Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

N-Sulfonylation of Azoles with Sulfonyl Hydrazides Enabled by Electrocatalysis

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Table of Contents

1. General Information

Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received. ^{1}H NMR spectra were recorded using Agilent ProPulse AM-400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 101 MHz and referenced to the internal solvent signals. ^{19}F NMR spectra were recorded at 376 MHz using $CDCl_3$ as solvent. Mass spectra were recorded using an Agilent 7890-5975C spectrometer. EPR spectra were recorded by X Band on a Bruker E500 spectrometer. All the electrochemical reactions were performed in an undivided cell unless otherwise noted. The electrolysis instrument used is an adjustable DC regulated power supply (HYELEC, HY3005B). Cyclic voltammograms were obtained on a DH7000C instrument. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products visualized by UV detection.

2. Reaction Setup

The electrolysis instrument used is an adjustable DC regulated power supply (HYELEC HY3005B) (made in China). All the materials used to make the electrolytic cell were commercially available. The anode used graphite felt (1.0 cm × 1.0 cm) and cathode used platinum sheet electrodes (1.0 cm × 1.0 cm).

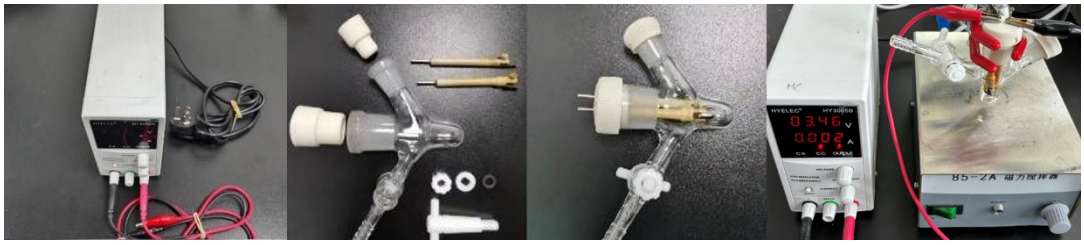
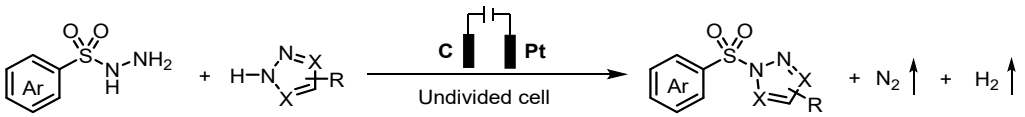


Figure S1. Reaction setup

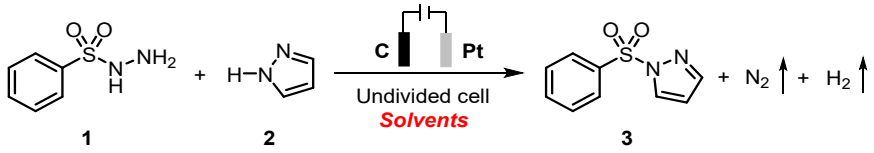
3. General Experimental Procedure for *N*-Sulfonylation of Azoles



A 3 mL reaction tube with magnetic stirring bar was charged with sulfonyl hydrazides substrates **1** (0.2 mmol, 1 equiv), azoles **2** (0.4 mmol, 2 equiv), $^{n}Bu_4NBr$ (0.2 mmol, 1 equiv) and 2.0 mL of CH_3CN, graphite felt (1.0 cm × 1.0 cm) as the anode, platinum sheet (1.0 cm × 1.0 cm) as cathode, was added in an undivided cell under air atmosphere for 2 h (constant current = 15 mA). After reaction, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired products.

4. Optimization of Conditions

Table S1. Optimization of solvents

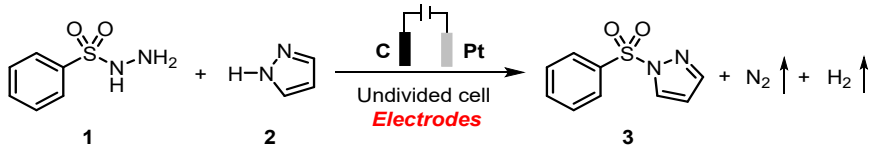


1 2 3

Entry	Change from standard conditions	Yield (%)
1	DCE instead of CH_3CN	45
2	DCM instead of CH_3CN	34
3	DMF instead of CH_3CN	26
4	DMSO instead of CH_3CN	N.R.
5	EtOH instead of CH_3CN	37
6	THF instead of CH_3CN	N.R.
7	H_2O instead of CH_3CN	23
8	CH_3CN : H_2O (5:1) instead of CH_3CN	39

Reaction condition: **1** (0.20 mmol, 1.0 equiv), **2** (0.40 mmol, 2.0 equiv), ^{n}Bu$_4$NBr (0.2 mmol, 1.0 equiv), were added into 2 mL of CH_3CN, graphite felt (1.0 cm × 1.0 cm) as the anode, platinum sheet (1.0 cm × 1.0 cm) as cathode, constant current = 15 mA, in an undivided cell under air atmosphere for 2 h at room temperature. Isolated yields. N.R. = No Reaction.

Table S2. Optimization of electrodes

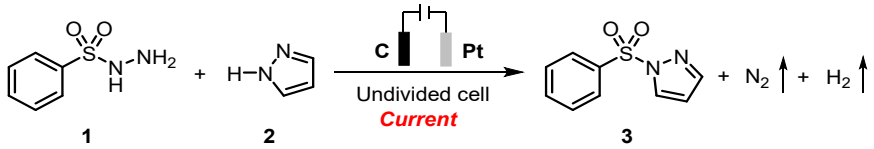


1 2 3

Entry	Change from standard conditions	Yield (%)
1	C(+)/Ni(-) instead of C(+)/Pt(-)	47
2	C(+)/Al(-) instead of C(+)/Pt(-)	30
3	C(+)/C(-) instead of C(+)/Pt(-)	56
4	C(+)/Zn(-) instead of C(+)/Pt(-)	38
5	Pt(+)/Pt(-) instead of C(+)/Pt(-)	N.R.
6	Pt(+)/C(-) instead of C(+)/Pt(-)	N.R.
7	Pt(+)/Zn(-) instead of C(+)/Pt(-)	N.R.
8	Pt(+)/Ni(-) instead of C(+)/Pt(-)	N.R.

Reaction condition: **1** (0.20 mmol, 1.0 equiv), **2** (0.40 mmol, 2.0 equiv), ^{n}Bu$_4$NBr (0.2 mmol, 1.0 equiv), were added into 2 mL of CH_3CN, graphite felt (1.0 cm × 1.0 cm) as the anode, platinum sheet (1.0 cm × 1.0 cm) as cathode, constant current = 15 mA, in an undivided cell under air atmosphere for 2 h at room temperature. Isolated yields. N.R. = No Reaction.

Table S3. Optimization of current

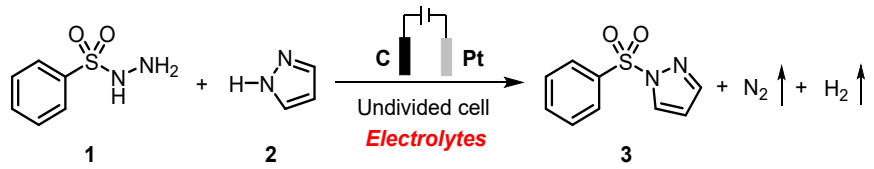


1 2 3

Entry	Change from standard conditions	Yield (%)
1	6 mA instead of 15 mA	83
2	8 mA instead of 15 mA	70
3	10 mA instead of 15 mA	76
4	12 mA instead of 15 mA	45
5	18 mA instead of 15 mA	52
6	20 mA instead of 15 mA	55

Reaction condition: **1** (0.20 mmol, 1.0 equiv), **2** (0.40 mmol, 2.0 equiv), $^{n}Bu_4NBr$ (0.2 mmol, 1.0 equiv), were added into 2 mL of CH_3CN, graphite felt (1.0 cm × 1.0 cm) as the anode, platinum sheet (1.0 cm × 1.0 cm) as cathode, constant current = 15 mA, in an undivided cell under air atmosphere for 2 h at room temperature. Isolated yields. N.R. = No Reaction.

Table S4. Optimization of electrolytes

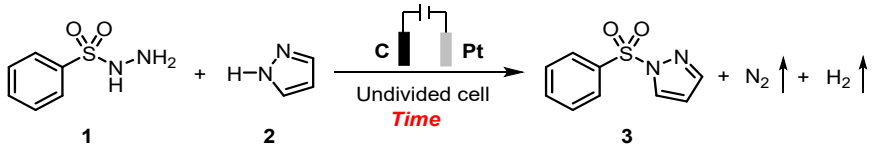


1 2 3

Entry	Change from standard conditions	Yield (%)
1	TEAB instead of $^{n}Bu_4NBr$	49
2	$^{n}Bu_4NBF_4$ instead of $^{n}Bu_4NBr$	84
3	$^{n}Bu_4NClO_4$ instead of $^{n}Bu_4NBr$	N.R.
4	$^{n}Bu_4NHSO_4$ instead of $^{n}Bu_4NBr$	N.R.
5	TBAI instead of $^{n}Bu_4NBr$	39
6	TBAF instead of $^{n}Bu_4NBr$	76
7	$^{n}Bu_4NCl$ instead of $^{n}Bu_4NBr$	51
8	$^{n}Et_4NCl$ instead of $^{n}Bu_4NBr$	54
9	$^{n}Et_4NBF_4$ instead of $^{n}Bu_4NBr$	71
10	$^{n}Bu_4NBF_4$ with KBr instead of $^{n}Bu_4NBr$	79
11	$^{n}Bu_4NBF_4$ with NaBr instead of $^{n}Bu_4NBr$	82

Standard condition: **1** (0.20 mmol, 1.0 equiv), **2** (0.40 mmol, 2.0 equiv), $^{n}Bu_4NBr$ (0.2 mmol, 1.0 equiv), were added into 2 mL of CH_3CN, graphite felt (1.0 cm × 1.0 cm) as the anode, platinum sheet (1.0 cm × 1.0 cm) as cathode, constant current = 15 mA, in an undivided cell under air atmosphere for 2 h at room temperature. Isolated yields. N.R. = No Reaction.

Table S5. Optimization of time

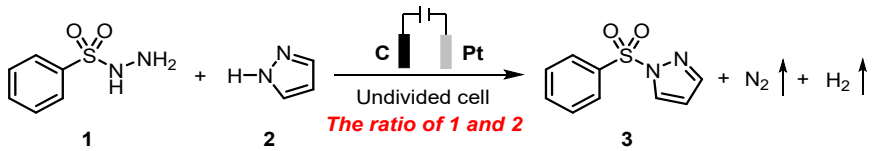


1 2 3

Entry	Change from standard conditions	Yield (%)
1	1 h instead of 2 h	53
2	3 h instead of 2 h	65
3	4 h instead of 2 h	55

Reaction condition: **1** (0.20 mmol, 1.0 equiv), **2** (0.40 mmol, 2.0 equiv), $^{n}Bu_4NBr$ (0.2 mmol, 1.0 equiv), were added into 2 mL of CH_3CN, Graphite felt (1.0 cm × 1.0 cm) as the anode, platinum sheet (1.0 cm × 1.0 cm) as cathode, constant current = 15 mA, in an undivided cell under air atmosphere for 2 h at room temperature. Isolated yields. N.R. = No Reaction.

Table S6. Optimization of the amount of sulfonyl hydrazides and azoles

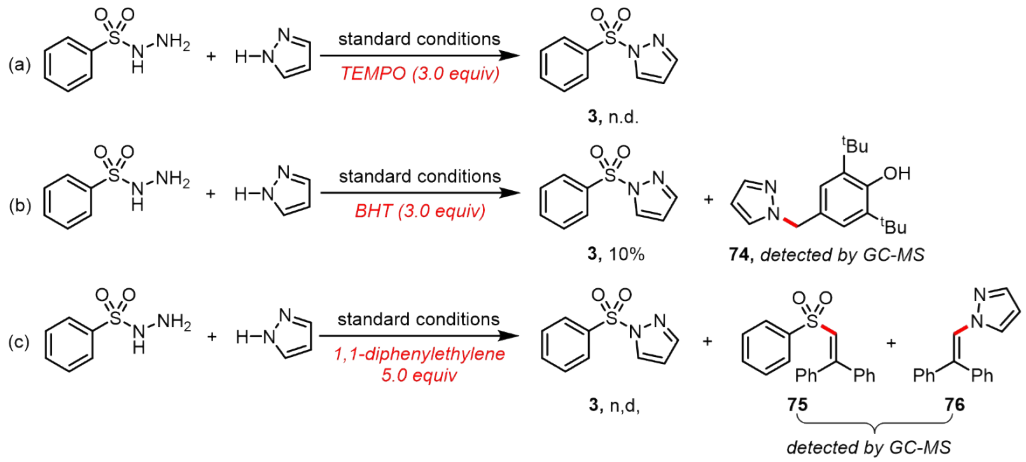


1 2 3

Entry	The ratio of sulfonyl hydrazides 1 and azoles 2	3 Yield (%)
1	1:1	51
2	1:2	87
3	1:3	82
4	2:1	67
5	3:1	68

Reaction condition: **1**, **2**, $^{n}Bu_4NBr$ (0.2 mmol, 1.0 equiv), were added into 2 mL of CH_3CN, Graphite felt (1.0 cm × 1.0 cm) as the anode, platinum sheet (1.0 cm × 1.0 cm) as cathode, constant current = 15 mA, in an undivided cell under air atmosphere for 2 h at room temperature. Isolated yields. N.R. = No Reaction.

5. Radical Trapping Reactions



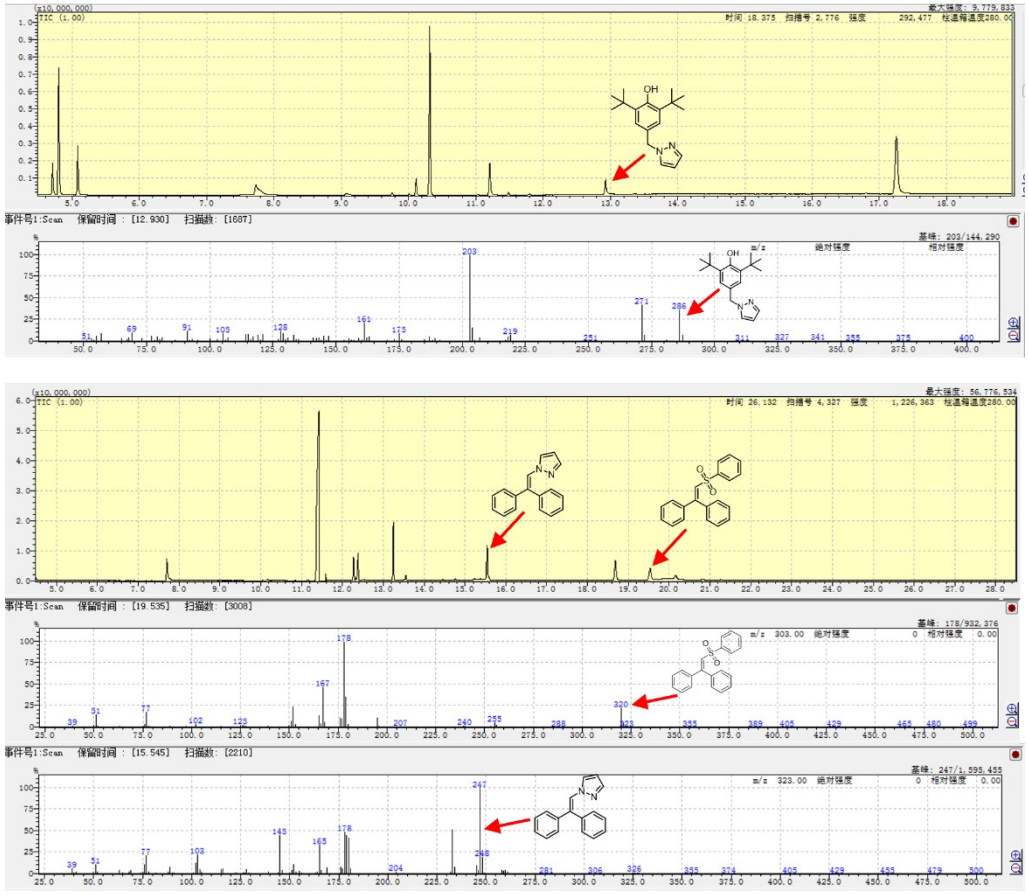


Figure S2 GC-MS of the crude reaction mixture

6. Electron Paramagnetic Resonance (EPR) Spectroscopy Experiments

EPR spectra were recorded by X Band on a Bruker E500 spectrometer. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.852 GHz. Typical spectrometer parameters are shown as follows, Center field set: 3510 G; Sweep width: 100G; Number of Points: 1024; Attenuation:10 dB; Modulation frequency: 100 kHz; Modulation Amplitude: 1.0 G; Conver Time :20.00 ms; Sweep Time: 20.48 s.

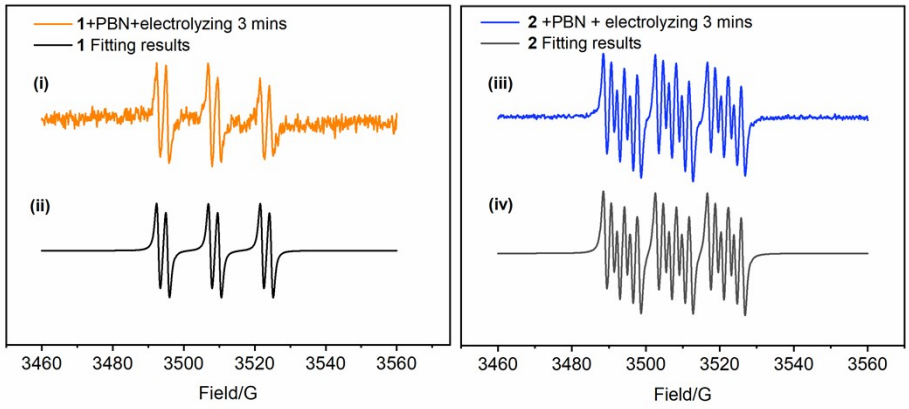


Figure S3. EPR experiments: (i) A solution containing PBN, **1**, and CH_3CN was electrolyzed for 3 mins under N_2 atmosphere, (iii) A solution containing PBN, **2**, and CH_3CN was electrolyzed for 3 mins under N_2 atmosphere; (ii and iv) Fitting results.

7. Cyclic Voltammetry Studies

Cyclic voltammetry was recorded on a DH7000C instrument. A 3 mm diameter glassy carbon electrode was used as the working electrode; a platinum wire electrode (0.5*37 mm) was used as the counter electrode; an Ag/AgCl was used as reference electrode under air at room temperature. The scan rate is 100 mVs^{-1}, ranging from 0 V to 3 V.

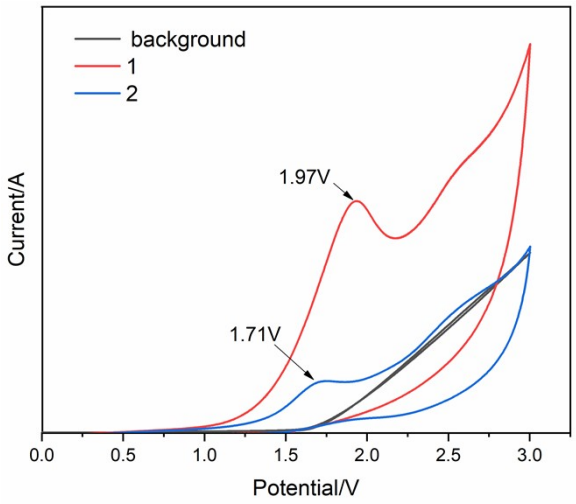


Figure S4. The cyclic voltammetry experiment of **1** and **2** in CH_3CN under air atmosphere.

(1) **1** (0.2 mmol) and the solvent (CH_3CN, 5 mL) containing $^{n}Bu_4NBF_4$ (0.2 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mVs^{-1}, ranging from 0 V to 3 V.

(2) **2** (0.2 mmol) and the solvent (CH_3CN, 5 mL) containing $^nBu_4NBF_4$ (0.2 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mVs^{-1}, ranging from 0 V to 3 V.

8. Electricity On/Off Experiment

Eight parallel reaction mixtures in 3 mL reaction tube with magnetic stirring bar was charged with benzenesulfonyl hydrazide **1** (0.02 mmol), 1*H*-pyrazole **2** (0.4 mmol, 2.0 equiv.), $^nBu_4NBr$ (0.2 mmol, 1.0 equiv), and 2.0 mL of CH_3CN at room temperature using a constant current of 15 mA. Graphite felt (1.0 cm × 1.0 cm) as the anode, platinum sheet (1.0 cm × 1.0 cm) as cathode. These reaction tubes were labeled by **A, B, C, D, E, F, G and H**.

The reaction **A** was electrolyzed for 0.5 h. After reaction, upon removal of solvent under vacuum, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product in 26% yield.

The reaction **B** was electrolyzed for 0.5 h. Then, the reaction **B** was stirred in the absence of electric current for 0.5 h. After reaction, upon removal of solvent under vacuum, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product in 29% yield.

The reaction **C** was electrolyzed for 0.5 h. Then, the reaction **C** was stirred in the absence of electric current for 0.5 h. Then, the reaction **C** was electrolyzed for 0.5 h. After reaction, upon removal of solvent under vacuum, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product in 53% yield.

The reaction **D** was electrolyzed for 0.5 h. Then, the reaction **D** was stirred in the absence of electric current for 0.5 h. Then, the reaction **D** was electrolyzed for 0.5 h. Then, the reaction **D** was stirred in the absence of electric current for 0.5 h. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product in 57% yield.

The reaction **E** was electrolyzed for 0.5 h. Then, the reaction **E** was stirred in the absence of electric current for 0.5 h. Then, the reaction **E** was electrolyzed for 0.5 h. Then, the reaction **E** was stirred in the absence of electric current for 0.5 h. Then, the reaction **E** was electrolyzed for 0.5 h. After reaction, upon removal of solvent under vacuum, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product in 72% yield.

The reaction **F** was electrolyzed for 0.5 h. Then, the reaction **F** was stirred in the absence of electric current for 0.5 h. Then, the reaction **F** was electrolyzed for 0.5 h. Then, the reaction **F** was stirred in the absence of electric current for 0.5 h. Then, the reaction **F** was electrolyzed for 0.5 h. Then, the reaction **F** was stirred in the absence of electric current for 0.5 h. After reaction, upon removal of solvent under vacuum, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product in 75% yield.

The reaction **G** was electrolyzed for 0.5 h. Then, the reaction **G** was stirred in the absence of electric current for 0.5 h. Then, the reaction **G** was electrolyzed for 0.5 h. Then, the reaction **G** was stirred in the absence of electric current for 0.5 h. Then, the reaction **G** was electrolyzed for 0.5 h. Then, the reaction **G** was stirred in the absence of electric current for 0.5 h. Then, the reaction **G** was electrolyzed for 0.5 h. After reaction, upon removal of solvent under vacuum, the crude residue was subjected to flash column chromatography on silica gel to yield the

desired product in 87% yield.

The reaction **H** was electrolyzed for 0.5 h. Then, the reaction **H** was stirred in the absence of electric current for 0.5 h. Then, the reaction **H** was electrolyzed for 0.5 h. Then, the reaction **H** was stirred in the absence of electric current for 0.5 h. Then, the reaction **H** was electrolyzed for 0.5 h. Then, the reaction **H** was stirred in the absence of electric current for 0.5 h. Then, the reaction **H** was electrolyzed for 0.5 h. Then, the reaction **H** was stirred in the absence of electric current for 0.5 h. After reaction, upon removal of solvent under vacuum, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product in 88% yield.

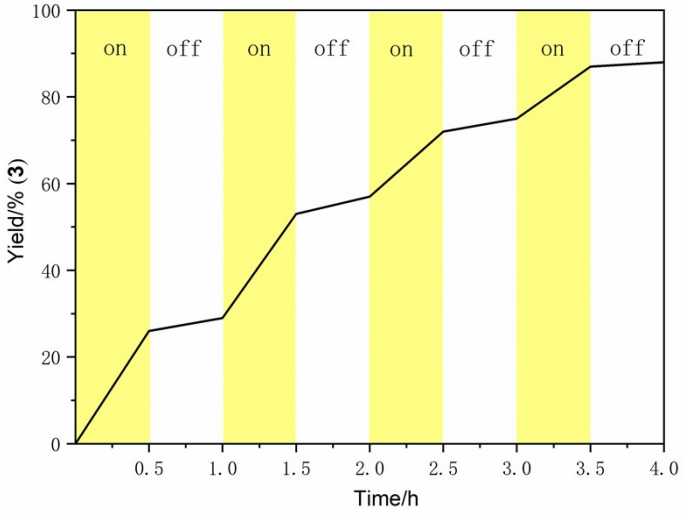
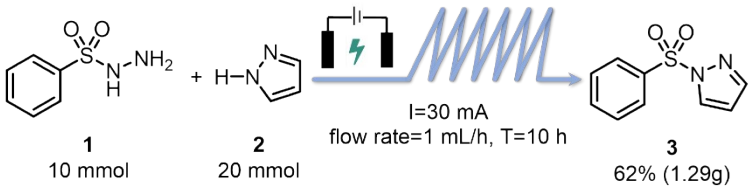


Figure S5. Electricity on / off Experiments

9. Electrochemical Continuous-flow Experiments



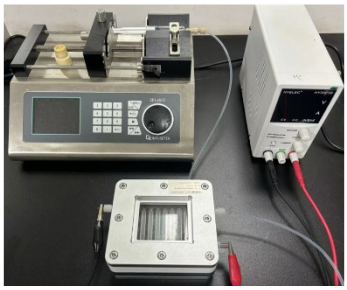
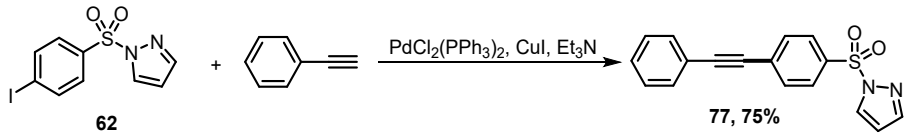


Figure S6. Components of flow chemistry: Micro syringe pump (DK INFUSETEK, SPLab02), DC stabilized power supply (HYELEC, HY3005B), Continuous flow panel (EZONE, PER-10).

A 10 mL reaction tube was charged with benzenesulfonyl hydrazide **1** (10 mmol), 1*H*-pyrazole **2** (20 mmol, 2.0 equiv), $^{n}Bu_4NBr$ (10 mmol, 1.0 equiv) and 10 mL of CH_3CN. The 10 mL mixture was swirled until homogeneous, placed in a 10 mL disposable syringe and mounted on a syringe pump. The mixture liquid feed was pumped into the flow reactor for electrolysis for 10 h at room temperature. After reaction, the solvent was extracted with ethyl acetate (3 × 20

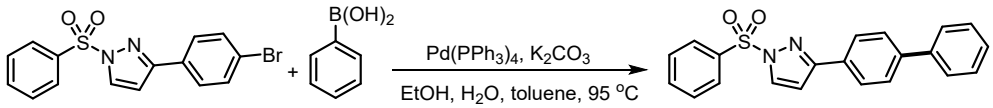
mL), the combined organic extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system (petroleum ether/ethyl acetate = 4 : 1) afforded the desired product **3** in 62% yield (1.29 g).

10. Experimental Procedure for Diversification



62 **77, 75%**

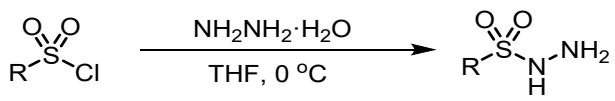
Prepared according to literature methods.[1] A suspension of 1-((4-iodophenyl)sulfonyl)-1*H*-pyrazole (0.5 mmol), $PdCl_2(PPh_3)_2$ (2 mol%), CuI (3 mol%) in 2 mL of triethylamine was degassed with nitrogen for 5 minutes. Then, a solution of phenyl acetylene (1.2 equiv.) was added drop-wise over 5 minutes via syringe and the reaction mixture was left to stir for 12 h. After completion, the solvent diluted with 10 mL ethyl acetate and washed with 5 mL brine and dried over anhydrous Na_2SO_4. After the solvent was evaporated *in vacuo*, the residues were purified by column chromatography, eluting with petroleum ether/ethyl acetate = 4:1 to afford **77** as a white solid.



33 **78, 68%**

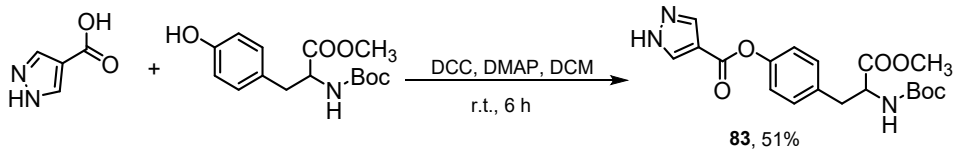
Prepared according to literature methods.[2] In an oven-dried round bottom flask, 4-bromo-1-(phenylsulfonyl)-1*H*-pyrazole **33** (0.3 mmol) was taken in a mixture of 2.0 mL EtOH, 1 mL water and 3 mL toluene and degassed for 20 mins. To the resulting mixture, Phenylboronic acid (0.4 mmol, 1.5 equiv.), K_2CO_3 (1.2 mmol, 4.0 equiv.) and $Pd(PPh_3)_4$ (0.024 mmol, 0.8 mol%) were added successively at room temperature. The resulting mixture was stirred at 95 °C (oil bath) under positive argon pressure for 12 h. The reaction mixture was cooled to room temperature, quenched with saturated NH_4Cl solution, and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, concentrated *in vacuo* to obtain a black oil which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to obtain 4-phenyl-1-(phenylsulfonyl)-1*H*-pyrazole **78** as a white solid.

11. Synthesis of Starting Materials

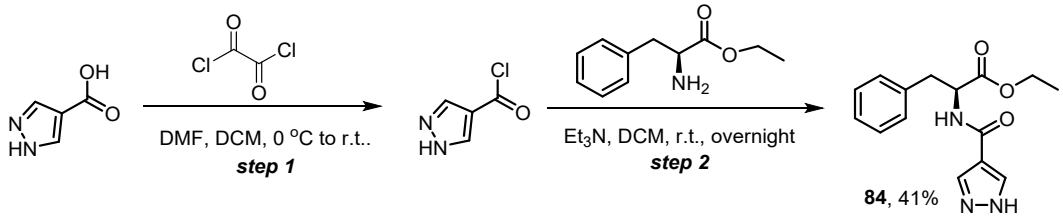


Synthesis of arylsulfonyl hydrazides. All sulfonyl hydrazides were prepared according to the literature procedure.[3-6] The hydrazine monohydrate (1.50 g, 30 mmol) was added dropwise into the solution of sulfonyl chloride (10 mmol) in THF (50 mL) under air at 0 °C. Subsequently, the mixture was further stirred at 0 °C for 30 mins. After the completion of the reaction, the solvent was removed by evaporation, and the residue was extracted with dichloromethane (3 × 20 mL), and the combined organic layer was washed with water and brine and dried over

Na_2SO_4. Concentration in vacuum followed by silica gel column purification with a petroleum ether/ethyl acetate eluent gave the desired products in yields ranging from 70% to 95%.

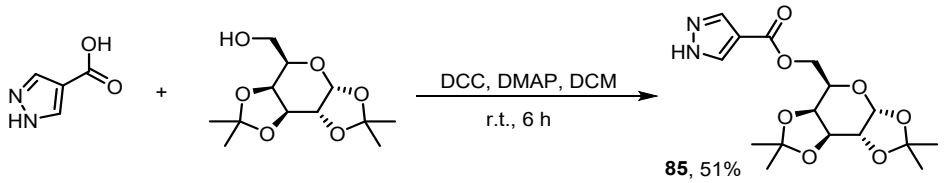


Synthesis of compound **83**. Prepared according to literature methods.[7] To the 100 mL round bottom flask, the 1H-pyrazole-4-carboxylic acid (230 mg, 2.0 mmol), tyrosine derivative (360 mg, 0.6 equiv), DCC (454 mg, 1.1 equiv), and DMAP (10 mg) were added in 20 mL DCM at room temperature and stirred about 6 hours. After the completion of the reaction, the solution was filtrated by the celite and remove the solvent. The crude product was purified directly by flash chromatograph using the mixture of hexane/ethyl acetate (1:1) to provide the desired product **83** (white solid, 356 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.23 – 6.98 (m, 4H), 5.18 (s, 1H), 4.61 (d, J = 7.4 Hz, 1H), 3.74 (s, 3H), 3.10 (dd, J = 20.5, 5.9 Hz, 2H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 161.4, 155.2, 149.5, 137.1, 133.7, 130.3, 121.8, 113.9, 80.1, 54.4, 52.3, 37.7, 28.3.

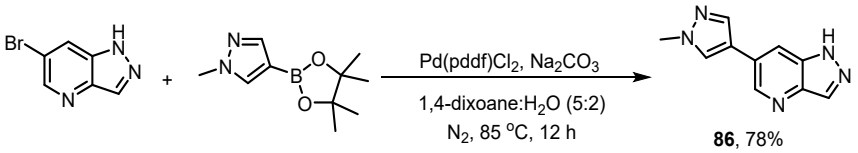


Synthesis of compound **84**. Prepared according to literature methods.[8] **Step 1:** A 100 mL round-bottom flask was charged with 1H-pyrazole-4-carboxylic acid (5 mmol), dry DCM (20 mL) and three drops of DMF. The reaction mixture was cooled to 0 °C. Then, $(COCl)_2$ (1.3 equiv) was added dropwise to the reaction mixture and stirred at room temperature for 5 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step 2: To a solution of ethyl *L*-phenylalaninate (6 mmol, 1.2 equiv) and Et_3N (7.5 mmol, 1.5 equiv) in dry DCM (20 mL), acid chloride prepared from Step-1 was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (10 mL) was added, the organic layer was separated and the aqueous layer was extracted three times with DCM. The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) solution. After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was then purified by flash column with petroleum ether/ethyl acetate (4/1 ratio) on silica gel to afford the compound **84** (706 mg, 41%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 9.9 Hz, 2H), 7.33 – 7.20 (m, 3H), 7.15 (dt, J = 7.9, 2.0 Hz, 2H), 5.04 (d, J = 7.8 Hz, 1H), 4.21 (d, J = 7.1 Hz, 3H), 3.21 (q, J = 4.9, 4.0 Hz, 2H), 1.28 (d, J = 7.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 162.5, 136.0, 134.3, 129.3, 128.5, 127.1, 117.5, 61.7, 53.3, 37.9, 14.0.



Synthesis of compound **85**. Prepared according to literature methods.[8] To the 100 mL round bottom flask, the 1H-pyrazole-4-carboxylic acid (230 mg, 2.0 mmol), ((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methanol (312 mg, 0.6 equiv), DCC (454 mg, 1.1 equiv), and DMAP (10 mg) were added in 20 mL DCM at room temperature and stirred about 6 hours. After the completion of the reaction, the solution was filtrated by the celite and remove the solvent. The crude product was purified directly by flash chromatograph using the mixture of hexane/ethyl acetate (4:1) to provide the white solid product **85** (362 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 5.58 (d, J = 5.0 Hz, 1H), 4.64 (m, 1H), 4.49 (dd, J = 11.6, 4.5 Hz, 1H), 4.41 – 4.28 (m, 3H), 4.21 – 4.09 (m, 1H), 1.53 (d, J = 4.2 Hz, 3H), 1.47 (d, J = 7.3 Hz, 3H), 1.36 (s, 3H), 1.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 136.6, 109.7, 109.4, 108.8, 108.7, 96.3, 71.1, 70.7, 70.5, 66.2, 63.3, 26.0, 25.9, 24.9, 24.4.



Synthesis of compound **86**. Prepared according to literature methods.[9] To a solution of 6-bromo-1*H*-pyrazolo[4,3-b]pyridine (5 mmol) and 1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (7.5 mmol, 1.5 equiv), Na_2CO_3 (20 mmol, 4 equiv), $Pd(pddf)Cl_2$ (5 mol%) in 1,4-dixoane:H_2O (5:2, v/v) under N_2 atmosphere and the reaction mixture was stirred at 85 °C for 12 h. Then water (10 mL) was added, the organic layer was separated and the aqueous layer was extracted three times with DCM. The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) solution. After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was then purified by flash column with petroleum ether/ethyl acetate (4/1 ratio) on silica gel to afford the compound **86** (776 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.32 (s, 1H), 7.88 (d, J = 15.5 Hz, 2H), 7.77 (s, 1H), 4.01 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 137.1, 131.9, 129.4, 126.8, 120.2, 113.5, 113.2, 103.6, 39.5.

12. Faraday Efficiency

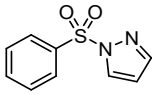
Faradaic efficiency was calculated according to the following equation[10]:

$$\text{Faradaic efficiency} = \left(\frac{n * z * F}{I * t}\right) * 100\% = \left(\frac{0.174\ \text{mmol} * 4 * 26.8\ \text{A·h}}{15\ \text{mA} * 2\ \text{h}}\right) * 100\% = 62.2\%$$

Where n represents the product's amount (mmol), z represents the number of electrons transferred，F represents Faraday constant (F = 96500 C/mol = 26.8 A·h)， I represents the current (mA), t represents the electrolysis time (h).

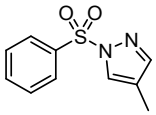
13. Characterization Data for All Compounds

1-(Phenylsulfonyl)-1*H*-pyrazole (3)



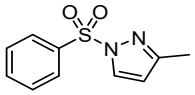
The compound was prepared according to the General procedure. White solid; mp 97.2-98.5 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 36.2 mg, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 2.7 Hz, 1H), 8.02 – 7.97 (m, 2H), 7.71 (d, J = 1.5 Hz, 1H), 7.62 (s, 1H), 7.51 (t, J = 7.7 Hz, 2H), 6.40 – 6.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 137.0, 134.6, 131.3, 129.4, 128.0, 108.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_9N_2O_2S$ 209.0379; Found: 209.0375.

4-Methyl-1-(phenylsulfonyl)-1*H*-pyrazole (4)



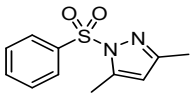
The compound was prepared according to the General procedure. White solid; mp 81.8-82.4 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 31.5 mg, yield 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dt, J = 7.3, 1.3 Hz, 2H), 7.84 – 7.79 (m, 1H), 7.58 (dt, J = 6.8, 1.6 Hz, 1H), 7.53 – 7.45 (m, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 137.3, 134.4, 129.3, 129.1, 127.8, 119.9, 8.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2O_2S$ 223.0536; Found: 223.0530.

3-Methyl-1-(phenylsulfonyl)-1*H*-pyrazole (5)



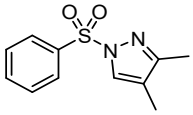
The compound was prepared according to the General procedure. White solid; mp 90.2-91.5 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 29.3 mg, yield 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.68 (m, 3H), 7.54 – 7.47 (m, 1H), 7.39 (t, J = 7.7 Hz, 2H), 6.08 (d, J = 2.7 Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 137.3, 134.2, 132.0, 129.2, 127.7, 109.7, 13.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2O_2S$ 223.0536; Found: 223.0534.

3,5-Dimethyl-1-(phenylsulfonyl)-1*H*-pyrazole (6)



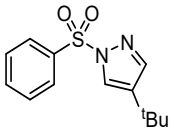
The compound was prepared according to the General procedure. White solid; mp 72.6-74.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 25.0 mg, yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.3, 1.4 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H), 5.89 (s, 1H), 2.48 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 144.2, 138.3, 134.0, 129.3, 127.5, 110.9, 13.8, 13.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}N_2O_2S$ 237.0692; Found: 237.0691.

3,4-Dimethyl-1-(phenylsulfonyl)-1*H*-pyrazole (7)



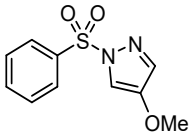
The compound was prepared according to the General procedure. White solid; mp 84.2-86.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 26.0 mg, yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.9 Hz, 2H), 7.72 (s, 1H), 7.59 – 7.53 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H), 2.12 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 137.6, 134.0, 129.6, 129.2, 127.7, 119.3, 12.1, 8.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}N_2O_2S$ 237.0692; Found: 237.0693.

4-(tert-Butyl)-1-(phenylsulfonyl)-1*H*-pyrazole (8)



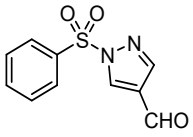
The compound was prepared according to the General procedure. White solid; mp 59.1-60.3 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 33.3 mg, yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.82 (d, J = 8.7 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.54 – 7.47 (m, 2H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 137.2, 136.1, 134.3, 129.2, 127.8, 126.2, 31.0(1), 30.9 (5). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2O_2S$ 265.1005; Found: 265.1004.

4-Methoxy-1-(phenylsulfonyl)-1*H*-pyrazole (9)



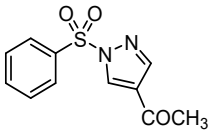
The compound was prepared according to the General procedure. White solid; mp 57.2-59.3 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 30.0 mg, yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.84 (m, 2H), 7.60 (d, J = 15.1 Hz, 2H), 7.49 (q, J = 6.0, 4.4 Hz, 3H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 137.0, 136.7, 134.4, 129.3, 127.8, 112.8, 58.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2O_3S$ 239.0485; Found: 239.0490.

1-(Phenylsulfonyl)-1*H*-pyrazole-4-carbaldehyde (10)



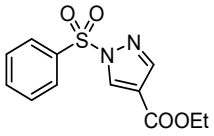
The compound was prepared according to the General procedure. White solid; mp 98.8-101.5 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 27.4 mg, yield 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.62 (d, 1H), 8.15 – 7.97 (m, 3H), 7.74 – 7.68 (m, 1H), 7.61 – 7.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.3, 143.7, 135.8, 135.4, 134.8, 129.7, 128.6, 125.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_9N_2O_3S$ 237.0328; Found: 237.0326.

1-(1-(Phenylsulfonyl)-1*H*-pyrazol-4-yl)ethan-1-one (11)



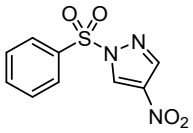
The compound was prepared according to the General procedure. White solid; mp 85.2-86.5 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 33.5 mg, yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 11.2 Hz, 1H), 8.03 (dt, J = 11.5, 4.1 Hz, 3H), 7.72 – 7.64 (m, 1H), 7.61 – 7.51 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 173.8, 165.3, 144.3, 135.3, 133.1, 129.7, 128.5, 28.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{11}N_2O_3S$ 251.0485; Found: 251.0489.

Ethyl 1-(phenylsulfonyl)-1*H*-pyrazole-4-carboxylate (12)



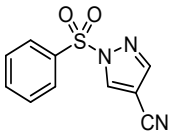
The compound was prepared according to the General procedure. White solid; mp 107.8-109.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 24.1 mg, yield 43%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.06 – 8.02 (m, 3H), 7.73 – 7.61 (m, 1H), 7.56 (t, J = 7.8 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 145.3, 136.2, 135.2, 134.1, 129.7, 128.5, 117.8, 61.1, 14.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{13}N_2O_4S$ 281.0591; Found: 281.0596.

4-Nitro-1-(phenylsulfonyl)-1*H*-pyrazole (13)



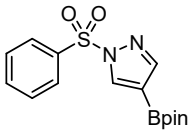
The compound was prepared according to the General procedure. White solid; mp 106.8-107.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 23.8 mg, yield 47%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.22 (s, 1H), 8.12 (d, J = 7.9 Hz, 2H), 7.79 (t, J = 7.5 Hz, 1H), 7.65 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 136.7, 136.0, 135.1, 130.0, 129.6, 128.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8N_3O_4S$ 254.0230; Found: 254.0234.

1-(Phenylsulfonyl)-1*H*-pyrazole-4-carbonitrile (14)



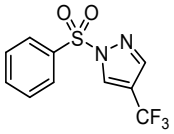
The compound was prepared according to the General procedure. White solid; mp 101.6-103.4 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 25.6 mg, yield 55%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 16.0 Hz, 1H), 8.11 – 8.01 (m, 2H), 7.93 (d, J = 15.8 Hz, 1H), 7.73 (q, J = 8.1, 7.4 Hz, 1H), 7.60 (q, J = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 136.1, 135.8, 135.3, 129.8, 128.7, 111.4, 95.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_8N_3O_2S$ 234.0332; Found: 234.0329.

1-(Phenylsulfonyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (15)



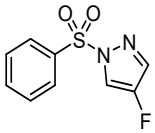
The compound was prepared according to the General procedure. White solid; mp 130.1-132.0 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 17.4 mg, yield 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.03 – 7.96 (m, 2H), 7.90 (s, 1H), 7.64 – 7.60 (m, 1H), 7.51 (t, J = 7.8 Hz, 2H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 138.0, 137.0, 134.6, 129.4, 128.2, 84.0, 24.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{20}BN_2O_4S$ 335.1231; Found: 335.1235.

1-(Phenylsulfonyl)-4-(trifluoromethyl)-1*H*-pyrazole (16)



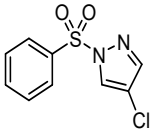
The compound was prepared according to the General procedure. Yellow liquid; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 27.1 mg, yield 49%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.09 – 8.04 (m, 2H), 7.87 (s, 1H), 7.73 – 7.69 (m, 1H), 7.59 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5 ($J_{C\text{-}F}$ = 3.0 HZ), 135.9, 135.4,130.4 ($J_{C\text{-}F}$ = 4.0 HZ), 129.7, 128.6, 127.6, 119.8 ($J_{C\text{-}F}$ = 268.7 HZ).^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_8F_3N_2O_2S$ 277.0253; Found: 277.0256.

4-Fluoro-1-(phenylsulfonyl)-1*H*-pyrazole (17)



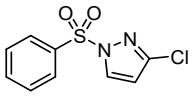
The compound was prepared according to the General procedure. White solid; mp 86.8-87.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 23.1 mg, yield 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 3H), 7.66 (t, J = 7.5 Hz, 1H), 7.62 (d, J = 4.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3($J_{C\text{-}F}$ = 258.6 HZ), 136.5, 134.8, 134.6($J_{C\text{-}F}$ = 17.2 HZ), 129.5, 128.1, 116.4($J_{C\text{-}F}$ = 28.3 HZ). ^{19}F NMR (376 MHz, $CDCl_3$) δ -171.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8FN_2O_2S$ 227.0285; Found: 227.0286.

4-Chloro-1-(phenylsulfonyl)-1*H*-pyrazole (18)



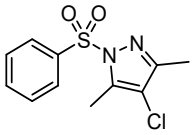
The compound was prepared according to the General procedure. White solid; mp 77.2-78.4 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 23.1 mg, yield 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.99 (dd, J = 8.4, 1.3 Hz, 2H), 7.70 – 7.58 (m, 2H), 7.53 (t, J = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 136.4, 135.0, 129.6, 128.4, 128.3, 114.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8ClN_2O_2S$ 242.9990; Found: 242.9988.

3-Chloro-1-(phenylsulfonyl)-1*H*-pyrazole (19)



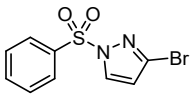
The compound was prepared according to the General procedure. White solid; mp 82.5-83.4 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 25.2 mg, yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 3H), 7.70 – 7.65 (m, 1H), 7.56 (t, J = 7.9 Hz, 2H), 6.33 (d, J = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 136.4, 134.9, 133.0, 129.5, 128.3, 109.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8ClN_2O_2S$ 242.9990; Found: 242.9988.

4-Chloro-3,5-dimethyl-1-(phenylsulfonyl)-1*H*-pyrazole (20)



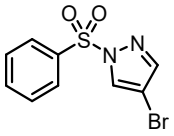
The compound was prepared according to the General procedure. White solid; mp 106.8-108.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 30.2 mg, yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.81 (m, 2H), 7.68 – 7.59 (m, 1H), 7.52 (dd, J = 8.5, 7.2 Hz, 2H), 2.48 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 139.4, 137.7, 134.4, 129.4, 127.7, 113.9, 11.8, 11.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}ClN_2O_2S$ 271.0303; Found: 271.0297.

3-Bromo-1-(phenylsulfonyl)-1*H*-pyrazole (21)



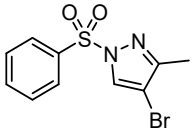
The compound was prepared according to the General procedure. White solid; mp 91.5-92.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 24.0 mg, yield 42%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dt, J = 10.2, 2.0 Hz, 3H), 7.69 – 7.64 (m, 1H), 7.55 (t, J = 7.8 Hz, 2H), 6.40 (d, J = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 135.0, 133.2, 132.9, 129.6, 128.3, 112.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8BrN_2O_2S$ 286.9484; Found: 286.9483.

4-Bromo-1-(phenylsulfonyl)-1*H*-pyrazole (22)



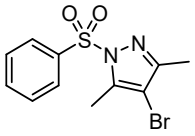
The compound was prepared according to the General procedure. White solid; mp 63.8-64.6 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 26.9 mg, yield 47%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 5.8 Hz, 1H), 8.04 (t, J = 6.6 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.58 (q, J = 7.5, 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 136.4, 135.0, 130.6, 129.6, 128.3, 97.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8BrN_2O_2S$ 286.9484; Found: 286.9481.

4-Bromo-3-methyl-1-(phenylsulfonyl)-1*H*-pyrazole (23)



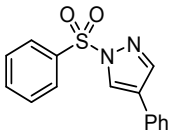
The compound was prepared according to the General procedure. White solid; mp 74.3-75.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 27.6 mg, yield 46%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.96 (d, J = 7.8 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 2.19 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 136.4, 135.0, 130.6, 129.6, 128.3, 97.7, 12.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{10}BrN_2O_2S$ 300.9641; Found: 300.9633.

4-Bromo-3,5-dimethyl-1-(phenylsulfonyl)-1*H*-pyrazole (24)



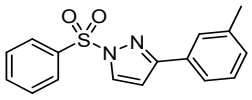
The compound was prepared according to the General procedure. White solid; mp 103.8-105.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 32.0 mg, yield 51%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.86 (m, 2H), 7.66 – 7.60 (m, 1H), 7.52 (t, J = 7.7 Hz, 2H), 2.50 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 141.2, 137.7, 134.4, 129.4, 127.7, 101.1, 12.8, 12.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}BrN_2O_2S$ 314.9797; Found: 314.9797.

4-Phenyl-1-(phenylsulfonyl)-1*H*-pyrazole (25)



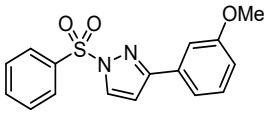
The compound was prepared according to the General procedure. White solid; mp 67.3-68.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 35.2 mg, yield 62%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.10 – 8.01 (m, 3H), 7.68 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.7 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.0, 134.7, 130.2, 129.5, 129.1, 128.2, 128.0, 127.0, 126.1, 126.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O_2S$ 285.0692; Found: 285.0689.

1-(Phenylsulfonyl)-3-(m-tolyl)-1*H*-pyrazole (26)



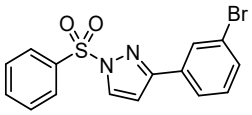
The compound was prepared according to the General procedure. White solid; mp 89.5-90.7 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 34.0 mg, yield 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.08 (d, J = 7.9 Hz, 2H), 7.69 – 7.54 (m, 5H), 7.31 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 6.73 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 138.4, 137.3, 134.4, 132.7, 131.3, 130.1, 129.4, 128.6, 128.1, 127.1, 106.9, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O_2S$ 299.0849; Found: 299.0851.

3-(3-Methoxyphenyl)-1-(phenylsulfonyl)-1*H*-pyrazole (27)



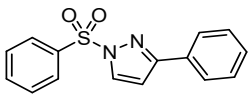
The compound was prepared according to the General procedure. White solid; mp 100.8-102.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 36.4 mg, yield 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 2.9 Hz, 1H), 8.07 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 7.5 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 6.94 (d, J = 8.3 Hz, 2H), 6.67 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 157.0, 137.4, 134.4, 132.7, 129.4, 128.1, 127.9, 124.1, 114.1, 106.5, 55.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O_3S$ 315.0798; Found: 315.0810.

3-(3-Bromophenyl)-1-(phenylsulfonyl)-1*H*-pyrazole (28)



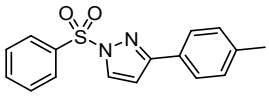
The compound was prepared according to the General procedure. White solid; mp 99.2-100.4 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 42.0 mg, yield 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 2.9 Hz, 1H), 8.08 (d, J = 7.9 Hz, 2H), 7.99 (s, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.49 (d, J = 8.1 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 6.71 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 137.0, 134.7, 133.4, 132.8, 132.2, 130.3, 129.5, 129.3, 128.2, 125.1, 122.9, 106.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{12}BrN_2O_2S$ 362.9797; Found: 362.9801.

3-Phenyl-1-(phenylsulfonyl)-1*H*-pyrazole (29)



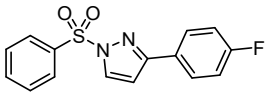
The compound was prepared according to the General procedure. White solid; mp 96.1-97.5 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 34.1 mg, yield 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 2.7 Hz, 1H), 8.05 (dd, J = 8.3, 1.5 Hz, 2H), 7.81 (dt, J = 5.8, 1.6 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.54 – 7.49 (m, 2H), 7.41 – 7.34 (m, 3H), 6.71 (d, J = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 137.2, 134.4, 132.7, 131.3, 129.3(4), 129.2(6), 128.7, 128.1, 126.4, 106.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O_2S$ 285.0692; Found: 285.0688.

1-(Phenylsulfonyl)-3-(p-tolyl)-1*H*-pyrazole (30)



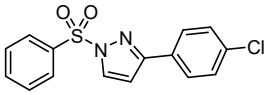
The compound was prepared according to the General procedure. White solid; mp 128.1-130.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 39.9 mg, yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 7.83 (m, 3H), 7.78 – 7.51 (m, 5H), 7.28 – 7.20 (m, 2H), 6.76 – 6.64 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 139.4, 137.3, 134.4, 132.6, 129.3(9), 129.3(5), 128.6, 128.1, 126.4, 106.7, 21.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O_2S$ 299.0849; Found: 299.0845.

3-(4-Fluorophenyl)-1-(phenylsulfonyl)-1*H*-pyrazole (31)



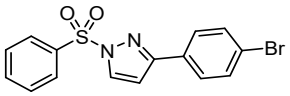
The compound was prepared according to the General procedure. White solid; mp 150.8-151.3 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 26.6 mg, yield 44%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 2.8 Hz, 1H), 8.04 (dd, J = 7.6, 1.7 Hz, 2H), 7.77 (dd, J = 8.6, 5.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.06 (t, J = 8.7 Hz, 2H), 6.65 (d, J = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 ($J_{C\text{-}F}$ = 249.5 HZ), 156.2, 137.2, 134.5, 132.8, 129.4, 128.3 ($J_{C\text{-}F}$ = 8.1 HZ), 128.1, 127.7 ($J_{C\text{-}F}$ = 3.0 HZ), 115.7 ($J_{C\text{-}F}$ = 21.2 HZ), 106.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.9. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{12}FN_2O_2S$ 303.0598; Found: 303.0608.

3-(4-Chlorophenyl)-1-(phenylsulfonyl)-1*H*-pyrazole (32)



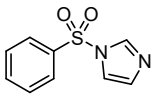
The compound was prepared according to the General procedure. White solid; mp 146.5-147.9 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 29.3 mg, yield 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.04 (d, J = 7.9 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.66 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 137.1, 135.2, 134.6, 132.8, 129.9, 129.5, 128.9, 128.2, 127.7, 106.6. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{12}ClN_2O_2S$ 319.0303; Found: 319.0315.

3-(4-Bromophenyl)-1-(phenylsulfonyl)-1*H*-pyrazole (33)



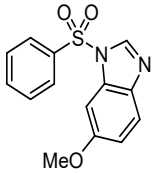
The compound was prepared according to the General procedure. White solid; mp 155.6-157.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 29.7 mg, yield 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.04 (dd, J = 7.7, 1.7 Hz, 2H), 7.68 – 7.62 (m, 3H), 7.56 – 7.50 (m, 4H), 6.67 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 137.1, 134.5, 132.8, 131.8, 130.3, 129.4, 128.1, 127.9, 123.4, 106.4. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{12}BrN_2O_2S$ 362.9797; Found: 362.9800.

1-(Phenylsulfonyl)-1*H*-imidazole (34)



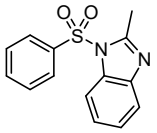
The compound was prepared according to the General procedure. Yellow liquid; R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 29.1 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.93 (d, J = 7.9 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.29 (s, 1H), 7.07 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 136.7, 134.9, 131.5, 129.8, 127.3, 117.5. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_9H_9N_2O_2S$ 209.0379; Found: 209.0379.

6-Methoxy-1-(phenylsulfonyl)-1*H*-benzo[d]imidazole (35)



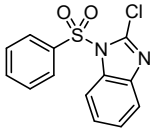
The compound was prepared according to the General procedure. White solid; mp 137.5-139.4 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 42.0 mg, yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.94 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 8.7 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.20 (d, J = 2.6 Hz, 1H), 6.98 (d, J = 8.9 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 145.2, 141.8, 137.6, 134.8, 129.8, 127.1, 125.0, 115.2, 112.9, 103.4, 55.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_3S$ 289.0641; Found: 289.0643.

2-Methyl-1-(phenylsulfonyl)-1*H*-benzo[d]imidazole (36)



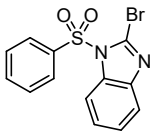
The compound was prepared according to the General procedure. White solid; mp 87.8-89.0 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 40.3 mg, yield 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 1H), 7.90 (d, J = 7.8 Hz, 2H), 7.59 (dd, J = 11.7, 7.1 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.31 (t, J = 6.7 Hz, 2H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 141.9, 138.3, 134.6, 133.1, 129.7, 126.7, 124.8, 124.7, 119.7, 113.4, 17.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_2S$ 273.0692; Found: 273.0690.

2-Chloro-1-(phenylsulfonyl)-1*H*-benzo[d]imidazole (37)



The compound was prepared according to the General procedure. White solid; mp 79.2-81.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 31.0 mg, yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.1 Hz, 1H), 8.01 (dd, J = 8.1, 1.6 Hz, 2H), 7.68 – 7.61 (m, 2H), 7.53 (t, J = 8.0 Hz, 2H), 7.44 – 7.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 138.4, 137.6, 135.2, 133.8, 129.7, 127.5, 125.8, 125.3, 120.0, 113.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{10}ClN_2O_2S$ 293.0146; Found: 293.0149.

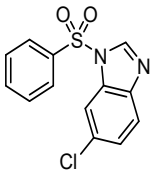
2-Bromo-1-(phenylsulfonyl)-1*H*-benzo[d]imidazole (38)



The compound was prepared according to the General procedure. White solid; mp 79.2-81.5 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 37.0 mg, yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 7.2 Hz, 2H), 7.64 (dt, J = 7.7, 4.2 Hz, 2H), 7.54 – 7.49

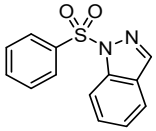
(m, 2H), 7.45 – 7.28 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 137.7, 135.2, 134.3, 129.7, 127.6, 126.0, 125.8, 125.2, 119.9, 114.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{10}BrN_2O_2S$ 336.9641; Found: 336.9640.

6-Chloro-1-(phenylsulfonyl)-1*H*-benzo[d]imidazole (39)



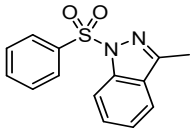
The compound was prepared according to the General procedure. White solid; mp 152.5-153.9 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 28.6 mg, yield 49%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 2.0 Hz, 1H), 7.66 (dd, J = 10.4, 8.1 Hz, 2H), 7.60 – 7.51 (m, 2H), 7.32 (dd, J = 8.6, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 141.8, 137.3, 135.2, 131.7, 131.4, 130.0, 127.2, 125.7, 121.9, 112.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{10}ClN_2O_2S$ 293.0146; Found: 293.0144.

1-(Phenylsulfonyl)-1*H*-indazole (40)



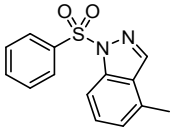
The compound was prepared according to the General procedure. White solid; mp 56.8-58.0 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 36.1 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.11 (m, 2H), 7.98 (d, J = 7.1 Hz, 2H), 7.69 (d, J = 8.4 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.45 (t, J = 7.8 Hz, 2H), 7.33 (t, J = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 140.3, 137.6, 134.2, 129.3, 129.2, 127.5, 125.8, 124.3, 121.4, 113.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{11}N_2O_2S$ 259.0536; Found: 259.0533.

3-Methyl-1-(phenylsulfonyl)-1*H*-indazole (41)



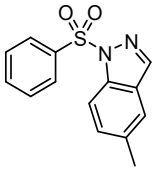
The compound was prepared according to the General procedure. White solid; mp 134.2-136.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 33.7 mg, yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 7.5 Hz, 2H), 7.56 – 7.46 (m, 3H), 7.38 (t, J = 7.8 Hz, 2H), 7.27 (t, J = 7.6 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 141.1, 137.6, 133.9, 129.2, 129.1, 127.4, 126.2, 124.0, 120.6, 113.3, 12.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_2S$ 273.0692; Found: 273.0686.

4-Methyl-1-(phenylsulfonyl)-1*H*-indazole (42)



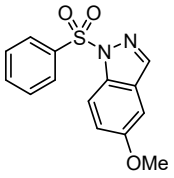
The compound was prepared according to the General procedure. White solid; mp 69.3-71.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 31.6 mg, yield 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 3.1 Hz, 1H), 7.99 (dd, J = 19.8, 8.0 Hz, 3H), 7.52 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 8.2 Hz, 3H), 7.08 (d, J = 7.1 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 138.9, 137.6, 134.2, 134.1, 131.2, 129.2, 127.5, 126.4, 120.7, 112.8, 21.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_2S$ 273.0692; Found: 273.0686.

5-Methyl-1-(phenylsulfonyl)-1*H*-indazole (43)



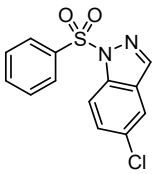
The compound was prepared according to the General procedure. White solid; mp 72.6-73.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 36.4 mg, yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (q, J = 6.3, 5.5 Hz, 2H), 7.99 – 7.92 (m, 2H), 7.55 – 7.50 (m, 1H), 7.45 – 7.35 (m, 4H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 140.3, 137.6, 134.2, 132.1, 129.5, 129.2, 127.5, 126.1, 124.6, 110.5, 18.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_2S$ 273.0692; Found: 273.0685.

5-Methoxy-1-(phenylsulfonyl)-1*H*-indazole (44)



The compound was prepared according to the General procedure. White solid; mp 66.8-68.6 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 42.6 mg, yield 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 10.2 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.39 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 6.8 Hz, 1H), 6.99 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 141.4, 137.4, 135.7, 134.2, 129.2, 127.4, 126.9, 120.4, 114.1, 101.4, 55.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_3S$ 289.0641; Found: 289.0637.

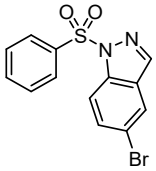
5-Chloro-1-(phenylsulfonyl)-1*H*-indazole (45)



The compound was prepared according to the General procedure. White solid; mp 68.9-70.6

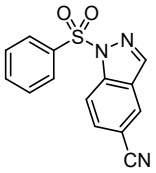
°C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 38.5 mg, yield 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 11.7 Hz, 2H), 7.99 (d, J = 7.9 Hz, 2H), 7.68 (s, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.51 (dt, J = 15.7, 8.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 138.8, 137.2, 134.5, 130.2, 129.9, 129.4, 127.6, 126.9, 120.8, 114.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{10}ClN_2O_2S$ 293.0146; Found: 293.0142.

5-Bromo-1-(phenylsulfonyl)-1*H*-indazole (46)



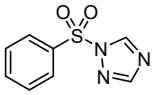
The compound was prepared according to the General procedure. White solid; mp 83.3-84.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 45.0 mg, yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 2H), 7.99 – 7.93 (m, 2H), 7.84 – 7.79 (m, 1H), 7.66 – 7.54 (m, 2H), 7.46 (q, J = 9.2, 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 139.1, 137.2, 134.5, 132.4, 129.3, 127.5, 127.4, 123.9, 117.6, 114.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{10}BrN_2O_2S$ 336.9641; Found: 336.9639.

1-(Phenylsulfonyl)-1*H*-indazole-5-carbonitrile (47)



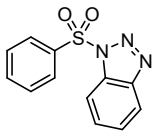
The compound was prepared according to the General procedure. White solid; mp 153.7-155.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 36.8 mg, yield 65%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.8 Hz, 1H), 8.25 (s, 1H), 8.06 (s, 1H), 7.98 (d, J = 7.9 Hz, 2H), 7.75 (d, J = 8.8 Hz, 1H), 7.59 (t, J = 5.9 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 140.8, 136.9, 134.9, 131.6, 129.5, 127.7, 127.2, 125.4, 118.4, 114.3, 108.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{10}N_3O_2S$ 284.0488; Found: 284.0492.

1-(Phenylsulfonyl)-1*H*-1,2,4-triazole (48)



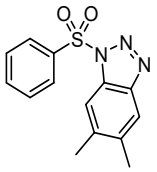
The compound was prepared according to the General procedure. White solid; mp 100.8-102.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 29.4 mg, yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.09 – 7.97 (m, 3H), 7.71 (d, J = 7.3 Hz, 1H), 7.62 – 7.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 144.7, 135.7, 135.6, 129.8, 128.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_8H_8N_3O_2S$ 210.0332; Found: 210.0332.

1-(Phenylsulfonyl)-1*H*-benzo[d][1,2,3]triazole (49)



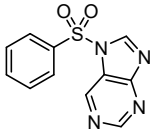
The compound was prepared according to the General procedure. White solid; mp 117.0-118.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 33.2 mg, yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.01 (m, 4H), 7.66 – 7.59 (m, 2H), 7.53 – 7.43 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 136.9, 135.3, 131.6, 130.4, 129.7, 127.9, 125.9, 120.9, 112.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{10}N_3O_2S$ 260.0488; Found: 260.0497.

5,6-Dimethyl-1-(phenylsulfonyl)-1*H*-benzo[d][1,2,3]triazole (50)



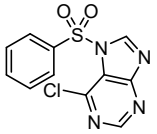
The compound was prepared according to the General procedure. White solid; mp 124.5-126.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 33.2 mg, yield 64%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.49 – 7.43 (m, 2H), 2.39 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 141.2, 137.1, 135.9, 135.0, 130.5, 129.6, 127.7, 119.6, 111.4, 21.1, 20.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}N_3O_2S$ 288.0807; Found: 288.0808.

7-(Phenylsulfonyl)-7*H*-purine (51)



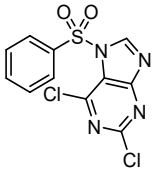
The compound was prepared according to the General procedure. White solid; mp 146.3-147.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 36.9 mg, yield 71%.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 9.19 (s, 1H), 8.65 (s, 1H), 8.02 (d, *J* = 6.7 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 155.3, 146.1, 142.3, 136.6, 135.9, 130.4, 127.5, 122.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_9N_4O_2S$ 261.0441; Found: 261.0437.

6-Chloro-7-(phenylsulfonyl)-7*H*-purine (52)



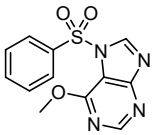
The compound was prepared according to the General procedure. White solid; mp 210.1-212.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 32.9 mg, yield 56%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.55 (s, 1H), 8.26 (d, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 152.3, 150.2, 142.4, 136.2, 135.8, 132.2, 129.8, 128.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_8ClN_4O_2S$ 295.0051; Found: 295.0048.

2,6-Dichloro-7-(phenylsulfonyl)-7*H*-purine (53)



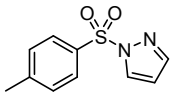
The compound was prepared according to the General procedure. White solid; mp 141.6-142.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 47.9 mg, yield 73%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.26 (d, J = 7.9 Hz, 2H), 7.73 (t, J = 7.5 Hz, 1H), 7.62 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 152.9, 151.2, 142.8, 136.1, 135.8, 131.3, 129.9, 128.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_7Cl_2N_4O_2S$ 328.9661; Found: 328.9663.

6-Methoxy-7-(phenylsulfonyl)-7*H*-purine (54)



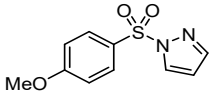
The compound was prepared according to the General procedure. White solid; mp 140.4-142.3 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 40.1 mg, yield 69%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.36 (s, 1H), 8.25 (dd, J = 8.5, 1.3 Hz, 2H), 7.66 (tt, J = 6.9, 1.3 Hz, 1H), 7.58 – 7.52 (m, 2H), 4.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 154.1, 150.6, 139.7, 136.8, 135.4, 129.6, 128.6, 122.1, 54.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{11}N_4O_3S$ 291.0546; Found: 291.0546.

1-Tosyl-1*H*-pyrazole (55)



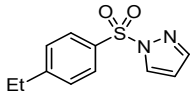
The compound was prepared according to the General procedure. White solid; mp 130.2-131.6 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 35.5 mg, yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 2.7 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.67 (s, 1H), 7.28 (d, J = 8.1 Hz, 2H), 6.37 – 6.32 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 145.3, 134.0, 131.2, 130.1, 128.2, 108.8, 21.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2O_2S$ 223.0536; Found: 223.0532.

1-((4-Methoxyphenyl)sulfonyl)-1*H*-pyrazole (56)



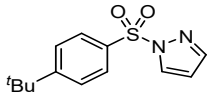
The compound was prepared according to the General procedure. White solid; mp 101.2-102.6 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 33.8 mg, yield 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 2.8 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.68 (d, J = 1.6 Hz, 1H), 6.97 – 6.92 (m, 2H), 6.38 – 6.31 (m, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 145.1, 131.0, 130.6, 128.2, 114.7, 108.6, 55.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2O_3S$ 239.0485; Found: 239.0480.

1-((4-Ethylphenyl)sulfonyl)-1*H*-pyrazole (57)



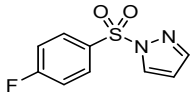
The compound was prepared according to the General procedure. White solid; mp 57.8-59.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 32.6 mg, yield 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 2.8 Hz, 1H), 7.93 (d, J = 8.1 Hz, 2H), 7.73 (s, 1H), 7.36 (d, J = 8.1 Hz, 2H), 6.40 (d, J = 2.2 Hz, 1H), 2.71 (q, J = 7.7 Hz, 2H), 1.23 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 145.2, 134.2, 131.2, 129.0, 128.3, 108.8, 28.9, 14.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}N_2O_2S$ 237.0692; Found: 237.0685.

1-((4-(tert-Butyl)phenyl)sulfonyl)-1*H*-pyrazole (58)



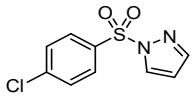
The compound was prepared according to the General procedure. White solid; mp 98.1-100.0 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 33.8 mg, yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.95 – 7.86 (m, 2H), 7.70 (s, 1H), 7.51 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 2.5 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 145.2, 134.0, 131.2, 128.0, 126.5, 108.7, 35.4, 30.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2O_2S$ 265.1005; Found: 265.1007.

1-((4-Fluorophenyl)sulfonyl)-1*H*-pyrazole (59)



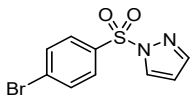
The compound was prepared according to the General procedure. White solid; mp 80.8-81.9 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 28.5 mg, yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.03 (m, 3H), 7.76 (s, 1H), 7.23 (t, J = 8.4 Hz, 2H), 6.43 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 ($J_{C\text{-}F}$ = 208.1 HZ), 145.6, 133.0 ($J_{C\text{-}F}$ = 2.0 HZ), 131.2, 131.1, 116.9 ($J_{C\text{-}F}$ = 19.2 HZ), 109.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8FN_2O_2S$ 227.0285; Found: 227.0280.

1-((4-Chlorophenyl)sulfonyl)-1*H*-pyrazole (60)



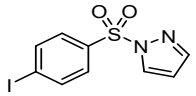
The compound was prepared according to the General procedure. White solid; mp 98.3-99.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 21.8 mg, yield 45%.^{1}H NMR (400 MHz, DMSO-d_6) δ 8.46 (s, 1H), 8.06 – 7.84 (m, 3H), 7.72 (d, J = 8.3 Hz, 2H), 6.59 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.7, 140.7, 135.6, 133.1, 130.6, 130.0, 110.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8ClN_2O_2S$ 242.9990; Found: 242.9987.

1-((4-Bromophenyl)sulfonyl)-1*H*-pyrazole (61)



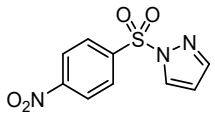
The compound was prepared according to the General procedure. White solid; mp 152.3-153.4 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 41.8 mg, yield 73%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.89 (d, J = 8.6 Hz, 2H), 7.76 (s, 1H), 7.69 (d, J = 8.7 Hz, 2H), 6.44 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 136.0, 132.8, 131.3, 130.2, 129.6, 109.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8BrN_2O_2S$ 286.9484; Found: 286.9484.

1-((4-Iodophenyl)sulfonyl)-1*H*-pyrazole (62)



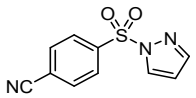
The compound was prepared according to the General procedure. White solid; mp 156.4-158.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 44.1 mg, yield 66%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 2.6 Hz, 1H), 7.92 – 7.84 (m, 2H), 7.70 (dd, J = 9.5, 7.7 Hz, 3H), 6.39 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 138.7, 131.2, 129.2, 128.1, 109.1, 102.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8IN_2O_2S$ 334.9346; Found: 334.9346.

1-((4-Nitrophenyl)sulfonyl)-1*H*-pyrazole (63)



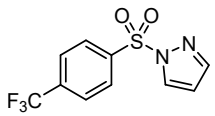
The compound was prepared according to the General procedure. White solid; mp 90.3-92.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 29.9 mg, yield 59%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 – 8.32 (m, 3H), 8.25 – 8.12 (m, 2H), 7.91 (s, 1H), 6.61 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.5, 147.3, 141.7, 133.5, 129.8, 125.6, 110.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_8N_3O_4S$ 254.0230; Found: 254.0235.

4-((1*H*-Pyrazol-1-yl)sulfonyl)benzonitrile (64)



The compound was prepared according to the General procedure. White solid; mp 121.3-122.7 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 30.3 mg, yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 8.5, 5.6 Hz, 3H), 7.86 (d, J = 7.9 Hz, 2H), 7.79 (s, 1H), 6.48 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 141.0, 133.2, 131.6, 128.8, 118.3, 116.9, 109.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_8N_3O_2S$ 234.0332; Found: 234.0326.

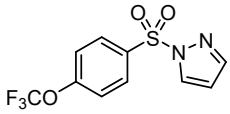
1-((4-(Trifluoromethyl)phenyl)sulfonyl)-1*H*-pyrazole (65)



The compound was prepared according to the General procedure. White solid; mp 74.8-75.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 38.6 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$)

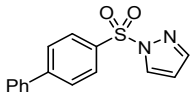
δ 8.16 – 8.09 (m, 3H), 7.78 (d, J = 8.2 Hz, 2H), 7.74 (s, 1H), 6.42 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 140.5, 136.0 ($J_{C\text{-}F}$ = 34.3 HZ), 131.5, 128.7, 126.5 ($J_{C\text{-}F}$ = 4.0 HZ), 121.5 ($J_{C\text{-}F}$ = 274.7 HZ), 109.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_8F_3N_2O_2S$ 277.0253; Found: 277.0256.

1-((4-(Trifluoromethoxy)phenyl)sulfonyl)-1*H*-pyrazole (66)



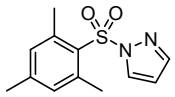
The compound was prepared according to the General procedure. White solid; mp 126.8-127.7 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 36.8 mg, yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.01 (m, 3H), 7.74 (s, 1H), 7.33 (d, J = 8.5 Hz, 2H), 6.41 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 145.8, 135.1, 131.3, 130.5, 118.8, 109.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_8F_3N_2O_3S$ 293.0202; Found: 293.0198.

1-([1,1'-Biphenyl]-4-ylsulfonyl)-1*H*-pyrazole (67)



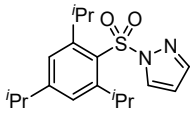
The compound was prepared according to the General procedure. White solid; mp 123.3-124.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 30.1mg, yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 2.8 Hz, 1H), 8.10 (d, J = 8.4 Hz, 2H), 7.82 – 7.72 (m, 3H), 7.59 (d, J = 6.8 Hz, 2H), 7.48 (dt, J = 16.2, 7.3 Hz, 3H), 6.45 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.4, 138.8, 135.4, 131.3, 129.2, 128.9, 128.7, 128.0, 127.4, 108.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O_2S$ 285.0692; Found: 285.0690.

1-(Mesitylsulfonyl)-1*H*-pyrazole (68)



The compound was prepared according to the General procedure. White solid; mp 134.2-136.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 35.0 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 2.8 Hz, 1H), 7.67 (d, J = 1.6 Hz, 1H), 6.96 (s, 2H), 6.40 – 6.32 (m, 1H), 2.61 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.4, 141.3, 132.4, 130.9, 130.7, 107.4, 22.9, 21.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O_2S$ 251.0849; Found: 251.0841.

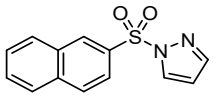
1-((2,4,6-Triisopropylphenyl)sulfonyl)-1*H*-pyrazole (69)



The compound was prepared according to the General procedure. White solid; mp 140.2-141.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 36.7 mg, yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 3.1 Hz, 1H), 7.72 (s, 1H), 7.28 (t, J = 3.2 Hz, 2H), 6.44 (s, 1H), 4.22 (dq, J = 6.8, 2.9 Hz, 2H), 3.13 – 2.84 (m, 1H), 1.59 (d, J = 2.8 Hz, 4H), 1.29 – 1.18 (m, 14H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 152.3, 143.9, 129.8, 124.4, 107.9, 34.3, 29.8, 24.6, 23.5. HRMS (ESI)

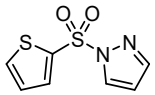
m/z: $[M + H]^+$ Calcd for $C_{18}H_{27}N_2O_2S$ 335.1788; Found: 335.1787.

1-(Naphthalen-2-ylsulfonyl)-1*H*-pyrazole (70)



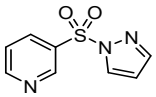
The compound was prepared according to the General procedure. White solid; mp 181.1-182 .8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 23.2 mg, yield 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.21 (d, J = 2.8 Hz, 1H), 8.05 – 7.91 (m, 4H), 7.76 – 7.64 (m, 3H), 6.43 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 135.6, 133.8, 131.9, 131.3, 130.4, 129.9(0), 129.8(3), 129.7, 128.0(3), 127.9(8), 122.3, 108.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{11}N_2O_2S$ 259.0536; Found: 259.0531.

1-(Thiophen-2-ylsulfonyl)-1*H*-pyrazole (71)



The compound was prepared according to the General procedure. White solid; mp >300 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 22.3 mg, yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 3.3 Hz, 1H), 7.87 (t, J = 4.2 Hz, 1H), 7.82 – 7.73 (m, 2H), 7.14 (d, J = 4.4 Hz, 1H), 6.44 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 136.8, 135.6, 131.1, 127.9, 109.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_7H_7N_2O_2S_2$ 214.9943; Found: 214.9939.

3-((1*H*-Pyrazol-1-yl)sulfonyl)pyridine (72)

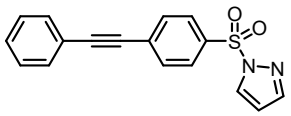


The compound was prepared according to the General procedure. White solid; mp 67.3-68.5 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 22.3 mg, yield 52%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 8.89 (d, J = 4.7 Hz, 1H), 8.50 (d, J = 3.0 Hz, 1H), 8.34 (d, J = 8.2 Hz, 1H), 7.91 (s, 1H), 7.67 (dd, J = 8.3, 4.6 Hz, 1H), 6.61 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.9, 148.2, 147.1, 136.3, 133.3, 125.3, 110.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_8H_8N_3O_2S$ 210.0332; Found: 210.0329.

1-(Methylsulfonyl)-1*H*-pyrazole (73)

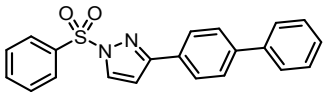
The compound was prepared according to the General procedure. White solid; mp 86.8-87.9 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 17.8 mg, yield 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.78 (s, 1H), 6.42 (s, 1H), 3.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 130.9, 108.6, 41.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_4H_7N_2O_2S$ 147.0223; Found: 147.0227.

1-((4-(Phenylethynyl)phenyl)sulfonyl)-1*H*-pyrazole (77)



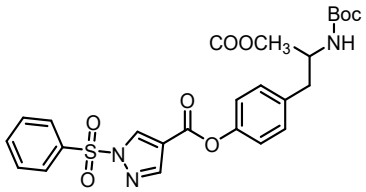
The compound was prepared according to the General procedure. White solid; mp 116.8-117.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 46.2 mg, yield 75%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 2.7 Hz, 1H), 7.96 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 1.6 Hz, 1H), 7.62 (d, J = 8.2 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.35 (dt, J = 5.2, 2.6 Hz, 3H), 6.39 (dd, J = 2.8, 1.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 135.8, 132.2, 131.8, 131.3, 130.1, 129.2, 128.5, 128.1, 122.0, 109.1, 94.3, 87.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_2S$ 309.0692; Found: 309.0691.

4-([1,1'-Biphenyl]-4-yl)-1-(phenylsulfonyl)-1*H*-pyrazole (78)



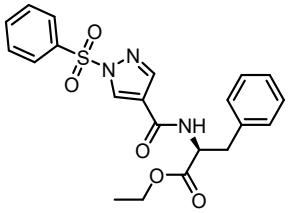
The compound was prepared according to the General procedure. White solid; mp 126.1-127.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 49.0 mg, yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 3H), 7.70 – 7.58 (m, 7H), 7.45 (t, J = 7.5 Hz, 3H), 7.36 (t, J = 7.3 Hz, 2H), 6.67 (d, J = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 140.9, 140.6, 133.3, 130.9, 128.9, 127.5(4), 127.4(8), 127.0, 126.2, 102.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{17}N_2O_2S$ 361.1005; Found: 361.1003.

4-(2-((tert-Butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl 1-(phenylsulfonyl)-1*H*-pyrazole-4-carboxylate (79)



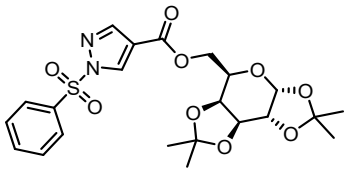
The compound was prepared according to the General procedure. White solid; mp 206.8-207.3 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 32.8 mg, yield 31%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.16 (s, 1H), 8.08 (d, J = 7.9 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.8 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 4.98 (d, J = 8.3 Hz, 1H), 4.57 (s, 1H), 3.70 (s, 3H), 3.24 – 2.93 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 159.9, 155.1, 149.1, 145.5, 136.0, 135.4, 134.8, 134.2, 130.5, 129.8, 128.6, 121.6, 116.9, 54.4, 52.4, 37.8, 29.7, 28.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{28}N_3O_8S$ 530.1592; Found: 530.1595.

Ethyl (1-(phenylsulfonyl)-1*H*-pyrazole-4-carbonyl)-L-phenylalaninate (80)



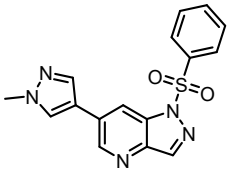
The compound was prepared according to the General procedure. White solid; mp 210.1-211.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 44.4 mg, yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 0.7 Hz, 1H), 8.08 – 7.99 (m, 2H), 7.87 (d, J = 0.7 Hz, 1H), 7.80 – 7.65 (m, 1H), 7.57 (dd, J = 8.5, 7.2 Hz, 2H), 7.40 – 7.20 (m, 4H), 7.19 – 7.12 (m, 2H), 6.76 (d, J = 7.8 Hz, 1H), 5.00 (dt, J = 7.8, 6.1 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.18 (qd, J = 13.8, 6.2 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 160.5, 143.6, 136.1, 135.8, 135.2, 131.9, 129.6, 129.3, 128.7, 128.5, 127.3, 120.3, 61.9, 53.4, 37.9, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{22}N_3O_5S$ 428.1275; Found: 428.1269.

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 1-(phenylsulfonyl)-1*H*-pyrazole-4-carboxylate (81)



The compound was prepared according to the General procedure. White solid; mp 226.5-227.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 52.4 mg, yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.03 (d, J = 6.9 Hz, 3H), 7.67 (d, J = 7.4 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 5.53 (dd, J = 14.5, 4.9 Hz, 1H), 4.61 (d, J = 8.6 Hz, 1H), 4.33 (d, J = 13.9 Hz, 3H), 4.09 (s, 1H), 3.85 (s, 1H), 1.57 (s, 3H), 1.47 (d, J = 14.7 Hz, 3H), 1.43 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 145.4, 136.1, 135.3, 134.3, 129.7, 128.6, 117.3, 109.8, 108.9, 96.3, 71.0, 70.7, 70.4, 66.0, 64.0, 26.0(3), 25.9(7), 25.0, 24.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{27}N_2O_9S$ 495.1432; Found: 495.1430.

6-(1-Methyl-1*H*-pyrazol-4-yl)-1-(phenylsulfonyl)-1*H*-pyrazolo[4,3-b]pyridine (82)



The compound was prepared according to the General procedure. White solid; mp 112.1-113.5 °C. R_f = 0.5 (petroleum ether/ethyl acetate 4:1); 31.9 mg, yield 47%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.47 (s, 1H), 8.35 (s, 1H), 7.99 (dd, J = 8.5, 1.3 Hz, 2H), 7.91 (s, 1H), 7.83 (s, 1H), 7.59 (t, 1H), 7.48 (t, J = 7.8 Hz, 2H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 142.0, 141.5, 137.3, 134.6, 129.4, 128.9, 128.0, 127.7, 123.0, 120.2, 119.6, 116.0, 39.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{14}N_5O_2S$ 340.0863; Found: 340.0862.

14. References

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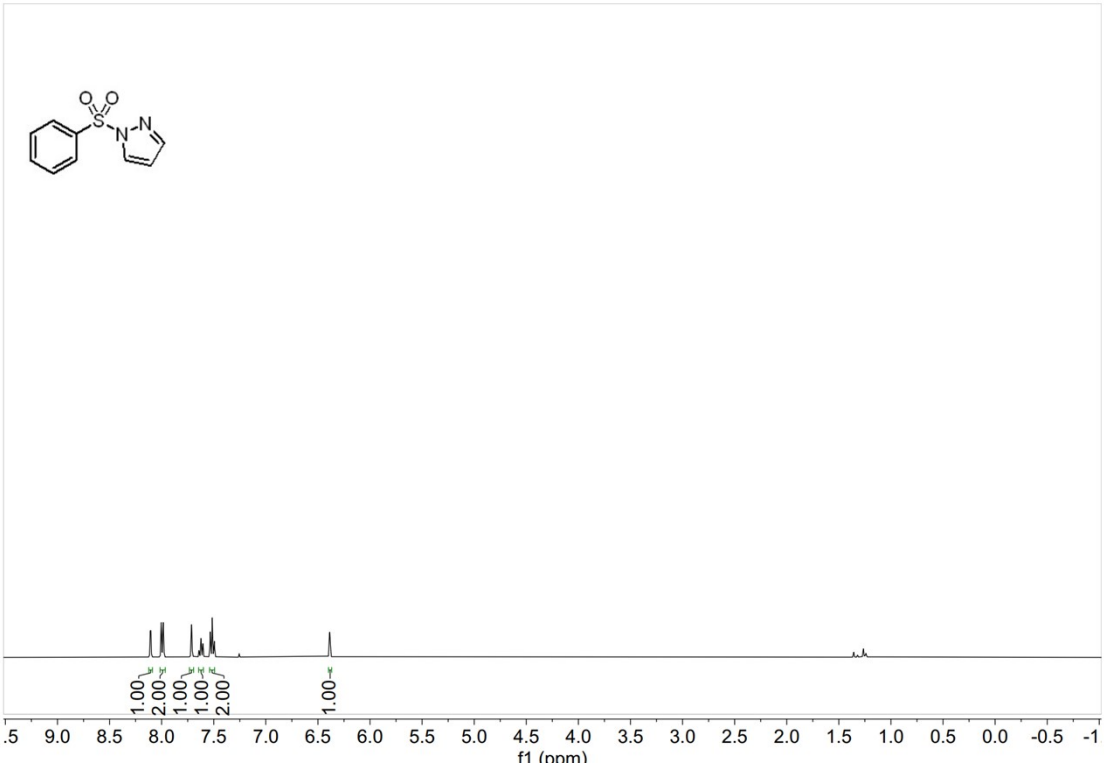
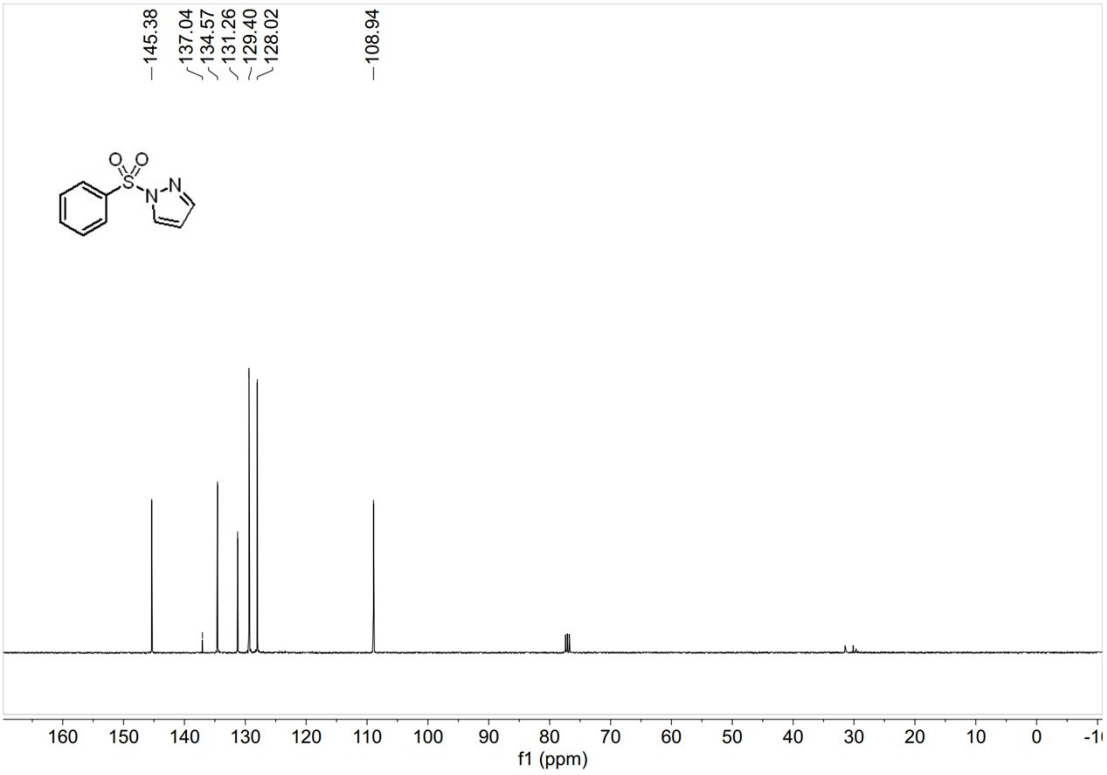
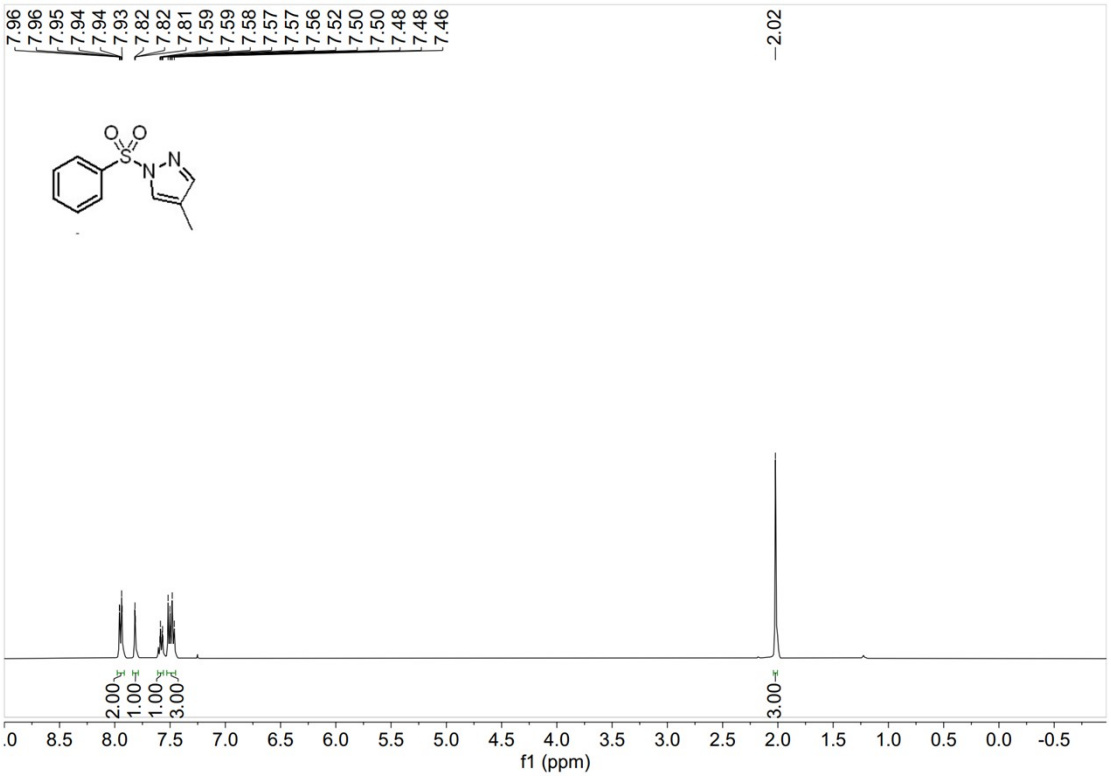
15. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR



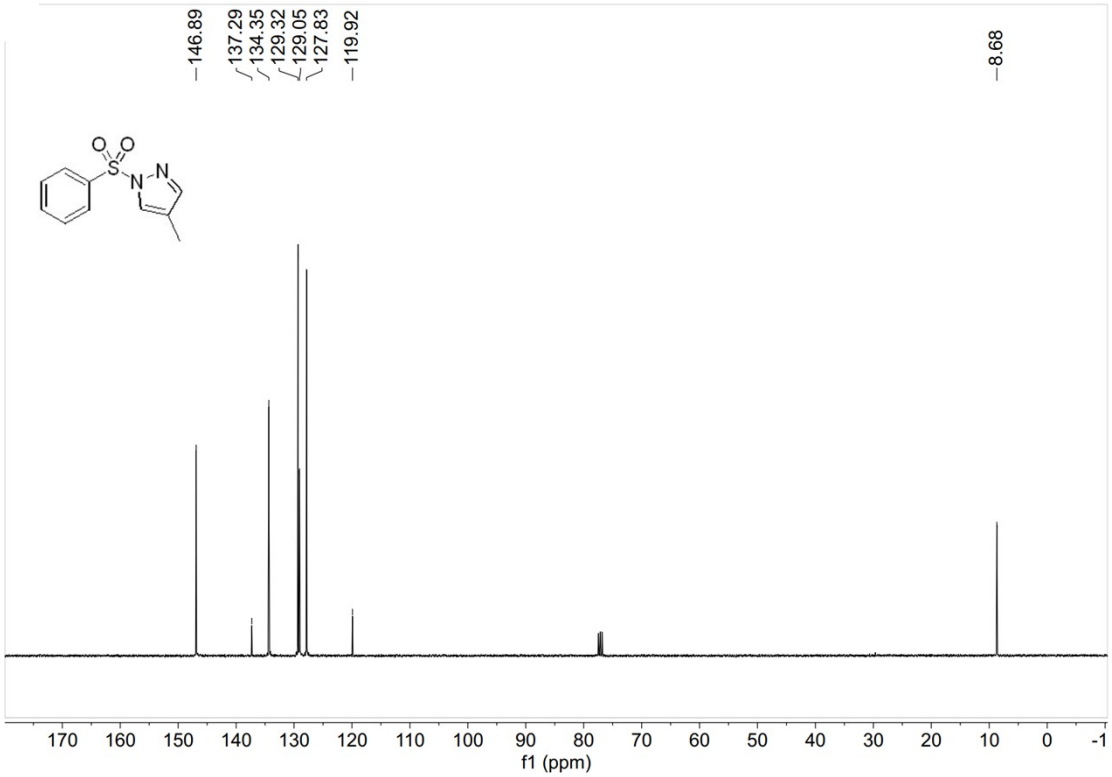
^{1}H NMR (400 MHz, $CDCl_3$) of **3**



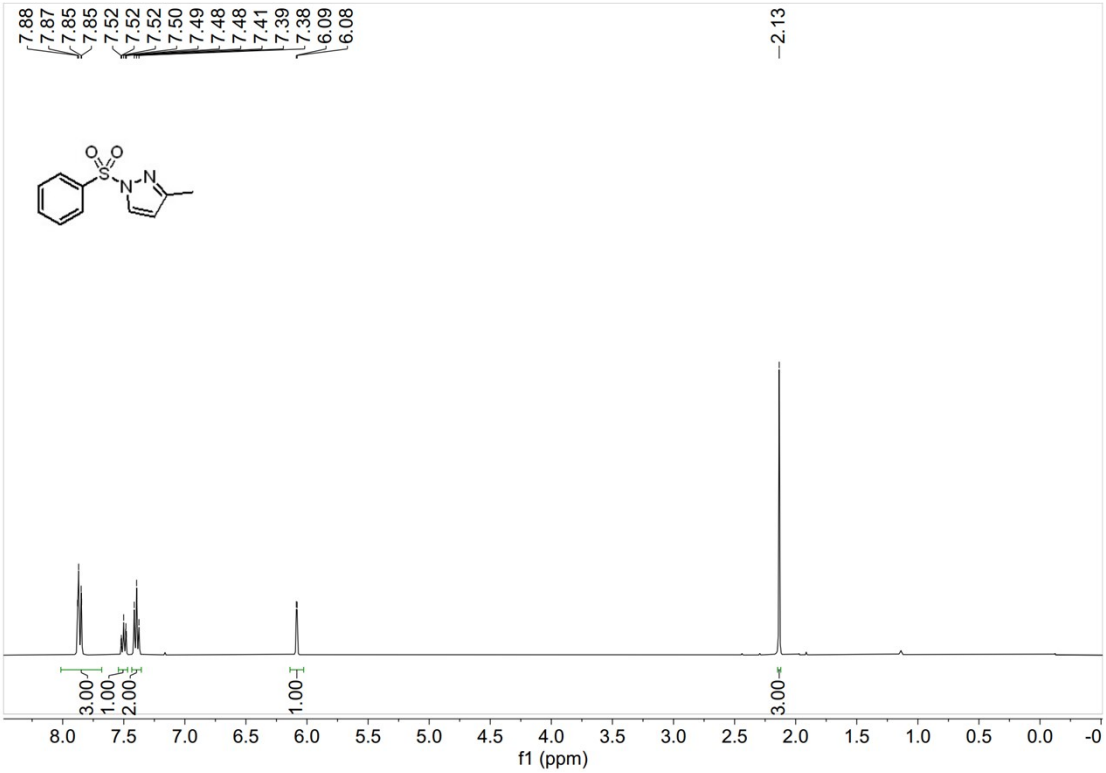
^{13}C NMR (101 MHz, $CDCl_3$) of **3**



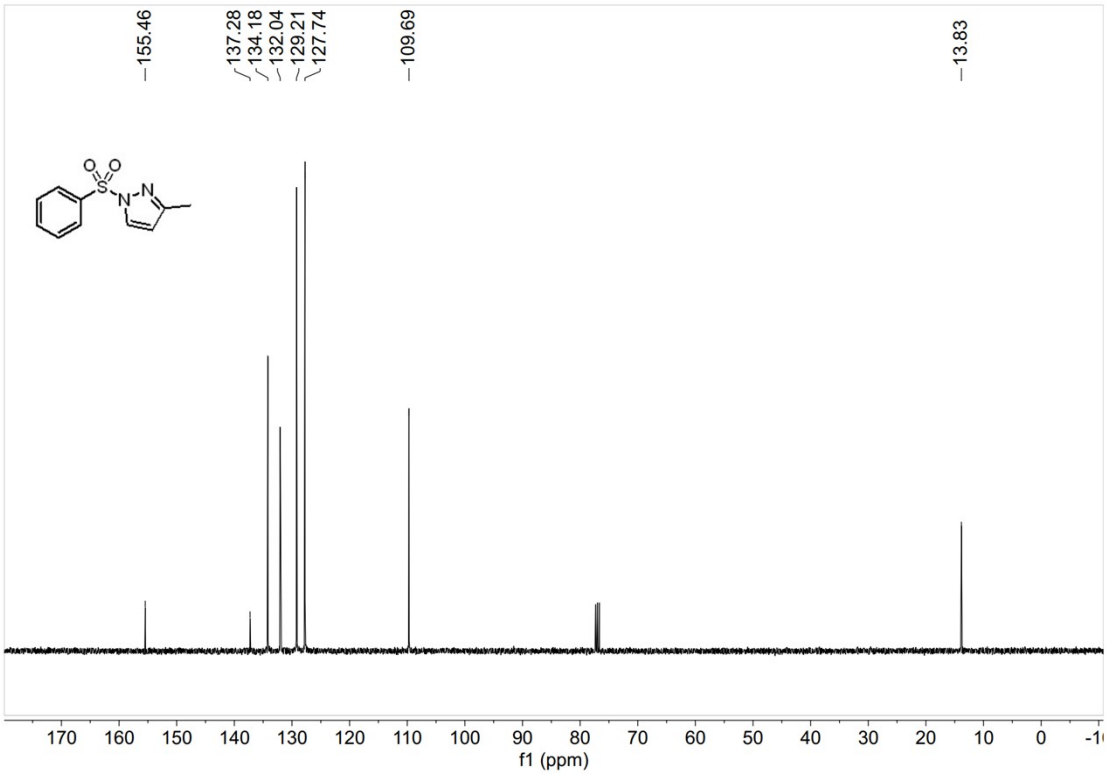
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



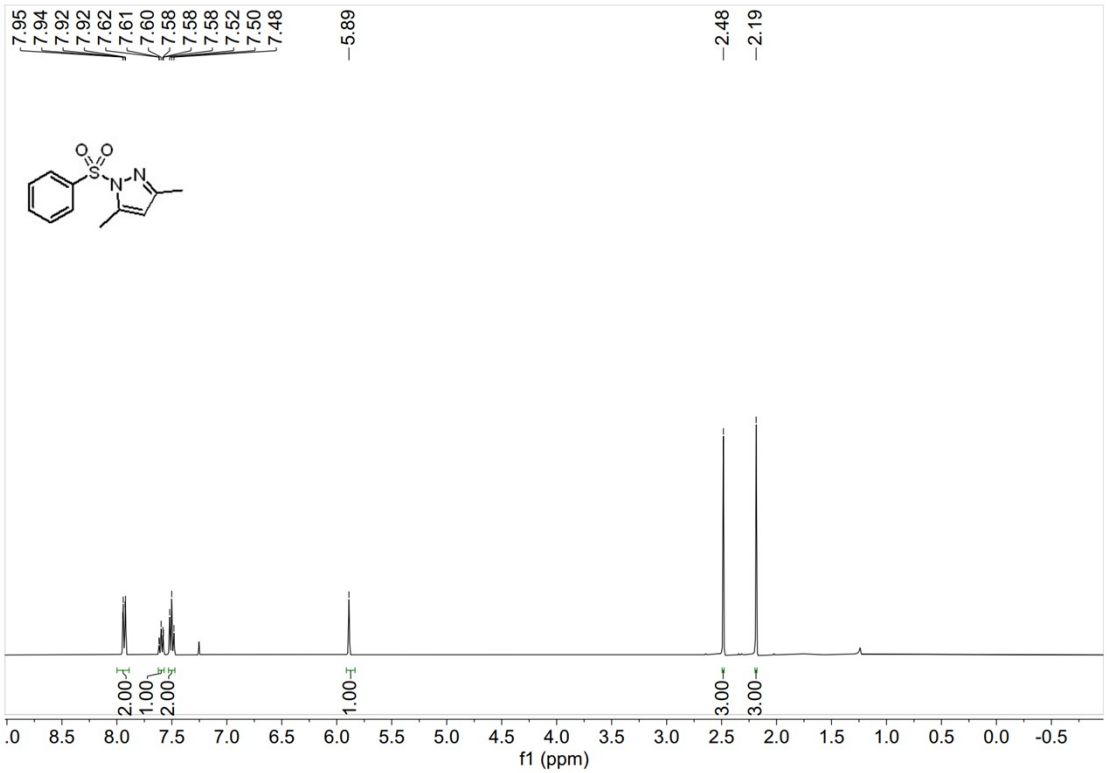
^{13}C NMR (101 MHz, $CDCl_3$) of **4**



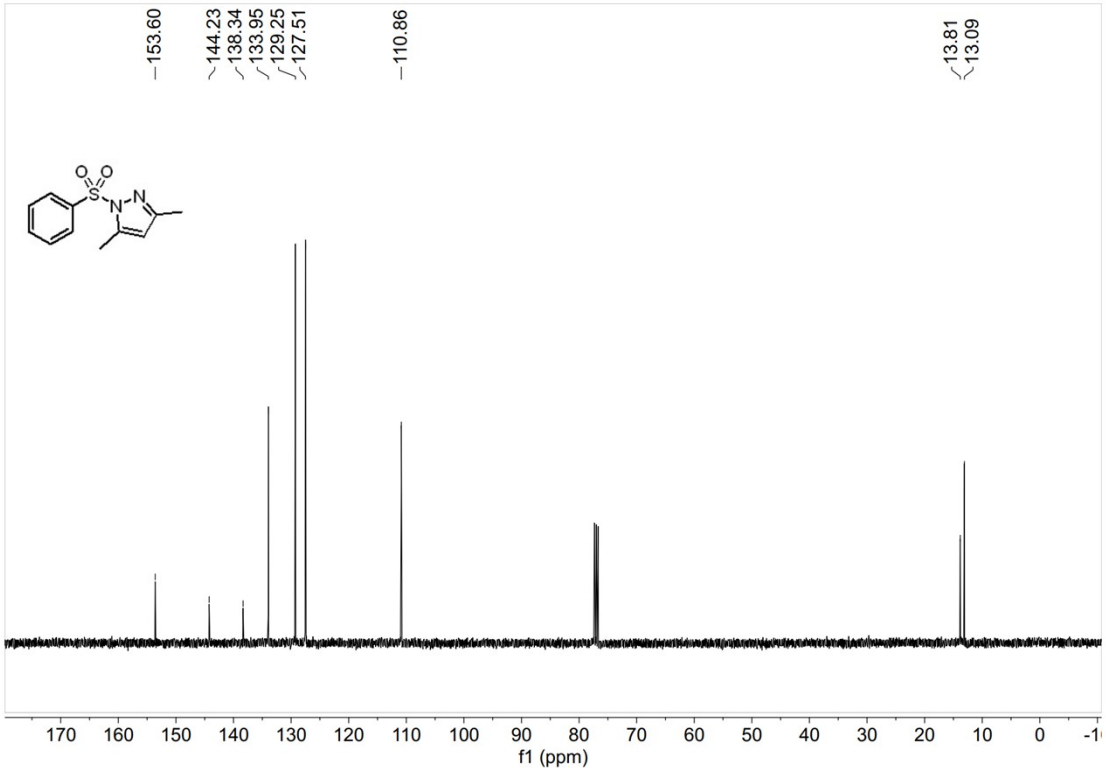
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



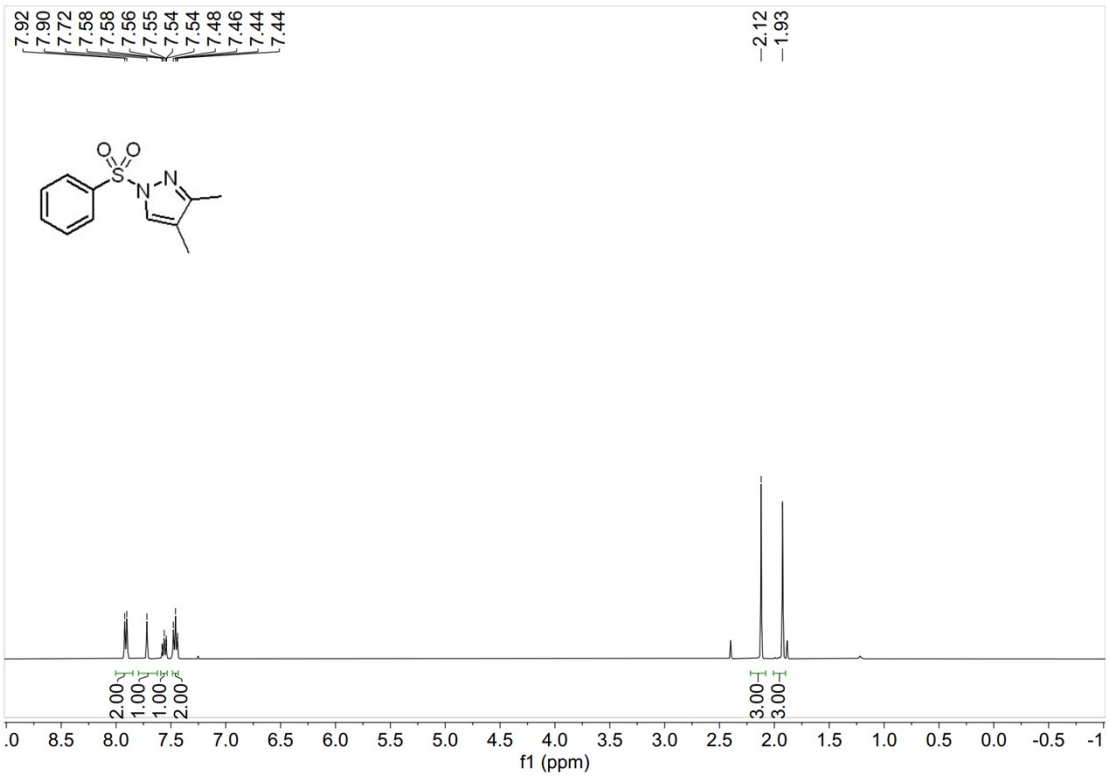
^{13}C NMR (101 MHz, $CDCl_3$) of **5**



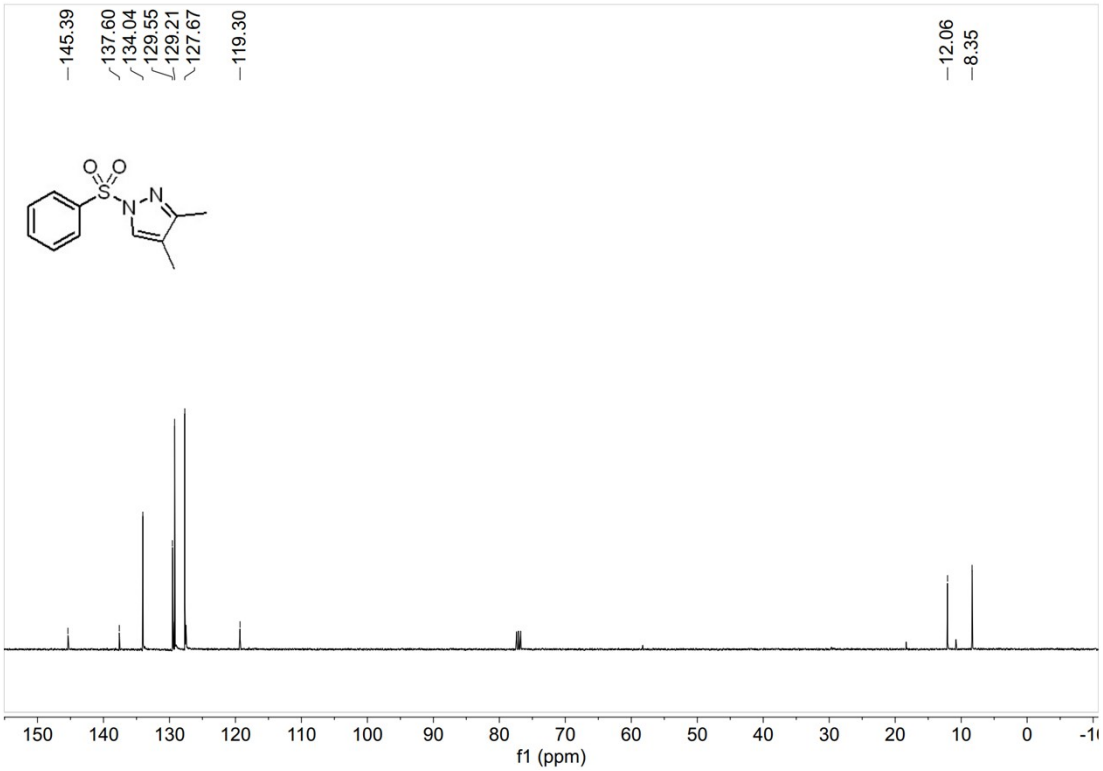
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



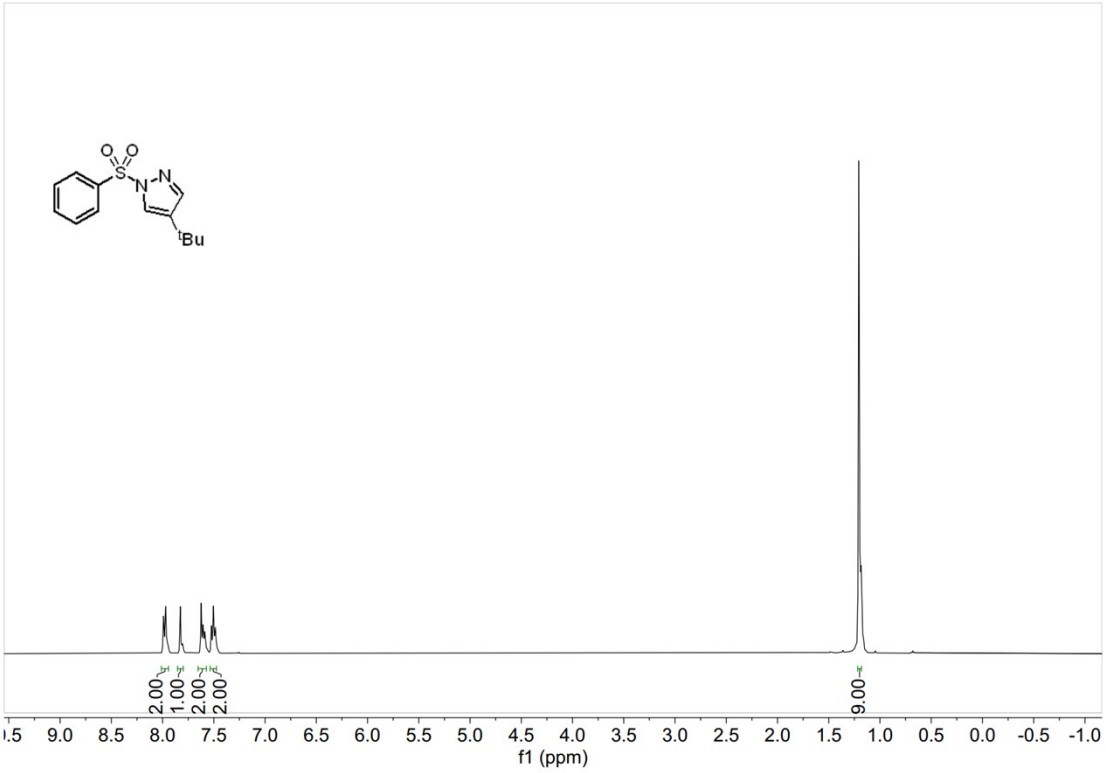
^{13}C NMR (101 MHz, $CDCl_3$) of **6**



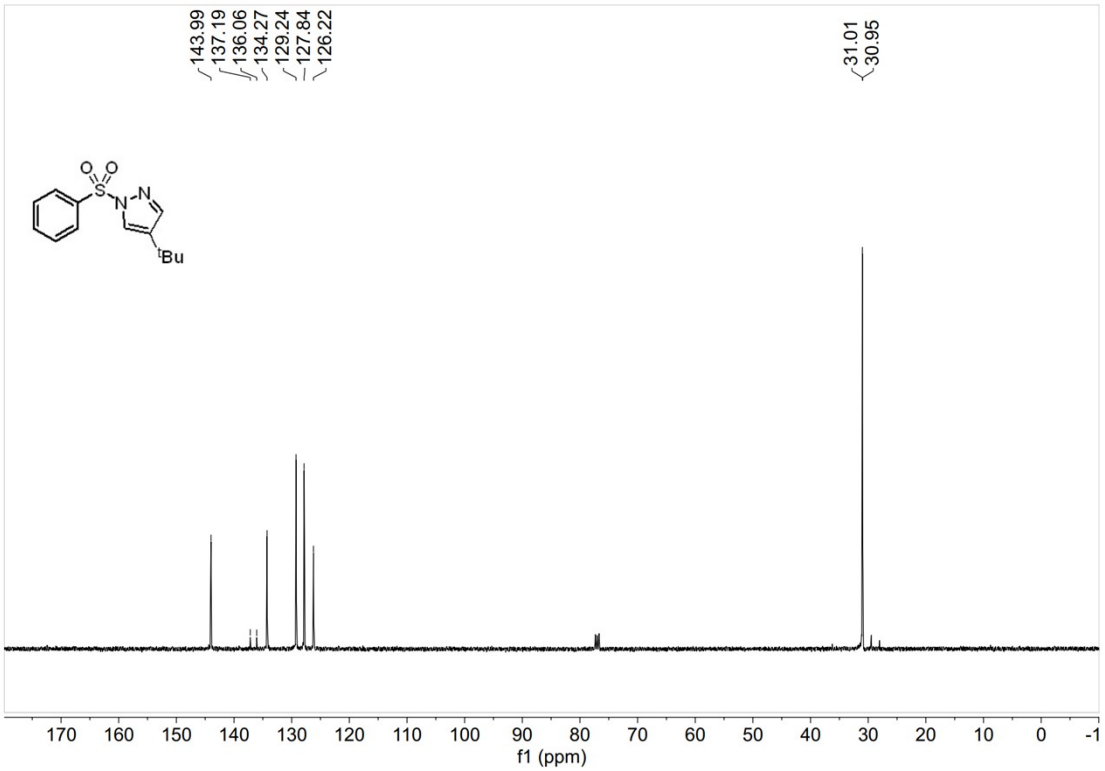
^{1}H NMR (400 MHz, $CDCl_3$) of **7**



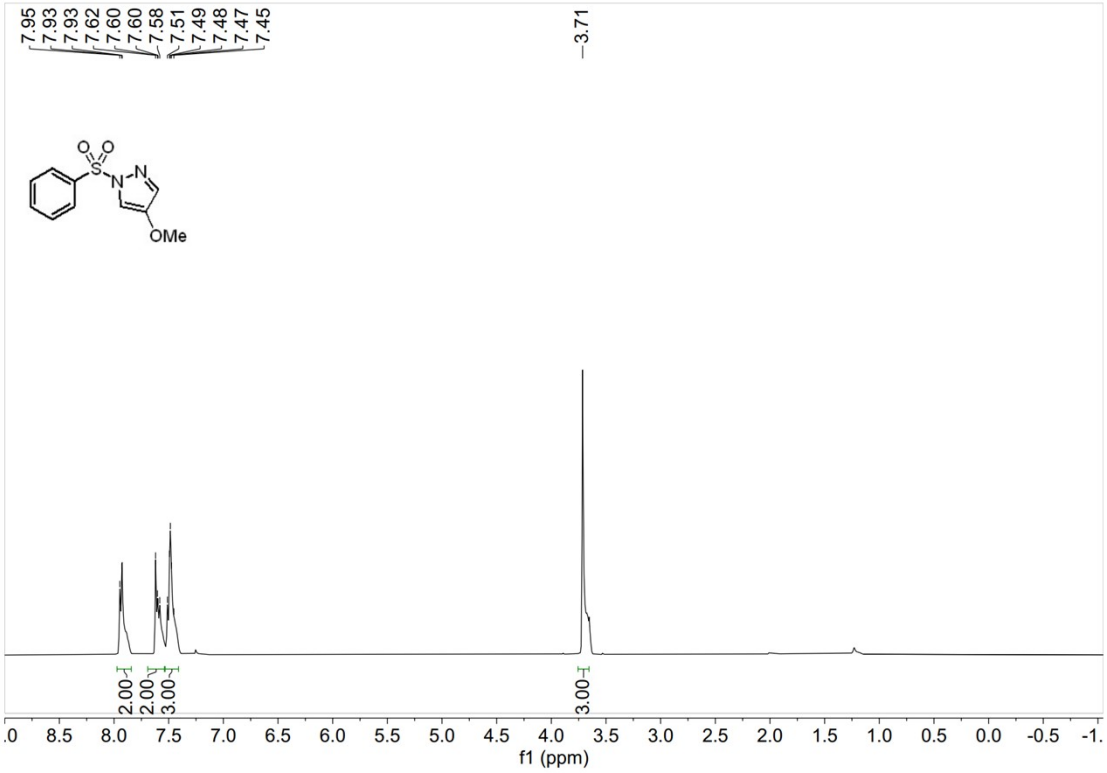
^{13}C NMR (101 MHz, $CDCl_3$) of **7**



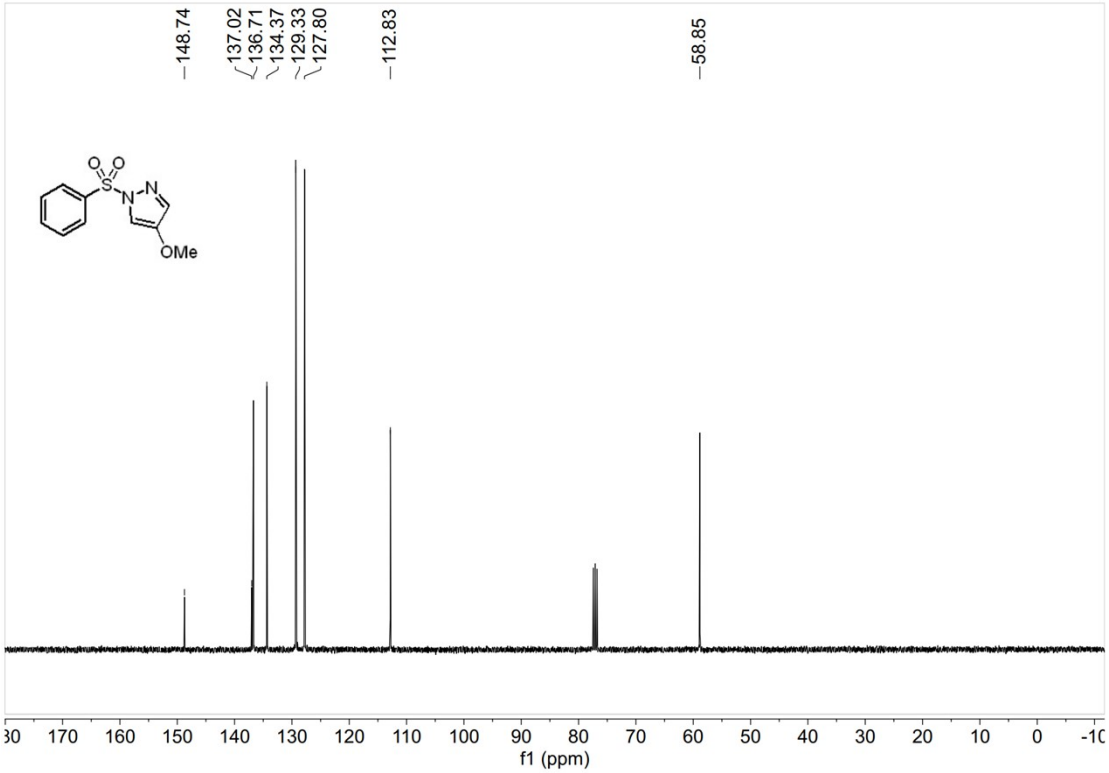
^{1}H NMR (400 MHz, $CDCl_3$) of **8**



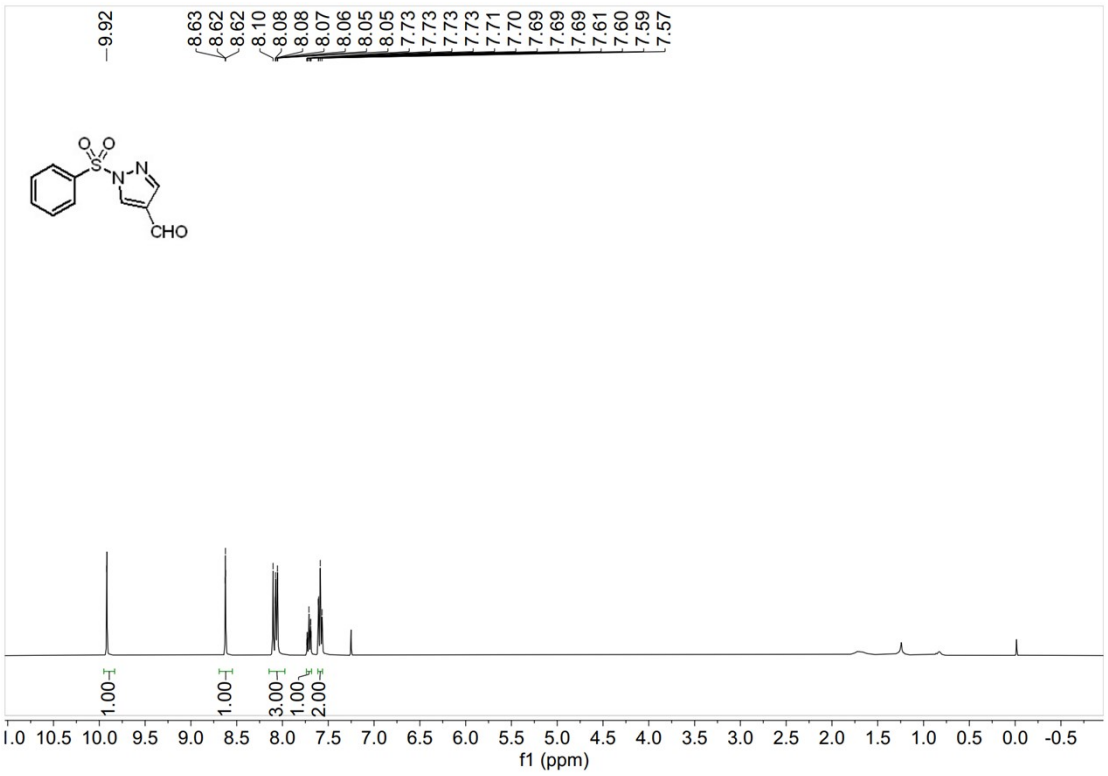
^{13}C NMR (101 MHz, $CDCl_3$) of **8**



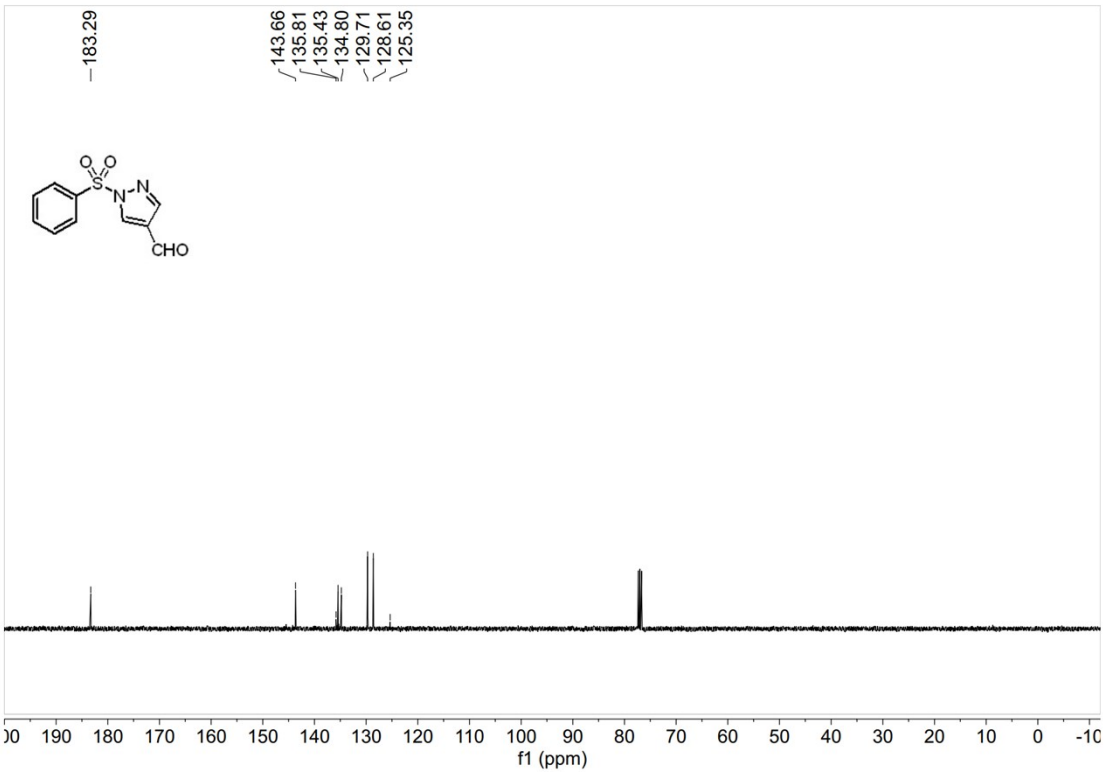
^{1}H NMR (400 MHz, $CDCl_3$) of **9**



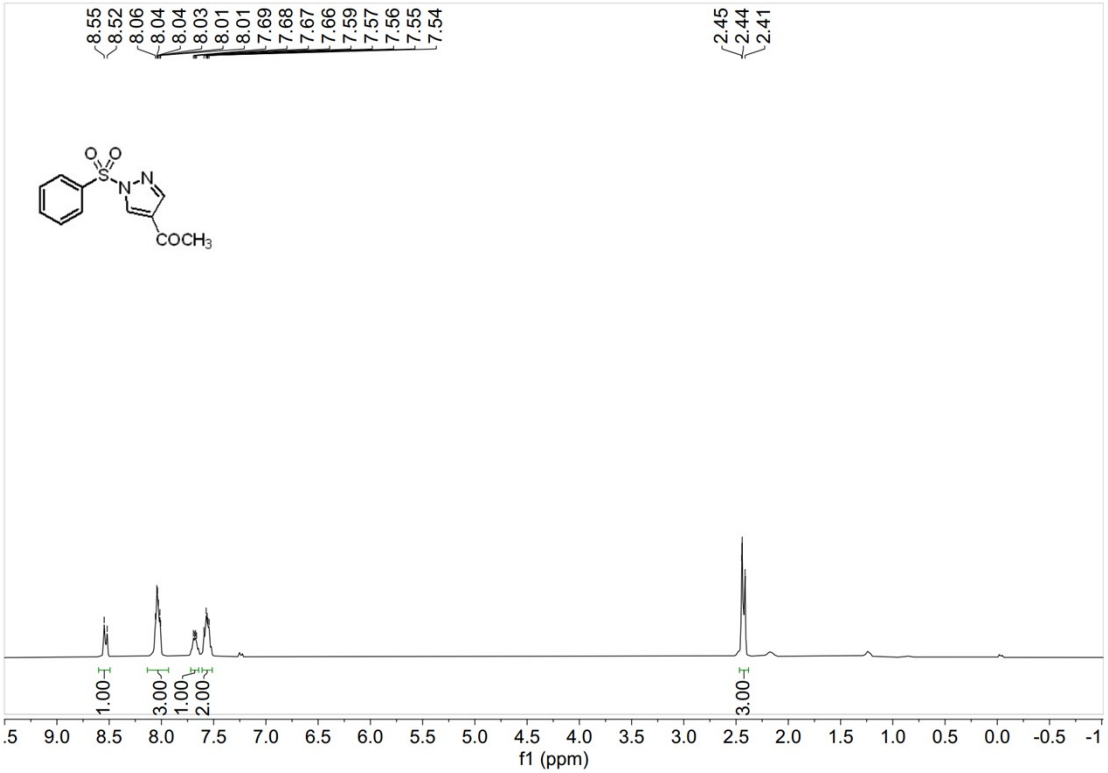
^{13}C NMR (101 MHz, $CDCl_3$) of **9**



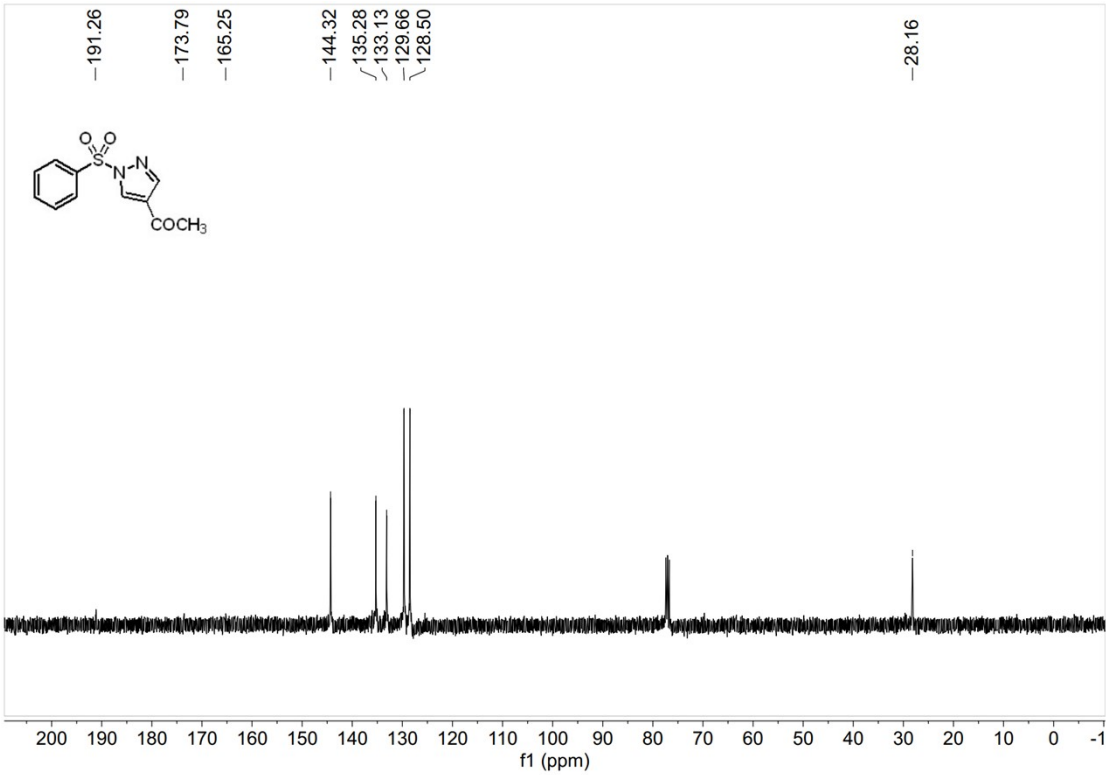
^{1}H NMR (400 MHz, $CDCl_3$) of **10**



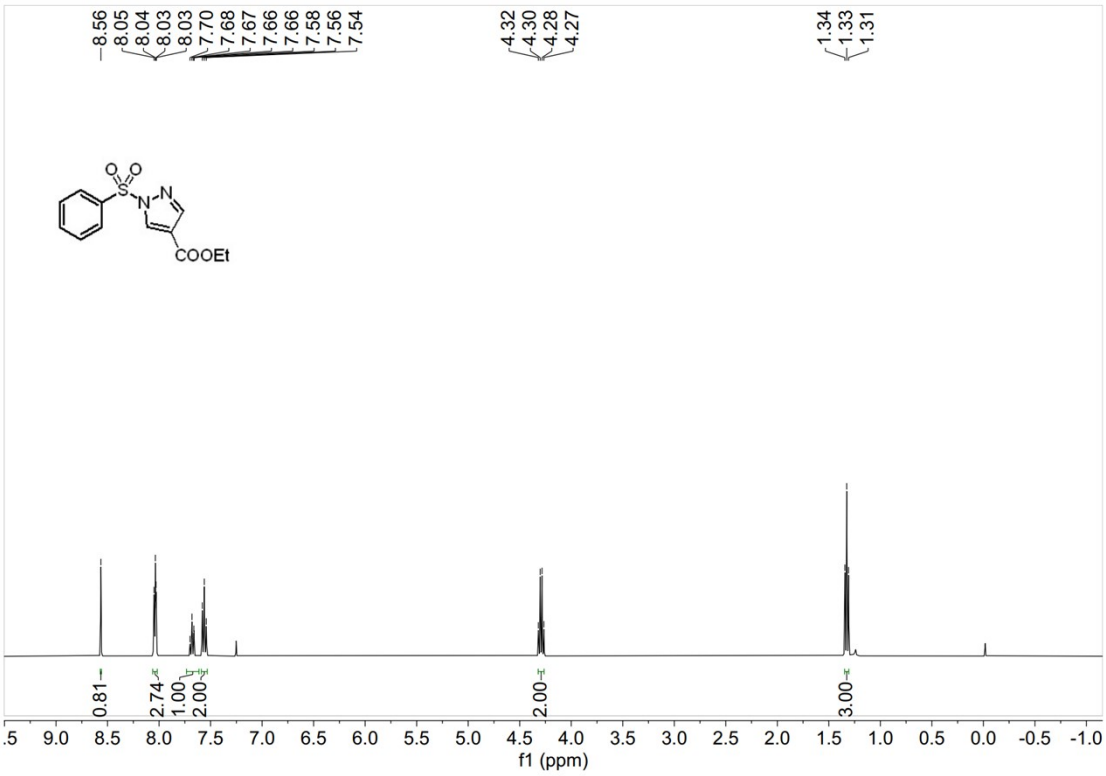
^{13}C NMR (101 MHz, $CDCl_3$) of **10**



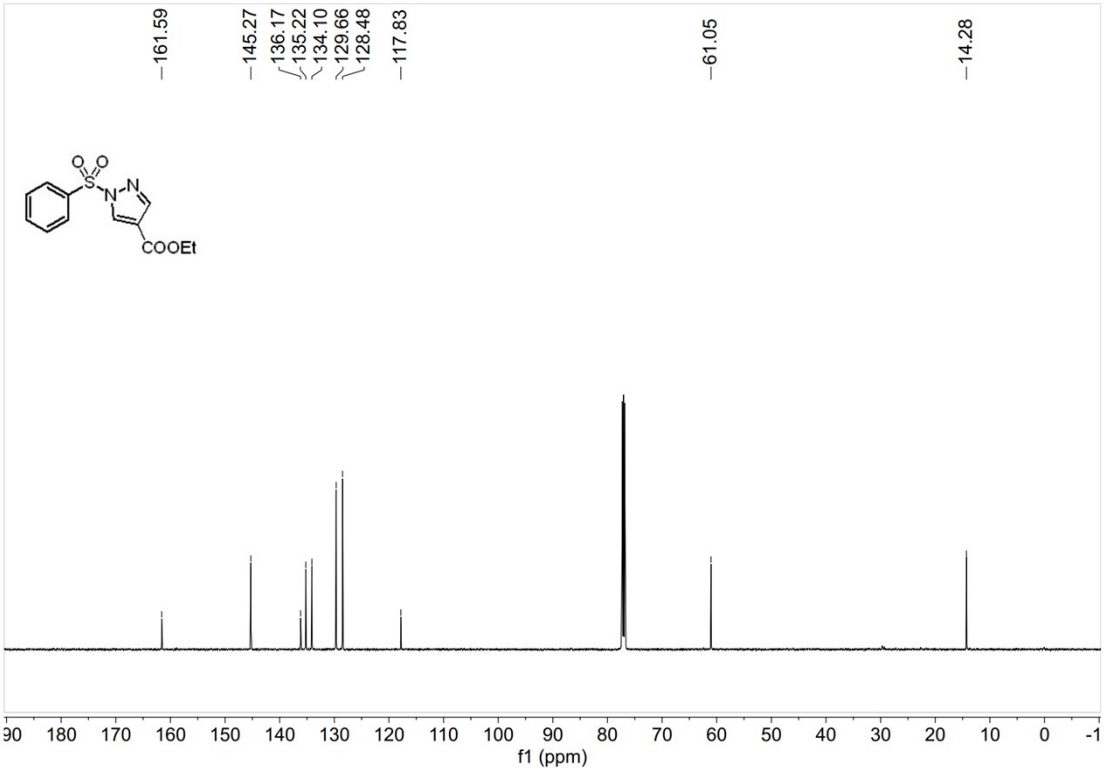
^{1}H NMR (400 MHz, $CDCl_3$) of **11**



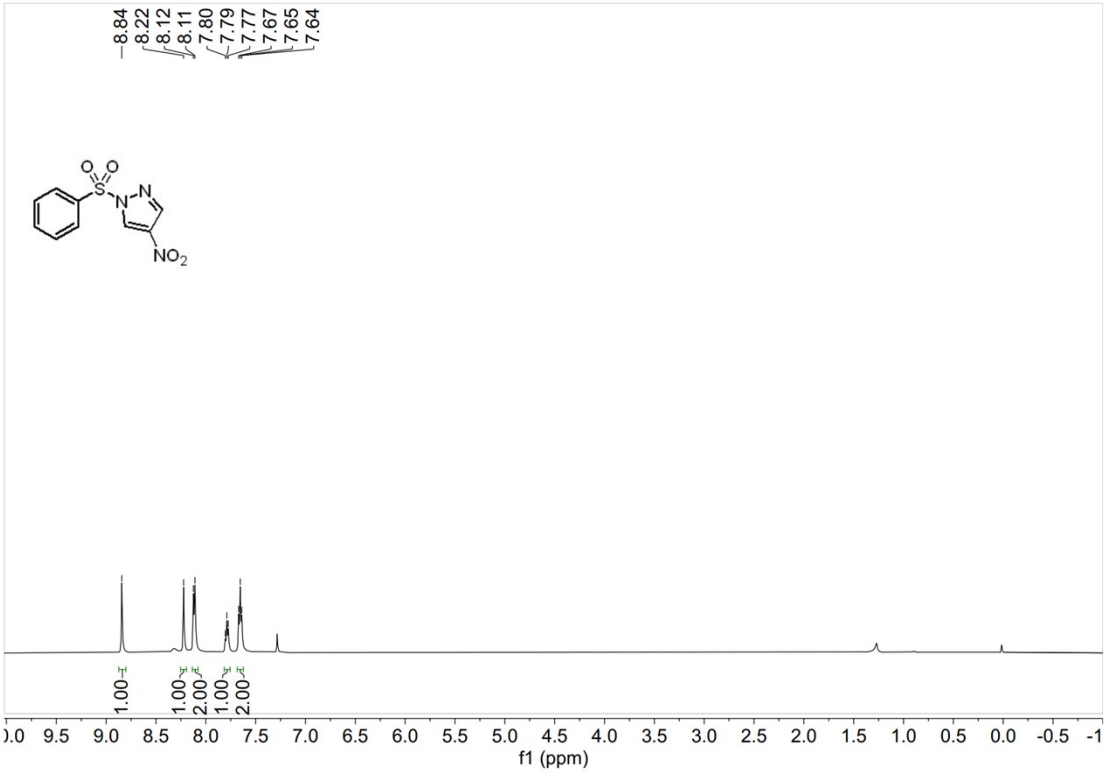
^{13}C NMR (101 MHz, $CDCl_3$) of **11**



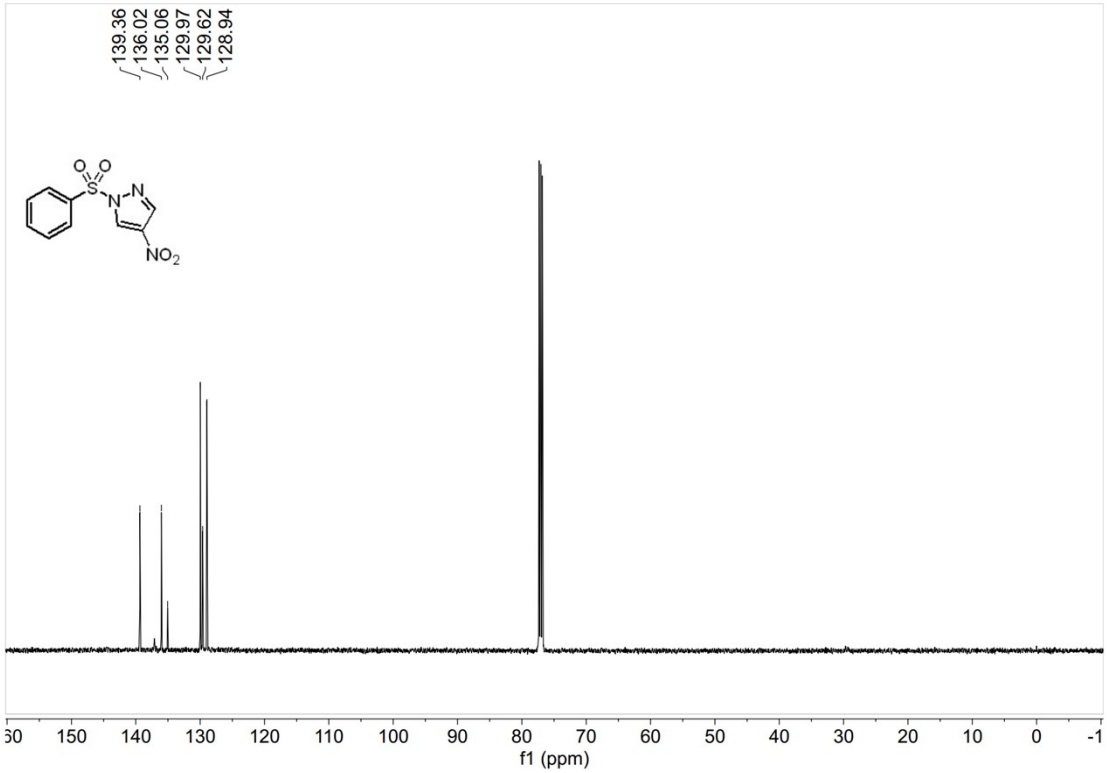
^{1}H NMR (400 MHz, $CDCl_3$) of **12**



^{13}C NMR (101 MHz, $CDCl_3$) of **12**



^{1}H NMR (400 MHz, $CDCl_3$) of **13**



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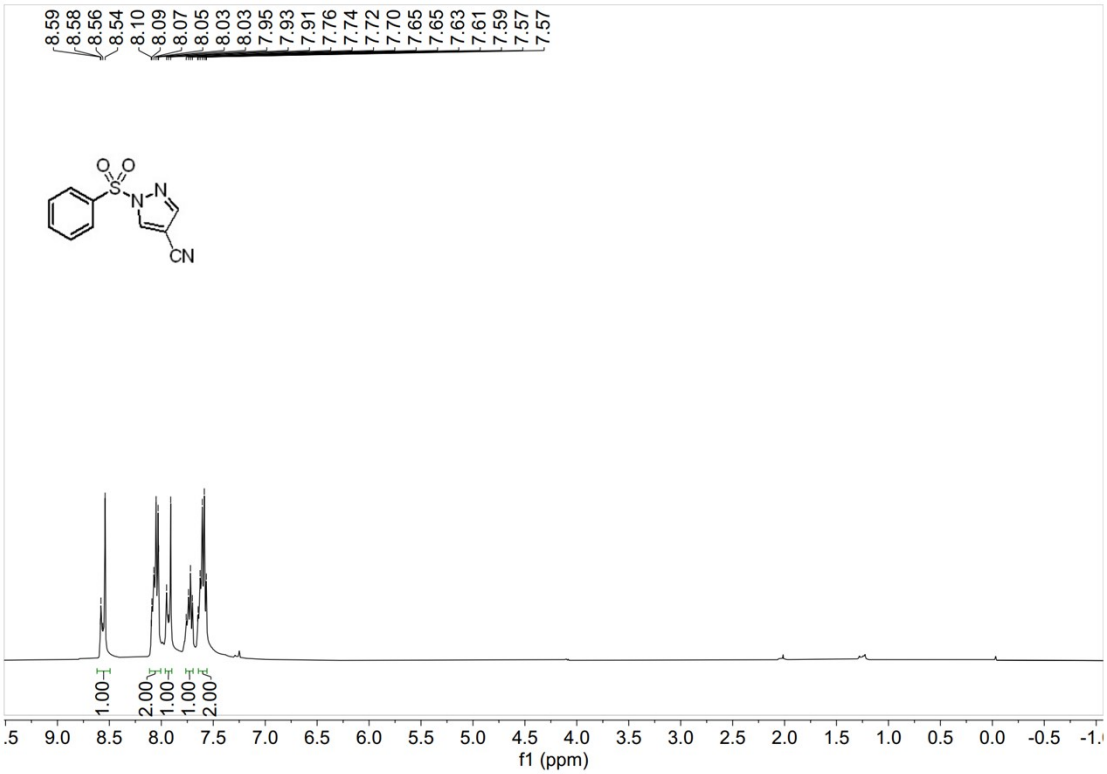
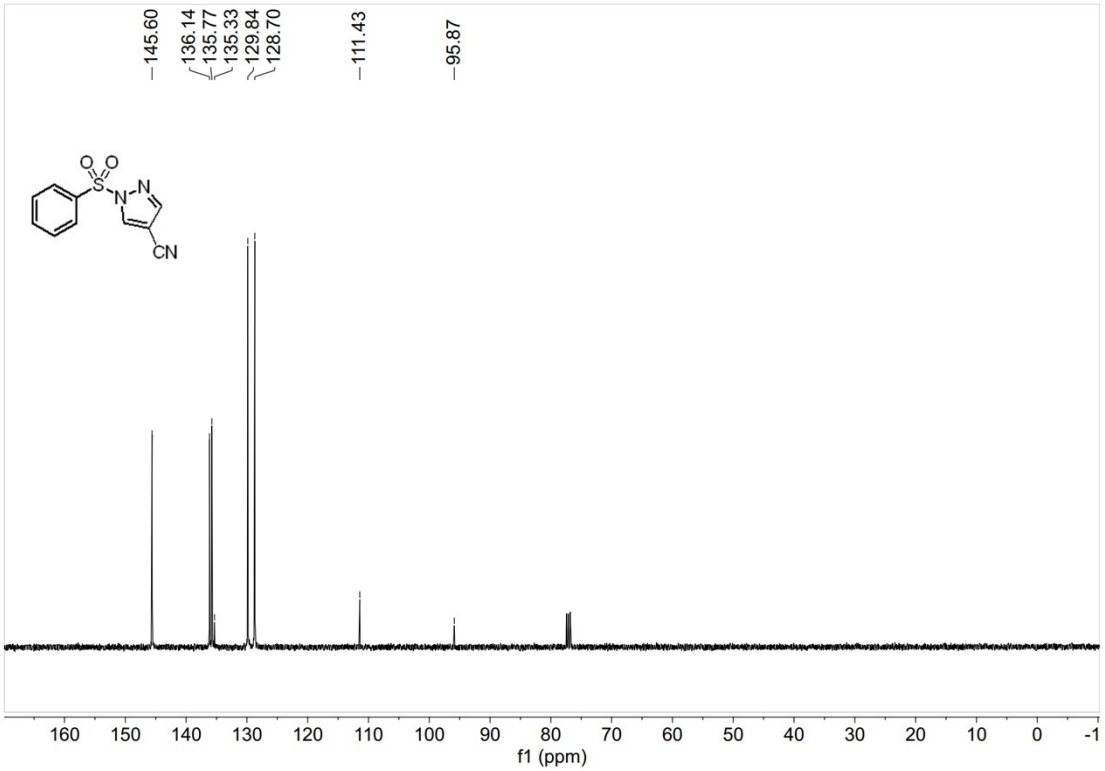
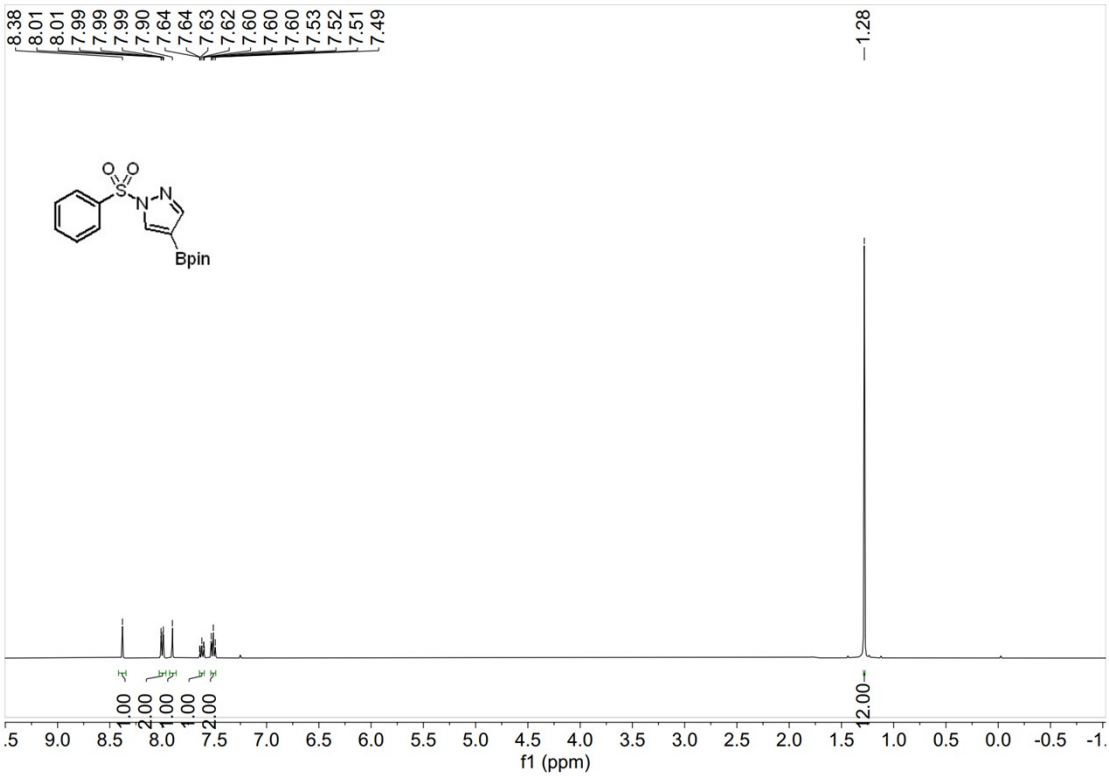


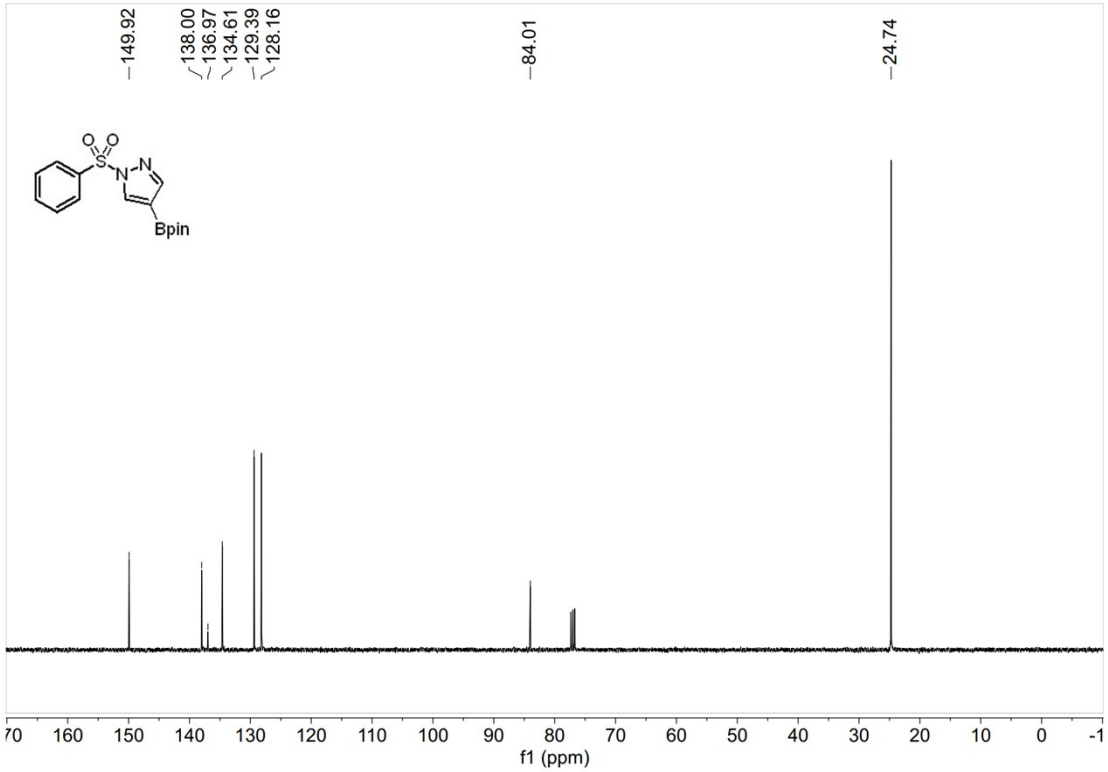
^{1}H NMR (400 MHz, $CDCl_3$) of **14**



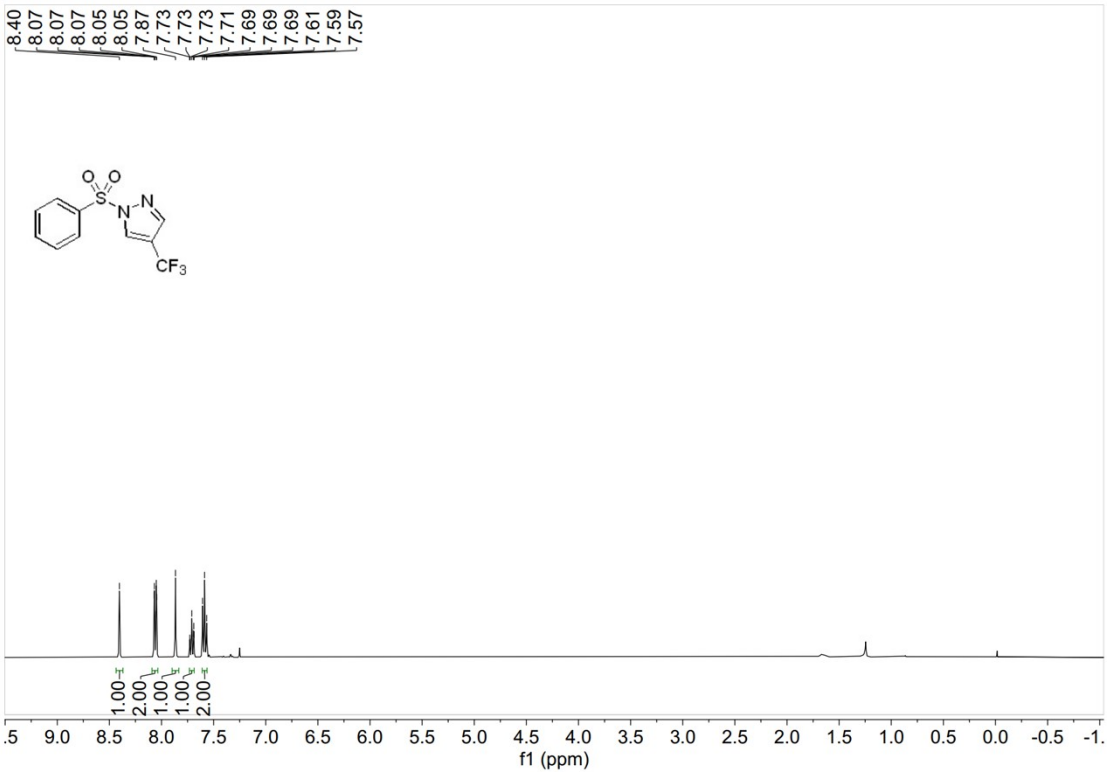
^{13}C NMR (101 MHz, $CDCl_3$) of **14**



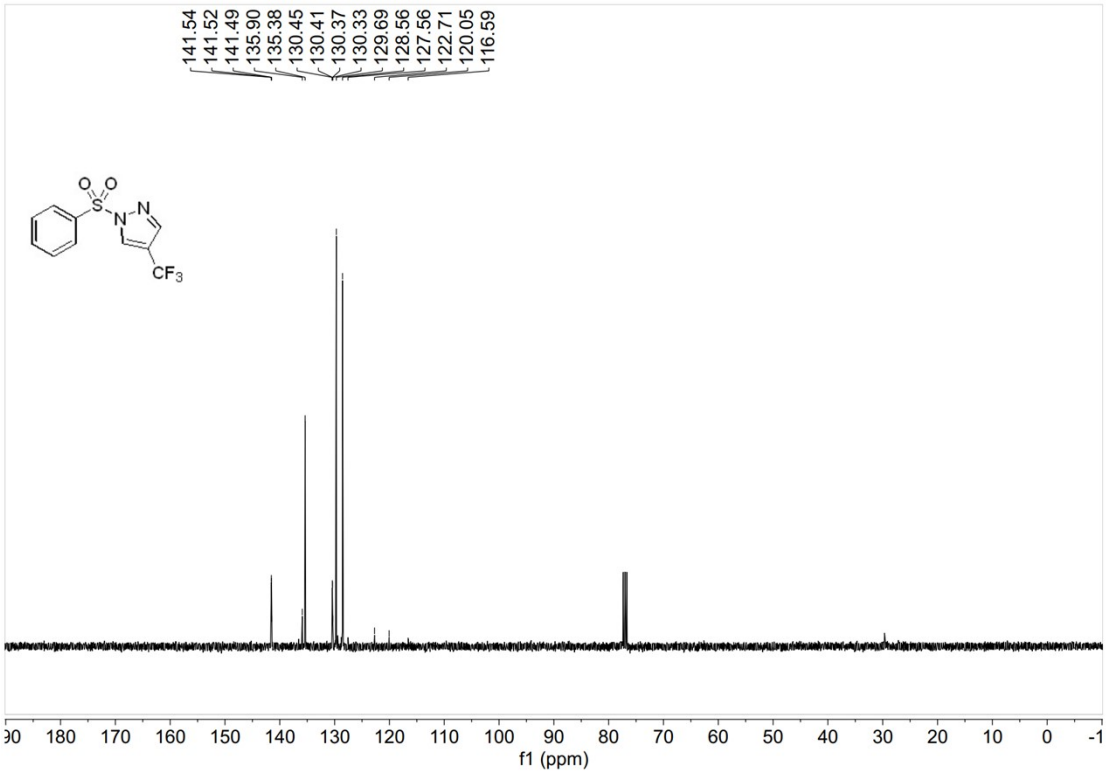
^{1}H NMR (400 MHz, $CDCl_3$) of **15**



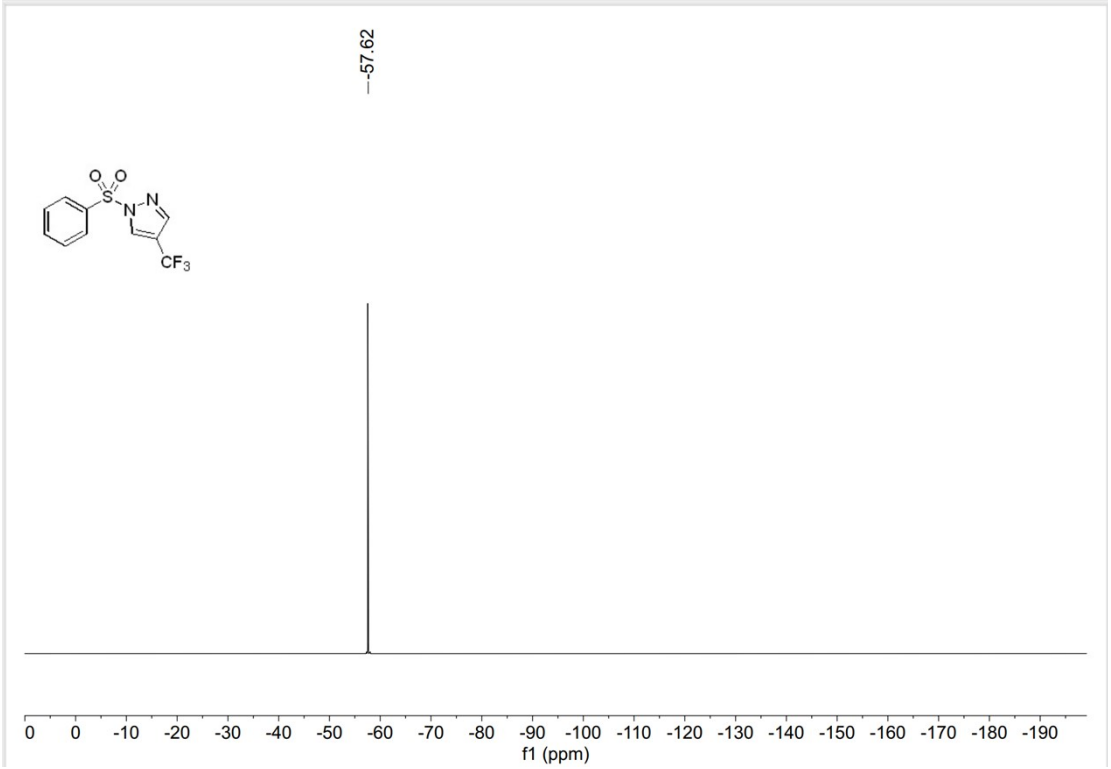
^{13}C NMR (101 MHz, $CDCl_3$) of **15**



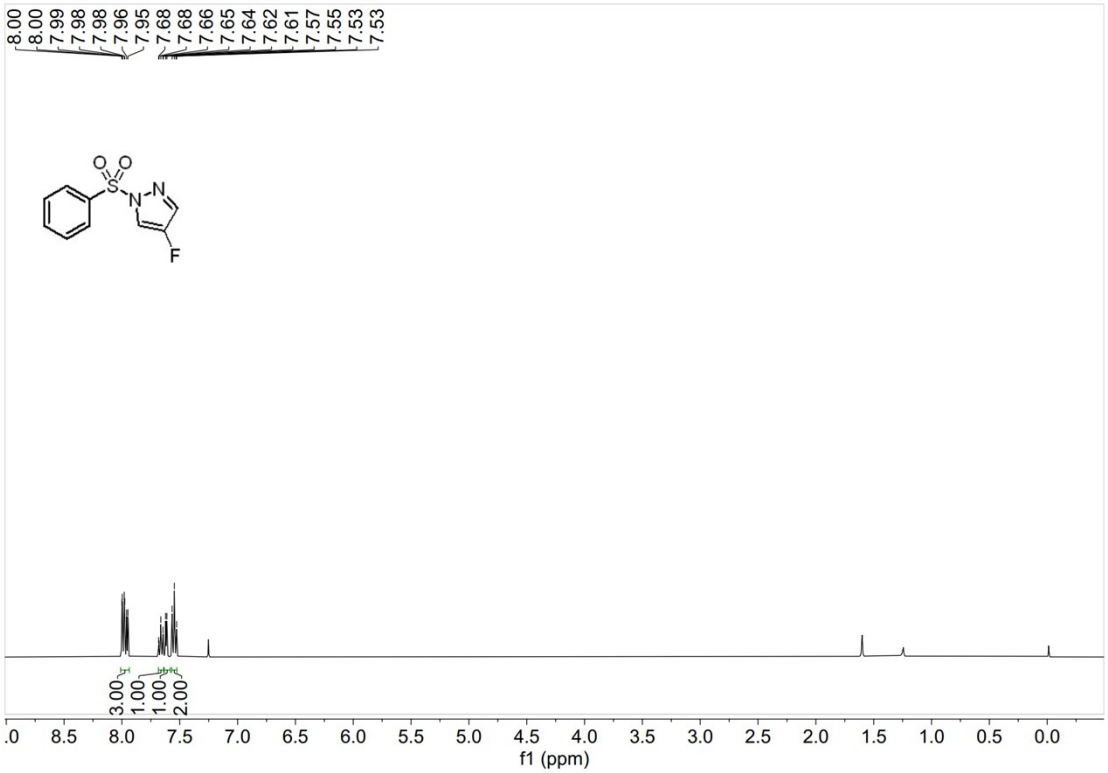
^{1}H NMR (400 MHz, $CDCl_3$) of **16**



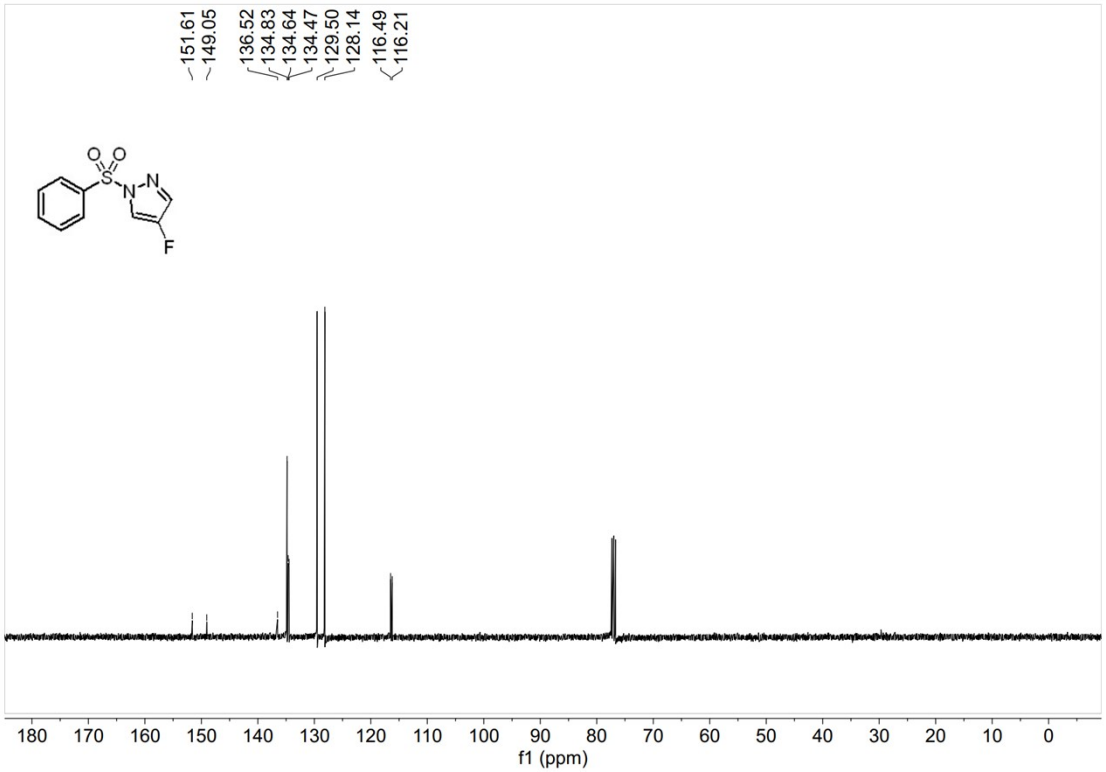
^{13}C NMR (101 MHz, $CDCl_3$) of **16**



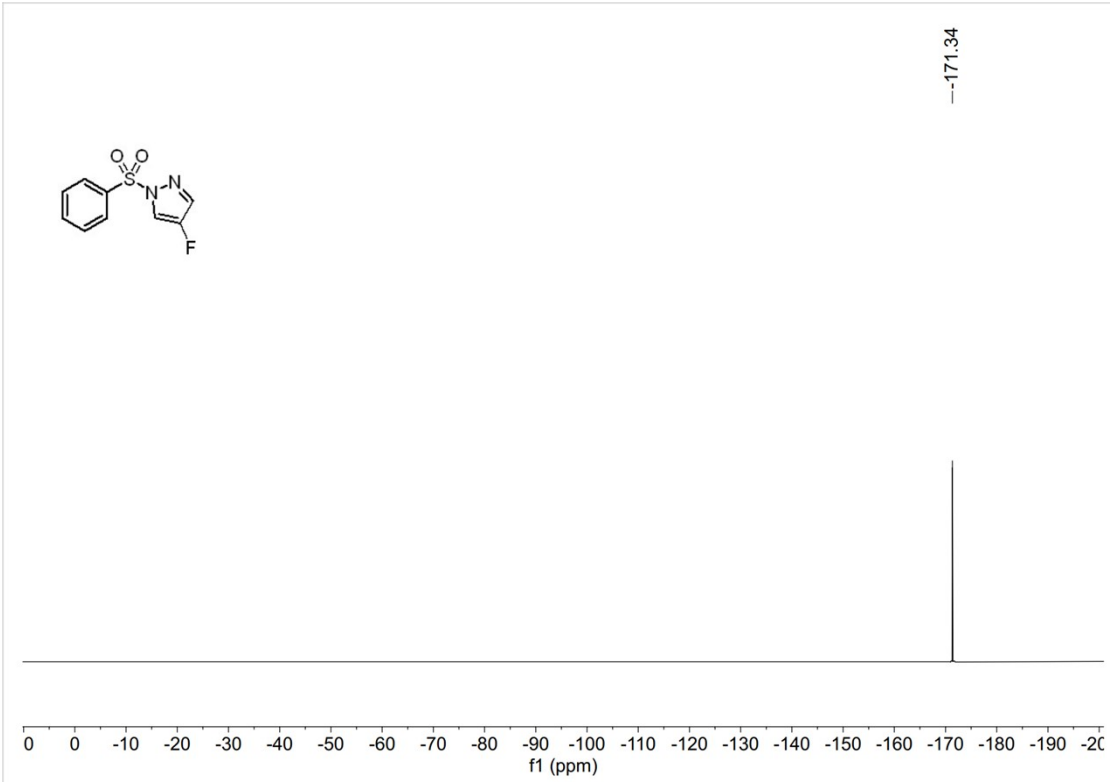
^{19}F NMR (376 MHz, $CDCl_3$) of **16**



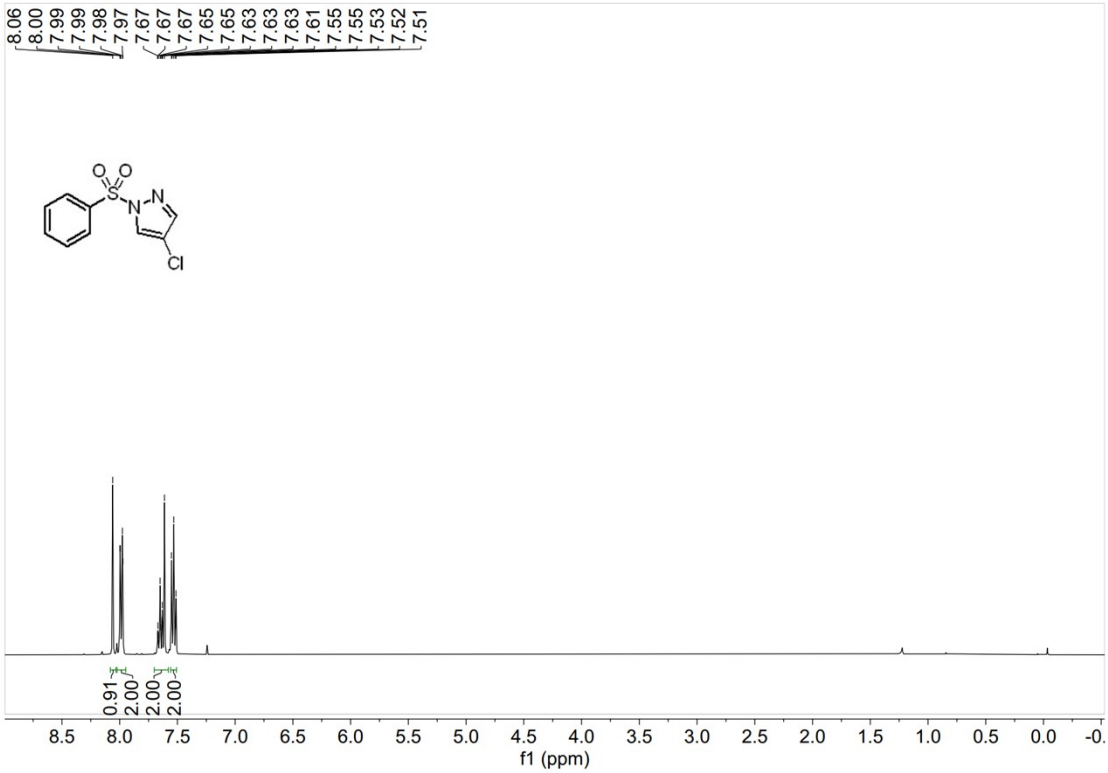
^{1}H NMR (400 MHz, $CDCl_3$) of **17**



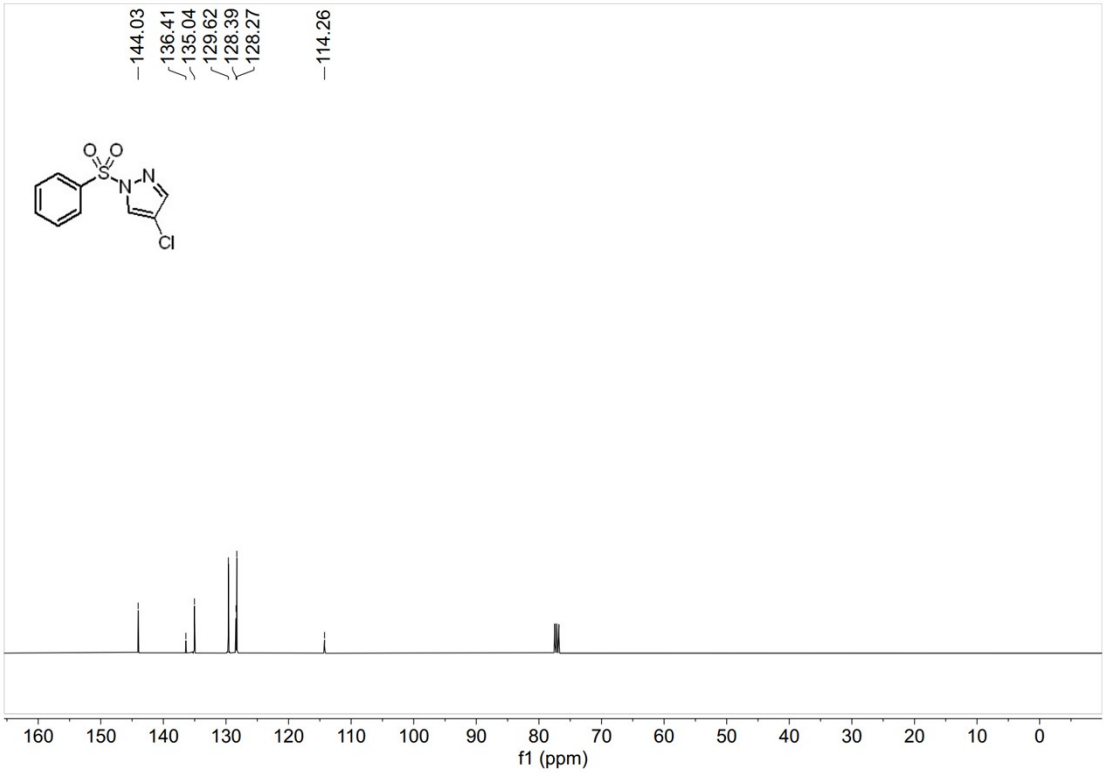
^{13}C NMR (101 MHz, $CDCl_3$) of **17**



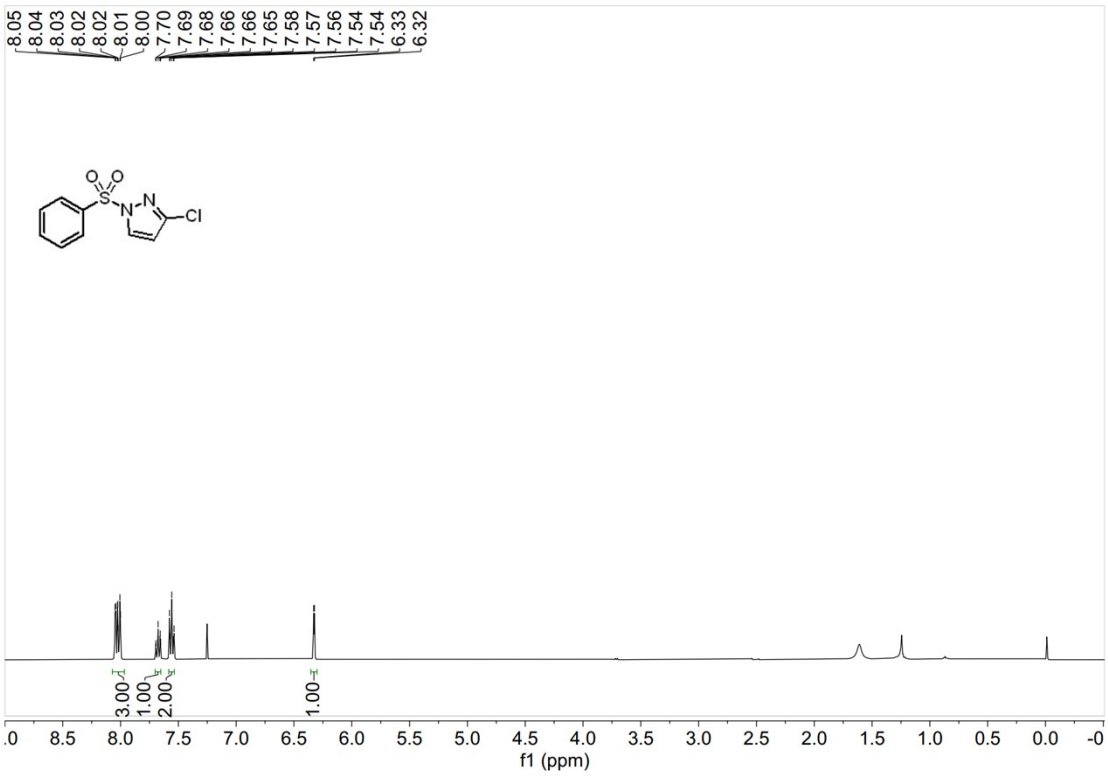
^{19}F NMR (376 MHz, $CDCl_3$) of **17**



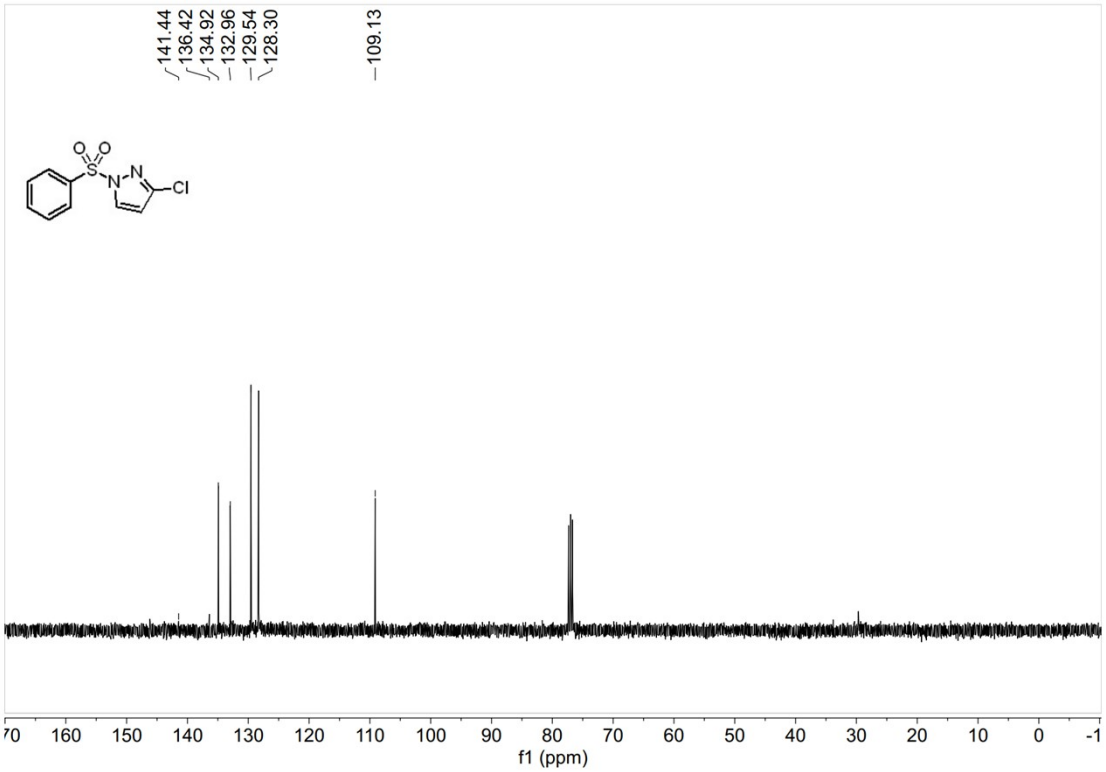
^{1}H NMR (400 MHz, $CDCl_3$) of **18**



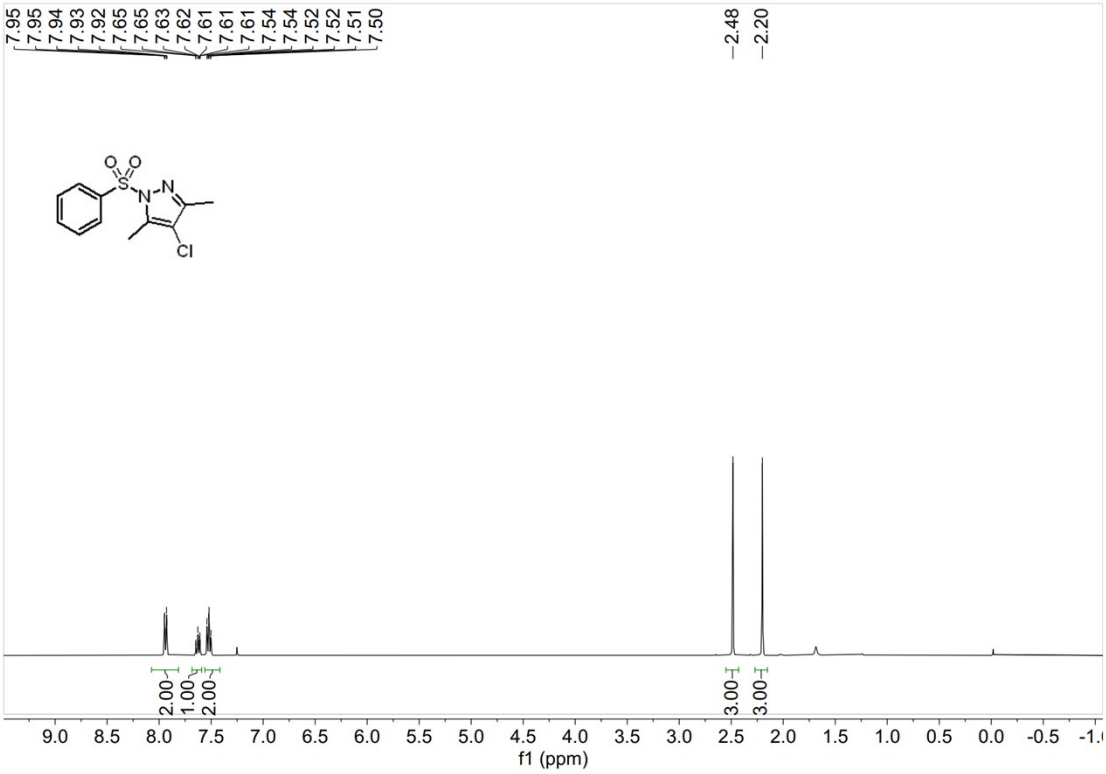
^{13}C NMR (101 MHz, $CDCl_3$) of **18**



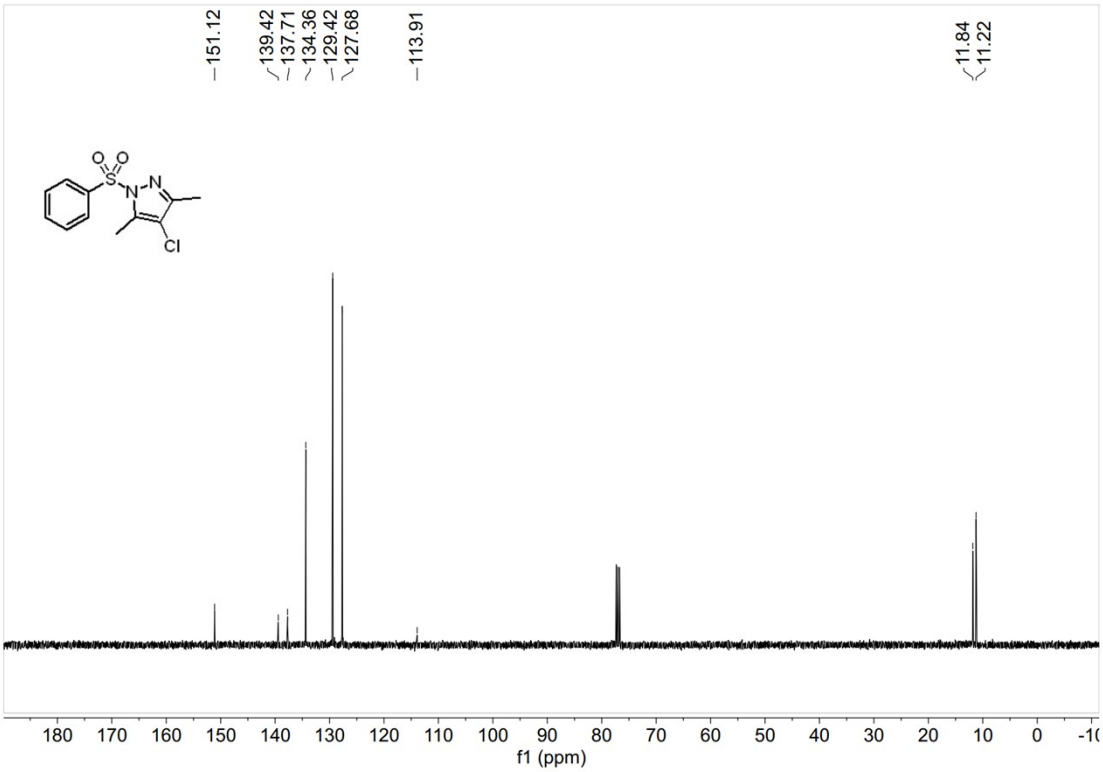
^{1}H NMR (400 MHz, $CDCl_3$) of **19**



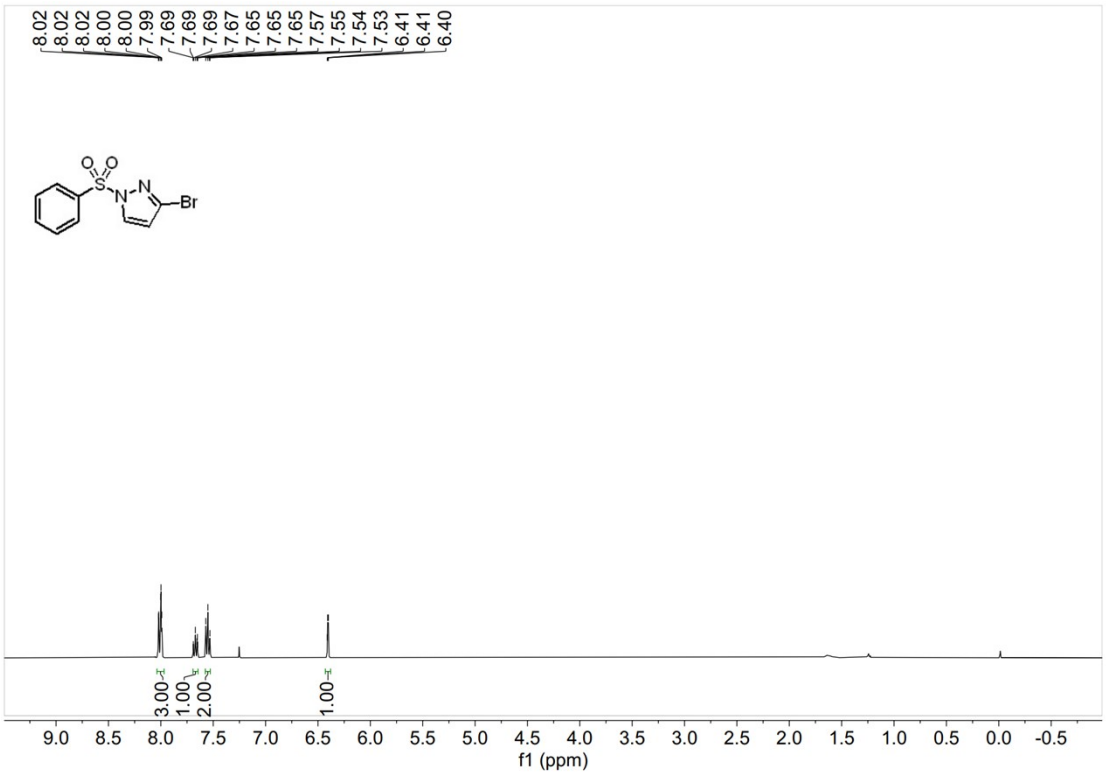
^{13}C NMR (101 MHz, $CDCl_3$) of **19**



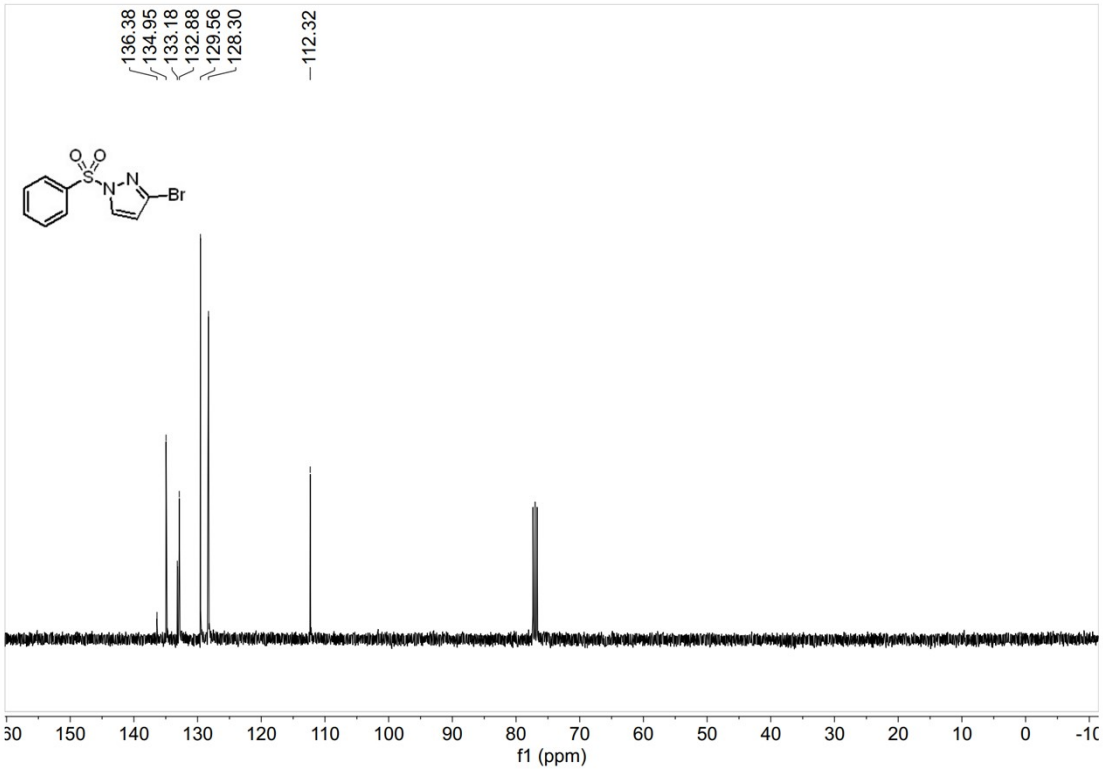
^{1}H NMR (400 MHz, $CDCl_3$) of **20**



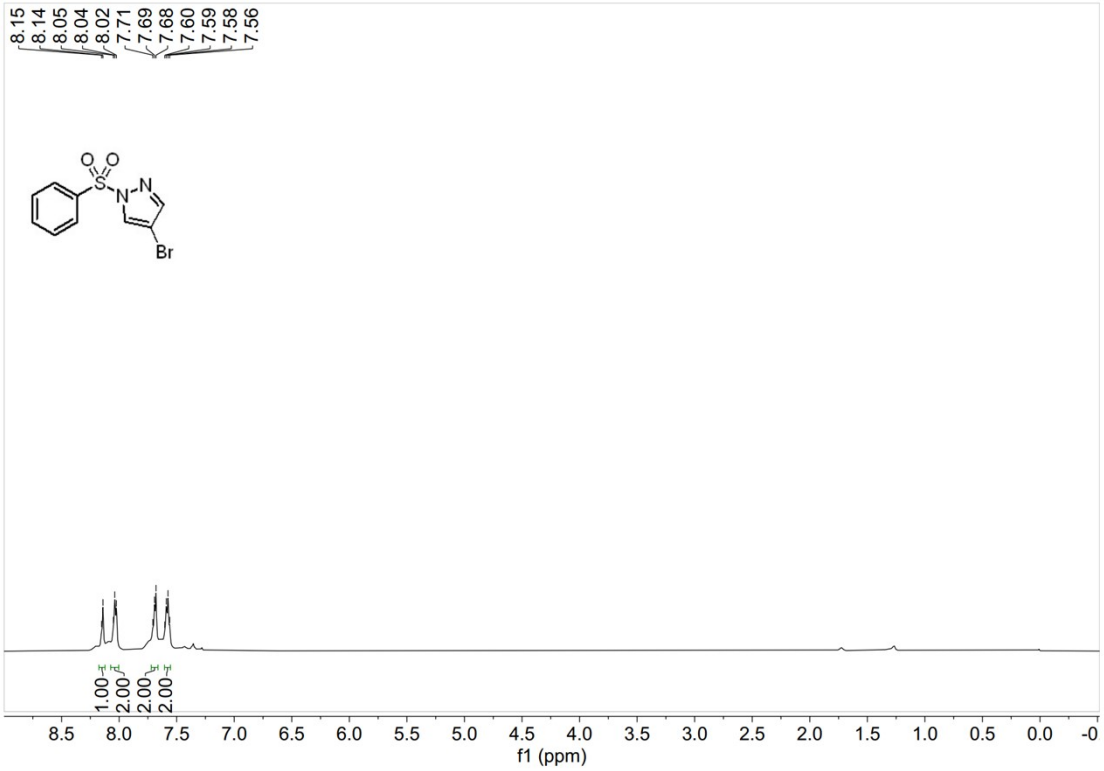
^{13}C NMR (101 MHz, $CDCl_3$) of **20**



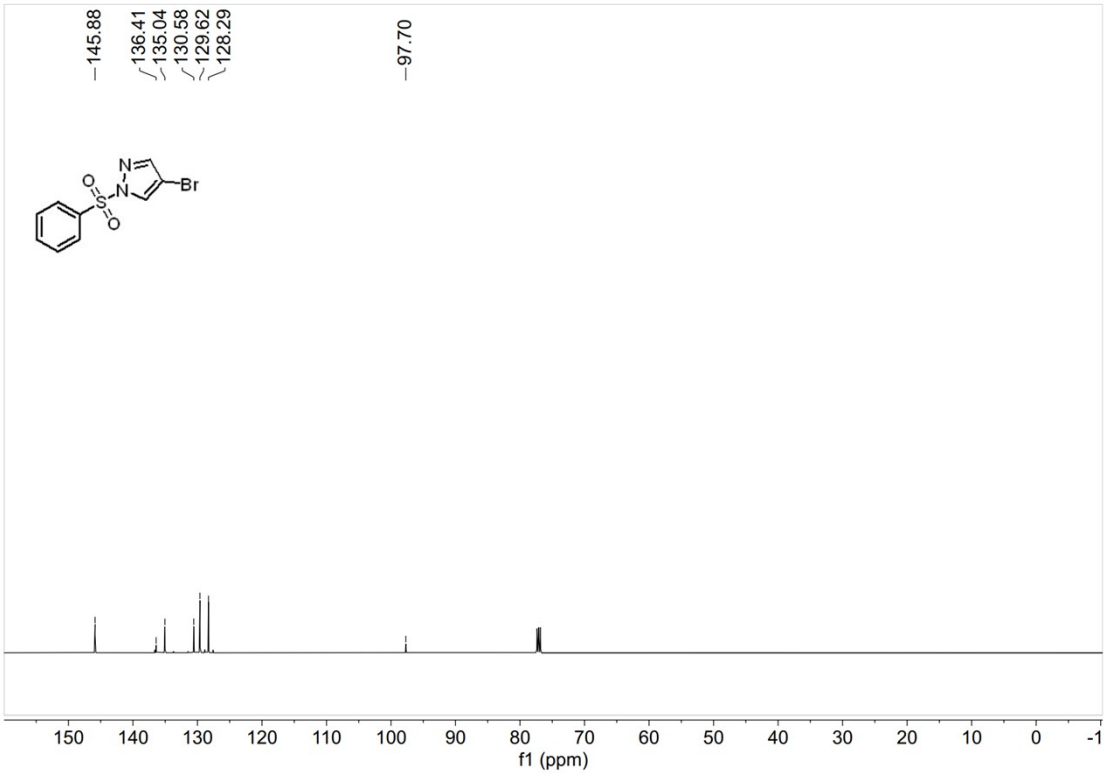
^{1}H NMR (400 MHz, $CDCl_3$) of **21**



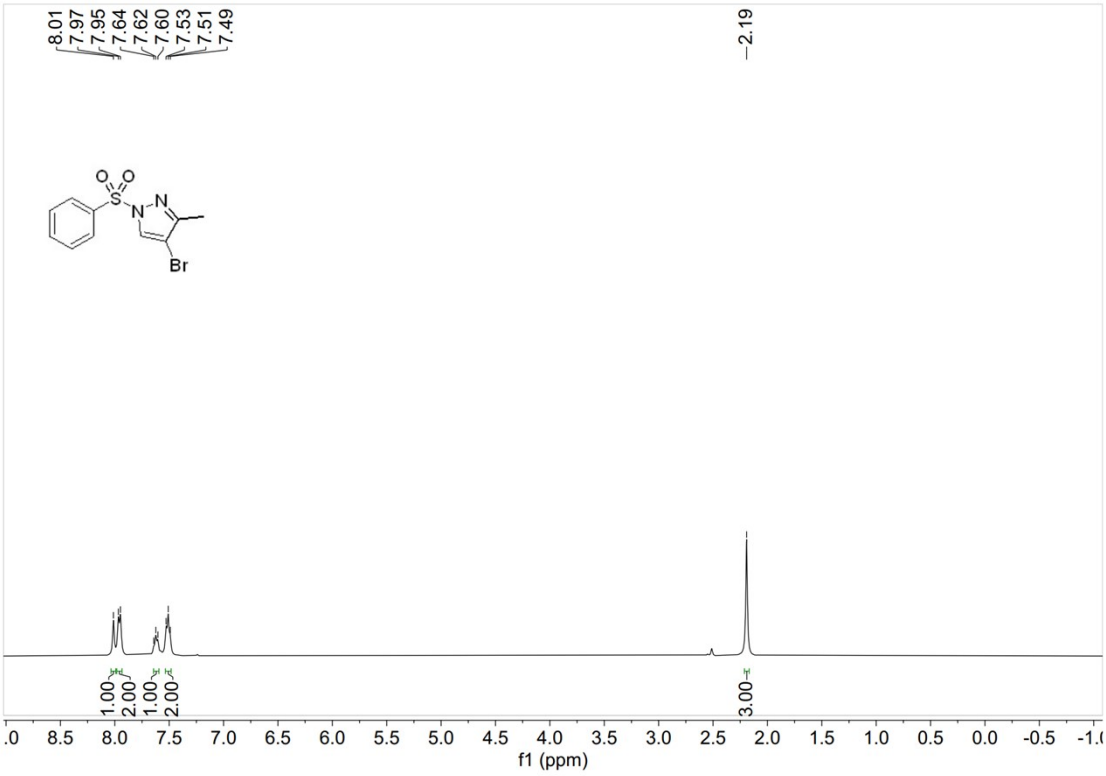
^{13}C NMR (101 MHz, $CDCl_3$) of **21**



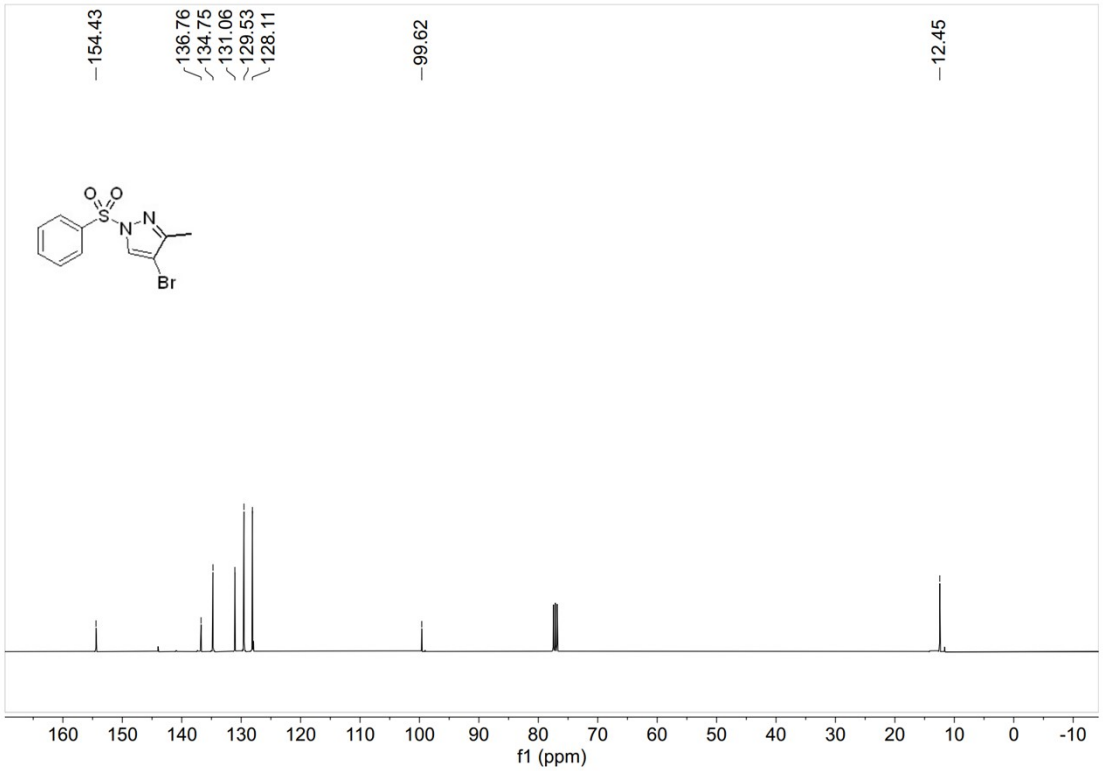
^{1}H NMR (400 MHz, $CDCl_3$) of **22**



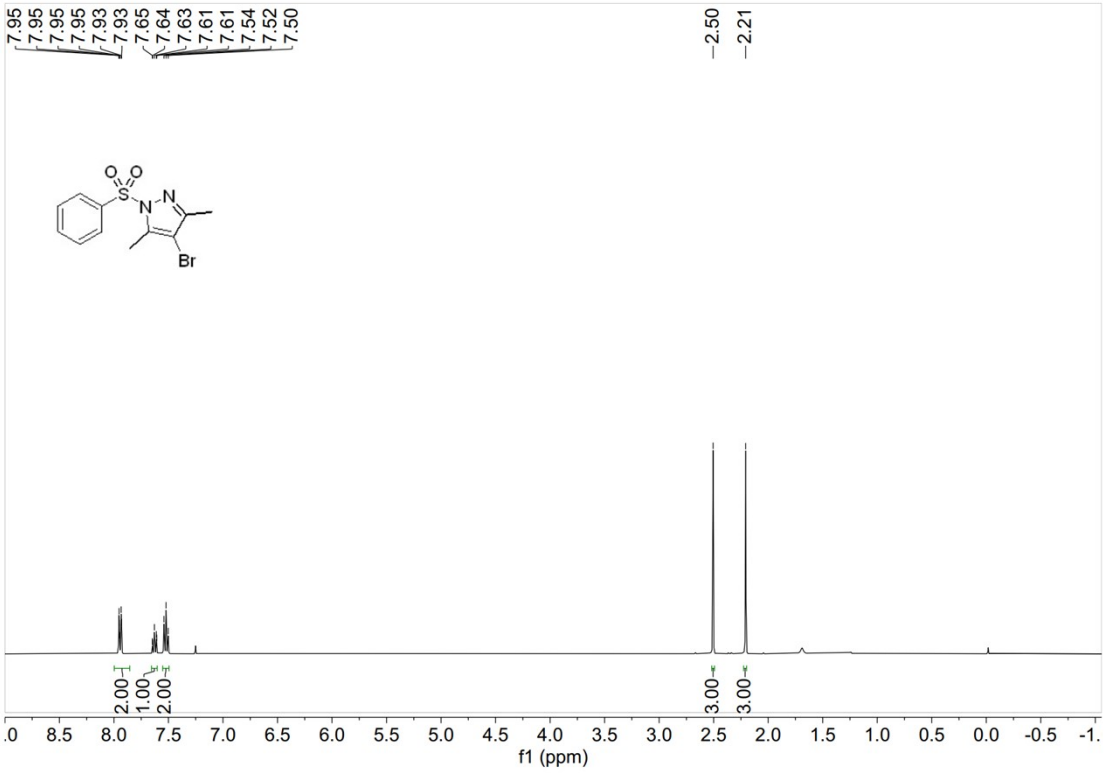
^{13}C NMR (101 MHz, $CDCl_3$) of **22**



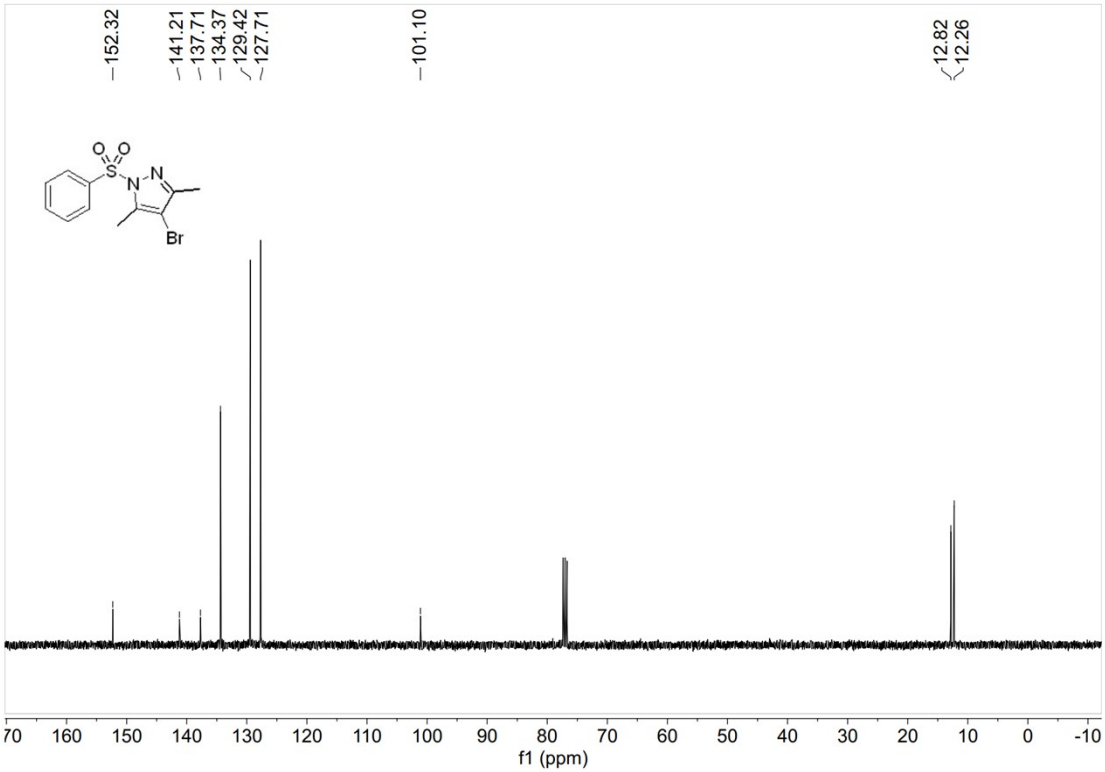
^{1}H NMR (400 MHz, $CDCl_3$) of **23**



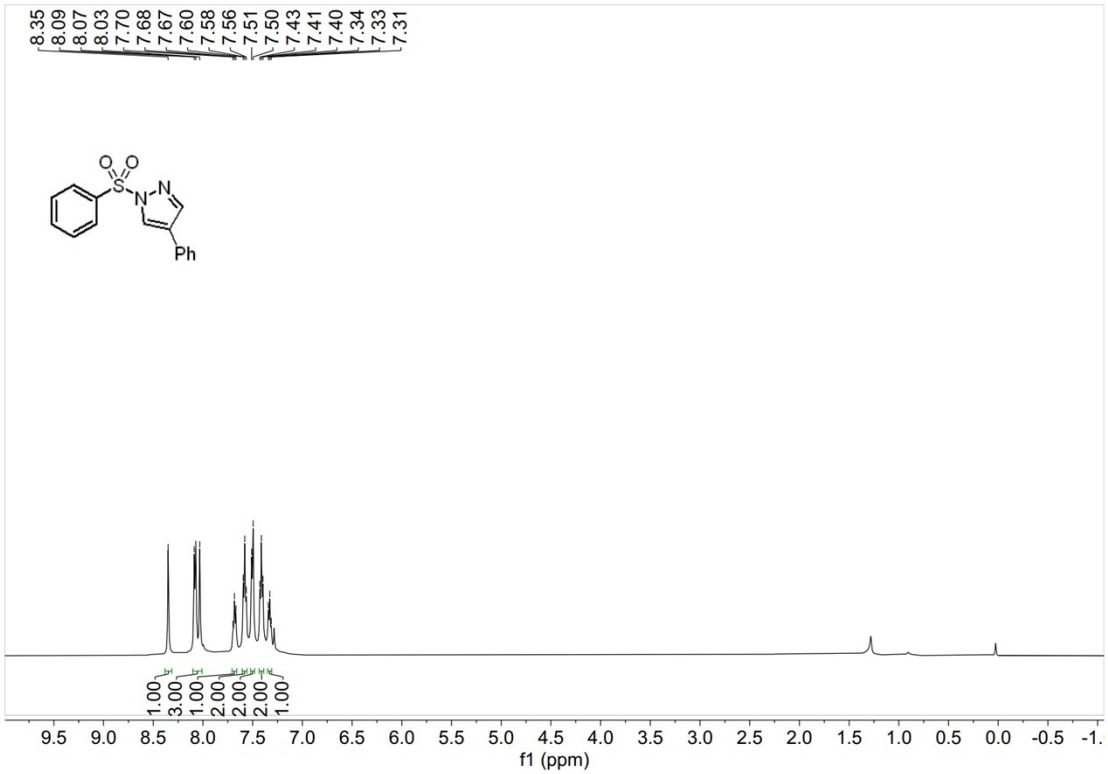
^{13}C NMR (101 MHz, $CDCl_3$) of **23**



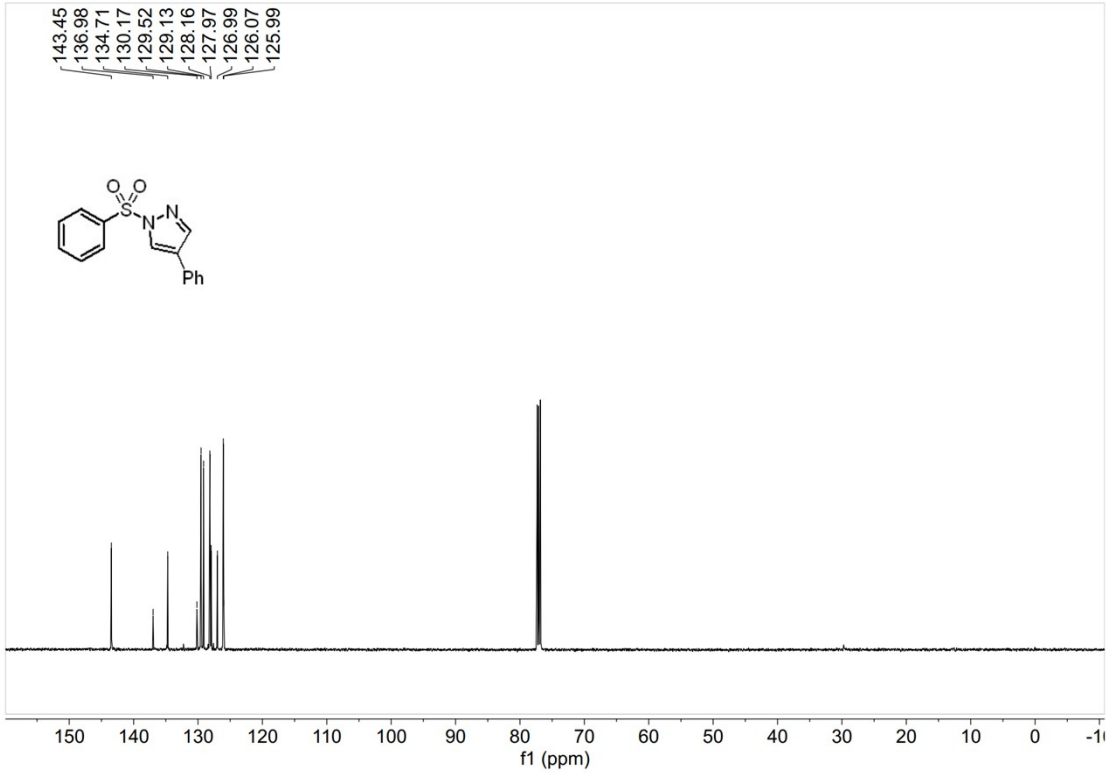
^{1}H NMR (400 MHz, $CDCl_3$) of **24**



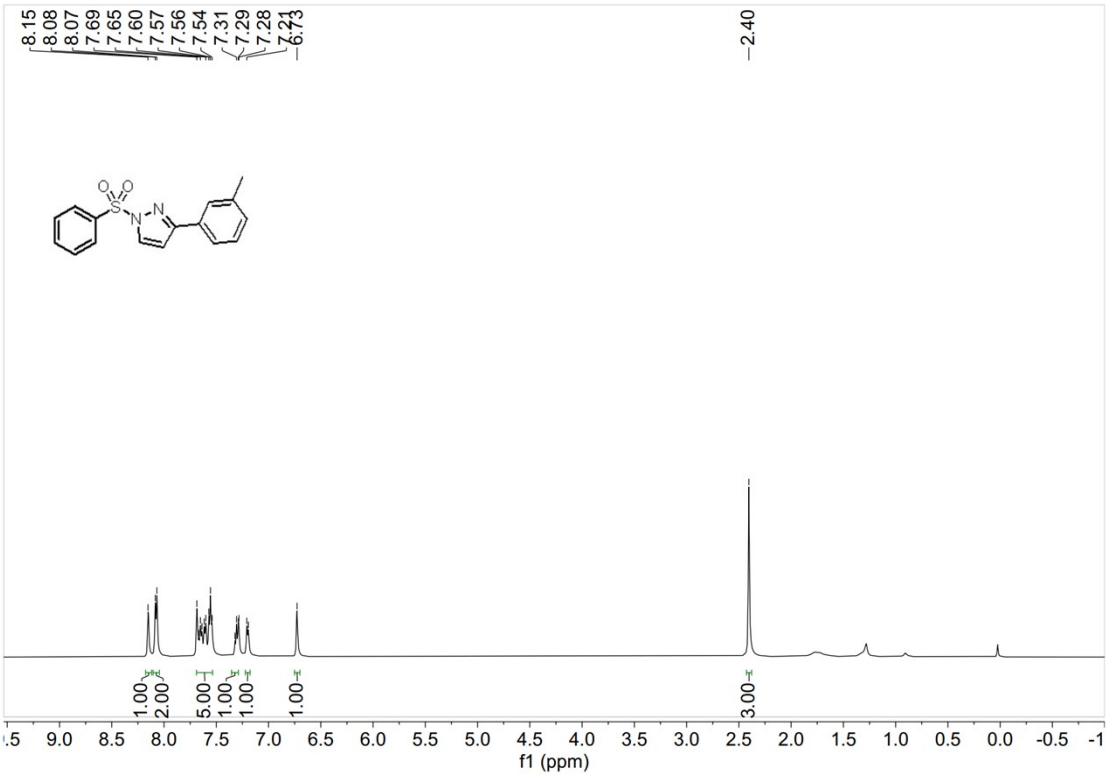
^{13}C NMR (101 MHz, $CDCl_3$) of **24**



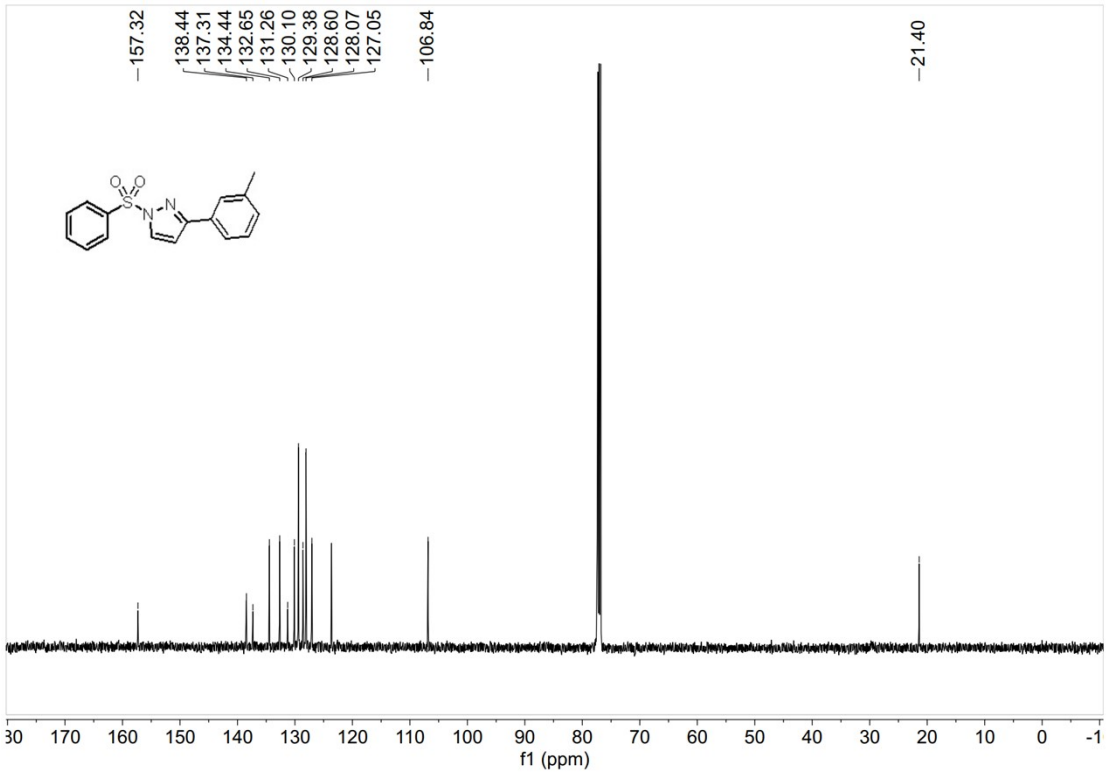
^{1}H NMR (400 MHz, $CDCl_3$) of **25**



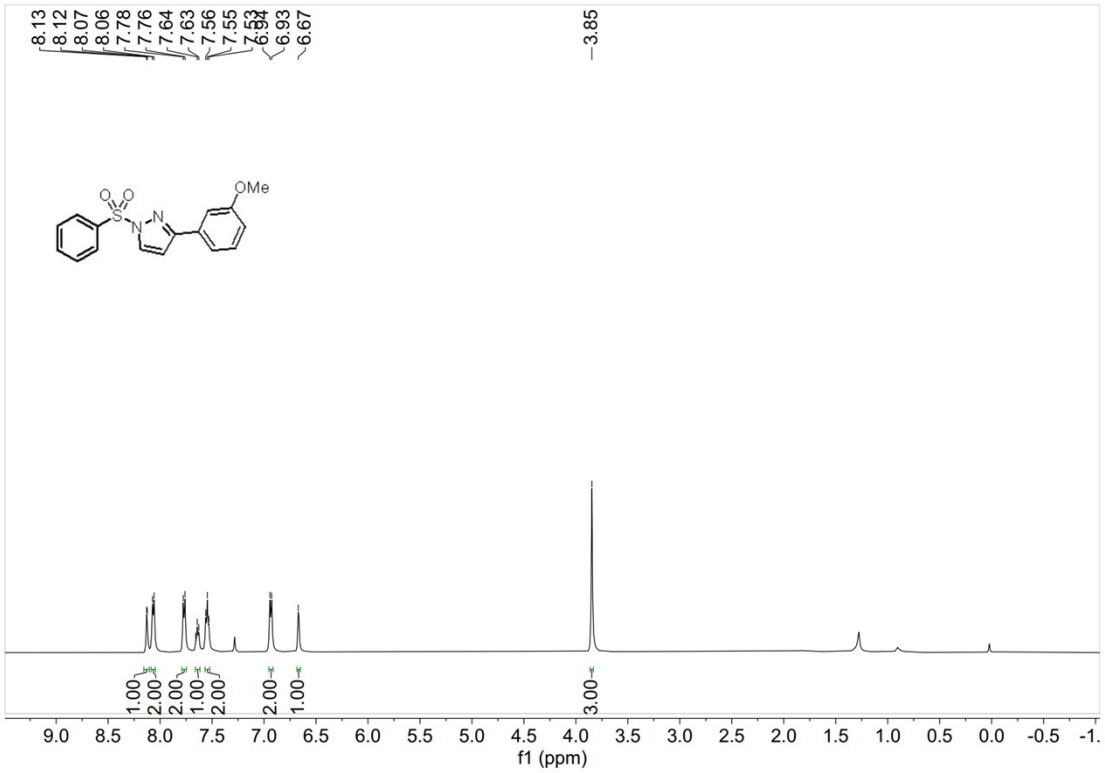
^{13}C NMR (101 MHz, $CDCl_3$) of **25**



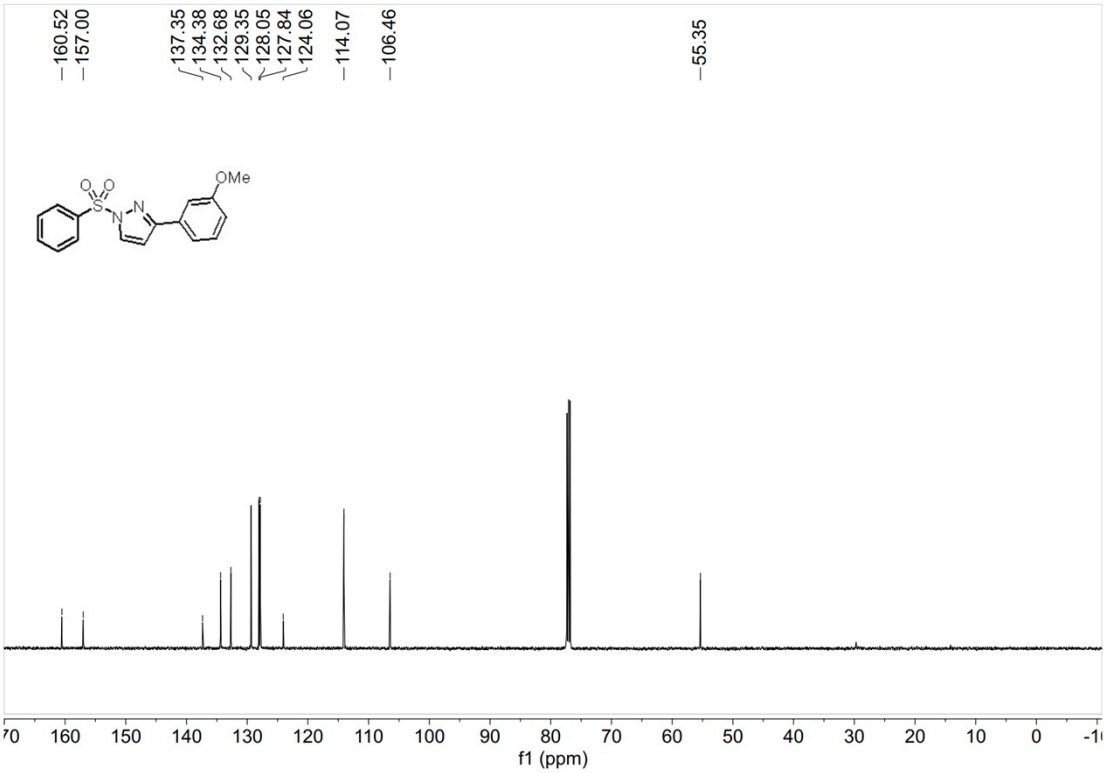
^{1}H NMR (400 MHz, $CDCl_3$) of **26**



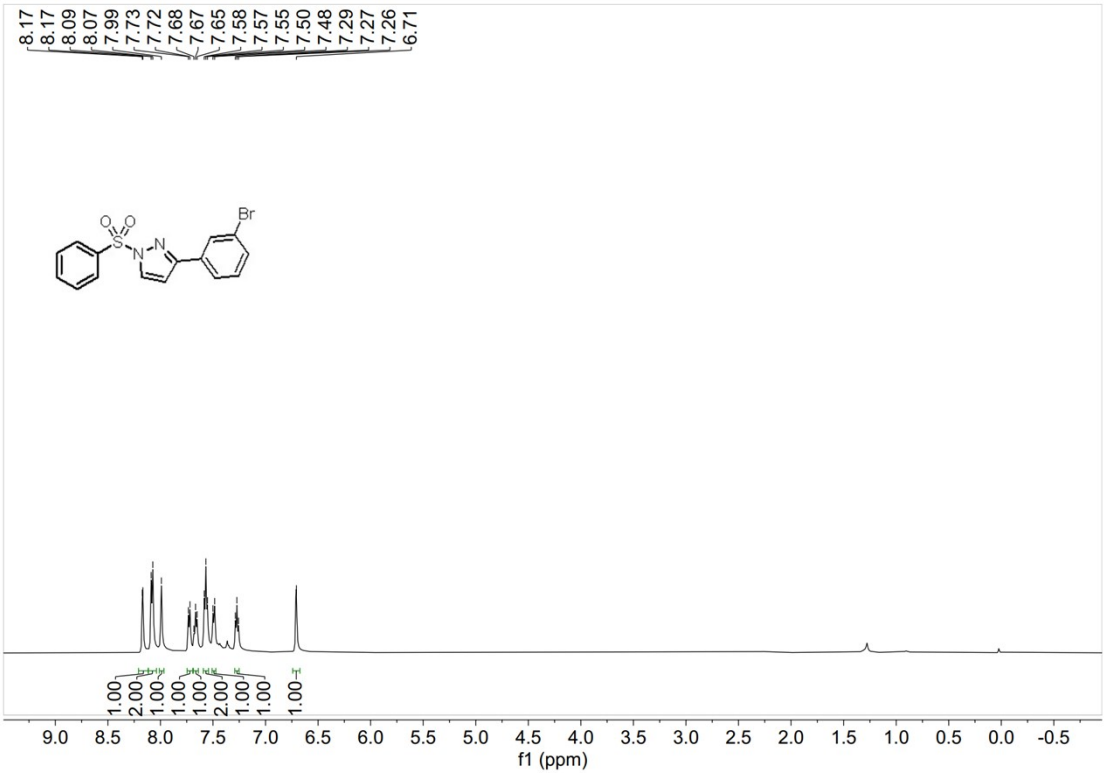
^{13}C NMR (101 MHz, $CDCl_3$) of **26**



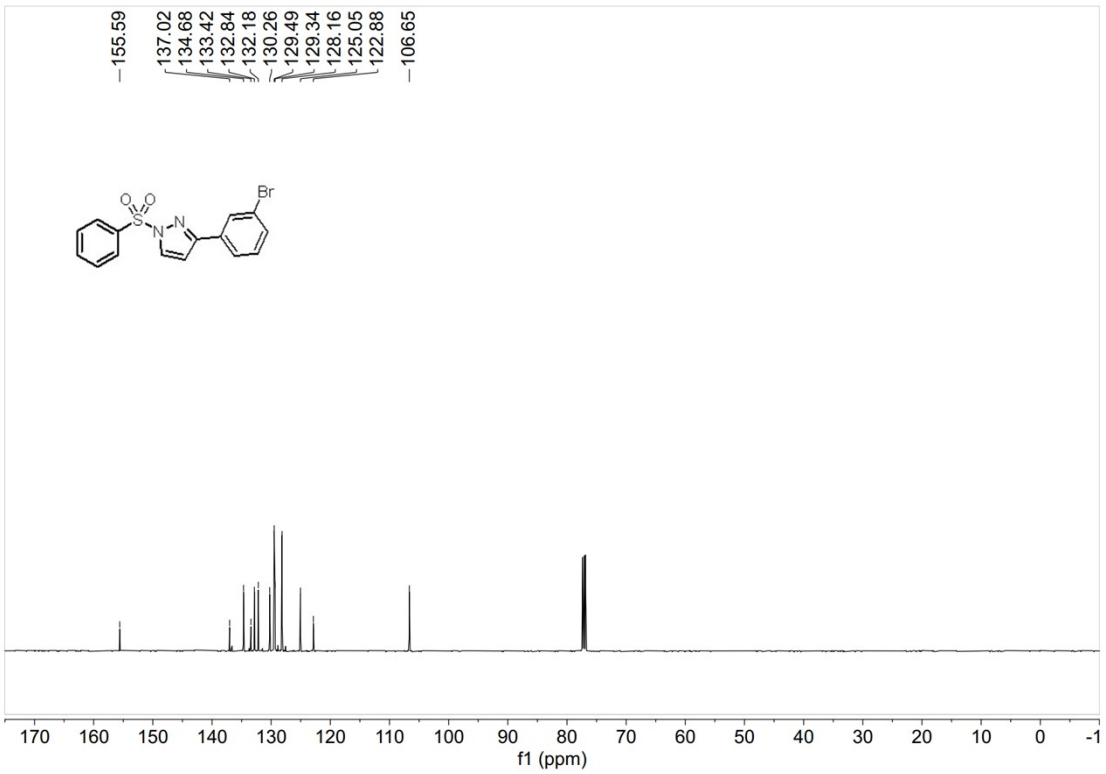
^{1}H NMR (400 MHz, $CDCl_3$) of **27**



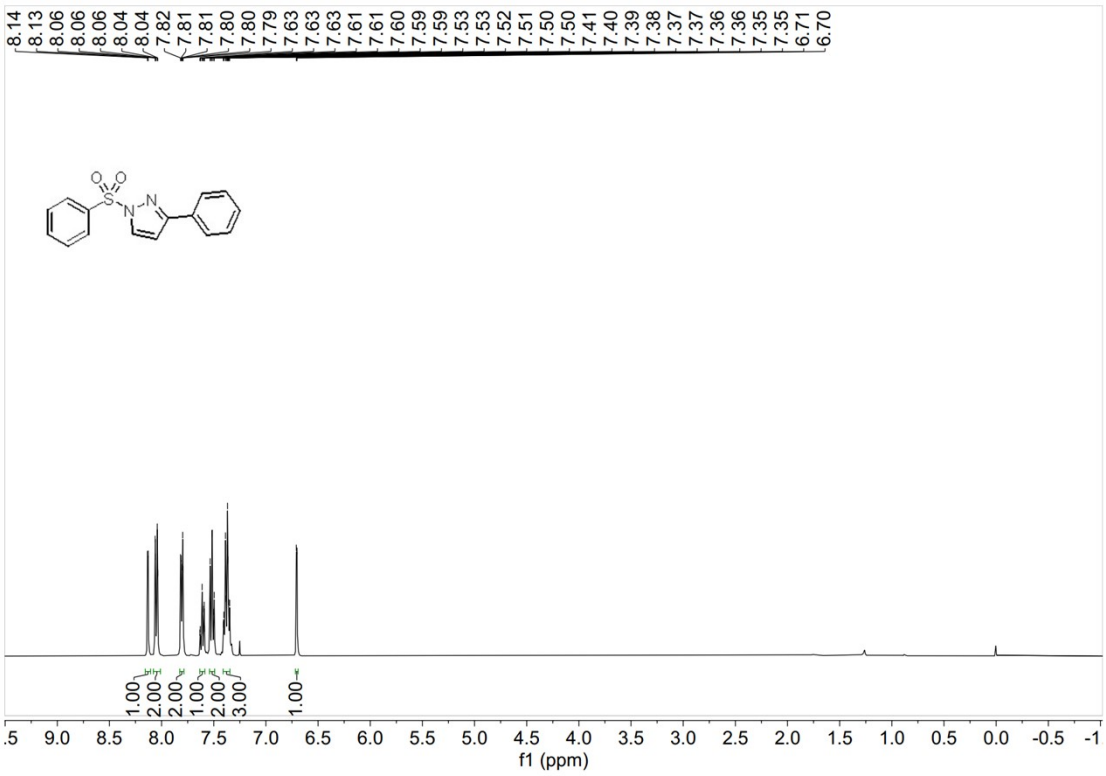
^{13}C NMR (101 MHz, $CDCl_3$) of **27**



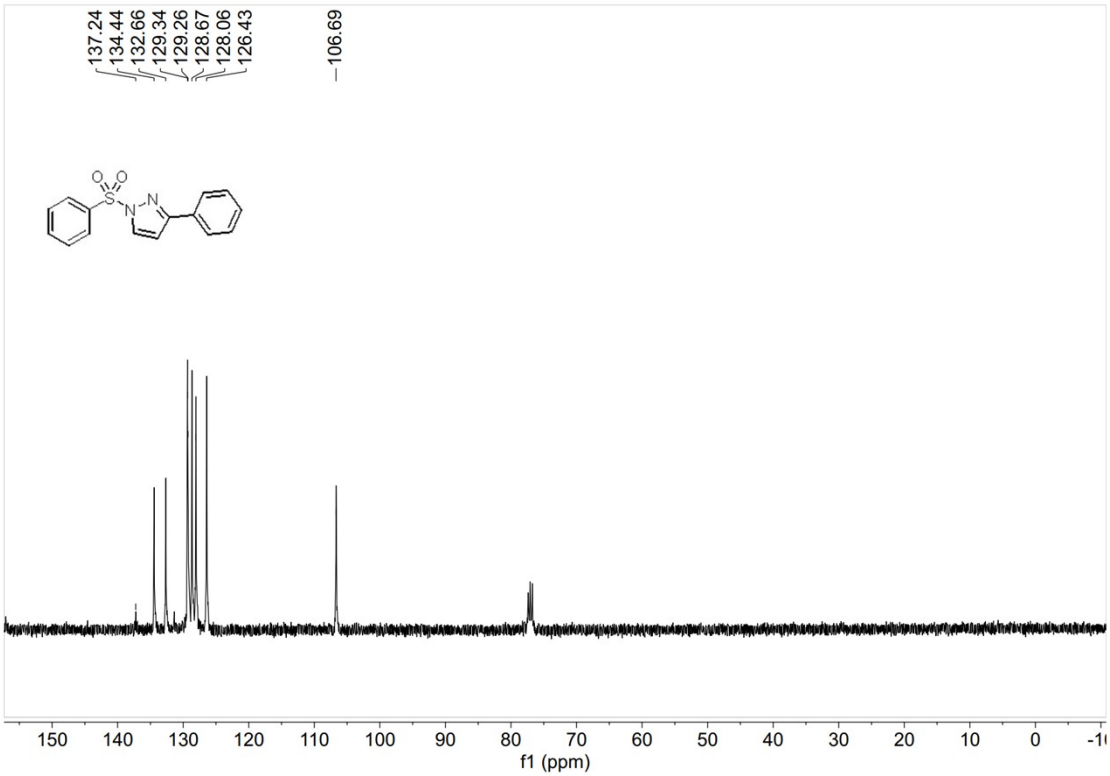
^{1}H NMR (400 MHz, $CDCl_3$) of **28**



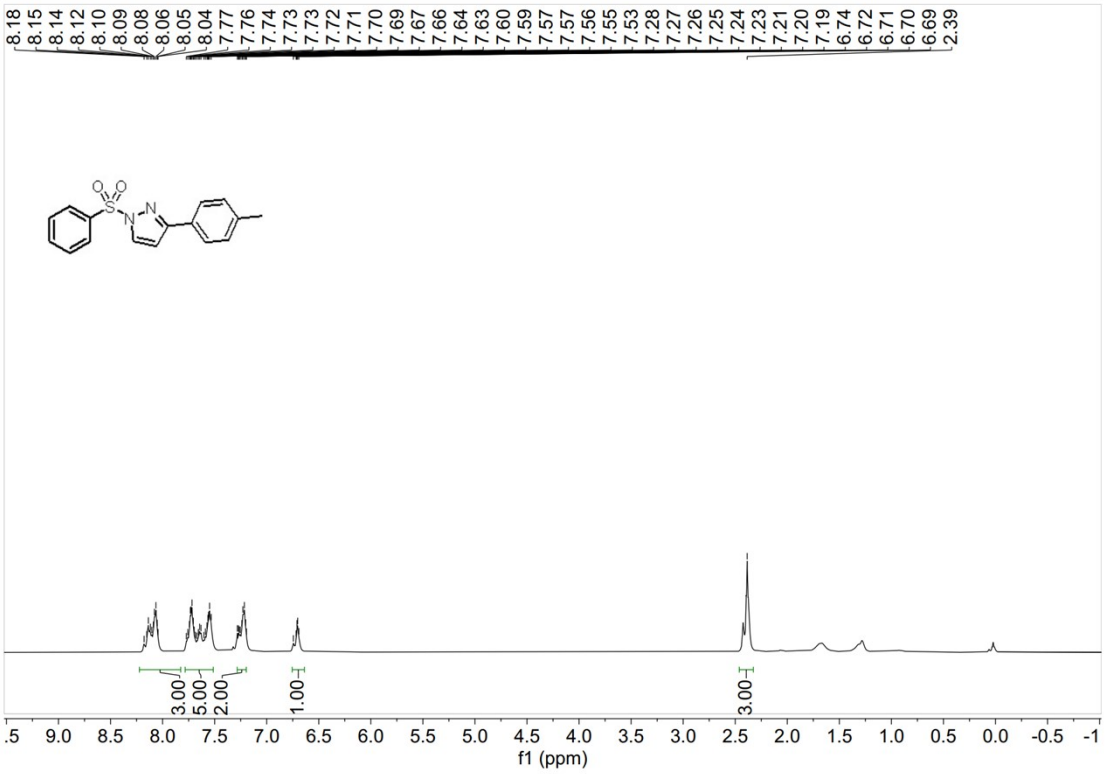
^{13}C NMR (101 MHz, $CDCl_3$) of **28**



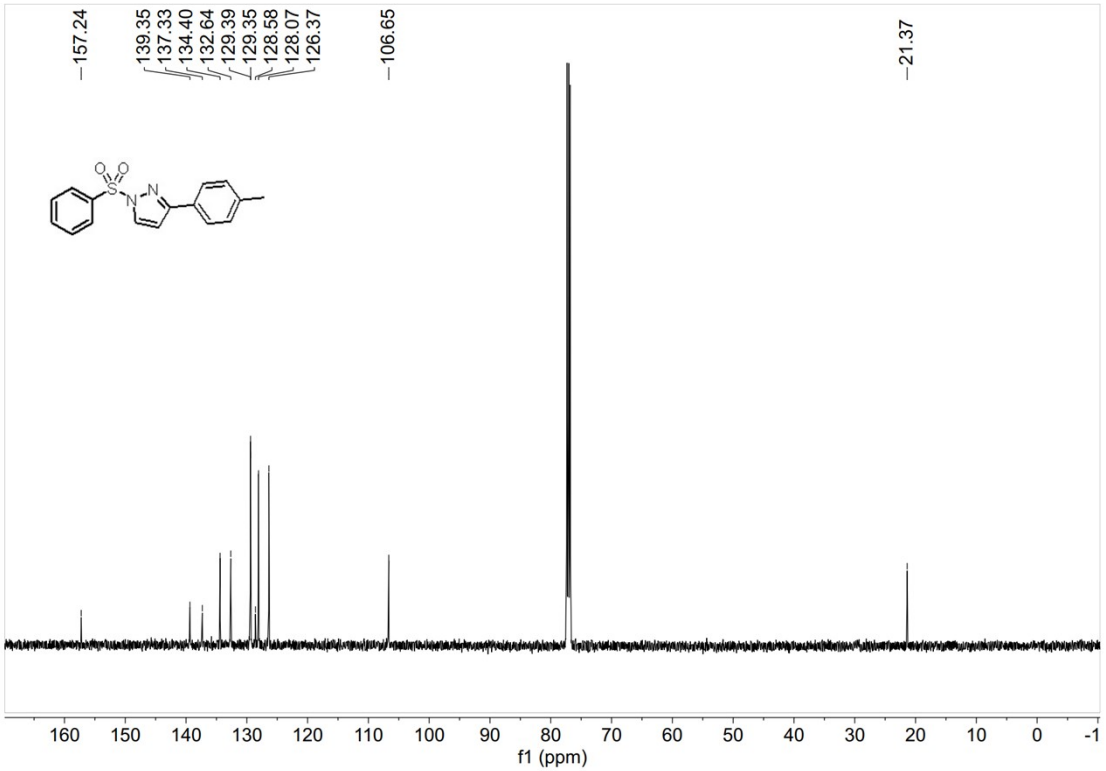
^{1}H NMR (400 MHz, $CDCl_3$) of **29**



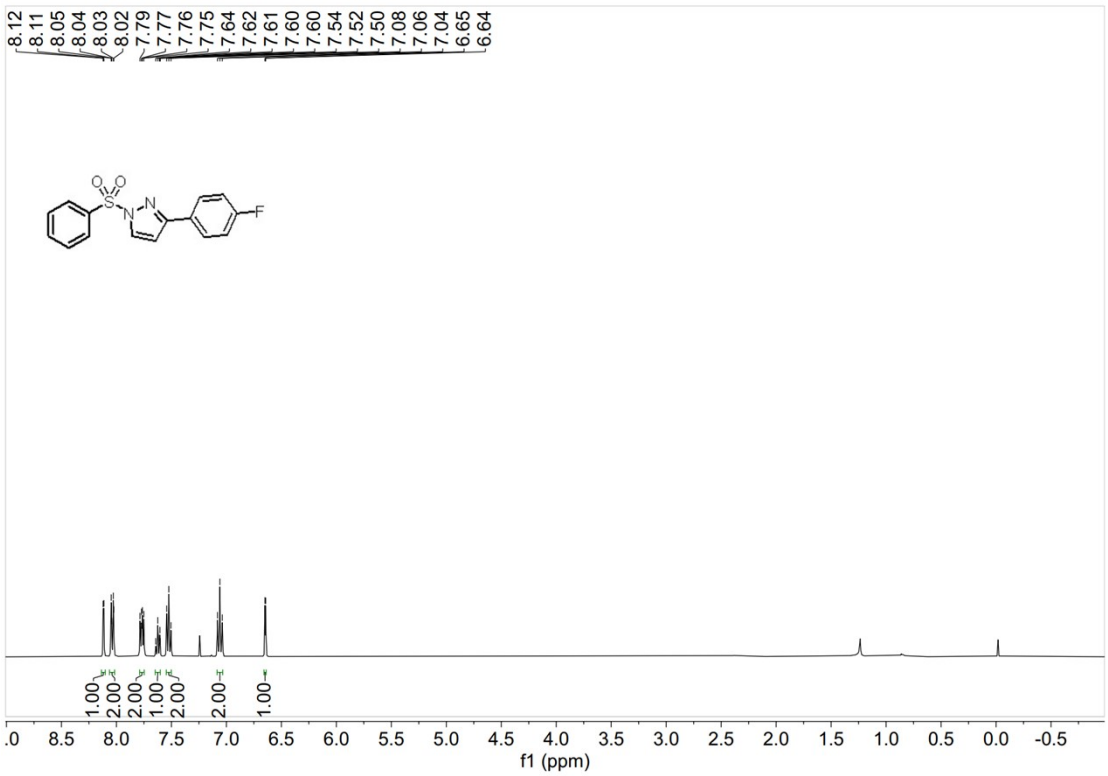
^{13}C NMR (101 MHz, $CDCl_3$) of **29**



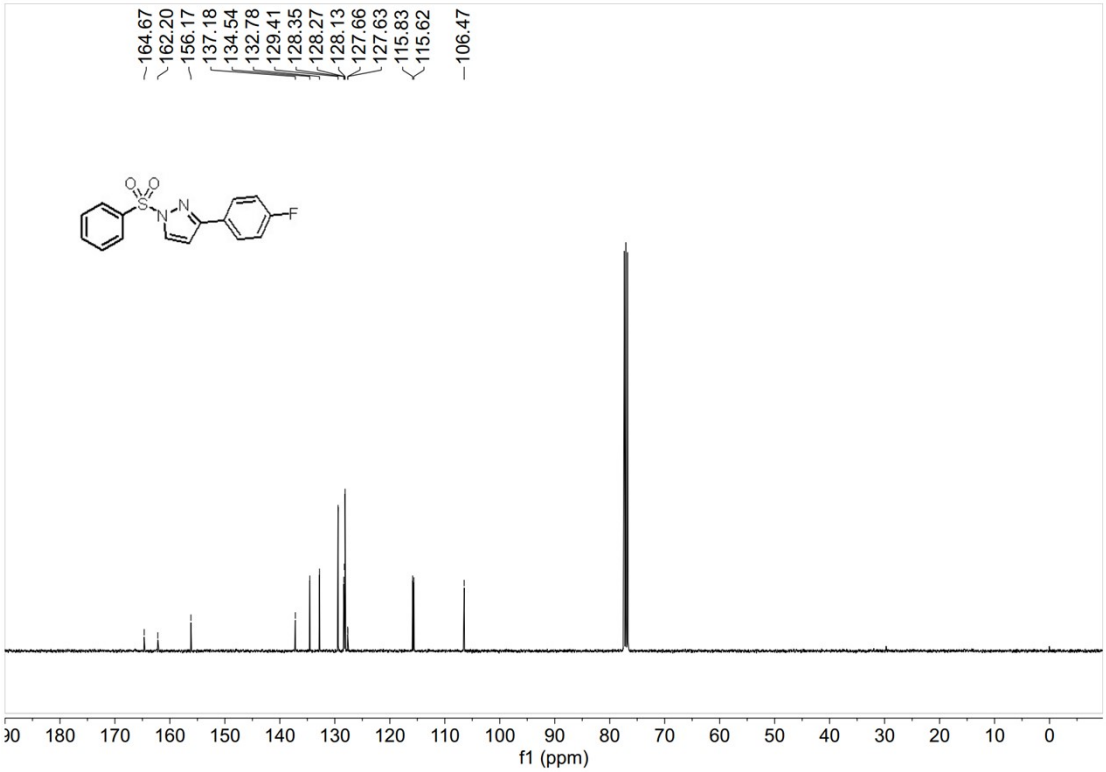
^{1}H NMR (400 MHz, $CDCl_3$) of **30**



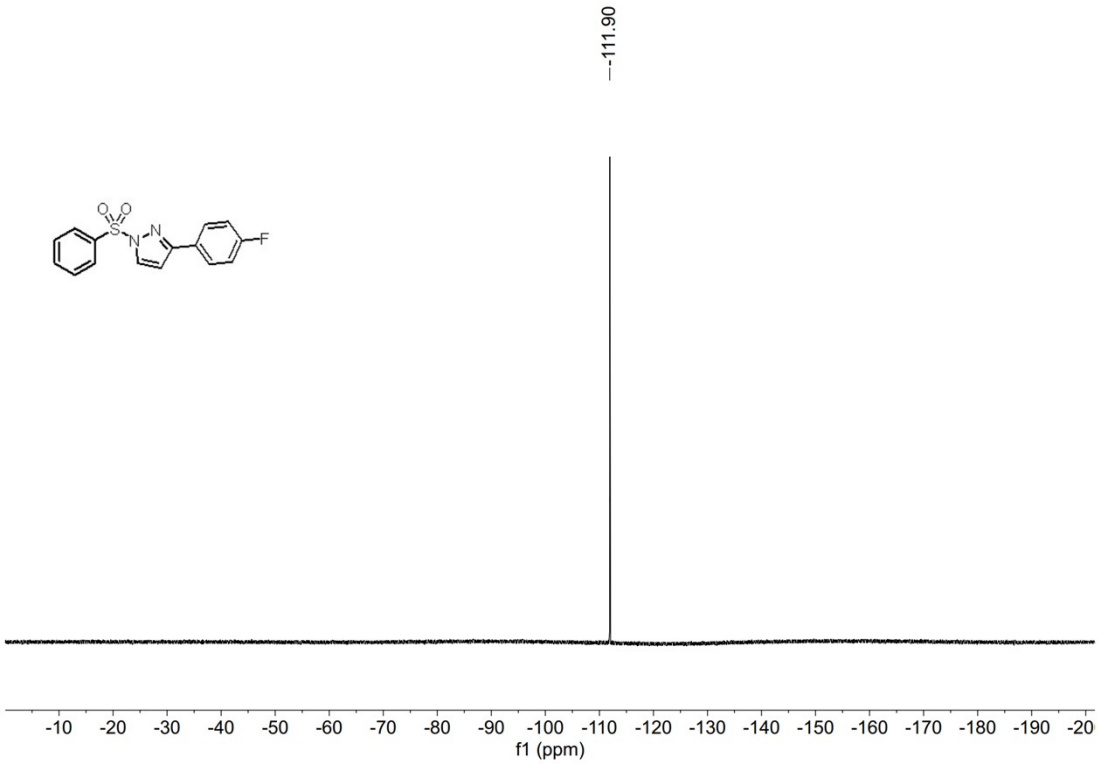
^{13}C NMR (101 MHz, $CDCl_3$) of **30**



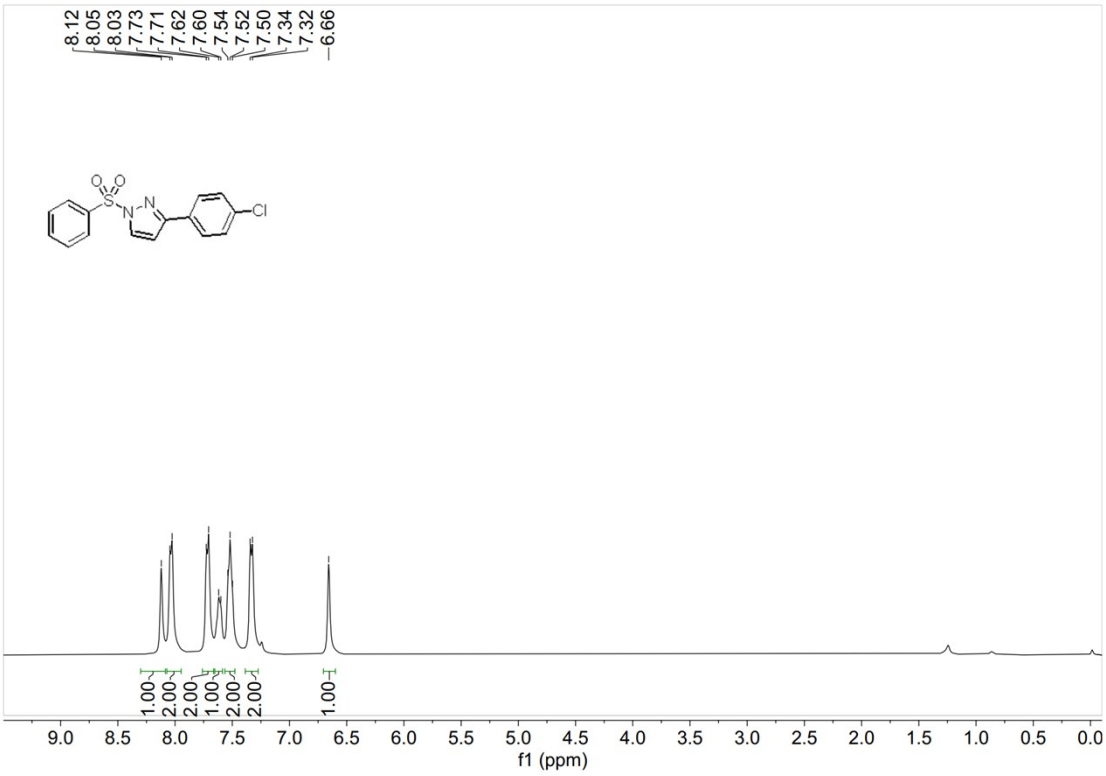
^{1}H NMR (400 MHz, $CDCl_3$) of **31**



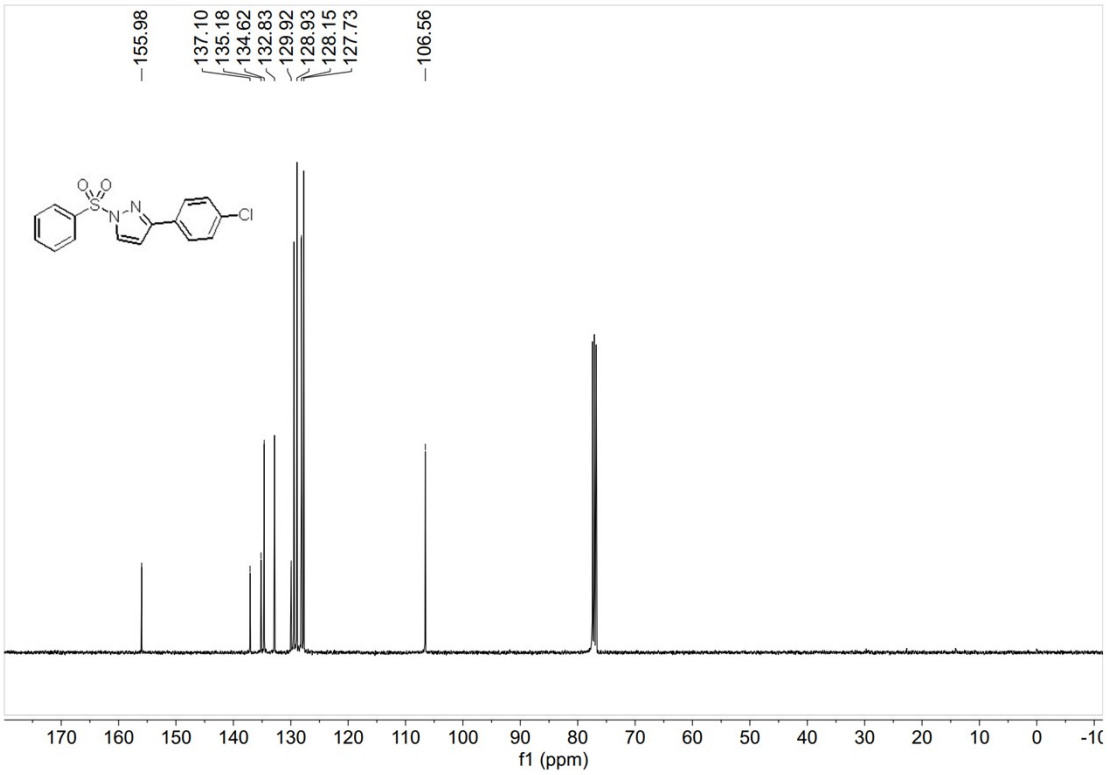
^{13}C NMR (101 MHz, $CDCl_3$) of **31**



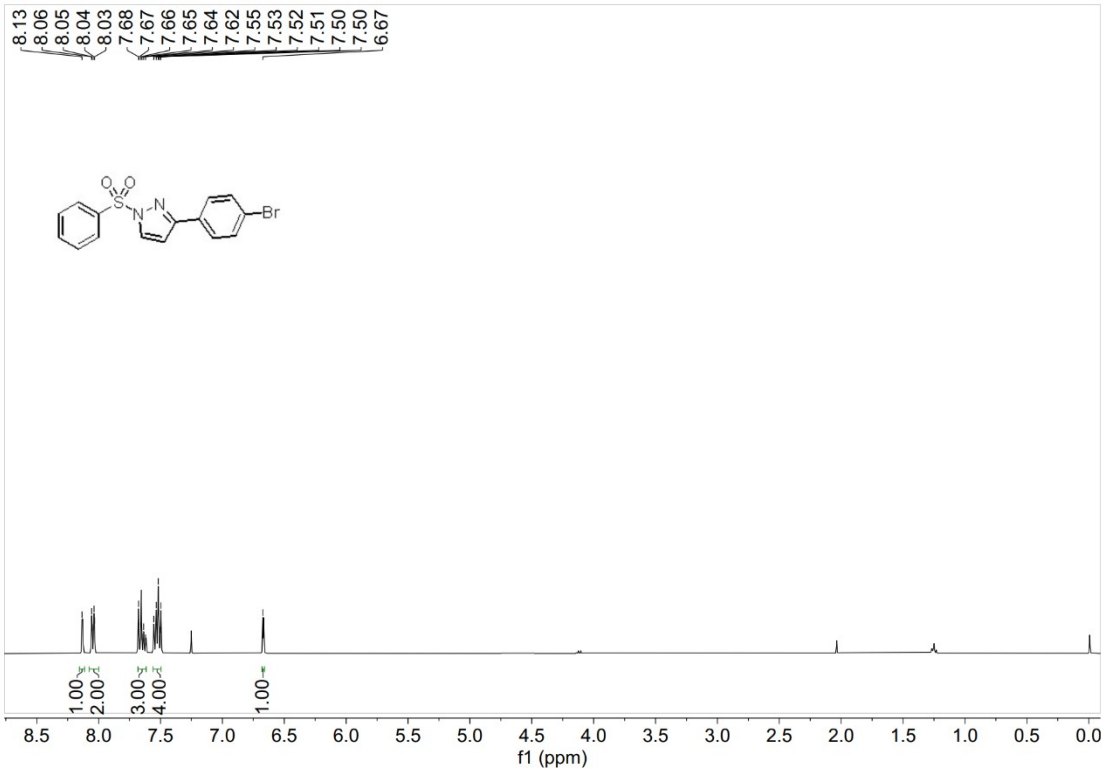
^{19}F NMR (376 MHz, $CDCl_3$) of **31**



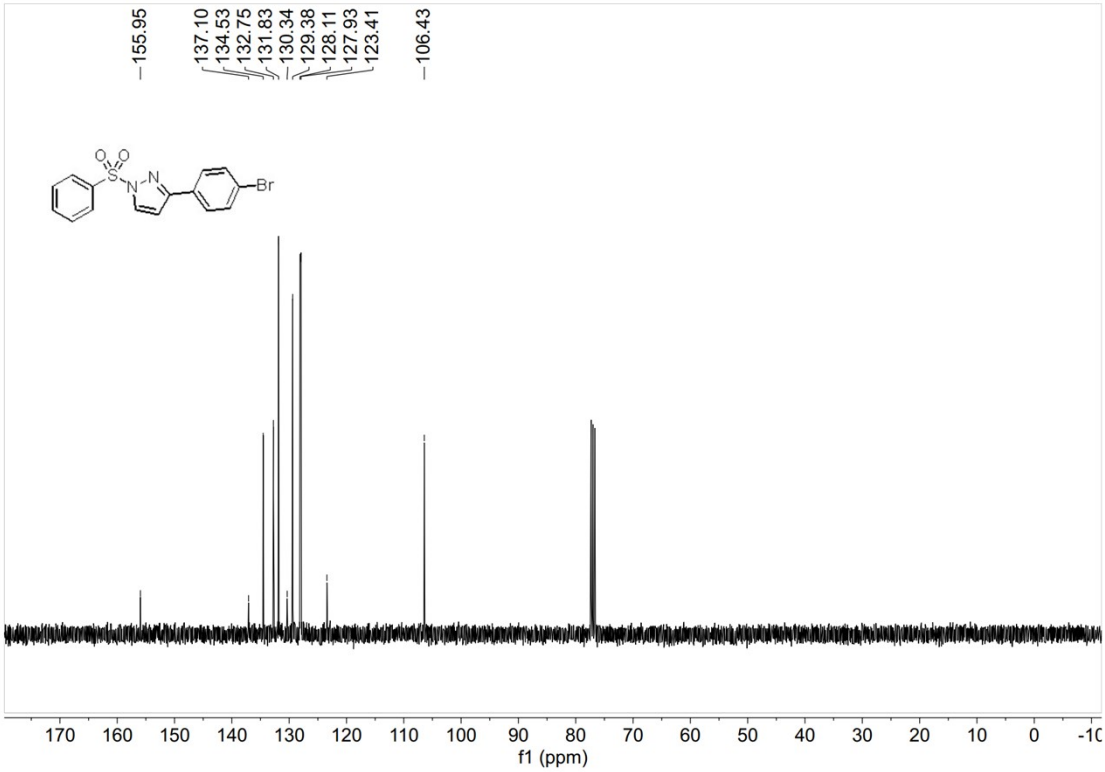
^{1}H NMR (400 MHz, $CDCl_3$) of **32**



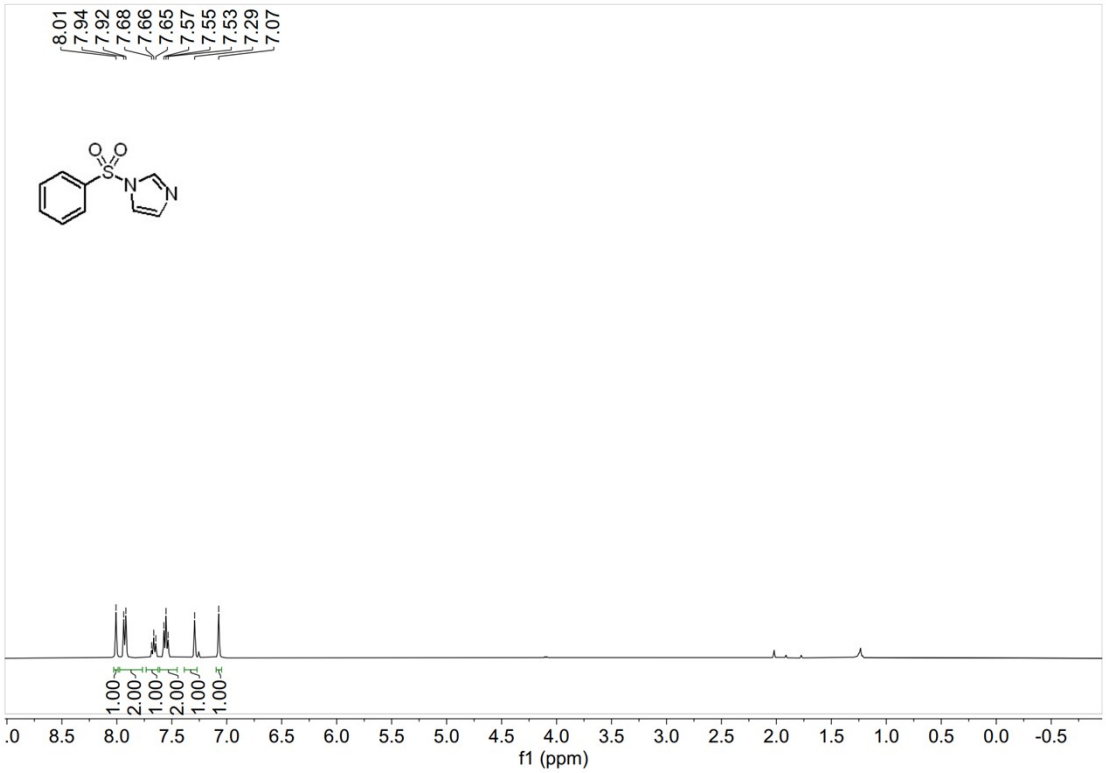
^{13}C NMR (101 MHz, $CDCl_3$) of **32**



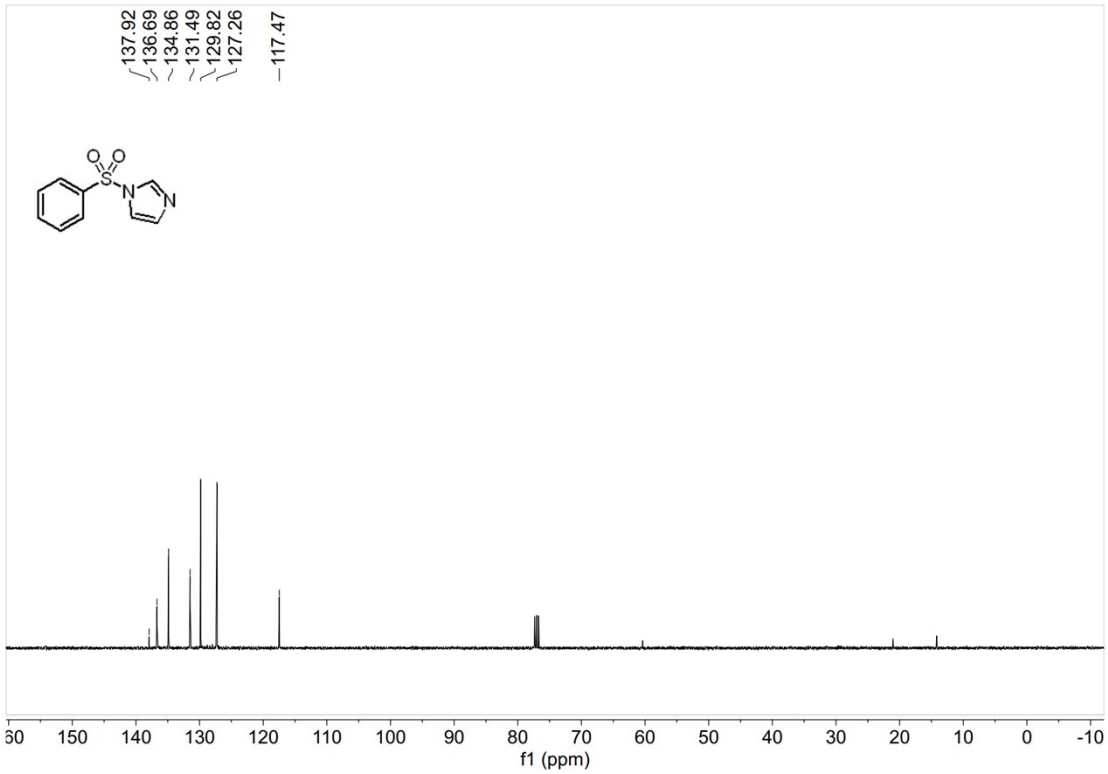
^{1}H NMR (400 MHz, $CDCl_3$) of **33**



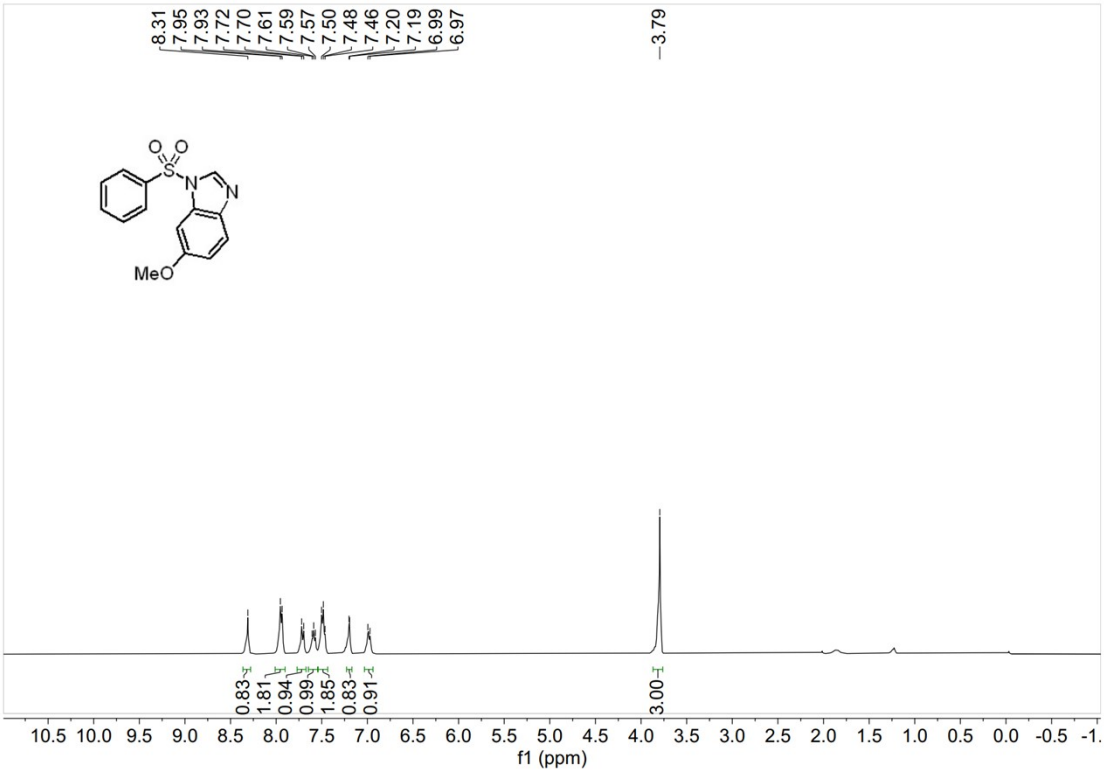
^{13}C NMR (101 MHz, $CDCl_3$) of **33**



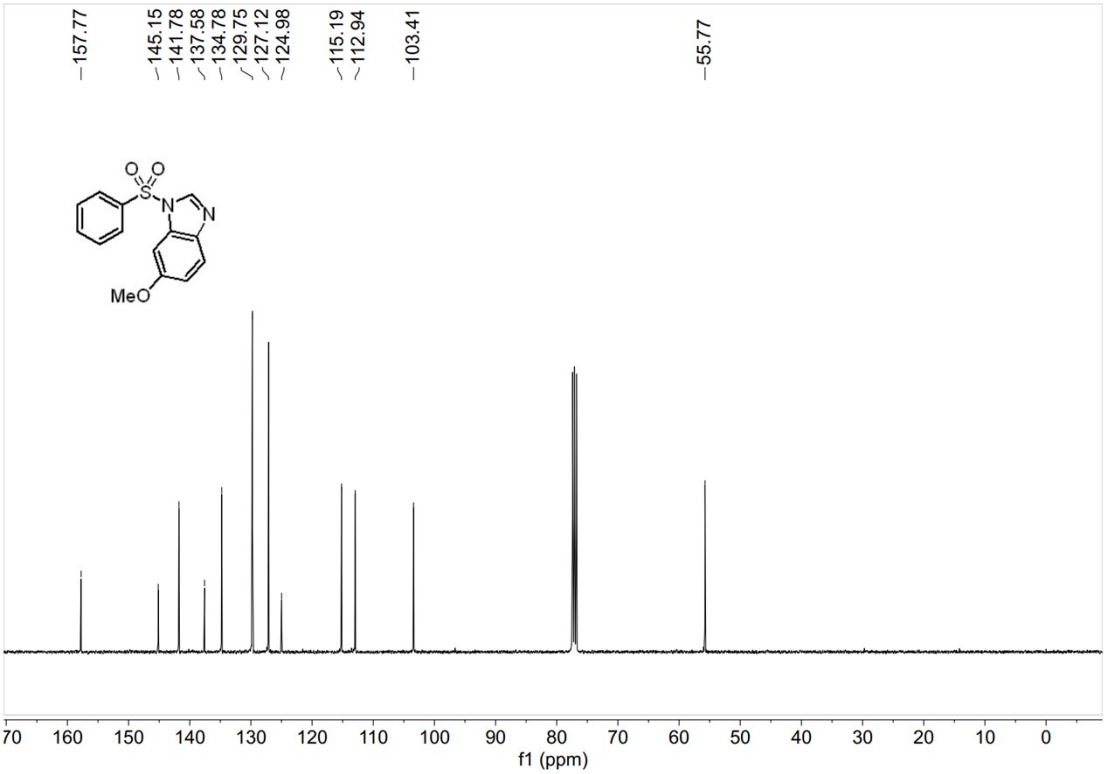
^{1}H NMR (400 MHz, $CDCl_3$) of **34**



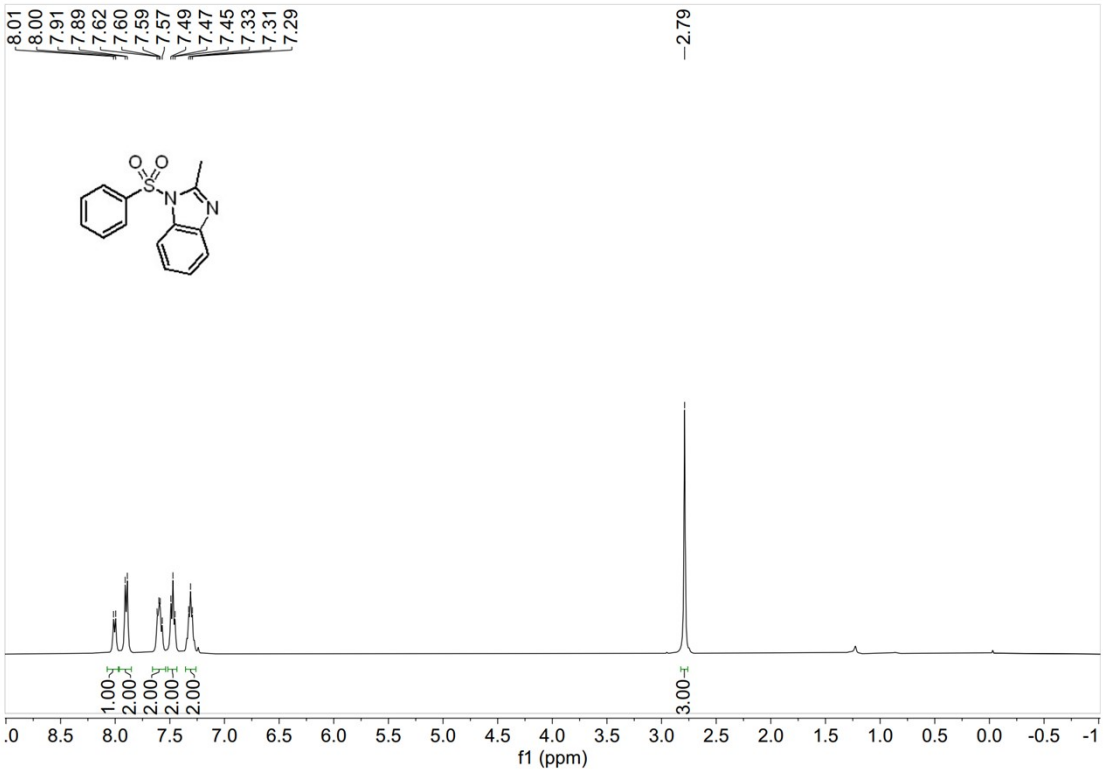
^{13}C NMR (101 MHz, $CDCl_3$) of **34**



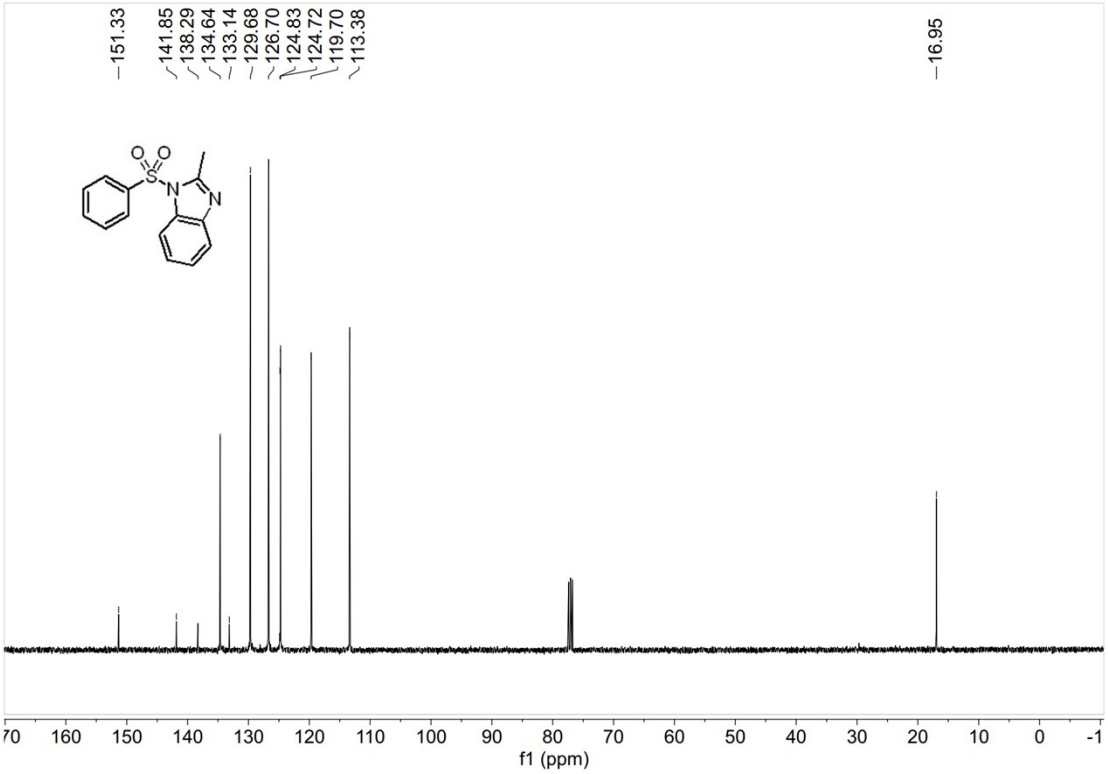
^{1}H NMR (400 MHz, $CDCl_3$) of **35**



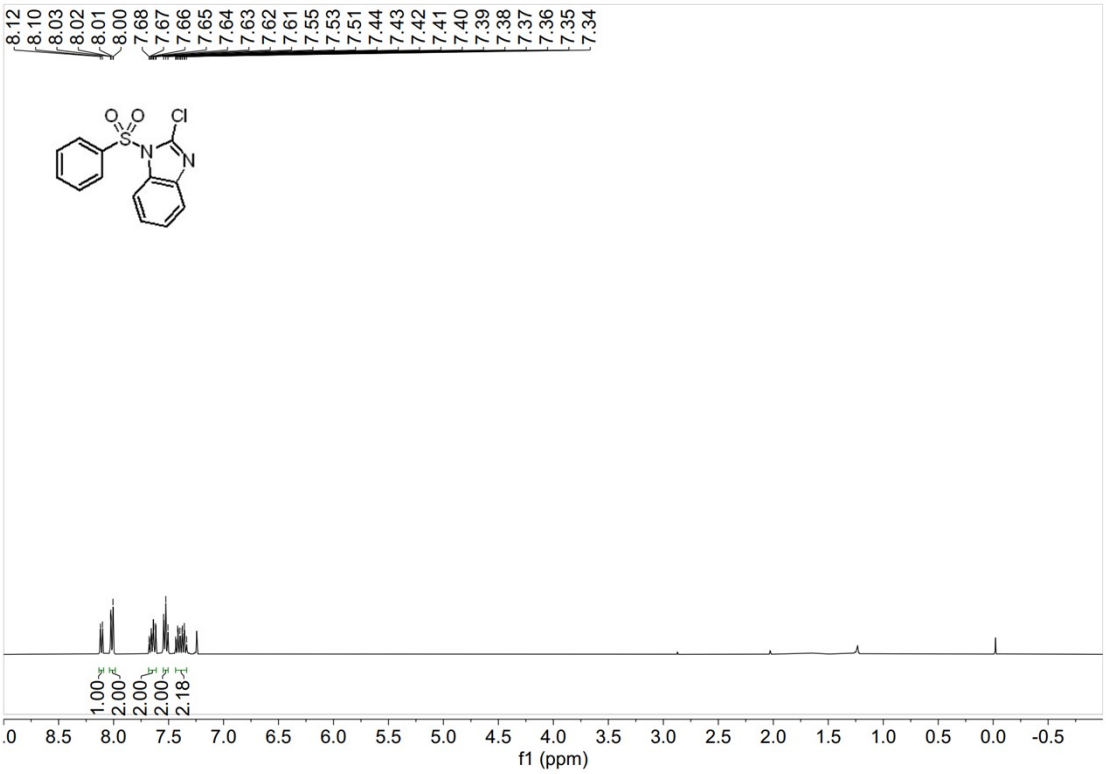
^{13}C NMR (101 MHz, $CDCl_3$) of **35**



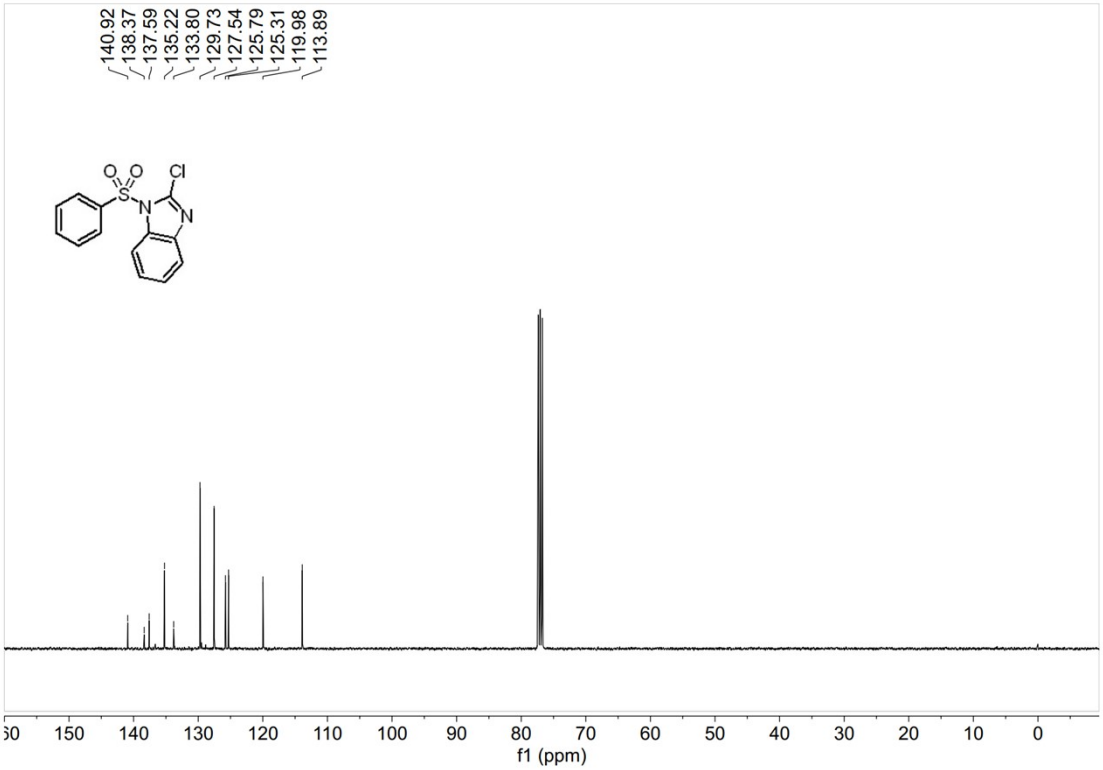
^{1}H NMR (400 MHz, $CDCl_3$) of **36**



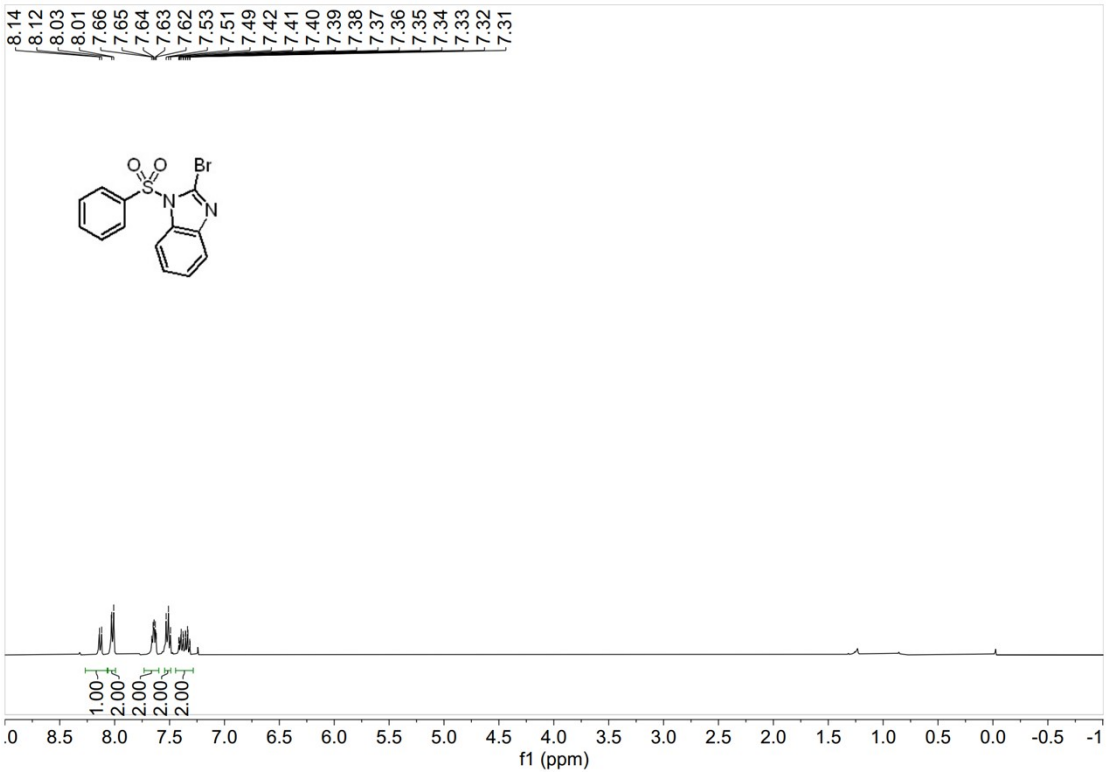
^{13}C NMR (101 MHz, $CDCl_3$) of **36**



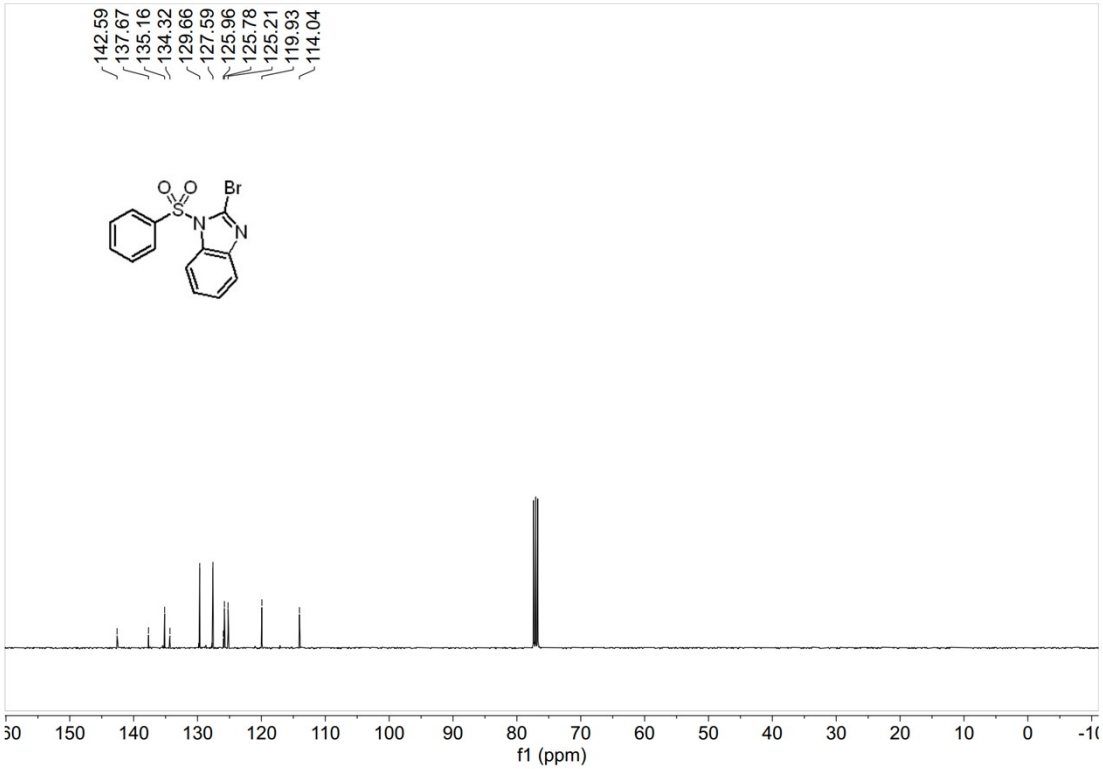
^{1}H NMR (400 MHz, $CDCl_3$) of **37**



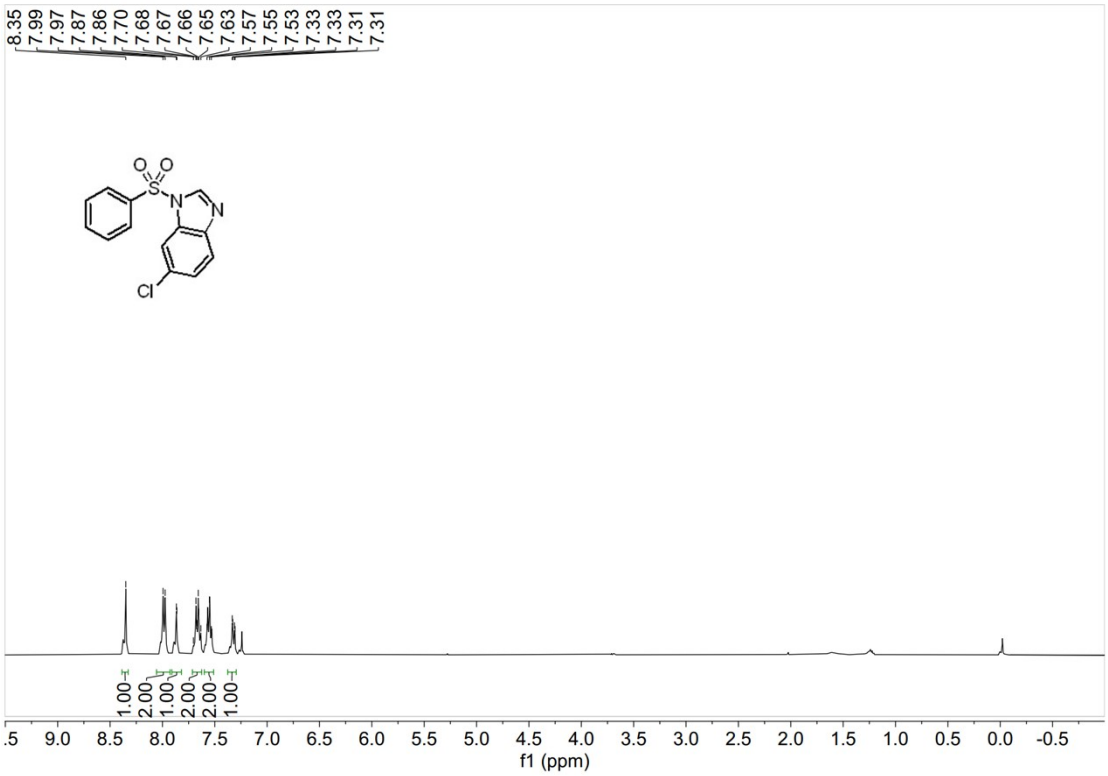
^{13}C NMR (101 MHz, $CDCl_3$) of **37**



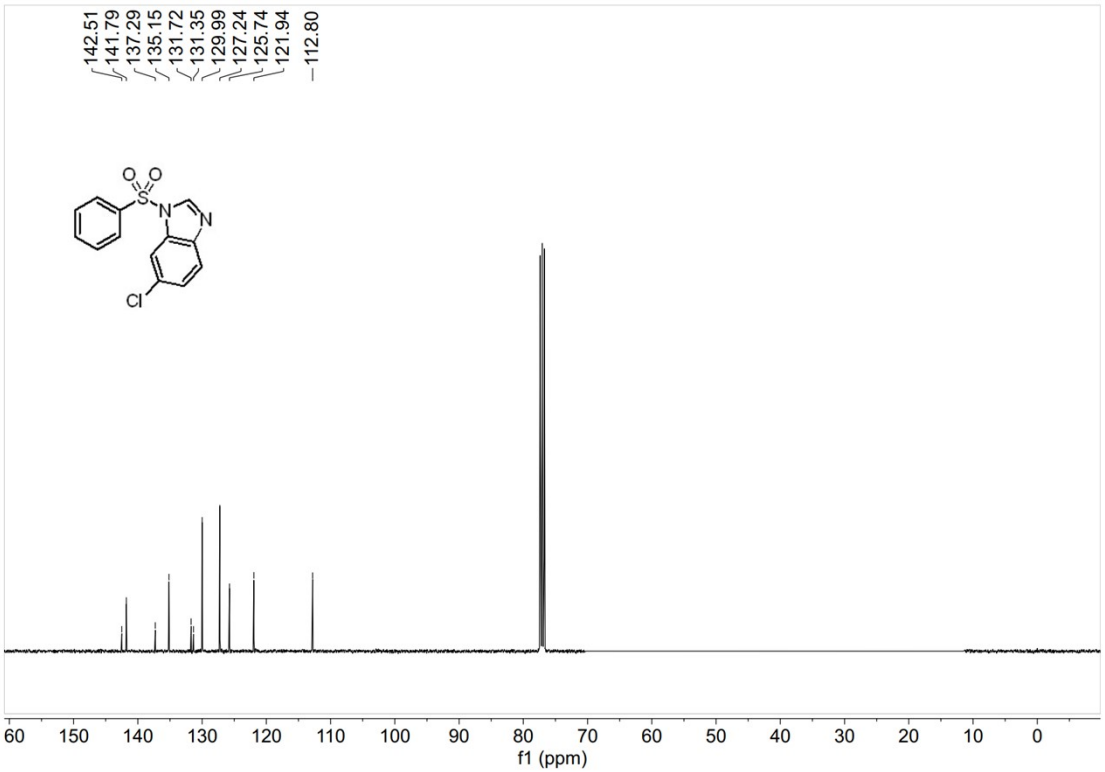
^{1}H NMR (400 MHz, $CDCl_3$) of **38**



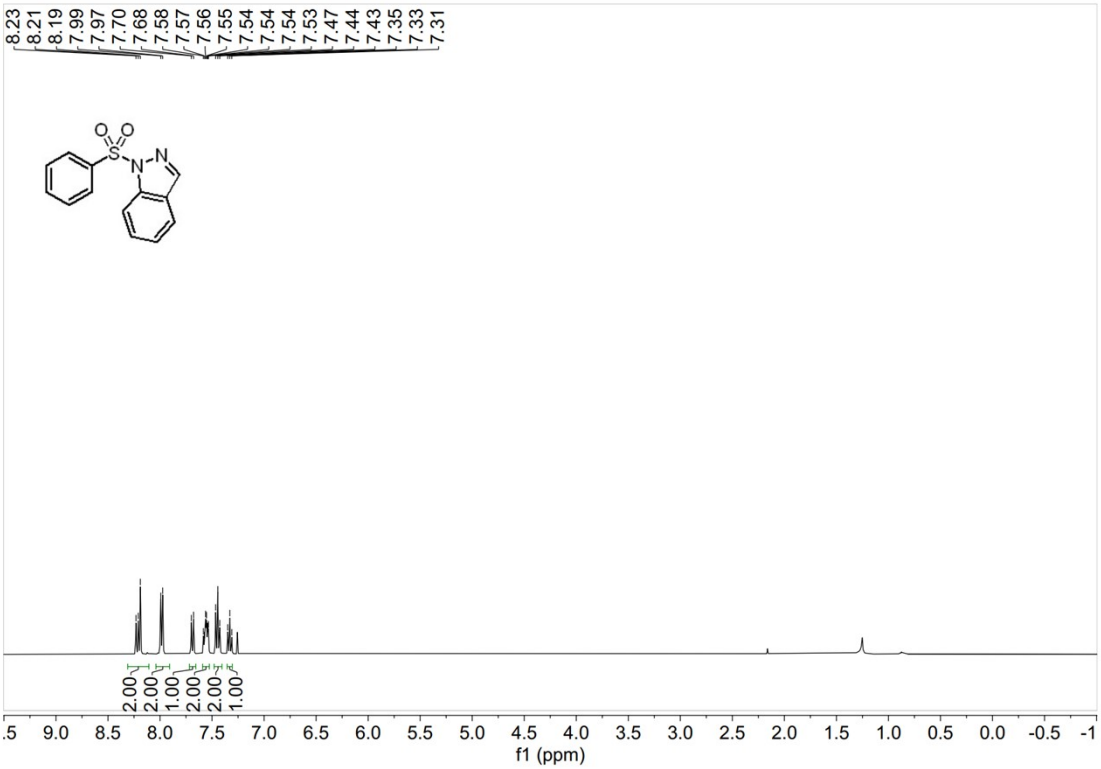
^{13}C NMR (101 MHz, $CDCl_3$) of **38**



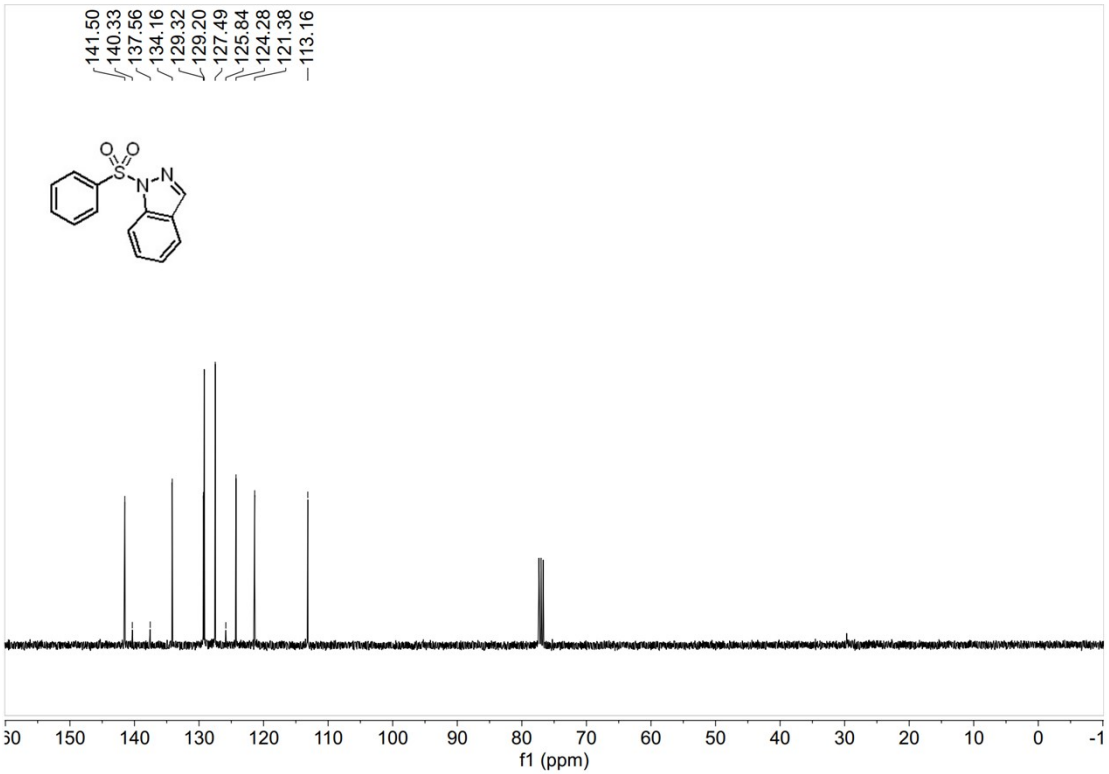
^{1}H NMR (400 MHz, $CDCl_3$) of **39**



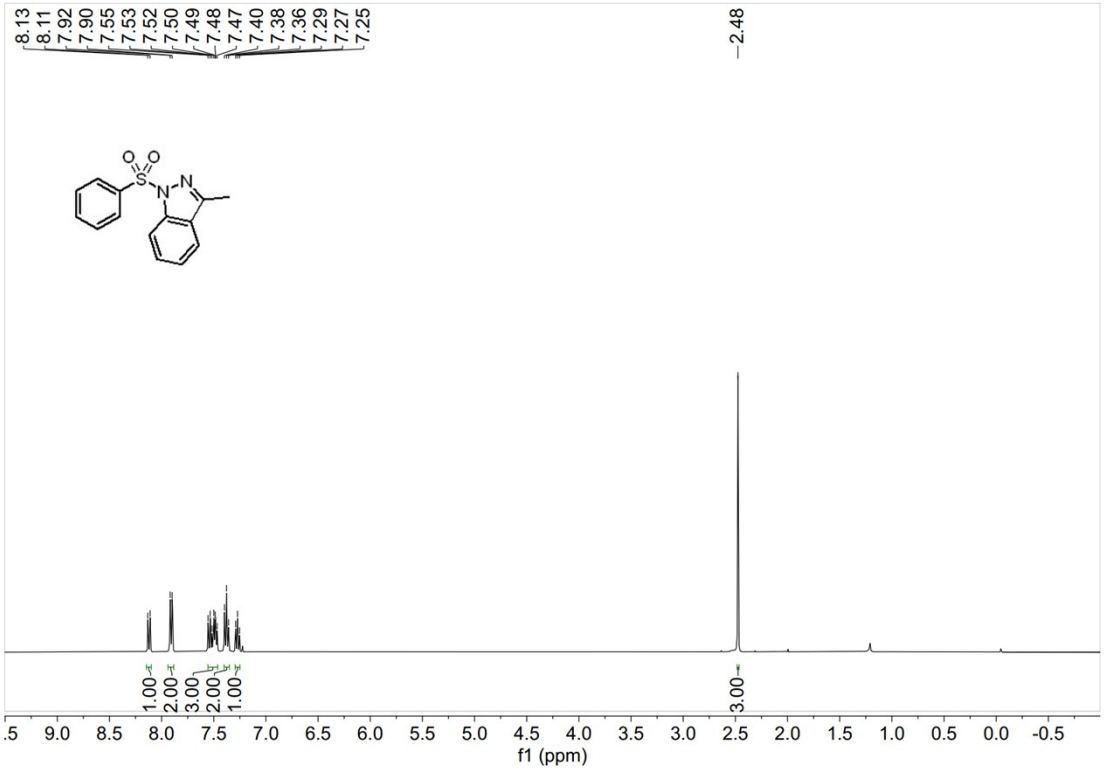
^{13}C NMR (101 MHz, $CDCl_3$) of **39**



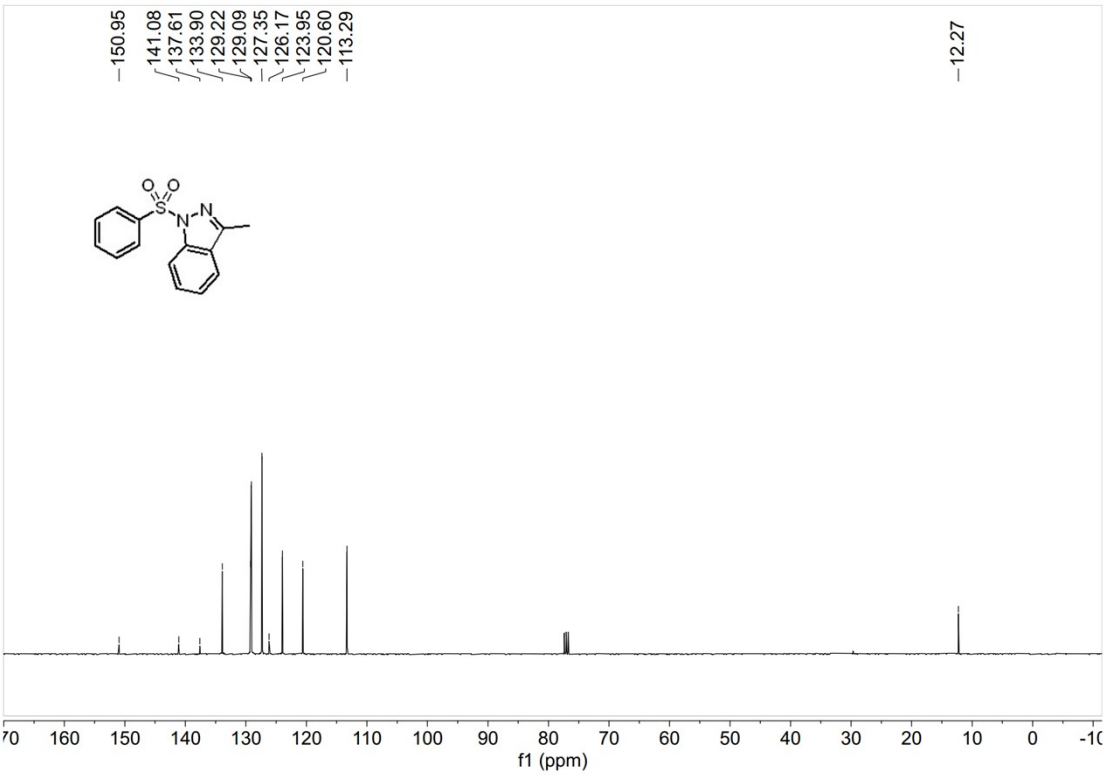
^{1}H NMR (400 MHz, $CDCl_3$) of **40**



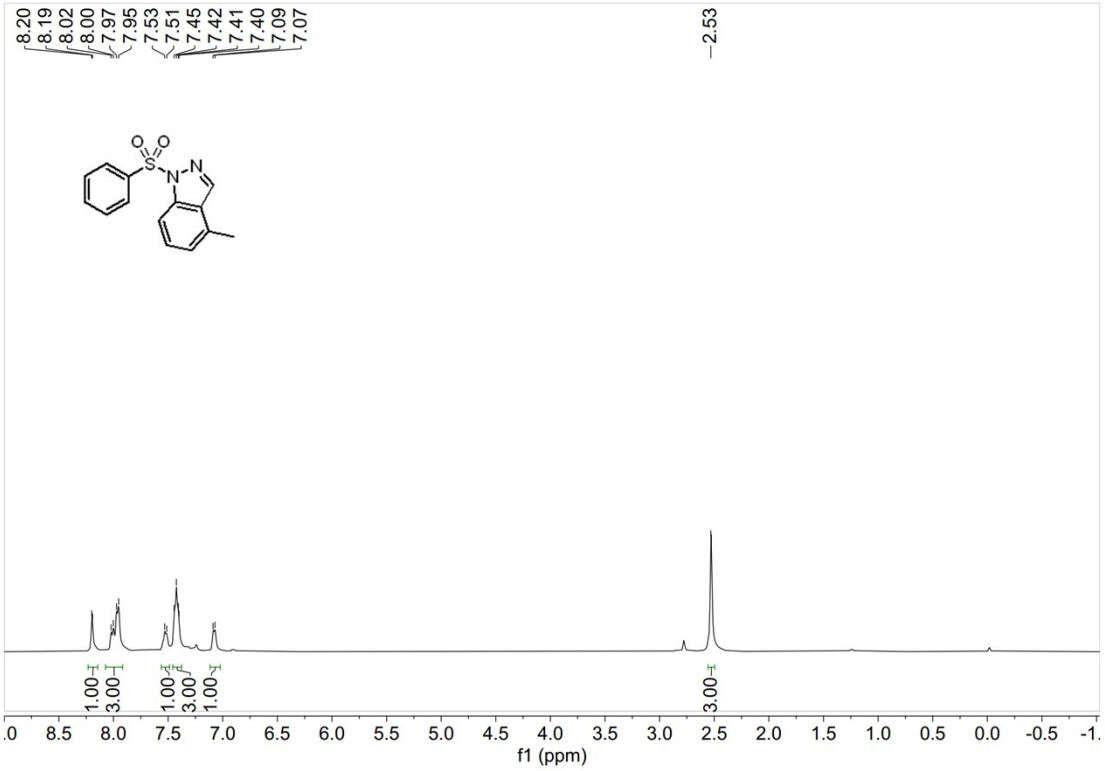
^{13}C NMR (101 MHz, $CDCl_3$) of **40**



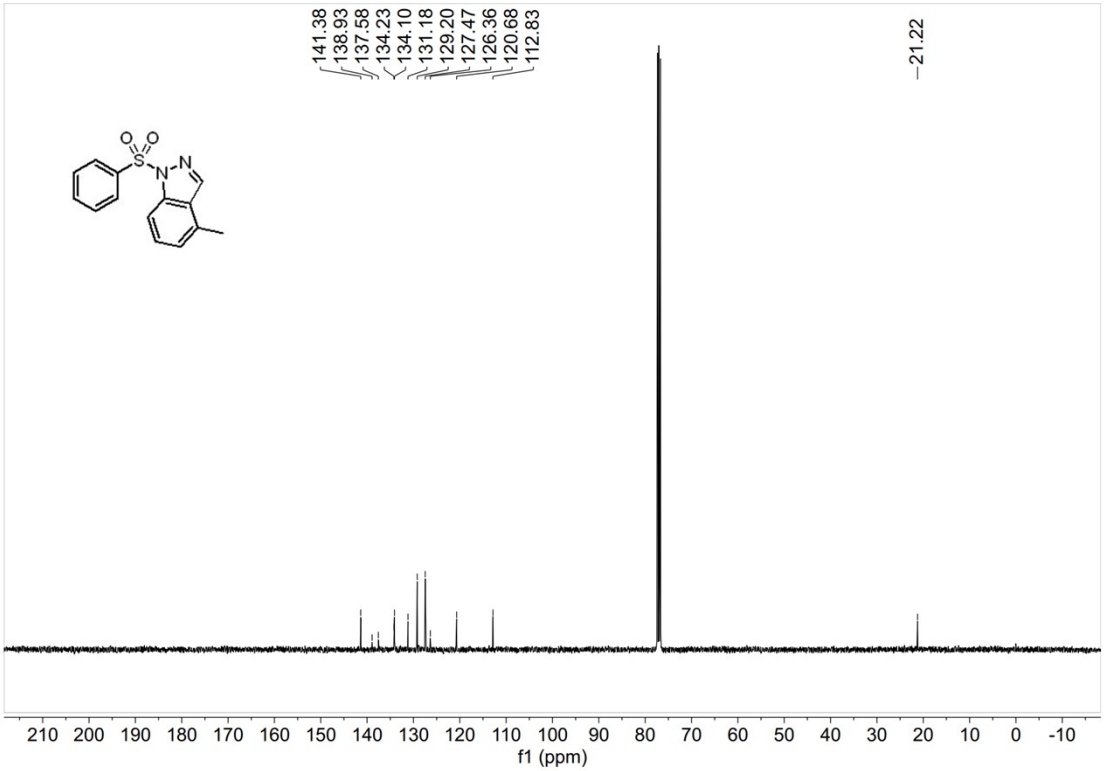
^{1}H NMR (400 MHz, $CDCl_3$) of **41**



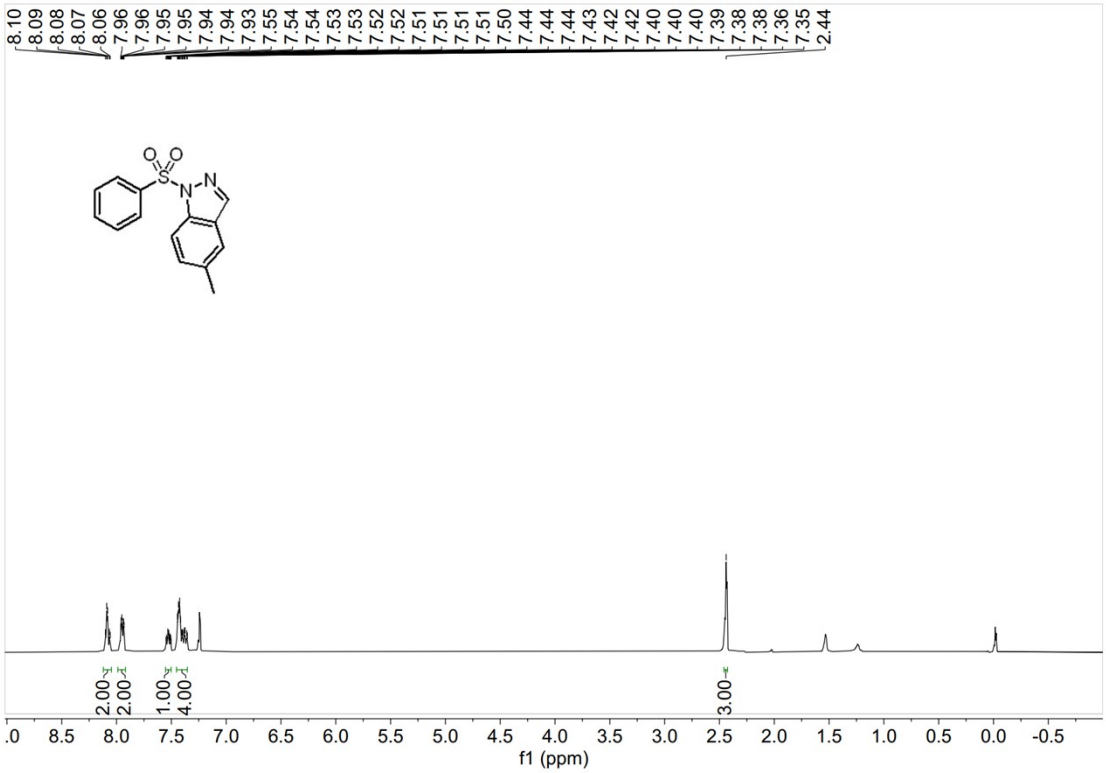
^{13}C NMR (101 MHz, $CDCl_3$) of **41**



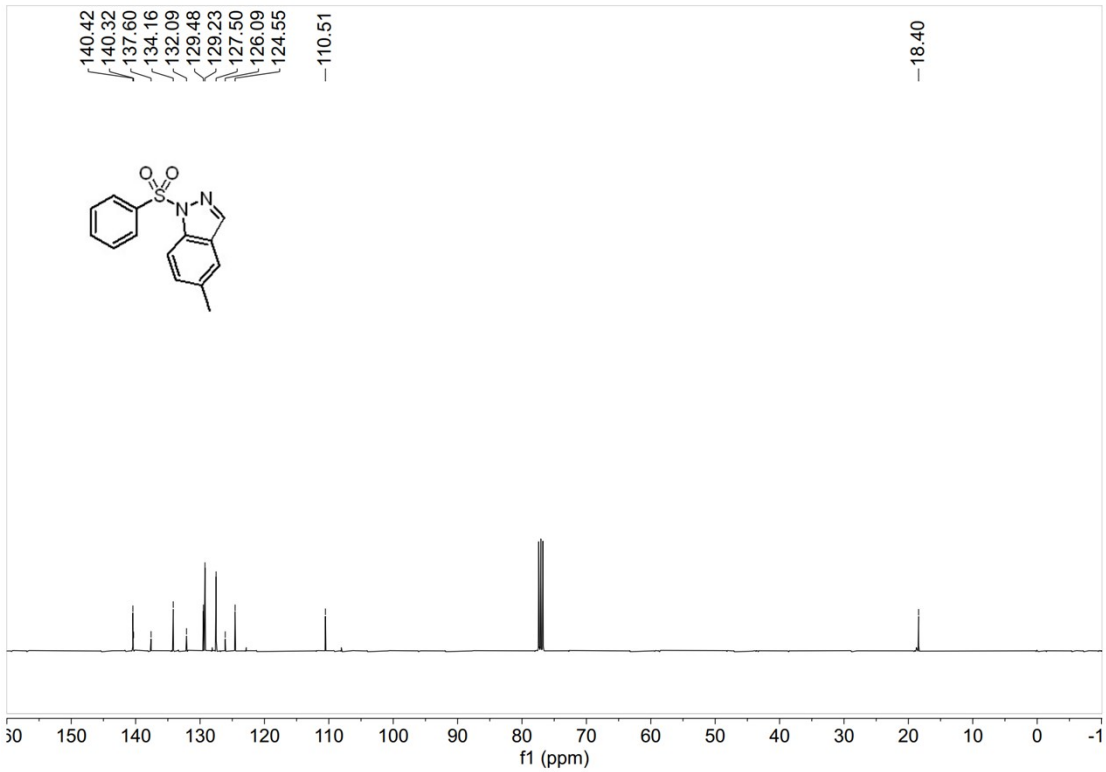
^{1}H NMR (400 MHz, $CDCl_3$) of **42**



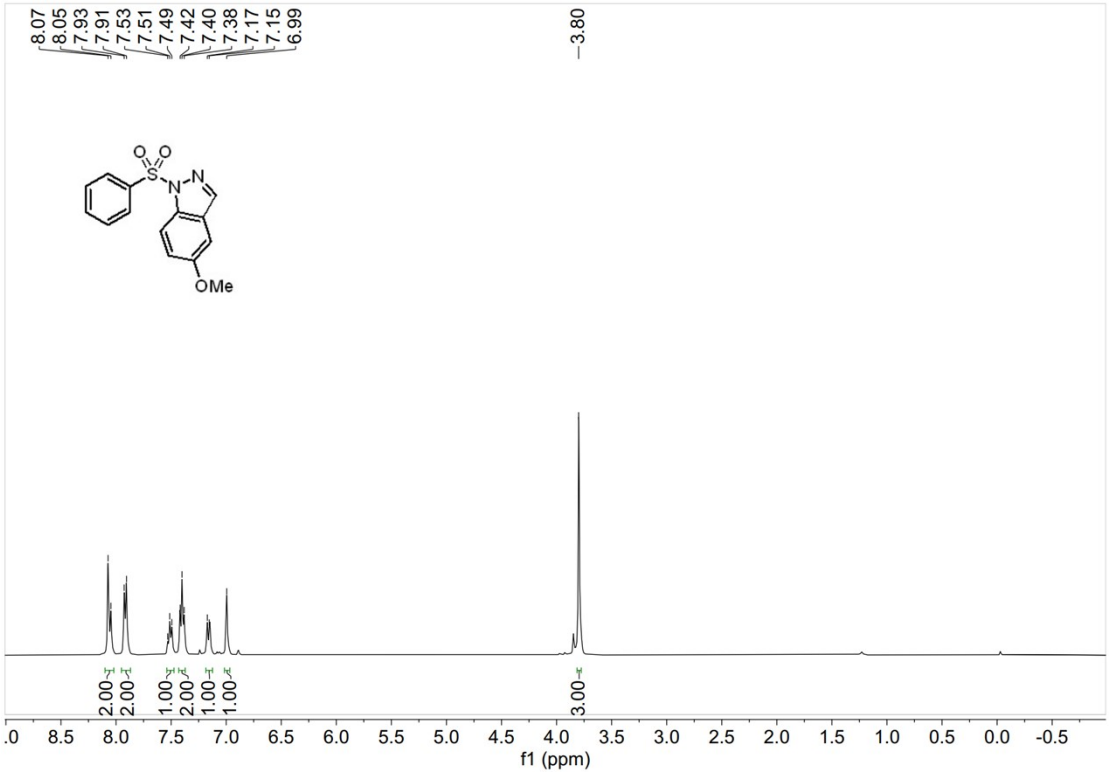
^{13}C NMR (101 MHz, $CDCl_3$) of **42**



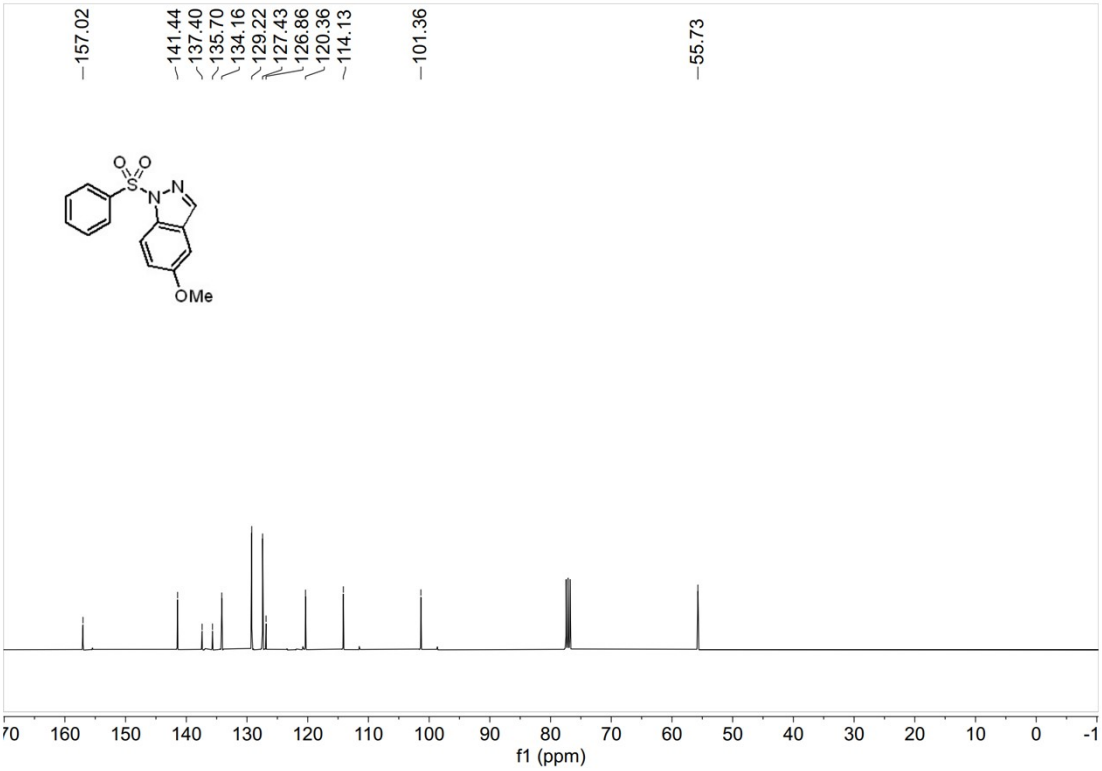
^{1}H NMR (400 MHz, $CDCl_3$) of **43**



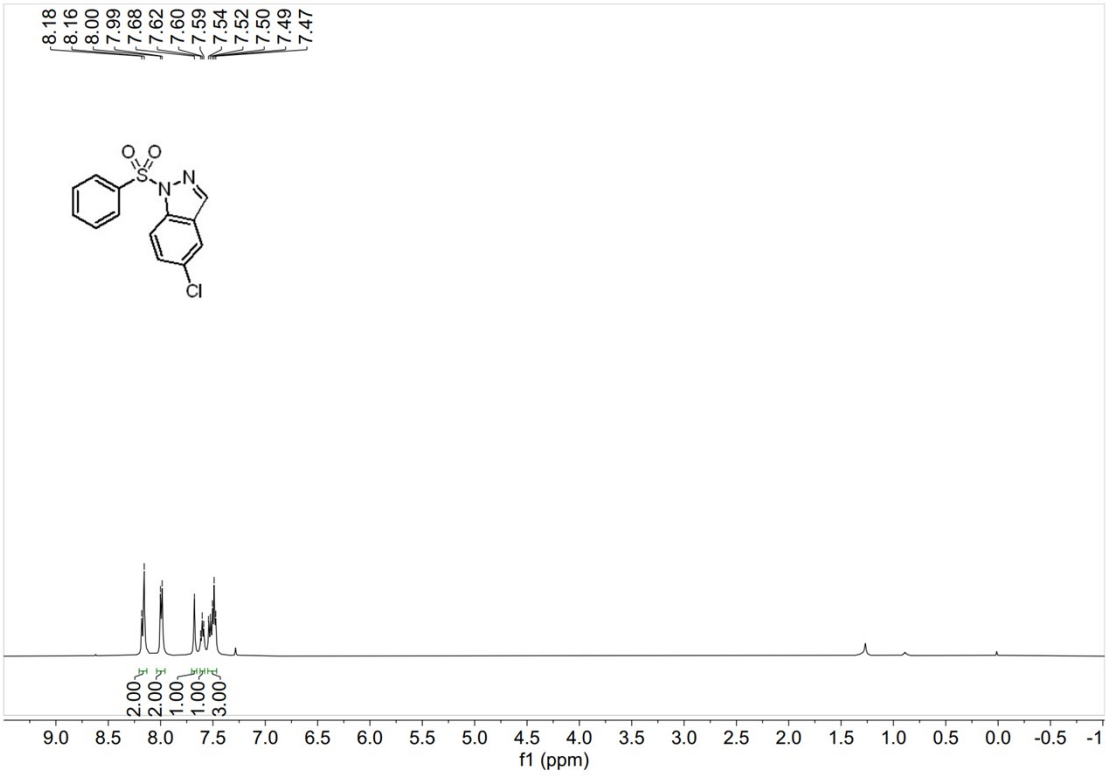
^{13}C NMR (101 MHz, $CDCl_3$) of **43**



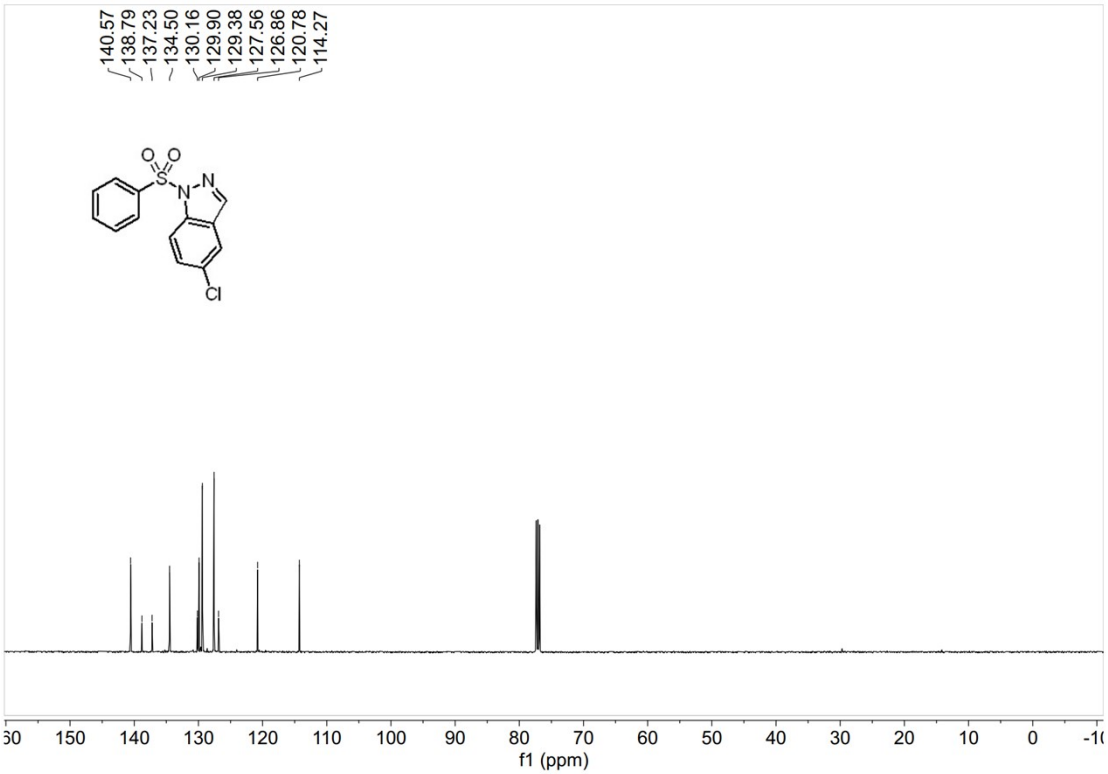
^{1}H NMR (400 MHz, $CDCl_3$) of **44**



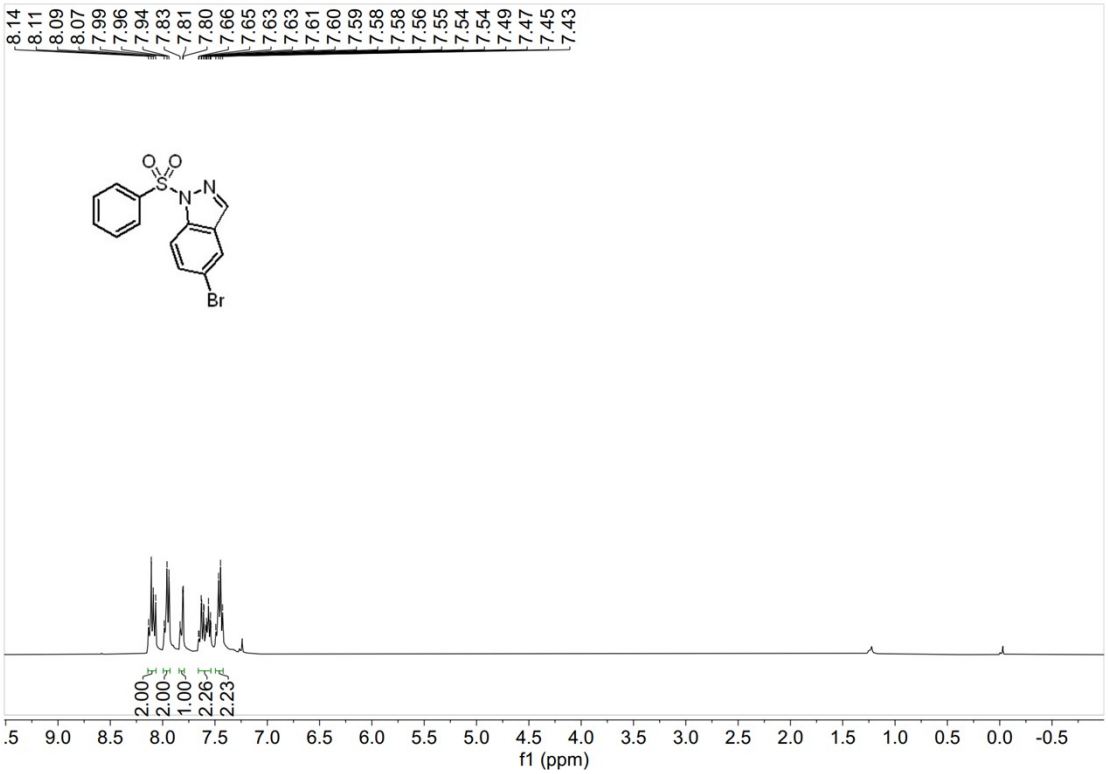
^{13}C NMR (101 MHz, $CDCl_3$) of **44**



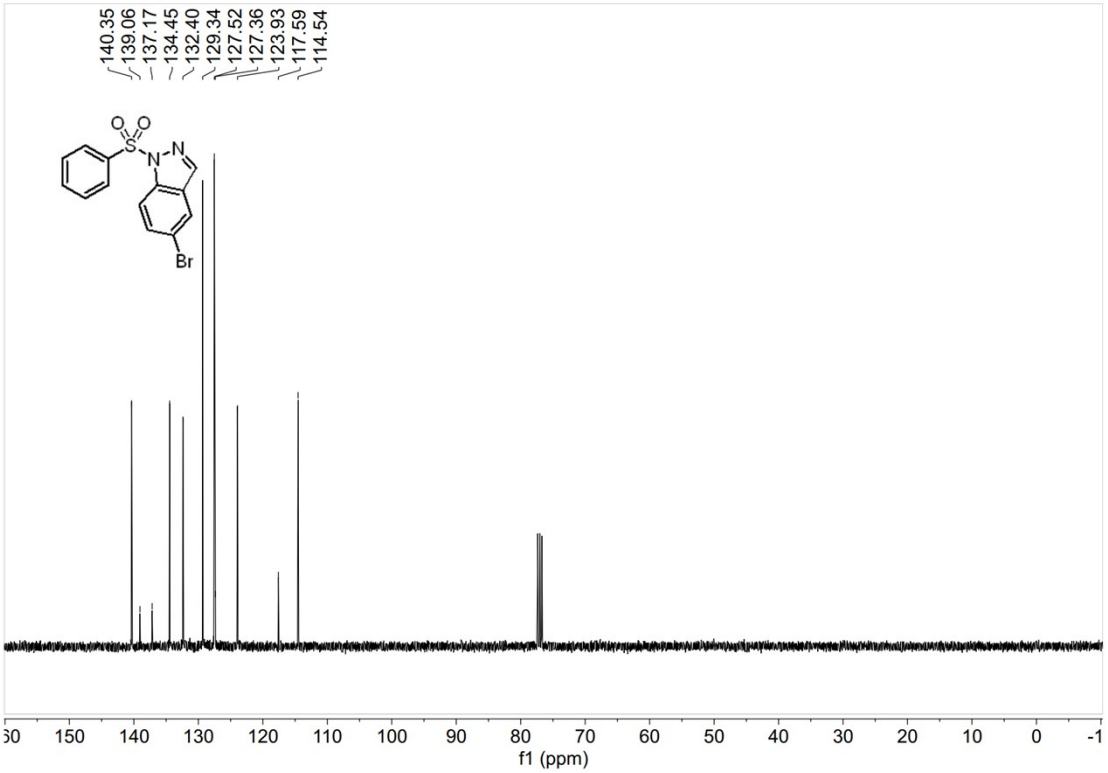
^{1}H NMR (400 MHz, $CDCl_3$) of **45**



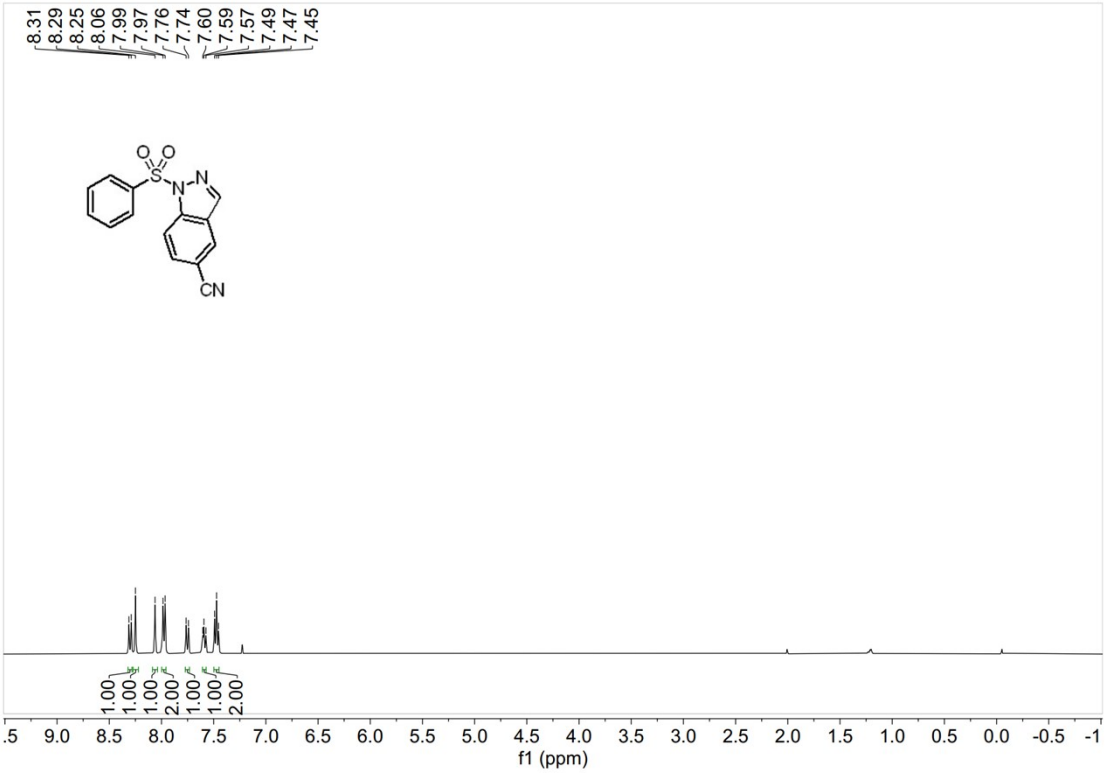
^{13}C NMR (101 MHz, $CDCl_3$) of **45**



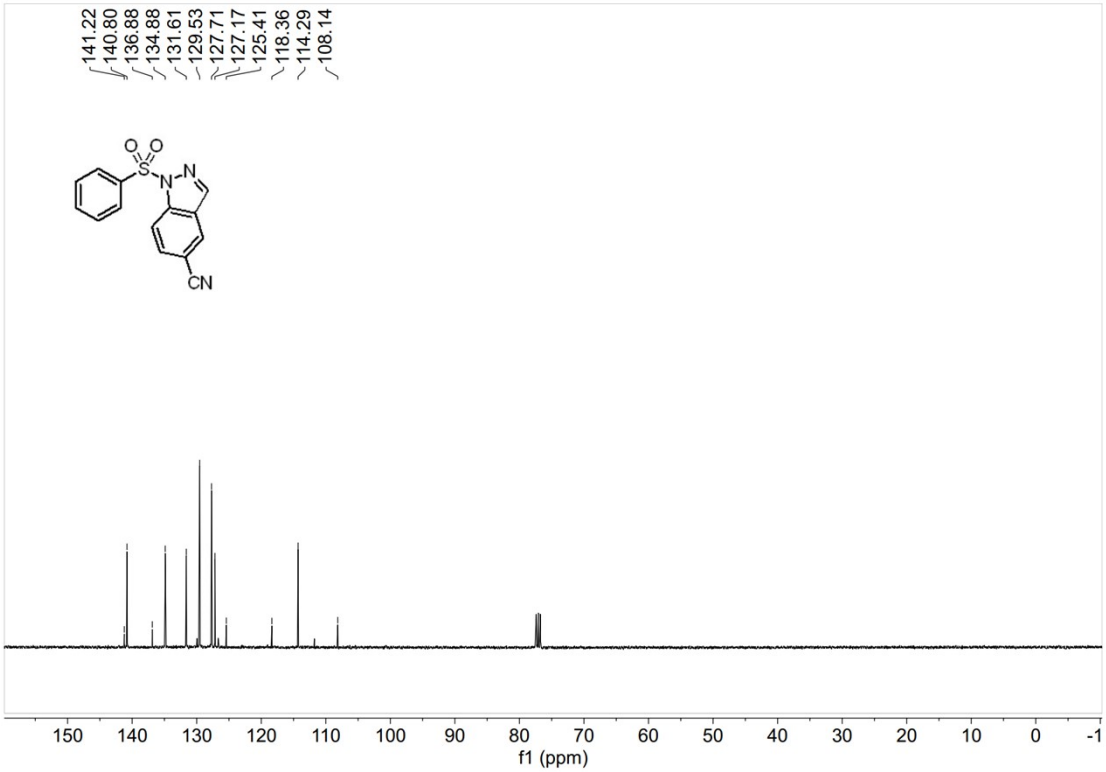
^{1}H NMR (400 MHz, $CDCl_3$) of **46**



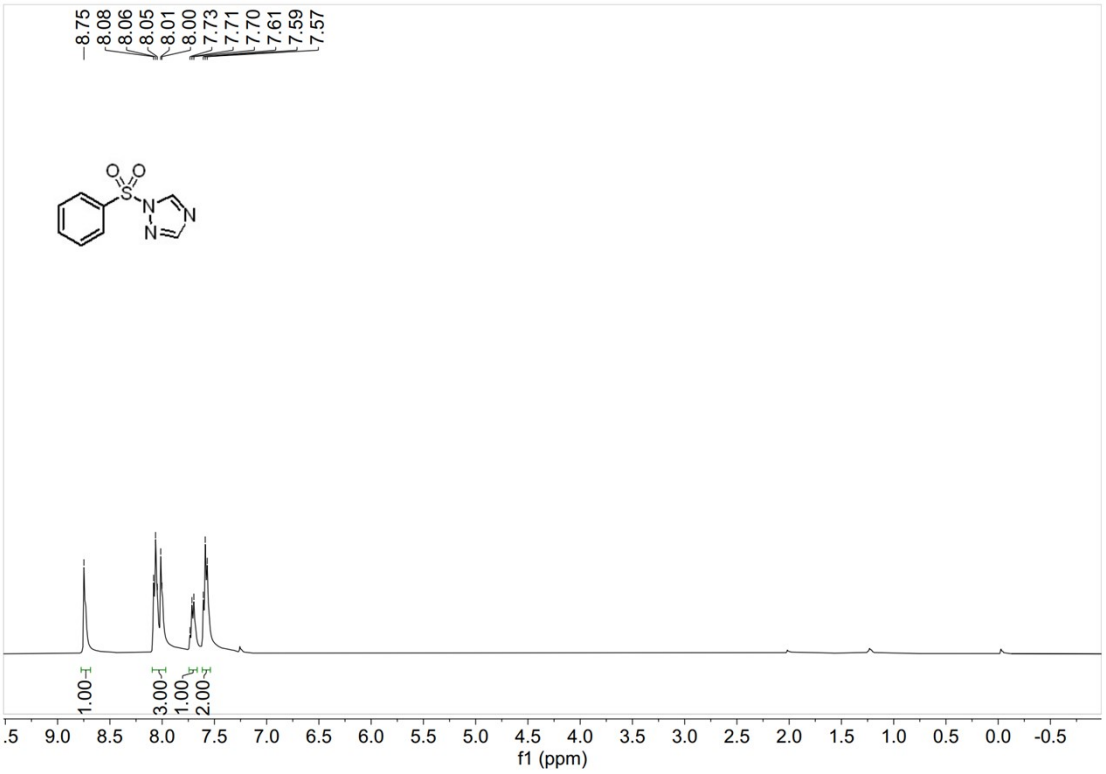
^{13}C NMR (101 MHz, $CDCl_3$) of **46**



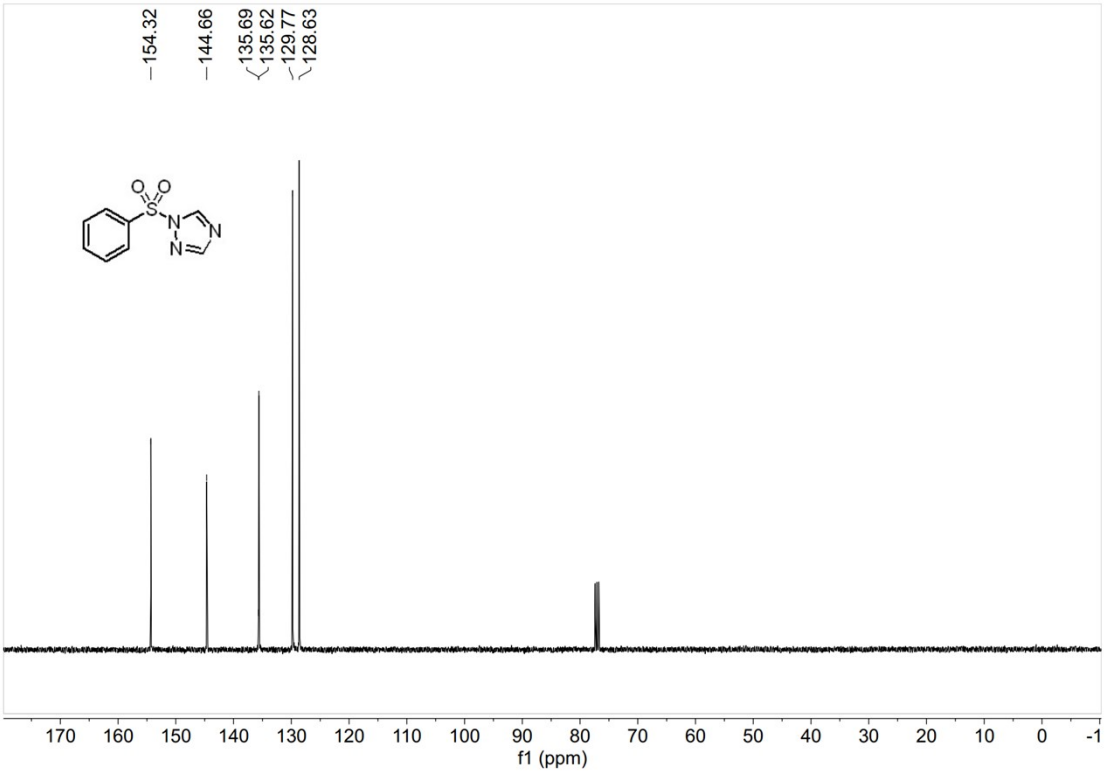
^{1}H NMR (400 MHz, $CDCl_3$) of **47**



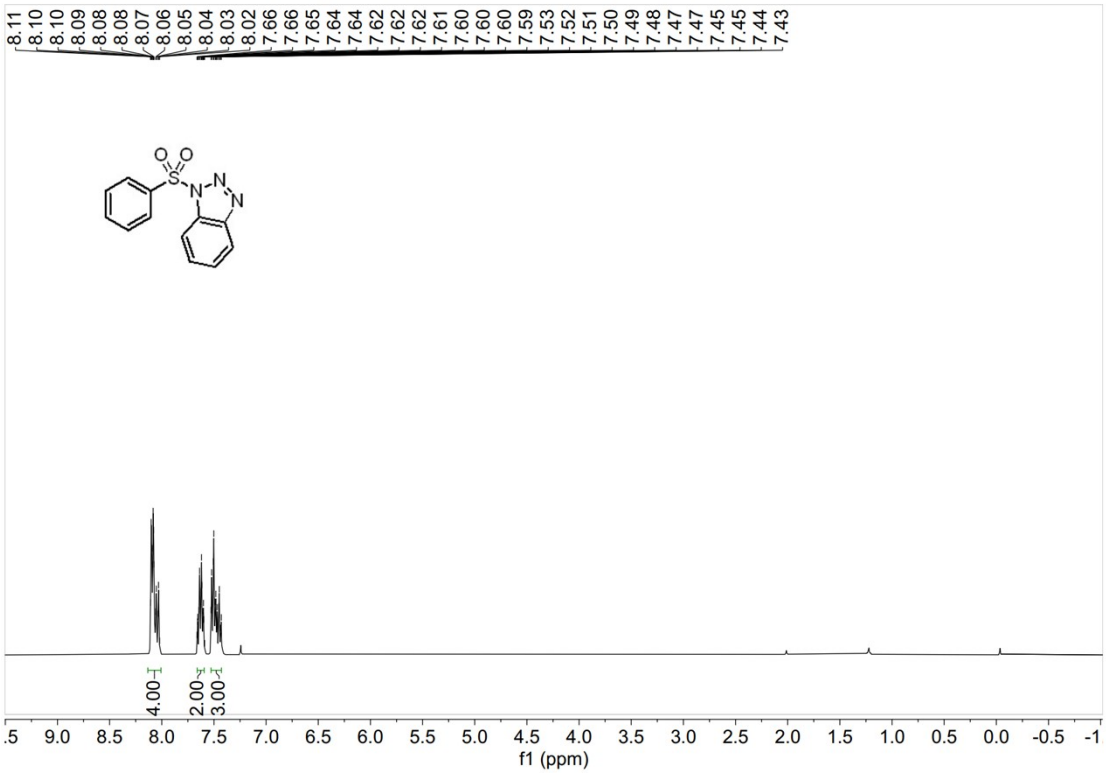
^{13}C NMR (101 MHz, $CDCl_3$) of **47**



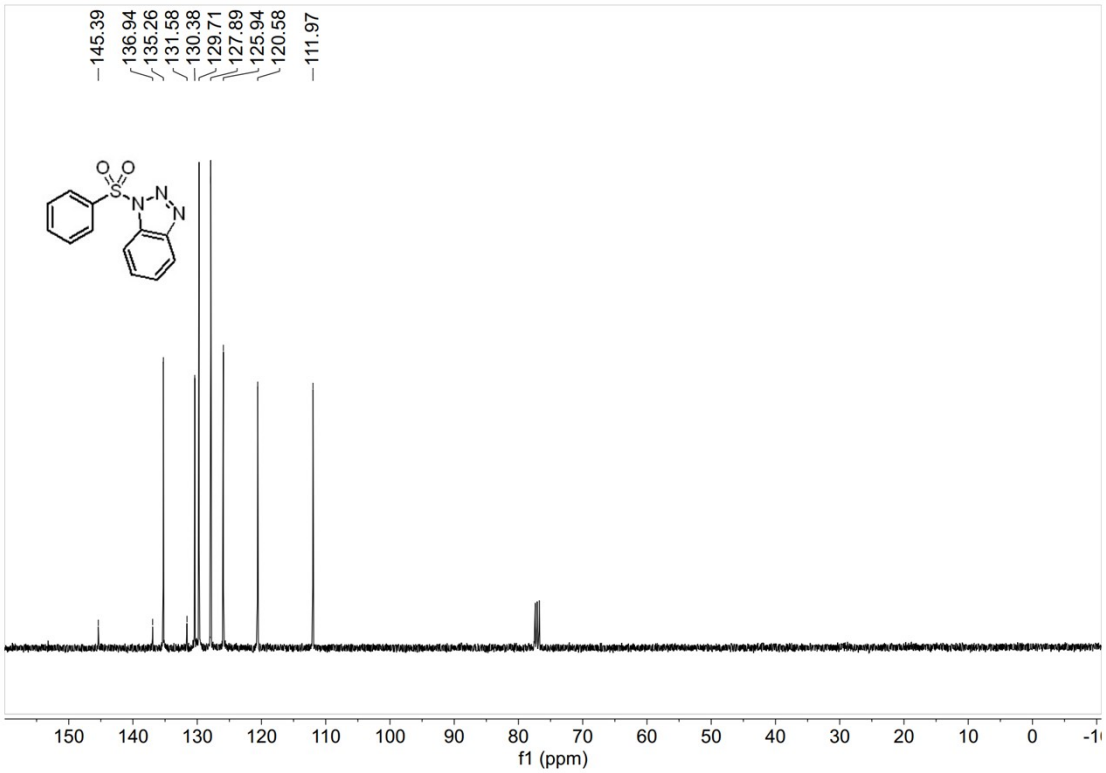
^{1}H NMR (400 MHz, $CDCl_3$) of **48**



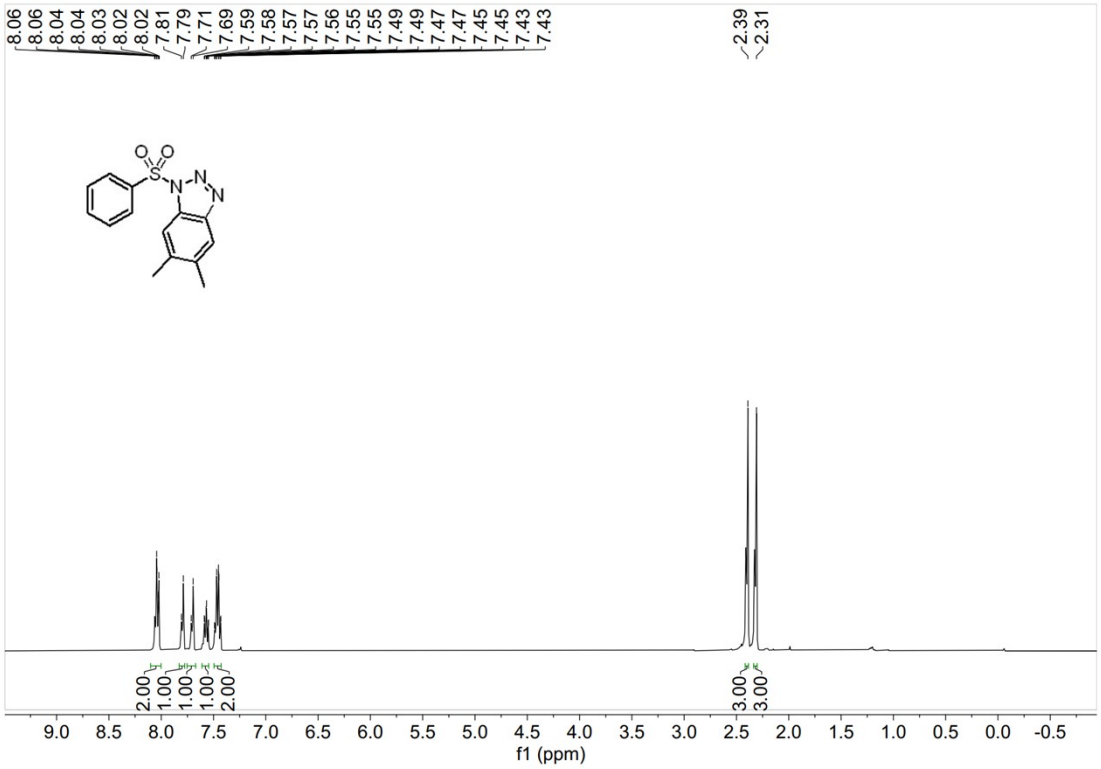
^{13}C NMR (101 MHz, $CDCl_3$) of **48**



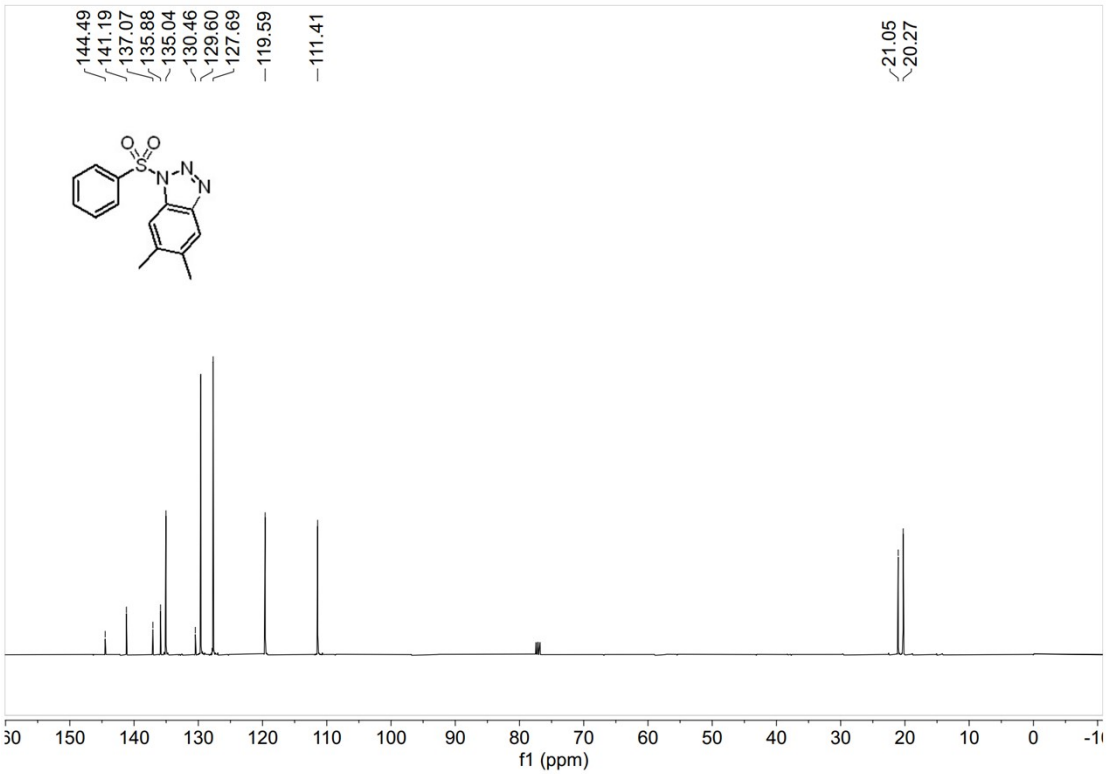
^{1}H NMR (400 MHz, $CDCl_3$) of **49**



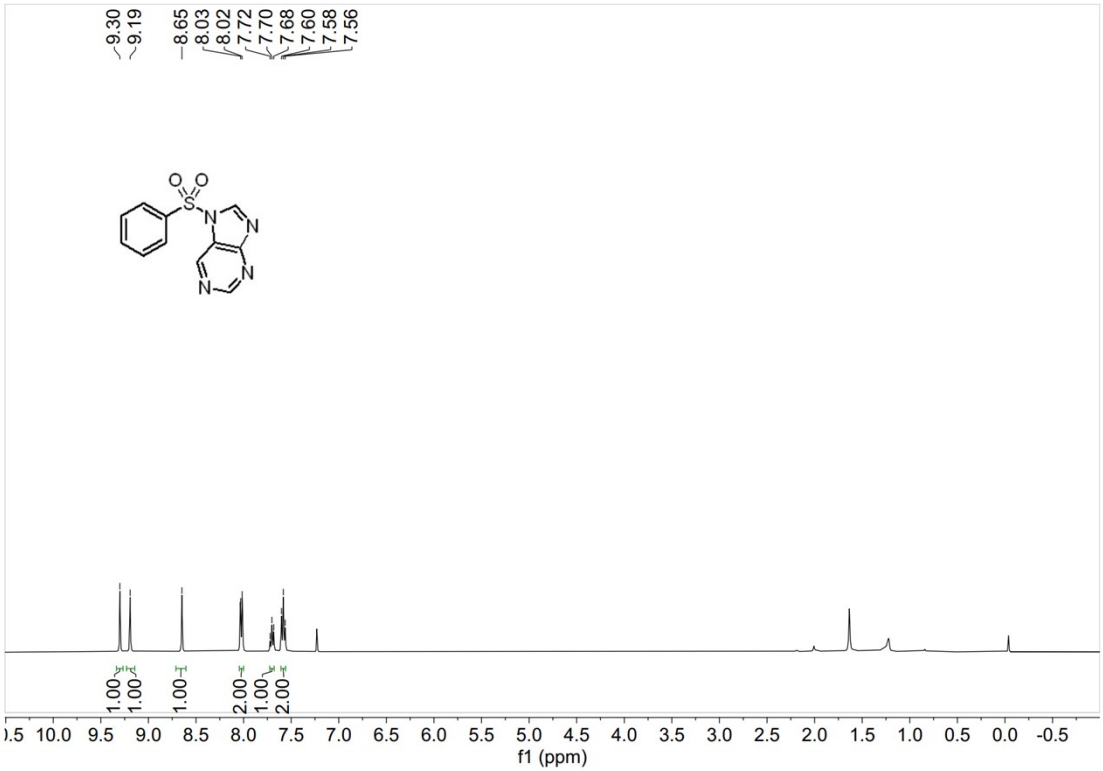
^{13}C NMR (101 MHz, $CDCl_3$) of **49**



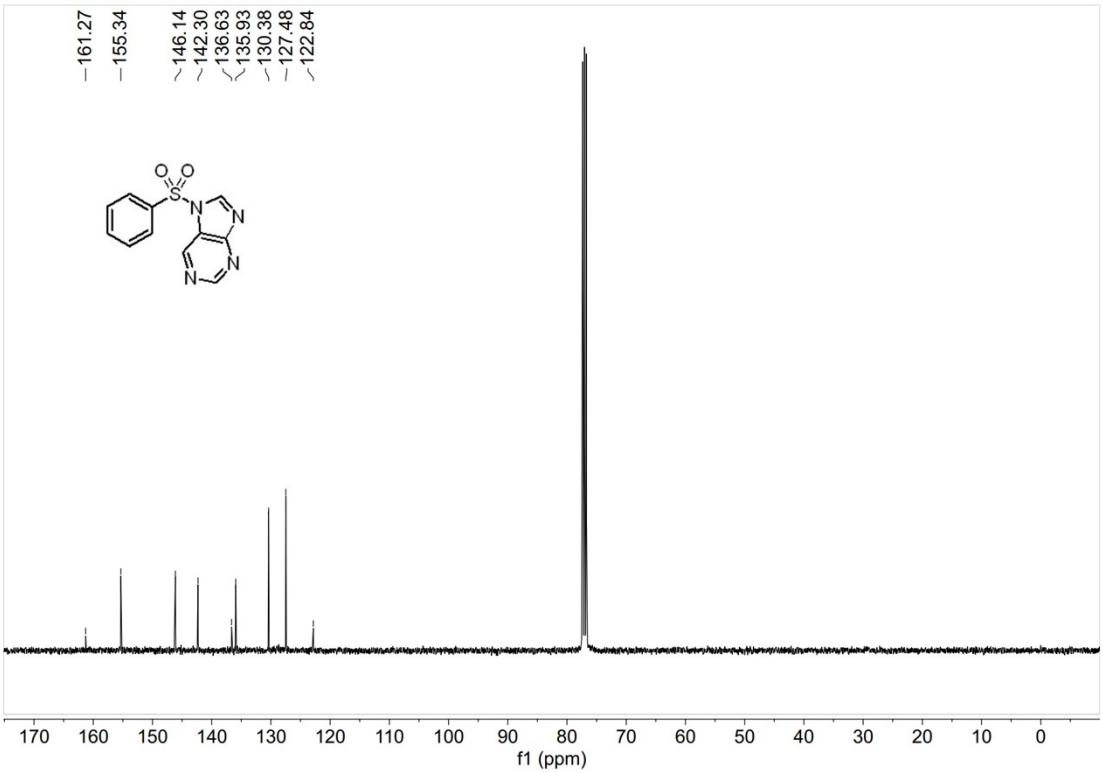
^{1}H NMR (400 MHz, $CDCl_3$) of **50**



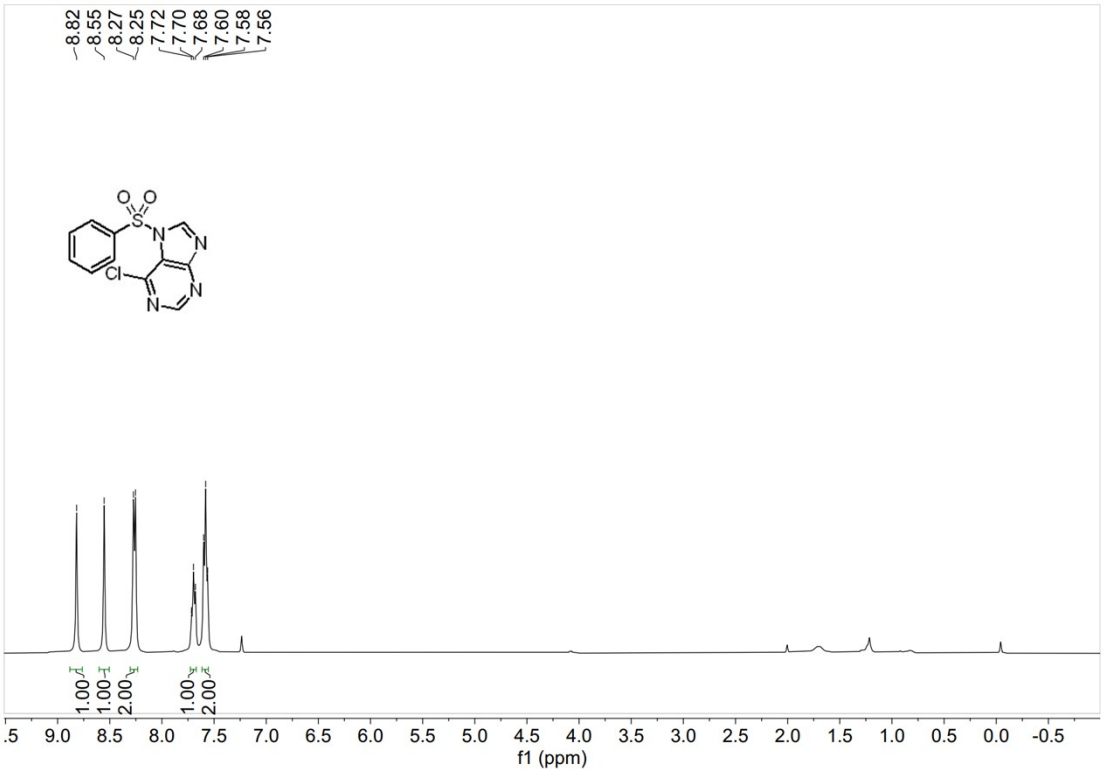
^{13}C NMR (101 MHz, $CDCl_3$) of **50**



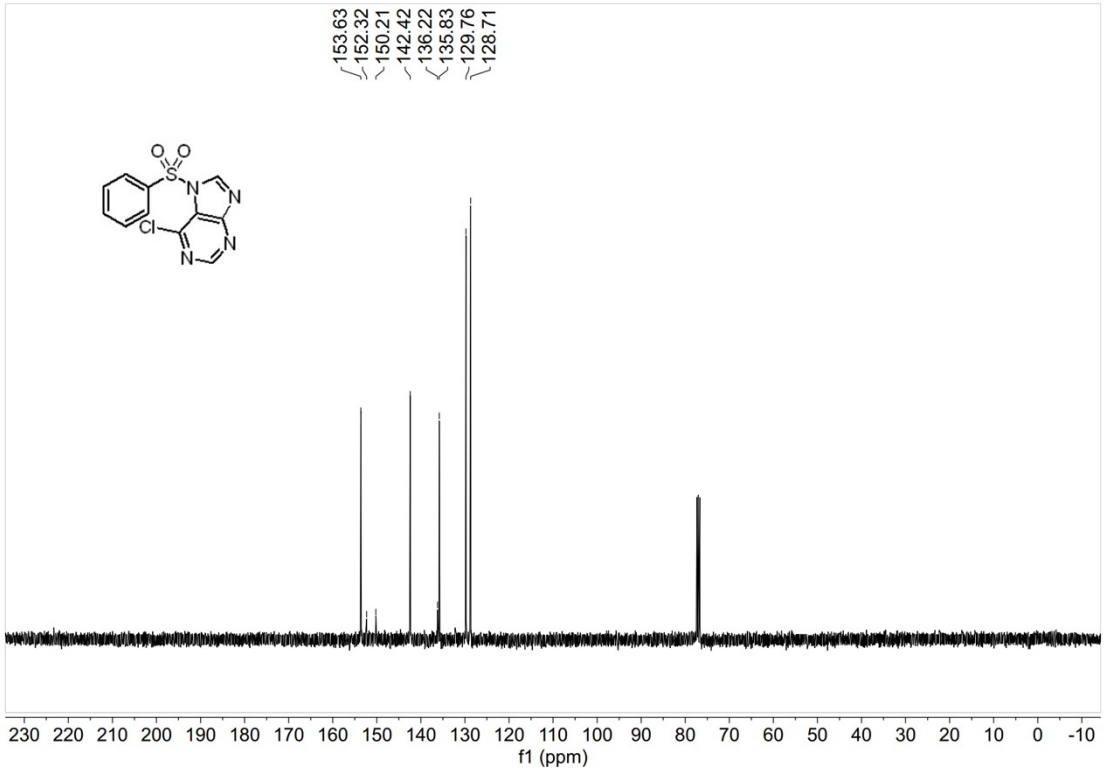
^{1}H NMR (400 MHz, $CDCl_3$) of **51**



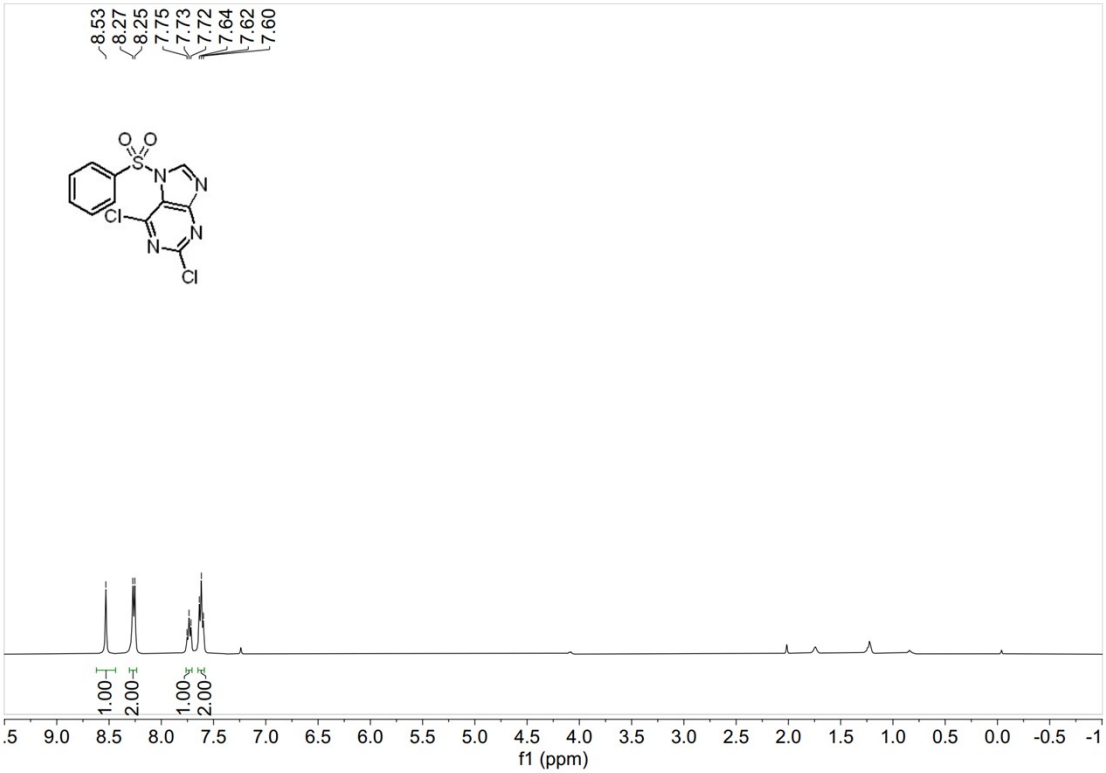
^{13}C NMR (101 MHz, $CDCl_3$) of **51**



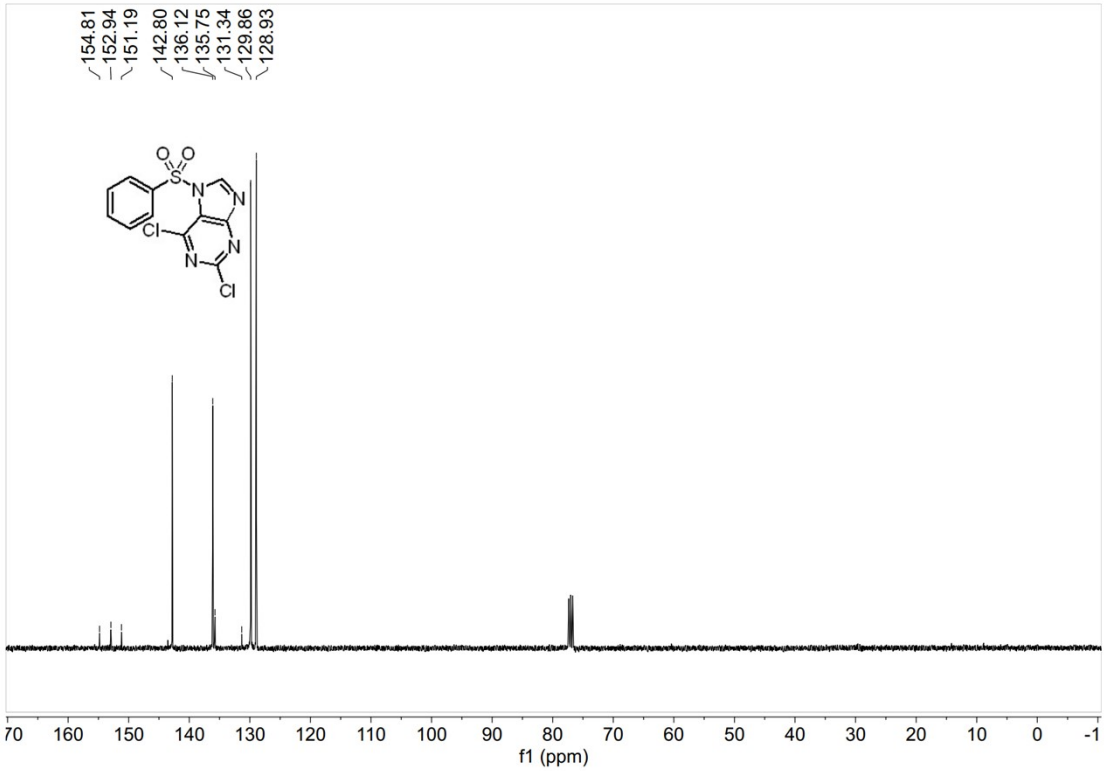
^{1}H NMR (400 MHz, $CDCl_3$) of **52**



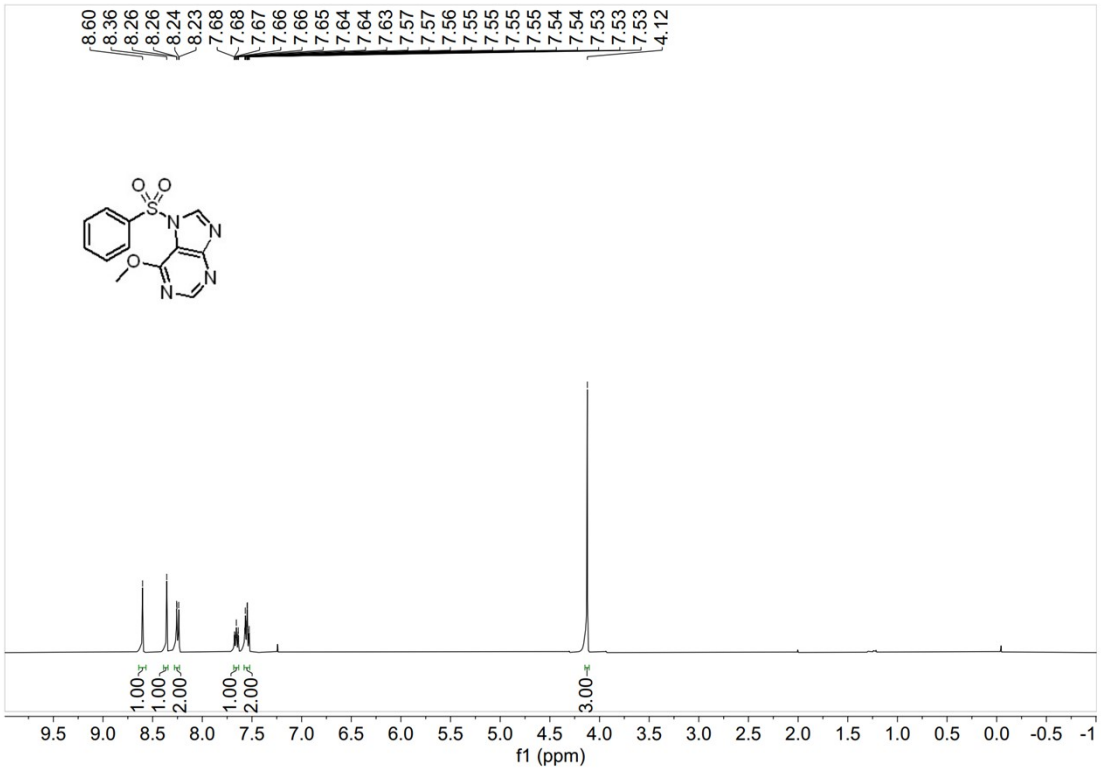
^{13}C NMR (101 MHz, $CDCl_3$) of **52**



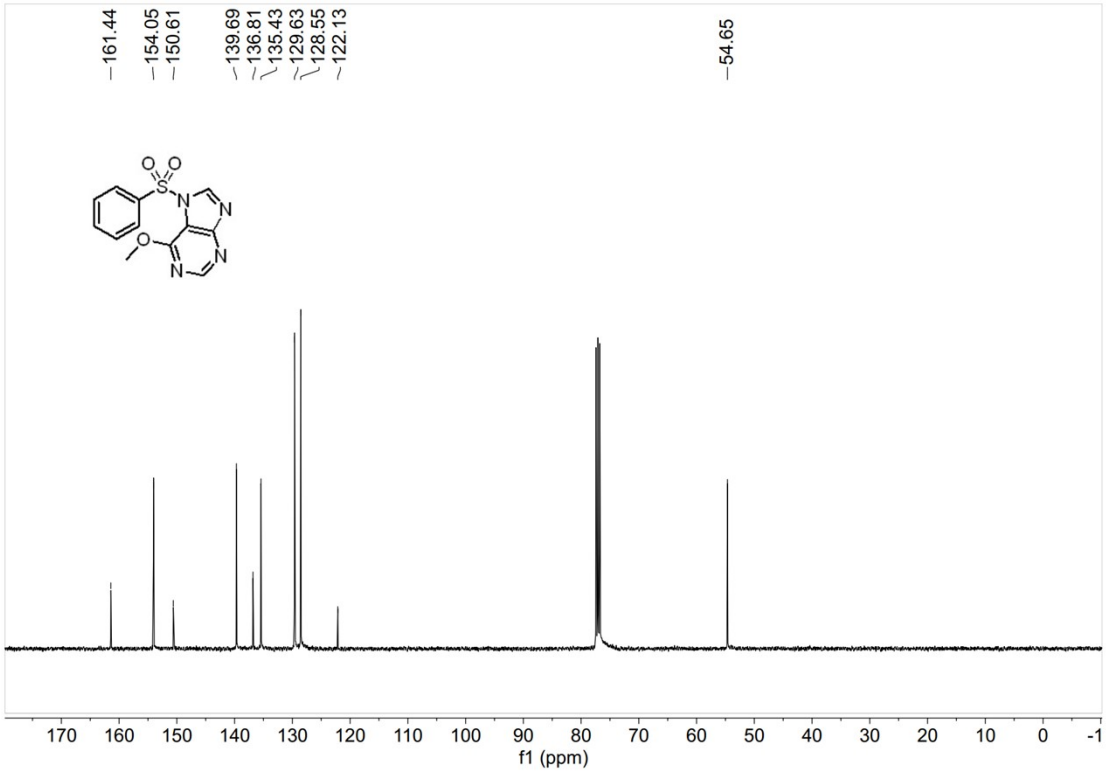
^{1}H NMR (400 MHz, $CDCl_3$) of **53**



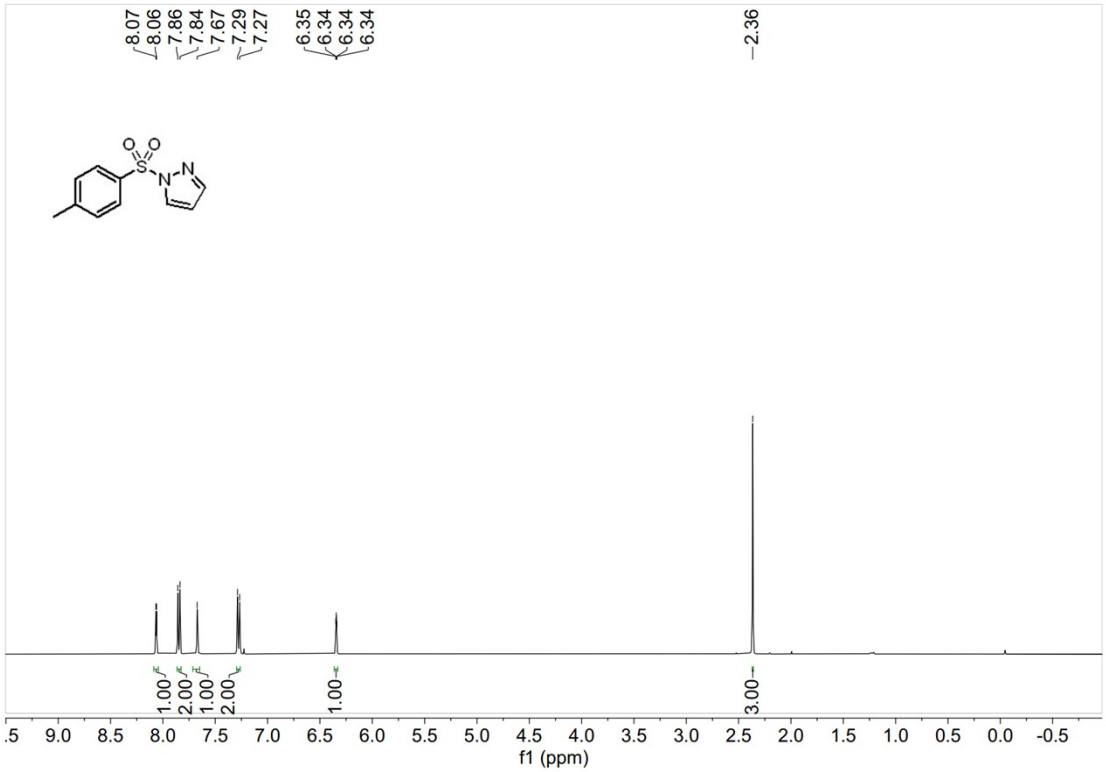
^{13}C NMR (101 MHz, $CDCl_3$) of **53**



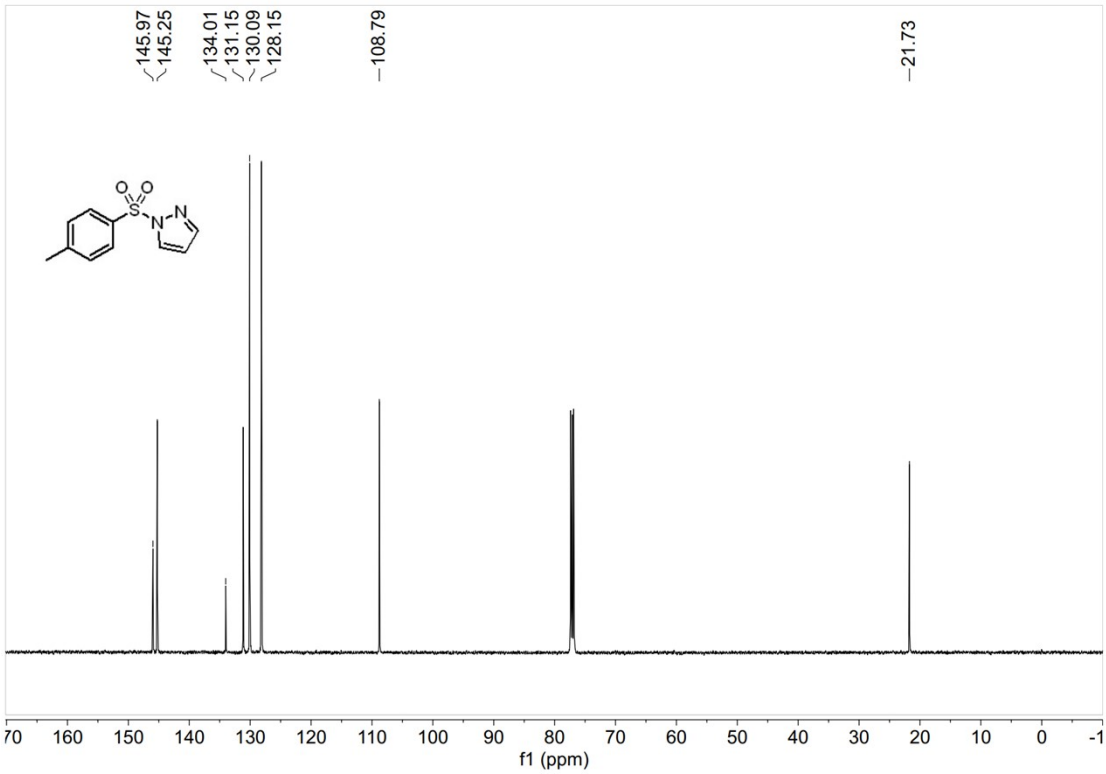
^{1}H NMR (400 MHz, $CDCl_3$) of **54**



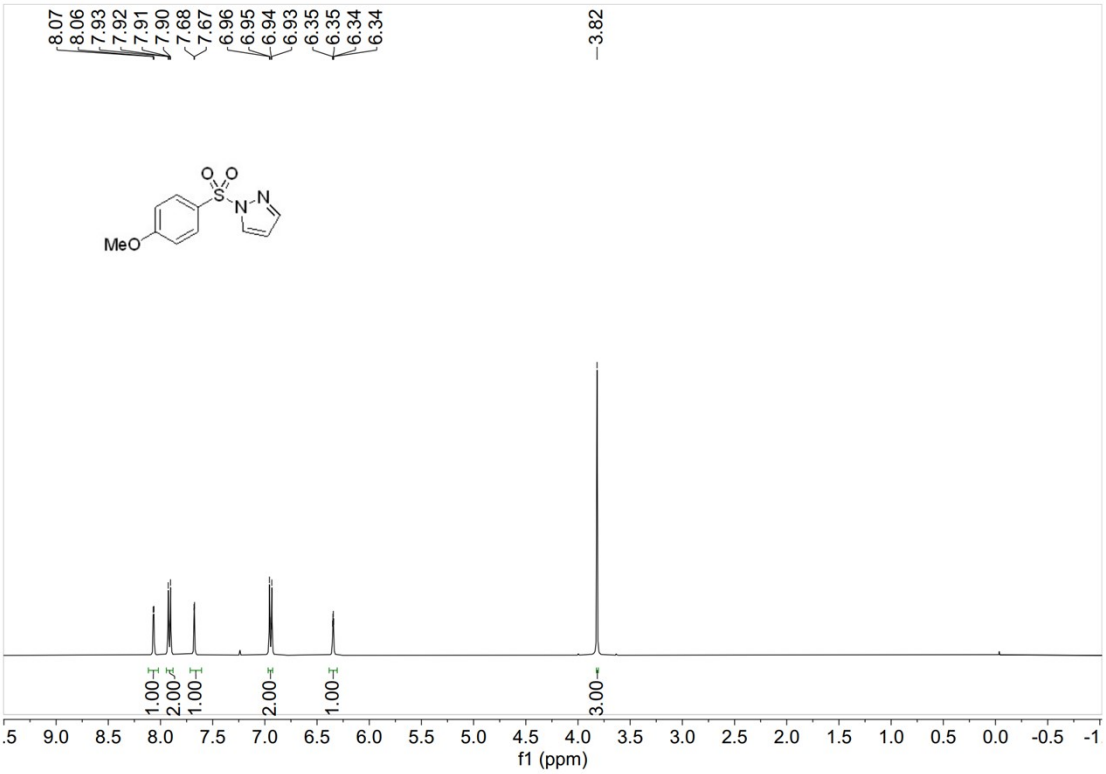
^{13}C NMR (101 MHz, $CDCl_3$) of **54**



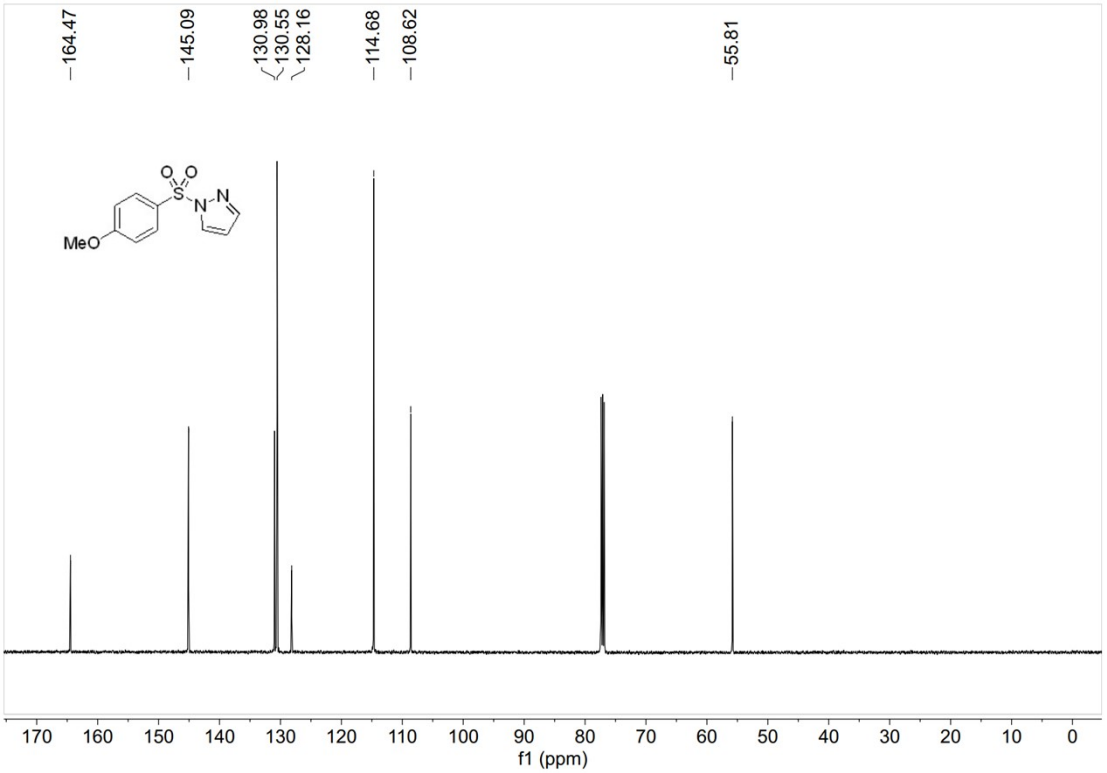
^{1}H NMR (400 MHz, $CDCl_3$) of **55**



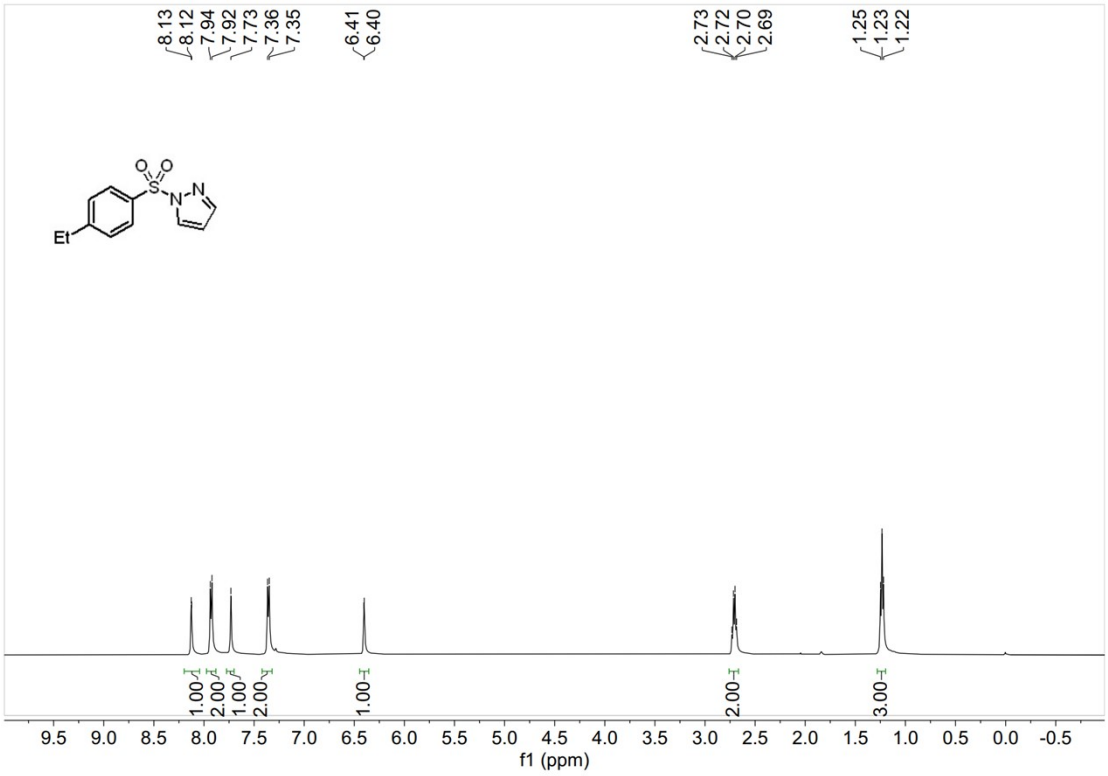
^{13}C NMR (101 MHz, $CDCl_3$) of **55**



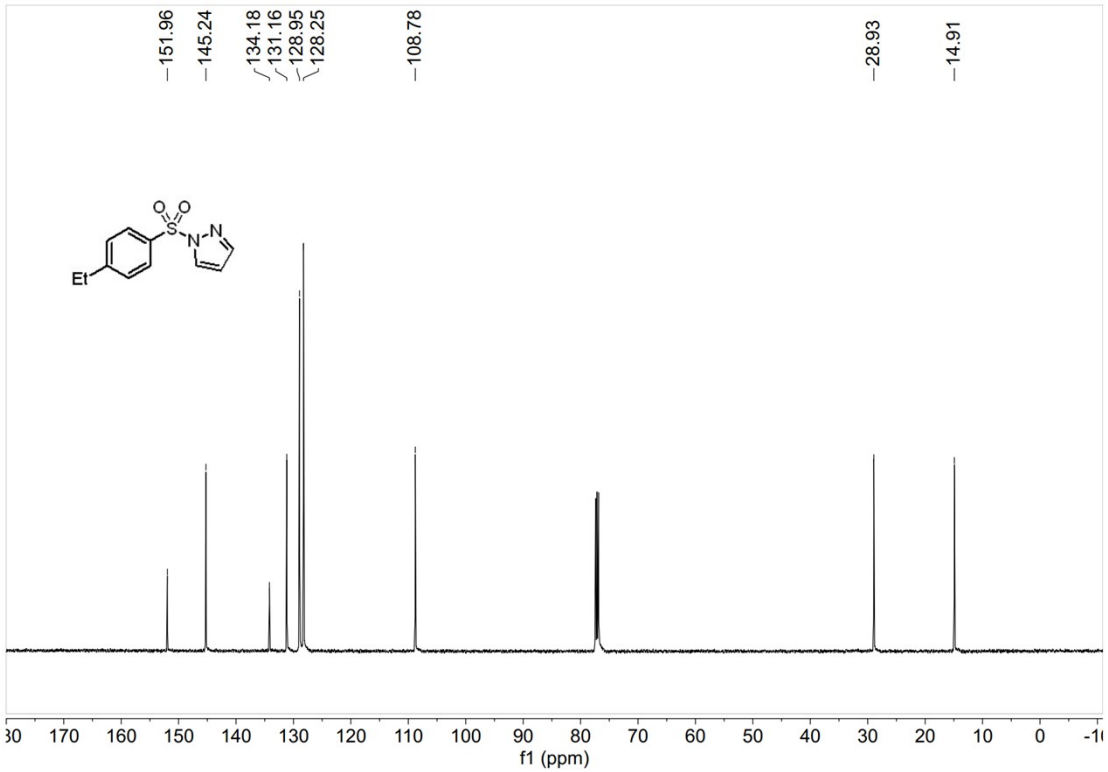
^{1}H NMR (400 MHz, $CDCl_3$) of **56**



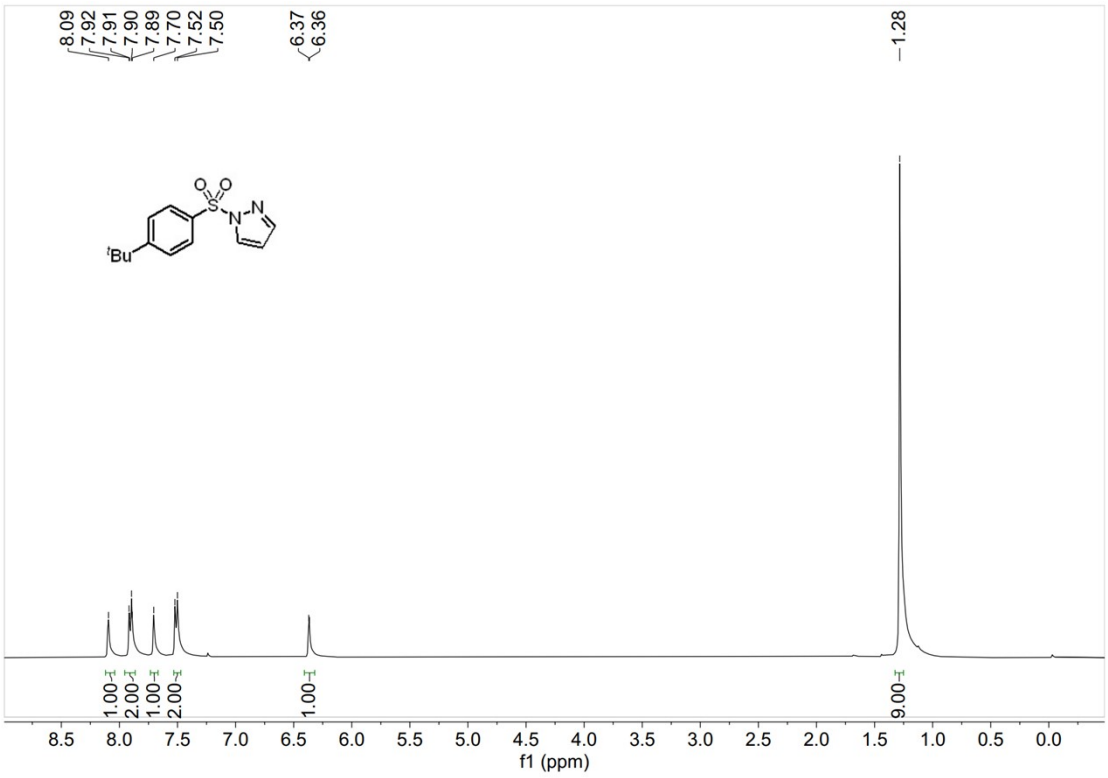
^{13}C NMR (101 MHz, $CDCl_3$) of **56**



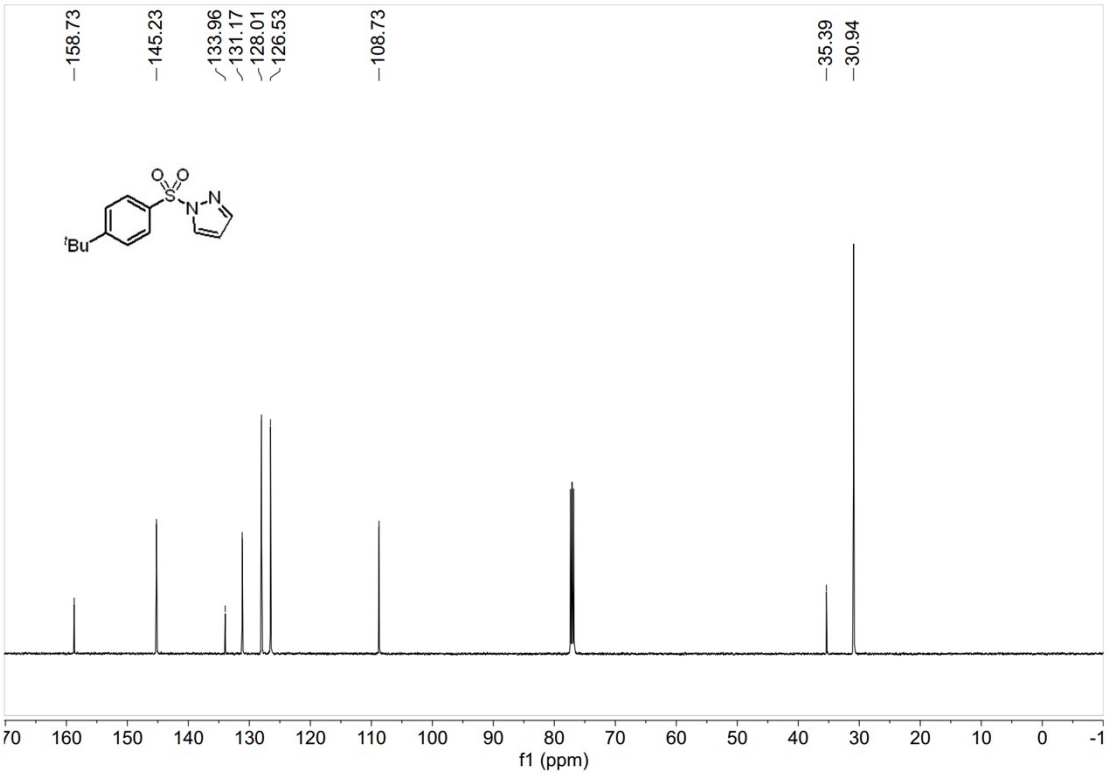
^{1}H NMR (400 MHz, $CDCl_3$) of **57**



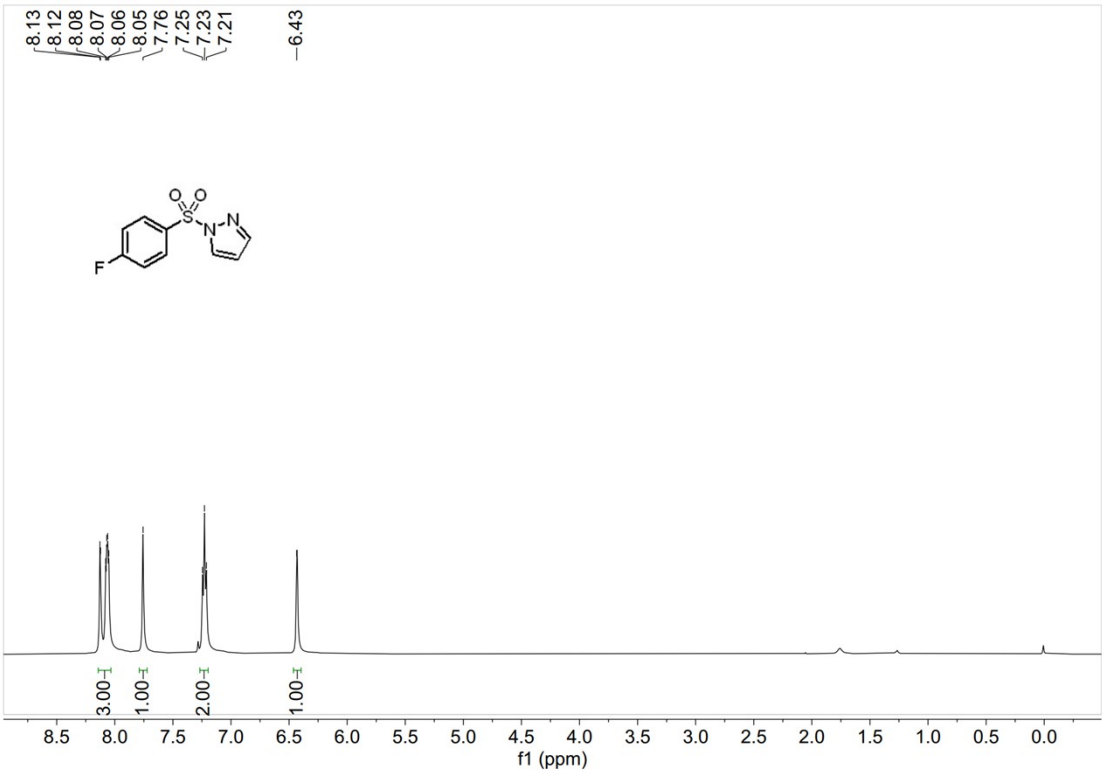
^{13}C NMR (101 MHz, $CDCl_3$) of **57**



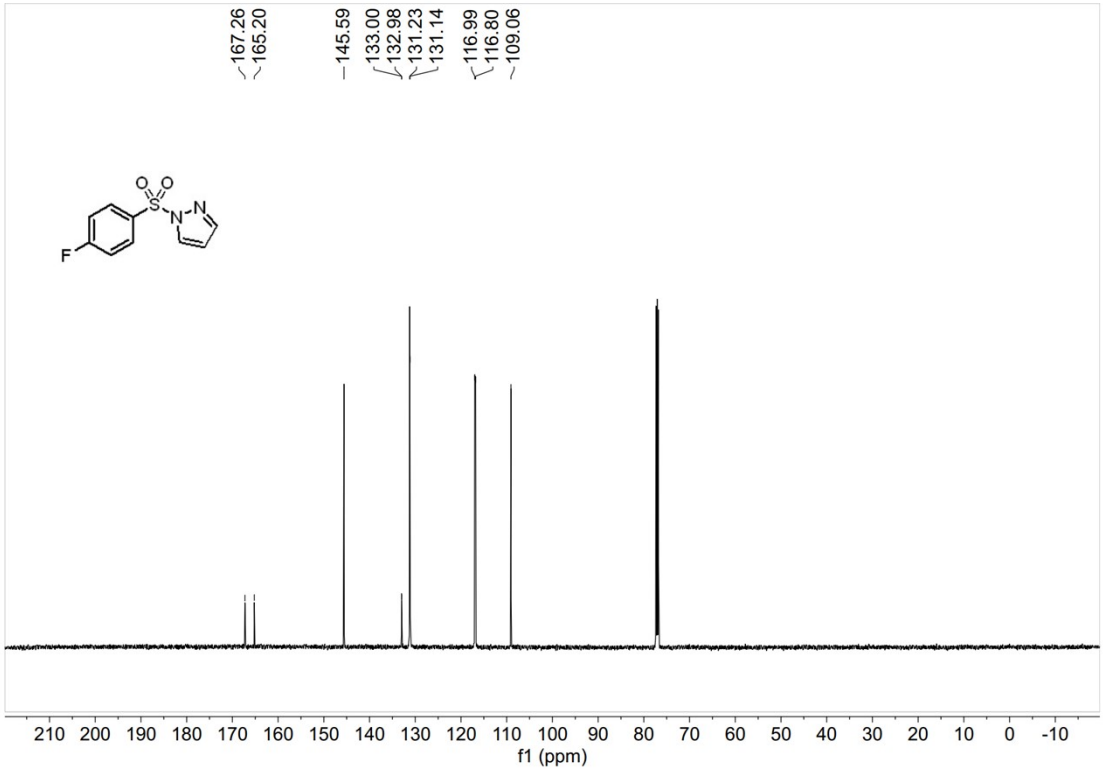
^{1}H NMR (400 MHz, $CDCl_3$) of **58**



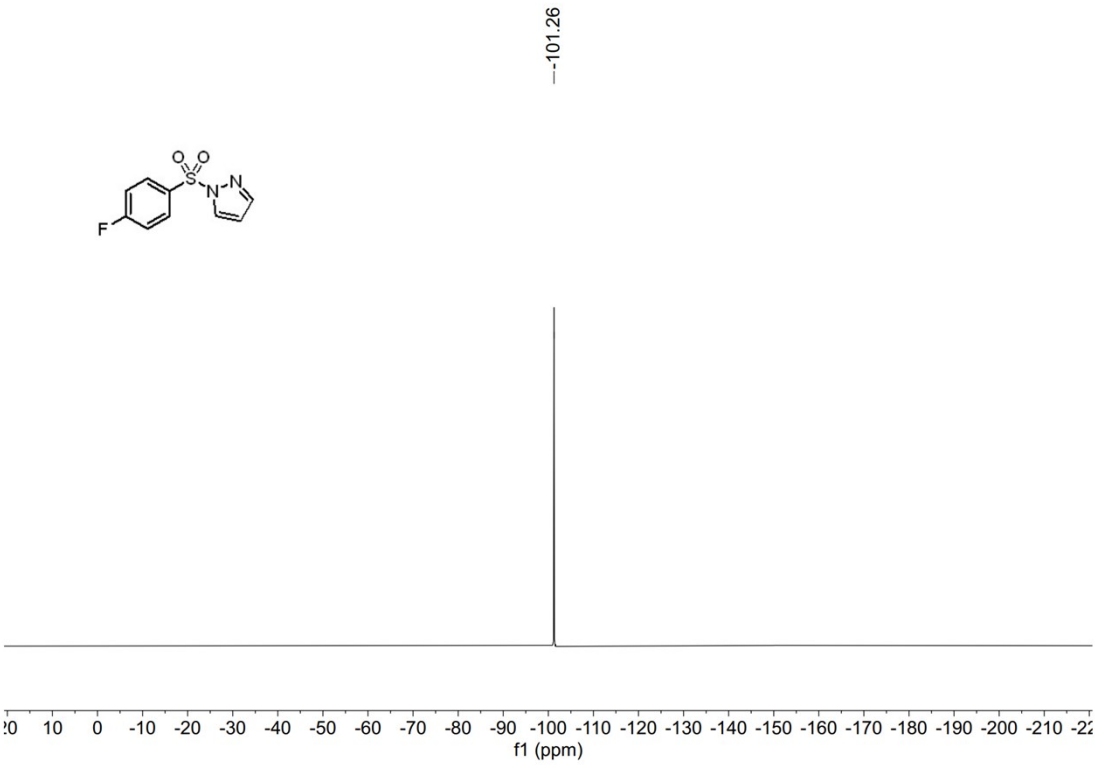
^{13}C NMR (101 MHz, $CDCl_3$) of **58**



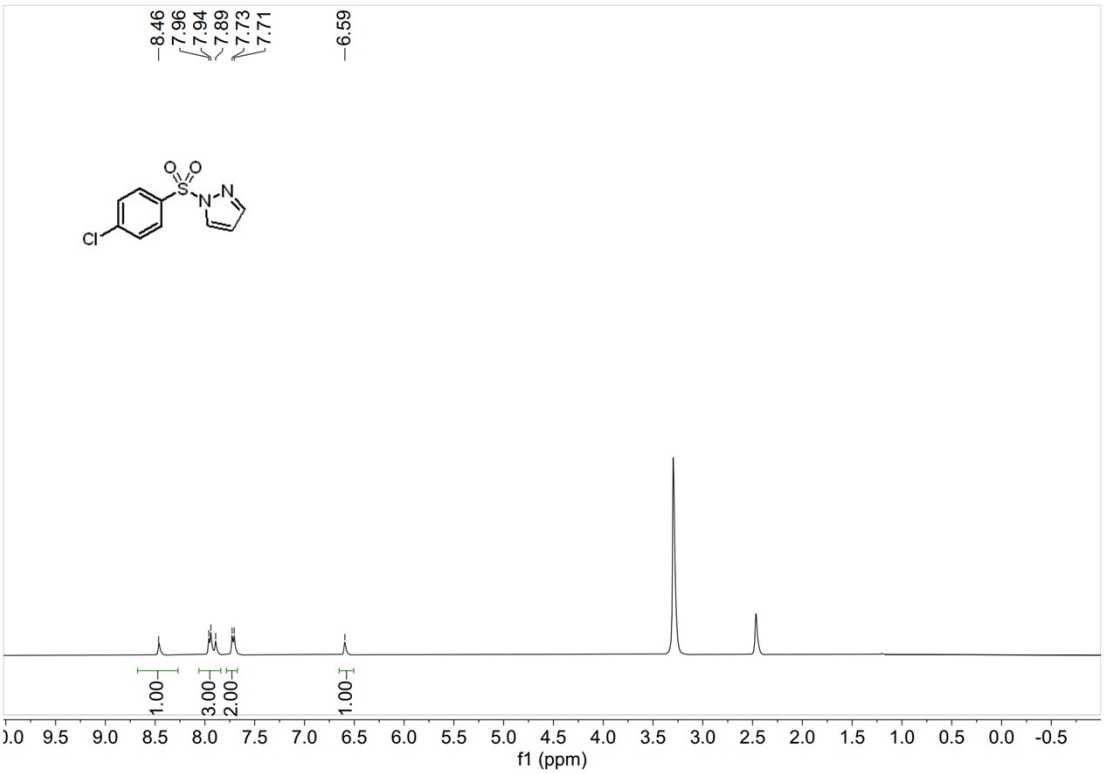
^{1}H NMR (400 MHz, $CDCl_3$) of **59**



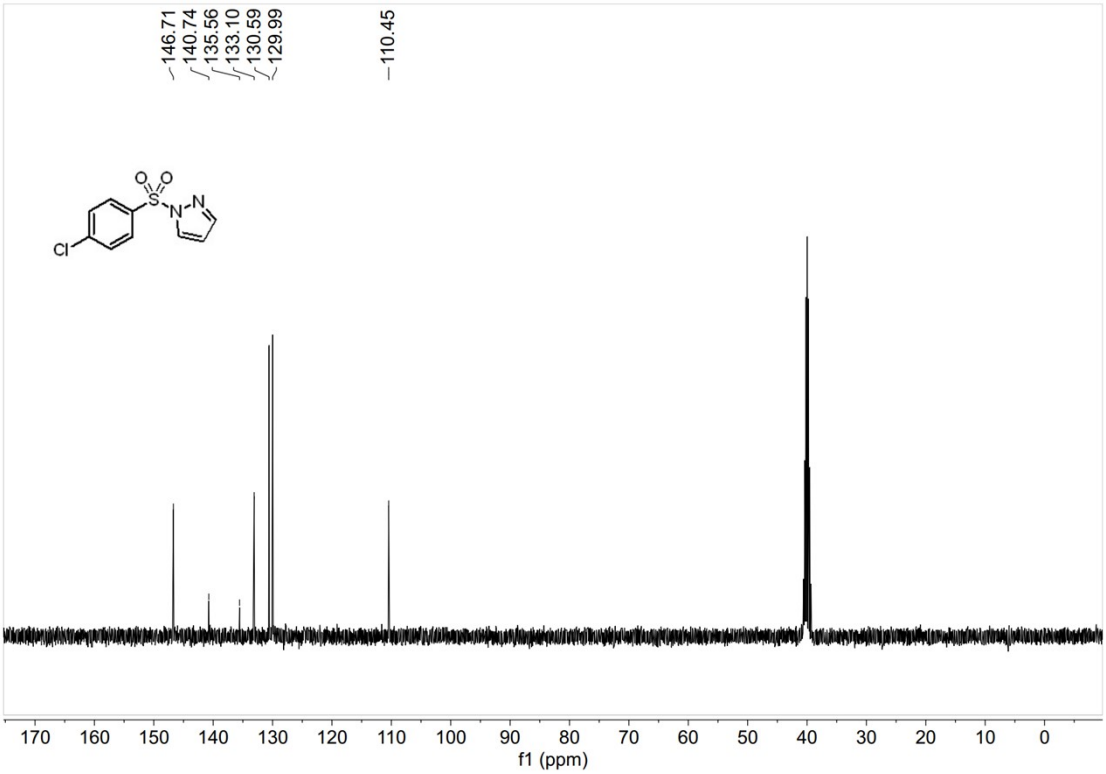
^{13}C NMR (101 MHz, $CDCl_3$) of **59**



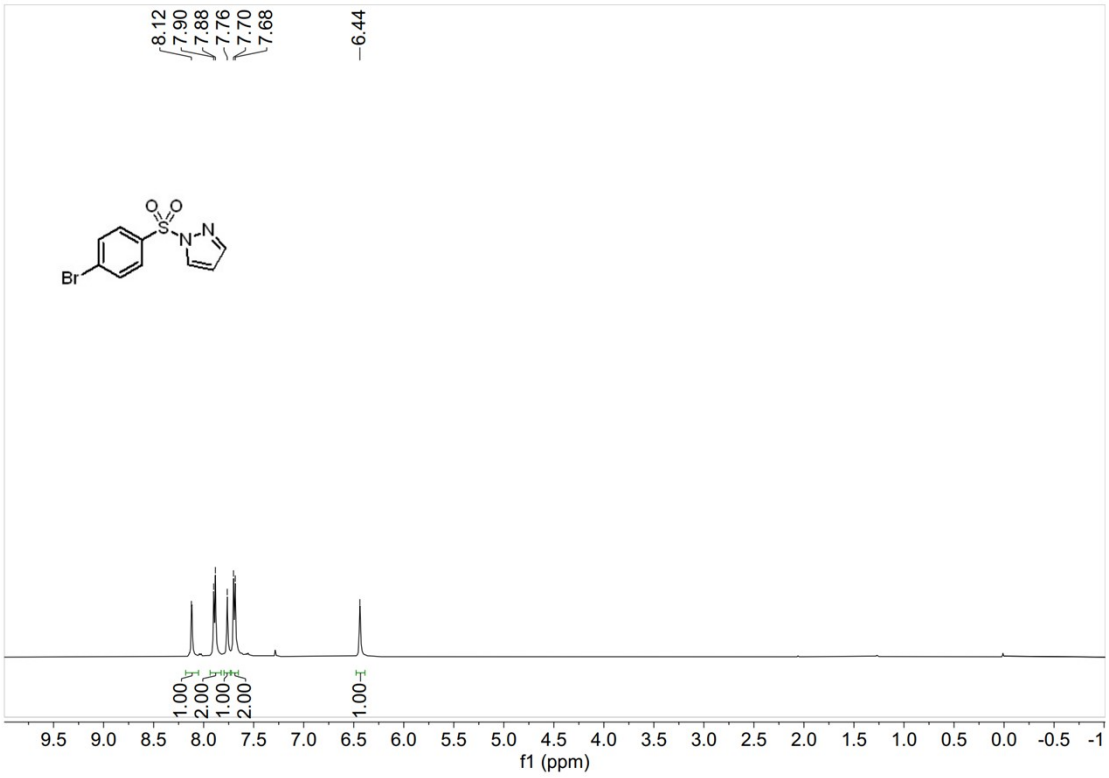
^{19}F NMR (376 MHz, $CDCl_3$) of **59**



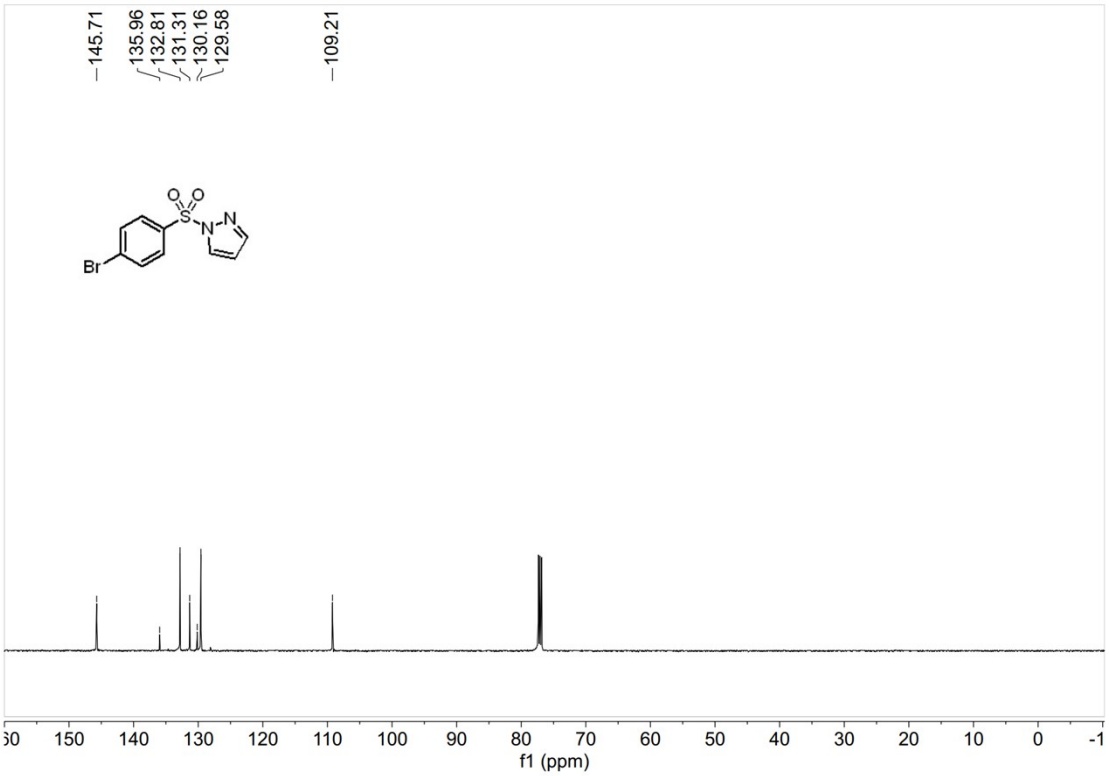
^{1}H NMR (400 MHz, DMSO-d_6) of **60**



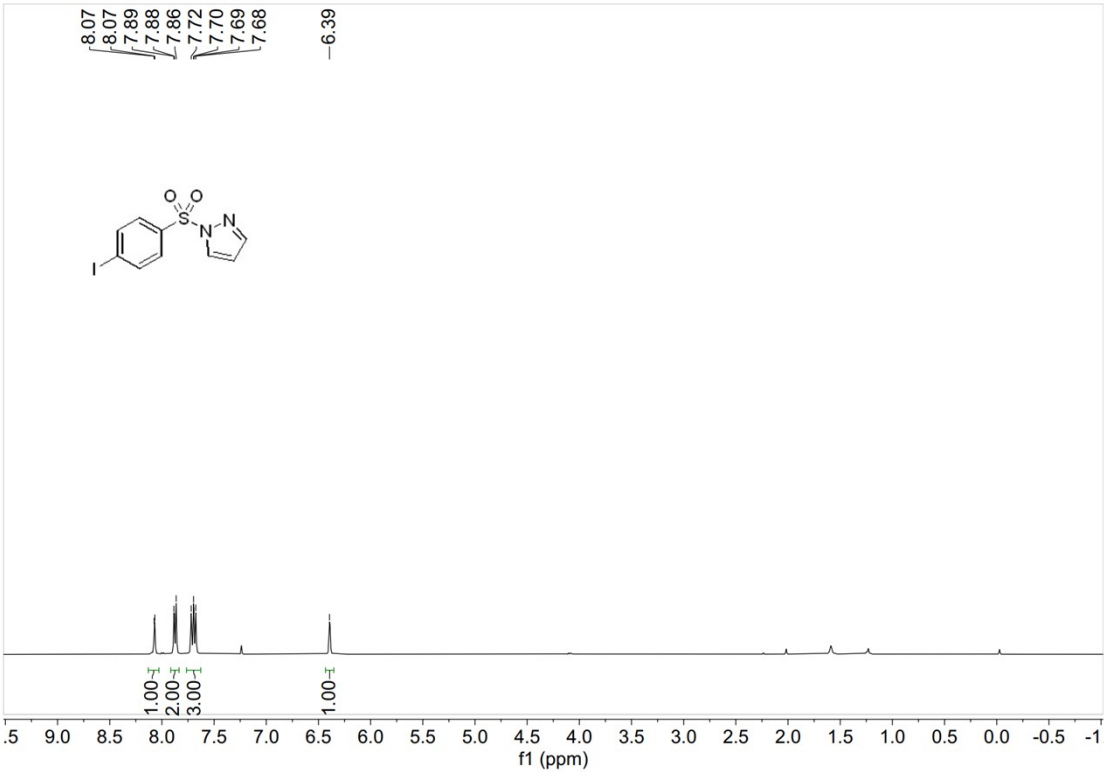
^{13}C NMR (101 MHz, DMSO-d_6) of **60**



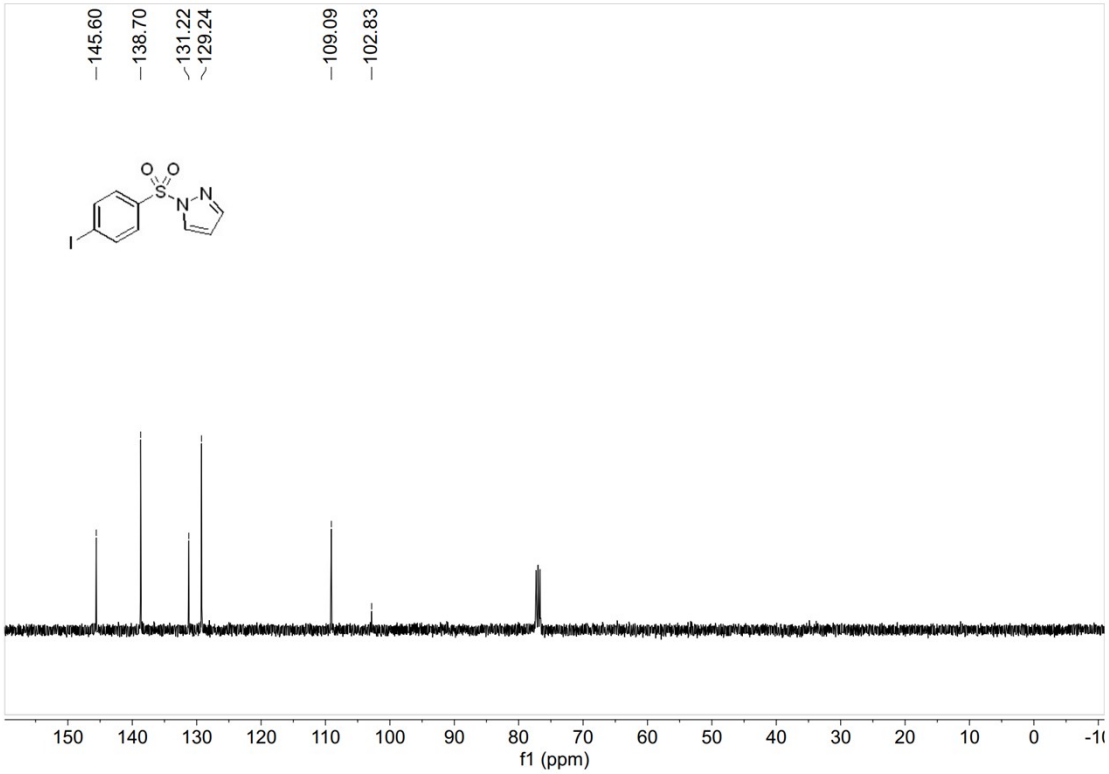
^{1}H NMR (400 MHz, $CDCl_3$) of **61**



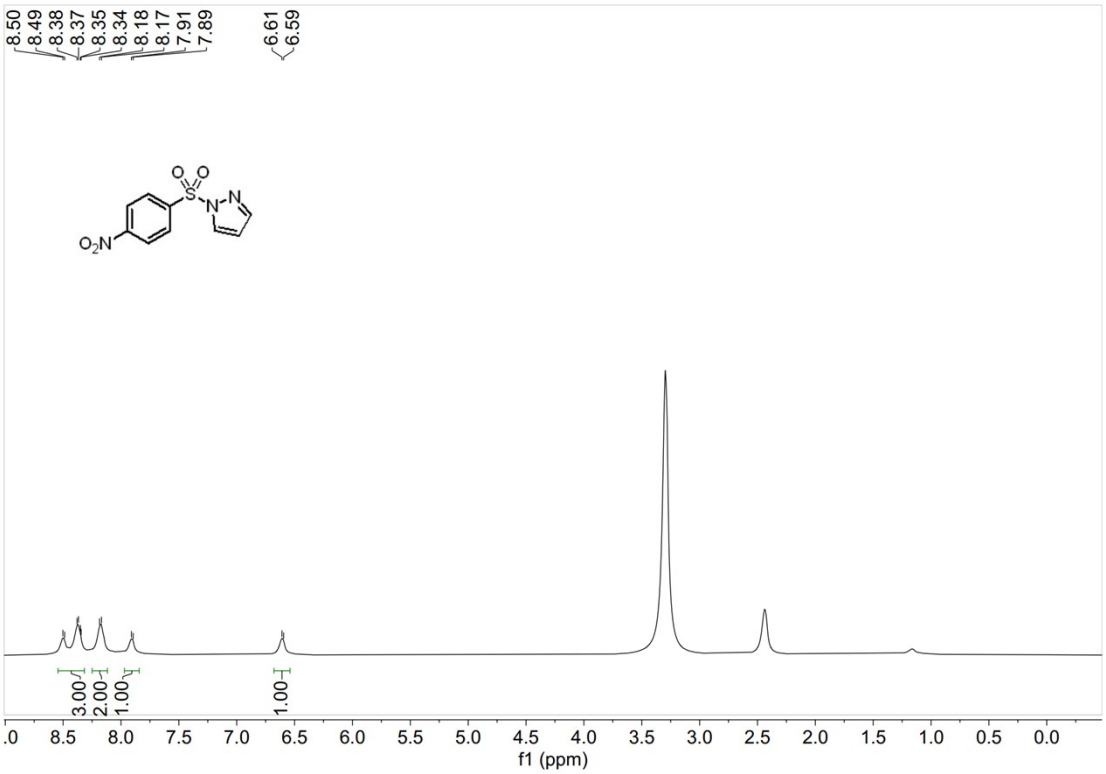
^{13}C NMR (101 MHz, $CDCl_3$) of **61**



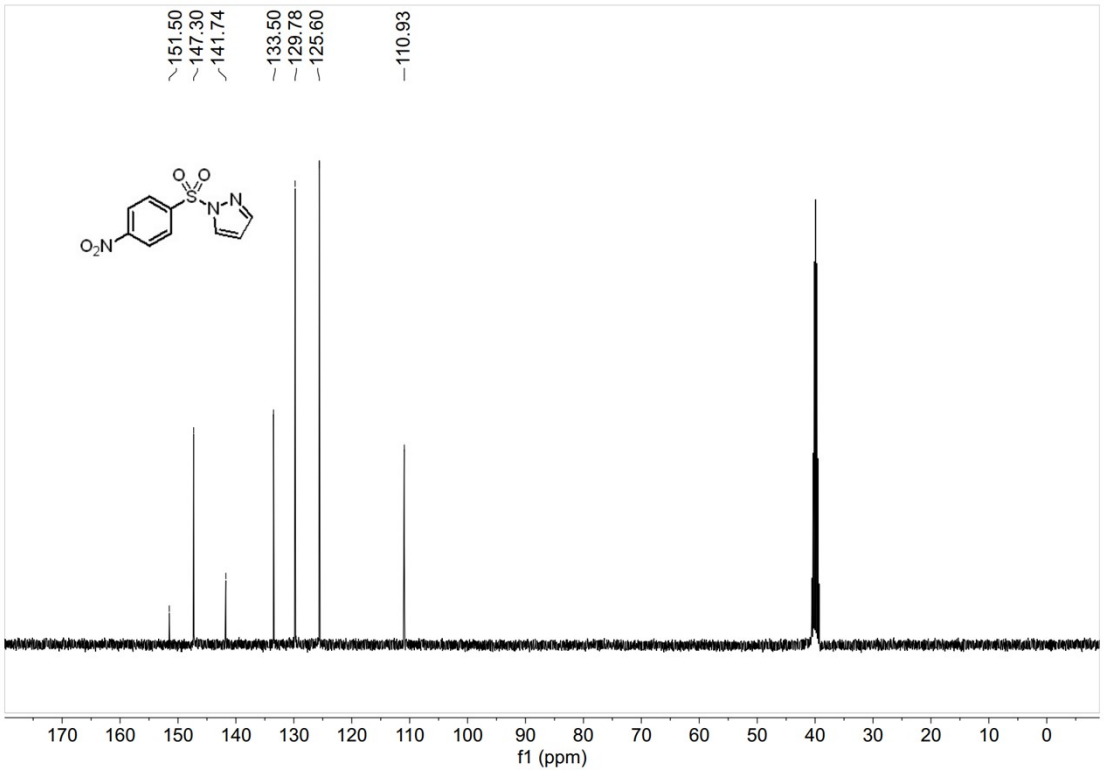
^{1}H NMR (400 MHz, $CDCl_3$) of **62**



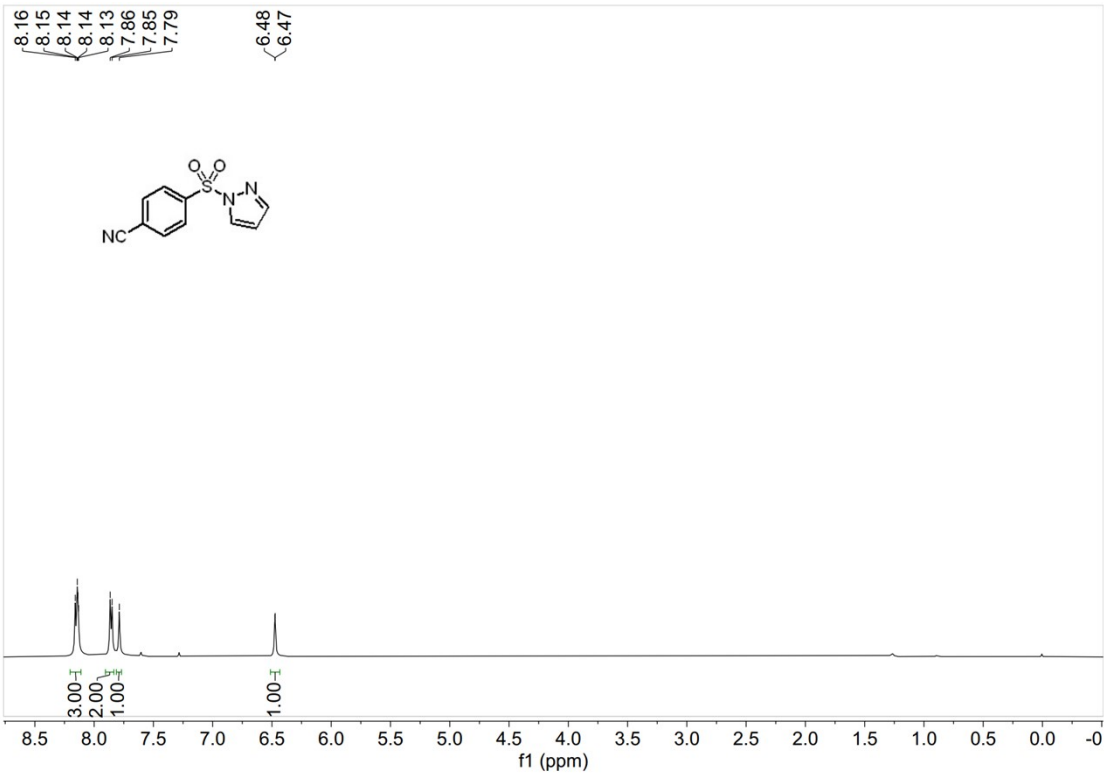
^{13}C NMR (101 MHz, $CDCl_3$) of **62**



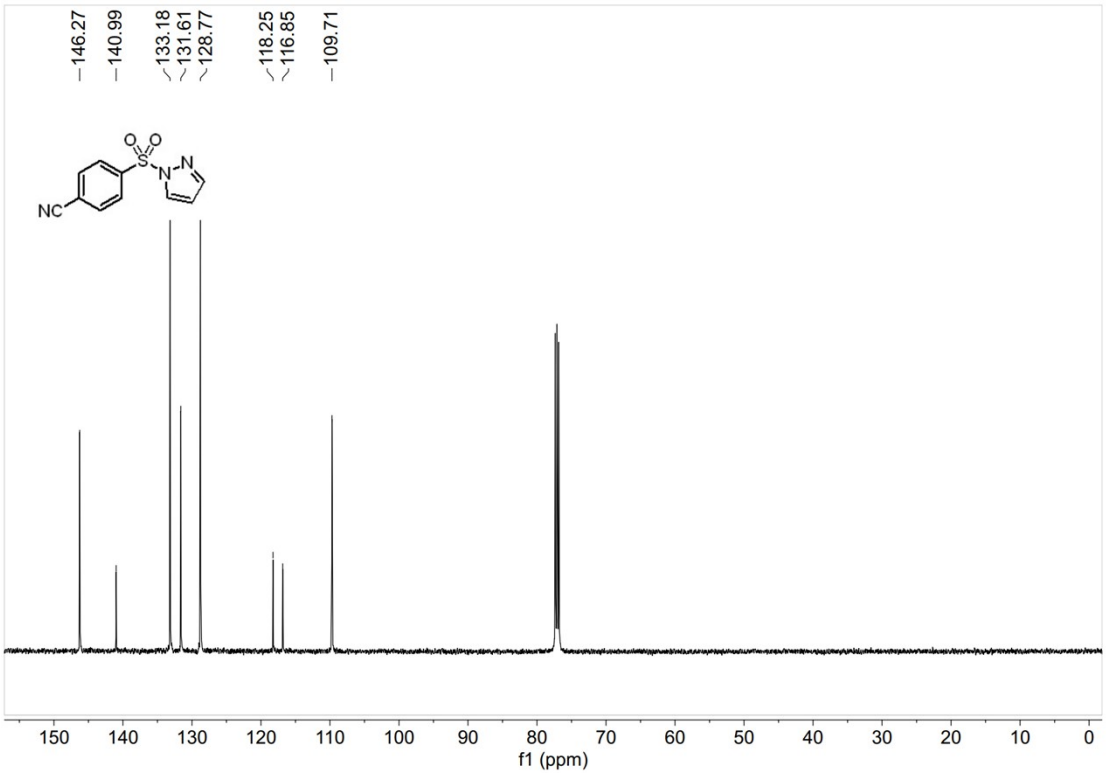
^{1}H NMR (400 MHz, DMSO-d_6) of **63**



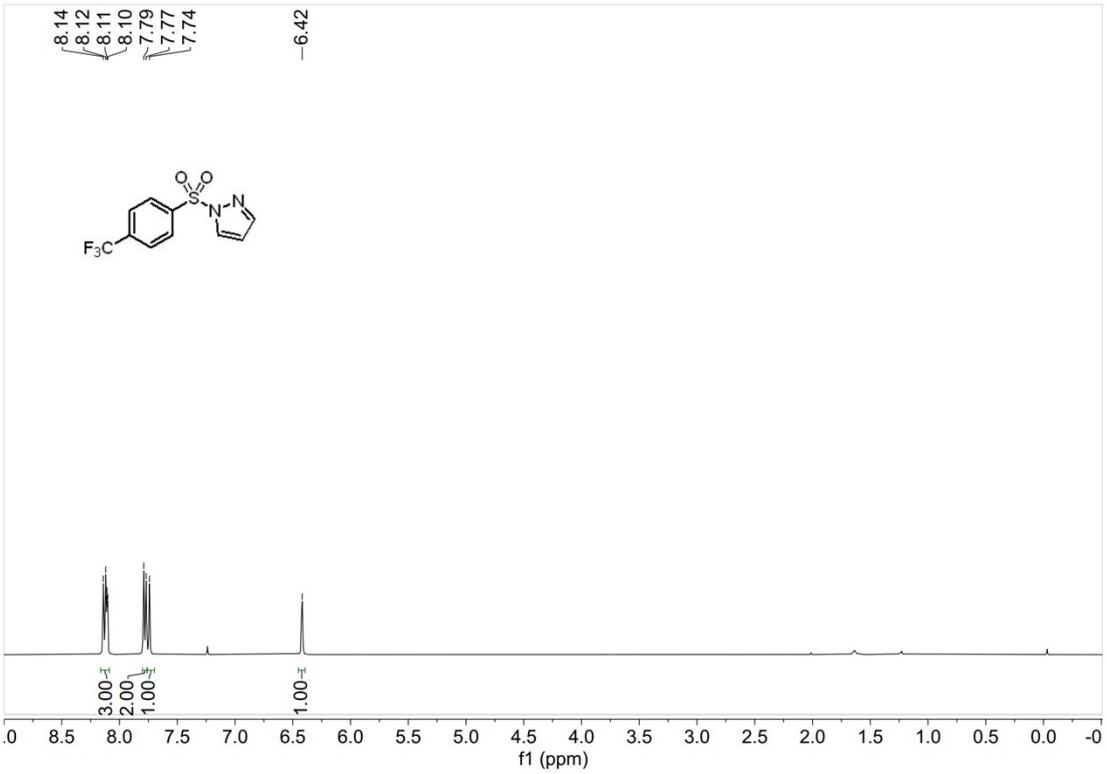
^{13}C NMR (101 MHz, DMSO-d_6) of **63**



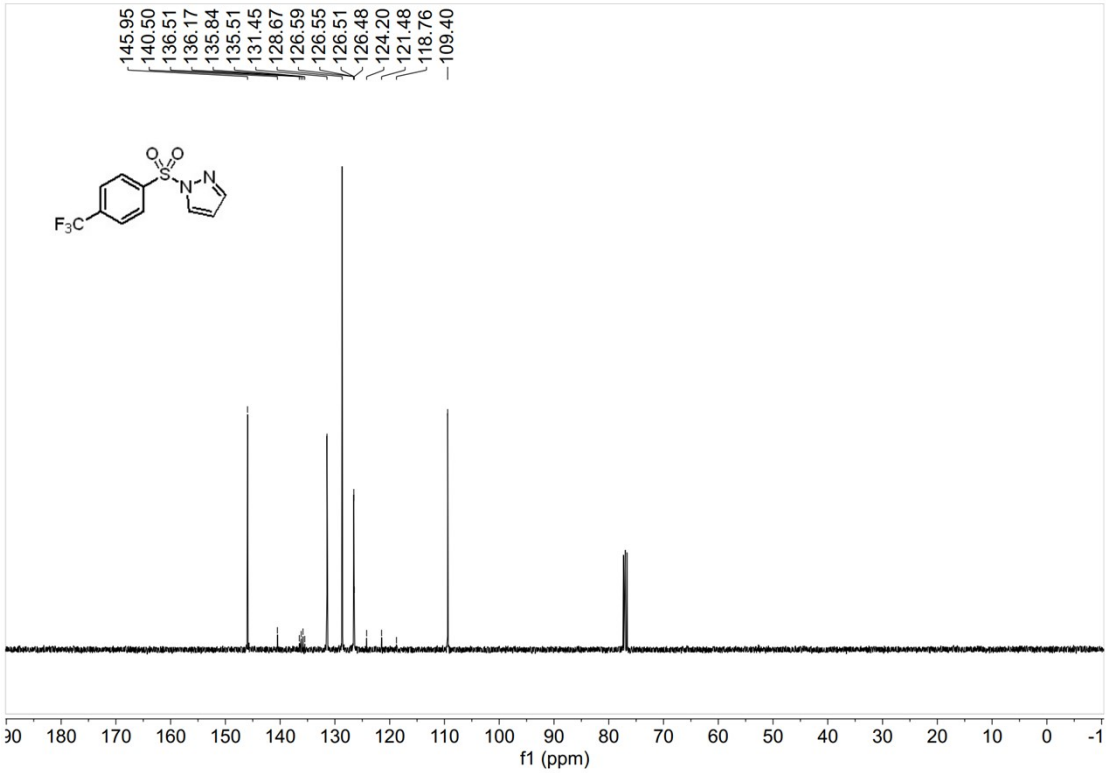
^{1}H NMR (400 MHz, $CDCl_3$) of **64**



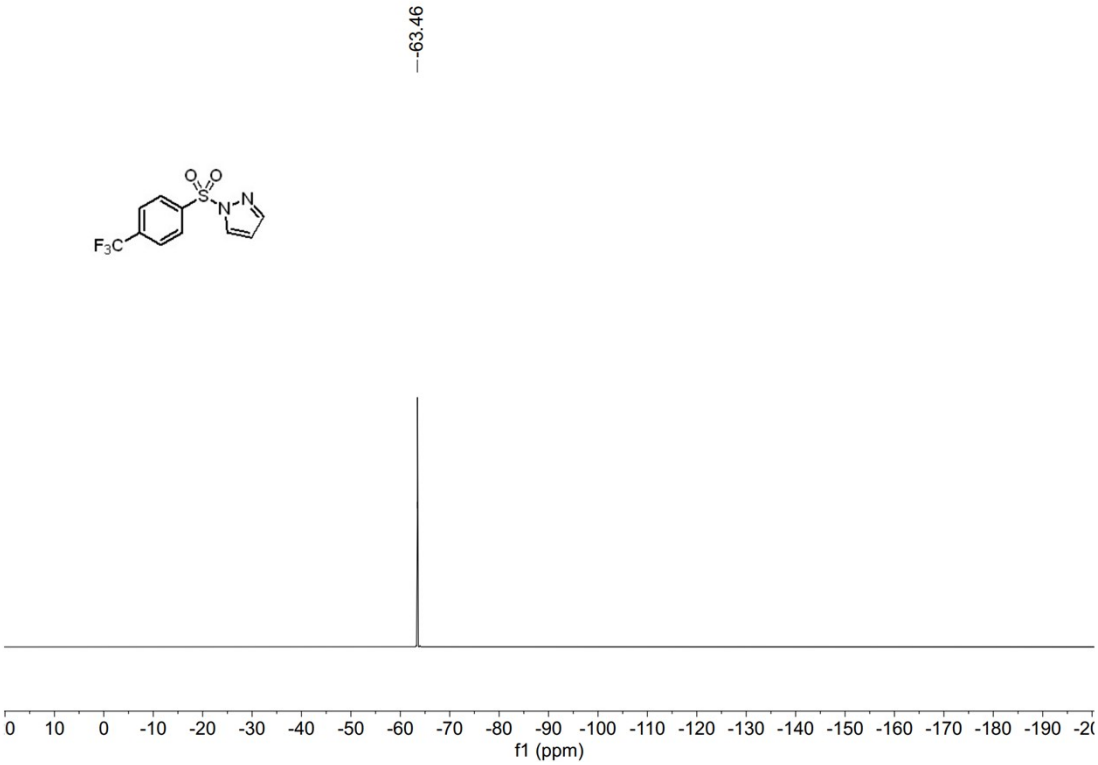
^{13}C NMR (101 MHz, $CDCl_3$) of **64**



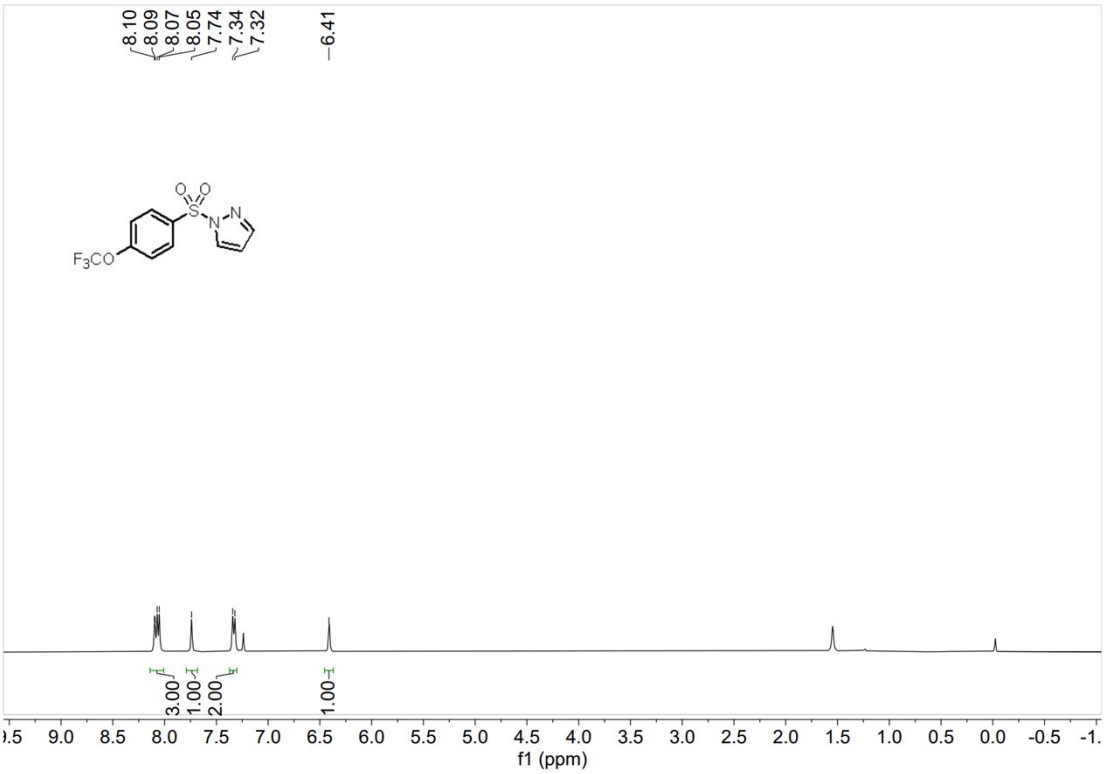
^{1}H NMR (400 MHz, $CDCl_3$) of **65**



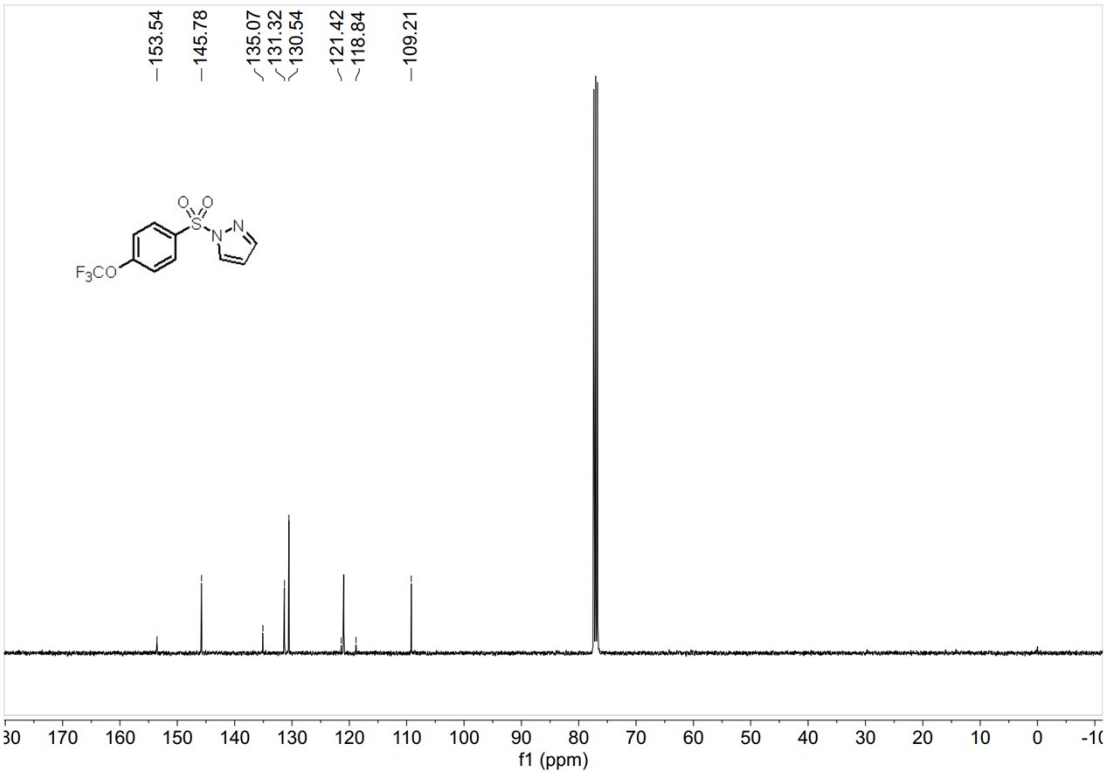
^{13}C NMR (101 MHz, $CDCl_3$) of **65**



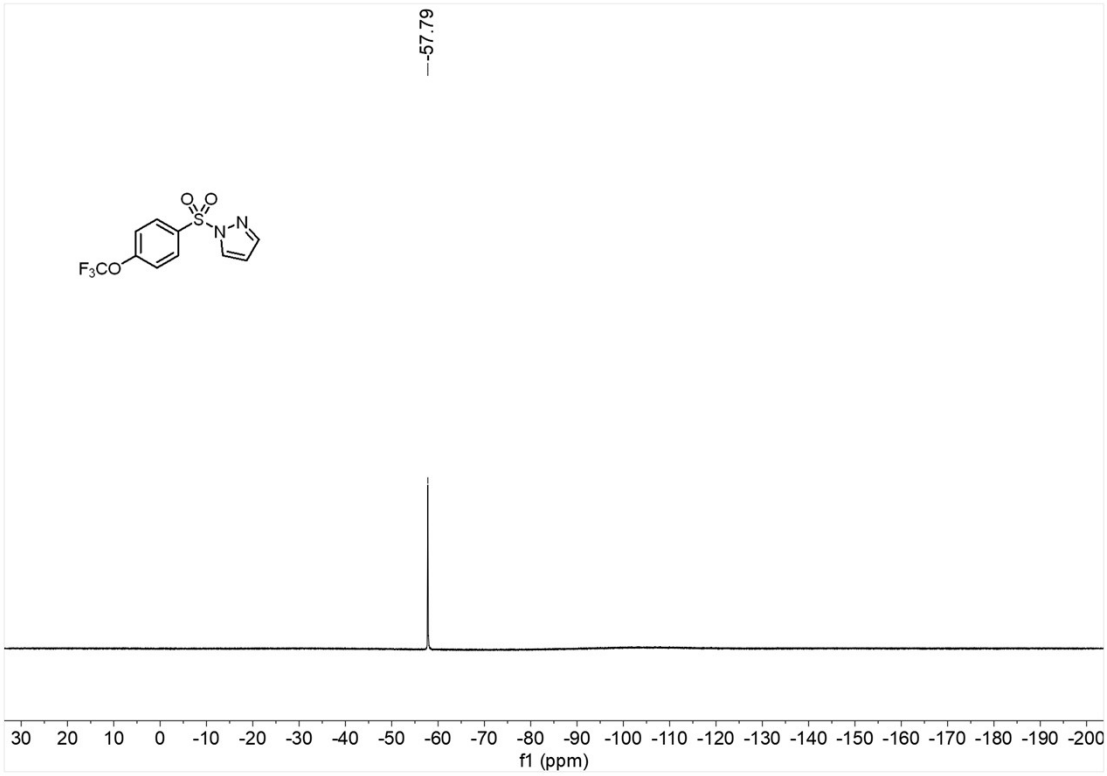
^{19}F NMR (376 MHz, $CDCl_3$) of **65**



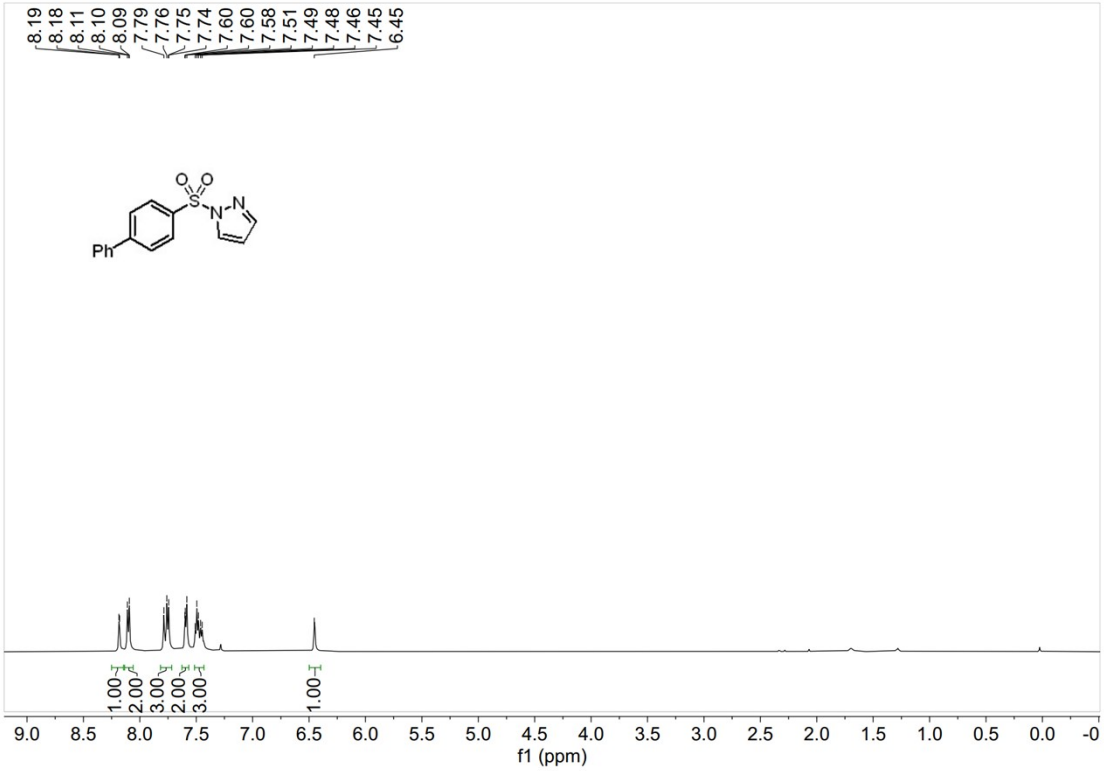
^{1}H NMR (400 MHz, $CDCl_3$) of **66**



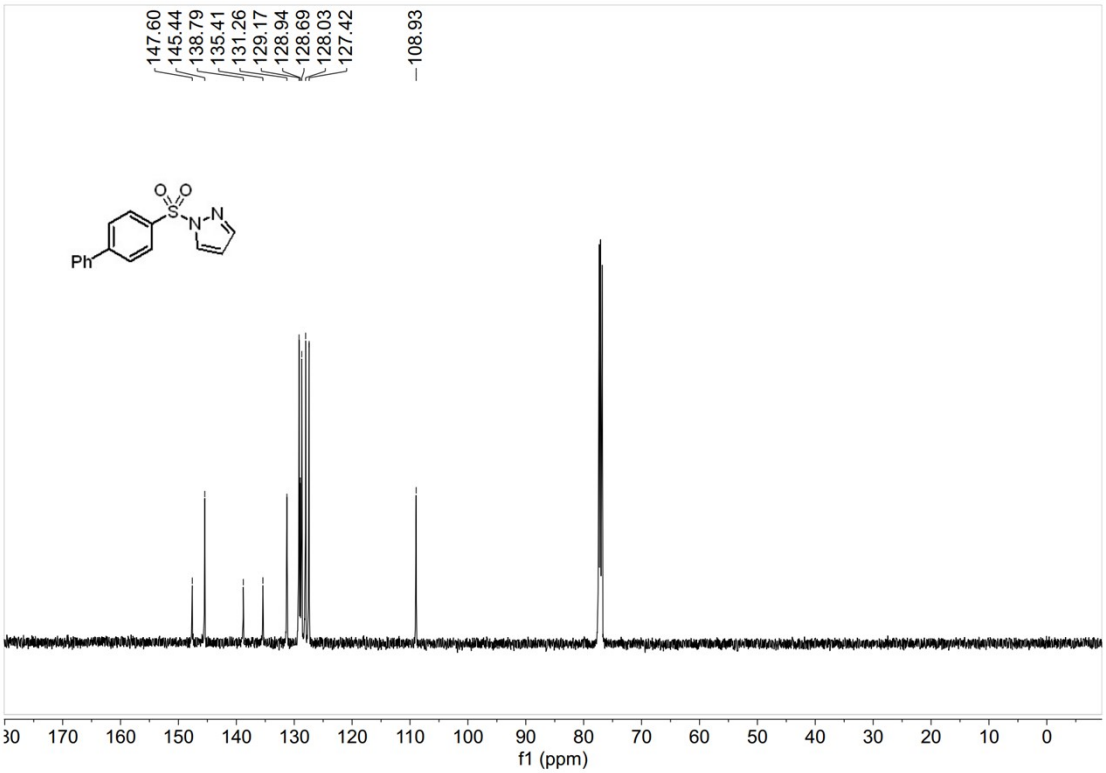
^{13}C NMR (101 MHz, $CDCl_3$) of **66**



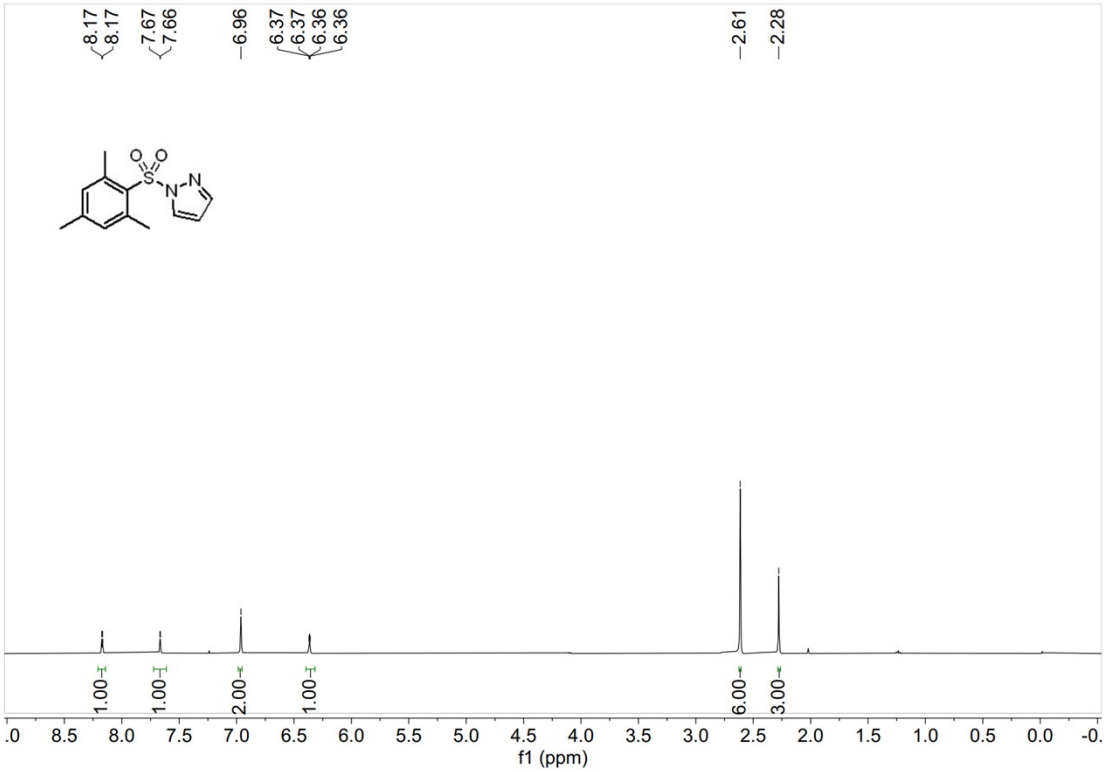
^{19}F NMR (376 MHz, $CDCl_3$) of **66**



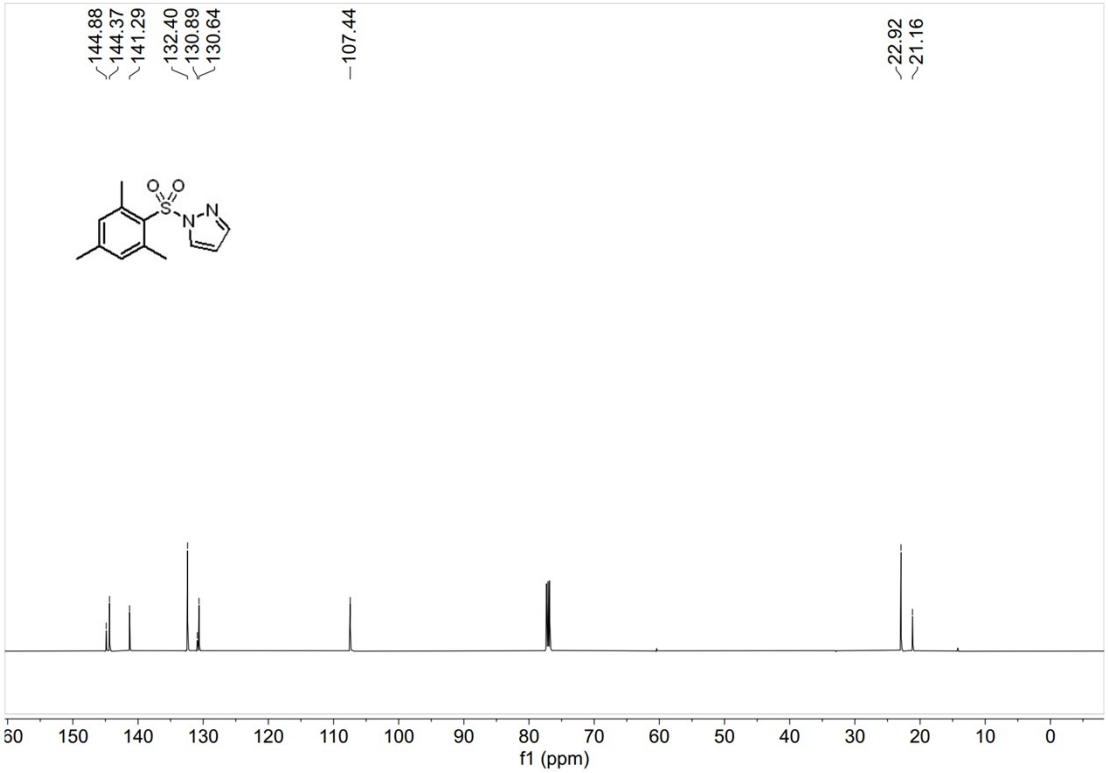
^{1}H NMR (400 MHz, $CDCl_3$) of **67**



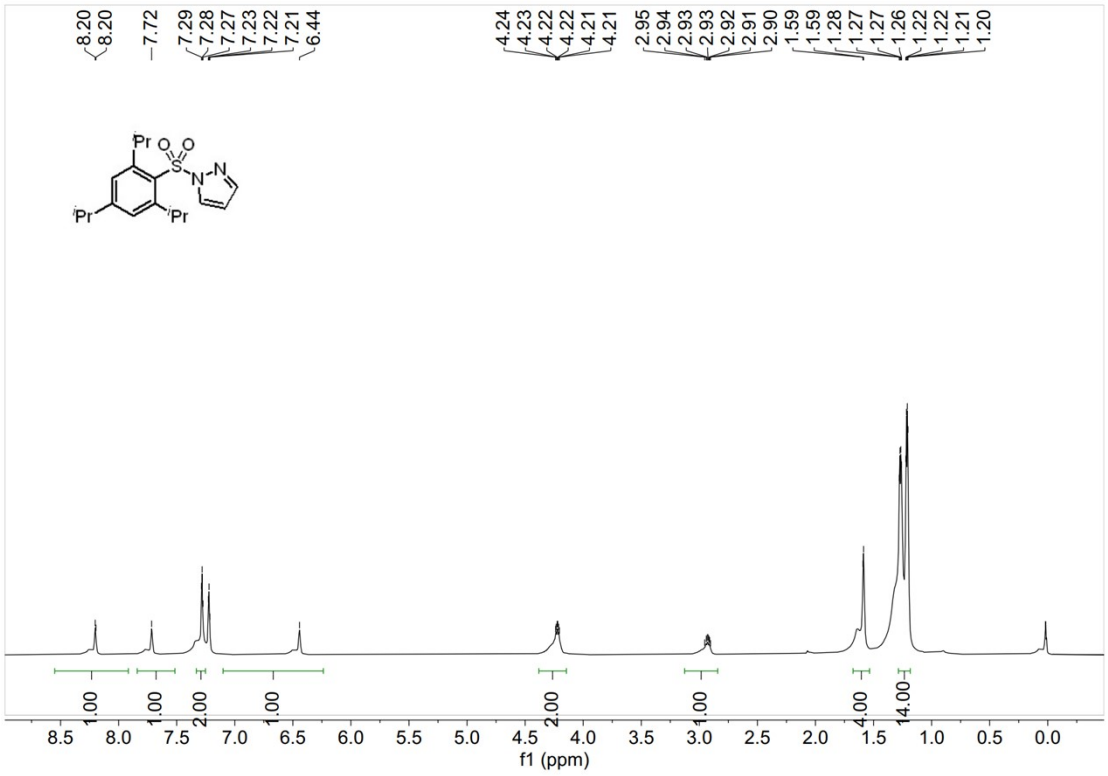
^{13}C NMR (101 MHz, $CDCl_3$) of **67**



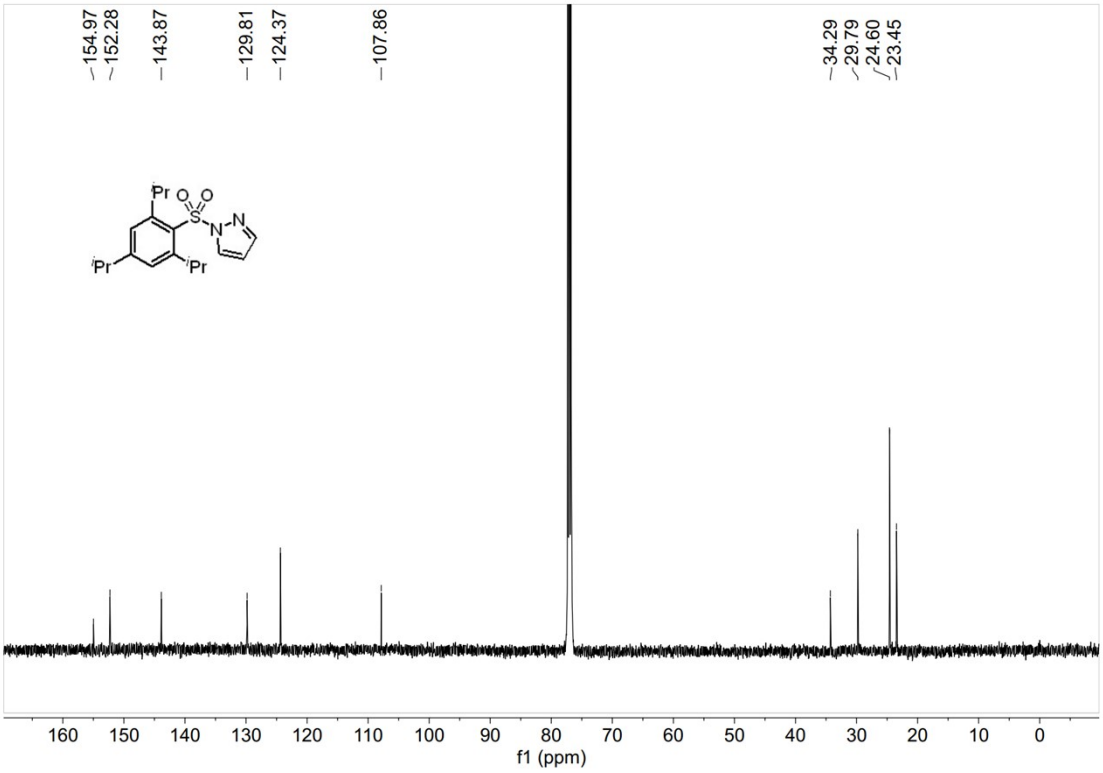
^{1}H NMR (400 MHz, $CDCl_3$) of **68**



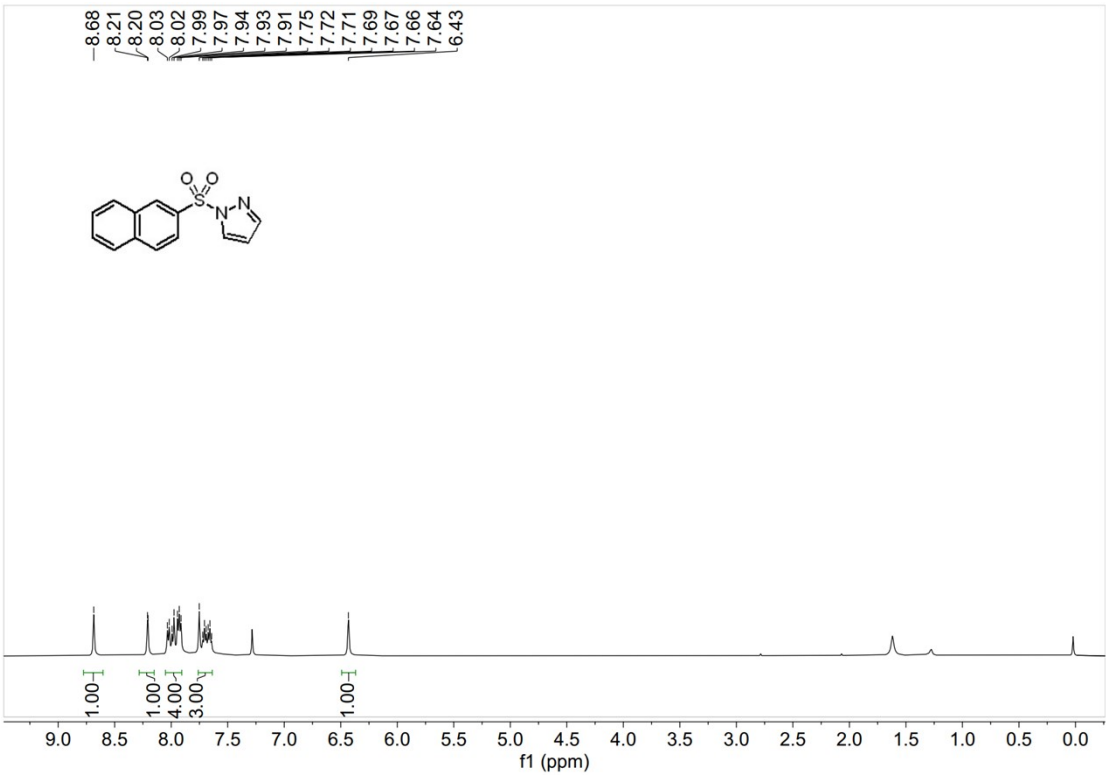
^{13}C NMR (101 MHz, $CDCl_3$) of **68**



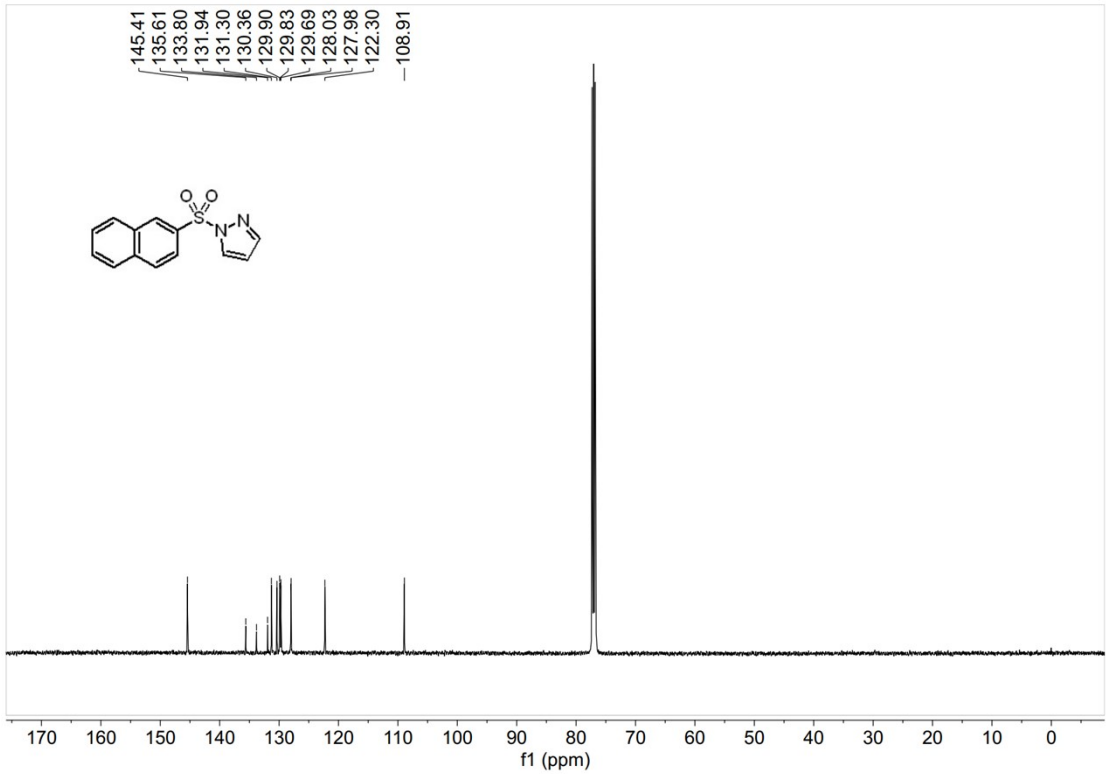
^{1}H NMR (400 MHz, $CDCl_3$) of **69**



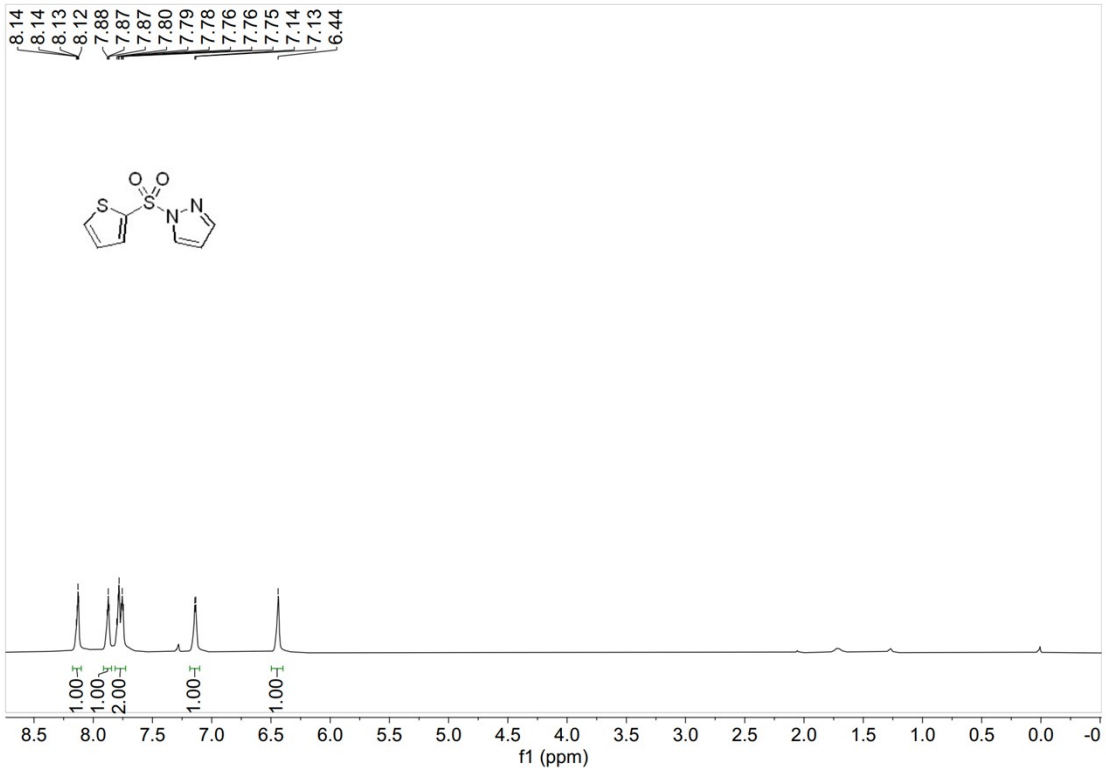
^{13}C NMR (101 MHz, $CDCl_3$) of **69**



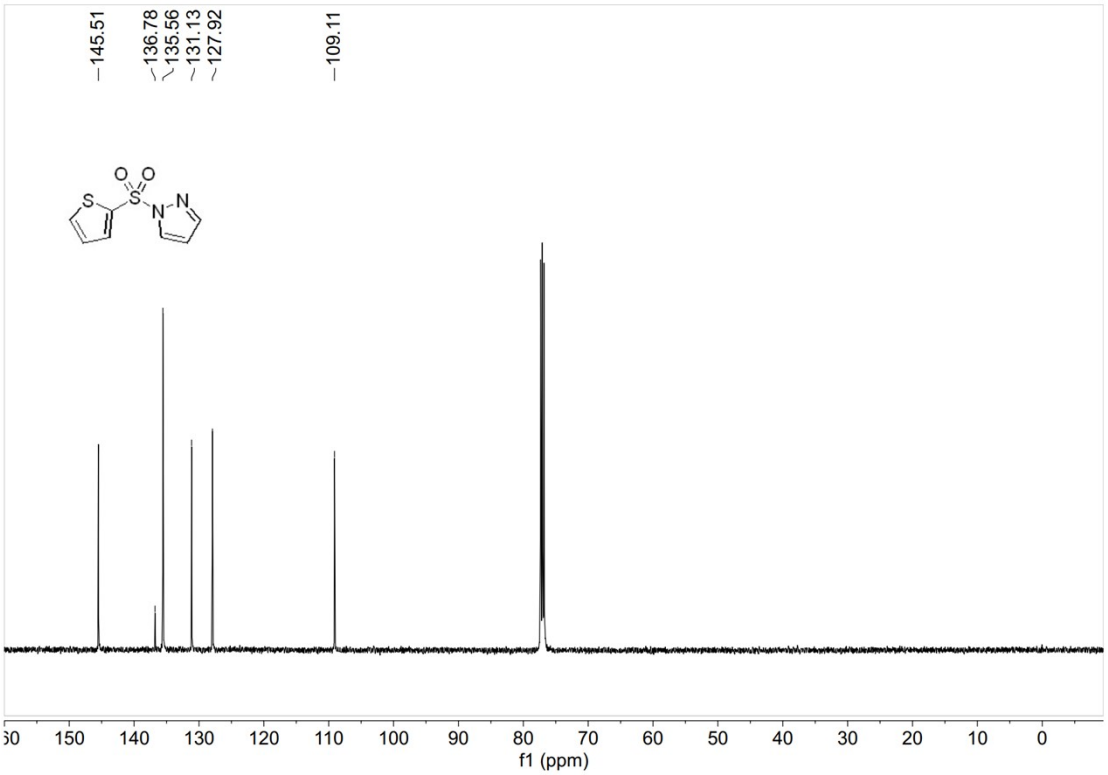
^{1}H NMR (400 MHz, $CDCl_3$) of **70**



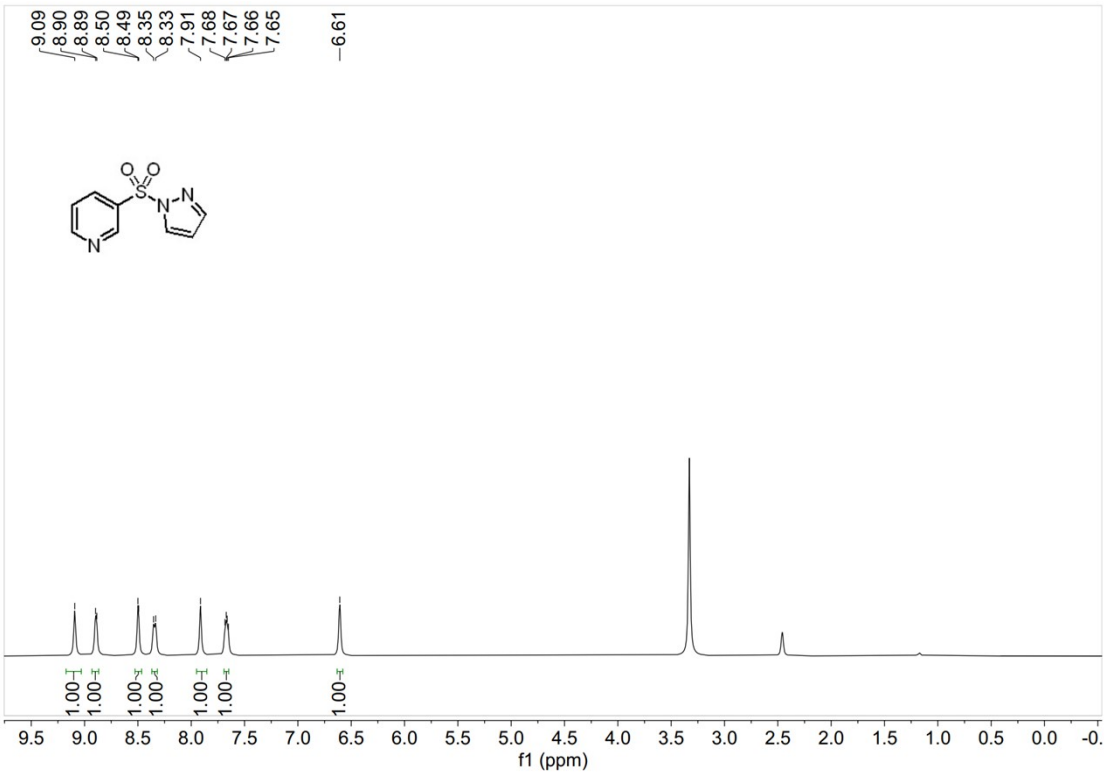
^{13}C NMR (101 MHz, $CDCl_3$) of **70**



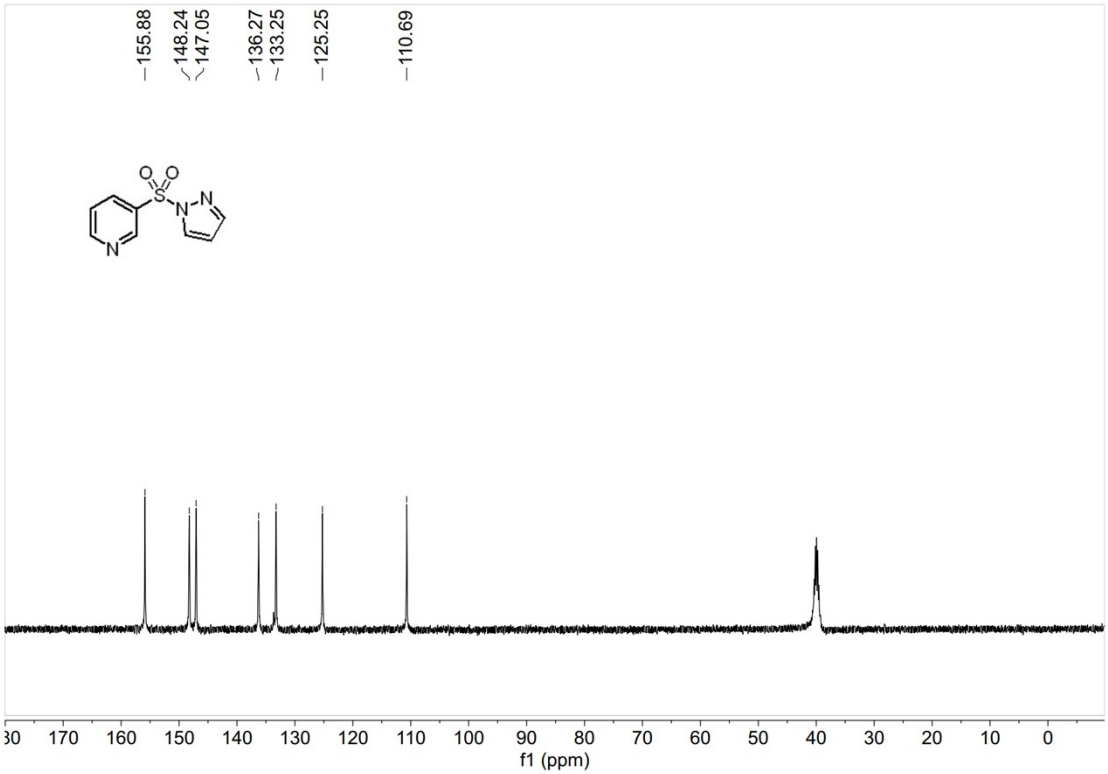
^{1}H NMR (400 MHz, $CDCl_3$) of **71**



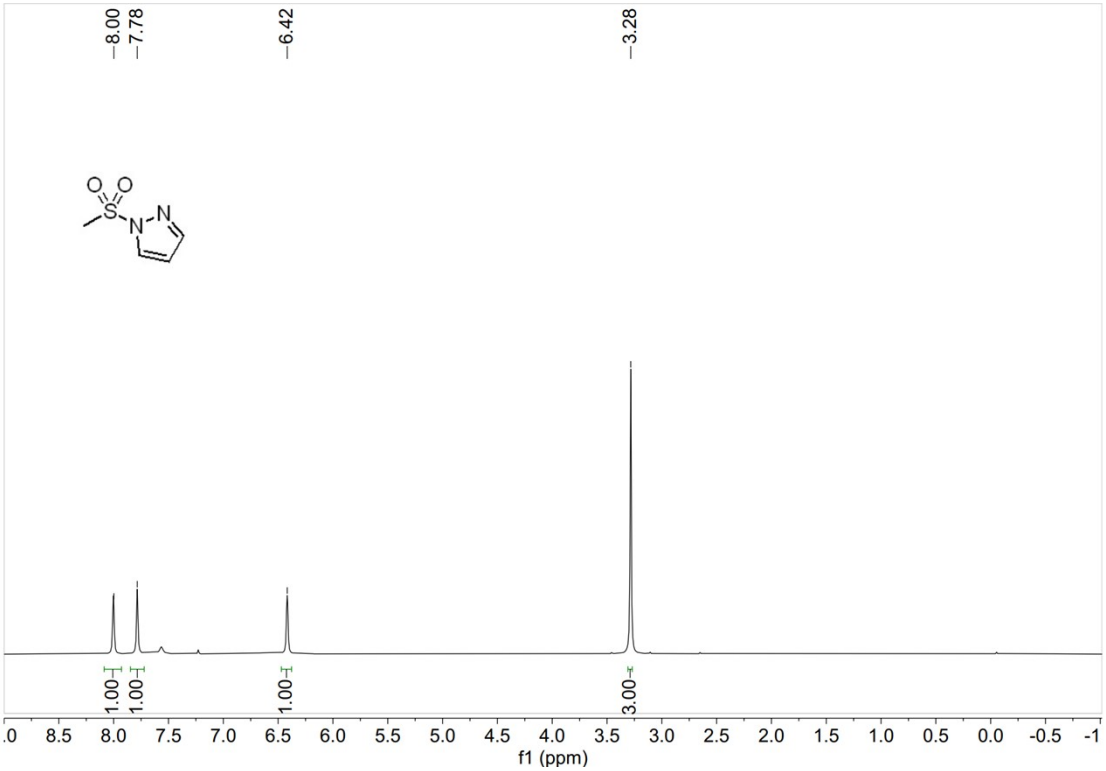
^{13}C NMR (101 MHz, $CDCl_3$) of **71**



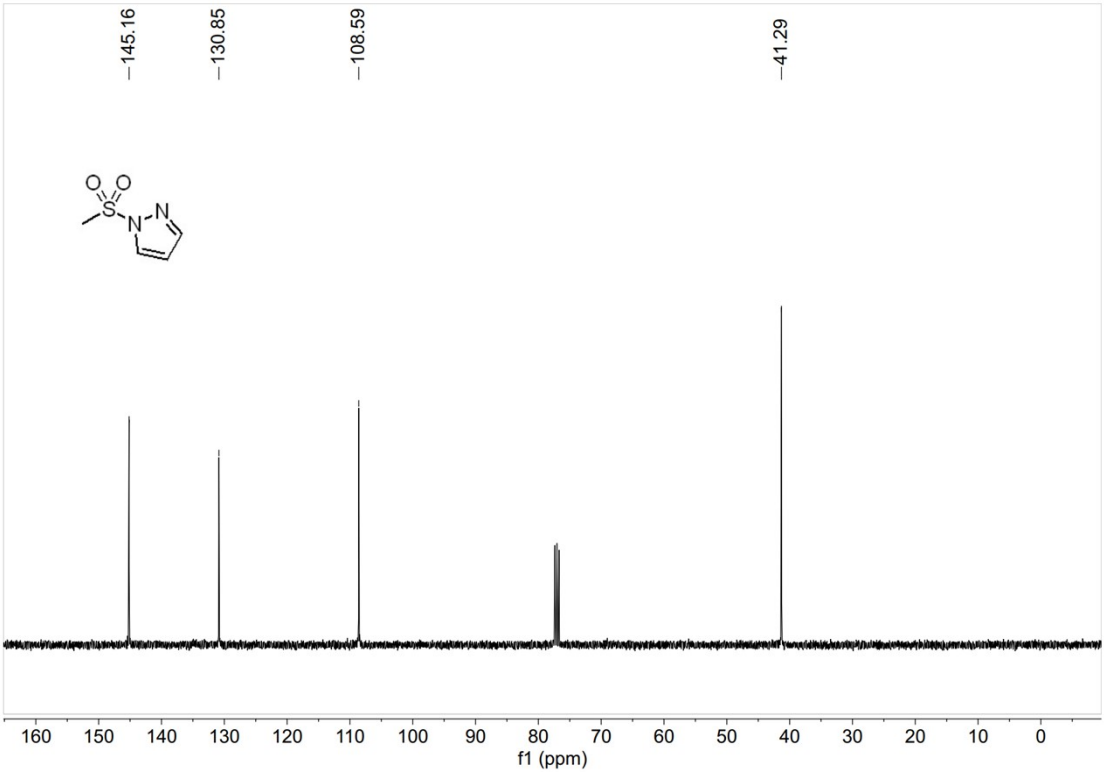
^{1}H NMR (400 MHz, DMSO-d_6) of **72**



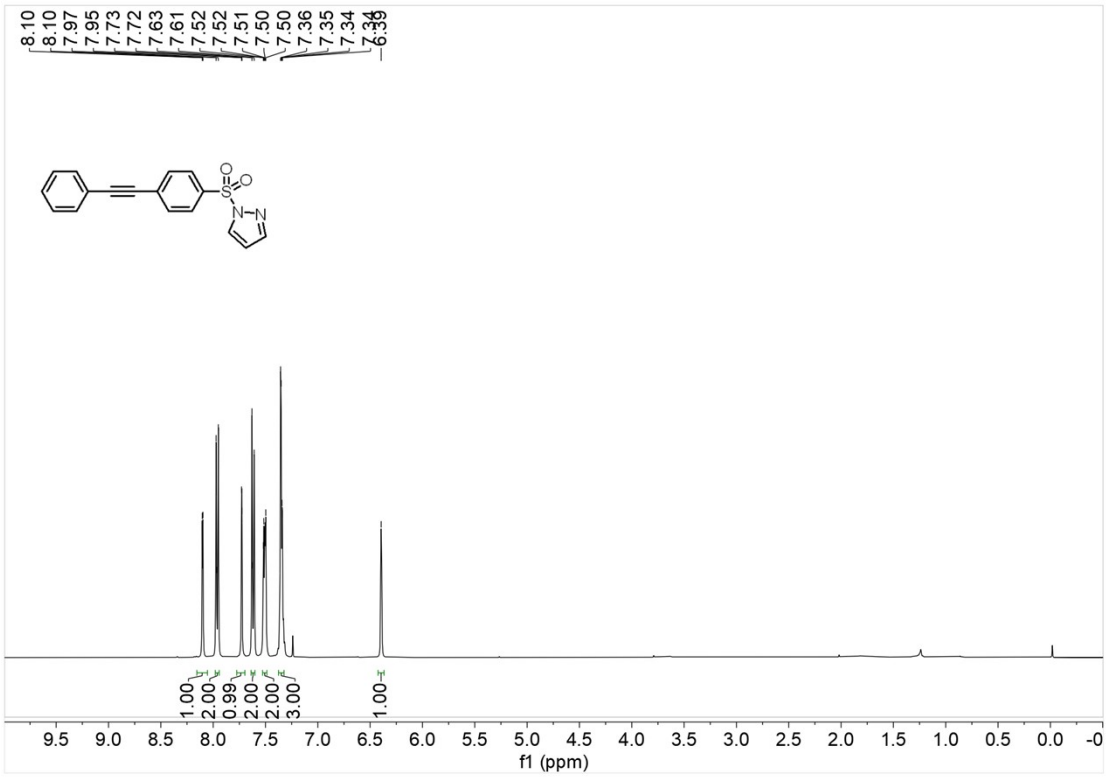
^{13}C NMR (101 MHz, DMSO-d_6) of **72**



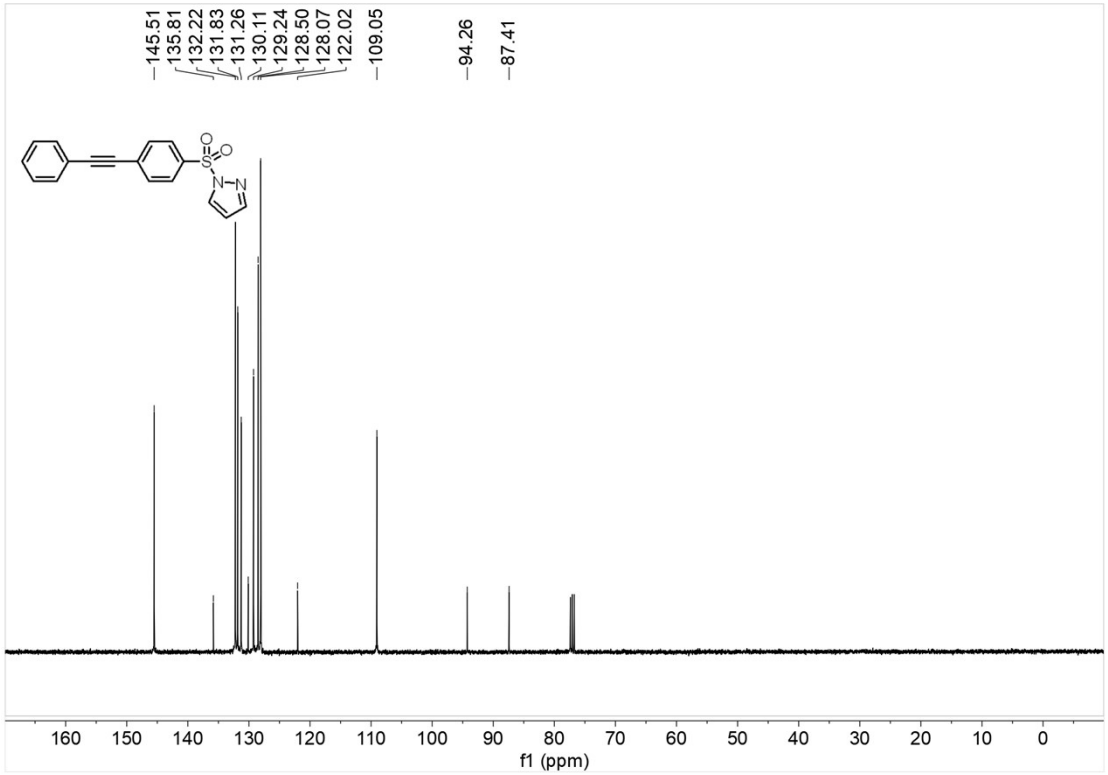
^{1}H NMR (400 MHz, $CDCl_3$) of **73**



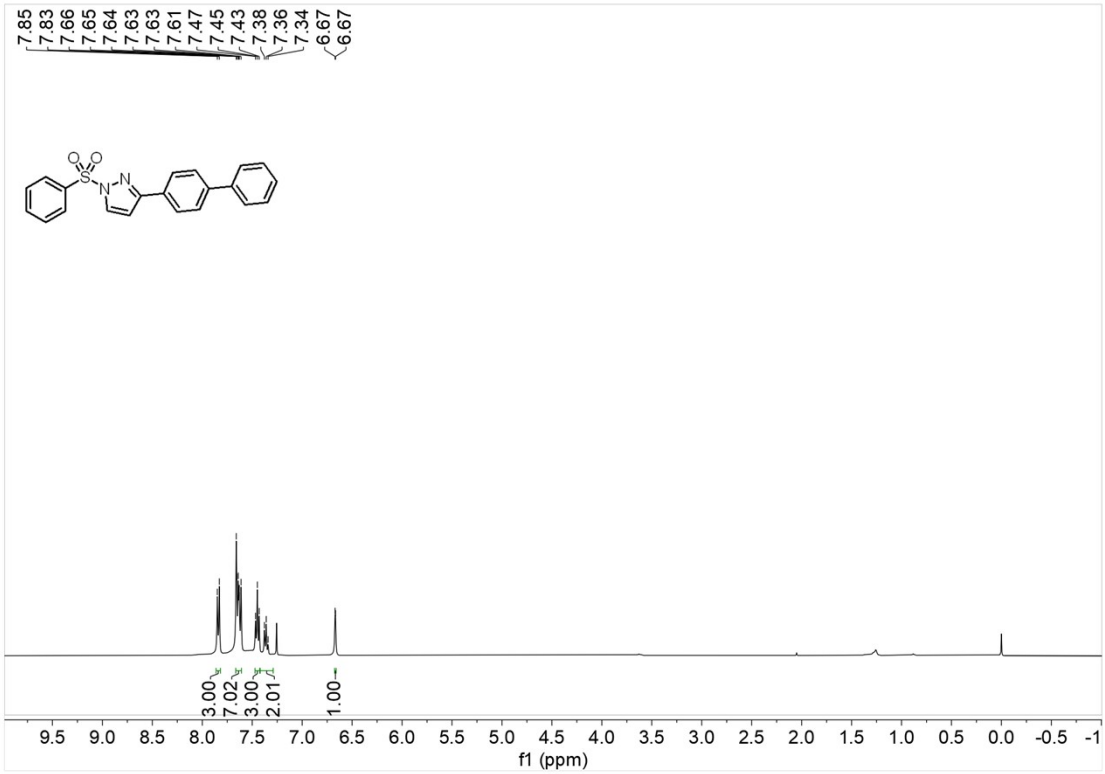
^{13}C NMR (101 MHz, $CDCl_3$) of **73**



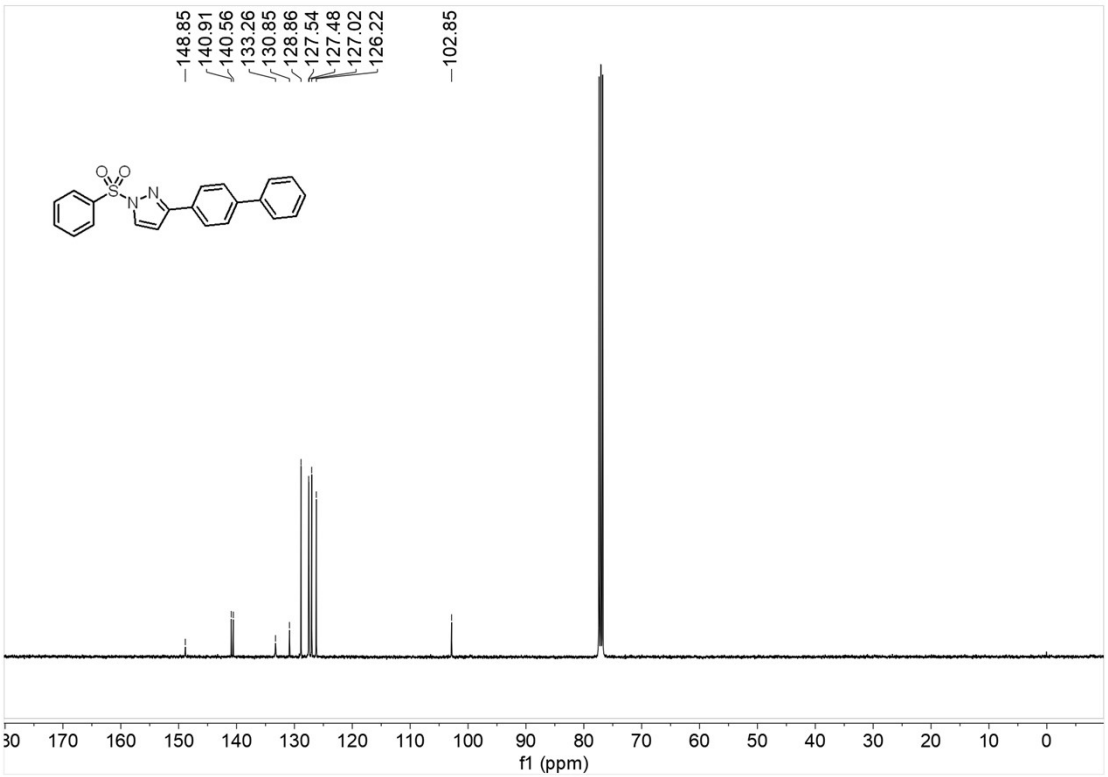
^{1}H NMR (400 MHz, $CDCl_3$) of **77**



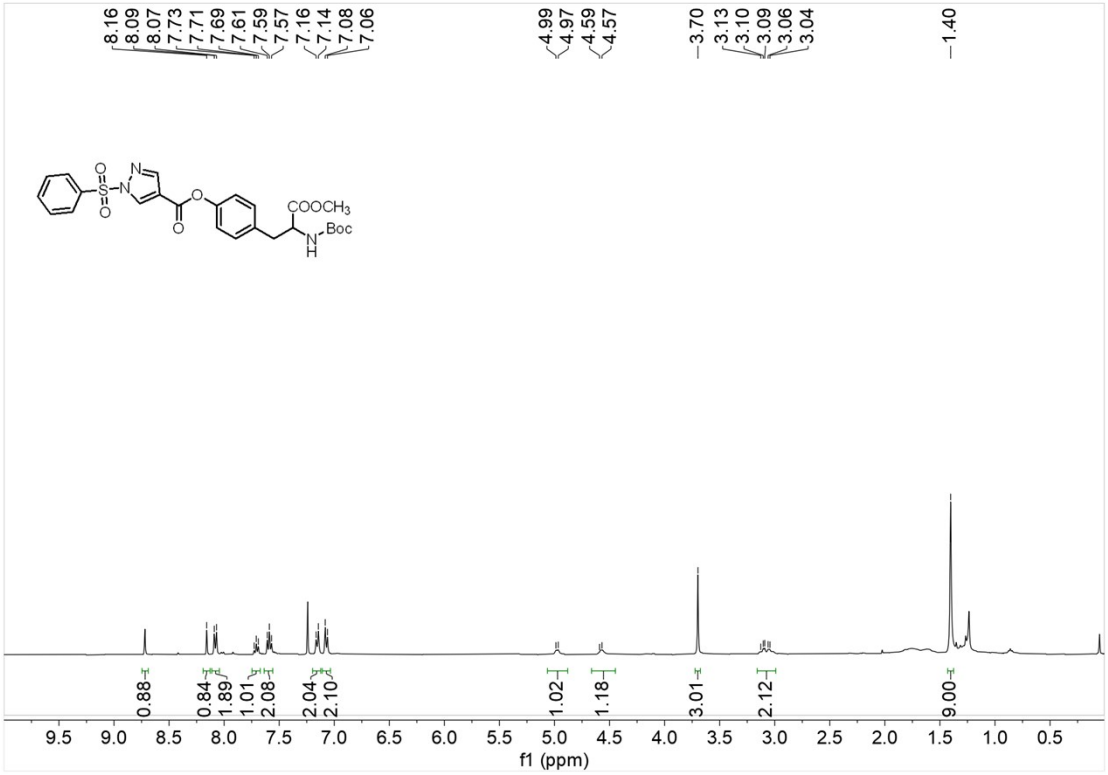
^{13}C NMR (101 MHz, $CDCl_3$) of **77**



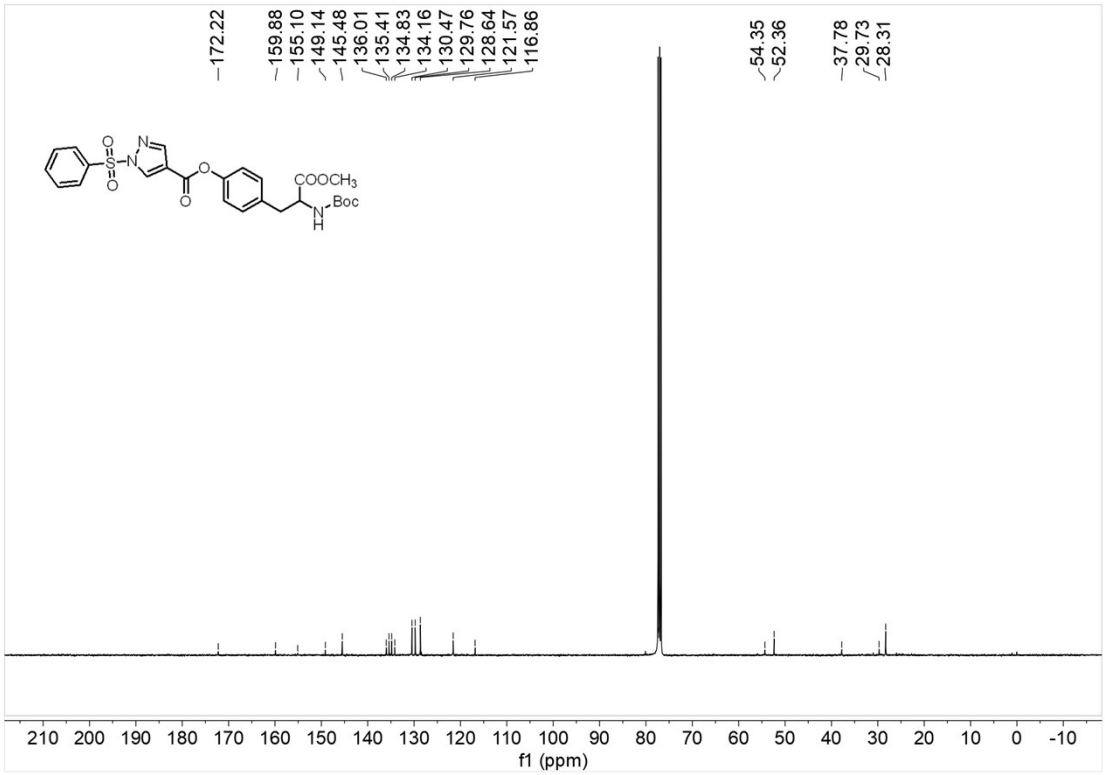
^{1}H NMR (400 MHz, $CDCl_3$) of **78**



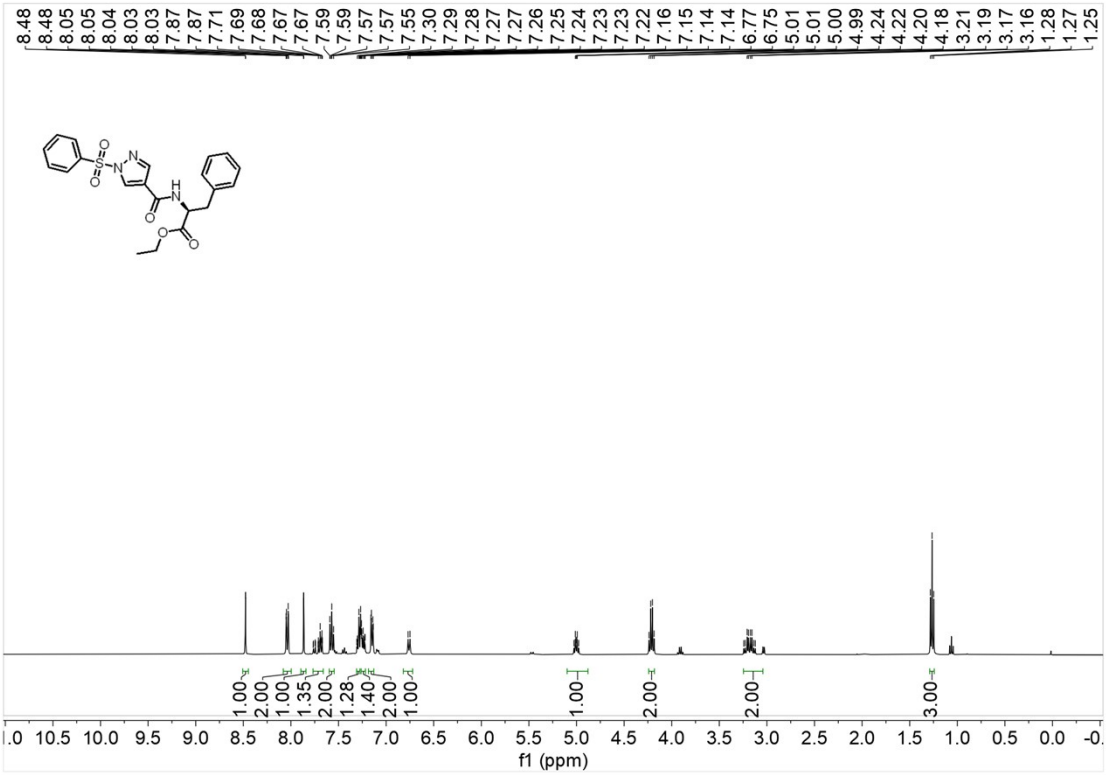
^{13}C NMR (101 MHz, $CDCl_3$) of **78**



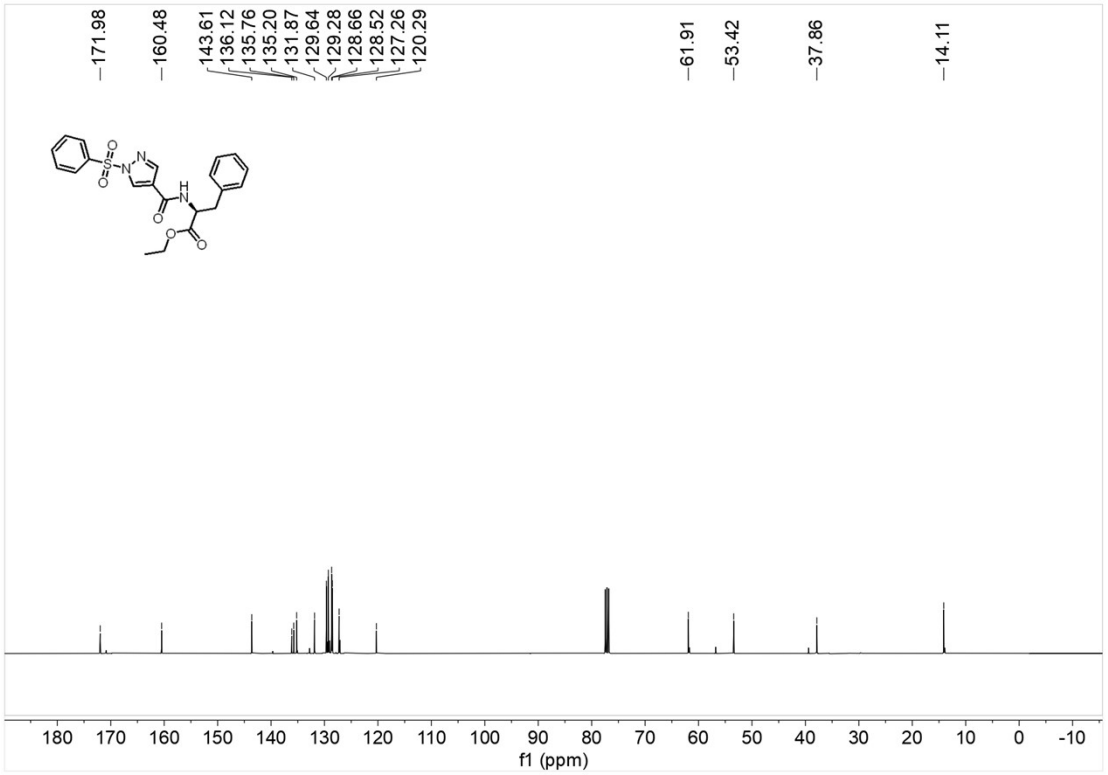
^{1}H NMR (400 MHz, $CDCl_3$) of **79**



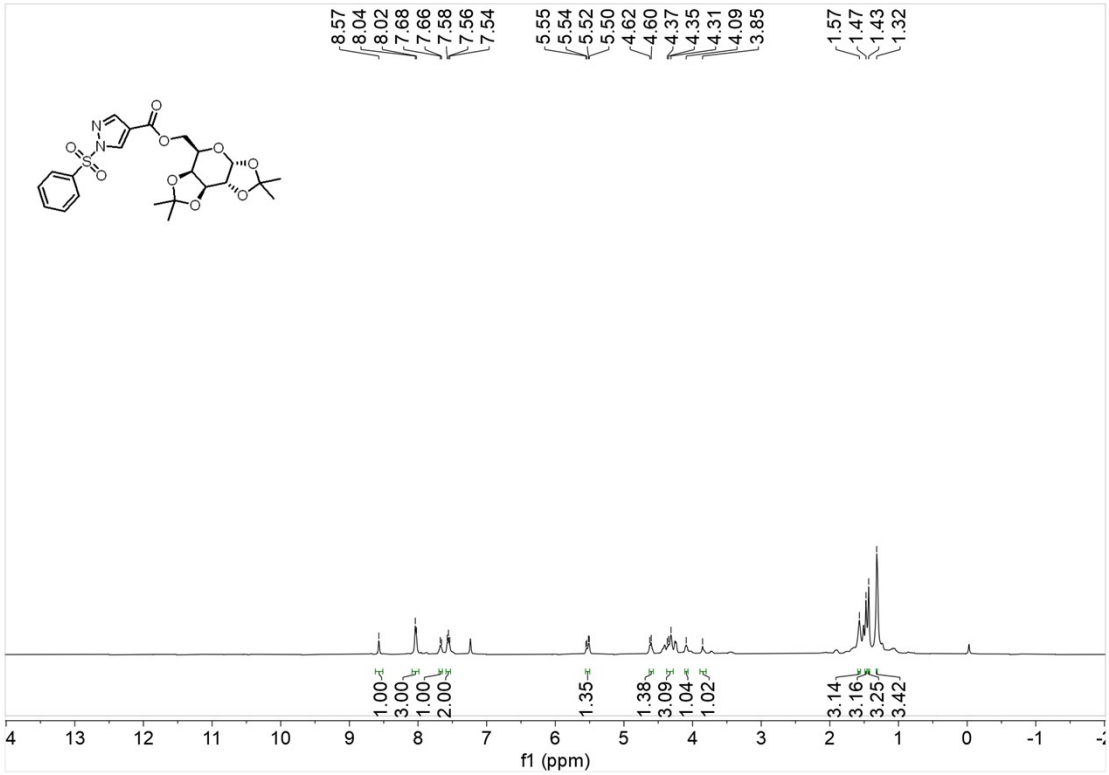
^{13}C NMR (101 MHz, $CDCl_3$) of **79**



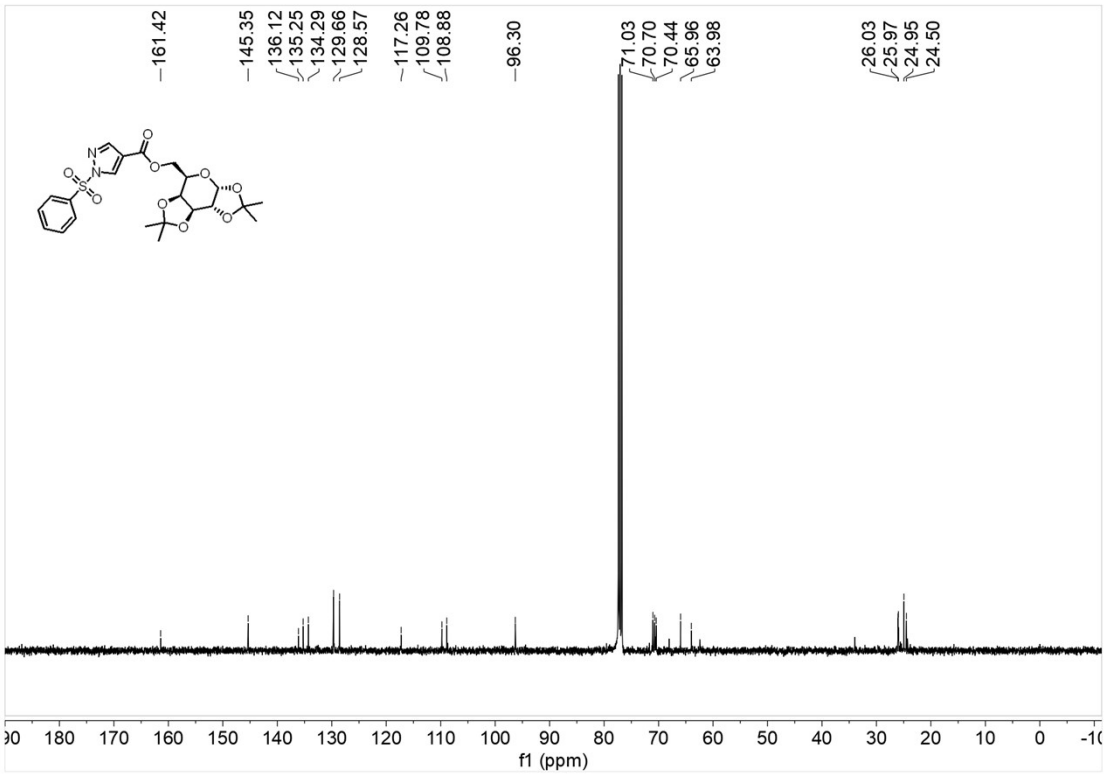
^{1}H NMR (400 MHz, $CDCl_3$) of **80**



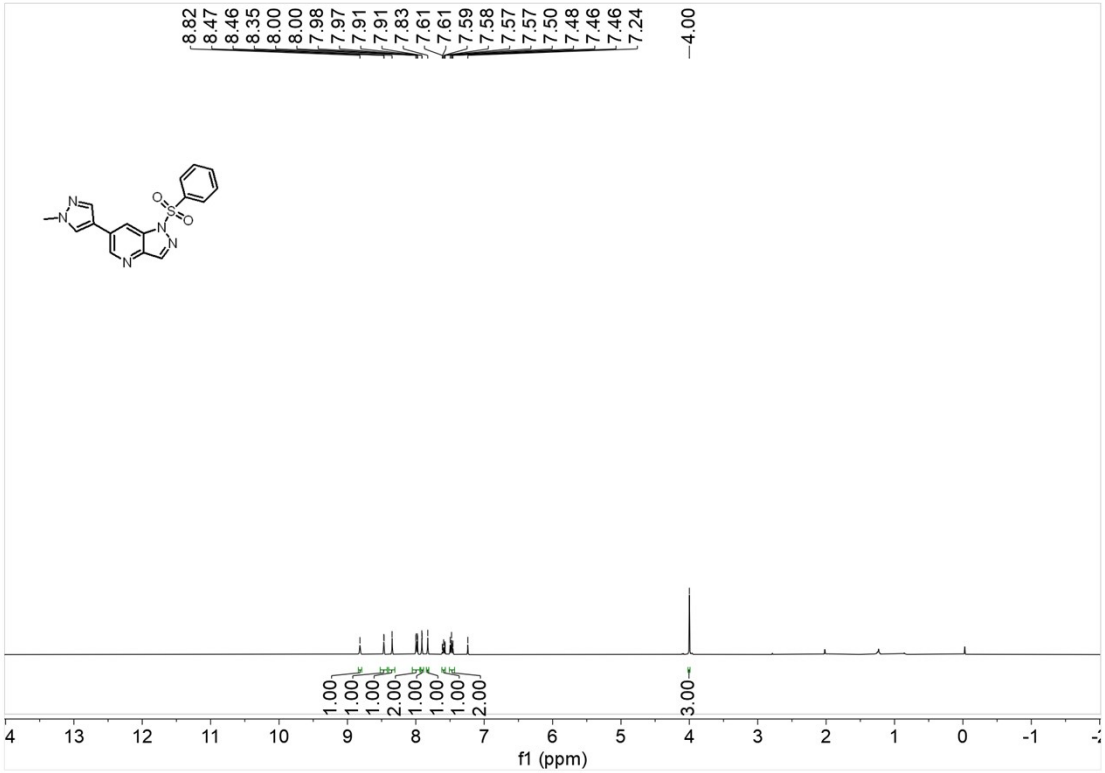
^{13}C NMR (101 MHz, $CDCl_3$) of **80**



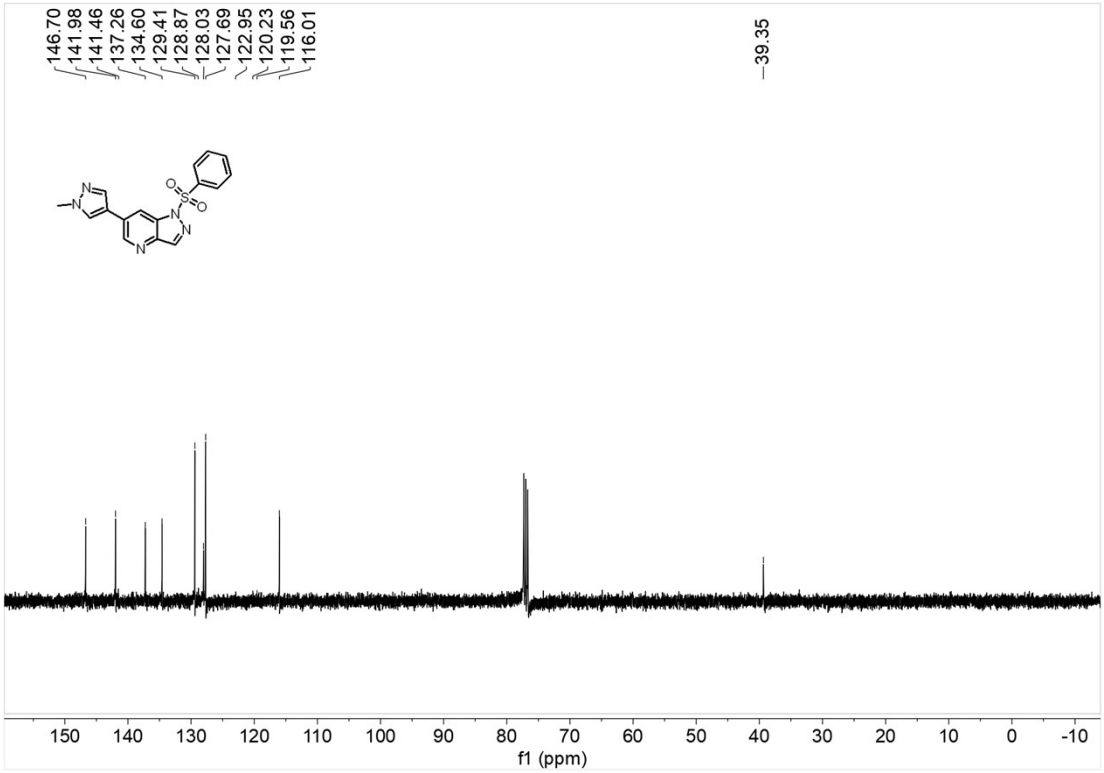
^{1}H NMR (400 MHz, $CDCl_3$) of **81**



^{13}C NMR (101 MHz, $CDCl_3$) of **81**



^{1}H NMR (400 MHz, $CDCl_3$) of **82**



^{13}C NMR (101 MHz, $CDCl_3$) of **82**

16. Crystal Structure Data

X-Ray crystal structure of compound **12**: Crystal of compound **12** were obtained by dissolving the product in Hexane/CH_2Cl_2 mixture and allowing the solvent to slowly evaporate at room temperature. A suitable crystal was selected and mounted onto the cryoloop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,1 the structure was solved with the SHELXT2 structure solution program using Intrinsic Phasing and refined with the SHELXL3 refinement package using Least Squares minimization.

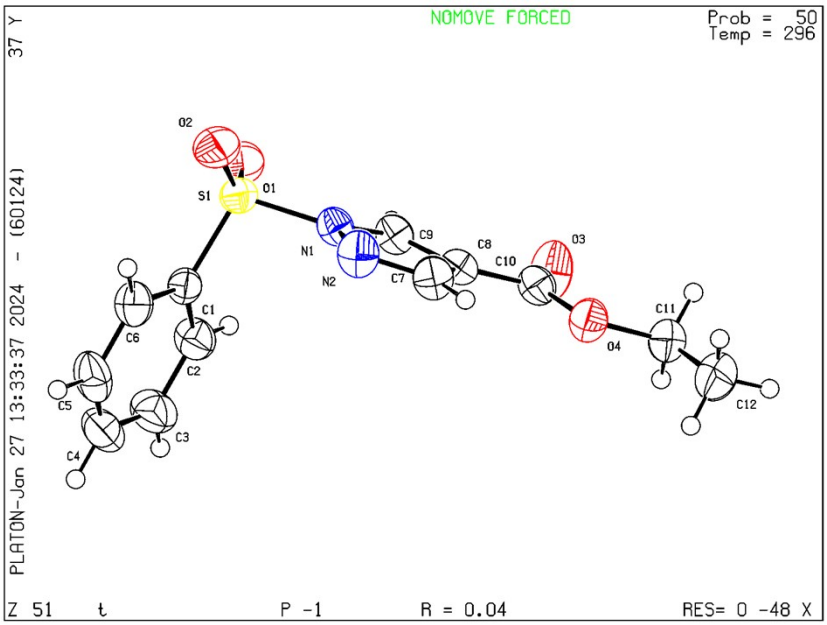


Figure S7. ORTEP diagram of compound **12** with ellipsoid shown at the 50% contour percent probability level (CCDC-2328852)

Identification code	12
Empirical formula	$C_{12}H_{12}N_2O_4S$
Formula weight	280.30
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	7.3939(16)
b/Å	7.7731(17)
c/Å	13.160(3)
α/°	84.179(4)
β/°	73.900(3)
γ/°	63.163(3)
Volume/Å^3	648.2(2)
Z	2
ρ_{calc}g/cm^3	1.436
μ/mm^{-1}	0.261
F(000)	292.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	5.876 to 55.368
Index ranges	-6 ≤ h ≤ 9, -8 ≤ k ≤ 10, -17 ≤ l ≤ 17
Reflections collected	3956
Independent reflections	2865 [R_{int} = 0.0220, R_{sigma} = 0.0372]
Data/restraints/parameters	2865/0/174
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.1040
Final R indexes [all data]	R_1 = 0.0511, wR_2 = 0.1127
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.33

X-Ray crystal structure of compound **23**: Crystal of compound **23** were obtained by dissolving the product in Hexane/CH_2Cl_2 mixture and allowing the solvent to slowly evaporate at room temperature. A suitable crystal was selected and mounted onto the cryoloop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,1 the structure was solved with the SHELXT2 structure solution program using Intrinsic Phasing and refined with the SHELXL3 refinement package using Least Squares minimization.

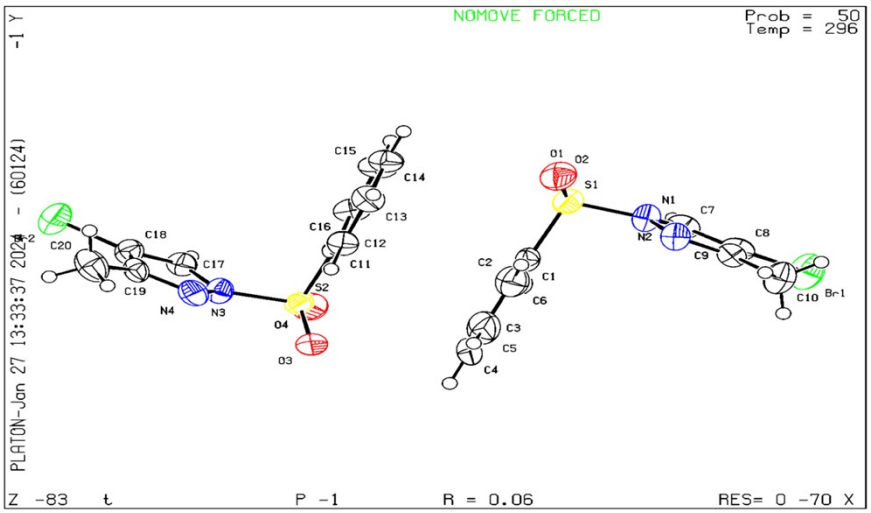


Figure S8. ORTEP diagram of compound **23** with ellipsoid shown at the 50% contour percent probability level (CCDC- 2328851)

Identification code	23
Empirical formula	$C_{10}H_9BrN_2O_2S$
Formula weight	301.16
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	7.976(3)
b/Å	12.668(4)
c/Å	12.714(4)
α/°	101.928(6)
β/°	102.068(6)
γ/°	105.796(6)
Volume/$Å^3$	1160.5(7)
Z	4
ρ_{calc}g/cm^3	1.724

μ/mm^{-1}	3.708
F(000)	600.0
Crystal size/mm^3	0.16 × 0.13 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.48 to 55.71
Index ranges	-8 ≤ h ≤ 10, -16 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	7022
Independent reflections	5121 [R_{int} = 0.0432, R_{sigma} = 0.1244]
Data/restraints/parameters	5121/0/291
Goodness-of-fit on F^2	0.994
Final R indexes [I>=2σ (I)]	R_1 = 0.0635, wR_2 = 0.1345
Final R indexes [all data]	R_1 = 0.1530, wR_2 = 0.1673
Largest diff. peak/hole / e $Å^{-3}$	1.13/-0.99