

## Supplementary Material

*N,N*-Dialkyl-*N'*-Chlorosulfonyl Chloroformamidines in Heterocyclic Synthesis.Part XI. Some Substitution Reactions of Pyrazolo[1,5-*b*][1,2,4,6]thiatriazine

## 1,1-Dioxides.

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## EXPERIMENTAL

### *Methods and Materials*

Reactions were carried out under an atmosphere of nitrogen. Solvents (dichloromethane, chloroform, acetonitrile, pyridine) and triethylamine were distilled from calcium hydride. Tetrahydrofuran was distilled from sodium benzophenone ketyl. DMF was distilled under vacuum onto 4Å molecular sieves. Samples of CDCl<sub>3</sub> were passed it through activated aluminium oxide 70–290 mesh (Scharlau, activity degree 1, grain size 0.05–0.2 mm) to remove residual HCl and stored over silver foil/molecular sieves. Other reagents were used without further purification. Analytical TLC was performed on Merck Kieselgel 60 F<sub>254</sub> silica aluminium backed sheets, and was visualised under UV light and/or developed using a ninhydrin dip. Column chromatography was performed on Merck Kieselgel (particle size: 0.04-0.063 mm) silica gel.

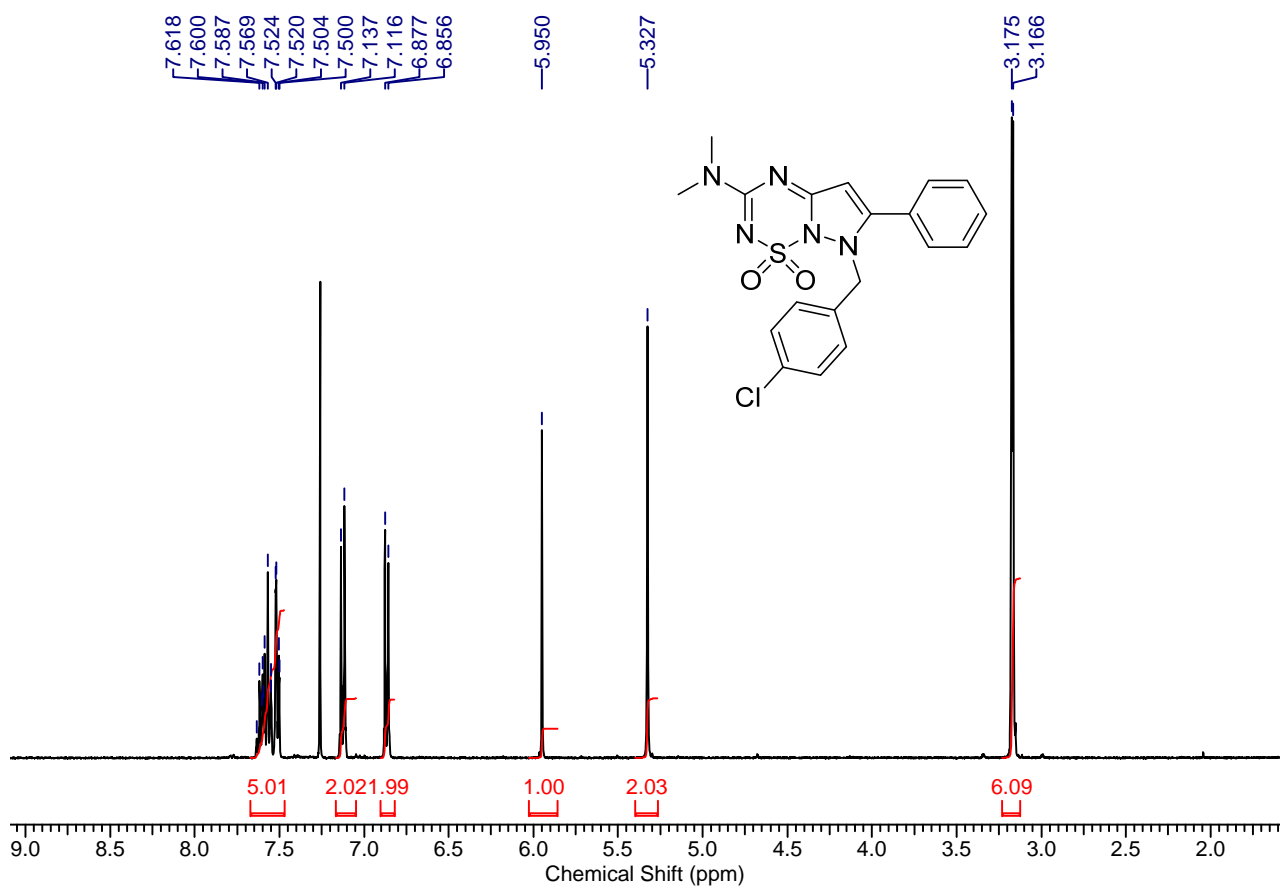
S1 NMR spectra were recorded with a Bruker UltraShield Avance III 400 MHz or 600 MHz NMR Spectrometer running the TopSpin 2.1 software package at 299 K and 293 K, respectively. CDCl<sub>3</sub> and (CD<sub>3</sub>)<sub>2</sub>SO (DMSO-*d*<sub>6</sub>) were used as solvents and as an internal lock. Chemical shifts (δ) are measured in ppm. <sup>1</sup>H NMR chemical shifts were referenced to δ 7.26 for CDCl<sub>3</sub> and δ 2.50 for DMSO-*d*<sub>6</sub>. <sup>13</sup>C NMR chemical shifts were referenced to δ 77.0 for CDCl<sub>3</sub> and δ 39.52 for DMSO-*d*<sub>6</sub>. Spectral data are reported using the following format: (1) chemical shift (ppm), (2) integration, (3) multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, dd=doublet of doublets, m=multiplet, br=broad), (4) *J*-coupling constant (Hz), (5) assignment. Copies of 2D NOESY NMR spectra are contained within the supplementary information. Chemical shifts and nOe cross peak patterns with significant correlations are circled in red.

Melting points were determined using a Gallenkamp hot-stage microscope and are uncorrected. X-Ray crystallography was performed at the Bragg Crystallography Facility at The University of Adelaide on a Mo-target Oxford Diffraction X-Calibur X-ray diffractometer. Electron Impact (EI) mass spectrometry (70eV) was performed on a ThermoQuest MAT95XP mass spectrometer. Only the major fragments are given with their relative abundances shown in parentheses. Accurate

mass measurements were taken with a resolution of 5000-10000 using PerFluoroKerosene (PFK) as an internal reference. High resolution mass spectrometry using electrospray ionization, positive ion with lockspray, was performed on a Waters Synapt HDMS instrument. Calibration: infusion of 0.5 mM sodium formate solution. Data acquisition: infusion of sample,  $m/z$  527.1588 from the sodium attached ion of raffinose employed as a lock mass signal in positive ion mode and the proton abstracted ion of raffinose ( $m/z$  503.1612) in the negative ion mode.

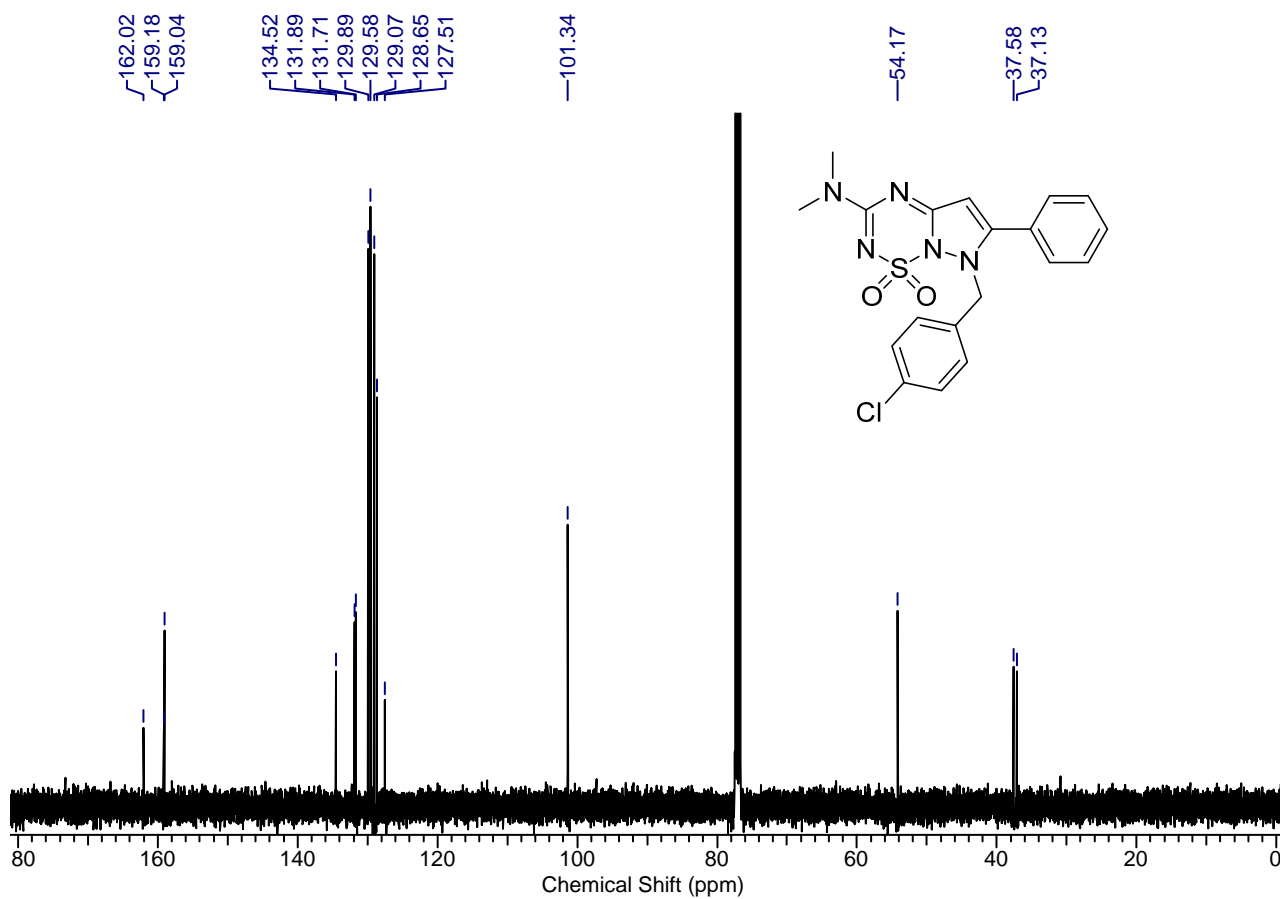
Experiments involving microwave irradiation were performed in a CEM Discover S-Class microwave reactor in reaction vessels (10 mL) loaded with combined starting materials in solvent (no more than 2 mL). The microwave reactor was operated in variable power (dynamic) mode with the following parameters: power 150 W, pressure maximum 20 bar, temperature 50 °C, stirring high, air/nitrogen cooling off. Ramp time to 50°C was 2 min. The sample was held at this temperature until the reaction reached completion, automatically modulating the power between 20–110W.

<sup>1</sup>H NMR spectrum of **6a** 400MHz (CDCl<sub>3</sub>)

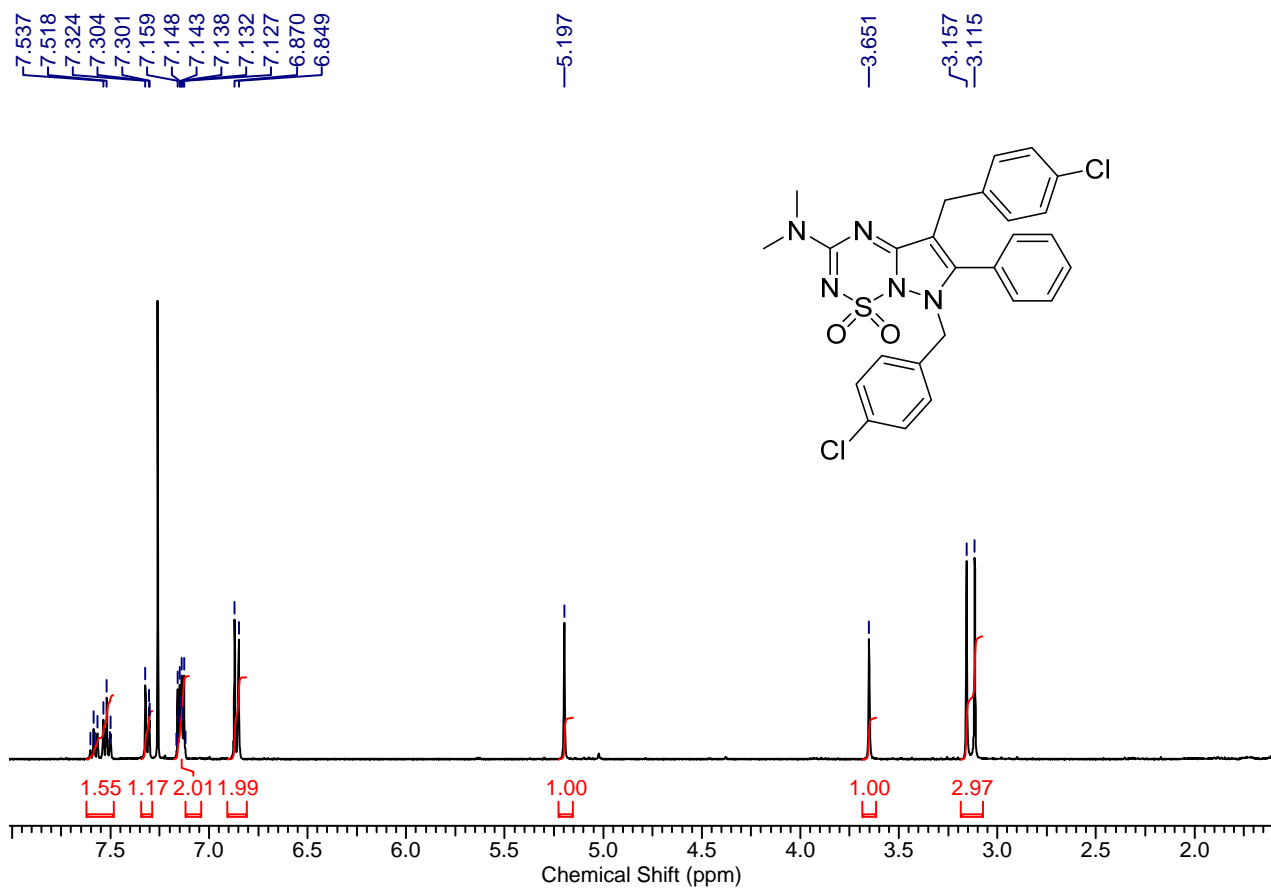


<sup>13</sup>C NMR spectrum of **6a** 100MHz (CDCl<sub>3</sub>)

S3

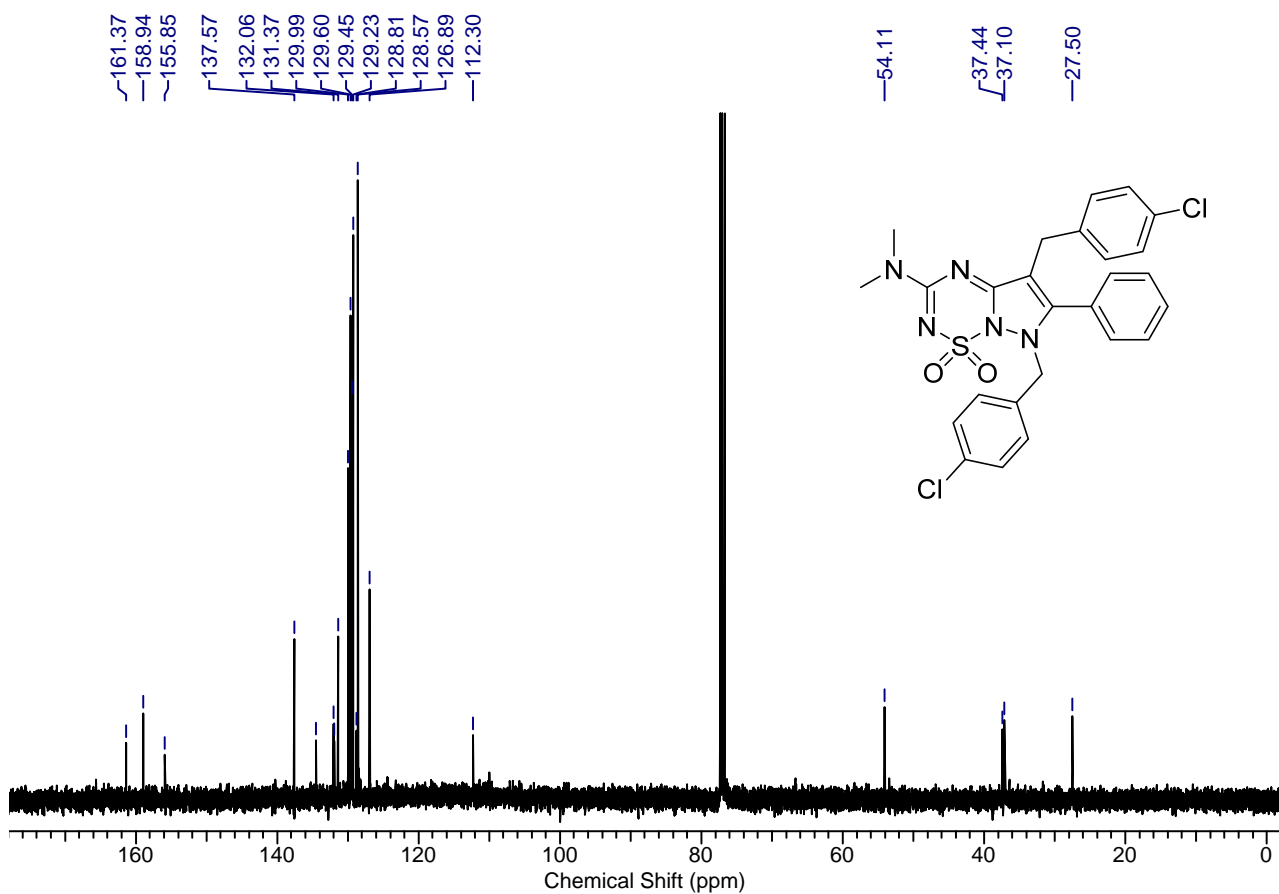


$^1\text{H}$  NMR spectrum of **7a** 400MHz ( $\text{CDCl}_3$ )

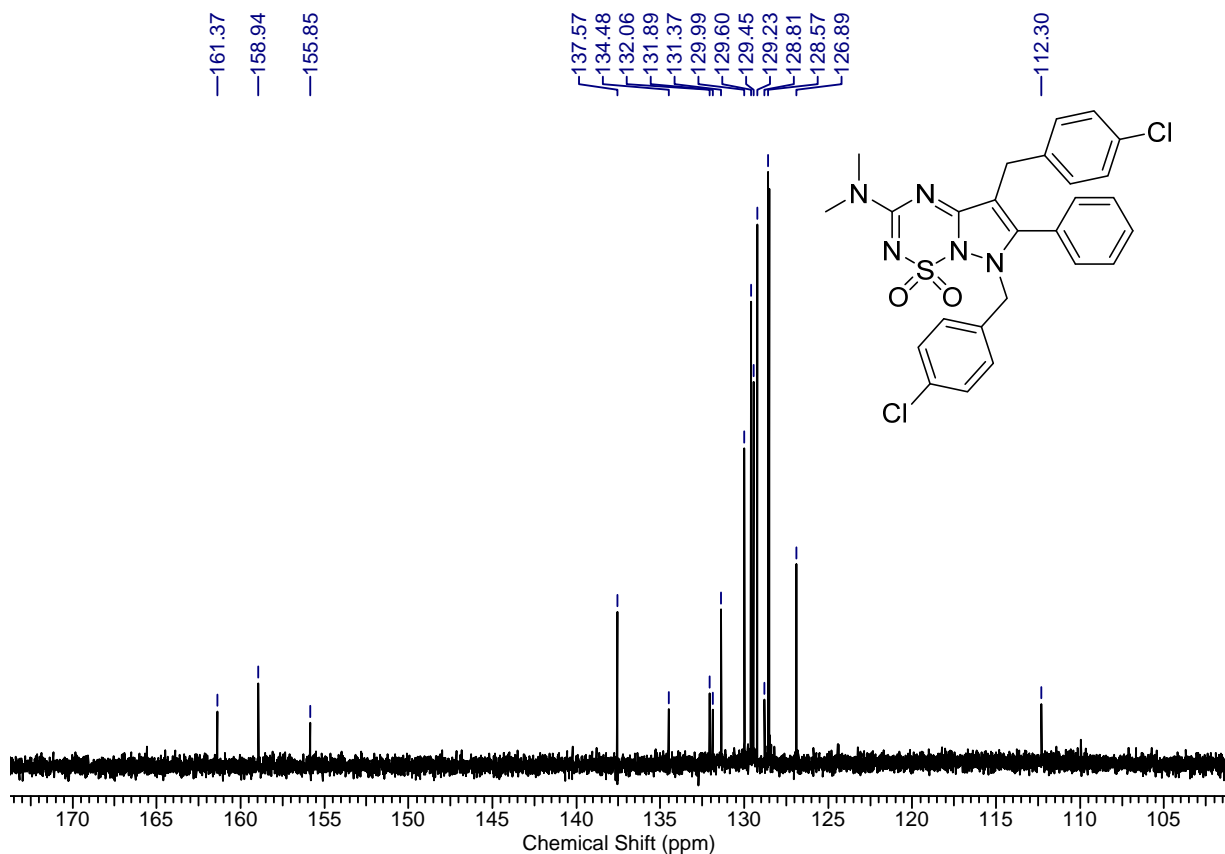


$^{13}\text{C}$  NMR spectrum of **7a** 100MHz ( $\text{CDCl}_3$ )

S4

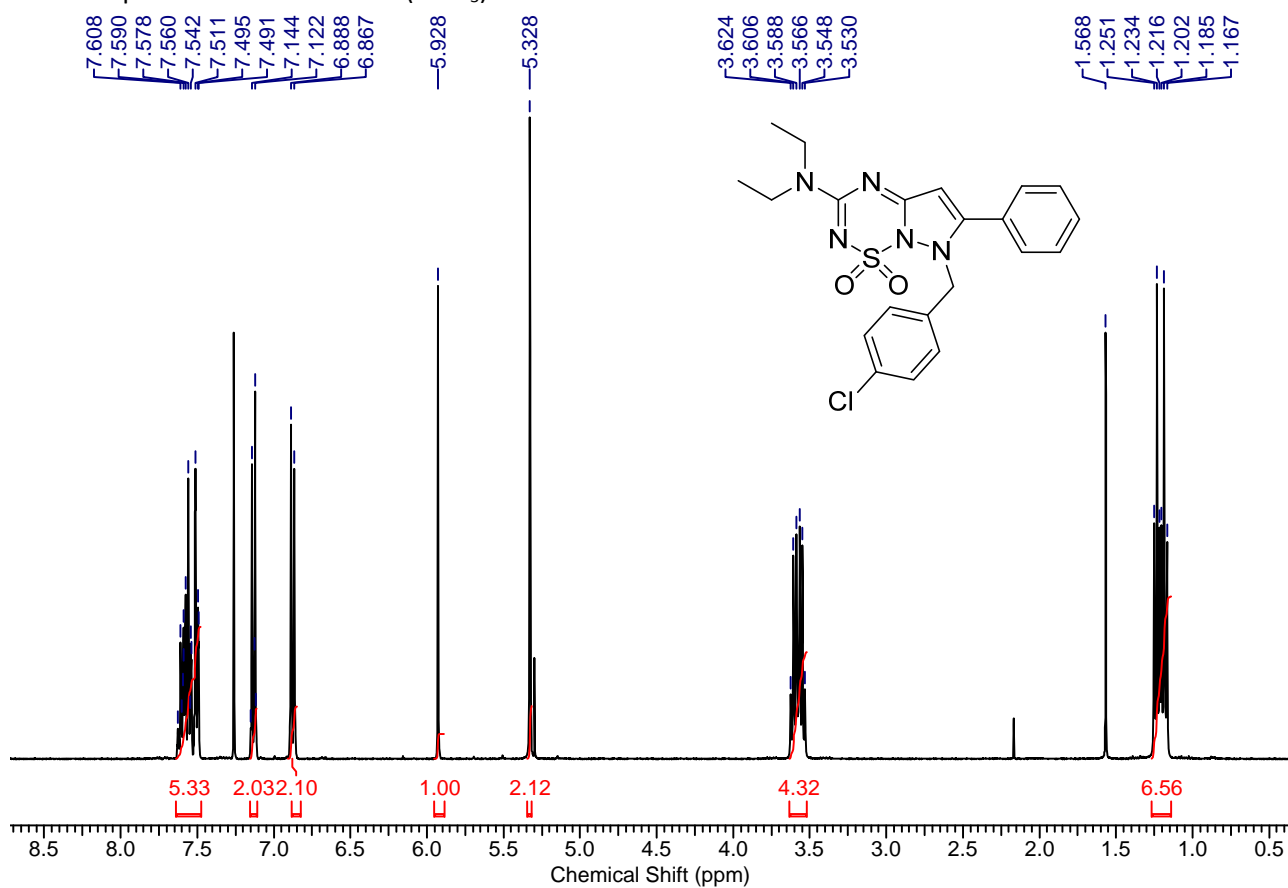


<sup>13</sup>C NMR spectrum of **7a** 100MHz (CDCl<sub>3</sub>) – expansion of region 100-175ppm

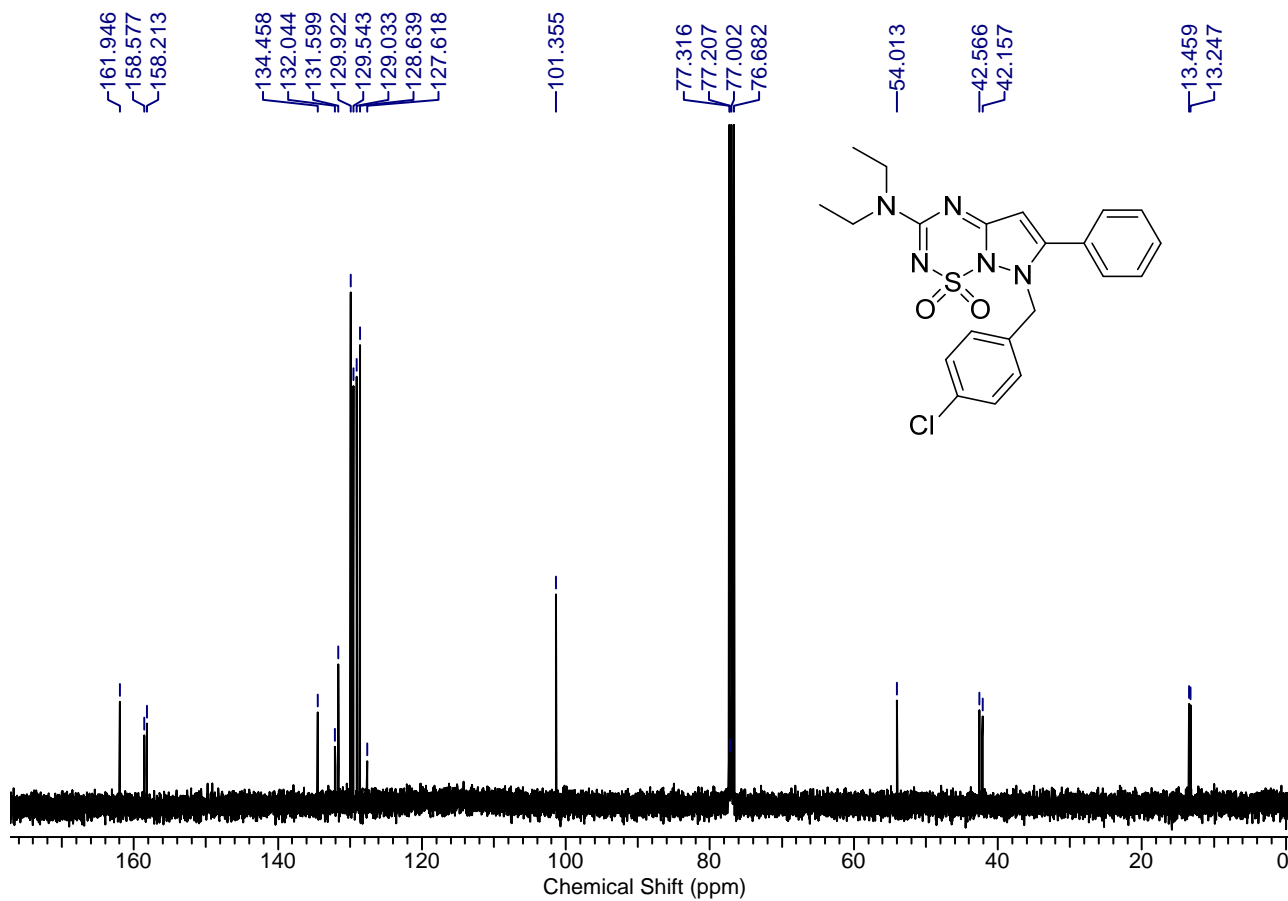


S5

<sup>1</sup>H NMR spectrum of **6b** 400MHz (CDCl<sub>3</sub>)

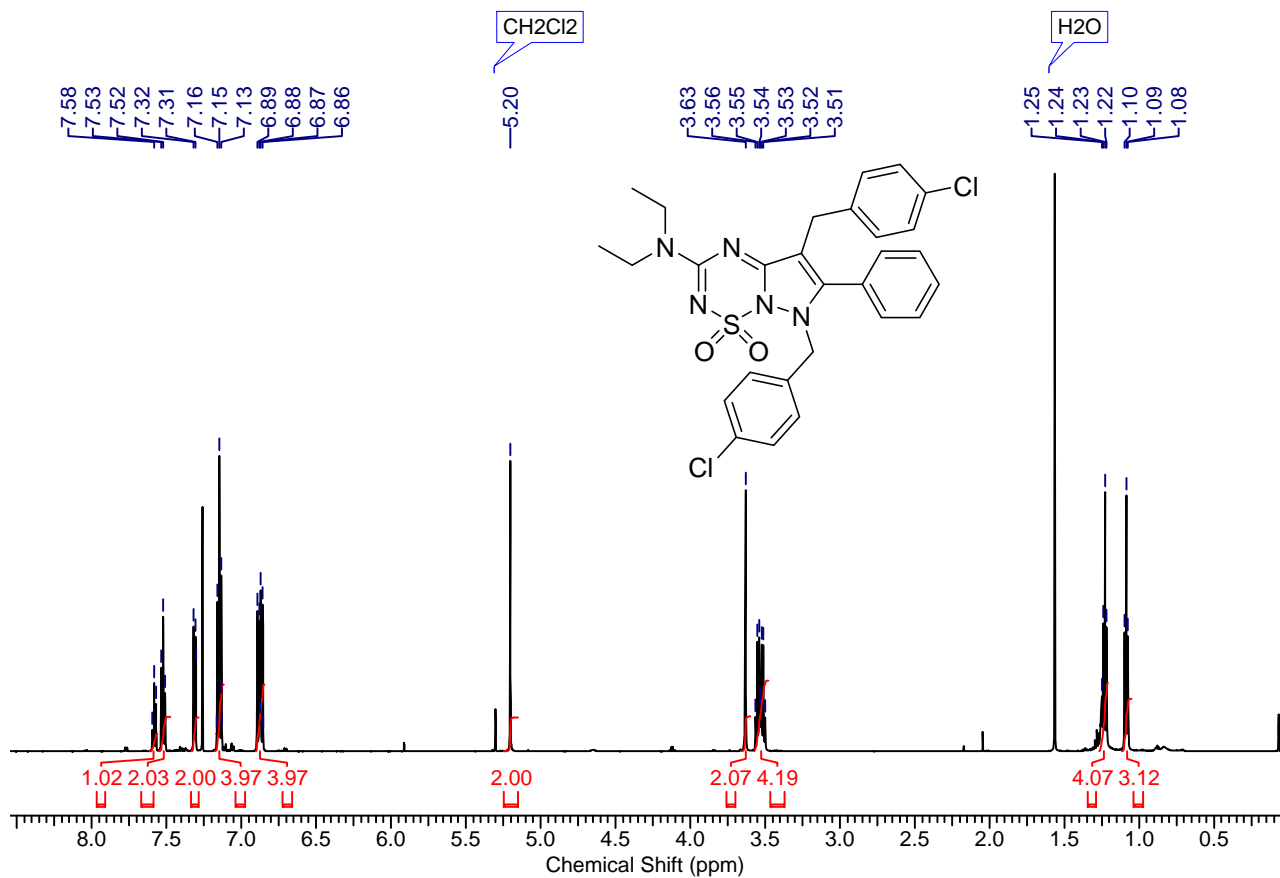


<sup>13</sup>C NMR spectrum of **6b** 100MHz (CDCl<sub>3</sub>)

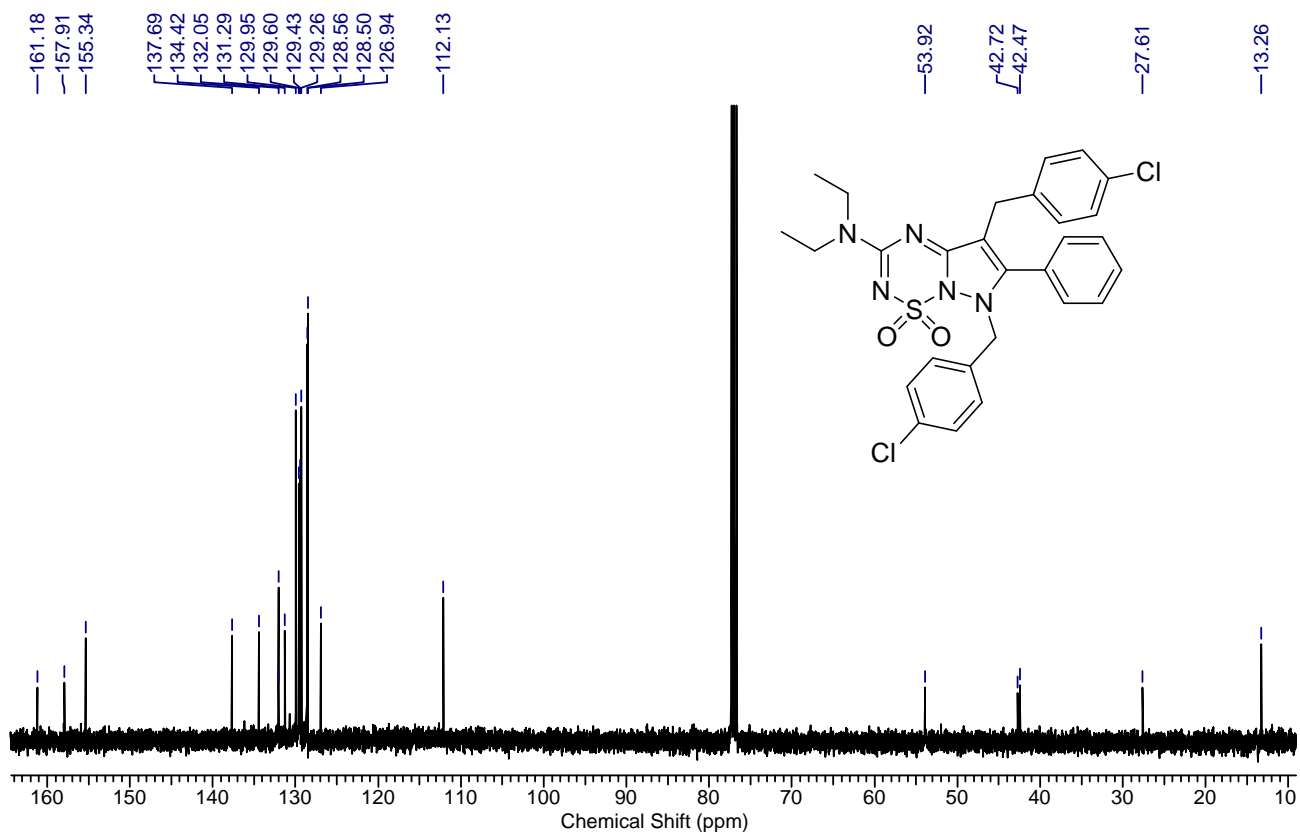


<sup>1</sup>H NMR spectrum of **7b** 600MHz (CDCl<sub>3</sub>)

S6

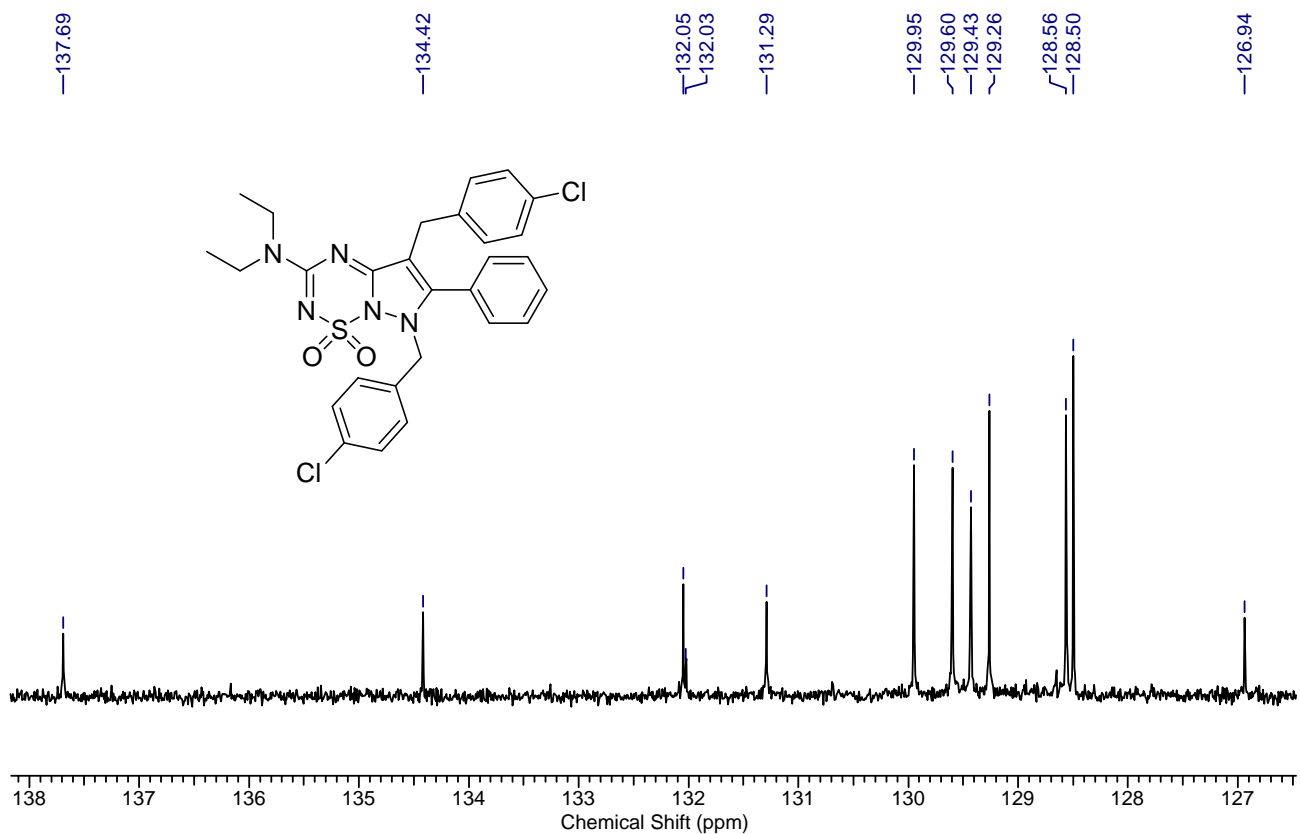


<sup>13</sup>C NMR spectrum of **7b** 100MHz (CDCl<sub>3</sub>)



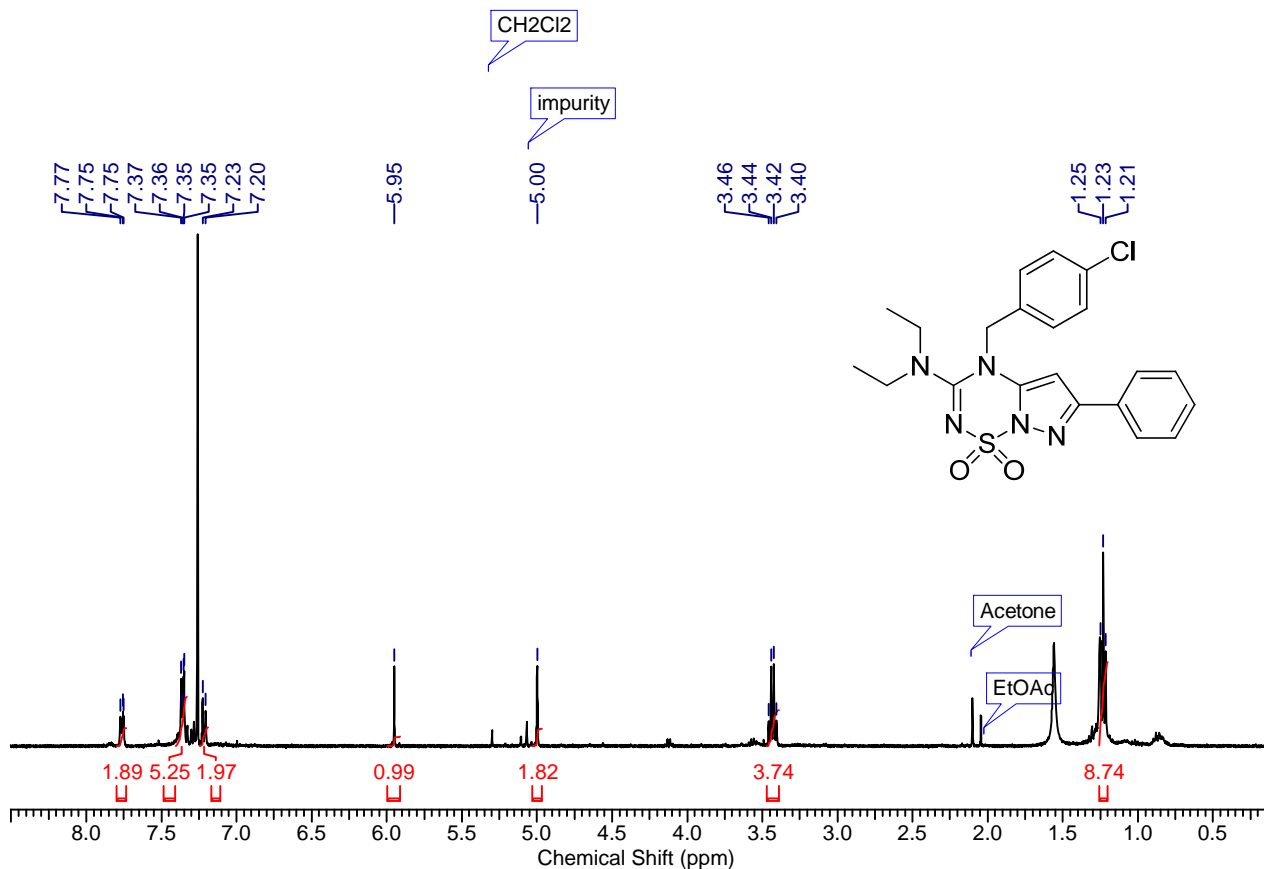
<sup>13</sup>C NMR spectrum of **7b** 100MHz (CDCl<sub>3</sub>) **zoom area of aromatic region**

S7



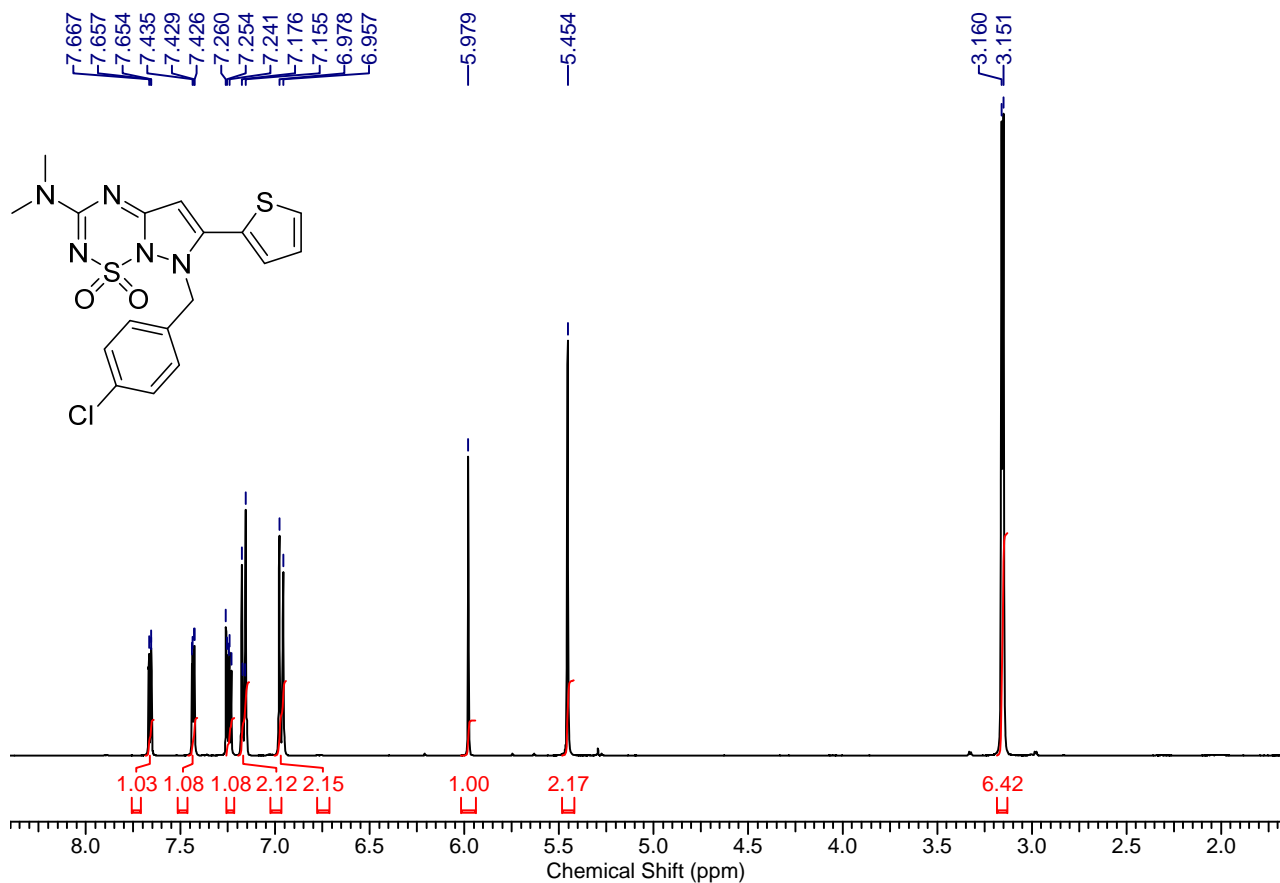


$^1\text{H}$  NMR spectrum of **8b** 400MHz ( $\text{CDCl}_3$ )

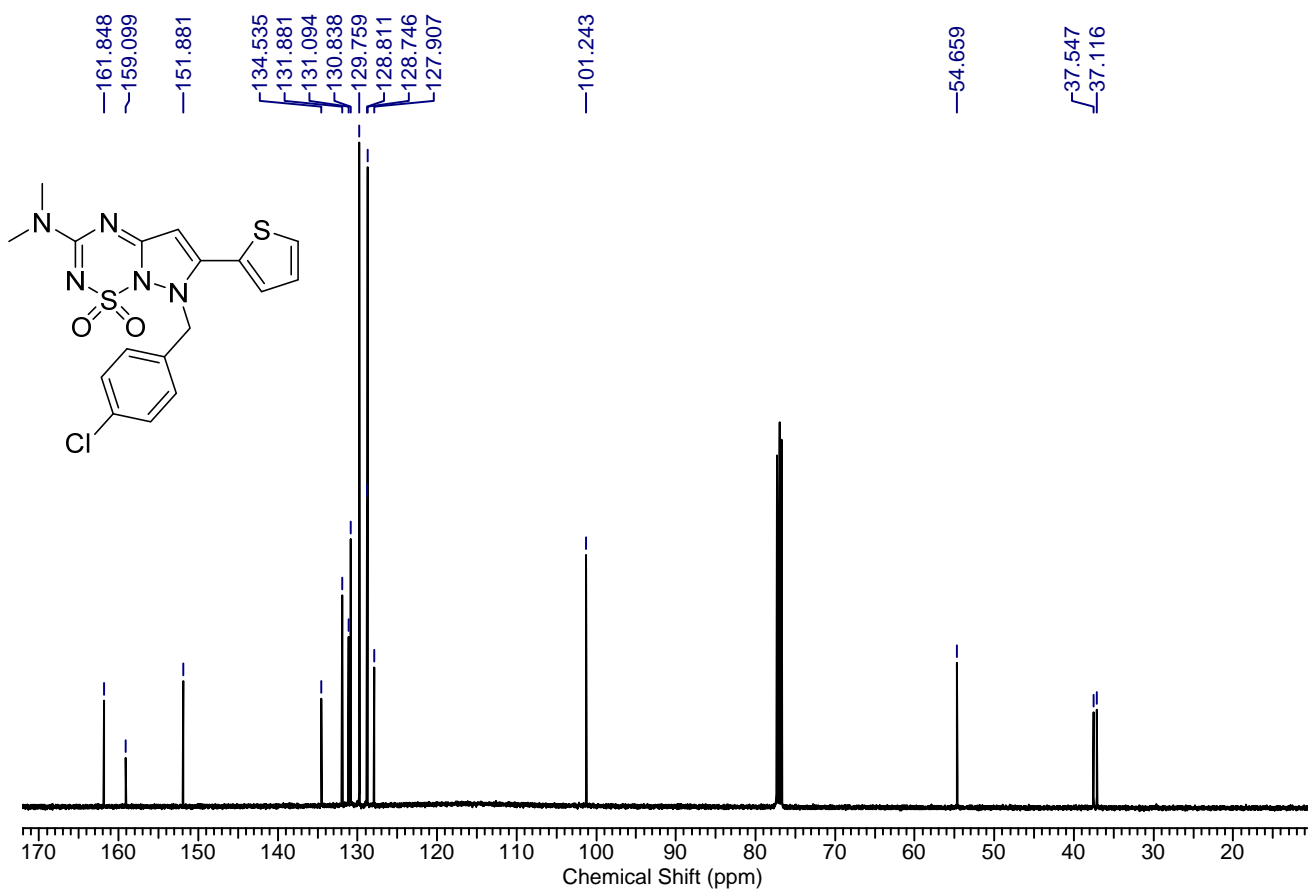


$^1\text{H}$  NMR spectrum of **6c** 400MHz ( $\text{CDCl}_3$ )

S8

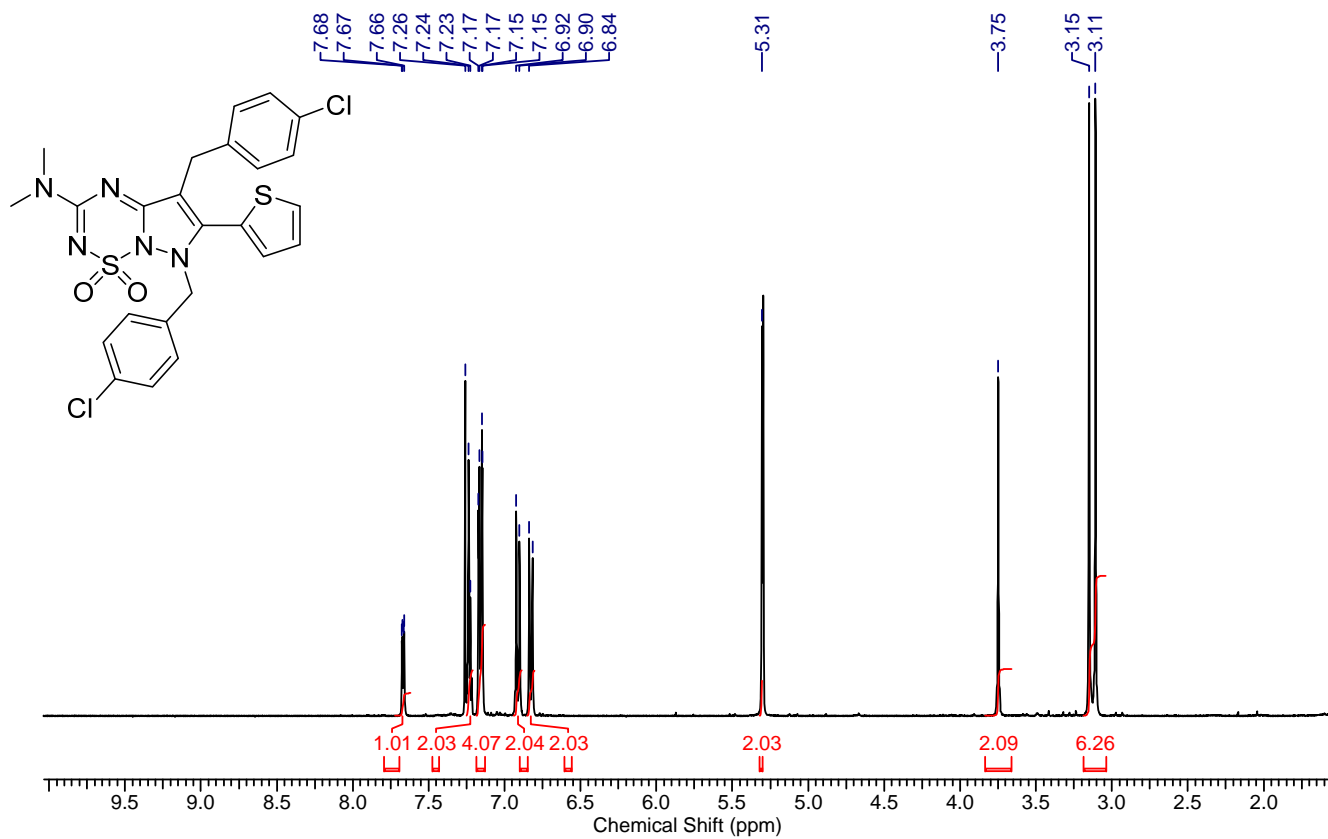


$^{13}\text{C}$  NMR spectrum of **6c** 100MHz ( $\text{CDCl}_3$ )

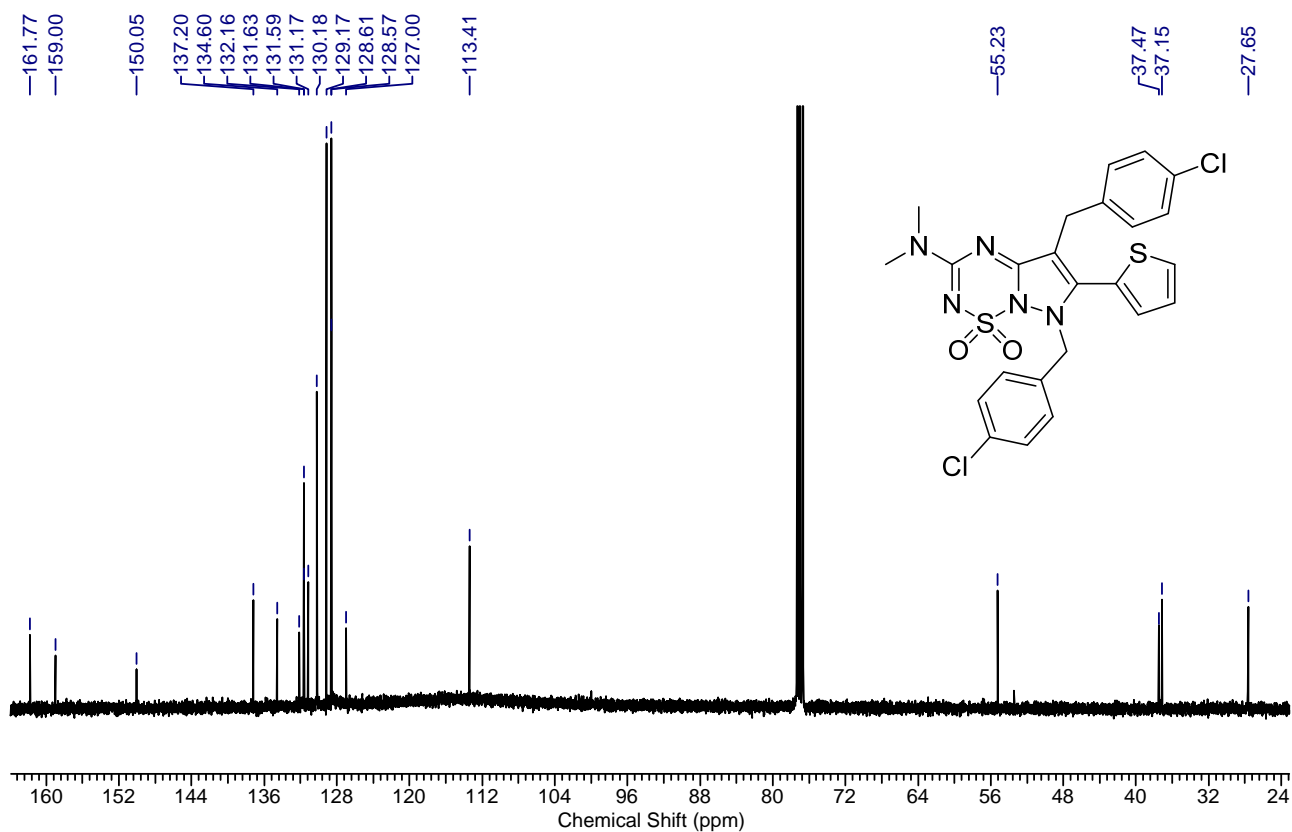


$^1\text{H}$  NMR spectrum of **7c** 400MHz ( $\text{CDCl}_3$ )

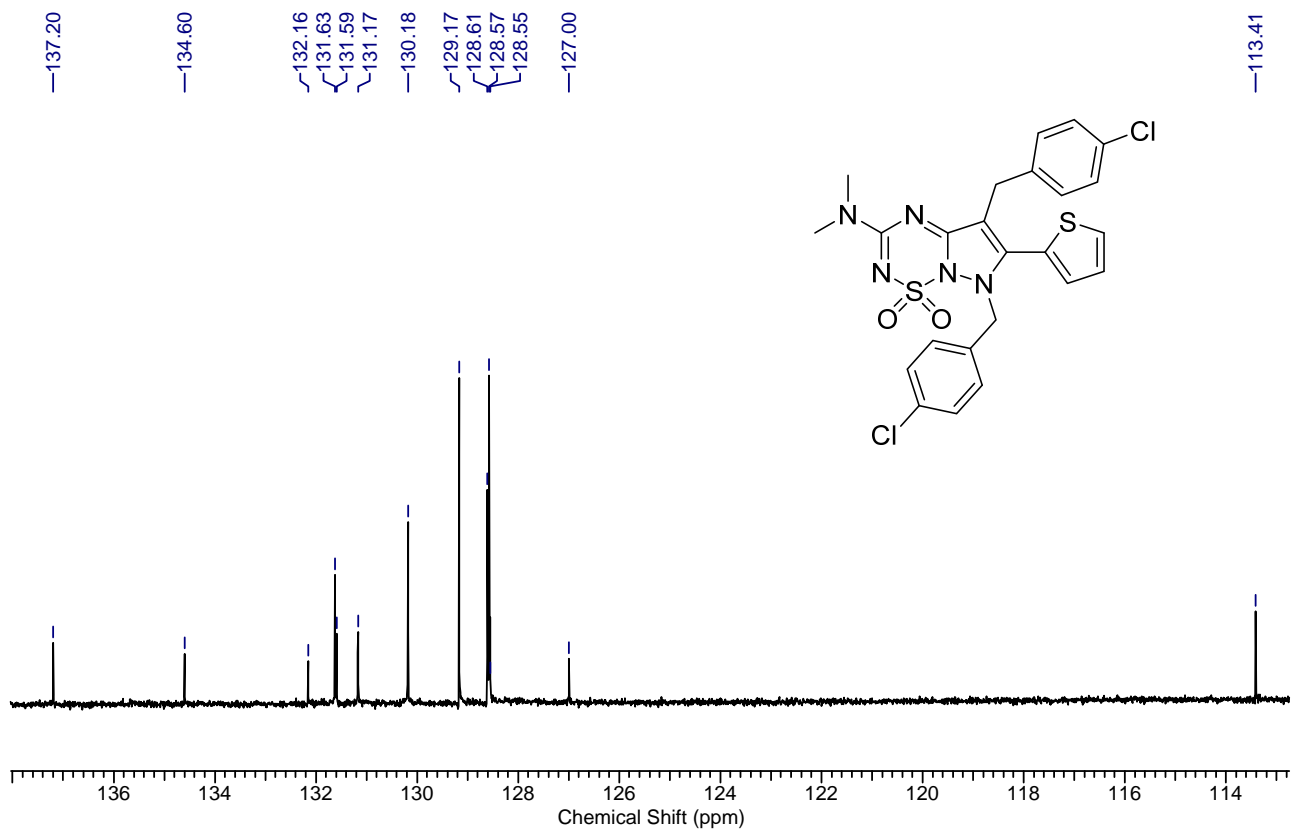
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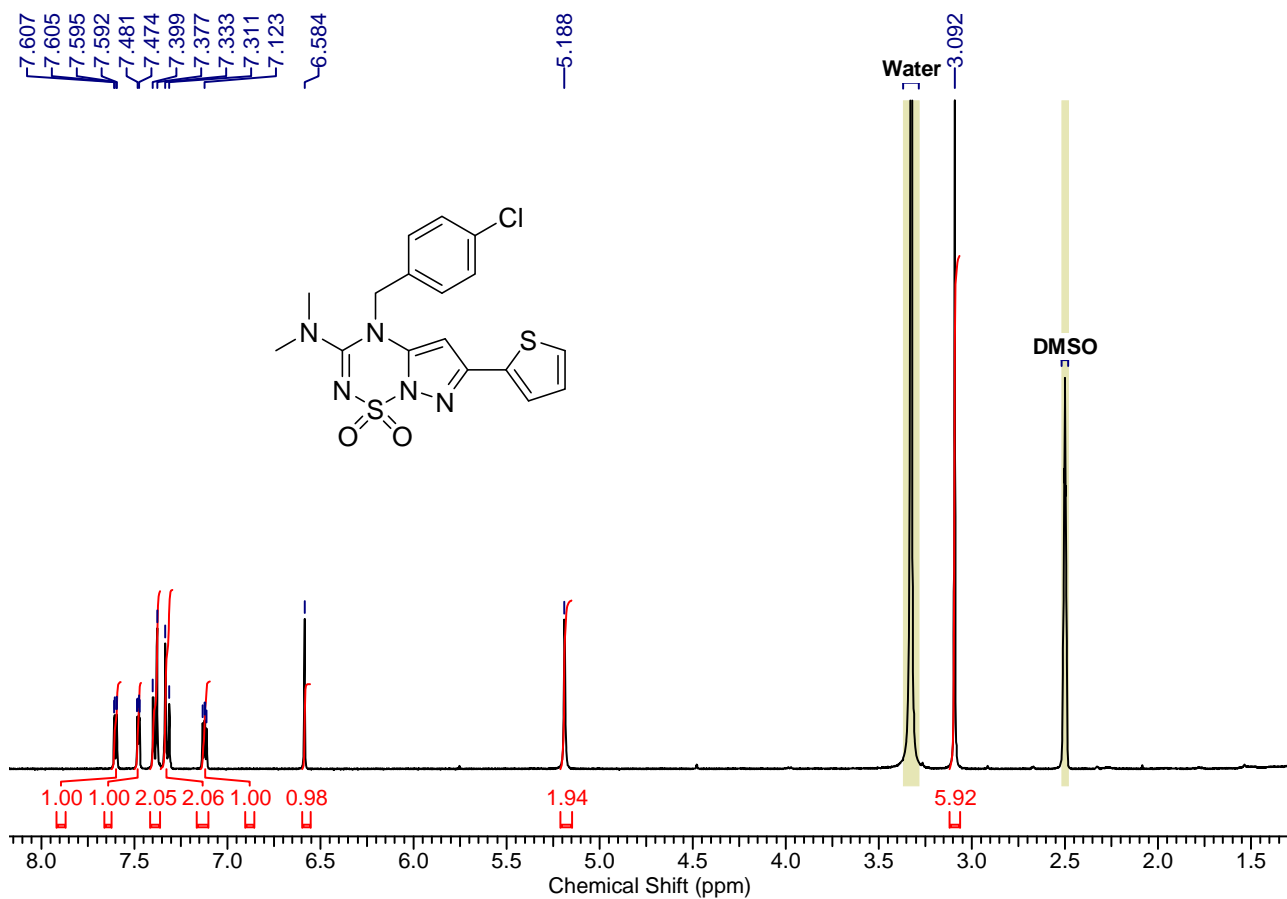
$^{13}\text{C}$  NMR spectrum of **7c** 100MHz ( $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR spectrum of **7c** 100MHz ( $\text{CDCl}_3$ ) **zoom area of aromatic region**

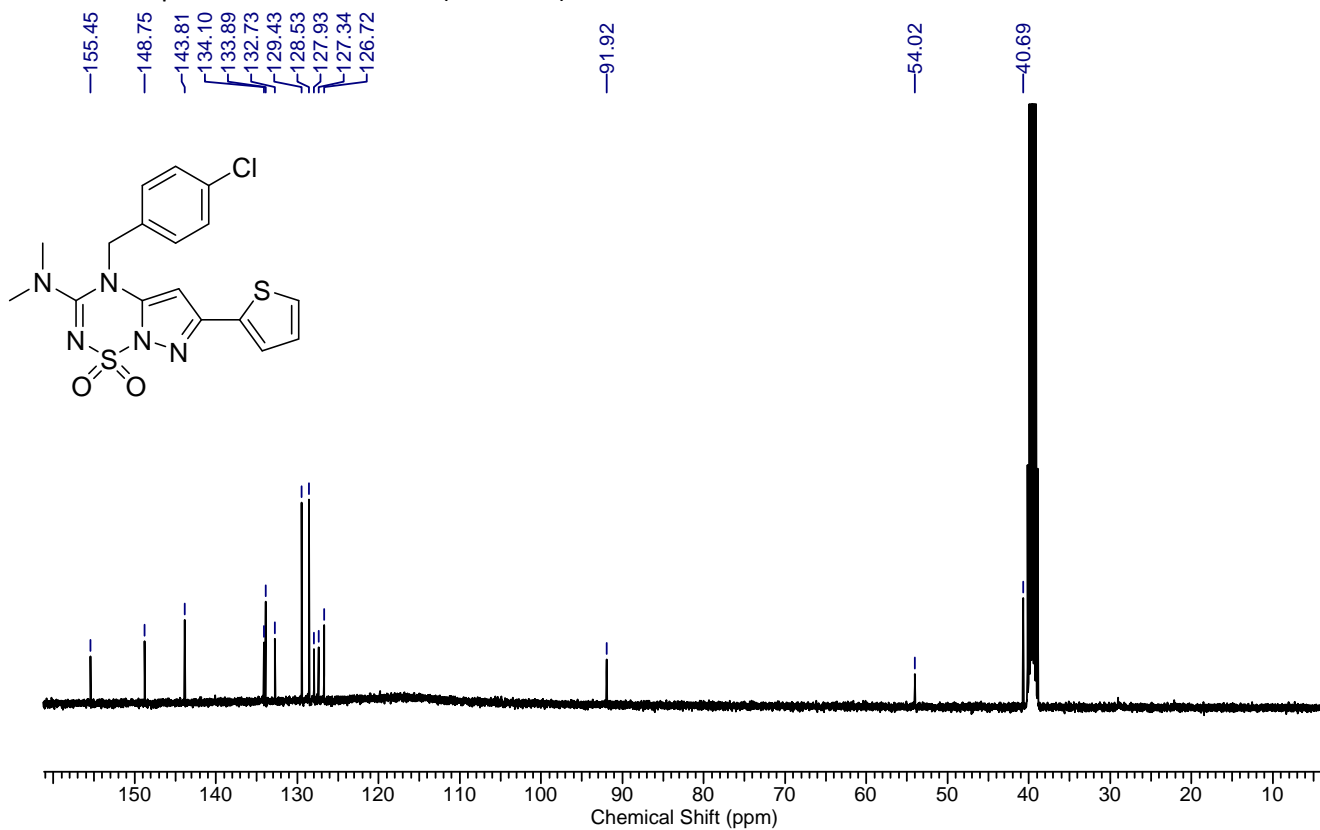


<sup>1</sup>H NMR spectrum of **8c** 400MHz (DMSO-*d*<sup>6</sup>)

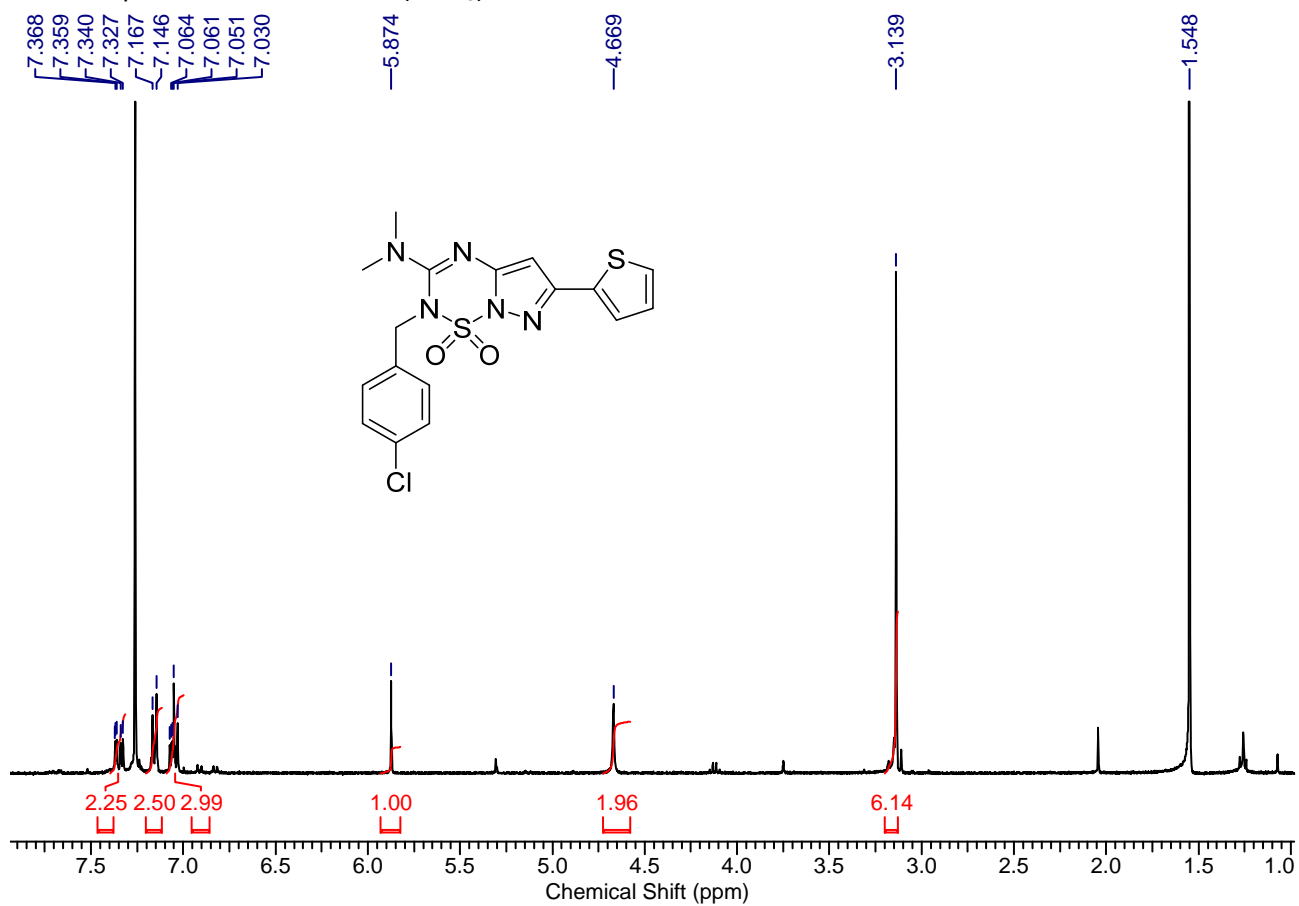


<sup>13</sup>C NMR spectrum of **8c** 100MHz (DMSO-*d*<sup>6</sup>)

S11

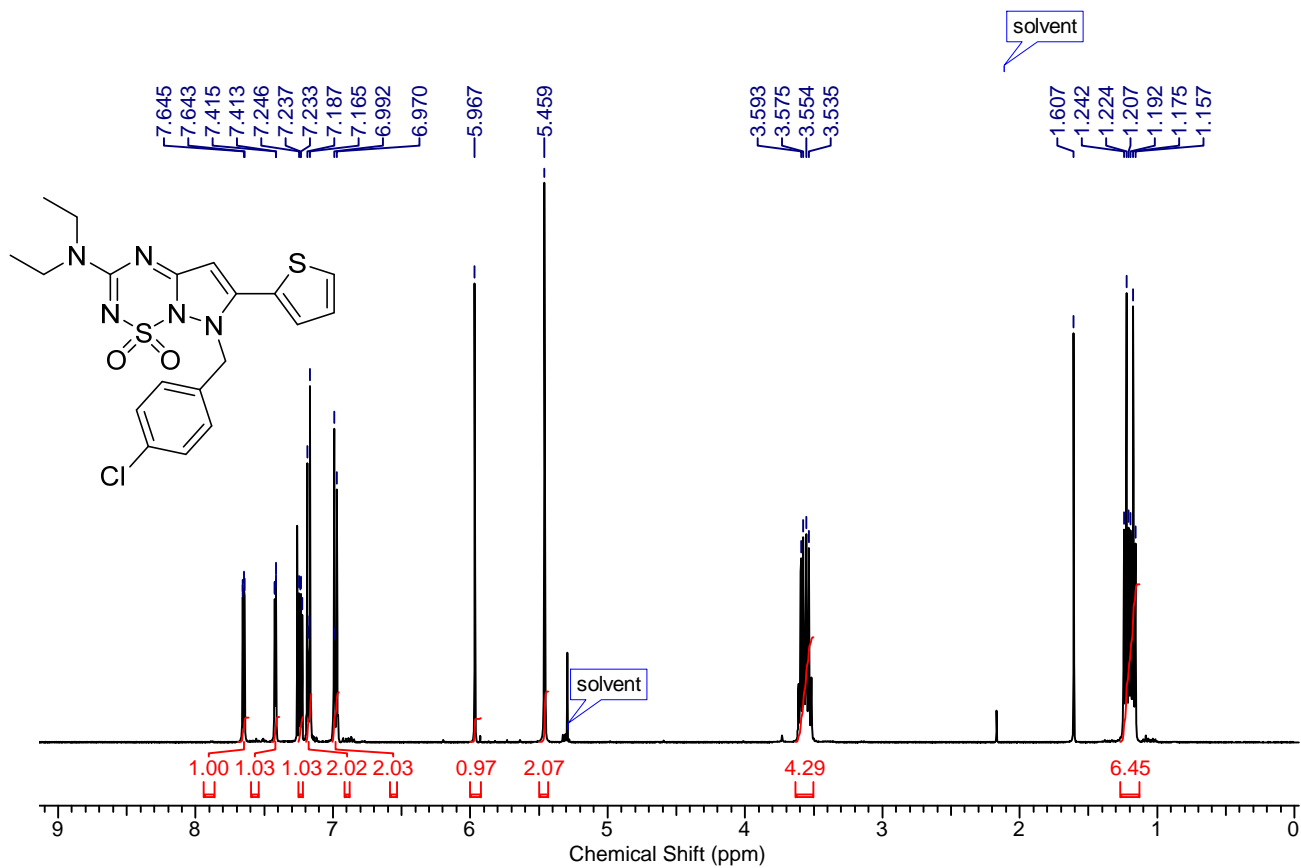


<sup>1</sup>H NMR spectrum of **9c** 400MHz (CDCl<sub>3</sub>)

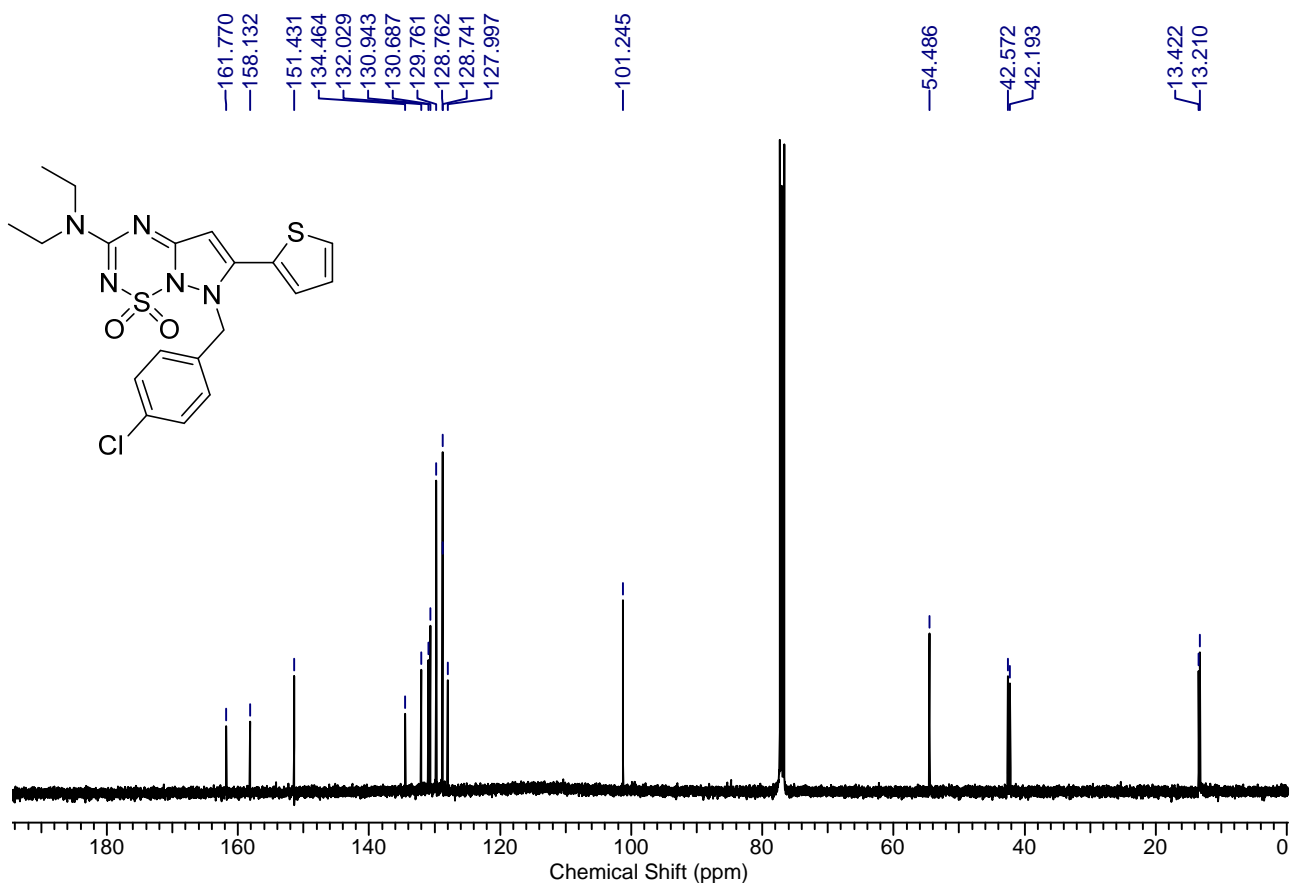


<sup>1</sup>H NMR spectrum of **6d** 400MHz (CDCl<sub>3</sub>)

S12

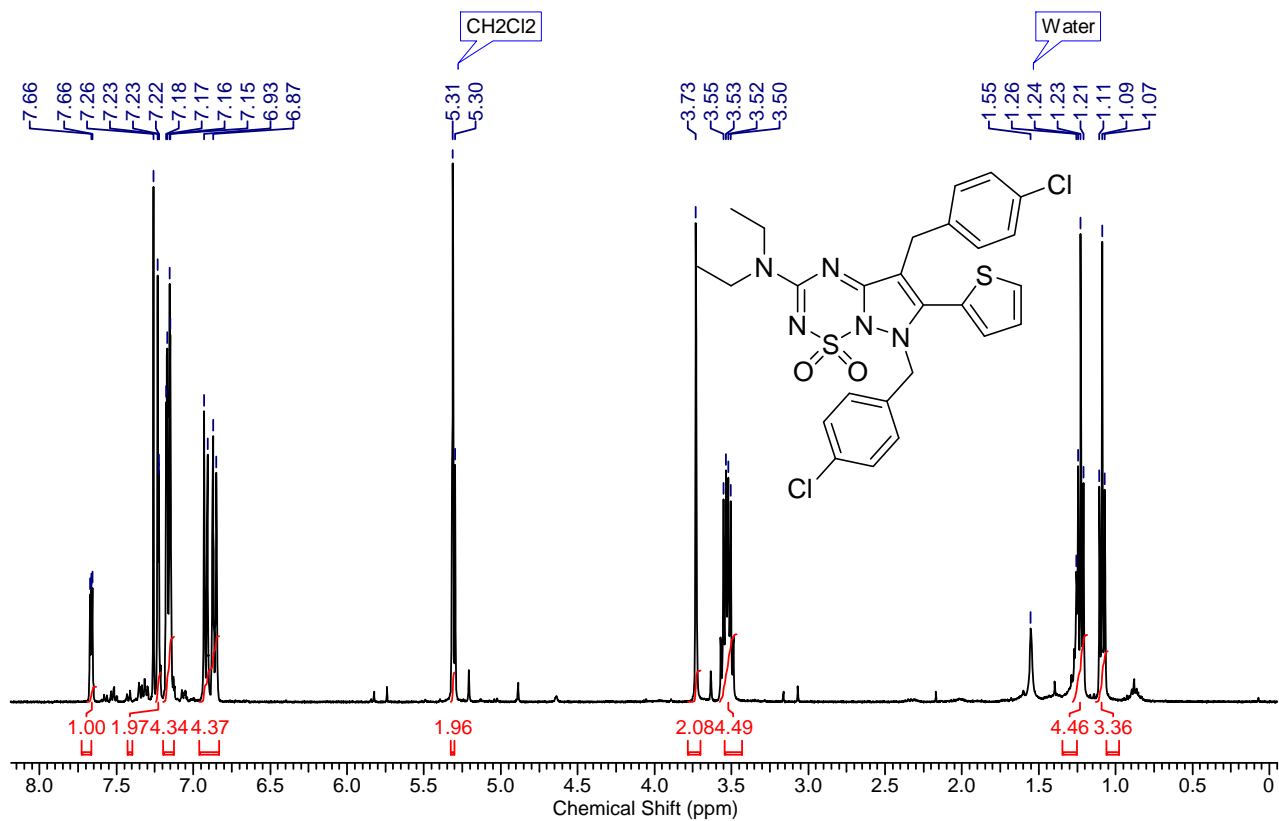


$^{13}\text{C}$  NMR spectrum of **6d** 100MHz ( $\text{CDCl}_3$ )

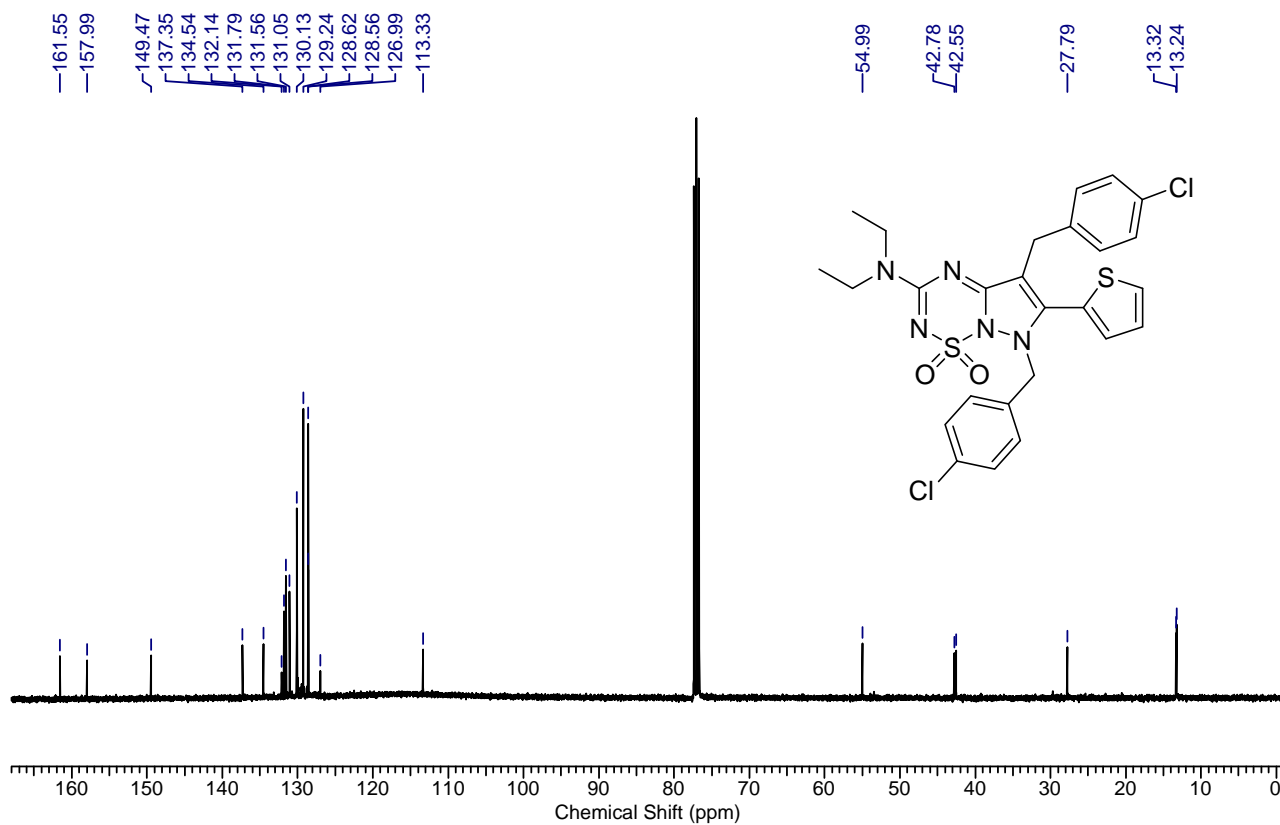


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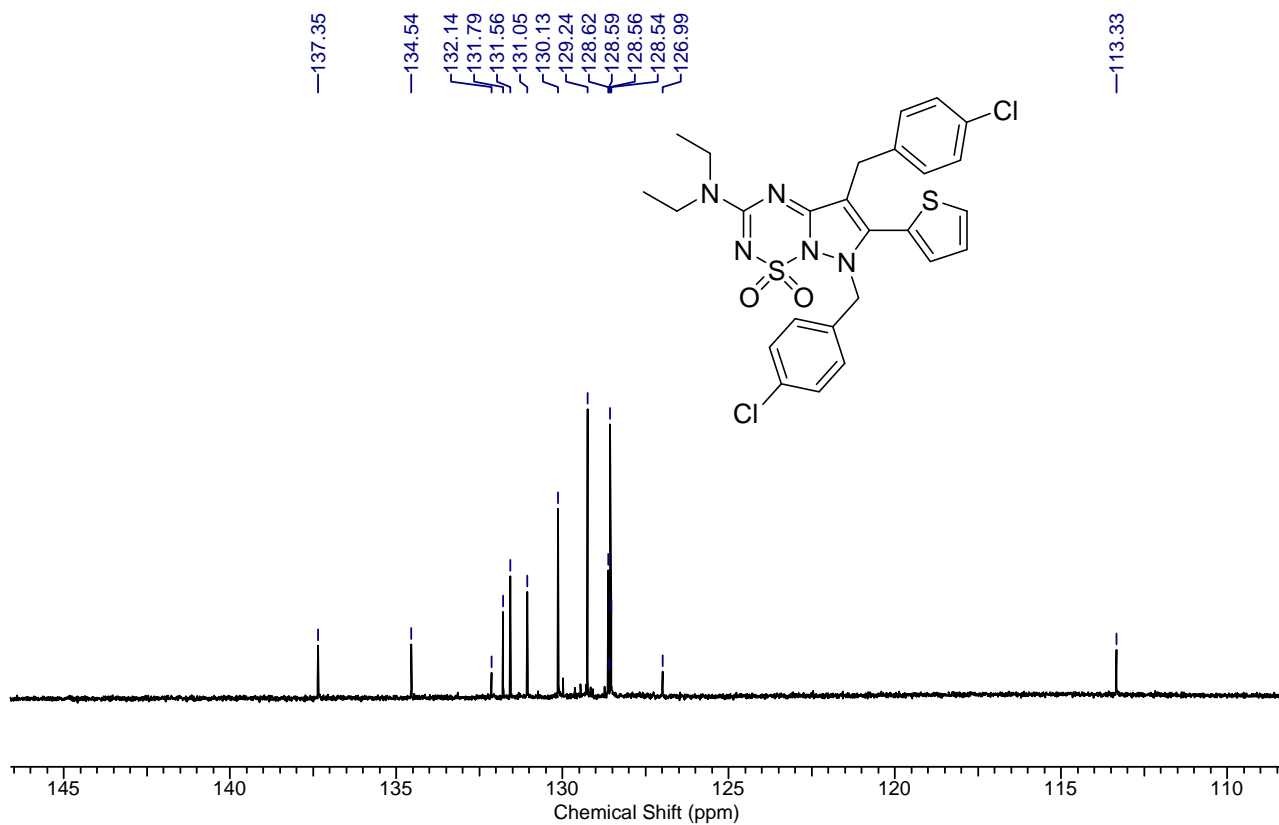
$^1\text{H}$  NMR spectrum of **7d** 400MHz ( $\text{CDCl}_3$ )



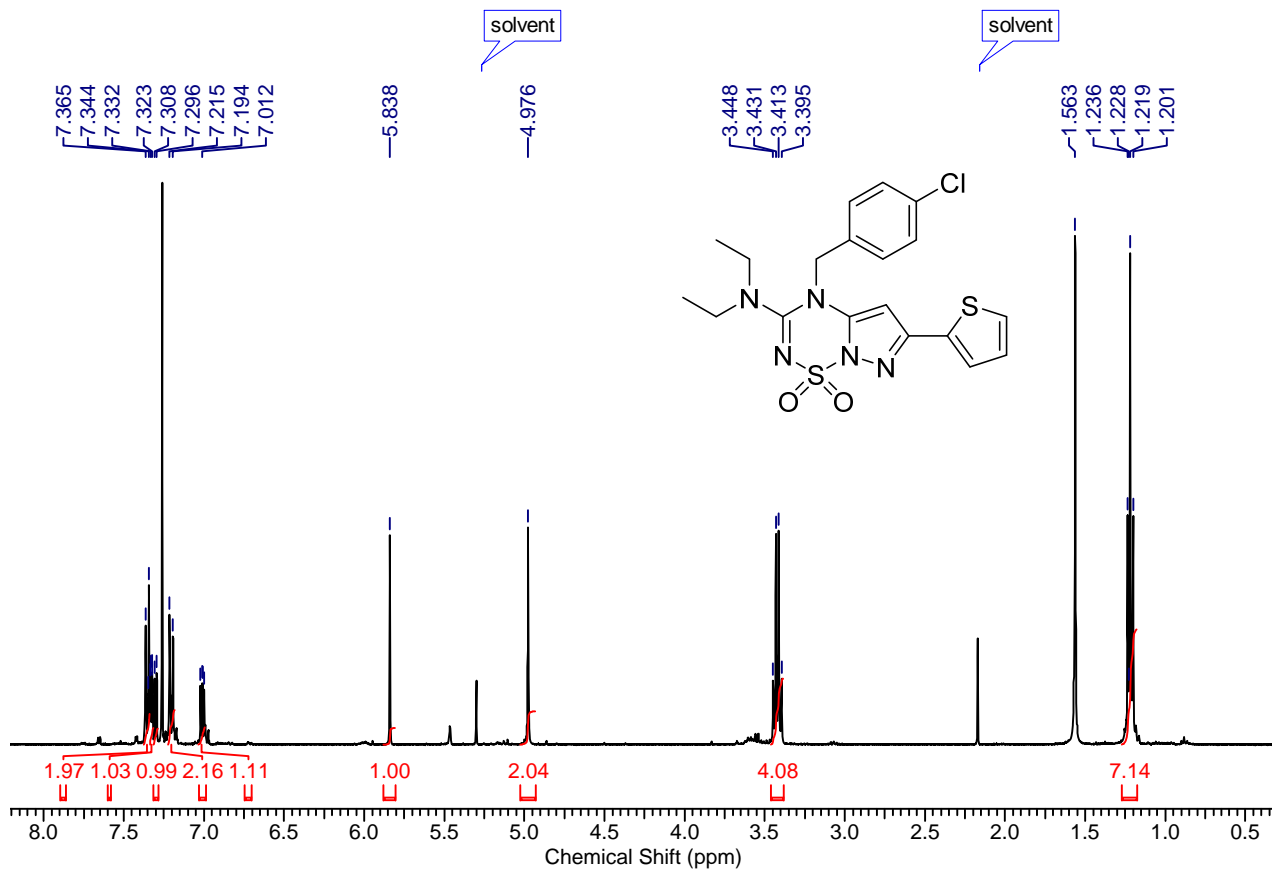
$^{13}\text{C}$  NMR spectrum of **7d** 100MHz ( $\text{CDCl}_3$ )



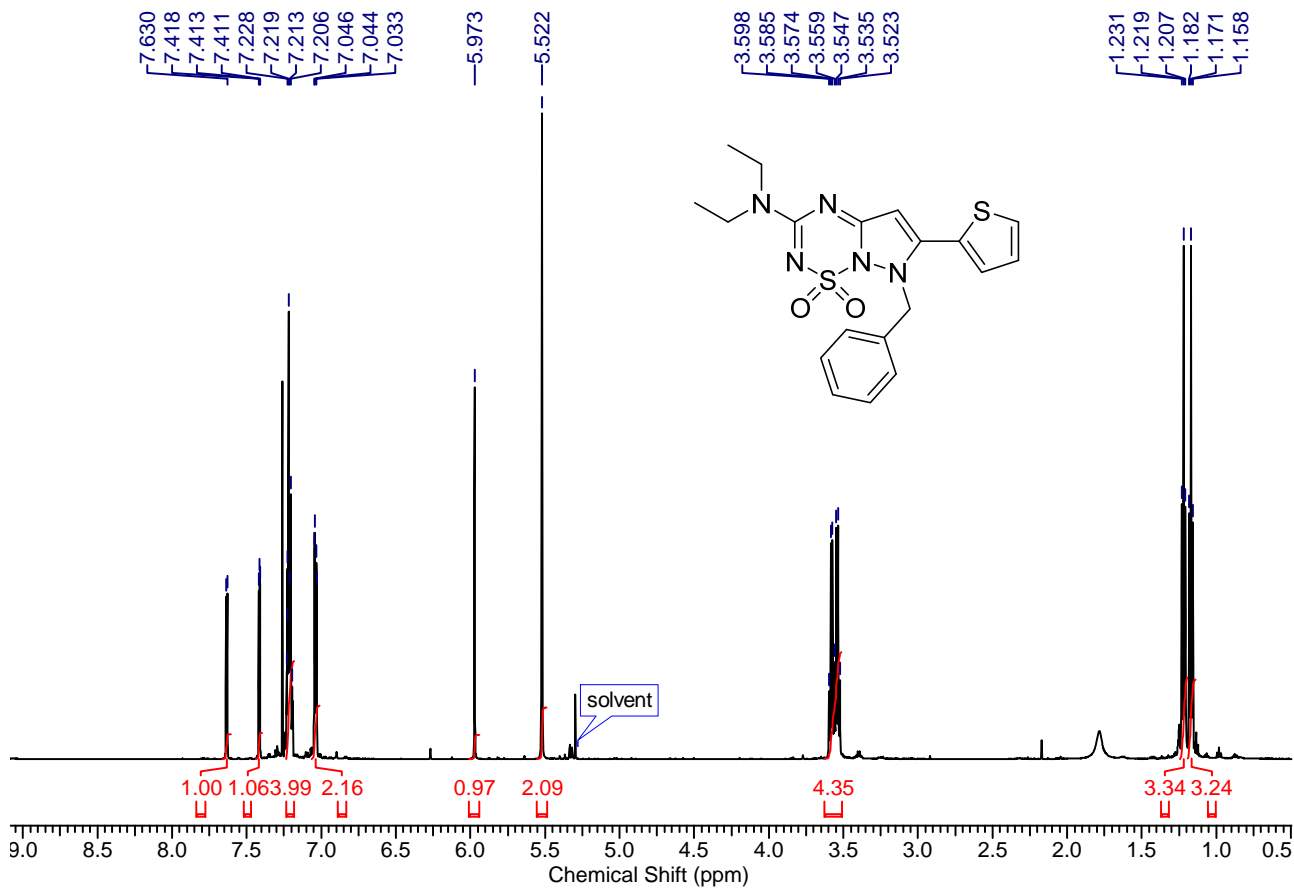
$^{13}\text{C}$  NMR spectrum of **7d** 100MHz ( $\text{CDCl}_3$ ) zoom area of aromatic region



$^1\text{H}$  NMR spectrum of **8d** 400MHz ( $\text{CDCl}_3$ )

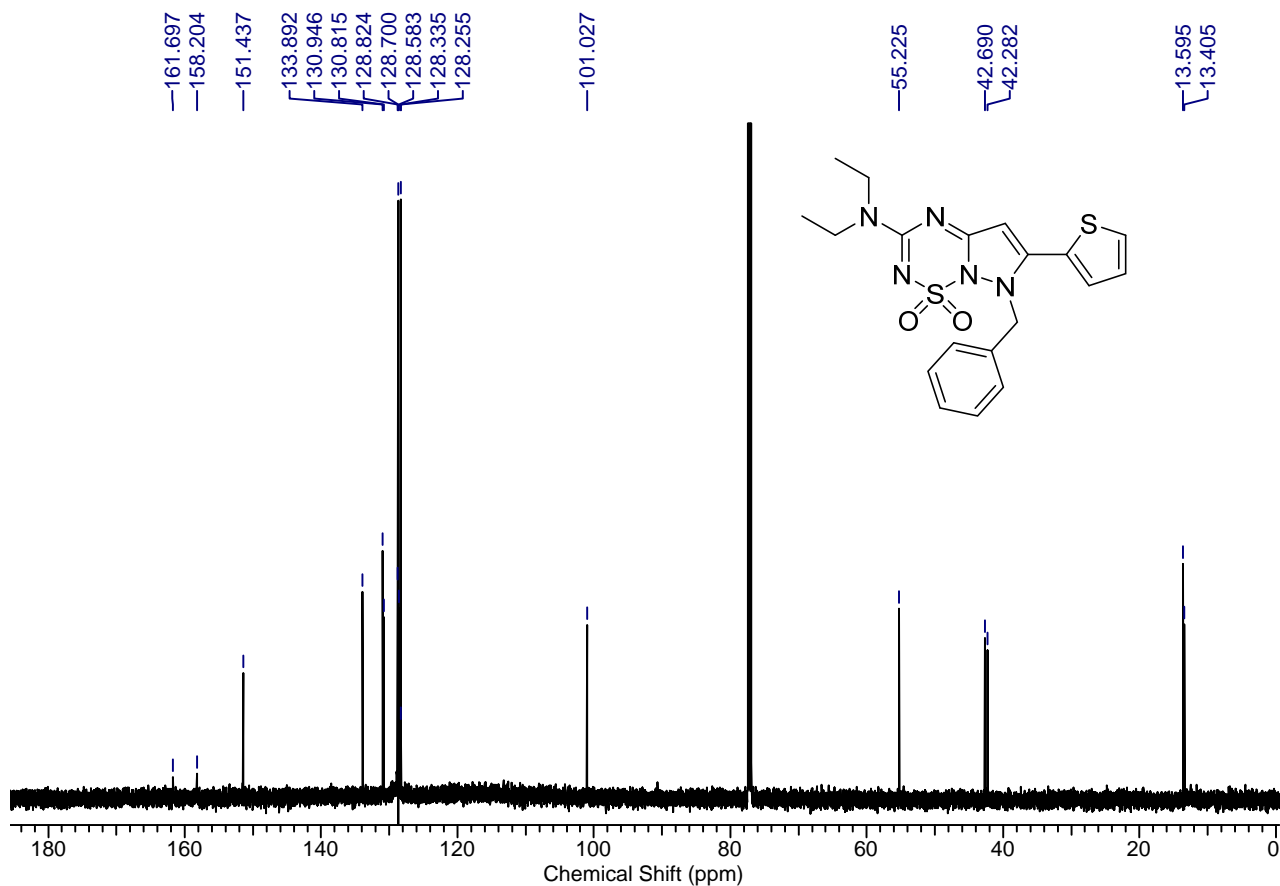


$^1\text{H}$  NMR spectrum of **6e** 600MHz ( $\text{CDCl}_3$ )



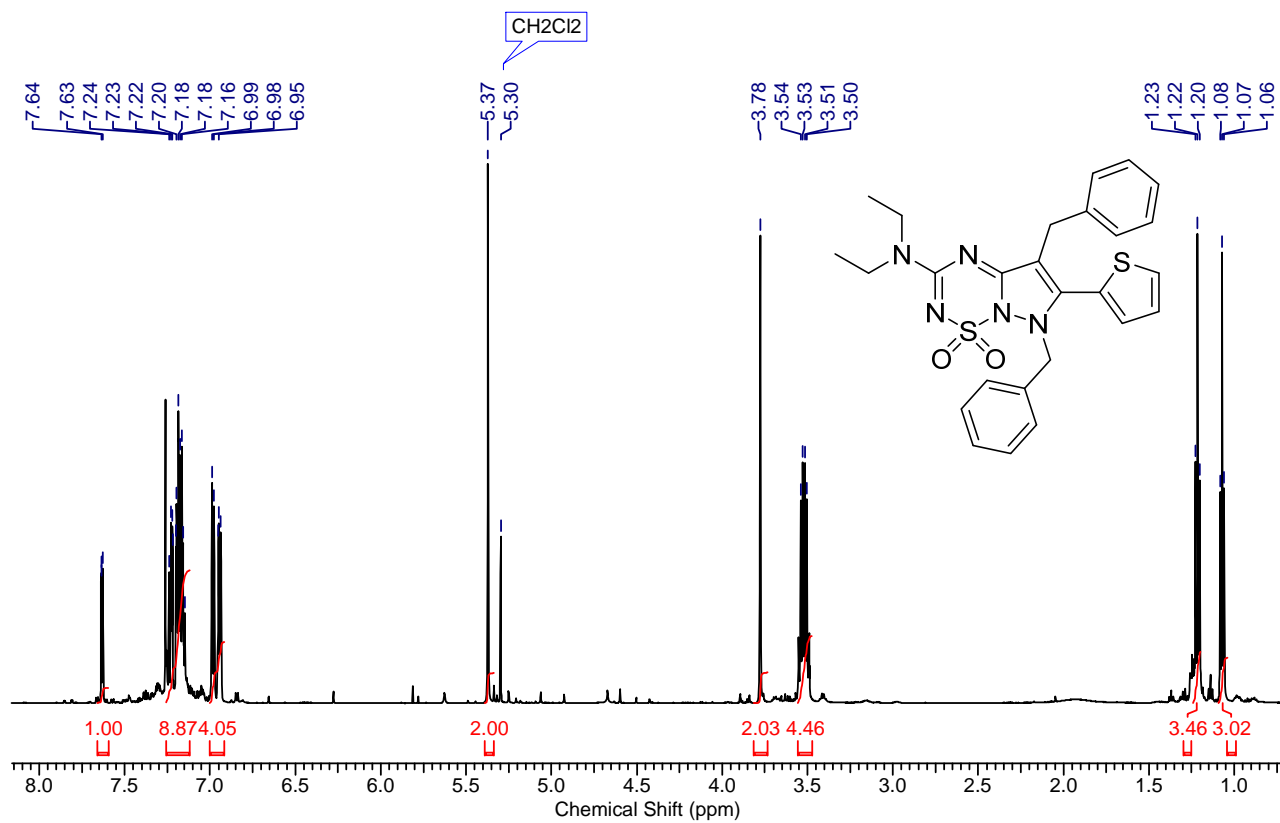


$^{13}\text{C}$  NMR spectrum of **6e** 150MHz ( $\text{CDCl}_3$ )

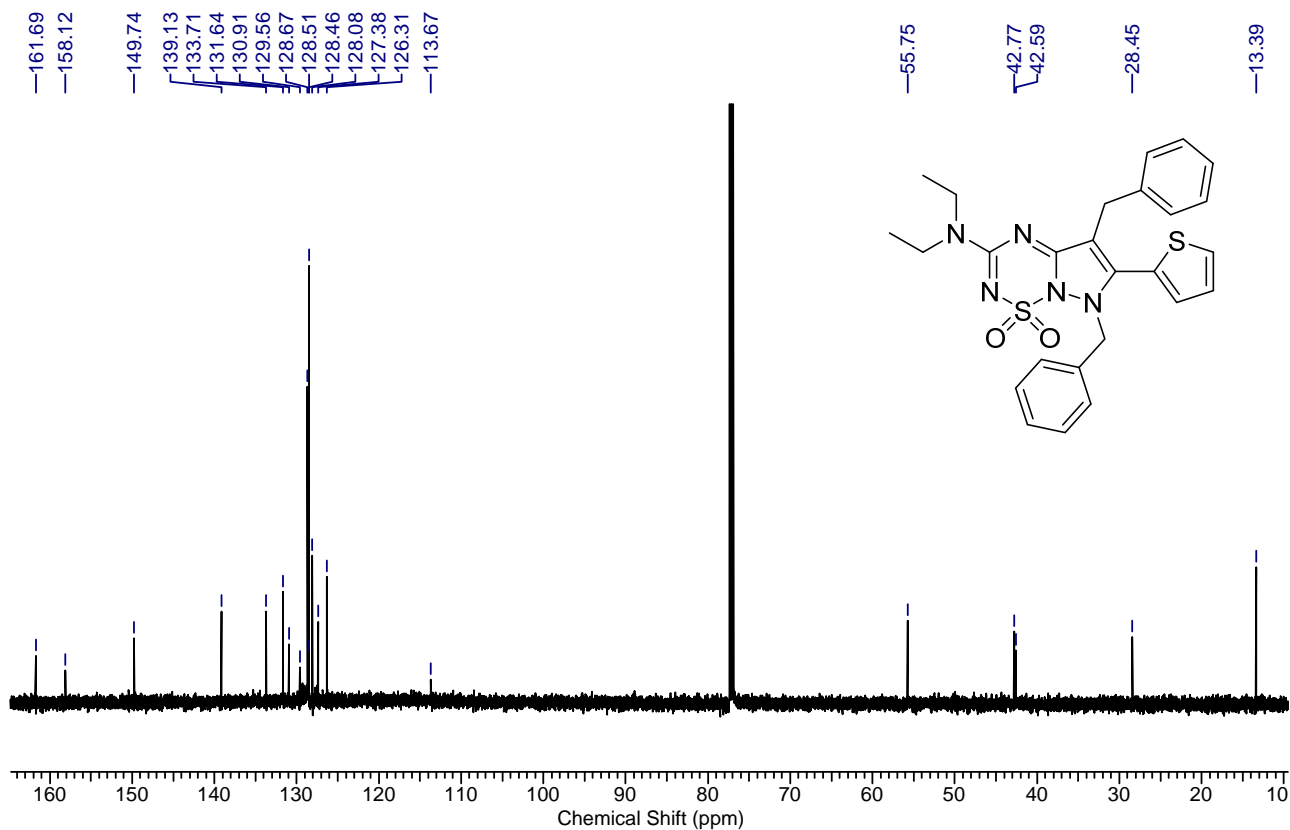


S16

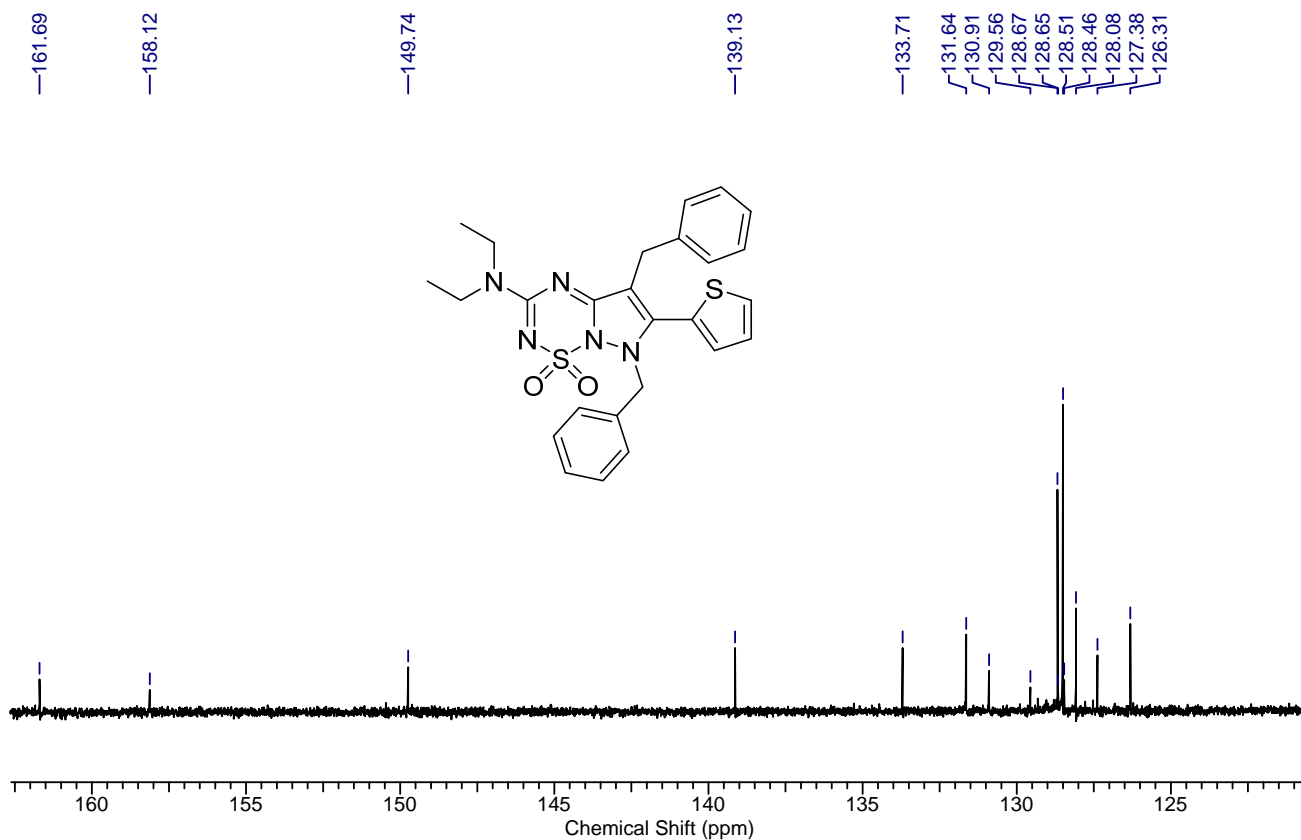
$^1\text{H}$  NMR spectrum of **7e** 600MHz ( $\text{CDCl}_3$ )



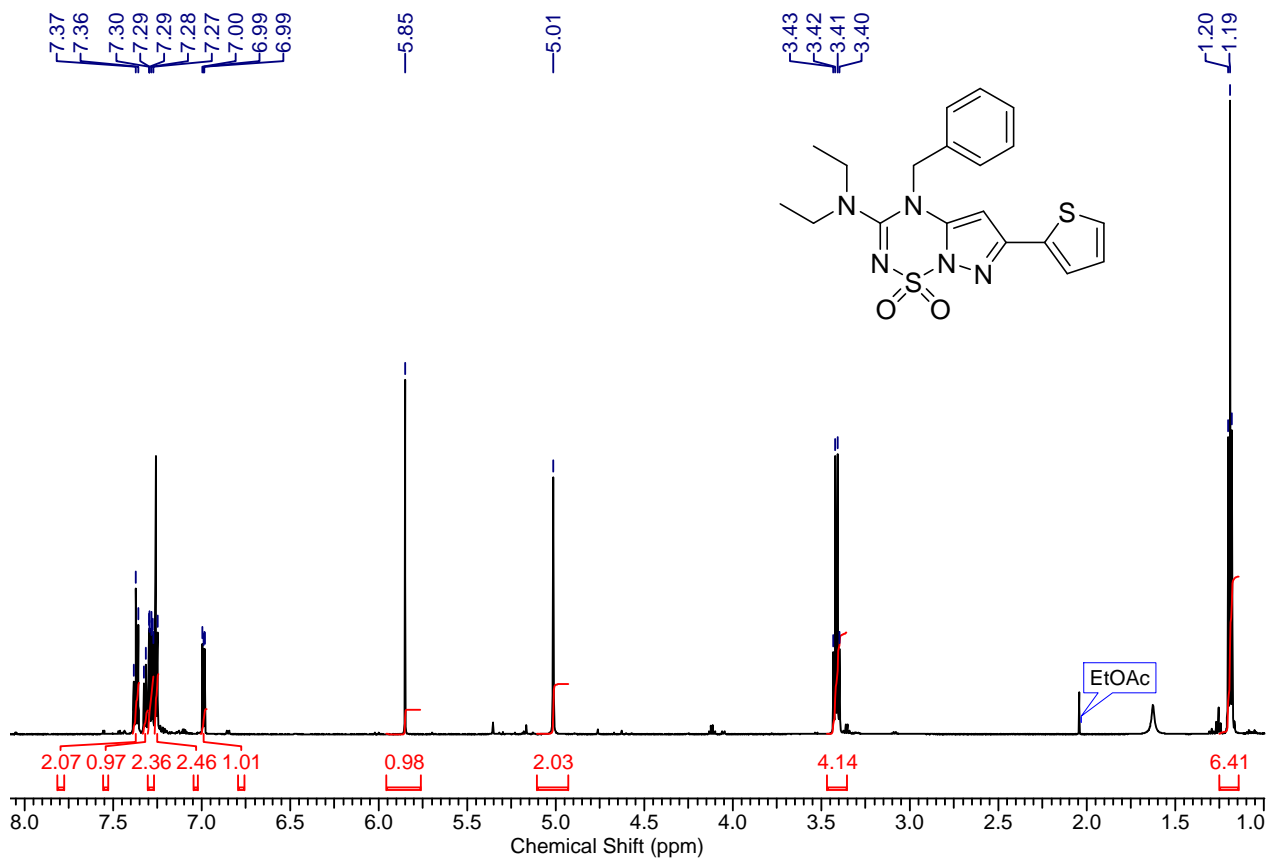
$^{13}\text{C}$  NMR spectrum of **7e** 150MHz ( $\text{CDCl}_3$ )



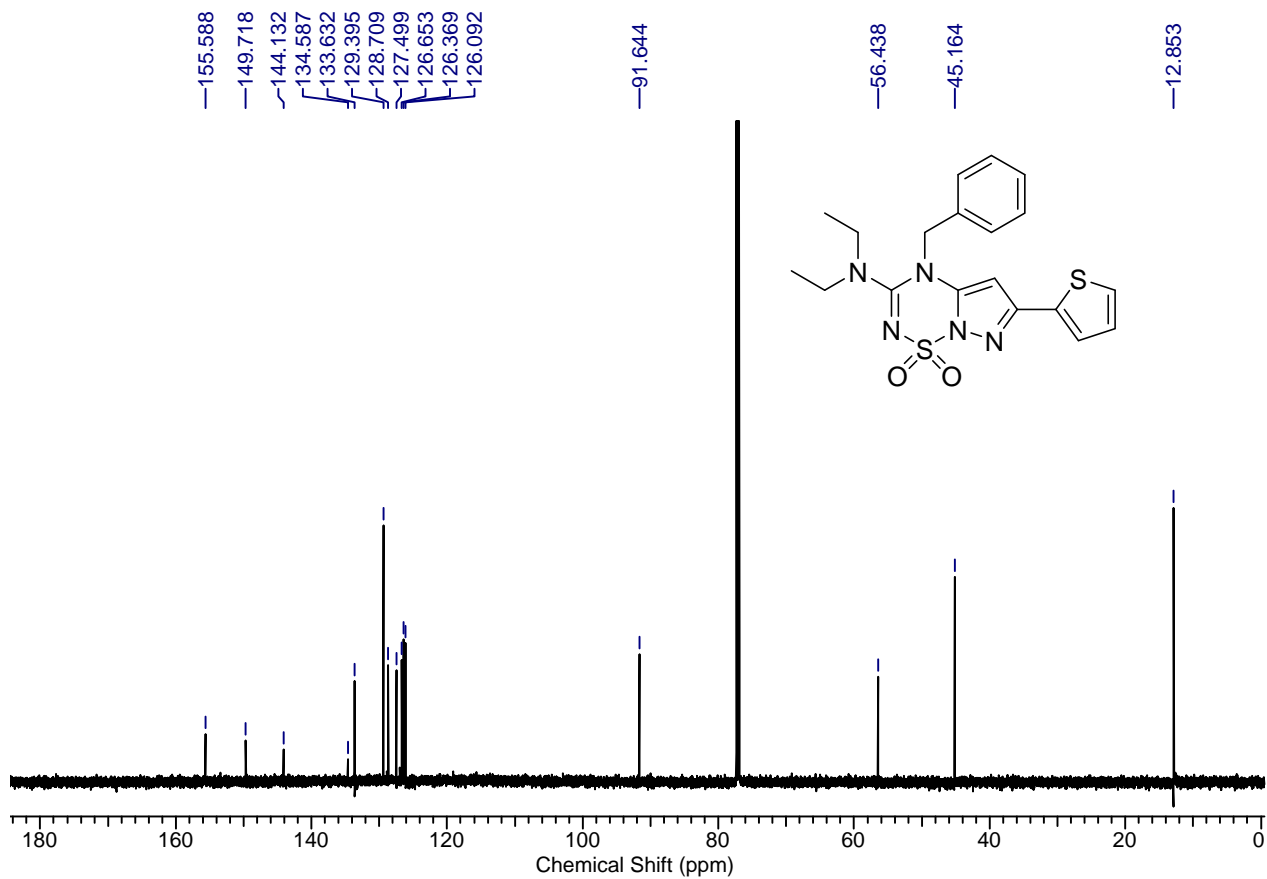
$^{13}\text{C}$  NMR spectrum of **7e** 100MHz ( $\text{CDCl}_3$ ) **zoom area of aromatic region**



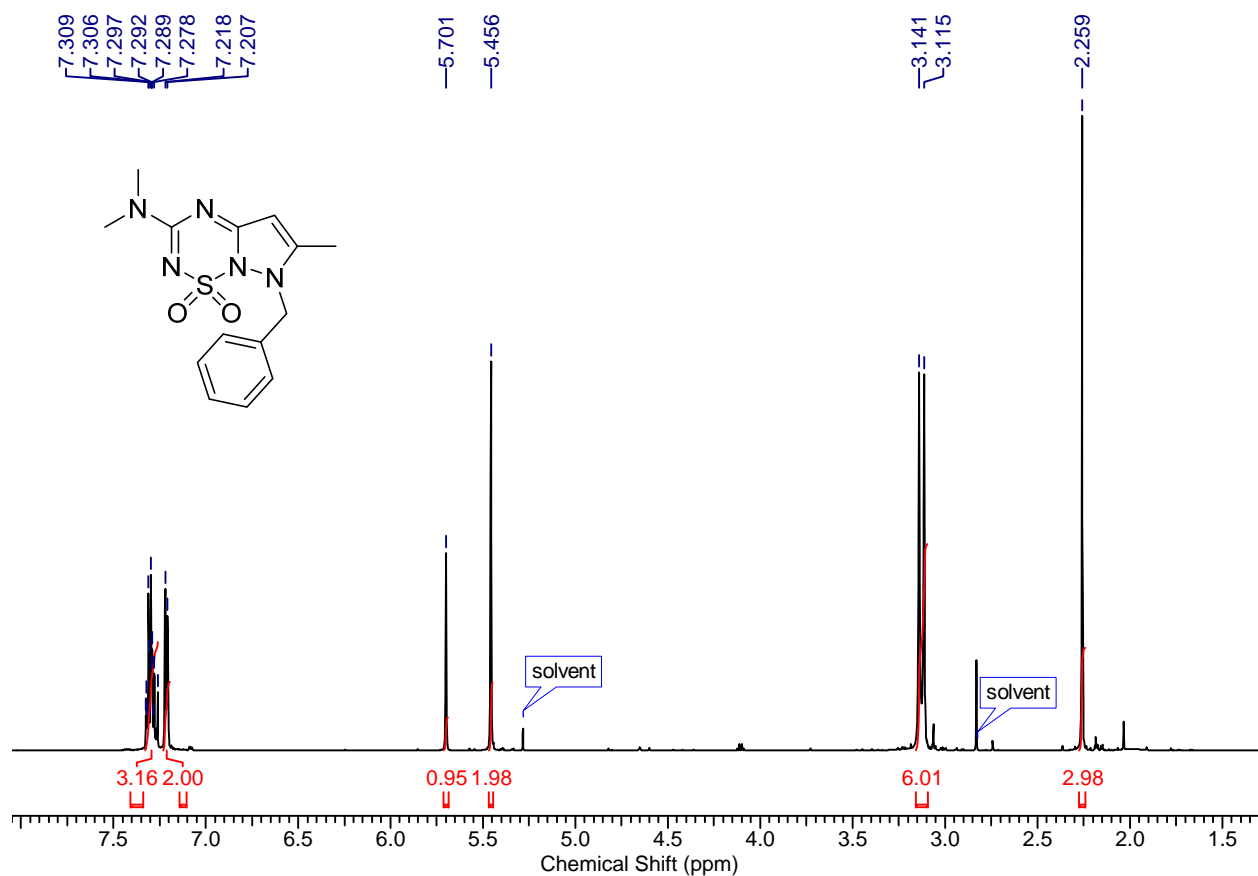
<sup>1</sup>H NMR spectrum of **8e** 600MHz (CDCl<sub>3</sub>)



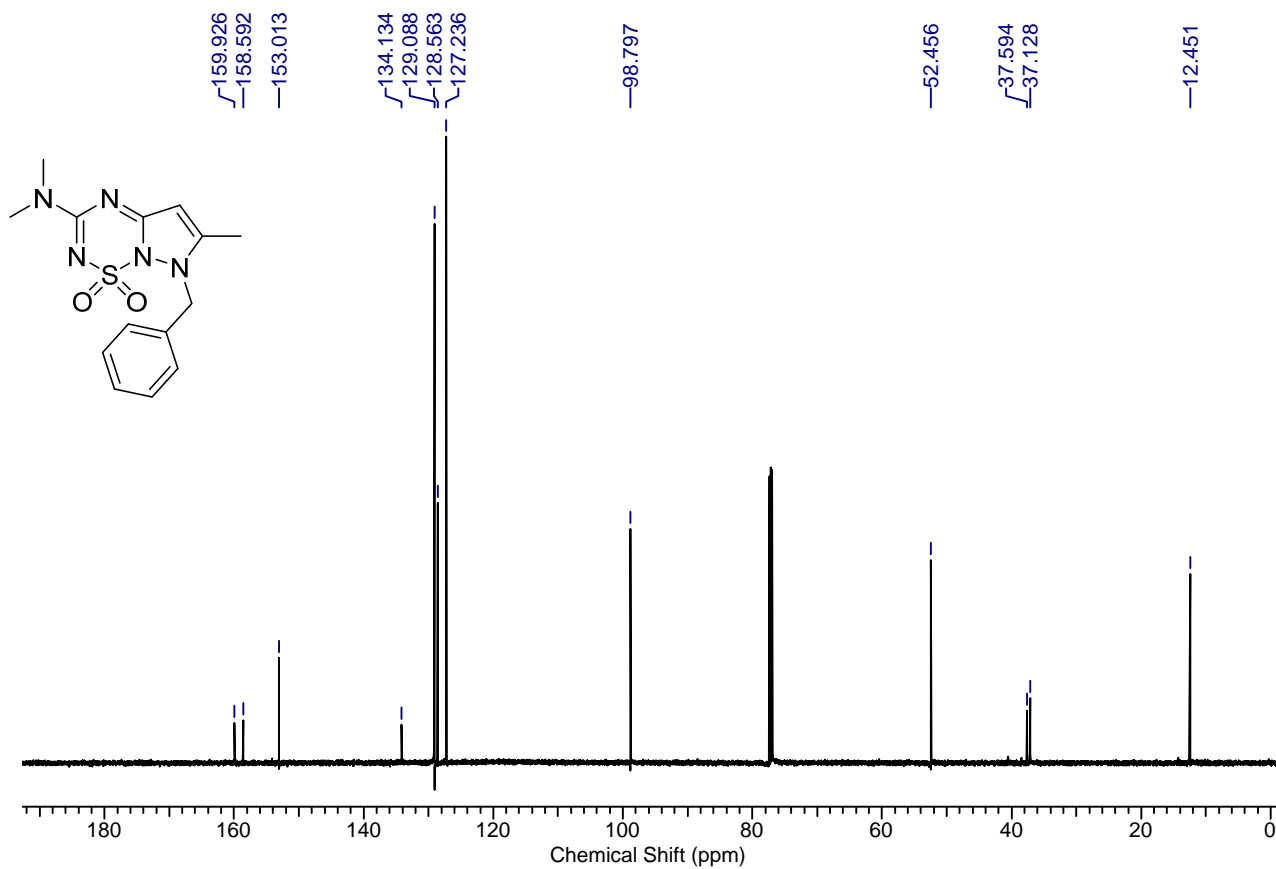
<sup>13</sup>C NMR spectrum of **8e** 150MHz (CDCl<sub>3</sub>)



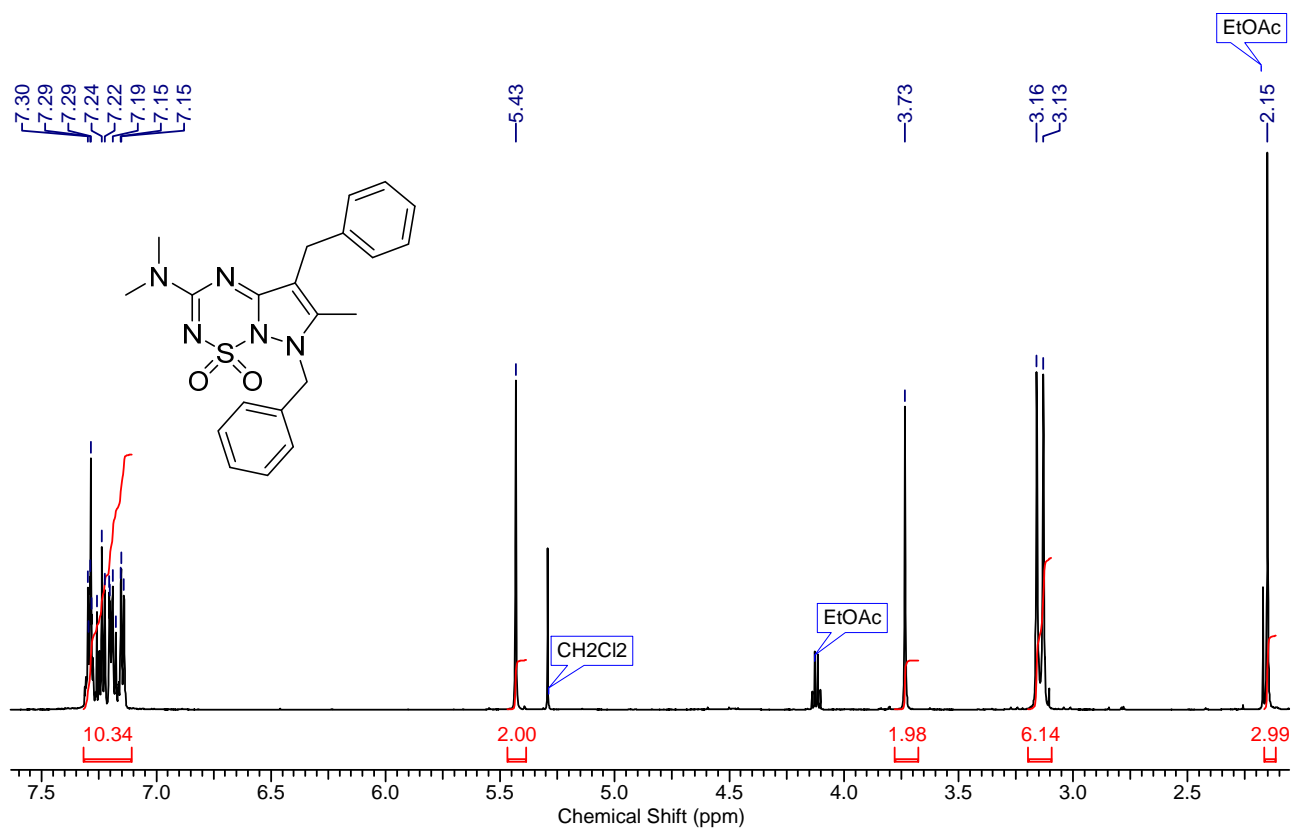
<sup>1</sup>H NMR spectrum of **6f** 600MHz (CDCl<sub>3</sub>)



<sup>13</sup>C NMR spectrum of **6f** 150MHz (CDCl<sub>3</sub>)

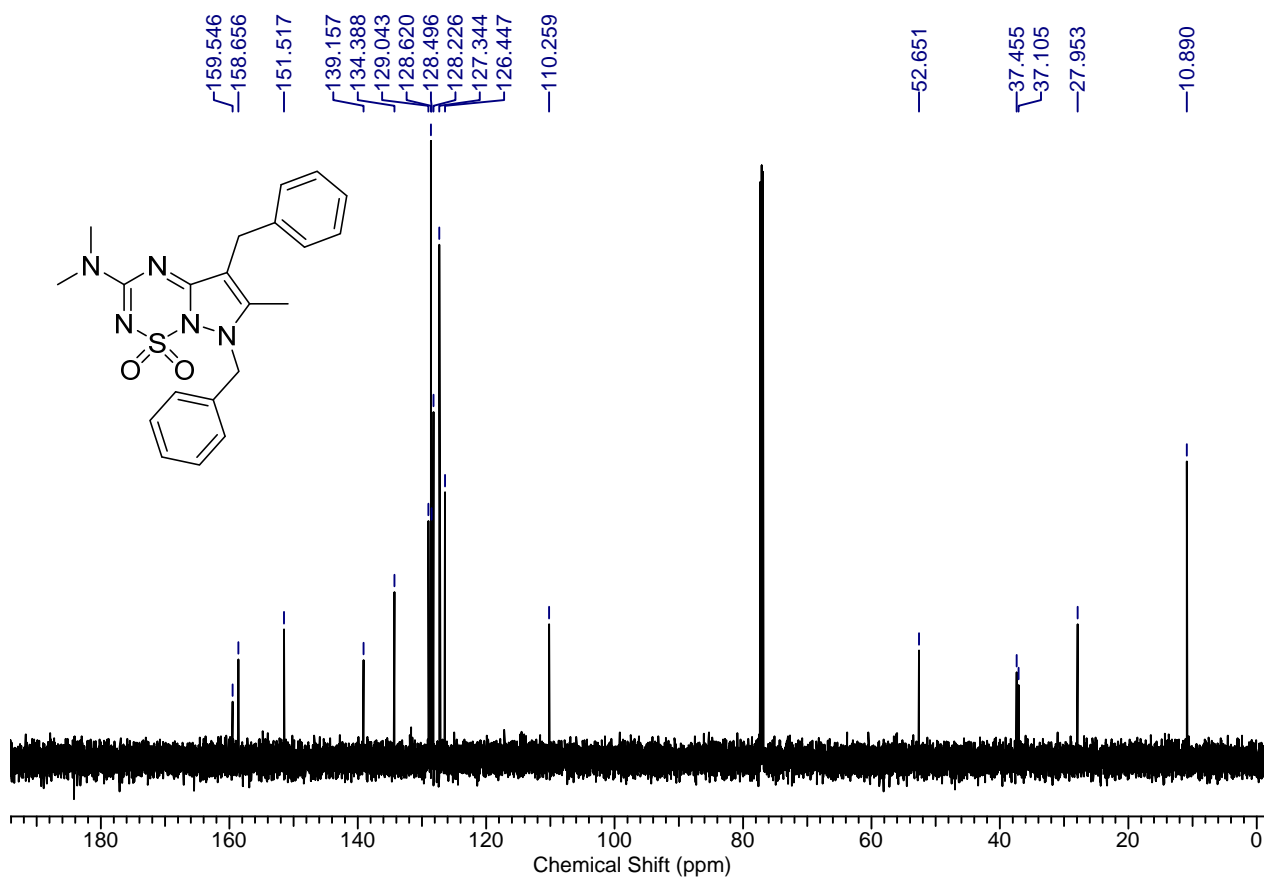


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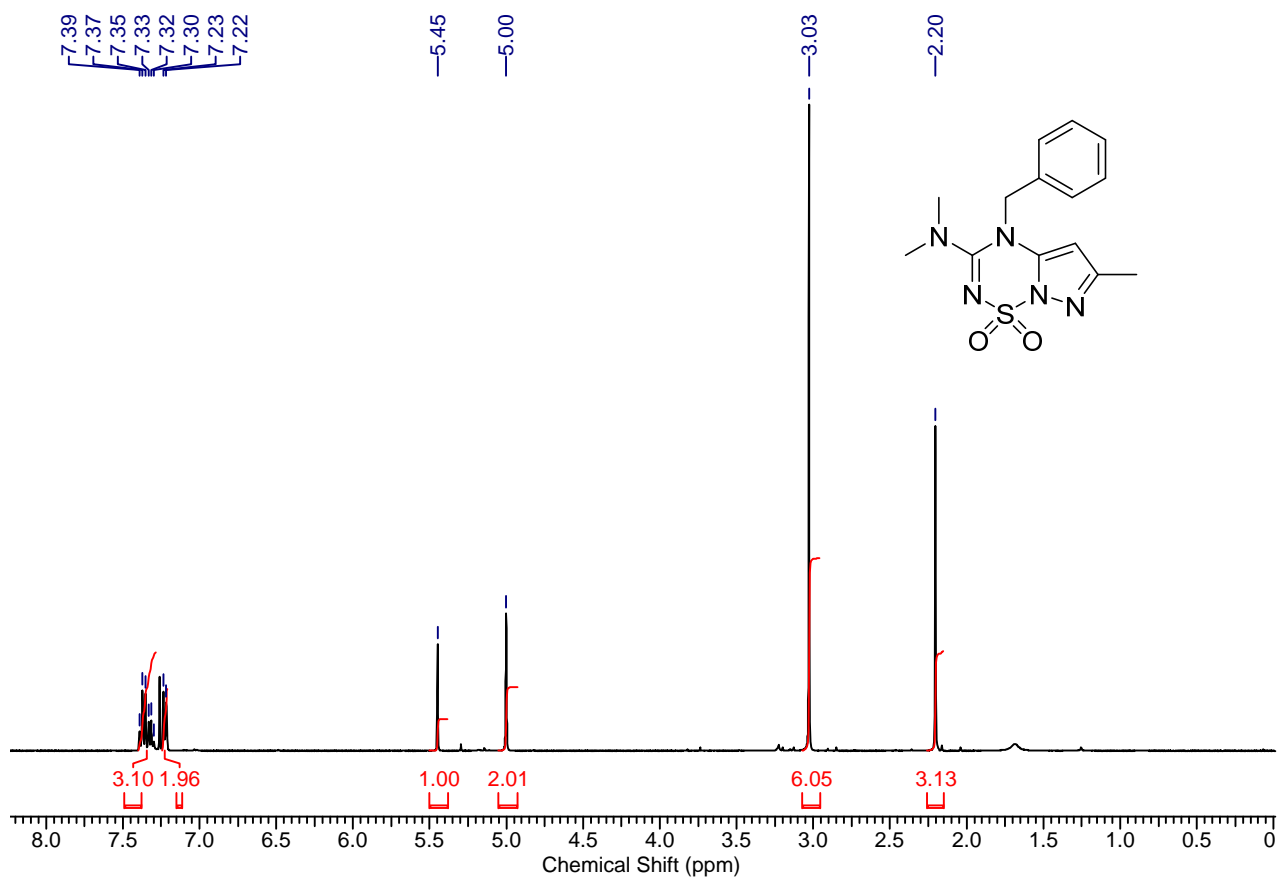


$^{13}\text{C}$  NMR spectrum of **7f** 150MHz ( $\text{CDCl}_3$ )

S20

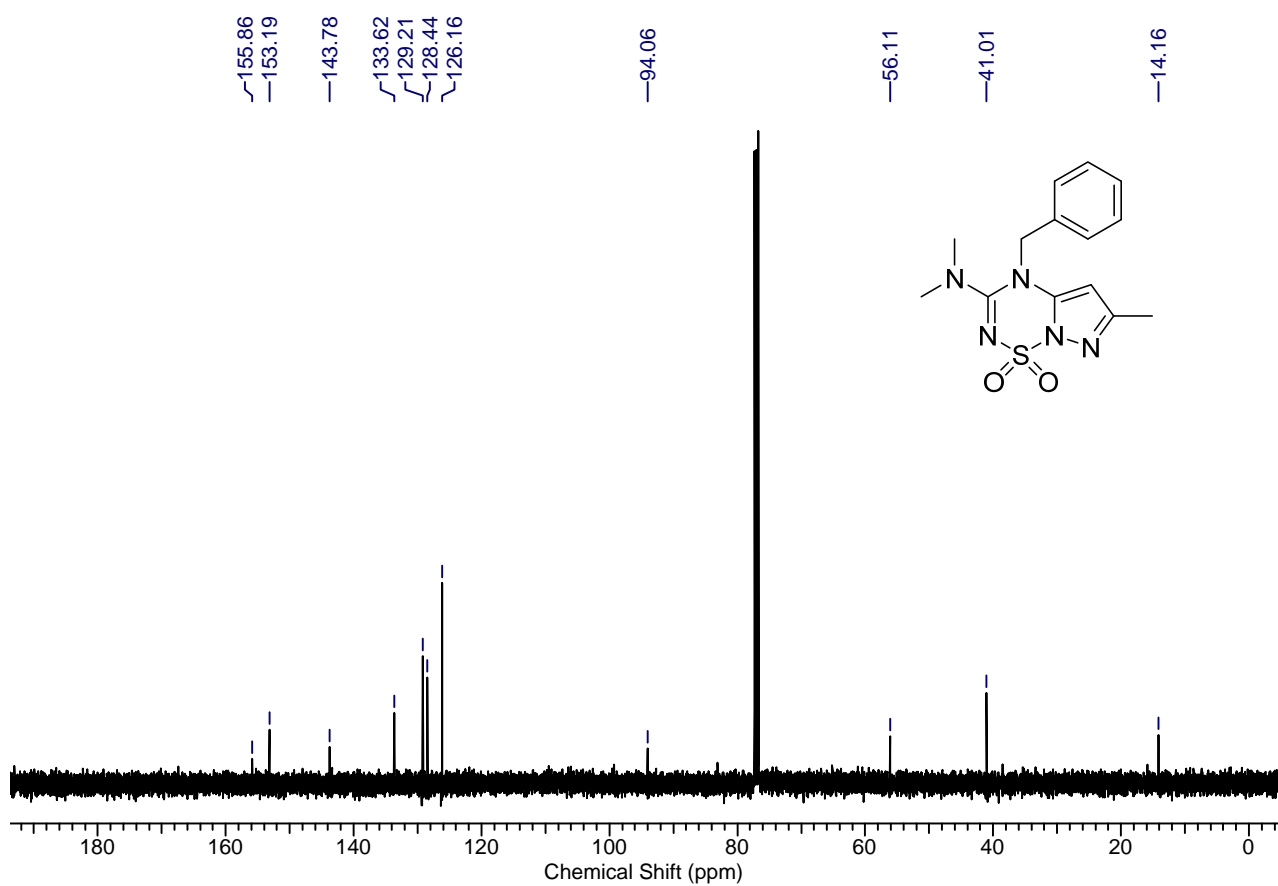


<sup>1</sup>H NMR spectrum of **8f** 400MHz (CDCl<sub>3</sub>)

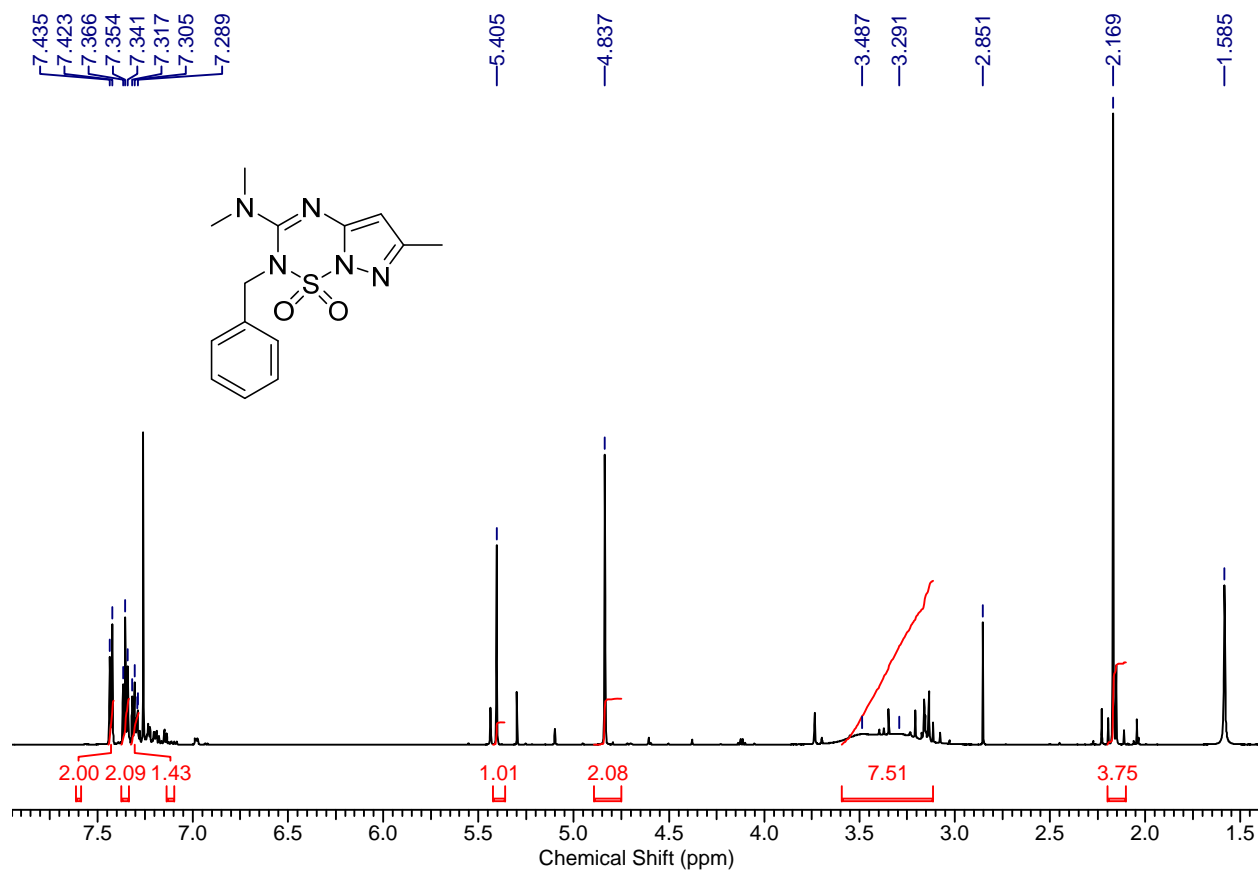


<sup>13</sup>C NMR spectrum of **8f** 400MHz (CDCl<sub>3</sub>)

S21

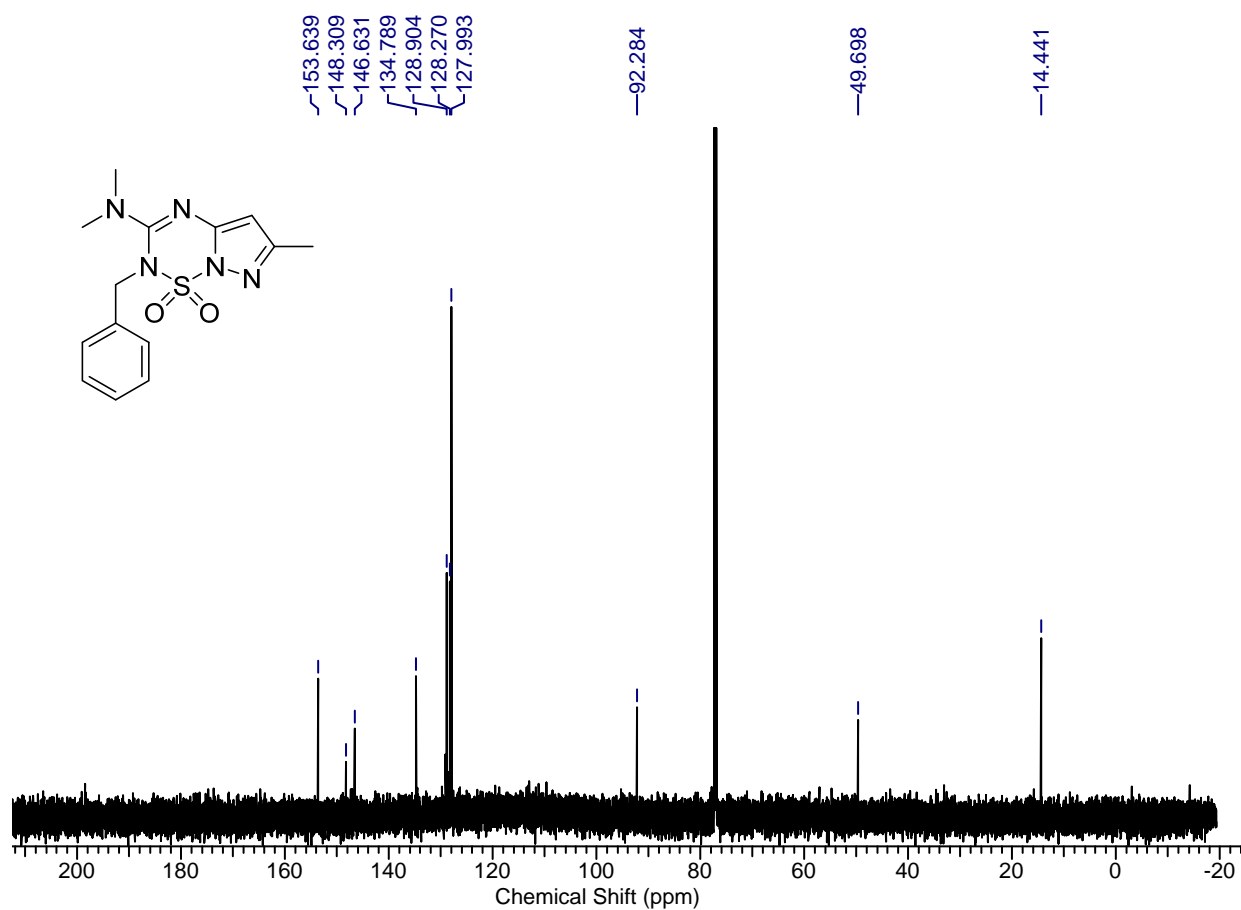


<sup>1</sup>H NMR spectrum of **9f** 600MHz (CDCl<sub>3</sub>)

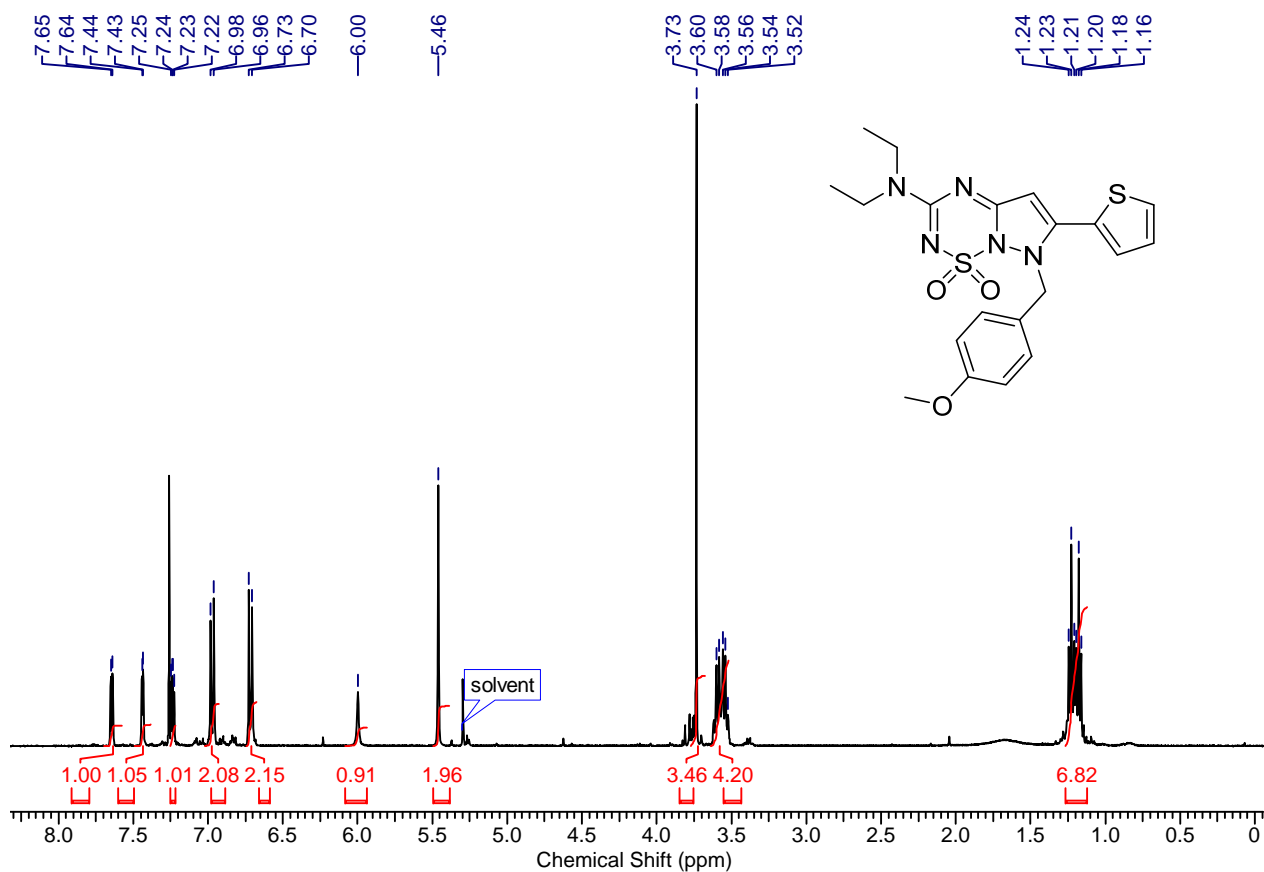


<sup>13</sup>C NMR spectrum of **9f** 150MHz (CDCl<sub>3</sub>)

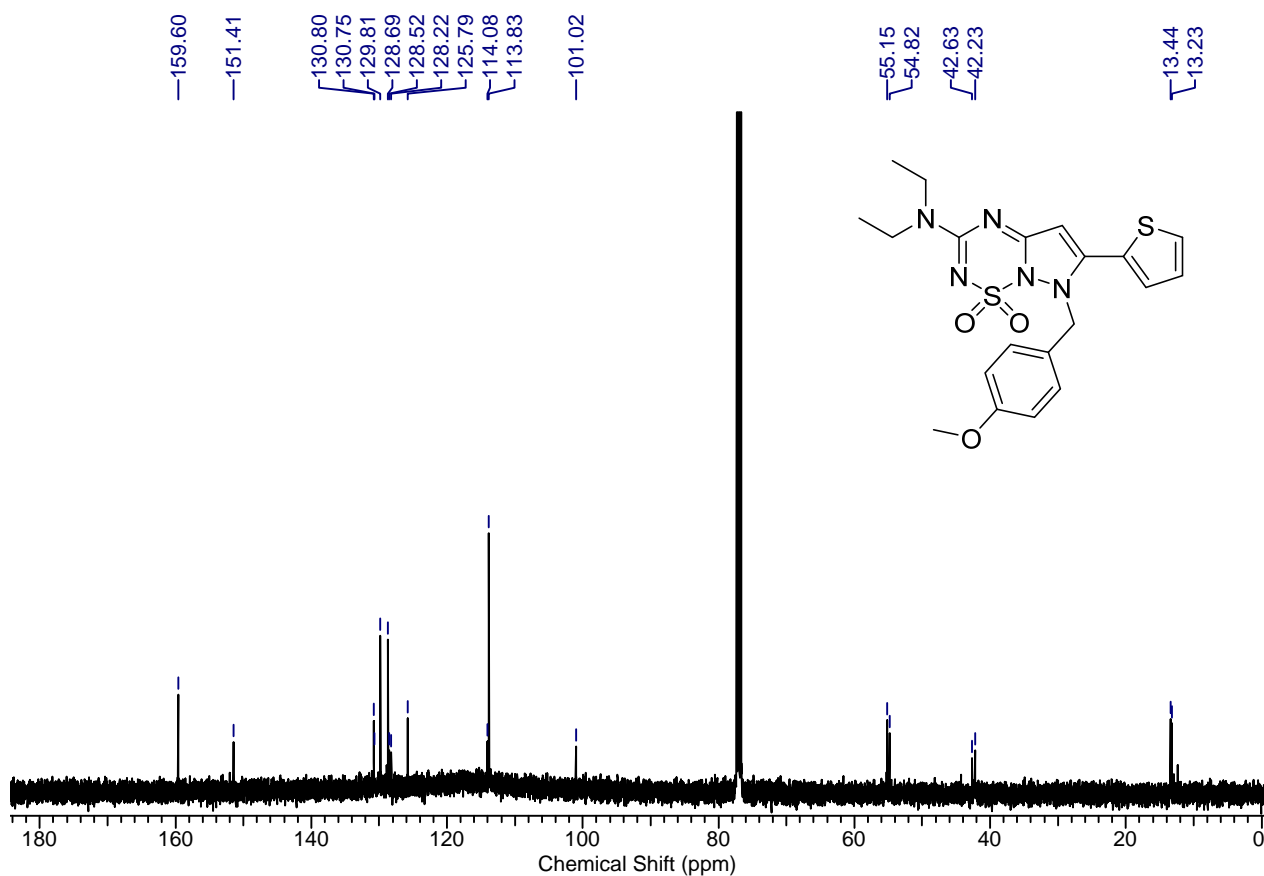
S22



<sup>1</sup>H NMR spectrum of **6g** 400MHz (CDCl<sub>3</sub>)

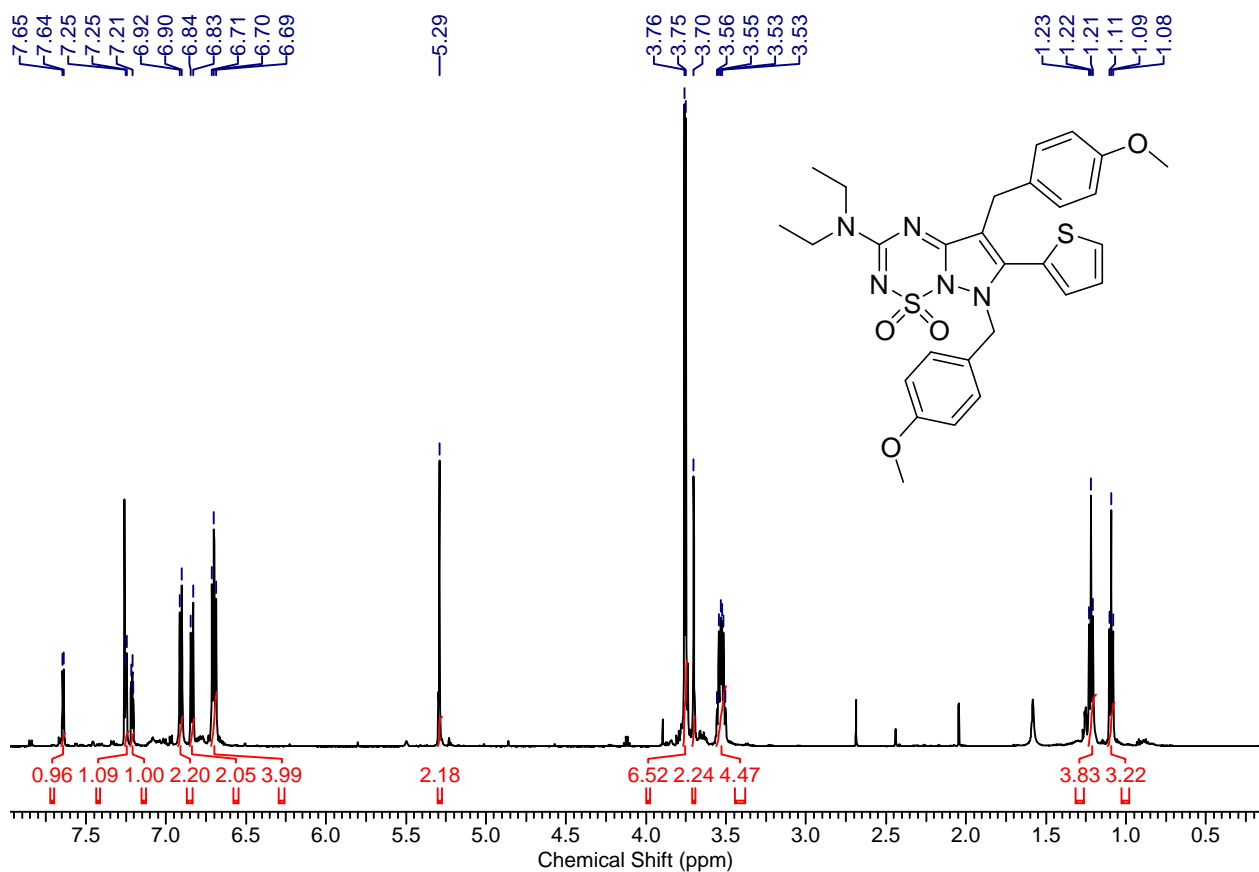


<sup>13</sup>C NMR spectrum of **6g** 100MHz (CDCl<sub>3</sub>)



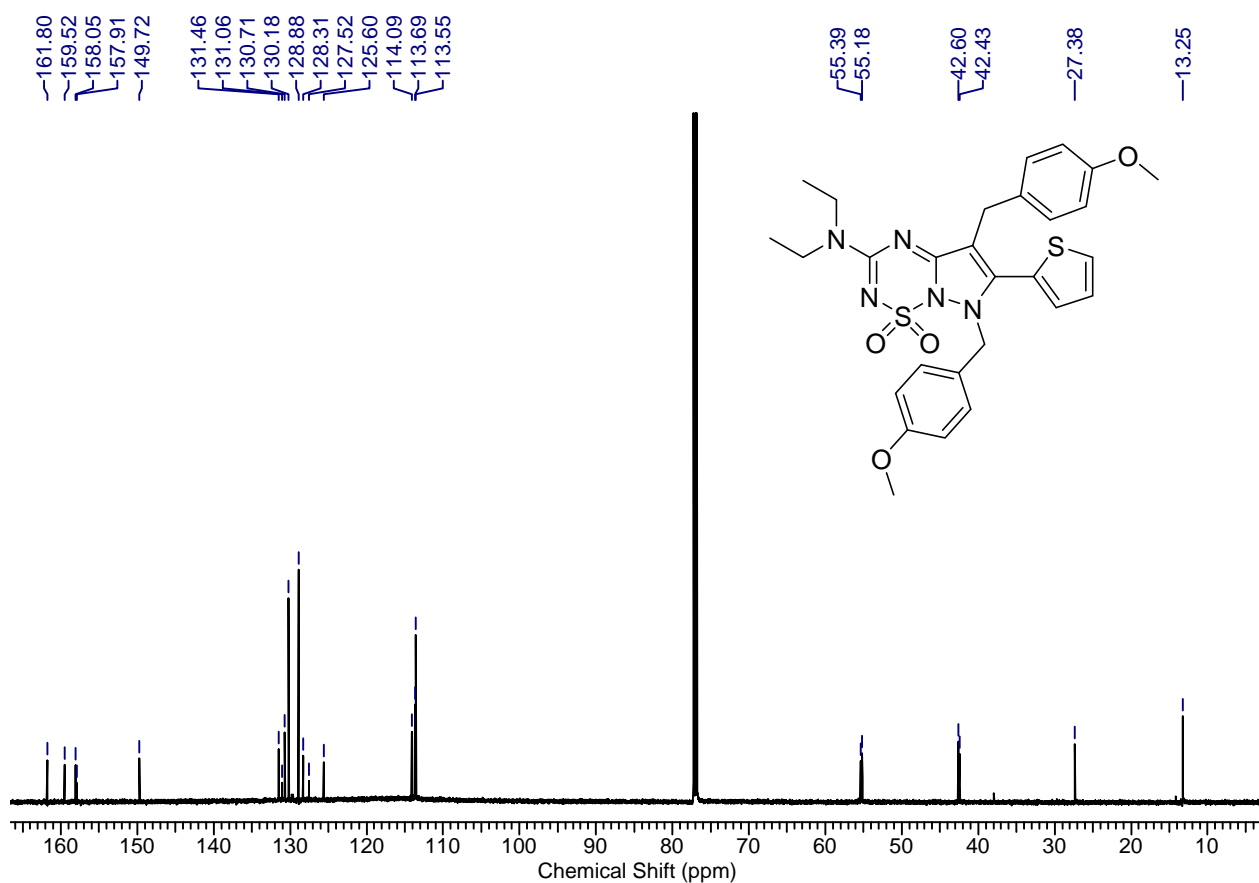


<sup>1</sup>H NMR spectrum of **7g** 400MHz (CDCl<sub>3</sub>)

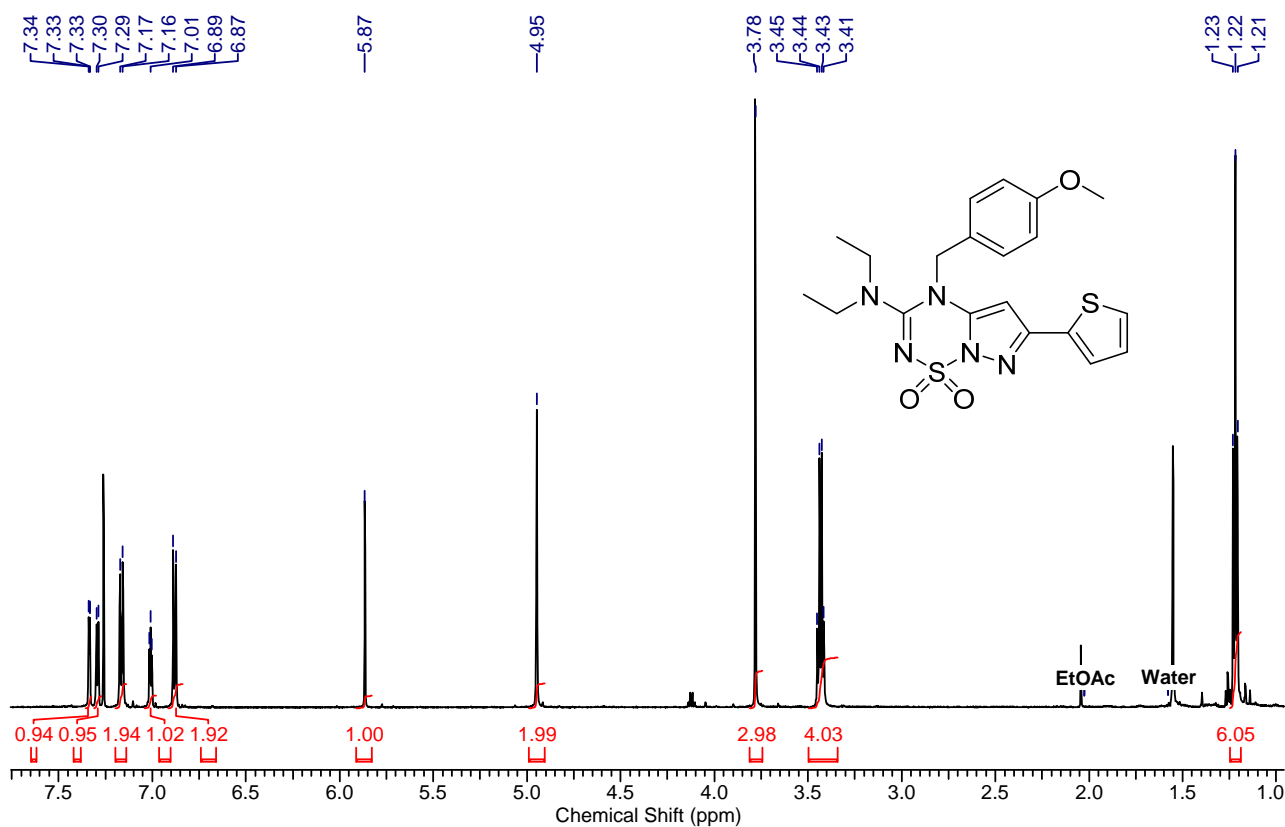


<sup>13</sup>C NMR spectrum of **7g** 100MHz (CDCl<sub>3</sub>)

S24

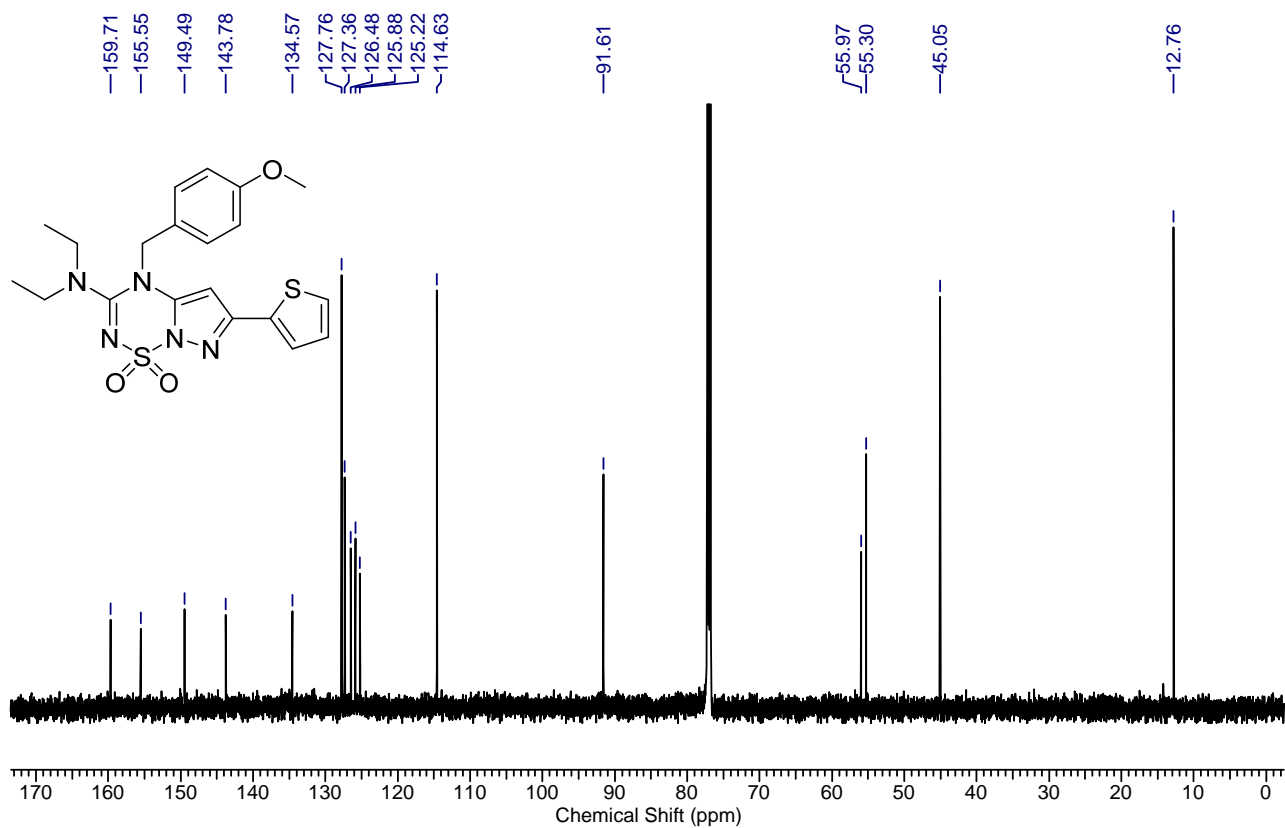


$^1\text{H}$  NMR spectrum of **8g** 600MHz ( $\text{CDCl}_3$ )

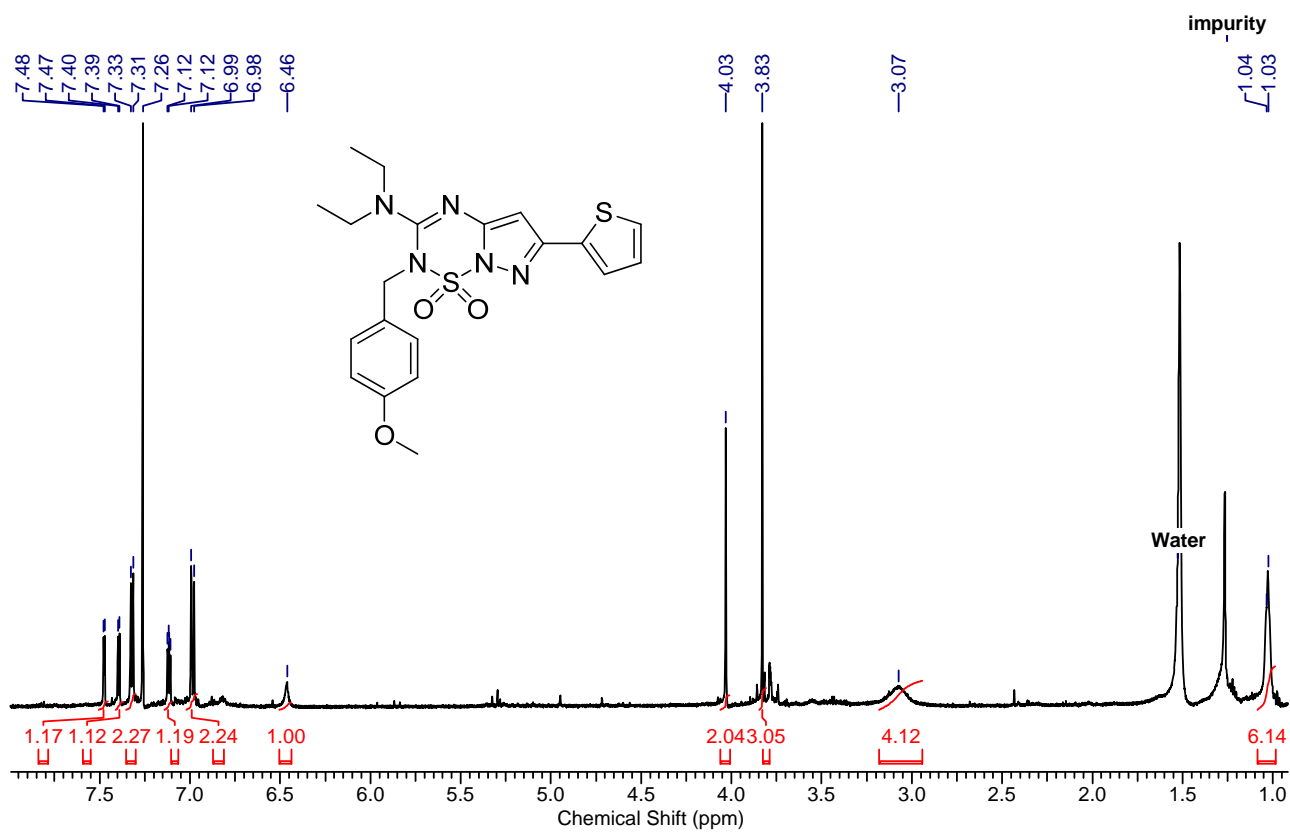


$^{13}\text{C}$  NMR spectrum of **8g** 150MHz ( $\text{CDCl}_3$ )

S25

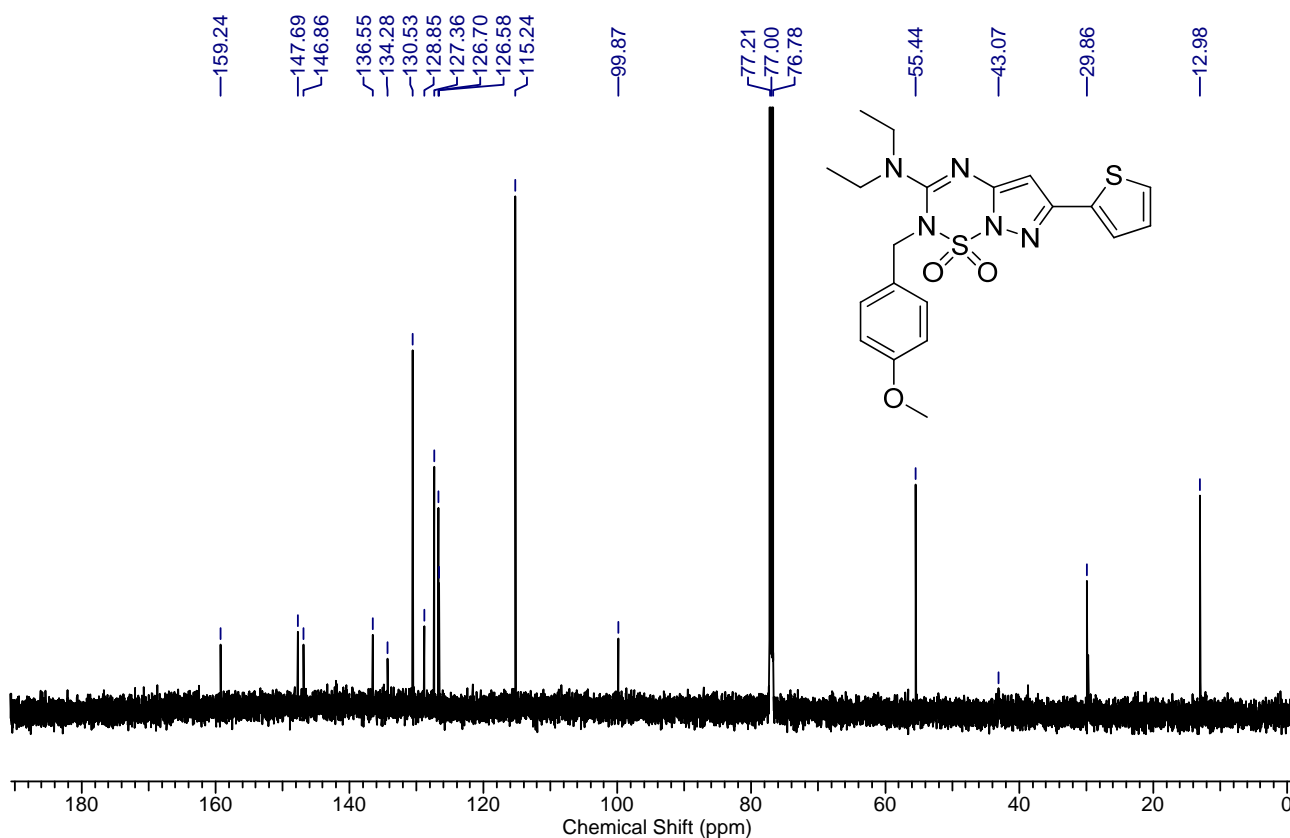


<sup>1</sup>H NMR spectrum of **9g** 600MHz (CDCl<sub>3</sub>) 40°C

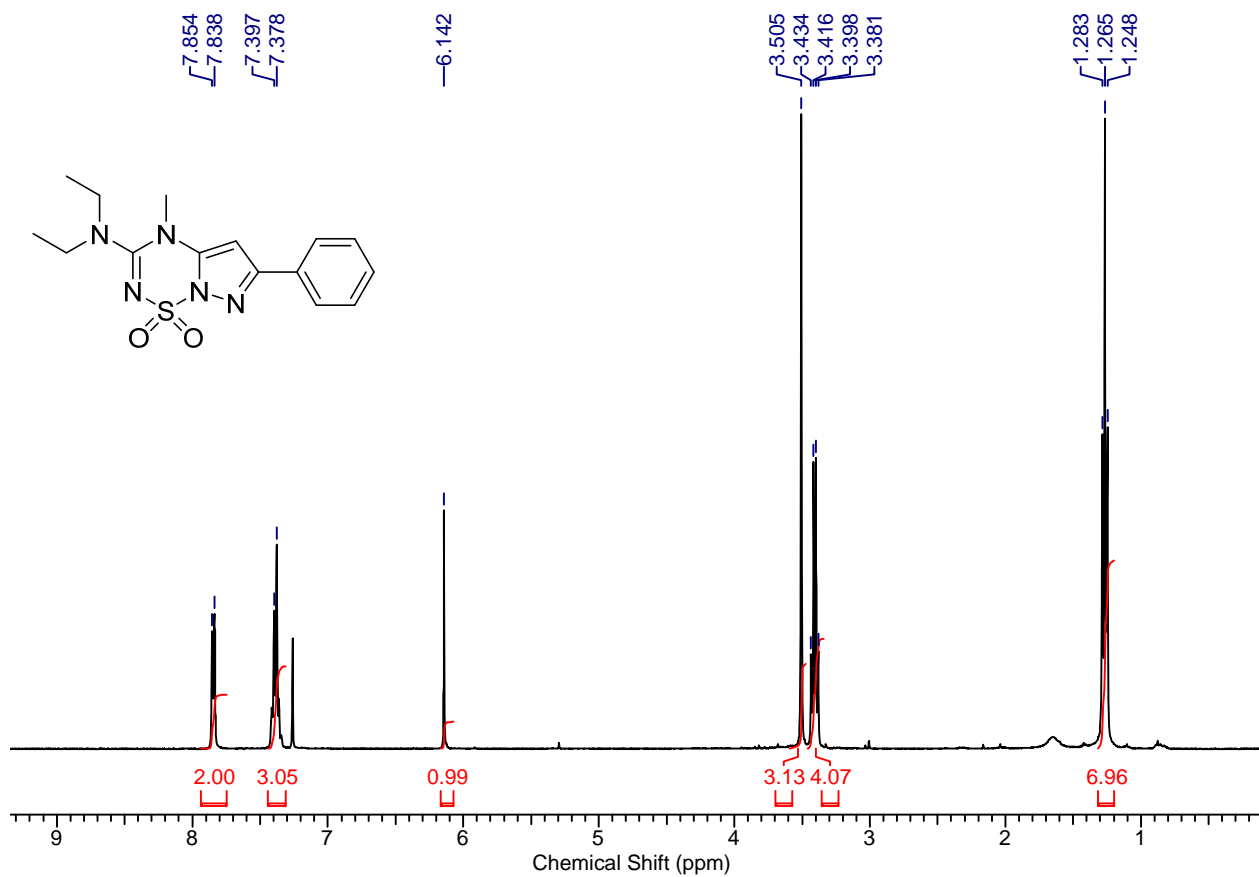


<sup>13</sup>C NMR Spectrum of **9g** 150MHz (CDCl<sub>3</sub>) 40°C

S26

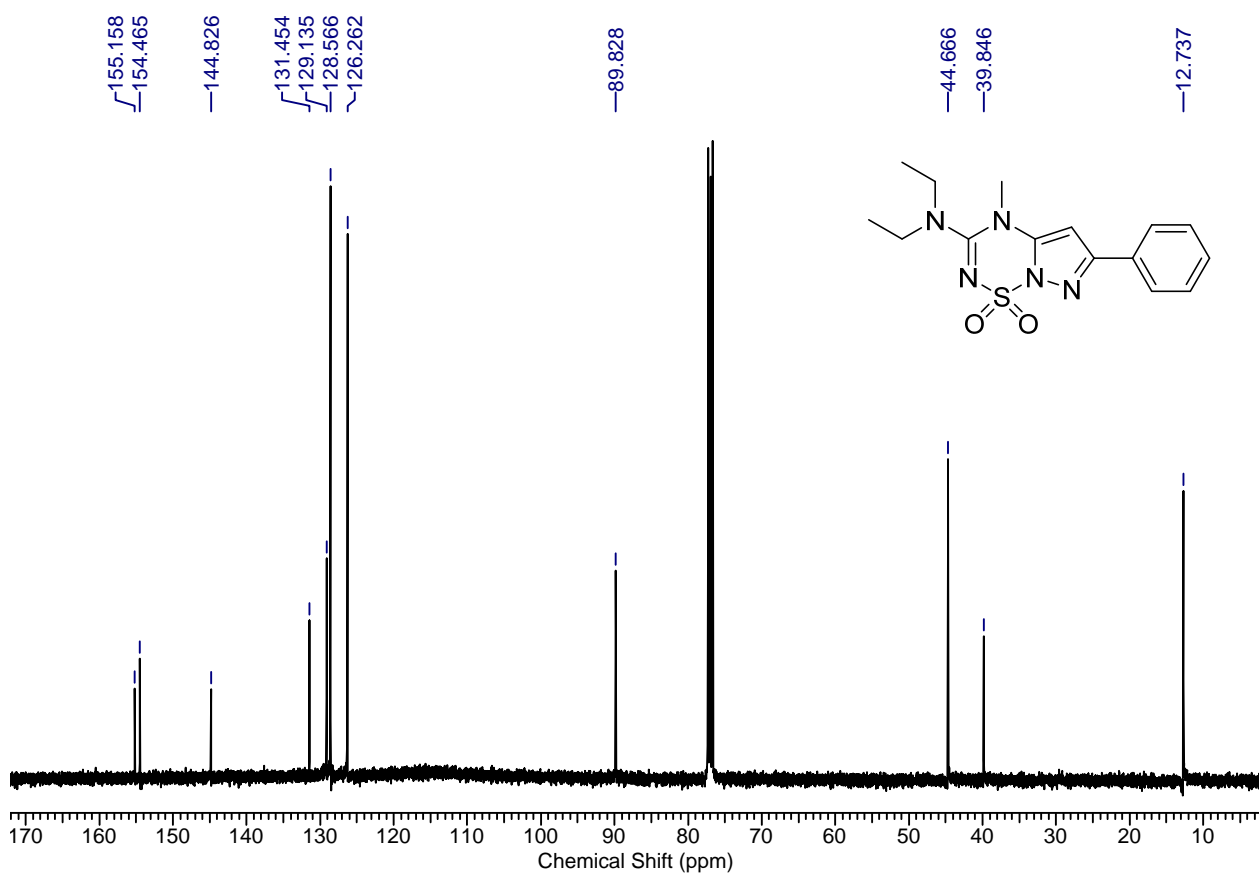


<sup>1</sup>H NMR spectrum of **10** 400MHz (CDCl<sub>3</sub>)

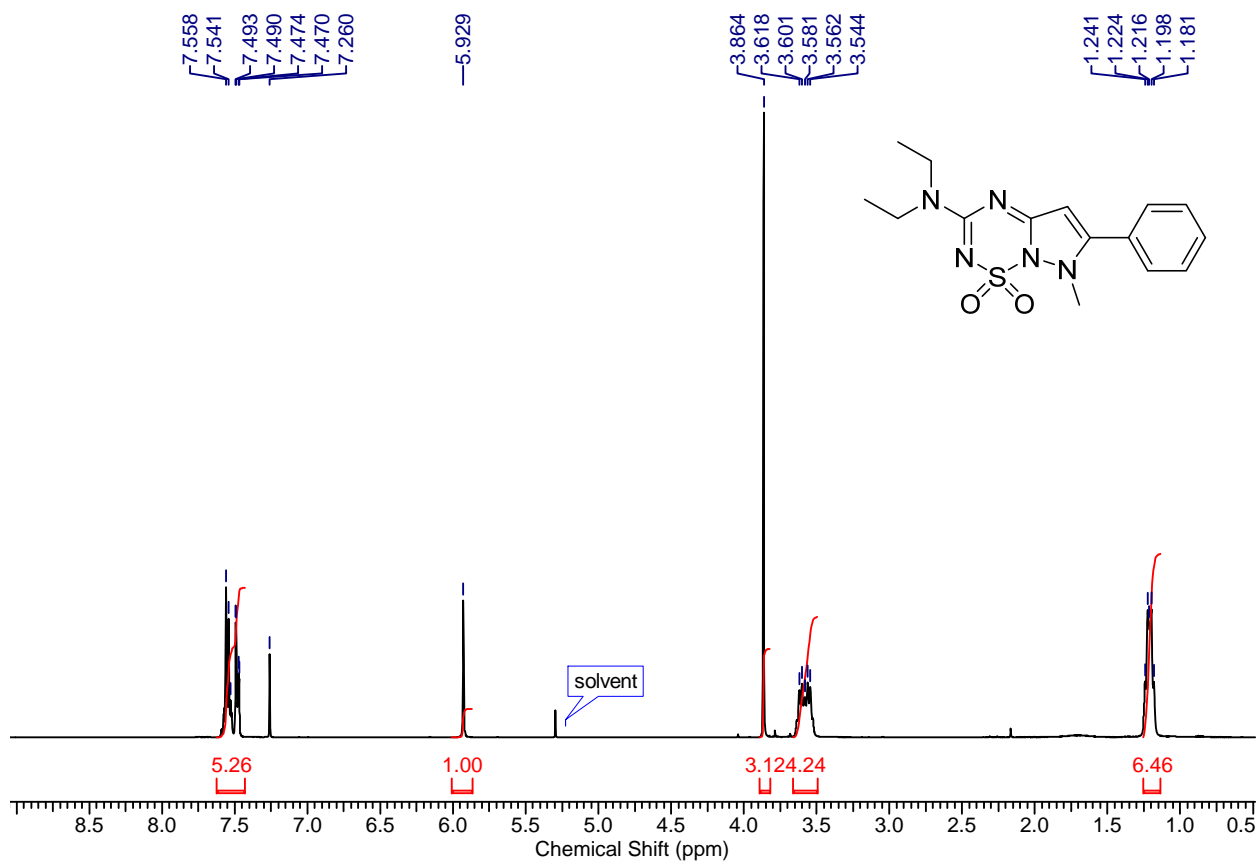


<sup>13</sup>C NMR spectrum of **10** 100MHz (CDCl<sub>3</sub>)

S27

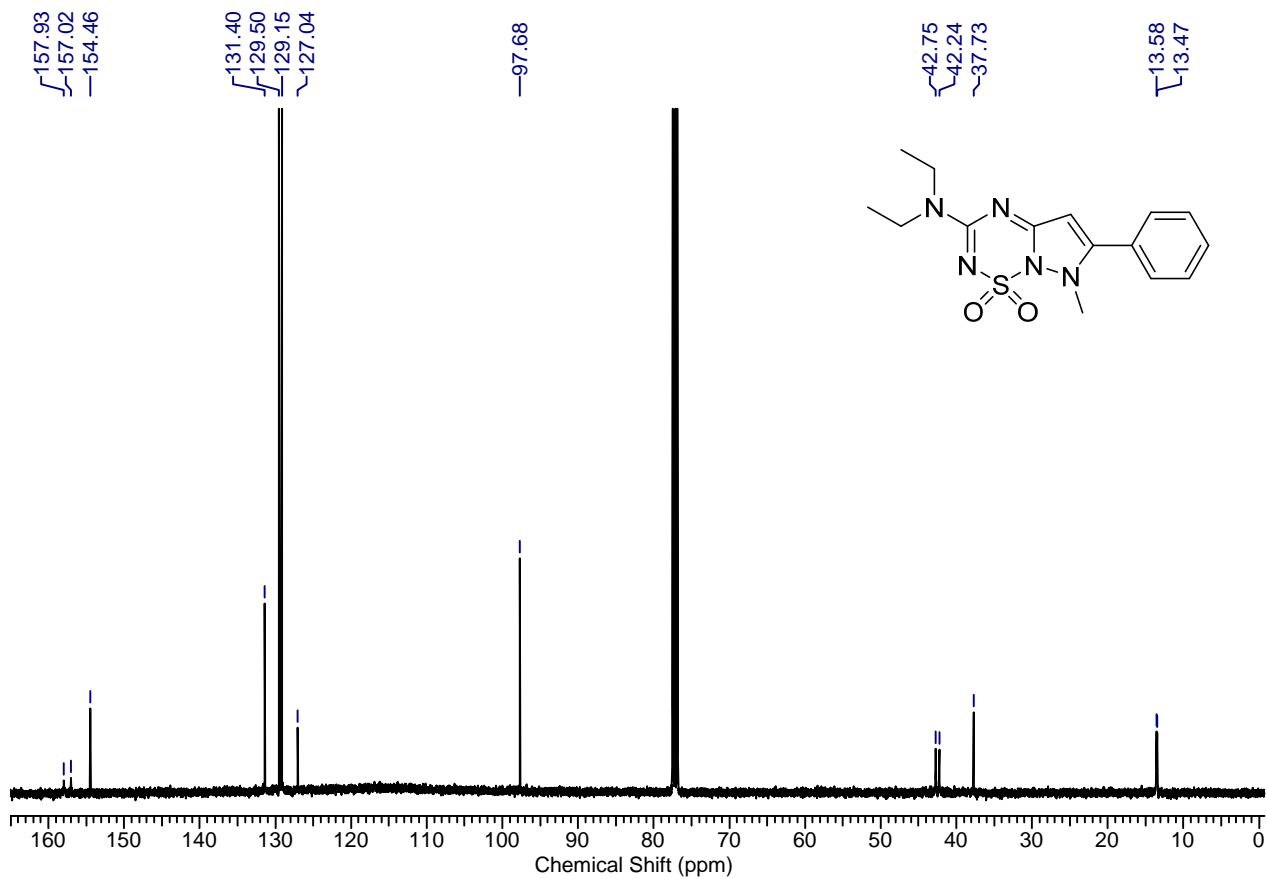


<sup>1</sup>H NMR spectrum of **11** 400MHz (CDCl<sub>3</sub>)

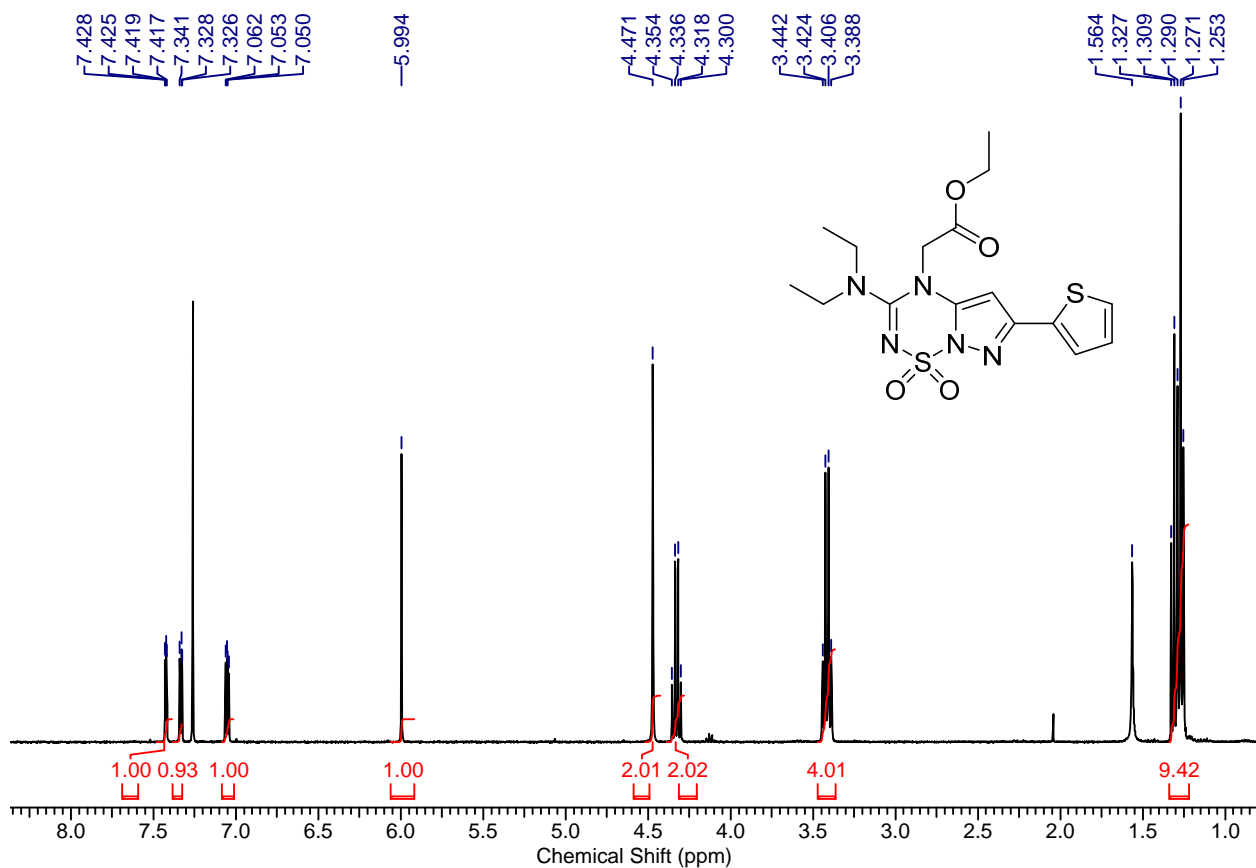


<sup>13</sup>C NMR spectrum of **11** 100MHz (CDCl<sub>3</sub>)

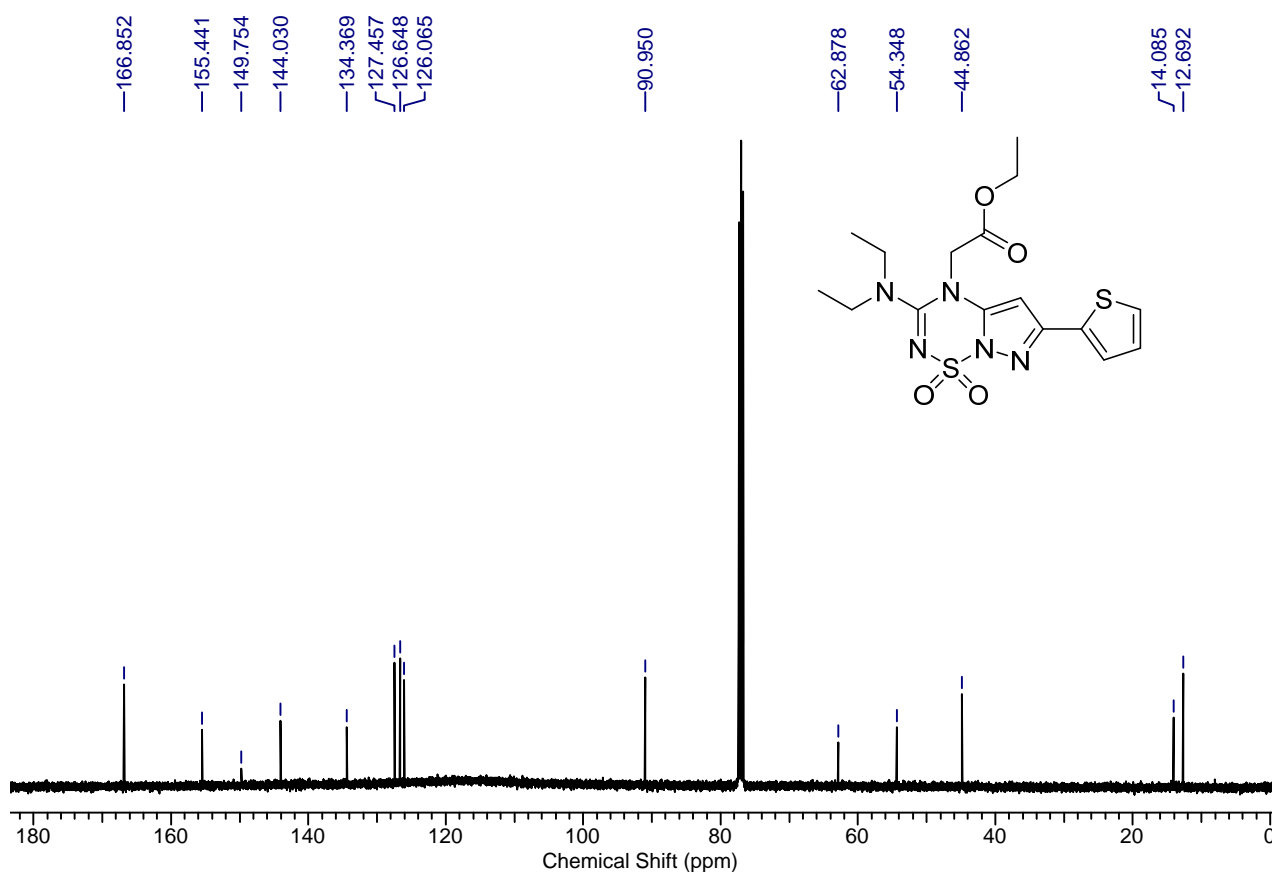
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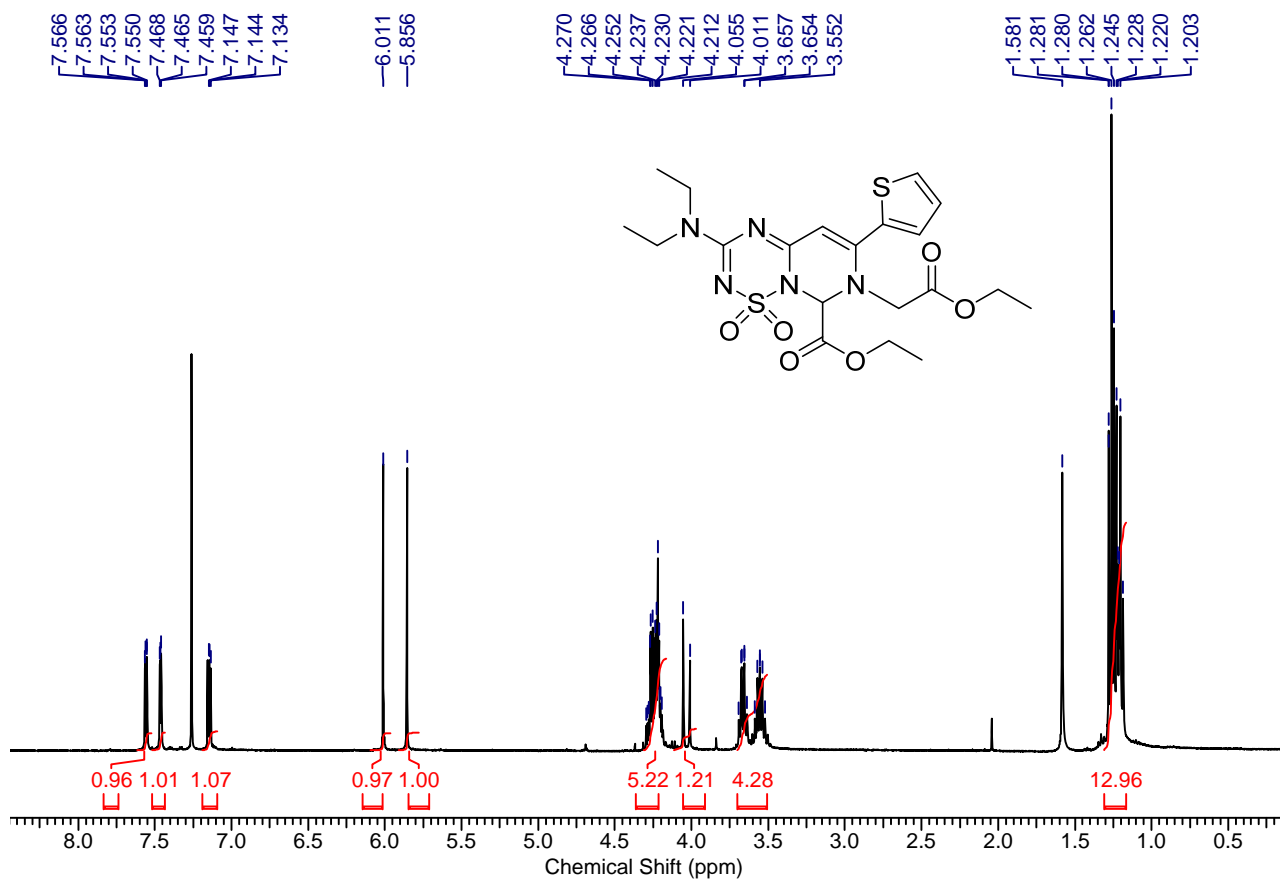
<sup>1</sup>H NMR spectrum of **12a** 600MHz (CDCl<sub>3</sub>)



<sup>13</sup>C NMR spectrum of **12a** 150MHz (CDCl<sub>3</sub>)

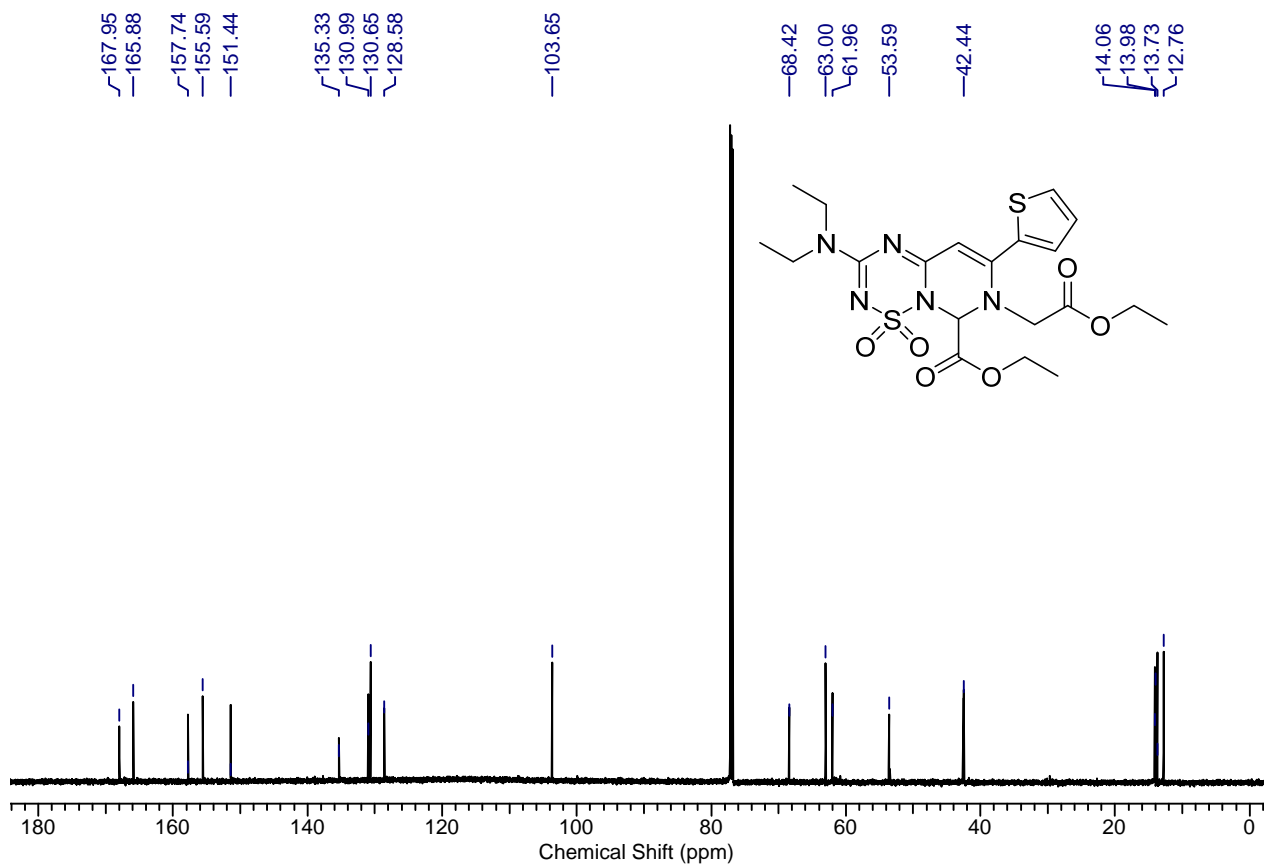


<sup>1</sup>H NMR spectrum of **14a** 600MHz (CDCl<sub>3</sub>)

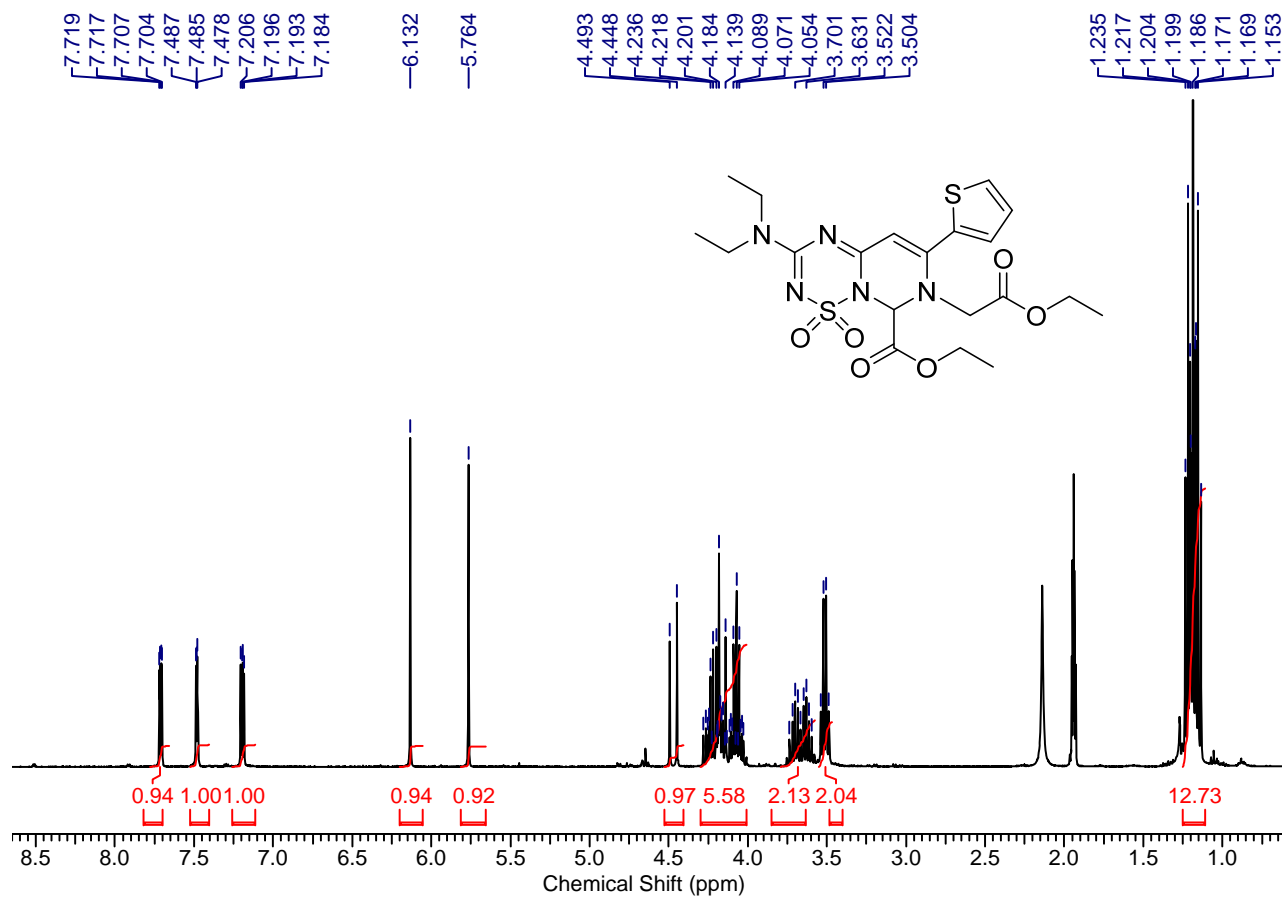


<sup>13</sup>C NMR spectrum of **14a** 150MHz (CDCl<sub>3</sub>)

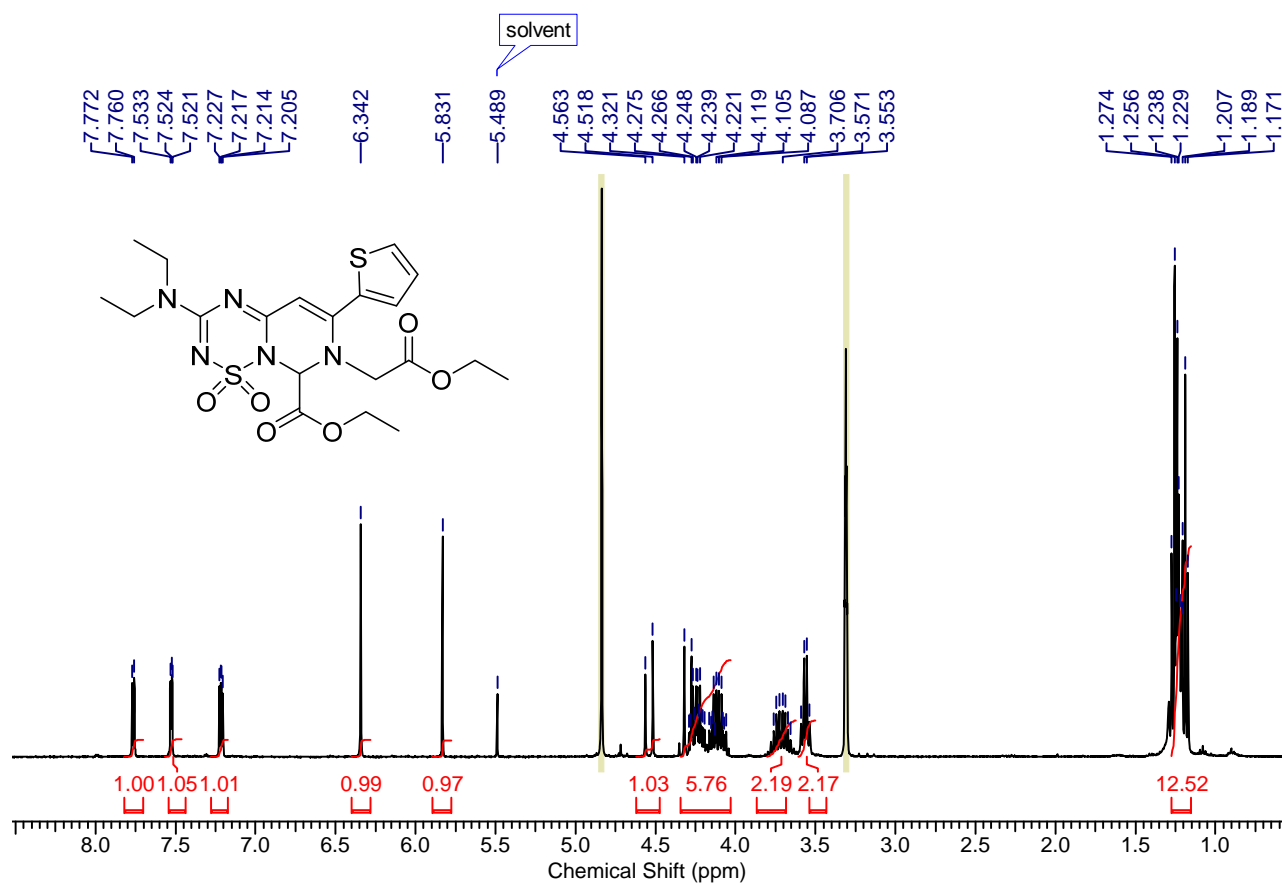
S30



<sup>1</sup>H NMR spectrum of **14a** 400MHz (CD<sub>3</sub>CN)

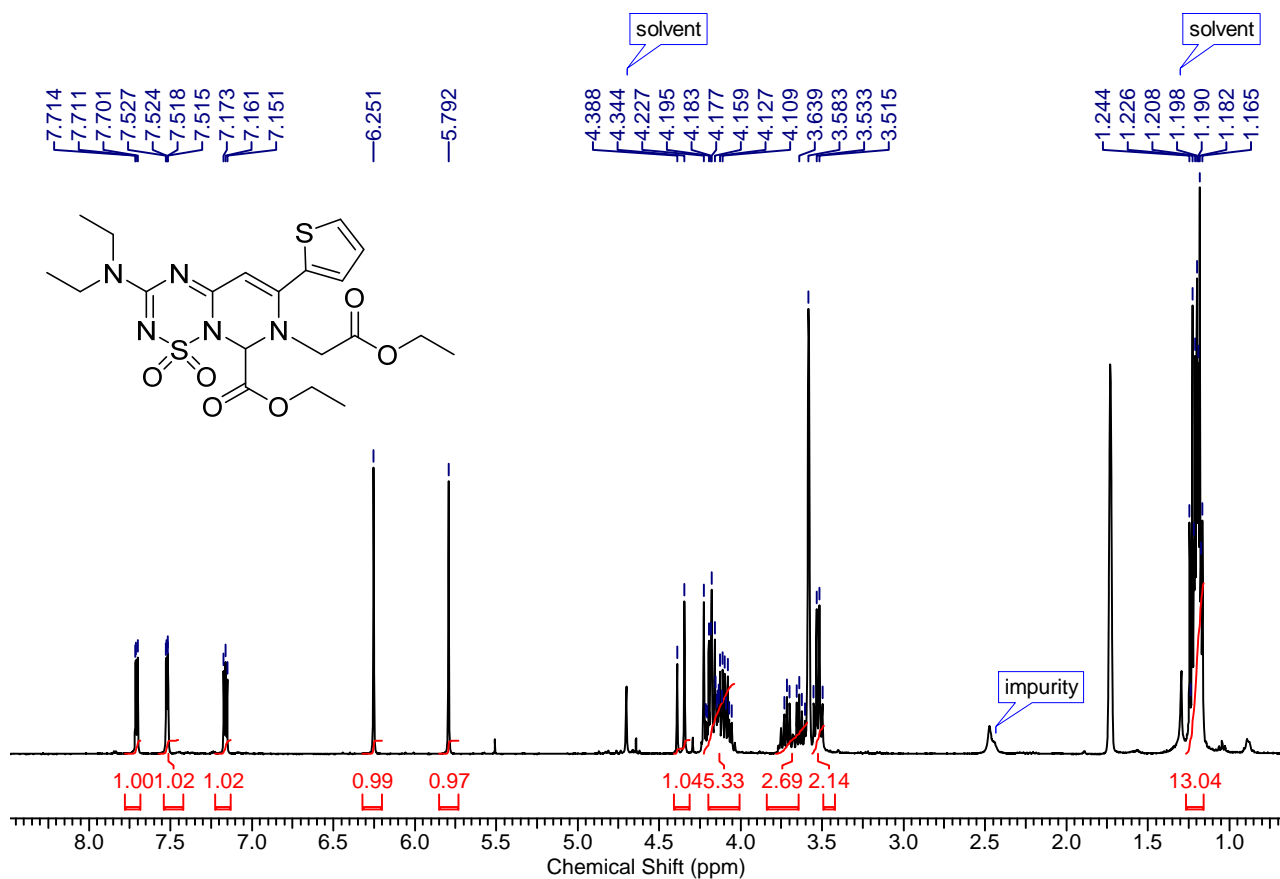


<sup>1</sup>H NMR spectrum of **14a** 400MHz (Methanol-*d*<sup>4</sup>)

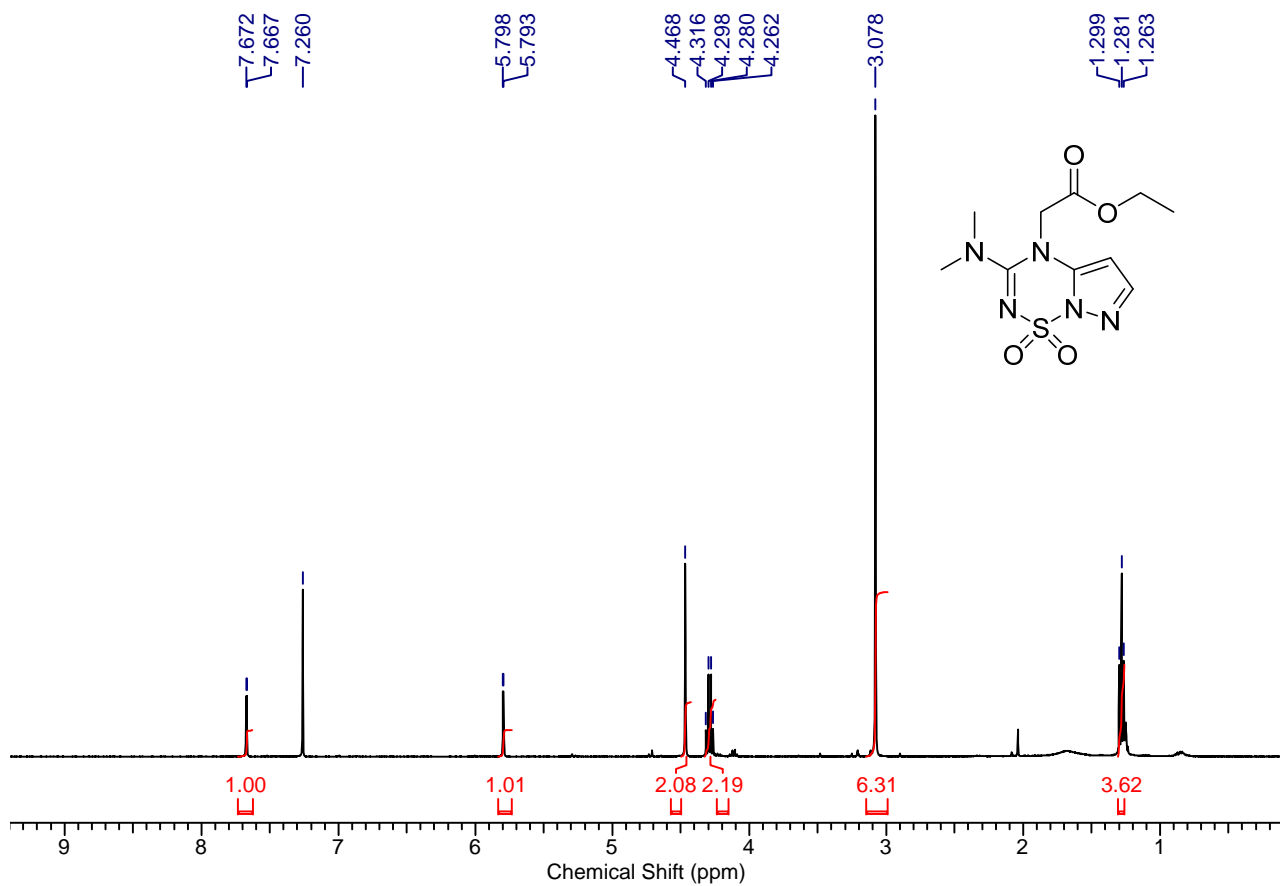




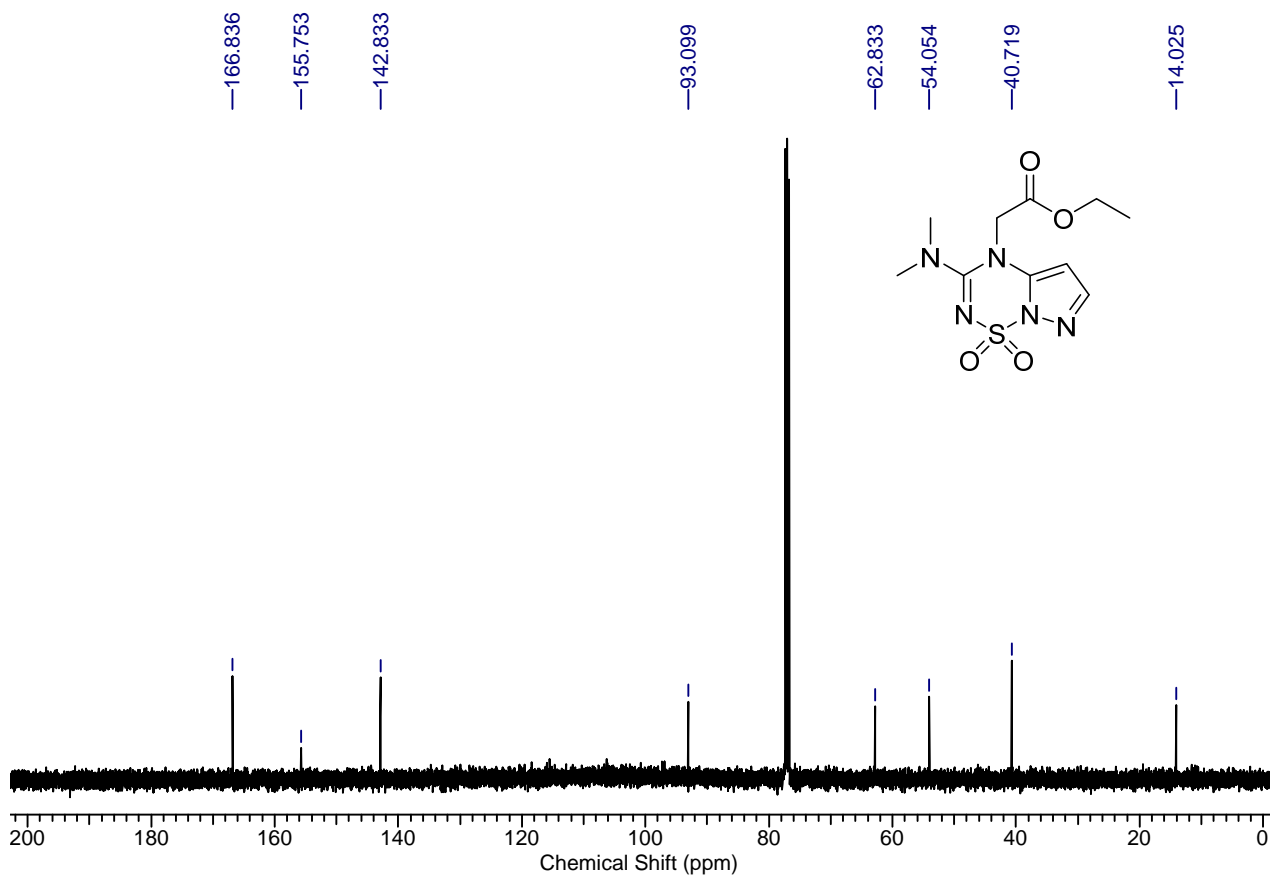
<sup>1</sup>H NMR spectrum of **14a** 400MHz (THF-*d*<sup>8</sup>)



<sup>1</sup>H NMR spectrum of **12b** 400MHz (CDCl<sub>3</sub>)

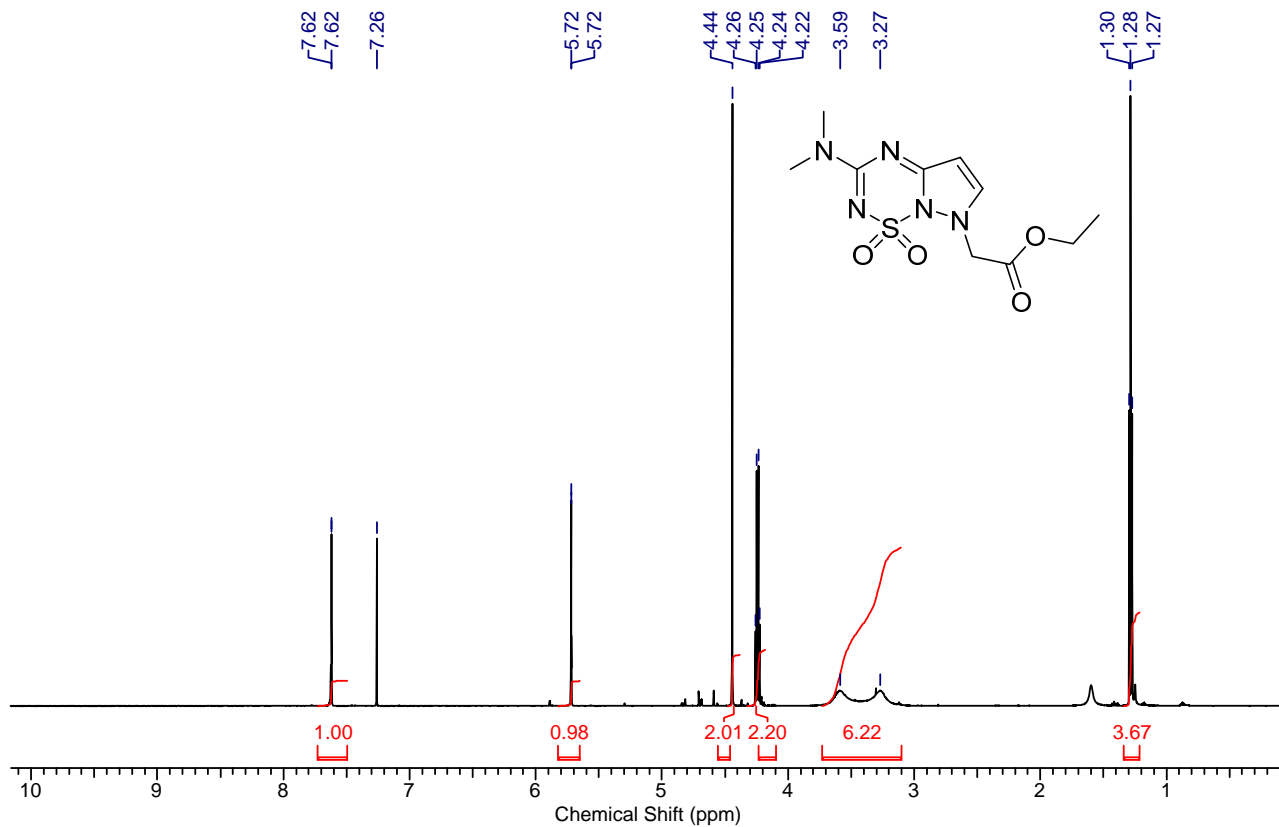


<sup>13</sup>C NMR spectrum of **12b** 100MHz (CDCl<sub>3</sub>)

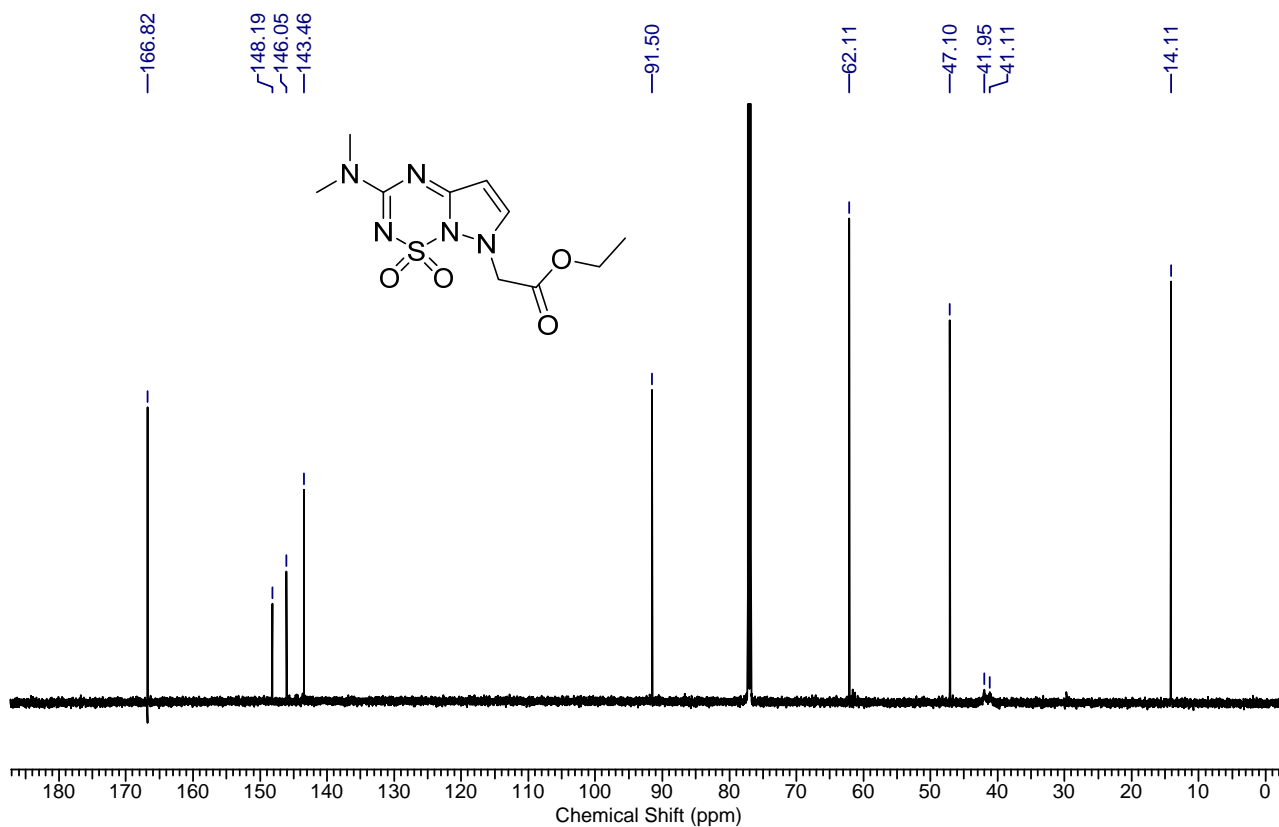


S33

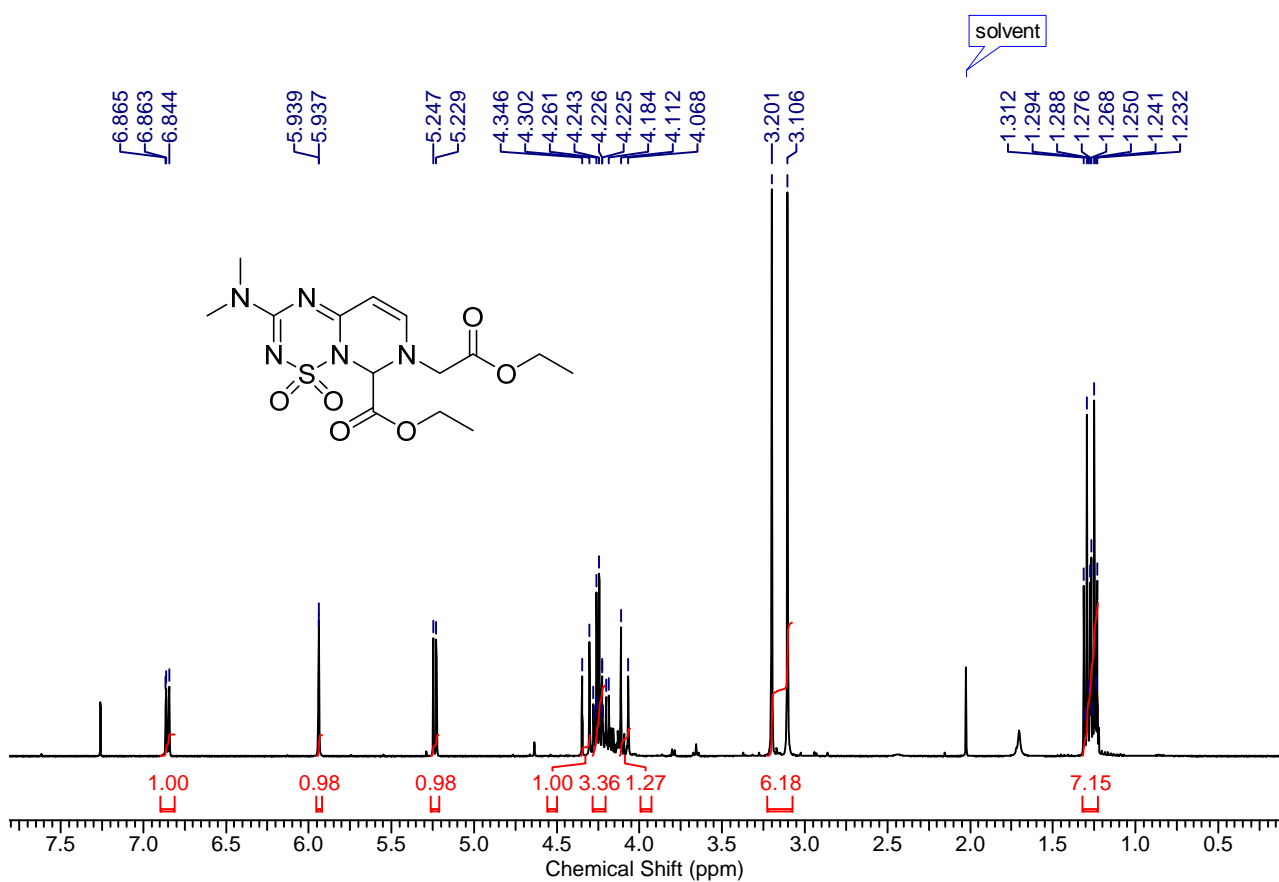
<sup>1</sup>H NMR spectrum of **13b** 600MHz (CDCl<sub>3</sub>)



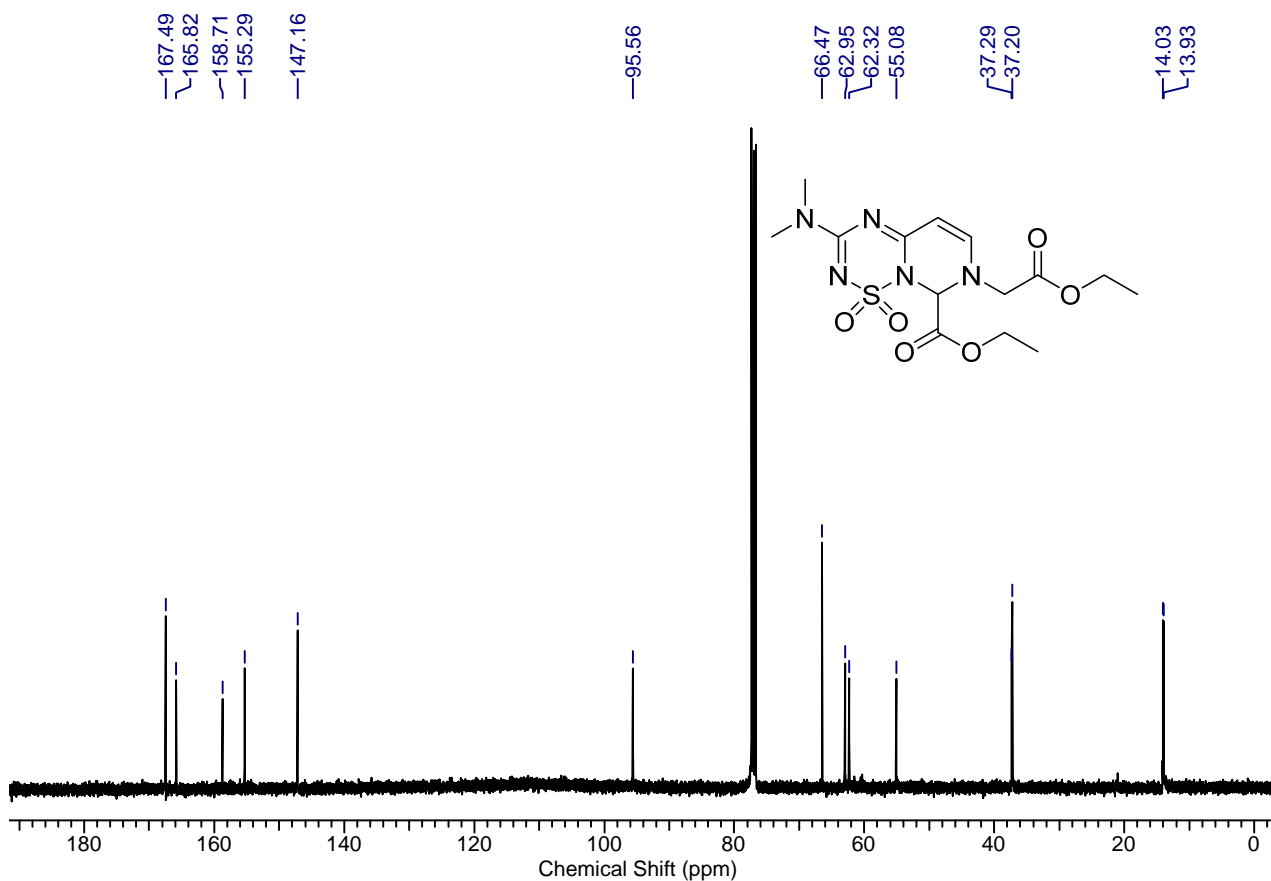
$^{13}\text{C}$  NMR spectrum of **13b** 100MHz ( $\text{CDCl}_3$ )



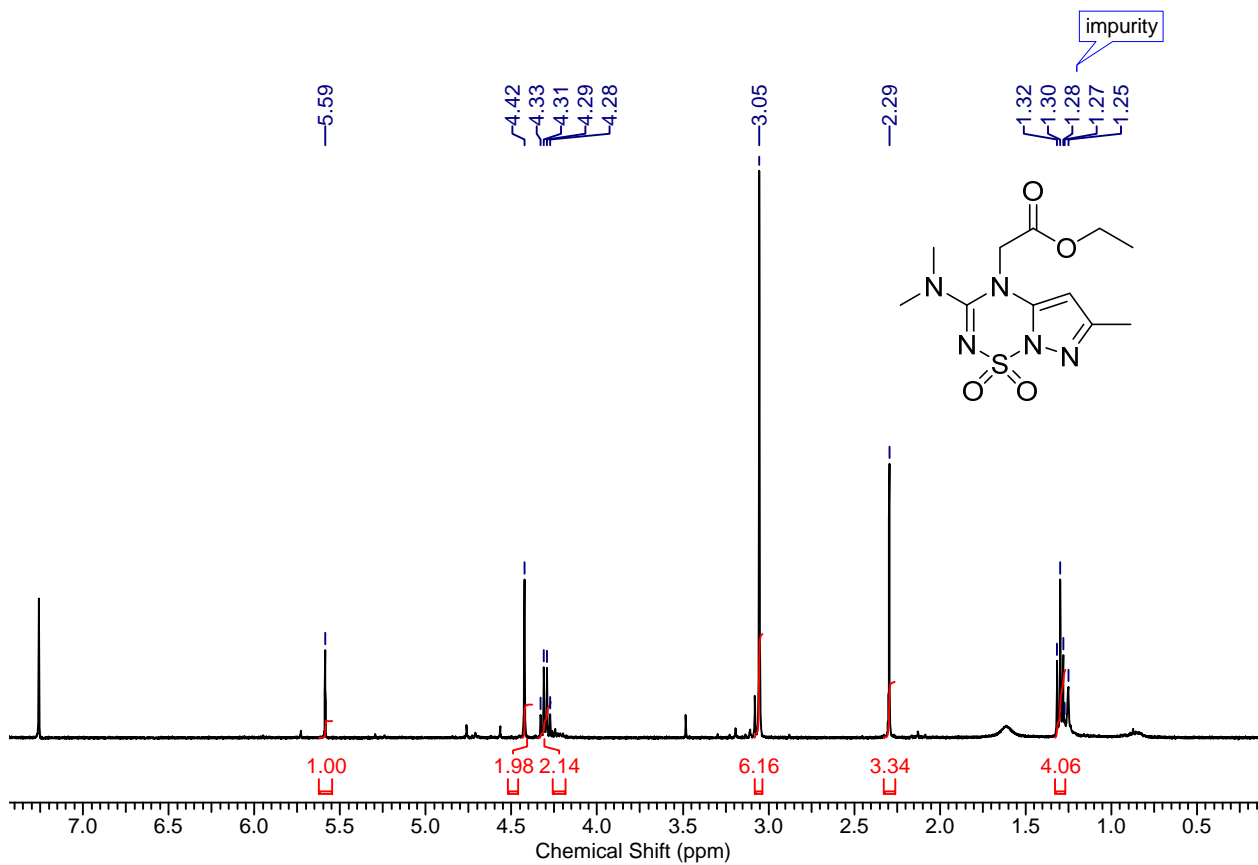
$^1\text{H}$  NMR spectrum of **14b** 400MHz ( $\text{CDCl}_3$ )



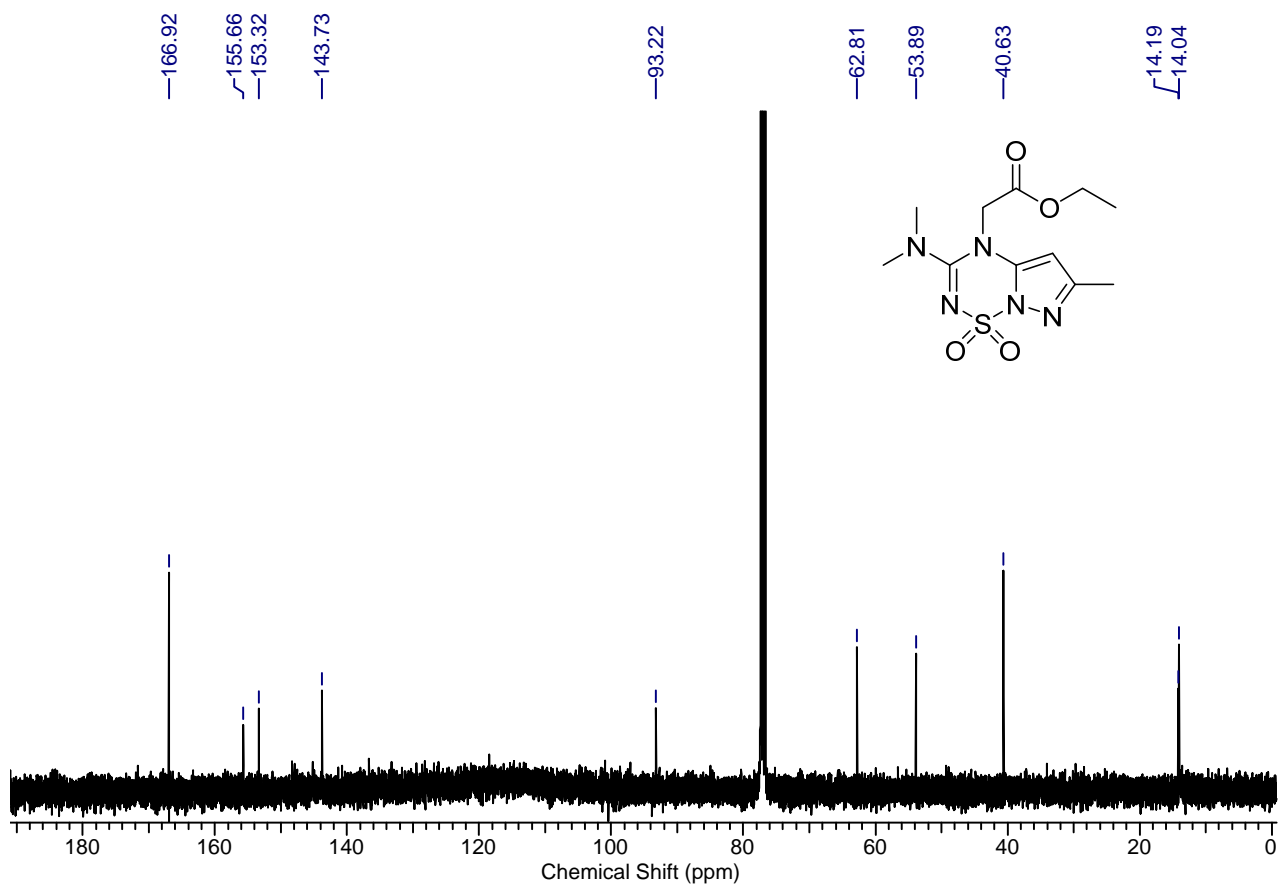
<sup>13</sup>C NMR spectrum of **14b** 100MHz (CDCl<sub>3</sub>)



<sup>1</sup>H NMR spectrum of **12c** 400MHz (CDCl<sub>3</sub>)

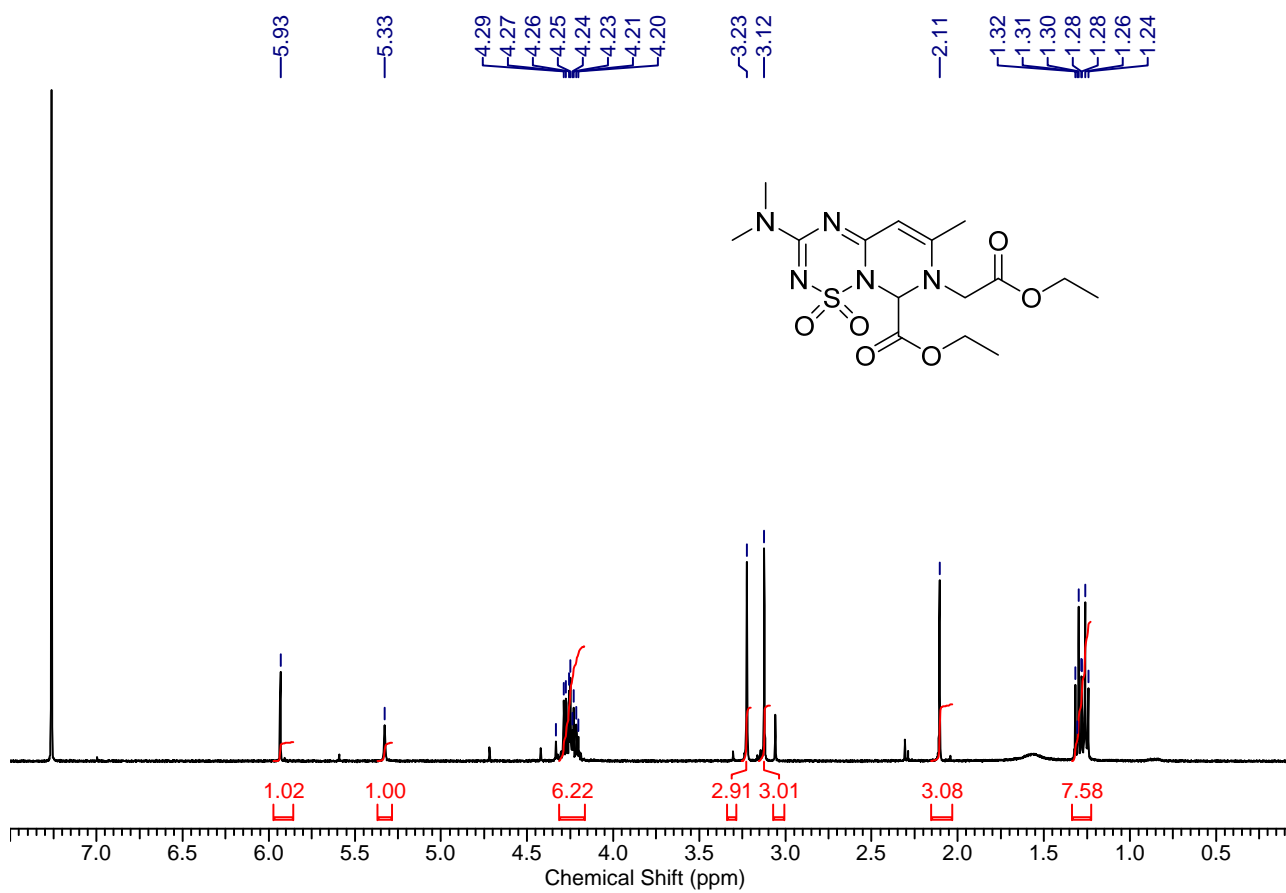


$^{13}\text{C}$  NMR spectrum of **12c** 100MHz ( $\text{CDCl}_3$ )

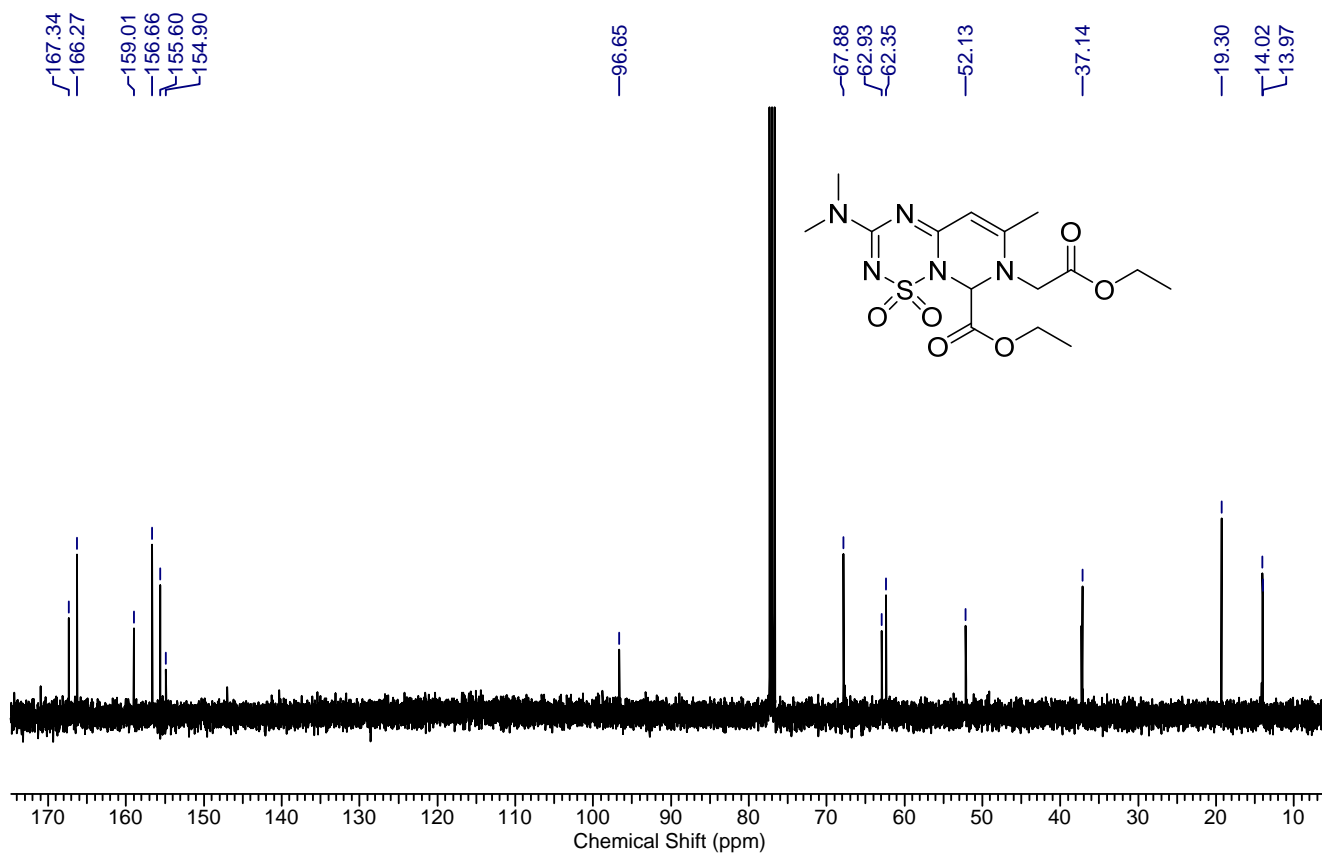


$^1\text{H}$  NMR spectrum of **14c** 400MHz ( $\text{CDCl}_3$ )

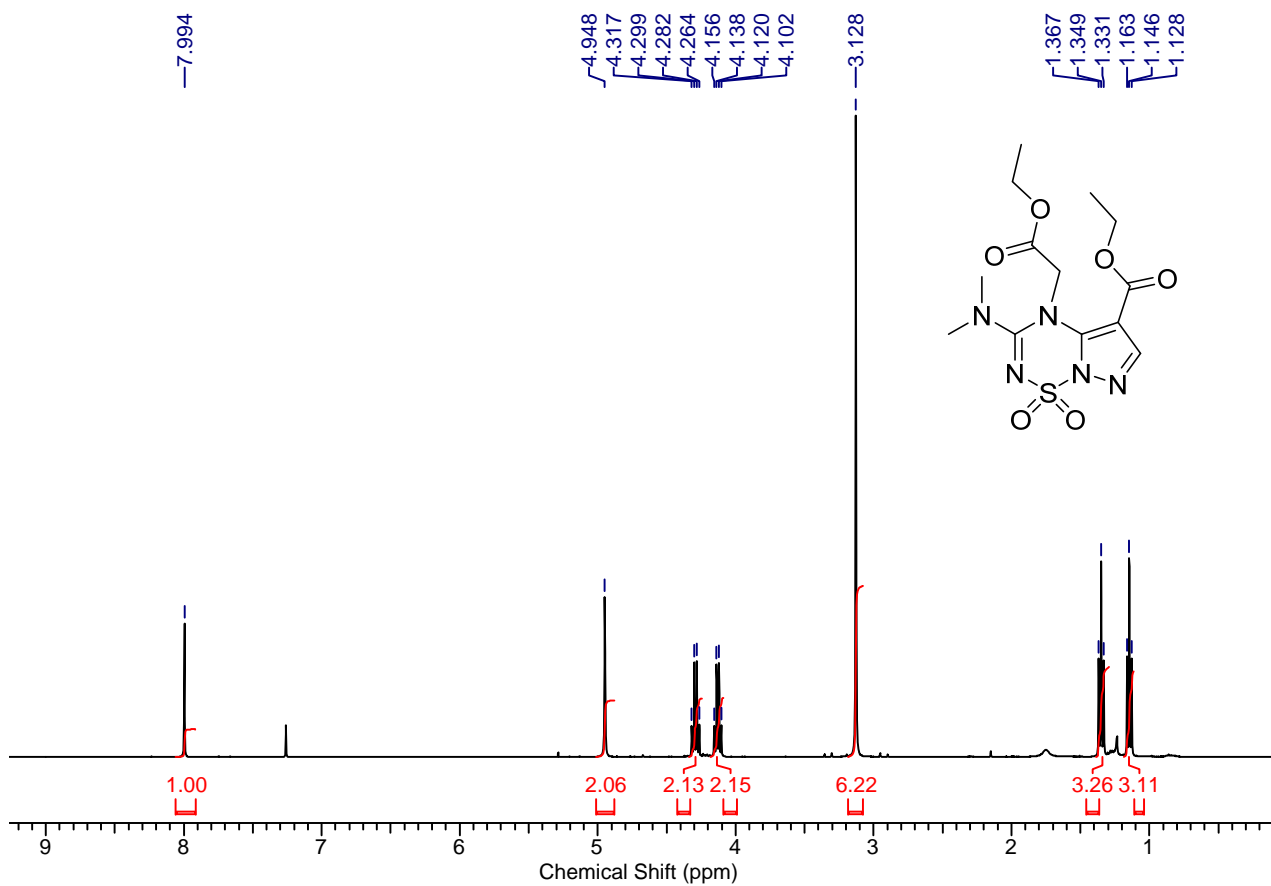
S36



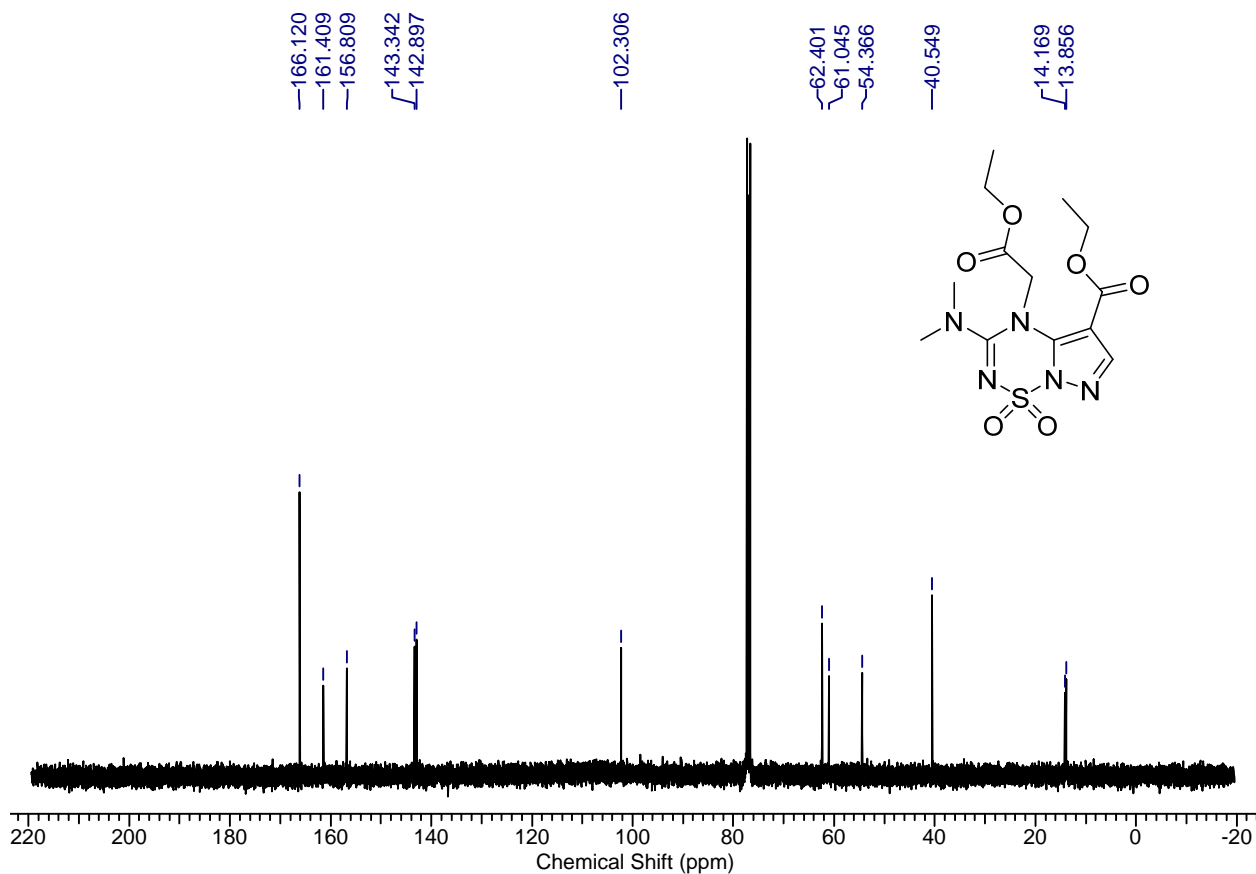
<sup>13</sup>C NMR spectrum of **14c** 100MHz (CDCl<sub>3</sub>)



<sup>1</sup>H NMR spectrum of **12d** 100MHz (CDCl<sub>3</sub>)

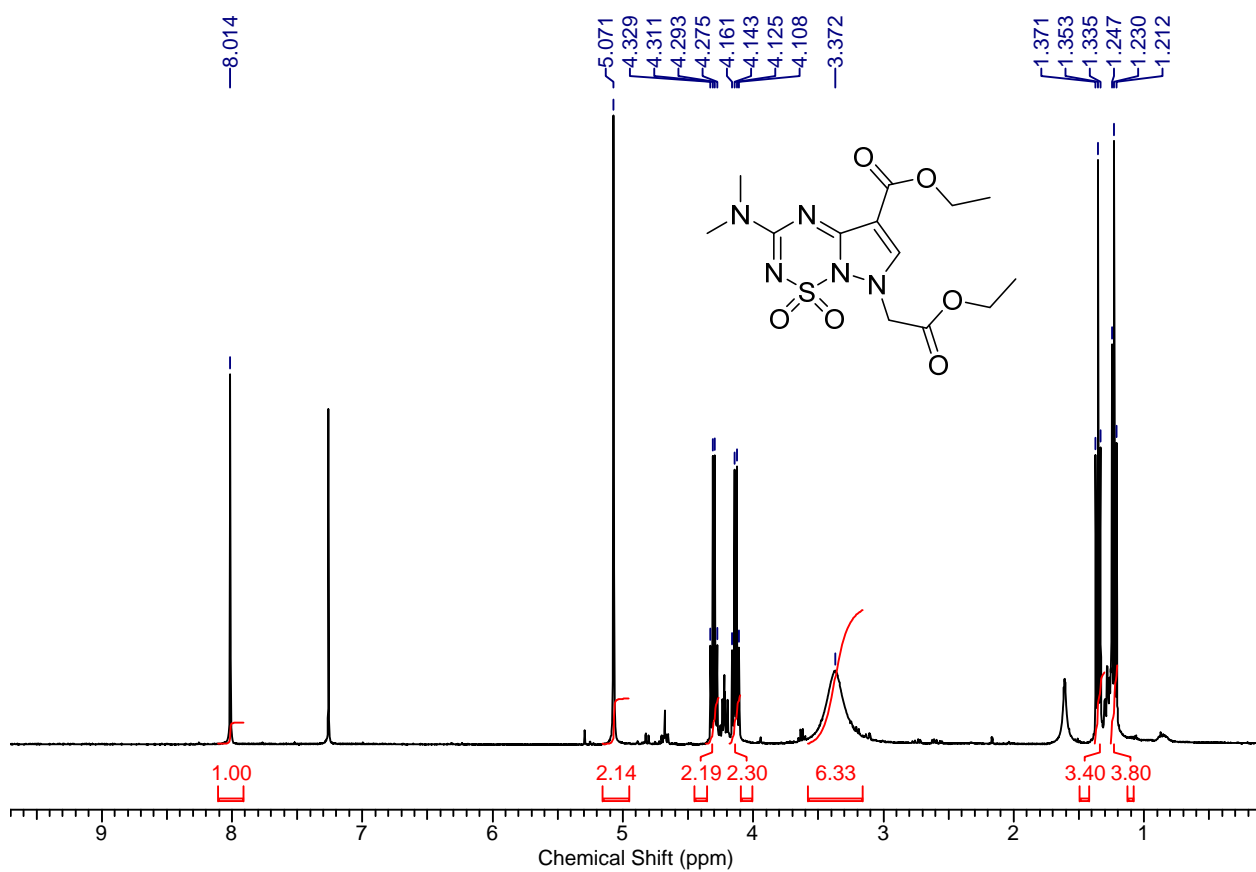


<sup>13</sup>C NMR spectrum of **12d** 100MHz (CDCl<sub>3</sub>)

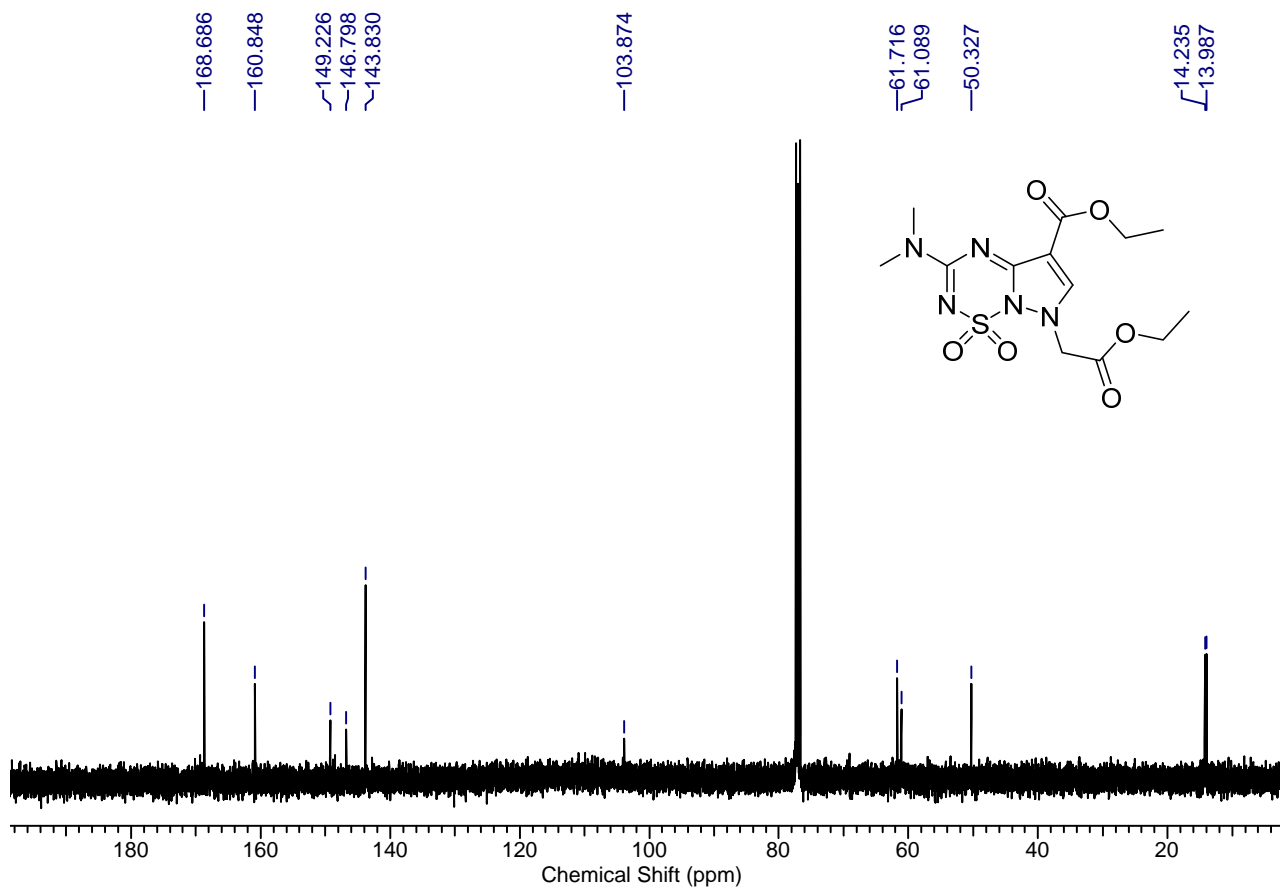


<sup>1</sup>H NMR spectrum of **13d** 400MHz (CDCl<sub>3</sub>)

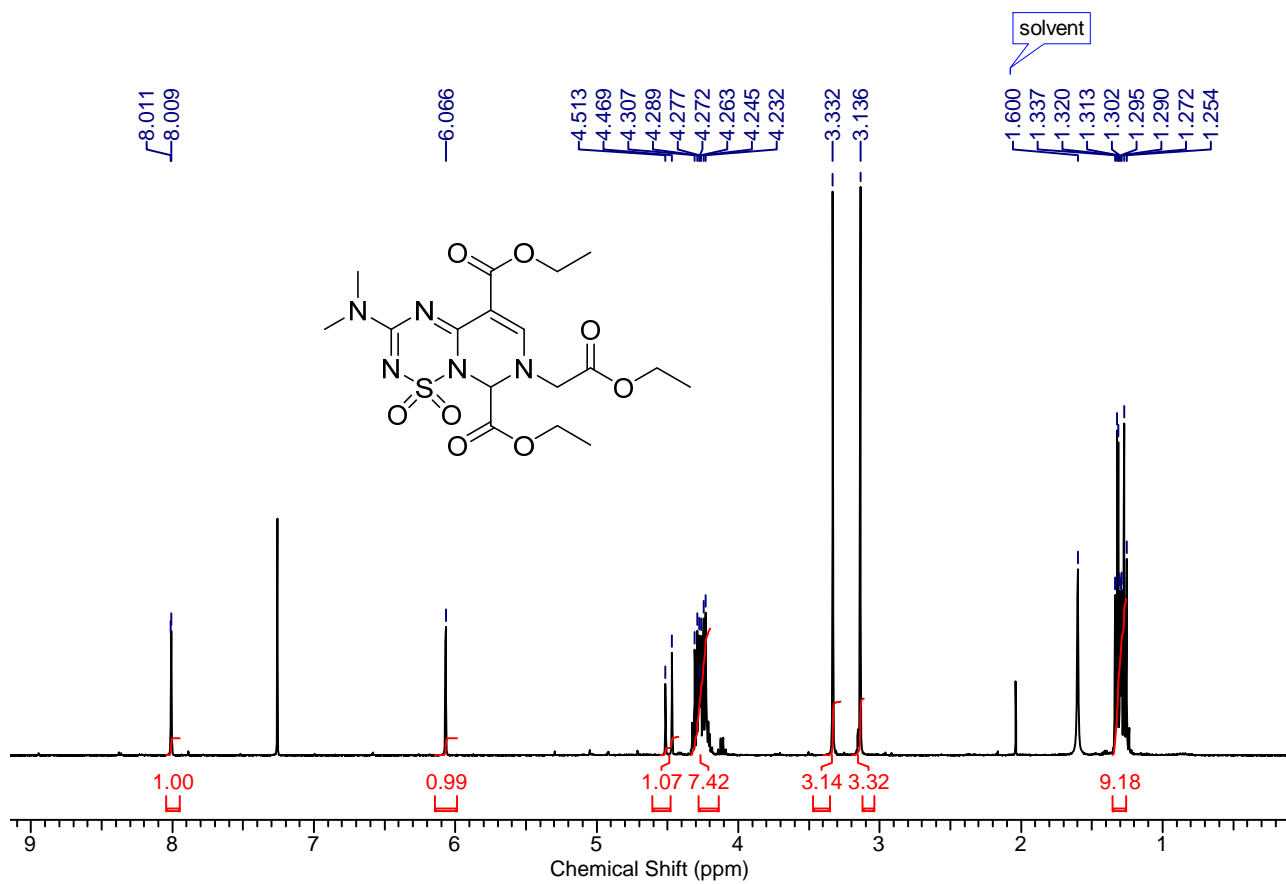
S38



<sup>13</sup>C NMR spectrum of **13d** 100MHz (CDCl<sub>3</sub>)

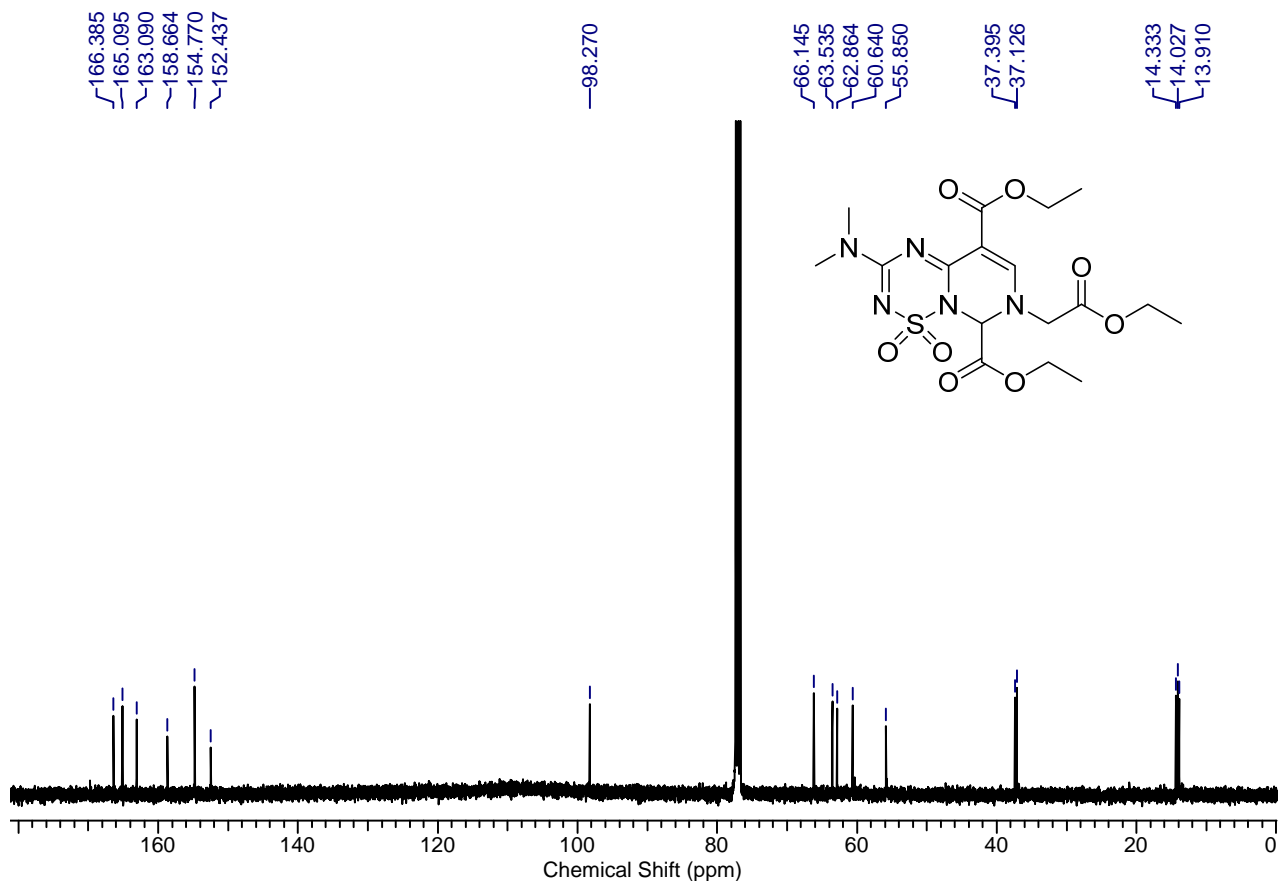


<sup>1</sup>H NMR spectrum of **14d** 400MHz (CDCl<sub>3</sub>)



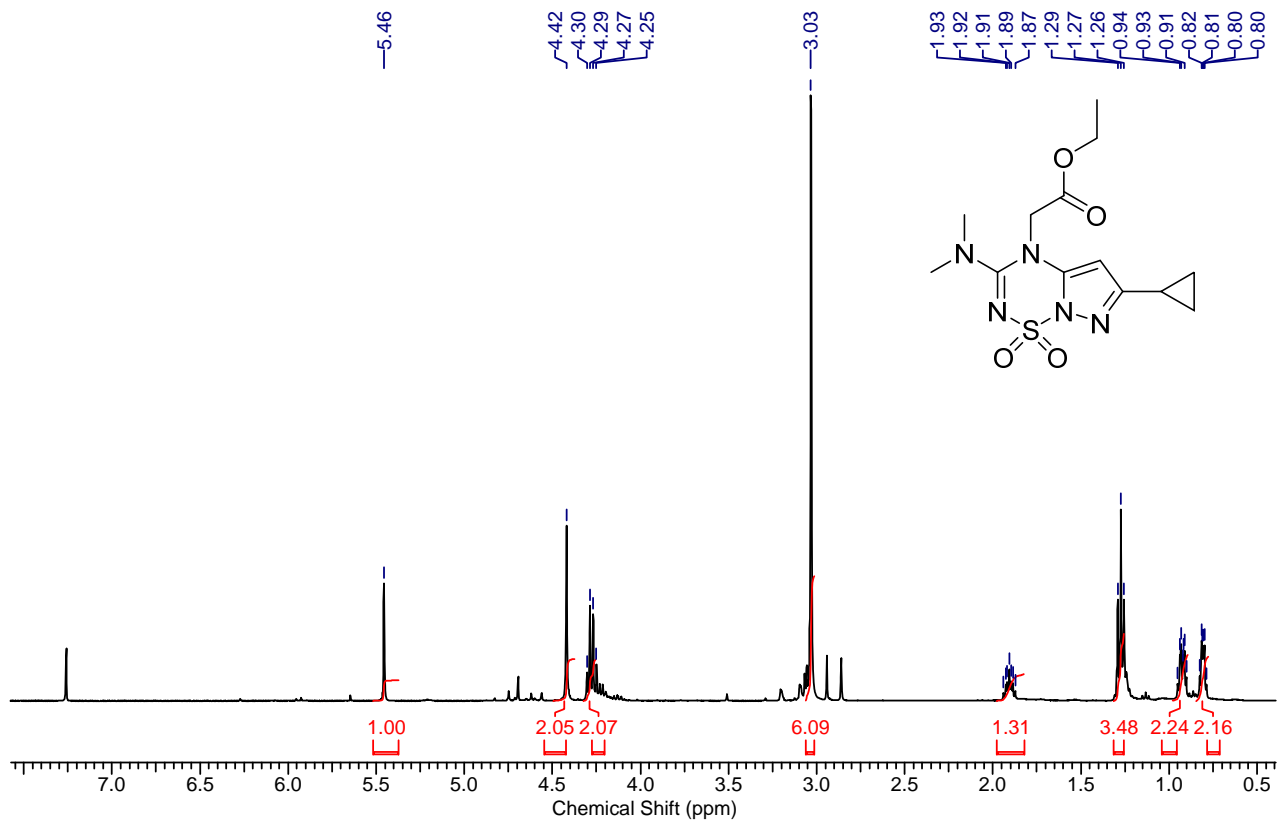


<sup>13</sup>C NMR spectrum of **14d** 100MHz (CDCl<sub>3</sub>)

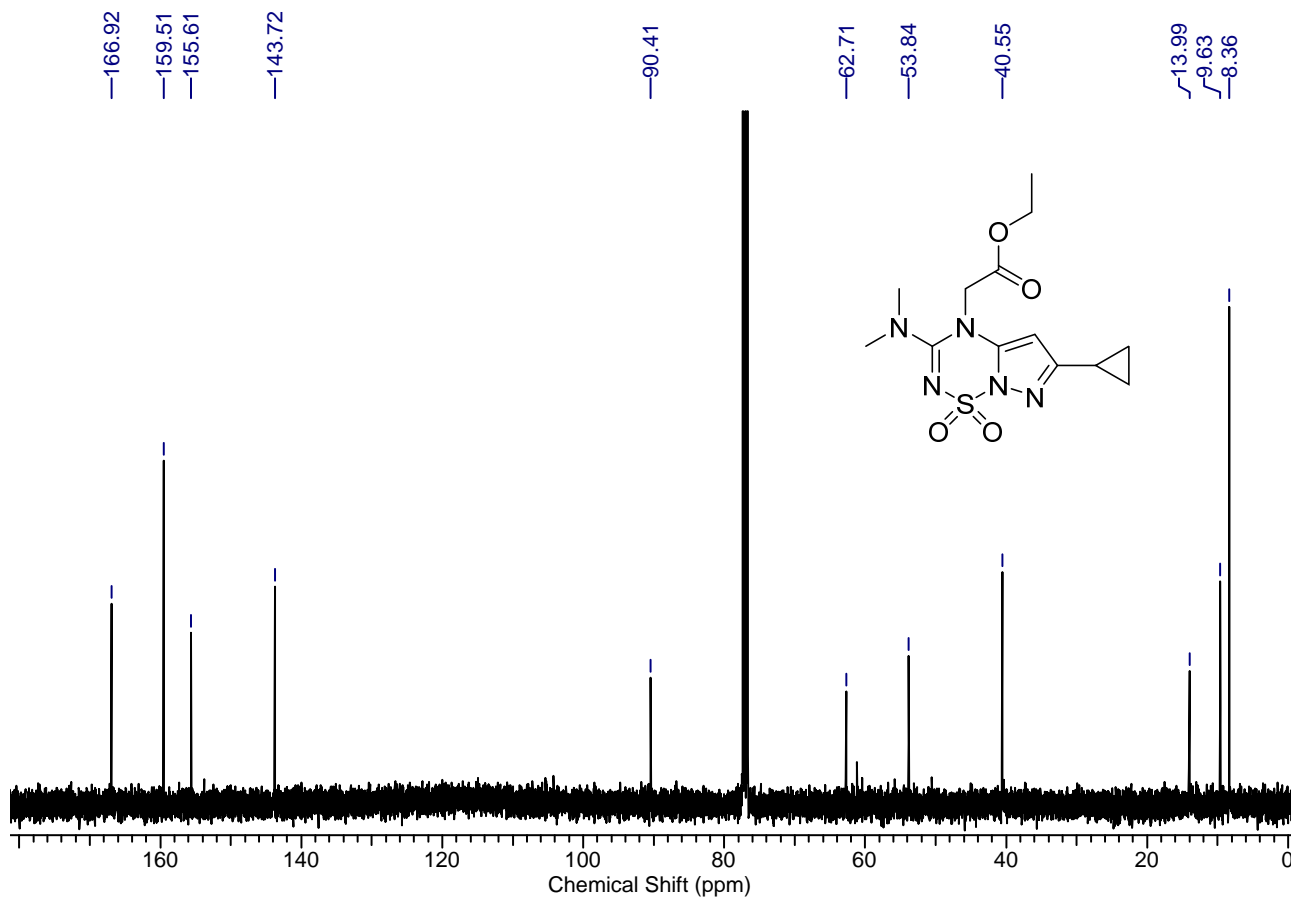


S40

<sup>1</sup>H NMR spectrum of **12e** 400MHz (CDCl<sub>3</sub>)

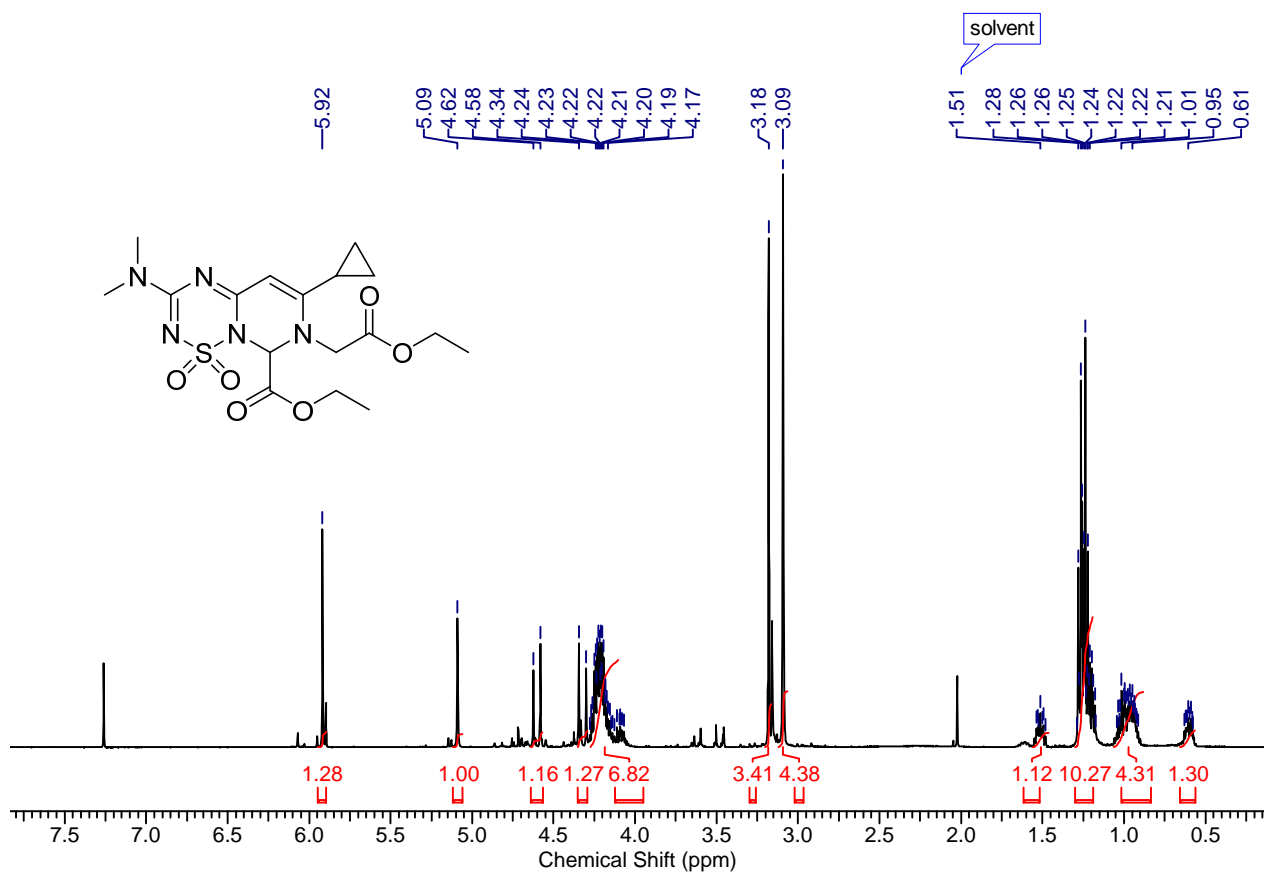


$^{13}\text{C}$  NMR spectrum of **12e** 100MHz ( $\text{CDCl}_3$ )

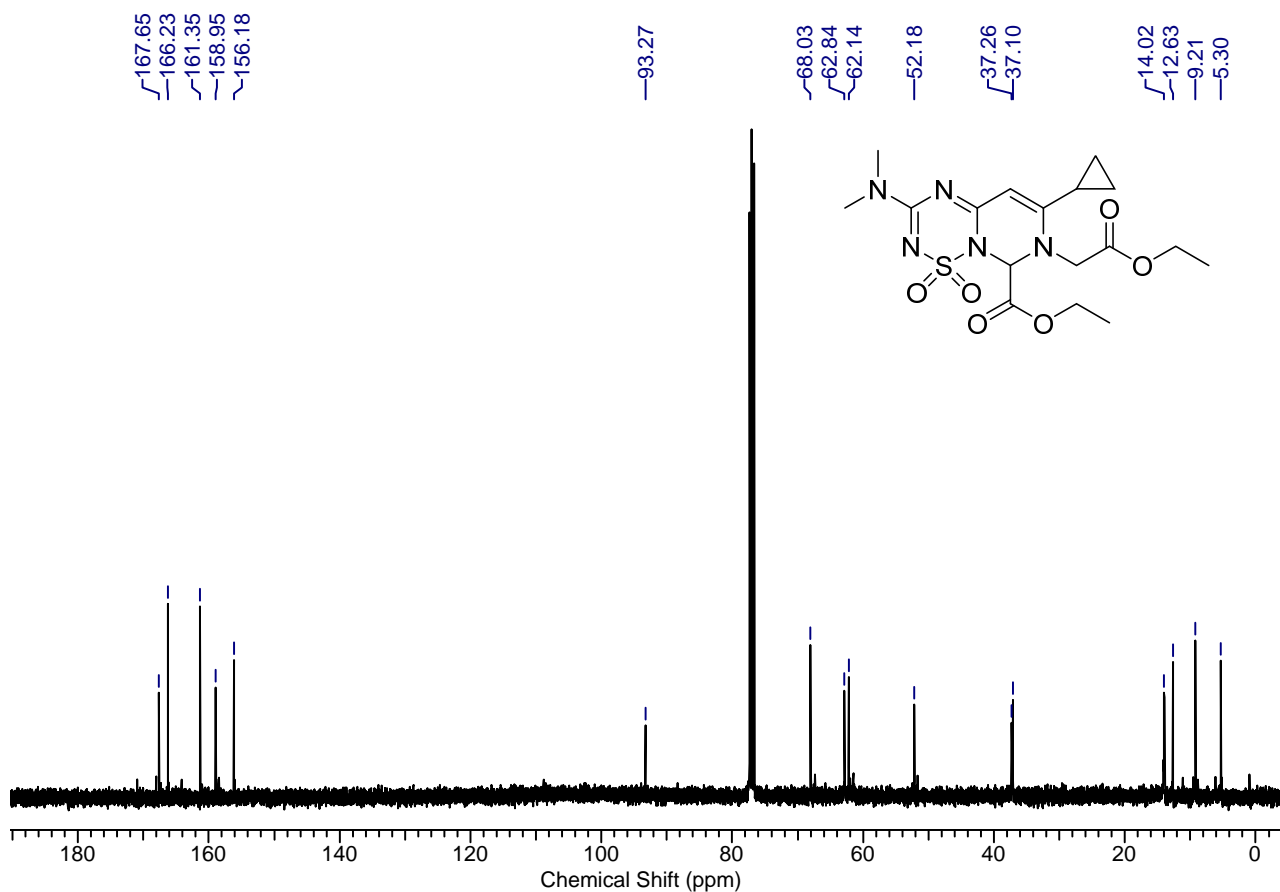


$^1\text{H}$  NMR spectrum of **14e** 400MHz ( $\text{CDCl}_3$ )

S41

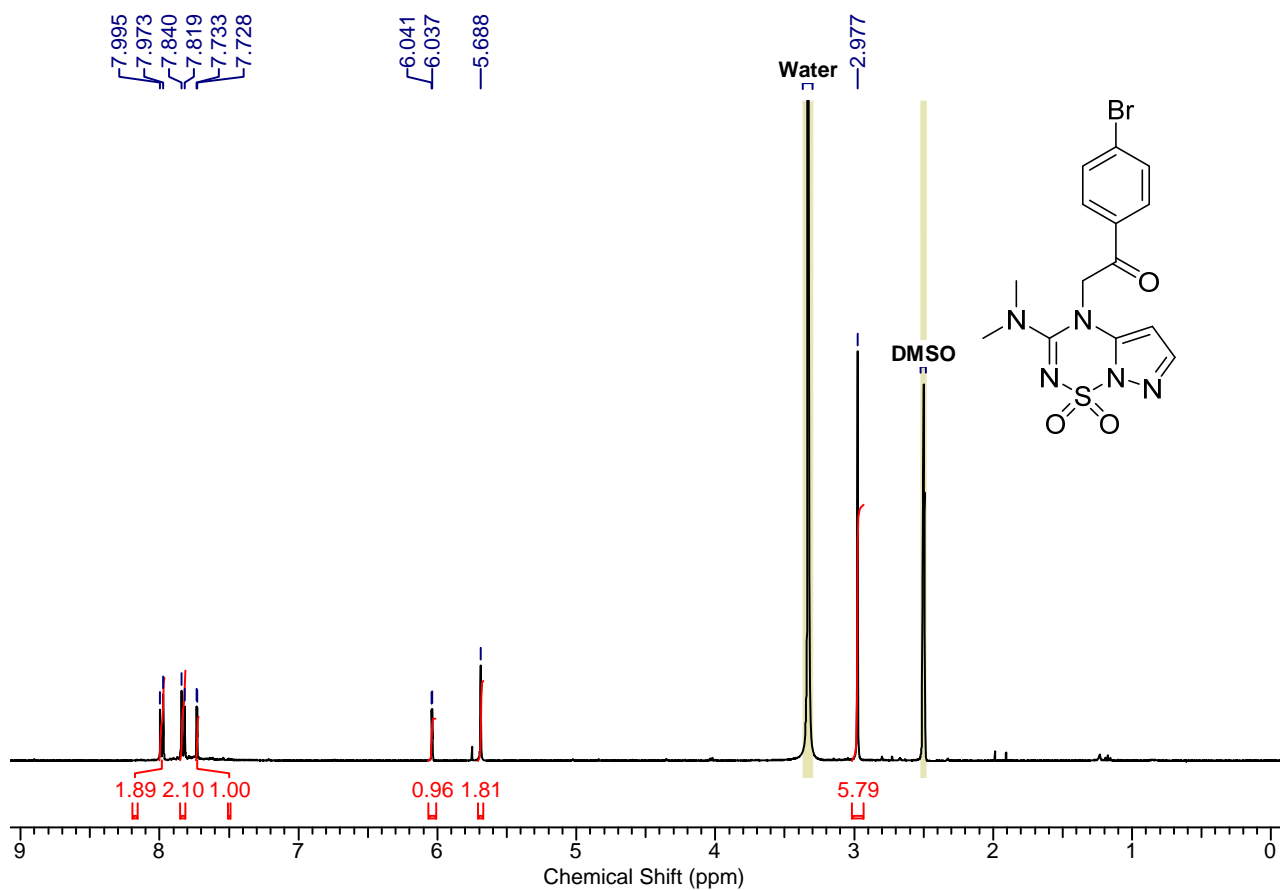


<sup>13</sup>C NMR spectrum of **14e** 100MHz (CDCl<sub>3</sub>)

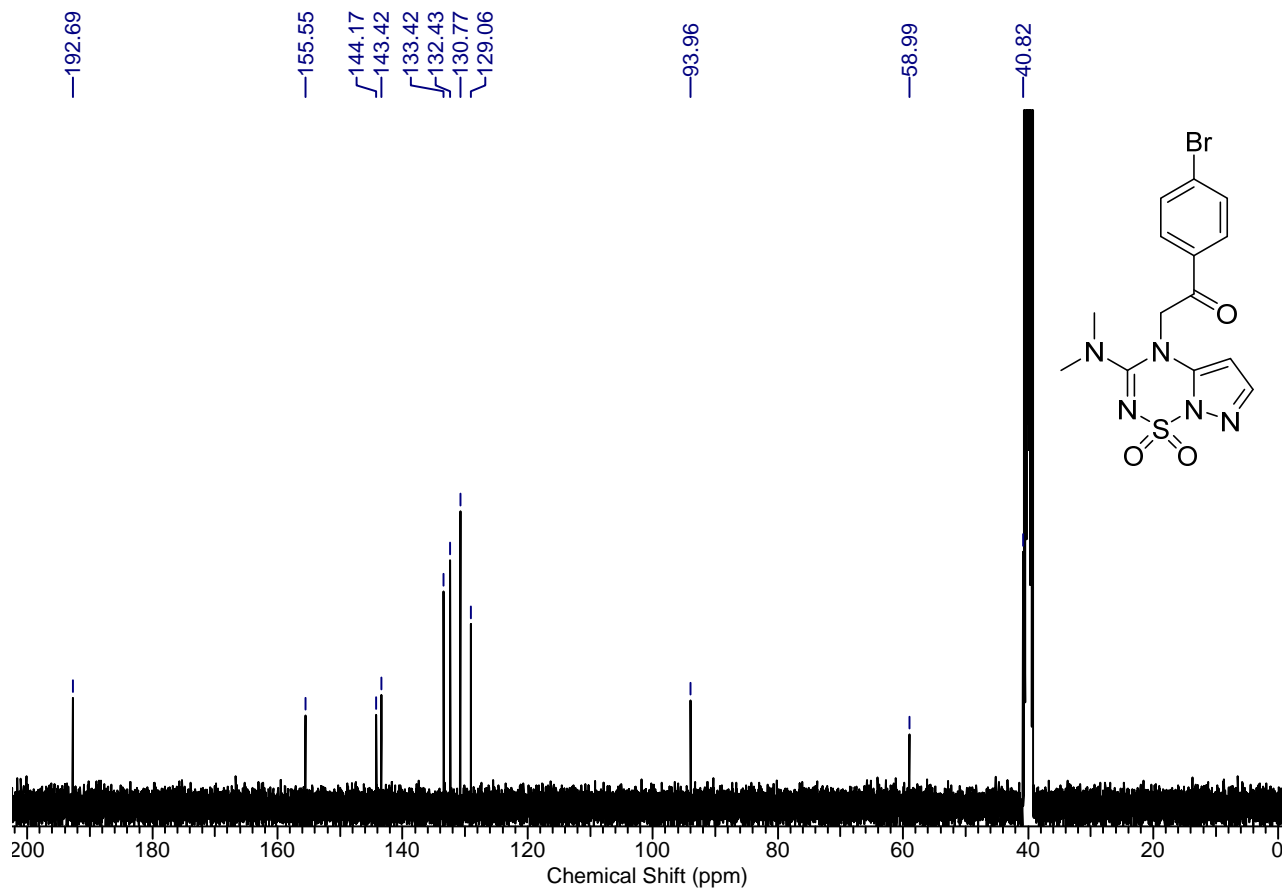


<sup>1</sup>H NMR spectrum of **12f** 400MHz (CDCl<sub>3</sub>)

S42

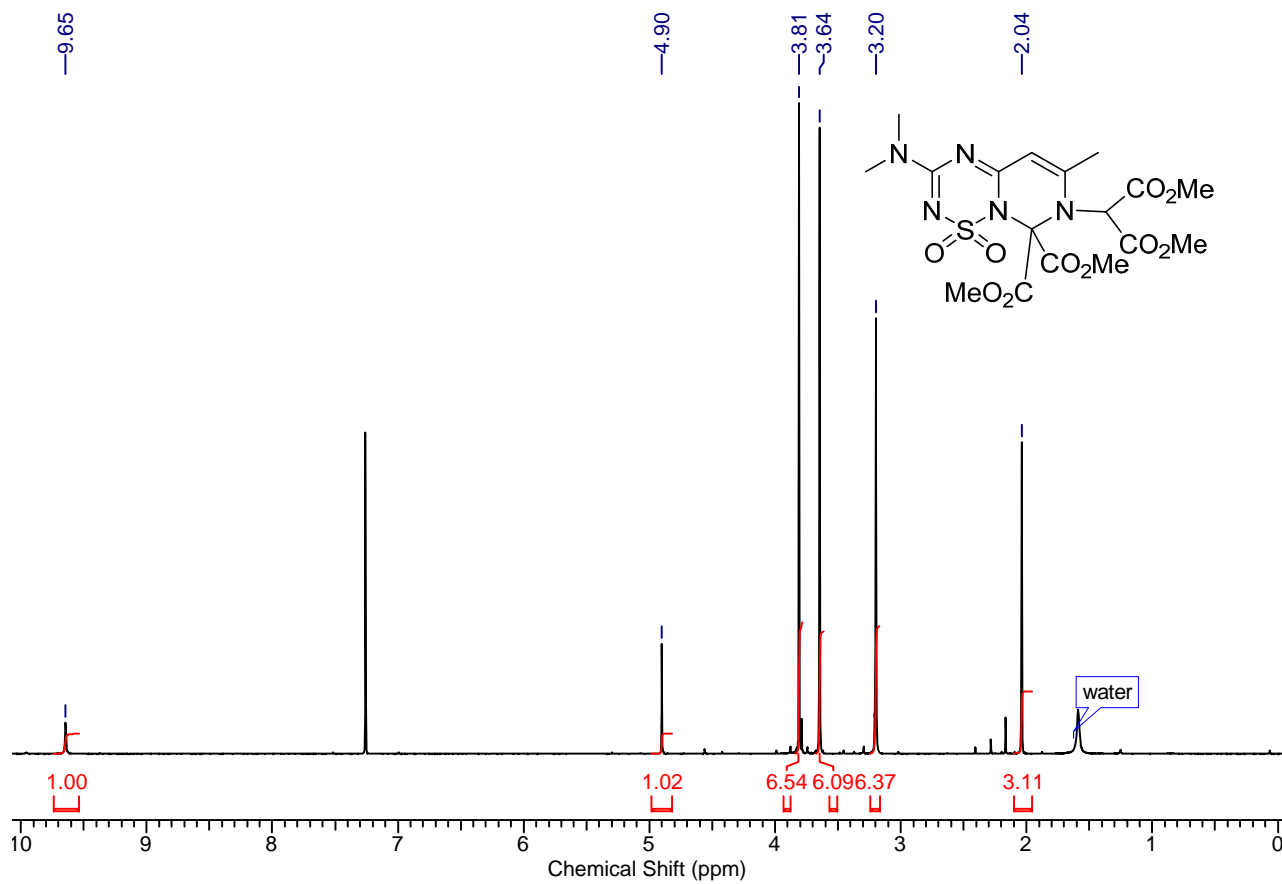


<sup>13</sup>C NMR spectrum of **12f** 100MHz (CDCl<sub>3</sub>)

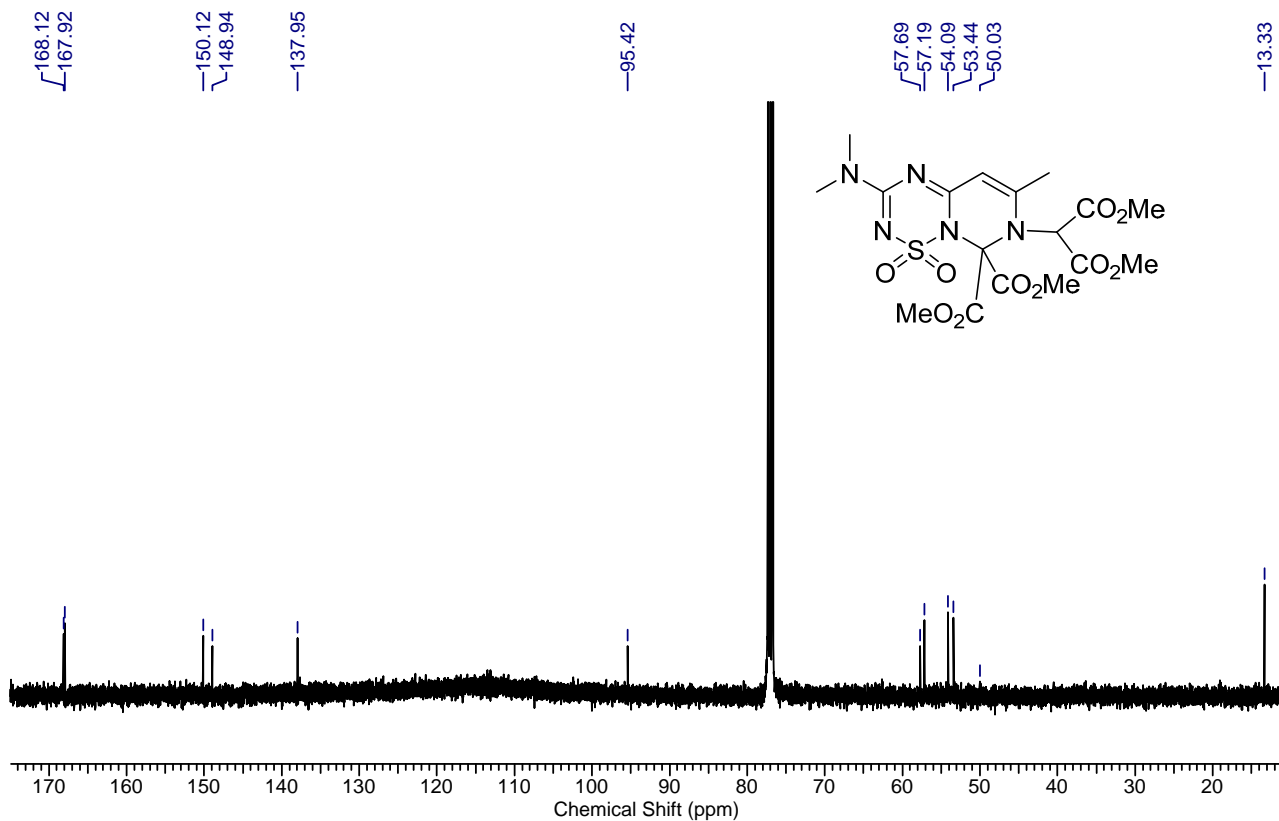


<sup>1</sup>H NMR spectrum of **14g** 400MHz (CDCl<sub>3</sub>)

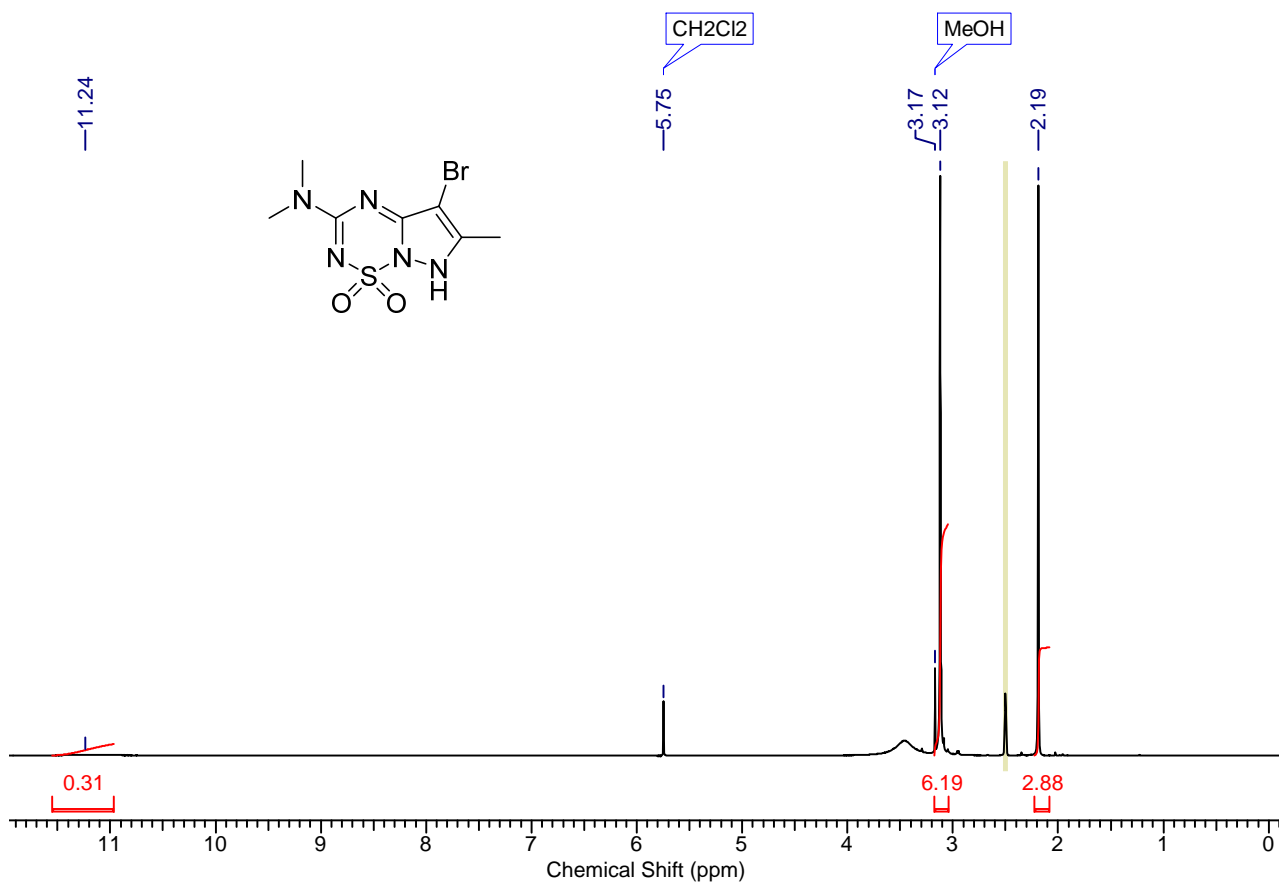
S43



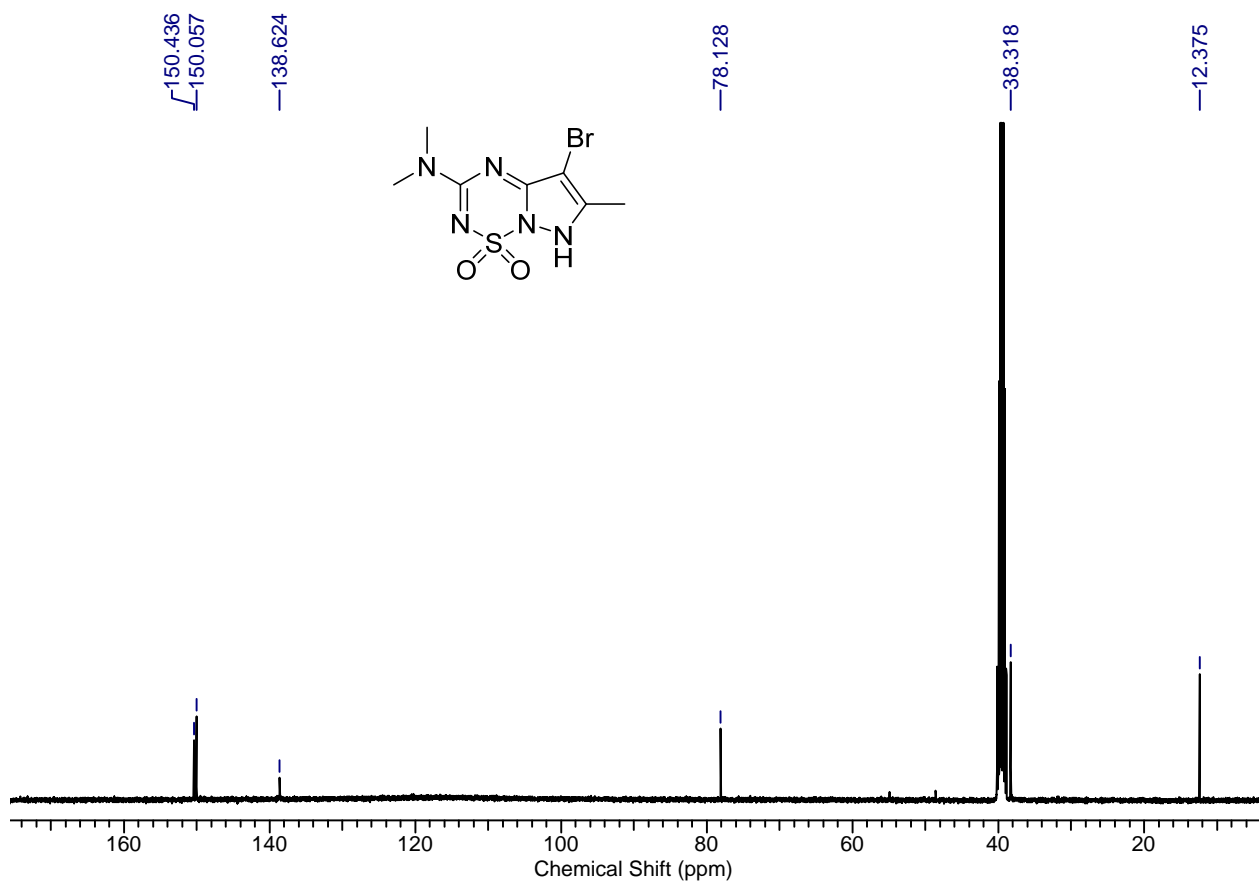
$^{13}\text{C}$  NMR spectrum of **14g** 100MHz ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR spectrum of **15a** 400MHz ( $\text{DMSO}-d_6$ )

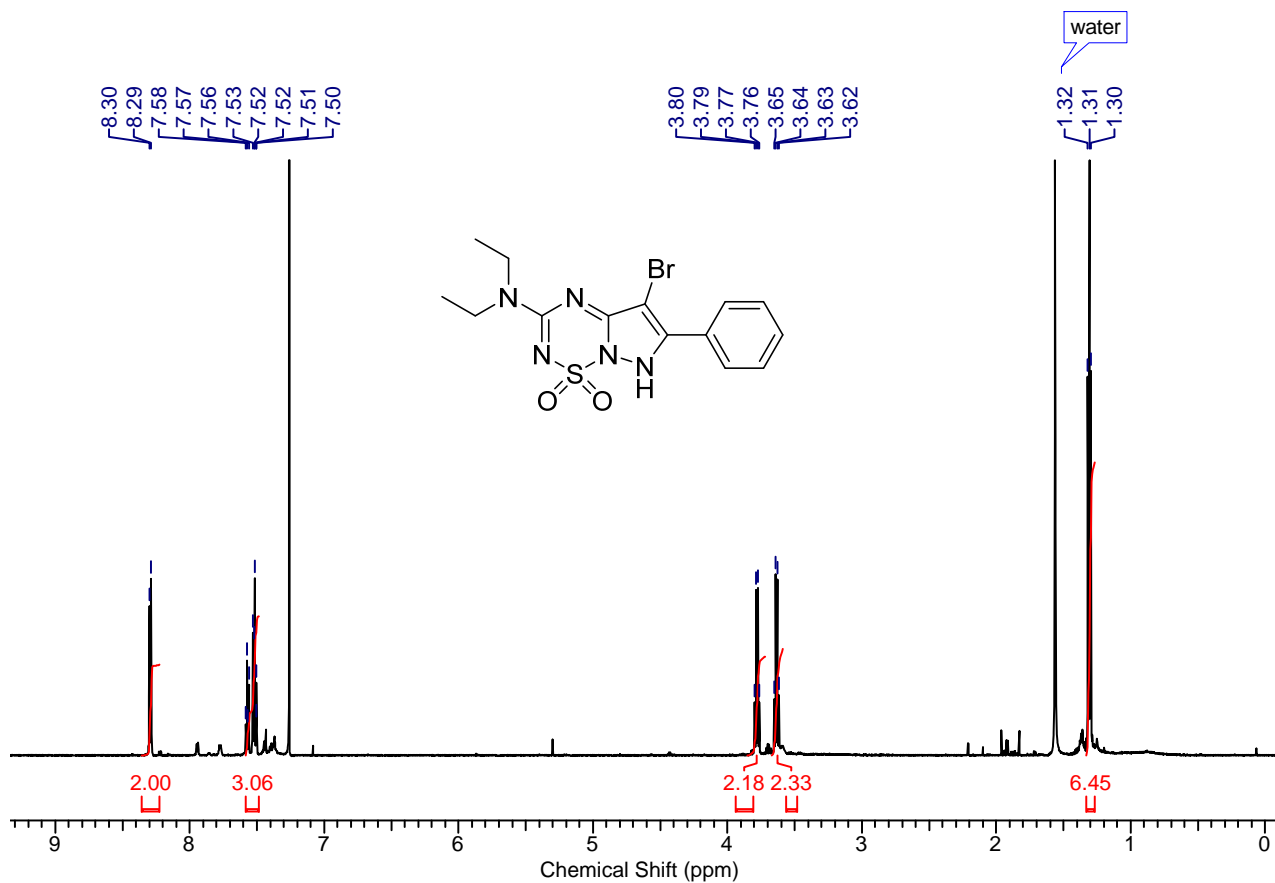


$^{13}\text{C}$  NMR spectrum of **15a** 100MHz (DMSO- $d_6$ )

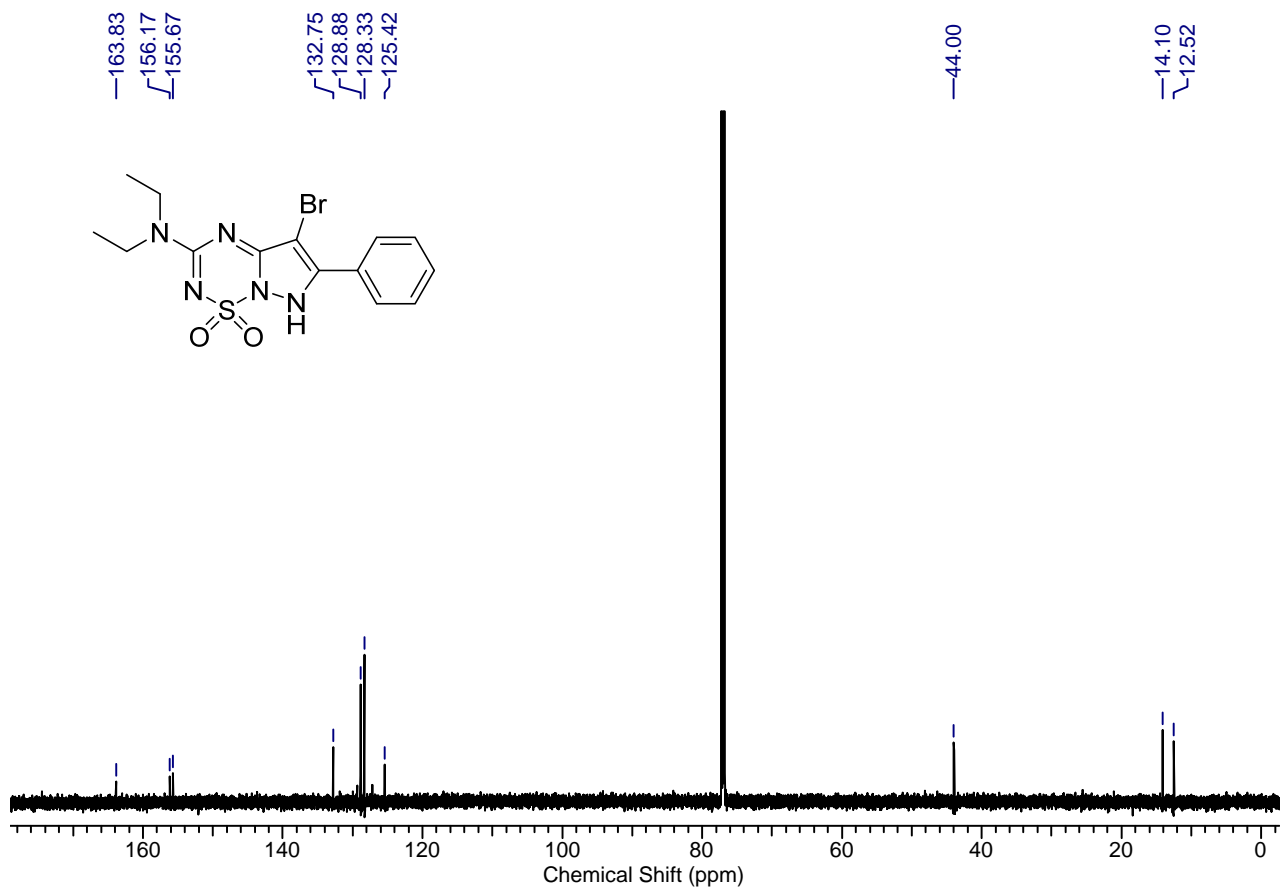


$^1\text{H}$  NMR spectrum of **15b** 600MHz (CDCl $_3$ )

S45

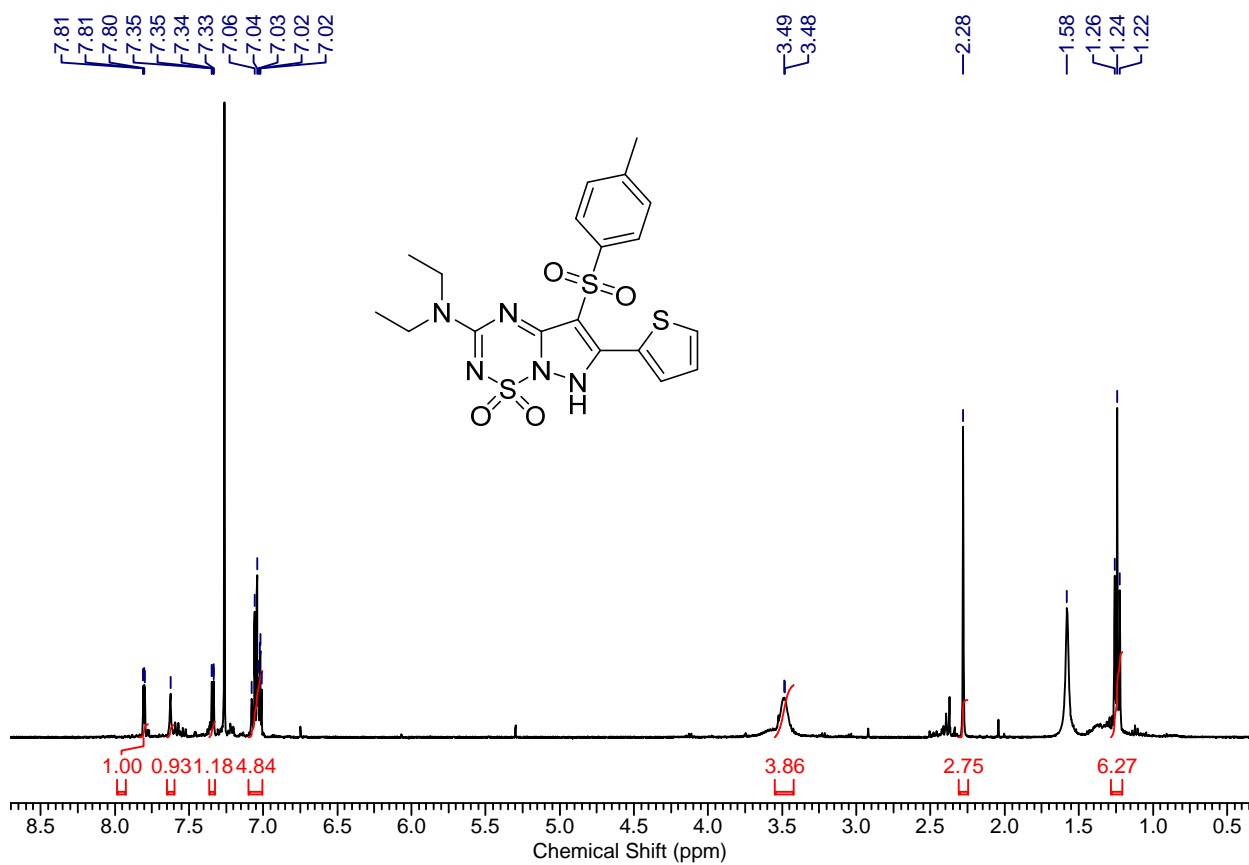


$^{13}\text{C}$  NMR spectrum of **15b** 150MHz ( $\text{CDCl}_3$ )

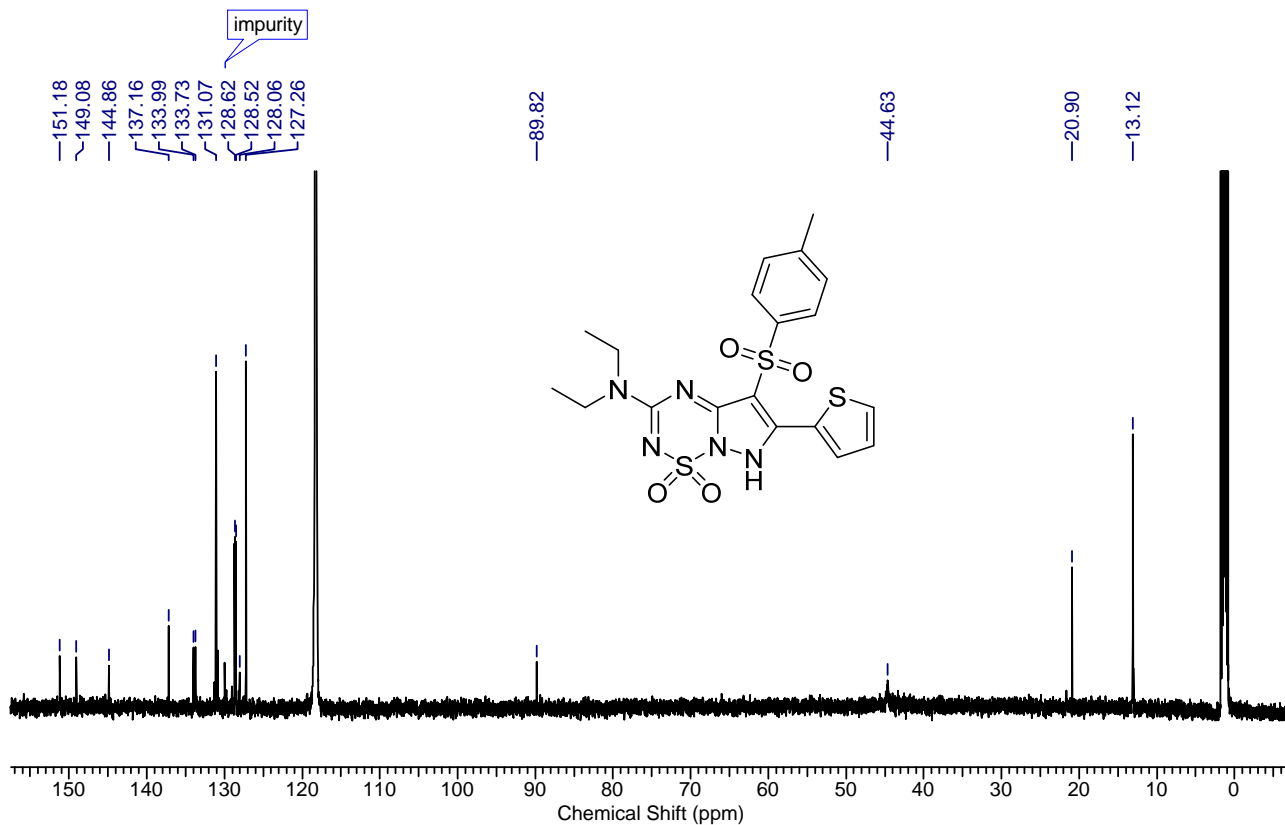


$^1\text{H}$  NMR spectrum of **16** 400MHz ( $\text{CDCl}_3$ )

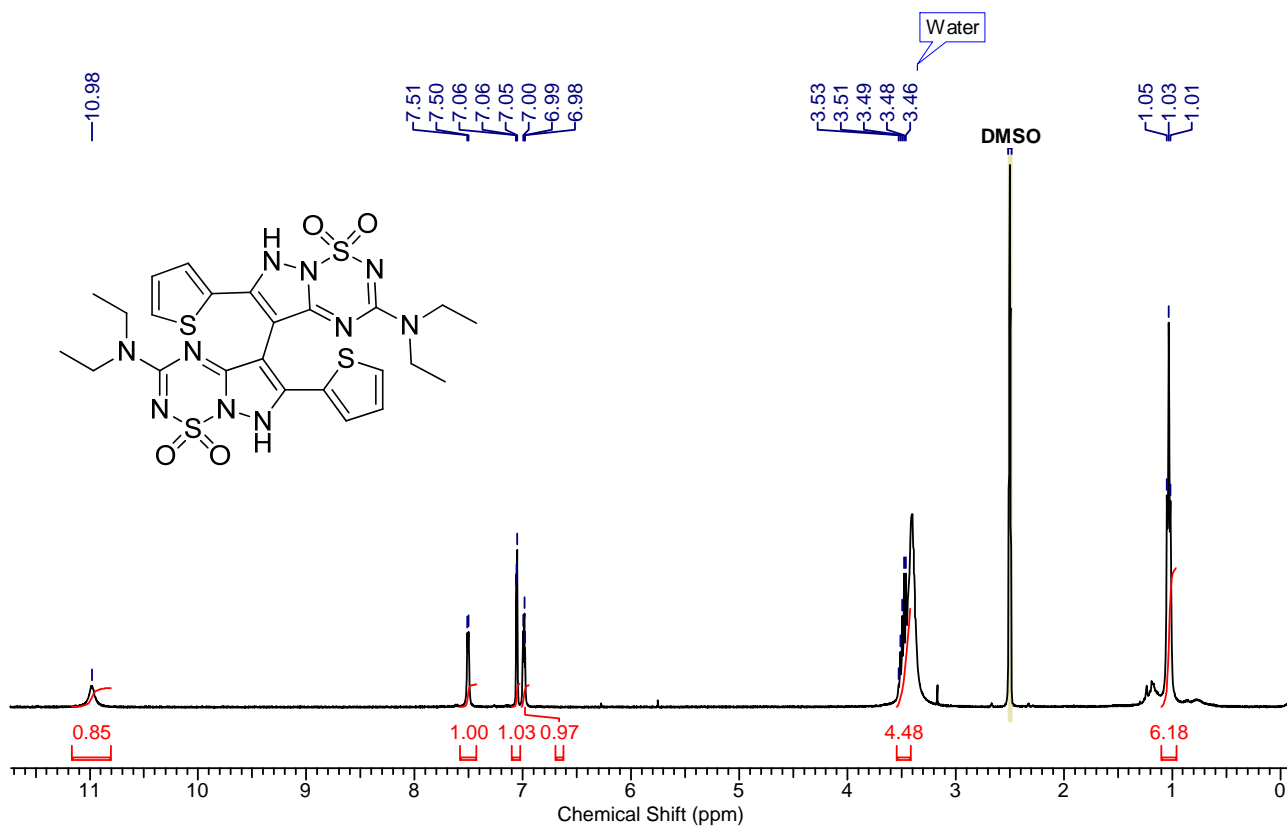
S46



$^{13}\text{C}$  NMR spectrum of **16** 150MHz ( $\text{CD}_3\text{CN}$ )  $35^\circ\text{C}$

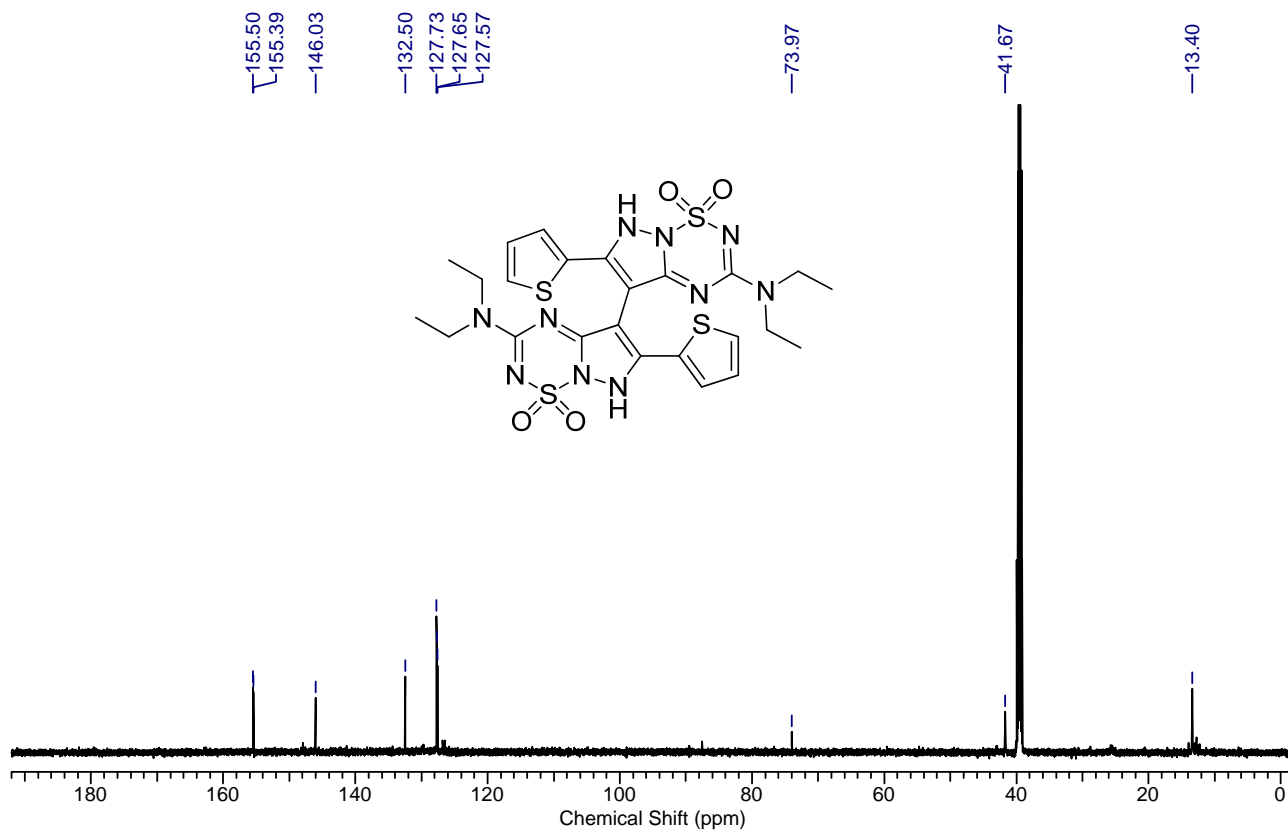


$^1\text{H}$  NMR spectrum of **17** 400MHz ( $\text{DMSO}-d_6$ )



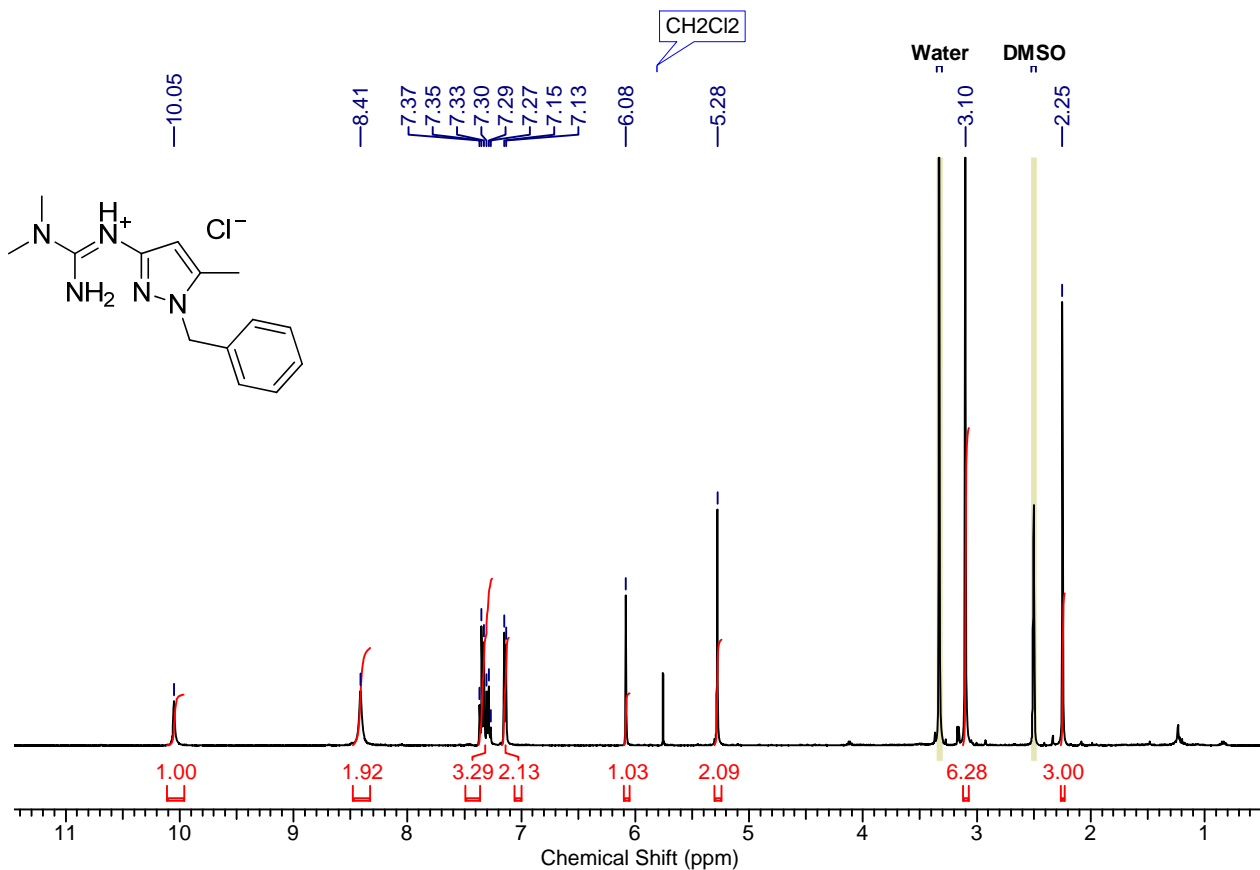


$^{13}\text{C}$  NMR spectrum of **17** 150MHz (DMSO- $d^6$ ) 40°C

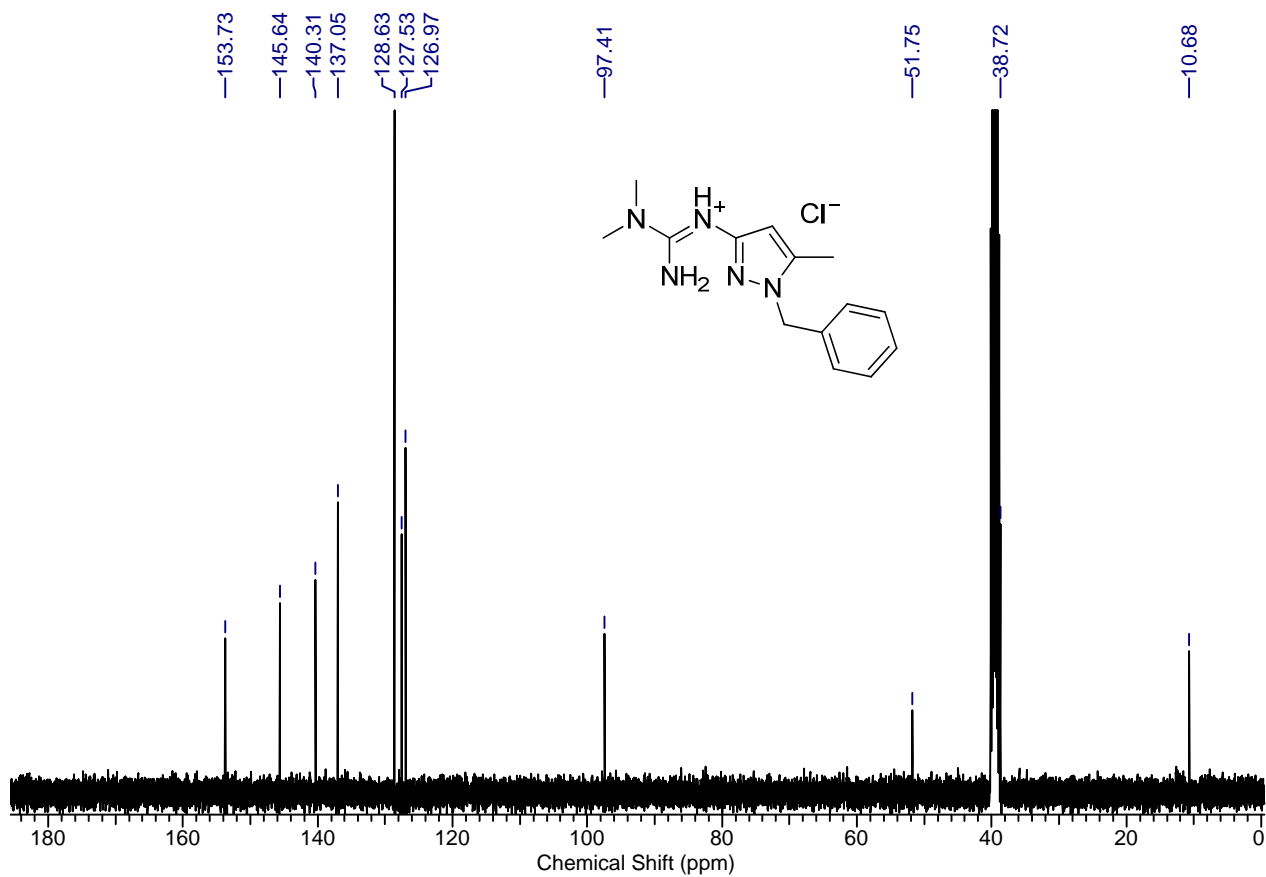


$^1\text{H}$  NMR spectrum of **18a** 400MHz (DMSO- $d^6$ )

S48

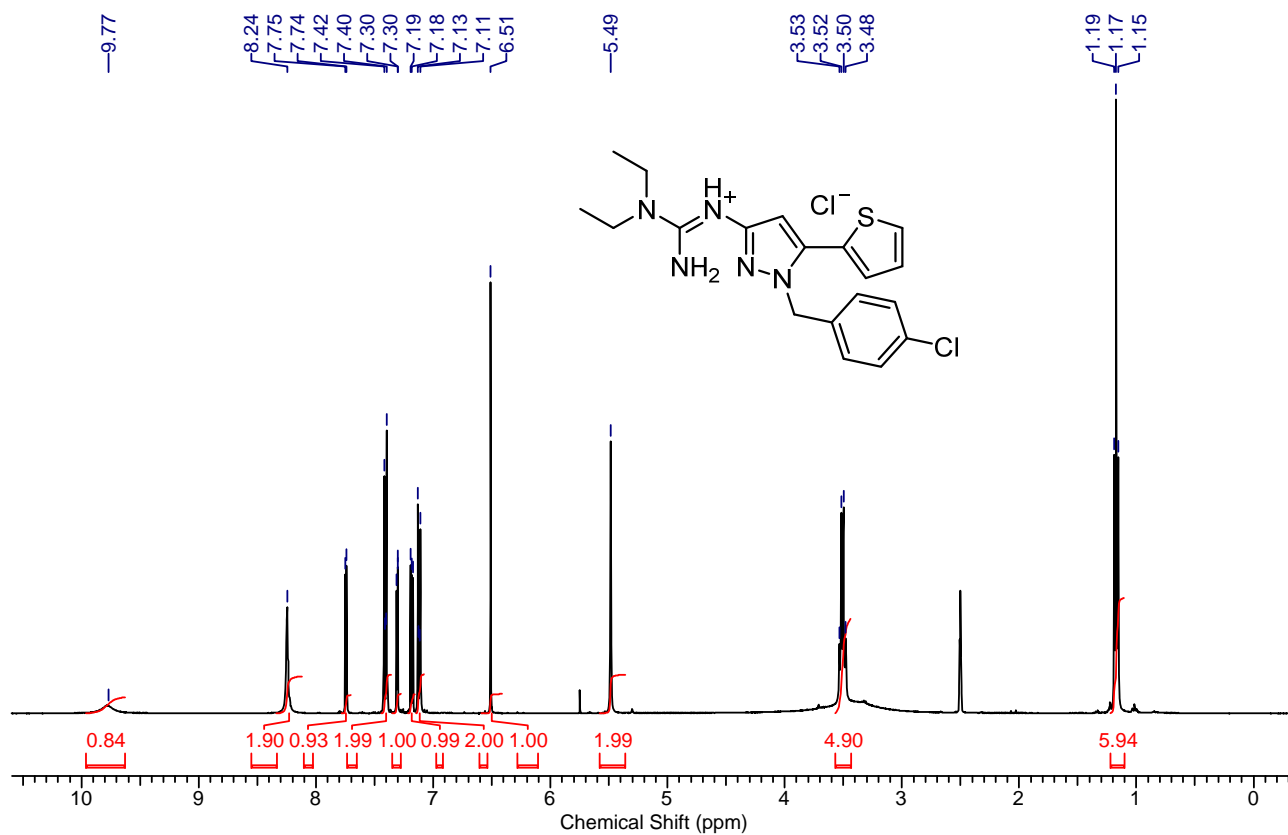


$^{13}\text{C}$  NMR spectrum of **18a** 100MHz (DMSO- $d^6$ )

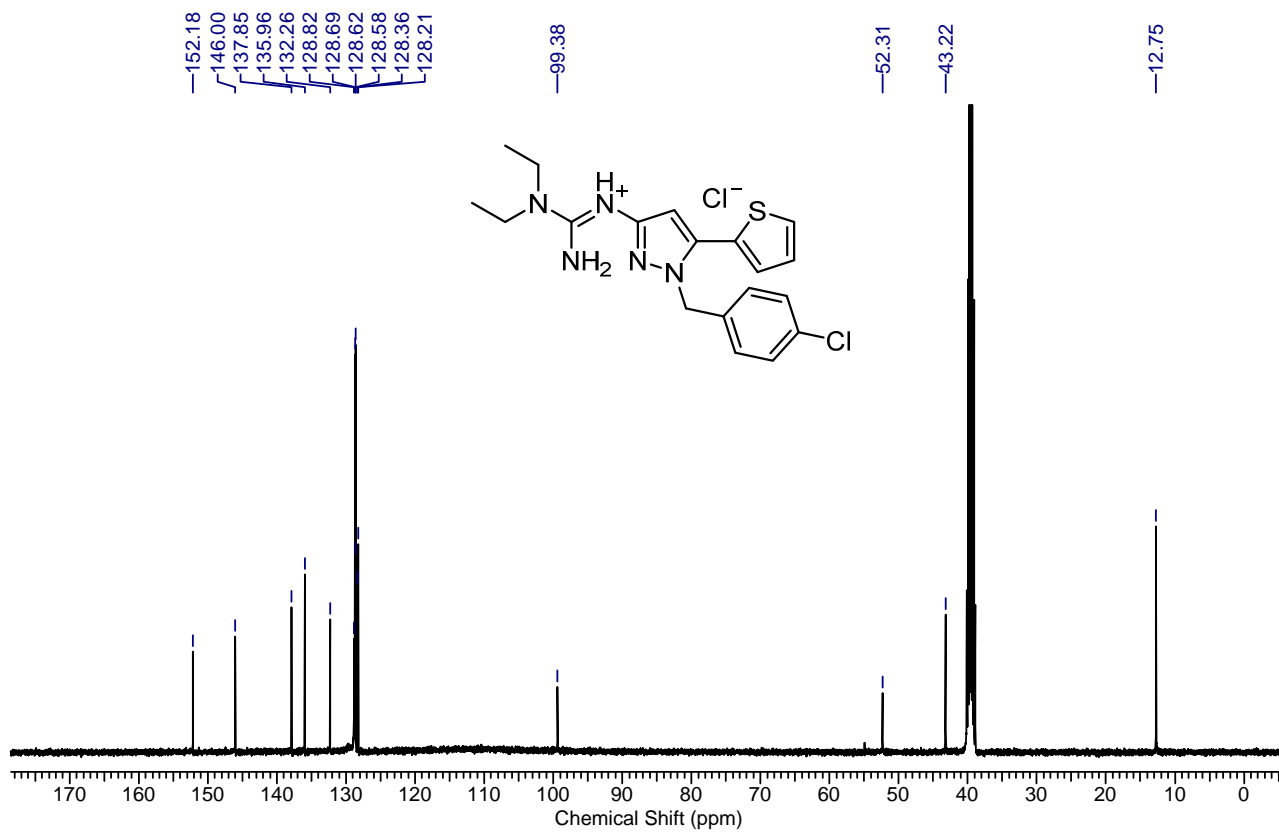


S49

$^1\text{H}$  NMR spectrum of **18b** 400MHz (DMSO- $d^6$ )

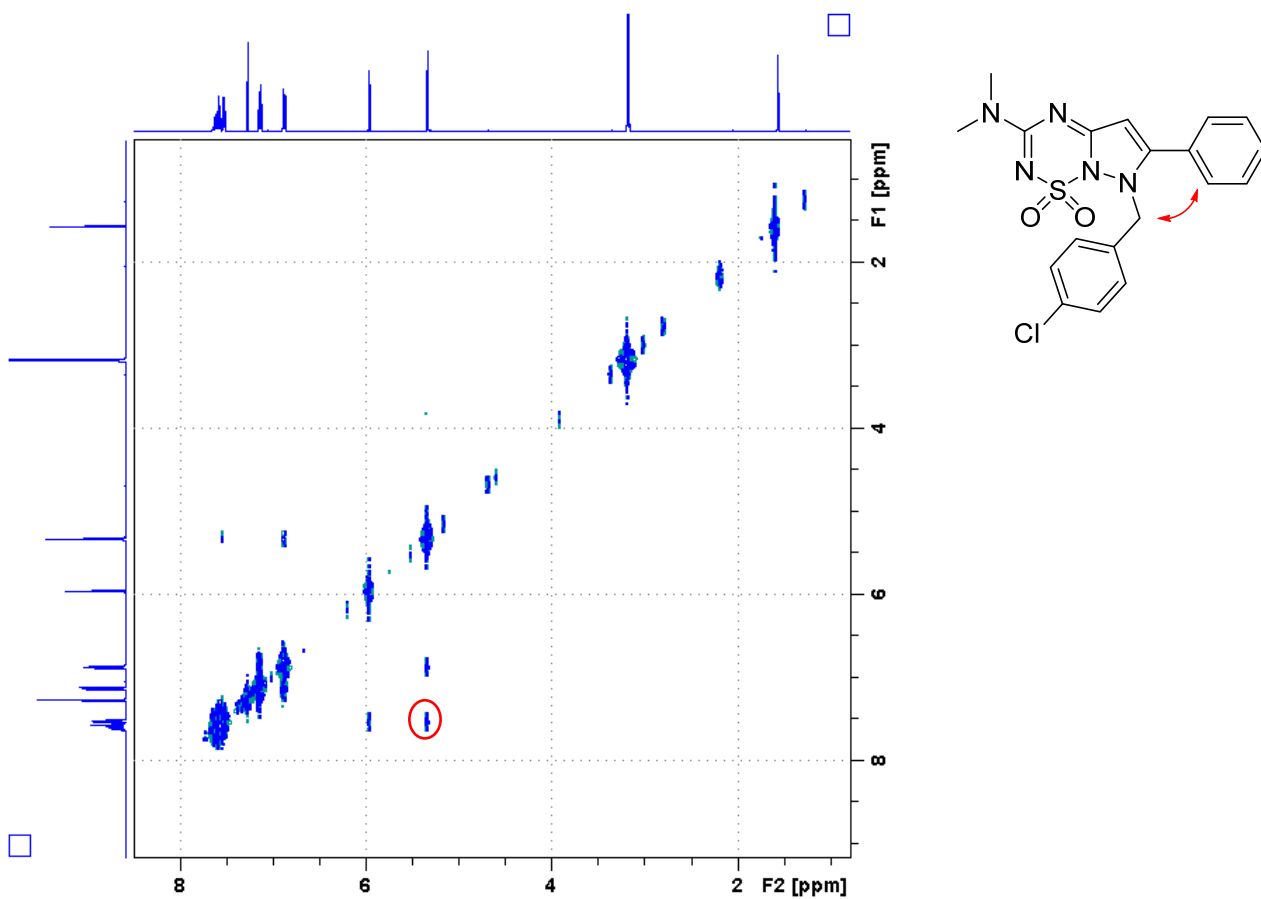


$^{13}\text{C}$  NMR spectrum of **18b** 100MHz (DMSO- $d_6$ )

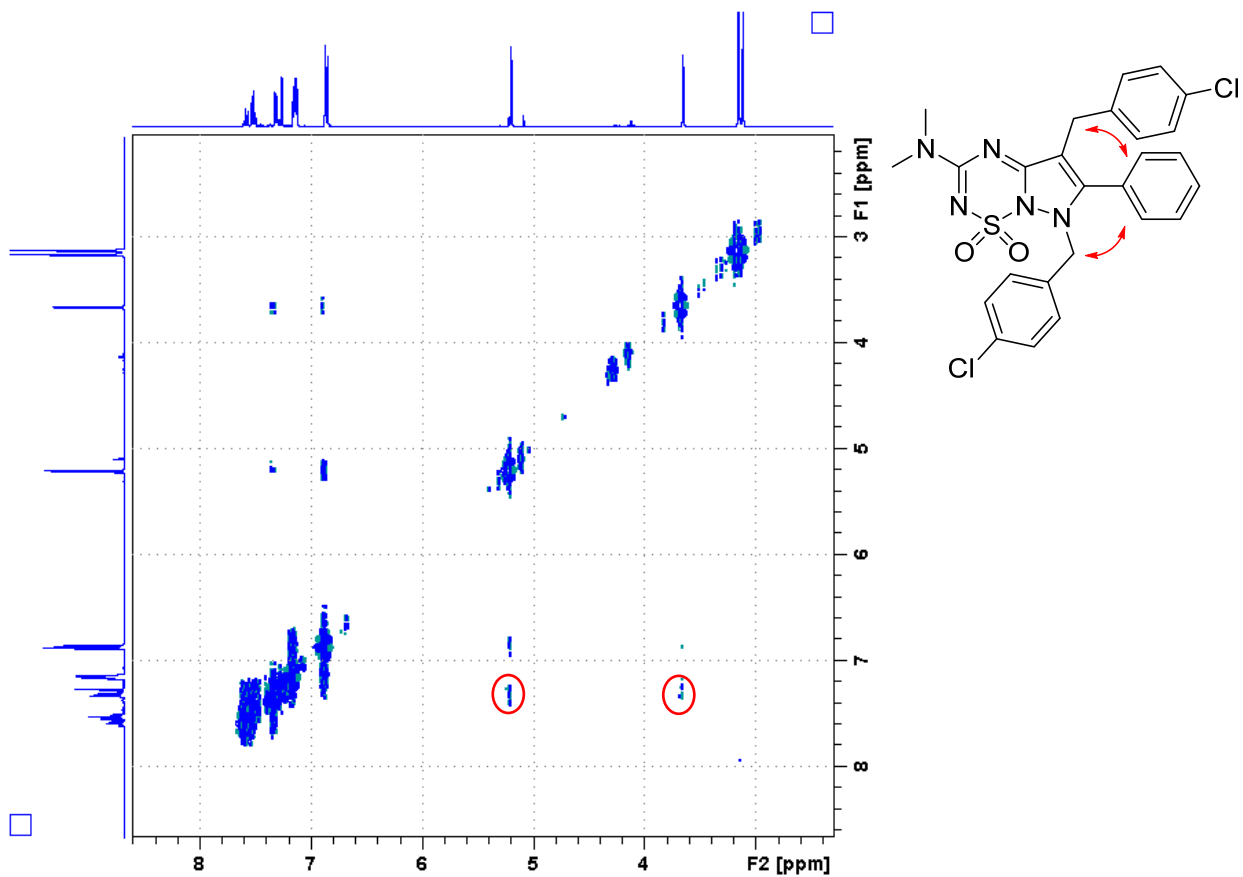


NOESY spectrum of **6a** 400MHz (CDCl<sub>3</sub>)

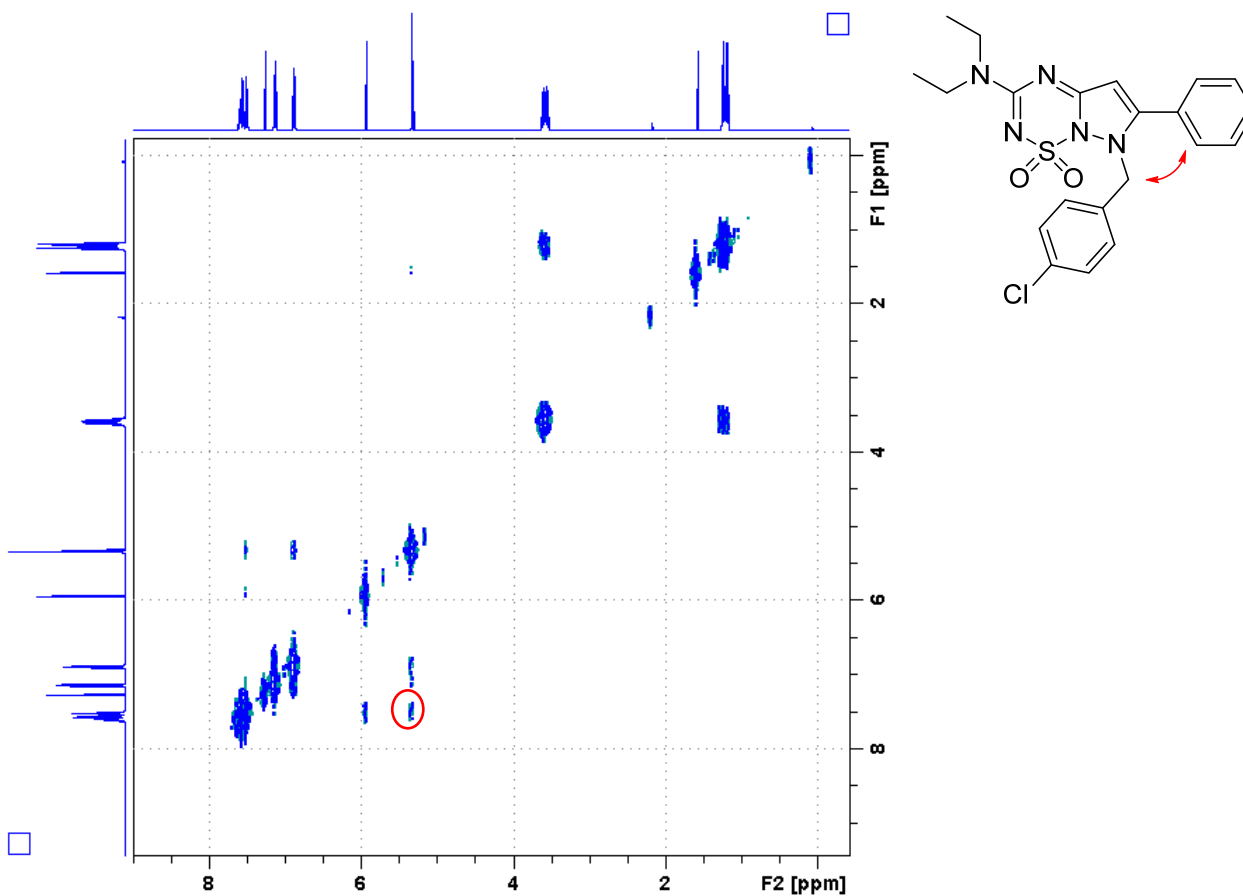
S50



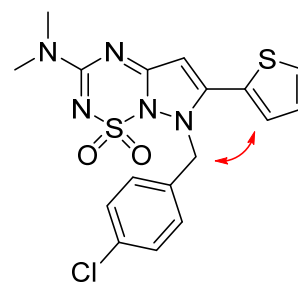
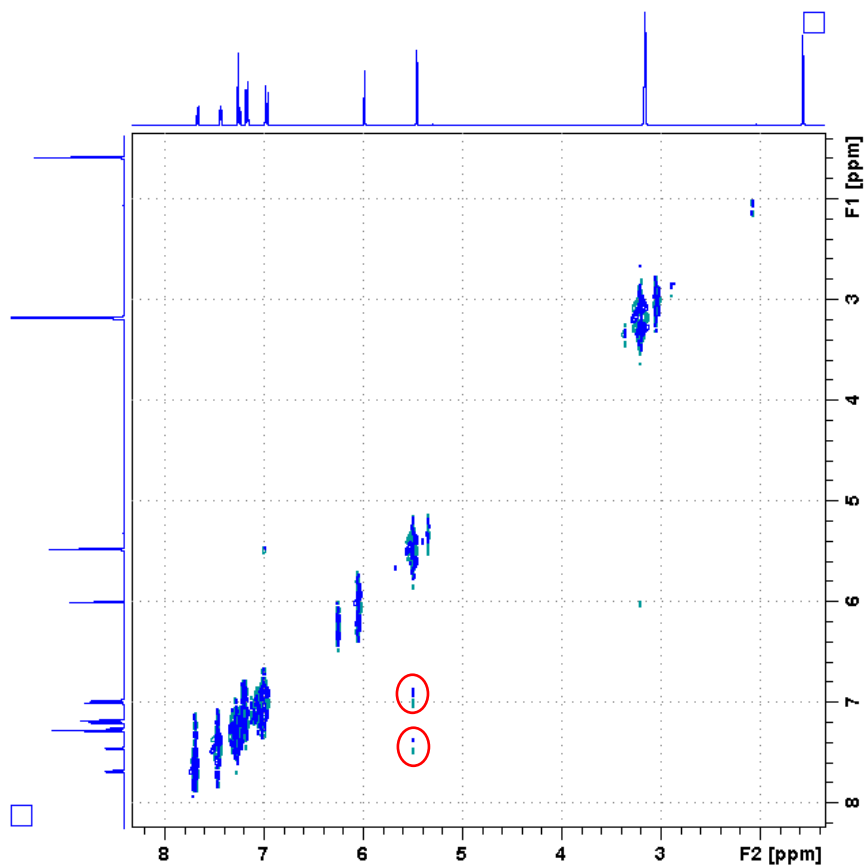
NOESY spectrum of **7a** 400MHz (CDCl<sub>3</sub>)



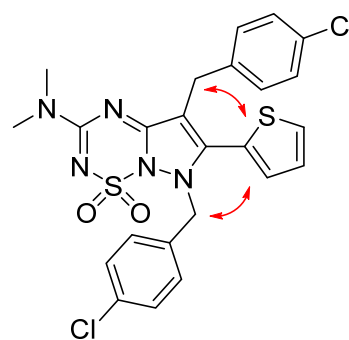
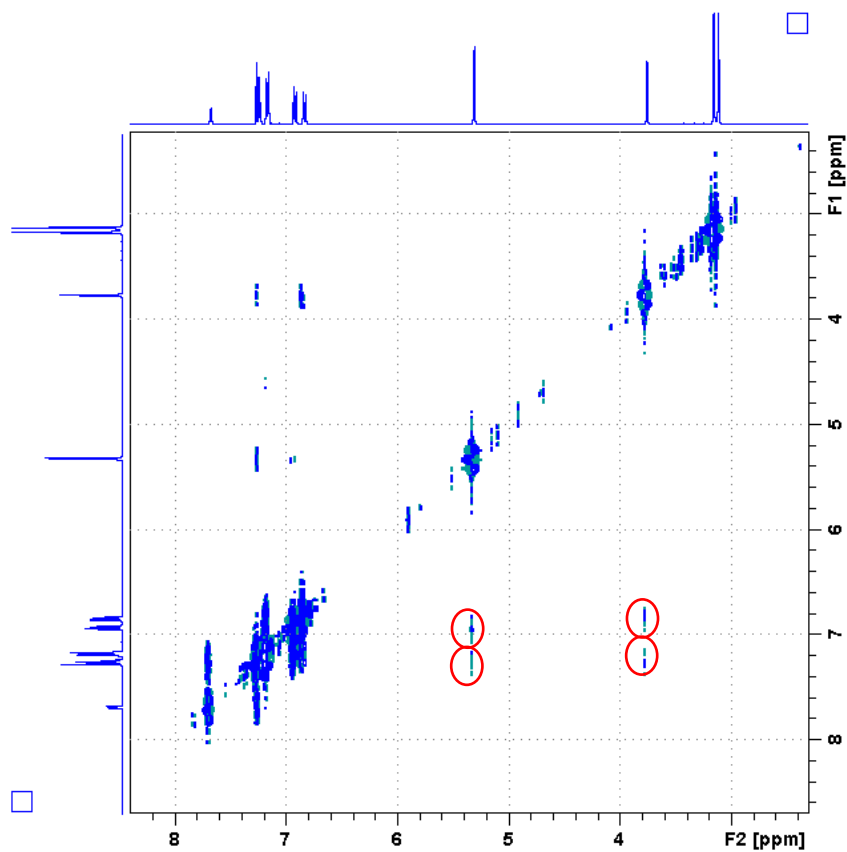
NOESY spectrum of **6b** 400MHz (CDCl<sub>3</sub>)



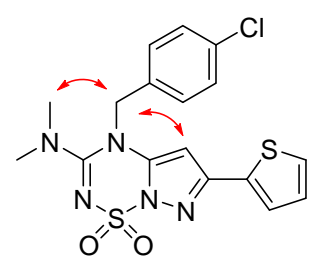
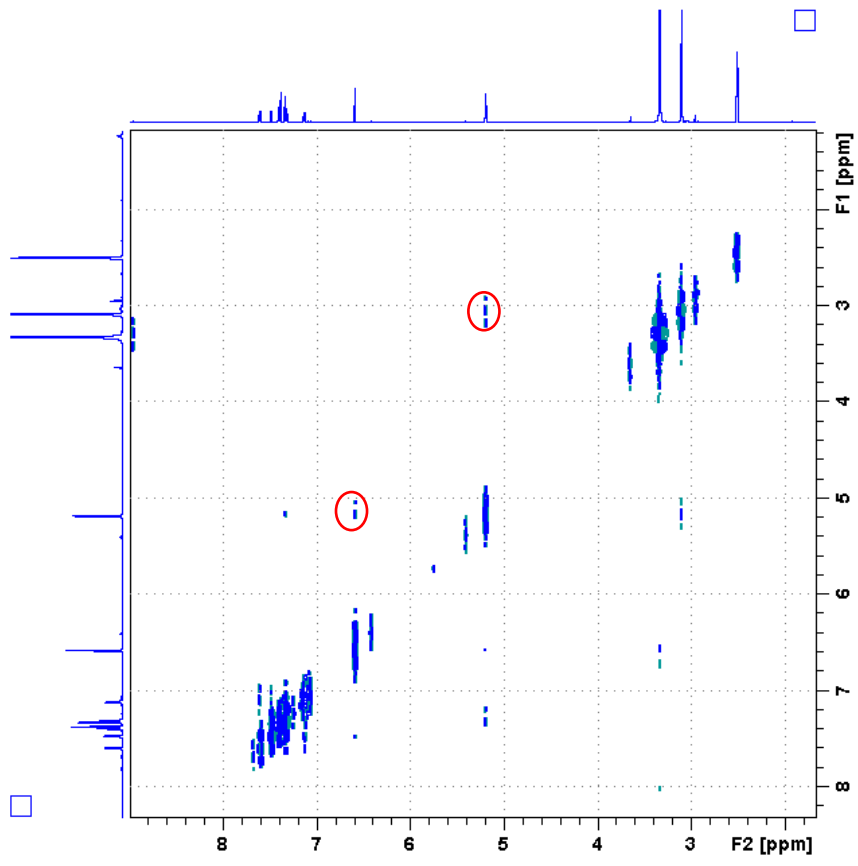
NOESY spectrum of **6c** 400MHz (CDCl<sub>3</sub>)



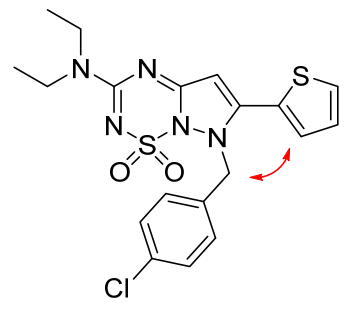
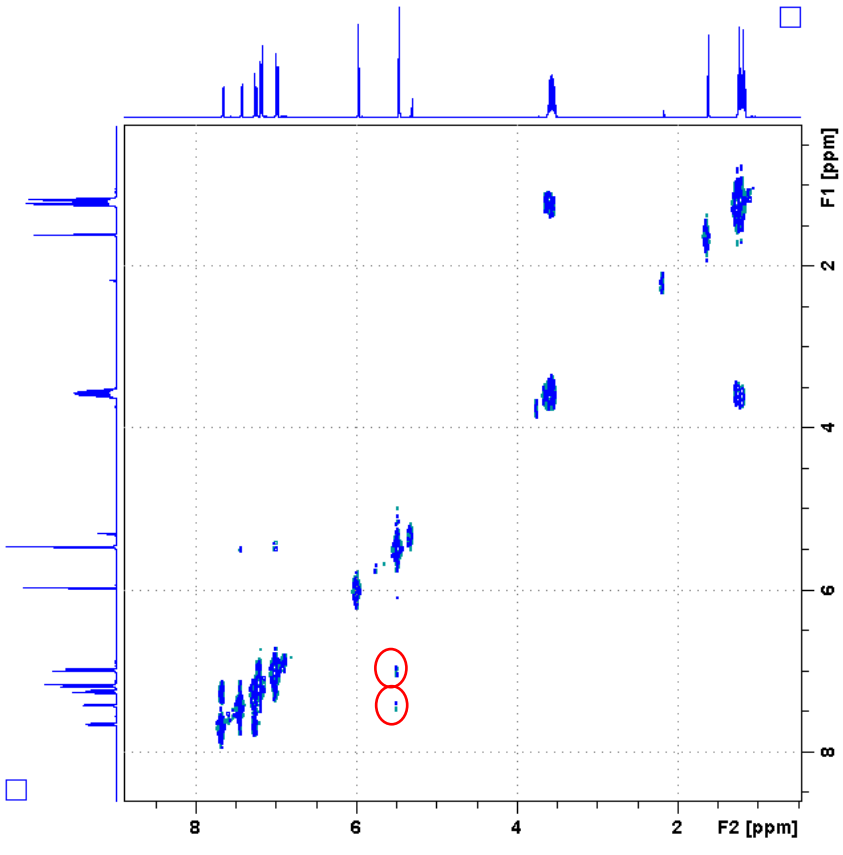
NOESY spectrum of **7c** 400MHz (CDCl<sub>3</sub>)



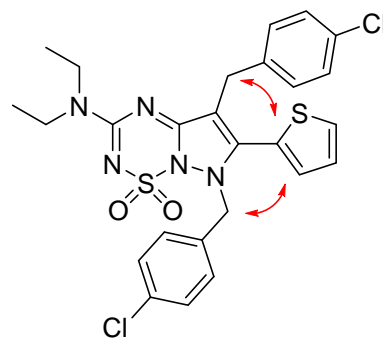
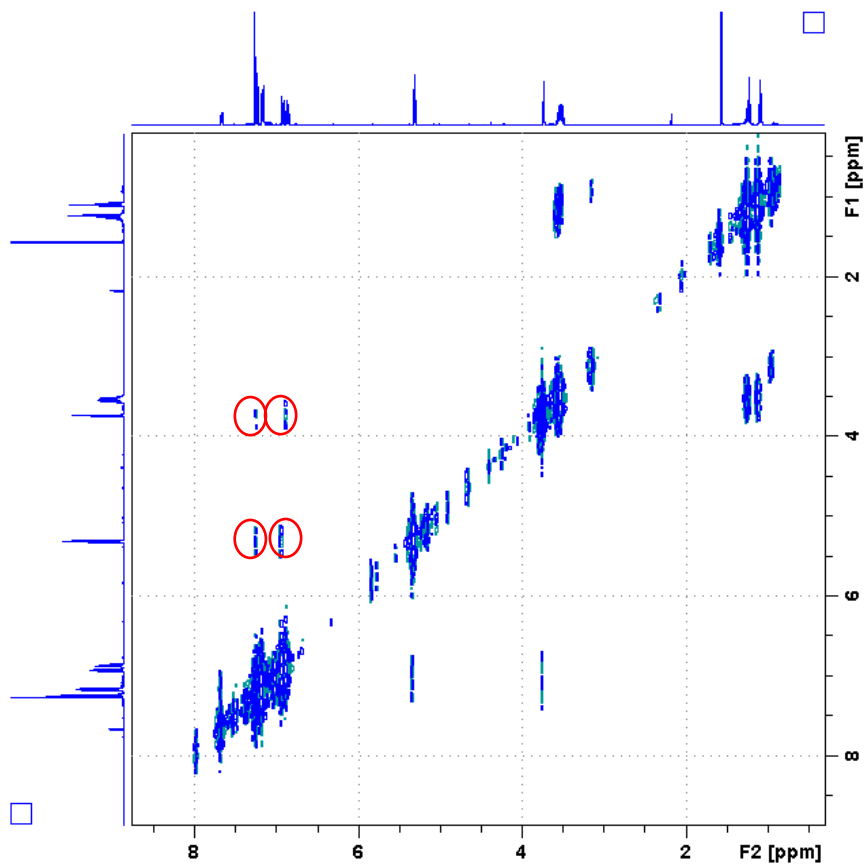
NOESY spectrum of **8c** 400MHz (DMSO- $d^6$ )



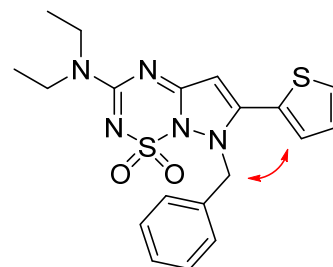
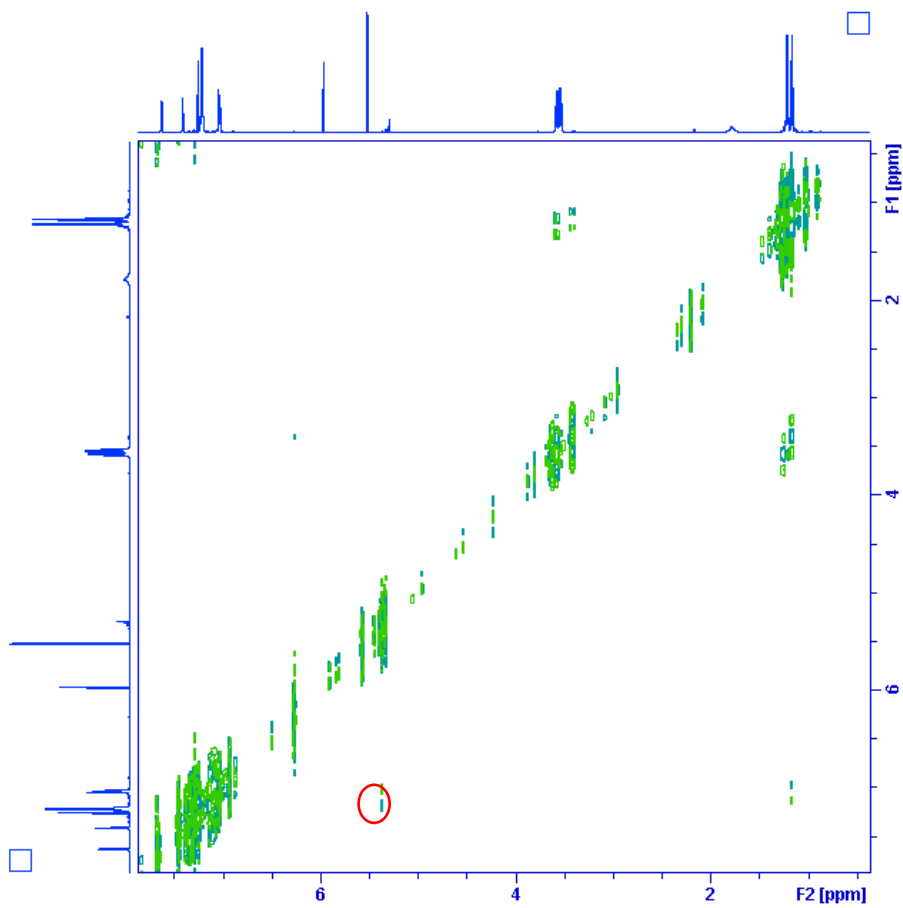
NOESY spectrum of **6d** 400MHz (CDCl<sub>3</sub>)



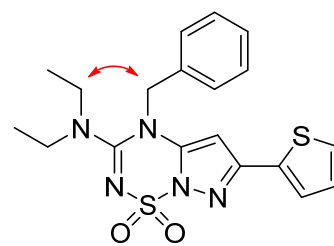
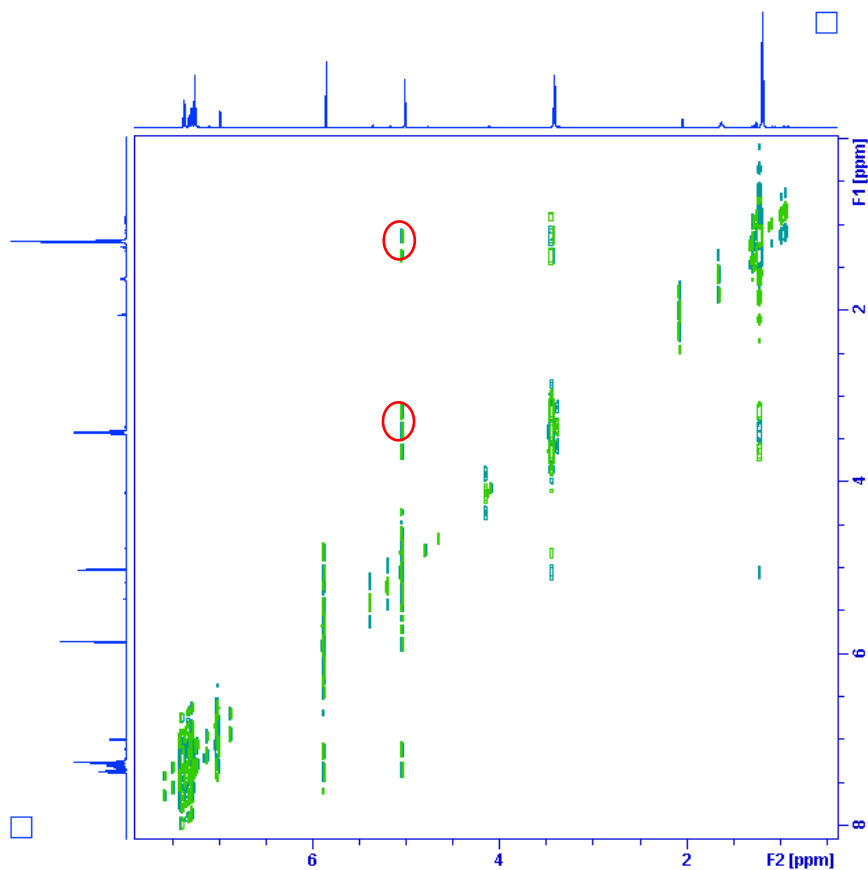
NOESY spectrum of **7d** 400MHz (CDCl<sub>3</sub>)



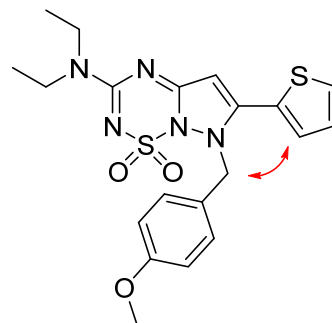
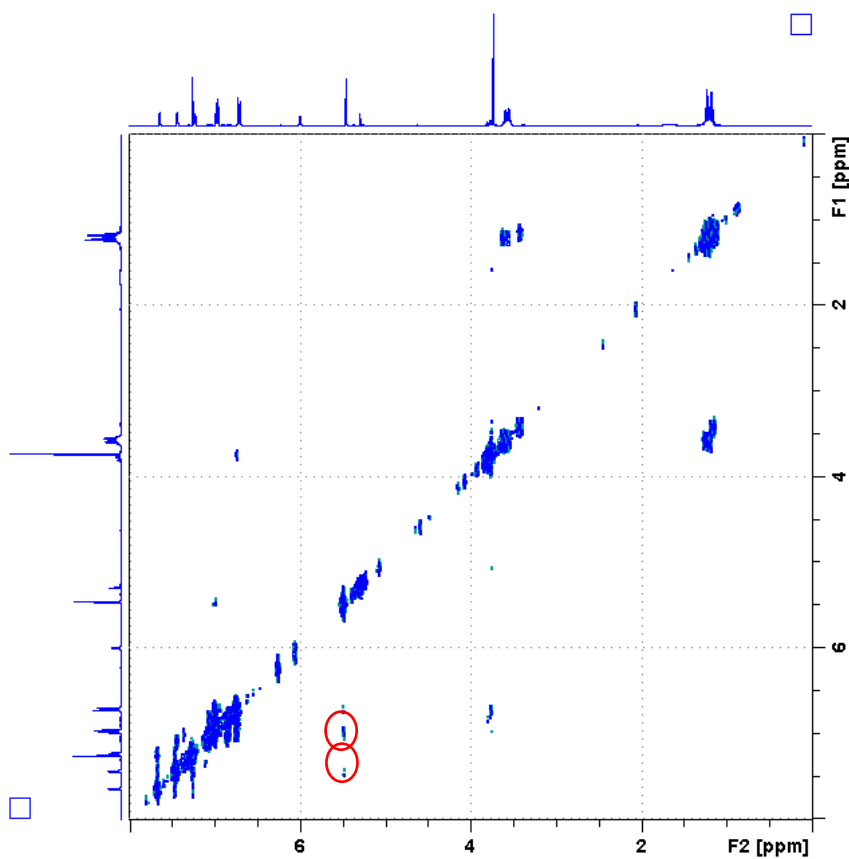
NOESY spectrum of **6e** 600MHz (CDCl<sub>3</sub>)



NOESY spectrum of **8e** 600MHz (CDCl<sub>3</sub>)

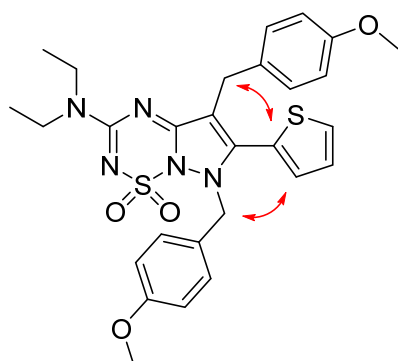
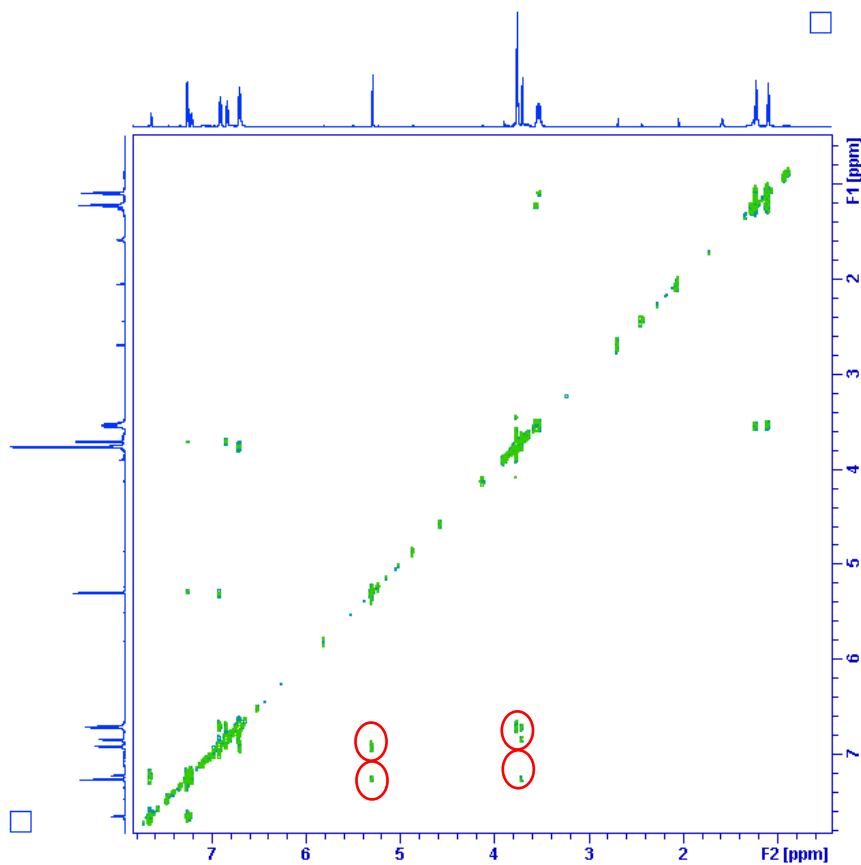


NOESY spectrum of **6g** 400MHz (CDCl<sub>3</sub>)



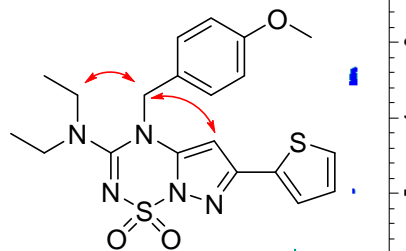
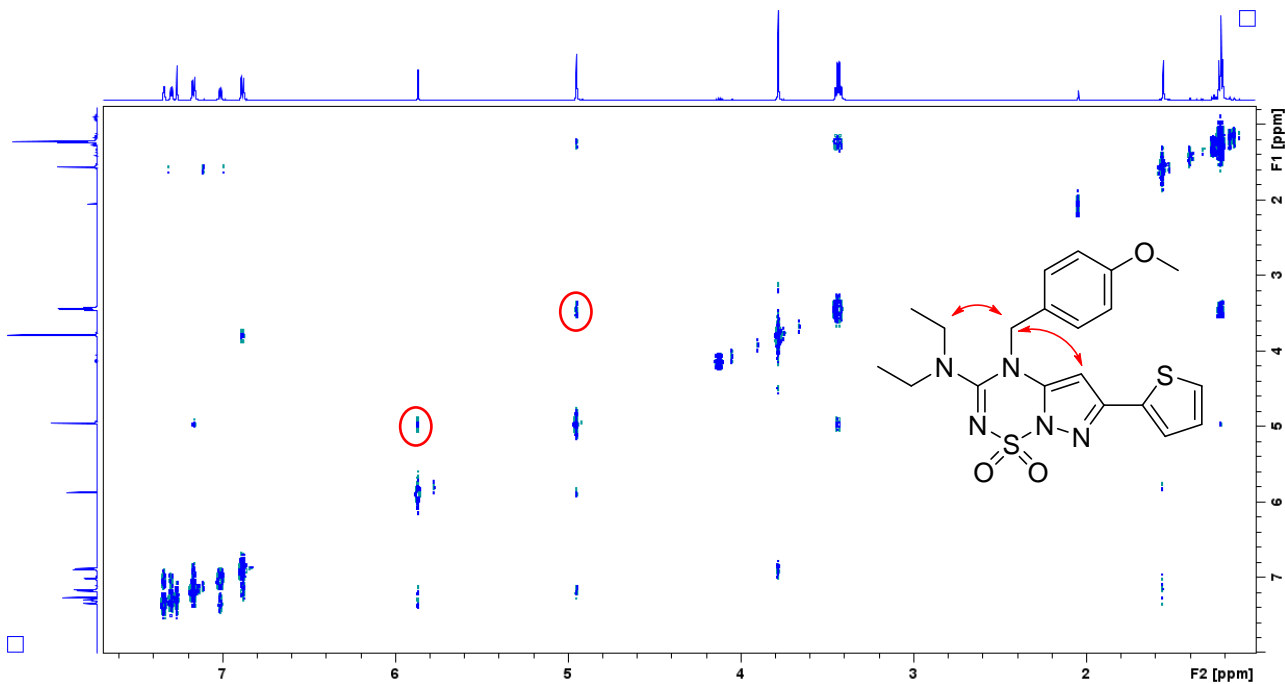


NOESY spectrum of **7g** 600MHz (CDCl<sub>3</sub>)

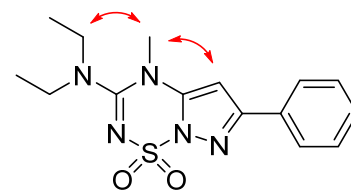
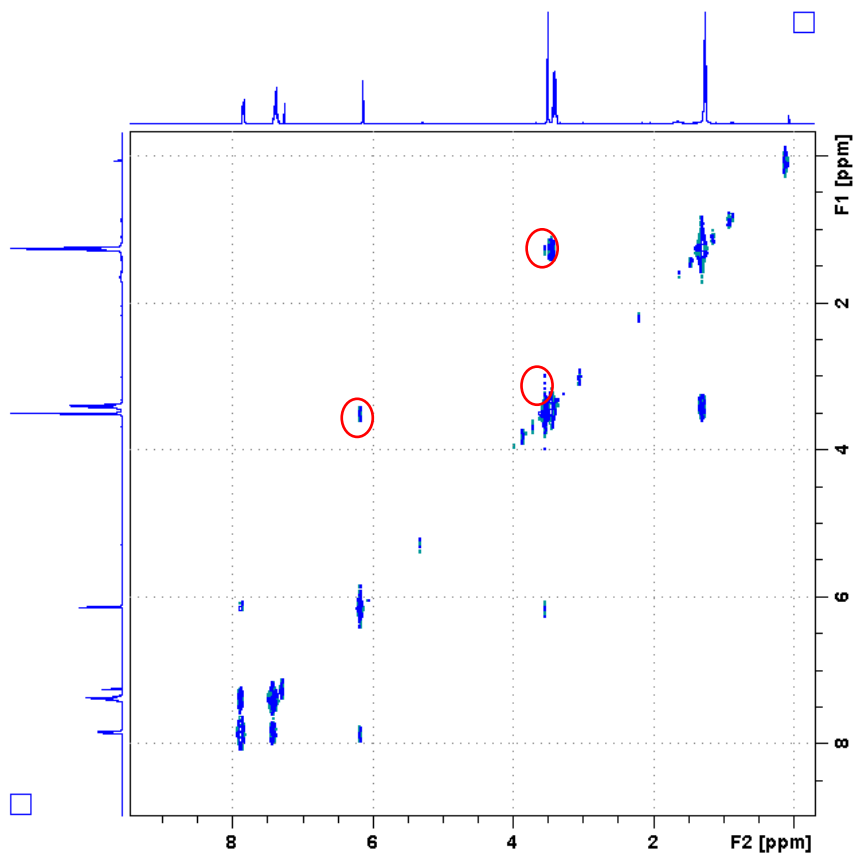


S56

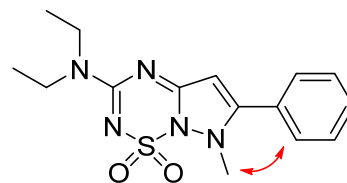
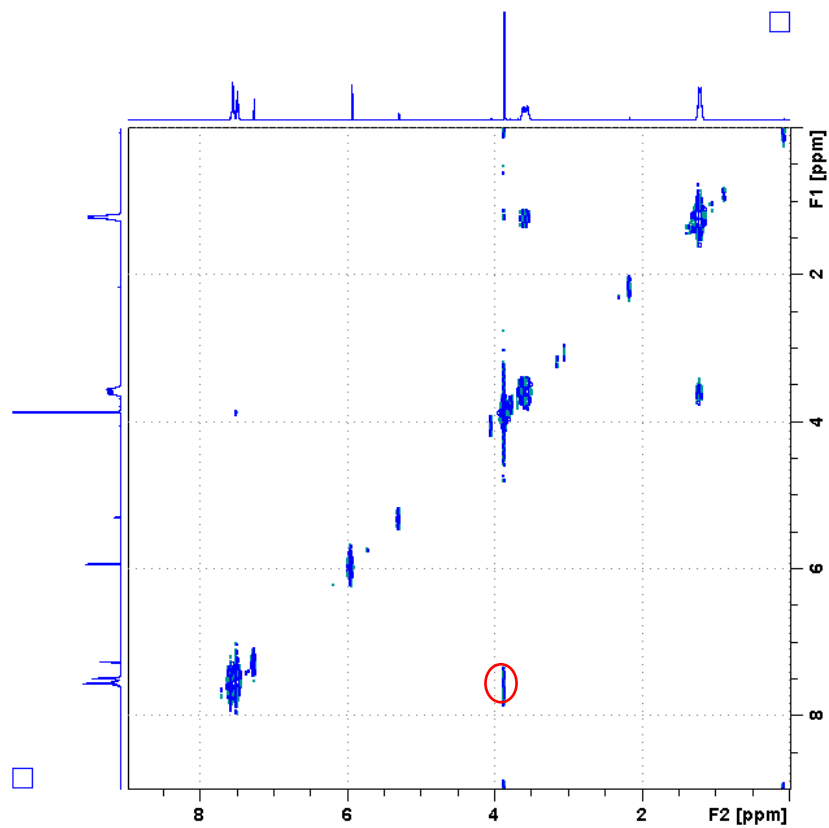
NOESY spectrum of **8g** 600MHz (CDCl<sub>3</sub>)



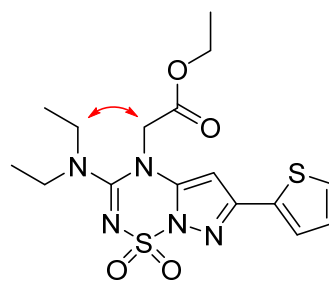
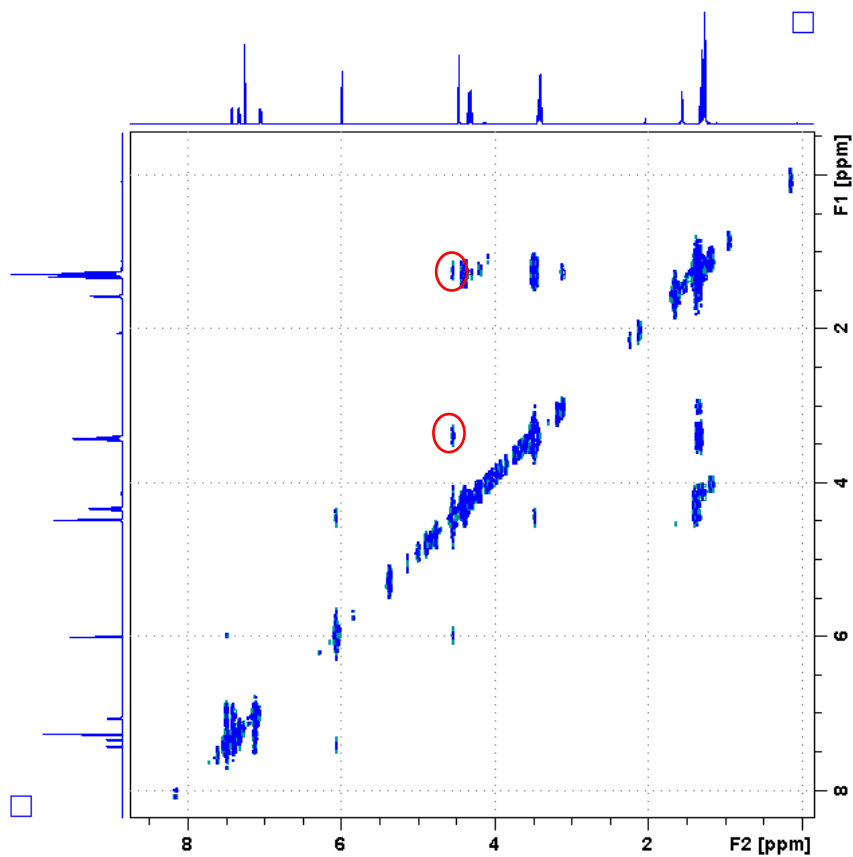
NOESY spectrum of **10** 400MHz (CDCl<sub>3</sub>)



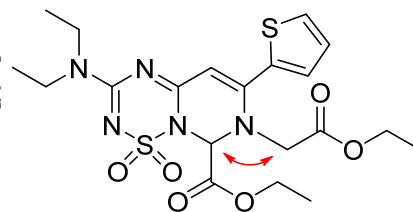
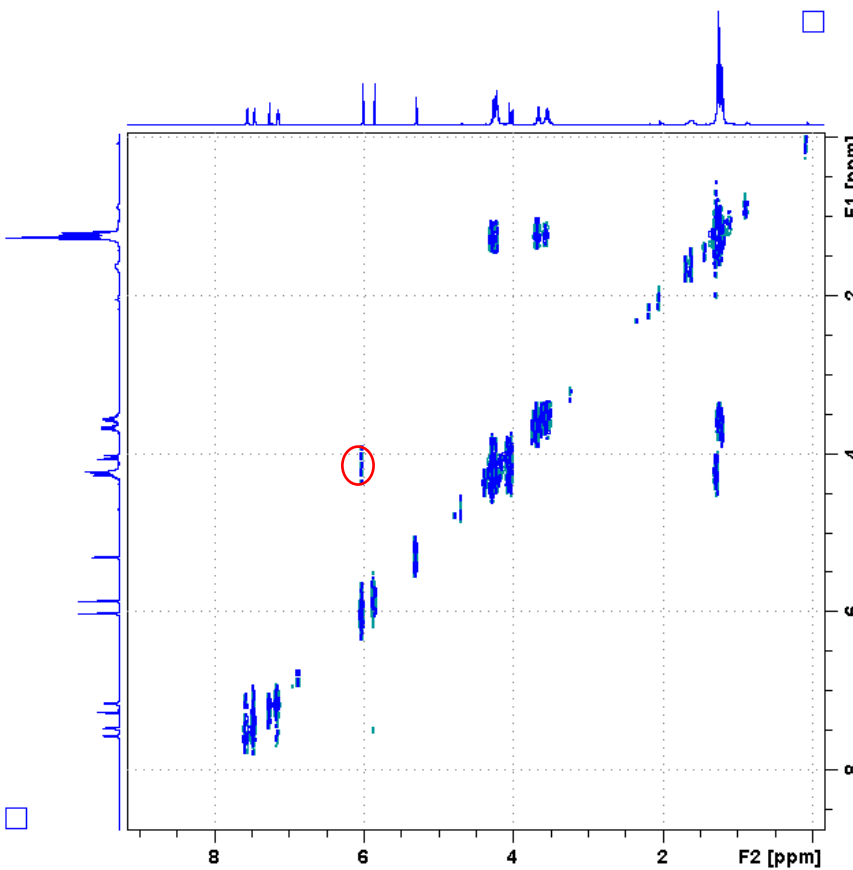
NOESY spectrum of **11** 400MHz (CDCl<sub>3</sub>)



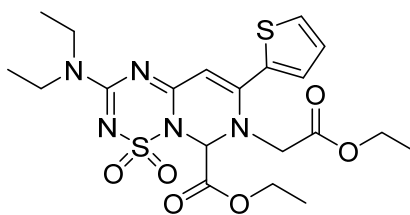
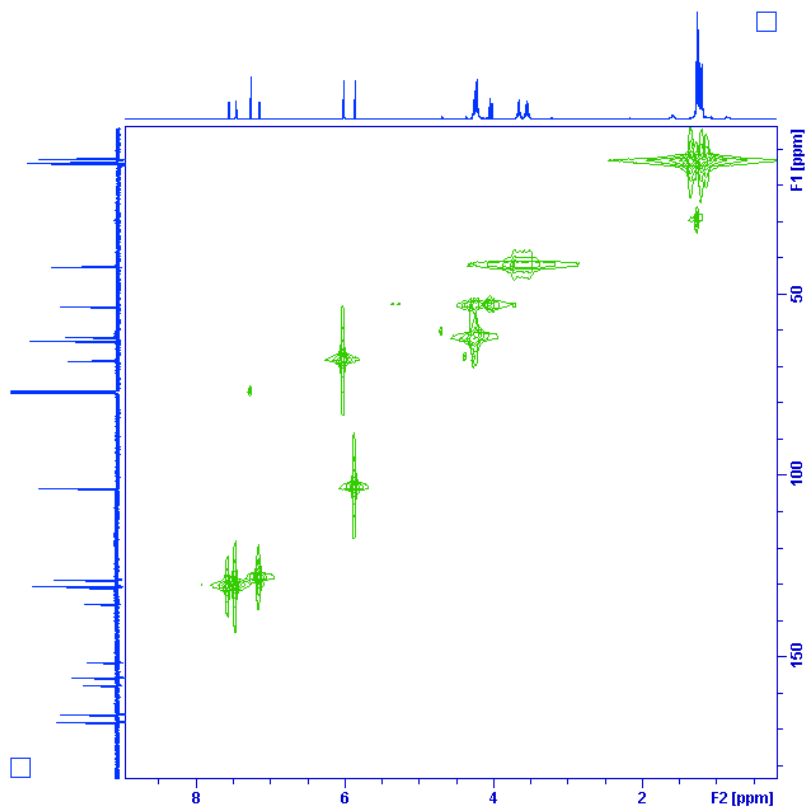
NOESY spectrum of **12a** 400MHz (CDCl<sub>3</sub>)



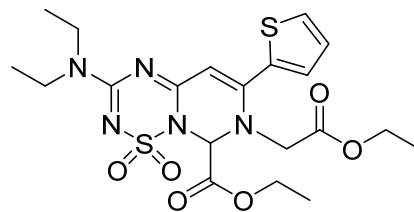
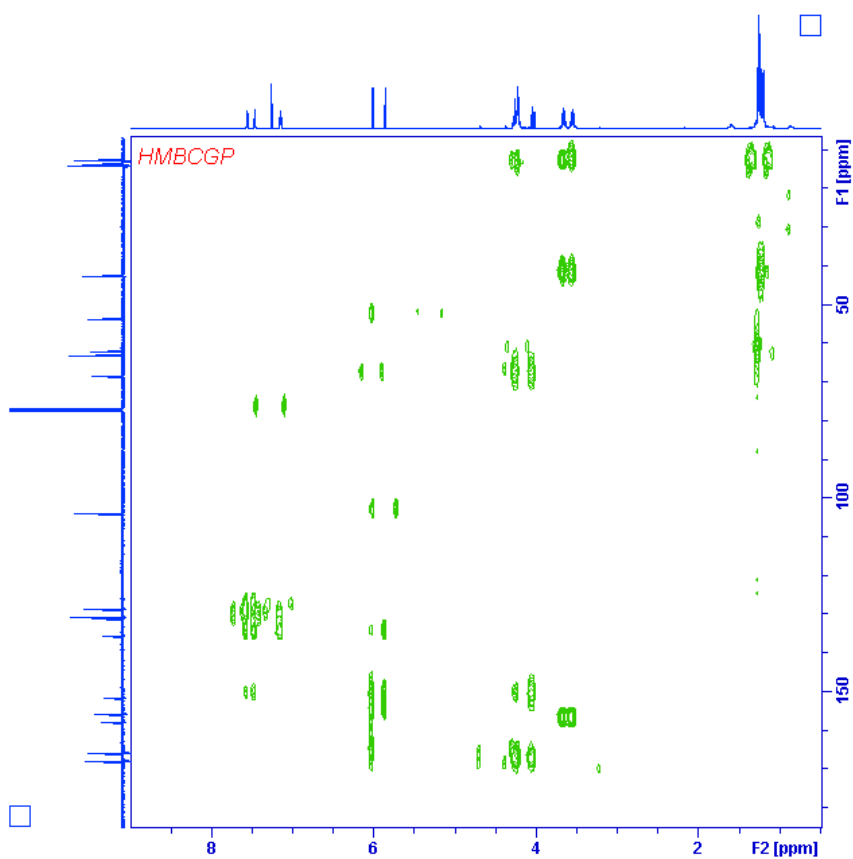
NOESY spectrum of **14a** 400MHz (CDCl<sub>3</sub>)



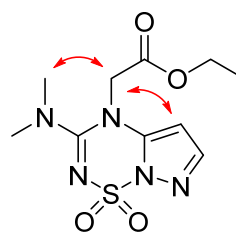
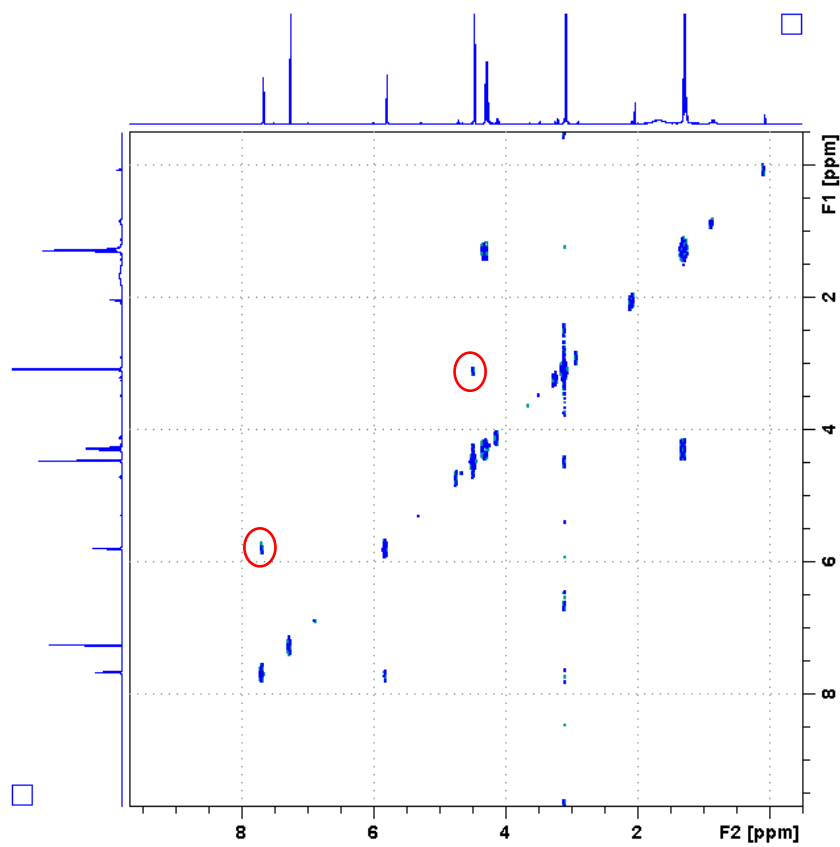
HMQC spectrum of **14a** 600MHz (CDCl<sub>3</sub>)



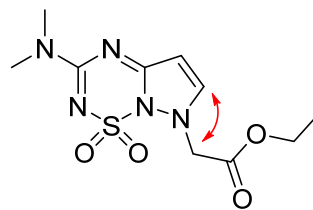
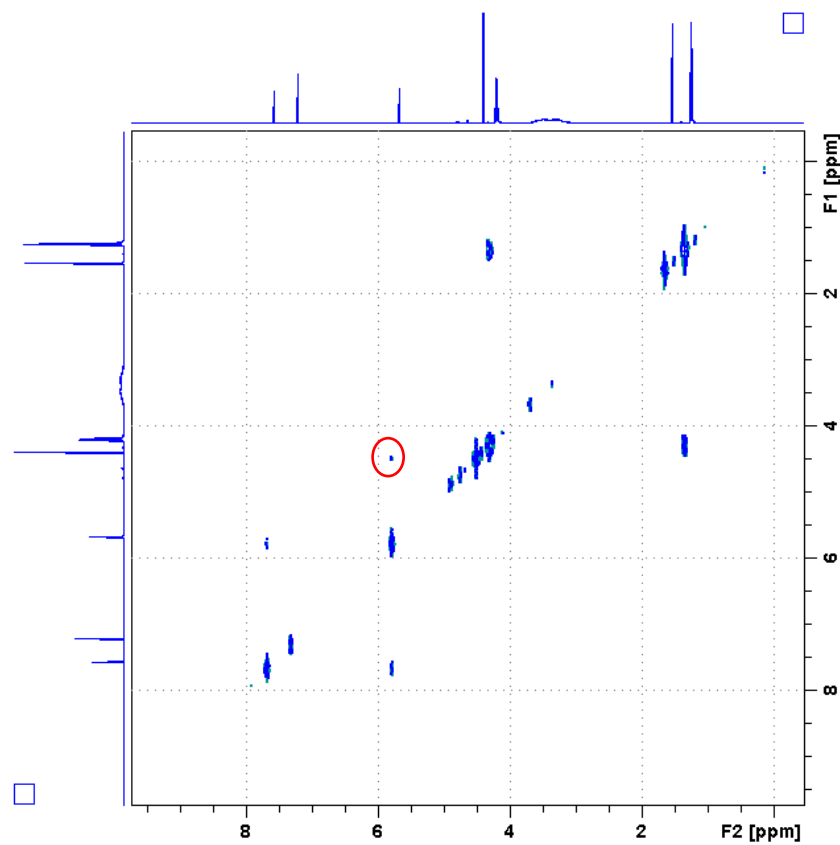
HMBC spectrum of **14a** 600MHz (CDCl<sub>3</sub>)



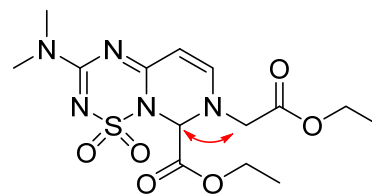
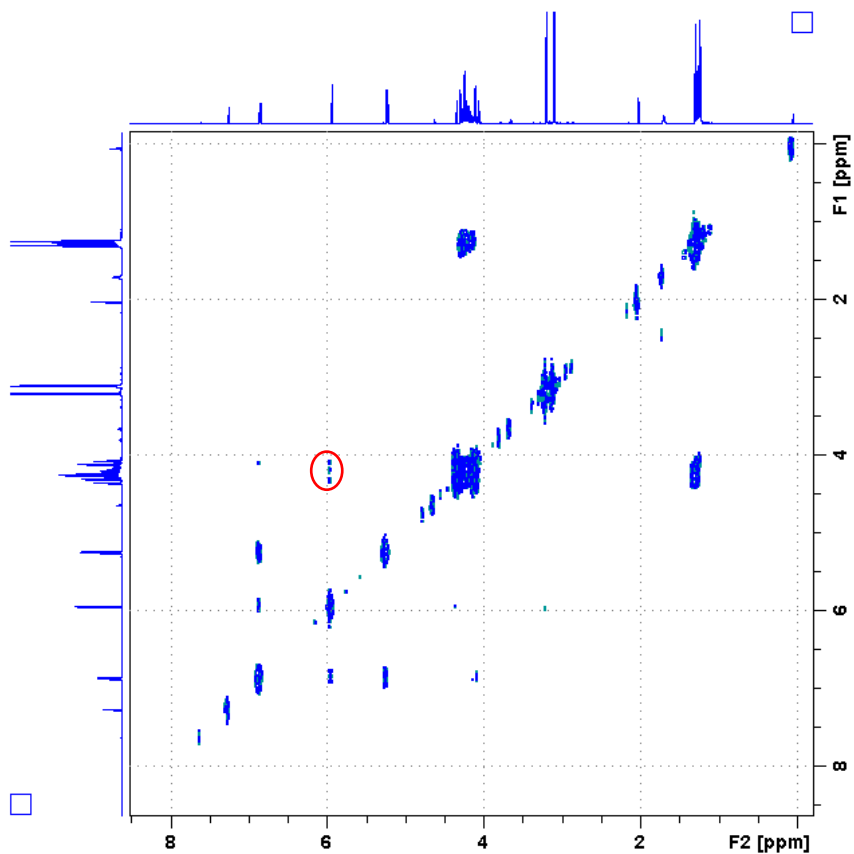
NOESY spectrum of **12b** 400MHz (CDCl<sub>3</sub>)



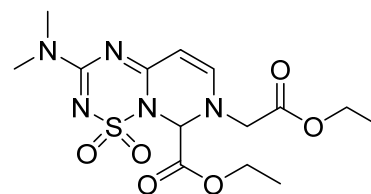
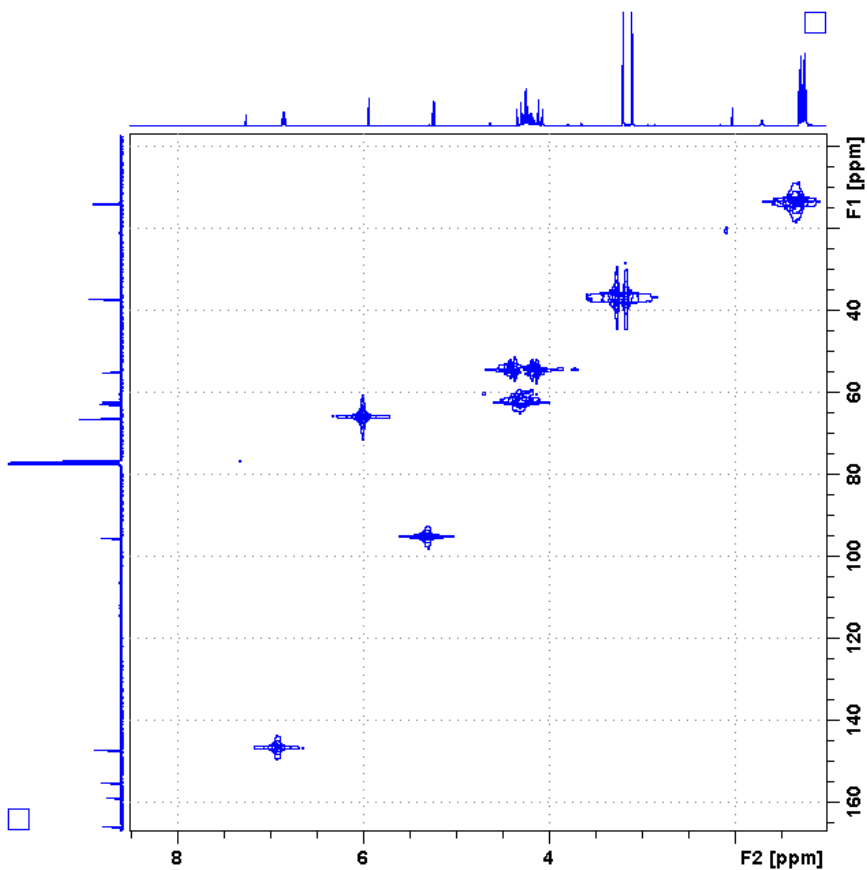
NOESY spectrum of **13b** 400MHz (CDCl<sub>3</sub>)



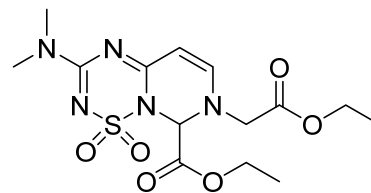
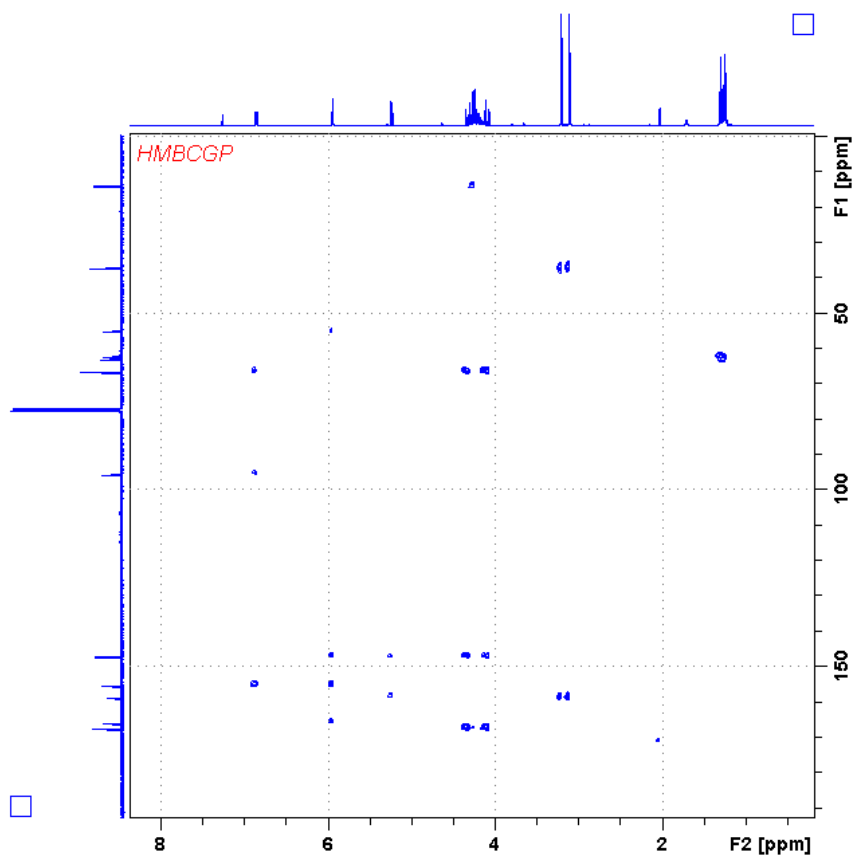
NOESY spectrum of **14b** 400MHz (CDCl<sub>3</sub>)



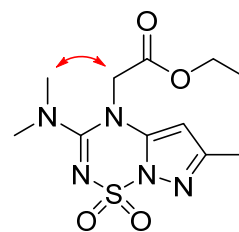
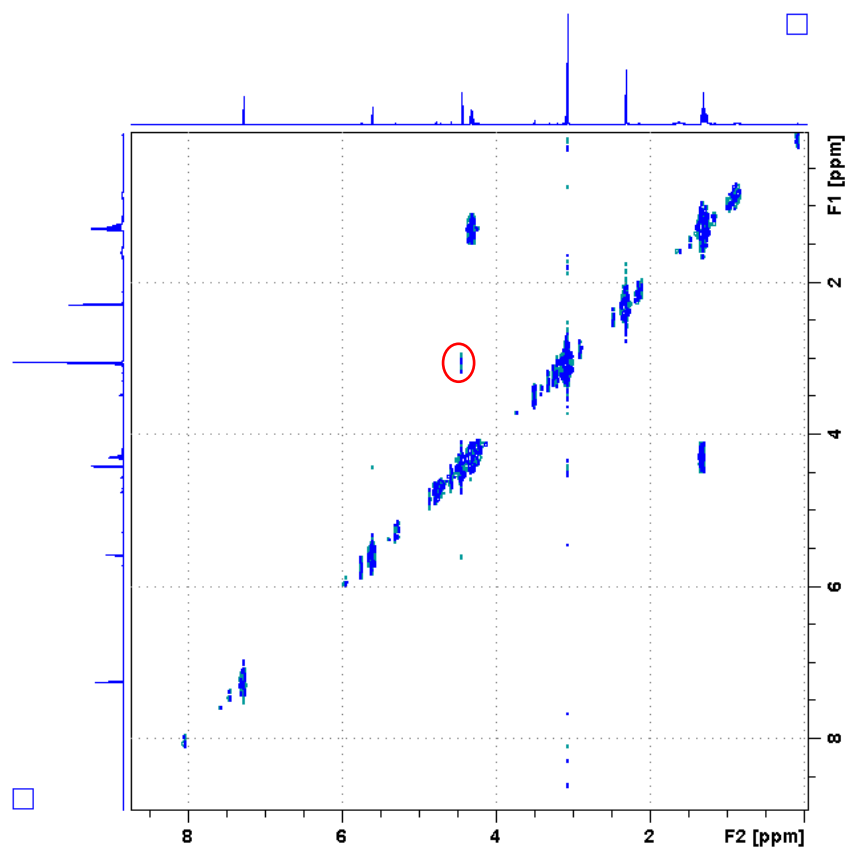
HMQC spectrum of **14b** 400MHz (CDCl<sub>3</sub>)



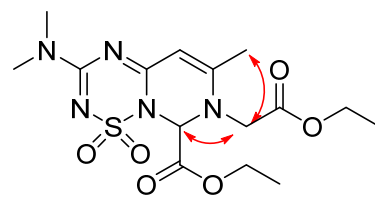
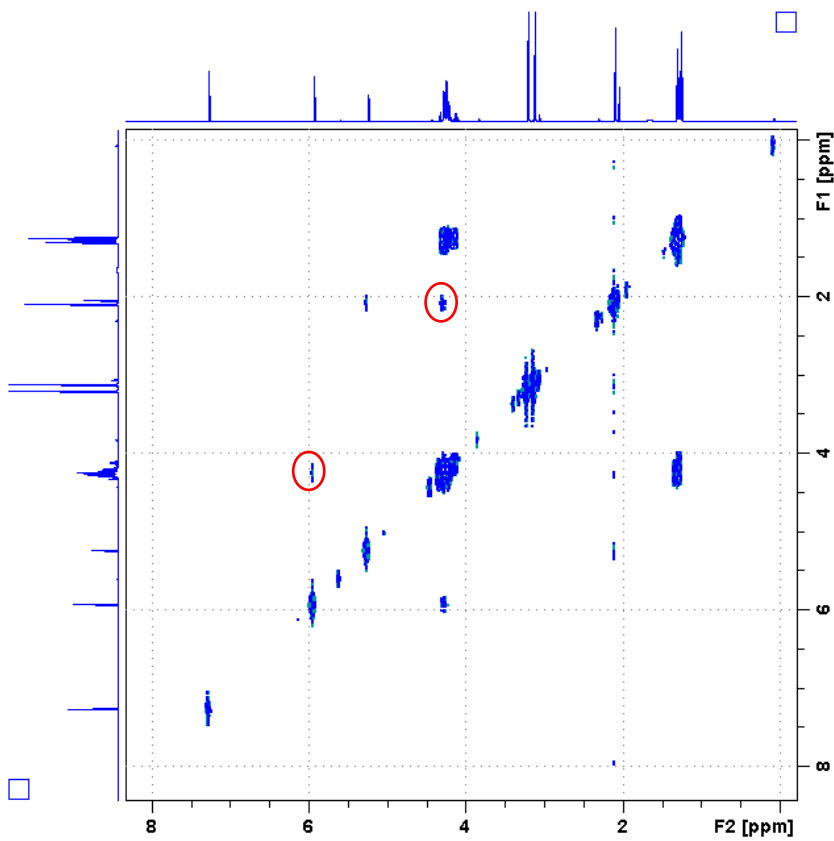
HMBC spectrum of **14b** 400MHz (CDCl<sub>3</sub>)



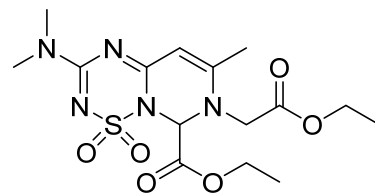
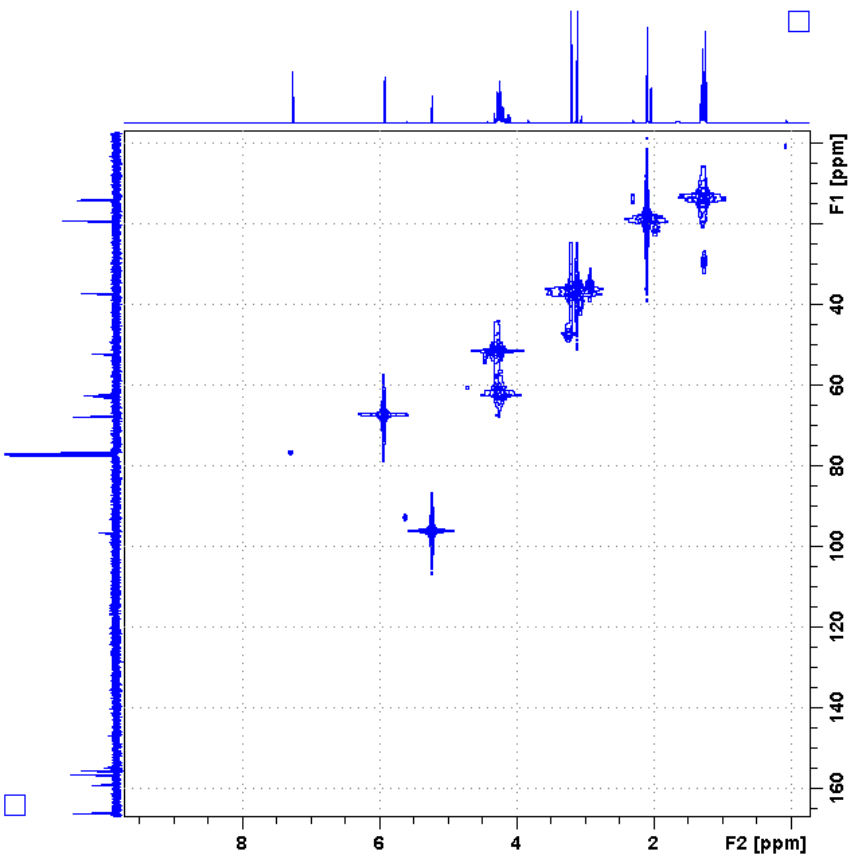
NOESY spectrum of **12c** 400MHz (CDCl<sub>3</sub>)



NOESY spectrum of **14c** 400MHz (CDCl<sub>3</sub>)

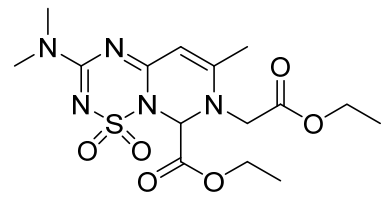
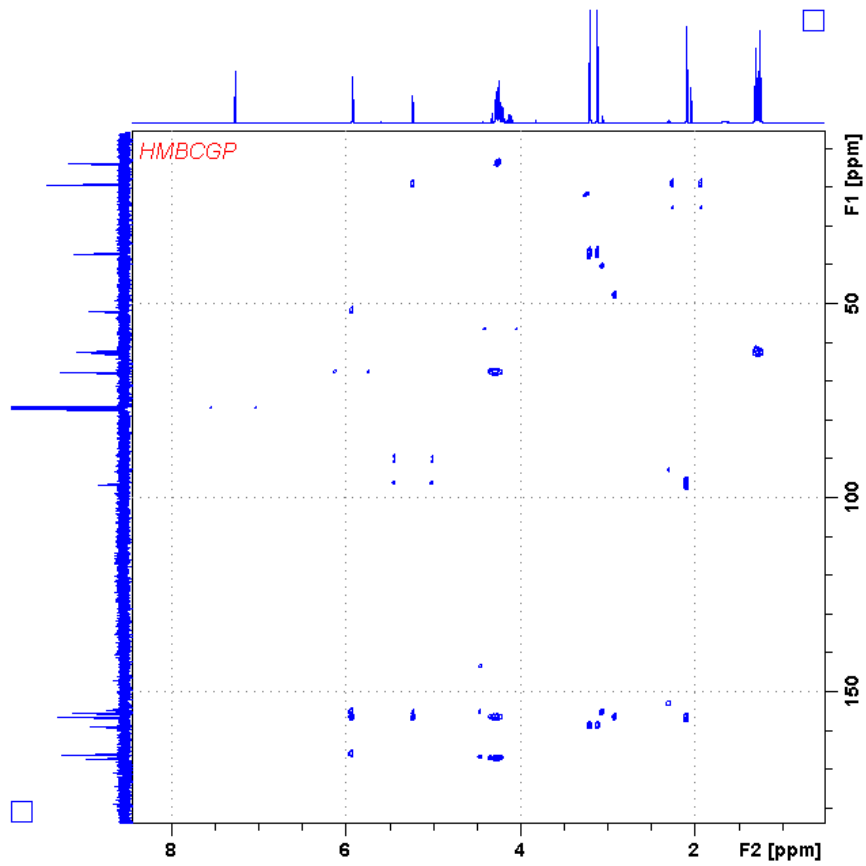


HMQC spectrum of **14c** 400MHz (CDCl<sub>3</sub>)

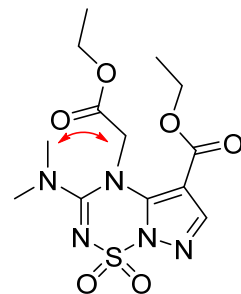
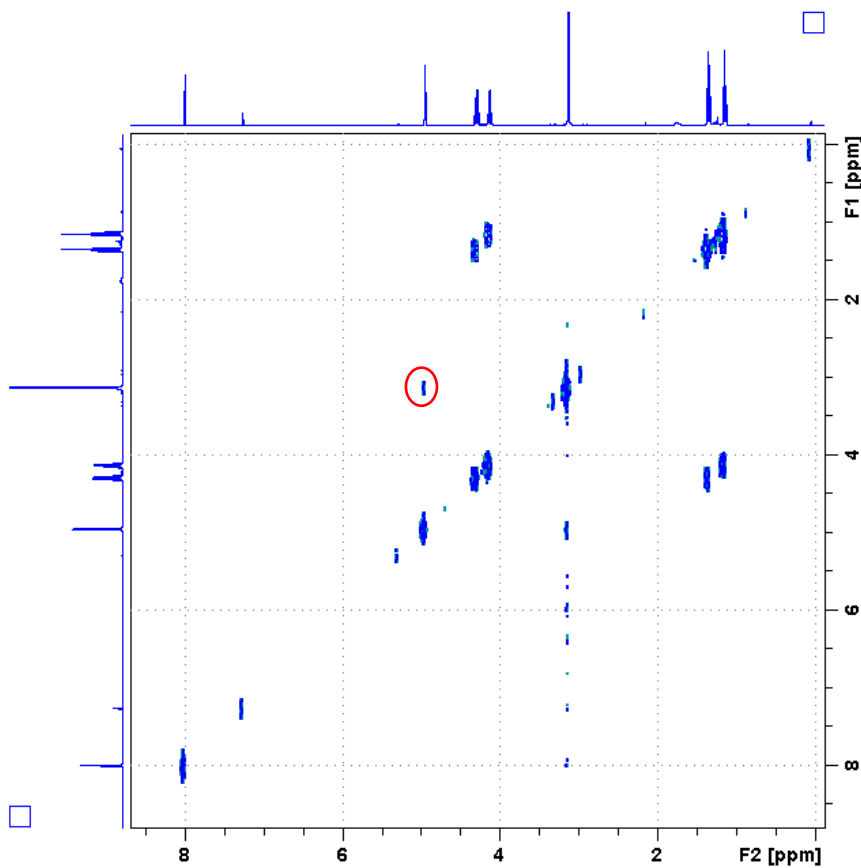




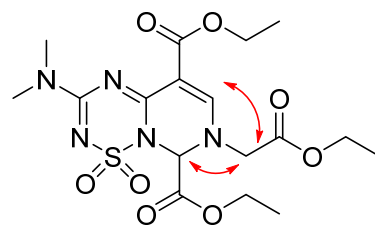
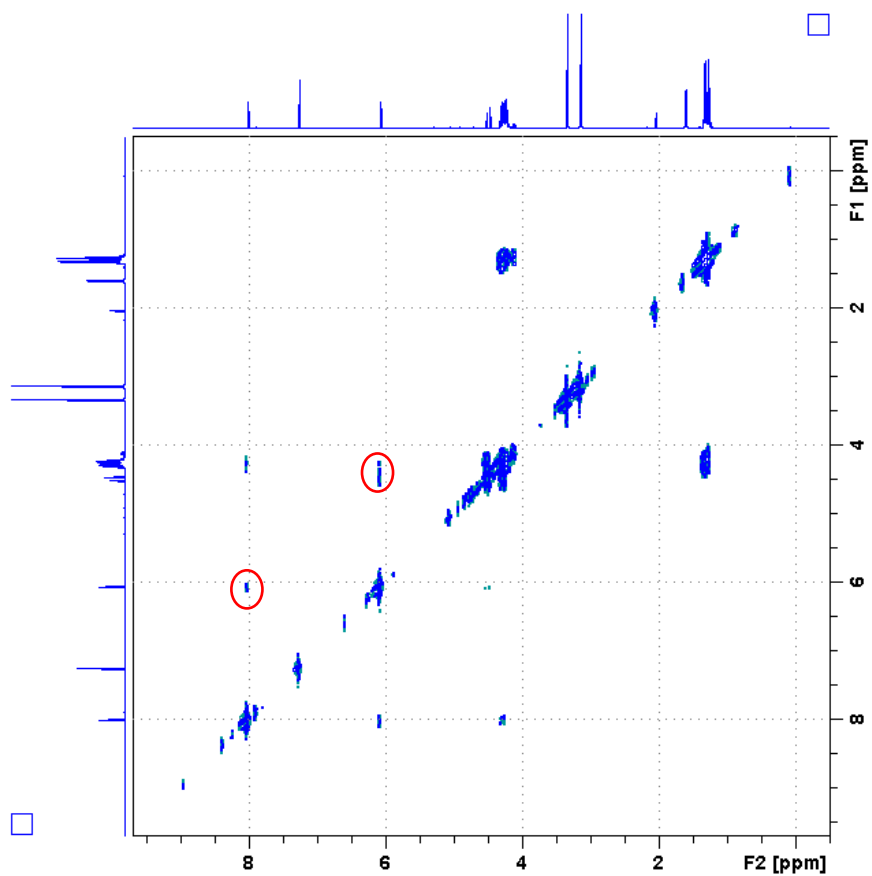
HMBC spectrum of **14c** 400MHz (CDCl<sub>3</sub>)



NOESY spectrum of **12d** 400MHz (CDCl<sub>3</sub>)

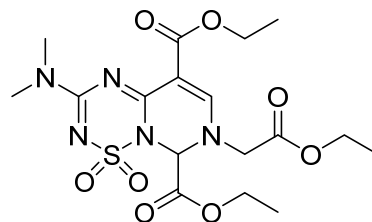
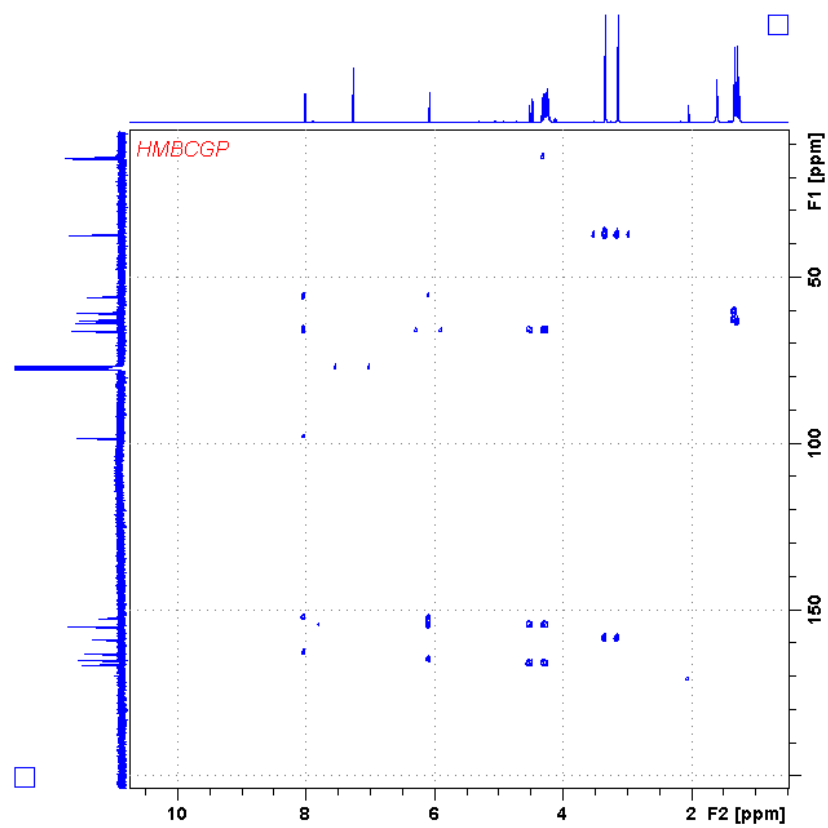


NOESY spectrum of **14d** 400MHz (CDCl<sub>3</sub>)

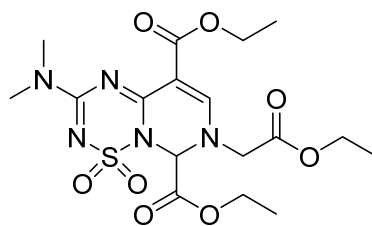
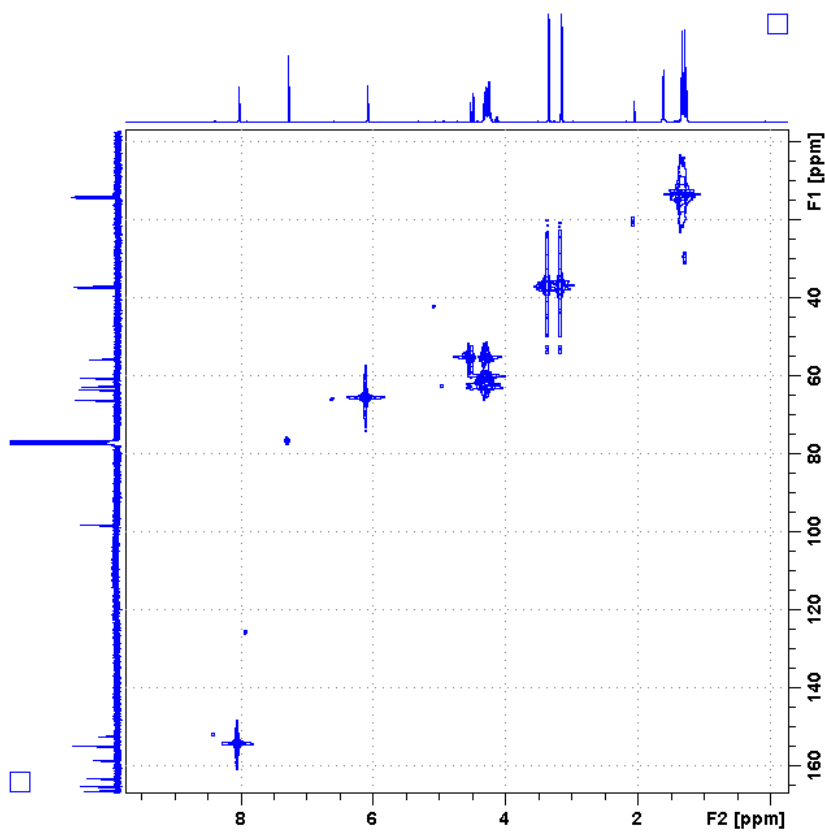


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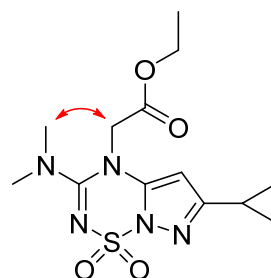
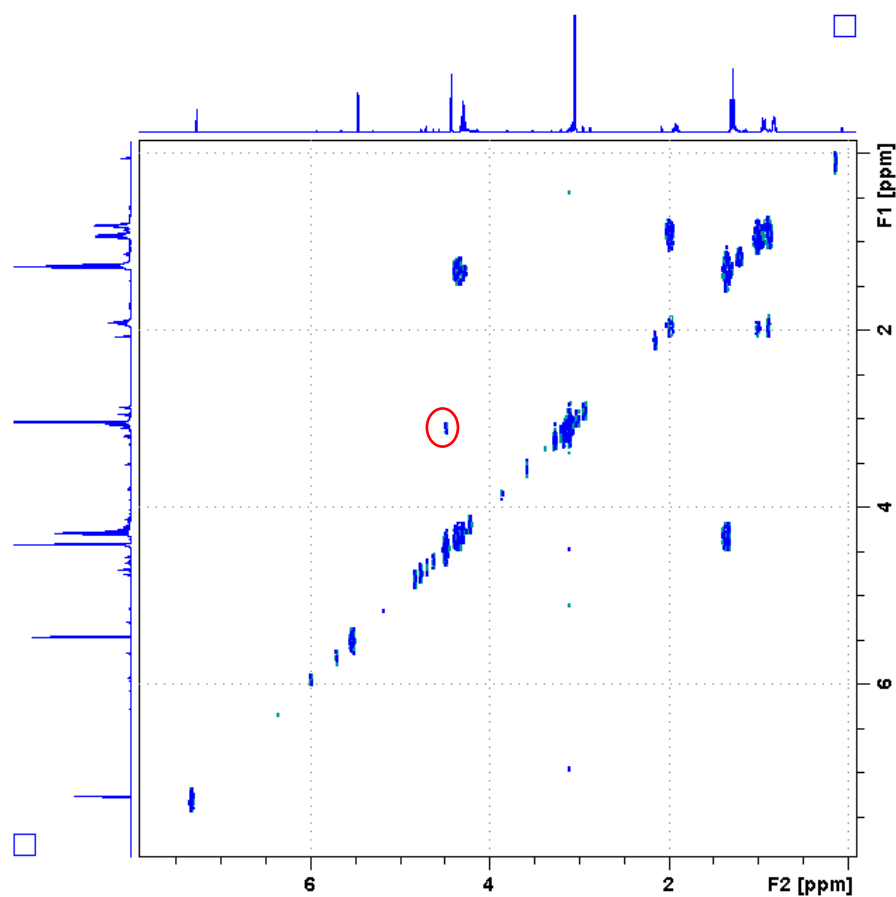
HMBC spectrum of **14d** 400MHz (CDCl<sub>3</sub>)



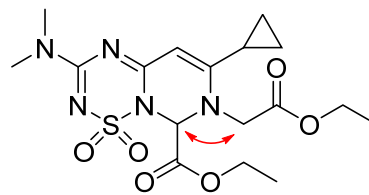
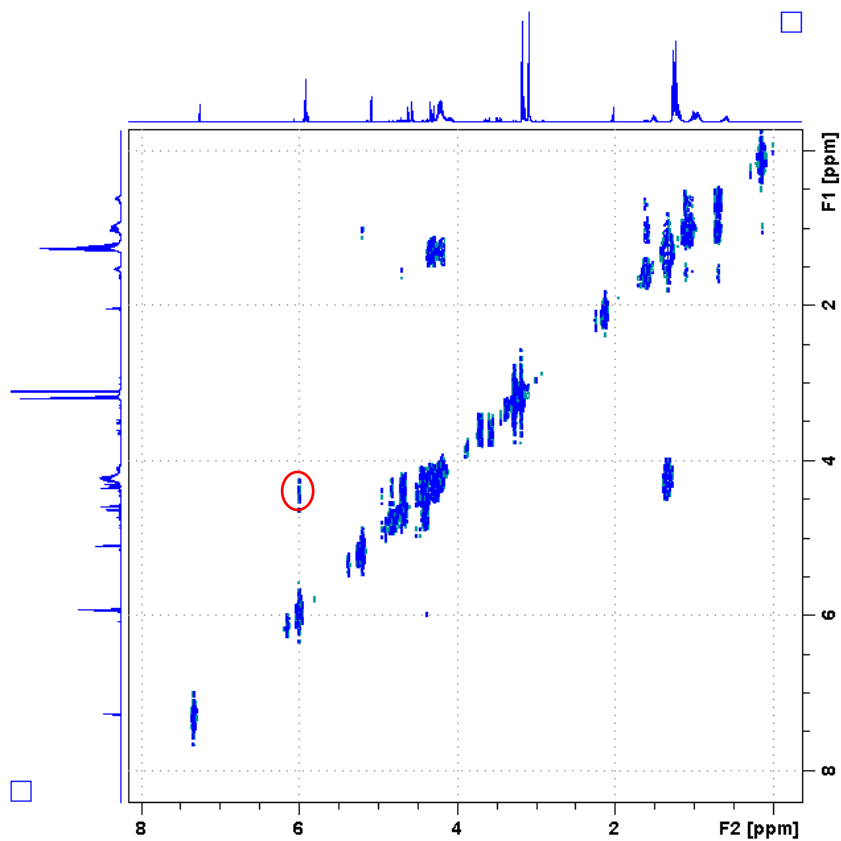
HMQC spectrum of **14d** 400MHz (CDCl<sub>3</sub>)



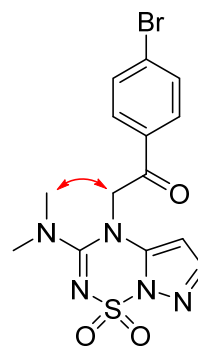
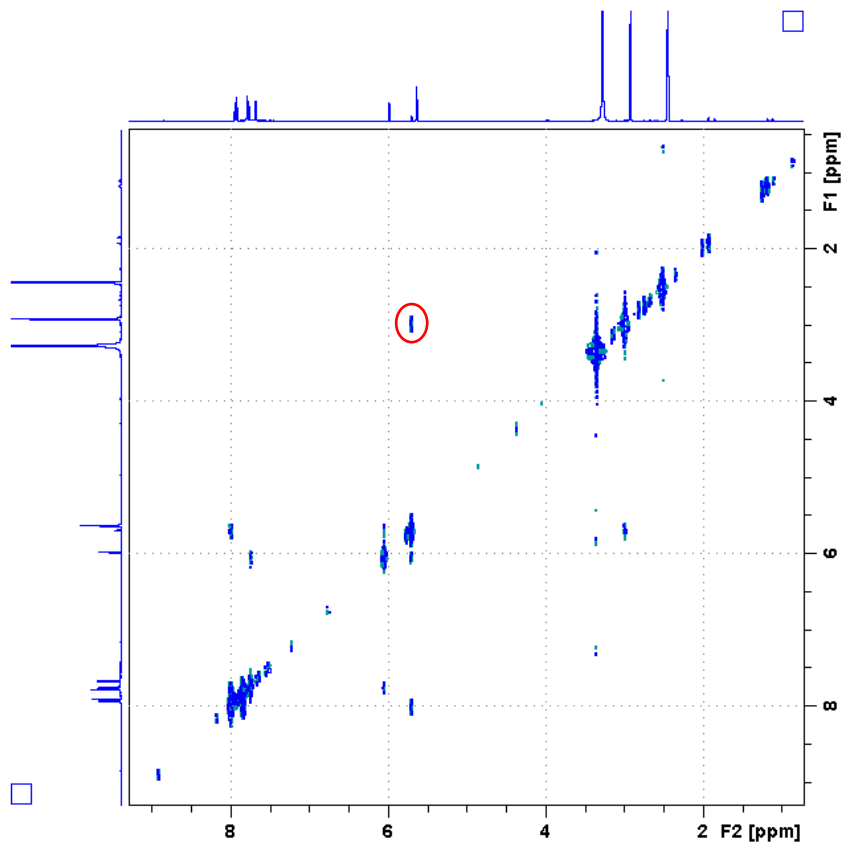
NOESY spectrum of **12e** 400MHz (CDCl<sub>3</sub>)



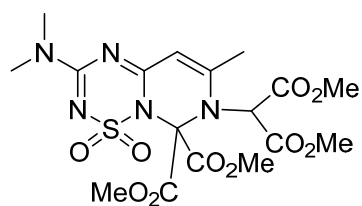
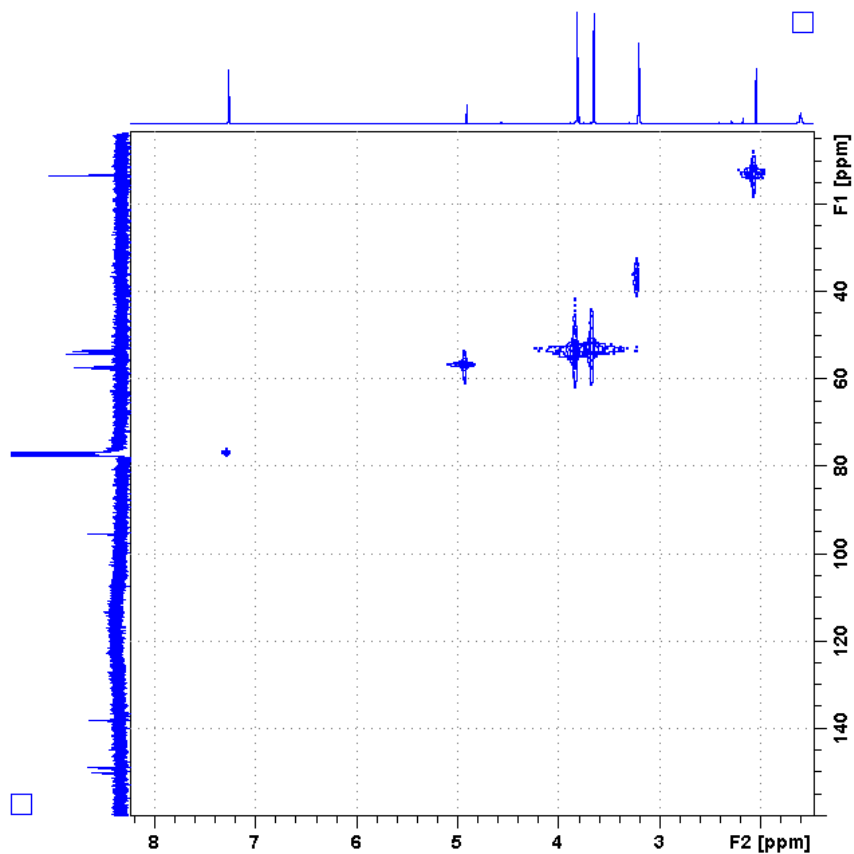
NOESY spectrum of **14e** 400MHz (CDCl<sub>3</sub>)



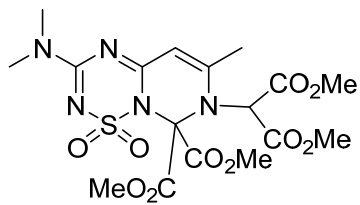
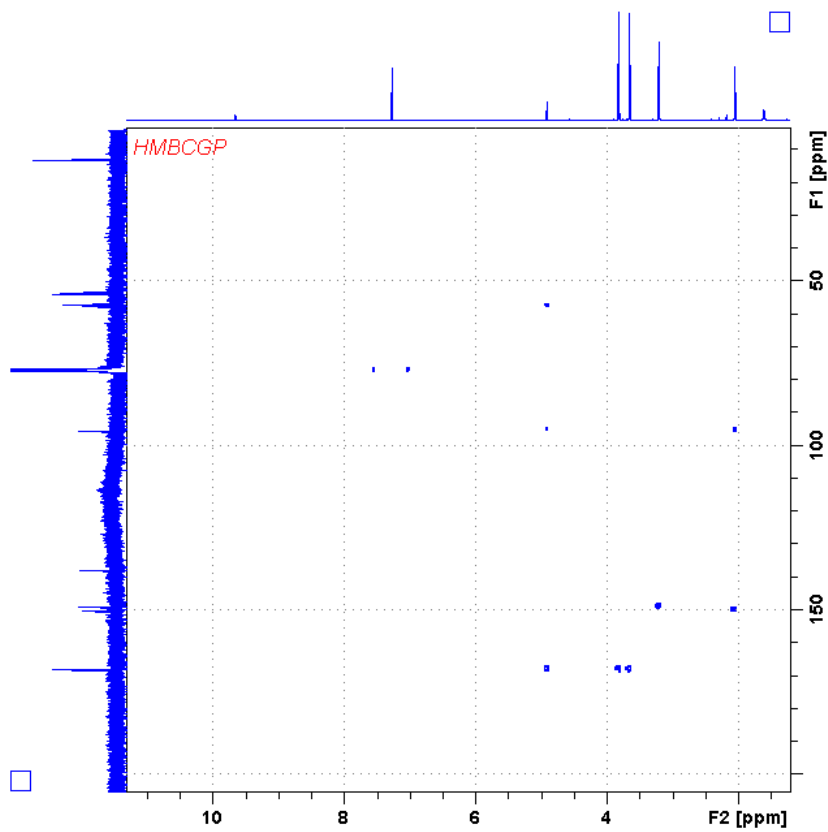
NOESY spectrum of **12f** 400MHz (CDCl<sub>3</sub>)



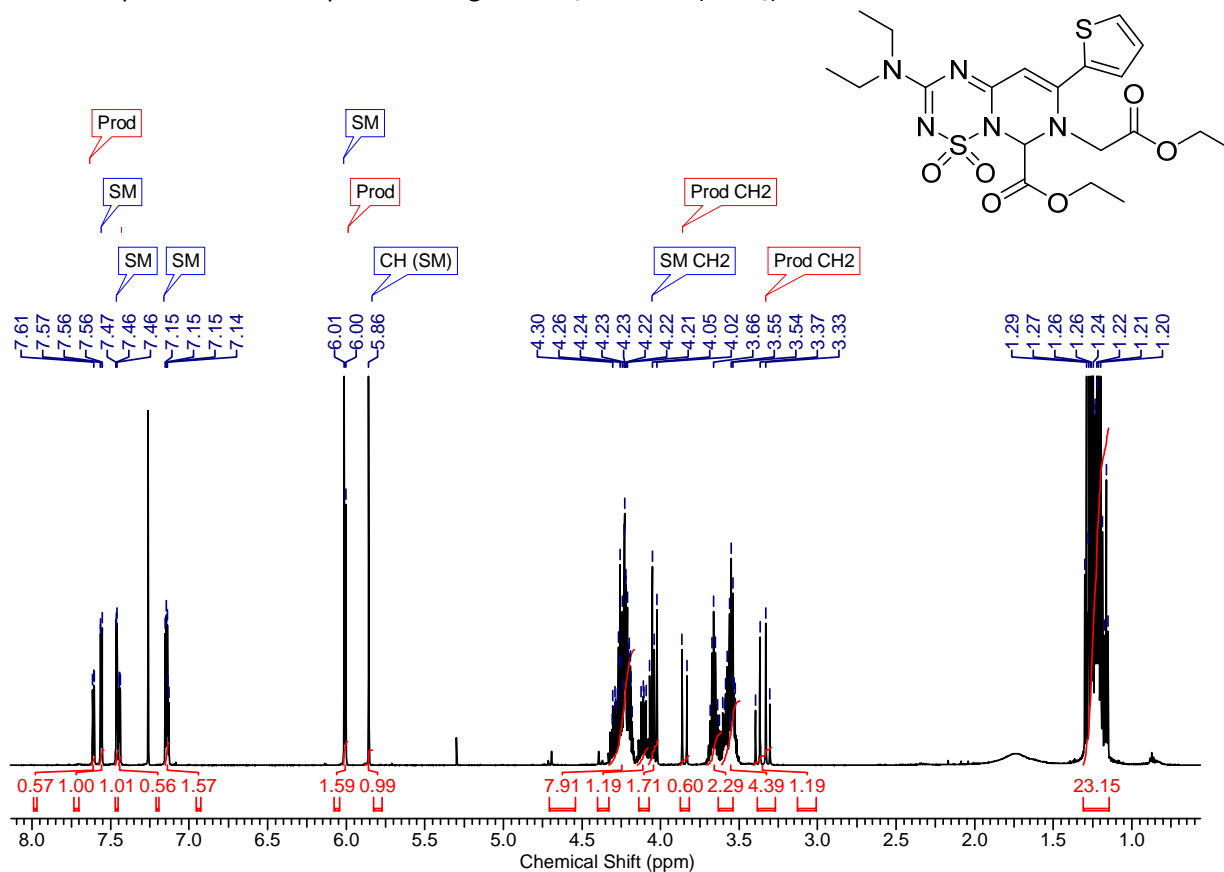
HMQC spectrum of **14g** 400MHz (CDCl<sub>3</sub>)



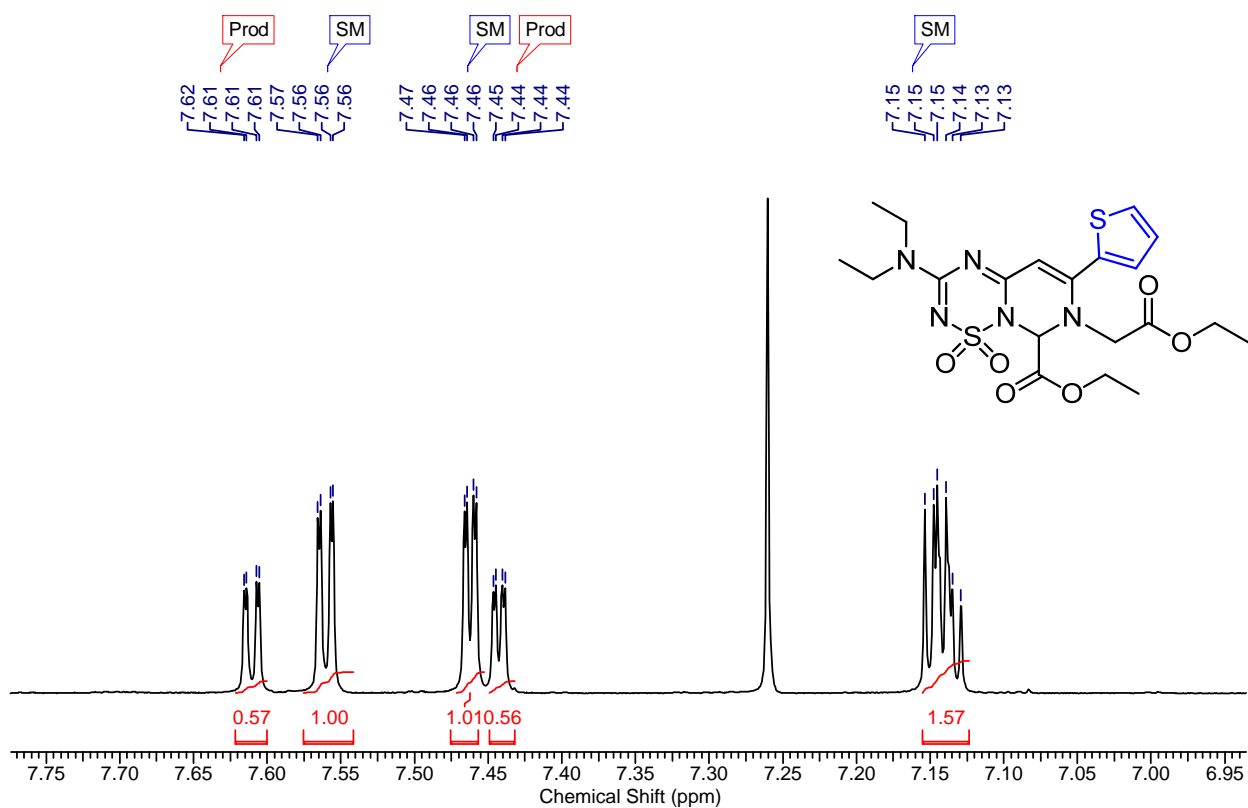
HMBC spectrum of **14g** 400MHz (CDCl<sub>3</sub>)

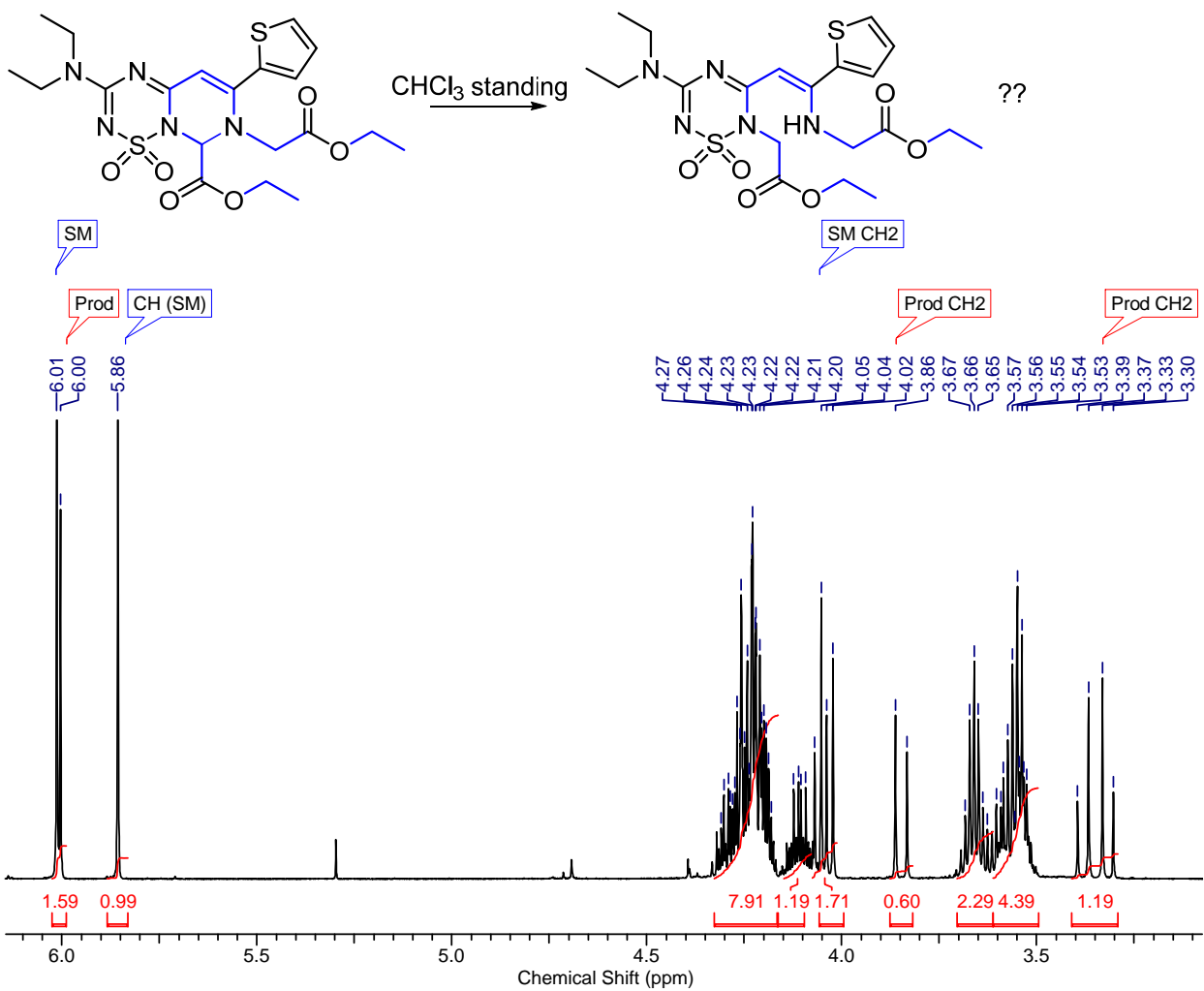


<sup>1</sup>H NMR spectrum of **14a** upon standing in CDCl<sub>3</sub> 600MHz (CDCl<sub>3</sub>)



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$^1\text{H}$  NMR spectrum of **7e** upon standing in  $\text{CDCl}_3$  600MHz (DMSO- $d_6$ )

