

Supporting Information for:

Thiocarbamate-Directed Tandem Olefination – Intramolecular Sulfuration of Two ortho C-H Bonds: Application to Synthesis of a COX-2 Inhibitor

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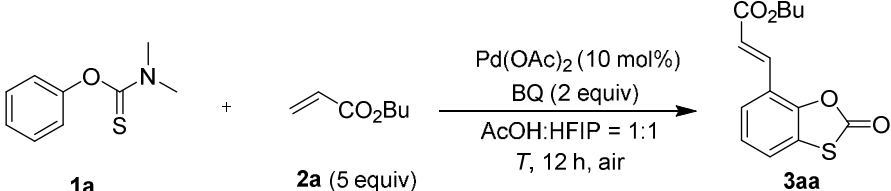
1. General information

Starting materials were purchased from Adamas Reagent, Energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd or Tansoole. Unless stated otherwise, reactions were performed in oven-dried or flame-dried glassware using a seal tube under air atmosphere. Flash column chromatography was performed over silica gel (200-300 mesh).

^1H -NMR and ^{13}C -NMR spectra were recorded in CDCl_3 on a Bruker Avance 500MHz/Avance III spectrometer (500 MHz ^1H , 125 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to CDCl_3 ($\delta = 7.26$ for ^1H -NMR, $\delta = 77.00$ for ^{13}C -NMR) as an internal reference. Coupling constants (J) were reported in Hertz (Hz). The following abbreviations are used to indicate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High resolution mass spectra were recorded using a Thermo Fisher Scientific LTQ FT Ultra or Waters Micromass GCT Premier instrument.

2. Optimization of the reaction conditions (Table S1-S5)

Table S1. Temperature and atmosphere

<div><div><div><div>1a</div><div>2a (5 equiv)</div><div>$\xrightarrow[\text{AcOH:HFIP = 1:1, T, 12 h, air}]{\text{Pd(OAc)}_2 \text{ (10 mol\%)}, \text{BQ (2 equiv)}}$</div><div>3aa</div></div></div></div>		
entry	T(°C)	yield (%) ^a
1	60	0
2	70	45
3	80	62
4	90	54
5	100	39
6	90	59 ^b
7	90	61 ^c

Conditions : ^a 0.2 mmol of **1a**, 1 mmol of **2a**, 0.02 mol of Pd catalyst, 0.4 mmol of BQ, 1 ml of solvent (the volume ratio of two components is 1 : 1), reaction under air atmosphere for 12 h;

^b N_2 instead of air; ^c O_2 instead of air.

Table S2. Catalyst

$\text{1a} + \text{2a (5 equiv)} \xrightarrow[\text{AcOH:HFIP = 1:1, 80 } ^\circ\text{C, 12h, air}]{\text{catalyst (10 mol\%), BQ (2 equiv)}} \text{3aa}$

entry	catalyst	yield (%) ^a
1	Cu(OAc) ₂	0
2	[Cp*RhCl ₂] ₂	0
3	Pd(OAc) ₂	62
4	Pd(OAc) ₂	36 ^b
5	Pd(TFA) ₂	40
6	PdCl ₂	0
7	Pd(PPh ₃) ₄	55
8	Pd ₂ (dba) ₂	50

Conditions : ^a 0.2 mmol of **1a**, 1 mmol of **2a**, 0.02 mmol of catalyst, 0.4 mmol of BQ, 1 ml of solvent (the volume ratio of two components is 1 : 1), 80 °C, reaction under air atmosphere for 12 h; ^b 0.01 mmol of Pd(OAc)₂.

Table S3. Solvent

$\text{1a} + \text{2a (5 equiv)} \xrightarrow[\text{80 } ^\circ\text{C, 12 h, air}]{\text{Pd(OAc)}_2 \text{ (10 mol\%), BQ (2 equiv), solvent}} \text{3aa}$

entry	solvent	yield (%) ^a
1	AcOH:HFIP=1:1	62
2	AcOH	0
3	HFIP	0
4	AcOH:DMF=1:1	trace
5	AcOH:Toluene=1:1	25
6	AcOH:TFE=1:1	55

Conditions : ^a 0.2 mmol of **1a**, 1 mmol of **2a**, 0.02 mmol of catalyst, 0.4 mmol of BQ, 1 ml of solvent (the volume ratio of two components is 1 : 1), 80°C, reaction under air atmosphere for 12 h.

Table S4. Amount of Olefin

entry	x	yield (%)
1	1.5	26
2	2	30
3	3	41
4	4	52
5	5	62
6	6	60

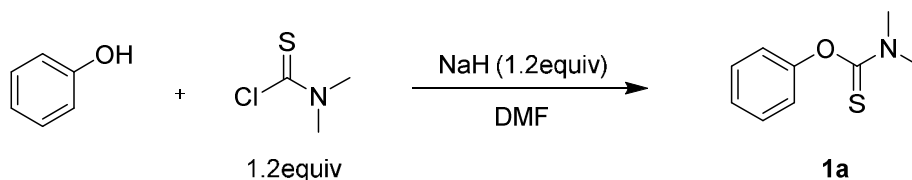
Condatons : ^a 0.2 mmol of **1a**, 0.02 mmol of catalyst, 0.4mmol BQ, 1 ml of solvent (the volume ratio of two components is 1 : 1), 80 °C, reaction under air atmosphere 12 h.

Table S4. Amount of BQ

entry	x	yield (%) ^a
1	1	25
2	1.5	40
3	2	62
4	2.5	58
5	3	53

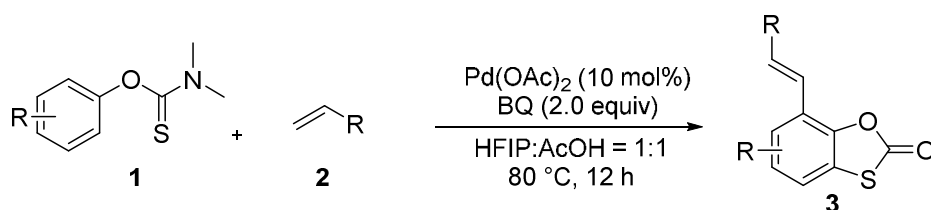
Conditions : ^a 0.2 mmol of **1a**, 1 mmol of **2a**, 0.02 mmol of catalyst, 1 ml of solvent (the volume ratio of two components is 1 : 1), 80 °C, reaction under air atmosphere 12 h.

3. General procedures for the dual C–H Bond Activation and product characterization



To a cooled solution of phenol (0.1 mol, 9.4 g) dissolved in of dimethylformamide (100ml) was added, in small portions, sodium hydride (0.12 mol, 4.8 g, 60% in mineral oil). After hydrogen evolution ceased the solution was cooled to 10°C in an ice bath and dimethylthiocarbamoyl chloride (0.12 mol, 14.9 g) added all at once. The temperature rose rapidly to 25°C and then slowly to 40 °C. The cooling bath was removed and the mixture heated during 1 h to 80 °C. After cooling, the mixture was poured into 200 mL of potassium hydroxide (1%). The resulting solution was saturated with sodium chloride and then extracted with ethyl acetate. Organic extracts were washed with 100 mL of water and then 100 mL of saturated sodium chloride, filtered through anhydrous sodium sulfate, and concentrated to dark oil. Chromatography on silica gel with ethyl acetate/petroleum ether (1:20) yielded 16.2 g (90%) product as colorless oil. Recrystallization under -20 °C in ethyl acetate/petroleum ether afforded pure O-phenyl dimethylcarbamothioate (1a) as a colorless crystal.

All the aryl thiocarbamates (**1a-1q**) were synthesized according to reported methods. (See: Zhao, Y.; Xie, Y.; Xia, C.; Huang, H., *Adv. Synth. Catal.* **2014**, 356, 2471; Zhao, Y.; Han, F.; Yang, L.; Xia, C., *Org. Lett.* **2015**, 17, 1477; Mai, S.; Song, Q., *Angew. Chem. Int. Ed.* **2017**, 56, 7952.)

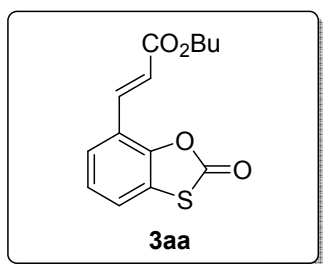


General procedure

To a 25 mL dry reaction tube added 0.2 mmol of aryl thicarbamate **1**, 1.0 mmol of olefin **2**, 0.02 mmol of Pd(OAc)₂, 0.4 mmol of benzoquinone (BQ), 0.5 mL of acetic acid, and 0.5 mL of HFIP. The reaction tube was then sealed and the mixture was allowed to react at 80 °C for 12 h. After cooled to room temperature, solvents of the obtained solution was evaporated under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate / petroleum ether (1:50) to give corresponding product **3**.

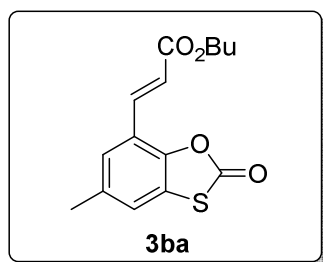
The NMR and HRMS data on the products:

Butyl (E)-3-(2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3aa): This product was



obtained from the reaction of **1a** with **2a** as a colorless oil (34.5 mg, yield 62%). ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 16.2 Hz, 1H), 7.46 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.27 (dd, *J* = 9.7, 6.0 Hz, 1H), 6.70 (d, *J* = 16.2 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 1.72 – 1.66 (m, 2H), 1.48 – 1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.0, 166.6, 146.1, 137.0, 127., 125.3, 124.0, 123.4, 122.8, 120.1, 64.8, 30.7, 19.2, 13.8; HRMS (ESI) *calcd* for C₁₄H₁₄O₄SNa (M+Na⁺): 301.0510, found 301.0507.

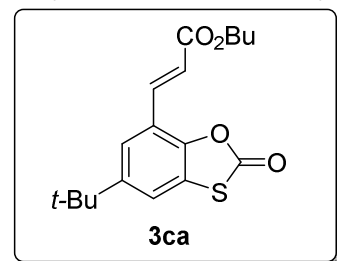
Butyl (E)-3-(5-methyl-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ba): This



product was obtained from the reaction of **1b** with **2a** as a white solid (32 mg, yield 55%). ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 16.2 Hz, 1H), 7.25 (s, 1H), 7.21 (s, 1H), 6.69 (d, *J* = 16.2 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 2.39 (s, 3H), 1.73–1.67 (m, 2H), 1.48–1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.3, 166.7, 144.2, 137.2, 135.3, 128.1, 123.8, 123.7, 122.6, 119.7, 64.7, 30.7, 21.1, 19.2, 13.8; HRMS (ESI) *calcd*

for C₁₅H₁₆O₄SNa (M+Na⁺): 315.0667, found 315.0662.

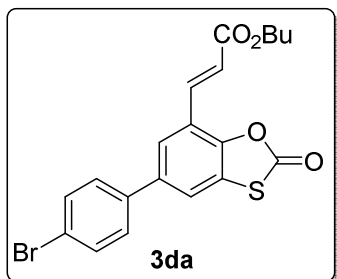
Butyl (E)-3-(5-(tert-butyl)-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ca): This



product was obtained from the reaction of **1c** with **2a** as a white solid (43 mg, yield 64%). ¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, *J* = 16.2 Hz, 1H), 7.45 (s, 1H), 7.41 (s, 1H), 6.72 (d, *J* = 16.2 Hz, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 1.73–1.66 (m, 2H), 1.48–1.40 (m, 2H), 1.33 (s, 9H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.4, 166.7, 148.9, 144.1, 137.7, 125.1, 123.7, 122.5,

120.5, 119.3, 64.7, 35.0, 31.3, 30.7, 19.2, 13.8.

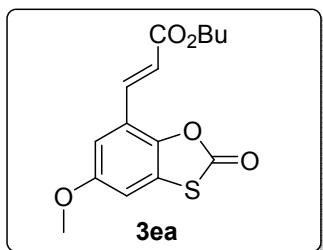
Butyl (E)-3-(5-(4-bromophenyl)-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3da):



This product was obtained from the reaction of **1d** with **2a** as a white solid (40.6 mg, yield 47%). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 16.2 Hz, 1H), 7.61–7.57 (m, 3H), 7.55 (d, *J* = 1.9 Hz, 1H), 7.42–7.38 (m, 2H), 6.77 (d, *J* = 16.2 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 1.74–1.67 (m, 2H), 1.49–1.41 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.7, 166.5, 145.6, 137.9, 137.8, 136.8, 132.3, 128.6, 126.3, 124.9, 123.4,

122.6, 121.6, 120.3, 64.9, 30.7, 19.2, 13.8. HRMS (ESI) *calcd* for C₂₀H₁₇BrO₄SNa (M+Na⁺): 454.9929, found 454.9922.

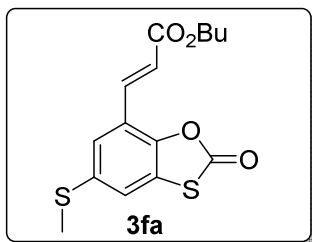
Butyl (E)-3-(5-methoxy-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ea): This



product was obtained from the reaction of **1e** with **2a** as a white solid (32.6 mg, yield 53%). ^1H NMR (500 MHz, CDCl_3) δ 7.70 (d, J = 16.2 Hz, 1H), 6.95 (q, J = 2.6 Hz, 2H), 6.68 (d, J = 16.1 Hz, 1H), 4.22 (t, J = 6.7 Hz, 2H), 3.83 (s, 3H), 1.74–1.66 (m, 2H), 1.48–1.40 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.1, 166.5, 156.9, 140.4, 137.0, 124.8, 123.0, 120.6, 112.6, 109.0, 64.8, 56.0, 30.7, 19.2, 13.8. HRMS (ESI)

calcd for $\text{C}_{15}\text{H}_{16}\text{O}_5\text{SNa}$ ($\text{M}+\text{Na}^+$): 331.0616, found 331.0612.

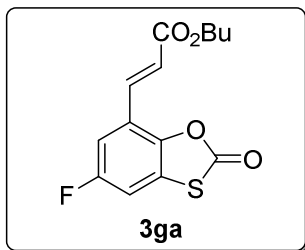
Butyl (E)-3-(5-(methylthio)-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3fa): This



product was obtained from the reaction of **1f** with **2a** as a white solid (26 mg, yield 40%). ^1H NMR (500 MHz, CDCl_3) δ 7.68 (d, J = 16.2 Hz, 1H), 7.30 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 1.9 Hz, 1H), 6.69 (d, J = 16.2 Hz, 1H), 4.22 (t, J = 6.7 Hz, 2H), 2.50 (s, 3H), 1.70 (dd, J = 14.4, 7.1 Hz, 2H), 1.48–1.39 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.7, 166.4, 143.9, 136.6,

136.2, 125.9, 124.9, 123.4, 121.3, 120.3, 64.9, 30.7, 19.2, 16.7, 13.8. HRMS (ESI) *calcd* for $\text{C}_{15}\text{H}_{16}\text{O}_4\text{S}_2\text{Na}$ ($\text{M}+\text{Na}^+$): 347.0388, found 347.0383.

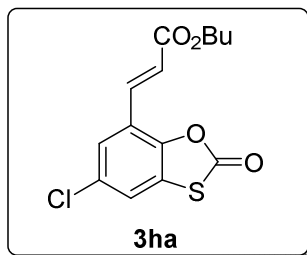
Butyl (E)-3-(5-fluoro-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ga): This product



was obtained from the reaction of **1g** with **2a** as a white solid (31.4 mg, yield 53%). ^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, J = 16.2 Hz, 1H), 7.22–7.14 (m, 2H), 6.69 (d, J = 16.2 Hz, 1H), 4.23 (t, J = 6.7 Hz, 2H), 1.70 (dt, J = 14.5, 6.7 Hz, 2H), 1.49–1.39 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.4, 159.3 (d, J = 247.2 Hz), 158.4, 142.3, 135.76 (d, J = 1.9 Hz), 125.20 (d, J = 10.6 Hz), 124.0, 121.26 (d, J = 8.2 Hz), 113.62 (d, J =

24.7 Hz), 110.70 (d, J = 28.2 Hz), 65.0, 30.7, 19.2, 13.7. HRMS (ESI) *calcd* for $\text{C}_{14}\text{H}_{14}\text{FO}_4\text{S}$ ($\text{M}+\text{H}^+$): 297.0591, found 297.0584.

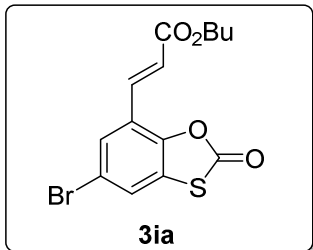
Butyl (E)-3-(5-chloro-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ha): This product



was obtained from the reaction of **1h** with **2a** as a white solid (26.8 mg, yield 43%). ^1H NMR (500 MHz, CDCl_3) δ 7.68 (d, J = 16.2 Hz, 1H), 7.45 (d, J = 2.2 Hz, 1H), 7.39 (d, J = 2.2 Hz, 1H), 6.70 (d, J = 16.2 Hz, 1H), 4.23 (t, J = 6.7 Hz, 2H), 1.74–1.66 (m, 2H), 1.48–1.40 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.1, 166.2, 144.5, 135.6, 130.9, 127.0, 125.4, 124.1, 122.9, 121.2, 65.0, 30.7, 19.2, 13.7. HRMS (ESI) *calcd* for

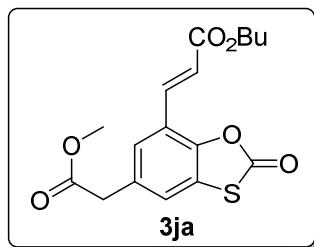
$\text{C}_{14}\text{H}_{14}\text{ClO}_4\text{S}$ ($\text{M}+\text{H}^+$): 313.0296, found 313.0292.

Butyl (E)-3-(5-bromo-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ia): This product



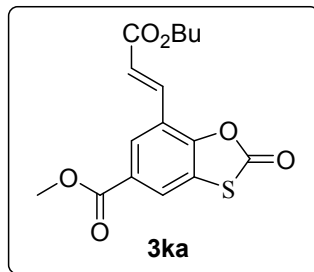
was obtained from the reaction of **1i** with **2a** as a white solid (40.6 mg, yield 57%). ¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, *J* = 16.2 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 6.69 (d, *J* = 16.2 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 1.73–1.67 (m, 2H), 1.48–1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.0, 166.1, 145.0, 135.5, 129.9, 125.7, 125.6, 124.1, 121.6, 117.9, 65.0, 30.7, 19.2, 13.7. HRMS (ESI) *calcd* for C₁₄H₁₄BrO₄S (M+H⁺): 356.9791, found 356.9786.

Butyl (E)-3-(5-(2-methoxy-2-oxoethyl)-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ja): This product was obtained from the reaction of **1j**



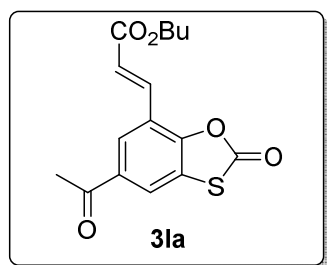
with **2a** as a white solid (30.1 mg, yield 43%). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 16.2 Hz, 1H), 7.36 (s, 2H), 6.71 (d, *J* = 16.2 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 3.72 (s, 3H), 3.65 (s, 2H), 1.74–1.66 (m, 2H), 1.48–1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 171.1, 167.9, 166.5, 145.3, 136.8, 131.5, 128.5, 124.4, 124.1, 123.2, 120.0, 64.8, 52.4, 40.4, 30.7, 19.2, 13.8. HRMS (ESI) *calcd* for C₁₇H₁₉O₆S (M+H⁺): 351.0897, found 351.0891.

Methyl (E)-7-(3-butoxy-3-oxoprop-1-en-1-yl)-2-oxobenzo[d][1,3]oxathiole-5-carboxylate (3ka): This product was obtained from the reaction of **1k** with **2a** as a white solid (24.2 mg, yield 36%).



¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, *J* = 1.7 Hz, 1H), 8.11 (d, *J* = 1.7 Hz, 1H), 7.78 (d, *J* = 16.2 Hz, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 3.95 (s, 3H), 1.74–1.67 (m, 2H), 1.48–1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.2, 166.3, 165.0, 148.8, 136.0, 128.9, 127.7, 124.5, 124.5, 123.9, 120.0, 64.9, 52.8, 30.7, 19.2, 13.7. HRMS (ESI) *calcd* for C₁₆H₁₇O₆S (M+H⁺): 337.0740, found 337.0736.

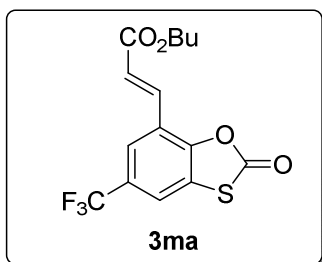
Butyl (E)-3-(5-acetyl-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3la): This product



was obtained from the reaction of **1l** with **2a** as a white solid (32 mg, yield 50%). ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 1.7 Hz, 1H), 8.04 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 16.2 Hz, 1H), 6.79 (d, *J* = 16.2 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 2.64 (s, 3H), 1.72 – 1.69 (m, 2H), 1.49 – 1.41 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 195.2, 167.2, 166.3, 148.8, 136.1, 134.4, 128.0, 125.0, 124.0, 123.2, 120.0, 65.0, 30.7, 26.57, 19.2,

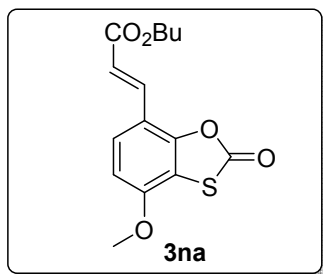
13.7. HRMS (ESI) *calcd* for C₁₆H₁₆O₅SNa (M+Na⁺): 343.0616, found 343.0612.

Butyl (E)-3-(2-oxo-5-(trifluoromethyl)benzo[d][1,3]oxathiol-7-yl)acrylate (3ma):



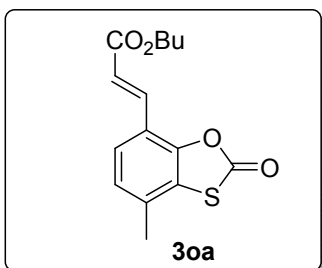
This product was obtained from the reaction of **1m** with **2a** as a white solid (22.1 mg, yield 32%). ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 16.3 Hz, 1H), 7.74–7.73 (m, 1H), 7.69 (d, *J* = 1.2 Hz, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.74–1.67 (m, 2H), 1.49 – 1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 166.7, 166.0, 147.8, 135.5, 128.2 (d, *J* = 33.7 Hz), 125.2, 124.6, 124.5 (q, *J* = 3.8 Hz), 123.1 (d, *J* = 272.7 Hz), 120.5, 120.2 (q, *J* = 3.8 Hz), 65.0, 30.7, 19.2, 13.7. HRMS (ESI) *calcd* for C₁₅H₁₄F₃O₄S (M+H⁺): 347.0559, found 347.0554.

Butyl (E)-3-(4-methoxy-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3na):



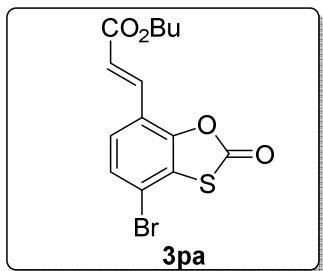
The product as isomer mixture was obtained from the reaction of **1n** with **2a** as a white solid. Pure **3na** was obtained from recrystallization in ethyl acetate/petroleum ether (42.3 mg, yield 75%). ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 16.2 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.62 (d, *J* = 16.1 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.95 (s, 3H), 1.72–1.66 (m, 2H), 1.46–1.41 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.7, 167.17, 154.7, 146.8, 137.3, 129.0, 120.1, 113.6, 111.7, 106.7, 64.6, 56.4, 30.8, 19.2, 13.8. HRMS (ESI) *calcd* for C₁₅H₁₆O₅SNa (M+Na⁺): 331.0616, found 331.0612.

Butyl (E)-3-(4-methyl-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3oa):



This product was obtained from the reaction of **1o** with **2a** as a colorless oil (26.3 mg, yield 45 %). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 16.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 16.2 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 2.38 (s, 3H), 1.73–1.66 (m, 2H), 1.48–1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.9, 166.8, 145.9, 137.2, 134.2, 127.2, 126.0, 123.9, 121.7, 117.5, 64.7, 30.7, 20.5, 19.2, 13.8. HRMS (ESI) *calcd* for C₁₅H₁₆O₄SNa (M+Na⁺): 315.0667, found 315.0663.

Butyl (E)-3-(4-bromo-2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3pa):

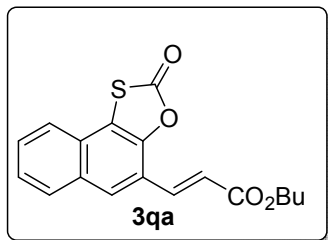


This product was obtained from the reaction of **1p** with **2a** as a white solid (30.6 mg, yield 43%). ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 16.2 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 16.2 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 1.77–1.67 (m, 2H), 1.47–1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.4, 166.0, 145.8, 136.2, 128.2, 128.1, 127.1, 123.2, 118.9, 116.0, 64.9, 30.7, 19.2, 13.7. HRMS (ESI)

calcd for $C_{14}H_{14}BrO_4S$ ($M+H^+$): 356.9791, found 356.9786.

Single crystal was obtained from recrystallization in ethyl acetate/ petroleum ether.

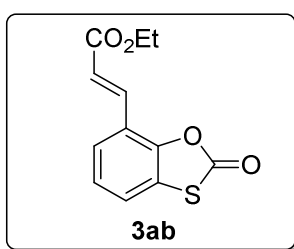
Butyl (E)-3-(2-oxonaphtho[2,3-d][1,3]oxathiol-9-yl)acrylate (3qa): This product



was obtained from the reaction of **1q** with **2a** as a white solid (36.1 mg, yield 53%). 1H NMR (500 MHz, $CDCl_3$) δ 7.91 (t, J = 4.5 Hz, 2H), 7.82 (d, J = 16.2 Hz, 1H), 7.65–7.60 (m, 1H), 7.57–7.53 (m, 2H), 6.87 (d, J = 16.2 Hz, 1H), 4.25 (t, J = 6.7 Hz, 2H), 1.75–1.69 (m, 2H), 1.50–1.42 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 166.8, 143.1, 137.8, 130.5, 129.6, 129.2, 129.0, 127.5, 126.7, 123.7, 123.0, 120.1, 119.0, 64.8, 30.8, 19.2, 13.8.

HRMS (ESI) *calcd* for $C_{18}H_{18}O_4S$ ($M+H^+$): 329.0848, found 329.0843.

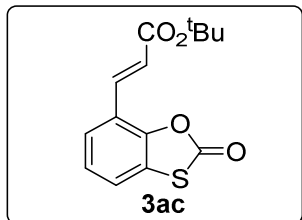
Ethyl (E)-3-(2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ab): This product was



obtained from the reaction of **1a** with **2b** as a white solid (27 mg, yield 54%). 1H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 16.2 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.41 (dd, J = 7.8, 1.0 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.71 (d, J = 16.2 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 166.5, 146.2, 137.0, 127.4, 125.3, 124.0, 123.4, 122.9, 120.1, 29.7, 14.3. HRMS (ESI)

calcd for $C_{12}H_{10}O_4SNa$ ($M+Na^+$): 273.0197, found 273.0211.

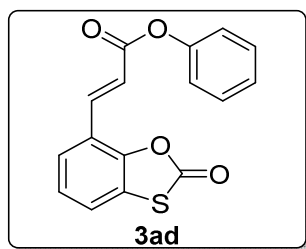
tert-Butyl (E)-3-(2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ac): This product was



obtained from the reaction of **1a** with **2c** as a white solid (26.1 mg, yield 47 %). 1H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 16.2 Hz, 1H), 7.44 (dd, J = 7.9, 0.8 Hz, 1H), 7.39 (dd, J = 7.8, 1.2 Hz, 1H), 7.25 (t, J = 7.9 Hz, 1H), 6.63 (d, J = 16.2 Hz, 1H), 1.54 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 165.8, 146.1, 136.0, 127.4, 125.3, 124.9, 123.9, 123.1, 120.4, 81.1, 28.2. HRMS (ESI) *calcd* for

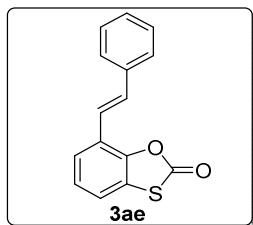
$C_{14}H_{14}O_4SNa$ ($M+Na^+$): 301.0510, found 301.0507.

Phenyl (E)-3-(2-oxobenzo[d][1,3]oxathiol-7-yl)acrylate (3ad): This product was



obtained from the reaction of **1a** with **2d** as a white solid (15 mg, yield 25 %). 1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 16.2 Hz, 1H), 7.53 (dd, J = 7.9, 0.8 Hz, 1H), 7.43 (ddt, J = 9.9, 4.1, 1.7 Hz, 3H), 7.32 (t, J = 7.9 Hz, 1H), 7.29–7.25 (m, 1H), 7.20–7.17 (m, 2H), 6.93 (d, J = 16.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 164.9, 150.7, 146.3, 138.9, 129.5, 127.7, 126.0, 125.4, 124.2, 123.9, 122.0, 121.5, 119.8. HRMS (ESI) *calcd* for $C_{16}H_{10}O_4SNa$ ($M+Na^+$): 321.0197, found 321.0192.

(E)-7-styrylbenzo[d][1,3]oxathiol-2-one (3ae): This product was obtained from the

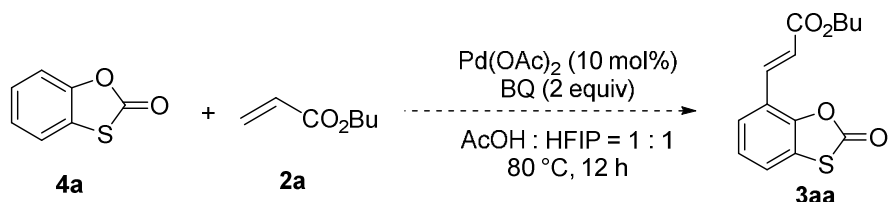


reaction of **1a** with **2e** as a white solid (14.2 mg, yield 28 %). 1H NMR (500 MHz, $CDCl_3$) δ 7.60–7.52 (m, 3H), 7.39 (dd, J = 10.4, 4.8 Hz, 2H), 7.36–7.30 (m, 2H), 7.28 (dt, J = 6.0, 3.2

Hz, 2H), 7.25–7.23 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 168.6, 145.3, 136.6, 132.8, 128.8, 128.5, 126.9, 125.2, 124.9, 123.6, 123.0, 121.0, 120.7. HRMS (ESI) *calcd* for $\text{C}_{15}\text{H}_{11}\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$): 255.0474, found 255.0471.

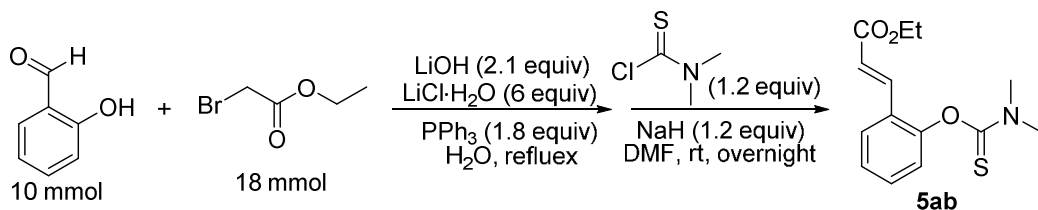
4. Control experiments and product characterization

Reaction of **4a** with **2a**



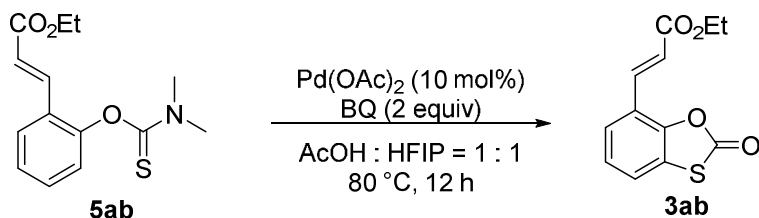
To a 25 mL dry reaction tube added 0.2 mmol of **4a**, 1.0 mmol of **2a**, 0.02 mmol of $\text{Pd}(\text{OAc})_2$, 0.4 mmol of benzoquinone (BQ), 0.5 mL of acetic acid, and 0.5 mL of HFIP. The reaction tube was then sealed and the mixture was allowed to react at 80 °C for 12 h. After cooled to room temperature, no **3aa** was detected by GC-MS.

Synthesis of Potential Reaction Intermediate (**5ab**)



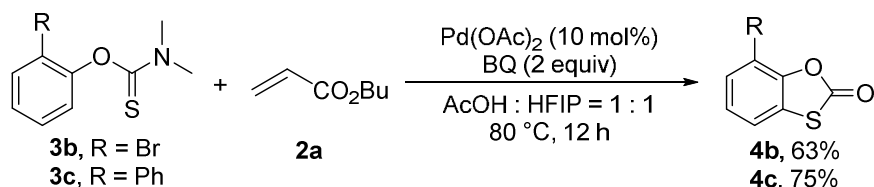
A suspension of the ethyl 2-bromoacetate (18 mmol), the 2-hydroxybenzaldehyde **1** (10 mmol), and PPh_3 (4.72 g, 18 mmol) in H_2O (50 mL) containing LiOH (504 mg, 21 mmol) and $\text{LiCl}\cdot\text{H}_2\text{O}$ (3.63 g, 60 mmol) was refluxed in air for the indicated time. After cooling to room temperature, the reaction mixture was extracted with EtOAc (50 mL \times 3), and the combined organic layer was washed with brine, dried over Na_2SO_4 , filtered, and condensed under reduced pressure, then DMF (30 mL) and NaH (480 mg, 12 equiv, 60% in mineral oil) were added under ice bath stirred 5 min, followed by addition of dimethylcarbamothioic chloride (1.23 g, 10 mmol). The mixture was stirred overnight under room temperature. Then reaction mixture was extracted with EtOAc (50 mL \times 3), and the combined organic layer was washed with sodium hydroxide solution and brine, dried over Na_2SO_4 , filtered, and condensed under reduced pressure and the residue was purified by flash column chromatograph to give the desired product (**5ab**) as a white solid (2.1 g, yield 75% in two steps). ^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, J = 16.1 Hz, 1H), 7.65 (dd, J = 7.8, 1.4 Hz, 1H), 7.41 (td, J = 8.1, 1.5 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 7.09 (dd, J = 8.1, 0.9 Hz, 1H), 6.43 (d, J = 16.1 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.47 (s, 3H), 3.41 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 187.1, 166.8, 152.62, 138.1, 130.8, 128.0, 127.2, 126.4, 124.4, 120.0, 60.6, 43.4, 38.8, 14.3.

Intramolecular sulfuration of 5ab



To a 25 mL dry reaction tube was added 0.2 mmol of **5ab**, 0.02 mmol of Pd(OAc)₂, 0.4 mmol of benzoquinone (BQ), 0.5 mL of acetic acid, and 0.5 mL of HFIP. The reaction tube was then sealed and the mixture was allowed to react at 80 °C for 12 h. After cooled to room temperature, solvents of the obtained solution was evaporated under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate / petroleum ether (1:50) to give corresponding product **3ab** as a white solid (42.5 mg, yeild 85%).

Reaction of ortho-substituted thiocarbamates with olefin 2a:



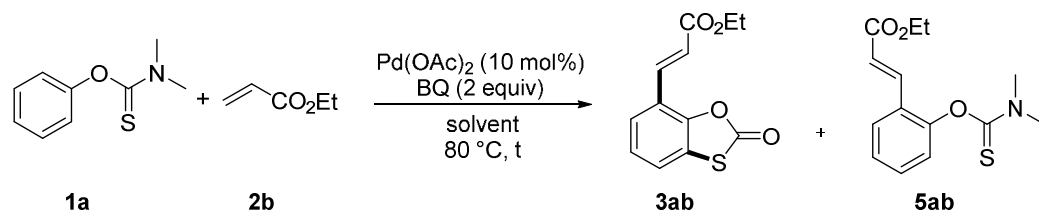
To a 25 mL dry reaction tube was added 0.2 mmol of **3b**, 0.2 mmol of **2a**, 0.02 mmol of Pd(OAc)₂, 0.4 mmol of benzoquinone (BQ), 0.5 mL of acetic acid, and 0.5 mL of HFIP. The reaction tube was then sealed and the mixture was allowed to react at 80 °C for 12 h. After cooled to room temperature, solvents of the obtained solution was evaporated under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate / petroleum ether (1:50) to give corresponding product **4b** as a white solid (29.0 mg, yield 63%). ¹H NMR (500 MHz, CDCl₃) δ 7.49 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.35 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 166.7, 145.9 131.0, 126.1, 124.0, 121.2, 105.0.

7-phenylbenzo[d][1,3]oxathiol-2-one. The reaction was performed following the same general procedure give corresponding product **4c** as a white solid (34.2 mg, yield 75 %). ¹H NMR (500 MHz, CDCl₃) δ 7.65 – 7.63 (m, 2H), 7.50 – 7.46 (m, 2H), 7.45 – 7.40 (m, 2H), 7.38 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 168.5, 145.3, 135.2, 128.7 (d, *J* = 4.7 Hz), 128.4, 128.1, 126.8, 125.4, 123.8, 121.2.

GC analysis for the concentration of the mixture varies with time

General Procedure. To a 25 mL dry reaction tube added 0.2 mmol of **1a**, 0.2 mmol of **2b**, 0.02 mmol of Pd(OAc)₂, 0.4 mmol of benzoquinone (BQ), 0.5 mL of acetic acid, and 0.5 mL of HFIP. The reaction tube was then sealed and the mixture was allowed to react at 80 °C. The data (% product versus time) was analyzed using the initial rates

method. Product yield from the corresponding reaction was monitored by GC analysis using dodecane as internal standard.



t (min)	1a (mol/L)	5ab (mol/L)	3ab (mol/L)
0	0.200	0	0
30	0.152	0.04	0
40	0.136	0.05	0
50	0.090	0.084	0
60	0.032	0.134	0.04
70	0.010	0.054	0.088
90	0	0.012	0.112
120	0	0.008	0.114
150	0	0	0.115

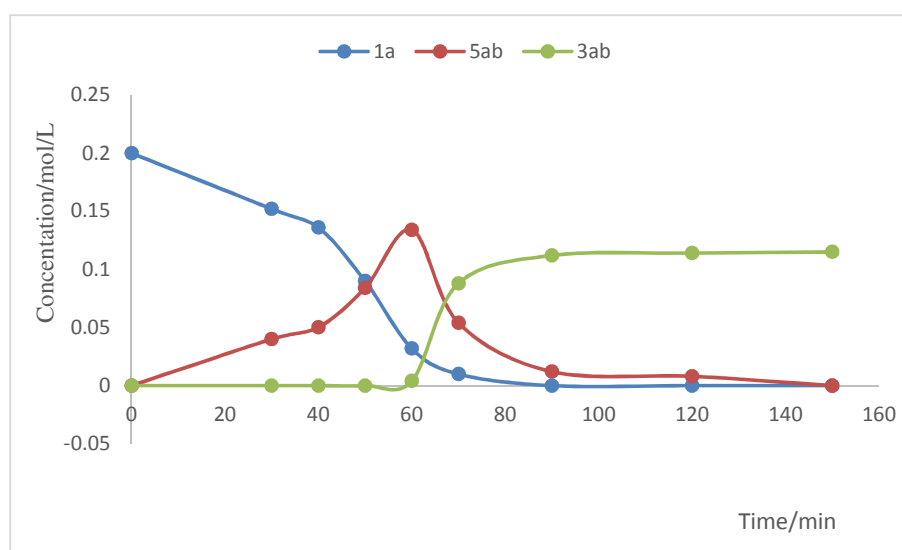
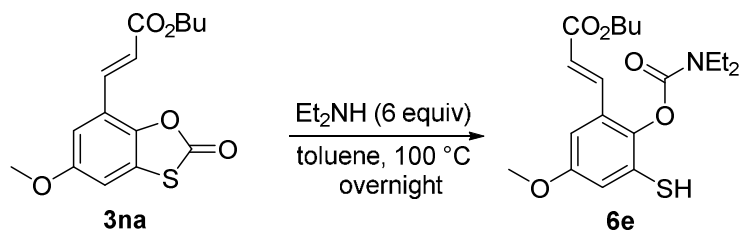


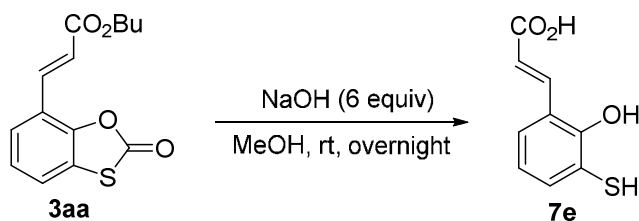
Figure S1

5. Synthetic application and product characterization

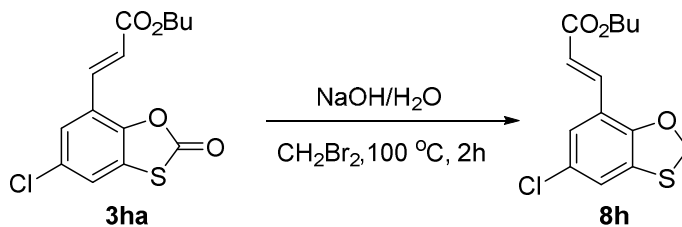


To a reaction tube was added **3na** (154 mg, 0.5 mmol), Et_2NH (6 equiv) and toluene (2 mL). The tube was sealed and heated at 100°C . After 12 hours, the reaction

mixture was cooled to room temperature. Then it was condensed under reduced pressure and the residue was purified by flash column chromatograph to give the desired product (**6e**) as an colorless oil (84 mg, yield 44%). ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, J = 16.1 Hz, 1H), 7.15 (d, J = 2.9 Hz, 1H), 6.96 (d, J = 2.9 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 4.18 (t, J = 6.6 Hz, 2H), 3.74 (s, 3H), 3.54 (d, J = 6.9 Hz, 2H), 3.39 (q, J = 7.0 Hz, 2H), 1.69–1.63 (m, 2H), 1.45–1.39 (m, 2H), 1.38–1.33 (m, 3H), 1.21 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.5, 157.5, 153.0, 141.0, 137.7, 132.1, 129.5, 121.0, 114.9, 111.0, 64.5, 55.8, 42.6, 42.1, 30.7, 19.2, 14.4, 13.7, 13.3. HRMS (ESI) *calcd* for $\text{C}_{19}\text{H}_{28}\text{NO}_5\text{S}$ ($\text{M}+\text{H}^+$): 382.1683, found 382.1677.

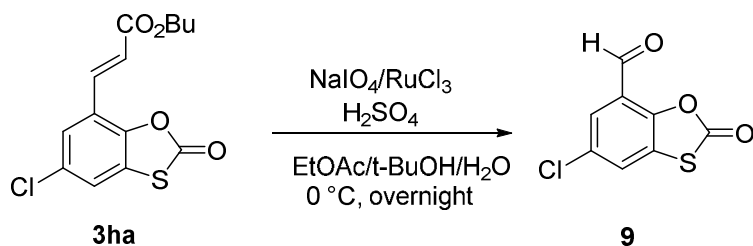


To a reaction tube was added **3aa** (139 mg, 0.5 mmol), NaOH (120 mg, 6 equiv) and MeOH (2 mL) and then sealed. The reaction mixture was stirred at room temperature for 12 hours, followed by addition of 5 ml HCl (1 M). Then the reaction mixture was extracted with EtOAc (10 mL x 3), and the combined organic layer was washed with sodium hydroxide solution and brine, dried over Na_2SO_4 , filtered, and condensed under reduced pressure and the residue was purified by flash column chromatograph to give the desired product (**7e**) as a white solid (55 mg, yield 56%). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.93 (d, J = 16.0 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 6.86 (t, J = 7.4 Hz, 1H), 6.50 (d, J = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 168.1, 153.9, 139.0, 131.1, 127.6, 125.5, 124.1, 121.6, 120.1.

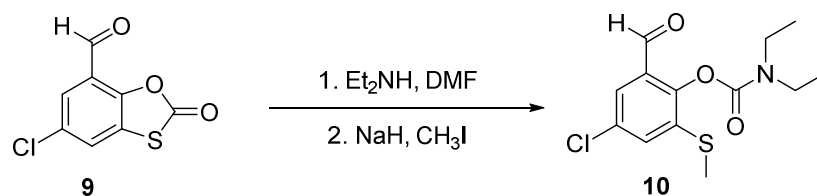


To a reaction tube was added **3ha** (314 mg, 1.0 mmol), 1 ml aq NaOH (5M), Bu_4NBr (30 mg) and 1 mL CH_2Br_2 . The tube was then sealed and heated at 100°C . After 2 hours, the reaction mixture was cooled to room temperature. Then it was condensed under reduced pressure and the residue was purified by flash column chromatograph to give the desired product (**8h**) as a white solid (283 mg, yield 95%). ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, J = 16.1 Hz, 1H), 7.10 (s, 2H), 6.56 (d, J = 16.1 Hz, 1H), 5.80 (s, 2H), 4.20 (t, J = 6.7 Hz, 2H), 1.72 – 1.64 (m, 2H), 1.47 – 1.39 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.9, 153.8, 137.9, 129.0, 127.4, 125.2, 122.9, 121.6, 119.1, 76.1, 64.6, 30.8, 19.2, 13.8. HRMS (ESI) *calcd* for $\text{C}_{14}\text{H}_{16}\text{ClO}_3\text{S}$ ($\text{M}+\text{H}^+$): 299.0503, found 299.0499.

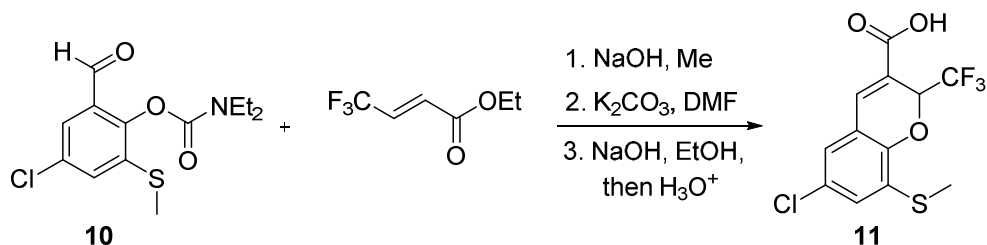
Synthesis of COX-2 inhibitor



To a reaction tube was added **3ha** (1.57g, 5.0 mmol), NaIO₄ (3.2g, 3 equiv, 15 mmol), RuCl₃ (aq., 0.1 M, 250 μ l), H₂SO₄ (20 mol%), EtOAc (3 ml), *t*-BuOH (3 ml) and H₂O (1 ml). The mixture was stirred at 0°C for 12 h. Then it was condensed under reduced pressure and the residue was purified by flash column chromatograph to give the desired product (**9**) as a white solid (642 mg, yield 60%). ¹H NMR (500 MHz, CDCl₃) δ 10.31 (s, 1H), 7.81 (d, *J* = 2.3 Hz, 1H), 7.64 (d, *J* = 2.3 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 185.0, 166.67, 147.4, 131.5, 127.2, 126.3, 126.1, 121.



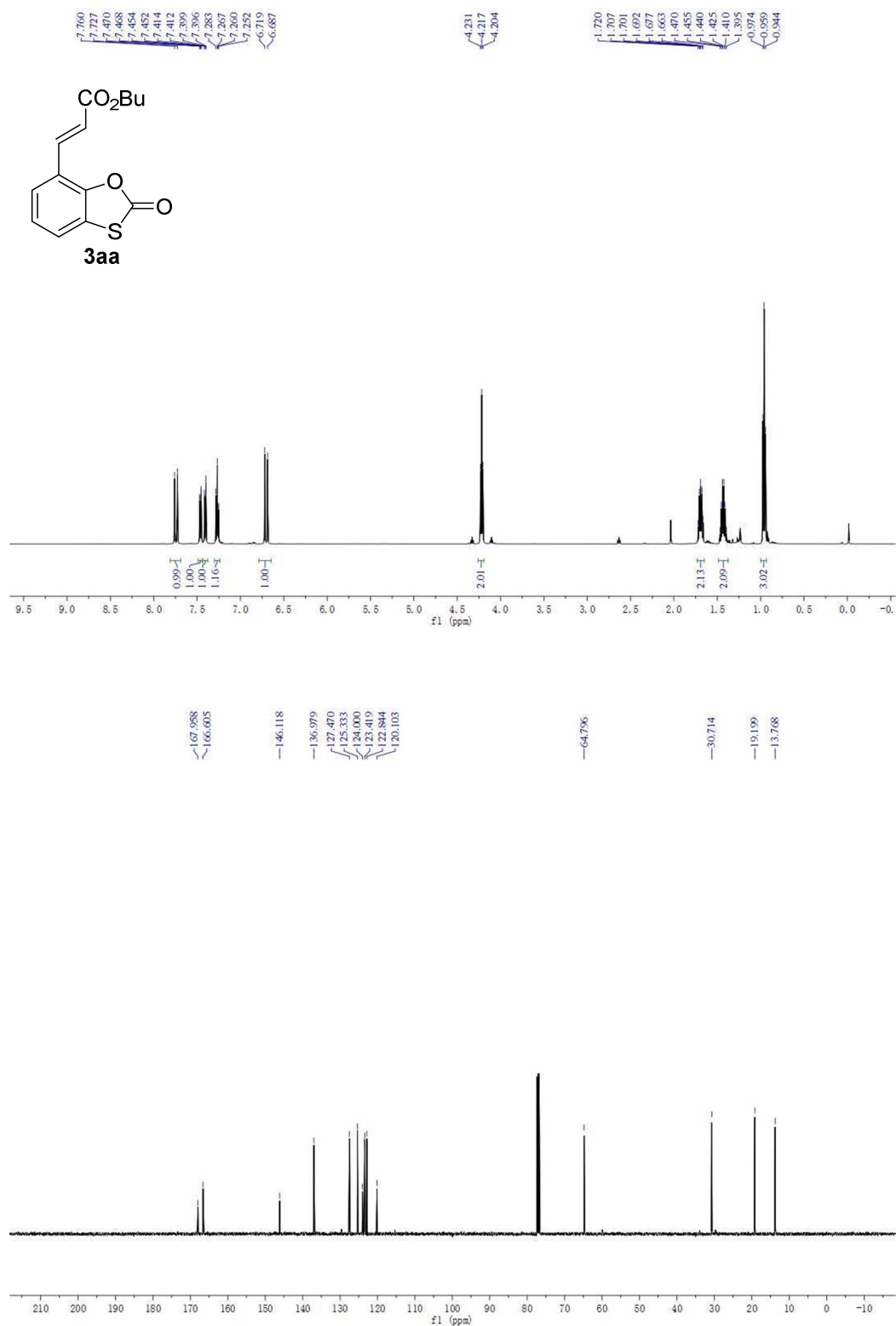
To a schlenk tube was added 1 mmol **9** (214 mg), 1.2 equiv Et₂NH and 2 ml DMF at 90 °C for 12 h, then added 1.2 equiv NaH and 2 equiv CH₃I under room temperature for 12 h, and condensed under reduced pressure and the residue was purified by flash column chromatograph to give the desired product (**10**) as a white solid (172 mg, yield 57% in two steps). ¹H NMR (500 MHz, DMSO) δ 9.90 (s, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.58 (d, *J* = 2.4 Hz, 1H), 3.48 (q, *J* = 7.1 Hz, 2H), 3.29 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, DMSO) δ 188.8, 152.3, 147.2, 138.0, 131.7, 130.3, 130.1, 125.5, 42.6, 42.2, 14.6, 14.1, 13.6. HRMS (ESI) *calcd* for C₁₃H₁₇ClNO₃S (M+H⁺): 302.0612, found 302.0608.

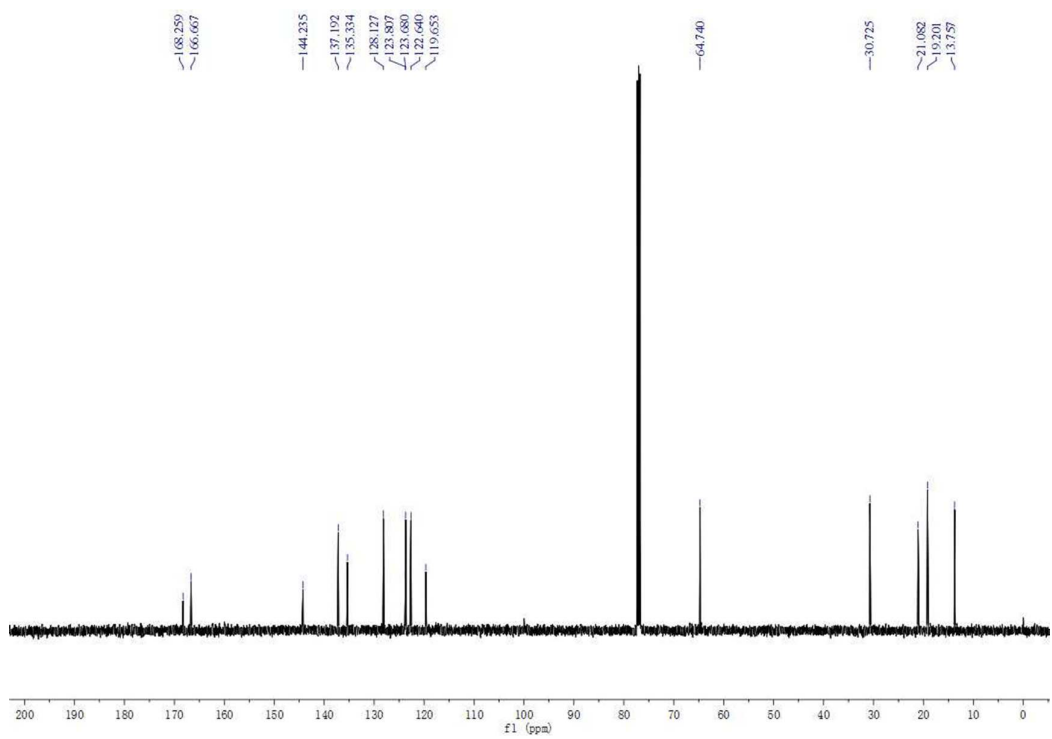
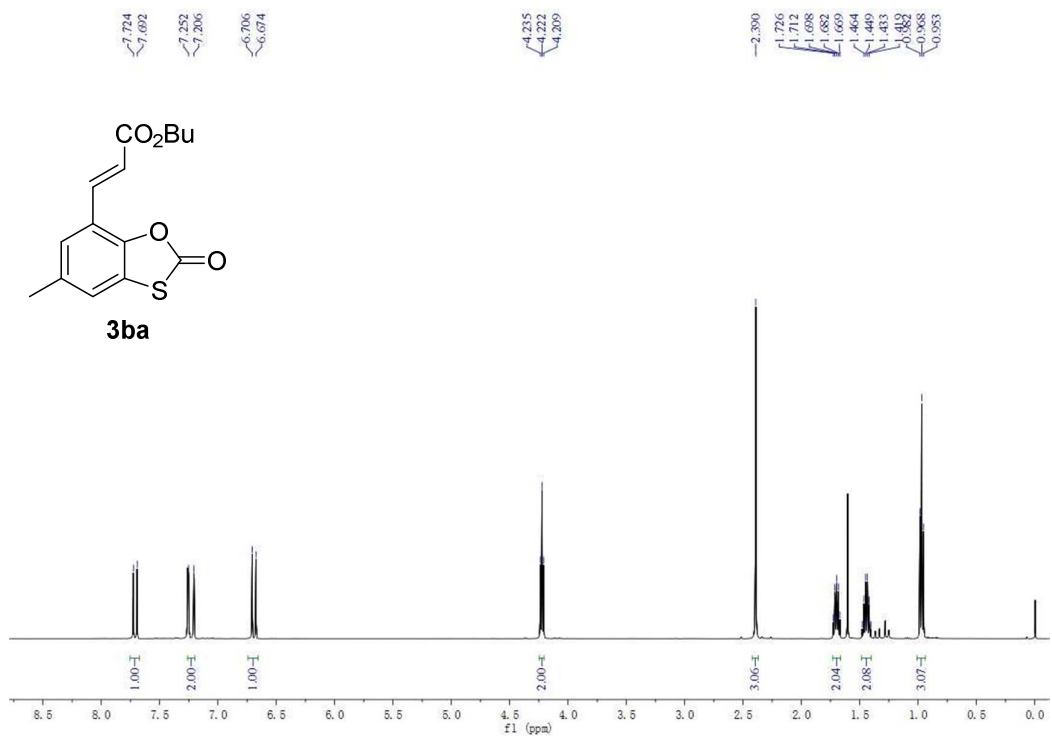


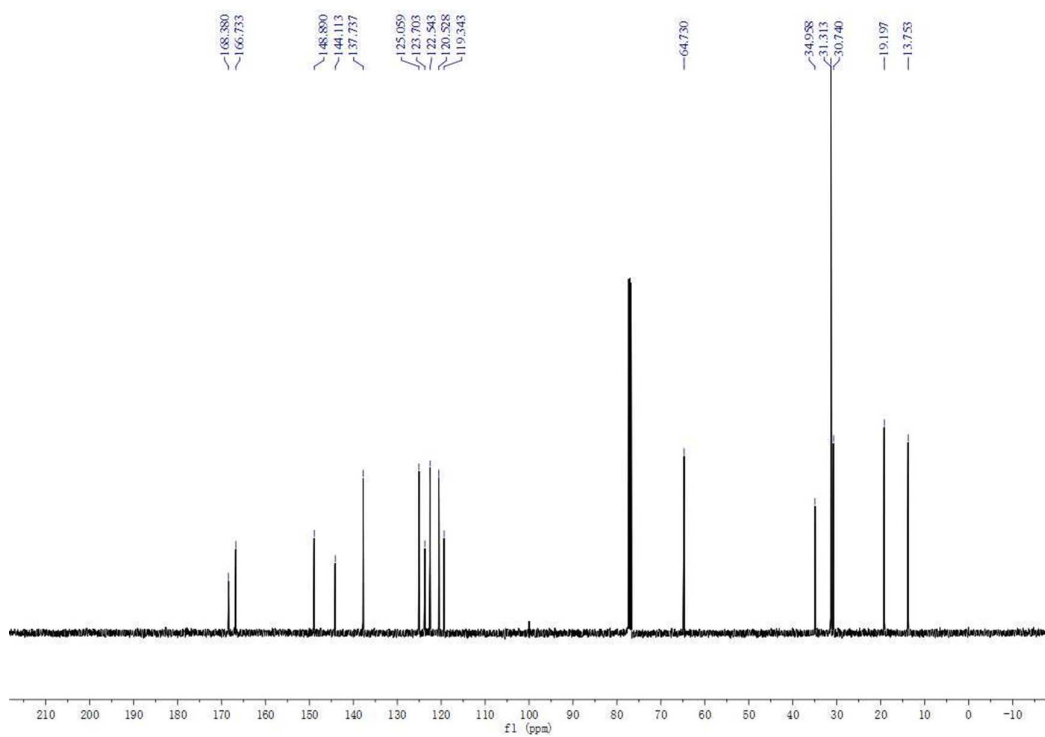
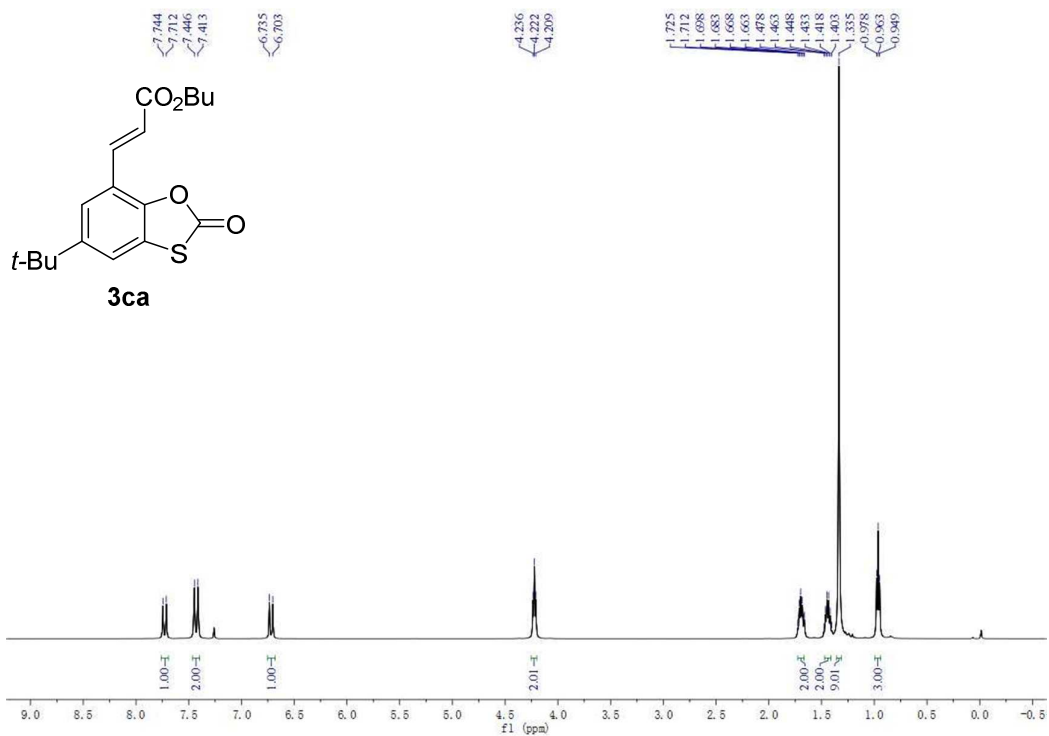
To a schlenk tube was added 0.5 mmol **10**, 2 mmol NaOH and 2 ml MeOH at room temperature for 12 h, remove the Me, then added 5 equiv ethyl (E)-4,4,4-trifluorobut-2-enoate, 2.5 equiv K₂CO₃ and 2 ml DMF at 90 °C for 24 h, the reaction mixture was extracted with aqueous NH₄Cl solution and EtOAc, and steam the organic phase, then added 0.5 ml NaOH(aq)(5 M) and 1 ml MeOH under room

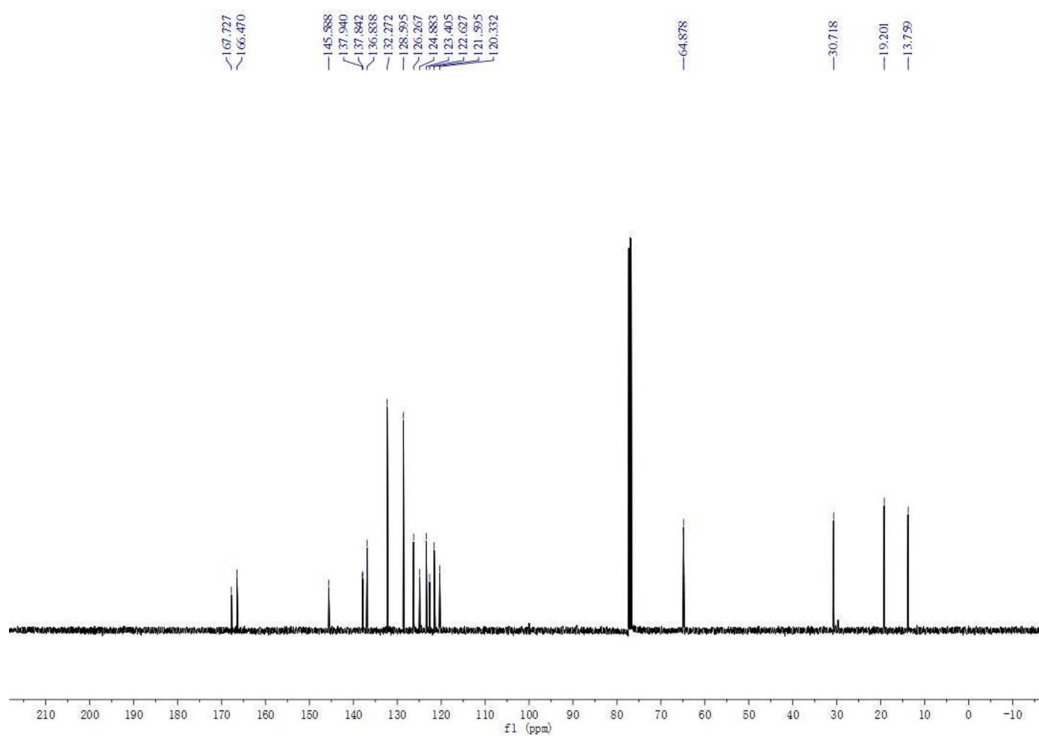
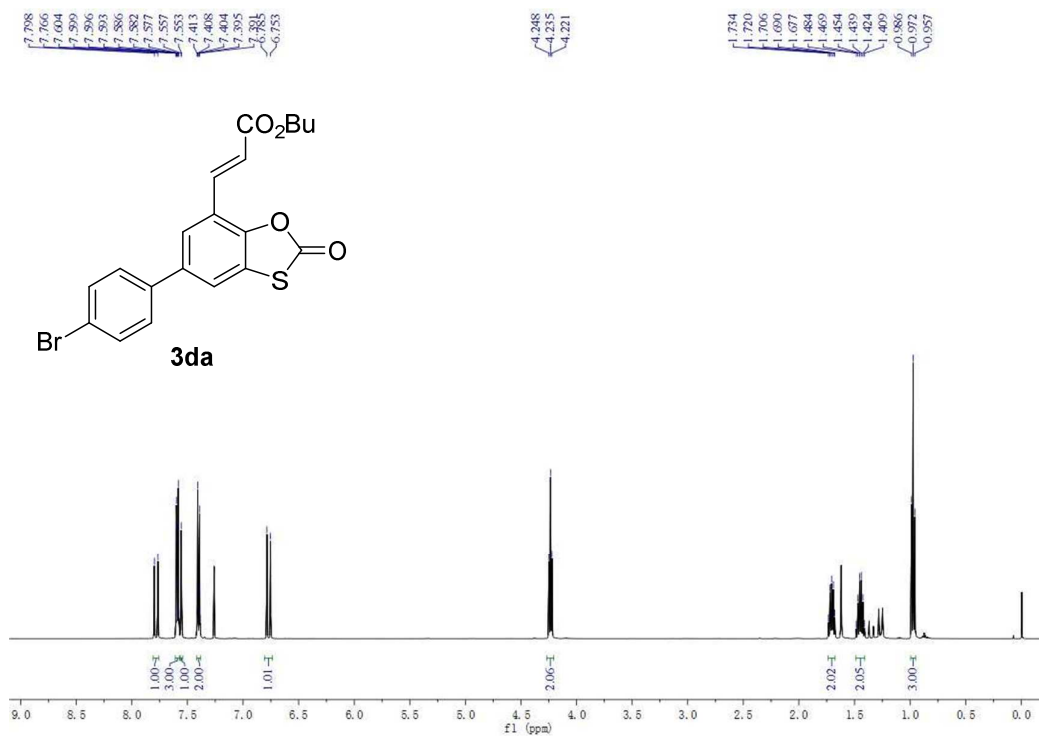
temperature for 24 h. Then condensed under reduced pressure and the residue was purified by flash column chromatograph to give the desired product (**11**) as a white solid 50 mg (yield 31%). ^1H NMR (500 MHz, DMSO) δ 7.83 (s, 1H), 7.40 (d, J = 2.4 Hz, 1H), 7.23 (d, J = 2.4 Hz, 1H), 6.04 (q, J = 7.1 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 164.9, 147.5, 135.4, 129.1, 127.5, 127.5, 125.1, 120.1, 119.1, 79.4 (t, J = 33.2 Hz), 70.7 (q, J = 32.3 Hz), 13.8.

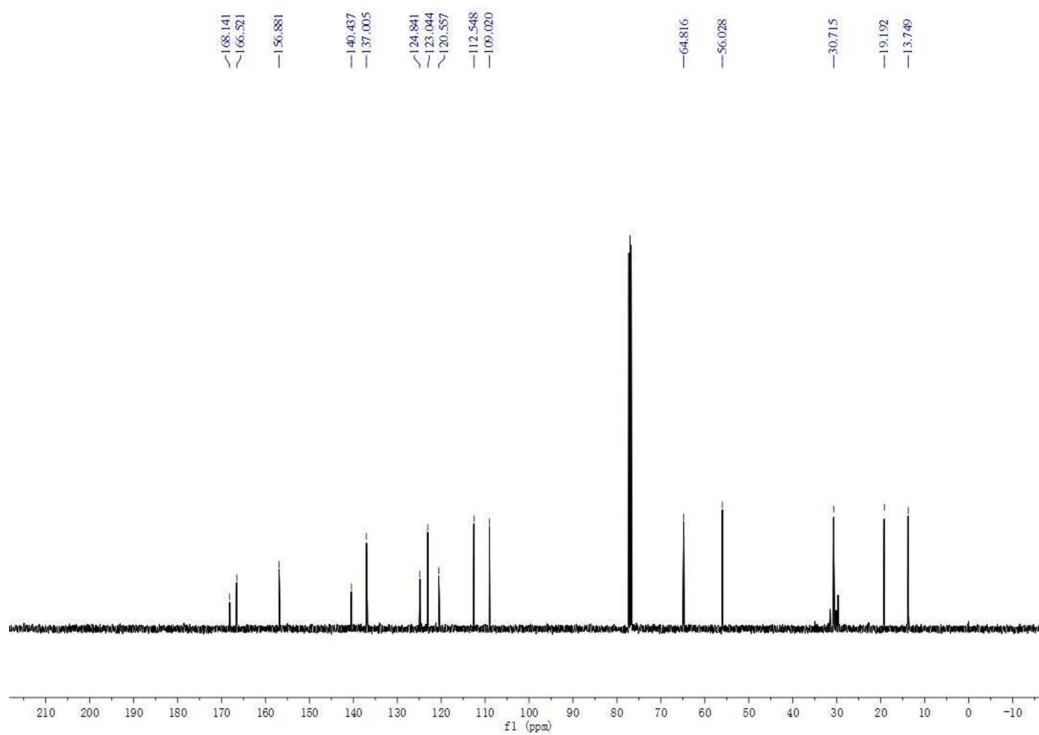
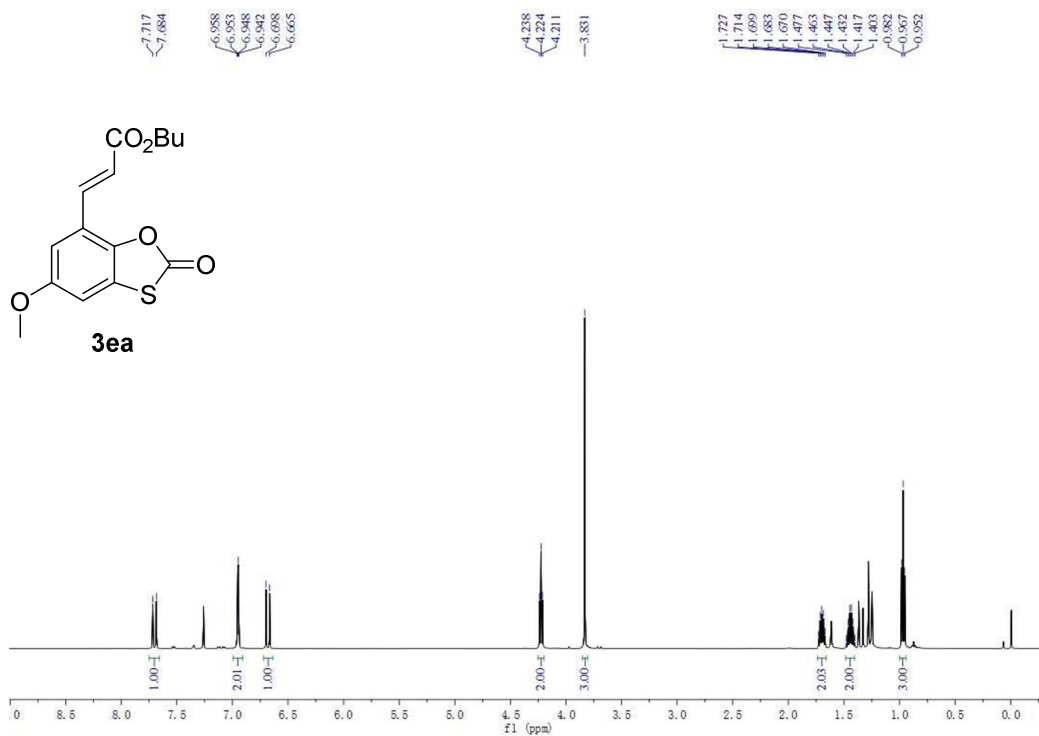
6. Copies for ^1H NMR and ^{13}C NMR spectrum

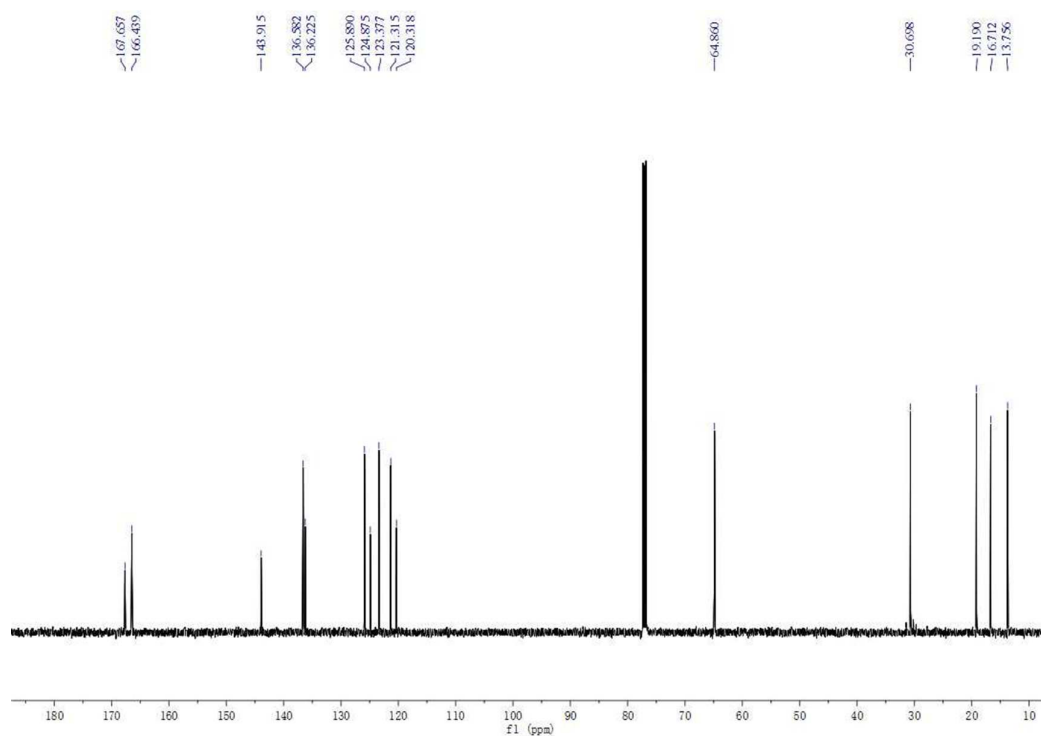
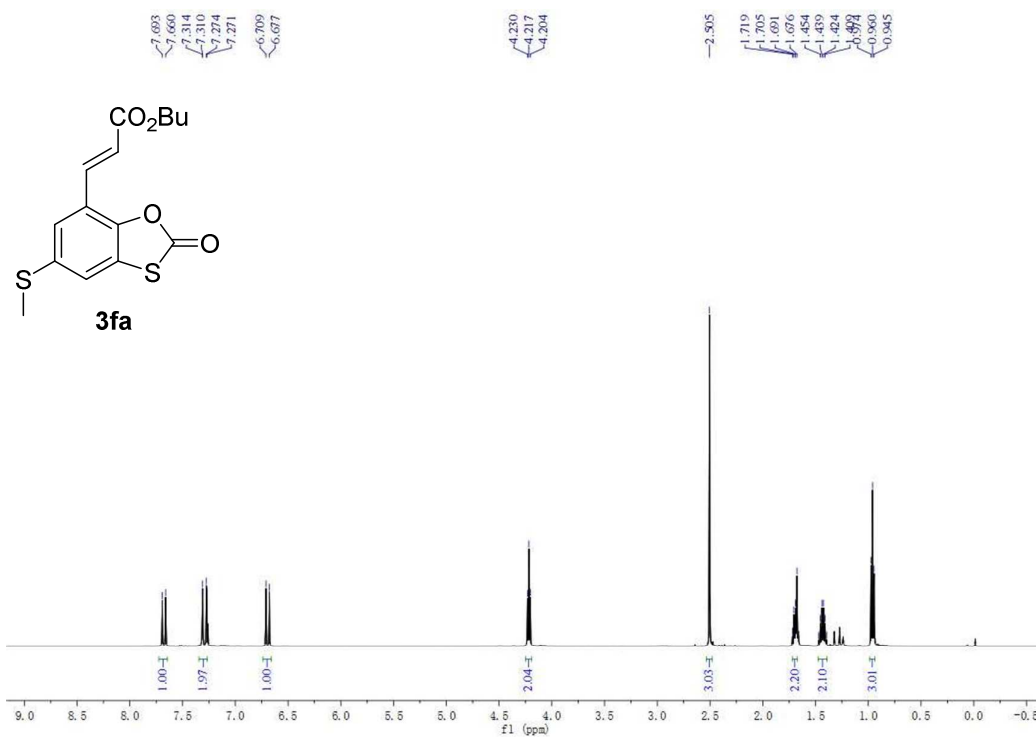


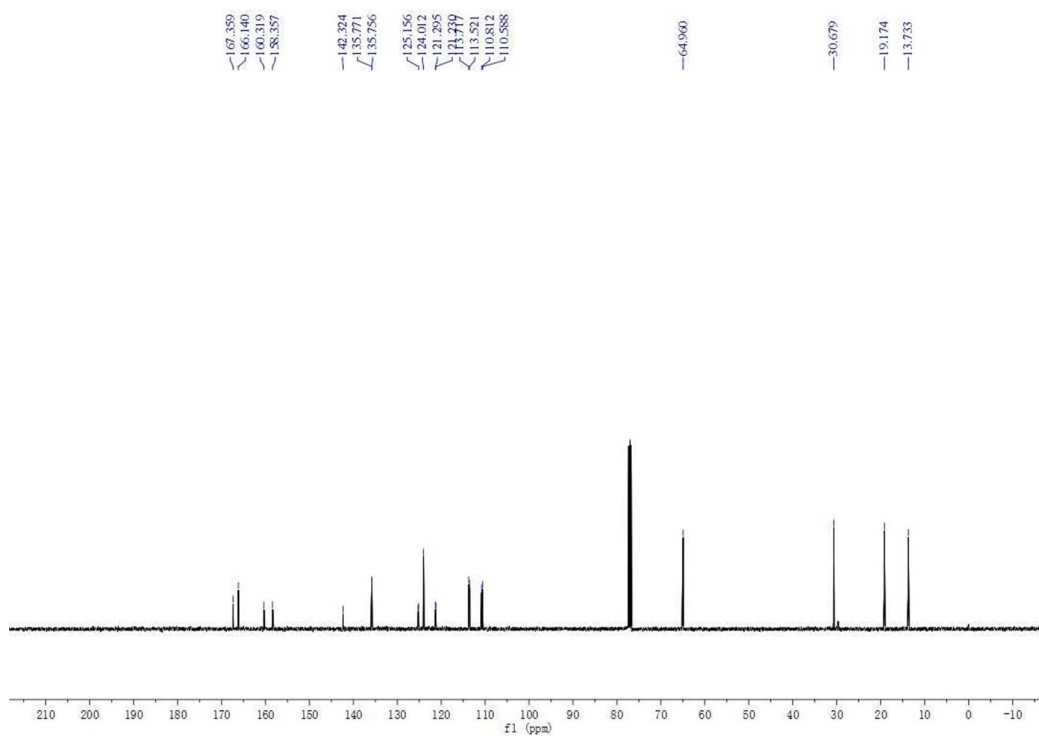
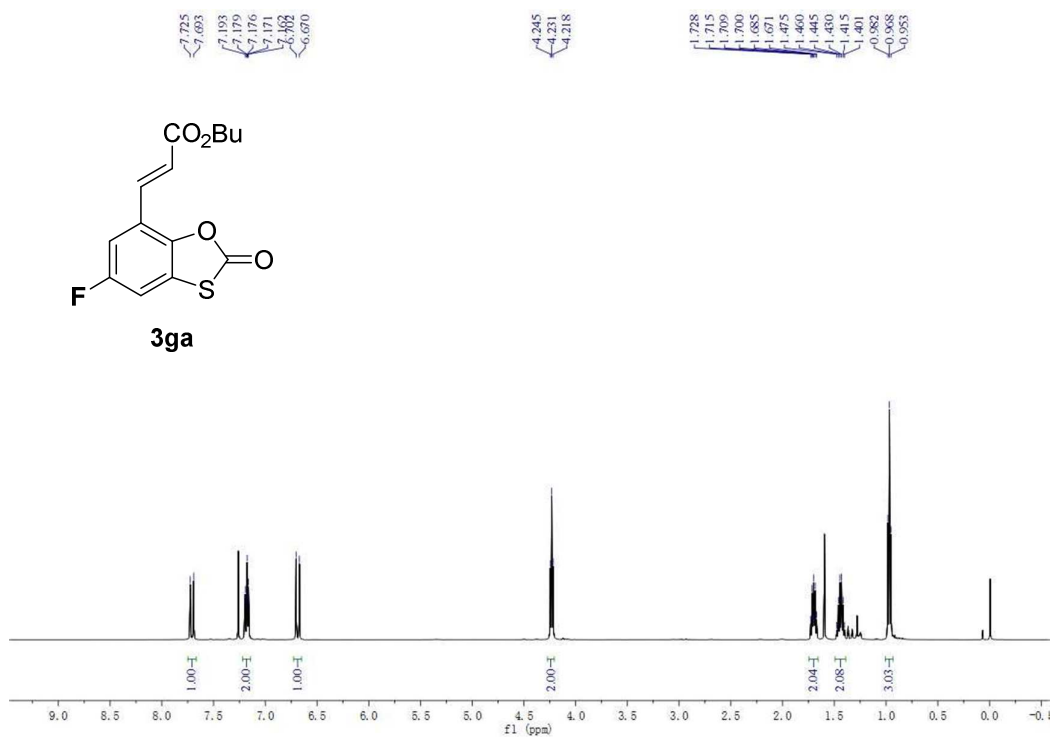
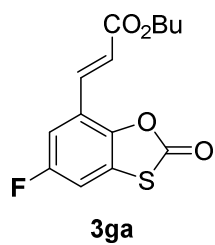


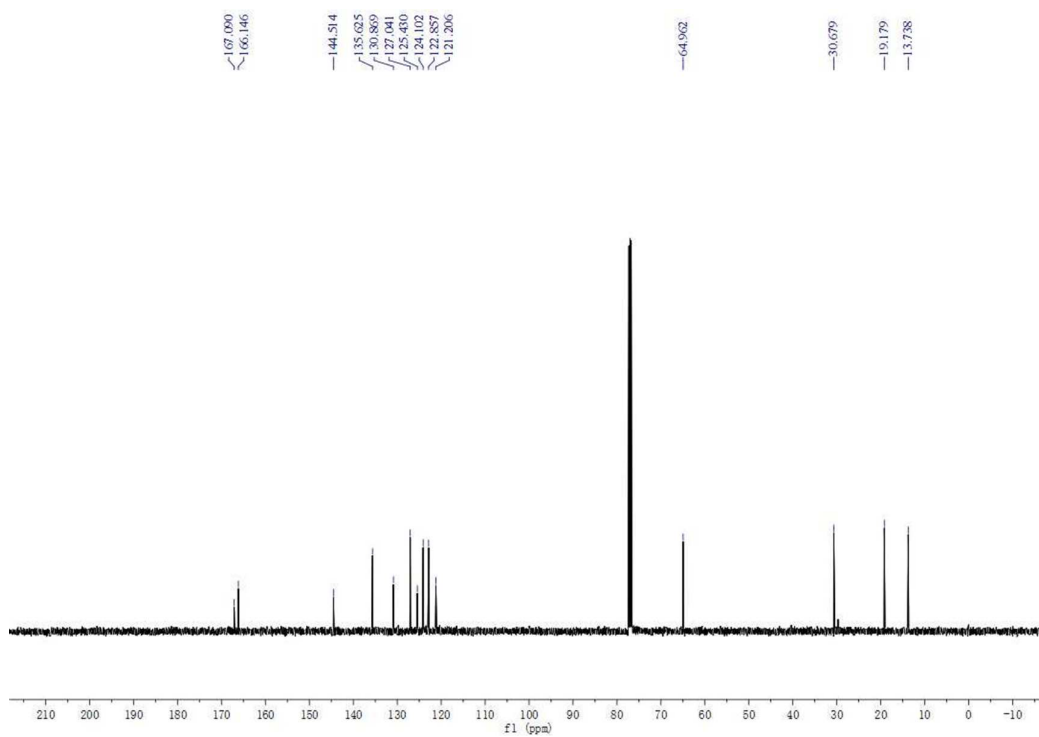
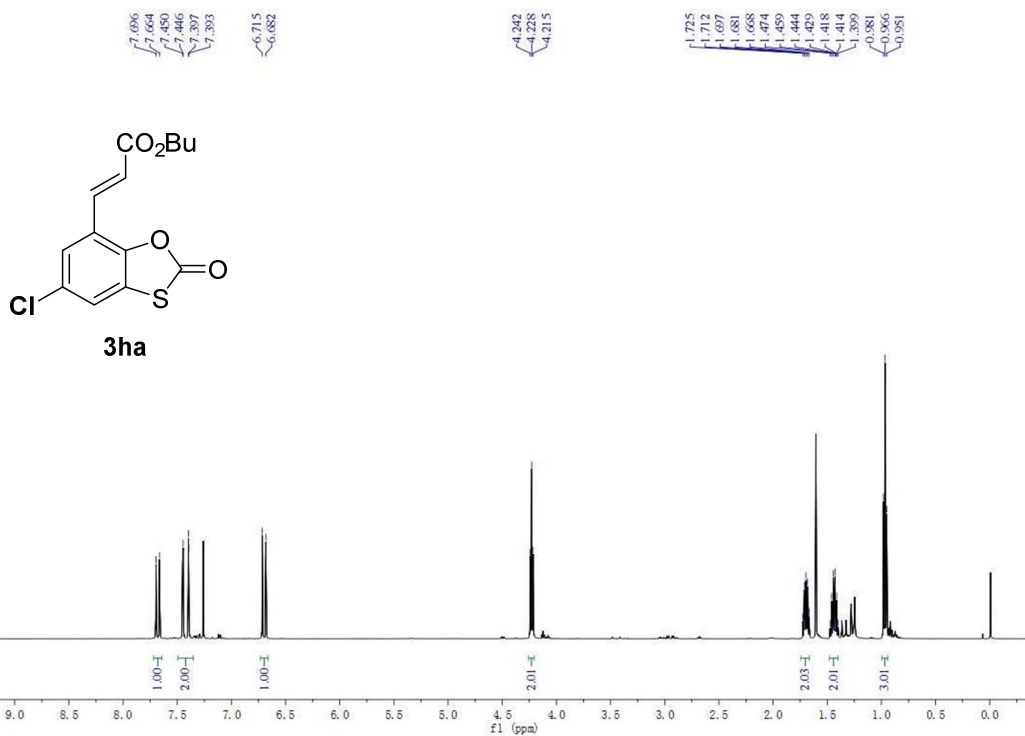


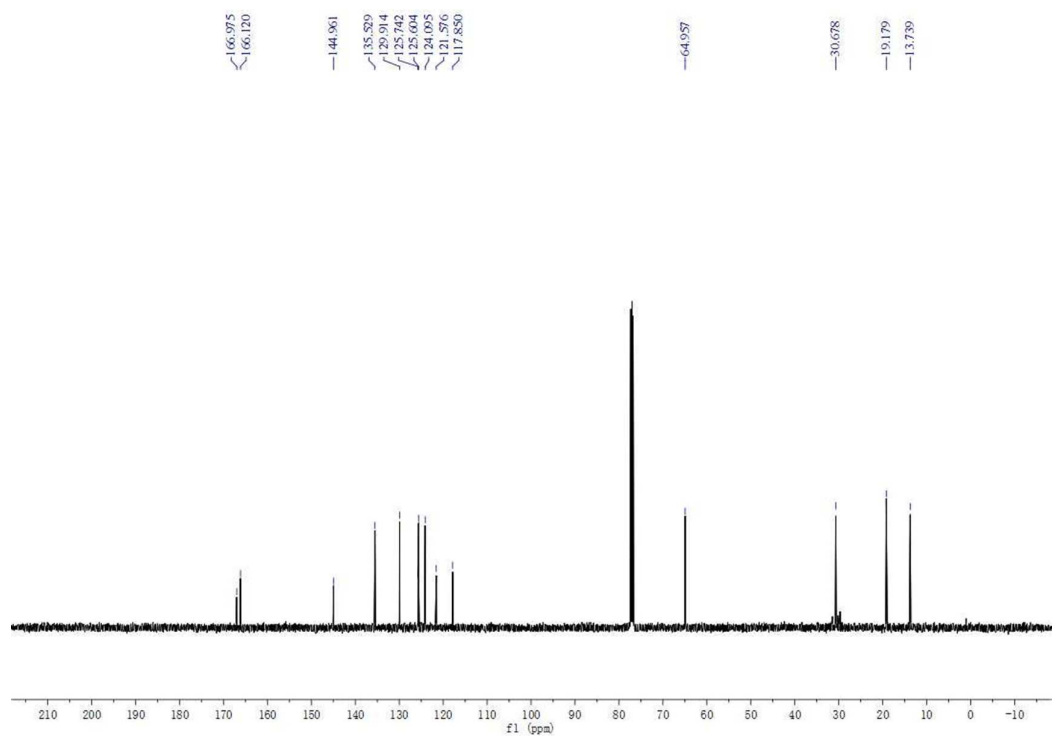
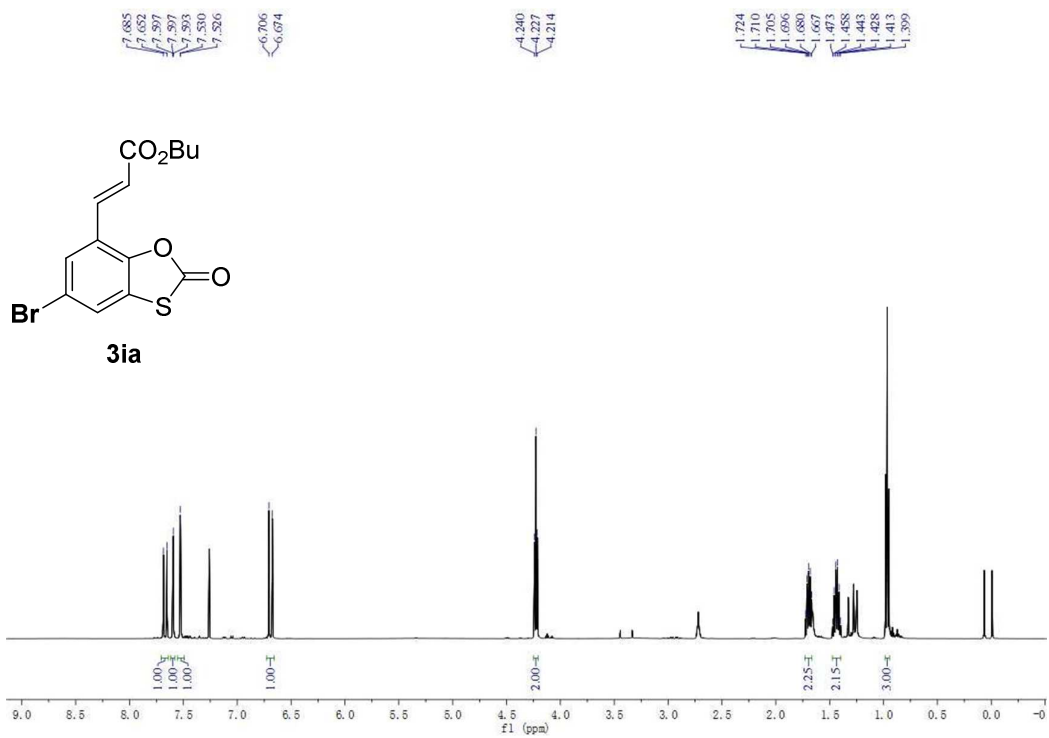


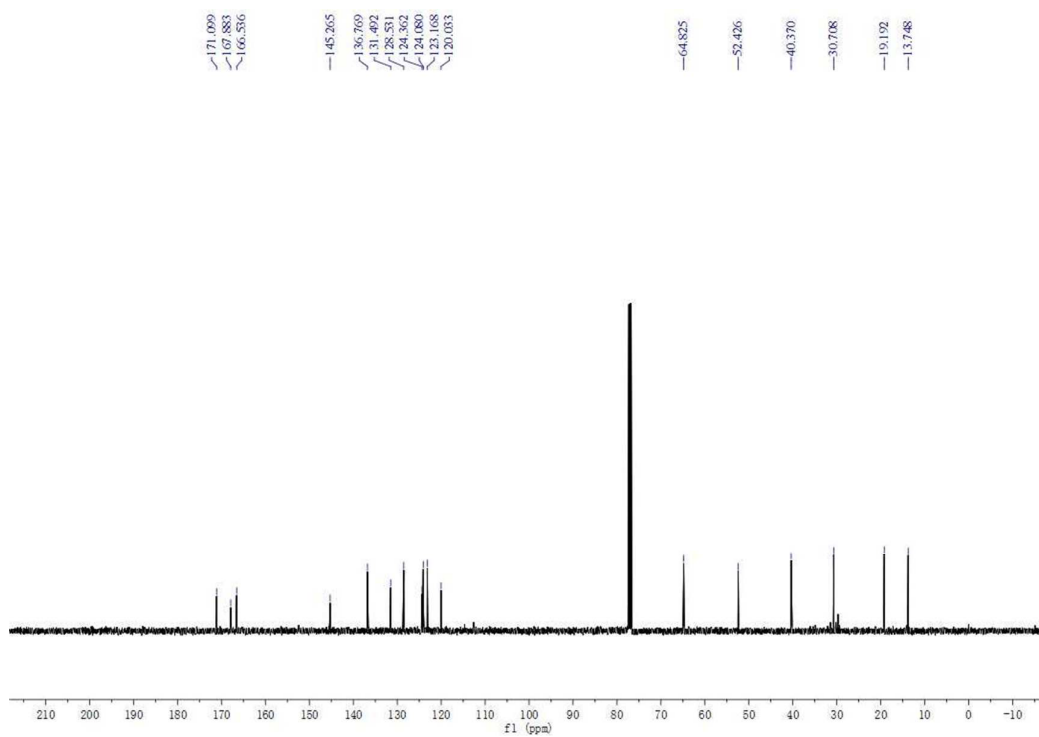
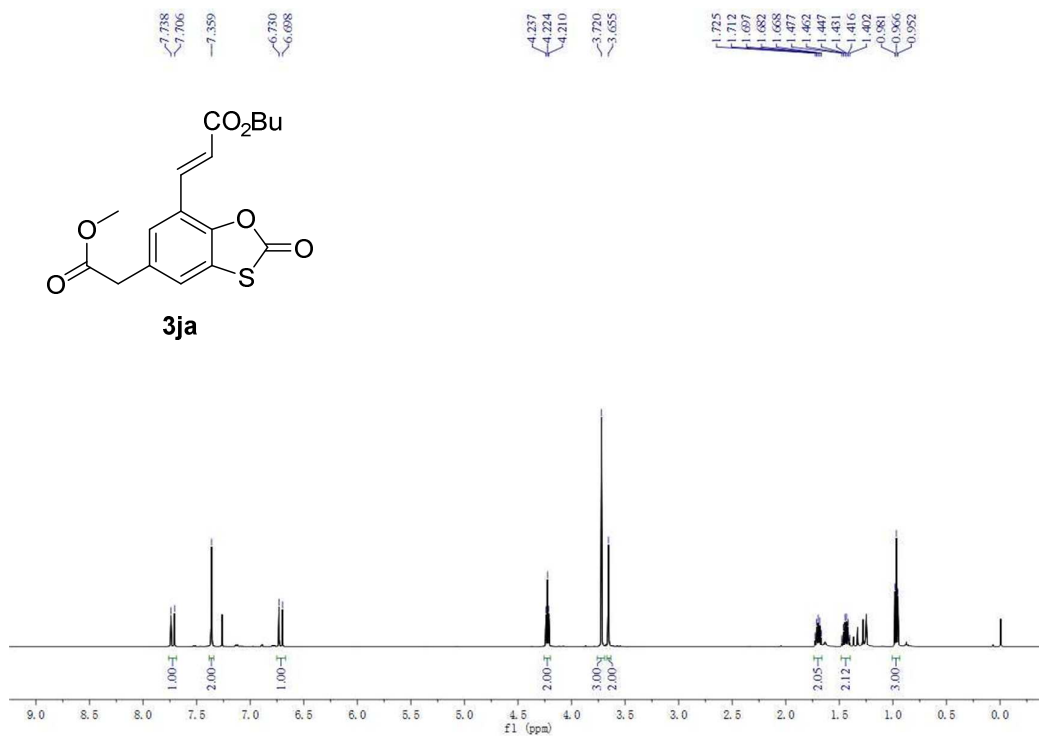
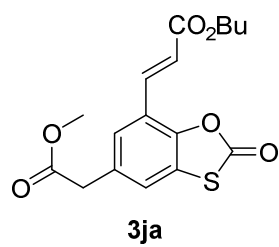


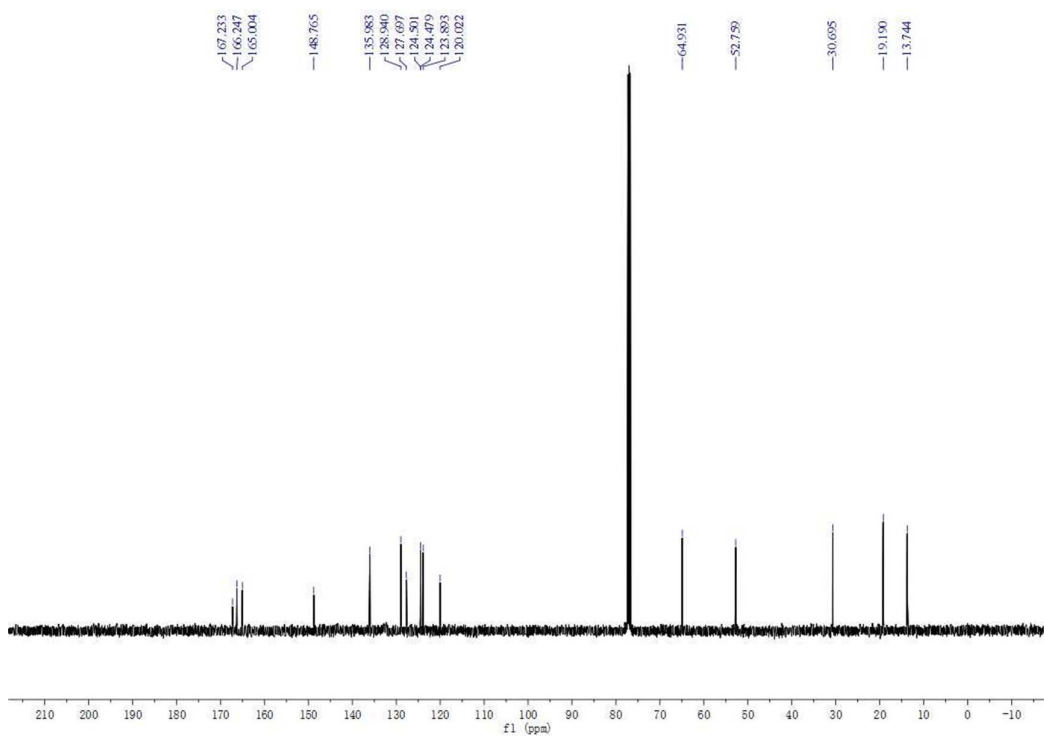
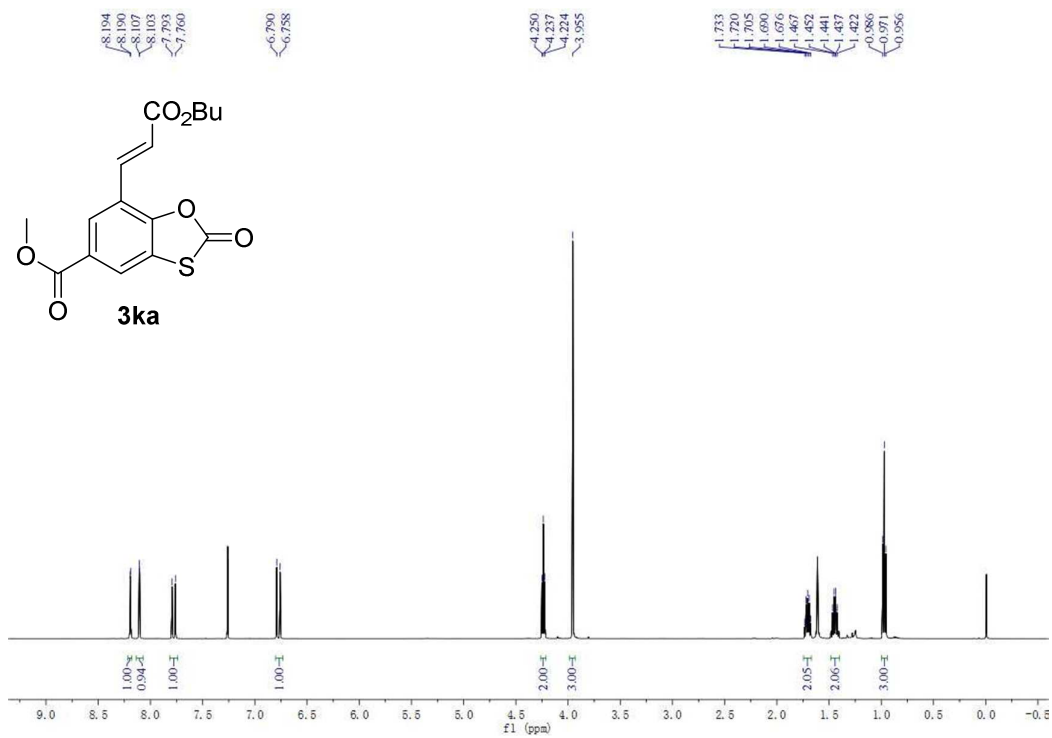


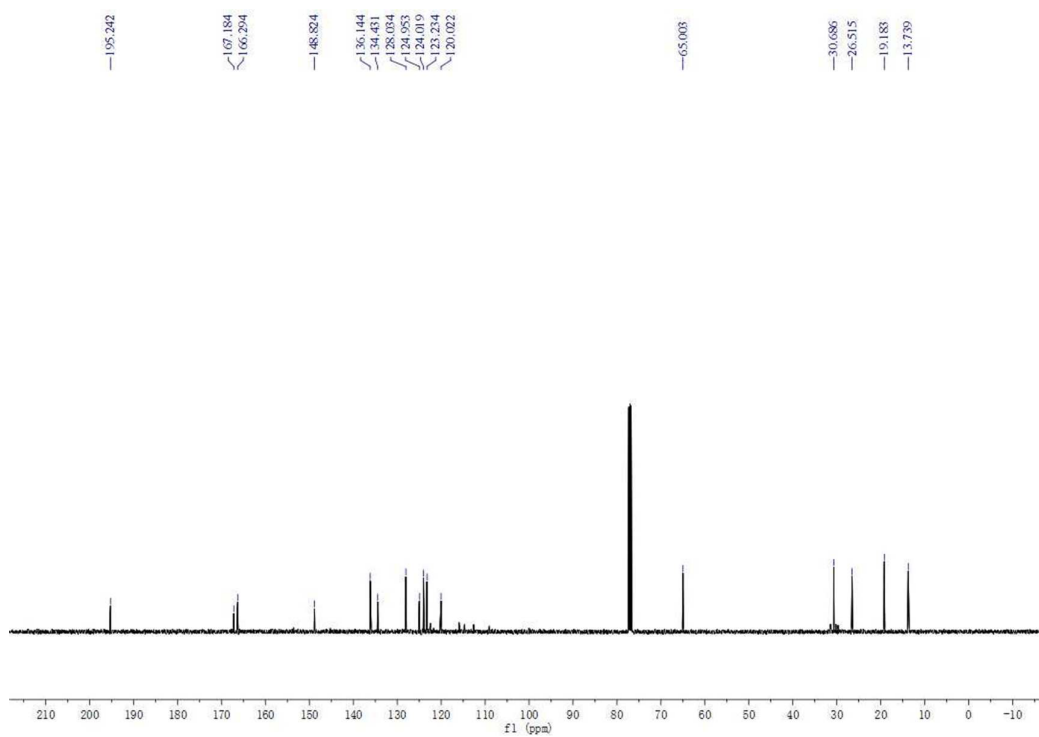
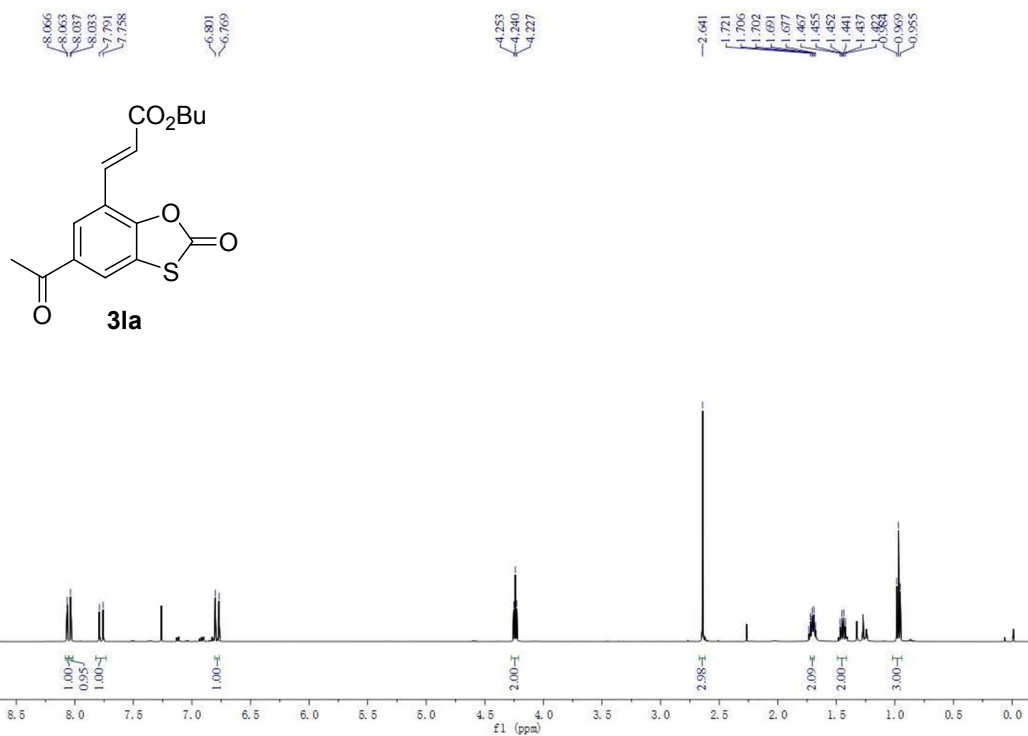


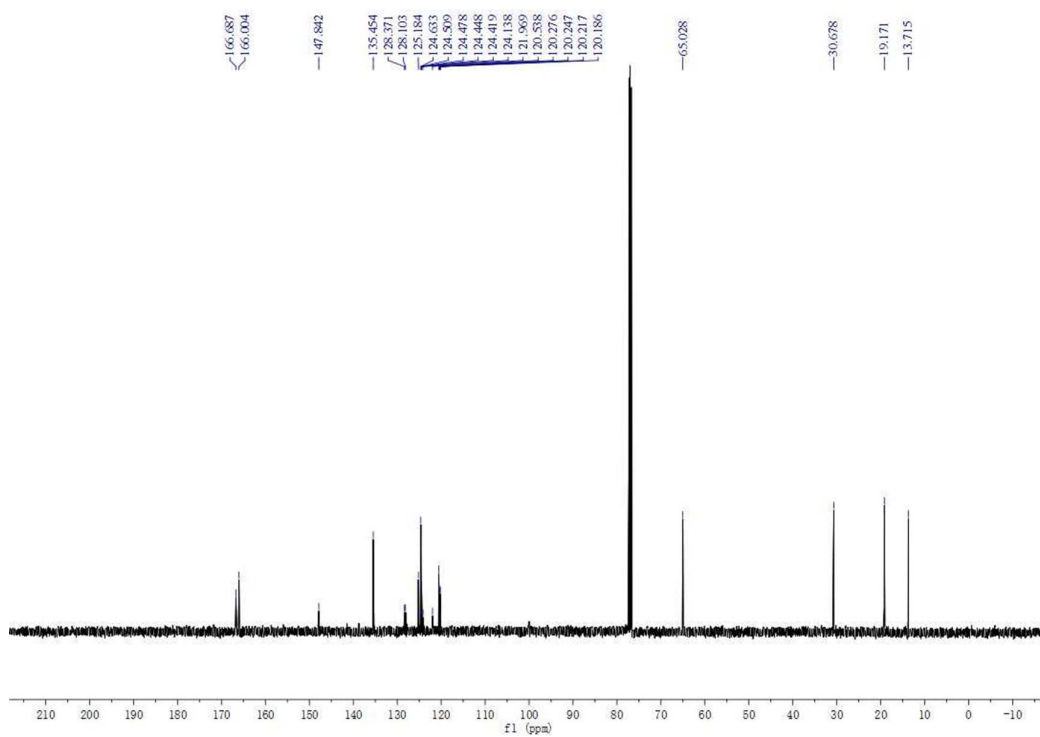
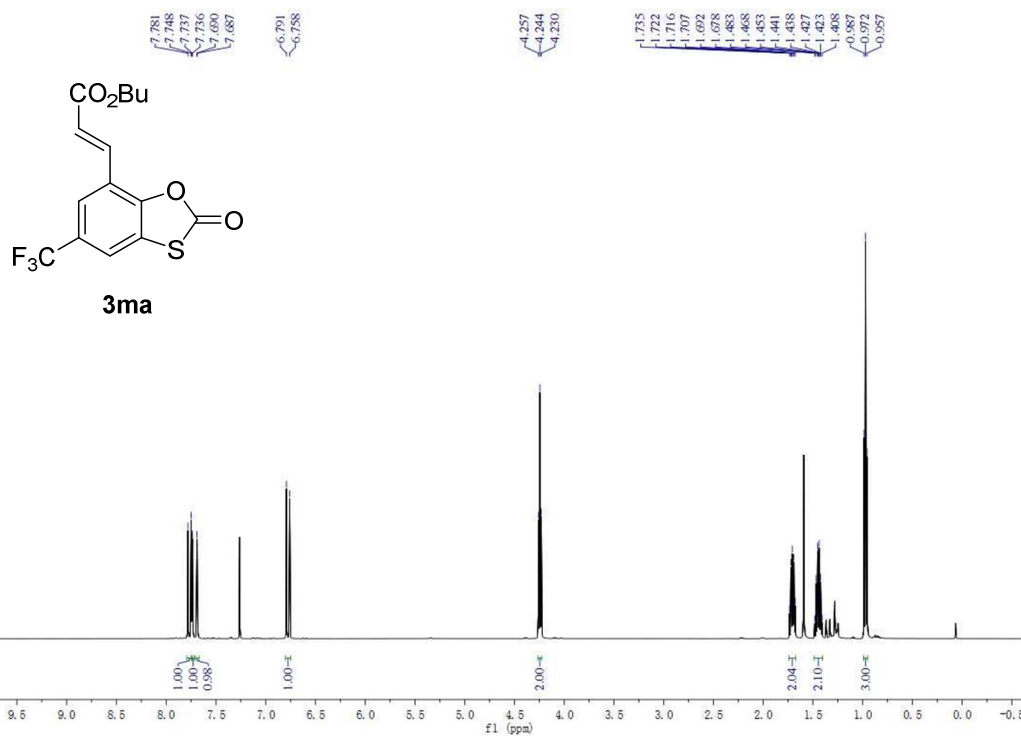


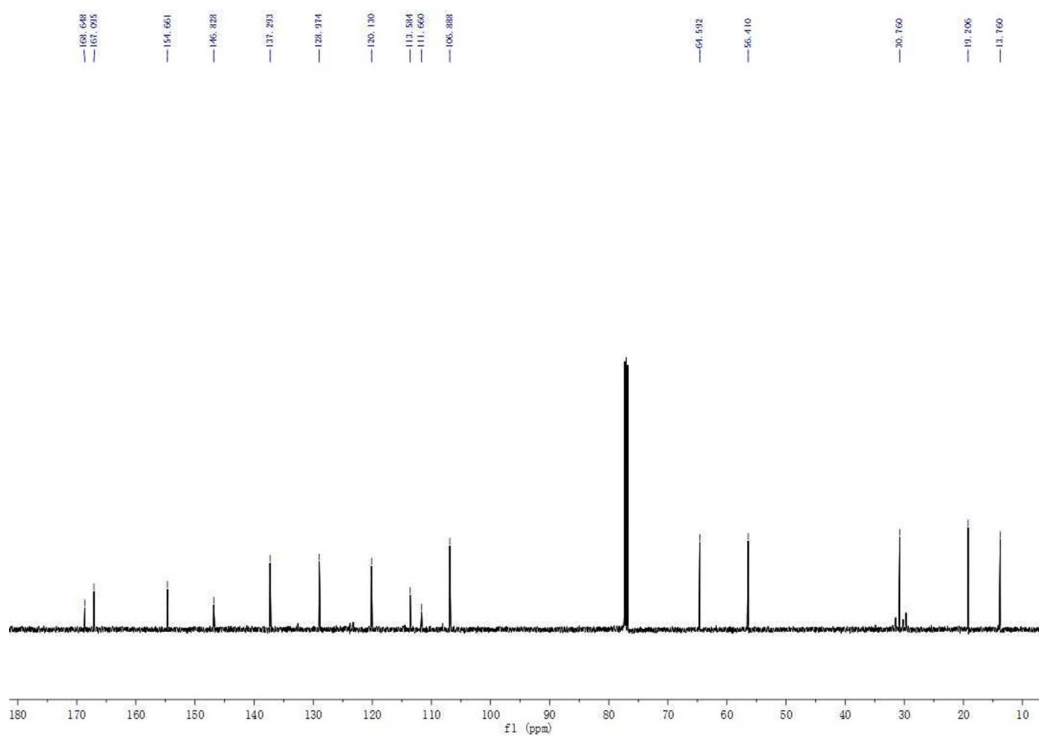
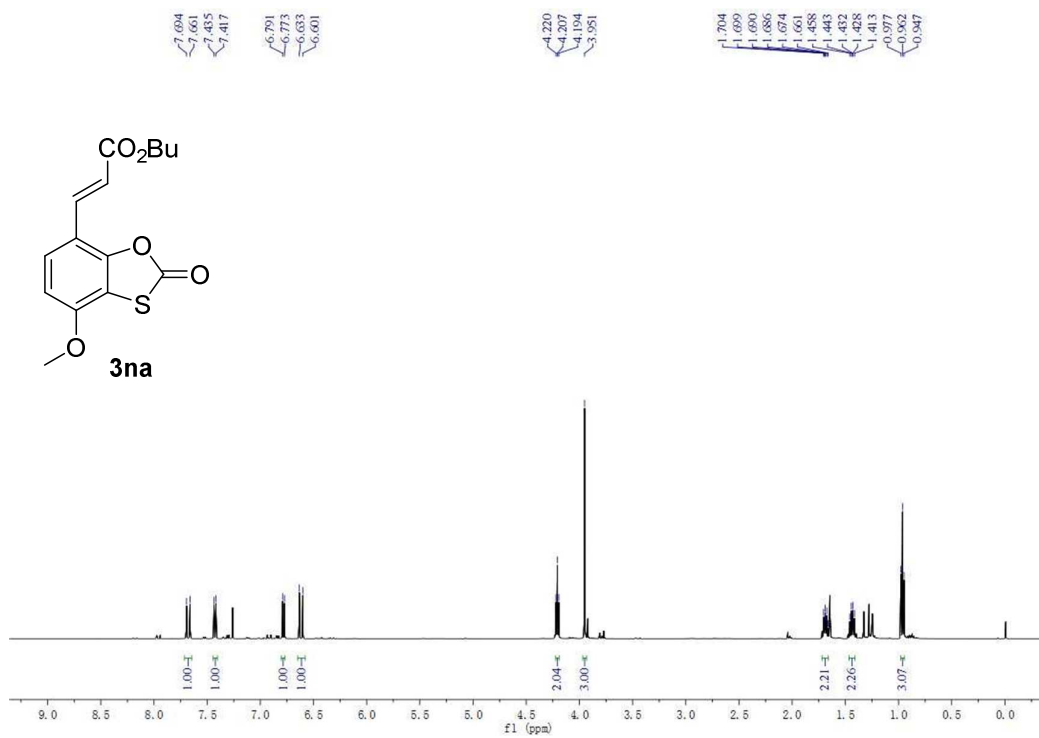


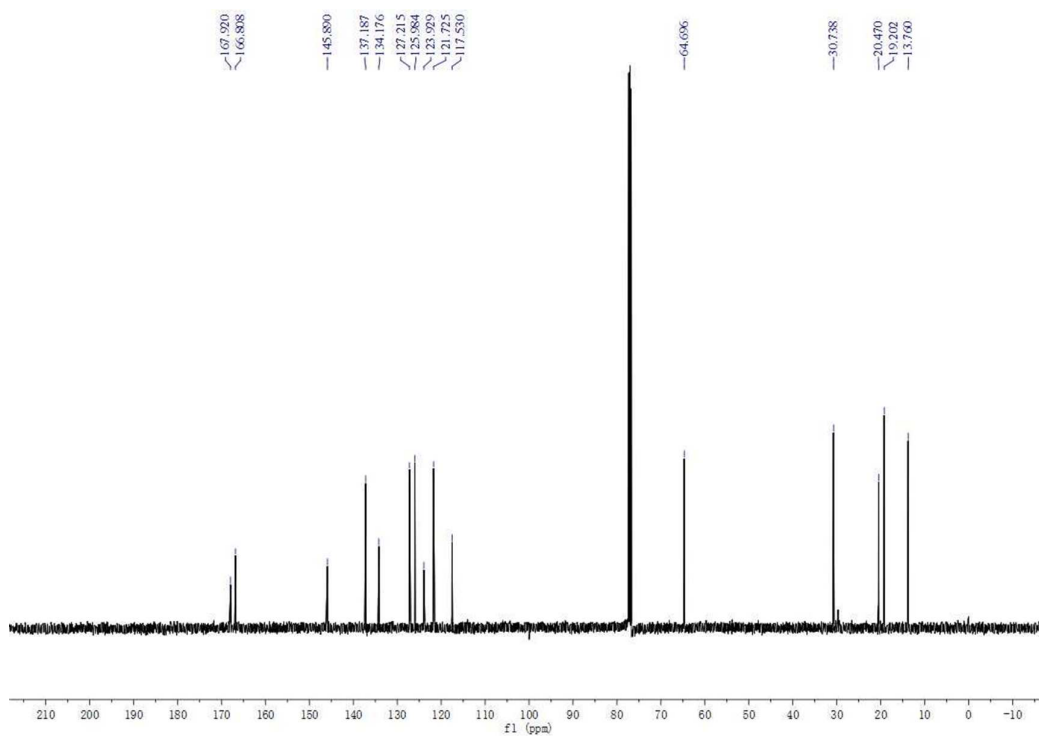
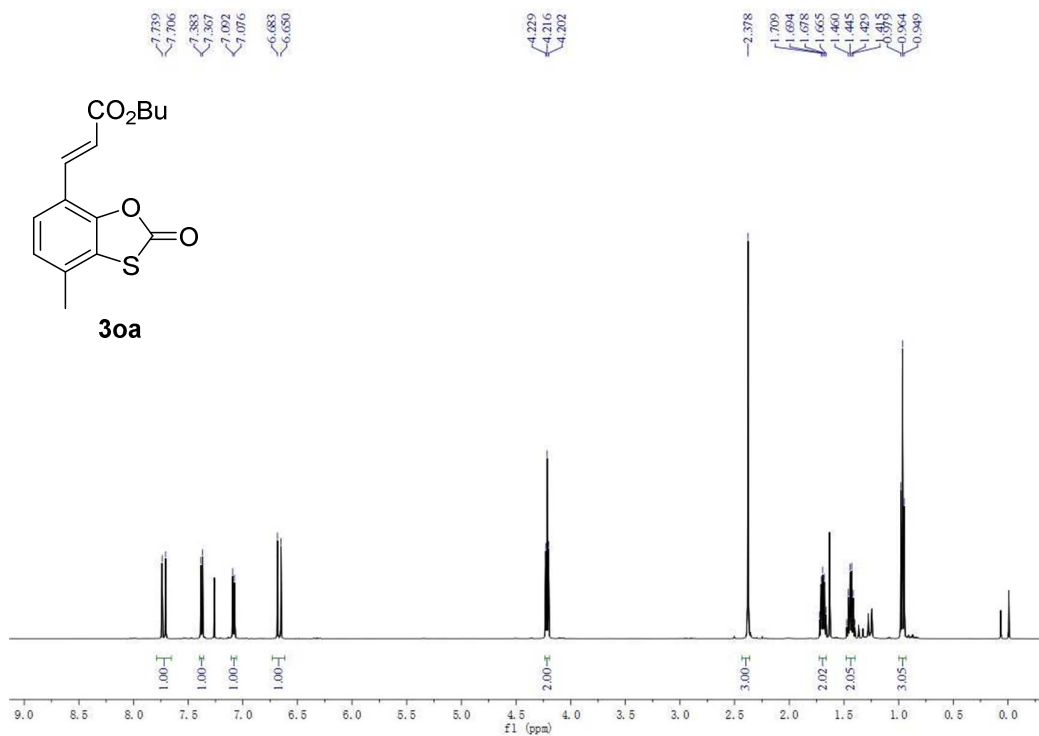


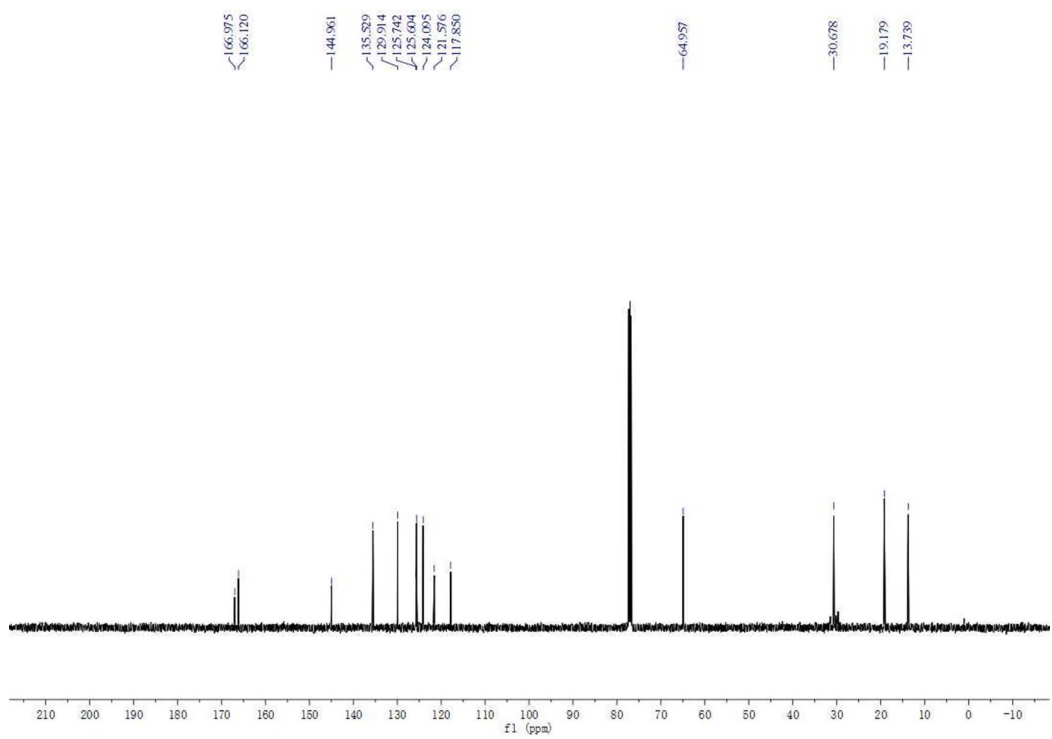
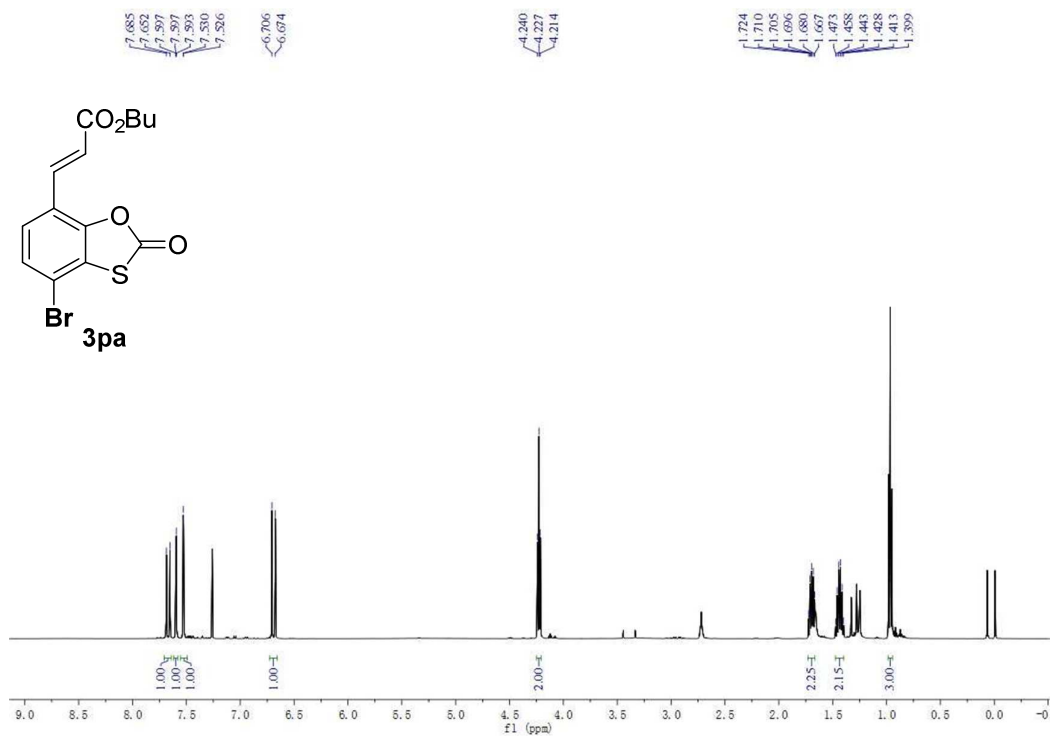








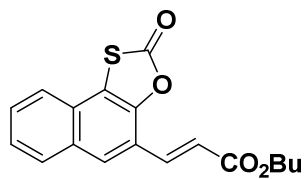




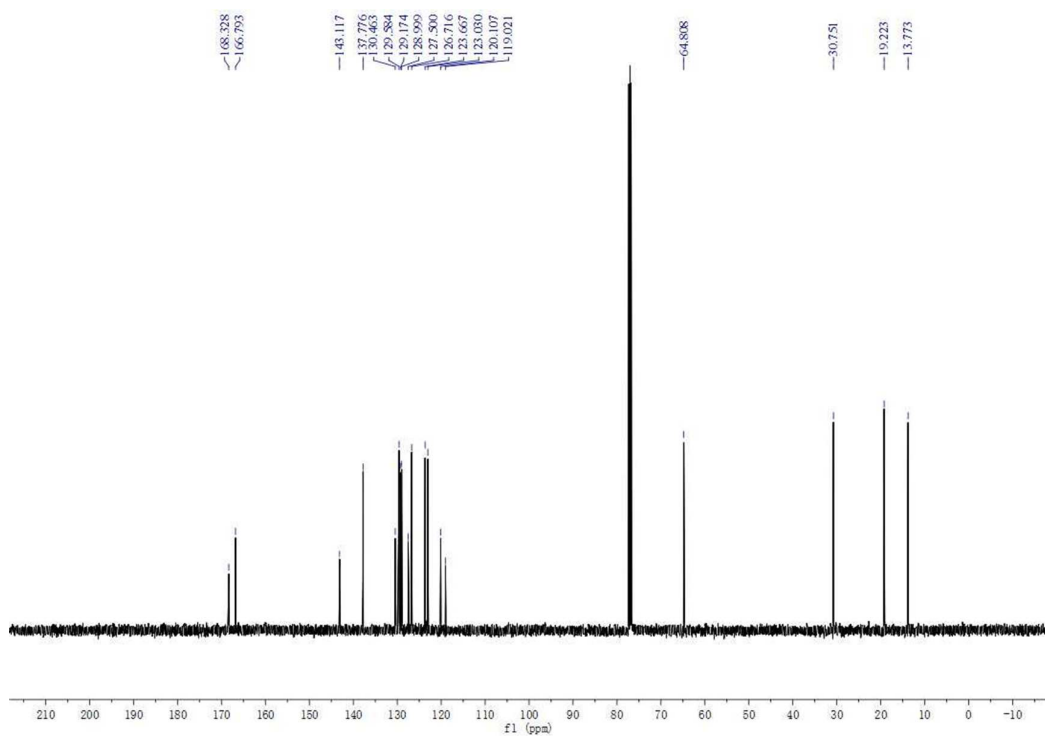
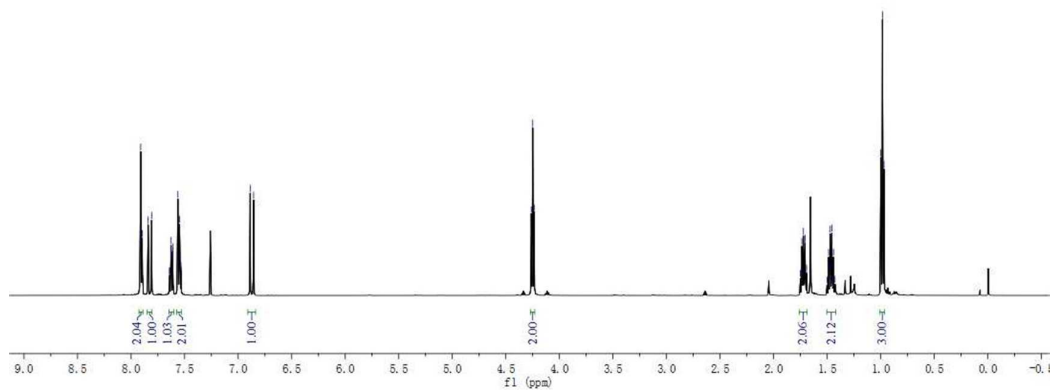
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7.528
7.526

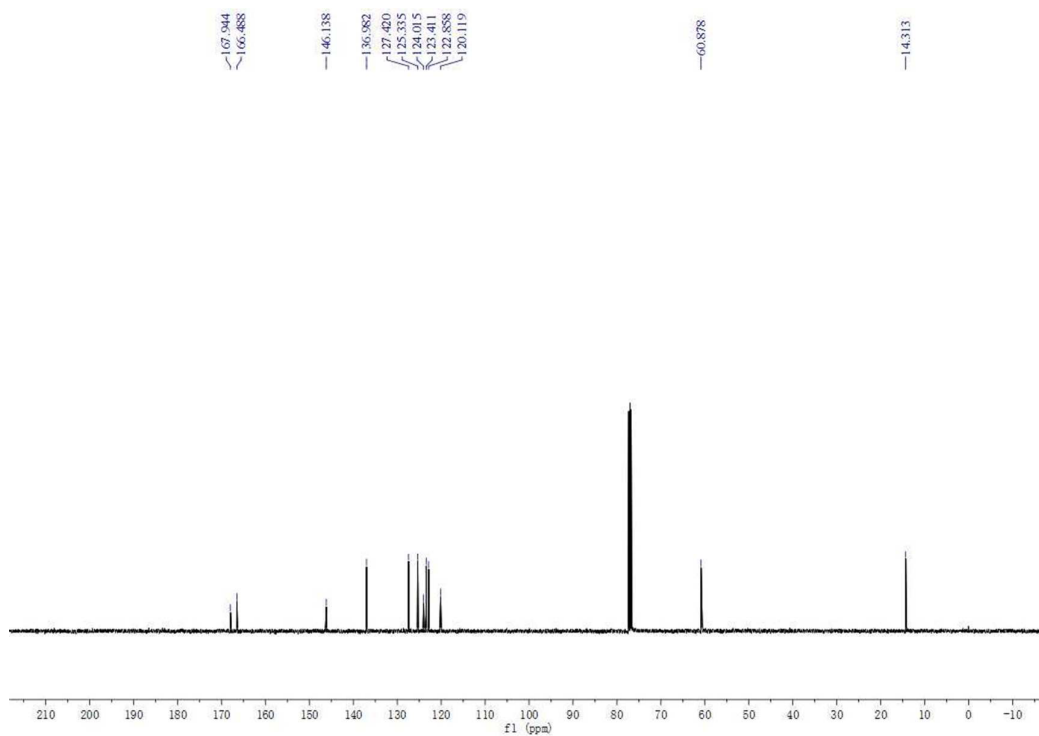
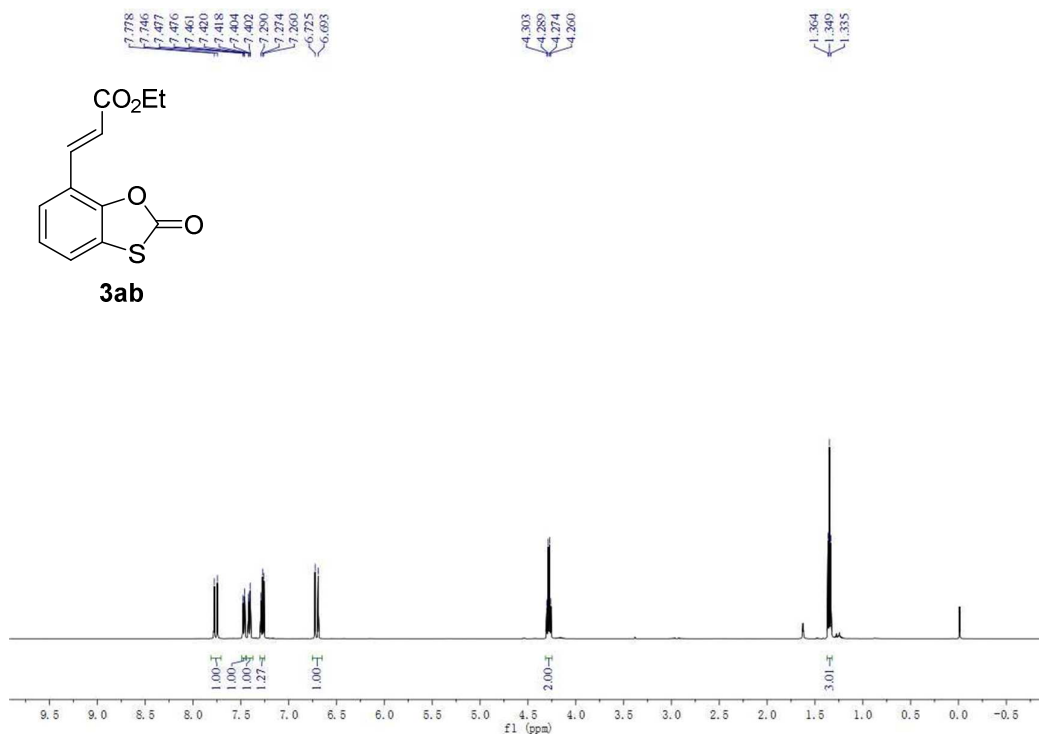
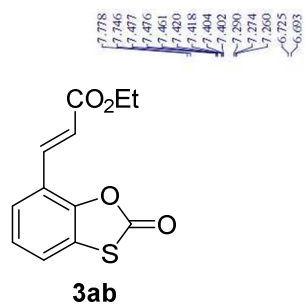
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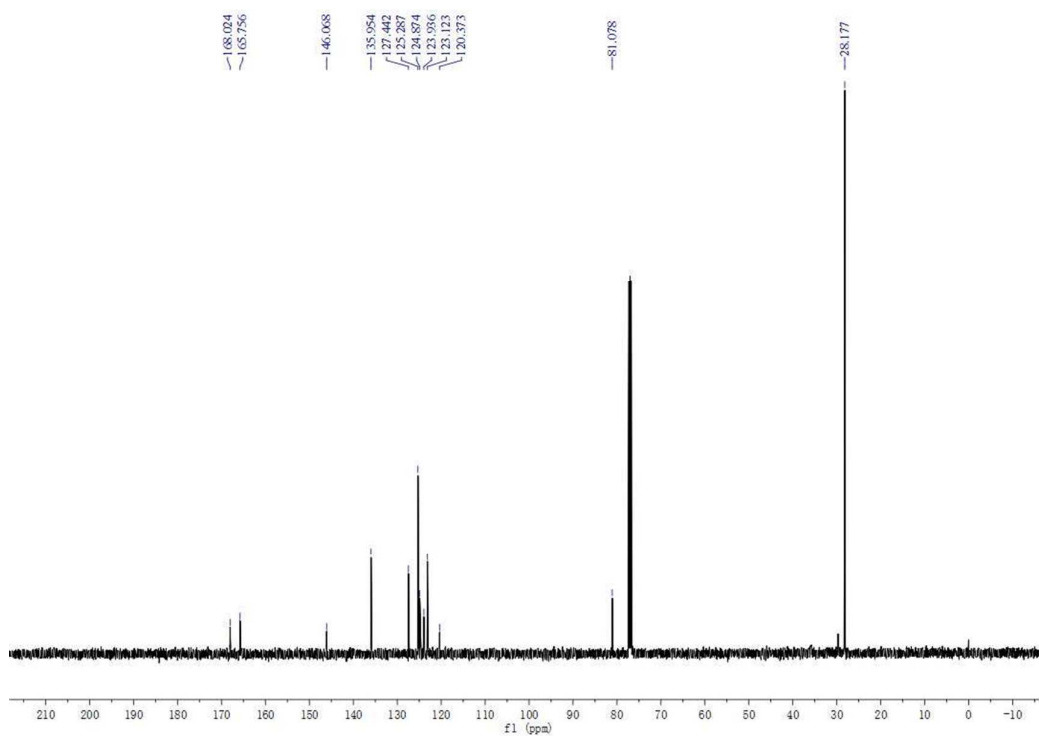
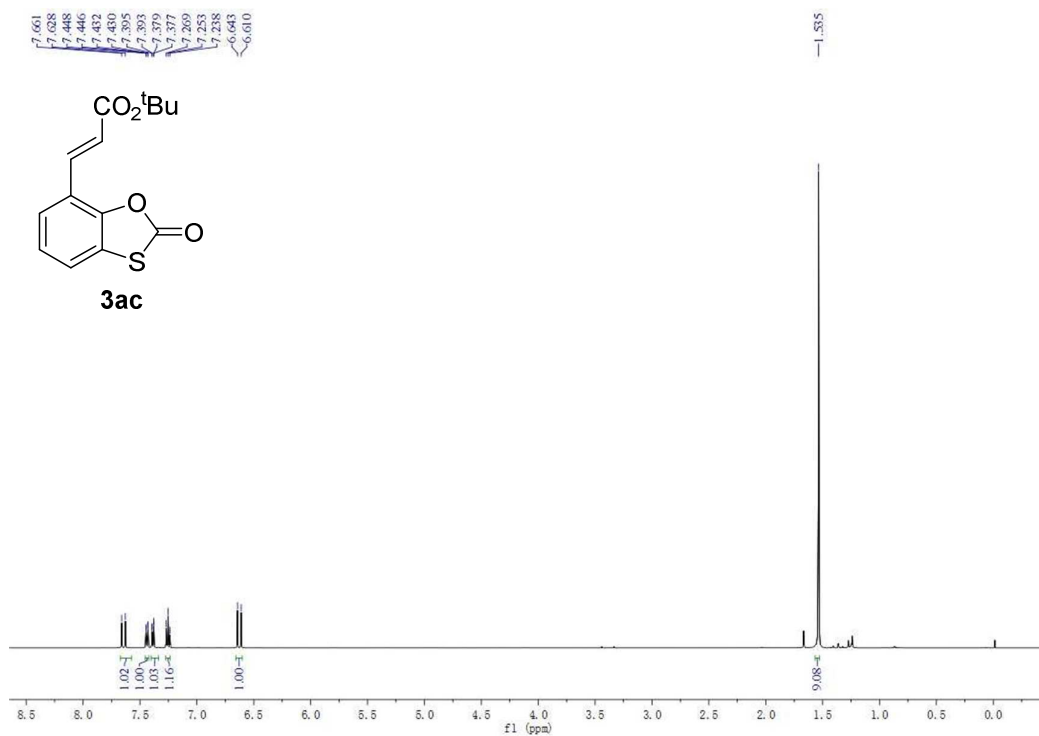
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0.983
0.969

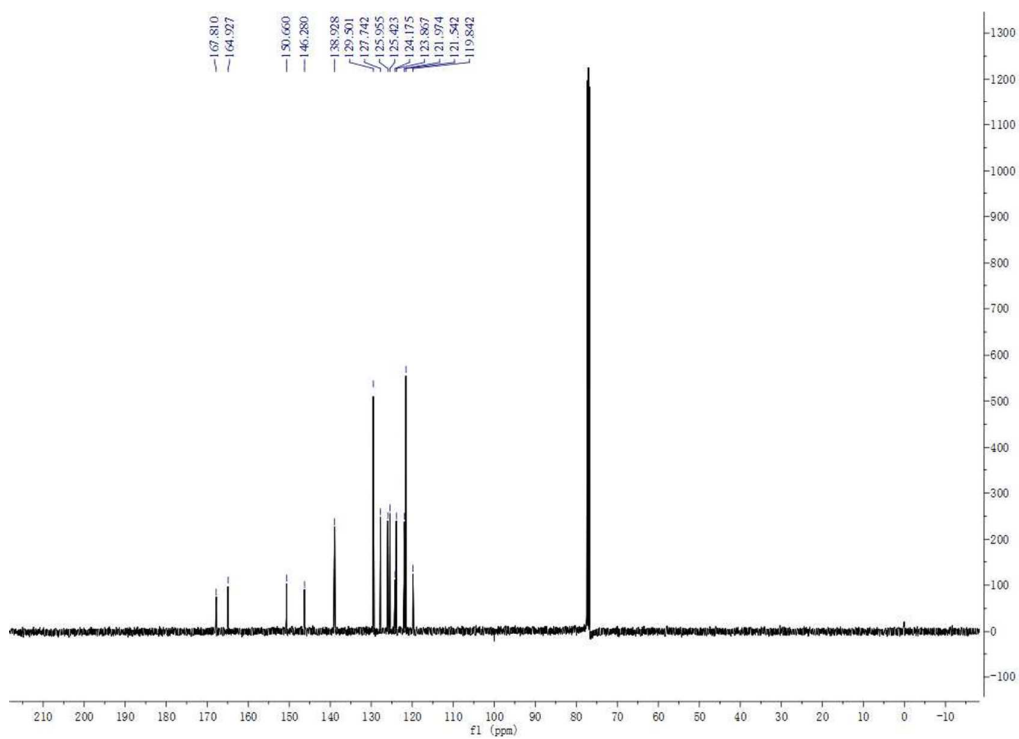
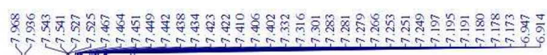


3qa

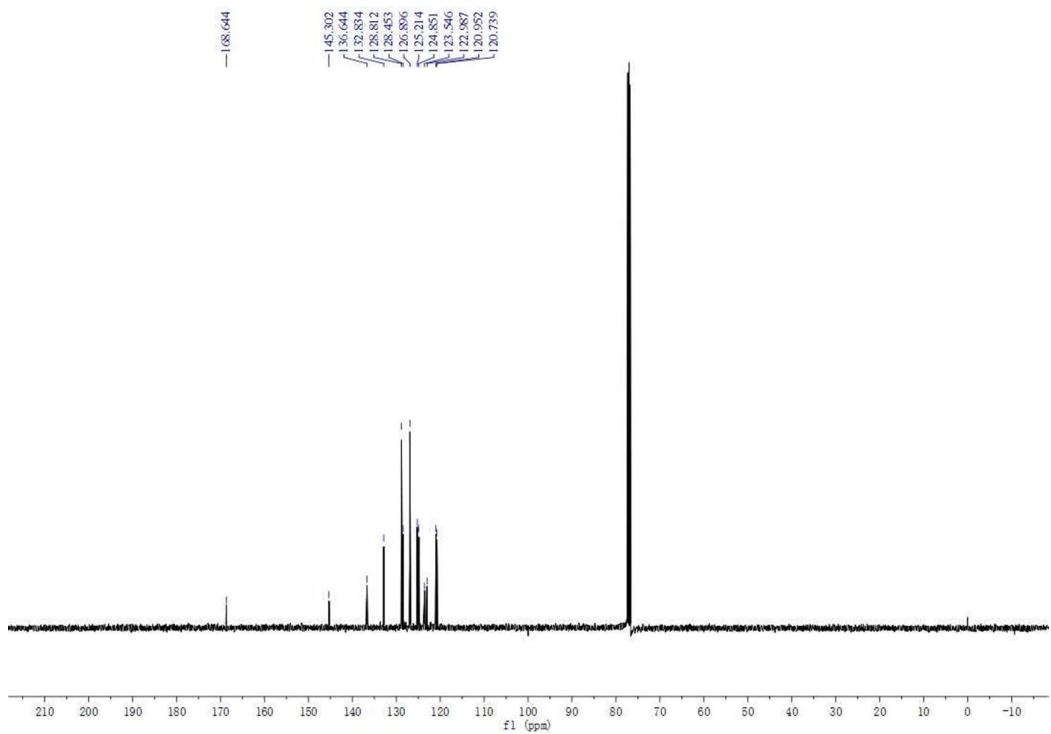
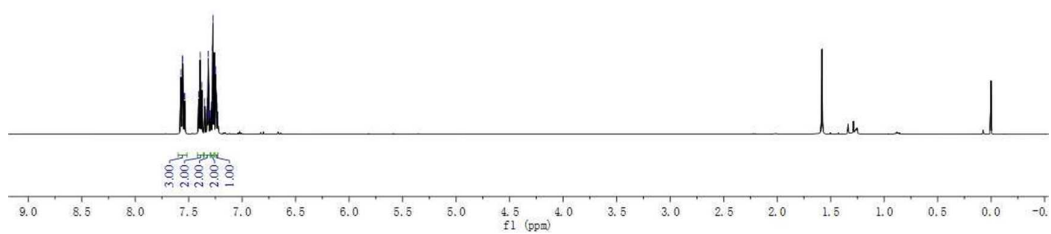
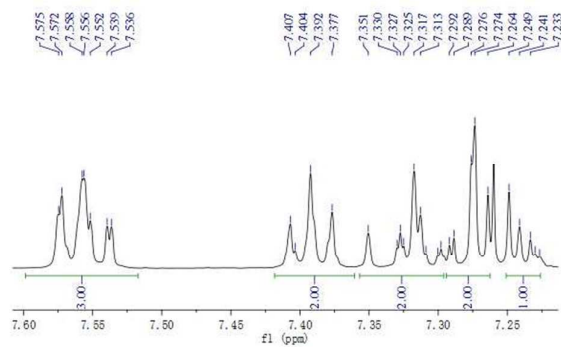
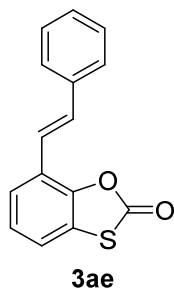


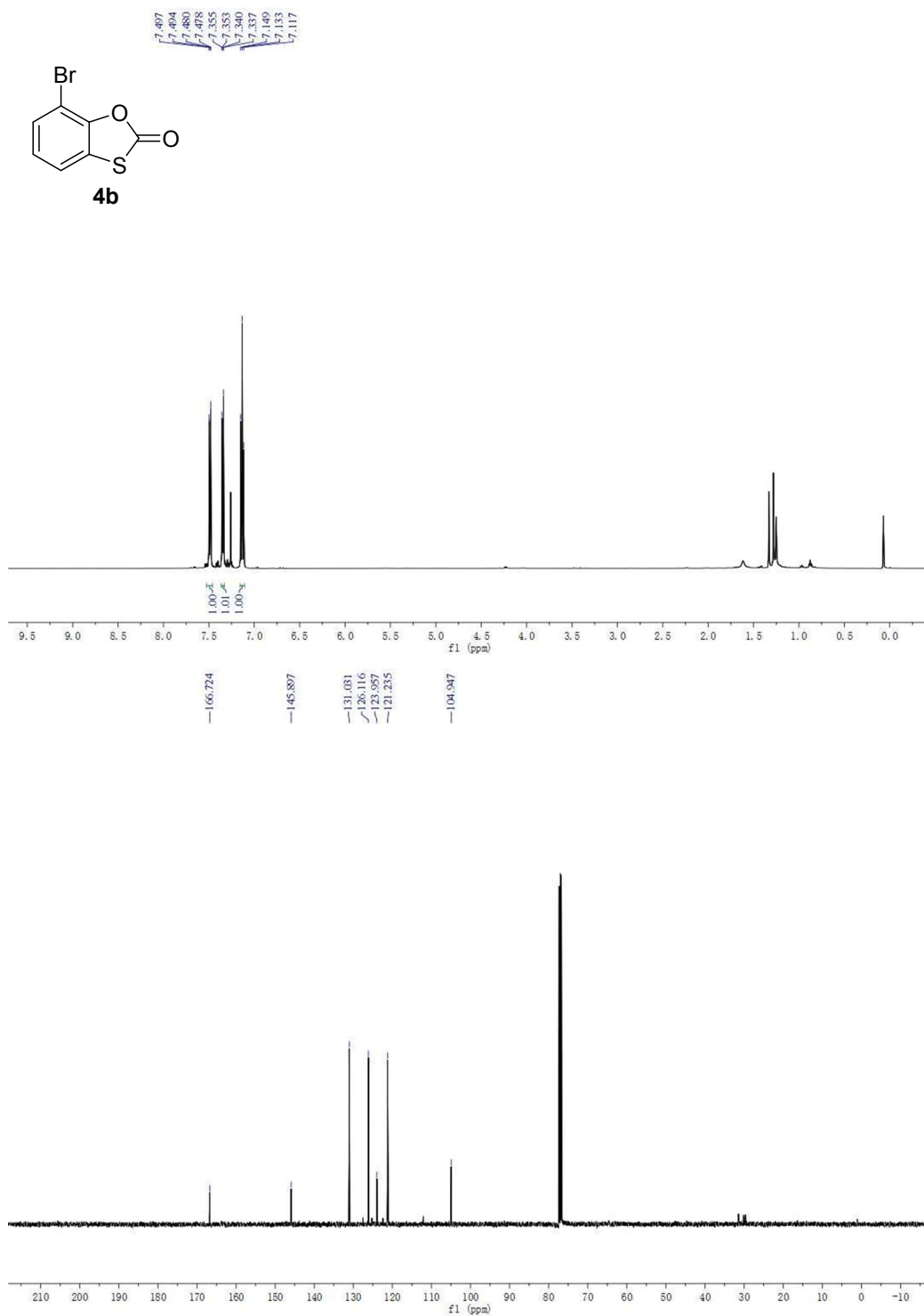




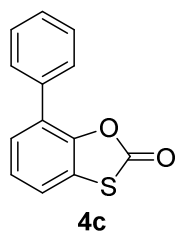


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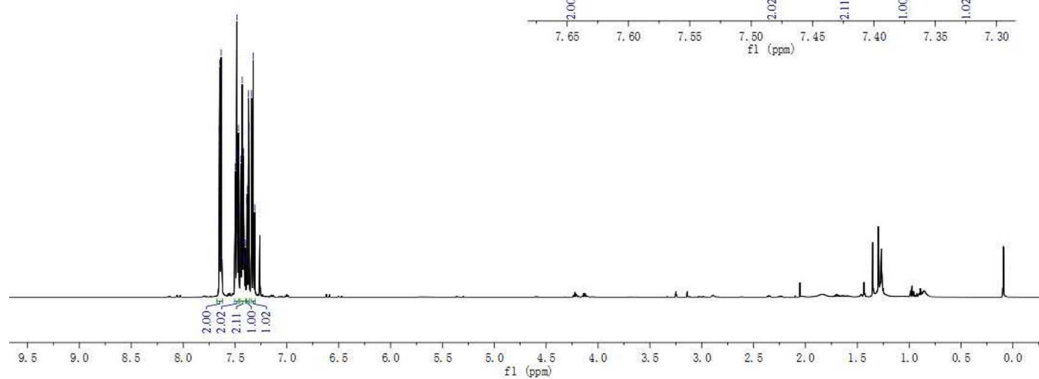
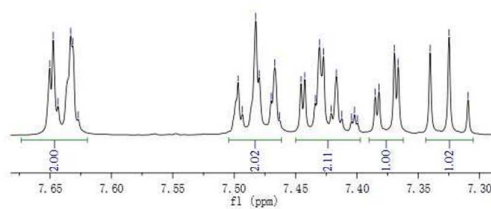




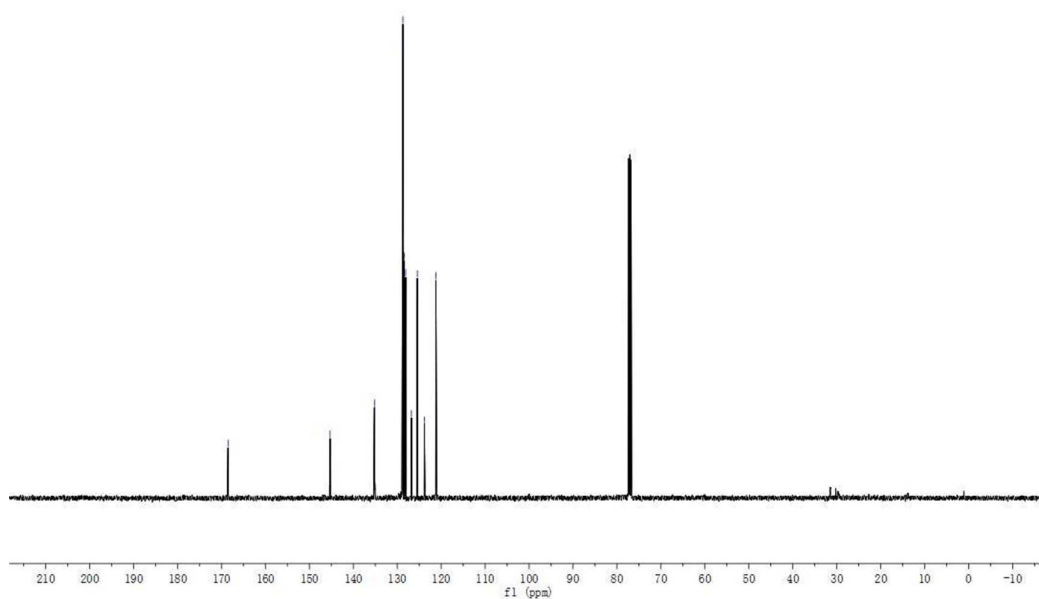
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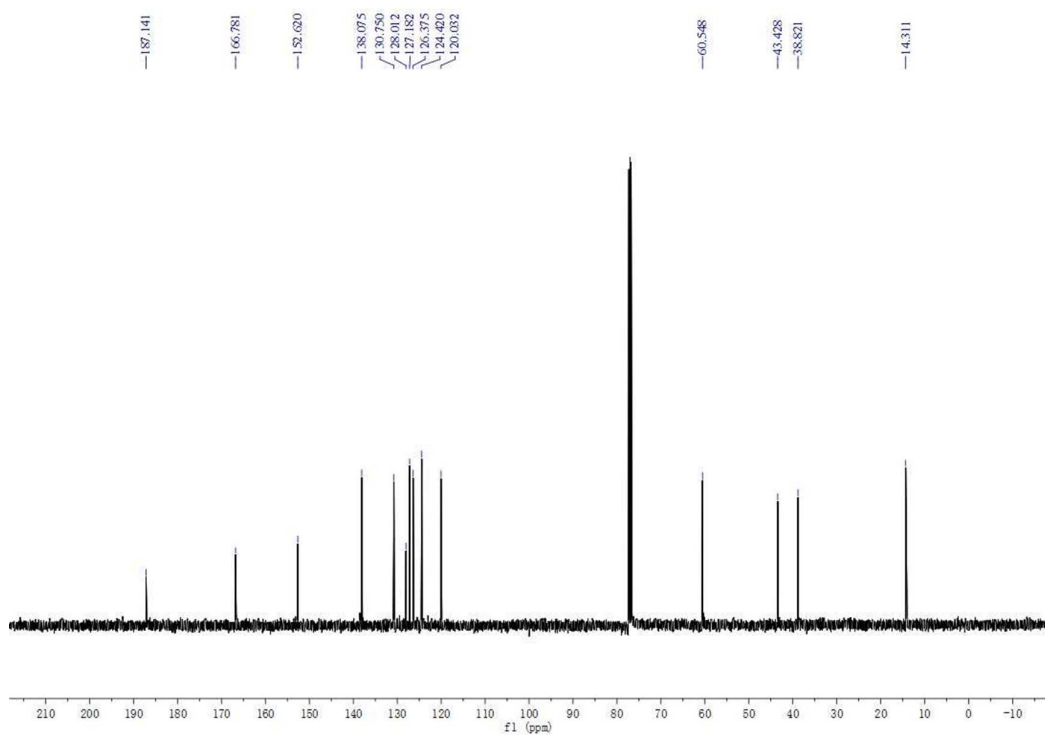
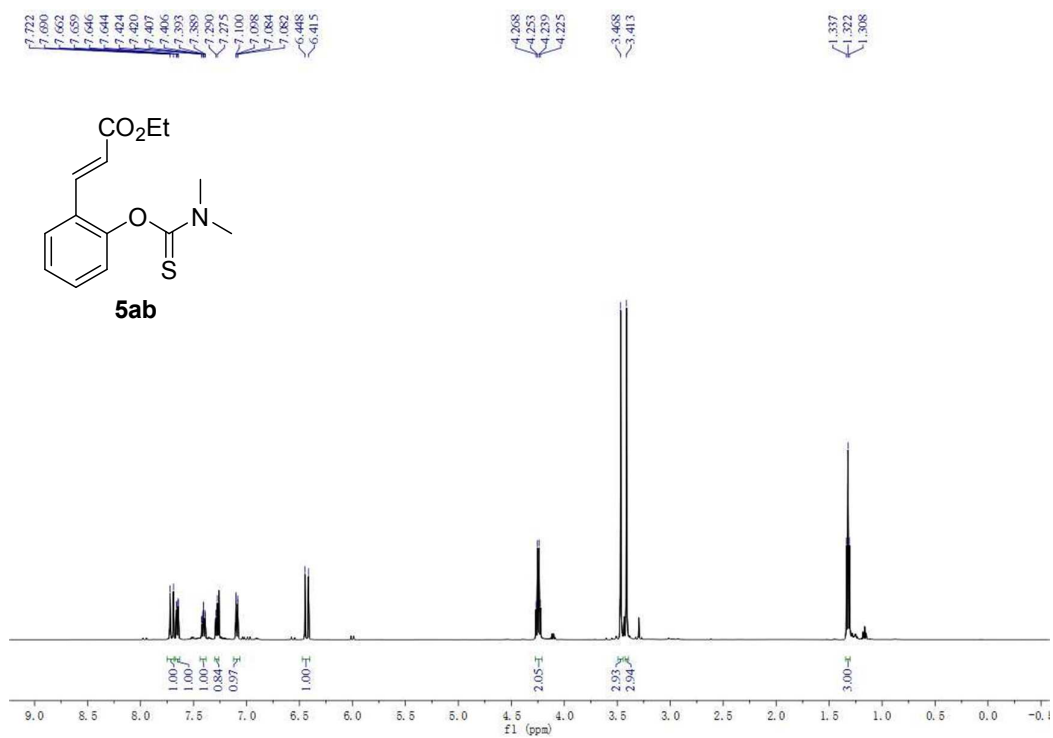


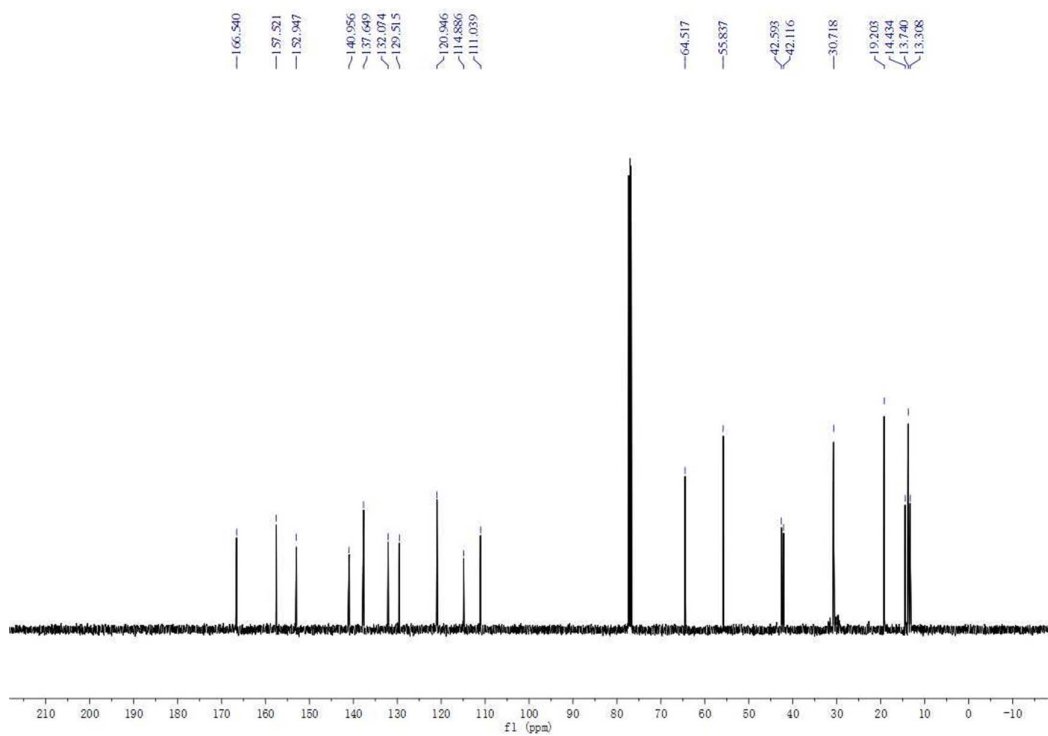
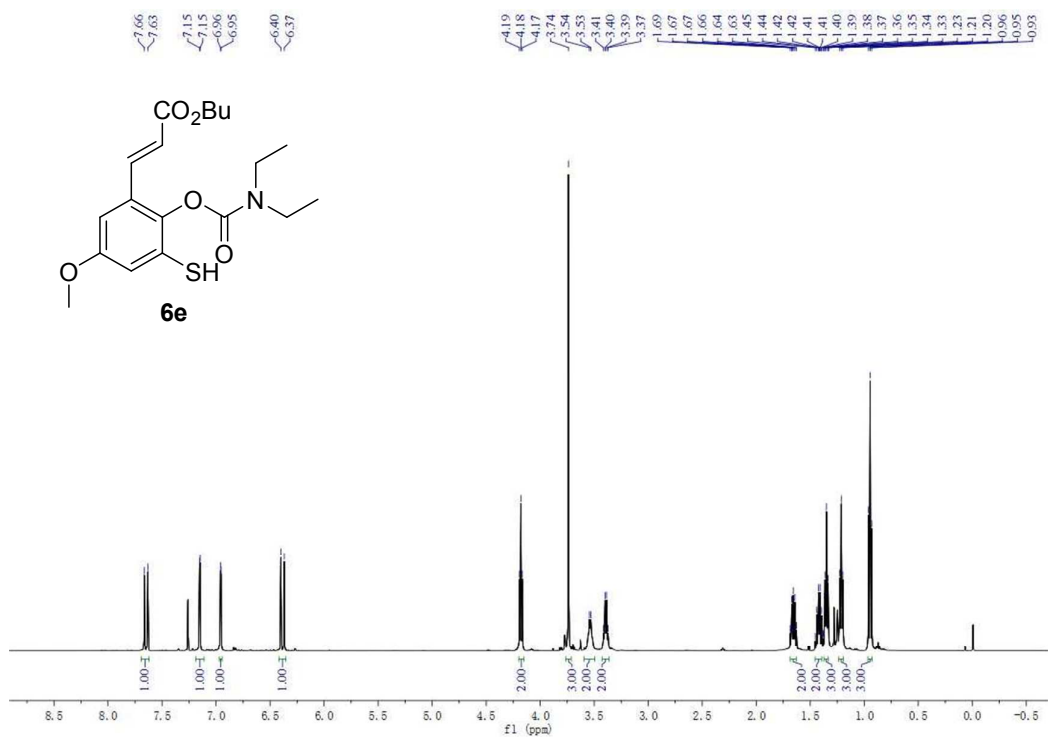
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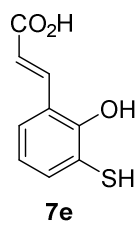


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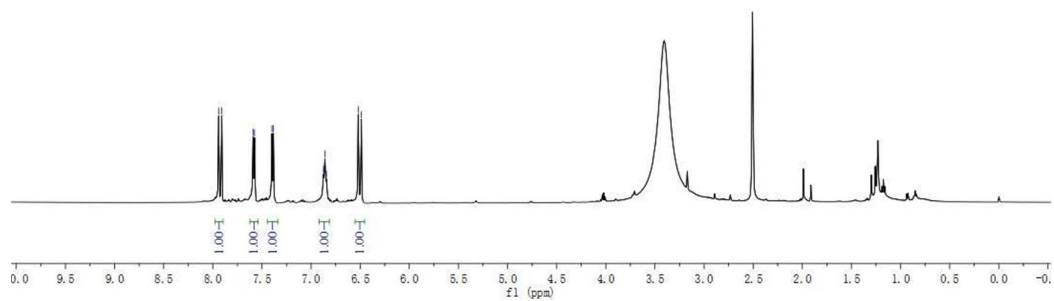




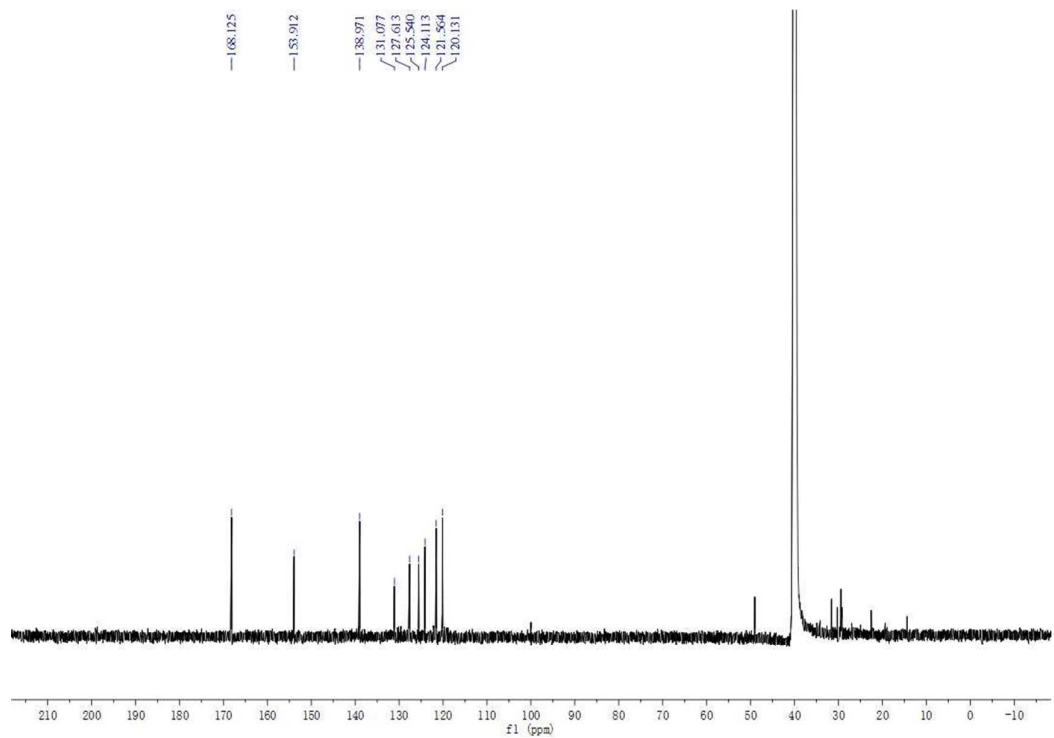


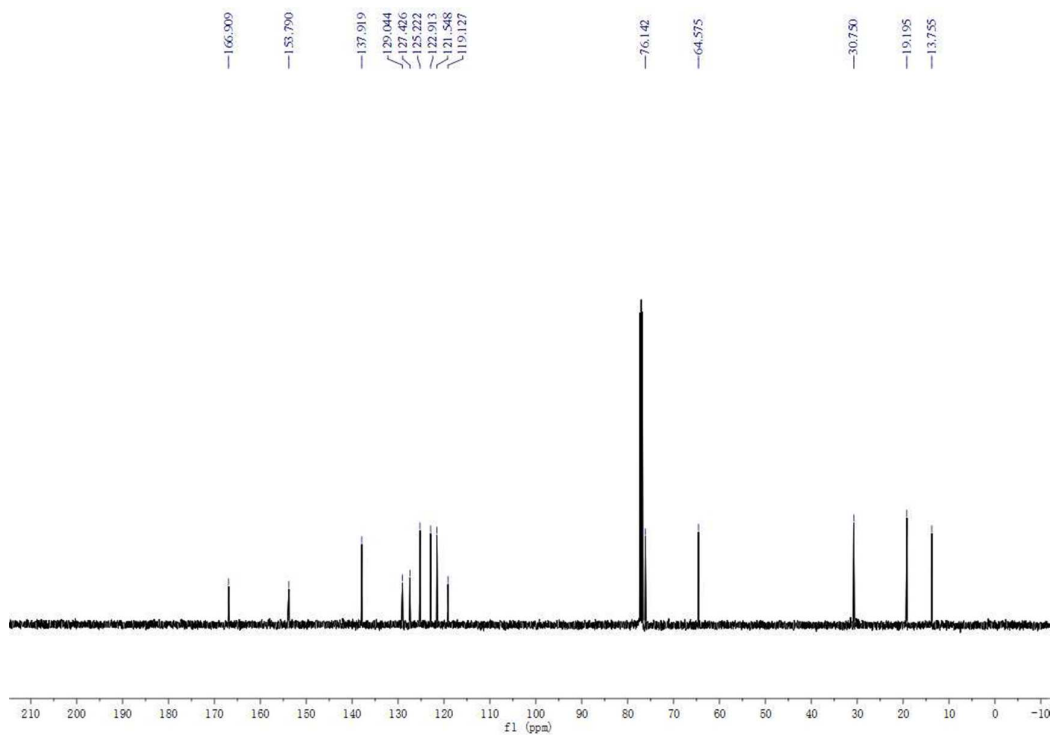
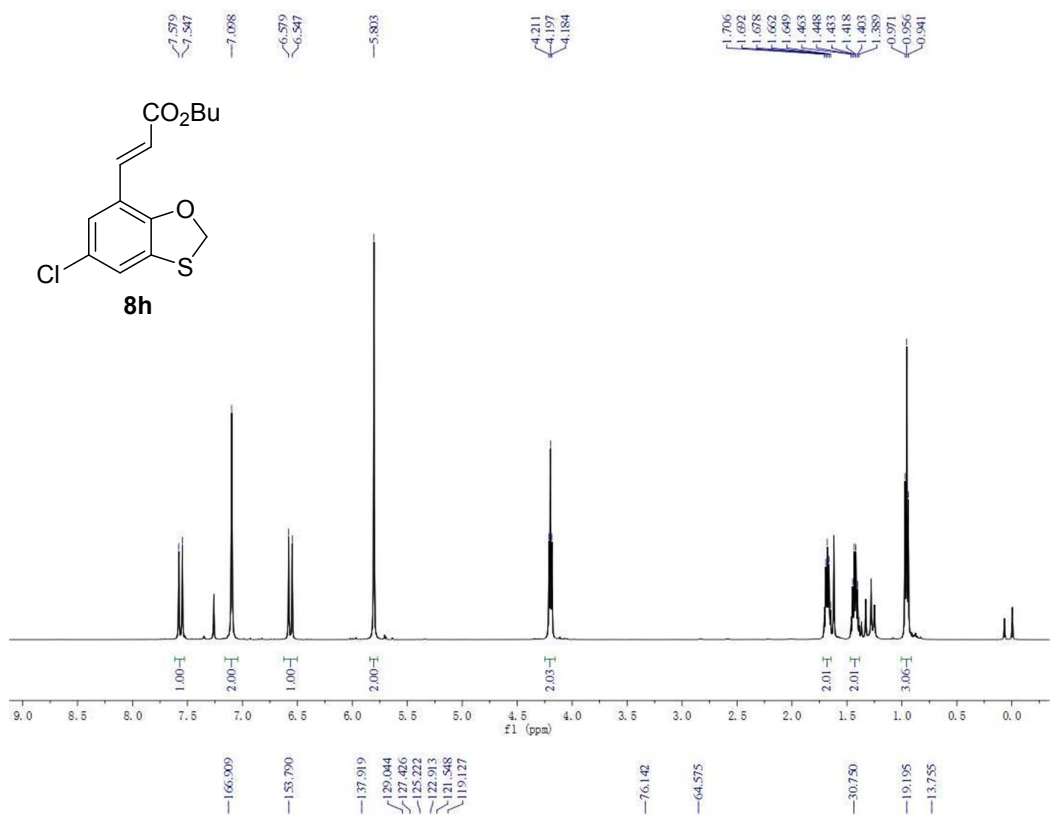


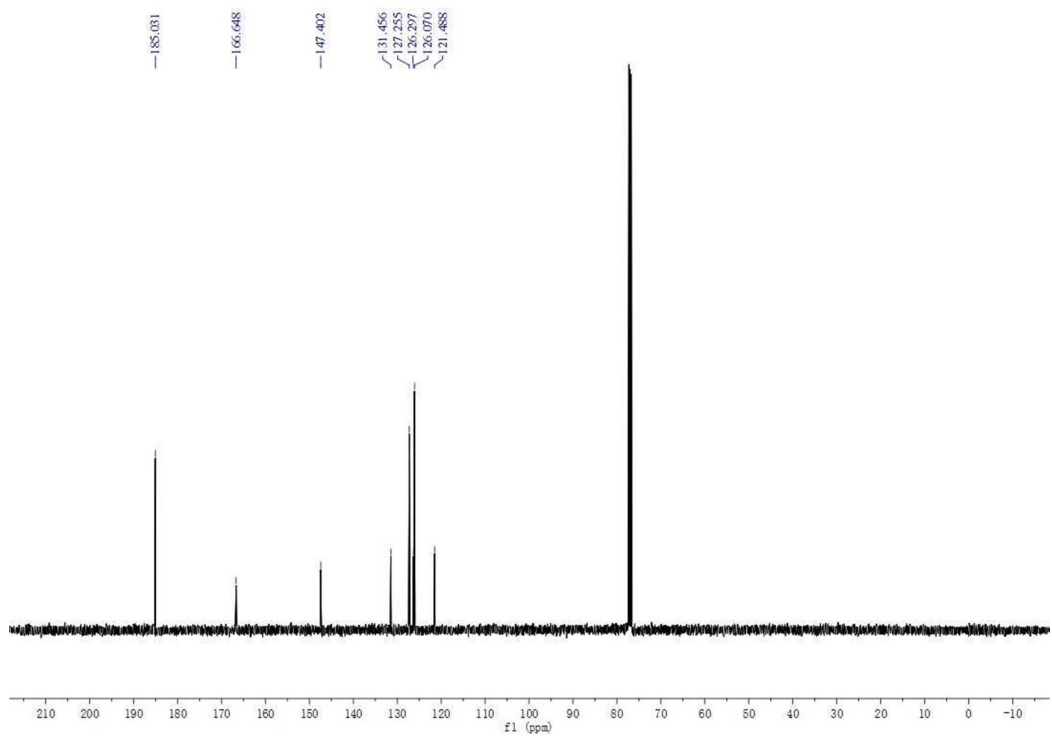
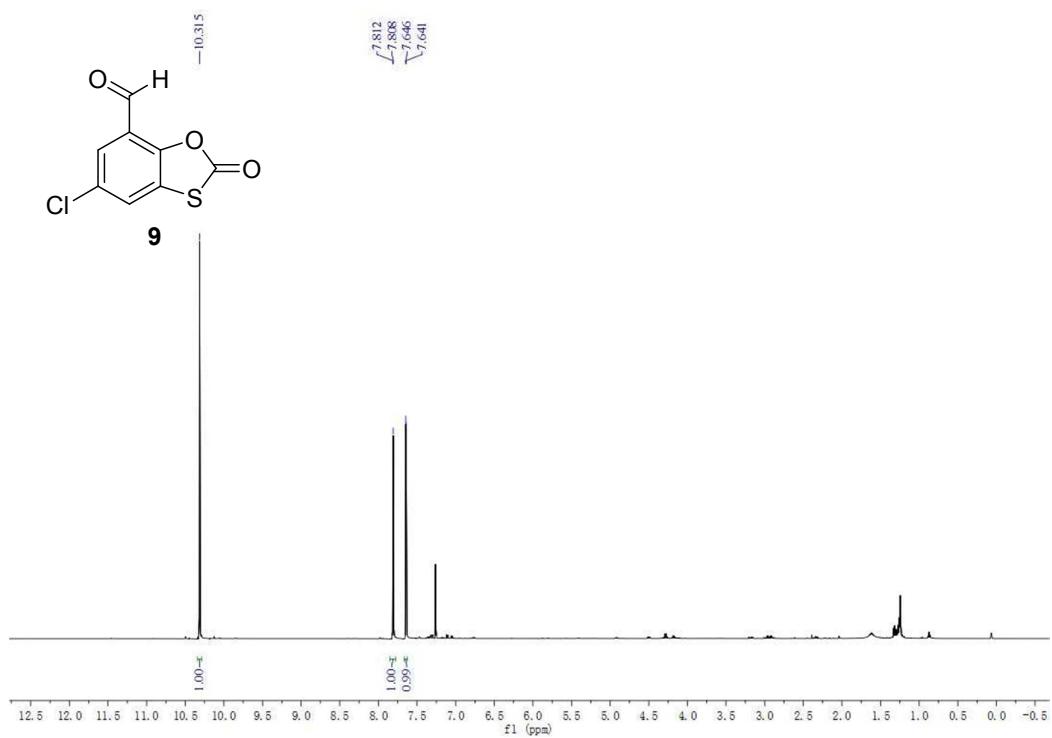
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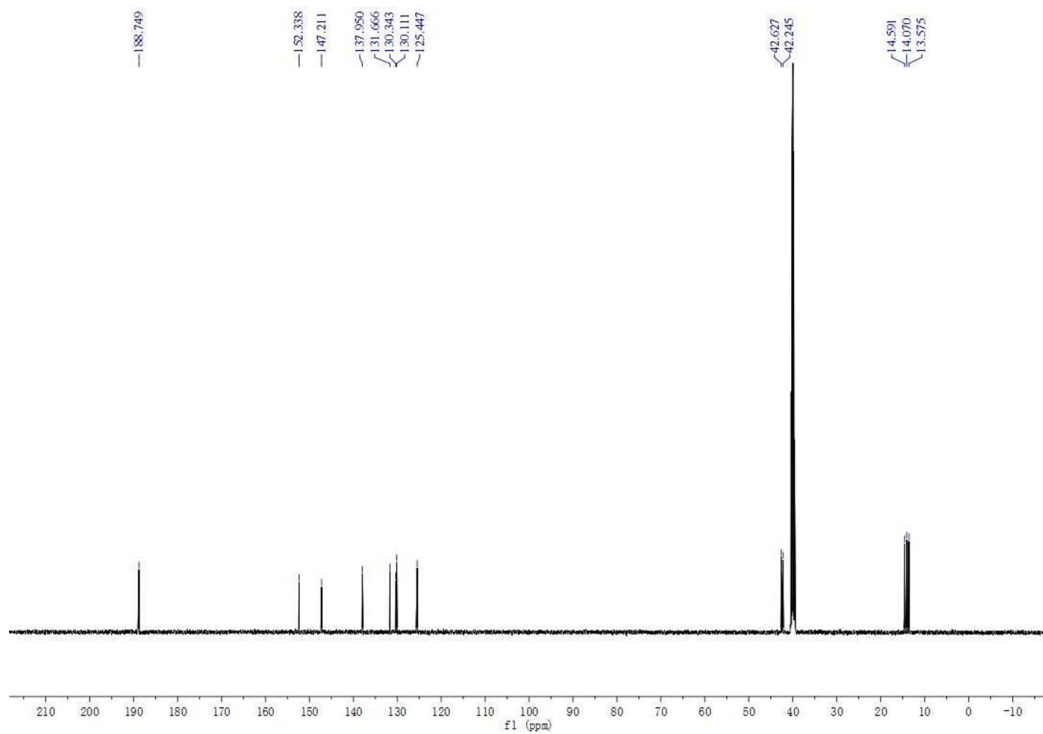
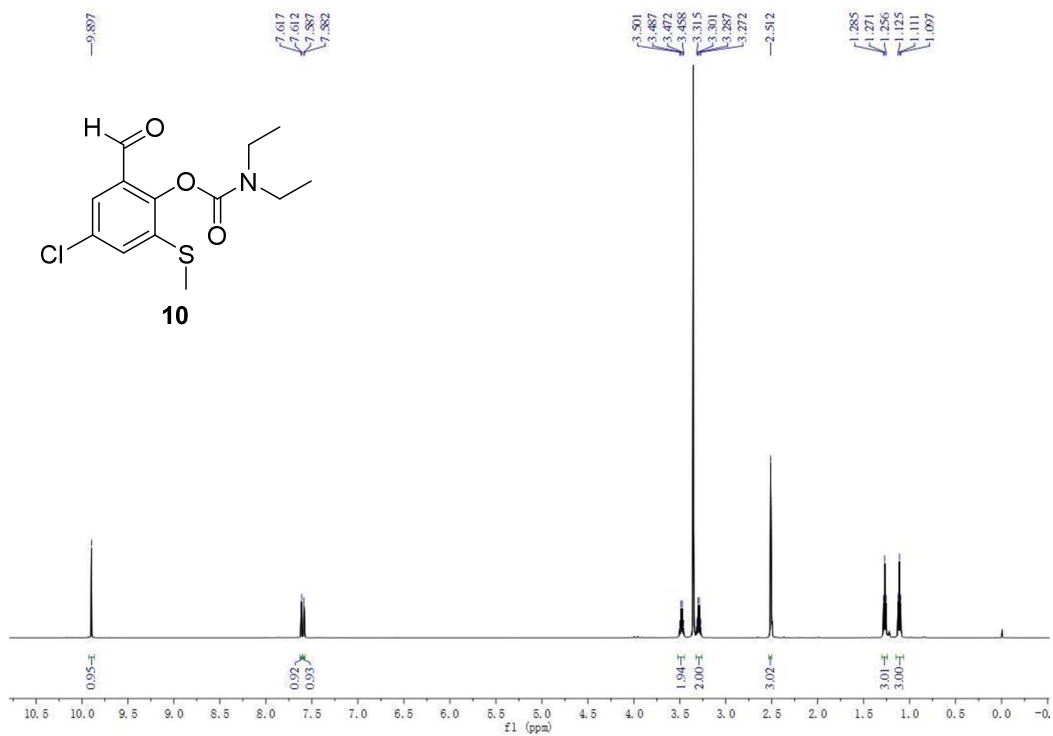


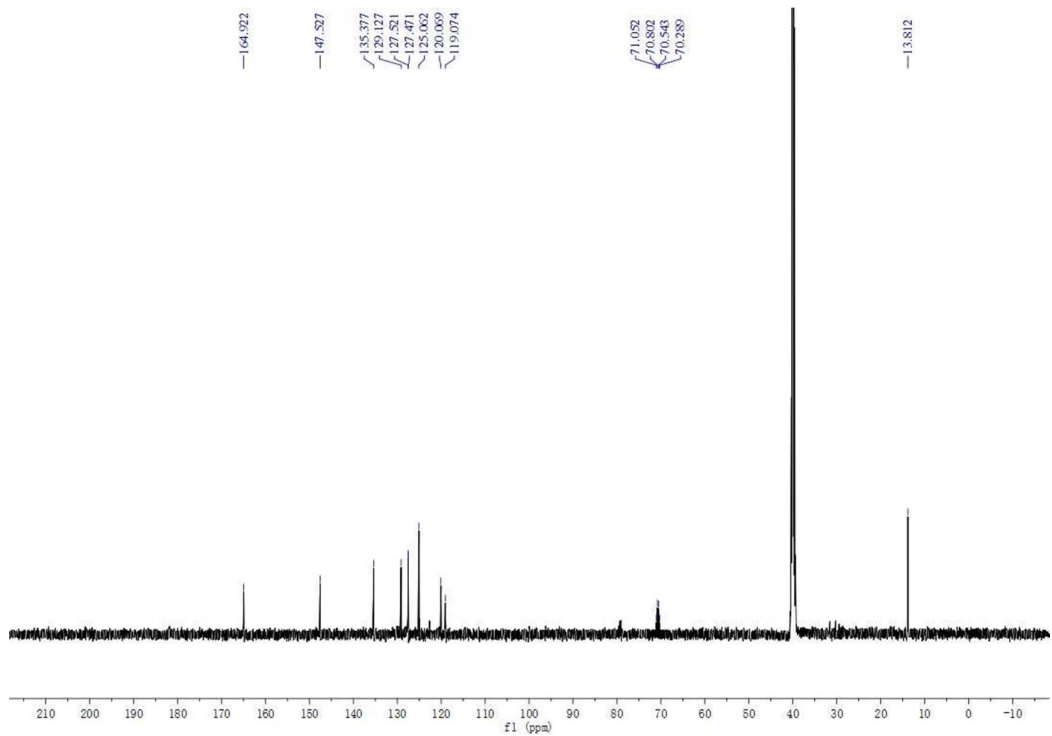
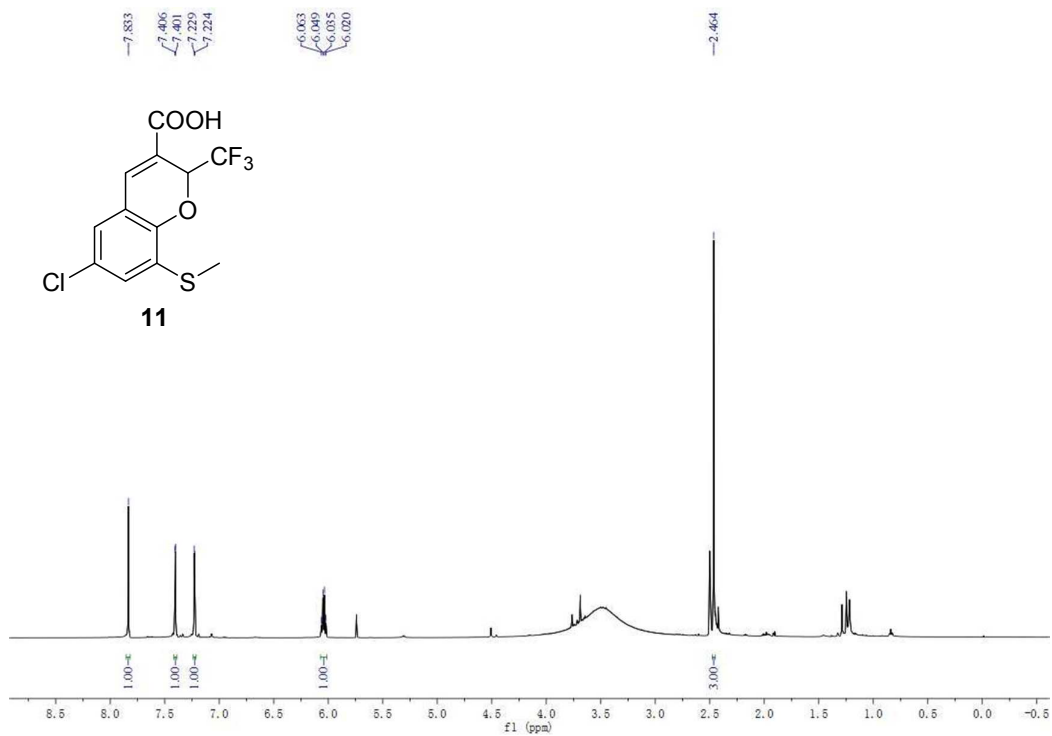
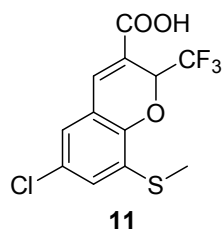
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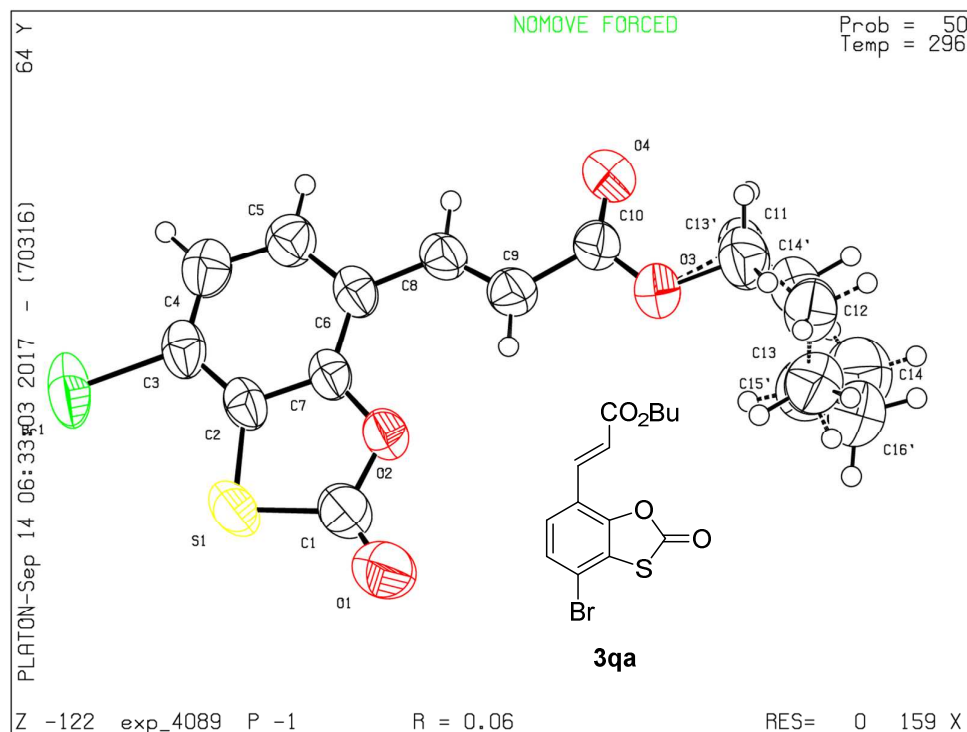








7. X-Ray crystallographic data for compound 3pa



Bond precision : C-C = 0.0086 Å Wavelength = 0.71073

Cell : a=6.9777(8) b=9.4206(13) c=12.6844(17)
alpha=68.487(13) beta=82.995(10) gamma=72.591(12)

Temperature : 296 K

	Calculated	Reported
Volume	740.11 (18)	740.11 (18)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₁₄ H ₁₃ BrO ₄ S	C ₁₄ H ₁₃ BrO ₄ S
Sum formula	C ₁₄ H ₁₃ BrO ₄ S	C ₁₄ H ₁₃ BrO ₄ S
Mr	357.20	357.21
Dx, g cm ⁻³	1.603	1.603
Z	2	2
Mu (mm ⁻¹)	2.927	2.927
F000	360.0	360.0
F000'	359.84	
h,k,lmax	8,11,15	8,11,15
Nref	2930	2927
Tmin,Tmax	0.596,0.704	0.505,1.000
Tmin'	0.436	

Correction method = # Reported T Limits: Tmin=0.505 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.999

R(reflections)= 0.0639(1773)

S = 1.037

Theta(max)= 26.020

wR2(reflections)= 0.1981(2927)

Npar= 219