

## Electronic Supplementary Information

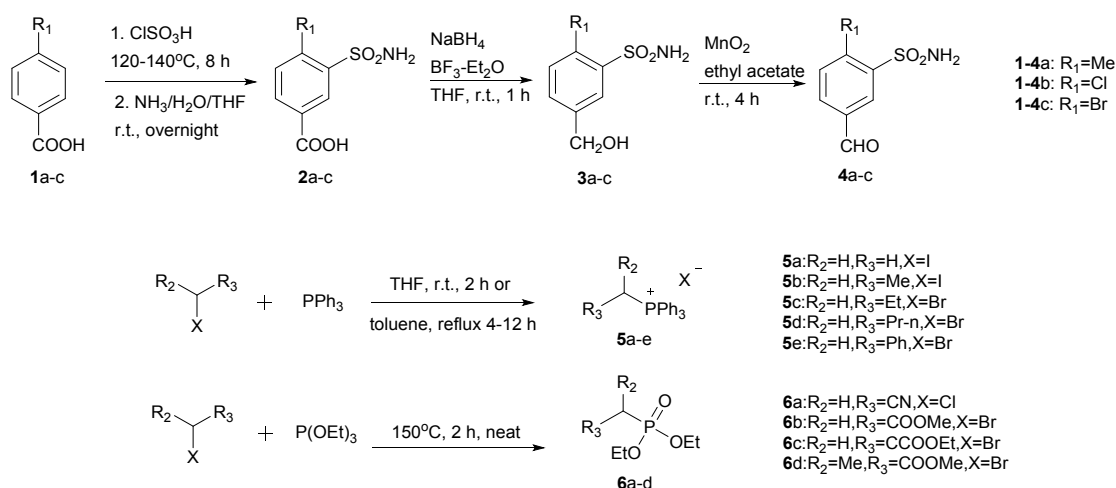
# Design, synthesis and SAR study of novel sulfonylureas containing an alkenyl moiety

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## 1. Synthesis of compounds 4



Scheme 1. Synthetic routes of the intermediates **4**, **5** and **6**

### General Synthetic Procedure for compound **2a-c**

0.1 mol of 4-methylbenzoic acid (**1a**) was slowly added to 40 ml ClSO<sub>3</sub>H, and the mixture was heated to 120°C for 8 hours, the HCl gas released from the reaction system was absorbed by aqueous NaOH. After the mixture was cooled to room temperature, it was carefully poured on to sufficient crushed ice. Collect the white solid by suction filtration and wash the solid with cold water. Then dissolve the white solid with THF and add this solution to 50 ml ammonium hydroxide at 0°C. The reaction mixture was heated to 50°C for 30 min and THF was removed *in vacuo*. Adjust the acidity to pH 1 with hydrochloric acid and collect the precipitated white solid to obtain 4-methyl-3-sulfamoylbenzoic acid (**2a**), yield 85.1%, white solid, m.p. 221-222°C, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.43 (d, *J* = 1.8 Hz, 1H, Ph-H), 8.01 (dd, *J* = 7.8, 1.9 Hz, 1H, Ph-H), 7.56 (s, 2H, SO<sub>2</sub>NH<sub>2</sub>), 7.52 (d, *J* = 8.0 Hz, 1H, Ph-H), 2.65 (s, 3H, CH<sub>3</sub>). **2b** and **2c** were synthesized by similar procedure except that the reaction temperature was 140°C.

4-chloro-3-sulfamoylbenzoic acid (**2b**), yield 83.0%, white solid, m.p. 254-256°C, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.60 (s, 1H, COOH), 8.51 (d, *J* = 2.0 Hz, 1H, Ph-H), 8.10 (dd, *J* = 8.2, 2.1 Hz, 1H, Ph-H), 7.82 (s, 2H, SO<sub>2</sub>NH<sub>2</sub>), 7.79 (d, *J* = 8.3 Hz, 1H, Ph-H).

4-bromo-3-sulfamoylbenzoic acid (**2c**), yield 81.2%, white solid, m.p. 258-259°C, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.59 (s, 1H, COOH), 8.53 (d, *J* = 1.5 Hz, 1H, Ph-H), 8.02 – 7.95 (m, 2H, Ph-H), 7.78 (s, 2H, SO<sub>2</sub>NH<sub>2</sub>).

### General Procedure for Preparation of the compound **3a-c**

To a solution of 100 mmol 4-methyl-3-sulfamoylbenzoic acid (**2a**) in THF was added 200 mmol NaBH<sub>4</sub> and the mixture was stirred until the gas evolution ceased. And then 266 mmol BF<sub>3</sub>·Et<sub>2</sub>O was added dropwisely at room temperature and stirring was continued for additional 1 hour. 1M HCl was added carefully to quench the reaction. THF was then removed *in vacuo*. The aqueous phase was extracted with ethyl acetate for 3 times. The combined organic phase was washed with saturated NaHCO<sub>3</sub> solution, brine and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was washed with small amount of ethyl acetate to give 5-(hydroxymethyl)-2-methylbenzenesulfonamide (**3a**), yield 82.4%, white crystals, m.p. 105-106°C, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.84 (s, 1H, Ph-H), 7.39 (d, *J* = 7.8 Hz, 1H, Ph-H), 7.34 (s, 2H, SO<sub>2</sub>NH<sub>2</sub>), 7.31 (d, *J* = 7.7 Hz, 1H, Ph-H), 4.51 (s, 2H, CH<sub>2</sub>), 2.56 (s, 3H, CH<sub>3</sub>). **3b** was purified by column chromatography (petroleum ether/acetone 4:1→1:1) and **3c** was synthesized by similar procedures with **3a**.

5-(hydroxymethyl)-2-chlorobenzenesulfonamide (**3b**), yield 75.0%, white crystals, m.p. 149-150°C, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.97 (s, 1H, Ph-H), 7.58 (d, *J* = 5.9 Hz, 3H, Ph-H, SO<sub>2</sub>NH<sub>2</sub>), 7.51 (d, *J* = 8.0 Hz, 1H, Ph-H), 5.49 (s, 1H, OH), 4.55 (s, 2H, CH<sub>2</sub>).

5-(hydroxymethyl)-2-bromobenzenesulfonamide (**3c**), yield 90.0%, white crystals, m.p. 160-161°C, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.01 (d, *J* = 2.1 Hz, 1H, Ph-H), 7.75 (d, *J* = 8.1 Hz, 1H, Ph-H), 7.55 (s, 2H, SO<sub>2</sub>NH<sub>2</sub>), 7.41 (dd, *J* = 8.1, 2.0 Hz, 1H, Ph-H), 5.49 (t, *J* = 5.6 Hz, 1H, OH), 4.53 (d, *J* = 5.6 Hz, 2H, CH<sub>2</sub>).

### General Procedure for Preparation of the compound **4a-c**

A mixture of 10 mmol 5-(hydroxymethyl)-2-methylbenzenesulfonamide (**3a**) and 100 mmol MnO<sub>2</sub> were stirred in ethyl acetate at room temperature for 4 hours. Remove the MnO<sub>2</sub> by suction filtration through a celite pad and wash the solid with ethyl acetate for several times. The filtrates was concentrated at reduced pressure to provide 5-formyl-2-methylbenzenesulfonamide (**4a**) in 91.1% yield, white solid, m.p. 95-96°C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.02 (s, 1H, CHO), 8.50 (s, 1H, Ph-H), 7.99 (d, *J* = 7.7 Hz, 1H, Ph-H), 7.52 (d, *J* = 7.8 Hz, 1H, Ph-H), 4.99 (s,

2H, SO<sub>2</sub>NH<sub>2</sub>), 2.79 (s, 3H, CH<sub>3</sub>). **4b** and **4c** were synthesized by similar procedures.

5-formyl-2-chlorobenzenesulfonamide (**4b**), yield 89.5%, white solid, m.p. 128-129°C, <sup>1</sup>H NMR (400 MHz, DMSO) δ 10.08 (s, 1H, CHO), 8.46 (d, *J* = 2.0 Hz, 1H, Ph-H), 8.13 (dd, *J* = 8.1, 2.0 Hz, 1H, Ph-H), 7.91 (d, *J* = 8.1 Hz, 1H, Ph-H), 7.84 (s, 2H, SO<sub>2</sub>NH<sub>2</sub>).

5-formyl-2-bromobenzenesulfonamide (**4c**), yield 95.0%, white solid, m.p. 135-136°C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.07 (s, 1H, CHO), 8.64 (d, *J* = 1.5 Hz, 1H, Ph-H), 7.98 – 7.95 (m, 2H, Ph-H), 5.25 (s, 2H, SO<sub>2</sub>NH<sub>2</sub>).

## 2. Herbicidal activities of compounds **9** at 375g/hm<sup>2</sup>

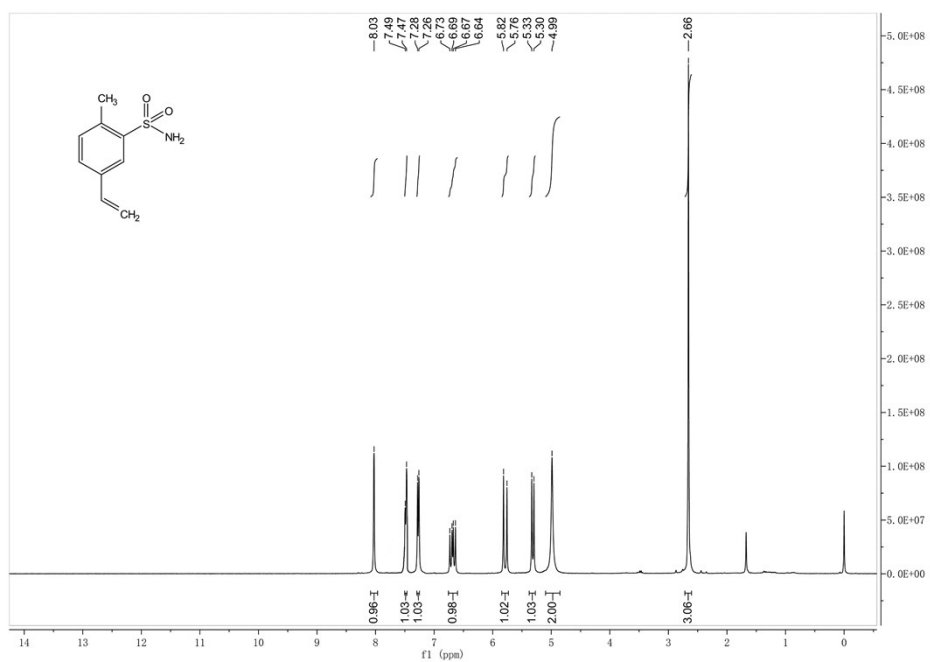
Table 1 Herbicidal Activities of Compounds **9a-w** at 375 g/hm<sup>2</sup> Dosage.

compd.	<i>Brassica napus</i>		<i>Amaranthus retroflexus</i>		compd.	<i>Brassica napus</i>		<i>Amaranthus retroflexus</i>	
	pre	post	pre	post		pre	post	pre	post
	<b>9a</b>	93.1	69.0	67.6		10.0	<b>9m</b>	10.0	23.4
<b>9b</b>	88.0	67.1	95.4	10.0	<b>9n</b>	0.0	21.1	5.0	68.2
<b>9c</b>	51.3	76.2	0.0	0.0	<b>9o</b>	30.0	25.8	0.0	23.9
<b>9d</b>	64.8	25.8	70.7	0.0	<b>9p</b>	20.0	25.0	0.0	61.9
<b>9e</b>	10.0	36.0	80.0	0.0	<b>9q</b>	15.0	87.7	10.0	33.2
<b>9f</b>	90.9	92.5	67.1	98.4	<b>9r</b>	15.0	89.9	15.0	85.1
<b>9g</b>	35.0	26.5	19.1	93.5	<b>9s</b>	10.0	66.1	0.0	32.7
<b>9h</b>	45.7	20.1	0.0	0.0	<b>9t</b>	98.0	97.0	99.0	85.6
<b>9i</b>	96.5	45.6	60.7	37.4	<b>9u</b>	89.2	98.0	99.0	66.9
<b>9j</b>	51.0	44.4	0.0	37.9	<b>9v</b>	99.1	85.9	98.8	80.6
<b>9k</b>	48.6	34.5	65.9	43.7	<b>9w</b>	10.0	5.0	0.0	5.0
<b>9l</b>	43.8	39.8	71.7	79.1	chlorsulfuron	98.6	100	79.8	62.7

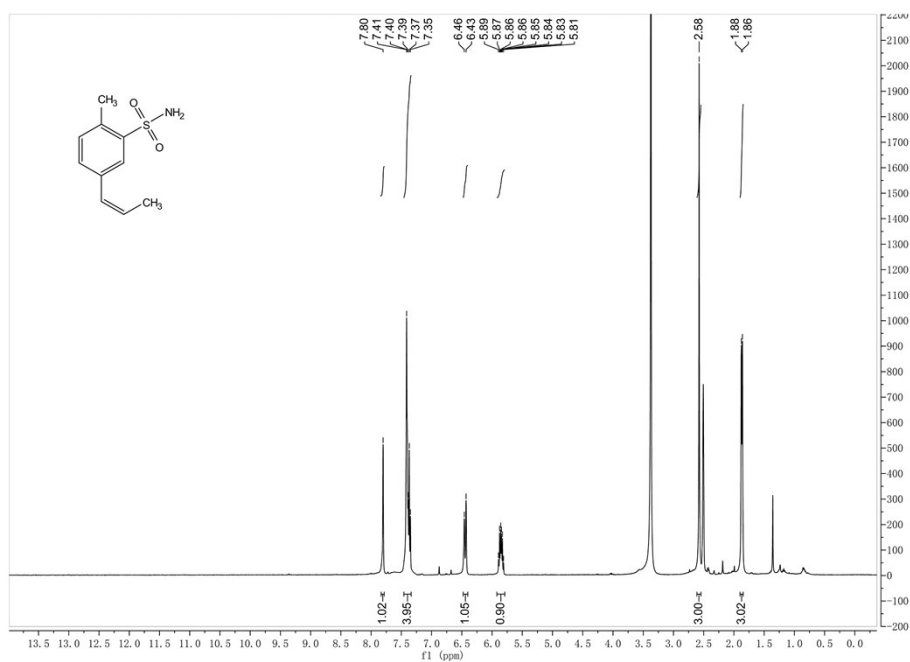
### 3. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of title compounds

#### $^1\text{H}$ NMR spectra of intermediate 7a-m

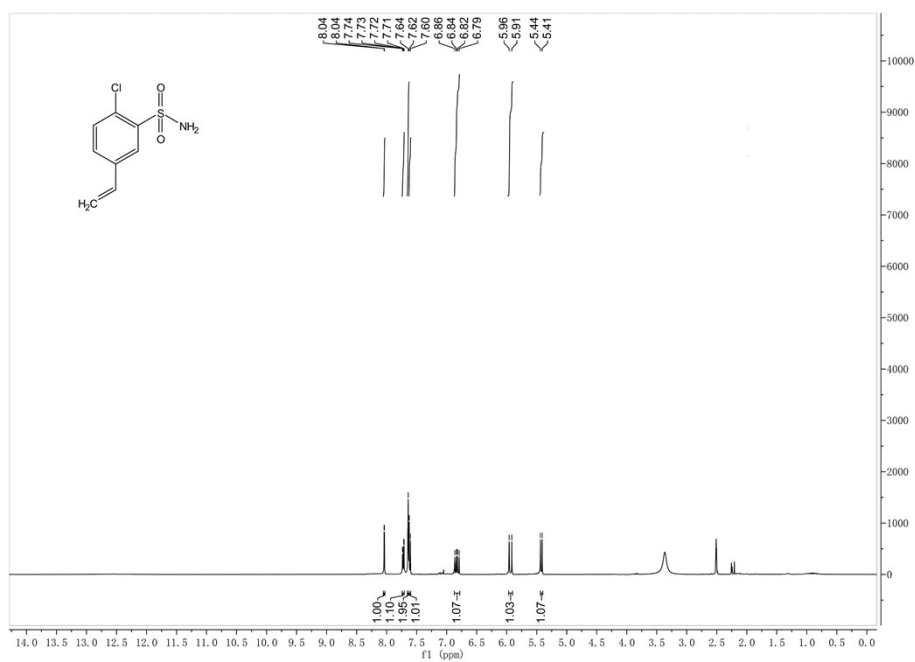
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of 7a



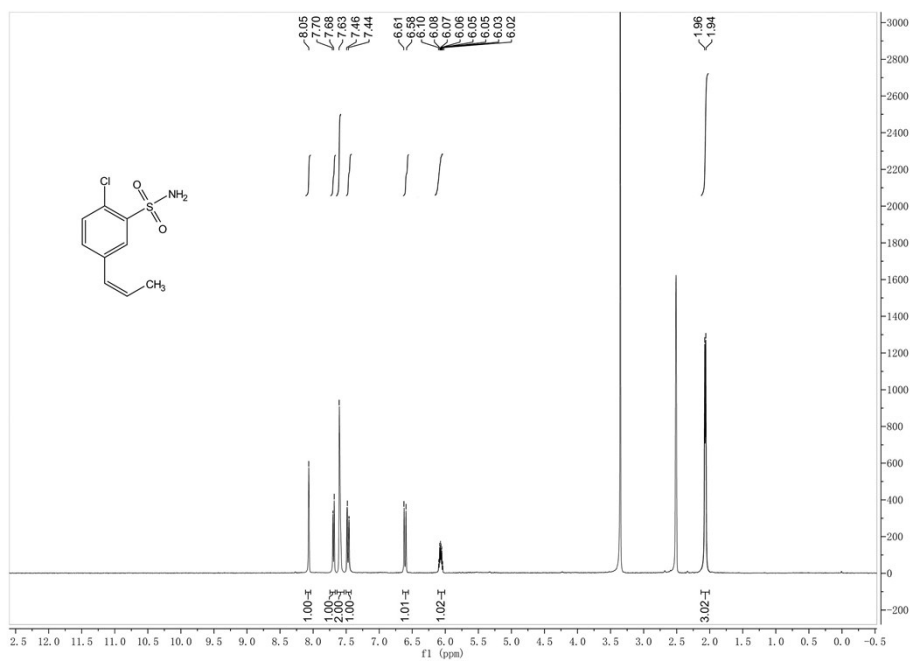
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of 7b



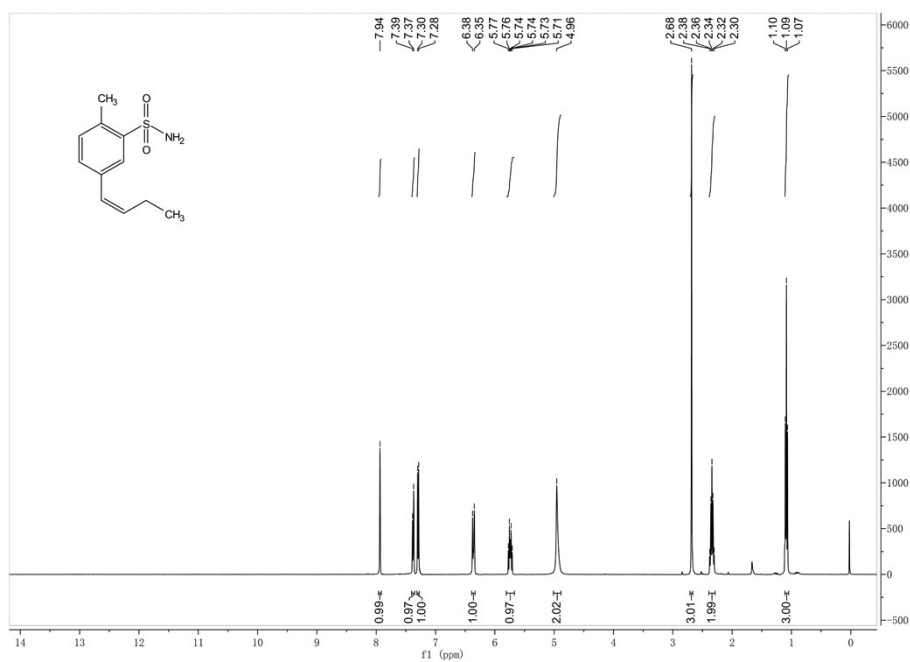
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of **7c**



$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of **7d**



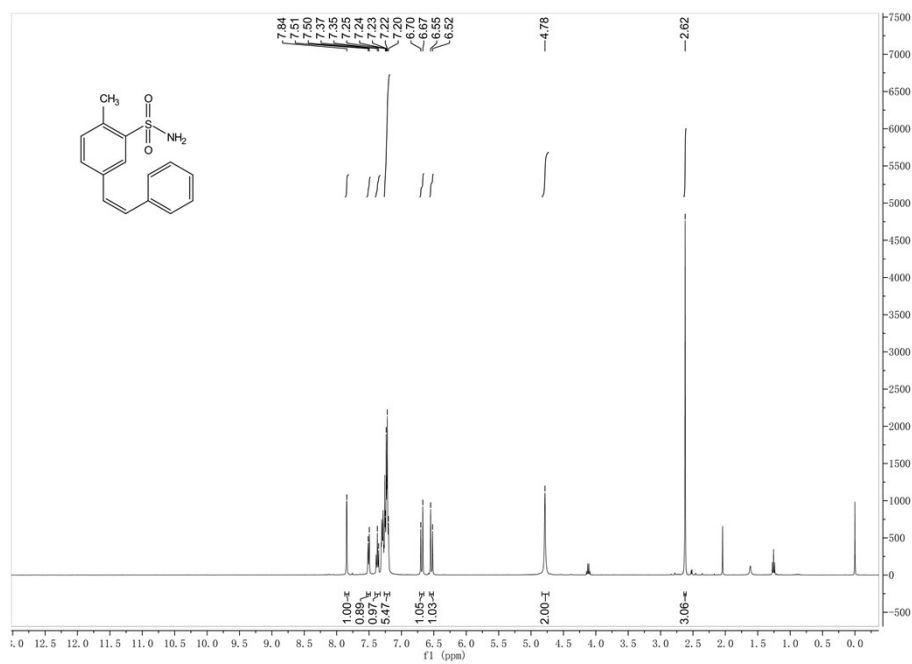
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **7e**



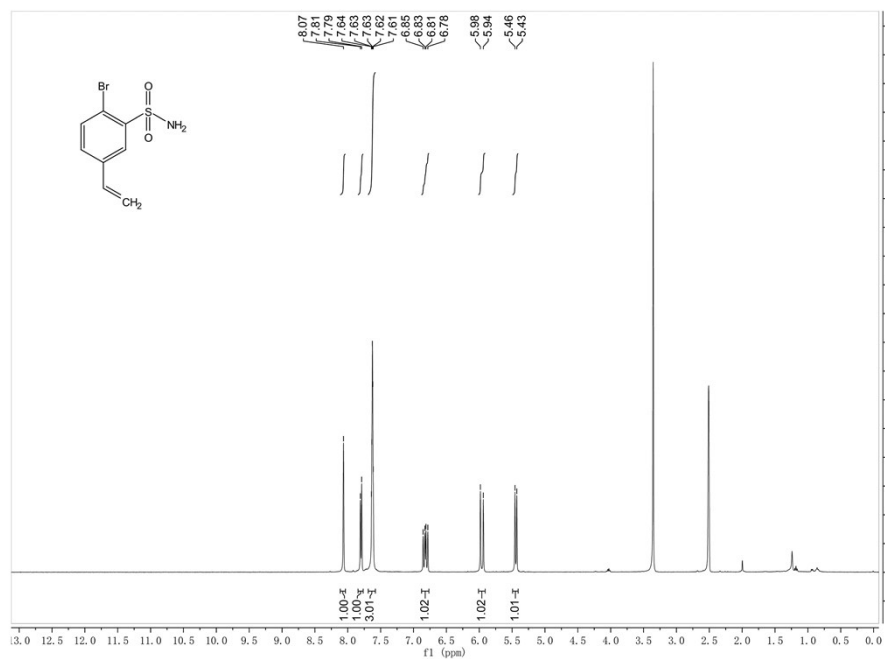
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **7f**



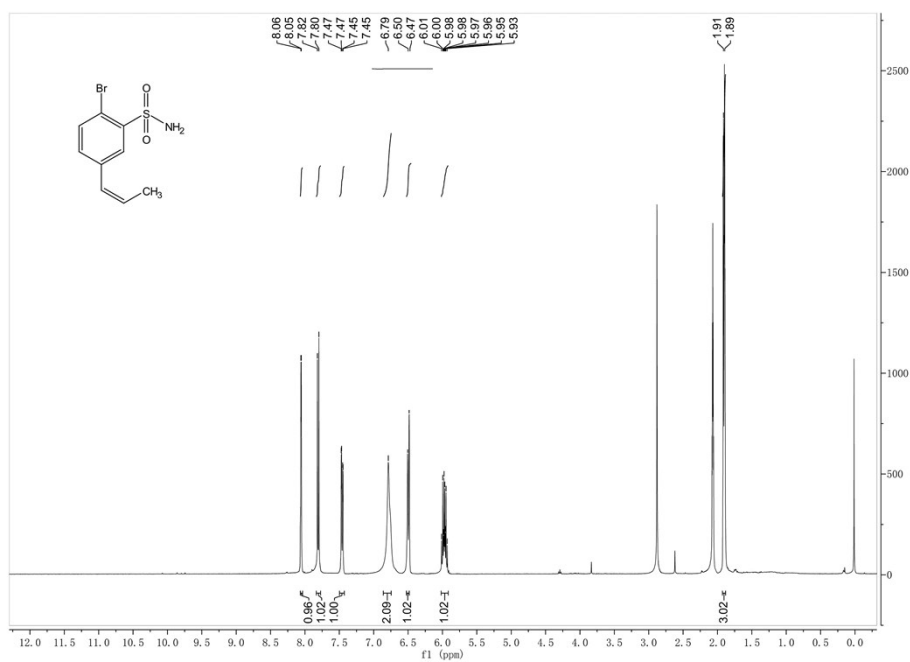
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **7g**



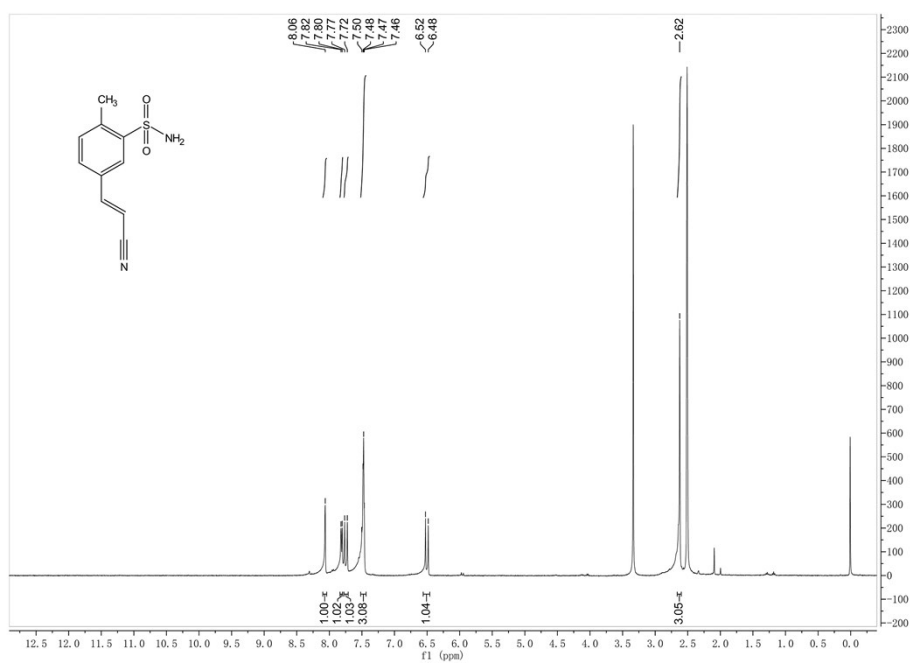
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) spectrum of **7h**



$^1\text{H}$  NMR (400 MHz, acetone- $d_6$ ) spectrum of **7i**

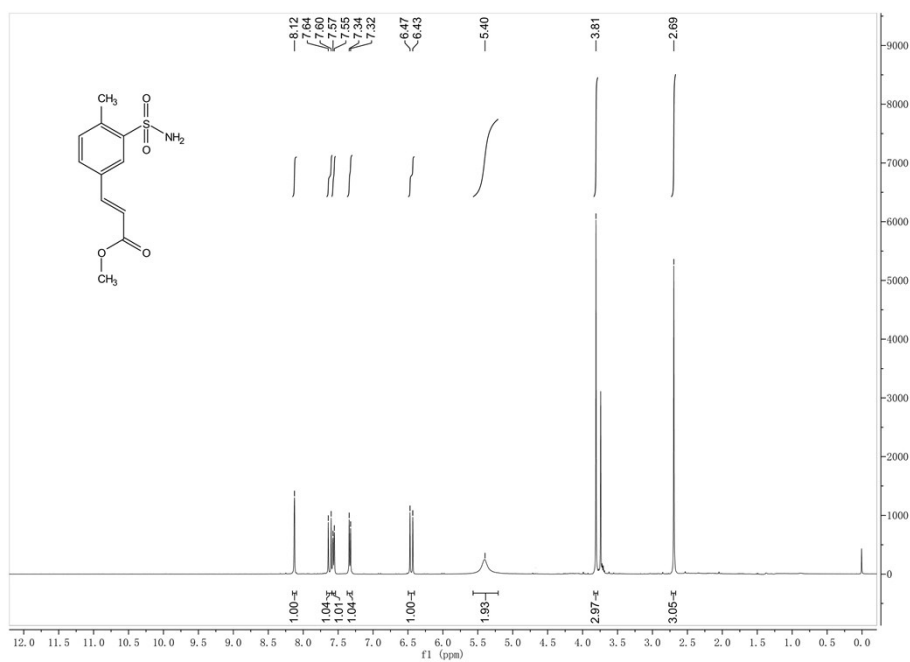


$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) spectrum of **7j**

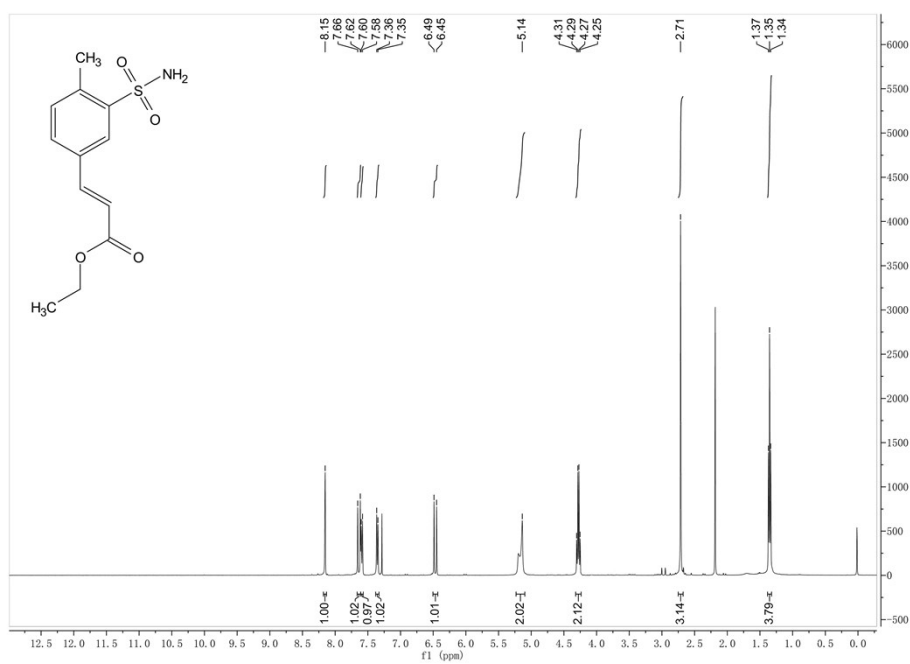




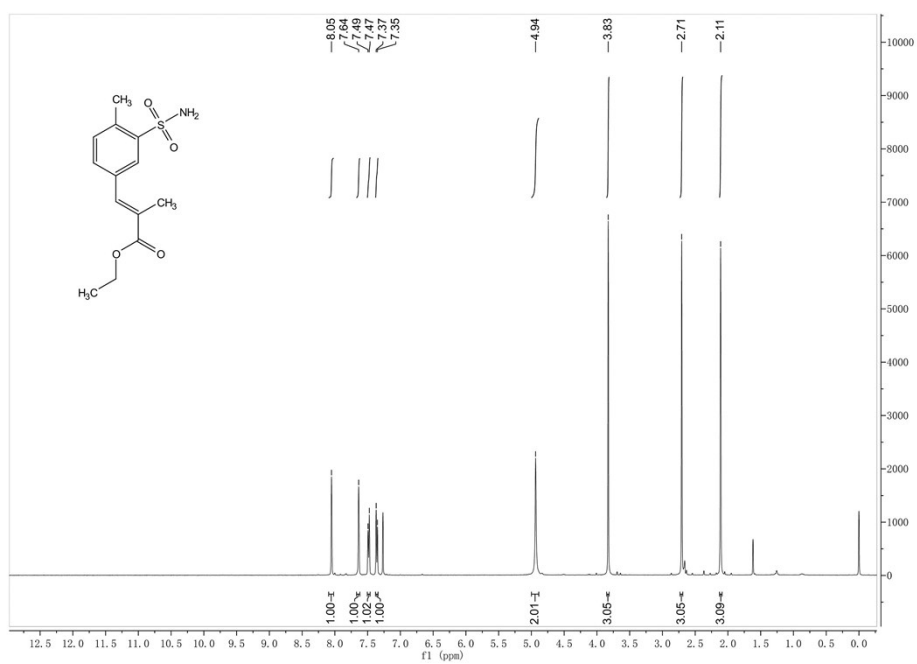
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **7k**



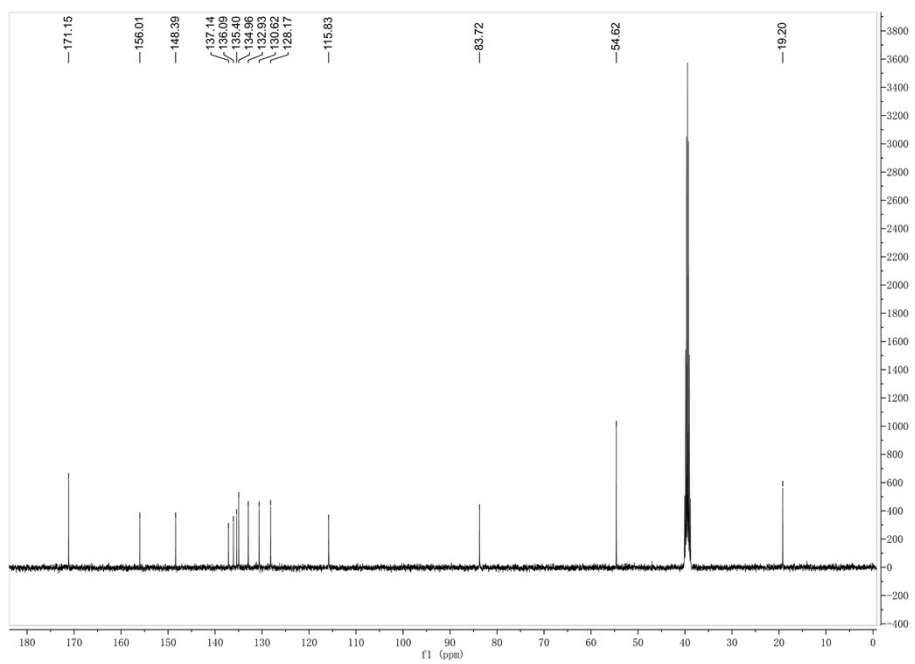
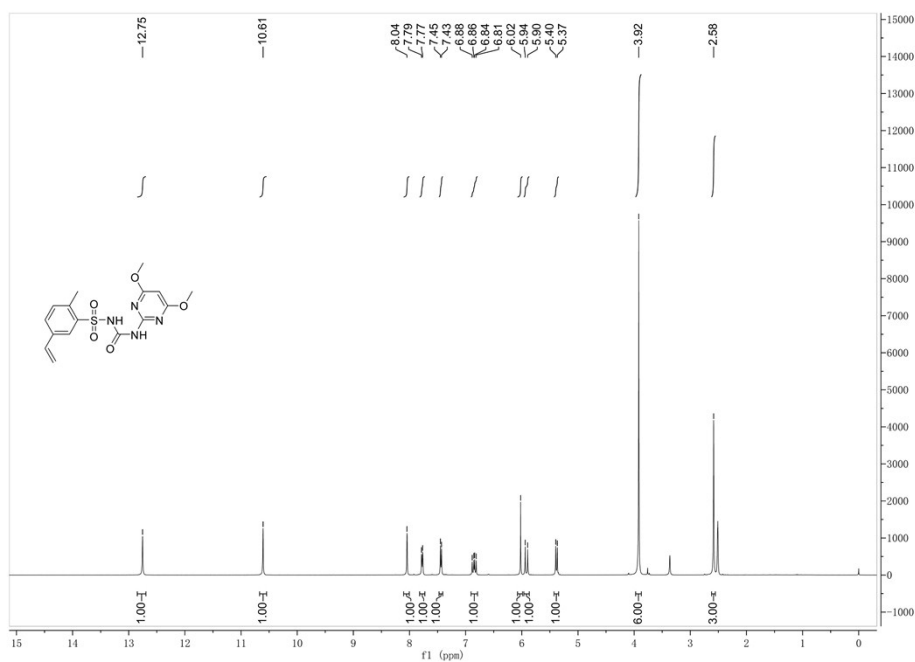
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **7l**



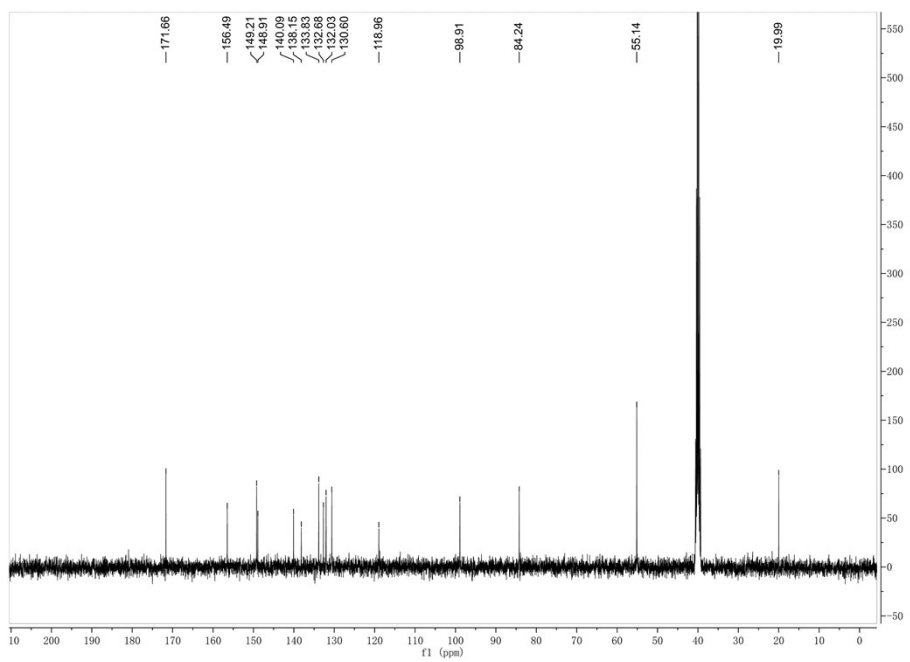
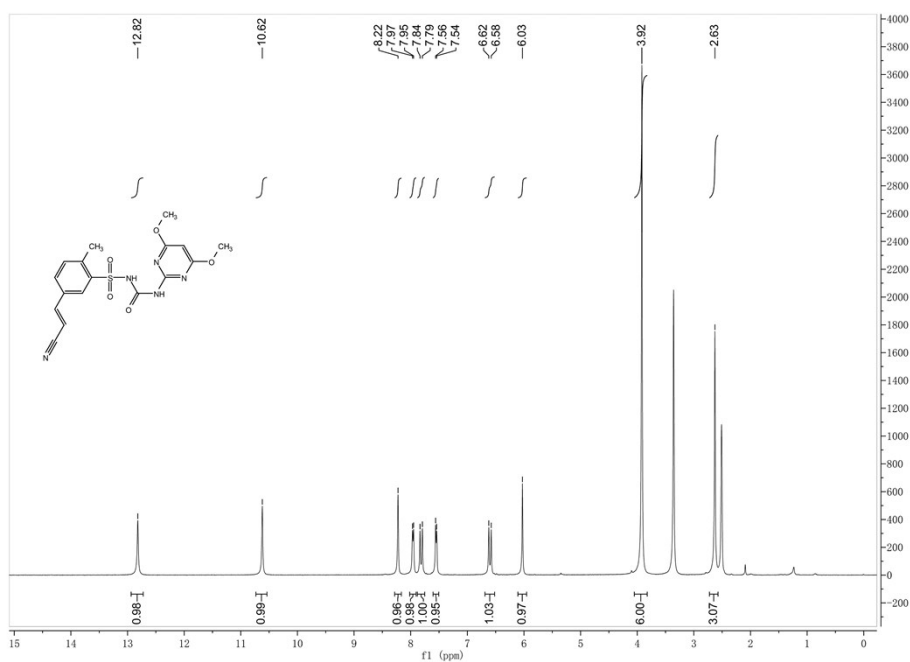
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of **7m**



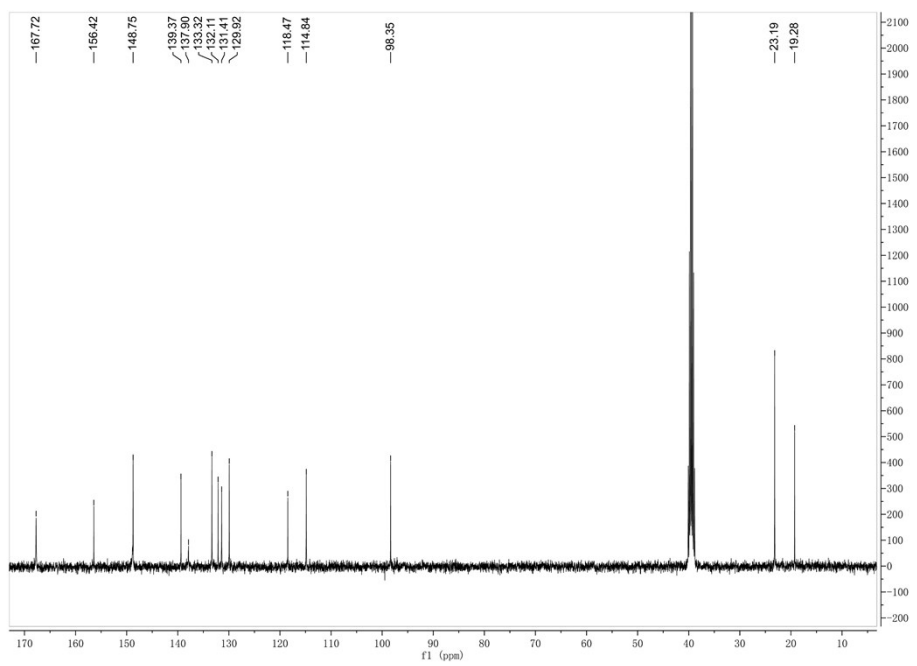
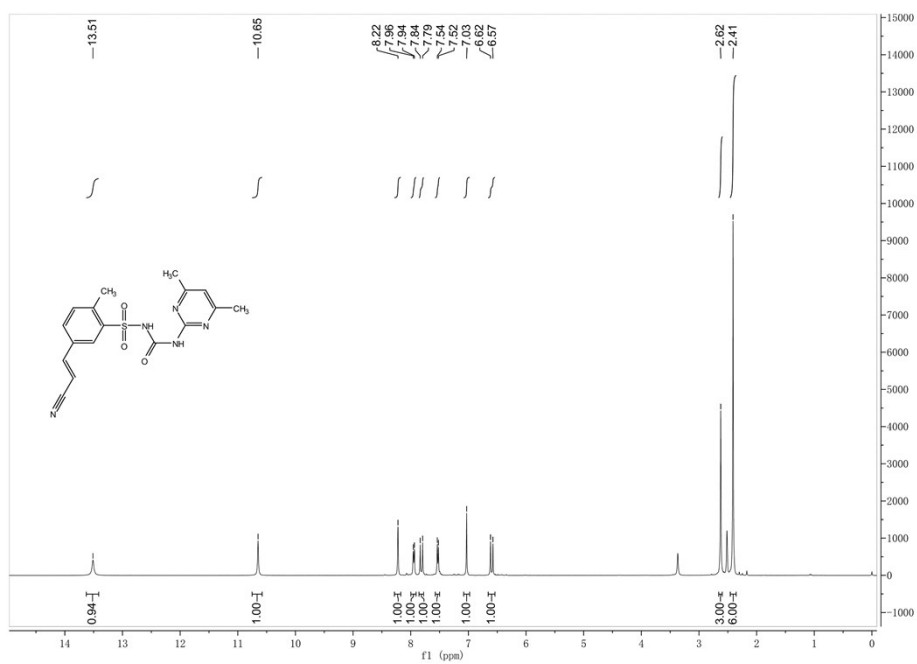
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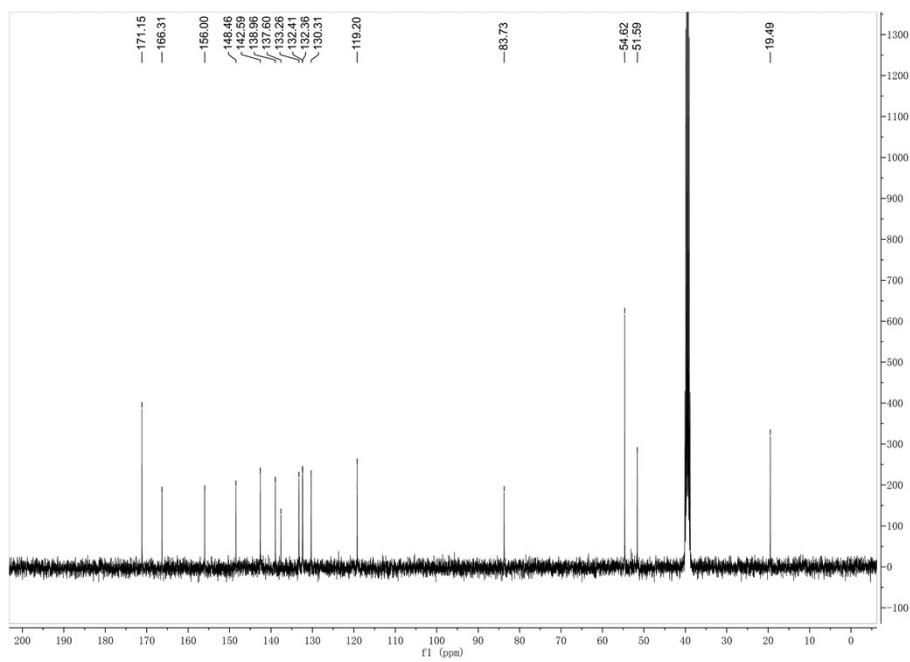
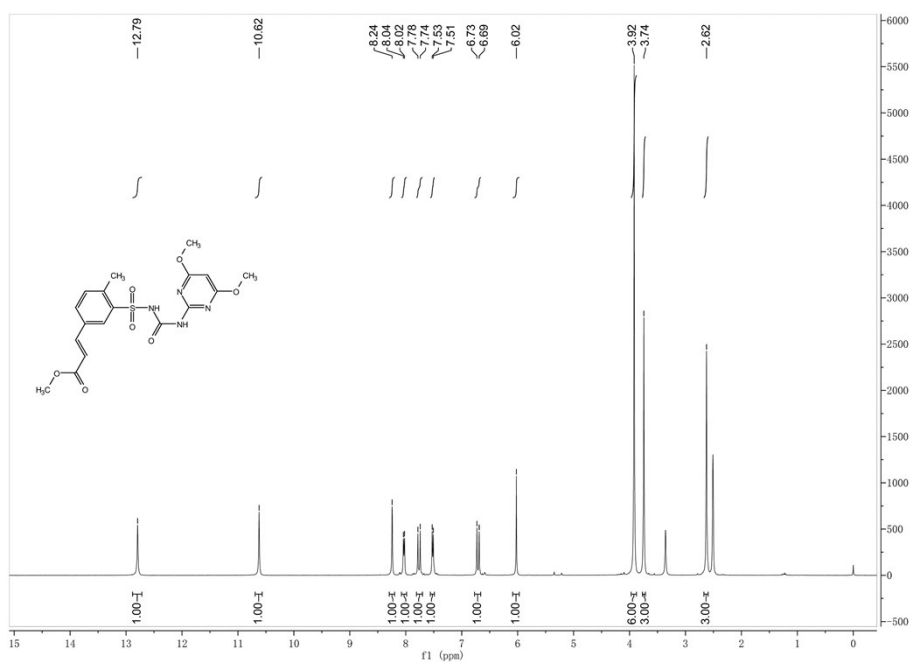
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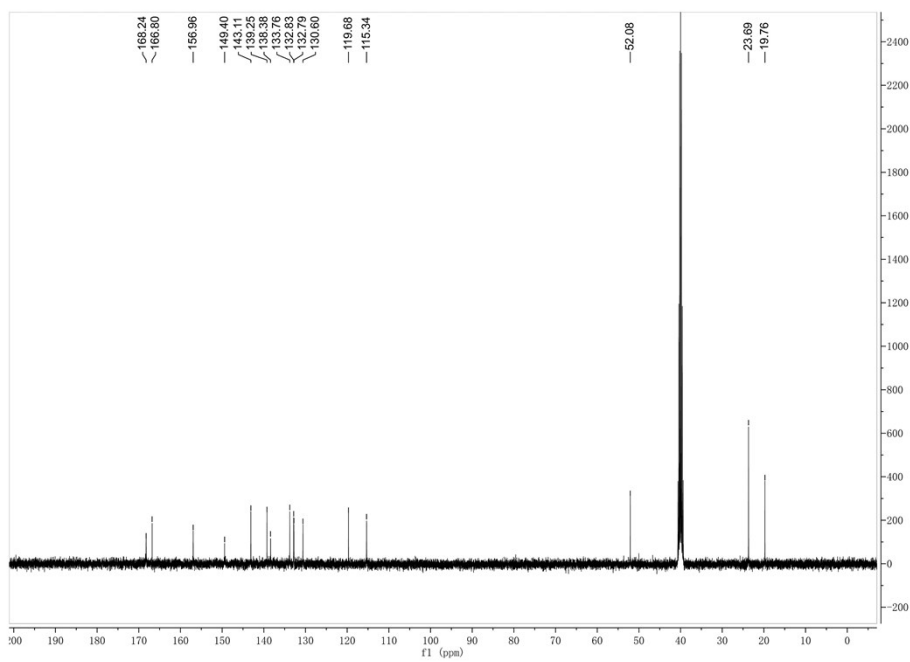
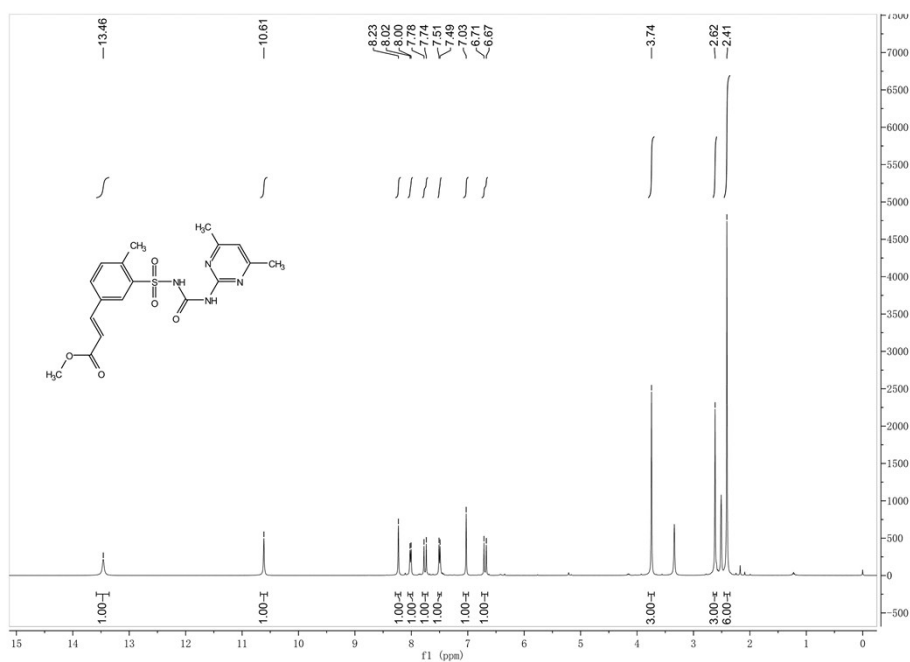
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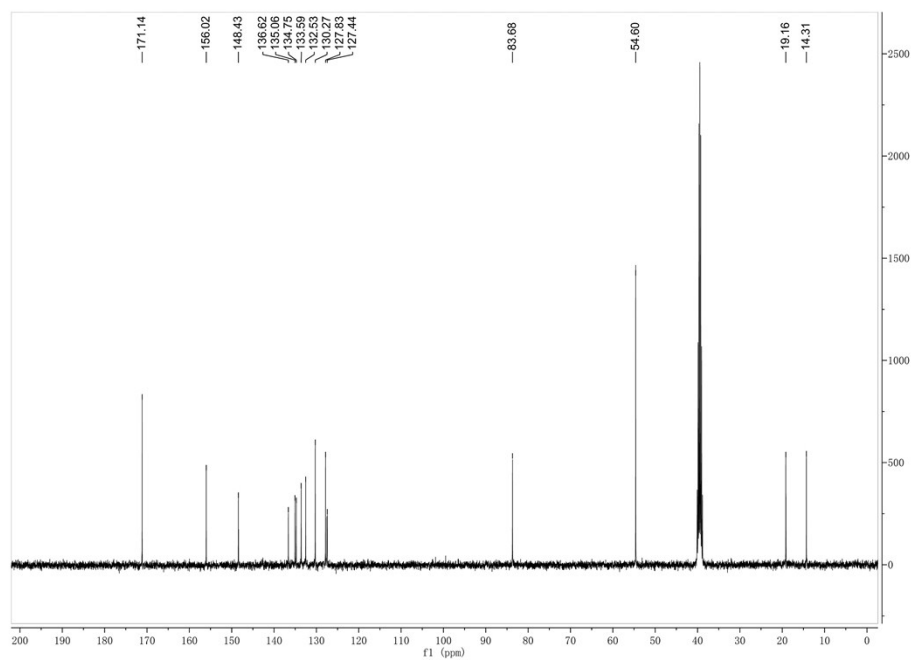
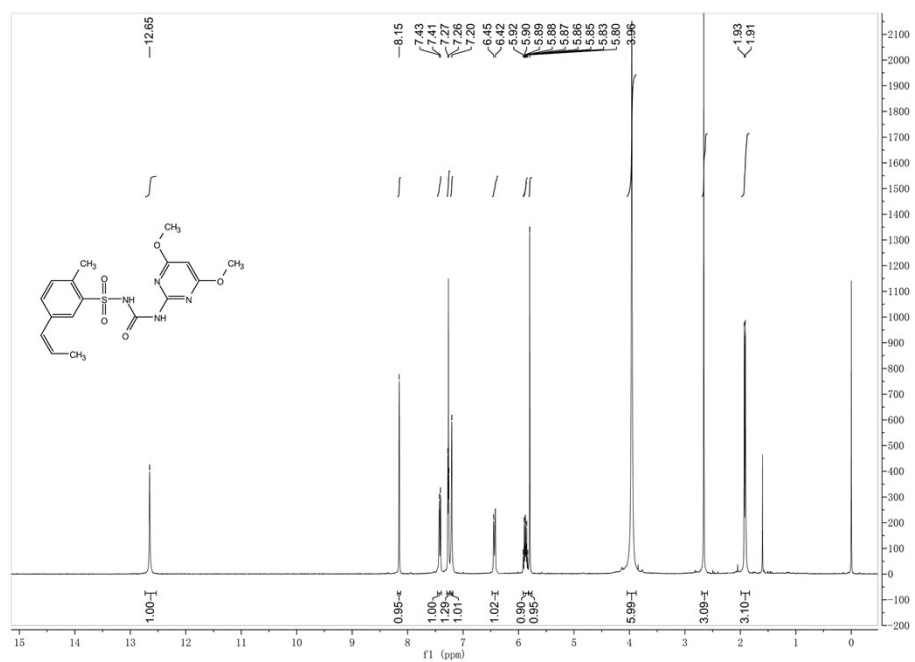
$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of 9d



$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of **9e**

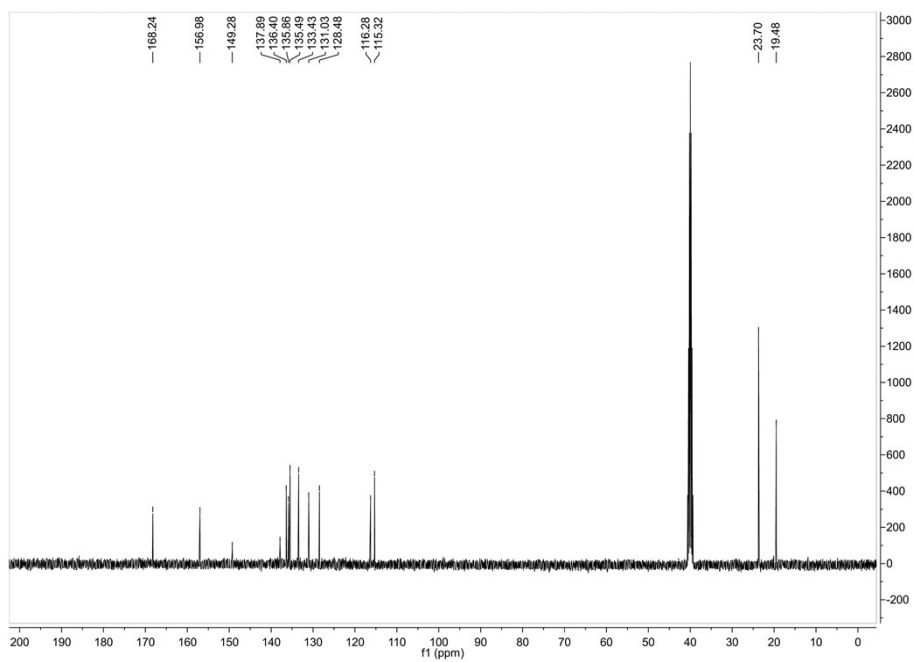
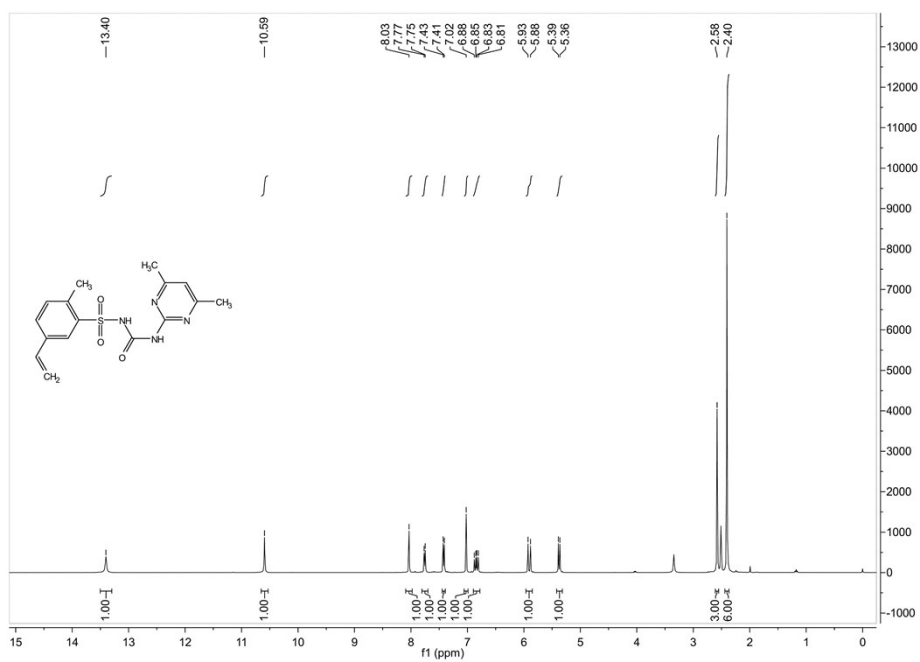


<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>) spectra of 9f

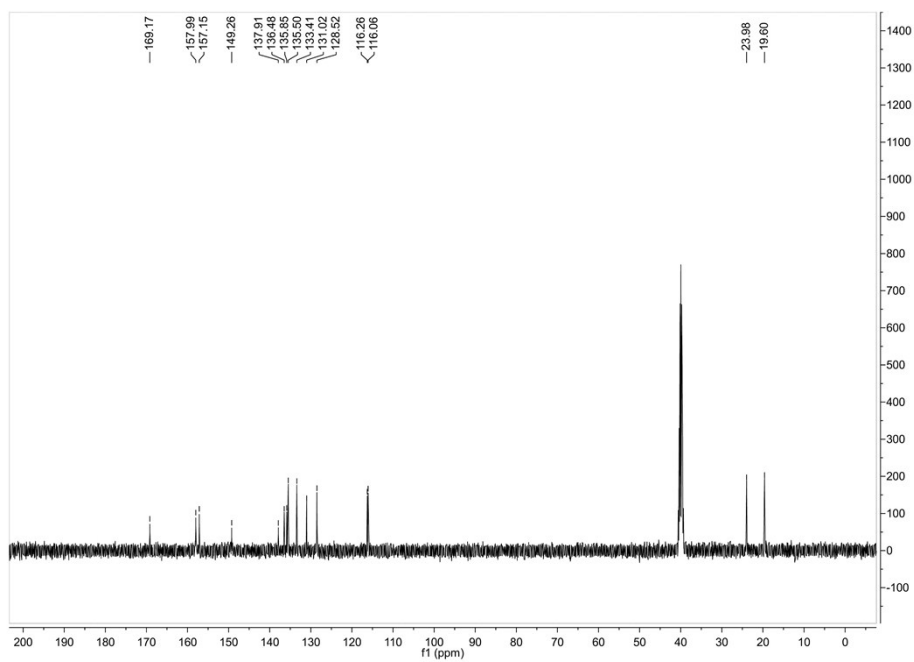
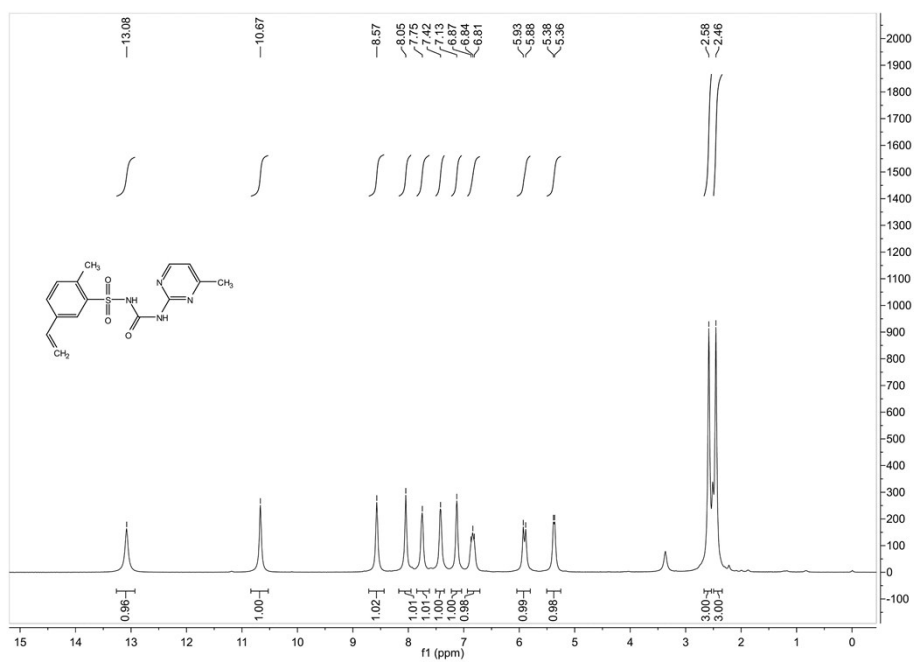




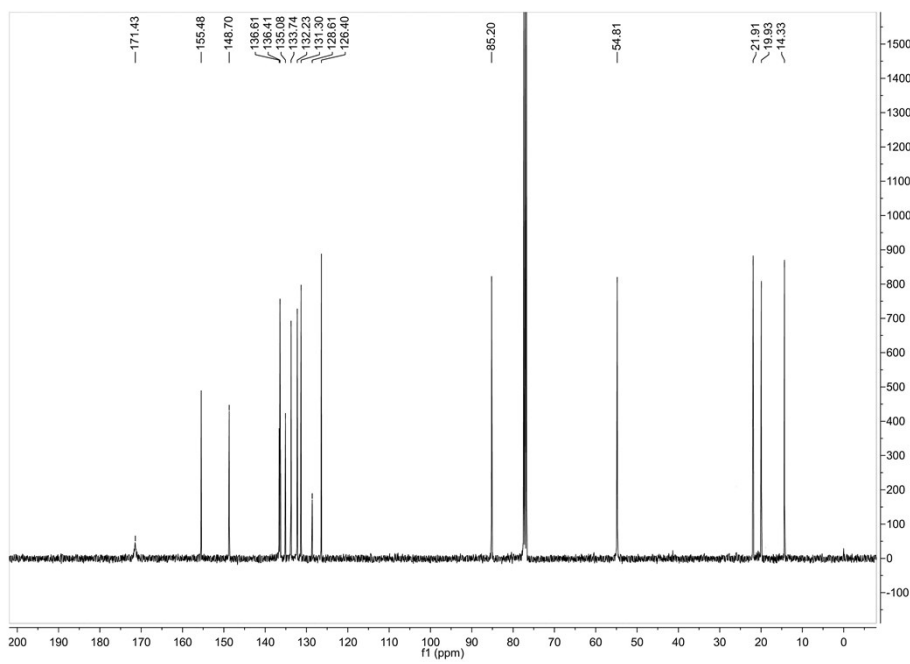
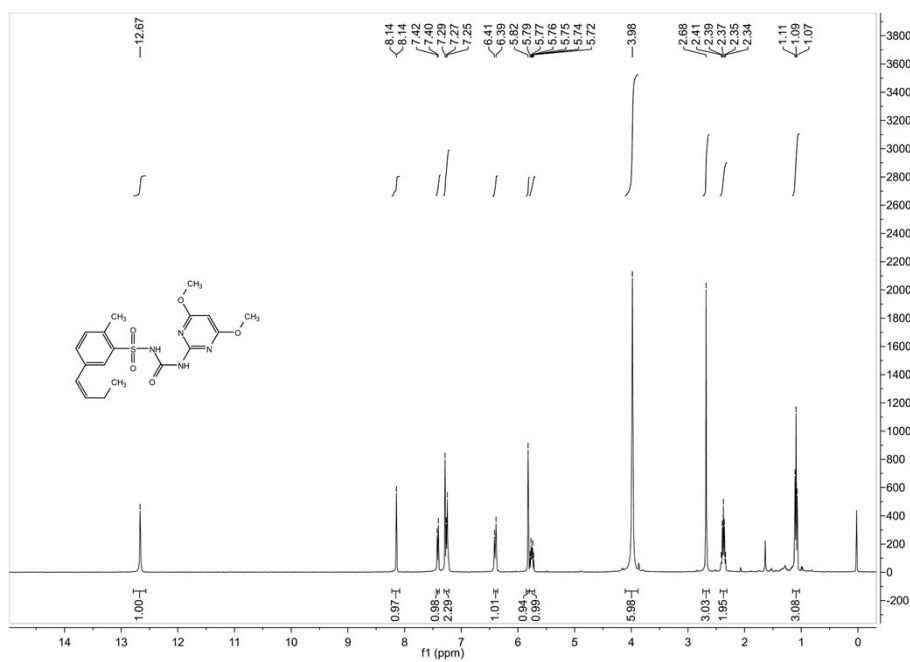
<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) and <sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>) spectra of **9g**



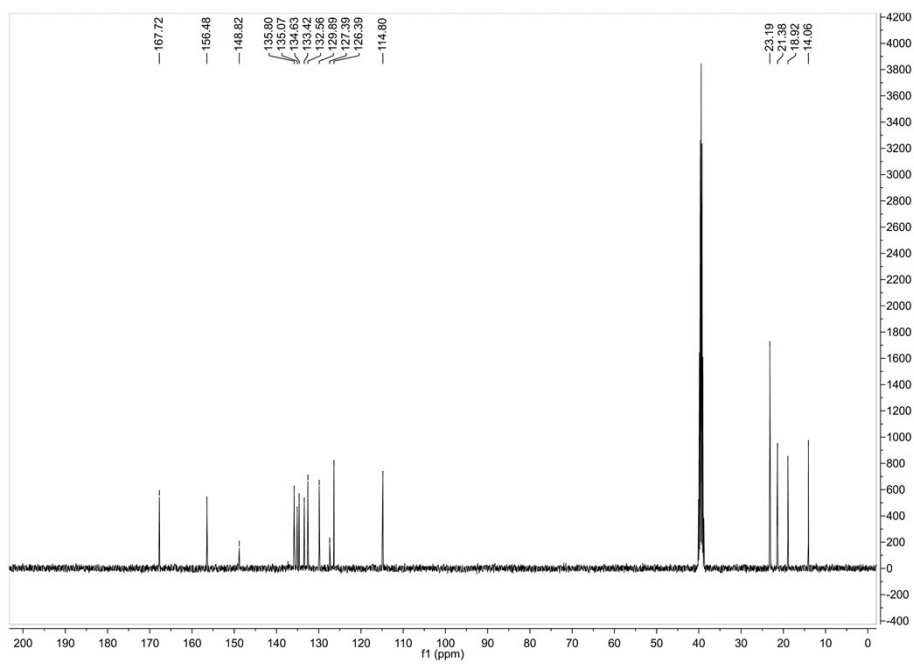
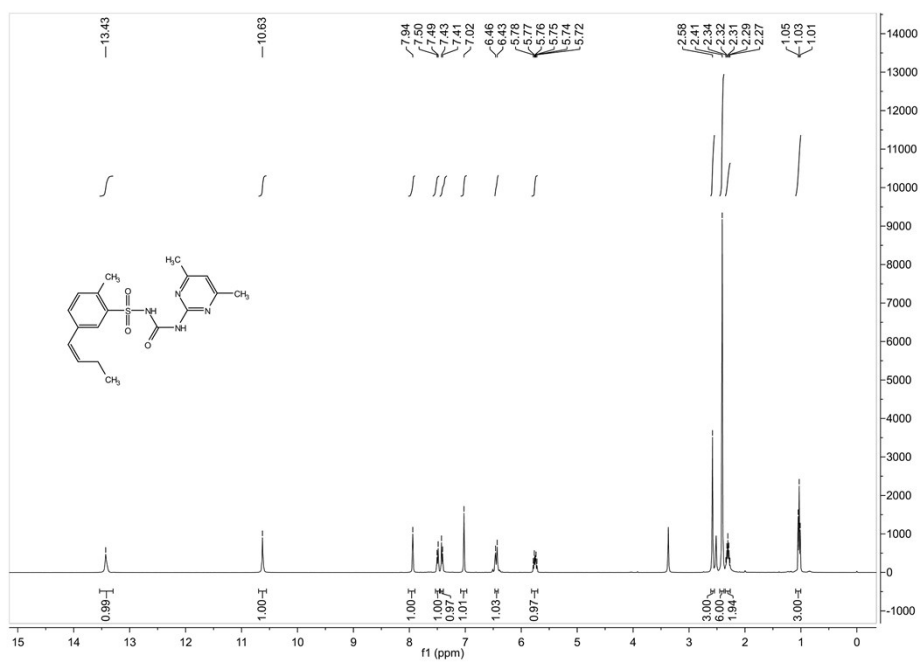
<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) and <sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>) spectra of 9h



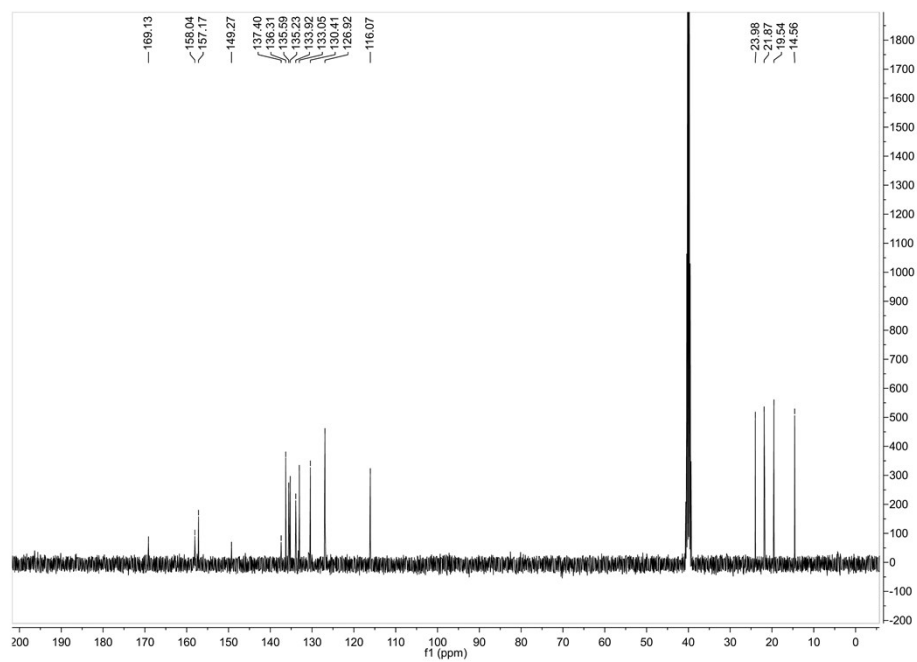
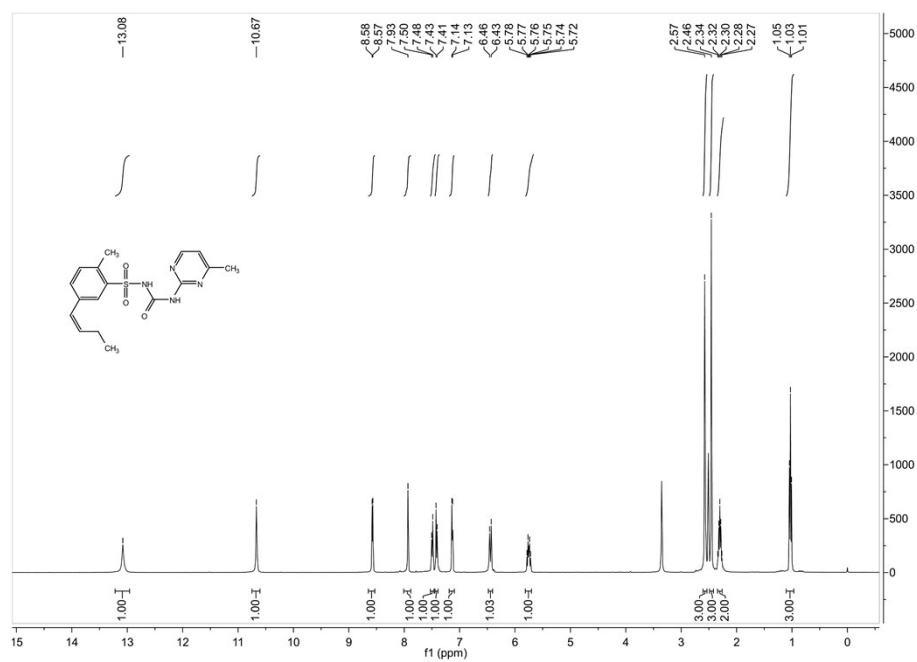
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of **9i**



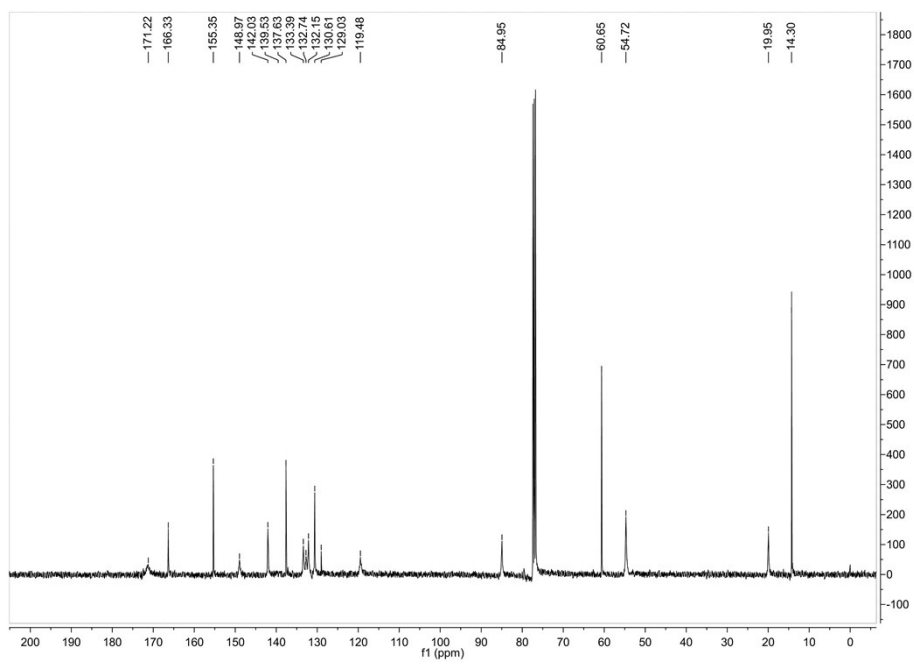
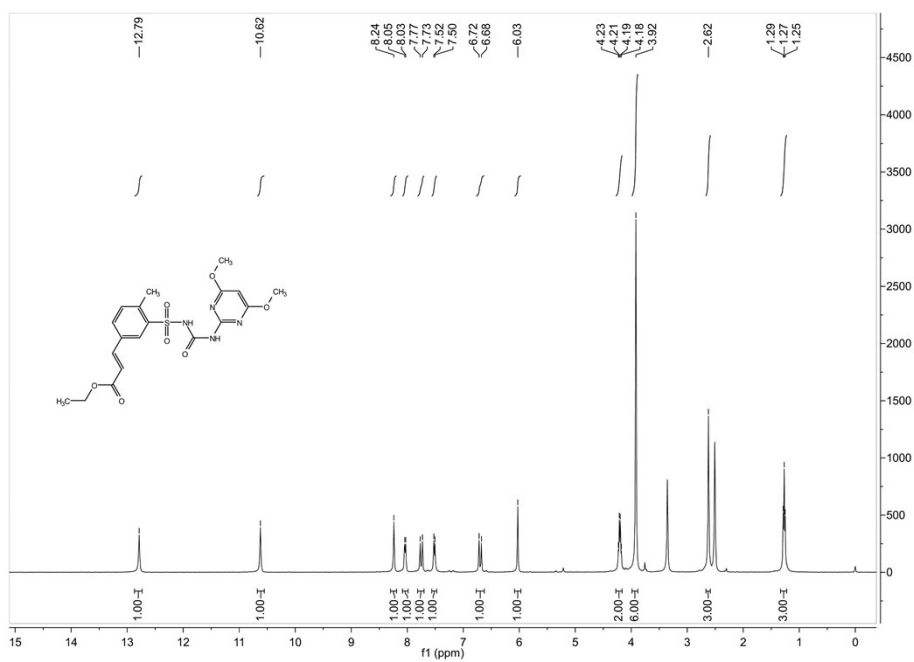
$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of 9j



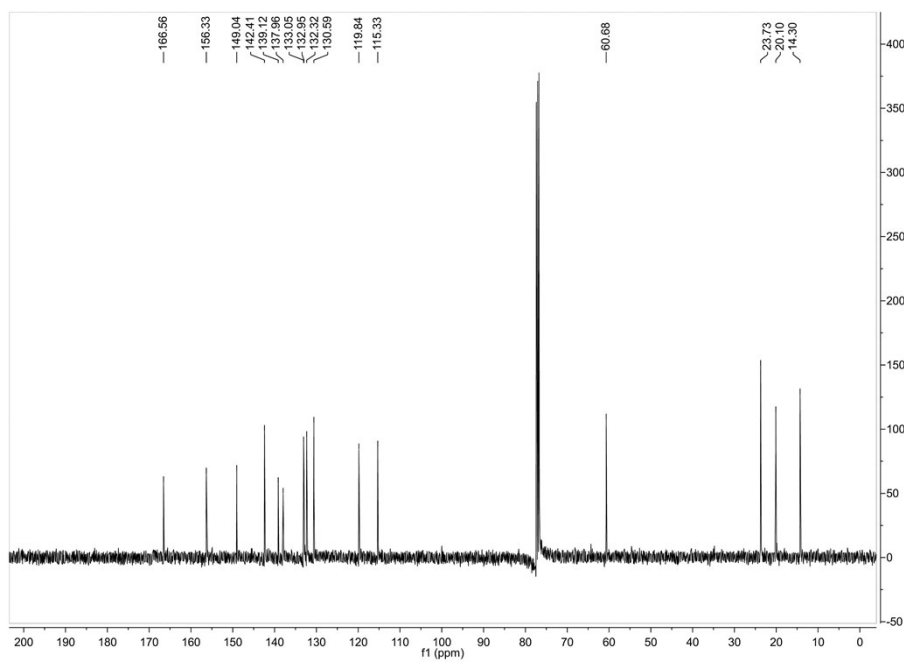
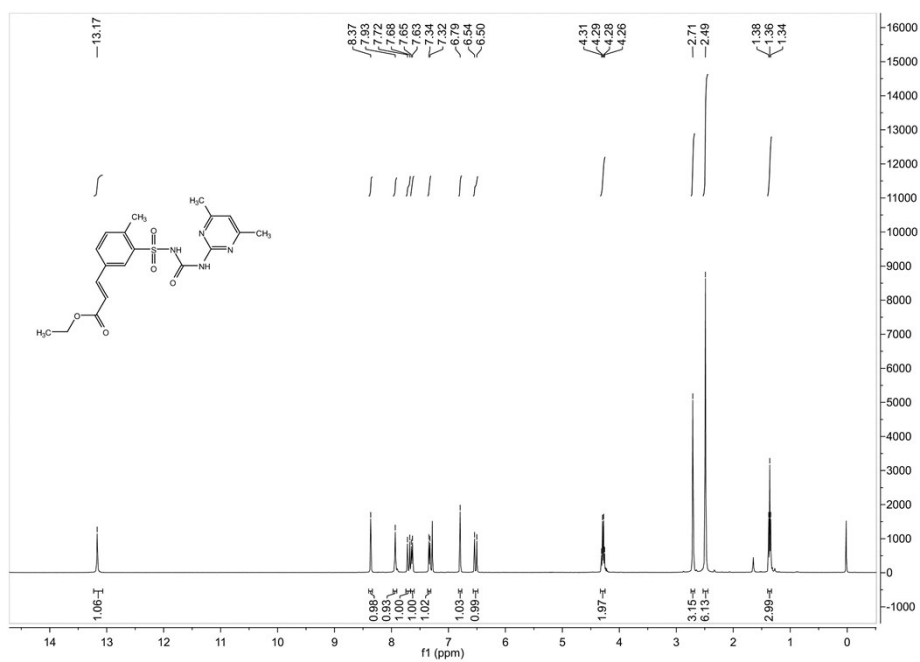
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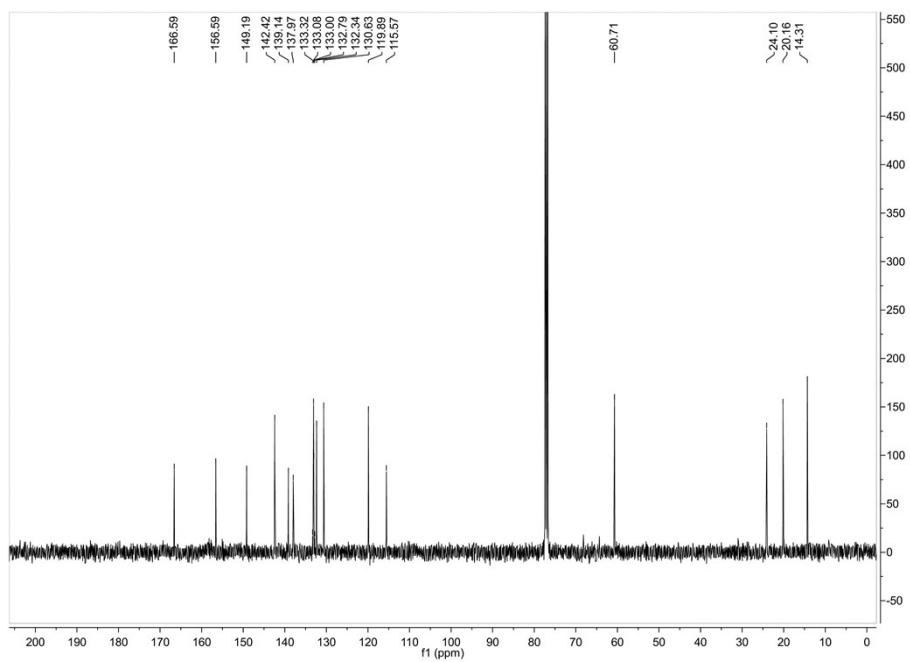
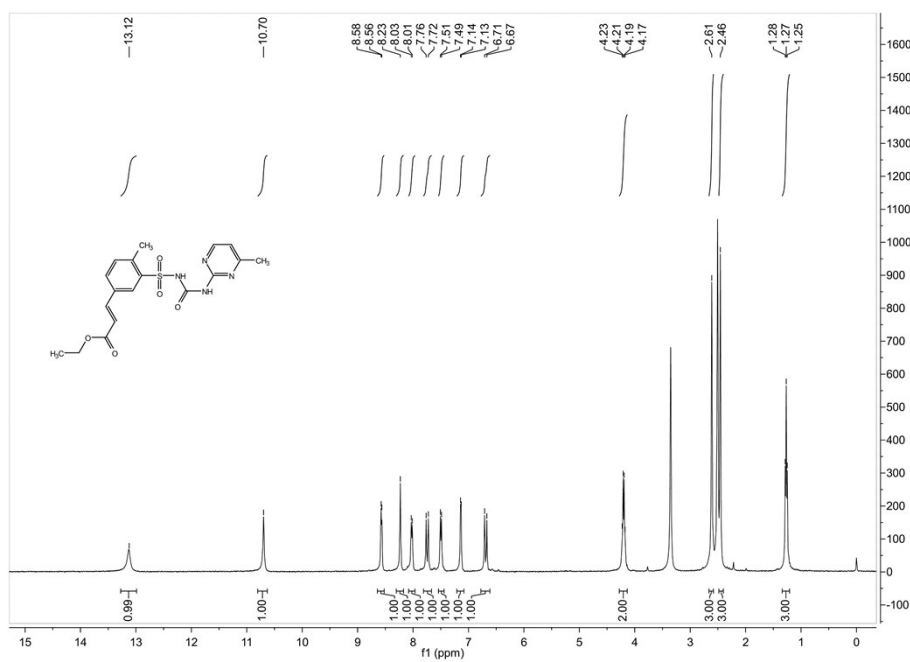
<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) and <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of 9l



$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of 9m

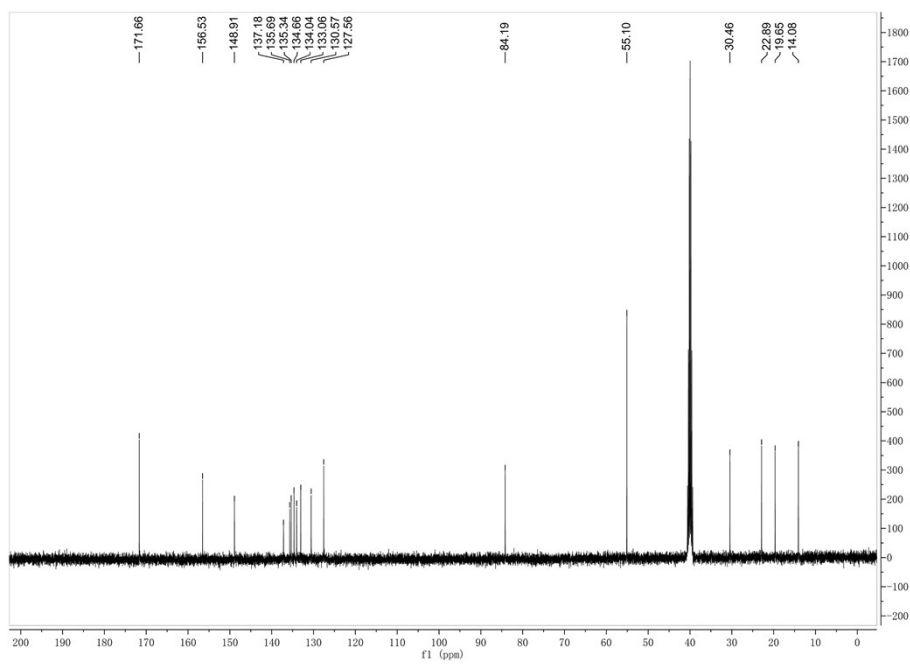
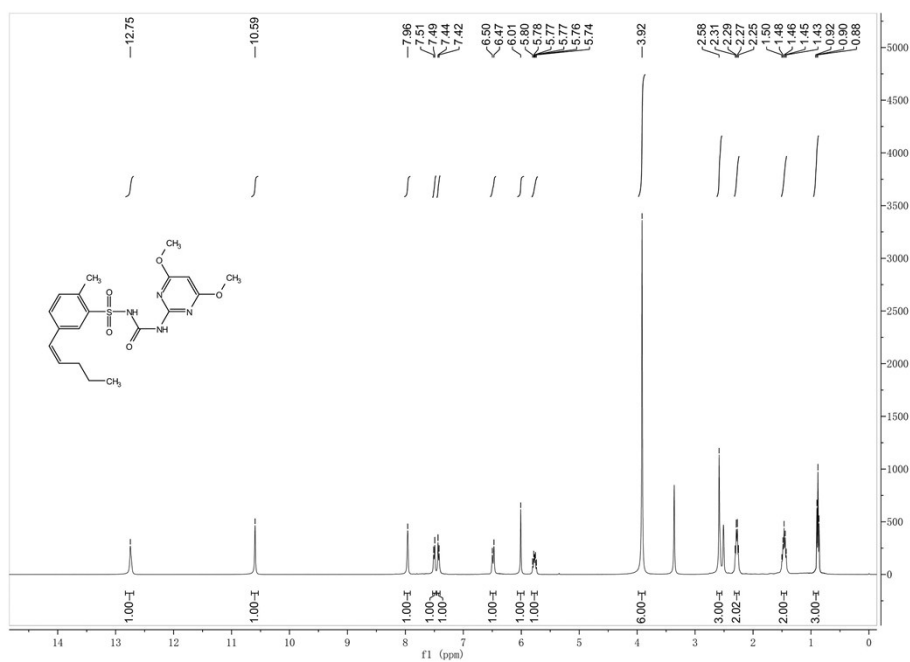


$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of **9n**

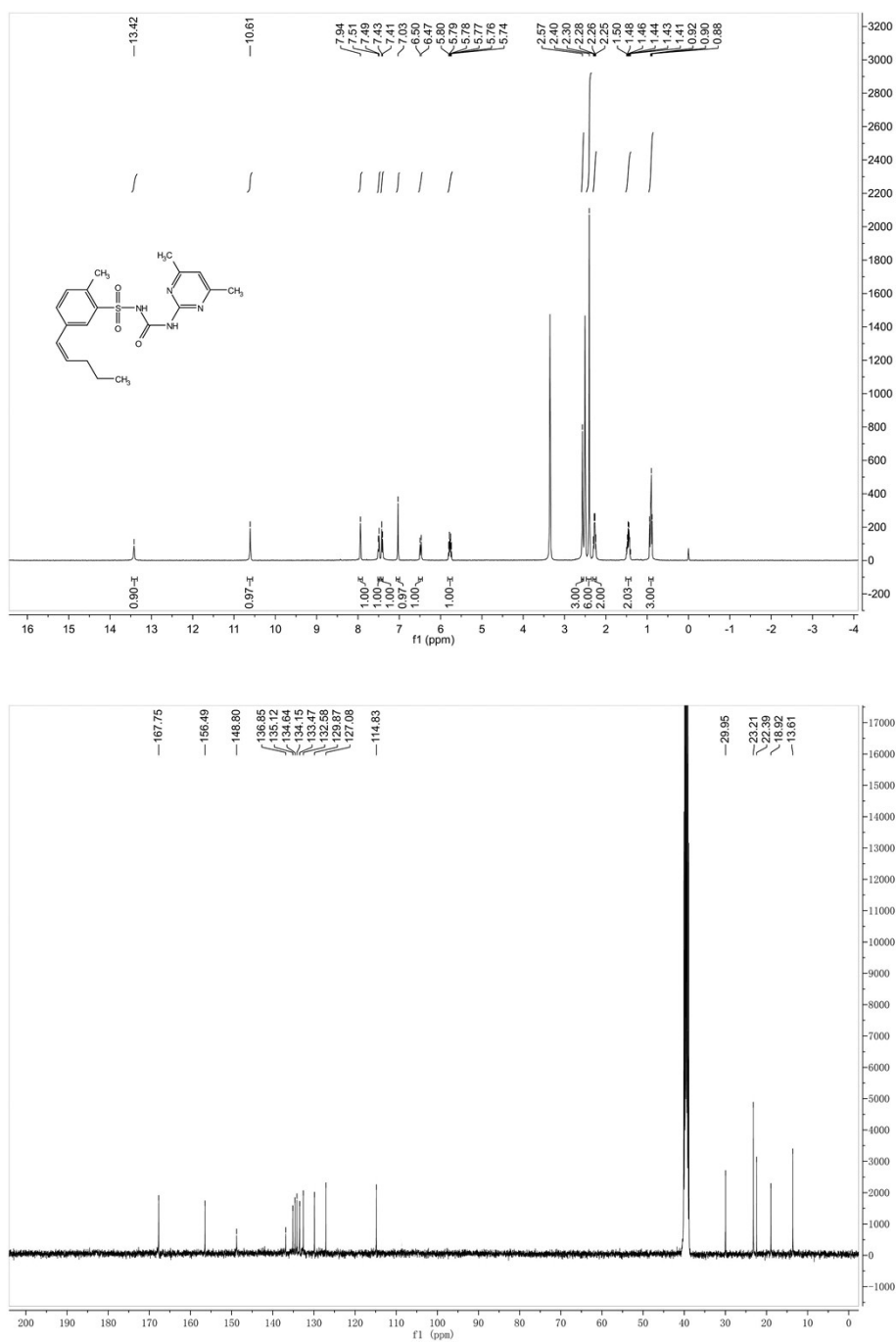




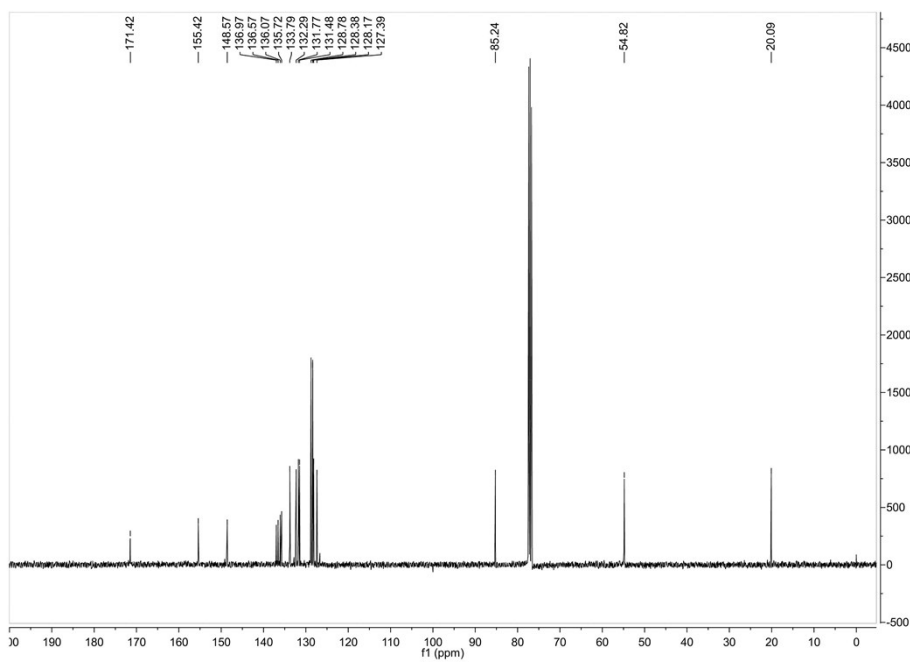
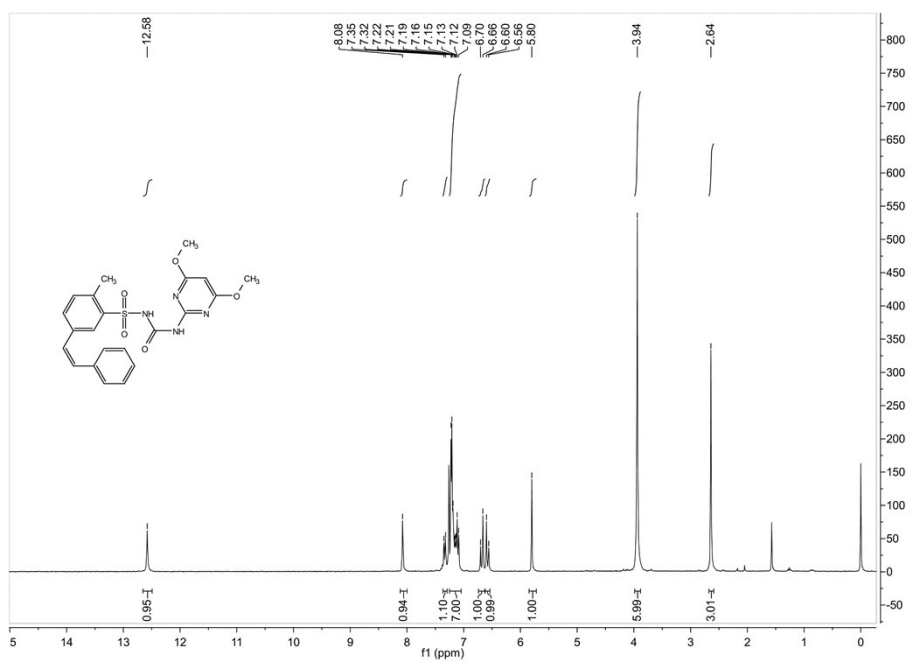
$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of **9o**



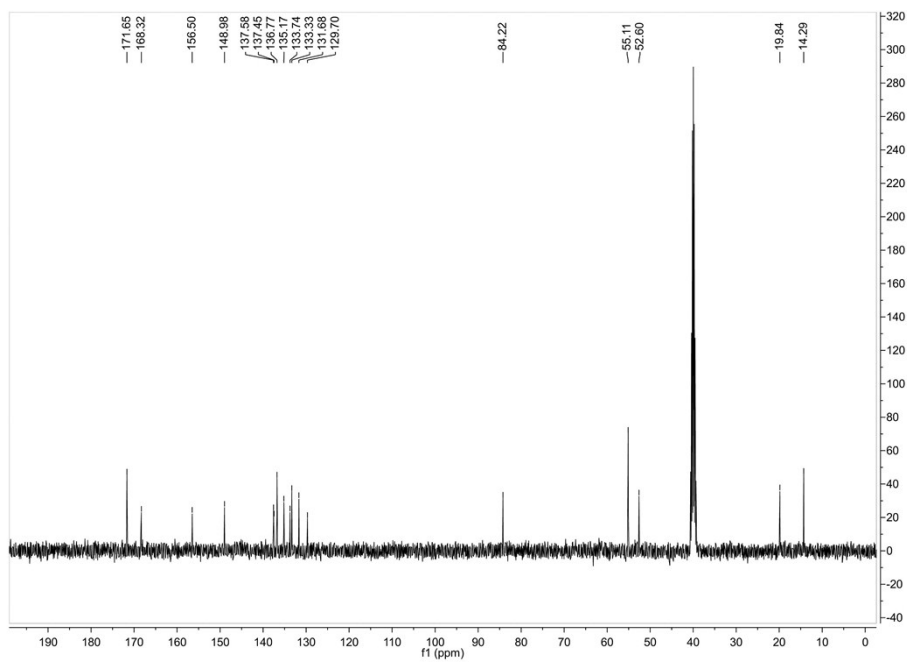
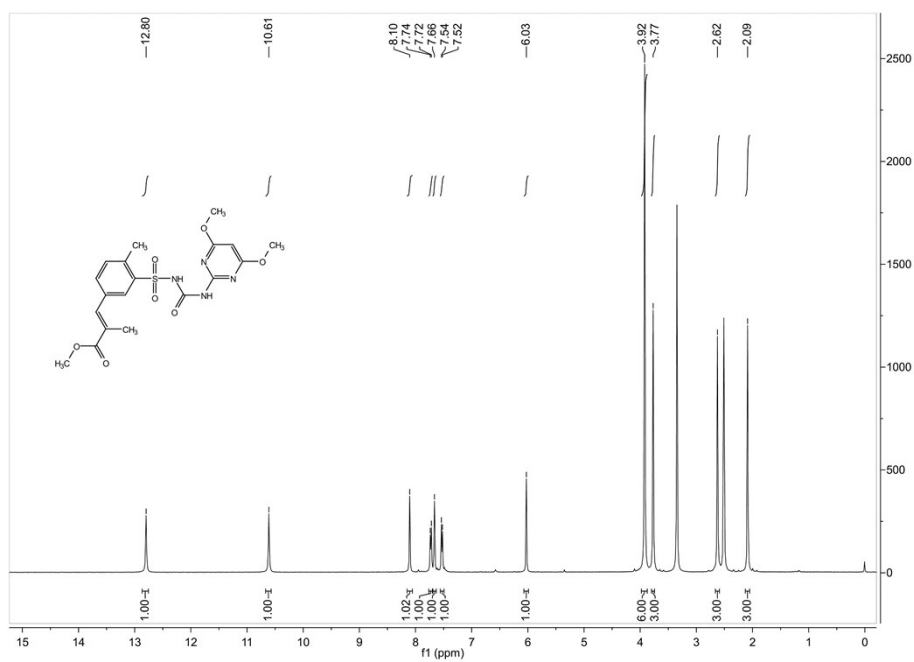
$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of **9p**



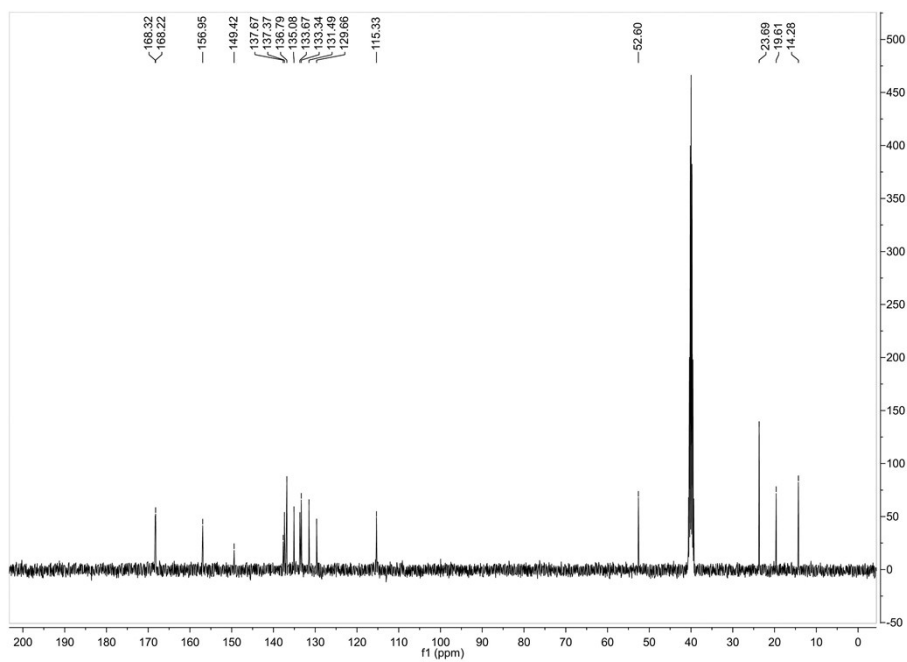
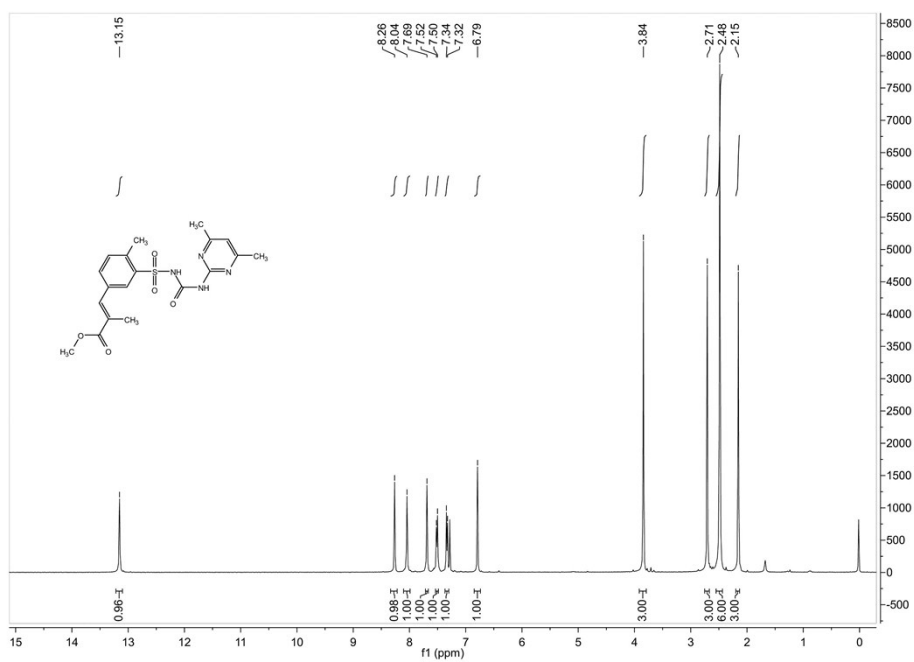
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO}-d_6$ ) spectra of **9q**



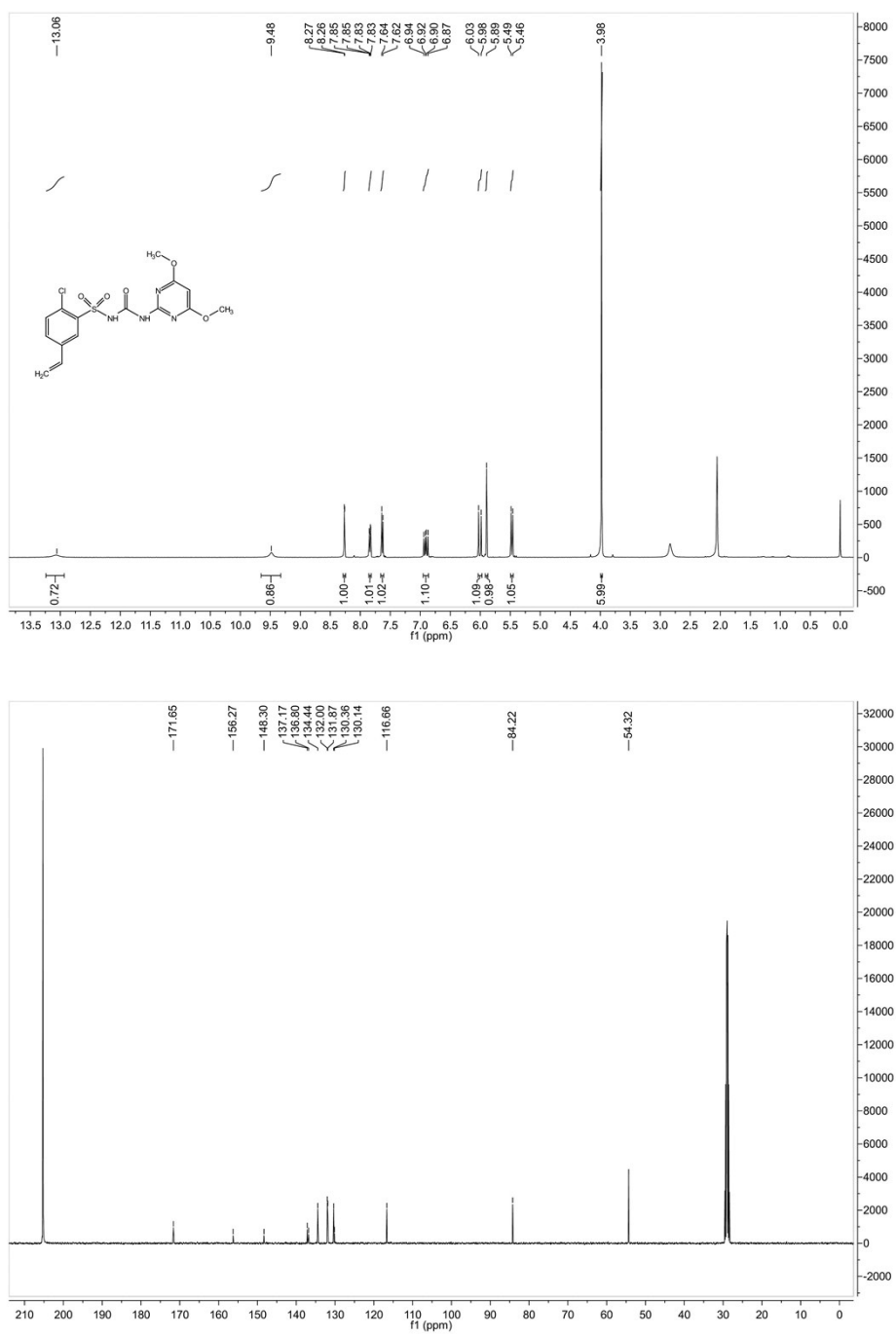
<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) and <sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>) spectra of **9r**



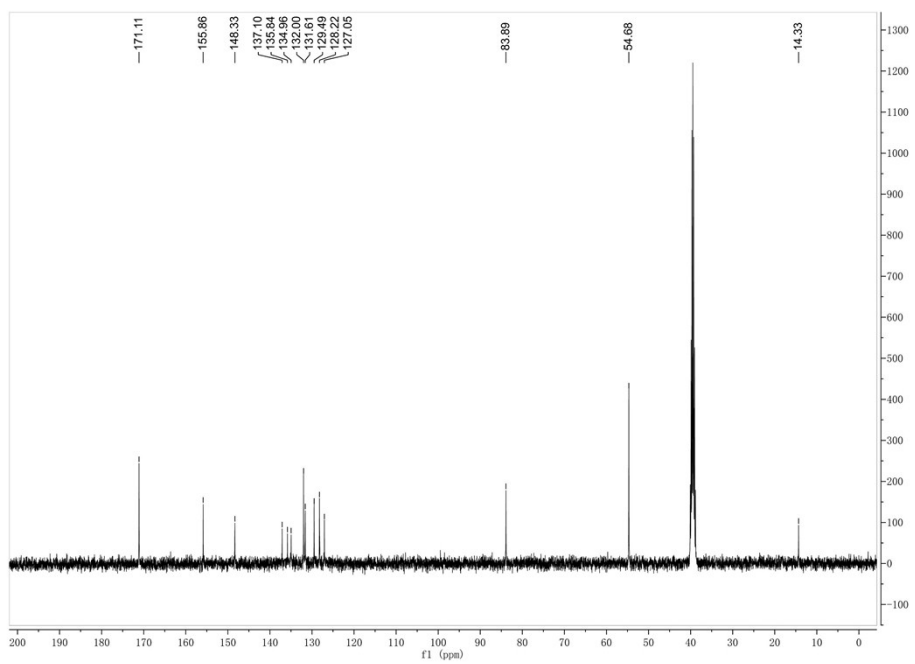
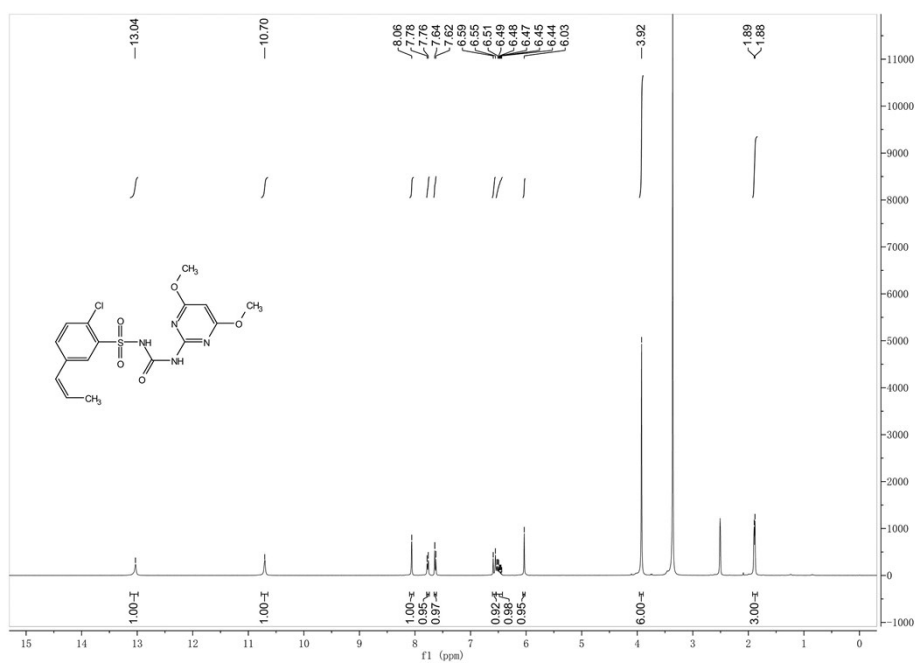
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of **9s**



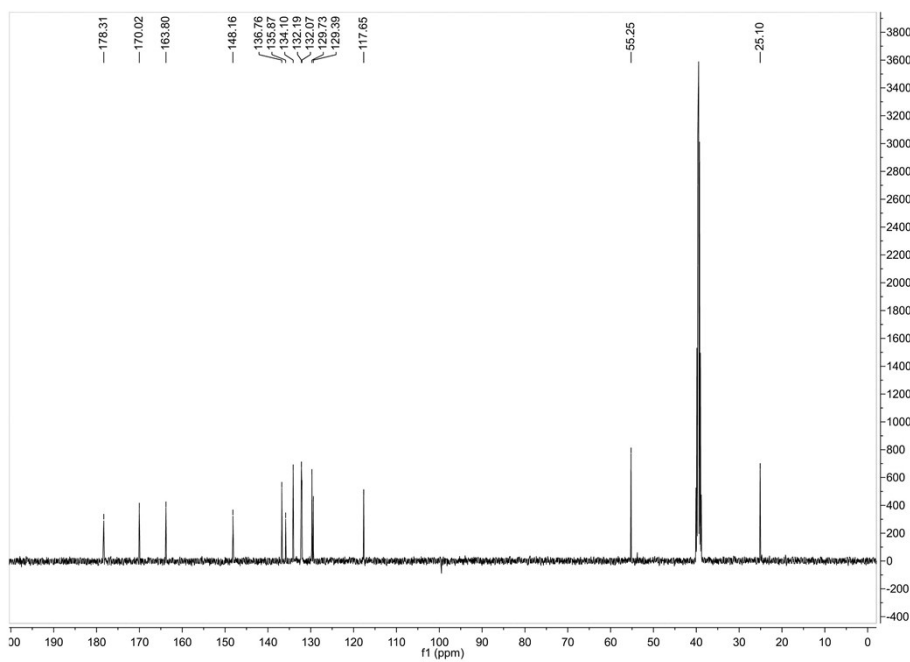
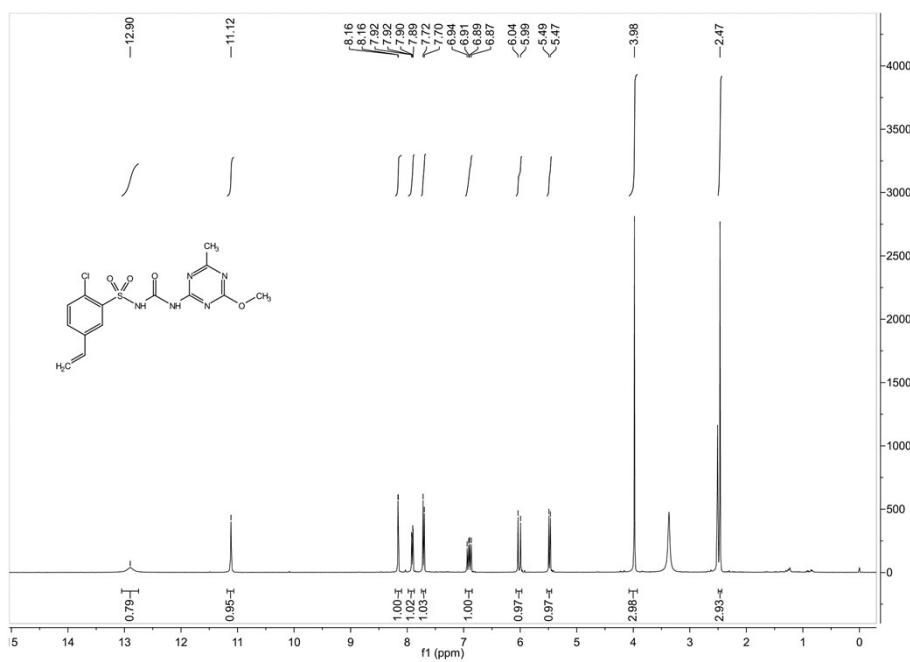
$^1\text{H}$  NMR (400MHz, acetone- $d_6$ ) and  $^{13}\text{C}$  NMR (100MHz, acetone- $d_6$ ) spectra of **9t**



<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) and <sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>) spectra of **9u**

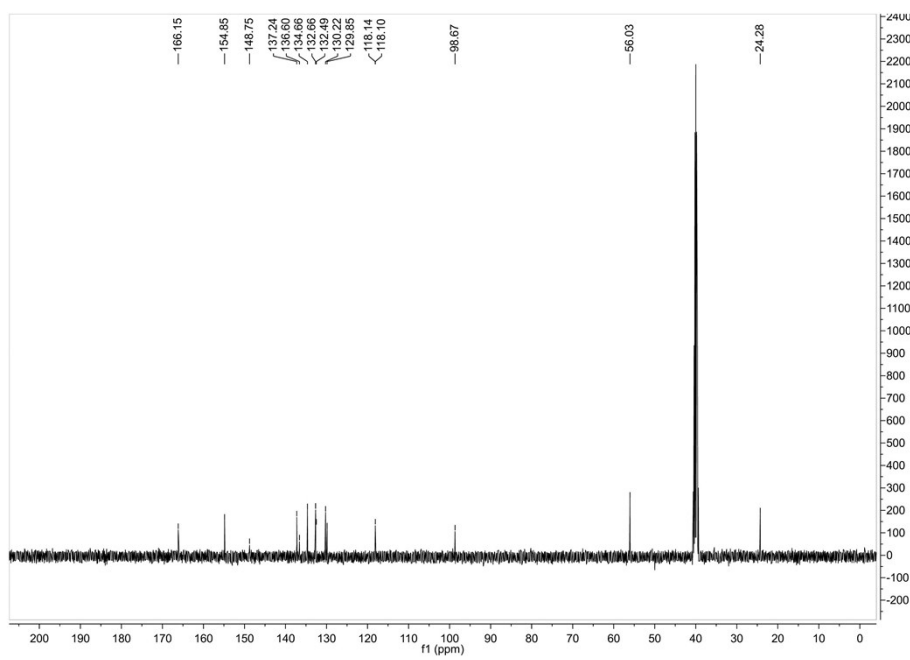
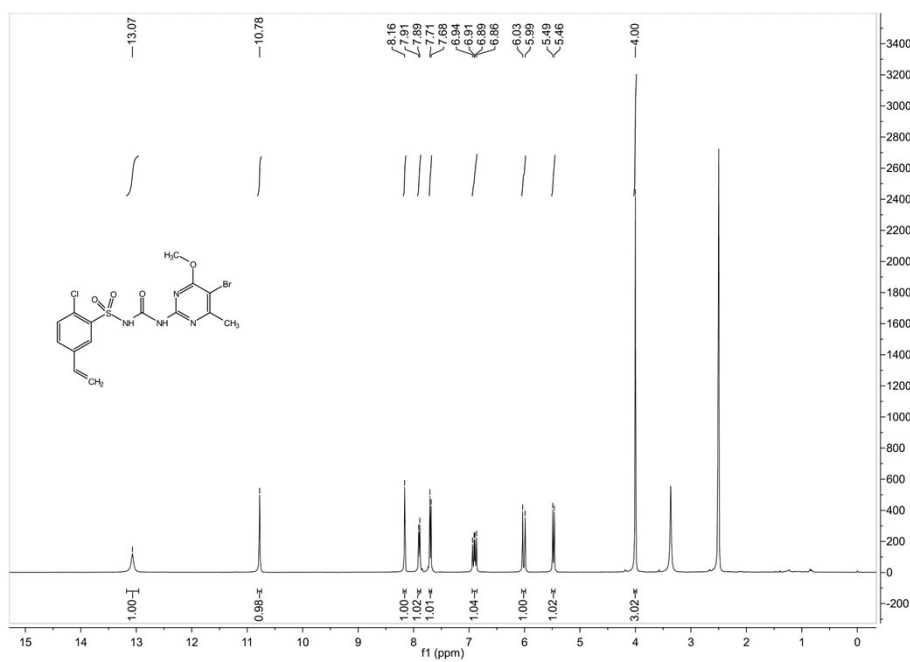


$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of **9v**

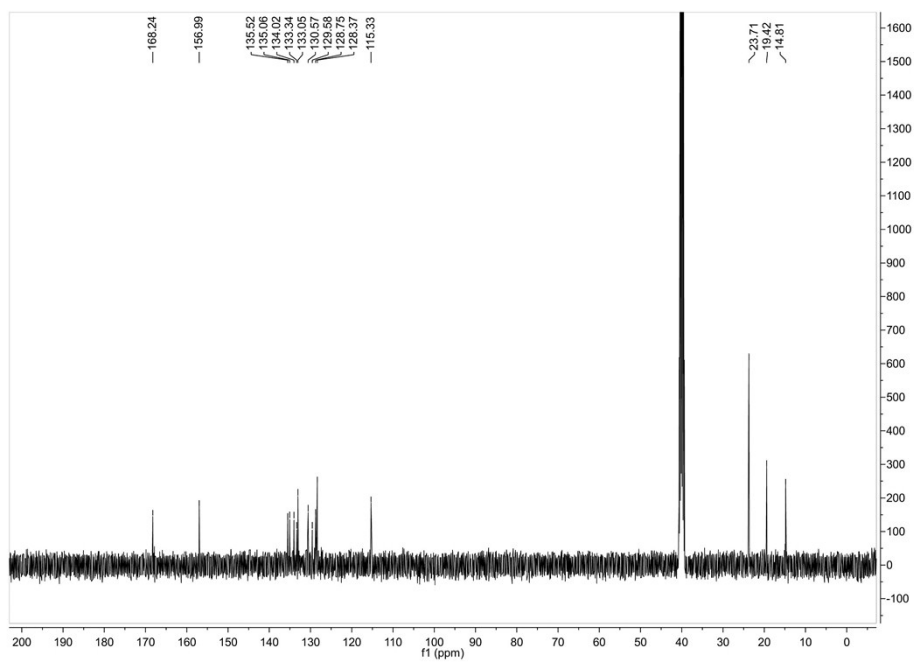
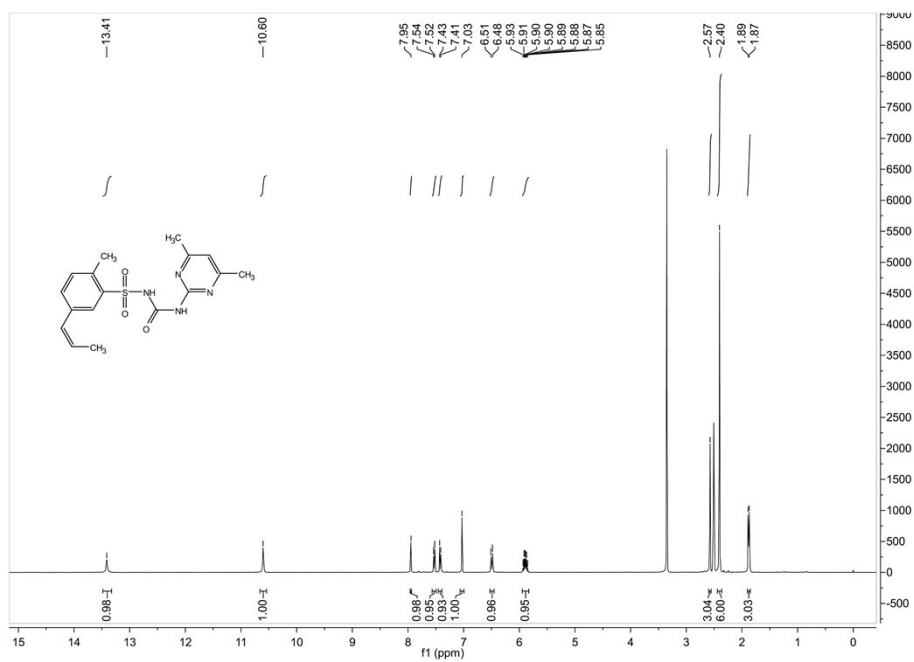




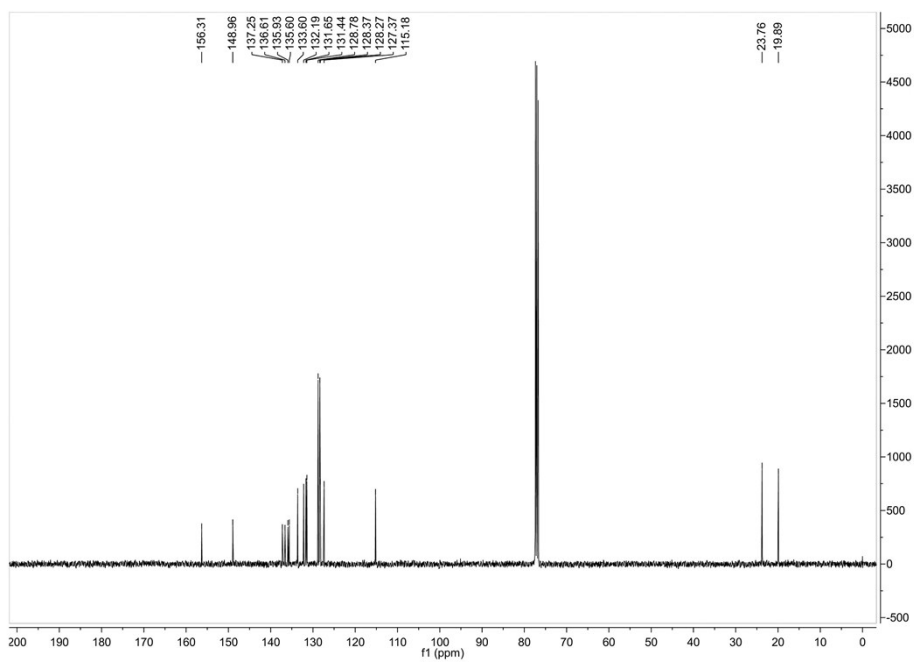
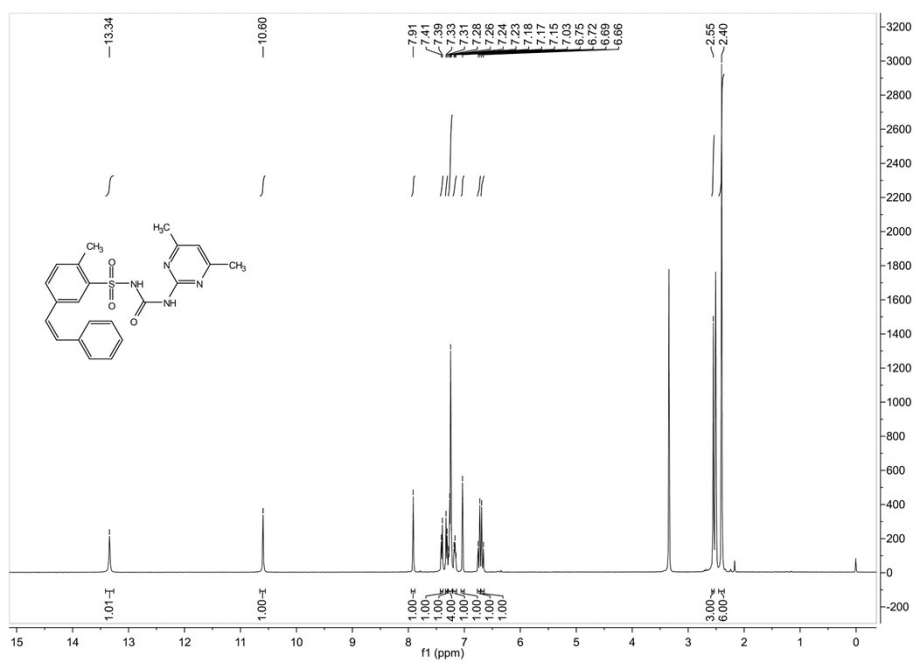
$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO-d}_6$ ) spectra of **9w**



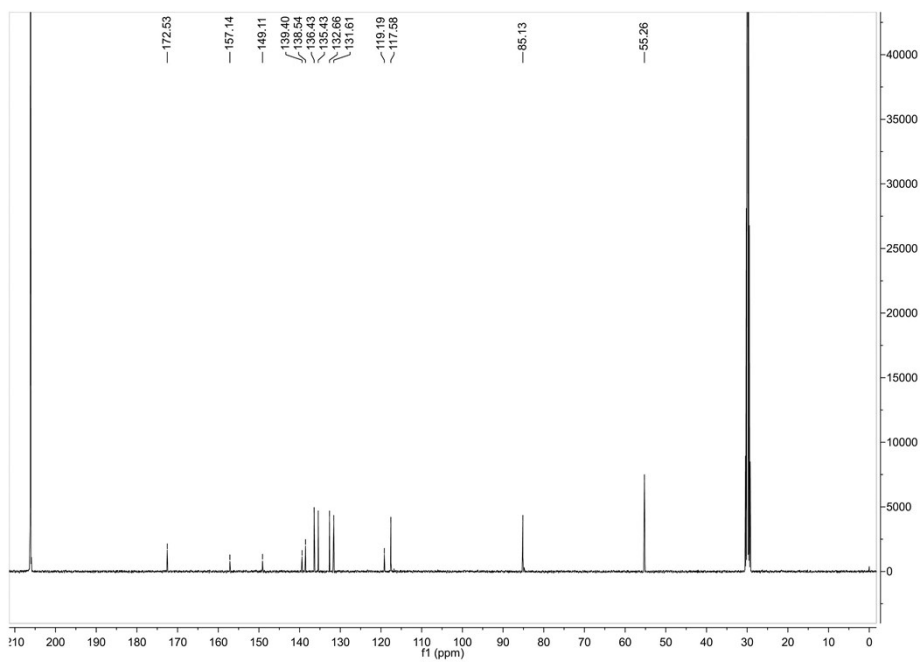
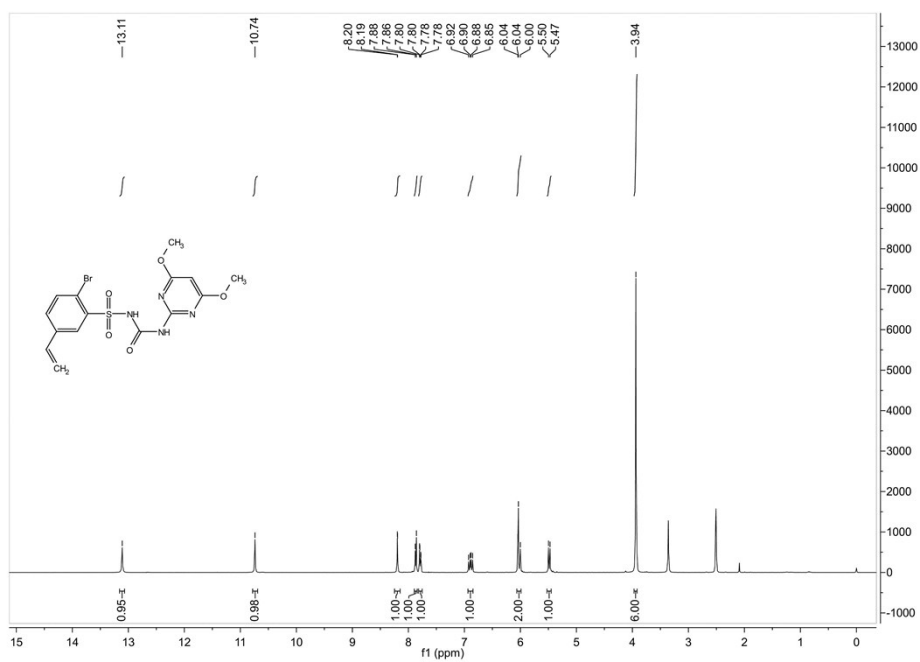
<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) and <sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>) spectra of 9x



$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ) spectra of **9y**



$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) and  $^{13}\text{C}$  NMR (100MHz,  $\text{acetone-d}_6$ ) spectra of **9z**



$^1\text{H}$  NMR (400MHz, acetone- $d_6$ ) and  $^{13}\text{C}$  NMR (100MHz, DMSO- $d_6$ ) spectra of **9aa**

