Visible Light Mediated Synthesis of Thioaryl sulfonamide *via* N-S Bond Formation

M.Sc. Thesis

by

Mirja Samim Ali

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY INDORE
MAY,2026

Visible Light Mediated Synthesis of Thioaryl sulfonamide *via* N-S Bond Formation

A Thesis

Submitted in partial fulfillment of the requirements for the award of the degree
of
Master of Science

by

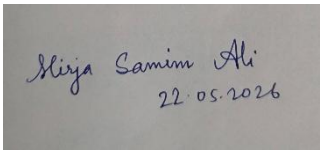
Mirja Samim Ali

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MAY,2026

INDIAN INSTITUTE OF TECHNOLOGY INDORE

Declaration

I hereby certify that the work being presented in the report entitled **"Visible Light Mediated Synthesis of Thioaryl sulfonamide *via* N-S bond Formation**" in the partial fulfillment of the requirements for the award of the degree of Master of Science and submitted in the **Deparment of Chemistry, Indian Institue of Technology Indore,** is an authentic record of my own work carried out during the period from July, 2025, to May, 2026, under the supervision of **Prof. Debayan Sarkar**, Professor, Department of Chemistry, IIT Indore.



Signature of Student with date

(Mirja Samim Ali)

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



22.05.2026

Signature of the Supervisor with date

(Prof. Debayan Sarkar)

Mirja Samim Ali has successfully given his M.Sc Oral Examination held on **21st May, 2026**



Signature of Supervisor M.Sc thesis

Acknowledgment

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I am deeply obliged to my parents, teachers and friends who encouraged me throughout this wonderful journey.

Mirja samim Ali

Abstract

Sulfonamide derivatives are important organic compounds because of their wide range of biological and pharmaceutical applications, including antibacterial, anti-inflammatory, and antiviral activities. Conventional methods for the synthesis of sulfonamides often require toxic amine sources, harsh reaction conditions, expensive catalysts, or environmentally harmful reagents. Therefore, the development of sustainable and environmentally benign approaches for sulfonamide synthesis remains highly desirable. In this work, a visible light-mediated protocol for the synthesis of thioarylsulfonamide derivatives *via* N–S bond formation has been developed under mild reaction conditions. The transformation was carried out using chloramine-T as the sulfonamide source and Riboflavin tetraacetate (RFTA) as the photocatalyst under blue LED irradiation.

Optimisation studies revealed that a mixed solvent system of ACN:H_2O (9:1) under open-air conditions yielded the highest reaction efficiency. A wide variety of aromatic and aliphatic thiols bearing electron-donating and electron-withdrawing substituents were successfully converted into the corresponding thioarylsulfonamides in moderate to excellent yields. However, substrates containing strongly electron-withdrawing substituents, such as nitro and cyano groups, showed little or no reactivity under the optimised conditions. Mechanistic investigations suggest that the reaction proceeds through a visible-light-driven photoredox pathway involving sulfur-centred and nitrogen-centred radical intermediates followed by radical cross-coupling to form the N–S bond.

The synthesized compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, confirming the successful formation of the desired products. This methodology provides a simple, efficient, and greener alternative for the synthesis of biologically important sulfonamide derivatives and highlights the potential of visible-light photoredox catalysis in modern organic synthesis

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ABBREVIATIONS

G	Gram
Mg	Milligram
H	Hour
Min	Minute
R.T.	Room Temperature
Equiv.	Equivalent
mL	Millilitres
mol	Mole
mmol	Millimole
ACN	Acetonitrile
PC	Photocatalyst
n.d.	not detected
DMSO	DimethylSulfoxide
MHz	mega hertz

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Chapter-1

Introduction

Nowadays, Sulfonamide compounds containing SO_2NH_2 are crucial compounds because of their broad range of applications. Currently, many sulfonyl derivatives are used for the treatment of various types of diseases, such as heart failure, HIV, cancer treatment, serious burns, and inflammatory diseases, and many other medical conditions.[1] Antimicrobial compounds containing the sulfonamide group are significant because of their distinct mode of action and their historical and contemporary use in the treatment of a variety of bacterial illnesses. Several antimicrobial drug molecules having a sulfonamide unit are traditionally prepared by the reactions between heterocyclic primary amines and aromatic sulfonyl halides, e.g., sulfacetamide, sulfodiazine, and sulfamethoxazole, etc. The classical approach to aryl sulfonamide scaffold synthesis relies on nucleophilic substitution between activated sulfonyl precursors (e.g., sulfonyl halides, sulfinate salts, or sulfonic acids) and amines as nitrogen nucleophiles.[2] However, most aromatic amines are a cause of toxicity, a pollutant of the environment, and some amines are considered hazardous to human health, causing significant toxicity, including the development of cancer. In the era of synthetic organic chemistry for sulfonamide synthesis, there are several reaction methodologies already reported using the reaction between N-atom-containing moieties (Amines) and S-atom-containing scaffolds. However, these methods have certain drawbacks, including the use of hazardous amine sources and expensive chemicals, among others. To date, extensive research efforts are still in process to design environmentally benign and sustainable approaches for the synthesis of structurally diverse sulfonamide analogues. Therefore, our research group aims to contribute to the advancement of sulfonamide development, and we have begun exploring greener and milder conditions for the synthesis of sulfonamide scaffolds

Sulfonamides are very important molecules, particularly in medicinal

chemistry, and are widely used as antibacterial drugs to treat infections. In addition to medicinal applications, they also serve as pesticides in agriculture and find use in materials science. Their simple structure and strong biological activity make them valuable building blocks in drug design. I have mentioned some Sulfonamides analogues, which are biologically very important for the treatment of various diseases, in Fig. 1.[3]

Sulfasalazine is an anti-inflammatory drug used to treat inflammatory bowel diseases and rheumatoid arthritis by reducing inflammation and controlling symptoms. Delavirdine is an antiretroviral drug used in the treatment of HIV infection by inhibiting reverse transcriptase and preventing viral replication. Recognizing the importance of sulfonamides, we decided to initiate our investigation into their synthesis using a visible light-mediated method, which offers a milder and greener approach for a more sustainable environment. So, we are finally able to demonstrate a novel and efficient method for the synthesis of numerous sulfonamide derivatives under visible light mediated, which is titled as Visible Light Mediated Synthesis of Thioaryl sulfonamide via N-S bond Formation.

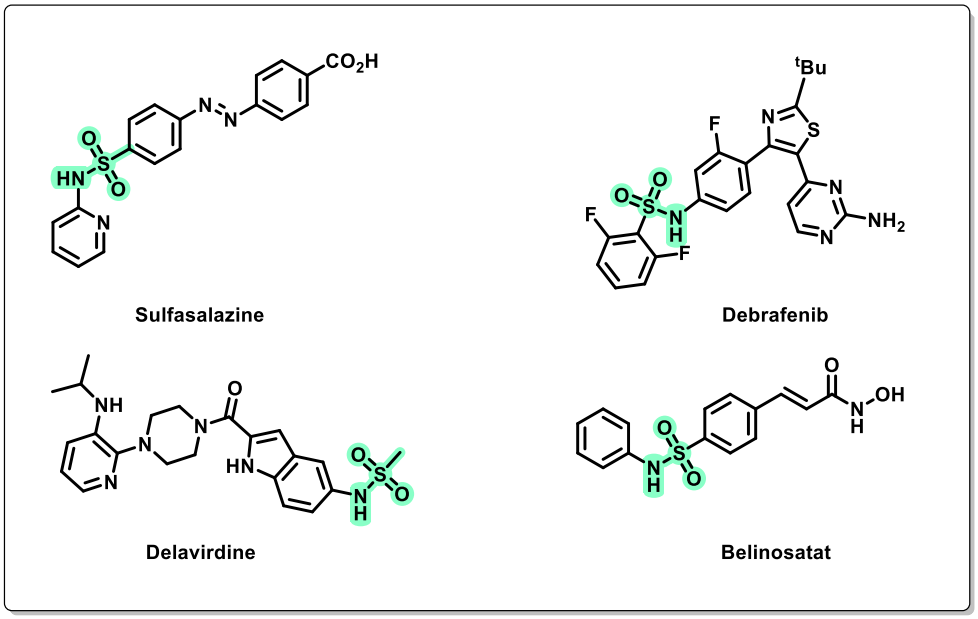


Fig. 1: Selected FDA-approved drugs with sulfonamide structure motif.

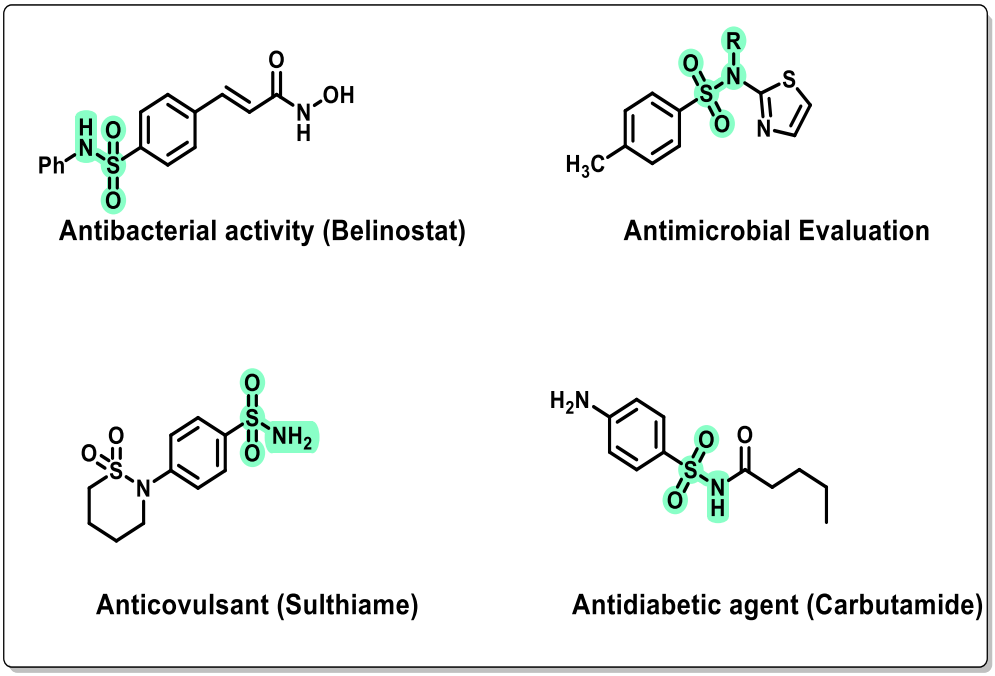
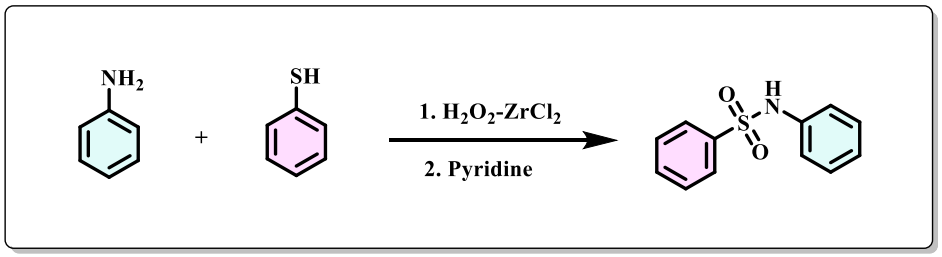


Fig. 2: Drugs with sulfonamide structure motif.

Chapter-2

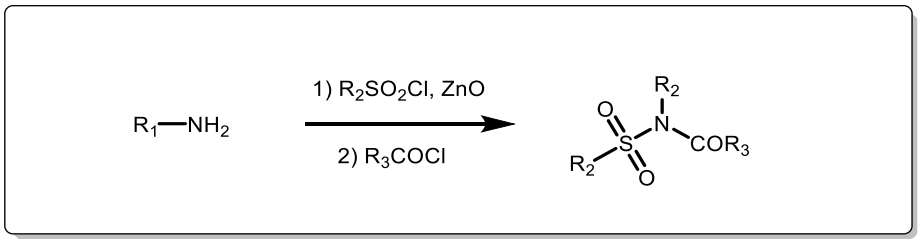
Literature Review

In **2010**, sulfonamide derivatives were synthesized in situ by **Bahrami** *et al*. using primary amine (Aniline) and benzene thiol (Thiophenol), where the SH group of Thiophenol gets oxidised by an oxidising agent, hydrogen peroxide, followed by chlorination. In the next step, they used Pyridine (Py) as a base to form the desired product in excellent yields of up to 98%. In this reaction, they used hydrogen peroxide (H_2O_2) as an oxidizing agent and Zirconium chloride as a chlorinating agent.



Scheme 1: Scheme for the synthesis of sulfonamide by Bahrami et al.

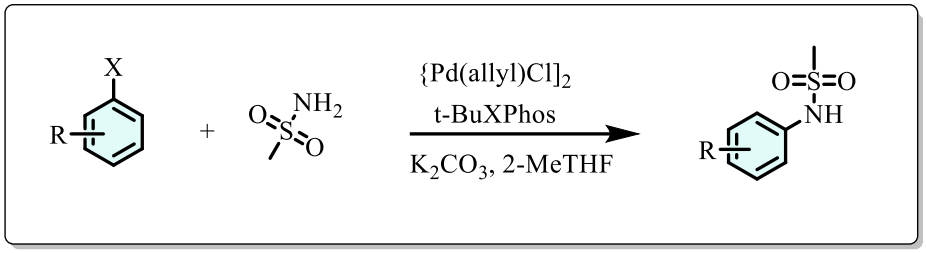
In **2011**, **Tamaddon** *et al.* developed a nanoparticle-catalysed and Solvent-free method for the synthesis of sulfonamide analogues using the reaction between a primary amine and a sulfonyl chloride, achieving excellent yields of up to 95%. In this transformation, zinc oxide (ZnO) nanoparticles were used as a catalyst, which helps to speed up the reaction and improve the overall efficiency. The use of ZnO nanoparticles along with solvent-free conditions highlights this method as a greener and sustainable approach for sulfonamide synthesis.



Scheme 2: Scheme for the synthesis of sulfonamide by Tamaddono et al.

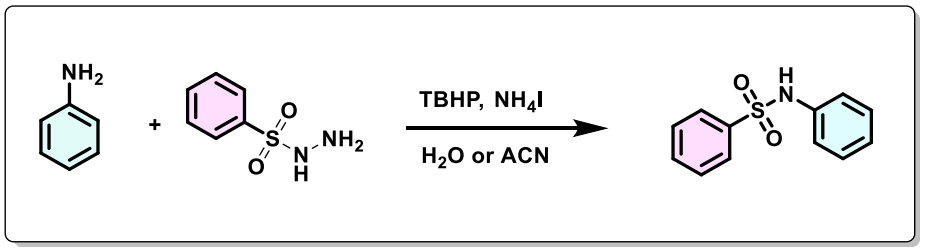
In **2011, Rosen** *et al.* reported a mild palladium-catalyzed N-arylation

method for methanesulfonamide and related nucleophiles, providing an efficient route to aryl sulfonamides. The reaction proceeds under relatively gentle conditions and avoids the use of potentially genotoxic reagents and harmful byproducts, which are commonly associated with traditional methods. A suitable ligand system enables effective C–N bond formation with good functional group tolerance and high yields. Overall, this methodology offers a safer and more practical alternative for the synthesis of sulfonamide derivatives.



Scheme 3: Scheme for the synthesis of sulfonamide by Rosen *et al*.

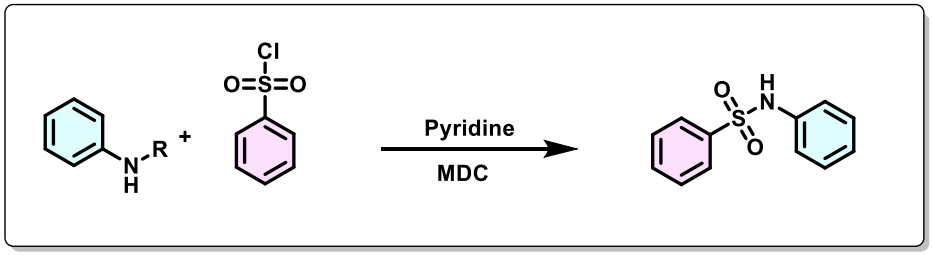
In **2016, Yu** *et al*. developed a method to prepare sulfonamides using benzenesulfonyl hydrazine and aniline as starting materials. In this reaction, tert-butyl hydroperoxide (TBHP) was used as an oxidizing agent, while ammonium iodide acted as a catalyst to promote the reaction. The process was carried out with water and acetonitrile (ACN) as solvents. This method provided moderate to good yields of the desired sulfonamide products, demonstrating it to be a useful and practical approach



Scheme 4: Scheme for the synthesis of sulfonamide by Yu *et al*.

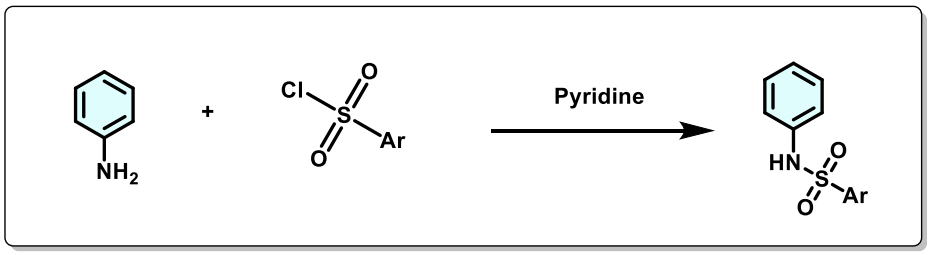
In **2016, Wang** *et al.* developed a method for the synthesis of sulfonamide moieties using secondary amines such as N-methylaniline and diphenylamine. Their study focused on understanding the reaction mechanism, particularly homolytic cleavage and radical-radical coupling involved in sulfonyl migration processes. The reaction was carried out using pyridine as a base in a chlorinated solvent, with

benzenesulfonyl chloride added slowly in portions. Under these conditions, the method provided excellent yields of up to 97%, demonstrating its high efficiency.



Scheme 5: Scheme for the synthesis of sulfonamide by Wang et al.

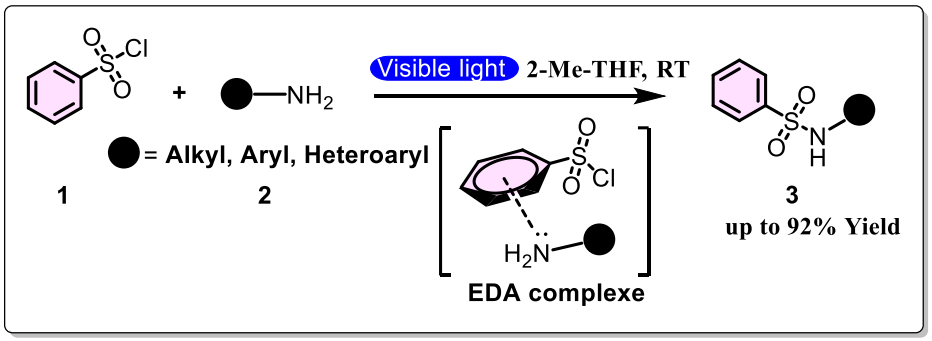
In **2017,** sulfonamide was synthesized by **Youn** *et al.*'s research group using aryl primary amine and aryl sulfonyl chloride. In this reaction, they used pyridine as a base, and the reaction occurred at 0-25°C. They found 100% yield when they used aniline as the primary amine and benzene sulfonyl chloride or 4-nitrobenzyl sulfonyl chloride as a sulfonylating agent under the same reaction conditions.



Scheme 6: Scheme for the synthesis of sulfonamide by Youn *et al.*

In **2023**, **S. Singh** *et al.* developed a visible-light-triggered method for the synthesis of sulfonamides through an electron donor–acceptor (EDA) complex strategy using green 2-methyltetrahydrofuran (2-MeTHF) as the solvent. The reaction proceeds efficiently at room temperature without the use of external photocatalysts, bases, or transition metals, making the process environmentally friendly and cost-effective. This approach provides high yields, excellent atom economy, and broad functional group compatibility under mild reaction conditions. The protocol also demonstrated practical applicability through gram-scale synthesis and successful operation under sunlight

irradiation.



Scheme 7: Scheme for the synthesis of sulfonamide by **S. Singh** *et al.* via EDA complex.

Chapter-3

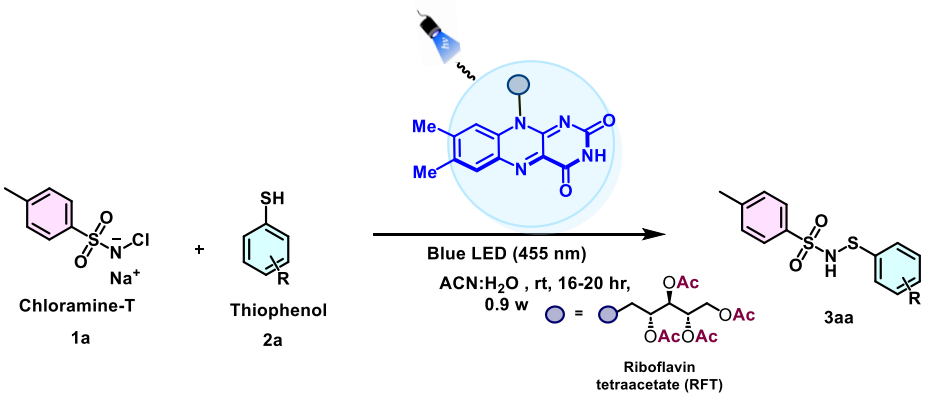
Objective

The main objective of this work was to develop a visible light-mediated, green, and efficient protocol for the synthesis of thioarylsulfonamide derivatives through N–S bond formation under mild reaction conditions. This study aimed to utilize chloramine-T as the sulfonamide source and Riboflavin tetraacetate (RFTA) as a photocatalyst under blue LED irradiation to achieve a sustainable synthetic transformation. Another important objective was to optimize the reaction conditions by examining the effects of solvents, photocatalysts, light, and atmospheric conditions in order to obtain better yields of the desired products. The work also focused on exploring the substrate scope using various aromatic and aliphatic thiols containing electron-donating and electron-withdrawing groups. Furthermore, the study aimed to investigate the plausible visible-light-driven photoredox mechanism involving sulfur-centred and nitrogen-centred radical intermediates. Finally, all synthesized compounds were characterized using spectroscopic techniques such as ^{1}H NMR and ^{13}C NMR spectroscopy to confirm the successful formation of thioarylsulfonamide derivatives.

Chapter-4

Results and Discussions

In order to determine the optimal conditions for the synthesis of thioarylsulfonamide, we initiated our study using paratoluenethiophenol (1 equiv.) as a model substrate, chloramine T (1.2 equiv.) as the source of SO_2N moieties, and RFTA as the photocatalyst, under blue LED irradiation in a polar aprotic solvent. In the presence of a photocatalyst, sulfur-centred radical intermediates are generated under mild conditions and several reports demonstrated that in the presence of visible light, N-centred radical is generated by homolytic cleavage of the N-Cl bond of chloramine T. We are speculating that the photocatalytic approach may be a direct and sustainable transformation of thiols into sulfonamide moieties. However, achieving selective N–S bond formation without disulfide byproduct requires careful and systematic optimization of the reaction conditions. Therefore, a detailed investigation of solvent, photocatalyst, catalyst loading, temperature, and atmospheric conditions was carried out in a stepwise manner.



Scheme 8: Schematic representation of our work.

Step 1: Solvent Screening and Initial Observations:

We did optimization studies for the above transformation to analyse the solvent effect on the substrate, as the solubility of the substrate depends on the solvents. Therefore, solvents have an important role. Initially, the reaction occurred in acetonitrile upon blue light irradiation in the

presence of a photocatalyst. We found only 47% yield in this condition after 20 hours. After reviewing the literature, we had expected a solubility issue with Chloramine-T in ACN solvent, which leads to a lower yield of the desired product. So, we continued our optimization process to enhance the yield of our isolated product.

To enhance the solubility of chloramine T, we tried with more polar solvents such as MeOH and DMSO individually, but we did not find any transformation. Then we used a 9:1 ratio of ACN:H_2O as a mixture of solvent, and we found yield is increased to 70%. Then we tried 9:1 ratio of H2O as a mixture of solvent, but we did not found any transformation. Then we could say the presence of water is responsible for the better solubility of chloramine-T and the increased efficiency of interaction between substrates.

Step 2: Screening of Photocatalysts:

After optimizing the solvent effect, we moved on to optimizing the photocatalyst. Initially, we performed the reaction in the presence of **$Ru(bpy)_3Cl_2$** as a photocatalyst. We found only 36% yield. After that, we used another photocatalyst, Rose Bengal, but we did not get a significant yield. Then we tried RFTA for this transformation, and we found a good yield of 70%. Based on these results, RFTA was taken as the optimal photocatalyst for further studies.

Step 3: Effect of Atmospheric Conditions:

To investigate the role of oxygen, we performed the reaction under different atmospheric conditions. When the reaction was carried out under open air, a comparable yield of 70% was obtained, indicating that excess oxygen does not significantly enhance the reaction efficiency. In contrast, performing the reaction under an inert atmosphere (N_2) resulted in no transformation occurring.

Table 1: Optimisation table of sulfonamide (3a) with different solvents and reaction environments[a]

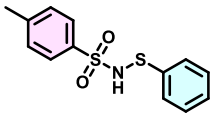
Entry	PC	Solvents	Light	Environment	Yield[b] (%)
1	RFTA	ACN: H_2O (9:1)	Present	O_2	70
2	RFTA	ACN	Present	N_2	n.d

3	RFTA	ACN	Present	O_2	47
4	RFTA	CH_3OH	Present	O_2	n.d
5	RFTA	DMSO	Present	O_2	n.d
6	-	ACN: H_2O (9:1)	Absent	O_2	Trace
7	RFTA	H_2O: ACN (9:1)	Absent	O_2	n.d
8	Rose bengal	ACN	Present	O_2	29
9	$Ru(bpy)_3Cl_2$	ACN	Present	O_2	36

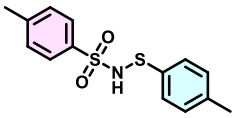
[a]Reaction condition: **1a** (0.30 mmol, 1.2 equiv.), **2a** (0.24 mmol,1 equiv.), PC (2 mol%), ACN (2 mL), rt. [b]isolated yield. n.d-not detected.

Substrate Scope

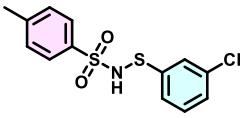
Under the optimized reaction conditions (thiol 1.0 equiv, Chloramine-T 1.2 equiv, RFTA 1 mol%, ACN:H_2O = 9:1, blue LED, room temperature, open air), the substrate scopes of this coupling reaction were investigated. For example, various aliphatic substitutions at the phenyl moiety were well tolerated (up to 80% yield). However, the fluorine-substituted moiety showed low yield. Notably, no sulfonamide product was obtained when the substrate contained an electron-donating amino group. Substrates with electron-withdrawing groups yielded the desired product with good yield but with strong electron-withdrawing such as nitro (-NO_2) or cyano (-CN) showed no reactivity under the standard conditions. We continued our investigation on the substrate scope. We moved aromatic thiol to aliphatic thiol and found that the transformation occurred with moderate yield. However, heterocyclic benzene sulfonamide showed low reactivity for this optimized reaction.



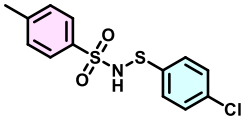
3aa, 71%



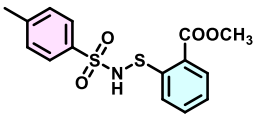
3ab, 70%



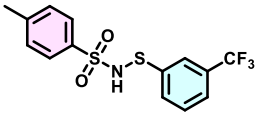
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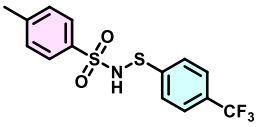
3ad, 75%



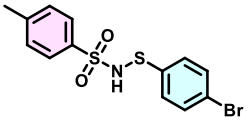
3ae, 80%



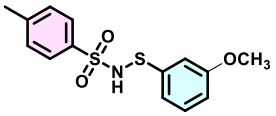
3af, 75%



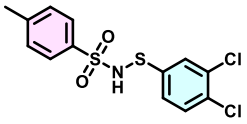
3ag, 50%



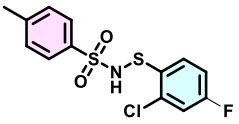
3ah, 55%



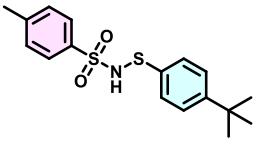
3ai, 72%



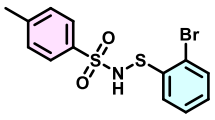
3aj, 76%



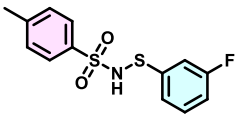
3ak, 76%



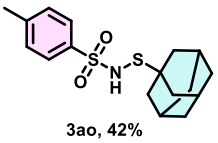
3al, 76%



3am, 75%



3an, 71%

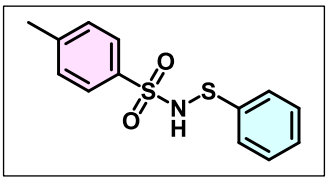


3ao, 42%

Chapter-5

Experimental Sections

4-methyl-N-(phenylthio)benzenesulfonamide (3aa):

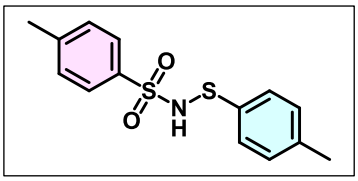


Following the general procedure, the reaction was carried out with Chloramine T(213.1, 0.9 mmol, 1.2 equiv.), PC (8.7 mg, 2 mol%, 0.02 equiv.) in CH_3CN (2 ml), was added PhSH (80 µL, 0.8 mmol, 1.0 equiv.). After the completion of the reaction followed by workup and silica gel column chromatography with Hexane : EtOAc (90:10) as eluent, afforded product (Yield: 71%) as a white solid,

^{1}H NMR (500 MHz, $CDCl_3$)δ 7.71 (d, 2H), 7.26 (d, 2H), 7.22-7.18 (m, 3H), 7.15-7.12 (m, 1H), 2.3 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$)δ 144.2, 137.3, 136.1, 129.6, 128.9, 127.7, 127.5, 126.2, 21.6.

4-methyl-*N*-(p-tolylthio)benzenesulfonamide (3ab):



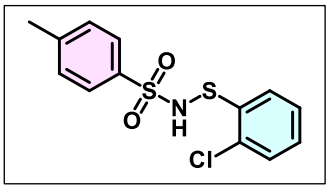
Following the general procedure, the reaction was carried out with Chloramine T (219.9, 0.9 mmol, 1.2 equiv.), PC (8 mg, 2 mol%, 0.02 equiv.) in CH_3CN (2 ml), was added 4-methylbenzenethiol (98 µL, 0.8 mmol, 1.0 equiv.). After the completion of the reaction of the reaction followed by workup and silica gel column chromatography with Hexane : EtOAc (85:15) as eluent, afforded product (Yield: 70%) as a redish solid.

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.49 (d, 1H), 7.39-7.35 (m, 2H), 7.22 (d, 1H), 7.18-7.11 (m, 4H), 7.06 (d, 1H), 2.35 (s, 3H), 2.30 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 135.4, 130.1, 129.8,

128.6, 124.3, 21.5.

***N*-((2-chlorophenyl)thio)-4-methylbenzenesulfonamide (3ac):**

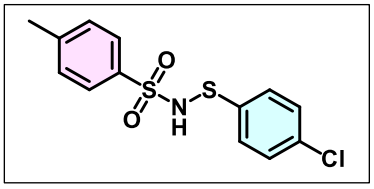


Following the general procedure, the reaction was carried out with Chloramine T (157 mg, 0.7 mmol, 1 equiv.), RFTA (7.5 mg, 2 mol%, 0.02 equiv.) in $CH_3CN:H_2O$ (9:1), 2-chlorobenzenethiol was added (100 mg, 0.7 mmol, 1.0 equiv.). After the completion of the reaction of the reaction followed by work up and silica gel column chromatography with Hexane: EtOAc (85:15) as eluent, afforded product (Yield: 76%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.7 (d, 2H), 7.39 (d, 1H), 7.18-7.02 (m, 4H), 6.26 (br, 1H), 2.32 (s, 3H).

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ 136.1, 135.8, 129.7, 129.4, 127.8, 127.6, 127.3, 126.4, 21.6.

N-((4-chlorophenyl)thio)-4-methylbenzenesulfonamide (3ad):

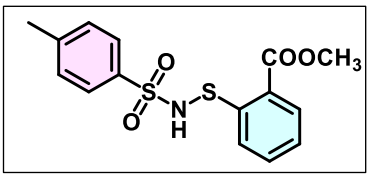


Following the general procedure, the reaction was carried out with Chloramine T (157 mg, 0.7 mmol, 1 equiv.), RFTA (7.5 mg, 2 mol%, 0.02 equiv.) in $CH_3CN:H_2O$ (9:1), 4-chlorobenzenethiol was added (100 mg, 0.7 mmol, 1.0 equiv.). After the completion of the reaction of the reaction followed by work up and silica gel column chromatography with Hexane: EtOAc (85:15) as eluent, afforded product (Yield: 73%) as a white solid

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.7 (d, 1H), 7.2 (m, 6H), 6.1 (br, 1H), 2.4 (s, 3H)

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ 144.5, 135.9,135.8, 129.7, 129.2, 129.1, 127.8, 127.7, 21.6.

methyl 2-(((4-methylphenyl)sulfonamido)thio)benzoate(3ae):

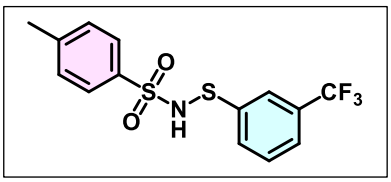


Following the general procedure, the reaction was carried out with Chloramine T (170 mg, 0.6 mmol, 1.2 equiv.), RFTA (6.5 mg, 2 mol%, 0.02 equiv.) in $CH_3CN:H_2O$ (9:1), was added methyl 2-mercaptobenzoate (81 µL, 0.6 mmol, 1.0 equiv.). After the completion of the reaction of the reaction followed by work up and silica gel column chromatography with Hexane: EtOAc (90:10) as eluent, afforded product (Yield: 80%) as a white solid

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.84 (d, 1H), 7.78 (d, 1H), 7.7 (d, 2H), 7.38 (m, 1H), 7.14 (d, 2H), 7.8 (m,1H), 6.47 (br, 1H), 3.76 (s,3H), 2.27 (s, 3H)

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ167.3,145.1, 144.1, 136.5, 133.3, 130.7, 129.7, 128.6, 127.44, 125.0, 123.9, 52.5, 21.7.

4-methyl-*N*-((3-(trifluoromethyl)phenyl)thio)benzenesulfonamide (3af):



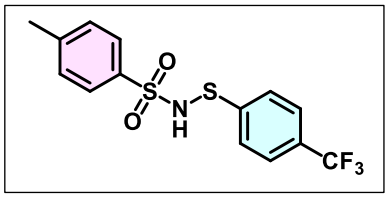
Following the general procedure, the reaction was carried out with Chloramine T (170 mg, 0.6 mmol, 1.2 equiv.), RFTA (6.5 mg, 2 mol%, 0.02 equiv.) in $CH_3CN:H_2O$ (9:1), was added 3-(trifluoromethyl)benzenethiol (77 µL, 0.6 mmol, 1.0 equiv.). After the completion of the reaction of the reaction followed by work up and silica gel column chromatography with Hexane: EtOAc (85:15) as eluent, afforded product (Yield: 75 %) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.78 (d, 2H), 7.51 (d, 1H), 7.40 (m, 2H), 6.26 (br, 1H), 2.40 (s, 3H).

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ144.7, 139.0, 135.6, 129.8, 129.44, 127.8, 123.9, 121.7, 29.7, 21.5.

4-methyl-*N*-((4-

(trifluoromethyl)phenyl)thio)benzenesulfonamide(3ag):

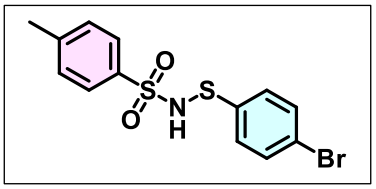


Following the general procedure, the reaction was carried out with Chloramine T (170 mg, 0.6 mmol, 1.2 equiv.), RFTA (6.5 mg, 2 mol%,0.02 equiv.) in $CH_3CN:H_2O$ (9:1), was added 4-(trifluoromethyl)benzenethiol (77 µL, 0.6 mmol, 1.0 equiv.). After the completion of the reaction of the reaction followed by work up and silica gel column chromatography with Hexane: EtOAc (85:15) as eluent, afforded product (Yield: 78%) as a white solid

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.78 (d, 2H), 7.51 (d, 2H), 7.3 (d, 2H), 7.38 (m, 1H), 7.14 (d, 2H), 7.8(m,1H), 6.47 (br, 1H), 3.76 (s,3H), 2.27 (s, 3H)

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ135.7, 129.8, 129.8, 127.8, 125.8, 124.1, 21.5.

***N*-((4-bromophenyl)thio)-4-methylbenzenesulfonamide(3ah):**



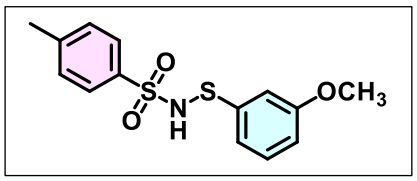
Following the general procedure, the reaction was carried out with Chloramine T (145 mg, 0.6 mmol, 1.2 equiv.), RFTA (6.0 mg, 2 mol%, 0.02 equiv.) in $CH_3CN:H_2O$ (9:1), 4-bromobenzenethiol (100 mg, 0.5 mmol, 1.0 equiv.) was added. After the completion of the reaction followed by work up and silica gel column chromatography with Hexane:EtOAc (88:12) as eluent, afforded product (Yield: 76%) as a white solid

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.77 (d, 2H), 7.39 (d, 2H), 7.27 (d, 2H), 7.20 (d, 2H), 6.10 (br, 1H), 2.43 (s, 3H)

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ 144.5, 132.0, 129.7, 129.7. 127.7, 127.7, 126.5, 121.5, 21.6.

***N*-((3-methoxyphenyl)thio)-4-**

methylbenzenesulfonamide(3ai):

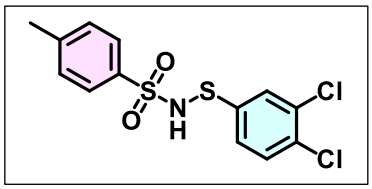


Following the general procedure, the reaction was carried out with Chloramine T (194 mg, 0.9 mmol, 1 equiv.), RFTA (6.0 mg, 2 mol%, 0.02 equiv.) in CH_3CN:H_2O (9:1), 3-methoxybenzenethiol (100 mg, 0.7 mmol, 1.0 equiv.) was added. After the completion of the reaction followed by workup and silica gel column chromatography with Hexane: EtOAc (88:12) as eluent, afforded product (Yield: 64%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.78 (d, 2H), 7.27 (d, 2H), 7.19 (d, 2H), 7.17 (m, 1H), 6.88 (d, 2H), 6.74 (d,1H), 6.07 (br, 1H) 3.77 (s, 3H), 2.41 (s, 3H)

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ 159.9, 144.3, 138.6, 136.1, 129.8, 129.65, 127.7, 117.85, 113.6, 55.3, 21.3.

***N*-((3,4-dichlorophenyl)thio)-4-methylbenzenesulfonamide(3aj):**



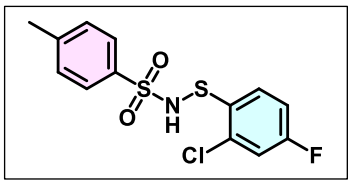
Following the general procedure, the reaction was carried out with Chloramine T (152 mg, 0.6 mmol, 1 equiv.), RFTA (6.0 mg, 2 mol%, 0.02 equiv.) in CH_3CN:H_2O (9:1), 3,4-dichlorobenzenethiol (100 mg, 0.7 mmol, 1.0 equiv.) was added. After the completion of the reaction of the reaction followed by work up and silica gel column chromatography with Hexane:EtOAc (70:30) as eluent, afforded product (Yield: 76%) as a white liquid.

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.76 (d, 2H), 7.32 (d, 1H), 7.27 (m, 3H), 7.16 (d, 1H), 6.22 (br, 1H), 2.42 (s, 3H).

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ 144.8, 137.4, 135.7, 130.7, 129.8, 129.7, 127.4, 125.0, 21.6.

***N*-((2-chloro-4-fluorophenyl)thio)-4-**

methylbenzenesulfonamide(3ak):

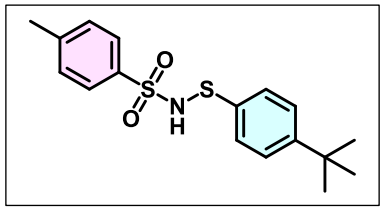


Following the general procedure, the reaction was carried out with Chloramine T (168 mg, 0.7 mmol, 1.2 equiv.), RFTA (6.0 mg, 2 mol%, 0.02 equiv.) in CH_3CN:H_2O (9:1), 2-chloro-4-fluorobenzenethiol (100 mg, 0.6 mmol, 1.0 equiv.) was added. After the completion of the reaction followed by work up and silica gel column chromatography with Hexane:EtOAc (88:12) as eluent, afforded product (Yield: 79%) as a solid.

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.75 (d, 2H), 7.49 (d, 1H), 7.27 (d, 2H), 7.05 (d, 1H), 6.93 (m, 1H), 6.18 (br, 1H), 2.41 (s, 3H).

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ 161.0, 144.6, 135.8, 129.7, 129.7, 127.7, 117.3, 117.1, 114.9, 114.9, 21.6.

***N*-((4-(tert-butyl)phenyl)thio)-4-methylbenzenesulfonamide(3al):**

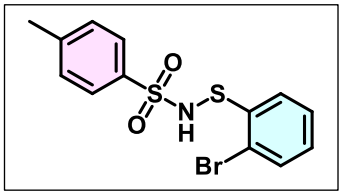


Following the general procedure, the reaction was carried out with Chloramine T (213 mg, 0.9 mmol, 1.2 equiv.), RFTA (6.0 mg, 2 mol%, 0.02 equiv.) in CH_3CN:H_2O (9:1), 4-(tert-butyl)benzenethiol (100 mg, 0.6 mmol, 1.0 equiv.) was added. After the completion of the reaction, followed by workup and silica gel column chromatography with Hexane:EtOAc (88:12) as eluent, afforded product (Yield: 66%) as a liquid.

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.75 (d, 2H), 7.25 (m, 4H), 7.23 (d, 2H), 6.09 (br, 1H), 2.40 (s, 3H), 1.29 (s, 9H),

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ 151.4, 144.04, 136.3, 133.5, 129.5, 127.8, 127.4, 126.0, 34.6, 31.2, 21.6.

***N*-((2-bromophenyl)thio)-4-methylbenzenesulfonamide(3am):**

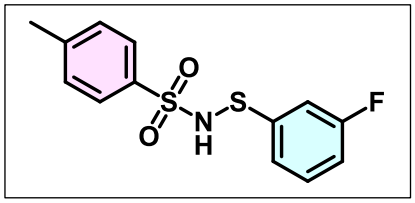


Following the general procedure, the reaction was carried out with Chloramine T (145 mg, 0.6 mmol, 1.2 equiv.), RFTA (6.0 mg, 2 mol%, 0.02 equiv.) in CH_3CN:H_2O (9:1), 2-bromobenzenethiol (100 mg, 0.8 mmol, 1.0 equiv.) was added. After the completion of the reaction followed by work up and silica gel column chromatography with Hexane:EtOAc (85:15) as eluent, afforded product (Yield: 72%) as a solid

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.80 (d, 2H), 7.48 (d, 4H), 7.43 (d, 1H), 7.28 (m, 1H), 7.06 (m, 1H), 6.07 (br, 1H), 2.42 (s, 3H),

^{13}C(^{1}H) NMR (126 MHz, $CDCl_3$), δ 144.5, 138.0, 135.9, 132.6, 129.8, 128.0, 127.9, 127.7, 126.3, 118.1, 21.6.

***N*-((3-fluorophenyl)thio)-4-methylbenzenesulfonamide(3an):**

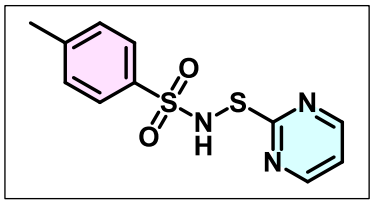


Following the general procedure, the reaction was carried out with Chloramine T (213 mg, 0.6 mmol, 1.2 equiv.), RFTA (6.0 mg, 2 mol%, 0.02 equiv.) in CH_3CN:H_2O (9:1), 3-fluorobenzenethiol (100 mg, 0.8 mmol, 1.0 equiv.) was added. After the completion of the reaction of the reaction followed by work up and silica gel column chromatography with Hexane:EtOAc (85:15) as eluent, afforded product (Yield: 55%) as a liquid.

^{1}H NMR (500 MHz, $CDCl_3$), δ 7.72 (d, 2H), 7.21 (m, 2H), 7..00 (d, 1H), 6.93 (d, 1H), 6.81 (m, 1H), 6.01 (br, 1H), 2.35 (s, 3H),

^{13}C(1H) NMR (126 MHz, $CDCl_3$), δ δ 144.5, 129.7, 127.7, 120.5, 114.3, 112.2, 21.6.

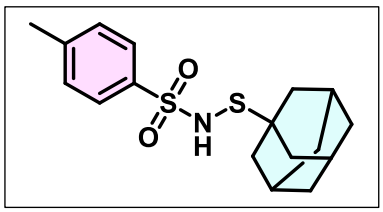
4-methyl-*N*-(pyrimidin-2-ylthio)benzenesulfonamide(3ao):



Following the general procedure, the reaction was carried out with Chloramine T (243 mg, 1.07 mmol, 1.2 equiv.), RFTA (9.0 mg, 2 mol%, 0.02 equiv.) in CH_3CN: H_2O (9:1), pyrimidine-2-thiol (100 mg, 0.9 mmol, 1.0 equiv.) was added. After the completion of the reaction followed by workup and silica gel column chromatography with Hexane: EtOAc (92:8) as eluent, afforded product (Yield: 37%) was obtained as a liquid.

^{1}H NMR (500 MHz, $CDCl_3$), δ 8.64 (d, 2H), 7.51 (d, 2H), 7.1 (d, 1H), 6.93 (d, 1H), 6.81 (m, 1H), 6.01 (br, 1H), 2.35 (s, 3H).

***N*-(adamantan-1-ylthio)-4-methylbenzenesulfonamide(3ap):**



Following the general procedure, the reaction was carried out with Chloramine T (162 mg, 0.71 mmol, 1.2 equiv.), RFTA (9.0 mg, 2 mol%, 0.02 equiv.) in CH_3CN: H_2O (9:1), adamantane-1-thiol (100 mg, 0.9 mmol, 1.0 equiv.) was added. After the completion of the reaction, followed by workup and silica gel column chromatography with Hexane: EtOAc (92:8) as eluent, afforded product (Yield: 52%) was obtained as a liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.20 (s, 5H), 2.33 (s, 3H), 2.30 (s, 3H), 1.98 (d, J = 18.0 Hz, 19H), 1.92 (s, 17H), 1.85 (s, 8H), 1.60 (s, 17H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.85, 140.99, 129.10, 126.11, 41.61, 40.82, 36.34, 29.71, 29.30, 24.66.

Plausible Mechanism:

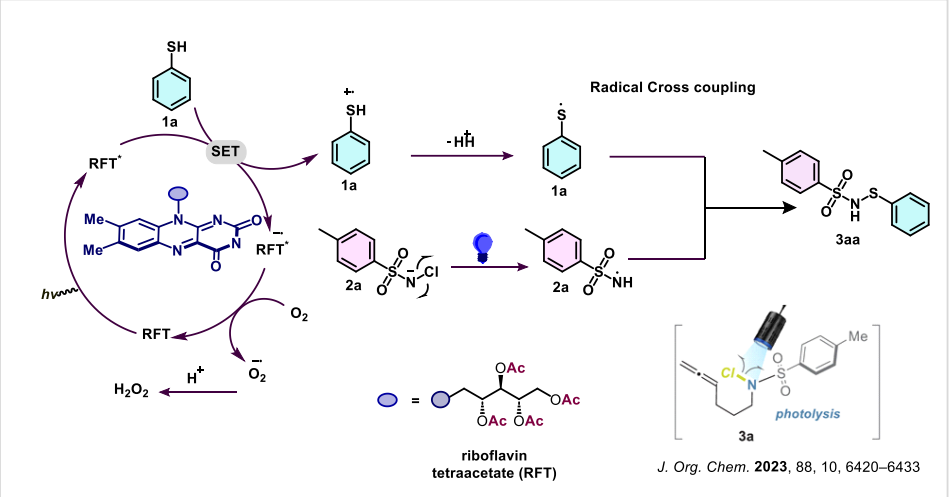
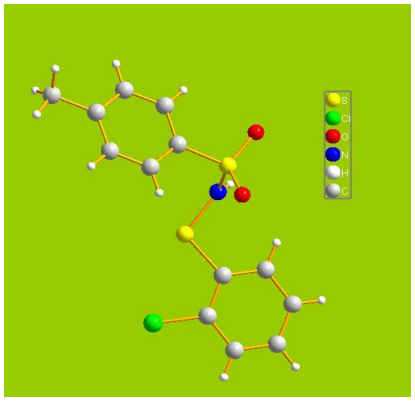
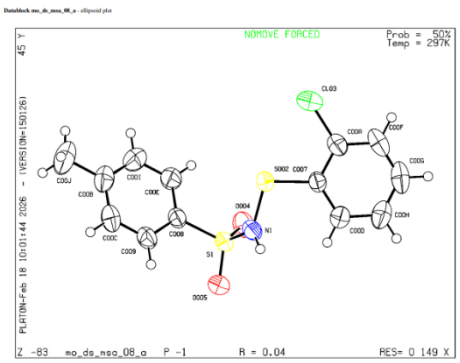


Fig. 3: Plausible reaction mechanism

The reaction proceeds through a visible-light-driven photoredox catalytic cycle using Riboflavin tetraacetate (RFT) as the photocatalyst. Upon light irradiation, the catalyst goes its excited state and undergoes single-electron transfer (SET) with thiophenol, generating a sulfur-centred thiyl radical upon proton loss. Simultaneously, the chloramine T precursor undergoes photolytic cleavage to produce a nitrogen-centred radical intermediate. These two radical species coupled with each other in radical cross-coupling, leading to the formation of the desired thioarylsulfonamide product through new N–S bond formation. During the catalytic cycle, molecular oxygen assists in regenerating the ground-state photocatalyst, producing the superoxide radical anion and, subsequently, formed hydrogen peroxide as byproducts. This mechanism highlights an efficient and mild photocatalytic strategy for constructing sulfur-containing sulfonamide derivatives under visible-light conditions.

X-RAY crystal Structure





Bond precision: C-C = 0.0027 A Wavelength=0.71073

Cell: a=7.9148(8) b=8.1411(9) c=11.5719(13)
alpha=103.194(3) beta=95.529(3) gamma=97.759(3)
Temperature: 297 K

	Calculated	Reported
Volume	713.03(13)	713.03(13)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C13 H12 Cl N O2 S2	0.25(C13 H12 Cl N O2 S2)
Sum formula	C13 H12 Cl N O2 S2	C3.25 H3 Cl0.25 N0.25 O0.50 S0.50
Mr	313.81	78.45
Dx,g cm-3	1.462	1.462
Z	2	8
Mu (mm-1)	0.556	0.556
F000	324.0	324.0
F000'	324.90	
h,k,lmax	10,10,15	10,10,15
Nref	3551	3530
Tmin,Tmax	0.946,0.946	0.693,0.746
Tmin'	0.946	

CCDC No: 2537606

Chapter 6

Conclusions

We have successfully developed a visible-light-mediated protocol for the synthesis of thioarylsulfonamide derivatives via N–S bond formation under mild, green conditions. The reaction was performed using chloramine-T as the sulfonamide source and RFTA as the photocatalyst under blue LED irradiation. During optimization studies, the solvent system ACN:H_2O (9:1) and open-air conditions were found to be the most effective, providing good yields of the desired products. The study also revealed that oxygen plays an important role in the catalytic cycle, while no significant transformation was observed under an inert atmosphere.

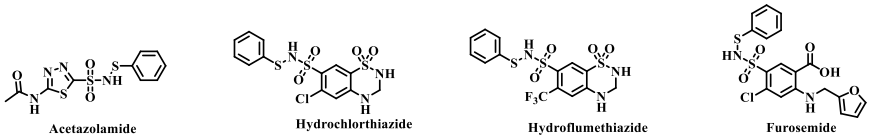
A wide range of aryl thiols containing electron-donating and electron-withdrawing substituents were successfully converted into the corresponding thioarylsulfonamides in moderate to excellent yields. However, strongly electron-withdrawing groups such as nitro and cyano substituents showed no reactivity under the optimized conditions. The developed methodology demonstrates good functional group tolerance and provides a simple, efficient, and sustainable alternative to conventional sulfonamide synthesis methods that often require harsh reagents or toxic amine sources.

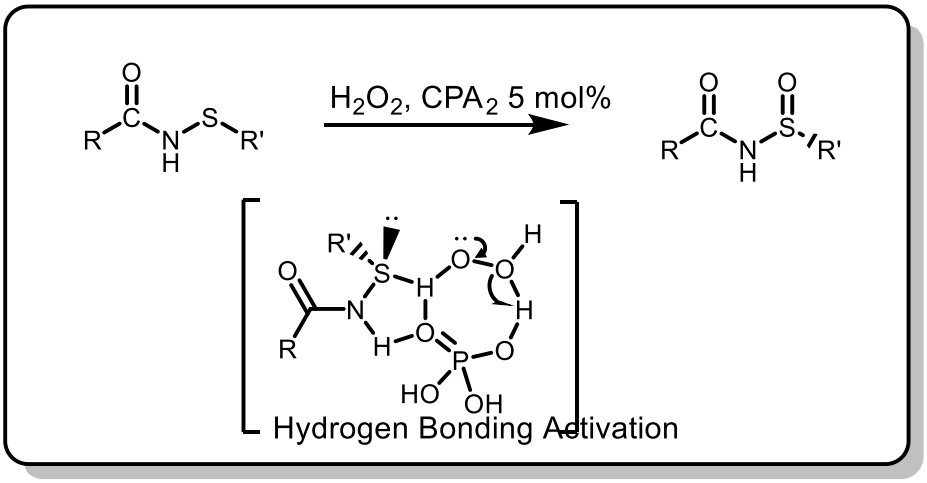
All synthesized compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, confirming the successful formation of the desired products. Mechanistic investigations suggest that the transformation proceeds through a visible-light-driven photoredox pathway involving sulfur-centred and nitrogen-centred radical intermediates, followed by radical cross-coupling to form the N–S bond.

Overall, this work highlights the potential of visible-light photoredox catalysis as a greener and practical strategy for the synthesis of biologically important sulfonamide derivatives.

Future Scope

In the Future, we will go for variation of sulfonamides and thiols to increase the number of N-thiosubstituted sulfonamides and late-stage functionalization for the synthesis of drugs and natural products and will develop enantioselective version of this reaction. Additionally, we will go through the detailed mechanistic studies.





Proposed mechanism for the enantioselective version of this reaction

NMR Spectrum

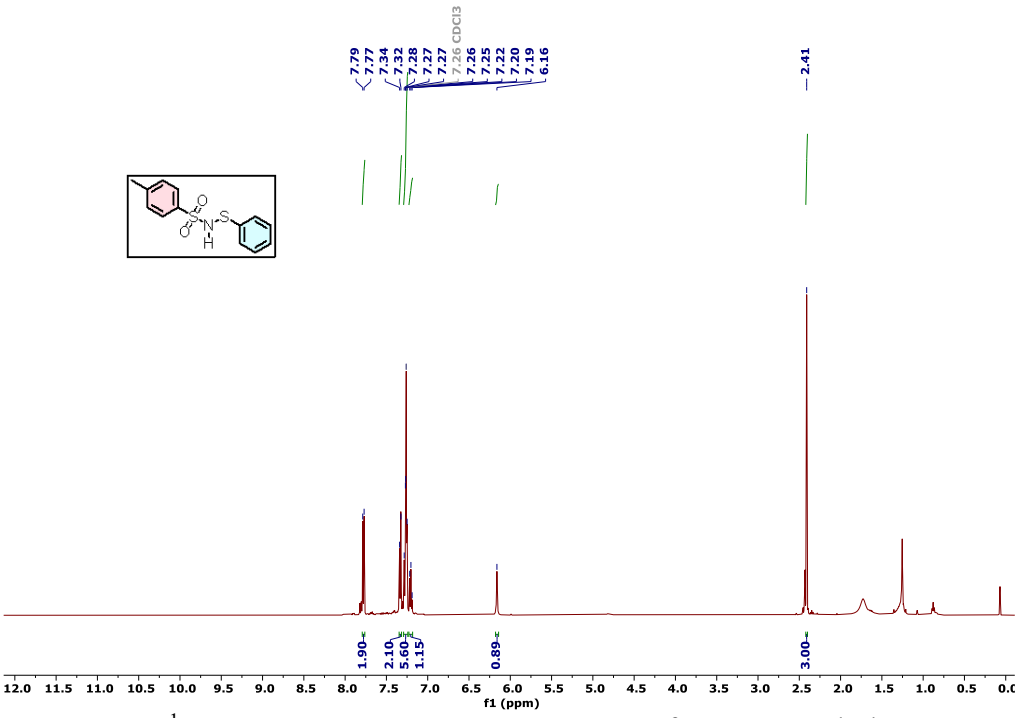


Fig-4: ^{1}H NMR spectrum of 4-methyl-*N*-(phenylthio)benzenesulfonamide.

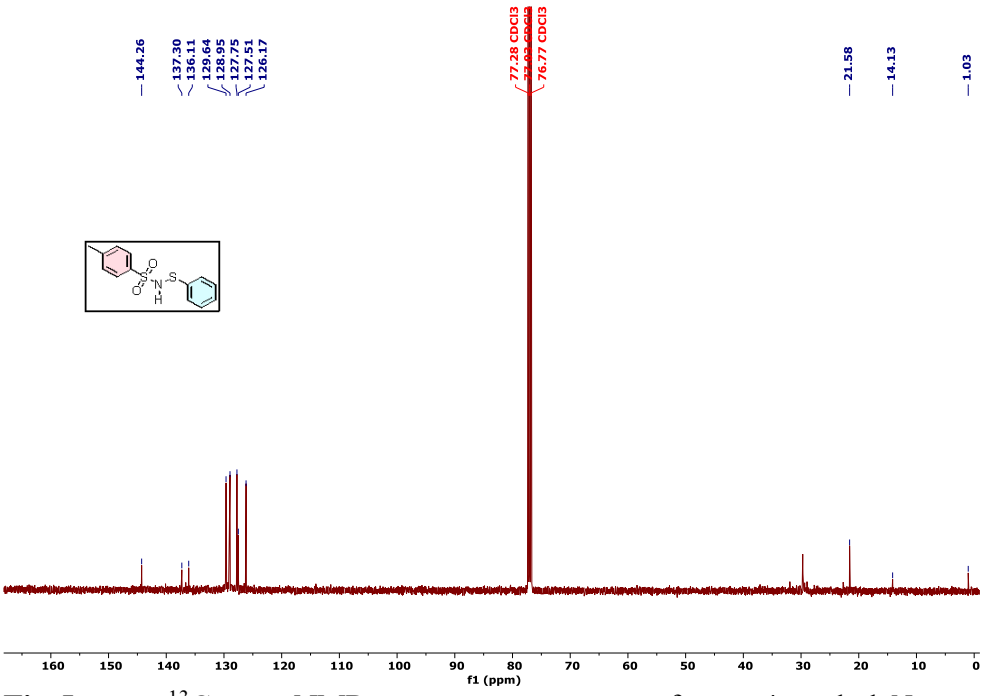


Fig-5: ^{13}C NMR spectrum of 4-methyl-*N*-(phenylthio)benzenesulfonamide

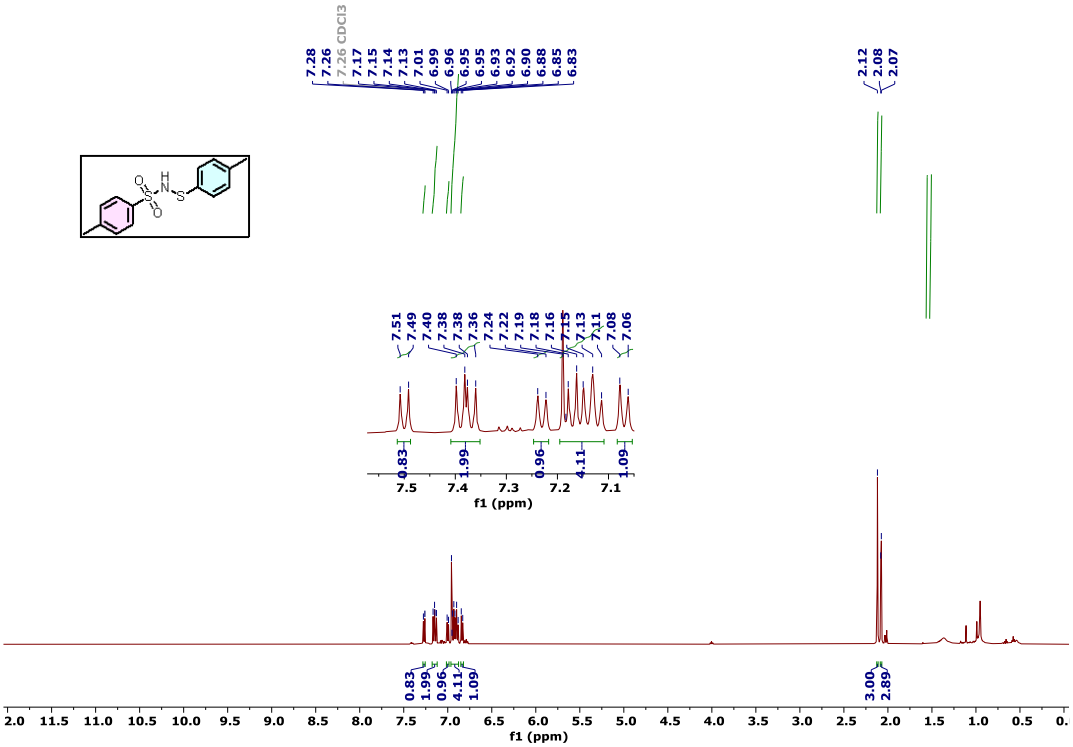


Fig-6: ^{1}H NMR spectrum of 4-methyl-*N*-(p-tolylthio)benzenesulfonamide.

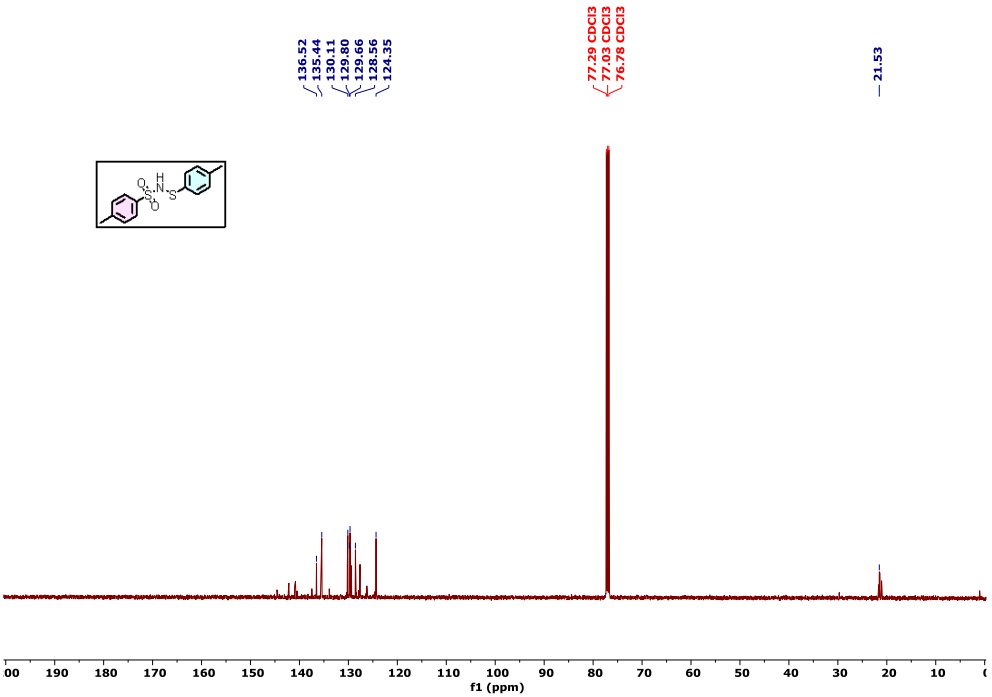


Fig-7: ^{13}C NMR spectrum of 4-methyl-*N*-(p-tolylthio)benzenesulfonamide.

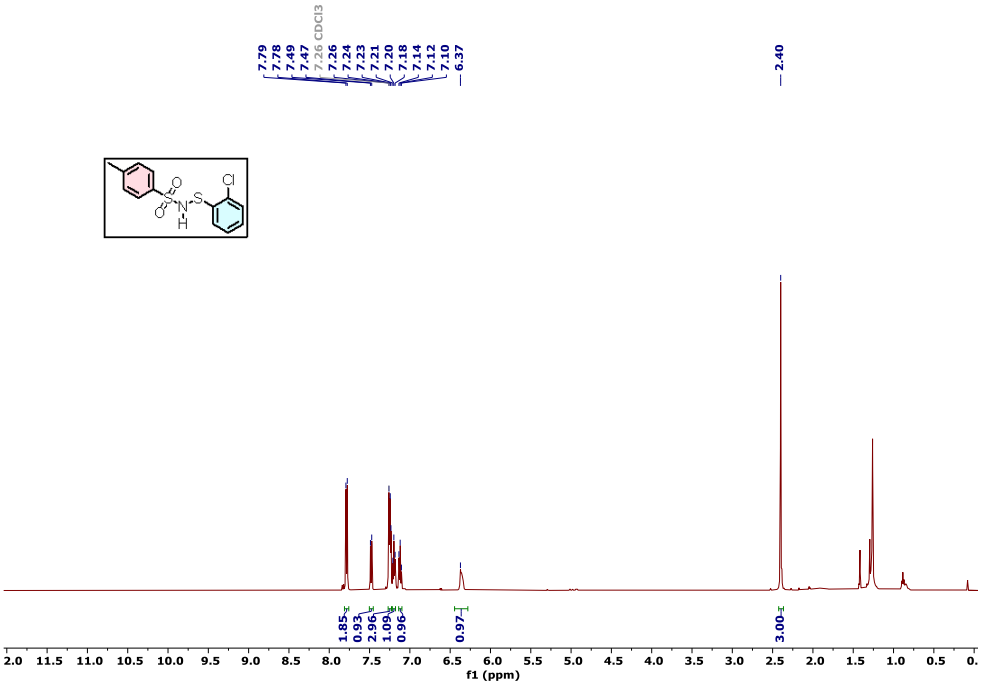


Fig-8: ^{1}H NMR spectrum of *N*-((2-chlorophenyl)thio)-4-methylbenzenesulfonamide.

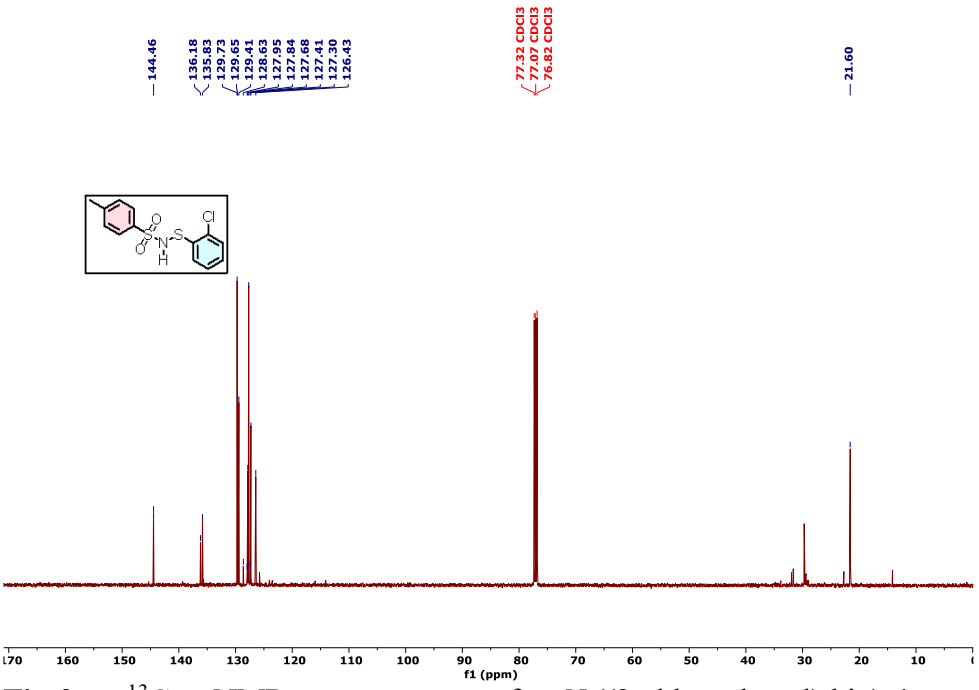


Fig-9: ^{13}C NMR spectrum of *N*-((2-chlorophenyl)thio)-4-methylbenzenesulfonamide.

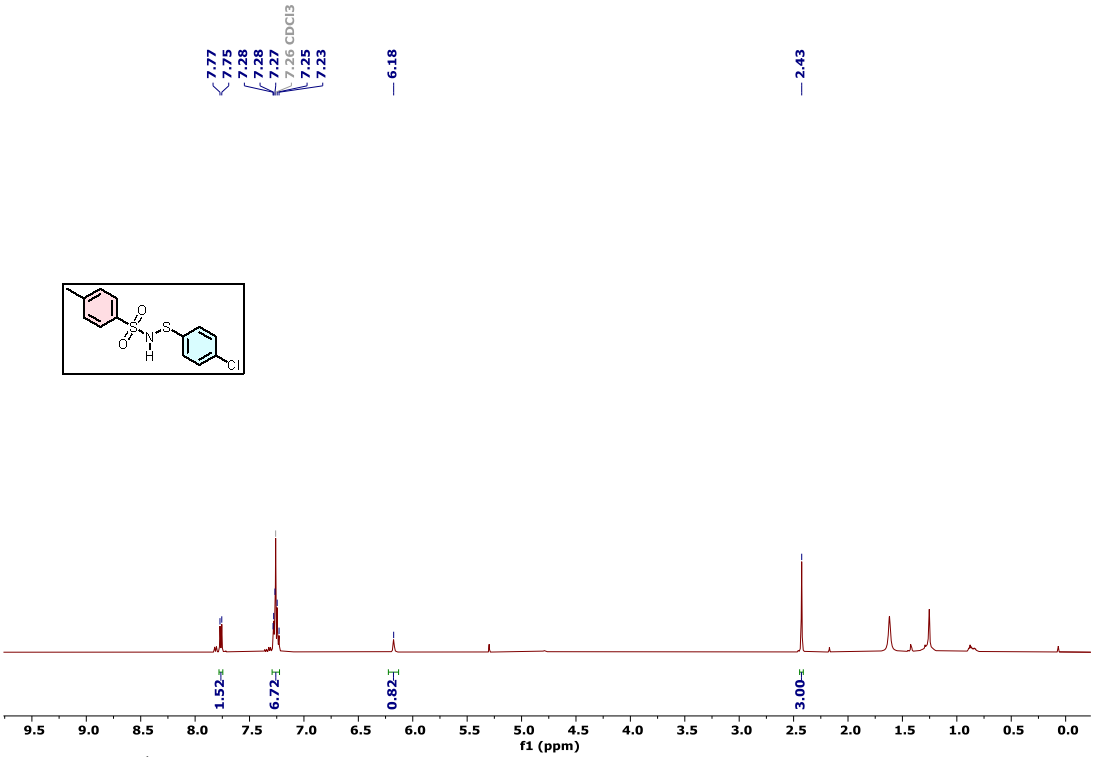


Fig-10: ^{1}H NMR spectrum of *N*-((4-chlorophenyl)thio)-4-methylbenzenesulfonamide.

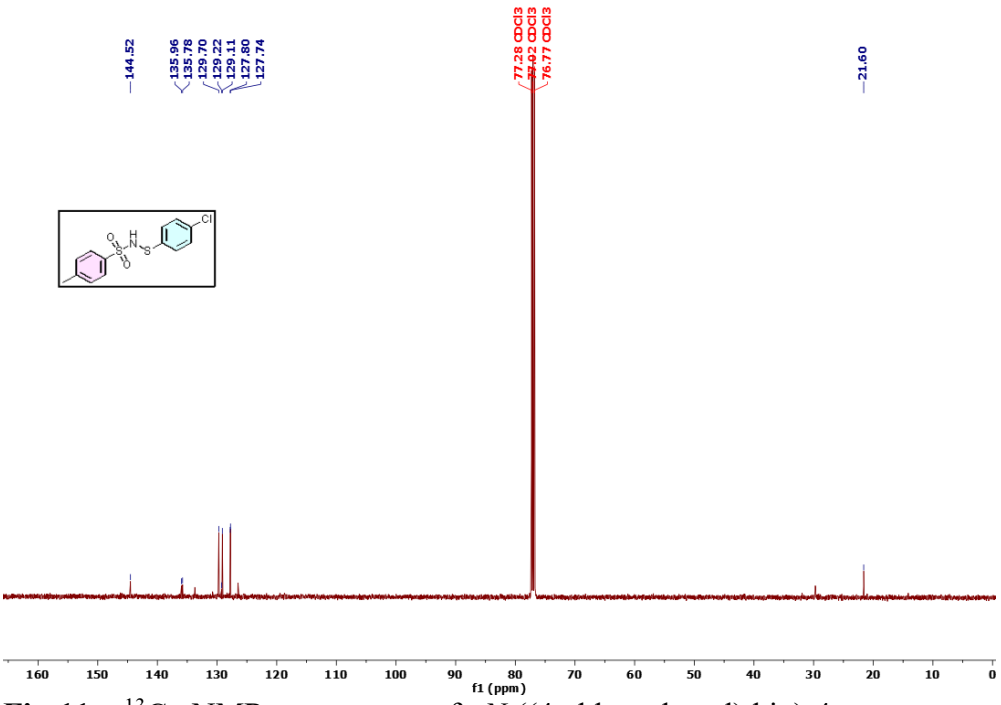


Fig-11: ^{13}C NMR spectrum of *N*-((4-chlorophenyl)thio)-4-methylbenzenesulfonamide.

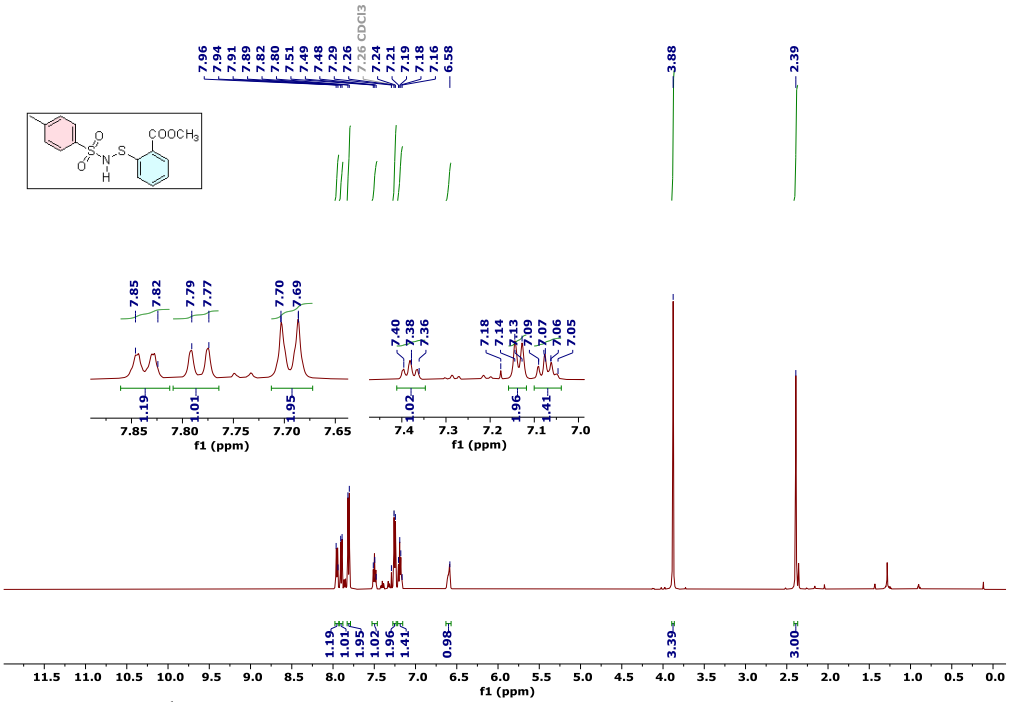


Fig-12: ^{1}H NMR spectrum of methyl 2-(((4-methylphenyl)sulfonamido)thio)benzoate.

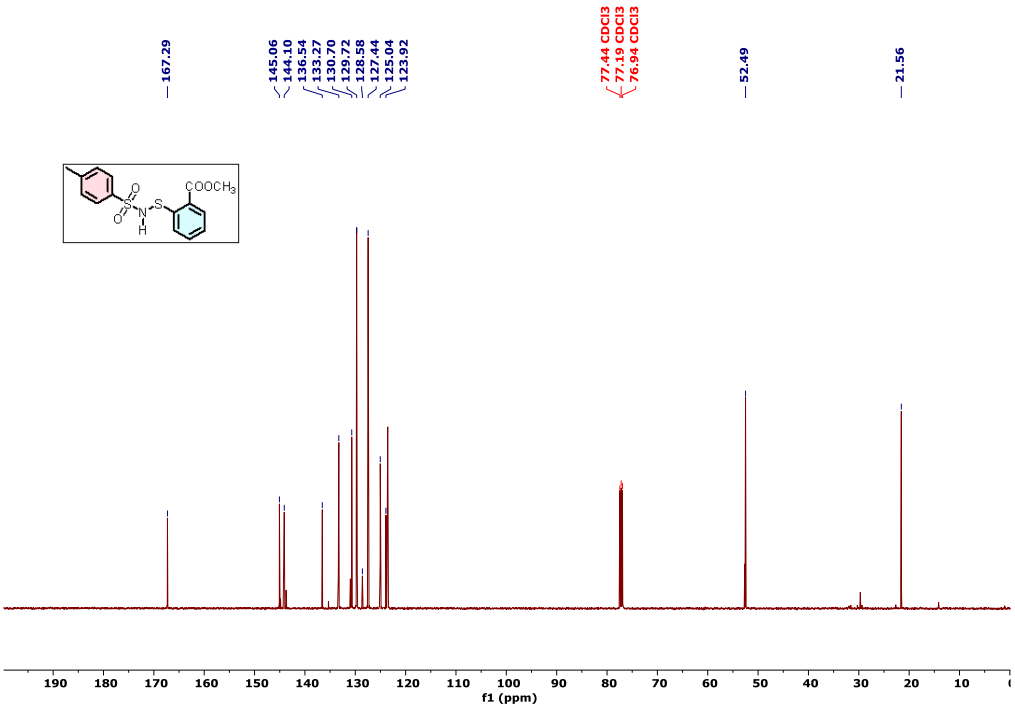


Fig-13: ^{13}C NMR spectrum methyl 2-(((4-methylphenyl)sulfonamido)thio)benzoate.

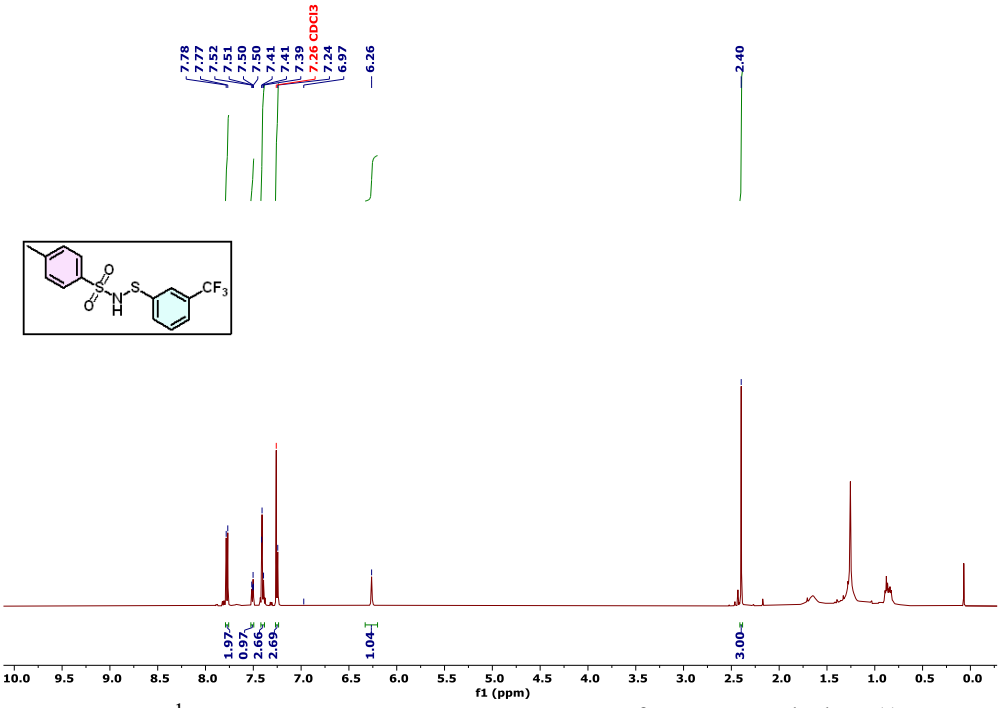


Fig-14: ^{1}H NMR spectrum of 4-methyl-*N*-((3-(trifluoromethyl)phenyl)thio)benzenesulfonamide.

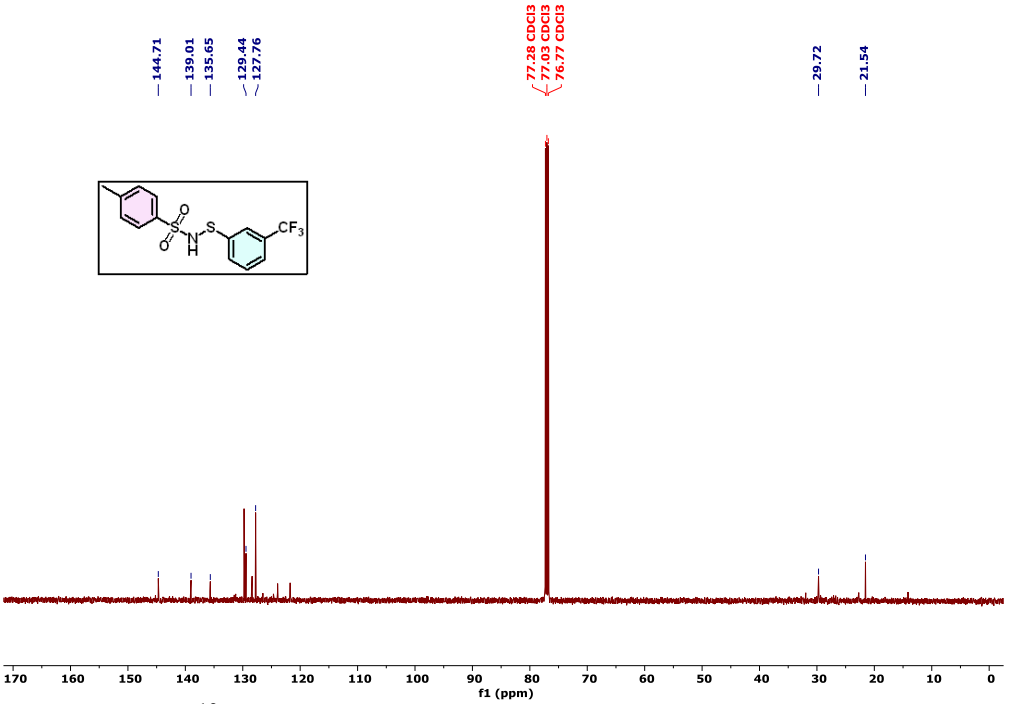


Fig-15: ^{13}C NMR spectrum 4-methyl-*N*-((3-(trifluoromethyl)phenyl)thio)benzenesulfonamide.

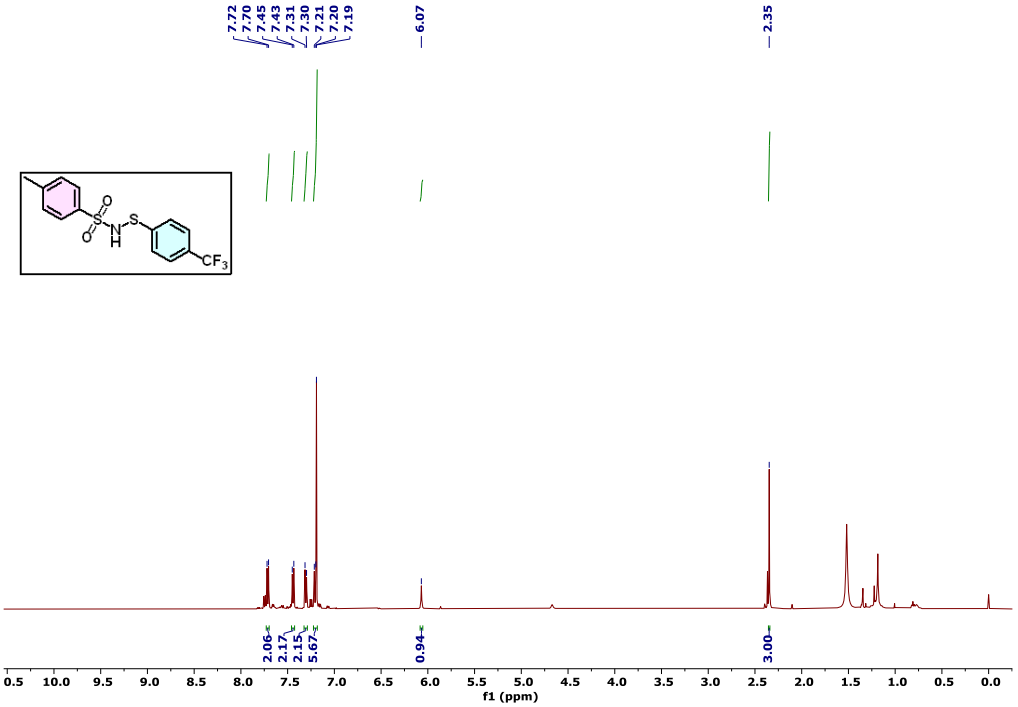


Fig-16: ^{1}H NMR spectrum of 4-methyl-*N*-((4-(trifluoromethyl)phenyl)thio)benzenesulfonamide.

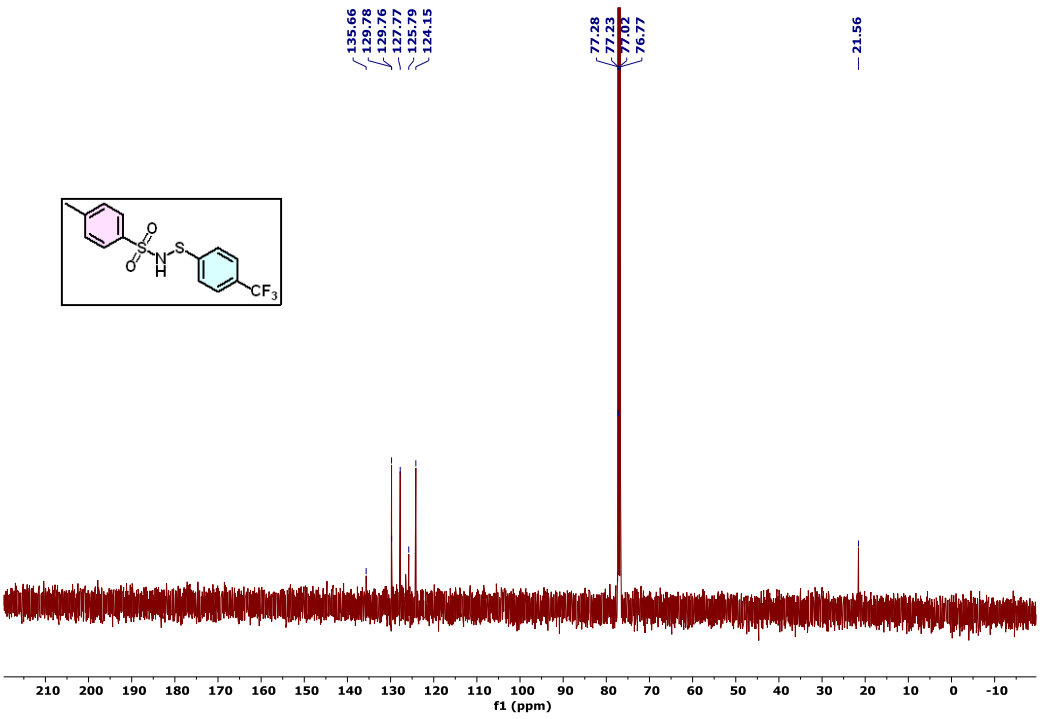


Fig-17: ^{13}C NMR spectrum 4-methyl-N-((4-(trifluoromethyl)phenyl)thio)benzenesulfonamide.

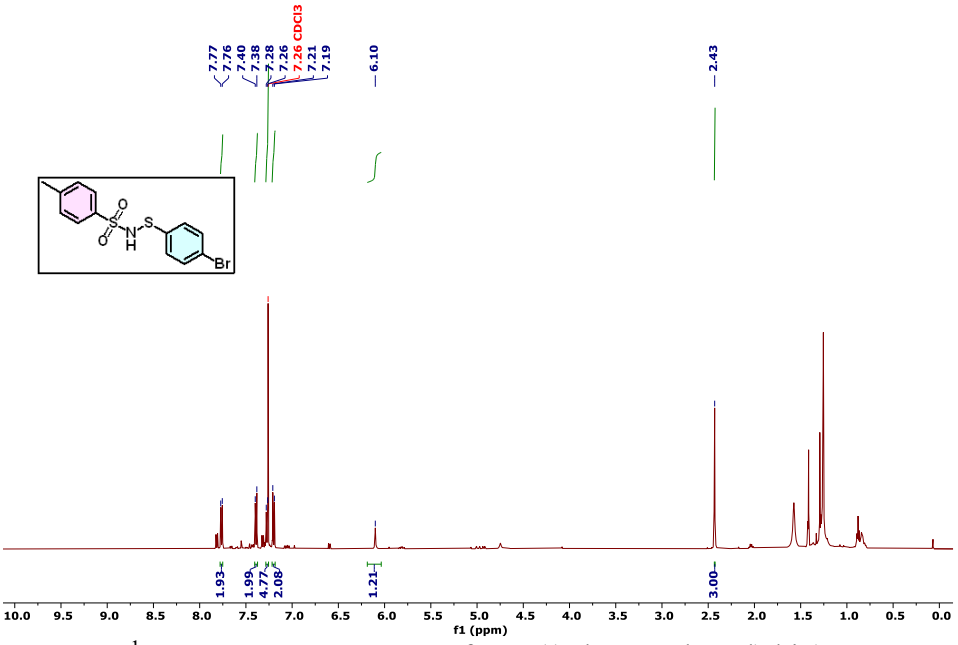


Fig-18: ^{1}H NMR spectrum of N-((4-bromophenyl)thio)-4-methylbenzenesulfonamide.

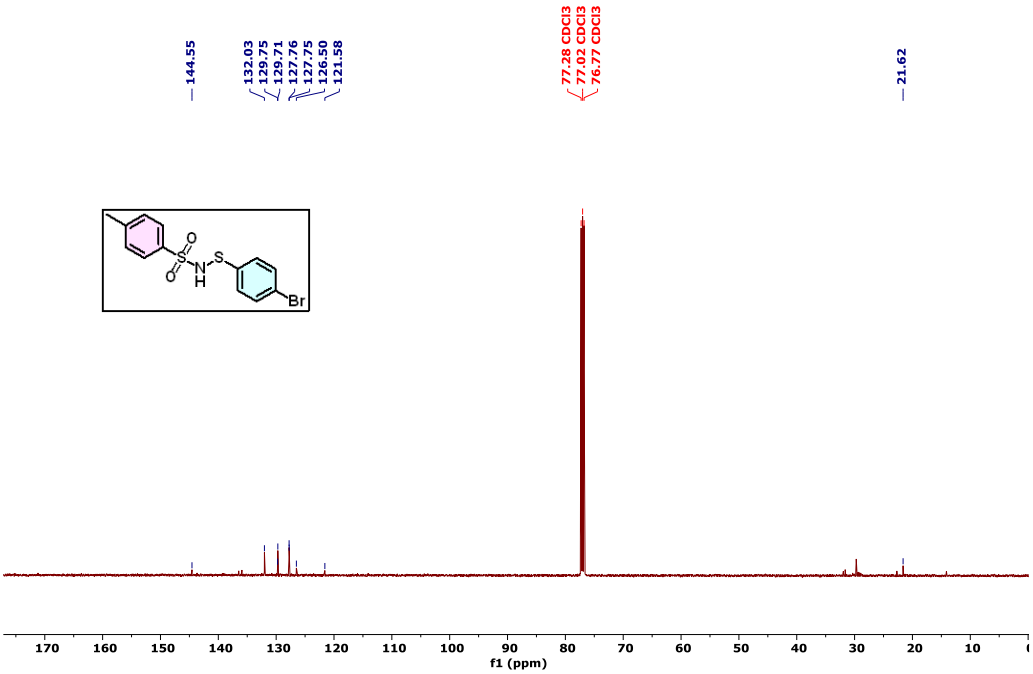


Fig-19: ^{13}C NMR spectrum *N*-((4-bromophenyl)thio)-4-methylbenzenesulfonamide

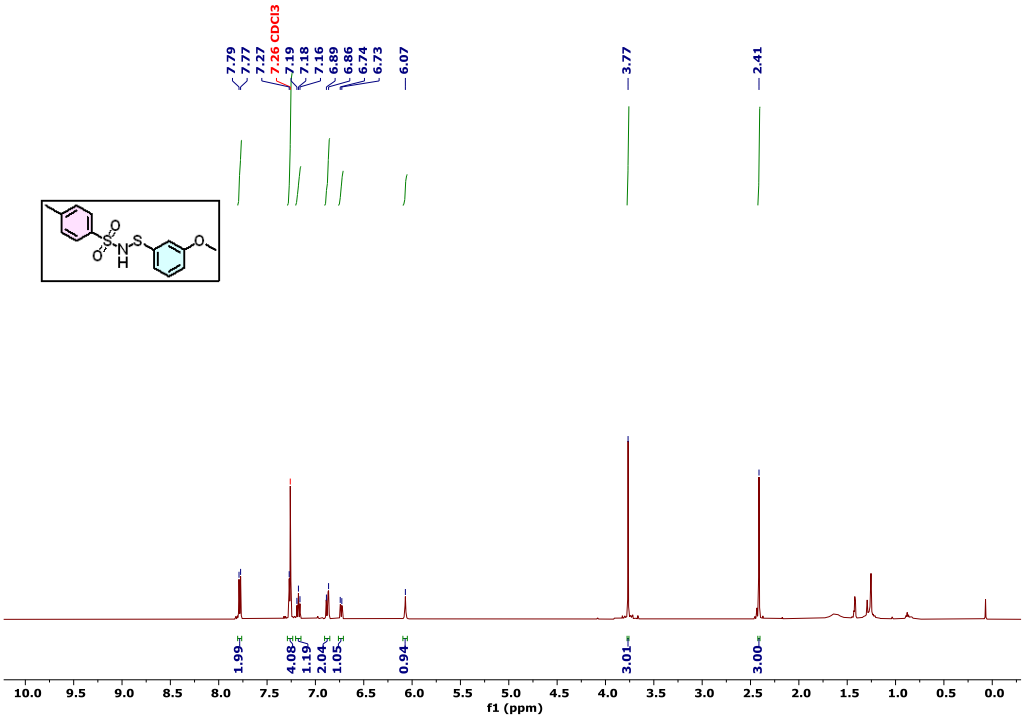


Fig-20: ^{1}H NMR spectrum of *N*-((3-methoxyphenyl)thio)-4-methylbenzenesulfonamide.

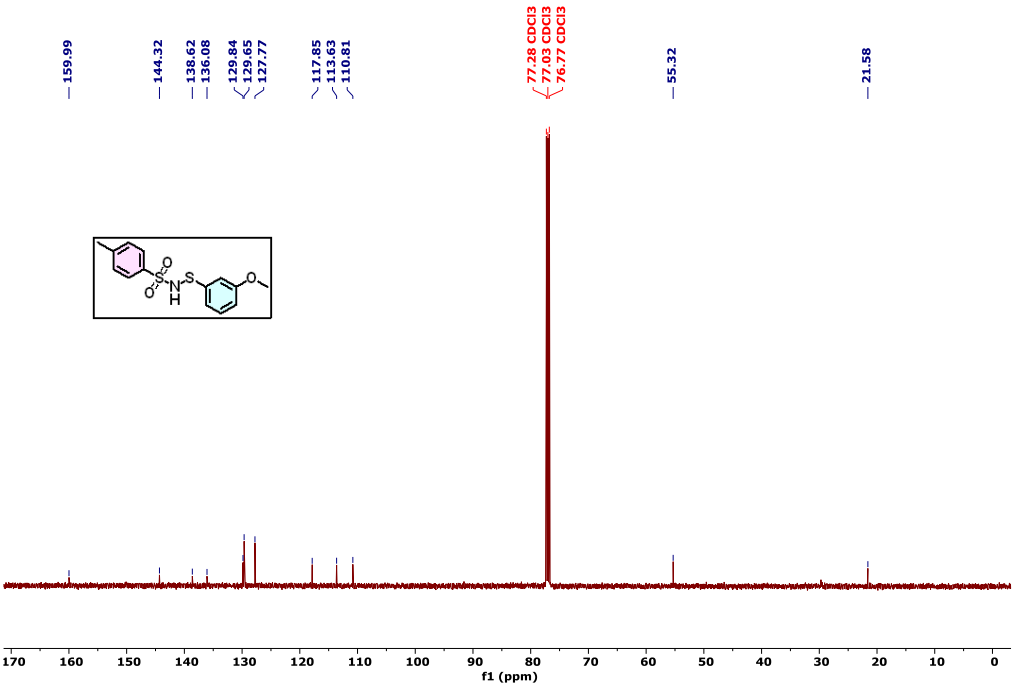


Fig-21: ^{13}C NMR spectrum *N*-((3-methoxyphenyl)thio)-4-methylbenzenesulfonamide.

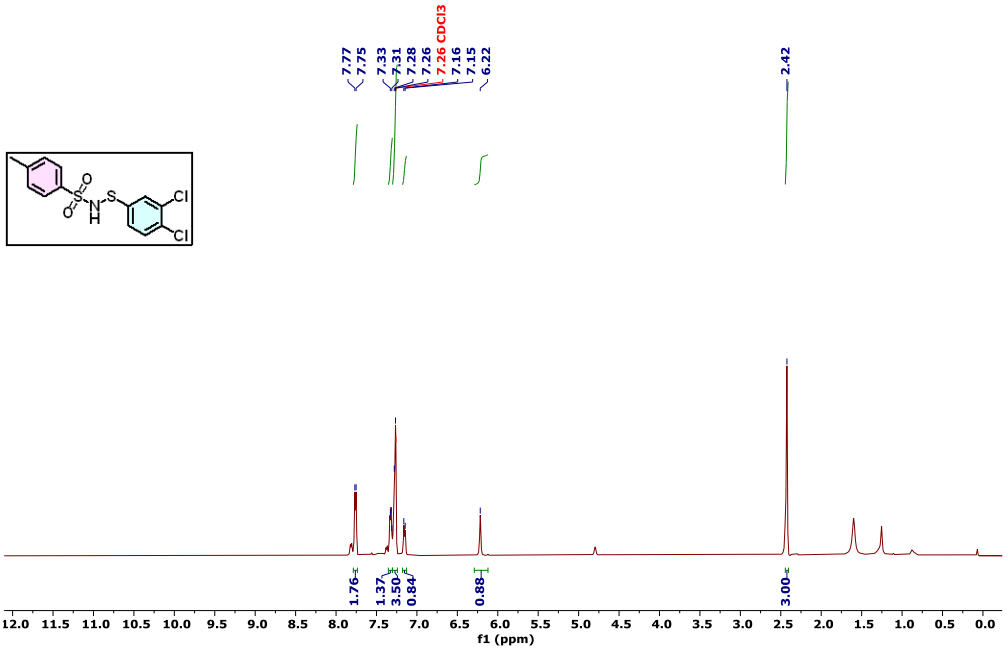


Fig-22: ^{1}H NMR spectrum of *N*-((3,4-dichlorophenyl)thio)-4-methylbenzenesulfonamide.

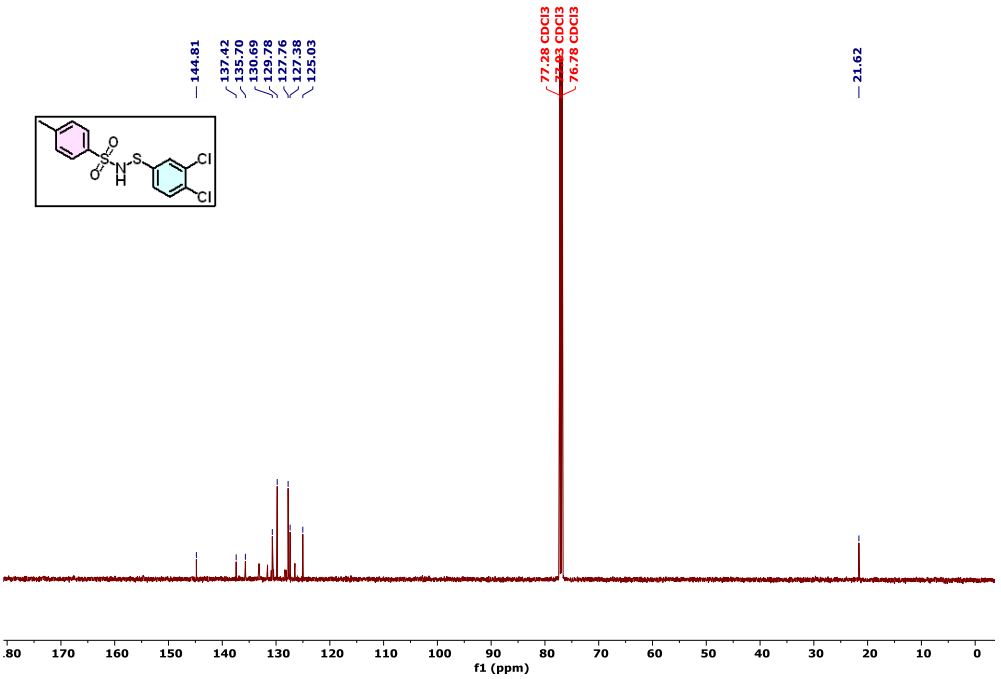


Fig-23: ^{13}C NMR spectrum *N*-((3,4-dichlorophenyl)thio)-4-methylbenzenesulfonamide.

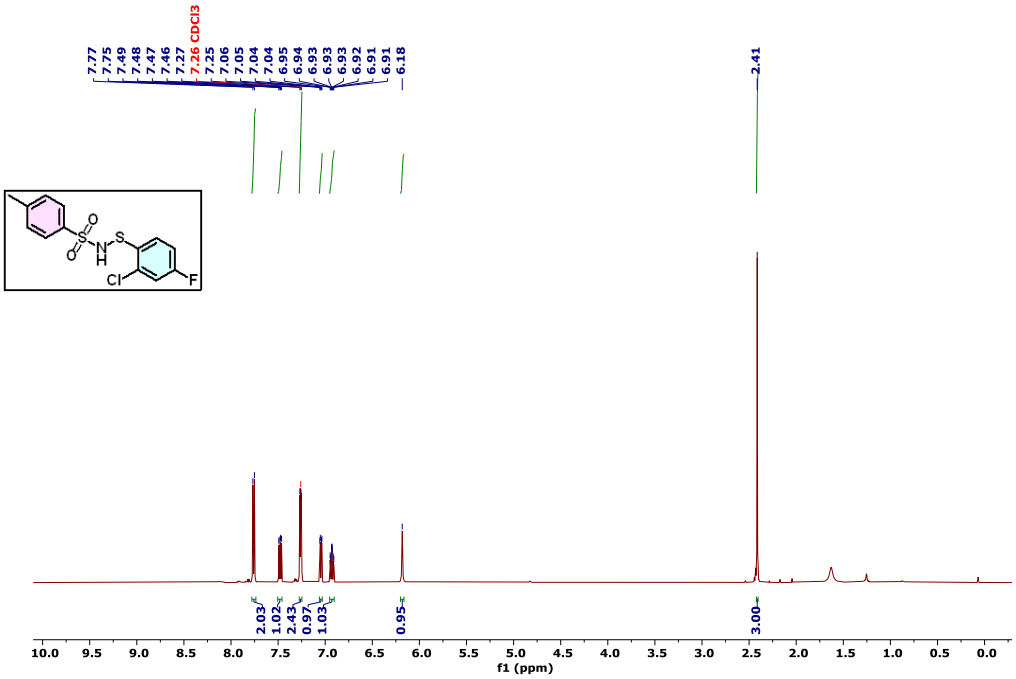


Fig-24: ^{1}H NMR spectrum of *N*-((2-chloro-4-fluorophenyl)thio)-4-methylbenzenesulfonamide.

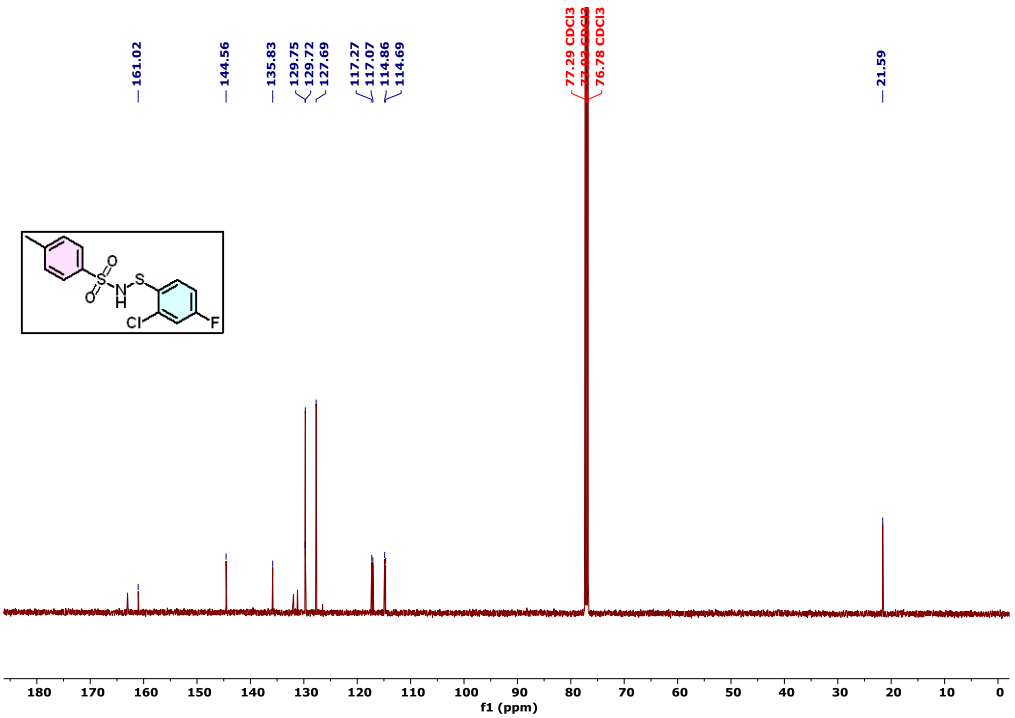


Fig-25: ^{13}C NMR spectrum *N*-((2-chloro-4-fluorophenyl)thio)-4-methylbenzenesulfonamide.

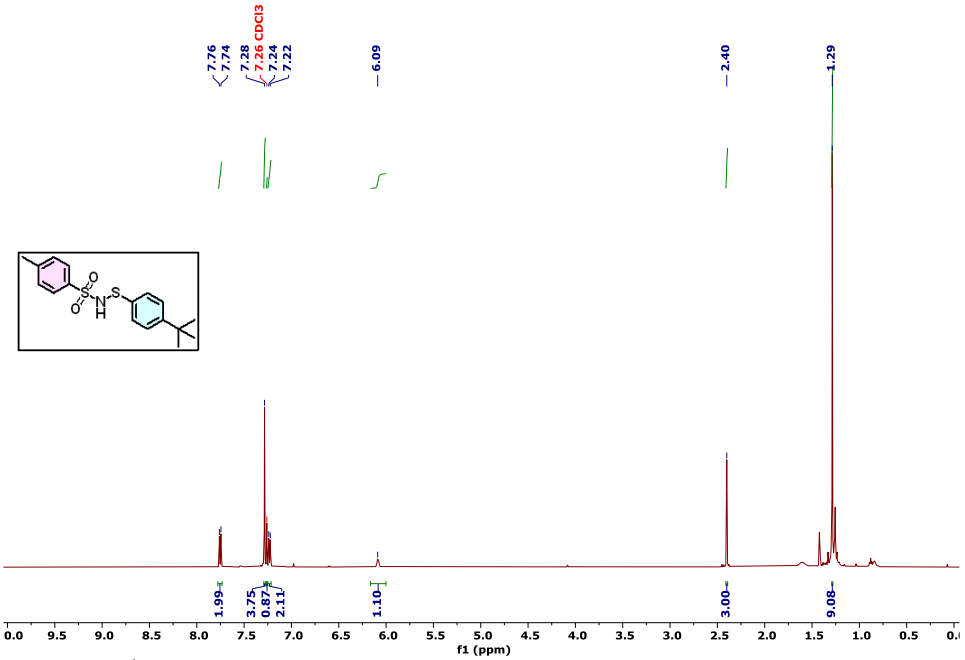


Fig-26: ^{1}H NMR spectrum of *N*-((4-(tert-butyl)phenyl)thio)-4-methylbenzenesulfonamide.

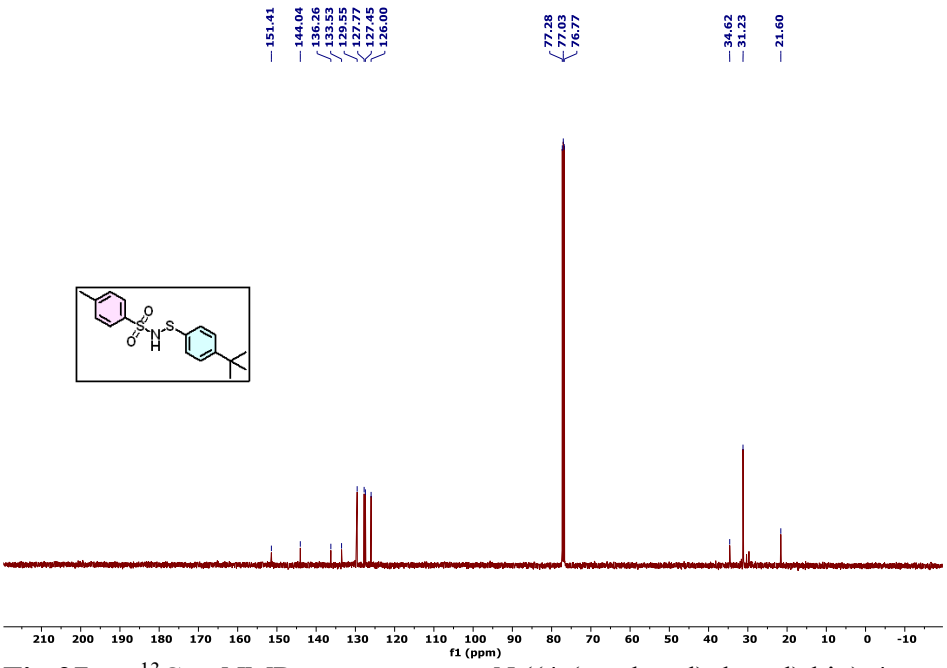


Fig-27: ^{13}C NMR spectrum *N*-((4-(tert-butyl)phenyl)thio)-4-methylbenzenesulfonamide.

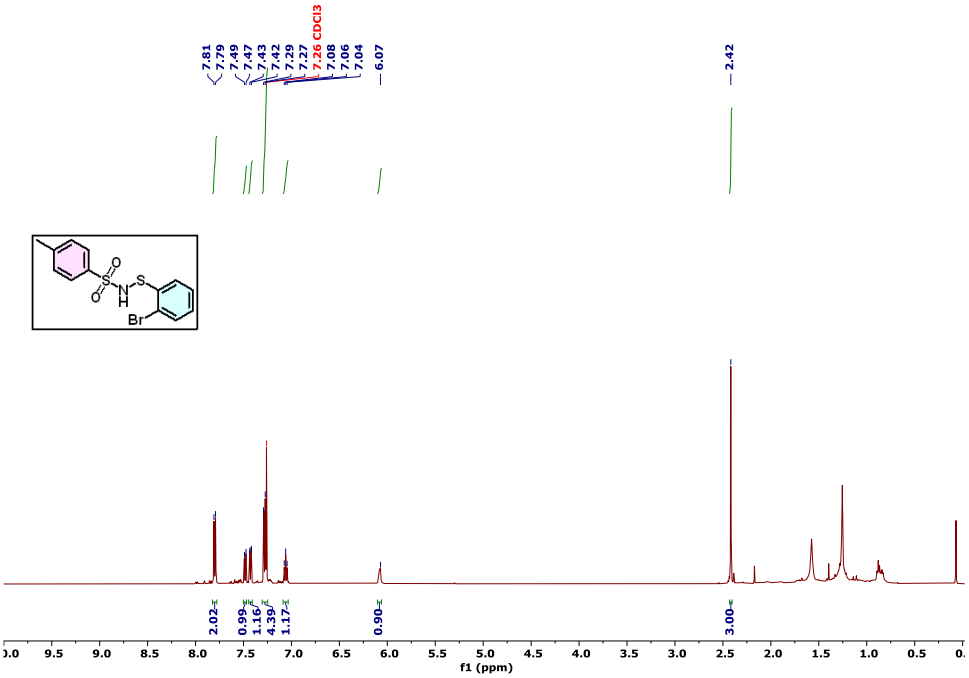


Fig-28: ^{1}H NMR spectrum of *N*-((2-bromophenyl)thio)-4-methylbenzenesulfonamide.

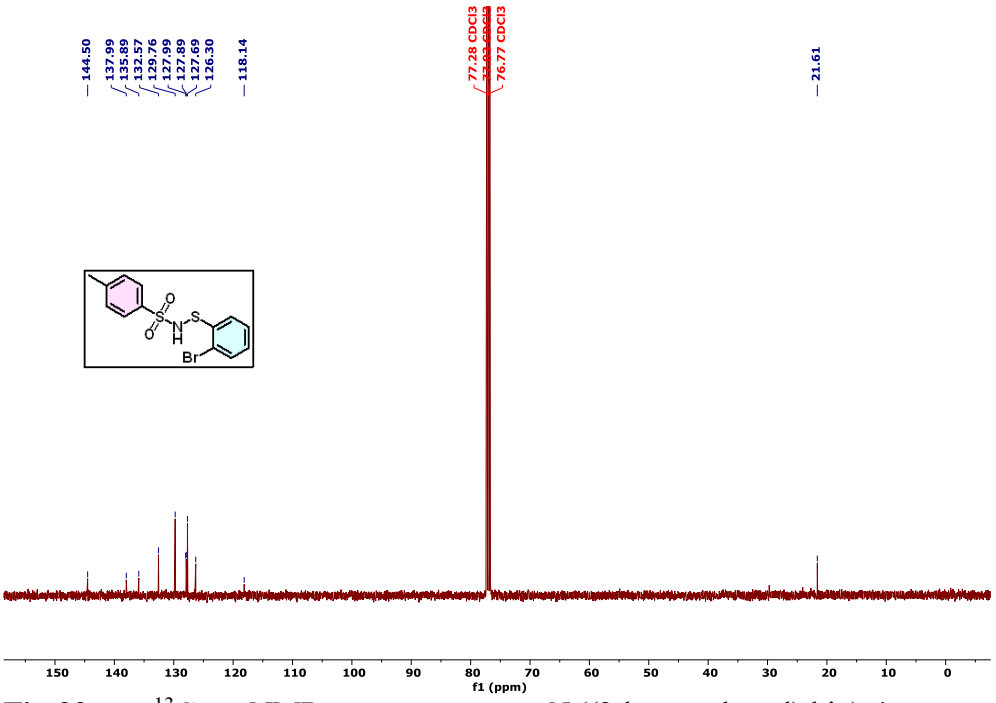


Fig-29: ^{13}C NMR spectrum *N*-((2-bromophenyl)thio)-4-methylbenzenesulfonamide.

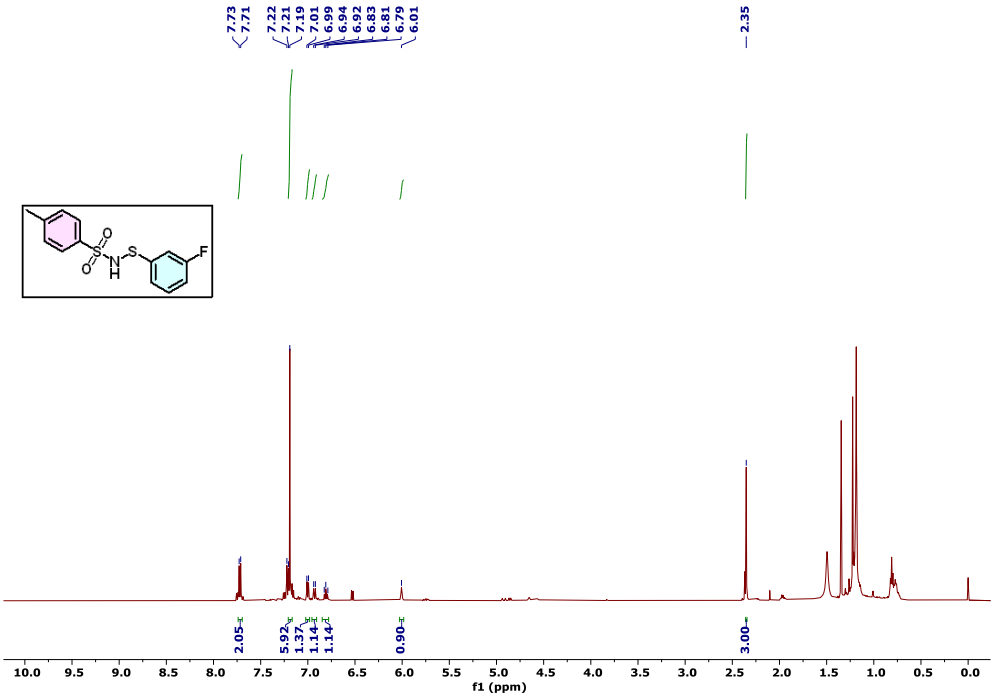


Fig-30: ^{1}H NMR spectrum of *N*-((3-fluorophenyl)thio)-4-methylbenzenesulfonamide.

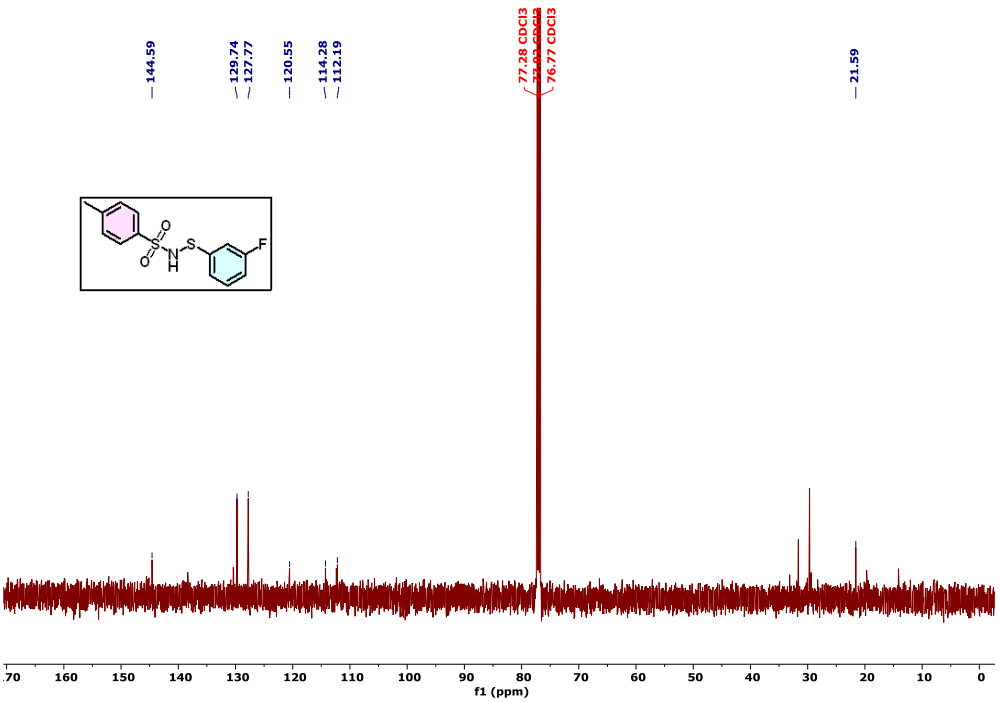


Fig-31: ^{13}C NMR spectrum *N*-((3-fluorophenyl)thio)-4-methylbenzenesulfonamide.

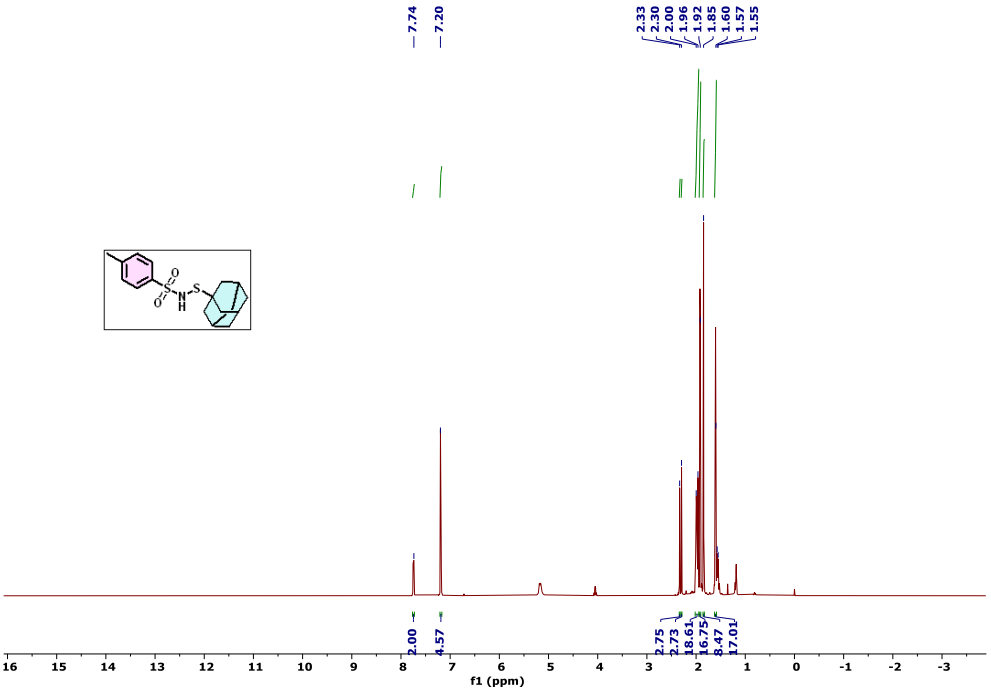


Fig-32: ^{1}H NMR spectrum of *N*-(adamantan-1-ylthio)-4-methylbenzenesulfonamide.

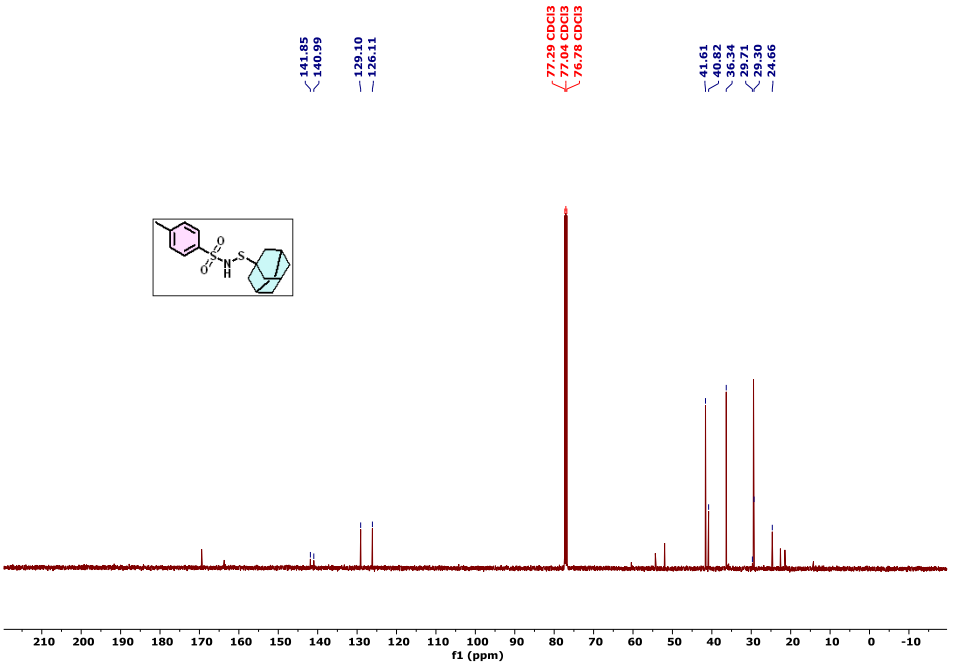


Fig-33: ^{13}C NMR spectrum *N*-(adamantan-1-ylthio)-4-methylbenzenesulfonamide

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