

**Supporting Information for**  
**Organocatalytic Cycloaddition of Carbonyl Sulfide with**  
**Propargylic Alcohols to 1,3-Oxithiolan-2-ones**

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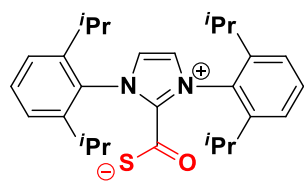
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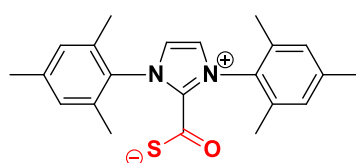
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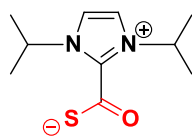
## 1. Spectral data of NHC-COS and NHO-COS adducts 1a-1e.



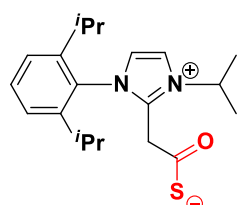
**1a:**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (t,  $J = 7.8$  Hz, 2H), 7.24 (d,  $J = 7.8$  Hz, 4H), 7.04 (s, 2H), 2.80 – 2.65 (m, 4H), 1.35 (d,  $J = 6.7$  Hz, 12H), 1.15 (d,  $J = 7.0$  Hz, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  187.7, 147.2, 146.0, 131.17, 130.7, 124.4, 121.0, 29.2, 25.5, 22.9.



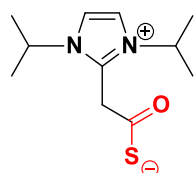
**1b:**  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.04 (s, 2H), 7.02 (s, 4H), 2.34 (s, 6H), 2.23 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  189.5, 146.5, 141.3, 135.9, 135.8, 131.4, 129.7, 129.7, 120.5, 100.4, 21.3, 18.1.



**1c:**  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  7.26 (s, 2H), 4.89 (hept,  $J = 6.7$  Hz, 2H), 1.45 (d,  $J = 6.7$  Hz, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  192.6, 146.0, 116.7, 51.7, 22.6.

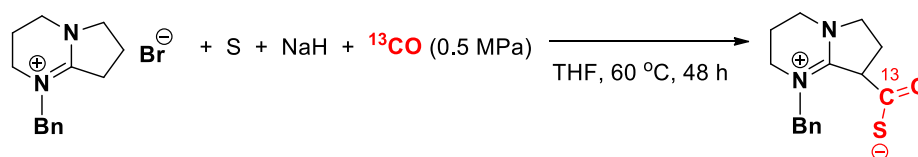


**1d:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (s, 1H), 7.58 (t,  $J = 7.8$  Hz, 1H), 7.35 (d,  $J = 7.9$  Hz, 2H), 5.24 (m,  $J = 13.3, 6.7$  Hz, 1H), 3.75 (s, 2H), 2.17 (m,  $J = 13.5, 6.8$  Hz, 2H), 1.91 – 1.80 (m, 1H), 1.74 (d,  $J = 6.7$  Hz, 6H), 1.19 (d,  $J = 6.9$  Hz, 6H), 1.15 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.0, 146.2, 144.5, 131.8, 129.4, 124.9, 123.2, 118.4, 67.9, 52.0, 45.2, 28.5, 25.2, 23.2, 22.7.



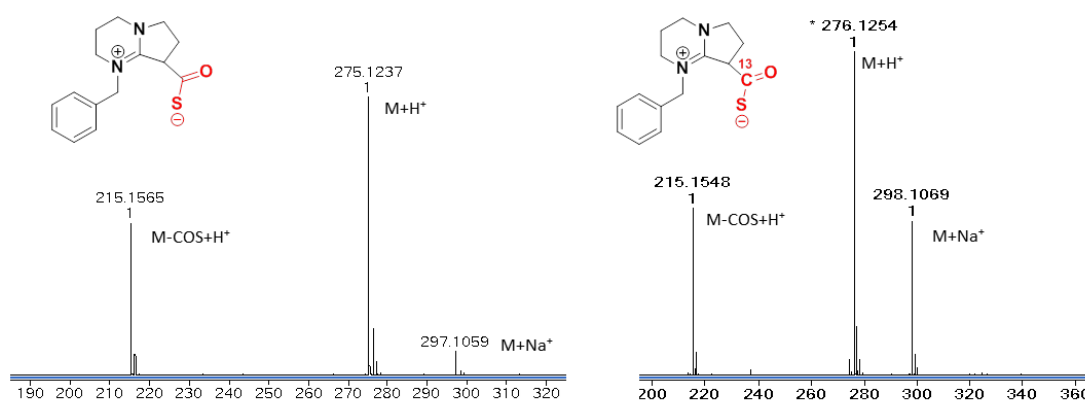
**1e:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (s, 2H), 4.91 (hept,  $J = 6.7$  Hz, 1H), 4.37 (s, 1H), 1.55 (d,  $J = 6.7$  Hz, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  203.4, 141.9, 117.8, 50.7, 45.3, 22.7.

## 2. Synthesis of $^{13}\text{C}$ labeled THPE-COS adducts **1g**

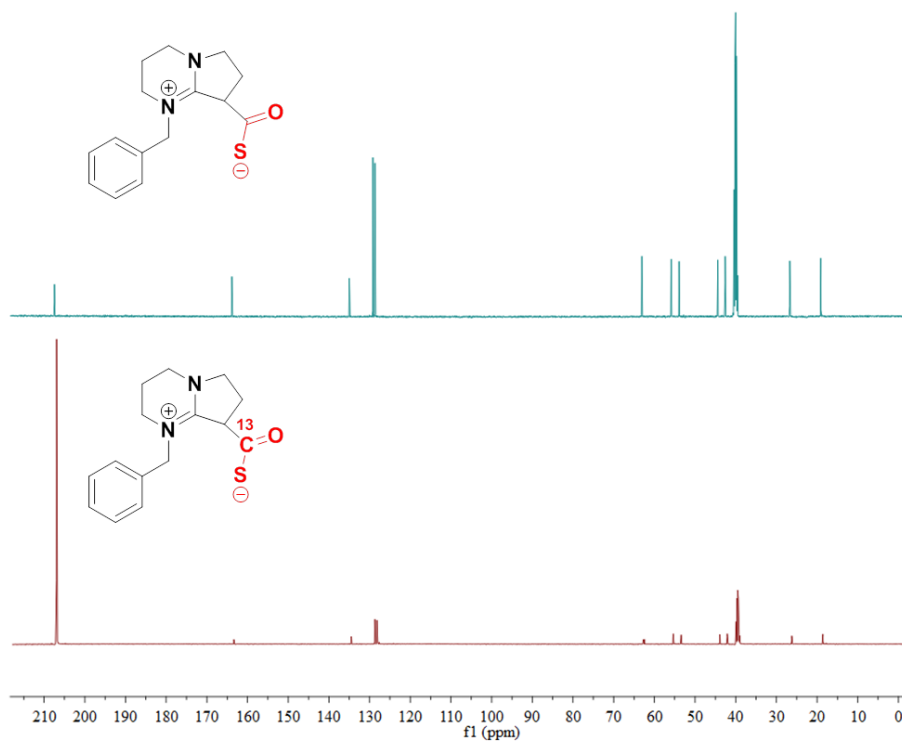


**Scheme S1.** Synthetic routes of  $^{13}\text{C}$  labeled THPE-COS adducts

In a glove box, a 10 ml autoclave containing a stirring bar was charged with elemental sulfur (64 mg, 2.0 mmol), DBN-salt (0.5 mmol), NaH (48 mg, 2.0 mmol) and THF (2.0 mL), then was pressurized to 0.5 MPa with  $^{13}\text{CO}$ . The reaction was carried out at 60 °C for 48 hours with continuous stirring. Then, the autoclave was cooled, and the excess CO was vented. The residue was purified by column chromatography ( $\text{CH}_2\text{Cl}_2$ :MeOH=15:1) to give  $^{13}\text{C}$  labeled **1g** (50 mg, 36 % yield).

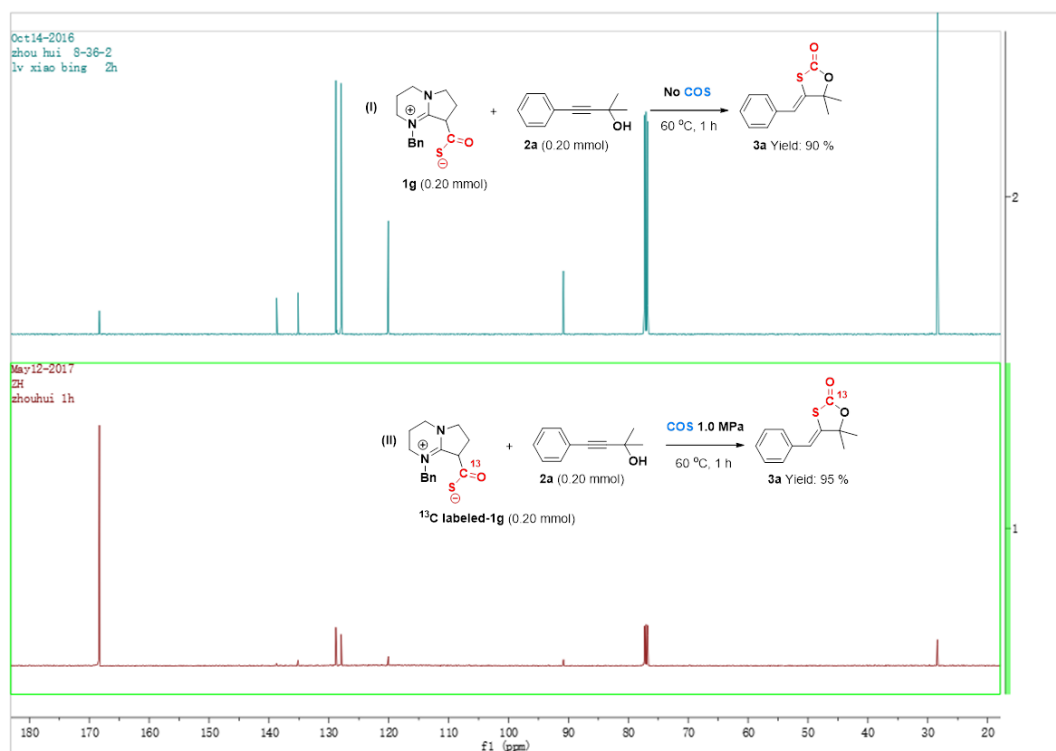


**Figure S1.** Comparison of HRMS spectra of normal and  $^{13}\text{C}$  labeled **1g**

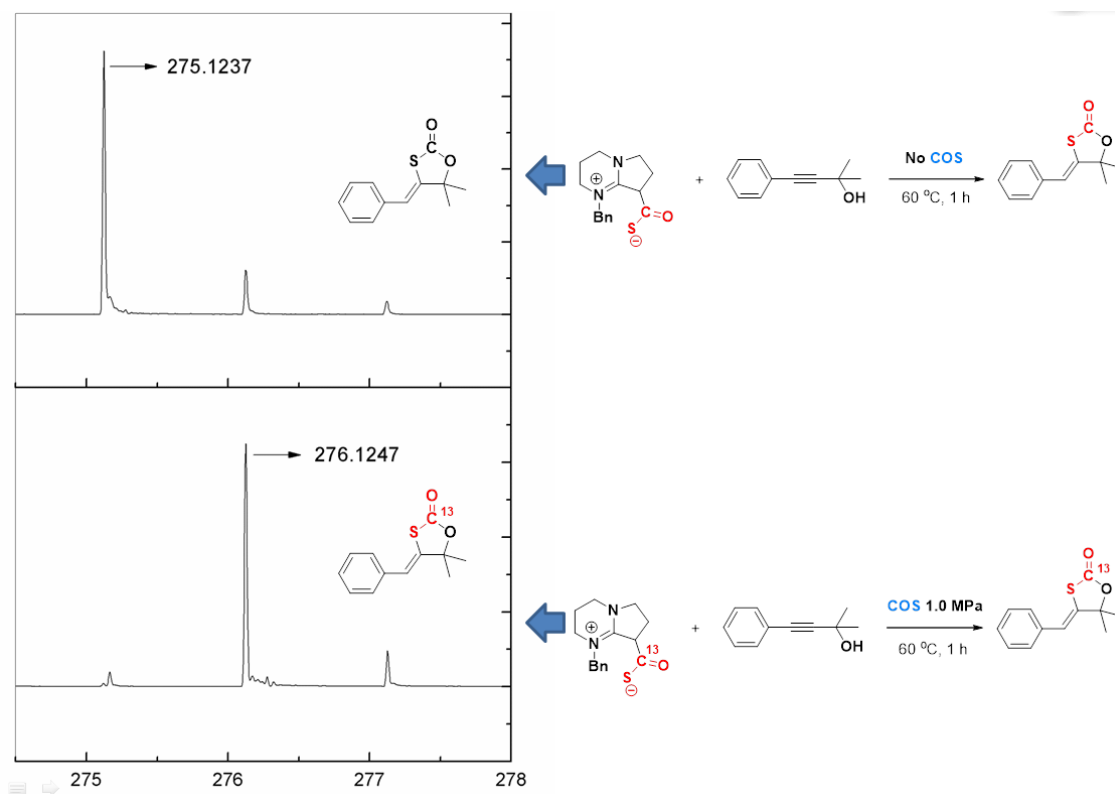


**Figure S2.** Comparison of  $^{13}\text{C}$  NMR spectra of normal and  $^{13}\text{C}$  labeled **1g**

### 3. $^{13}\text{C}$ -NMR and HRMS data for preliminary mechanistic studies



**Figure S3.**  $^{13}\text{C}$  NMR spectra of control experiments in Scheme 4.



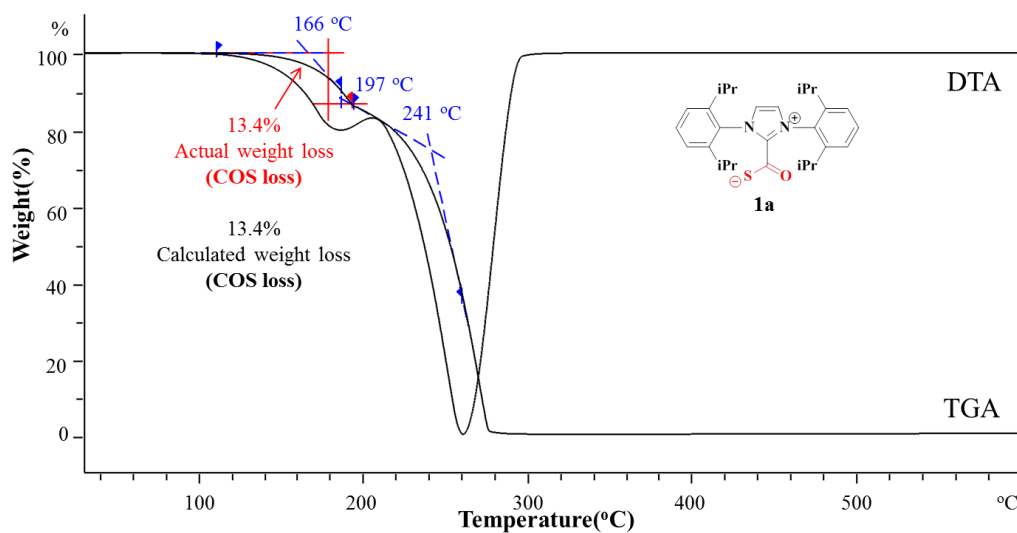
**Figure S4.** Enlarged HRMS spectra of control experiments in Scheme 4.

From the  $^{13}\text{C}$ -NMR and HRMS data (Figure S3 and Figure S4), we could draw a conclusion that the COS moiety of product should entirely come from activated COS of THPE-COS adducts, and the reaction tends to proceed via the THPE-COS adducts mediated nucleophilic addition mechanism (Scheme3, Pathway A).

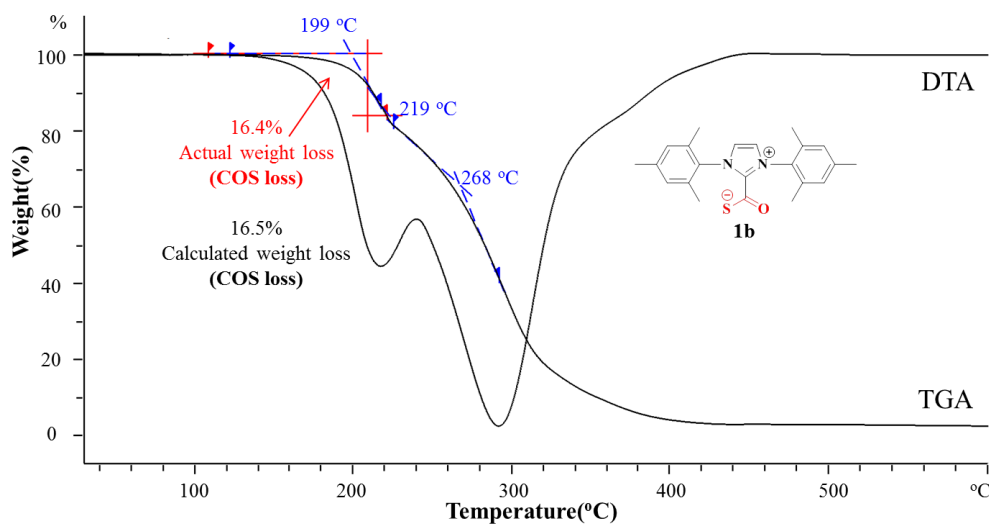
#### 4. TGA of LB-COS Adducts (1a-1g).

The thermal stability of all reported LB-COS adducts (NHC-COS, NHO-COS, and THPE-COS adducts) in this manuscript were investigated by thermogravimetric analysis (TGA), and the thermogravimetric analysis data were shown below. Clean loss of 13.4%, 16.4% and 21.8% of the weight of adducts **1a**, **1b** and **1g** (corresponding to the mass of COS) was observed under high temperature, respectively (Figure S5, S6, and S11). In contrast, other LB-COS adducts (**1c-1f**) have almost identical dethiocarboxylation/decomposition temperature. During the

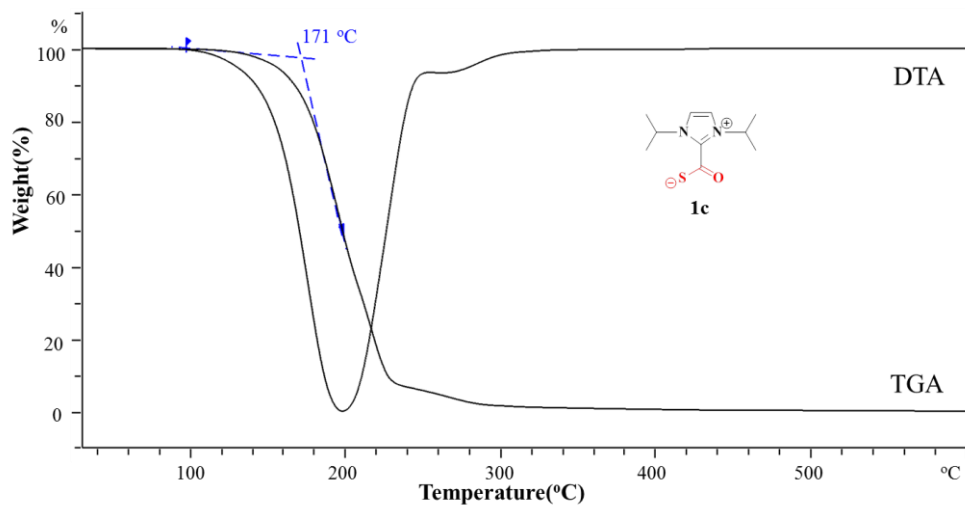
investigation, we found that part of LB-COS adducts obviously dethiocarboxylated under high temperature and reversibly released LB and free COS, so LB-COS adducts and free LB should have a certain catalytic activity to promote this process.



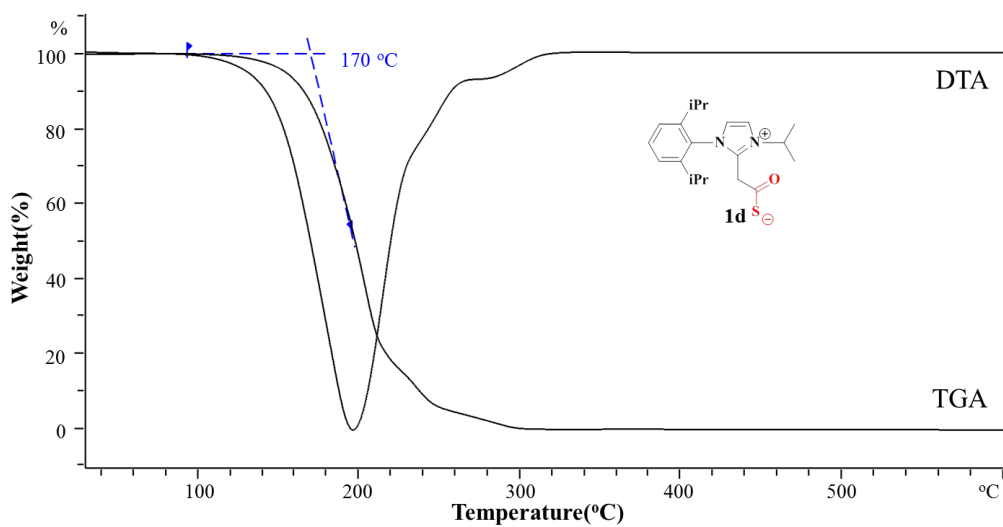
**Figure S5.** TGA of LB-COS adduct **1a**



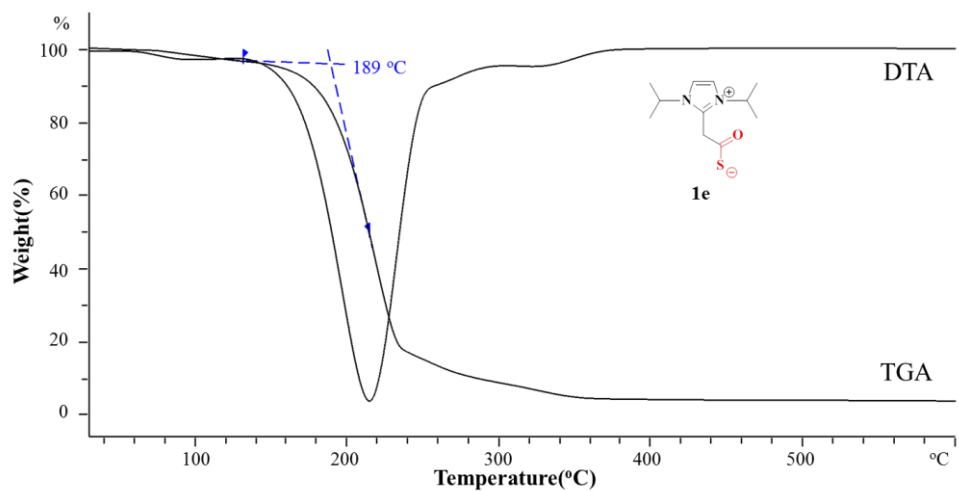
**Figure S6.** TGA of LB-COS adduct **1b**



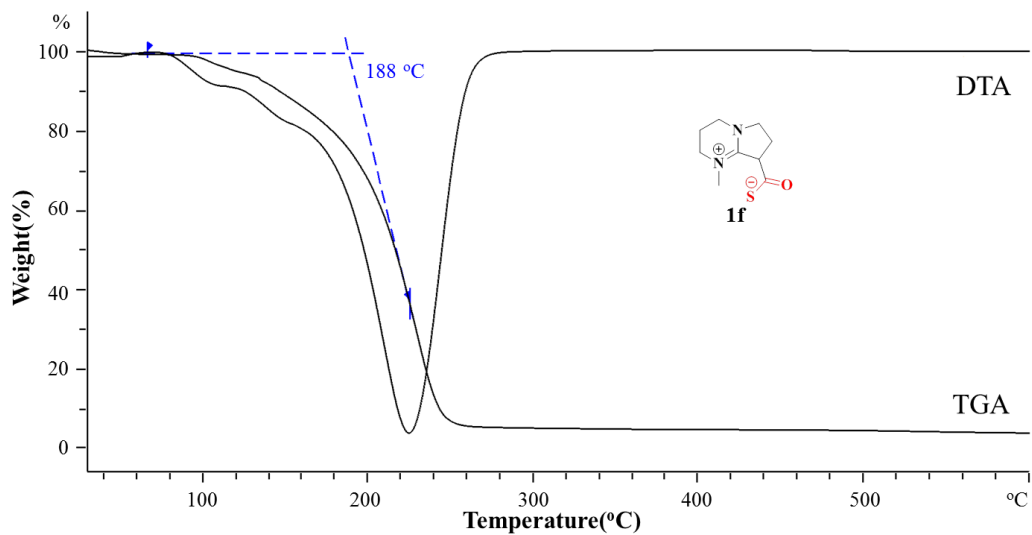
**Figure S7.** TGA of LB-COS adduct **1c**



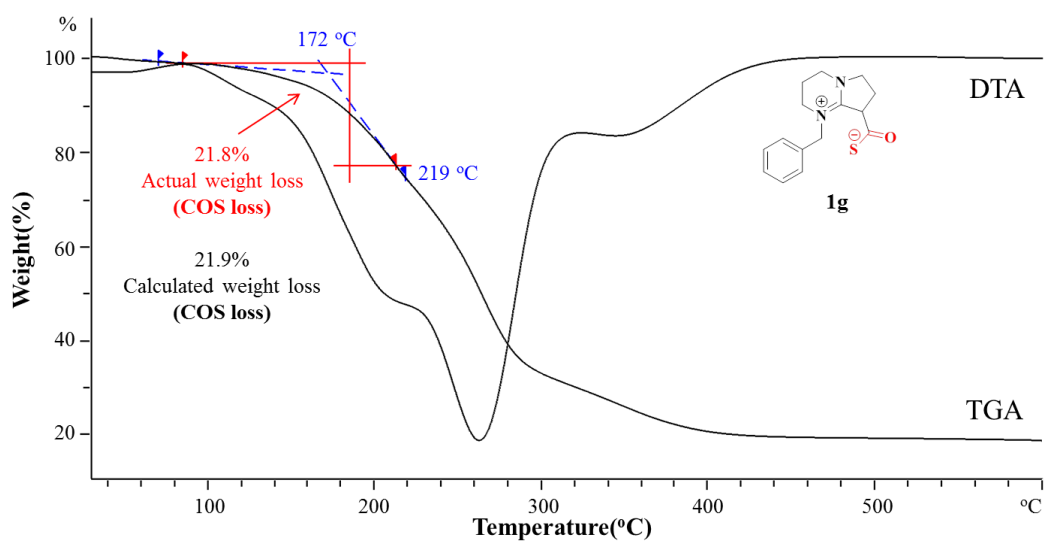
**Figure S8.** TGA of LB-COS adduct **1d**



**Figure S9.** TGA of LB-COS adduct **1e**



**Figure S10.** TGA of LB-COS adduct **1f**

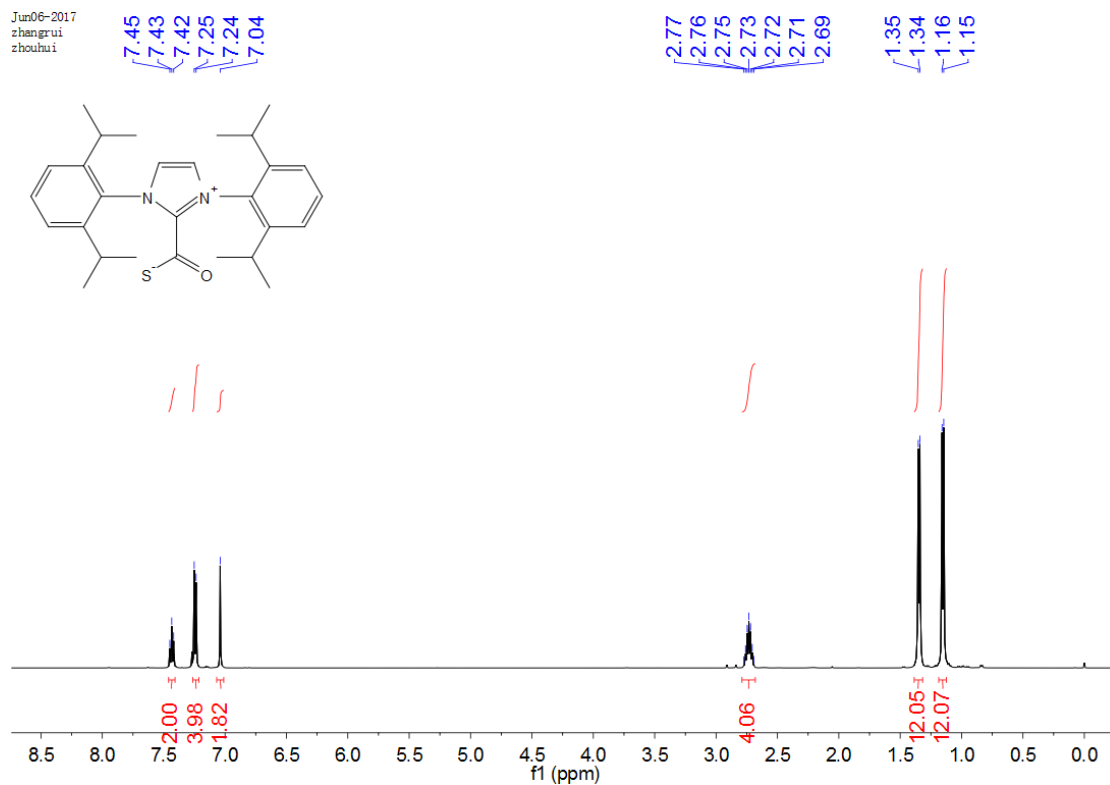


**Figure S11.** TGA of LB-COS adduct **1g**

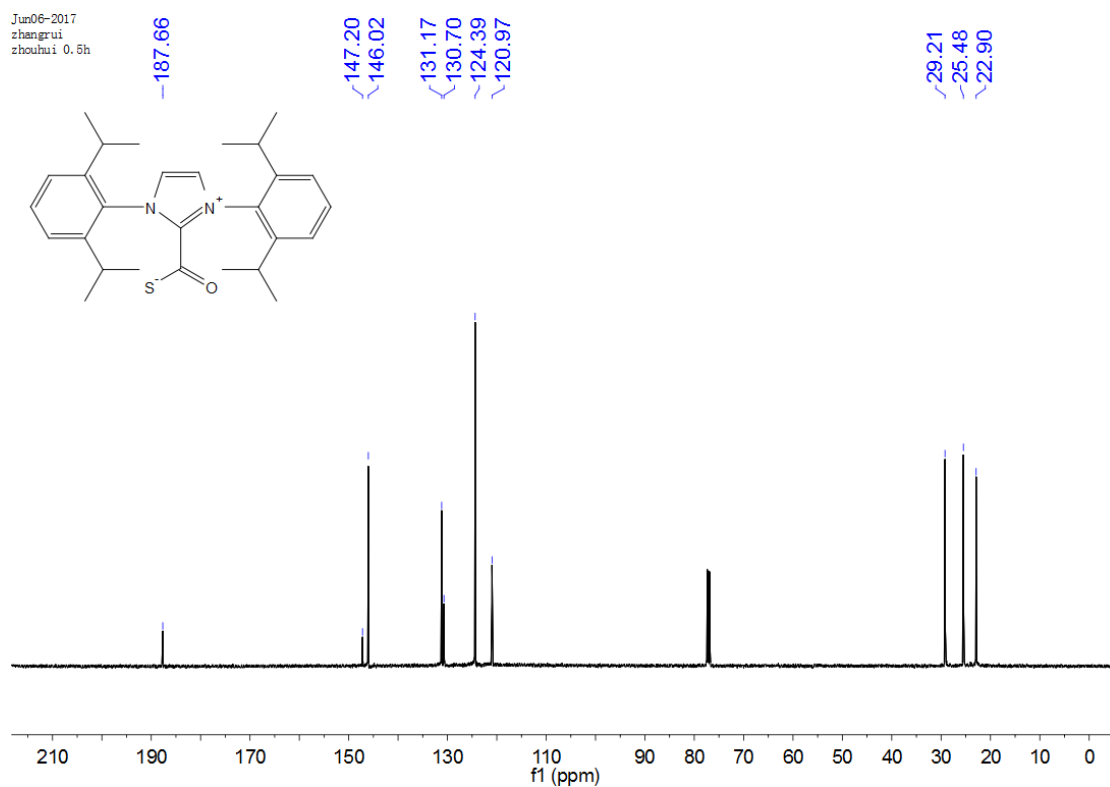


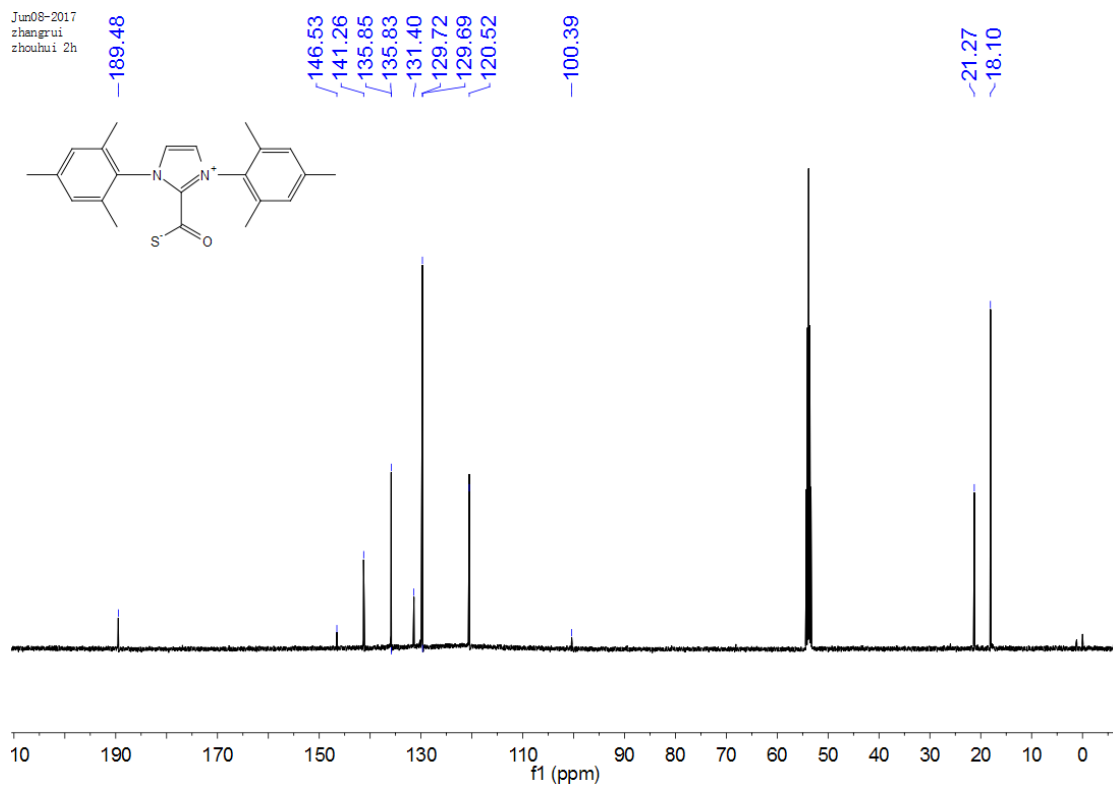
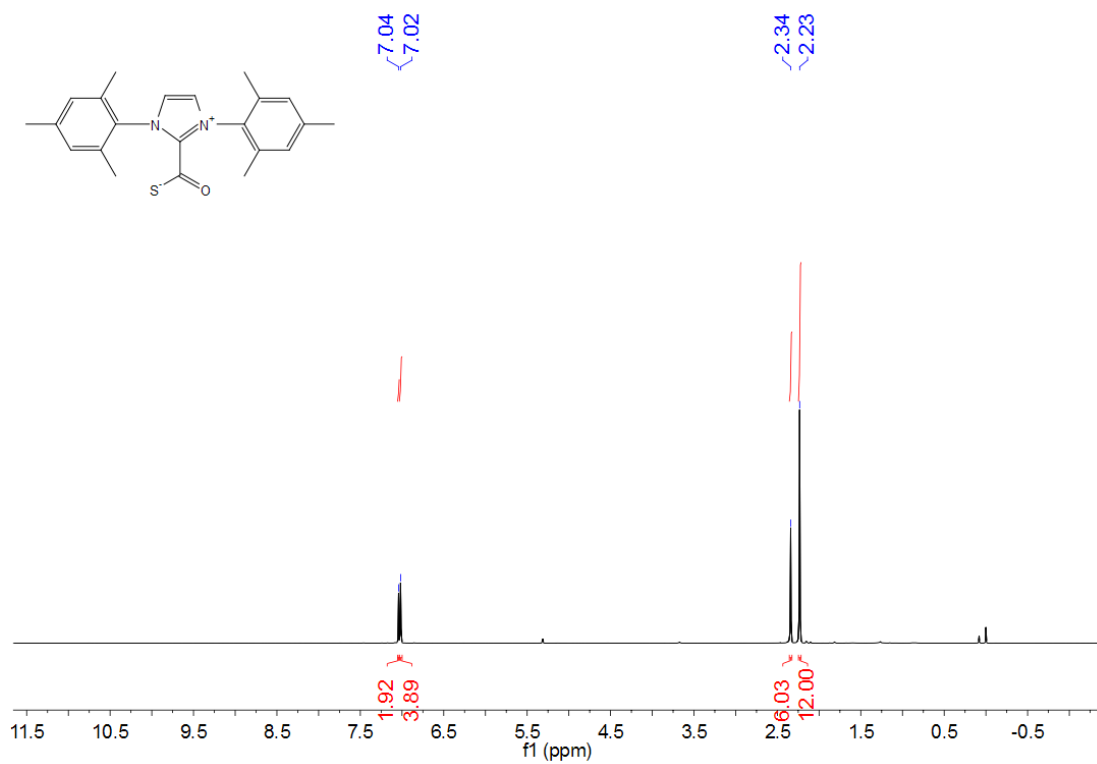
## 5. NMR spectra

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zhouhui

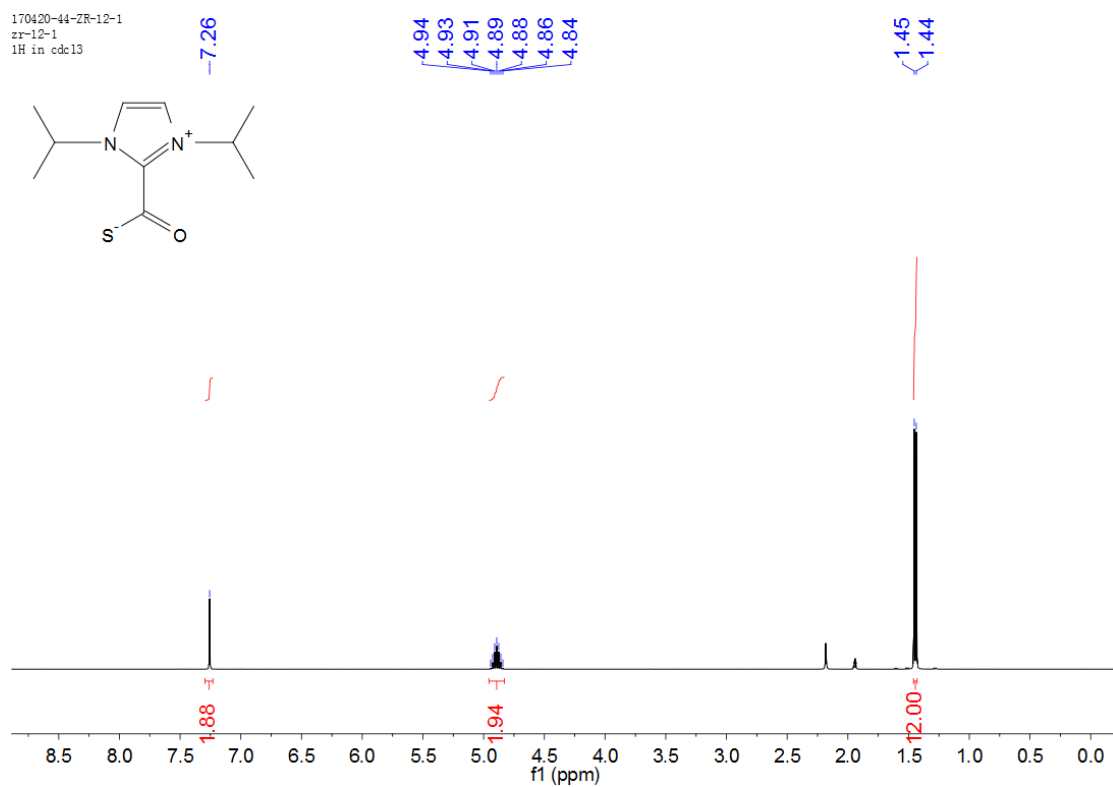


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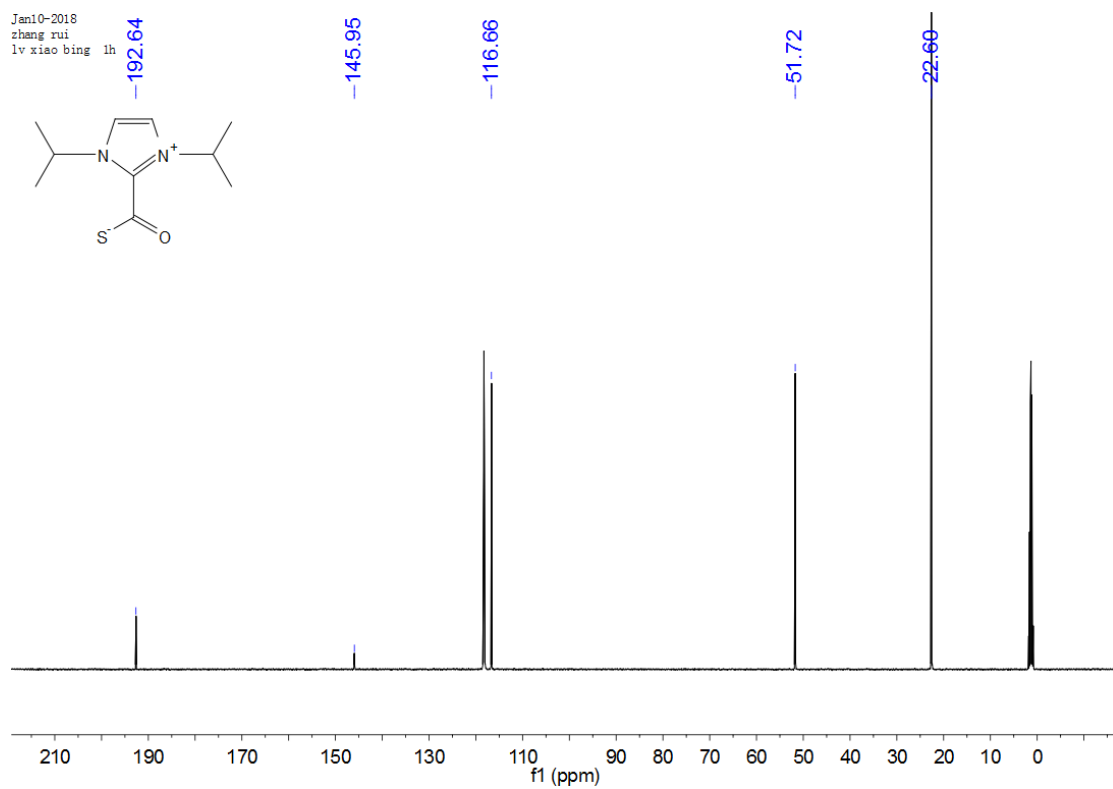




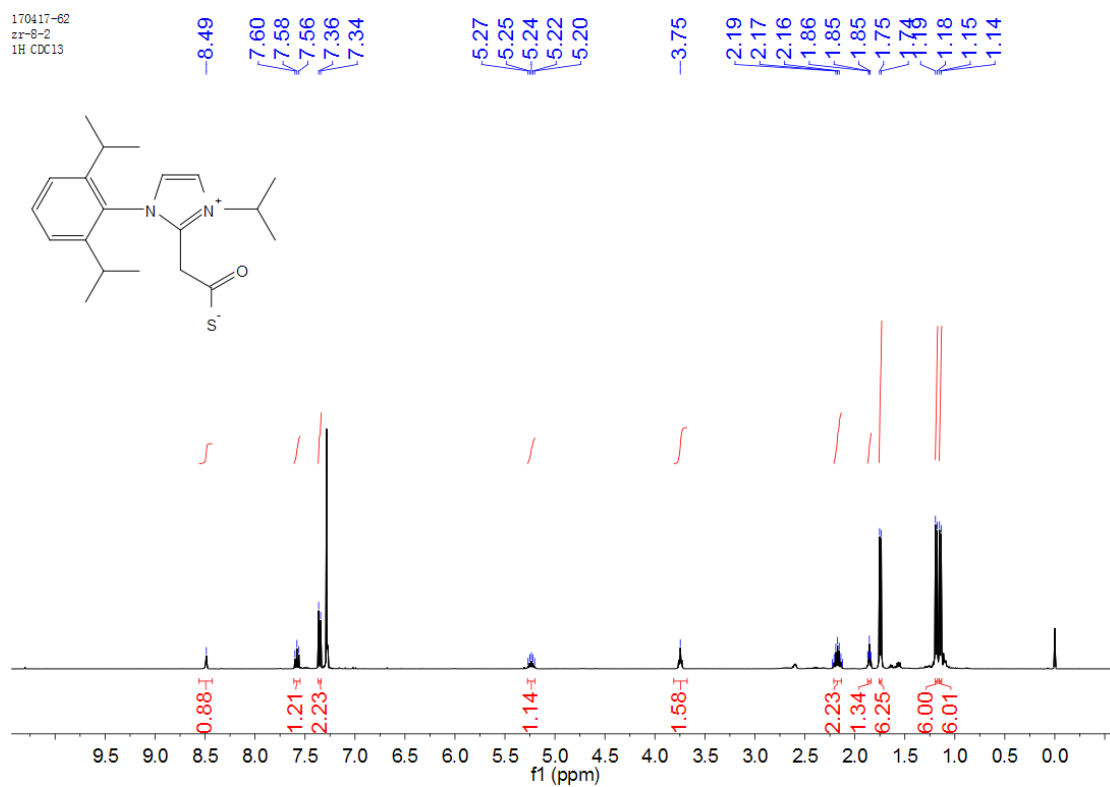
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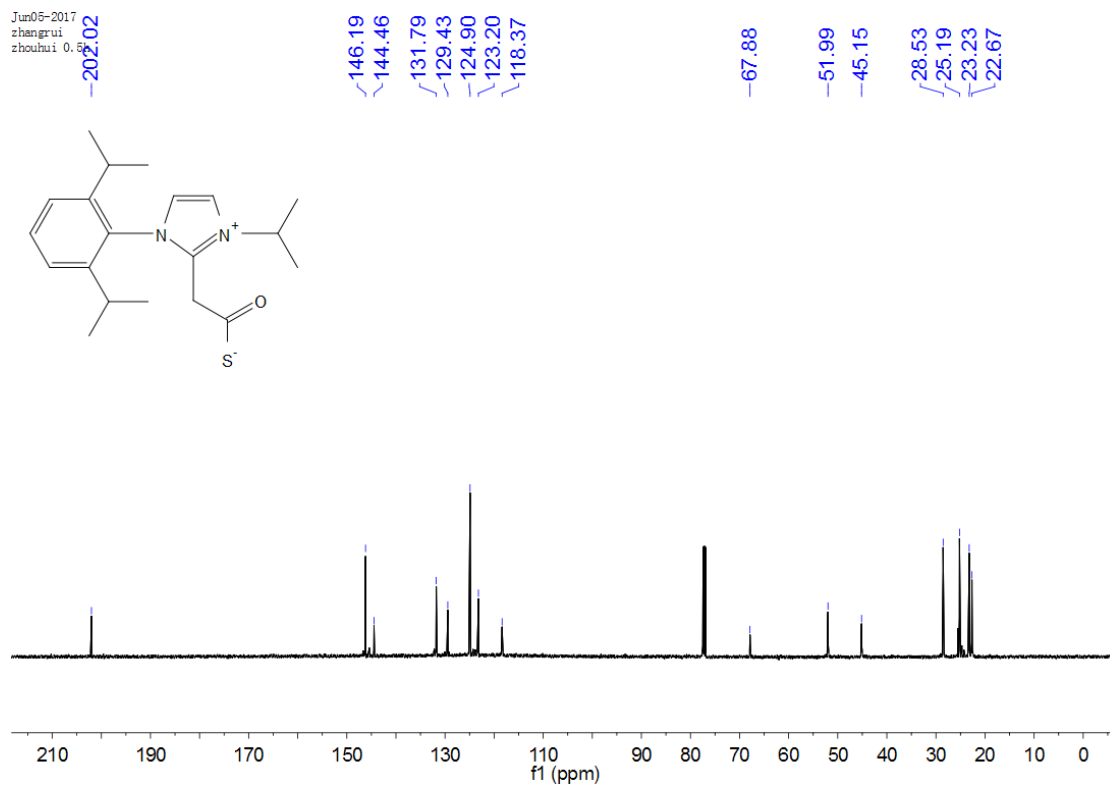
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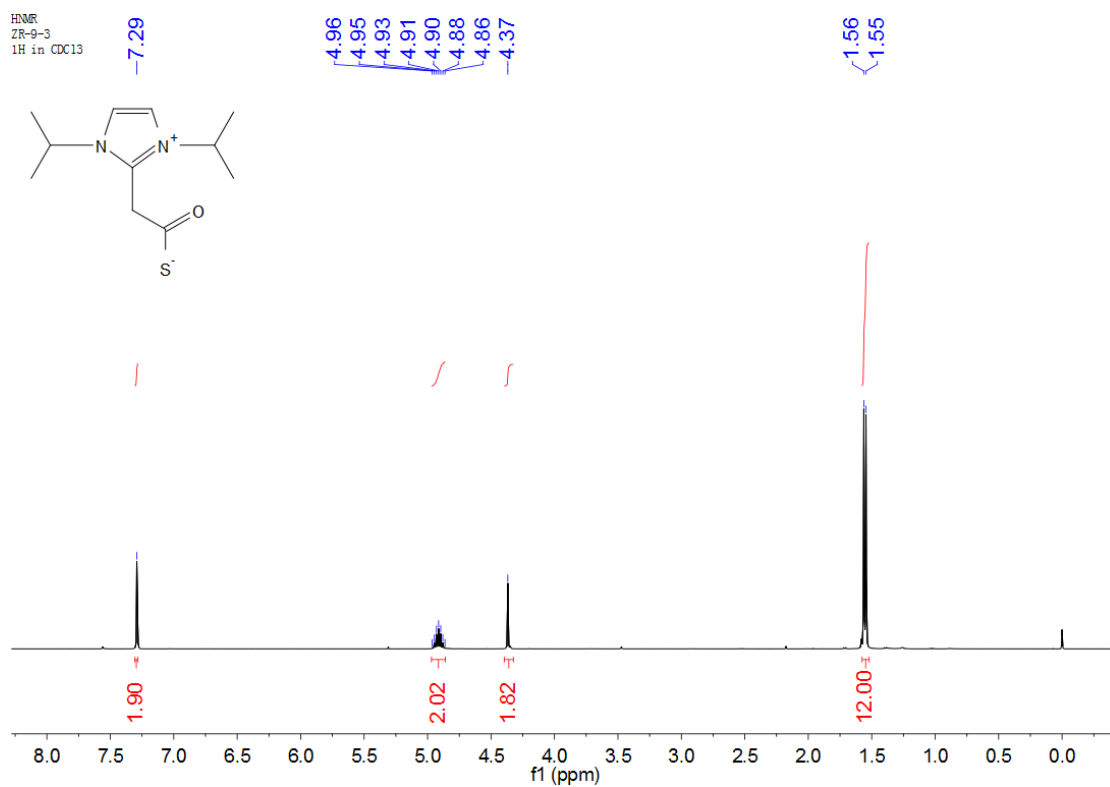
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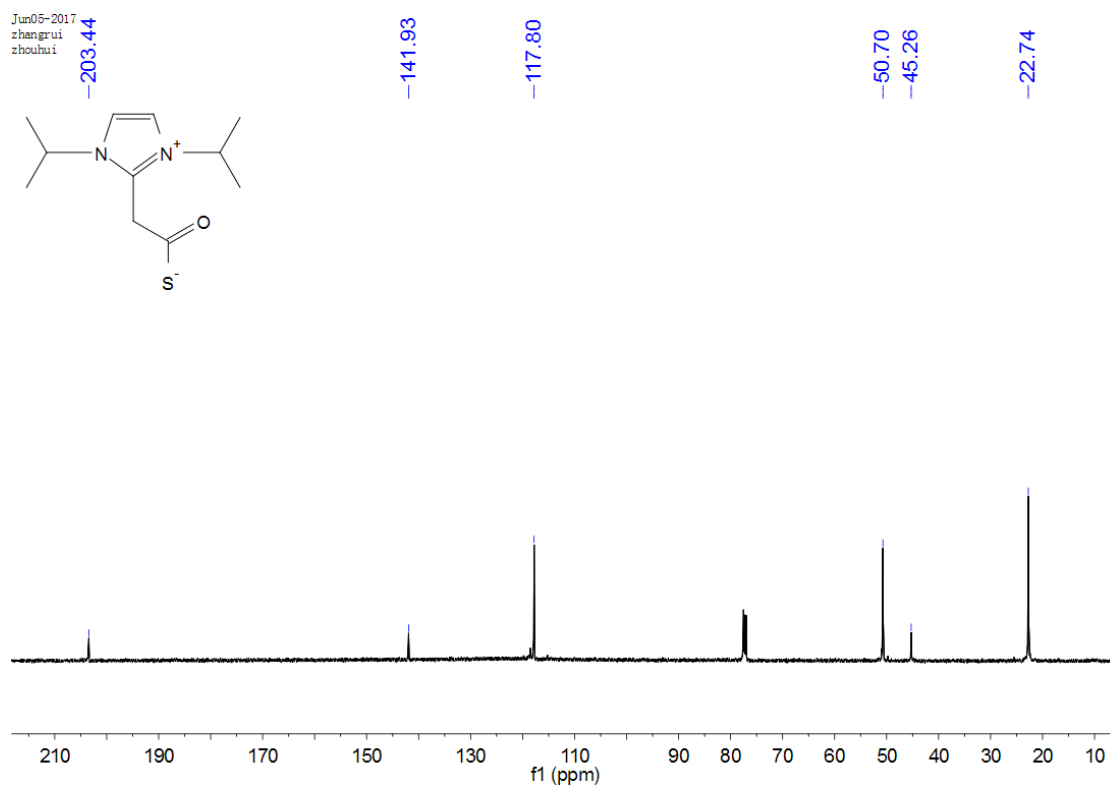
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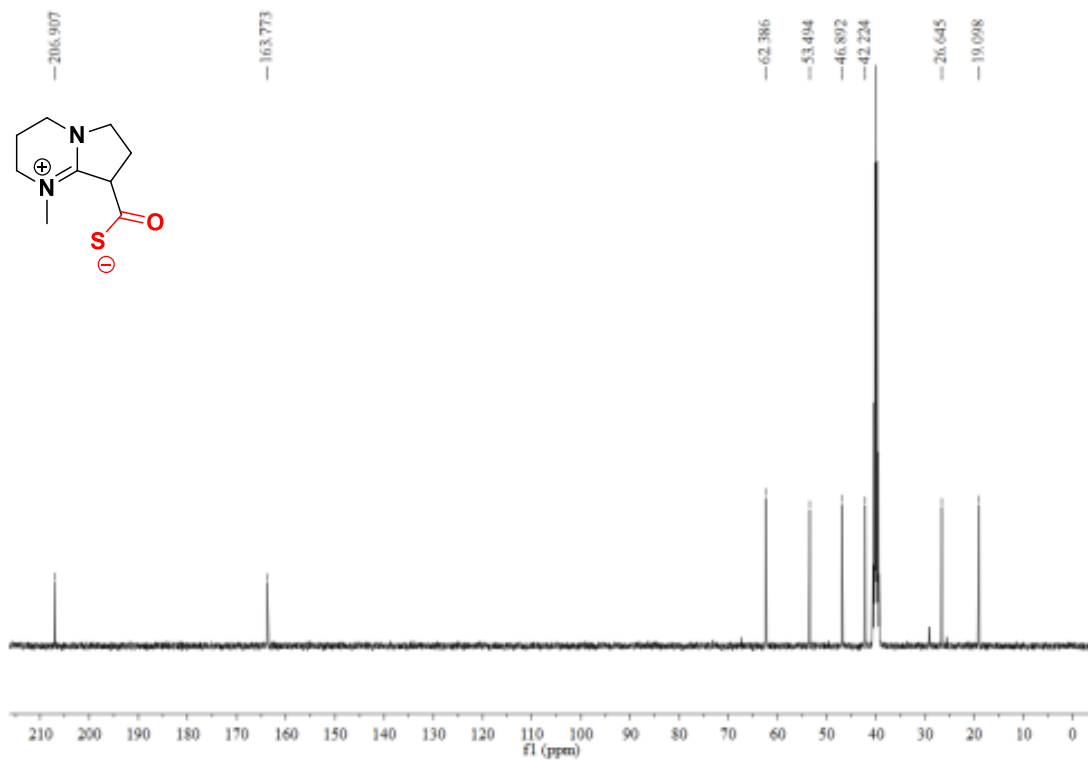
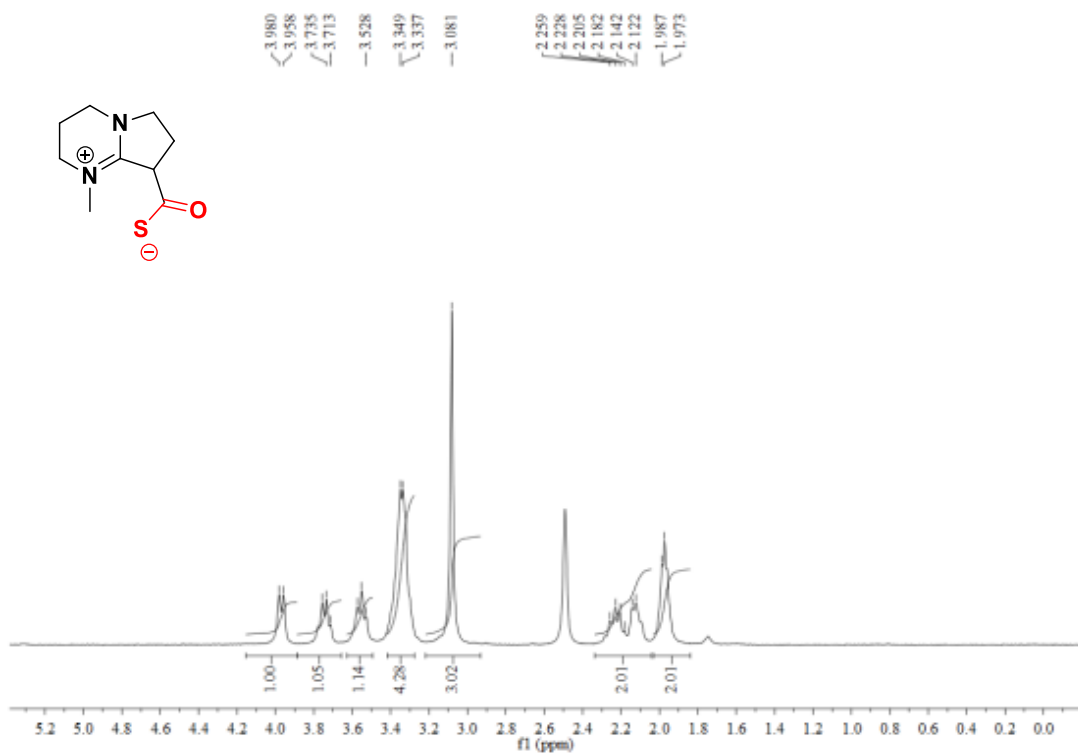


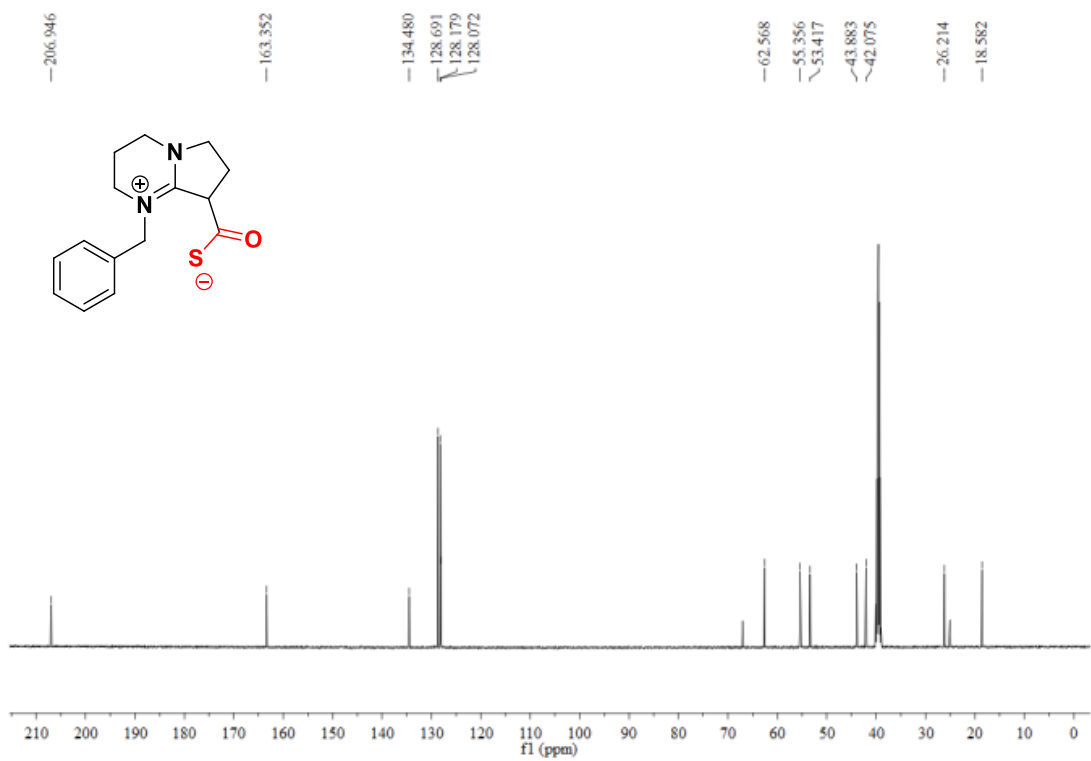
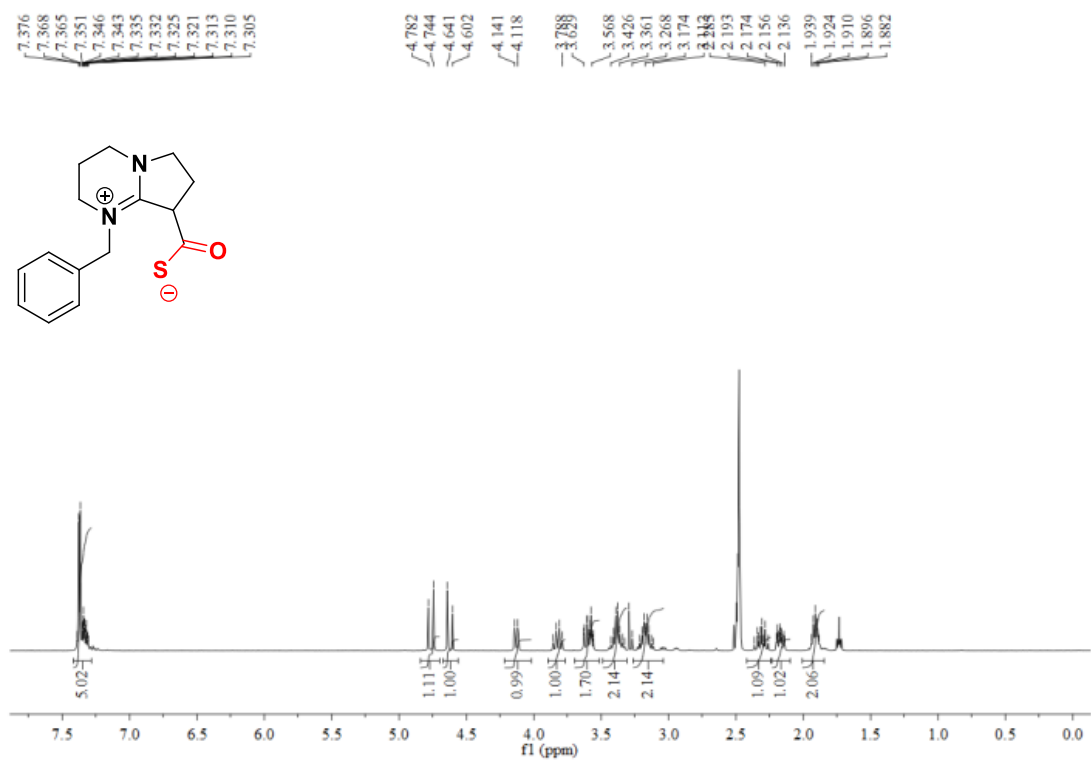
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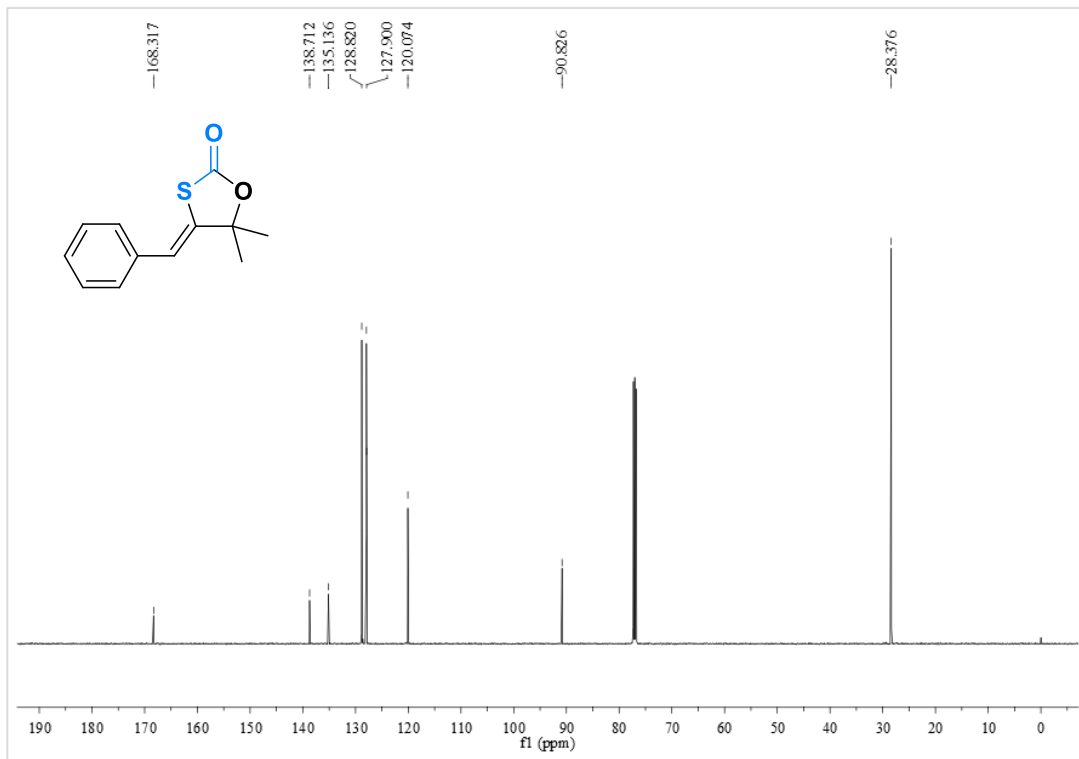
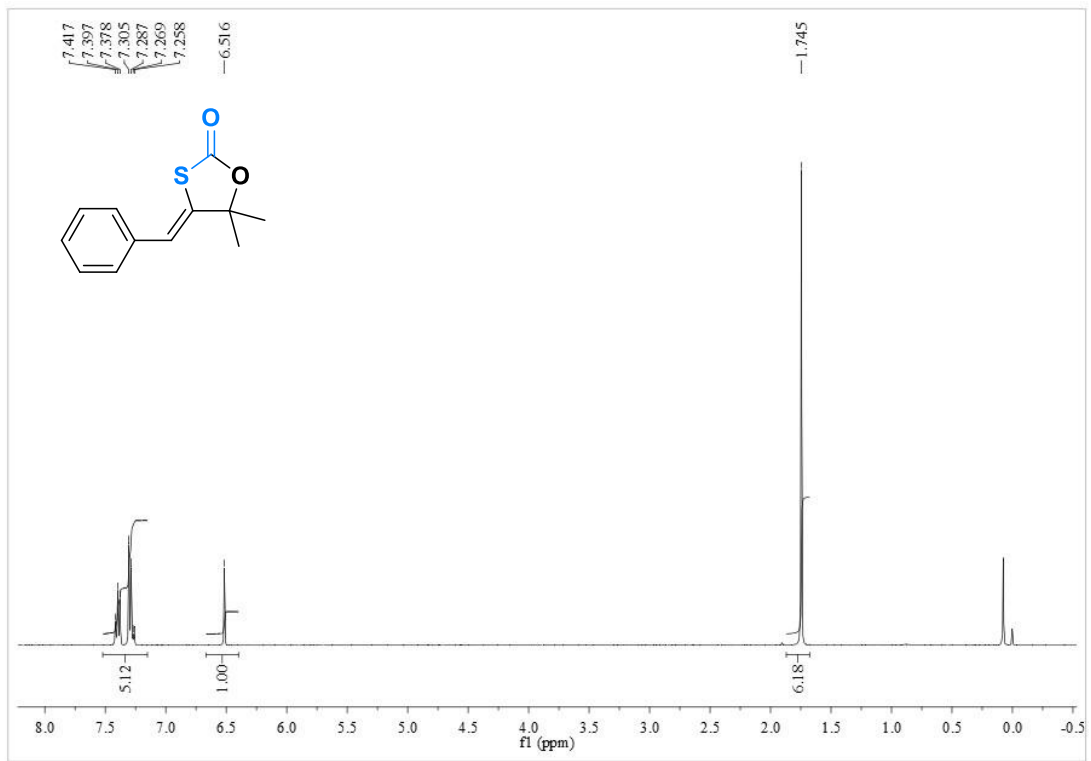


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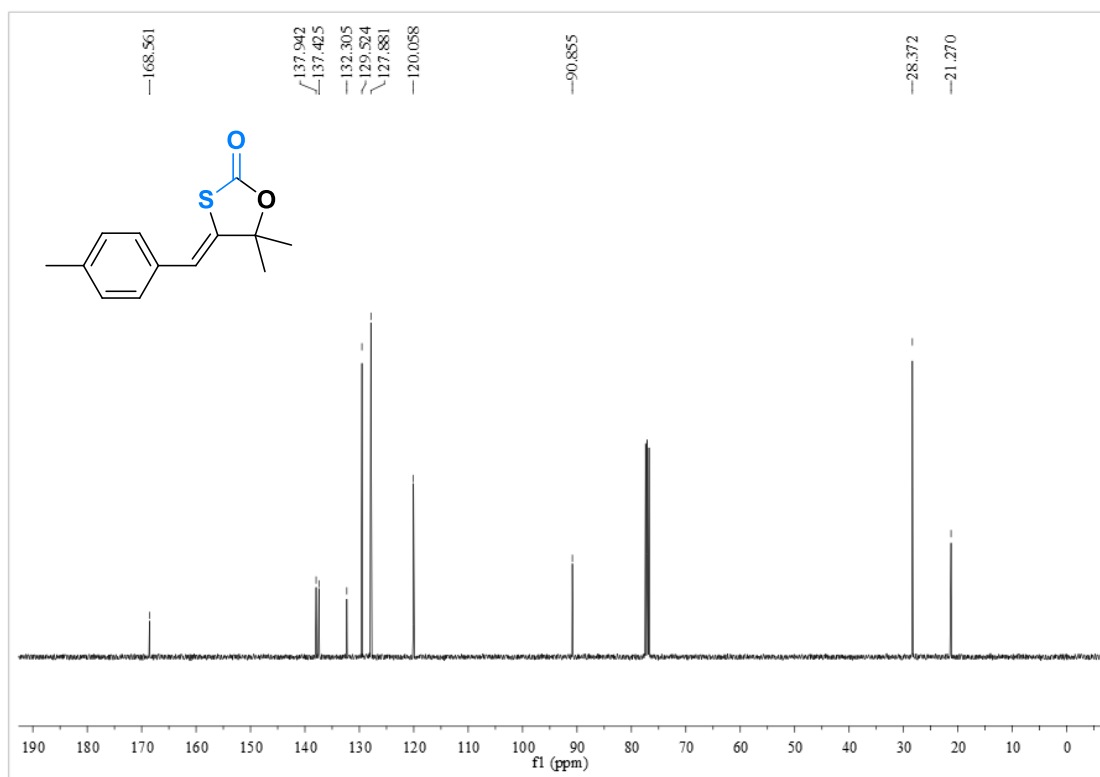
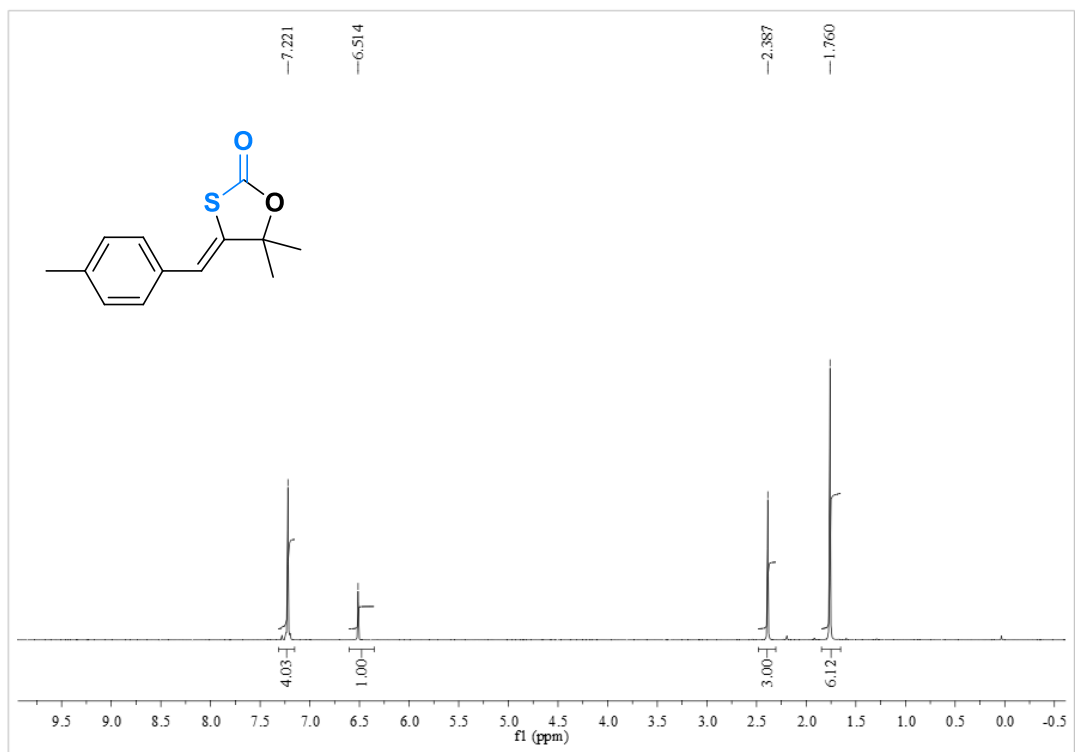


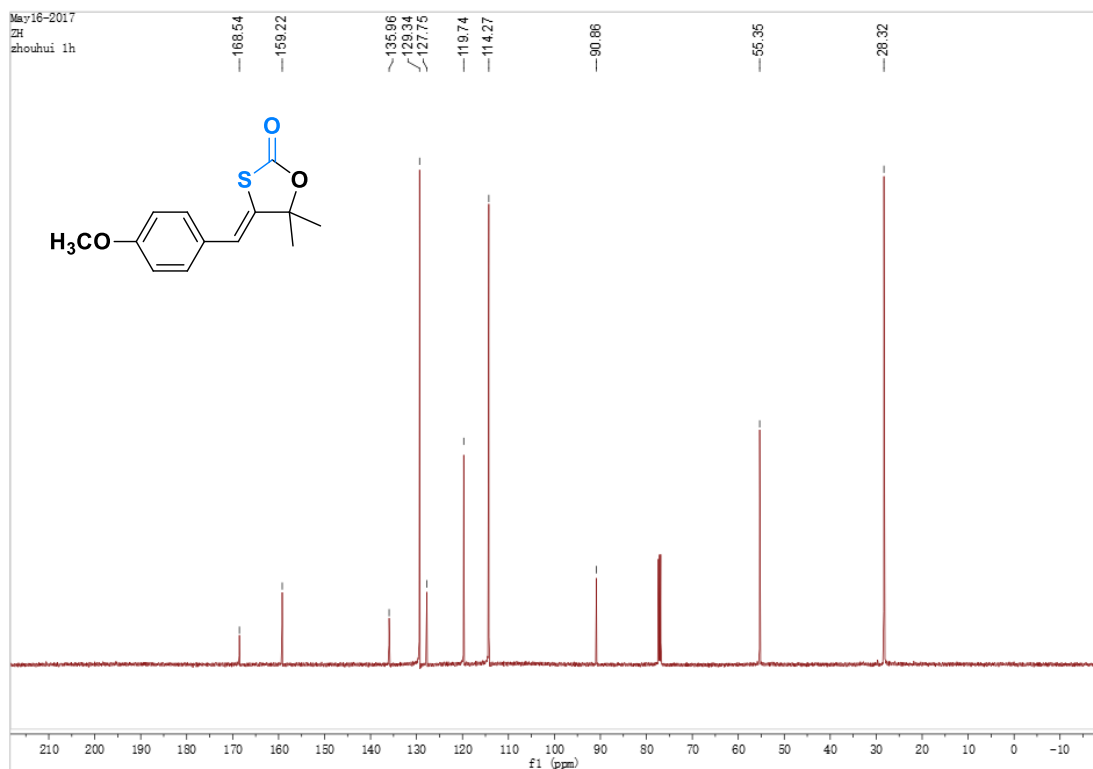
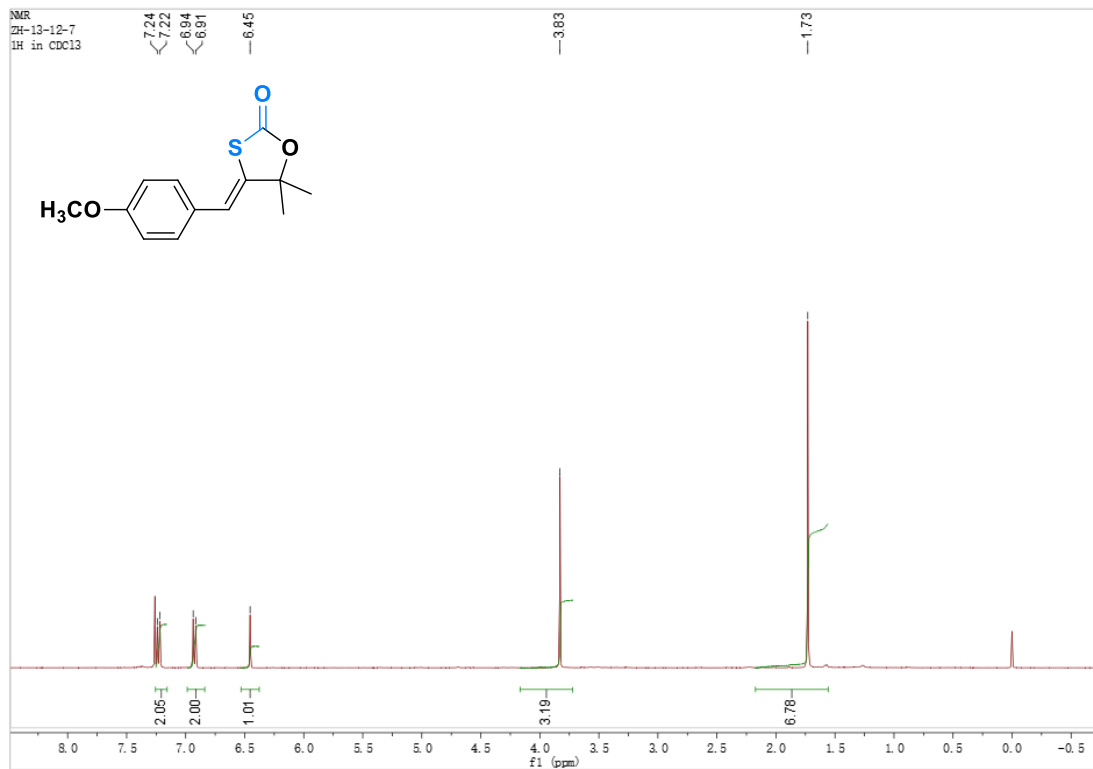


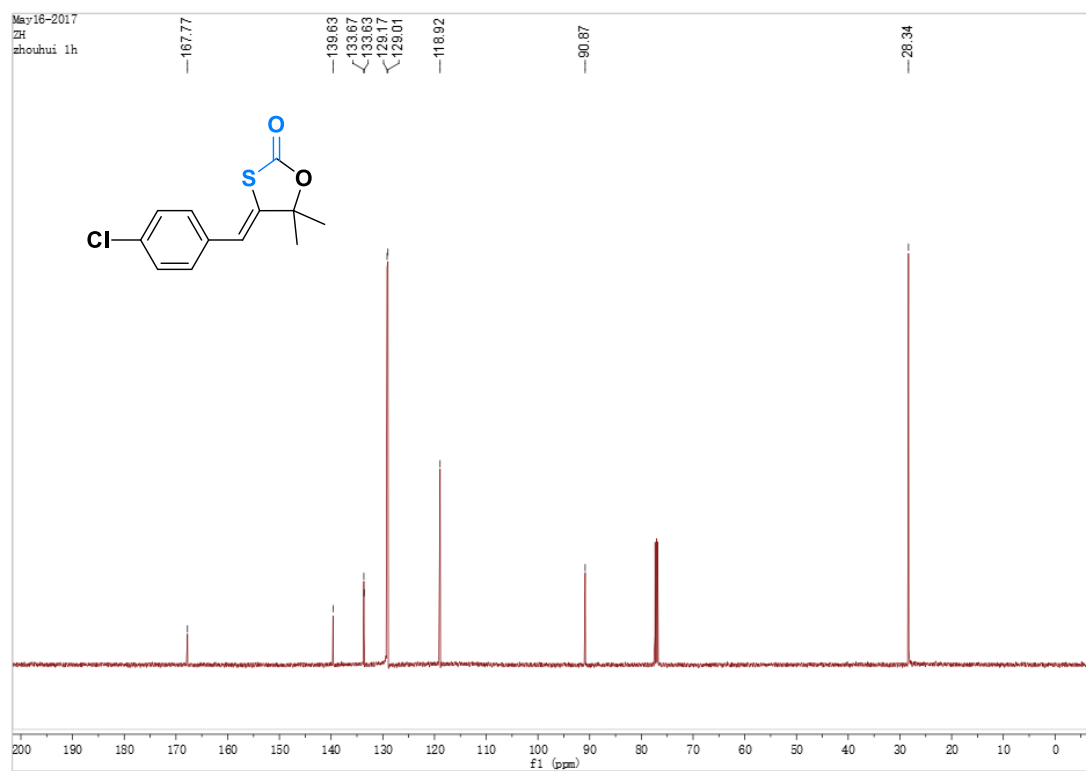
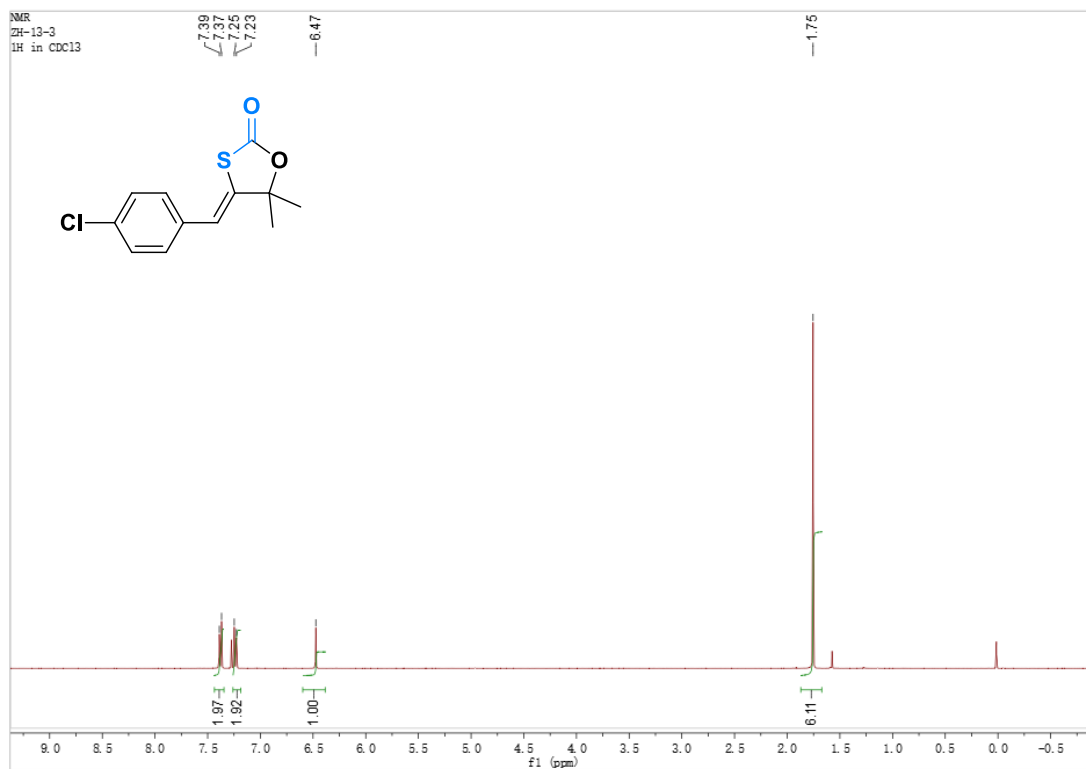


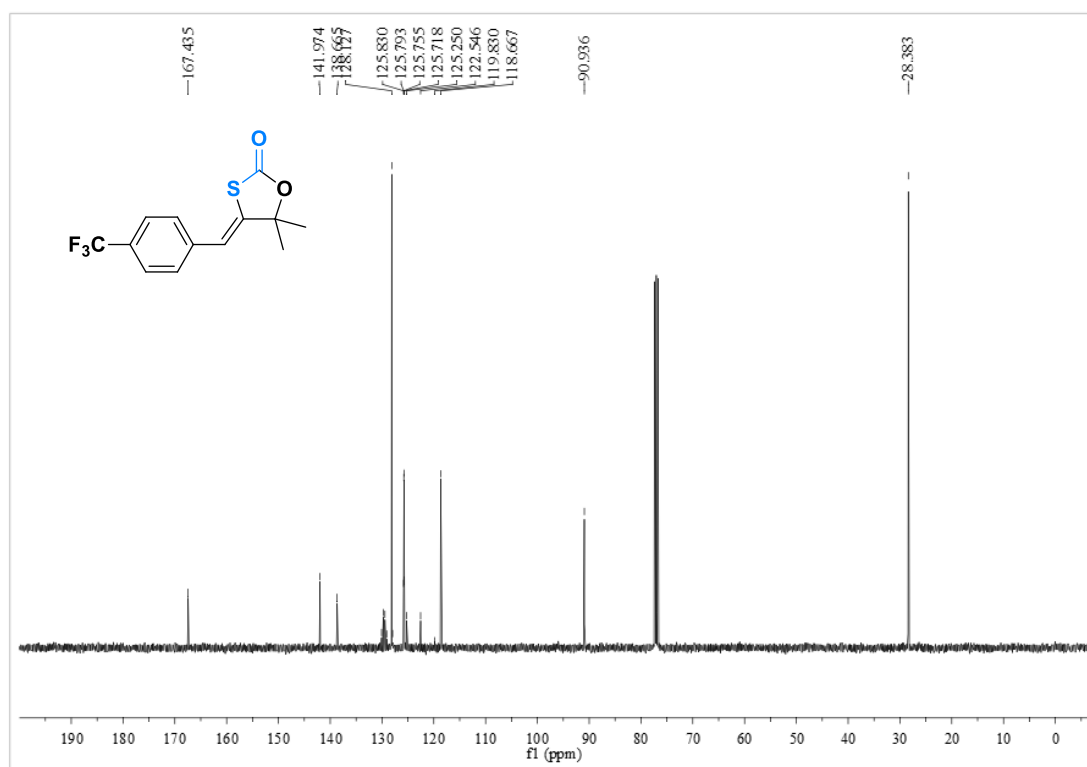
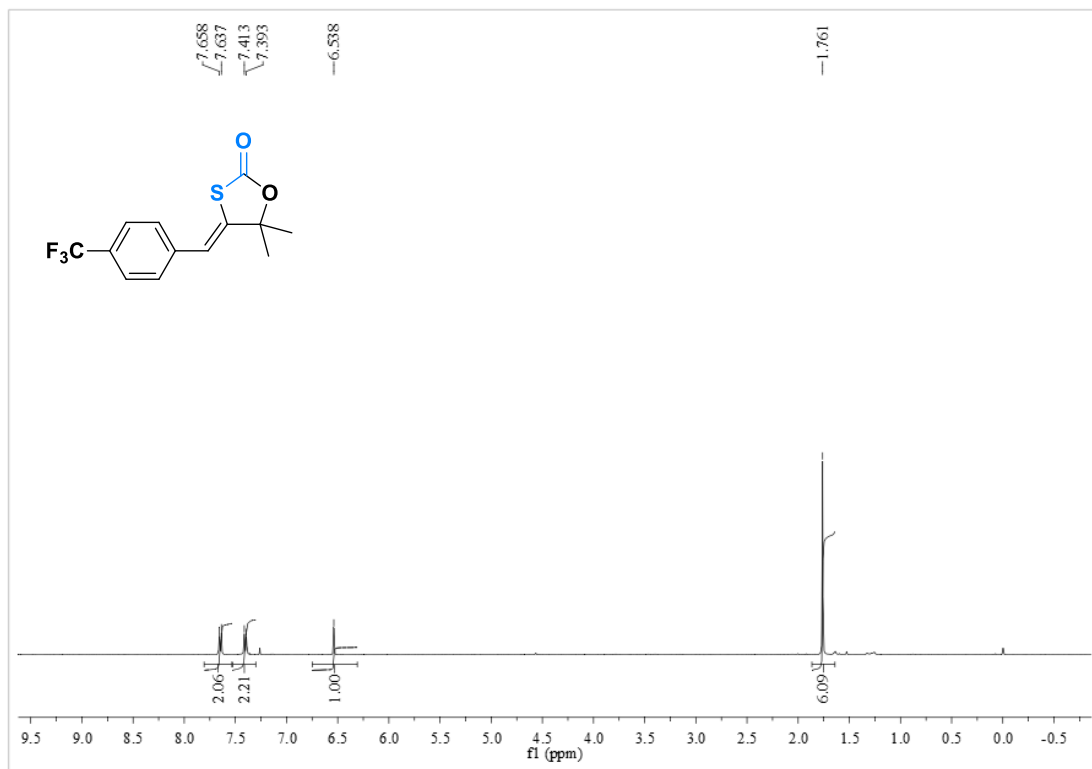


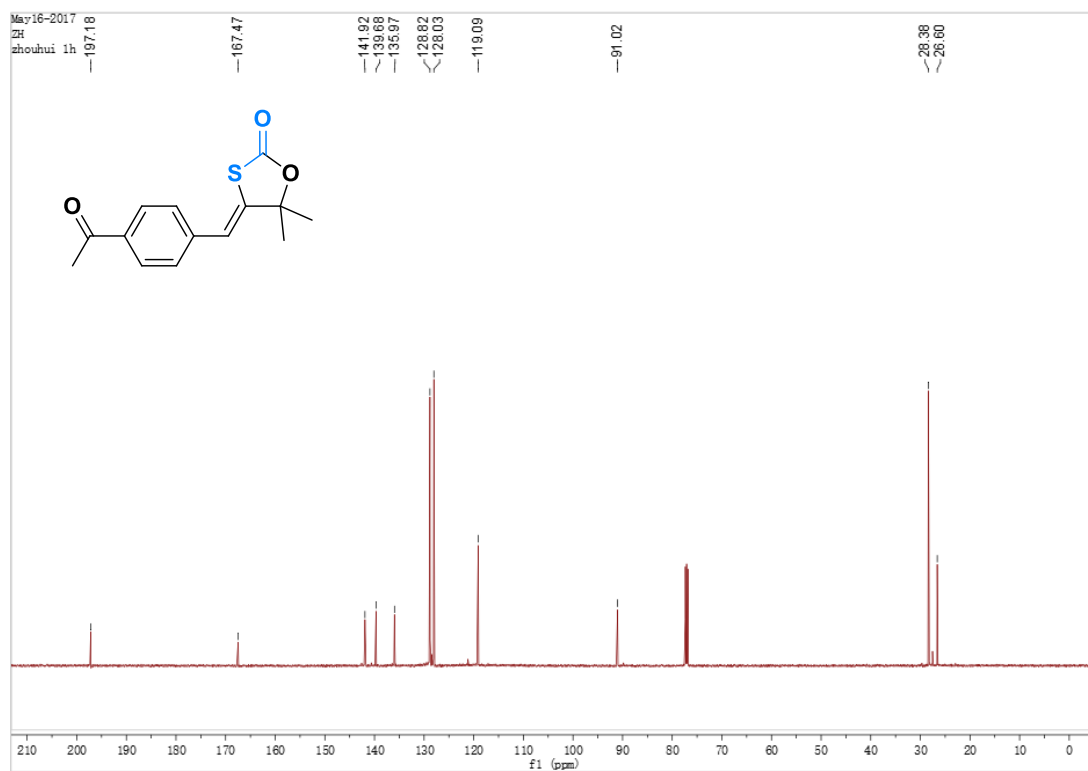
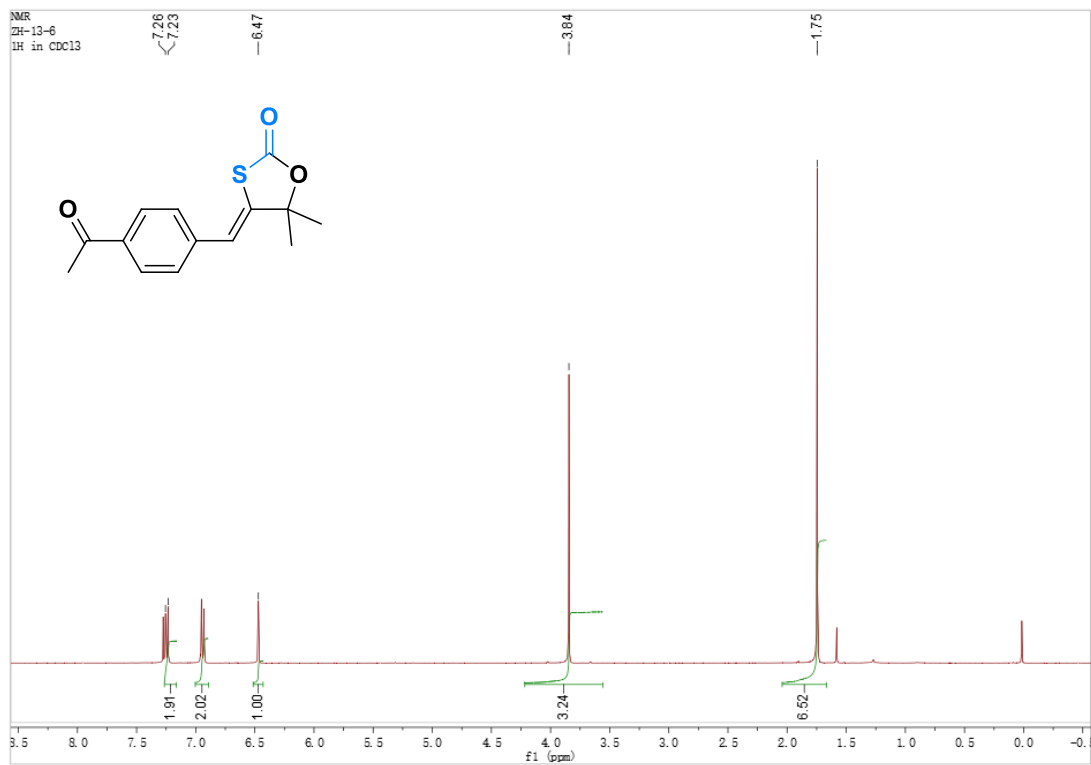


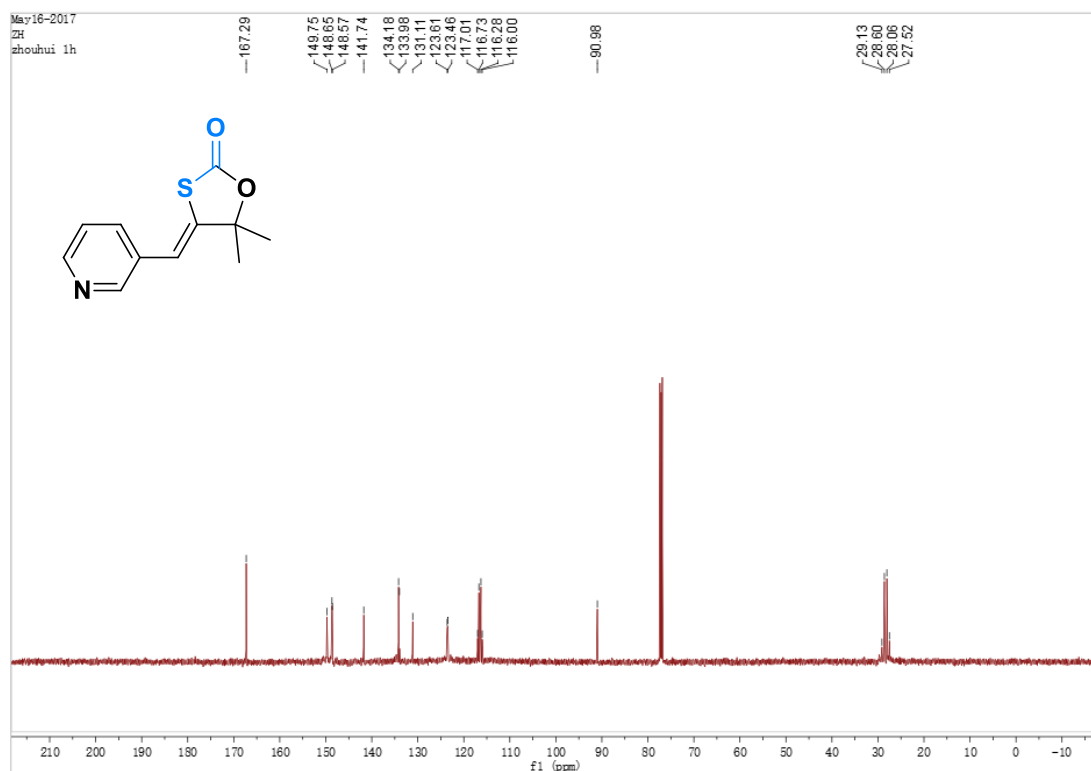
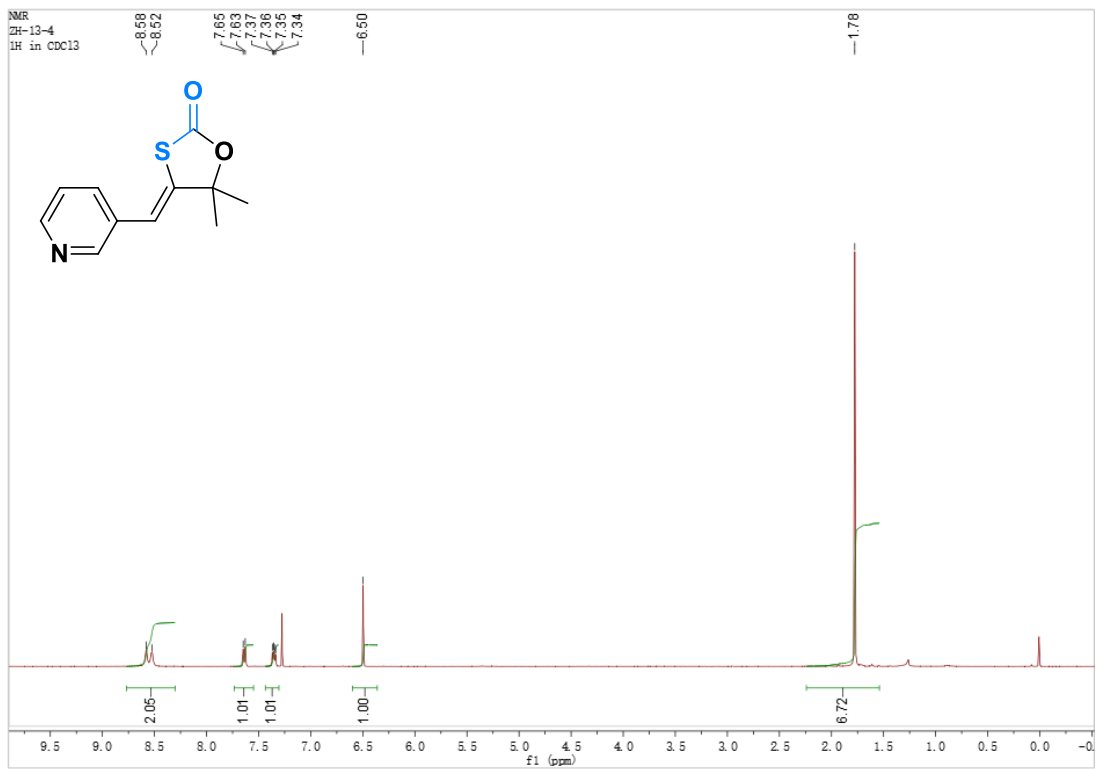


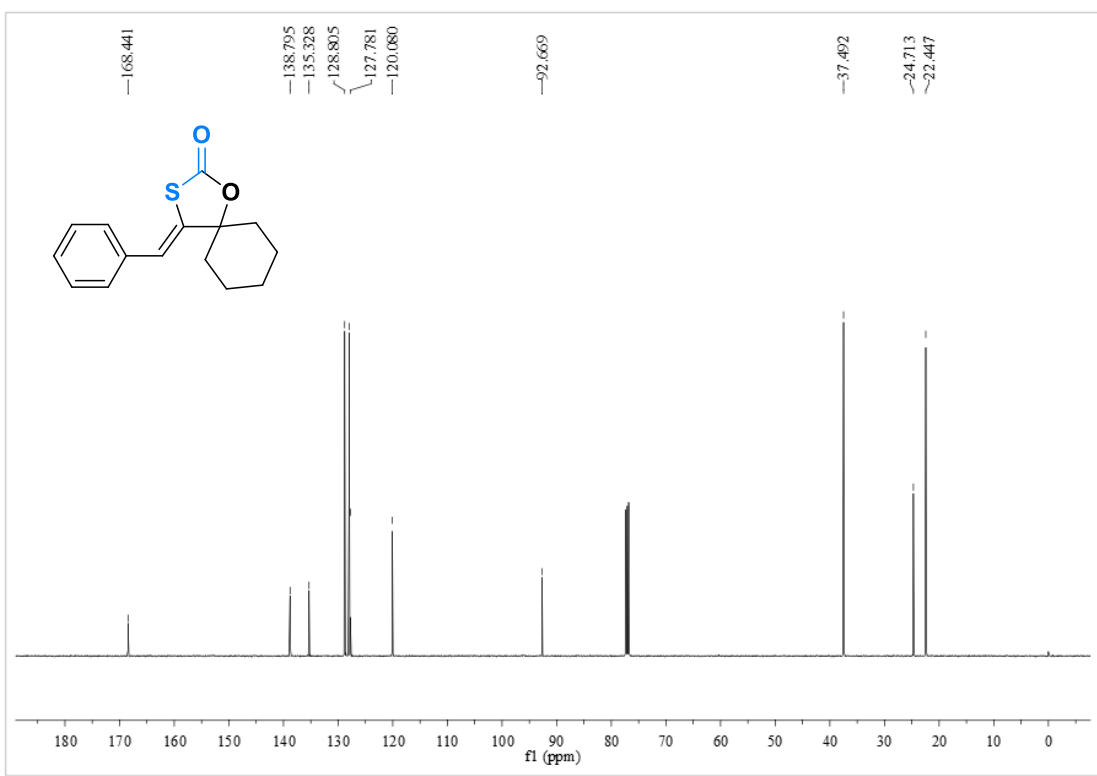
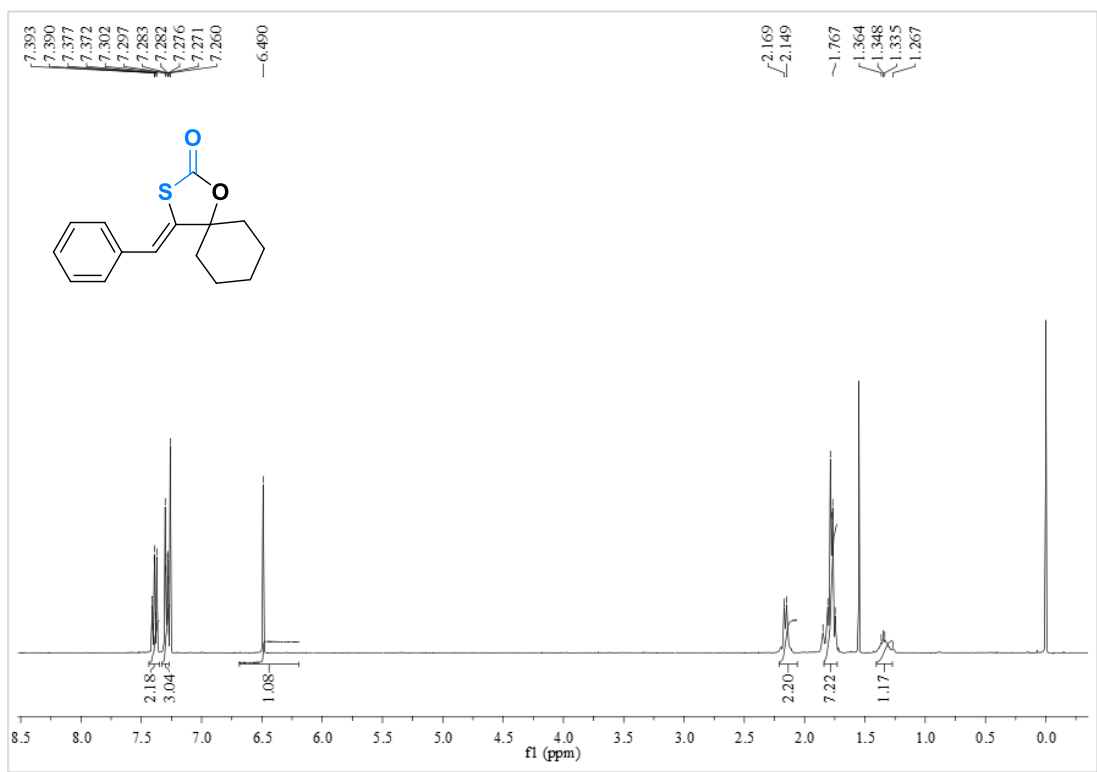




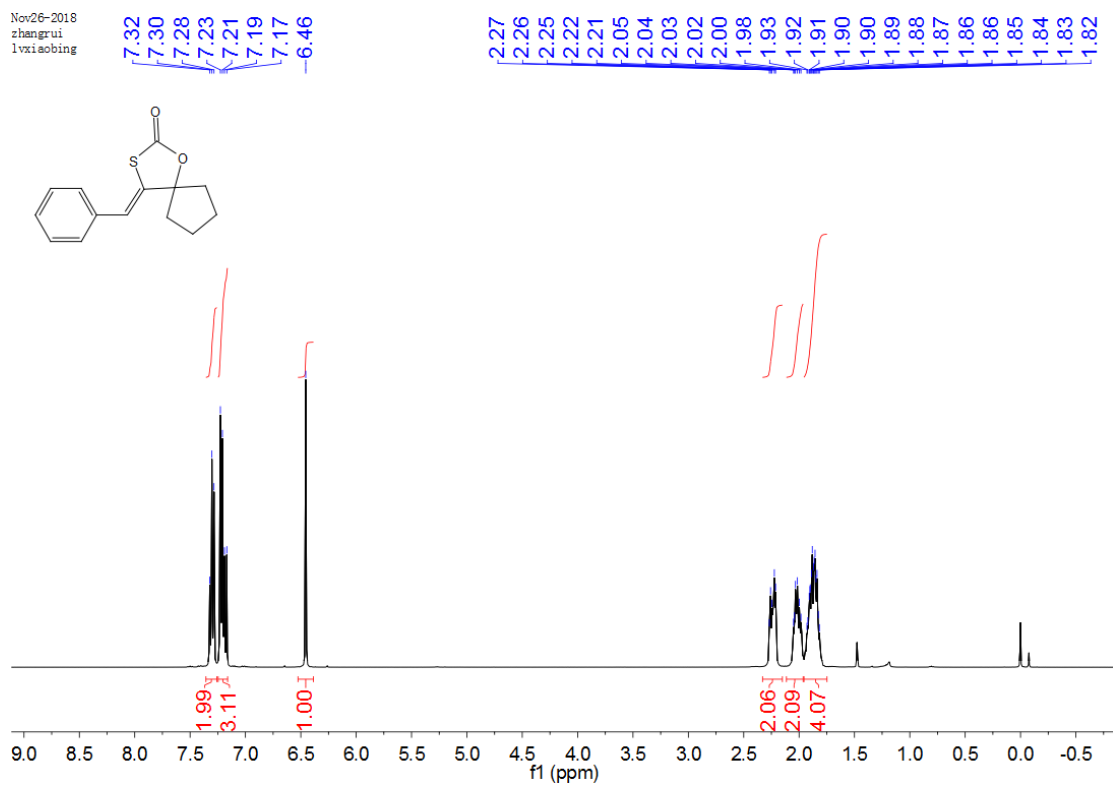








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