.p. 37–39 °C (lit.<sup>[9]</sup> 38–40 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.78–7.84 (m, 4H), 7.60 (tt, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 7.49–7.54 (m, 4H), 1.39 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 196.5, 156.2, 137.9, 134.8, 132.2, 130.2, 130.1, 128.2, 125.3, 35.1, 31.2.

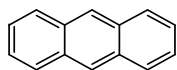
**2-Methylbenzophenone** (Product from entry 9 in Table 2):



Known compound,<sup>[9]</sup> yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.80 (d, *J* = 7.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.39 (dt, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 1.0 Hz, 1H), 7.23–7.32 (m, 3H), 2.33 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 198.7, 138.6, 137.8, 136.8, 133.2, 131.0, 130.3, 130.2, 128.5, 128.48, 125.2, 20.0.

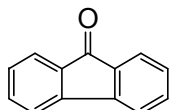


**Anthracene** (Product from entry 10 in Table 2):



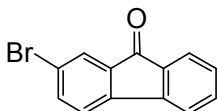
Known compound,<sup>[12]</sup> white solid, m.p. 153–154 °C (lit.<sup>[12]</sup> 150–152 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.47 (s, 2H), 8.04–8.06 (m, 4H), 7.50–7.52 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 131.7, 128.2, 126.2, 125.4.

**9H-flouren-9-one** (Product from entry 14 in Table 2):



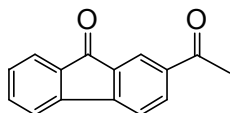
Known compound,<sup>[13]</sup> white solid, m.p. 82–83 °C (lit.<sup>[13]</sup> 82–84 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.66 (d, *J* = 7.5 Hz, 2H), 7.47–7.52 (m, 4H), 7.30 (t, *J* = 7.0 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 193.8, 144.8, 134.7, 134.2, 129.1, 124.3, 120.3.

**2-Bromo-9H-flouren-9-one** (Product from entry 15 in Table 2):



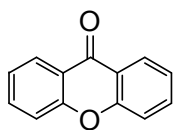
Known compound,<sup>[14]</sup> pale yellow solid, m.p. 137–138 °C (lit.<sup>[14]</sup> 139–141 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.78 (d, *J* = 1.5 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.62 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H), 7.52 (d, *J* = 4.5 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.33–7.36 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 192.3, 143.7, 143.0, 137.1, 135.8, 135.0, 133.8, 129.4, 127.6, 124.6, 122.9, 121.7, 120.4.

**2-Acetyl-9H-flouren-9-one** (Product from entry 16 in Table 2):



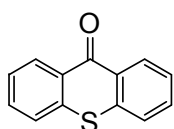
Known compound,<sup>[14]</sup> pale yellow solid, m.p. 158–160 °C (lit.<sup>[14]</sup> 159–160 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.22 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.57 (t, *J*<sub>1</sub> = 7.5 Hz 1H), 7.41 (t, *J* = 7.0 Hz, 1H), 2.66 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 196.5, 192.7, 148.5, 143.3, 137.9, 135.0, 134.9, 134.88, 134.4, 130.2, 124.7, 124.1, 121.3, 120.4, 26.7.

**9H-xanthen-9-one** (Product from entry 17 in Table 2):



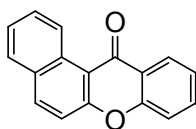
Known compound,<sup>[13]</sup> white solid, m.p. 172–173 °C (lit.<sup>[13]</sup> 174–176 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.35 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.5$  Hz, 2H), 7.70-7.74 (m, 2H), 7.48 (d,  $J = 8.0$  Hz, 2H), 7.36-7.40 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 177.1, 156.2, 134.8, 126.7, 123.9, 121.9, 118.0.

**9H-thioxanthen-9-one** (Product from entry 18 in Table 2):



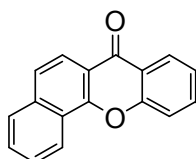
Known compound,<sup>[13]</sup> yellow solid, m.p. 209–210 °C (lit.<sup>[13]</sup> 209–212°C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.64 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.0$  Hz, 2H), 7.62-7.66 (m, 2H), 7.59-7.60 (m, 2H), 7.49-7.52 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 180.0, 137.3, 132.3, 129.9, 129.3, 126.3, 126.0.

**12H-benzo[a]xanthen-12-one** (Product from entry 19 in Table 2):



Known compound,<sup>[14]</sup> white solid, m.p. 140–141 °C (lit.<sup>[14]</sup> 143 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 10.10 (d,  $J = 9.0$  Hz, 1H), 8.43 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.5$  Hz, 1H), 8.07 (d,  $J = 9.0$  Hz, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.76-7.80 (m, 1H), 7.69-7.72 (m, 1H), 7.57-7.60 (m, 1H), 7.49-7.52 (m, 2H), 7.41-7.44 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 178.4, 157.6, 154.6, 136.6, 133.8, 131.1, 130.1, 129.5, 128.3, 127.0, 126.6, 126.1, 124.3, 123.6, 118.0, 117.5, 114.5.

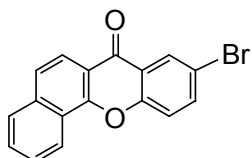
**7H-benzo[c]xanthen-7-one** (Product from entry 20 in Table 2):



Known compound,<sup>[15]</sup> white solid, m.p. 160 °C (lit.<sup>[15]</sup> 159–160 °C); <sup>1</sup>H NMR (500

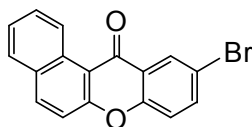
MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.67 (dd,  $J_1 = 7.5$  Hz,  $J_2 = 0.5$  Hz, 1H), 8.43 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.5$  Hz, 1H), 8.29 (d,  $J = 9.0$  Hz, 1H), 7.94 (d,  $J = 7.5$  Hz, 1H), 7.59-7.79 (m, 5H), 7.47 (dt,  $J_1 = 7.0$  Hz,  $J_2 = 1.0$  Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 176.9, 155.8, 153.7, 136.6, 134.3, 129.5, 128.1, 126.9, 126.6, 124.4, 124.1, 124.0, 122.9, 122.5, 121.5, 118.1, 117.6.

**9-Bromo-7H-benzo[c]xanthen-7-one** (Product from entry 21 in Table 2):



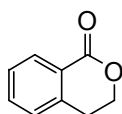
Known compound,<sup>[14]</sup> pale yellow solid, m.p. 206–209 °C (lit.<sup>[14]</sup> 207–209 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.65 (d,  $J = 8.0$  Hz, 1H), 8.53 (d,  $J = 2.5$  Hz, 1H), 8.26 (d,  $J = 9.0$  Hz, 1H), 7.96 (d,  $J = 7.5$  Hz, 1H), 7.88 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 2.5$  Hz, 1H), 7.72-7.78 (m, 3H), 7.60 (d,  $J = 9.0$  Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 175.8, 154.5, 153.8, 137.4, 136.8, 129.9, 129.3, 128.2, 127.1, 124.6, 124.0, 123.7, 122.9, 121.5, 120.1, 117.7, 117.5.

**10-Bromo-12H-Benzo[a]xanthen-12-one** (Product from entry 22 in Table 2):



Known compound,<sup>[14]</sup> pale yellow solid, m.p. 195–196 °C (lit.<sup>[14]</sup> 196 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 10.05 (d,  $J = 8.5$  Hz, 1H), 8.57 (s, 1H), 8.17 (d,  $J = 9.0$  Hz, 1H), 7.93 (d,  $J = 8.0$  Hz, 1H), 7.81-7.84 (m, 2H), 7.64 (t,  $J = 7.5$  Hz, 1H), 7.57 (d,  $J = 9.0$  Hz, 1H), 7.47 (d,  $J = 9.0$  Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 177.1, 157.6, 153.5, 137.1, 136.8, 131.0, 130.2, 129.8, 129.3, 128.4, 126.9, 126.4, 124.9, 119.5, 117.9, 117.6, 114.5.

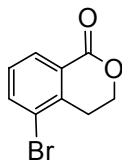
**Isochroman-1-one:** (Product from entry 1 in Table 3):



Known compound,<sup>[15]</sup> colorless liquid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.09 (d,  $J = 8.0$  Hz, 1H), 7.54 (t,  $J = 7.0$  Hz, 1H), 7.39 (t,  $J = 7.5$  Hz, 1H), 7.27 (d,  $J = 7.5$  Hz,

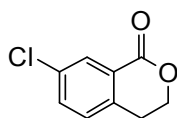
1H), 4.54 (t,  $J = 6.0$  Hz, 2H), 3.07 (t,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 165.1, 139.6, 133.7, 130.4, 127.7, 127.3, 125.3, 67.3, 27.8$ .

**5-Bromo-isochroman-1-one** (Product from entry 2 in Table 3):



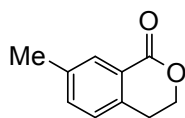
Known compound,<sup>[15]</sup> white solid, m.p. 90 °C (lit.<sup>[15]</sup> 89–90 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.09 (d,  $J = 8.0$  Hz, 1H), 7.78–7.80 (m, 1H), 7.30 (t,  $J = 8.0$  Hz, 1H), 4.56 (t,  $J = 6.0$  Hz, 2H), 3.16 (t,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 164.1, 139.4, 137.3, 129.7, 128.8, 127.3, 122.8, 66.6, 28.1.

**7-Chloro-isochroman-1-one** (Product from entry 3 in Table 3):



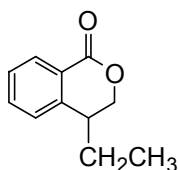
Known compound,<sup>[15]</sup> white solid, m.p. 65–67 °C (lit.<sup>[15]</sup> 67–69 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.10 (s, 1H), 7.53 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 2.0$  Hz, 1H), 7.25 (d,  $J = 8.5$  Hz, 1H), 4.56 (t,  $J = 6.0$  Hz, 2H), 3.06 (t,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 163.9, 137.8, 133.8, 133.7, 130.2, 128.8, 126.8, 67.3, 27.3.

**7-Methyl-isochroman-1-one** (Product from entry 4 in Table 3):



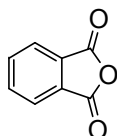
Known compound,<sup>[15]</sup> colorless liquid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.91 (s, 1H), 7.36 (d,  $J = 7.5$  Hz, 1H), 7.17 (d,  $J = 8.0$  Hz, 1H), 4.52 (t,  $J = 6.0$  Hz, 2H), 3.02 (t,  $J = 6.0$  Hz, 2H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 165.4, 137.5, 136.6, 134.6, 130.6, 127.1, 125.0, 67.5, 27.5, 21.0.

**4-Ethyl-isochroman-1-one** (Product from entry 5 in Table 3):



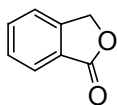
Known compound,<sup>[14]</sup> colorless liquid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.08 (d, *J* = 7.5 Hz, 1H), 7.56 (dt, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 7.40 (dt, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 0.5 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 4.45-4.56 (m, 2H), 2.76-2.80 (m, 1H), 1.74-1.79 (m, 2H), 1.02 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 165.1, 143.7, 133.6, 130.4, 127.6, 127.0, 124.5, 70.3, 39.0, 25.7, 11.7.

***o*-Phthalic anhydride** (Product from entries 6 and 7 in Table 3):



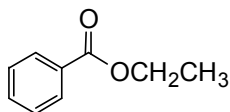
Known compound,<sup>[16]</sup> yellow solid, m.p. 131–134 °C (lit.<sup>[16]</sup> 130–132 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.04-8.07 (m, 2H), 7.93-7.97 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 162.8, 136.1, 131.3, 125.7.

**Phthalide** (Product from entry 6 in Table 3):



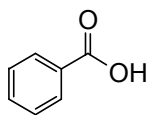
Known compound,<sup>[17]</sup> white solid, m.p. 72–74 °C (lit.<sup>[17]</sup> 74–76 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.91 (d, *J* = 7.5 Hz, 1H), 7.69 (t, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 7.5 Hz, *J*<sub>3</sub> = 1.0 Hz, 1H), 7.51-7.55 (m, 2H), 5.33 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 171.2, 146.6, 134.1, 129.0, 125.7, 122.2, 69.7.

**Ethyl benzoate** (Product from entry 8 in Table 3):



Known compound,<sup>[18]</sup> colorless liquid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.08 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 166.6, 132.8, 130.5, 129.5, 128.3, 61.0, 14.3.

**Benzoic acid** (Product from entry 8 in Table 3):



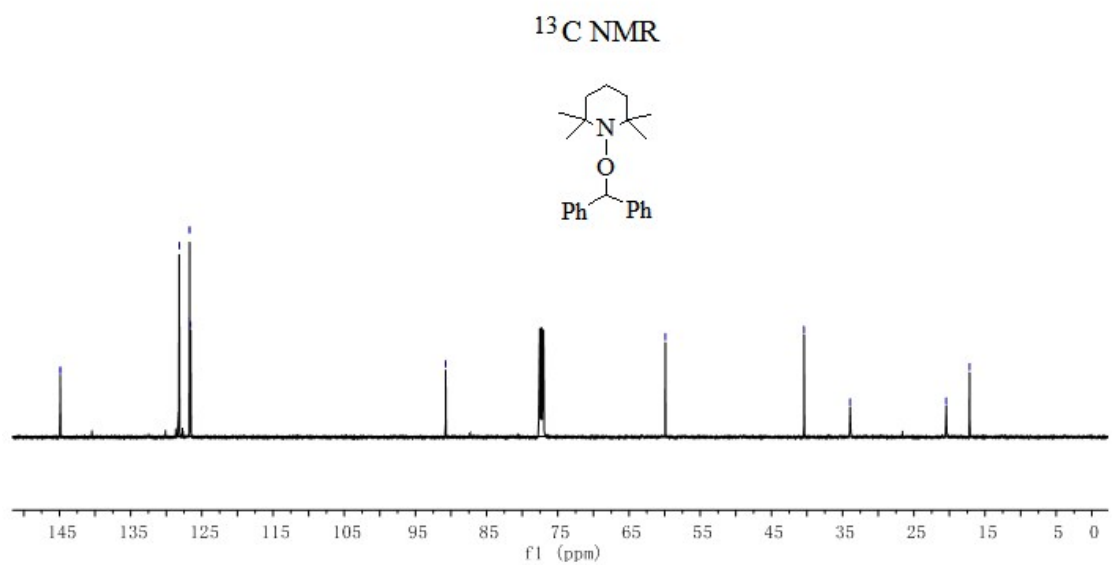
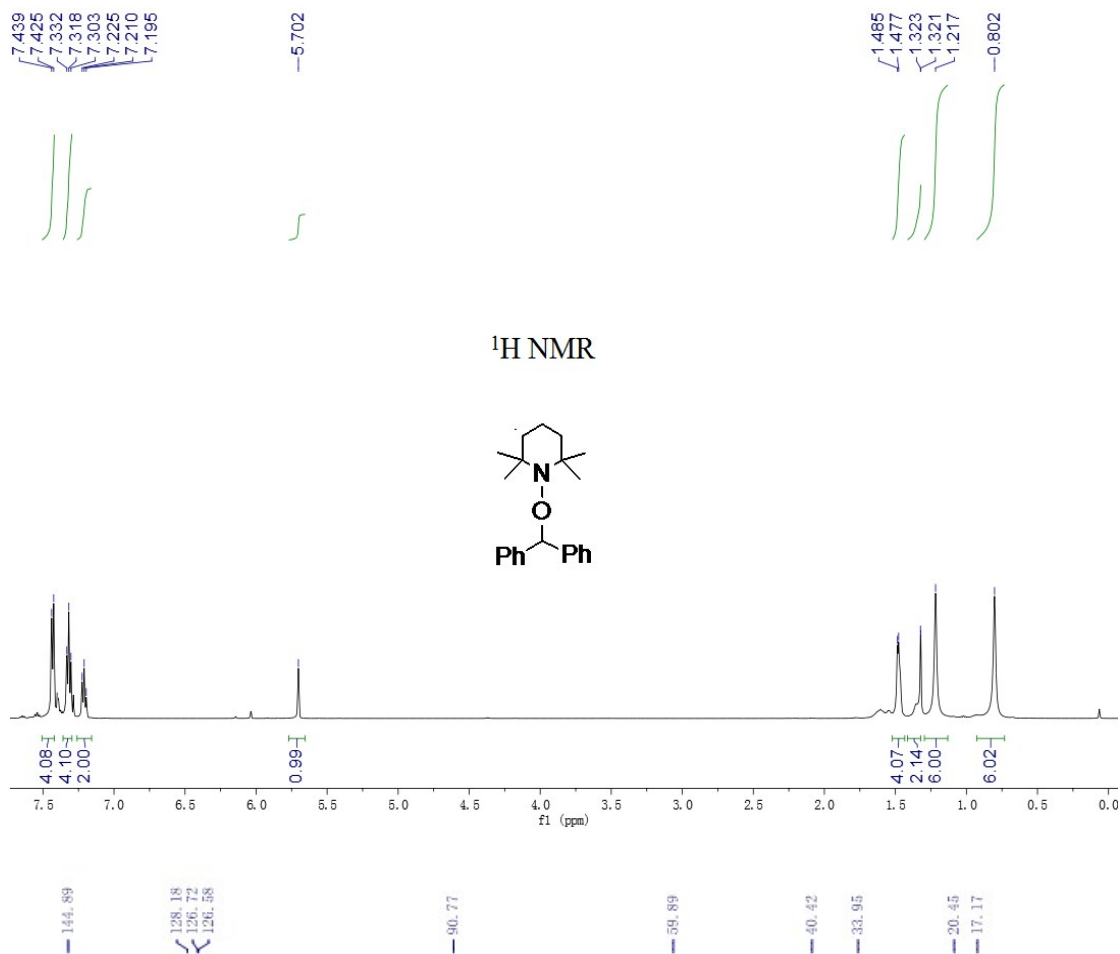
Known compound,<sup>[19]</sup> pale yellow solid, m.p. 122–123 °C (lit.<sup>[19]</sup> 123°C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 12.36 (br, 1H), 8.17 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 1.0$  Hz, 2H), 7.66 (t,  $J = 7.5$  Hz, 1H), 7.52 (t,  $J = 7.5$  Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 172.6, 133.9, 130.3, 129.4, 128.5.

## 5. Reference

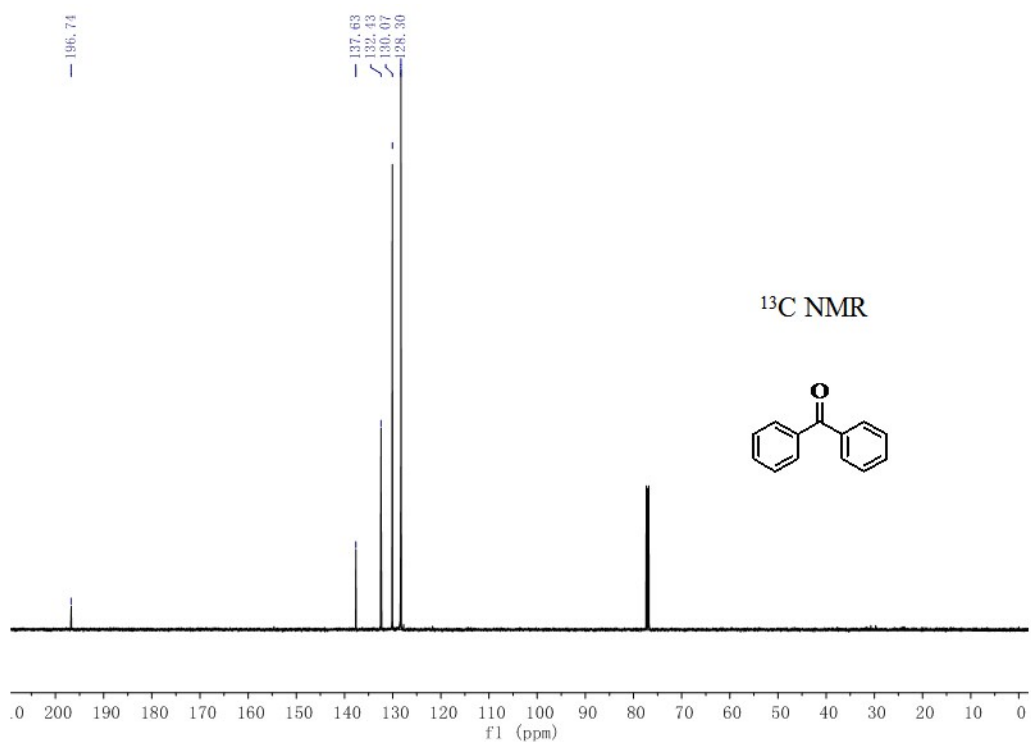
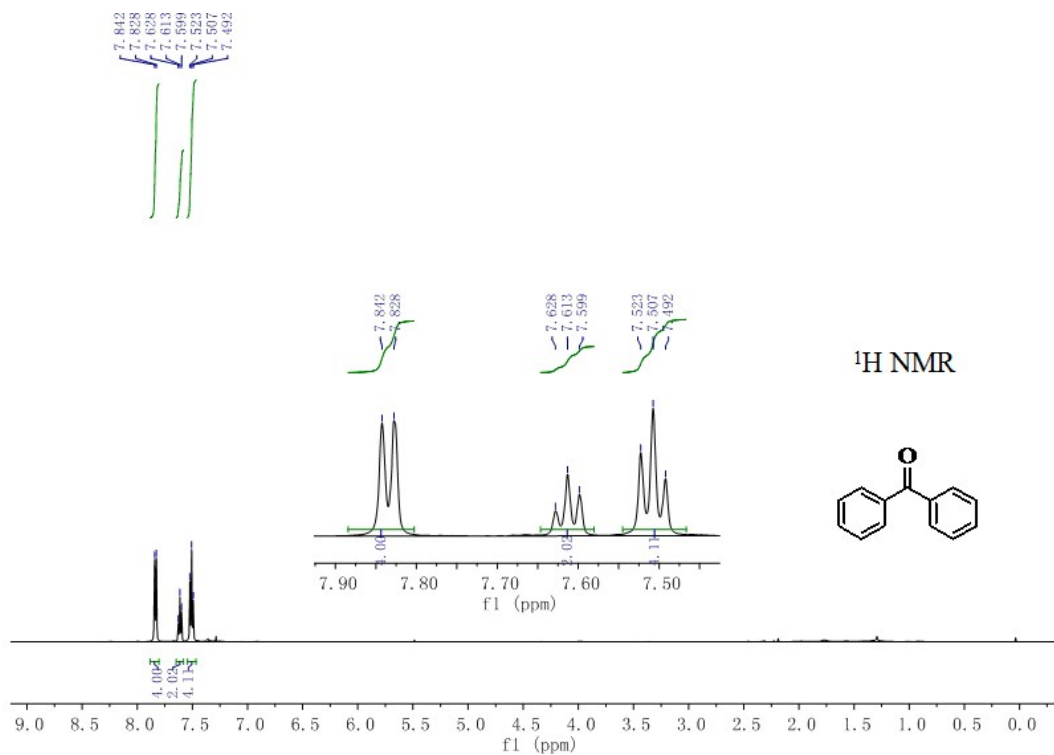
- [1] S. M. Nobre, A. L. Monteiro, *Tetrahedron Lett.* **2004**, *45*, 8225–8228.
- [2] Z. G. Zhang, Y. Gao, Y. Liu, J. J. Li, H. X. Xie, H. Li, W. Wang, *Org. Lett.* **2015**, *17*, 5492–5495.
- [3] L. Y. Li, Z. W. Yu, Z. M. She, *Adv. Synth. Catal.* **2015**, *357*, 3495–3500.
- [4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, *et. al.* Gaussian 09, revision C.01, Gaussian, Inc., Wallingford CT, **2010**.
- [5] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [6] a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654; b) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213–222; c) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261.
- [7] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.* **2005**, *105*, 2999–3093.
- [8] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
- [9] A. J. Yu, L. Shen, X. L. Cui, D. P. Peng, Y. J. Wu, *Tetrahedron* **2012**, *68*, 2283–2288.
- [10] B. W. Zhao, X. Y. Lu, *Org. Lett.* **2006**, *8*, 5987–5990.
- [11] M. Keenan, M. J. Abbott, P. W. Alexander, *et. al.* *J. Med. Chem.* **2012**, *55*, 4189–4204.
- [12] X. F. Yu, X. Y. Lu, *Adv. Synth. Catal.* **2011**, *353*, 569–574.
- [13] R. Prebil, G. Stavber, S. Stavber, *Eur. J. Org. Chem.* **2014**, 395–402.
- [14] X. Z. Tian, F. P. Ren, B. Zhao, Y. L. Ren, S. Zhao, J. J. Wang, *Catal. Commun.*, **2018**, *106*, 44–49.
- [15] C. Hong, J. Q. Ma, M. C. Li, L. Q. Jin, X. Q. Hu, W. M. Mo, B. X. Hu, N. Sun, Z. L. Shen, *Tetrahedron* **2017**, *73*, 3002–3009.

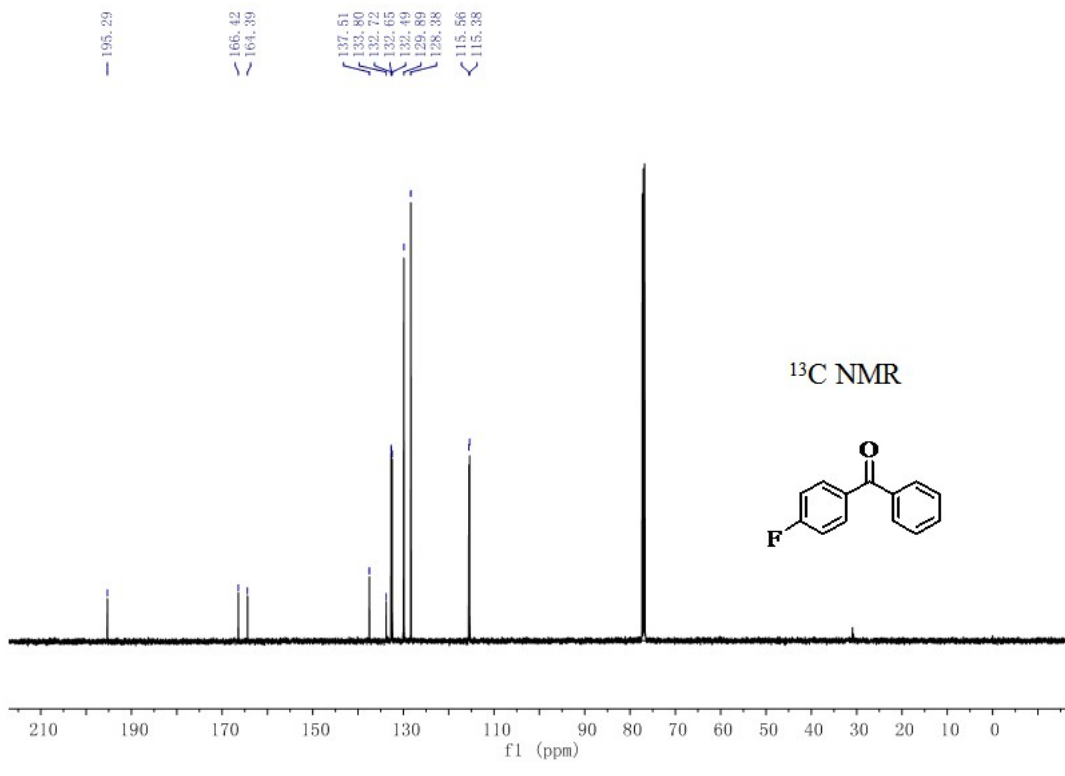
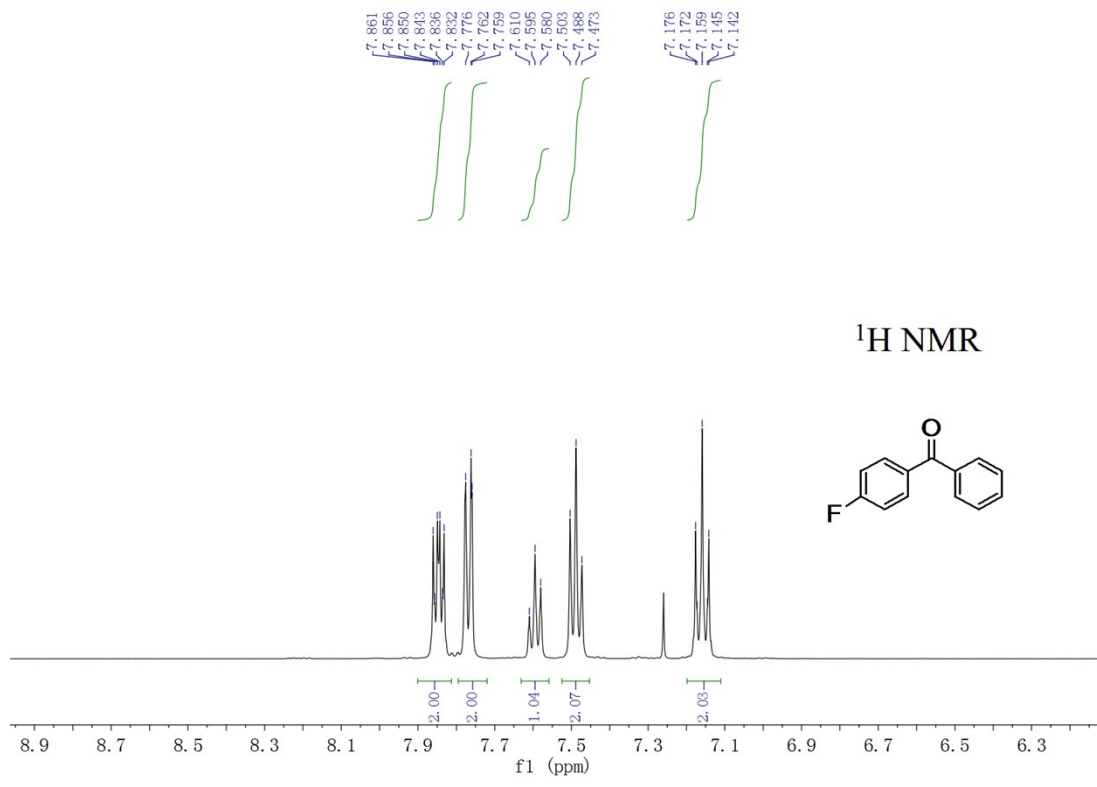
- [16] M. D. Konieczynska, C. H. Dai, C. R. J. Stephenson, *Org. Biomol. Chem.* **2012**, *10*, 4509–4511.
- [17] P. Losch, A. S. Felten, P. Palea, *Adv. Synth. Catal.* **2015**, *357*, 2931–2938.
- [18] Y. F. Guo, S. Mahmood, B. H. Xu, X. Q. Yao, H. Y. He, S. J. Zhang, *J. Org. Chem.* **2017**, *82*, 1591–1599.
- [19] P. K Prasad, A. Sudalai, *Adv. Synth. Catal.* **2014**, *356*, 2231–2238.

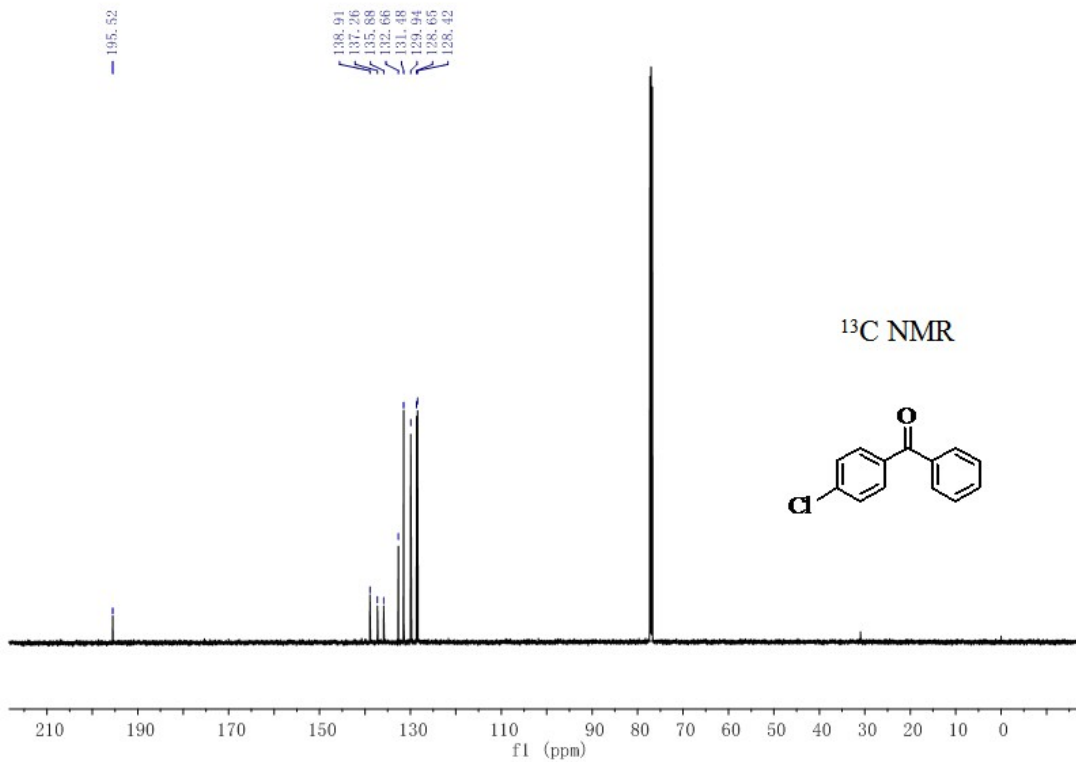
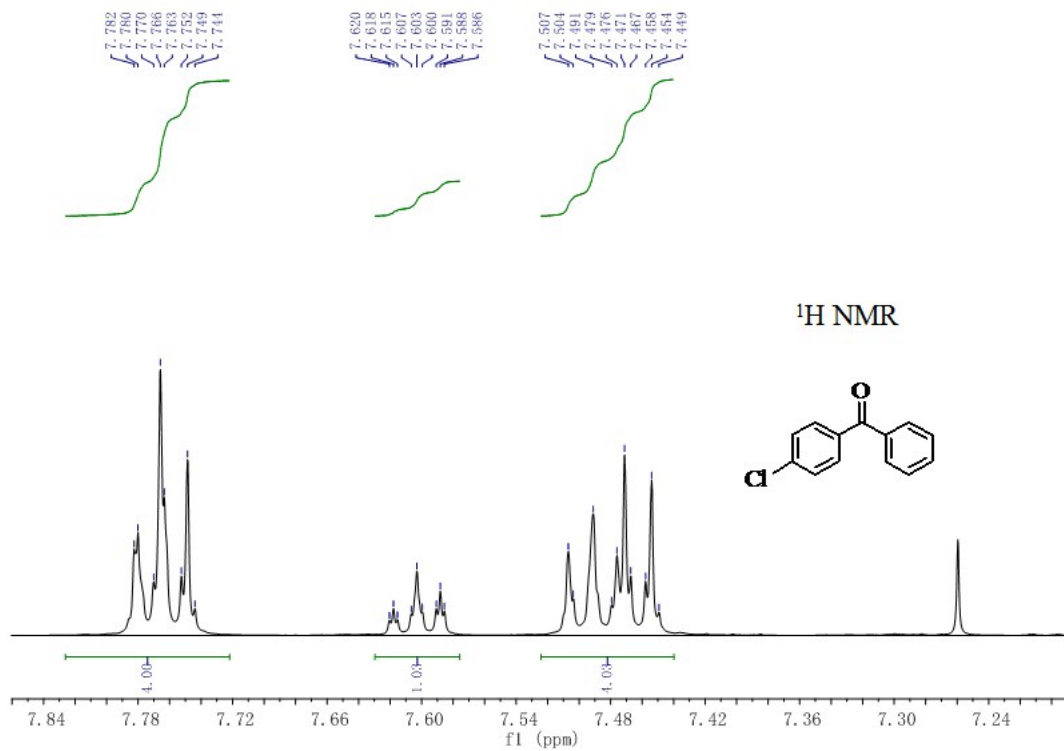
## 6. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR for the isolated products

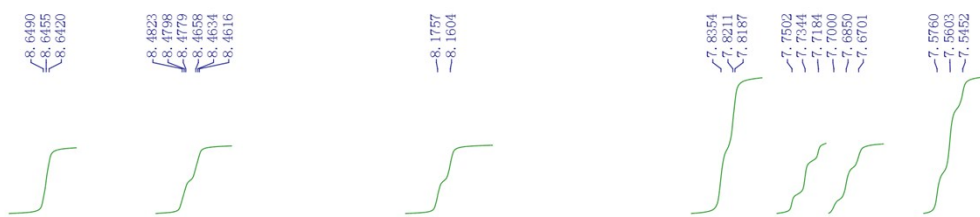




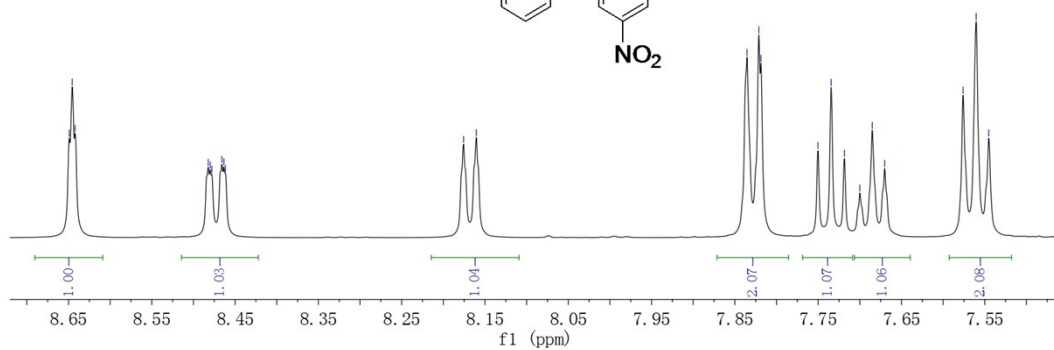
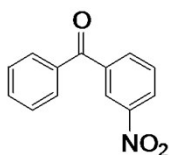




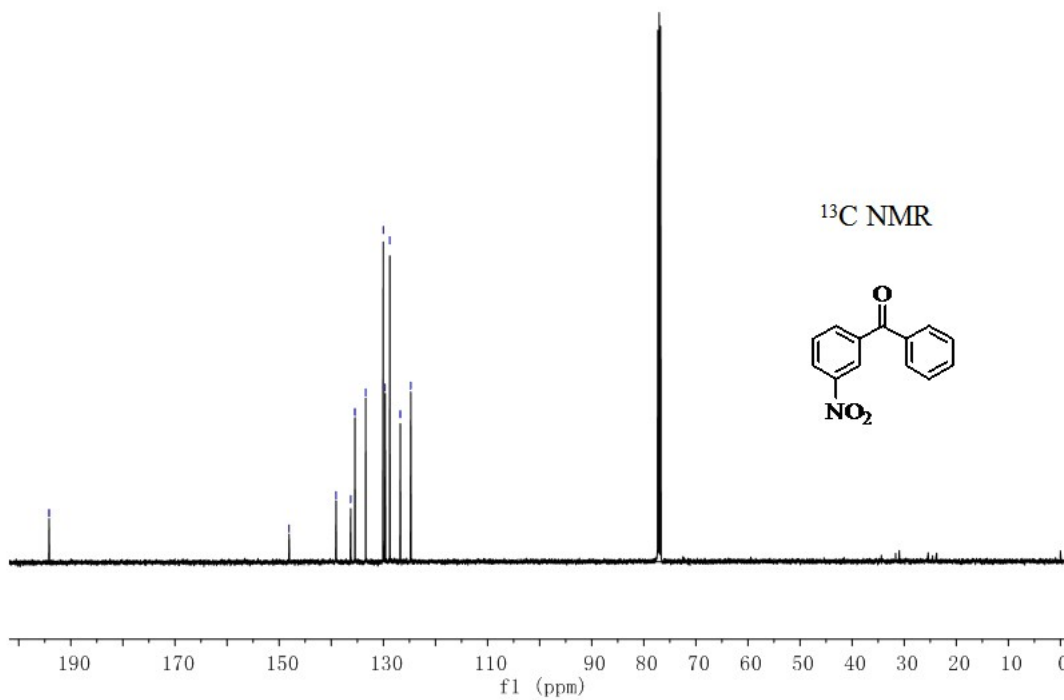
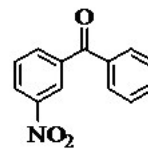


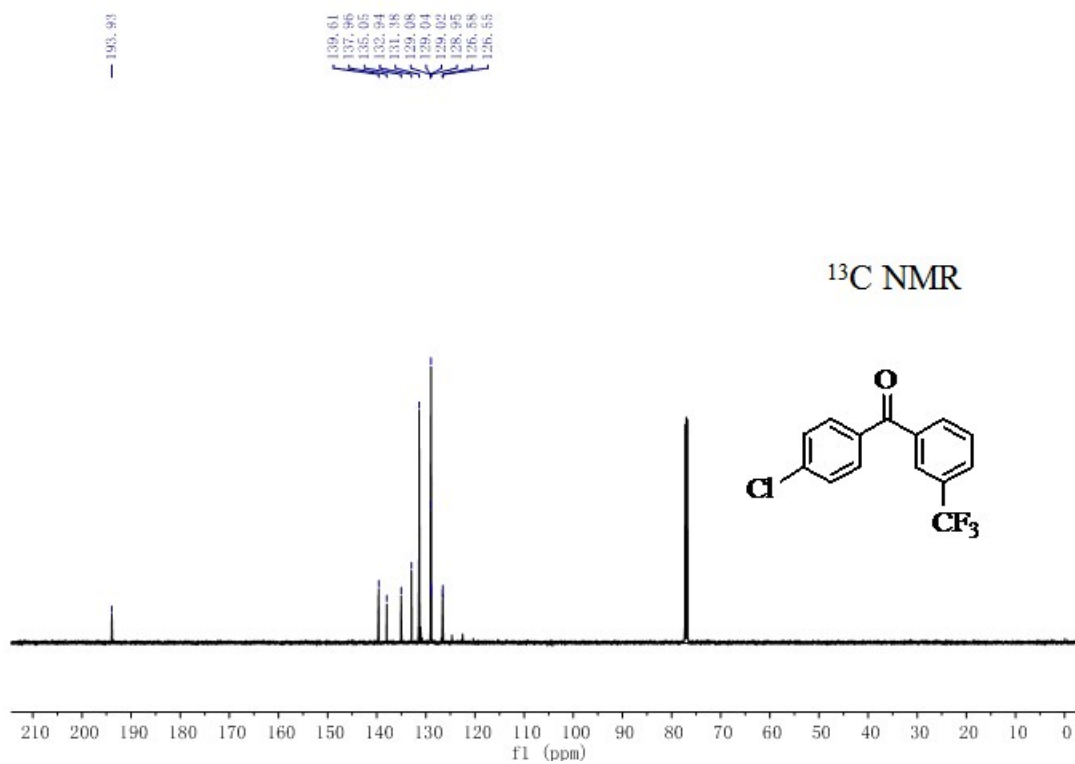
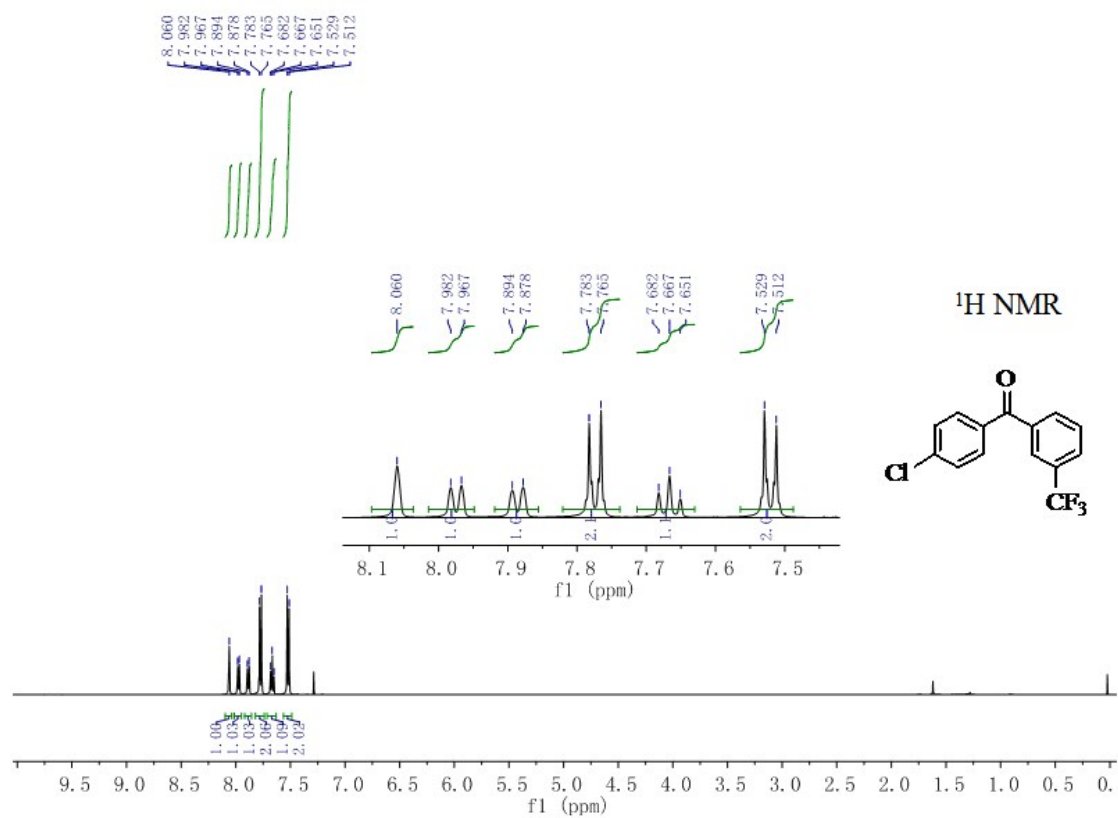


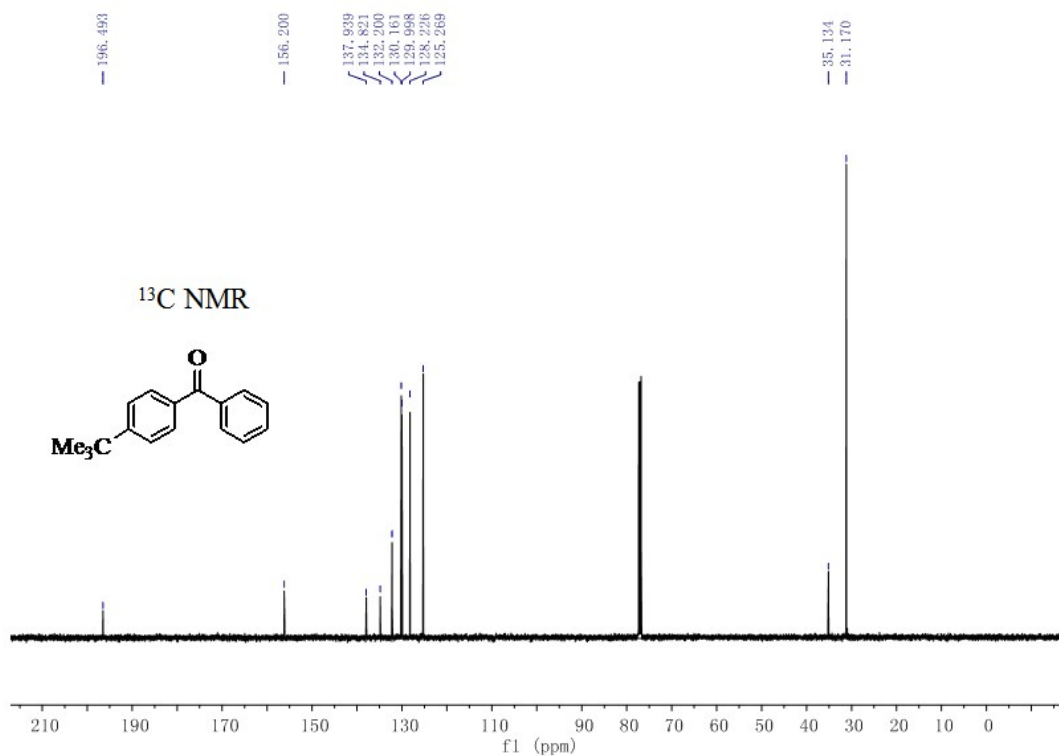
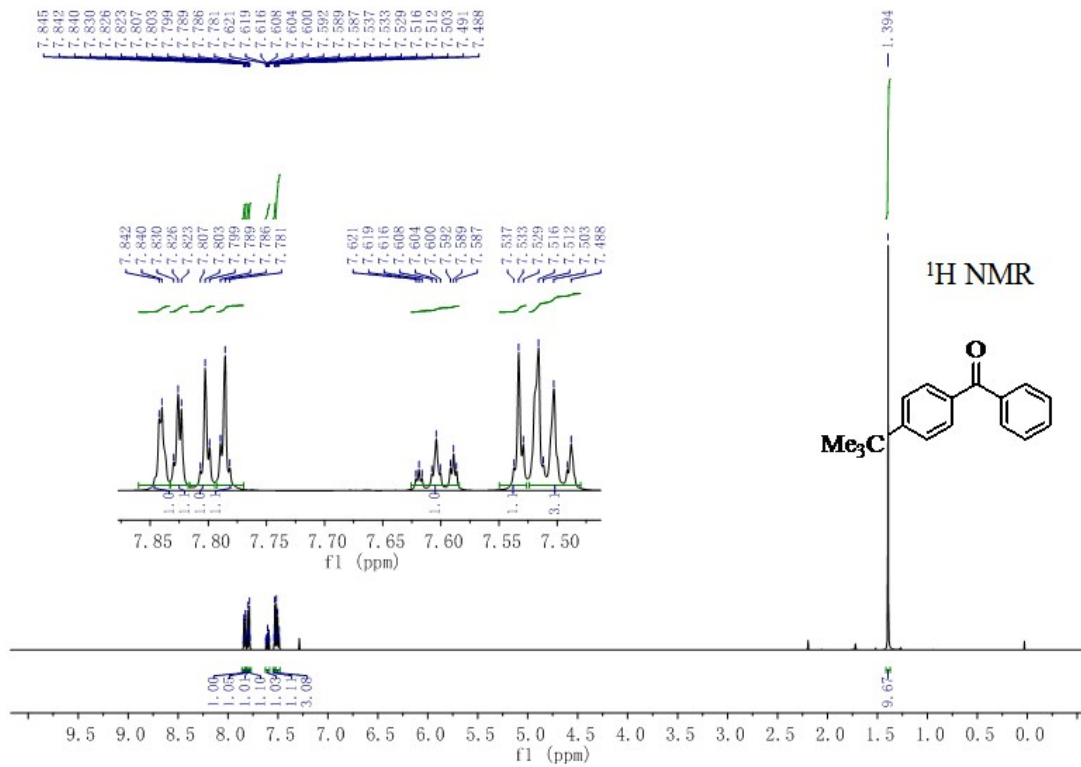
<sup>1</sup>H NMR

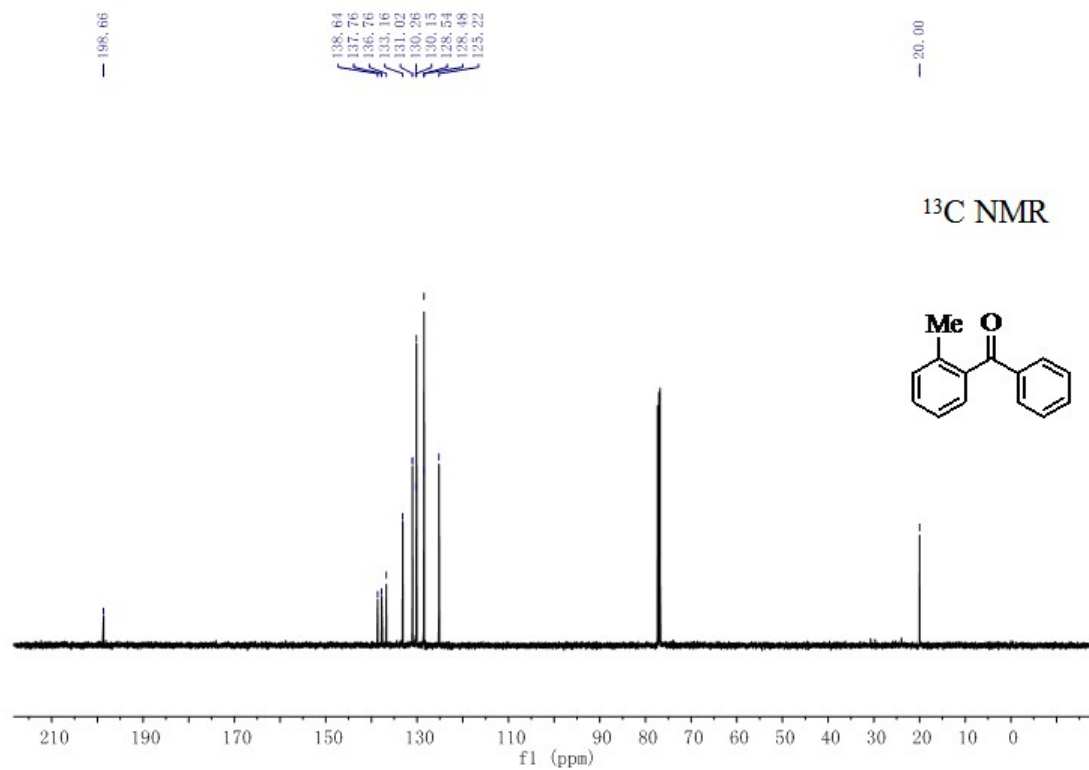
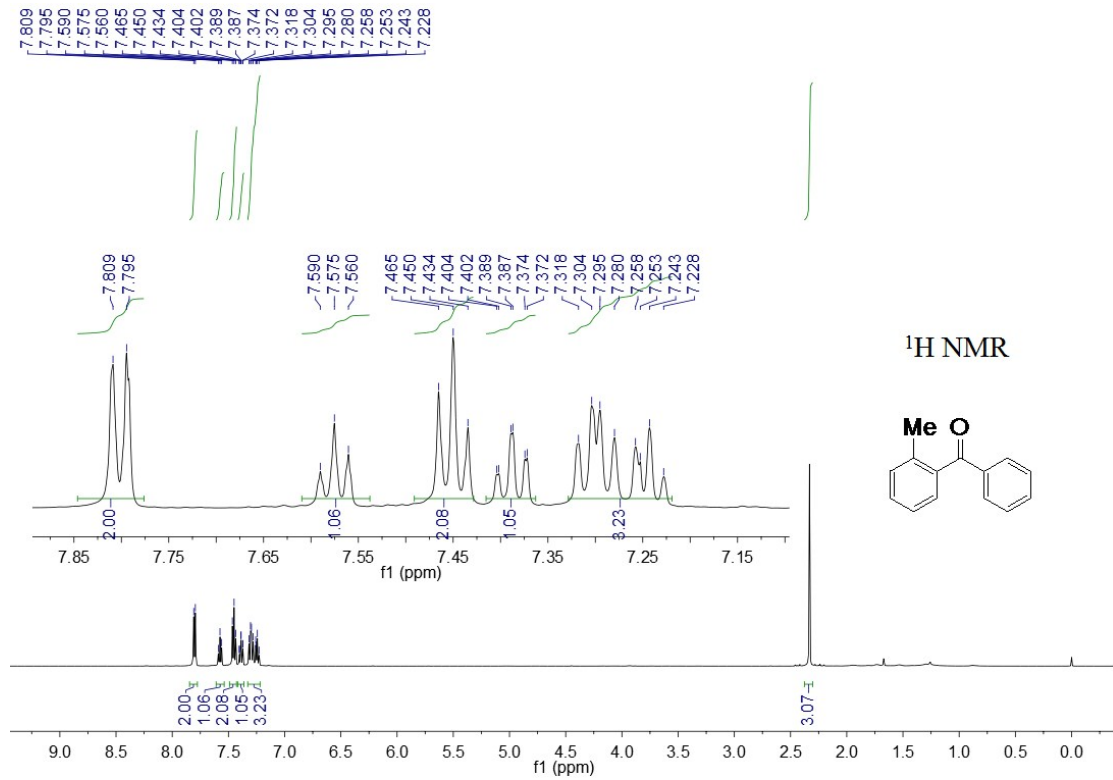


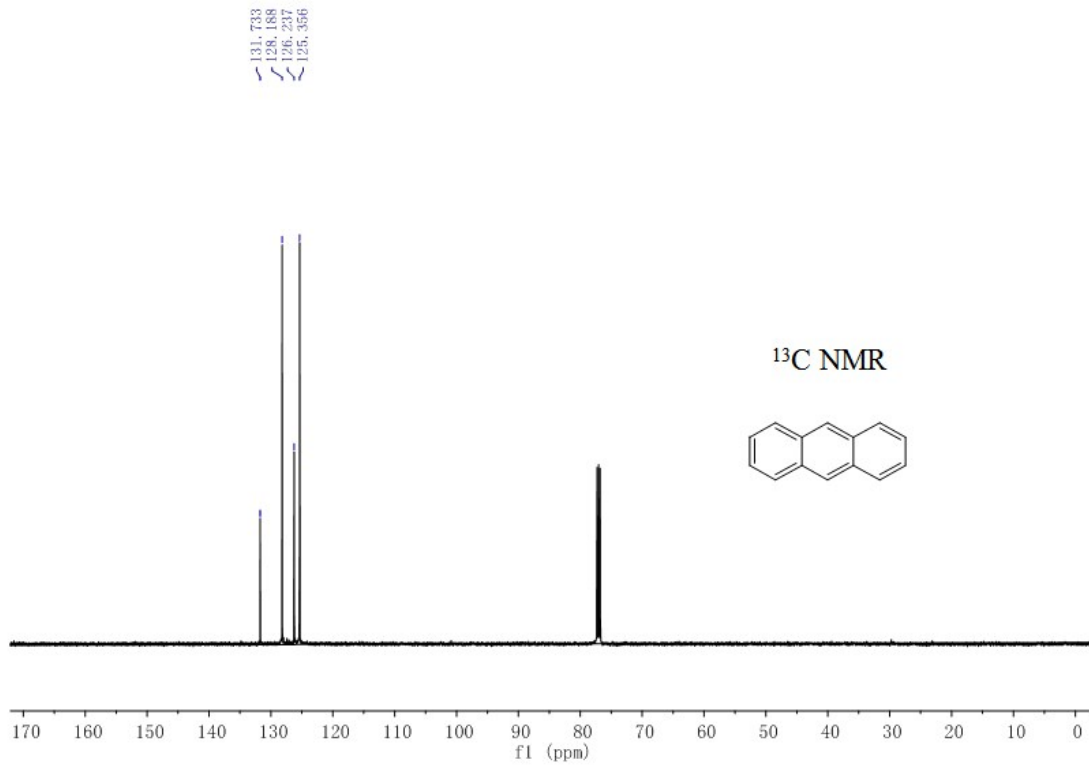
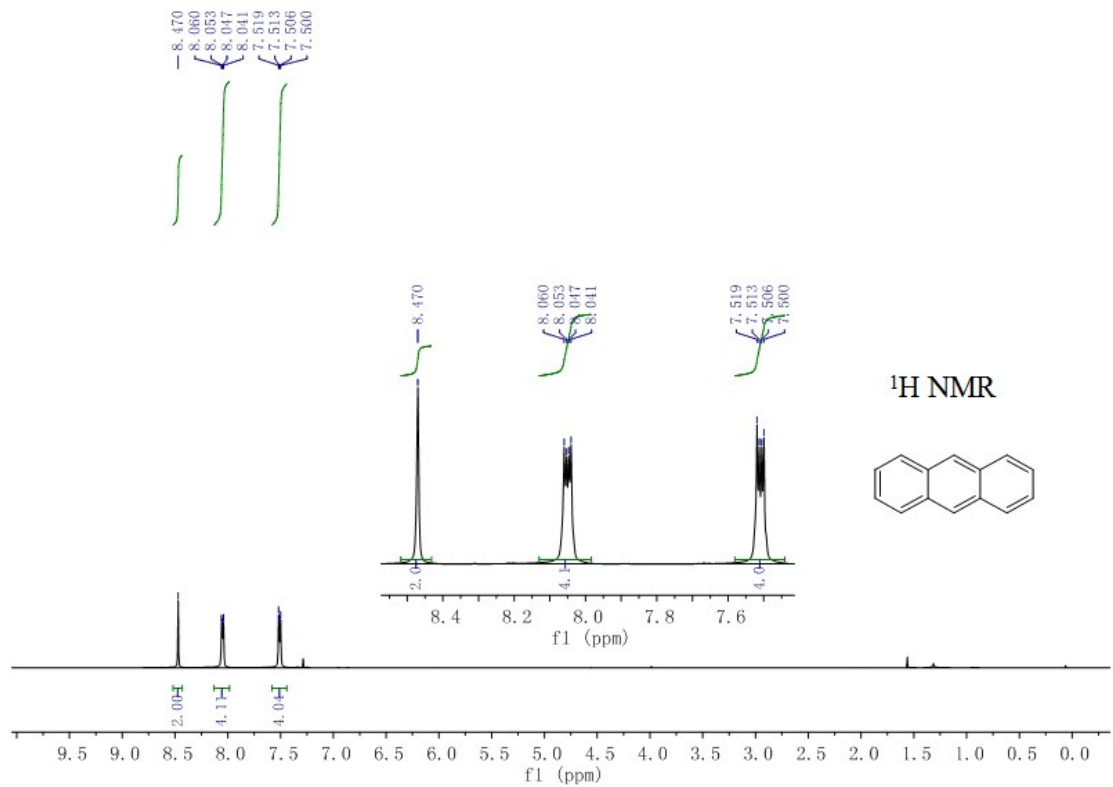
<sup>13</sup>C NMR



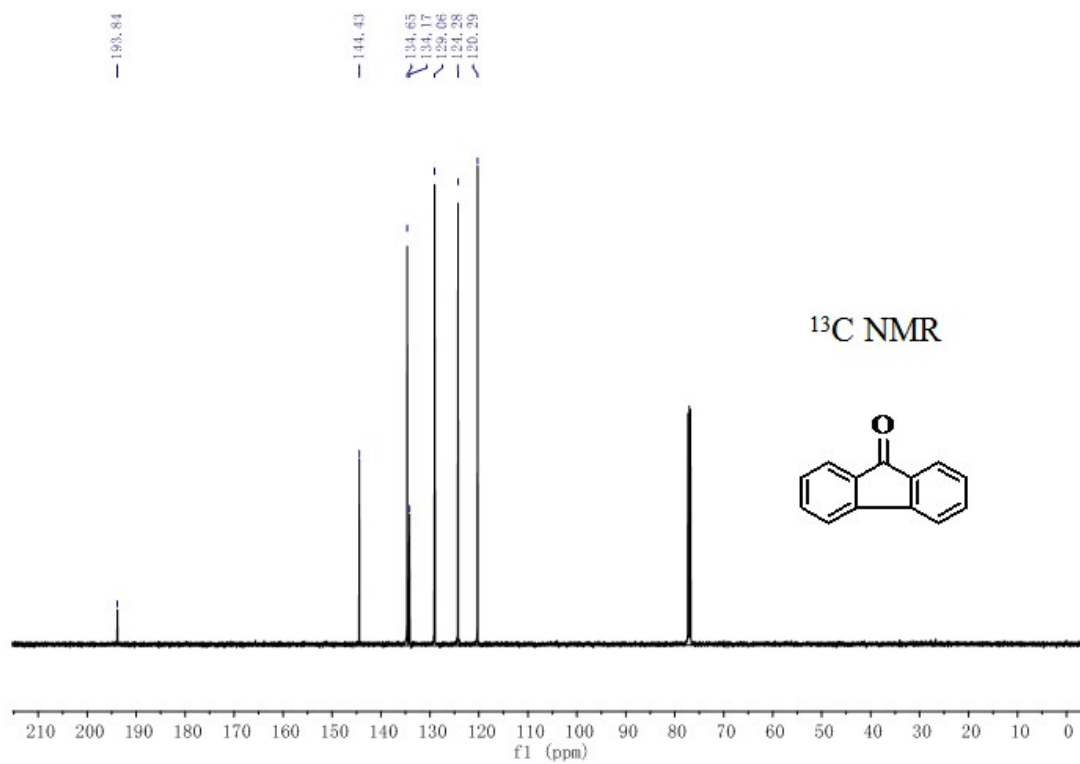
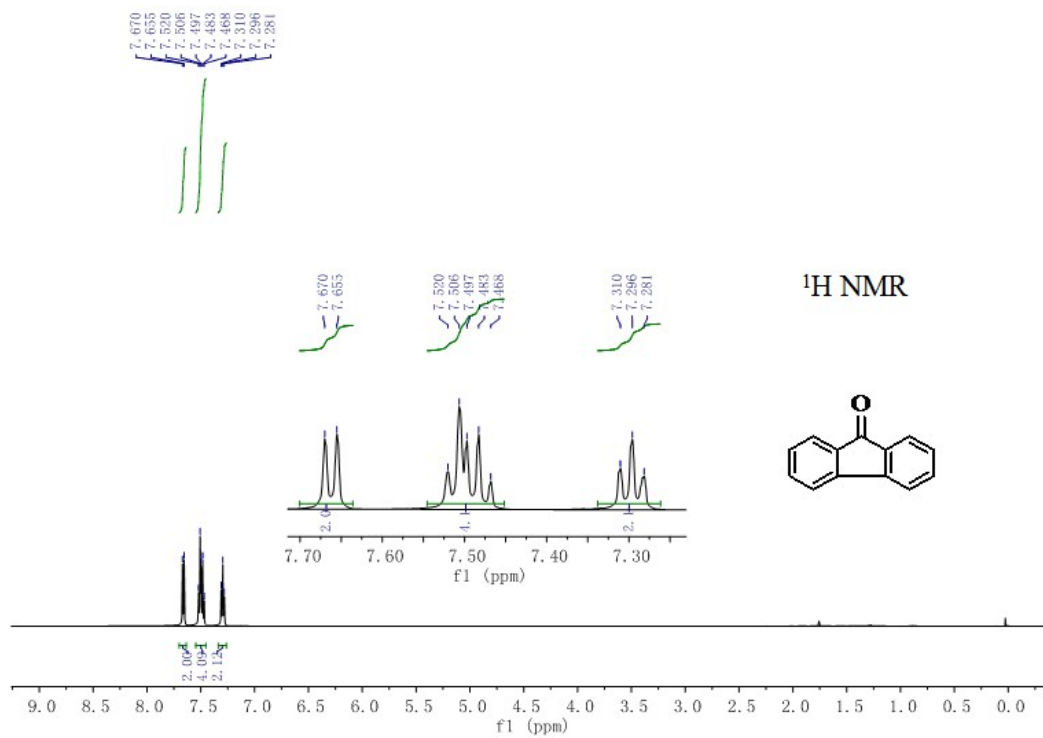


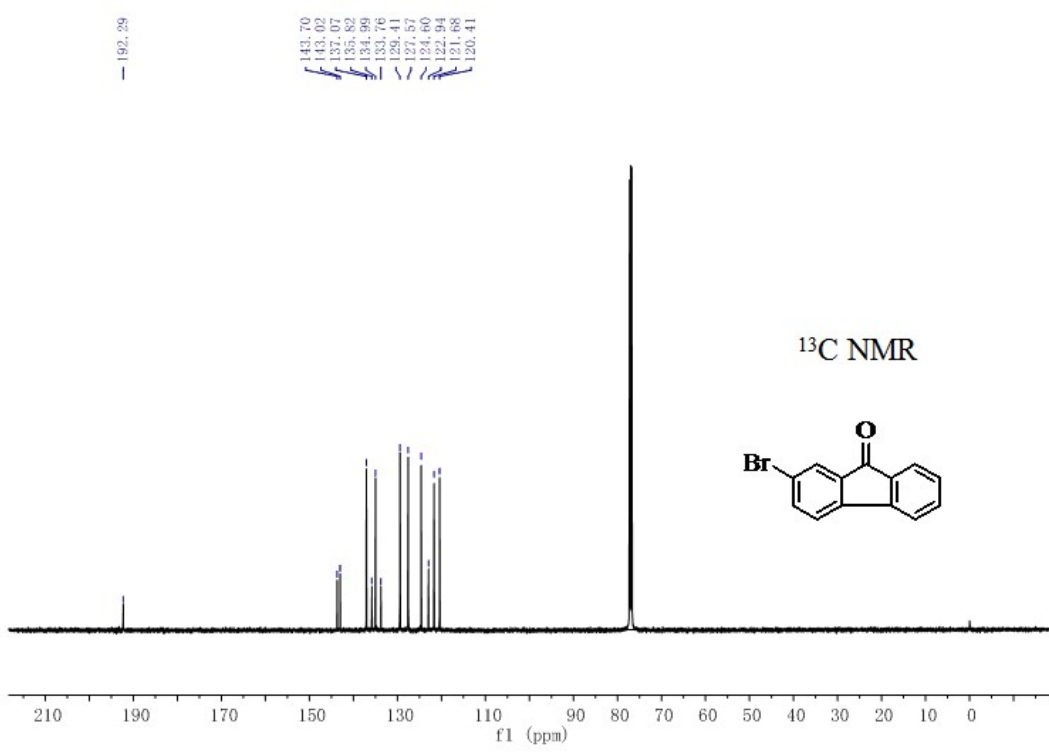
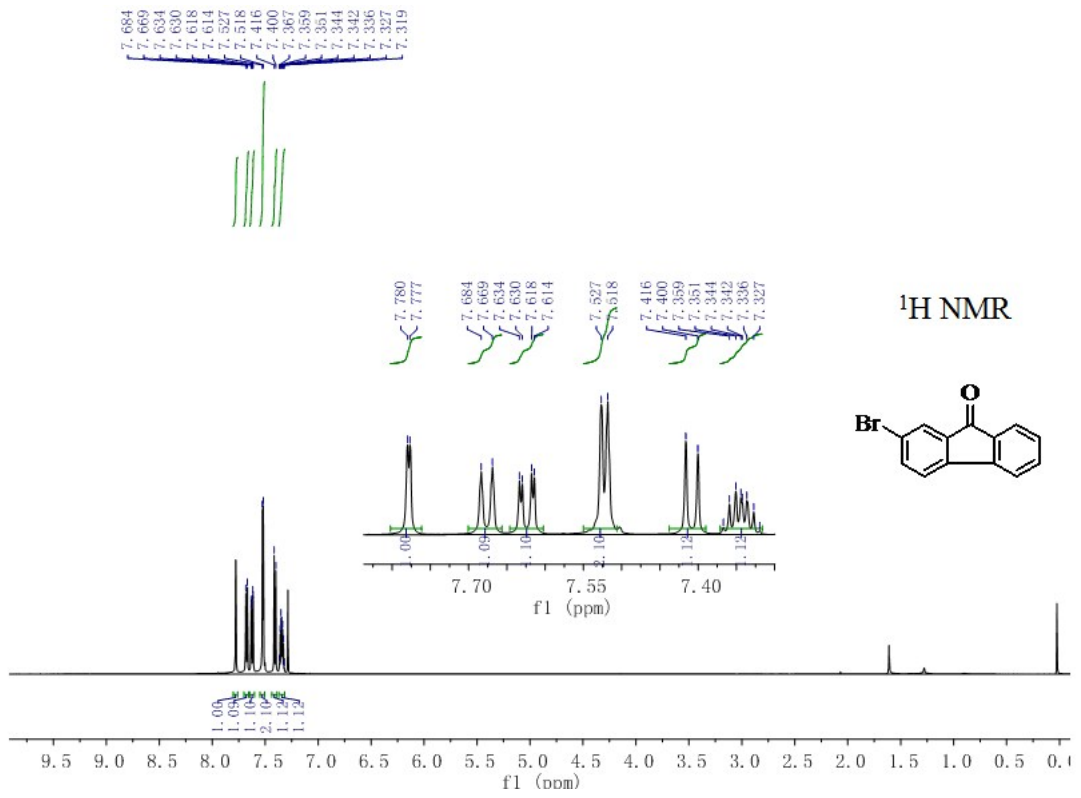


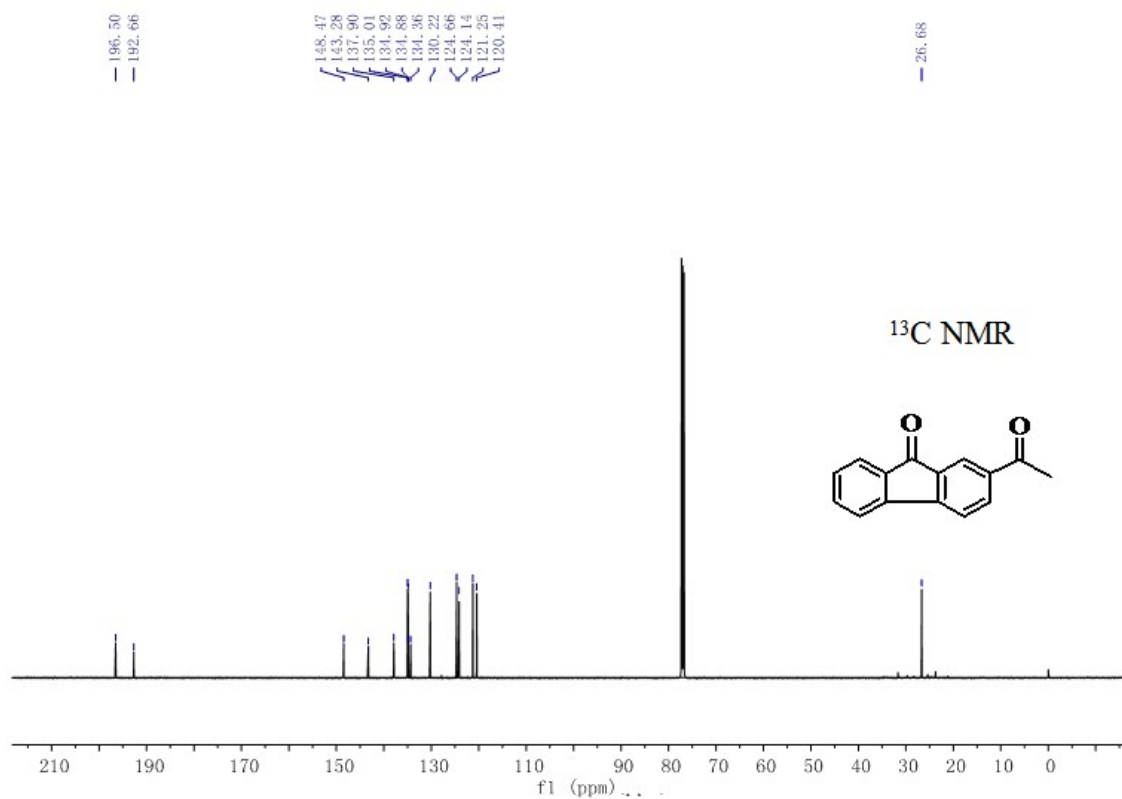
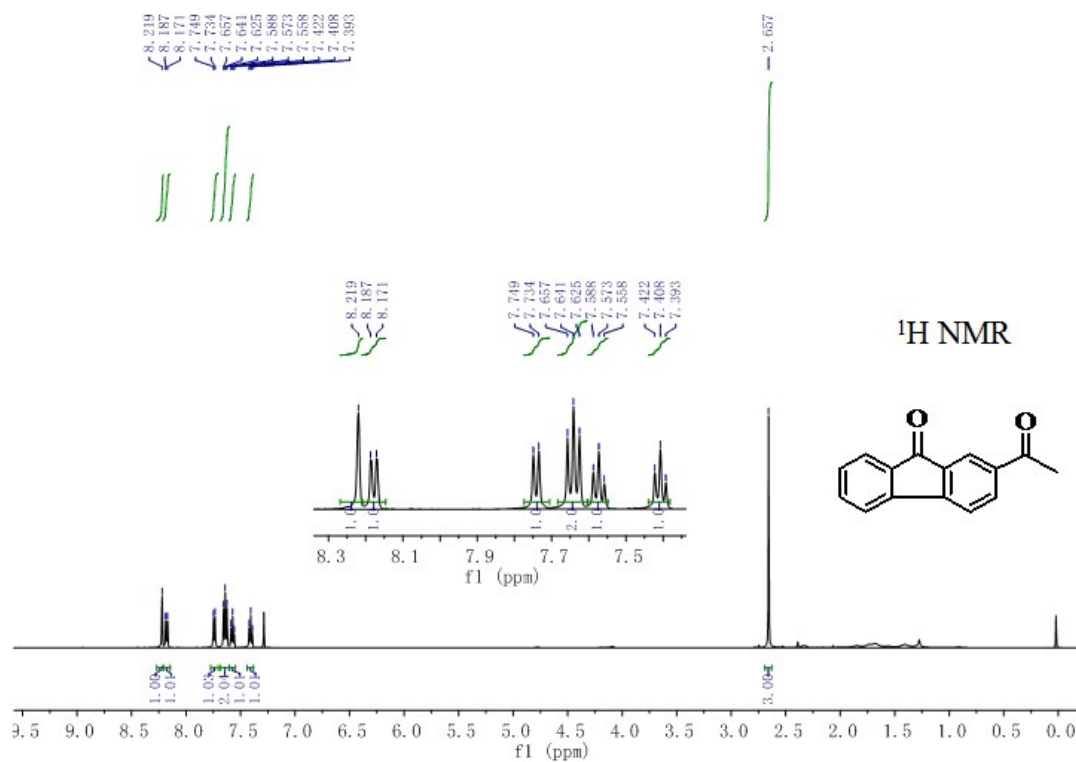




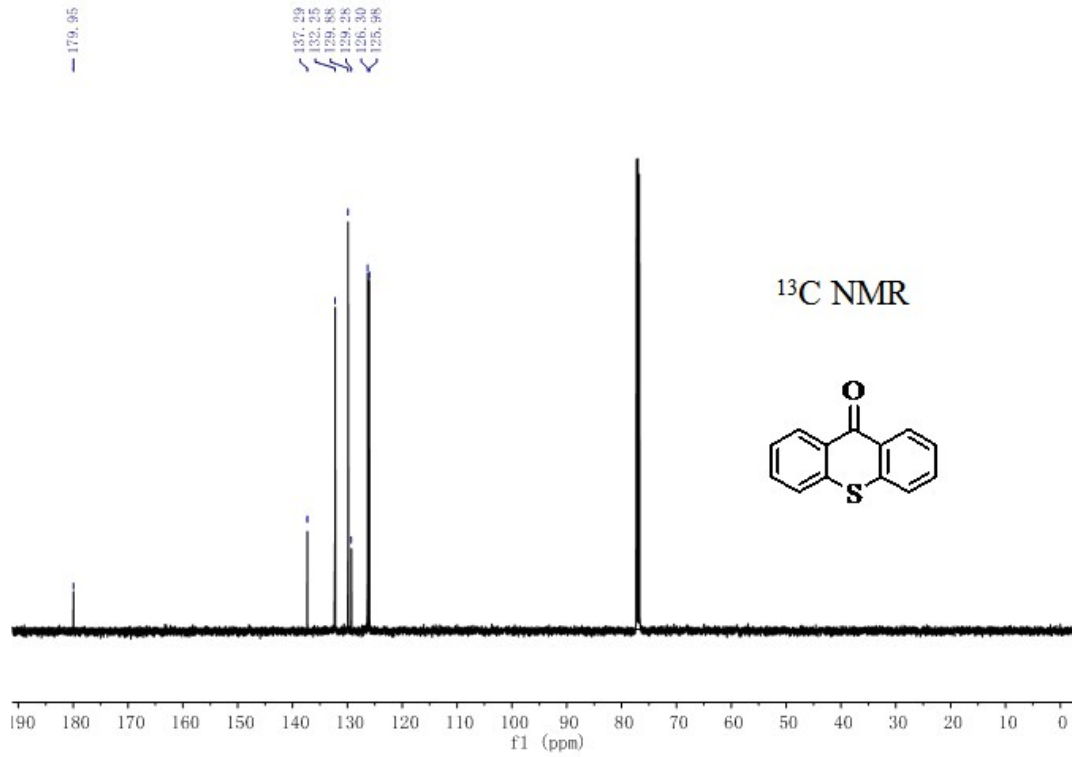
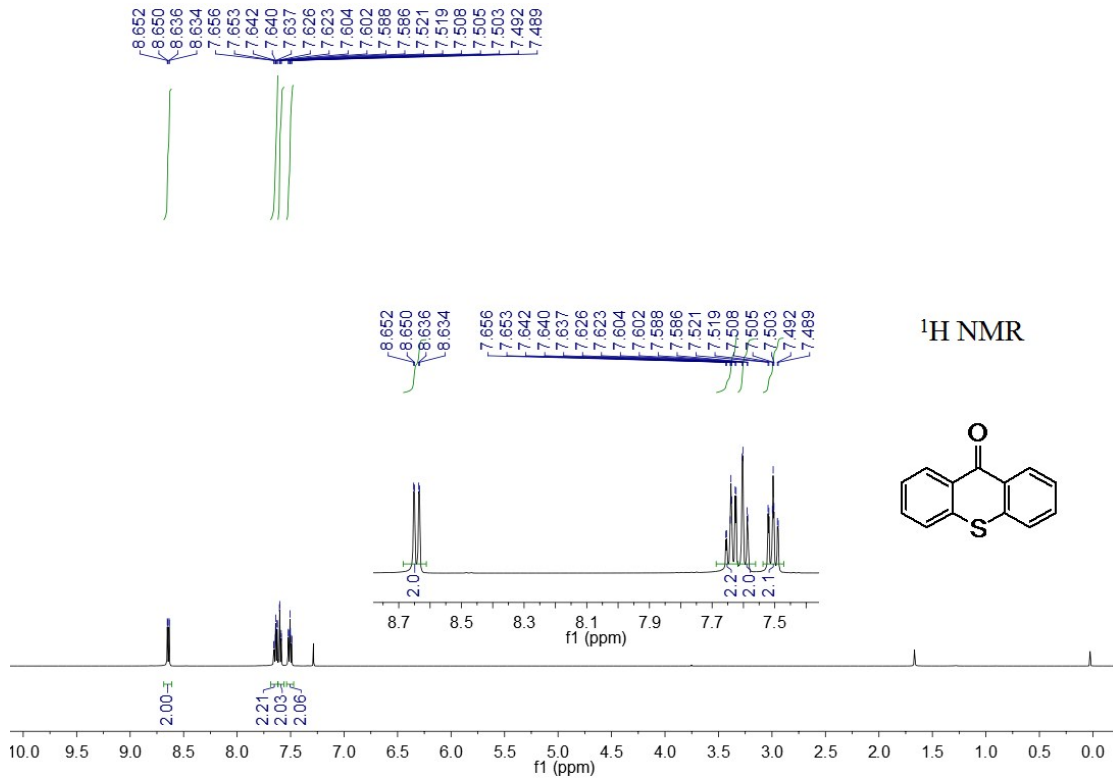




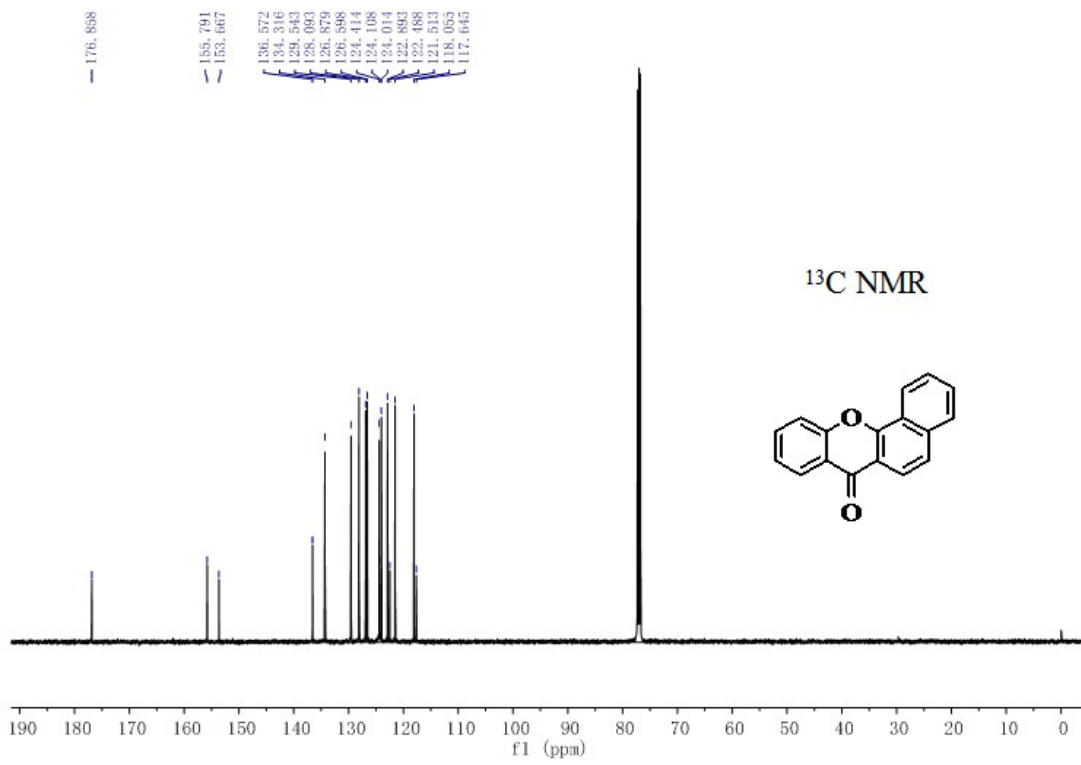
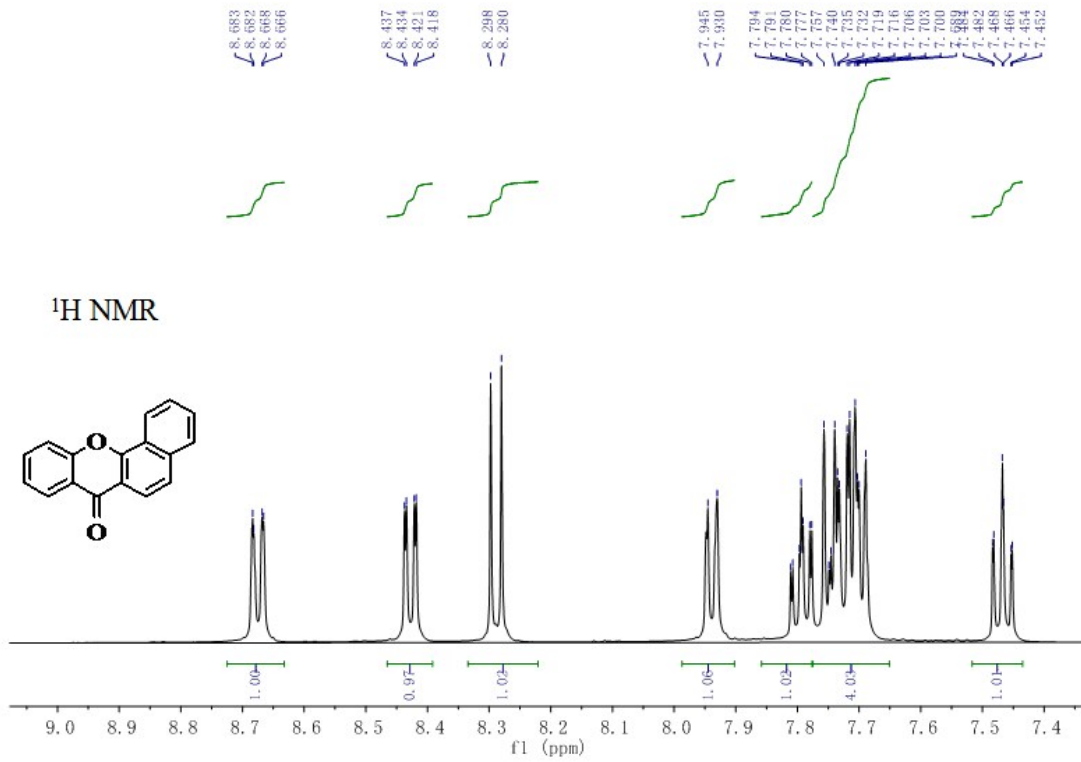


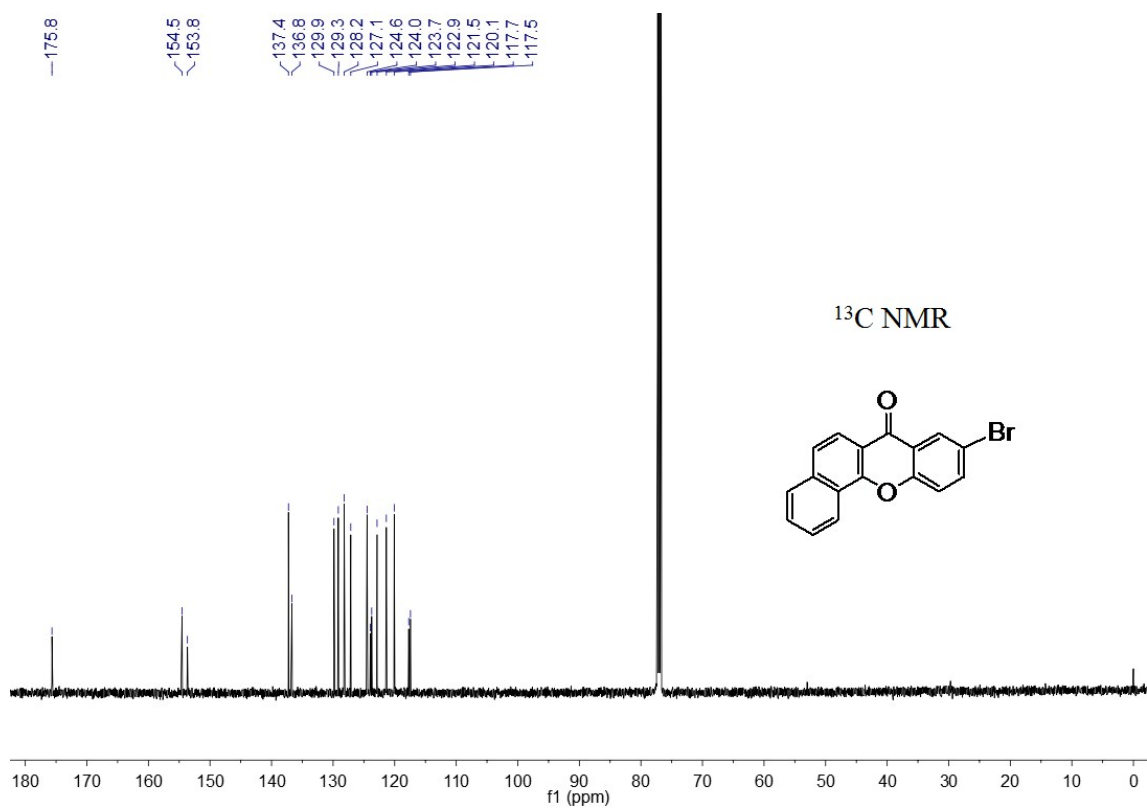
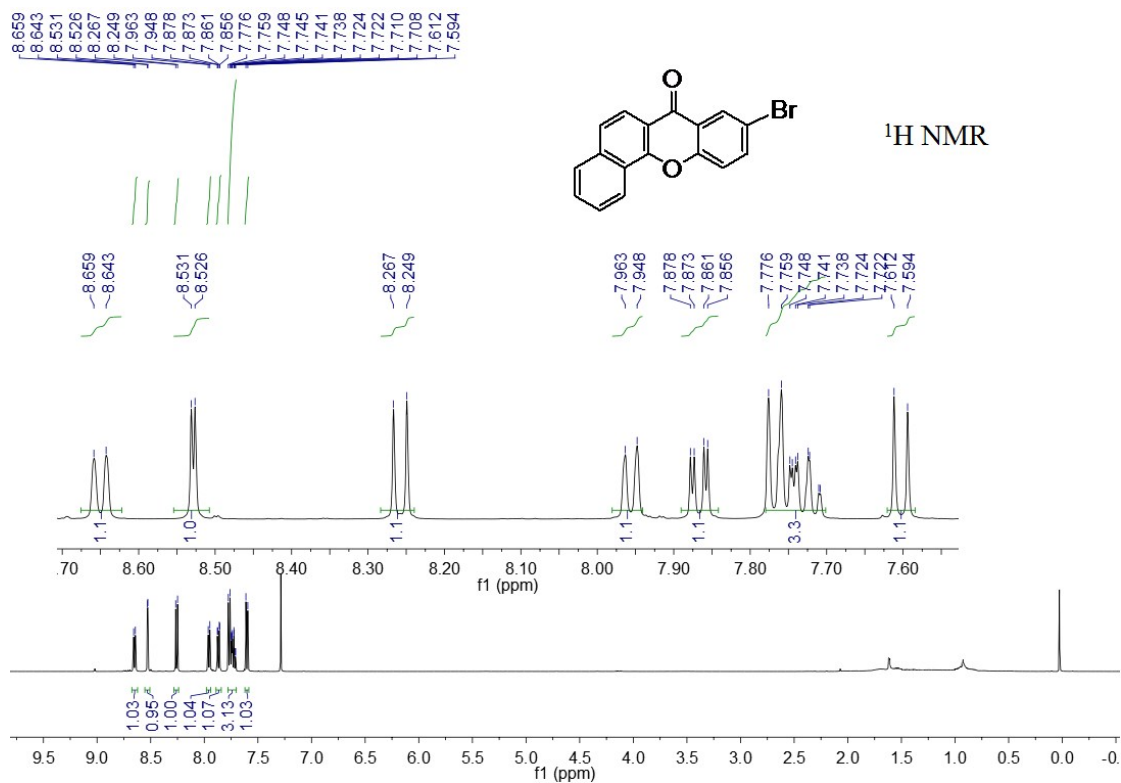




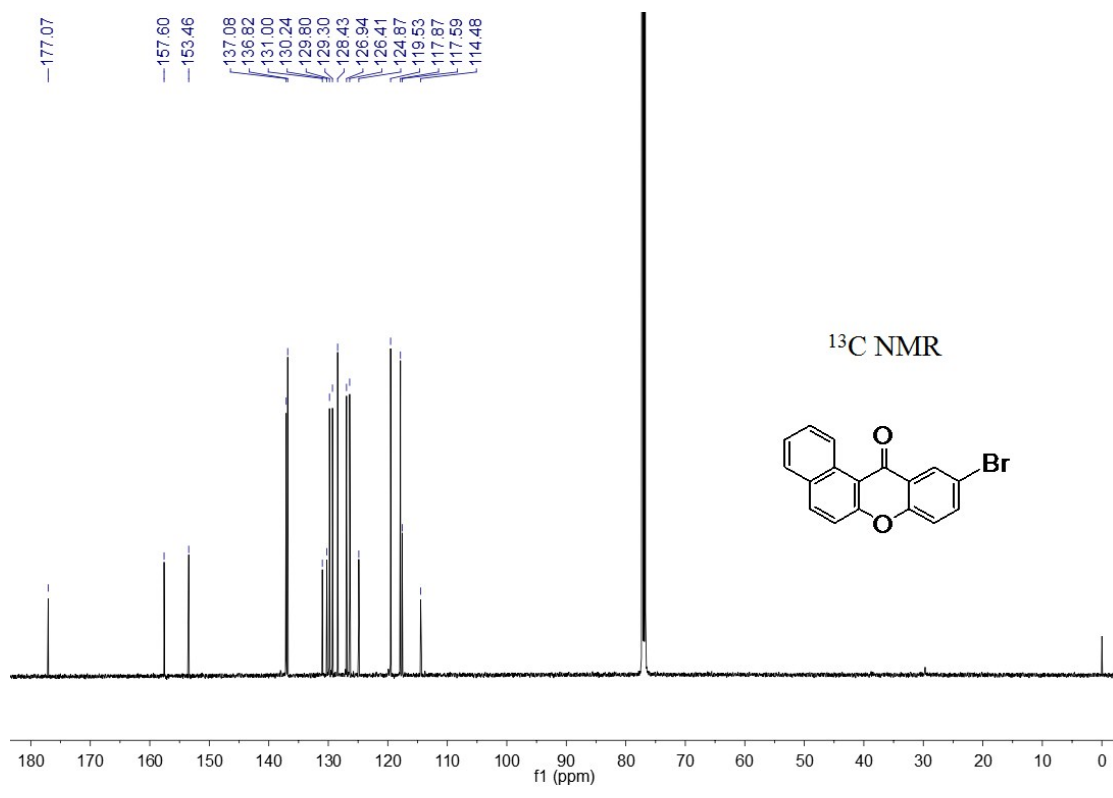
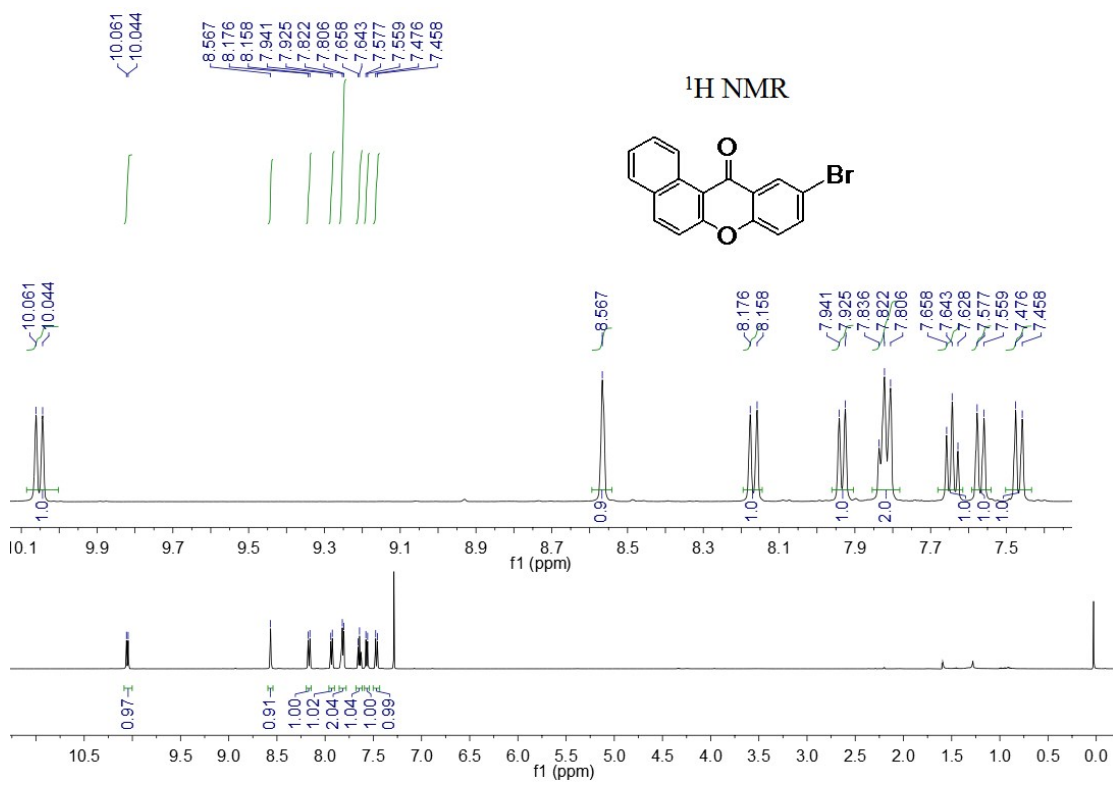


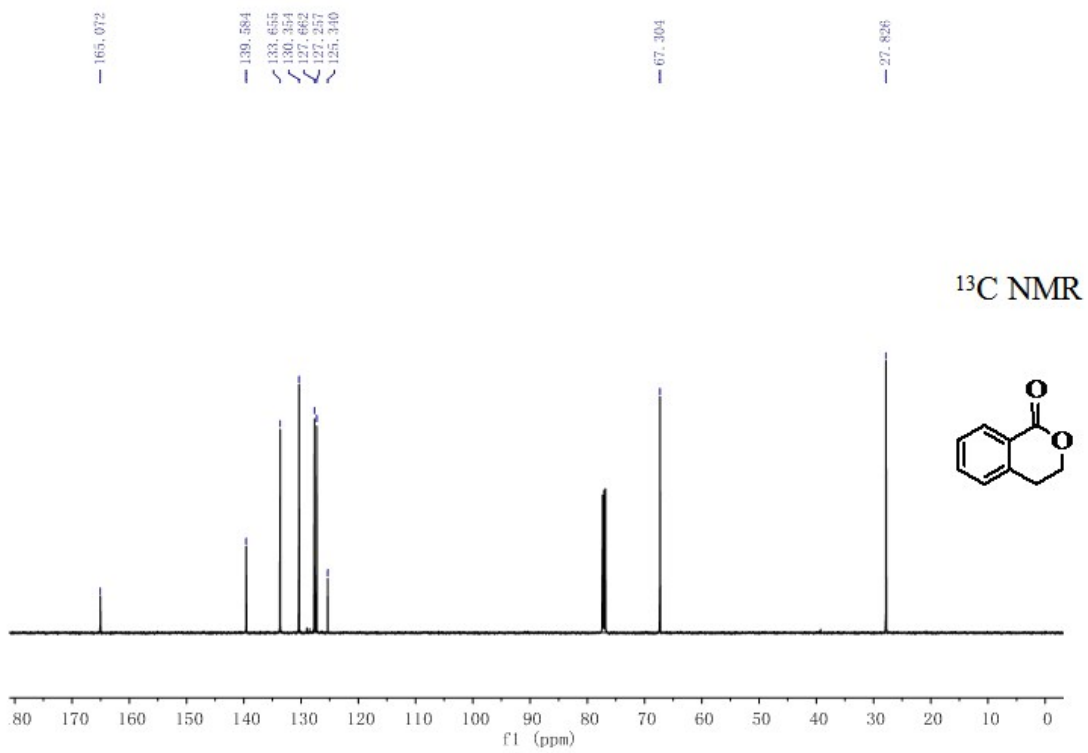
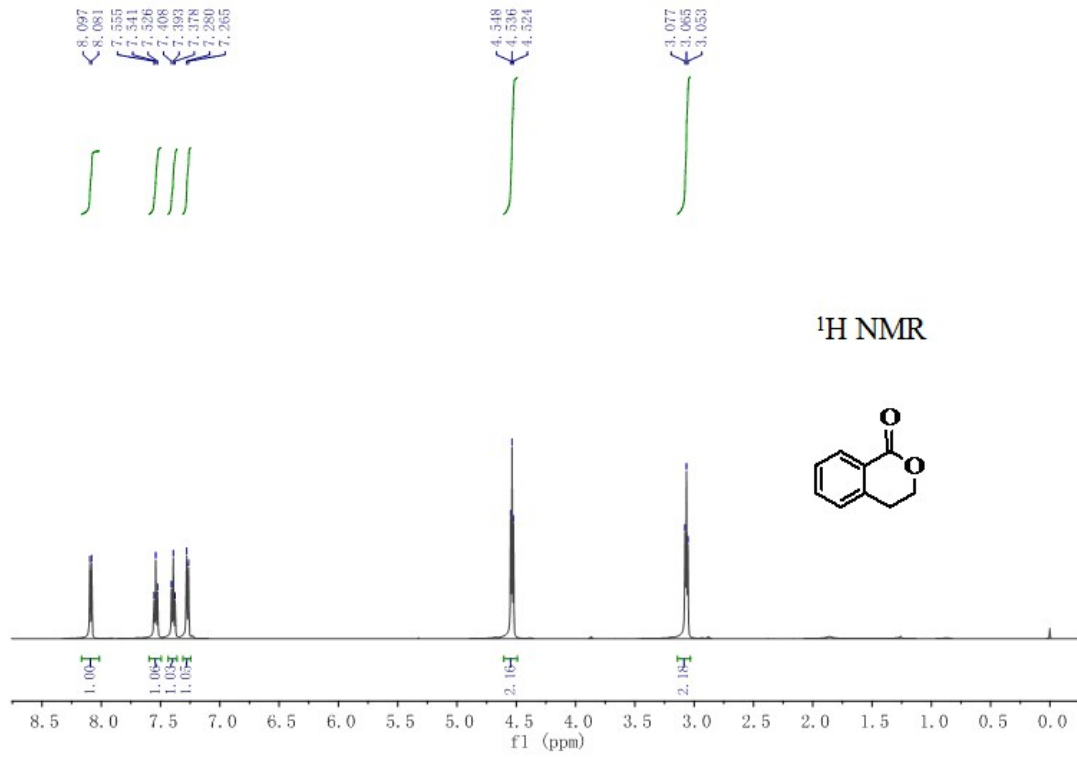


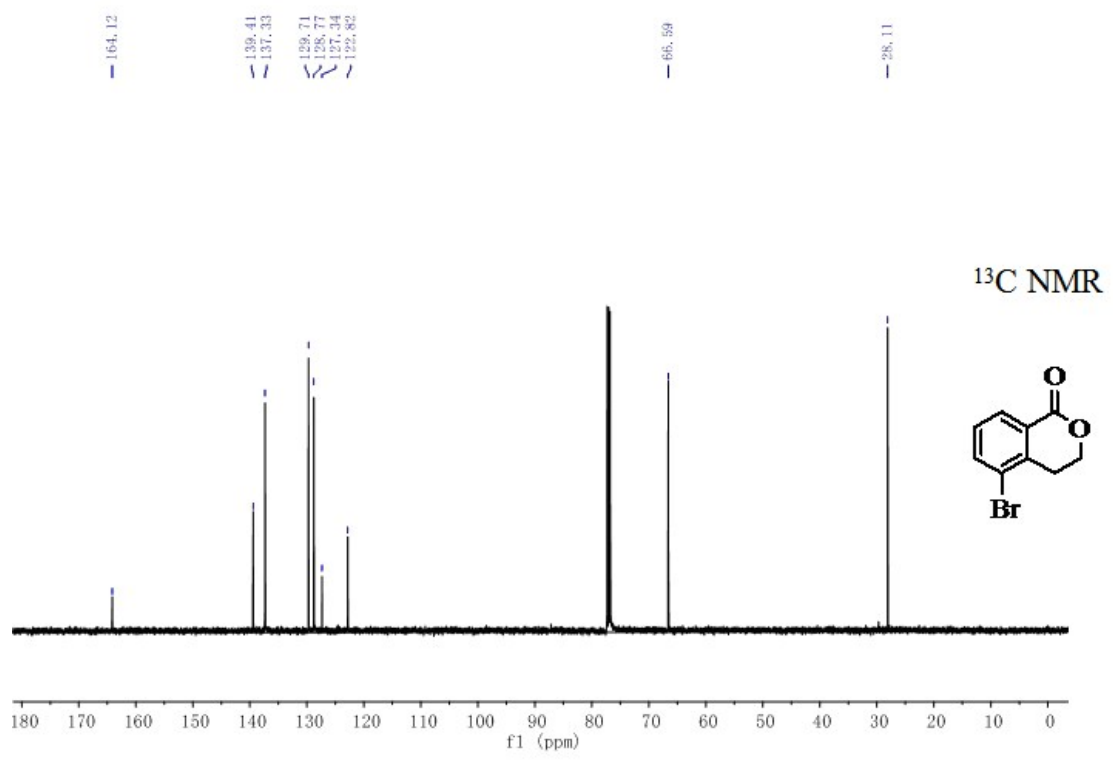
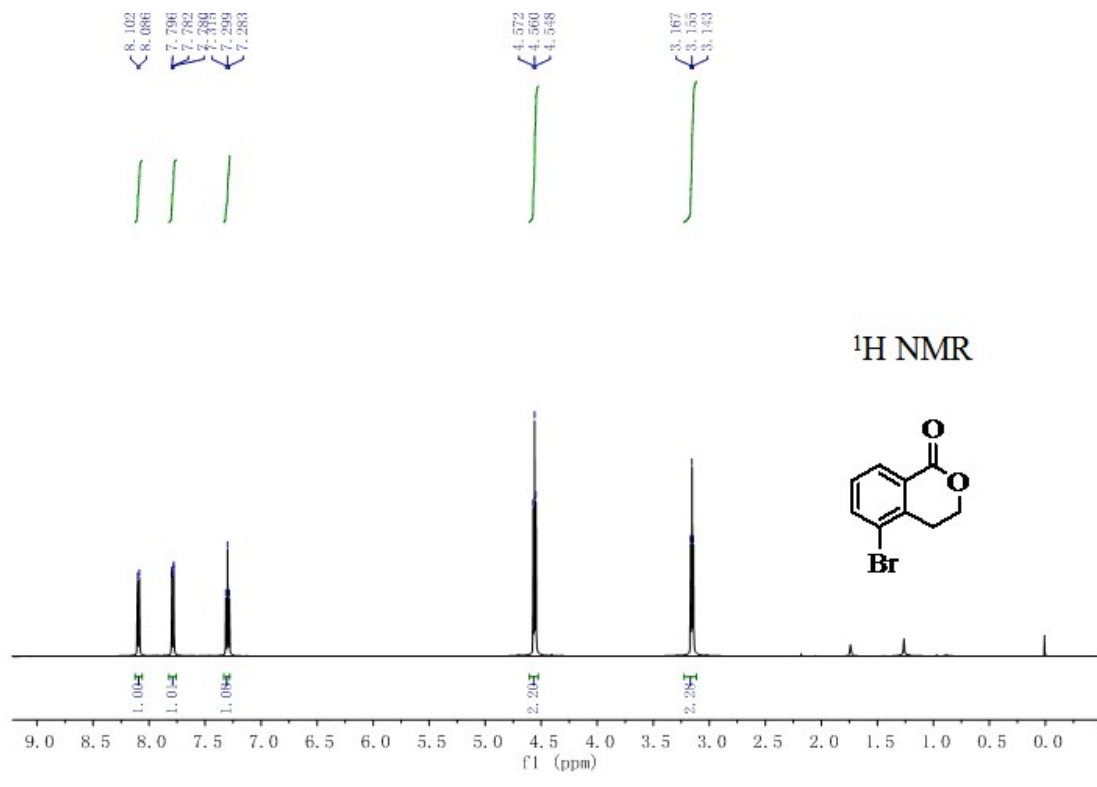


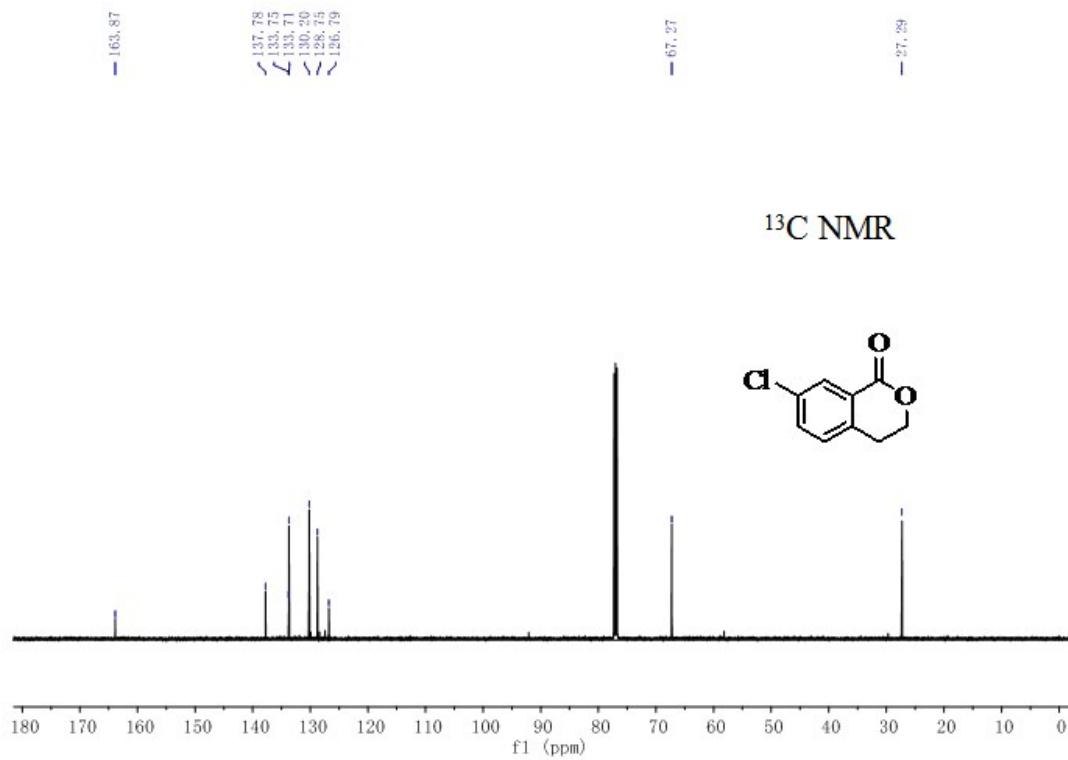
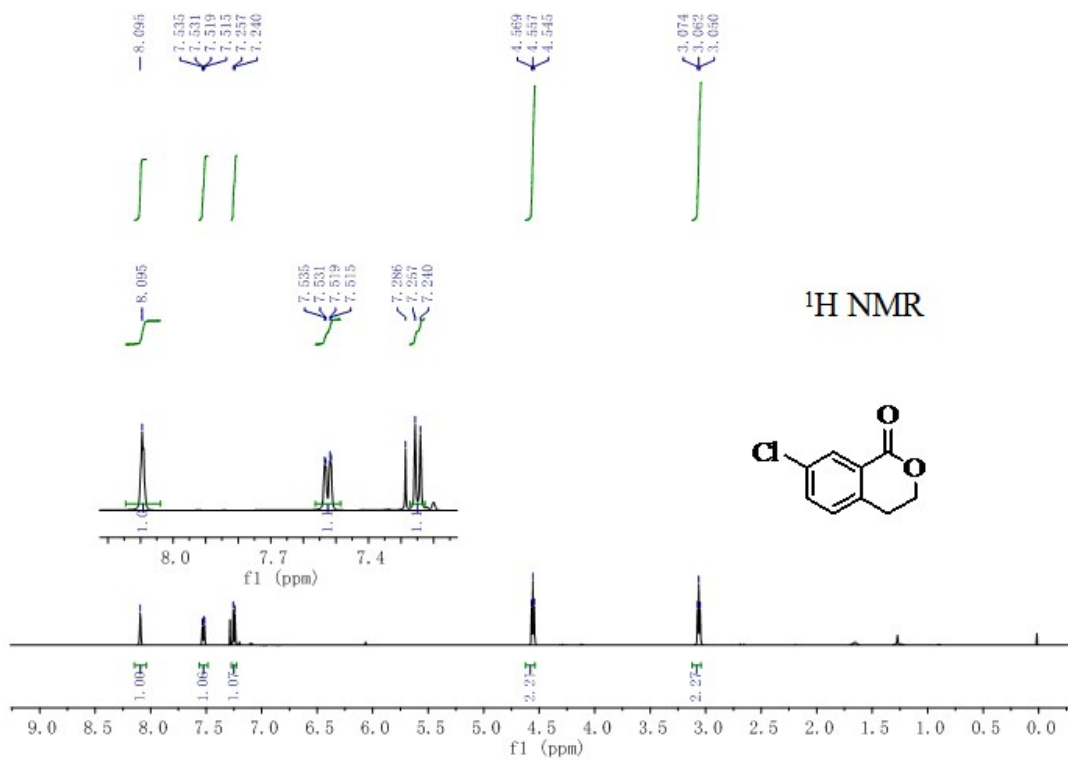


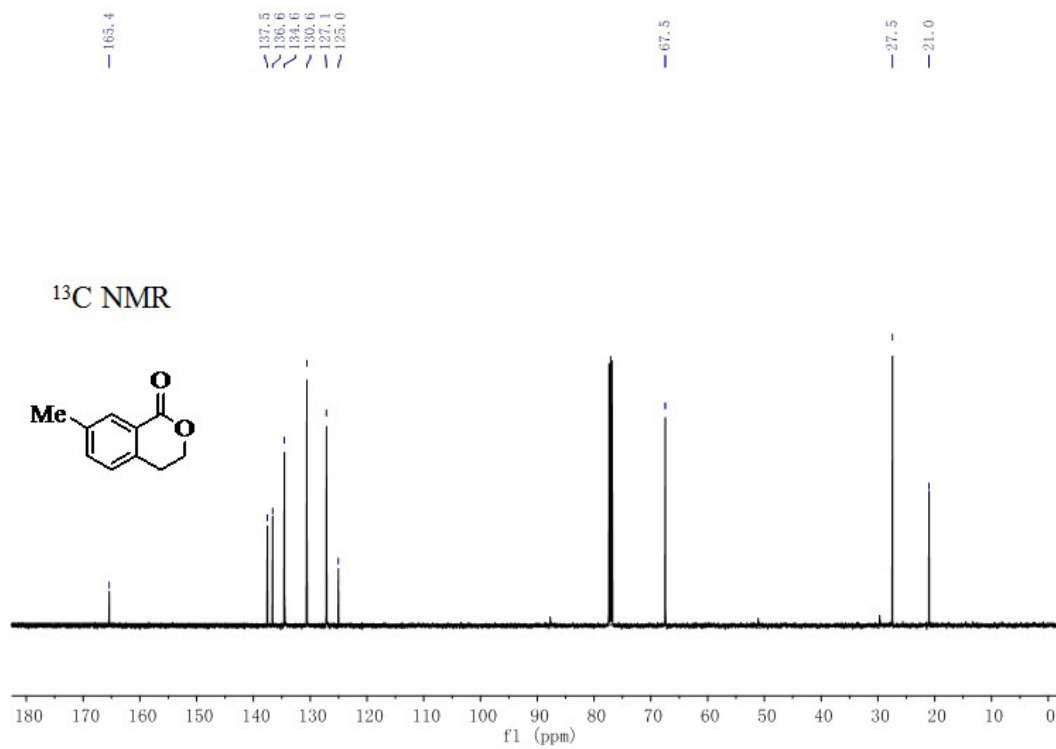
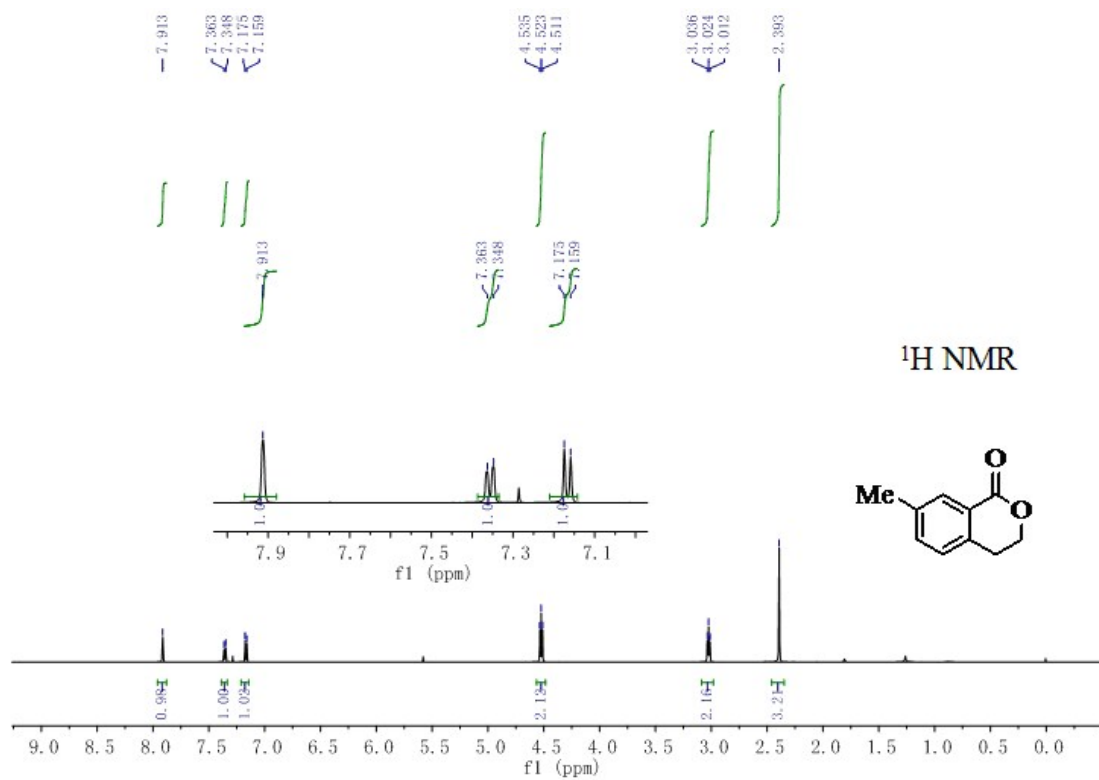




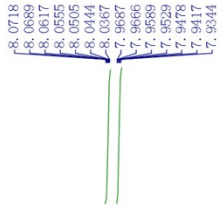




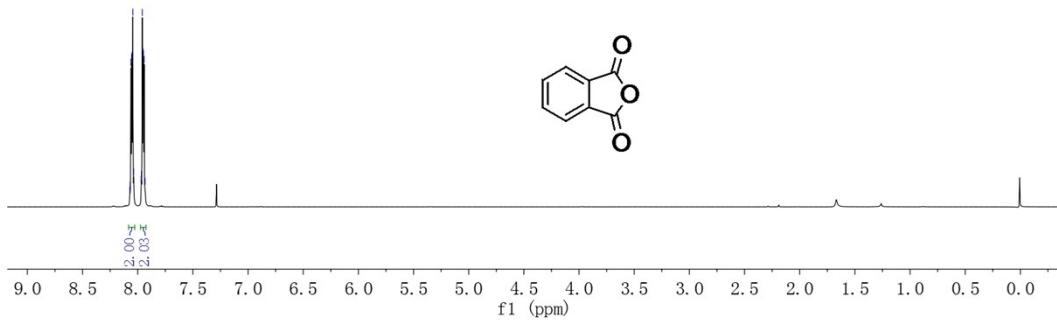








<sup>1</sup>H NMR



<sup>13</sup>C NMR

