Synthesis and Characterization of 2-Iminocoumarins and Cyclic *N*-Sulfonyl Ketimines

M.Sc. Research Thesis

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By

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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Synthesis and Characterization of 2-Iminocoumarins and Cyclic *N*-Sulfonyl Ketimines

A THESIS

Submitted in partial fulfilment of the

Requirements for the award of the degree

Of

Master of science

by

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CANDIDATE'S DECLARATION

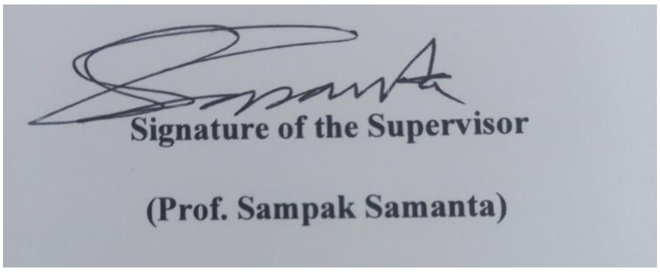
I hereby declare that the work being presented in the thesis entitled "**Synthesis and Characterization of 2-Iminocoumarins and Cyclic *N*-Sulfonyl Ketimines"** is an authentic record of my work carried out during the period from July 2024 to May 2025 under the supervision of **Prof. Sampak Samanta**, Professor, IIT Indore.

Sanjay yadav 23/05/2025

Signature of the student with date

(Sanjay Yadav)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.



Signature of the Supervisor

(Prof. Sampak Samanta)

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Sanjay Yadav

M.Sc. 2nd Year

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ACRONYMS

^{1}H NMR	Proton nuclear magnetic resonance spectroscopy
^{13}C NMR	^{13}C nuclear magnetic resonance spectroscopy
MeCN	Acetonitrile
DCM	Dichloromethane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene
DABCO	1,8-Diazabicyclo[5.4.0]undec-7-ene
DIPEA	*N*,*N*-Diisopropylethylamine

NOMENCLATURE

equiv.	equivalent
mmol	millimole
mg	milligram
h	hour
rt	room temperature
°C	Degree Celsius
mL	millilitre
δ	chemical shift

CHAPTER 1

1. INTRODUCTION

1.1. OBJECTIVE

There is a growing interest in creating synthetic processes that are friendly to the environment. These processes are for making important heterocycles, like cyclic *N*-sulfonyl ketimines, using C-C functionalization. This is especially true when these methods follow the principles of green chemistry. The main goal is to improve how efficiently these reactions work while also considering financial and environmental issues.

1.2. Motivation

Nitrogen-containing heterocycles are commonly utilized as fundamental components in the field of synthesis and serve as essential structural units in the drug discovery process. Cyclic *N*-sulfonyl ketimines have served important roles in the synthesis of various products possessing heteroatomic functional groups.[1-2] cyclic *N*-sulfonyl ketimines represent a very suitable platform for the preparation of this interesting class of heterocyclic compounds for their application in the pharmaceutical industry and drug discovery.[3] *N*-sulfonyl enamine as a suitable donor would possibly make a C-C bond. The Cyclic *N*-sulfonyl ketimines as nucleophilic partners were efficiently coupled with a diverse range of nucleophilic acceptors to construct interesting classes of a wide array of heterocyclic molecules.[4]

1.3. Literature review

Cyclic *N*-sulfonyl ketimines as fundamental building blocks in organic synthesis are widely implicated in medicinal chemistry, and the compounds containing *N*-sulfonyl imine moieties are normally biologically active molecules. Cyclic *N*-sulfonyl ketimines are important for creating various products that contain functional groups with heteroatoms. The proton of alcohols as the sole hydrogen source in diborane-mediated nickel-catalysed asymmetric transfer hydrogenation of cyclic *N*-sulfonyl ketimines has been developed, providing the chiral cyclic *N*-sulfonyl in excellent enantioselectivities.[5] The mechanistic investigations suggested that the proton of alcohols could be activated by tetrahydroxydiboron to form active nickel hybrid species. *N*-sulfonyl imines are important chemicals used in making other molecules in organic chemistry. [8-9] They are commonly found in medicinal chemistry because molecules with *N*-sulfonyl imine structures often have biological activity, meaning they can affect living organisms in useful ways.

2-Iminocoumarin is a colourless to white powder-like water-insoluble substance, but 4-hydroxy substitution confers weakly acidic properties to the molecule that make it water soluble under slightly alkaline conditions. Coumarins are natural compounds made of fused benzene and α-pyrone rings, and they have the potential to treat various health problems like cancer, and metabolic, and degenerative diseases. They are found both in nature and can also be synthesized, offering a wide range of biological and therapeutic properties. It also compares various methods for synthesizing the coumarin core, highlighting both traditional and environmentally friendly (green) approaches. Conventional methods include Pechmann, Knoevenagel, Perkin, Wittig, and metal-catalysed reactions like Heck and Suzuki reactions. Green methods involve energy sources like microwaves or ultrasounds.[6] The chromene moiety is indeed a significant structural unit found in a variety of biologically active and natural compounds. It features prominently in natural products such as alkaloids, flavonoids, tocopherols, and anthocyanins, which are known for their wide range of biological activities. Chromene derivatives, particularly 2-amino-4H-chromenes, hold great promise in medicinal chemistry due to their versatility and pharmacological importance.[7]

Key Features of 2-Iminocoumarin

- **Medicinal Applications**: They act as privileged scaffolds in drug design, offering spasmolytic, diuretic, anti-coagulant, and anti-anaphylactic activities.
- **Synthetic Versatility**: These compounds are valuable for developing small-molecule ligands, contributing to therapeutic innovations.

Synthetic Methods

The synthesis of 2-amino-3-nitrile-4*H*-chromenes typically involves:

1. The most common approach uses *ortho*-hydroxy salicylaldehyde and malononitrile as key precursors.
2. Various catalysts have been explored to enhance the efficiency and yield of these reactions, reflecting their significance in medicinal chemistry and industrial applications.

Research and Development

The development of catalytic methods for Coumarin derivatives has gained momentum due to their extensive applications in pharmaceutical research. These methods aim to improve reaction conditions, minimize environmental impact, and achieve higher selectivity and yields, aligning with green chemistry principles.

1.4. Scope of work

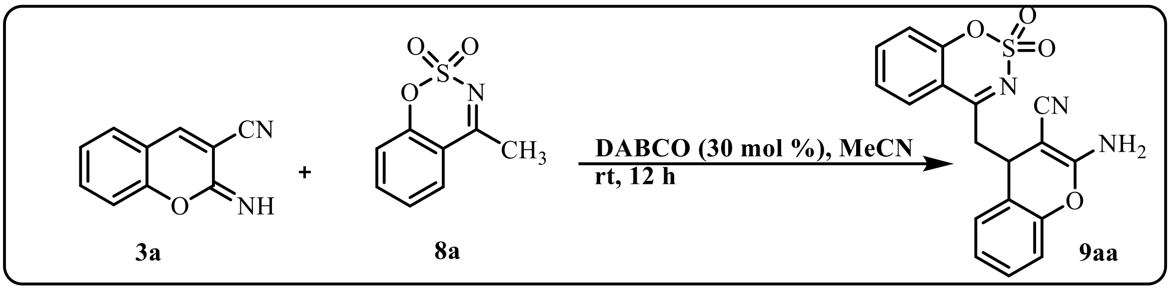
For substrate scope, we will perform the C-C bond-forming reaction involving different substituted cyclic *N*-sulfonyl ketimines and 2-iminocoumarin derivatives to establish the substrate scope of this alkylation reaction under optimal conditions. Additionally, we will conduct control experiments to better understand the reaction pathway.

CHAPTER 2

2. RESULTS AND DISCUSSION

To start our investigation, we chose substituted 2-Iminocoumarin (1) and substituted cyclic *N*-sulfonyl ketimine (2), and the results are summarized in Table 1

2.1. Optimization of the reaction conditions



Scheme 1: Synthesis of 4-chromenyl-substituted *N*-sulfonyl ketimine

Entry	Base	Solvent	Equivalent	Temperature(°C)	Time(h)	Yield (9) (%)
1.	DABCO	MeCN	0.15	rt	12	52
2.	**DABCO**	**MeCN**	**0.30**	**rt**	**12**	**69**
3.	DABCO	MeCN	0.50	rt	12	55
4.	DABCO	MeCN	1.00	rt	12	60
5.	DABCO	MeCN	1.50	rt	12	63
6.	DABCO	MeCN	2.00	rt	12	65
7.	DABCO	DCM	0.30	rt	12	54
8.	DABCO	DCE	0.30	rt	12	10
9.	DABCO	Toluene	0.30	rt	12	15
10.	DABCO	THF	0.30	rt	12	23
11.	DABCO	1,4-Dioxane	0.30	rt	12	56
12.	DABCO	EtOH	0.30	rt	12	63
13.	DBU	MeCN	0.30	rt	12	60
14.	DBN	MeCN	0.30	rt	12	45
15.	NEt_3	MeCN	0.30	rt	12	28
16.	DIPEA	MeCN	0.30	rt	12	48

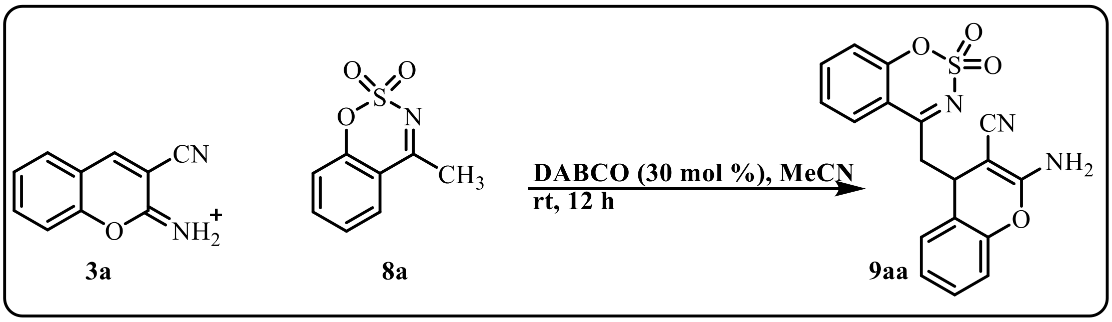
Table 1: Optimization of different reaction conditions

All the reactions are carried out with **3a** (0.29 mmol, 1.0 equiv.), **8a** (0.29 mmol, 1.0 equiv.), and base (0.30 equiv.) in dry solvent (0.5 mL) at room temperature. Yield is isolated product **9aa**.

We did the model reaction between 2-Iminocoumarin **(3a)** and cyclic *N*-sulfonyl ketimine (**8a**) in Acetonitrile using DABCO as a robust base at room temperature and observed by TLC. After 12 h, the reaction was completed, and **9aa** was isolated in good yield at rt. To improve the yield further, several common solvents such as THF, DCE, MeCN, 1,4-dioxane, toluene, and EtOH were tested for this reaction. Most of the solvents gave moderate to good yields. Thus, considering the yield, MeCN was the best solvent for this reaction at rt (entry 2). Further, we screened other bases such as DBU, DBN, DIPEA, NEt_3, and Lewis's acid (silver triflate). Therefore, considering the yield of the desired product **9aa**, DABCO in MeCN at rt is the best-optimized condition for the reaction **(Scheme 1).**

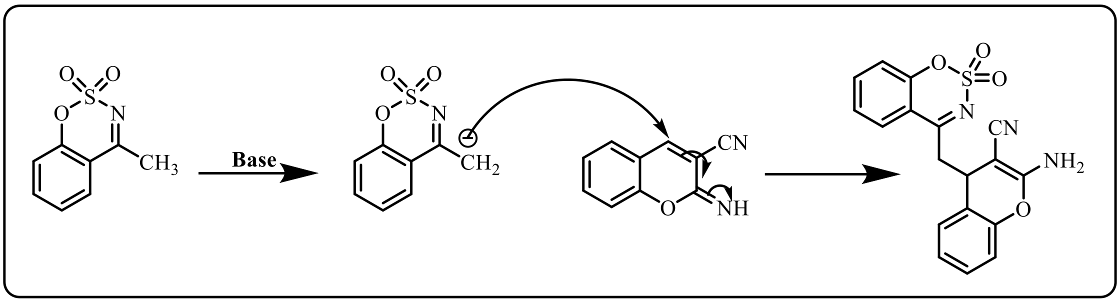
2.2 Substrate Scope

Having optimal reaction parameters in hand, we demonstrated the substrate scope of the reaction by taking various 2-Iminocoumarins and cyclic *N*-sulfonyl ketimines in MeCN at rt in the presence of DABCO under the present conditions.



2.3 Plausible Reaction Mechanism

The plausible mechanism is drawn in **Scheme (2)**. cyclic *N*-sulfonyl ketimines behave as nucleophiles after the abstraction of proton with the help of strong base (DABCO) attack on 2-Iminocoumarin (act as electrophile) then undergoes Michael addition form the desired product **9aa**(2-Amino-4-((2,22-dioxidobenzo[*e*][1,2,3]oxathiazine-4-yl)methyl)-4*H*-chromene-3-carbonitrile).



Scheme 2: Plausible reaction mechanism

CHAPTER 3

3. EXPERIMENTAL WORK

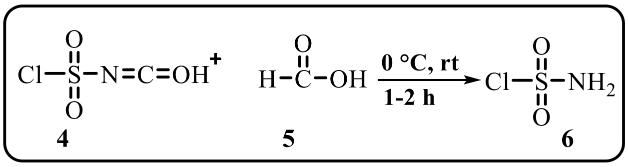
3.1 Required Materials and Instrumentation:

All the chemicals were bought from Sigma Aldrich and Spectrochem. All the reactions were in a closed tube and observed by TLC using a Merck 60 F_{254} pre-coated silica gel plate, and the product was apprehended by UV detection. Silica gel (60-120 mesh) was used for column chromatography. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) data were taken in $CDCl_3$ and DMSO-d_6 solvents using Bruker Advance 500. NMR data were processed by MestReNova.

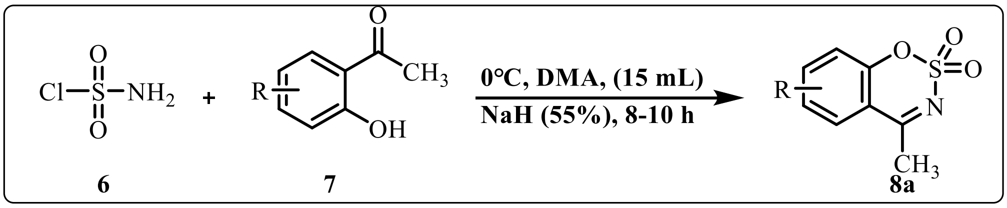
3.2 Standard procedure for the synthesis:

3.2.1 Synthesis of cyclic *N*-sulfonyl ketimine:

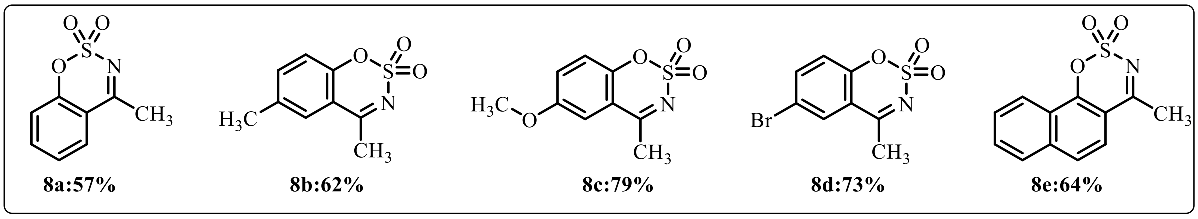
Step:1



Step:2



Scheme 3: Synthesis of cyclic *N*-sulfonyl ketimines

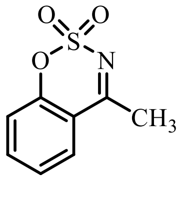


8a:57% 8b:62% 8c:79% 8d:73% 8e:64%

Synthesized cyclic *N*-sulphonyl ketimines

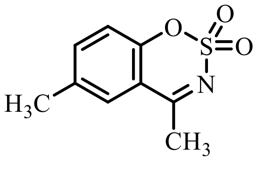
Firstly, anhydrous formic acid (921 mg, 20.0 mmol, 0.75 mL) was added dropwise to a neat chlorosulfonyl isocyanate (20.0 mmol) was taken in a double neck 250 mL round bottom flask at 0 °C with rapid stirring, vigorous gas evolution observed during the addition process. After that, stir the resulting viscous suspension at room temperature until gas evolution ceased (1-2 hours), after we add 2′-hydroxyacetophenone (10.0 mmol) to the resulting sulfamoyl chloride, then cool the mixture under ice-cooling, we add 15 mL of DMA slowly to the mixture and then move the mixture to ice-cooling, after that stir the mixture for 10 minutes and then add sodium hydride(480 mg of 60% dispersion in mineral oil, 12.0 mmol) in portions. After stirring for 30 minutes at room temperature, add sodium hydride (480 mg of 60% dispersion in mineral oil, 12.0 mmol) in portions again, stir the mixture for 1 hour at room temperature and stir the reaction mixture to overnight (8-12 hours) at 50 ^{0}C and finally quench the reaction by the addition of 30 mL of water. Then, extract the aqueous layer with 20 mL of EtOAc and then wash the combined organic layers with 40 mL of water and 40 mL of brine. Concentrate the combined organic layer under reduced pressure. Purify the product by column chromatography on silica gel (Ethyl acetate and hexane,1:9**) (Scheme 3).**

4-Methylbenzo[*e*][1,2,3] oxathiazine-2,2-dioxide(8a):



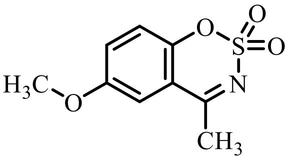
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.72 (ddd, *J* = 8.7, 7.5, 1.6 Hz, 1H), 7.40 (td, *J* = 7.7, 1.2 Hz, 1H), 7.29 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.73 (s, 3H) ppm**. ^{13}C NMR (125 MHz, CDCl$_3$) δ** 177.4, 153.5, 137.2, 128.6, 126.0, 119.2, 116.5, 23.8 ppm.

4,6-Dimethylbenzo[*e*][1,2,3]oxathiazine-2,2-dioxide(8b):



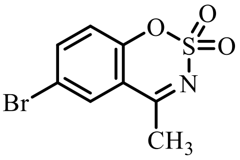
^{1}H NMR (500 MHz, CDCl3) δ 7.57 (s,1H), 7.51 (d, J = 8.4 Hz, 1H), 7.17 (dd, J = 8.3, 1.3 Hz,1H), 2.70 (s, 3H), 2.44(s, 3H) ppm; **^{13}C NMR (125 MHz, CDCl$_3$) δ** 177.5, 151.5, 138.0, 136.0, 128.4, 118.9, 116.2, 23.8, 21.0 ppm.

6-Methoxy-4-methylbenzo[*e*][1,2,3] oxathiazine-2,2-dioxide(8c):



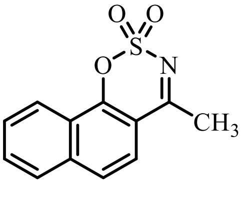
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.57 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.17 (dd, *J* = 8.3, 1.3 Hz, 1H), 2.70 (s, 3H), 2.44 (s, 3H) ppm; **^{13}C NMR (125 MHz, CDCl$_3$) δ** 177.3, 156.9, 147.2, 123.35, 120.0, 116.9, 112.0, 56.2, 23.8 ppm.

6-bromo-4-methylbenzo[*e*][1,2,3]oxathiazine-2,2-dioxide(8d):



^{1}H NMR (500 MHz, CDCl$_3$) δ 7.91 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.20 (dd, *J* = 8.8, 1.8 Hz, 1H), 2.72 (s, 3H) ppm.**^{13}C NMR (125 MHz, CDCl$_3$) δ** 176.2, 152.4, 139.8, 131.1, 121.0, 118.6, 117.8, 23.8 ppm.

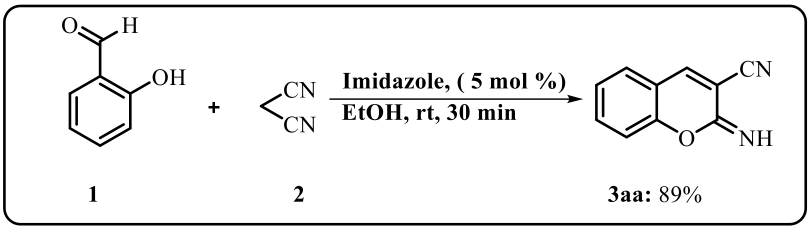
4-Methylnaphtho[2, 1-*e*][1,2,3]oxathiazine-2,2-dioxide(8e):



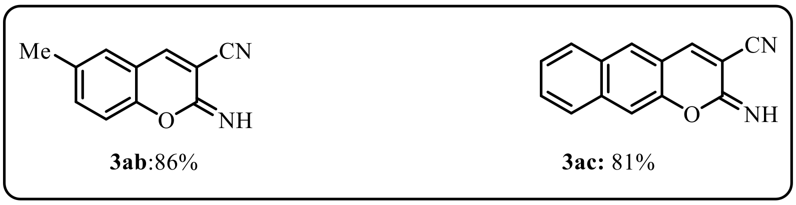
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 – 8.40 (m, 1H), 7.94 – 7.88 (m, 1H), 7.80 – 7.74 (m, 2H), 7.73 – 7.67 (m, 2H), 2.81 (s, 3H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 178.1, 152.4, 137.5, 131.3, 128.4, 128.0, 125.4, 123.6, 123.1, 121.8, 111.7, 24.5 ppm.

3.2.2 Synthesis of 2-Iminocoumarin (3aa):

Take a 100 mL round-bottom flask, add a solution of aryl aldehyde (244 mg, 2.0 mmol) and malononitrile (132 mg, 2.0 mmol), in an ethanol solution (3.0 mL) containing imidazole (5 mol%) at room temperature for 30 minutes, and monitor the reaction progress using TLC. After completion of the reaction, the pure crystalline product could be isolated from ethanol without further separation and purification. Separate the crystal obtained from the supernatant solution by a simple decanting procedure **(Scheme 4).**

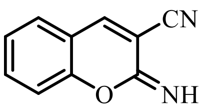


Scheme 4: Synthesis of 2-Iminocoumarin



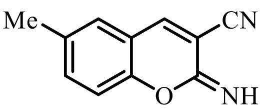
Synthesized 2-Iminocoumarins

2-Imino-2*H*-chromene-3-carbonitrile (3aa):



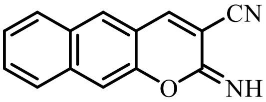
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.85 (s, 1H), 8.37 (s, 1H), 7.60 – 7.58 (m, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 8.9 Hz, 1H) ppm**;** **^{13}C NMR (125 MHz, DMSO-d_6) δ** 154.2, 151.9, 147.4, 134.6, 130.0, 124.7, 117.8, 116.0, 115.7, 104.7 ppm.

2-Imino-6-methyl -2*H*-chromene-3-carbonitrile (3ab):



^{1}H NMR (500 MHz, DMSO-d$_6$) δ 7.89 (s, 1H), 7.44 (s, 1H), 6.53 (s, 2H), 6.23 (s, 1H), 1.43 (s, 3H) ppm; **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** 151.8, 151.7, 146.9, 134.8, 133.4, 129.1, 117.0, 115.3, 104.1, 19.9 ppm.

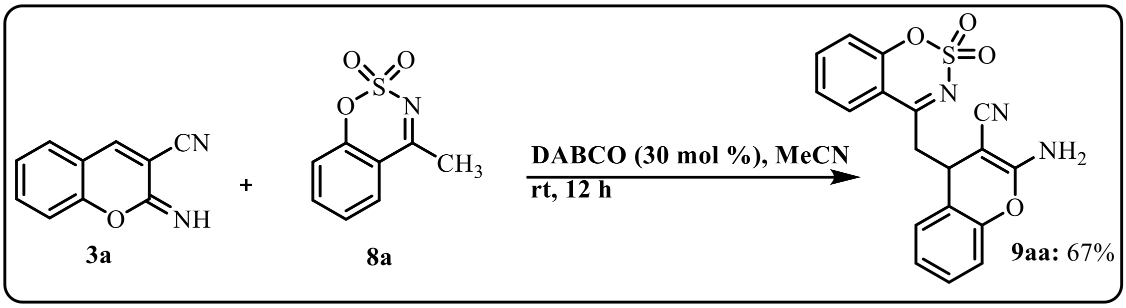
2-Imino-2*H*-benzo[*g*]chromene-3-carbonitrile(3ac):



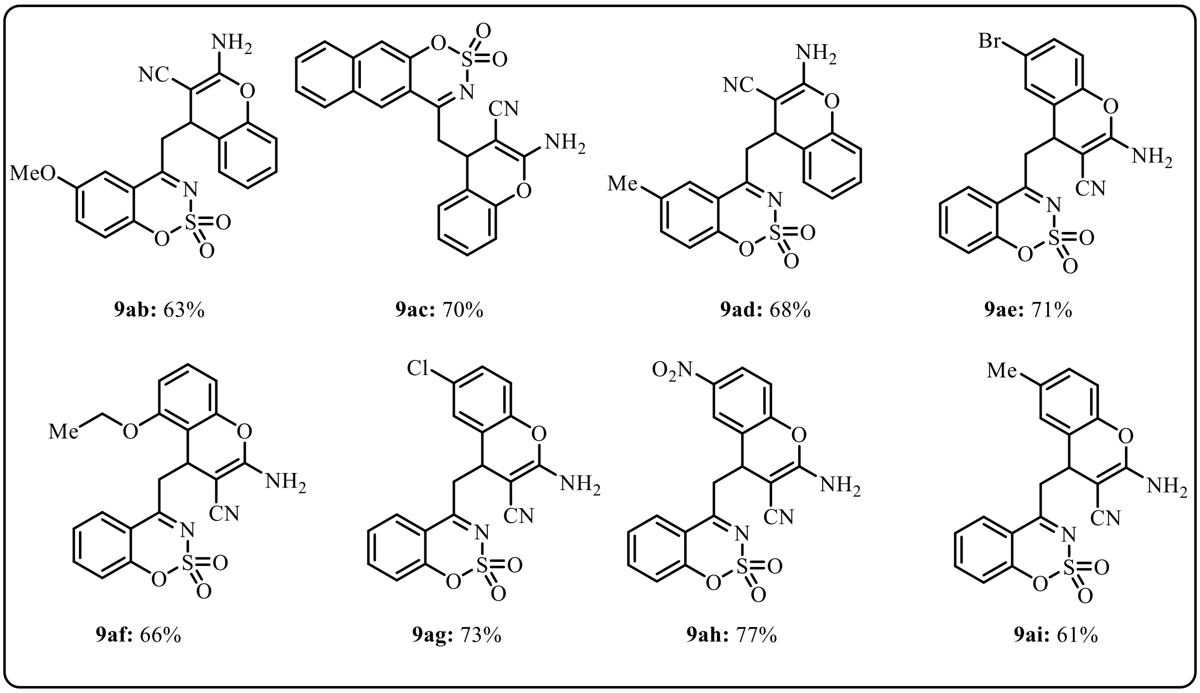
^{1}H NMR (500 MHz, DMSO-d$_6$) δ 8.31 (s, 1H), 7.92 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.30 (d, J = 9.0 Hz, 1H), 7.12 (d, J = 8.1 Hz, 1H), 6.83 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 6.73 – 6.67 (m, 1H), 6.49 (d, J = 9.0 Hz, 1H) ppm; **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** 153.4, 151.1, 142.6, 134.8, 129.0, 128.4, 128.2, 125.4, 121.6, 115.5, 115.0, 110.6, 102.6 ppm.

3.2.3 One-pot procedure for the synthesis of 2-Amino-4-((2,2-dioxidobenzo[*e*][1,2,3] oxathiazin-4-yl)-4*H*-chromine-3-carbonitrile:

In a dry closed test tube, the mixture of 2-Iminocoumarin (50 mg, 0.294 mmol, 1.0 equiv.), cyclic *N*-sulfonyl ketimine (57.9 mg, 0.294 mmol, 1.0 equiv.), DABCO (9.9 mg, 0.088 mmol, 0.30 equiv.) and Acetonitrile (0.5 mL) were taken, then stirred at room temperature for 12h. The completion of the reaction was judged by TLC. Then the reaction mixture was extracted with ethyl acetate (30 mL), washed with brine, and dried using Na_2SO_4. After that, concentrated using a rotary evaporator under reduced pressure to yield the crude, which was purified using column chromatography over silica gel (60-120 mesh) with EtOAc/hexane (1:4, v/v). ^{1}H and ^{13}C data were used to characterize the product with MestreNova **(Scheme 5).**



Scheme 5: Synthesis of 4-chrominyl-substituted *N*-sulfonyl ketimines

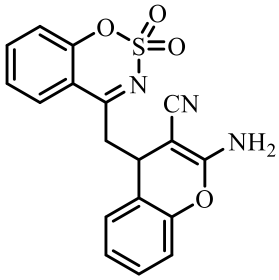


Synthesized 4-chrominyl-substituted *N*-sulfonyl ketimines

CHAPTER 4

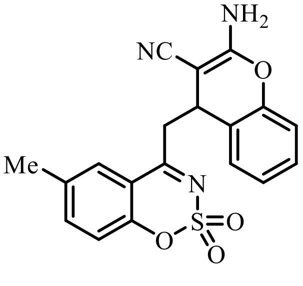
4.1 Data of all synthesized compounds

2-Amino-4-((2,2-dioxidobenzo[*e*][1,2,3]oxathiazin-4-yl)-4*H*-chromene-3-carbonitrile(9aa):



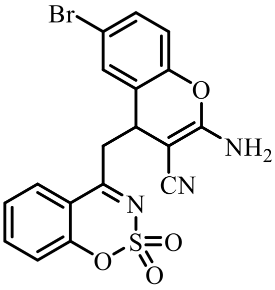
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.64 (s, 1H), 7.57 (s, 1H), 7.22 (s, 2H), 7.15 (s, 1H), 7.10 (s, 1H), 7.05 (s, 1H), 6.93 (s, 1H), 4.67 (s, 2H), 4.29 (s, 1H), 3.33 (d, *J* = 47.8 Hz, 2H) ppm; **NMR (125 MHz, CDCl$_3$) δ** 176.9, 161.4, 153.7, 149.5, 137.2, 129.0, 128.3, 128.3, 125.9, 125.4, 121.6, 119.5, 119.3, 116.7, 116.6, 57.7, 44.2, 34.1 ppm.

2-Amino-4-((6-methyl-2,2-dioxidobenzo[*e*/[1,2,3]oxathiazin-4-yl)methyl)-4*H*-chromene-3-carbonitrile(9ad).



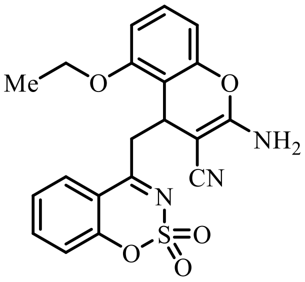
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 (s, 1H), 7.35 (s, 1H), 7.20 (s, 1H), 7.15 (s, 2H), 7.08 (s, 1H), 6.96 (s, 1H), 4.71 (s, 2H), 4.31 (s, 1H), 3.36 (d, J = 39.1 Hz, 2H), 2.35 (s, 3H) ppm; **^{13}C NMR (125 MHz, CDCl$_3$)) δ**176.6, 161.2, 151.4, 149.3, 137.7, 135.7, 128.7, 128.1, 128.0, 125.1, 121.5, 118.7, 116.4, 116.1, 57.5, 43.9, 33.8, 20.7 ppm.

2-Amino-6-bromo-4-((2,2-dioxidobenzo[*e*][1,2,3]oxathiazin-4-yl)methyl)-4*H*-chromene-3-carbonitrile(9ae):



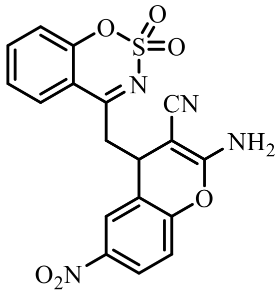
^{1}H NMR (500 MHz, , DMSO-d$_6$) δ 8.10 (s, 1H), 7.83 (s, 1H), 7.60 (s, 1H), 7.46 (s, 2H), 7.37 (s, 1H), 7.06 (s, 2H), 6.90 (s, 1H), 4.19 (s, 1H), 3.47 (d, J = 44.3 Hz, 2H) ppm; **^{13}C NMR (125 MHz, , DMSO-d$_6$) δ** 179.2, 161.8, 152.6, 148.8, 138.0, 131.3, 131.1, 130.1, 126.3, 125.1, 120.0, 118.7, 118.6, 118.3, 116.4, 116.2, 52.7, 44.1, 34.2 ppm.

2-Amino-4-((2,2-dioxidobenzo[*e*][1,2,3]oxathiazin-4-yl)-4*H*-chromene-3-carbonitrile(9af):



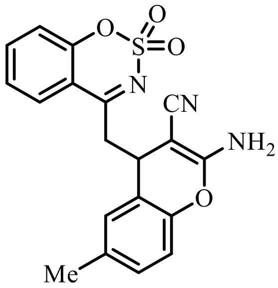
^{1}H NMR (500 MHz, , DMSO-d$_6$) δ 179.20, 161.84, 152.61, 148.89, 138.02, 131.37, 131.10, 130.16, 126.36, 125.10, 120.07, 118.72, 118.67, 118.31, 116.40, 116.22, 52.70, 44.11, 34.23 ppm; **^{13}C NMR (125 MHz, , DMSO-d$_6$)δ** 176.9, 161.5, 153.7, 147.1, 139.3, 137.1, 128.3, 125.8, 125.2, 122.8, 119.5, 119.3, 116.7, 112.6, 64.8, 57.7, 44.6, 34.5, 14.8 ppm.

2-Amino-4-((7-nitro-2,2-dioxidobenzo[*e*][1,2,3]oxathiazin-4-yl)methyl)-4*H*-chromene-3-carbonitrile(9ah)



^{1}H NMR (500 MHz, , DMSO-d$_6$) δ 8.39 – 8.29 (m, 1H), 8.15 – 8.06 (m, 2H), 7.84 (t, *J* = 7.9 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.27 – 7.14 (m, 3H), 4.37 (t, *J* = 5.6 Hz, 1H), 3.57 (dd, *J* = 5.7, 2.9 Hz, 2H) ppm; **^{13}C NMR (125 MHz,, DMSO-d$_6$) δ** 178.9, 161.1, 154.0, 152.4, 143.5, 137.9, 129.96, 126.2, 124.7, 124.2, 123.8, 119.5, 118.5, 117.3, 116.2, 52.6, 43.4, 33.5 ppm.

2-Amino-4-((7-methyl-2,2-dioxidobenzo[*e*][1,2,3]oxathiazin-4-yl)methyl)-4*H*-chromene-3-carbonitrile(9ai):



^{1}H NMR (500 MHz, , DMSO-d$_6$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.85 (q, *J* = 12.3 Hz, 1H), 7.54 – 7.39 (m, 2H), 7.12 – 6.93 (m, 4H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.10 (t, *J* = 6.0 Hz, 1H), 3.47 – 3.36 (m, 2H), 2.18 (s, 3H) ppm; **^{13}C NMR (125 MHz,, DMSO-d$_6$)** δ 178.7, 161.4, 151.8, 146.6, 137.2, 132.9, 129.3, 128.3, 127.9, 125.6, 121.3, 119.6, 117.9, 115.7, 115.1, 52.2, 44.0, 34.2, 19.5 ppm.

CHAPTER 5: CONCLUSION

In summary, we have synthesized an eco-friendly alkylation method for synthesizing 4-chromenyl-substituted *N*-sulfonyl ketimine in good yield via a C-C bond formation from 2-iminocoumarin and Cyclic *N*-sulfonyl ketimines in the presence of DABCO.

APPENDIX A

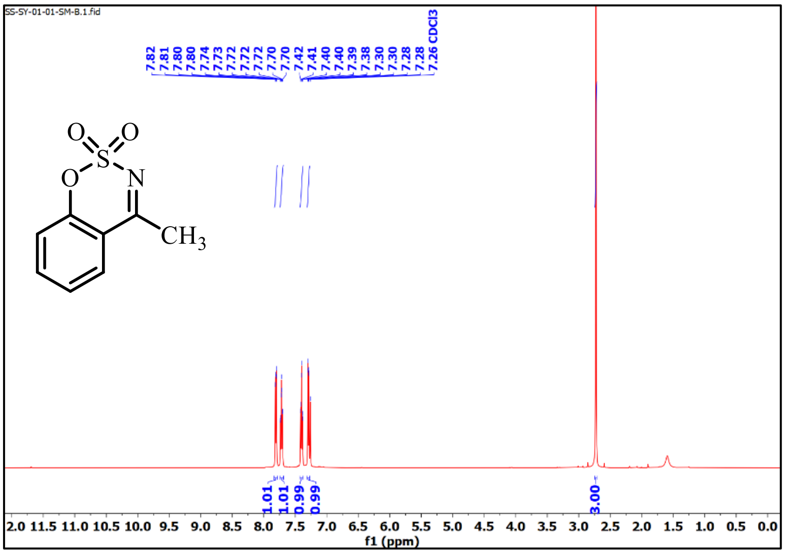


Figure1: ^{1}H NMR spectrum (500 MHz) of **8a** in $CDCl_3$

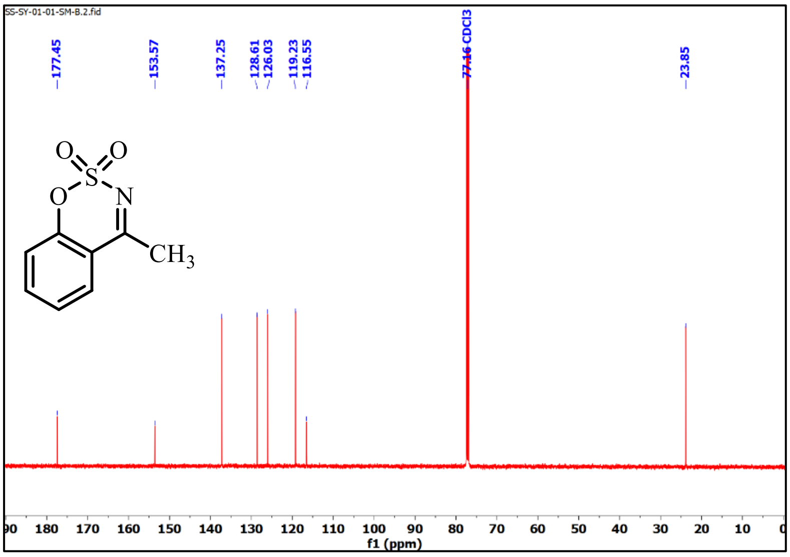


Figure 2: ^{13}C NMR spectrum (125 MHz) of **8a** in $CDCl_3$

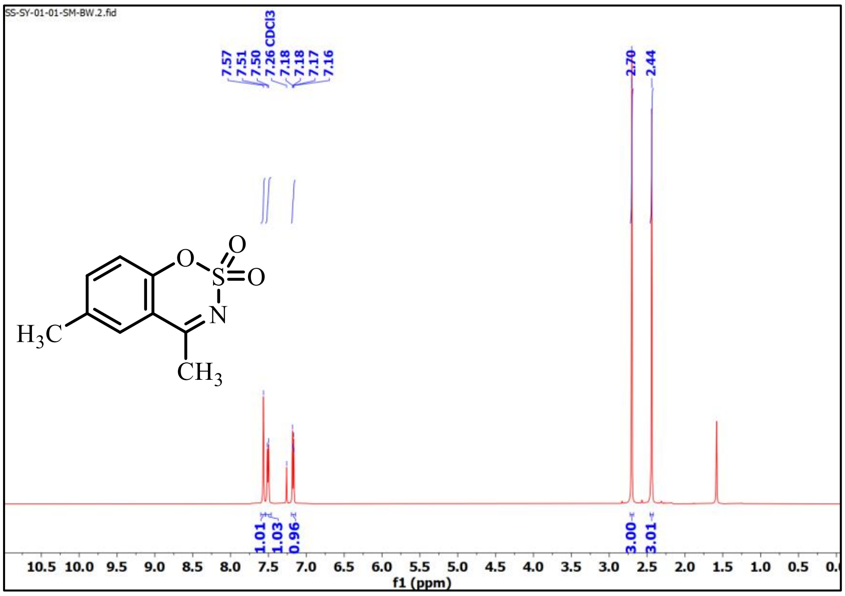


Figure 3: ^{1}H NMR spectrum (500 MHz) of **8b** in $CDCl_3$

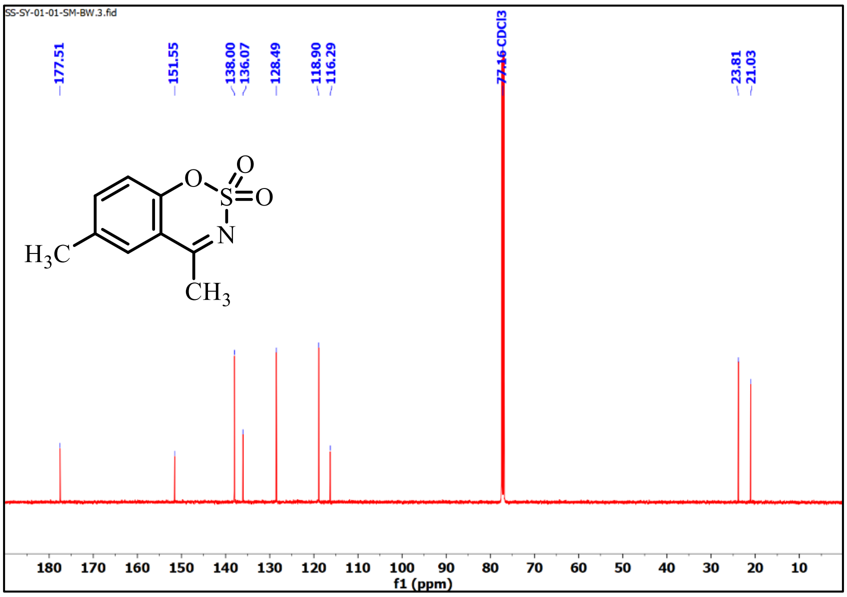


Figure 4: ^{13}C NMR spectrum (125 MHz) of **8b** in $CDCl_3$

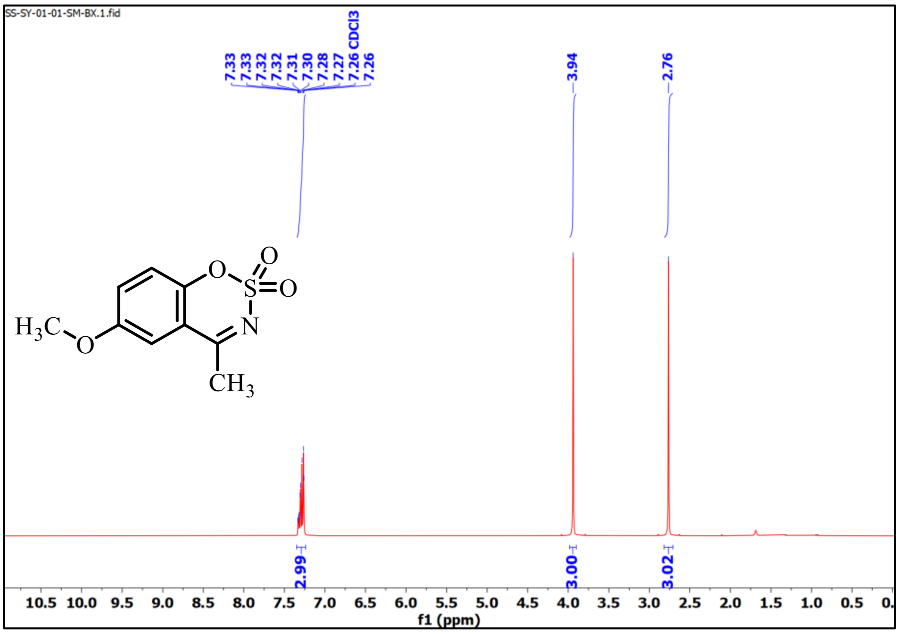


Figure 5: ^{1}H NMR spectrum (500 MHz) of **8c** in CDCl$_3$

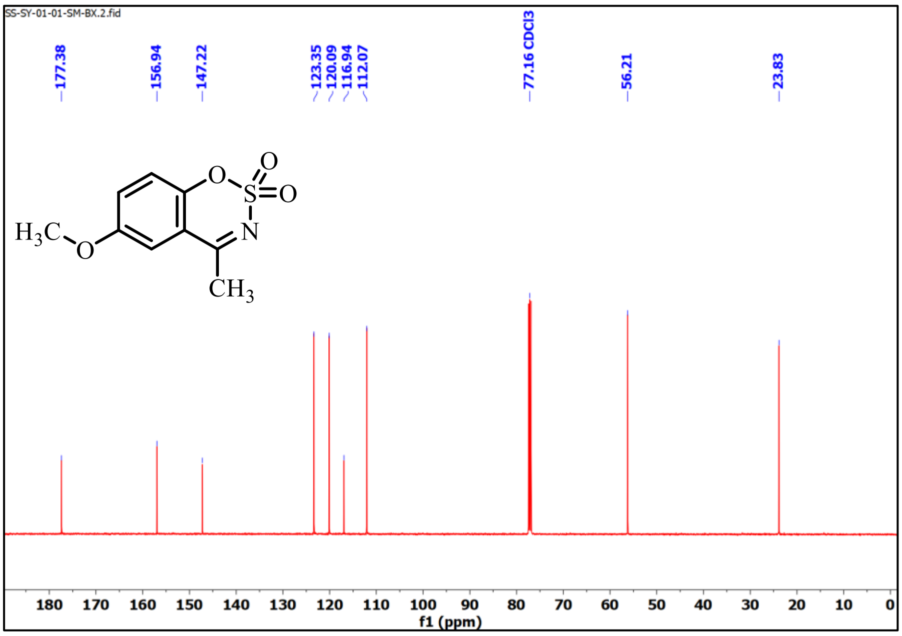


Figure 6: ^{13}C NMR spectrum (500 MHz) of **8c** in CDCl$_3$

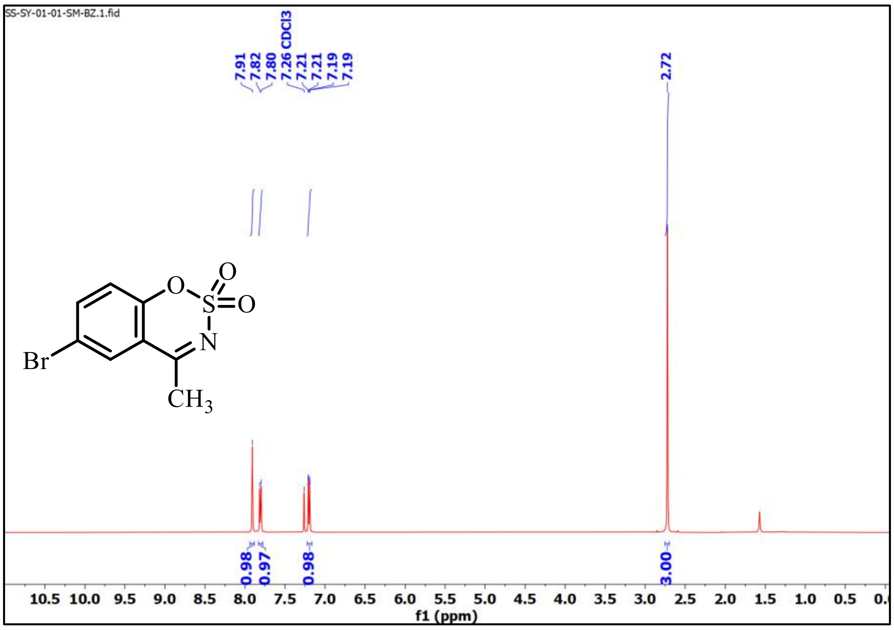


Figure 7: ^{1}H NMR spectrum (500 MHz) of **8d** in $CDCl_3$

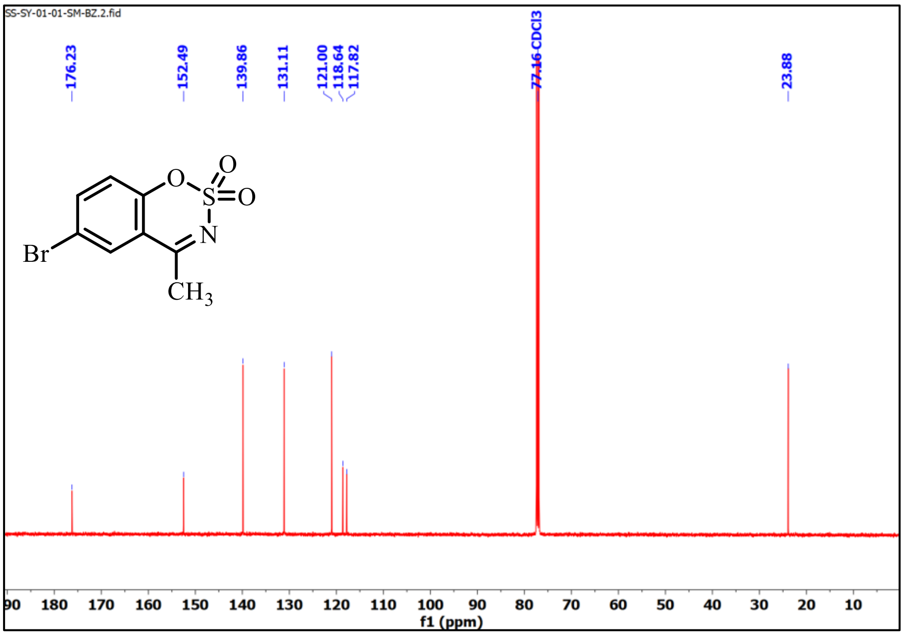


Figure 8: ^{13}C NMR spectrum (125 MHz) of **8d** in $CDCl_3$

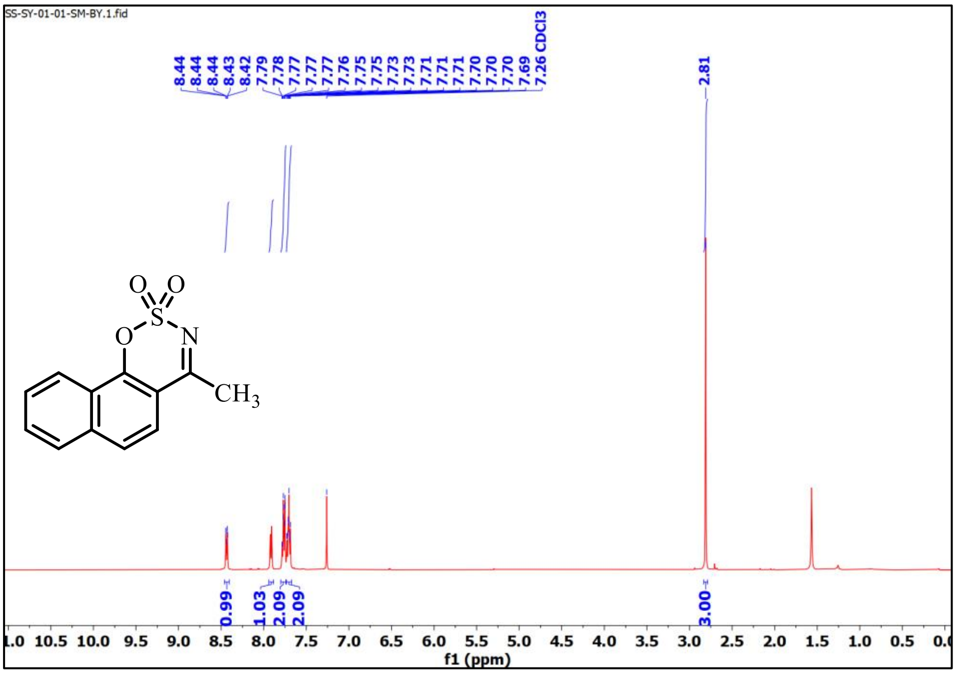


Figure 9: ^{1}H NMR spectrum (500 MHz) of **8e** in $CDCl_3$

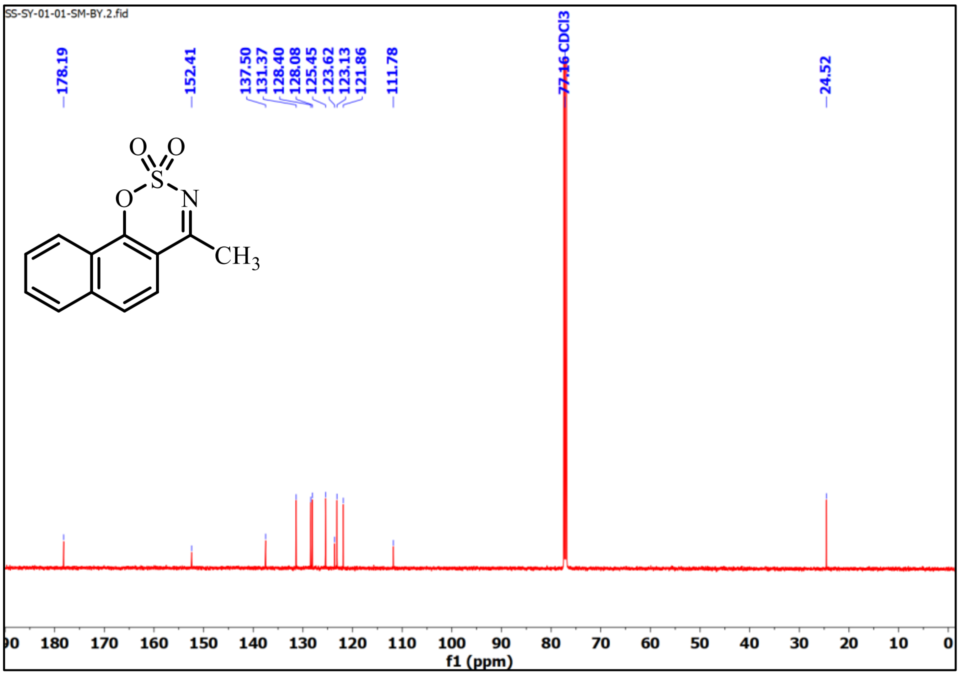


Figure 10: ^{13}C NMR spectrum (125 MHz) of **8e** in $CDCl_3$

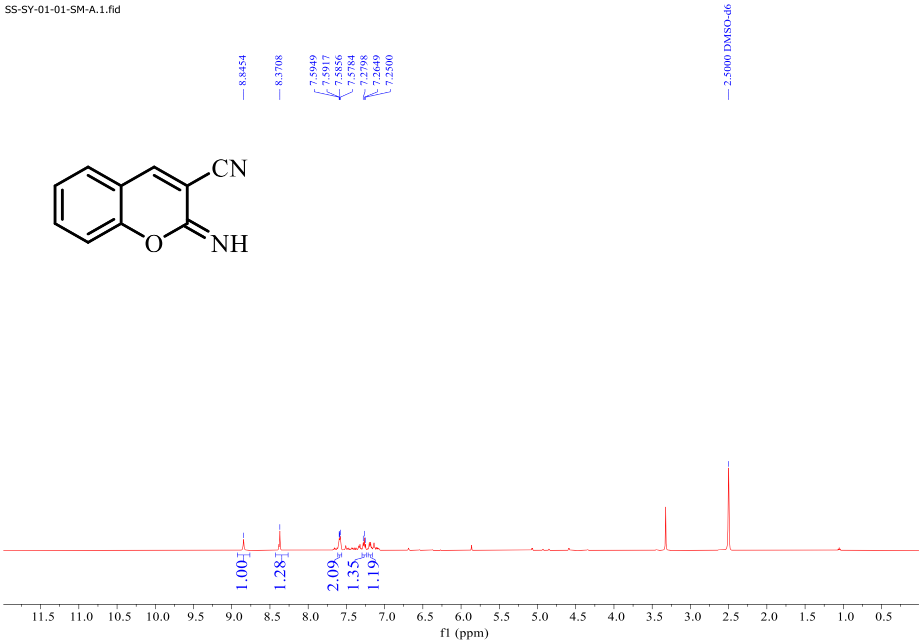


Figure 11: ^{1}H NMR spectrum (500 MHz) of **3aa** in DMSO-d$_6$

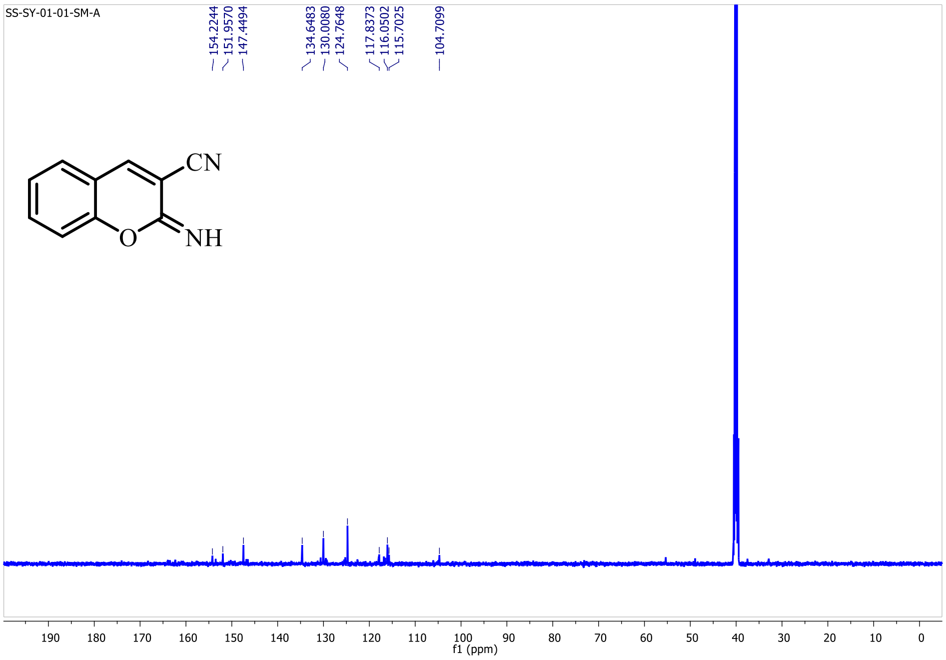


Figure 12: ^{13}C NMR spectrum (125 MHz) of **3aa** in DMSO-d$_6$

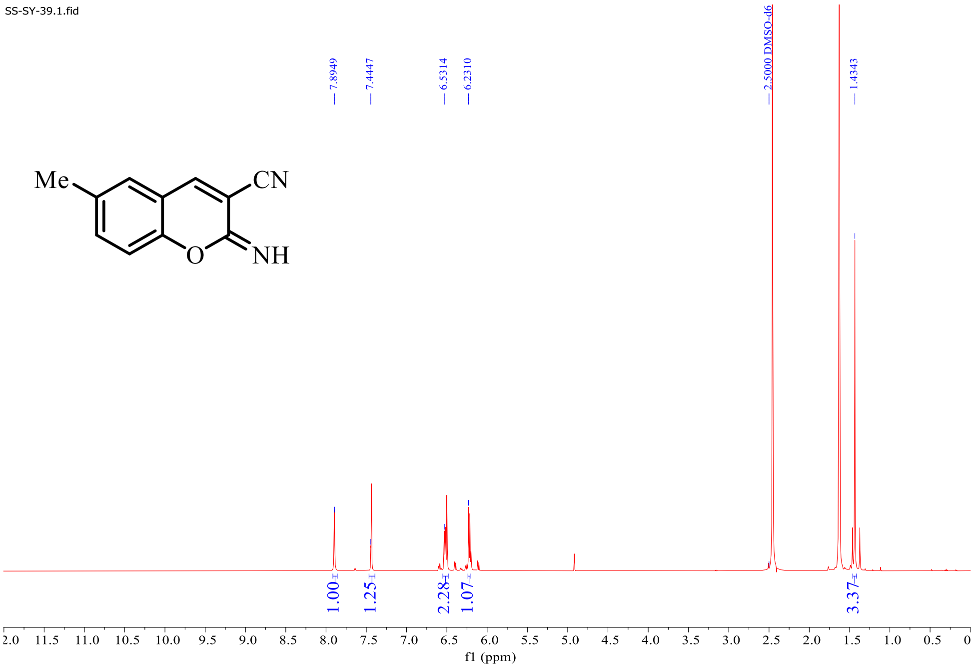


Figure 13: ^{1}H NMR spectrum (500MHz) of **3ab** in DMSO-d$_6$

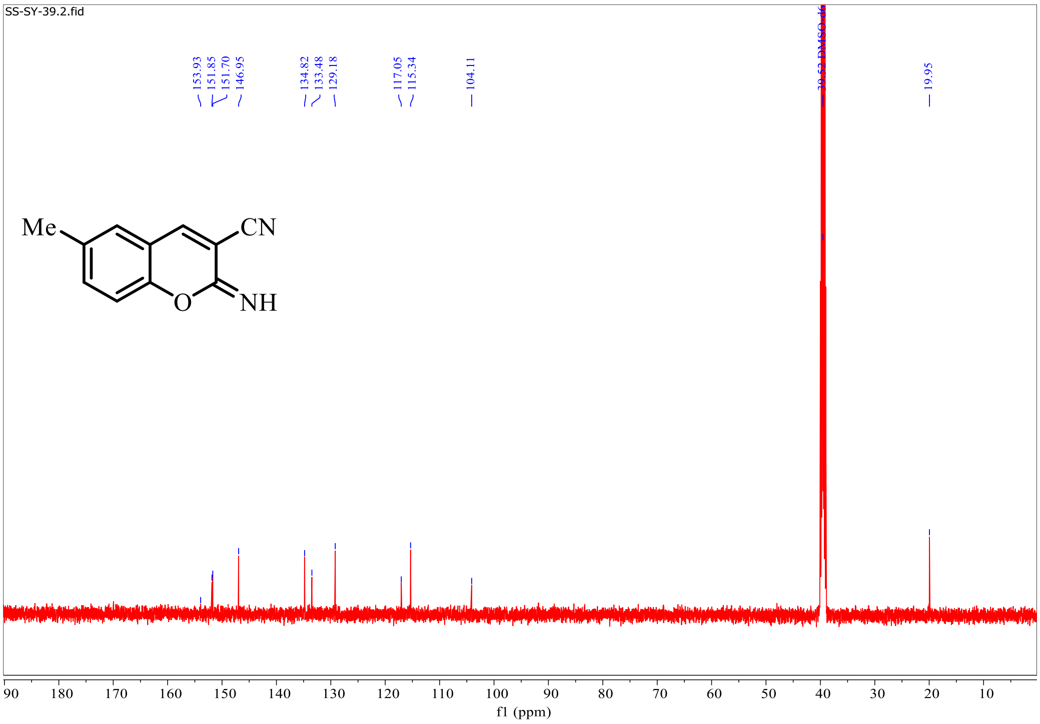


Figure 14: ^{13}C NMR spectrum (125MHz) of **3ab** in DMSO-d$_6$

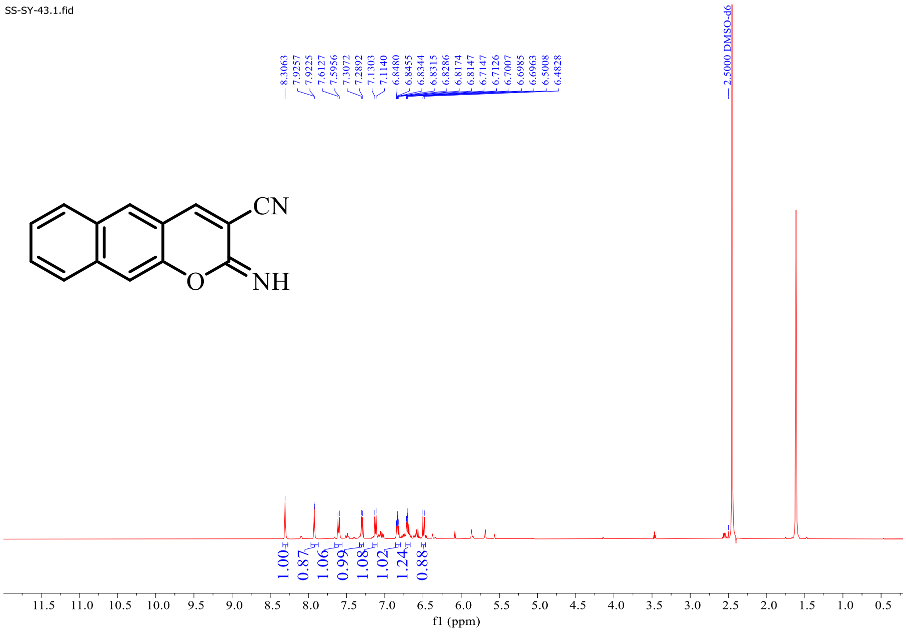


Figure 15: ^{1}H NMR spectrum (500MHz) of **3ac** in DMSO-d$_6$

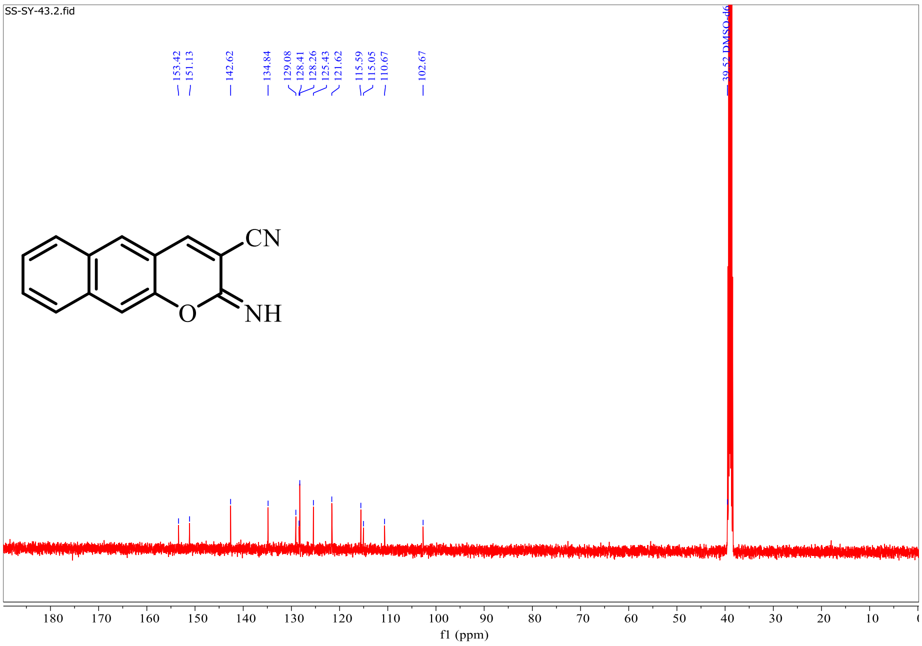


Figure 16: ^{13}C NMR spectrum (125MHz) of **3ac** in DMSO-d$_6$

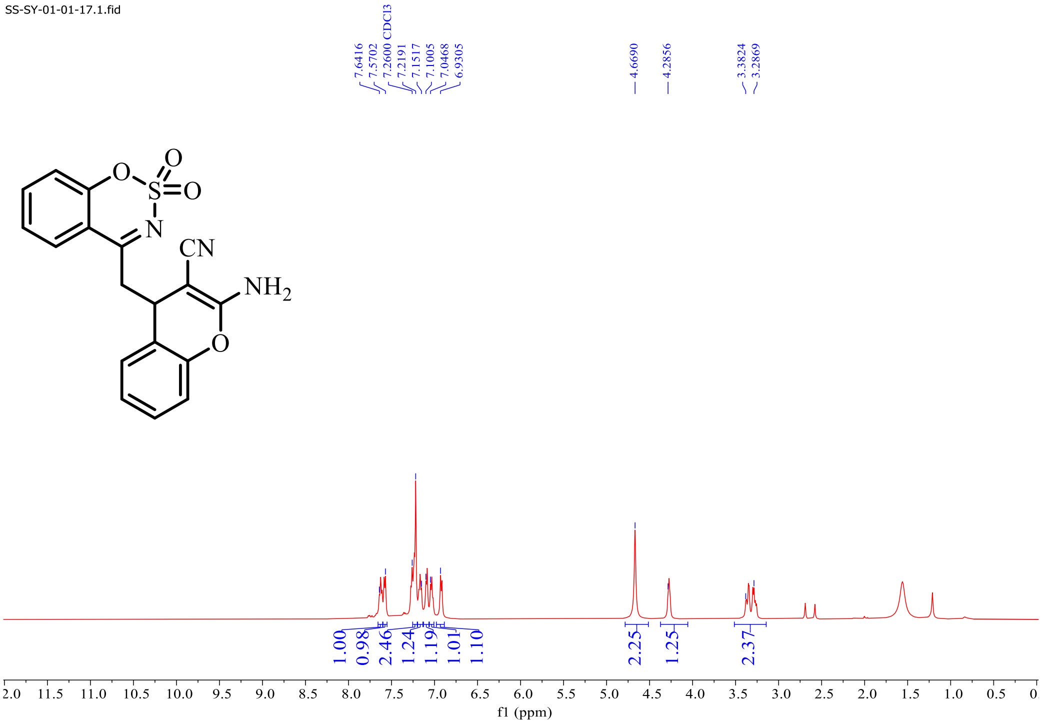


Figure 17: ^{1}H NMR spectrum (500MHz) of **9aa** in CDCl$_3$

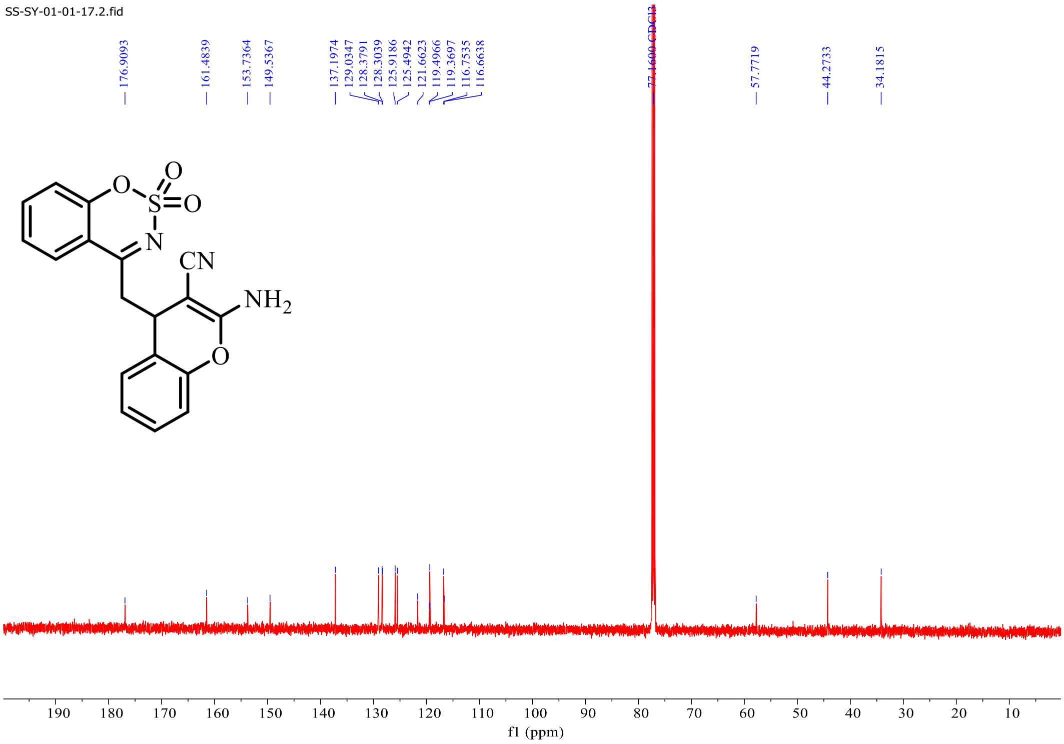


Figure 18: ^{13}C NMR spectrum (125 MHz) of **9aa** in CDCl$_3$

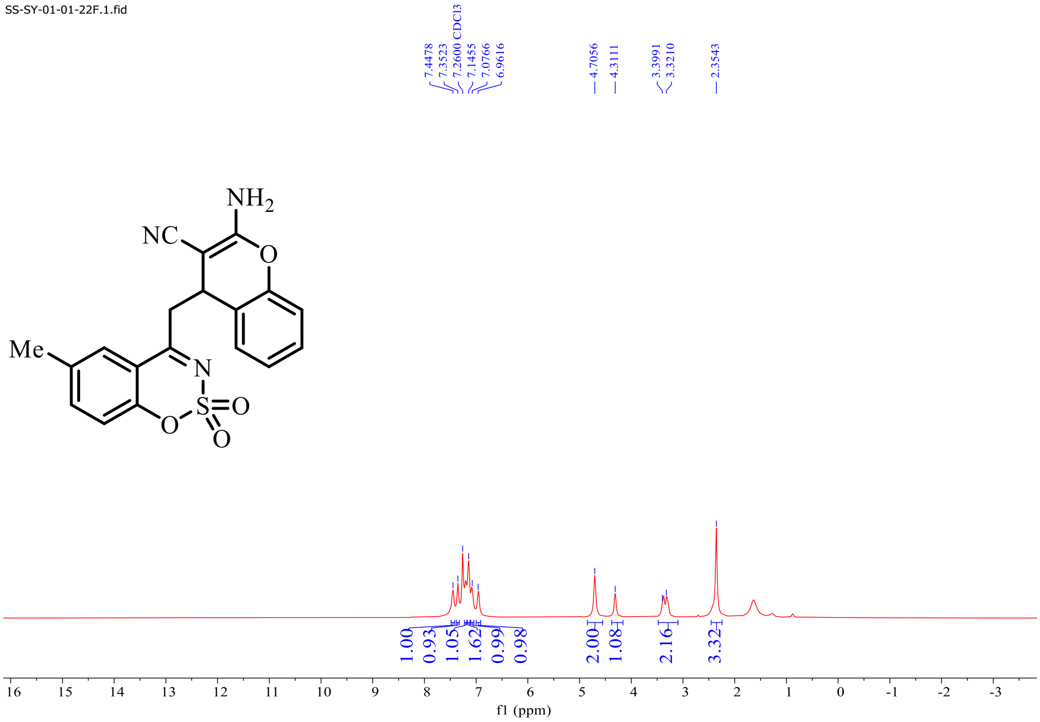


Figure 19: ^{1}H NMR spectrum (500 MHz) of **9ad** in CDCl$_3$

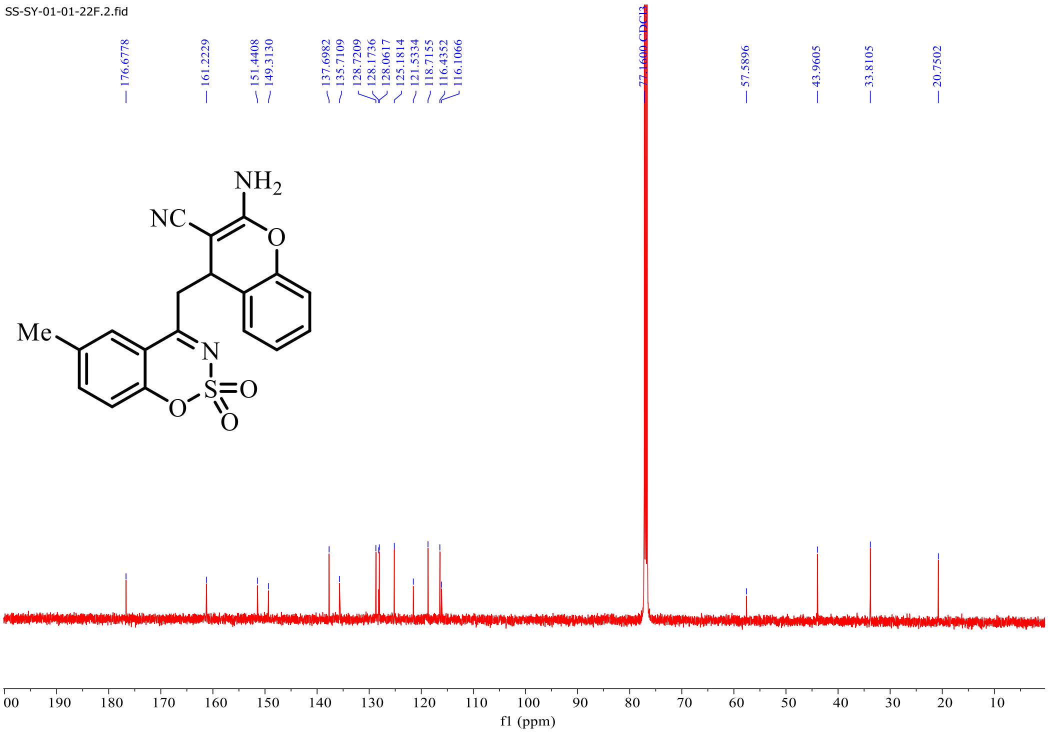


Figure 20: ^{13}C NMR spectrum (125 MHz) of **9ad** in CDCl$_3$

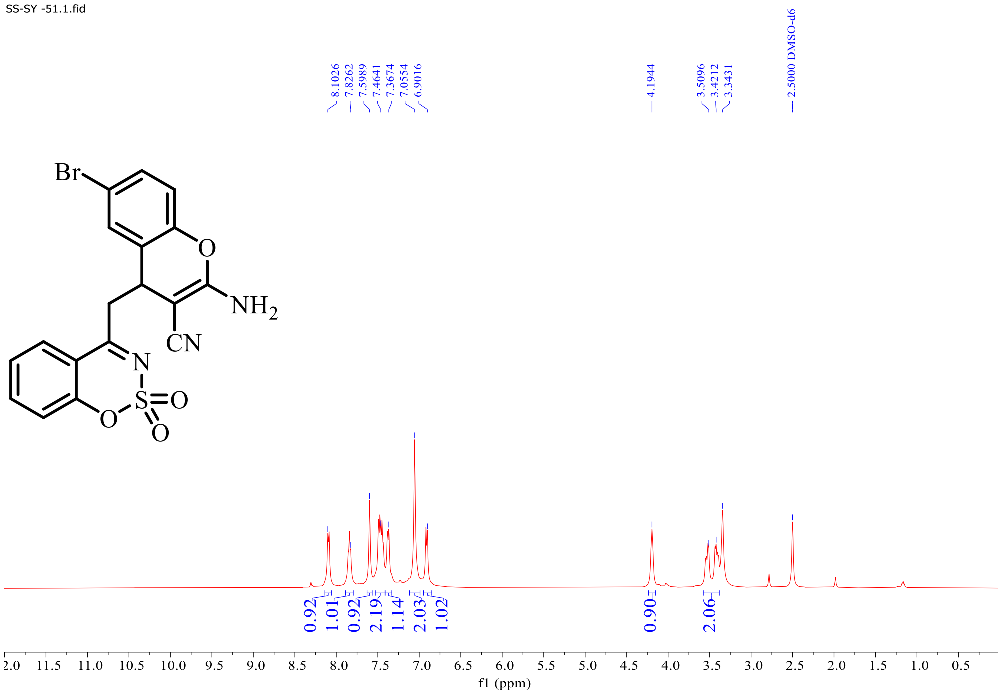


Figure 21: ^{1}H NMR spectrum (500 MHz) of **9ae** in DMSO-d_6

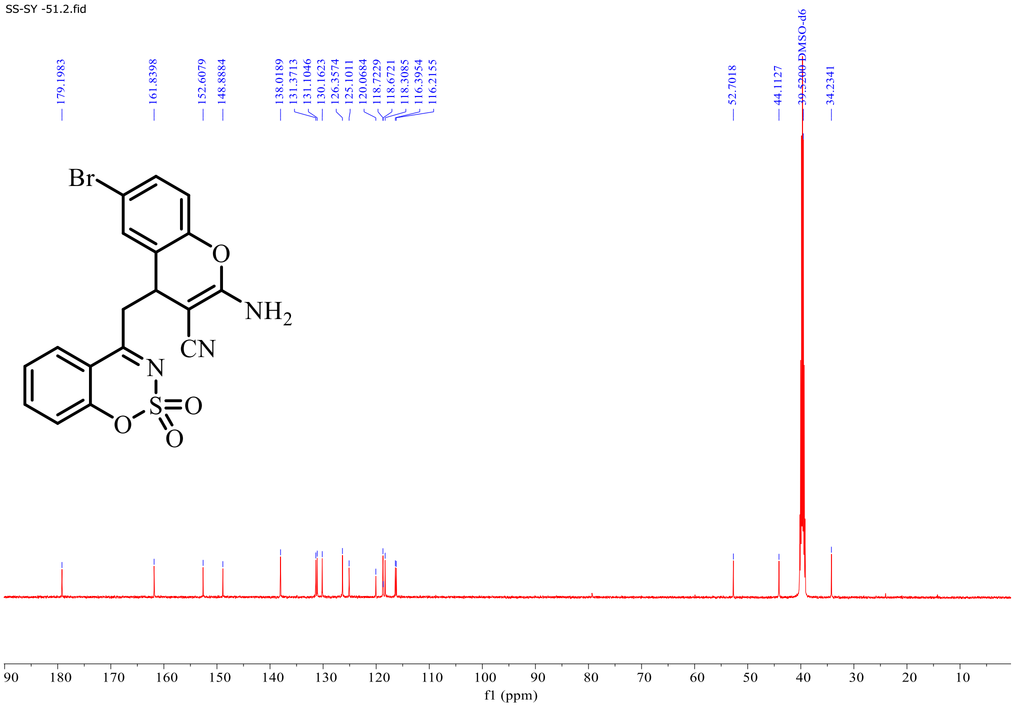


Figure 22: ^{13}C NMR spectrum (125 MHz) of **9ae** in DMSO-d_6

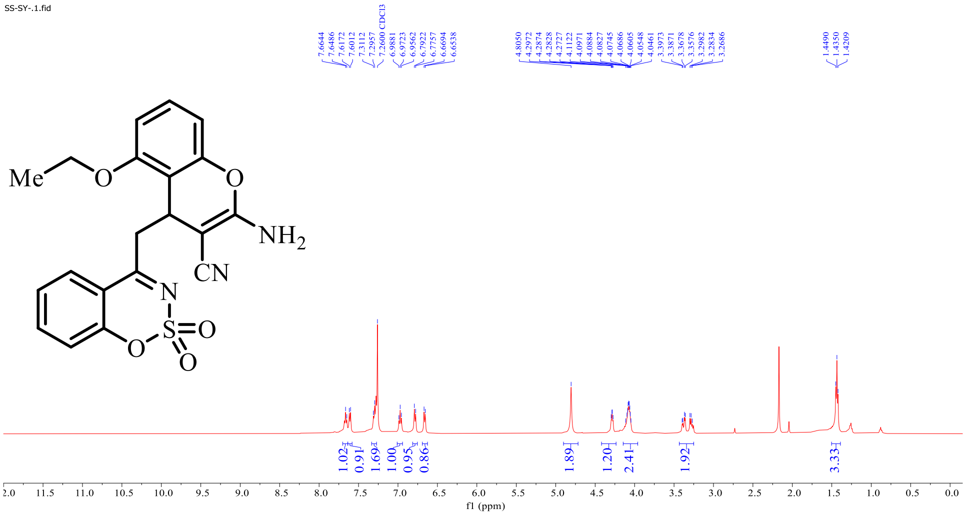


Figure 23: ^{1}H NMR spectrum (500 MHz) of **9af** in DMSO-d$_6$

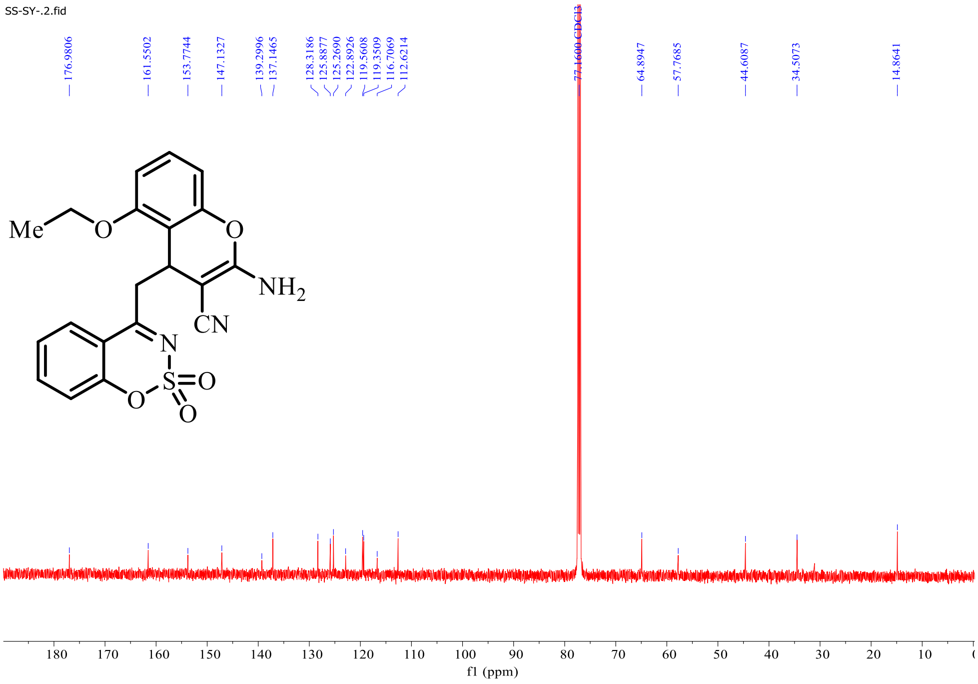


Figure 24: ^{13}C NMR spectrum (125 MHz) of **9af** in DMSO-d$_6$

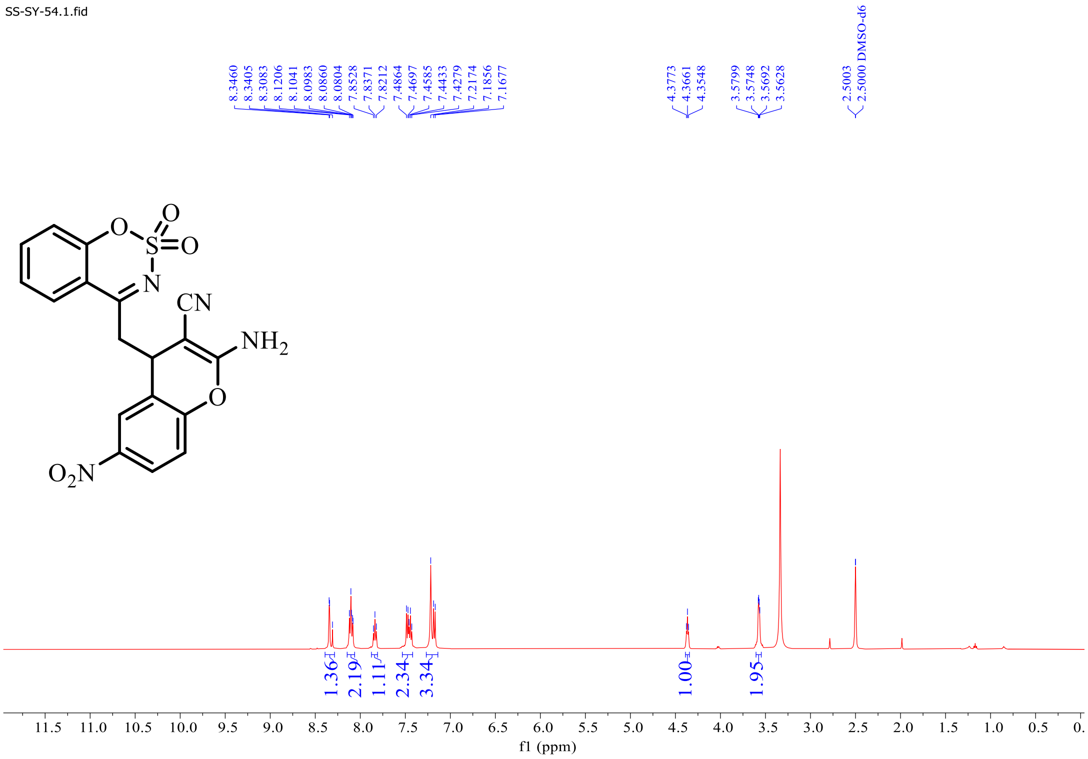


Figure 25: ^{1}H NMR spectrum (500 MHz) of **9ah** in DMSO-d_6

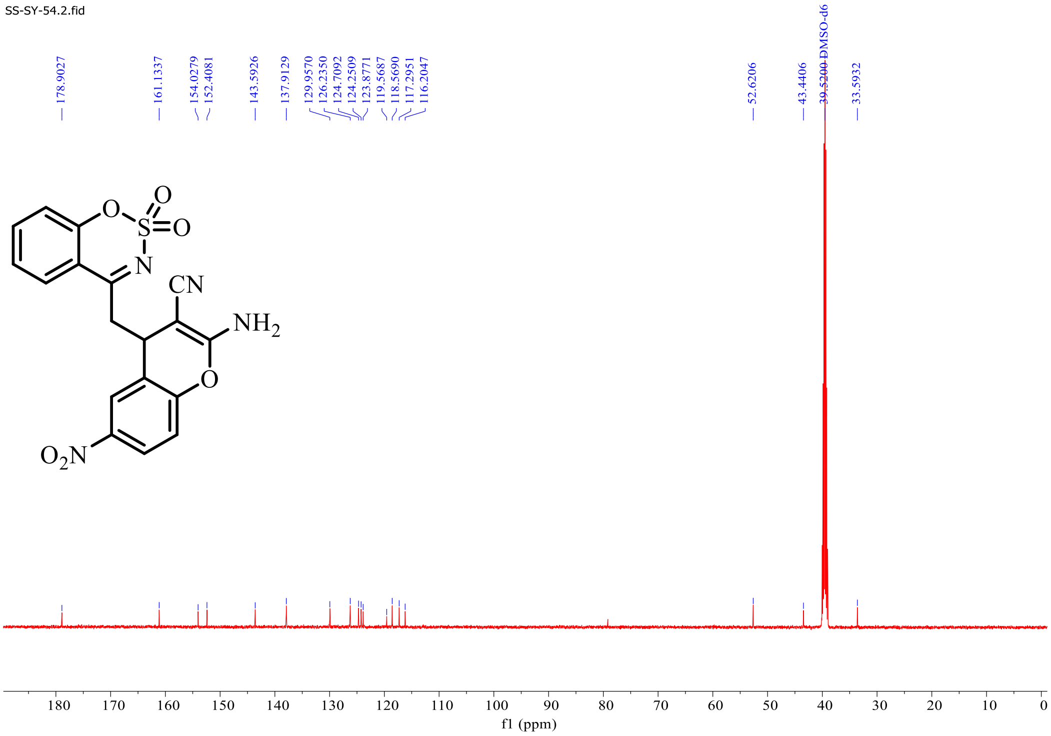


Figure 26: ^{13}C NMR spectrum (125 MHz) of **9ah** in DMSO-d_6

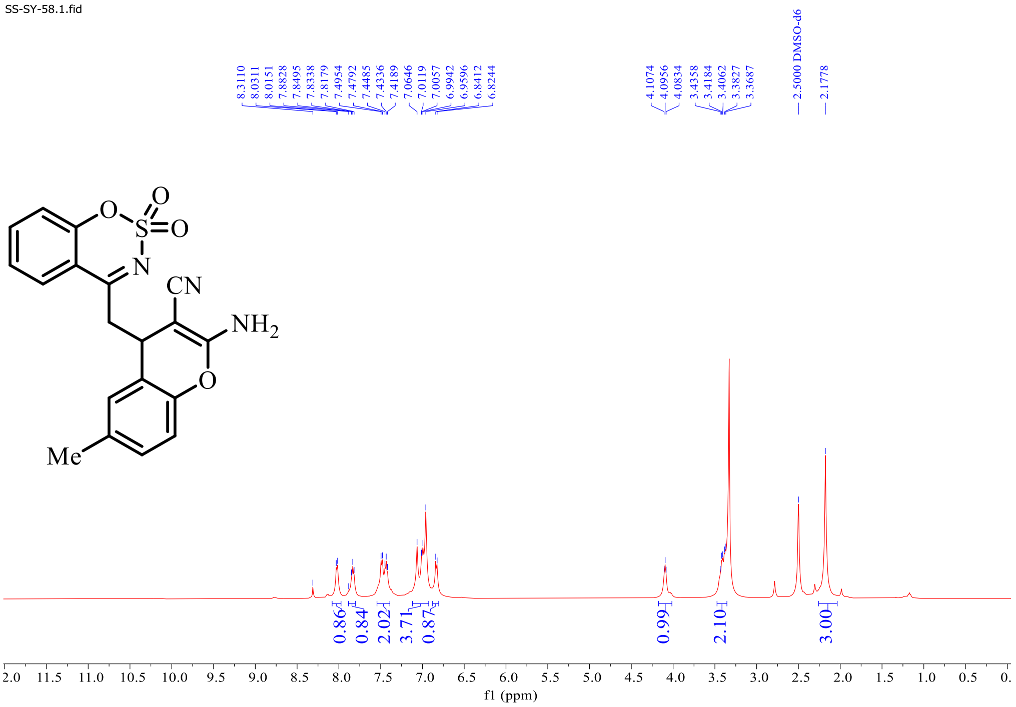


Figure 27: ^{1}H NMR spectrum (500 MHz) of **9ai** in DMSO-d_6

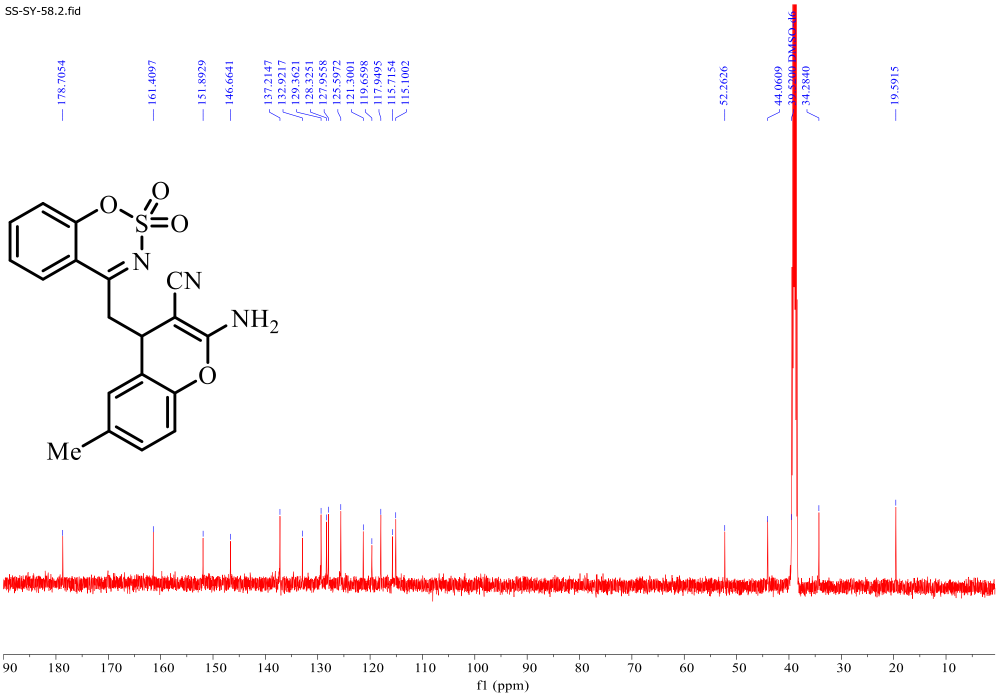


Figure 28: ^{13}C NMR spectrum (125 MHz) of **9ai** in DMSO-d_6

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