Supporting Information

Electrochemical selective incorporation of SO_2 to synthesize the fused-ring framework

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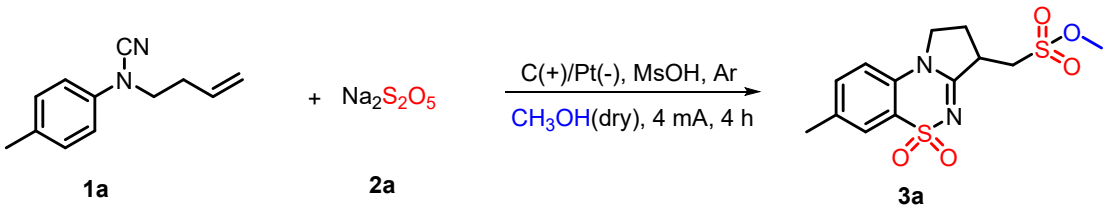
1. General methods

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 ^{o}C petroleum ether and analytical grade EtOAc (without further purification). ^{1}H and ^{13}C and ^{19}F spectra were recorded on a 400 MHz or 600MHz spectrometer. Chemical shifts were reported in ppm. ^{1}H and ^{19}F NMR spectra were referenced to $CDCl_3$ (7.26 ppm) or DMSO (2.5 ppm) or MeOD (4.87 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm) or DMSO (39.5 ppm) or MeOD (49.0 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. The HRMS spectrum was measured by micromass $QTOF_2$ Quadrupole/Time of Flight Tandem mass spectrometer with electron spray ionization. Potentiostat was purchased from Shanghai Xinrui Companyand the model is DJS-292B.

2.Supplementary experiments

Table S1 Reaction conditions for insertion of two-component SO_2 into fused-ring framework compounds[a]



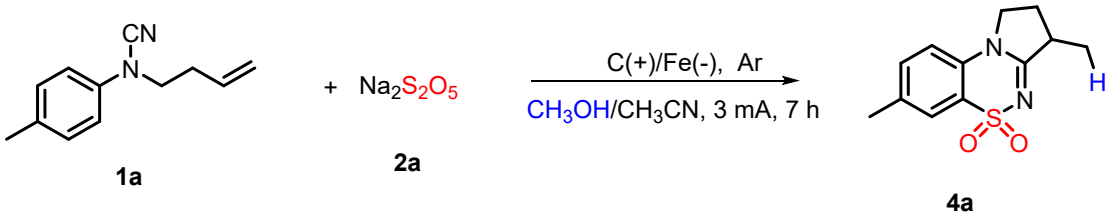
1a 2a 3a

Entry	Electrode	Current (mA)	additive	"SO_2"	Solvent	time	Yield (%)[b]
1	C(+)|C(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH	2 h	40%
2	C(+)|C(-)	8 mA	HCOOH	$Na_2S_2O_5$	MeOH	2 h	25%
3	C(+)|C(-)	8 mA	CH_3OOH	$Na_2S_2O_5$	MeOH	2 h	33%
4	C(+)|C(-)	8 mA	*p*-Toluenesulfonic acid	$Na_2S_2O_5$	MeOH	2 h	18%
5	C(+)|C(-)	8 mA	-	$Na_2S_2O_5$	MeOH	2 h	trace
6	C(+)|C(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH/CH_3CN (1 : 1)	2 h	17%
7	C(+)|C(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH/HFIP (1 : 1)	2 h	27%
8	C(+)|C(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH/DCE (1 : 1)	2 h	28%
9	C(+)|C(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH/DCM (1 : 1)	2 h	18%
10	C(+)|C(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH/DMA (1 : 1)	2 h	0%
11	C(+)|C(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH/DMSO (1 : 1)	2 h	0%
12	C(+)|Pt(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH	2 h	51%
13	C(+)|Ni(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH	2 h	23%
14	GF(+)|GF(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH	2 h	9%
15	Pt(+)|Pt(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH	2 h	35%
16	RVC(+)|RVC(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH	2 h	19%
17	C(+)|Pt(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH (dry)	2 h	51%
18	C(+)|Pt(-)	6 mA	MsOH	$Na_2S_2O_5$	MeOH (dry)	3 h	60%
19	**C(+)|Pt(-)**	**4 mA**	**MsOH**	**$Na_2S_2O_5$**	**MeOH (dry)**	**4 h**	**71%**
20	C(+)|Pt(-)	4 mA	MsOH	$K_2S_2O_5$	MeOH (dry)	4 h	44%
21	C(+)|Pt(-)	4 mA	MsOH	DABSO	MeOH (dry)	4 h	25%
22	C(+)|Pt(-)	8 mA	MsOH	$K_2S_2O_8$	MeOH (dry)	4 h	0%
23	C(+)|Pt(-)	0 mA	MsOH	$Na_2S_2O_5$	MeOH (dry)	4 h	0%
24	C(+)|Pt(-)	8 mA	MsOH	$Na_2S_2O_5$	MeOH (dry)	4 h	0%[c]
25	C(+)|C(-)	4 mA	MsOH	$Na_2S_2O_5$	MeOH (dry)	4 h	24%
26	GF(+)|GF(-)	4 mA	MsOH	$Na_2S_2O_5$	MeOH (dry)	4 h	14%

27	C(+)|Pt(-)	4 mA	MsOH	$Na_2S_2O_5$	MeOH/H_2O(1 : 1)	4 h	0%
28	C(+)|Pt(-)	4 mA	MsOH	$Na_2S_2O_5$	MeOH/DCM (1 : 1)	4 h	19%
29	C(+)|C(-)	4 mA	HCOOH	$Na_2S_2O_5$	MeOH(dry)	4 h	27%
30	C(+)|C(-)	4 mA	CH_3COOH	$Na_2S_2O_5$	MeOH(dry)	4 h	33%

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (1 mmol), MeOH (dry) as solvent (10 mL), electrolysis at a constant current of 4 mA for 4 h in an undivided cell. [b] Yield determined by ^{1}H NMR analysis based on **1a** (using 1,3,5-trimethoxybenzene as the internal standard). [c] In the air atmosphere.

Table S2 Reaction conditions for insertion of single-component SO_2 into fused-ring framework compounds[a]

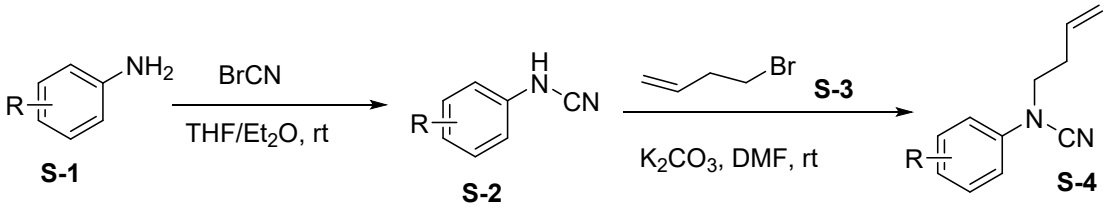


1a **2a** **4a**

Entry	Electrode	Current (mA)	"SO_2"	Solvent	time	Yield (%)[b]
1	C(+)|C(-)	5 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	5 h	28%
2	C(+)|Pt(-)	5 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	5 h	21%
3	C(+)|SS(-)	5 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	5 h	17%
4	Pt(+)|SS(-)	5 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	5 h	7%
5	C(+)|Pb(-)	5 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	5 h	36%
6	C(+)|Cu(-)	5 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	5 h	18%
7	C(+)|Fe(-)	5 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	5 h	50%
8	C(+)|Zn(-)	5 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	5 h	21%
9	Al(+)|Fe(-)	5 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	5 h	trace
10	C(+)|Fe(-)	3 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	11 h	39%
11	**C(+)|Fe(-)**	**3 mA**	**$Na_2S_2O_5$**	**CH_3OH/CH_3CN (1:1)**	**7 h**	**76%**
12	C(+)|Fe(-)	8 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	4 h	34%
13	C(+)|C(-)	8 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	4 h	61%
14	C(+)|C(-)	3 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	7 h	70%
15	C(+)|Pt(-)	3 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	7 h	12%
16	C(+)|Fe(-)	3 mA	$Na_2S_2O_5$	H_2O/CH_3CN (1:1)	7 h	0%
17	C(+)|Fe(-)	3 mA	$Na_2S_2O_5$	CH_3OH/DCM (1:1)	7 h	12%
18	C(+)|Fe(-)	6 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	4.5 h	45%
19	C(+)|Fe(-)	0 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	7 h	0%
20	C(+)|Fe(-)	3 mA	$K_2S_2O_5$	CH_3OH/CH_3CN (1:1)	7 h	22%
21	C(+)|Fe(-)	3 mA	$K_2S_2O_8$	CH_3OH/CH_3CN (1:1)	7 h	0%
22	C(+)|Fe(-)	3 mA	DABSO	CH_3OH/CH_3CN (1:1)	7 h	31%
23	C(+)|Fe(-)	4 mA	$Na_2S_2O_5$	CH_3OH (dry)	6 h	23%
24	C(+)|Fe(-)	4 mA	$Na_2S_2O_5$	CH_3OH/CH_3CN (1:1)	6 h	67%

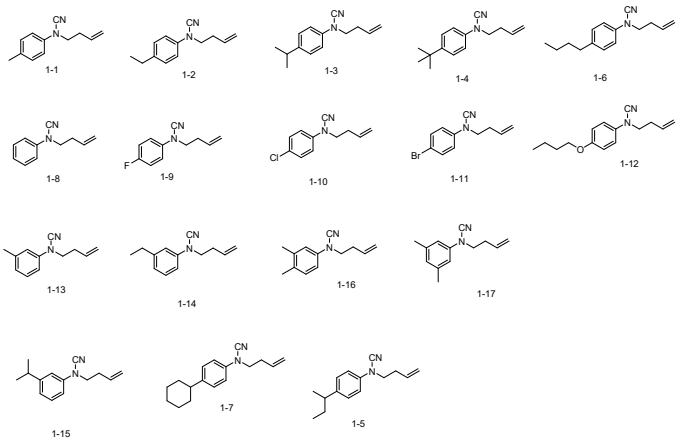
[a] Reaction conditions: **1a** (0.25 mmol), **2a** (1.25 mmol), MeOH /CH_3CN (1:1) as solvent (10 mL), electrolysis at a constant current of 3 mA for 7 h in an undivided cell. [b] Yield determined by ^1H NMR analysis based on **1a** (using 1,3,5-trimethoxybenzene as the internal standard).

3. Synthesis of substrates



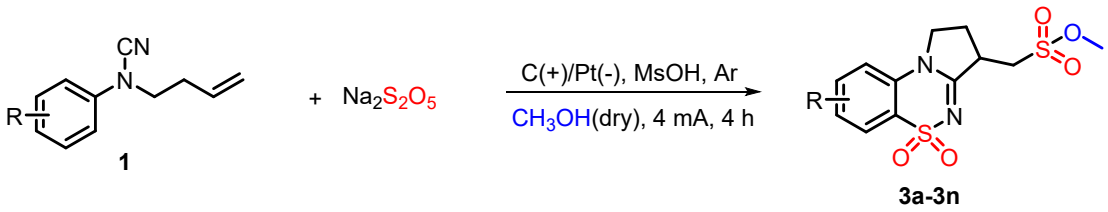
To a solution of cyanogen bromide (1.0 equiv.) in Et_2O and THF (0. 75 M) was added **S-1** (1.7 equiv.) at 0 °C. Then the mixture was stirred at room temperature for the desired time before being diluted with Et_2O. Following was purified by flash column chromatography (silica gel, EtOAc/Petroleum ether) to afford the ponding compounds **S-2**.

Under a N_2 atmosphere, to a two neck round bottom flask was added **S-2** (1.0 equiv.), $K_2C_2O_3$, (2.0 equiv.) and DMF at 0 °C, bromide **S-3** (1.1 equiv.) was added dropwise at 0 °C after the reaction mixture was stirred for half an hour. Then the reaction mixture was warmed to room temperature and stirred for 14 h. Upon completion, H_2O was added and the mixture was extracted with EtOAc, and the combined organic layers were washed by brine and dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, EtOAc/Petroleum ether) to give the desired substrate **S-4**. The following substrates are synthesized based on reported literatures [1-3]



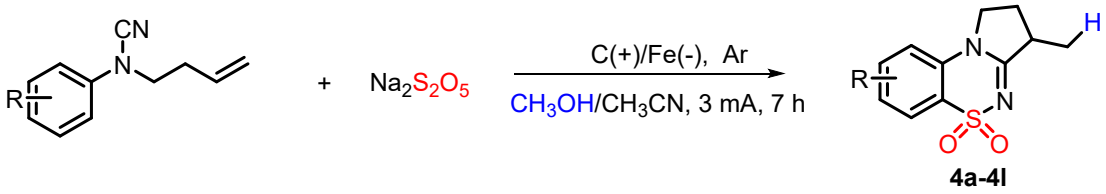
4. General procedure for the preparation of products

General method for synthesis of two-component SO_2 into fused-ring framework compounds **3a**-**3n**.



A 10 ml three-necked round-bottomed flask was charged sequentially with **1a** (0.25 mmol, 1.0 eq.), **2a** (1 mmol, 4.0 eq.) and MsOH (5 eq.). The electrolytic cell was equipped with a graphite rod anode (Φ6 mm) and a platinum plate cathode (1 cm × 1 cm). The three-necked flask was pumped and vented three times to fill the interior with argon. The three-neck flask was then filled with dry MeOH. Electrolysis was carried out at room temperature at a constant current of 4 mA for the appropriate time. At the end of the reaction, the reaction mixture was washed with water and extracted with dichloromethane (3 × 10 mL). The organic layers were combined, dried with Na_2SO_4 and concentrated. Flash column chromatography on silica gel gave the pure product .

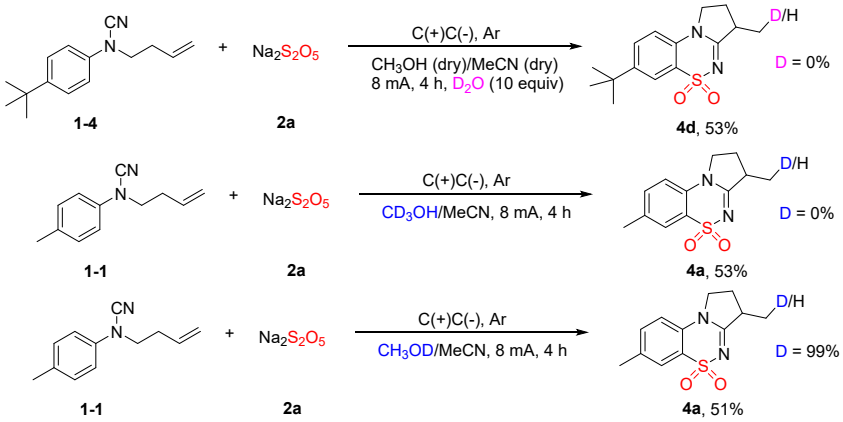
General method for synthesis of single-component SO_2 into fused-ring framework compounds **4a**-**4l**.

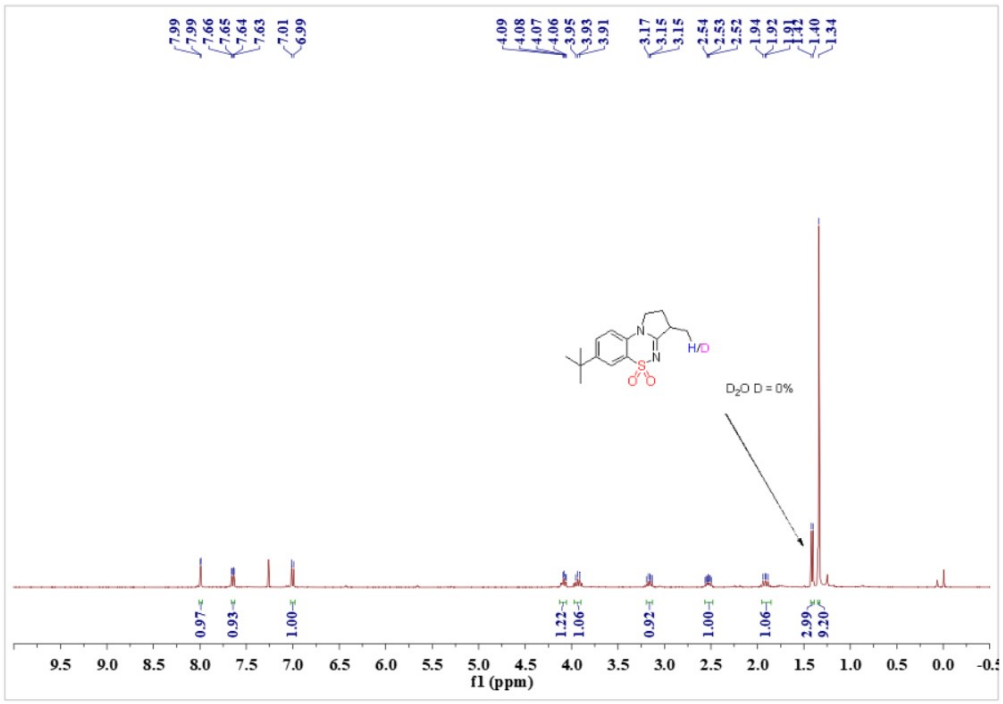


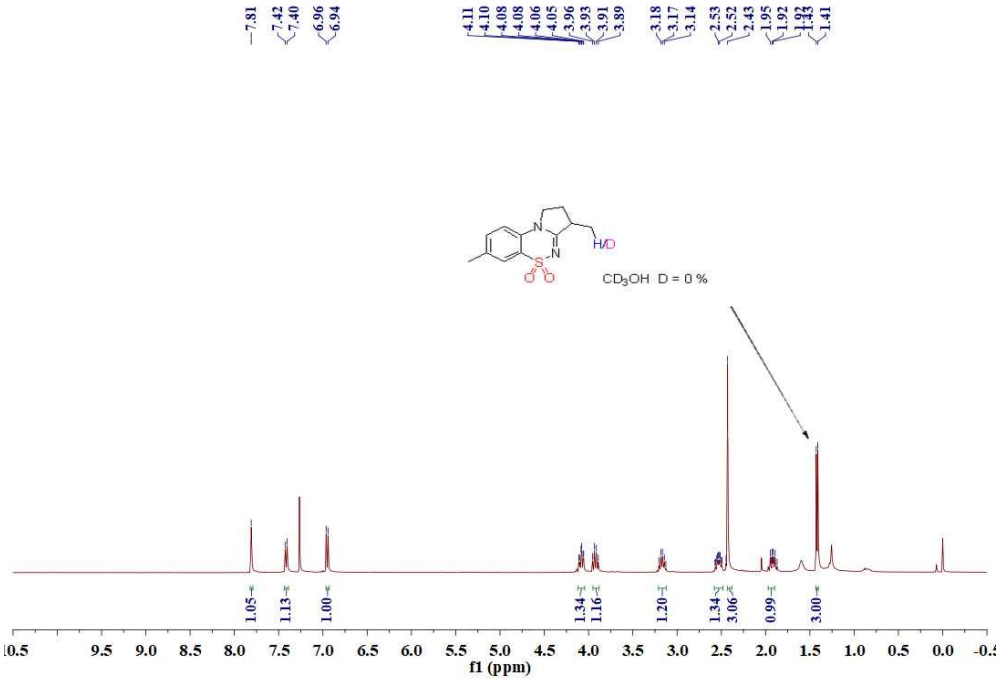
A 10 ml three-necked round-bottomed flask was filled with **1a** (0.25 mmol, 1.0 eq.), **2a** (1.25 mmol, 5.0 eq.). The electrolytic cell was equipped with a graphite rod anode (Φ6 mm) and an iron sheet cathode (1 cm × 1 cm). The three-necked flask was pumped and vented three times to fill the interior with argon. The three-neck flask was then charged with MeCN and MeOH. Electrolysis was carried out at room temperature at a constant current of 3 mA for the appropriate time. At the end of the reaction, the reaction mixture was washed with water and extracted with dichloromethane (3 × 10 mL). The organic layers were combined, dried with Na_2SO_4 and concentrated. Flash column chromatography on silica gel gave the pure product .

5.Control experiments

5.1 Labeling experiment




7.99
7.99
7.66
7.65
7.64
7.63
7.01
6.99
4.09
4.08
4.07
4.06
3.95
3.93
3.91
3.17
3.15
3.15
2.54
2.53
2.52
1.94
1.92
1.91
1.40
1.34
H/D
D2O D = 0%
0.97
0.93
1.00
1.22
1.06
0.92
1.00
1.06
2.99
9.20
f1 (ppm)


7.81
7.42
7.40
6.96
6.94
4.11
4.10
4.08
4.08
4.06
4.05
3.96
3.93
3.91
3.89
3.18
3.17
3.14
2.53
2.52
2.43
1.95
1.92
1.41
H/D
CD3OH D = 0 %
1.05
1.13
1.00
1.34
1.16
1.20
1.34
3.06
0.99
3.00
f1 (ppm)

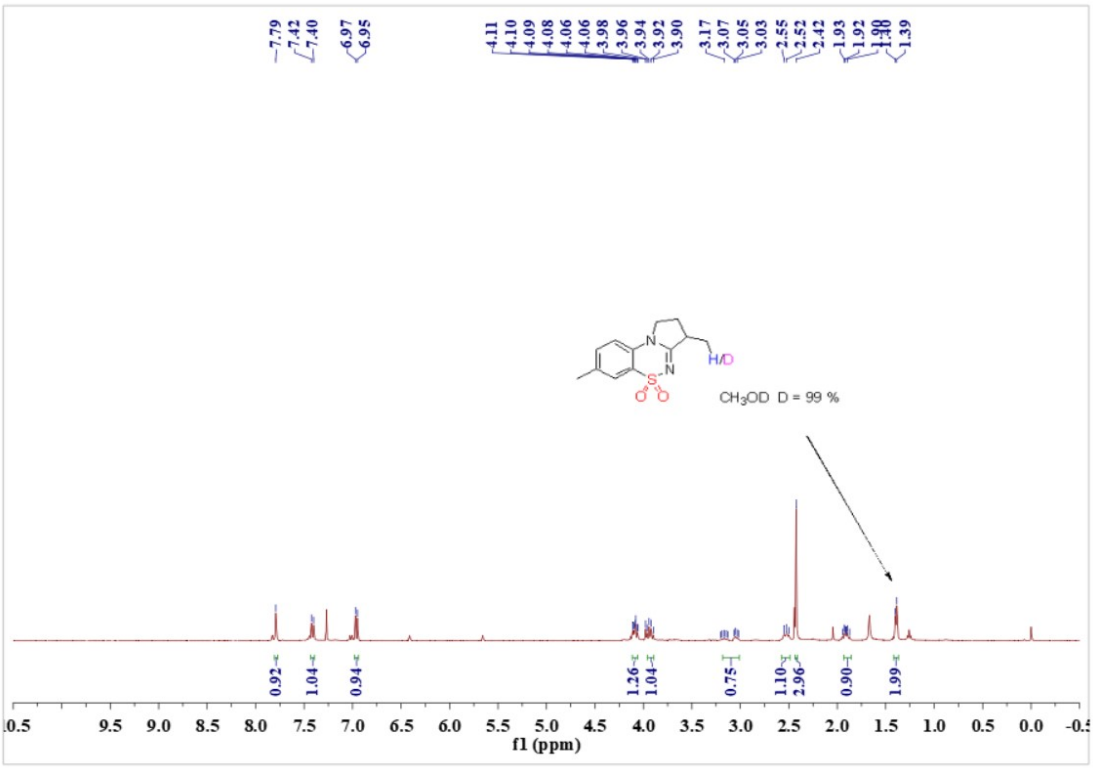


Fig. S1: Labeling experiment

6.Cyclic voltammetry studies

The cyclic voltammograms were recorded in an electrolyte solution of nBu_4NBF_4 (0.1 M) in CH_3OH using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 100 mV/s.

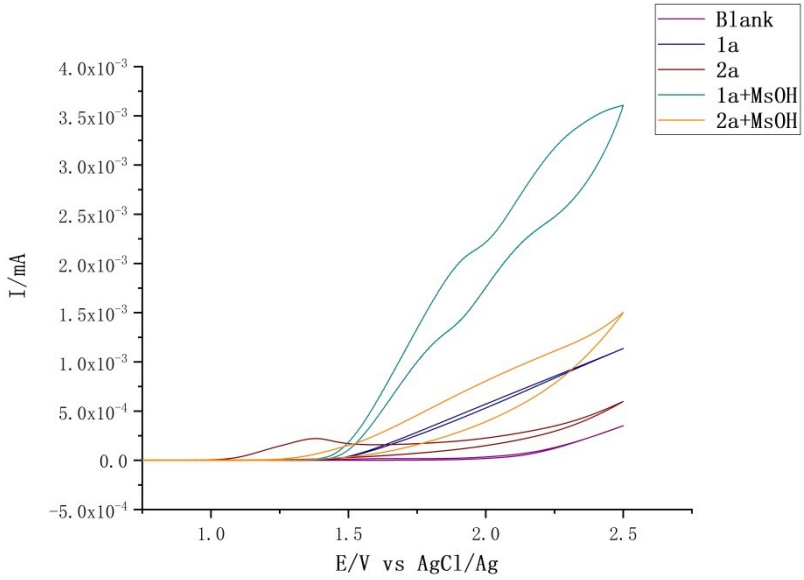


Fig. S2: Cyclic voltammograms in CH_3OH (4 mL) + 0.1 M nBu_4NBF_4. a) pink line：Blank. b) blue

line：**1a** (0.15 mmol). c) wine red line：**2a** (0.45 mmol). d) olive-green line：MsOH (0.75 mmol) and **1a** (0.45 mmol). e) olive-green line：MsOH (0.75 mmol) and **2a** (0.45 mmol).

The cyclic voltammograms were recorded in an electrolyte solution of nBu_4NBF_4 (0.1 M) in CH_3OH/CH_3CN using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 100 mV/s.

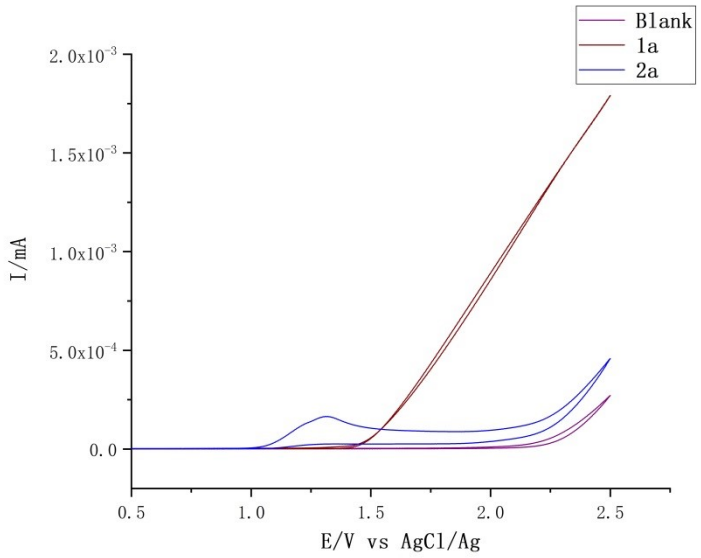


Fig. S3: Cyclic voltammograms in CH_3OH/ CH_3CN (2 mL / 2 mL) + 0.1 M nBu_4NBF_4. a) pink line：Blank. b) wine red line：**1a** (0.15 mmol). c) blue line：**2a** (0.45 mmol).

The cyclic voltammograms were recorded in an electrolyte solution of nBu_4NBF_4 (0.1 M) in CH_3OH/CH_3CN using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 100 mV/s.

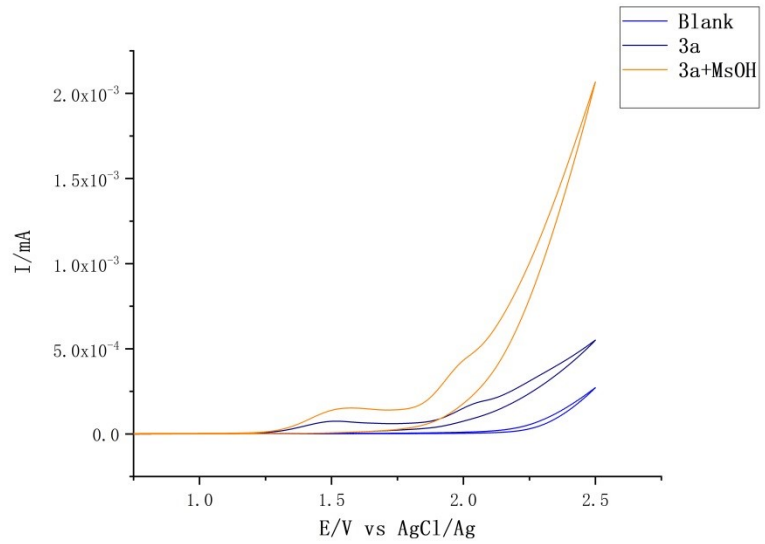


Fig. S4: Cyclic voltammograms in CH_3OH/ CH_3CN (2 mL / 2 mL) + 0.1 M nBu_4NBF_4. a) blue line：Blank. b) purple line：**3a** (0.1 mmol). c) orange line：MsOH (0.6 mmol) and **3a** (0.1 mmol).

The cyclic voltammograms were recorded in an electrolyte solution of nBu_4NBF_4 (0.1 M) in CH_3OH/CH_3CN using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 100 mV/s.

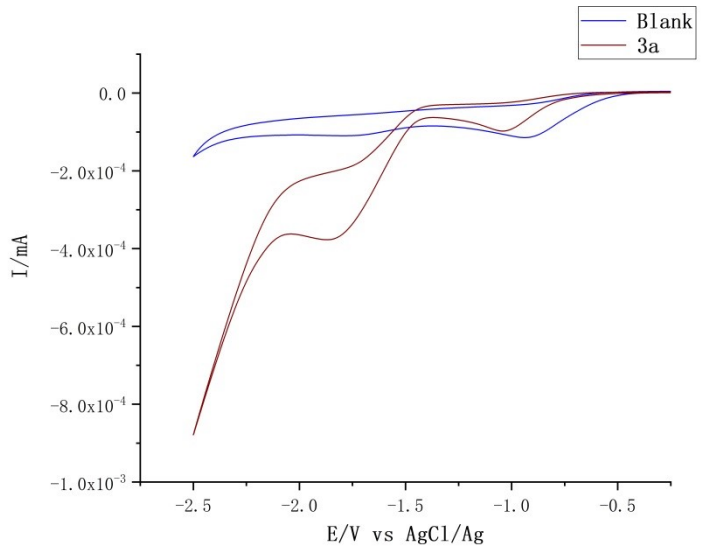


Fig. S5: Cyclic voltammograms in CH_3OH/ CH_3CN (2 mL / 2 mL) + 0.1 M nBu_4NBF_4. a) blue line：Blank. b) brown line：**3a** (0.1 mmol).

The cyclic voltammograms were recorded in an electrolyte solution of nBu_4NBF_4 (0.1 M) in CH_3OH/CH_3CN using a glassy carbon disk working electrode (diameter, 3 mm),

a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 100 mV/s.

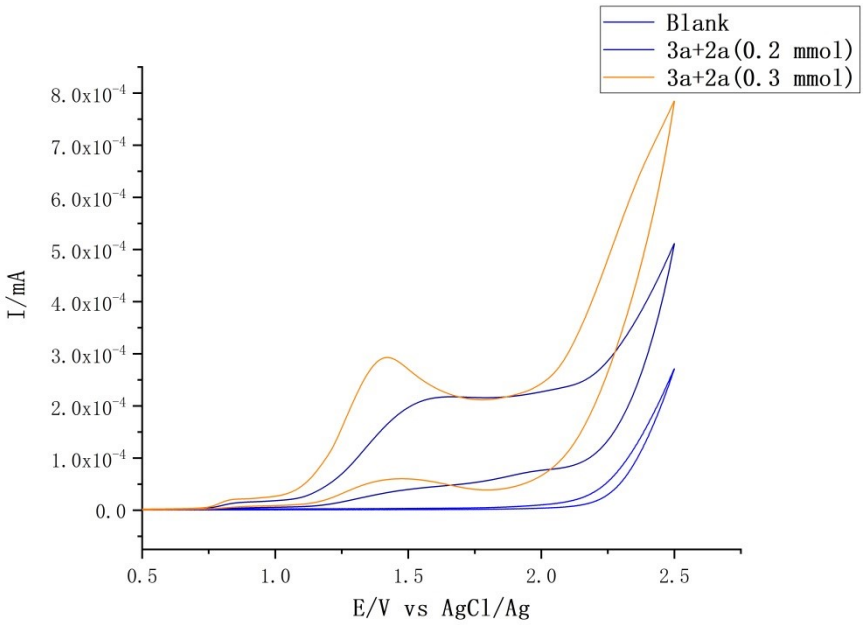


Fig. S6: Cyclic voltammograms in CH_3OH/ CH_3CN (2 mL / 2 mL) + 0.1 M nBu_4NBF_4. a) blue line：Blank. b) dark blue line：**3a** (0.1 mmol) and **2a** (0.2 mmol). c) orange line：**3a** (0.1 mmol) and **2a** (0.3 mmol).

6.1 Charge measurement

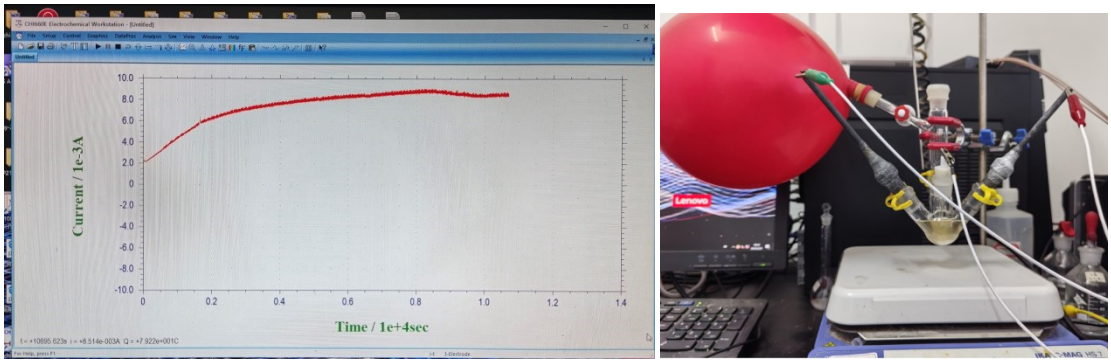


Fig. S7: Amplifying device

Q = +7.922e+0.001C=79.22C

$$n_e = \frac{Q}{F} = \frac{79.22C}{96485} = 0.00082mol$$

$$n_2 = \frac{n_e}{n_1} = \frac{0.00082mol}{0.00025mol} = 3.28 \approx 3$$

F: Faraday constant. Q: Total charge. n_e: Electron molar number. n_1: The number of moles of

reaction. n_2: The number of electrons transferred.

6.2 Current efficiency

Current efficiency calculation[4] of **3a**

$$Q = I \times t = 0.004\ A \times 14400\ s = 57.6\ C$$

$$n_1 = \frac{Q}{n \times F} = \frac{57.6}{2 \times 96485} \approx 0.2985\ mmol$$

$$n_2 = 0.25 mmol \times 71\ \% = 0.1775 mmol$$

$$CE\ \% = \frac{n_2}{n_1} \times 100\ \% = \frac{0.1775}{0.2985} \times 100\ \% \approx 59.5\ \%$$

F: Faraday constant. Q: Total charge. n: Electron transfer number. n_1: Theoretical product quantity. n_2: Actual product quantity. CE: Current efficiency.

Current efficiency calculation of **3a** (2 mmol)

$$Q = I \times t = 0.010\ A \times 36000\ s = 360\ C$$

$$n_1 = \frac{Q}{n \times F} = \frac{360}{2 \times 96485} \approx 1.865\ mmol$$

$$n_2 = 2\ mmol \times 48\ \% = 0.96\ mmol$$

$$CE\ \% = \frac{n_2}{n_1} \times 100\ \% = \frac{0.96}{1.865} \times 100\ \% \approx 51.5\ \%$$

F: Faraday constant. Q: Total charge. n: Electron transfer number. n_1: Theoretical product quantity. n_2: Actual product quantity. CE: Current efficiency.

Current efficiency calculation of **4a**

$$Q = I \times t = 0.003\ A \times 25200\ s = 75.6\ C$$

$$n_1 = \frac{Q}{n \times F} = \frac{75.6}{3 \times 96485} \approx 0.2613\ mmol$$

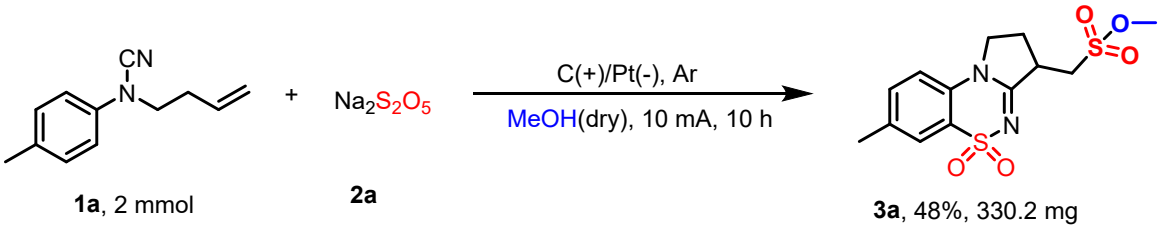
$$n_2 = 0.25 mmol \times 76\ \% = 0.19 mmol$$

$$CE\ \% = \frac{n_2}{n_1} \times 100\ \% = \frac{0.19}{0.2613} \times 100\ \% \approx 72.7\ \%$$

F: Faraday constant. Q: Total charge. n: Electron transfer number. n_1: Theoretical product quantity. n_2: Actual product quantity. CE: Current efficiency.

7. Electrochemical applications

7.1 Preparation of scale-up reactions



1a, 2 mmol

2a

3a, 48%, 330.2 mg

A 25 ml round-bottomed flask was filled sequentially with **1a** (2 mmol, 1.0 eq.), **2a** (8 mmol, 4.0 eq.). The cell was equipped with a graphite rod anode (Φ6 mm) and a Pt plate cathode (1 cm × 1 cm). MeOH (20 ml) were added to a round-bottomed flask and the flask was filled with argon. Electrolysis was carried out at room temperature at a constant current of 10 mA for the appropriate time. At the end of the reaction, the reaction mixture was washed with water and extracted with dichloromethane (3 × 20 mL). The organic layers were combined, dried with Na_2SO_4 and concentrated. Flash column chromatography on silica gel gave the pure product **3a** in 48% (0.330 g) yield (DCM: MeOH = 100 : 1).

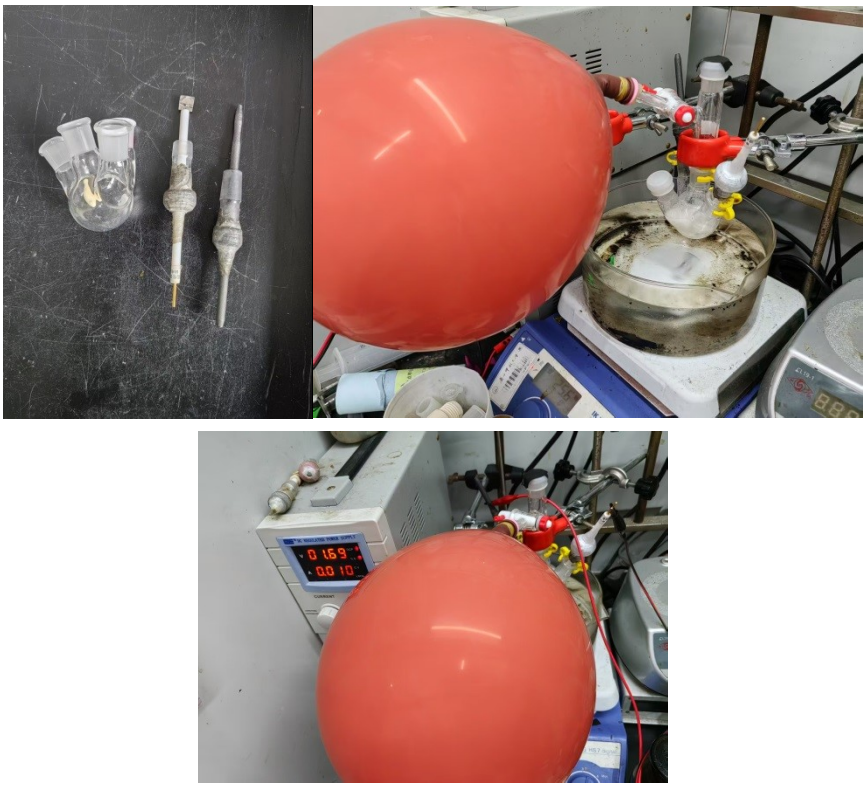
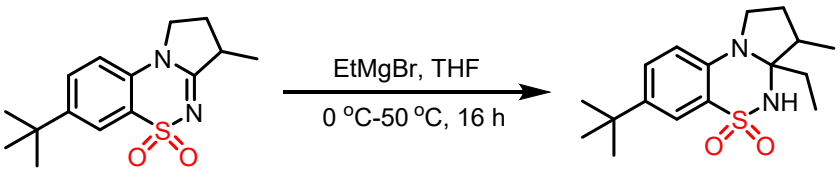


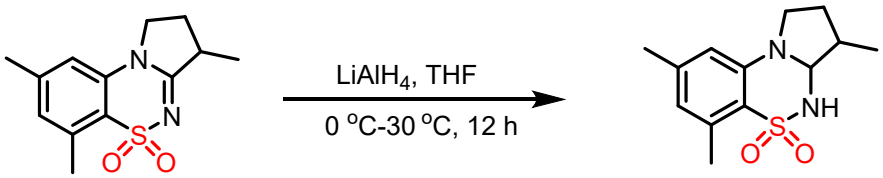
Fig. S8: Amplifying device

7.2 Derivatisation of products



4d **7d**, 68%

To solution of **4d** (0.2 mmol) in THF (0.2M) was added EtMgBr (2.3 equiv.) at 0°C.Then, the mixture was stirred at 50 °C for 16 h. Upon completion, the reaction was quenched with saturated ammonium chloride solution at 0 °C, and the mixture was extracted with DCM. The combined organic phases were washed with brine before being dried Na_2SO_4 and concentrated in vacuo. Purification by column chromatography on silica gel (EtOAc/petroleum ether = 1/1) to afford **7d** (68%,) as colorless oil.



4h **8h**, 72%

To solution of **4h** (0.2 mmol) in THF (0.2 M) was added $LiAlH_4$ (1.3 equiv.) dropwise at 0 °C. Then the reaction mixture was warmed to 30 °C and allowed to proceed for 12 h. The resulting mixture was cooled to 0 °C and quenched by dropwise addition the solution of NaOH (1 N). The aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on a silica gel column (EtOAc/petroleum ether = 1/12) to afford **8h** (72%) as white solid.

8. Single-crystal X-Ray diffraction

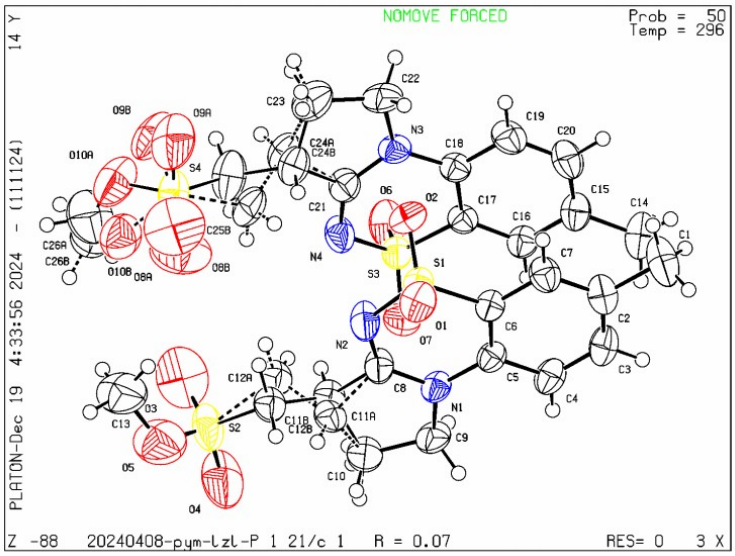


Fig. S9: X-ray molecular structure of **3a**

Table S3. Crystal data and structure refinement for **3a**

Identification code	**3a**
Empirical formula	C13H16N2O5S2
Formula weight	344.40
Temperature/K	295.81(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	11.27430(10)
b/Å	24.3447(3)
c/Å	11.0893(2)
α/°	90
β/°	96.9450(10)
γ/°	90
Volume/Å^3	3021.34(7)
Z	8
ρcalcg/cm^3	1.514
μ/mm-1	3.438
F(000)	1440.0
Crystal size/mm^3	0.2 × 0.18 × 0.14
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.262 to 154.778
Index ranges	-13 ⩽ h ⩽ 14, -30 ⩽ k ⩽ 28, -12 ⩽ l ⩽ 14
Reflections collected	23617
Independent reflections	6084 [Rint = 0.0576, Rsigma = 0.0419]

Data/restraints/parameters	6084/190/476
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R1 = 0.0686, wR2 = 0.1843
Final R indexes [all data]	R1 = 0.0807, wR2 = 0.1916
Largest diff. peak/hole / e $Å^{-3}$	0.79/-0.58

Table S4. Selected bond distances and angles for **3a.**

Bond Distances(Å)			
N3-C18	1.398(4)	C24A-C25A	1.511(8)
N3-C21	1.336(5)	C24B-C25B	1.497(15)
N3-C22	1.475(4)	C1-C2	1.514(6)
S3-N4	1.610(3)	N1-C5	1.396(4)
S3-O6	1.425(3)	N1-C8	1.343(4)
S3-O7	1.423(3)	N1-C9	1.472(4)
S3-C17	1.743(3)	O1-S1	1.426(3)
N4-C21	1.294(5)	S1-N2	1.609(3)
S4-O8A	1.356(6)	S1-O2	1.419(3)
S4-O8B	1.452(12)	S1-C6	1.756(3)
S4-O9A	1.440(5)	C2-C3	1.386(6)
S4-O9B	1.311(10)	C2-C7	1.382(5)
S4-O10A	1.543(5)	N2-C8	1.295(4)
S4-O10B	1.625(11)	S2-O3	1.417(6)
S4-C25A	1.782(6)	S2-O4	1.360(4)
S4-C25B	1.745(10)	S2-O5	1.522(5)
O10A-C26A	1.272(10)	S2-C12A	1.806(9)
O10B-C26B	1.254(18)	S2-C12B	1.773(5)
C14-C15	1.508(5)	C3-C4	1.376(6)
C15-C16	1.386(5)	C4-C5	1.401(5)
C15-C20	1.383(6)	C5-C6	1.393(4)
C16-C17	1.396(5)	O5-C13	1.435(7)
C17-C18	1.391(4)	C6-C7	1.389(5)
C18-C19	1.398(5)	C8-C11A	1.545(11)
C19-C20	1.376(6)	C8-C11B	1.530(6)
C21-C24A	1.528(6)	C9-C10	1.503(6)
C21-C24B	1.545(13)	C10-C11A	1.495(11)
C22-C23	1.504(7)	C10-C11B	1.538(7)
C23-C24A	1.478(8)	C11A-C12A	1.518(13)
C23-C24B	1.513(14)	C11B-C12B	1.504(8)
Bond Angles (Å)			
C18-N3-C22	123.3(3)	C24A-C25A-S4	110.7(4)
C21-N3-C18	122.0(3)	C24B-C25B-S4	117.9(9)
C21-N3-C22	112.9(3)	C5-N1-C9	123.9(3)
N4-S3-C17	104.32(16)	C8-N1-C5	122.5(3)

O6-S3-N4	109.0(2)	C8-N1-C9	112.9(3)
O6-S3-C17	108.50(17)	O1-S1-N2	108.8(2)
O7-S3-N4	107.89(19)	O1-S1-C6	108.40(16)
O7-S3-O6	116.1(2)	N2-S1-C6	105.62(15)
O7-S3-C17	110.29(17)	O2-S1-O1	116.18(18)
C21-N4-S3	119.7(3)	O2-S1-N2	107.38(19)
O8-S4-O9A	117.4(5)	O2-S1-C6	109.96(17)
O8A-S4-O10A	116.5(4)	C3-C2-C1	121.0(4)
O8A-S4-C25A	112.6(5)	C7-C2-C1	121.2(4)
O8B-S4-O10B	97.2(8)	C7-C2-C3	117.8(3)
O8B-S4-C25B	102.2(8)	C8-N2-S1	121.5(3)
O9A-S4-O10A	104.2(4)	O3-S2-O5	106.3(3)
O9A-S4-C25A	108.5(4)	O3-S2-C12A	86.8(4)
O9B-S4-O8B	108.2(12)	O3-S2-C12B	114.3(3)
O9B-S4-O10B	111.6(7)	O4-S2-O3	113.8(4)
O9B-S4-C25B	121.4(8)	O4-S2-O5	111.6(3)
O10A-S4-C25A	95.1(3)	O4-S2-C12A	111.7(4)
O10B-S4-C25B	112.7(7)	O4-S2-C12B	112.7(3)
C26A-O10-AS4	129.9(8)	O5-S2-C12A	123.9(4)
C26B-O10B-S4	139(2)	O5-S2-C12B	96.7(3)
C16-C15-C14	120.6(4)	C4-C3-C2	122.8(3)
C20-C15-C14	121.5(4)	C3-C4-C5	119.4(3)
C20-C15-C16	117.9(3)	N1-C5-C4	121.1(3)
C15-C16-C17	120.3(3)	C6-C5-N1	120.6(3)
C16-C17-S3	119.7(2)	C6-C5-C4	118.3(3)
C18-C17-S3	119.2(3)	C13-O5-S2	121.2(4)
C18-C17-C16	120.9(3)	C5-C6-S1	119.7(3)
N3-C18-C19	121.9(3)	C7-C6-S1	119.1(3)
C17-C18-N3	119.4(3)	C7-C6-C5	121.1(3)
C17-C18-C19	118.6(3)	C2-C7-C6	120.7(4)
C20-C19-C18	119.3(3)	N1-C8-C11A	108.0(5)
C19-C20-C15	122.9(3)	N1-C8-C11B	109.1(3)
N3-C21-C24A	107.5(3)	N2-C8-N1	128.8(3)
N3-C21-C24B	110.4(6)	N2-C8-C11A	121.3(5)
N4-C21-N3	128.7(3)	N2-C8-C11B	121.4(4)
N4-C21-C24A	123.2(4)	N1-C9-C10	103.8(3)
N4-C21-C24B	119.3(6)	C9-C10-C11B	105.8(3)
N3-C22-C23	102.9(3)	C11A-C10-C9	108.9(5)
C22-C23-C24B	110.7(6)	C10-C11A-C8	102.8(7)
C24A-C23-C22	105.9(4)	C10-C11A-C12A	115.3(9)
C23-C24A-C21	103.1(4)	C12A-C11A-C8	103.5(8)
C23-C24A-C25A	118.2(6)	C8-C11B-C10	101.5(4)
C25A-C24A-C21	110.6(5)	C12B-C11B-C8	109.0(4)

C23-C24B-C21	100.7(8)	C12B-C11B-C10	120.2(6)
C25B-C24B-C21	100.8(9)	C11A-C12A-S2	110.0(8)
C25B-C24B-C23	122.0(13)	C11B-C12B-S2	109.6(4)

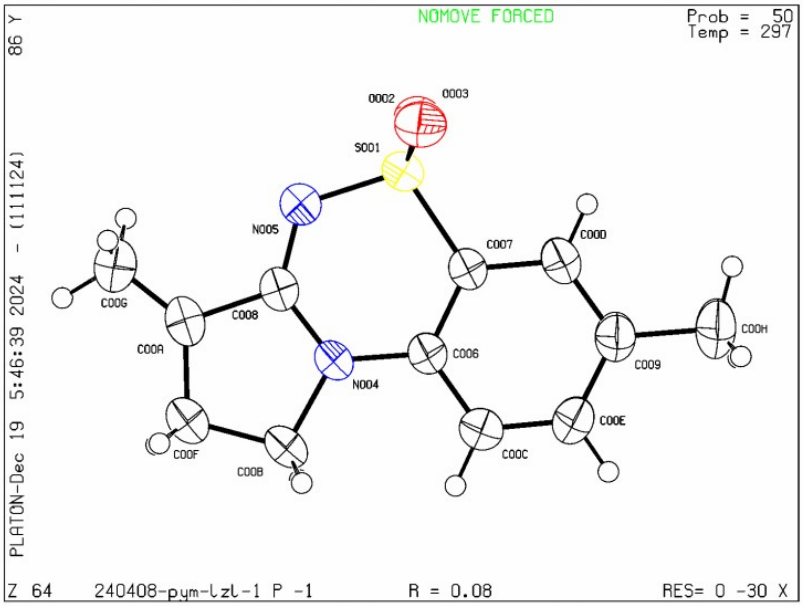


Fig. S10: X-ray molecular structure of **4a**

Table S5. Crystal data and structure refinement for **4a**

Identification code	**4a**
Empirical formula	$C_{12}H_{14}N_2O_2S$
Formula weight	250.31
Temperature/K	296.74(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.5524(4)
b/Å	8.9178(5)
c/Å	9.3580(5)
α/°	83.619(4)
β/°	80.454(5)
γ/°	66.215(5)
Volume/Å^3	568.07(6)
Z	2
ρcalcg/cm^3	1.463
μ/mm-1	2.469
F(000)	264.0
Crystal size/mm^3	0.22 × 0.18 × 0.11
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.596 to 153.966
Index ranges	-7 ⩽ h ⩽ 9, -11 ⩽ k ⩽ 11, -11 ⩽ l ⩽ 11

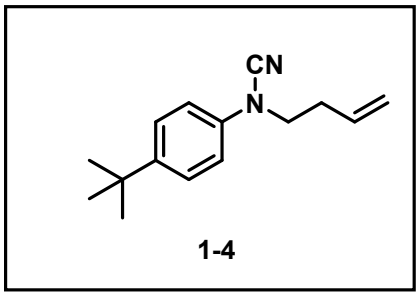
Reflections collected	5277
Independent reflections	2201 [Rint = 0.0369, Rsigma = 0.0372]
Data/restraints/parameters	2201/0/156
Goodness-of-fit on F^2	1.116
Final R indexes [I>=2σ (I)]	R1 = 0.0844, wR2 = 0.2608
Final R indexes [all data]	R1 = 0.0918, wR2 = 0.2676
Largest diff. peak/hole / e $Å^{-3}$	0.94/-0.41

Table S6. Selected bond distances and angles for **4a.**

Bond Distances(Å)			
S001-O002	1.431(3)	C009-C00D	1.396(6)
S001-O003	1.431(3)	C009-C00E	1.395(6)
S001-N005	1.604(4)	C009-C00H	1.506(6)
S001-C007	1.751(4)	C00A-C00F	1.483(6)
N004-C006	1.402(5)	C00A-C00G	1.332(7)
N004-C008	1.339(5)	C00B-C00F	1.521(6)
N004-C00B	1.476(5)	C00C-C00E	1.379(6)
N005-C008	1.306(5)	C007-C00D	1.396(5)
C006-C007	1.397(5)	C008-C00A	1.486(5)
C006-C00C	1.386(6)		

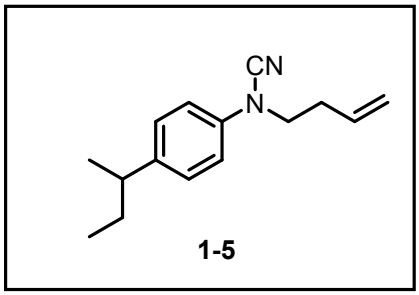
Bond Angles (Å)			
O002-S001-N005	109.1(2)	C00D-C007-C006	120.6(4)
O002-S001-C007	108.67(19)	N004-C008-C00A	108.8(3)
O003-S001-O002	114.6(2)	N005-C008-N004	128.3(4)
O003-S001-N005	108.9(2)	N005-C008-C00A	122.9(4)
O003-S001-C007	109.42(19)	C00D-C009-C00H	120.8(4)
N005-S001-C007	105.82(18)	C00E-C009-C00D	117.7(4)
C006-N004-C00B	123.2(3)	C00E-C009-C00H	121.4(4)
C008-N004-C006	123.3(3)	C00F-C00A-C008	107.4(4)
C008-N004-C00B	113.4(3)	C00G-C00A-C008	122.6(4)
C008-N005-S001	122.0(3)	C00G-C00A-C00F	130.0(4)
C007-C006-N004	119.8(3)	N004-C00B-C00F	104.1(3)
C00C-C006-N004	121.2(3)	C00E-C00C-C006	119.9(4)
C00C-C006-C007	119.0(4)	C009-C00D-C007	120.4(4)
C006-C007-S001	120.7(3)	C00C-C00E-C009	122.2(4)
C00D-C007-S001	118.6(3)	C00A-C00F-C00B	106.3(3)

9. Characterization data for the products



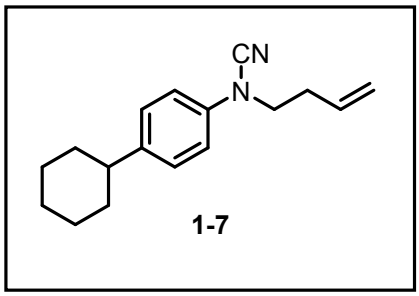
1-4

***N*-(but-3-en-1-yl)-*N*-(4-(tert-butyl)phenyl)cyanamide (1-4).** yellow liquid (74%).**^{1}H NMR** (400 MHz, Chloroform-d) δ7.39-7.37 (m, 2H), 7.07-7.04 (m, 2H), 5.84- 5.80 (m, 1H), 5.21-5.14 (m, 2H), 3.63 (t, *J* = 7.3 Hz, 2H), 2.58-2.53 (m, 3H), 1.30 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 146.7, 137.3, 133.2, 126.6, 118.5, 115.8, 113.9, 48.9, 34.3, 31.7, 31.4. **HRMS**(m/z)(ESI): calcd for $C_{15}H_{21}N_2^+$ $[M+H]^+$ 229.1700, found 229.1705.



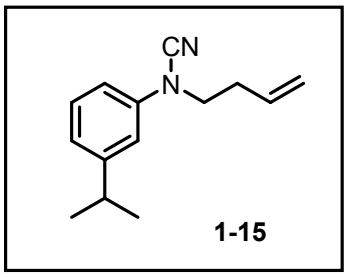
1-5

***N*-(but-3-en-1-yl)-*N*-(4-(sec-butyl)phenyl)cyanamide (1-5).** yellow liquid (64%).**^{1}H NMR** (500 MHz, Chloroform-d) δ7.22-7.20 (m, 2H), 7.09-7.07 (m, 2H), 5.90- 5.84 (m, 1H), 5.24-5.18 (m, 2H), 3.66 (t, *J* = 7.3 Hz, 2H), 2.63-2.57 (m, 3H), 1.62- 1.58 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ143.3, 137.6, 133.2, 128.2, 118.5, 116.1, 113.9, 49.0, 40.9, 31.8, 31.2, 21.9, 12.2. **HRMS**(m/z)(ESI): calcd for $C_{15}H_{21}N_2^+$ $[M+H]^+$ 229.1700, found 229.1702.

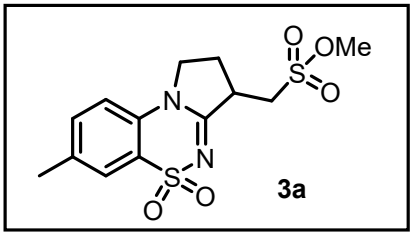


1-7

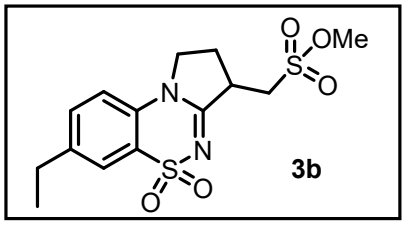
***N*-(but-3-en-1-yl)-*N*-(4-cyclohexylphenyl)cyanamide (1-7).** red liquid (69%).**^{1}H NMR** (500 MHz, Chloroform-d) δ7.25-7.23 (m, 2H), 7.10-7.08 (m, 2H), 5.90-5.83 (m, 1H), 5.24-5.18 (m, 2H), 3.65 (t, *J* = 7.3 Hz, 2H), 2.60-2.52 (m, 2H), 2.52-2.50 (m, 1H), 1.89-1.85 (m, 4H), 1.81-1.78 (m, 1H), 1.45-1.38 (m, 4H), 1.31-1.27 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ143.7, 137.6, 133.3, 128.0, 118.5, 116.1, 113.9, 49.0, 43.8, 34.5, 31.8, 26.9, 26.1. **HRMS**(m/z)(ESI): calcd for $C_{17}H_{23}N_2^+$ $[M+H]^+$ 255.1856, found 255.1860.



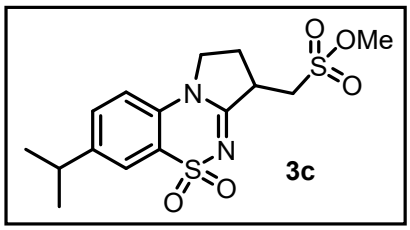
***N*-(but-3-en-1-yl)-*N*-(3-isopropylphenyl)cyanamide.** red liquid (70%). **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.33-7.30 (m, 1H), 7.04-7.03 (m, 1H), 7.01-7.00 (m, 1H), 6.95-6.93 (m, 1H), 5.90-5.85 (m, 1H), 5.24-5.18 (m, 2H), 3.69-3.66 (m, 2H), 2.95- 2.92 (m, 1H), 2.63-2.58 (m, 2H), 1.28 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 151.0, 139.8, 133.2, 129.6, 121.8, 118.6, 114.5, 113.8, 113.3, 48.9, 34.3, 31.8, 23.9. **HRMS**(m/z)(ESI): calcd for $C_{14}H_{19}N_2^+$ $[M+H]^+$ 215.1453, found 215.1451.



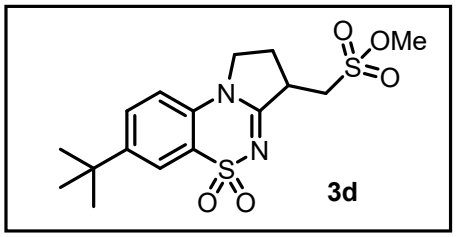
methyl(7-methyl-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3a). white solid (71%). m.p. 90.2-92.5 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.78 (m, 1H), 7.46-7.44 (m, 1H), 6.99-6.97 (m, 1H), 4.20-4.16 (m, 1H), 4.01-3.99 (m, 1H), 3.98 (s, 3H), 3.96-3.82 (m, 1H), 3.70-3.64 (m, 1H), 3.30- 3.25(m, 1H), 2.86-2.81 (m, 1H), 2.44 (s, 3H), 2.36-2.26 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.4, 137.7, 134.2, 132.0, 125.0, 121.8, 115.0, 56.6, 50.4, 48.0, 40.4, 25.4, 21.1. **HRMS**(m/z)(ESI): calcd for $C_{12}H_{17}N_2O_5S_2^+$ $[M+H]^+$ 345.0574, found 345.0578.



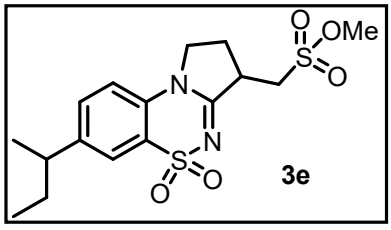
methyl(7-ethyl-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3b). white solid (65%). m.p. 94.2-94.5 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.81 (m, 1H), 7.50-7.47 (m, 1H), 7.02-7.00 (m, 1H), 4.22-4.11 (m, 1H), 4.03-3.98 (m, 1H), 3.97 (s, 3H), 3.95–3.89 (m, 1H), 3.74-3.63 (m, 1H), 3.31-3.21 (m, 1H), 2.88-2.80 (s, 1H), 2.77-2.71 (m, 2H), 2.34-2.19 (m, 1H), 1.29-1.25 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.5, 144.0 133.2, 132.2, 123.9, 121.9, 115.1, 56.7, 50.5, 48.1, 40.4, 28.4, 25.4, 15.1. **HRMS**(m/z)(ESI): calcd for $C_{14}H_{18}NaN_2O_5S_2^+$ $[M+Na]^+$ 381.0555, found 381.0553.



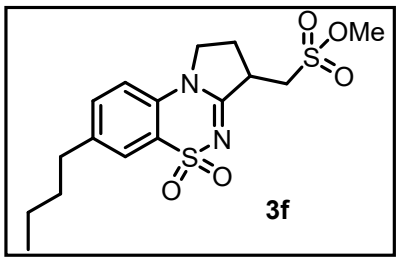
methyl(7-isopropyl-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3c). white solid (70%). m.p. 89.1-90.3 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.84-7.83 (m, 1H), 7.53-7.50 (m, 1H), 7.03-7.01 (m, 1H), 4.18-4.16 (m, 1H), 4.00-.99 (m, 1H), 3.97 (s, 3H), 3.95-3.93 (m, 1H), 3.70-3.62 (m, 1H), 3.31-3.25 (m, 1H), 3.03-2.96 (m, 1H), 2.86-2.79 (m, 1H), 2.31-2.25 (m, 1H), 1.28-1.26 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.5, 148.6, 132.2, 131.9, 122.5, 121.9, 115.2, 56.6, 50.4, 48.1, 40.4, 33.9, 25.4, 23.7. **HRMS**(m/z)(ESI): calcd for $C_{15}H_{20}NaN_2O_5S_2^+$ $[M+Na]^+$ 395.0711, found 395.0711.



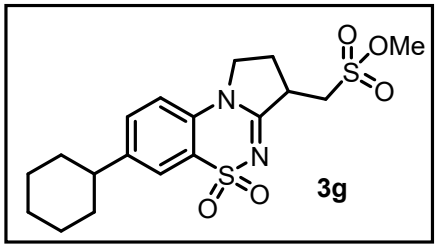
methyl(7-(tert-butyl)-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3d). white solid (78%). m.p. 94.9-95.1 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.97-7.96 (m, 1H), 7.69-7.67 (m, 1H), 7.04-7.03 (m, 1H), 4.21-4.10 (m, 1H), 4.02-3.97 (m, 1H), 3.96 (s, 3H), 3.94 -3.93 (m, 1H), 3.71-3.62 (m, 1H), 3.31-3.25 (m, 1H), 2.86-2.79 (m, 1H), 2.33-2.25 (m, 1H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.5, 151.1, 132.0, 131.0, 121.6, 121.4, 114.9, 56.7, 50.4, 48.0, 40.3, 35.2, 31.1, 25.4. **HRMS**(m/z)(ESI): calcd for $C_{16}H_{23}N_2O_5S_2^+$ $[M+H]^+$ 387.1043, found 387.1043. **HRMS**(m/z)(ESI): calcd for $C_{16}H_{22}NaN_2O_5S_2^+$ $[M+Na]^+$ 409.0863, found 409.0866.



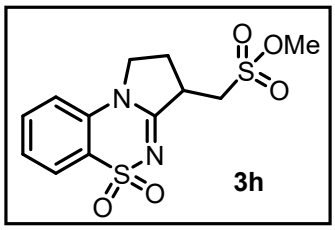
methyl(7-(sec-butyl)-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3e). white solid (70%). m.p. 88.7-91.0 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.81 (m, 1H), 7.49-7.46 (m, 1H), 7.03-7.01 (m, 1H), 4.19-4.17 (m, 1H), 3.99 (m, 1H), 3.98 (s, 3H), 3.96 (m, 1H), 3.68-3.64 (m, 1H), 3.30-3.25 (m, 1H), 2.86-2.83 (m, 1H), 2.73-2.69 (m, 1H), 2.32-2.26 (m, 1H), 1.63-1.58 (m, 2H), 1.26-1.25 (m, 3H), 0.83-0.80 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.6, 147.5, 132.3, 123.0, 121.8, 115.3, 56.7, 50.4, 48.1, 41.3, 40.4, 30.9, 25.3, 21.5, 12.1. **HRMS**(m/z)(ESI): calcd for $C_{16}H_{23}N_2O_5S_2^+$ $[M+H]^+$ 387.1043, found 387.1042.



methyl(7-butyl-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3f). white solid (73%). m.p. 91.7-92.1 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.80 (s, 1H), 7.47-7.45 (m, 1H), 7.01-6.99 (m, 1H), 4.21-4.17 (m, 1H), 4.02-4.00 (m, 1H), 3.98 (s, 3H), 3.95-3.94 (m, 1H), 3.71-3.36 (m, 1H), 3.31-3.22 (m, 1H), 2.88-2.81 (m, 1H), 2.71-2.67 (m, 2H), 2.34-2.25 (m, 1H), 1.64-1.60 (m, 2H), 1.38-1.33 (m, 2H), 0.95-0.91 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.4, 142.8, 133.6, 132.1, 124.4, 121.8, 115.0, 56.6, 50.4, 48.1, 40.4, 35.1, 33.1, 25.4, 22.2, 13.9. **HRMS**(m/z)(ESI): calcd for $C_{16}H_{22}NaN_2O_5S_2^+$ $[M+Na]^+$ 409.0864, found 409.0868.

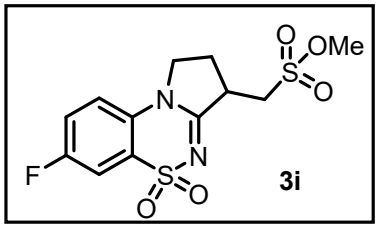


methyl(7-cyclohexyl-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3g). white solid (65%). m.p. 94.0-94.3 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.83 (m, 1H), 7.51-7.48 (m, 1H), 7.02-7.00 (m, 1H), 4.18-4.15 (m, 1H), 4.06-3.99 (m, 1H), 3.97 (s, 3H), 3.95-3.89 (m, 1H), 3.73-3.64 (m, 1H), 3.30-3.24 (m, 1H), 2.87-2.80 (m, 1H), 2.59-2.57 (m, 1H), 2.33-2.22 (m, 1H), 1.86-1.74 (m, 5H), 1.43-1.38 (m, 3H), 1.28-1.25 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.5, 147.8, 132.2, 123.5, 122.8, 121.8, 115.1, 56.6, 50.4, 48.1, 44.1, 40.4, 34.1, 26.8, 25.9, 25.4. **HRMS**(m/z)(ESI): calcd for $C_{18}H_{24}NaN_2O_5S_2^+$ $[M+Na]^+$ 435.1019, found 435.1025.

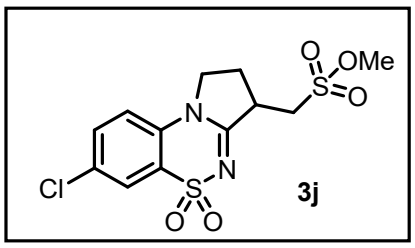


methyl(5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3h). white solid (70%). m.p. 87.9-88.3 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.89-7.87 (m, 1H), 7.65-6.21 (m, 1H), 7.45-7.41 (m, 1H), 7.08-7.06 (m, 1H), 4.20-4.15 (m, 1H), 4.03-3.98 (m, 1H), 3.97-3.93 (m, 3H), 3.92-3.83 (m, 1H), 3.70-3.62 (m, 1H), 3.31-3.24 (m, 1H), 2.81-2.78 (m, 1H), 2.29-2.23 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 161.0, 134.3, 133.3, 127.1, 125.0, 121.8, 115.3, 56.7, 50.4,

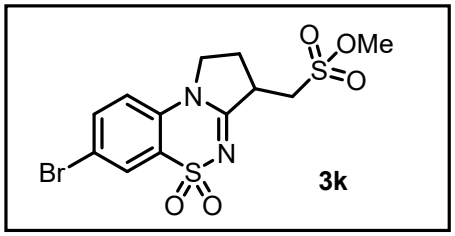
48.2, 40.4, 25.3. **HRMS**(m/z)(ESI): calcd for $C_{12}H_{14}NaN_2O_5S_2^+$ $[M+Na]^+$ 353.0242, found 353.0237.



methyl(7-fluoro-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3i). white solid (66%). m.p. 86.4-87.3 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.57-7.54 (m, 1H), 7.40-7.34 (m, 1H), 7.12-7.08 (m, 1H), 4.22-4.16 (m, 1H), 4.06-4.02 (m, 1H), 3.99 (s, 3H), 3.97-3.93 (m, 1H), 3.81-3.66 (m, 1H), 3.33-3.22 (m, 1H), 2.87-2.80 (m, 1H), 2.32-2.27 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 161.2, 160.0 (d, J = 252.5 Hz), 130.9, 122.8 (d, J = 10.1 Hz), 121.1 (d, J = 20.2 Hz), 117.9 (d, J = 10.1 Hz), 111.3, (d, J = 20.2 Hz), 56.6, 50.4, 48.5, 40.4, 25.1. **^{19}F NMR** (376 MHz, Chloroform-d) δ -110.98. **HRMS**(m/z)(ESI): calcd for $C_{12}H_{13}NaFN_2O_5S_2^+$ $[M+Na]^+$ 371.0143, found 371.0145.

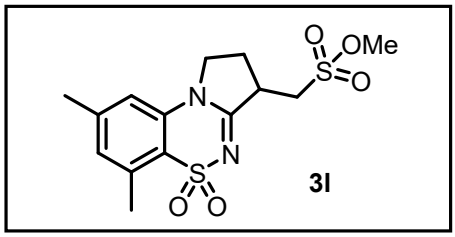


methyl(7-chloro-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3j). white solid (65%). m.p. 90.8-92.1 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.93-7.92 (m, 1H), 7.62-7.60 (m, 1H), 7.05-7.03 (m, 1H), 4.21-4.17 (m, 1H), 4.043-4.01 (m, 1H), 3.99 (s, 3H), 3.96 (m, 1H), 3.94-3.93 (m, 1H), 3.34-3.27 (m, 1H), 2.90-2.84 (m, 1H), 2.34-2.29 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 161.1, 133.5, 132.8, 132.4, 125.0, 122.9, 116.8, 56.6, 50.4, 48.3, 40.4, 25.2. **HRMS**(m/z)(ESI): calcd for $C_{12}H_{13}ClNaN_2O_5S_2^+$ $[M+Na]^+$ 386.9847, found 386.9850.

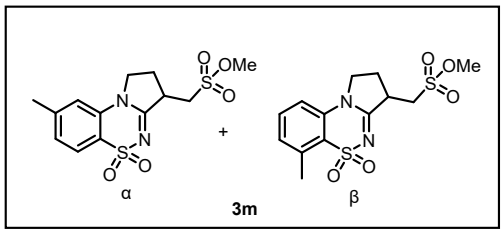


methyl(7-bromo-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3k). white solid (66%). m.p. 91.1-92.6 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.05 (m, 1H), 7.76-7.74 (m, 1H), 6.98-6.96 (m, 1H), 4.21-4.15 (m, 1H), 4.04-4.00 (m, 1H), 3.98 (s, 3H), 3.96-3.90 (m, 1H), 3.70-3.66 (m, 1H), 3.33-3.27 (m, 1H), 2.88-2.84 (m, 1H), 2.34-2.28 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 161.0, 136.3, 128.0, 123.1, 119.7, 116.9, 56.7, 50.3, 48.3, 40.4, 25.3. **HRMS**(m/z)(ESI): calcd for $C_{12}H_{13}BrN_2O_5S_2Na^+$ $[M+Na]^+$ 430.9347, found

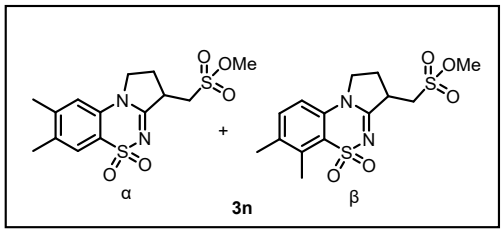
430.9347.



methyl(6,8-dimethyl-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3l). white solid (77%). m.p. 94.3-94.5 °C. **^{1}H NMR** (400 MHz, Chloroform-d/Tetrahydrofuran-d) δ 7.16 (s, 1H), 7.10 (s, 1H), 4.27-4.22 (m, 1H), 4.06-3.97 (m, 1H), 3.96 (s, 3H), 3.79-3.69 (m, 3H), 2.62 (s, 3H), 2.60-2.56 (m, 1H), 2.42 (s, 3H), 2.29-2.23 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d/Tetrahydrofuran-d) δ 160.3, 143.2, 136.4, 135.2, 130.0, 118.7, 114.6, 57.1, 49.6, 48.9, 21.1, 19.4. **HRMS**(m/z)(ESI): calcd for $C_{14}H_{18}N_2O_5S_2Na^+$ $[M+Na]^+$ 381.0550, found 381.0552.

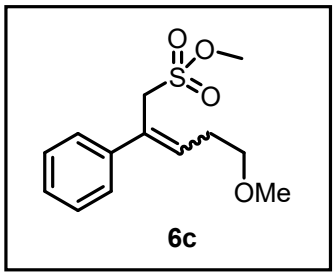


α:methyl(8-methyl-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate,β:methyl(6-methyl-5,5-dioxido-2,3-dihydro-1H-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3m). white solid (75%). m.p. 90.3-91.1 °C. Major isomer (α):**^{1}H NMR** (400 MHz, Chloroform-d) δ 7.84-7.82 (m, 1H), 7.28-7.27 (m, 1H), 6.87 (m, 1H), 6.87 (s, 1H), 4.20-4.16(m, 1H), 4.11-4.07 (m, 1H), 3.98 (s, 3H), 3.95-3.93 (m, 1H), 3.70-3.65 (m, 1H), 3.31-3.25 (m, 1H), 2.84-2.77 (m, 1H), 2.47 (s, 3H), 2.30-2.27 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 159.1, 138.2, 134.3, 132.5, 129.9, 125.1, 120.9, 115.2, 53.5, 50.4, 48.0, 40.4, 25.3, 20.0. Minor isomer (β): **^{1}H NMR** (400 MHz, Chloroform-d) 7.53-7.49 (m, 1H), 7.26-7.24 (m, 1H), 6.93-6.91 (m, 1H), 4.20-4.16(m, 1H), 4.11-4.07 (m, 1H), 3.99 (s, 3H), 3.95-3.93 (m, 1H), 3.70-3.65 (m, 1H), 3.31-3.25 (m, 1H), 2.84-2.77 (m, 1H), 2.75 (s, 3H), 2.30-2.27 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.8, 144.5, 134.6, 132.5, 128.1, 120.9, 115.2, 56.6, 50.4, 48.5, 40.4, 25.4, 22.0. **HRMS**(m/z)(ESI): calcd for $C_{12}H_{17}N_2O_5S_2^+$ $[M+H]^+$ 345.0574, found 345.0575.



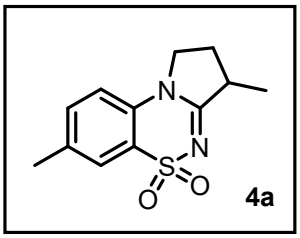
α:methyl(7,8-dimethyl-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate,β:methyl(6,7-dimethyl-5,5-dioxido-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazin-3-yl)methanesulfonate (3n).

white solid (74%). m.p. 92.3-94.0 °C. Major isomer (α):**^{1}H NMR** (400 MHz, Chloroform-d) δ 7.64 (m, 1H), 6.83 (m, 1H), 4.15-4.13 (m, 1H), 4.00-3.98 (m, 1H), 3.94 (s, 3H), 3.89-3.87 (m, 1H), 3.68-3.59 (m, 1H), 3.29-3.22 (m, 1H), 2.80-2.75 (m, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 2.27-2.21 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 158.7, 137.0, 135.9, 132.7, 125.0, 119.3, 112.9, 53.5, 50.4, 48.0, 40.2, 25.2, 20.3, 16.4. Minor isomer (β): **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.37-7.35 (m, 1H), 6.82-6.80 (m, 1H), 4.15-4.13 (m, 1H), 4.00-3.98 (m, 1H), 3.95 (s, 3H), 3.89-3.87 (m, 1H), 3.68-3.59 (m, 1H), 3.29-3.22 (m, 1H), 2.80-2.75 (m, 1H), 2.60 (s, 3H), 2.34 (s, 3H), 2.27-2.21 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 160.5, 143.3, 136.5, 134.0, 132.3, 125.0, 119.3, 115.8, 56.6, 50.4, 48.4, 40.3, 25.3, 20.5, 19.5. **HRMS**(m/z)(ESI): calcd for $C_{14}H_{18}N_2O_5S_2Na^+$ $[M+Na]^+$ 381.0550, found 381.0557.



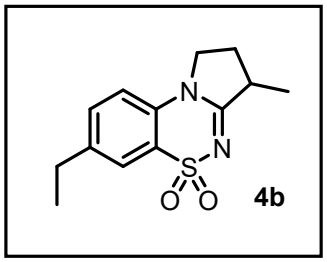
6c

methyl 5-methoxy-2-phenylpent-2-ene-1-sulfonate (6c). colourless liquid (28%,).**^{1}H NMR** (400 MHz, Chloroform-d) δ 7.41-7.33 (m, 4H), 7.30-7.26 (m, 1H), 6.20-6.17 (m, 1H), 4.37 (s, 2H), 3.65 (s, 3H), 3.56-3.52 (m, 2H), 3.36 (s, 3H), 2.66-2.61 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 140.7, 135.2, 128.9, 128.6, 127.7, 126.5, 71.5, 58.8, 56.1, 51.5, 30.1. **HRMS**(m/z)(ESI): calcd for $C_{13}H_{18}O_4SNa^+$ $[M+Na]^+$ 293.0818, found 293.0820.



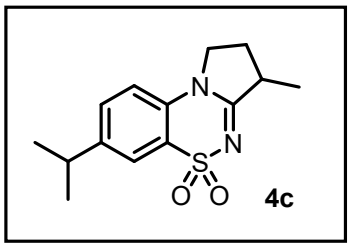
4a

3,7-dimethyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine 5,5-dioxide (4a). white solid (76%). m.p. 100.1-102.6 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.79 (m, 1H), 7.42-7.39 (m, 1H), 6.96-6.94 (m, 1H), 4.10-4.05 (m, 1H), 3.95-3.89 (m, 1H), 3.19-3.13 (m, 1H), 2.55-2.50 (m, 1H), 2.42 (s, 3H), 1.94-1.98 (m, 1H), 1.40 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.0, 136.9, 133.9, 132.5, 125.0, 121.6, 114.8, 47.8, 39.8, 27.3, 21.0, 16.6. **HRMS**(m/z)(ESI): calcd for $C_{12}H_{15}N_2O_2S^+$ $[M+H]^+$ 251.0849, found 251.0852.

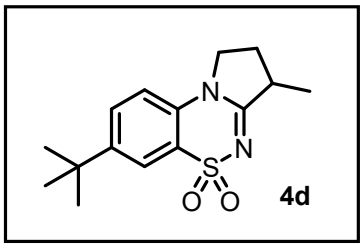


4b

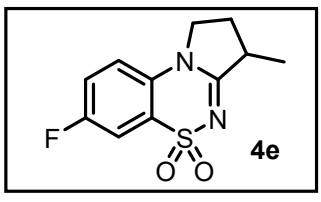
7-ethyl-3-methyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide (4b). white solid (68%). m.p. 101.1-101.6 °C. **^{1}H NMR** (400 MHz, Chloroform-d)
δ 7.85-7.84 m, 1H), 7.46-7.43 (m, 1H), 6.99-6.97 (m, 1H), 4.10-4.06 (m, 1H), 3.94-3.89 (m, 1H), 3.21-3.14 (m, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.57-2.49 (m, 1H), 1.95-1.89 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 2.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.0, 143.2, 132.8, 132.7, 123.9, 121.7, 114.8, 47.7, 39.8, 28.4, 27.3, 16.6, 15.1. **HRMS**(m/z)(ESI): calcd for $C_{13}H_{17}N_2O_2S^+$ $[M+H]^+$ 265.1006, found 265.1010.



7-isopropyl-3-methyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide (4c). white solid (70%). m.p. 100.9-101.1 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.80 (m, 1H), 7.43-7.40 (m, 1H), 6.93-6.91 (m, 1H), 4.04 -3.99 (m, 1H), 3.89-3.82 (m, 1H), 3.13-3.07 (m, 1H), 2.96-2.89 (m, 1H), 2.48-2.43 (m, 1H), 1.88-1.82 (m, 1H), 1.35 (d, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.0, 147.9, 132.8, 131.5, 122.6, 121.7, 114.8, 47.7, 39.8, 33.9, 27.3, 23.7, 16.6. **HRMS**(m/z)(ESI): calcd for $C_{14}H_{19}N_2O_2S^+$ $[M+H]^+$ 279.1162, found 279.1166.

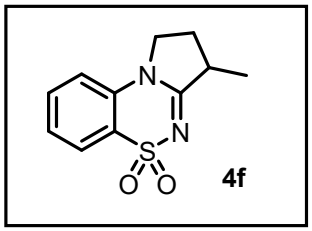


7-(tert-butyl)-3-methyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide (4d). white solid (76%). m.p. 101.2-101.5 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.99 (m, 1H), 7.66-7.63 (m, 1H), 7.01-6.99 (m, 1H), 4.11-4.06 (m, 1H), 3.95-3.89 (m, 1H), 3.20-3.13 (m, 1H), 2.55-2.50 (m, 1H), 1.94-1.89 (m, 1H), 1.41 (d, *J* = 7.0 Hz, 3H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.1, 150.3, 132.5, 130.6, 121.4, 114.6, 47.7, 39.8, 35.1, 31.1, 27.3, 16.6. **HRMS**(m/z)(ESI): calcd for $C_{15}H_{21}N_2O_2S_+$ $[M+H]^+$ 293.1124, found 293.1121.

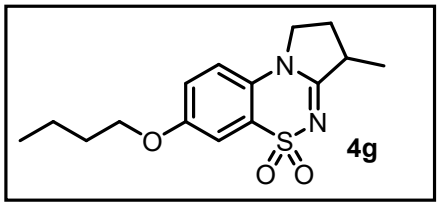


7-fluoro-3-methyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide (4e). white solid (59%). m.p. 100.4-100.5 °C. **^{1}H NMR** (400 MHz,

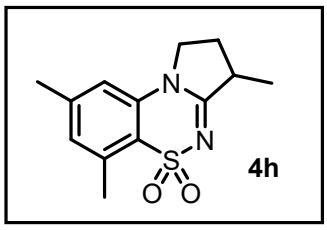
Chloroform-d) δ 7.69-7.66 (m, 1H), 7.37-7.32 (m, 1H), 7.09-7.06 (m, 1H), 4.13-4.07 (m, 1H), 3.99-3.92 (m, 1H), 3.22-3.16 (m, 1H), 2.57-2.52 (m, 1H), 1.96 -1.91 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 165.3, 159.9 (d, *J* = 241.6 Hz), 131.3, 123.1 (d, *J* = 15.1 Hz), 120.8 (d, *J* = 30.2 Hz), 117.1 (d, *J* = 15.1 Hz), 111.9, (d, *J* = 30.2 Hz), 48.0, 39.8, 27.1, 16.5. **^{19}F NMR** (376 MHz, Chloroform-d) δ -111.79. **HRMS**(m/z)(ESI): calcd for $C_{11}H_{11}NaFN_2O_2S^+$ $[M+Na]^+$ 277.0418, found 3277.0420.



3-methyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine 5,5-dioxide (4f). white solid (56%). m.p. 103.2-103.5 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.02-8.00 (m, 1H), 7.63-7.61 (m, 1H), 7.47-7.45 (m, 1H), 7.07-7.05 (m, 1H), 4.13-4.08 (m, 1H), 3.98-3.91 (m, 1H), 3.22-3.14(m, 1H), 2.59-2.51 (m, 1H), 1.99-1.89 (m, 1H), 1.43 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.3, 134.8, 133.0, 126.5, 125.3, 121.9, 114.7, 47.8, 39.9, 27.3, 16.5. **HRMS**(m/z)(ESI): calcd for $C_{11}H_{13}N_2O_2S^+$ $[M+H]^+$ 237.0693, found 237.0695.



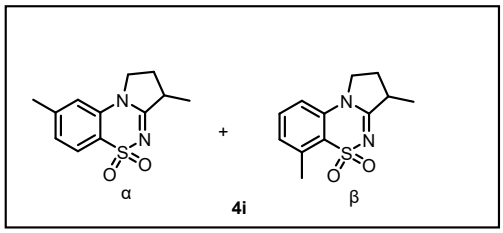
7-butoxy-3-methyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide (4g). white solid (72%). m.p. 100.0-100.5 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.42 (m, 1H), 7.17-7.14 (m, 1H), 7.01-6.99 (m, 1H), 4.11-4.05 (m, 1H), 4.04-4.00 (m, 2H), 3.96-3.90 (m, 1H), 3.20-3.14 (m, 1H), 2.57-2.49 (m, 1H), 1.93-1.88 (m, 1H), 1.82-1.74 (m, 2H), 1.52-1.46 (m, 2H), 1.41 (d, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 164.6, 157.4, 128.2, 122.5, 121.8, 116.6, 107.4, 68.6, 47.9, 39.7, 31.0, 27.2, 19.1, 16.6, 13.8. **HRMS**(m/z)(ESI): calcd for $C_{15}H_{21}N_2O_3S^+$ $[M+H]^+$ 309.1268, found 309.1266.



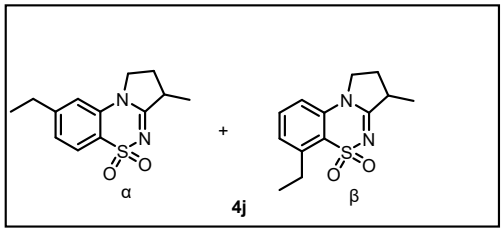
3,6,8-trimethyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide (4h). white solid (72%). m.p. 101.2-101.3 °C. **^{1}H NMR** (400 MHz, Chloroform-d)

δ 7.00 (m, 1H), 6.67 (m, 1H), 4.08-4.02 (m, 1H), 3.93-3.87 (m, 1H), 3.16-3.12 (m, 1H), 2.71 (s, 3H), 2.54-2.46 (m, 1H), 2.37 (s, 3H), 1.90-1.84 (m, 1H), 1.39 (d, *J* = 7.0 Hz,

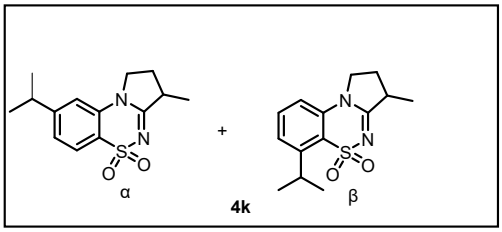
3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 163.5, 142.9, 137.8, 135.1, 130.2, 118.2, 113.1, 48.1, 39.7, 27.2, 21.7, 19.9, 16.5. **HRMS**(m/z)(ESI): calcd for $C_{13}H_{17}N_2O_2S^+$ $[M+H]^+$ 265.1006, found 265.1010.



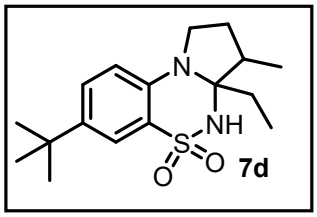
α:3,8-dimethyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide,β:3,6-dimethyl-2,3-dihydro-1H-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide (4i). white solid (78%). m.p. 101.3-101.6 °C. Major isomer (α):**^{1}H NMR** (400 MHz, Chloroform-d) δ 7.85-7.83 (m, 1H), 6.89-6.87 (m, 1H), 6.84 (m, 1H), 4.10-4.05 (m, 1H), 3.96-3.88 (m, 1H), 3.20-3.13 (m, 1H), 2.56-2.46 (m, 1H), 2.45 (s, 3H), 1.93 -1.87 (m, 1H), 1.40 (d, *J* = 3.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 163.6, 138.1, 134.8, 129.3, 125.1, 119.2, 112.8, 47.7, 39.8, 27.2, 20.0, 16.5.Minor isomer (β): **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.48-7.44 (m, 1H), 7.24-7.19 (m, 2H), 4.10-4.05 (m, 1H), 3.96-3.88 (m, 1H), 3.20-3.13 (m, 1H), 2.76 (s, 3H), 2.56-2.46 (m, 1H), 1.93 -1.87 (m, 1H), 1.41 (d, *J* = 3.8 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.2, 144.0, 135.1, 132.2, 127.4, 119.2, 115.0, 48.2, 39.8, 27.3, 22.0, 16.5. **HRMS**(m/z)(ESI): calcd for $C_{12}H_{17}N_2O_5S_2^+$ $[M+H]^+$ 345.0574, found 345.0575.



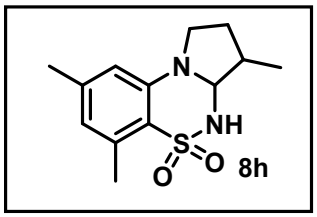
α:8-ethyl-3-methyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide,β:6-ethyl-3-methyl-2,3-dihydro-1H-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine 5,5-dioxide (4j). white solid (67%). m.p. 102.3-102.6 °C. Major isomer (α):**^{1}H NMR** (400 MHz, Chloroform-d) δ 7.92-7.91 (m, 1H), 6.89-6.87 (m, 1H), 6.85 (m, 1H), 4.10-4.07 (m, 1H), 3.95-3.91 (m, 1H), 3.18-3.14 (m, 2H), 2.77 -2.71 (m, 1H), 2.26-2.19 (m, 1H), 1.95-1.87 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 163.6, 138.1, 134.8, 129.3, 125.1, 119.2, 112.8, 47.7, 39.8, 27.2, 20.0, 16.5. Minor isomer (β): **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.54-7.50 (m, 1H), 7.30-7.29 (m, 1H), 6.89-6.87 (m, 1H), 4.10-4.07 (m, 1H), 3.95-3.91 (m, 1H), 3.25-3.20 (m, 2H), 2.77 -2.71 (m, 1H), 2.26-2.19 (m, 1H), 1.95-1.87 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 3H), 1.36 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 165.2, 144.0, 135.1, 132.2, 127.4, 119.2, 115.0, 48.2, 39.8, 27.3, 22.0, 16.5. **HRMS**(m/z)(ESI): calcd for $C_{13}H_{17}N_2O_2S^+$ $[M+H]^+$ 265.1006, found 265.1008.



α:8-isopropyl-3-methyl-2,3-dihydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine5,5-dioxide,β:6-ethyl-3-methyl-2,3-dihydro-1H-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine 5,5-dioxide (4j). white solid (68%). m.p. 101.2-101.9 °C. Major isomer (α):**^{1}H NMR** (400 MHz, Chloroform-d) δ 7.93-7.91 (m, 1H), 7.33-7.31 (m, 1H), 6.86 (m, 1H), 4.14-4.09 (m, 1H), 3.99-3.92 (m, 1H), 3.18-3.16 (m, 1H), 3.01-2.98 (m, 1H), 2.28-2.19 (m, 1H), 1.95-1.89 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 3H), 1.34 (d, *J* = 6.3 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 165.2, 154.8, 134.9, 125.3, 125.0, 119.5, 112.5, 47.7, 39.8, 34.6, 27.3, 23.7, 16.6. **HRMS**(m/z)(ESI): calcd for $C_{14}H_{19}N_2O_2S^+$ $[M+H]^+$ 279.1162, found 279.1160.

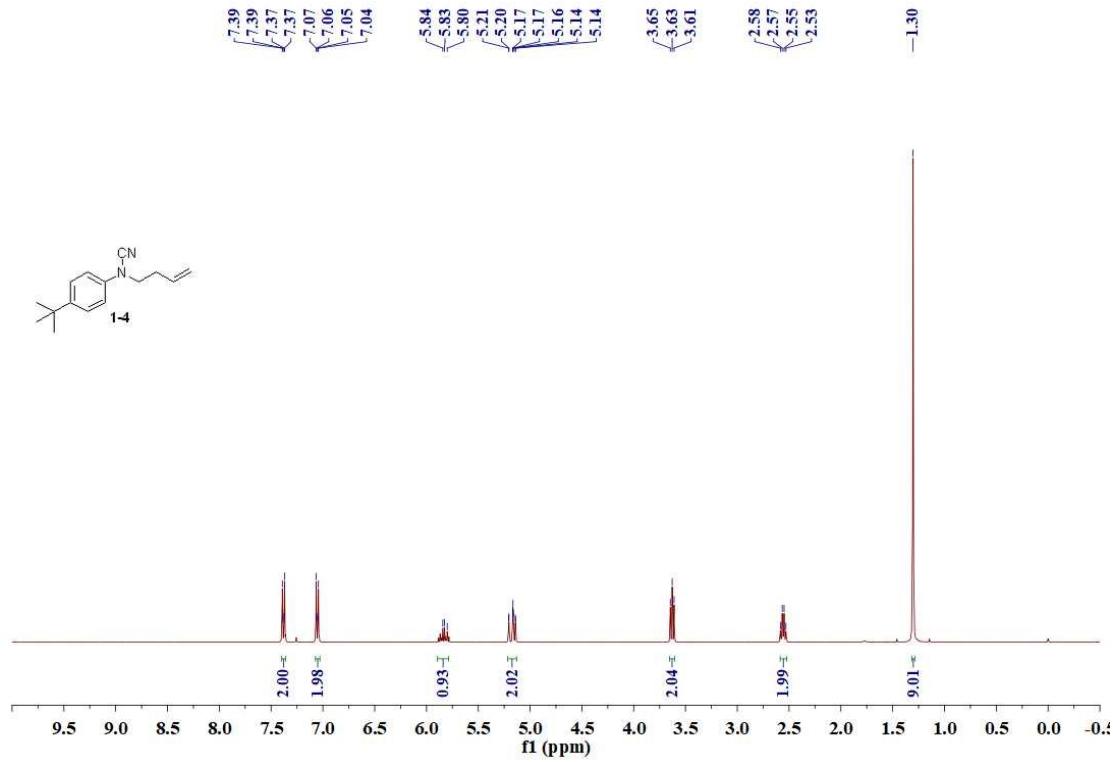


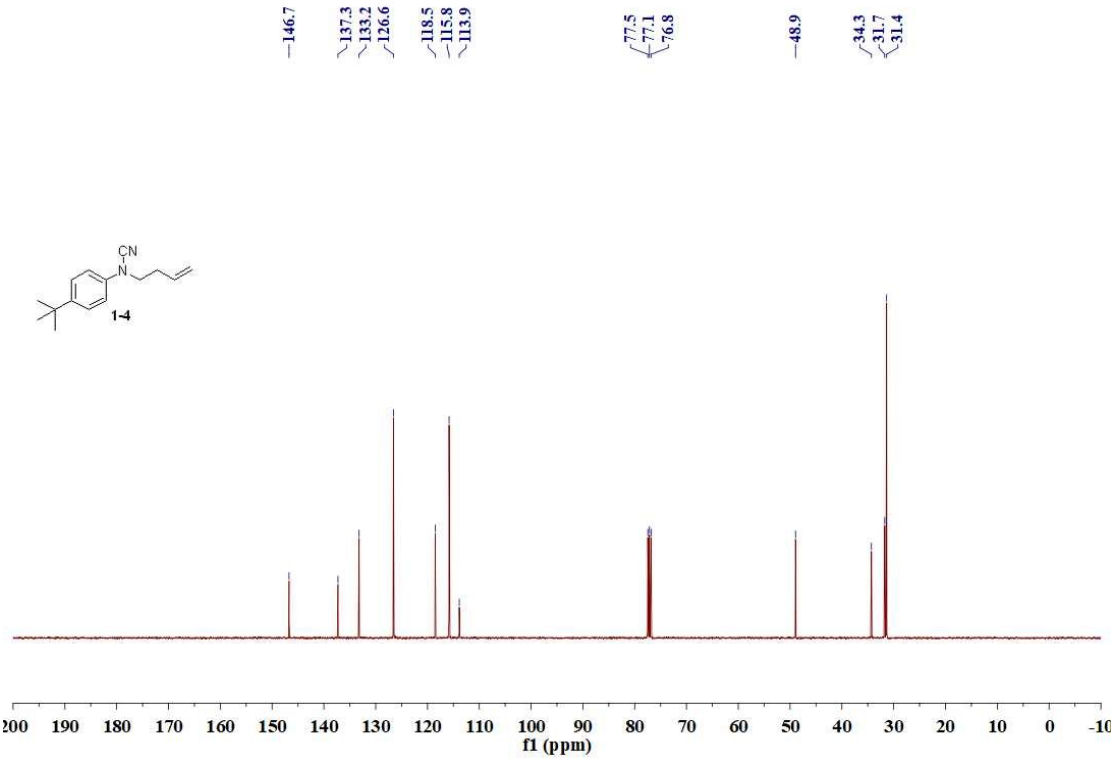
3a-ethyl-3,7-dimethyl-2,3,3a,4-tetrahydro-1*H*-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine 5,5-dioxide (7d). colorless liquid (68%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.68-7.67 (m, 1H), 7.43-7.40 (m, 1H), 6.57-6.55 (m, 1H), 3.43-3.40 (m, 1H), 2.55-2.51 (m, 1H), 2.40-2.27 (m, 2H), 1.75-1.70 (m, 1H), 1.29 (s, 9H), 1.25-1.22 (m, 2H), 1.07 (d, *J* = 7.1 Hz, 3H), 1.03-0.98 (m, 3H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 139.8, 138.8, 131.2, 121.0, 120.0, 114.3, 81.8, 45.1, 38.7, 34.1, 31.2, 29.4, 27.7, 14.9, 9.0 . **HRMS**(m/z)(ESI): calcd for $C_{17}H_{26}N_2NaO_2S^+$ $[M+Na]^+$ 345.1608, found 345.1613.

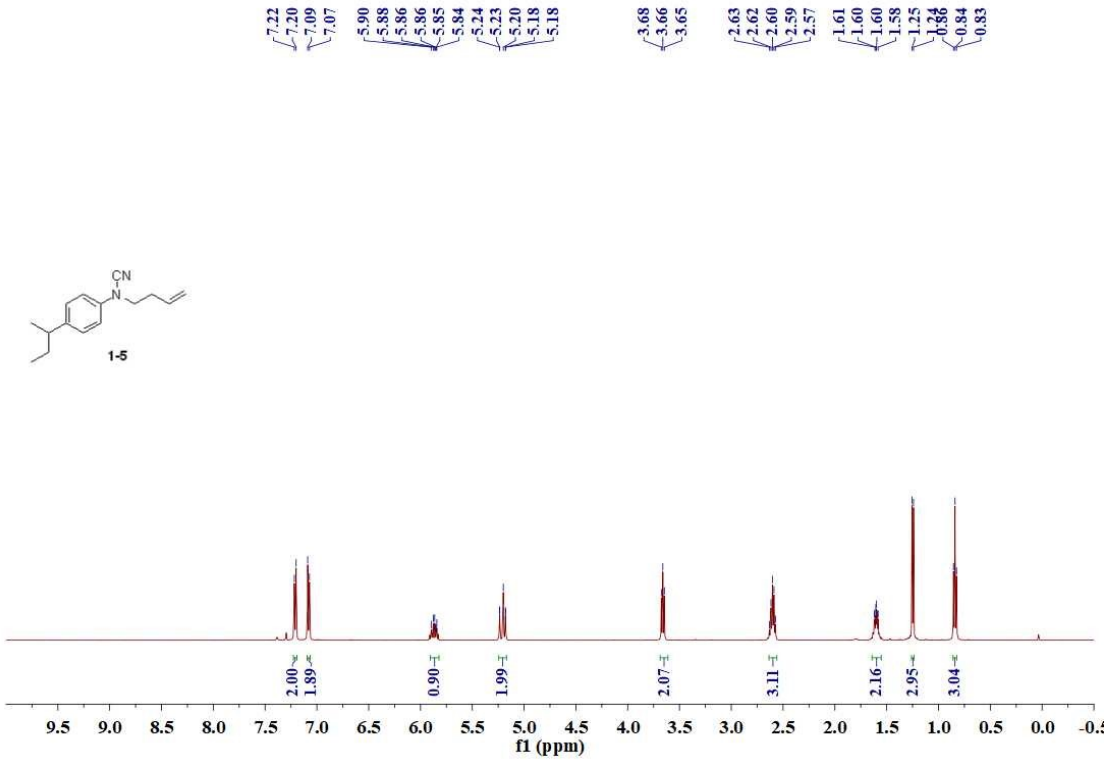


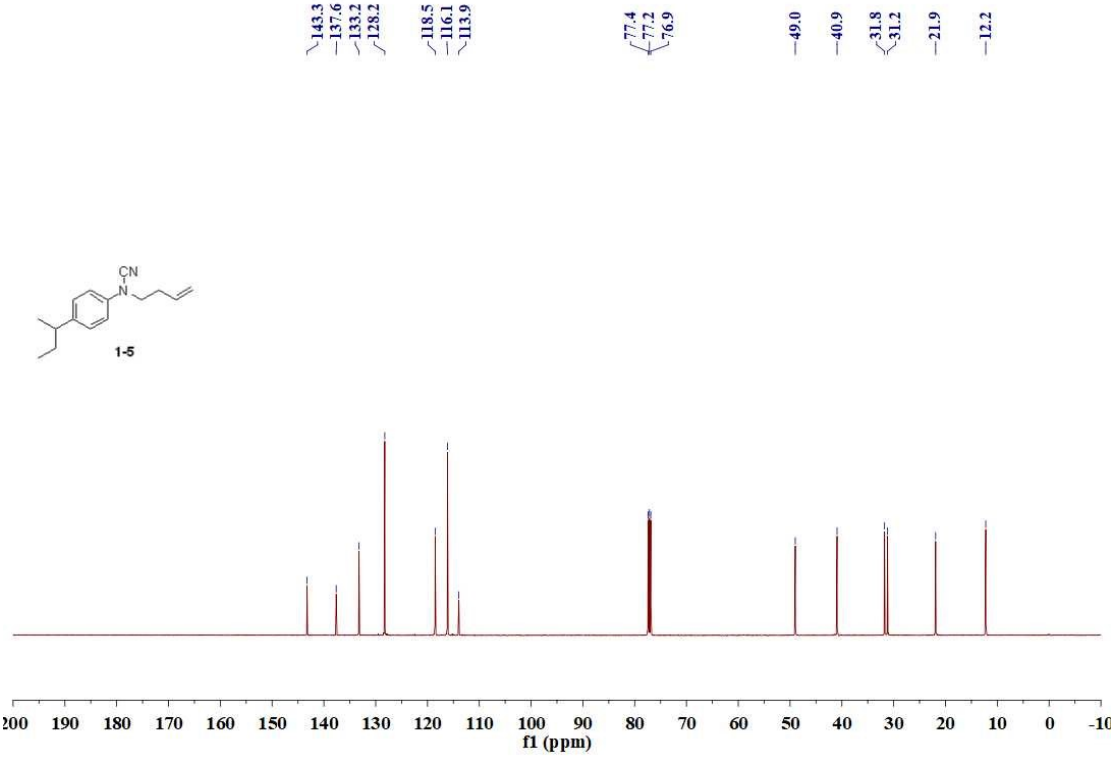
3a-ethyl-3,6,8-trimethyl-2,3,3a,4-tetrahydro-1H-benzo[e]pyrrolo[2,1-c][1,2,4]thiadiazine 5,5-dioxide (8h). white solid (72%). **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.45 (s, 1H), 6.26 (s, 1H), 4.66-4.62 (m, 1H), 4.28-4.25 (m, 1H), 3.50-3.45 (m, 1H), 3.43-3.39 (m, 1H), 2.64 (s, 3H), 2.30 (s, 3H), 2.18-2.12 (m, 1H), 1.76-1.69 (m, 1H), 1.29 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 143.3, 142.4, 137.3, 120.9, 117.7, 111.0, 75.4, 45.5, 40.4, 29.7, 21.8, 20.3, 15.6. **HRMS**(m/z)(ESI): calcd for $C_{13}H_{19}N_2O_2S^+$ $[M+H]^+$ 267.1162, found 267.1165.

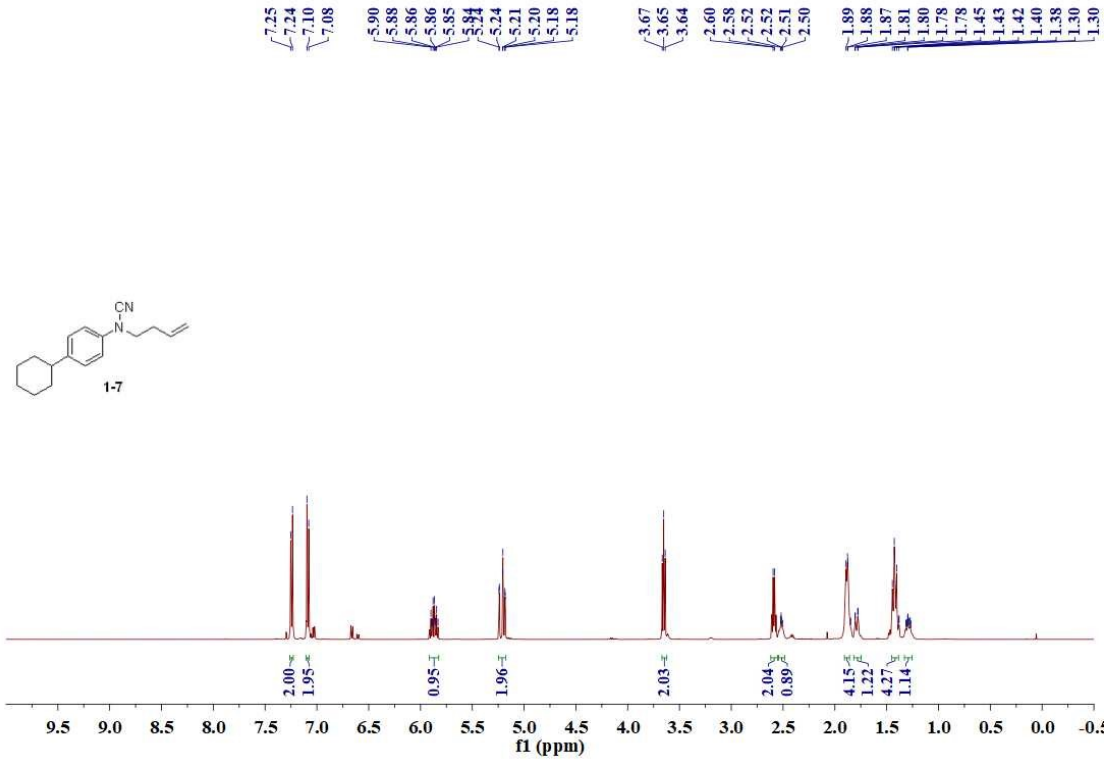
10. Copies of the NMR spectra

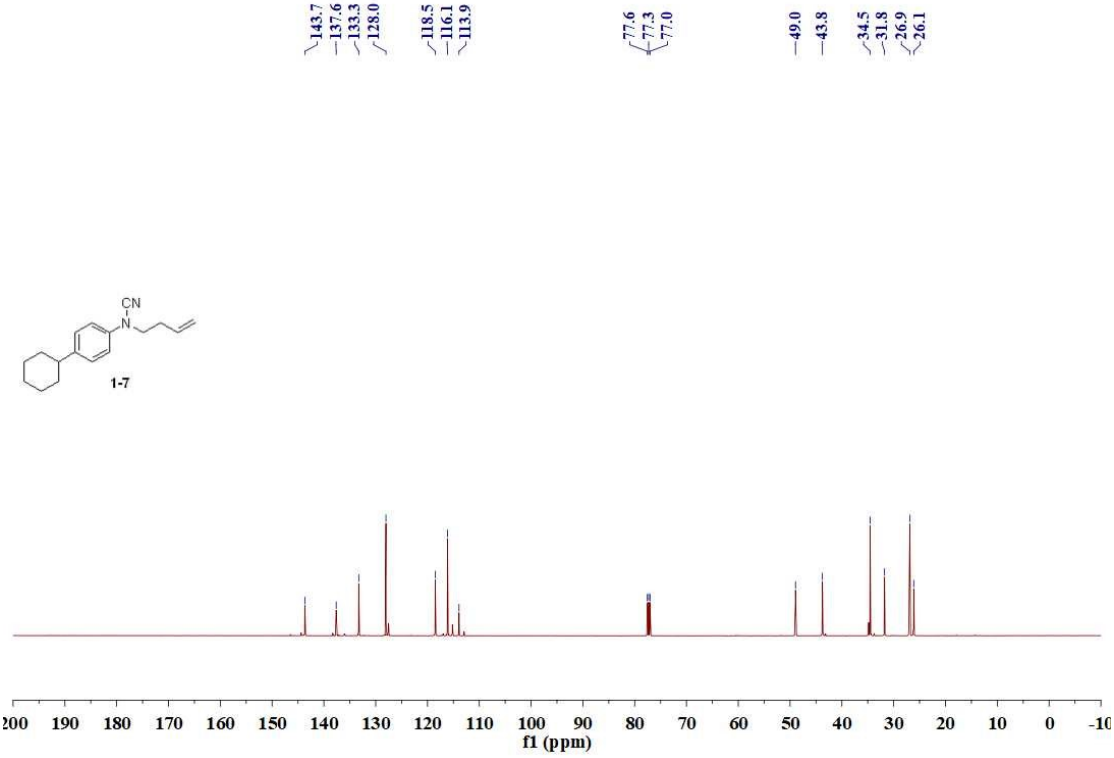


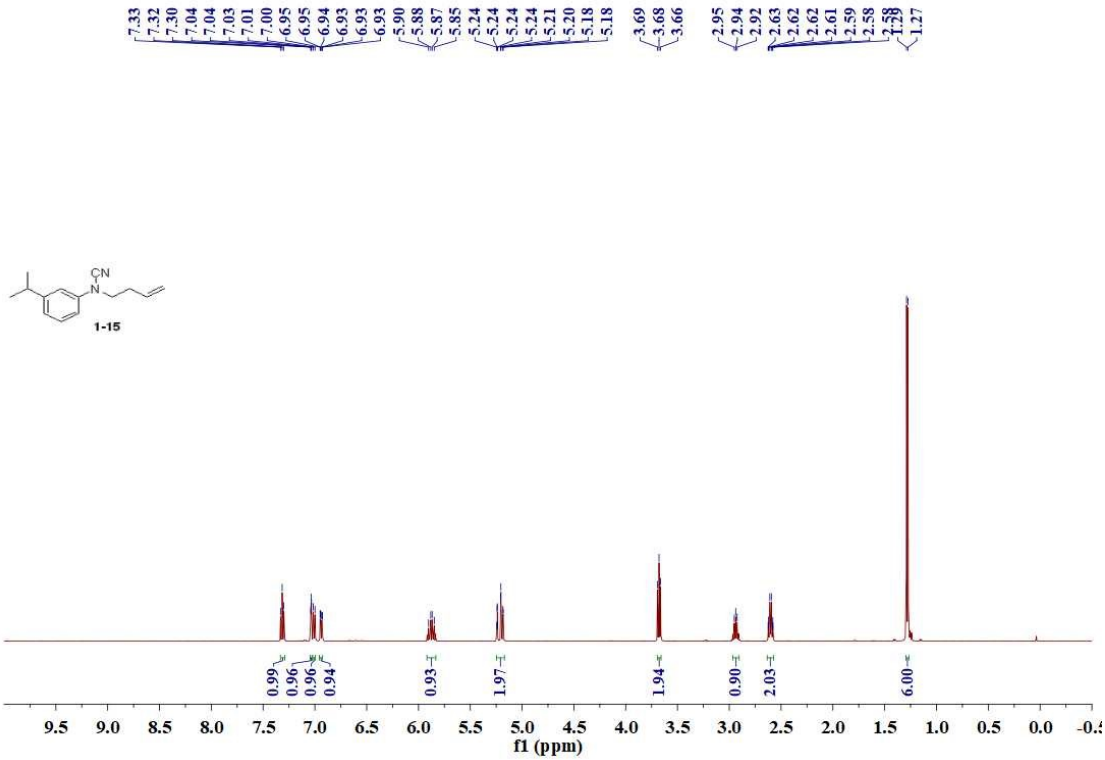


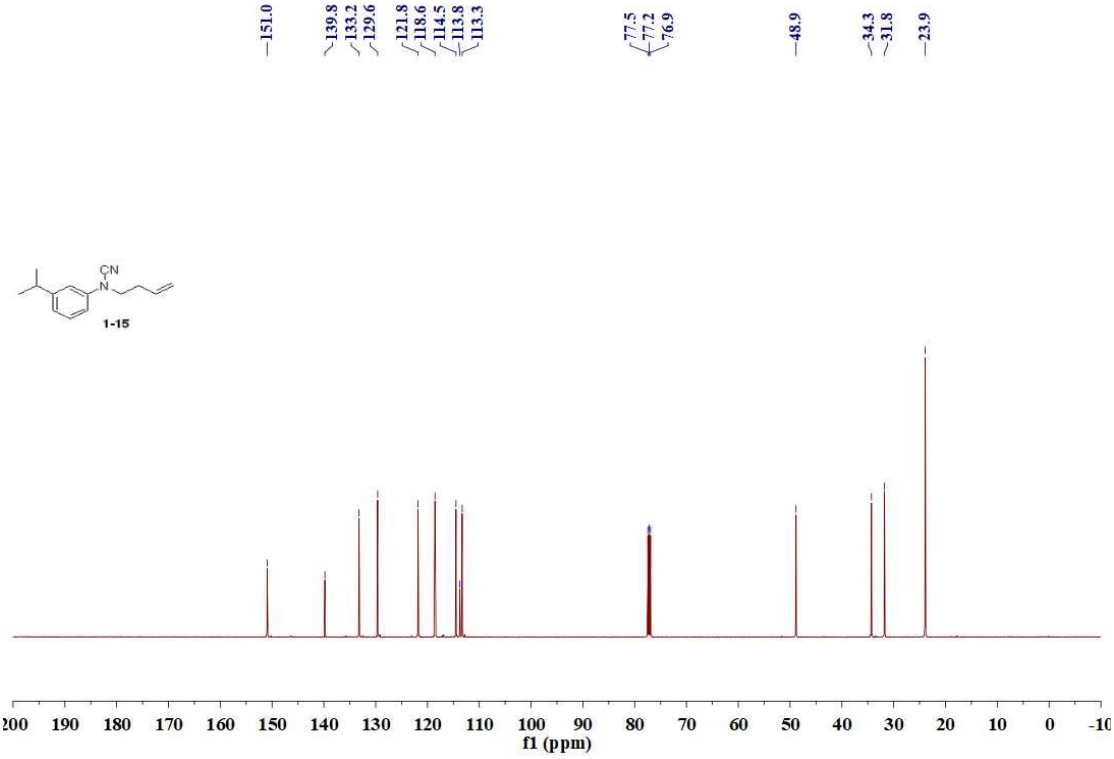

7.22
7.20
7.09
7.07
5.90
5.88
5.86
5.86
5.85
5.84
5.24
5.23
5.20
5.18
5.18
3.68
3.66
3.65
2.63
2.62
2.60
2.59
2.57
1.61
1.60
1.60
1.58
1.25
1.24
0.86
0.84
0.83
CN
N
1-5
2.00
1.89
0.90
1.99
2.07
3.11
2.16
2.95
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

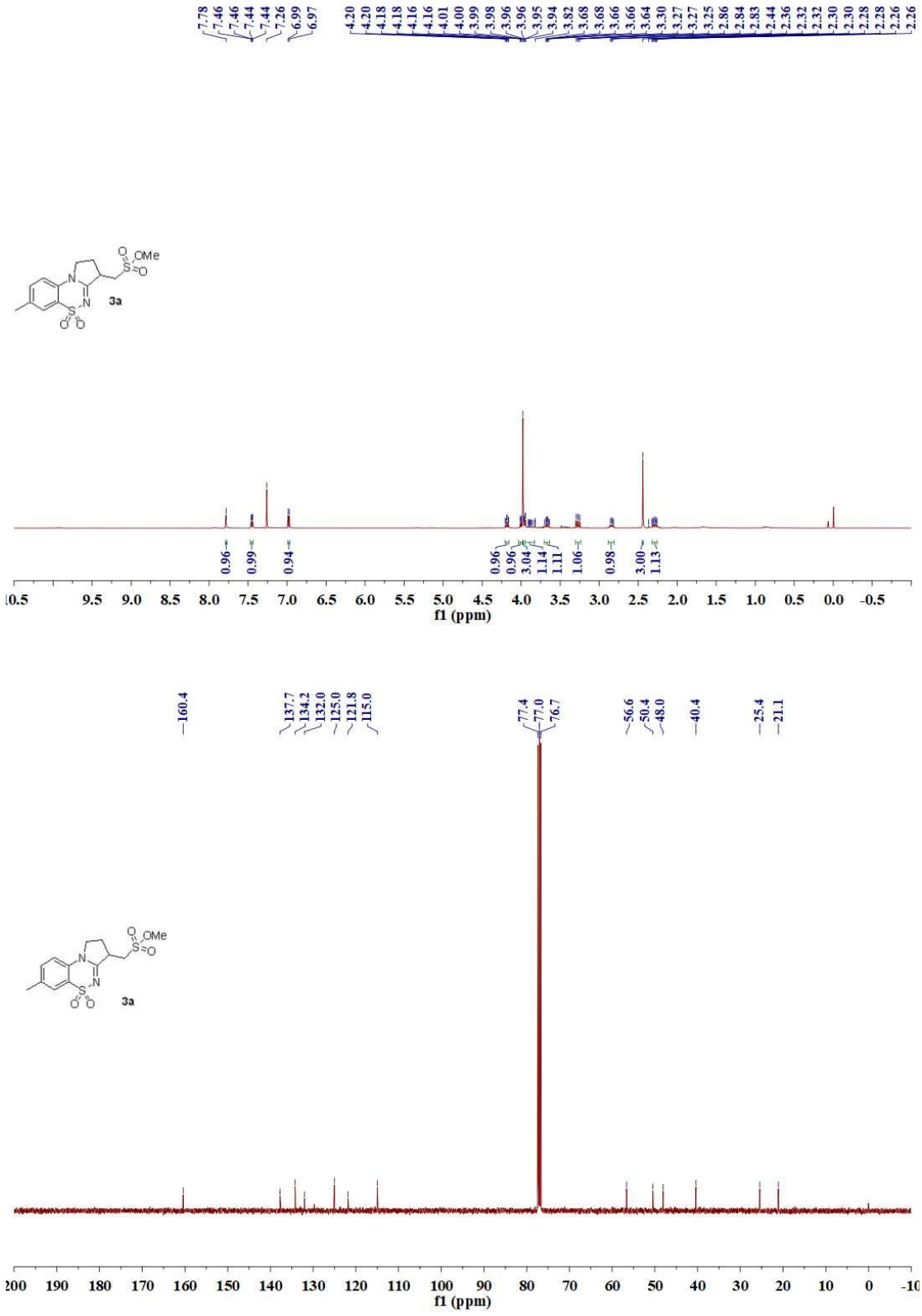

143.3
137.6
133.2
128.2
118.5
116.1
113.9
77.4
77.2
76.9
49.0
40.9
31.8
31.2
21.9
12.2
CN
N
1-5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.25
7.24
7.10
7.08
5.90
5.88
5.86
5.86
5.85
5.84
5.24
5.21
5.20
5.18
5.18
3.67
3.65
3.64
2.60
2.58
2.52
2.52
2.51
2.50
1.89
1.88
1.87
1.81
1.80
1.78
1.78
1.45
1.43
1.42
1.40
1.38
1.30
1.30
CN
N
1-7
2.00
1.95
0.95
1.96
2.03
2.04
0.89
4.15
1.22
4.27
1.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

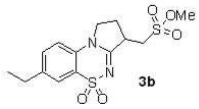

143.7
137.6
133.3
128.0
118.5
116.1
113.9
77.6
77.3
77.0
49.0
43.8
34.5
31.8
26.9
26.1
CN
N
1-7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

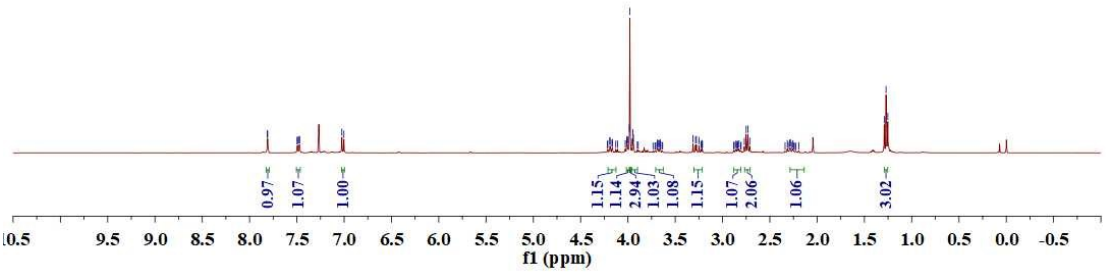

7.33
7.32
7.30
7.04
7.04
7.03
7.01
7.00
6.95
6.95
6.94
6.93
6.93
5.90
5.88
5.87
5.85
5.24
5.24
5.24
5.21
5.20
5.18
5.18
3.69
3.68
3.66
2.95
2.94
2.92
2.63
2.62
2.62
2.61
2.59
2.58
1.27
CN
N
1-15
0.99
0.96
0.96
0.94
0.93
1.97
1.94
0.90
2.03
6.00
f1 (ppm)


151.0
139.8
133.2
129.6
121.8
118.6
114.5
113.8
113.3
77.5
77.2
76.9
48.9
34.3
31.8
23.9
CN
N
1-15
f1 (ppm)

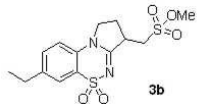

7.78
7.46
7.46
7.44
7.44
7.26
6.99
6.97
4.20
4.20
4.18
4.18
4.16
4.16
4.01
4.00
3.99
3.98
3.96
3.96
3.95
3.94
3.82
3.68
3.66
3.66
3.64
3.30
3.27
3.27
3.25
2.86
2.84
2.83
2.44
2.36
2.32
2.32
2.30
2.28
2.28
2.26
2.26
OMe
3a
0.96
0.99
0.94
0.96
0.96
3.04
1.14
1.11
1.06
0.98
3.00
1.13
f1 (ppm)
160.4
137.7
134.2
132.0
125.0
121.8
115.0
77.4
77.0
76.7
56.6
50.4
48.0
40.4
25.4
21.1
OMe
3a
f1 (ppm)


7.81
7.81
7.50
7.49
7.48
7.47
7.02
7.00
4.22
4.21
4.19
4.19
4.17
4.16
4.13
4.11
4.03
4.01
4.01
4.00
3.99
3.98
3.96
3.95
3.94
3.90
3.89
3.69
3.69
3.68
3.67
3.66
3.65
3.31
3.29
3.28
3.25
3.23
3.22
3.21
2.88
2.86
2.85
2.84
2.84
2.83
2.77
2.75
2.73
2.71
2.31
2.29
2.28
2.26
1.29
1.27
1.25

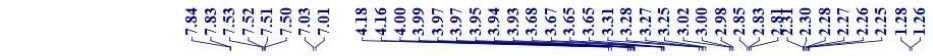

OMe
3b

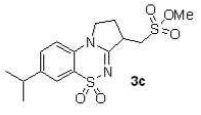

0.97
1.07
1.00
1.15
1.14
2.94
1.03
1.08
1.15
1.07
2.06
1.06
3.02
f1 (ppm)

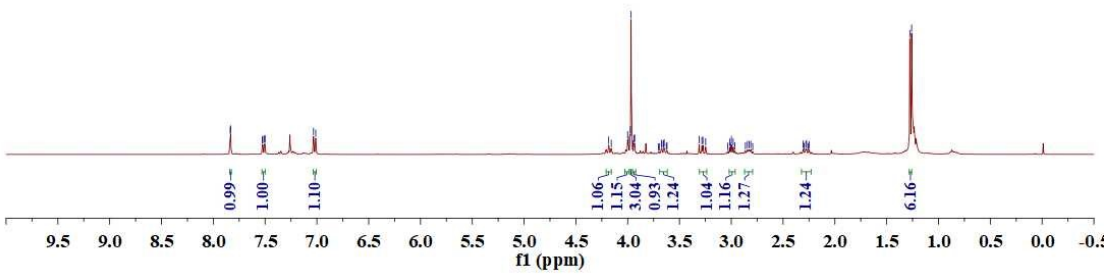

160.5
144.0
133.2
132.2
123.9
121.9
115.1
77.3
77.1
76.8
56.7
50.5
48.1
40.4
28.4
25.4
15.1


OMe
3b

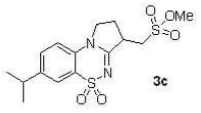
f1 (ppm)

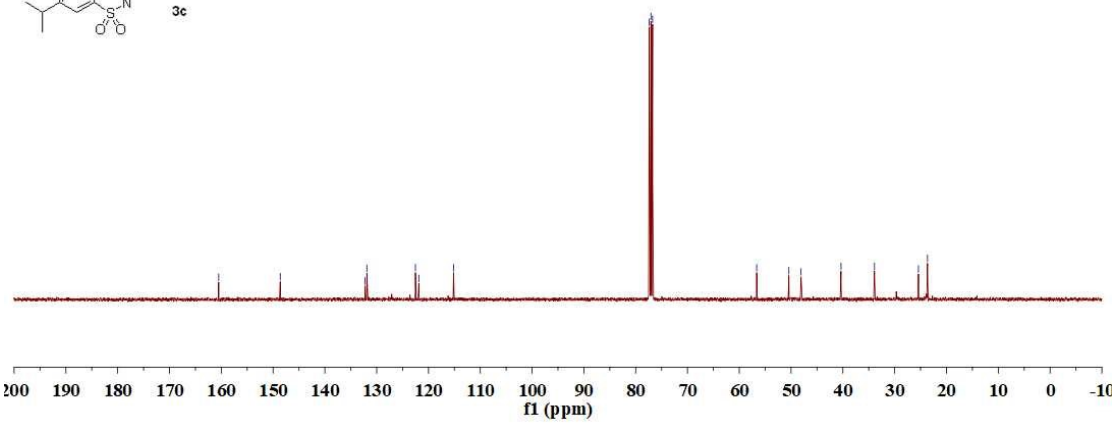

7.84
7.83
7.53
7.52
7.51
7.50
7.03
7.01
4.18
4.16
4.00
3.99
3.97
3.97
3.95
3.94
3.93
3.68
3.67
3.65
3.65
3.31
3.28
3.27
3.25
3.02
3.00
2.98
2.85
2.83
2.30
2.28
2.27
2.26
2.25
1.28
1.26

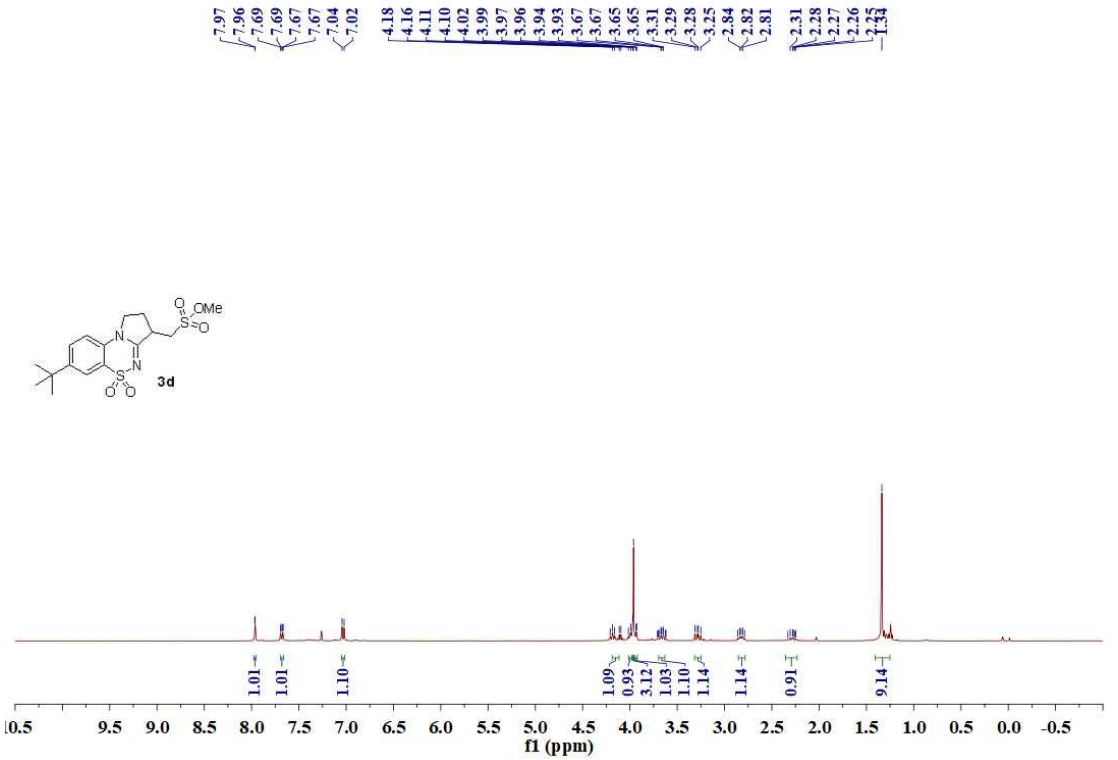

OMe
3c

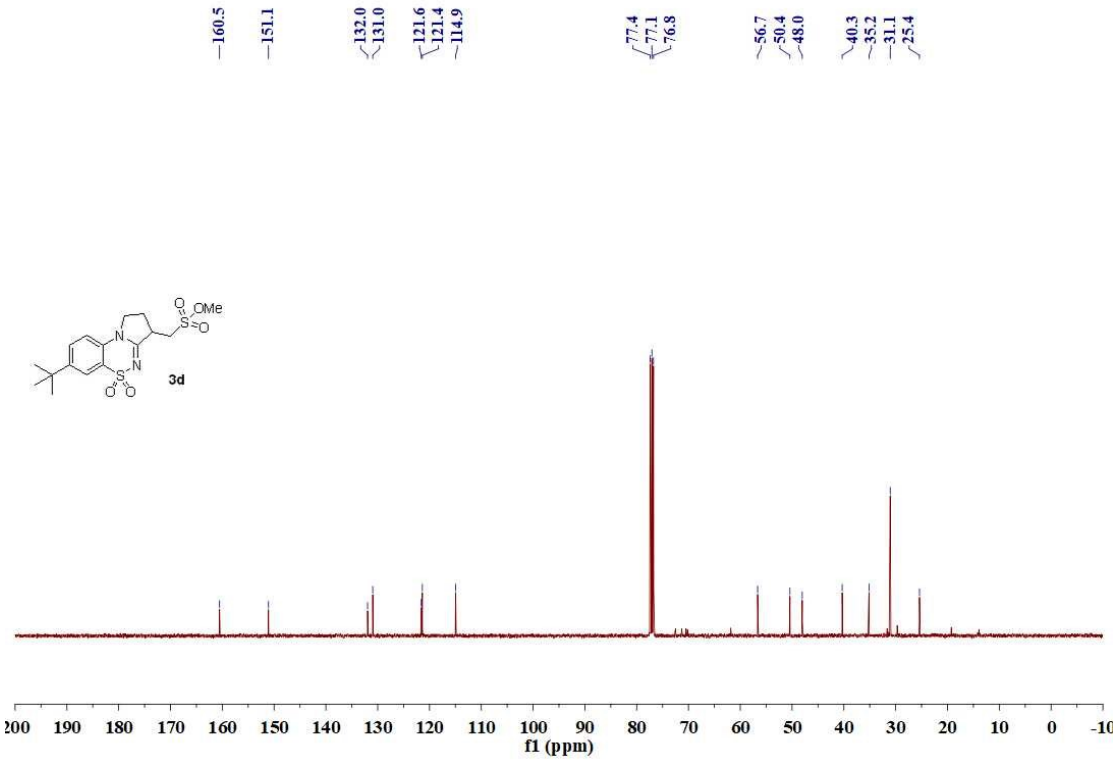

0.99
1.00
1.10
1.06
1.15
3.04
0.93
1.24
1.04
1.16
1.27
1.24
6.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

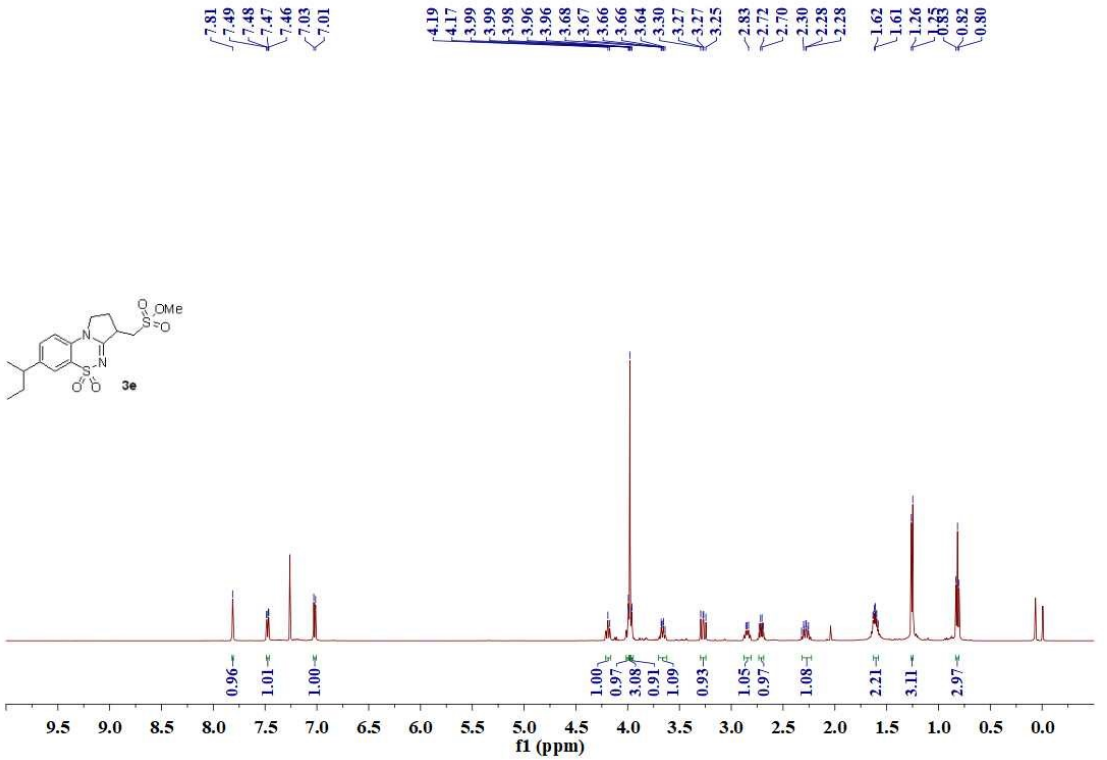

160.5
148.6
132.2
131.9
122.5
121.9
115.2
77.4
77.1
76.7
56.6
50.4
48.1
40.4
33.9
25.4
23.7

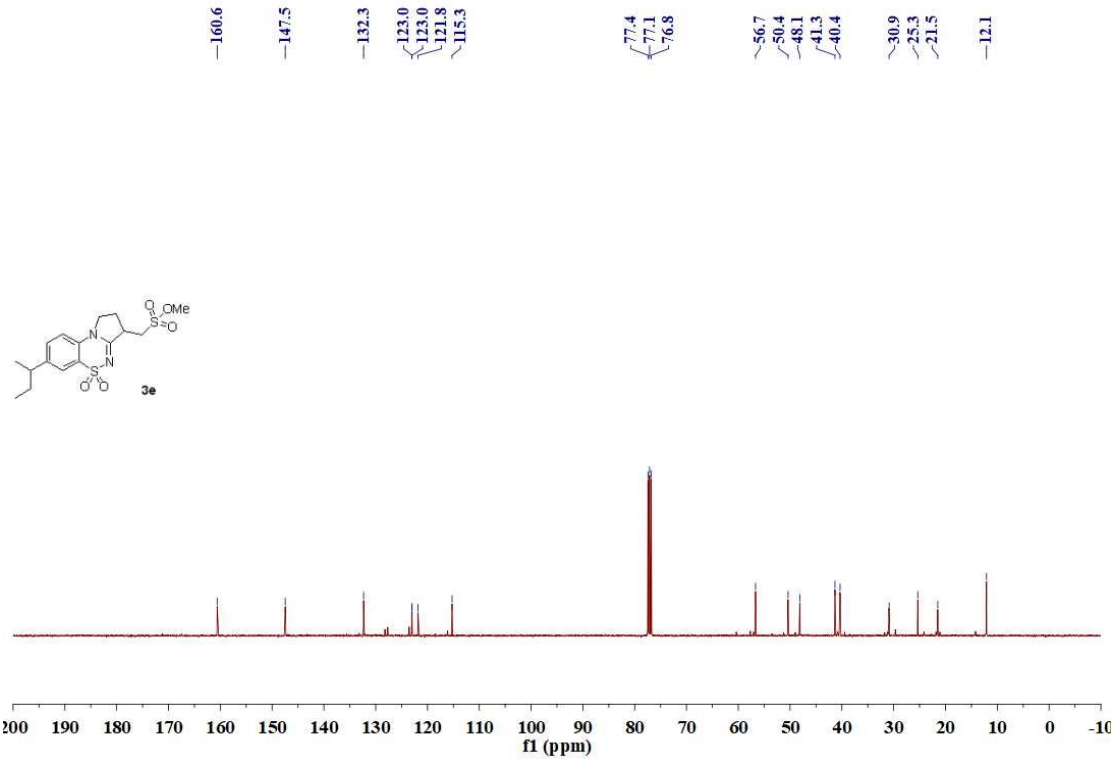

OMe
3c

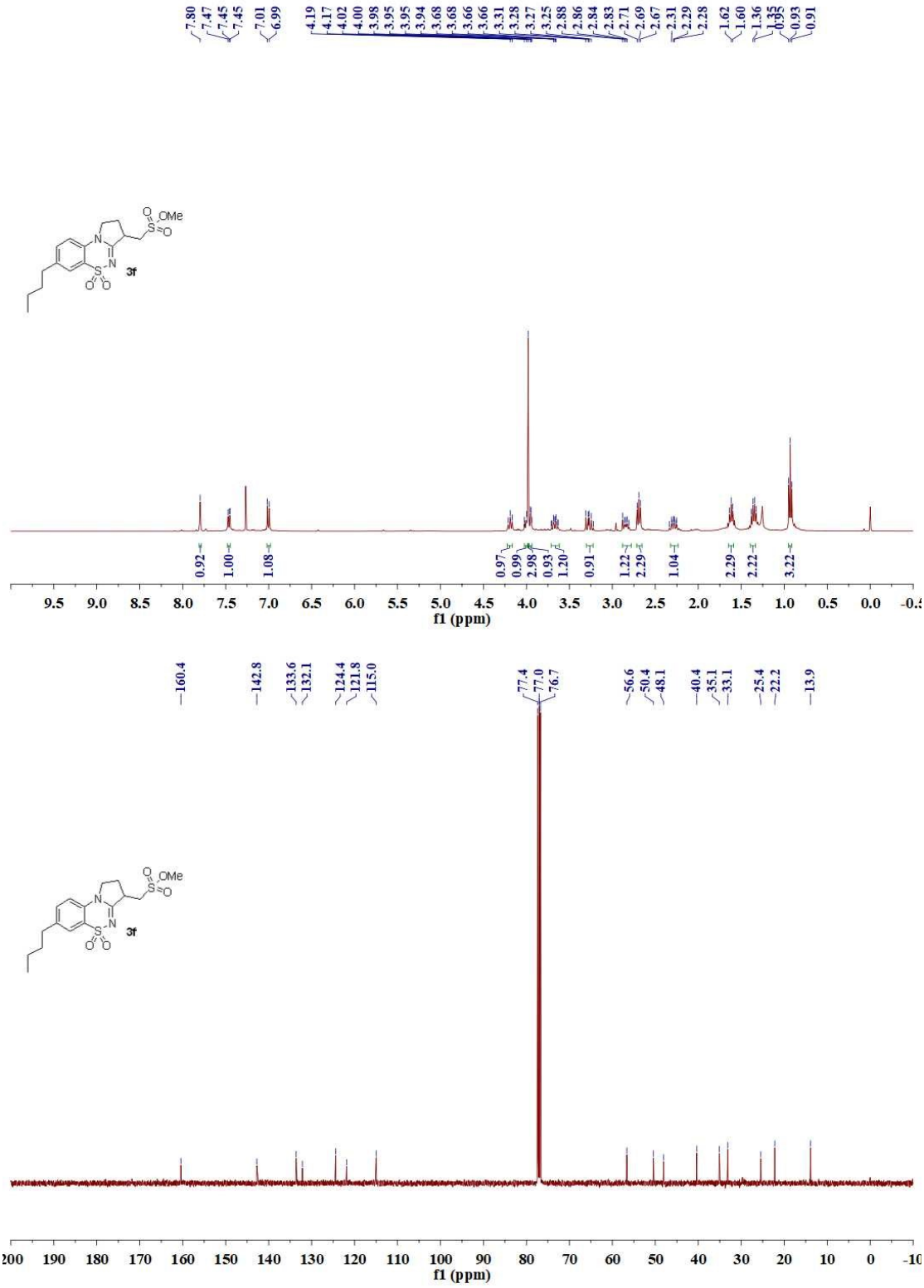

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

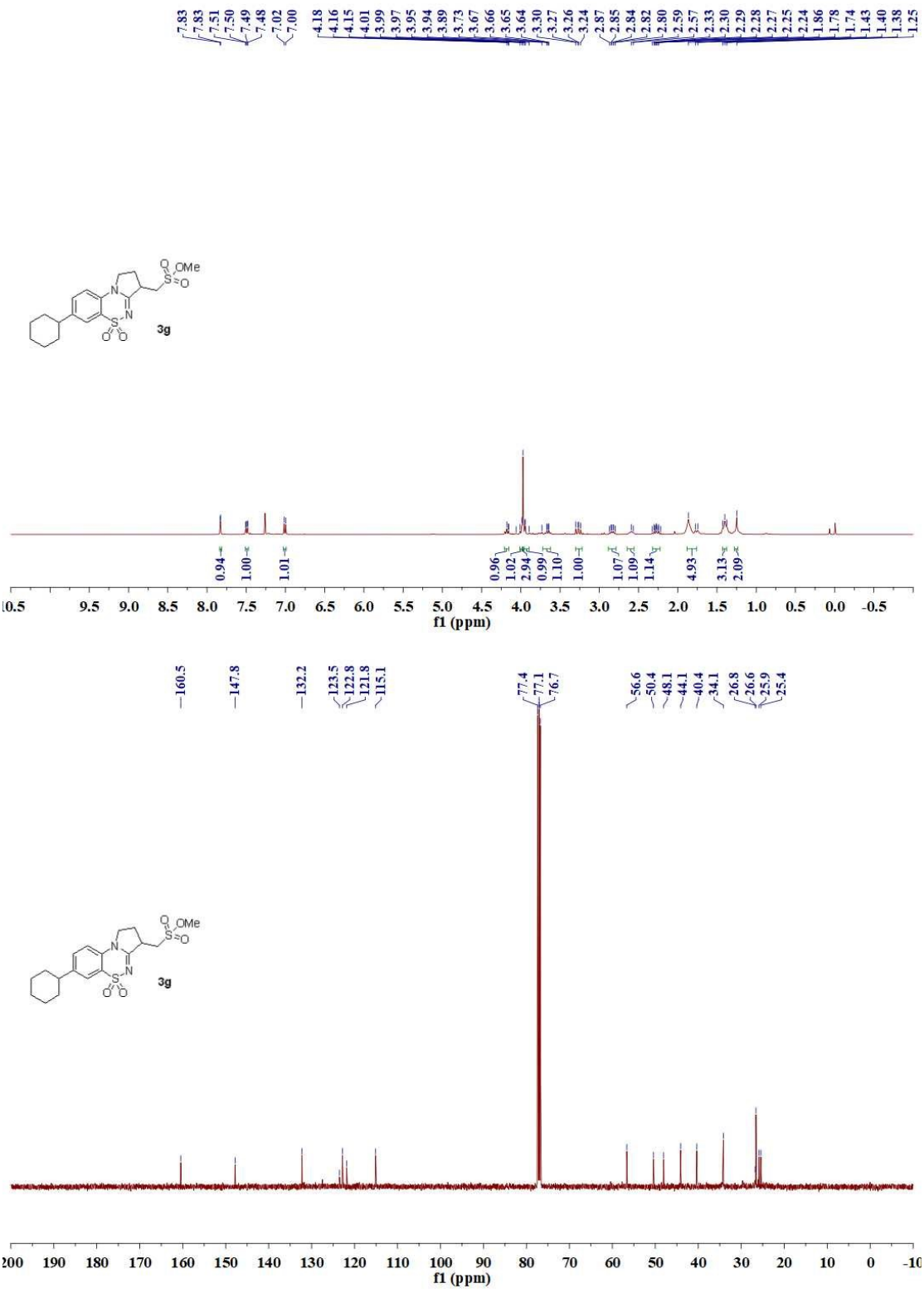

7.97
7.96
7.69
7.69
7.67
7.67
7.04
7.02
4.18
4.16
4.11
4.10
4.02
3.99
3.97
3.96
3.94
3.93
3.67
3.67
3.65
3.65
3.31
3.29
3.28
3.25
2.84
2.82
2.81
2.31
2.28
2.27
2.26
2.25
1.34
OMe
3d
1.01
1.01
1.10
1.09
0.93
3.12
1.03
1.10
1.14
1.14
0.91
9.14
f1 (ppm)


160.5
151.1
132.0
131.0
121.6
121.4
114.9
77.4
77.1
76.8
56.7
50.4
48.0
40.3
35.2
31.1
25.4
OMe
3d
f1 (ppm)


7.81
7.49
7.48
7.47
7.46
7.03
7.01
4.19
4.17
3.99
3.98
3.96
3.68
3.67
3.66
3.64
3.30
3.27
3.25
2.83
2.72
2.70
2.30
2.28
2.28
1.62
1.61
1.26
1.25
0.83
0.82
0.80
OMe
3e
0.96
1.01
1.00
1.00
0.97
3.08
0.91
1.09
0.93
1.05
0.97
1.08
2.21
3.11
2.97
f1 (ppm)


160.6
147.5
132.3
123.0
123.0
121.8
115.3
77.4
77.1
76.8
56.7
50.4
48.1
41.3
40.4
30.9
25.3
21.5
12.1
OMe
3e
f1 (ppm)


7.80
7.47
7.45
7.45
7.01
6.99
4.19
4.17
4.02
4.00
3.98
3.95
3.95
3.94
3.68
3.68
3.66
3.66
3.31
3.28
3.27
3.25
2.88
2.86
2.84
2.83
2.71
2.69
2.67
2.31
2.29
2.28
1.62
1.60
1.36
1.35
0.95
0.93
0.91
OMe
3f
0.92
1.00
1.08
0.97
0.99
2.98
0.93
1.20
0.91
1.22
2.29
1.04
2.29
2.22
3.22
f1 (ppm)
160.4
142.8
133.6
132.1
124.4
121.8
115.0
77.4
77.0
76.7
56.6
50.4
48.1
40.4
35.1
33.1
25.4
22.2
13.9
OMe
3f
f1 (ppm)


7.83
7.83
7.51
7.50
7.49
7.48
7.02
7.00
4.18
4.16
4.15
4.01
3.99
3.97
3.95
3.94
3.89
3.73
3.67
3.66
3.65
3.64
3.30
3.27
3.26
3.24
2.87
2.85
2.84
2.82
2.80
2.59
2.57
2.33
2.30
2.29
2.28
2.27
2.25
2.24
1.86
1.78
1.74
1.43
1.40
1.38
1.25
OMe
3g
0.94
1.00
1.01
0.96
1.02
2.94
0.99
1.10
1.00
1.07
1.09
1.14
4.93
3.13
2.09
f1 (ppm)
160.5
147.8
132.2
123.5
122.8
121.8
115.1
77.4
77.1
76.7
56.6
50.4
48.1
44.1
40.4
34.1
26.8
26.6
25.9
25.4
OMe
3g
f1 (ppm)


7.89
7.89
7.87
7.87
7.65
7.65
7.63
7.61
7.61
7.45
7.45
7.43
7.41
7.08
7.06
4.20
4.19
4.17
4.17
4.15
4.15
4.03
4.01
4.00
4.00
3.99
3.99
3.98
3.97
3.96
3.95
3.94
3.93
3.92
3.91
3.90
3.90
3.87
3.87
3.83
3.67
3.66
3.65
3.64
3.64
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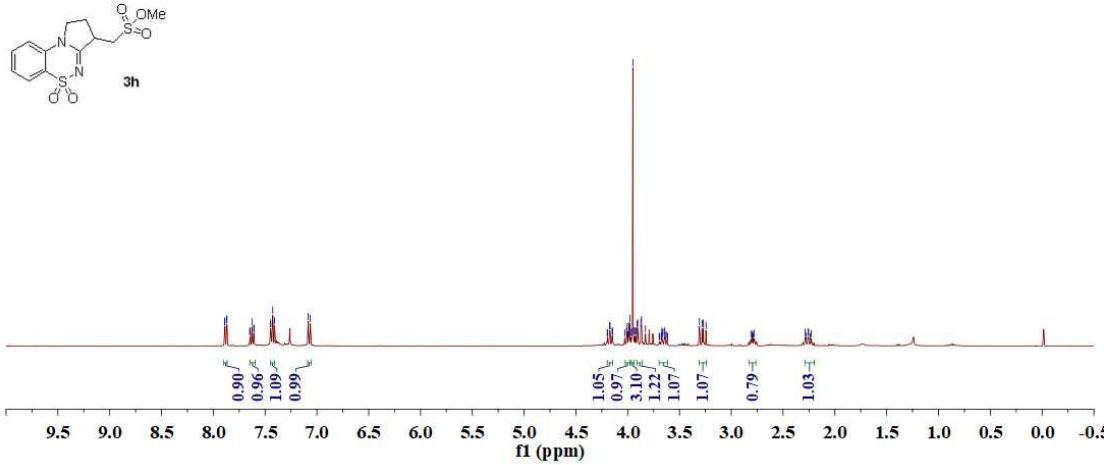
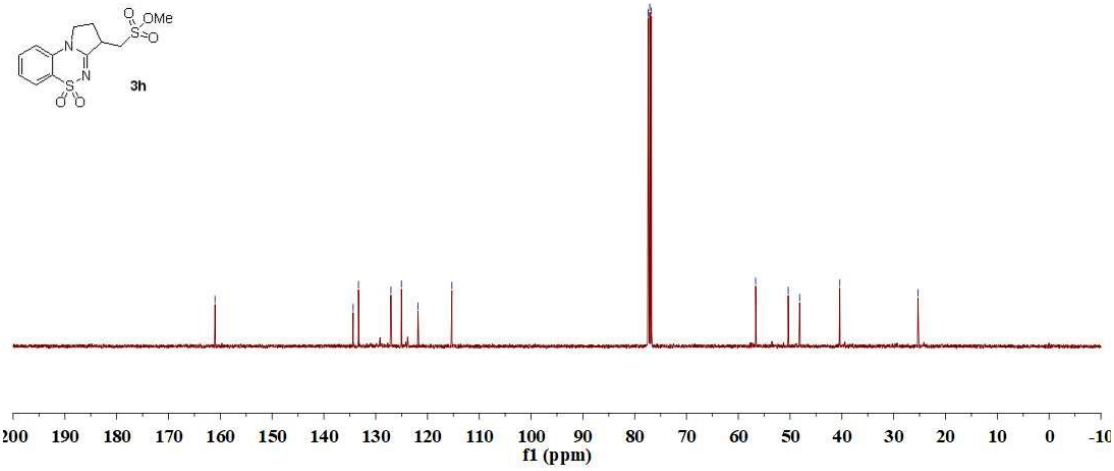
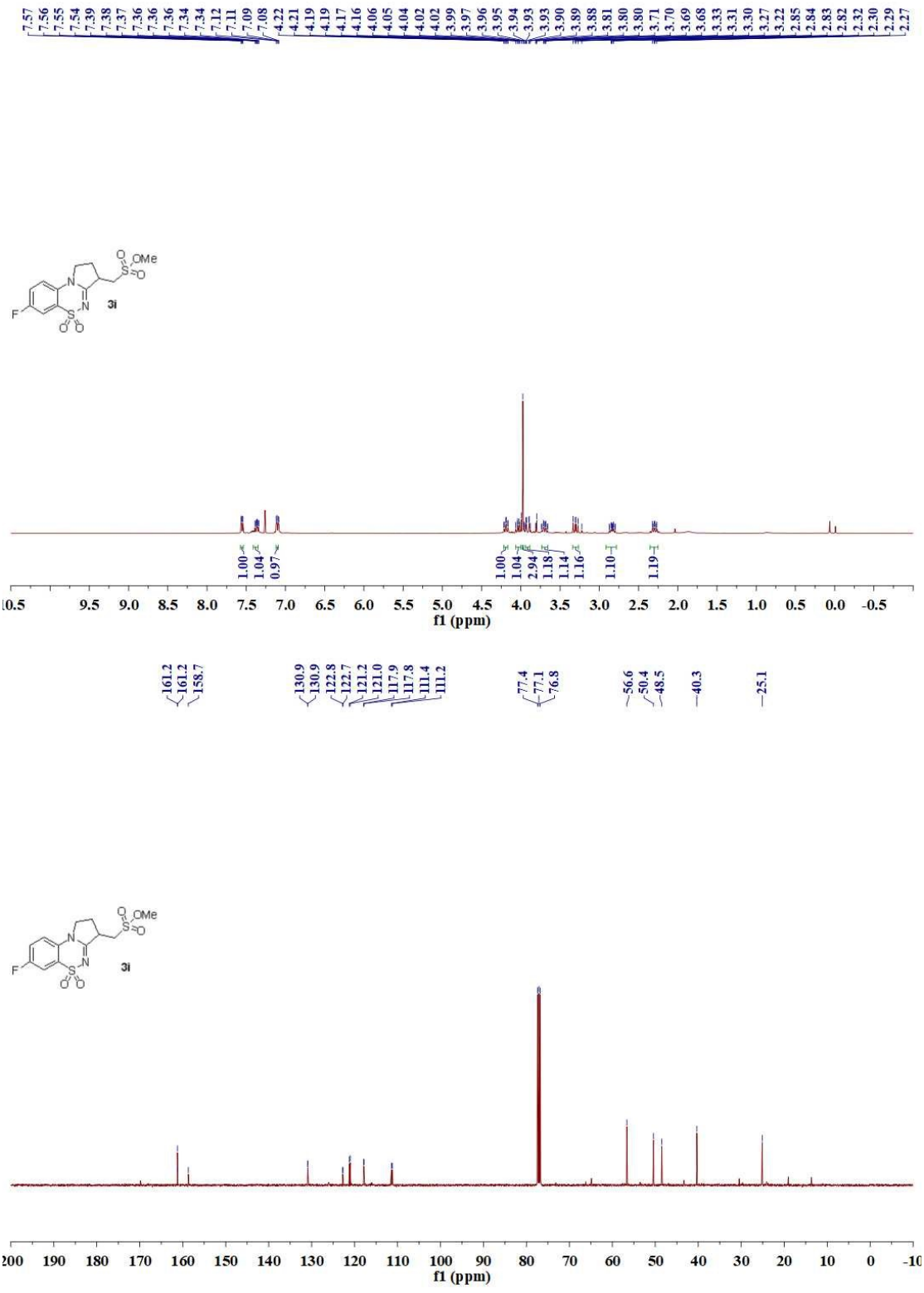
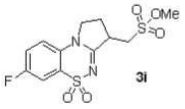
2.79
2.78
2.29
2.26
2.25
2.23


OMe
3h
0.90
0.96
1.09
0.99
1.05
0.97
3.10
1.22
1.07
1.07
0.79
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.0
134.3
133.3
127.1
125.0
121.8
115.3
77.4
77.1
76.8
56.7
50.4
48.2
40.4
25.3


OMe
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

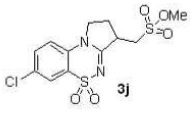

7.57 7.56 7.55 7.54 7.39 7.38 7.37 7.36 7.36 7.36 7.34 7.34 7.12 7.11 7.09 7.08 4.22 4.21 4.19 4.19 4.17 4.16 4.06 4.05 4.04 4.02 4.02 3.99 3.97 3.96 3.95 3.94 3.93 3.93 3.90 3.89 3.88 3.81 3.80 3.80 3.71 3.70 3.69 3.68 3.33 3.31 3.30 3.27 3.22 2.85 2.84 2.83 2.82 2.32 2.30 2.29 2.27
OMe
F
3i
1.00 1.04 0.97 1.00 1.04 2.94 1.18 1.14 1.16 1.10 1.19
f1 (ppm)
161.2 161.2 158.7 130.9 130.9 122.8 122.7 121.2 121.0 117.9 117.8 111.4 111.2 77.4 77.1 76.8 56.6 50.4 48.5 40.3 25.1
OMe
F
3i
f1 (ppm)



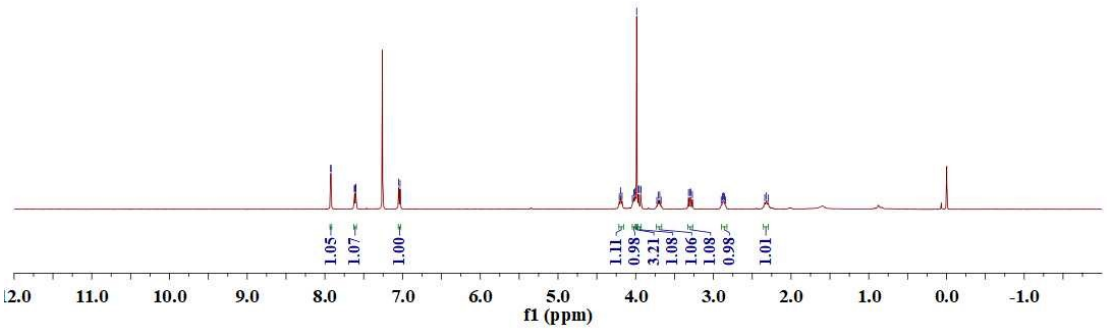
3i

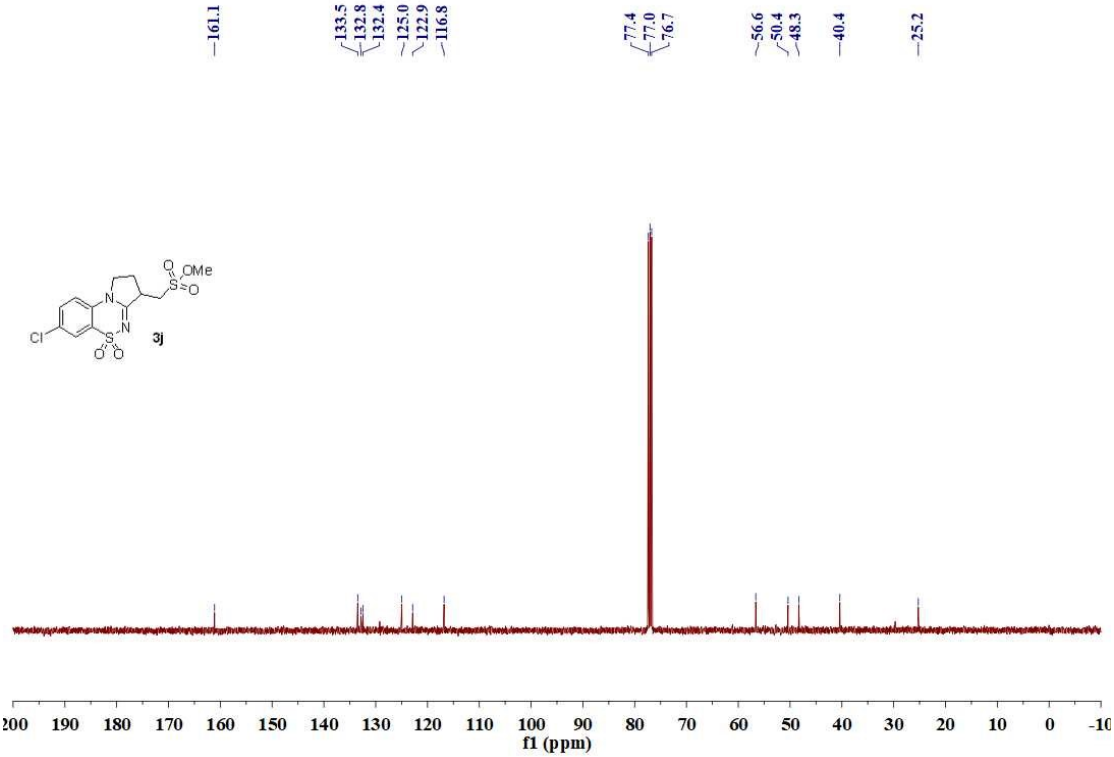
-110.98
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

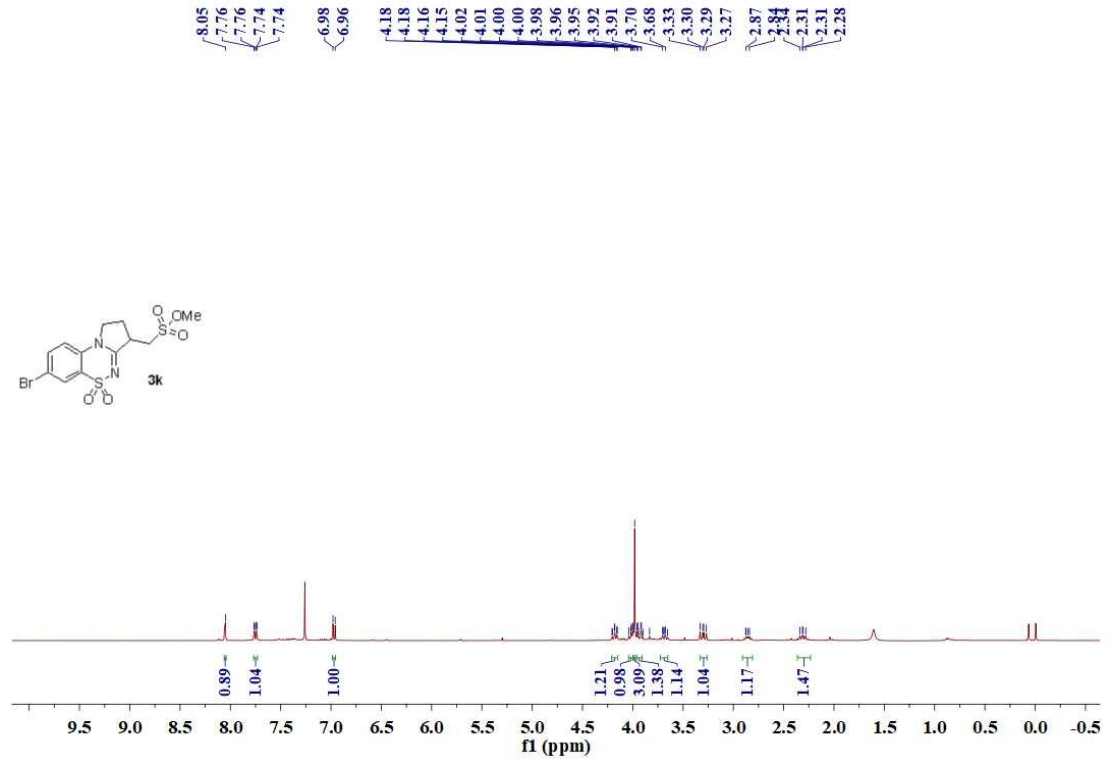

7.93
7.92
7.62
7.62
7.60
7.60
7.05
7.03
4.19
4.17
4.02
4.01
3.99
3.96
3.96
3.94
3.93
3.71
3.69
3.32
3.30
3.29
3.27
2.87
2.32
2.29

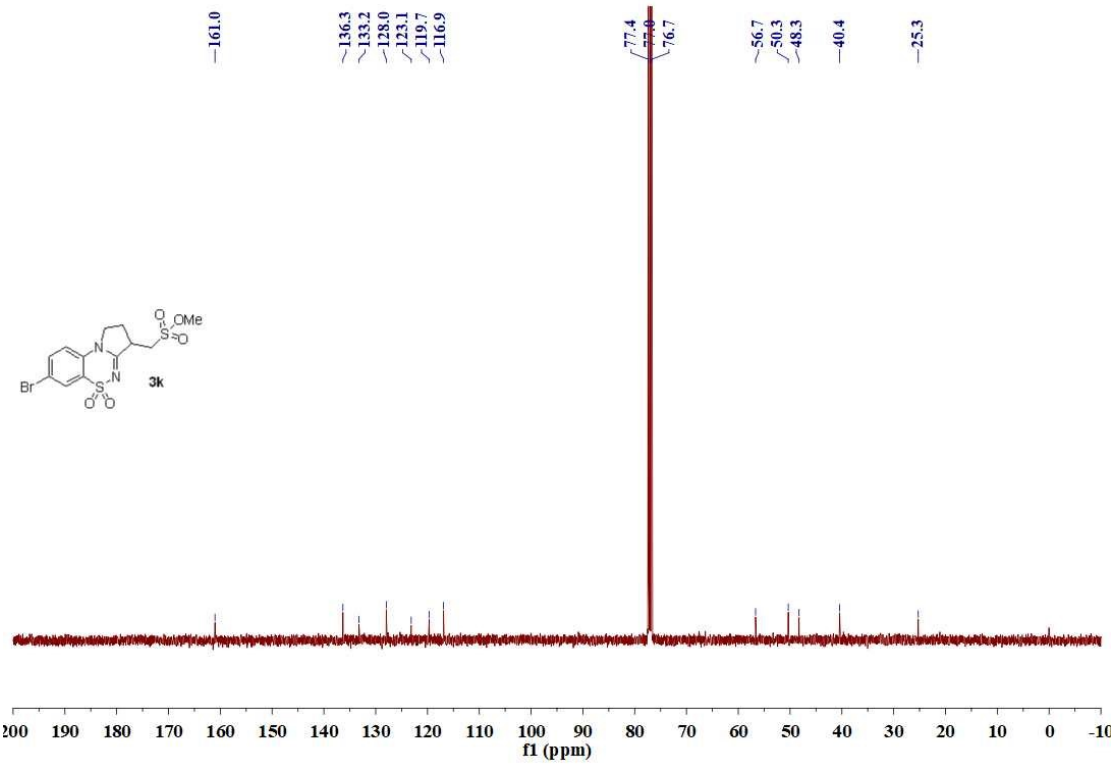


3j


1.05
1.07
1.00
1.11
0.98
3.21
1.08
1.06
1.08
0.98
1.01
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


161.1
133.5
132.8
132.4
125.0
122.9
116.8
77.4
77.0
76.7
56.6
50.4
48.3
40.4
25.2
OMe
Cl
3j
f1 (ppm)


8.05
7.76
7.76
7.74
7.74
6.98
6.96
4.18
4.18
4.16
4.15
4.02
4.01
4.00
4.00
3.98
3.96
3.95
3.92
3.91
3.70
3.68
3.33
3.30
3.29
3.27
2.87
2.31
2.31
2.28
OMe
Br
3k
0.89
1.04
1.00
1.21
0.98
3.09
1.38
1.14
1.04
1.17
1.47
f1 (ppm)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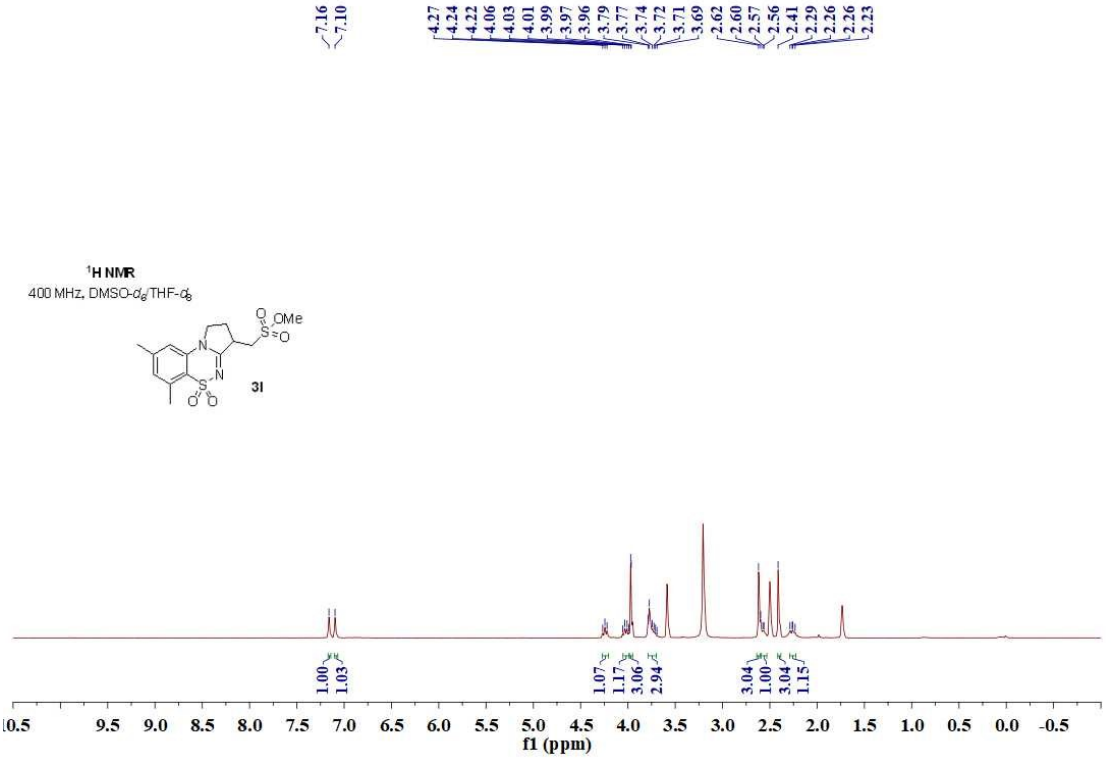
133.2
128.0
123.1
119.7
116.9
77.4
77.0
76.7
56.7
50.3
48.3
40.4
25.3
OMe
Br
3k
f1 (ppm)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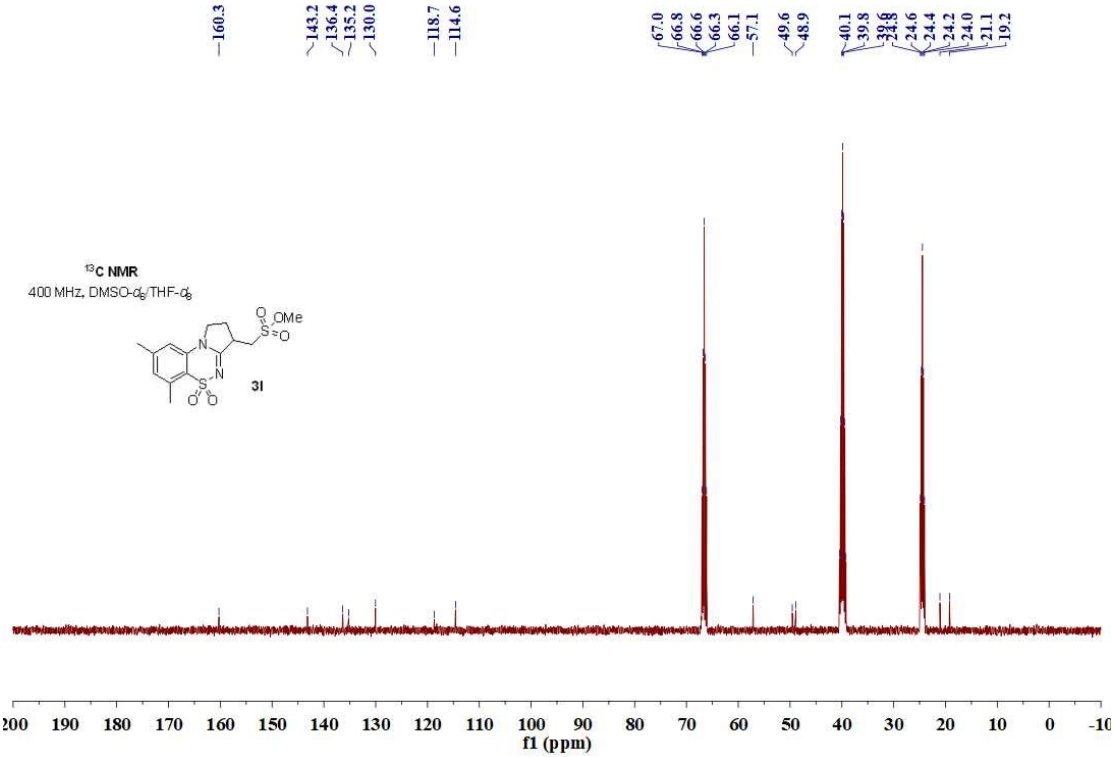
7.10
4.27
4.24
4.22
4.06
4.03
4.01
3.99
3.97
3.96
3.79
3.77
3.74
3.72
3.71
3.69
2.62
2.60
2.57
2.56
2.41
2.29
2.26
2.26
2.23
1H NMR
400 MHz, DMSO-d6/THF-d8
OMe
3l
1.00
1.03
1.07
1.17
3.06
2.94
3.04
1.00
3.04
1.15
f1 (ppm)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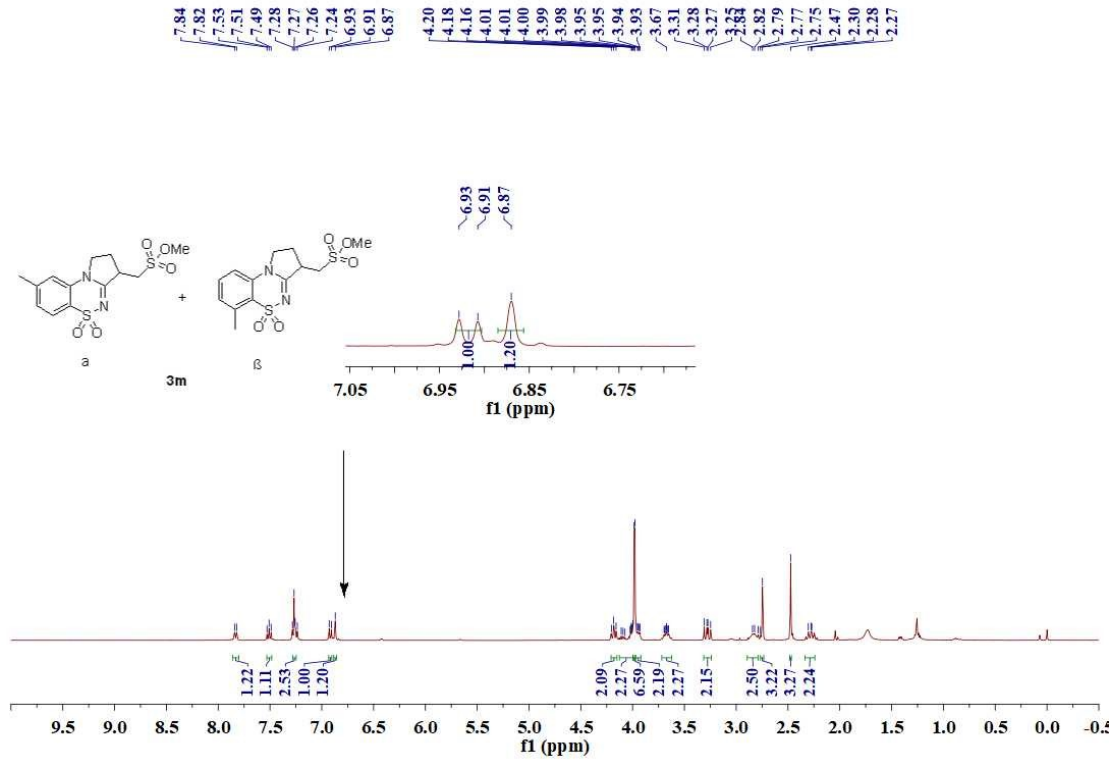
143.2
136.4
135.2
130.0
118.7
114.6
67.0
66.8
66.6
66.3
66.1
57.1
49.6
48.9
40.1
39.8
24.6
24.4
24.2
24.0
21.1
19.2
13C NMR
400 MHz, DMSO-d6/THF-d8
OMe
3l
f1 (ppm)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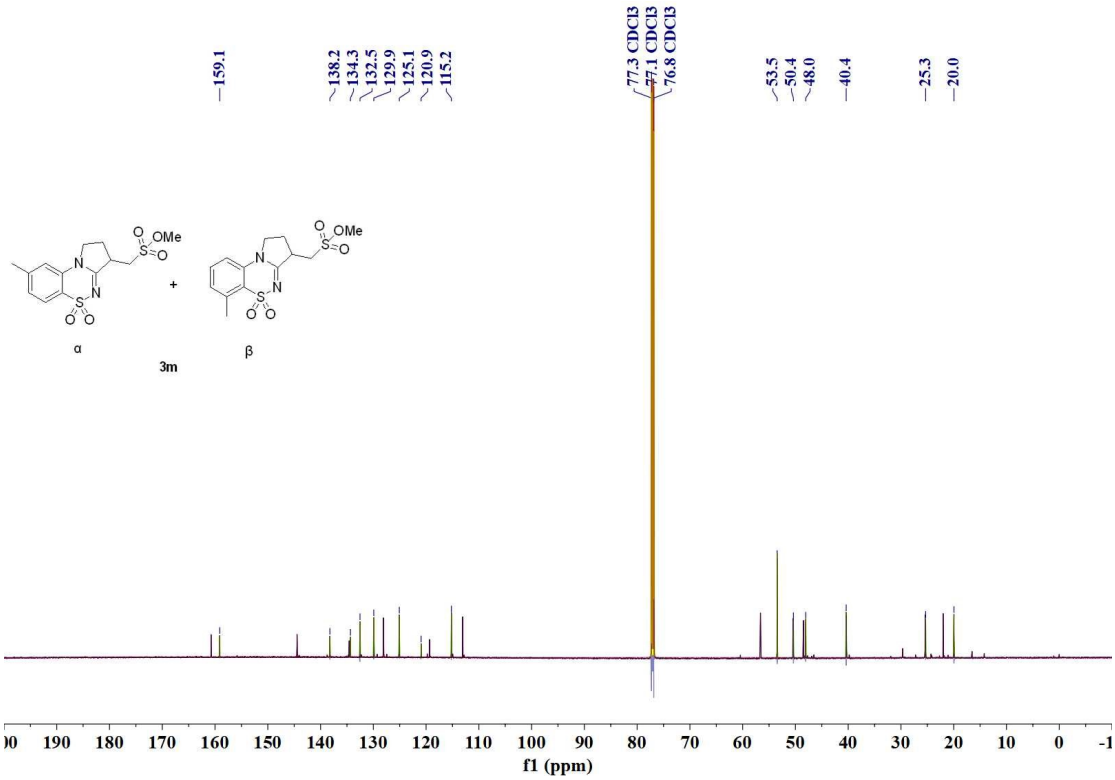
7.82
7.53
7.51
7.49
7.28
7.27
7.26
7.24
6.93
6.91
6.87
4.20
4.18
4.16
4.01
4.01
4.00
3.99
3.98
3.95
3.95
3.94
3.93
3.67
3.31
3.28
3.27
2.82
2.79
2.77
2.75
2.47
2.30
2.28
2.27
OMe
a
ß
3m
6.93
6.91
6.87
1.00
1.20
7.05
6.95
6.85
6.75
f1 (ppm)
1.22
1.11
2.53
1.00
1.20
2.09
2.27
6.59
2.19
2.27
2.15
2.50
3.22
3.27
2.24
f1 (ppm)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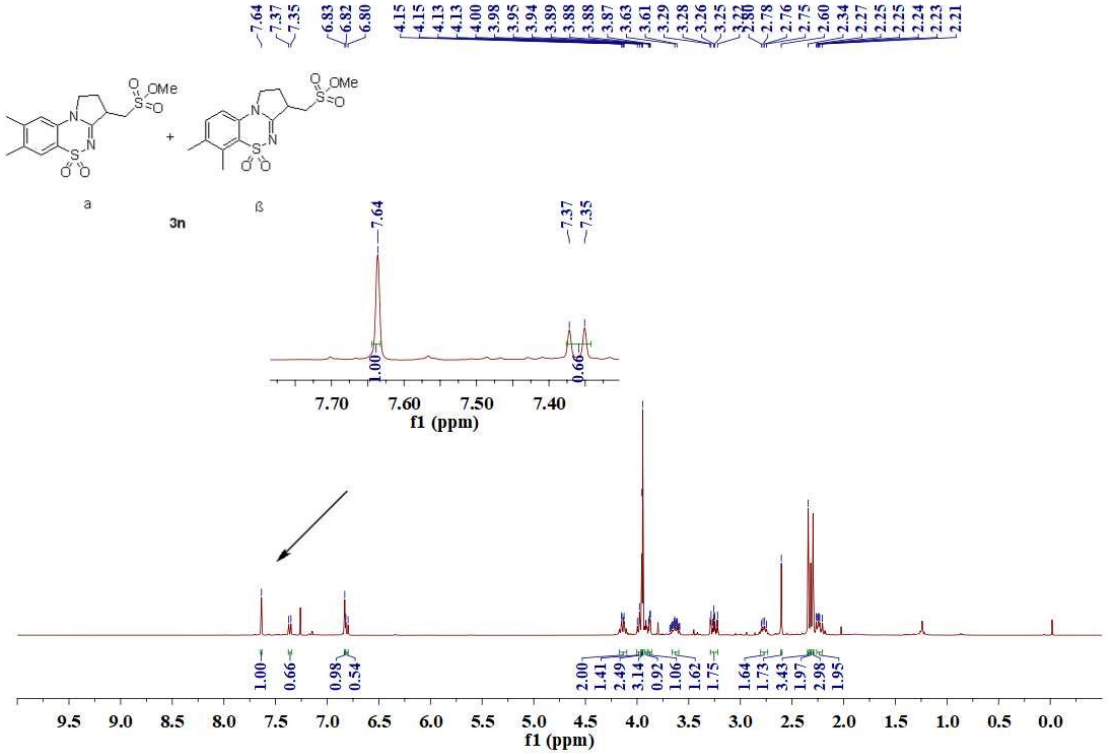
138.2
134.3
132.5
129.9
125.1
120.9
115.2
77.3 CDCl3
77.1 CDCl3
76.8 CDCl3
53.5
50.4
48.0
40.4
25.3
20.0
α
β
3m
f1 (ppm)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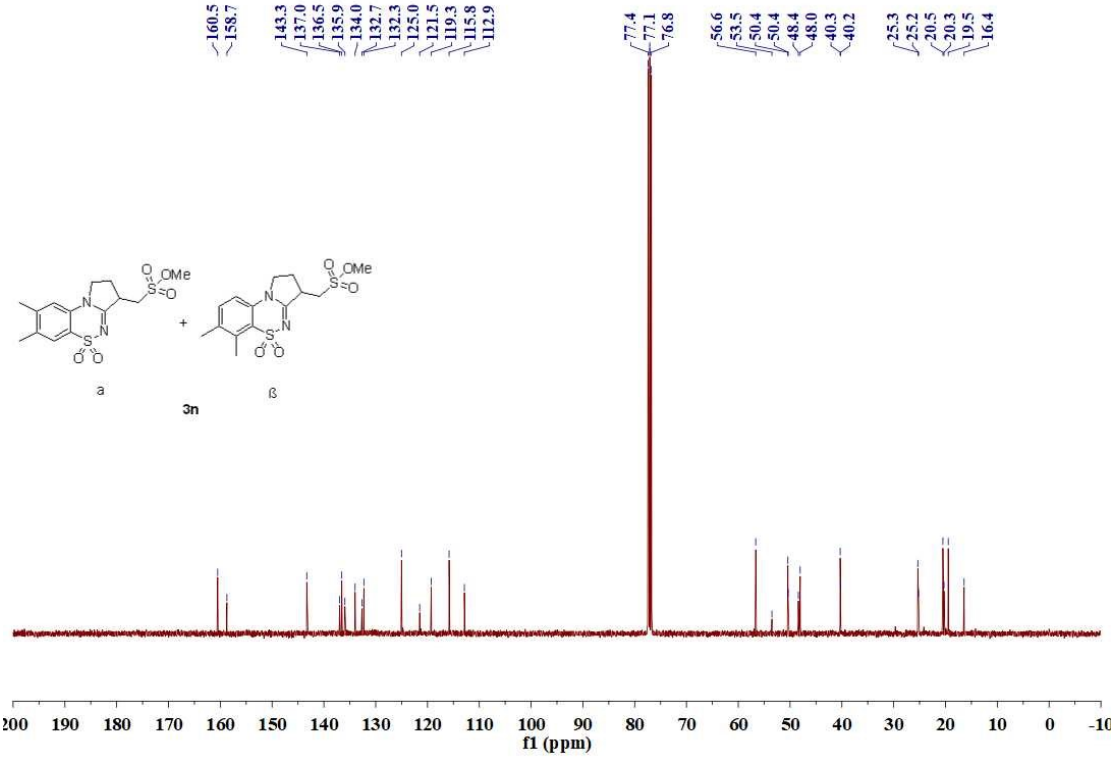
7.37
7.35
6.83
6.82
6.80
a
ß
3n
1.00
0.66
0.98
0.54
2.00
1.41
2.49
3.14
0.92
1.06
1.62
1.75
1.64
1.73
3.43
1.97
2.98
1.95
f1 (ppm)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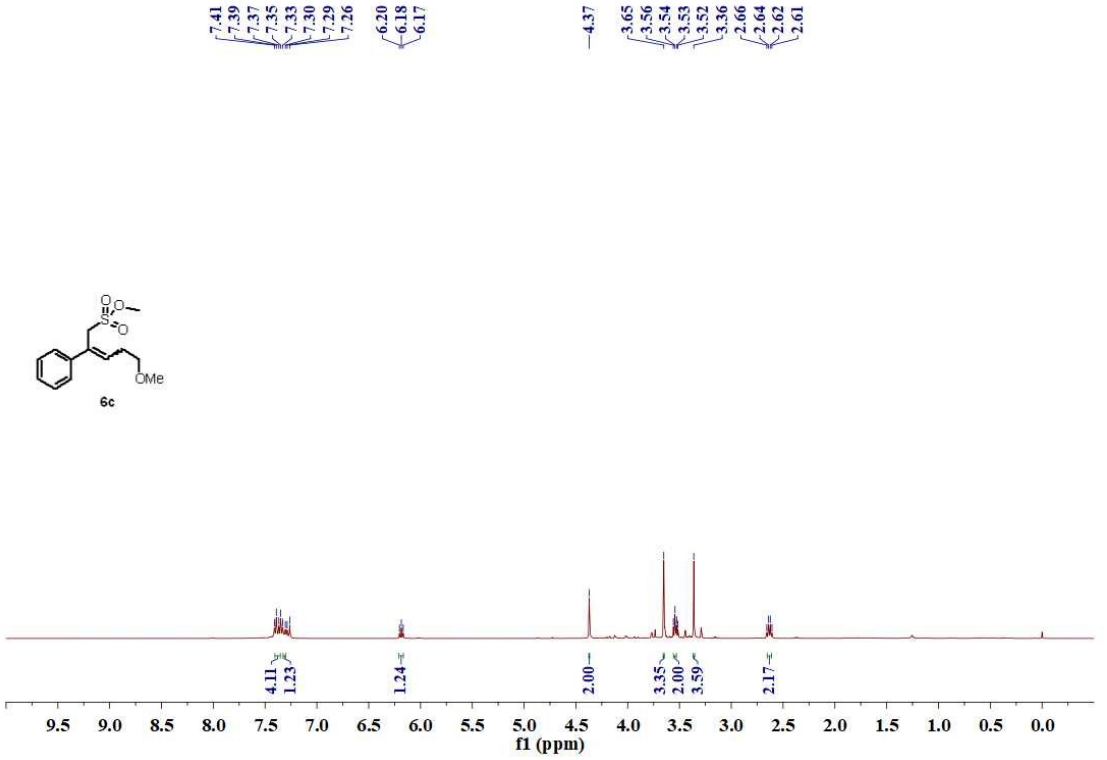
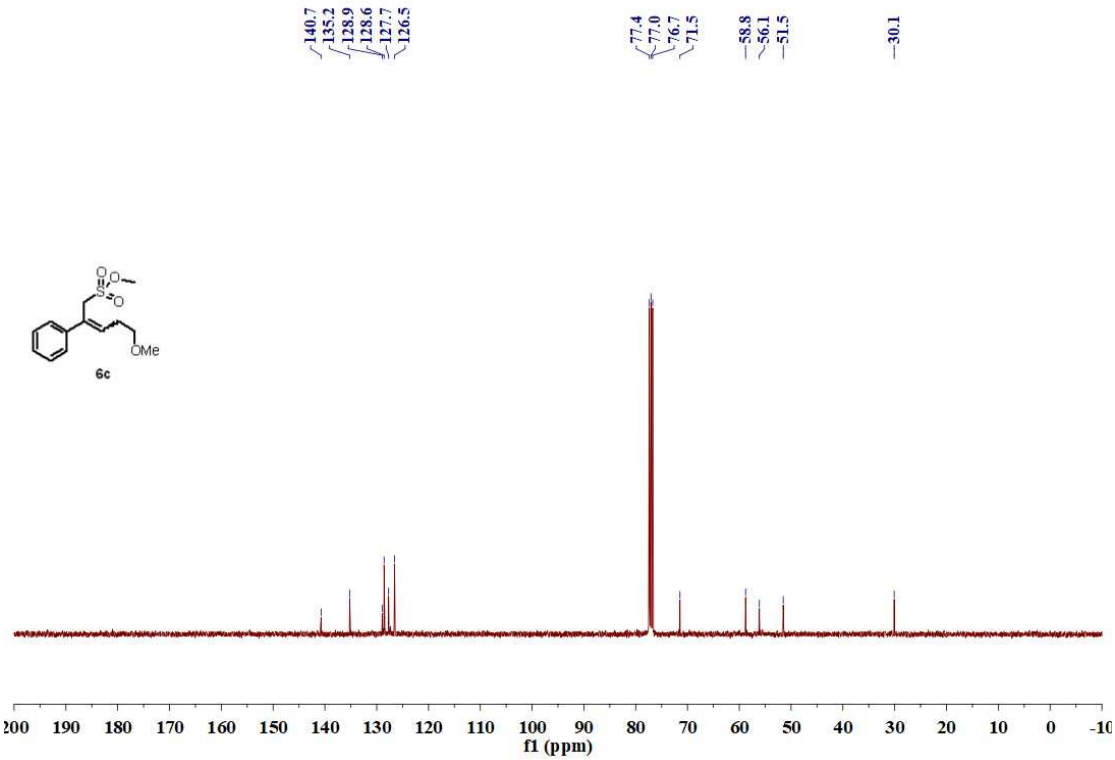
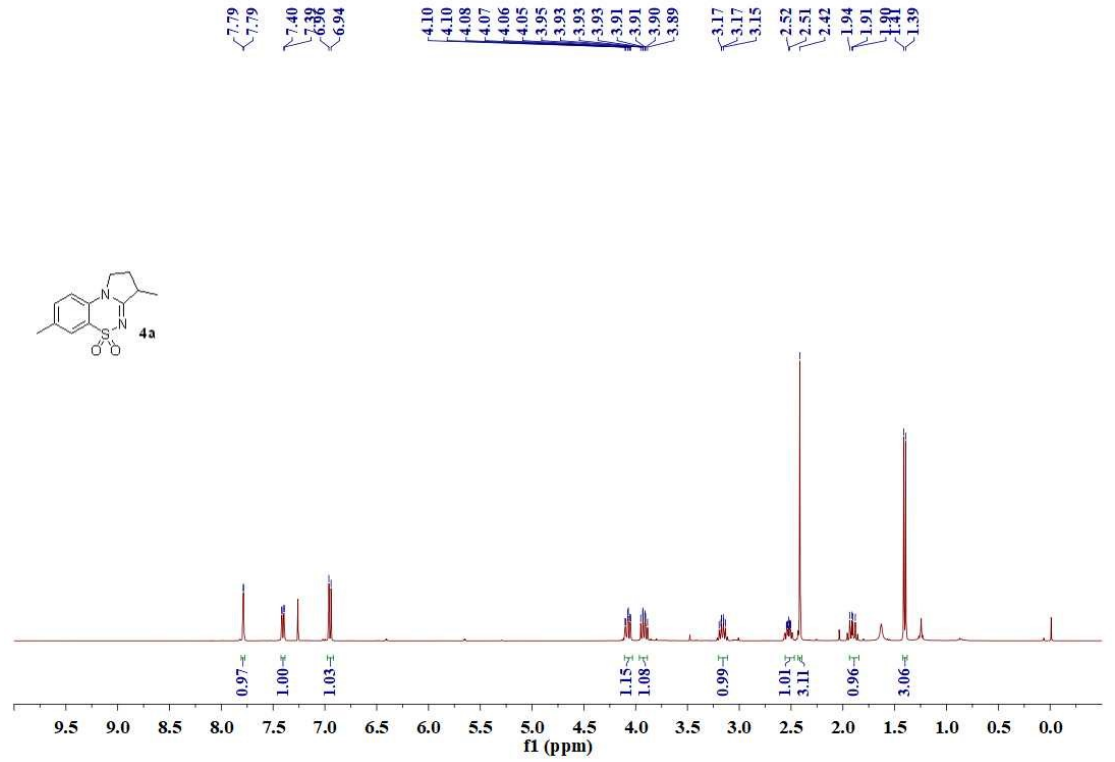
158.7
143.3
137.0
136.5
135.9
134.0
132.7
132.3
125.0
121.5
119.3
115.8
112.9
77.4
77.1
76.8
56.6
53.5
50.4
50.4
48.4
48.0
40.3
40.2
25.3
25.2
20.5
20.3
19.5
16.4
OMe
a
ß
3n
f1 (ppm)


7.41
7.39
7.37
7.35
7.33
7.30
7.29
7.26
6.20
6.18
6.17
4.37
3.65
3.56
3.54
3.53
3.52
3.36
2.66
2.64
2.62
2.61
OMe
6c
4.11
1.23
1.24
2.00
3.35
2.00
3.59
2.17
f1 (ppm)


140.7
135.2
128.9
128.6
127.7
126.5
77.4
77.0
76.7
71.5
58.8
56.1
51.5
30.1
OMe
6c
f1 (ppm)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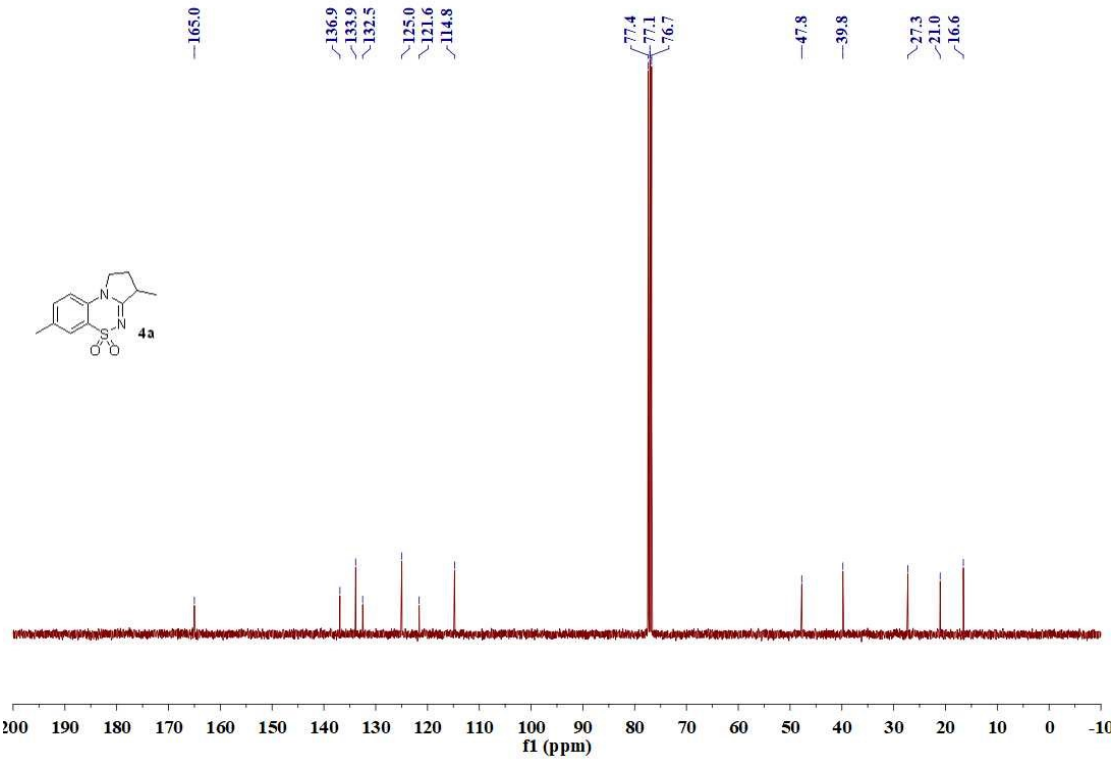
7.79
7.40
7.39
6.96
6.94
4.10
4.10
4.08
4.07
4.06
4.05
3.95
3.93
3.93
3.93
3.91
3.91
3.90
3.89
3.17
3.17
3.15
2.52
2.51
2.42
1.94
1.91
1.90
1.41
1.39
4a
0.97
1.00
1.03
1.15
1.08
0.99
1.01
3.11
0.96
3.06
f1 (ppm)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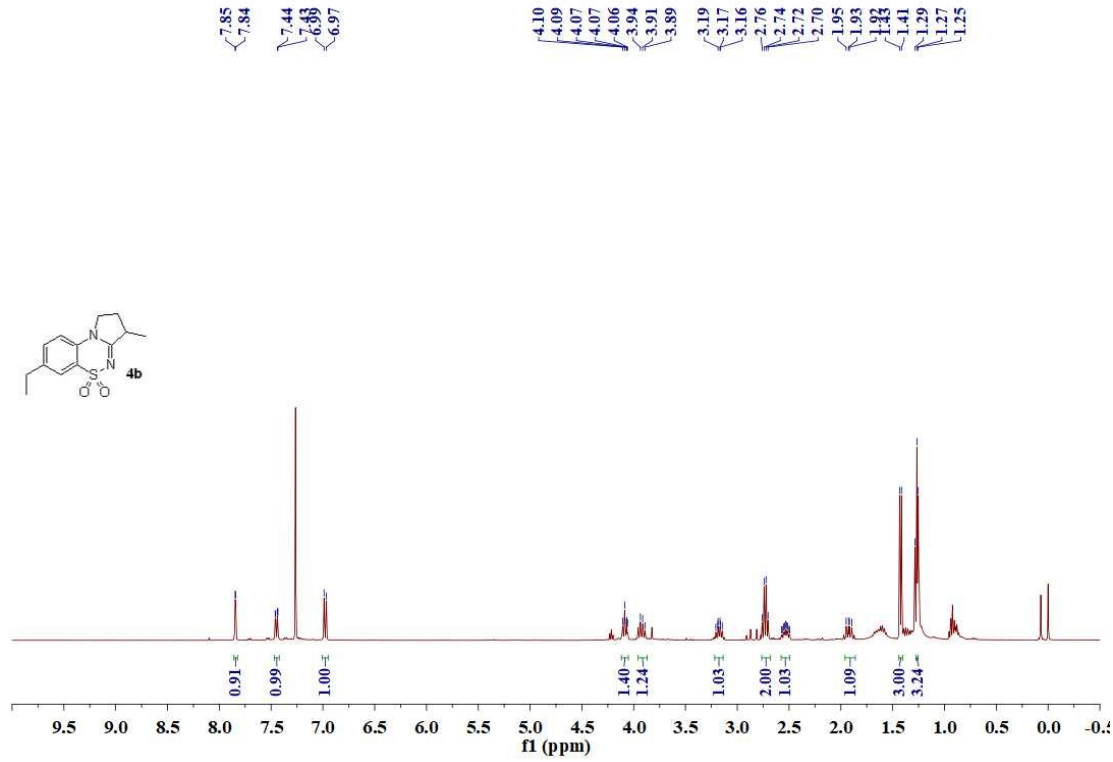
136.9
133.9
132.5
125.0
121.6
114.8
77.4
77.1
76.7
47.8
39.8
27.3
21.0
16.6
4a
f1 (ppm)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7.84
7.44
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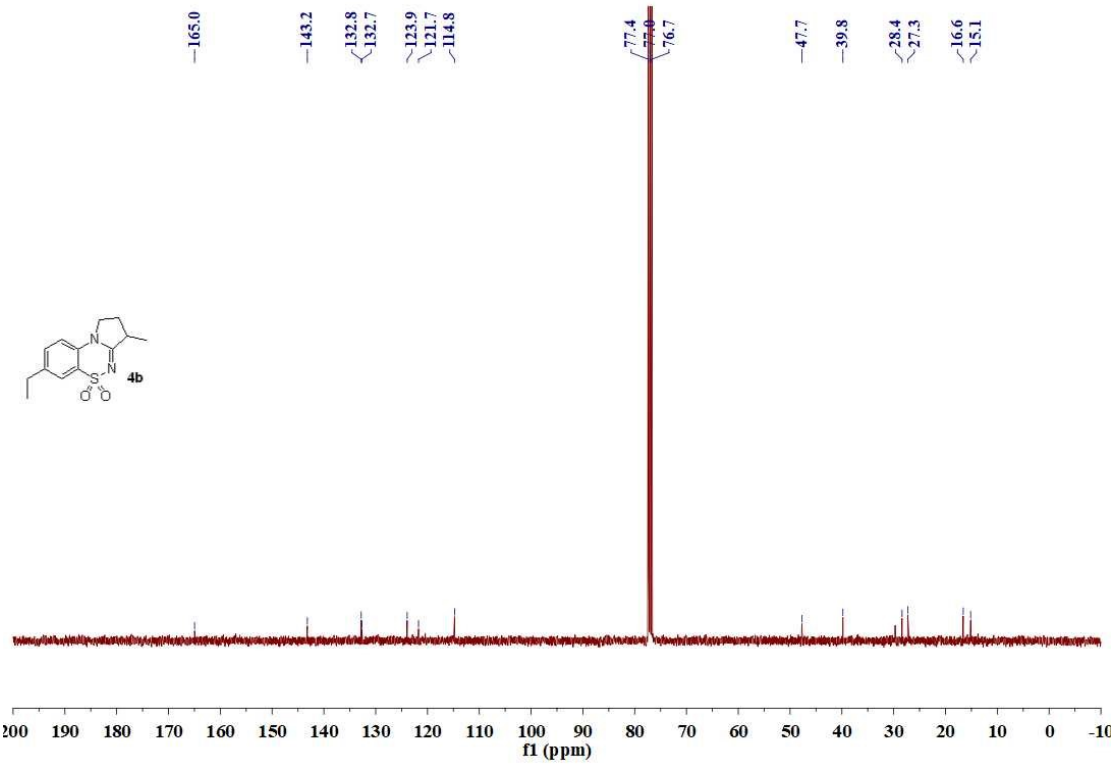
4.09
4.07
4.06
3.94
3.91
3.89
3.19
3.17
3.16
2.76
2.74
2.72
2.70
1.95
1.93
1.41
1.29
1.27
1.25
4b
0.91
0.99
1.00
1.40
1.24
1.03
2.00
1.03
1.09
3.00
3.24
f1 (ppm)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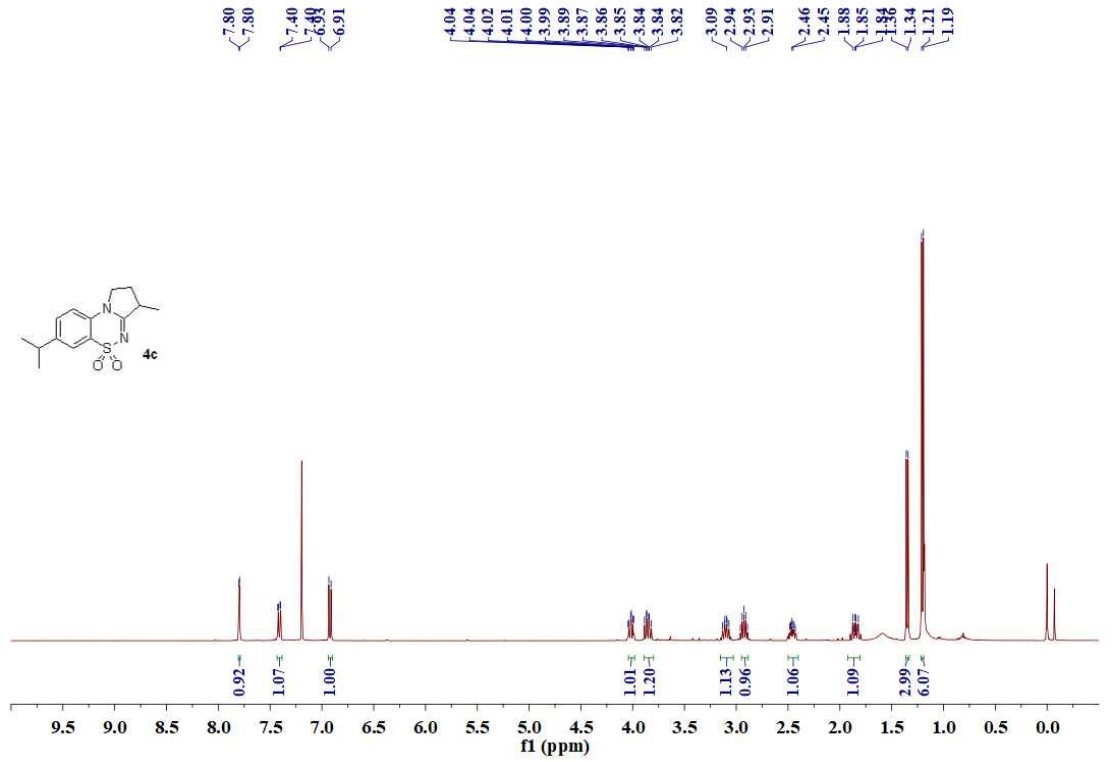
143.2
132.8
132.7
123.9
121.7
114.8
77.4
77.0
76.7
47.7
39.8
28.4
27.3
16.6
15.1
4b
f1 (ppm)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7.80
7.40
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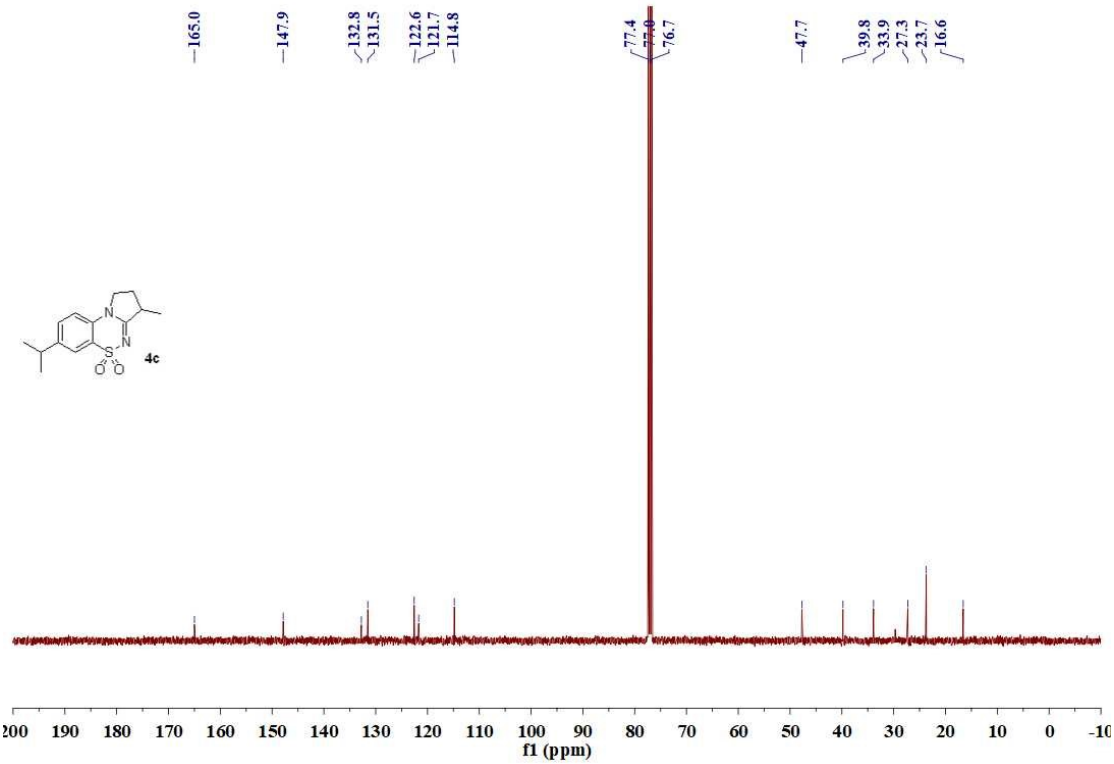
6.91
4.04
4.04
4.02
4.01
4.00
3.99
3.89
3.87
3.86
3.85
3.84
3.84
3.82
3.09
2.94
2.93
2.91
2.46
2.45
1.88
1.85
1.34
1.21
1.19
4c
0.92
1.07
1.00
1.01
1.20
1.13
0.96
1.06
1.09
2.99
6.07
f1 (ppm)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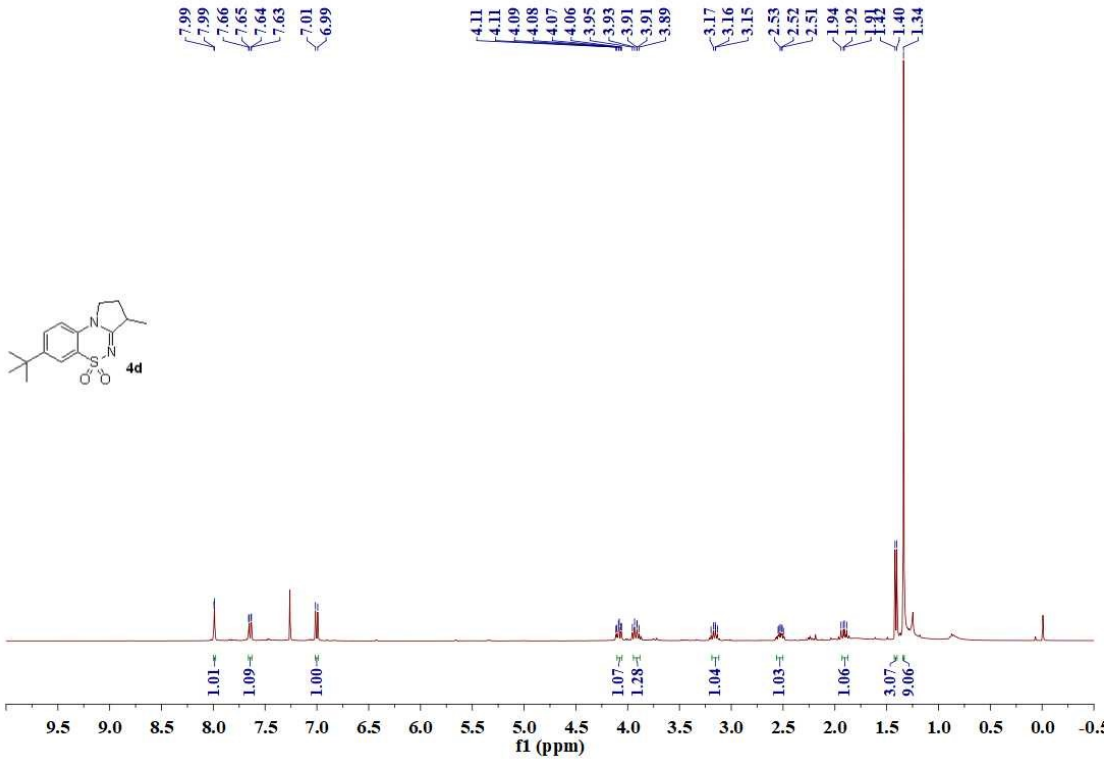
147.9
132.8
131.5
122.6
121.7
114.8
77.4
77.0
76.7
47.7
39.8
33.9
27.3
23.7
16.6
4c
f1 (ppm)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7.65
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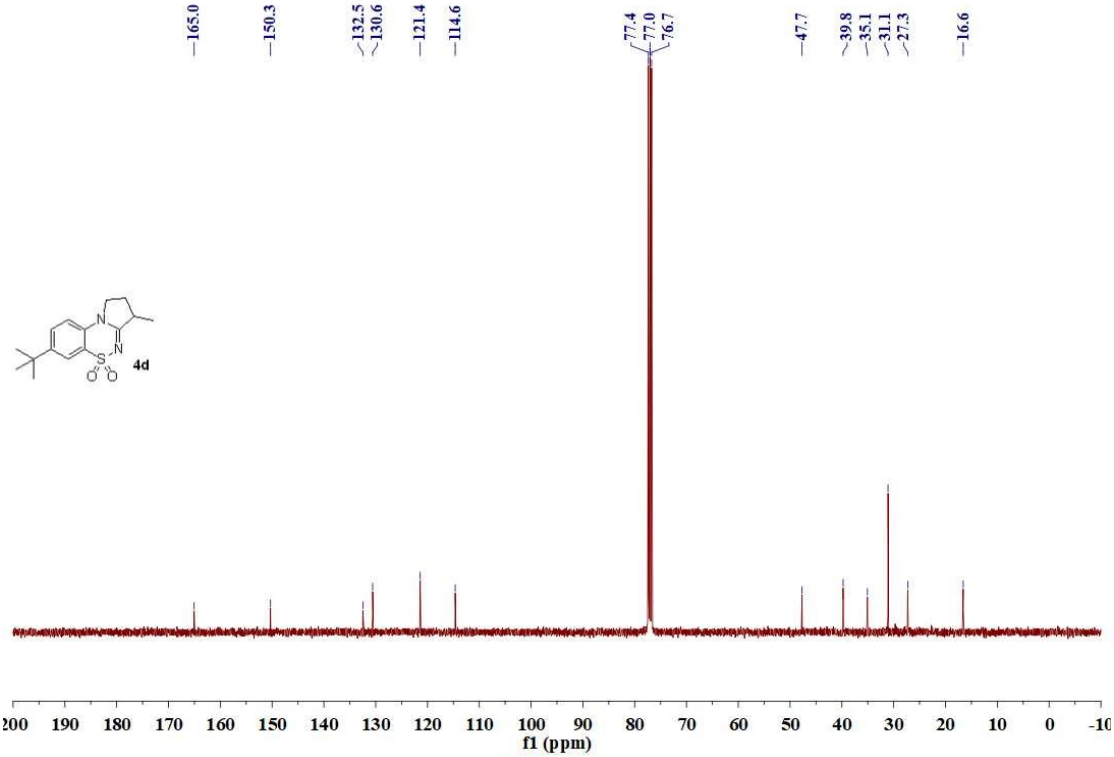
7.63
7.01
6.99
4.11
4.11
4.09
4.08
4.07
4.06
3.95
3.93
3.91
3.91
3.89
3.17
3.16
3.15
2.53
2.52
2.51
1.94
1.92
1.91
1.42
1.40
1.34
4d
1.01
1.09
1.00
1.07
1.28
1.04
1.03
1.06
3.07
9.06
f1 (ppm)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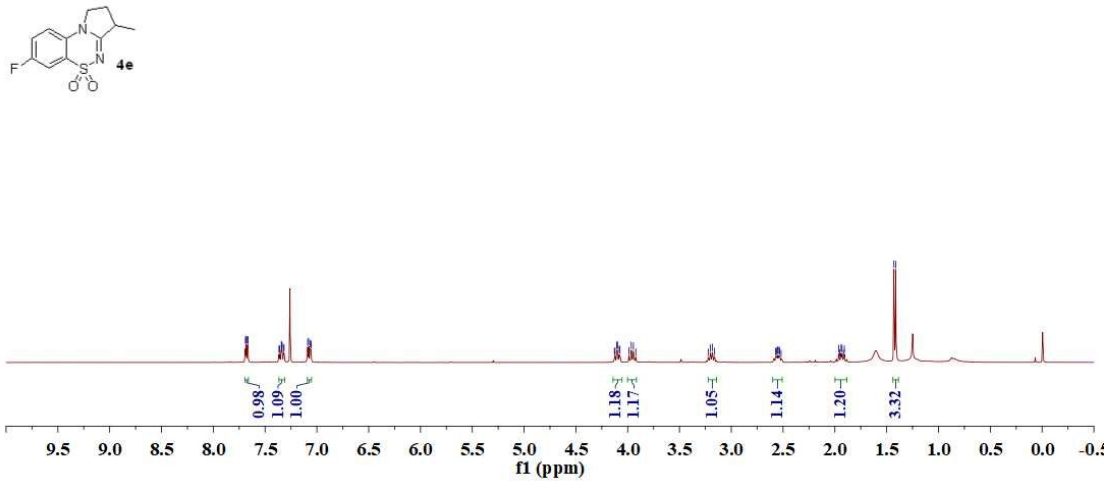
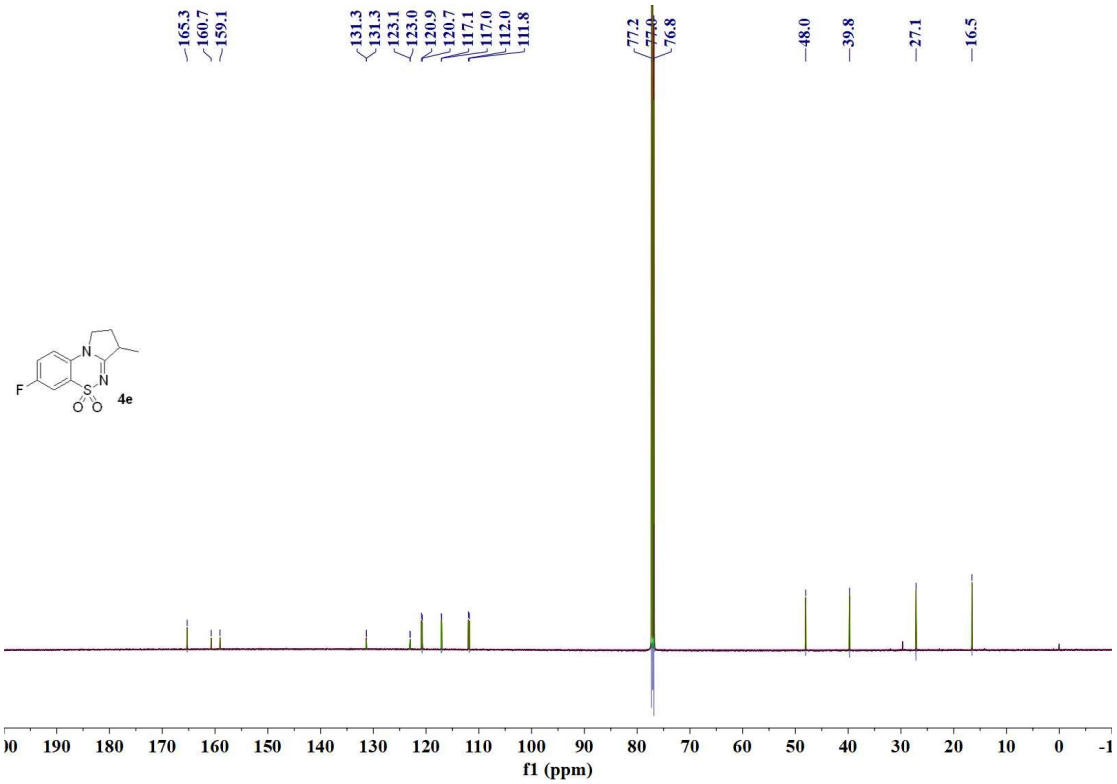
150.3
132.5
130.6
121.4
114.6
77.4
77.0
76.7
47.7
39.8
35.1
31.1
27.3
16.6
4d
f1 (ppm)


7.69
7.68
7.67
7.66
7.37
7.36
7.34
7.34
7.34
7.32
7.32
7.09
7.08
7.07
7.06
4.13
4.12
4.10
4.10
4.08
4.07
3.99
3.97
3.94
3.92
3.20
3.18
3.16
2.55
2.54
2.53
1.96
1.94
1.41


4e
0.98
1.09
1.00
1.18
1.17
1.05
1.14
1.20
3.32
f1 (ppm)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160.7
159.1
131.3
131.3
123.1
123.0
120.9
120.7
117.1
117.0
112.0
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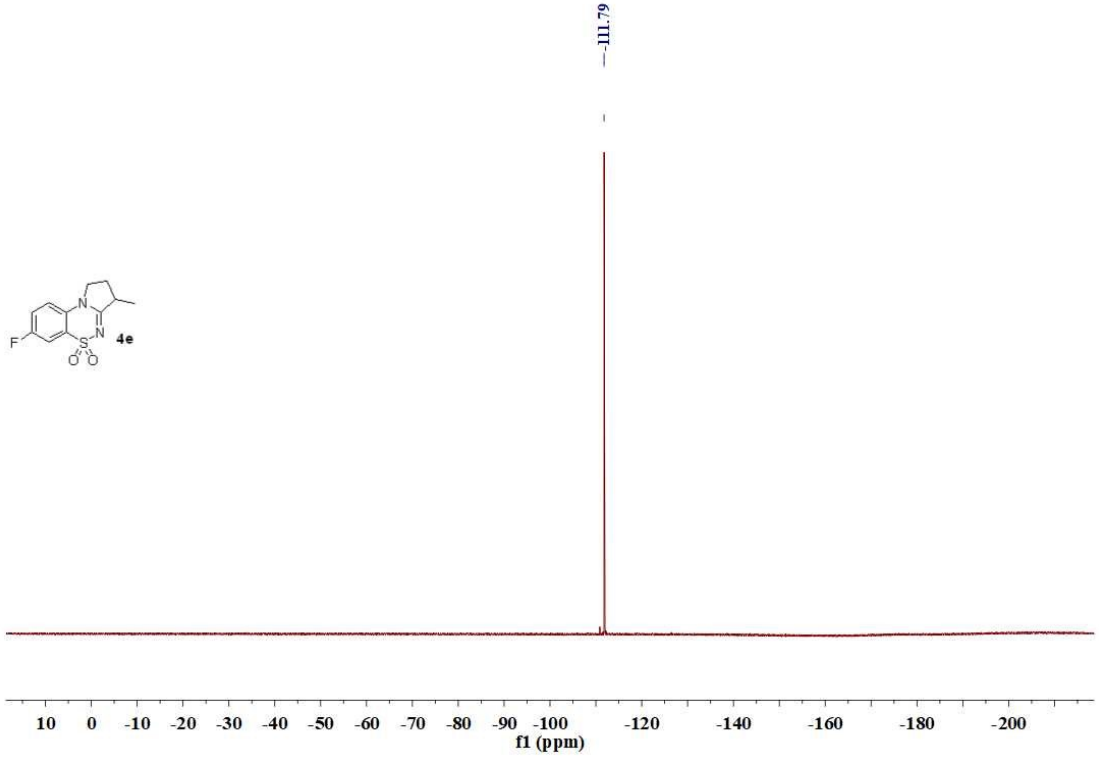
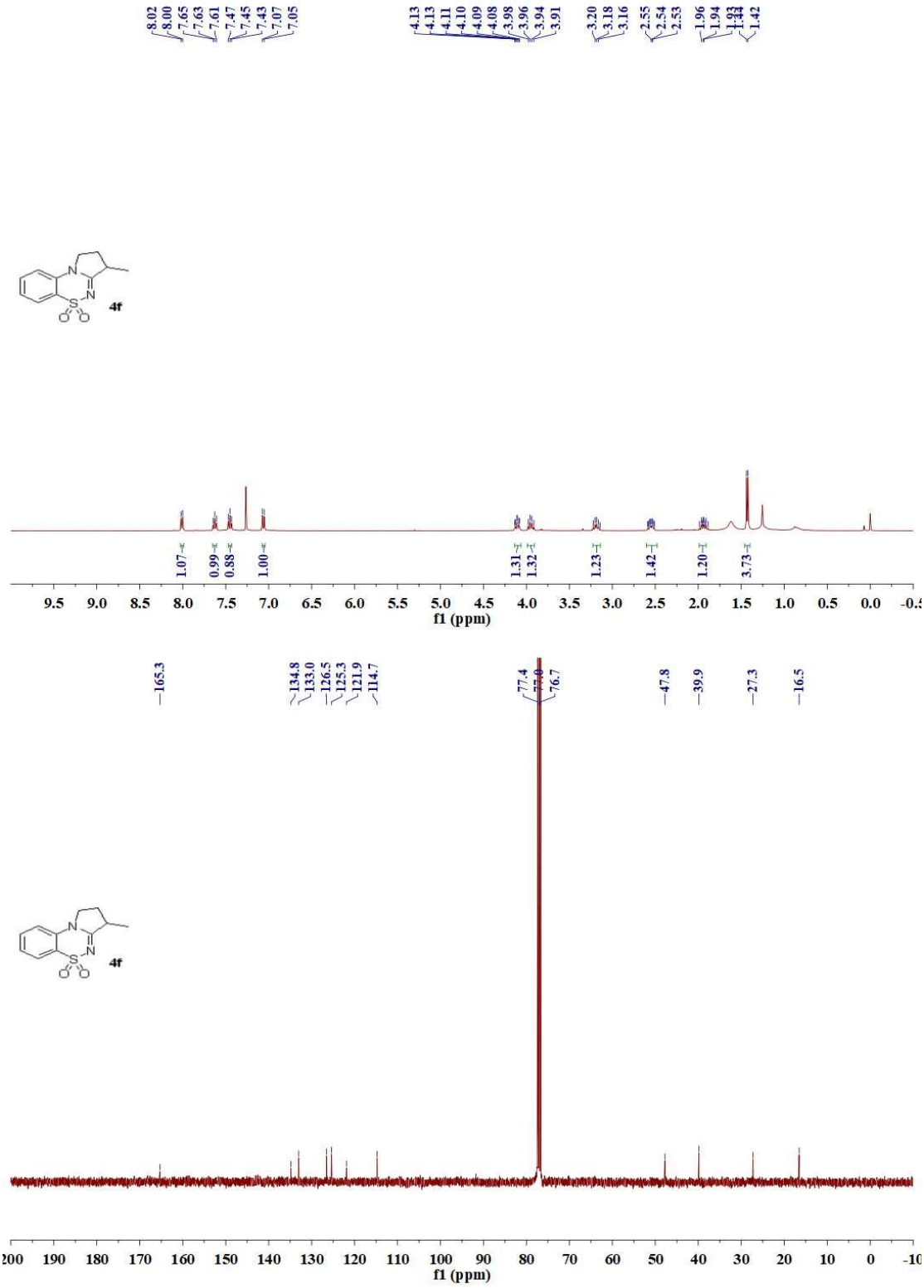
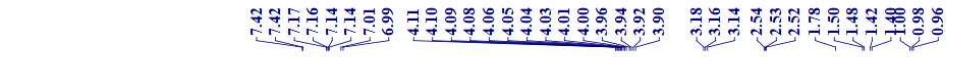
39.8
27.1
16.5
4e
f1 (ppm)


111.79
4e
f1 (ppm)


8.02
8.00
7.65
7.63
7.61
7.47
7.45
7.43
7.07
7.05
4.13
4.13
4.11
4.10
4.09
4.08
3.98
3.96
3.94
3.91
3.20
3.18
3.16
2.55
2.54
2.53
1.96
1.94
1.93
1.42
4f
1.07
0.99
0.88
1.00
1.31
1.32
1.23
1.42
1.20
3.73
f1 (ppm)
165.3
134.8
133.0
126.5
125.3
121.9
114.7
77.4
77.0
76.7
47.8
39.9
27.3
16.5
4f
f1 (ppm)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7.14
7.01
6.99
4.11
4.10
4.09
4.08
4.06
4.05
4.04
4.03
4.01
4.00
3.96
3.94
3.92
3.90
3.18
3.16
3.14
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2.53
2.52
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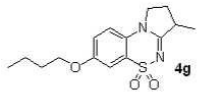
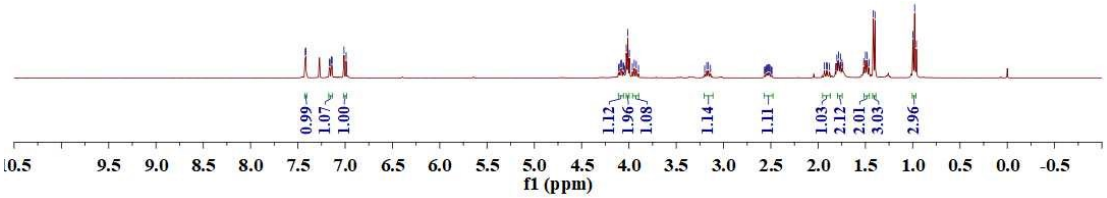
1.50
1.48
1.42
1.40
1.00
0.98
0.96


4g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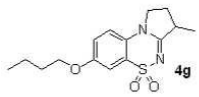
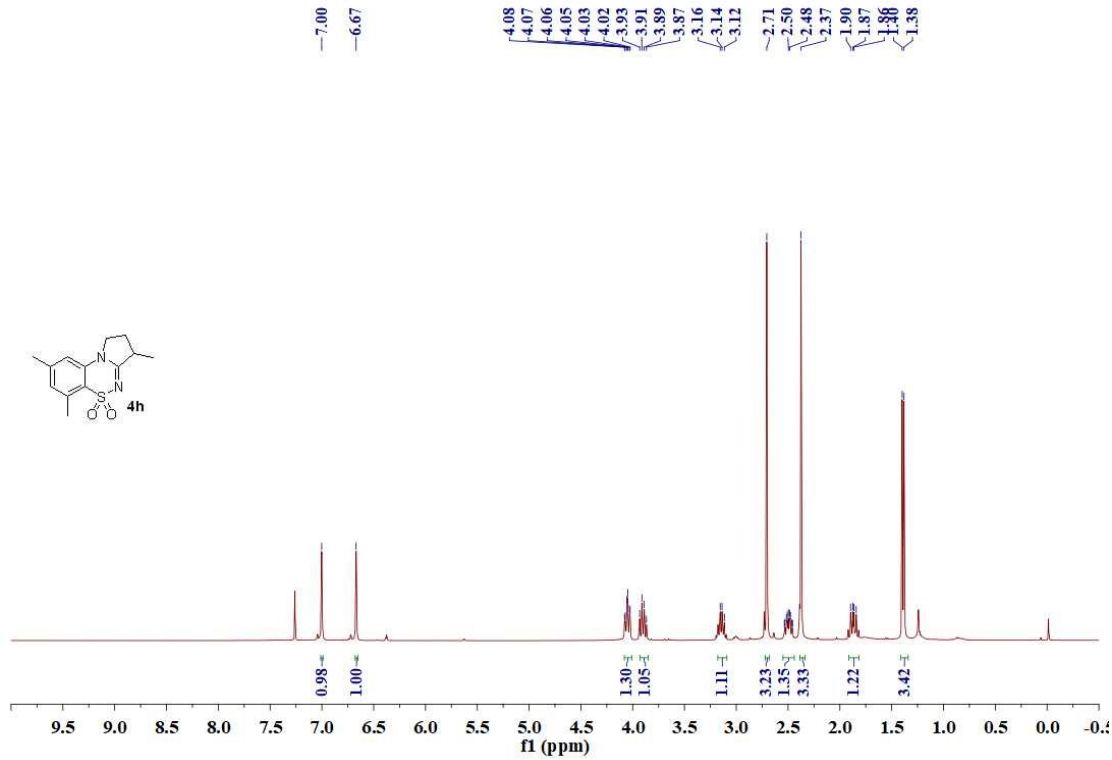
1.07
1.00
1.12
1.96
1.08
1.14
1.11
1.03
2.12
2.01
3.03
2.96
f1 (ppm)


164.6
157.4
128.2
122.5
121.8
116.6
107.4
77.4
77.1
76.7
68.6
47.9
39.7
31.0
27.2
19.1
16.6
13.8


4g

f1 (ppm)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4.06
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4.03
4.02
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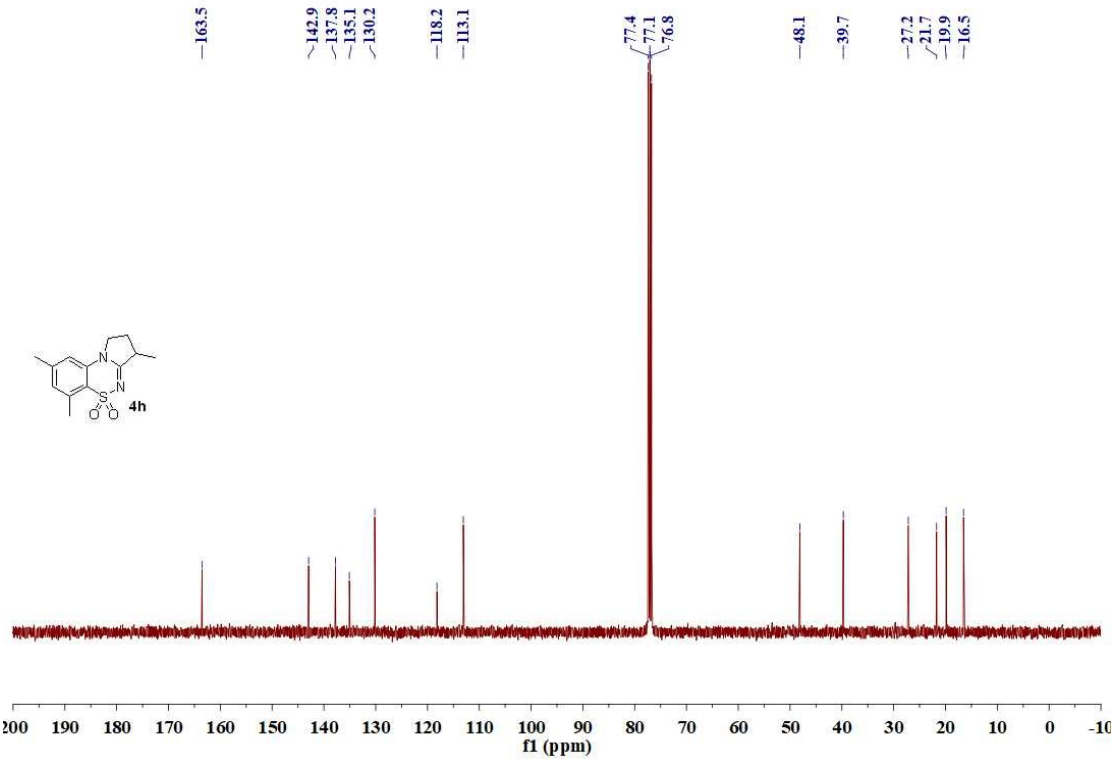
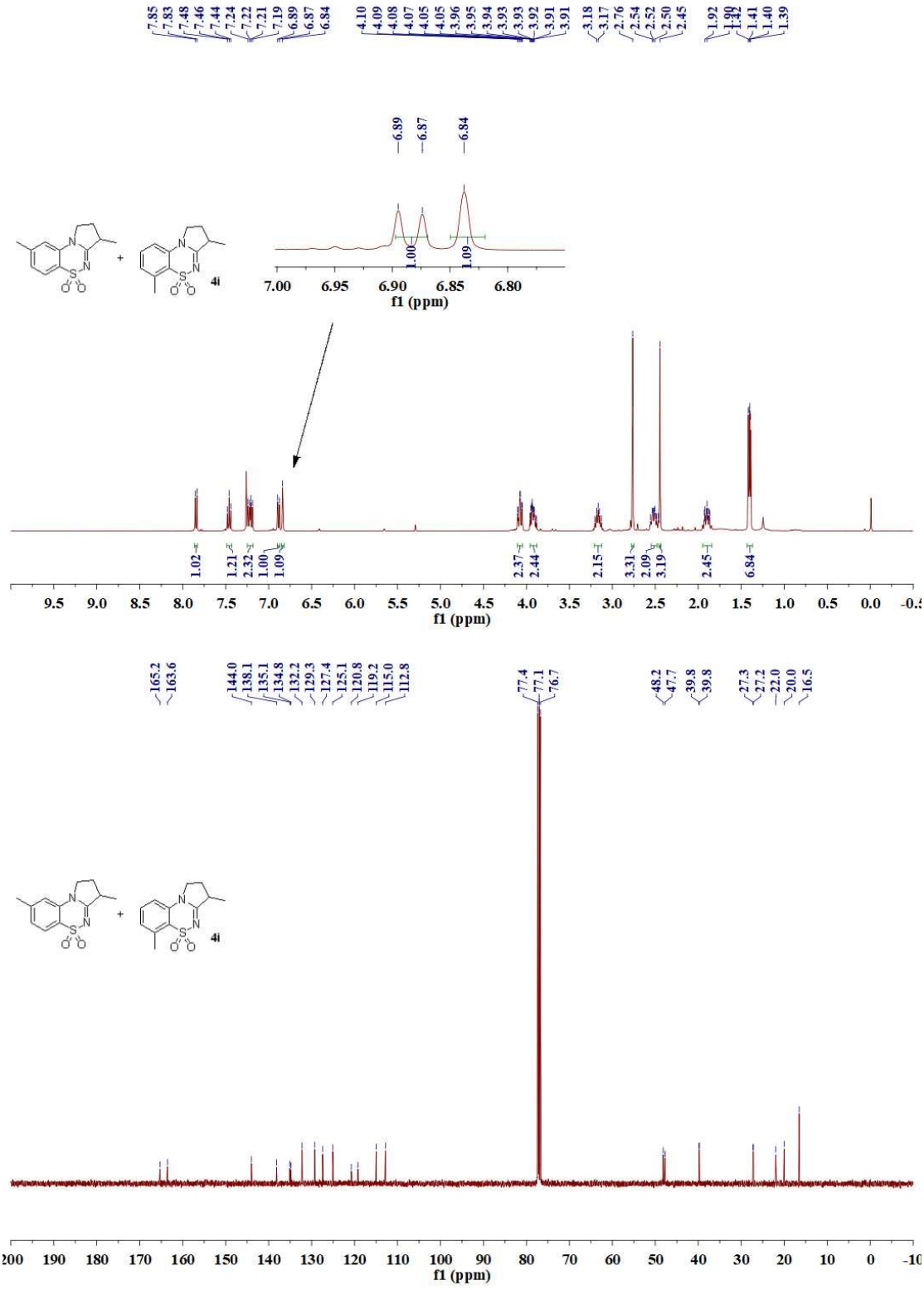
3.91
3.89
3.87
3.16
3.14
3.12
2.71
2.50
2.48
2.37
1.90
1.87
1.38
4h
0.98
1.00
1.30
1.05
1.11
3.23
1.35
3.33
1.22
3.42
f1 (ppm)


163.5
142.9
137.8
135.1
130.2
118.2
113.1
77.4
77.1
76.8
48.1
39.7
27.2
21.7
19.9
16.5
4h
f1 (ppm)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7.24
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7.21
7.19
6.89
6.87
6.84
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4.09
4.08
4.07
4.05
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1.41
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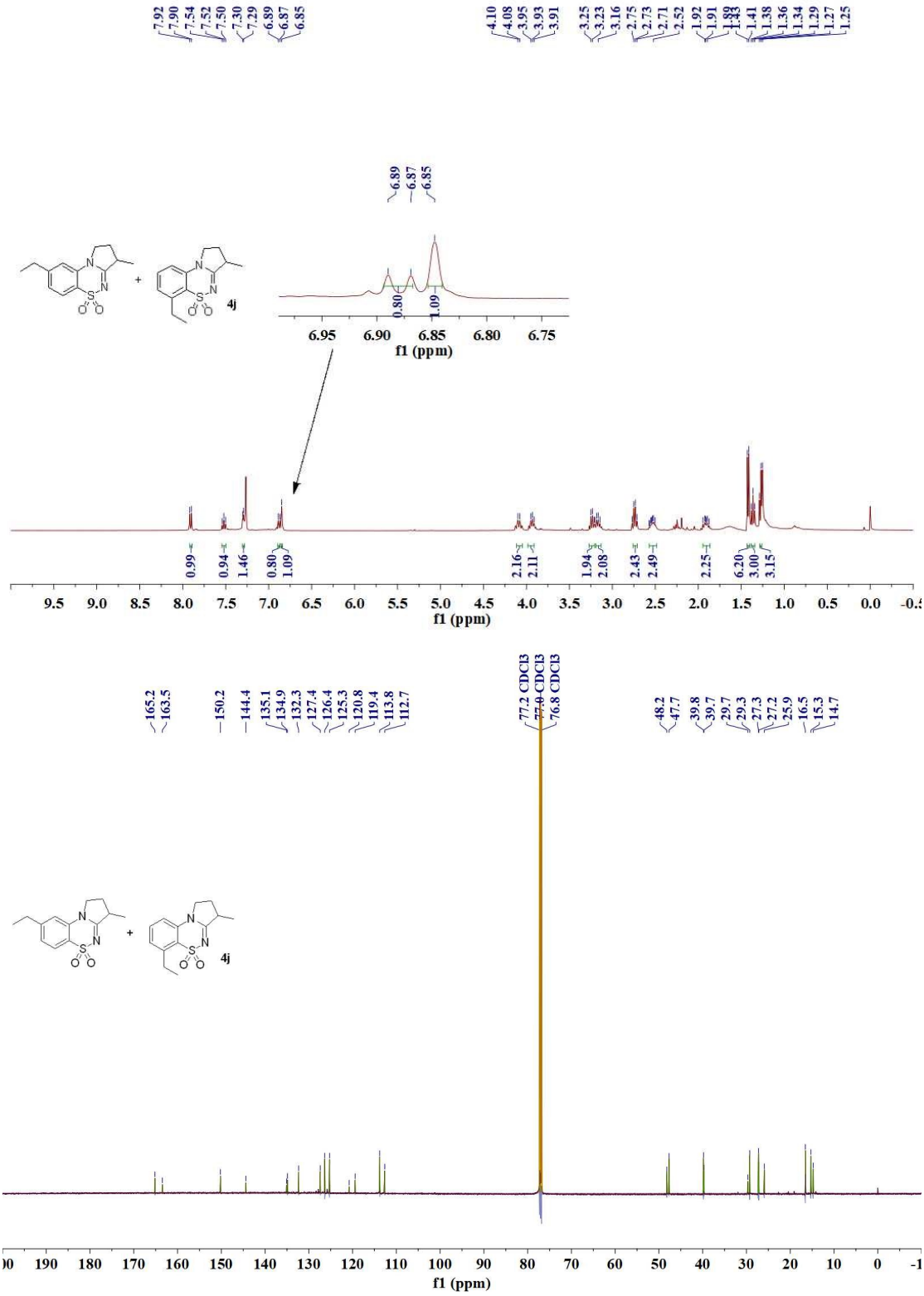
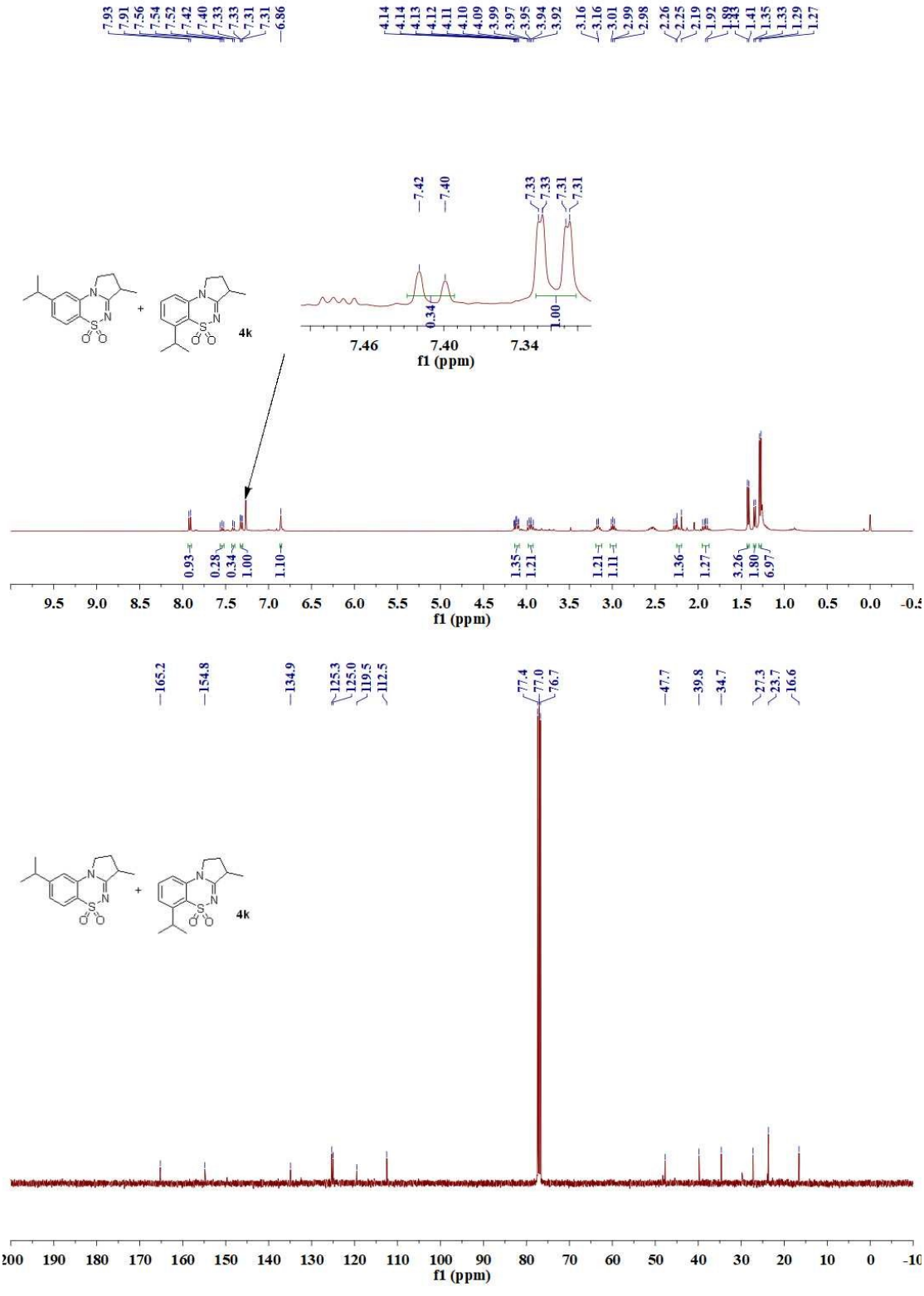
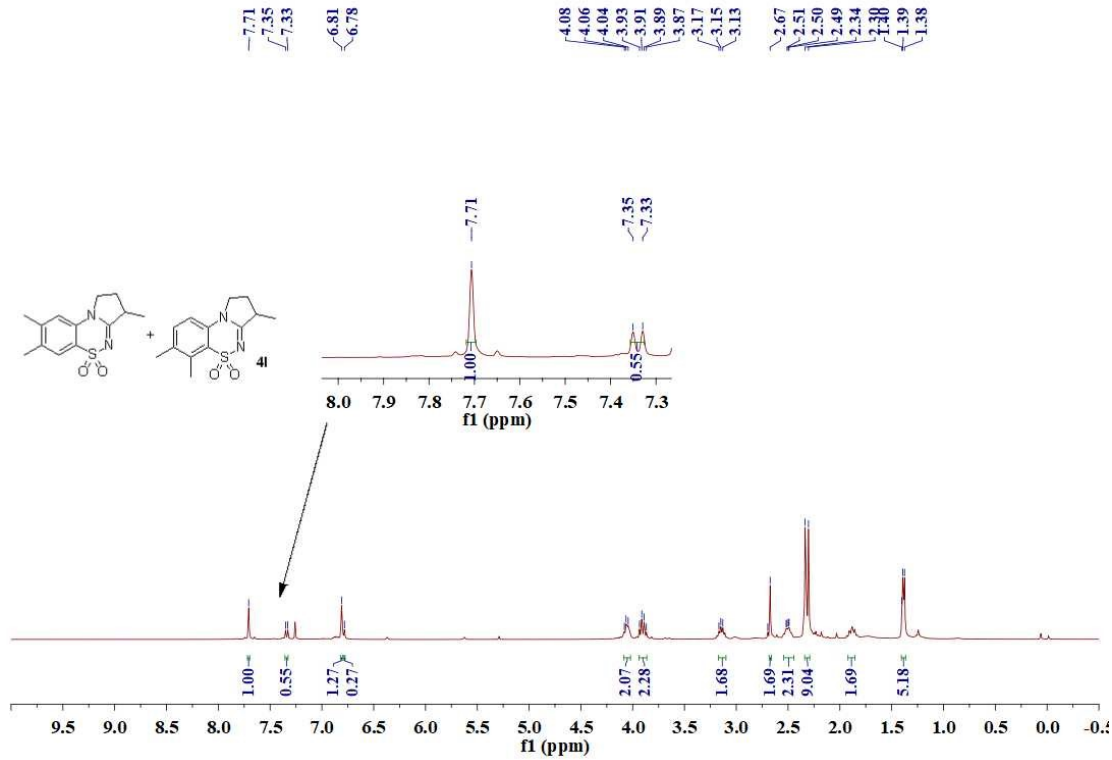
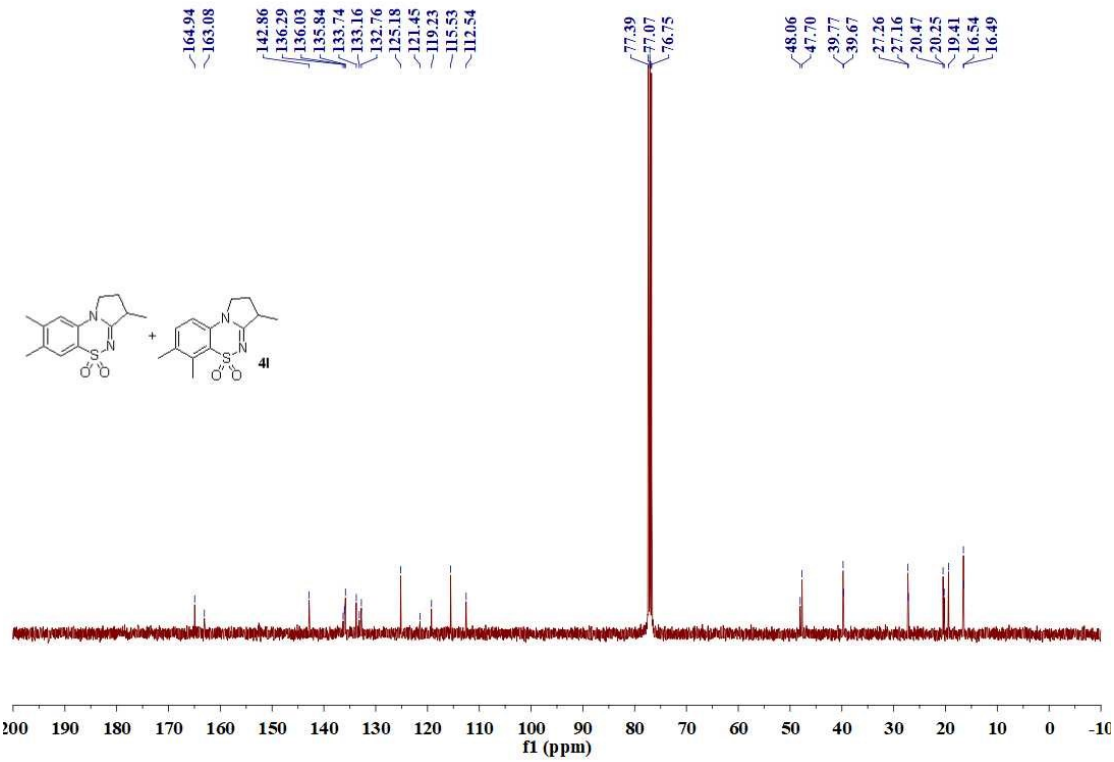
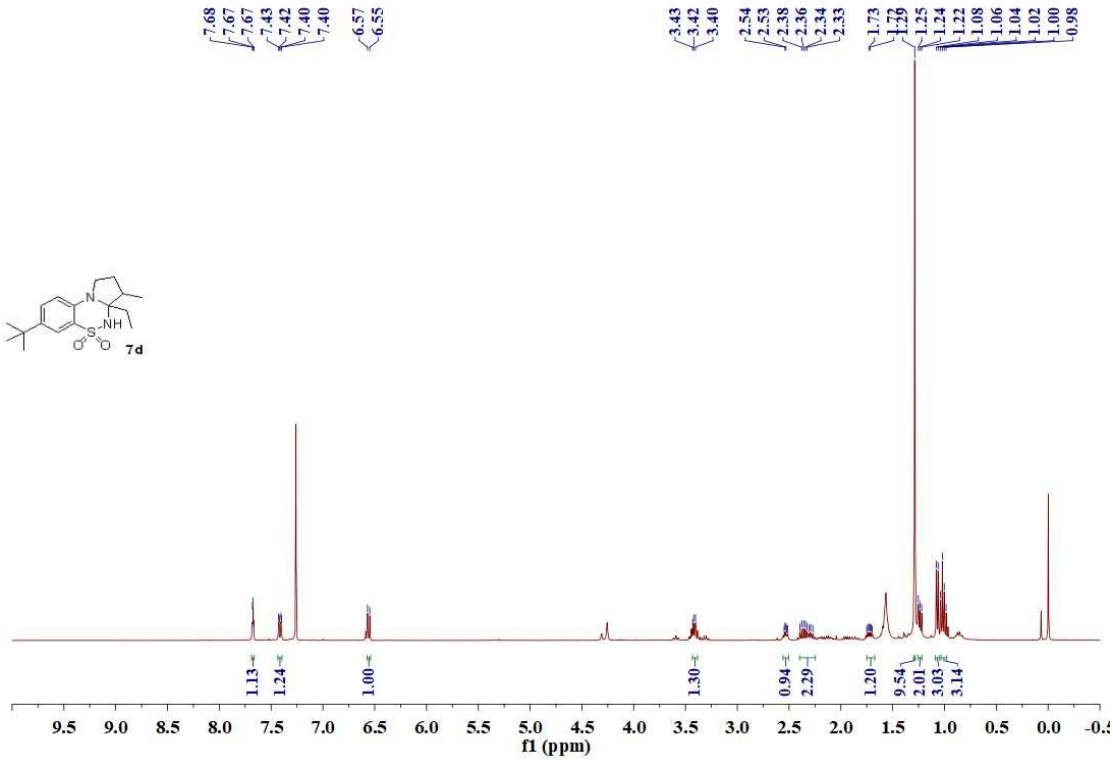
1.39
6.89
6.87
6.84
1.00
1.09
7.00
6.95
6.90
6.85
6.80
f1 (ppm)
4i
1.02
1.21
2.32
1.00
1.09
2.37
2.44
2.15
3.31
2.09
3.19
2.45
6.84
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
165.2
163.6
144.0
138.1
135.1
134.8
132.2
129.3
127.4
125.1
120.8
119.2
115.0
112.8
77.4
77.1
76.7
48.2
47.7
39.8
39.8
27.3
27.2
22.0
20.0
16.5
4i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

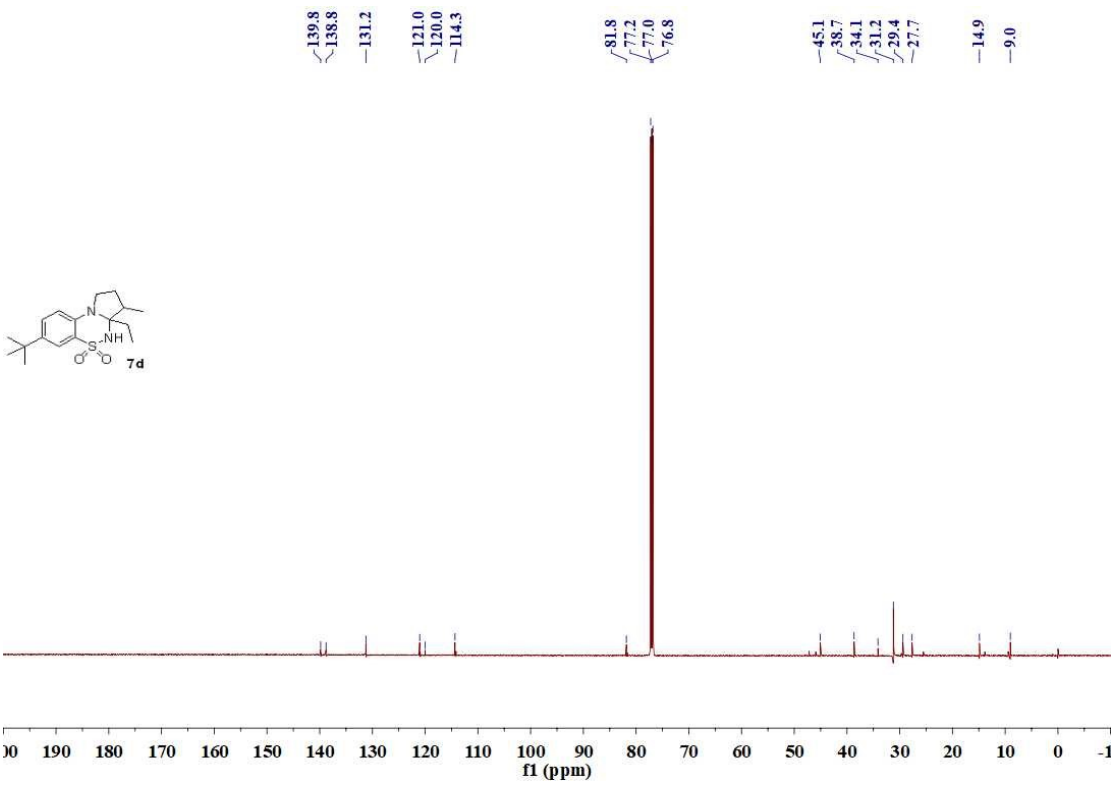

7.92
7.90
7.54
7.52
7.50
7.30
7.29
6.89
6.87
6.85
4.10
4.08
3.95
3.93
3.91
3.25
3.23
3.16
2.75
2.73
2.71
2.52
1.92
1.91
1.41
1.38
1.36
1.34
1.29
1.27
1.25
4j
0.80
1.09
f1 (ppm)
0.99
0.94
1.46
0.80
1.09
2.16
2.11
1.94
2.08
2.43
2.49
2.25
6.20
3.00
3.15
f1 (ppm)
165.2
163.5
150.2
144.4
135.1
134.9
132.3
127.4
126.4
125.3
120.8
119.4
113.8
112.7
77.2 CDCl3
77.0 CDCl3
76.8 CDCl3
48.2
47.7
39.8
39.7
29.7
29.3
27.3
27.2
25.9
16.5
15.3
14.7
4j
f1 (ppm)

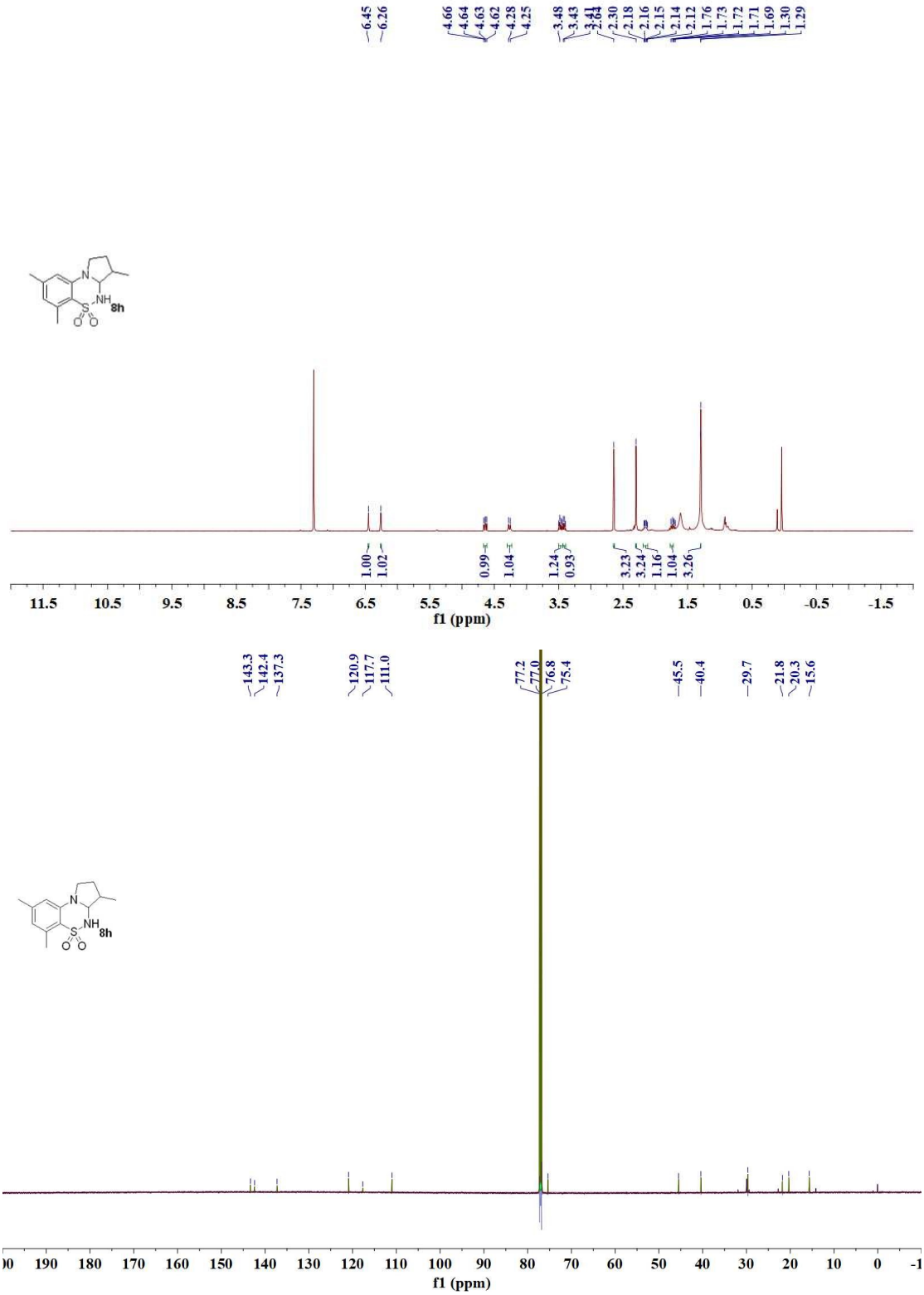

4k
f1 (ppm)
4k
f1 (ppm)


7.71
7.35
7.33
6.81
6.78
4.08
4.06
4.04
3.93
3.91
3.89
3.87
3.17
3.15
3.13
2.67
2.51
2.50
2.49
2.34
1.39
1.38
4l
f1 (ppm)
1.00
0.55
1.27
0.27
2.07
2.28
1.68
1.69
2.31
9.04
1.69
5.18


164.94
163.08
142.86
136.29
136.03
135.84
133.74
133.16
132.76
125.18
121.45
119.23
115.53
112.54
77.39
77.07
76.75
48.06
47.70
39.77
39.67
27.26
27.16
20.47
20.25
19.41
16.54
16.49
4l
f1 (ppm)


7.68
7.67
7.67
7.43
7.42
7.40
7.40
6.57
6.55
3.43
3.42
3.40
2.54
2.53
2.38
2.36
2.34
2.33
1.73
1.72
1.25
1.24
1.22
1.08
1.06
1.04
1.02
1.00
0.98
1.13
1.24
1.00
1.30
0.94
2.29
1.20
9.54
2.01
3.03
3.14
f1 (ppm)
7d


139.8
138.8
131.2
121.0
120.0
114.3
81.8
77.2
77.0
76.8
45.1
38.7
34.1
31.2
29.4
27.7
14.9
9.0
f1 (ppm)
7d



11. References

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