Supporting Information

An efficient catalyst-free synthesis of vinyl sulfides in aqueous-phase

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1. Experimental Section

1.1 Materials and Measurements

All reagents and solvents were acquired from commercially available suppliers and used without further purification, unless specified. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ using TMS as the internal standard. IR spectra were recorded on a Nicollet 740 FT-IR spectrometer. HRMS were measured on an Agilent Technologies 6510, Q-TOFLC/MS ESI Technique. Melting points were determined in capillaries and are uncorrected. All reactions were monitored using thin layer chromatography (TLC) on pre-coated silica gel 60 F_{254} (mesh); spots were observed under UV light.

1.2 X-ray single crystal structure determination

X-ray diffraction single-crystal data were measured on a Bruker Apex II CCD diffractometer at 296 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction was made with the Bruker SAINT program. The structure was solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package1. Displacement parameters were refined anisotropically, and the positions of the hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement.

1.3 General procedure for the synthesis of compounds 3 and 5.

A solution of benzo[d]thiazole-2-thiol **1a** (or the corresponding compounds **1c** and **4**) (5 mmol), dimethyl acetylenedicarboxylate **2a** (or diethyl acetylenedicarboxylate **2b**) (6 mmol) in water (10 mL) was completed by stirring at 80 °C for 2 h (TLC tracking). After the reaction was completed, the solid was filtered and recrystallized with 95% EtOH and dried. The pure products **3a** and **5** were obtained (the oily substance was extracted with ethyl acetate, dried, and the solvent was evaporated to obtain other product **3b, 3c and 3d**).

Dimethyl 2-(benzo[d]thiazol-2-ylthio)fumarate (**3a)**

Yellow powder, yield: 88%. mp 157-158 °C; IR (KBr) *v*: 3060, 2950, 1732, 1600, 1427, 994, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H, ArH), 7.78 (d, *J* = 7.5 Hz, 1H, ArH), 7.46-7.39 (m, 1H, ArH), 7.34 (m, 1H, ArH), 6.92 (s, 1H, CH), 3.81 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3); HRMS (ESI) calcd for $C_{13}H_{11}NO_4S_2$ $[M+H]^+$ 310.0207, found 310.0208.

Diethyl 2-(benzo[d]thiazol-2-ylthio)fumarate (**3b)**

Pale yellow oil, yield: 83%; IR (KBr) *v*: 3061, 2981, 1732, 1598, 1463, 856, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H, ArH), 7.77 (d, *J* = 7.9 Hz, 1H, ArH), 7.41 (t, *J* = 9.0 Hz, 1H, ArH), 7.33 (t, *J* = 7.6 Hz, 1H, ArH), 6.91 (s, 1H, CH), 4.25 (m, 2H, OCH_2), 4.04 (m, 2H, OCH_2), 1.30 (t, *J* = 7.1 Hz, 3H, CH_3), 0.96 (t, *J* = 7.1 Hz, 3H, CH_3); HRMS (ESI) calcd for $C_{15}H_{15}NO_4S_2$ $[M+H]^+$ 338.0534, found 338.0521.

Dimethyl 2-(benzo[d]oxazol-2-ylthio)fumarate (**3c)**

Pale yellow oil, yield: 84%; IR (KBr) *v*: 3064, 2952, 1751, 1603, 1501, 891, 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66-7.59 (m, 1H, ArH), 7.49-7.41 (m, 1H, ArH), 7.34-7.25 (m, 2H, ArH), 7.01 (s, 1H, CH), 3.82 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3); HRMS (ESI) calcd for $C_{13}H_{11}NO_5S$ $[M+H]^+$ 294.0437, found 294.0436.

Diethyl 2-(benzo[d]oxazol-2-ylthio)fumarate (**3d)**

Orange oil, yield:, yield: 82%; IR (KBr) *v*: 3064, 2983, 1732, 1600, 1473, 804, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66-7.55 (m, 1H, ArH), 7.49-7.37 (m, 1H, ArH), 7.34 – 7.21 (m, 2H, ArH), 7.00 (s, 1H, CH), 4.26 (m, 2H, OCH_2), 4.07 (m, 2H, OCH_2), 1.30 (t, *J* = 7.1 Hz, 3H, CH_3), 0.96 (t, *J* = 7.1 Hz, 3H, CH_3); HRMS (ESI) calcd for $C_{15}H_{15}NO_5S$ $[M+H]^+$ 322.0749, found 322.0749.

Dimethyl 2-(5-amino-1,3,4-thiadiazol-2-ylthio)fumarate (**5a)**

Yellow powder, yield: 87%; mp 154-156 °C; IR (KBr) *v*: 3429, 3110, 1730, 1698, 1505, 1255, 861, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1H, CH), 5.78 (s, 2H, NH_2), 3.82 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3); ^{13}C NMR (400 MHz, d_6-DMSO) δ 172.2, 165.3, 163.7, 145.3, 144.9, 122.1, 53.7, 52.7; HRMS (ESI) calcd for $C_8H_9N_3O_4S_2$ $[M+H]^+$ 276.0120,found 276.0113.

Diethyl 2-(5-amino-1,3,4-thiadiazol-2-ylthio)fumarate (**5b)**

Yellow powder, yield: 86%; mp 110-112 °C; IR (KBr) *v*: 3287, 3103, 1735, 1500, 1247, 865, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.70 (s, 1H, CH), 5.79 (s, 2H, NH_2), 4.27 (m, 2H, OCH_2),

4.14 (m, 2H, OCH_2), 1.33 (t, J = 7.1 Hz, 3H, CH_3), 1.19 (t, J = 7.1 Hz, 3H, CH_3); HRMS (ESI) calcd for $C_{10}H_{13}N_3O_4S_2$ $[M+H]^+$304.0433, found 304.0426.

1.4 General procedure for the synthesis of compounds 6.

A solution of 1*H*-benzo[*d*]imidazole-2-thiol **1c** (5 mmol), dimethyl acetylenedicarboxylate **2a** (or diethyl acetylenedicarboxylate **2b**) (6 mmol) in water (10 mL) was refluxed at 80 °C for 2 h. After the reaction was completed, the solid was filtered and recrystallized with 95% ethanol and dried. The pure products **6** were obtained. *(Z)-methyl 2-(3-oxobenzo[d]thiazolo[3,2-a]imidazol-2(3H)-ylidene)acetate* (**6a)**

Yellow powder, yield: 85%; mp 190-191 °C; IR (KBr) *v*: 3061, 1725, 1698, 1514, 1451, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.4 Hz, 1H, ArH), 7.67 (d, J = 8.3 Hz, 1H, ArH), 7.37 (m, 2H, ArH), 7.23 (s, 1H, CH), 3.92 (s, 3H, CH_3); HRMS (ESI) calcd for $C_{12}H_8N_2O_3S$ $[M+H]^+$: 261.0335, found 261.0334.

(Z)-ethyl 2-(3-oxobenzo[d]thiazolo[3,2-a]imidazol-2(3H)-ylidene)acetate (**6b)**

Yellow powder, yield: 85%; mp 156-157 °C; IR (KBr) *v:* 3065, 1732, 1685, 1476, 932, 75 7cm^{-1}; ^1H NMR (400 MHz, CDCl3) δ 7.95 (d, J = 7.4 Hz, 1H, ArH), 7.67 (d, J = 8.3 Hz, 1H, ArH), 7.37 (m, 2H, ArH), 7.23 (s, 1H, CH), 3.92 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 165.3, 157.6, 155.2, 148.9, 144.8, 130.1, 126.5, 124.9, 122.0, 120.1, 112.9, 62.4, 14.2; HRMS (ESI) calcd for $C_{13}H_{10}N_2O_3S$ $[M+H]^+$ 275.0484, found 275.0490.

1.5 General procedure for the synthesis of compounds 8 and 9.

The synthetic methods of compounds **8** and **9** are similar to those of compounds **6**, except that the corresponding starting materials are used.

(Z)-methyl 3-(benzo[d]thiazol-2-ylthio)acrylate (**8a**)

Yellow powder, yield: 85%; mp 190-191 °C; IR(KBr): 3061, 1725, 1698, 1514, 1451, 762cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 12.0 Hz, 1H, CH), 7.69 (d, J = 8.0 Hz, 1H, ArH), 7.54 (d, J = 8.0 Hz, 1H, ArH), 7.38 – 7.34 (m, 2H), 6.29 (d, J = 12.0 Hz, 1H, CH), 3.86 (s, 3H, CH_3); HRMS (ESI) calcd for $C_{11}H_9NO_2S_2$ $[M+H]^+$ 252.0156, found 252.0153.

(Z)-methyl 3-(benzo[d]oxazol-2-ylthio)acrylate (**8b**)

Yellow powder, yield: 85%; mp 156-157 °C; IR(KBr): 3065, 1732, 1685, 1476, 932, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.0 Hz, 1H, CH), 7.99 (d, J = 8.0 Hz, 1H, ArH), 7.85 (d, J = 8.0 Hz, 1H, ArH), 7.52 (t, J = 8.0 Hz, 1H, ArH), 7.41 (t, J = 8.0 Hz, 1H, CH), 6.22 (d,

J = 8.0 Hz, 1H, CH), 3.84 (s, 3H, CH_3); HRMS (ESI) calcd for $C_{11}H_9NO_3S$ $[M+H]^+$ 236.0385, found 236.0381.

(Z)-methyl 3-(1H-benzo[d]imidazol-2-ylthio)acrylate (**8c**)

White powder, yield: 85%; mp 143-146 ^oC; IR (KBr) *v*: 3265, 1780, 1569, 1437, 813, 735cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 12.0 Hz, 1H, CH), 7.63 (s, 2H, ArH), 7.33-7.32 (m, 3H, ArH), 6.28 (d, *J* = 12.0 Hz, 1H, CH), 3.90 (s, 3H, CH_3); HRMS (ESI) calcd for $C_{11}H_{10}N_2O_2S$ $[M+H]^+$ 235.0497, found 235.0501.

(Z)-methyl 3-(5-amino-1,3,4-thiadiazol-2-ylthio)acrylate (**9**)

White powder, yield: 85%; mp 93-95 ^oC; IR (KBr) *v*: 3262, 3123, 1693, 1510, 1222, 1165, 932, 798cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 12.0 Hz, 1H, CH), 6.14 (d, *J* = 12.0 Hz, 1H, CH), 5.13 (s, 2H, NH_2), 3.82 (s, 3H, CH_3); ^{13}C NMR (400 MHz, d_6-DMSO) δ 171.3, 166.6, 148.7, 145.5, 115.0, 52.1; HRMS (ESI) calcd for $C_6H_7N_3O_2S_2$ $[M+H]^+$ 218.0061, found 218.0058.

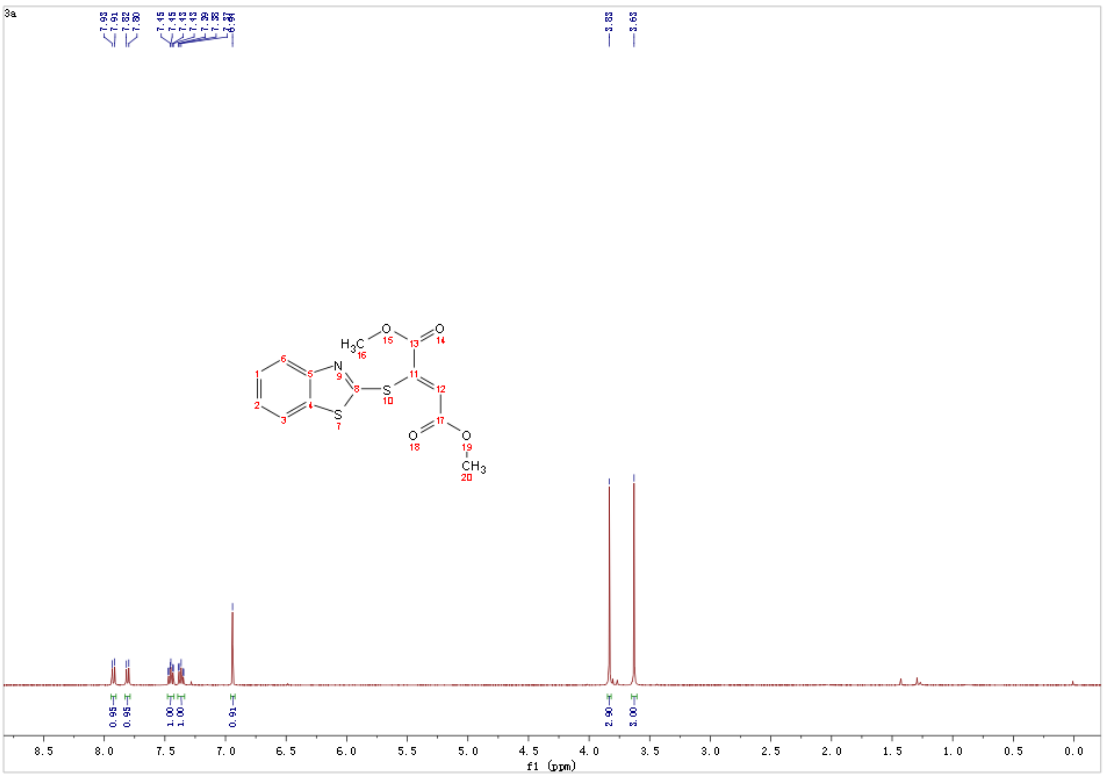
2. X-ray crystal structure data for compounds **5b, 6b** and **8a**

Table S1. Crystal data and structure refinement for **5b, 6b** and **8a**.

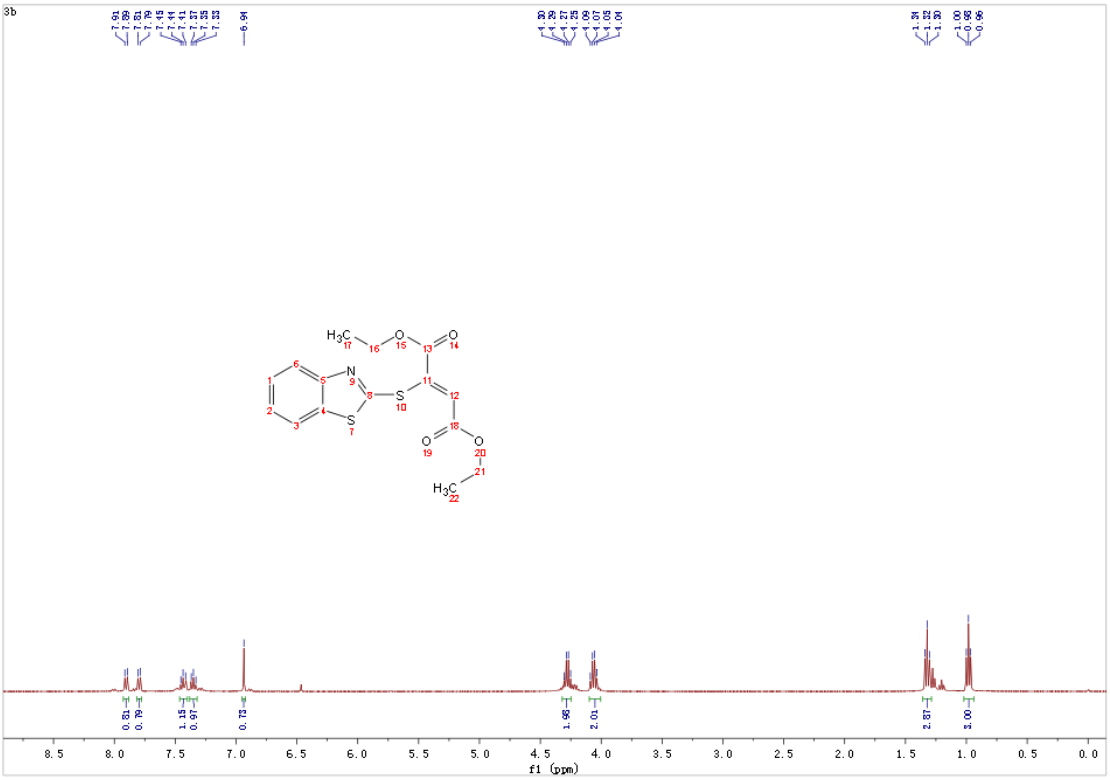
	5b	**6b**	**8a**
Empirical formula	$C_{10}H_{13}N_3O_4S_2$	$C_{26}H_{20}N_4O_6S_2$	$C_{11}H_9NO_2S_2$
Formula weight	303.37	548.6	251.31
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P-1*	*P-1*	*P2₁/n*
Unit cell dimensions(Å, °)	*a* = 5.8072(4)	*a* = 5.5645(2)	*a* = 9.901(2)
	b = 10.1034(7)	*b* = 8.3728(2)	*b* = 5.6108(14)
	c = 12.5372(9)	*c* = 13.3704(4)	*c* = 20.644(5)
	α = 83.745(4)	*α* = 82.2150(10)	*α* = 90
	β = 76.844(4)	*β* = 80.871(2)	*β* = 92.708(3)
	γ = 79.794(4)	γ = 84.664(2)	γ = 90
Volume/ nm^3	703.14(9)	607.74	1145.6(5)
Z	2	1	4
Density (calc.) /$g\cdot cm^{-3}$	1.433	1.499	1.457
μ/mm^{-1}	0.391	0.271	0.447
Limiting indices	-8≤h≤8; -13≤k≤13; -17≤l≤17	-7≤h≤7; -10≤k≤10; -17≤l≤16	-13≤h≤12; -4≤k≤7; -26≤l≤25
Reflection collected	10977	10235	6583
Independent reflection	3750 (R_{int} = 0.0350)	2781 (R_{int} = 0.0190)	2663 (R_{int} = 0.0329)
Data/restraints/ parameters	3750 / 0 / 182	2781 / 0 / 2524	2663 / 0 / 146
Goodness-of-fit on F^2	1.026	1.057	1.026
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0399, wR_2 = 0.1063	R_1 = 0.0333, wR_2 = 0.098	R_1 = 0.0446, wR_2 = 0.1249
R indices (all data)	R_1 = 0.0512, wR_2 = 0.1156	R_1 = 0.0403, wR_2 = 0.1132	R_1 = 0.0522, wR_2 = 0.1307
Largest diff. peak and hole / $e\cdot Å^{-3}$	0.380 and -0.250	0.320 and -0.440	0.347 and -0.269

3. NMR spectra of compounds **3**, **5**, **6, 8** and **9**

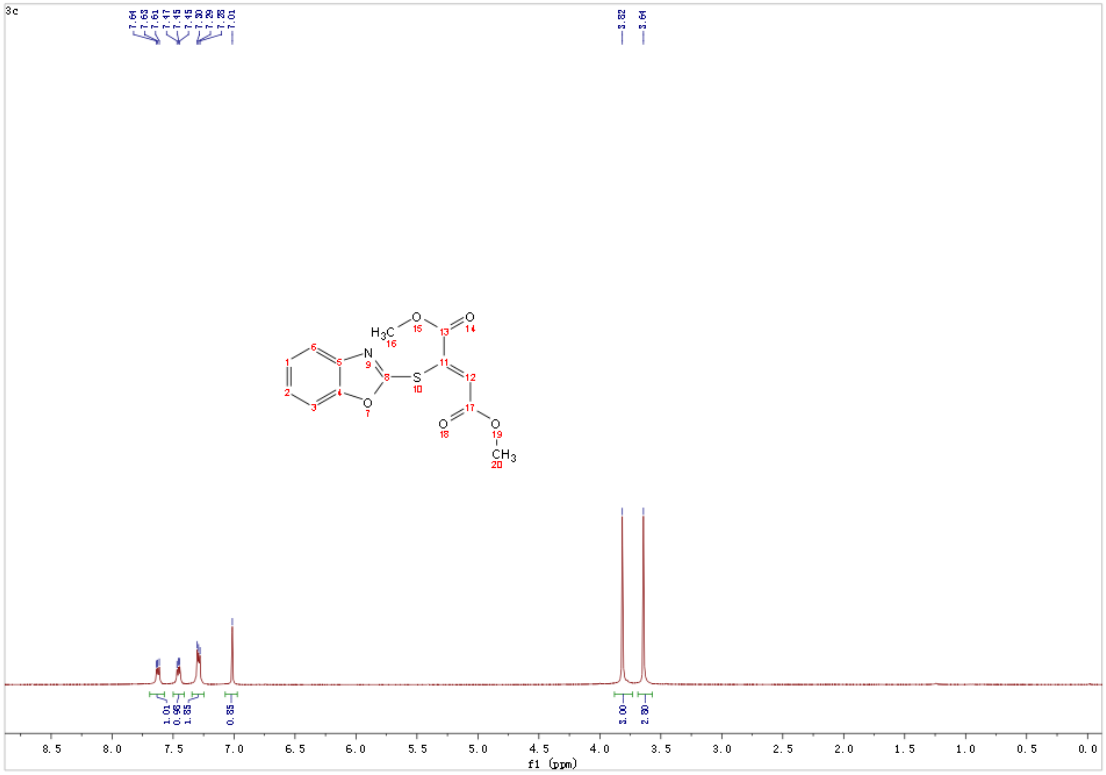
^{1}H NMR spectrum of compound 3a in $CDCl_3$, 400 MHz



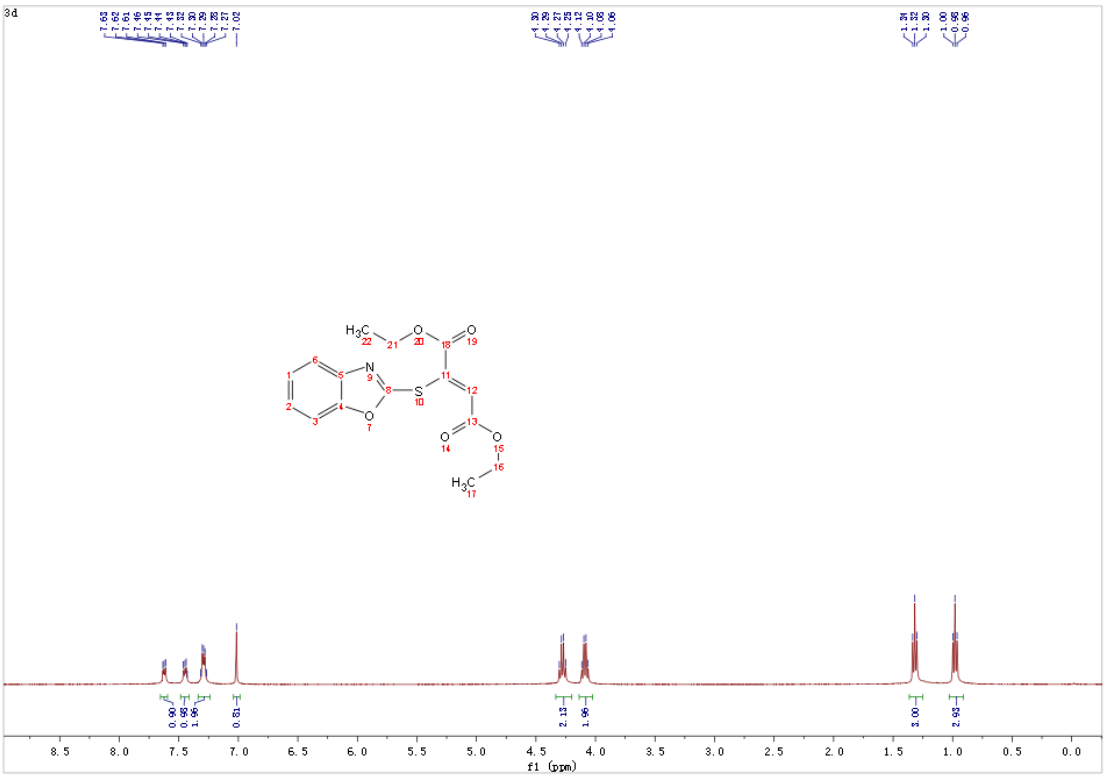
^{1}H NMR spectrum of compound 3b in $CDCl_3$, 400 MHz



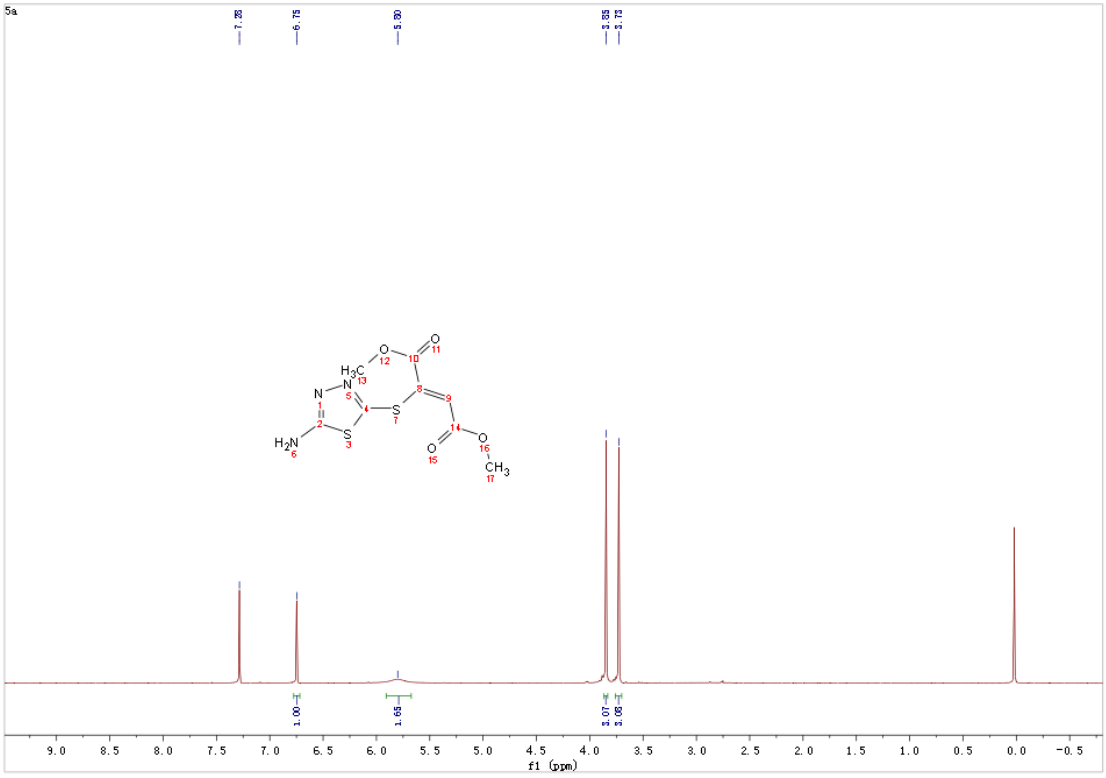
^{1}H NMR spectrum of compound 3c in $CDCl_3$, 400 MHz



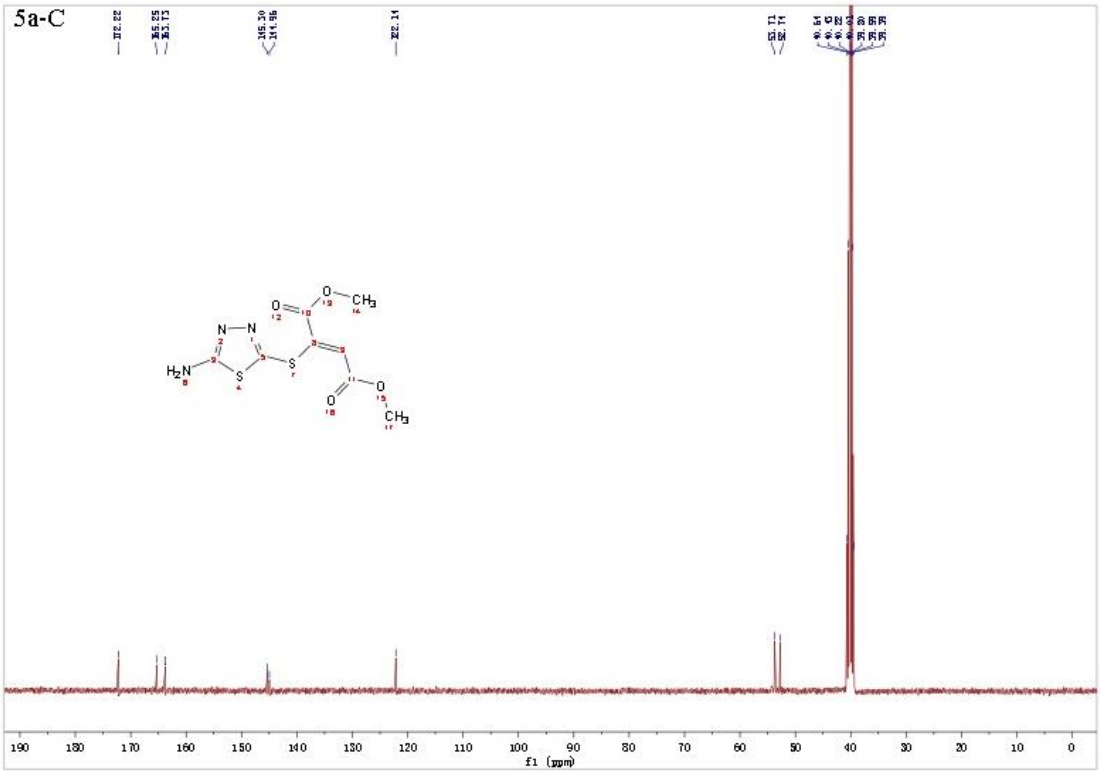
^{1}H NMR spectrum of compound 3d in $CDCl_3$, 400 MHz



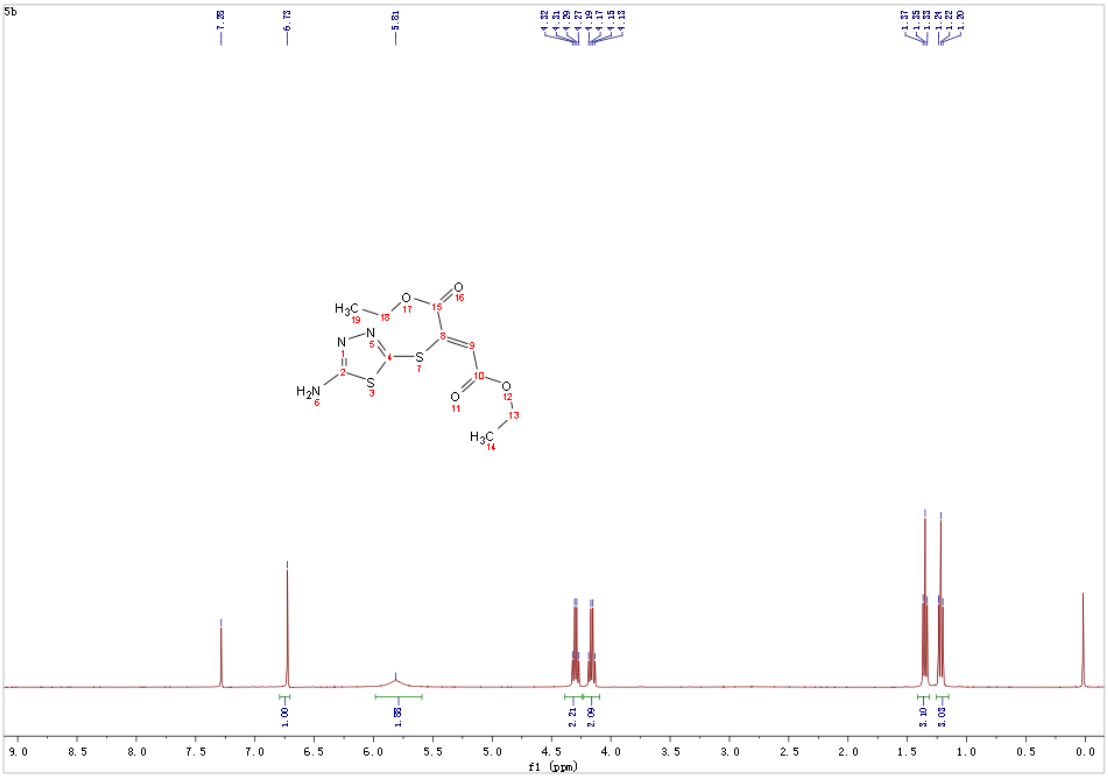
^{1}H NMR spectrum of compound 5a in $CDCl_3$, 400 MHz



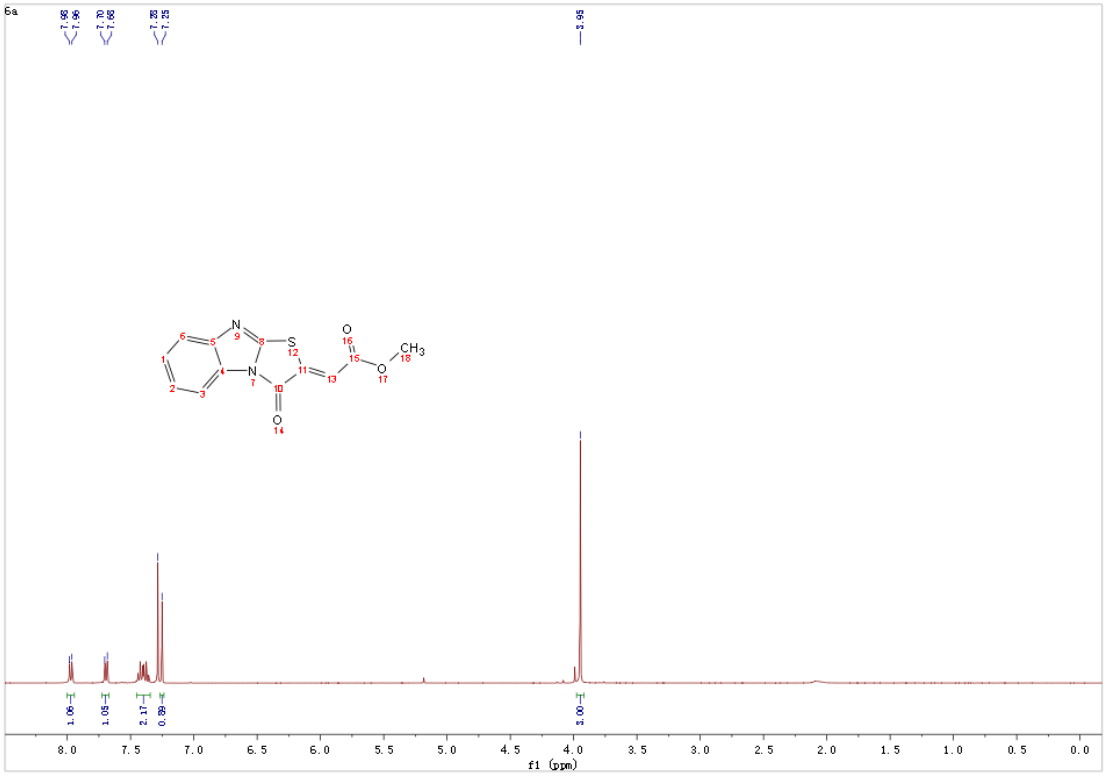
^{13}C NMR spectrum of compound 5a in $(CD_3)_2SO$, 400 MHz



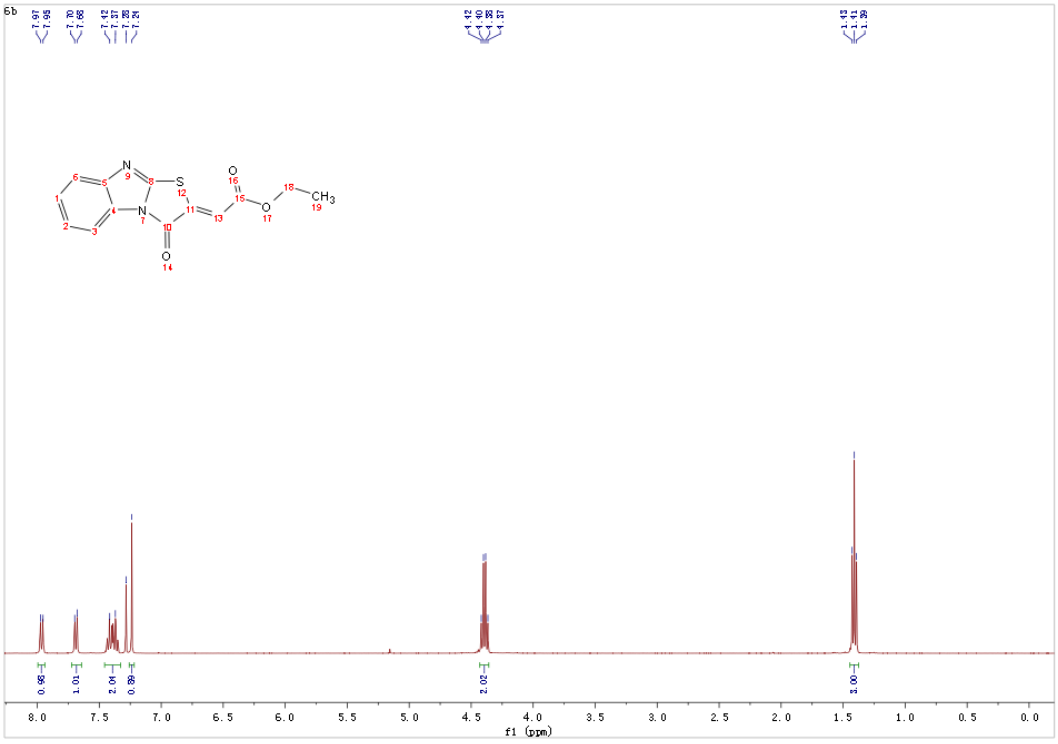
^{1}H NMR spectrum of compound 5b in $CDCl_3$, 400 MHz



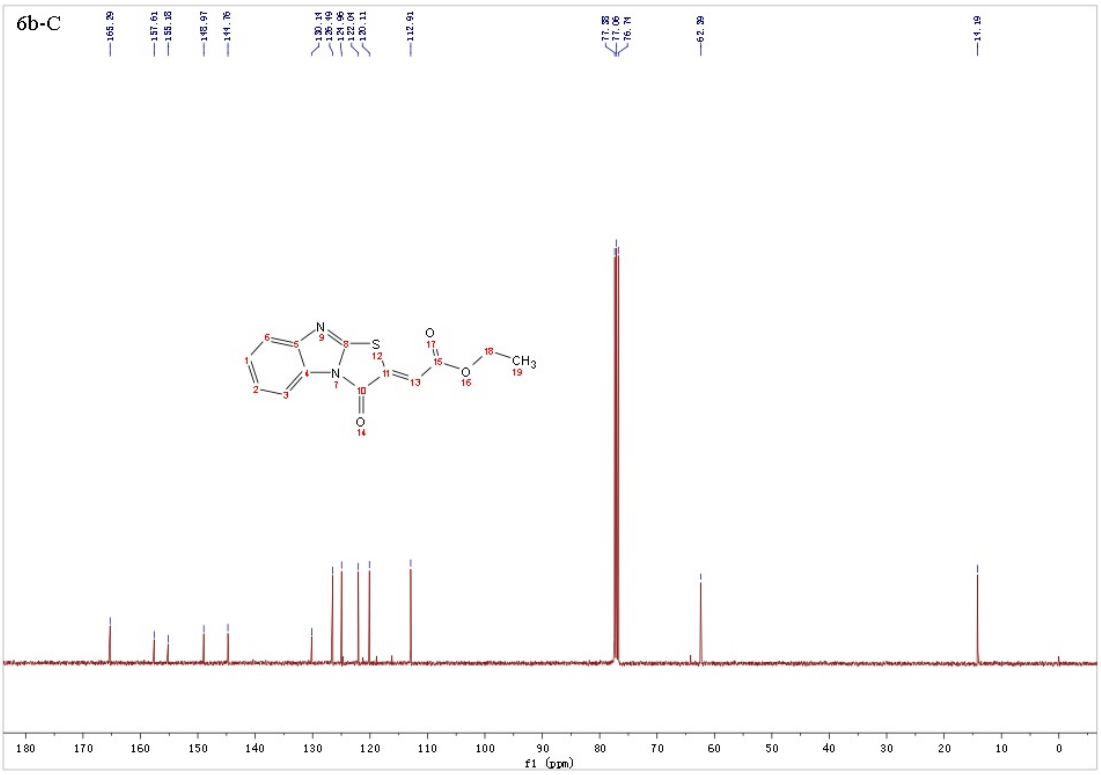
^{1}H NMR spectrum of compound 6a in $CDCl_3$, 400 MHz



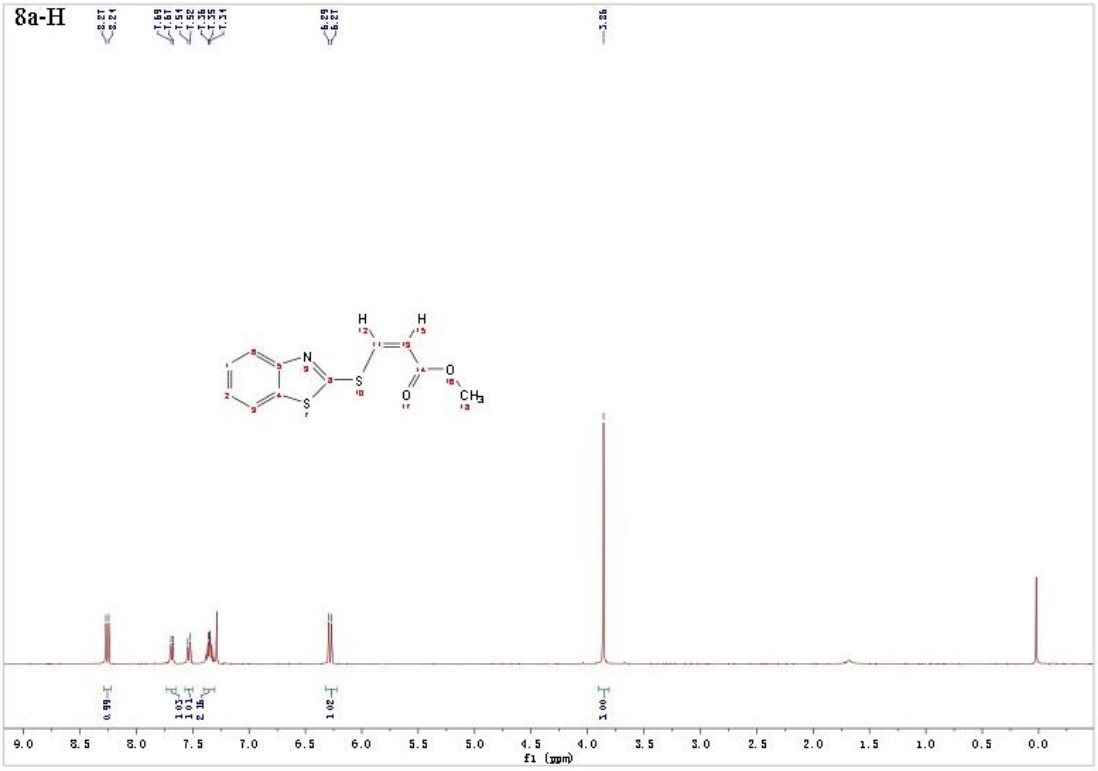
^{1}H NMR spectrum of compound 6b in $CDCl_3$, 400 MHz



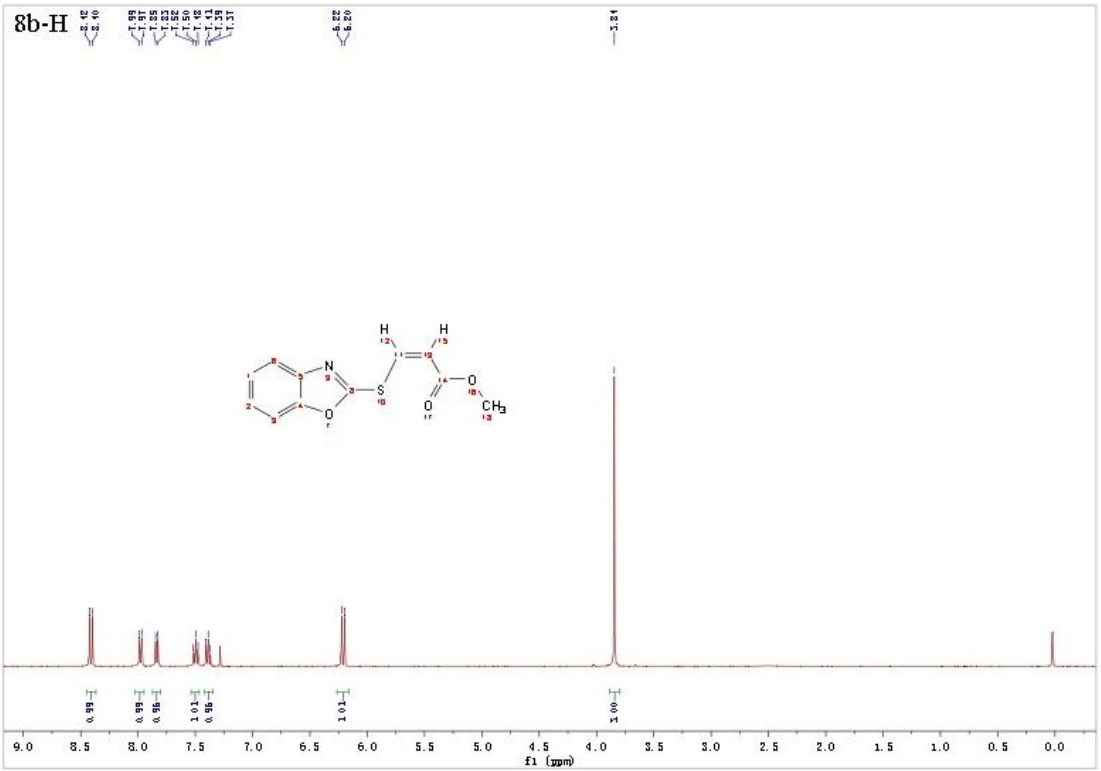
^{13}C NMR spectrum of compound 6b in $CDCl_3$, 400 MHz



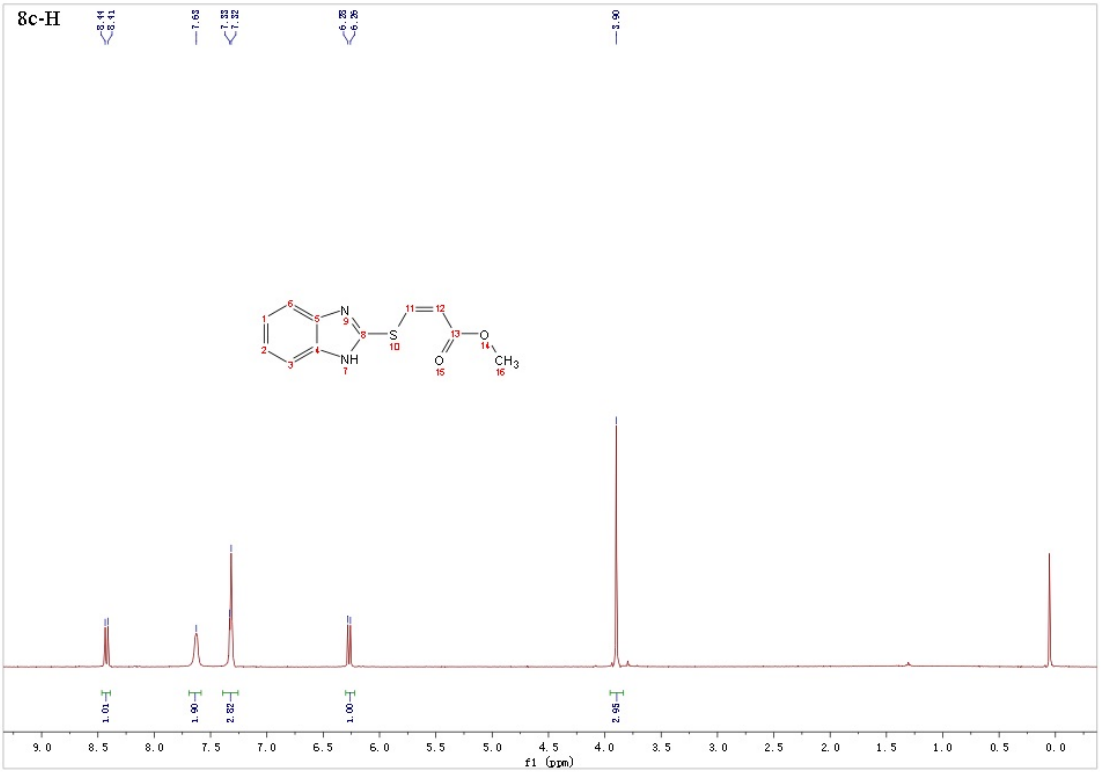
^{1}H NMR spectrum of compound 8a in $CDCl_3$, 400 MHz



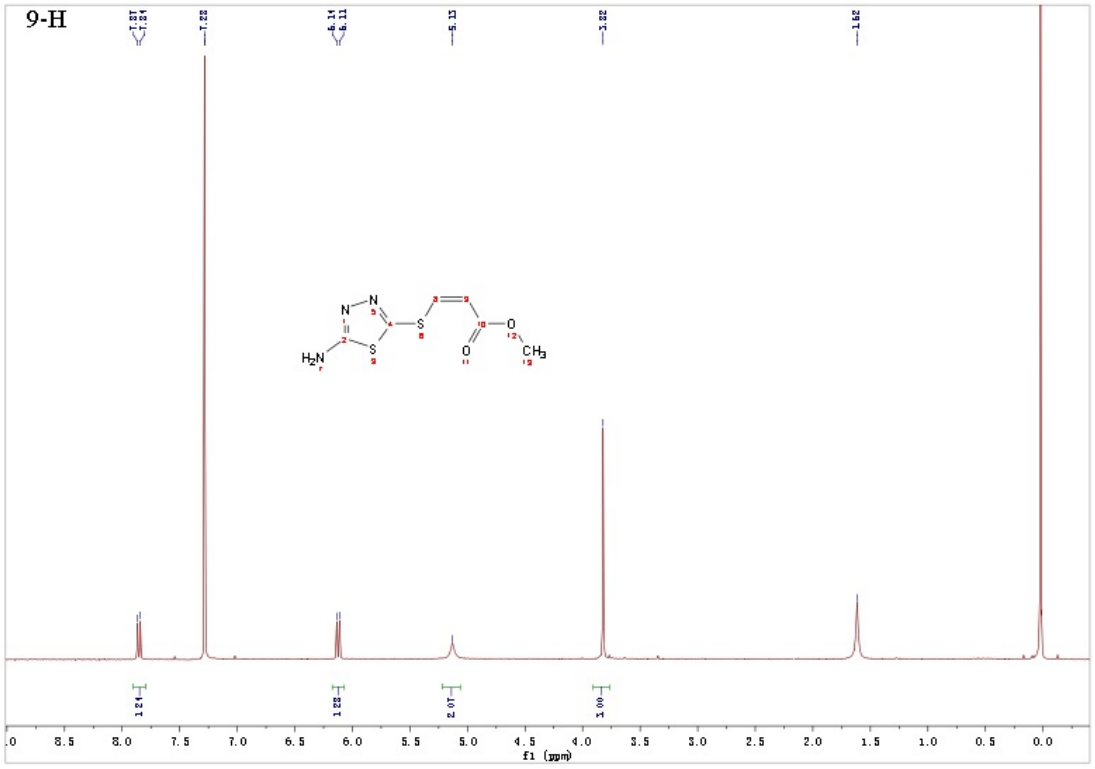
^{1}H NMR spectrum of compound 8b in $CDCl_3$, 400 MHz



^{1}H NMR spectrum of compound 8c in $CDCl_3$, 400 MHz



^{1}H NMR spectrum of compound 9 in $CDCl_3$, 400 MHz



^{13}C NMR spectrum of compound 9 in $(CD_3)_2SO$, 400 MHz