

Supplementary Materials

# Synthesis of Novel Amino Acid-Fipronil Conjugates and Study on their Phloem Loading Mechanism

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Figures S1-S50. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all compounds

Table S1. The fatality rates of **4a-1** and fipronil against *Plutella xylostella*

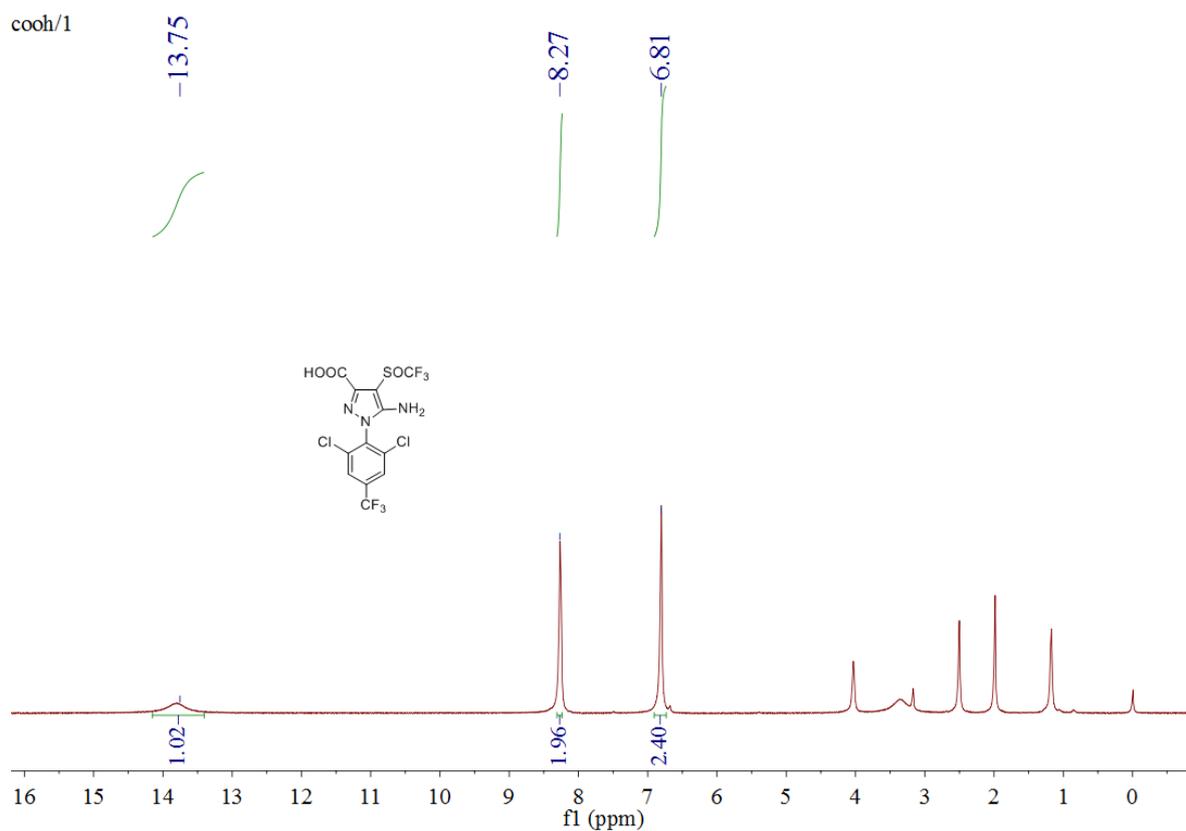


Figure S1  $^1\text{H}$  NMR spectra of 2 in  $\text{DMSO-}d_6$

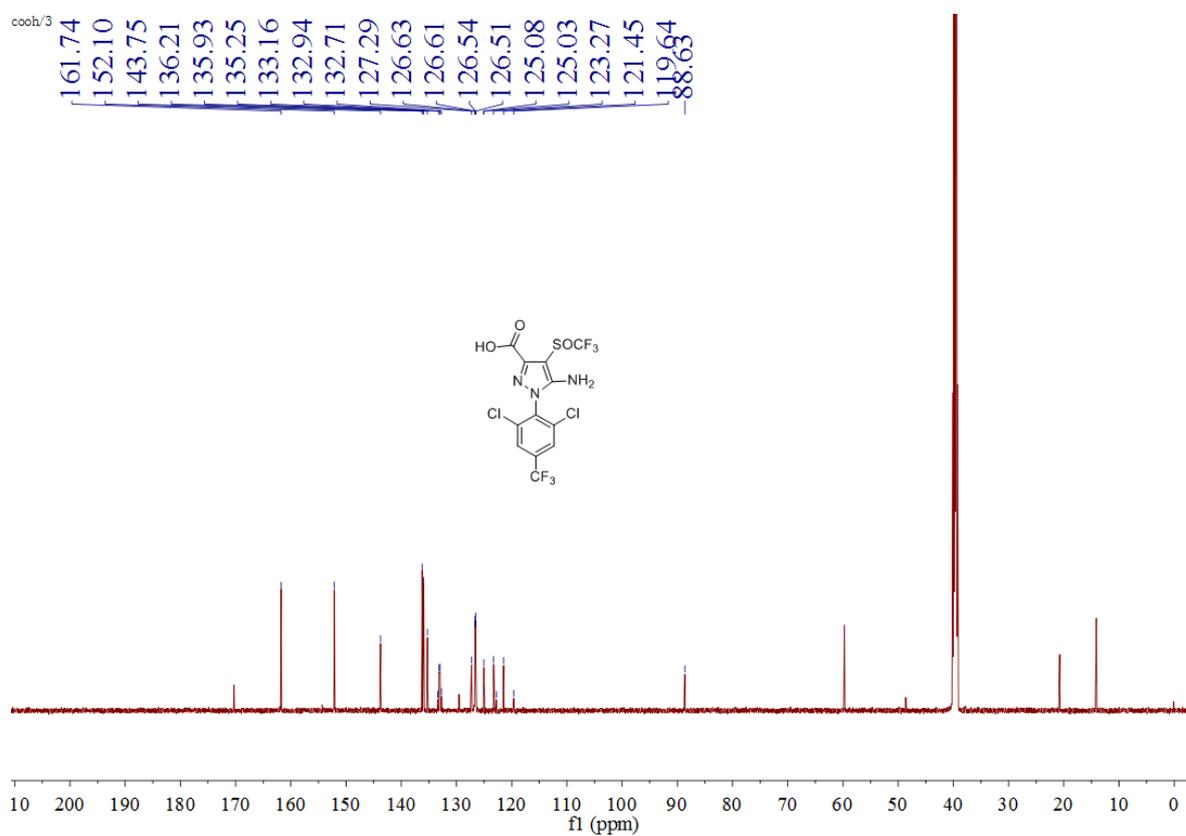
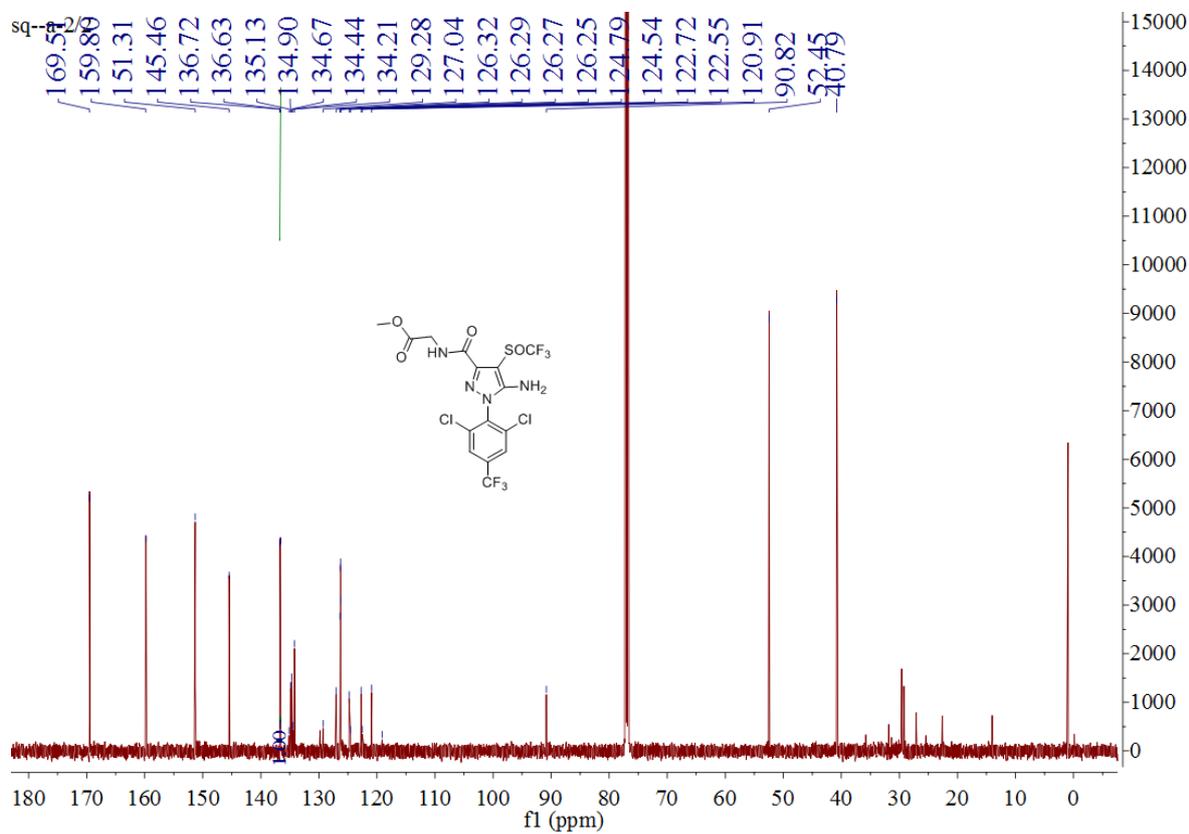
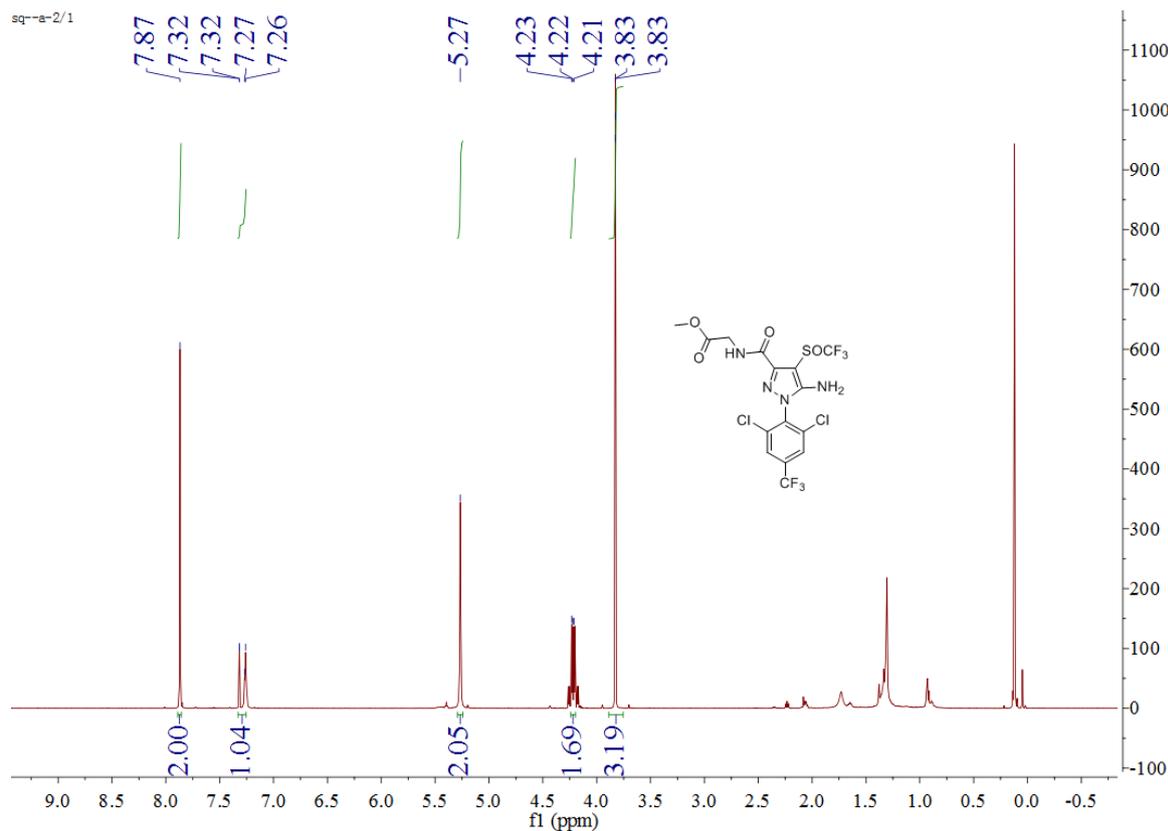
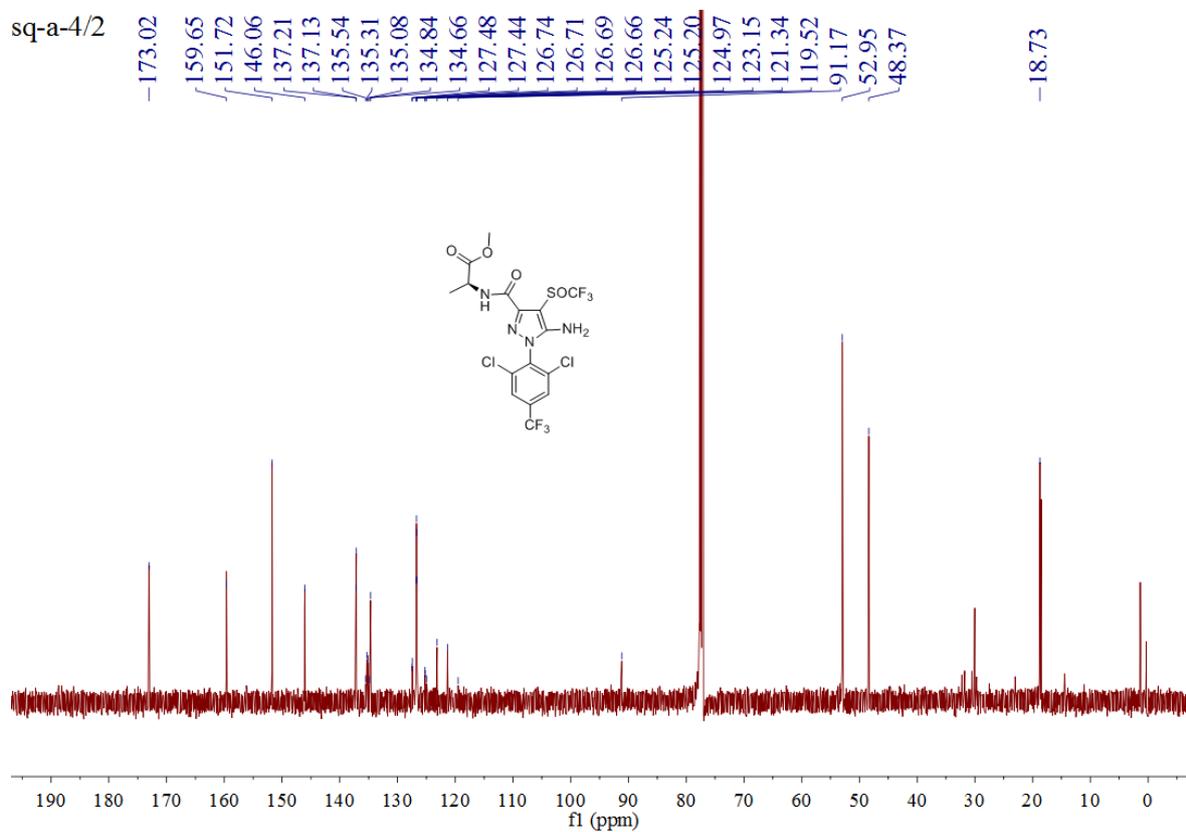
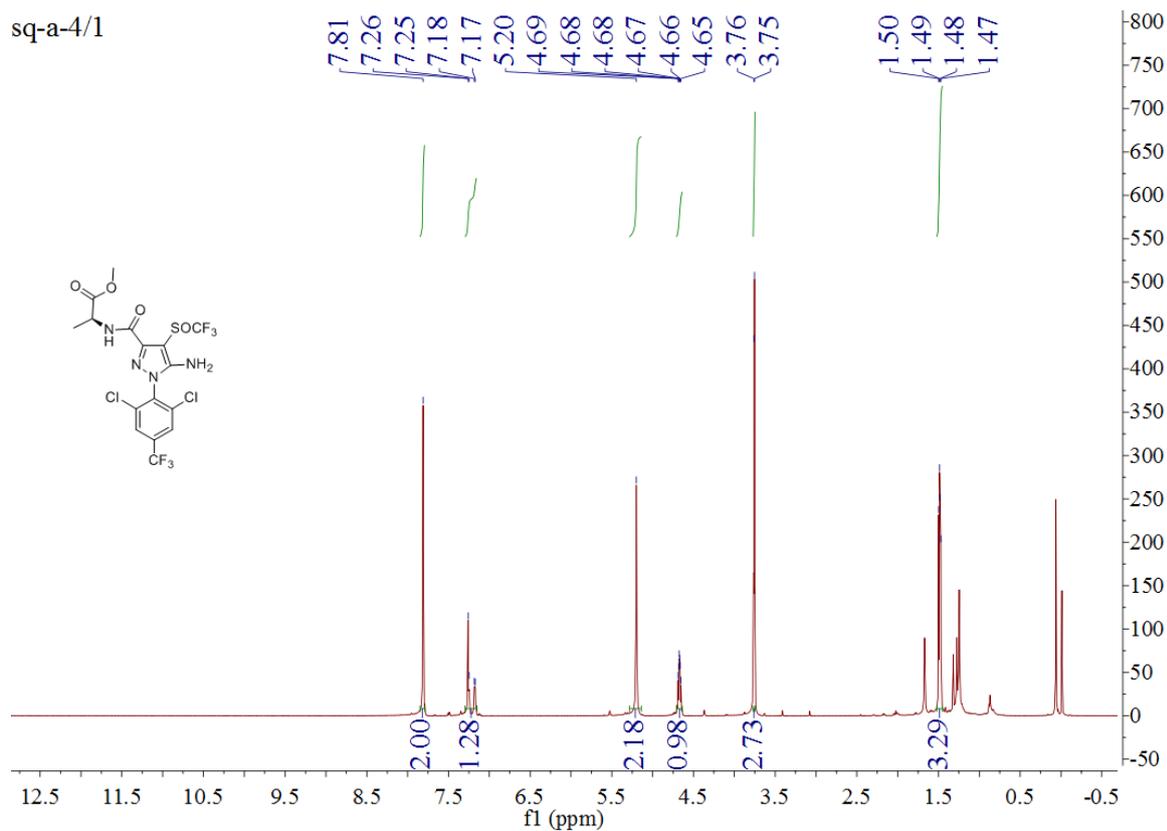
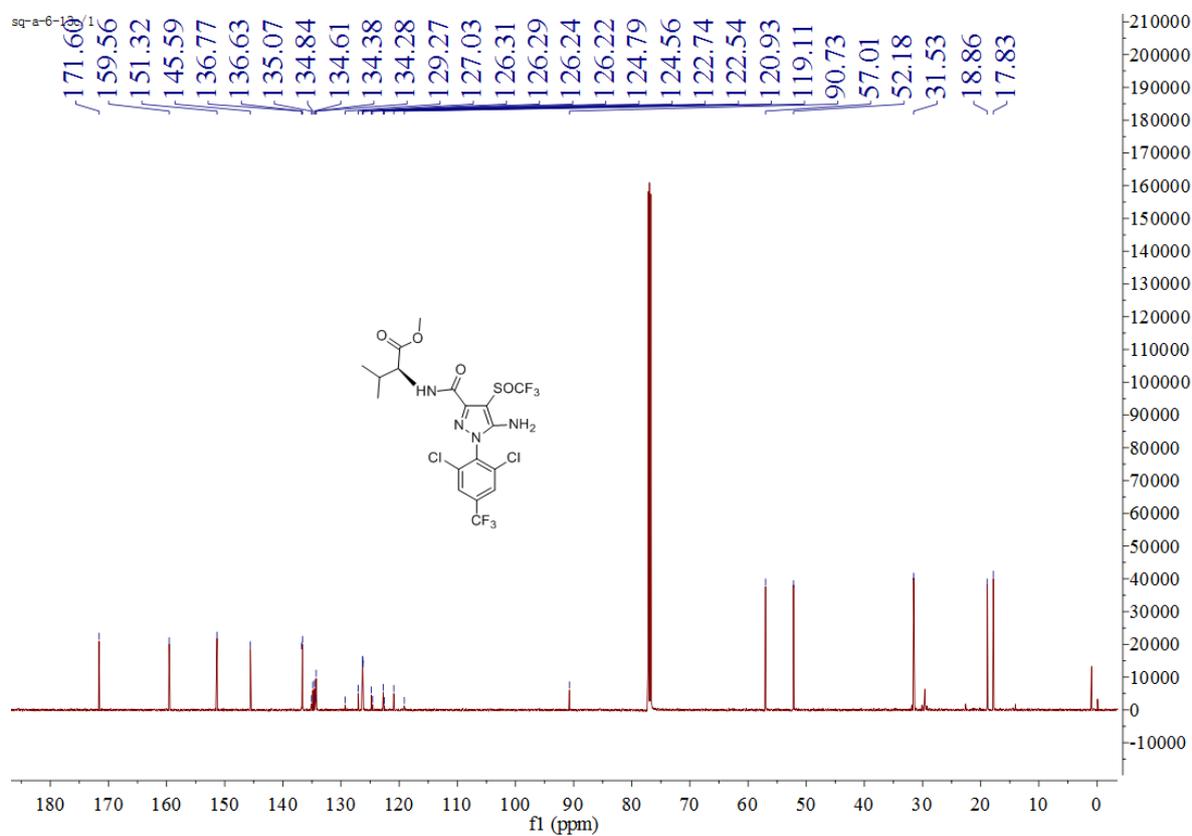
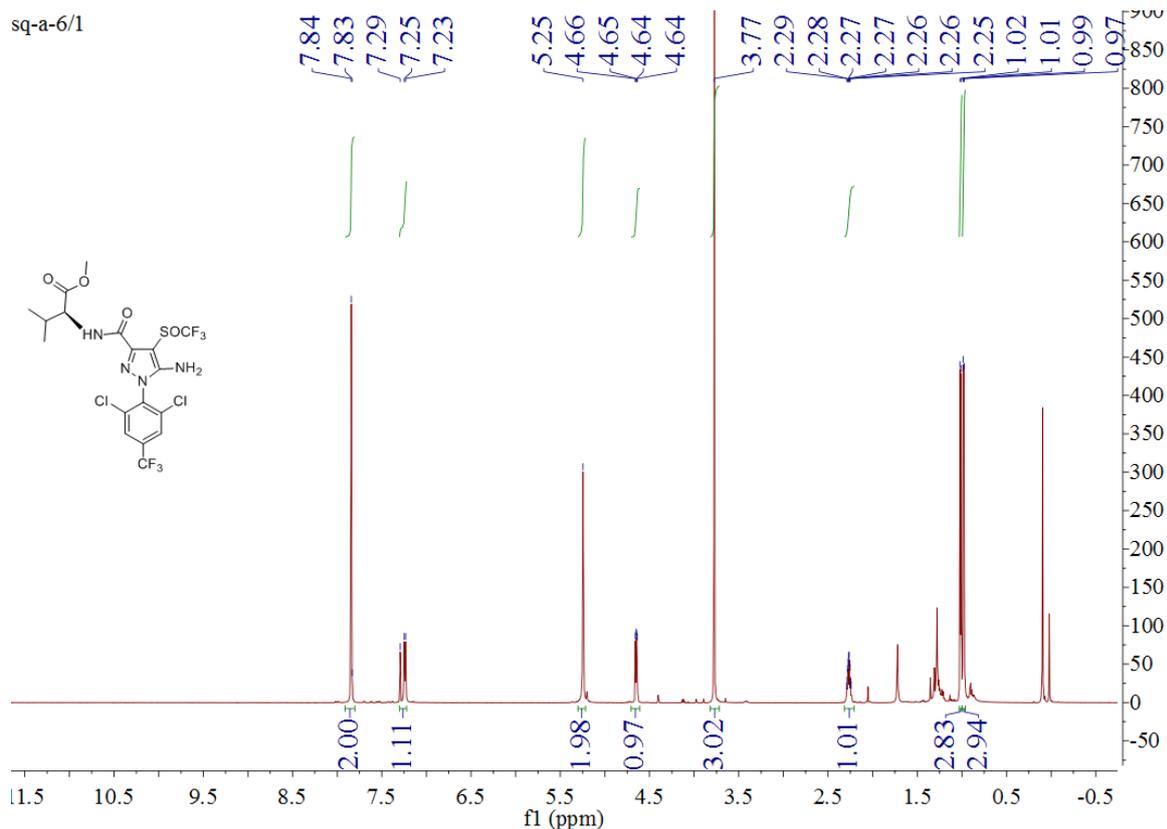
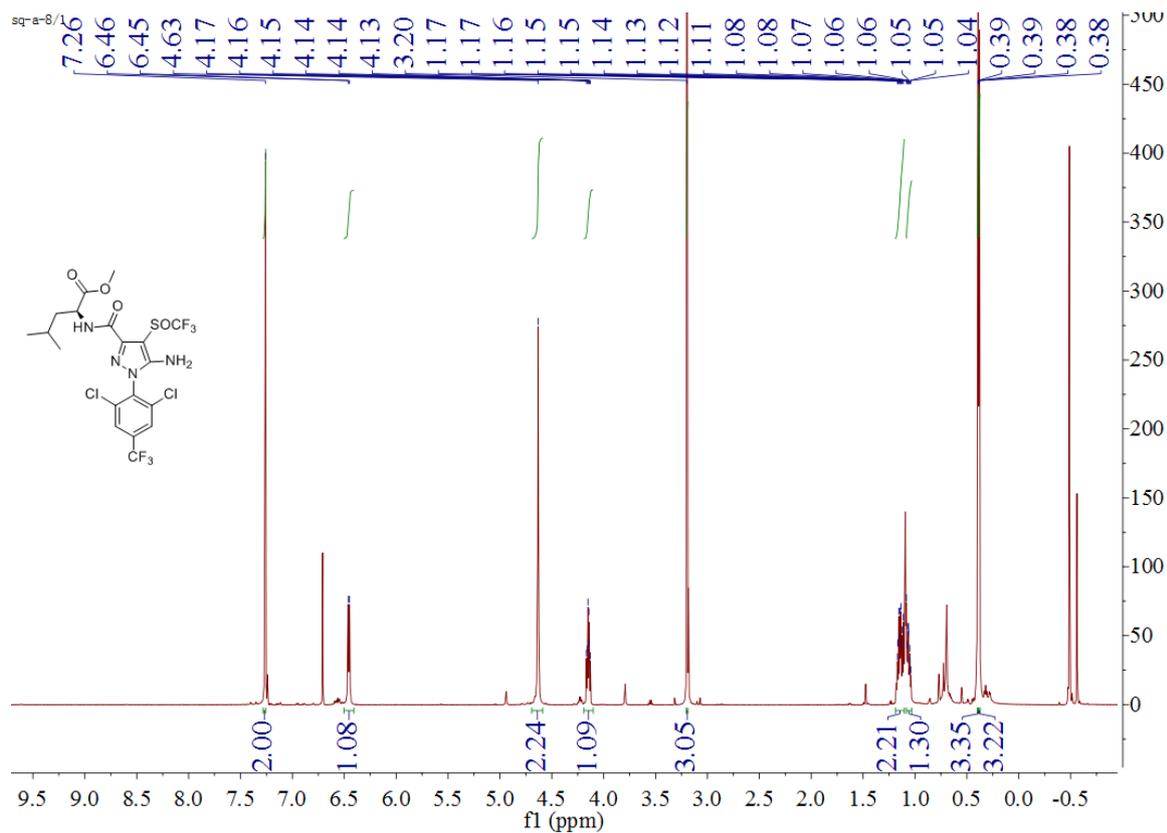
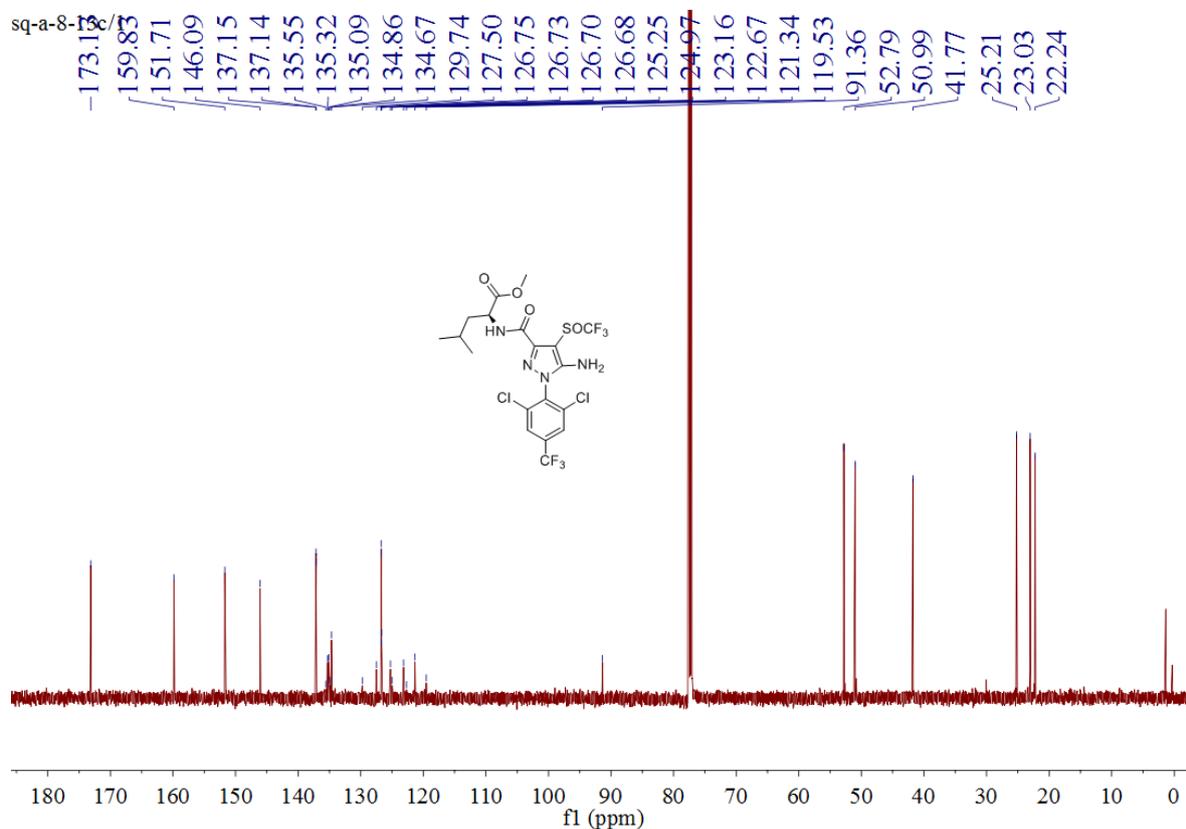


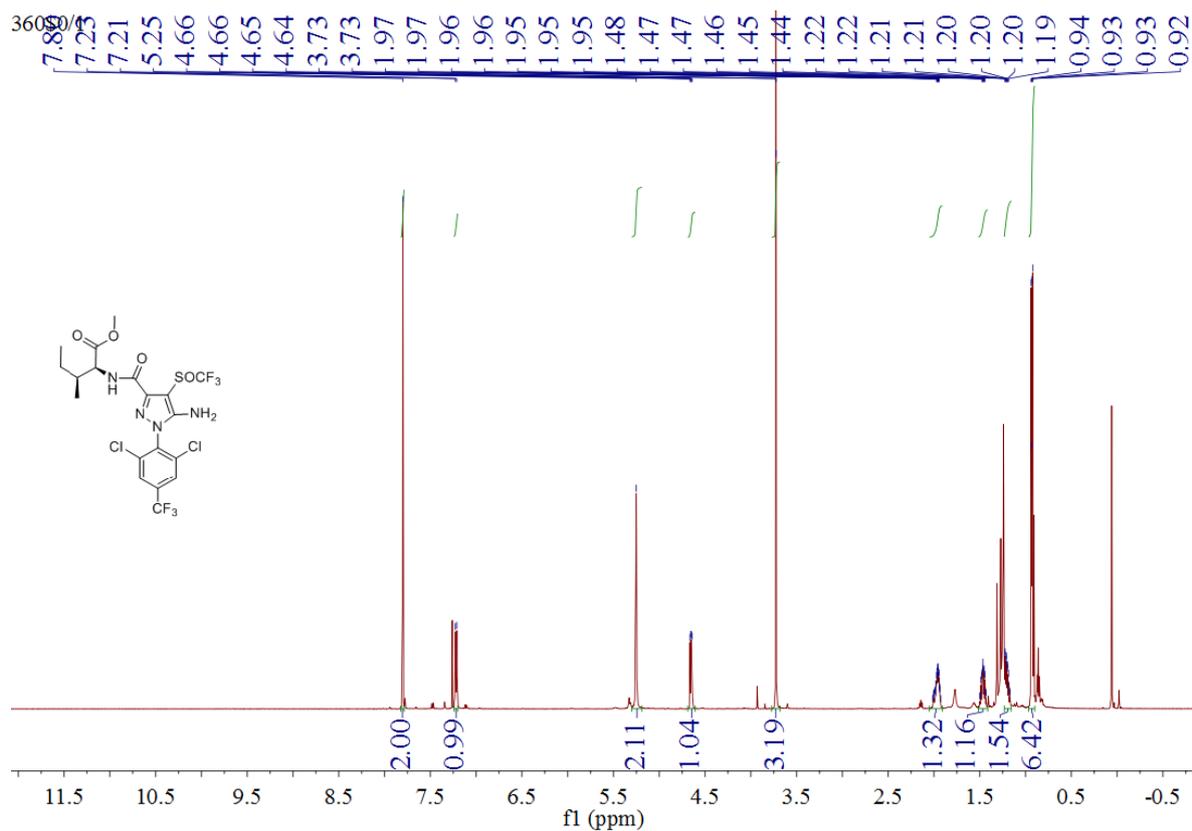
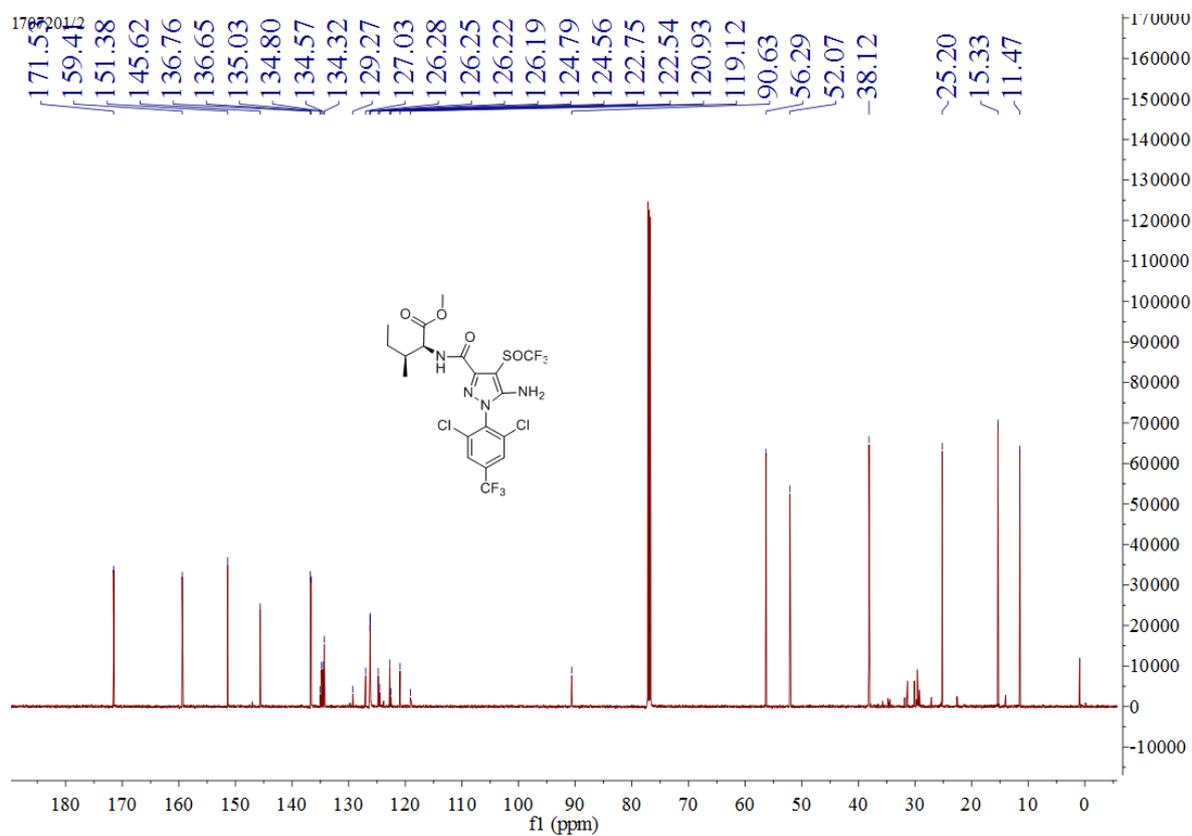
Figure S2  $^{13}\text{C}$  NMR spectra of 2 in  $\text{DMSO-}d_6$

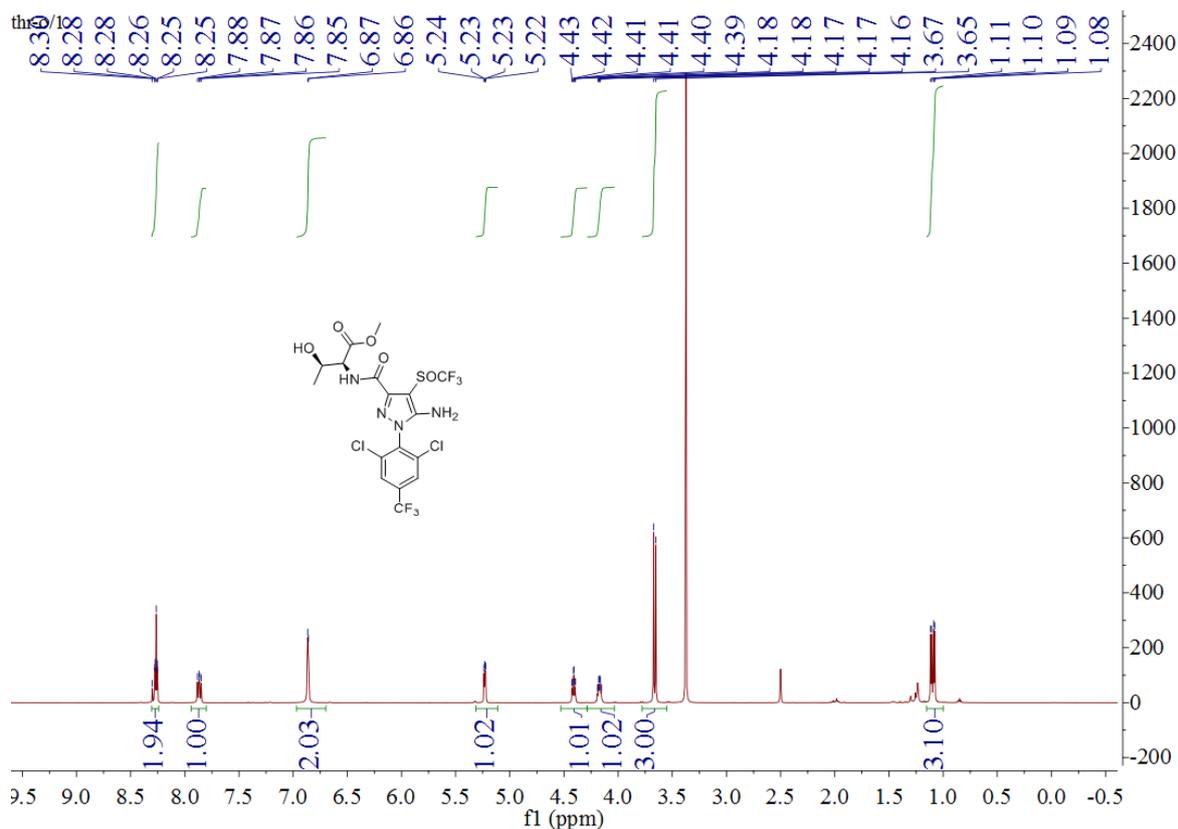
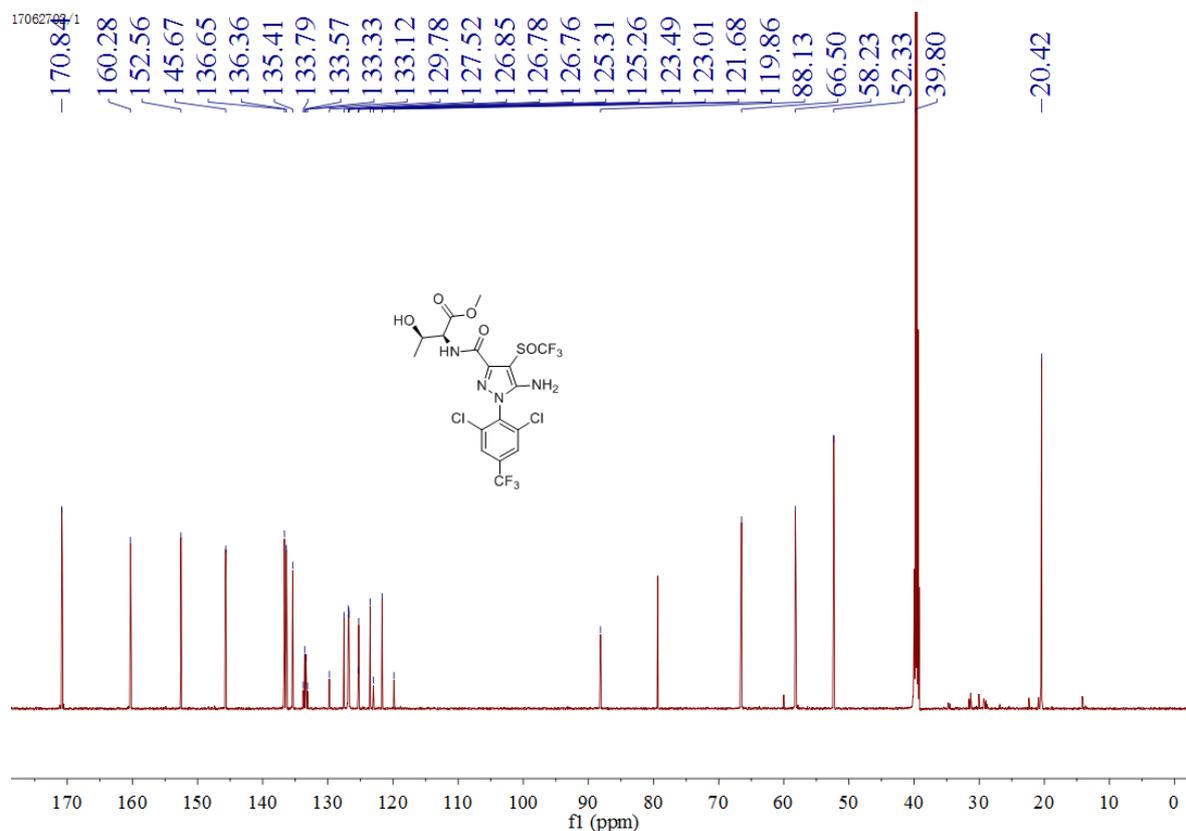


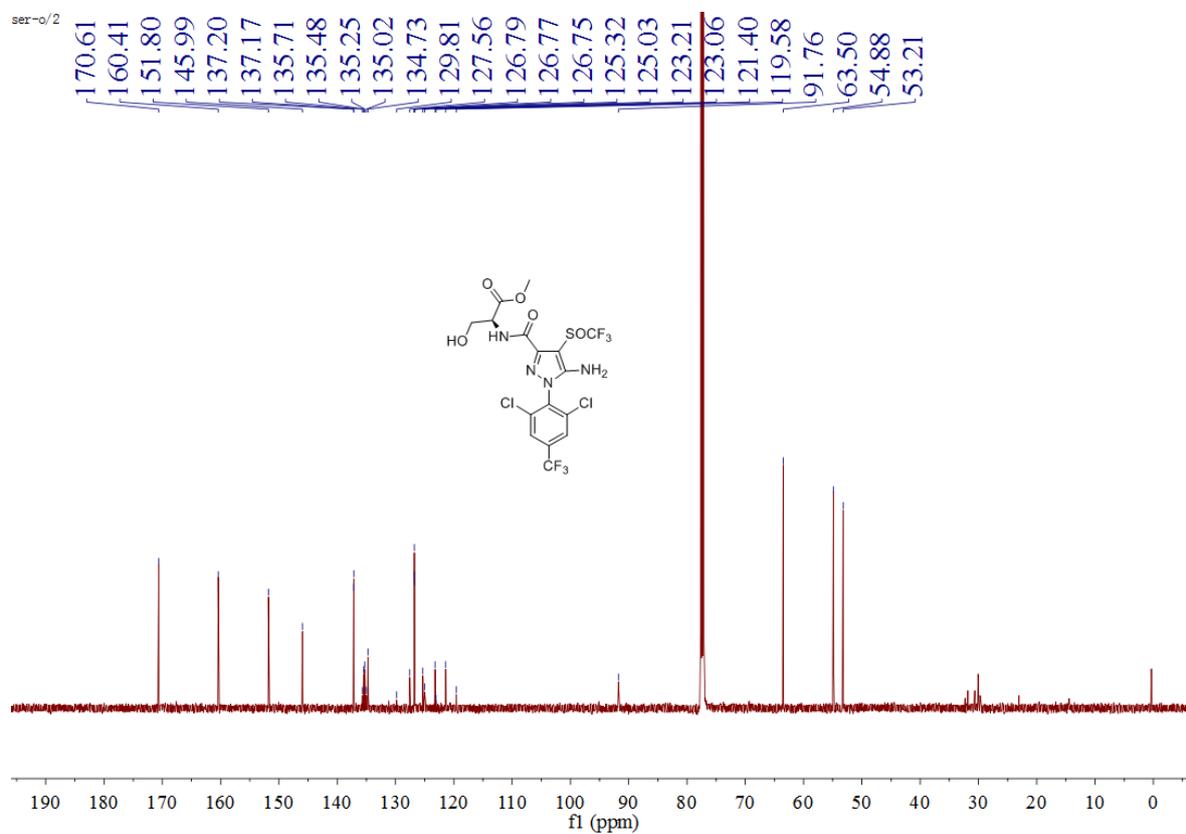
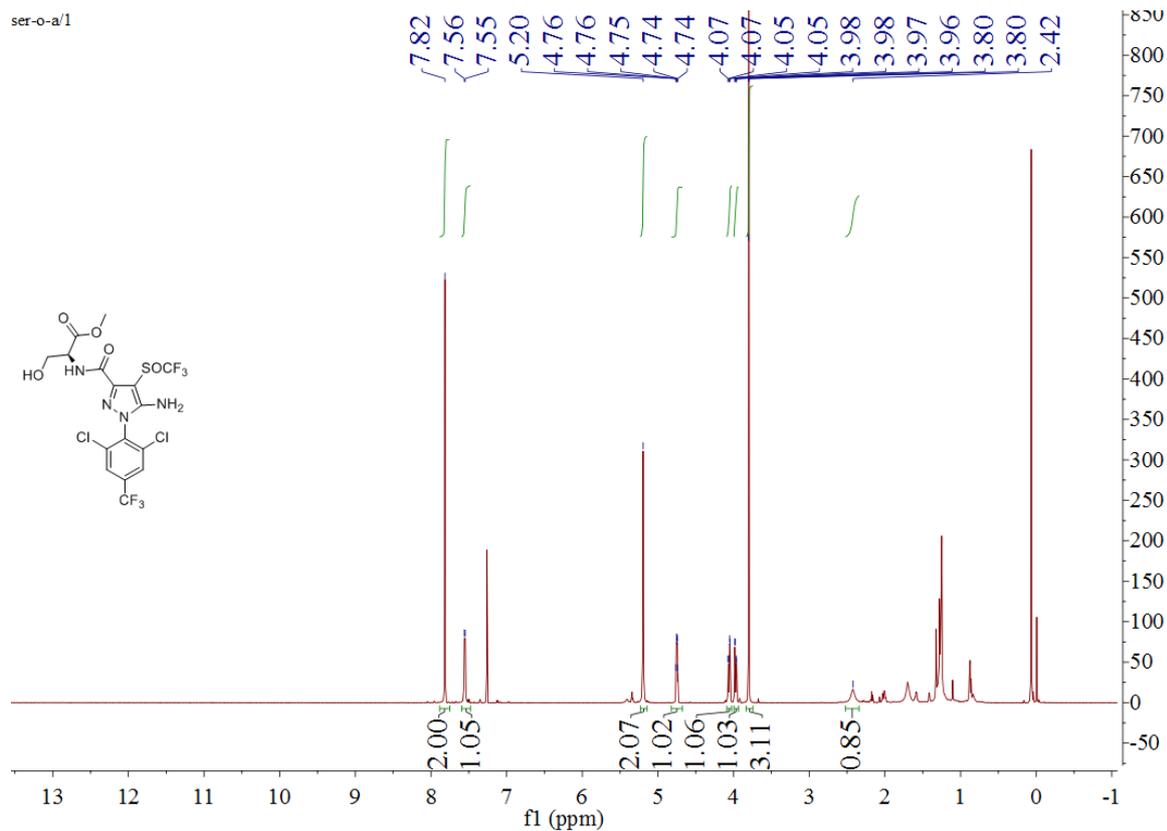


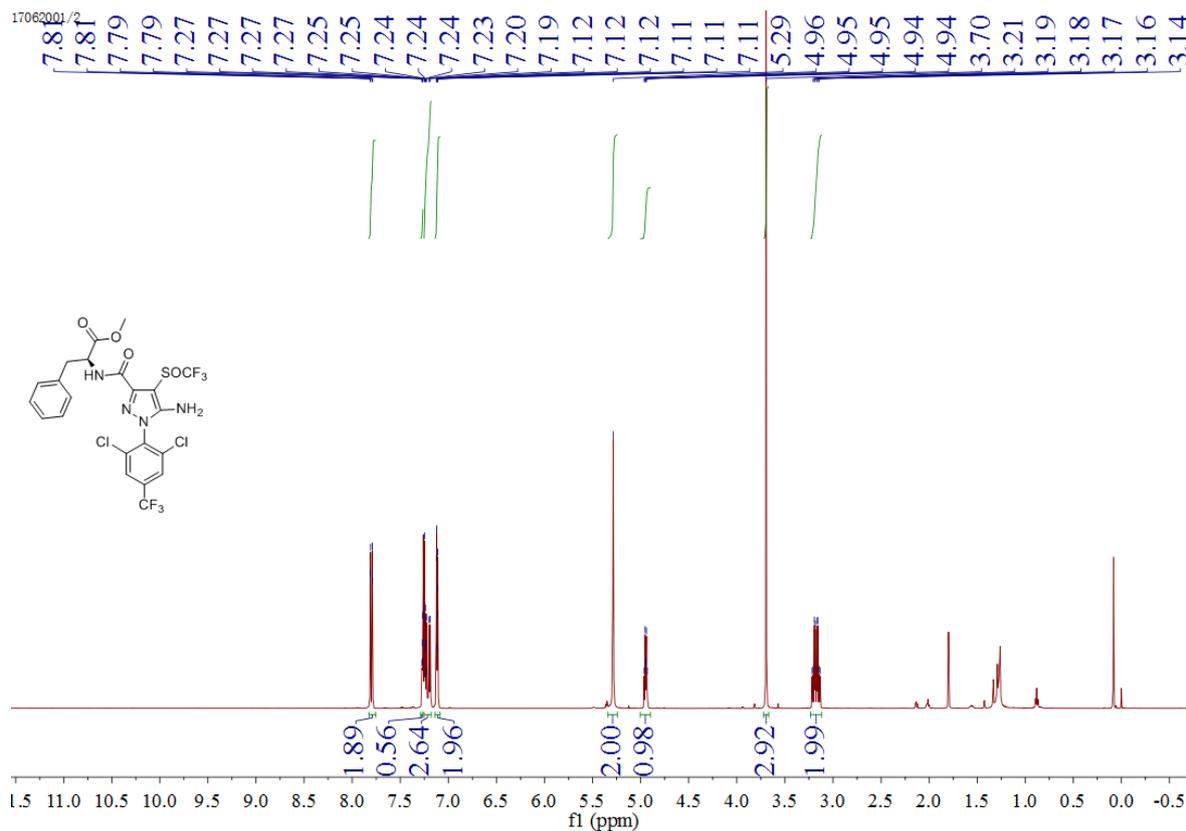
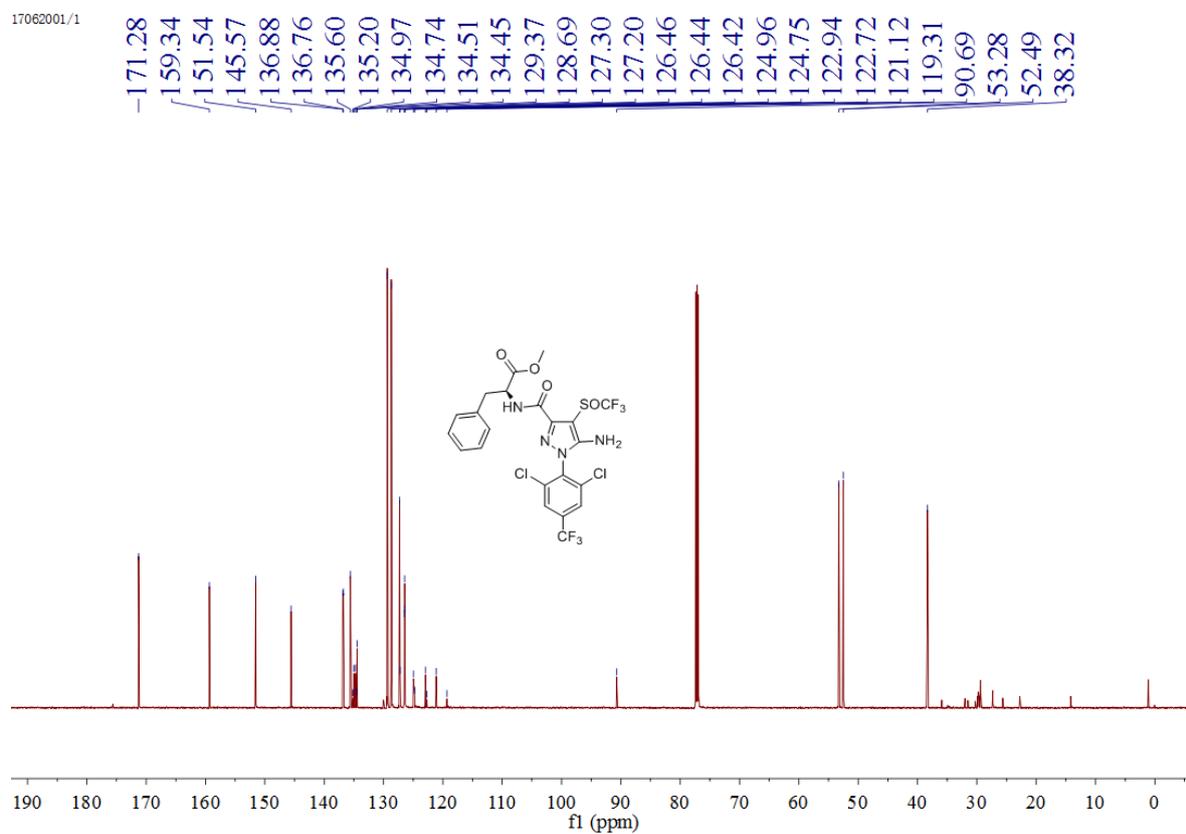


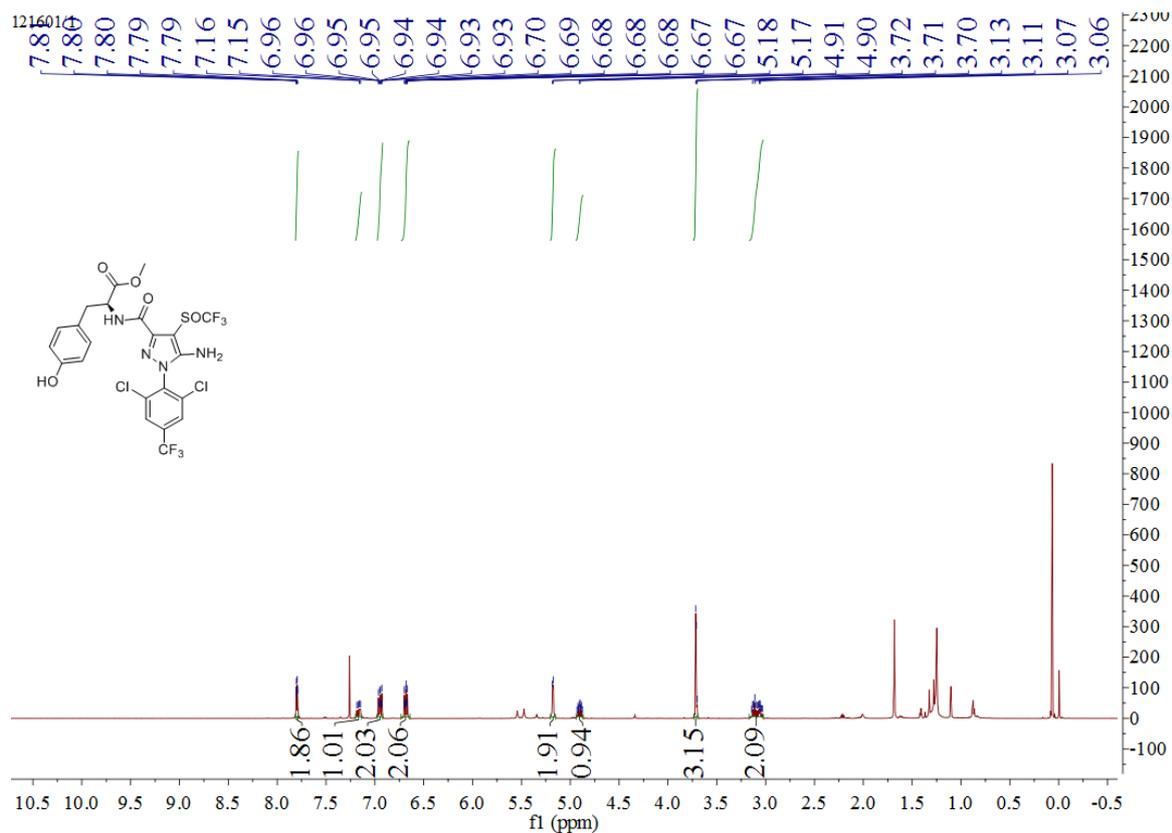
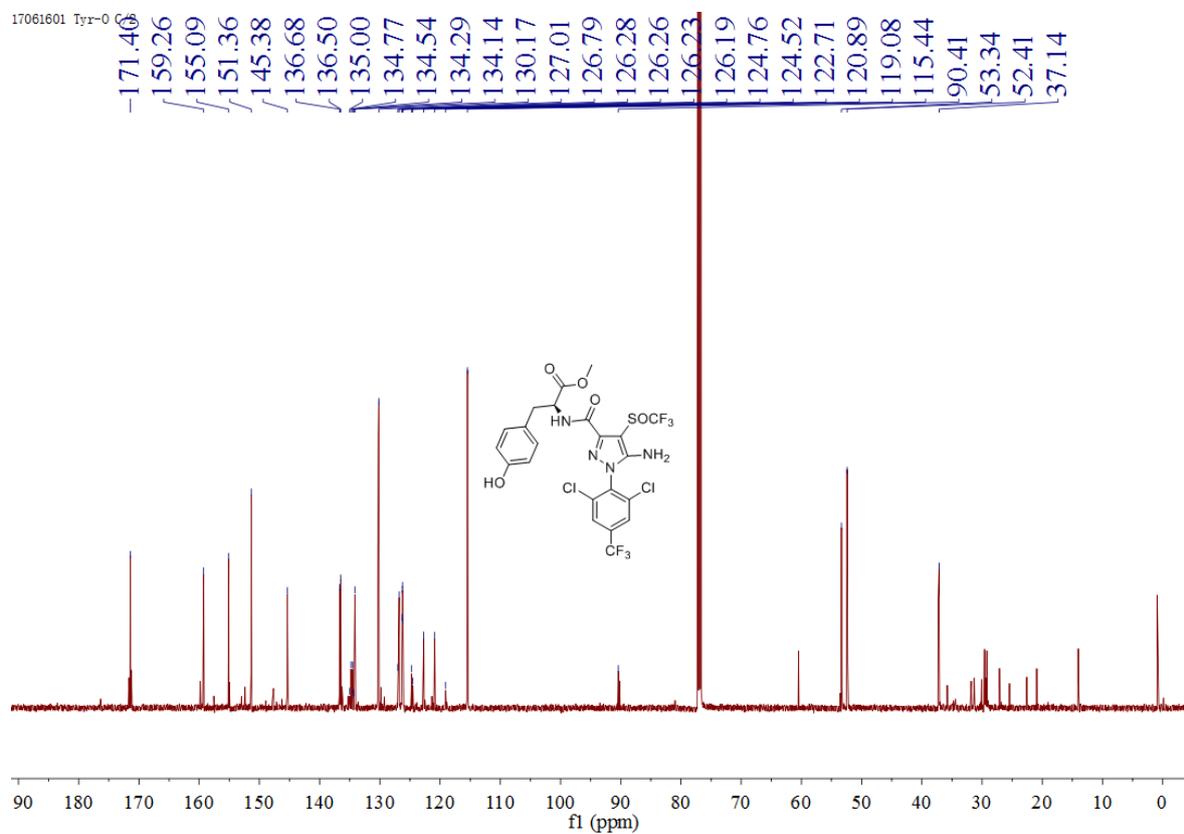
Figure S9  $^1\text{H}$  NMR spectra of 3d in Chloroform-*d*Figure S10  $^{13}\text{C}$  NMR spectra of 3d in Chloroform-*d*

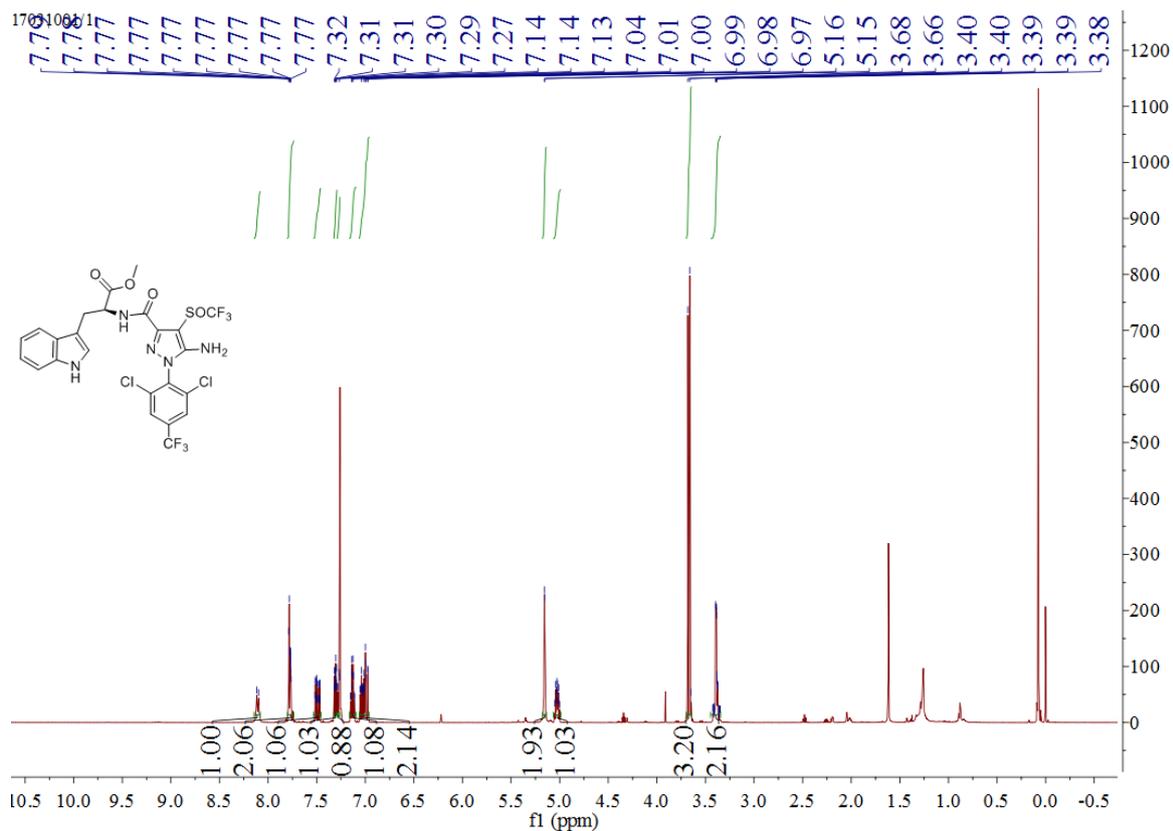
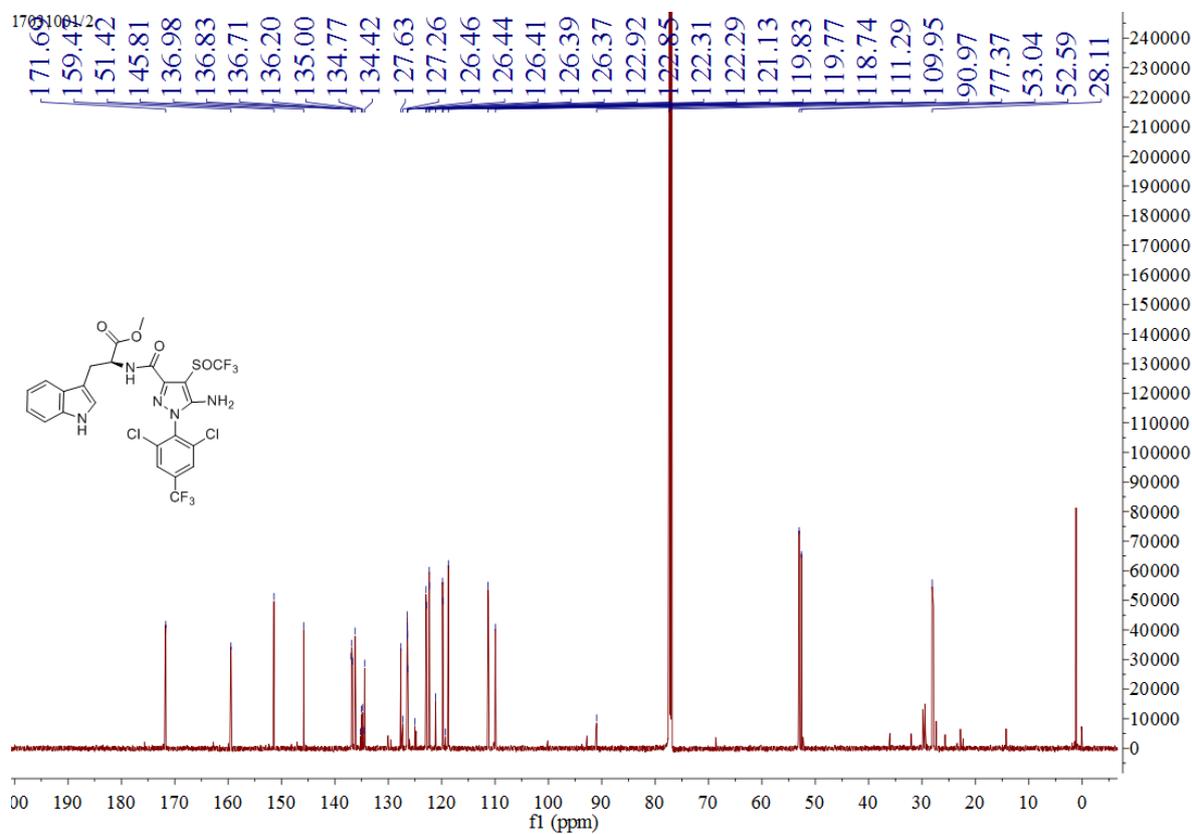
Figure S11 <sup>1</sup>H NMR spectra of 3e in Chloroform-*d*Figure S12 <sup>13</sup>C NMR spectra of 3e in Chloroform-*d*

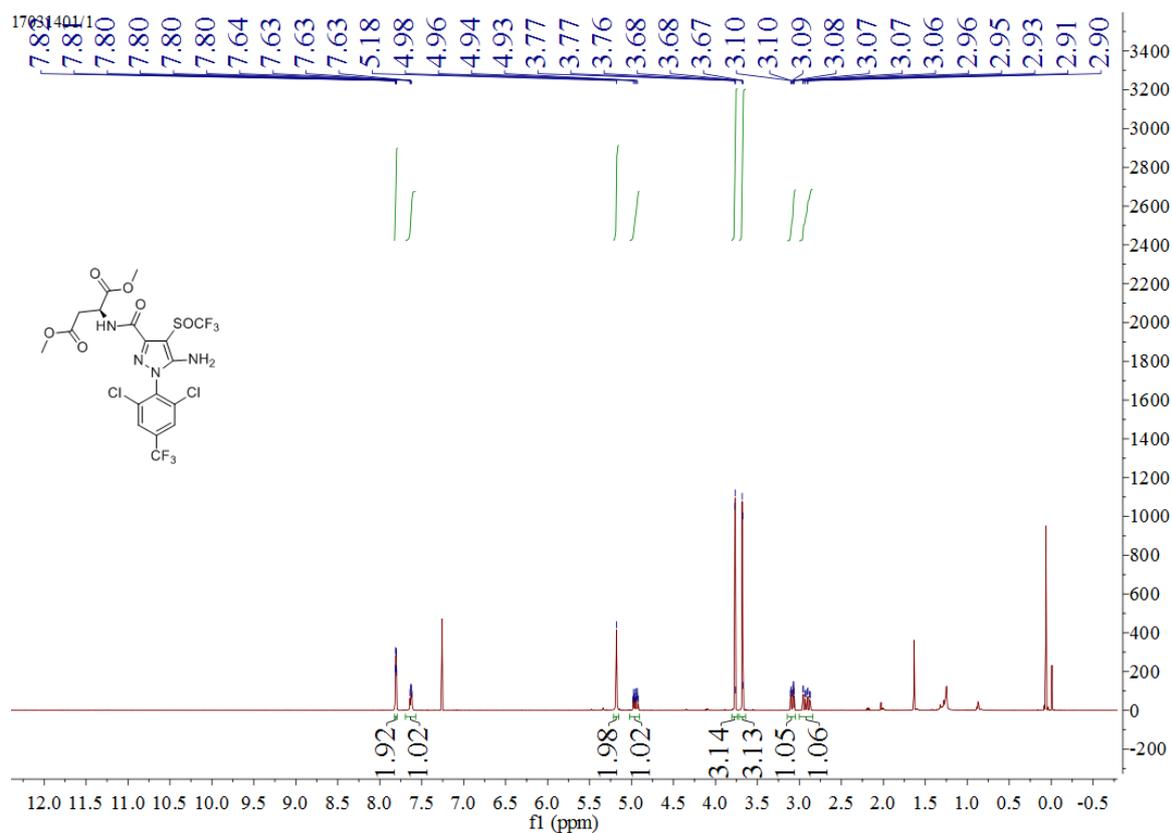
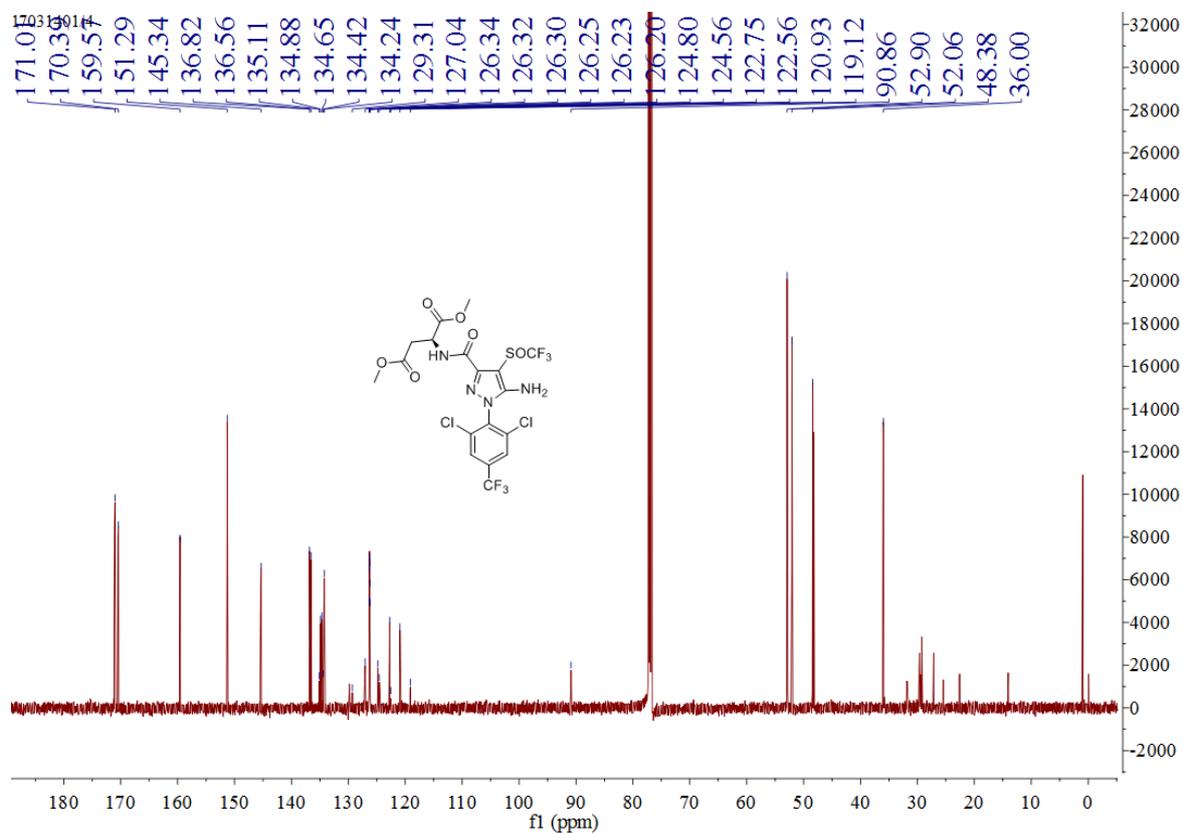
Figure S13  $^1\text{H}$  NMR spectra of 3f in  $\text{DMSO-}d_6$ Figure S14  $^{13}\text{C}$  NMR spectra of 3f in  $\text{DMSO-}d_6$

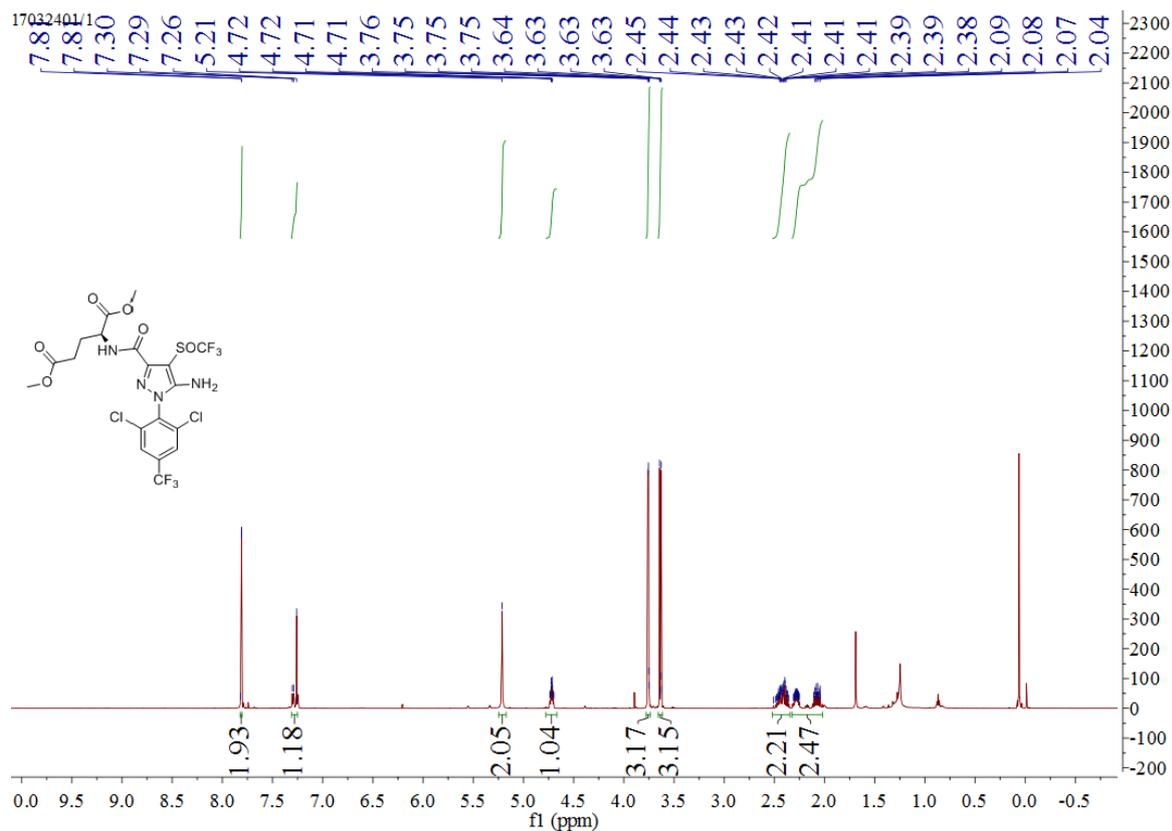


Figure S17  $^1\text{H}$  NMR spectra of 3h in Chloroform-*d*Figure S18  $^{13}\text{C}$  NMR spectra of 3h in Chloroform-*d*

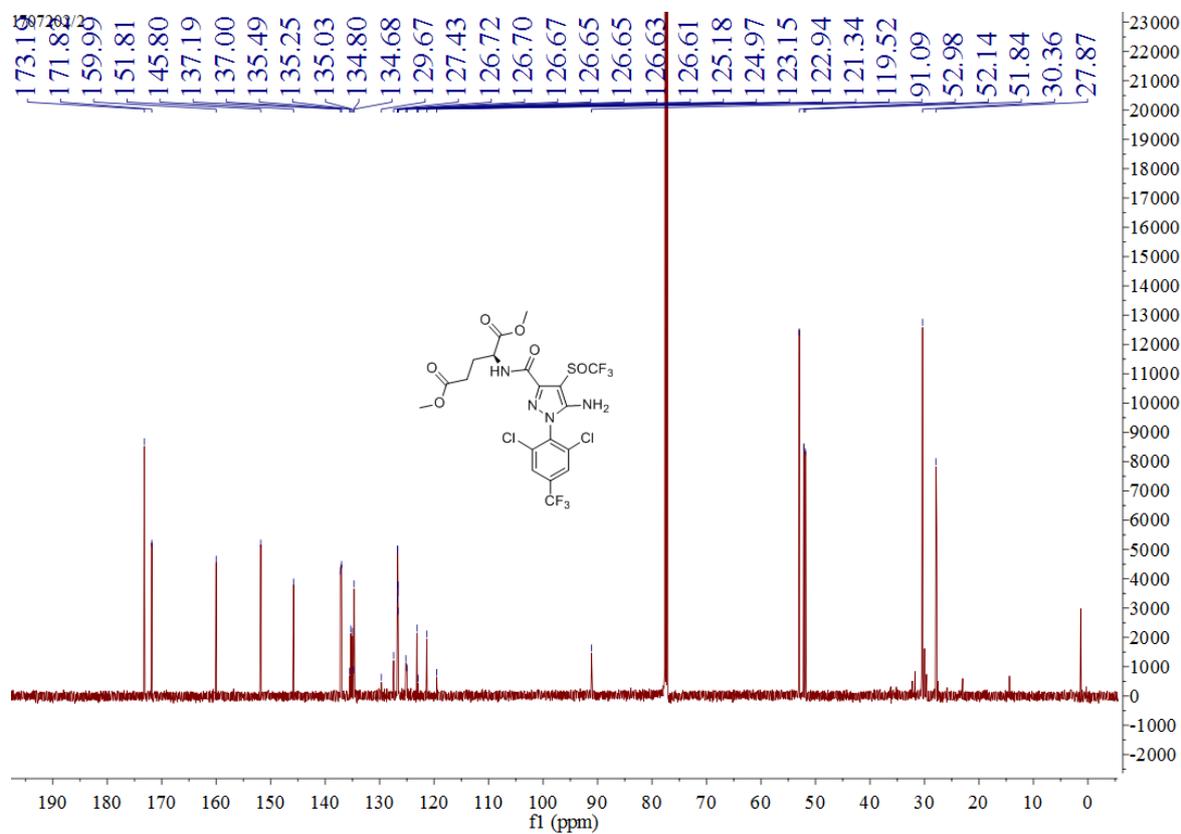
Figure S19  $^1\text{H}$  NMR spectra of 3i in Chloroform-*d*Figure S20  $^{13}\text{C}$  NMR spectra of 3i in Chloroform-*d*

Figure S21  $^1\text{H}$  NMR spectra of 3j in Chloroform-*d*Figure S22  $^{13}\text{C}$  NMR spectra of 3j in Chloroform-*d*

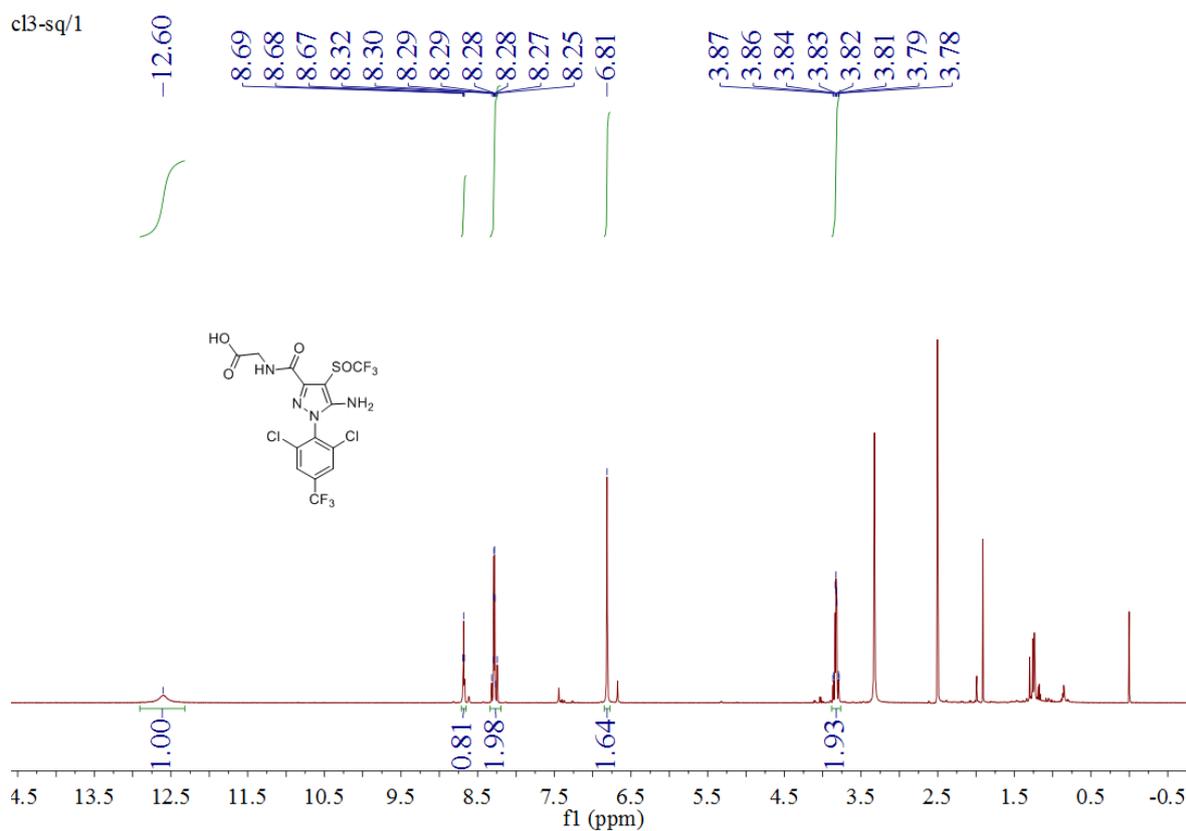
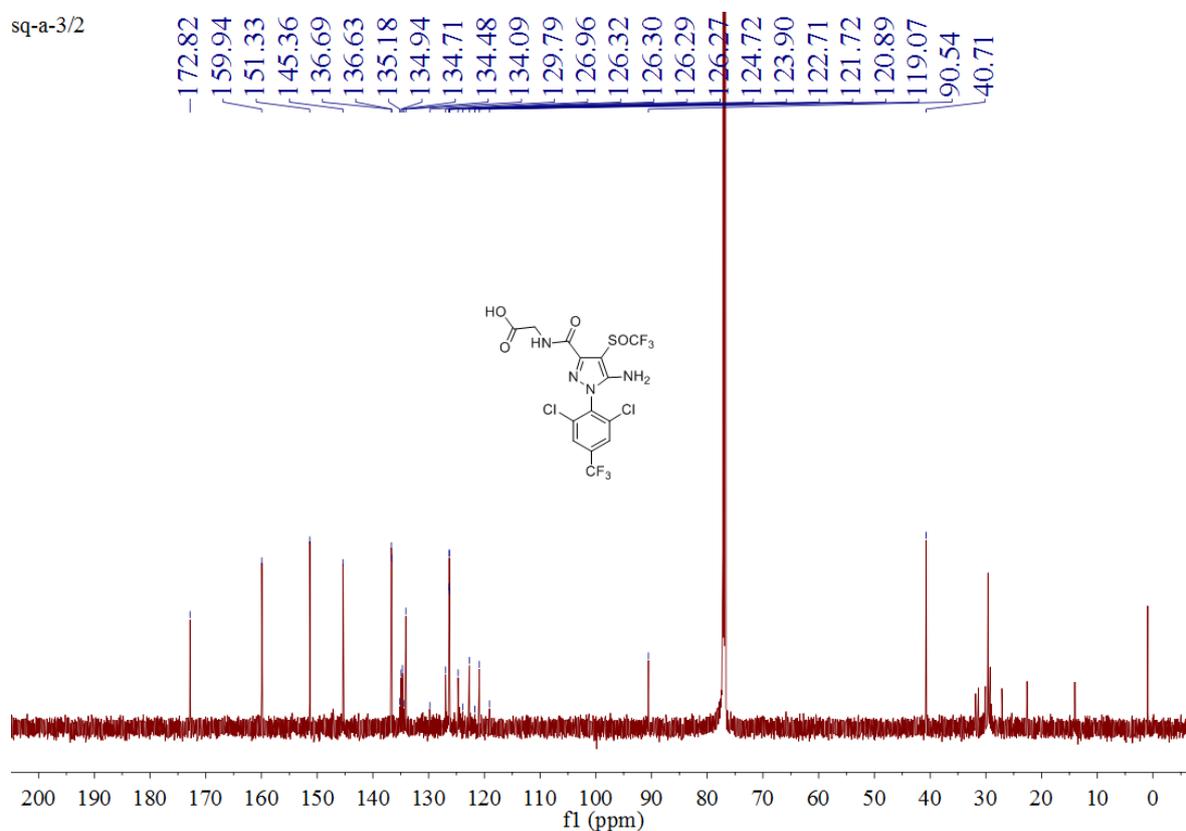
Figure S23  $^1\text{H}$  NMR spectra of 3k in Chloroform-*d*Figure S24  $^{13}\text{C}$  NMR spectra of 3k in Chloroform-*d*

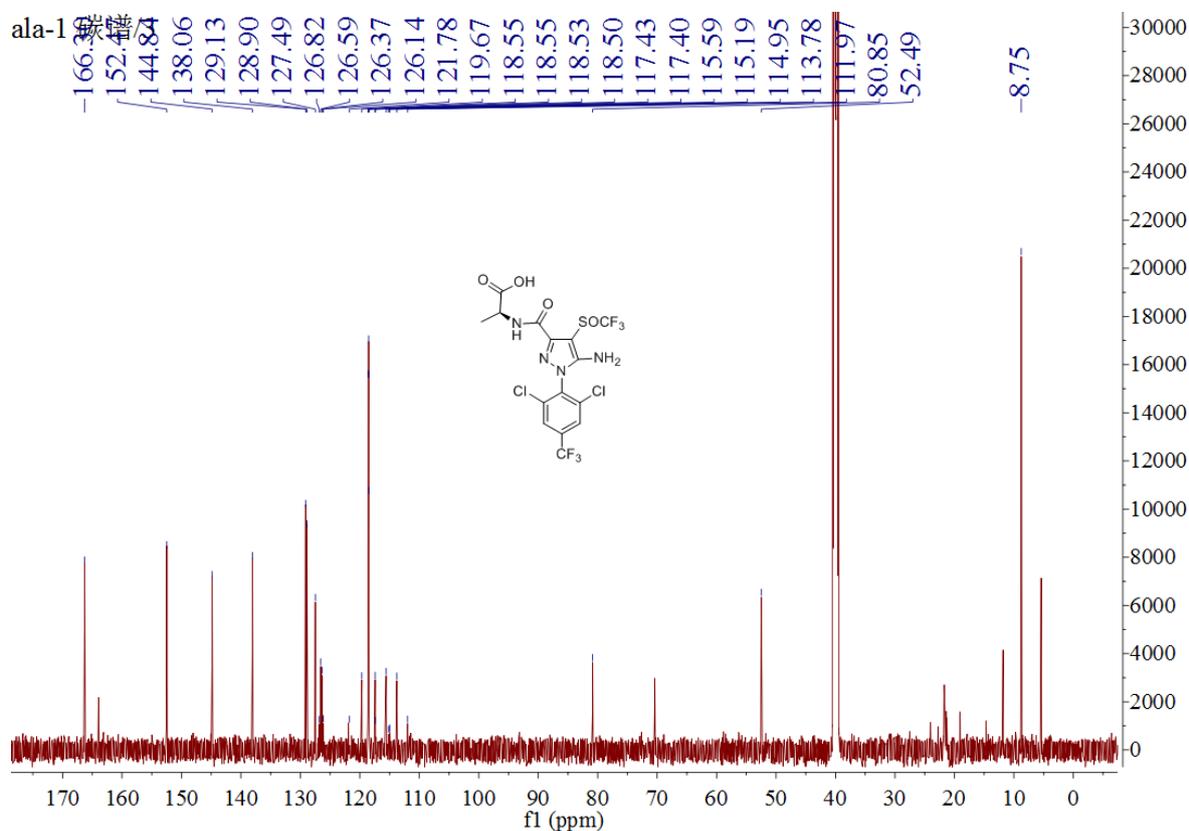
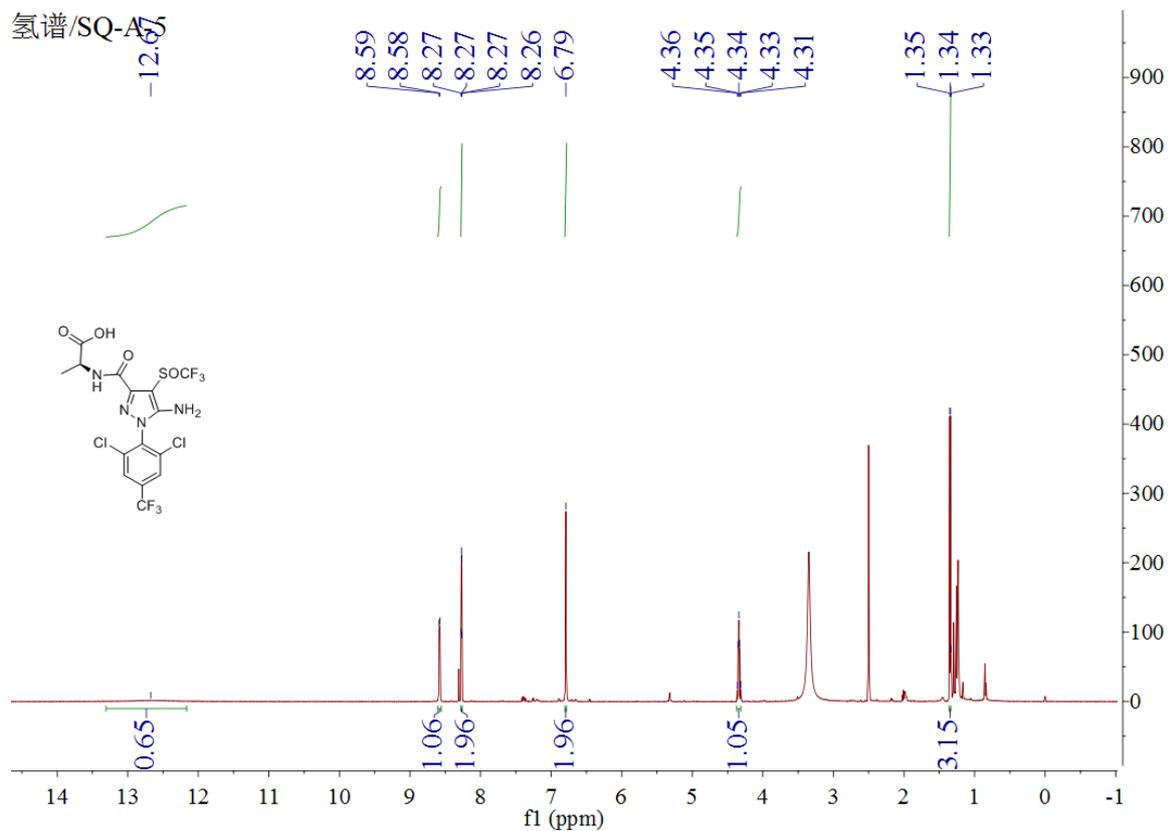


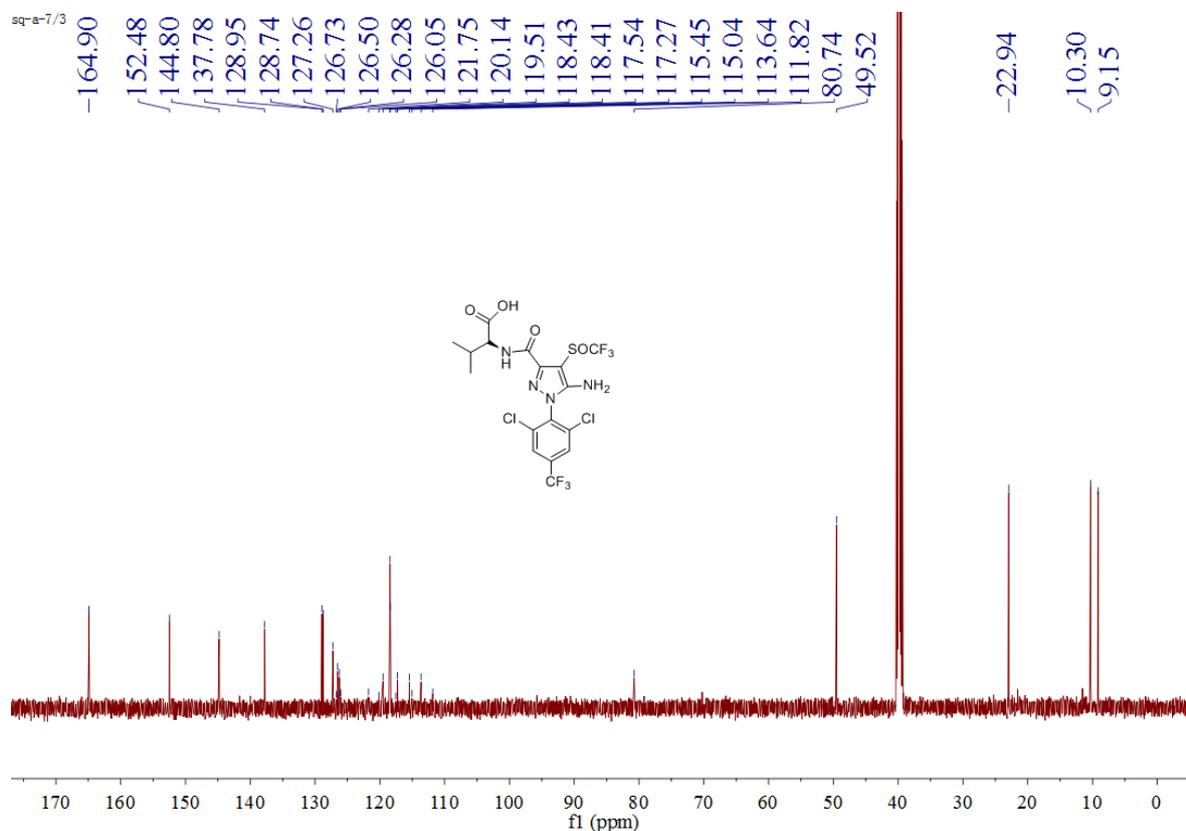
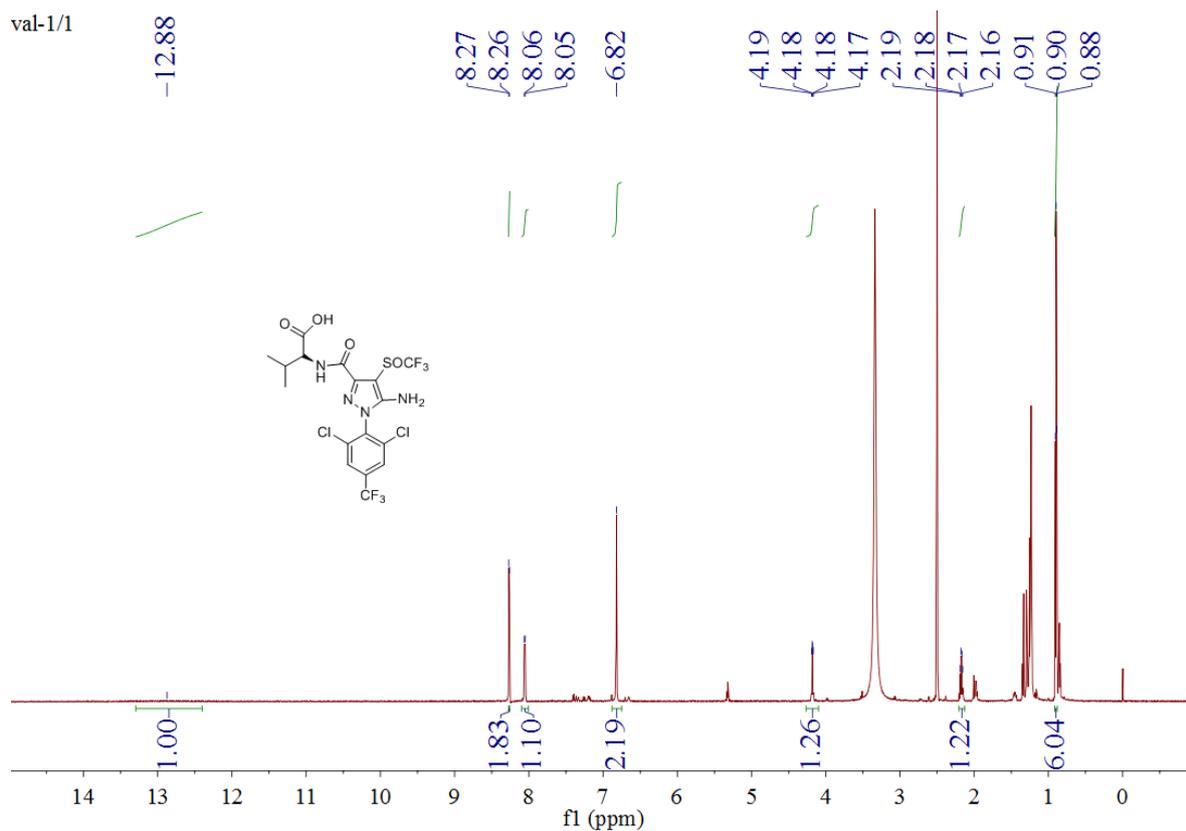
**Figure S25**  $^1\text{H}$  NMR spectra of **31** in Chloroform-*d*

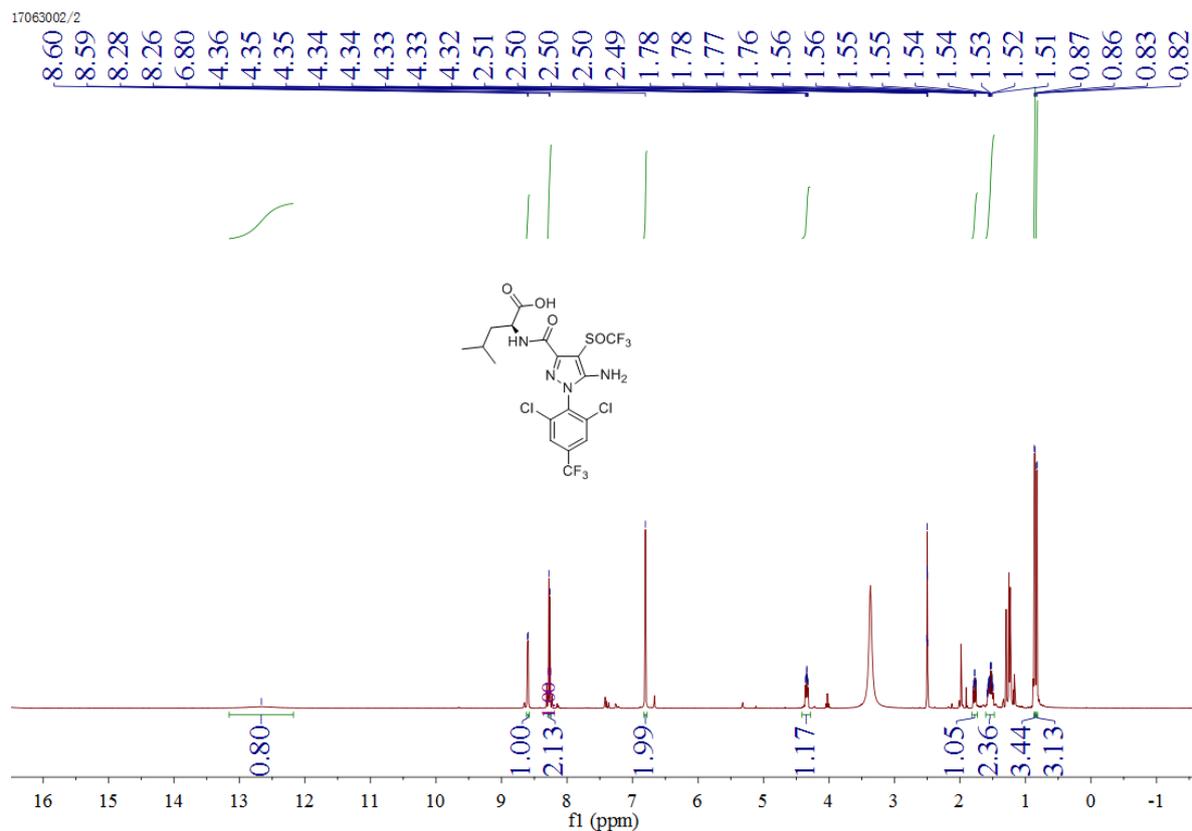
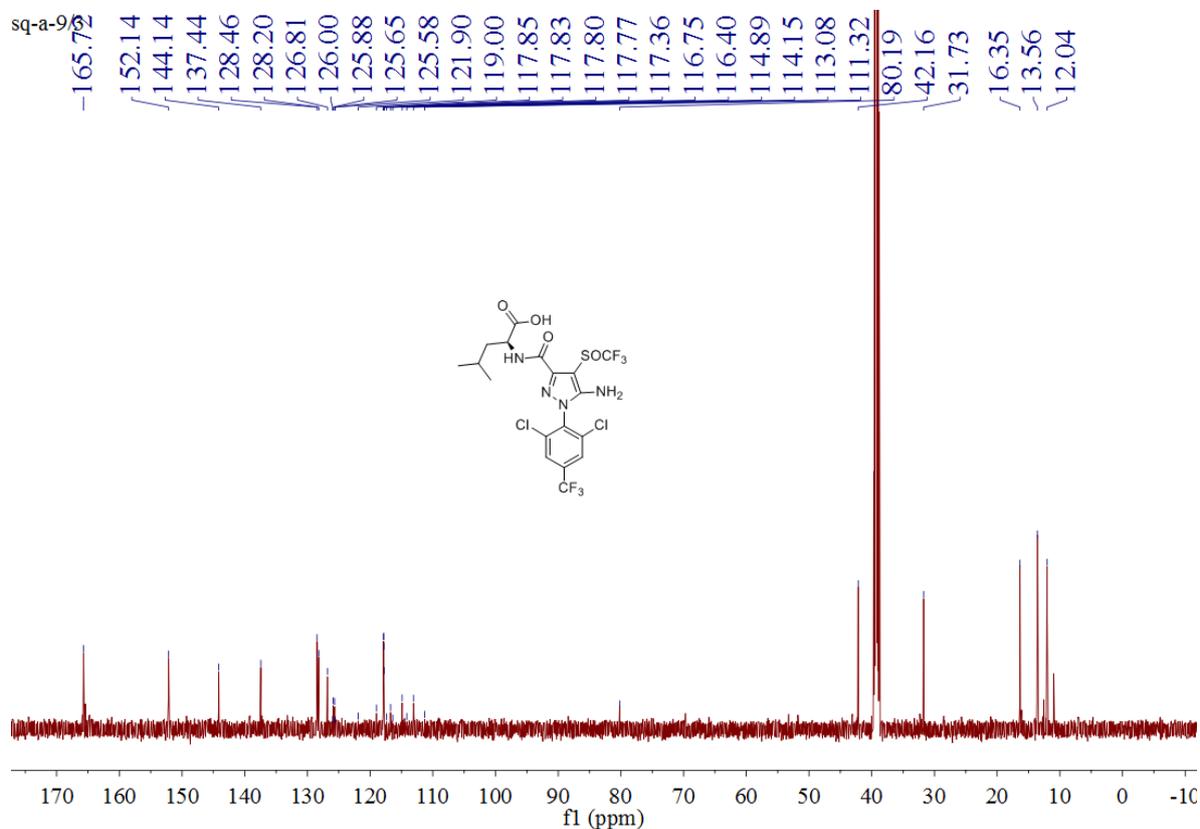


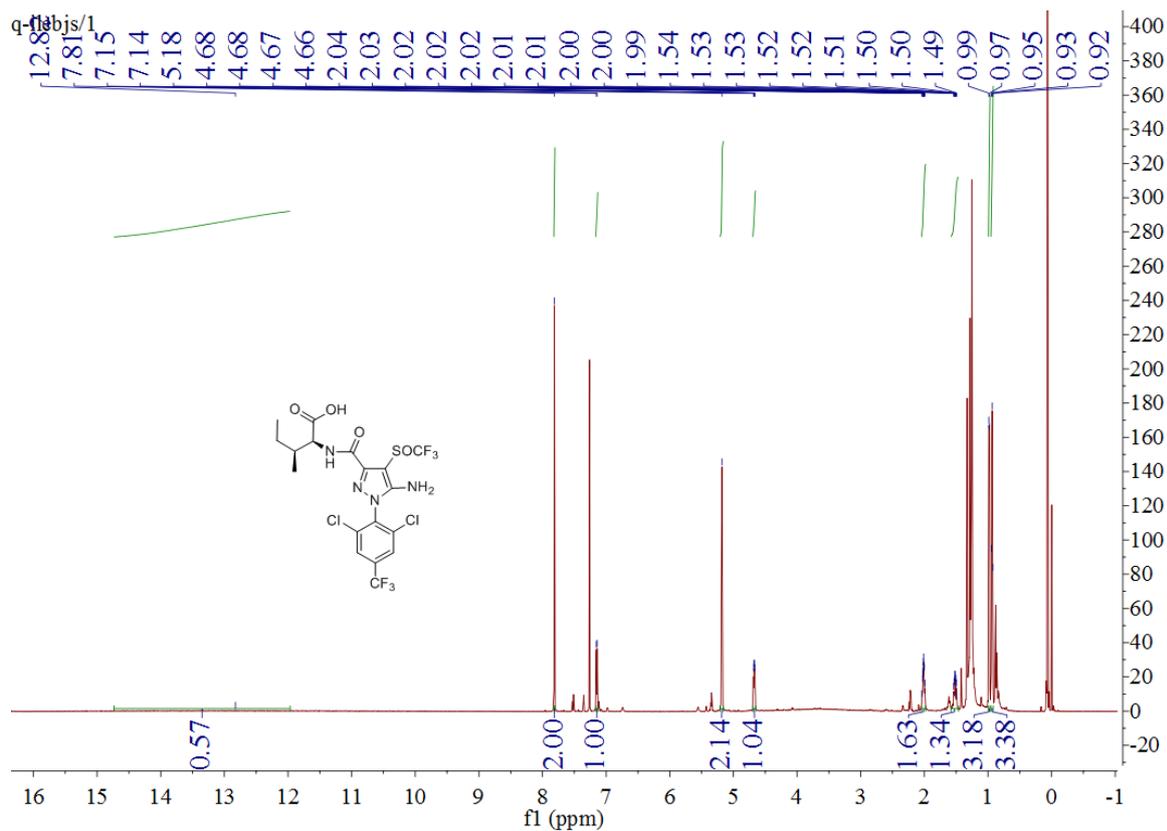
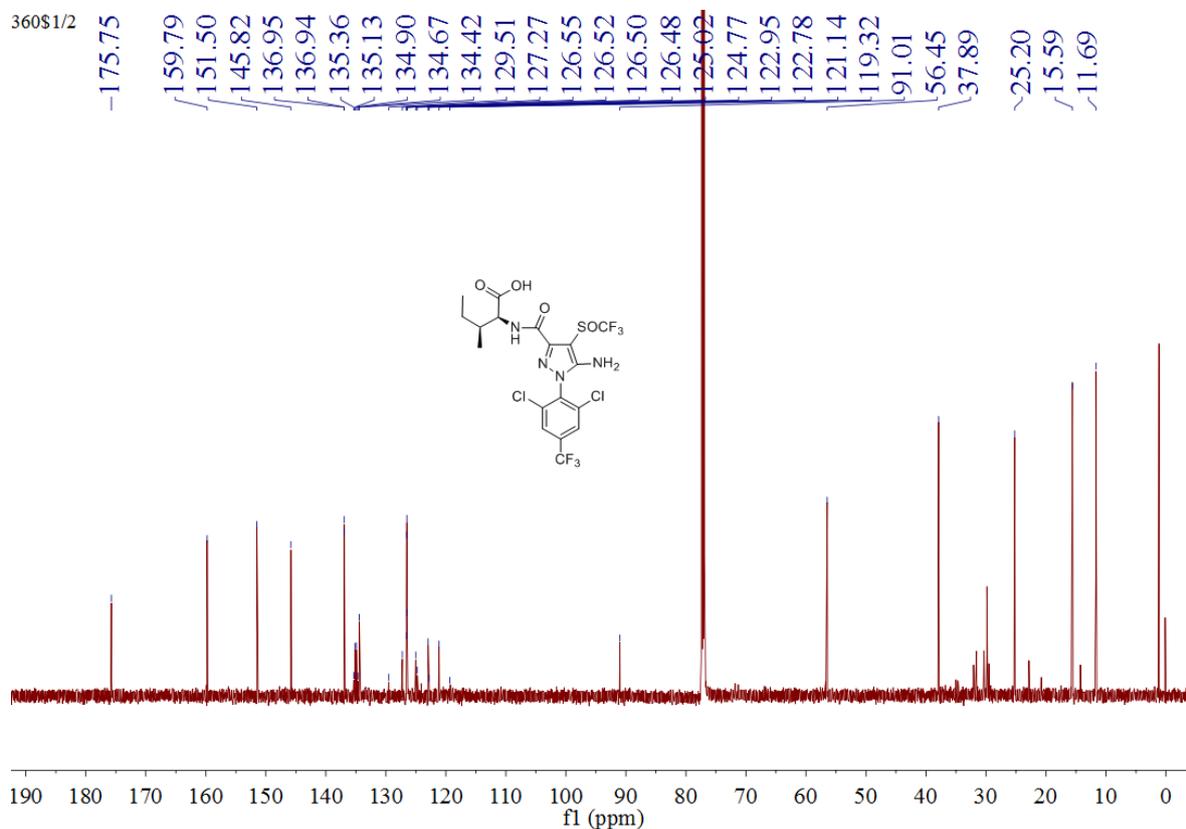
**Figure S26**  $^{13}\text{C}$  NMR spectra of **31** in Chloroform-*d*

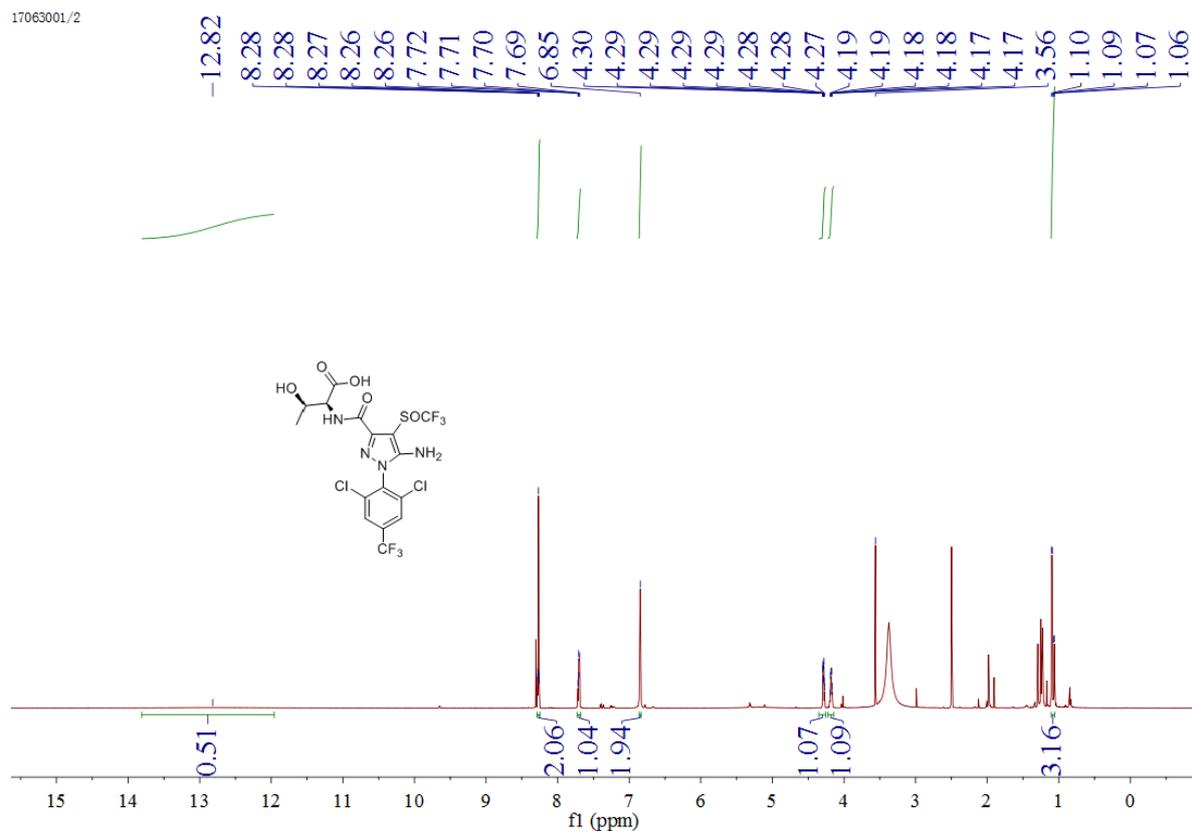
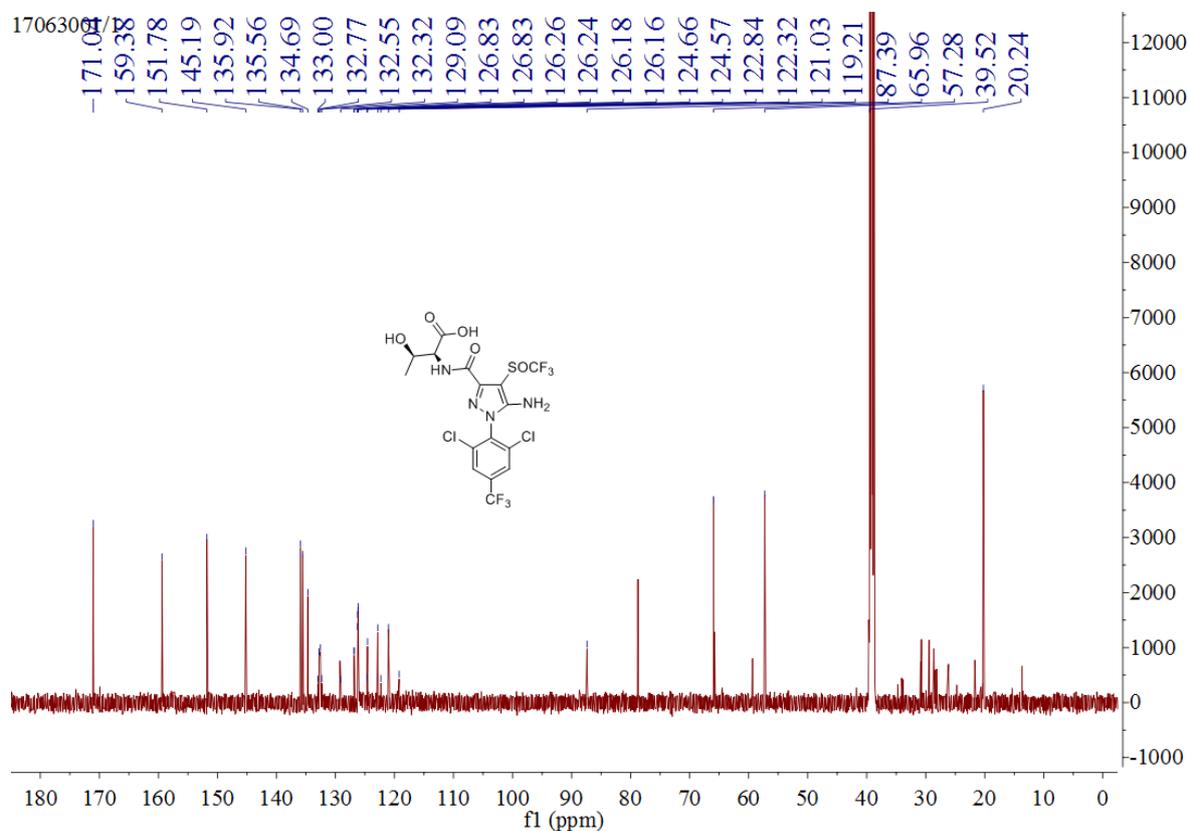
Figure S27  $^1\text{H}$  NMR spectra of 4a in Chloroform-*d*Figure S28  $^{13}\text{C}$  NMR spectra of 4a in Chloroform-*d*

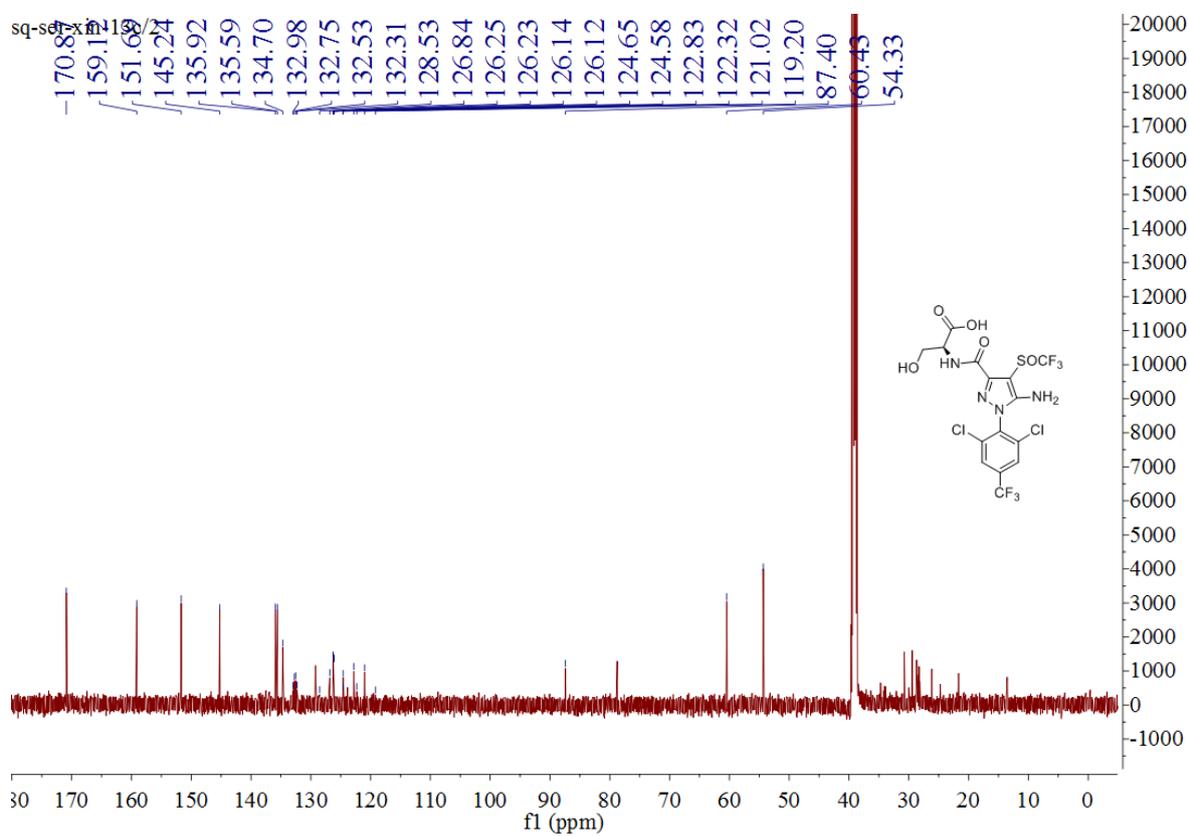
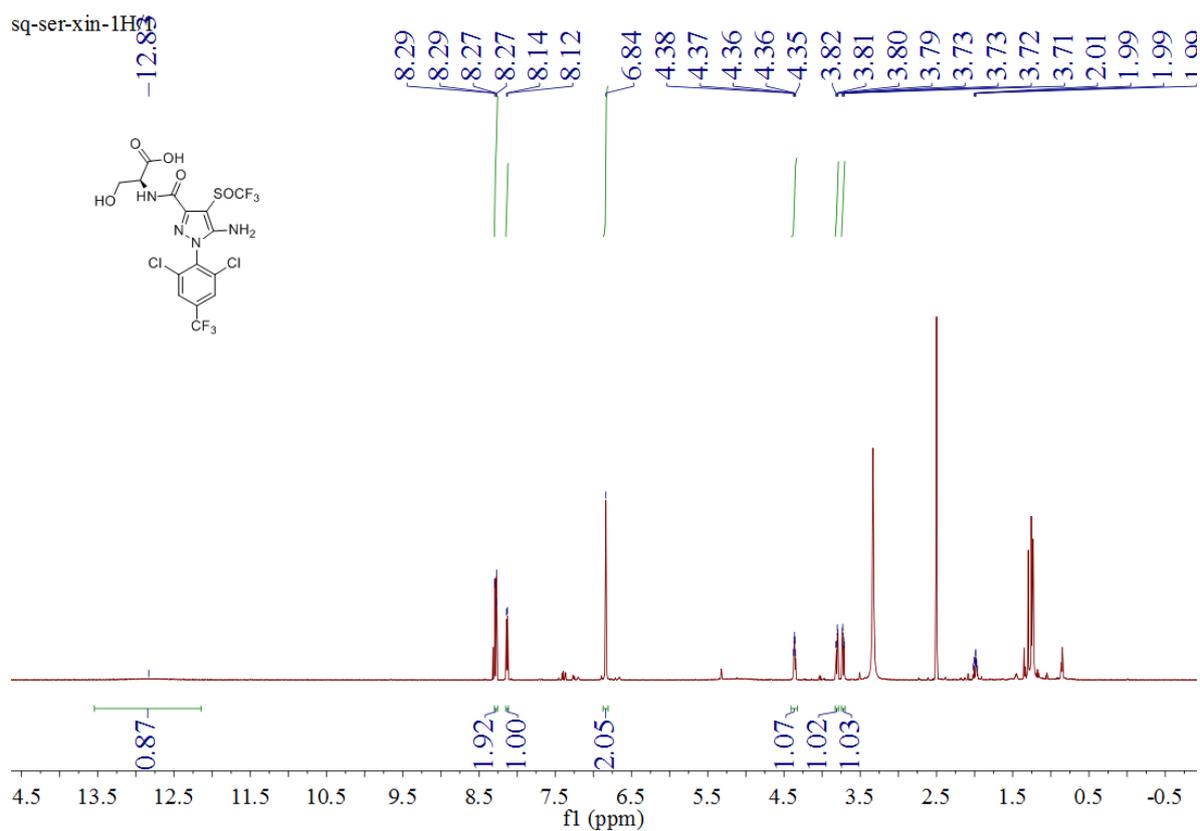


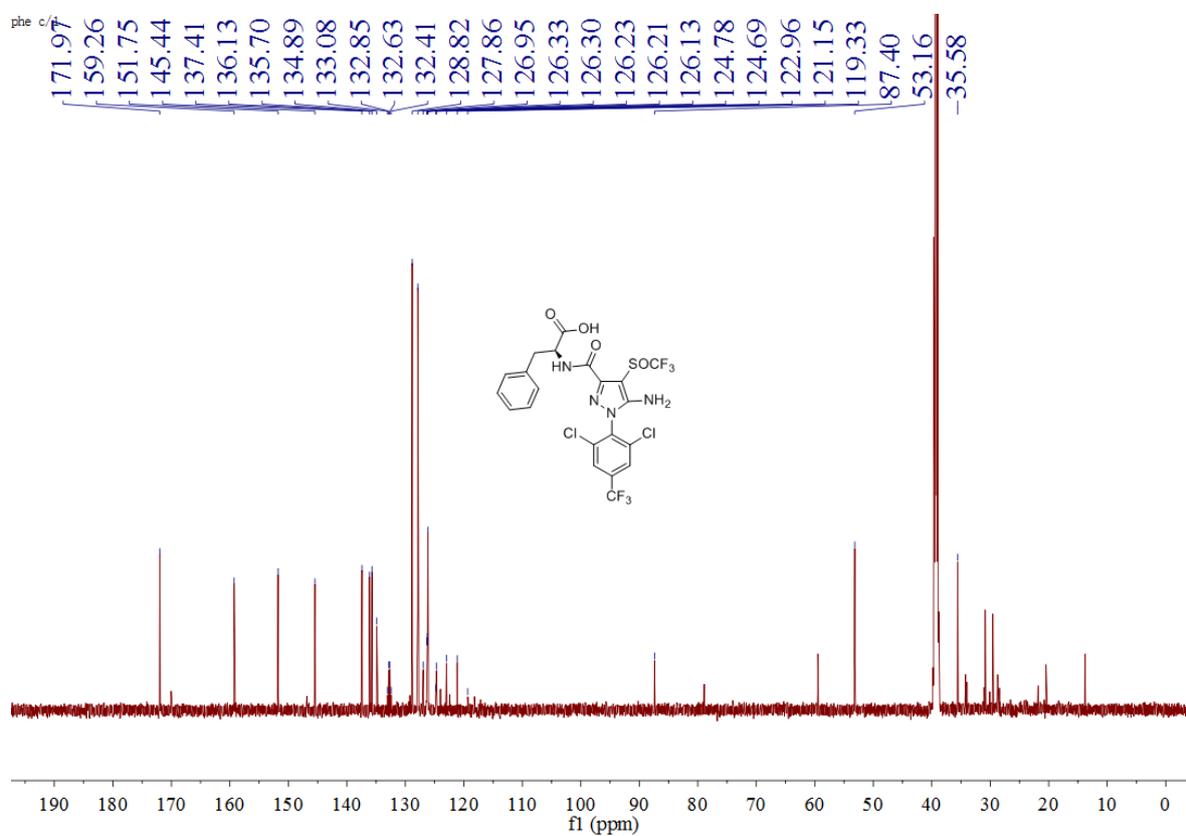
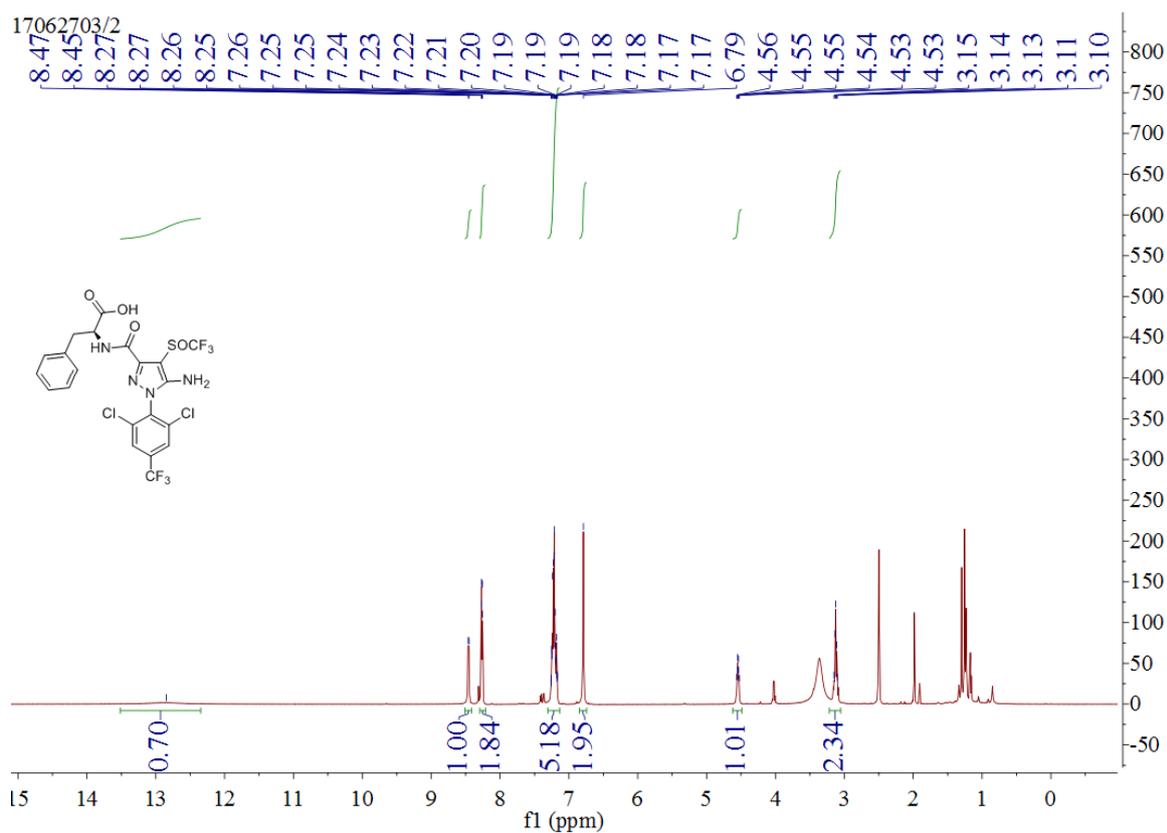


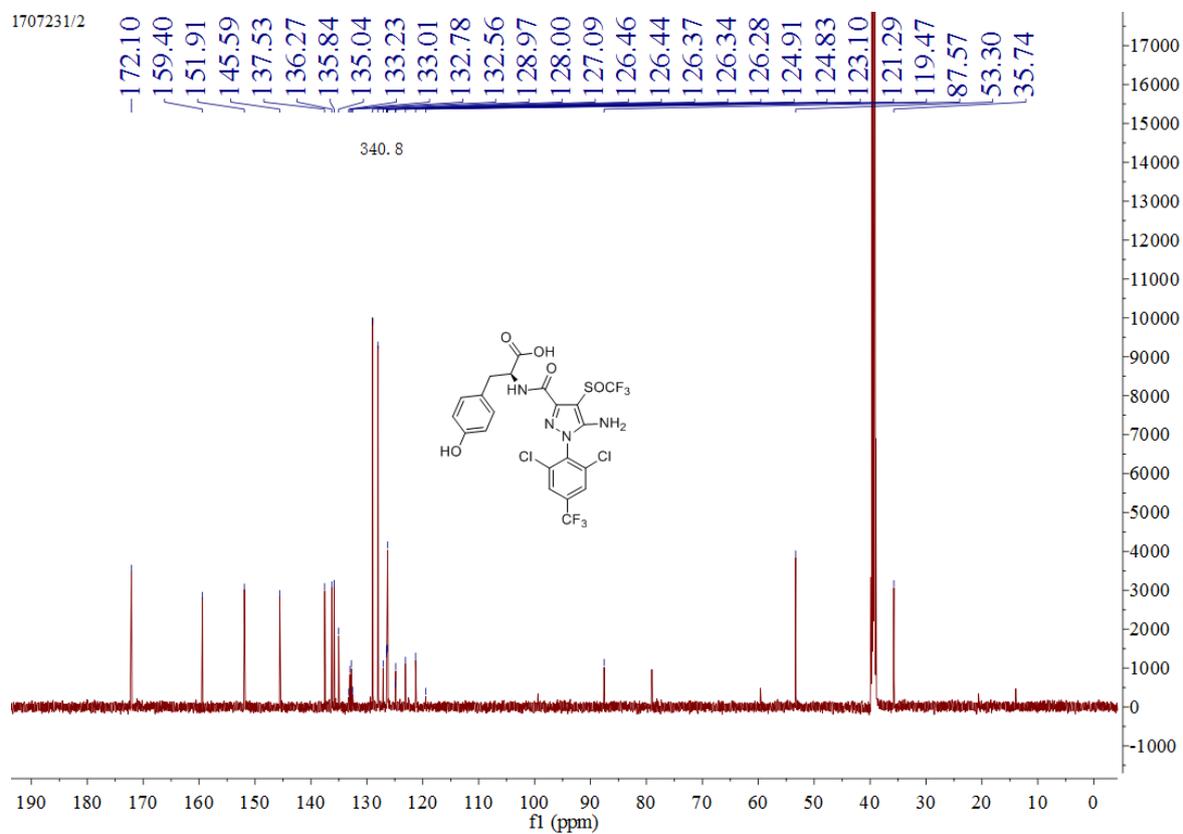
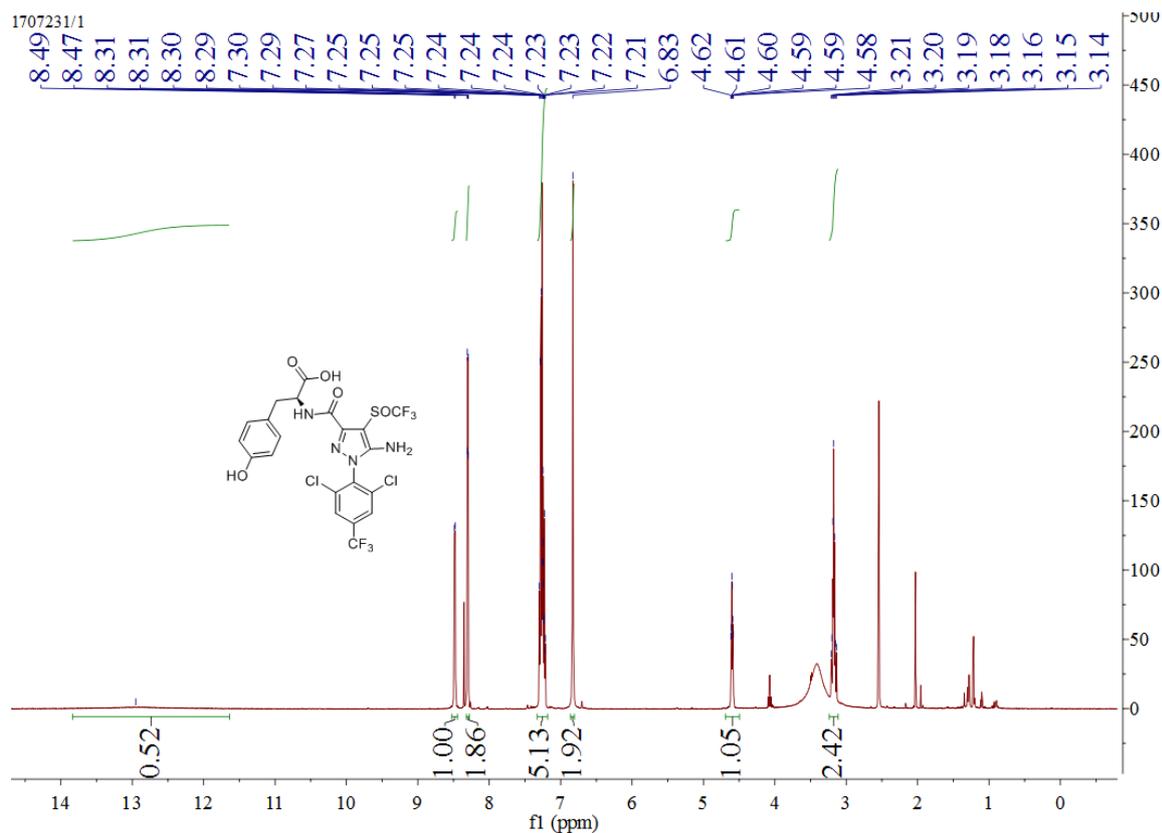
Figure S33 <sup>1</sup>H NMR spectra of 4d in DMSO-*d*<sub>6</sub>Figure S34 <sup>13</sup>C NMR spectra of 4d in DMSO-*d*<sub>6</sub>

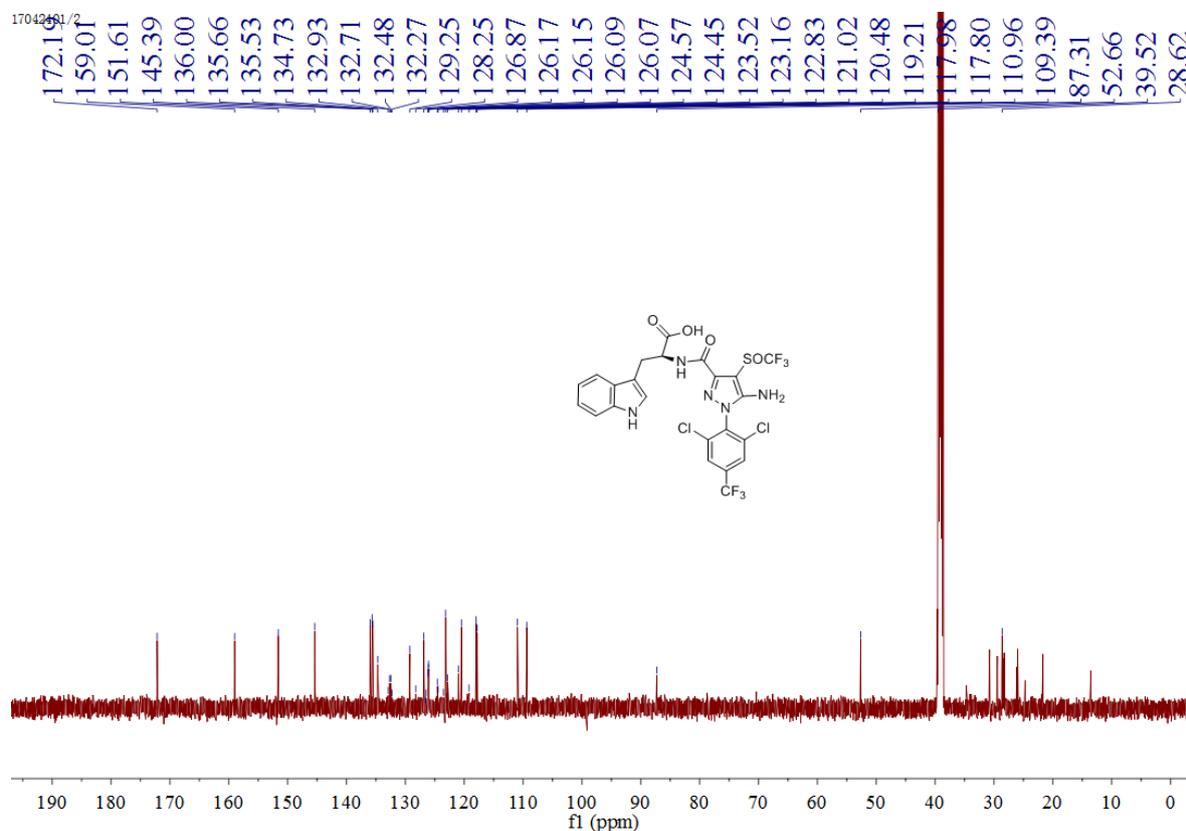
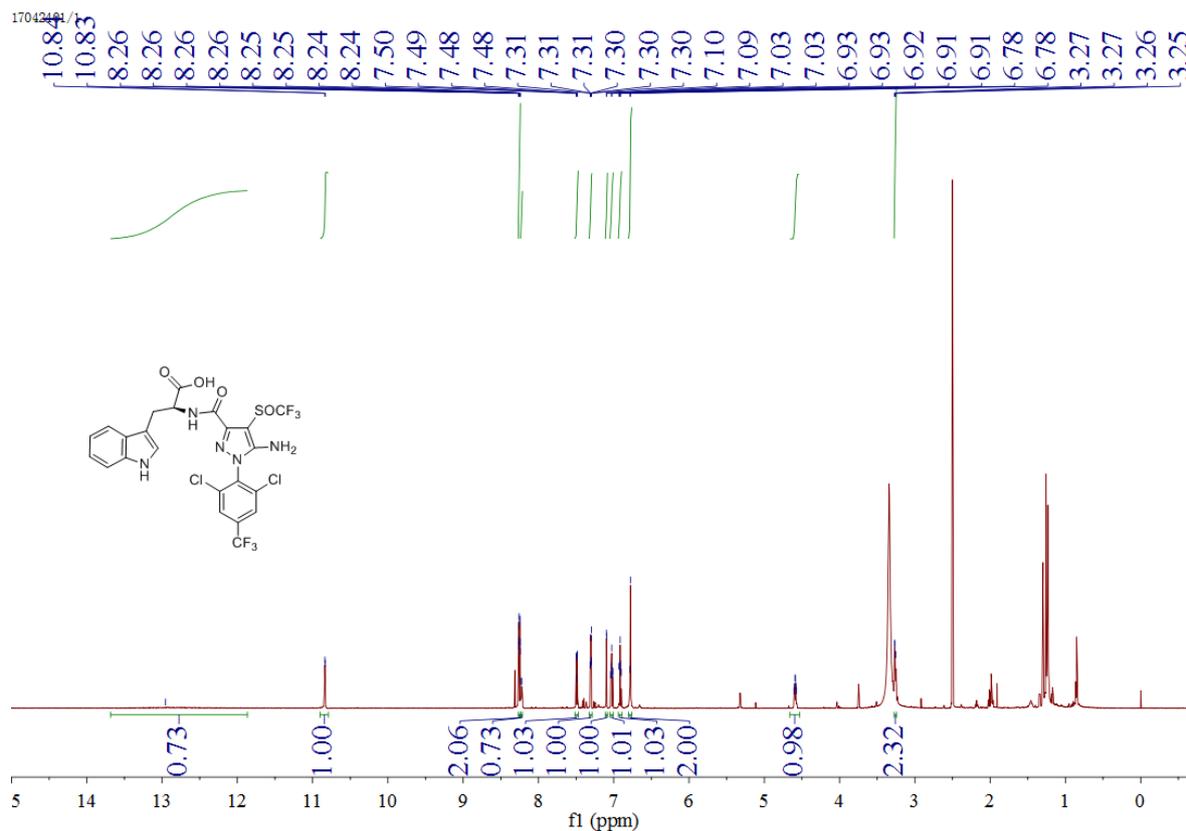
Figure S35  $^1\text{H}$  NMR spectra of **4e** in Chloroform-*d*Figure S36  $^{13}\text{C}$  NMR spectra of **4e** in Chloroform-*d*

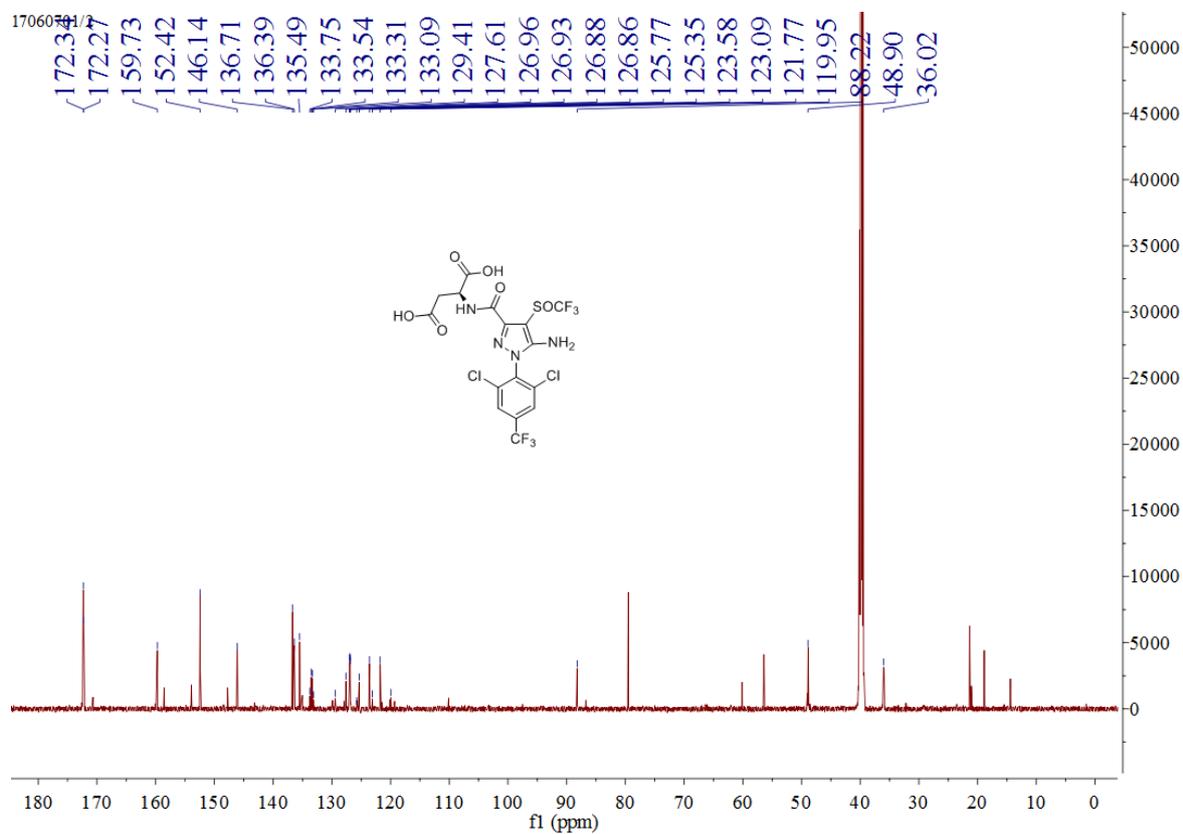
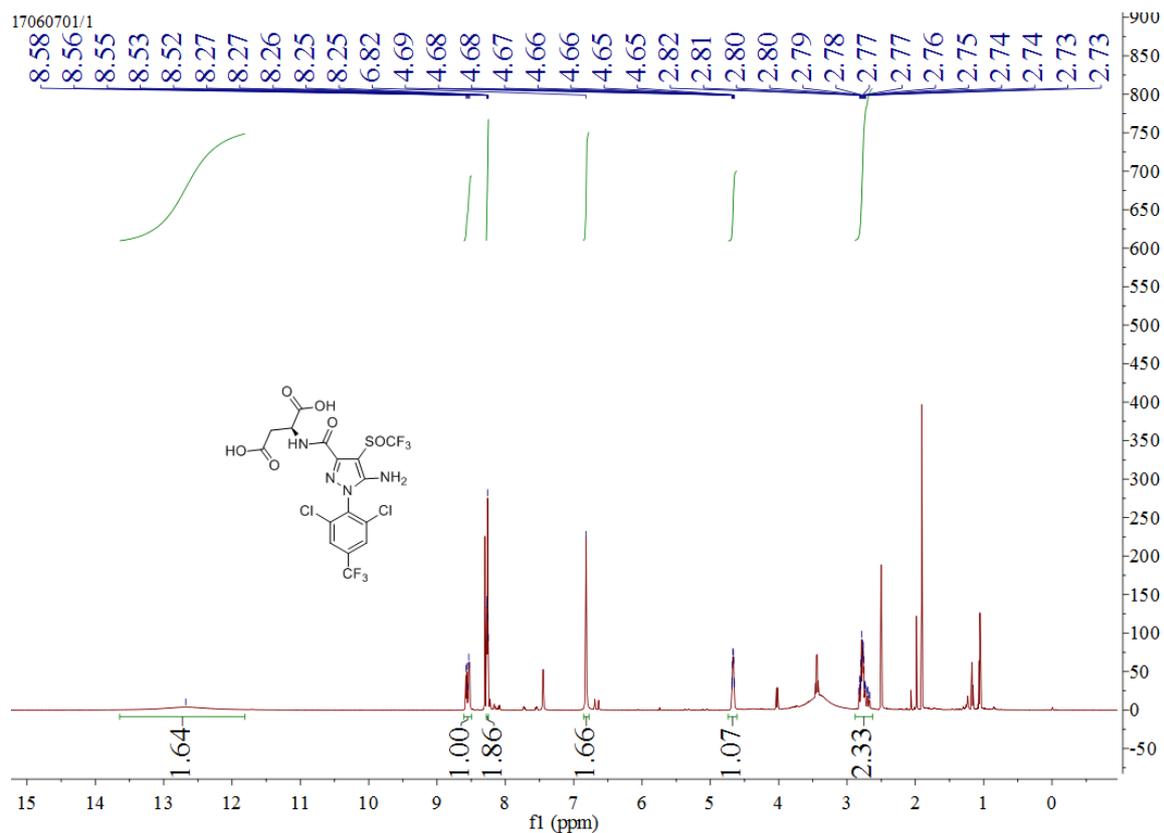
Figure S37  $^1\text{H}$  NMR spectra of 4f in  $\text{DMSO-}d_6$ Figure S38  $^{13}\text{C}$  NMR spectra of 4f in  $\text{DMSO-}d_6$

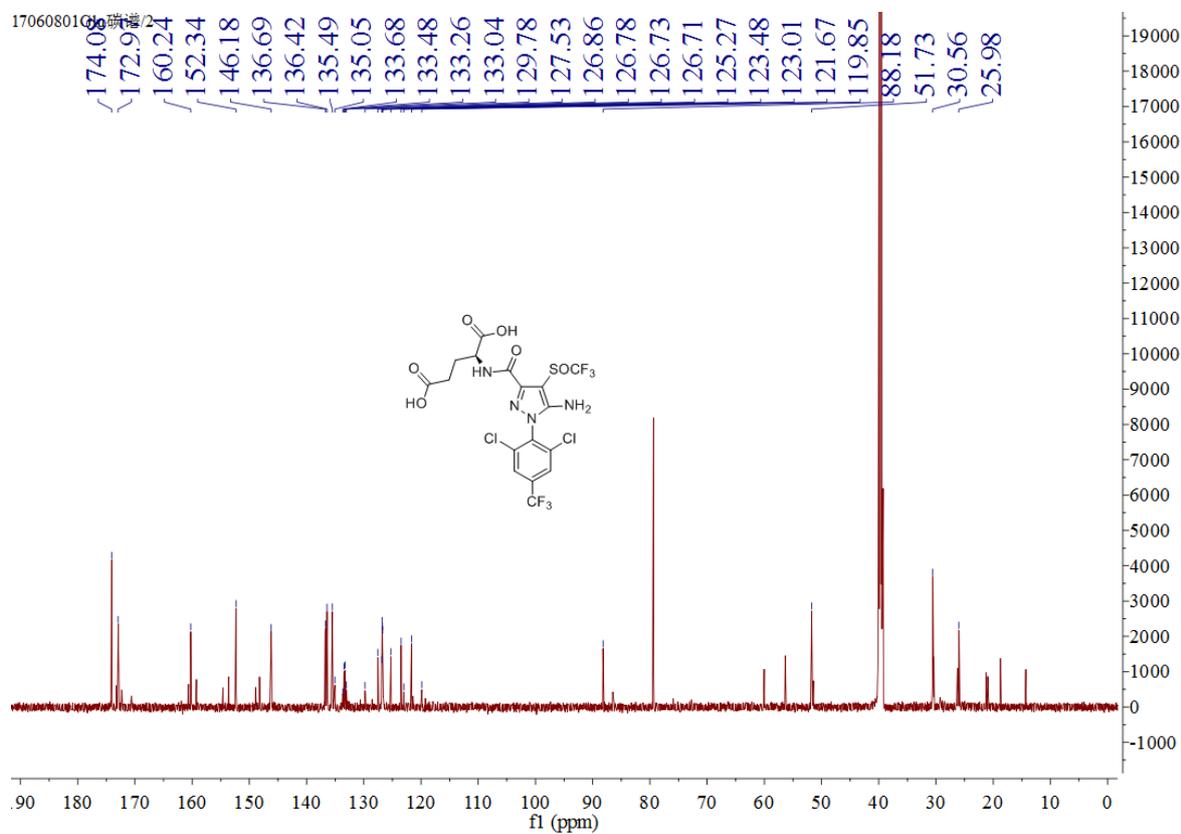
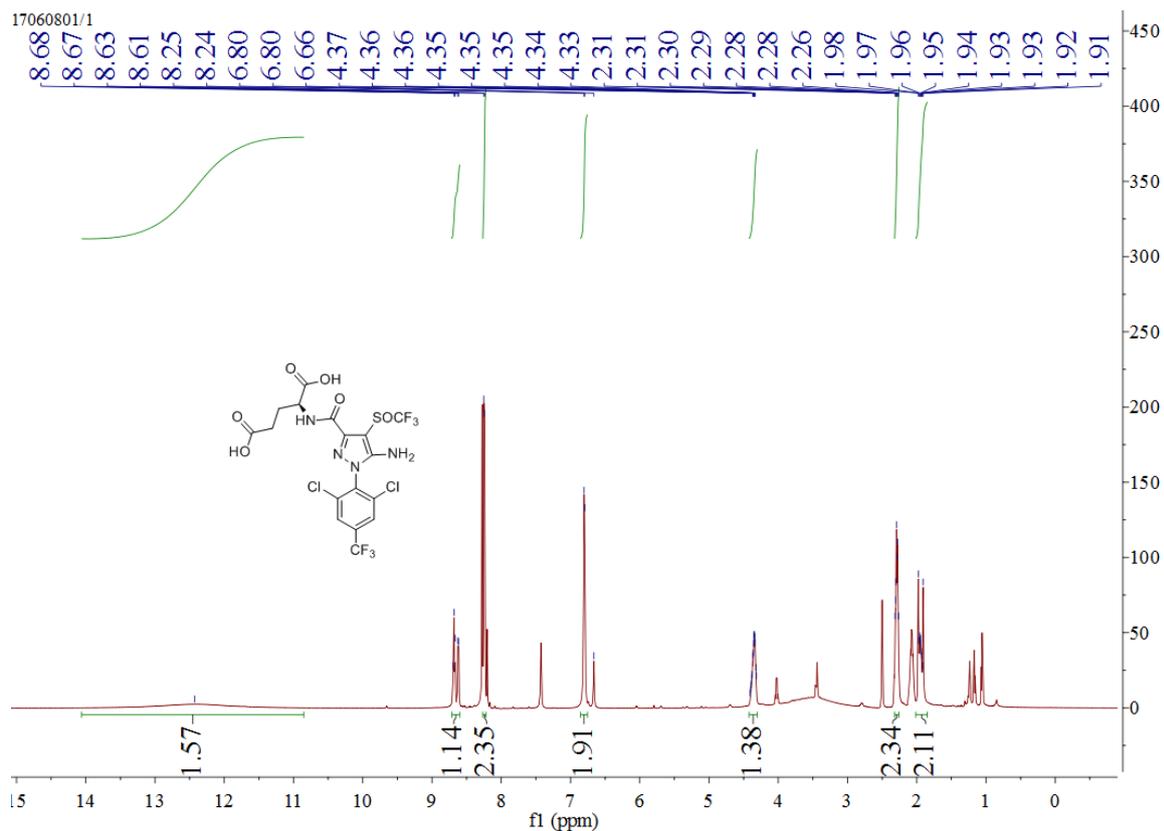












**Table S1.** The fatality rates of **4a-1** and fipronil against *Plutella xylostella*

Compounds <sup>a</sup>	12 h Fatality rate (%)	24 h Fatality rate (%)
<b>4a</b>	15.15	48.48
<b>4b</b>	32.26	80.65
<b>4c</b>	3.33	66.67
<b>4d</b>	6.06	84.85
<b>4e</b>	9.09	78.79
<b>4f</b>	8.11	40.54
<b>4g</b>	3.33	55.67
<b>4h</b>	0.00	32.26
<b>4i</b>	8.57	68.57
<b>4j</b>	0.00	12.50
<b>4k</b>	15.63	81.25
<b>4l</b>	46.67	86.67
Fipronil	100.00	100.00

<sup>a</sup> at the concentration of 100 mg/mL.