

Development of Nitrene Transfer Reactions and Modification of Sulfur-Containing Compounds via Photocatalytic Nitrene and Carbene Transfer

Von der Fakultät für Mathematik und Naturwissenschaften der RWTH Aachen University zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation

vorgelegt von

Ivan Sliusarevskyi

Aus

Kyiv, Ukraine

Berichter: Prof. Dr. Rene M. Koenigs

Prof. Dr. Frederic W. Patureau

Tag der mündlichen Prüfung: 19.05.2026

Diese Dissertation ist auf den Internetseiten der Universitätsbibliothek verfügbar.

The work reported in this thesis was performed at the Institute of Organic Chemistry at the RWTH Aachen University in Aachen from March 2023 until February 2026 under the supervision of Prof. Dr. Rene M. Koenigs.

Acknowledgement

At the very beginning, I would like to dedicate this work to the memory of my grandmother, Svitlana Sliusarevska, who passed away during this period.

I would like to express my sincere gratitude to my supervisor, Prof. Dr. Rene M. Koenigs, for his patience, guidance, and continuous support throughout my doctoral journey. When I joined the group, he skillfully directed my efforts in the right direction, providing a strong foundation for a successful start. Throughout the entire period of my doctoral studies, he shared invaluable scientific insights and professional experience. His fresh perspective often reignited my enthusiasm at moments when projects seemed to have reached a dead end. Equally important were his life and career-related advices, which helped me to set meaningful goals and identify the right paths to achieve them. I am also deeply grateful for the excellent conditions for both living and working in Germany that he helped to create.

I would further like to thank Jun. Prof. Dr. Claire Empel, who, during her time in our group, provided invaluable advice and contributed significantly to many organizational aspects, both in structuring the working process and in the preparation of high-quality scientific publications. Special thanks go to Dr. Hoang Pham, Dr. Yaseen Hussain, and Dr. Haripriyo Mondal for sharing their experience and for their leadership qualities, which made an important contribution to creating a productive and comfortable working atmosphere.

Additionally, I am grateful to have met many friendly and supportive people within our group. Suyuan He consistently offered thoughtful advice and support during difficult times, thanks to her natural ability to connect with people. Karabo Mike Bopape was always willing to help and, through his life experience, often identified non-obvious solutions to complex problems. Lennard Kloene, friendly and always ready to assist, never hesitated to take on extraordinary challenges, drawing on his unique skill set. Sudip Senapati provided constant support during difficult periods and was always willing to lend a helping hand.

Finally, I would like to express my deepest gratitude to my parents Maksym Sliusarevskyi and Mariana Sliusarevska as well as my sister Khrystyna Sliusarevska, who have always been a reliable source of support, encouragement, and care. I am also sincerely thankful to all other members of my family for believing in me throughout this journey.

The following parts of this work have already been published:

Photocatalytic Synthesis of Unprotected Sulfonimidamides and Their Application in Photochemical Nitrene Transfer Reactions

I. Sliusarevskyi, J. Diaz, S. Senapati, B. J. Ebel, N. J. Linnartz, I. M. Oppel, C. Empel, P. W. H. Chan, R. M. Koenigs, *Angew. Chem. Int. Ed.* 64, e202509870 (**2025**)

A metal-catalyzed triplet relay strategy for aza-Pauson-Khand reactions

Q. H. Pham, **I. Sliusarevskyi**, A. Saha, L. Kloene, N. J. Linnartz, C. Empel, I. M. Oppel, D. Maiti, R. M. Koenigs, *Chin. Chem. Lett.* 112306 (**2025**)

Photocatalytic S-alkylation of sulfinamides: access to sulfoximines

I. Sliusarevskyi, H. Mondal, R. M. Koenigs, accepted by: *Chem. Commun.* (**2026**)

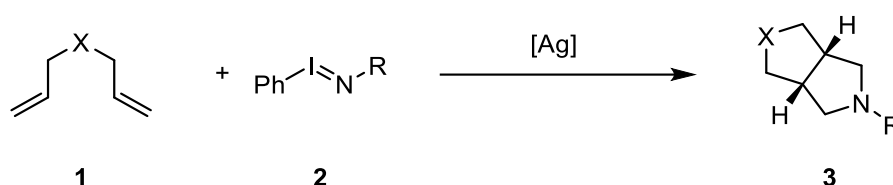
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Summary

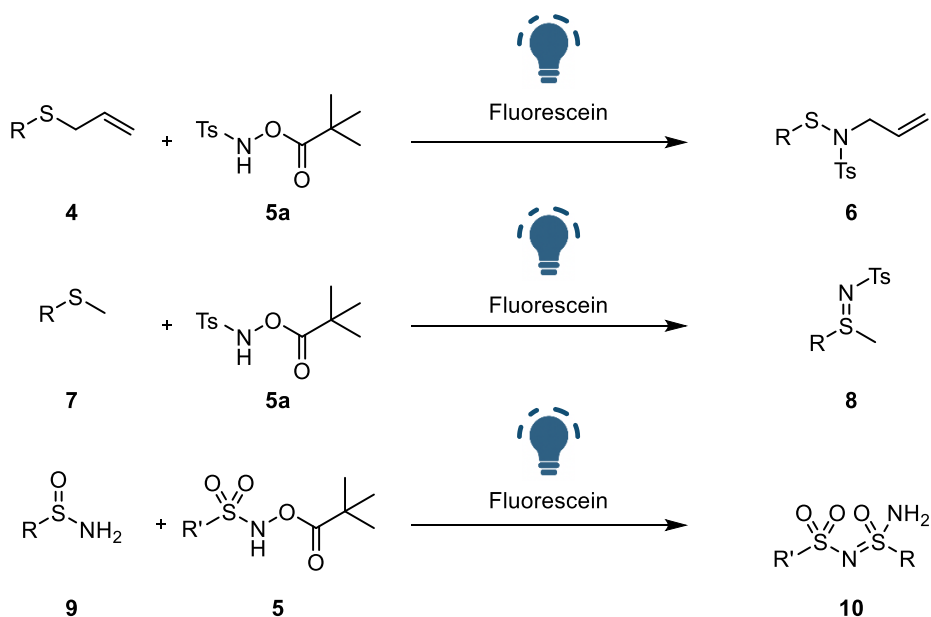
This PhD thesis is divided into two, although related, independent blocks: transition metal-catalyzed nitrene transfer reactions in cycloaddition chemistry and the synthesis of various sulfur-containing compounds via photocatalytic nitrene and carbene transfer reactions.

In the first part, we decided to expand the modified version of the Pauson-Khand reaction that was already studied by our group. Specifically, we considered a metal-catalyzed conditions transformation to extend its applicability beyond the present photochemical version. We successfully developed a method for a silver-catalyzed nitrene transfer reaction via a triplet relay strategy to obtain the desired product. Moreover, we managed to present a diverse scope, using various non-conjugated 1,6-dienes **1** and various iminodiodanes **2**.



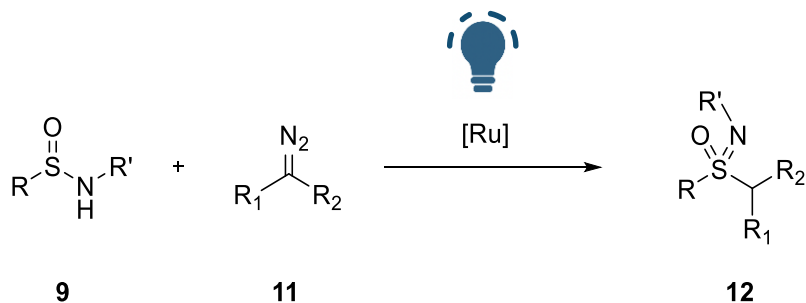
Scheme 1: metal-catalyzed nitrene Pauson-Khand-like reaction.

In the second part, we modified the sulfur(II) **4,7** and sulfur(IV) **9** substrates via photocatalytic activation of the hydroxylamine bond, leading to nitrene transfer. This strategy is poorly described in the literature. For this reason, we were able to obtain a broad scope of sulfenamides **6**, sulfilimines **8** and sulfonimidamides **9**. Moreover, we extended the application of sulfonimidamides in further nitrene transfer reactions, highlighting the possibility of performing consecutive nitrene transfers within a single chain of transformations.



Scheme 2: modification of sulfocompounds with hydroxylamine-based nitrene sources.

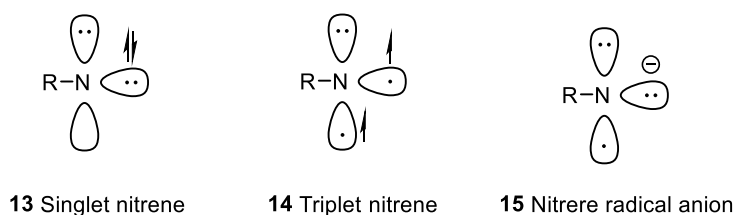
Lastly, we explored the modification of organosulfonyl compounds through photocatalytic direct S-C coupling of sulfinamides **9** with diazo compounds **11**. This transformation proved to tolerate a wide range of function groups. In addition, this reaction, afforded the synthesis of a methylene group, which could be activated by the presence of two acceptors, thus, providing an excellent platform for various modifications.



Scheme 3: photocatalytic S-Alkylation of Sulfinamides with diazo compounds.

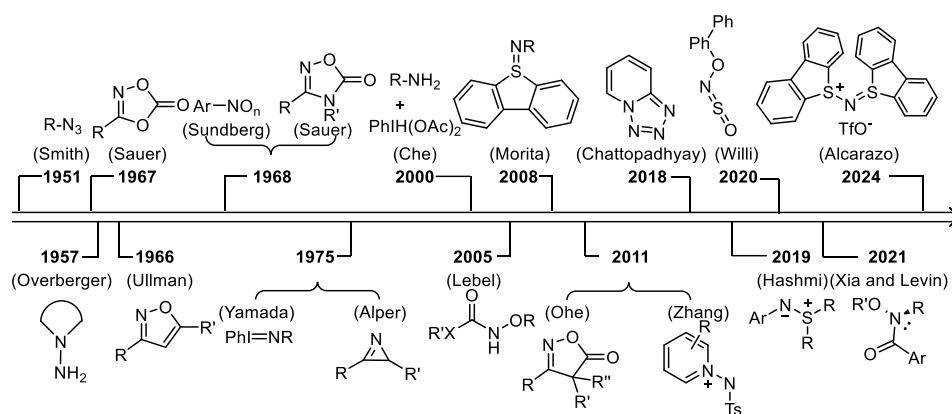
1. Introduction to nitrene

Modern organic chemistry is built on the study of highly reactive species. A lot of these intermediates are extremely short-lived. However, they participate in numerous valuable and diverse chemical reactions. One such class of intermediates is nitrenes; electron-deficient, nitrogen-containing species known for their high reactivity. Nitrenes share close structural and electronic similarities with their "chemical siblings", carbenes, and share many comparable properties.¹ Due to their electron structure, nitrenes can exist in different spin states.² The singlet state **13** features a lone pair of electrons along with an empty orbital. In contrast, the triplet state **14** is characterized by two unpaired electrons on two different orbitals, giving nitrenes biradical-like behavior. This duality in electronic structure opens up a wide range of synthetic applications.³ Recently, another nitrene-like species based on single-electron transfer (SET) gained increasing attention. This strategy allows the formation of anion radicals **15** through activation by metal-based or organic photocatalysts, opening new possibilities for radical-mediated transformations (Scheme 4).⁴



Scheme 4: Types of nitrene and their structure

Some of the widely studied nitrene-mediated reactions include C-H insertion, aziridination, and reactions with heteroatoms such as oxygen, sulfur, and phosphorus.^{5,6} Due to their extreme reactivity and fleeting nature, nitrenes can not usually be isolated. It is necessary to generate these chemical species in the reaction mixture. As a result, numerous nitrene precursors have been developed for this purpose.⁷⁻¹⁸ As a result, a historical chain of sustained development of these precursors has since been established (Scheme 5).⁵ There has been a notable growth in the types of compounds developed for nitrene generation, thus growing the scope of the mechanistic pathways for synthesis development.

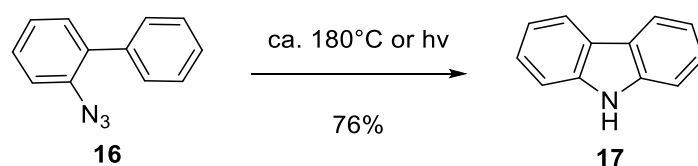


Scheme 5: Types of nitrene precursors

Azides were the first nitrene precursor discovered, in a period when the nature of the species was not yet defined. They are highly reactive compounds. Azide organic motifs, such as phenyl azide, have been known since the mid-19th century,¹⁹ whilst inorganic azide compounds have been studied by Curtius at the end of the 19th century.²⁰ Since then, they are used in countless organic reactions. Their most important transformation is the click reaction [3+2]^{21,22} and other heterocyclizations,^{23,24} which have become simple and cheap ways to combine two scaffolds in organic synthesis.

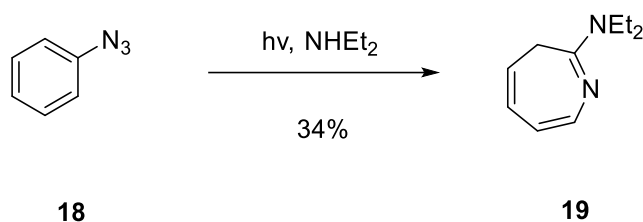
An additional advantage of azide chemistry is its ability to eliminate chemically neutral gas N_2 . In the Staudinger reactions^{25–27} and noble-metal hydrogenation, this process occurs gradually. First is the addition of a nucleophile, followed by the subsequent cleavage of a gas. Alternative to this, thermal or photo-irradiation activation may cause the azide group to cleave nitrogen, thereby generating a nitrene species. In 1951, Smith and Brown carried out one of the first free nitrene reactions. The authors did not realize it, but this was the first use of nitrenes, obtained by thermal or UV activation of aromatic azides **16** (Scheme 6).²⁸

Smith and Brown 1951



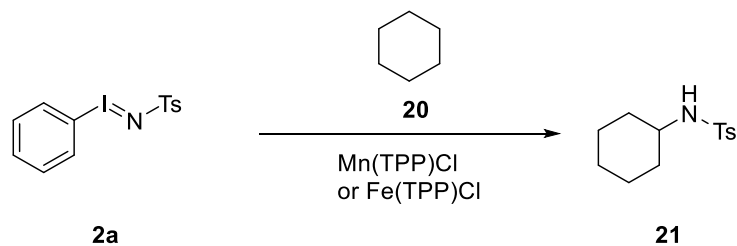
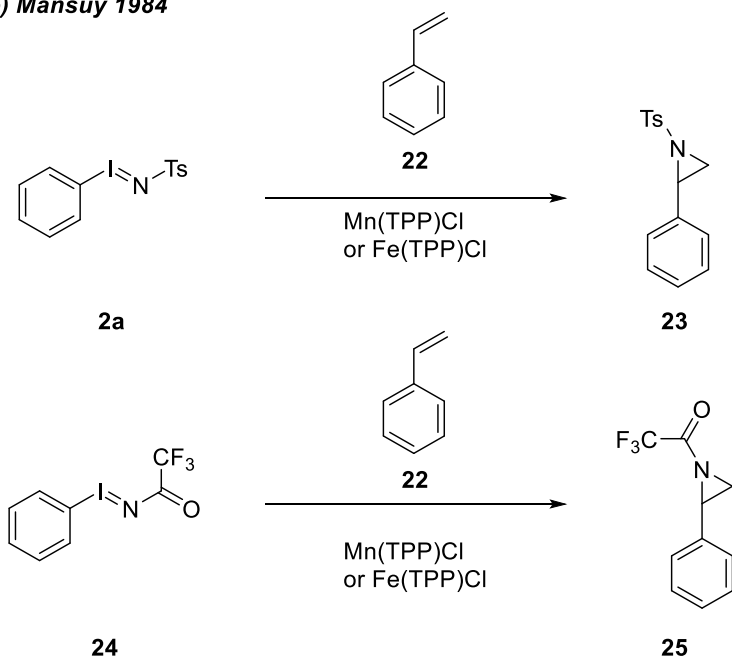
Scheme 6: Thermal or UV activation of azides reported by Smith and Brown

Later, in 1966, Odum demonstrated that aryl azides **18** can react with their own aromatic rings, leading to intramolecular insertion and ring modification **19**.²⁹ This rearrangement transformation was eventually controlled by employing appropriate catalysts, which resulted in directing the reactivity more selectively (Scheme 7).³⁰

Odum 1966**Scheme 7: UV intramolecular insertion reported by Odum**

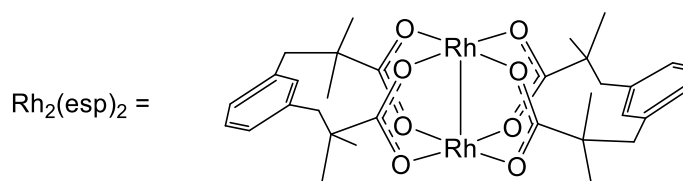
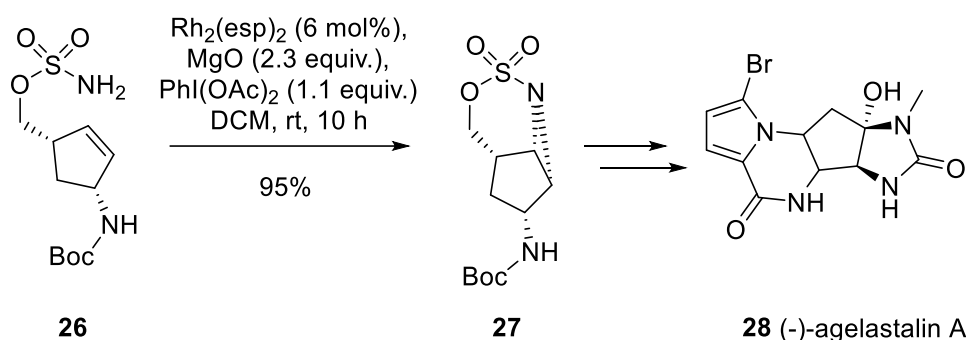
Although azides have proven to be highly effective nitrene-generating precursors, they are also known to be dangerous compounds due to their tendency to decompose, and their explosive nature. These risks can occur both during their preparation, and in chemical reactions involving them.³¹ These serious safety concerns were a strong motivation to develop alternative nitrene precursors that are more stable and safer.

Hypervalent iodine(III) compounds are one of the oldest and most well-established sources of nitrenes. In 1975, Yamada published a study describing the synthesis of PhINTs.³² This method, with only minor modifications, remains a reliable preparative technique to date. These reagents gained popularity due to their low cost, relative stability in laboratory conditions, and high reactivity under catalytic conditions. However, this class of compounds is not without issues. A significant environmental concern is the formation of iodobenzene as a byproduct, which is toxic and poses challenges for green chemistry.^{33,34} The first successful use of iminoiodinanes in nitrene transfer reactions was reported by Breslow in 1982. He showed that manganese and iron complexes could catalyse the C-H insertion of a nitrene into cyclohexane **20** (Scheme **8a**).³⁵ Two years later, Mansuy used similar catalytic systems to obtain aziridines **23**, **25** from alkenes **22**. He also successfully synthesized trifluoroacetyl iminoiodinane **24**, which is a rare example of a carbonyl-derived nitrene precursor (Scheme **8b**). This compound is an exception because most amide-based iminoiodinanes are too unstable and prone to rearrangements, making it difficult to isolate or use them.³⁶

a) Breslow 1982**b) Mansuy 1984**

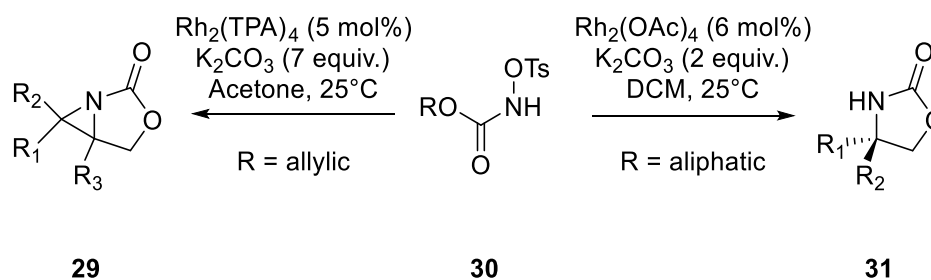
Scheme 8: a) Metal-catalysed insertion reported by Breslow, b) Metal-catalysed aziridination reported by Mansuy

Certain natural products and aliphatic sulfinylamides are challenging to synthesize or isolate directly from reaction mixtures. For such cases, Che and coworkers developed a solution: *in-situ* generation techniques.⁸ These approaches simplify the reaction process and, in some cases, have proven to be more effective than traditional methods. A good example is the work of Du Bois in 2009, where diacetoxyiodobenzene was used to prepare a nitrene precursor from sulfamate **26** during one of the steps in the synthesis of the complex natural product (–)-agelastatin A **28** (Scheme 9).³⁷

Du Bois 2009**Scheme 9: In situ iminoiodane formation in natural product synthesis**

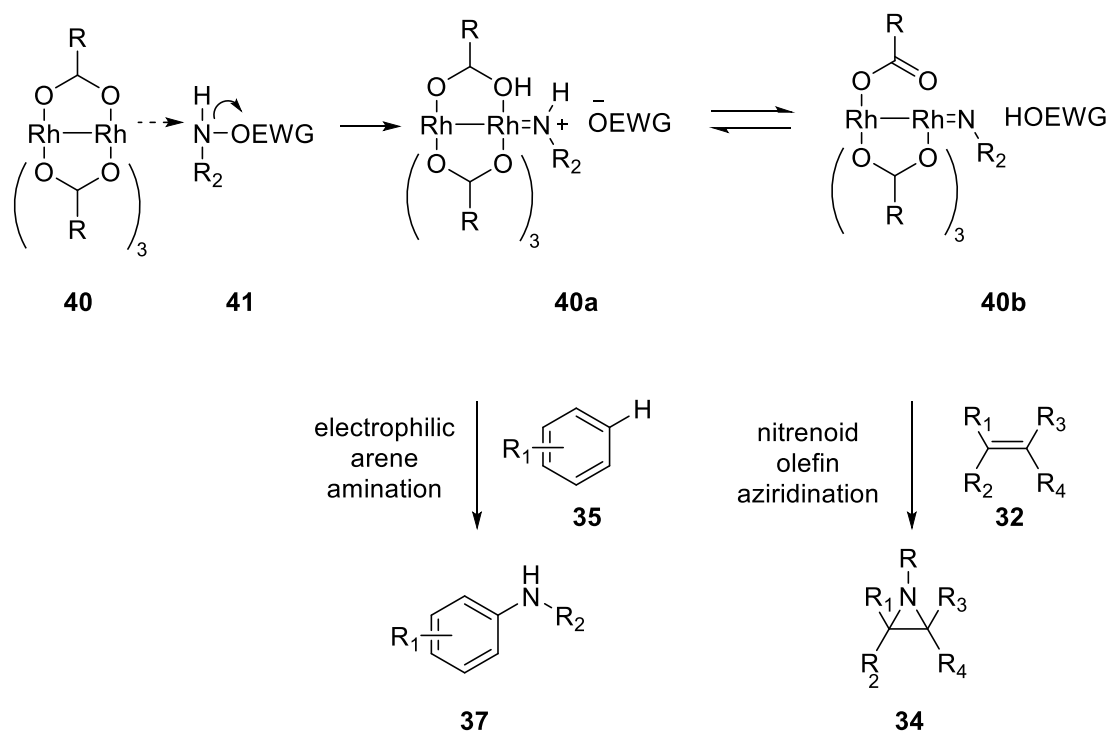
Hydroxylamine derivatives are widely used across various scientific fields, including chemistry, biology, and environmental science.^{38–40} In organic chemistry, hydroxylamines and their derivatives play an essential role as reagents and intermediates in many nitrogen-based transformations.⁴¹ A typical application is their condensation with carbonyl compounds such as aldehydes and ketones, which serves as a key step in the Beckmann rearrangement: a method used to synthesize amides and lactams.⁴² They could be catalytically reduced to amines,^{43,44} and they are often used in heterocyclization reactions.⁴⁵

In the field of nitrene generation, *O*-acylated hydroxylamines have gained attention. Although there are some exceptions, which help to better understand the processes. These compounds can undergo intramolecular elimination to form nitrene intermediates. In 2005, Lectard demonstrated the use of *O*-acylated hydroxylamines **30** as nitrene precursors. His work showed that they could be used under mild conditions to achieve C-H insertion **31** or aziridination of double bonds **29** (Scheme 10).⁷

Lectard 2005**Scheme 10: First application of hydroxylamines as nitrene precursor**

organic and inorganic, are used, aziridination remains feasible, but aromatic amination is completely inhibited. At the same time, addition of *p*-toluenesulfonic acid suppresses aziridination, confirming the protonation-dependent equilibrium between the two catalytic forms (Scheme 12).⁴⁷

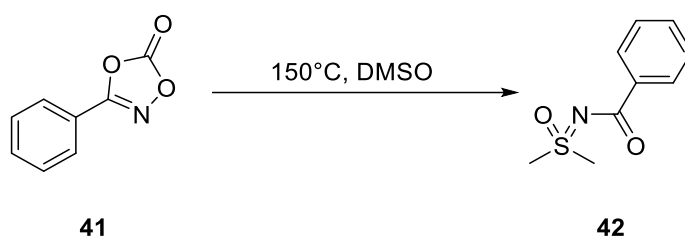
Proposed Mechanism



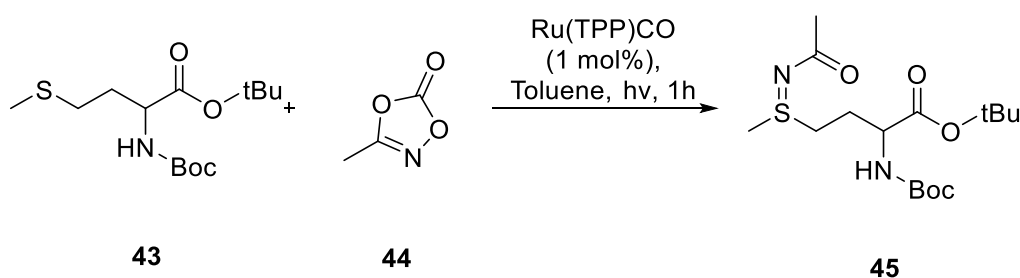
Scheme 12: Differences in the mechanisms of the leaving groups in hydroxylamines

There are many examples demonstrating the potential of hydroxylamine-based compounds in nitrene chemistry. Despite this fact, the use of *N*-sulfonamide fragments as nitrenoid sources from hydroxylamine precursors remains underexplored in modern literature, with only a few reported cases.^{34,48,49} This leaves potential for future research, as the sulfonamide group is commonly found in many biologically active molecules and widely used as a protecting group due to its high stability under various reaction conditions. Additionally, many studies focus on the activation of hydroxylamines by various transition-metal catalysts.^{50–55} However, there are far fewer studies describing the photocatalytic activation of such compounds.⁵⁶ This gives us a direction for potential research in this field.

One of the newest and under-explored classes of nitrene precursors is dioxazolones **41**. Related structures have been known since the mid-20th century,⁵⁷ and in 1968 Sauer and Mayer demonstrated their ability to transfer nitrene groups to DMSO to get corresponding sulfoximine **42** (Scheme 13).⁵⁸

Sauer and Mayer 1968**Scheme 13: Thermal activation of dioxazolones**

These compounds attracted little attention from the scientific community until Bolm's breakthrough study in 2014.⁵⁹ In their work, dioxazolone **44** was used in a photocatalytic process, which triggered a new wave of interest in this class of molecules by modifying protected methionine **43** (Scheme 14). Dioxazolones offer several significant advantages. They are considered safer and more environmentally friendly than many other nitrene sources, their byproduct is carbon dioxide, in contrast with iodobenzene. Additionally, they show reduced tendency toward rearrangements, making them more stable and selective in many reactions.⁶⁰ Despite this, dioxazolones remain poorly studied in the context of nitrene chemistry. However, recent scientific work offers hope for the increasing use of this class of compounds in nitrene-transfer reactions.

Bolm 2014**Scheme 14: Methionine functionalisation by dioxazolone**

The chemistry of nitrene intermediates is a dynamically evolving field, with a wide range of precursors offering distinct advantages and solutions to specific challenges. Each class of nitrene precursors remains essential to modern synthetic chemistry. At the same time, all of them contain unexplored areas and questions that continue to challenge researchers and offer opportunities for future discovery. The growing diversity of nitrene precursors, coupled with advancements in catalysis and activation methods, points toward broader, more controlled applications of nitrene chemistry in modern synthetic strategies.

2. Silver-catalyzed triplet relay strategy for 2+2+1 reactions

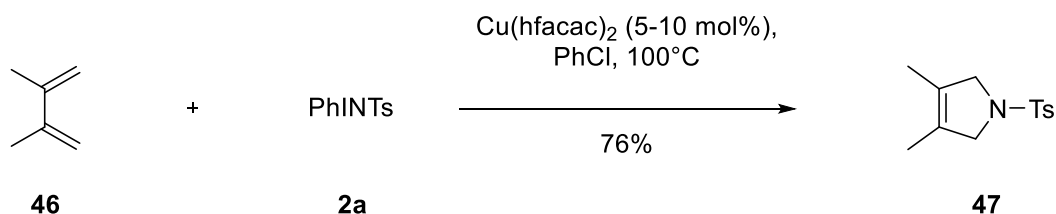
This work was done in collaboration with Hoang Pham and Lennard Kloene. Reactions shown in this chapter were conducted by Ivan Sliusarevskyi.

2.1 Background and aim of the project

Cycloaddition is an important method for the synthesis of heterocycles. In many cases, it is an easier and sometimes the only possible way to solve a synthetic challenge.⁶¹ The expansion of this direction has been a key vector of the development of chemistry throughout its existence. Despite the rapid development of nitrene chemistry, the number of known cycloaddition reactions involving nitrene transfer remains limited, and [2+1] aziridination remains one of the most researched reactions.^{36,62–75}

In recent years, more studies have begun to expand the horizons of nitrene-based cycloaddition. In 2011, Zhou reported a notable [4+1] cycloaddition involving conjugated diene **46** and an iminoiodinane **2a**, opening a new direction in the field (Scheme 15a).⁷⁶ Later, in 2019, Hilinski introduced a [5+1] cycloaddition that enabled the formation of dihydropiperidines **50** from vinylcyclopropanes **48** and a nitrene precursor **49** (Scheme 15b).⁷⁷

a) Zhou y 2011



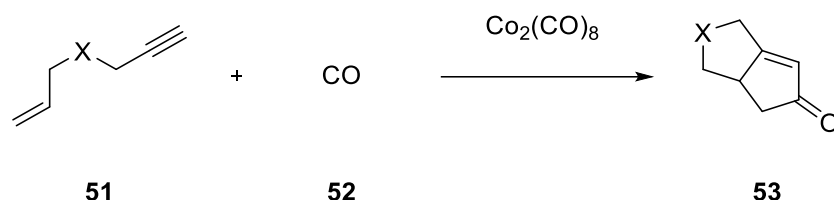
b) Hilinski 2019



Scheme 15: a) nitrene-based formation of five membered ring, b) nitrene-based formation of six membered ring.

The work reported by Pauson and Khand demonstrated that cobalt catalyst can form complexes with acetylene **51** and in the presence of carbon monoxide **52** can lead to cyclization **53** (Scheme 16).^{78,79}

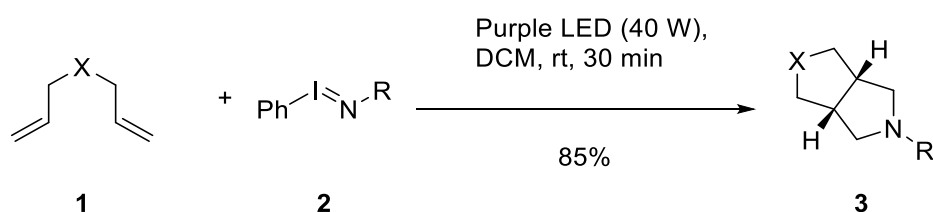
Pauson and Khand 1977



Scheme 16: Pauson–Khand reaction

Most recently, in 2024, our group, inspired by the Pauson–Khand reaction, developed a [2+2+1] cycloaddition method that combined a non-conjugated diene system **1** and a light-activated nitrene precursor **2**. This transformation afforded two joined five-membered rings via a mechanism similar to the Pauson-Khand reaction. This work highlights the growing potential of complex cycloadditions in expanding the synthetic utility of nitrene intermediates beyond traditional frameworks (Scheme 17).⁸⁰

Koenigs 2024



Scheme 17: Free nitrene Pauson–Khand-like reaction.

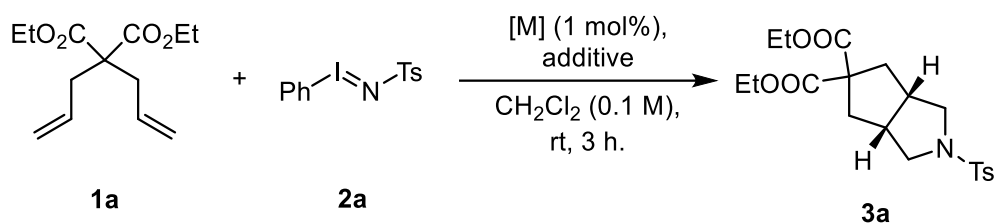
In our work, we extended the concept reported by our group in 2024, which demonstrated that photoactivated triplet nitrene reactivity can be translated into metal-catalysed conditions. This strategy offers a promising method to expand the synthetic utility of nitrenes beyond light-dependent systems.

2.2 Result and discussion

To achieve this goal, we conducted a series of experiments with known metal catalysts that have proven their ability to initiate nitrene transfer. We increased the reaction time from 30 minutes, as reported in the initial paper, to 3 hours. This was necessary because the transfer of nitrenes with the help of a catalyst was much slower than the transfer of free nitrenes. Exploring CoTPP, FeTPPCL, FePC, and Ru₂(esp)₂Cl (Table 1, entries 1-4) afforded moderate yields (around 30%). To our satisfaction, significantly higher yields were achieved with Ag(TP)^{Br3} (49%) (Table 1, entry 5). It is important to note that no product formation was observed when Rh₂(esp)₂ was used (Table 1, entry 6), suggesting that not all transition metal

complexes are equally effective in this transformation. To improve reaction yields, we added HFIP (hexafluoroisopropanol), a weak acid (Table 1, entry 7). This was done to neutralize basic elements that could form during the reaction and negatively affect the process. This addition improved the yield increasing it to 52%. Removal of catalyst, resulted in only 8% yield observed (Table 1, entry 8). We then conducted the experiment in the absence of the metal catalyst with HFIP, observing a yield of 20% (Table 1, entry 9). Confirming the positive role of HFIP, but at the same time, the presence of a metal catalyst remains significant for the reaction process.

Table 1: Investigation of different metal catalysts.



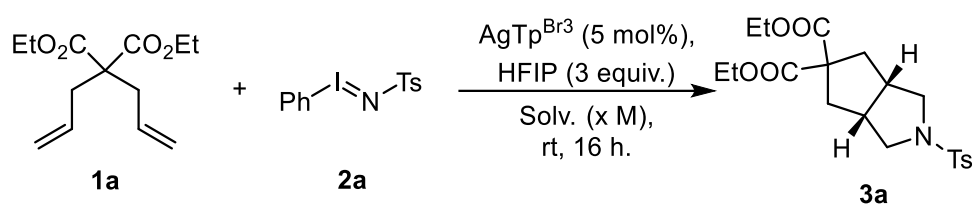
Entry	Catalyst (x mol%)	Additive	% Yield NMR ^b
1	CoTPP (5 mol%)	-	36%
2	FeTPPCl (5 mol%)	-	33%
3	FePC (5 mol%)	-	31%
4	Ru ₂ (esp) ₂ Cl (2.5 mol%)	-	32%
5	AgTP ^{Br3} (5 mol%)	-	49%
6	Rh ₂ (esp) ₂ (5 mol%)	-	0%
7	AgTP ^{Br3} (5 mol%)	HFIP (3 equiv.)	52%
8	-	-	8%
9	-	HFIP (3 equiv.)	20%

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), [M] (x mol%), CH₂Cl₂ (0.1 M), rt, time.

^bCalculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene or mesytilene), isolated yield in parentheses.

In the next stage of the study, the reaction conditions were further optimized by varying stoichiometry, solvent, and concentration. The addition of 5 equivalents of iminoiodinane **2a** (Table 2, entry 2) did not lead to a significant increase in yield. Similar results were observed when the initial solvent screening was conducted. Firstly, we explored chlorinated solvents (Table 2, entries 1-4). In all cases the same result was observed, therefore, we decided to proceed with the most common and easiest to work with - DCM. We further assessed other solvent classes, such as THF (Table 2, entry 5), toluene (Table 2, entry 6), acetonitrile (Table 2, entry 7), and DMF (Table 2, entry 8). In all of them we observed no product formation. Next, we focused on concentration. Dilution of the reaction mixture by half (Table 2, entry 9) gave only a minor increase in yield. A further dilution to 0.0125 M (Table 2, entry 10) increases the crude NMR yield to 67%, and the isolated yield after purification was 65%. Unfortunately, further dilution (Table 2, entry 11) led to a decrease in yield.

Table 2: Investigation of different solvents and concentration.

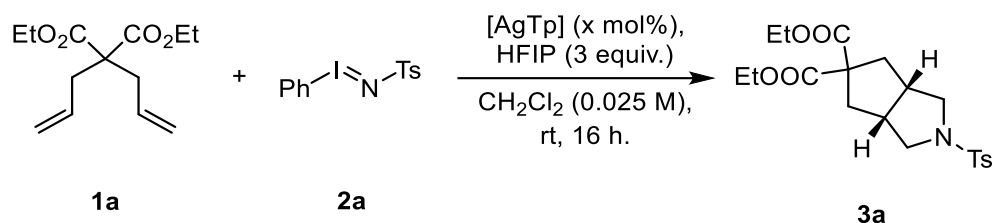


Entry	Solvent	Concentration	% Yield NMR ^b
1 ^c	DCM	0.1 M	52%
2 ^d	DCM	0.1 M	53%
3	CHCl_3	0.1 M	53%
4	DCE	0.1 M	52%
5	THF	0.1 M	0%
6	PhMe	0.1 M	0%
7	MeCN	0.1 M	0%
8	DMF	0.1 M	0%
9	DCM	0.05 M	54%
10	DCM	0.025 M	67% (65%)
11	DCM	0.0125 M	57%

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), $\text{AgTp}^{\text{Br}3}$ (5 mol%), solvent (x M), additive(s), rt. ^bCalculated yields were determined by ^1H NMR integration against an internal standard (1,3,5-trimethoxybenzene or mesytilene), isolated yield in parentheses. ^cdata were obtained from previously described experiments. ^d**2a** (5.0 equiv.) was used.

Next, a series of silver scorpionate catalysts was investigated.^{81,82} As shown in Table 3, we did not obtain an increase in yield from the various catalysts in comparison to $\text{AgTp}^{\text{Br}3}$ (Table 3, entries 1-5). Then we explored whether catalyst loading would influence the outcome, by doubling the $\text{AgTp}^{\text{Br}3}$ loading (Table 3, entry 6). Unfortunately, this led to a decrease in yield. Thus, we learned that a higher catalyst concentration can negatively affect the reaction's efficiency under these conditions.

Table 3: Investigation of different silver catalysts.



Entry	Catalyst (mol%)	% Yield NMR ^b
1 ^c	$\text{AgTp}^{\text{Br}3}$ (5 mol%)	67%
2	$\text{AgTp}^{*\text{Br}}$ (5 mol%)	47%
3	$\text{AgTp}^{3,5\text{Me}}$ (5 mol%)	54%
4	$\text{AgTp}^{3,5i\text{-Pr}}$ (5 mol%)	55%

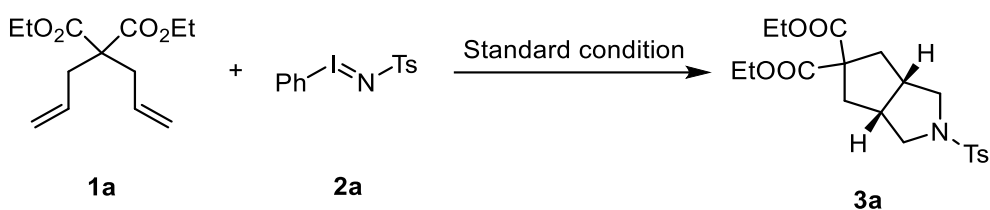
5	AgTp ^{3,5Ph} (5 mol%)	50%
6	AgTp ^{Br3} (10 mol%)	62%

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), [AgTp], CH₂Cl₂ (0.025 M), rt, 16 h.

^bCalculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene or mesitylene). ^cdata were obtained from previously described experiments.

Lastly, various factors were screened to observe the impact on the yield. We have observed that air had a negative effect, reducing the yield to 5% (Table 4, entry 1). Additionally, the presence of water also reduced the reaction yield to 28% (Table 4, entry 2). Also, an increase in the reaction temperature led to a reduction in yield to 55% (Table 4, entry 3). Based on these results, the reaction optimization process was completed at this stage.

Table 4: Influence of different deviations from standard conditions of reaction.



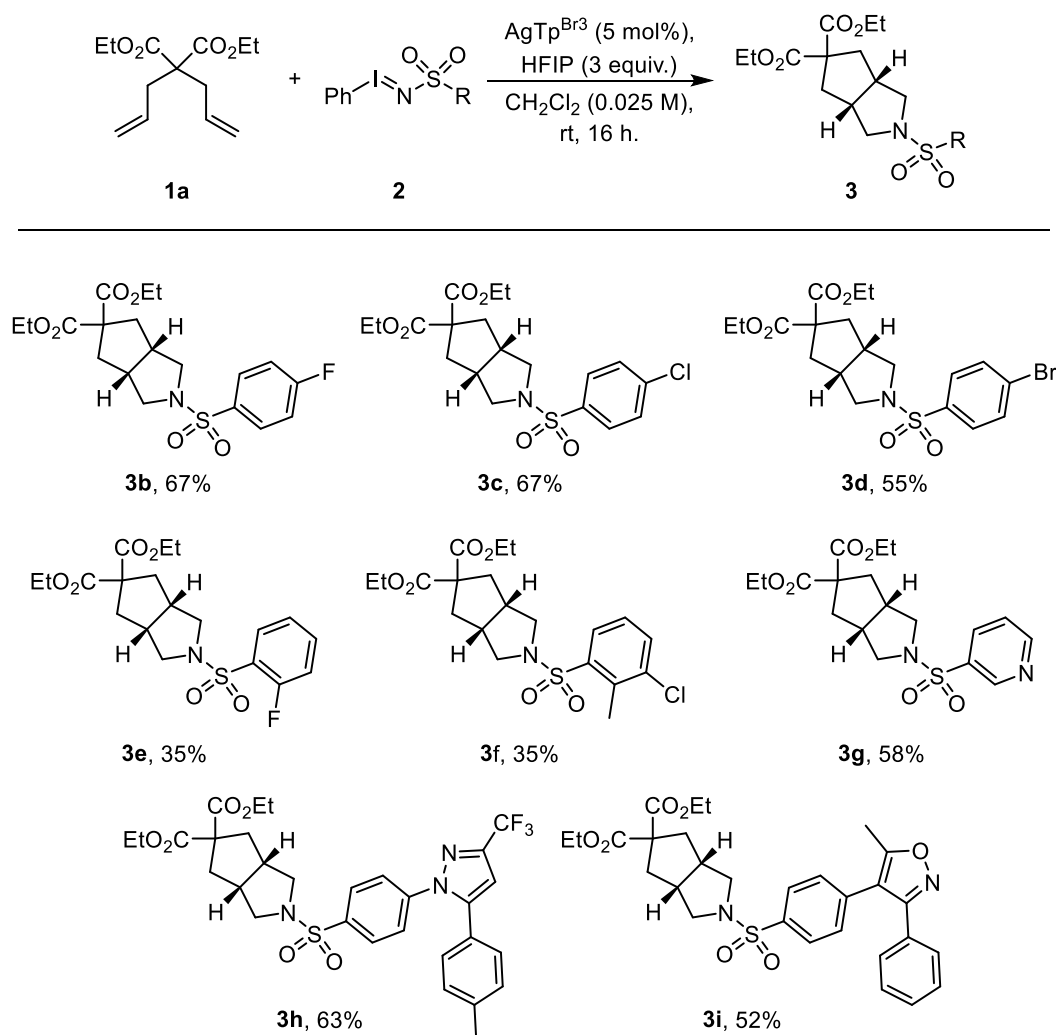
Entry	Deviation	% Yield NMR ^b
1	Air	5%
2	H ₂ O (50 μL)	28%
3	40 °C	55%

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), [AgTp] (x mol%), CH₂Cl₂ (0.025 M), rt, 16 h. ^bCalculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene or mesitylene).

To summarize the optimization results, the following methodology was established as the optimal procedure for conducting the reaction: An oven-dried test tube equipped with a magnetic stir bar was charged with compound **1** (0.2 mmol, 1.0 equiv), AgTp^{Br3} (0.01 mmol, 5 mol%), and HFIP (0.6 mmol, 3.0 equiv). The tube was sealed with a rubber septum, evacuated, and backfilled with argon three times. Anhydrous dichloromethane (CH₂Cl₂, 8 mL) was added via syringe, followed by the addition of iminoiodine **2** (0.6 mmol, 3.0 equiv) in a single portion under a continuous argon flow. The reaction vessel was then sealed with parafilm and stirred at ambient temperature for 16 hours. Upon completion, the mixture was concentrated in vacuo and purified by column chromatography.

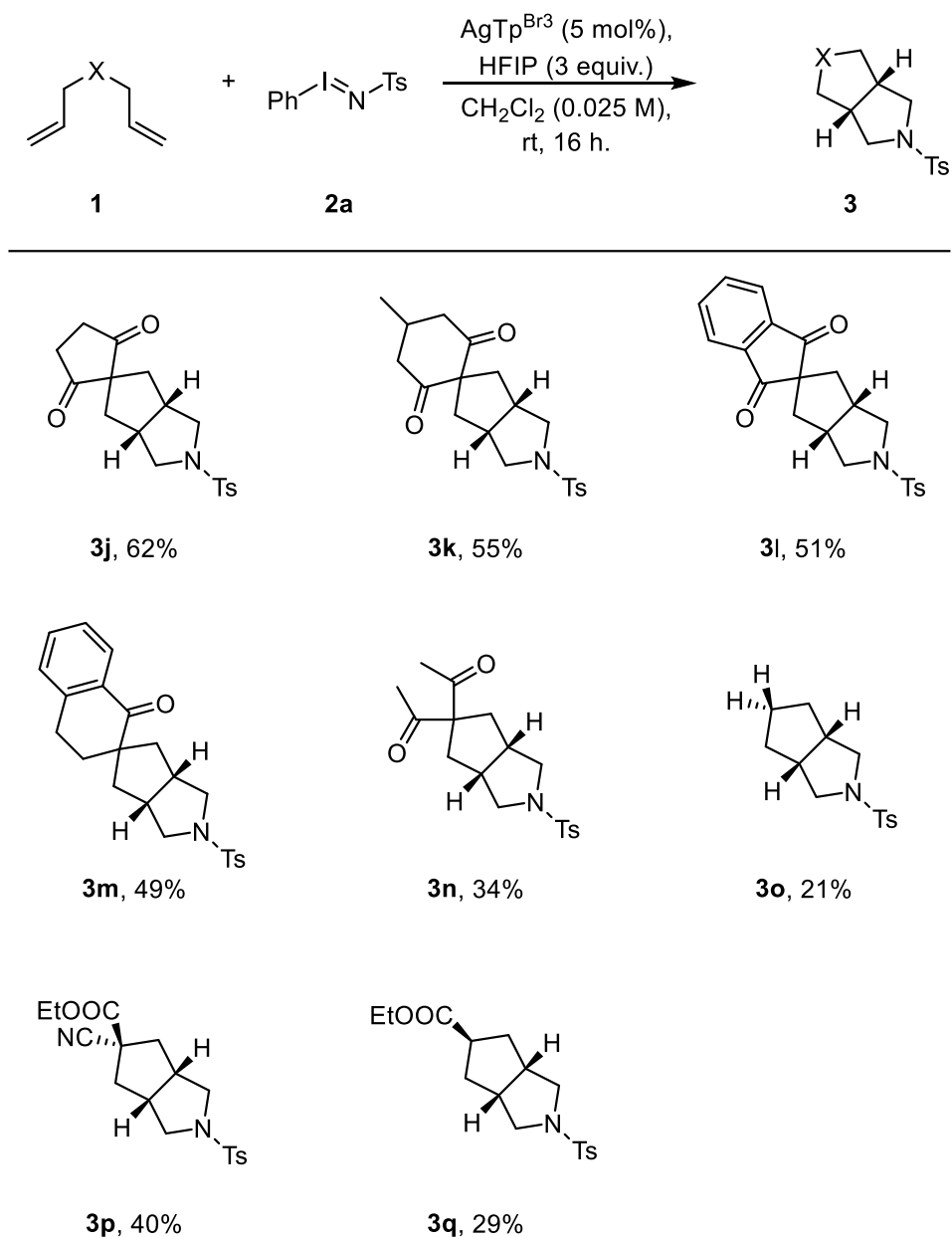
With the optimized reaction conditions in hand, the substrate scope of this reaction was then investigated. We began our study with various iminoiodinanes and examined how their structures affected our reaction. (Scheme 18). For the *p*-halogenated derivatives **3b-d**, yields were similar to the model reaction, indicating good tolerance toward halogen groups in the *p*-position. However, with the *m*-substituted compound **3e** and the *o,m*-disubstituted variant **3f**, the reaction yield decreased to 35%, which is most likely due to a steric effects limiting the transformation. Incorporation of a β-pyridyl fragment in product **3g** afforded the

product in a moderate yield of 58%. This indicates the tolerance to the basic heterocyclic groups. Additionally, we explored iminoiodinanes derived from biologically active drug molecules. Specifically, our goal was to synthesize derivatives from Valdecoxib **3h** and Celecoxib **3i**. These transformations were successful, delivering the modified drug-like products **3h** in 63% and **3i** in 52% yields, highlighting the potential of this method for late-stage functionalization of pharmaceutically relevant compounds.



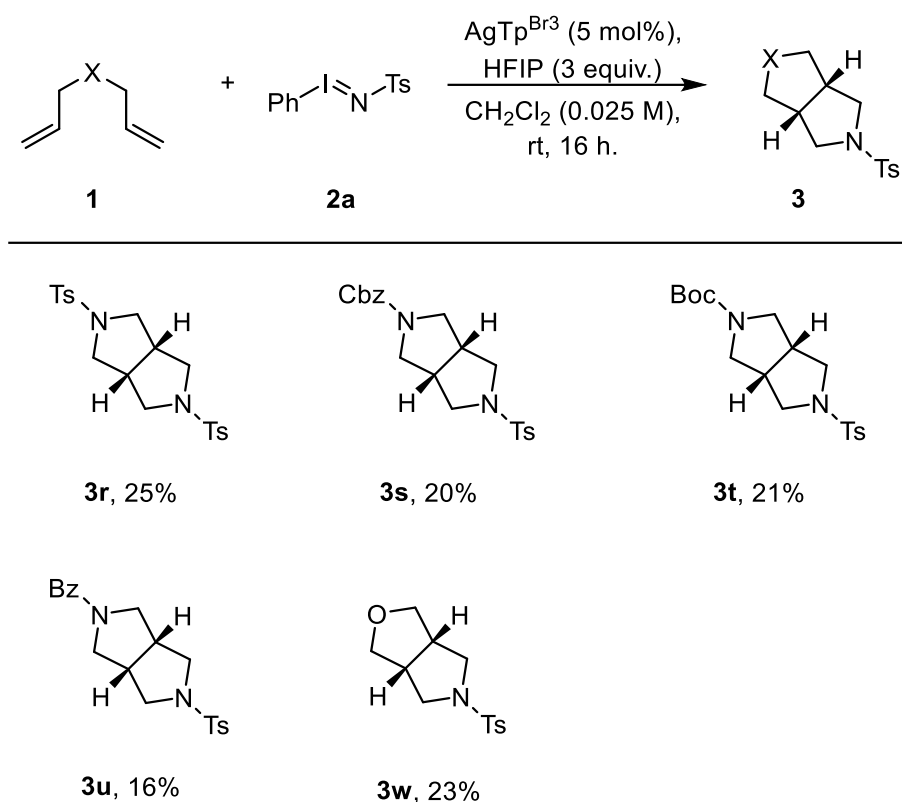
Scheme 18: Substrate scope of different iminoiodinanes.

Next, we moved to assess the scope by studying the effects of the variation in a wide range of products from various dienes (Scheme 19). The reaction conditions showed afforded products with yields ranging from 49% to 62%, in reactions where spirocyclic products **3j-m** were formed. Notably, with an open ring as in the substance **3n**, a significant drop in yield is observed. Further, we replaced one of the esters with a nitrile group **3p**, which further exhibited decreased yields. After double substitution, the reaction stops. The removal of one ester group **3q** or both of them **3o** leads to a significant drop in yield, indicating the importance of acceptor groups in stabilizing the reaction's transition states.



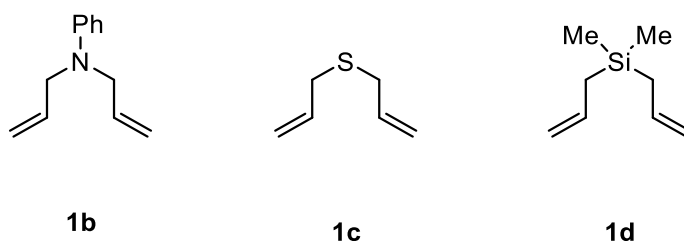
Scheme 19: Substrate scope of different acceptors containing dienes.

Further developing strategies for increasing the diene scope, we synthesized compounds using our methodology in which heteroatoms replaced the carbon atom between the two allylic groups. The synthesis of amine-containing substances with a deactivated electron pair **3r–3u** yields varied from 16% to 25%. A product with an oxygen atom **3w** was also successfully synthesized with 23% yield.



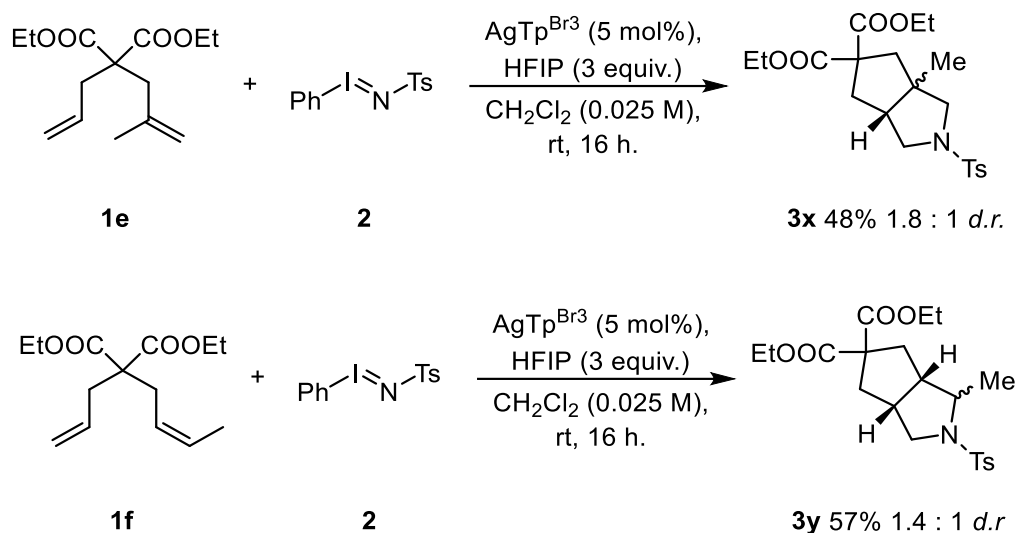
Scheme 20: Substrate scope of different heteroatom-containing dienes.

Using a diene with an aliphatic amine **1b** did not yield the product. As well as, incorporation both sulfur (II) **1c** and silicon **1d** atoms bonded to two allylic moieties did not work. This is a good indication of what heteroatoms our reaction tolerates (Scheme 21).



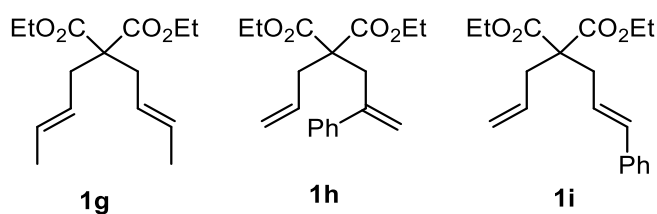
Scheme 21: Substrate scope of different unreactive heteroatoms containing dienes.

To conclude the study of substrate scope, we investigated the reaction with some dienes bearing additional substituents on the double bond (Scheme 22). The use of starting materials bearing substituents on the internal **1e** and terminal **1f** carbon atoms of the double bond led to the formation of compounds **3x** and **3y** in good yields.



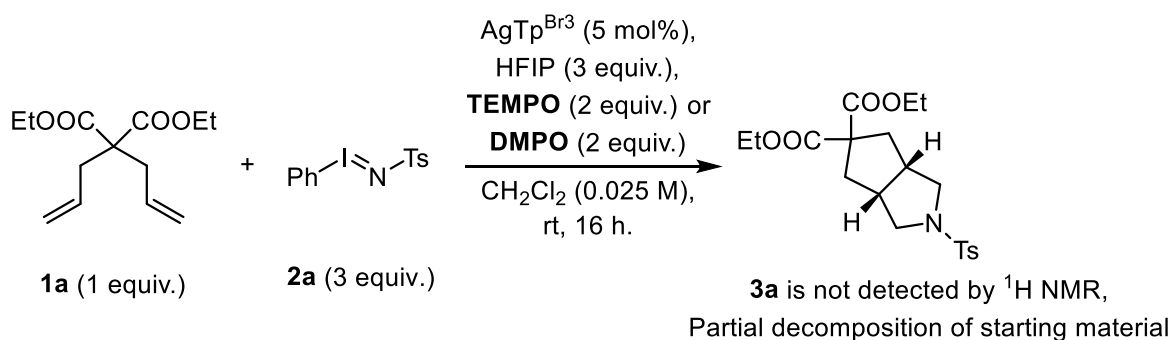
Scheme 22: Substrate scope of functionalized double bond dienes.

Reaction with a compound in which the diene had substituents on both of its double bonds **1g**, or in which there were bulky substituents such as phenyl rings **1h** and **1i**, did not lead to the formation of the product. The most likely explanation for this is steric effects (Scheme 23).



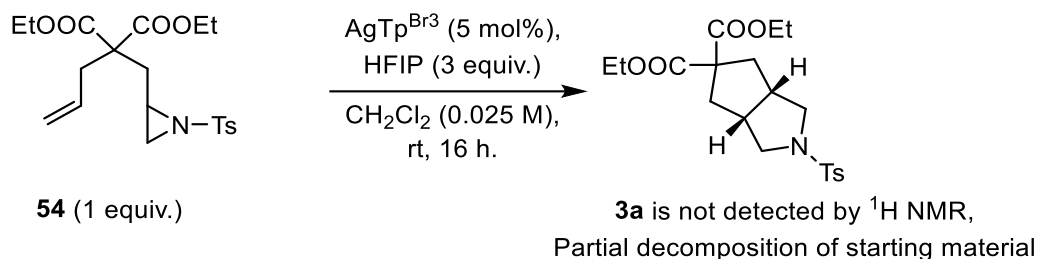
Scheme 23: Substrate scope of unreactive functionalized by double bond dienes.

The final stage of this research was the investigation of the reaction mechanism. Firstly, we did a radical trap experiment. Under standard reaction conditions, TEMPO and DMPO were added separately at the final stage of the reaction. In both cases, the reaction was inhibited, and we could not detect the product. This leads us to the conclusion on the presence of radical species in the transformation (Scheme 24).



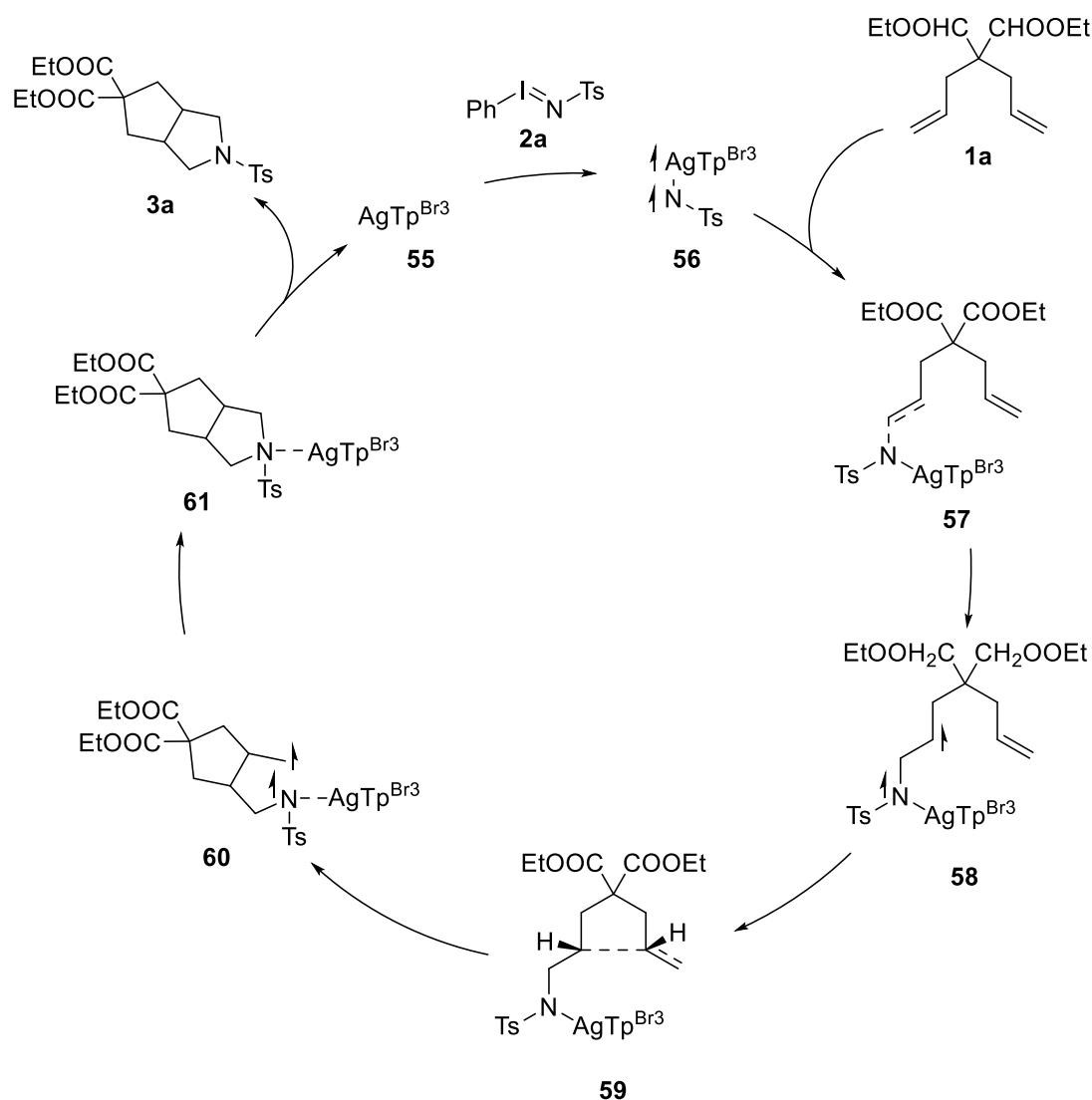
Scheme 24: Radical trap experiment.

Secondly, we examined the potential intermediate product of the reaction. We took the aziridine **54**, which did not lead to the formation of the target product **3a**. This indicates the absence of such an intermediate. Instead, the process is likely to go via a concerted pathway without the formation of aziridine intermediates (Scheme 25).



Scheme 25: Investigation of the potential intermediate.

Based on our data, as well as on the DFT calculations we propose our mechanism. After the generation of silver-nitrenoid species **56** out of the silver complex **55** proposed by Pérez.⁶² After the interaction with diene **1a**, intermediate **57** formed, which subsequently converts into the active species **58**. The resulting structure reacts with the adjacent double bond, leading to the closure of the inner ring and formation of intermediate **59**. Upon regaining a reactive configuration **60**, the second ring closure occurs through interaction with the remaining unpaired electron of the nitrenoid fragment, resulting in the formation of complex **61**. Elimination of the silver complex **55** affords the final product **3a**, thereby completing the catalytic cycle (Scheme 26).



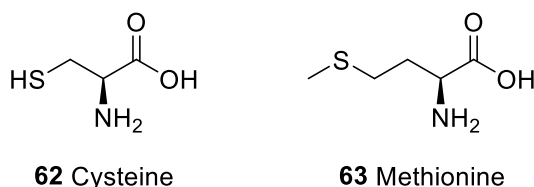
Scheme 26: Proposed mechanism.

2.3 Conclusion

In this work, a new metal-catalyzed methodology for nitrene transfer reactions was developed and expanded the principles of its photoactivated analogue. We successfully translated triplet nitrene reactivity into silver-catalysed conditions. We established a synthetically useful and operationally simple method that avoids the limitations of photochemical initiation. Overall, this methodology opens new possibilities for nitrene-based heterocycle synthesis under transition metal-catalysis and provides a foundation for further development in late-stage functionalization, green chemistry, and medicinal chemistry applications.

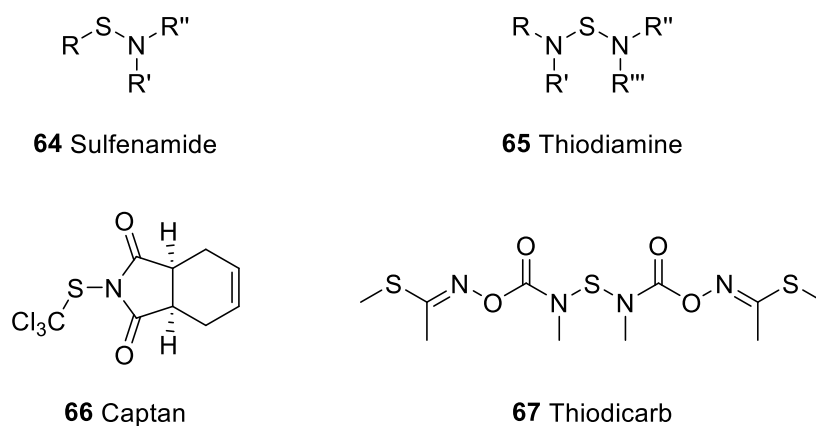
3. Organosulfur compounds

Organosulfur compounds are known for their unique chemical properties and rich diversity, which can only be compared to the diversity of carbon-containing compounds. They are also the basis of life, as they are present in amino acids such as cysteine **62** and methionine **63**, which are the building blocks of proteins, and therefore, all living things on our planet (Scheme 27). The ability to exist in three different oxidation states and form covalent bonds with many non-metals leads to an incredible combination of elements. There are compounds with S-O, S-P, S-Hal, and S-N bonds, and even with the combination of these bonds in one functional group. Among them, sulfur-nitrogen bonds are of great interest to work with. It is used in different situations as an alternative to oxygen. It can perform the same role, but at the same time, it can create an additional bond that can be combined with a variety of molecules. This allows chemists to expand the variability and biological interaction of existing molecules and synthesise entirely new scaffolds.⁸³



Scheme 27: Sulfur-containing amino acids.

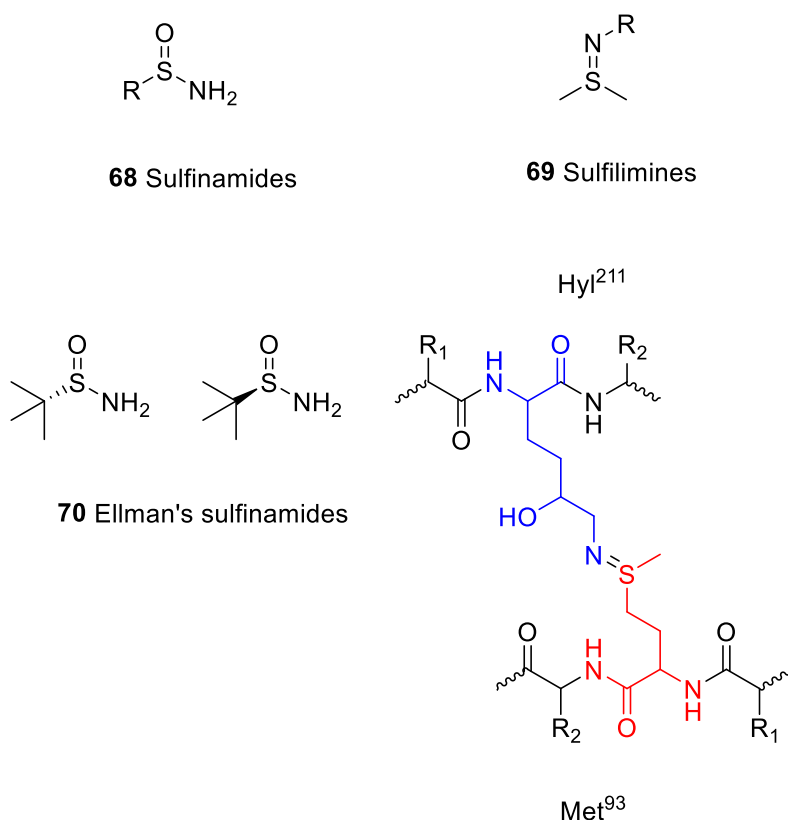
Among organic S(II) compounds connected to the nitrogen atom, only two variants are known: sulfenamides **64** and thiodiamines **65**. Sulfenamides are widely used in agriculture. Captan **66** is a typical pesticide.⁸⁴ On the other hand, they are effectively used in the synthesis of biodegradable polymers used for drug delivery.⁸⁵ Sulfenamide bonds are formed in proteins as post-translational modifications that play essential roles in redox biology and protein regulation.⁸⁶ Thiodiamines, known for their linear structures, have been widely used in agriculture. A striking example is the Thiodicarb **67**. Due to their detrimental effects on human health and documented fatal cases, pesticides of this class were banned in the EU.⁸⁷



Scheme 28: Examples of compounds containing S-N bond with S(II).

Compounds with S(IV) have an additional factor. In the presence of three substituents on the sulfur atom and a pair of electrons, it becomes a stereocenter. This makes such compounds even more interesting for various biological studies, as different isomers can exhibit markedly distinct properties *in vivo*.

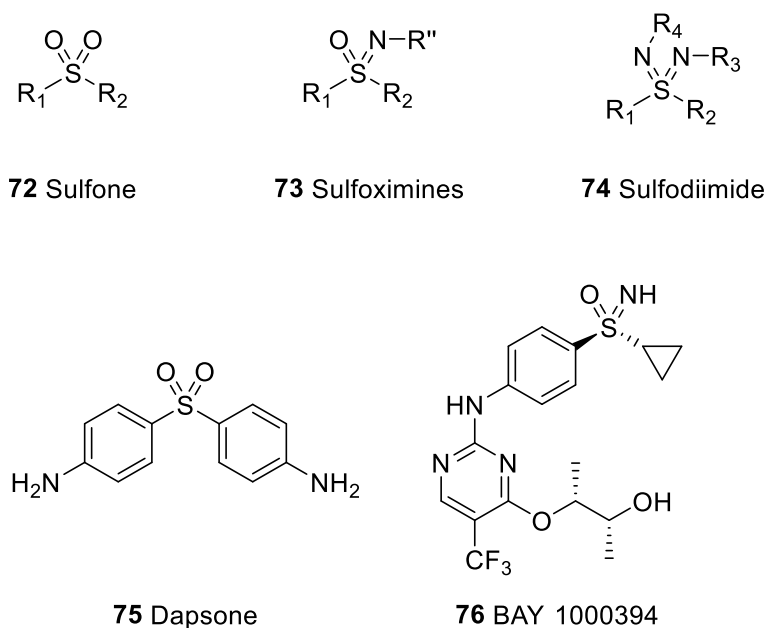
Sulfinamides **68** are excellent examples of chirality. Structurally, they consist of a single C-S bond, a single S-N bond, and an S=O bond, which is an intermediate of a dative bond and a polarized double bond, and of course, a pair of electrons that gives the necessary condition for chirality. The most prominent representative of this class is Ellman's sulfinamides **70**, which have become indispensable in the synthesis of chiral amines. Their role is to coordinate the big tert-butyl group, which enables stereoselective control of the chirality of secondary amines.⁸⁸ Sulfimides **69** are compounds that have a double bond between sulfur and nitrogen, which may be considered a single bond with a formal charge of +1 on the sulfur and a formal charge of -1 on the nitrogen. They also have two C-S bonds. The most prominent example of sulfilimine is the natural process of S=N cross-linking in collagen IV **71**. In 2009, Vanacore and colleagues showed that in the NC1 domains of collagen IV there is a covalent bond between Met93 and (hydroxy)lysine-211, which, according to mass spectrometric and NMR data, corresponds to the sulfilimine-type S=N (Scheme 29).⁸⁹



71 A Sulfilimine Bond Identified in Collagen IV

Scheme 29: Examples of compounds containing S-N bond with S(IV).

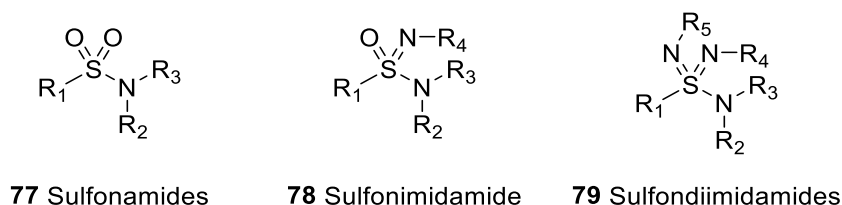
Sulfur(VI)-nitrogen compounds include a broad range of structures, which can generally be divided into two main categories: sulfone-like and sulfamide-like derivatives. Sulfones **72** are functional groups where a sulfur atom is double-bonded to two oxygen atoms and connected to two carbon-based substituents. This moiety is highly relevant in medicinal chemistry. The most well-known example is Dapsone **75**, a synthetic sulfone used as an antibacterial agent in the treatment of leprosy, dermatitis herpetiformis, and other skin conditions.⁹⁰ Sulfone-containing compounds have demonstrated a wide range of biological activities, including antimicrobial, antifungal, antimalarial, anti-HIV, anticancer, and anti-inflammatory effects.⁹¹ Replacing one of the sulfone oxygen atoms with an amino group leads to the formation of sulfoximines **73**. These compounds have attracted significant attention over the last decade, especially in the development of a new class of insecticides.⁹² In pharmaceutical research, a good example is BAY 1000394 **76**, a pan-CDK inhibitor developed by Bayer that contains a sulfoximine fragment. In this molecule, substituting oxygen with nitrogen improved water solubility, enhanced the ADME profile, strengthened CDK inhibition, and enabled new molecular interactions via the N-substituent.⁹³ Additionally, it inhibits the growth of various human tumor xenografts on athymic mice.⁹⁴ Further substitution, replacing both oxygen atoms with nitrogen, yields sulfodiimides **74**. These compounds remain underexplored, but recent studies have begun to uncover promising and practical applications in synthetic chemistry (Scheme 30a).⁹⁵



Scheme 30a: Examples of compounds containing S-N bond with S(VI).

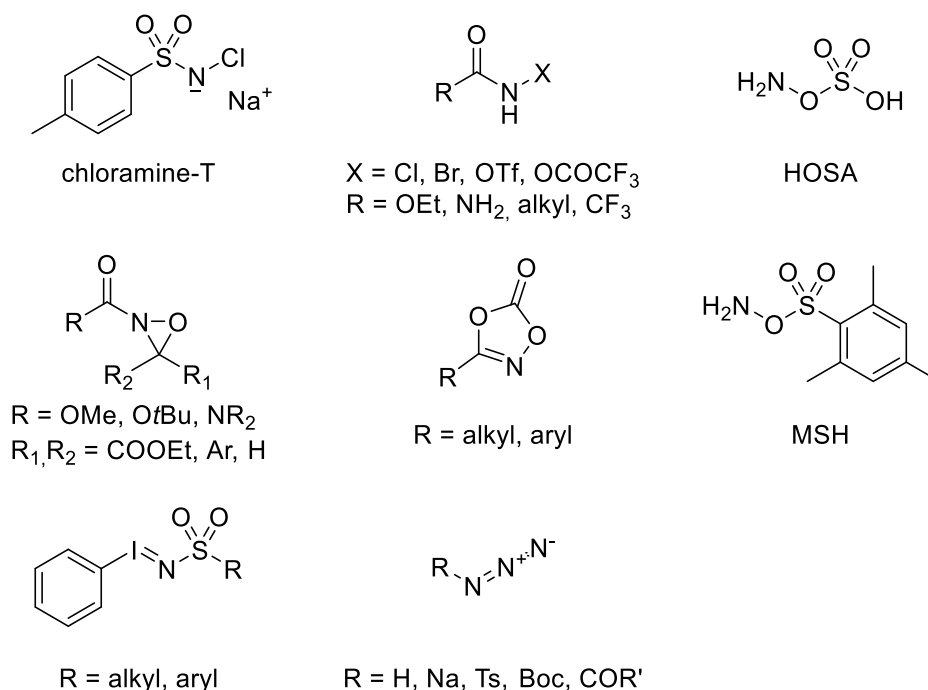
Sulfonamides **77** are groups with hexavalent sulfur connected by a single bond to the nitrogen atom S-N, as well as two double bonds to the oxygen atoms S=O. They play an essential role in medicine, becoming the first antibacterial drugs, even before the invention of antibiotics.⁹⁶ The sulfonamide motif is also widely used in non-antibacterial medications, for example, carbonic anhydrase inhibitors, diuretics, and sulfonylureas, which play a key role in binding to the target.^{97,98} Replacing one of the oxygen atoms with a nitrogen atom,

gives us sulfonimidamides **78**, which are used as bioisosteres of sulfenyl amides. The main difference is that the integration of this nitrogen atom confers chiral properties to the group. The optional presence of another hydrogen atom or bond expands the possibilities for functionalization and, therefore, provides additional advantages in the scaffold construction.⁹⁹ Replacing the next oxygen atom with nitrogen, we obtain Sulfondiimidamides **79**. This represents a relatively new class of compounds that has so far received limited attention but is attracting increasing interest. (Scheme 30b).¹⁰⁰



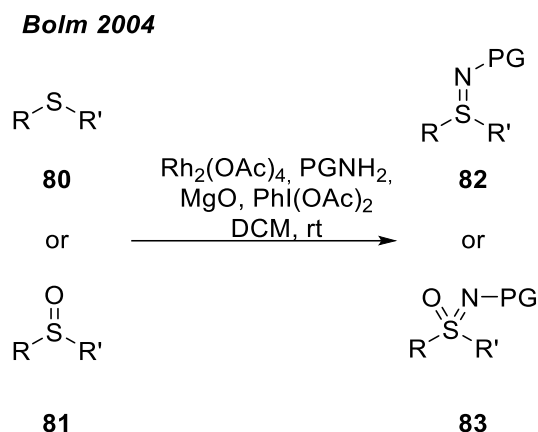
Scheme 30b: Examples of compounds containing S-N bond with S(VI).

Molecules with sulfur(II) and sulfur(IV) atoms in their composition are electron-rich due to the presence of lone electron pairs.¹⁰¹ That is why carbenes and nitrenes, which lack a full octet on their outer orbitals, actively react with sulfur-containing compounds. This strategy opens a large field of research. Sulfides with S(II) and sulfoxides or sulfinamides with S(IV) can incorporate nitrogen as a target for nitrene transfer or form S-ylides reacting with carbenes. From a broad review by Hendriks and Bolm (2015), it is clear that most nitrene precursors are capable of participating in transformations with organic sulfur compounds (Scheme 31).¹⁰² This provides wide variability in selecting the method to overcome the set synthetic tasks, thereby enabling maximum yield and avoiding unwanted side products.



Scheme 31: Examples of nitrene precursors used in modification of Organosulfur compounds

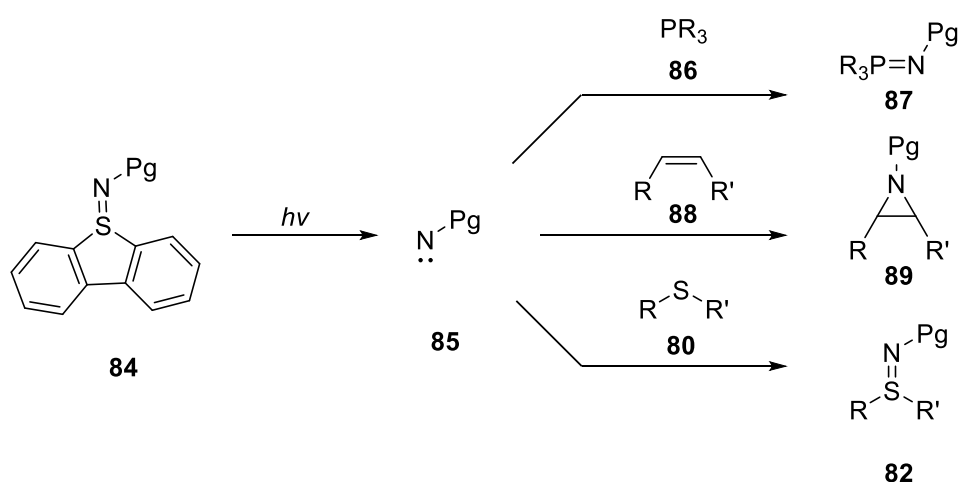
The key study was reported by Okamura and Bolm in 2004, which proposed the in situ generation of nitrenes for the synthesis of sulfilimines **82** and sulfonimidamides **83**, which were synthesized with the help of a Rhodium catalyst (Scheme 32).¹⁰³ This allows obtaining the products of such additions quickly, without the preparation required for the nitrene source. This work prompted a series of publications on in situ transformations that could integrate even unprotected nitrogen.^{104–107}



Scheme 32: in situ modification of organosulfur compounds

Additionally, a significant contribution was reported by Toscano and co-workers in 2007. This work describes the ability of sulfilimines **84** in photochemical conditions to act as sources of nitrenes **85**.¹⁰⁸ Based on this study, in 2008, Akasaka and colleagues carried out a series of experiments with nucleophilic compounds and proved previous data with broad results. They were able to interact with double bonds **88**, phosphorus(III) **86** compounds, and even with other sulfides **80** (Scheme 33).⁹

Akasaka 2008

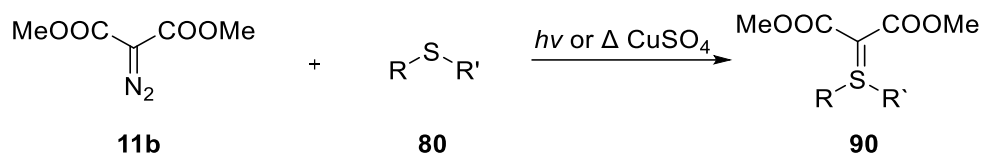


Scheme 33: Sulfilimines as nitrene precursor.

Interactions of carbene **11b** with sulfur-containing compounds lead to the formation of sulfur ylides. Ando and colleagues reported the photoinitiated formation of sulfur ylides **90** in 1969,

and three years later, they published a thermal method as well. According to their studies, metal carbenoids have lower energy than carbenes generated by photolysis. The authors explain their improved yield by this (Scheme 34).^{109,110}

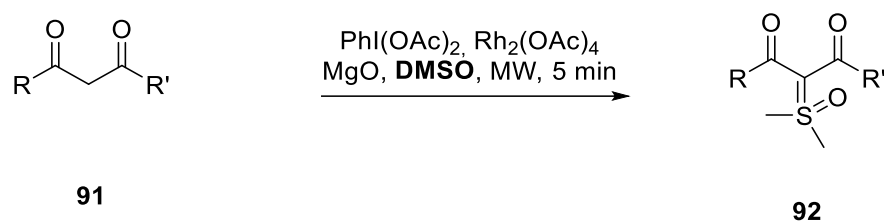
Ando 1969 and 1972



Scheme 34: Modification of sulfide with carbene.

Sulfones can also form ylides. In 2017, Vaitla and colleagues developed a convenient strategy for the synthesis of sulfur ylides under mild conditions. A method involving the rhodium-catalysed coupling of in situ generated carbenes to form ylides **92** with sulfoxides was developed (Scheme 35).¹¹¹

Vaitla 2017



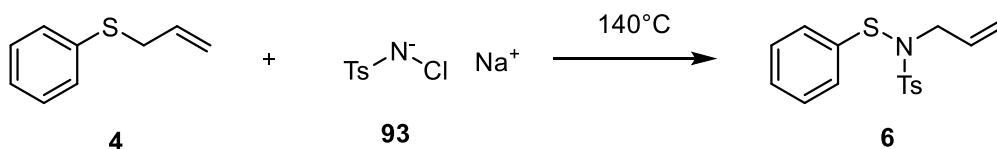
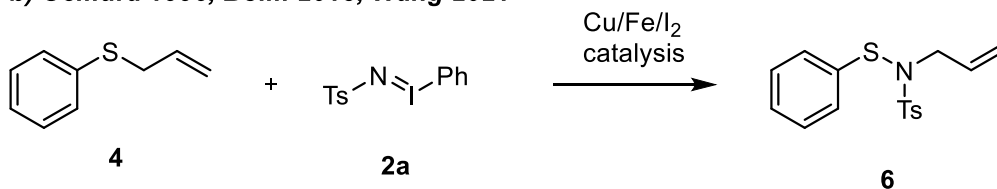
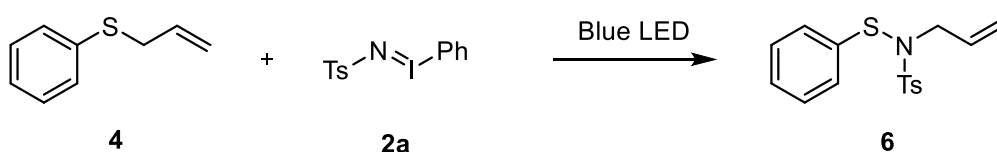
Scheme 35: Modification of sulfoxide with in situ generated carbene.

4. Photocatalytic nitrene transfer to organic sulfur compounds

This work was done in collaboration with Sudip Senapati. Reactions shown in this chapter were conducted by Ivan Sliusarevskiy.

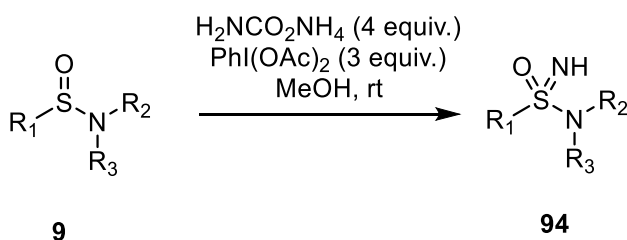
4.1 Background and aim of the project

Organic sulfides S(II) are among the most reactive substrates for nitrene transfer. The high electron density at the sulfur atom favors rapid formation of intermediates and usually outcompetes other potential targets for nitrene transfer. The main products of these reactions are sulfimides, which can serve as an intermediate in different reactions, such as cyclopropanation, epoxidation, and [2,3]-sigmatropic rearrangements. Sigmatropic rearrangements are a class of reactions in which a group bonded through a σ -bond migrates to a system with a π -bond, which changes the position of the σ bond and rearranges the π system. There are several types of such rearrangements, but in the context of S(II) interactions with nitrenes, [2,3]-sigmatropic rearrangements are significant. This rearrangement involves a concerted electron movement through a five-membered transition state. The attempt to run a reaction with sulfide **4** to obtain allylic sulfilimines triggers a rearrangement, leading to a relatively rare nitrogen-sulfur(II) compound **6**. Unlike the similar reaction with carbenes, the nitrene variant is much less described. The first mention of this transformation as a thermal method was documented using Chloramine-T **93** (Scheme **36a**).^{112,113} More recent studies have focused on the use of iodinated compounds. Several methods based on metal catalysis, Cu,^{114,115} Fe,¹¹⁶ as well as I₂ catalysis (Scheme **36b**),¹¹⁷ have been reported. In 2022, our group reported a similar transformation under the influence of light. (Scheme **36c**).¹¹⁸

a) Tsuchiya 1986**b) Uemura 1996, Bolm 2013, Wang 2021****c) Koenigs 2022**

Scheme 36: a) Thermal activated nitrene based [2,3]-sigmatropic rearrangement, b) Catalysis of nitrene based [2,3]-sigmatropic rearrangement, c) Photo activated nitrene based [2,3]-sigmatropic rearrangement

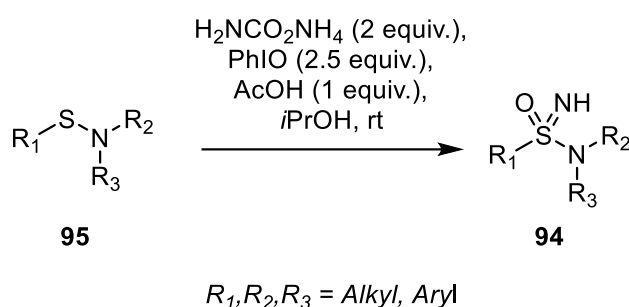
Nitrene transfer reactions on S(IV) have been widely reported in the scientific literature. For example, Lücking and Stockman in 2017 presented an efficient one-pot method for the addition of an unprotected NH moiety to tertiary sulfinamides **9**. They achieved high yields, affording sulfoximidamides **94**, and demonstrated a wide range of substrates, including aryl, alkyl, and heterocyclic substituents (Scheme 37).¹¹⁹

Lücking and Stockman 2017

Scheme 37: Modification of sulfinamides with in situ generated carbene.

A continuation of this concept is the work of Bull and Luisi in 2019, in which the synthesis of sulfoximidamides **94** from sulfenamides **95** was achieved for the first time. This transformation combines two oxidation processes into a single process, helping to save resources (Scheme 38).¹²⁰

Bull and Luisi 6 2019

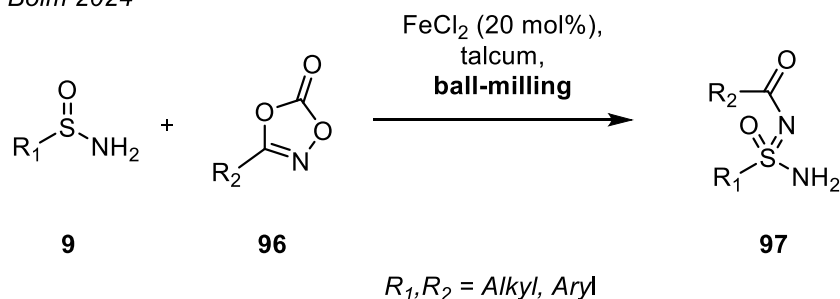


Scheme 38: Modification of sulfenamide with in situ generated carbene.

However, both strategies have similar limitations. The transformation can be carried out mainly with N,N-disubstituted amines, while side reactions or low yields are observed with primary or unsubstituted amines. In both methods, the effect of this transfer on the sulfur atom's stereochemistry is not investigated.

In contrast to these works, Bolm et al. (2024) proposed a novel mechanochemical approach to the synthesis of sulfoximidamides **97** via Fe(II)-catalyzed nitrene transfer from dioxazolones **96**. This method allows the preparation of N-acylated sulfoximidamides without the use of solvents, under mild ball-milling conditions, and importantly, it is successfully implemented with both unsubstituted and mono- and disubstituted amines, expanding the synthetic possibilities compared to previous methods (Scheme 39).¹²¹

Bolm 2024



Scheme 39: Mechanochemical modification of sulfinamides with dioxazolones.

In our study, we set out to investigate the use of a to this moment unconventional nitrene source, TsNHOPiv **5a**, under photocatalyzed conditions to expand and complement the known methods for nitrene precursors of this type.

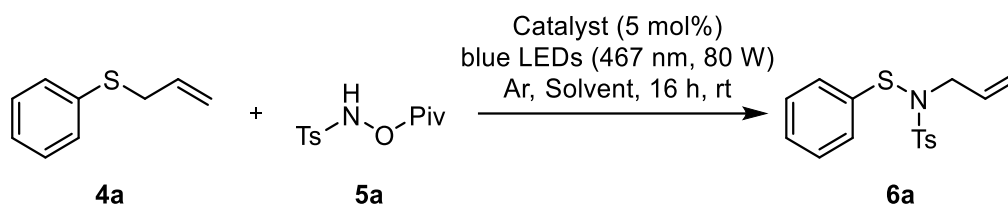
4.2 Result and discussion

4.2.1 Photocatalytic nitrene transfer to allyl sulfides

Initially, we investigated the reaction's ability to proceed in the presence of various photocatalysts under visible light irradiation. The results exhibited that multiple types of photocatalysts can initiate this reaction. Interestingly, the organophotocatalyst fluorescein yielded the best results (Table 5, entry 1), so this catalyst was chosen for further studies. Notably, no product formation was observed when employing Ru(bpy)₃Cl₂ as a photocatalyst

(Table 5, entry 3). It was noted that in the absence of a photocatalyst in the presence of blue LEDs (Table 5, entry 6), the reaction does not occur. Similarly, in the absence of light, but in the presence of a catalyst (Table 5, entry 7), we observed no product formation. In the next step we studied the effects of the solvents. Using the most popular representatives of their solvent classes led to either negligible yields or no reaction. Acetonitrile (Table 5, entry 1) showed the highest yields, and acetone (Table 5, entry 10), although with lower yields, could still serve as a medium for the reaction, unlike other solvents (Table 5, entries 11-15).

Table 5: Investigation of different photocatalysts and solvents.



Entry	[X] (5 mol%)	Solvent	% Yield NMR
1	Fluorescein	MeCN	61%
2	Ir(ppy) ₃	MeCN	25%
3	Eosin Y	MeCN	53%
4	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O	MeCN	0%
5	4-CzIPN	MeCN	57%
6	-	MeCN	0%
7	Fluorescein, no light	DCM	0%
10	Fluorescein	Acetone	54%
11	Fluorescein	Toluene	0%
12	Fluorescein	CHCl ₃	22%
13	Fluorescein	DCM	18%
14	Fluorescein	EtOAc	0%
15	Fluorescein	THF	10%

Reaction conditions: **4a** (1 equiv), **5a** (1.5 equiv), Catalyst (5 mol%), solvent (0.1 M wrt **1**), 16 h, rt.

The effect of the stoichiometric ratio of the reactants on reaction yield was explored. We observed the best yield when an excess of the nitrene reagent **5a** was used (Table 6, entry 4). Increasing the excess of the sulfoallyl **4a** (Table 6, entry 1-2) decreased the yield, as did an excessive excess of compound **5a** (Table 6, entry 5). After that, we conducted experiments with varying reaction time (Table 6, entries 6-8). The results showed that 8 hours was insufficient to achieve optimal results; therefore, we set the reaction time to 16 hours.

Table 6: Investigation of different starting material ratios and reaction time

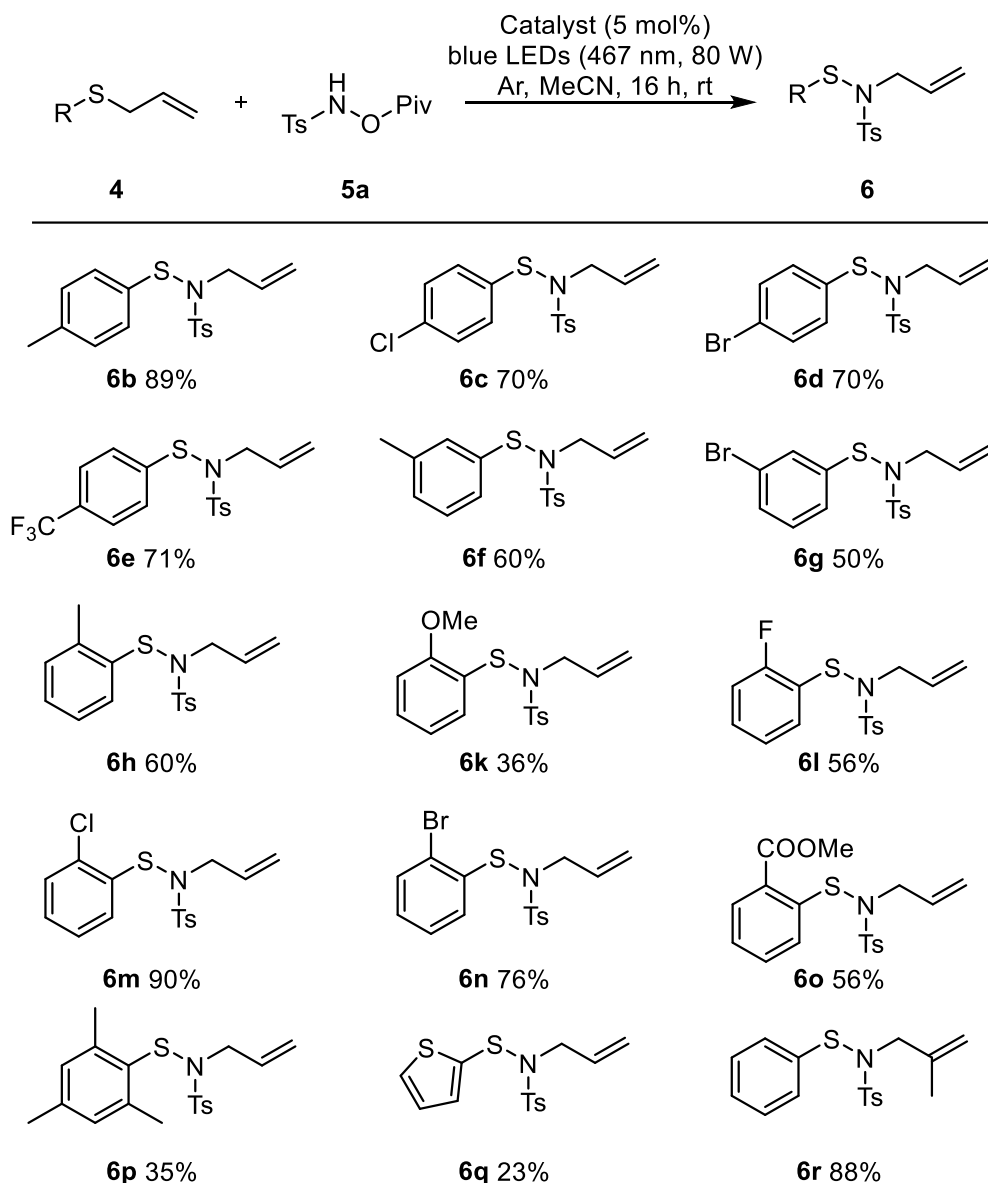
C=CCSc1ccccc1 (**4a**) + CC(C)(C)ONc1ccccc1 (**5a**) $\xrightarrow[\text{Ar, MeCN, time, rt}]{\text{Fluorescein (5 mol\%), blue LEDs (467 nm, 80 W)}}$ C=CCN(C(=O)C(C)(C)C)Sc1ccccc1 (**6a**)

Entry	Equivalents (4a : 5a)	Time	% Yield NMR
1	4 : 1	16 h	28%
2	2 : 1	16 h	38%
3	1 : 1	16 h	44%
4	1 : 2	16 h	89%
5	1 : 4	16 h	11%
6	1 : 2	4 h	25%
7	1 : 2	8 h	61%
8	1 : 2	24 h	88%

Reaction conditions: **4a**, **5a**, Fluorescein (5 mol%), MeCN (0.1 M wrt **1**), x h, rt.

After optimization, the final procedure was established: To a reaction tube equipped with a magnetic stir bar, hydroxylamine **5** (0.4 mmol, 2.0 equiv.) and Fluorescein (5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of allyl sulfide **4** (0.2 mmol, 1.0 equiv) dissolved in 2 mL dry acetonitrile (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was purified by column chromatography.

Following successful optimization, we investigated the range of substrate scope. Studies on allyl sulfides **4** demonstrated that the reaction can proceed in the presence of both donor and acceptor groups. Specifically, the reaction shows excellent results in the presence of halogens in all positions **6c**, **6d**, **6g**, **6l-n**, which are weak acceptors. A product with a trifluoromethyl group in the para position **6e** was also obtained. Weak electron donor groups, such as methyl, were obtained in all positions **6b**, **6f**, **6h** with excellent yields. However, strong donors, such as OMe **6k**, can reduce yield. As well as steric effects can negatively affect ortho-substituted sulfides **6p**, leading to noticeable decreases in yield and indicating the reaction's sensitivity to bulky groups. Replacing the phenyl ring with a thiophene ring **6q** also reduced the yield, which could be negatively affected by possible competitive processes involving sulfur. As shown by compound **6r**, the presence of substituents on the double bond does not affect the reaction yield, thereby confirming the [2,3]-sigmatropic rearrangement mechanism, which changes the position of the methyl group (Scheme 40).



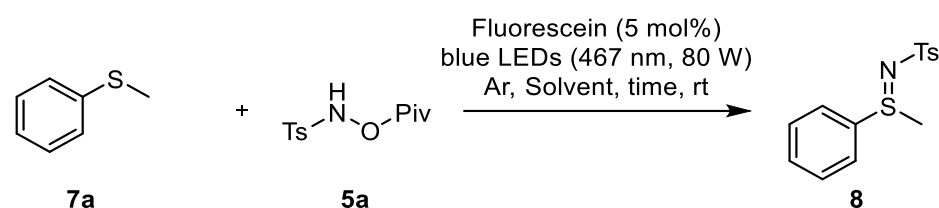
Scheme 40: Substrate scope of different allyl sulfides.

4.2.2 Photocatalytic nitrene transfer to sulfides

Based on the previously obtained results, it was decided to test the reaction conditions on methyl sulfides, which, in the absence of the allyl group, would form ordinary sulfilimines.

To do this, we conducted an additional optimization stage. Initially, we used solvents from different classes. The best yields were obtained with acetonitrile (Table 7, entry 1), but acetone (Table 7, entry 2) also showed promising results, as with the previous substrates. Methylene chloride (Table 7, entry 3) showed high yields, as well. All changes in reaction time led to a decrease in yield (Table 7, entries 7-9). Four hours were determined to be optimal. Evaluation of the reagent ratios proved the need for a slight excess of nitrene precursor **5a** (Table 7, entry 11).

Table 7: Investigation of different solvents, starting material ratio and reaction time

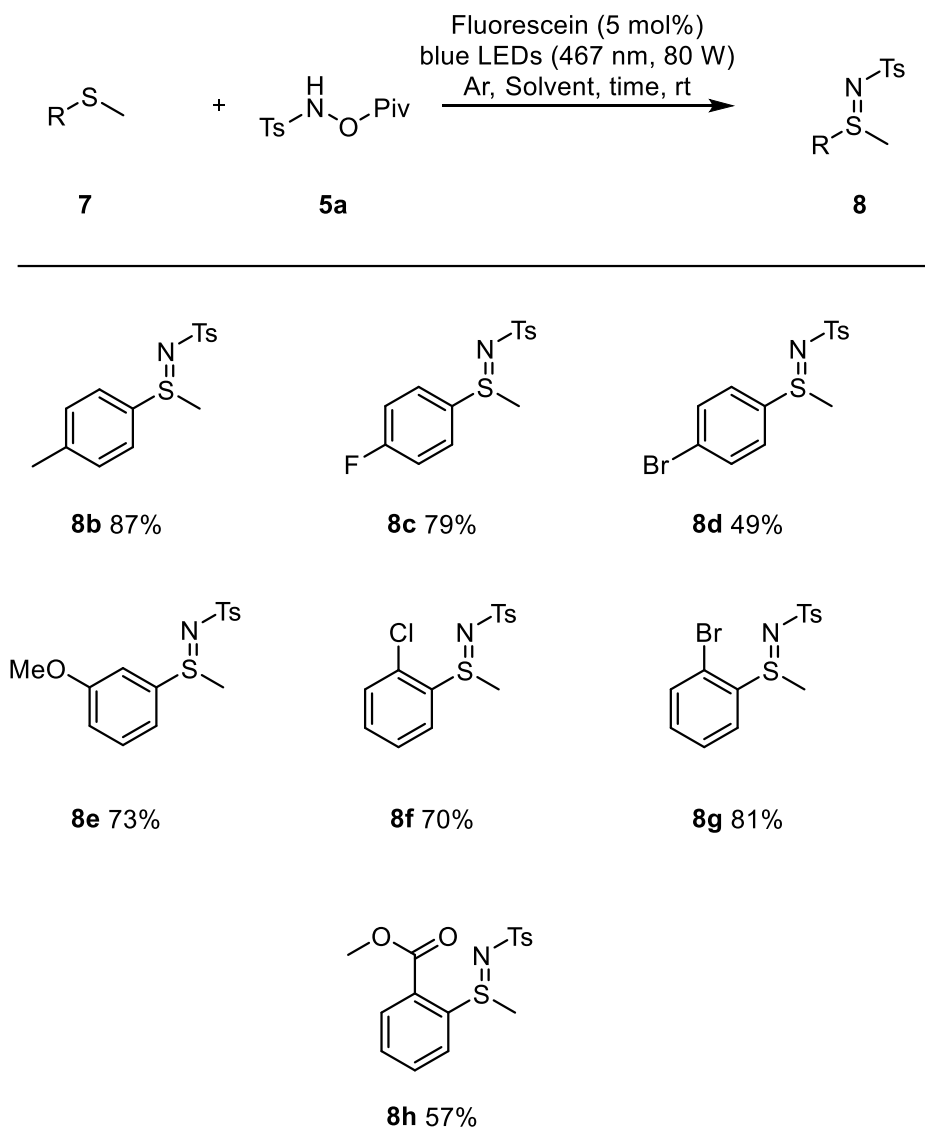


Entry	Solvent	Equivalents (7a : 5a)	Time	% Yield NMR
1	MeCN	1 : 1	4 h	70%
2	Acetone	1 : 1	4 h	64%
3	DCM	1 : 1	4 h	67%
4	Toluene	1 : 1	4 h	0%
5	EtOAc	1 : 1	4 h	20%
6	THF	1 : 1	4 h	17%
7	MeCN	1 : 1	2 h	40%
8	MeCN	1 : 1	3 h	61%
9	MeCN	1 : 1	6 h	71%
10	MeCN	1.5 : 1	4 h	54%
11	MeCN	1 : 1.5	4 h	88%
12	MeCN	1 : 2	4 h	87%

Reaction conditions: **7a**, **5a**, Fluorescein (5 mol%), Solvent (0.1 M wrt 1), x h, rt.

After optimization, the final procedure was established: To a reaction tube equipped with a magnetic stir bar, hydroxylamine **5** (0.3 mmol, 1.5 equiv.) and Fluorescein (5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of sulfide **7** (0.2 mmol, 1.0 equiv) dissolved in 2 mL dry acetonitrile (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was purified by column chromatography.

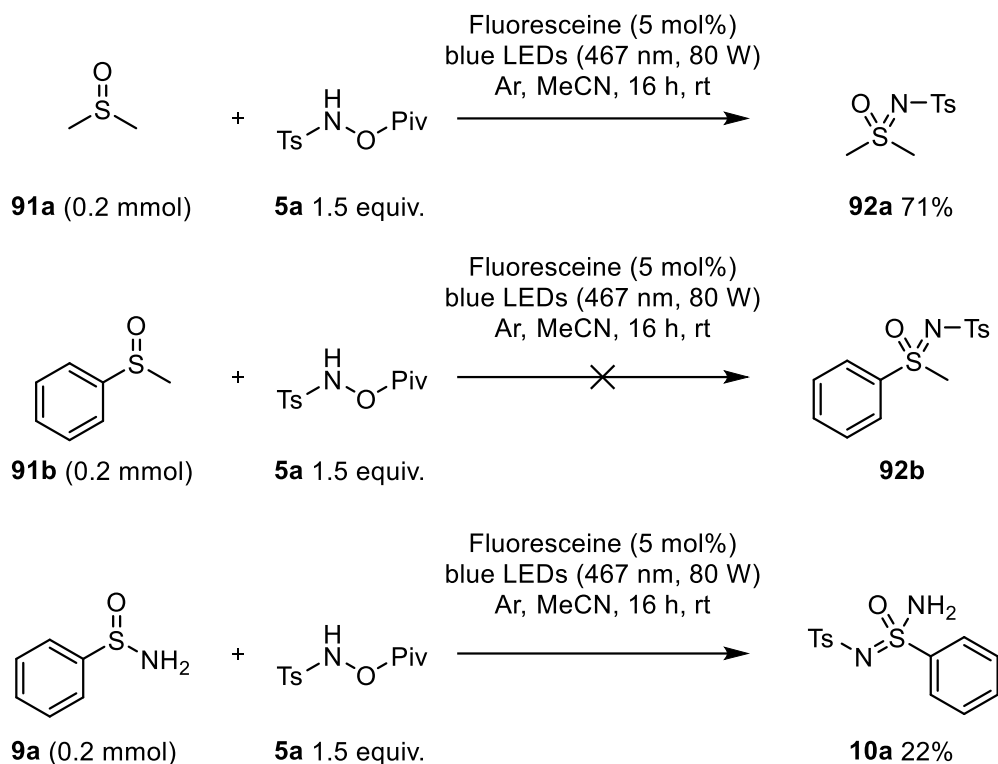
With these optimized conditions, we moved on to the scope. The methyl **8b** and methoxy **8e** groups, which are electron-donating substituents, gave good yields under the chosen conditions. Halogen-containing substrates **8c**, **8d** reacted efficiently, indicating tolerance to electron-withdrawing groups. The presence of the strongly accepting COOMe **8h** also demonstrates good yields. The yields remain high even in the presence of ortho-substituents **8f**, **8g**, demonstrating the broad applicability of the studied methodology (Scheme 41).



Scheme 41: Substrate scope of different sulfides.

4.2.3 Photocatalytic nitrene transfer to sulfinamides

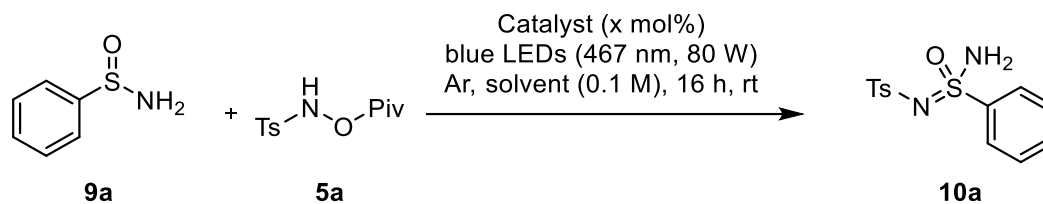
The next step was to use sulfur(IV) compounds as starting materials. With this aim, we used dimethyl sulfoxide and obtained an excellent result in the synthesis of sulfoximine **92a**. Unfortunately, when we tried to replace the methyl with a phenyl ring, the reaction stopped. So we decided not to continue working with sulfoxides due to potential scope issues and focused on another S(IV) representative – sulfinamides. Using our method, we were able to obtain sulfonimidamide **10a**, out of sulfinamide **9a**, which still has only a few synthetic routes via the nitrene strategy. (Scheme 42).



Scheme 42: Application of the reaction condition to sulfoxides and sulfinamides.

Initially, we assessed whether Fluorescein was the optimal performing catalyst as previously observed. We conducted the reactions with different photocatalysts in DCM. Fluorescein (Table 8, entry 2) showed the best result, 4-CzIPN (Table 8, entry 3) was also able to catalyze the reaction, although with a lower yield. Other photocatalysts (Table 8, entries 4-6) were unable to activate the reaction. The next move was to study the effect of catalyst loading on the reaction process (Table 8, entries 7-9). Unfortunately, this also did not have a significant impact on the reaction yield. Acetone was chosen as the reaction solvent (Table 8, entry 10), which increased our yield to 52%. Other solvents of different classes did not show even similar yields (Table 8, entries 11-15).

Table 8: Investigation of different photocatalysts and solvents

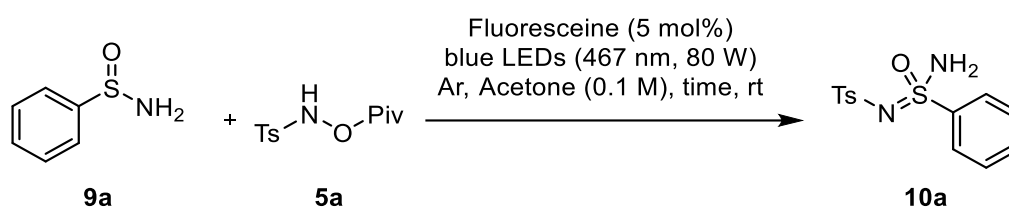


Entry	Catalyst (x mol%)	Solvent	% Yield NMR ^a
1	Fluorescein (5 mol%)	MeCN	22%
2	Fluorescein (5 mol%)	DCM	24%
3	4-CzIPN (5 mol%)	DCM	18%
4	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O (5 mol%)	DCM	0%
5	Eosin Y (5 mol%)	DCM	0%
6	IrCl ₃ (5 mol%)	DCM	0%
7	Fluorescein (7.5 mol%)	DCM	24%
8	Fluorescein (10 mol%)	DCM	25%
9	Fluorescein (20 mol%)	DCM	18%
10	Fluorescein (5 mol%)	Acetone	57%
11	Fluorescein (5 mol%)	Toluene	0%
12	Fluorescein (5 mol%)	CHCl ₃	13%
13	Fluorescein (5 mol%)	HFIP	0%
14	Fluorescein (5 mol%)	1,4-Dioxane	18%
15	Fluorescein (5 mol%)	THF	10%

Reaction conditions: **9a** (1 equiv), **5a** (1.5 equiv), Catalyst, solvent (0.1 M wrt **1**), 16 h, rt. ^a Calculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene), isolated yield in parentheses.

The attempt to increase the yield of the reaction by increasing the reaction time (Table 9, entries 1-2) did not meet our expectations. As a result, we switched to using additives. Molecular sieves (Table 9, entry 4), which can absorb unwanted water molecules, stopped the reaction entirely. The attempt to add a portion of the catalyst after six hours did not lead to improvement in the yield (Table 9, entry 3). The addition of HFIP as a possible scavenger of basic particles and to promote the regeneration of the fluorescein catalyst by protonation increased the yield (Table 9, entries 5-7). The attempt to add a larger amount of this alcohol, on the contrary, led to a decrease in yields. In parallel, there were experiments to use diphenyl sulfide, which Song and co-workers used as an additive to improve the nitrene transfer process (Table 9, entries 8-9).¹²² Both additives individually showed excellent performance; however, their simultaneous use led to a further increase in yield. (Table 9, entry 10). After a small optimization of their ratio (Entry 11-13), complete conversion of sulfonamide was achieved. After workup, the expected product was obtained with 95% yield (Table 9, entry 14).

Table 9: Investigation of different reaction time and additives

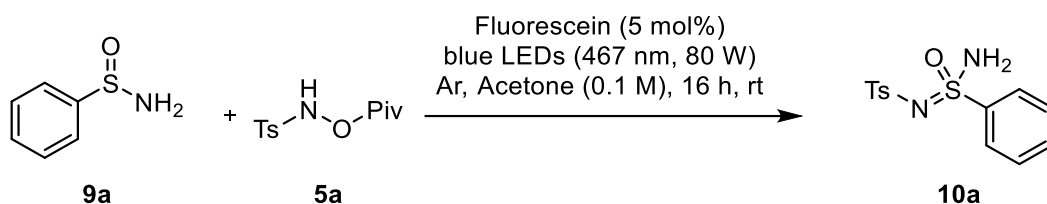


Entry	Additive	Time	% Yield NMR ^a
1	-	48 h	60%
2	-	72 h	61%
3	After 6 h second portion of Fluorescein (5 mol%) was added	24 h	60%
4	MS (3Å)	16 h	0%
5	HFIP (1 equiv.)	16 h	87%
6	HFIP (2 equiv.)	16 h	77%
7	HFIP (3 equiv.)	16 h	76%
8	Ph ₂ S (10 mol%)	16 h	76%
9	Ph ₂ S (1 equiv.)	16 h	83%
10	Ph ₂ S (10 mol%), HFIP (2 equiv.)	16 h	90%
11	Ph ₂ S (1 equiv.) HFIP(1 equiv.)	16 h	74%
12	Ph ₂ S (1 equiv.), HFIP (3 equiv.)	16 h	67%
13	Ph ₂ S (10 mol%), HFIP (3 equiv.)	16 h	87%
14	Ph ₂ S (10 mol%), HFIP (1 equiv.)	16 h	99% (95%)

Reaction conditions: **9a** (1 equiv), **5a** (2 equiv), Fluorescein (5 mol%), solvent (0.1 M wrt **1**), 16 h, rt. ^a Calculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene), isolated yield in parentheses.

After completing the main optimization stage, several additional control experiments were conducted to evaluate the effects of various factors on the reaction outcome. An attempt to carry out the reaction in the presence of light without a catalyst (Table 10, entry 1) did not yield the desired product **10a**. A negative result was also obtained in the opposite case, in the absence of irradiation but with the presence of the organophotocatalyst (Table 10, entry 2). When thermal initiation was used (Table 10, entry 3), the product was not obtained. Alternative nitrogen sources, such as PhINTs **2a** (Table 10, entry 4) and TsN=S(Ph)₂ (Table 10, entry 5), were also used. Analysis of the reaction mixtures from these attempts revealed no spectral confirmation of the expected product. Different irradiation lengths resulted in a reduction in yield, both with shorter wavelengths (Table 10, entry 6) and with longer wavelengths (Table 10, entry 7).

Table 10: Influence of different deviations from standard conditions on reaction

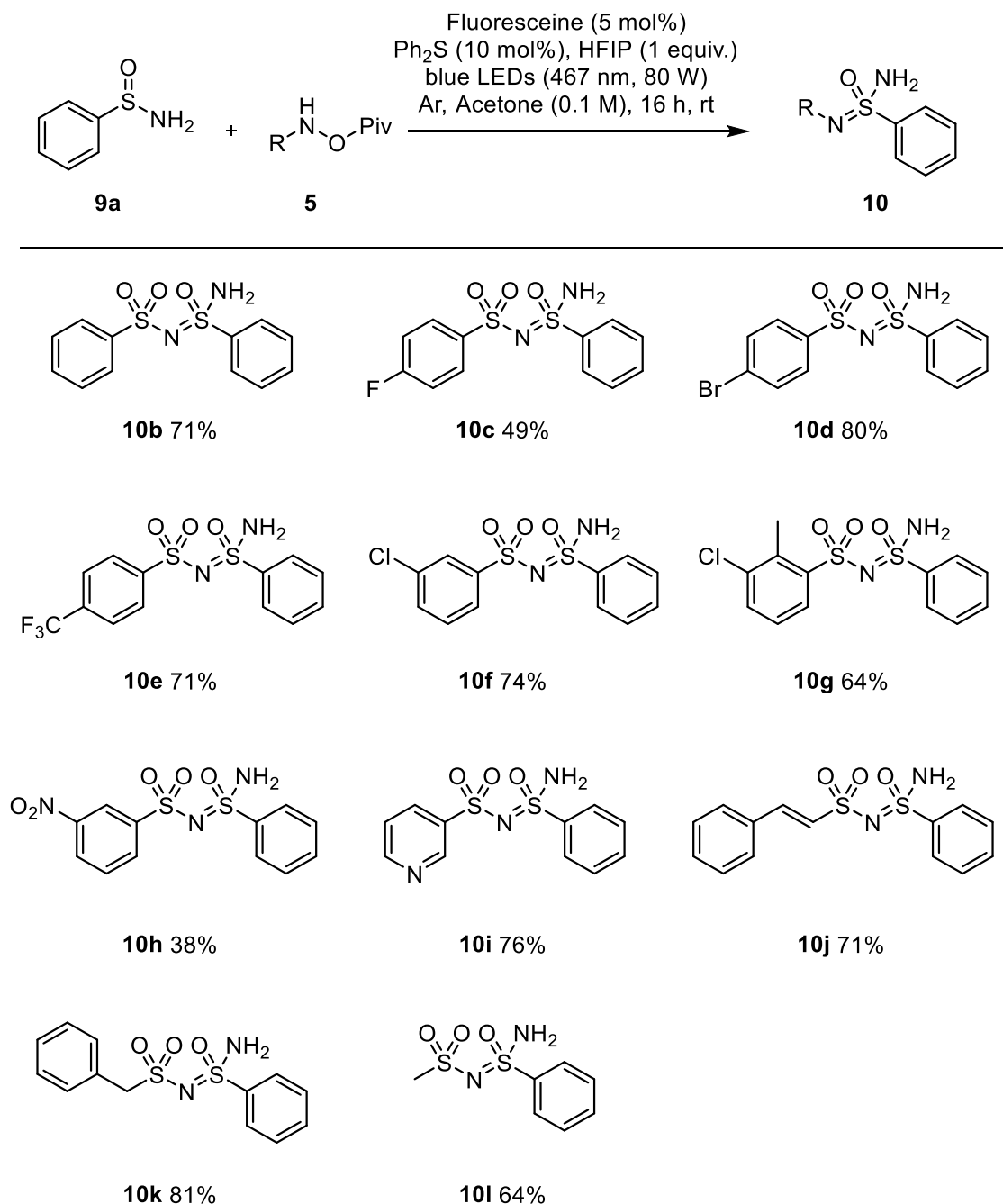


Entry	deviation	% Yield NMR ^a
1	No catalyst	trace
2	No light	trace
3	no light, 60°C	trace
4	PhINTs 2a instead of 5a	trace
5	TsN=S(Ph) ₂ instead of 5a	trace
6	370 nm light	37
7	520 nm light	48

Reaction conditions: **9a** (1 equiv.), **5a** (2 equiv.), Fluorescein (5 mol%), Acetone (0.1 M wrt 1), 16 h, rt. ^a Calculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene), isolated yield in parentheses.

Finally, the final procedure was established: To a reaction tube equipped with a magnetic stir bar, sulfinamide **9** (0.2 mmol, 1.0 equiv), hydroxylamine **5a** (0.4 mmol, 2.0 equiv.), and Fluorescein (5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times, followed by the addition of HFIP (0.2 mmol, 1.0 equiv.) and Diphenyl sulfide (0.02 mmol, 0.1 equiv.) dissolved in 2 mL dry acetone (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was purified by column chromatography.

With the optimal conditions at hand, the substrate scope was explored. We started with various hydroxylamine derivatives. The obtained *p*-phenyl compounds **10c–e** demonstrate good yields, as well as *m*-phenyl derivatives **10f, g**. However, the *m*-nitro compound **10h** shows lower yields, in which the nitro group can be triggered by light, and therefore competitive processes could interfere with a better yield. The pyridine fragment **10i** was also introduced, which, despite its basic nature, gave good yields. Vinyl **10j** and the aliphatic products **10k, 10l** are also present in our scope and demonstrate high yields. (Scheme 43).



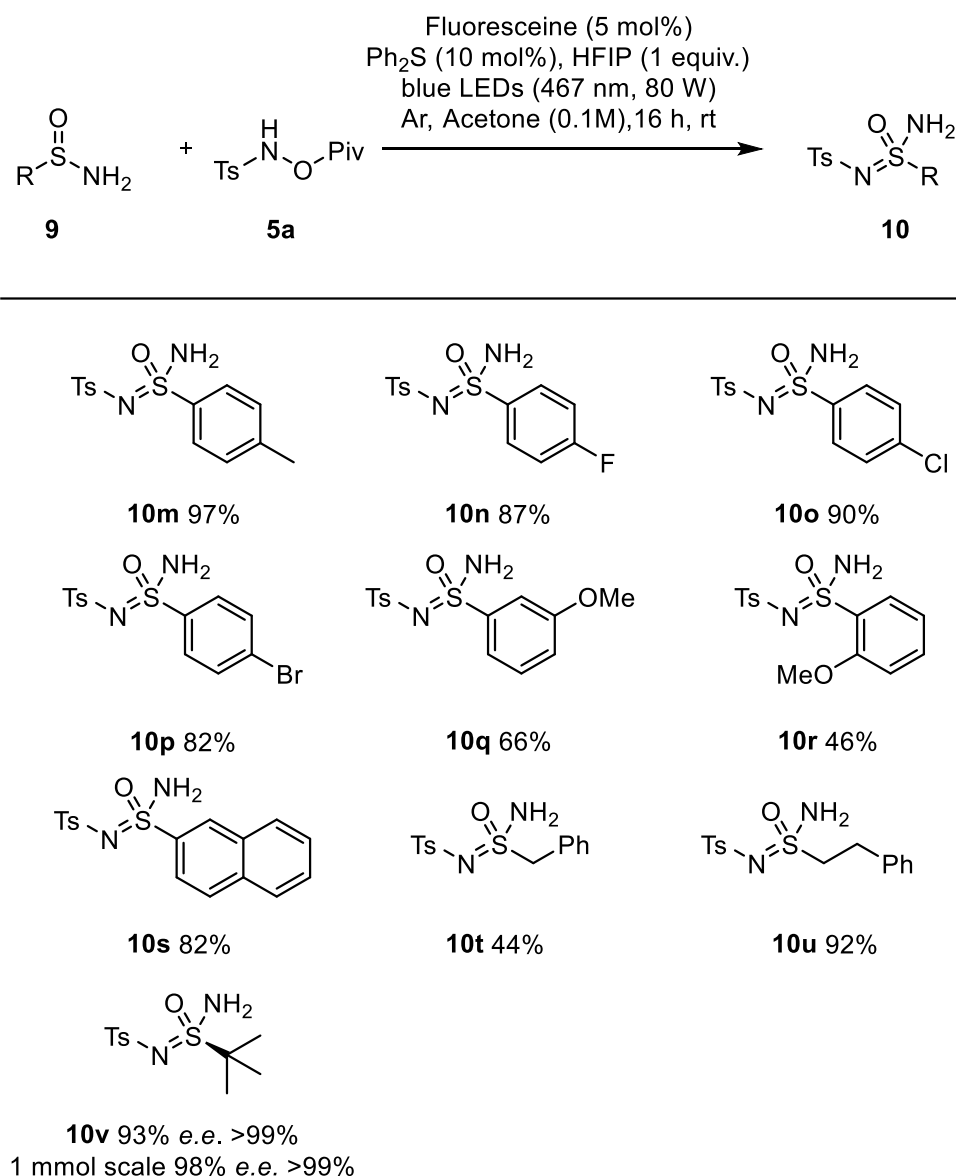
Scheme 43: Substrate scope of different hydroxylamines.

Applying amide-type substrates **98a**, **98b** instead of sulfonamide derivatives did not lead to the formation of the products. This indicates a specific dependence of this transformation on the sulfonamide framework (Scheme 44).



Scheme 44: Substrate scope of unreactive hydroxylamines.

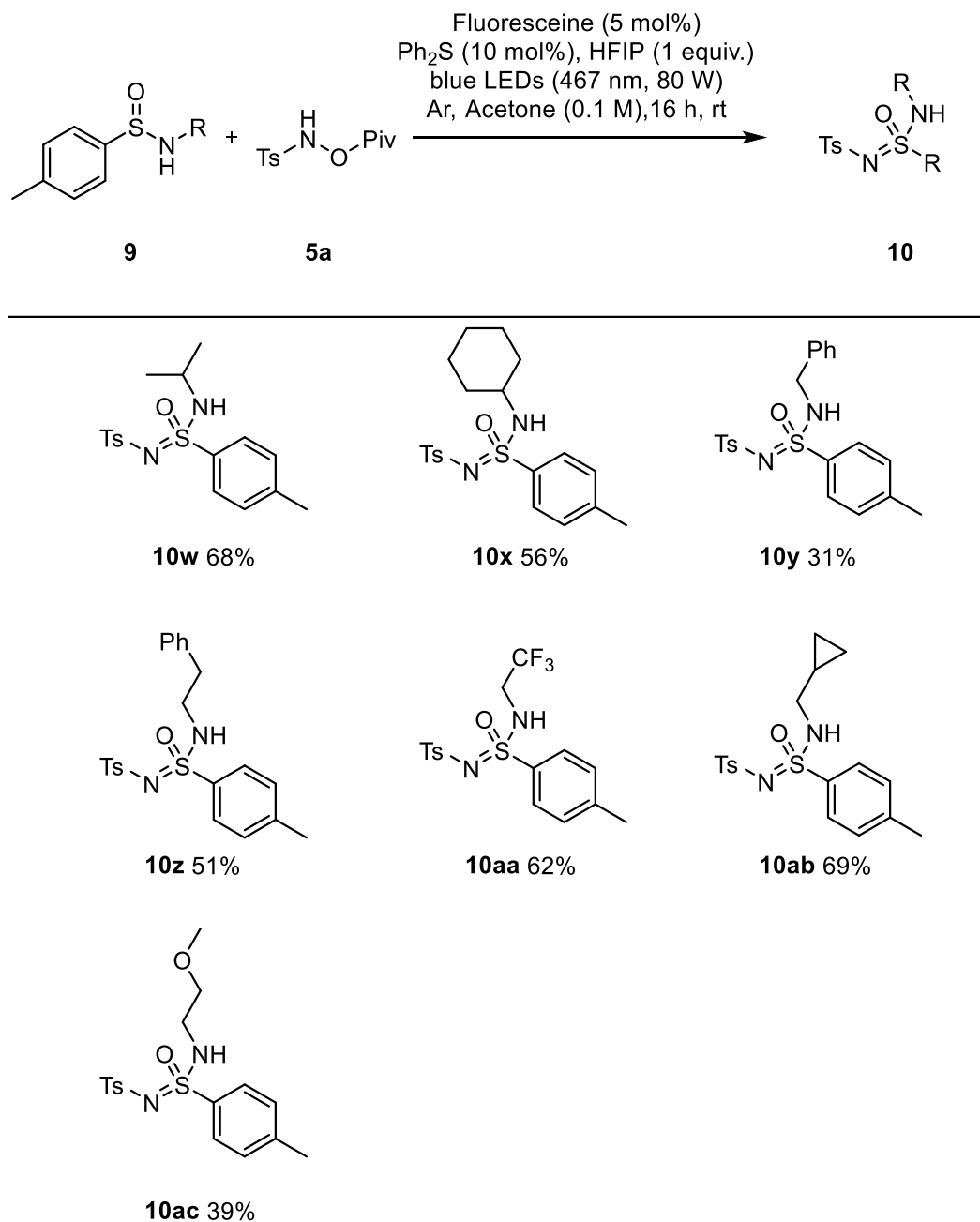
In the following step, variations of the sulfinamide fragment were tested. The tested arylsulfinamides bearing substituents at all positions of the aromatic ring generally tolerated reaction conditions, giving the corresponding sulfoximidamides **10m-p** in good yields. A slight decrease in yield was observed for the *o*-substituted arylsulfinamide derivative **10r** compared to the *m*-substituted derivative **10q**, probably due to steric hindrance. We further investigated the applicability of the reaction to aliphatic sulfinamides **10u**. Only the compound with an active methylene group **10t** showed a significant decrease in yield, likely due to possible side reactions. As well as the successful conversion of the chiral Ellman sulfinamides to the corresponding sulfoximidamide **10v** with a high level of stereoselectivity (Scheme 45).



Scheme 45: Substrate scope of different sulfinamides.

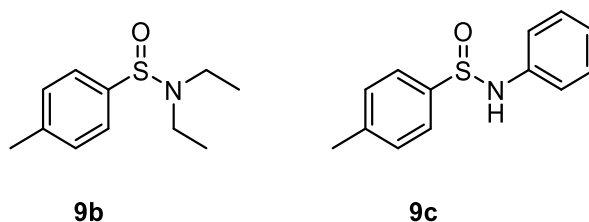
Further investigations focused on testing the ability of *N*-substituted arylsulfinamides to form the corresponding sulfoximidamides. We were able to obtain several secondary amines

10w, **10x** in good yields. Several products were also obtained with primary amines **10y**, **10z**. There were products that had specific functional groups: esters **10ac**, cyclopropanes **10ab**, and trifluoromethyl groups **10aa**. These groups were well tolerated and efficiently yielded the desired products (Scheme 46).



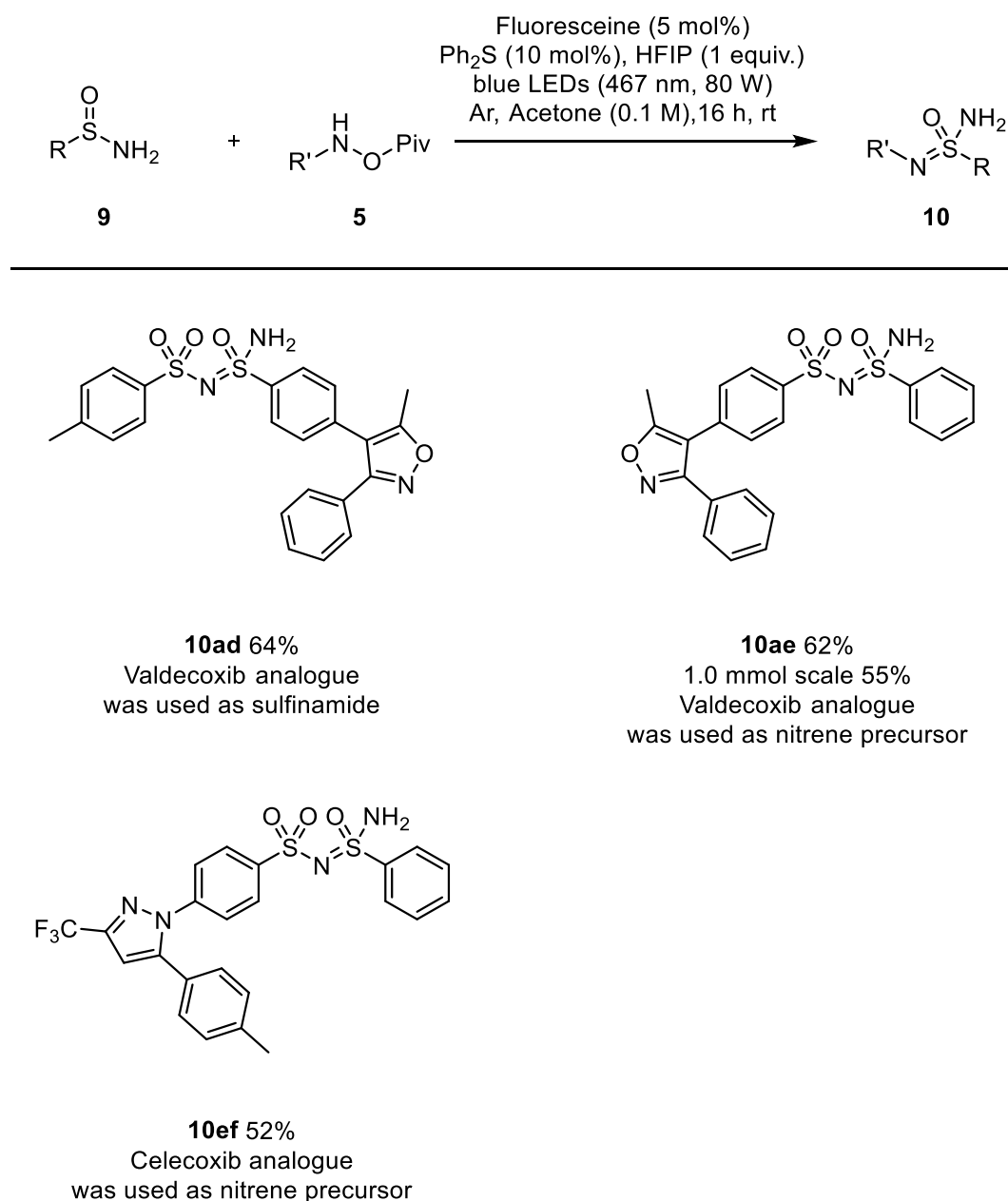
Scheme 46: Substrate scope of different N-substituted sulfonamides.

Despite the broad tolerance to various functional groups, it was observed that N,N-dialkylated sulfonamides **9b** do not exhibit the ability to transform. A similar situation is observed with N-aryl substituted sulfonamides **9c**. (Scheme 47).



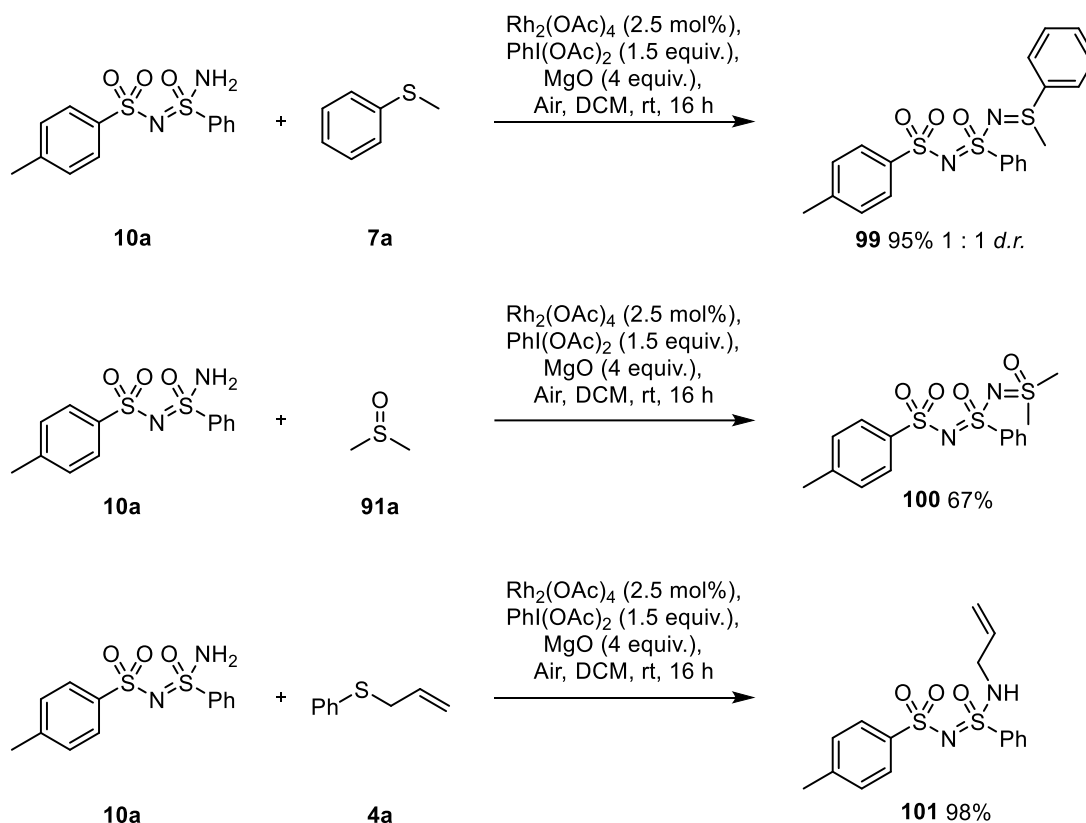
Scheme 47: Substrate scope of unreactive N-substituted sulfinamides.

The scope of this methodology was then expanded to assess its broader applicability. We investigated its compatibility with drug molecules. Valdecoxib derivatives were used as both the nitrene precursor **10ae** and the sulfinamide reagent **10ad**. In both cases, the transformation proceeded smoothly, providing the corresponding sulfonylimidamides in good yields. These two products differ only in the location of the unprotected amine functional group and the pharmacophore, which offers distinct vectors for the introduction of additional substituents. Similarly, celecoxib could be used as a precursor for the transfer of the nitrene to the sulfinamide, forming sulfoximidamides **10af** (Scheme 48).



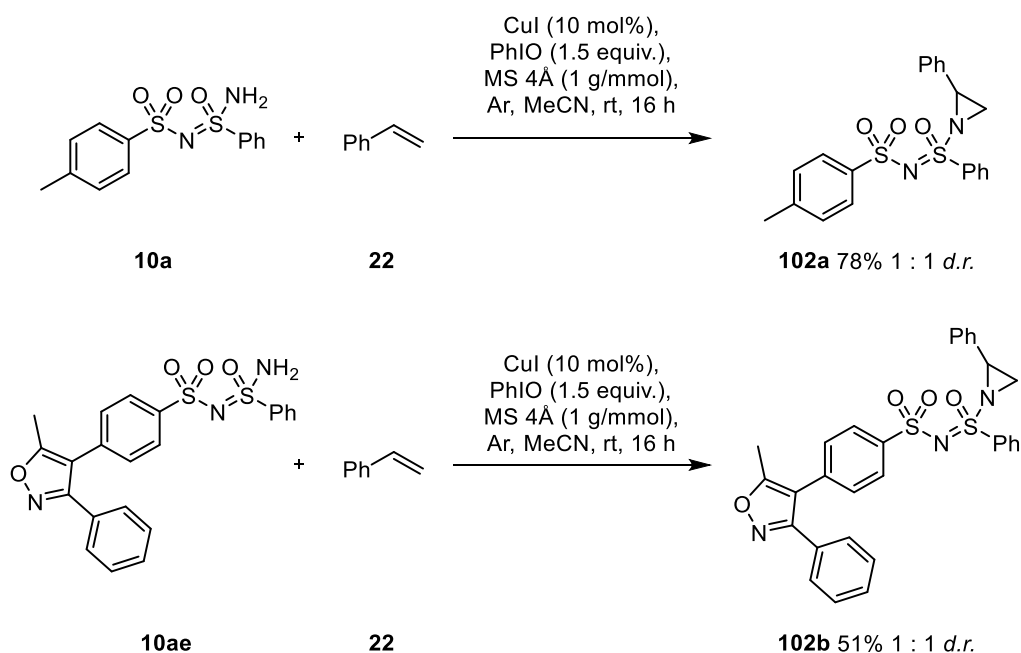
Scheme 48: Substrate scope of modified bioactive compounds.

Building on previous work from our group,^{4,80,118,123} we further investigated the utility of unprotected amine-containing sulfonimidamide **10a** in nitrene transfer reactions. In the first series of experiments, we examined the direct transfer of the entire sulfonimidamide unit to different organosulfur substrates under oxidative conditions. This was done to synthesize a nitrene precursor in situ using $\text{Rh}_2(\text{OAc})_4$ as a nitrene transfer catalyst.¹⁰³ Depending on the type of organosulfur compound used, this method allows for efficient synthesis of structures **99**, **100** with high yields. These frameworks, which consist only of sulfur and nitrogen atoms in the backbone, are still challenging to create but are highly sought after in modern sulfur–nitrogen chemistry. However, in an attempt to obtain the product of the [2,3]-sigmatropic rearrangement, thiophenol was eliminated, leading to the addition of the allyl group to the nitrogen atom **101** (Scheme 49).



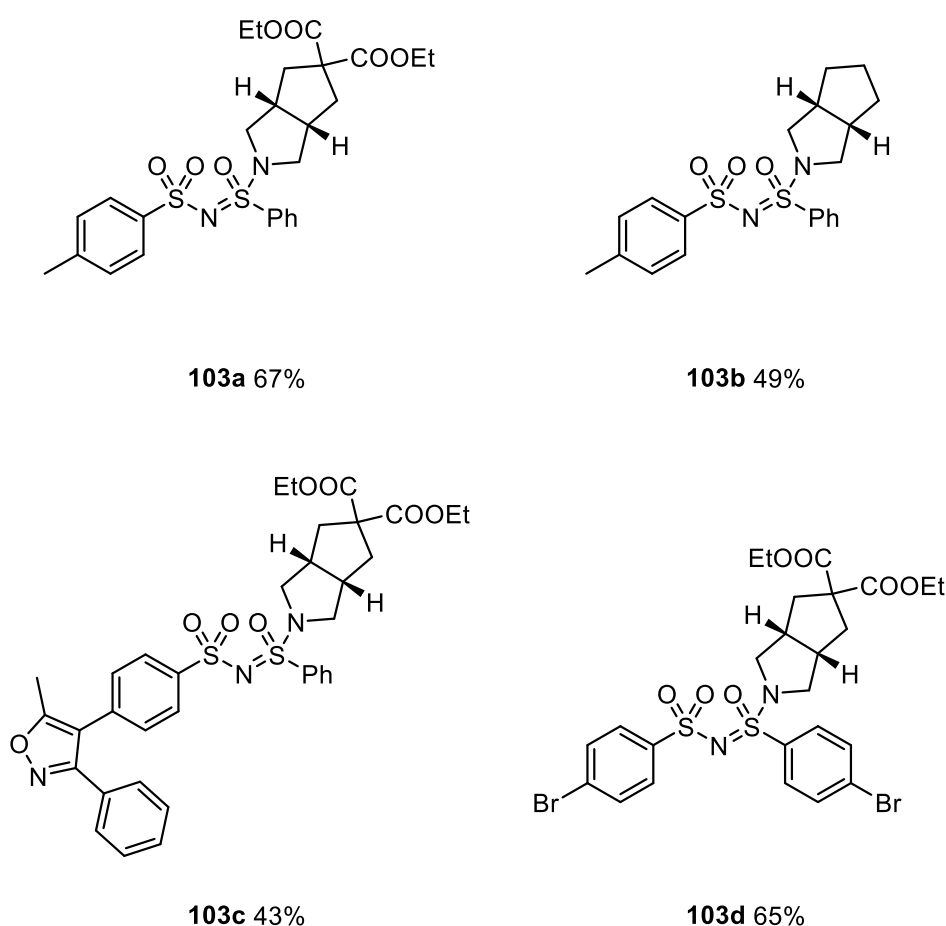
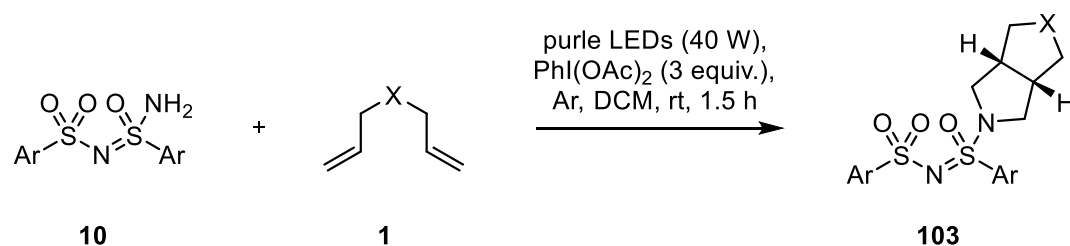
Scheme 49: Post-synthetic modification of sulfonimidamides.

The research was continued by synthesizing sulfonimidamide-substituted aziridines. In this method, the nitrene was generated from iodosobenzene in the presence of copper(I) iodide, which catalyzes the process.¹²⁴ We were able to obtain the aziridine **102a** using the model framework, as well as the Valdecoxib derivative **102b**, in good yields (Scheme 50).



Scheme 50: Post-synthetic modification of sulfonimidamides.

Finally, we were able to apply unprotected sulfonimidamides in a photochemical [2+2+1] cyclization with non-conjugated dienes. This reaction allows the formation of free triplet nitrogens under photochemical conditions.⁸⁰ We were able to synthesize several interesting products with acceptors present in the diene **103a**, as well as with a diene having a straight, unsubstituted carbon chain between the double bonds **103b**. We were also able to obtain a product derived from the Valdecocib scaffold **103c** in good yields (Scheme 51).

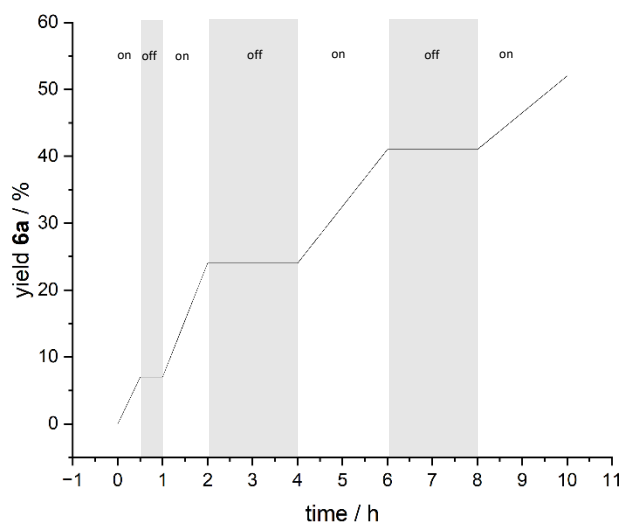
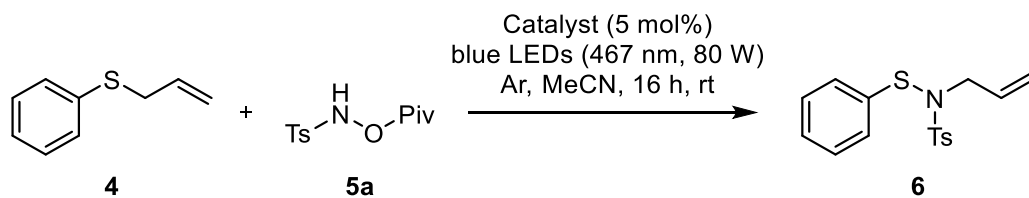


Scheme 51: Post-synthetic modification of sulfonimidamides.

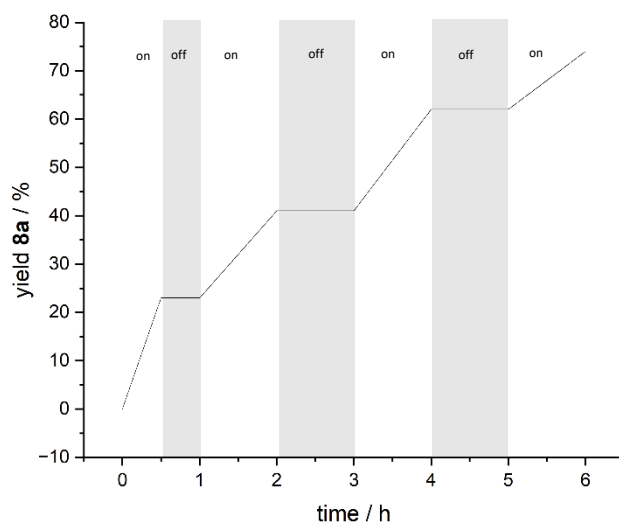
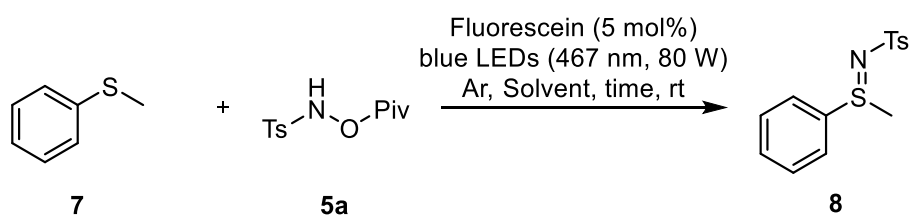
4.2.4 Mechanistic Investigation of the Photocatalytic Nitrene Transfer Process

To establish the mechanism of the reaction, a series of control experiments was conducted. The first one was an on/off experiment. After the reaction started, we removed the sample

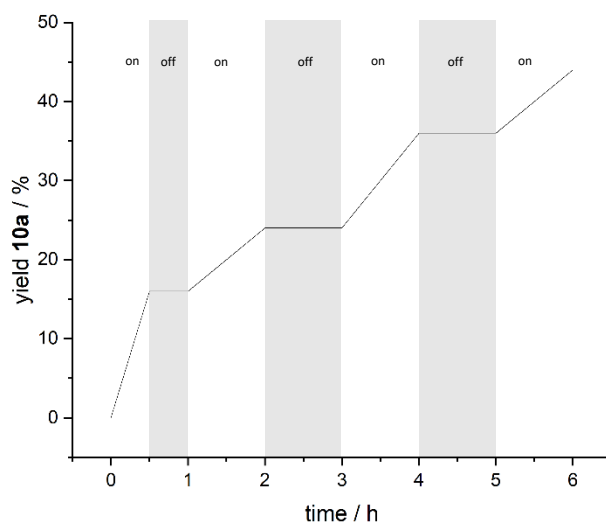
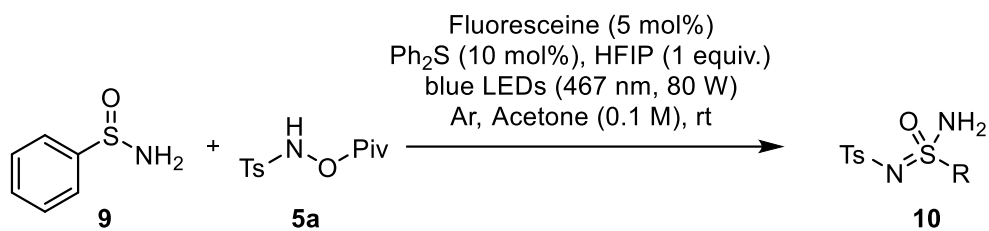
from the light at a specific time. In an argon atmosphere, the aliquot was taken. We left the reaction in the dark for a specific period of time, then took another aliquot and placed it under light. Several cycles were carried out to obtain a more reliable result. All three graphs demonstrate the absence of reaction during periods without light and a stable increase in product content during periods with light irradiation. The obtained data prove the absence of a radical-chain mechanism (Schemes 51, 52, 53).



Scheme 51: on/off experiment

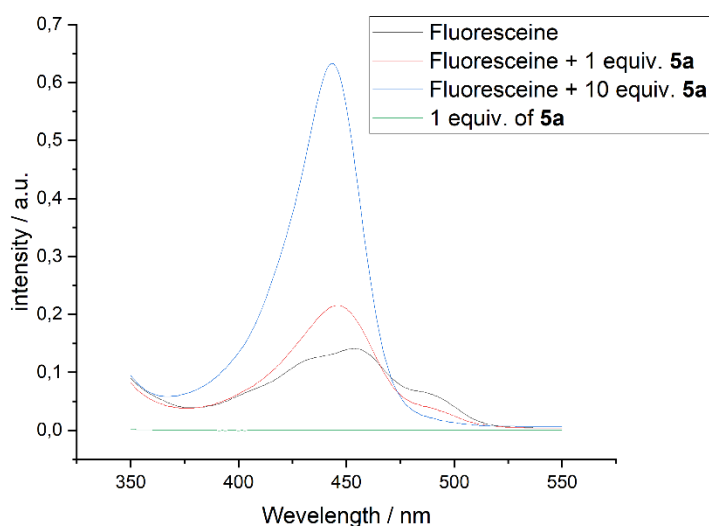


Scheme 52: on/off experiment



Scheme 53: on/off experiment

We also conducted a series of absorption spectra of the catalyst and other reagents. UV/Vis studies show that nitrene reagent **5a** does not absorb light in the (near-)visible region. However, subsequent studies have shown that it affects Fluorescein's absorption properties. After the addition of 1 and 10 equivalents of **5a** to the catalyst solution, we observe a significant increase in peak intensity and a change in its shape, which may indicate a non-chemical interaction between the reagents (Scheme 54).

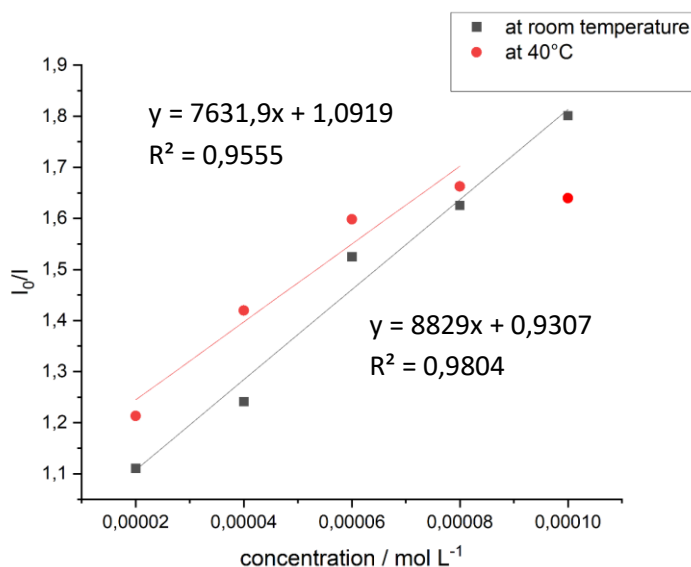


Scheme 54: Absorption spectra of Fluorescein in acetone in the presence of **5a**.

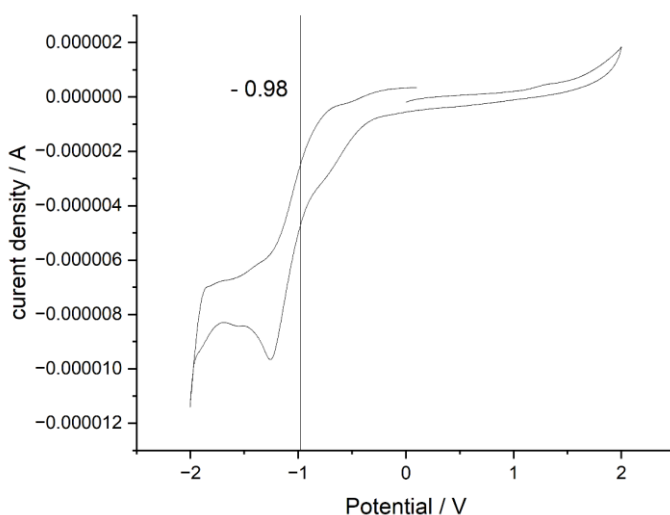
Fluorescence quenching was subsequently investigated. The data analysis was carried out using the Stern-Volmer equation $I_0/I = 1 + K_{sv} [Q]$, where $K_{sv} = K_q \tau_0$ and the fluorescence lifetime was taken from the literature.¹²⁵ It was found (Table 11, entry 1) that the quenching constant of our hydroxylamine **5a** is higher than the diffusion limit, which can be explained by the presence of several types of quenching, namely dynamic and static. To confirm this theory, an additional fluorescence-quenching experiment was conducted with samples heated to 40°C (Table 11, entry 2). New data indicate a decrease in the fluorescence quenching constant, confirming the presence of a static quenching component whose effect decreases with increasing temperature.

Table 11: Results of Stern-Volmer calculations.

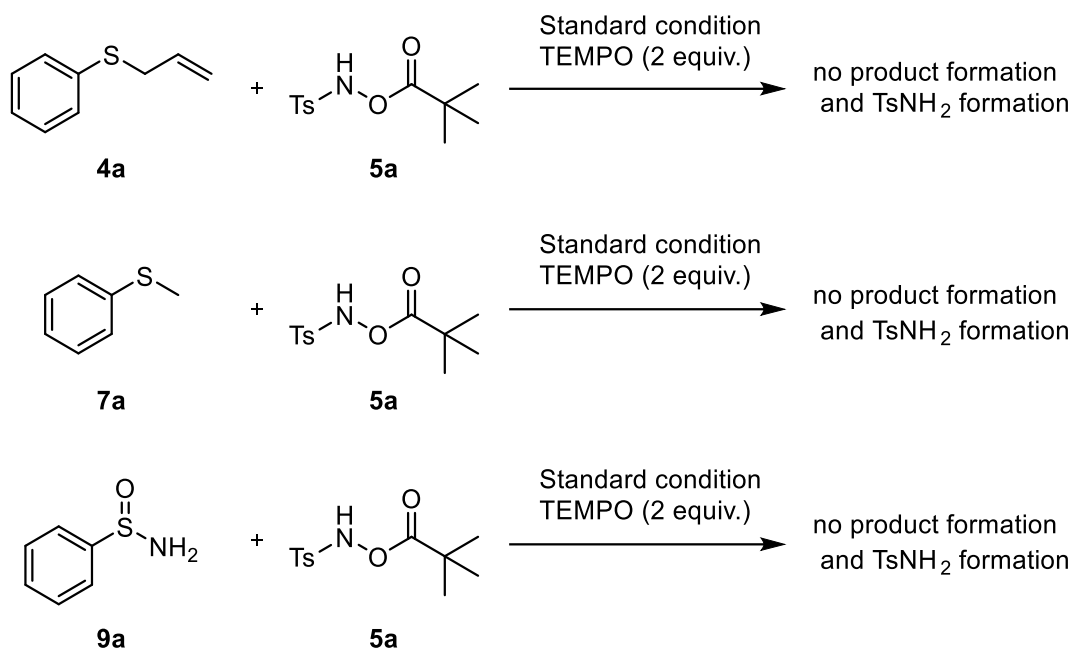
Entry	Name	$K_{sv} \text{ M}^{-1}$	$K_q 10^{12} \text{ M}^{-1}\text{s}^{-1}$
1	5a rt	8829	2.2
2	5a 40°C	7631	1.9

Scheme 55: Stern-Volmer plot of fluorescein with **5a**

The cyclic voltammogram (CV) of **5a** was recorded. The measurements were carried out within a potential range of -2.0 to $+2.0$ V vs. Ag/AgCl. Irreversible waves were observed; therefore, the redox potentials were estimated at half of the maximum current, following the procedure described by Nicewicz.¹²⁶ The spectrum of compound **5a** showed a prominent irreversible cathodic peak with a half-wave potential of -0.98 . These data probably correspond to the cleavage of the N-O bond in the hydroxamate fragment. Analyzing the positive potential, a smooth current increase was observed. This indicates the absence of a mild oxidation stage. (Scheme **56**).

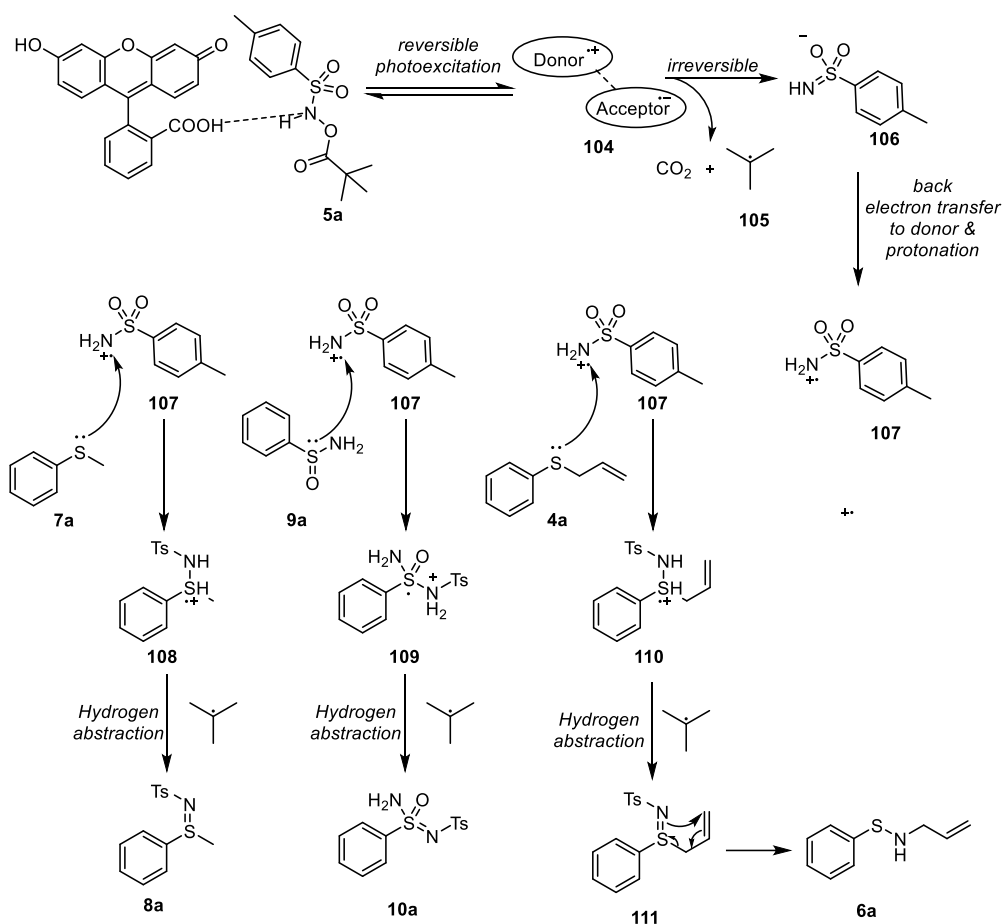
Scheme 56: A 0.005 M solution of **5a** was analysed in a 0.1 M MeCN solution of NBu₄PF₆ used as electrolyte.

In addition, we confirmed the presence of radical elements in our reaction. This was done by adding TEMPO to the reaction mixture. In all three cases, the reaction stopped, indicating the presence of radicals (Scheme 57).



Scheme 57: Radical trap experiment.

These observations led to the conclusion that the reaction mechanism involves the initial excitation state of a non-covalent complex **104** between substance **5a** and the photocatalyst. The next stage is the irreversible decomposition of substance **5a**, leading to the formation of the anion **106**. This intermediate **106** transforms into the intermediate **107** via the reverse transfer of one electron to the donor. In all variants, the attack of the sulfur electron pair on the radical cation **107** occurs. The resulting intermediate compounds **108**, **109**, and **110** react with the radical decomposition products of pivaloyl **105**, forming the reaction products **8a** and **10a**. In the presence of an Allyl fragment, after the formation of compound **111**, a [2,3]-sigmatropic rearrangement occurs, which leads to the formation of the expected product **6a** (Scheme 58).



Scheme 58: Proposed mechanism.

4.3 Conclusion

In summary, this work proposes a methodology for the preparation of unprotected sulfonimidamides, sulfilimines, and sulfonamides. This reaction involves hydroxylamine derivatives in a single-electron transition under mild, metal-free conditions. The reaction procedure has proven effective for reactions with substrates bearing substituents of various natures. The obtained sulfonimidamides were successfully used in subsequent nitrene transfer reactions, thereby facilitating the formation of both complex sulfur-nitrogen skeletons and cycloaddition products to these skeletons. The reaction mechanism was also studied. These studies suggest the presence of a single-electron transfer process. This strategy provides a broadly applicable platform for the formation of sulfur-nitrogen bonds.

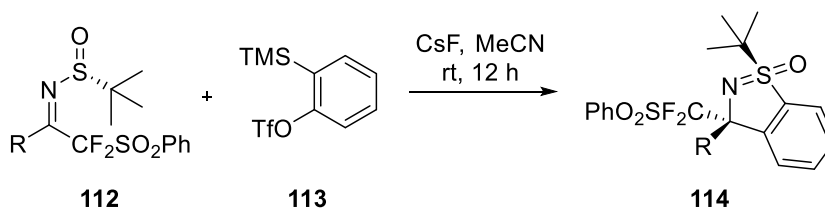
5. Photocatalytic S-Alkylation of Sulfinamides: access to sulfoximines

5.1 Brief Introduction

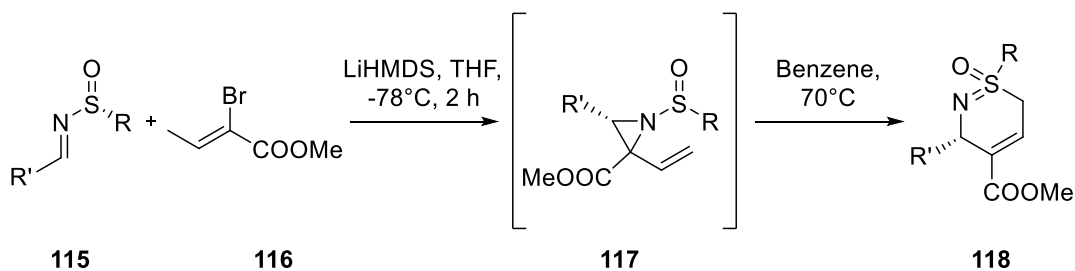
There are numerous strategies for preparing sulfoximines. However, the main one is the nitrene transfer process and its modifications, which have many variations and already have their preparative value. There are alternatives, one pathway gaining popularity is the formation of sulfoximines via S-C bond formation with sulfinamides.

In 2014, Hu and co-workers developed a novel [3+2] cycloaddition between imides derived from Ellman's sulfinamide **112** and aryl groups **113**, providing a stereoselective method for the synthesis of cyclic sulfoximines **114**. This transformation is facilitated by a PhSO_2CF_2 group, which can be removed under basic conditions (Scheme **59a**).¹²⁷ In 2016, Stockman demonstrated a synchrotopropic rearrangement that allowed the synthesis of six-membered rings bearing a sulfinamide group **118** from pre-synthesized aziridine sulfinamides **117** under thermally promoted conditions (Scheme **59b**).¹²⁸

a) Hu 2014



b) Stockman 2016

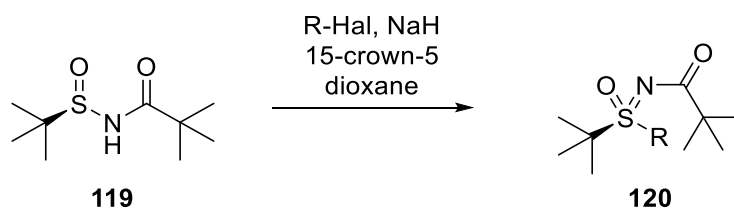


Scheme 59: a) five-membered sulfoximines formation from sulfinamides imines reported by Hu, b) six-membered sulfoximines formation from sulfinamides imines reported by Stockman.

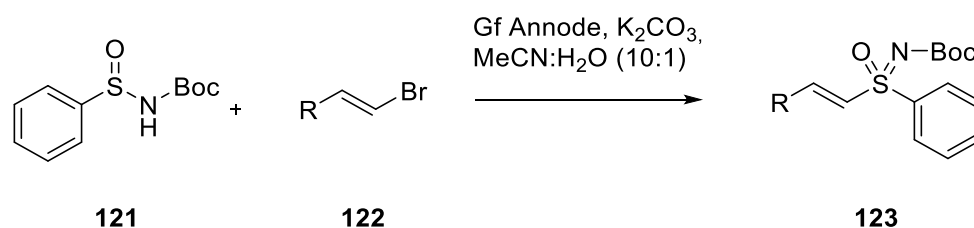
In Maruoka and colleagues' work from 2019, a method for the formation of N-acylated sulfoximines **120** from sulfonamides **119** under the influence of a base and an alkylating agent was reported. This work provides access to previously unavailable chiral structures and describes a reversible process for converting sulfoximines to sulfonamides (Scheme **60a**).¹²⁹ In 2025, our group reported a study in which electrochemical conditions were explored to form sulfoximines **123** from sulfonamides **121** and vinyl halides **122**, a direction that is still

gaining attention from scientists. Unfortunately, both transformations can only be applied to N-acylated sulfonamides (Scheme 60b).¹³⁰

a) Maruoka 2019



b) Koenigs 2025



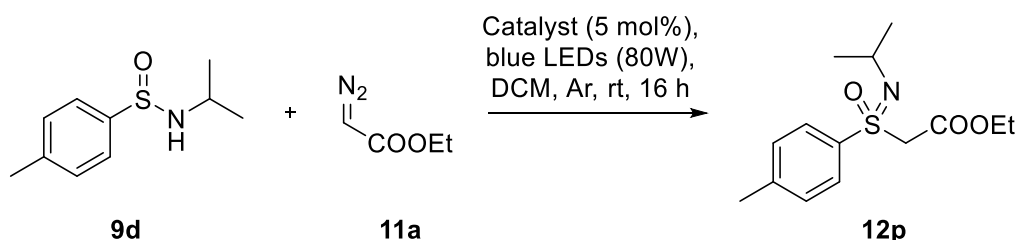
Scheme 60: a) S-C bond formation by Maruoka, b) electrochemical S-C bond formation by Koenigs.

Based on this literature, we decided to develop a photocatalytic method for converting sulfonamides to sulfoximines using diazo compounds. Diazo compounds are well-known agents for forming C-C bonds but have so far been poorly represented in this transformation, despite their ability to participate in single-electron transfer (SET) in the presence of a photocatalyst.

5.2 Result and discussion

To prove our hypothesis, several catalysts were used to test the ability of sulfonamides **9** to be converted into sulfoximines **12** by diazo compounds **11**. Organic photocatalysts (Table 12, entries 1-3) did not show any efficiency for this conversion. In contrast, the Ru-based catalyst (Table 12, entry 4). demonstrated the ability to catalyze the process of C-S bond formation. In the absence of a photocatalyst under irradiation, no product formation was observed (Table 12, entry 5).

Table 12: Investigation of different photocatalysts.



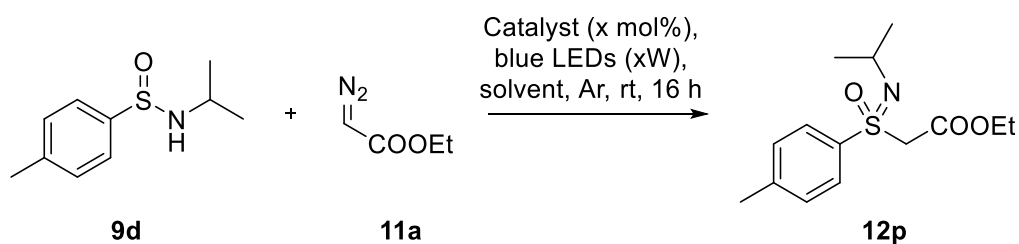
Entry	Catalyst (1 mol%)	% Yield NMR ^a
1	4-CzIPN	trace
2	Fluorescein	trace

3	Eosin Y	trace
4	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O	47%
5	-	trace

Reaction conditions: **9d** (1 equiv), **11a** (5 equiv), Catalyst (5 mol%), MeCN (0.1 M wrt **1**), 16 h, rt. ^a Calculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene), isolated yield in parentheses.

After determining the catalyst, the selection of the optimal solvent began. Most solvent classes demonstrated the ability to carry out the reaction (Table **13**, entries 1-5). Nevertheless, the best result was obtained with acetonitrile (Table **13**, entry 6). In the reaction with it, 60% yield was achieved. Next, we explored the effects of reducing the light intensity (Table **13**, entries 7-8). In such conditions, a dramatic decrease in yields was observed. Increasing the catalyst loading to 2.5 mol% (Table **13**, entry 9) results in a higher reaction output. With a further increase (Table **13**, entry 10-11), no improvement in yields is observed.

Table 13: Investigation of different solvents, light intensity, amount of photocatalyst.



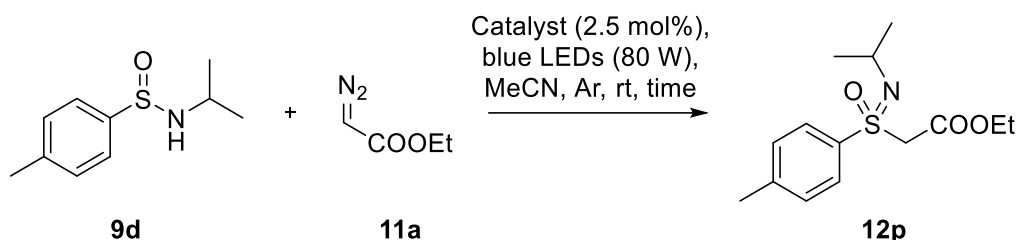
Entry	Solvent	Light intensity	Catalyst loading	% Yield NMR ^a
1	CHCl ₃	40W·2	1 mol%	36
2	DCE	40W·2	1 mol%	50
3	THF	40W·2	1 mol%	22
4	Toluen	40W·2	1 mol%	43
5	Acetone	40W·2	1 mol%	55
6	MeCN	40W·2	1 mol%	60
7	MeCN	20W·2	1 mol%	21
8	MeCN	30W·2	1 mol%	33
9	MeCN	40W·2	2.5 mol%	78
10	MeCN	40W·2	5 mol%	73
11	MeCN	40W·2	10 mol%	74

Reaction conditions: **9d** (1 equiv.), **11a** (5 equiv.), [Ru(bpy)₃]Cl₂·6H₂O, solvent (0.1 M wrt **1**), 16 h, rt. ^a Calculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene), isolated yield in parentheses.

Next, we evaluated the stoichiometric ratio of the reactants. We observed an increase in the yield with an increase of the diazo component (Table **14**, entries 1-7), reaching 92% yield with a six-fold advantage (Table **14**, entry 7) of the diazo compound **11a** over sulfonamide

9d. Also, attempts were made to reduce the reaction time (Table **14**, entries 8-11). It was determined that more than 4 hours were required for the complete reaction, during which only 44% yield was achieved. Therefore, the reaction time was left at 16 hours.

Table 14: Investigation of different starting material ratios and reaction time

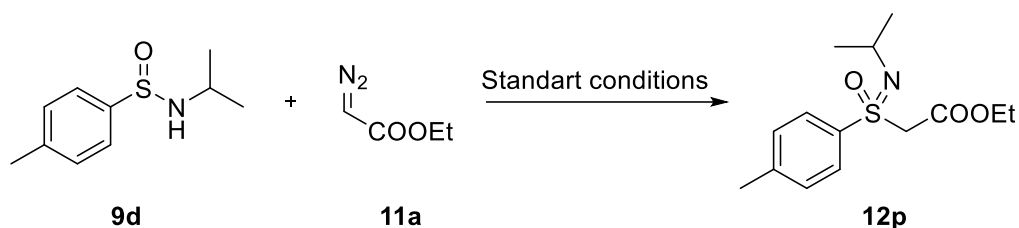


Entry	9b:11a (equiv.)	time	% Yield NMR ^a
1	2:1	16 h	18
2	1:1	16 h	30
3	1:2	16 h	47
4	1:3	16 h	64
5	1:4	16 h	71
6	1:5	16 h	78
7	1:6	16 h	96
8	1:6	0.5 h	12
9	1:6	1 h	20
10	1:6	2 h	28
11	1:6	4 h	44

Reaction conditions: **9d**, **11a**, [Ru(bpy)₃]Cl₂·6H₂O (2.5 mol%), MeCN (0.1 M wrt **1**), x h, rt. ^a Calculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene), isolated yield in parentheses.

Following the initial optimization, additional studies were conducted on the influence of various factors on the reaction. The addition of weakly acidic HFIP (Table 15, entry 1) yielded a decrease in the yields to 61%. Adding water reduced the conversion to 27% (Table 15, entry 3). Triethylamine (Table 15, entry 2) had an even more negative effect on the reaction, reducing the conversion to 21%. An attempt to abandon the inert atmosphere (Table 15, entry 4) also disastrously reduced the yield to 24%. The next unsuccessful effort was to use photoinitiation without a photocatalyst (Table 15, entry 5). The replacement of the light source with shorter wavelengths (Table 15, entry 6) reduced the yield. An attempt to provoke the reaction by heating (Table 15, entry 7) rather than by light failed, with both reagents remaining completely preserved in the reaction mixture.

Table 15: Influence of different deviations from standard conditions on reaction

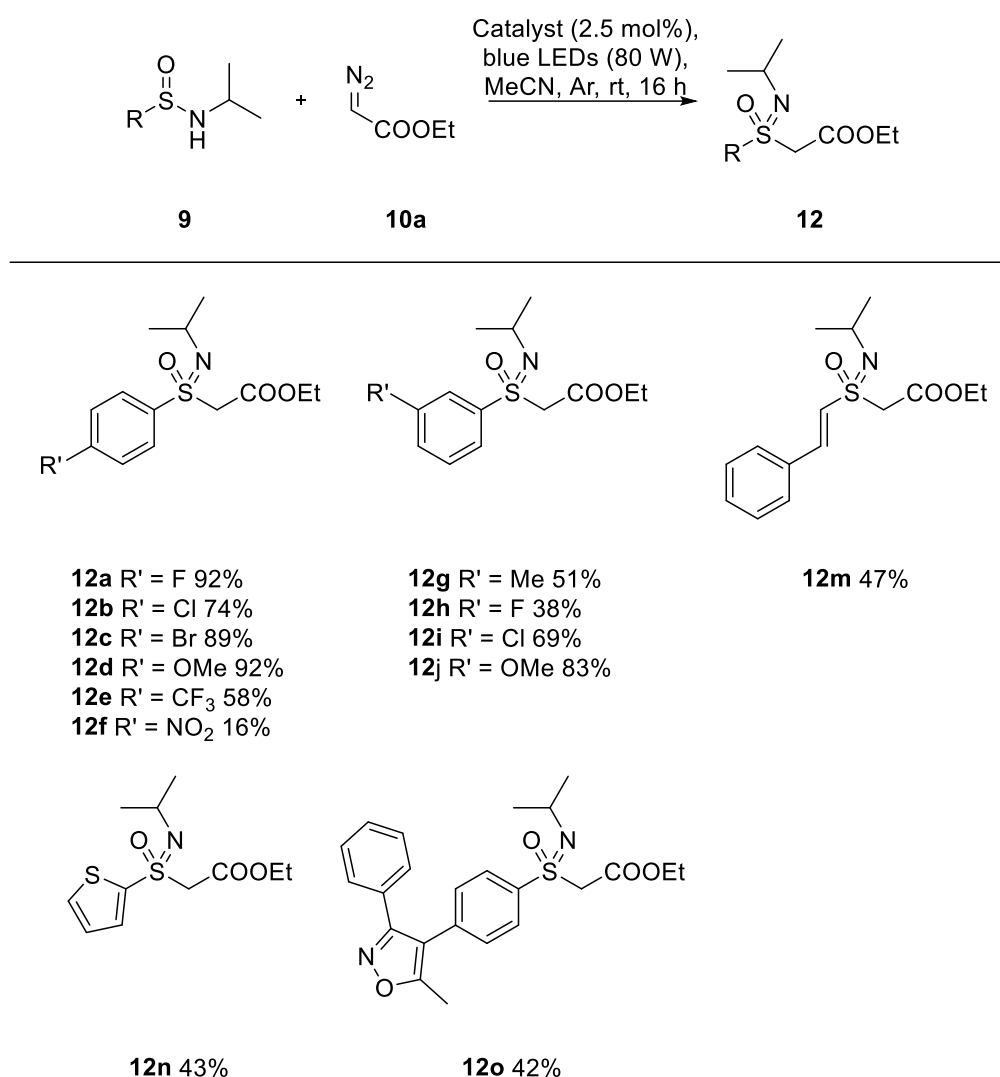


Entry	deviation	% Yield NMR ^a
1	HFIP (1 equiv.)	61
2	NEt ₃ (1 equiv.)	21
3	H ₂ O (2 equiv.)	27
4	under air	24
5	no Catalyst	trace
6	370 nm light	21
7	no light, 60°C	trace

Reaction conditions: **9d** (1 equiv.), **11a** (6 equiv.), [Ru(bpy)₃]Cl₂·6H₂O (2.5 mol%), solvent (0.1 M wrt **1**), 16 h, rt. ^a Calculated yields were determined by ¹H NMR integration against an internal standard (1,3,5-trimethoxybenzene), isolated yield in parentheses.

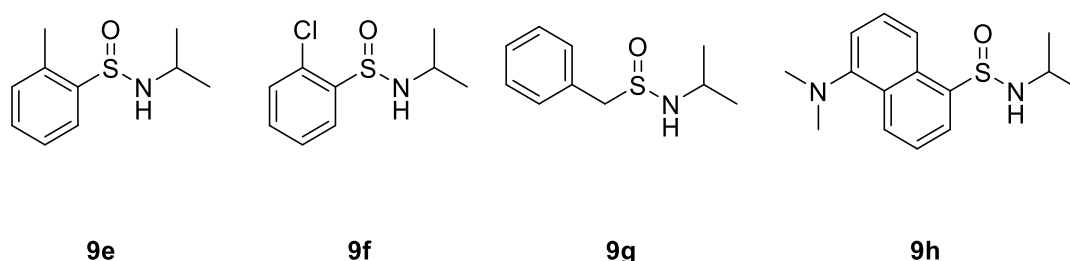
After optimization, the final procedure was established: To a reaction tube equipped with a magnetic stir bar, sulfinamide **9** (0.2 mmol, 1.0 equiv) and [Ru(bpy)₃]Cl₂·6H₂O (2.5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of diazo compound **11** (1.2 mmol, 6.0 equiv.) dissolved in 2 mL anhydrous Acetonitrile (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h.

With the optimal conditions at hand, we investigated the substrate scope. The first part focused on investigating changes in substituents in the aromatic series. Halides in the *p*- **12a-c** and *m*-position **12h-i** afforded the corresponding product in good yields. Donor substituents **12d**, **12j** demonstrate high yields. Using a trifluoromethyl electron acceptor group **12e** resulted in a reduced yield, though, the decrease is not dramatic. The product with a nitro group **12f**, which also has electron acceptor properties, unfortunately, gave a poor yield, probably due to possible side effects arising from its interaction with light. We successfully applied our methodology to the vinyl fragment **12m**. Thiophene **12n** was tested, which showed a moderate yield. We also successfully obtained a Celecoxib-based product **12o**, demonstrating the feasibility of modifying drugs using our methodology (Scheme 61).



Scheme 61: Substrate scope of different sulfinamides.

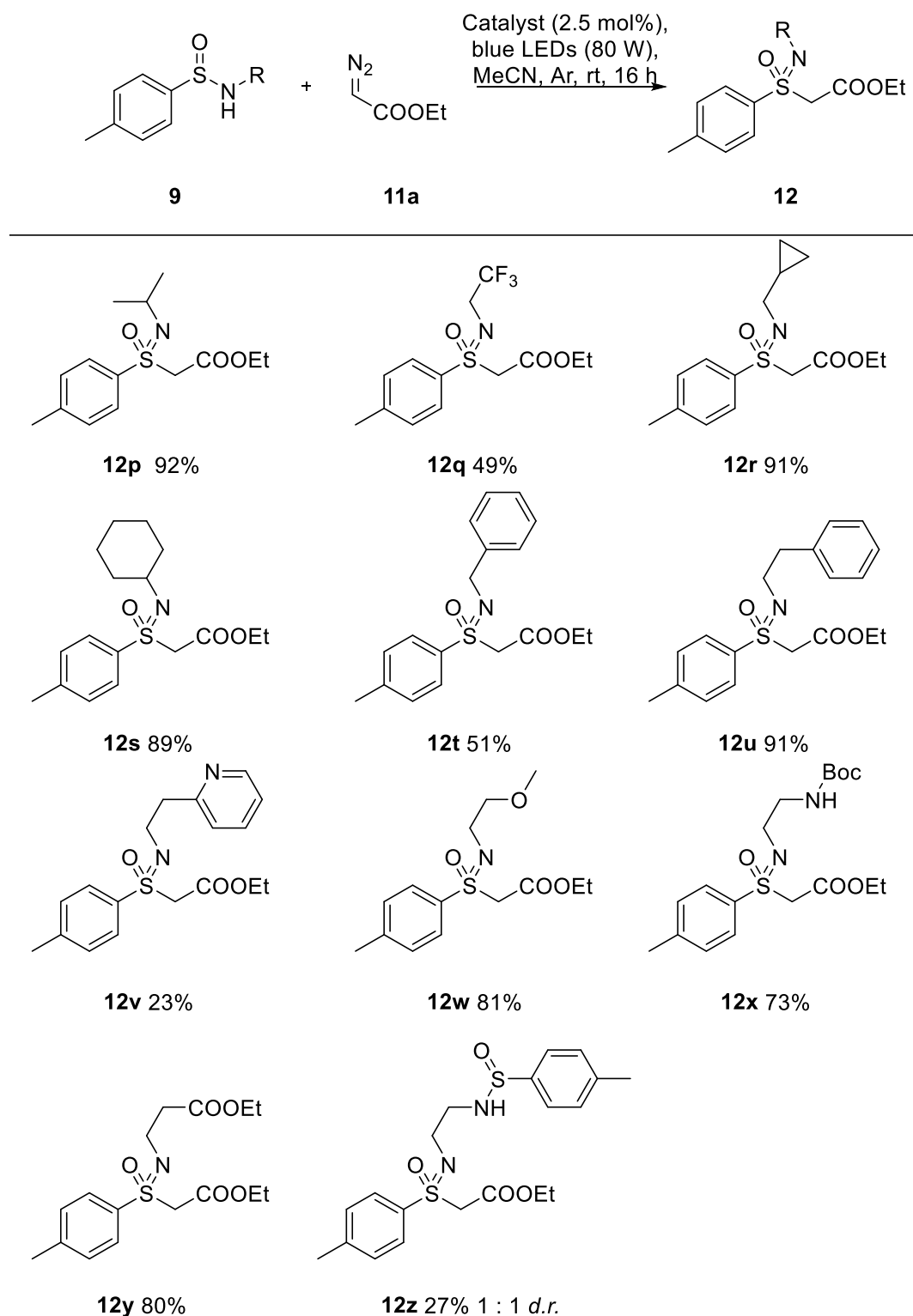
During the study, several structural patterns were discovered that interfered with our transformation. The use of starting materials containing *o*-substituted aromatic fragments **9e**, **9f**, completely inhibited the reaction. Aliphatic sulfonamides **9g** were also unable to react under our conditions. We observed a similar trend when using the basic nitrogen atom **9h** (Scheme 62).



Scheme 62: Substrate scope of unreactive sulfinamides.

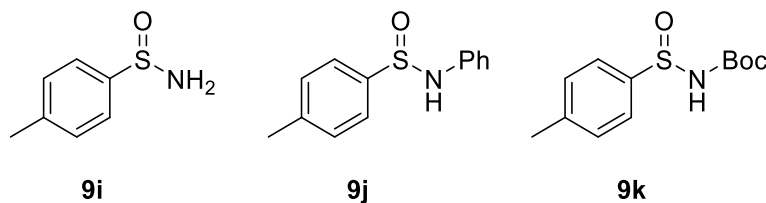
Next, we investigated different substituents attached to the nitrogen group. Isopropyl **12p**, trifluoromethyl **12q**, phenyl fragments connected by an aliphatic chain **12t**, **12u**, pyridyl **12v**,

methoxy **12w**, ester **12y**, and Boc-protected amine groups attached to the alkyl chain **12x** were found to be suitable for the reaction transformation, affording the corresponding sulfoximines in good to excellent yields. Using a starting material containing two sulfamide fragments leads to the monoaddition product **12z**, which was obtained, albeit in low yield, with a 1:1 diastereomer ratio (Scheme 63).



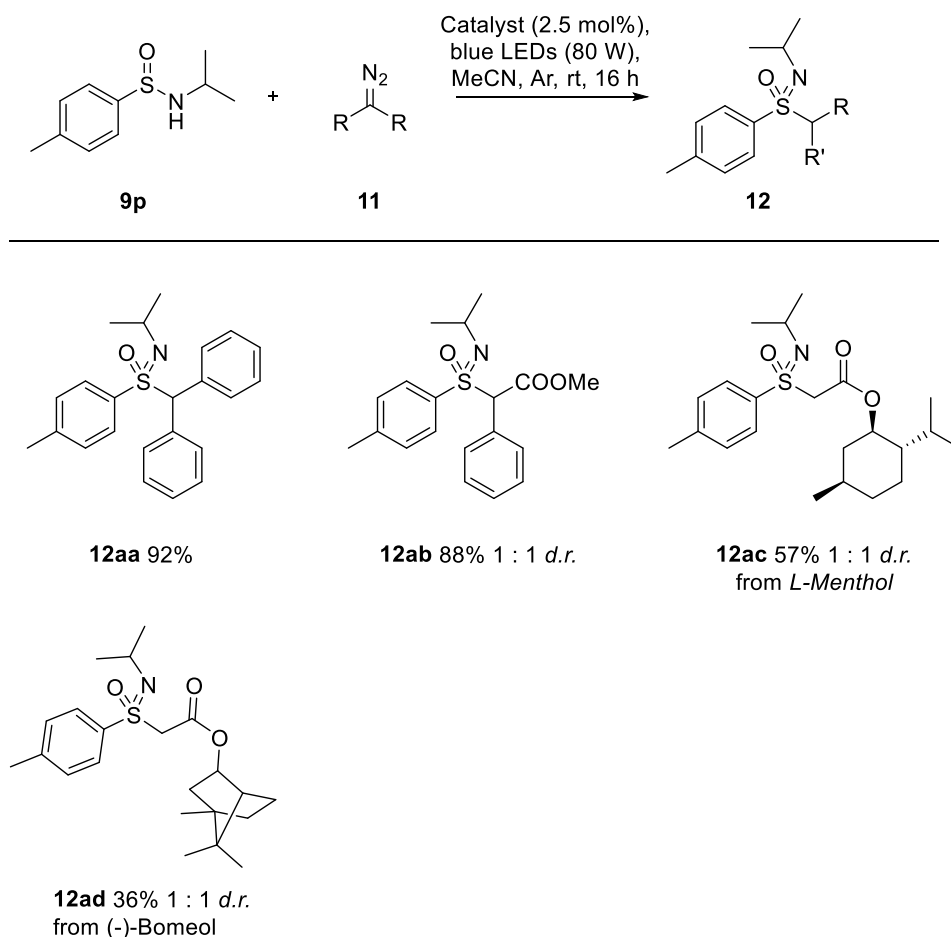
Scheme 63: Substrate scope of different N-substituted sulfinamides.

In contrast, substrates bearing *N*-aryl substituents **9j** did not produce the expected products, and the use of unsubstituted *N*-H sulfonamide **9i** also resulted in no observable conversion. Similarly, direct Boc-protected substrate **9k** failed to undergo the transformation (Scheme 64).



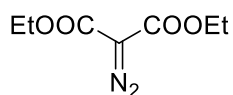
Scheme 64: Substrate scope of unreactive *N*-substituted sulfinamides.

We managed to obtain several products based on diazo compounds containing esters of natural substances **12ac**, **12ad**. Diazo compounds of different classes were also used. The **12aa** product of the reaction of donor/donor with a diazo compound and the **12ab** product of the reaction of donor/acceptor with a diazo compound were obtained in high yields (Scheme 65).



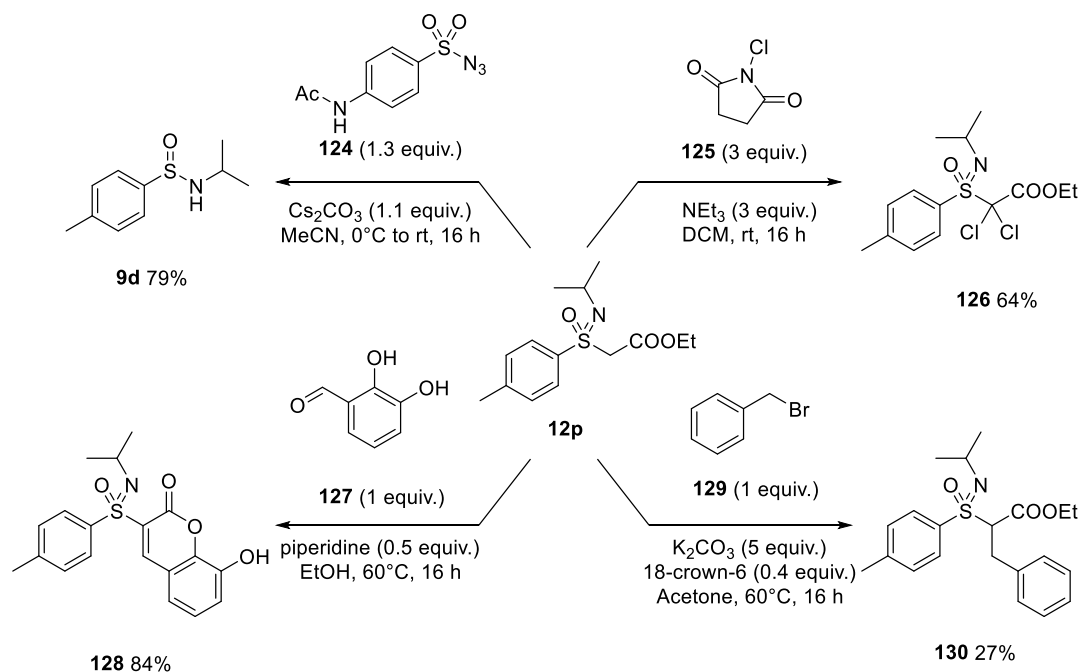
Scheme 65: Substrate scope of different diazo compounds.

However, when acceptor/acceptor diazo compounds **11b** were used, no formation of the expected product was observed (Scheme 66).

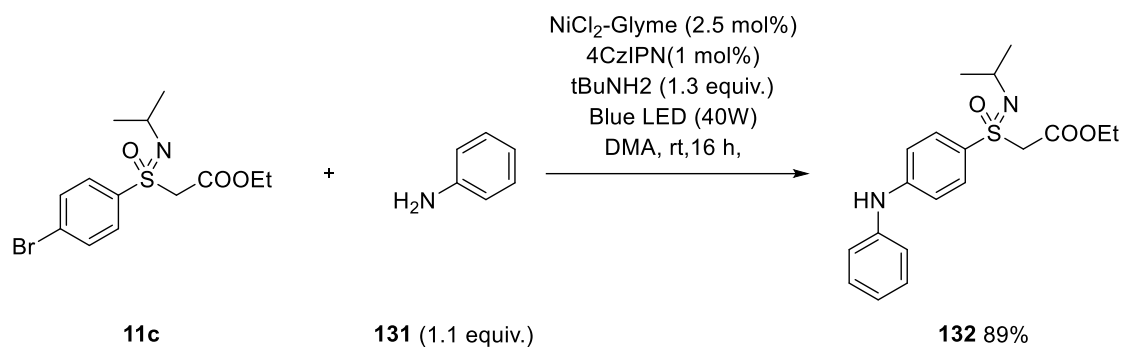
**11b****Scheme 66: Unreactive diazo compound**

After exploring the substrate scope of the described transformation, we conducted a series of experiments to demonstrate the synthetic utility of the obtained sulfoximine products.

We investigated that when treating substance **12p** with azide **124** under basic conditions, it was possible to regenerate the starting sulfonamide **9d**. The ability to obtain the product of alkylation **130**¹³¹ and chlorination **126** with NCS **125**¹³² was shown. The target of this reaction was an activated methylene, located between two acceptor groups. Condensation was also carried out, allowing the preparation of a representative of the coumarin class **128** (Scheme 67).¹³³

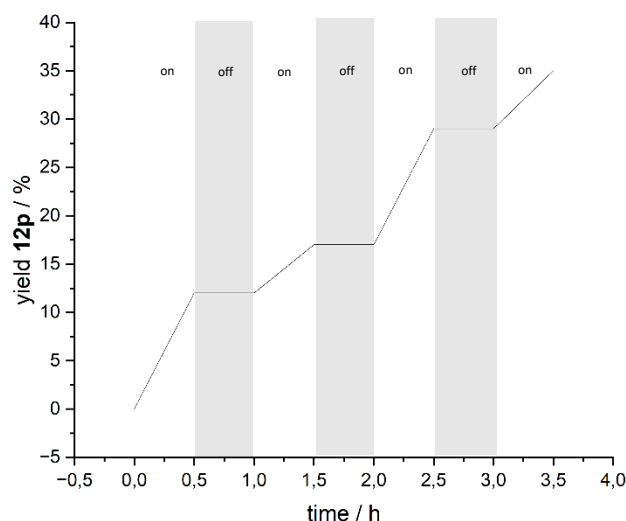
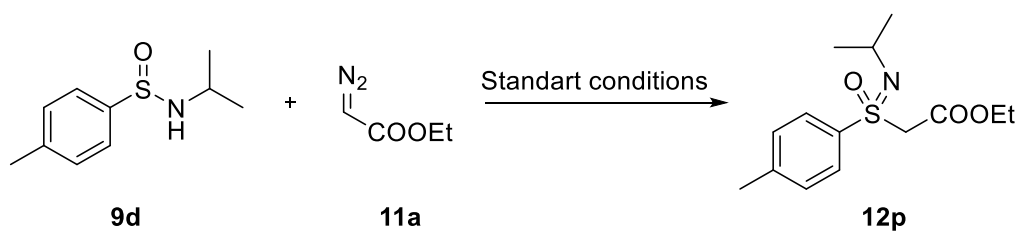
**Scheme 67: Post-synthetic modification of acceptor-activated methylene group.**

Finally, amination of compound **11c** with aniline **131** was carried out under photocatalytic conditions, leading to the formation of the corresponding aminated product **132** (Scheme 68).¹³⁴



Scheme 68: Post-synthetic modification of aromatic bromine.

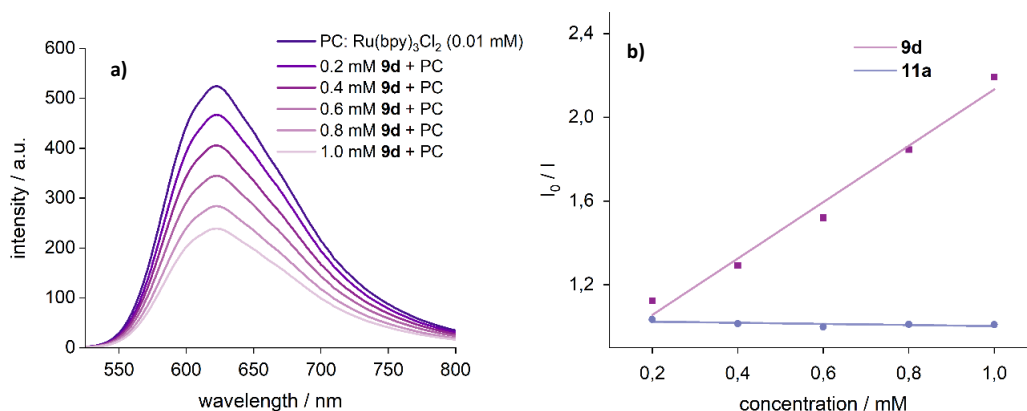
To establish the reaction mechanism, a series of control experiments was conducted. The first step was an on/off experiment. After the reaction started, we removed the sample from the light at a specific time. In an argon atmosphere, we took an aliquot. We left the reaction in the dark for some period, then took another aliquot and placed it under light. Several cycles were carried out to obtain a more reliable result. The data indicate that there is no reaction during periods without light and a stable increase in product content during periods with light irradiation. The obtained data prove the absence of a radical-chain mechanism (Scheme 69).



Scheme 69: on/off experiment.

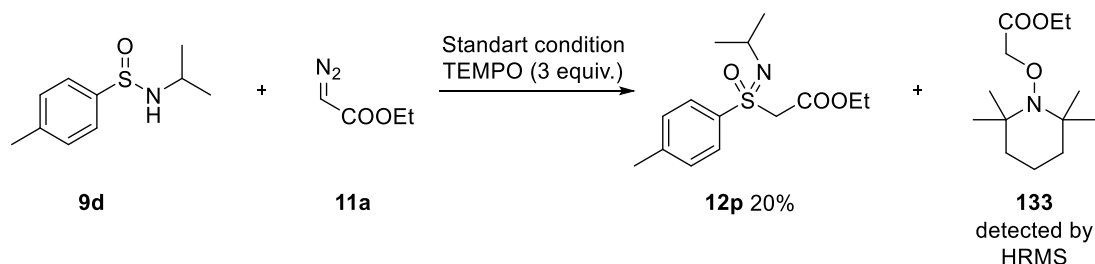
The next step was the study of fluorescence quenching. The data analysis was carried out using the Stern-Volmer plot $I_0/I = 1 + K_{sv} [Q]$. It was determined that the sulfonamide

substrate **9d** quench catalyst, unlike the diazo compound **11a**, does not exhibit similar properties. The results of our experiment are consistent with previously reported data (Scheme 71).¹³⁵



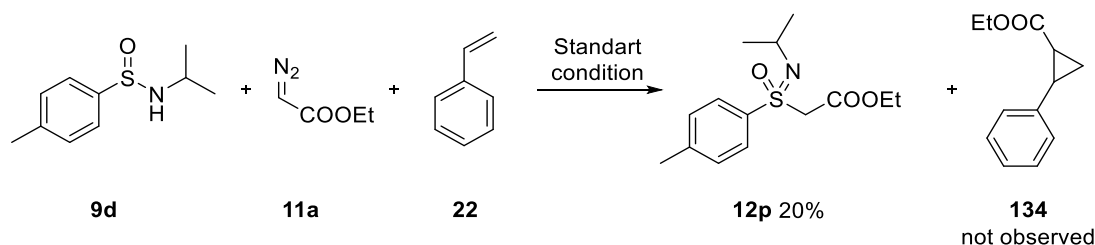
Scheme 70: a) fluorescence quenching of Ru(bpy)₃Cl₂ with **9d**, b) Stern-Volmer plot of **9b**, **11a**

After it, a radical-trap experiment was also conducted. During which TEMPO was added at the last stage of the reaction setup. It has a radical nature, reducing the yield of our reaction to 20%. Also, GC-MS analysis detected trace amounts of substance **133**, indicating the reaction's radical nature (Scheme 71).



Scheme 71: Radical trap experiment.

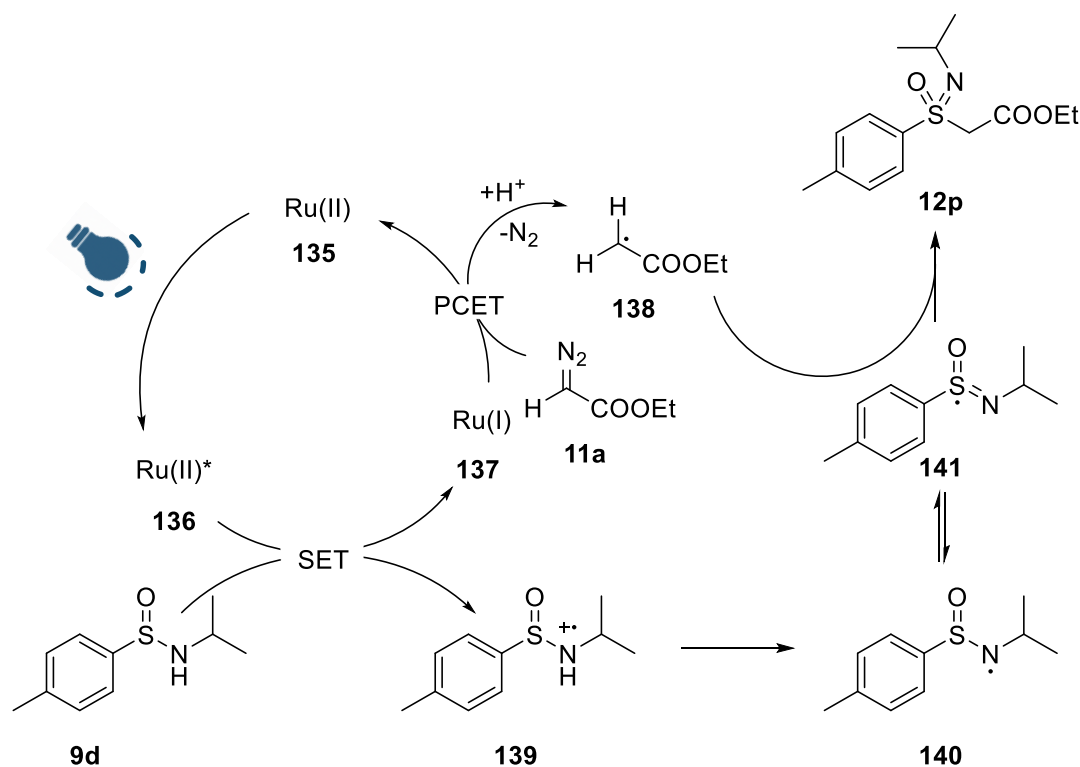
The reaction was also carried out in the presence of equimolar amounts of sulfonamide **9d** and styrene **22**. According to the reaction results, no cyclopropane product **134** was detected, indicating the absence of triplet carbene formation (Scheme 72).



Scheme 72: Competition reaction of styrene and sulfinamide.

Based on these data, we presented a possible mechanism for this transformation. At the first stage, the Ruthenium catalyst is photoexcited **136**, after which sulfonamide **9d** quenches our catalyst, reducing it to Ru(I) **138**, and obtaining a radical cation **139**, which, after

deprotonation **140**, completes its transformations with a radical located on the sulfur atom **141**. On the other hand, the catalyst, reduced to Ru(I) **137**, can donate an electron to the diazo compound **11a**, thereby completing its catalytic cycle. And the diazo compound, after oxidation and protonation, forms a radical **138**, which will interact with our S-radical **141**, forming our expected product **12p**. (Scheme 73).



Scheme 72: Proposed mechanism.

5.3 Conclusion

In summary, we have developed a photocatalytic methodology for converting sulfinamides into sulfoximidamides using diazo compounds. The conversion was tested on a wide range of substrates, enabling us to identify most of the reaction's limitations. A series of experiments was also performed to confirm the feasibility of further synthetic conversions for our products. Finally, we proposed a detailed mechanism for this reaction, supported by many experimental data.

6. Outlook

Despite its long-standing history, nitrene chemistry remains a vibrant and evolving field. At the same time, the creation of heterocyclic compounds will always be a key goal in organic synthesis. Further research at the intersection of these two vectors is always valuable. The ability to obtain such products under different conditions remains a desirable direction of development. The [2+2+1] cycloaddition reaction could benefit greatly from the exploration of new substrate classes. Iminoiodinanes are reliable, but not universal, sources of nitrenes, due to the difficulties in obtaining their different classes. Unconjugated dienes are not the most obvious substrates for cyclization, and further searches can expand the capabilities of this transformation. No one has yet presented a carbene transformation using a [2+2+1] strategy.

The transformation of S-containing compounds by nitrenes and carbenes will not leave people's minds for long, because their full diversity has not yet been studied, both chemically and biomedically. The ability of sulfur to form various bonds, although well researched, leaves many blanks. It is also important to remember the sulfur atom's chiral properties. The development of inexpensive, synthetically simple methods for controlling this isomerism is a primary challenge for chemists.

7. Experimental Data

7.1 General Information

NMR spectroscopy

^1H -, ^{13}C - and ^{19}F -NMR spectra were recorded on either Varian AV600/AV400 or an Agilent DD2 400 NMR spectrometer using CDCl_3 as solvents. Spectra are referenced to the corresponding solvents. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated b (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)); coupling constants (J) are in Hertz (Hz).

HRMS spectra

HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization or on a Finnigan MAT 95 using EI ionization at 70 eV.

GC/MS spectra

GC/MS were recorded on a Shimadzu GCMS-QP2010 SE Gas chromatograph mass spectrometer. GC column: Optima 5 MS column, 30 m. Carrier gas: Helium.

HPLC spectra

HPLC was carried out on a JASCO UV- 2077 Plus with a PU-2080 Plus solvent pump. Operation and analysis were under control of JASCO ChromPass software. As chiral columns for determination of enantiomeric excess the following prefabricated columns from Daicel were used: Chiralcel OD-H (250 x 4.6 mm, 5 μm).

Thin layer chromatography

Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light.

Solvents

Solvents used in reactions were p.A. grade and dried only if indicated. Solvents for chromatography were technical grade and distilled before use.

UV-Vis spectra

UV-Vis spectra were recorded on a UV-2600 machine from Shimadzu.

Emission spectra

Emission spectra were recorded on a Simazu RF-6000 Spectro Fluorophotometer

LEDs

LEDs used in this manuscript were purchased from LUMITRONIX: Blue LED (470 nm) Module: rigid strips of 12 LEDs at 25 W and 30 lm, 2 single LEDs of this strip were used for each reaction.

Reagents

Unless otherwise noted, all commercially available compounds were used as provided without further purification.

7.2 Experimental Data

7.2.1 Silver-catalyzed triplet relay strategy for 2+2+1 reactions

Typical experimental procedure: An oven-dried test tube equipped with a magnetic stir bar was charged with compound **1** (0.2 mmol, 1.0 equiv), AgTp^{Br3} (0.01 mmol, 5 mol%), and HFIP (0.6 mmol, 3.0 equiv). The tube was sealed with a rubber septum, evacuated, and backfilled with argon three times. Anhydrous dichloromethane (CH₂Cl₂, 8 mL) was added via syringe, followed by the addition of iminoiodinane **2** (0.6 mmol, 3.0 equiv) in a single portion under a continuous argon flow. The reaction vessel was then sealed with parafilm and stirred at ambient temperature for 16 hours. Upon completion, the mixture was concentrated in vacuo and purified by column chromatography.

Diethyl 2-tosylhexahydrocyclopenta[c]pyrrole-5,5(1*H*)-dicarboxylate (**3a**)

¹H NMR (600 MHz, CDCl₃): δ = 7.70 – 7.62 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.14 (qd, *J* = 7.1, 3.7 Hz, 4H), 3.14 (dd, *J* = 9.9, 1.9 Hz, 2H), 2.83 (dq, *J* = 10.9, 7.0 Hz, 2H), 2.65 (td, *J* = 9.9, 8.6, 4.7 Hz, 2H), 2.55 – 2.47 (m, 2H), 2.42 (s, 4H), 1.93 (dd, *J* = 13.4, 7.1 Hz, 2H), 1.21 (dt, *J* = 11.6, 7.1 Hz, 8H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 171.6, 170.7, 143.7, 131.9, 129.6, 128.0, 62.3, 61.5, 53.6, 41.7, 39.7, 21.5, 14.0, 13.9 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₀H₂₇NO₆SN⁺: 432.15413; Found: 432.14433.

Diethyl 2-((4-fluorophenyl)sulfonyl)hexahydrocyclopenta[c]pyrrole-5,5(1*H*)-dicarboxylate (**3b**)

¹H NMR (600 MHz, CDCl₃): δ = 7.88 – 7.77 (m, 2H), 7.23 – 7.15 (m, 2H), 4.14 (qd, *J* = 7.1, 2.7 Hz, 4H), 3.15 (dd, *J* = 9.8, 2.0 Hz, 2H), 2.96 – 2.82 (m, 2H), 2.68 (dtd, *J* = 7.8, 5.9, 2.7 Hz, 2H), 2.58 – 2.45 (m, 2H), 1.92 (dd, *J* = 13.5, 7.2 Hz, 2H), 1.21 (dt, *J* = 9.8, 7.1 Hz, 6H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 171.6, 170.8, δ 165.3 (d, *J* = 255.0 Hz), 131.2 (d, *J* = 3.1 Hz), 130.6 (d, *J* = 9.1 Hz), 116.36 (d, *J* = 22.4 Hz), 62.2, 61.6, 61.6, 53.5, 41.8, 39.6, 14.0, 13.9 ppm. **¹⁹F NMR** (565 MHz, CDCl₃): δ = -105.04 (td, *J* = 8.8, 4.4 Hz) ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₉H₂₄FNO₆SN⁺: 436.12006; Found: 436.11920.

Diethyl 2-((4-chlorophenyl)sulfonyl)hexahydrocyclopenta[c]pyrrole-5,5(1*H*)-dicarboxylate (**3c**)

¹H NMR (600 MHz, CDCl₃): δ = 7.78 – 7.68 (m, 1H), 7.61 – 7.38 (m, 1H), 4.14 (qd, *J* = 7.1, 1.6 Hz, 2H), 3.15 (dd, *J* = 9.9, 2.1 Hz, 1H), 2.94 – 2.81 (m, 1H), 2.68 (ddq, *J* = 8.0, 6.3, 2.7 Hz, 1H), 2.60 – 2.39 (m, 1H), 1.92 (dd, *J* = 13.5, 7.2 Hz, 1H), 1.21 (dt, *J* = 9.8, 7.1 Hz, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 171.7, 170.9, 139.5, 133.7, 129.4, 129.4, 62.3, 61.7, 61.7, 53.6, 42.0, 39.7, 14.1, 14.0 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₉H₂₄NO₆SClNa⁺: 452.09051; Found: 452.08961.

Diethyl 2-((4-bromophenyl)sulfonyl)hexahydrocyclopenta[c]pyrrole-5,5(1*H*)-dicarboxylate (**3d**)

¹H NMR (600 MHz, CDCl₃): δ = 7.77 – 7.58 (m, 4H), 4.13 (qd, *J* = 7.1, 1.3 Hz, 4H), 3.14 (dd, *J* = 9.8, 2.1 Hz, 2H), 2.97 – 2.80 (m, 1H), 2.68 (tt, *J* = 7.2, 2.6 Hz, 2H), 2.55 – 2.46 (m, 2H), 1.91 (dd, *J* = 13.4, 7.0 Hz, 2H), 1.21 (dt, *J* = 10.2, 7.1 Hz, 6H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 171.6, 170.8, 134.2, 132.4, 129.5, 128.0, 62.2, 61.7, 61.6, 53.6, 41.9, 39.6, 14.1, 14.1 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₉H₂₄NO₆SBrNa⁺: 496.03999; Found: 496.03948.

Diethyl 2-((2-fluorophenyl)sulfonyl)hexahydrocyclopenta[c]pyrrole-5,5(1H)-dicarboxylate (3e)

¹H NMR (600 MHz, CDCl₃): δ = 7.83 – 7.74 (m, 1H), 7.57 – 7.45 (m, 1H), 7.26 – 7.20 (m, 1H), 7.15 (ddd, J = 9.6, 8.3, 1.1 Hz, 1H), 4.09 (q, J = 7.1 Hz, 4H), 3.20 (dd, J = 10.2, 2.3 Hz, 2H), 3.17 – 3.01 (m, 2H), 2.77 – 2.56 (m, 2H), 2.52 – 2.39 (m, 2H), 1.90 (dd, J = 13.5, 7.2 Hz, 2H), 1.16 (td, J = 7.1, 6.0 Hz, 6H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 171.7, 170.8, 160.0, 158.3, 135.1, 135.0, 131.5, 124.4, 124.4, 117.4, 117.2, 62.2, 61.6, 53.1, 53.18, 42.0, 39.4, 14.0, 13.9 ppm.

¹⁹F NMR (565 MHz, CDCl₃): δ = -106.99 (dt, J = 11.1, 6.1 Hz) ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₉H₂₄NO₆SFNa⁺: 436.12006; Found: 436.11921.

Diethyl 2-((3-chloro-2-methylphenyl)sulfonyl)hexahydrocyclopenta[c]pyrrole-5,5(1H)-dicarboxylate (3f)

¹H NMR (600 MHz, CDCl₃): δ = 7.89 (dd, J = 7.9, 1.3 Hz, 1H), 7.58 (dd, J = 8.0, 1.3 Hz, 1H), 7.30 – 7.21 (m, 1H), 4.17 (q, J = 7.1 Hz, 4H), 3.18 – 3.10 (m, 4H), 2.77 (ddt, J = 10.6, 7.7, 4.3 Hz, 2H), 2.70 (s, 3H), 2.56 (ddt, J = 13.7, 7.7, 5.3 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.23 (td, J = 7.1, 5.5 Hz, 6H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 171.5, 170.9, 137.9, 137.3, 136.3, 133.9, 128.9, 126.5, 62.2, 61.6, 61.6, 52.9, 41.9, 39.8, 17.3, 14.02, 14.01 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₀H₂₆NO₆SClNa⁺: 466.10616; Found: 466.10559.

Diethyl 2-(pyridin-3-ylsulfonyl)hexahydrocyclopenta[c]pyrrole-5,5(1H)-dicarboxylate (3g)

¹H NMR (400 MHz, CDCl₃): δ = 8.99 (s, 1H), 8.81 (d, J = 5.1 Hz, 1H), 8.07 (dd, J = 7.8, 2.0 Hz, 1H), 7.49 (dd, J = 8.2, 4.7 Hz, 1H), 4.13 (qd, J = 7.2, 2.0 Hz, 4H), 3.19 (dd, J = 9.8, 2.0 Hz, 2H), 3.09 – 2.79 (m, 2H), 2.70 (d, J = 6.7 Hz, 2H), 2.51 (dd, J = 13.9, 8.0 Hz, 2H), 1.92 (dd, J = 13.7, 7.4 Hz, 2H), 1.20 (q, J = 7.0 Hz, 6H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 171.5, 170.7, 153.2, 148.4, 135.7, 132.1, 123.8, 62.1, 61.6, 61.6, 53.5, 41.9, 39.5, 14.0 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₈H₂₄N₂O₆SNa⁺: 419.12473; Found: 419.12473.

Diethyl 2-((4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl)sulfonyl)hexahydrocyclopenta[c]pyrrole-5,5(1H)-dicarboxylate (3h)

¹H NMR (600 MHz, CDCl₃): δ = 7.82 – 7.72 (m, 2H), 7.52 – 7.45 (m, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.12 – 7.04 (m, 2H), 6.74 (s, 1H), 4.15 (qd, J = 7.1, 4.5 Hz, 4H), 3.15 (dd, J = 9.9, 2.0 Hz, 2H), 2.87 (dd, J = 9.8, 7.0 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.52 (ddd, J = 13.5, 6.1, 2.3 Hz, 2H), 2.37 (s, 3H), 1.93 (dd, J = 13.5, 7.1 Hz, 2H), 1.22 (td, J = 7.1, 1.0 Hz, 6H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 171.7, 170.9, 145.4, 144.3 (q, J = 38.6 Hz), 142.8, 140.0, 134.7, 129.8, 129.0, 128.8, 125.7, 125.6, 121.2 (q, J = 269.2 Hz), 106.4, 62.3, 61.8, 61.7, 53.7, 42.0, 39.7, 21.4, 14.1 ppm.

¹⁹F NMR (565 MHz, CDCl₃): δ = -62.47 (s) ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{30}H_{32}F_3N_3O_6SNa^+$: 642.18561; Found: 642.18478.

Diethyl 2-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonyl)hexahydrocyclopenta[c]pyrrole-5,5(1H)-dicarboxylate (3i)

1H NMR (600 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.4 Hz, 2H), 7.43 – 7.28 (m, 7H), 4.13 (dq, J = 11.6, 7.1 Hz, 4H), 3.17 (dd, J = 9.9, 2.2 Hz, 2H), 2.96 (dq, J = 11.2, 7.3 Hz, 2H), 2.70 (tq, J = 8.0, 6.4, 2.8 Hz, 2H), 2.55 – 2.50 (m, 1H), 2.49 (s, 3H), 1.92 (dd, J = 13.5, 7.2 Hz, 2H), 1.21 (td, J = 7.1, 4.5 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.7, 170.9, 167.3, 161.2, 135.5, 134.5, 130.2, 129.8, 128.8, 128.5, 128.4, 114.5, 62.2, 61.7, 53.6, 42.0, 39.6, 14.1, 11.9 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{29}H_{32}N_2O_7SNa^+$: 575.18224; Found: 575.18148.

2'-Tosylhexahydro-1'H-spiro[cyclopentane-1,5'-cyclopenta[c]pyrrole]-2,5-dione (3j)

1H NMR (600 MHz, $CDCl_3$): δ = 7.73 – 7.65 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.17 (dd, J = 10.0, 2.5 Hz, 2H), 3.03 (dd, J = 9.9, 7.0 Hz, 2H), 2.89 – 2.80 (m, 2H), 2.75 (s, 4H), 2.44 (s, 3H), 2.02 (dt, J = 13.2, 7.1 Hz, 2H), 1.66 (dd, J = 13.2, 7.1 Hz, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 215.6, 213.3, 143.7, 132.4, 129.7, 127.9, 65.1, 52.7, 43.2, 39.0, 35.6, 34.4, 21.5 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{18}H_{21}NO_4SNa^+$: 370.10835; Found: 370.10777.

4-Methyl-2'-tosylhexahydro-1'H-spiro[cyclohexane-1,5'-cyclopenta[c]pyrrole]-2,6-dione (3k)

1H NMR (600 MHz, $CDCl_3$): δ = 7.73 – 7.65 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.17 (dd, J = 10.0, 2.5 Hz, 2H), 3.03 (dd, J = 9.9, 7.0 Hz, 2H), 2.89 – 2.80 (m, 2H), 2.75 (s, 4H), 2.44 (s, 3H), 2.02 (dt, J = 13.2, 7.1 Hz, 2H), 1.66 (dd, J = 13.2, 7.1 Hz, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 215.6, 213.3, 143.7, 132.4, 129.7, 127.9, 65.1, 52.7, 43.2, 39.0, 35.6, 34.4, 21.5 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{20}H_{25}NO_4SNa^+$: 398.13965; Found: 398.13894.

2-Tosyl-2,3,3a,4,6,6a-hexahydro-1H-spiro[cyclopenta[c]pyrrole-5,2'-indene]-1',3'-dione (3l)

1H NMR (600 MHz, $CDCl_3$): δ = 8.05 – 7.90 (m, 1H), 7.90 – 7.82 (m, 1H), 7.81 – 7.66 (m, 1H), 7.42 – 7.34 (m, 1H), 3.27 (dd, J = 9.8, 2.3 Hz, 1H), 3.10 (dd, J = 9.7, 7.1 Hz, 1H), 3.04 (qd, J = 7.4, 6.7, 2.8 Hz, 1H), 2.46 (s, 1H), 2.07 (dd, J = 13.6, 7.4 Hz, 1H), 1.88 (dd, J = 13.3, 7.1 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 202.0, 143.6, 143.4, 133.2, 131.8, 131.1, 129.6, 128.7, 128.1, 127.7, 126.6, 56.1, 54.2, 42.3, 41.9, 35.5, 27.3, 21.6 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{22}H_{21}NO_4SNa^+$: 418.10835; Found: 418.10778.

2-Tosyl-2,3,3a,3',4,4',6,6a-octahydro-1H,1'H-spiro[cyclopenta[c]pyrrole-5,2'-naphthalen]-1'-one (3m)

1H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.4 Hz, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.45 (t, J = 7.8 Hz, 1H), 7.34 (d, J = 8.3 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 7.4 Hz, 1H), 3.21 (d, J = 10.1 Hz, 3H), 2.98 (t, J = 6.0 Hz, 3H), 2.76 (q, J = 6.0, 5.5 Hz, 3H), 2.70 (dd, J = 9.7, 6.9 Hz, 2H), 2.44 (s, 4H), 2.37 (dd, J = 13.8, 8.3 Hz, 3H), 2.12 (t, J = 6.4 Hz, 3H), 1.44 (dd, J = 12.9, 8.3 Hz, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 202.0, 143.6, 143.4, 133.2, 131.8, 131.1, 129.6, 128.7, 128.1, 127.7, 126.6, 56.1, 54.2, 42.3, 41.9, 35.5, 27.3, 21.6 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₃H₂₅NO₃Na⁺: 418.14474; Found: 418.14401.

1,1'-(2-Tosyloctahydrocyclopenta[c]pyrrole-5,5-diyl)bis(ethan-1-one) (3n)

¹H NMR (600 MHz, CDCl₃): δ = 7.69 – 7.65 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.15 (dd, *J* = 9.8, 1.6 Hz, 2H), 2.87 – 2.80 (m, 2H), 2.58 – 2.47 (m, 4H), 2.45 (d, *J* = 2.8 Hz, 4H), 2.09 (d, *J* = 4.8 Hz, 6H), 1.81 (h, *J* = 6.1 Hz, 2H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 205.0, 204.7, 143.8, 132.0, 130.0, 129.8, 129.7, 129.6, 128.0, 53.5, 41.4, 37.2, 27.0, 25.9, 21.5 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₈H₂₂NO₄Na⁺: 372.12400; Found: 372.12336.

2-Tosyloctahydrocyclopenta[c]pyrrole (3o)

¹H NMR (600 MHz, CDCl₃): δ = 7.67 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 3.16 – 3.06 (m, 2H), 2.88 (dd, *J* = 9.2, 3.7 Hz, 2H), 2.54 (h, *J* = 3.7 Hz, 2H), 2.43 (s, 3H), 1.72 (dt, *J* = 13.8, 7.4 Hz, 2H), 1.64 – 1.54 (m, 1H), 1.50 – 1.41 (m, 1H), 1.41 – 1.33 (m, 2H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 143.4, 132.2, 129.6, 129.5, 128.0, 128.0, 54.6, 42.6, 32.7, 26.1, 21.5 ppm.

Ethyl 5-cyano-2-tosyloctahydrocyclopenta[c]pyrrole-5-carboxylate (3p)

¹H NMR (600 MHz, CDCl₃) (7.0 : 1 mixture of two diastereoisomers, distinguishable resonances of the major diastereoisomer): δ = 7.68 – 7.65 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.28 (d, *J* = 9.8 Hz, 2H), 2.87 (pd, *J* = 9.6, 8.3, 6.2 Hz, 2H), 2.77 – 2.70 (m, 2H), 2.52 (ddd, *J* = 13.3, 6.1, 1.9 Hz, 2H), 2.15 – 2.03 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃) (7.0 : 1 mixture of two diastereoisomers, distinguishable resonances of the major diastereoisomer): δ = 167.3, 144.0, 131.3, 129.7, 128.1, 128.0, 119.5, 63.1, 53.0, 50.3, 42.2, 41.3, 21.6, 14.0 ppm.

IR (KBr): 3420, 2945, 2862, 2242, 2064, 1933, 1727, 1658, 1598, 1448, 1343, 1294, 1246, 1202, 1164, 1129, 1092, 1061, 1009, 897, 841, 754, 661 cm⁻¹.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₈H₂₂N₂O₄Na⁺: 385.11925; Found: 385.11857.

Ethyl 2-tosyloctahydrocyclopenta[c]pyrrole-5-carboxylate (3q)

¹H NMR (600 MHz, CDCl₃): δ = 7.70 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.14 (dd, *J* = 9.7, 2.3 Hz, 2H), 3.03 – 2.90 (m, 2H), 2.67 (tt, *J* = 11.1, 7.0 Hz, 1H), 2.58 (dd, *J* = 8.7, 5.4 Hz, 2H), 2.45 (s, 3H), 2.24 – 2.12 (m, 2H), 1.72 – 1.58 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 174.2, 143.6, 132.2, 129.6, 128.0, 60.5, 53.6, 46.00, 42.4, 35.8, 21.5, 14.2 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₇H₂₃NO₄Na⁺: 360.12400; Found: 360.12355.

2,5-Ditosyloctahydropyrrolo[3,4-c]pyrrole (3r)

¹H NMR (400 MHz, CDCl₃): δ = 7.67 – 7.60 (m, 4H), 7.33 (d, *J* = 7.8 Hz, 4H), 3.27 – 3.18 (m, 4H), 2.87 (dd, *J* = 10.1, 3.7 Hz, 4H), 2.75 (s, 2H), 2.45 (s, 6H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 144.0, 131.9, 129.8, 127.8, 52.3, 41.7, 21.6 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₀H₂₄N₂O₄S₂Na⁺: 443.10697; Found: 443.10590.

Benzyl 5-tosylhexahydropyrrolo[3,4-c]pyrrole-2(1H)-carboxylate (3s)

¹H NMR (600 MHz, CDCl₃): δ = 7.77 – 7.67 (m, 2H), 7.44 – 7.30 (m, 6H), 5.11 (d, *J* = 8.5 Hz, 2H), 3.61 (s, 2H), 3.43 (s, 2H), 3.17 (s, 2H), 3.10 (dd, *J* = 10.2, 4.0 Hz, 2H), 2.84 (s, 2H), 2.45 (s, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 154.6, 143.8, 136.6, 133.0, 129.8, 128.5, 128.1, 127.9, 127.6, 67.0, 52.0, 21.6 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₁H₂₄N₂O₄SNa⁺: 423.13490; Found: 423.13407.

tert-Butyl 5-tosylhexahydropyrrolo[3,4-c]pyrrole-2(1H)-carboxylate (3t)

¹H NMR (600 MHz, CDCl₃): δ = 7.70 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 3.53 – 3.44 (m, 2H), 3.44 – 3.37 (m, 2H), 3.06 (dd, *J* = 10.2, 3.8 Hz, 4H), 2.78 (s, 2H), 2.44 (s, 3H), 1.41 (s, 9H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 154.2, 143.8, 133.0, 129.8, 128.7, 127.7, 79.6, 52.11, 49.7, 28.4, 21.6 ppm.

Phenyl(5-tosylhexahydropyrrolo[3,4-c]pyrrol-2(1H)-yl)methanone (3u)

¹H NMR (600 MHz, MeOH-*d*₄): δ = 7.71 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.50 – 7.39 (m, 5H), 7.36 – 7.32 (m, 2H), 3.70 (t, *J* = 10.7 Hz, 1H), 3.57 (t, *J* = 9.9 Hz, 1H), 3.48 – 3.36 (m, 2H), 3.30 – 3.28 (m, 1H), 3.17 – 3.11 (m, 1H), 3.07 (dd, *J* = 11.9, 4.8 Hz, 1H), 2.99 (dd, *J* = 11.0, 3.9 Hz, 1H), 2.92 (s, 1H), 2.84 (s, 1H), 2.46 (s, 3H) ppm.

¹³C NMR (151 MHz, MeOH-*d*₄): δ = 170.4, 144.1, 136.0, 132.5, 129.9, 129.5, 128.1, 127.5, 126.6, 52.8, 52.3, 51.7, 49.6, 42.4, 40.8, 20.1 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₀H₂₂N₂O₃SNa⁺: 393.12433; Found: 393.12393.

5-Tosylhexahydro-1H-furo[3,4-c]pyrrole (3w)

¹H NMR (600 MHz, CDCl₃): δ = 7.68 – 7.55 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.74 (dd, *J* = 9.3, 6.6 Hz, 1H), 3.44 (dd, *J* = 9.1, 3.4 Hz, 2H), 3.18 (dd, *J* = 9.9, 7.3 Hz, 1H), 2.86 (dd, *J* = 9.9, 3.6 Hz, 2H), 2.77 (dq, *J* = 7.3, 4.0 Hz, 2H), 2.37 (s, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 143.9, 132.0, 129.7, 128.0, 73.0, 52.7, 43.6, 21.6 ppm.

HRMS (ESI): *m/z*: [M+H]⁺ Calcd. for C₁₄H₁₉NO₂S⁺: 265.11310; Found: 265.11334.

Diethyl 3a-methyl-2-tosylhexahydrocyclopenta[c]pyrrole-5,5(1H)-dicarboxylate (3x)

¹H NMR (600 MHz, CDCl₃) (2.0 : 1 mixture of two diastereoisomers, distinguishable resonances of the major diastereoisomer): δ = 7.66 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.26 – 4.02 (m, 5H), 3.18 (d, *J* = 9.7 Hz, 1H), 3.14 (dd, *J* = 9.9, 2.7 Hz, 1H), 3.07 (dd, *J* = 9.9, 7.0 Hz, 1H), 2.94 – 2.81 (m, 1H), 2.73 (d, *J* = 9.7 Hz, 1H), 2.53 (ddd, *J* = 13.6, 7.8, 1.2 Hz, 1H), 2.41 (s, 3H), 2.37 (d, *J* = 14.1 Hz, 1H), 2.17 (dd, *J* = 14.1, 1.2 Hz, 1H), 1.80 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.20 (td, *J* = 7.3, 4.9 Hz, 9H), 0.97 (s, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃) (2.0 : 1 mixture of two diastereoisomers): δ = 172.4, 172.1, 171.7, 171.3, 143.6, 143.4, 135.4, 132.7, 129.8, 129.78, 127.9, 127.1, 64.8, 61.9, 61.8, 61.7, 61.7, 61.12, 60.2, 57.1, 52.7, 51.9, 50.6, 50.0, 49.7, 46.0, 45.6, 41.1, 39.5, 30.9, 25.7, 21.6, 21.6, 17.4, 14.1, 14.0 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{21}H_{29}NO_6SNa^+$: 446.16078; Found: 446.16040.

Diethyl 1-methyl-2-tosylhexahydrocyclopenta[c]pyrrole-5,5(1H)-dicarboxylate (3y)

1H NMR (600 MHz, $CDCl_3$) (1.2 : 1 mixture of two diastereoisomers): δ = 7.72 – 7.68 (m, 2H), 7.68 – 7.63 (m, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 4.15 – 4.10 (m, 4H), 4.05 (qd, J = 7.1, 5.9 Hz, 2H), 3.55 (dt, J = 8.5, 6.5 Hz, 1H), 3.50 (qd, J = 6.4, 2.7 Hz, 1H), 3.25 (dd, J = 10.7, 4.7 Hz, 1H), 3.11 – 3.02 (m, 2H), 2.99 (dd, J = 10.4, 5.7 Hz, 1H), 2.80 – 2.69 (m, 1H), 2.56 (ddt, J = 11.1, 9.3, 7.2 Hz, 1H), 2.53 – 2.47 (m, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.38 – 2.29 (m, 3H), 2.29 – 2.23 (m, 2H), 2.09 (dd, J = 13.1, 11.0 Hz, 1H), 1.94 (dd, J = 13.6, 6.5 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.37 (d, J = 6.5 Hz, 3H), 1.28 – 1.13 (m, 16H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) (1.2 : 1 mixture of two diastereoisomers): δ = 171.93, 171.85, 171.23, 171.16, 143.7, 143.3, 135.1, 133.1, 129.9, 129.8, 129.73, 129.67, 127.9, 127.5, 127.4, 127.3, 61.7, 61.69, 61.66, 61.6, 61.5, 61.4, 61.2, 58.2, 55.2, 52.7, 51.7, 48.3, 41.3, 39.2, 38.9, 38.1, 38.0, 34.6, 21.7, 21.62, 21.60, 17.0, 14.1, 14.09, 14.07, 14.04 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{21}H_{29}NO_6SNa^+$: 446.16078; Found: 446.16005.

7.2.2 Photocatalitical nitrene transfer to organic sulfur compounds

Photocatalitical nitrene transfer to allyl sulfides.

Typical experimental procedure: to a reaction tube equipped with a magnetic stir bar, hydroxylamine **5** (0.4 mmol, 2.0 equiv.) and Fluorescein (5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of allyl sulfide **4** (0.2 mmol, 1.0 equiv) dissolved in 2 mL dry acetonitrile (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was purified by column chromatography.

N-Allyl-*N*-(mesitylthio)-4-methylbenzenesulfonamide (6a)

1H NMR (600 MHz, $CDCl_3$): δ = 7.83 – 7.78 (m, 2H), 7.40 – 7.37 (m, 1H), 7.34 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 5.81 – 5.62 (m, 1H), 5.20 – 5.09 (m, 2H), 4.15 (d, J = 6.4 Hz, 2H), 2.43 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 144.0, 137.0, 136.2, 132.3, 129.6, 128.9, 127.8, 127.4, 126.3, 119.7, 56.9, 21.5 ppm.

The data is in accordance with the literature.¹¹⁸

N-Allyl-4-methyl-*N*-(*p*-tolylthio)benzenesulfonamide (6b)

1H NMR (600 MHz, $CDCl_3$): δ = 7.85 – 7.73 (m, 2H), 7.40 – 7.32 (m, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 5.72 (ddt, J = 16.7, 10.2, 6.4 Hz, 1H), 5.24 – 5.12 (m, 2H), 4.12 (d, J = 6.4 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 143.9, 138.2, 136.3, 133.1, 132.6, 129.6, 129.5, 128.3, 127.8, 119.4, 56.7, 21.5, 21.1 ppm.

The data is in accordance with the literature.¹¹⁸

N-Allyl-*N*-((4-chlorophenyl)thio)-4-methylbenzenesulfonamide (6c)

¹H NMR (600 MHz, CDCl₃) δ = 7.79 (d, J = 8.3 Hz, 2H), 7.39 – 7.22 (m, 6H), 5.77 – 5.62 (m, 1H), 5.27 – 5.09 (m, 2H), 4.13 – 4.10 (d, 2H), 2.44 (s, 3H). ppm

¹³C NMR (151 MHz, CDCl₃) δ = 144.2, 135.9, 135.6, 133.5, 132.1, 129.6, 129.0, 128.0, 127.8, 119.9, 57.0, 29.7, 21.6. ppm

The data is in accordance with the literature.¹¹⁸

***N*-Allyl-*N*-((4-bromophenyl)thio)-4-methylbenzenesulfonamide (6d)**

¹H NMR (600 MHz, CDCl₃): δ = 7.83 (d, J = 8.3 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.32 (d, J = 7.5, 2H), 7.30 – 7.25 (m, 2H), 5.75 – 5.64 (m, 1H), 5.19 – 5.11 (m, 2H), 4.15 – 4.10 (m, 2H), 2.44 (s, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 144.3, 136.5, 135.9, 132.1, 132.0, 129.7, 127.9, 127.8, 121.4, 120.0, 57.0, 21.6 ppm.

HRMS (ESI): m/z : [M+H]⁺ Calcd. for C₁₆H₁₆BrNO₂S₂Na⁺: 419.96980; Found: 419.96980.

***N*-Allyl-4-methyl-*N*-((4-(trifluoromethyl)phenyl)thio)benzenesulfonamide (6e)**

¹H NMR (400 MHz, CDCl₃) δ = 7.79 (d, J = 8.3 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 5.77 – 5.63 (m, 1H), 5.21 – 5.09 (m, 2H), 4.15 (d, J = 6.6 Hz, 2H), 2.42 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃) δ = 144.4, 142.9, 135.7, 131.8, 129.7, 128.7 (q, J = 32.7 Hz), 127.8, 125.8 (q, J = 4.8 Hz), 124.8, 123.9 (q, J = 271.3 Hz), 120.4, 57.1, 21.6 ppm

¹⁹F NMR (376 MHz, CDCl₃): δ = -62.54 ppm.

The data is in accordance with the literature.¹¹⁸

***N*-Allyl-4-methyl-*N*-(*m*-tolylthio)benzenesulfonamide (6f)**

¹H NMR (400 MHz, CDCl₃): δ = 7.79 (d, J = 8.3 Hz, 2H), 7.31 – 7.25 (J = 7.9 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.13 – 7.08 (m, 1H), 7.03 – 6.99 (m, 1H), 5.78 – 5.65 (m, 1H), 5.20 – 5.09 (m, 2H), 4.14 (dt, J = 6.5, 1.3 Hz, 2H), 2.42 (s, 3H), 2.29 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ = 143.9, 138.7, 136.7, 136.3, 132.4, 129.5, 128.7, 128.3, 127.8, 126.8, 123.5, 119.5, 77.3, 77.0, 76.6, 56.8, 21.5, 21.3 ppm

HRMS (ESI): m/z : [M+H]⁺ Calcd. for C₁₇H₁₉NO₂S₂⁺: 333.08517; Found: 333.08512.

***N*-Allyl-*N*-((3-bromophenyl)thio)-4-methylbenzenesulfonamide (6g)**

¹H NMR (600 MHz, CDCl₃): δ = 7.79 (d, J = 8.2 Hz, 2H), 7.39 – 7.24 (m, 5H), 7.16 (t, J = 7.9 Hz, 1H), 5.72 (ddt, J = 16.7, 10.1, 6.5 Hz, 1H), 5.22 – 5.12 (m, 2H), 4.15 (dt, J = 6.6, 1.2 Hz, 2H), 2.44 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ = 144.3, 139.6, 135.8, 132.1, 130.2, 130.1, 129.7, 128.0, 127.8, 124.0, 122.8, 120.0, 56.9, 21.5 ppm

HRMS (ESI): m/z : [M+H]⁺ Calcd. for C₁₆H₁₆BrKNO₂S₂⁺: 435.94374; Found: 435.94374.

***N*-Allyl-*N*-((2-methoxyphenyl)thio)-4-methylbenzenesulfonamide(6h)**

¹H NMR (400 MHz, CDCl₃) δ = 7.81 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 7.3 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.08 (dd, J = 6.8, 1.5 Hz, 2H), 5.78– 5.64 (m, 1H), 5.20 – 5.05 (m, 2H), 4.15 (d, J = 6.5 Hz, 2H), 2.42 (s, 3H), 2.21 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 144.0, 136.2, 132.8, 132.1, 130.1, 129.5, 127.8, 126.6, 126.2, 124.5, 119.6, 56.8, 21.5, 18.7.

The data is in accordance with the literature.¹¹⁷

***N*-Allyl-*N*-((2-methoxyphenyl)thio)-4-methylbenzenesulfonamide (6k)**

¹H NMR (400 MHz, CDCl₃) δ = 7.84 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 7.7 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.19 (t, J = 7.8, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 5.83 – 5.69 (m, 1H), 5.23 – 5.10 (m, 2H), 4.21 (d, J = 6.4 Hz, 2H), 3.85 (s, 3H), 2.45 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃) δ = 154.2, 143.9, 136.3, 132.2, 129.5, 127.8, 127.3, 126.1, 125.1, 121.4, 119.5, 110.2, 56.8, 55.7, 21.5 ppm

HRMS (ESI): *m/z*: [M+H]⁺ Calcd. for C₁₇H₂₀NO₃S₂⁺: 350.08791; Found: 350.08685.

***N*-Allyl-*N*-((2-fluorophenyl)thio)-4-methylbenzenesulfonamide (6l)**

¹H NMR (600 MHz, CDCl₃) δ = 7.80 (d, J = 8.3 Hz, 2H), 7.58 (td, J = 7.6, 1.7 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.14 (td, J = 7.6, 1.4 Hz, 1H), 7.01 (td, J = 8.9, 1.4 Hz, 1H), 5.77 – 5.67 (m, 1H), 5.23 – 5.11 (m, 2H), 4.18 (d, J = 6.5 Hz, 2H), 2.43 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃) δ = 158.5 (d, J = 244.9 Hz), 144.1, 136.0, 132.0, 129.6, 129.2 (d, J = 7.4 Hz), 127.8, 124.7 (d, J = 3.6 Hz), 124.5 (d, J = 16.6 Hz), 119.9, 115.4 (d, J = 21.0 Hz), 57.0, 21.5 ppm

¹⁹F NMR (564 MHz, CDCl₃): δ = -111.87 ppm.

The data is in accordance with the literature.¹¹⁸

***N*-Allyl-*N*-((2-chlorophenyl)thio)-4-methylbenzenesulfonamide (6m)**

¹H NMR (600 MHz, CDCl₃) δ = 7.86 – 7.81 (m, 2H), 7.49 (dd, J = 8.0, 1.5 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.25 (m, 2H), 7.14 – 7.09 (m, 1H), 5.76 – 5.66 (m, 1H), 5.21 – 5.09 (m, 2H), 4.18 (dt, J = 6.5, 1.2 Hz, 2H), 2.44 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃) δ = 144.3, 136.9, 135.8, 131.6, 129.7, 129.3, 127.8, 127.5, 127.3, 126.9, 124.7, 120.3, 57.0, 21.6 ppm

HRMS (ESI): *m/z*: [M+H]⁺ Calcd. for C₁₆H₁₇ClNO₂S₂⁺: 354.03837; Found: 354.03837.

***N*-Allyl-*N*-((2-bromophenyl)thio)-4-methylbenzenesulfonamide (6n)**

¹H NMR (400 MHz, CDCl₃) δ = 7.86 (d, J = 8.5 Hz, 2H), 7.55 – 7.40 (m, 2H), 7.40 – 7.32 (m, 3H), 7.07 (td, J = 7.6, 1.5 Hz, 1H), 5.81 – 5.66 (m, 1H), 5.25 – 5.09 (m, 2H), 4.20 (d, J = 6.6 Hz, 2H), 2.46 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃) δ 144.3, 138.7, 135.9, 132.4, 131.6, 129.7, 127.9, 127.8, 127.1, 124.7, 120.3, 116.1, 57.0, 21.6 ppm

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₆H₁₅BrNO₂S₂Na⁺: 419.96980; Found: 419.96980.

Methyl 2-(((*N*-allyl-4-methylphenyl)sulfonamido)thio)benzoate (6o)

¹H NMR (600 MHz, CDCl₃) δ = 8.03 - 7.99 (m, 1H), 7.86 – 7.80 (m, 3H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.27 – 7.20 (m, 1H), 5.78 – 5.65 (m, 1H), 5.17 – 5.03 (m, 2H), 4.15 (t, *J* = 7.7 Hz, 2H), 3.91 (s, 3H), 2.43 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃) δ = 167.2, 145.1, 144.0, 136.3, 133.3, 131.8, 130.8, 129.6, 127.7, 124.9, 123.8, 123.5, 119.9, 56.5, 52.4, 21.5 ppm

HRMS (ESI): mass found: 400.06517, calculated mass for C₁₈H₁₉NO₄S₂Na⁺: 400.06477.

***N*-Allyl-*N*-(mesitylthio)-4-methylbenzenesulfonamide (6p)**

¹H NMR (400 MHz, CDCl₃) δ = 7.69 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.18 (m, 2H), 6.88 (s, 2H), 5.71 – 5.57 (m, 1H), 5.16 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.07 (dd, *J* = 10.2, 1.4 Hz, 1H), 4.14 (dt, *J* = 6.2, 1.4 Hz, 2H), 2.54 (s, 6H), 2.39 (s, 3H), 2.25 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃) δ 143.5, 142.6, 140.2, 136.5, 133.1, 130.5, 129.3, 129.3, 127.7, 118.5, 56.7, 22.1, 21.5, 21.0.

The data is in accordance with the literature.¹¹⁸

***N*-Allyl-4-methyl-*N*-(thiophen-2-ylthio)benzenesulfonamide (6q)**

¹H NMR (600 MHz, CDCl₃) δ 7.78 – 7.73 (m, 2H), 7.51 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.32 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.31 – 7.26 (m, 2H), 6.98 (dd, *J* = 5.3, 3.6 Hz, 1H), 5.90 – 5.62 (m, 1H), 5.35 – 5.12 (m, 2H), 4.08 (dt, *J* = 6.3, 1.4 Hz, 2H), 2.43 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 143.8, 137.8, 136.5, 133.6, 133.2, 132.8, 129.5, 127.8, 127.4, 119.4, 55.2, 21.5.

The data is in accordance with the literature.¹¹⁸

4-Methyl-*N*-(2-methylallyl)-*N*-(phenylthio)benzenesulfonamide (6r)

¹H NMR (600 MHz, CDCl₃) δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.32 - 7.27 (m, 4H), 7.26 – 7.22 (m, 1H), 4.91 – 4.79 (m, 2H), 4.05 (s, 2H), 2.43 (s, 3H), 1.56 (t, *J* = 1.2 Hz, 3H) ppm

¹³C NMR (101 MHz, CDCl₃) δ = 141.68, 132.39, 129.94, 129.16, 126.24, 125.79, 77.19, 39.07, 21.34.

HRMS (ESI): *m/z*: [M+H]⁺ Calcd. for C₁₇H₁₉NO₂S₂⁺: 333.08517; Found: 333.08527.

Photocatalitical nitrene transfer to sulfides

Typical experimental procedure: To a reaction tube equipped with a magnetic stir bar, hydroxylamine **5** (0.3 mmol, 1.5 equiv.) and Fluorescein (5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of sulfide **7** (0.2 mmol, 1.0 equiv) dissolved in 2 mL dry acetonitrile (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was purified by column chromatography.

4-Methyl-*N*-(methyl(phenyl)- λ 4-sulfaneylidene)benzenesulfonamide (8a)

¹H NMR (400 MHz, CDCl₃) δ = 7.69 (dd, *J* = 17.5, 7.7 Hz, 4H), 7.57 – 7.40 (m, 3H), 7.14 (d, *J* = 7.8 Hz, 2H), 2.82 (s, 3H), 2.33 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃) δ 141.6, 141.2, 136.0, 132.3, 129.9, 129.1, 126.2, 125.7, 77.1, 39.0, 21.3.

The data is in accordance with the literature.¹¹⁸

4-methyl-*N*-(methyl(*p*-tolyl)-λ⁴-sulfaneylidene)benzenesulfonamide(8b)

¹H NMR (400 MHz, CDCl₃) δ = 7.70 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 2.80 (s, 3H), 2.37 (s, 3H), 2.32 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃) δ = 143.3, 141.6, 141.2, 132.6, 130.6, 129.6, 129.1, 126.2, 125.8, 115.0, 39.0, 21.4, 21.3 ppm

HRMS (ESI): *m/z*: [M+H]⁺ Calcd. for C₁₇H₁₈NO₂S₂⁺: 308.07735; Found: 308.07800.

***N*-((4-fluorophenyl)(methyl)-λ⁴-sulfaneylidene)-4-methylbenzenesulfonamide(8c)**

¹H NMR (400 MHz, CDCl₃) δ = 7.74 - 7.63 (m, 4H), 7.21 - 7.10 (m, 4H), 2.82 (s, 3H), 2.33 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃) δ = 164.9 (d, *J* = 254.6 Hz), 141.8, 141.0, 131.5, 129.2, 128.3 (d, *J* = 9.1 Hz), 117.3 (d, *J* = 22.4 Hz), 39.2, 21.3 ppm

¹⁹F NMR (376 MHz, CDCl₃) δ = -105.34 ppm

HRMS (ESI): *m/z*: [M+H]⁺ Calcd. for C₁₄H₁₅NO₂S₂F⁺: 312.05227; Found: 312.05291.

***N*-((4-Bromophenyl)(methyl)-λ⁴-sulfaneylidene)-4-methylbenzenesulfonamide(8d)**

¹H NMR (400 MHz, CDCl₃) δ = 8.06 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.34 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 2.84 (s, 3H), 2.32 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃) δ = 141.8, 141.0, 136.6, 133.5, 133.4, 129.2, 129.1, 127.8, 126.2, 120.0, 38.0, 21.3 ppm

The data is in accordance with the literature.¹¹⁸

***N*-((3-methoxyphenyl)(methyl)-λ⁴-sulfaneylidene)-4-methylbenzenesulfonamide (8e)**

¹H NMR (600 MHz, CDCl₃) δ = 7.70 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 2.2 Hz, 1H), 7.17 – 7.12 (m, 3H), 7.02 – 6.99 (m, 1H), 3.76 (s, 3H), 2.82 (s, 3H), 2.32 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃) δ = 160.6, 141.7, 141.2, 137.1, 130.8, 129.1, 126.2, 118.9, 117.7, 109.9, 55.6, 39.1, 21.3.

HRMS (ESI): *m/z*: [M+K]⁺ Calcd. for C₁₅H₁₇NO₃S₂K⁺: 362.02814; Found: 362.02858.

***N*-((2-Chlorophenyl)(methyl)-λ⁴-sulfaneylidene)-4-methylbenzenesulfonamide (8f)**

Compound **XXX** was prepared according to the general procedure GP-2 and was obtained after column chromatography (*n*-hexane : EtOAc 4:1 → 1:2); 70% (46 mg); colorless oil.

¹H NMR (600 MHz, CDCl₃) δ = 8.12 – 8.08 (m, 1H), 7.78 – 7.73 (m, 2H), 7.50 – 7.41 (m, 3H), 7.19 (d, *J* = 7.7 Hz, 2H), 2.86 (s, 3H), 2.35 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃) δ = 141.9, 140.9, 134.6, 133.3, 131.1, 130.3, 129.3, 128.6, 127.4, 126.2,

37.7, 21.4 ppm

HRMS (ESI): m/z : $[M+K]^+$ Calcd. for $C_{14}H_{14}ClNO_2S_2K^+$: 365,97861; Found: 365.97916.

***N*-((2-bromophenyl)(methyl)- λ^4 -sulfaneylidene)-4-methylbenzenesulfonamide (8g)**

1H NMR (400 MHz, $CDCl_3$) δ = 8.06 (dd, J = 7.8, 1.6 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.44 – 7.34 (m, 1H), 7.16 (d, J = 8.2 Hz, 2H), 2.84 (s, 3H), 2.32 (s, 3H) ppm

^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.8, 141.0, 136.6, 133.5, 133.4, 129.2, 129.1, 127.8, 126.2, 120.0, 38.0, 21.3 ppm

The data is in accordance with the literature.¹¹⁸

Methyl 2-(methyl-*N*-tosylsulfinimidoyl)benzoate (8h)

1H NMR (600 MHz, $CDCl_3$) δ = 8.55 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 7.7 Hz, 1H), 7.82 – 7.76 (m, 3H), 7.62 (t, J = 7.8 Hz, 1H), 7.20 (d, J = 8.1 Hz, 2H), 3.97 (s, 3H), 2.90 (s, 3H), 2.37 (s, 3H) ppm

^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.7, 141.6, 140.3, 134.5, 131.5, 131.1, 129.2, 127.2, 126.6, 126.2, 53.1, 39.9, 21.4 ppm

HRMS (ESI): m/z : $[M+K]^+$ Calcd. for $C_{16}H_{17}NO_4S_2K^+$: 390,02306; Found: 390.02356.

Photocatalitical nitrene transfer to sulfinamides

Typical experimental procedure: to a reaction tube equipped with a magnetic stir bar, sulfinamide **9** (0.2 mmol, 1.0 equiv), hydroxylamine **5a** (0.4 mmol, 2.0 equiv.) and Fluorescein (5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of HFIP (0.2 mmol, 1.0 equiv.) and Diphenyl sulfide (0.02 mmol, 0.1 equiv.) dissolved in 2 mL dry acetone (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was purified by column chromatography.

***N*-(dimethyl(oxo)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (92a)**

1H NMR (400 MHz, DMSO) δ = 7.71 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 3.43 (s, 6H), 2.37 (s, 3H) ppm

^{13}C NMR (101 MHz, DMSO) δ = 142.6, 141.7, 129.7, 126.4, 43.3, 21.3 ppm

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_9H_{13}NO_3S_2Na^+$: 270.02291; Found: 270.02323.

***N*-(amino(oxo)(phenyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10a)**

1H NMR (600 MHz, $DMSO-d_6$): δ = 8.07 (s, 2H), 7.85 – 7.73 (m, 2H), 7.71 – 7.60 (m, 1H), 7.60 – 7.47 (m, 4H), 7.24 (d, J = 8.5 Hz, 2H), 2.33 (s, 3H) ppm.

^{13}C NMR (151 MHz, $DMSO-d_6$): δ = 142.7, 142.3, 141.5, 133.2, 129.4, 129.4, 126.9, 126.43, 21.3 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{13}H_{14}N_2O_3S_2Na^+$: 333.03380; Found: 333.03362.

***N*-(amino(oxo)(phenyl)- λ^6 -sulfaneylidene)benzenesulfonamide (10b)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.12 (s, 2H), 7.78 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.68 – 7.60 (m, 3H), 7.53 (ddd, *J* = 9.1, 8.1, 7.1 Hz, 3H), 7.45 (dd, *J* = 8.4, 7.1 Hz, 2H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 144.1, 142.5, 133.3, 132.2, 129.4, 129.1, 126.9, 126.3 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₂H₁₂N₂O₃S₂Na⁺: 319.01816; Found: 319.01857.

***N*-(amino(oxo)(phenyl)-λ⁶-sulfaneylidene)-4-fluorobenzenesulfonamide (10c)**

¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.14 (s, 2H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.72 – 7.58 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 8.9 Hz, 2H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 164.1 (d, *J* = 249.8 Hz), 142.3, 140.5, 133.4, 129.4, 129.3 (d, *J* = 9.9 Hz), 127.0, 116.1 (d, *J* = 23.0 Hz) ppm.

¹⁹F NMR (564 MHz, DMSO-*d*₆): δ = -107.99 (ddd, *J* = 14.1, 8.9, 5.2 Hz) ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₂H₁₁N₂O₃FS₂Na⁺: 337.00873; Found: 337.00912.

***N*-(amino(oxo)(phenyl)-λ⁶-sulfaneylidene)-4-bromobenzenesulfonamide (10d)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.20 (s, 2H), 7.78 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.68 – 7.62 (m, 3H), 7.61 – 7.50 (m, 4H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 143.3, 142.2, 133.4, 132.1, 129.5, 128.5, 127.0, 125.9 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₂H₁₁N₂O₃BrS₂Na⁺: 396.92867; Found: 396.92933.

***N*-(amino(oxo)(phenyl)-λ⁶-sulfaneylidene)-4-(trifluoromethyl)benzenesulfonamide (10e)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.27 (s, 2H), 7.84 (q, *J* = 8.6 Hz, 4H), 7.77 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.55 – 7.51 (m, 2H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 147.6, 141.9, 133.5, 132.0 (q, *J* = 32.2 Hz), 129.5, 127.4, 127.0, 126.3 (q, *J* = 4.1 Hz), 124.0 (q, *J* = 272.5 Hz), 118.4 ppm.

¹⁹F NMR (564 MHz, DMSO-*d*₆): δ = -61.62 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₅H₁₁N₂O₃F₃S₂Na⁺: 387.00554; Found: 387.00527.

***N*-(amino(oxo)(phenyl)-λ⁶-sulfaneylidene)-3-nitrobenzenesulfonamide (10f)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.40 – 8.35 (m, 1H), 8.32 (s, 3H), 8.22 (t, *J* = 2.0 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.81 – 7.70 (m, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 3H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 147.8, 145.2, 141.5, 133.6, 132.6, 131.4, 129.5, 127.0, 126.9, 121.1 ..

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₂H₁₁N₃O₅S₂Na⁺: 364.00323; Found: 364.00388.

***N*-(amino(oxo)(phenyl)-λ⁶-sulfaneylidene)-3-chlorobenzenesulfonamide (10g)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.24 (s, 2H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.60 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.52 – 7.47 (m, 2H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 145.7, 141.8, 133.6, 133.5, 132.2, 131.3, 129.4, 127.0, 126.0, 125.1 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{12}H_{11}N_2O_3ClS_2Na^+$: 352.97918; Found: 352.97900.

***N*-(amino(oxo)(phenyl)- λ^6 -sulfaneylidene)-3-chloro-2-methylbenzenesulfonamide (10h)**

1H NMR (600 MHz, DMSO- d_6): δ = 8.15 (s, 0H), 7.69 (d, J = 7.6 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.21 (t, J = 8.0 Hz, 0H), 2.56 (s, 1H) ppm.

^{13}C NMR (151 MHz, DMSO- d_6): δ = 144.1, 141.6, 135.6, 134.4, 133.4, 132.9, 129.3, 127.2, 126.8, 126.7, 17.2 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{13}H_{13}N_2O_3ClS_2Na^+$: 366.99483; Found: 366.99465.

***N*-(amino(oxo)(phenyl)- λ^6 -sulfaneylidene)pyridine-3-sulfonamide (10i)**

1H NMR (600 MHz, DMSO- d_6): δ = 8.78 (s, 1H), 8.71 (d, J = 5.2 Hz, 1H), 8.27 (s, 2H), 8.02 – 7.97 (m, 1H), 7.82 – 7.75 (m, 2H), 7.67 – 7.61 (m, 1H), 7.59 – 7.52 (m, 2H), 7.50 (dd, J = 8.0, 4.8 Hz, 1H) ppm.

^{13}C NMR (151 MHz, DMSO- d_6): δ = 152.8, 147.0, 141.9, 140.2, 134.3, 133.6, 129.5, 127.0, 124.3 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{11}H_{11}N_3O_3S_2Na^+$: 320.01340; Found: 320.01226.

***(E)*-*N*-(amino(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-phenylethene-1-sulfonamide (10j)**

1H NMR (600 MHz, DMSO- d_6): δ = 8.14 (s, 2H), 7.92 – 7.85 (m, 2H), 7.62 – 7.52 (m, 5H), 7.41 – 7.36 (m, 3H), 7.10 (s, 2H) ppm.

^{13}C NMR (151 MHz, DMSO- d_6): δ = 142.5, 137.3, 133.3, 130.7, 130.6, 129.4, 129.3, 128.6, 127.0 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{14}H_{14}N_2O_3S_2Na^+$: 345.03377; Found: 345.03268.

***N*-(amino(oxo)(phenyl)- λ^6 -sulfaneylidene)-1-phenylmethanesulfonamide (10k)**

1H NMR (600 MHz, Chloroform- d): δ = 7.97 – 7.87 (m, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 7.45 – 7.38 (m, 2H), 7.35 – 7.28 (m, 3H), 5.29 (s, 2H), 4.41 (s, 2H) ppm.

^{13}C NMR (151 MHz Chloroform- d): δ = 140.5, 133.7, 131.1, 129.3, 129.2, 128.5, 126.8, 62.2 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{13}H_{14}N_2O_3S_2Na^+$: 333.03380; Found: 333.03264.

***N*-(amino(oxo)(phenyl)- λ^6 -sulfaneylidene)methanesulfonamide (10l)**

1H NMR (600 MHz, DMSO- d_6): δ = 8.10 (s, 2H), 7.90 (d, J = 7.1 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.61 (t, J = 7.5 Hz, 2H), 2.94 (s, 3H) ppm.

^{13}C NMR (151 MHz, DMSO- d_6): δ = 143.0, 133.3, 129.5, 126.8, 44.6 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_7H_{10}N_2O_3S_2Na^+$: 257.00250; Found: 257.00227.

***N*-(amino(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10m)**

1H NMR (600 MHz, Chloroform- d): δ = 7.83 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 9.5 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.41 (s, 2H), 2.41 (s, 3H), 2.39 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): δ = 144.7, 142.9, 140.0, 137.4, 129.7, 129.2, 127.1, 126.6, 21.5, 21.5 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{15}H_{18}N_2O_3S_2Na^+$: 361.06511; Found: 361.06456.

***N*-(amino(4-fluorophenyl)(oxo)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10n)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.15 (s, 2H), 7.86 – 7.69 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.38 (t, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 164.7 (d, *J* = 252.3 Hz), 142.4, 141.2, 138.7, 130.1 (d, *J* = 10.3 Hz), 129.5, 126.4, 116.5 (d, *J* = 23.4 Hz), 21.3 ppm.

¹⁹F NMR (564 MHz, DMSO-*d*₆): δ = -106.37 (ddd, *J* = 13.9, 8.8, 5.0 Hz) ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₃H₁₃N₂O₃FS₂Na⁺: 351.02438; Found: 351.02396.

***N*-(amino(4-chlorophenyl)(oxo)-λ⁶-sulfaneylidene)-4-methylbenzenesulfonamide (10o)**

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.90 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.28 – 7.26 (m, 2H), 5.76 (s, 2H), 2.41 (s, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ 143.3, 140.5, 139.6, 138.7, 129.4, 129.3, 128.5, 128.5, 126.6, 21.5 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₃H₁₄N₂O₃ClS₂Na⁺: 345.01289; Found: 345.01303.

***N*-(amino(4-bromophenyl)(oxo)-λ⁶-sulfaneylidene)-4-methylbenzenesulfonamide (10p)**

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.80 (dd, *J* = 11.0, 8.5 Hz, 4H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.23 (m, 3H), 5.81 (s, 2H), 2.41 (s, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 143.3, 139.6, 139.3, 132.4, 129.3, 129.3, 129.0, 128.5, 126.6, 116.3, 21.5 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₃H₁₄N₂O₃BrS₂Na⁺: 388.96237; Found: 388.96241.

***N*-(amino(3-methoxyphenyl)(oxo)-λ⁶-sulfaneylidene)-4-methylbenzenesulfonamide (10q)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.05 (s, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.14 (m, 2H), 3.74 (s, 3H), 2.32 (s, 3H) ppm.

¹³C NMR (600 MHz, DMSO-*d*₆): δ = 159.5, 143.6, 142.3, 141.2, 129.4, 126.4, 119.1, 119.0, 111.9, 56.0, 21.3 ppm.

HRMS (ESI): *m/z*: [M+H]⁺ Calcd. for C₁₄H₁₇N₂O₄S₂⁺: 341.06243; Found: 341.06141.

***N*-(amino(2-methoxyphenyl)(oxo)-λ⁶-sulfaneylidene)-4-methylbenzenesulfonamide (10r)**

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.95 (dt, *J* = 8.0, 1.4 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.57 (td, *J* = 8.0, 7.4, 1.5 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.69 (s, 2H), 3.95 (s, 3H), 2.39 (s, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 156.0, 142.7, 140.3, 135.5, 129.1, 129.0, 128.4, 126.6, 120.7, 112.5, 56.5, 21.5 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₄H₁₆N₂O₄S₂Na⁺: 363.04437; Found: 363.04397.

***N*-(amino(naphthalen-2-yl)(oxo)-λ⁶-sulfaneylidene)-4-methylbenzenesulfonamide (10s)**

¹H NMR (600 MHz, Chloroform-*d*): δ = 8.49 (s, 1H), 7.93 – 7.85 (m, 4H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.62 – 7.58 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.93 (s, 2H), 2.32 (s, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 143.0, 139.7, 136.6, 135.1, 131.7, 129.6, 129.5, 129.4, 129.2, 128.7, 127.8, 127.7, 126.6, 121.8, 21.4 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₇H₁₆N₂O₃S₂Na⁺: 383.04946; Found: 383.04892.

***N*-(amino(benzyl)(oxo)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10t)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 7.64 (d, *J* = 8.2 Hz, 2H), 7.56 (s, 2H), 7.44 – 7.35 (m, 5H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.65 – 4.58 (m, 2H), 2.34 (s, 3H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 142.2, 142.1, 131.9, 129.5, 129.3, 129.0, 128.8, 126.4, 62.3, 21.3 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₄H₁₆N₂O₃S₂Na⁺: 347.04945; Found: 347.04926.

***N*-(amino(oxo)(phenethyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10u)**

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.85 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.20 (m, 5H), 7.16 (d, *J* = 6.9 Hz, 2H), 5.61 (s, 2H), 3.65 – 3.52 (m, 2H), 3.21 – 3.08 (m, 2H), 2.40 (s, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 143.2, 140.0, 136.6, 129.4, 128.9, 128.5, 127.1, 126.5, 58.8, 29.3, 21.5.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₅H₁₈N₂O₃S₂Na⁺: 361.06511; Found: 361.06456.

(*R*)-*N*-(amino(*tert*-butyl)(oxo)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10v)

HPLC (ADH, *n*-hexane/2-propanol = 90/10, flow rate = 0.75 mL/min, λ = 220 nm, temp = rt) *t*_R = 23.1 min (major), 27.9 min (minor), *er* = 99.98:0.02.

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.84 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.46 (s, 2H), 2.39 (s, 3H), 1.43 (s, 9H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 142.8, 140.4, 129.3, 126.4, 62.8, 23.1, 21.5 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₁H₁₈N₂O₃S₂Na⁺: 313.06510; Found: 313.06476.

***N*-((isopropylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10w)**

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.84 – 7.77 (m, 3H), 7.24 (dd, *J* = 23.1, 7.8 Hz, 4H), 5.95 (d, *J* = 6.9 Hz, 1H), 3.48 – 3.38 (m, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 1.20 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 144.5, 142.7, 140.4, 136.1, 129.7, 129.1, 127.8, 126.7, 46.2, 24.0, 22.9, 21.5, 21.5 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₇H₂₂N₂O₃S₂Na⁺: 389.09641; Found: 389.09604.

***N*-((cyclohexylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10x)**

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.87 – 7.74 (m, 4H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.87 (d, *J* = 7.7 Hz, 1H), 3.13 (dtt, *J* = 10.1, 7.0, 3.8 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 1.96 – 1.89 (m, 1H), 1.73 – 1.65 (m, 1H), 1.56 (ddt, *J* = 18.5, 10.8, 5.0 Hz, 2H), 1.50 (t, *J* = 7.5 Hz, 1H), 1.33 (ddd, *J* = 12.8, 10.0, 3.5 Hz, 1H), 1.29 – 1.19 (m, 2H), 1.15 – 1.10 (m, 2H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 144.5, 142.7, 140.3, 136.4, 129.7, 129.1, 127.7, 126.7, 52.6, 34.1, 33.0, 25.0, 24.5, 21.58, 21.53 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{20}H_{26}N_2O_3S_2Na^+$: 429.12771; Found: 429.12712.

***N*-(((benzylamino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide(10y)**

1H NMR (600 MHz, Chloroform-*d*): δ = 7.82 (dd, J = 8.4, 6.4 Hz, 4H), 7.31 – 7.20 (m, 7H), 7.20 – 7.12 (m, 2H), 6.03 (s, 1H), 4.18 (dd, J = 13.8, 4.1 Hz, 1H), 4.07 (dd, J = 13.5, 3.9 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 144.9, 142.8, 140.3, 135.2, 134.8, 129.8, 129.2, 128.7, 128.0, 127.8, 126.7, 46.7, 21.5, 21.5 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{21}H_{22}N_2O_3S_2Na^+$: 437.09641; Found: 437.09663.

4-methyl-*N*-(oxo(phenethylamino)(*p*-tolyl)- λ^6 -sulfaneylidene)benzenesulfonamide (10z)

1H NMR (600 MHz, Chloroform-*d*): δ = 7.80 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.29 – 7.20 (m, 7H), 7.08 (d, J = 6.8 Hz, 2H), 5.67 – 5.57 (m, 1H), 3.26 (dq, J = 13.1, 6.6 Hz, 1H), 3.16 (dq, J = 12.8, 6.7 Hz, 1H), 2.77 (td, J = 7.0, 3.3 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 144.8, 142.8, 140.3, 137.2, 134.8, 129.8, 129.2, 128.78, 128.72, 127.7, 126.9, 126.6, 43.8, 35.4, 21.58, 21.53.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{22}H_{24}N_2O_3S_2Na^+$: 451.11206; Found: 451.11149.

4-methyl-*N*-(oxo(*p*-tolyl)((2,2,2-trifluoroethyl)amino)- λ^6 -sulfaneylidene)benzenesulfonamide (10aa)

1H NMR (600 MHz, Chloroform-*d*): δ = 7.84 (t, J = 8.3 Hz, 4H), 7.31 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 3H), 6.39 (s, 1H), 3.78 – 3.62 (m, 2H), 2.43 (s, 3H), 2.41 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ 145.4, 143.3, 139.8, 134.9, 129.9, 129.3, 127.6, 126.7, 123.3 (q, J = 278.4 Hz), 43.8 (q, J = 35.6 Hz), 21.6, 21.5 ppm.

^{19}F NMR (565 MHz, Chloroform-*d*): δ = -72.04 (t, J = 8.6 Hz) ppm.

HRMS (ESI): m/z : $[M+H]^+$ Calcd. for $C_{16}H_{18}N_2O_3F_3S_2^+$: 407.07054; Found: 407.06920.

***N*-(((cyclopropylmethyl)amino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10ab)**

1H NMR (600 MHz, Chloroform-*d*): δ = 7.82 (dd, J = 14.1, 8.4 Hz, 4H), 7.29 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 5.82 (t, J = 5.8 Hz, 1H), 2.88 (ddd, J = 13.1, 7.0, 6.1 Hz, 1H), 2.75 (ddd, J = 12.9, 7.4, 5.5 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 0.89 (dddd, J = 15.2, 10.4, 5.2, 2.6 Hz, 1H), 0.52 – 0.42 (m, 2H), 0.12 (dddd, J = 13.0, 11.1, 9.4, 4.7, 3.5 Hz, 2H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 144.7, 142.8, 140.4, 135.1, 129.7, 129.1, 127.8, 126.7, 47.9, 21.58, 21.53, 10.4, 3.8, 3.6 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{18}H_{22}N_2O_3S_2Na^+$: 401.09641; Found: 401.09574.

***N*-(((2-methoxyethyl)amino)(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10ac)**

1H NMR (600 MHz, Chloroform-*d*): δ = 7.83 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 5.78 (s, 1H), 3.43 – 3.36 (m, 2H), 3.29 (s, 3H), 3.18 – 3.05 (m, 2H), 2.42 (s, 3H), 2.39 (s, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 144.8, 142.8, 140.4, 135.0, 129.8, 129.1, 127.7, 126.7, 69.9, 58.8, 42.3, 21.5, 21.5 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₇H₂₂N₂O₄S₂Na⁺: 405.09132; Found: 405.09076.

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.39 – 8.35 (m, 1H), 8.32 (s, 2H), 8.22 (s, 1H), 8.07 (dd, J = 8.0, 1.7 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.62 – 7.57 (m, 1H), 7.52 (t, J = 7.7 Hz, 2H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 147.8, 145.2, 141.5, 133.5, 132.6, 131.4, 129.5, 127.0, 126.9, 121.1 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₂H₁₁N₃O₅S₂Na⁺: 364.00323; Found: 364.00388.

***N*-(amino(4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)(oxo)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (10ad)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 7.91 (s, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.40 (dd, J = 8.2, 6.7 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.22 (d, J = 7.9 Hz, 2H), 2.46 (s, 3H), 2.30 (s, 3H) ppm.

¹³C NMR (151 MHz DMSO-*d*₆): δ = 168.1, 161.1, 142.5, 142.1, 141.7, 130.2, 129.4, 129.2, 128.7, 128.6, 127.3, 126.4, 122.0, 114.5, 21.3, 11.8, 2.1 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₂₃H₂₁N₃O₄S₂Na⁺: 490.08657; Found: 490.08605.

***N*-(amino(oxo)(phenyl)- λ^6 -sulfaneylidene)-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfonamide (10ae)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.18 (s, 2H), 7.84 – 7.74 (m, 2H), 7.65 – 7.59 (m, 3H), 7.53 (t, J = 7.9 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.41 (t, J = 7.3 Hz, 2H), 7.32 (d, J = 6.9 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 2.45 (s, 3H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 168.0, 161.0, 143.1, 142.3, 133.6, 133.4, 130.2, 130.1, 129.4, 129.2, 128.8, 128.6, 127.0, 126.8, 114.6, 11.8 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₂₂H₁₉N₃O₄S₂Na⁺: 476.07092; Found: 476.07094.

***N*-(amino(oxo)(phenyl)- λ^6 -sulfaneylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (10af)**

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.23 (s, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.19 – 7.14 (m, 3H), 2.30 (s, 3H) ppm.

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 145.6, 144.0, 142.6 (q, J = 38.0 Hz), 142.3, 141.5, 139.5, 133.5, 129.8, 129.5, 129.1, 127.6, 127.0, 126.2, 125.7, 121.7 (q, J = 268.7 Hz), 106.5, 21.2 ppm.

¹⁹F NMR (564 MHz, DMSO-*d*₆): δ = -60.90 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₂₃H₂₀N₄O₃F₃S₂Na⁺: 521.09234; Found: 521.09251.

4-methyl-*N*-(((methyl(phenyl)- λ^4 -sulfaneylidene)amino)(oxo)(phenyl)- λ^6 -sulfaneylidene)benzenesulfonamide (99)

¹H NMR (600 MHz, Chloroform-*d*) (1 : 1 mixture of two diastereoisomers): δ = 7.86 (dd, J = 8.5, 1.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.75 (dd, J = 8.5, 1.3 Hz, 2H), 7.72 – 7.69 (m, 2H), 7.68 (d, J = 8.2 Hz, 2H),

7.64 – 7.61 (m, 2H), 7.57 – 7.47 (m, 4H), 7.47 – 7.40 (m, 3H), 7.38 – 7.32 (m, 3H), 7.28 – 7.24 (m, 2H), 7.17 (d, $J = 7.8$ Hz, 2H), 7.08 (d, $J = 7.8$ Hz, 2H), 3.04 (s, 3H), 3.01 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 142.6, 142.2, 142.0, 141.6, 141.2, 141.0, 135.5, 134.6, 132.8, 132.7, 132.2, 132.0, 130.12, 130.11, 128.9, 128.7, 128.6, 126.8, 126.7, 126.6, 126.2, 126.1, 126.0, 39.2, 38.5, 21.48, 21.42$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_3\text{S}_3^+$: 433.07088; Found: 433.07088.

N -(((dimethyl(oxo)- λ^6 -sulfaneylidene)amino)(oxo)(phenyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide(100)

^1H NMR (600 MHz, Chloroform- d): $\delta = 7.94$ (d, $J = 8.7$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.9$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 3.60 (s, 3H), 3.35 (s, 3H), 2.37 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 142.3, 142.1, 140.8, 132.9, 129.0, 128.8, 126.56, 126.56, 44.47, 44.40, 21.4$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_4\text{S}_2\text{Na}^+$: 409.03209; Found: 409.03183.

4*N*-((allylamino)(oxo)(phenyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (101)

^1H NMR (600 MHz, Chloroform- d): $\delta = 7.94$ (dd, $J = 8.5, 1.3$ Hz, 2H), 7.83 (d, $J = 8.3$ Hz, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.52 – 7.47 (m, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 6.00 (s, 1H), 5.68 (ddt, $J = 17.0, 10.2, 5.9$ Hz, 1H), 5.22 – 5.15 (m, 1H), 5.10 (dq, $J = 10.2, 1.2$ Hz, 1H), 3.60 (dddt, $J = 51.9, 15.0, 6.1, 1.5$ Hz, 2H), 2.39 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 142.9, 140.2, 138.2, 133.6, 132.0, 129.26, 129.22, 127.7, 126.7, 118.5, 45.1, 21.5$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_3\text{S}_2^+$: 351.08316; Found: 351.08265.

4-methyl- N -(oxo(phenyl)(2-phenylaziridin-1-yl)- λ^6 -sulfaneylidene)benzenesulfonamide (102a)

^1H NMR (600 MHz, Chloroform- d) (1 : 1 mixture of two diastereoisomers): $\delta = 8.01 - 7.95$ (m, 4H), 7.82 (d, $J = 8.3$ Hz, 2H), 7.78 (d, $J = 8.3$ Hz, 2H), 7.65 – 7.60 (m, 2H), 7.50 (dt, $J = 8.5, 7.1$ Hz, 4H), 7.30 – 7.25 (m, 6H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.19 (dt, $J = 7.0, 2.4$ Hz, 4H), 7.14 – 7.11 (m, 2H), 4.02 (dd, $J = 7.3, 4.8$ Hz, 1H), 3.87 (dd, $J = 7.3, 4.8$ Hz, 1H), 3.27 (d, $J = 7.5$ Hz, 1H), 3.14 (d, $J = 7.3$ Hz, 1H), 2.62 (dd, $J = 4.8, 0.8$ Hz, 1H), 2.47 (d, $J = 4.9$ Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 142.8, 142.7, 140.3, 137.6, 137.5, 137.4, 134.2, 133.8, 133.7, 129.29, 129.26, 129.21, 129.1, 128.6, 128.6, 127.8, 126.7, 126.6, 126.5, 43.7, 42.3, 37.9, 36.2, 21.5$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{K}]^+$ Calcd. for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3\text{S}_2\text{K}^+$: 451.05469; Found: 451.05382.

4-(5-methyl-3-phenylisoxazol-4-yl)- N -(oxo(phenyl)(2-phenylaziridin-1-yl)- λ^6 -sulfaneylidene)benzenesulfonamide (102b)

^1H NMR (600 MHz, Chloroform- d) (1 : 1 mixture of two diastereoisomers): $\delta = 8.02$ (dt, $J = 8.6, 1.5$ Hz, 2H), 7.94 (d, $J = 8.5$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 7.68 – 7.63 (m, 2H), 7.53 (q, $J = 8.1$ Hz, 4H), 7.37 (ddd, $J = 7.2, 3.0, 1.6$ Hz, 5H), 7.35 – 7.31 (m, 5H), 7.31 – 7.26 (m, 7H), 7.25 (d, $J = 8.5$ Hz, 3H), 7.23 – 7.20 (m, 3H), 7.15 – 7.12 (m, 3H), 4.08 (dd, $J = 7.4, 4.9$ Hz, 1H), 3.89 (dd, $J = 7.3, 4.8$ Hz, 1H), 3.32 (dd,

$J = 7.4, 0.9$ Hz, 1H), 3.16 (d, $J = 7.3$ Hz, 1H), 2.68 (dd, $J = 4.8, 0.9$ Hz, 1H), 2.52 (d, $J = 4.9$ Hz, 1H), 2.47 (s, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 167.1, 161.0, 142.3, 134.4, 133.6, 129.85, 129.82, 129.6, 129.38, 129.35, 128.8, 128.7, 128.6, 128.4, 127.8, 127.1, 127.0, 126.7, 126.5, 114.6, 43.9, 42.5, 38.0, 36.4, 11.7$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{30}\text{H}_{25}\text{N}_3\text{O}_4\text{S}_2\text{Na}^+$: 578.11787; Found: 578.11820.

Diethyl(3a*R*,6a*S*)-2-(*N*-tosylphenylsulfonimidoyl)hexahydrocyclopenta[*c*]pyrrole-5,5(1*H*)-dicarboxylate (103a)

^1H NMR (600 MHz, Chloroform- d): $\delta = 7.92 - 7.85$ (m, 4H), 7.63 (t, $J = 7.5$ Hz, 1H), 7.56 – 7.50 (m, 2H), 7.25 (d, $J = 7.9$ Hz, 2H), 4.18 – 4.11 (m, 4H), 3.33 (dd, $J = 9.8, 2.8$ Hz, 1H), 3.15 (td, $J = 9.9, 7.1$ Hz, 2H), 3.09 (dd, $J = 9.9, 2.9$ Hz, 1H), 2.82 – 2.68 (m, 2H), 2.56 – 2.47 (m, 2H), 2.39 (s, 3H), 1.98 (dd, $J = 13.4, 8.0$ Hz, 1H), 1.89 (dd, $J = 13.4, 8.0$ Hz, 1H), 1.22 (td, $J = 7.1, 2.5$ Hz, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 171.5, 170.8, 142.7, 140.7, 135.1, 133.7, 129.1, 127.8, 126.8, 62.1, 61.5, 53.7, 53.5, 41.9, 41.7, 39.3, 39.2, 21.5, 14.0$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{26}\text{H}_{32}\text{N}_2\text{O}_7\text{S}_2\text{Na}^+$: 571.15431; Found: 571.15431.

***N*-(((3a*R*,6a*S*)-hexahydrocyclopenta[*c*]pyrrol-2(1*H*)-yl)(oxo)(phenyl)- λ^6 -sulfaneylidene)-4-methylbenzenesulfonamide (103b)**

^1H NMR (600 MHz, Chloroform- d): $\delta = 7.91 - 7.85$ (m, 4H), 7.65 – 7.59 (m, 1H), 7.52 (dd, $J = 8.5, 7.4$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 3.30 (dt, $J = 9.9, 7.8$ Hz, 2H), 3.09 (dd, $J = 9.7, 3.5$ Hz, 1H), 2.96 (dd, $J = 9.8, 3.5$ Hz, 1H), 2.61 (tq, $J = 7.7, 4.4$ Hz, 2H), 2.38 (s, 3H), 1.74 (ddd, $J = 12.8, 7.5, 5.5$ Hz, 2H), 1.63 (dt, $J = 12.1, 6.7$ Hz, 1H), 1.48 (dt, $J = 12.5, 6.5$ Hz, 1H), 1.44 – 1.40 (m, 1H), 1.36 (dq, $J = 10.4, 4.1, 3.1$ Hz, 1H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 142.6, 140.9, 135.3, 133.5, 129.1, 129.0, 127.7, 126.7, 126.6, 54.8, 54.6, 42.6, 42.5, 32.5, 32.4, 29.6, 25.9, 24.2, 21.5$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_3\text{S}_2\text{Na}^+$: 427.11206; Found: 427.11194.

diethyl(3a*R*,6a*S*)-2-(*N*-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonyl)phenylsulfonimidoyl)hexahydrocyclopenta[*c*]pyrrole-5,5(1*H*)-dicarboxylate (103c)

^1H NMR (600 MHz, Chloroform- d): $\delta = 7.98$ (d, $J = 8.4$ Hz, 2H), 7.95 – 7.90 (m, 2H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.9$ Hz, 2H), 7.40 – 7.36 (m, 3H), 7.34 – 7.31 (m, 2H), 7.27 – 7.25 (m, 2H), 4.22 – 4.05 (m, 4H), 3.38 – 3.34 (m, 1H), 3.20 (dt, $J = 9.5, 7.3$ Hz, 2H), 3.13 (dd, $J = 9.9, 2.8$ Hz, 1H), 2.77 (tdd, $J = 11.9, 6.1, 2.0$ Hz, 2H), 2.55 – 2.46 (m, 5H), 2.00 (dd, $J = 13.5, 7.8$ Hz, 1H), 1.89 (dd, $J = 13.4, 7.9$ Hz, 1H), 1.22 (td, $J = 7.1, 4.6$ Hz, 7H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 171.5, 170.8, 167.1, 161.0, 142.6, 135.1, 134.5, 133.8, 129.8, 129.5, 129.3, 128.6, 128.4, 127.8, 127.1, 114.7, 62.0, 61.6, 53.8, 53.5, 41.9, 41.8, 39.3, 39.2, 14.0, 11.7$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{35}\text{H}_{37}\text{N}_3\text{O}_8\text{S}_2\text{Na}^+$: 714.19143; Found: 714.19086.

diethyl(3a*R*,6a*S*)-2-(4-bromo-*N*-((4-bromophenyl)sulfonyl)phenylsulfonimidoyl)hexahydrocyclopenta[*c*]pyrrole-5,5(1*H*)-dicarboxylate (103d)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.83 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 4.23 – 4.09 (m, 4H), 3.30 (dd, *J* = 9.9, 2.7 Hz, 1H), 3.18 – 3.08 (m, 3H), 2.77 (dddd, *J* = 17.9, 10.7, 8.1, 2.7 Hz, 2H), 2.52 (dddd, *J* = 13.4, 11.8, 7.8, 6.4 Hz, 2H), 1.97 (dd, *J* = 13.5, 7.7 Hz, 1H), 1.89 (dd, *J* = 13.5, 7.8 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*) δ = 171.4, 170.8, 142.3, 134.1, 132.6, 131.8, 129.3, 129.2, 128.4, 127.1, 62.0, 61.68, 61.65, 53.8, 53.5, 41.9, 41.8, 39.3, 39.2, 14.0, 13.9 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₅H₂₈N₂O₇S₂Br₂Na⁺: 714.95764; Found: 714.95755.

7.2.3 Photocatalytic *S*-Alkylation of Sulfinamides: access to sulfoximines

Typical experimental procedure: to a reaction tube equipped with a magnetic stir bar, sulfinamide **9** (0.2 mmol, 1.0 equiv) and [Ru(bpy)₃]Cl₂·6H₂O (2.5 mol%) were added. The tube was then sealed, evacuated, and backfilled with argon three times followed by the addition of diazo compound **11** (1.2 mmol, 6.0 equiv.) dissolved in 2 mL anhydrous Acetonitrile (2.0 mL, 0.1 M) via a syringe. The resulting solution was irradiated with a 2 x 40 W blue LED (467 nm) with stirring at a distance of ~1.5 cm with an external cooling fan for 16 h. After completion, the crude mixture was purified by column chromatography on silica gel using n-hexane/ethyl acetate mixtures as eluent, affording the desired products.

ethyl 2-(4-fluoro-*N*-isopropylphenylsulfonimidoyl)acetate (11a)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.97 – 7.92 (m, 2H), 7.24 – 7.17 (m, 2H), 4.13 (s, 2H), 4.13 – 4.06 (m, 2H), 3.56 – 3.47 (m, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.20 – 1.15 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 165.6 (d, *J* = 255.0 Hz), 162.9, 134.7, 132.1 (d, *J* = 9.6 Hz), 116.1 (d, *J* = 22.5 Hz), 62.0, 60.6, 46.7, 26.6, 26.4, 13.8 ppm.

¹⁹F NMR (564 MHz, Chloroform-*d*): δ = -105.04 (ddd, *J* = 13.4, 8.5, 5.1 Hz) ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₃H₁₈NO₃FSNa⁺: 310.08836; Found: 310.08804.

ethyl 2-(4-chloro-*N*-isopropylphenylsulfonimidoyl)acetate (11b)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.87 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 4.13 (s, 2H), 4.13 – 4.06 (m, 2H), 3.55 – 3.45 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.19 – 1.16 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.8, 139.8, 137.4, 130.8, 129.2, 62.0, 60.7, 46.7, 26.6, 26.4, 13.8 ppm.

HRMS (ESI): *m/z*: [M-CH₃]⁺ Calcd. for C₁₂H₁₅NO₃ClS⁺: 288.04612; Found: 288.04577.

ethyl 2-(4-bromo-*N*-isopropylphenylsulfonimidoyl)acetate (11c)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.82 – 7.78 (m, 2H), 7.69 – 7.65 (m, 2H), 4.13 (s, 2H), 4.12 – 4.08 (m, 2H), 3.54 – 3.45 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.20 – 1.16 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.8, 138.0, 132.2, 130.9, 128.4, 62.0, 60.6, 46.8, 26.6, 26.4, 13.9 ppm.

HRMS (ESI): m/z : [M+H]⁺ Calcd. for C₁₃H₁₉NO₃BrS⁺: 348.02635; Found: 348.02515.

ethyl 2-(N-isopropyl-4-methoxyphenylsulfonimidoyl)acetate (11d)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.84 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 4.11 (s, 2H), 4.12 – 4.05 (m, 2H), 3.86 (s, 3H), 3.50 (h, J = 6.3 Hz, 1H), 1.20 (d, J = 6.3 Hz, 3H), 1.19 – 1.14 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 163.4, 163.2, 131.4, 130.0, 114.1, 61.8, 60.8, 55.6, 46.6, 26.7, 26.5, 13.9 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₄H₂₁NO₄SN⁺: 322.10835; Found: 322.10804.

ethyl 2-(N-isopropyl-4-(trifluoromethyl)phenylsulfonimidoyl)acetate (11e)

¹H NMR (600 MHz, Chloroform-*d*): δ = 8.09 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 4.17 (s, 2H), 4.14 – 4.06 (m, 2H), 3.55 – 3.48 (m, 1H), 1.23 (d, J = 6.2 Hz, 3H), 1.20 – 1.15 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.7, 142.8, 134.8 (q, J = 32.9 Hz), 129.9, 126.0 (q, J = 3.7 Hz), 123.2 (q, J = 273.4 Hz), 62.1, 60.6, 46.9, 26.6, 26.4, 13.8 ppm.

¹⁹F NMR (564 MHz, Chloroform-*d*): δ = -63.11 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₄H₁₈NO₃F₃SN⁺: 360.08517; Found: 360.08484.

ethyl 2-(N-isopropyl-4-nitrophenylsulfonimidoyl)acetate (11f)

¹H NMR (600 MHz, Chloroform-*d*): δ = 8.38 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 4.19 (s, 2H), 4.16 – 4.09 (m, 2H), 3.57 – 3.49 (m, 1H), 1.24 (d, J = 6.3 Hz, 3H), 1.22 – 1.17 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.5, 150.5, 145.1, 130.7, 124.0, 62.2, 60.6, 47.0, 26.5, 26.3, 13.9 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₃H₁₈N₂O₅SN⁺: 337.08286; Found: 337.08329.

ethyl 2-(N-isopropyl-3-methylphenylsulfonimidoyl)acetate (11g)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.76 – 7.71 (m, 2H), 7.43 – 7.39 (m, 2H), 4.13 (s, 2H), 4.12 – 4.05 (m, 2H), 3.57 – 3.49 (m, 1H), 2.43 (s, 3H), 1.23 (d, J = 6.3 Hz, 3H), 1.19 (d, J = 6.3 Hz, 3H), 1.15 (t, J = 7.2 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 163.0, 139.1, 138.7, 133.9, 129.5, 128.8, 126.3, 61.8, 60.6, 46.7, 26.6, 26.5, 21.3, 13.8 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₄H₂₁NO₃SN⁺: 306.11344; Found: 306.11244.

ethyl 2-(3-fluoro-N-isopropylphenylsulfonimidoyl)acetate (11h)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.75 – 7.73 (m, 1H), 7.67 – 7.65 (m, 1H), 7.51 – 7.55 (m, 1H), 7.33 – 7.31 (m, 1H), 4.15 (s, 2H), 4.14 – 4.07 (m, 2H), 3.56 – 3.48 (m, 1H), 1.23 (d, J = 6.3 Hz, 3H), 1.20 – 1.16 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.7, 162.4 (d, J = 251.3 Hz), 141.3 (d, J = 6.4 Hz), 130.6 (d, J = 7.6 Hz), 124.9 (d, J = 3.4 Hz), 120.3 (d, J = 21.3 Hz), 116.7 (d, J = 24.2 Hz), 62.0, 60.7, 46.8, 26.6, 26.4, 13.8 ppm.

¹⁹F NMR (564 MHz, Chloroform-*d*): δ = -109.95 (td, J = 8.2, 5.3 Hz) ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₃H₁₈NO₃SFNa⁺: 310.08836; Found: 310.08752.

ethyl 2-(3-chloro-N-isopropylphenylsulfonimidoyl)acetate (11i)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.94 (t, J = 1.9 Hz, 1H), 7.83 (dt, J = 7.9, 1.4 Hz, 1H), 7.59 – 7.58 (m, 1H), 7.50 – 7.47 (m, 1H), 4.14 (s, 2H), 4.14 – 4.06 (m, 2H), 3.56 – 3.48 (m, 1H), 1.23 (d, J = 6.3 Hz, 3H), 1.21 – 1.15 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.7, 140.8, 135.2, 133.2, 130.1, 129.4, 127.3, 62.1, 60.7, 46.8, 26.6, 26.4, 13.8 ppm.

HRMS (ESI): m/z : [M+H]⁺ Calcd. for C₁₃H₁₉NO₃ClS⁺: 304.07687; Found: 304.07623.

ethyl 2-(N-isopropyl-3-methoxyphenylsulfonimidoyl)acetate (11j)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.52 – 7.50 (m, 1H), 7.46 – 7.41 (m, 2H), 7.14 – 7.12 (m, 1H), 4.13 (s, 2H), 4.13 – 4.04 (m, 2H), 3.86 (s, 3H), 3.56 – 3.46 (m, 1H), 1.22 (d, J = 6.3 Hz, 3H), 1.20 – 1.15 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.9, 159.9, 140.2, 129.9, 121.3, 119.5, 113.8, 61.9, 60.8, 55.6, 46.7, 26.7, 26.4, 13.8 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₄H₂₁NO₄SN⁺: 322.10835; Found: 322.10701.

ethyl (E)-2-(N-isopropyl-2-phenylvinylsulfonimidoyl)acetate (11m)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.56 (d, J = 15.5 Hz, 1H), 7.53 (dd, J = 7.4, 2.1 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.01 (d, J = 15.4 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 4.18 – 4.07 (m, 2H), 3.68 – 3.60 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 6.0 Hz, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 163.5, 159.0, 144.4, 132.6, 130.9, 129.0, 128.5, 125.6, 62.0, 59.5, 46.5, 41.9, 26.7, 26.5, 22.3, 14.0 ppm.

HRMS (ESI): m/z : [M+H]⁺ Calcd. for C₁₅H₂₂NO₃S⁺: 296.13149; Found: 296.13078.

ethyl 2-(N-isopropylthiophene-2-sulfonimidoyl)acetate (11n)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.70 (dd, J = 5.0, 1.2 Hz, 1H), 7.61 (dd, J = 3.8, 1.3 Hz, 1H), 7.17 – 7.12 (m, 1H), 4.26 – 4.19 (m, 2H), 4.19 – 4.10 (m, 2H), 3.60 – 3.51 (m, 1H), 1.25 – 1.20 (m, 6H), 1.17 (d, J = 6.3 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.7, 140.4, 134.7, 134.3, 127.8, 62.6, 62.1, 47.0, 26.7, 26.2, 13.9 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₁H₁₇NO₃S₂Na⁺: 398.05421; Found: 298.05351.

ethyl 2-(N-isopropyl-4-(5-methyl-3-phenylisoxazol-4-yl)phenylsulfonimidoyl)acetate (11o)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.95 (d, J = 8.4 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.35 – 7.31 (m, 4H), 4.18 (s, 2H), 4.12 – 4.08 (m, 2H), 3.64 – 3.57 (m, 1H), 2.49 (s, 3H), 1.25 (d, J = 6.3 Hz, 3H), 1.22 (d, J = 6.3 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 163.0, 161.1, 138.1, 135.7, 130.1, 129.6, 129.6, 128.6, 128.4, 114.5, 61.9, 60.3, 46.8, 26.6, 26.5, 13.9, 11.7 ppm.

HRMS (ESI): m/z : [M+H]⁺ Calcd. for C₂₃H₂₇N₂O₄S⁺: 427.16860; Found: 427.16816.

ethyl 2-(N-isopropyl-4-methylphenylsulfonimidoyl)acetate (12p)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.81 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.13 (s, 2H), 4.12 – 4.05 (m, 2H), 3.55 – 3.45 (m, 1H), 2.43 (s, 3H), 1.22 (d, J = 6.3 Hz, 3H), 1.19 – 1.15 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 163.1, 144.0, 135.7, 129.6, 129.3, 61.9, 60.7, 46.6, 26.7, 26.4, 21.5, 13.8 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₄H₂₁NO₃SNa⁺: 306.11344; Found: 306.11287.

ethyl 2-(4-methyl-N-(2,2,2-trifluoroethyl)phenylsulfonimidoyl)acetate (12q)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.81 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 7.7 Hz, 2H), 4.18 (s, 2H), 4.18 – 4.09 (m, 2H), 3.59 – 3.66 (m, 1H), 3.47 – 3.53 (m, 1H), 2.46 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.4, 145.0, 133.9, 130.0, 129.3, 125.18 (q, J = 278.0 Hz), 62.3, 61.2, 45.18 (q, J = 34.0 Hz), 44.8, 21.6, 13.8 ppm.

¹⁹F NMR (564 MHz, Chloroform-*d*): δ = -72.57 (t, J = 9.2 Hz) ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₃H₁₆NO₃F₃SNa⁺: 346.06952; Found: 346.06899.

ethyl 2-(N-(cyclopropylmethyl)-4-methylphenylsulfonimidoyl)acetate (12r)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.81 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.17 – 4.13 (m, 2H), 4.13 – 4.06 (m, 2H), 3.02 – 2.91 (m, 2H), 2.43 (s, 3H), 1.17 (t, J = 7.1 Hz, 2H), 1.05 – 1.03 (m, 1H), 0.48 – 0.44 (m, 2H), 0.23 – 0.12 (m, 2H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 163.0, 144.1, 135.3, 129.7, 129.3, 61.9, 60.8, 48.7, 21.5, 13.8, 13.3, 3.8, 3.7 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₅H₂₁NO₃SNa⁺: 318.11344; Found: 318.11315.

ethyl 2-(N-cyclohexyl-4-methylphenylsulfonimidoyl)acetate (12s)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.81 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.13 – 4.10 (m, 2H), 4.10 – 4.05 (m, 2H), 3.18 – 3.09 (m, 1H), 2.43 (s, 3H), 1.89 – 1.78 (m, 2H), 1.74 – 1.65 (m, 2H), 1.55 – 1.48 (m, 1H), 1.48 – 1.34 (m, 2H), 1.28 – 1.18 (m, 3H), 1.16 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 163.1, 143.9, 136.0, 129.6, 129.3, 61.8, 60.9, 54.2, 37.0, 36.7, 25.6, 25.2, 25.1, 21.5, 13.8 ppm.

HRMS (ESI): m/z : [M+Na]⁺ Calcd. for C₁₇H₂₅NO₃SNa⁺: 346.14474; Found: 346.14452.

ethyl 2-(N-benzyl-4-methylphenylsulfonimidoyl)acetate (12t)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.85 (d, J = 8.3 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 4.37 – 4.22 (m, 2H), 4.18 (s, 2H), 4.10 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.9, 144.3, 141.0, 134.9, 129.8, 129.3, 128.2, 127.3, 126.5, 62.0, 60.9, 47.0, 21.6, 13.8 ppm.

HRMS (ESI): m/z : $[M+K]^+$ Calcd. for $C_{18}H_{21}NO_3SK^+$: 370.08737; Found: 370.08739.

ethyl 2-(4-methyl-N-phenethylphenylsulfonimidoyl)acetate (12u)

1H NMR (600 MHz, Chloroform- d): δ = 7.70 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.21 (d, J = 6.6 Hz, 2H), 7.22 – 7.19 (m, 1H), 4.12 – 3.99 (m, 4H), 3.37 – 3.22 (m, 2H), 2.94 – 2.88 (m, 2H), 2.43 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): δ = 162.9, 144.1, 140.3, 134.9, 129.7, 129.3, 129.0, 128.2, 126.0, 61.9, 60.5, 45.6, 39.3, 21.5, 13.8 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{19}H_{23}NO_3SNa^+$: 368.12909; Found: 368.12959.

ethyl 2-(4-methyl-N-(2-(pyridin-2-yl)ethyl)phenylsulfonimidoyl)acetate (12v)

1H NMR (600 MHz, Chloroform- d): δ = 8.51 (d, J = 4.5 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.60 – 7.57 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.24 (s, 1H), 7.12 – 7.10 (m, 1H), 4.13 – 3.99 (m, 4H), 3.54 – 3.41 (m, 2H), 3.08 (td, J = 7.1, 1.6 Hz, 2H), 2.42 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): δ = 162.9, 160.3, 149.1, 144.2, 136.0, 129.7, 129.3, 123.8, 121.1, 64.6, 61.9, 60.5, 43.8, 41.3, 21.5, 13.8 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{18}H_{22}N_2O_3SNa^+$: 369.12433; Found: 369.12482.

ethyl 2-(N-(2-methoxyethyl)-4-methylphenylsulfonimidoyl)acetate (12w)

1H NMR (600 MHz, Chloroform- d): δ = 7.82 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.20 – 4.13 (m, 2H), 4.13 – 4.07 (m, 2H), 3.54 – 3.51 (m, 2H), 3.36 (s, 3H), 3.33 – 3.20 (m, 2H), 2.43 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): δ = 163.0, 144.2, 134.9, 129.7, 129.3, 74.0, 61.9, 60.7, 58.8, 43.4, 21.5, 13.8 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{14}H_{21}NO_4SNa^+$: 322.10835; Found: 322.10809.

Ethyl 2-(N-(2-((tert-butoxycarbonyl)amino)ethyl)-4-methylphenylsulfonimidoyl) acetate (12x)

1H NMR (600 MHz, Chloroform- d): δ = 7.79 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 5.16 (s, 1H), 4.16 – 4.07 (m, 4H), 3.28 (t, J = 5.7 Hz, 2H), 3.17 (t, J = 5.6 Hz, 2H), 2.44 (s, 3H), 1.43 (s, 9H), 1.17 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): δ = 162.8, 156.0, 144.5, 134.6, 129.8, 129.2, 62.0, 60.6, 43.8, 42.4, 28.4, 21.5, 13.8 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{18}H_{28}N_2O_5SNa^+$: 407.16111; Found: 407.16055.

Ethyl 3-(((2-ethoxy-2-oxoethyl)(oxo)(p-tolyl)- λ^6 -sulfaneylidene)amino)propanoate (12y)

1H NMR (600 MHz, Chloroform- d): δ = 7.79 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 4.17 – 4.05 (m, 6H), 3.43 – 3.31 (m, 2H), 2.60 – 2.57 (m, 2H), 2.43 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): δ = 172.3, 162.9, 144.3, 134.9, 129.7, 129.3, 61.9, 60.4, 60.2, 39.6, 37.6, 21.5, 14.2, 13.8 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{16}H_{23}NO_5SNa^+$: 364.11891; Found: 364.11777.

ethyl 2-(4-methyl-N-(2-((p-tolylsulfinyl)amino)ethyl)phenylsulfonimidoyl)acetate (12z)

¹H NMR (600 MHz, Chloroform-*d*) (1 : 1 mixture of two diastereoisomers): δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 8.1, 5.2 Hz, 4H), 7.30 – 7.26 (m, 3H), 5.00 (t, *J* = 5.9 Hz, 2H), 4.23 – 4.10 (m, 2H), 4.10 – 4.02 (m, 2H), 3.31 – 3.16 (m, 3H), 2.99 – 2.82 (m, 1H), 2.44 (d, *J* = 3.4 Hz, 6H), 2.40 (s, 3H), 2.39 (s, 3H), 1.16 – 1.12 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 144.5, 140.9, 129.87, 129.83, 129.49, 129.46, 129.3, 129.2, 126.1, 126.1, 62.1, 62.0, 60.3, 60.1, 44.8, 44.5, 42.9, 42.4, 21.6, 21.3, 13.8 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₀H₂₆N₂O₄S₂Na⁺: 445.12262; Found: 445.12232.

benzhydryl(isopropylimino)(phenyl)- λ^6 -sulfanone (12aa)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.49 (d, *J* = 7.1 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 7.24 – 7.17 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.1 Hz, 2H), 5.78 (s, 1H), 3.80 – 3.68 (m, 1H), 2.31 (s, 3H), 1.26 – 1.22 (m, 3H), 1.09 (d, *J* = 6.6 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 141.8, 141.0, 140.5, 140.4, 129.9, 129.1, 128.6, 128.1, 128.0, 127.2, 126.9, 126.1, 62.3, 48.8, 29.6, 23.3, 21.2 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₃H₂₅NOSNa⁺: 386.15491; Found: 386.15393.

methyl 2-(N-isopropyl-4-methylphenylsulfonimidoyl)-2-phenylacetate (12ab)

¹H NMR (600 MHz, Chloroform-*d*) (1 : 1 mixture of two diastereoisomers): δ = 7.44 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.27 – 7.22 (m, 4H), 7.22 – 7.15 (m, 6H), 7.15 – 7.11 (m, 2H), 5.25 (s, 2H), 3.80 (s, 3H), 3.73 (s, 3H), 3.67 – 3.61 (m, 1H), 3.58 – 3.52 (m, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 1.22 – 1.17 (m, 9H), 1.16 (d, *J* = 6.3 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 143.8, 143.7, 130.9, 130.4, 130.3, 129.0, 129.0, 128.9, 128.7, 128.0, 128.0, 75.5, 74.4, 52.8, 52.6, 46.9, 46.6, 26.7, 26.6, 26.6, 26.4, 21.5, 21.5 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₁₉H₂₃NO₃SN⁺: 368.12909; Found: 368.12789.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-(N-isopropyl-4-methylphenylsulfonimidoyl)acetate (12ac)

¹H NMR (600 MHz, Chloroform-*d*) (1 : 1 mixture of two diastereoisomers): δ = 7.80 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.66 – 4.53 (m, 1H), 4.16 – 4.03 (m, 2H), 3.52 – 3.38 (m, 1H), 2.43 (s, 3H), 1.87 – 1.85 (m, 1H), 1.77 – 1.79 (m, 1H), 1.65 – 1.62 (m, 2H), 1.41 – 1.39 (m, 1H), 1.34 – 1.23 (m, 3H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.02 – 0.94 (m, 1H), 0.87 (dd, *J* = 6.6, 2.3 Hz, 3H), 0.83 (dd, *J* = 7.1, 1.9 Hz, 3H), 0.67 (dd, *J* = 7.0, 1.9 Hz, 3H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 162.6, 143.9, 129.6, 129.4, 76.2, 60.96, 60.91, 46.6, 46.56, 46.53, 34.04, 34.01, 31.3, 31.2, 29.6, 26.78, 26.76, 26.4, 25.69, 25.67, 23.08, 23.06, 21.9, 21.5, 20.7, 16.0 ppm.

HRMS (ESI): *m/z*: [M+Na]⁺ Calcd. for C₂₂H₃₅NO₃SN⁺: 416.22299; Found: 416.22134.

(2R)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(N-isopropyl-4-methylphenylsulfonimidoyl)acetate (12ad)

¹H NMR (600 MHz, Chloroform-*d*) (1 : 1 mixture of two diastereoisomers): δ = 7.82 (d, *J* = 7.0 Hz, 2H), 7.33 (d, *J* = 6.8 Hz, 2H), 4.82 – 4.78 (m, 1H), 4.19 – 4.13 (m, 2H), 3.52 – 3.42 (m, 1H), 2.43 (s, 3H), 2.27

– 2.24 (m, 1H), 1.78 – 1.65 (m, 4H), 1.22 (dd, $J = 6.3, 1.0$ Hz, 3H), 1.16 (dd, $J = 6.3, 2.3$ Hz, 3H), 0.89 – 0.86 (m, 2H), 0.84 (dd, $J = 4.9, 2.2$ Hz, 6H), 0.75 (d, $J = 7.0$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 163.4, 163.3, 143.9, 135.99, 135.91, 129.77, 129.75, 129.2, 82.0, 60.98, 60.94, 48.7, 47.85, 47.82, 46.6, 44.6, 36.2, 36.1, 27.8, 27.7, 26.88, 26.86, 26.81, 26.49, 26.47, 21.5, 19.66, 19.62, 18.8, 18.7, 13.38, 13.31$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{22}\text{H}_{34}\text{NO}_3\text{S}^+$: 392.22539; Found: 392.22443.

***N*-isopropyl-4-methylbenzenesulfinamide (9d)**

^1H NMR (600 MHz, Chloroform- d): $\delta = 7.58$ (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 7.9$ Hz, 2H), 3.82 (d, $J = 6.4$ Hz, 1H), 3.63 – 3.55 (m, $J = 6.4$ Hz, 1H), 2.40 (s, 3H), 1.28 (d, $J = 6.4$ Hz, 3H), 1.14 (d, $J = 6.6$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 142.2, 141.1, 129.4, 125.7, 46.0, 24.8, 24.4, 21.3$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{10}\text{H}_{16}\text{NOS}^+$: 198.09471; Found: 198.09481.

ethyl 2,2-dichloro-2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)acetate (126)

^1H NMR (600 MHz, Chloroform- d): $\delta = 7.89$ (d, $J = 8.4$ Hz, 2H), 7.32 – 7.27 (m, 2H), 4.31 – 4.18 (m, 2H), 2.43 (s, 3H), 1.31 (d, $J = 6.3$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.25 (d, $J = 6.3$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 162.9, 144.9, 131.6, 130.7, 129.0, 64.7, 47.3, 26.6, 25.6, 21.6, 13.6$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{SCl}_2\text{Na}^+$: 374.03549; Found: 374.03563.

8-hydroxy-3-(*N*-isopropyl-4-methylphenylsulfonimidoyl)-2H-chromen-2-one (128)

^1H NMR (600 MHz, DMSO- d_6): $\delta = 10.39$ (s, 1H), 8.96 (s, 1H), 7.96 – 7.82 (m, 2H), 7.44 (d, $J = 7.4$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.26 – 7.17 (m, 2H), 3.40 – 3.35 (m, 1H), 2.36 (s, 3H), 1.13 (d, $J = 6.2$ Hz, 3H), 1.08 (d, $J = 6.3$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, DMSO- d_6): $\delta = 155.0, 150.6, 144.9, 143.9, 143.8, 135.9, 129.7, 129.6, 126.9, 125.5, 121.3, 121.0, 119.1, 46.5, 27.4, 26.6, 21.4$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_4\text{SNa}^+$: 380.09270; Found: 380.09298.

ethyl 2-(*N*-isopropyl-4-methylphenylsulfonimidoyl)-3-phenylpropanoate (130)

^1H NMR (600 MHz, Chloroform- d): $\delta = 7.80$ (t, $J = 8.7$ Hz, 4H), 7.37 – 7.32 (m, 4H), 7.23 – 7.21 (m, 4H), 7.20 – 7.15 (m, 2H), 7.12 – 7.09 (m, 2H), 7.08 – 7.03 (m, 2H), 4.33 (dd, $J = 12.3, 3.3$ Hz, 1H), 4.28 (dd, $J = 12.2, 3.2$ Hz, 1H), 4.08 (q, $J = 7.1$ Hz, 2H), 3.99 – 3.91 (m, 2H), 3.60 – 3.50 (m, 2H), 3.39 (dd, $J = 13.5, 3.3$ Hz, 1H), 3.21 (dd, $J = 13.6, 3.3$ Hz, 1H), 3.05 (dd, $J = 13.6, 12.3$ Hz, 1H), 2.94 (t, $J = 12.9$ Hz, 1H), 2.45 (s, 6H), 1.26 (d, $J = 6.4$ Hz, 3H), 1.22 (dd, $J = 6.3, 2.7$ Hz, 6H), 1.17 (d, $J = 6.3$ Hz, 3H), 1.10 (t, $J = 7.1$ Hz, 3H), 1.02 (t, $J = 7.1$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform- d): $\delta = 166.3, 144.0, 130.6, 130.2, 129.5, 129.4, 128.8, 128.7, 128.6, 128.5, 126.95, 126.91, 71.8, 71.0, 61.7, 61.5, 46.6, 46.3, 34.2, 33.4, 26.89, 26.83, 26.6, 26.5, 21.5, 13.9, 13.7$ ppm.

HRMS (ESI): m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{21}\text{H}_{27}\text{NO}_3\text{SNa}^+$: 396.16039; Found: 396.16065.

ethyl 2-(*N*-isopropyl-4-(phenylamino)phenylsulfonimidoyl)acetate (132)

¹H NMR (600 MHz, Chloroform-*d*): δ = 7.74 (d, J = 8.8 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.18 – 7.17 (m, 2H), 7.08 – 7.11 (m, 1H), 7.03 (d, J = 8.8 Hz, 2H), 6.16 (s, 1H), 4.17 – 4.05 (m, 4H), 3.56 – 3.48 (m, 1H), 1.22 (d, J = 6.3 Hz, 3H), 1.21 – 1.18 (m, 6H) ppm.

¹³C NMR (151 MHz, Chloroform-*d*): δ = 163.3, 148.5, 140.2, 131.3, 129.5, 127.6, 123.7, 121.0, 114.5, 61.8, 60.8, 46.5, 26.7, 26.5, 13.9 ppm.

HRMS (ESI): m/z : $[M+Na]^+$ Calcd. for $C_{19}H_{24}N_2O_3SNa^+$: 383.13998; Found: 383.13980.

7. Abbreviations

AgTp	Silver scorpionate
Ar	Aryl
aq.	Aqueous
Bn	Benzyl
Bu	Butyl
2,2'-bpy	2,2'-Bipyridine
cat.	Catalyst
Cy	Cyclohexyl
4CzIPN	1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene
CuTC	Copper(I) thiophene-2-carboxylate hydrate
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DFT	Density Functional Theory
DMA	<i>N,N</i> -Dimethylacetamide
DMAP	Dimethylaminopyridine
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
dppb	1,4-Bis(diphenylphosphino)butane
dtbbpy	4,4'-Di-tert.-butyl-2,2'-dipyridyl
d.r	Diastereoselective ratio
EDG	Electron-donating group
Ee	Enantioselective excess
eq.	Equivalent
Et	Ethyl
EDA	Ethyl diazoacetate
EtOAc	Ethyl acetate
EWG	Electron-withdrawing group
FeTPPCI	5,10,15,20-Tetraphenyl-21H, 23H-prophine iron(III) chloride
GC	Gas chromatography
hfacac	Hexafluoroacetylacetonate
HFIP	Hexafluoroisopropanol
iPr	<i>iso</i> -Propyl
LED	Light emitting diode
Me	Methyl
MeCN	Acetonitrile
MS	Mass spectrometry
Mw	Micro wave
n.d	Not detected
n.r	No reaction
NMR	Nuclear Magnetic Resonance
Nu	Nucleophile
PC	Phthalocyanine
PG	Protecting Group
Piv	Pivaloyl
PTSA	<i>p</i> -Toluenesulfonic acid
PCET	Proton-coupled electron transfer
P(nBu)Ad ₂	Di-(1-adamantyl)- <i>n</i> -butylphosphine
rac	Racemic
Rh ₂ (piv) ₄	Rhodium (II) pivalate
Rh ₂ (oct) ₄	Rhodium(II) octanoate dimer
Rh ₂ esp ₂	Bis[rhodium($\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-benzenedipropionic acid)]

Rh ₂ (OAc) ₄	Rhodium (II) acetate
Rh ₂ (TFA) ₄	Rhodium (II) trifluoroacetate
rt	Room temperature
SET	Single electron transfer
<i>t</i> Bu	<i>tert.</i> Butyl
TEMPO	2,2,6,6-Tetramethyl-piperidine- <i>N</i> -oxide
TFA	Trifluoroacetic acid
TFE	Trifluoroethanol
THF	Tetrahydrofuran
TM	Transition metal
TPP	Tetraphenylporphyrin
TTP	Tetraphenylporphyrin
UV	Ultraviolet
Vis	Visible

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