# Continuous-flow electro-oxidative coupling of sulfide with activated methylene compound leading to sulfur ylide

Chengkou Liu,[a] Yang Lin,[a] Chen Cai,[a] Chengcheng Yuan,[a] Zheng Fang,[a] and Kai Guo*[,a,b]

[a]College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing, 211816 China

[b]State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing, 211816 China

E-mail: guok@njtech.edu.cn.

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# 1. General Information

Commercially available reagents and solvents were of reagent grade quality without any further purification. Flash column chromatography was performed using silicycle silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV lamp (254 nm). $^{1}H$ NMR and $^{13}C$ NMR were recorded on magnet system 400'54 ascend purchased from Bruker Biospin AG. ESI-MS spectra were recorded on Agilent Q-TOF 6520. All continuous-flow electrosynthesis of sulfur ylides was conducted under the Asia Flux Module purchased from Syrris. And, electro-oxidative coupling of sulfides with activated methylene compounds in batch was carried out in an undivided electrochemical cell equipped with a carbon cloth anode and a platinum plate cathode, which were purchased from Shanghai Jing Chong Electronic Technology Development Co., Ltd Contract. Graphite rod (⌀ 6 mm) was also purchased from the company above. And, electrolysis was conducted under an AXIOMET AX3003P potentiostat in constant current mode. Cyclic voltammogram experiments were investigated using a Metrohm Autolab PGSTAT204 workstation and Nova 2.0 software.

# 2. General Material Information for Batch Setup and Continuous-Flow Electrochemical Reactor

## 2.1 General Material Information for Batch setup

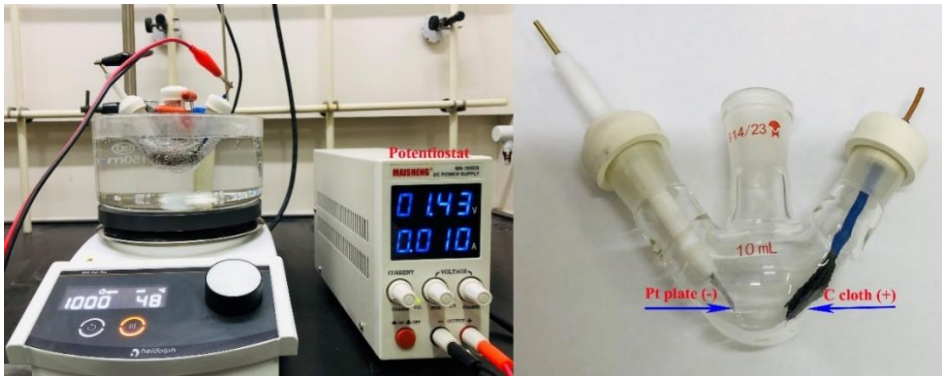



Figure **S1** pictures of batch setup

The batch electrolysis setup used is shown in Figure **S1**.

## 2.2 General Material Information for Continuous-Flow Electrochemical Reactor

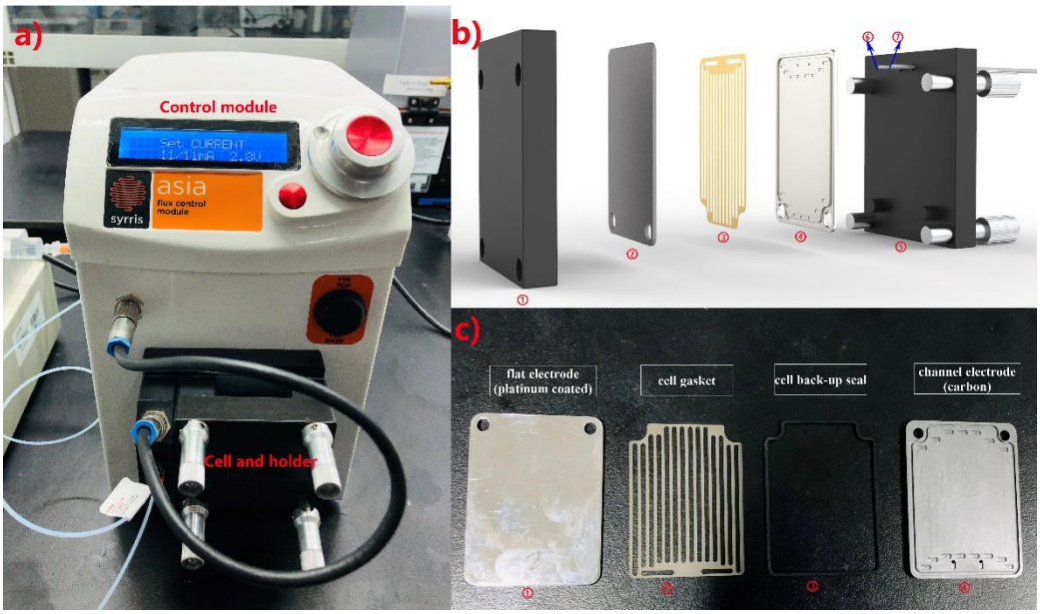


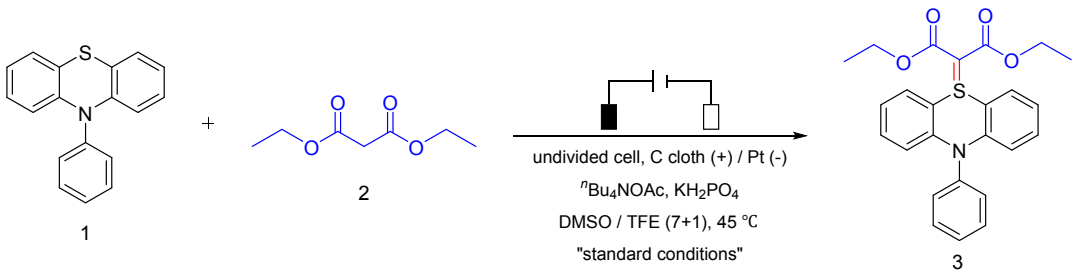

Figure **S2** pictures of continuous-flow electrochemical reactor

a) the outside views of control module and cell; b) the diagram of reactor. ① and ⑤: electrode holder; ②: cathode; ③ channel reactor; ④: Anode; ⑥ and ⑦: inlet and outlet. c) the pictures of the continuous-flow electrochemical setups. ①: Pt-plated flat electrode (5.0 × 4.0 cm); ②: cell gasket (channel reactor); ③: cell back-up seal; ④: C gasket electrode (carbon filled PPS, 5.0 × 4.0 cm).

# 3. Reaction Optimization

## 3.1 Optimization of the electrosynthesis of sulfur ylides in batch

Table **S1**: General optimization of electrolysis conditions in batch.[a]

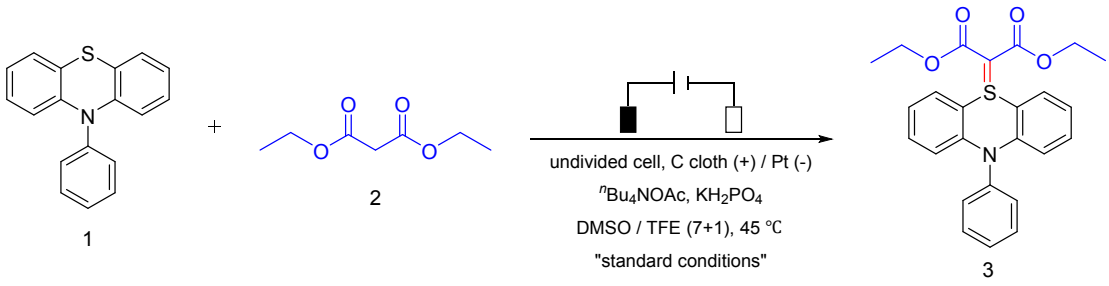



| Entry | Variation(s) from the standard conditions | | | Yield[b] |
|---|---|---|---|---|
| | Electrolyte | Base | Solvent | (%) |
| 1 | | none | | 89 |
| 2 | $^{n}Bu_4NPF_6$ as electrolyte | | | trace |

| | | | | |
|---|---|---|---|---|
| 3 | $^{n}Bu_4NBF_4$ as electrolyte | | | trace |
| 4 | $^{n}Bu_4NClO_4$ as electrolyte | | | 27 |
| 5 | $LiClO_4$ as electrolyte | | | 38 |
| 6 | $^{n}Bu_4NI$ as electrolyte | | | trace |
| 7 | $^{n}Bu_4NBr$ as electrolyte | | | trace |
| 8 | $^{n}Bu_4NCl$ as electrolyte | | | 21 |
| 9 | NaI | | | trace |
| 10 | NaBr | | | trace |
| 11 | NaCl | | | 24 |
| 12 | No electrolyte | | | N.R |
| 13 | | $K_2CO_3$ as base | | 10 |
| 14 | | $K_3PO_4$ as base | | 51 |
| 15 | | $K_2HPO_4$ as base | | 43 |
| 16 | | $Na_2CO_3$ as base | | trace |
| 17 | | $NaHCO_3$ as base | | trace |
| 18 | | KOAc as base | | trace |
| 19 | | | TFA instead of TFE | N.R |
| 20 | | | HFIP instead of TFE | 70 |
| 21 | | | EtOH instead of TFE | 60 |
| 22 | | | MeOH instead of TFE | 65 |
| 23 | | | DMF instead of DMSO | 40 |
| 24 | | | ACN instead of DMSO | 37 |
| 25 | | | DCE instead of DMSO | trace |
| 26 | | | Dioxane instead of DMSO | trace |

[a]Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), $^{n}Bu_4NOAc$ (0.4 mmol), $KH_2PO_4$ (0.4 mmol), solvent (DMSO/TFE = 7 mL/1 mL), 45℃, 2.5 h, 4.67 F/mol, undivided cell, carbon cloth anode (40 mm x 20 mm), platinum plate cathode (10 mm x 10 mm x 0.1 mm), constant current = 10 mA, TFE: 2,2,2-trifluoroethanol, TFA: trifluoroacetic acid; HFIP: 1,1,1,3,3,3-Hexafluoro-2-propanol. [b]isolated Yield.

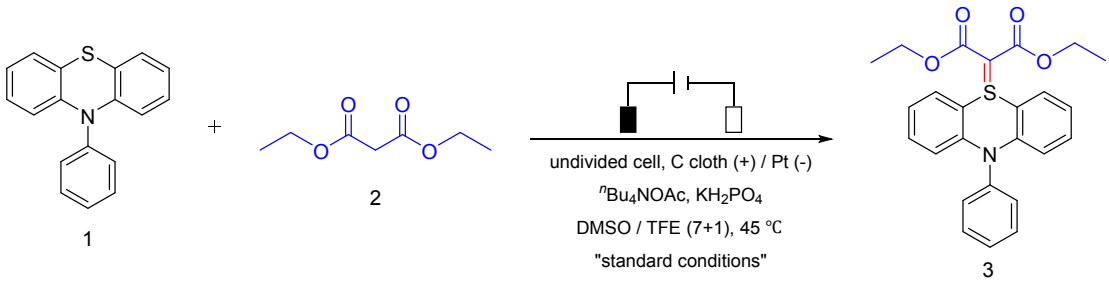
Table **S2**. Effect of electrode and temperature.[a]




| Entry | Variation(s) from the standard conditions | | Yield[b] (%) |
|---|---|---|---|
| | electrode | temperature | |
| 1 | none | | 89 |
| 2 | Pt(+)/Pt(-) | | 10 |
| 3 | Graphite(+)/Pt(-) | | 21 |
| 4 | Graphite(+)/Graphite(-) | | 30 |
| 5 | Pt(+)/Graphite(-) | | 13 |
| 6 | Pt(+)/Carbon cloth(-) | | 33 |
| 7 | | 25 | trace |
| 8 | | 35 | 57 |
| 9 | | 55 | 73 |
| 10 | | 65 | 67 |
| 11 | | 75 | 39 |
| 12 | | 85 | 41 |
| 13[c] | none | | 49 |

[a]Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), $^{n}Bu_4NOAc$ (0.4 mmol), $KH_2PO_4$ (0.4 mmol), solvent (DMSO/TFE = 7 mL/1 mL), 45℃, 2.5 h, 4.67 F/mol, constant current = 10 mA, undivided cell, graphite rod (⌀ 6 mm), [b]isolated Yield, [c]under $N_2$.

Table **S3**. Effect of equiv. of 2 and electrolyte, concentration and current.[a]

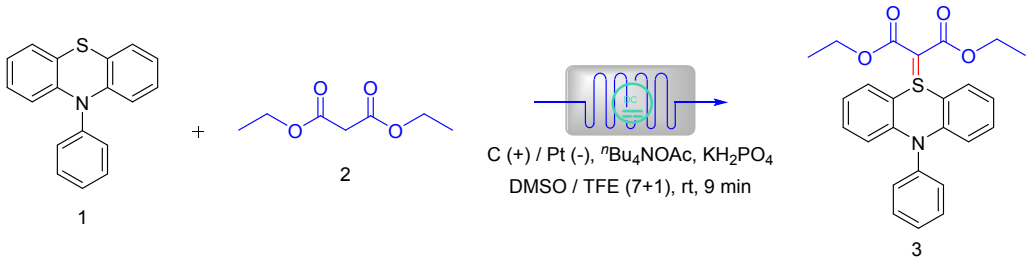



| Entry | Variation(s) from the standard conditions | | | | Yield[b] (%) |
|---|---|---|---|---|---|
| | equiv. of 2 | equiv. of $^{n}Bu_4NOAc$ | Concentration (based on 1) | Current (A) | |
| 1 | none | | | | |
| 2 | 1 | | | | 62 |
| 3 | 1.5 | | | | 71 |
| 4 | | 1 | | | 57 |
| 5 | | 1.5 | | | 69 |
| 6 | | | 0.025 M | | 89 |
| 7 | | | 0.05 M | | 80[c] |
| 8 | | | 0.075 M | | 74[d] |
| 9 | | | | 8 | 83 |
| 10 | | | | 12 | 76 |
| 11 | | | | 15 | 67 |
| 12 | | | | 20 | 61 |

[a]Reaction conditions: 1 (0.2 mmol), 2 (0.4 mmol), $^{n}Bu_4NOAc$ (0.4 mmol), $KH_2PO_4$ (0.4 mmol), solvent (DMSO/TFE = 7 mL/1 mL), 45℃, 2.5 h, 4.67 F/mol, undivided cell, constant current = 10 mA. [b]isolated Yield. [c]5 h. [d]7 h.

3.2 Optimization of the electrosynthesis of sulfur ylides in continuous-flow.[a]

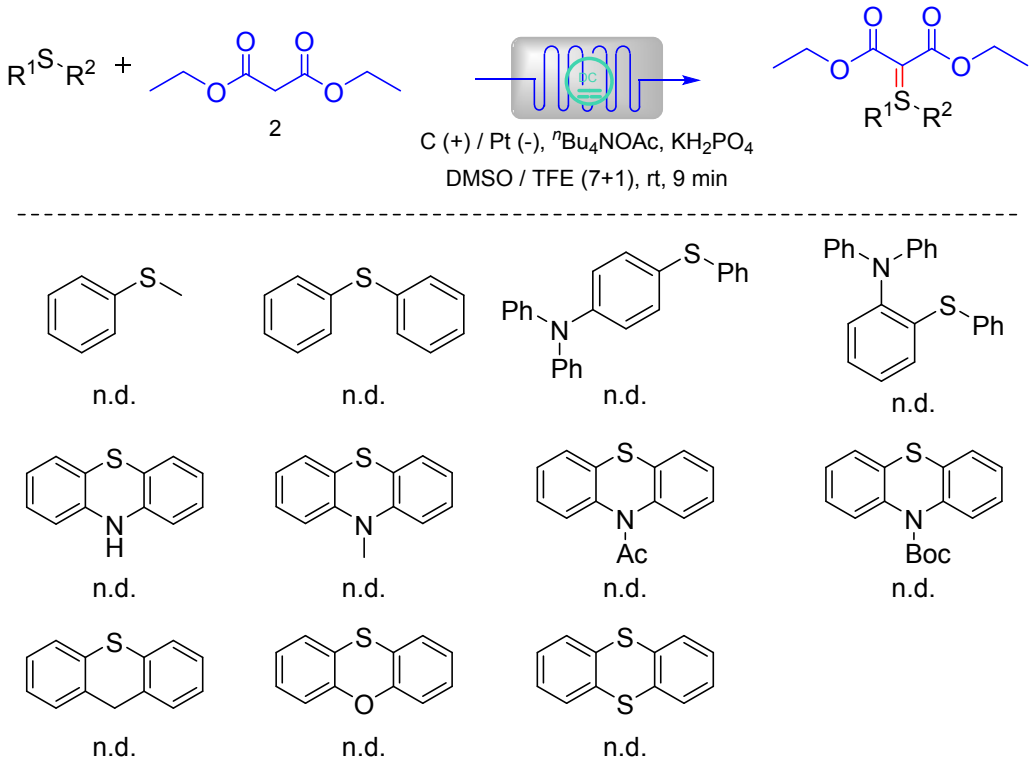
Table **S4**: Effect of equiv. of 2 and electrolyte in continuous-flow.[a]




| Entry | Variation(s) from the standard conditions | | Yield[b] (%) |
|---|---|---|---|
| | equiv. of 2 | equiv. of $^{n}Bu_4NOAc$ | |
| 1 | none | | 94 |
| 2 | 1 | | 61 |
| 3 | 1.5 | | 69 |
| 4 | | 1 | 59 |
| 5 | | 1.5 | 57 |

[a]Reaction conditions: 1 (0.6 mmol), 2 (1.2 mmol), $^{n}Bu_4NOAc$ (1.2 mmol), $KH_2PO_4$ (1.2 mmol), DMSO/TFE (7 mL/1 mL), C (carbon filled PPS, 5.0 × 4.0 cm) anode, Pt (SS 316L Platinum coated, 5.0 × 4.0 cm) cathode, volume (0.225 mL), 0.025 mL/min, residence time 9 min, 11 mA, rt, 3.65 F/mol.

# 4. Sulfide scope

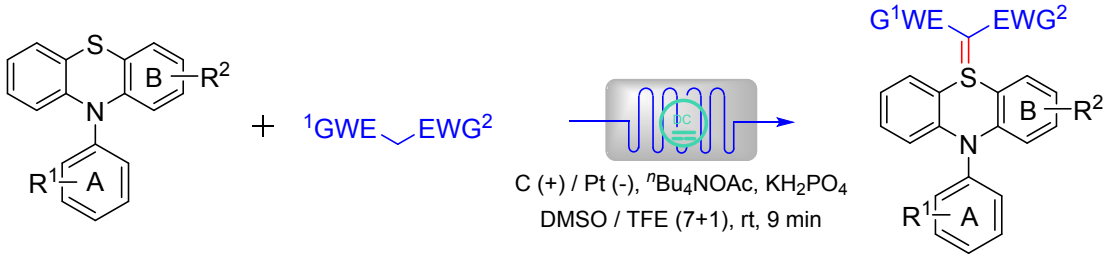



Scheme **S1** Sulfide screening for continuous-flow electrosynthesis of sulfur ylides

Reaction conditions: sulfide (0.6 mmol), 2 (1.2 mmol), $^{n}Bu_4NOAc$ (1.2 mmol), $KH_2PO_4$ (1.2 mmol), DMSO/TFE (7 mL/1 mL), C (carbon filled PPS, 5.0 × 4.0 cm) anode, Pt (SS 316L Platinum coated, 5.0 × 4.0 cm) cathode, volume (0.225 mL), 9 min, 11 mA, rt, 3.65 F/mol.

## 5. General Procedure for the electrosynthesis of sulfur ylides

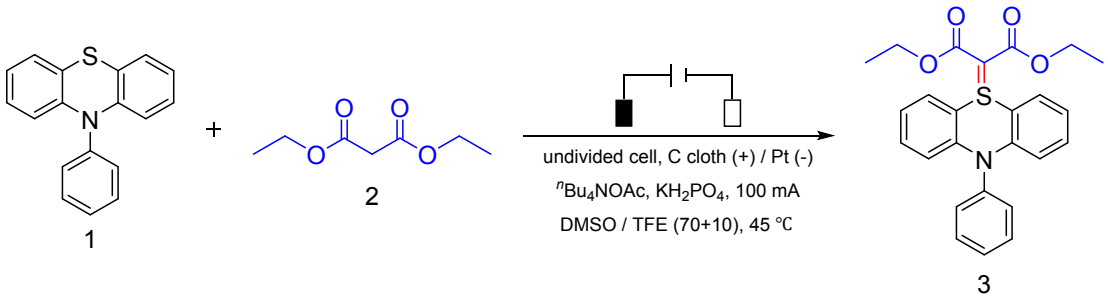
General Procedure for the continuous-flow electrosynthesis of sulfur ylides




The corresponding sulfide (0.6 mmol), active methylene (1.2 mmol), $^{n}Bu_4NOAc$ (1.2 mmol, 361.8 mg) and $KH_2PO_4$ (1.2 mmol, 163.3 mg) were dissolved in a mixed solvent of DMSO/TFE [(7+1) mL]. At ambient temperature, the reaction mixtures were introduced into the reactor at 0.025 mL/min at a constant current of 11 mA. The reaction solution was diluted with ethyl acetate (50 mL) and washed with brine (50 mL) and $H_2O$ (50 mL). The separated organic layer was dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate).

## 6. Gram-Scale Synthesis of 3 in Batch and Continuous-Flow Reactor

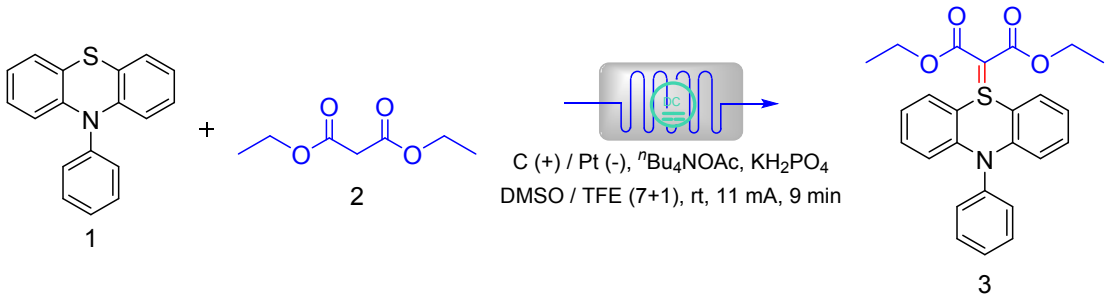
### 6.1 In Batch




In a 150 mL beaker equipped with a carbon cloth (100 mm × 50 mm) anode and a Pt (40 mm ×40 mm × 0.1 mm) cathode, sulfide 1 (4 mmol, 1.10 g), diethyl malonate (8 mmol, 1.28 g), $^{n}Bu_4NOAc$ (8 mmol, 2.41 g) and $KH_2PO_4$ (8 mmol, 1.09 g) were dissolved in a mixed solvent of DMSO/TFE [(70+10) mL]. At 45 °C, the reaction was started at a constant current of 100 mA for 6 h. The

reaction solution was diluted with ethyl acetate (150 mL) and washed with brine (150 mL) and $H_2O$ (150 mL). The separated organic layer was dried over anhydrous $Na_2SO_4$ (2 g) and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 3/1, white solid, 1.37 g, 79%).

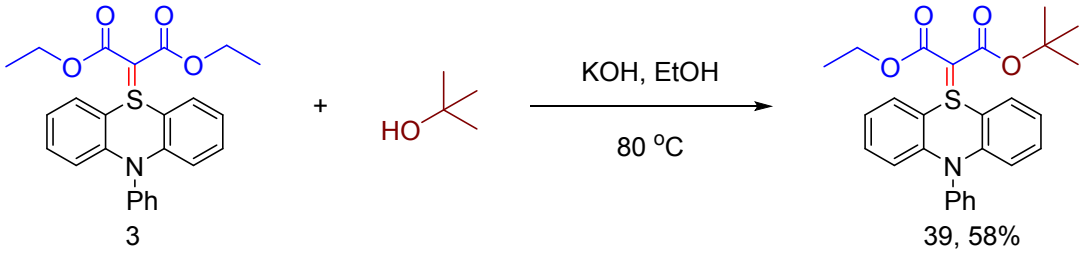
### 6.2 In continuous-flow




The sulfide 1 (6 mmol, 1.65 g), diethyl malonate 2 (12 mmol, 1.92 g), $^{n}Bu_4NOAc$ (12 mmol, 3.62 g) and $KH_2PO_4$ (12 mmol, 1.63 g) were dissolved in a mixed solvent of DMSO/TFE [(70+10) mL]. At ambient temperature, the reaction mixtures were introduced into the reactor at 0.025 mL/min at a constant current of 11 mA. 53 mL reaction solution was diluted with ethyl acetate (150 mL) and washed with brine (150 mL) and $H_2O$ (150 mL). The separated organic layer was dried over anhydrous $Na_2SO_4$ (2 g) and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 3/1, white solid, 1.63 g, 94%).

## 7 Derivatization of α-carbonyl sulfonium ylide 3

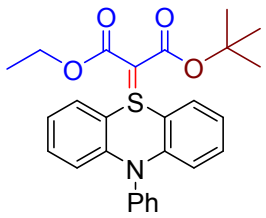
### 7.1 transesterification




3 39, 58%

Procedure for the synthesis of compound **39**:

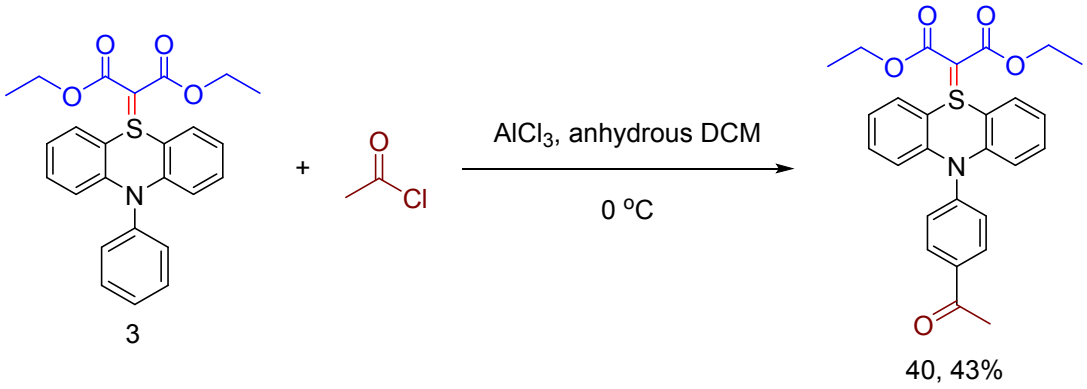
To solution of compound of 3 (433.1 mg, 1.0 mmol, 1.0 equiv) and KOH (57 mg, 1.0 mmol, 1.0 equiv) in 5 mL EtOH, *t*-butyl alcohol (75 mg, 1.0 mmol, 1.0 equiv) was added. The solution was heated at 80 °C for 12 h then another 1.0 equivalence of *t*-butyl alcohol was added and continued for another 12 h at 80 °C. The solvent was removed in vacuo. The crude product was purified by column chromatography [petroleum/ethyl acetate (3:1)] to obtain the compound **39** (267.5 mg, 58%) as white solid.




1-(*tert*-butyl) -3-ethyl 2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**39**):

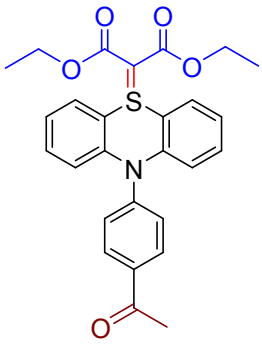
$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.77 (t, $J$ = 7.7 Hz, 2H), 7.65 (t, $J$ = 7.4 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.49 (dd, $J$ = 8.0, 1.5 Hz, 2H), 7.33 - 7.25 (m, 2H), 7.12 (t, $J$ = 7.3 Hz, 2H), 6.29 (d, J = 8.5 Hz, 2H), 3.92 (brs, 2H), 1.31 (brs, 9H), 1.06 (brs, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 166.88, 165.41, 142.79, 140.61, 133.07, 132.86, 131.72, 130.78, 130.37, 123.52, 117.35, 111.07, 78.92, 59.48, 29.60, 15.75. HRMS (ESI) Calcd for $C_{27}H_{28}NSO_4$ [M+H]$^+$: 462.1734; found: 462.1723.

7.2 acetylation




Procedure for the synthesis of compound **40**:

A pre-dried tube equipped with a magnetic stirring bar was charged with the sulfur ylide 3 (433.1 mg, 1.0 mmol, 1.0 equiv), $AlCl_3$ (146.7 mg, 1.1 mmol, 1.1 equiv) and anhydrous DCM (3 mL) under a nitrogen atmosphere. The tube was stirred at 0 ℃ for 5 min before addition of acetyl chloride (87 mg, 1.1 mmol, 1.1 equiv) in anhydrous DCM (2 mL) solution dropwise in 2 min. The reaction mixture was stirred at the same temperature for 12 h and washed with 50 mL sodium hydroxide solution (5%) then extracted with 20 mL ethyl acetate for 3 times. The organic layer was dried over with $Na_2SO_4$ (2 g). Concentration under reduced pressure afforded the crude product was purified by column chromatography [petroleum/ethyl acetate (1:1)] to obtain the compound **40** (204.3 mg, 43 %) as white solid.

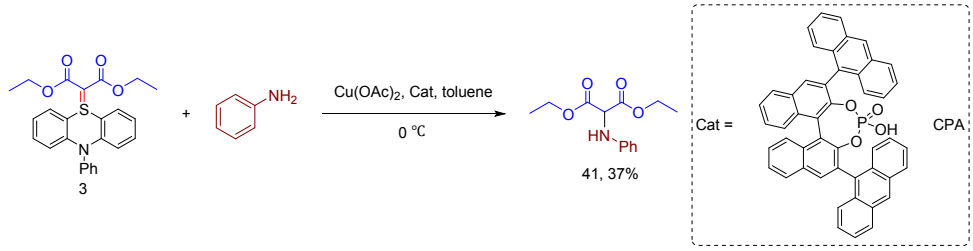


diethyl 2-(10-(4-acetylphenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**40**):

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.37 - 8.29 (m, 2H), 7.72 - 7.66 (m, 2H), 7.53 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.34 - 7.26 (m, 2H), 7.16 - 7.09 (m, 2H), 6.29 (d, $J$ = 8.6 Hz, 2H), 3.97 (q, $J$ = 7.7 Hz, 4H), 2.70 (s, 3H), 1.08 (t, $J$ = 7.0 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 197.83, 165.48, 143.91, 142.01, 137.82, 132.57, 132.03, 131.47, 130.28, 122.96, 116.56, 109.76, 75.10, 58.79, 27.45, 14.98.

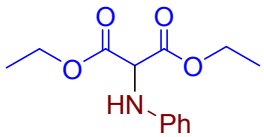
HRMS (ESI) Calcd for $C_{27}H_{26}NSO_5$ $[M+H]^+$: 476.1526; found: 476.1498.

7.3 protonation-aminationdiethyl 2-(phenylamino)malonate




Procedure for the synthesis of compound **41**:

A pre-dried 20-mL schlenk tube equipped with a magnetic stirring bar was charged with the sulfur ylide 3 (433.1 mg, 1.0 mmol, 1.0 equiv) and the CPA catalyst (70.1 mg, 0.1 mmol, 10 mol%). The tube was sealed with a puncturable screw-cap, toluene (10.0 mL) was added and the resulted suspension was stirred at -40 ℃ for 5 min before addition of aniline (112.1 mg ,1.2 mmol, 1.2 equiv). The reaction mixture was stirred at the same temperature for another 48 h. Then, $Cu(OAc)_2$ (20.0 mg, 0.1 mol, 10 mol%) was directly added and the reaction mixture was warmed to room temperature and stirred for 48 h. Then the toluene was removed in vacuo and the crude product was purified by column chromatography [petroleum/ethyl acetate (100:1)] to obtain the compound **41** (92.9 mg, 37%) as yellow oil.




diethyl 2-(phenylamino)malonate (**41**):

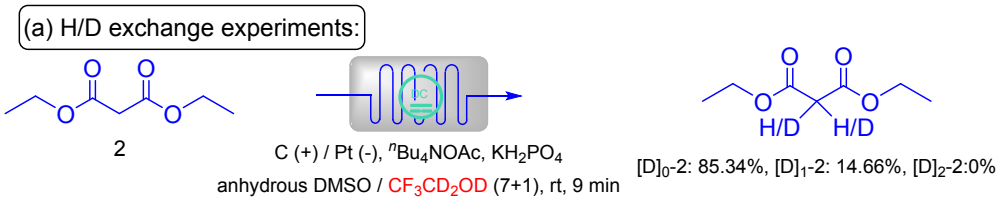
$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.18 - 7.06 (m, 2H), 6.80 - 6.70 (m, 2H), 6.65 (tt, $J$ = 7.2, 1.1 Hz, 1H), 6.21 (d, $J$ = 8.8 Hz, 1H), 5.01 (d, $J$ = 8.7 Hz, 1H), 4.27 - 4.13 (m, 4H), 1.20 (t, $J$ = 7.1 Hz, 6H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 168.18, 146.80, 129.34, 117.92, 113.42, 62.02, 60.31, 14.31.

HRMS (ESI) Calcd for $C_{13}H_{18}NO_4$ $[M+H]^+$: 252.1230; found: 252.1192.

# 8 Mechanistic Studies

8.1 H/D exchange experiments




Diethyl malonate 2 (1.2 mmol, 192.1 mg), $^{n}Bu_4NOAc$ (1.2 mmol, 361.8 mg) and $KH_2PO_4$ (1.2 mmol, 163.3 mg) were dissolved in a mixed solvent of anhydrous DMSO/$CF_3CD_2OD$ [(7+1) mL]. At ambient temperature, the reaction mixtures were introduced into the reactor at 0.025 mL/min at a constant current of 11 mA. The crude mixture was analyzed by HRMS (ESI), which revealed that the ratio between $[D]_0$-2, $[D]_1$-2 and $[D]_2$-2 was 85.34:14.66:0. (Fig. **S3**).

$[D]_0$-2: HRMS (ESI-TOF) Calcd for $C_7H_{12}O_4Na$ $[M+Na]^+$: 183.0628; found: 183.0627.

$[D]_1$-2: HRMS (ESI-TOF) Calcd for $C_7H_{11}DO_4Na$ $[M+Na]^+$: 184.0691; found: 184.0671.

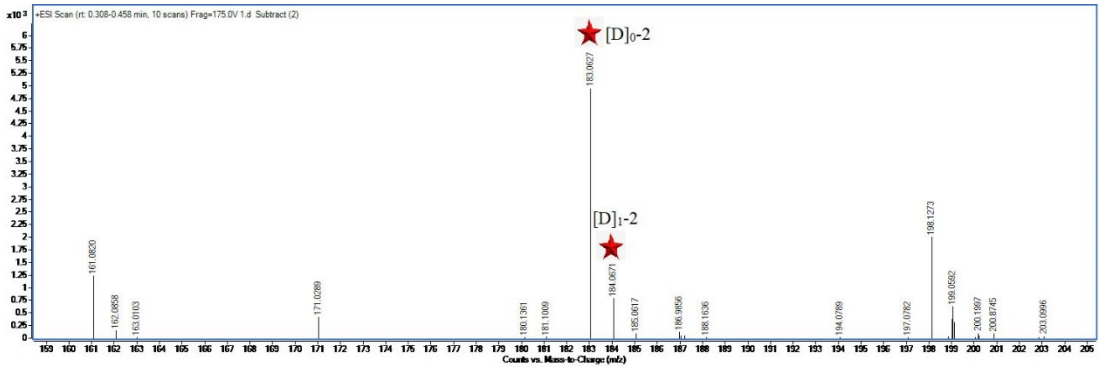
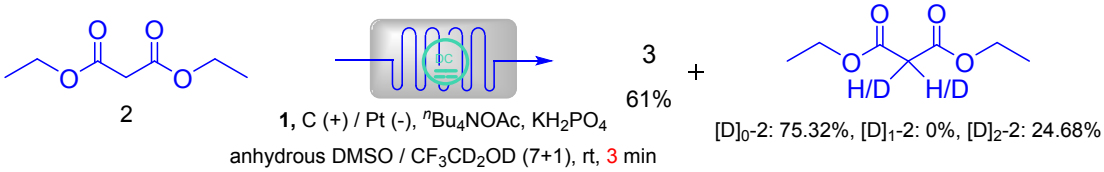



Figure **S3** HRMS (ESI) analysis of electrochemically generated $[D]_0$-2, $[D]_1$-2 and $[D]_2$-2 using the mixed solvent of anhydrous DMSO/$CF_3CD_2OD$ in the absence of 1




The sulfide 1 (0.6 mmol, 165.0 mg), Diethyl malonate 2 (1.2 mmol, 192.1 mg), $^{n}Bu_4NOAc$ (1.2 mmol, 361.8 mg) and $KH_2PO_4$ (1.2 mmol, 163.3 mg) were dissolved in a mixed solvent of anhydrous DMSO/$CF_3CD_2OD$ [(7+1) mL]. At ambient temperature, the reaction mixtures were introduced into the reactor at 0.075 mL/min at

a constant current of 11 mA. The crude mixture was analyzed by HRMS (ESI), which revealed that the ratio between $[D]_0$-2, $[D]_1$-2 and $[D]_2$-2 was 75.32:0:24.68. (Fig. **S4**).

$[D]_0$-2: HRMS (ESI-TOF) Calcd for $C_7H_{13}O_4$ $[M+H]^+$: 161.0808; found: 161.0897.

$[D]_2$-2: HRMS (ESI-TOF) Calcd for $C_7H_{11}D_2O_4$ $[M+H]^+$: 163.0934; found: 163.0904.

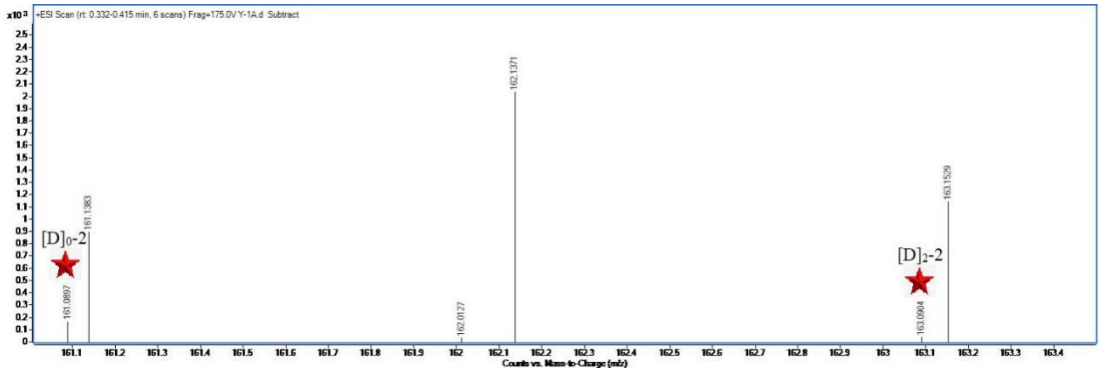
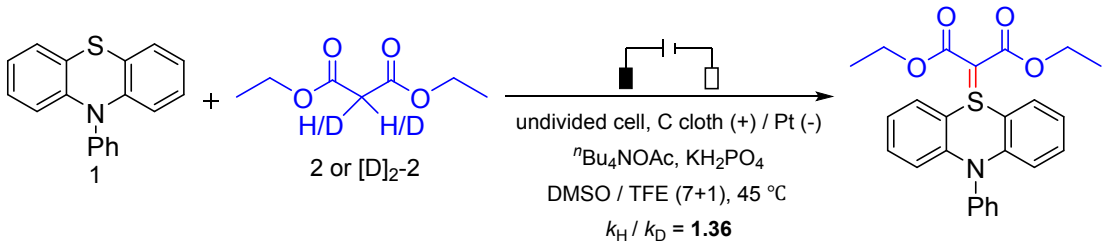



Figure **S4** HRMS (ESI) analysis of electrochemically generated $[D]_0$-2, $[D]_1$-2 and $[D]_2$-2 using the mixed solvent of anhydrous DMSO/$CF_3CD_2OD$ in the presence of 1

## 8.2 KIE studies




In an undivided cell equipped with a carbon cloth (40 mm x 20 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, sulfide 1 (0.2 mmol, 55.0 mg, 1.0 equiv), diethyl malonate (0.4 mmol, 64.03 mg, 2.0 equiv), $^n$Bu$_4$NOAc (0.4 mmol, 120.6 mg, 2.0 equiv) and $KH_2PO_4$ (0.4 mmol, 54.4 mg, 2.0 equiv) were dissolved in a mixed solvent of DMSO/TFE [(7+1) mL]. At 45 °C, the reaction was started at a constant current of 10 mA. Aliquots of 0.2 mL were removed from the cell every 20 minutes and 1 mL $CDCl_3$ solution was added, which was analyzed by $^1$H-NMR using 1, 4-dinitrobenzene (0.0025 mmol/mL in $CDCl_3$ solution) as the internal standard. (Fig. **S5** and Fig. **S6**).

| Time [min] | 20 | 40 | 60 | 80 | 100 | 120 |
|---|---|---|---|---|---|---|
| 2 [%] | 10.10 | 21.70 | 36.20 | 50.10 | 64.10 | 77.01 |
| $[D]_2$-2 [%] | 12.02 | 24.44 | 34.15 | 43.84 | 52.70 | 63.77 |

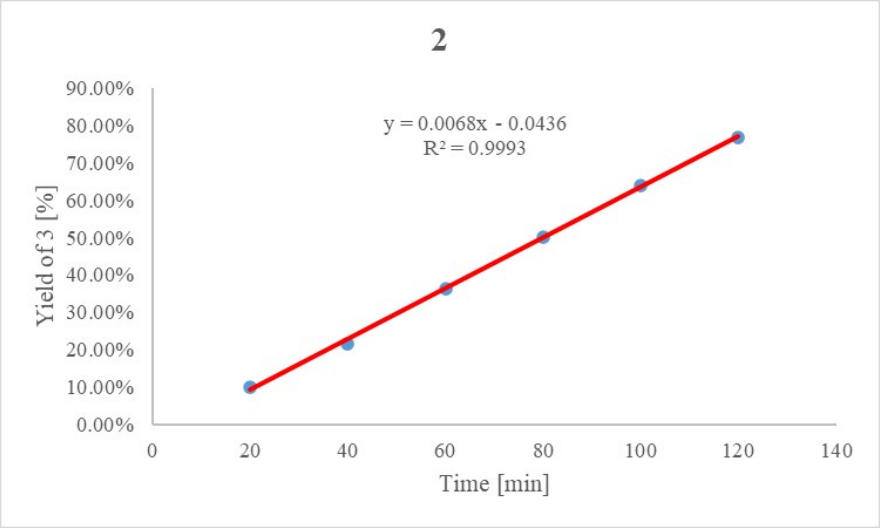



Figure **S5** Parallel experiment of 2

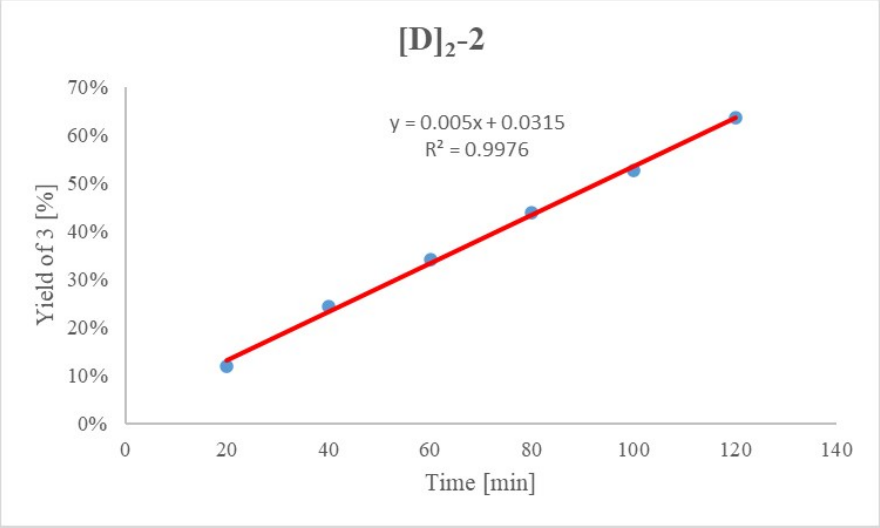
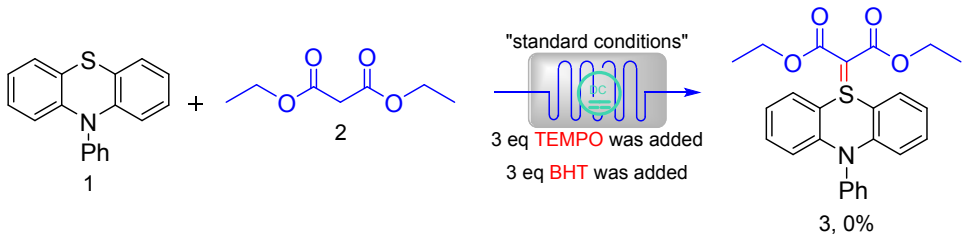



Figure **S6** Parallel experiment of $[D]_2$-2

## 8.3 Radical-trapping experiments




The sulfide 1 (0.6 mmol, 165.0 mg, 1.0 equiv), Diethyl malonate 2 (1.2 mmol, 192.1 mg, 2.0 equiv), $^{n}Bu_4NOAc$ (1.2 mmol, 361.8 mg, 2.0 equiv), $KH_2PO_4$ (1.2 mmol, 163.3 mg, 2.0 equiv) and the corresponding radical scavenger [TEMPO (1.8 mmol, 281.2 mg, 3.0 equiv) or BHT (1.8 mmol, 396.6 mg, 3.0 equiv)] were dissolved in a mixed solvent of anhydrous DMSO/$CF_3CD_2OD$ [(7+1) mL]. At ambient temperature, the reaction mixtures were introduced into the reactor at 0.075 mL/min at a constant current of 11 mA. However, no desired product was detected.

## 8.4 Cyclic voltammetry

The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. The Ag/AgCl was used as reference electrode. The scan range was 0.0 V to 2.5 V. The scan rate was 100 mVs-1 (Fig. S10). Anhydrous DMSO/TFE = 7 mL/1 mL containing 1.2 mmol $^{n}Bu_4NOAc$ (1.2 mmol, 361.8 mg) were poured into the electrochemical cell in all experiments.

### 8.4.1 Cyclic voltammetry (CV) experiment of substrates

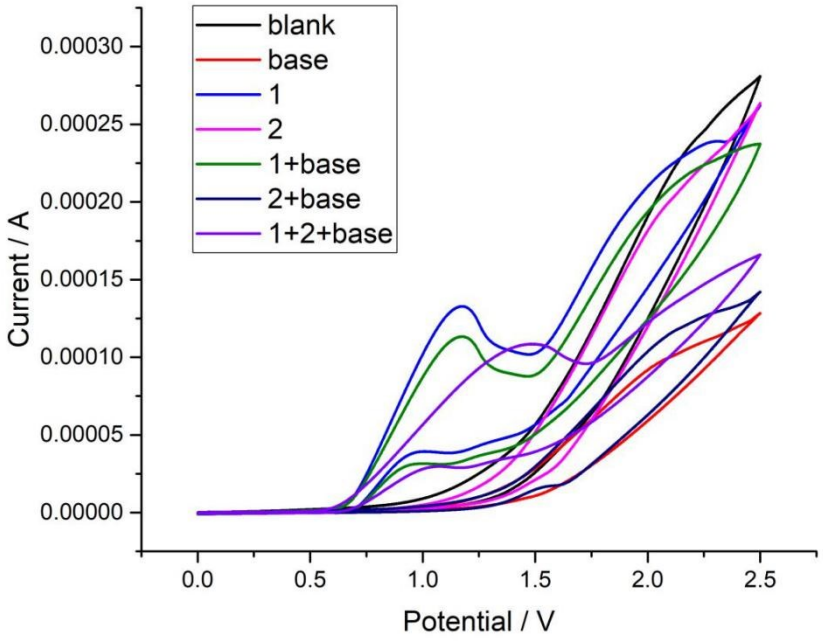



Figure **S7** Cyclic Voltammetry experiment of substrate

100 mVs-1: (black) blank; (red) $KH_2PO_4$ (1.2 mmol, 163.3 mg); (blue) sulfide 1 (0.6 mmol, 165.0 mg); (pink) diethyl malonate 2 (1.2 mmol, 192.1 mg); (green) sulfide 1 (0.6 mmol, 165.0 mg) and $KH_2PO_4$ (1.2 mmol, 163.3 mg); (indigo) diethyl malonate 2 (1.2 mmol, 192.1 mg) and $KH_2PO_4$ (1.2 mmol, 163.3 mg); (violet) sulfide 1 (0.6 mmol, 165.0 mg), diethyl malonate 2 (1.2 mmol, 192.1 mg) and $KH_2PO_4$ (1.2 mmol, 163.3 mg).

8.4.2 Cyclic voltammetry (CV) experiment of radical scavengers

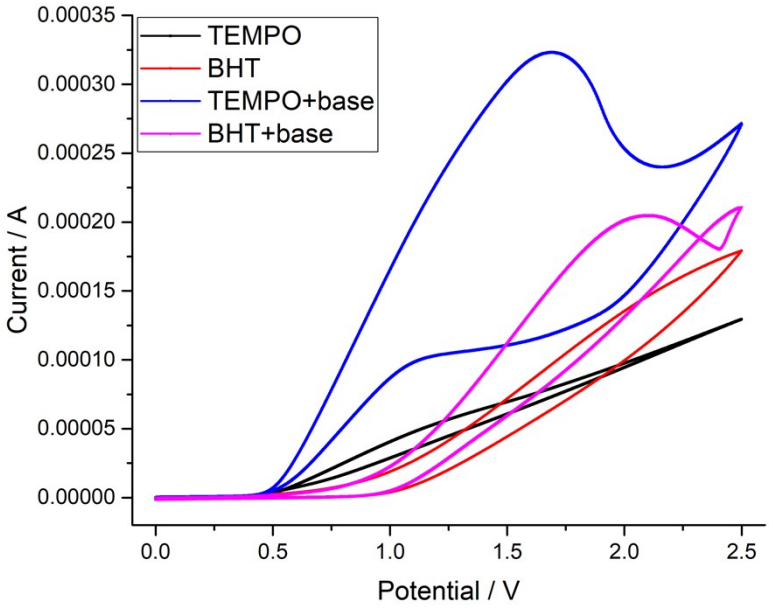



Figure **S8** Cyclic voltammetry experiment of radical scavenger

100 mVs-1: (black) TEMPO (1.8 mmol, 281.2 mg); (red) BHT (1.8 mmol, 396.6 mg); (blue) TEMPO (1.8 mmol, 281.2 mg) and $KH_2PO_4$ (1.2 mmol, 163.3 mg); (pink) BHT (1.8 mmol, 396.6 mg) and $KH_2PO_4$ (1.2 mmol, 163.3 mg).

8.5 Procedures for the electron paramagnetic resonance (EPR) experiment

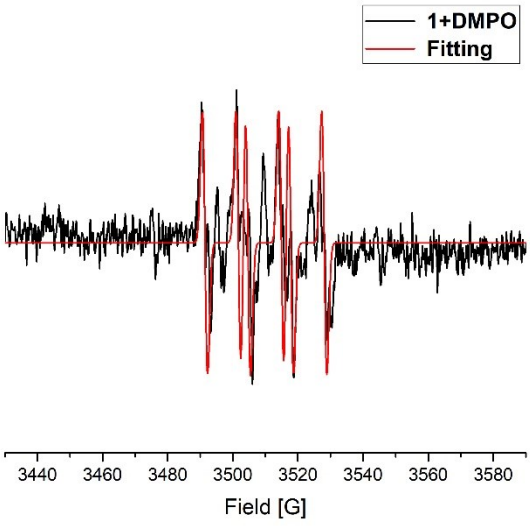


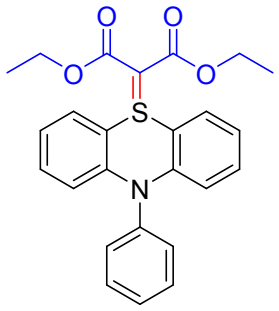

Figure **S9** Electron paramagnetic resonance (EPR) spectra

A dried three-necked flask equipped with a stir bar was loaded with **1** (0.20 mmol),

$^{n}Bu_4NOAc$ (0.4 mmol) and $KH_2PO_4$ (0.4 mmol) in mixture solvent of DMSO/TFE [(7+1) mL] was stirred at a constant current of 10 mA under 45 ºC. After 20 minutes, DMPO (5,5-dimethyl-1-pyrroline *N*-oxide, 15 μL) was added to the reaction mixture and continued to react for 2 minutes. The solution sample was taken out into a small tube and analyzed by EPR.

EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.868 GHz. Typical spectrometer parameters are shown as follows, sweep range: 200 G; center field set: 3518.65 G; time constant: 40.96 msec; sweep time: 81.92 sec, modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 2.00×103; microwave power: 5.63×10-1 mW.

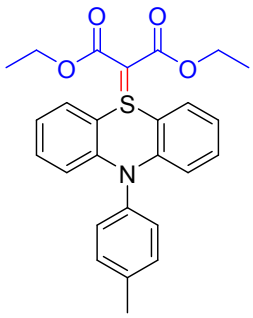
## 9 Characterization Data for Electrolysis Products




3

diethyl 2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**3**):

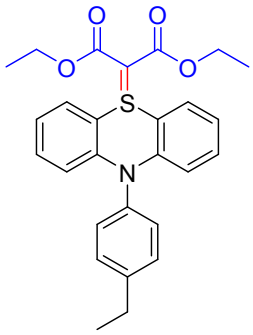
White solid; Eluent: petroleum ether/ethyl acetate 3:1; 244.3 mg, 94%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.80 - 7.73 (m, 2H), 7.66 (tt, $J$ = 7.5, 1.2 Hz, 1H), 7.57 - 7.46 (m, 4H), 7.33 - 7.25 (m, 2H), 7.14 - 7.04 (m, 2H), 6.27 (dd, $J$ = 8.5, 1.1 Hz, 2H), 3.98 (p, $J$ = 7.3 Hz, 4H), 1.08 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.02, 141.94, 139.29, 132.03, 131.65, 130.42, 129.78, 129.57, 122.24, 116.10, 109.00, 74.93, 58.30, 14.54. HRMS (ESI) Calcd for $C_{25}H_{24}NSO_4$ $[M+H]^+$: 434.1421; found: 434.1434.



4

diethyl 2-(10-(p-tolyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**4**):

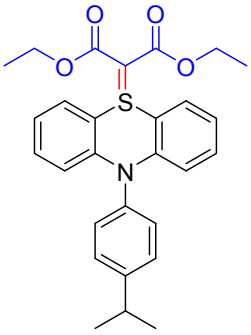
White solid; Eluent: petroleum ether/ethyl acetate 3:1; 217.3 mg, 81%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.55 (d, $J$ = 7.9 Hz, 2H), 7.49 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.40 - 7.35 (m, 2H), 7.32 - 7.26 (m, 2H), 7.13 - 7.05 (m, 2H), 6.30 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.96 (q, $J$ = 7.1 Hz, 4H), 2.46 (s, 3H), 1.06 (t, $J$ = 7.6 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 164.98, 141.98, 139.07, 136.62, 132.07, 131.94, 130.03, 129.64, 122.13, 116.12, 109.03, 74.78, 58.23, 20.86, 14.48. HRMS (ESI) Calcd for $C_{26}H_{26}NSO_4$ $[M+H]^+$: 448.1577; found: 448.1561.



5

diethyl 2-(10-(4-ethylphenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**5**):

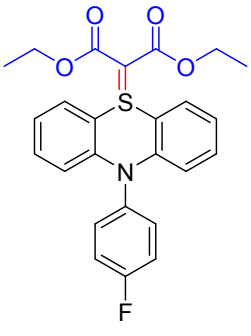
Colorless oil; Eluent: petroleum ether/ethyl acetate 3:1; 213.0 mg, 77%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.61 - 7.57 (m, 2H), 7.50 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.43 - 7.38 (m, 2H), 7.33 - 7.27 (m, 2H), 7.12 - 7.06 (m, 2H), 6.29 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.96 (q, $J$ = 6.7 Hz, 4H), 2.77 (q, $J$ = 7.6 Hz, 2H), 1.30 (t, $J$ = 7.6 Hz, 3H), 1.08 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 164.94, 145.12, 141.97, 136.79, 131.94, 130.82, 130.07, 129.63, 122.13, 116.09, 109.05, 74.71, 58.19, 27.86, 15.23, 14.47. HRMS (ESI) Calcd for $C_{27}H_{28}NSO_4$ $[M+H]^+$: 462.1734; found: 462.1740.



6

diethyl 2-(10-(4-isopropylphenyl)-10H-5λ$^4$-phenothiazin-5-ylidene)malonate (**6**):

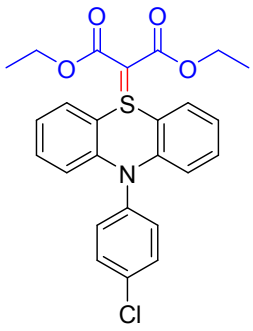
Colorless oil; Eluent: petroleum ether/ethyl acetate 3:1; 211.0 mg, 74%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.61 (d, $J$ = 8.2 Hz, 2H), 7.49 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.44 - 7.37 (m, 2H), 7.31 - 7.24 (m, 2H), 7.12 - 7.03 (m, 2H), 6.27 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.96 (q, $J$ = 7.2 Hz, 4H), 3.05 (hept, $J$ = 6.9 Hz, 1H), 1.30 (d, $J$ = 6.9 Hz, 6H), 1.11 - 1.01 (m, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 164.98, 149.69, 142.03, 136.86, 131.96, 130.09, 129.70, 129.39, 122.16, 116.09, 109.01, 74.80, 58.25, 33.24, 23.78, 14.50. HRMS (ESI) Calcd for $C_{28}H_{30}NSO_4$ $[M+H]^+$: 476.1890; found: 476.1866.



7

diethyl 2-(10-(4-fluorophenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**7**):

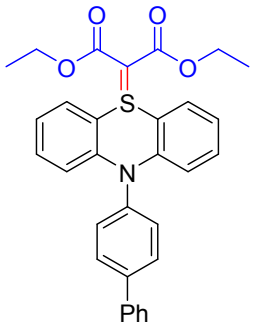
White solid; Eluent: petroleum ether/ethyl acetate 3:1; 194.9 mg, 72%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.60 (d, $J$ = 6.8 Hz, 4H), 7.52 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.35 - 7.28 (m, 2H), 7.16 - 7.07 (m, 2H), 6.32 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.96 (q, $J$ = 7.2 Hz, 4H), 1.08 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.01, 163.28, 160.83, 142.05, 135.53 (d, $J$ = 3.3 Hz), 132.76 (d, $J$ = 8.9 Hz), 132.08, 129.79, 122.33, 118.67, 118.44, 116.13, 109.06, 74.81, 58.28, 14.49. $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ -111.59. HRMS (ESI) Calcd for $C_{25}H_{23}NSO_4F$ $[M+H]^+$: 452.1326; found: 452.1342.




8

diethyl 2-(10-(4-chlorophenyl)-10H-5λ$^4$-phenothiazin-5-ylidene)malonate (**8**):

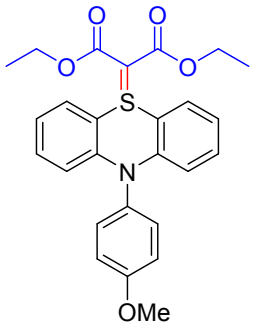
White solid; Eluent: petroleum ether/ethyl acetate 3:1; 221.4 mg, 79%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.86 - 7.81 (m, 2H), 7.59 - 7.55 (m, 2H), 7.52 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.35 - 7.29 (m, 2H), 7.15 - 7.09 (m, 2H), 6.32 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.96 (q, $J$ = 7.1 Hz, 4H), 1.09 (t, $J$ = 7.4 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.00, 141.80, 138.20, 134.10, 132.53, 132.13, 131.77, 129.79, 122.41, 116.14, 109.14, 74.75, 58.29, 14.50. HRMS (ESI) Calcd for $C_{25}H_{23}NSO_4Cl$ $[M+H]^+$: 468.1031; found: 468.1035.




9

diethyl 2-(10-([1,1'-biphenyl]-4-yl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**9**):

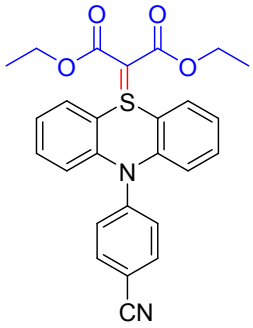
White solid; Eluent: petroleum ether/ethyl acetate 3:1; 281.0 mg, 92%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.09 - 8.01 (m, 2H), 7.86 - 7.78 (m, 2H), 7.64 - 7.58 (m, 2H), 7.57 - 7.48 (m, 4H), 7.45 (tt, $J$ = 7.4, 1.2 Hz, 1H), 7.35 - 7.28 (m, 2H), 7.15 - 7.07 (m, 2H), 6.39 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.98 (q, $J$ = 7.3 Hz, 4H), 1.09 (t, $J$ = 6.7 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.03, 141.95, 141.12, 139.01, 138.52, 132.08, 130.93, 129.78, 129.14, 128.09, 126.98, 122.29, 116.20, 109.08, 74.88, 58.30, 14.53. HRMS (ESI) Calcd for $C_{31}H_{28}NSO_4$ $[M+H]^+$: 510.1734; found: 510.1734.




10

diethyl 2-(10-(4-methoxyphenyl)-10H-5λ$^4$-phenothiazin-5-ylidene)malonate (**10**):

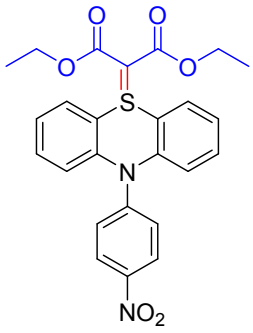
Pink solid; Eluent: petroleum ether/ethyl acetate 2:1; 200.0 mg, 72%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.50 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.44 - 7.40 (m, 2H), 7.33 - 7.26 (m, 4H), 7.12 - 7.07 (m, 2H), 6.34 (dd, $J$ = 8.6, 1.2 Hz, 2H), 3.96 (q, $J$ = 7.0 Hz, 4H), 3.88 (s, 3H), 1.07 (t, $J$ = 7.0 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 164.97, 159.50, 142.28, 131.98, 131.64, 131.42, 129.69, 122.13, 116.65, 116.18, 108.99, 74.88, 58.23, 55.51, 14.51. HRMS (ESI) Calcd for $C_{26}H_{26}NSO_5$ $[M+H]^+$: 464.1526; found: 464.1534.




11

diethyl 2-(10-(4-cyanophenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**11**):

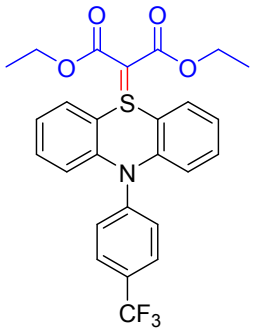
White solid; Eluent: petroleum ether/ethyl acetate 1:1; 239.1 mg, 87%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.28 - 8.22 (m, 2H), 7.80 - 7.74 (m, 2H), 7.53 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.34 - 7.28 (m, 2H), 7.14 (td, $J$ = 7.6, 1.1 Hz, 2H), 6.29 (dd, $J$ = 8.6, 1.0 Hz, 2H), 3.96 (q, $J$ = 7.2 Hz, 4H), 1.09 (t, $J$ = 7.7 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.10, 143.68, 141.48, 135.91, 132.26, 132.08, 129.90, 122.74, 118.32, 116.25, 112.49, 109.42, 74.56, 58.43, 14.54. HRMS (ESI) Calcd for $C_{26}H_{23}N_2SO_4$ $[M+H]^+$: 459.1373; found: 459.1364.



12

diethyl 2-(10-(4-nitrophenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**12**):

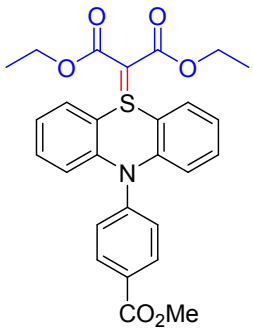
Yellow solid; Eluent: petroleum ether/ethyl acetate 1:2; 218.0 mg, 76%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.63 - 8.58 (m, 2H), 7.87 - 7.82 (m, 2H), 7.55 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.35 - 7.29 (m, 2H), 7.19 - 7.13 (m, 2H), 6.35 (dd, *J* = 8.5, 1.1 Hz, 2H), 3.97 (q, *J* = 7.2 Hz, 4H), 1.10 (t, *J* = 7.6 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.01, 147.73, 145.28, 141.32, 132.22, 132.17, 129.81, 127.03, 122.79, 116.32, 109.72, 74.18, 58.35, 14.50. HRMS (ESI) Calcd for $C_{25}H_{23}N_2SO_6$ $[M+H]^+$: 479.1271; found: 479.1280.



13

diethyl 2-(10-(4-(trifluoromethyl)phenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**13**):

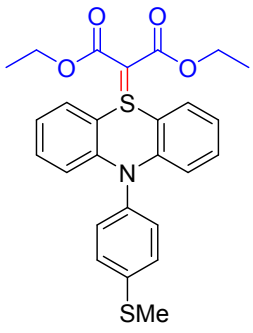
White solid; Eluent: petroleum ether/ethyl acetate 3:1; 267.6 mg, 89%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.54 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.34 - 7.28 (m, 2H), 7.16 - 7.09 (m, 2H), 6.27 (dd, *J* = 8.6, 1.1 Hz, 2H), 3.97 (q, *J* = 7.3 Hz, 4H), 1.09 (t, *J* = 7.0 Hz, 6H).$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.50, 143.57, 142.04, 132.66, 132.34, 130.34 (q, *J* = 32.3 Hz), 130.31, 129.32 (q, *J* = 3.5 Hz), 128.47, 125.76, 123.03, 116.59, 109.77, 75.09, 58.80, 14.96. $^{19}$F NMR (376 MHz, DMSO) δ -61.04. HRMS (ESI) Calcd for $C_{26}H_{23}NSO_6F_3$ $[M+H]^+$: 502.1294; found: 502.1269.




14

diethyl 2-(10-(4-(methoxycarbonyl)phenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**14**):

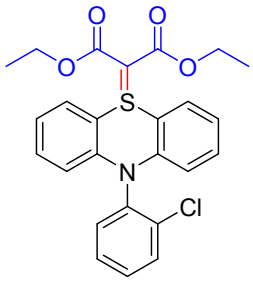
White solid; Eluent: petroleum ether/ethyl acetate 1:1; 226.9 mg, 77%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.32 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.69 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.53 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.33 - 7.26 (m, 2H), 7.15 - 7.09 (m, 2H), 6.28 (dd, *J* = 8.6, 1.1 Hz, 2H), 3.97 (q, *J* = 5.7 Hz, 4H), 3.93 (s, 3H), 1.09 (t, *J* = 6.8 Hz, 6H).$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 166.05, 165.48, 144.08, 141.97, 133.02, 132.58, 131.63, 131.02, 130.27, 122.96, 116.57, 109.79, 75.08, 58.78, 53.01, 14.98. HRMS (ESI) Calcd for $C_{27}H_{26}NSO_6$ $[M+H]^+$: 492.1475; found: 492.1476.




15

diethyl 2-(10-(4-(methylthio)phenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**15**):

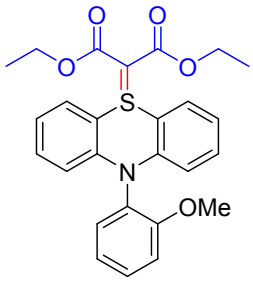
White solid; Eluent: petroleum ether/ethyl acetate 2:1; 189.7 mg, 66%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.65 - 7.57 (m, 2H), 7.54 - 7.48 (m, 2H), 7.47 - 7.41 (m, 2H), 7.35 - 7.27 (m, 2H), 7.15 - 7.06 (m, 2H), 6.42 - 6.30 (m, 2H), 3.96 (brs, 4H), 2.58 (d, *J* = 2.5 Hz, 3H), 1.08 (brs, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 164.97, 141.98, 140.18, 135.69, 132.02, 130.80, 129.72, 128.17, 122.23, 116.14, 109.05, 74.81, 58.25, 14.50, 14.37. HRMS (ESI) Calcd for $C_{26}H_{26}NS_2O_4$ $[M+H]^+$: 480.1298; found: 480.1307.




16

diethyl 2-(10-(2-chlorophenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**16**):

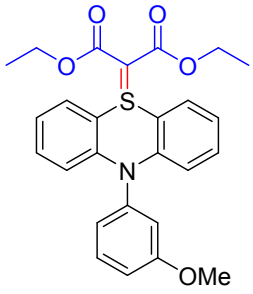
White solid; Eluent: petroleum ether/ethyl acetate 3:1; 179.4 mg, 64%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.80 (t, $J$ = 7.6 Hz, 2H), 7.73 - 7.66 (m, 1H), 7.60 - 7.49 (m, 4H), 7.36 - 7.30 (m, 1H), 7.20 - 7.12 (m, 2H), 6.29 (dd, $J$ = 8.5, 1.1 Hz, 1H), 6.16 (d, $J$ = 2.1 Hz, 1H), 3.98 (q, $J$ = 7.2 Hz, 4H), 1.09 (t, $J$ = 7.4 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.43, 143.46, 141.87, 139.23, 136.76, 132.70, 132.35, 132.21, 130.65, 130.43, 130.29, 123.37, 122.46, 116.83, 115.49, 109.82, 108.73, 75.43, 58.89, 14.97. HRMS (ESI) Calcd for $C_{25}H_{23}NSO_4Cl$ $[M+H]^+$: 468.1031; found: 468.1043.




17

diethyl 2-(10-(2-methoxyphenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**17**):

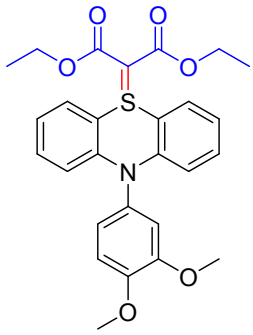
Colorless oil; Eluent: petroleum ether/ethyl acetate 2:1; 144.5 mg, 52%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.64 (t, $J$ = 8.5 Hz, 2H), 7.55 - 7.43 (m, 2H), 7.40 (d, $J$ = 8.3 Hz, 1H), 7.35 - 7.22 (m, 3H), 7.09 (t, $J$ = 7.5 Hz, 2H), 6.26 (d, $J$ = 8.6 Hz, 2H), 3.98 (q, $J$ = 4.6 Hz, 4H), 3.72 (s, 3H), 1.08 (brs, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.51, 156.95, 142.31, 132.68, 131.85, 131.38, 130.47, 127.37, 123.36, 122.69, 116.37, 113.85, 109.23, 75.80, 58.71, 56.17, 14.95. HRMS (ESI) Calcd for $C_{26}H_{26}NSO_5$ $[M+H]^+$: 464.1526; found: 464.1570.



18

diethyl 2-(10-(3-methoxyphenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**18**):

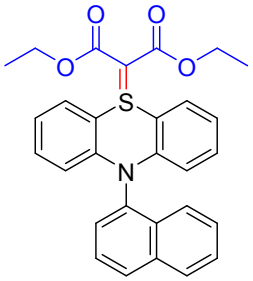
White solid; Eluent: petroleum ether/ethyl acetate 2:1; 161.2 mg, 58%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.71 - 7.64 (t, $J$ = 8.1 Hz, 1H), 7.51 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.35 - 7.28 (m, 2H), 7.23 (ddd, $J$ = 8.5, 2.6, 0.9 Hz, 1H), 7.17 - 7.05 (m, 4H), 6.37 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.96 (q, $J$ = 7.1 Hz, 4H), 3.81 (s, 3H), 1.07 (d, $J$ = 7.7 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.00, 161.77, 141.84, 140.41, 132.22, 132.07, 129.71, 122.24, 122.20, 116.21, 115.43, 115.28, 108.89, 74.93, 58.28, 55.43, 14.52. HRMS (ESI) Calcd for $C_{26}H_{26}NSO_5$ [M+H]$^+$: 464.1526; found: 464.1542.



19

diethyl 2-(10-(3,4-dimethoxyphenyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**19**):

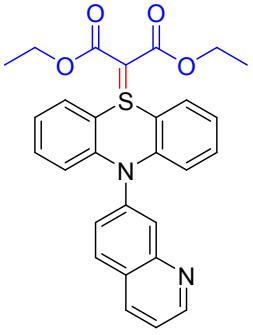
White solid; Eluent: petroleum ether/ethyl acetate 1:1; 142.0 mg, 48%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.50 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.35 - 7.26 (m, 3H), 7.14 (d, $J$ = 2.3 Hz, 1H), 7.13 - 7.04 (m, 3H), 6.43 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.96 (q, $J$ = 7.3 Hz, 4H), 3.88 (s, 3H), 3.74 (s, 3H), 1.08 (t, $J$ = 7.1 Hz, 6H).$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.45, 151.40, 149.66, 142.77, 132.51, 132.19, 130.09, 122.78, 122.62, 116.88, 113.59, 113.33, 109.33, 75.38, 58.71, 56.16, 56.05, 14.99. HRMS (ESI) Calcd for $C_{27}H_{28}NSO_6$ [M+H]$^+$: 494.1632; found: 494.1636.



20

diethyl 2-(10-(naphthalen-1-yl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (20):

White solid; Eluent: petroleum ether/ethyl acetate 3:1; 260.9 mg,90%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.62 (dd, *J* = 8.4, 1.1 Hz, 0.5H), 8.28 – 8.21 (m, 1H), 8.20 - 8.14 (m, 1H), 7.90 – 7.84 (m, 1H), 7.79 (dd, *J* = 8.3, 7.2 Hz, 0.5H), 7.68 - 6.60 (m, 1H), 7.59 – 7.45 (m, 4H), 7.21 - 7.12 (m, 2H), 7.12 - 7.04 (m, 2H), 6.05 - 5.94 (m, 2H), 4.04 (q, *J* = 8.2, 7.6 Hz, 4H), 1.15 (t, *J* = 7.2 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.79, 165.54, 142.31, 141.83, 136.09, 135.97, 135.57, 135.37, 132.58, 132.51, 131.21, 130.75, 130.47, 130.42, 130.38, 129.75, 129.57, 129.20, 128.97, 128.51, 128.31, 128.12, 127.84, 127.79, 127.69, 123.67, 122.88, 122.73, 122.62, 116.44, 116.24, 109.95, 109.82, 75.98, 75.12, 58.92, 58.76, 15.03. HRMS (ESI) Calcd for $C_{29}H_{26}NSO_4$ $[M+H]^+$: 484.1577; found: 484.1576.

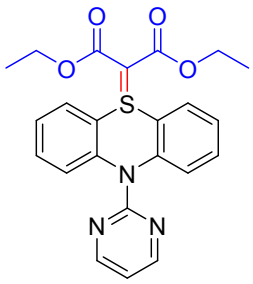


21

diethyl 2-(10-(quinolin-7-yl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**21**):

White solid; Eluent: petroleum ether/ethyl acetate 1:3; 136.5 mg, 47%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.07 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.54 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.40 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 2.3 Hz, 1H), 7.85 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.67 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.54 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.29 - 7.23 (m, 2H), 7.14 - 7.09 (m, 2H), 6.35 (dd, *J* = 8.6, 1.2 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 4H), 1.15 - 1.07 (brs, 6H).$^{13}$C NMR (101 MHz, DMSO-*d6*) δ 165.53, 152.46, 147.89, 142.36,

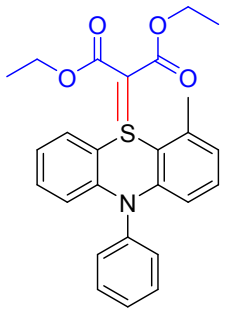
137.42, 137.05, 133.56, 132.59, 131.81, 130.76, 130.24, 129.77, 122.88, 122.72, 116.83, 109.72, 75.21, 58.81, 15.01. HRMS (ESI) Calcd for $C_{28}H_{25}N_2SO_4$ $[M+H]^+$: 485.1530; found: 485.1497.



22

diethyl 2-(10-(pyrimidin-2-yl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**22**):

White solid; Eluent: petroleum ether/ethyl acetate 1:5; 114.9 mg, 44%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.59 (d, $J$ = 4.8 Hz, 2H), 7.97 - 7.94 (m, 2H), 7.69 - 7.60 (m, 2H), 7.51 - 7.44 (m, 4H), 7.18 (t, $J$ = 4.8 Hz, 1H), 3.88 (q, $J$ = 7.0 Hz, 4H), 0.90 (t, $J$ = 7.0 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-*d6*) δ 164.77, 159.34, 159.03, 136.51, 130.66, 128.93, 127.54, 127.06, 124.79, 116.60, 59.04, 49.80, 14.64. HRMS (ESI) Calcd for $C_{23}H_{22}N_3SO_4$ $[M+H]^+$: 436.1326; found: 436.1356.

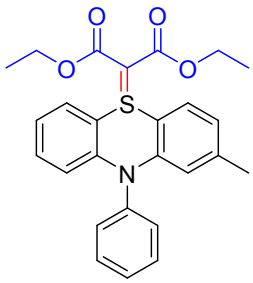


23

diethyl 2-(4-methyl-10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**23**):

Colorless oil; Eluent: petroleum ether/ethyl acetate 3:1; 217.3 mg, 81%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.76 (t, $J$ = 7.3 Hz, 2H), 7.67 - 7.62 (m, 1H), 7.56 (d, $J$ = 7.6 Hz, 2H), 7.50 (dd, $J$ = 7.9, 1.6 Hz, 1H), 7.32 - 7.26 (m, 1H), 7.19 (dd, $J$ = 8.6, 7.3 Hz, 1H), 7.12 - 7.07 (m, 1H), 6.97 (dt, $J$ = 7.4, 1.0 Hz, 1H), 6.25 (dd, $J$ = 8.6, 1.1 Hz, 1H), 6.17 (d, $J$ = 8.5, 1H), 3.97 (q, $J$ = 7.0 Hz, 4H), 2.50 (s, 3H), 1.10 (t, $J$ = 7.1 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-*d6*) δ 165.50, 143.89, 142.69, 140.17, 139.37, 132.60, 131.98, 131.83, 130.92, 130.58, 129.93, 124.32, 122.58, 116.38, 114.83,

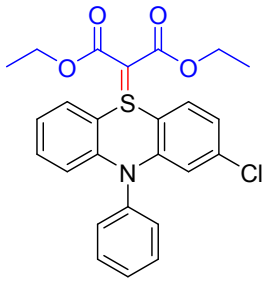
108.65, 106.89, 74.59, 58.68, 19.67, 15.04. HRMS (ESI) Calcd for $C_{26}H_{26}NSO_4$ $[M+H]^+$: 448.1577; found: 448.1573.



24

diethyl 2-(2-methyl-10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**24**):

White solid; Eluent: petroleum ether/ethyl acetate 3:1; 211.9 mg, 79%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.76 (t, *J* = 7.6 Hz, 2H), 7.69 – 7.62 (m, 1H), 7.55 - 7.45 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.31 - 7.24 (m, 1H), 7.11 - 7.06 (m, 1H), 6.93 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.24 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.06 (d, *J* = 1.6 Hz, 1H), 3.96 (q, *J* = 7.2 Hz, 4H), 2.11 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-*d6*) δ 165.50, 142.54, 142.39, 139.73, 132.42, 132.06, 130.89, 130.29, 130.24, 130.03, 123.79, 122.61, 116.64, 116.56, 109.40, 106.38, 75.68, 58.71, 21.86, 14.99. HRMS (ESI) Calcd for $C_{26}H_{26}NSO_4$ $[M+H]^+$: 448.1577; found: 448.1586.

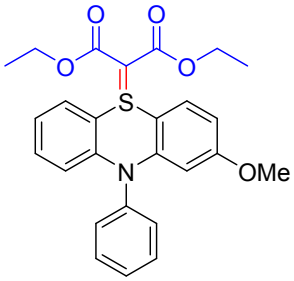


25

diethyl 2-(2-chloro-10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**25**):

White solid; Eluent: petroleum ether/ethyl acetate 3:1; 213.0 mg, 76%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.80 (tt, *J* = 7.7, 2.4 Hz, 2H), 7.70 (tt, 7.5, 1.3 Hz, 1H), 7.58 - 7.51 (m, 4H), 7.36 - 7.3 (m, 1H), 7.19 - 7.12 (m, 2H), 6.28 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.16 (d, *J* = 2.1 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 4H), 1.09 (t, *J* = 8.4 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-*d6*) δ 164.97, 143.00, 141.41, 138.77, 136.30, 132.25, 131.89, 131.76, 130.19, 129.97, 129.83, 122.91, 122.00, 116.37, 115.03, 109.36,

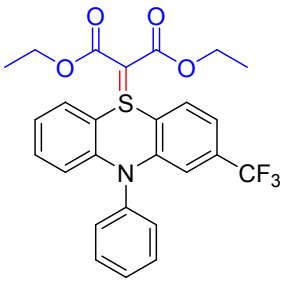
108.28, 74.98, 58.43, 14.52. HRMS (ESI) Calcd for $C_{25}H_{23}NSO_4Cl$ $[M+H]^+$: 468.1031; found: 468.1003.




26

diethyl 2-(2-methoxy-10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**26**):

White solid; Eluent: petroleum ether/ethyl acetate 2:1; 194.5 mg, 70%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.71 - 7.64 (t, $J$ = 8.1 Hz, 1H), 7.51 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.35 - 7.28 (m, 2H), 7.23 (ddd, $J$ = 8.5, 2.6, 0.9 Hz, 1H), 7.17 - 7.05 (m, 4H), 6.37 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.96 (q, $J$ = 7.1 Hz, 4H), 3.81 (s, 3H), 1.07 (d, $J$ = 7.7 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO-*d6*) δ 165.00, 161.77, 141.84, 140.41, 132.22, 132.07, 129.71, 122.24, 122.20, 116.21, 115.43, 115.28, 108.89, 74.93, 58.28, 55.43, 14.52. HRMS (ESI) Calcd for $C_{26}H_{26}NSO_5$ $[M+H]^+$: 464.1526; found: 464.1538.

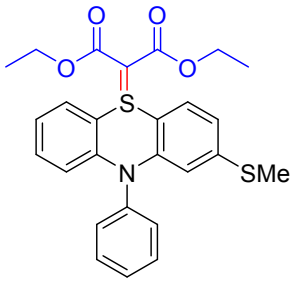



27

diethyl 2-(10-phenyl-2-(trifluoromethyl)-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**27**):

White solid; Eluent: petroleum ether/ethyl acetate 3:1; 231.5 mg, 77%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.83 - 7.75 (m, 3H), 7.71 (tt, $J$ = 7.5, 1.0 Hz, 1H), 7.59 - 7.53 (m, 3H), 7.42 (dd, $J$ = 8.4, 1.8 Hz, 1H), 7.37 - 7.31 (m, 1H), 7.20 - 7.14 (m, 1H), 6.40 (d, $J$ = 1.7 Hz, 1H), 6.31 (dd, $J$ = 8.6, 1.1 Hz, 1H), 3.98 (q, $J$ = 5.0 Hz, 4H), 1.09 (brs, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 164.97, 142.27, 141.34, 138.66, 132.33, 131.99, 131.63 (d, $J$ = 32.3 Hz), 131.37, 130.16, 130.09, 129.68, 124.49, 123.12, 121.78, 118.07 (d, $J$ = 3.1 Hz), 116.43, 113.83, 111.74 (d, $J$ = 4.4 Hz), 109.46, 74.50, 58.53,

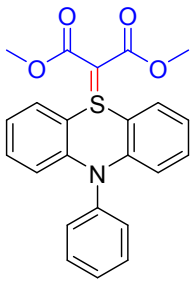
14.47. $^{19}$F NMR (376 MHz, DMSO-*d6*) δ -62.34. HRMS (ESI) Calcd for $C_{26}H_{23}NSO_4F_3$ $[M+H]^+$: 502.1294; found: 502.1276.




28

diethyl 2-(2-(methylthio)-10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**28**):

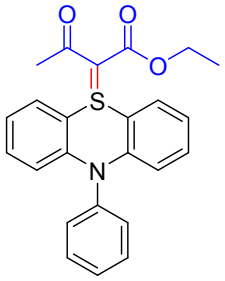
White solid; Eluent: petroleum ether/ethyl acetate 2:1; 189.7 mg, 66%; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 - 7.63 (m, 2H), 7.58 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.54 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 - 7.46 (m, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.17 - 7.11 (m, 1H), 7.02 - 6.96 (m, 1H), 6.83 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.32 (dd, *J* = 8.6, 1.2 Hz, 1H), 6.11 (d, *J* = 1.8 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 4H), 2.22 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.48, 143.90, 142.45, 142.29, 139.61, 131.63, 131.45, 130.87, 130.38, 130.27, 129.54, 122.17, 119.15, 116.52, 112.75, 109.71, 105.48, 75.17, 59.37, 14.86, 14.72. HRMS (ESI) Calcd for $C_{26}H_{26}NS_2O_4$ $[M+H]^+$: 480.1298; found: 480.1266.




29

dimethyl 2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)malonate (**29**):

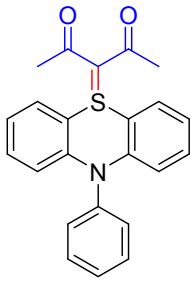
White solid; Eluent: petroleum ether/ethyl acetate 2:1; 192.0 mg, 79%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.78 (tt, *J* = 7.4, 1.6 Hz, 2H), 7.68 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.58 - 7.51 (m, 4H), 7.35 - 7.27 (m, 2H), 7.14 - 7.07 (m, 2H), 6.29 (dd, *J* = 8.6, 1.1 Hz, 2H), 3.50 (s, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.90, 142.60, 139.69, 132.63, 132.09, 130.90, 130.47, 130.05, 122.72, 116.57, 108.91, 75.88, 50.69. HRMS (ESI) Calcd for $C_{23}H_{20}NSO_4$ $[M+H]^+$: 406.1108; found: 406.1110.



30

ethyl 3-oxo-2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)butanoate (**30**):

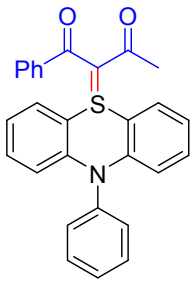
White solid; Eluent: petroleum ether/ethyl acetate 4:1; 195.9 mg, 81%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.76 (t, *J* = 7.6 Hz, 2H), 7.69 - 7.58 (m, 3H), 7.44 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.31 - 7.20 (m, 2H), 7.10 - 6.99 (m, 2H), 6.26 (d, *J* = 8.4 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.16 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 189.14, 165.83, 142.94, 139.89, 132.40, 132.01, 131.02, 130.07, 129.97, 122.55, 116.40, 108.44, 89.48, 59.05, 29.60, 15.09. HRMS (ESI) Calcd for $C_{24}H_{22}NSO_3$ $[M+H]^+$: 404.1315; found: 404.1287.



31

3-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)pentane-2,4-dione (**31**):

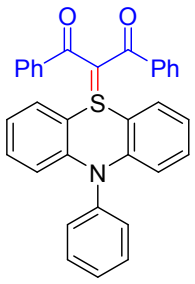
Yellow solid; Eluent: petroleum ether/ethyl acetate 3:1; 163.4 mg, 73%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.82 - 7.75 (m, 2H), 7.71 - 7.58 (m, 5H), 7.32 - 7.25 (m, 2H), 7.11 - 7.01 (m, 2H), 6.27 (dd, *J* = 8.6, 1.1 Hz, 2H), 2.35 (s, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 143.32, 139.96, 132.49, 131.99, 131.09, 130.40, 129.98, 122.40, 116.33, 108.13, 29.99. HRMS (ESI) Calcd for $C_{23}H_{20}NSO_2$ $[M+H]^+$: 374.1209; found: 374.1231.



32

1-phenyl-2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)butane-1,3-dione (**32**):

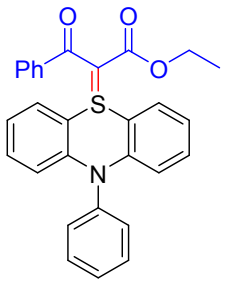
Yellow solid; Eluent: petroleum ether/ethyl acetate 3:1; 188.0 mg, 72%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.80 - 7.74 (m, 2H), 7.69 - 7.63 (m, 3H), 7.59 - 7.43 (m, 7H), 7.32 - 7.25 (m, 2H), 7.13 - 7.04 (m, 2H), 6.27 (dd, $J$ = 8.6, 1.0 Hz, 2H), 2.02 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 189.12, 188.63, 143.53, 143.00, 139.84, 132.58, 132.01, 131.05, 130.01, 129.84, 129.65, 128.85, 127.74, 122.66, 116.56, 107.95, 104.09, 30.36. HRMS (ESI) Calcd for $C_{28}H_{22}NSO_2$ $[M+H]^+$: 436.1366; found: 436.1326.



33

1,3-diphenyl-2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)propane-1,3-dione (**33**):

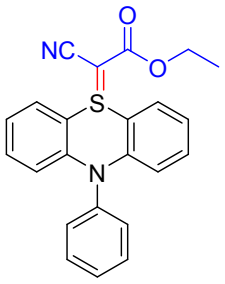
White solid; Eluent: petroleum ether/ethyl acetate 3:1; 250.6 mg, 84%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.79 (t, $J$ = 7.7 Hz, 2H), 7.74 - 7.66 (m, 3H), 7.64 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.34 - 7.29 (m, 2H), 7.28 - 7.22 (m, 4H), 7.18 - 7.06 (m, 8H), 6.33 (dd, $J$ = 8.5, 1.1 Hz, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 188.99, 142.95, 142.41, 139.84, 132.73, 132.05, 131.07, 130.07, 130.03, 128.61, 127.93, 122.85, 116.74, 108.08, 102.83. HRMS (ESI) Calcd for $C_{33}H_{24}NSO_2$ $[M+H]^+$: 498.1522; found: 498.1486.




34

ethyl 3-oxo-3-phenyl-2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)propanoate (**34**):

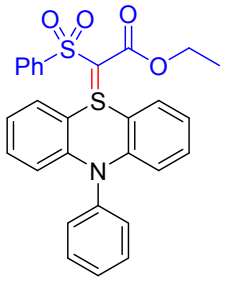
White solid; Eluent: petroleum ether/ethyl acetate 3:1; 189.8 mg, 68%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.77 (tt, *J* = 7.7, 1.1 Hz, 2H), 7.70 - 7.57 (m, 5H), 7.37 - 7.22 (m, 7H), 7.15 - 7.09 (m, 2H), 6.31 (dd, *J* = 8.6, 1.1 Hz, 2H), 3.83 (q, *J* = 7.1 Hz, 2H), 0.82 (t, *J* = 7.1 Hz, 3H).$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 188.85, 165.51, 143.26, 142.82, 139.81, 132.63, 132.05, 131.00, 130.27, 130.03, 129.50, 127.89, 127.59, 122.79, 116.62, 108.43, 89.80, 58.85, 14.40. HRMS (ESI) Calcd for $C_{29}H_{24}NSO_3$ $[M+H]^+$: 466.1471; found: 466.1474.




35

ethyl 2-cyano-2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)acetate (**35**):

Yellow solid; Eluent: petroleum ether/ethyl acetate 2:1; 136.7 mg, 59%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.85 - 7.73 (m, 4H), 7.71 - 7.65 (m, 1H), 7.60 - 7.54 (m, 2H), 7.53 - 7.45 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 6.55 (d, *J* = 8.5 Hz, 2H), 4.24 - 3.89 (m, 2H), 1.39 - 1.00 (m, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 165.12, 141.37, 138.26, 133.39, 131.50, 130.54, 129.86, 129.63, 123.52, 118.92, 117.13, 107.59, 59.18, 55.72, 14.64. HRMS (ESI) Calcd for $C_{23}H_{19}N_2SO_2$ $[M+H]^+$: 387.1162; found: 387.1161.

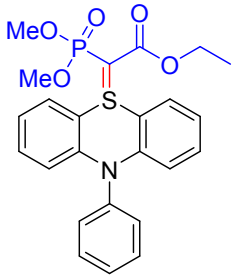


36

ethyl 2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)-2-(phenylsulfonyl)acetate (**36**):

Yellow solid; Eluent: petroleum ether/ethyl acetate 3:1; 198.4 mg, 66%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.10 - 7.72 (m, 3H), 7.71 - 7.22 (m, 11H), 7.21 - 7.10 (m, 2H), 6.37 (d, $J$ = 8.6 Hz, 2H), 3.83 (brs, 2H), 0.93 (brs, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 145.75, 142.68, 139.44, 133.11, 132.14, 132.06, 130.74, 130.17, 128.89, 126.98, 123.09, 117.03, 108.68, 82.41, 59.43, 14.63.

HRMS (ESI) Calcd for $C_{28}H_{24}NS_2O_4$ $[M+H]^+$: 502.1141; found: 502.1148.

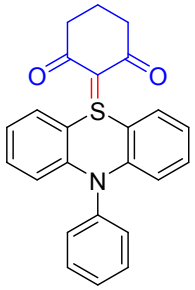


37

ethyl 2-(dimethoxyphosphoryl)-2-(10-phenyl-10*H*-5λ$^4$-phenothiazin-5-ylidene)acetate (**37**):

White solid; Eluent: petroleum ether/ethyl acetate 1:3; 242.1 mg, 86%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.76 (t, $J$ = 7.7 Hz, 2H), 7.66 (tt, $J$ = 7.4, 1.3 Hz, 1H), 7.60 (dd, $J$ = 7.9, 1.6 Hz, 2H), 7.58 - 7.53 (m, 2H), 7.34 - 7.26 (m, 2H), 7.17 - 7.09 (m, 2H), 6.29 (dd, $J$ = 8.6, 1.1 Hz, 2H), 3.85 (q, $J$ = 5.3 Hz, 2H), 3.47 (brs, 6H), 0.96 (brs, 3H).$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 166.16, 142.23, 139.29, 131.99, 131.52, 130.43, 130.03, 129.51, 122.27, 116.07, 109.83, 58.25, 55.07, 51.64, 14.42.

HRMS (ESI) Calcd for $C_{24}H_{25}NSO_5P$ $[M+H]^+$: 470.1186; found: 470.1182




38

2-(10-phenyl-10*H*-5λ$^4$phenothiazin-5-ylidene)cyclohexane-1,3-dione (**38**):

Pink solid; Eluent: petroleum ether/ethyl acetate 1:1; 175.6 mg, 76%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.82 - 7.75 (m, 2H), 7.74 - 7.69 (m, 2H), 7.69 - 7.64 (m, 1H), 7.42 (dd, $J$ = 7.8, 1.6 Hz, 2H), 7.34 - 7.26 (m, 2H), 7.11 - 7.02 (m, 2H), 6.31 (dd, $J$ = 8.6, 1.1 Hz, 2H), 2.22 (t, $J$ = 6.3 Hz, 4H), 1.74 - 1.64 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 190.57, 143.24, 139.80, 132.70, 131.97, 131.12, 130.32, 130.02, 122.80, 116.56, 106.92, 102.67, 37.63, 20.26. HRMS (ESI) Calcd for $C_{24}H_{20}NSO_2$ $[M+H]^+$: 386.1209; found: 386.1220

## 10 X-ray Crystallography Studies of Compound **8**

Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a saturated solution of compound **8** (cyclohexane/$CH_2Cl_2$) in a loosely capped vial.

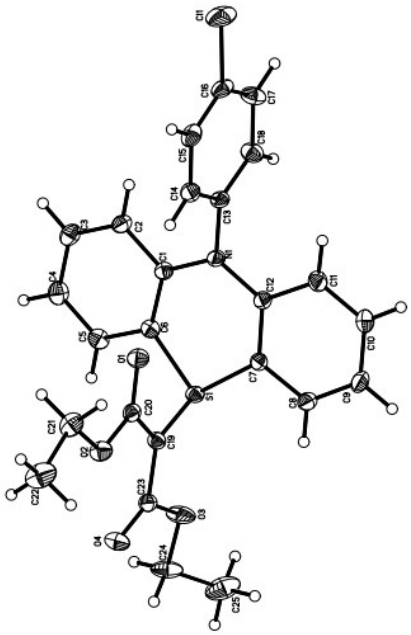
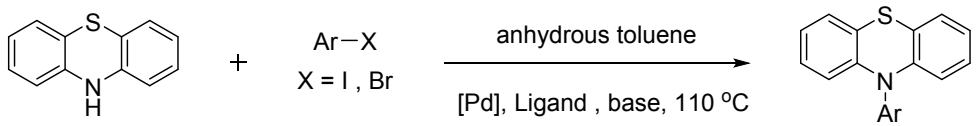


Figure **S10** Structure of 8 by X-Ray Crystallographic (CCDC 2056830)

Table **S5**. Crystal data and structure refinement for 8

| | |
|---|---|
| Empirical formula | $C_{25}H_{22}ClNO_4S$ |
| Formula weight | 467.95 |
| Temperature/K | 296(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 12.3598(5) |
| b/Å | 12.8606(5) |
| c/Å | 15.4574(6) |
| α/° | 81.9760(10) |
| β/° | 75.4550(10) |
| γ/° | 70.6690(10) |
| Volume/Å$^3$ | 2239.90(15) |
| Z | 4 |
| ρcalcg/cm$^3$ | 1.388 |
| μ/mm$^{-1}$ | 0.297 |
| F(000) | 976.0 |
| Crystal size/mm$^3$ | 0.2 × 0.2 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.4 to 55.0 |
| Index ranges | -16 ≤ h ≤ 14, -16 ≤ k ≤ 15, -20 ≤ l ≤ 19 |
| Reflections collected | 20598 |
| Independent reflections | 10117 [Rint = 0.119] |
| Data/restraints/parameters | 10117/0/577 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.13/-0.56 |

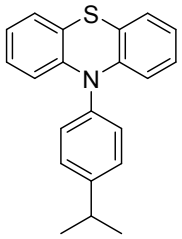
# 11 Synthesis and characterization of substrates




General procedure for the synthesis of substrates from phenothiazine:[1]

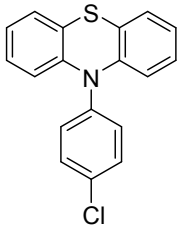
An oven-dried round bottom flask equipped with a magnetic stirring bar was charged with the phenothiazine (5 mmol, 1 eq, 0.995 g), 2,2'-Bis-(diphenylphosphino)-1,1'-binaphthyl (BINAP) (0.4 mmol, 0.08 eq, 0.249 g), *t*-BuOK (10.0 mmol, 2 eq, 1.122 g), tris(dibenzylideneacetone)dipalladium (1 mmol, 0.2 eq, 0.916 g) under nitrogen atmosphere. Then, anhydrous toluene was added into the mixture followed by the addition of substituted iodobenzene or bromobenzene (5.5 mmol, 1.1 eq). The reaction mixture was stirred at 110 °C overnight. Upon the consumption of starting materials, the toluene was removed in vacuo and the crude product was purified by column chromatography to give the desired substrates.

Note: When the iodobenzene or bromobenzene is solid, all the reactants were directly added into the round bottom flask before nitrogen replacement followed by addition of anhydrous toluene.



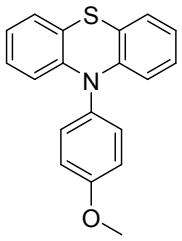

10-(4-isopropylphenyl)-10*H*-phenothiazine:

White solid; Eluent: petroleum ether; 1.474 g, 93%; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 7.59 - 7.44 (m, 2H), 7.29 (d, $J$ = 7.5 Hz, 2H), 7.03 (d, $J$ = 7.5 Hz, 2H), 6.95 - 6.77 (m, 4H), 6.12 (d, $J$ = 8.2 Hz, 2H), 3.08 - 2.90 (m, 1H), 1.26 (d, $J$ = 6.8 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 149.13, 144.27, 138.26, 130.79, 129.30, 127.69, 127.05, 123.02, 119.52, 116.22, 33.60, 24.27. HRMS (ESI) Calcd for $C_{21}H_{20}NS$ $[M+H]^+$: 318.1311; found: 318.1298.



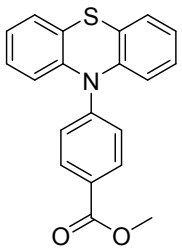

10-(4-chlorophenyl)-10*H*-phenothiazine:

White solid; Eluent: petroleum ether; 1.406 g, 91%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.71 – 7.64 (m, 2H), 7.45 – 7.39 (m, 2H), 7.10 (dd, $J$ = 7.5, 1.7 Hz, 2H), 6.99 – 6.93 (m, 2H), 6.89 (td, $J$ = 7.4, 1.3 Hz, 2H), 6.24 (dd, $J$ = 8.2, 1.3 Hz, 2H). $^{13}$C NMR (101 MHz, DMSO) δ 143.71, 140.02, 132.95, 132.05, 131.50, 127.86, 127.33, 123.59, 120.79, 117.19. HRMS (ESI) Calcd for $C_{18}H_{13}NSCl$ $[M+H]^+$: 310.0452; found: 310.0456.



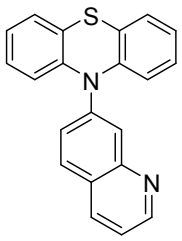

10-(4-methoxyphenyl)-10*H*-phenothiazine:

White solid; Eluent: petroleum ether; 1.311 g, 86%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.36 – 7.31 (m, 2H), 7.23 – 7.17 (m, 2H), 7.03 (dd, $J$ = 7.4, 1.6 Hz, 2H), 6.90 (ddd, $J$ = 8.2, 7.3, 1.7 Hz, 2H), 6.82 (td, $J$ = 7.4, 1.3 Hz, 2H), 6.13 (dd, $J$ = 8.2, 1.3 Hz, 2H), 3.85 (s, 3H).$^{13}$C NMR (101 MHz, DMSO) δ 159.42, 144.51, 132.92, 132.42, 127.72, 127.01, 122.93, 119.18, 116.64, 116.02, 55.89. HRMS (ESI) Calcd for $C_{19}H_{16}NSO$ $[M+H]^+$: 306.0947; found: 306.0895.



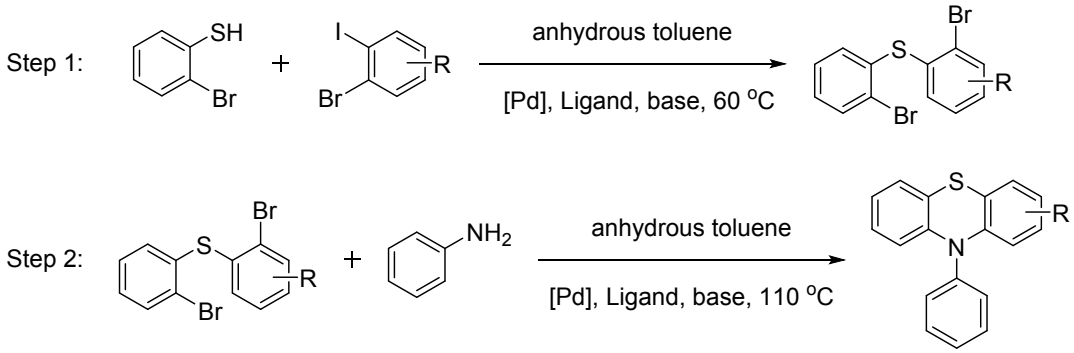

methyl 4-(10*H*-phenothiazin-10-yl)benzoate:

Yellow solid; Eluent: petroleum ether/ethyl acetate 80:1 to 20:1; 1.282 g, 67%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.98 – 7.92 (m, 2H), 7.37 (dd, $J$ = 7.7, 1.6 Hz, 2H), 7.26 - 7.17 (m, 4H), 7.13 (td, $J$ = 7.5, 1.3 Hz, 2H), 6.98 (dd, $J$ = 8.1, 1.3 Hz, 2H), 3.82 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 166.20, 147.97, 142.04, 131.80, 128.56, 128.47, 128.13, 125.70, 125.15, 123.36, 121.14, 52.44. HRMS (ESI) Calcd for $C_{20}H_{16}NSO_2$ $[M+H]^+$: 334.0896; found: 333.0887.



10-(quinolin-7-yl)-10H-phenothiazine:

Yellow solid; Eluent: petroleum ether/ethyl acetate 50:1 to 8:1; 0.852 g, 52%; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 8.99 (d, $J$ = 4.2 Hz, 1H), 8.42 (d, $J$ = 8.3 Hz, 1H), 8.26 (d, $J$ = 8.9 Hz, 1H), 8.09 (s, 1H), 7.76 (dd, $J$ = 8.8, 2.5 Hz, 1H), 7.59 (dd, $J$ = 8.3, 4.2 Hz, 1H), 7.13 (d, $J$ = 7.1 Hz, 2H), 6.97 – 6.84 (m, 4H), 6.28 (d, $J$ = 7.9 Hz, 2H). $^{13}$C NMR (101 MHz, DMSO) δ 151.78, 147.28, 143.92, 138.91, 136.64, 132.35, 131.84, 129.85, 128.70, 127.88, 127.34, 123.58, 122.43, 120.81, 117.39. HRMS (ESI) Calcd for $C_{21}H_{15}N_2S$ $[M+H]^+$: 327.0950; found: 327.0938.

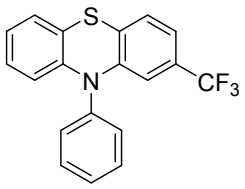



General procedure for the synthesis of phenothiazine ring:[2]

**Step 1**: An oven-dried round bottom flask equipped with a magnetic stirring bar was charged with subsitituted 1-bromo-2-iodobenzene (5.5 mmol, 1.1 eq), bis(2-diphenylphosphinophenyl)ether (DPE·phos) (0.5 mmol, 0.1 eq, 0.269 g), *t*-BuONa (10.0 mmol, 2 eq, 0.961 g), $Pd(OAc)_2$ (0.25 mmol, 0.05 eq, 0.056 g) under nitrogen atmosphere. Then, anhydrous toluene was added into the mixture followed by the addition of 2-bromothiophenol (5 mmol, 1 eq, 0.940 g). The reaction mixture was stirred at 60 °C for 24 h. Upon the consumption of starting materials, the reaction mixture was concentrated and purified by column chromatography (petroleum) to give the crude product thioether.

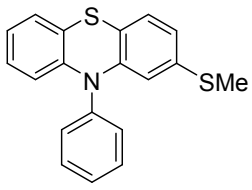
Step 2: An oven-dried round bottom flask equipped with a magnetic stirring bar was charged with crude product thioether (3 mmol, 2 eq), 2,2'-Bis-(diphenylphosphino)-

1,1'-binaphthyl (BINAP) (0.3 mmol, 0.1 eq, 0.187 g), *t*-BuOK (6.0 mmol, 2 eq, 0.673 g), tris(dibenzylideneacetone) dipalladium (0.15 mmol, 0.05 eq, 0.137 g) under nitrogen atmosphere. Then, anhydrous toluene was added into the mixture followed by the addition of aniline (3.3 mmol, 1.1 eq, 0.307 g). The reaction mixture was stirred at 110 °C for 24 h. The solution was washed with saturated $NH_4Cl$ solution (200 mL), and extracted with ethyl acetate (60 mL) for 3 times. The organic layer was dried over with $Na_2SO_4$. Then it was concentrated under reduced pressure to afford the crude product and purified by column chromatography to give the desired substrates.




10-phenyl-2-(trifluoromethyl)-10*H*-phenothiazine:

Step 1: Colorless oil; Eluent: petroleum ether; 1.762 g, 86%. Step 2: White solid; Eluent: petroleum ether; 0.762 g, 74%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.70 (t, $J$ = 7.7 Hz, 2H), 7.63 – 7.54 (m, 1H), 7.50 – 7.42 (m, 2H), 7.24 (d, $J$ = 8.0 Hz, 1H), 7.13 (dd, $J$ = 8.1, 1.8 Hz, 1H), 7.06 (dd, $J$ = 7.4, 1.8 Hz, 1H), 6.89 (dtd, $J$ = 20.3, 7.5, 1.6 Hz, 2H), 6.20 (d, $J$ = 1.8 Hz, 1H), 6.10 (dd, $J$ = 8.1, 1.4 Hz, 1H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 144.64, 143.16, 139.89, 131.92, 130.97, 129.64, 129.37, 128.71, 128.39, 128.27, 128.17, 128.08, 127.79, 127.17, 125.56, 125.11 (d, $J$ = 1.1 Hz), 123.79, 122.86, 119.46 (q, $J$ = 4.0 Hz), 118.29, 116.52, 111.37 (q, $J$ = 4.1 Hz). $^{19}$F NMR (376 MHz, DMSO) δ -61.89. HRMS (ESI) Calcd for $C_{19}H_{13}NSF_3$ $[M+H]^+$: 344.0715; found: 344.0666,




2-(methylthio)-10-phenyl-10*H*-phenothiazine:

Step 1: Colorless oil; Eluent: petroleum ether; 1.512 g, 78%. Step 2: White solid; Eluent: petroleum ether; 0.617 g, 64%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.70 - 7.63 (m, 2H), 7.55 (tt, $J$ = 7.4, 1.1 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.06 (dd, $J$ = 7.4, 1.7 Hz, 1H), 7.01 (d, $J$ = 8.0 Hz, 1H), 6.93 – 6.88 (m,

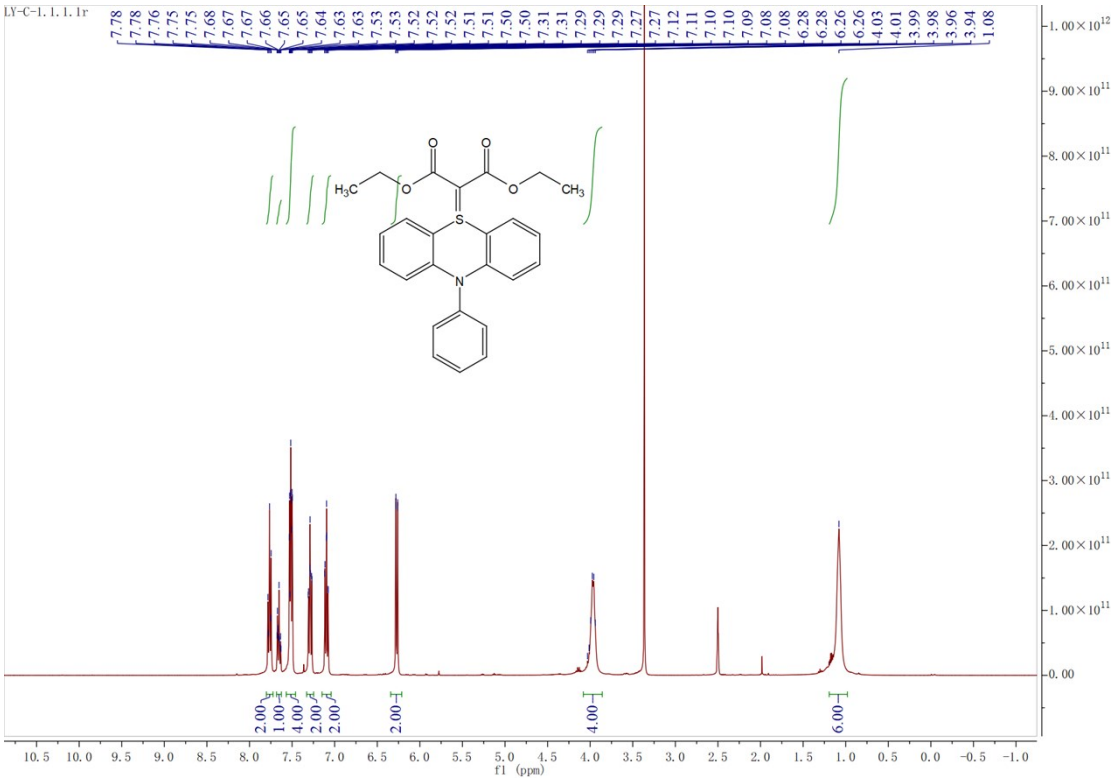
1H), 6.84 (td, *J* = 7.4, 1.3 Hz, 1H), 6.76 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.14 (dd, *J* = 8.1, 1.4 Hz, 1H), 5.98 (d, *J* = 1.9 Hz, 1H), 2.23 (s, 3H).$^{13}$C NMR (101 MHz, DMSO) δ 144.43, 143.77, 140.50, 137.62, 131.59, 130.84, 129.15, 127.72, 127.49, 127.14, 123.31, 120.57, 119.83, 116.61, 116.27, 114.12, 15.30. HRMS (ESI) Calcd for $C_{19}H_{16}NS_2$ $[M+H]^+$: 322.0719; found: 322.0695.

## 12 References

1 F. Speck, D. Rombach and H.-A. Wagenknecht, Beilstein *J. Org. Chem.,* 2019, **15**, 52-59.

2 L. Zhang, X. Huang, S. Zhen, J. Zhao, H. Li, B. Yuan and G. Yang, *Org. Biomol. Chem.,* 2017, **15**, 6306-6309.

## 13 NMR Spectra for Electrolysis Products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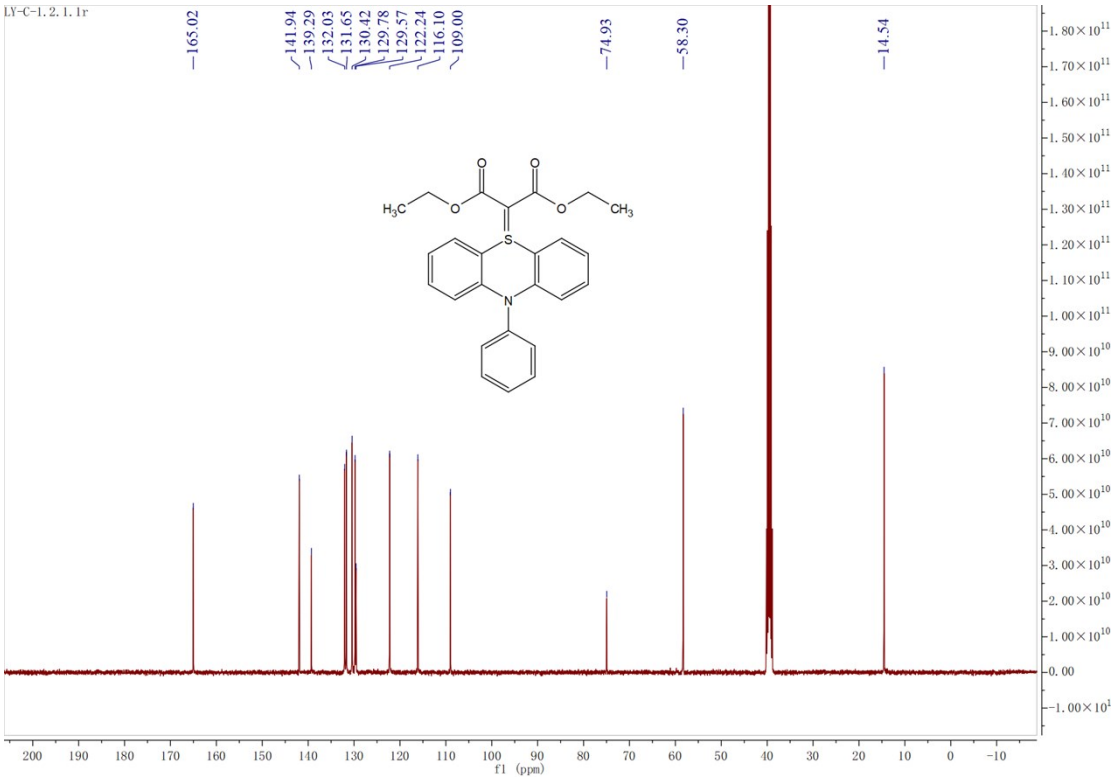
f1 (ppm)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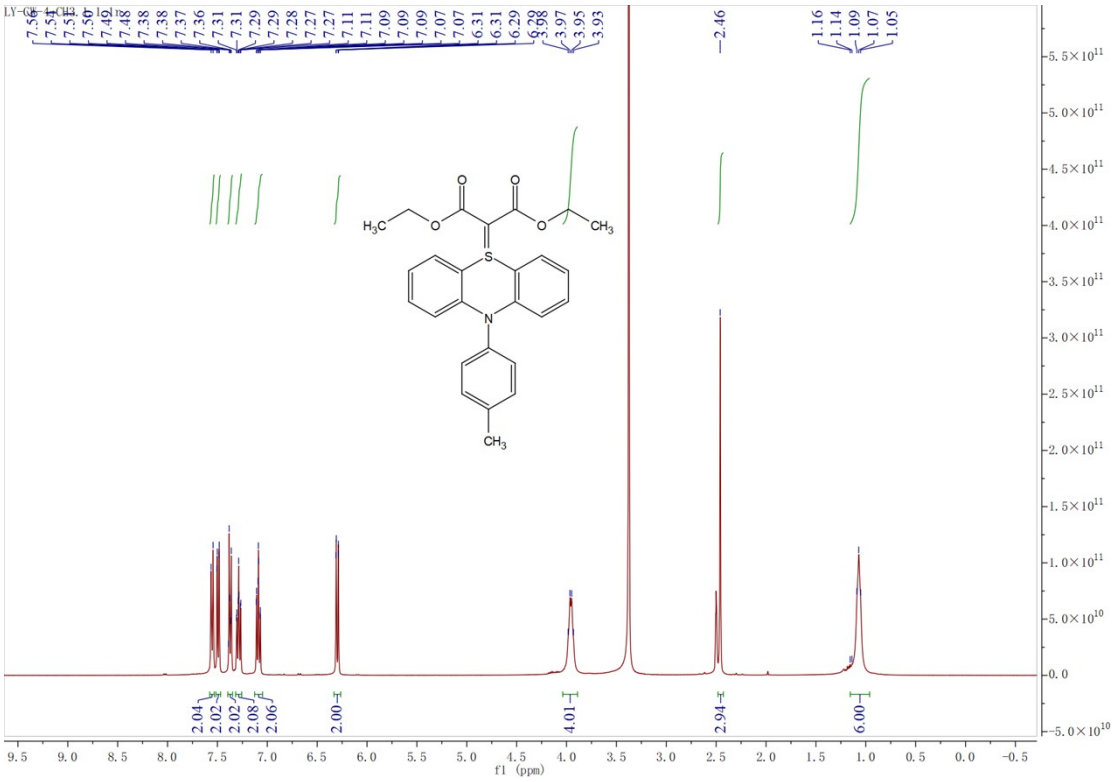
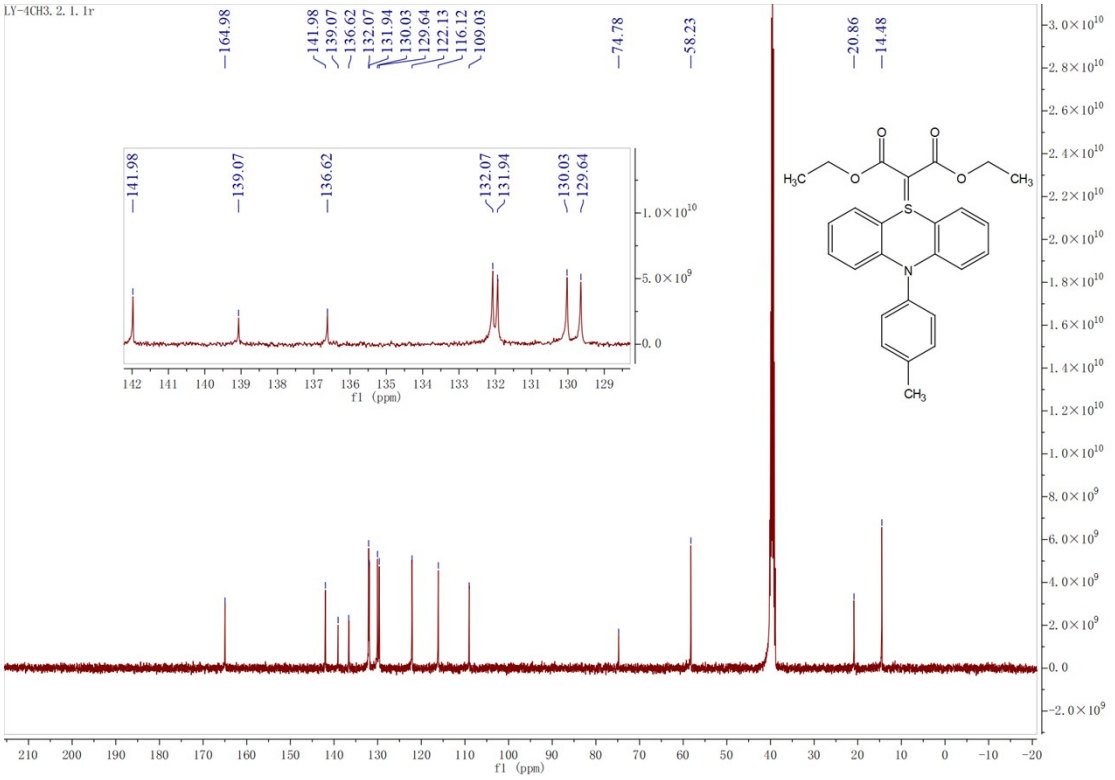
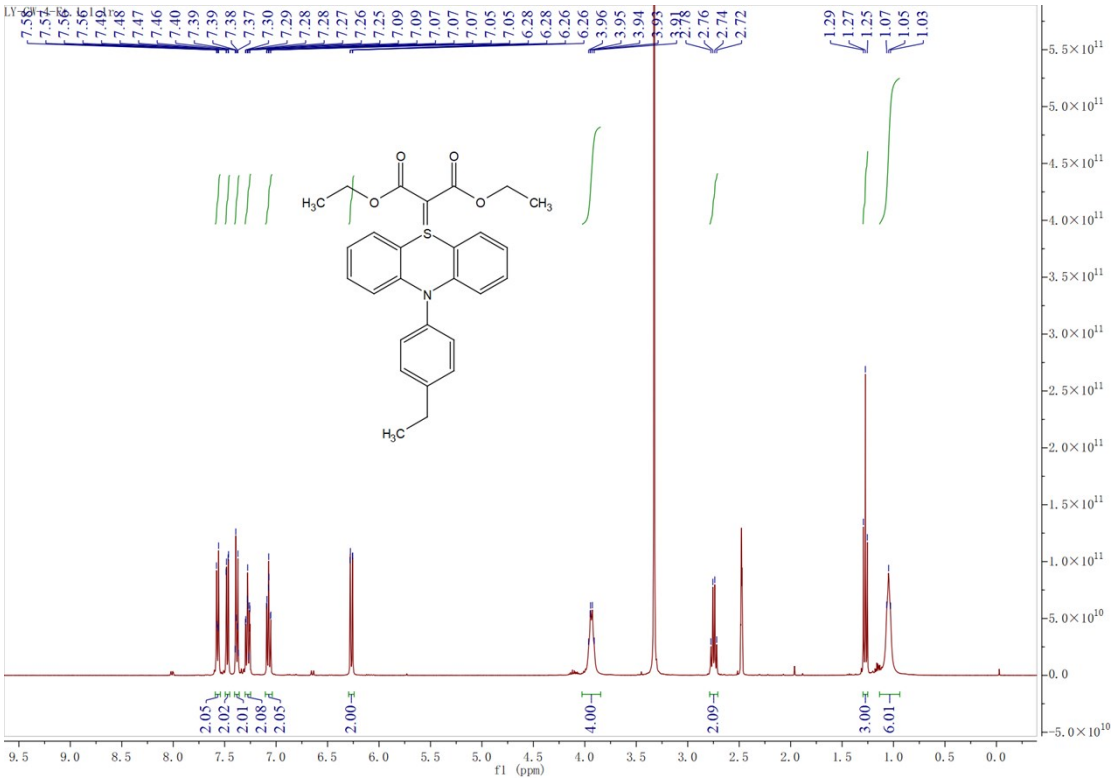
f1 (ppm)



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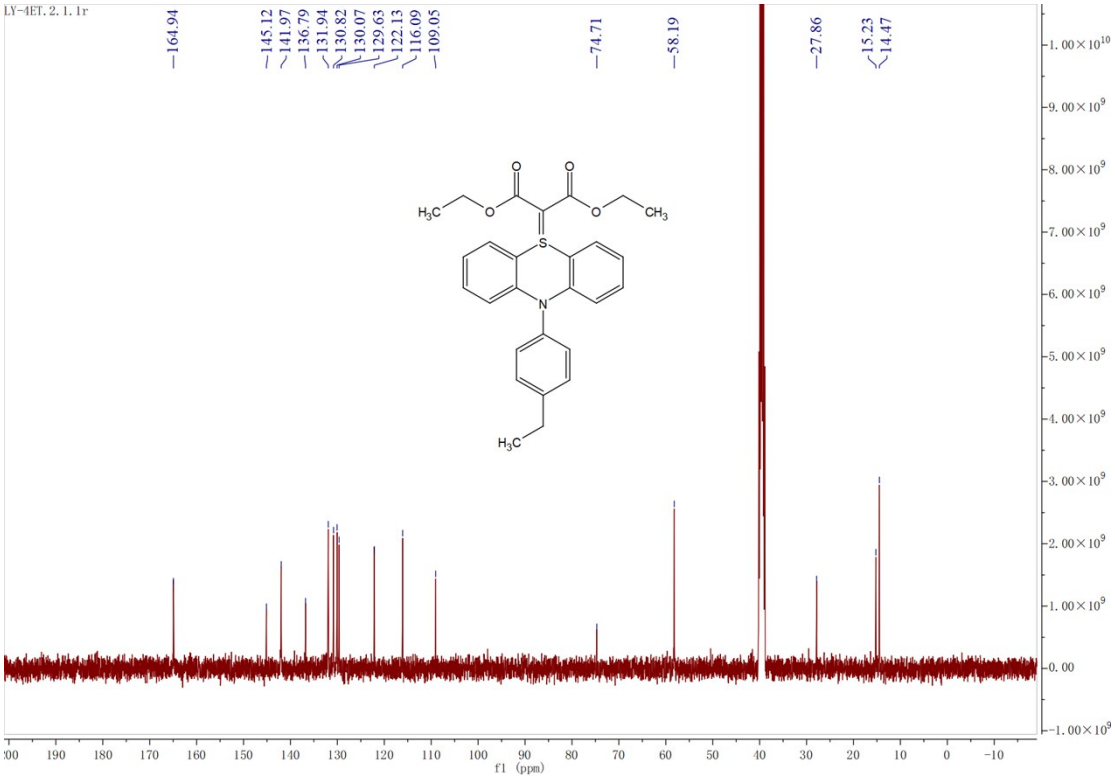
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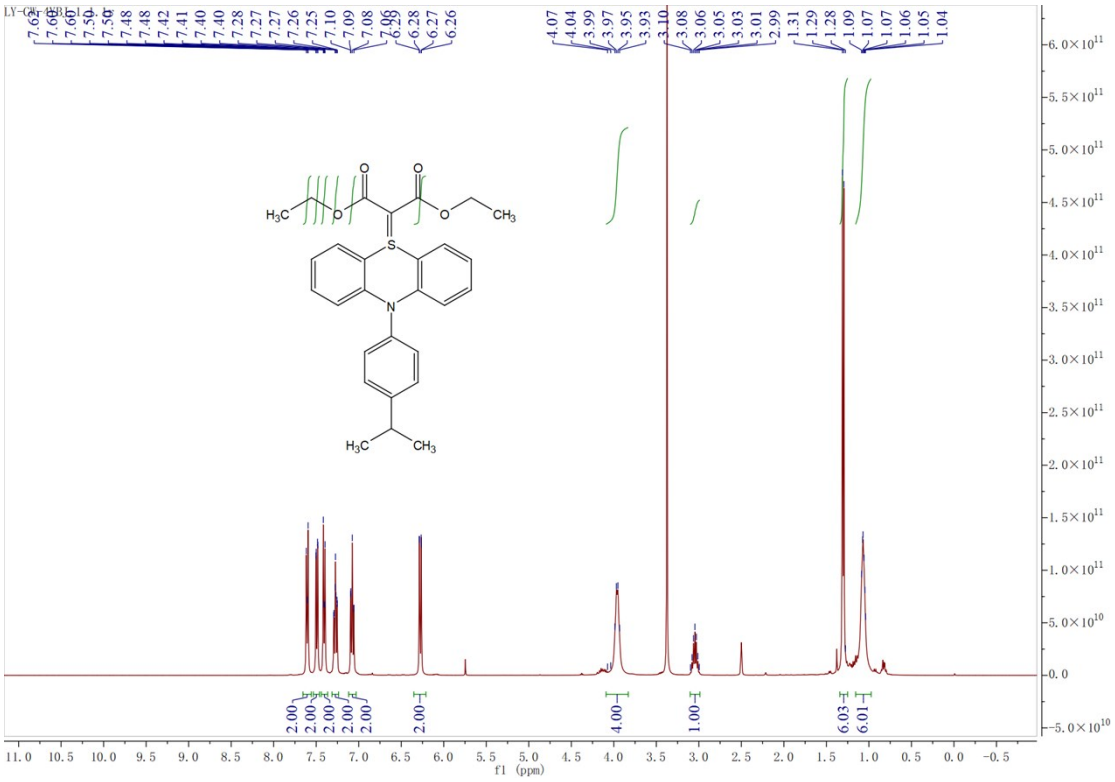
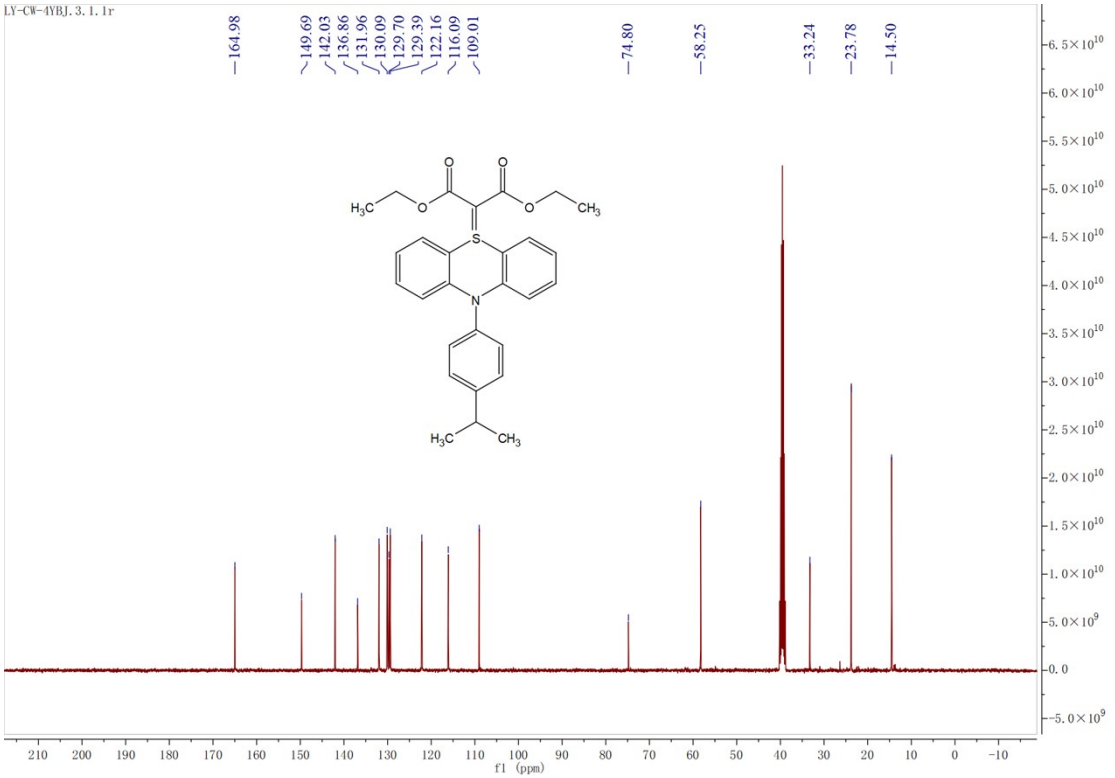
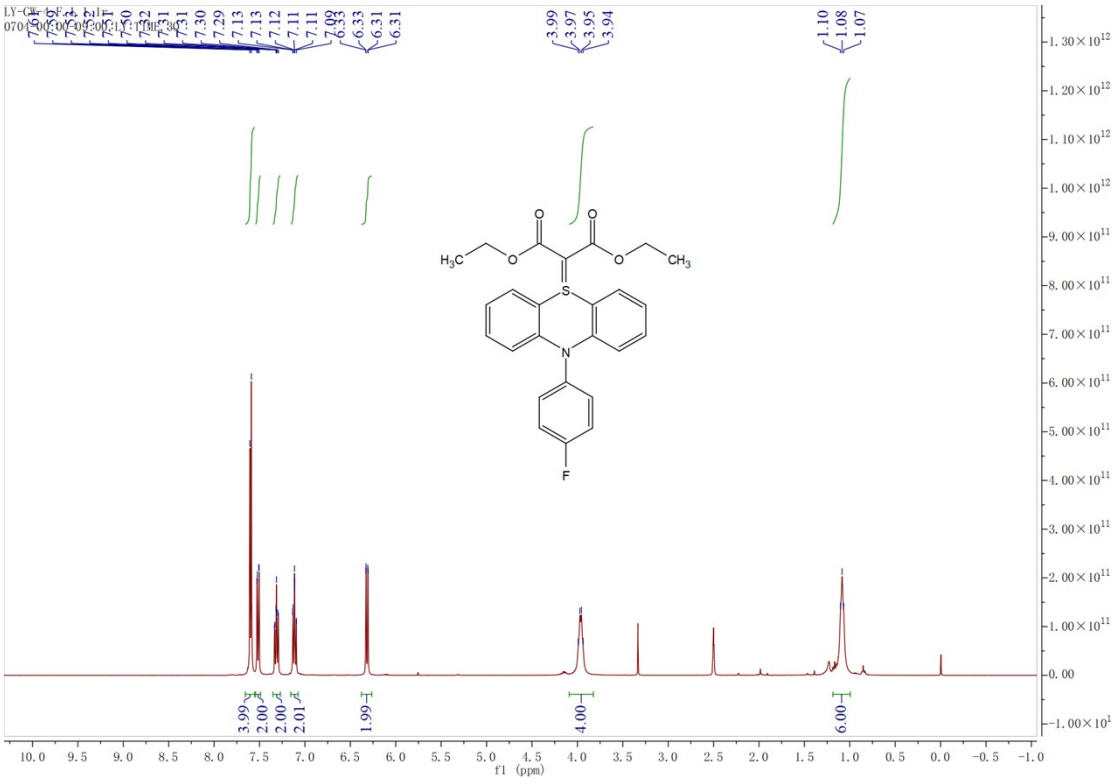
f1 (ppm)



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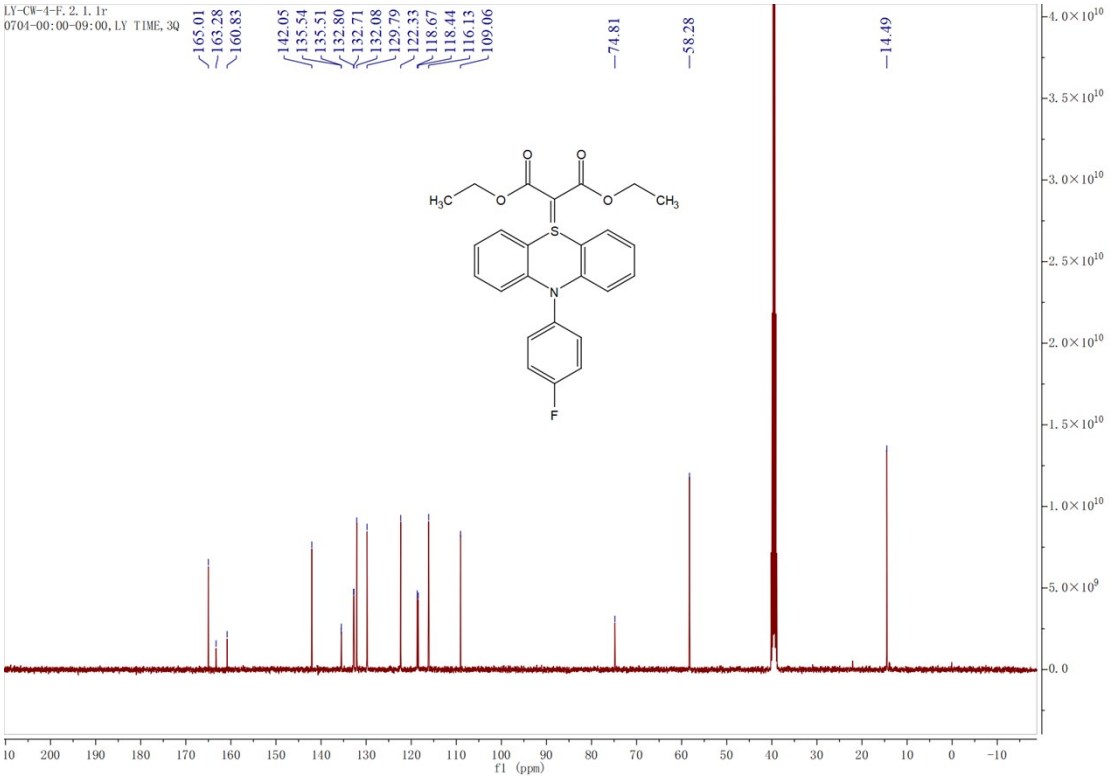
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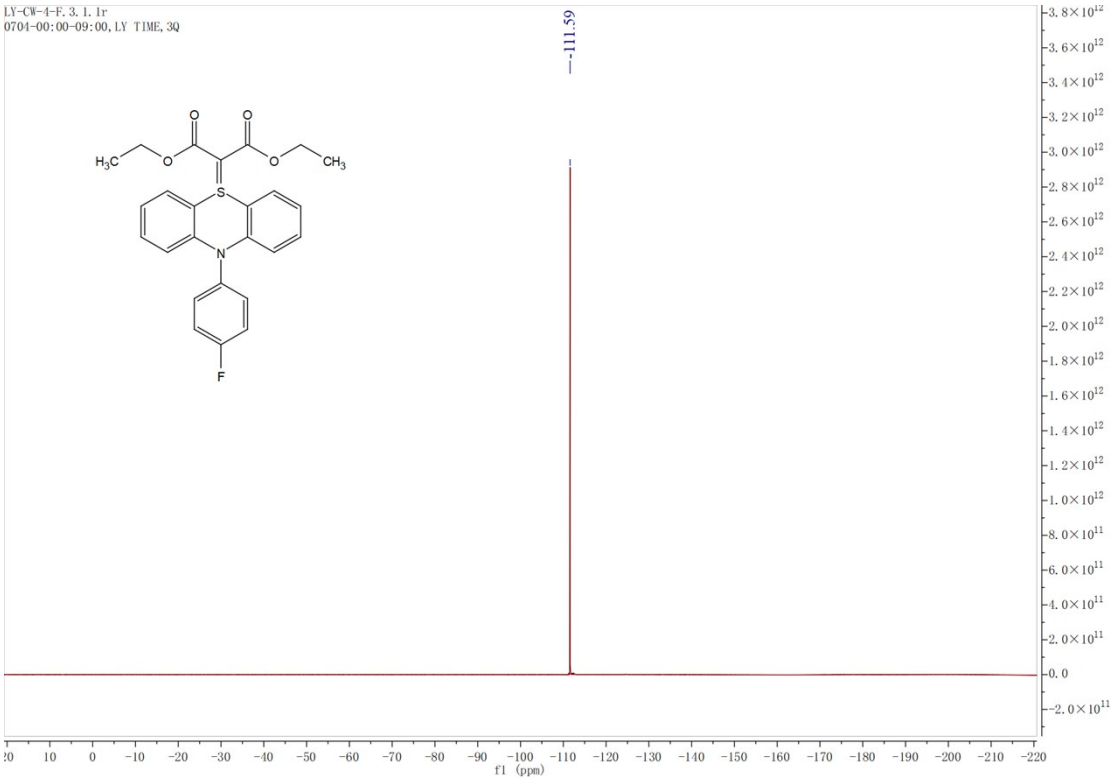
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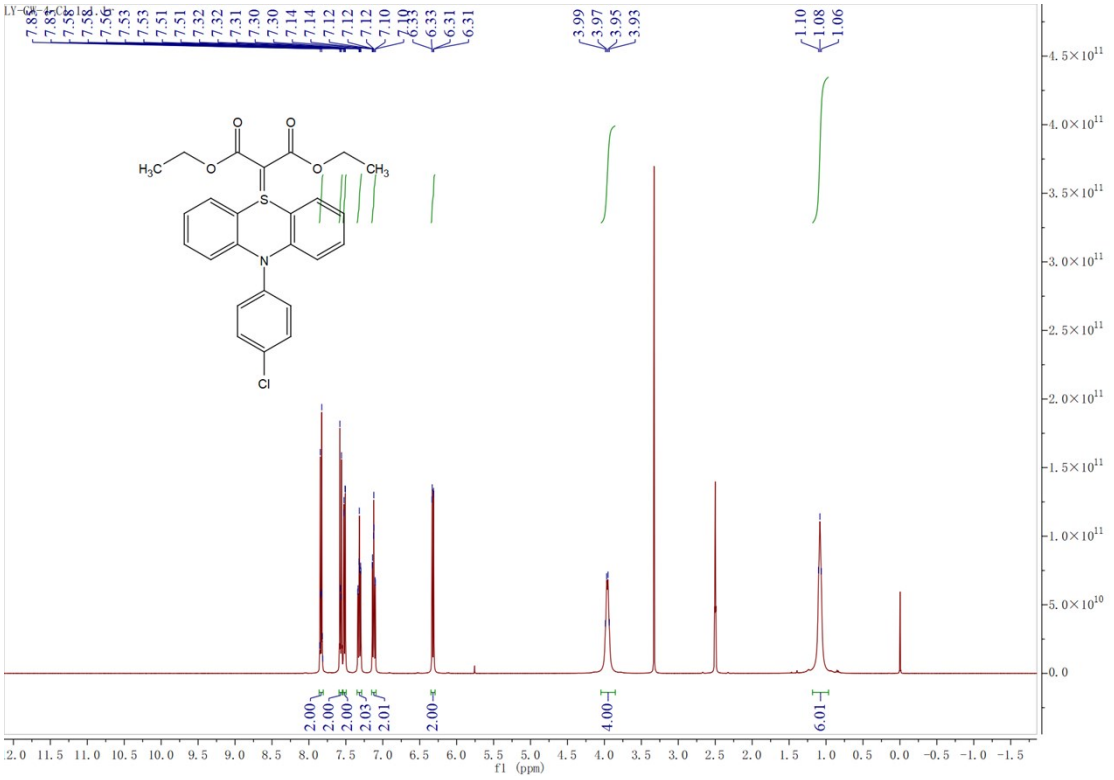
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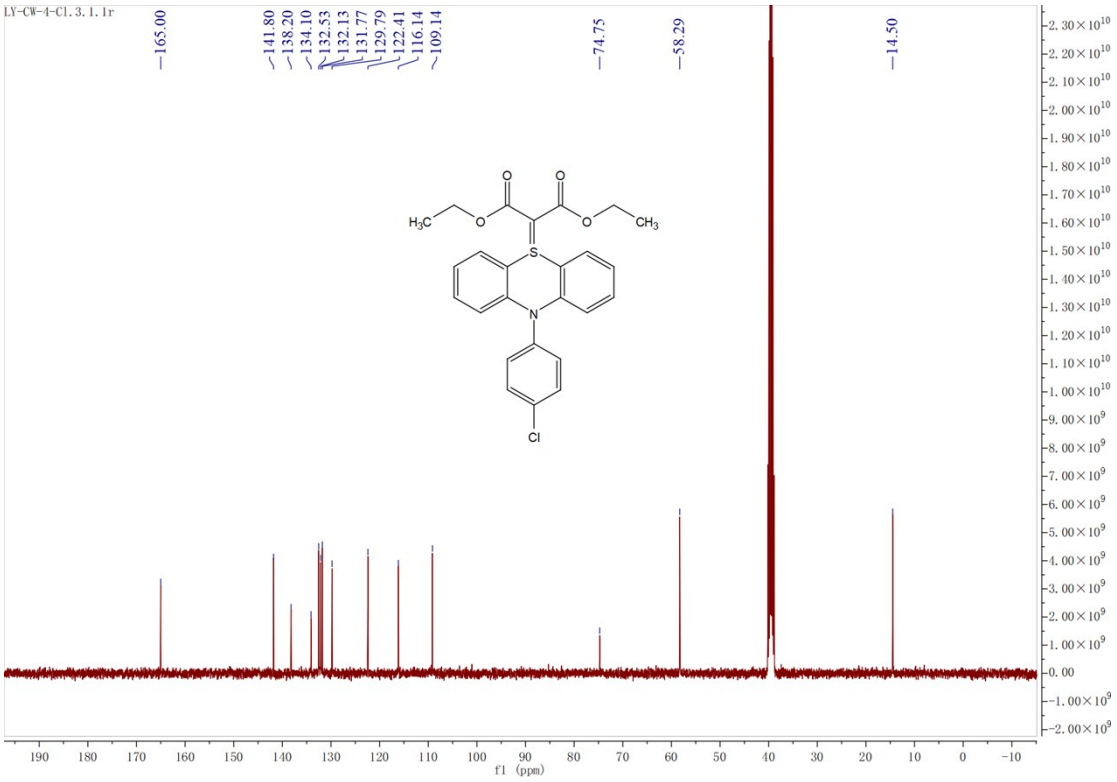
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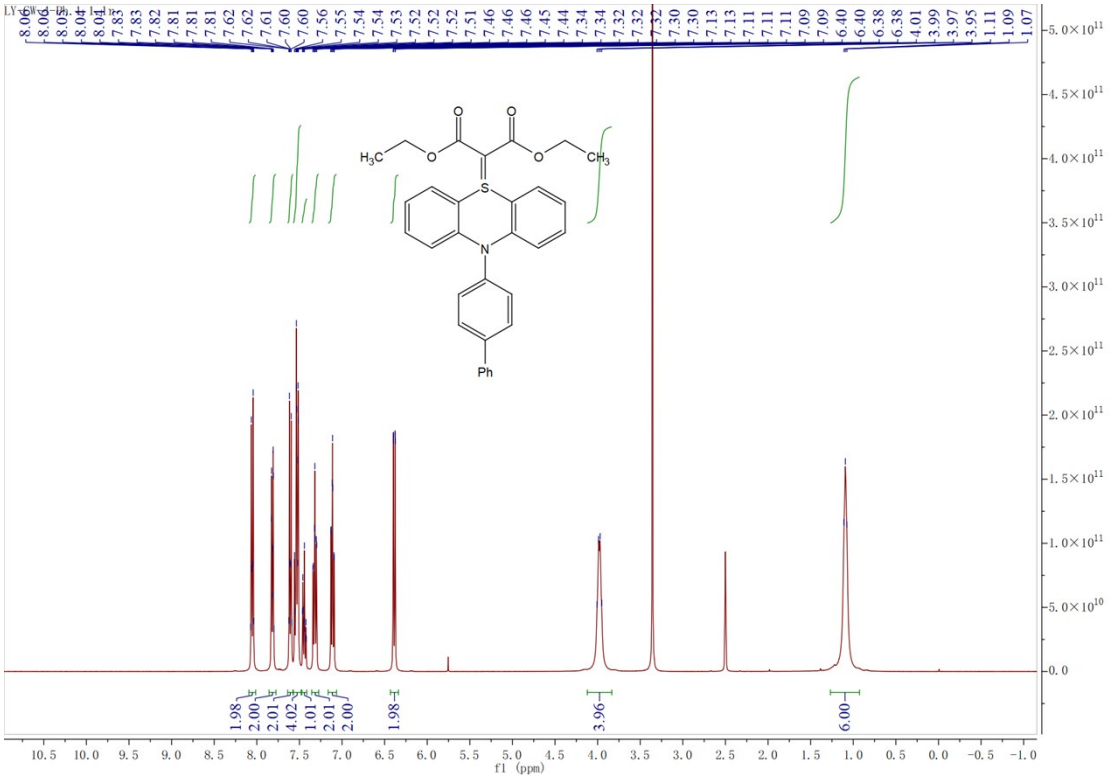
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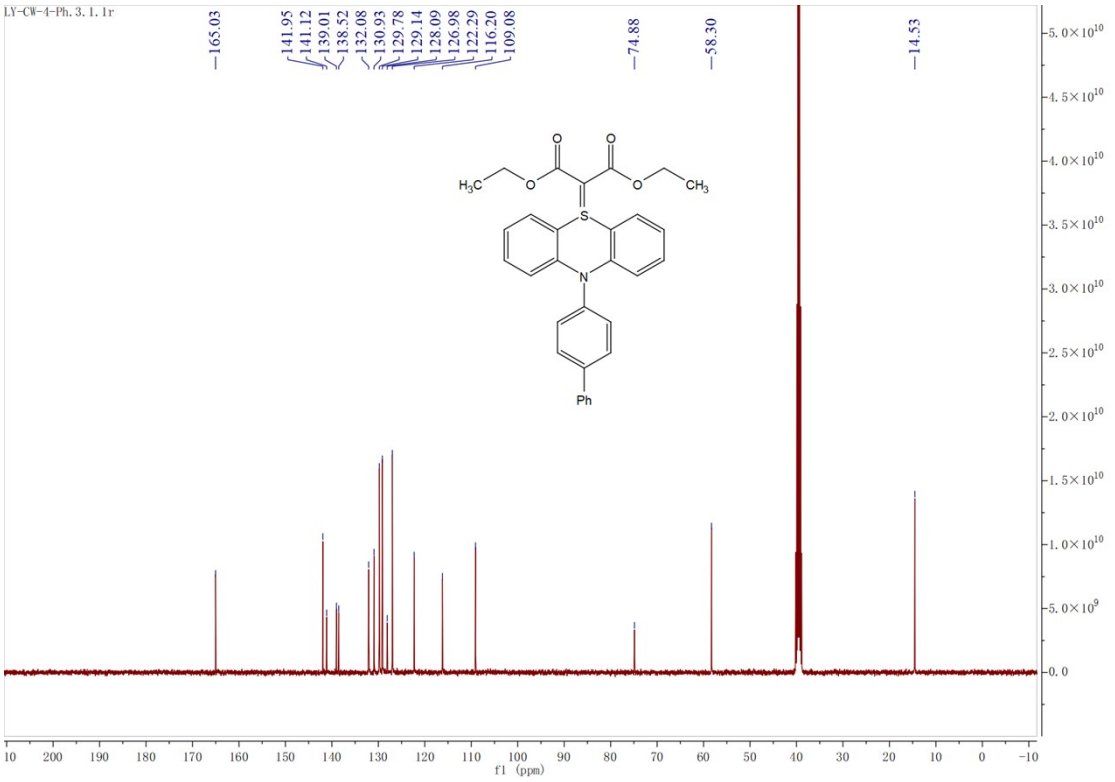
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Ph
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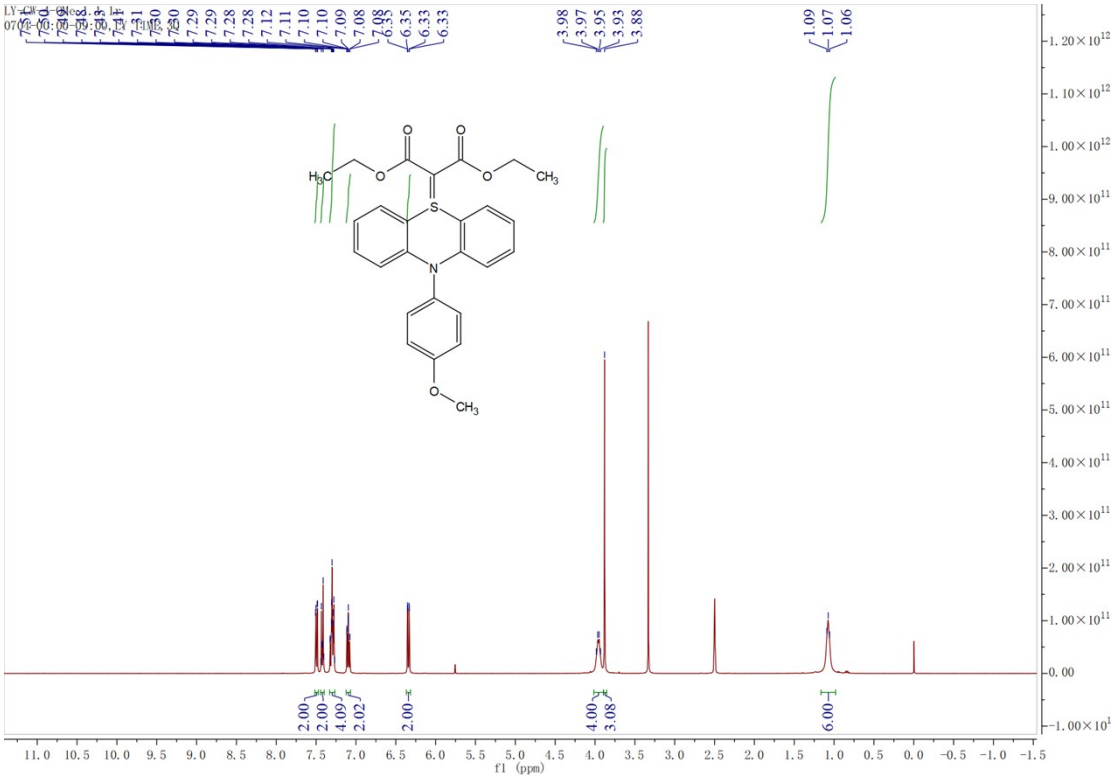
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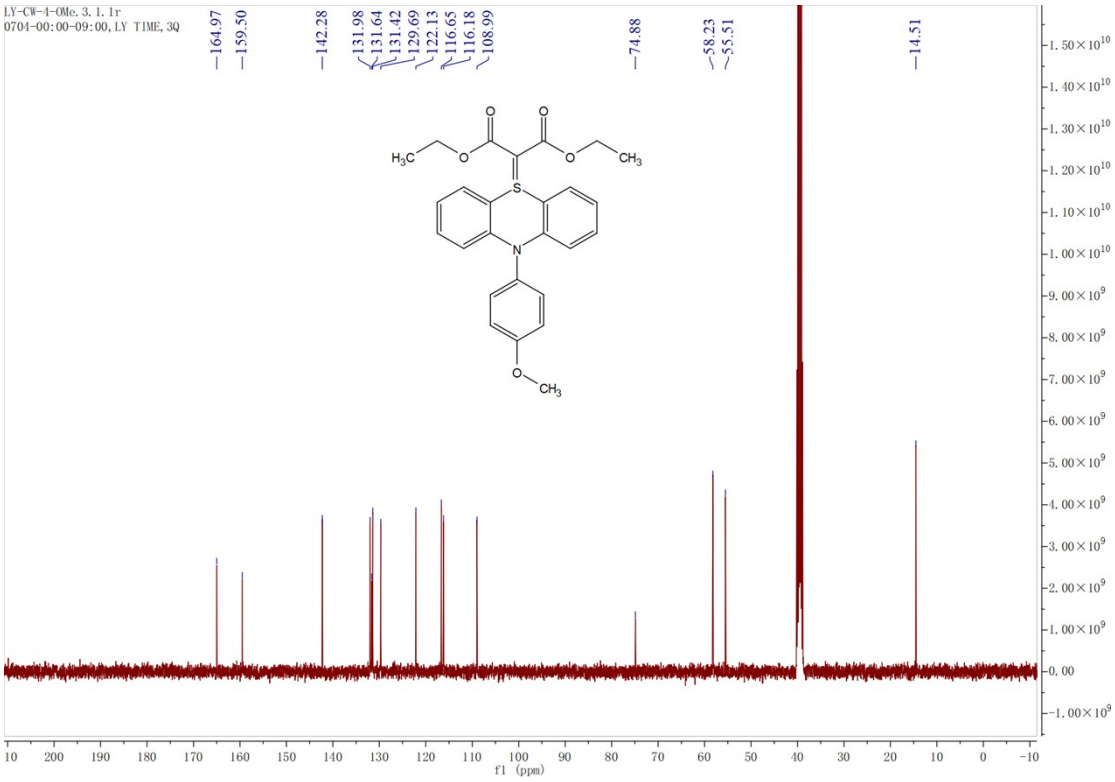
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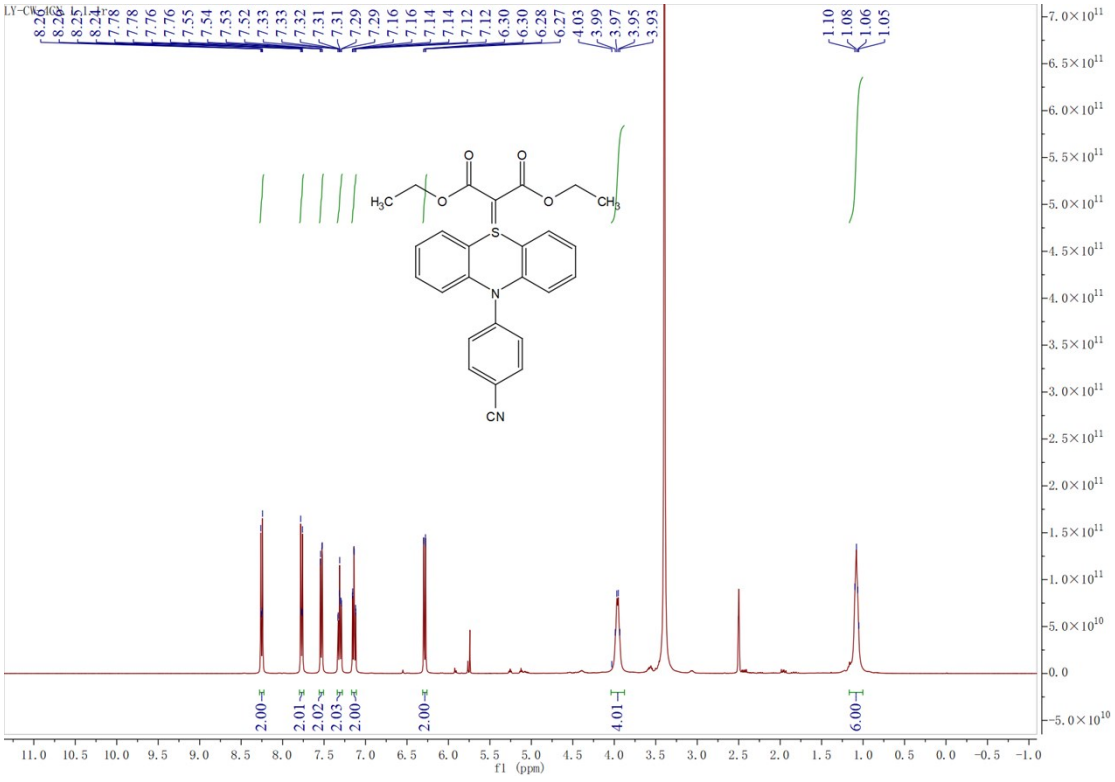
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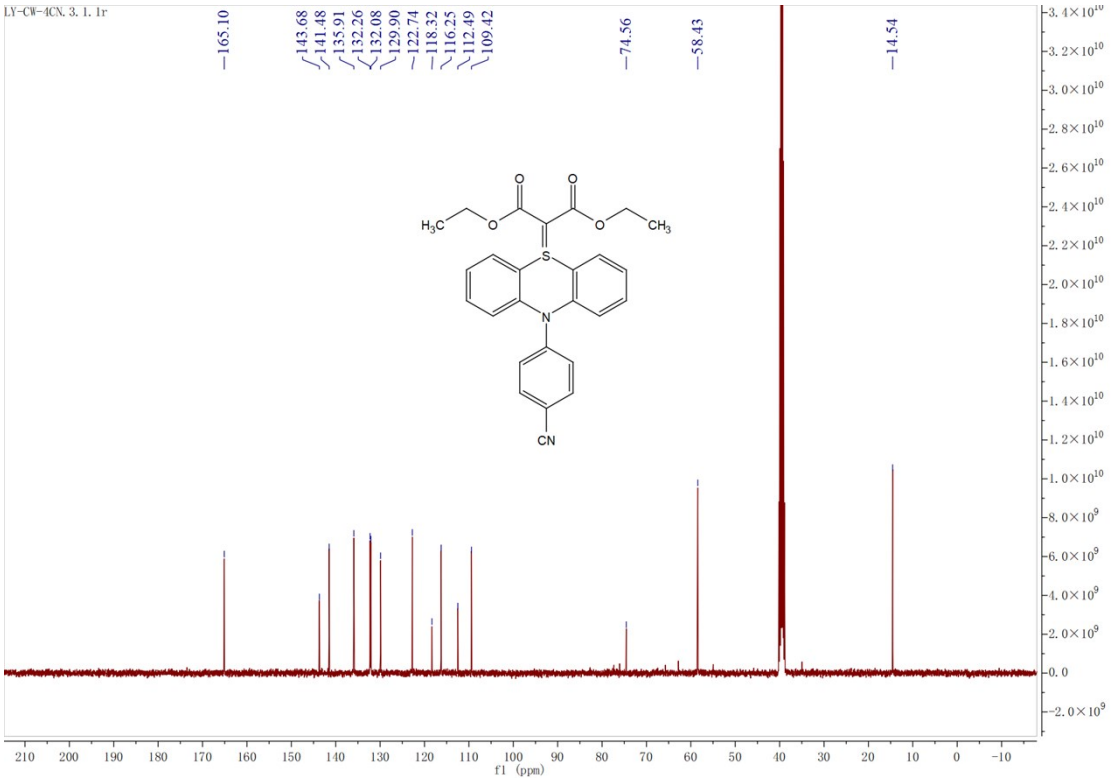
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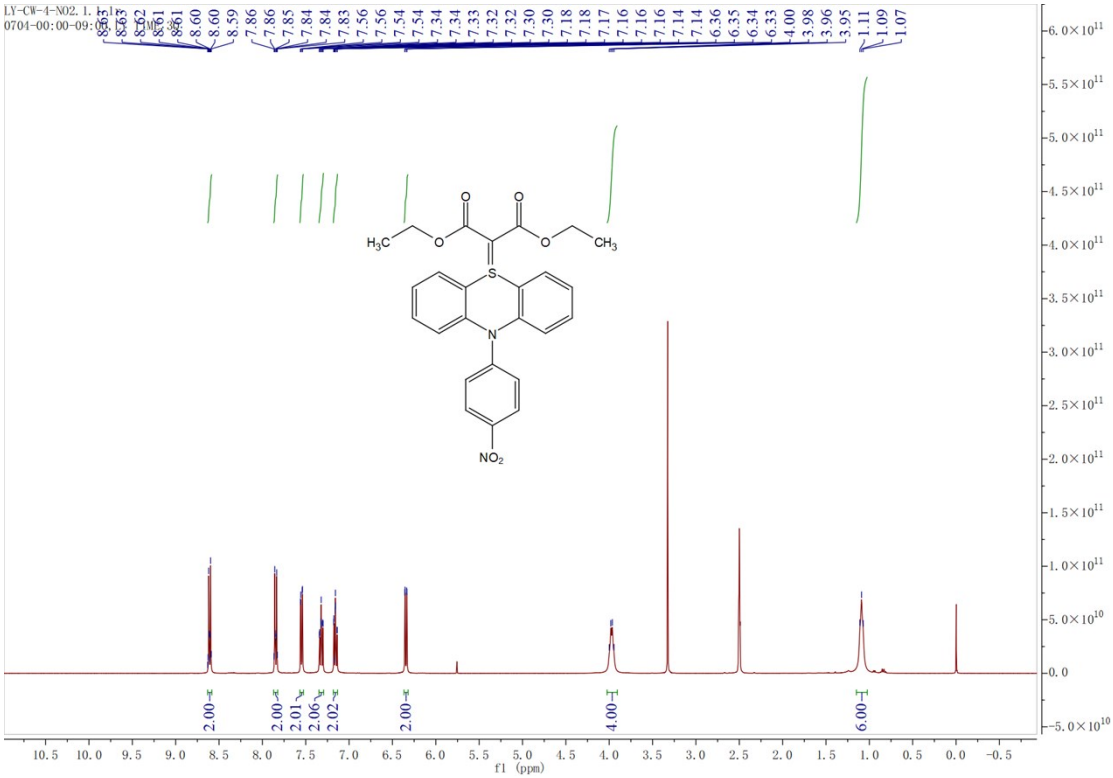
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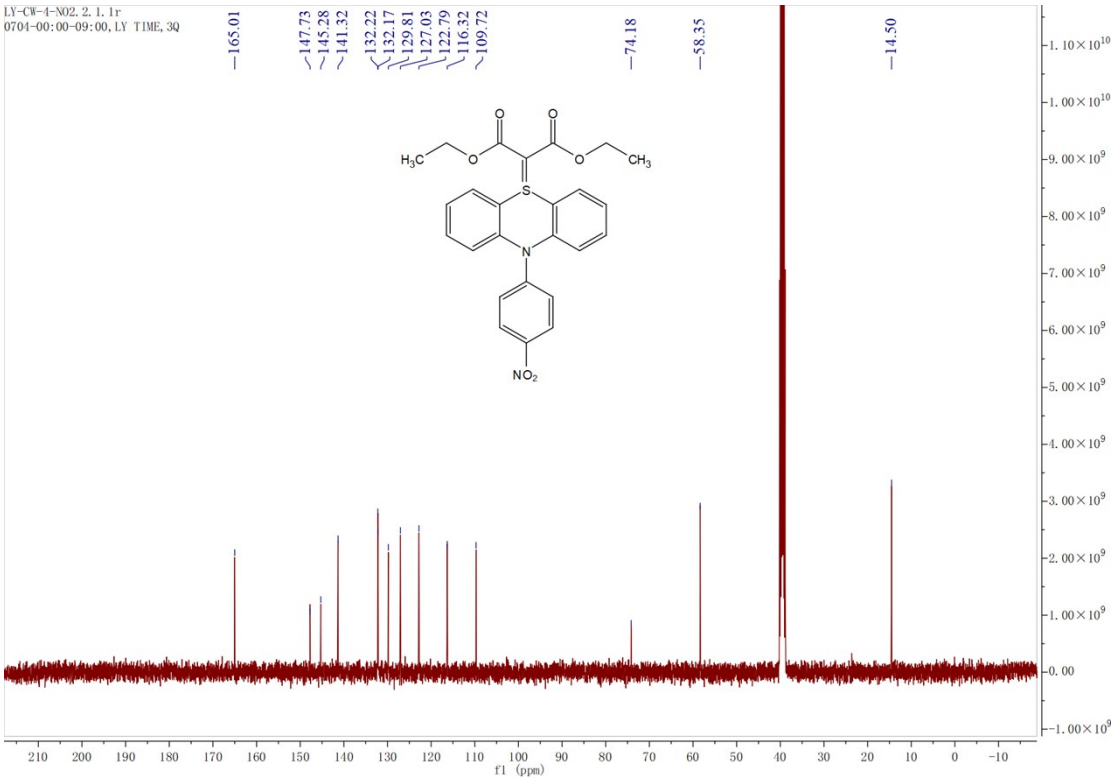
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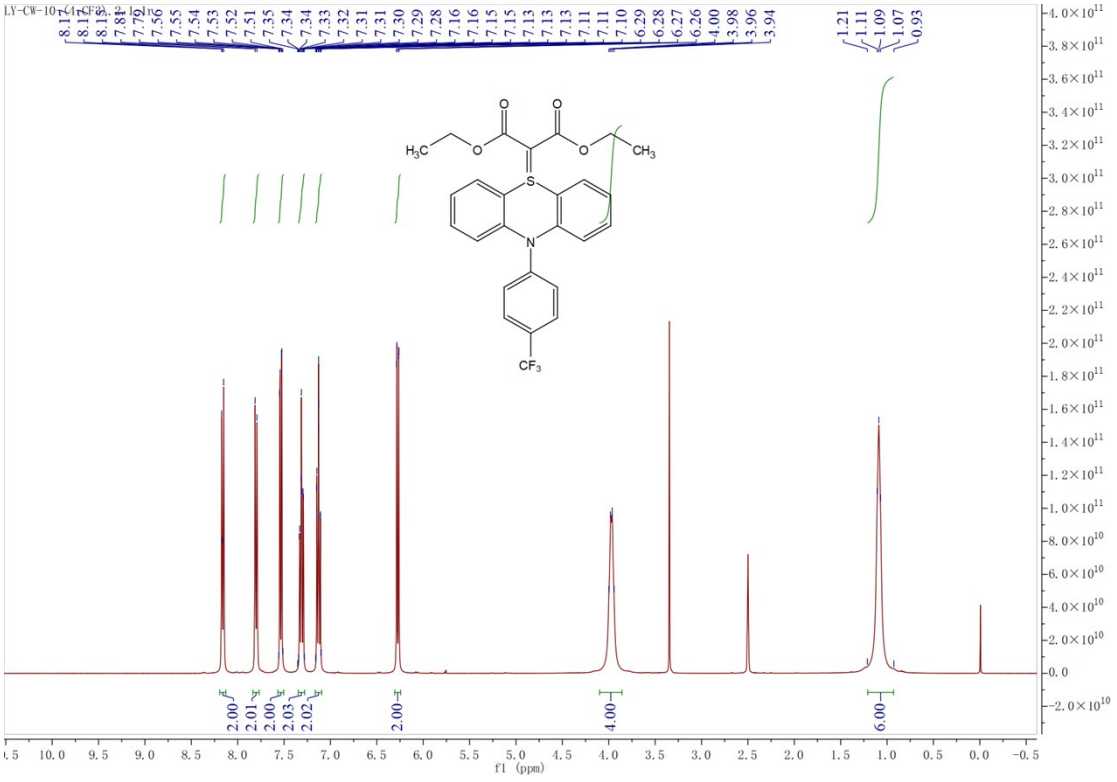
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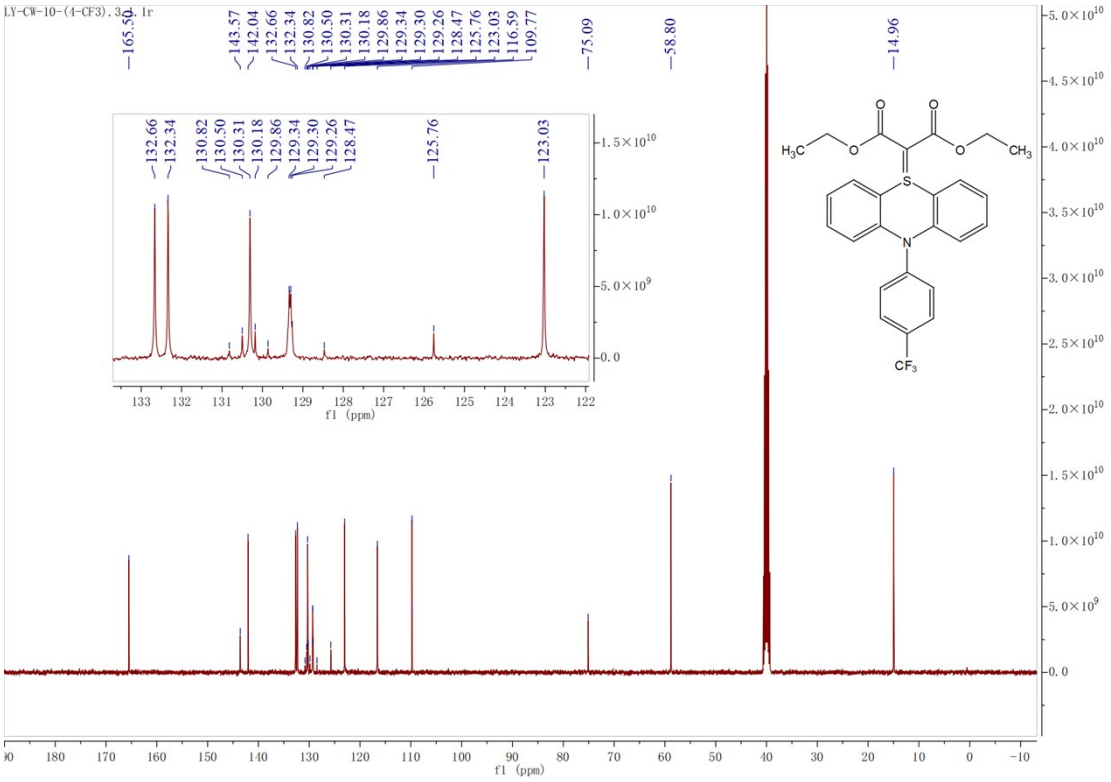
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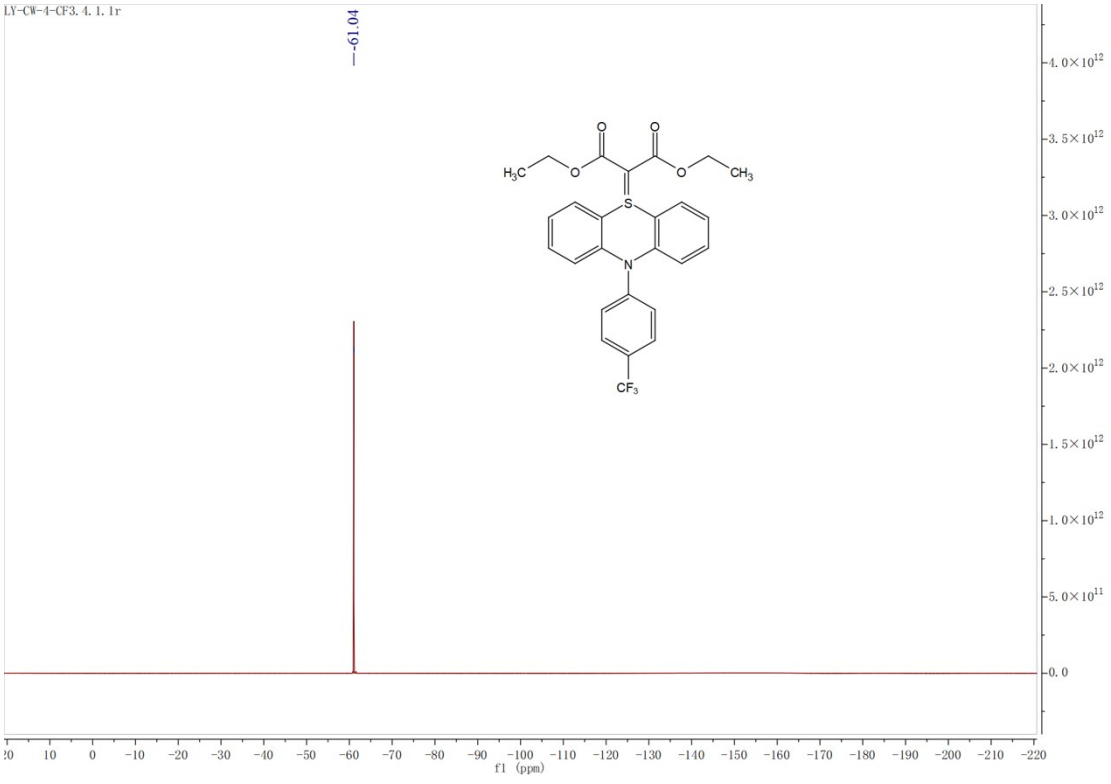
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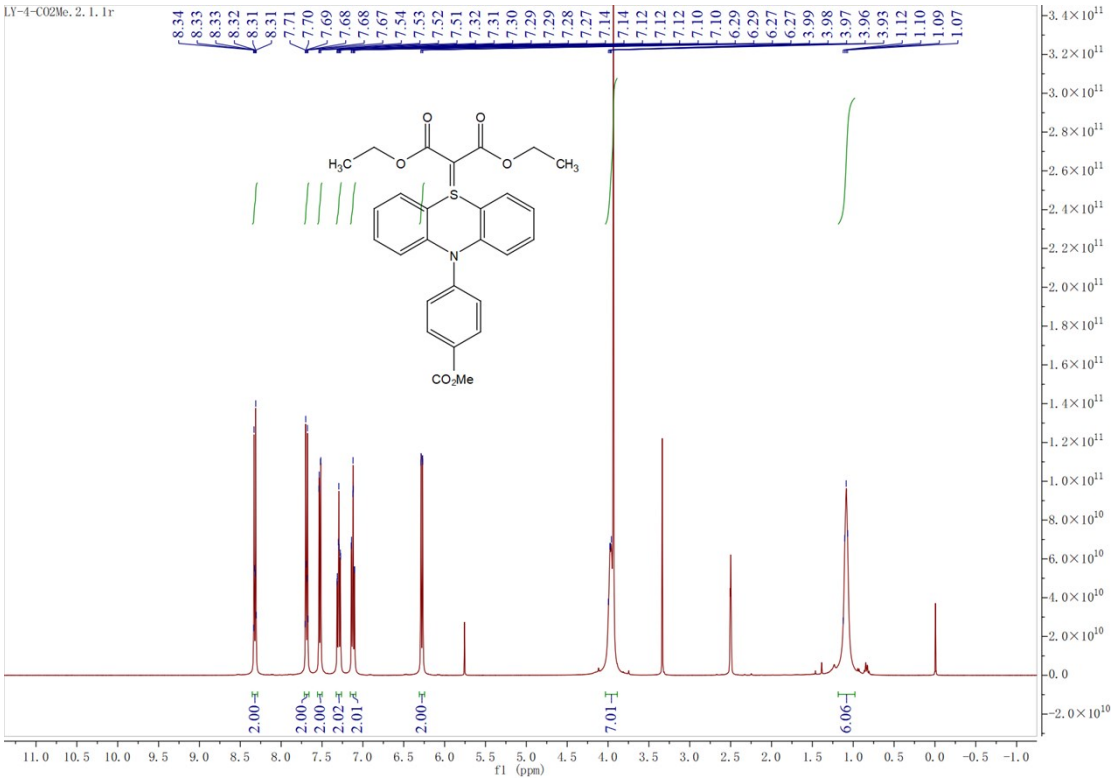
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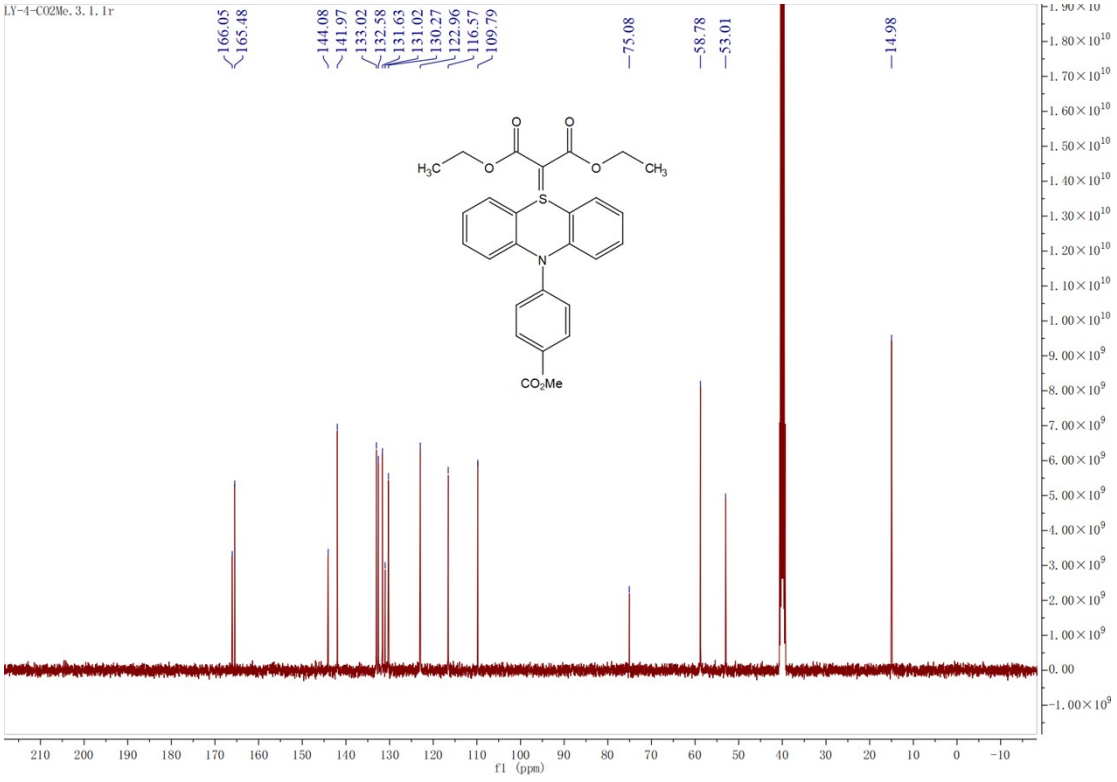
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116.57
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58.78
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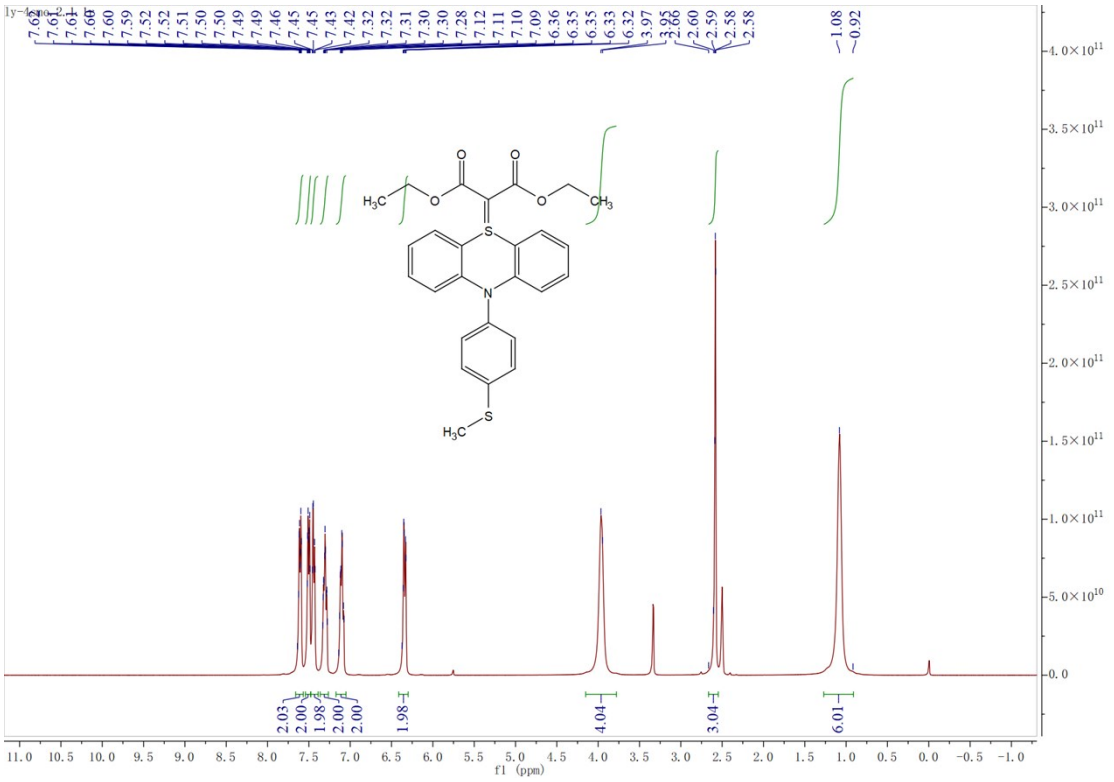
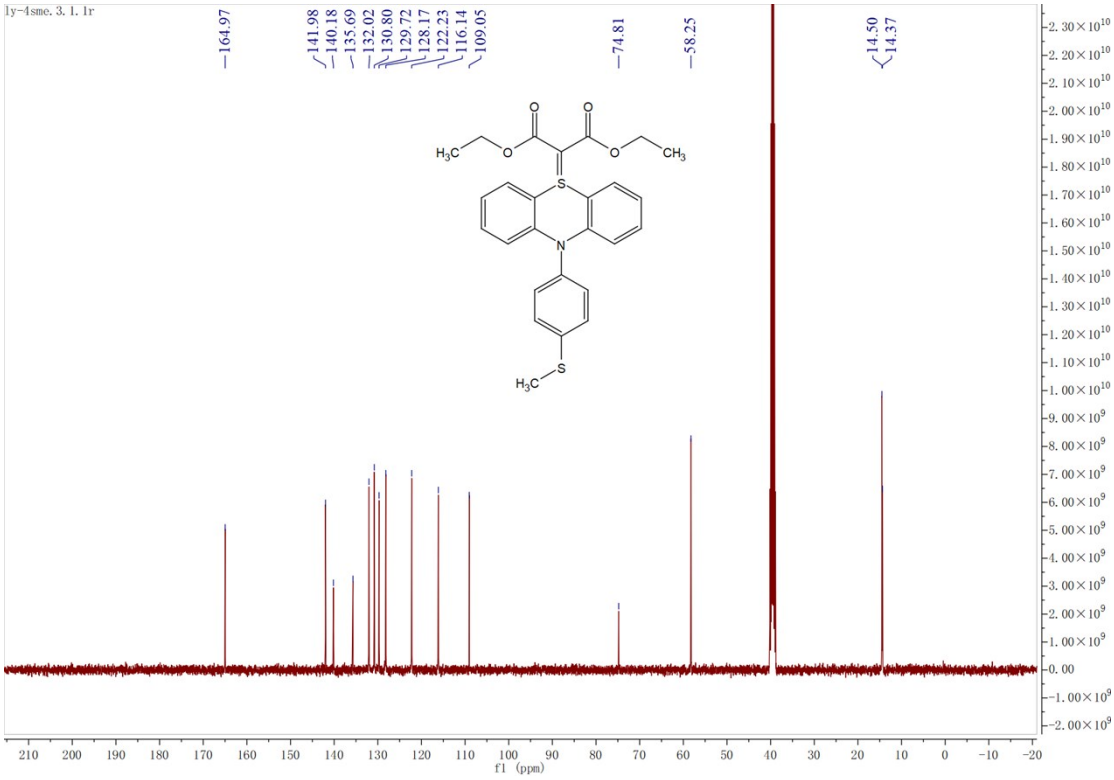
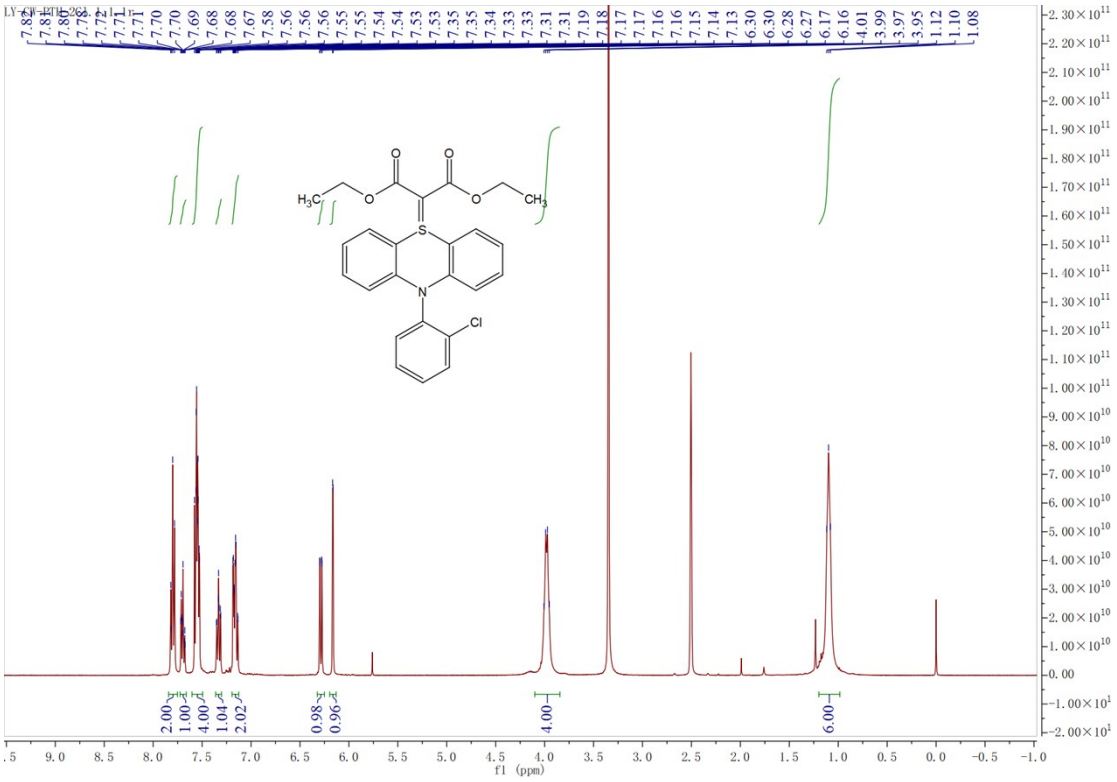
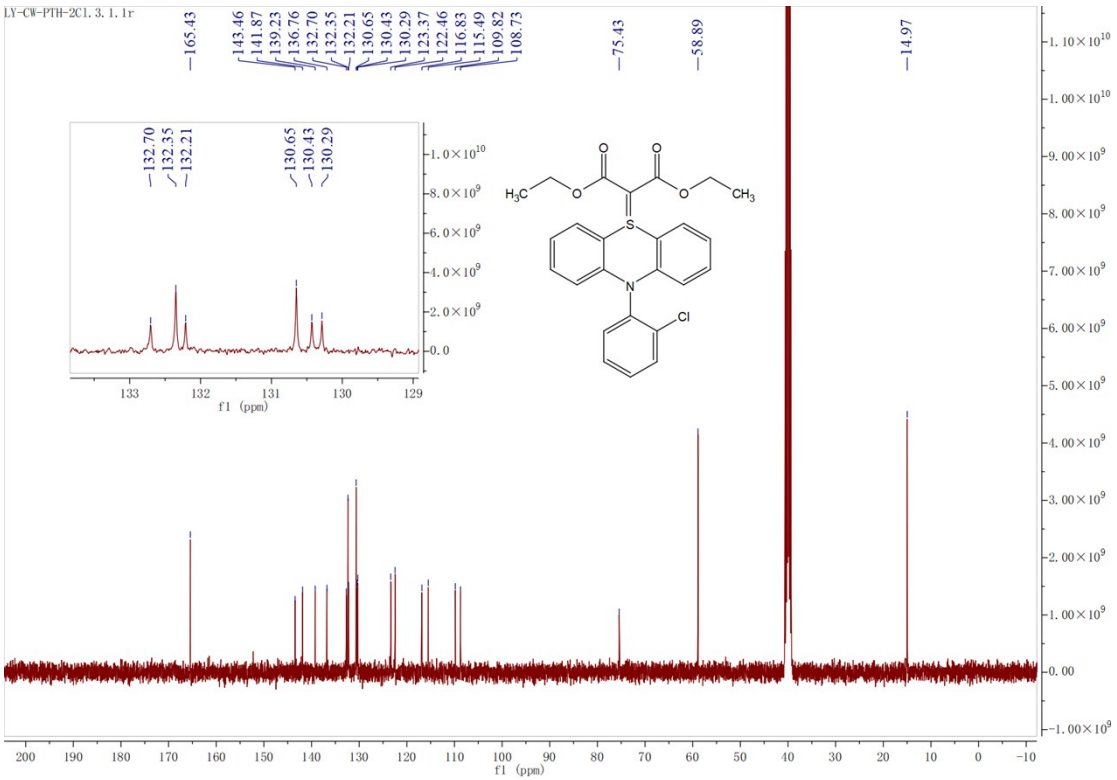
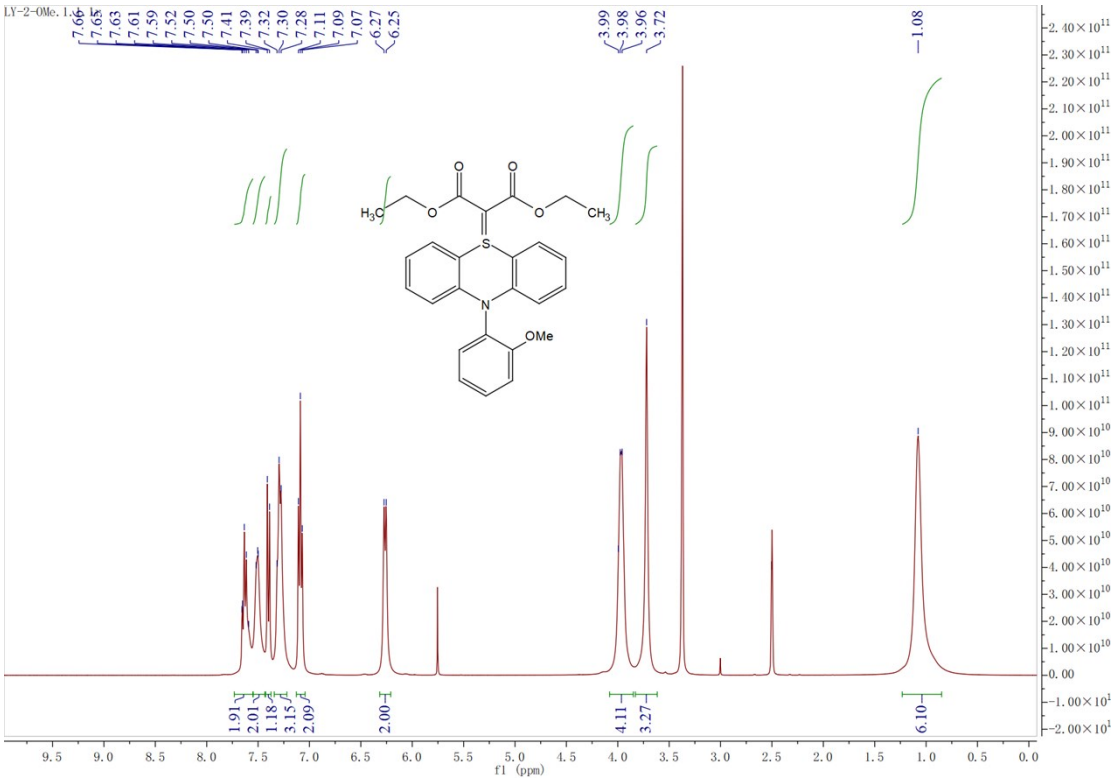
14.98
f1 (ppm)

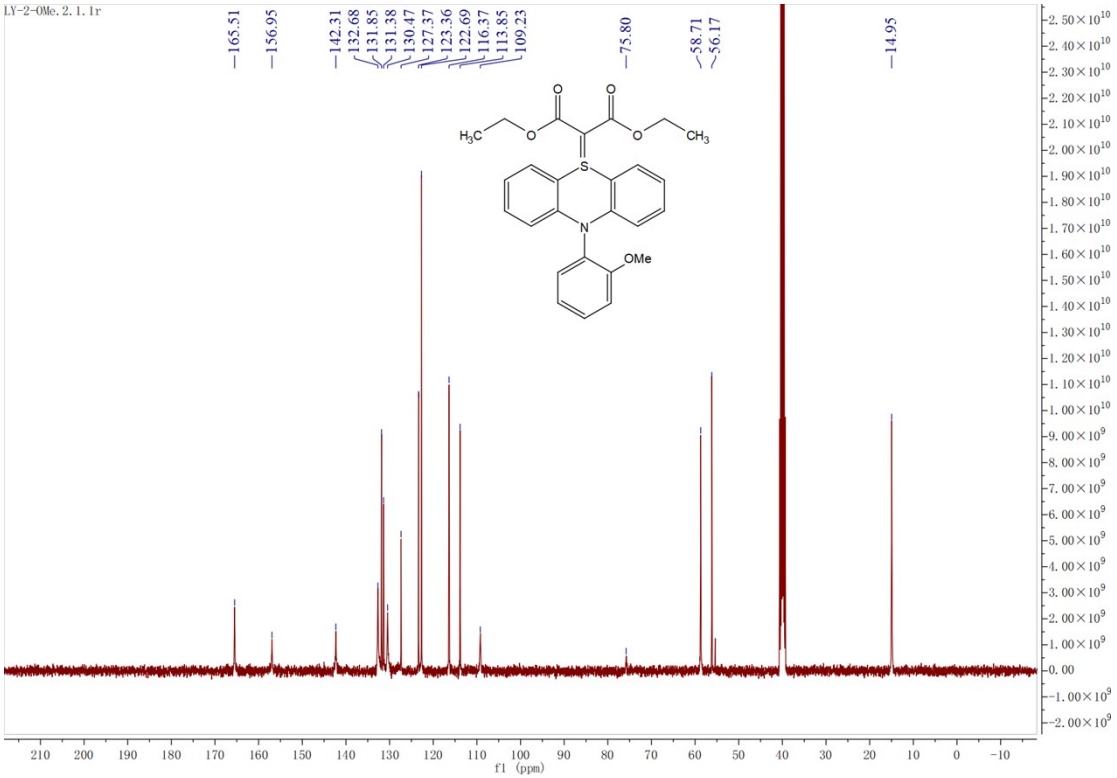


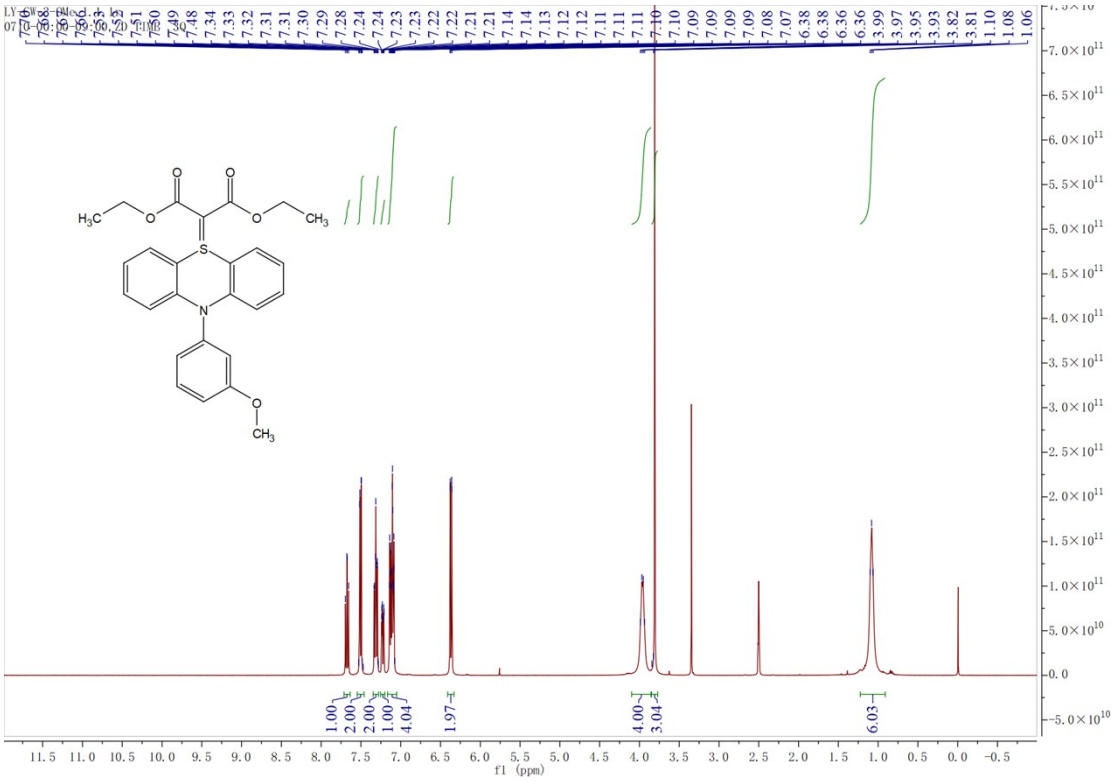


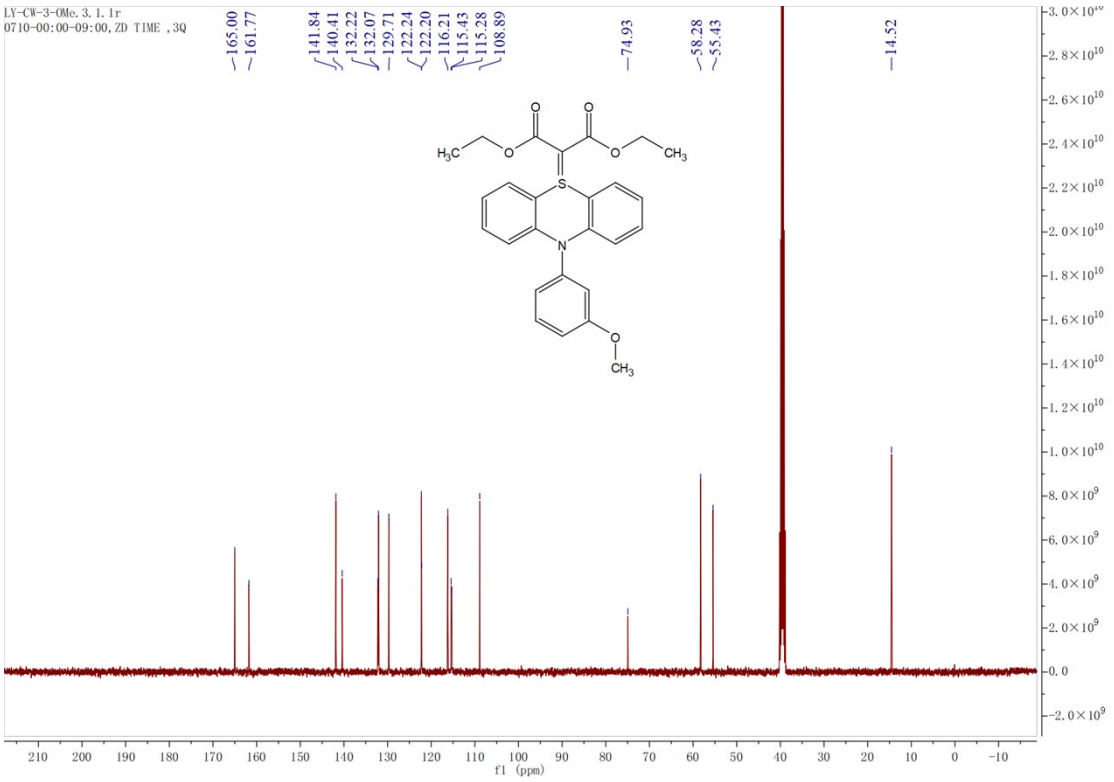


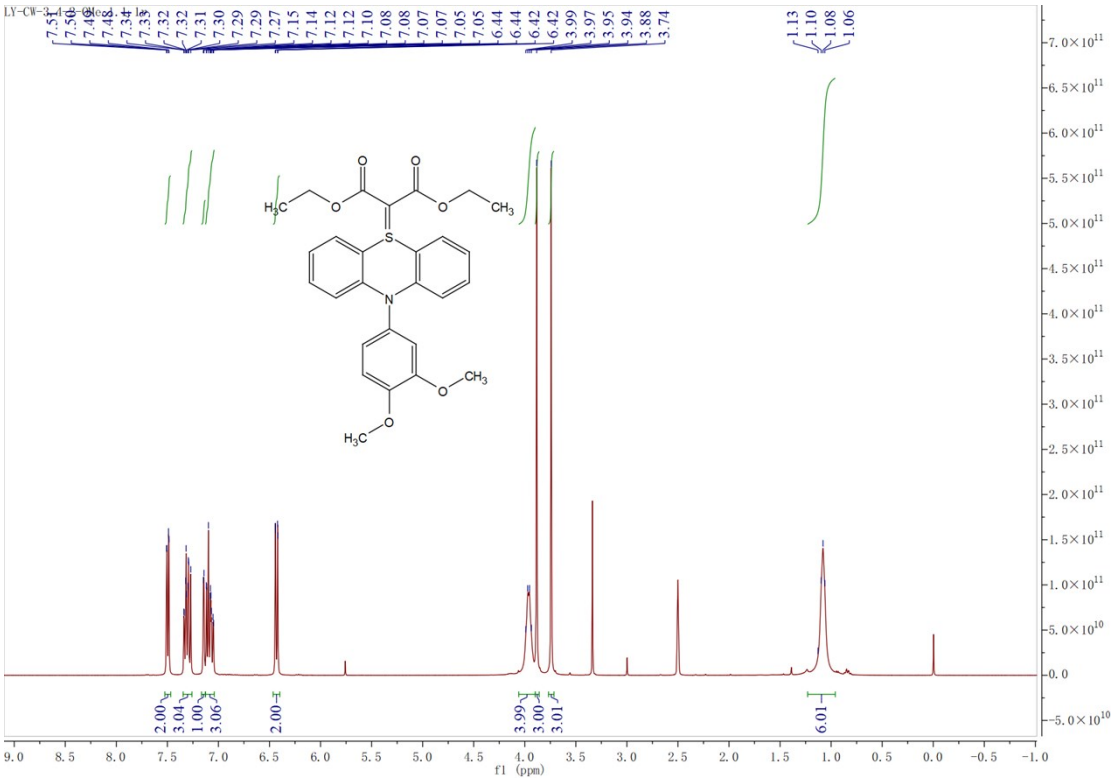


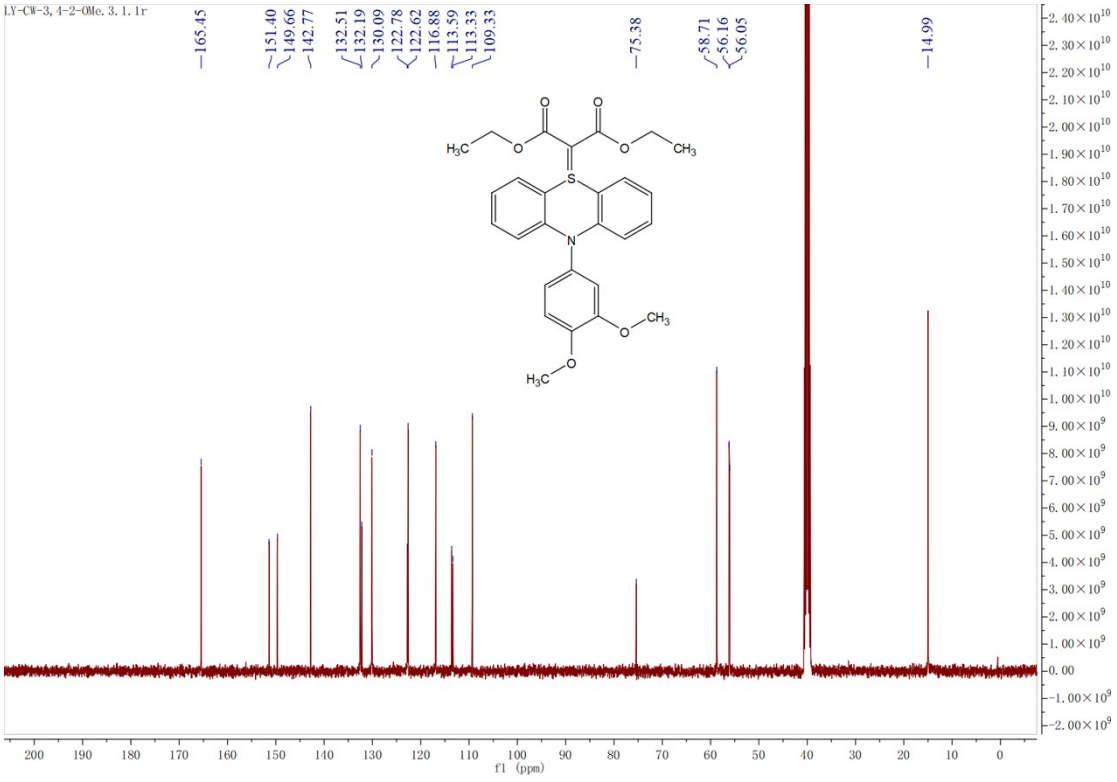

LY-2-OMe.1.1r
7.66
7.65
7.63
7.61
7.59
7.52
7.50
7.50
7.41
7.39
7.32
7.30
7.28
7.11
7.09
7.07
6.27
6.25
3.99
3.98
3.96
3.72
1.08
H3C
O
O
O
O
CH3
S
N
OMe
1.91
2.01
1.18
3.15
2.09
2.00
4.11
3.27
6.10
f1 (ppm)

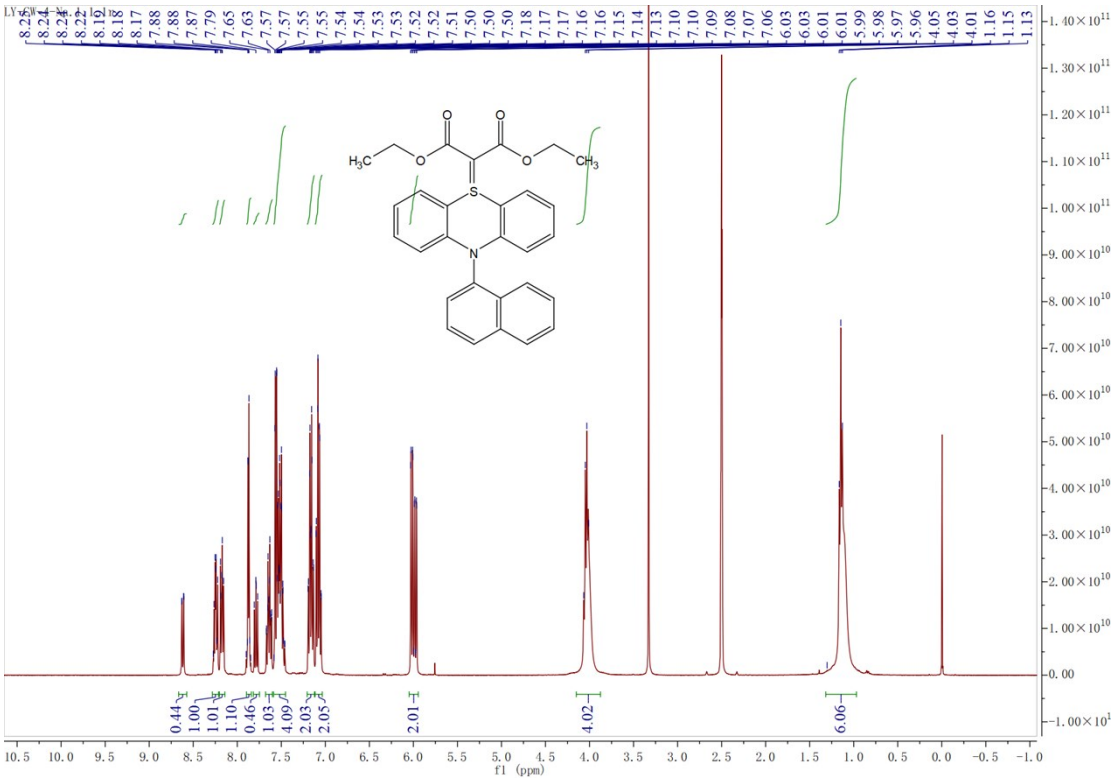

LY-2-OMe.2.1.1r
165.51
156.95
142.31
132.68
131.85
131.38
130.47
127.37
123.36
122.69
116.37
113.85
109.23
75.80
58.71
56.17
14.95
H3C
O
O
O
O
CH3
S
N
OMe
f1 (ppm)

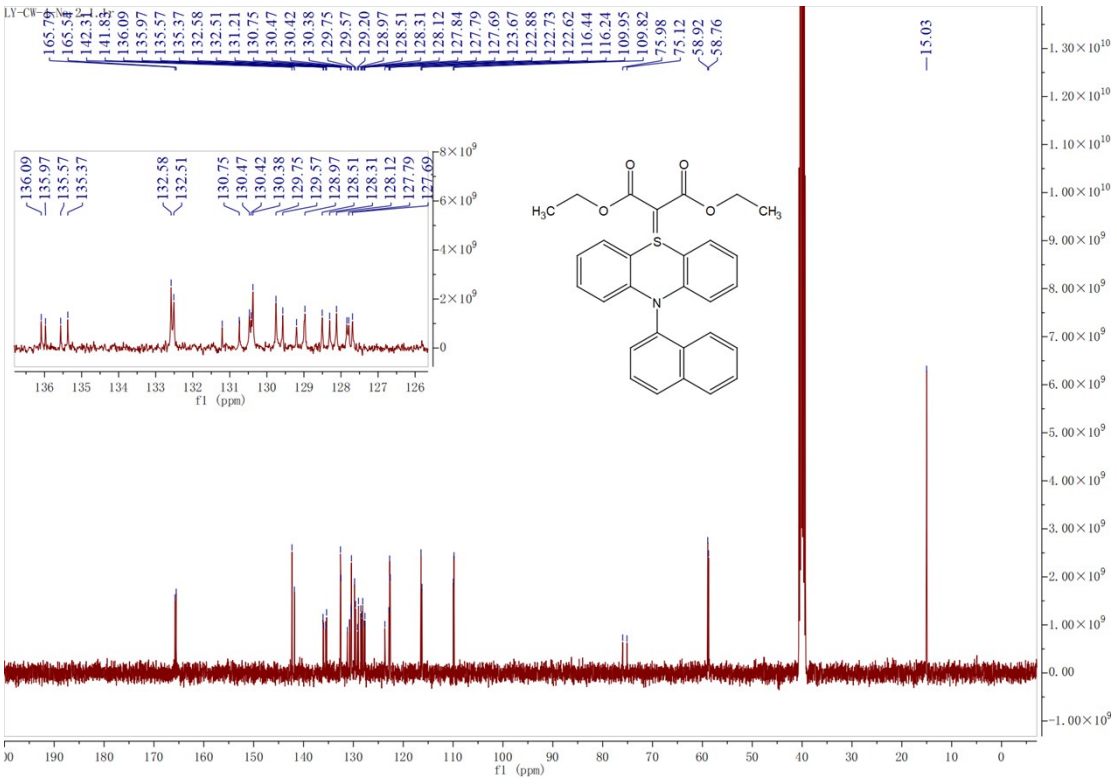


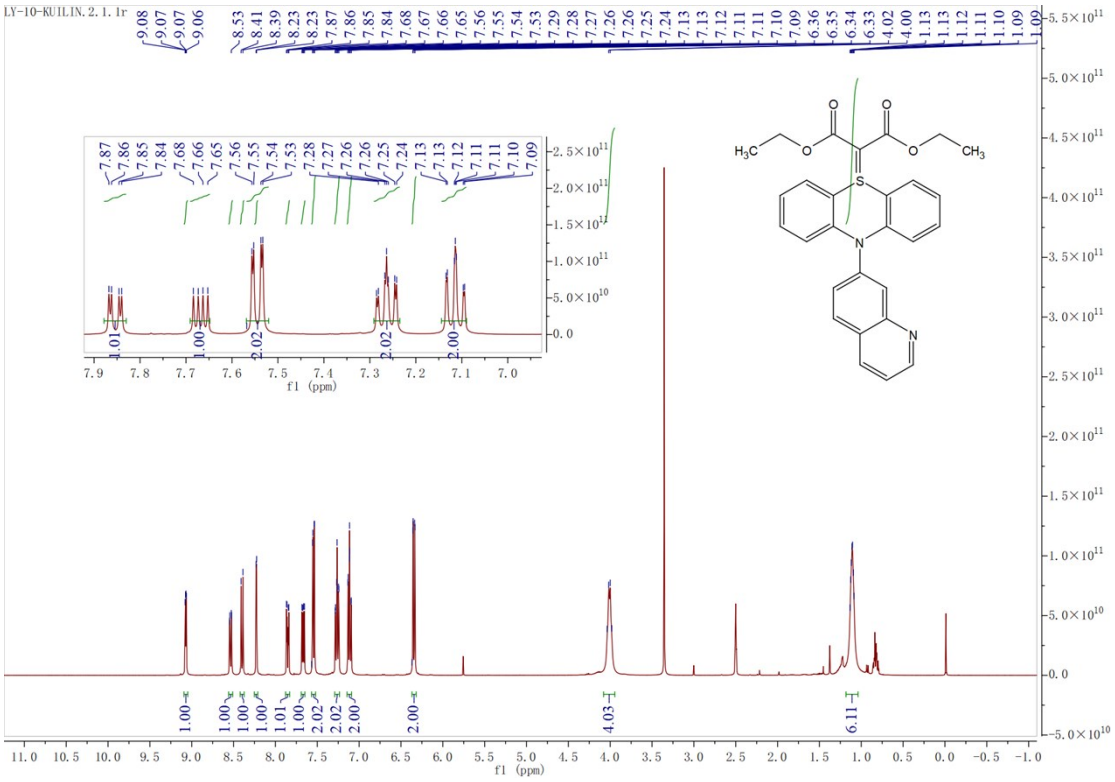


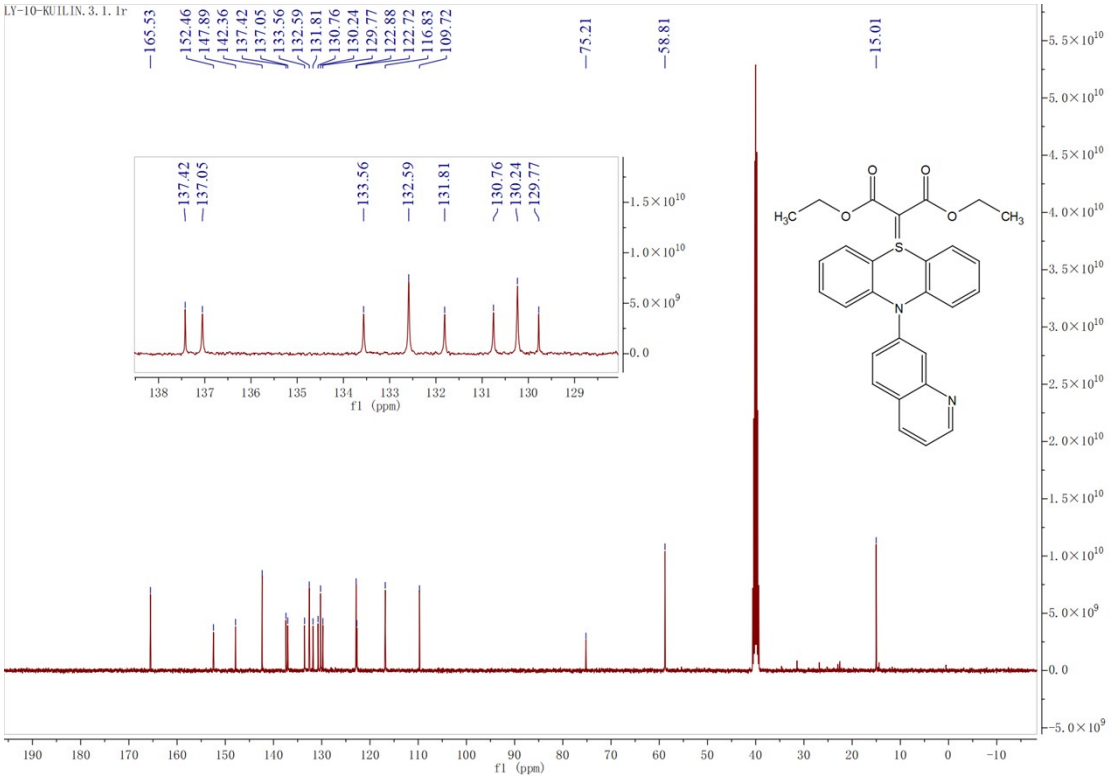


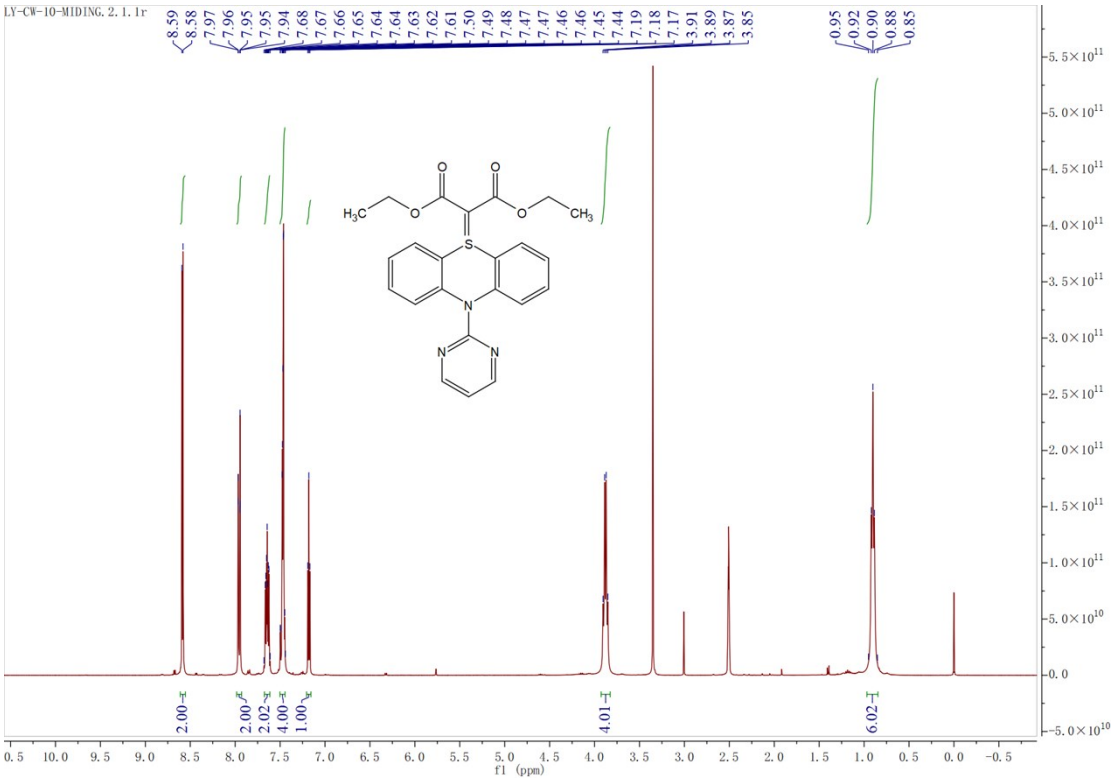


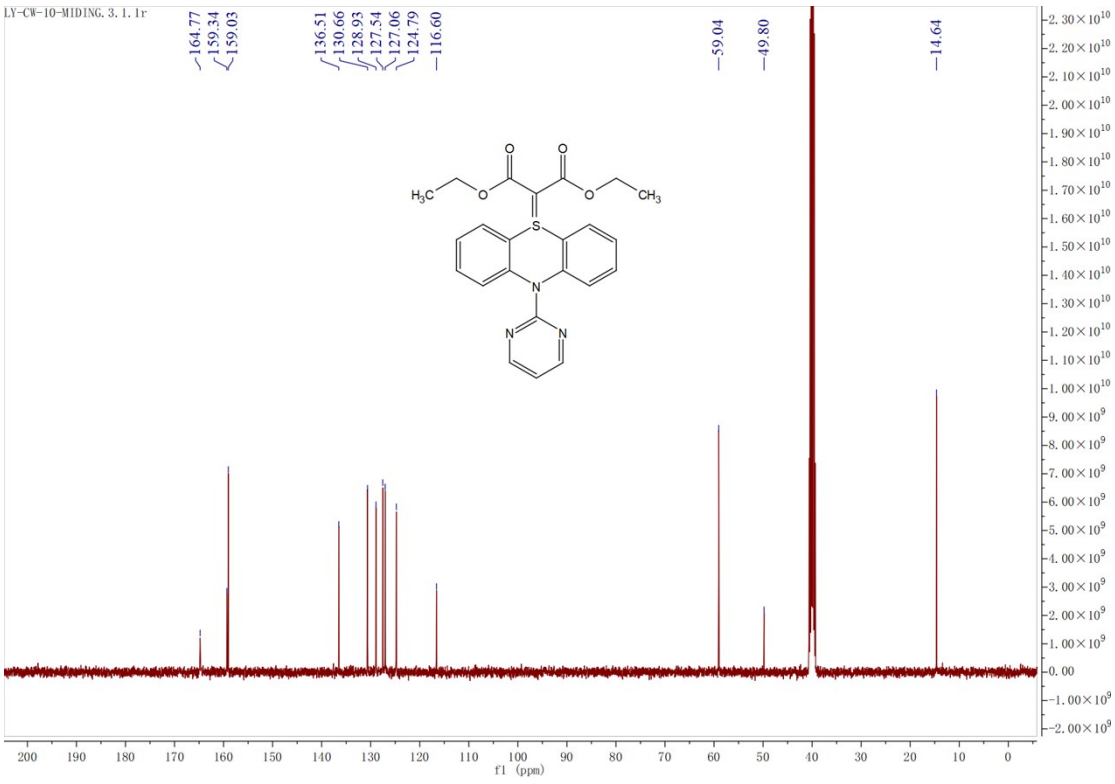


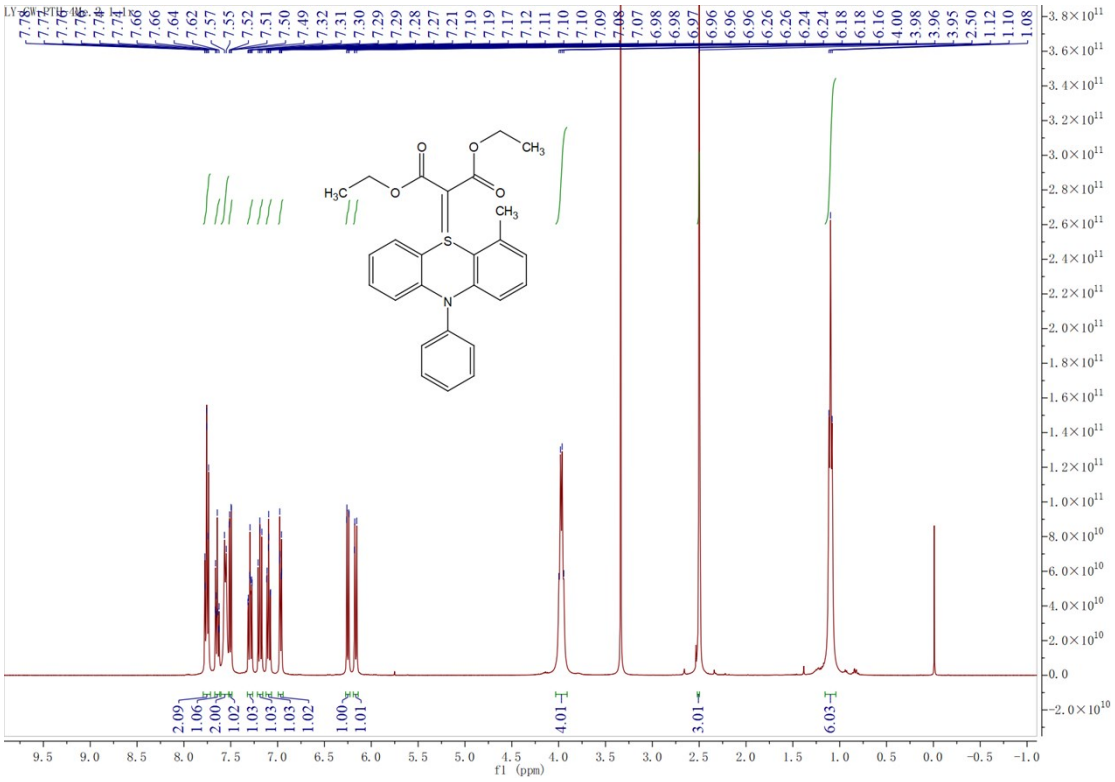



LY-10-KUILIN.2.1.1r
f1 (ppm)


LY-10-KUILIN.3.1.1r
f1 (ppm)


LY-CW-10-MIDING.2.1.1r
8.59
8.58
7.97
7.96
7.95
7.95
7.94
7.68
7.67
7.66
7.65
7.64
7.64
7.63
7.62
7.61
7.50
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.19
7.18
7.17
3.91
3.89
3.87
3.85
0.95
0.92
0.90
0.88
0.85
2.00
2.00
2.02
4.00
1.00
4.01
6.02
f1 (ppm)


LY-CW-10-MIDING.3.1.1r
164.77
159.34
159.03
136.51
130.66
128.93
127.54
127.06
124.79
116.60
59.04
49.80
14.64
f1 (ppm)


7.78
7.77
7.76
7.75
7.74
7.73
7.66
7.64
7.62
7.57
7.55
7.52
7.51
7.50
7.49
7.32
7.31
7.30
7.29
7.28
7.27
7.21
7.19
7.17
7.12
7.11
7.10
7.09
7.08
7.07
6.98
6.97
6.96
6.26
6.24
6.18
6.16
4.00
3.98
3.96
3.95
2.50
1.12
1.10
1.08
2.09
1.06
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1.02
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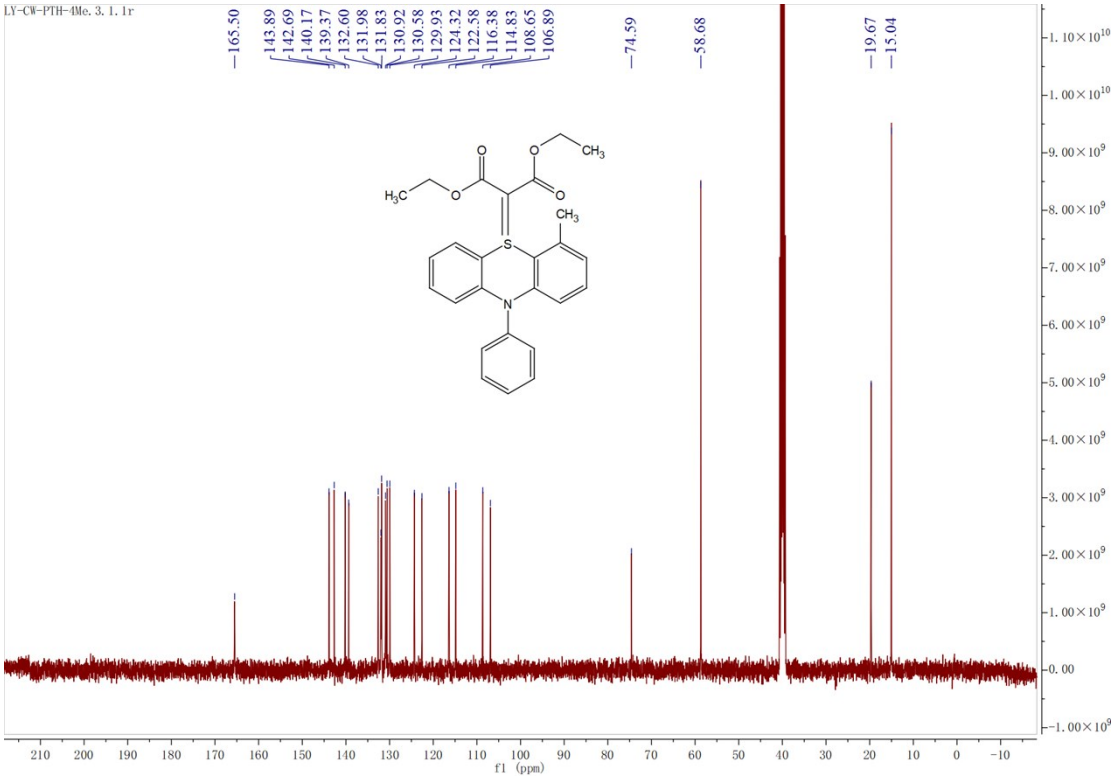
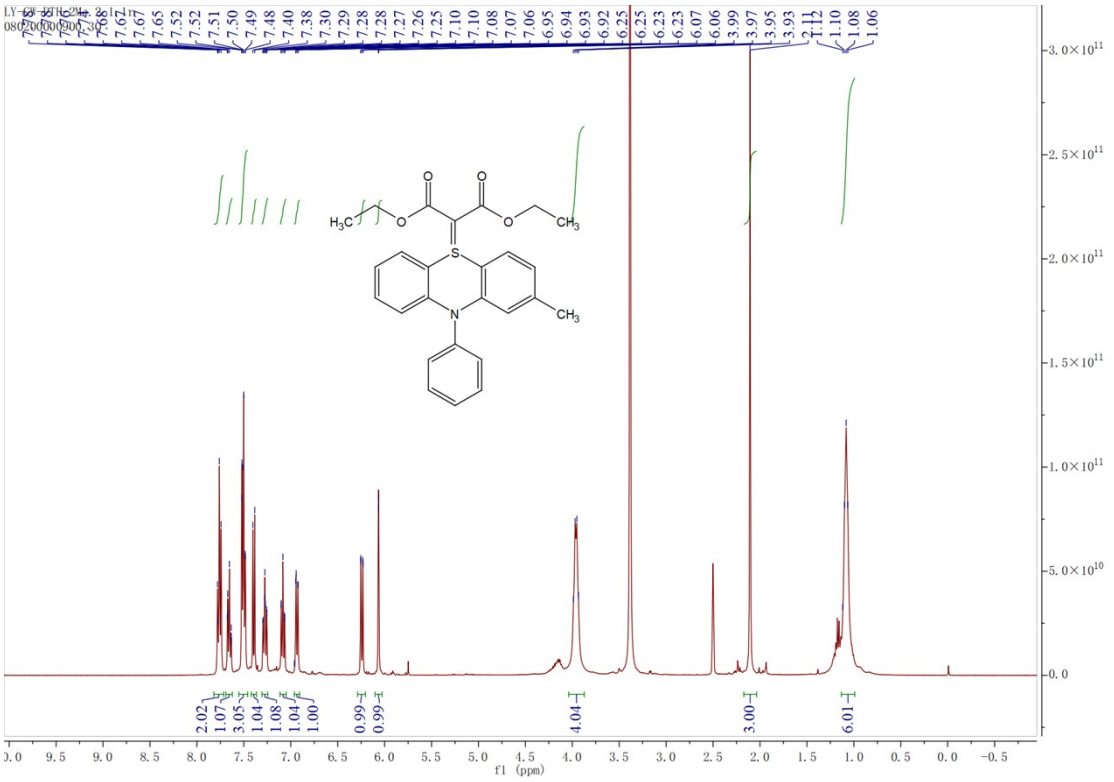
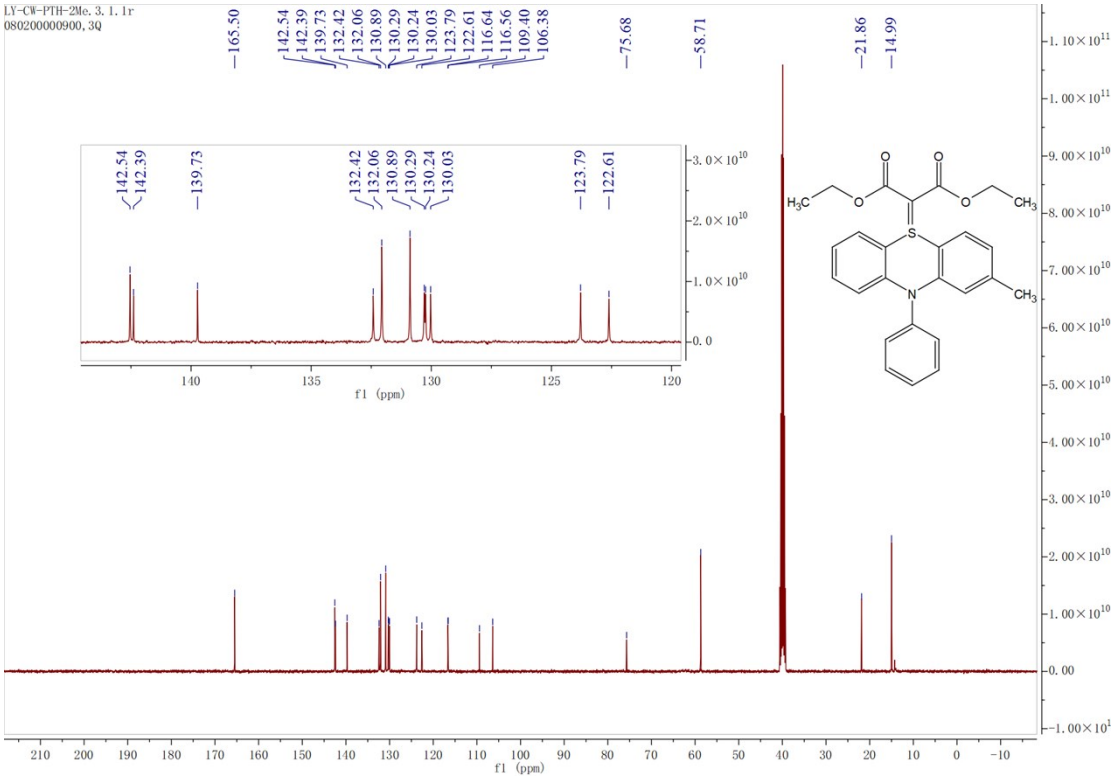
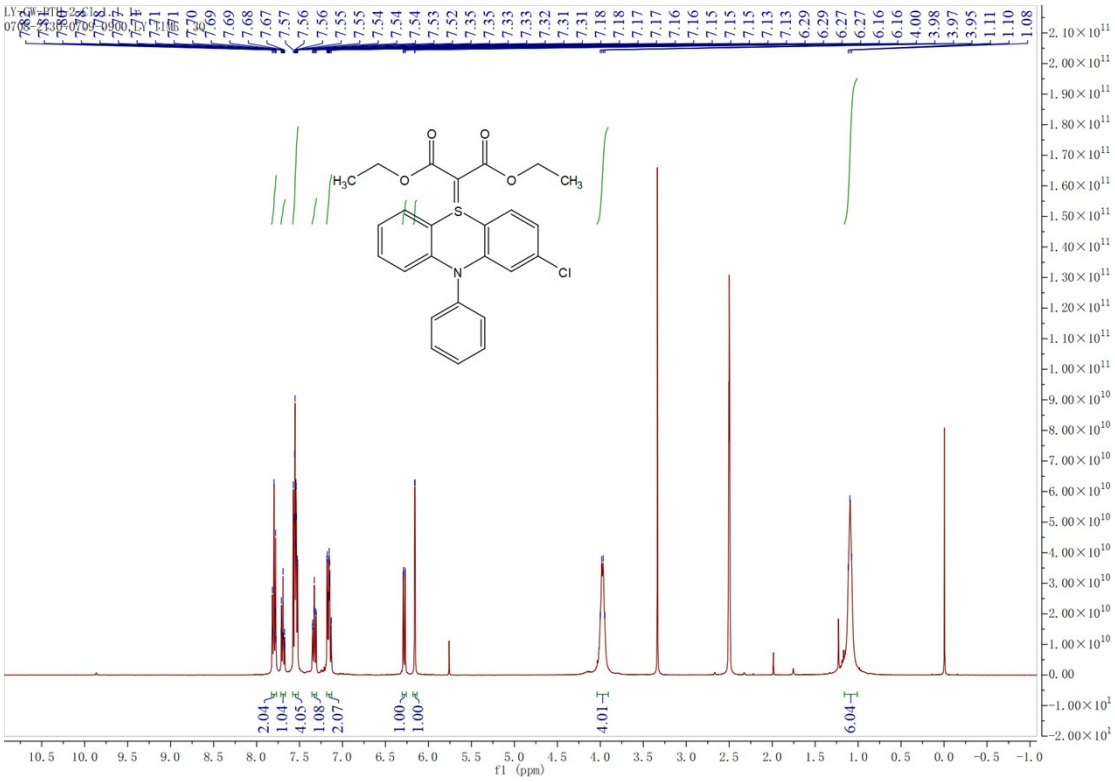
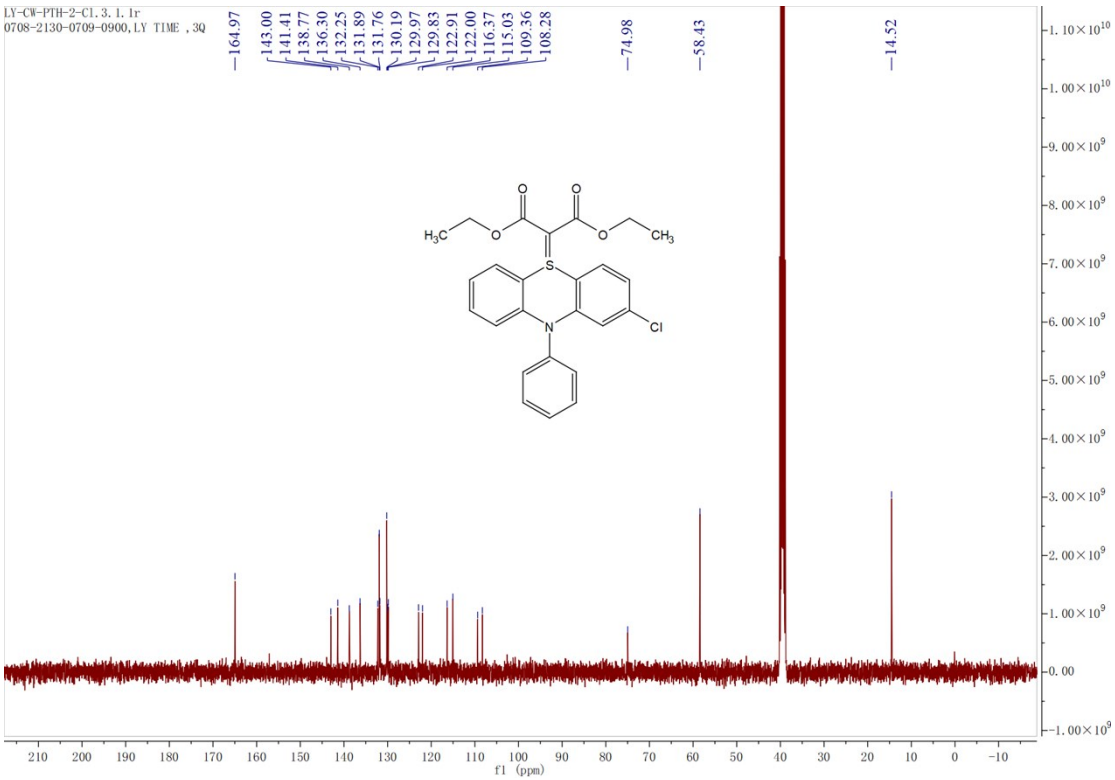
1.03
1.03
1.02
1.00
1.01
4.01
3.01
6.03
f1 (ppm)

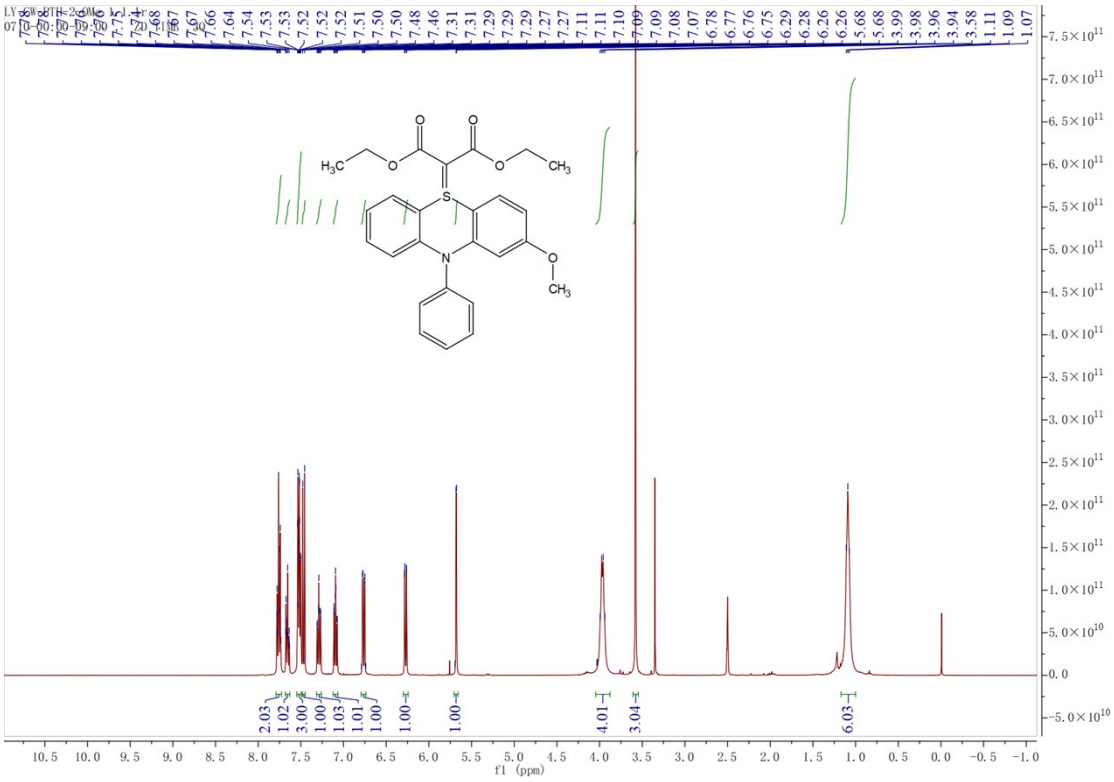

LY-CW-PTH-4Me.3.1.1r
165.50
143.89
142.69
140.17
139.37
132.60
131.98
131.83
130.92
130.58
129.93
124.32
122.58
116.38
114.83
108.65
106.89
74.59
58.68
19.67
15.04
f1 (ppm)

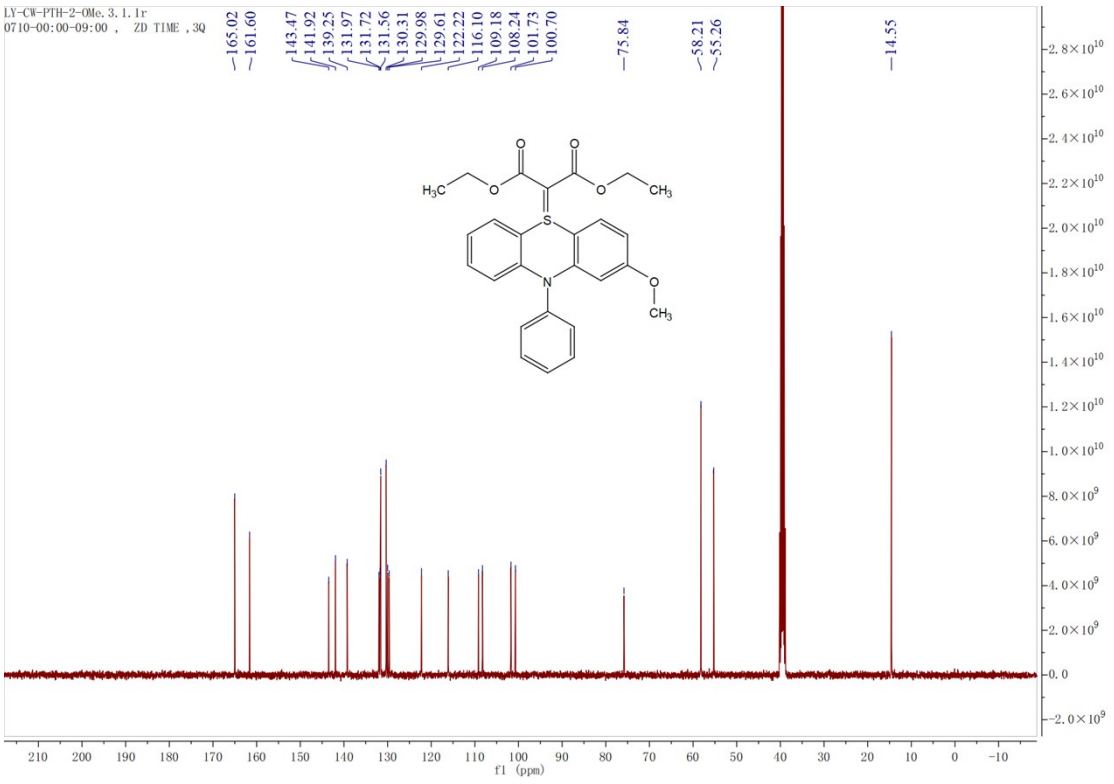


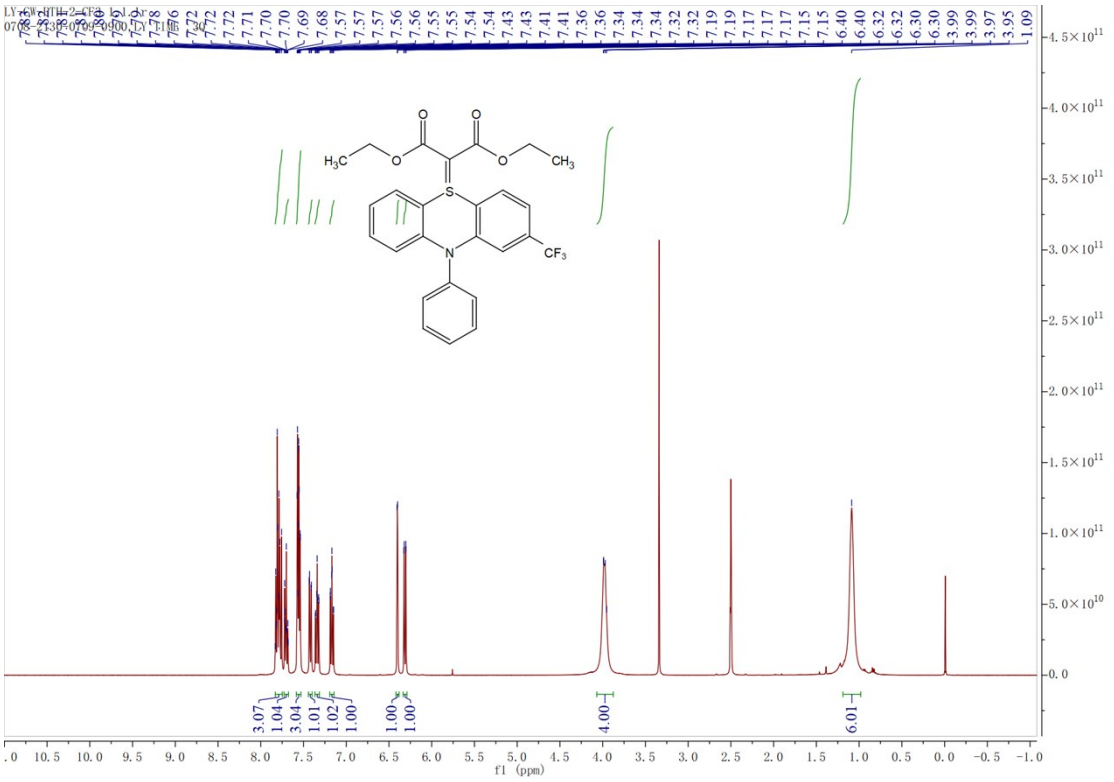


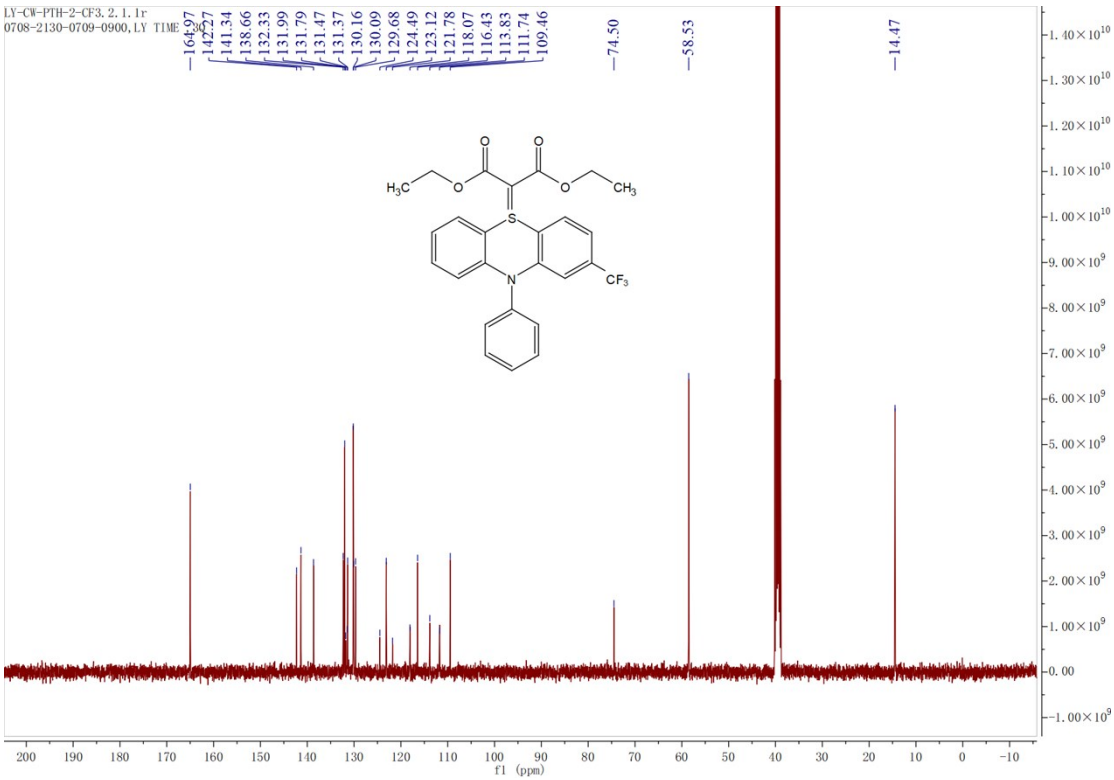

2.04
1.04
4.05
1.08
2.07
1.00
1.00
4.01
6.04
f1 (ppm)

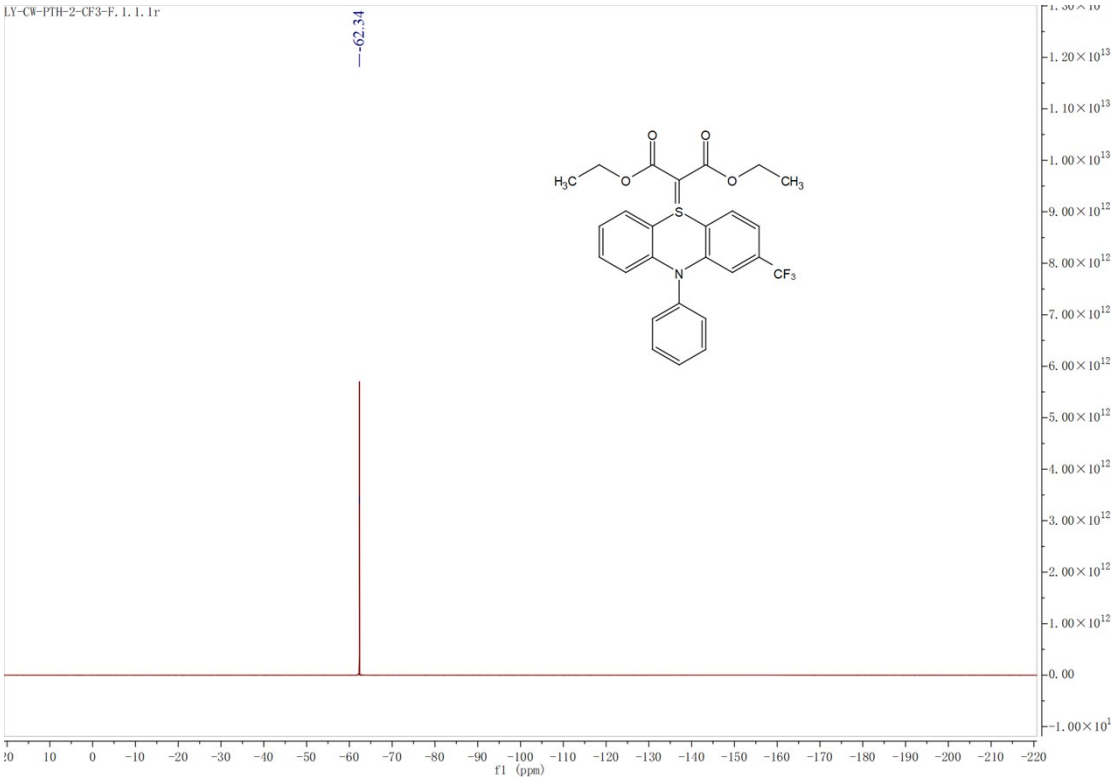

LY-CW-PTH-2-C1.3.1.1r
0708-2130-0709-0900,LY TIME ,3Q
164.97
143.00
141.41
138.77
136.30
132.25
131.89
131.76
130.19
129.97
129.83
122.91
122.00
116.37
115.03
109.36
108.28
74.98
58.43
14.52
f1 (ppm)

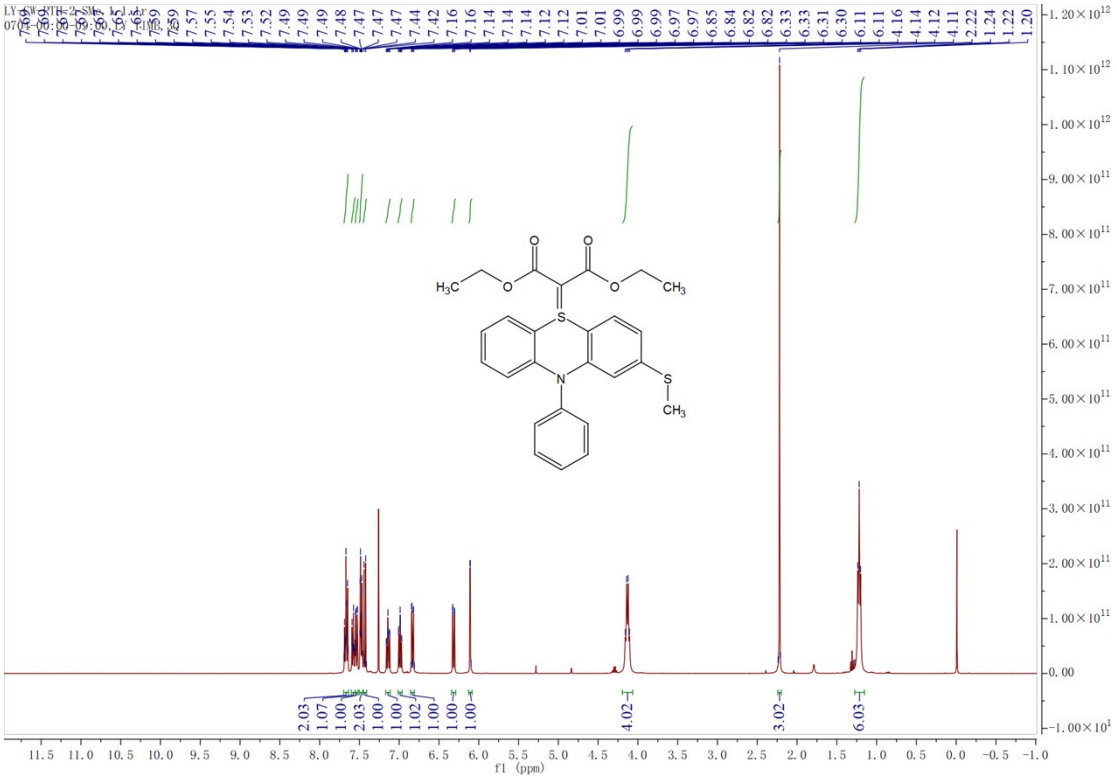


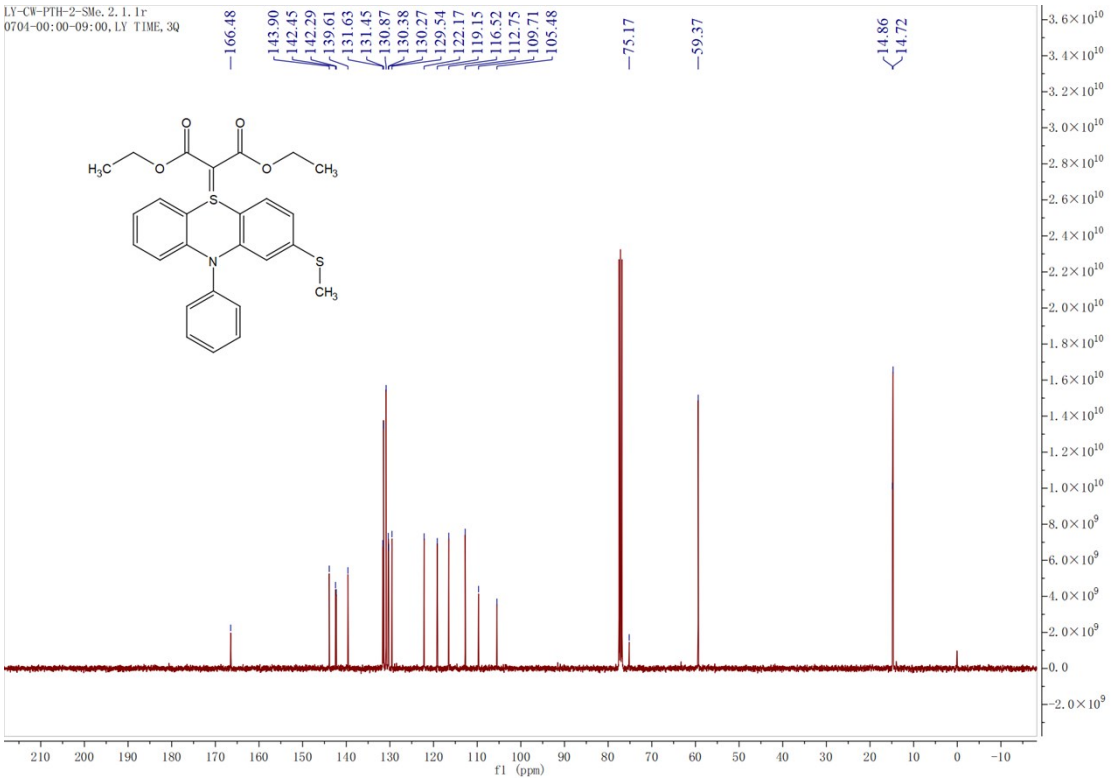


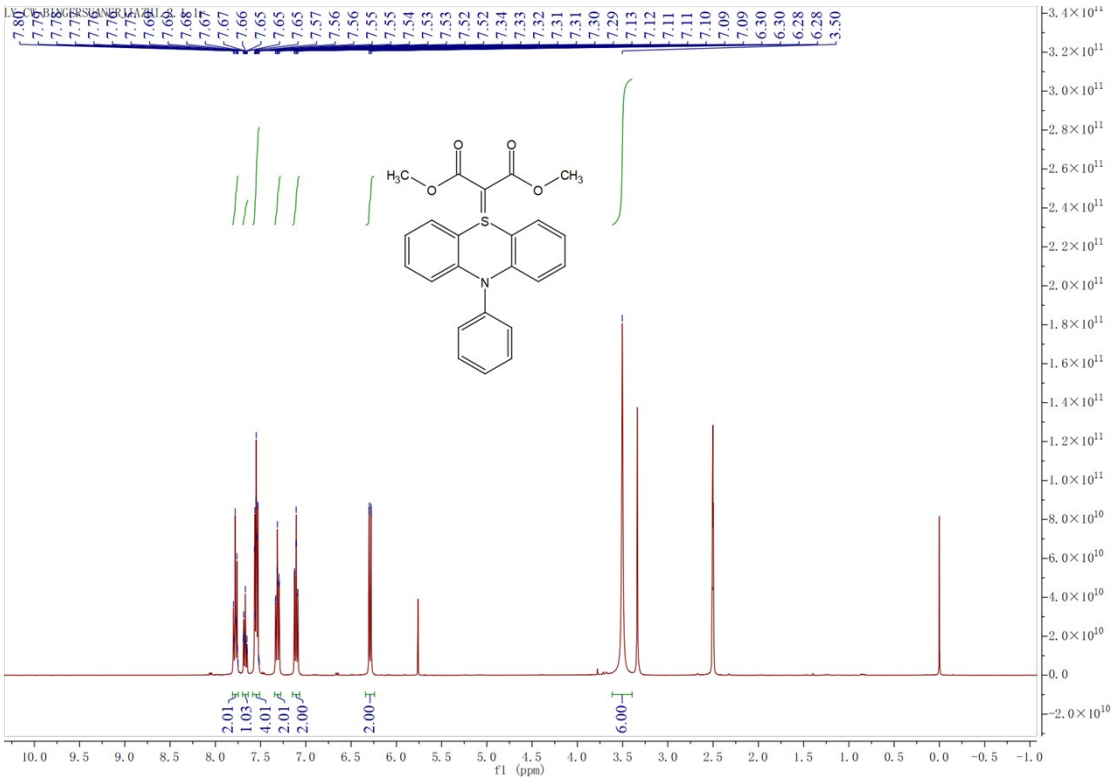

3.07
1.04
3.04
1.01
1.02
1.00
1.00
1.00
4.00
6.01
f1 (ppm)

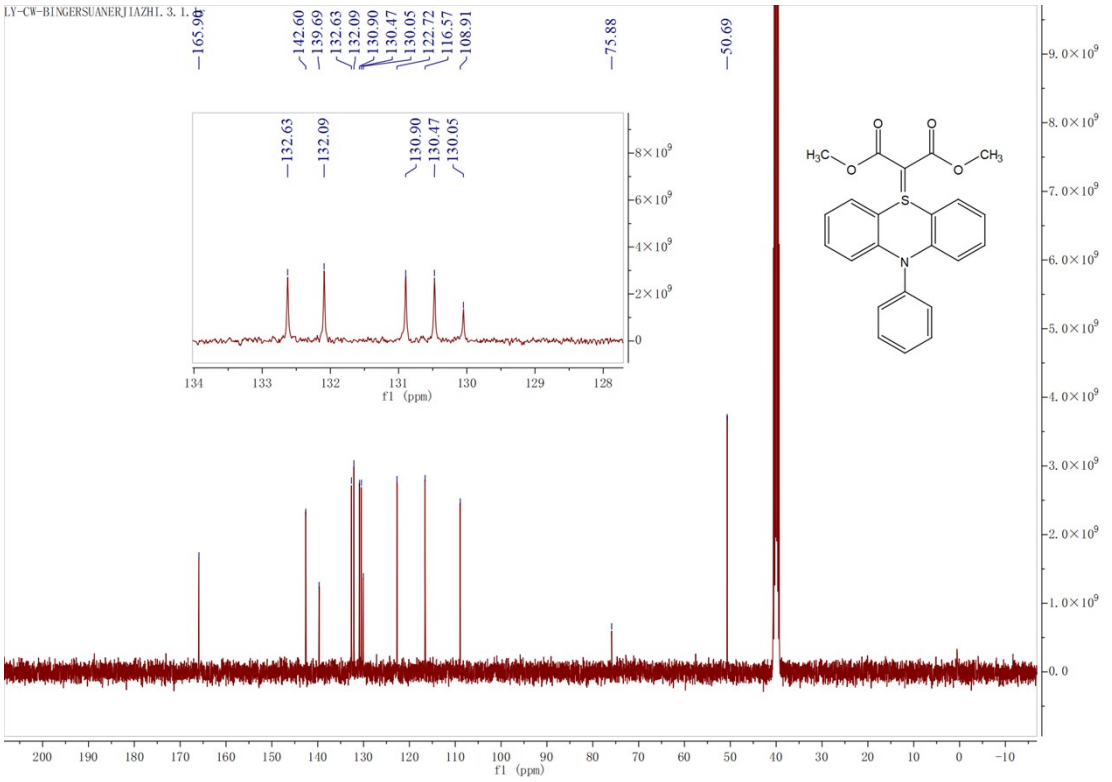

164.97
142.27
141.34
138.66
132.33
131.99
131.79
131.47
131.37
130.16
130.09
129.68
124.49
123.12
121.78
118.07
116.43
113.83
111.74
109.46
74.50
58.53
14.47
f1 (ppm)

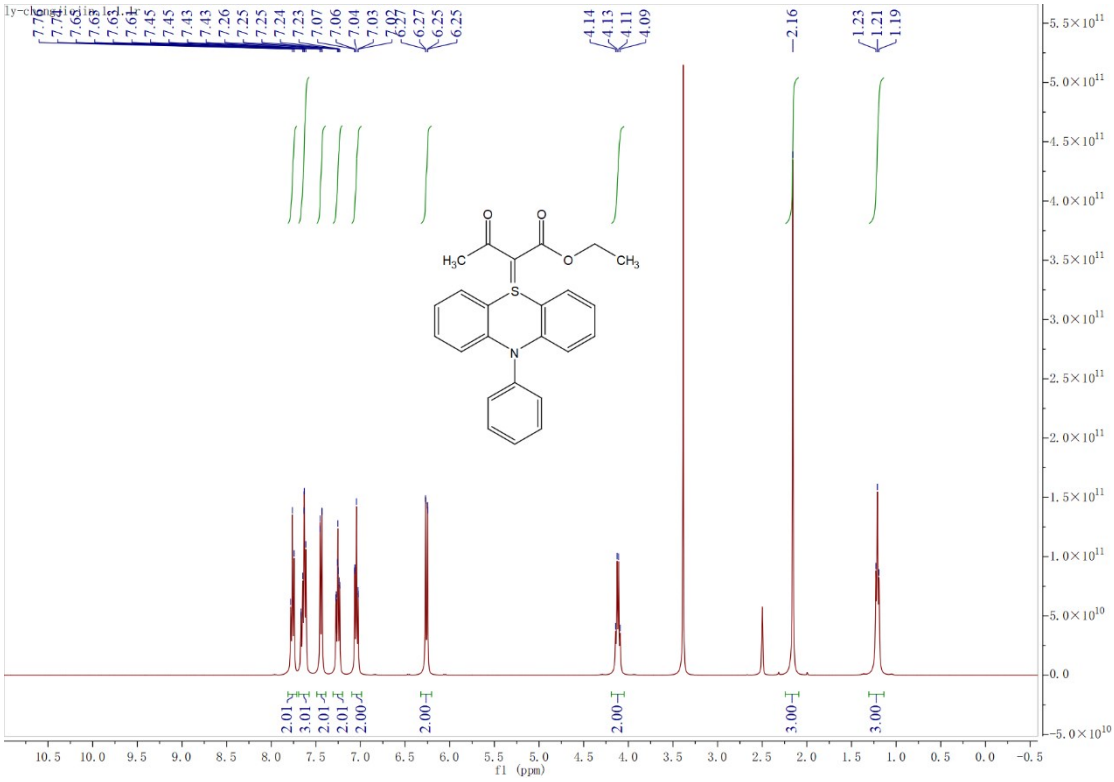

LY-CW-PTH-2-CF3-F.1.1.1r
-62.34
f1 (ppm)

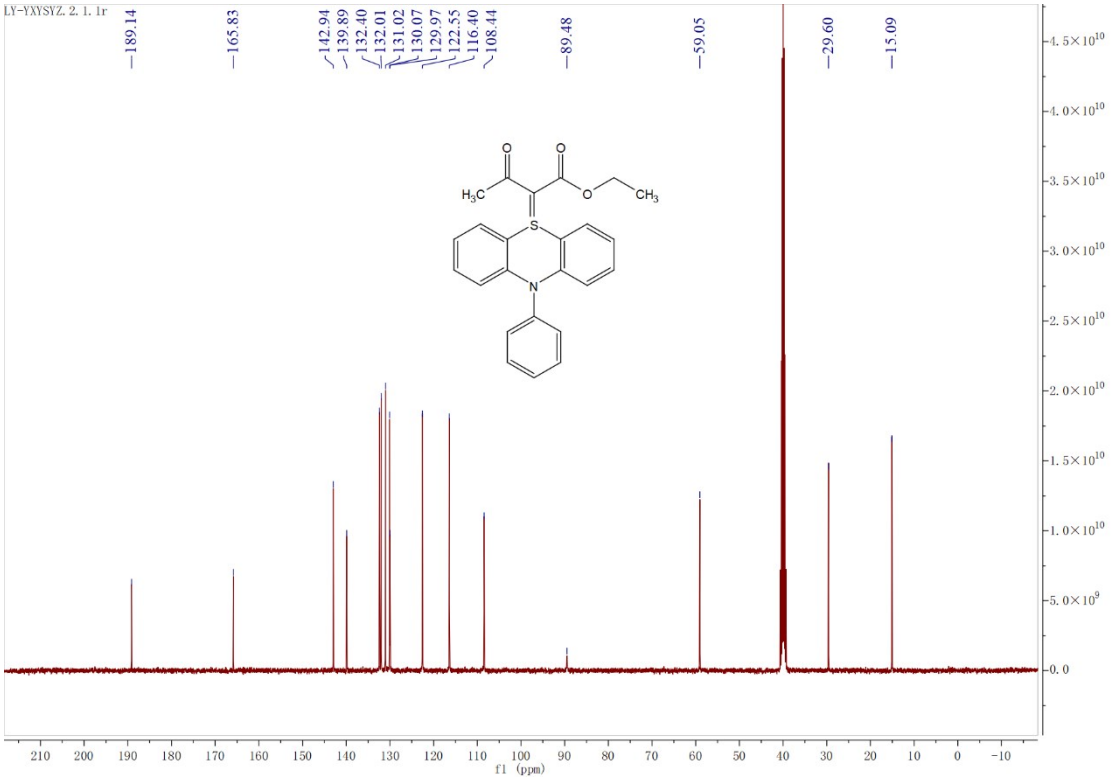

2.03
1.07
1.00
2.03
1.00
1.00
1.02
1.00
1.00
1.00
4.02
3.02
6.03
f1 (ppm)

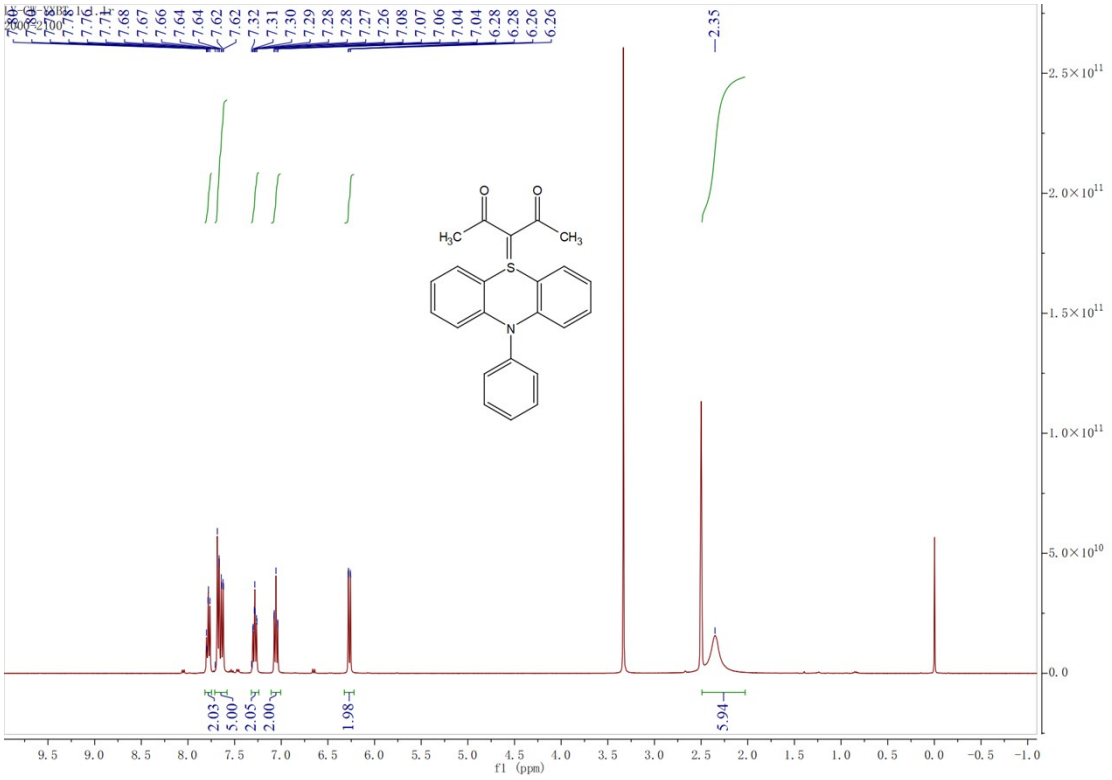

LY-CW-PTH-2-SMe. 2. 1. 1r
0704-00:00-09:00, LY TIME, 3Q
166.48
143.90
142.45
142.29
139.61
131.63
131.45
130.87
130.38
130.27
129.54
122.17
119.15
116.52
112.75
109.71
105.48
75.17
59.37
14.86
14.72
f1 (ppm)

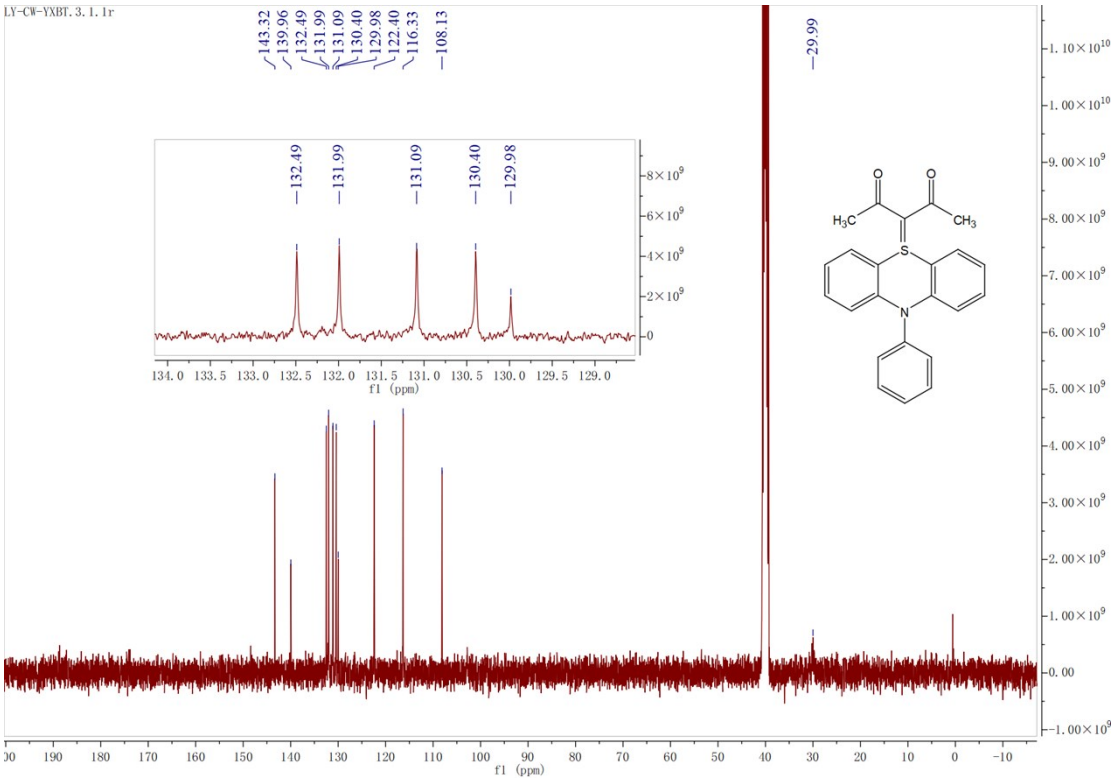

7.80
7.79
7.78
7.77
7.76
7.75
7.68
7.67
7.66
7.65
7.57
7.56
7.55
7.54
7.53
7.52
7.34
7.33
7.32
7.31
7.30
7.29
7.13
7.12
7.11
7.10
7.09
6.30
6.28
3.50
2.01
1.03
4.01
2.01
2.00
2.00
6.00
f1 (ppm)

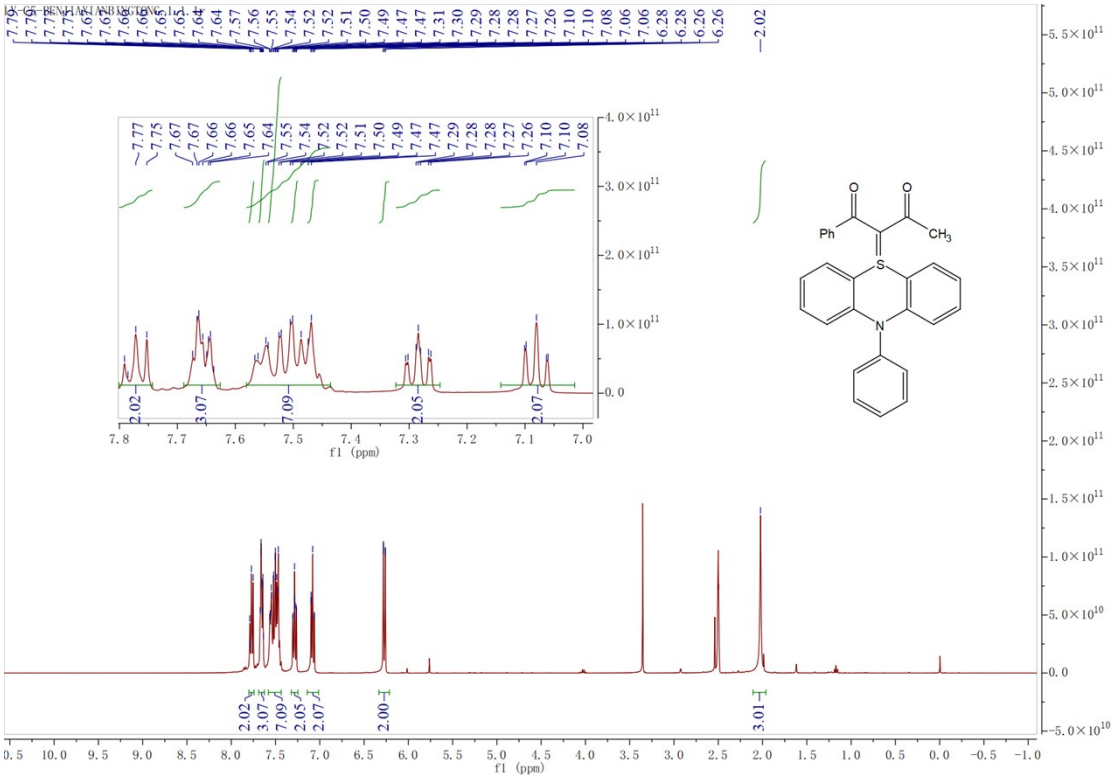

LY-CW-BINGERSUANERJIAZHI. 3. 1. 1
165.90
142.60
139.69
132.63
132.09
130.90
130.47
130.05
122.72
116.57
108.91
75.88
50.69
132.63
132.09
130.90
130.47
130.05
f1 (ppm)
f1 (ppm)

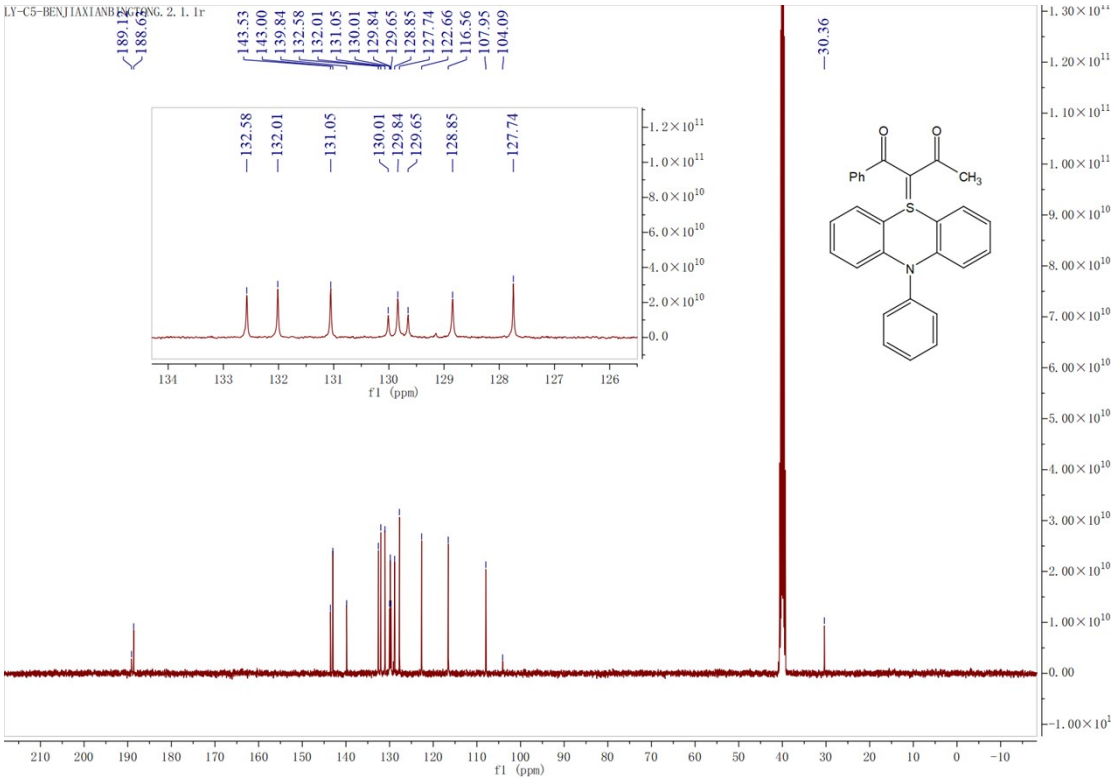

7.76
7.74
7.65
7.63
7.61
7.45
7.43
7.26
7.25
7.24
7.23
7.07
7.06
7.04
7.03
7.02
6.27
6.25
6.25
4.14
4.13
4.11
4.09
2.16
1.23
1.21
1.19
2.01
3.01
2.01
2.01
2.00
2.00
2.00
3.00
3.00
f1 (ppm)


LY-YXYSYZ. 2. 1. 1r
189.14
165.83
142.94
139.89
132.40
132.01
131.02
130.07
129.97
122.55
116.40
108.44
89.48
59.05
29.60
15.09
f1 (ppm)


7.78
7.76
7.71
7.68
7.67
7.66
7.64
7.64
7.62
7.62
7.32
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.08
7.07
7.06
7.04
7.04
6.28
6.26
6.26
2.35
2.03
5.00
2.05
2.00
1.98
5.94
f1 (ppm)


LY-CW-YXBT.3.1.1r
143.32
139.96
132.49
131.99
131.09
130.40
129.98
122.40
116.33
108.13
29.99
f1 (ppm)


2.02
3.07
7.09
2.05
2.07
2.00
3.01
f1 (ppm)


LY-C5-BENJIAXIANBENGTONG. 2. 1. 1r
189.12
188.62
143.53
143.00
139.84
132.58
132.01
131.05
130.01
129.84
129.65
128.85
127.74
122.66
116.56
107.95
104.09
30.36
132.58
132.01
131.05
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129.84
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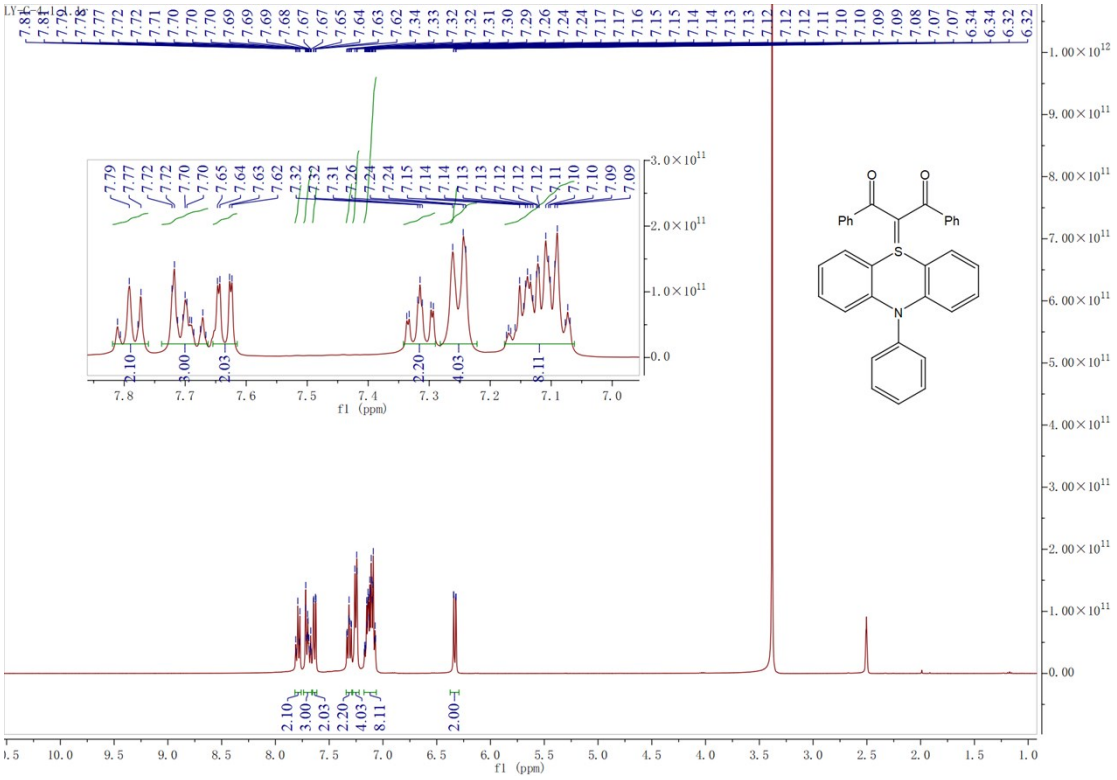
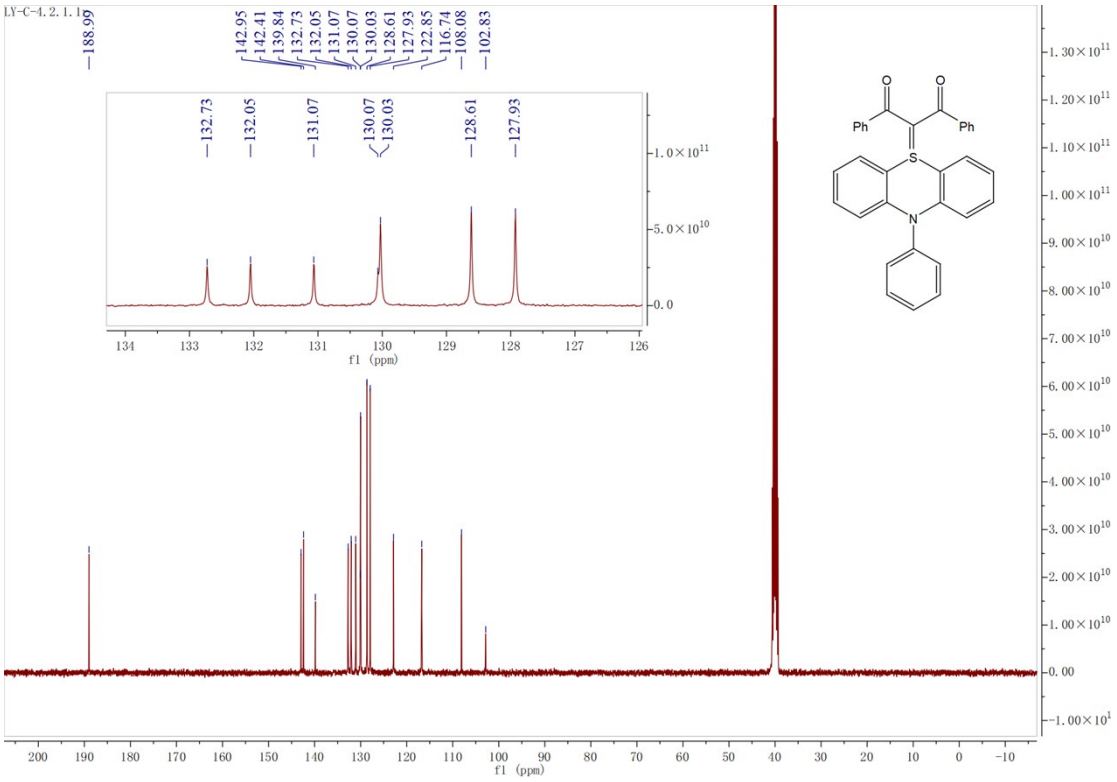
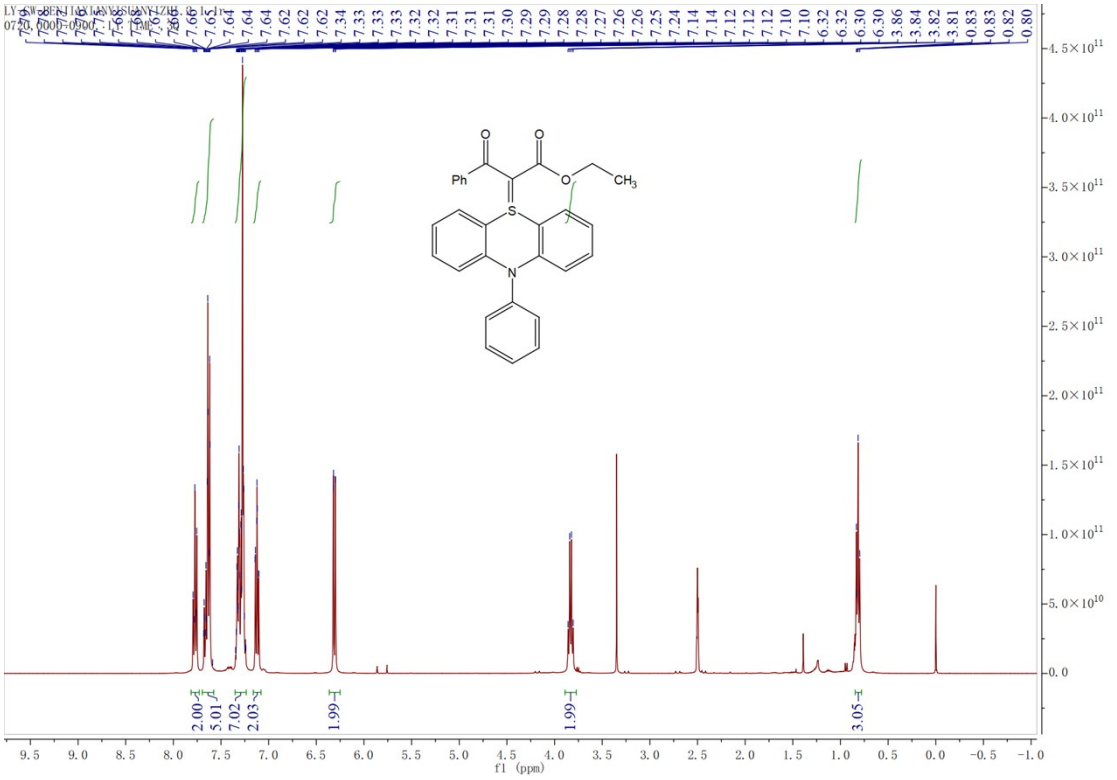
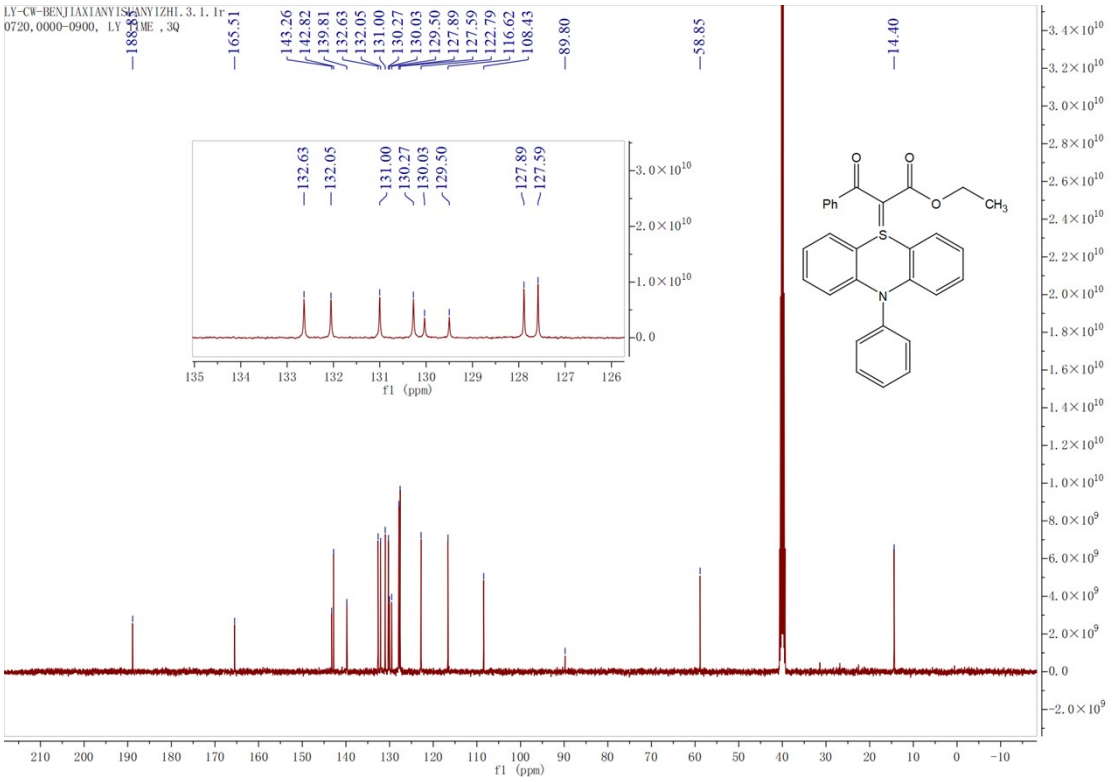
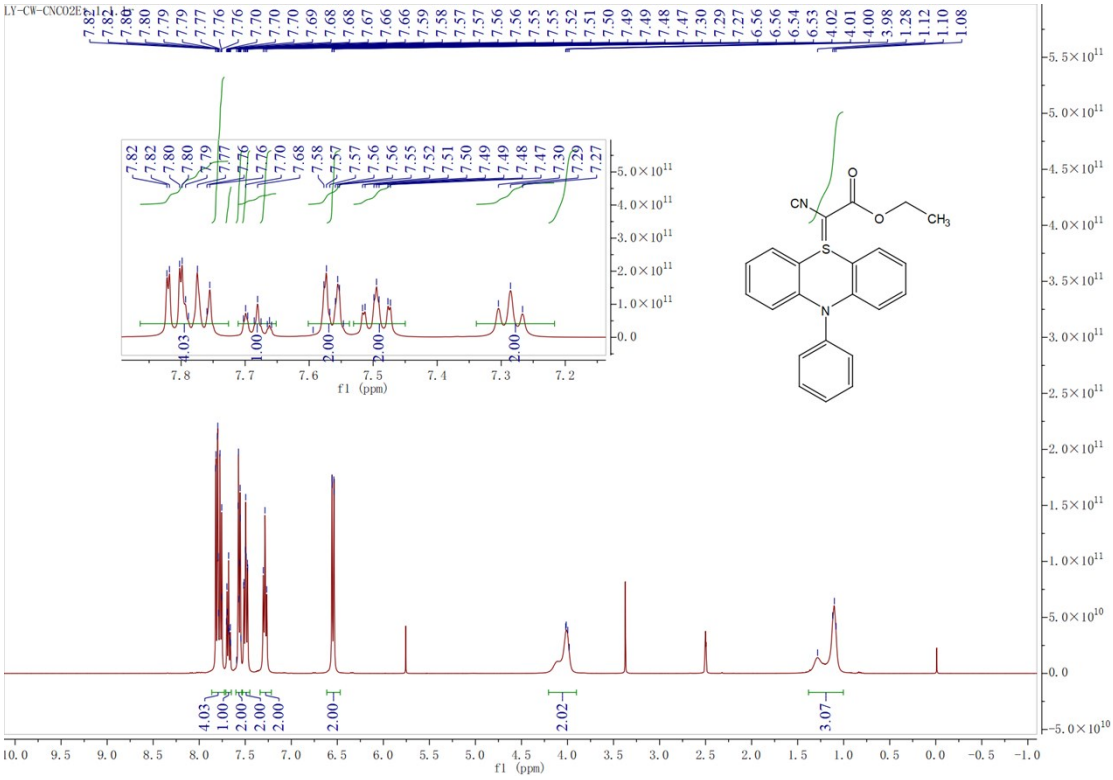
127.74
f1 (ppm)
Ph
CH3
S
N
f1 (ppm)

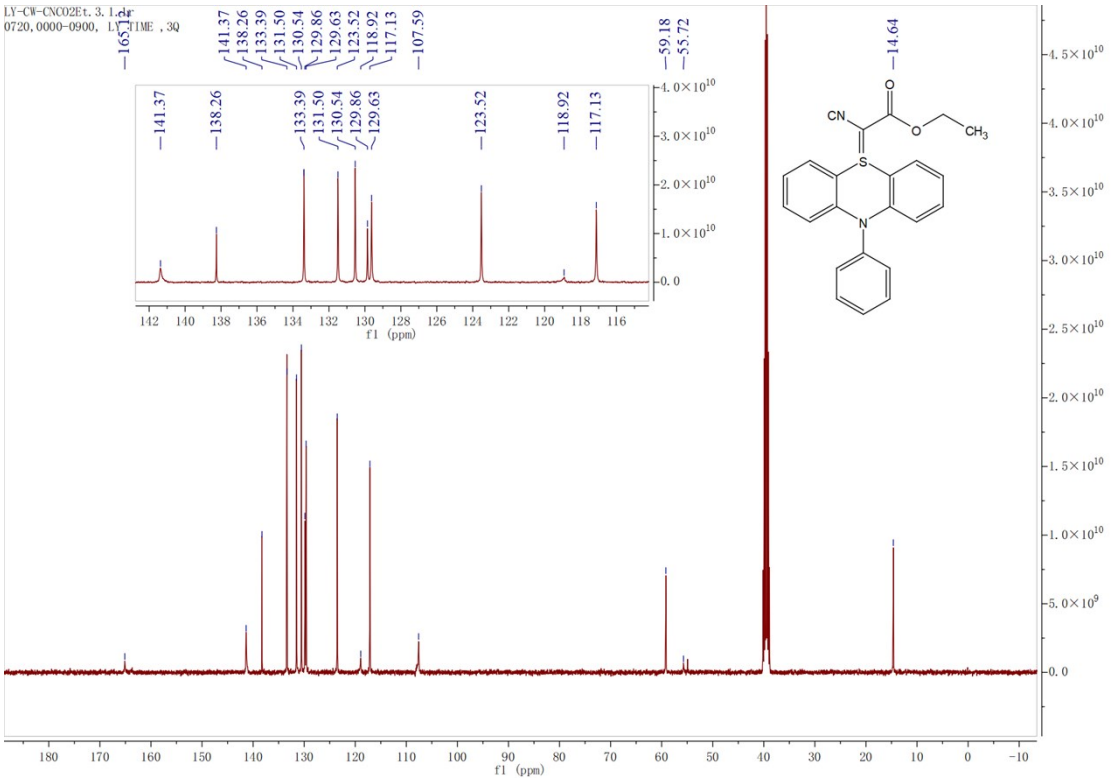

7.79
7.77
7.72
7.72
7.70
7.70
7.65
7.64
7.63
7.62
7.32
7.32
7.31
7.26
7.24
7.24
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.12
7.11
7.10
7.10
7.09
7.09
2.10
3.00
2.03
2.20
4.03
8.11
f1 (ppm)
Ph
Ph
S
N
2.10
3.00
2.03
2.20
4.03
8.11
2.00
f1 (ppm)

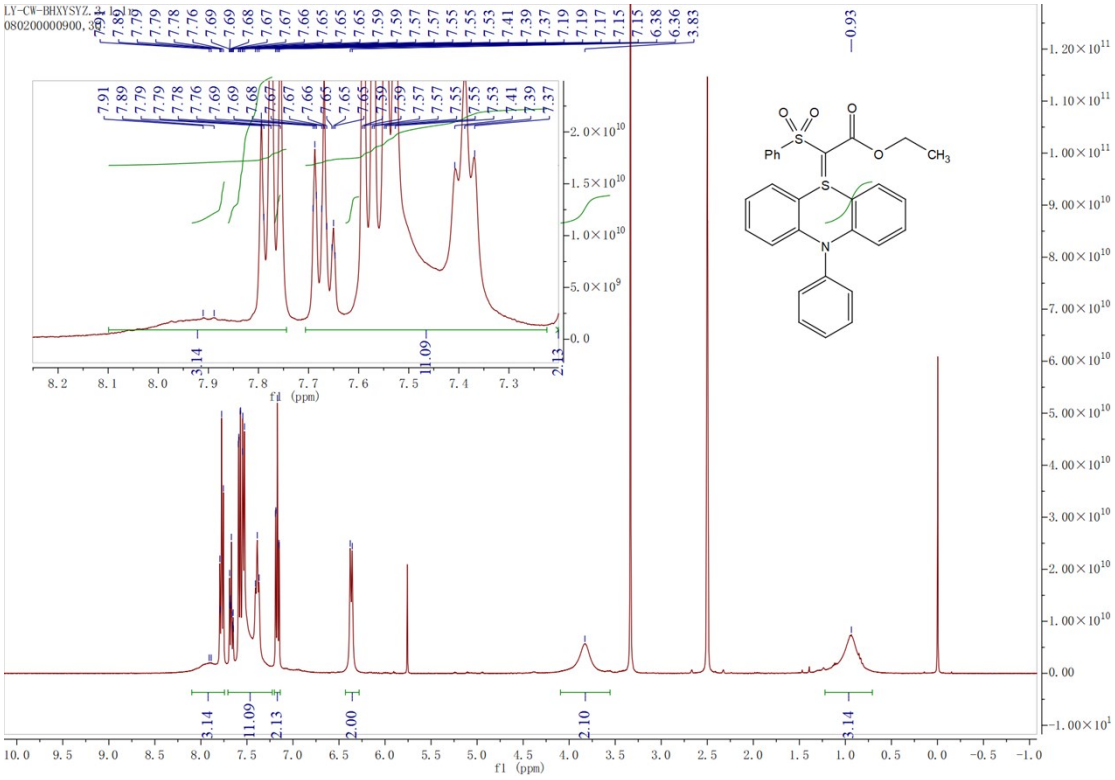

LY-C-4.2.1.1
188.99
142.95
142.41
139.84
132.73
132.05
131.07
130.07
130.03
128.61
127.93
122.85
116.74
108.08
102.83
f1 (ppm)

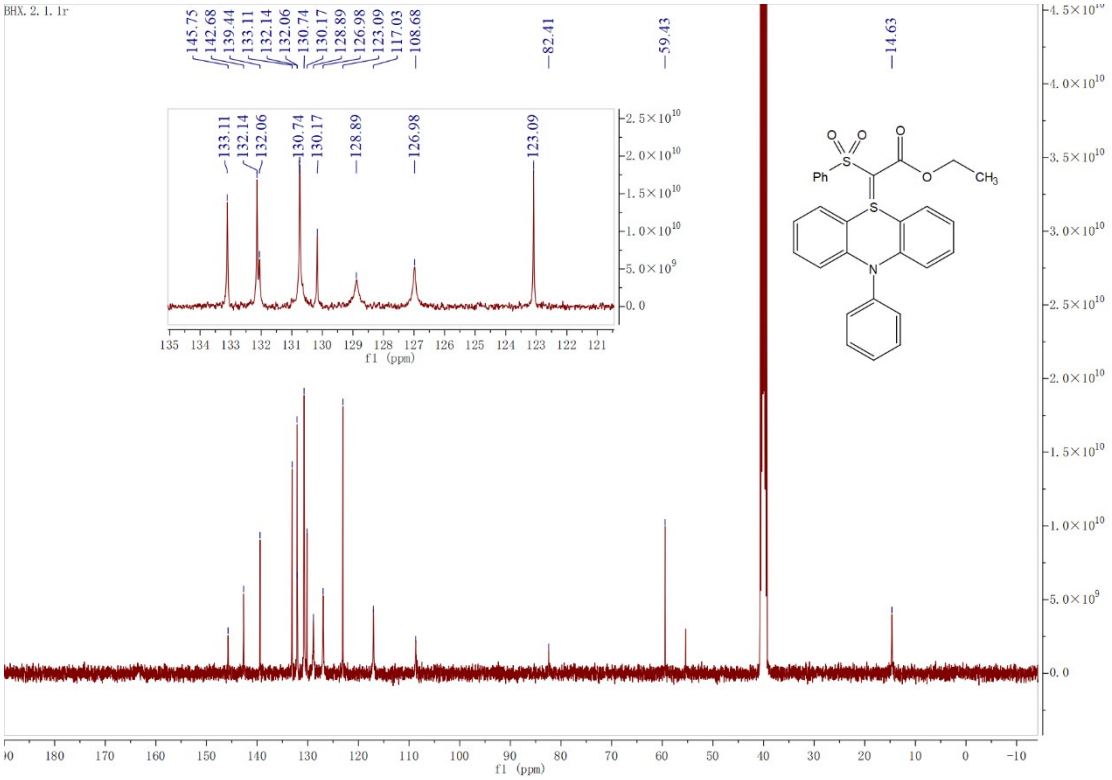

f1 (ppm)

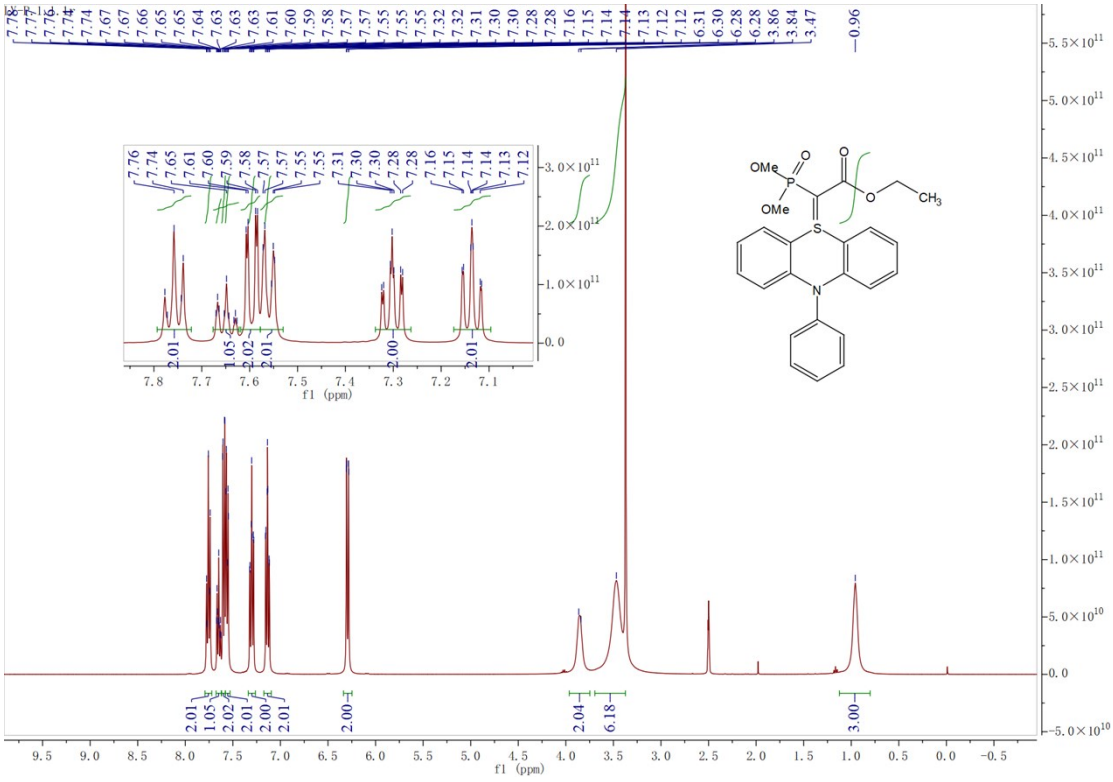

LY-CW-BENJIAXIANYISHANYIZHI.3.1.1r
0720,0000-0900, LY ME ,3Q
188.38
165.51
143.26
142.82
139.81
132.63
132.05
131.00
130.27
130.03
129.50
127.89
127.59
122.79
116.62
108.43
89.80
58.85
14.40
f1 (ppm)
Ph
O
O
CH3
S
N

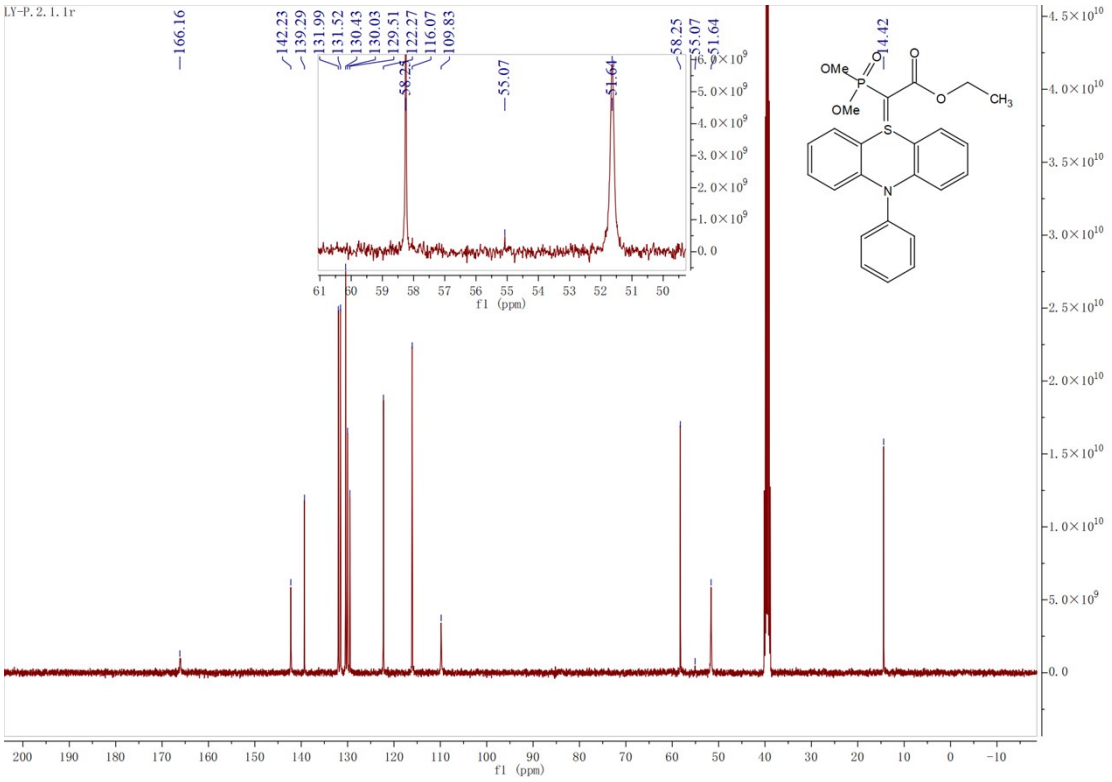

LY-CW-CNCO2Et-1
f1 (ppm)
CN
O
O
CH3
S
N
4.03
1.00
2.00
2.00
2.00
2.00
2.02
3.07

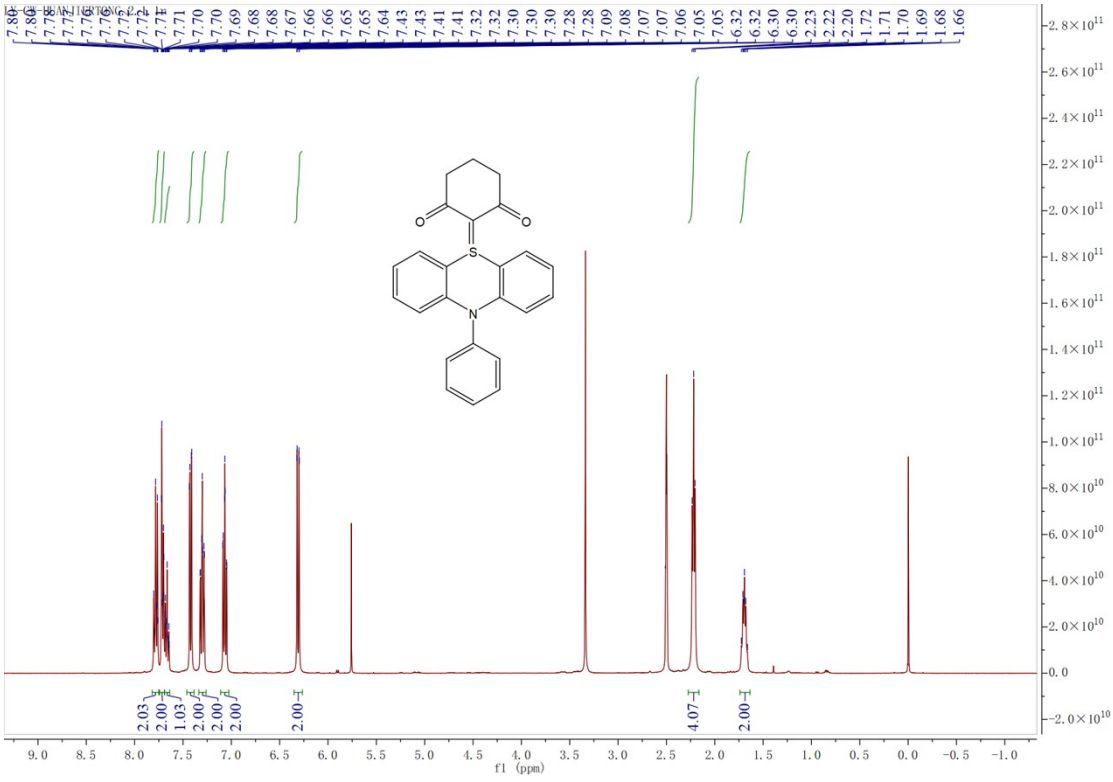

141.37
138.26
133.39
131.50
130.54
129.86
129.63
123.52
118.92
117.13
107.59
59.18
55.72
14.64
CN
O
CH3
S
N
f1 (ppm)

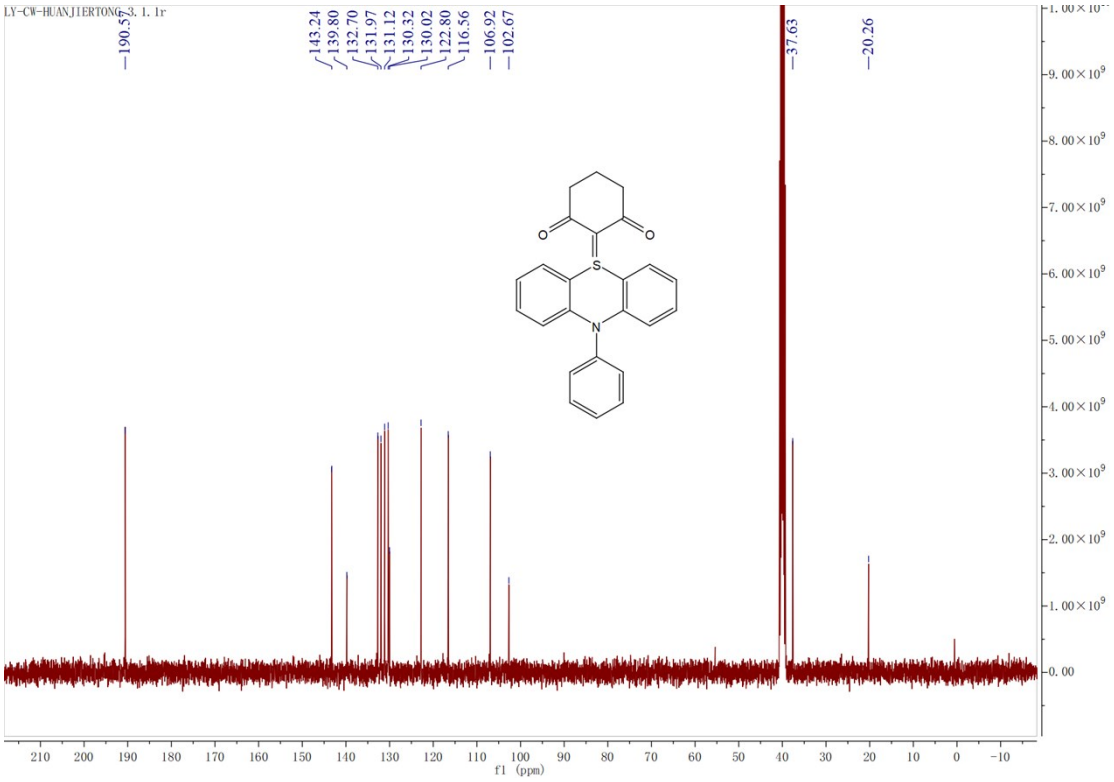

7.91
7.89
7.79
7.79
7.78
7.76
7.69
7.69
7.68
7.67
7.67
7.66
7.65
7.65
7.65
7.59
7.59
7.57
7.57
7.55
7.55
7.53
7.41
7.39
7.37
7.19
7.17
7.15
6.38
6.36
3.83
0.93
Ph
S
O
CH3
N
3.14
11.09
2.13
2.00
2.10
3.14
f1 (ppm)

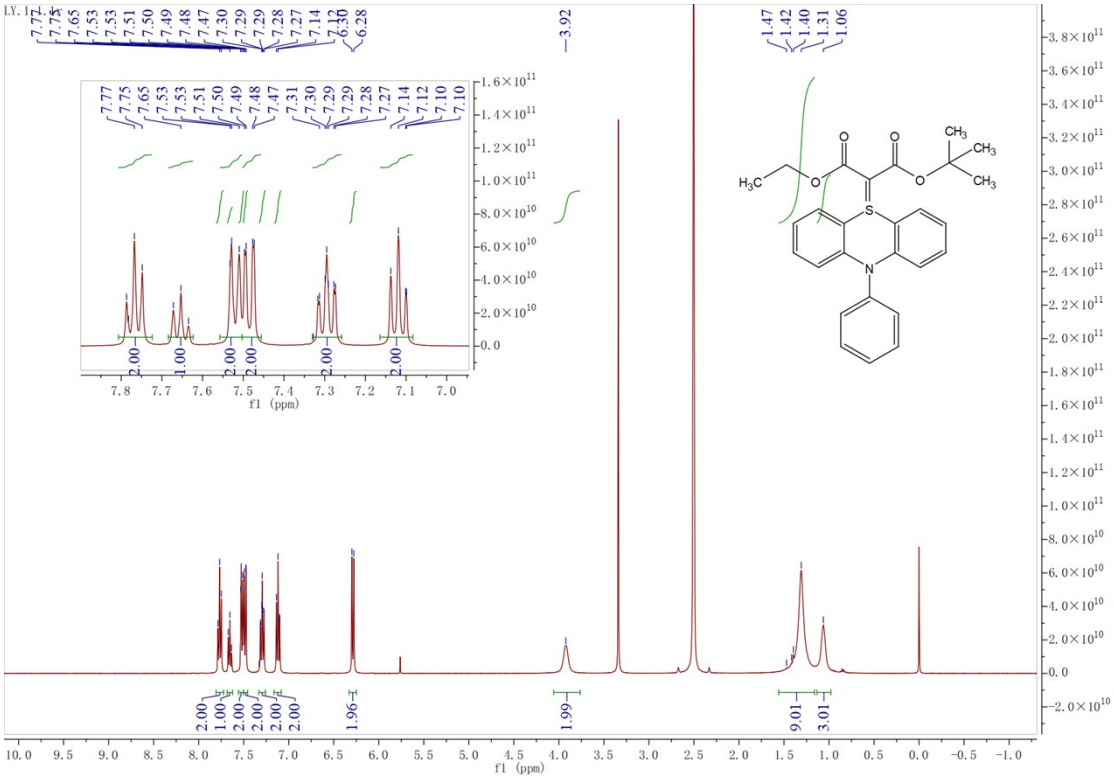

BHX. 2. 1. 1r
145.75
142.68
139.44
133.11
132.14
132.06
130.74
130.17
128.89
126.98
123.09
117.03
108.68
82.41
59.43
14.63
Ph
CH3
f1 (ppm)

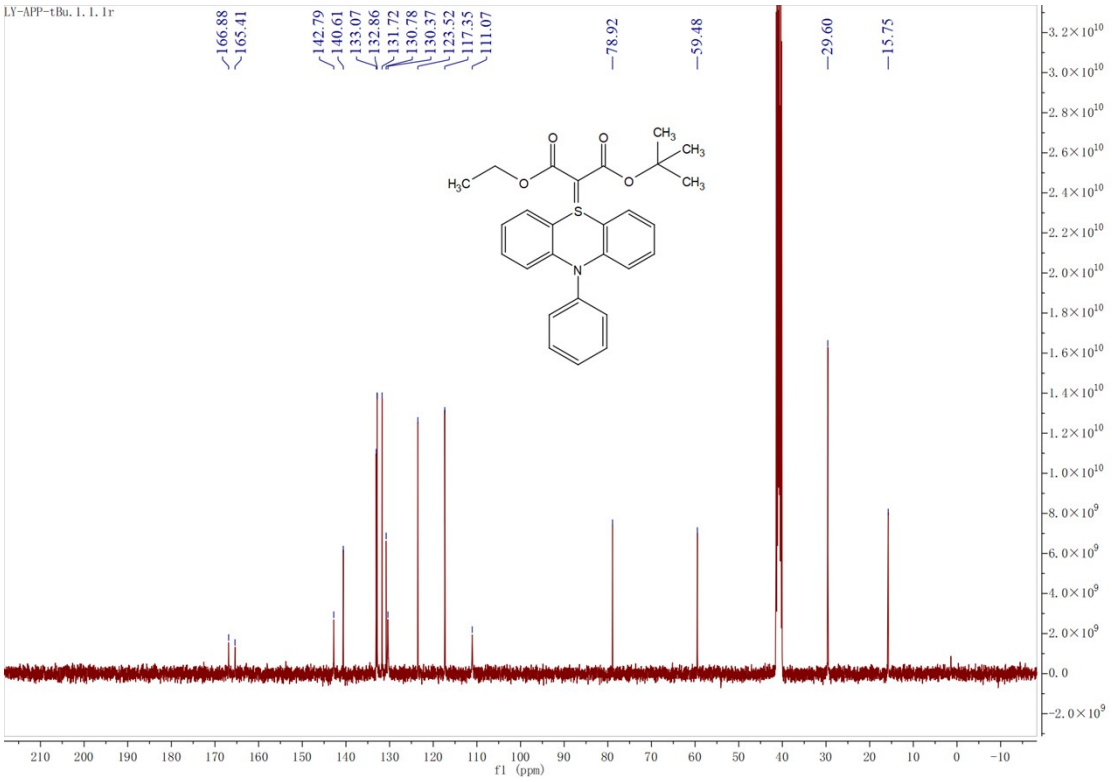

0.96
OMe
OMe
CH3
f1 (ppm)

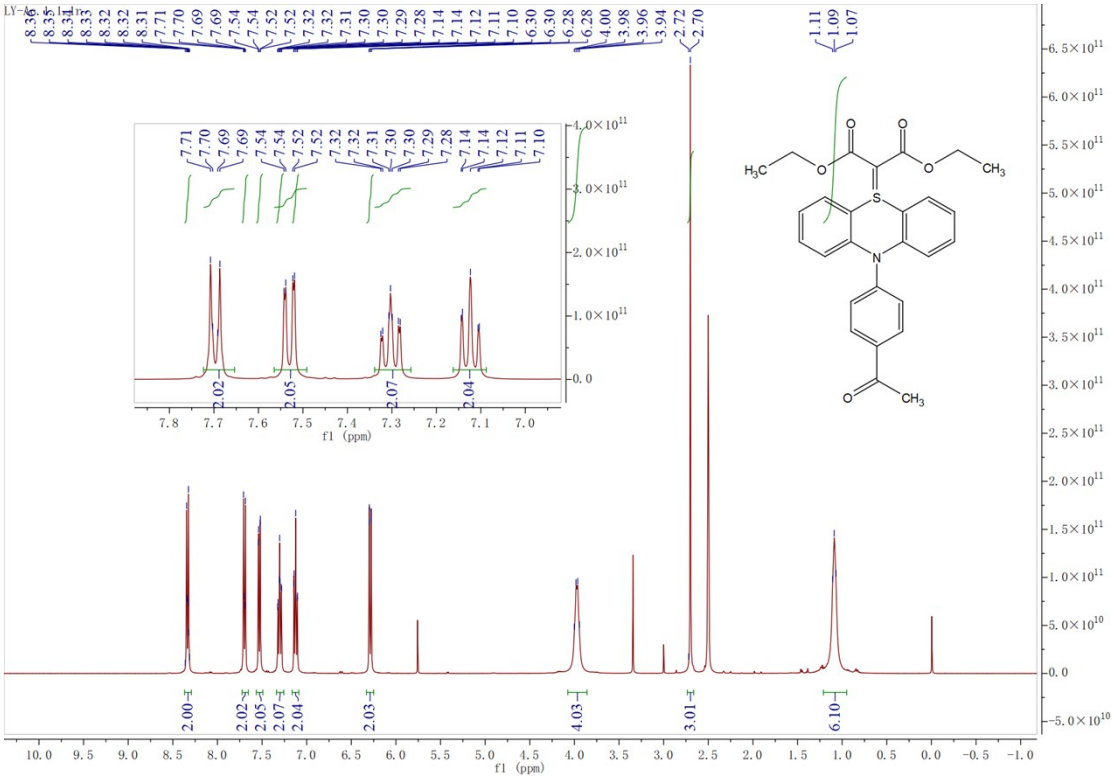

LY-P.2.1.1r
166.16
142.23
139.29
131.99
131.52
130.43
130.03
129.51
122.27
116.07
109.83
58.25
55.07
51.64
14.42
f1 (ppm)

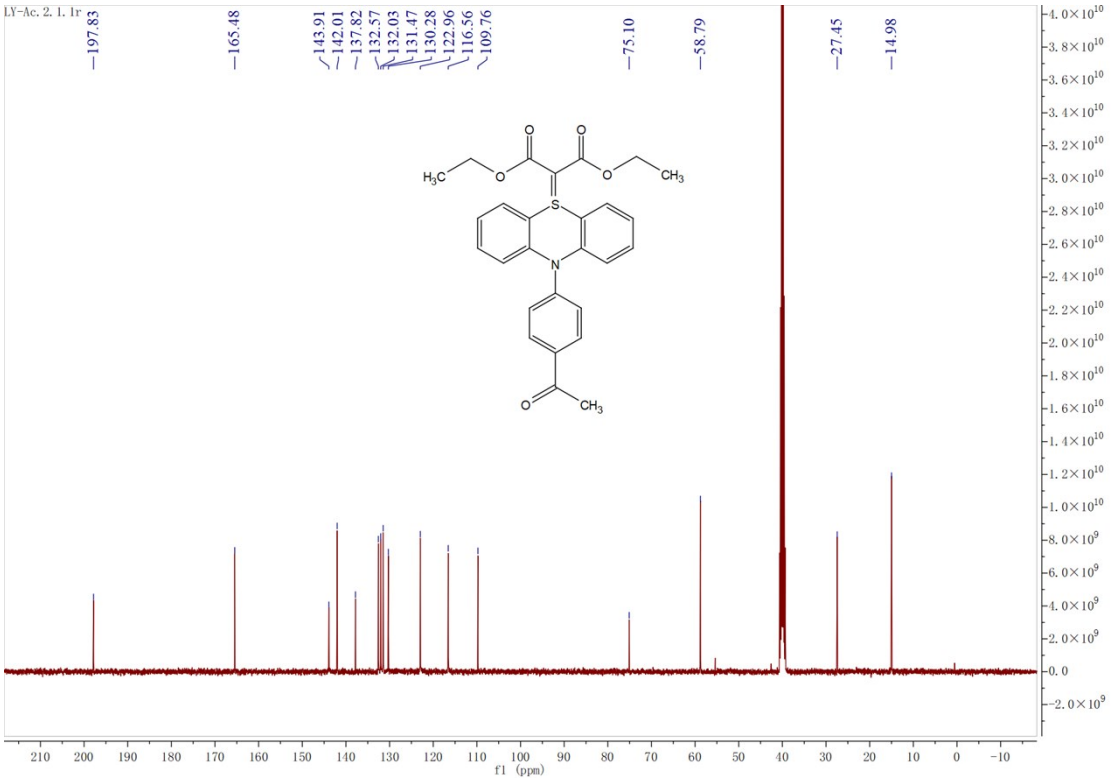

2.03
2.00
1.03
2.00
2.00
2.00
2.00
4.07
2.00
f1 (ppm)

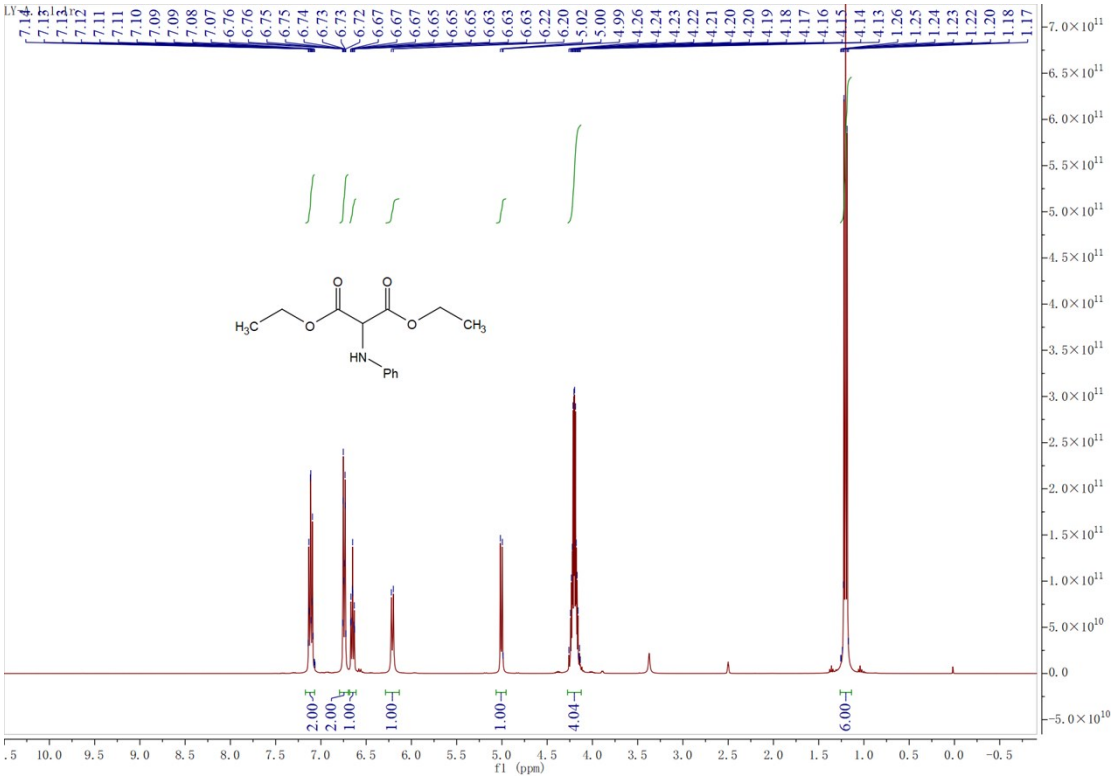

LY-CW-HUANJIERTONG-3.1.1r
190.57
143.24
139.80
132.70
131.97
131.12
130.32
130.02
122.80
116.56
106.92
102.67
37.63
20.26
f1 (ppm)

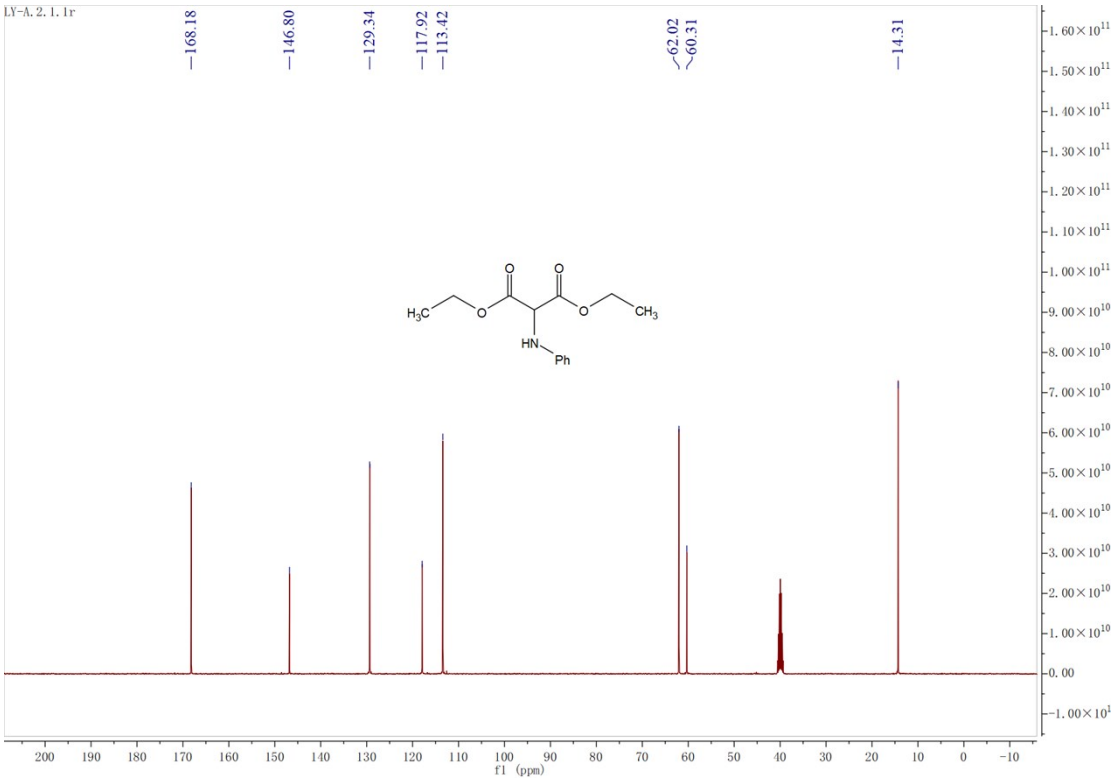

7.77
7.75
7.65
7.53
7.53
7.51
7.50
7.49
7.48
7.47
7.30
7.29
7.29
7.28
7.27
7.14
7.12
6.30
6.28
3.92
1.47
1.42
1.40
1.31
1.06
2.00
1.00
2.00
2.00
2.00
2.00
1.96
1.99
9.01
3.01
f1 (ppm)


LY-APP-tBu. 1. 1. 1r
166.88
165.41
142.79
140.61
133.07
132.86
131.72
130.78
130.37
123.52
117.35
111.07
78.92
59.48
29.60
15.75
f1 (ppm)


7.71
7.70
7.69
7.54
7.52
7.32
7.31
7.30
7.29
7.28
7.14
7.12
7.11
7.10
6.30
6.28
4.00
3.98
3.96
3.94
2.72
2.70
1.11
1.09
1.07
2.02
2.05
2.07
2.04
2.00
2.03
4.03
3.01
6.10
f1 (ppm)


LY-Ac. 2. 1. 1r
197.83
165.48
143.91
142.01
137.82
132.57
132.03
131.47
130.28
122.96
116.56
109.76
75.10
58.79
27.45
14.98
f1 (ppm)


LY-1
7.14
7.13
7.12
7.11
7.10
7.09
7.08
7.07
6.76
6.75
6.74
6.73
6.72
6.67
6.65
6.63
6.22
6.20
5.02
5.00
4.99
4.26
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
1.26
1.25
1.24
1.23
1.22
1.20
1.18
1.17
2.00
2.00
1.00
1.00
1.00
4.04
6.00
f1 (ppm)


LY-A.2.1.1r
168.18
146.80
129.34
117.92
113.42
62.02
60.31
14.31
O
O
H3C
O
O
CH3
HN
Ph
1.60×10^11
1.50×10^11
1.40×10^11
1.30×10^11
1.20×10^11
1.10×10^11
1.00×10^11
9.00×10^10
8.00×10^10
7.00×10^10
6.00×10^10
5.00×10^10
4.00×10^10
3.00×10^10
2.00×10^10
1.00×10^10
0.00
-1.00×10^1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)