

## Supporting Information

### **Diacyl Disulfide: A Reagent for Chemoselective Acylation of Phenols Enabled by 4-(*N,N*-Dimethylamino)pyridine Catalysis**

Hongxin Liu,<sup>†,‡</sup> Yaqian Dang,<sup>†</sup> Yunfei Yuan,<sup>†</sup> Zhifang Xu,<sup>†</sup> Shengxiang Qiu,<sup>†,\*</sup> and Haibo Tan<sup>†,\*</sup>

<sup>†</sup>Program for Natural Product Chemical Biology, Key Laboratory Plant Resources Conservation and Sustainable Utilization, South China Botanical Garden, Chinese Academy of Sciences, Guangzhou 510650, China

<sup>‡</sup>State Key Laboratory of Applied Microbiology Southern China, Guangdong Provincial Key Laboratory of Microbial Culture Collection and Application, Guangdong Open Laboratory of Applied Microbiology, Guangdong Institute of Microbiology, Guangzhou 510070, China

Tel: +86-20-37081190; E-mails: sxqiu@scbg.ac.cn, tanhaibo@scbg.ac.cn.

## **Table of contents**

**(79 pages)**

Abbreviations	S3
General information	S4
General procedure for synthesis of diacyl disulfides <b>6</b>	S5
Characterization spectra data of compounds <b>6</b>	S6
General procedure for acylation of phenols	S10
Characterization spectra data of compounds <b>3</b>	S10
Characterization spectra data of compounds <b>5</b>	S11
Characterization spectra data of compounds <b>7</b>	S14
Characterization spectra data of compounds <b>9</b>	S19
Characterization spectra data of compounds <b>12</b>	S23
General procedure for acylation of aliphatic alcohols <b>10</b>	S24
Characterization spectra data of compounds <b>11</b>	S25
Procedure for acylation with acyl chlorides or acid anhydrides	S29
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of <b>3</b> and <b>6</b>	S30
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of <b>5</b>	S41
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of <b>7</b>	S50
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of <b>9</b>	S60
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of <b>11</b>	S69
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of <b>12</b>	S78
<sup>1</sup> H NMR detections of the crude reaction mixtures	S79

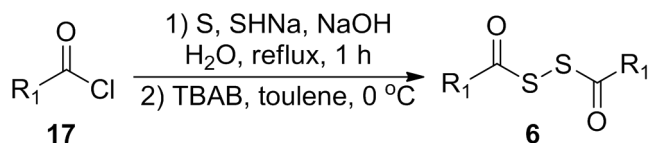
## Abbreviations

Ac	Acetyl
ACN	Acetonitrile
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DMAP	4-( <i>N,N</i> -Dimethylamino)pyridine
THF	Tetrahydrofuran
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
TBAB	Tetrabutyl ammonium bromide
Tol	<i>p</i> -Tolyl
Ph	Phenyl
HRMS	High resolution mass spectroscopy
NMR	Nuclear magnetic resonance
HPLC	High performance liquid chromatography
rt	Room temperature
ESI	Electron spray ionization
TLC	Thin layer chromatography

## General Information

All reactions were carried out under an air atmosphere with dry solvents unless otherwise noted. All of reagents were purchased at highly commercial quality and used without further purification. Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Silica gel (ZCX-II, 200-300 mesh) used for flash column chromatography was purchased from Qing Dao Hai Yang Chemical Industry Co. of China.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Brüker Advance 500 ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 125 MHz). Chemical shifts reported in parts per million relative to  $\text{CDCl}_3$  ( $^1\text{H}$  NMR; 7.27 ppm,  $^{13}\text{C}$  NMR; 77.00 ppm),  $\text{CD}_3\text{OD}$  ( $^1\text{H}$  NMR; 3.33 ppm,  $^{13}\text{C}$  NMR; 47.60 ppm), and  $\text{C}_3\text{D}_6\text{O}$  ( $^1\text{H}$  NMR; 2.88 ppm,  $^{13}\text{C}$  NMR; 28.96 ppm). Mass spectrometric data were obtained using ABI-Q Star Elite high resolution mass spectrometer. Anhydrous THF was distilled from sodium-benzophenone until a deep blue color persisited, acetonitrile (ACN), DCE, and DCM was distilled from calcium hydride. Yields referred to chromatographically purified products unless otherwise stated. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

## General procedure for synthesis of diacyl disulfides **6**



### For 0.5-gram scale synthesis of diacyl disulfides:

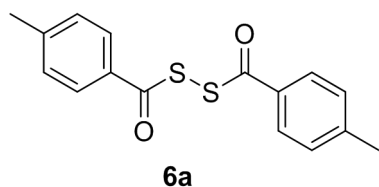
A flame-dried 10 mL flask was charged with sodium hydrosulfide hydrate (160 mg, 2.0 mmol, 70%) and sulfur powder (64 mg 2.0 mmol). 2.0 mL water was added in one portion followed by NaOH (80 mg 2.0 mmol). The mixture was refluxed for 1 h to prepare the aqueous solution of disodium sulfide in situ. After cooling the mixture to 0 °C with ice bath, toluene (2.0 mL) and tetrabutyl ammonium bromide (64 mg, 0.2 mmol) were added and stirred for another 10 min. Then, acetyl chloride **17** (4.0 mmol) was carefully added dropwise. After the completion of the dropwise addition, the mixture was allowed to stir at room temperature for another 1 h. The mixture was poured into water (5 mL), extracted with EtOAc (4 x 5 mL), washed with 1 N NaOH (10 mL) and brine (10 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude organic phase was concentrated in vacuum. The result crude product could then be successfully purified by recrystallization from methanol or flash column chromatography (silica gel, hexane/EtOAc = 30:1), to afford the corresponding diacyl disulfide product **6**.

### Example for 10-gram scale synthesis of diacyl disulfide:

A flame-dried 10 mL flask was charged with sodium hydrosulfide hydrate (3.2 g, 40 mmol, 70%) and sulfur powder (1.28 g, 40 mmol). 40.0 mL water was added in one portion followed by NaOH (1.6 g 40 mmol). The mixture was refluxed for 1 h to prepare the aqueous solution of disodium sulfide in situ. After cooling the mixture to 0 °C with ice bath, toluene (40.0 mL) and tetrabutyl ammonium bromide (1.28 g, 4 mmol) were added and stirred for another 10 min. Then, 4-Methylbenzoic chloride **17** (12.3 g, 80 mmol) was carefully added dropwise. After the completion of the dropwise addition, the mixture was allowed to stir at room temperature for another 1 h.

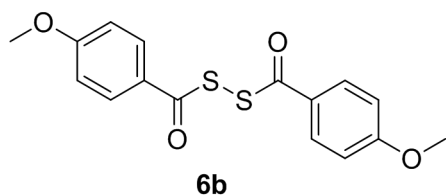
The mixture was poured into water (50 mL), extracted with EtOAc (4 x 50 mL), washed with 1 N NaOH (100 mL) and brine (100 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude organic phase was concentrated in vacuum. The result crude product was then recrystallized from methanol (50 mL), filtrated and washed with 10 mL methanol, recrystallization was repeated to give the pure diacyl disulfide product **6a** (9.8 g, 81% yield).

### Characterization spectra data of compounds 6



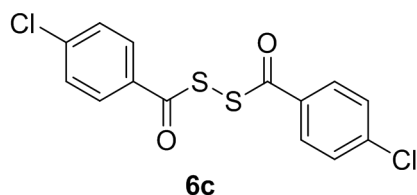
#### ***4-Methylbenzoic dithioperoxyanhydride 6a:***

Following the typical procedure, **6a** was obtained in 83% yield (503 mg) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.00 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 2.46 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 185.7, 145.4, 132.7, 129.6, 128.2, 21.8. HRMS (ESI): calculated for C<sub>16</sub>H<sub>15</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>, [M + H<sup>+</sup>] 303.0513, found 303.0495.



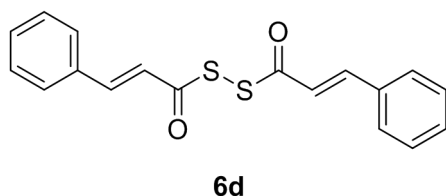
#### ***4-Methoxybenzoic dithioperoxyanhydride 6b:***

Following the typical procedure, **6b** was obtained in 89% yield (594 mg) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.07 (m, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 184.6, 164.5, 130.4, 128.0, 114.1, 55.6. HRMS (ESI): calculated for C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup>, [M - H<sup>+</sup>] 333.0261, found 333.0775.



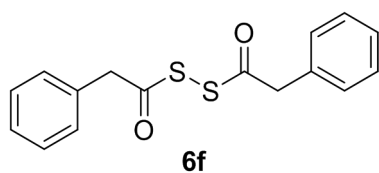
***4-Chlorobenzoic dithioperoxyanhydride 6c:***

Following the typical procedure, **6c** was obtained in 80% yield (545 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.03 (m, 2H), 7.53 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 184.9, 141.1, 133.5, 131.9, 129.4. HRMS (ESI): calculated for  $\text{C}_{14}\text{H}_9\text{Cl}_2\text{O}_2\text{S}_2^+$ ,  $[\text{M} + \text{H}^+]$  342.9421, found 342.9965.



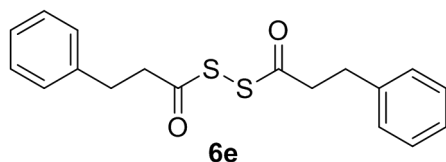
***cinnamic dithioperoxyanhydride 6d:***

Following the typical procedure, **6d** was obtained in 87% yield (567 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.80 (d,  $J$  = 15.8 Hz, 2H), 7.61 (dd,  $J$  = 7.6, 1.6 Hz, 4H), 7.54-7.40 (m, 6H), 6.92 (d,  $J$  = 15.8 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 184.2, 144.1, 133.6, 131.3, 129.1, 128.7, 122.0. HRMS (ESI): calculated for  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{S}_2^+$ ,  $[\text{M} + \text{H}^+]$  327.0513, found 327.0487.



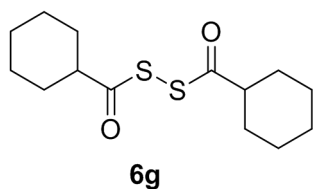
***3-Phenylethanoic dithioperoxyanhydride 6f:***

Following the typical procedure, **6f** was obtained in 80% yield (514 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.35 (m, 5H), 4.02 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 191.4, 132.1, 129.8, 128.9, 127.9, 49.2. HRMS (ESI): calculated for  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{S}_2^+$ ,  $[\text{M} + \text{H}^+]$  303.0513, found 303.0530.



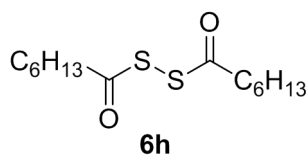
***3-Phenylpropanoic dithioperoxyanhydride 6e:***

Following the typical procedure, **6e** was obtained in 78% yield (514 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.34 (t,  $J$  = 7.4 Hz, 2H), 7.26 (m, 3H), 3.08 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.6, 139.3, 128.6, 128.3, 126.6, 44.3, 31.1. HRMS (ESI): calculated for  $\text{C}_{18}\text{H}_{19}\text{O}_2\text{S}_2^+$ ,  $[\text{M} + \text{H}^+]$  331.0826, found 331.0809.



***Cyclohexanecarboxylic dithioperoxyanhydride 6g:***

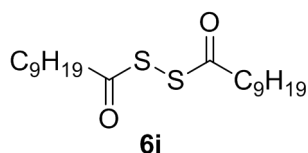
Following the typical procedure, **6g** was obtained in 75% yield (429 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.73 (tt,  $J$  = 11.3, 3.6 Hz, 1H), 2.03 (m, 2H), 1.82 (m, 2H), 1.68 (m, 1H), 1.54 (m, 1H), 1.30 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.5, 51.9, 29.4, 25.4, 25.3. HRMS (ESI): calculated for  $\text{C}_{14}\text{H}_{23}\text{O}_2\text{S}_2^+$ ,  $[\text{M} + \text{H}^+]$  287.1139, found 287.1124.



***Heptanoic dithioperoxyanhydride 6h:***

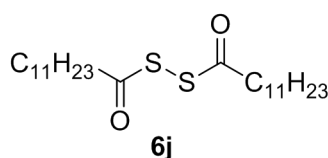
Following the typical procedure, **6h** was obtained in 81% yield (469 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.76 (q,  $J$  = 6.9 Hz, 2H), 1.73 (dt,  $J$  = 15.1, 7.5 Hz, 2H), 1.47-1.26 (m, 6H), 0.90 (t,  $J$  = 6.9 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 193.4, 42.9, 31.3, 28.5, 25.4, 22.4, 13.9. HRMS (ESI): calculated for  $\text{C}_{14}\text{H}_{27}\text{O}_2\text{S}_2^+$ ,  $[\text{M} + \text{H}^+]$  291.1452, found 291.1427.





***decanoic dithioperoxyanhydride 6i:***

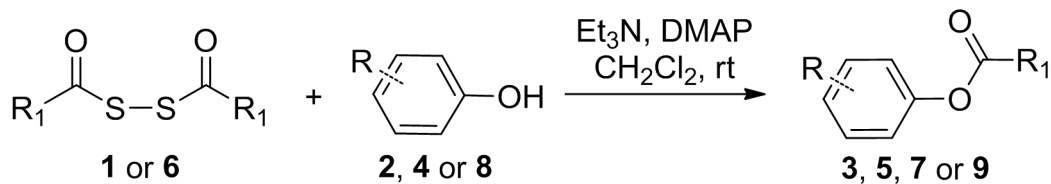
Following the typical procedure, **6i** was obtained in 82% yield (613 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.75 (t,  $J$  = 7.5 Hz, 2H), 1.73 (m, 2H), 1.33 (m, 12H), 0.89 (t,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 193.4, 42.8, 31.8, 29.3, 29.2, 29.1, 28.8, 25.4, 22.6, 14.0. HRMS (ESI): calculated for  $\text{C}_{20}\text{H}_{39}\text{O}_2\text{S}_2^+$ ,  $[\text{M} + \text{H}^+]$  375.2391, found 375.2386.



***dodecanoic dithioperoxyanhydride 6j:***

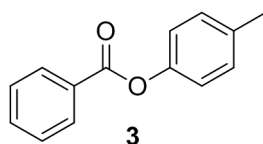
Following the typical procedure, **6j** was obtained in 72% yield (619 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.76 (t,  $J$  = 7.5 Hz, 2H), 1.74 (dt,  $J$  = 15.0, 7.4 Hz, 2H), 1.29 (d,  $J$  = 12.1 Hz, 16H), 0.90 (t,  $J$  = 6.9 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 193.5, 42.9, 31.9, 29.6, 29.5, 29.3, 29.3, 29.1, 28.8, 25.5, 22.7, 14.1. HRMS (ESI): calculated for  $\text{C}_{24}\text{H}_{47}\text{O}_2\text{S}_2^+$ ,  $[\text{M} + \text{H}^+]$  431.3017, found 431.2989.

### General procedure for acylation of phenols



A flame-dried 10 mL flask was charged with diacyl disulfides **6** (0.5 mmol), phenol **4** (0.5 mmol) and DCM (5 mL). Et<sub>3</sub>N (1.0 mmol, 75 mg, 0.1 mL) and DMAP (0.1 mmol, 12 mg) was added to the mixture. The mixture was allowed to stir at room temperature for 0.5-3 h until all of the starting material disappeared. Then, the mixture was poured into water (5 mL), extracted with EtOAc (4 x 5 mL), washed with 1 N HCl (10 mL) and brine (10 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude organic phase was concentrated in vacuo and purified with a short flash column chromatography (silica gel, hexane/EtOAc = 20:1) to afford the corresponding product **3**, **5**, **7** or **9**.

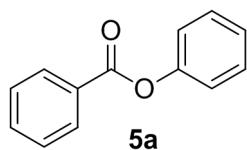
### Characterization spectra data of compounds **3**



#### *p*-Tolyl benzoate **3**:

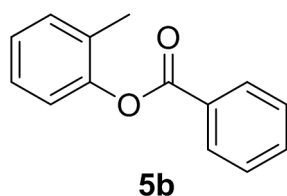
Following the typical procedure, 2 h, **3** was obtained in 94% yield (99.6 mg) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.25 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.66 (m, 1H), 7.54 (m, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.14 (m, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 165.3, 148.7, 135.5, 133.4, 130.1, 130.0, 129.7, 128.5, 121.3, 20.9. HRMS (ESI): calculated for C<sub>14</sub>H<sub>13</sub>O<sub>2</sub><sup>+</sup>, [*M* + H<sup>+</sup>] 213.0916, found 213.0575.

## Characterization spectra data of compounds 5



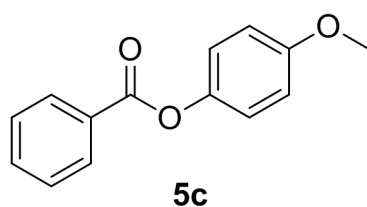
### *Phenyl benzoate 5a:*

Following the typical procedure, 2 h, **5a** was obtained in 92% yield (91.1 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.26 (dd,  $J$  = 8.0, 0.8 Hz, 2H), 7.67 (m, 1H), 7.55 (t,  $J$  = 7.8 Hz, 2H), 7.48 (t,  $J$  = 7.8 Hz, 2H), 7.32 (t,  $J$  = 7.4 Hz, 1H), 7.27 (dd,  $J$  = 6.0, 5.2 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.1, 150.9, 122.5, 130.1, 129.4, 128.5, 125.8, 121.7. HRMS (ESI): calculated for  $\text{C}_{13}\text{H}_{11}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  199.0759, found 199.0749.



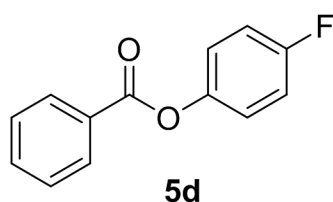
### *o*-Tolyl benzoate 5b:

Following the typical procedure, 3 h, **5b** was obtained in 91% yield (96.5 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.27 (dd,  $J$  = 8.3, 1.2 Hz, 2H), 7.68 (m, 1H), 7.56 (dd,  $J$  = 11.0, 4.5 Hz, 2H), 7.30 (dt,  $J$  = 7.5, 4.5 Hz, 2H), 7.23 (dd,  $J$  = 7.5, 1.2 Hz, 1H), 7.18 (dd,  $J$  = 8.3, 1.0 Hz, 1H), 2.28 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.8, 149.5, 133.5, 131.2, 130.3, 130.1, 129.5, 128.6, 127.0, 126.1, 122.0, 16.2. HRMS (ESI): calculated for  $\text{C}_{14}\text{H}_{13}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  213.0916, found 213.1136.



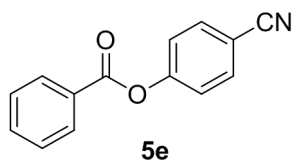
### *4*-Methoxyphenyl benzoate 5c:

Following the typical procedure, 2 h, **5c** was obtained in 96% yield (109.4 mg) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.23 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.65 (m, 1H), 7.54 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.98 (m, 2H), 3.85 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 165.5, 157.3, 144.4, 135.5, 130.1, 129.6, 129.3, 128.5, 122.4, 114.5, 55.6. HRMS (ESI): calculated for C<sub>14</sub>H<sub>13</sub>O<sub>3</sub><sup>+</sup>, [M + H<sup>+</sup>] 229.0865, found 229.0877.



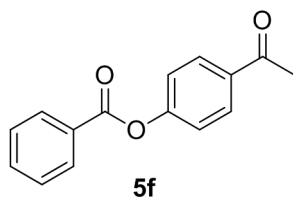
***4-Fluorophenyl benzoate 5d:***

Following the typical procedure, 1 h, **5d** was obtained in 93% yield (100.4 mg) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.23 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.67 (m, 1H), 7.55 (dd, *J* = 11.0, 4.5 Hz, 2H), 7.22 (m, 2H), 7.15 (ddd, *J* = 12.7, 6.4, 2.9 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 165.2, 161.3, 159.3, 146.8, 146.7, 133.7, 130.2, 129.3, 128.6, 123.1, 123.1, 116.2, 116.0. HRMS (ESI): calculated for C<sub>13</sub>H<sub>10</sub>FO<sub>2</sub><sup>+</sup>, [M + H<sup>+</sup>] 217.0665, found 217.0933.



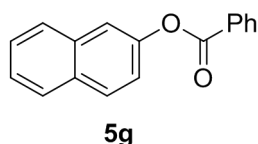
***4-Cyanophenyl benzoate 5e:***

Following the typical procedure, 0.5 h, **5e** was obtained in 87% yield (97.0 mg) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.22 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.69 (m, 1H), 7.56 (dd, *J* = 11.1, 4.5 Hz, 2H), 7.40 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 164.3, 154.3, 134.2, 133.8, 130.3, 128.8, 128.7, 123.0, 118.3, 109.9. HRMS (ESI): calculated for C<sub>14</sub>H<sub>10</sub>NO<sub>2</sub><sup>+</sup>, [M + H<sup>+</sup>] 224.0712, found 224.0698.



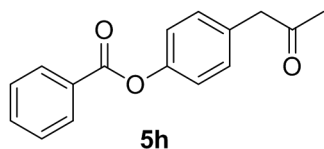
***4-Acetylphenyl benzoate 5f:***

Following the typical procedure, 1 h, **5f** was obtained in 90% yield (108.0 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.23 (dd,  $J$  = 8.3, 1.2 Hz, 2H), 8.07 (dd,  $J$  = 8.3, 1.2 Hz, 2H), 7.67 (m, 1H), 7.55 (m, 2H), 7.35 (m, 2H), 2.64 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.8, 164.6, 154.7, 134.8, 133.9, 130.2, 130.0, 129.0, 128.6, 121.9, 26.6. HRMS (ESI): calculated for  $\text{C}_{15}\text{H}_{13}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  241.0865, found 241.0869.



***Naphthalen-2-yl benzoate 5g:***

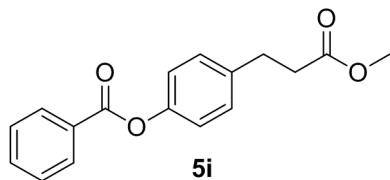
Following the typical procedure, 2 h, **5g** was obtained in 97% yield (120.3 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.30 (dd,  $J$  = 8.3, 1.2 Hz, 2H), 7.95-7.85 (m, 3H), 7.74 (d,  $J$  = 2.2 Hz, 1H), 7.69 (t,  $J$  = 7.5 Hz, 1H), 7.65-7.45 (m, 4H), 7.40 (dd,  $J$  = 8.8, 2.3 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.3, 148.6, 133.8, 133.6, 131.5, 130.2, 129.6, 129.4, 128.6, 127.8, 127.7, 126.6, 125.7, 121.2, 118.7. HRMS (ESI): calculated for  $\text{C}_{17}\text{H}_{13}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  249.0916, found 249.1015.



***4-(2-Oxopropyl)phenyl benzoate 5h:***

Following the typical procedure, 2 h, **5h** was obtained in 91% yield (115.6 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.22 (dd,  $J$  = 8.2, 1.0 Hz, 2H), 7.65 (dd,  $J$  = 11.7, 4.3 Hz, 1H), 7.53 (t,  $J$  = 8.2 Hz, 2H), 7.27 (m, 2H), 7.15 (m, 2H), 2.94 (t,  $J$  = 7.6 Hz, 2H), 2.80 (t,  $J$  = 7.6 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 207.6, 165.2,

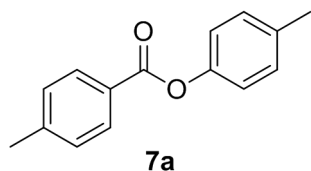
149.2, 138.6, 133.5, 130.1, 129.5, 129.3, 128.5, 121.6, 45.0, 30.0, 29.0. HRMS (ESI): calculated for  $C_{16}H_{15}O_3^+$ ,  $[M + H^+]$  255.1021, found 255.1087.



***4-(3-Methoxy-3-oxopropyl)phenyl benzoate 5i:***

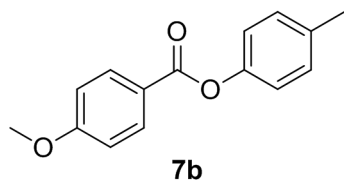
Following the typical procedure, 2 h, **5i** was obtained in 95% yield (134.9 mg) as white solid.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 8.22 (dd,  $J$  = 8.3, 1.3 Hz, 1H), 7.65 (m, 1H), 7.53 (m, 2H), 7.28 (m, 2H), 7.16 (m, 2H), 3.71 (s, 3H), 3.01 (t,  $J$  = 7.8 Hz, 2H), 2.68 (t,  $J$  = 7.8 Hz, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 173.2, 165.2, 149.3, 138.1, 133.5, 130.1, 129.6, 129.3, 128.5, 121.7, 51.6, 35.6, 30.3. HRMS (ESI): calculated for  $C_{17}H_{17}O_4^+$ ,  $[M + H^+]$  285.1127, found 285.1139.

**Characterization spectra data of compounds 7**



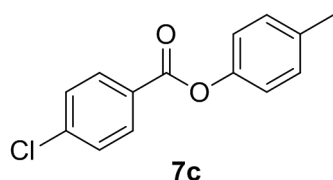
***p-Tolyl 4-methylbenzoate 7a:***

Following the typical procedure, 2 h, **7a** was obtained in 93% yield (105.1 mg) as white solid.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 8.12 (d,  $J$  = 8.2 Hz, 2H), 7.33 (d,  $J$  = 8.0 Hz, 2H), 7.25 (d,  $J$  = 8.2 Hz, 2H), 7.12 (m, 2H), 2.48 (s, 3H), 2.40 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 1165.4, 148.8, 144.3, 135.4, 130.2, 129.9, 129.2, 126.9, 121.4, 21.7, 20.9. HRMS (ESI): calculated for  $C_{15}H_{15}O_2^+$ ,  $[M + H^+]$  227.1072, found 227.1065.



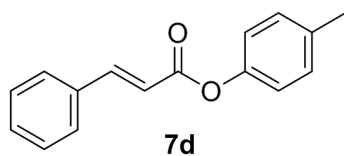
***p*-Tolyl 4-methoxybenzoate 7b:**

Following the typical procedure, 3 h, **7b** was obtained in 96% yield (116.2 mg) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.18 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 165.1, 163.8, 148.8, 135.3, 132.2, 129.9, 122.0, 121.4, 113.8, 113.6, 55.5, 20.9. HRMS (ESI): calculated for C<sub>15</sub>H<sub>15</sub>O<sub>3</sub><sup>+</sup>, [M + H<sup>+</sup>] 243.1021, found 243.1011.



***p*-Tolyl 4-chlorobenzoate 7c:**

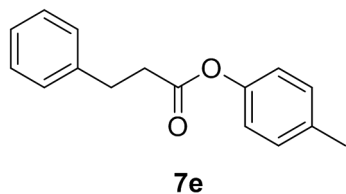
Following the typical procedure, 1.5 h, **7c** was obtained in 90% yield (110.7 mg) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.16 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.16-7.08 (m, 2H), 2.41 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 164.5, 148.5, 140.0, 135.7, 131.5, 130.0, 128.9, 128.1, 121.2, 20.9. HRMS (ESI): calculated for C<sub>14</sub>H<sub>12</sub>ClO<sub>2</sub><sup>+</sup>, [M + H<sup>+</sup>] 247.0526, found 247.0518.



***p*-Tolyl cinnamate 7d:**

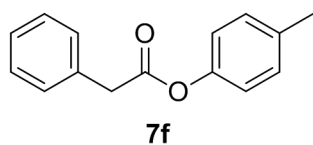
Following the typical procedure, 2 h, **7d** was obtained in 94% yield (111.9 mg) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.89 (d, *J* = 16.0 Hz, 1H), 7.61 (m, 2H), 7.45 (dd, *J* = 6.7, 3.5 Hz, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 2.39 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 165.6, 148.5,

146.4, 135.4, 134.2, 130.6, 129.9, 129.0, 128.3, 127.4, 121.3, 117.4, 20.9. HRMS (ESI): calculated for  $C_{16}H_{15}O_2^+$ ,  $[M + H^+]$  239.1072, found 239.1080.



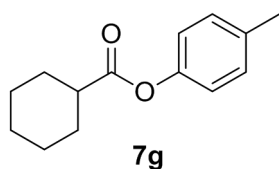
***p*-Tolyl 3-phenylpropanoate 7e:**

Following the typical procedure, 1 h, **7e** was obtained in 95% yield (114.0 mg) as white solid.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 7.44-7.25 (m, 5H), 7.22 (d,  $J$  = 8.4 Hz, 2H), 6.96 (d,  $J$  = 8.2 Hz, 2H), 3.14 (t,  $J$  = 7.7 Hz, 2H), 2.94 (t,  $J$  = 7.7 Hz, 2H), 2.40 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 171.5, 148.4, 140.1, 135.3, 129.8, 128.5, 126.4, 121.1, 35.9, 30.9, 20.8. HRMS (ESI): calculated for  $C_{16}H_{17}O_2^+$ ,  $[M + H^+]$  241.1229, found 241.1218.



***p*-Tolyl 2-phenylacetate 7f:**

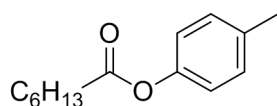
Following the typical procedure, 2 h, **7f** was obtained in 90% yield (101.7 mg) as white solid.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 7.46-7.37 (m, 4H), 7.34 (d,  $J$  = 6.9 Hz, 1H), 7.18 (d,  $J$  = 8.2 Hz, 2H), 6.97 (m, 2H), 3.88 (s, 2H), 2.36 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 170.2, 148.5, 135.6, 133.5, 129.3, 128.7, 127.3, 121.1, 41.4, 20.8. HRMS (ESI): calculated for  $C_{15}H_{15}O_2^+$ ,  $[M + H^+]$  227.1072, found 227.1086.



***p*-Tolyl cyclohexanecarboxylate 7g:**



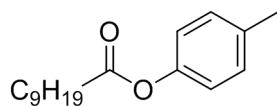
Following the typical procedure, 3 h, **7g** was obtained in 91% yield (99.2 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.18 (d,  $J$  = 8.4 Hz, 2H), 6.96 (d,  $J$  = 8.4 Hz, 2H), 2.56 (m, 1H), 2.36 (s, 3H), 2.08 (dd,  $J$  = 13.1, 2.9 Hz, 2H), 1.84 (m, 2H), 1.71 (m, 1H), 1.61 (m, 3H), 1.48-1.24 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 174.8, 148.6, 135.2, 129.8, 121.2, 43.2, 29.0, 25.7, 25.4, 20.8. HRMS (ESI): calculated for  $\text{C}_{14}\text{H}_{19}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  219.1385, found 219.1379.



**7h**

***p*-Tolyl heptanoate **7h**:**

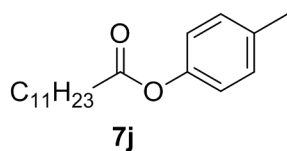
Following the typical procedure, 1 h, **7h** was obtained in 96% yield (105.6 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.19 (d,  $J$  = 8.2 Hz, 2H), 6.98 (m, 2H), 2.56 (t,  $J$  = 7.5 Hz, 2H), 2.36 (s, 3H), 1.77 (m, 2H), 1.50-1.27 (m, 7H), 0.94 (dd,  $J$  = 9.2, 4.6 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 172.5, 148.5, 135.3, 129.9, 121.2, 34.4, 31.4, 28.8, 24.9, 22.5, 20.8, 14.0. HRMS (ESI): calculated for  $\text{C}_{14}\text{H}_{21}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  221.1542, found 221.1541.



**7i**

***p*-Tolyl decanoate **7i**:**

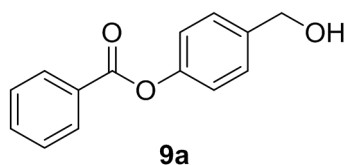
Following the typical procedure, 0.5 h, **7i** was obtained in 94% yield (123.1 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.19 (d,  $J$  = 8.1 Hz, 2H), 6.98 (d,  $J$  = 8.4 Hz, 2H), 2.56 (t,  $J$  = 7.5 Hz, 2H), 2.36 (s, 3H), 1.77 (dd,  $J$  = 15.1, 7.5 Hz, 2H), 1.50-1.23 (m, 14H), 0.91 (t,  $J$  = 6.9 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 172.5, 148.5, 135.3, 129.9, 121.2, 34.4, 31.8, 29.4, 29.2, 29.1, 25.0, 22.6, 20.8, 14.1. HRMS (ESI): calculated for  $\text{C}_{17}\text{H}_{27}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  263.2011, found 263.2079.



***p*-Tolyl decanoate 7j:**

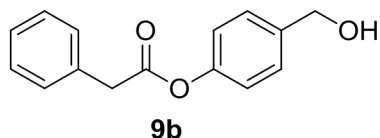
Following the typical procedure, 0.5 h, **7j** was obtained in 95% yield (137.8 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.19 (d,  $J$  = 8.1 Hz, 1H), 6.98 (d,  $J$  = 8.4 Hz, 1H), 2.56 (t,  $J$  = 7.5 Hz, 1H), 2.36 (s, 2H), 1.82-1.73 (m, 1H), 1.49-1.20 (m, 11H), 0.91 (t,  $J$  = 6.9 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 172.5, 148.5, 135.3, 129.9, 121.2, 34.4, 31.9, 29.6, 29.4, 29.2, 29.1, 25.0, 22.6, 20.8, 14.1. HRMS (ESI): calculated for  $\text{C}_{19}\text{H}_{31}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  291.2324, found 291.2320.

## Characterization spectra data of compounds 9



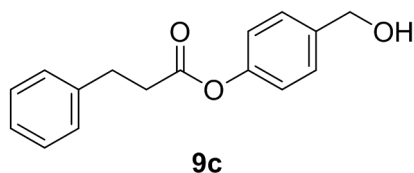
### *4-(Hydroxymethyl)phenyl benzoate 9a:*

Following the typical procedure, 1.5 h, **9a** was obtained in 89% yield (101.5 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.23 (m, 2H), 7.66 (m, 1H), 7.54 (t,  $J$  = 7.8 Hz, 2H), 7.46 (d,  $J$  = 8.5 Hz, 2H), 7.24 (m, 2H), 4.74 (d,  $J$  = 5.2 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.3, 150.4, 138.6, 133.7, 130.2, 129.5, 128.6, 128.2, 121.8, 64.8. HRMS (ESI): calculated for  $\text{C}_{14}\text{H}_{13}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  229.0865, found 229.0852.



### *4-(Hydroxymethyl)phenyl 2-phenylacetate 9b:*

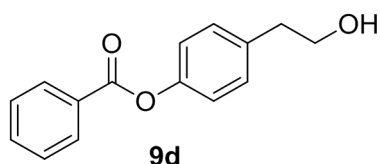
Following the typical procedure, 1 h, **9b** was obtained in 82% yield (99.2 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.48-7.39 (m, 4H), 7.36 (d,  $J$  = 8.5 Hz, 3H), 7.06 (d,  $J$  = 8.5 Hz, 2H), 4.65 (d,  $J$  = 3.1 Hz, 2H), 3.89 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 170.1, 150.0, 138.5, 133.3, 129.3, 129.7, 128.0, 127.3, 121.5, 64.6, 41.3. HRMS (ESI): calculated for  $\text{C}_{15}\text{H}_{15}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  243.1021, found 243.1025.



### *4-(Hydroxymethyl)phenyl 3-phenylpropanoate 9c:*

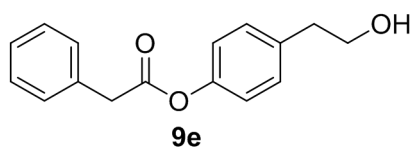
Following the typical procedure, 1 h, **9c** was obtained in 86% yield (110.1 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.36 (m, 4H), 7.28 (t,  $J$  = 8.7 Hz, 3H),

7.02 (m, 2H), 4.70 (s, 2H), 3.10 (t,  $J = 7.7$  Hz, 2H), 2.91 (t,  $J = 7.7$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 171.5, 150.1, 140.1, 138.5, 128.6, 128.4, 128.0, 126.5, 121.6, 64.8, 36.0, 30.9$ . HRMS (ESI): calculated for  $\text{C}_{16}\text{H}_{17}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  257.1178, found 257.1188.



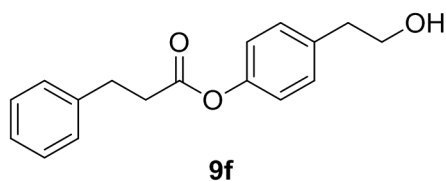
***4-(2-Hydroxyethyl)phenyl benzoate 9d:***

Following the typical procedure, 1.5 h, **9b** was obtained in 88% yield (106.5 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.23$  (dd,  $J = 8.3, 1.2$  Hz, 2H), 7.65 (d,  $J = 7.5$  Hz, 1H), 7.54 (t,  $J = 7.5$  Hz, 2H), 7.30 (t,  $J = 9.2$  Hz, 2H), 7.18 (d,  $J = 8.5$  Hz, 2H), 3.88 (t,  $J = 6.6$  Hz, 2H), 2.91 (t,  $J = 6.6$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 165.4, 149.5, 136.3, 133.6, 130.2, 130.1, 129.6, 128.6, 121.8, 63.6, 38.6$ . HRMS (ESI): calculated for  $\text{C}_{15}\text{H}_{15}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  243.1021, found 243.1277.



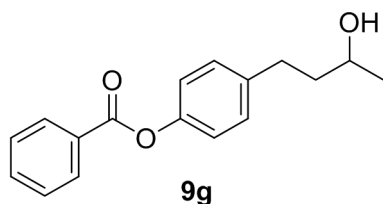
***4-(2-Hydroxyethyl)phenyl 2-phenylacetate 9e:***

Following the typical procedure, 1 h, **9e** was obtained in 85% yield (108.8 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.45\text{--}7.37$  (m, 4H), 7.34 (d,  $J = 6.6$  Hz, 1H), 7.23 (d,  $J = 8.5$  Hz, 2H), 7.07–6.97 (m, 2H), 3.88 (s, 2H), 3.83 (t,  $J = 6.5$  Hz, 2H), 2.85 (t,  $J = 6.5$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 170.3, 149.3, 136.3, 133.5, 130.0, 129.3, 128.8, 127.4, 121.5, 63.5, 41.4, 38.6$ . HRMS (ESI): calculated for  $\text{C}_{16}\text{H}_{17}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  257.1178, found 257.1174.



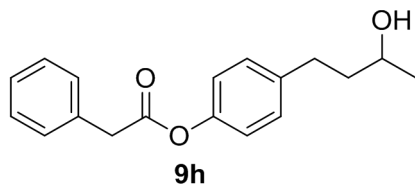
**4-(2-Hydroxyethyl)phenyl 3-phenylpropanoate 9f:**

Following the typical procedure, 0.5 h, **9f** was obtained in 87% yield (117.5 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.5-7.20 (m, 7H), 6.97 (d,  $J$  = 8.2 Hz, 1H), 3.87 (s, 2H), 3.10 (t,  $J$  = 6.2 Hz, 2H), 2.89 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 171.5, 149.2, 140.1, 136.1, 130.0, 128.6, 128.4, 121.6, 63.5, 38.6, 36.0, 31.0. HRMS (ESI): calculated for  $\text{C}_{17}\text{H}_{19}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  271.1334, found 271.1350.



**4-(3-Hydroxybutyl)phenyl benzoate 9g:**

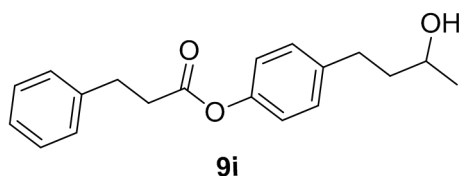
Following the typical procedure, 3 h, **9g** was obtained in 95% yield (128.3 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.23 (m, 2H), 7.66 (m, 1H), 7.53 (dd,  $J$  = 10.7, 4.8 Hz, 2H), 7.28 (m, 2H), 7.16 (m, 2H), 3.86 (dq,  $J$  = 12.4, 6.2 Hz, 1H), 2.81 (m, 1H), 2.72 (ddd,  $J$  = 13.9, 9.3, 7.0 Hz, 1H), 1.81 (m, 2H), 1.27 (d,  $J$  = 6.2 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.3, 149.0, 139.7, 133.5, 130.1, 129.6, 129.3, 128.5, 121.5, 67.3, 40.7, 31.5, 23.6. HRMS (ESI): calculated for  $\text{C}_{18}\text{H}_{21}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  285.1491, found 285.1690.



**4-(3-Hydroxybutyl)phenyl 2-phenylacetate 9h:**

Following the typical procedure, 1 h, **9h** was obtained in 92% yield (131.6 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.40 (m, 4H), 7.33 (dt,  $J$  = 9.3, 4.2 Hz, 1H), 7.20 (d,  $J$  = 8.6 Hz, 2H), 6.99 (d,  $J$  = 8.6 Hz, 2H),

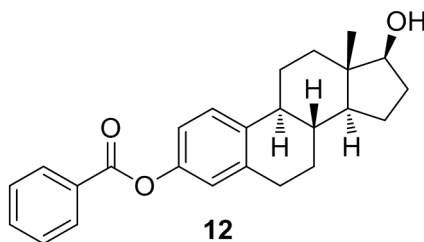
3.87 (s, 2H), 3.83 (dd,  $J = 12.4, 6.2$  Hz, 1H), 2.81-2.72 (m, 1H), 2.67 (ddd,  $J = 13.9, 9.2, 7.1$  Hz, 1H), 1.76 (m, 2H), 1.24 (d,  $J = 6.2$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 170.1, 148.8, 139.7, 135.5, 129.3, 129.2, 128.7, 127.3, 121.2, 67.4, 41.4, 40.8, 31.5, 23.7$ . HRMS (ESI): calculated for  $\text{C}_{17}\text{H}_{19}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  271.1334, found 271.1350.



***4-(3-Hydroxybutyl)phenyl 3-phenylpropanoate 9i:***

Following the typical procedure, 0.5 h, **9i** was obtained in 93% yield (138.2 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.34$  (dd,  $J = 10.2, 4.6$  Hz, 2H), 7.28 (m, 3H), 7.21 (d,  $J = 8.5$  Hz, 2H), 6.94 (m, 2H), 3.84 (dd,  $J = 12.4, 6.2$  Hz, 1H), 3.10 (t,  $J = 7.7$  Hz, 2H), 2.90 (t,  $J = 7.7$  Hz, 2H), 2.77 (m, 1H), 2.68 (ddd,  $J = 13.9, 9.2, 7.1$  Hz, 1H), 1.77 (m, 2H), 1.25 (d,  $J = 6.2$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 171.5, 148.7, 140.1, 139.6, 129.2, 128.6, 128.4, 126.4, 121.3, 67.4, 40.7, 36.0, 31.5, 31.0, 23.7$ . HRMS (ESI): calculated for  $\text{C}_{19}\text{H}_{23}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  299.1647, found 299.1658.

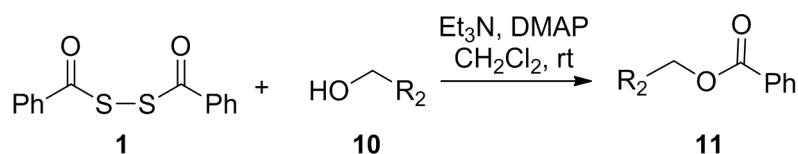
## Characterization spectra data of compound 12



***(8R,9S,13S,14S,17S)-17-Hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl benzoate 12:***

Following the typical procedure, 1 h, **12** was obtained in 92% yield (173.0 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  =  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (m, 2H), 7.65 (t,  $J$  = 7.4 Hz, 1H), 7.53 (t,  $J$  = 7.8 Hz, 2H), 7.36 (d,  $J$  = 8.5 Hz, 1H), 7.00 (dd,  $J$  = 8.4, 2.4 Hz, 1H), 6.95 (d,  $J$  = 2.2 Hz, 1H), 3.77 (t,  $J$  = 8.2 Hz, 1H), 2.92 (dd,  $J$  = 9.9, 6.6 Hz, 2H), 2.38 (ddd,  $J$  = 13.2, 6.9, 3.9 Hz, 1H), 2.28 (td,  $J$  = 11.1, 3.9 Hz, 1H), 2.16 (m, 1H), 2.00 (dt,  $J$  = 12.5, 3.2 Hz, 1H), 1.93 (m, 1H), 1.74 (m, 1H), 1.66 (s, 2H), 1.55 (m, 4H), 1.35 (m, 5H), 0.82 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.5, 148.7, 138.3, 138.1, 133.5, 130.2, 129.8, 128.5, 126.5, 121.6, 118.7, 81.9, 50.1, 44.2, 43.3, 38.5, 36.7, 30.6, 29.6, 27.1, 26.2, 23.2, 11.1. HRMS (ESI): calculated for  $\text{C}_{25}\text{H}_{29}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  377.2117, found 377.2100.

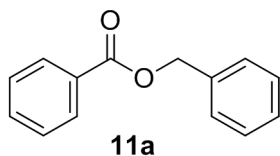
## General procedure for acylation of aliphatic alcohols **10**



A flame-dried 10 mL flask was charged with diacyl disulfides **6** (1.0 mmol), aliphatic alcohol **10** (0.5 mmol) and DCM (5 mL). DMAP (2.0 mmol, 244 mg) was added to the mixture. The mixture was allowed to stir at room temperature for 3-12 h until all of the starting material disappeared. Then, the mixture was poured into water (5 mL), extracted with EtOAc (4 x 5 mL), washed with 1 N HCl (10 mL) and brine (10 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude organic phase was concentrated in vacuo and purified with a short flash column chromatography (silica gel, hexane/EtOAc = 20:1) to afford the corresponding product **11**.

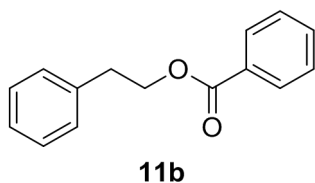


## Characterization spectra data of compounds 11



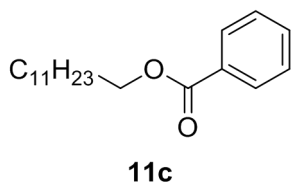
### *Benzyl benzoate 11a:*

Following the typical procedure, 5 h, **11a** was obtained in 86% yield (91.6 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.12 (dd,  $J$  = 8.2, 1.4 Hz, 2H), 7.58 (m, 1H), 7.35-7.55 (m, 7H), 5.42 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.4, 136.0, 133.0, 130.1, 129.6, 128.5, 128.3, 128.2, 128.1, 66.6. HRMS (ESI): calculated for  $\text{C}_{14}\text{H}_{13}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  213.0916, found 213.0905.



### *Phenethyl benzoate 11b:*

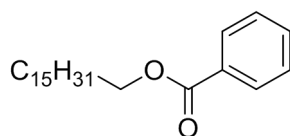
Following the typical procedure, 5 h, **11b** was obtained in 93% yield (105.1 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.08 (dd,  $J$  = 8.3, 1.3 Hz, 2H), 7.58 (m, 1H), 7.47 (m, 2H), 7.36 (m, 4H), 7.29 (m, 1H), 4.59 (t,  $J$  = 7.0 Hz, 2H), 3.13 (t,  $J$  = 7.0 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.4, 137.8, 132.8, 130.2, 129.5, 128.9, 128.3, 126.5, 65.4, 35.2. HRMS (ESI): calculated for  $\text{C}_{15}\text{H}_{15}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  227.1072, found 227.1065.



### *Dodecyl benzoate 11c:*

Following the typical procedure, 3 h, **11c** was obtained in 95% yield (131.1 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.07 (dd,  $J$  = 8.2, 1.1 Hz, 2H), 7.57 (d,

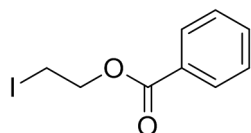
$J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.7$  Hz, 2H), 4.34 (t,  $J = 6.7$  Hz, 2H), 1.79 (m, 2H), 1.47 (m, 2H), 1.34 (m, 16H), 0.91 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 166.7, 132.7, 130.5, 129.5, 128.3, 65.1, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 28.7, 26.4, 22.7, 14.1$ . HRMS (ESI): calculated for  $\text{C}_{19}\text{H}_{31}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  291.2324, found 291.2197.



**11d**

***Hexadecyl benzoate 11d:***

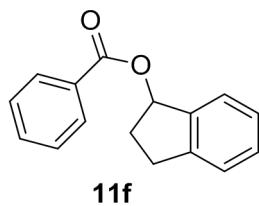
Following the typical procedure, 3 h, **11d** was obtained in 92% yield (152.7 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.07$  (dd,  $J = 8.2, 1.2$  Hz, 1H), 7.57 (m, 1H), 7.46 (dd,  $J = 10.7, 4.8$  Hz, 1H), 4.34 (t,  $J = 6.7$  Hz, 2H), 1.78 (dd,  $J = 14.8, 6.9$  Hz, 1H), 1.46 (m, 2H), 1.34 (m, 24H), 0.91 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 166.8, 132.7, 130.6, 129.5, 128.3, 65.1, 31.9, 29.7, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 28.7, 26.0, 22.7, 14.1$ . HRMS (ESI): calculated for  $\text{C}_{23}\text{H}_{39}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  347.2950, found 347.2997.



**11e**

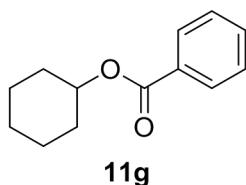
***2-Iodoethyl benzoate 11e:***

Following the typical procedure, 6 h, **11e** was obtained in 90% yield (152.7 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.10$  (dd,  $J = 8.2, 1.2$  Hz, 1H), 7.60 (m, 1H), 7.47 (m, 1H), 4.60 (t,  $J = 6.7$  Hz, 2H), 3.45 (d,  $J = 6.7$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 165.9, 133.2, 129.7, 129.7, 128.4, 77.1, 64.9$ . HRMS (ESI): calculated for  $\text{C}_9\text{H}_{10}\text{IO}_2^+$ ,  $[\text{M} + \text{H}^+]$  276.9725, found 276.8884.



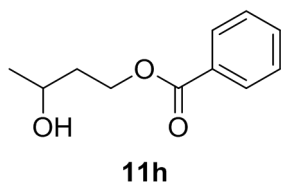
***2,3-Dihydro-1H-inden-1-yl benzoate 11f:***

Following the typical procedure, 12 h, **11f** was obtained in 72% yield (85.7 mg) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.07 (dd,  $J$  = 8.3, 1.3 Hz, 2H), 7.55 (m, 2H), 7.47 (m, 2H), 7.26 (m, 1H), 6.48 (dd,  $J$  = 7.0, 4.1 Hz, 1H), 3.22 (m, 1H), 2.98 (m, 1H), 2.66 (m, 1H), 2.27 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.6, 144.4, 141.1, 132.9, 130.5, 129.7, 128.9, 128.3, 126.7, 125.7, 124.8, 78.9, 32.5, 30.3. HRMS (ESI): calculated for  $\text{C}_{16}\text{H}_{15}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  239.1072, found 239.1031.



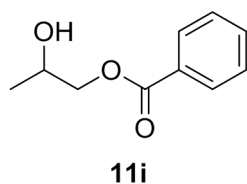
***Cyclohexyl benzoate 11g***

Following the typical procedure, 12 h, **11g** was obtained in 67% yield (68.3 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.08 (dd,  $J$  = 8.1, 1.0 Hz, 2H), 7.56 (m, 1H), 7.46 (m, 2H), 5.06 (m, 1H), 1.97 (m, 2H), 1.82 (ddd,  $J$  = 9.5, 5.9, 2.8 Hz, 2H), 1.61 (tt,  $J$  = 18.4, 6.1 Hz, 3H), 1.48 (dtt,  $J$  = 13.2, 9.9, 3.4 Hz, 2H), 1.38 (ddt,  $J$  = 13.3, 9.8, 3.3 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.0, 132.6, 131.0, 129.5, 128.2, 73.0, 31.6, 25.5, 23.6. HRMS (ESI): calculated for  $\text{C}_{13}\text{H}_{17}\text{O}_2^+$ ,  $[\text{M} + \text{H}^+]$  205.1229, found 205.1213.



***3-Hydroxybutyl benzoate 11h:***

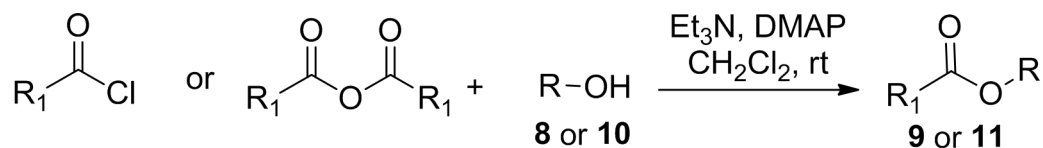
Following the typical procedure, 5 h, **11h** was obtained in 78% yield (75.7 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.06 (m, 2H), 7.66-7.54 (m, 1H), 7.46 (dd,  $J$  = 10.7, 4.8 Hz, 2H), 4.62 (ddd,  $J$  = 11.3, 8.6, 5.1 Hz, 1H), 4.41 (dt,  $J$  = 11.2, 5.6 Hz, 1H), 4.00 (m, 1H), 1.96 (m, 1H), 1.87 (m, 1H), 1.29 (d,  $J$  = 6.2 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.9, 133.0, 130.1, 129.6, 128.4, 64.8, 62.2, 38.2, 23.5. HRMS (ESI): calculated for  $\text{C}_{11}\text{H}_{15}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  195.1021, found 195.1037.



***2-Hydroxypropyl benzoate 11i:***

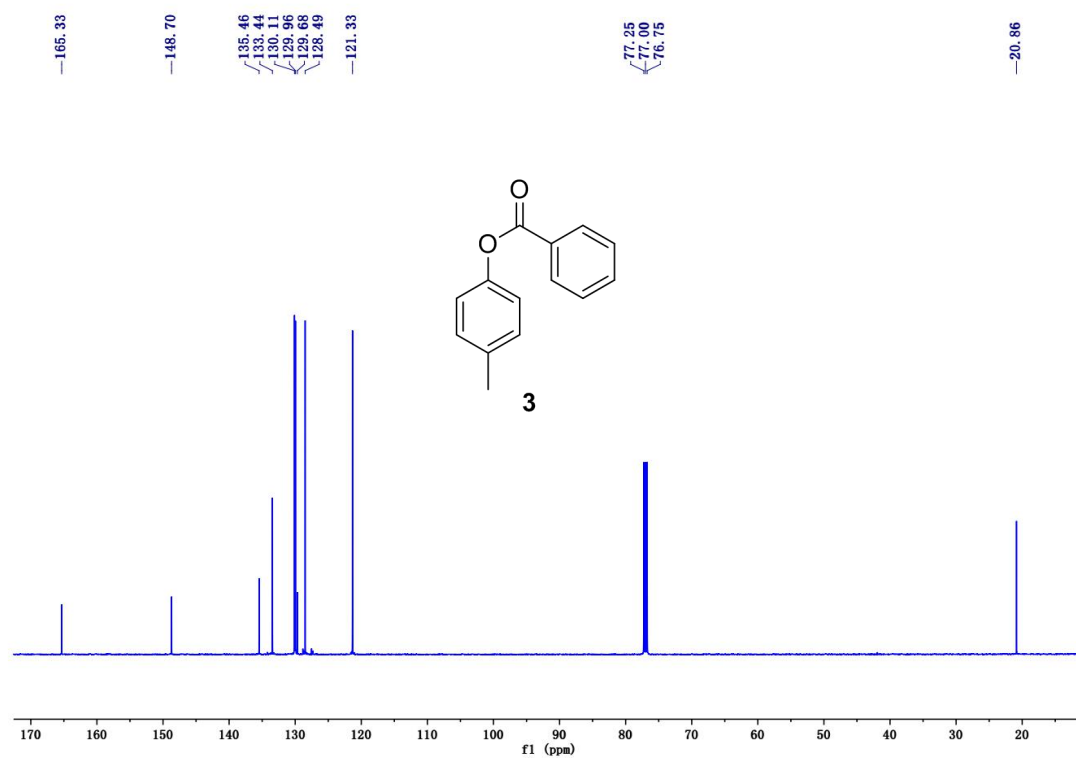
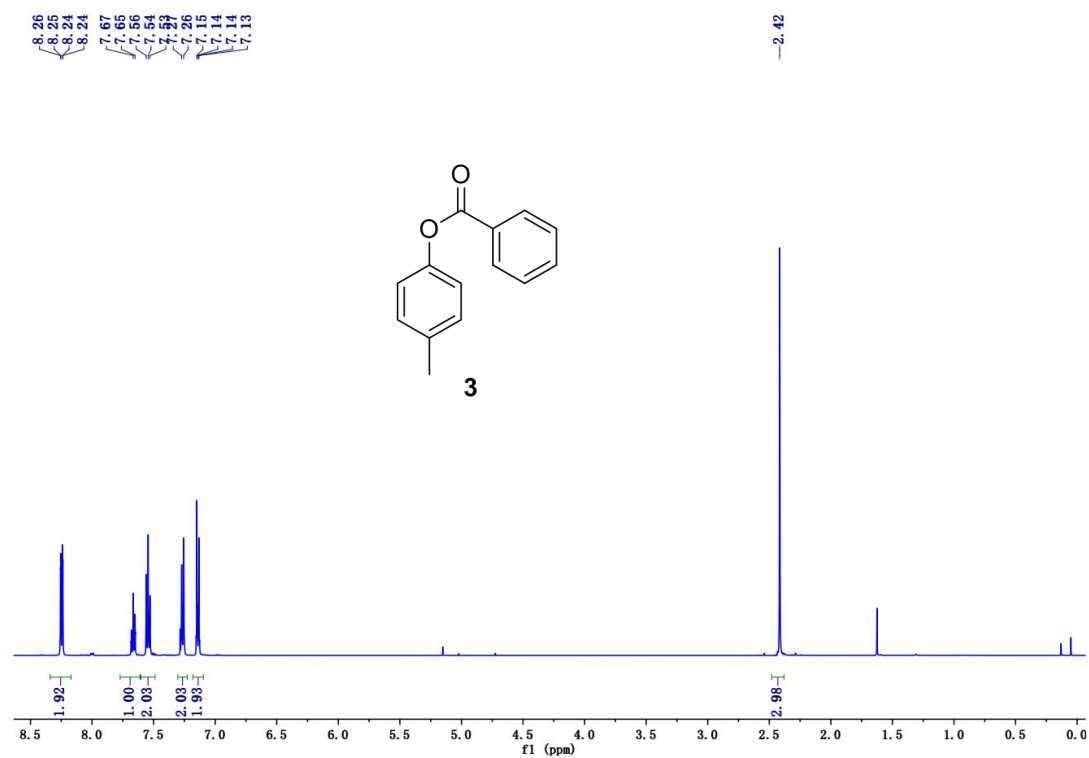
Following the typical procedure, 5 h, **11i** was obtained in 83% yield (74.7 mg) as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.08 (m, 2H), 7.59 (m, 1H), 7.47 (m, 2H), 4.37 (q,  $J$  = 2.3 Hz, 1H), 4.23 (dt,  $J$  = 6.1, 5.4 Hz, 2H), 1.32 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.7, 133.2, 129.9, 129.6, 128.4, 70.1, 66.3, 19.3. HRMS (ESI): calculated for  $\text{C}_{10}\text{H}_{13}\text{O}_3^+$ ,  $[\text{M} + \text{H}^+]$  181.0865, found 181.0854.

### Procedure for acylation with acyl chlorides or acid anhydrides

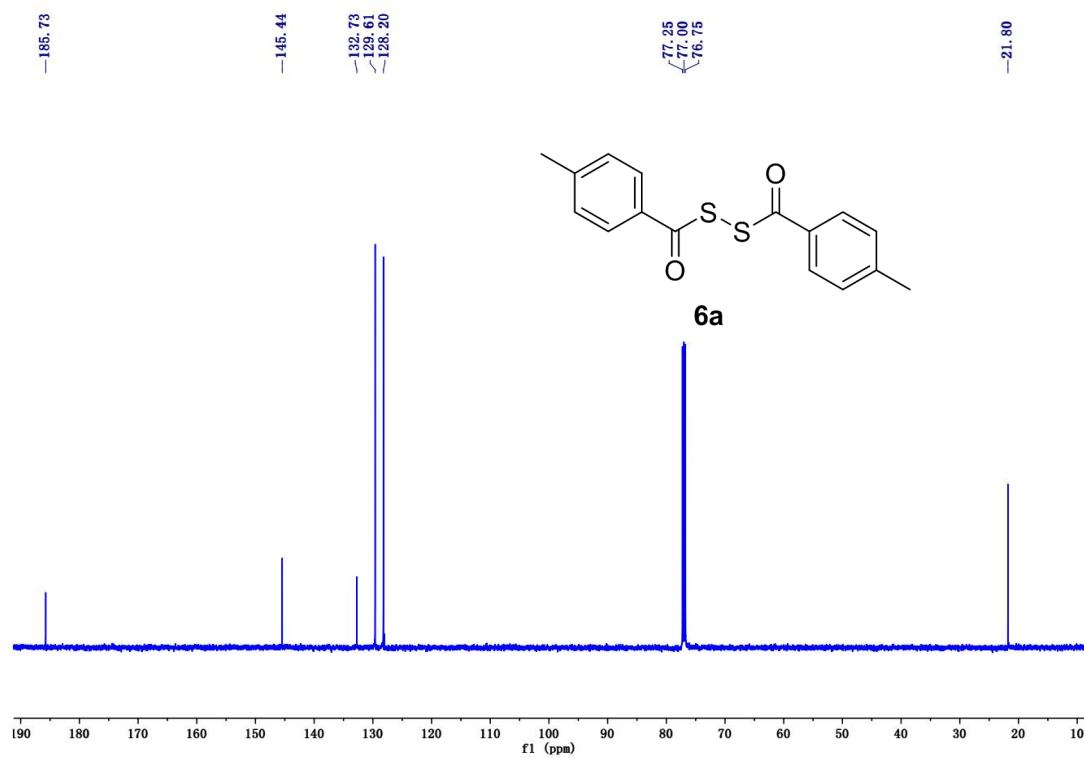
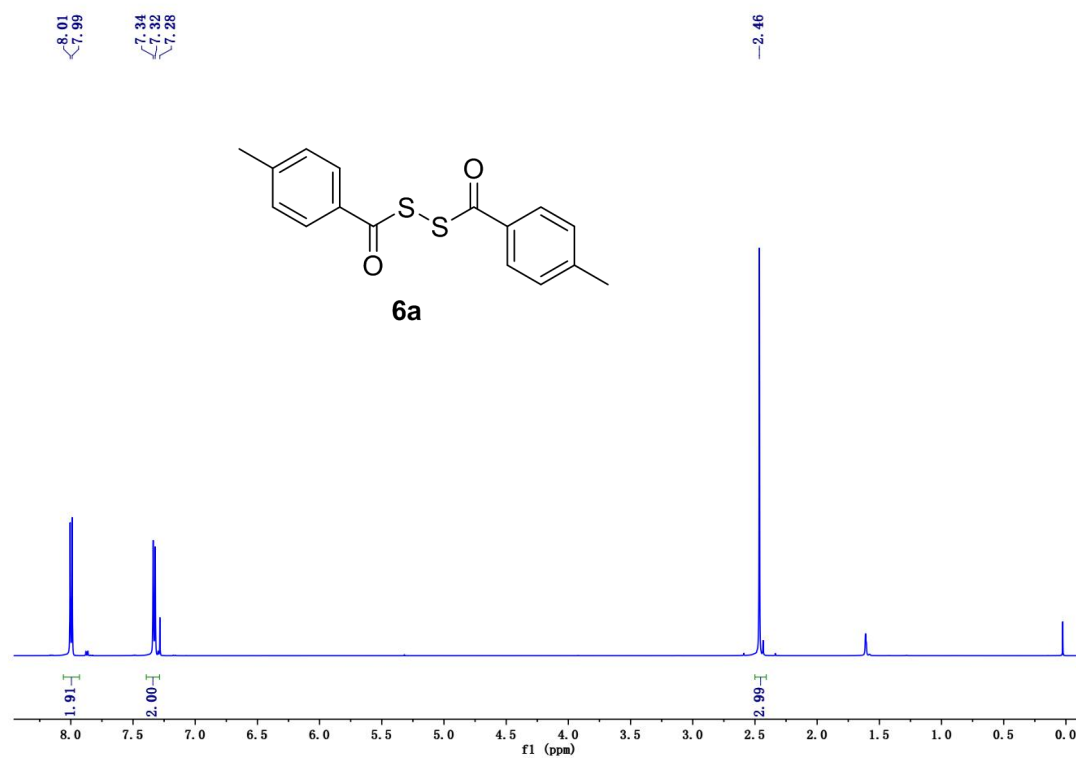


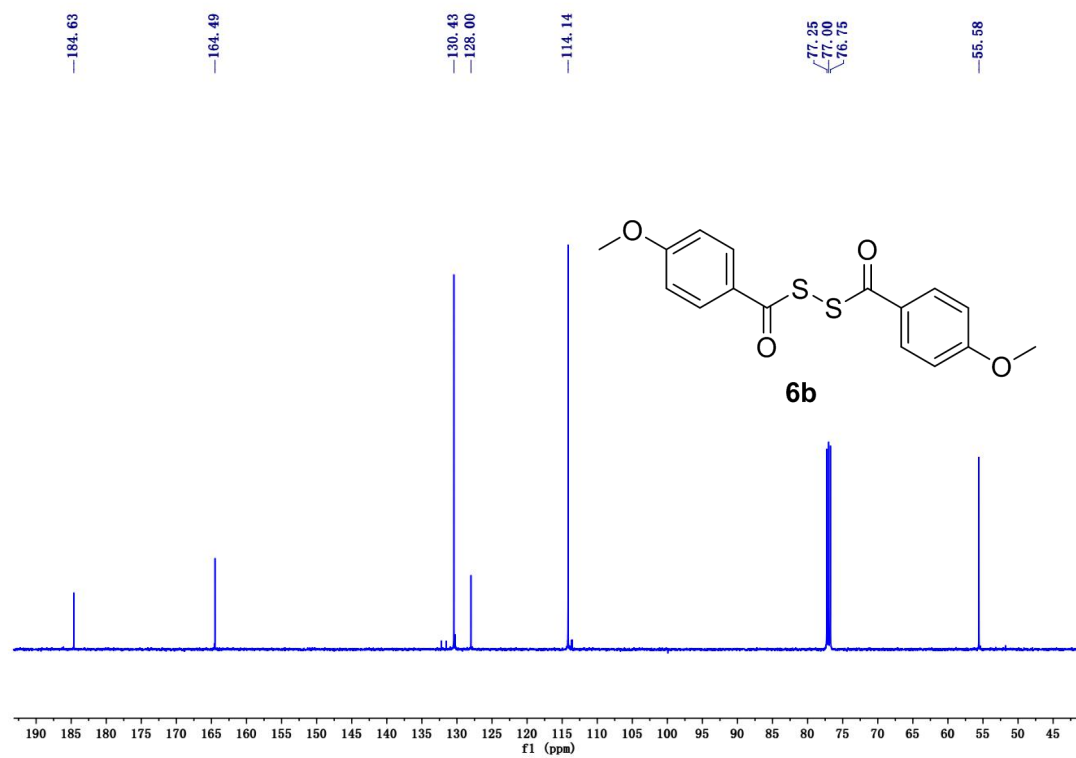
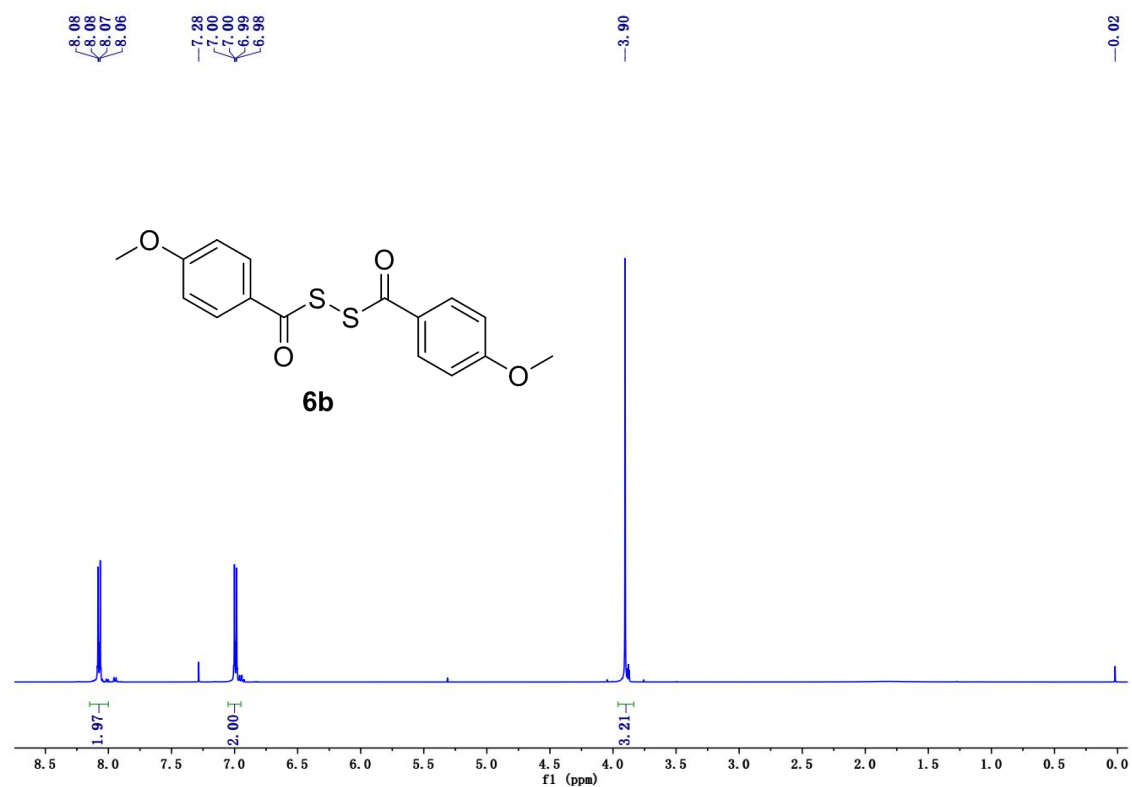
A flame-dried 10 mL flask was charged with phenol **4** (0.5 mmol), DCM (5 mL), Et<sub>3</sub>N (1.0 mmol, 75 mg, 0.1 mL) and DMAP (0.1 mmol, 12 mg), acyl chlorides or acid anhydrides (0.5 mmol) was added in one portion to the mixture. The mixture was allowed to stir at room temperature for 1-10 mins until all of the starting material disappeared. Then, the mixture was poured into water (5 mL), extracted with EtOAc (4 x 5 mL), washed with 1 N HCl (10 mL) and brine (10 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude organic phase was concentrated in vacuo and purified with a short flash column chromatography (silica gel, hexane/EtOAc = 20:1-5:1) to afford the corresponding product **9**. Yields for acyl chlorides: **9a** (71%), **9b** (46%), **9c** (53%), **9d** (82%), **9e** (61%), **9f** (68%), **9g** (88%), **9h** (77%), **9i** (83%), **11h** (66%), **11i** (72%). Yields for acid anhydrides: **9a** (77%), **9b** (59%), **9c** (67%), **9d** (84%), **9e** (69%), **9f** (81%), **9g** (91%), **9h** (84%), **9i** (89%), **11h** (74%), **11i** (80%).

# <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **3**

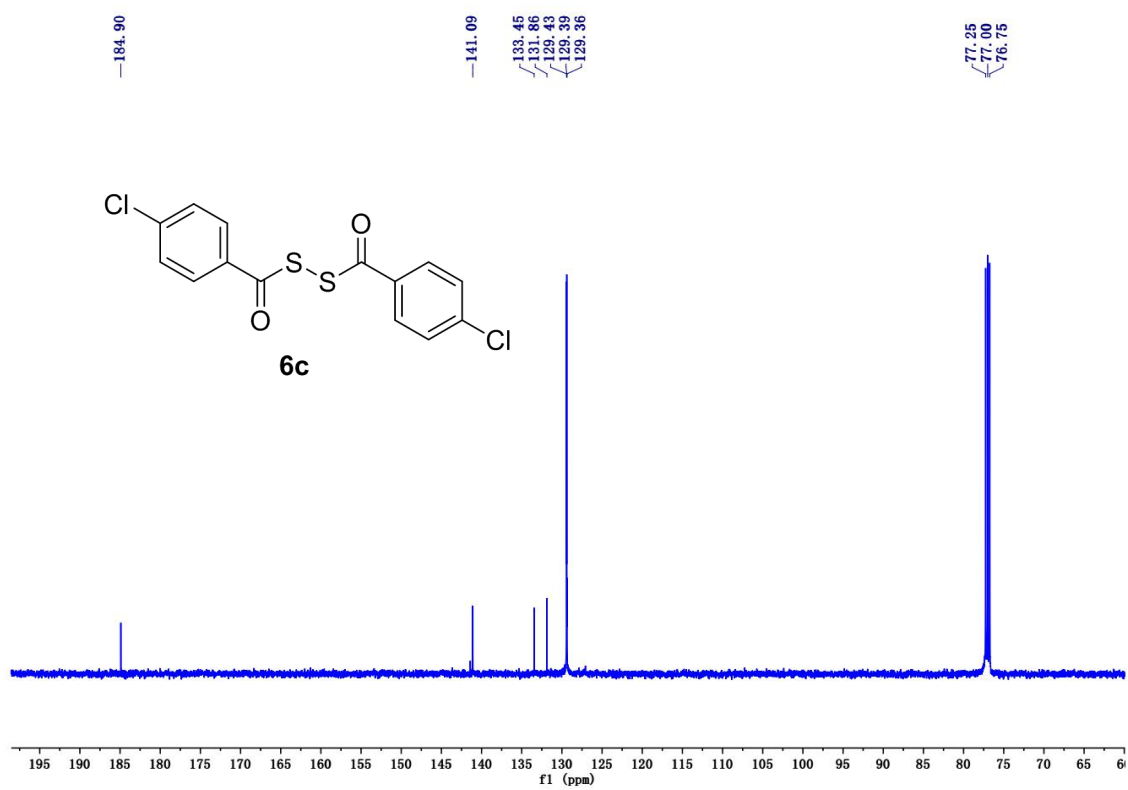
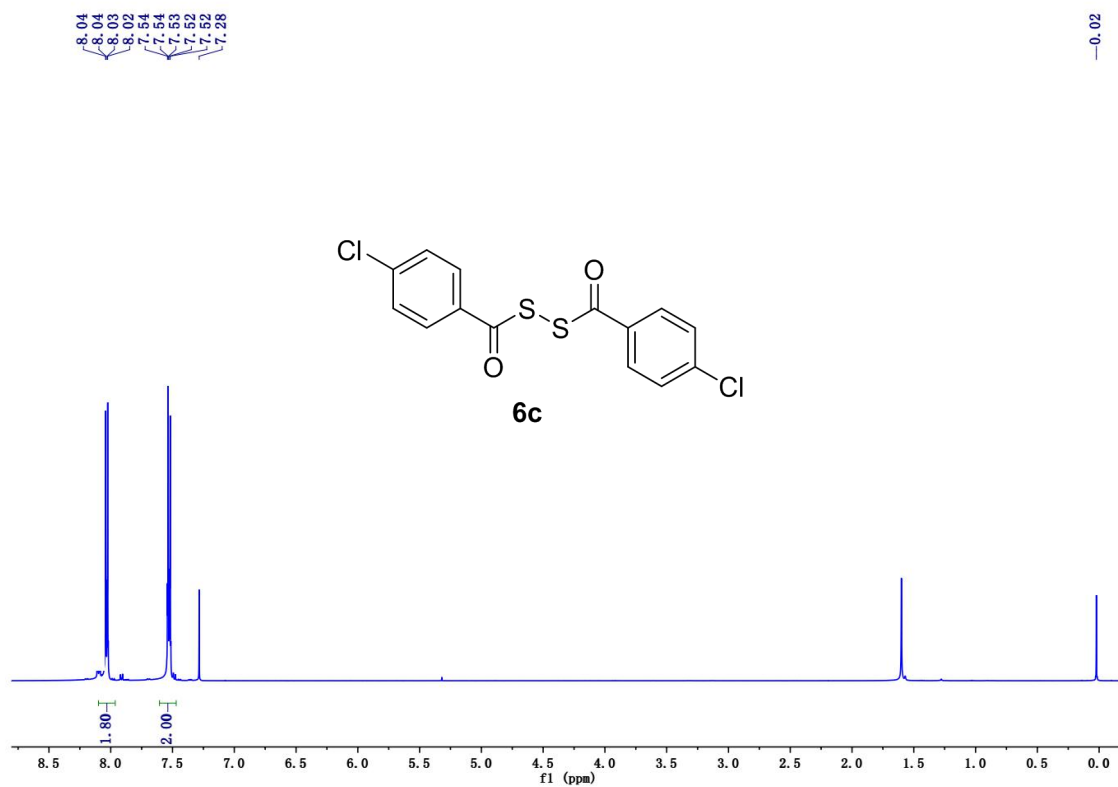


# <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 6

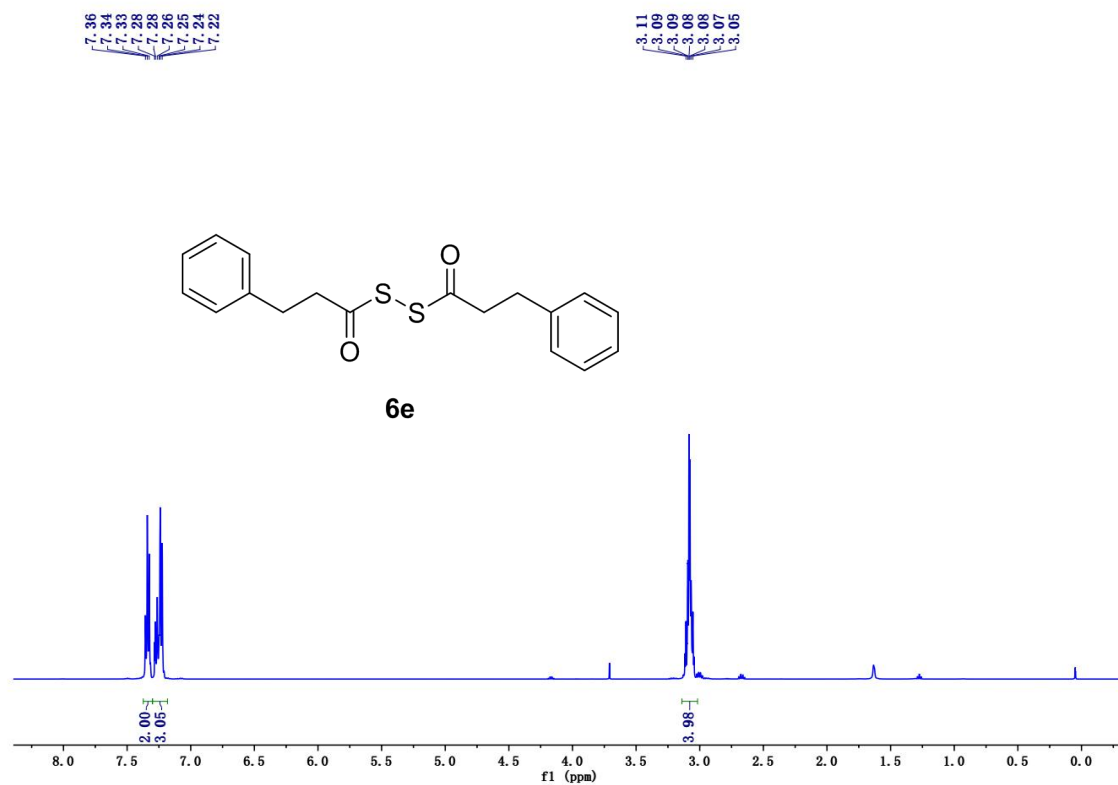


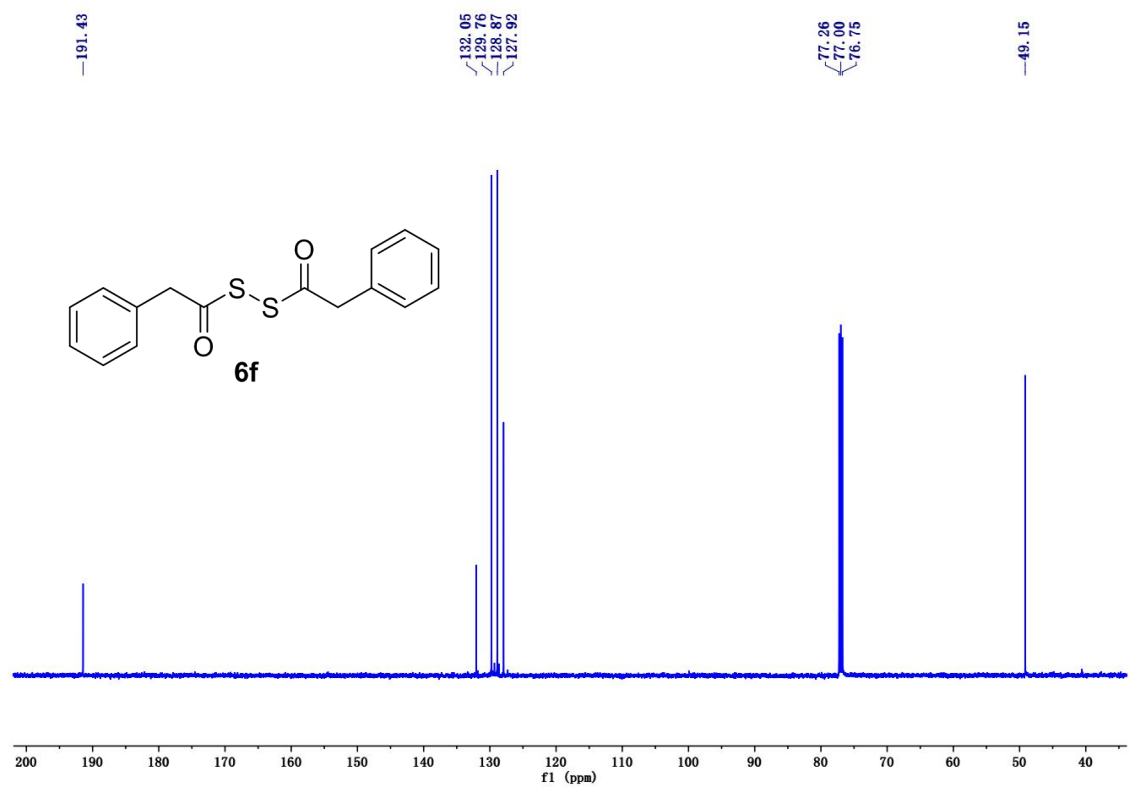
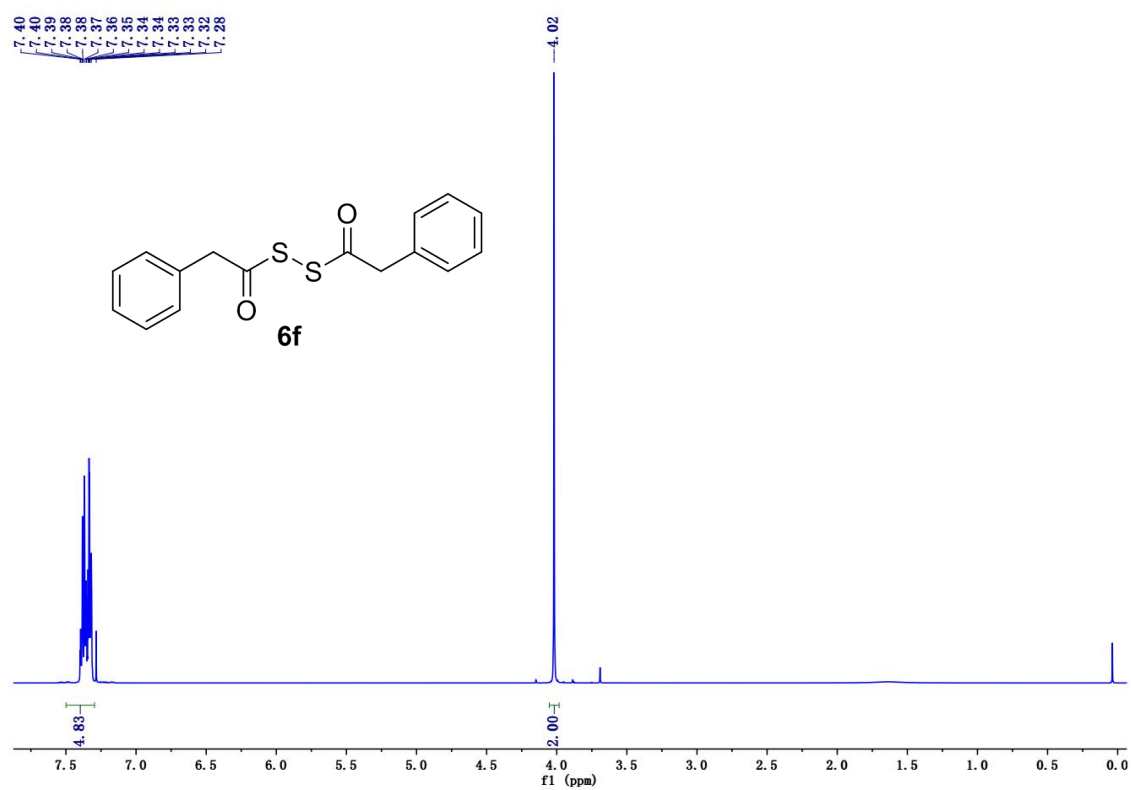


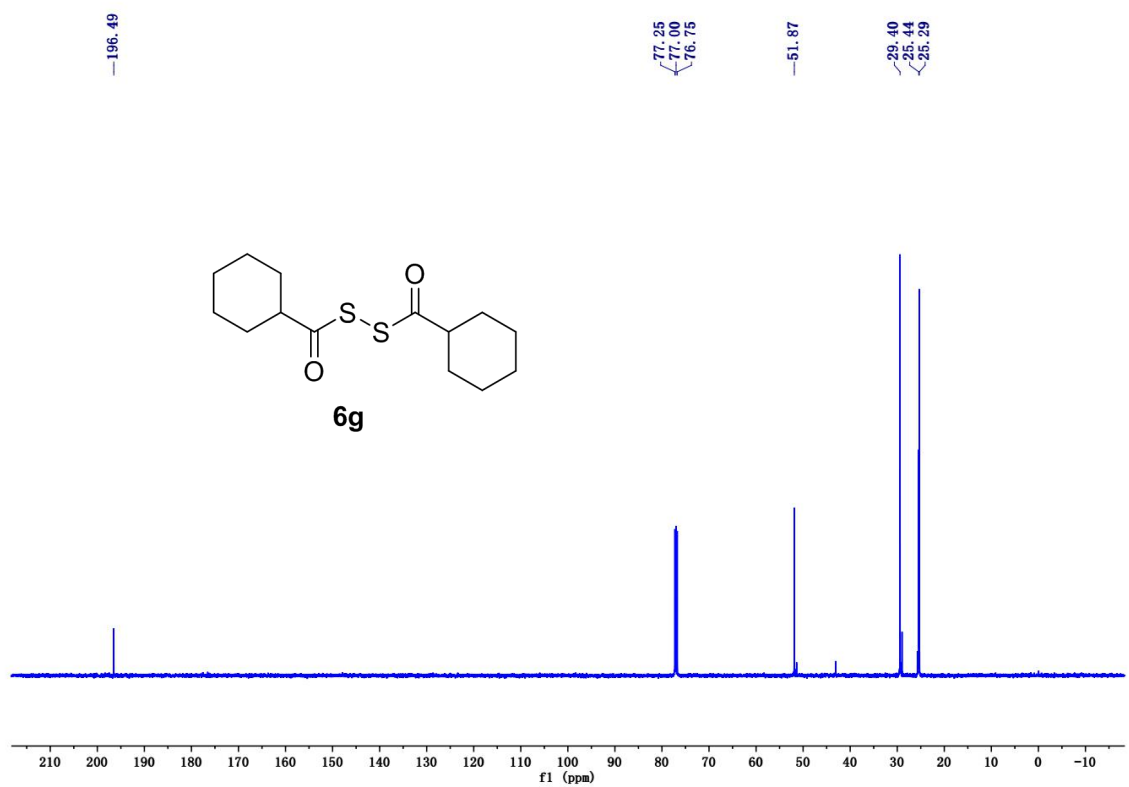
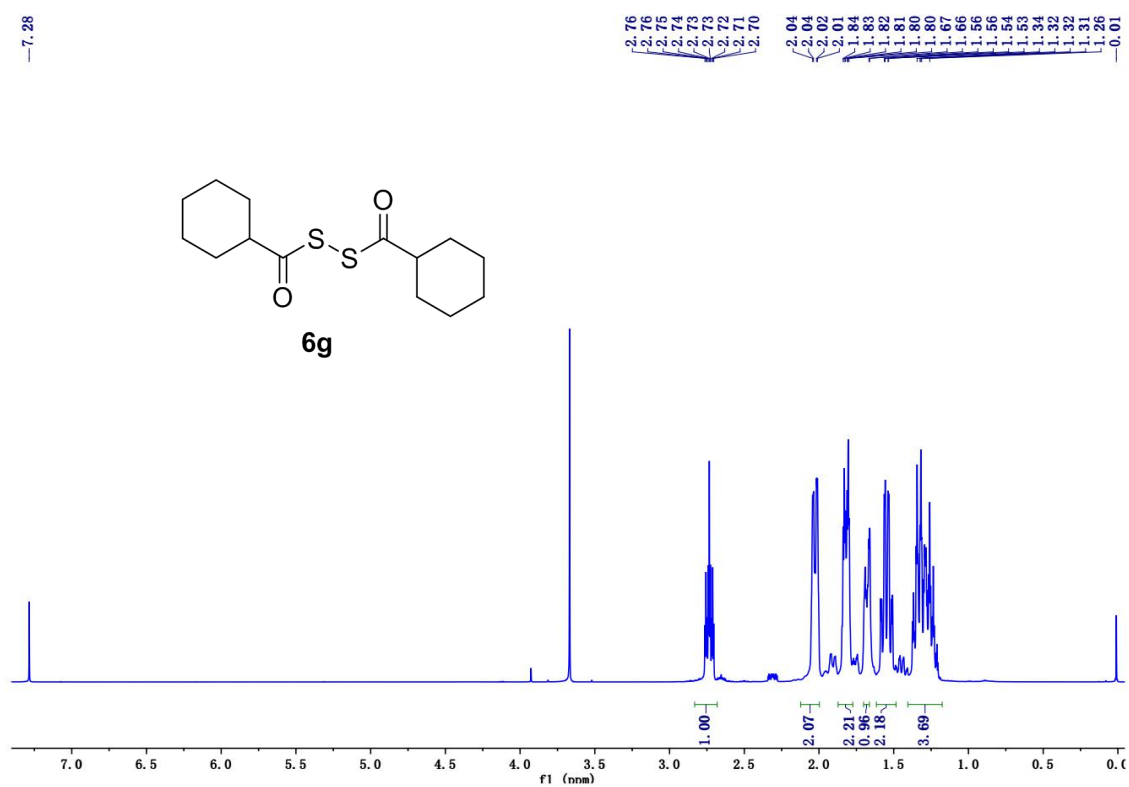


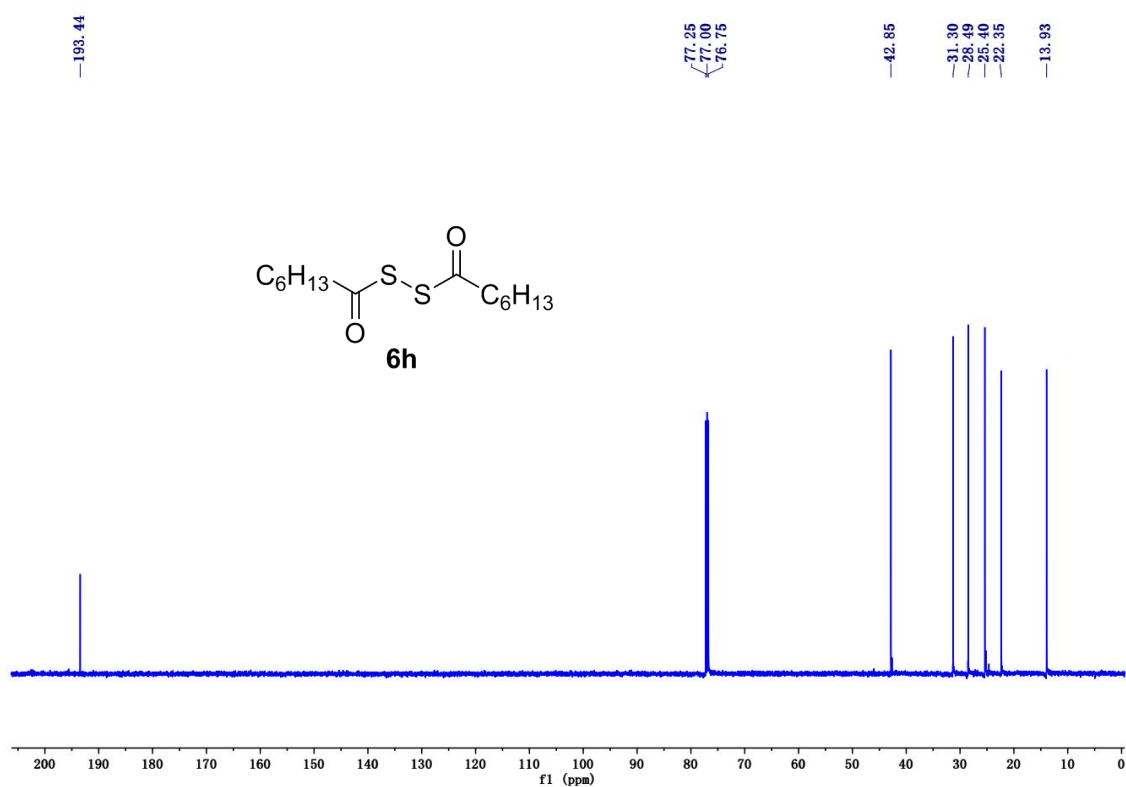
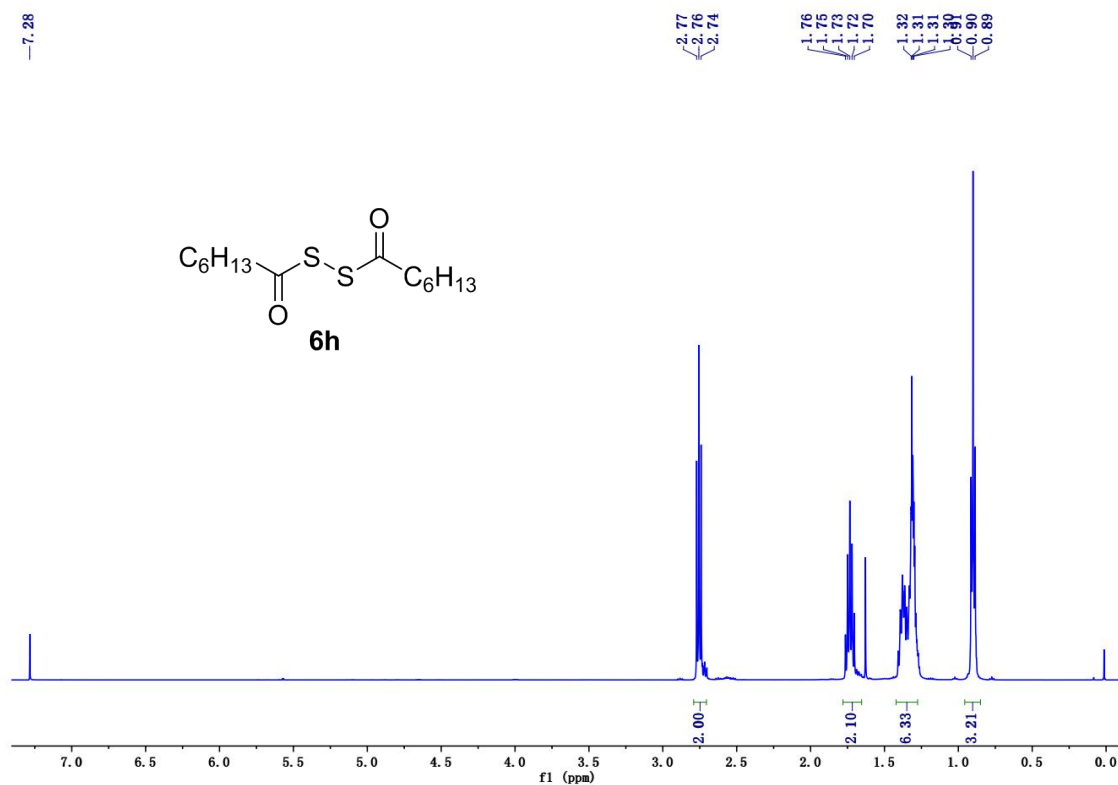


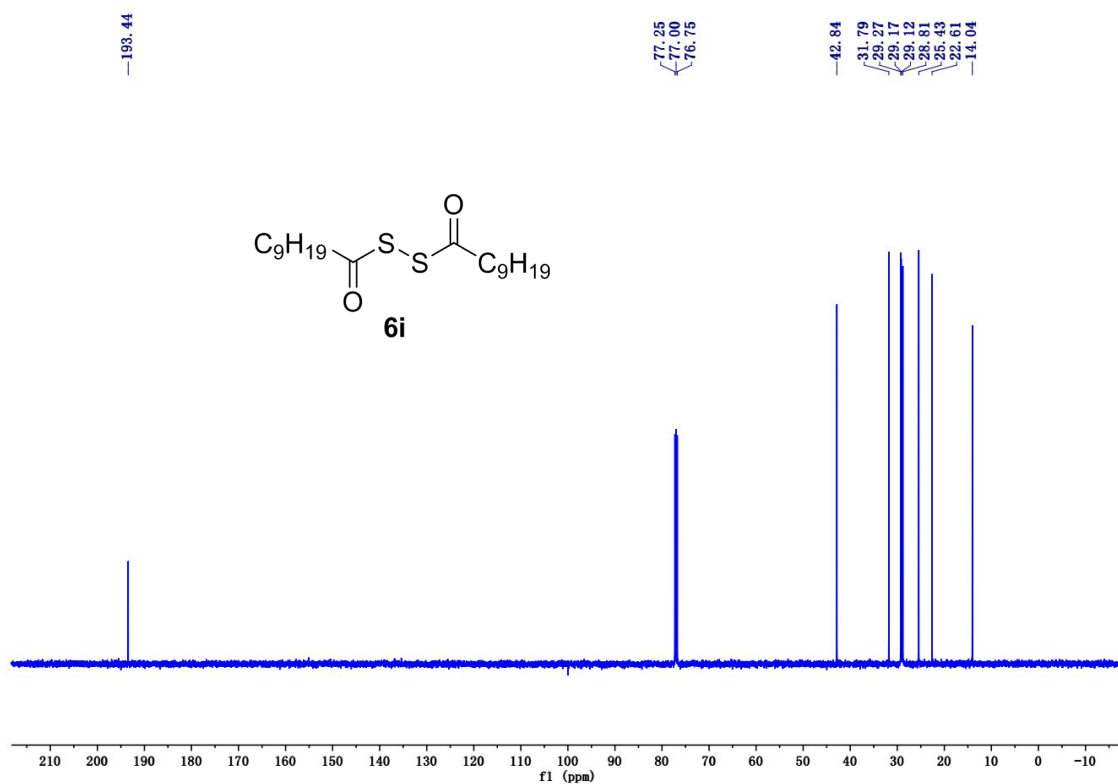
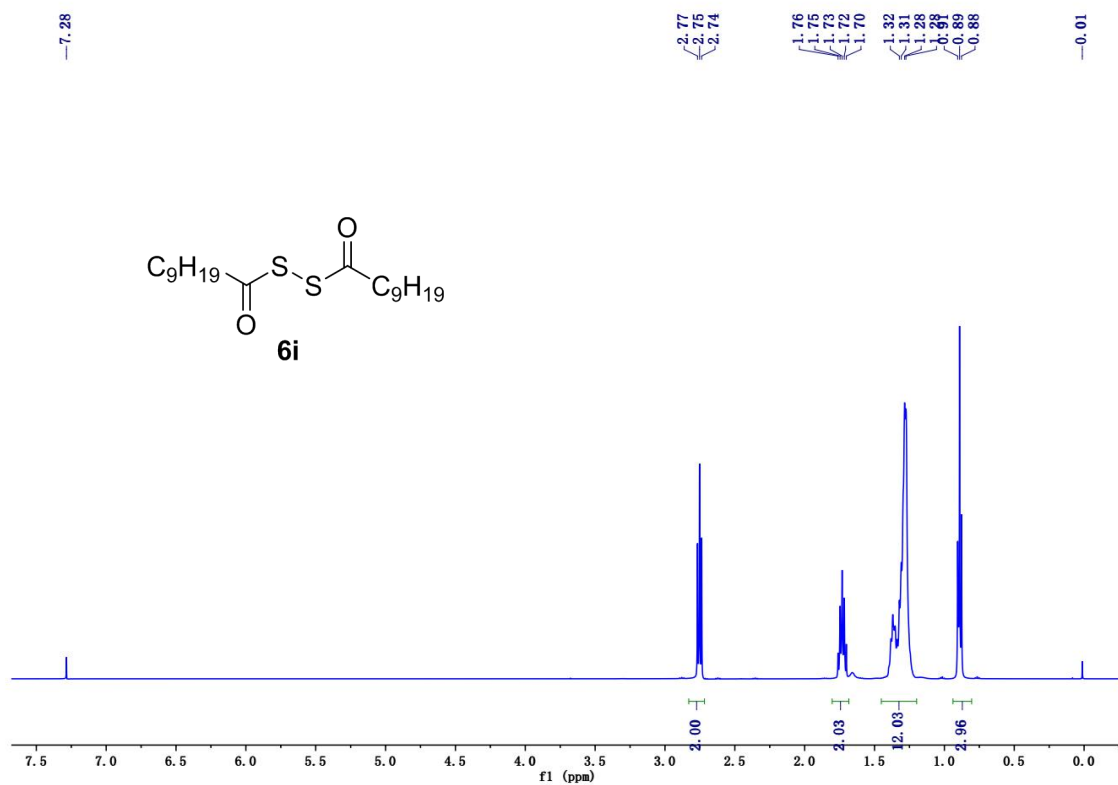


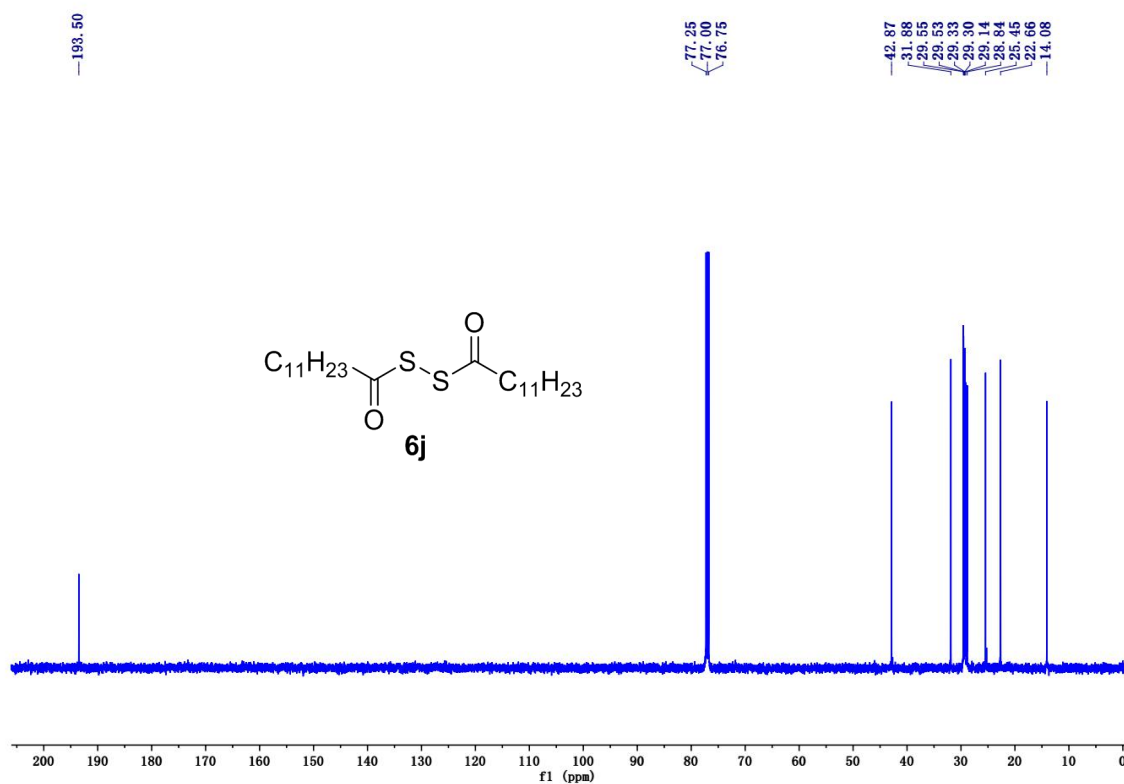
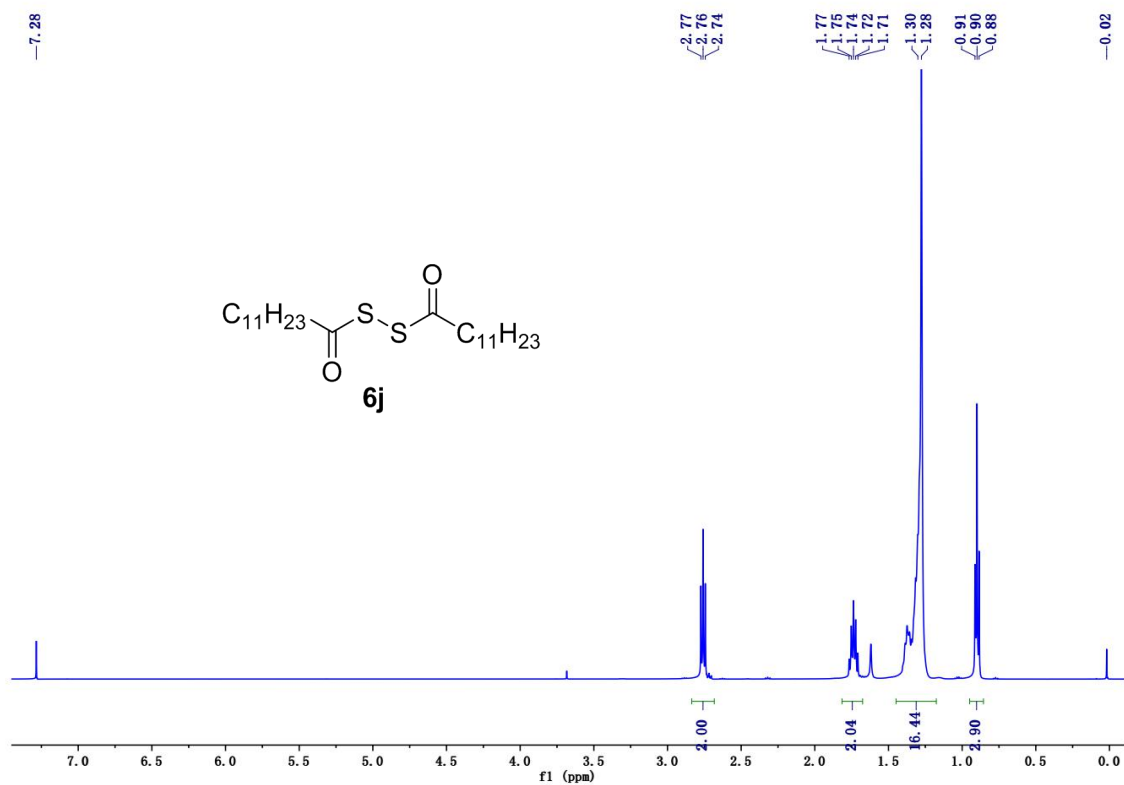






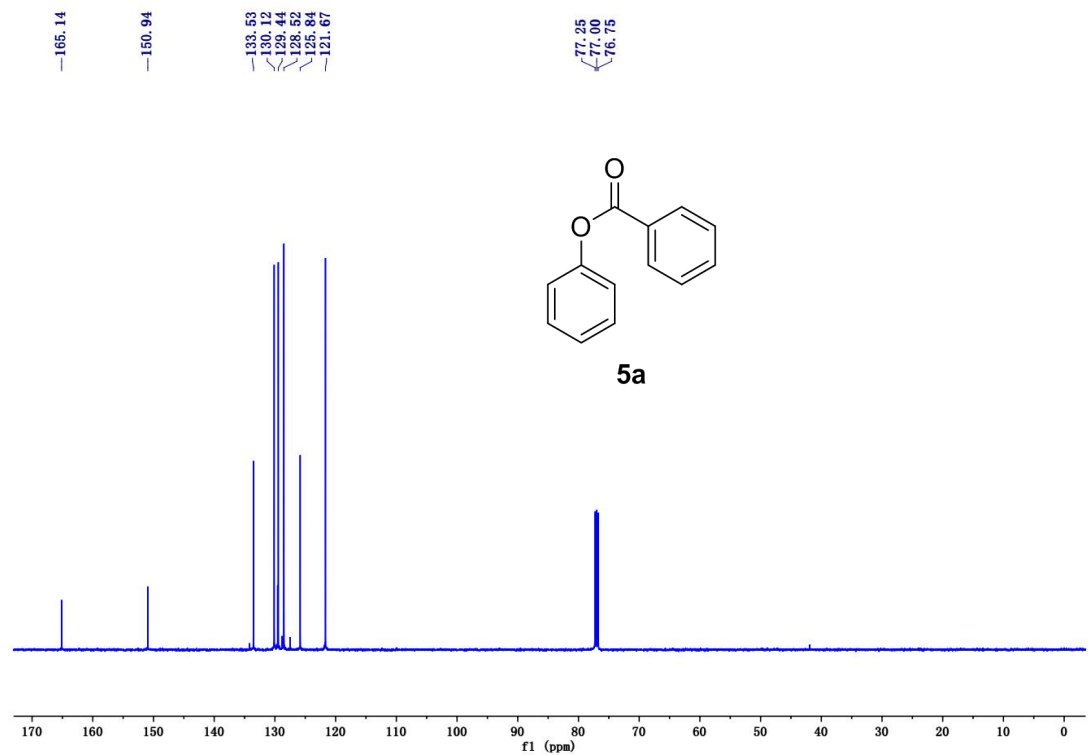
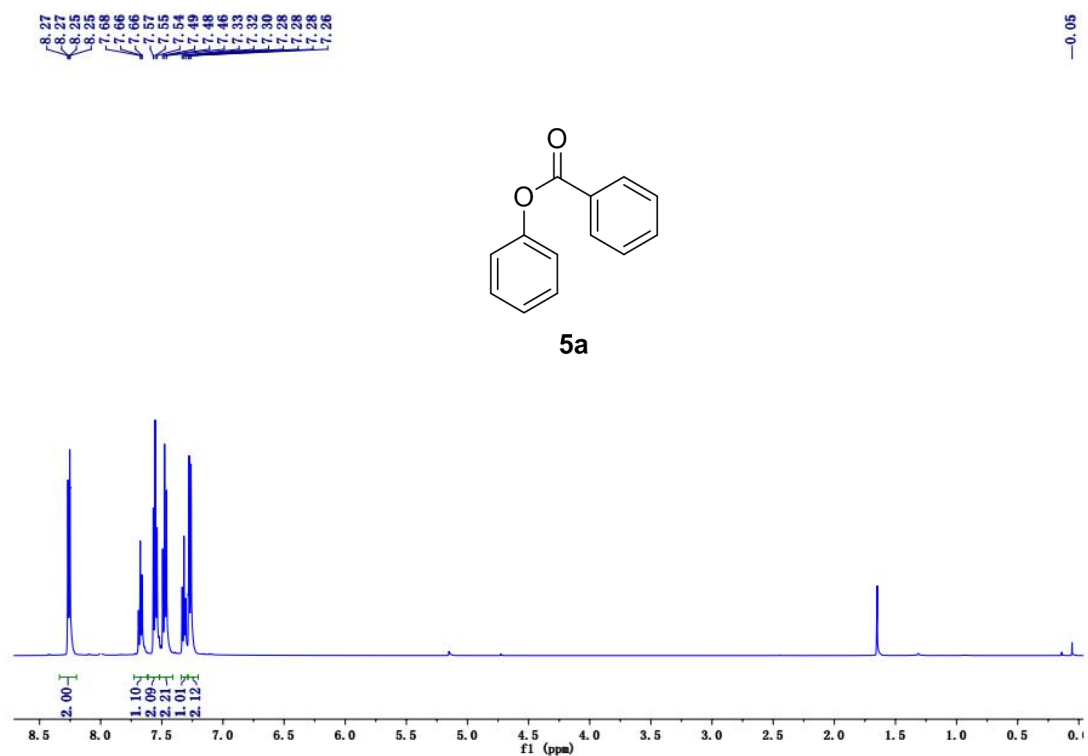


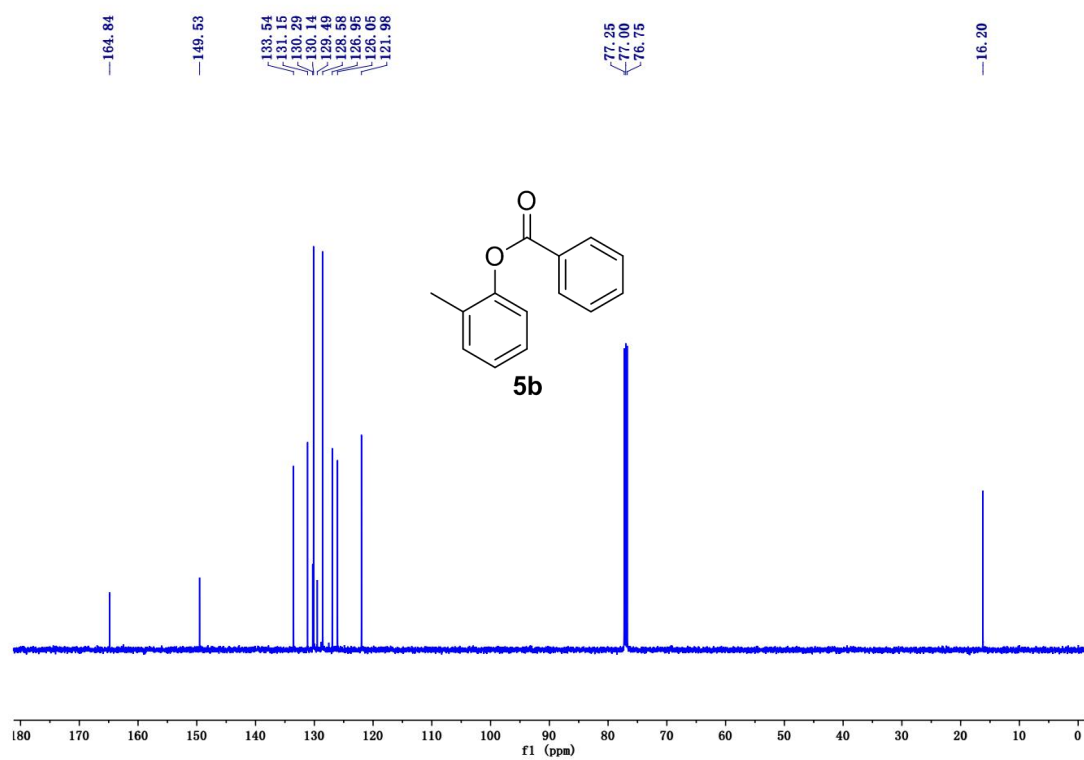
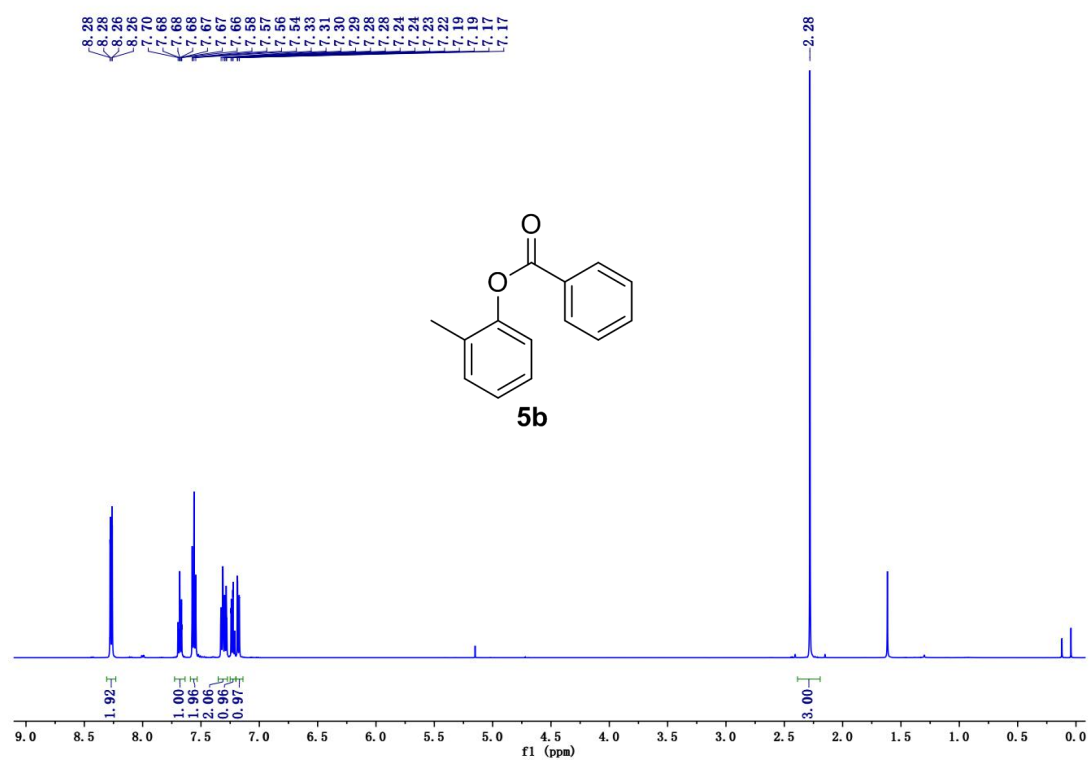


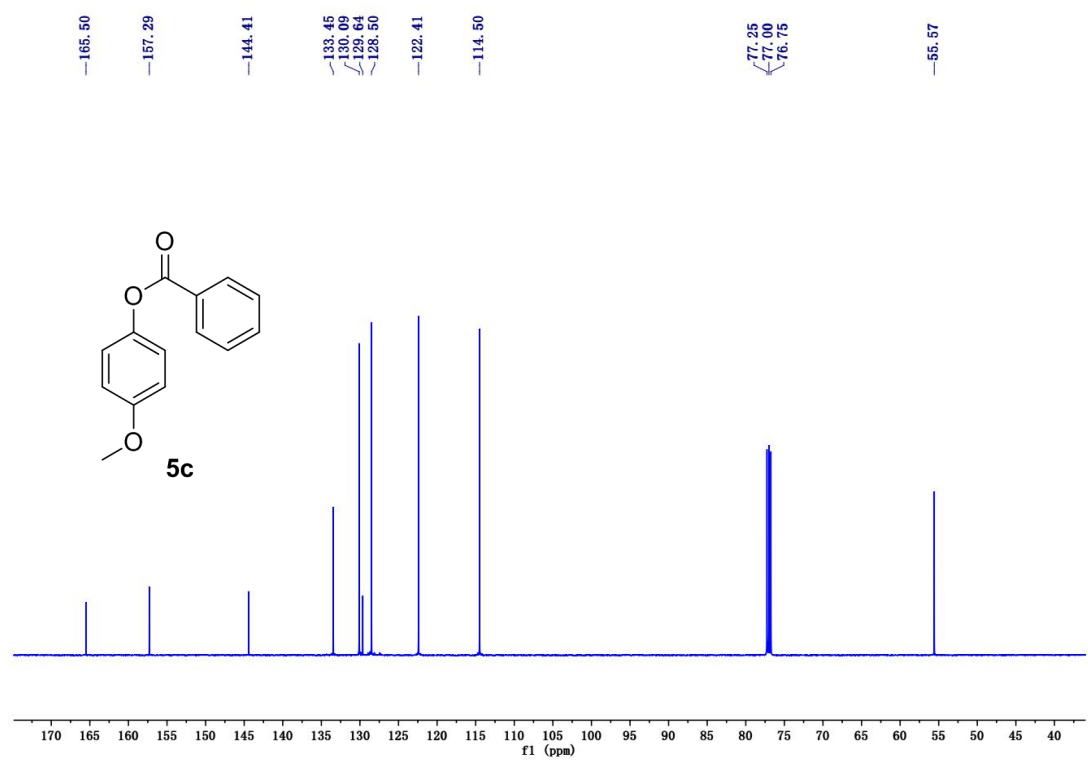
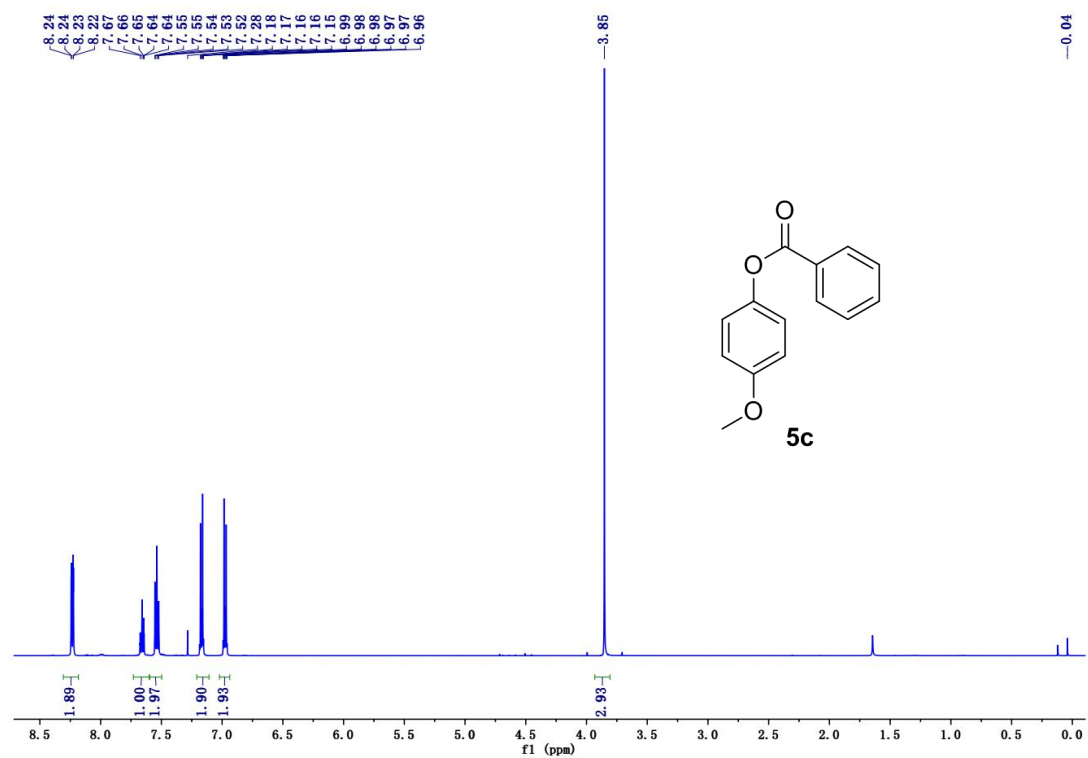


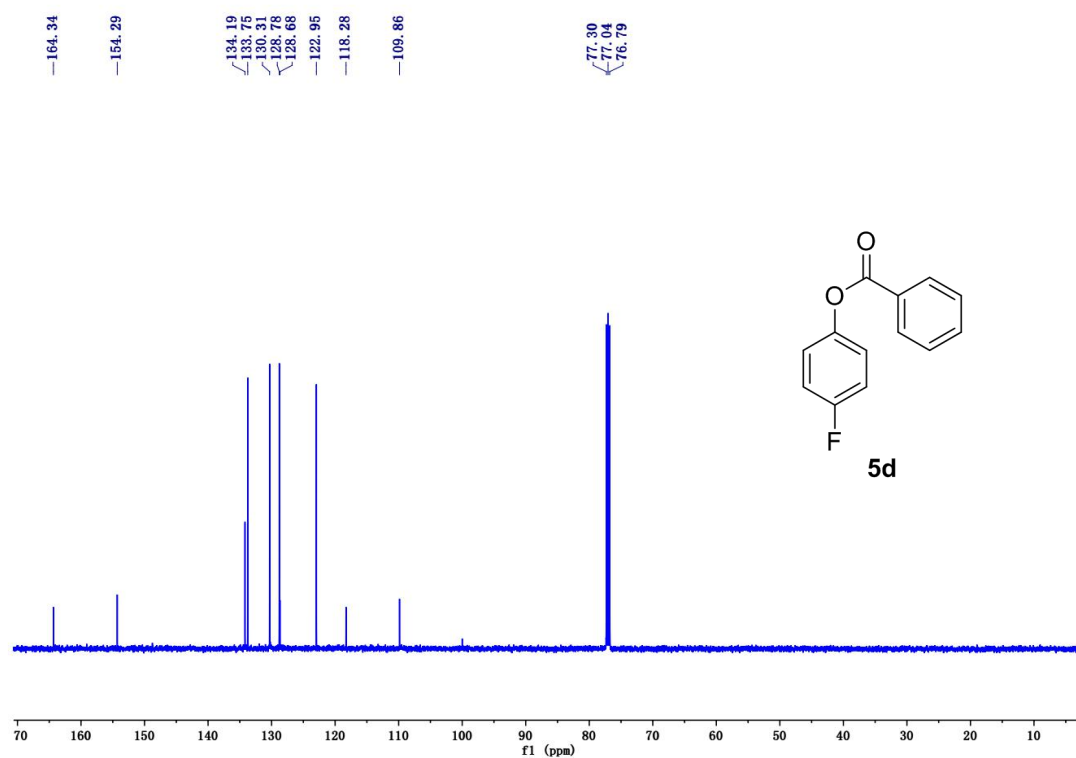
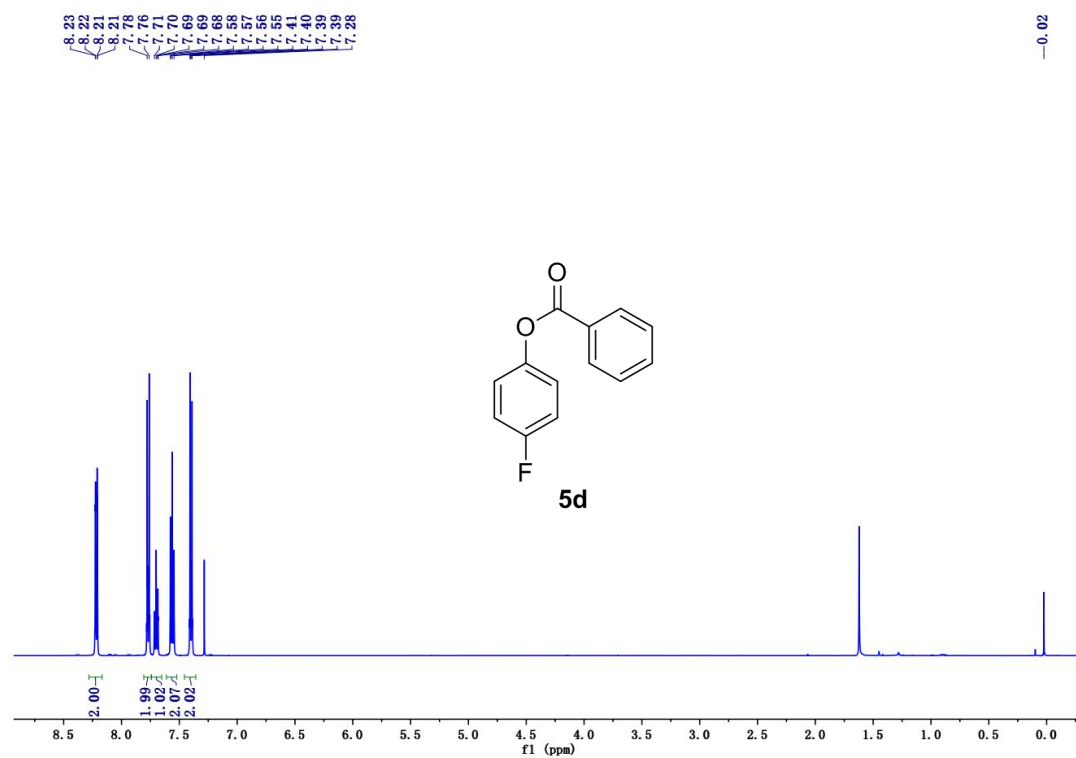


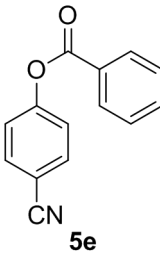
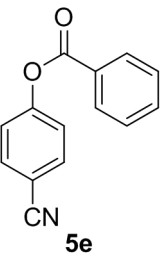
# <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **5**

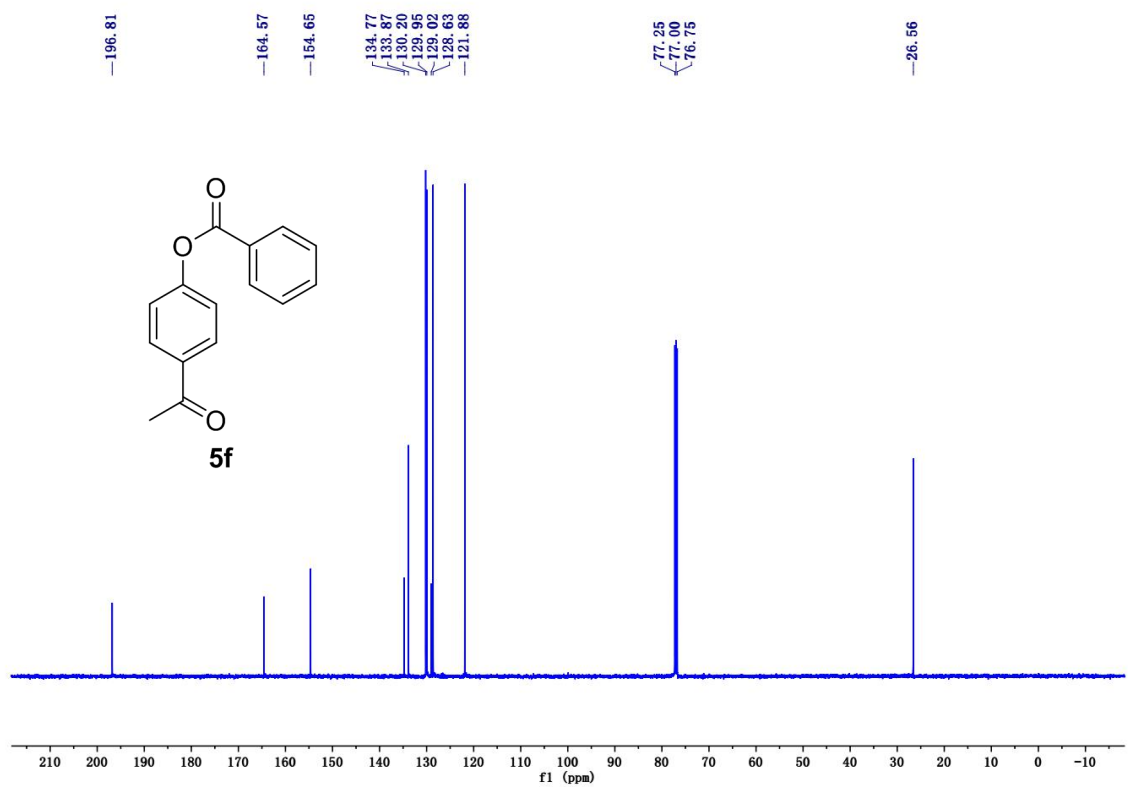
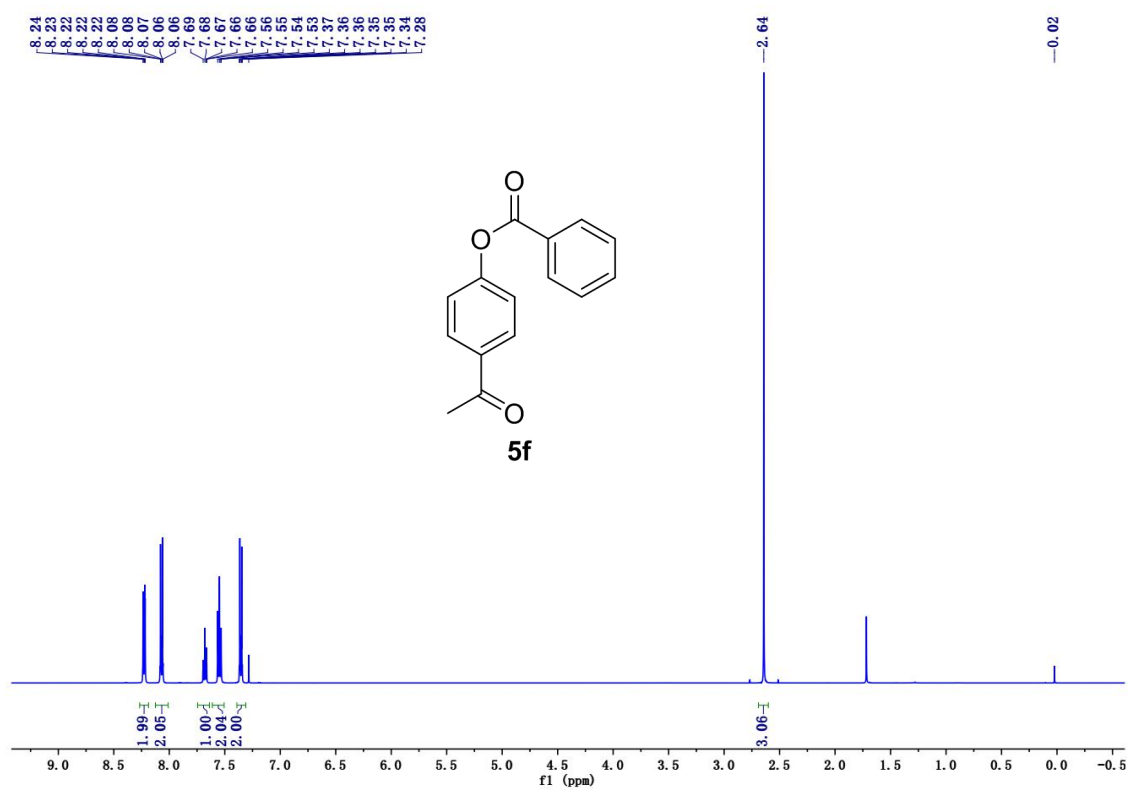


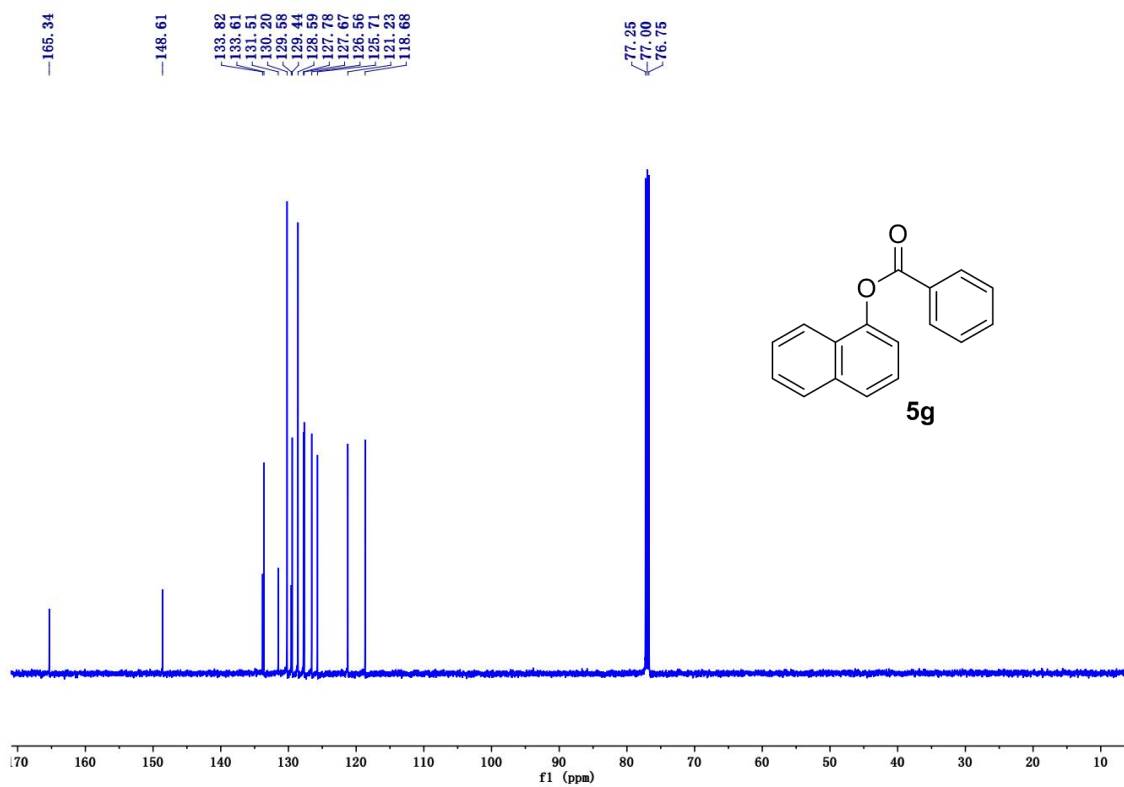
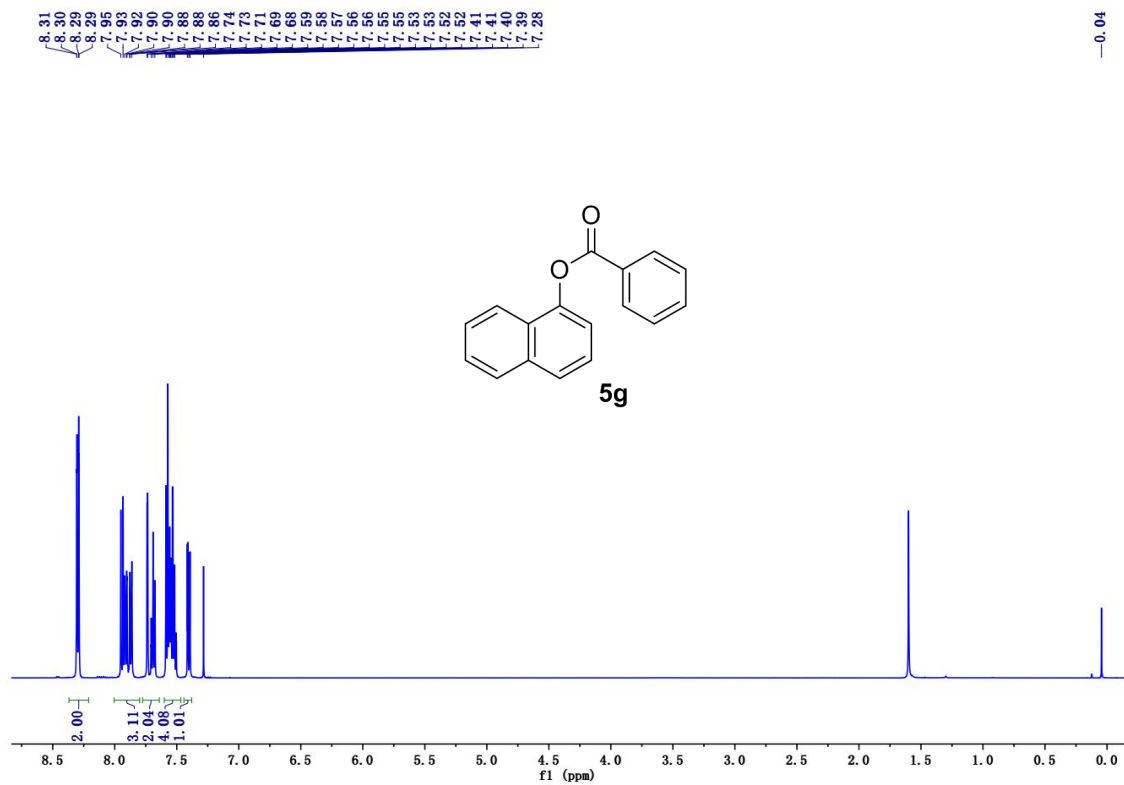


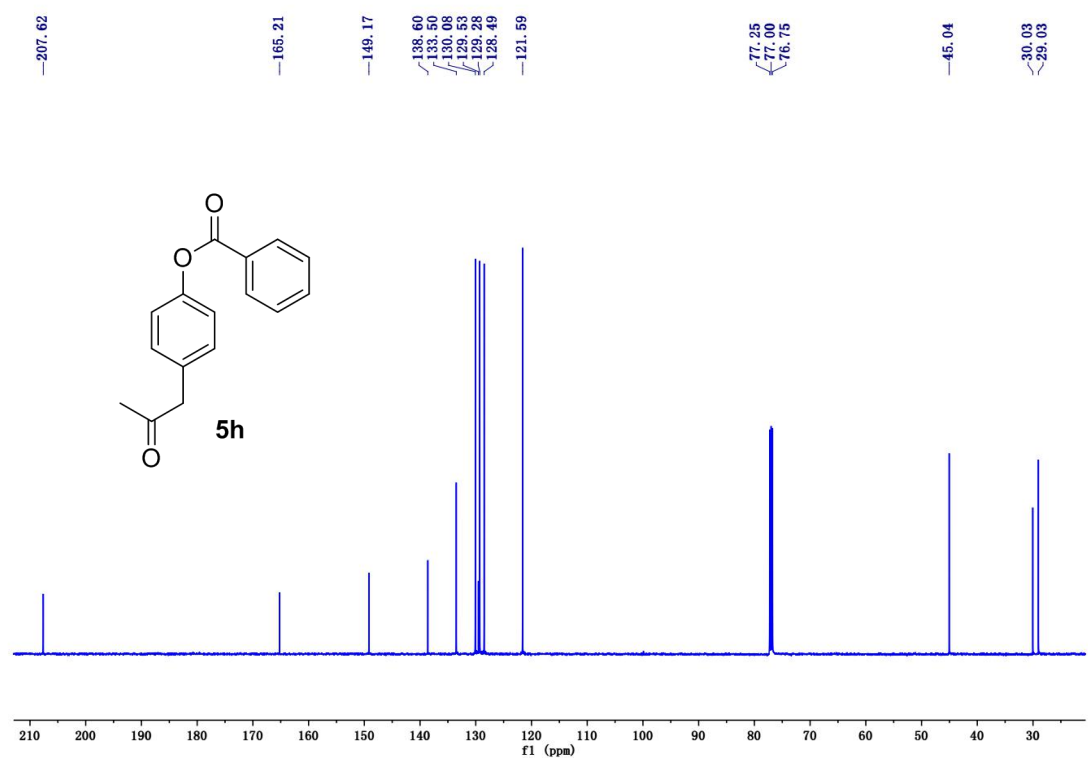
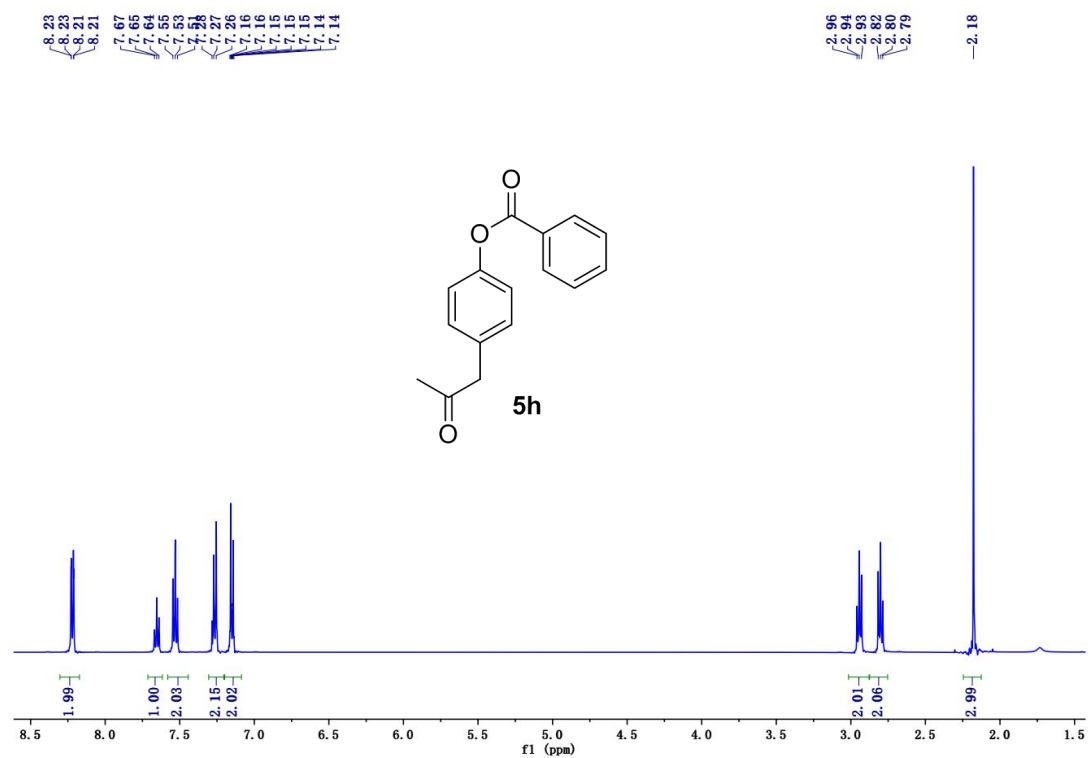




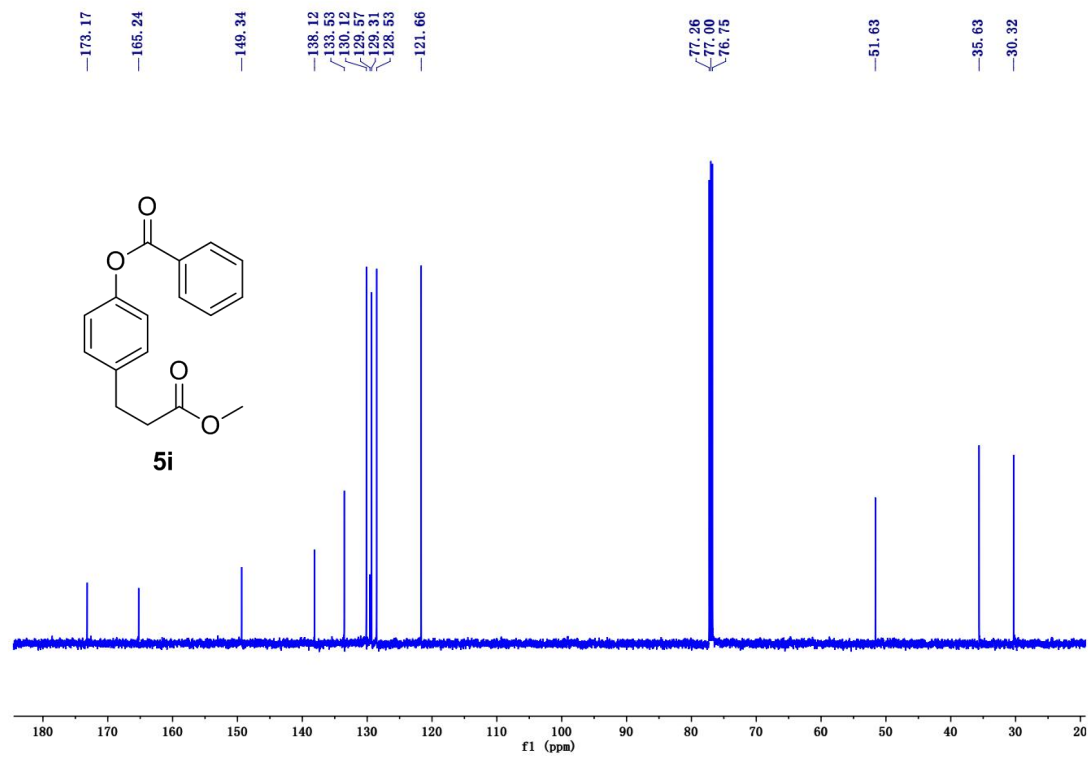
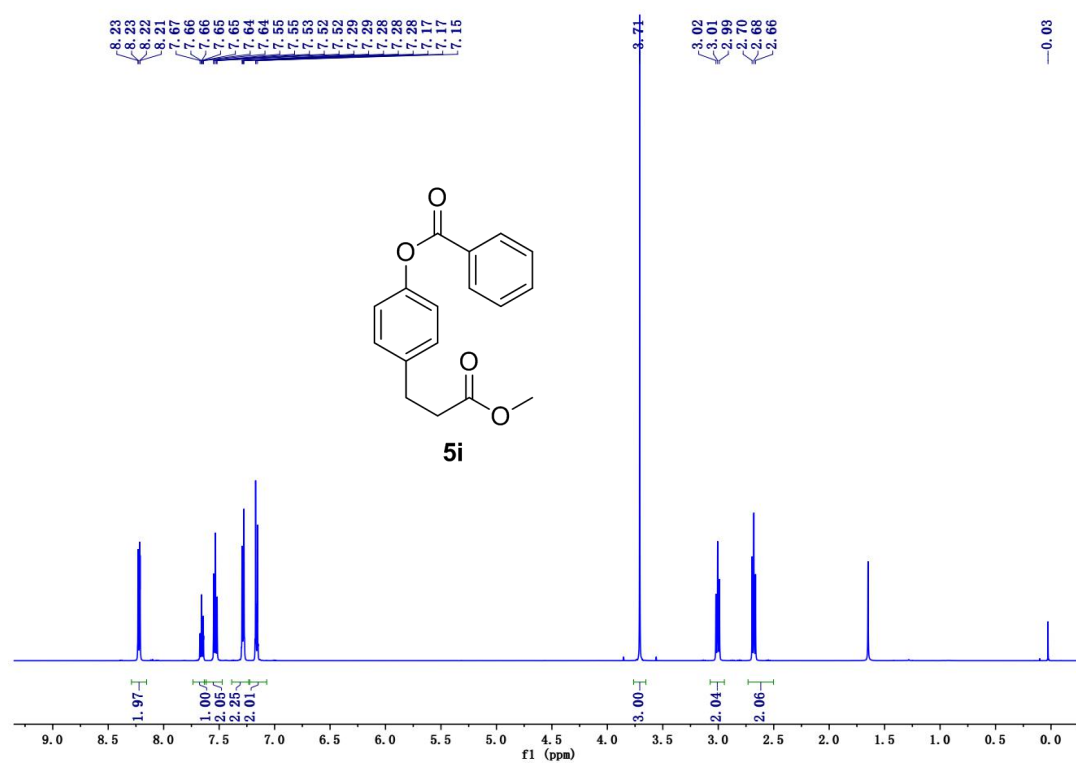




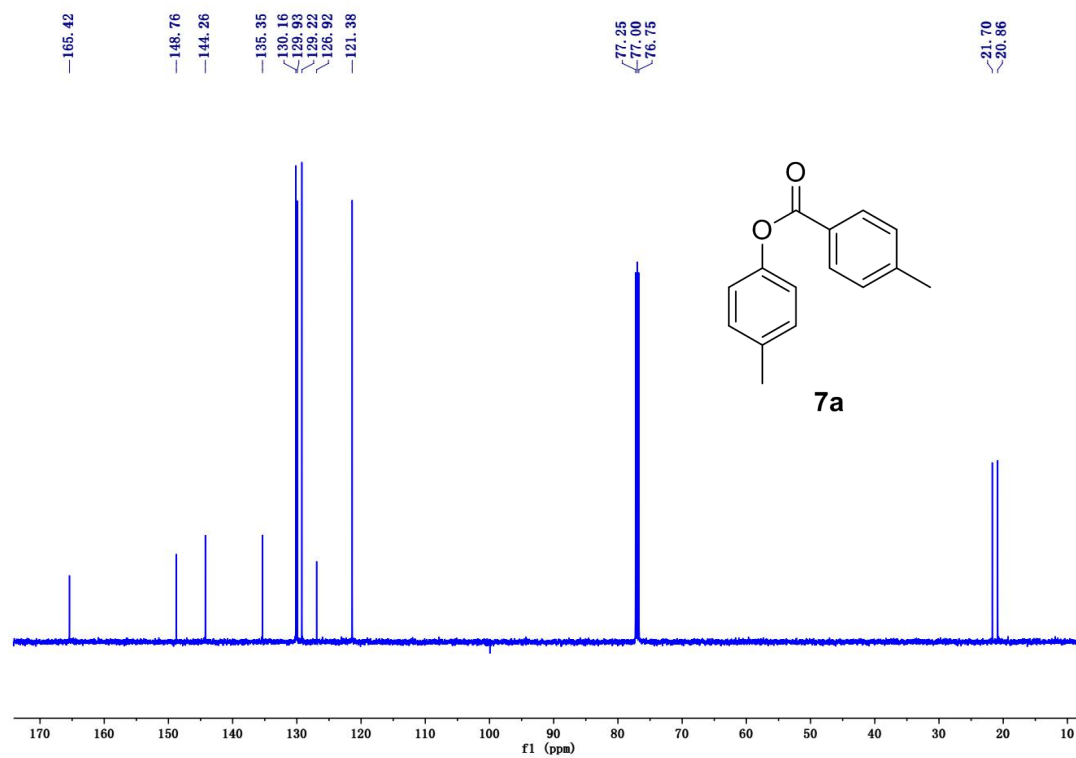
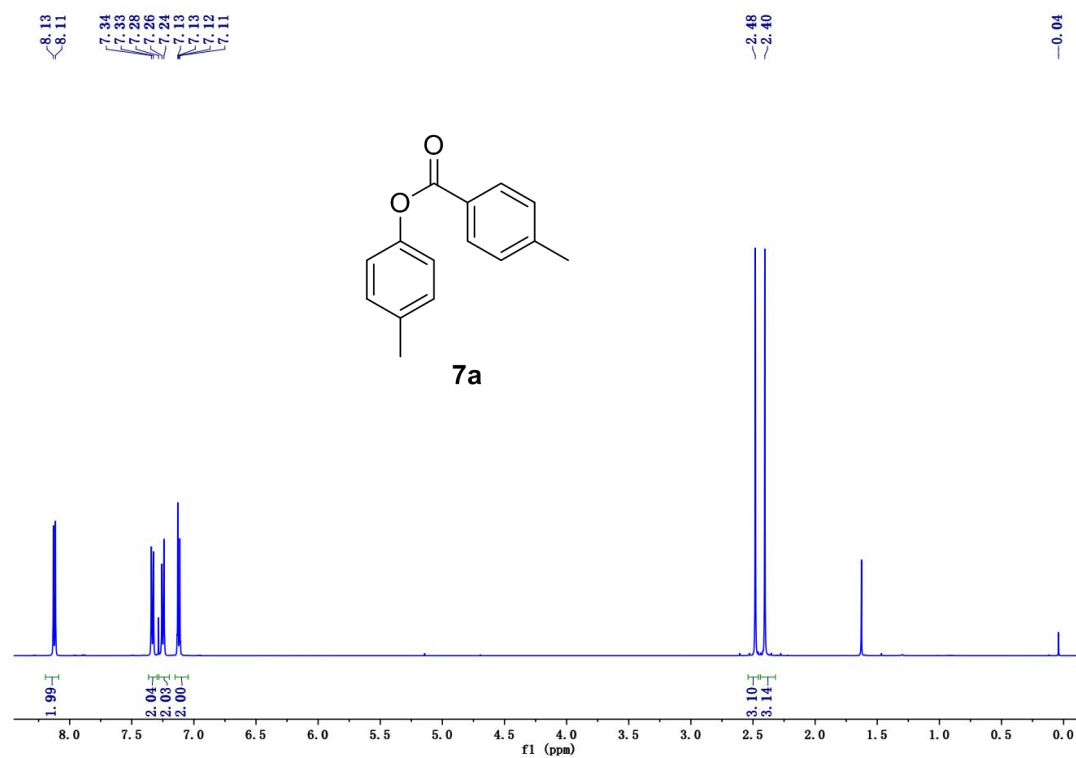


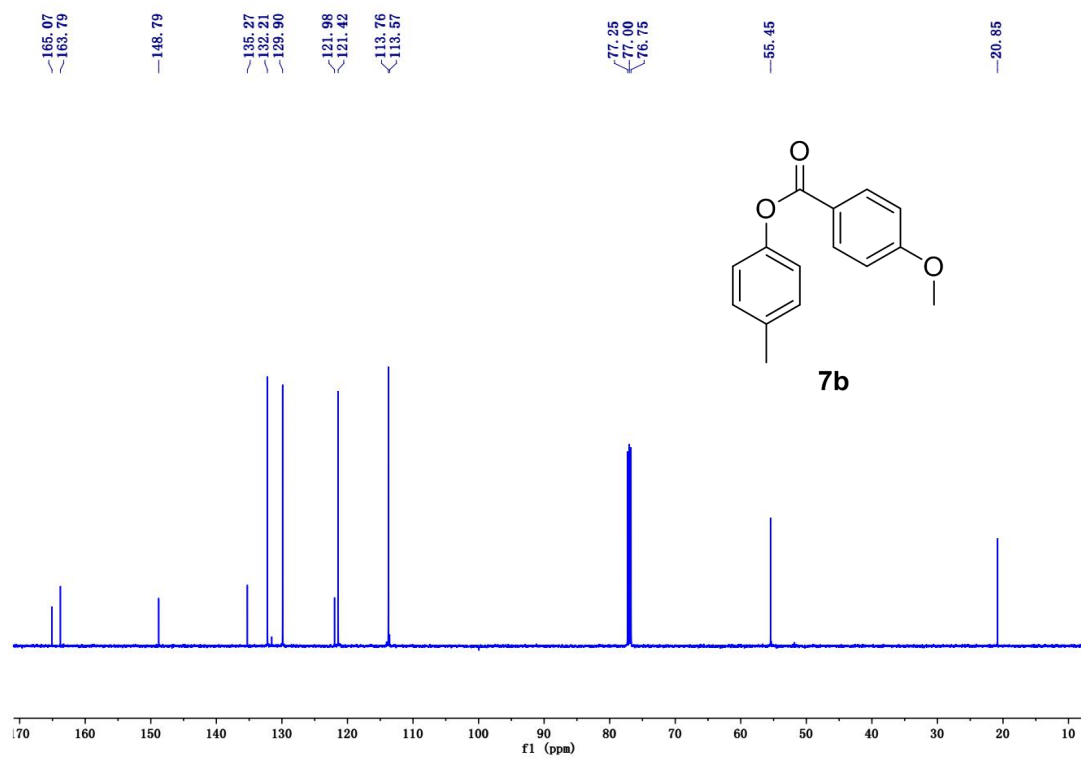
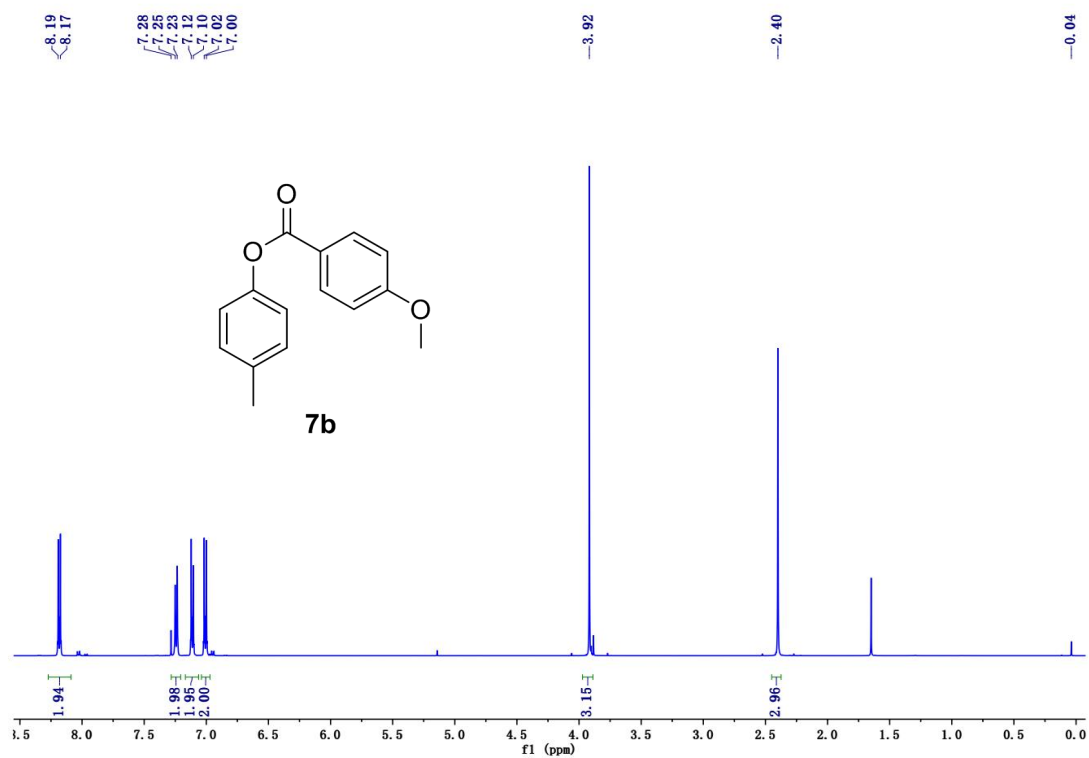


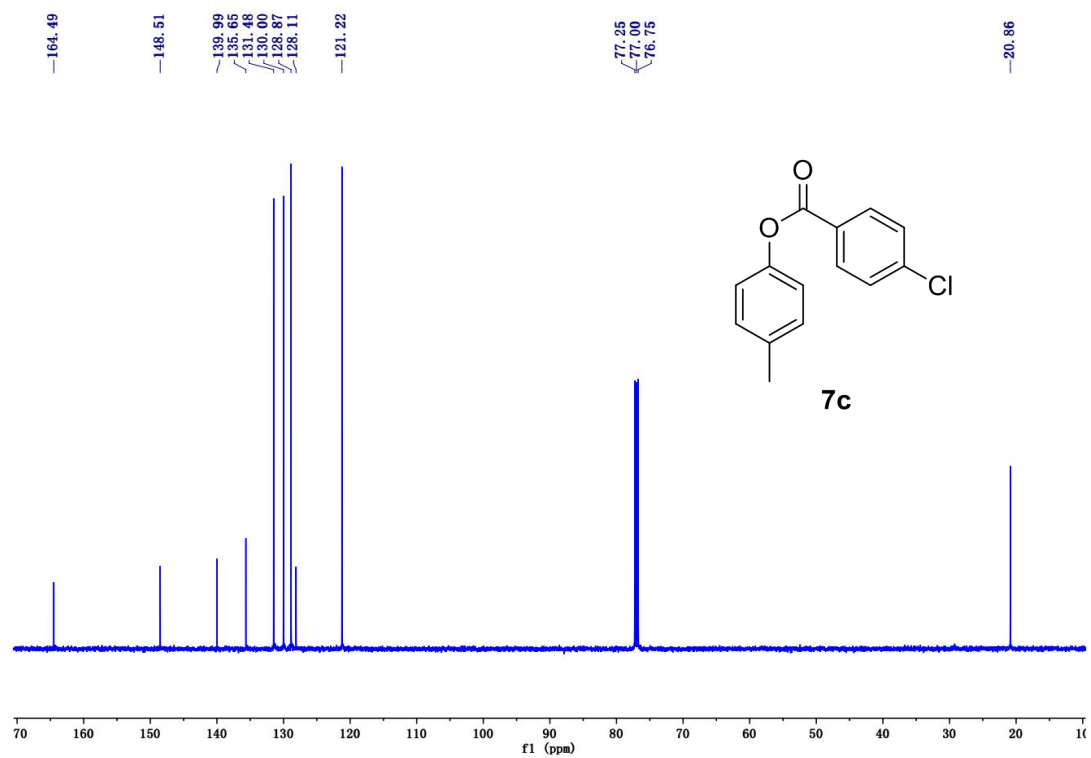
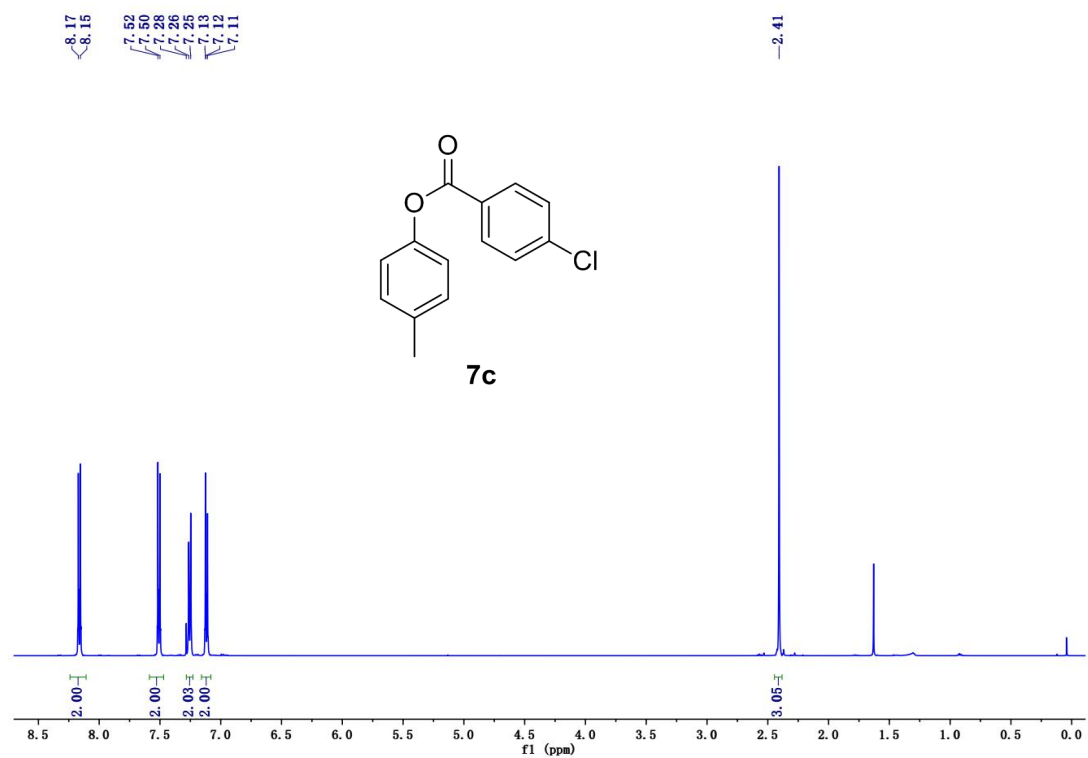


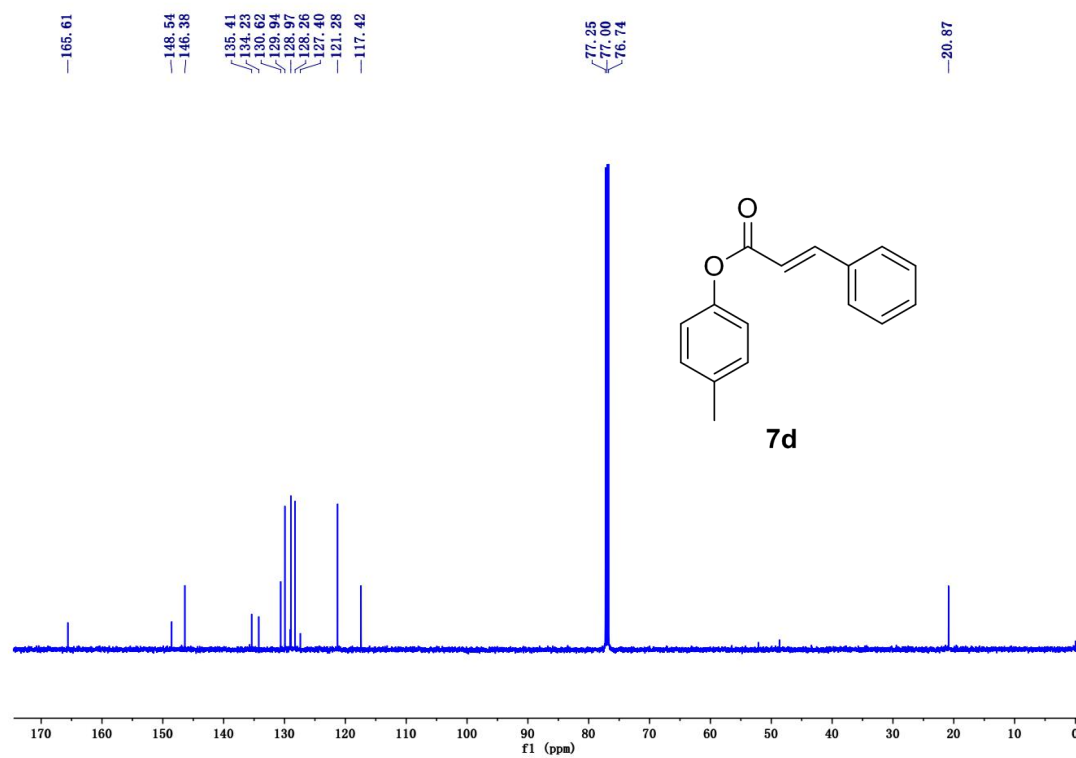
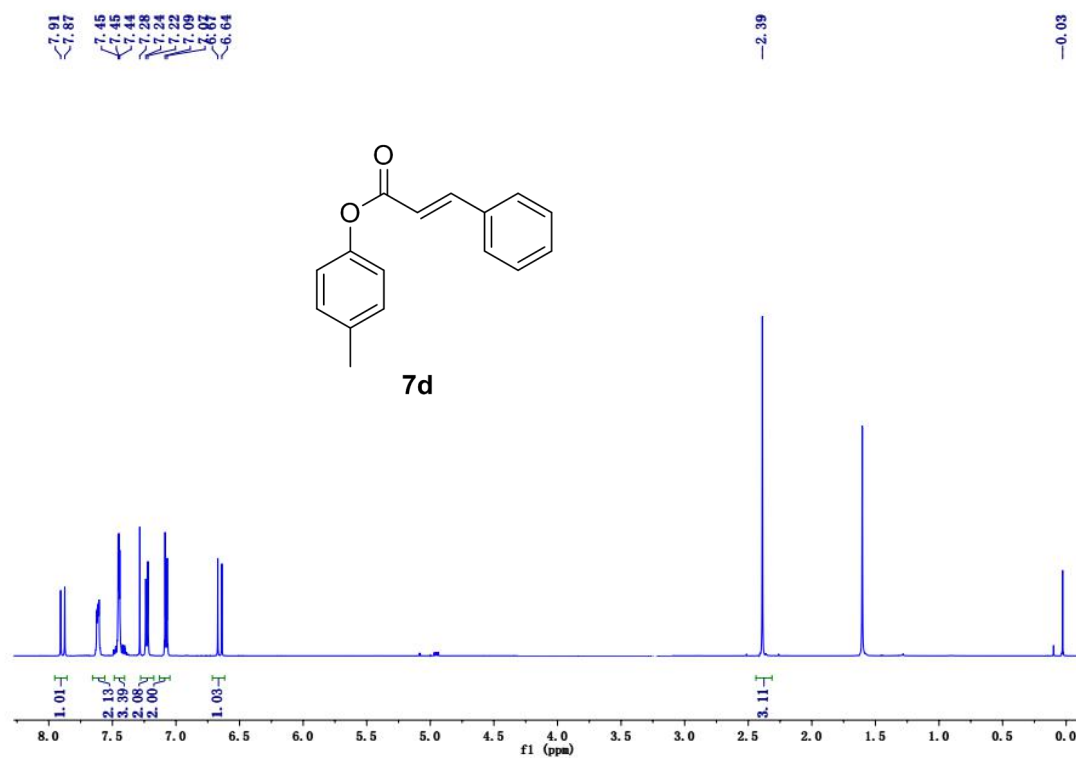


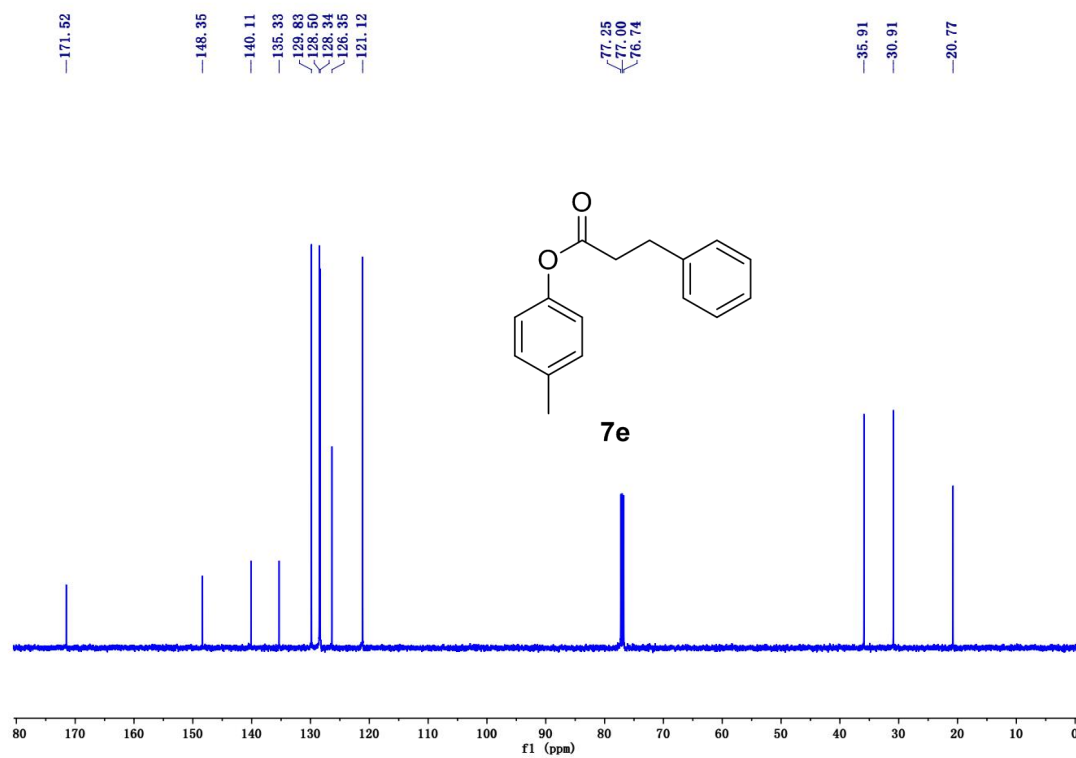
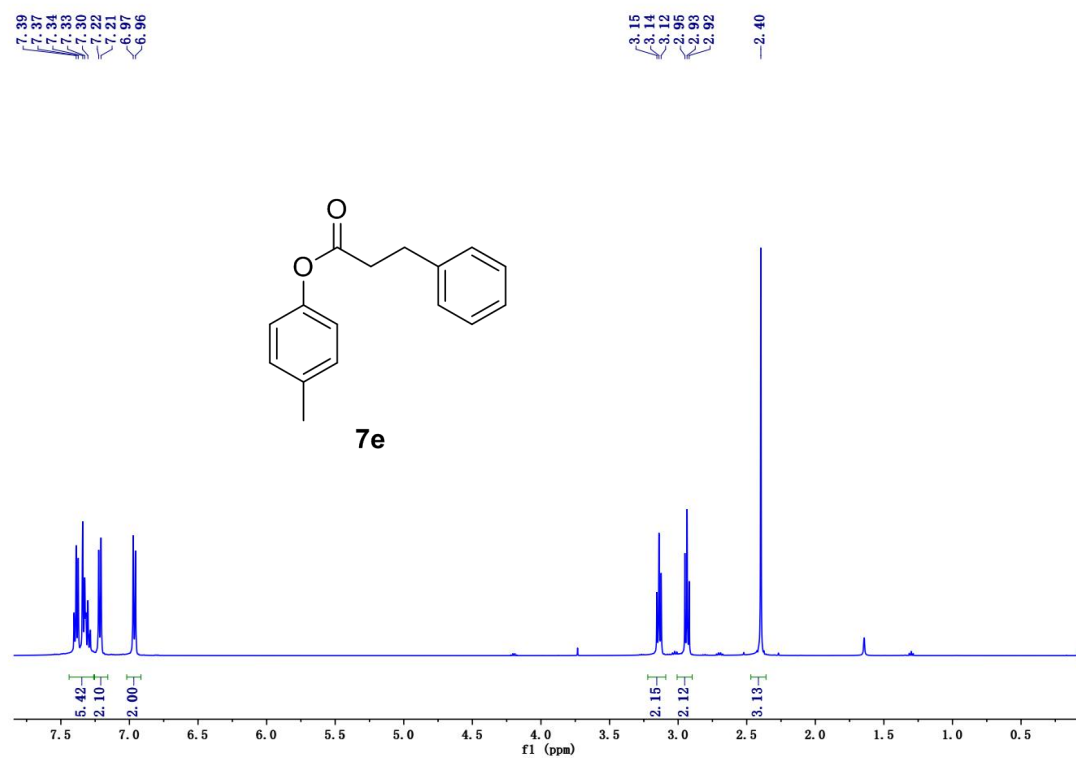
# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of 7

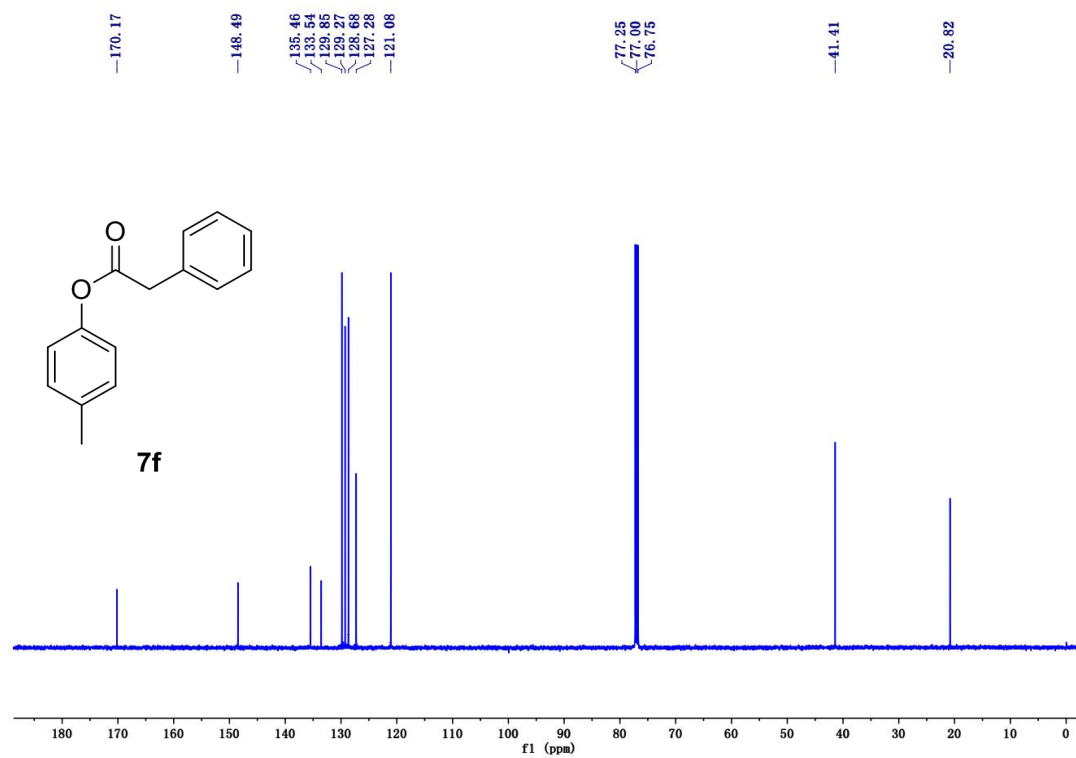
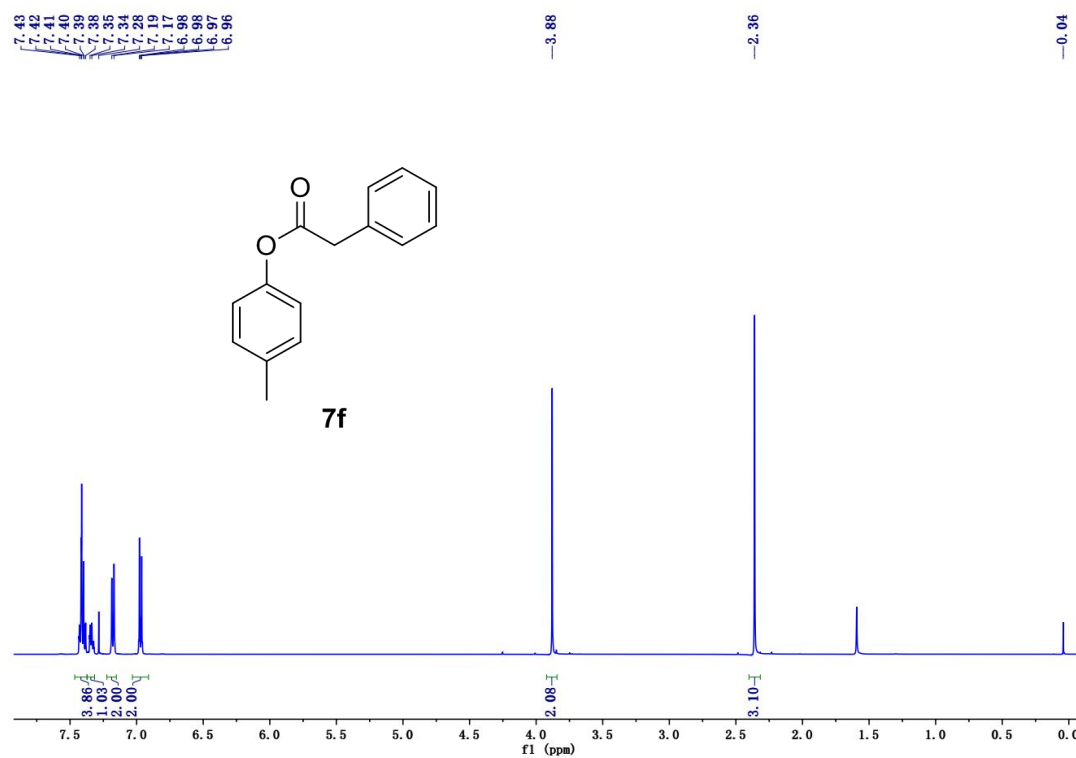


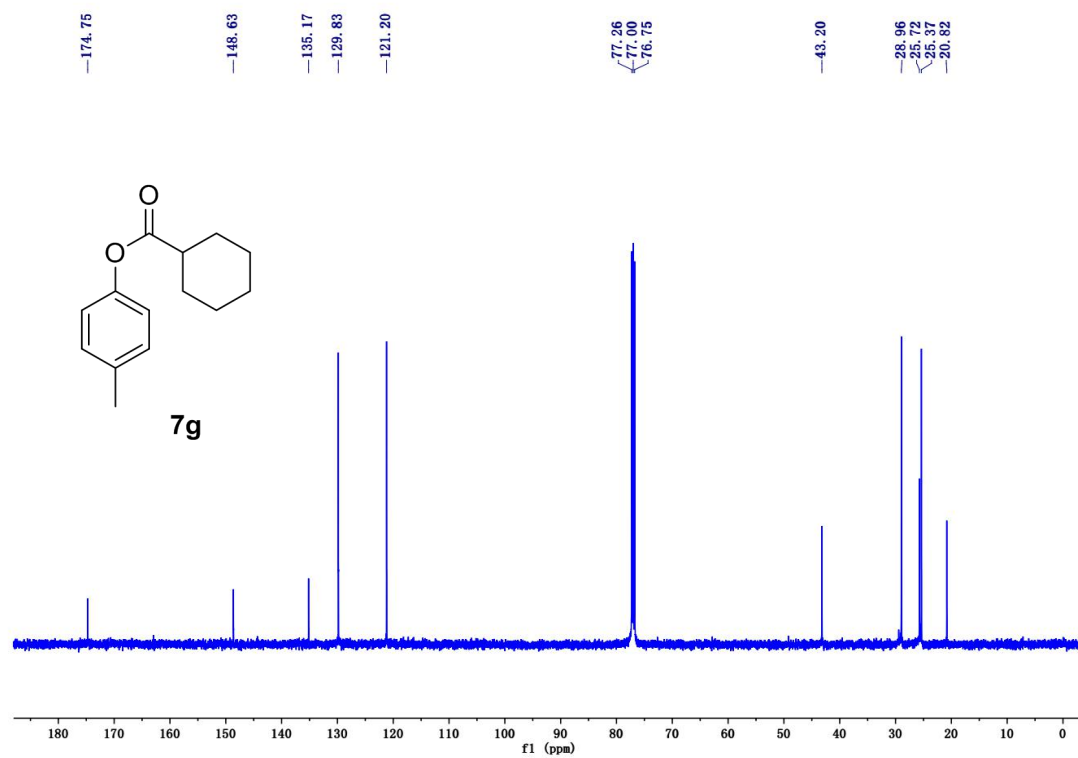
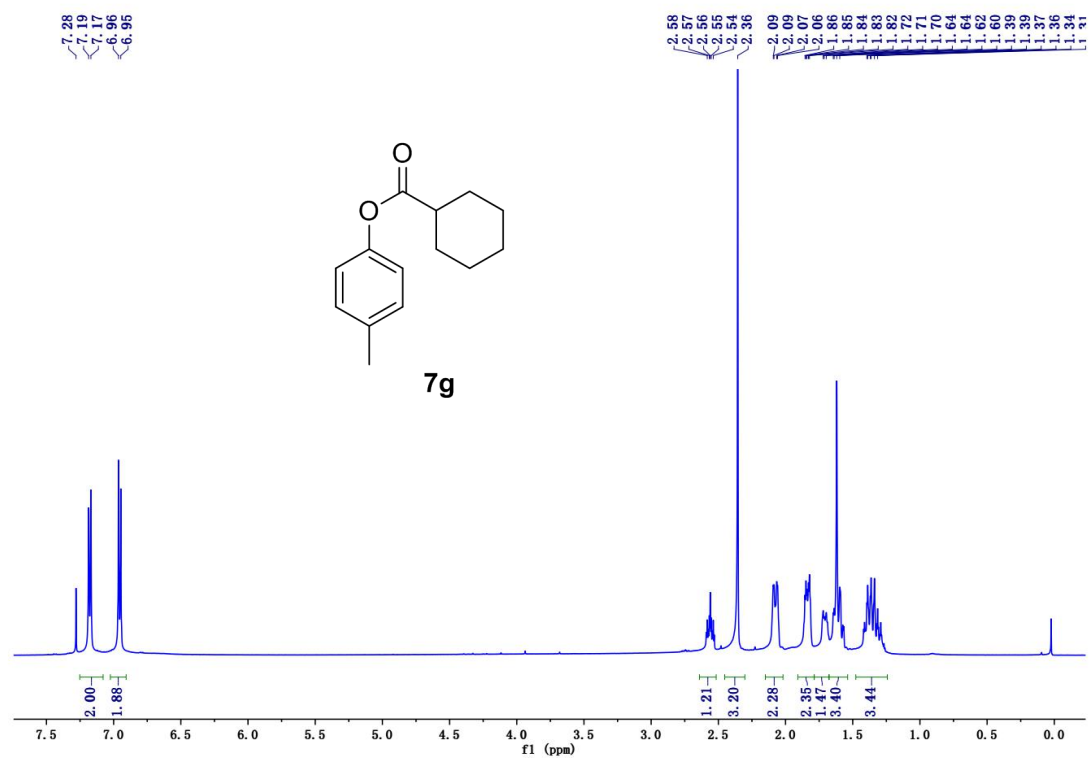




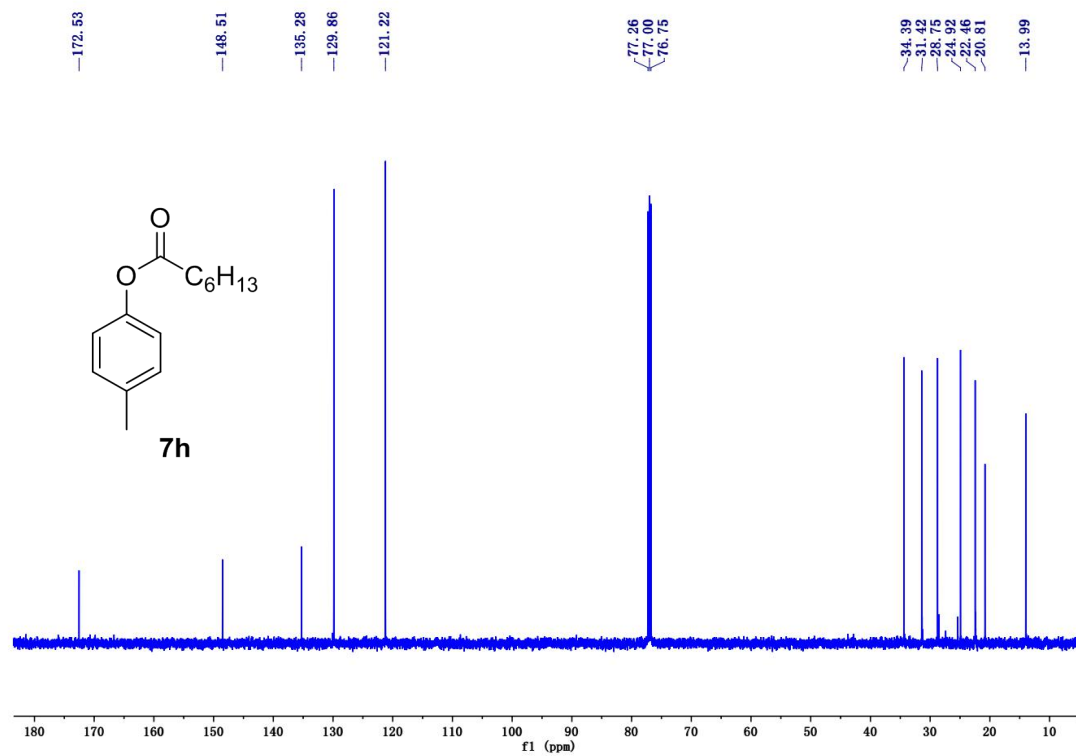
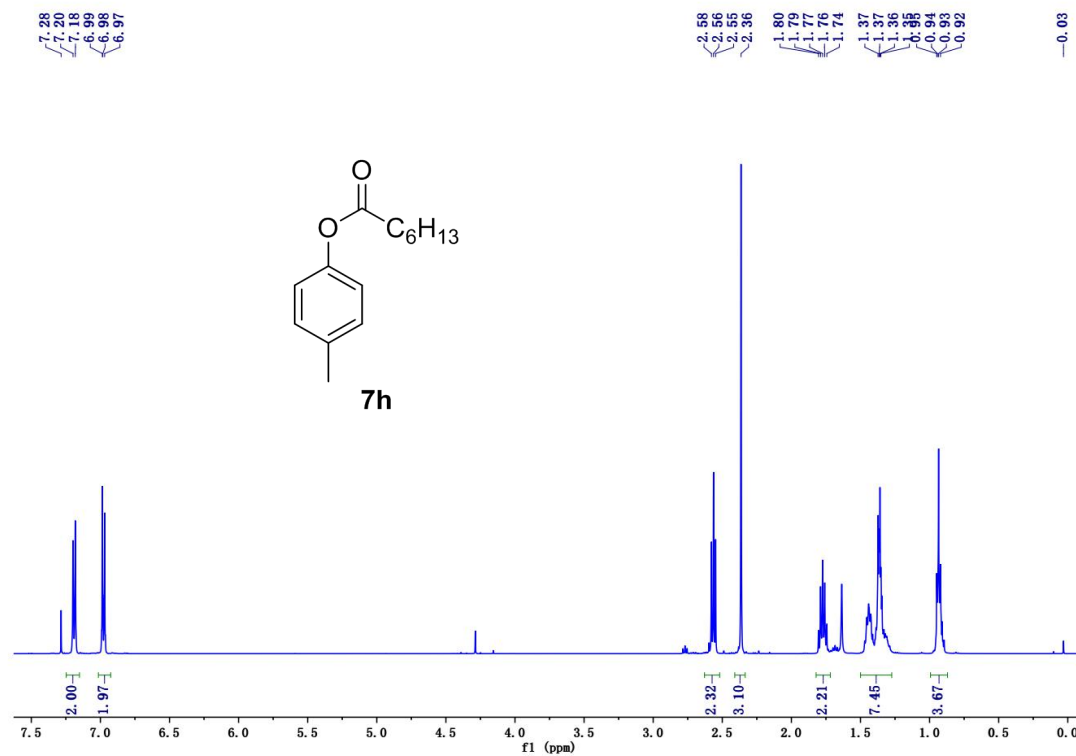


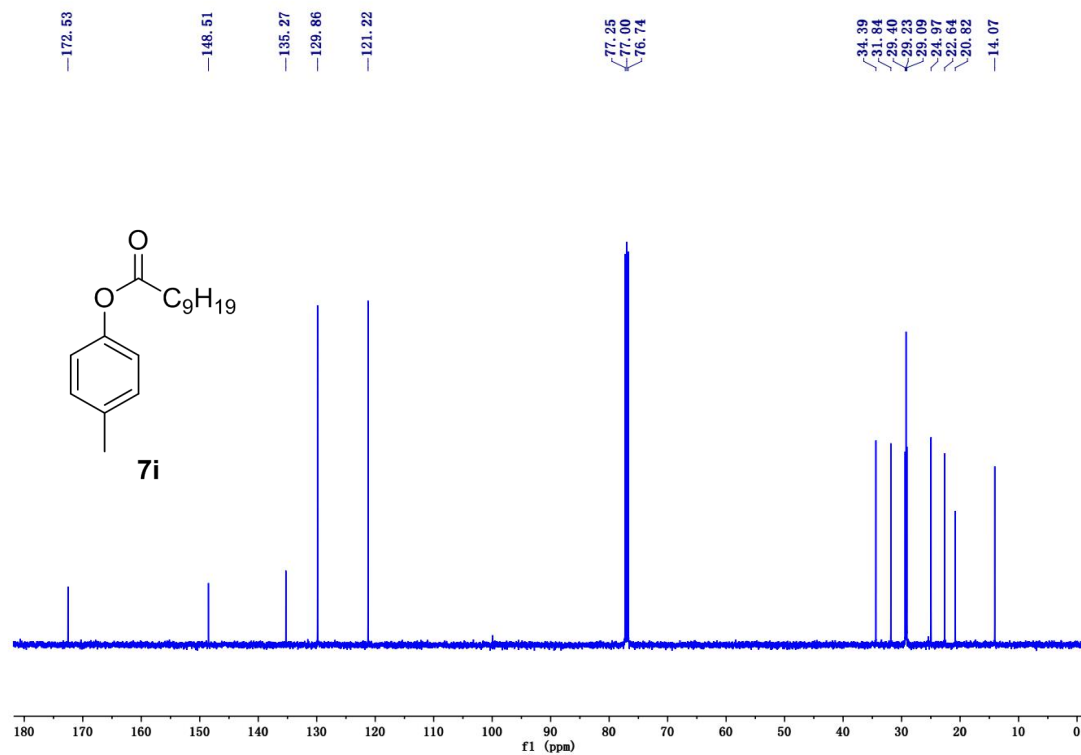
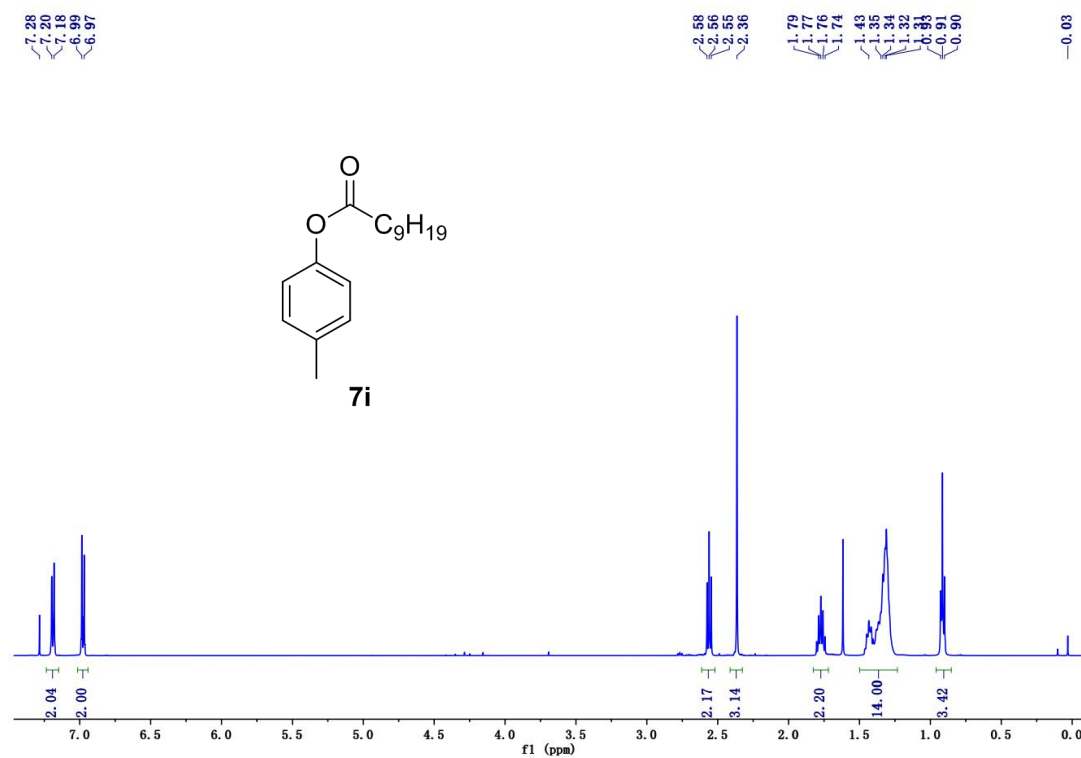


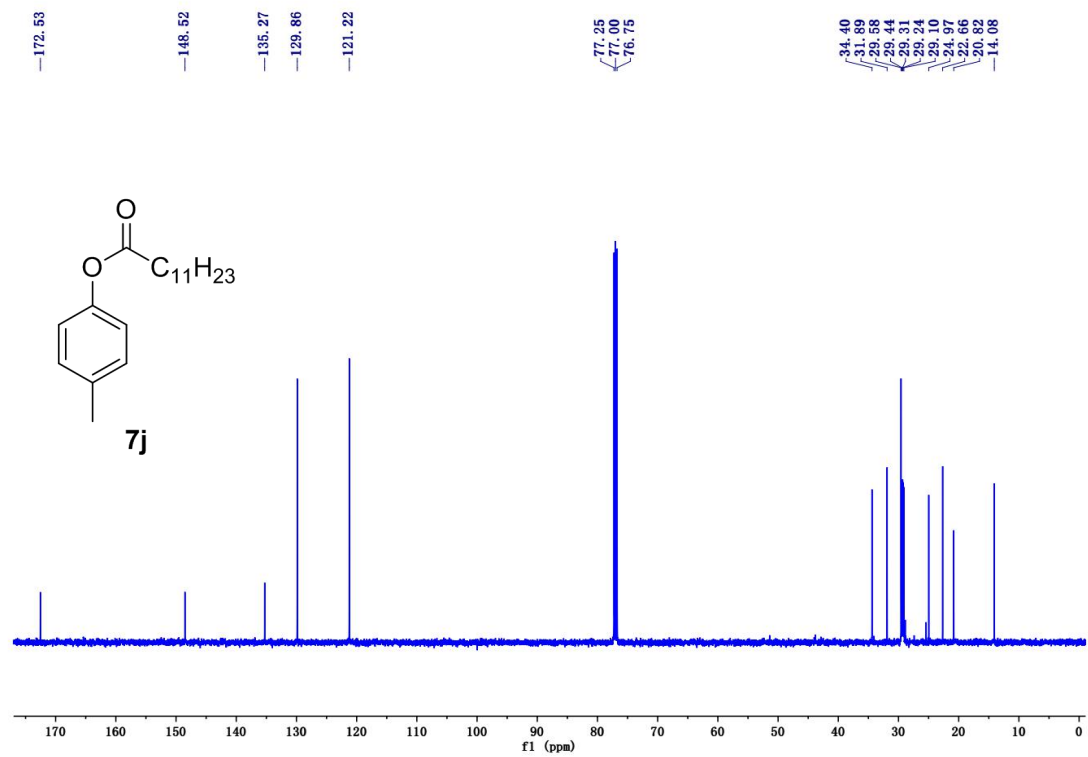
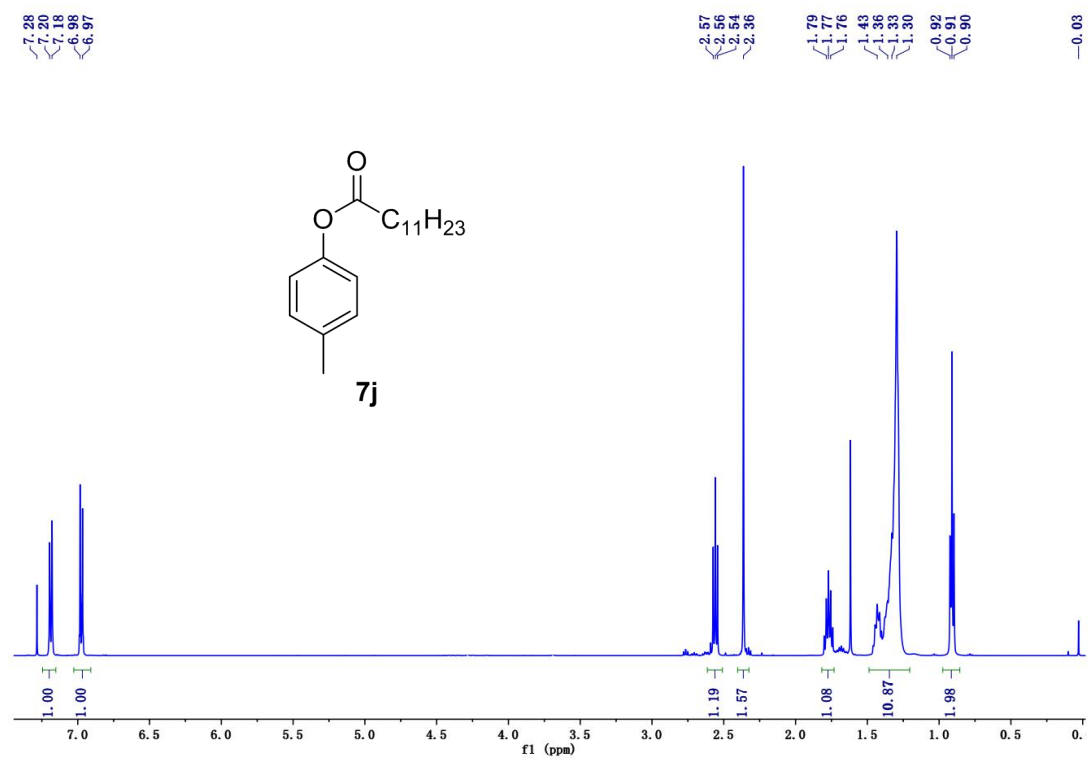




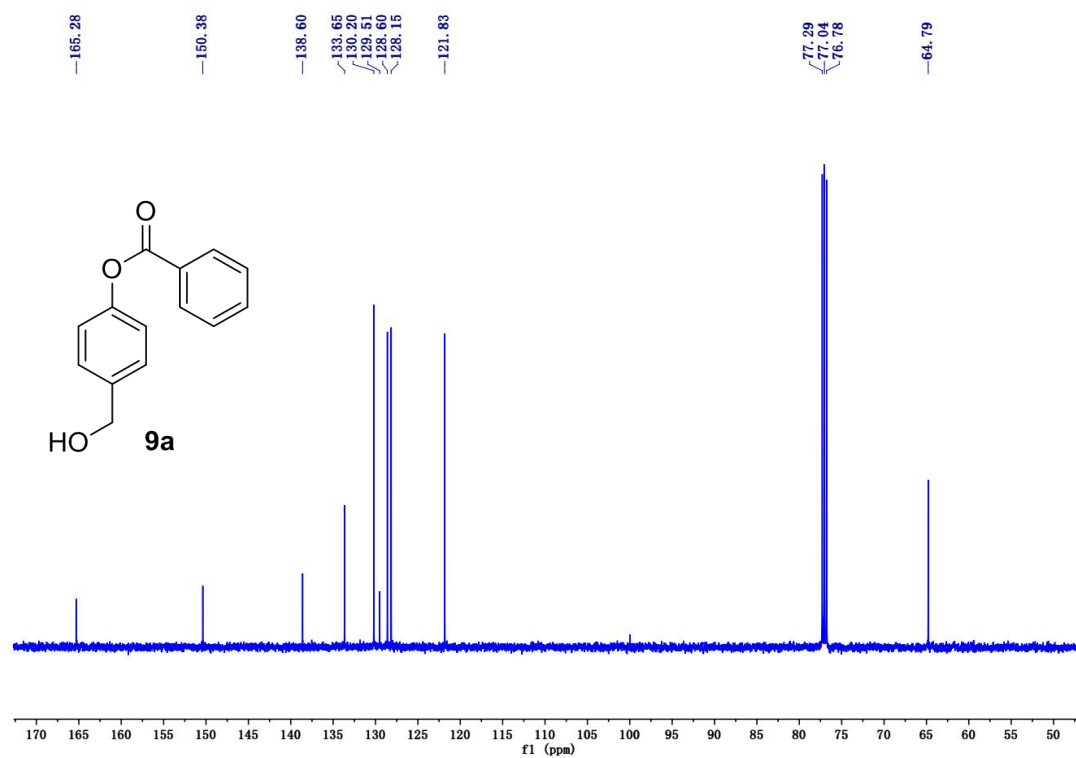
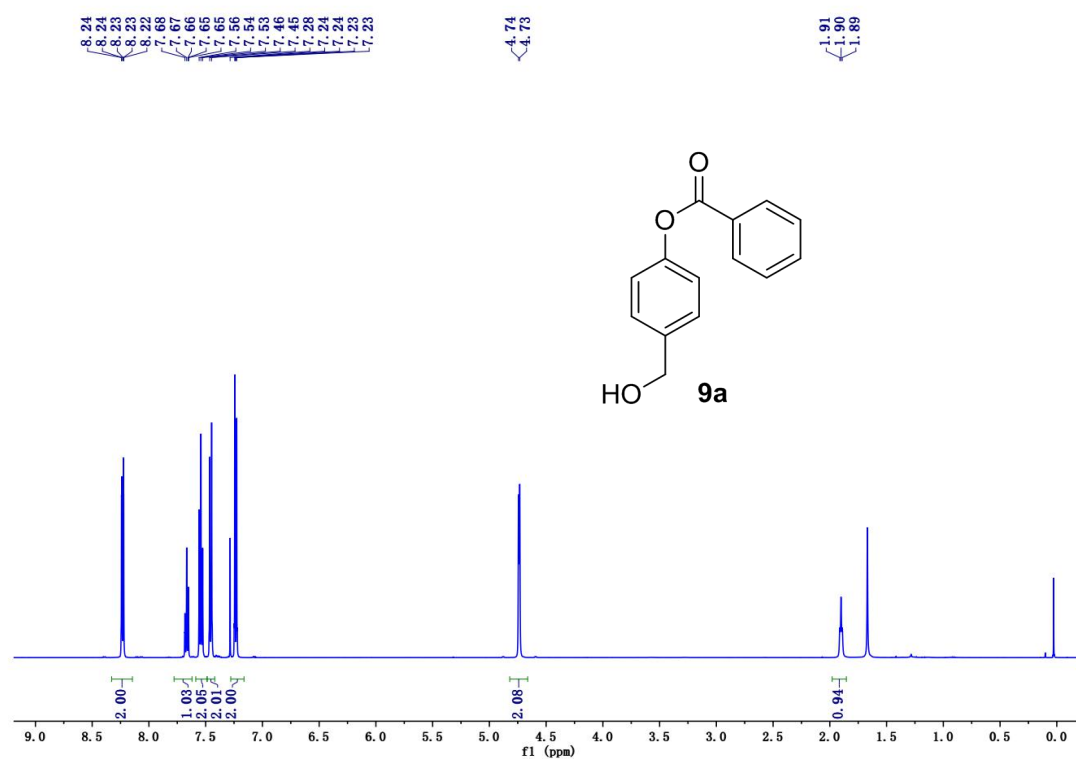


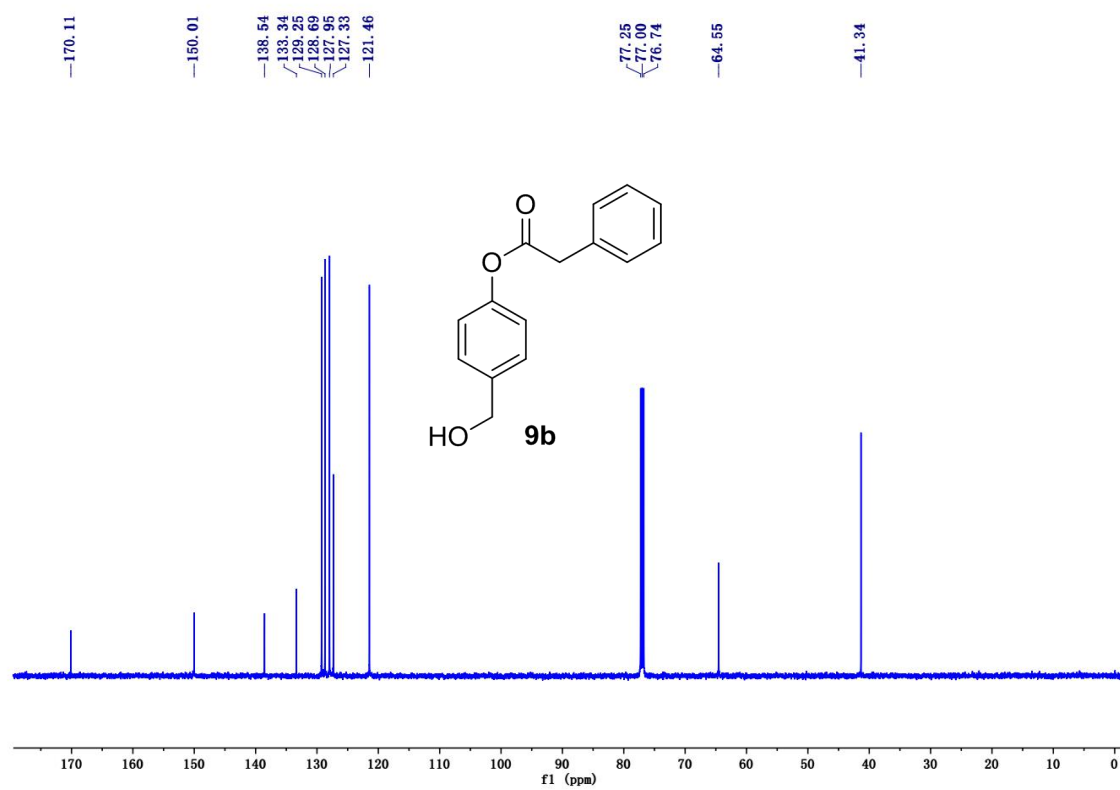
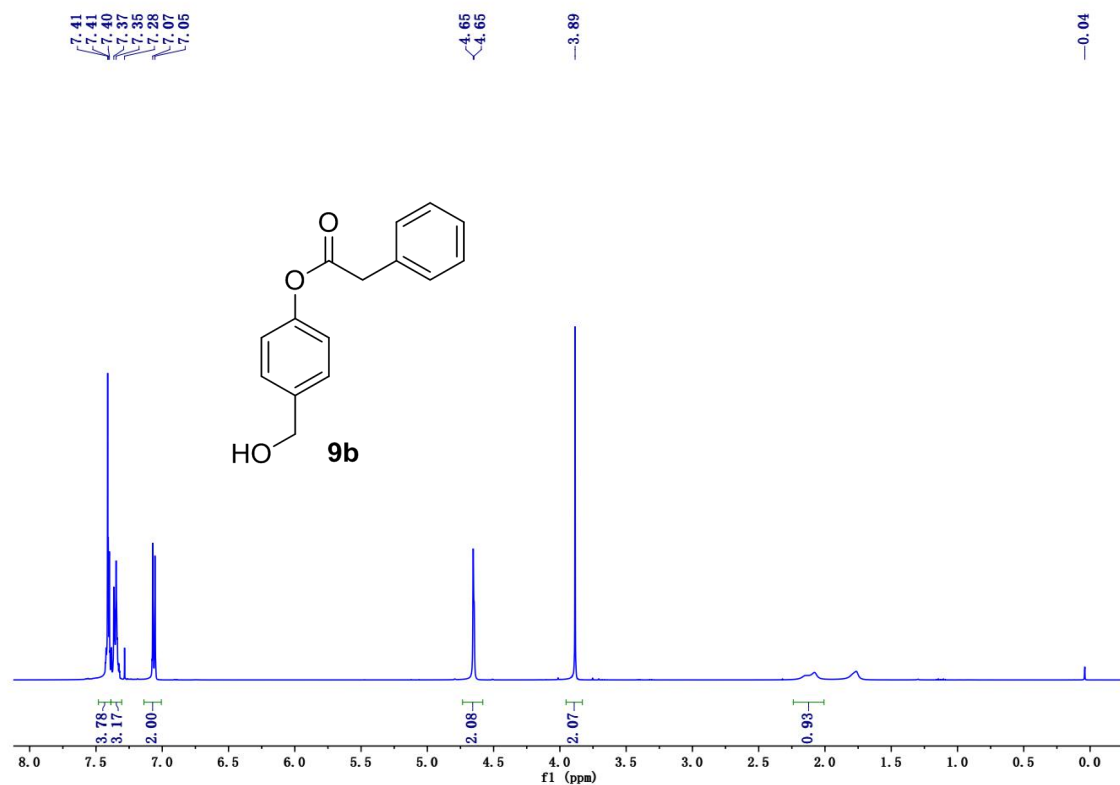


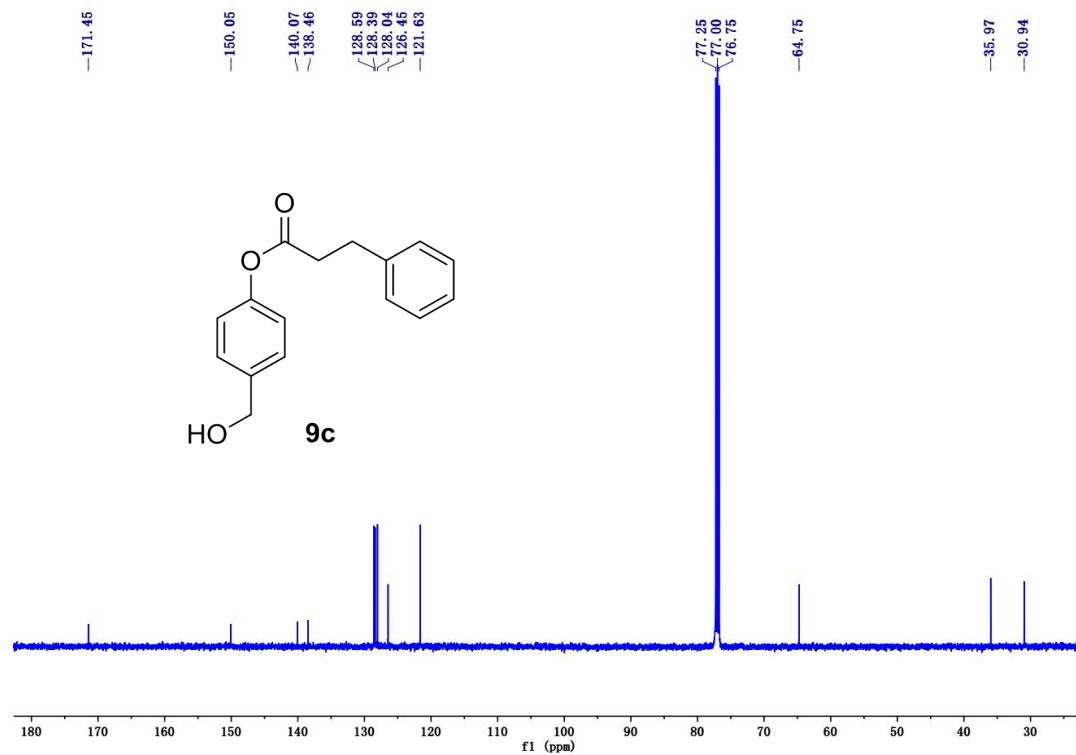
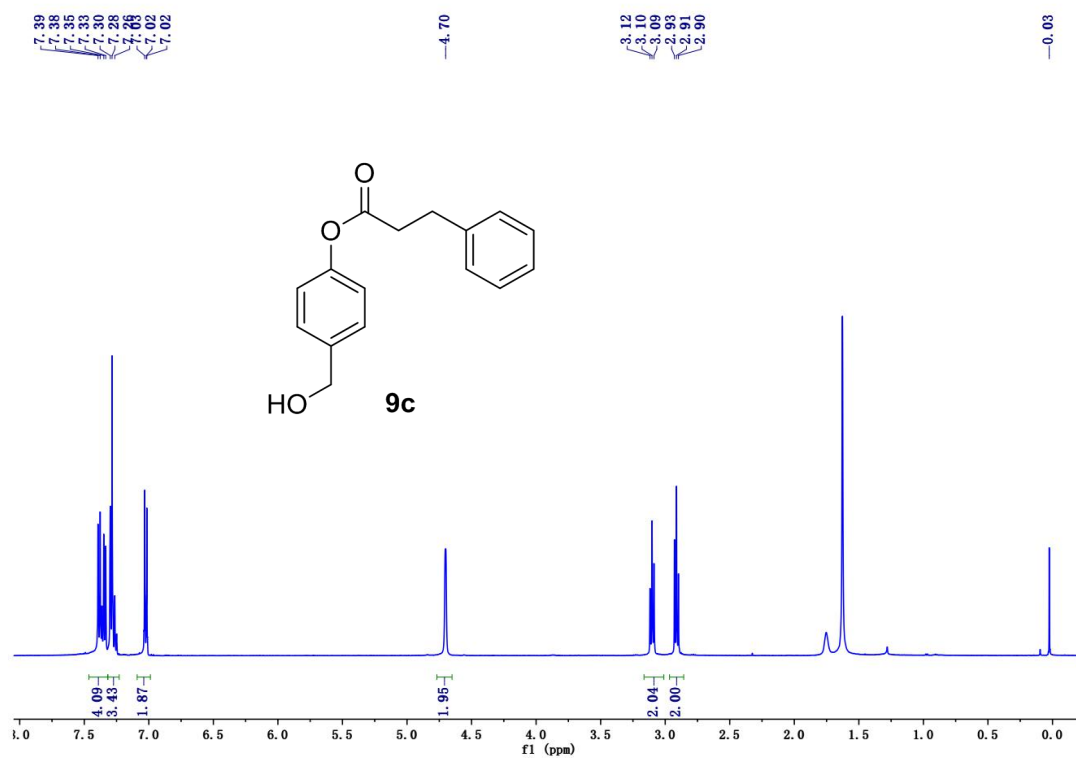


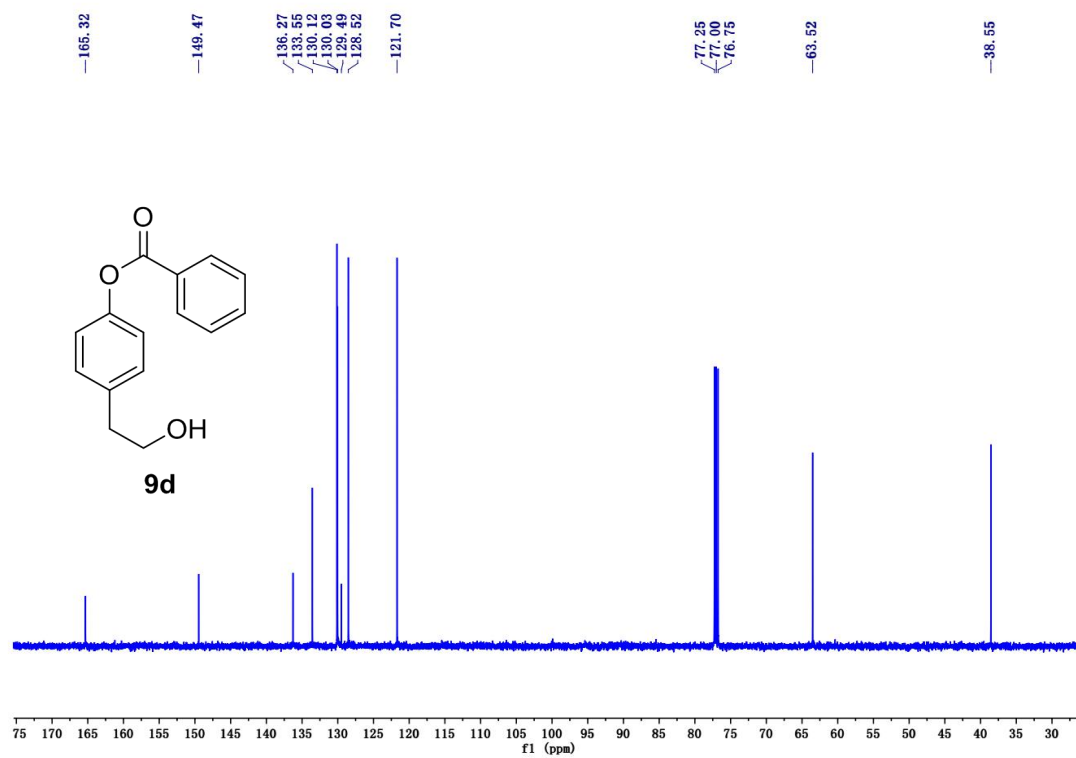
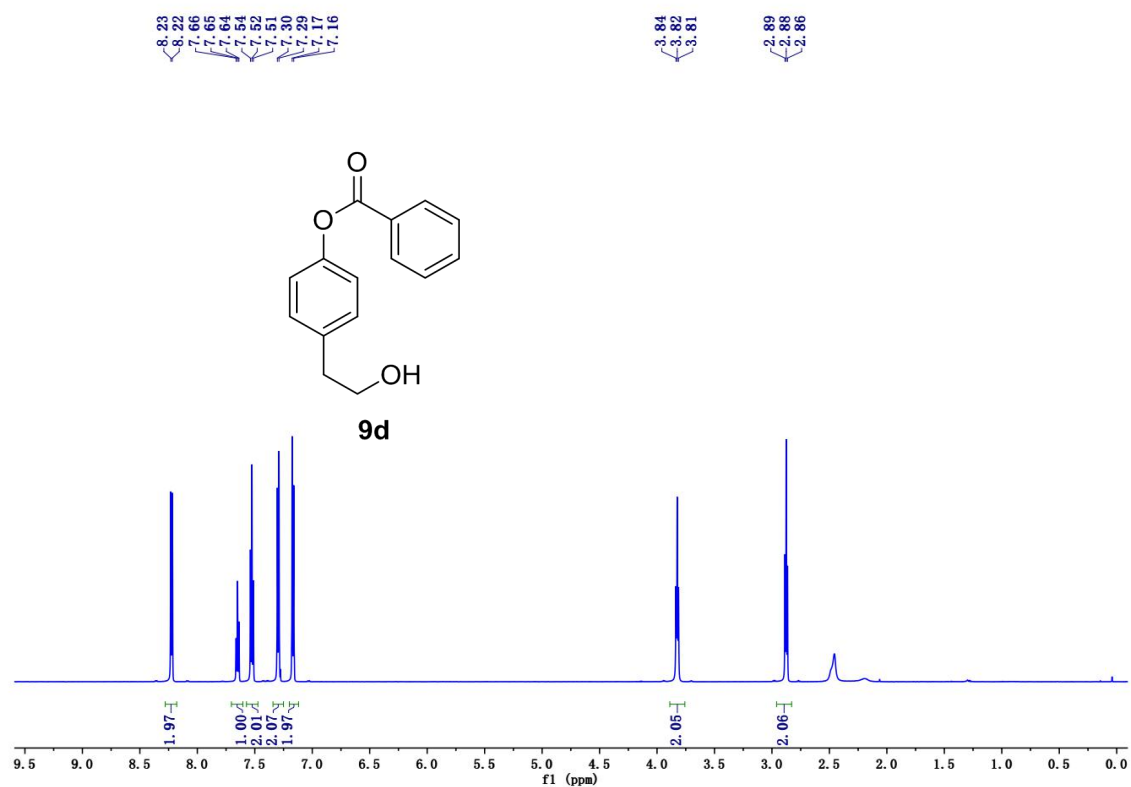


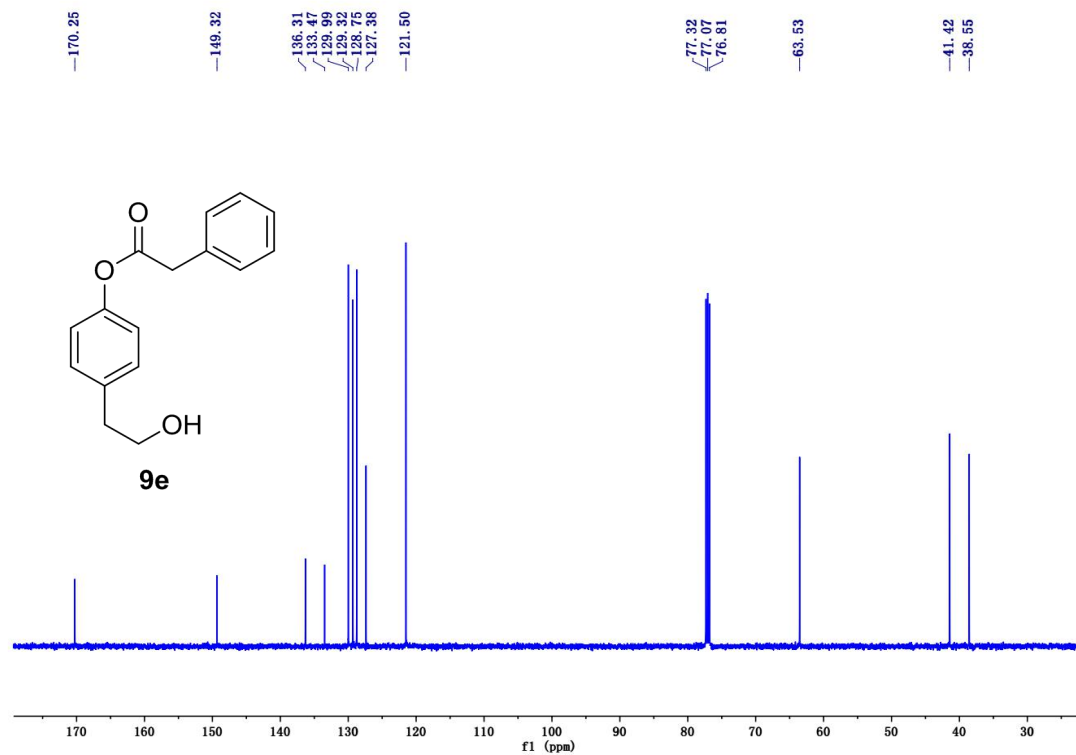
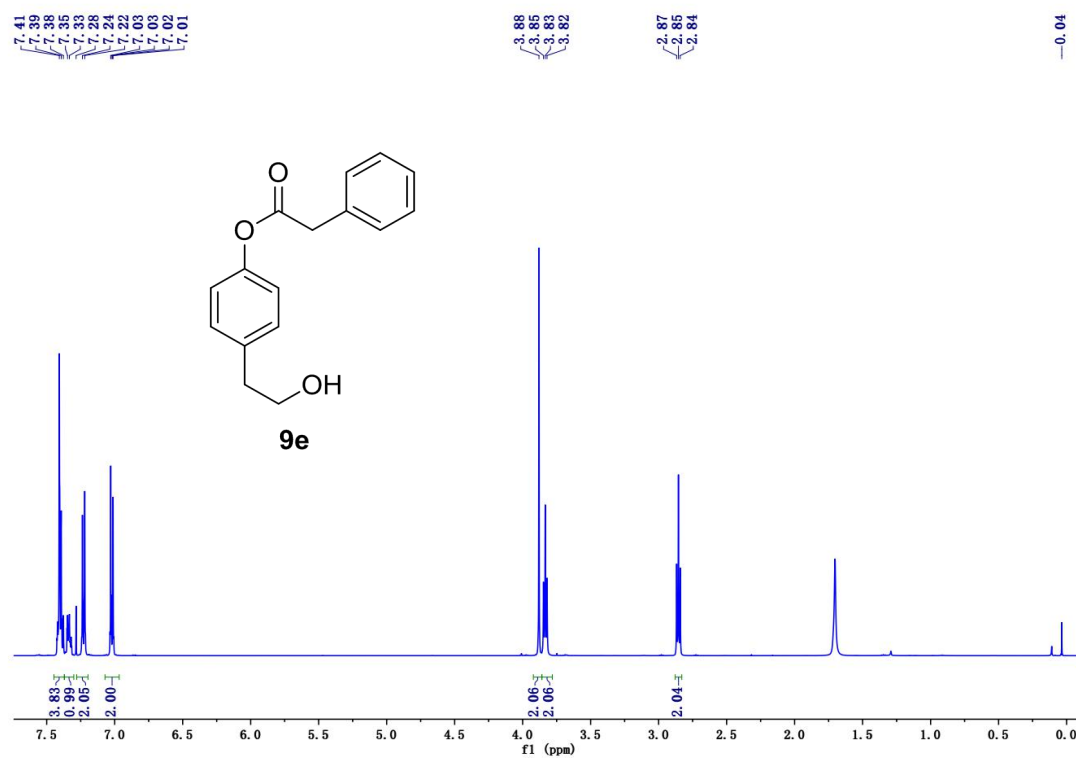
# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of **9**



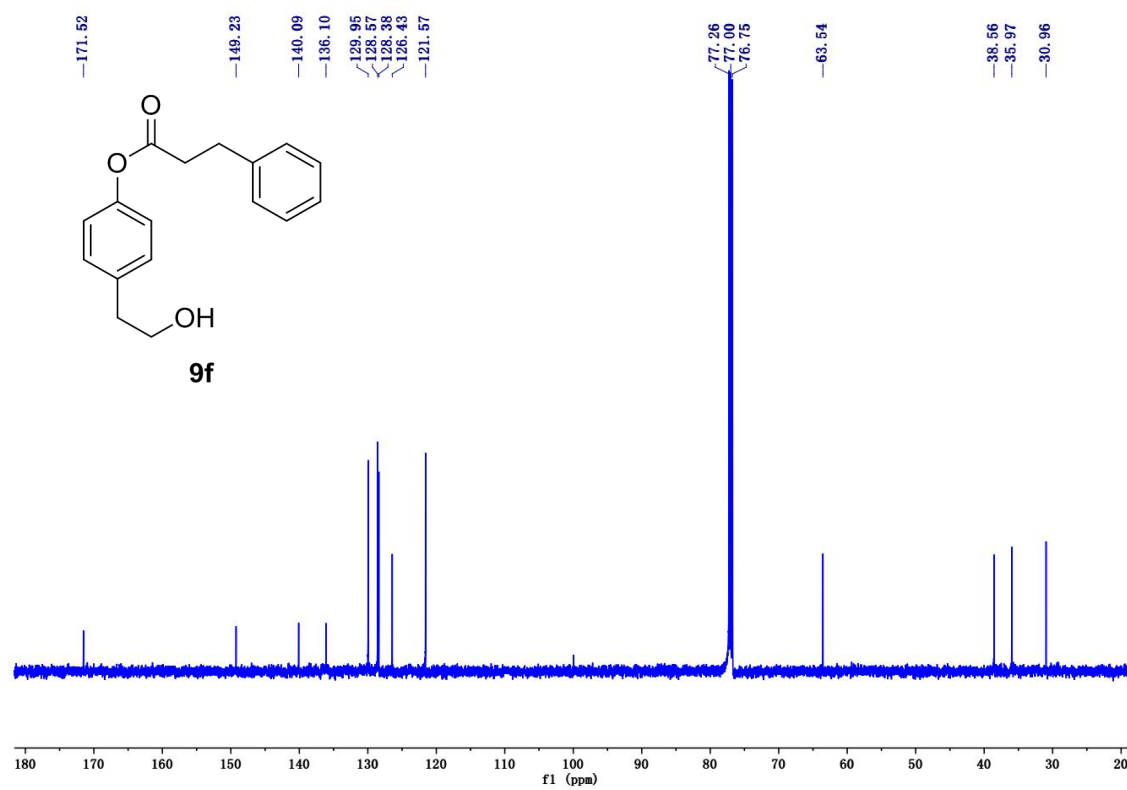
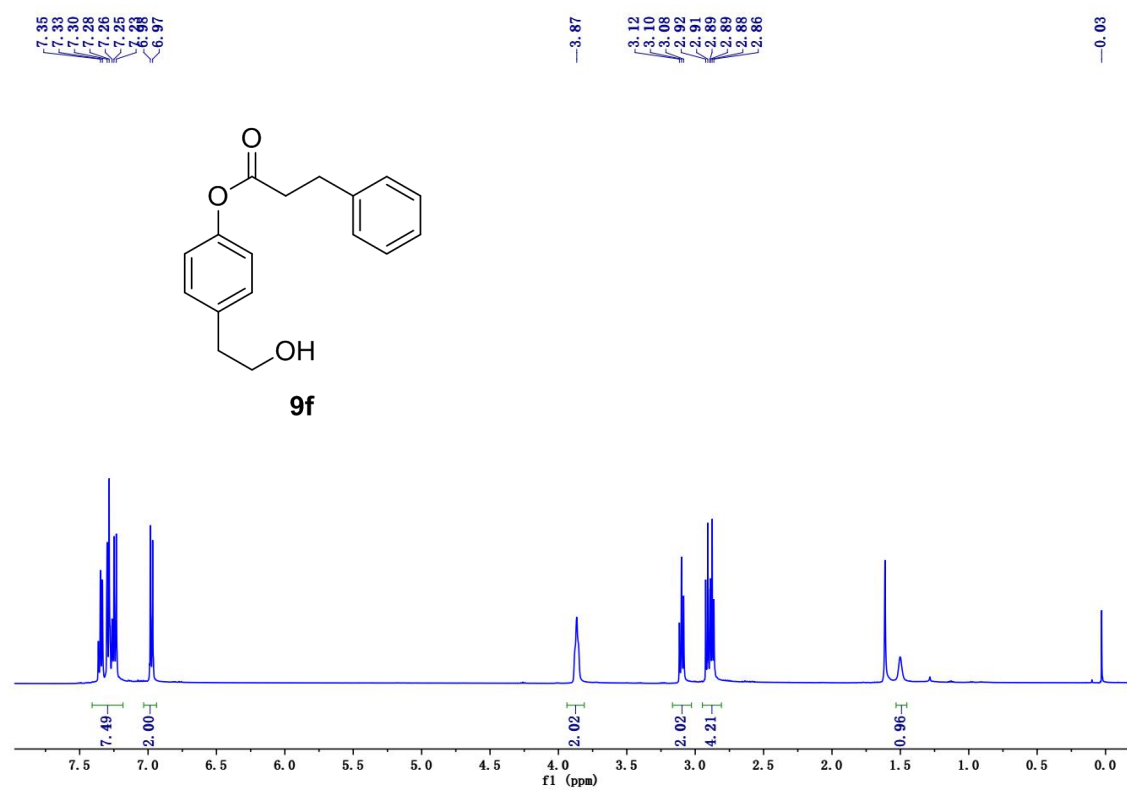


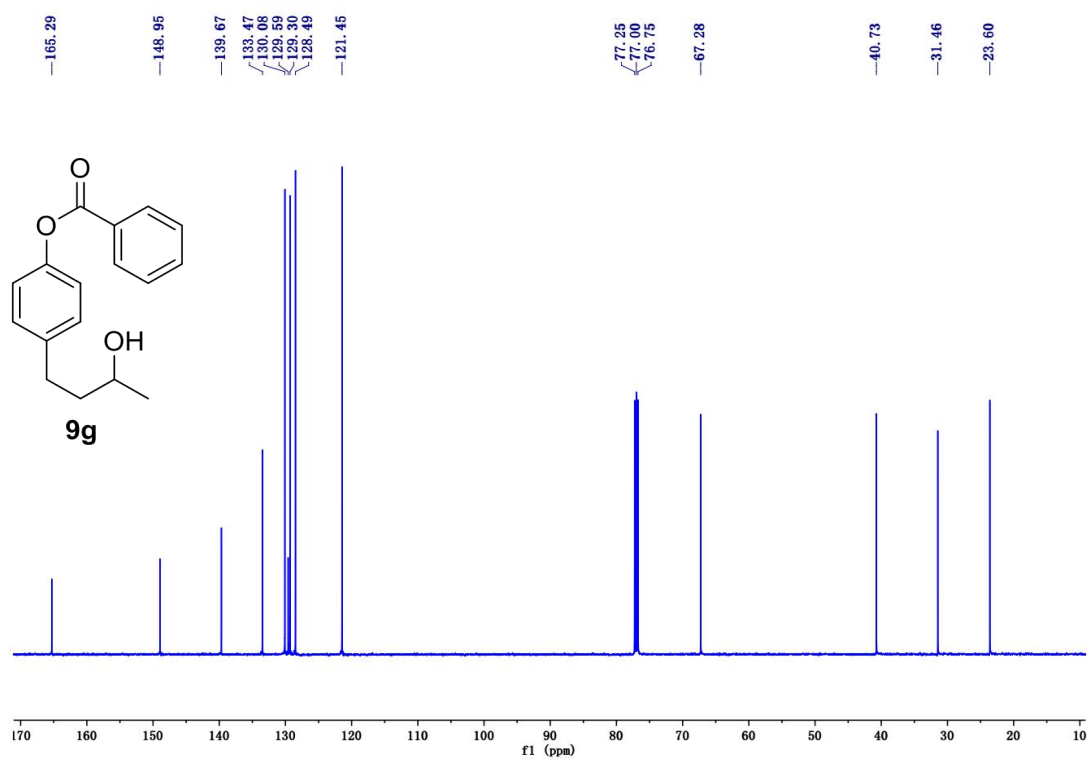
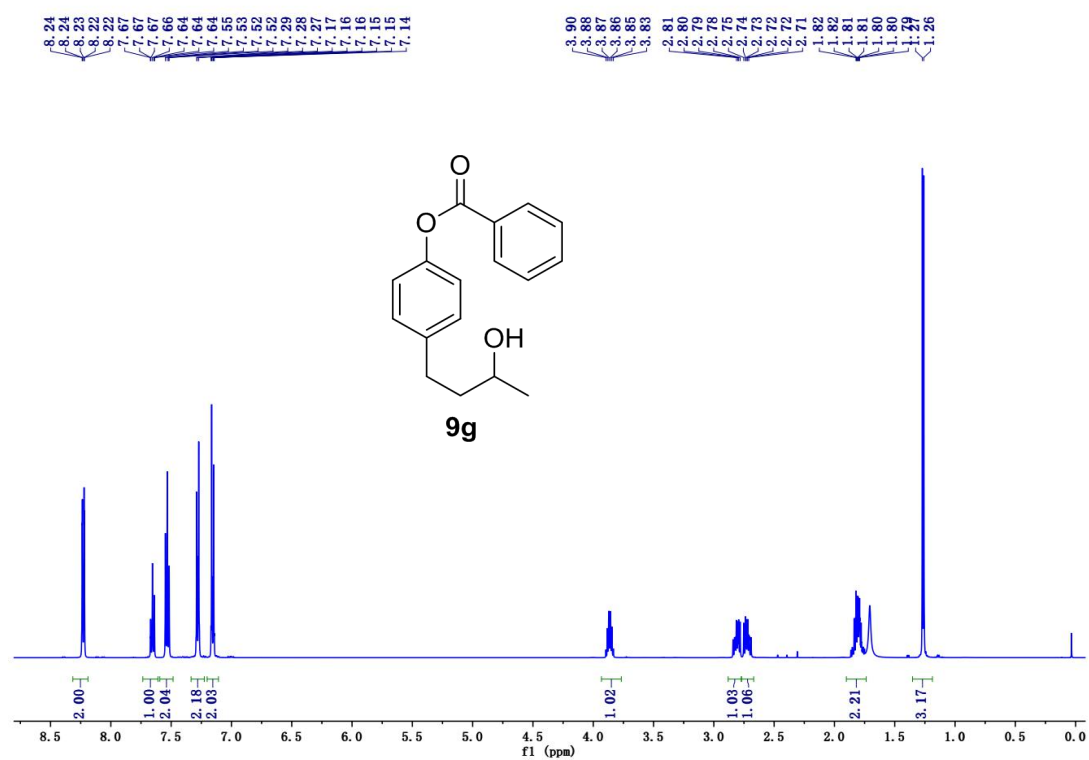


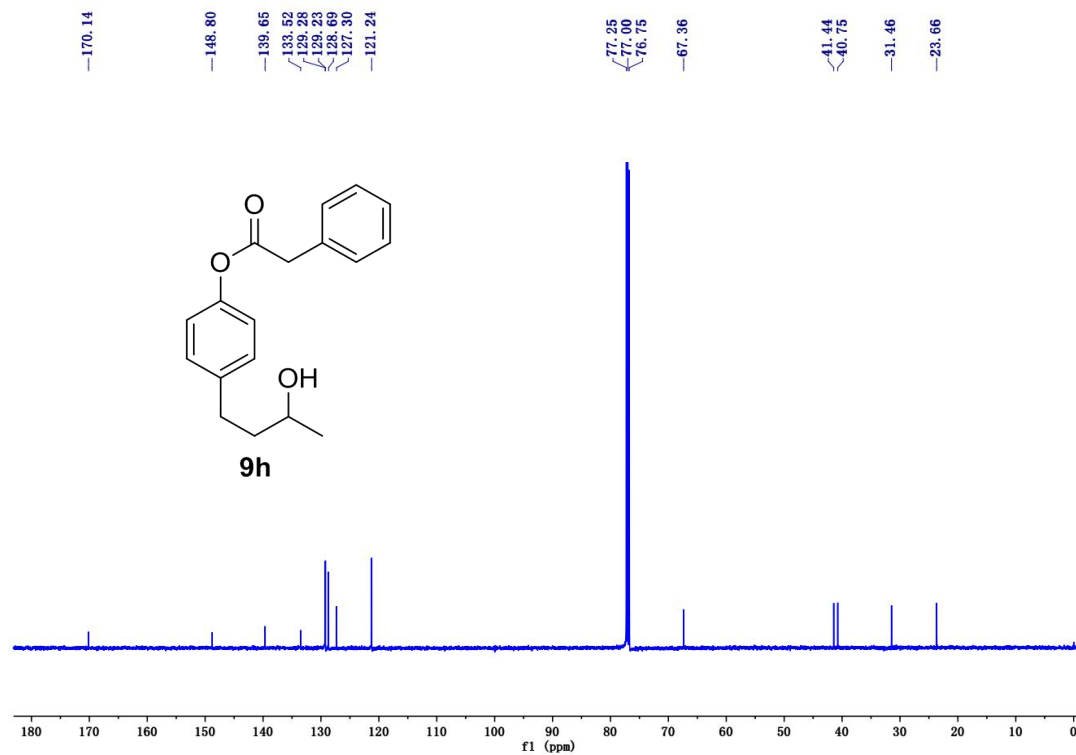
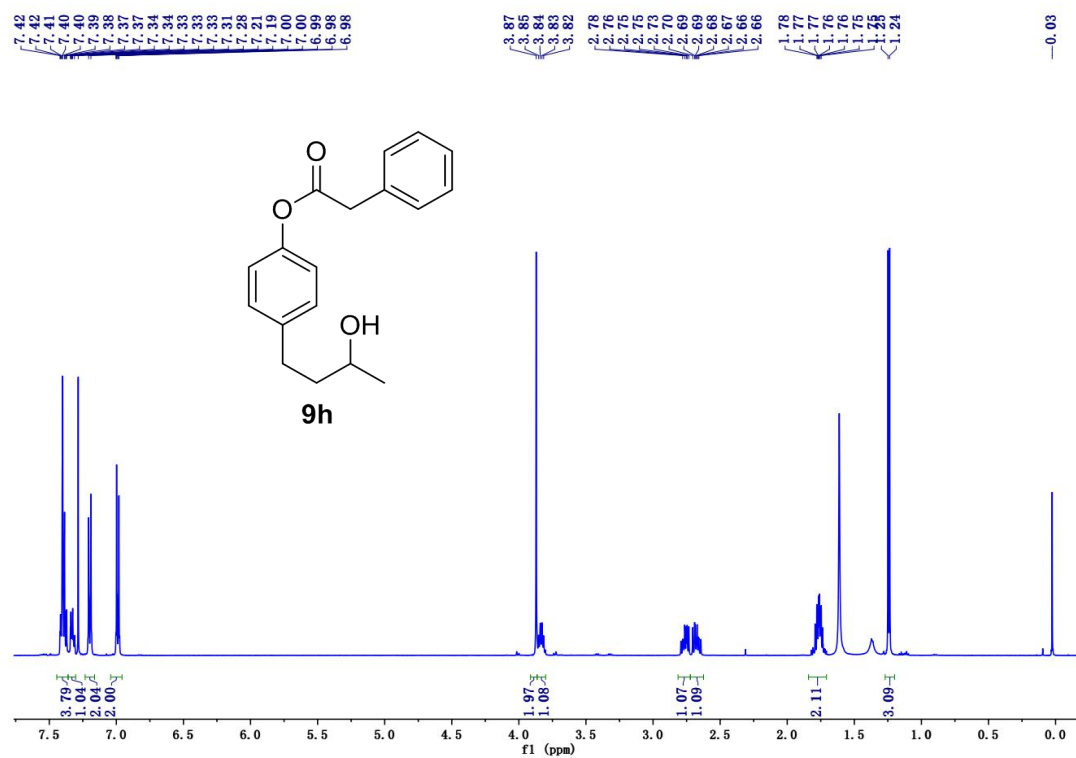


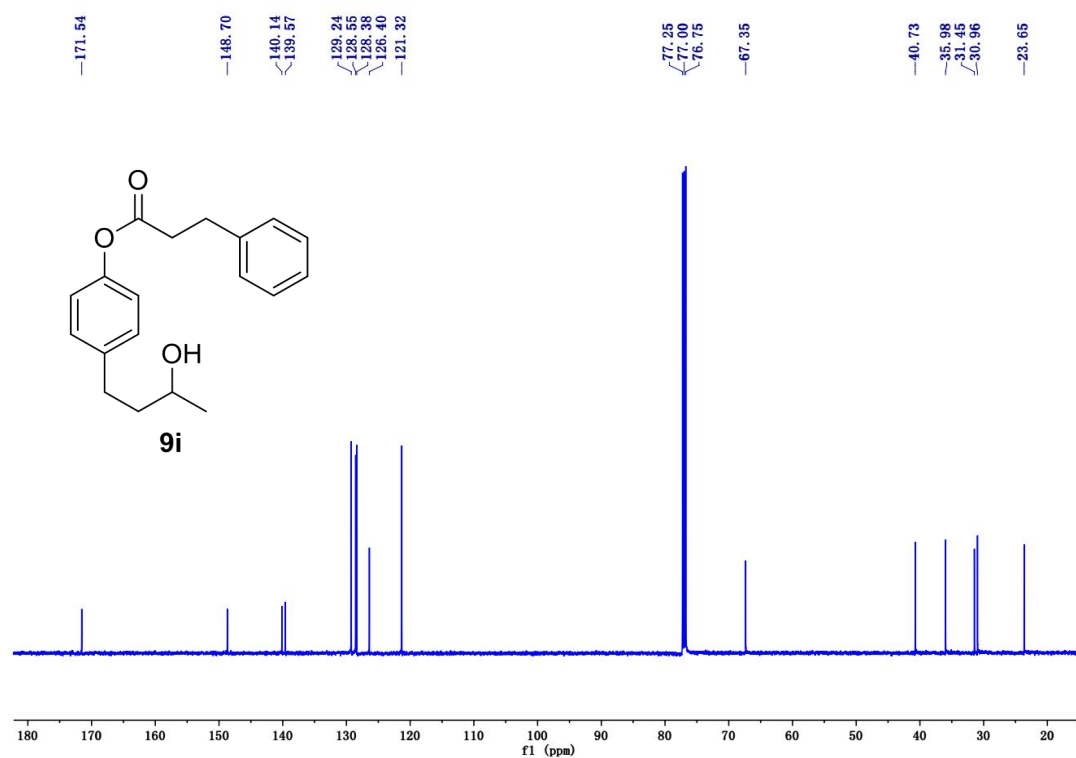
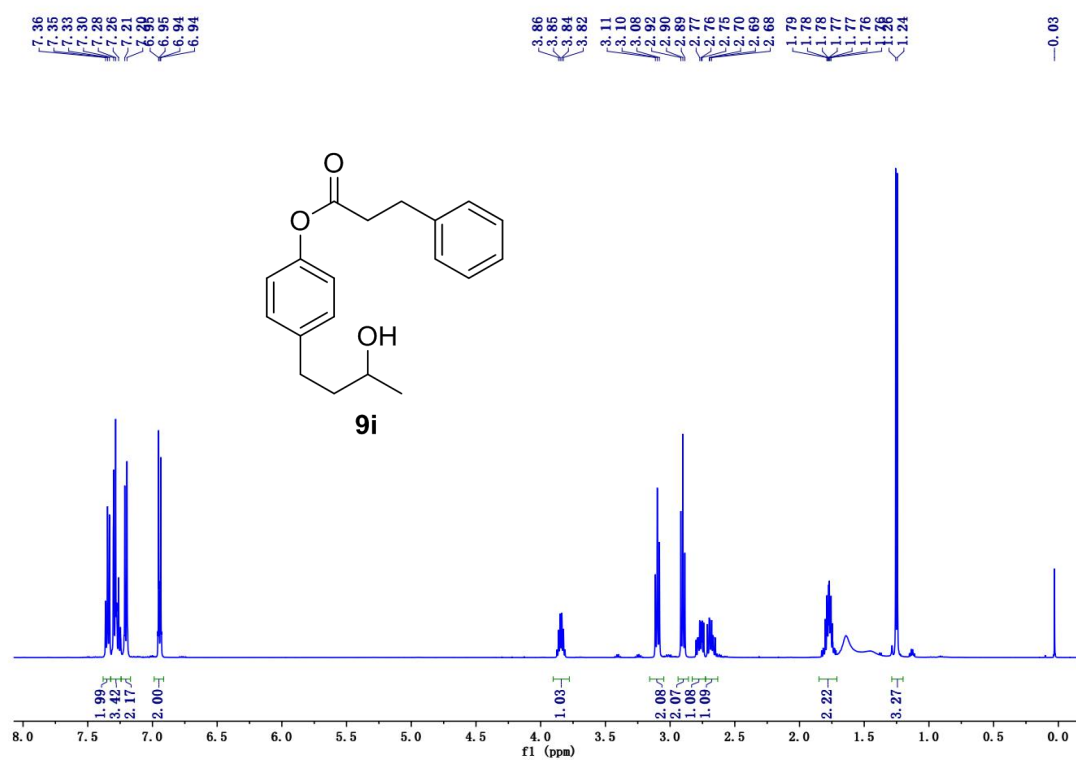




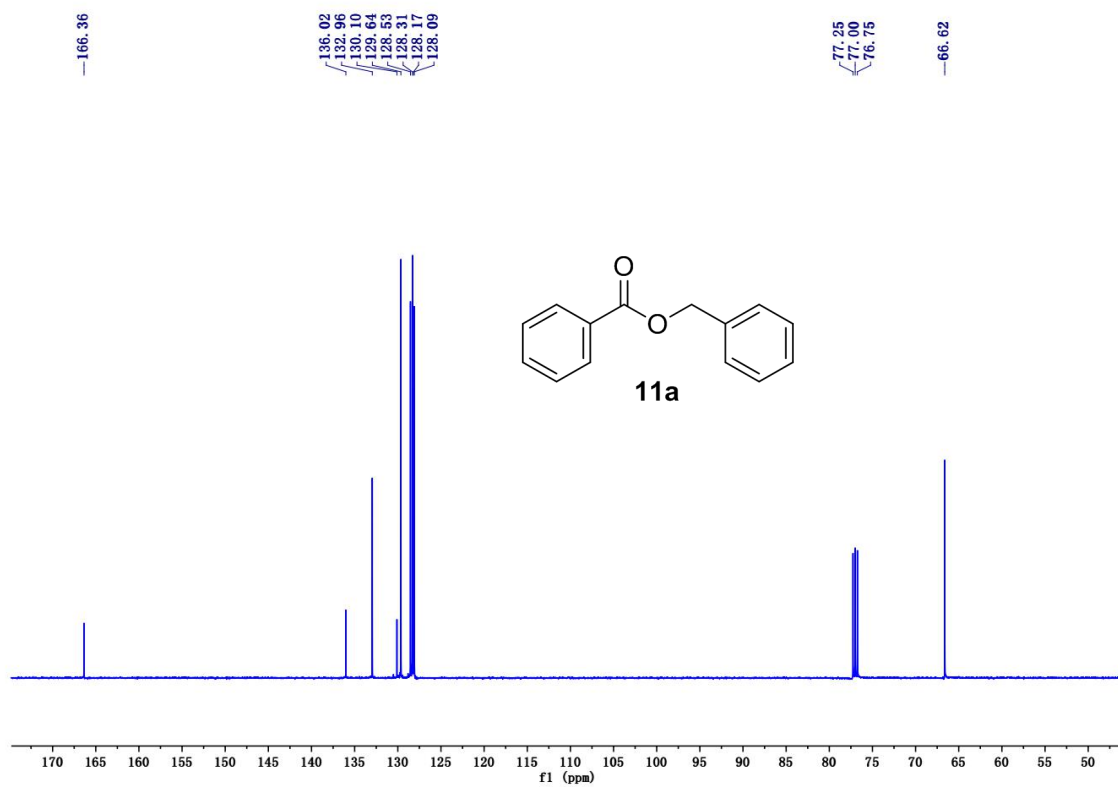
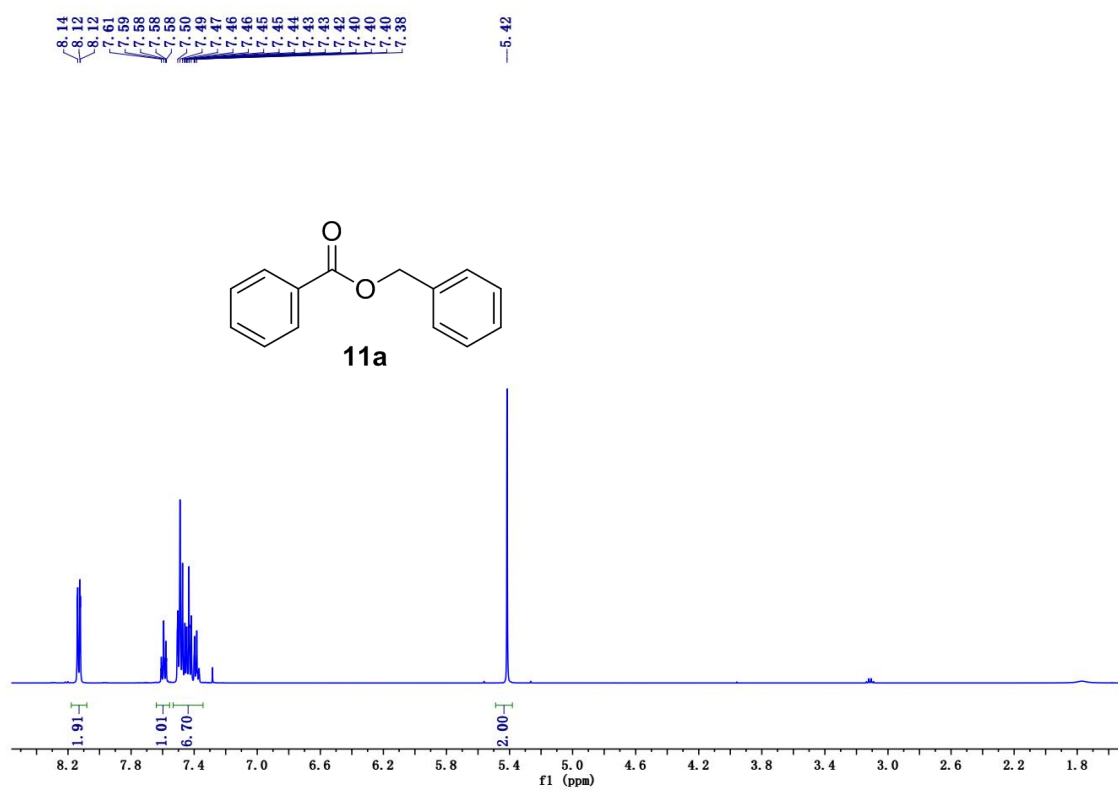


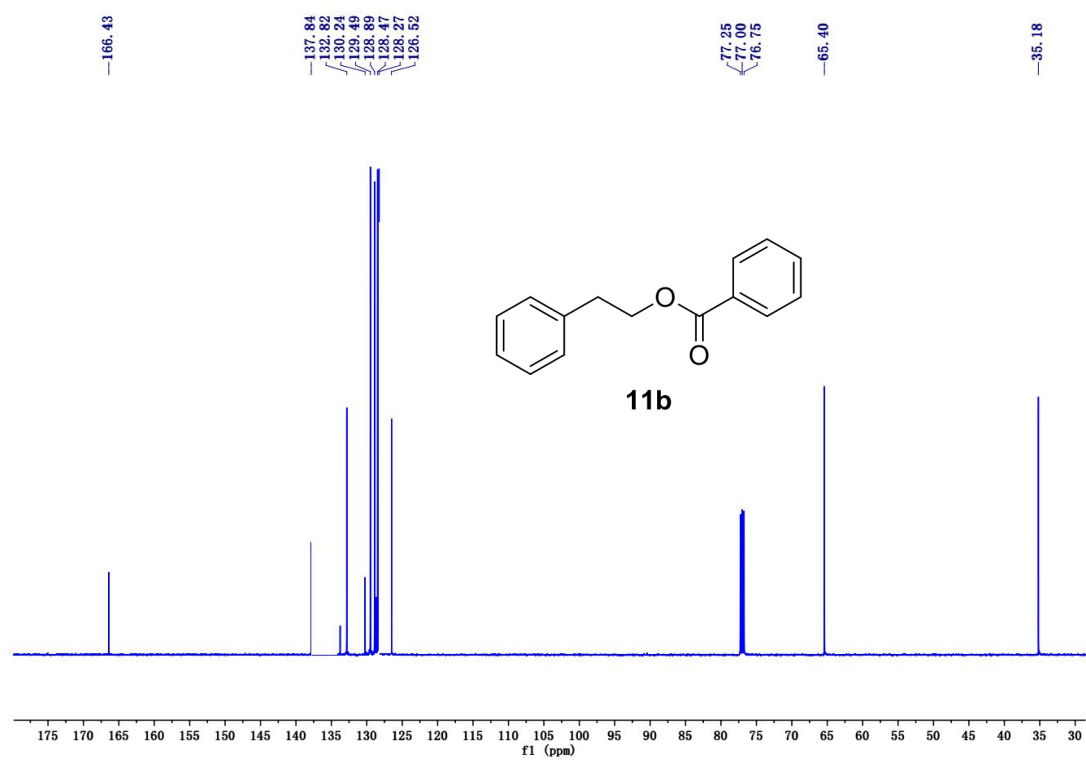
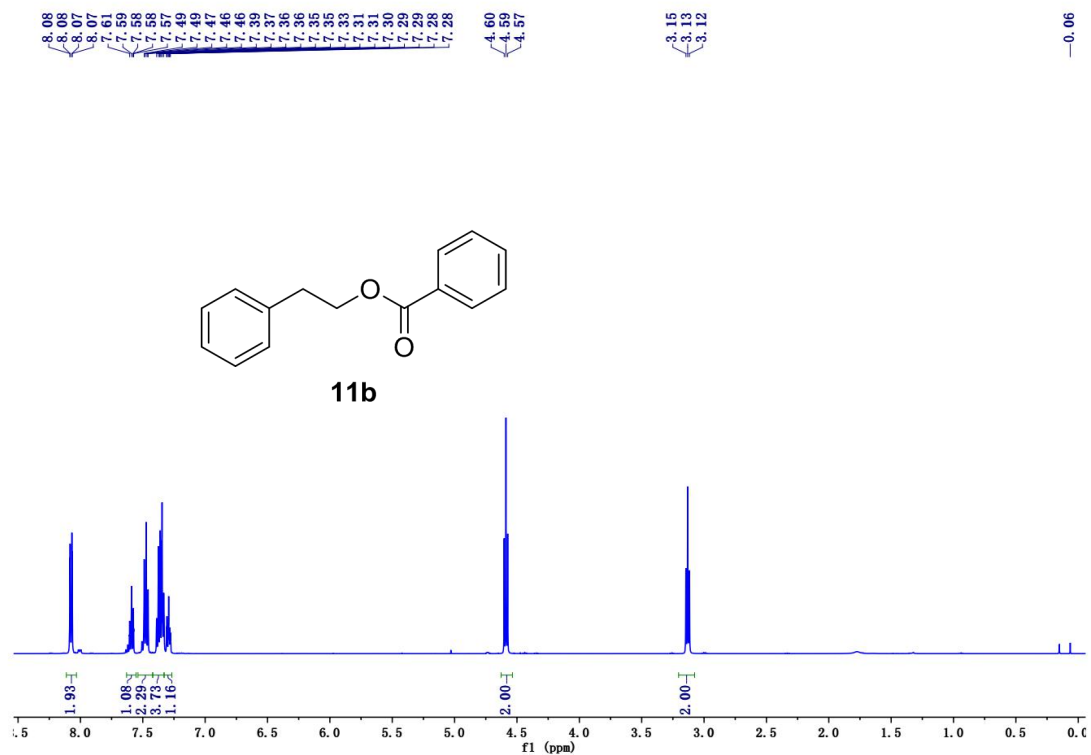


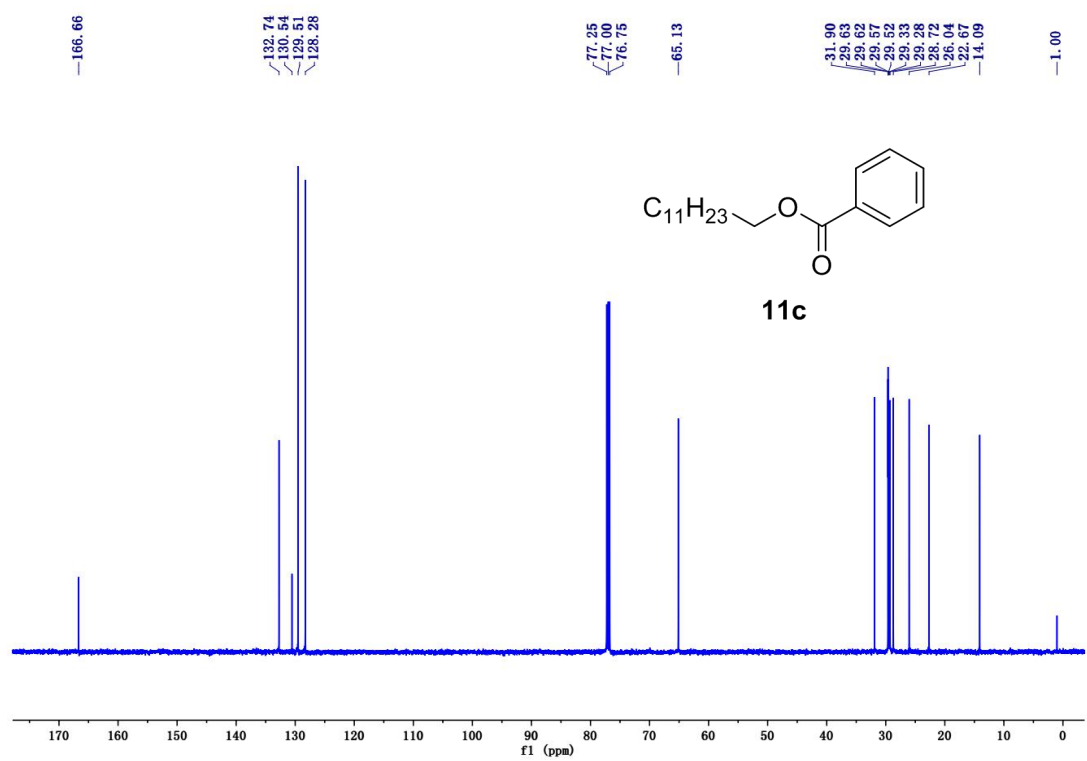
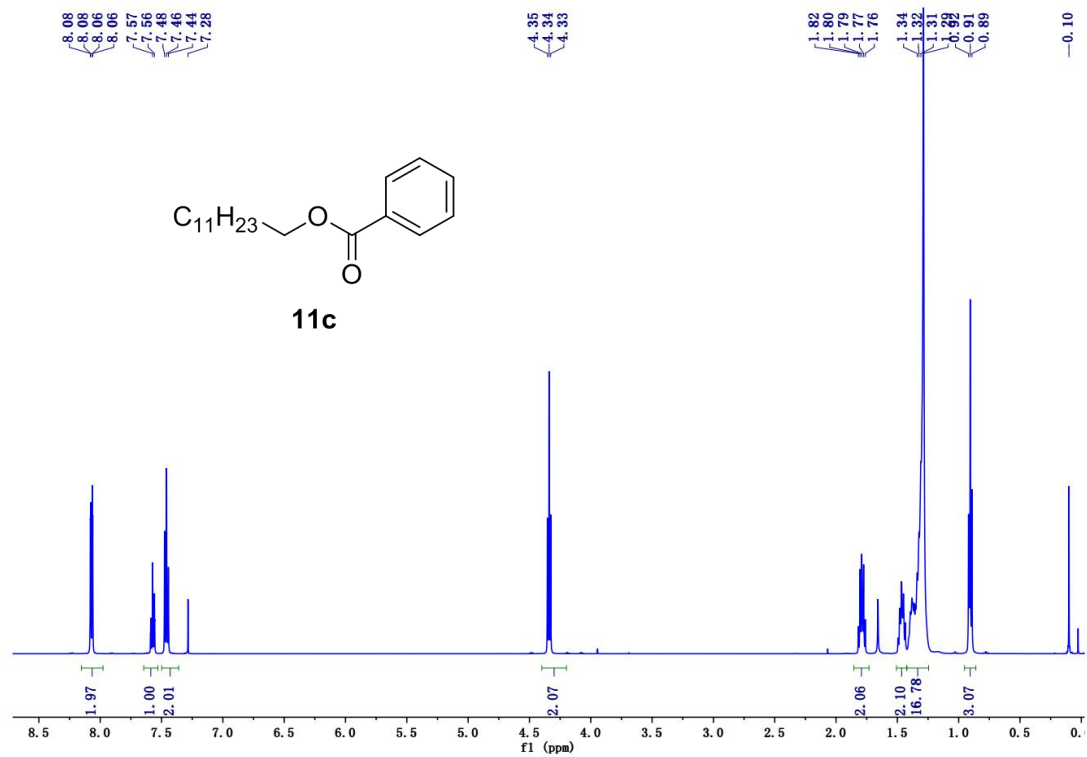


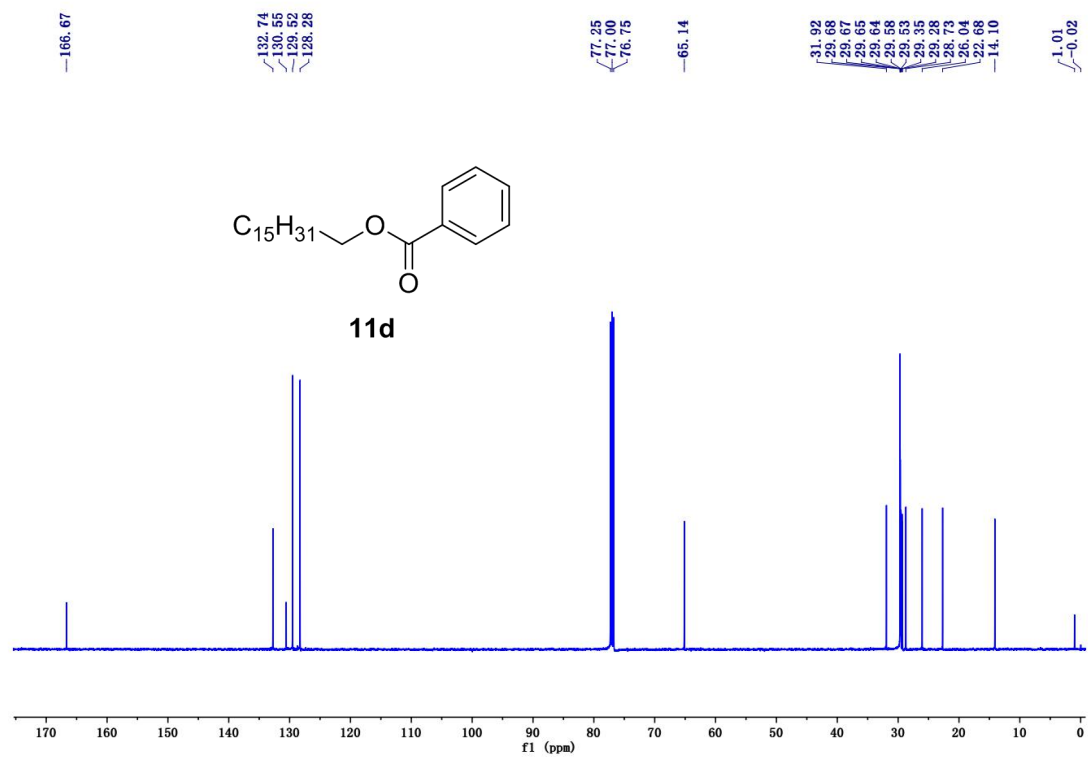
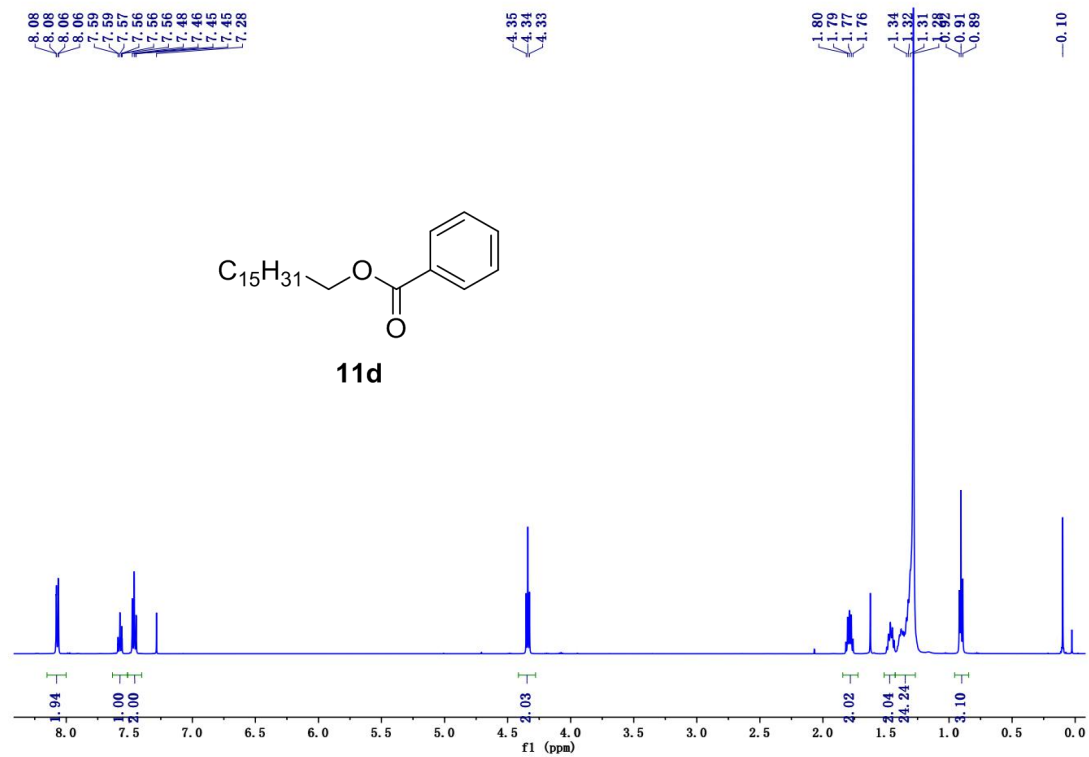


<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **11**

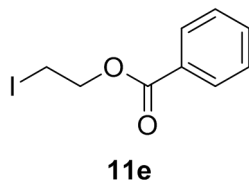
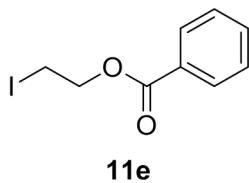


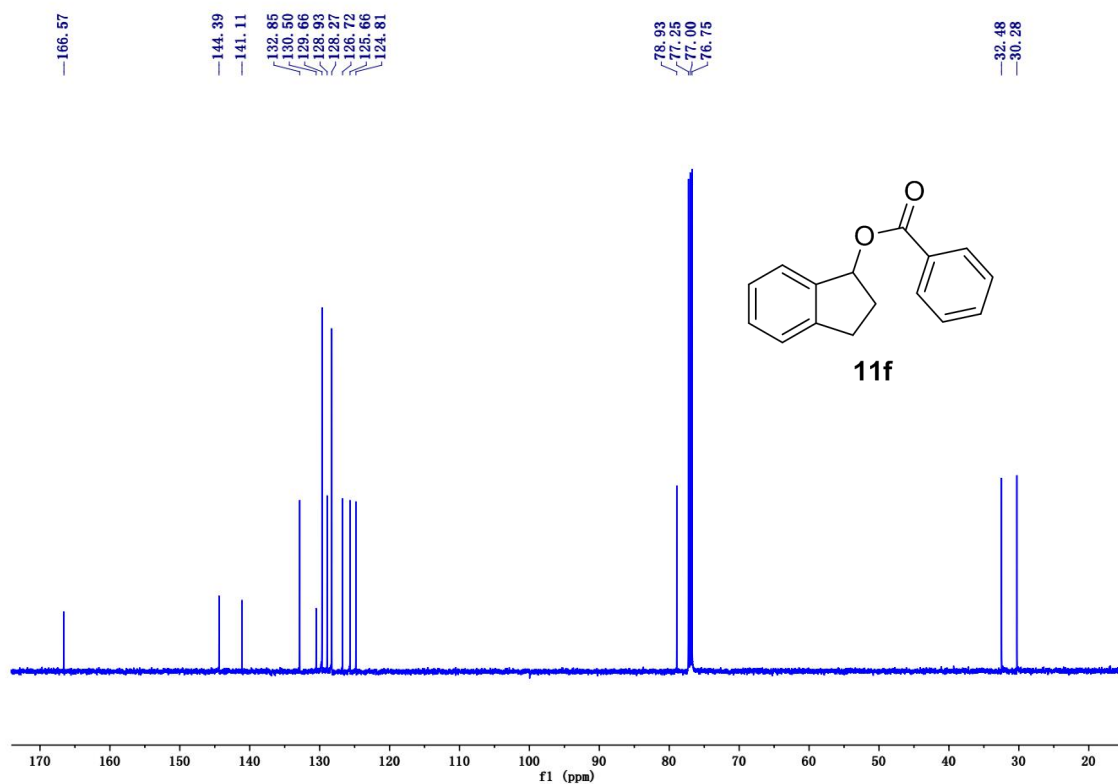
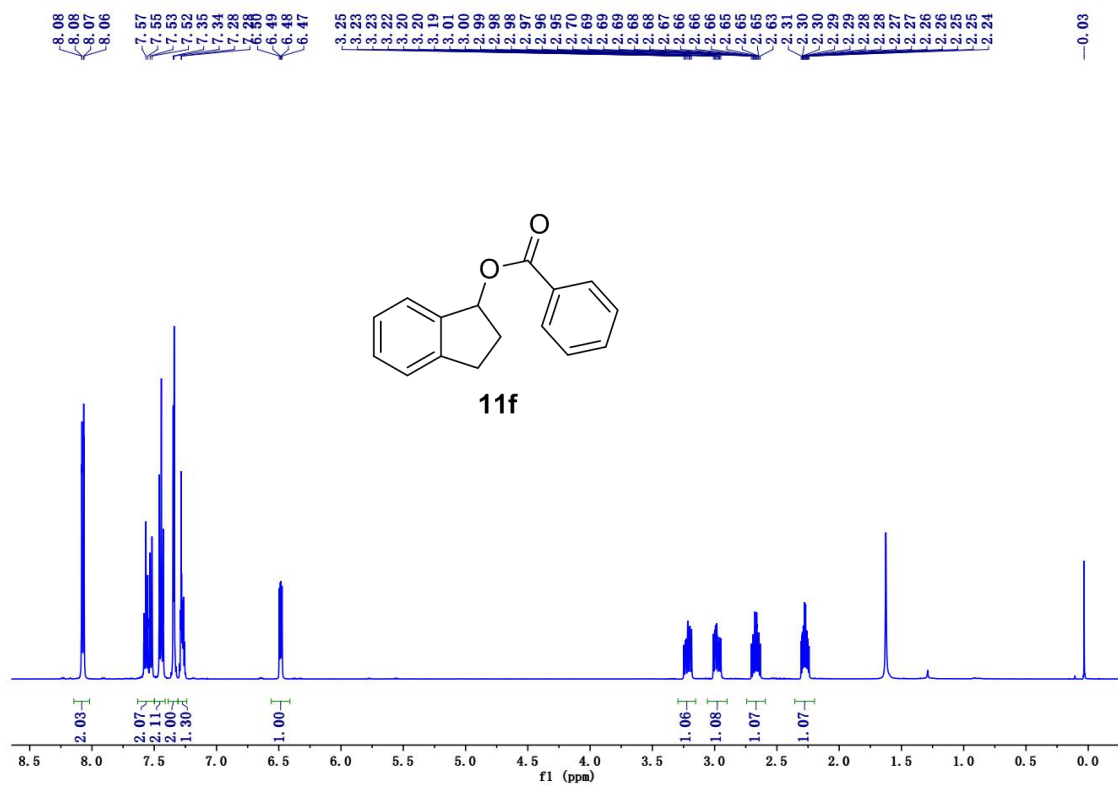


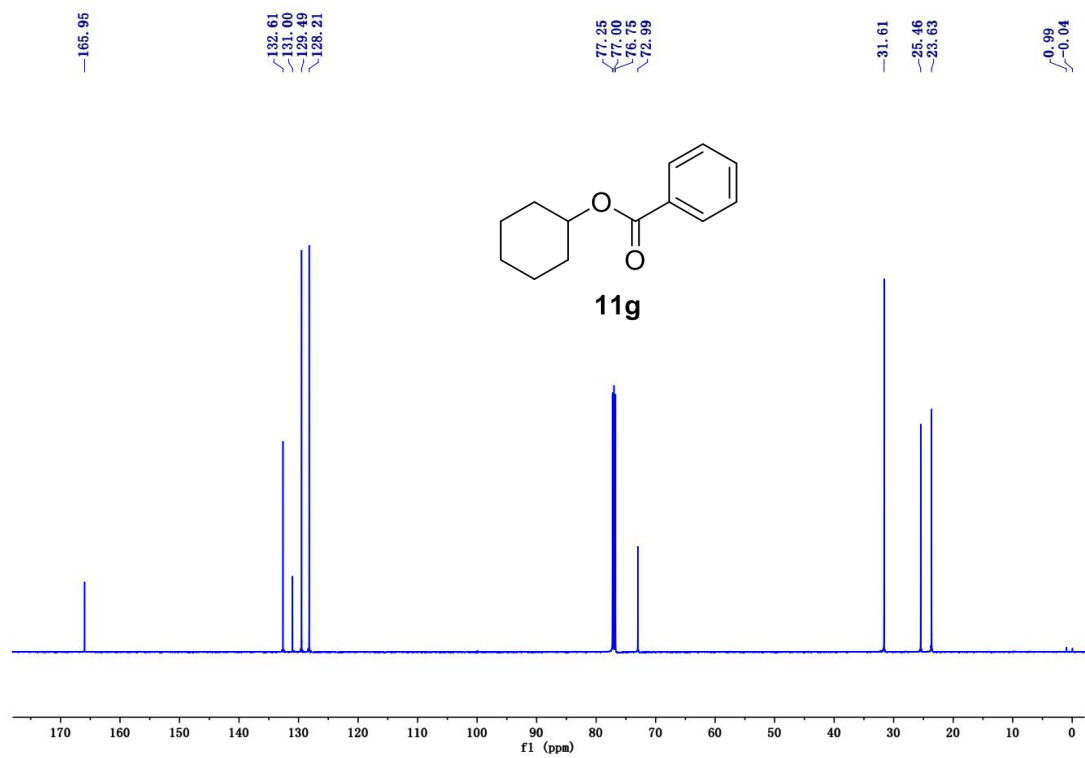
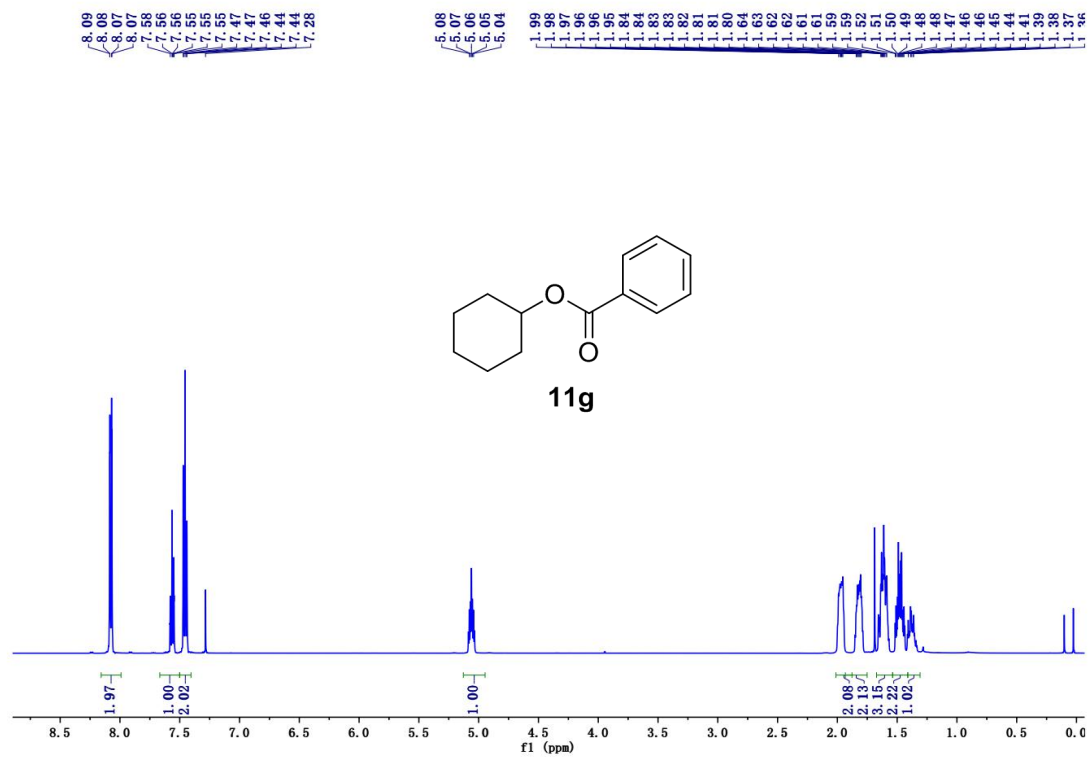


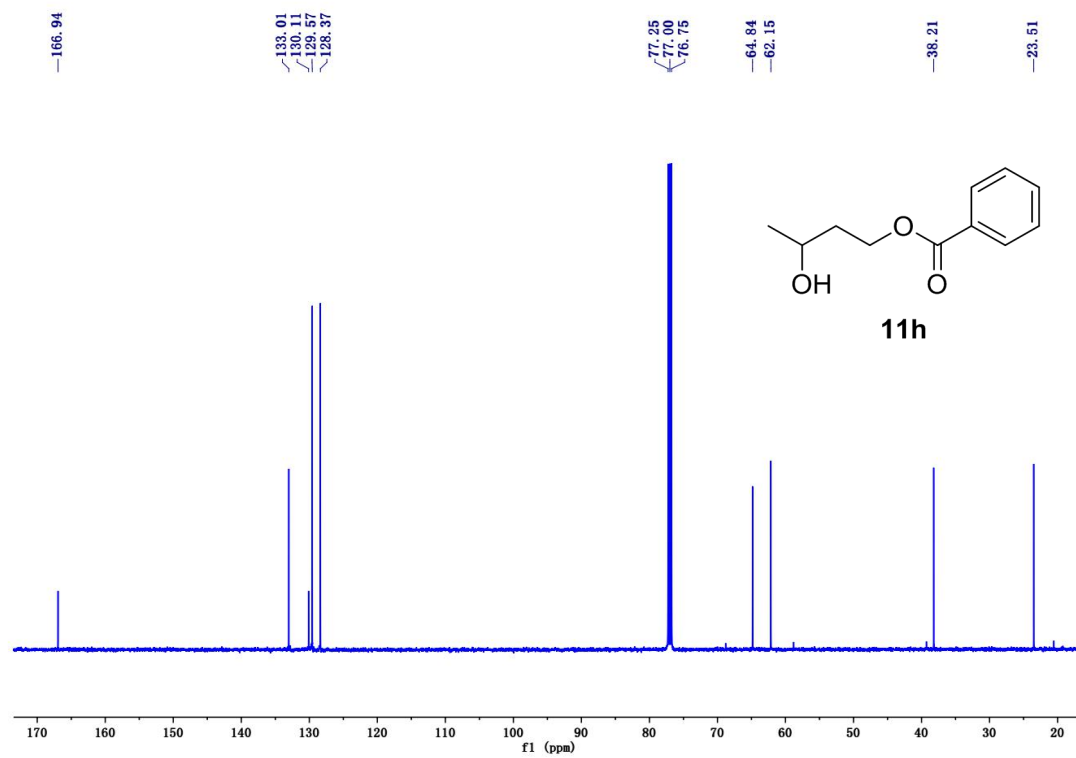
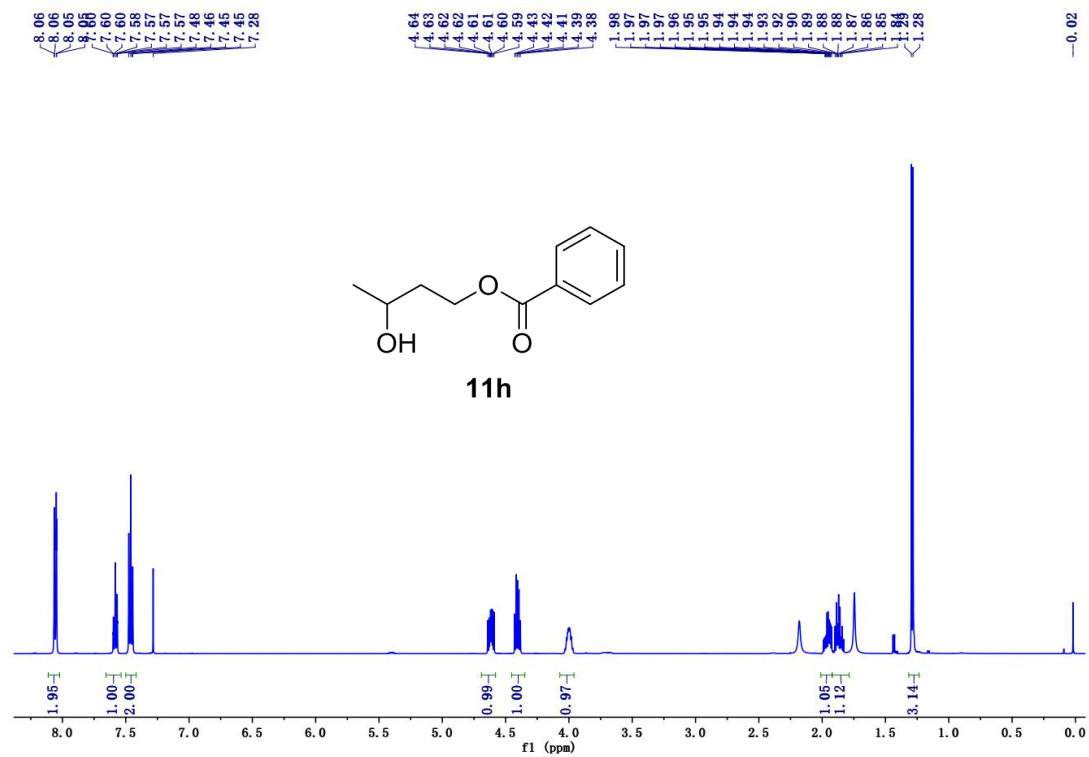


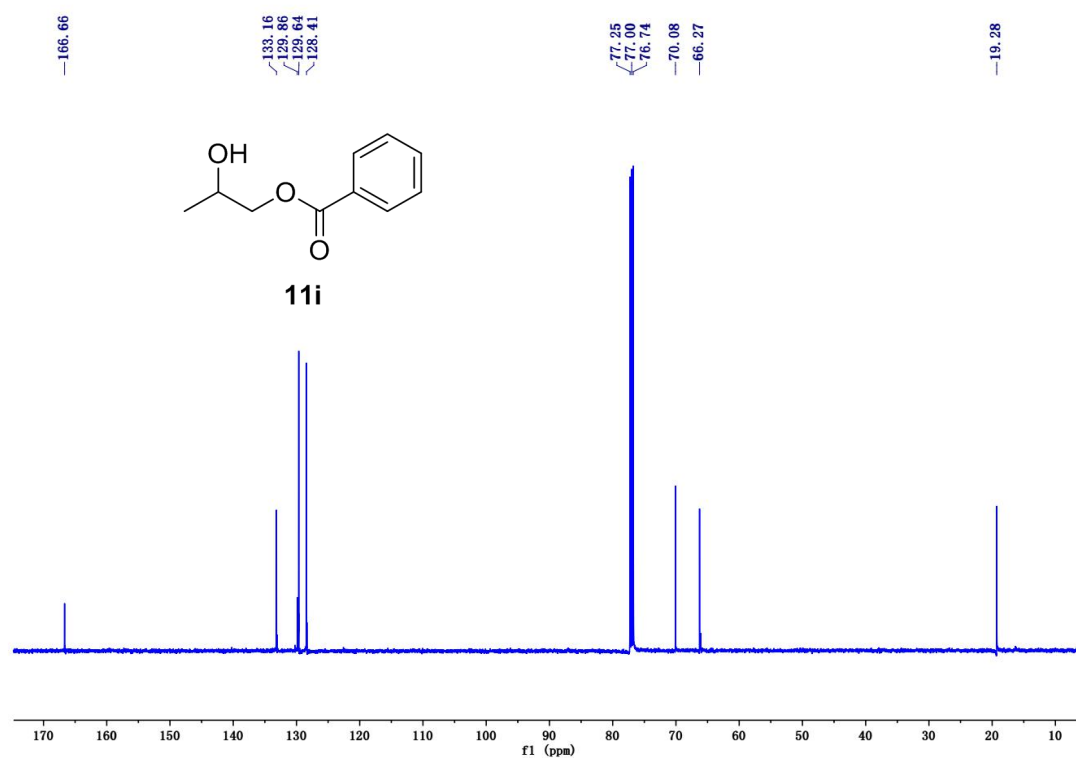
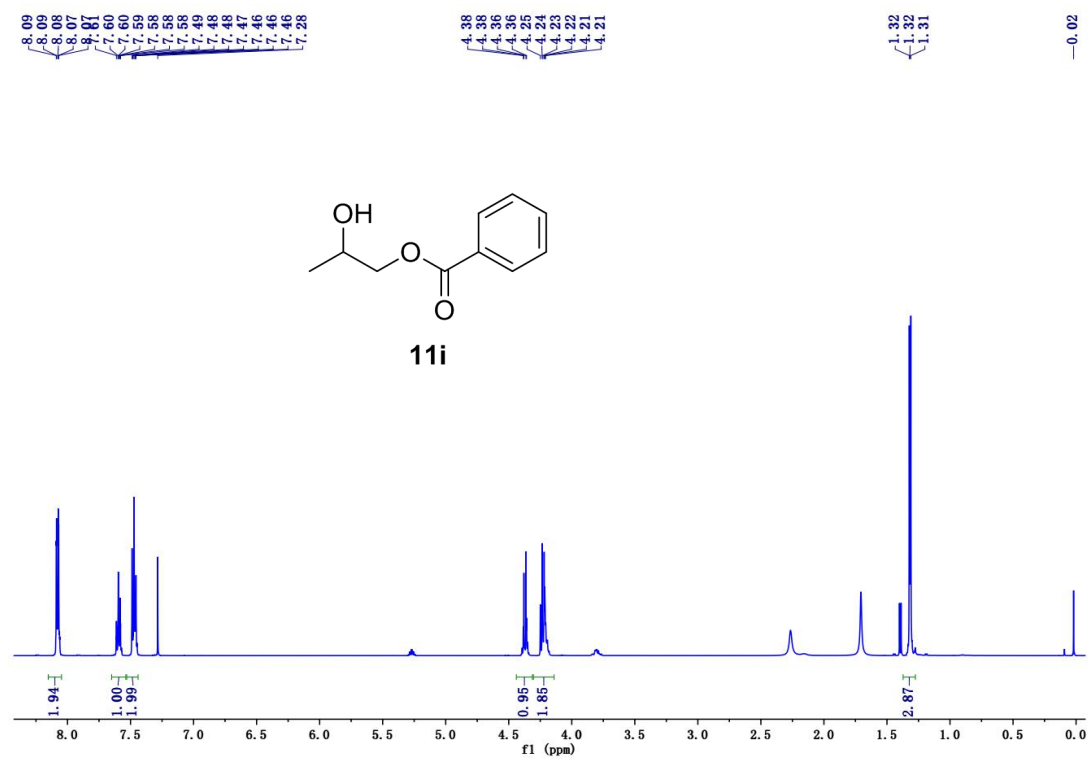




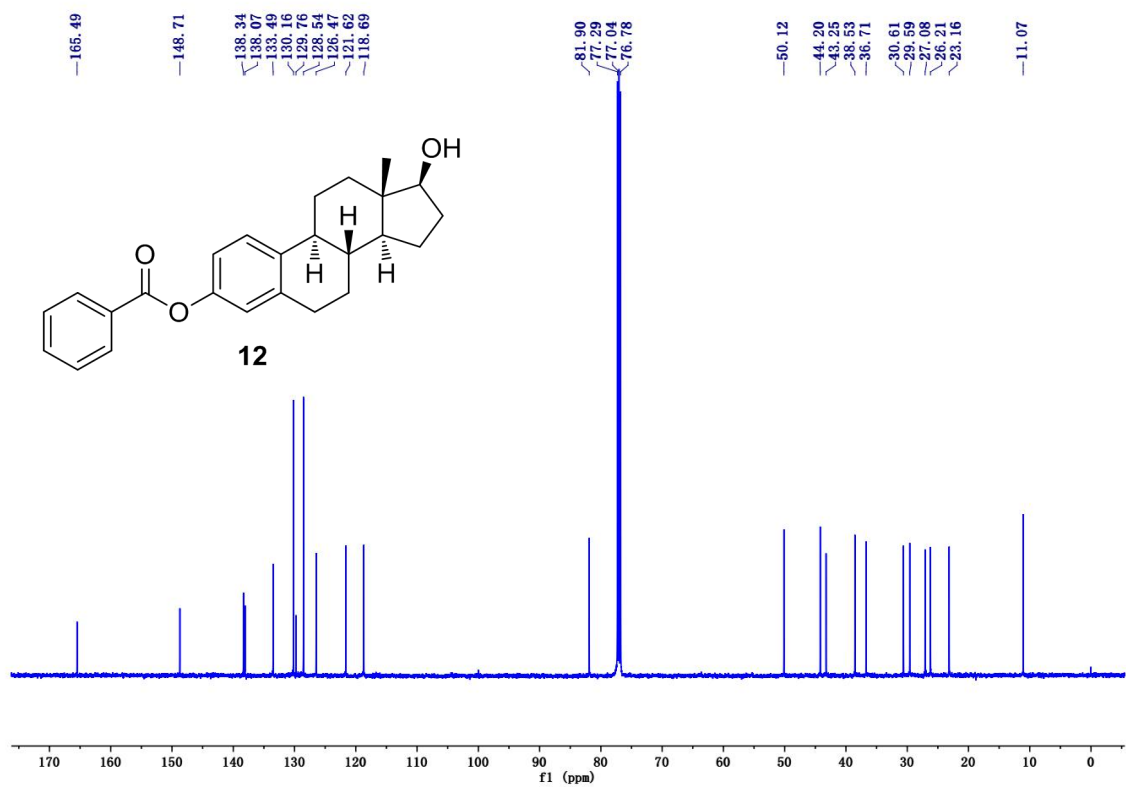
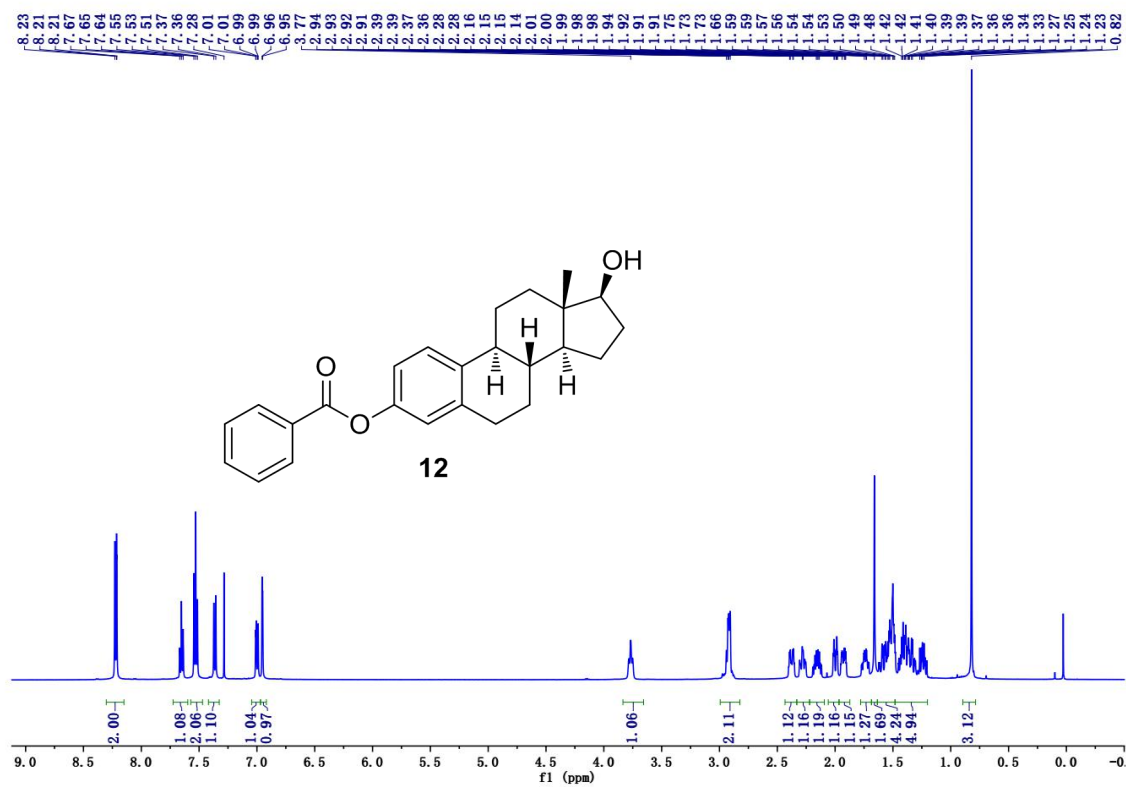




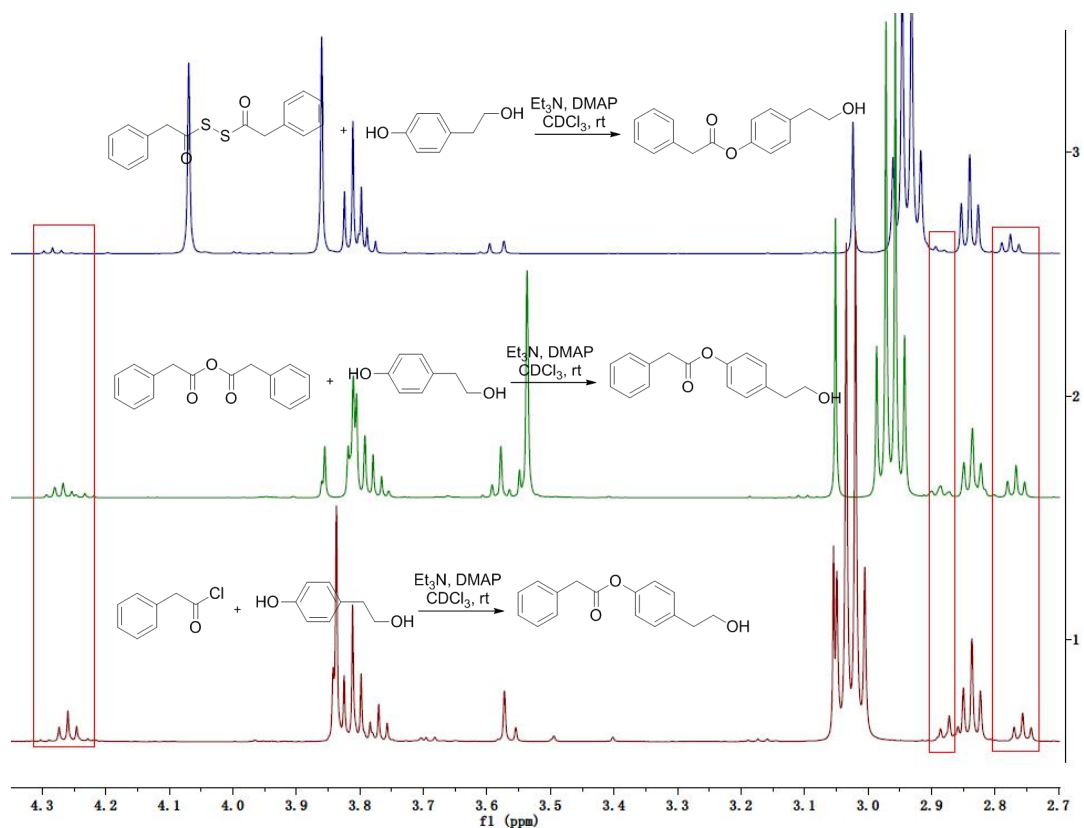
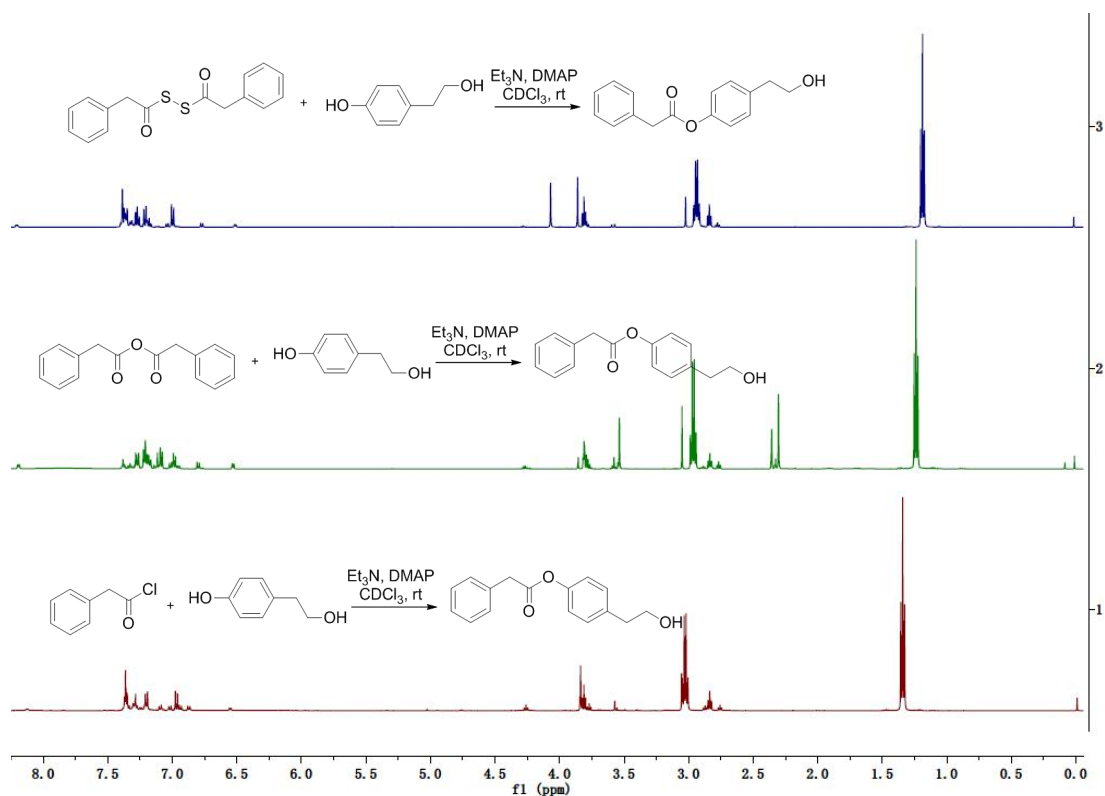




# <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 12



# <sup>1</sup>H NMR detections of the crude reaction mixtures



Note: The marked signals were the characteristic peaks of the byproducts and unreacted start material.