Photocatalyzed Generation and Application of Sulfoximidoyl Radicals

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I. Introduction

1. General introduction of sulfoximines

An interesting compound called sulfoximine 1 (MSO, methionine sulfoximine) was first unearthed in 1949 by Bentley and co-workers. They isolated compound 1 from a toxic mixture, which was generated by reacting NCl₃ with methionine (2) (Figure 1).[1] Since then, this new family of sulfur compounds has attracted growing interest among chemists. Over the past decades, sulfoximines have found numerous applications in organic synthesis, medicinal chemistry, biochemistry and agricultural chemistry.[2]

Figure 1: MSO (1), the first reported sulfoximine

The special chemical properties of sulfoximines are shown in Figure 2. Structurally, sulfoximines have a sulfur(VI)-centered core, which make them closely related to sulfones and sulfonic acid amides, therefore, they are also understood as mono–aza analogues of sulfones.[2b,d,g,3] The sulfoximine skeleton possesses several interesting features, which allow different reaction pathways for further applications: (a) an asymmetric sulfur center (R¹ ≠ CHR²R³); (b) a nucleophilic and basic nitrogen atom; and (c) the presence of an acidic hydrogen atom. Other properties also make them attractive, such as stability in air and water, and insensitively to base and acid.[4]

Figure 2: Chemical properties of sulfoximines
2. Photocatalytic reactions

The photophysics and photochemistry of transition metal coordination compounds have been studied for over half a century. In the past two decades, visible light photocatalysis has emerged as a powerful method to facilitate activation of organic molecules and engineer new chemical processes selectively.\[^5\] For instance, the classic Hofmann-Löffler-Freytag (HLF)\[^6\] reaction has been used for the functionalization of non-activated skeletal positions to construct pyrrolidines and related heterocyclic compounds (Scheme 1).

![Scheme 1: Hofmann-Löffler-Freytag (HLF) reaction](image)

Alternatively, by using visible light-mediated catalysts as initiators, the atom transfer radical addition (ATRA)\[^7\] protocol can be performed under mild reaction conditions, with minimal side reactions, optimal catalytic efficiency and straightforward purification (Scheme 2).

![Scheme 2: Generic atom transfer radical addition (ATRA) cycle](image)
3. Generation and application of nitrogen-centered radicals (NCRs)

To date, nitrogen-centered radicals (NCRs) have received increasing attention as a class of appealing intermediates in synthetic methods. Over recent years, a series of methods have been used to generate NCRs, such as visible light photocatalysis, metal catalysis, and thermolysis.

3.1 Generation and application of NCRs by N–C bond cleavage

N–C bonds are ubiquitous motifs in nature, especially in amino acids. Most of N–C bonds are stable under standard conditions. A very important type of free nitrogen-centered radicals generated from aziridinylcarbinyl radicals were found in 1976 by the Murphy group. As shown in Scheme 3, after a two-step reaction, the aminyl radical 5 was formed by C–N bond cleavage of aziridinylcarbinyl radical 4 in 70% yield.

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Inspired by this elegant work, a number of efficient methods have been developed to generate aminyl radicals (Scheme 3). In addition, the groups of De Kimpe, Schwan and Refvik, and Molander and Stenge have reported aziridinylcarbinyl radicals as precursors for the aminyl radical, giving the N–C bond cleavage products smoothly.

Scheme 3: Aminyl radical formation from aziridinylcarbinyl radical
In 2005, an example of NCRs generated by N–C bond cleavage was devised by Studer and co-workers\textsuperscript{[13a]} In their system, the most efficient NCR precursors 19a and 19b were synthesized and reacted with unactivated alkene 20 to give the desired hydroamination products 21a and 21b in moderate yields under the initiation of DTBP and heating conditions. The possible mechanism in Scheme 5 shows a chain reaction process.
Scheme 5: Synthesis of NCR precursors 19 and the possible mechanism for the
generation and reaction of aminyl radicals

The success in the generation of these NCRs by N–C bond cleavage inspired the authors to continue exploring other new NCR precursors (Scheme 6).\textsuperscript{[13b]} In 2007, the same group presented a series of cyclohexadienes 19 and 30 as the new NCR precursors for the synthesis of hydroamination products by using the same strategy. They expanded the family of NCR precursors in hydroamination and synthesized NCR precursors in moderate yields.
Scheme 6: Synthesis of new NCR precursors and their application in hydroamination reactions

More recently, Stephenson developed a photocatalytic preparation of N-alkylated heteroarenes (Scheme 7).\textsuperscript{[14]} The proposed mechanism suggested that the nitrogen-centered radical was generated by homolytic cleavage of the C–N bond through a 1,4-aryl migration from nitrogen to carbon, conceptually analogous to a radical Smiles rearrangement (Scheme 8). Under these conditions, 15 products were obtained in yields ranging from 50% to 90%.

Scheme 7: Preparation of aminoalkylated heteroarenes
3.2 Generation and application of NCRs by N–N bond cleavage

Since the energy of the N–N bond is relatively low, the nitrogen-centered free radical could be generated by N–N bond cleavage. In 1961, Rosich and co-workers\[^{15}\] described the first example of nitrogen-centered radical generation from N-nitrosamines by photolysis (Scheme 9).

Over the past few decades, various N-containing precursors with relatively weak N–N bonds have been used for the generation of nitrogen-centered radicals, such as N-aminobenzotriazole, azides, N-acyltri azenes, dihydropyridines, and thiosemicarbazides. The application of those precursor was reported by El Kaim and Meyer,\[^{16}\] Kim,\[^{17}\] Li,\[^{18}\] Studer,\[^{19}\] Zard,\[^{20}\] and Callier-Dublanchet\[^{21}\] under thermolysis, UV irradiation or by chemical initiation (Scheme 10).
Despite the existence of many ways to generate nitrogen-centered radicals by N–N bond cleavage, there are still several limitations. Therefore, developing new reagents and using more efficient methods to generate nitrogen-centered radicals still remains a worthy challenge.

Recently, Studer and co-workers[22] developed reagents based on N-aminopyridinium salts, which can be used as precursors for nitrogen-centered radicals in the amidation of arenes and heteroarenes (Scheme 11). The amidation products 59 were isolated in 46-89% yield by using 55 as reaction partner. 56 and 57 as the NCR precursors gave the amidation products 61, which were isolated in 31-95% yield (Scheme 12).

Scheme 10: Precursors of NCRs bearing an N–N bond

Scheme 11: Synthesis of N-aminopyridinium salt reagents
Scheme 12: Applications of N-aminopyridinium salts reagents

3.3 Generation and application of NCRs by N-O bond cleavage

Previous studies indicated that the N–O bond is weaker than the N–N bond and is more likely to form free radicals more easily. Therefore, it is another important precursor of nitrogen-centered radicals.

As early as the 1990s, Newcomb\textsuperscript{[23]} showed the utilization of N-hydroxypyridine-2-thione carbamates (62, PTOC carbamates) in the formation of aminyl radicals and aminium radicals in cyclizations by N–O bond cleavage.

Scheme 13: First example for the generation of NCRs by the N–O cleavage

In previous reports, acyl oximes were employed as important building blocks for the generation of NCRs by metal catalysis, microwave irradiation, photocatalysis, and other efficient methods (Scheme 14).\textsuperscript{[24]} A common feature in these reactions is that the N–O bond can be cleaved to give iminyl radicals for the construction of nitrogen-containing compounds.
Scheme 14: N–O cleavage of acyl oximes 68 to form N-containing heterocycles

Based on these results, Yu[24] and co-workers investigated a visible light promoted cyclization reaction of acyl oximes by Ir(III)-catalyzed generation of the iminyl radicals (Scheme 15). Under the optimized conditions, 27 phenanthridines 74 (Scheme 15, a) could be obtained in high yields. This method also allowed construction of quinoline derivatives 76 (Scheme 15, b) and polysubstituted pyridines 78 (Scheme 15, c). The authors also demonstrated the applicability of this method in the synthesis of two natural products — alkaloids noravicine and nornitidine — using this approach as the key step.

Scheme 15: Ir(III)-catalyzed generation and reaction of the iminyl radicals from acyl oximes

Further investigations of NCRs were described by the same group (Scheme 16).[25] In 2017, they used Et₃N (82) to prepare electron-donor-acceptor (EDA) complexes 83 with O-2,4-dinitrophenyl oximes 81. Upon visible light irradiation, EDA complexes
absorbed photons and were elevated to their excited states 84. A single electron transfer chain reaction is initiated, and the products were obtained by the formation of NCRs.

Scheme 16: Et$_3$N (82) promoted the generation of NCRs

3.4 Generation and application of NCRs by N–S bond cleavage

The N–S bond has similar properties as the N–O bond, which has a weak bond energy and high activity. Therefore, homolysis of N–S bonds has proved a feasible approach for the formation of NCRs.

In 1997, Lewis[26] and co-workers indicated that sulfenamides can serve as precursors of aminyl radicals in the cyclization reaction for the synthesis of 5-exo cyclized
products (Scheme 17). Landry and Zard\cite{27} reported the similar generation of NCRs under the initiation by AIBN and reduction by Bu$_3$SnH.

Scheme 17: Synthesis of sulfonamide precursors for cyclization via $\alpha$-amino acid aminyl radicals

In 2013, the Xiao group\cite{28} used tosyl amides 102 under visible-light irradiation giving desulfonylation products through N–S bond cleavage (Scheme 18). To demonstrate the utility of this approach, a gram-scale reaction of 102 was performed in 85% yield under the optimized reaction conditions. When a chiral substrate was used, the configuration of the product 104b was conserved with an ee value of 99%. Furthermore, a high chemoselectivity of the reaction could be demonstrated by using a tosylamide substituted starting material and thereby obtaining product 104c.

Scheme 18: Generation of desulfonylation products by N–S bond cleavage

3.5 Generation and application of NCRs by N–X (halo) bond cleavage

NCRs can be easily generated from commercially available $N$-bromosuccinimide
(NBS), \(N\)-chlorosuccinimide (NCS), \(N\)-iodosuccinimide (NIS) and their related derivatives under visible-light irradiation, thermal reaction conditions, and metal-catalyzed reactions. Lessar\(^ {29}\) used \(N\)-chloroamide as the precursor of NCRs under thermal conditions. Thus, lactams could be accessed through a radical chain reaction in excellent yields. Furthermore, the HLF reaction is known as an important method for the generation of NCRs in the synthesis of pyrrolidines and related heterocyclic structures,\(^ {30}\) especially in the functionalization of non-activated skeletal positions in organic compounds.

In 2015, Herrera\(^ {31}\) developed a chemoselective intramolecular functionalization of \(N\)-iodosulfonamides \(105\) for the synthesis of aminated five-membered heterocycles (Scheme 19). Various pyrrolidines \(106\) and 2-pyrrolidonones \(107\) could be obtained in good yields, from \(105\) following either a single hydrogen atom transfer (SHAT) or a multiple (triple) hydrogen atom transfer (MHAT). Stoichiometric iodine was used in this work.

![Scheme 19: Generation of NCRs from SHAT and MHAT processes](image)

In 2016, Nagib\(^ {32}\) reported a similar cyclization reaction of unbiased amines \(105\) to pyrrolidines \(106\) (Scheme 20) using an \(I_3^-\) system.

![Scheme 20: Generation of NCRs by \(N\)-halo bond cleavage](image)

Similarly, Muñiz\(^ {60}\) established an iodine-catalyzed visible light-induced \(C-H\) amination reaction (Scheme 21). In this reaction, molecular iodine and \(\text{PhI}(m\text{CPBA})_2\) were combined to lead to the formation of \(\text{I}(m\text{CPBA})\) which is the active catalyst. Once \(\text{I}(m\text{CPBA})\) is generated, this compound promotes the \(N-I\) bond formation to generate the NCR precursor.
Photocatalysts and common organic compounds can be used as initiators for the generation of NCRs. The Yu group described a photoredox catalytic intermolecular difunctionalization reaction of olefins by employing $N$-chlorosulfonamides as both an nitrogen-centered radical precursor and as a chlorine source (Scheme 22).[33] The photocatalyst Ir(III) was known to readily accept a photon from weak fluorescent light to generate a strongly reducing excited state Ir(III)$^+$. Single electron transfer (SET) from Ir(III)$^+$ to $N$-chlorosulfonamides led to the formation of a PC$^+$-species and induced N–Cl bond cleavage to generate a NCR and chloride.

**Scheme 22:** Photoredox catalytic intermolecular difunctionalization reaction

Our group has focused on new synthetic methods towards sulfoximine-base NCR precursors and modifying existing structures with sulfoximidoyl motifs for years. Recently an efficient photocatalyzed radical oxy-sulfoximidation reaction of styrenes has been developed by our group (Scheme 23)[34] with sulfoximidoyl-containing hypervalent iodine(III) reagents through a photoredox radical process. In this reaction the reactivity profile of sulfoximidoyl radicals is affected by solvents, and Eosin Y acted as an unexpected bifunctional catalyst to introduce diastereoselectivity (Scheme 23).
3.6 Generation and application of NCRs by N–H bond cleavage

The N–H bond has a relatively high bond energy. Therefore, the development of mild methods for the direct conversion of N–H bonds into NCRs is still an attractive but challenging task for organic chemists.

In the first example shown by the Nicolaou group (Scheme 24), they developed an effective method for the generation of NCRs by homolysis of the N–H bond under the oxidation with IBX.

Scheme 23: Photoredox catalytic intermolecular difunctionalization of sulfoximines

Scheme 24: Generation of NCRs under the oxidation with IBX
oxidation with IBX and thermal conditions. The NCRs reacted with double bonds to obtain the carbon-centered radical 118. The simple anhydrous conditions or IBX hydrous conditions afforded 119, 120, and 122, respectively. Inspired by this work, Janza and co-workers[36] extended the generation of NCRs with IBX to N-acetylhydroxylamines 121. Thus, acetamido alcohol 123 could be obtained by reduction of N-acetylhydroxylamine 122.

In 2012, the Chiba group[37] reported an intramolecular [3+2] annulation reaction of N-pentenylamidines 124 using Cu-catalyzed aerobic conditions to give bi- and tricyclic amidines 128 (Scheme 25).

Scheme 25: Intramolecular [3+2] annulation reaction via NCRs

Simultaneously, Chiba and co-workers disclosed the synthesis of dihydrooxazoles 130 using CuBr·SMe₂/2,2′-bipyridine catalytic system (Scheme 26).[38] The proposed reaction mechanism showed that Cu(II) was generated by the oxidation of O₂ with CuBr·SMe₂/2,2′-bipyridine. Cu(II) reacted with 131 giving intermediate 132 which could produce intermediate 133 after regeneration of Cu(I).
The generation of NCRs through cleavage of N–H bonds is an inherently more atom- and step-economical method and has attracted much attention and challenge. Electrocatalysis has emerged as a conceptually and chemically attractive method for organic synthesis and have enabled the generation of NCRs in a highly efficient manner.

Recently, Xu investigated an atom-economical and sustainable electrocatalytic method to access NCRs through the cleavage of N–H bonds (Scheme 27). In the reaction, a diverse range of amidinyl radicals can be generated under the electrocatalysis to afford the polycyclic benzimidazoles and pyridoimidazoles in good to excellent yield.

Based on the above studies, we know that the research of NCRs can promote the development of synthetic strategies and medicinal chemistry. Design and application of novel nitrogen-centered radical precursors in the reactions to afford new NCRs is becoming more and more important.
4. Generation and application of sulfur-centered radicals

Polyvalent sulfur atoms make up a large number of organosulfur compounds and generate many different types of sulfur-centered radicals,\(^4\) including sulfanyl, sulfenyl, persulfenyl, sulfinyl, hydro sulfinyl, sulfonyl, and hydro sulfonyl radicals.\(^5\) Meanwhile, many methods for the generations of sulfur-centered radicals were well-developed in previous reports.

4.1 S(II)–centered sulphenyl radicals [RS•]

In general, five methods could be used to generate sulphenyl radicals. 1) photolysis of thiols, 2) photolysis or thermolysis of disulfides, 3) using azobis(isobutyronitrile) (AIBN) and 1,10-azobis(cyclohexanecarbonitrile) (ACCN) as azo radical initiators in the reactions of thiols, 4) using Mn(OAc)\(_3\) and (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) (CAN) as single electron transfer (SET) agents in the reactions of thiols, 5) cleavage of the S–X (S–H, S–N, and S–S) bonds in sulfur compounds.

In 2009, Dondoni and co-workers reported a thiol-ene coupling (TEC) reaction for sulphenyl radicals \(^\text{144}\), which demonstrated a chain-reaction-type mechanism (Scheme 28).\(^6\)

\[ \text{Scheme 28 General mechanism for thiol-ene coupling (TEC) reaction} \]

S-Linked disaccharide \(^\text{151}\), through TEC reaction under visible light (\(\lambda_{\text{max}}\) 365 nm) conditions, can be obtained in excellent yield with high \(dr\) value, as shown in Scheme 29.\(^7\)
Scheme 29: Synthesis of 1,6-linked S-disaccharide

Almost simultaneously, the Borbás group described a photoinduced free radical selective hydrothiolation reaction of unsaturated monosaccharide derivative 152 with endo-cyclic double bond (Scheme 30).[^44]

![Scheme 29](image)

Scheme 30: Free radical addition of thiols to 2-acetoxy glycal

In order to demonstrate the applicability of the synthetic method, the Johansson group used a two-step free-radical approach to synthesize natural terpene derivative 156 (Scheme 31).[^45] The TEC step enables high conversion to product without significant influence of side-reactions.

![Scheme 30](image)

Scheme 31: Synthesis of natural terpene derivative

The groups of Davis,[^46] Oba,[^47] Seeberger,[^48] and Stoddart[^49] reported photolysis of thiols with alkene, that utilizes TEC reactions similar to Scheme 30 showed good yields and high selectivity.

Transition metal complexes are typical catalysts in visible light photocatalysis to generate S(II)-centered radicals. In 2014, Yoon and co-workers described an efficient polypyridyl based transition metal photocatalytic TEC reaction to generate the thiy radical, which reacts with olefins 110 through a chain radical process, giving thioethers 158 under mild conditions with moderate to high yields (Scheme 32).[^50]
In 2018, the Scanlan group\cite{51} described an intramolecular acyl thiol–ene (ATE) and acyl thiol–yne (ATY) reaction of acylthioyl radicals in the corresponding unsaturated alkene and alkyne compounds to access thiolactones in the presence of visible light. The possible intermediates are shown in Scheme 33.

**Scheme 33:** Acylthiroyl radicals intermediates

Irradiation of ammonium thiocyanate is usually transformed into sulfenyl radicals under the visible light using a photocatalyst. In 2014, Akita and co-workers reported a direct C-3 thiocyanation of indoles 161 in the presence of rose bengal at room temperature, giving 3-thiocyanoindoles 165 derivatives good to excellent yields (Scheme 34).\cite{52}
Scheme 34: Synthesis of 3-thiocyanoindoles through sulfenyl radicals

Alternatively, S–S bond cleavage can also generate sulfur-centered radicals. In 2005, Kati and co-workers utilized 2,2’-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) as a water-soluble radical initiator and disulfides 167 as the thioesterification reagents to prepare thioesters 168 (Scheme 35). Furthermore, the thioester products 168 could be used in the amidation of aldehydes with amines in one-pot syntheses with high yields and broad substrate suitability.

Scheme 35: Thioesterification by the cleavage of an S-S bond

Other applications for thioesters proved that pentafluorophenyl thioesters were useful intermediates in organic synthesis.

In 2014, an elegant work for the synthesis of trifluoromethylthiolated isoxazoline 170 through a Cu(II)-catalyzed intramolecular oxytrifluoromethylthiolation of unactivated alkene 169 with AgSCF₃ as the sulfur-centered radical precursor under heating was reported by the group of Xu and Wang (Scheme 36). In a further study, the isoxazoline derivative 170 was used as a starting material for the synthesis of the Csp³–SCF₃-containing building block 171.
In 2017, the Lei group developed a novel electrocatalytic dehydrogenative C–H/S–H cross-coupling with electron-rich arenes and aryl/heteroaryl thiols (Scheme 37).\[^{[55]}\] At the anode, sulfur radical generation was easy though single-electron-transfer (SET) oxidation of the thiophenol. Thiols with a range of structures, substituted indoles, and electron-rich arenes were tolerated in this process to form the corresponding products.

**Scheme 36:** Synthesis of trifluoromethylthiolated isoxazoline derivative 170

4.2 S(IV)–centered sulfinyl radicals [RSO•]

Sulfinyl radicals are an important part of sulfur–centered free radicals. However, they have not been studied deeply, which may be related to its instability. Despite this, there are still many available methods to form the sulfinyl free radicals, such as photo-cleavage of sulfoxides, thermolysis of sulfinimines, and oxidation of disulfides and vicinal disulfoxides.\[^{[56]}\]

As early as 1982, Hehre and co-workers\[^{[57]}\] noted that sulfinyl radicals 181 and 182 were generated by the homolytic scission of the S–S bond in 180, leading to four different sulfenyl sulfinates (Scheme 38, 183, 185, 187 and 189).
Scheme 38: Generation and application of sulfinyl radicals

Based on literature reported and the work by predecessors, we know that Folkins,[58] Harpp,[59] Nakayama, and Ishii groups[60] separated a series of stable vic-disulfoxides 194 successfully. Those stable vic-disulfoxides result from the thermal rearrangement reactions of the intermediate sulfinyl radicals that take place in situ under the oxidation conditions (Scheme 39).

Scheme 39: Thermal rearrangement reactions of vic-disulfoxides via sulfinyl radicals

After that, two novel and thermally stable diastereomeric vic-disulfoxides 197 and 198 were synthesized and isolated by Kariuki and co-workers (Scheme 40).[61] The structures of vic-disulfoxides 197 and 198 were confirmed by X-ray crystallographic analysis. Upon heating trans vic-disulfoxide 197 and cis vic-disulfoxide 198 in mesitylene at 167 °C (reflux), both compounds were converted into thiosulfonate 199. However, heating vic-disulfoxides only to a temperature ranging from 80 °C to 132 °C, the additional byproducts 197, 198, and 200 were formed.
Scheme 40: Synthesis and application of trans vic-disulfoxide and cis vic-disulfoxide

Jenks group mentioned the photocatalyzed cleavage of C–S reactions and the generation to sulfinyl radicals (Scheme 41). The CH$_2$–SO bond in sulfoxide 201 was cleaved by well-chosen wavelengths (i.e., <280 nm) and solvents (e.g., tBuOH) in an excited singlet state.

Scheme 41: Generation of S(IV)-centered radical by cleavage of C–S bond

Vicent and co-workers showed the transformation of 2-arylsulfinyl esters 206 to 3-arylsulfinyl esters 208 (Scheme 42). The mechanism of the dehydrosulfenylation of 2-arylsulfinyl esters 206 for furnishing enoates has been determined to be a homolytic process. The capturing of radical intermediate 181 using TEMPO and MS techniques were useful for drawing a comprehensive picture of the intermediates involved in the dehydrosulfenylation of 2-arylsulfinyl esters 206 and suggest that a radical-mediated process is operating.
Scheme 42: Preparation and elimination of 2-aryl sulfinyl esters to 3-aryl sulfinyl esters by generation of sulfinyl radicals

In 2014, the Stockman group noted that thermolysis of N–S bonds in S-aryl sulfinimines 211 was homolytic cleavage to form sulfinyl 216 and sulfenyl radicals 217, followed by free radical homo dimerisation giving disulfoxides 180a and disulfides 213 (Scheme 43). Those products have the potential to be used as ligands for transition metal catalysis reactions.

Scheme 43: Proposed mechanism for the generation of disulfoxides and disulfides

4.3 S(VI)–centered sulfonyl radicals [RSO₂•]

Sulfonyl radical, as well-studied sulfur(VI) radicals, have been efficiently generated by several methods. For instance, 1) the reduction reactions of sulfonyl halides, sulfonyl selenides, sulfonyl azides, and sulfonyl cyanides in the presence of radical initiators, light, or catalysts. 2) Oxidation reactions of sulfinates, sulfinic acids, and sulfonyl hydrazides also provide efficient methods for the generation of sulfonyl radicals. 3) The addition reactions of other radicals to sulfur dioxide leads to various sulfonyl radicals.

In 1964, Asscher and Vofs reported a copper chloride-catalyzed addition of sulfonyl
chlorides 218 to vinylic monomers. The reaction underwent a sulfonyl free radicals pathway (Scheme 44).\textsuperscript{[65]}

\[
\text{Cu}^+ + \text{RSO}_2\text{Cl} \xleftrightarrow{\text{Scheme 44}} \text{RSO}_2 + \text{CuCl}^+ \tag{218}\tag{219}
\]

**Scheme 44:** Copper-catalysed generation of sulfonyl free radicals

More recently, Reiser and co-workers extended a visible light-mediated photocatalyzed reaction utilizing novel Cu(II) complexes as catalysts to convert a large variety of olefins 145 to their corresponding vicinal chlorsulfonylated products 220 (Scheme 45).\textsuperscript{[66]} Moreover, elimination of hydrogen chloride and double elimination reactions can produce the corresponding vinyl sulfones 222 and alkynes 221.

**Scheme 45:** Chlorosulfonylation of olefins and the applications

In 1994, Simpkins and co-workers revealed that TolSO\textsubscript{2}SePh 227 could serve as sulfonyl free radical source in the cyclization reaction with a number of 1,6-dienes 225 or enynes 223 resulting the selenosulfonylation products in good yield in the presence of the free radical initiator AIBN (Scheme 46).\textsuperscript{[67]}

**Scheme 46:** Generation sulfonyl free radical from TolSO\textsubscript{2}SePh

In 2008, Renaud and co-workers realized that the sulfonyl radical ion formation of
sulfonyl azides could be used as the radical reagents to convert terminal alkynes for an irreversible 5-exo-trig rearrangement cyclization (Scheme 47). [68]

Scheme 47: Cyclization of terminals alkynes by sulfonyl radical

Toluenesulfonyl cyanide (TsCN) could be used to generate sulfonyl free radical in the presence of an initiator (AIBN) through chain reaction. Difunctionalization products 237 were obtained by Fang and co-workers in the reaction of toluenesulfonyl cyanide (TsCN) and unsaturated hydrocarbons with high regioselectivity (Scheme 48). [69]

Scheme 48: Chain reaction for the generation of a sulfonyl radical

The Jiang group developed a simple and efficient metal-free synthesis of vinyl sulfones 222 through cross-decarboxylative/coupling reactions between sodium sulfinates 238 and cinnamic acids 239 (Scheme 49). [70]

Scheme 49: CDC reactions of sodium sulfinates and cinnamic acids

In 2013, Kuhakarn and co-workers synthesized vinyl sulfones from alkynes 221 and sulfinates 238 in a molecular iodine-mediated one-pot iodosulfonation reaction (Scheme 50). [71] The corresponding products of (E)-β-iodovinyl sulfones 240 derived
from phenylacetylene derivatives were obtained by a radical pathway.

\[
\text{Me} \overset{238}{\text{SO}_2\text{Na}} + \overset{221}{\text{H}} \equiv \text{R} \xrightarrow{\text{I}_2 (1.5 \text{ equiv}) \text{ NaOAc (1.5 equiv)}} \overset{240}{\text{R}} \equiv \text{Ts}
\]

**Scheme 50**: Iodosulfonation of alkynes with sodium sulfinates

In addition to iodine and base-catalyzed reactions, metal catalysts can generate sulfonyl free radicals from sulfinates. Recently, the Rueping group displayed a nickel/photoredox dual catalysis cross-coupling of sodium sulfinates 238 using wide range of aryl, heteroaryl, and vinyl bromides and iodides as shown in Scheme 51.[72]

Then, redox potential of the photocatalyst and the sodium sulfinates were measured, showing that sodium sulfinates with the lower reduction potential could be used to generate sulfonyl radical under the photoredox conditions.

**Scheme 51**: Photoredox/nickel catalyzed synthesis of aromatic sulfones

Pratt and co-workers revealed that sulfinic acids 244 with H-atom donor ability could be used to generate sulfonyl radicals 181 by kinetic and thermochemical experiments as depicted in Scheme 52.[73]

**Scheme 52**: Generation of sulfonyl radicals from sulfinic acids

The Lei group reported an oxysulfonylation of alkene 249 using sulfinic acid 244a as shown in Scheme 53.[74] The simple one pot synthesis allowed for a wide range of functional groups as well as for the formation of new C–O and C–S bonds. Radical capture by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and
2,4-di-tert-butyl-4-methylphenol (BHT) revealed that this reaction indeed proceeds via radical intermediates. An $^{18}$O isotope labeling experiment indicated that the hydroxyl O-atom in 248 was produced from the oxygen gas.

Scheme 53: Oxysulfonylation of alkene using sulfinic acid and oxygen

In 2013, the Li group reported tetrabutylammonium iodide (TBAI) catalyzed sulfonylations of Baylis–Hillman acetates 250 with sulfonylhydrazides 251 to give products 252 in moderate yields and with high Z:E value. In this work, sulfonyl radicals were generated by the oxidation of TBHP and N$_2$ elimination from sulfonylhydrazide (Scheme 54).$^{[75]}$

Scheme 54: Tetrabutylammonium iodide catalyzed sulfonylation of acetates

Sulfonyl radicals could be generated in situ by metal catalysis and oxidants in the presence of unsaturated compounds. The reaction proceeded by addition of sulfonyl radicals to unsaturated carbon-carbon bonds to give the desired products. For example, metal-catalyzed C–S bond generation by oxidants, O$_2$ and DTBP have been reported by the group of Wang,$^{[76]}$ Zhang,$^{[77]}$ and Taniguchi$^{[78]}$ (Scheme 55).

Wang's work

$$\text{R'SO}_2\text{NNH}_2 + \text{Ar=CH}_2 \xrightarrow{\text{Cu(OAc)}_2 (5 \text{ mol} \%) \text{ O}_2 \text{ balloon}} \text{ArSO}_2\text{R'}$$

50–72% yield

Zhang's work

$$\text{R'SO}_2\text{NNH}_2 + \text{X} = \text{H, COOH} \xrightarrow{\text{Fe/Cu catalyst}} \text{R'SO}_2\text{R'}$$

21–59% yield
Scheme 55: Metal-catalyzed generation of sulfonyl radicals from sulfonyl hydrazides

The Wu group have demonstrated that DABCO·(SO$_2$)$_2$ could be used to generate sulfonyl radicals in combination with aryl diazonium tetrafluoroborates 256 under catalyst-free conditions (Scheme 56).$^{[79]}$ In this novel protocol, 3-sulfonated coumarin formations occurred by radical addition, spirocyclization, and 1,2-migration of esters. However, alkyl groups (R$_3^2$) at position 4 either led to poor results or no desired product formation.

Scheme 56: Synthesis of 3-sulfonated coumarins by generation sulfonyl radicals of DABCO·(SO$_2$)$_2$

In 2017, Huang and co-workers developed electrocatalytic decarboxylative sulfonylation reactions between $\alpha,\beta$-unsaturated carboxylic acids 239 and aromatic sulfonylhydrazides 251. This protocol was used to synthesize various vinyl sulfones 222 under mild conditions (Scheme 57).$^{[80]}$

Scheme 57: Decarboxylative sulfonylation of $\alpha,\beta$-unsaturated carboxylic acids

The Lei group has used electrocatalysis of redox reactions, which involved carbon rod anode, nickel plate cathode and an undivided cell to synthesize alkoxysulfonylation from alkenes 249b. In this seminal work, sulfonyl radicals were generated by the deprotonation of sulfonyl hydrazines 251 and liberation of H$_2$ and N$_2$ (Scheme 58).$^{[81]}$
Scheme 58: Alkoxysulfonylation of alkenes

Visible-light photoredox catalysis, electrocatalysis, and metal catalysis have been established as powerful tools for the construction of organosulfur compounds. Ongoing research in sulfonyl radicals has given significant inspiration for our future research.
II. Experimental section

5. Iodine-mediated Hofmann-Löffler-Freytag reaction of sulfoximines

Sulfur- and nitrogen-containing scaffolds are key pillars for crop protection and medicinal chemistry.\(^{[2k,1]}\) Previously, our group has prepared related compounds through metal-catalyzed \textit{ortho} C–H functionalization of S-arylsulfoximines (Scheme 59, 1)\(^{[82]}\) and synthesized various sulfoximines which undergo intramolecular ring-closing to afford the sulfoximidoyl moieties (Scheme 59, 2).\(^{[83]}\) In addition to those effective methods to construct heterocyclic compounds, the Hofmann-Löffler-Freytag (HLF) reaction is a very important method for the synthesis of pyrrolidines and related heterocyclic structures, especially in the functionalization of non-activated skeletal positions in organic compounds.

1) Rhodium-catalyzed \textit{ortho} C–H functionalization

![Diagram of Rhodium-catalyzed functionalization](attachment:diagram1.png)

2) Intramolecular ring-closing reaction

![Diagram of Intramolecular ring-closing reaction](attachment:diagram2.png)
5.1 Results and discussion

5.1.1 Research objective
A previous work\textsuperscript{[84]} showed that the N–I bond can be easily cleaved. Therefore, herein, we study the formation and the cleavage of a sulfoximidoic N–I bond in detail. S-Phenyl-S-phenylpropyl sulfoximine (274a) was chosen as model substrate. In the presence of iodine and (diacetoxyiodo)benzene (PIDA) under visible light an N–I bond is formed and cleaved, giving a sulfoximidoyl radical as NCR. Subsequently, the intermediate sulfoximidoyl radical reacts through the HLF reaction which yields 275a by 1,5-\(H\) migration and following cyclization. (Scheme 60).

\textbf{Scheme 60:} Cyclization of S-phenyl-S-phenylpropyl sulfoximine

5.1.2 Optimization of HLF reactions
Initial examination of S-phenyl-S-phenylpropyl sulfoximine (274a) and KI in the presence of PIDA under visible light gave the desired product 275a in 12\% yield (Table 1, entry 1). Then, various iodide reagents, such as NaI, NIS, TBAI and iodine (Table 1, entries 2-5) were screened. The latter proved to be the best iodide reagent (Table 1, entry 5). Among the oxidants PIDA, PIFA, and K\(_2\)S\(_2\)O\(_8\), only PIDA led to reactivity (Table 1, entry 5 vs entries 6-7). Testing the influence of the solvents showed that DCE was the optimal choice (Table 1, entry 5 vs entries 8-12), giving 275a as 95\% yield (NMR analysis). No product was observed when the reaction was carried out in the dark, or heated up to 50 °C (Table 1, entries 13-14), confirming the necessity of light. The optimized reaction conditions were identified as follows: sulfoximine (1.0 equiv), iodine (1.0 equiv), PIDA (3.0 equiv) and DCE (1 mL) under
the visible light for 16 hours.

**Table 1. Optimization of the reaction conditions**

![Reaction Diagram](image.png)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Iodide source</th>
<th>Oxidants</th>
<th>Solvents</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KI</td>
<td>PIDA</td>
<td>DCE</td>
<td>12%</td>
</tr>
<tr>
<td>2</td>
<td>NaI</td>
<td>PIDA</td>
<td>DCE</td>
<td>NR</td>
</tr>
<tr>
<td>3</td>
<td>NIS</td>
<td>PIDA</td>
<td>DCE</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
<td>TBAI</td>
<td>PIDA</td>
<td>DCE</td>
<td>NR</td>
</tr>
<tr>
<td>5</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PIDA</td>
<td>DCE</td>
<td>95% (78%&lt;sup&gt;c&lt;/sup&gt;)</td>
</tr>
<tr>
<td>6</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PIFA</td>
<td>DCE</td>
<td>NR</td>
</tr>
<tr>
<td>7</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;</td>
<td>DCE</td>
<td>NR</td>
</tr>
<tr>
<td>8</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PIDA</td>
<td>DCM</td>
<td>92%</td>
</tr>
<tr>
<td>9</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PIDA</td>
<td>THF</td>
<td>NR</td>
</tr>
<tr>
<td>10</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PIDA</td>
<td>dioxane</td>
<td>20%</td>
</tr>
<tr>
<td>11</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PIDA</td>
<td>DMF</td>
<td>68%</td>
</tr>
<tr>
<td>12</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PIDA</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>4%</td>
</tr>
<tr>
<td>13</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PIDA</td>
<td>DCE&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2%</td>
</tr>
<tr>
<td>14</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PIDA</td>
<td>DCE&lt;sup&gt;e&lt;/sup&gt;</td>
<td>5%</td>
</tr>
</tbody>
</table>

<sup>a</sup>All reactions were conducted with 274a (0.1 mmol), iodide source (0.1 mmol, 1.0 equiv), oxidants (0.3 mmol, 3.0 equiv) and solvent (1 mL) under argon in the visible light-initiated at room temperature. <sup>b</sup>The yield was determined by <sup>1</sup>H NMR using the CH<sub>2</sub>Br<sub>2</sub> as the internal standard. <sup>c</sup>Yield after column chromatography. <sup>d</sup>In the dark. <sup>e</sup>In the dark at 50 °C.

### 5.1.3 Substrate scope of sulfoximines

Variously substituted sulfoximines 274 were subjected to the optimized reaction conditions (Table 1, entry 5). The results are summarized in Table 2. The sulfoximines 274b-d bearing methyl substituents at the ortho-, meta- and para- position reacted
well, affording the products 275b-d in yields of 80%, 73%, and 57%, respectively. Additionally, the presence of various substituents at the para-position, such as chloro, fluoro or nitro groups, allowed for the synthesis of 275e-g in yields ranging from 56-73% (entries 5-7). Sulfoximines with ortho-methoxy 274h or bromo groups 274i led to products 275h and 275i in yields of 71% and 78% (entries 8-9). The reaction of S-naphthyl-S-phenylpropyl sulfoximine and [3-(phenylsulphonimidoyl)]pentane-1,5-diyl]dibenzene afforded products 275j and 275k in good yields (entries 10-11). It was discovered that the reaction selectively took place at the relatively active benzyl carbon position. For example, substrate 274l gave the corresponding product 275l in 80% yield with dr to 5:1, whereas only a trace amount of product 275m was detected using substrate 274m (entries 12-13). To examine the reaction selectivity, we further conducted the reactions using sulfoximines 275n-o containing two benzyl carbons. The results showed that the reactions proceeded smoothly with poor regioselectivity at both two benzyl carbons. The two isolable isomers were obtained with the ratio close to 1:1 (275n and 275n’, 275o and 275o’, entries 14-15).

**Table 2: Synthesis of cyclic sulfoximines**

<table>
<thead>
<tr>
<th>Entry</th>
<th>274</th>
<th>Products (275a-o’)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="274a" /></td>
<td><img src="image" alt="275a" /></td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="274b" /></td>
<td><img src="image" alt="275b" /></td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="274c" /></td>
<td><img src="image" alt="275c" /></td>
<td>73</td>
</tr>
</tbody>
</table>
All reactions were conducted with substrate 274 on 0.1 mmol scale under the argon and visible light at room temperature. Yield after column chromatography.

### 5.1.4 Plausible mechanism

A plausible reaction pathway for this HLF reaction is shown in Scheme 61. Initially, PIDA reacts with iodine leading to intermediate I(OAc) (A), and intermediate B is formed by the oxidation of A. The photolysis of the N–I bond to generate an nitrogen radical results in the formation of intermediate C, which is converted to radical D by an 1,5-\( H \) migration. Then, intermediate D reacts with PIDA or I radical to give carbocation E, which can be easily transformed to product 275a by deprotonation. The products 275l, 275n, and 275o are formed via intermediates F.
and G.

Scheme 61: Plausible mechanism

5.1.5 Application

We illustrated the utility of this product in the synthesis of 1-(4-aminophenyl)-3-phenyl-4,5-dihydro-3H-isothiazole 1-oxide (276). Reduction of 275g with NiCl₂ and NaBH₄ in CH₃OH/H₂O at room temperature gave 276 in 93% yield (Scheme 61).

Scheme 62: Reduction of substrate 275g with NiCl₂ and NaBH₄.

5.1.6 Summary

In summary, we have demonstrated an important iodine and visible light controlled HLF reaction. In most of the cases, dihydroisothiazole oxides were obtained in moderate to high yields under mild and efficient conditions.
5.2 Experimental

5.2.1 General information

Unless otherwise noted, the reagents were purchased from commercial suppliers and used without purification. Reactions were tracked by thin layer chromatography (TLC) from Merck. Column chromatography was performed using silica gel 60 (63 - 200 µm) from Merck. 1H NMR spectra were recorded on an Agilent 400 or 600 MHz spectrometer in deuterated chloroform. The chemical shifts were given in ppm relative to the residual peak of the non-deuterated solvent was used as internal standard (CDCl₃: δ = 7.26 ppm). 1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad), coupling constants (in Hz), integration. 13C {1H} NMR data were collected at 100 or 150 MHz with complete proton decoupling (CDCl₃ δ 77.16 ppm). IR spectra were recorded on a Perkin Elmer 100 FT/IR spectrometer, and the wave numbers of the absorption peaks are given in cm⁻¹. Mass (MS) were acquired on a Finnigan SSQ 7000 spectrometer [electron ionization (EI), 70 eV; chemical ionization (CI), 100 eV] and peaks were listed according to their m/z [also inconsistent use in the MS data later] values. High resolution mass spectra (HRMS) analyses were recorded on a Thermo Scientific LTQ Orbitrap XL with positive ion mode. Melting points (m.p.) were measured on a Büchi B-540 melting point apparatus. Visible light irradiation was provided by a fluorescent lamp.

5.2.2 General procedures and characterization data

Procedure for the preparation of 274a and 274k.\textsuperscript{[86]}

A mixture of S-methyl-S-phenyl sulfoximine (5.0 g, 32.0 mmol) and hexamethyldisilazane (HMDS, 33.7 mL, 161.0 mmol) was kept at 125 °C under an inert atmosphere for 12 h. The excess HMDS was removed under reduced pressure to afford a quantitative yield of the corresponding N-TMS-sulfoximine as a pale yellow oil. The crude material was used for the subsequent alkylation reaction. A solution of the N-TMS-sulfoximine in THF (25.0 mL) was stirred in an oven-dried two-neck round bottom flask under an argon atmosphere at 0 °C. nBuLi (20.0 mL, 1.0 equiv, 1.6 M in THF) was introduced over 0.5 h at 0 °C. After an additional 2 h stirring, (2-bromoethyl)benzene (6.5 g, 35.2 mmol, 1.1 equiv) was added at 0 °C. The resulting mixture was stirred for 0.5 h, slowly warmed to room temperature and
stirring was continued for 12 h. Then, MeOH (20.0 mL) was added to the reaction mixture. After stirring for 1 h, the reaction mixture was quenched with saturated aqueous solution NH₄Cl (40.0 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (3 × 50.0 mL). The combined extracts were dried over Na₂SO₄, filtered and the liquid was evaporated under reduced pressure. The products 274a and 274k were purified using column chromatography on silica gel, affording 581.1 mg of 274k (byproduct) in 5% yield as pale yellow solid (ethyl acetate/\(n\)-pentane = 1/4) and 3.5 g of 274a in 42% yield as pale yellow solid (ethyl acetate/\(n\)-pentane = 1/2).

**General procedure for the preparation of 274b–j and 274l–o.**[87]

The respective thiophenol derivative (5.0 mmol, 1.0 equiv) and K₂CO₃ (760.1 mg, 5.5 mmol, 1.1 equiv) in acetone (10.0 mL) were treated with the alkyl bromide (6.0 mmol, 1.2 equiv) and stirred at 45 °C for 12 h. Water was added to the mixture and the contents were cooled to room temperature. The resulting mixture was extracted with ethyl acetate (3 × 30 mL) and the organic phase was concentrated under reduced pressure.

A mixture of the sulfide (5.0 mmol, 1.0 equiv) and a solution of H₂O₂ (5.5 mmol, 0.33 mL, 30% in water; 1.1 equiv) was kept at 40 °C for 12 h in MeOH (10.0 mL). Then, the reaction mixture was cooled to room temperature, and water (10.0 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 30 mL) and the organic phase was concentrated under reduced pressure to give the crude sulfoxide, which was reacted further without purification.

The sulfoxide (277, 5.0 mmol, 1.0 equiv), PhI(OAc)₂ (15.0 mmol, 4.8 g, 3.0 equiv) and ammonium carbamate (20 mmol, 1.5 g, 4.0 equiv) were added to a round bottom
flask containing a stir bar. Then, MeOH (0.5 mL \* mmol⁻¹ of sulfoxide) was added and the reaction was stirred for 30 min at 25 ºC in an open flask. The solvent was removed under vacuum, and the product was purified by flash column chromatography to give the corresponding sulfoximine.

**General procedure for the preparation of 275a–o (as illustrated for the synthesis of 275a)**

![Chemical structure](image)

Under argon, S-phenyl-S-(3-phenylpropyl) sulfoximine (274a, 25.9 mg, 0.1 mmol, 1.0 equiv), PhI(OAc)₂ (96.9 mg, 0.3 mmol, 3.0 equiv) and iodine (25.4 mg, 0.1 mmol, 1.0 equiv) were added into a 5.0 mL sealable reaction tube. Then, DCE (1.0 mL) was added and the reaction was stirred for 16 h under the visible light. Subsequently, the mixture was quenched by the addition of a sat. aqueous solution of Na₂S₂O₃ (2.0 mL) and extracted with DCM (3 × 5.0 mL). The organic layer was concentrated under vacuum, the solvent was removed in vacuum, and the product was purified by flash column chromatography (ethyl acetate/ n-pentane = 1/2) to give 20.1 mg of 275a (78% yield). The diastereomeric ratio of 275a was determined by ¹H NMR of the crude product mixture.

**Preparation of 276**

Under air, 1-(4-nitrophenyl)-3-phenyl-4,5-dihydro-3H-isothiazole 1-oxide (275g, 15.1 mg, 0.05 mmol, 1.0 equiv) and NiCl₂ (0.4 mg, 0.0025 mmol, 0.05 equiv) were loaded into a 5.0 mL reaction tube. Then, MeOH (1.0 mL) and H₂O (1.0 mL) were added. Next, NaBH₄ (7.6 mg, 0.2 mmol, 4.0 equiv) was added and the mixture was stirred at room temperature until 275g was completely converted (2.0 h). Then, the reaction mixture was extracted with DCM (3 × 3.0 mL). The organic layer was concentrated and the product was purified by flash column chromatography (ethyl acetate/ n-pentane = 1/1) to give 12.6 mg of product 276 (93% yield). The diastereomeric ratio was determined by ¹H NMR of the crude product mixture.

**5.2.2. Characterization Data**

*S-Phenyl-S-(3-Phenylpropyl)sulfoximine (274a)*
Light yellow solid, 3.5 g (42%), melting point: 71–72 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 – 7.89 (m, 2H), 7.64 – 7.57 (m, 1H), 7.56 – 7.48 (m, 2H), 7.27 – 7.20 (m, 2H), 7.19 – 7.14 (m, 1H), 7.06 (d, $J$ = 6.9 Hz, 2H), 3.22 – 3.07 (m, 2H), 2.81 (s, 1H), 2.65 (t, $J$ = 7.5 Hz, 1H), 2.17 – 1.89 (m, 2H).

$^{13}$C {$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 141.9, 140.0, 133.0, 129.2, 128.5, 128.4, 128.3, 126.3, 56.7, 34.1, 24.7.

MS (EI,70 eV): $m/z$ (%) = 259.2 (8, M$^+$), 194.5 (15), 193.1 (16), 125.1 (28), 118.1 (100), 117.2 (40), 116.2 (36), 91.4 (64), 77.5 (22). MS (ESI) [M+H]$^+$: 260.11.

HRMS (ESI) ($m/z$) [C$_{15}$H$_{18}$NOS]$^+$: Calcd. 260.1104, found, 260.1103.

IR (ATR): $\nu$ = 3467, 3287, 3034, 2935, 2650, 2320, 2095, 1742, 1601, 1448, 1204, 1113, 972, 700.

$S$-($2$-Methylphenyl)-$S$-($3$-phenylpropyl)sulfoximine (274b)

Light yellow oil, 232.1 mg (17%),

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.02 (dd, $J$ = 8.0, 1.1 Hz, 1H), 7.44 (td, $J$ = 7.5, 1.1 Hz, 1H), 7.32 (t, $J$ = 7.6 Hz, 1H), 7.26 (d, $J$ = 7.5 Hz, 1H), 7.22 (t, $J$ = 7.5 Hz, 2H), 7.16 (t, $J$ = 7.4 Hz, 1H), 7.05 (d, $J$ = 7.2 Hz, 2H), 3.20 – 3.10 (m, 2H), 2.82 (s, 1H), 2.65 (td, $J$ = 7.4, 2.1 Hz, 2H), 2.60 (s, 3H), 2.10 – 1.91 (m, 2H).

$^{13}$C {$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 140.0, 139.9, 137.8, 132.98, 132.9, 130.3, 128.5, 128.4, 126.5, 126.3, 54.7, 34.0, 24.4, 20.7.

MS (EI,70 eV): $m/z$ (%) = 272.6 (8, M$^+$), 271.7 (22), 182.4 (22), 181.6 (16), 180.9 (33), 139.2 (25), 118.2 (54), 117.6 (15), 116.7 (37), 106.2 (17), 91.6 (34), 90.7 (25).


HRMS (ESI) ($m/z$) [C$_{16}$H$_{20}$NOS]$^+$: Calcd. 274.1260, found, 274.1256.

IR (ATR): $\nu$ = 3779, 3541, 3275, 3026, 2931, 2863, 2661, 2325, 2098, 1995, 1887, 1741, 1596, 1453, 1274, 1215, 1111, 1064, 969, 806, 747, 702.

$S$-($3$-Methylphenyl)-$S$-($3$-phenylpropyl)sulfoximine (274c)

Light yellow solid, 177.5 mg (13%), melting point: 64–65 °C.
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.76 – 7.71 (m, 2H), 7.42 (dd, $J = 5.2$, 0.8 Hz, 2H), 7.25 (t, $J = 6.0$, 2H), 7.18 (t, $J = 6.0$, 1H), 7.08 (dd, $J = 7.8$, 0.8 Hz, 2H), 3.23 – 3.11 (m, 2H), 2.66 (t, $J = 7.5$ Hz, 1H), 2.43 (s, 3H), 2.24 (s, 1H), 2.11 – 2.04 (m, 1H), 2.03 – 1.96 (m, 1H).

$^{13}$C $^1$H NMR (151 MHz, CDCl$_3$) $\delta$ 141.2, 140.0, 139.5, 134.0, 129.1, 128.7, 128.5, 128.4, 126.3, 125.5, 56.6, 34.1, 24.6, 21.4.

MS (EI,70 eV): m/z (%) = 139.3 (14), 119.4 (10), 118.4 (98), 117.3 (51), 105.3 (11), 92.4 (14), 91.4 (100), 77.3 (12). MS (ESI) [M+H]$^+$: 274.126.

HRMS (ESI) (m/z) [C$_{16}$H$_{20}$NOS]$^+$: Calcd. 274.1260, found, 274.1260.

IR (ATR): $\nu$ = 3280, 3046, 2935, 2372, 2093, 1747, 1603, 1209, 1102, 973, 734.

S-(4-Methylphenyl)-S-(3-phenylpropyl)sulfoximine (274d)

Light yellow solid, 122.9 mg (9%), melting point: 68-69 °C.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.24 (t, $J = 8.3$ Hz, 2H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.08 (d, $J = 7.2$ Hz, 2H), 3.18 – 3.06 (m, 2H), 2.65 (t, $J = 7.6$ Hz, 2H), 2.57 (s, 1H), 2.43 (s, 3H), 2.10 – 2.02 (m, 1H), 2.02 – 1.93 (m, 1H).

$^{13}$C $^1$H NMR (151 MHz, CDCl$_3$) $\delta$ 143.9, 140.1, 138.9, 129.8, 128.5, 128.4, 126.3, 56.8, 34.1, 24.7, 21.5.

MS (EI,70 eV): m/z (%) = 208.5 (12), 139.4 (38), 119.4 (11), 118.4 (99), 117.3 (58), 108.3 (11), 107.3 (12), 106.3 (15), 105.3 (16), 92.4 (14), 91.4 (100), 77.3 (12). MS (ESI) [M+H]$^+$: 274.13.

HRMS (ESI) (m/z) [C$_{16}$H$_{19}$NOSNa]$^+$: Calcd. 296.1080, found, 289.1073.

IR (ATR): $\nu$ = 3461, .3305, 3203, 3025, 2928, 2867, 2651, 2326, 2103, 1913, 1879, 1739, 1648, 1593, 1489, 1453, 1371, 1301, 1207, 1119, 968, 812, 743, 695.

S-(4-Chlorophenyl)-S-(3-phenylpropyl)sulfoximine (274e)

Light yellow oil. 146.5 mg (10%),

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.88 -7.83 (m, 2H), 7.52 – 7.47 (m, 2H), 7.29 – 7.22
(m, 2H), 7.22 – 7.16 (m, 1H), 7.12 – 7.04 (m, 2H), 3.19 – 3.07 (m, 2H), 2.67 (t, J = 7.5 Hz, 2H), 2.33 (s, 1H), 2.11 – 2.03 (m, 1H), 2.03 – 1.94 (m, 1H).

$^{13}$C $^{1}$H NMR (151 MHz, CDCl$_3$) δ 140.3, 139.8, 139.8, 129.9, 129.5, 128.6, 128.3, 126.4, 56.7, 34.3, 24.6.

MS (EI, 70 eV): m/z (%) = 159.3 (11), 119.4 (11), 118.4 (100), 117.3 (69), 111.2 (14), 91.3 (90). MS (ESI) [M+H]$^+$: 294.07.

HRMS (ESI) (m/z) [C$_{15}$H$_{16}$NOSClNa]$^+$: Calcd. 316.0533, found, 316.0533.

IR (ATR): $\nu$ = 3838, 3552, 3273, 3071, 3028, 2929, 2862, 2660, 2323, 2108, 1914, 1657, 1576, 1467, 1392, 1218, 1084, 977, 828, 749, 700.

$\text{S-(4-Fluorophenyl)-S-(3-phenylpropyl)sulfoximine (274f)}$

Light yellow solid, 290.9 mg (21%), melting point: 74-75 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.97 – 7.90 (m, 2H), 7.25 (t, J = 6.0, 2H), 7.22 – 7.17 (m, 3H), 7.08 (d, J = 7.2 Hz, 2H), 3.19 – 3.05 (m, 2H), 2.67 (t, J = 7.5 Hz, 2H), 2.55 (s, 1H), 2.11 – 2.03 (m, 1H), 2.02 – 1.94 (m, 1H).

$^{13}$C $^{1}$H NMR (151 MHz, CDCl$_3$) δ 165.5 (d, $J_{C-F}$ = 255.3 Hz), 139.9, 137.8 (d, $J_{C-F}$ = 3.0 Hz), 131.2, (d, $J_{C-F}$ = 9.0 Hz), 128.5 (d, $J_{C-F}$ = 37.5 Hz), 126.4, 116.5, 116.3, 56.9, 34.4, 24.7.

$^{19}$F NMR (564 MHz, CDCl$_3$) δ -105.2.

MS (EI, 70 eV): m/z (%) = 143.3 (14), 119.4 (11), 118.4 (100), 117.4 (59), 95.3 (12), 91.4 (58). MS [M+H]$^+$ (ESI): 278.10.

HRMS (ESI) (m/z) [C$_{15}$H$_{17}$NOS]$^+$: Calcd. 278.1010, found, 278.1012.

IR (ATR): $\nu$ = 3298, 3062, 3028, 2929, 2864, 2647, 2326, 2108, 1900, 1771, 1657, 1587, 1487, 1409, 1298, 1206, 1124, 1079, 971, 832, 743, 699.

$\text{S-(4-Nitrophenyl)-S-(3-phenylpropyl)sulfoximine (274g)}$

Light yellow solid, 410.5 mg (27%), melting point: 48-49 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.36 (d, J = 8.6 Hz, 2H), 8.12 (d, J = 8.6 Hz, 2H), 7.26 (t, J = 12.0, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 7.3 Hz, 2H), 3.26 – 3.07 (m, 2H), 2.69 (t, J = 7.4 Hz, 2H), 2.52 (s, 1H), 2.18 – 2.05 (m, 1H), 2.05 – 1.95 (m, 1H).
$^{13}$C {$^{1}$H} NMR (151 MHz, CDCl$_3$) δ 150.5, 148.0, 139.6, 129.8, 128.7, 128.3, 126.5, 124.3, 56.5, 34.0, 24.5.

MS (EI, 70 eV): m/z (%) = 286.6 (39), 181.4 (16), 168.4 (24), 167.3 (11), 151.3 (25), 150.3 (27), 149.3 (12). MS (ESI) [M+H]$^+$: 305.10.

HRMS (ESI) (m/z) [C$_{15}$H$_{17}$N$_2$O$_3$S]$^+$: Calcd. 305.0954, found, 305.0955.


S-(2-Methoxyphenyl)-S-(3-phenylpropyl)sulfoximine (274h)

Light yellow oil. 549.3 mg (38%),

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (dd, J = 7.8, 1.7 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.25 – 7.19 (m, 2H), 7.18 – 7.12 (m, 1H), 7.08 – 7.01 (m, 3H), 6.95 (d, J = 7.9 Hz, 1H), 3.79 (s, 3H), 3.46 – 3.27 (m, 2H), 2.72 – 2.62 (m, 2H), 2.57 (s, 1H), 2.09 – 1.88 (m, 2H).

$^{13}$C {$^{1}$H} NMR (101 MHz, CDCl$_3$) δ 156.7, 140.3, 134.7, 130.2, 129.5, 128.4, 126.2, 120.6, 112.2, 56.0, 54.2, 34.0, 24.5.

MS (EI, 70 eV): m/z (%) = 289.6 (1, M$^+$), 155.3 (12), 152.3 (10), 118.4 (11), 117.3 (24), 92.3 (22), 91.3 (93), 77.3 (29). MS (ESI) [M+H]$^+$: 290.12. HRMS (ESI) (m/z) [C$_{16}$H$_{20}$NO$_2$S]$^+$: Calcd. 290.1209, found, 290.1212.

IR (ATR): ν = 3552, 3271, 3067, 2936, 2852, 2324, 2083, 1938, 1812, 1707, 1590, 1522, 1471, 1348, 1273, 1216, 1126, 1083, 976, 853, 806, 744.

S-(2-Bromophenyl)-S-(3-phenylpropyl)sulfoximine (274i)

Light yellow oil. 337.0 mg (20%),

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.18 (dd, J = 7.9, 1.7 Hz, 1H), 7.72 (dd, J = 7.9, 1.2 Hz, 1H), 7.47 (td, J = 7.6, 1.2 Hz, 1H), 7.40 (td, J = 7.6, 1.7 Hz, 1H), 7.25 (t, J = 12, 2H), 7.20 – 7.14 (m, 1H), 7.13 – 7.06 (m, 2H), 3.56 – 3.48 (m, 1H), 3.45 – 3.37 (m, 1H), 2.90 – 2.50 (m, 3H), 2.12 – 2.03 (m, 1H), 2.02 – 1.94 (m, 1H).

$^{13}$C {$^{1}$H} NMR (151 MHz, CDCl$_3$) δ 141.1, 140.0, 135.6, 134.0, 131.9, 128.55, 128.4, 128.0, 126.4, 120.8, 53.4, 34.1, 24.3.
MS (EI, 70 eV): \( m/z \) (%) = 119.4 (16), 118.4 (100), 117.4 (66), 91.4 (66). MS (ESI) [M+Na]+: 360.00.

HRMS (ESI) (m/z) [C_{11}H_{15}NOSNa]+: Calcd. 360.0028, found, 360.0030.

IR (ATR): \( \nu = 3841, 3568, 3278, 3058, 2933, 2670, 2330, 2096, 1741, 1573, 1433, 1221, 1106, 969, 738. \)

\[ S-(2-Naphthyl)-S-(3-phenylpropyl)sulfoximine (274j) \]

Light yellow solid, 170.0 mg (11%), melting point: 109–110 °C.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \): 8.51 (d, \( J = 1.3 \) Hz, 1H), 7.98 (dd, \( J = 8.3, 3.0 \) Hz, 2H), 7.95 – 7.88 (m, 2H), 7.69 – 7.65 (m, 1H), 7.64 – 7.60 (m, 1H), 7.22 (t, \( J = 7.3 \) Hz, 2H), 7.18 – 7.14 (m, 1H), 7.06 (d, \( J = 7.0 \) Hz, 2H), 3.31 – 3.16 (m, 2H), 2.66 (t, \( J = 7.5 \) Hz, 2H), 2.36 (s, 1H), 2.17 – 2.07 (m, 1H), 2.07 – 1.97 (m, 1H).

\(^{13}\)C \{\(^1\)H\} NMR (151 MHz, CDCl\(_3\)) \( \delta \): 139.9, 138.6, 135.0, 132.3, 129.9, 129.5, 129.4, 129.0, 128.5, 128.4, 127.9, 127.6, 126.3, 123.4, 56.7, 34.1, 24.7.

MS (EI, 70 eV): \( m/z \) (%) = 245.5 (10), 244.6 (46), 191.4 (31), 176.4 (13), 175.4 (76), 144.4 (58), 143.3 (81), 142.4 (14), 141.4 (29), 128.4 (22), 127.4 (56), 118.4 (100), 117.4 (67), 115.4 (34), 91.4 (99), 77.4 (14). MS (ESI) [M+H]+: 310.13.

IR (ATR): \( \nu = 3754, 3470, 3248, 2937, 2336, 2094, 1744, 1433, 1210, 968, 739. \)

\[ S-Phenyl-S-(1-phenethyl-3-phenylpropyl)sulfoximine (274k) \]

Light yellow solid, 581.1 mg (5%), melting point: 52–53 °C.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \): 7.93 – 7.87 (m, 2H), 7.60 (dd, \( J = 10.7, 4.1 \) Hz, 1H), 7.52 (t, \( J = 7.8 \) Hz, 2H), 7.24 (dd, \( J = 16.3, 8.0 \) Hz, 4H), 7.18 (q, \( J = 7.2 \) Hz, 2H), 7.03 (dd, \( J = 13.1, 7.2 \) Hz, 4H), 2.99 (dq, \( J = 6.8, 4.9 \) Hz, 1H), 2.80 – 2.73 (m, 2H), 2.65 – 2.55 (m, 2H), 2.34 – 2.19 (m, 2H), 1.98 – 1.86 (m, 2H).

\(^{13}\)C \{\(^1\)H\} NMR (151 MHz, CDCl\(_3\)) \( \delta \): 140.7, 140.6, 140.6, 132.9, 129.0, 129.0, 128.5, 128.5, 128.4, 128.4, 126.2, 126.2, 63.4, 33.0, 32.8, 30.3, 30.2.
MS (EI, 70 eV): \( m/z \) (%) = 363.4 (24, M\(^+\)), 222.5 (17), 220.8 (35), 144.9 (15), 143.8 (14), 142.7 (19), 141.5 (36), 131.5 (33), 130.5 (100), 124.9 (41), 117.4 (51), 115.0 (12), 104.6 (23), 103.5 (16), 92.7 (20), 91.6 (48), 91.1 (100), 77.4 (21). MS (ESI) [M+H\(^+\)]\(^+\): 364.17.

HRMS (ESI) (\( m/z \)) \([C_{23}H_{25}NOSNa]\)\(^+\): Calcd. 386.1550, found, 386.1550. IR (ATR): \( \nu = 3273, 3205, 3027, 2934, 2866, 2330, 2088, 1891, 1740, 1598, 1491, 1449, 1364, 1299, 1215, 1090, 976, 836, 741, 695.\)

Note: \textbf{274k} was the byproduct from the synthesis of \textbf{274a}.

\textbf{S-(2-Ethylphenyl)-S-(3-propyl)sulfoximine (274l)}

\[
\begin{array}{c}
\text{S-} \big/ \text{NH} \big/ \text{Me} \\
\text{Et}
\end{array}
\]

Light yellow oil. 52.8 mg (5%),

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.04 (dd, \( J = 8.0, 1.3 \) Hz, 1H), 7.52 (td, \( J = 7.5, 1.3 \) Hz, 1H), 7.38 (d, \( J = 7.7 \) Hz, 1H), 7.35 – 7.31 (m, 1H), 3.26 – 2.09 (m, 4H), 2.58 (s, 1H), 1.80 – 1.66 (m, 2H), 1.30 (t, \( J = 7.5 \) Hz, 3H), 0.97 (t, \( J = 7.5 \) Hz, 3H).

\(^{13}\)C \{\(^1\)H\} NMR (151 MHz, CDCl\(_3\)) \( \delta \) 144.3, 139.7, 133.1, 131.2, 130.4, 126.3, 58.4, 26.0, 16.7, 16.3, 12.9.

MS (EI, 70 eV): \( m/z \) (%) = 152.3 (23), 137.3 (12), 136.3 (15), 135.3 (50), 109.3 (19), 105.3 (16), 104.3 (46), 103.3 (67), 102.3 (15), 91.3 (42), 90.2 (10), 89.3 (41), 79.3 (41), 78.3 (65), 77.3 (100). MS (ESI) [M+H\(^+\)]\(^+\): 212.11.

HRMS (ESI) (\( m/z \)) \([C_{11}H_{18}NOS]\)\(^+\): Calcd. 212.1104, found, 212.1100.

IR (ATR): \( \nu = 3269, 3044, 2934, 2362, 2093, 1747, 1599, 1455, 1209, 1089, 980, 708.\)

\textbf{S-Phenyl-S-(3-methylbutyl)sulfoximine (274m)}

\[
\begin{array}{c}
\text{O-} \big/ \text{NH} \big/ \text{Me} \\
\text{Ph}
\end{array}
\]

Light yellow oil. 200.5 mg (19%),

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.95 – 7.87 (m, 2H), 7.64 – 7.55 (m, 1H), 7.54 – 7.46 (m, 2H), 7.12 – 7.07 (m, 2H), 2.54 (s, 1H), 1.66 – 1.45 (m, 3H), 0.81 (dd, \( J = 6.4, 1.4 \) Hz, 6H).

\(^{13}\)C \{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)) \( \delta \) 142.0, 132.9, 129.1, 128.3, 55.9, 31.4, 27.2, 22.1, 22.0.
MS (EI, 70 eV): m/z (\%) = 211.1 (100), 141.7 (12), 140.5 (13), 124.7 (29), 93.7 (12), 91.4 (13), 77.5 (12). MS (ESI) [M+Na]^+: 234.09.

HRMS (ESI) (m/z) [C_{11}H_{17}NOSNa]^+: Calcd. 234.0929, found, 234.0922.

IR (ATR): \nu = 3280, 3049, 2935, 2327, 2093, 1747, 1603, 1452, 1209, 1102, 973, 743.

S-(2-Ethylphenyl)-S-(3-phenylpropyl)sulfoximine (274n)

Light yellow oil. 71.8 mg (5%),

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \delta 8.02 (dd, J = 8.0, 1.3 Hz, 1H), 7.50 (td, J = 7.6, 1.4 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.28 -7.20 (m, 2H), 7.19 -7.12 (m, 1H), 7.08 – 7.01 (m, 2H), 3.23 – 3.09 (m, 2H), 3.03 (q, J = 7.5 Hz, 2H), 2.66 (t, J = 7.4 Hz, 2H), 2.52 (s, 1H), 2.12 -1.92 (m, 2H), 1.20 (t, J = 7.5 Hz, 3H).

\(^1\)C \{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)) \delta 144.3, 140.0, 139.6, 133.1, 131.2, 130.4, 128.5, 128.3, 126.3, 126.3, 55.7, 34.0, 25.8, 24.4, 16.1.

MS (EI, 70 eV): m/z (\%) = 196.4 (41), 135.1 (27), 118.2 (38), 117.2 (26), 104.2 (12), 103.2 (16), 92.2 (10), 91.2 (100), 79.2 (14), 78.2 (13), 77.2 (27). MS (ESI) [M+H]^+: 288.14.

HRMS (ESI) (m/z) [C_{17}H_{22}NOS]^+: Calcd. 288.1417, found, 288.1421.

IR (ATR): \nu = 3277, 2943, 2339, 2093, 1745, 1603, 1453, 1208, 1094, 970, 741.

S-(2,6-Dimethylphenyl)-S-(3-phenylpropyl)sulfoximine (274o)

Light yellow oil. 86.1 mg (6%),

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \delta 7.28 – 7.22 (m, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 3.18 (t, J = 8.4 Hz, 2H), 2.73 – 2.63 (m, 8H), 2.22 – 2.13 (m, 1H), 2.04 – 1.95 (m, 1H).

\(^1\)C \{\(^1\)H\} NMR (151 MHz, CDCl\(_3\)) \delta 140.1, 139.8, 138.9, 138.9, 132.0, 131.8, 128.5, 128.4, 126.3, 55.6, 34.1, 24.0, 23.5.

MS (EI, 70 eV): m/z (\%) = 286.6 (20, M^+), 197.8 (11), 195.9 (100), 194.3 (24), 168.9 (21), 152.7 (17), 151.7 (20), 150.4 (22), 121.1 (30), 118.7 (22), 117.3 (56), 105.7 (11), 104.7 (10), 91.3 (60), 77.5 (14). MS (ESI) [M+H]^+: 288.14.
HRMS (ESI) (m/z) [C_{17}H_{22}NOS]^+: Calcd. 288.1417, found, 288.1407.

1,3-Diphenyl-4,5-dihydro-3H-isothiazole 1-oxide (275a)

Light yellow solid, 20.0 mg, 78% yield, melting point: 74–75 °C. dr = 1:1.

^1^H NMR (600 MHz, CDCl₃, mixture of diastereomers) δ 8.11 – 8.01 (m, 4H), 7.70 – 7.61 (m, 2H), 7.61 – 7.52 (m, 8H), 7.43 – 7.34 (m, 4H), 7.31 – 7.25 (m, 2H), 5.33 (dd, J = 7.9, 6.0 Hz, 1H), 5.22 – 5.17 (m, 1H), 3.61 – 3.49 (m, 3H), 3.28 (td, J = 12.1, 8.5 Hz, 1H), 2.92 – 2.86 (m, 1H), 2.78 – 2.72 (m, 1H), 2.32 – 2.24 (m, 1H), 2.10 – 2.03 (m, 1H).

^1^3^C {^1^H} NMR (151 MHz, CDCl₃, mixture of diastereomers) δ 144.7, 144.5, 139.6, 139.3, 133.6, 133.5, 129.4, 129.4, 129.3, 129.2, 128.5, 128.4, 127.2, 127.1, 126.2, 126.1, 72.4, 69.6, 57.8, 57.6, 35.9, 34.7.

MS (EI, 70 eV): m/z (%) = 256.6 (11, M^+), 229.5 (30), 181.5 (43), 126.4 (16), 125.4 (100), 104.4 (13), 97.4 (20), 78.4 (15), 77.4 (51). MS (ESI) [M+H]^+: 258.09.

HRMS (ESI) (m/z) [C_{15}H_{16}NOS]^+: Calcd. 258.0947, found, 258.0945.

IR (ATR): ν = 3563, 3026, 2930, 2863, 2327, 2112, 1903, 1822, 1684, 1597, 1448, 1361, 1309, 1205, 1104, 1063, 943, 904, 853, 804, 745, 692.

3-Phenyl-1-(o-tolyl)-4,5-dihydro-3H-isothiazole 1-oxide (275b)

Light yellow oil, 21.7 mg, 80% yield. dr = 1:1.

^1^H NMR (600 MHz, CDCl₃, mixture of diastereomers) δ 8.31 (d, J = 7.5 Hz, 1H), 8.21 – 8.16 (m, 1H), 7.56 (d, J = 7.4 Hz, 2H), 7.50 (td, J = 7.4, 3.2 Hz, 2H), 7.46 (d, J = 7.4 Hz, 2H), 7.39 – 7.34 (m, 8H), 7.29 – 7.25 (m, 2H), 5.36 – 5.32 (m, 1H), 4.97 (dd, J = 8.0, 6.3 Hz, 1H), 3.70 – 3.56 (m, 3H), 3.32 (td, J = 12.1, 8.4 Hz, 1H), 2.91 – 2.85 (m, 1H), 2.75 (s, 3H), 2.73 (s, 3H), 2.70 – 2.65 (m, 1H), 2.27 – 2.20 (m, 1H), 2.04 – 1.97 (m, 1H).

^1^3^C {^1^H} NMR (151 MHz, CDCl₃, mixture of diastereomers) δ 144.5, 144.4, 138.7, 138.4, 138.1, 138.0, 133.2, 133.2, 132.6, 132.5, 129.7, 129.7, 128.4, 127.1, 127.1,
126.5, 126.3, 126.1, 70.7, 69.2, 56.0, 55.6, 35.2, 34.7, 21.1, 20.8.

MS (EI, 70 eV): m/z (%) = 270.8 (72, M⁻), 269.6 (62), 253.2 (24), 243.8 (21), 242.2 (43), 221.7 (18), 195.7 (28), 194.0 (86), 140.7 (18), 139.4 (99), 138.5 (64), 137.4 (58), 132.4 (33), 130.9 (19), 121.1 (18), 117.2 (16), 116.2 (16), 111.0 (93), 104.7 (24), 103.4 (25), 91.4 (32), 77.4 (100). MS (ESI) [M+H]^+: 272.11.

HRMS (ESI) (m/z) [C_{16}H_{18}NO_S]^+: Calcd. 272.1104, found, 272.1103.


3-Phenyl-1-(m-tolyl)-4,5-dihydro-3H-isothiazole 1-oxide (275c)

Light yellow solid, 19.9 mg, 73% yield, melting point: 57-58 °C. dr = 1:1.

^1H NMR (600 MHz, CDCl₃, mixture of diastereomers) δ 7.90 – 7.82 (m, 4H), 7.54 (dd, \( J = 11.4, 4.0 \) Hz, 4H), 7.45 (dd, \( J = 5.9, 1.8 \) Hz, 4H), 7.38 (dt, \( J = 16.8, 7.6 \) Hz, 4H), 7.31 – 7.24 (m, 2H), 5.32 (dd, \( J = 7.7, 6.1 \) Hz, 1H), 5.22 – 5.17 (m, 1H), 3.59 – 3.47 (m, 3H), 3.28 (td, \( J = 12.1, 8.4 \) Hz, 1H), 2.91 – 2.84 (m, 1H), 2.79 – 2.71 (m, 1H), 2.45 (d, \( J = 1.0 \) Hz, 6H), 2.31 – 2.24 (m, 1H), 2.10 – 2.03 (m, 1H).

^13C {^1H} NMR (151 MHz, CDCl₃, mixture of diastereomers) δ 144.7, 144.5, 139.5, 139.5, 139.4, 139.0, 134.4, 134.3, 129.8, 129.6, 129.1, 129.1, 128.5, 128.4, 127.2, 127.0, 126.5, 126.2, 126.1, 72.3, 69.6, 57.8, 57.6, 35.8, 34.6, 21.4, 21.3.

MS (EI, 70 eV): m/z (%) = 270.6 (16, M⁻), 195.5 (37), 140.4 (16), 139.4 (100), 92.4 (10), 91.4 (27), 77.4 (31). MS (ESI) [M+H]^+: 272.11.

HRMS (ESI) (m/z) [C_{16}H_{18}NO_S]^+: Calcd. 272.1104, found, 272.1103.


3-Phenyl-1-(p-tolyl)-4,5-dihydro-3H-isothiazole 1-oxide (275d)

Light yellow oil, 20.7 mg, 76% yield. dr = 1:1.

^1H NMR (600 MHz, CDCl₃, mixture of diastereomers) δ 7.94 (d, \( J = 8.2 \) Hz, 2H), 7.58 – 7.51 (m, 2H), 7.38 (dd, \( J = 16.4, 8.1 \) Hz, 4H), 7.29 (t, \( J = 7.3 \) Hz, 1H), 5.35 – 5.28 (m, 1H), 3.59 – 3.47 (m, 2H), 2.94 – 2.84 (m, 1H), 2.46 (s, 3H), 2.11 – 2.09 (m,
\(^{13}\)C \({}^1\)H NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta\) 144.6, 144.5, 136.0, 129.9, 129.5, 128.5, 127.2, 126.1, 69.4, 57.9, 35.8, 21.6.

MS (EI,70 eV): \(m/z\) (%) = 270.8 (6, M\(^+\)), 243.7 (11), 242.6 (11), 139.7 (12), 139.0 (100), 105.6 (20), 104.8 (23), 91.3 (27), 77.4 (37). MS (ESI) [M+H]\(^+\): 272.11.

HRMS (ESI) (\(m/z\)) [C\(_{16}\)H\(_{18}\)NOS]\(^+\): Calcd. 272.1104, found, 272.1100.


1-(4-Chlorophenyl)-3-phenyl-4,5-dihydro-3\(H\)-isothiazole 1-oxide (275e)

\[
\text{Cl} \\
\text{O} \\
\text{S} \\
\text{N} \\
\text{Ph}
\]

Light yellow oil, 16.4 mg, 56% yield. \(dr = 1:1\).

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta\) 8.02 – 7.95 (m, 3.2H), 7.53 (dd, \(J = 17.9, 9.1\) Hz, 6.4H), 7.38 (dt, \(J = 15.4, 7.7\) Hz, 3.2H), 7.29 (dd, \(J = 17.9, 7.3\) Hz, 1.6H), 5.32 (dd, \(J = 7.7, 6.1\) Hz, 0.6H), 5.21 – 5.16 (m, 1H), 3.61 – 3.50 (m, 2.2H), 3.28 (td, \(J = 12.1, 8.5\) Hz, 1H), 2.92 – 2.87 (m, 0.6H), 2.79 – 2.73 (m, 1H), 2.31 - 2.25 (m, 1H), 2.10 – 2.03 (m, 0.6H).

\(^{13}\)C \({}^1\)H NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta\) 144.4, 144.2, 140.5, 140.4, 138.0, 130.9, 130.9, 129.6, 129.5, 128.6, 128.5, 127.3, 127.2, 126.1, 126.0, 72.2, 69.6, 57.9, 57.6, 35.7, 34.6.

MS (EI,70 eV): \(m/z\) (%) = 291.2 (1, M\(^+\)), 262.4 (23), 215.6 (15), 161.6 (15), 160.7 (18), 159.0 (100), 111.2 (18), 105.6 (31), 104.7 (30), 77.4 (33). MS (ESI) [M+H]\(^+\): 292.06.

HRMS (ESI) (\(m/z\)) [C\(_{15}\)H\(_{13}\)NOSCl]\(^+\): Calcd. 292.0557, found, 292.0555.

IR (ATR): \(\nu\) = 3350, 3064, 2931, 2866, 2651, 2323, 2107, 1908, 1682, 1588, 1485, 1314, 1215, 1150, 1099, 1022, 944, 901, 832, 745, 694.

1-(4-Fluorophenyl)-3-phenyl-4,5-dihydro-3\(H\)-isothiazole 1-oxide (275f)

\[
\text{F} \\
\text{O} \\
\text{S} \\
\text{N} \\
\text{Ph}
\]

Light yellow oil, 20.1 mg, 73% yield. \(dr = 1:1\).

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta\) 8.11 – 8.04 (m, 3.4H), 7.52
(t, \(J = 7.3\) Hz, 3.4H), 7.41 – 7.35 (m, 3.4H), 7.32 – 7.28 (m, 1H), 7.27 – 7.23 (m, 4.1H), 5.32 (dd, \(J = 7.8, 6.0\) Hz, 0.7H), 5.22 – 5.18 (m, 1H), 3.61 – 3.52 (m, 2.4H), 3.29 (td, \(J = 12.1, 8.5\) Hz, 1H), 2.92 – 2.87 (m, 0.7H), 2.79 – 2.73 (m, 1H), 2.33 – 2.25 (m, 1H), 2.09 – 2.04 (m, 0.7H).

\(^{13}\text{C}\ {\{^1\text{H}\}}\) NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta 166.9, 165.2, 165.2, 144.3, 144.2, 135.1, 135.0, 132.3, 132.3, 132.3, 132.2, 128.6, 128.5, 127.3, 127.2, 126.1, 126.0, 116.6, 116.6, 116.48, 116.4, 72.1, 69.5, 57.9, 57.7, 35.7, 34.6.

\(^{19}\text{F}\) NMR (564 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta -104.39, -104.53.

MS (EI, 70 eV): \(m/z\) (\%) = 275.0 (6, M\(^+\)), 273.5 (12), 247.8 (14), 246.3 (44), 198.4 (21), 143.0 (100), 104.7 (11), 95.3 (11), 77.4 (15). MS (ESI) [M+H]\(^+\): 276.09.

HRMS (ESI) (\(m/z\)) \([\text{C}_{15}\text{H}_{15}\text{NOSF}]^+\): Calcd. 276.0853, found, 276.0851.

IR (ATR): \(\nu = 3363, 3065, 2936, 2860, 2654, 2325, 2106, 1909, 1862, 1588, 1487, 1449, 1210, 1150, 1102, 945, 901, 833, 747, 694.

1-(4-Nitrophenyl)-3-phenyl-4,5-dihydro-3\(H\)-isothiazole 1-oxide (275g)

Light yellow solid, 18.2 mg, 57% yield; melting point: 107-108 °C. \(dr = 1:1\).

\(^1\text{H}\) NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta 8.40\) (dd, \(J = 8.8, 1.1\) Hz, 4H), 8.24 (d, \(J = 8.8\) Hz, 4H), 7.54 – 7.48 (m, 4H), 7.39 (dt, \(J = 15.2, 7.7\) Hz, 4H), 7.34 – 7.27 (m, 2H), 5.41 – 5.36 (m, 1H), 5.24 – 5.19 (m, 1H), 3.67 – 3.56 (m, 3H), 3.35 – 3.28 (m, 1H), 2.98 – 2.91 (m, 1H), 2.81 – 2.77 (m, 1H), 2.35 – 2.28 (m, 1H), 2.15 – 2.09 (m, 1H).

\(^{13}\text{C}\ {\{^1\text{H}\}}\) NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta 150.9, 146.0, 145.5, 143.9, 143.7, 130.7, 130.7, 128.7, 128.6, 127.5, 127.4, 126.1, 125.9, 124.4, 124.3, 72.6, 69.9, 57.8, 57.5, 35.5, 34.6.

MS (EI, 70 eV): \(m/z\) (\%) = 301.6 (4, M\(^+\)), 274.5 (19), 226.5 (59), 170.4 (33), 152.4 (15), 124.3 (15), 105.4 (11), 104.4 (49), 103.4 (11), 96.3 (12), 91.4 (12), 78.4 (21), 77.4 (100). MS (ESI) [M+H]\(^+\): 303.08.

HRMS (ESI) (\(m/z\)) \([\text{C}_{15}\text{H}_{15}\text{N}_{2}\text{O}_{3}\text{S}]^+\): Calcd. 303.0798, found, 303.0791.

IR (ATR): \(\nu = 3459, 3097, 2928, 2854, 2684, 2337, 2109, 1924, 1739, 1675, 1601, 1524, 1452, 1402, 1347, 1206, 1103, 1008, 929, 848, 804, 742, 691.

1-(2-Methoxyphenyl)-3-phenyl-4,5-dihydro-3\(H\)-isothiazole 1-oxide (275h)
Light yellow oil, 20.4 mg, 71% yield. dr = 1:1.

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 8.22 (dd, $J = 7.9$, 1.7 Hz, 1H), 8.14 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.60 – 7.52 (m, 4H), 7.41 (d, $J = 7.5$ Hz, 2H), 7.33 (dt, $J = 23.2$, 7.6 Hz, 4H), 7.24 (dt, $J = 14.6$, 5.1 Hz, 2H), 7.14 – 7.07 (m, 2H), 7.04 (dd, $J = 8.3$, 4.0 Hz, 2H), 5.29 (dd, $J = 7.9$, 5.8 Hz, 1H), 4.93 (dd, $J = 8.7$, 5.9 Hz, 1H), 4.00 (s, 3H), 3.93 (s, 3H), 3.90 (dt, $J = 8.9$, 4.2 Hz, 1H), 3.69 (td, $J = 12.4$, 8.4 Hz, 1H), 3.58 – 3.49 (m, 2H), 2.87 – 2.81 (m, 1H), 2.72 – 2.64 (m, 1H), 2.20 – 2.09 (m, 2H).

$^{13}$C {$^1$H} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 157.0, 156.7, 145.1, 144.5, 135.0, 134.9, 130.8, 130.7, 128.3, 128.3, 127.0, 126.9, 126.3, 126.1, 120.7, 120.6, 112.2, 112.1, 70.8, 69.8, 56.4, 55.9, 55.6, 55.0, 35.4, 34.4.

MS (EI, 70 eV): $m/z$ (%) = 286.6 (1, M$^+$), 155.4 (44), 125.3 (47), 104.4 (17), 97.3 (54), 92.3 (15), 78.4 (15), 77.4 (100). MS (ESI) [M+H]$^+$: 288.104.

HRMS (ESI) ($m/z$) [C$_{16}$H$_{18}$NO$_2$S]$^+$: Calcd. 288.1053, found, 288.1047.

IR (ATR): $\nu$ = 3582, 3065, 2938, 2858, 2659, 2328, 2102, 1899, 1821, 1687, 1588, 1454, 1205, 1100, 1009, 905, 852, 805, 744.

1-(2-Bromophenyl)-3-phenyl-4,5-dihydro-3H-isothiazole 1-oxide (275i)

Light yellow oil, 17.8 mg, 78% yield. dr = 1:1.

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 8.47 (dd, $J = 7.8$, 1.7 Hz, 1H), 8.38 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 2H), 7.56 – 7.53 (m, 2H), 7.53 – 7.49 (m, 2H), 7.47 – 7.41 (m, 4H), 7.35 (dt, $J = 18.7$, 7.7 Hz, 4H), 7.29 – 7.26 (m, 2H), 5.38 – 5.32 (m, 1H), 4.99 (dd, $J = 8.5$, 6.1 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.76 – 3.67 (m, 3H), 2.93 – 2.86 (m, 1H), 2.77 – 2.71 (m, 1H), 2.27 – 2.19 (m, 1H), 2.13 – 2.06 (m, 1H).

$^{13}$C {$^1$H} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 144.2, 140.1, 139.8, 135.2, 135.1, 134.2, 134.1, 131.9, 131.5, 128.5, 128.4, 127.9, 127.7, 127.2, 127.1, 126.2, 126.1, 121.6, 121.3, 70.7, 69.3, 55.5, 55.1, 34.8, 34.5.

MS (EI, 70 eV): $m/z$ (%) = 334.5 (2, M$^+$), 261.4 (51), 260.4 (14), 259.4 (69), 206.2 (14), 205.3 (100), 204.3 (14), 203.3 (86), 181.4 (21), 152.3 (15), 117.3 (12), 108.3
(13), 104.3 (36), 103.2 (12), 96.3 (32), 91.3 (11), 78.4 (13), 77.4 (74). MS (ESI) [M+H]+: 336.01.
HRMS (ESI) (m/z) [C15H15NOBrS]+: Calcd. 336.0052, found, 336.0051.
IR (ATR): ν = 3409, 3062, 2936, 2855, 2668, 2324, 2109, 1886, 1682, 1568, 1490, 1440, 1314, 1214, 1100, 1020, 944, 904, 852, 806, 747, 701, 653.

1-(Naphthalen-2-yl)-3-phenyl-4,5-dihydro-3H-isothiazole 1-oxide (275j)

Light yellow solid, 23.7 mg, 77% yield, melting point: 114-115 °C. dr = 1:1.

1H NMR (400 MHz, CDCl3, mixture of diastereomers) δ 8.65 (s, 2H), 8.01 – 7.91 (m, 7H), 7.68 – 7.56 (m, 7H), 7.44 – 7.34 (m, 4H), 7.33 – 7.25 (m, 2H), 5.38 (dd, J = 7.6, 6.1 Hz, 1H), 5.29 – 5.24 (m, 1H), 3.66 – 3.52 (m, 3H), 3.36 (td, J = 12.1, 8.4 Hz, 1H), 2.96 – 2.87 (m, 1H), 2.82 – 2.74 (m, 1H), 2.37 – 2.25 (m, 1H), 2.18 – 2.07 (m, 1H).

13C {1H} NMR (101 MHz, CDCl3, mixture of diastereomers) δ 144.5, 144.5, 136.1, 135.9, 135.3, 132.4, 132.3, 131.5, 131.3, 129.6, 129.4, 129.4, 129.4, 129.2, 129.2, 128.5, 128.4, 127.9, 127.6, 127.2, 127.1, 126.2, 126.1, 123.8, 115.0, 72.2, 69.7, 57.8, 57.5, 35.7, 34.6.

MS (EI, 70 eV): m/z (%) = 279.4 (11), 231.1 (12), 201.3 (16), 176.2 (14), 175.2 (100), 147.1 (16), 128.2 (11), 127.2 (22), 115.1 (13), 77.2 (15). MS (ESI) [M+H]+: 308.11.
HRMS (ESI) (m/z) [C19H18NOS]+: Calcd. 308.1104, found, 308.1104.
IR (ATR): ν = 3591, 3063, 2937, 2857, 2693, 2322, 2106, 1949, 1682, 1569, 1491, 1441, 1314, 1216, 1101, 1021, 946, 905, 854, 812, 751, 700.

5-Phenethyl-1,3-diphenyl-4,5-dihydro-3H-isothiazole 1-oxide (275k)

Light yellow oil, 33.4 mg, 92% yield. dr = 1:1.

1H NMR (400 MHz, CDCl3, mixture of diastereomers) δ 8.11 – 7.98 (m, 2H), 7.69 – 7.61 (m, 1H), 7.61 – 7.45 (m, 4H), 7.40 – 7.29 (m, 2H), 7.29 – 7.22 (m, 1H), 7.22 – 7.10 (m, 3H), 6.96 (dd, J = 9.5, 2.7 Hz, 1H), 6.91 – 6.85 (m, 1H), 5.31 – 5.25 (m, 0.5H), 5.01 (dd, J = 9.6, 5.9 Hz, 0.5H), 3.42 – 3.29 (m, 1H), 2.82 – 2.75 (m, 0.5H), 2.73 – 2.54 (m, 2H), 2.54 – 2.43 (m, 1H), 2.40 – 2.24 (m, 1H), 2.16 – 2.04 (m, 1H), 2.14 – 2.07 (m, 1H), 2.07 – 1.99 (m, 1H), 1.99 – 1.91 (m, 1H), 1.91 – 1.83 (m, 1H), 1.83 – 1.77 (m, 1H), 1.77 – 1.71 (m, 1H), 1.71 – 1.67 (m, 1H), 1.67 – 1.61 (m, 1H), 1.61 – 1.57 (m, 1H), 1.57 – 1.53 (m, 1H), 1.53 – 1.49 (m, 1H), 1.49 – 1.45 (m, 1H), 1.45 – 1.41 (m, 1H), 1.41 – 1.37 (m, 1H), 1.37 – 1.32 (m, 1H), 1.32 – 1.28 (m, 1H), 1.28 – 1.24 (m, 1H), 1.24 – 1.20 (m, 1H), 1.20 – 1.16 (m, 1H), 1.16 – 1.12 (m, 1H), 1.12 – 1.08 (m, 1H), 1.08 – 1.04 (m, 1H), 1.04 – 1.00 (m, 1H), 1.00 – 0.96 (m, 1H), 0.96 – 0.92 (m, 1H), 0.92 – 0.88 (m, 1H), 0.88 – 0.84 (m, 1H).
1.87 (td, \( J = 13.3, 9.6 \) Hz, 0.5H).

\(^{13}\)C \{\(^1\)H\} NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 145.4, 144.9, 140.3, 140.1, 139.1, 138.4, 133.5, 129.9, 129.8, 129.3, 128.5, 128.4, 128.2, 128.1, 127.00, 126.9, 126.3, 126.1, 126.0, 69.2, 68.3, 66.4, 65.7, 40.0, 39.0, 33.9, 33.4, 30.7, 30.1.

MS (EI, 70 eV): \( m/z \) (%) = 127.2 (14), 105.4 (45), 91.4 (100), 77.4 (81). MS (ESI) \([\text{M+H}]^+\): 362.16.

HRMS (ESI) \( (m/z) \) \([\text{C}_{23}\text{H}_{24}\text{NOS}]^+\): Calcd. 362.1573, found, 362.1574.

IR (ATR): \( \nu = 3187, 3061, 2929, 226, 2107, 1906, 1678, 1600, 1492, 1447, 1361, 1299, 1222, 1151, 1080, 1016, 914, 841, 739, 695. \)

3-Methyl-1-propylbenzo[\(d\)]isothiazole 1-oxide (275l)

![3-Methyl-1-propylbenzo[\(d\)]isothiazole 1-oxide](image)

Light yellow oil, 16.8 mg, 80% yield. \( dr = 1:1. \)

\(^1\)H NMR (400 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.74 – 7.44 (m, 1.2H), 7.59 (td, \( J = 7.5, 1.0 \) Hz, 1.2H), 7.52 – 7.41 (m, 2.4H), 5.13 (dd, \( J = 13.6, 6.8 \) Hz, 0.2H), 4.88 (q, \( J = 6.8 \) Hz, 1H), 3.51 – 3.43 (m, 1.2H), 3.42 – 3.34 (m, 1.2H), 1.72 – 1.63 (m, 1.2H), 1.57 (d, \( J = 6.8 \) Hz, 3H), 1.51 – 1.39 (m, 1.8H), 1.04 (t, \( J = 7.4 \) Hz, 0.6H), 0.93 (t, \( J = 7.4 \) Hz, 3H).

\(^{13}\)C \{\(^1\)H\} NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 151.8, 135.2, 132.6, 130.0, 128.6, 126.2, 124.0, 123.6, 122.2, 122.0, 65.7, 64.7, 57.7, 57.0, 24.9, 23.1, 18.1, 17.4, 12.8, 12.7.

MS (EI, 70 eV): \( m/z \) (%) = 208.5 (1, M\(^+\)), 194.5 (24), 166.4 (17), 152.4 (100), 151.4 (22), 135.3 (14), 134.3 (68), 132.4 (17), 121.4 (43), 109.3 (14), 103.4 (11), 97.3 (11), 91.4 (11), 77.4 (18). MS (ESI) \([\text{M+H}]^+\): 210.09.

HRMS (ESI) \( (m/z) \) \([\text{C}_{11}\text{H}_{16}\text{NOS}]^+\): Calcd. 210.0947, found, 210.0947.

IR (ATR): \( \nu = 3573, 3061, 2935, 2870, 2321, 2115, 1826, 1679, 1583, 1448, 1212, 1092, 1025, 976, 950, 905, 859, 752, 699. \)

1-(2-Ethylphenyl)-3-phenyl-4,5-dihydro-3\(H\)-isothiazole 1-oxide (275n)

![1-(2-Ethylphenyl)-3-phenyl-4,5-dihydro-3\(H\)-isothiazole 1-oxide](image)

Light yellow oil, 13.1 mg, 46% yield. \( dr = 1:1. \)
$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 8.31 (dd, $J = 8.0$, 1.2 Hz, 1H), 8.18 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.58 – 7.53 (m, 4H), 7.48 – 7.42 (m, 4H), 7.39 – 7.33 (m, 6H), 7.29 – 7.26 (m, 2H), 5.37 – 5.31 (m, 1H), 4.95 (dd, $J = 8.0$, 6.1 Hz, 1H), 3.70 – 3.57 (m, 3H), 3.35 – 3.28 (m, 1H), 3.25 – 3.15 (m, 2H), 3.12 – 3.02 (m, 2H), 2.91 – 2.85 (m, 1H), 2.70 – 2.63 (m, 1H), 2.27 – 2.20 (m, 1H), 2.04 – 1.96 (m, 1H), 1.37 (td, $J = 7.5$, 3.3 Hz, 6H).

$^{13}$C {$^1$H} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 144.5, 144.4, 144.3, 144.2, 138.7, 138.2, 133.3, 130.7, 130.6, 129.7, 129.5, 128.4, 127.2, 127.1, 126.3, 126.2, 126.1, 70.6, 69.1, 56.7, 56.4, 35.3, 34.8, 26.5, 26.4, 15.5, 15.4.

MS (EI, 70 eV): $m/z$ (%) = 285.3 (12, M$^+$), 284.4 (47), 283.4 (21), 167.3 (14), 153.9 (11), 152.7 (15), 151.6 (20), 150.2 (16), 135.7 (52), 134.4 (100), 132.7 (25), 131.5 (37), 116.9 (27), 106.0 (19), 103.3 (38), 91.3 (35), 78.8 (10), 77.7 (25). MS (ESI) [M+H]$^+$: 286.13.

HRMS (ESI) ($m/z$) [C$_{17}$H$_{20}$NOS]$^+$: Calcd. 286.1260, found, 286.1260.

IR (ATR): $\nu$ = 3926, 3782, 3709, 3373, 2948, 2651, 2319, 2171, 2109, 1910, 1671, 1583, 1521, 1450, 1400, 1324, 1197, 1022, 912, 807, 752, 676.

3-Methyl-1-(3-phenylpropyl)benzo[d]isothiazole 1-oxide (275n$^+$)

Light yellow oil, 12.4 mg, 44% yield. $dr = 1:1$.

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.71 – 7.55 (m, 2.6H), 7.54 – 7.37 (m, 2.6H), 7.26 – 7.21 (m, 2.6H), 7.19 – 7.14 (m, 1.3H), 7.11 – 7.01 (m, 2.6H), 5.13 (q, $J = 6.7$ Hz, 0.3H), 4.88 (q, $J = 6.8$ Hz, 1H), 3.55 – 3.38 (m, 2.6H), 2.65 (dt, $J = 7.5$, 6.2 Hz, 2.6H), 2.01 – 1.95 (m, 1.3H), 1.75 – 1.66 (m, 1.3H), 1.57 (d, $J = 6.8$ Hz, 3H), 1.48 (d, $J = 6.8$ Hz, 0.9H).

$^{13}$C {$^1$H} NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 151.8, 140.0, 134.9, 132.7, 132.6, 128.7, 128.5, 128.3, 126.4, 124.1, 123.7, 122.2, 122.0, 65.7, 64.7, 55.2, 54.5, 34.1, 34.0, 25.9, 25.3, 24.9, 23.2.

MS (EI, 70 eV): $m/z$ (%) = 166.4 (13), 152.0 (33), 150.6 (30), 149.5 (14), 134.7 (13), 133.4 (17), 120.9 (14), 118.0 (70), 116.8 (55), 114.7 (11), 96.7 (11), 91.6 (53), 90.9 (100). MS (ESI) [M+H]$^+$: 286.13.

HRMS (ESI) ($m/z$) [C$_{17}$H$_{20}$NOS]$^+$: Calcd. 286.1260, found, 286.1260.
IR (ATR): ν = 3440, 3028, 2927, 2863, 2323, 2209, 2072, 1945, 1680, 1594, 1453, 1363, 1220, 1098, 1024, 980, 863, 749, 700.

Note: 275n and 275n’ could be separated by flash column chromatography.
Conditions for 275n: (ethyl acetate/ n-pentane = 1/4) and conditions for 275n’: (ethyl acetate/ n-pentane = 1/1).

1-(2,6-Dimethylphenyl)-3-phenyl-4,5-dihydro-3H-isothiazole 1-oxide (275o)

Light yellow oil, 10.1 mg, 35% yield. dr = 1:1.

1H NMR (400 MHz, CDCl3, mixture of diastereomers) δ 7.53 (d, J = 7.5 Hz, 1H), 7.38 – 7.20 (m, 5H), 7.14 (dd, J = 11.3, 7.6 Hz, 2H), 5.35 (t, J = 6.5 Hz, 0.5H), 4.88 (dd, J = 8.4, 6.0 Hz, 0.5H), 3.80 – 3.72 (m, 0.5H), 3.71 – 3.62 (m, 1H), 3.38 (td, J = 12.1, 8.4 Hz, 0.5H), 2.88 – 2.78 (m, 3.5H), 2.77 (s, 3H), 2.65 – 2.58 (m, 0.5H), 2.15 – 2.08 (m, 0.5H), 2.02 – 1.93 (m, 0.5H).

13C {1H} NMR (101 MHz, CDCl3, mixture of diastereomers) δ 144.6, 139.1, 138.2, 131.7, 131.4, 131.2, 128.4, 128.3, 127.1, 126.9, 126.3, 126.0, 70.2, 69.6, 58.8, 57.5, 33.7, 33.5, 23.4, 22.7.

MS (EI, 70 eV): m/z (%) = 153.4 (32), 152.4 (18), 151.4 (25), 135.3 (17), 132.4 (60), 125.4 (47), 117.4 (33), 115.4 (10), 105.4 (21), 104.3 (37), 103.3 (35), 92.4 (27), 91.4 (100), 79.4 (26), 78.4 (31), 77.4 (99). MS (ESI) [M+H]+: 286.13.

HRMS (ESI) (m/z) [C17H20NOS]+: Calcd. 286.1260, found, 286.1260.


7-Methyl-1-(3-phenylpropyl)benzo[d]isothiazole 1-oxide (275o’)

Light yellow oil, 10.2 mg, 36% yield.

1H NMR (600 MHz, CDCl3) δ 7.48 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.27 – 7.22 (m, 3H), 7.19 (t, J = 7.4 Hz, 1H), 7.08 – 7.05 (m, 2H), 4.91 (d, J = 17.1 Hz, 1H), 4.70 (d, J = 17.1 Hz, 1H), 3.66 – 3.59 (m, 1H), 3.55 – 3.47 (m, 1H), 2.76 – 2.68 (m, 1H), 2.63 – 2.57 (m, 1H), 2.48 (s, 3H), 1.97 – 1.91 (m, 1H), 1.58 – 1.50 (m, 1H).

13C {1H} NMR (151 MHz, CDCl3) δ 147.5, 140.0, 134.4, 133.0, 130.0, 128.6, 128.4,
126.4, 121.6, 57.9, 55.3, 33.9, 25.4, 17.2.

MS (EI, 70 eV): m/z (%) = 121.4 (28), 118.4 (27), 117.4 (36), 92.4 (11), 91.4 (100), 77.4 (20). MS (ESI) [M+H]^+: 286.13.

HRMS (ESI) (m/z) [C₁₇H₂₀NOS]^+: Calcd. 286.1260, found, 286.1259.


Note: 275o and 275o’ could be separated by flash column chromatography.

Conditions for 275o: (ethyl acetate/ n-pentane = 1/4) and conditions for 275o’: (ethyl acetate/ n-pentane = 1/1 to 2/1).
6. Photocatalyzed difunctionalizations of alkenes with N–SCN sulfoximines

Organic thiocyanates are important motifs and precursors in organic chemistry.[88] For instance, thiocyanates are often used as intermediates in the synthesis of sulfur-containing compounds,[89] such as thiols,[90] thioethers,[91] disulfides,[92] isothiocyanates,[93] trifluoromethylthiolate,[94] thiocarbamates[95] and phosphonothioates.[96] Our research group is committed to the study of sulfoximines, developing synthetic methods for N–CN,[97] N–halogen,[98] N–CF₃,[99] N–SCF₃[98] sulfoximines and sulfoximidoyl-containing hypervalent iodine reagents.[100]

6.1 Results and discussion

6.1.1 Research objective

Here, we demonstrate the synthesis of new NCR precursors (N–SCN sulfoximines) as thiocyanosulfoximidation reagents and demonstrate their use in photocatalyzed difunctionalizations of alkenes under the appropriate conditions (Scheme 63 and Scheme 64).

![Scheme 63: Synthesis of the N–SCN sulfoximines 279](image1)

![Scheme 64: Photocatalytic difunctionalizations of alkenes with N–SCN sulfoximines](image2)

6.1.2 Synthesis of the N–SCN sulfoximines

Based on previous observations, N–Br sulfoximines (Table 3, 278a-k) and ammonium thiocyanate were chosen as substrates. N–SCN sulfoximines were synthesized under ambient conditions. Generally, the N–SCN sulfoximines (279a-k) were obtained in yields ranging from 51 to 90%.
Table 3: Synthesis of the N-SCN sulfoximines\textsuperscript{a}

![Chemical structures](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Products (279a-k)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>278a - 279a</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>278b - 279b</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>278c - 279c</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>278d - 279d</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>278e - 279e</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>278f - 279f</td>
<td>68</td>
</tr>
<tr>
<td>7</td>
<td>278g - 279g</td>
<td>51</td>
</tr>
<tr>
<td>8</td>
<td>278h - 279h</td>
<td>69</td>
</tr>
</tbody>
</table>
6.1.3 Optimization of the reaction conditions

For the initial screening and optimization of the reaction conditions, \(N\)-SCN sulfoximine 279a and styrene (110a) were chosen as substrates. In the initial screening, different photocatalysts were tested in DCM (Table 4, entries 1-4). Among them, Ir(ppy)₃ (ppy = 2-phenylpyridine) exhibited the best results under the conditions given in entry 4 of Table 4 (78% yield). Changing the solvent to either DCE, MeCN or tetrahydrofuran (THF), resulted in lower yields than DCM (Table 4,
entries 5-7). In the absence of the photocatalyst, no product was detected (Table 4, entry 8). Increasing the concentration from 0.05 M to 0.1 M and 0.2 M resulted in lower yields of 65% and 56%, respectively (Table 4, entry 9). Without blue-LED irradiation or iridium catalyst, no reaction occurred (Table 4, entries 10-11).

**Table 4. Optimization of reaction conditions**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru(bpy)_3(PF_6)_2</td>
<td>DCM</td>
<td>24</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>Ir(ppy)_3</td>
<td>DCM</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>Ir-[dF(CF_3)ppy]_2(dtbbpy)PF_6</td>
<td>DCM</td>
<td>24</td>
<td>n.d.</td>
</tr>
<tr>
<td>4</td>
<td>Ir(ppy)_3</td>
<td>DCM</td>
<td>40</td>
<td>78 (72)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>Ir(ppy)_3</td>
<td>DCE</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>Ir(ppy)_3</td>
<td>MeCN</td>
<td>40</td>
<td>42</td>
</tr>
<tr>
<td>7</td>
<td>Ir(ppy)_3</td>
<td>THF</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>--</td>
<td>DCM</td>
<td>40</td>
<td>n.d.</td>
</tr>
<tr>
<td>9</td>
<td>Ir(ppy)_3</td>
<td>DCM</td>
<td>40</td>
<td>64,&lt;sup&gt;d&lt;/sup&gt; 56&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>Ir(ppy)_3</td>
<td>DCM</td>
<td>40</td>
<td>n.d.&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>--</td>
<td>DCM</td>
<td>40</td>
<td>n.d.&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: **279a** (31.8 mg, 0.15 mmol, 1.0 equiv.), **110a** (78.2 mg, 0.75 mmol, 5.0 equiv), photocatalyst (1.0 mol%), DCM (3.0 mL) under argon with 5 W blue-LEDs as the visible light source at room temperature. n.d. = no detected. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy with CH_2Br_2 as the internal standard. <sup>c</sup>After column chromatography. <sup>d</sup>Solvent (0.10 M). <sup>e</sup>Solvent (0.15 M). <sup>f</sup>In the dark at 80 °C.

### 6.1.4 Substrate scope of N–SCN sulfoximines
We explored the scope of difunctionalizations by assaying the reactions of styrenes 110 (Table 5). In general, styrenes with different substituents on the phenyl were found to be feasible for this photoredox reaction providing the corresponding products (Table 5, 280aa-ak) in moderate to good yields. The ortho-, meta- and para-substituted styrenes afforded products 280ab-ad in yields ranging from 38% to 52% (entries 2-4). It is also noteworthy that styrenes with various substituents in the para position of the S-aryl group reacted well, leading to products 280ae-aj in moderate yield (entries 5-10). Lastly, the sterically hindered 2,4,6-trimethylstyrene gave 280ak in 33% yield.

Table 5: Photocatalyzed addition of N–thiocyanato sulfoximine 279a to styrene 110a

<table>
<thead>
<tr>
<th>Entry</th>
<th>R, 110a-k</th>
<th>Products (280aa-ak)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H, 110a</td>
<td>280aa</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>o-Me, 110b</td>
<td>280ab</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>m-Me, 110c</td>
<td>280ac</td>
<td>51</td>
</tr>
<tr>
<td>4</td>
<td>p-Me, 110d</td>
<td>280ad</td>
<td>52</td>
</tr>
<tr>
<td>5</td>
<td>tBu, 110e</td>
<td>280ae</td>
<td>60</td>
</tr>
</tbody>
</table>
Next, we studied the scope of the $N$–SCN sulfoximines (Table 6). A range of $N$–SCN sulfoximines were tolerated in this reaction (Table 6, entries 1-11). Substrates bearing an electron-donating or -withdrawing substituent on the para position of the S-aryl group reacted well, giving the corresponding products 280ba-280fa (entries 1-5) in yields ranging from 55% to 81%. Notably, the difunctionalization reagents with steric hinderance also reacted easily with styrene, providing the desired products 280ga-280la in moderate yields (entries 6-11). $N$–SCN S-Phenyl-S-ethyl sulfoximine 279m gave product 280ma in 46% yield (entry12). $N$–SCN S-Phenyl-S-ethyl sulfoximine 279n led to 280na in 55% yield (entry13).
Table 6: Photocatalysed addition of N-thiocyanation sulfoximines 279 to styrene$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>R, 279b-n</th>
<th>Products (280ba-na)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>p-MeO, 279b</td>
<td><img src="" alt="280ba" /></td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>p-Me, 279c</td>
<td><img src="" alt="280ca" /></td>
<td>71</td>
</tr>
<tr>
<td>3</td>
<td>p-Br, 279d</td>
<td><img src="" alt="280da" /></td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>p-Cl, 279e</td>
<td><img src="" alt="280ea" /></td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>p-F, 279f</td>
<td><img src="" alt="280fa" /></td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>m-MeO, 279g</td>
<td><img src="" alt="280ga" /></td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>m-Br, 279h</td>
<td><img src="" alt="280ha" /></td>
<td>44</td>
</tr>
</tbody>
</table>
8 \( m\)-Cl, 279i

\[
\begin{array}{c}
\text{SCN} \\
\text{Ph} \\
\text{N} \\
\text{Me} \\
\text{Cl}
\end{array}
\]

280ia

9 \( o\)-Br, 279j

\[
\begin{array}{c}
\text{SCN} \\
\text{Ph} \\
\text{N} \\
\text{Me} \\
\text{Br}
\end{array}
\]

280ja

10 \( o\)-Cl, 279k

\[
\begin{array}{c}
\text{SCN} \\
\text{Ph} \\
\text{N} \\
\text{Me} \\
\text{Cl}
\end{array}
\]

280ka

11 3,5-Cl\(_2\), 279l

\[
\begin{array}{c}
\text{SCN} \\
\text{Ph} \\
\text{N} \\
\text{Me} \\
\text{Cl}
\end{array}
\]

280la

12 \( 279m \)

\[
\begin{array}{c}
\text{SCN} \\
\text{Ph} \\
\text{N} \\
\text{Me} \\
\text{Ph}
\end{array}
\]

280ma

13 \( 279n \)

\[
\begin{array}{c}
\text{SCN} \\
\text{Ph} \\
\text{N} \\
\text{Me} \\
\text{Ph}
\end{array}
\]

280na

\(^{279}\) (0.15 mmol, 1.0 equiv), 110a (78.2 mg, 0.75 mmol, 5.0 equiv), fac-Ir(ppy)_3 (1.0 mg, 1.0 mol%), DCM (0.05 M) under argon with 5 W blue-LED irradiation as the visible light source at room temperature for 40 h, yields after column chromatography.

6.1.6 Plausible mechanism

On the basis of control experiments and previous reports,\(^{[5, 102]}\) we proposed the mechanism shown in Scheme 6.5. It involves an initiation by the excitation of PC with blue light. The excited photocatalyst can subsequently reduce the N–SCN S-phenyl-S-methyl sulfoximine 279, formally oxidizing the fac-*Ir(ppy)_3 (PC*) to fac-Ir(ppy)_3\(^{3+}\) (PC\(^{3+}\)). The generated radical B is sufficiently nucleophilic to add to
styrene 110. Then, radical B can be oxidized to a carbocation by $\text{fac-Ir(ppy)$_3$$}^{+}$ (PC$^+$) to complete the catalytic cycle and generate the ATRT products 280 through nucleophilic trapping of the SCN anion. In the control experiment, diphenyl disulfide was added to the reaction, which gave product 281 in 12% yield (Figure 6, eq. 1). Formation of product 281 showed that the reaction went through a free radical addition.

Scheme 65: Plausible mechanism

6.1.7 Applications

Finally, to demonstrate the synthetic potential of the products, 280aa was explored as a representative starting material (Scheme 66). Accordingly, compound 280aa was reduced with LiAlH$_4$ and then reacted with benzyl bromide under air to give sulfide 283 in 78% yield (Scheme 66, eq. 1). Furthermore, 280aa was used to produce the asymmetric disulfide compound 285 under microwave irradiation in 32% yield (Scheme 66, eq. 2).
6.1.8 Summary
In summary, a series of $N$–SCN sulfoximines was synthesized in moderate to good yields. $N$–SCN sulfoximines can be used in the photocatalyzed difunctionalization as NCR precursors, successfully granting access to the products. The mechanism of the reaction has been proposed as an ATRA reaction, and the applications illustrate the synthetic value of the products.

6.2 Experimental

6.2.1 General information
Visible light was provided by irradiation with blue-LEDs (5 W, 455 nm). The microwave reactor (CEM Discover) was purchased from CEM Company. The respective temperature (90 °C) was measured externally. $N$–Bromo sulfoximines 278 were prepared according to literature procedures.[98]

6.2.2 General procedures and characterization data
Synthesis of $N$–SCN sulfoximines, using $N$–Br sulfoximines 278 as starting materials

Scheme 66: Synthetic transformations of 280aa
*N*-Bromo sulfoximine 278 (0.2 mmol) and NH₄SCN (22.8 mg, 0.3 mmol, 1.5 equiv) were added to a 5.0 mL sealable reaction tube. Then, DCM (1.0 mL) was added and the reaction was stirred for 16 h at 25 °C in air. The product was purified by flash column chromatography (ethyl acetate/ n-pentane = 1/4 to 1/1) to give the corresponding *N*-SCN sulfoximines 279.

Note: The *N*-SCN sulfoximines were transferred to the small glass bottle. Then, they were kept under vacuum until they were used in the next step.

**Synthesis of *N*-SCN sulfoximines, using *N*-H sulfoximines 260 as starting materials**

The *N*-H sulfoximine (0.2 mmol), NH₄SCN (22.8 mg, 0.3 mmol, 1.5 equiv) and NBS (0.24 mmol, 42.7 mg, 1.2 equiv) were added to a 5.0 mL sealable reaction tube. Then, DCM (1.0 mL) was added and the reaction was stirred for 16 h at 25 °C in air.

**General method for the synthesis of 280 (as illustrated for 280aa)**

Under argon, freshly prepared *N*-SCN sulfoximine 279a (31.8 mg, 0.15 mmol, 1.0 equiv), styrene 110a (78.2 mg, 0.75 mmol, 5.0 equiv) and fac-[Ir(ppy)₃] (1.0 mg, 1.0 mol%, 0.01 equiv) were added into a 5.0 mL sealable reaction tube. Then, DCM (3 mL, 0.05 mL·mmol⁻¹ of *N*-SCN sulfoximine) was added, and the mixture was stirred under argon with blue-LED irradiations (5 W) at room temperature for 40 h. Subsequently, the product was purified by flash column chromatography (ethyl acetate/ n-pentane = 1/2) to give 280aa in 72% yield. The diastereomeric ratio of 280 was determined by ¹H NMR of the crude product mixture.

Note: In all reactions freshly prepared *N*-SCN sulfoximines were used.

**Transformations of 280aa into thioether 283 and disulfide 285**

[(2-(Benzylthio)-2-phenylethyl)imino](methyl)(phenyl)-2₆-sulfanone (283)

A mixture of 280aa (15.6 mg, 0.05 mmol), lithium aluminum hydride (5.4 mg, 0.14 mmol), benzylbromide (15.0 uL, 0.125 mmol) in THF (0.6 mL) was stirred in air at room temperature for 48 h. Purification by column chromatography (n-pentane: ethyl acetate = 2:1) gave 14.8 mg (78%) of product 283 as a light yellow oil.
Note: The protocol followed a literature procedure applied for converting related compounds. Accordingly, we expected to isolate the corresponding dimerized disulfide. That product, however, remained undetected.

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.80 (d, $J = 7.7$ Hz, 1H), 7.56 (dd, $J = 16.5$, 7.5 Hz, 2H), 7.50 (t, $J = 7.7$ Hz, 1H), 7.42 (t, $J = 7.7$ Hz, 1H), 7.33 – 7.18 (m, 10H), 3.98 – 3.86 (m, 1H), 3.60 – 3.48 (m, 2H), 3.44 – 3.38 (m, 1H), 3.22 – 3.07 (m, 1H), 2.97 (s, 3H).

$^{13}$C {1H} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 141.2, 141.0, 139.3, 139.0, 138.3, 132.9, 132.7, 129.4, 129.3, 129.0, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 127.2, 127.1, 126.8, 126.8, 52.0, 51.6, 49.5, 49.5, 45.0, 44.8, 35.7, 35.7. MS (EI, 70 eV): $m/z$ (%) = 168.0 (78), 141.0 (53), 125.0 (16), 124.0 (12), 121.0 (14), 104.1 (12), 91.1 (100). MS (ESI) [M+Na]$^+$: 404.11

HRMS (ESI) ($m/z$) [C$_{22}$H$_{23}$NOS$_2$Na]$^+$: Calcd. 404.1119. found, 404.1096.

IR (ATR): $\nu$ = 3570, 3027, 2917, 2845, 2667, 2330, 2108, 1900, 1815, 1726, 1595, 1489, 1447, 1239, 1136, 1082, 974, 737, 696.

[(2-(Hexylthio)-2-phenylethyl)imino](methyl)(phenyl)-$\lambda^6$-sulfanone (285)

A mixture of 280aa (15.6 mg, 0.05 mmol), 1-bromohexane (12.4 mg, 0.075 mmol), thiourea (4.6 mg, 0.06 mmol), $K_3$PO$_4$ (12.7 mg, 0.06 mmol), KI (12.4 mg, 0.075 mmol) and TBAH (49.0 mg, 0.075 mmol, 40% in water) in water (1.0 mL) was put into the cavity of the microwave reactor (with a power of 50 W at 90 °C for 10 min). Then, the reaction mixture was extracted by DCM (3 x 2.0 mL). The combined organic extract was concentrated, and the product was purified by column chromatography (n-pentane : ethyl acetate = 2:1) to give 6.5 mg (32%) of 285 as a light yellow oil.

Note: The protocol followed a procedure reported in the literature.$^{[103]}$
H NMR (600 MHz, CDCl3, mixture of diastereomers) δ 7.89 – 7.86 (m, 1H), 7.72 – 7.69 (m, 1H), 7.62 – 7.47 (m, 4H), 7.31 – 7.26 (m, 4H), 4.11 – 4.03 (m, 1H), 3.63 (dd, J = 12.7, 5.9 Hz, 0.5H), 3.51 (dd, J = 12.8, 6.8 Hz, 0.5H), 3.39 (dd, J = 12.8, 7.5 Hz, 0.5H), 3.27 (dd, J = 12.6, 8.7 Hz, 0.5H), 3.03 (d, J = 4.4 Hz, 3H), 2.35 – 2.29 (m, 1H), 2.19 – 2.15 (m, 1H), 1.51 – 1.42 (m, 2H), 1.28 – 1.23 (m, 4H), 1.20 – 1.17 (m, 2H), 0.87 – 0.85 (m, 3H).

13C {1H} NMR (151 MHz, CDCl3, mixture of diastereomers) δ 140.2, 132.9, 132.8, 129.4, 129.3, 128.7, 128.6, 128.5, 128.3, 128.2, 127.4, 57.9, 57.6, 48.2, 47.5, 45.0, 45.0, 38.9, 38.7, 31.3, 28.9, 28.1, 22.5, 14.0.

MS (EI, 70 eV): m/z (%) = 258.0 (52), 168.0 (80), 141.0 (100), 125.0 (16), 124.0 (13), 91.1 (33). MS (ESI) [M+H]+: 408.15

HRMS (ESI) (m/z) [M+Na]+: Calcd. 408.1490. found, 408.1484.


Characterization Data

**Methyl(phenyl)(thiocyanatoimino)-6-sulfanone (279a)**

Colourless oil, 38.2 mg, 90% yield,

1H NMR (600 MHz, CDCl3) δ 7.94 – 7.89 (m, 2H), 7.75 (t, J = 7.5 Hz, 1H), 7.66 (t, J = 7.9 Hz, 2H), 3.31 (s, 3H).

13C NMR (151 MHz, CDCl3) δ 135.8, 134.8, 130.0, 128.6, 115.3, 43.8, 43.8.

MS (EI, 70 eV): m/z (%) = 212.0 (100, M+), 186.0 (14), 156.0 (15), 140.1 (90), 125.0 (76), 97.1 (22), 77.2 (25).

HRMS (ESI) (m/z) [M+Na]+: Calcd. [C8H8N2O3SNa]+: 234.9976, found, 234.9977.

IR (ATR): ν = 3524, 3008, 2918, 2326, 2193, 2132, 2053, 1925, 1740, 1571, 1448, 1321, 1217, 1091, 973, 744, 678.

**(4-Methoxyphenyl)(methyl)(thiocyanatoimino)-6-sulfanone (279b)**
Colourless oil, 25.1 mg, 52% yield,
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.83 (dd, \(J = 8.8, 1.5 \text{ Hz}, 2\text{H})\), 7.10 (dd, \(J = 8.8, 1.5 \text{ Hz}, 2\text{H})\), 3.91 (d, \(J = 1.5 \text{ Hz}, 3\text{H})\), 3.28 (d, \(J = 1.5 \text{ Hz}, 3\text{H})\).
\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 164.6, 130.9, 126.4, 115.5, 115.2, 55.9, 44.2.
MS (EI, 70 eV): \(m/\ell\) \(\%\) = 242.0 (9, M\(^+\)), 155.1 (100), 76.3 (3).
HRMS (ESI) (m/z) [M+Na]\(^+\): Calcd. [C\(_9\)H\(_{10}\)N\(_2\)O\(_2\)S\(_2\)Na]\(^+\): 265.0081, found, 265.0077.
IR (ATR): \(\nu\) = 3492, 3002, 2914, 2666, 2299, 2054, 1910, 1638, 1546, 1447, 1400, 1322, 1219, 1101, 1007, 843, 743, 681.

Methyl(thiocyanatoimino)(\(p\)-toly)-\(\lambda^6\)-sulfanone (279c)

Colourless oil, 26.2 mg, 58% yield,
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.79 (d, \(J = 8.4 \text{ Hz}, 2\text{H})\), 7.45 (d, \(J = 8.2 \text{ Hz}, 2\text{H})\), 3.29 (s, 3H), 2.48 (s, 3H).
\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 146.1, 132.6, 130.6, 128.6, 115.4, 44.0, 21.8.
MS (EI, 70 eV): \(m/\ell\) \(\%\) = 226.0 (18, M\(^+\)), 194.1 (18), 139.0 (64), 91.2 (29), 77.2 (23), 65.3 (57), 63.2 (41), 58.2 (13), 46.2 (100).
HRMS (ESI) (m/z) [M+Na]\(^+\): Calcd. [C\(_9\)H\(_{10}\)N\(_2\)OS\(_2\)Na]\(^+\): 249.0232, found, 249.0127.
IR (ATR): \(\nu\) = 3893, 3745, 2922, 2344, 2095, 1746, 1597, 1397, 1215, 1091, 969, 795, 692.

(4-Bromophenyl)(methyl)(thiocyanatoimino)-\(\lambda^6\)-sulfanone (279d)

Colourless oil, 44.1 mg, 76% yield,
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 – 7.73 (m, 4H), 3.29 (s, 3H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 134.8, 133.3, 130.4, 130.1, 115.0, 43.9.
MS (EI, 70 eV): \(m/\ell\) \(\%\) = 289.9 (72, M\(^+\)), 219.9 (100), 218.0 (97), 204.9 (80), 202.9 (78), 156.9 (16), 155.0 (16), 75.2 (28), 50.2 (40).
HRMS (ESI) (m/z) [M+Na]\(^+\): Calcd. [C\(_8\)H\(_7\)N\(_2\)OS\(_2\)BrNa]\(^+\): 312.9081, found, 312.9076.
IR (ATR): \(\nu\) = 3876, 2913, 2337, 2101, 1740, 1528, 1349, 1221, 1094, 975, 854, 728.
(4-Chlorophenyl)(methyl)(thiocyanatoimino)-2₆-sulfanone (279e)

![Chemical Structure]

Colourless oil, 31.9 mg, 65% yield,

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.88 – 7.80 (m, 2H), 7.66 – 7.56 (m, 2H), 3.30 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl₃) \(\delta\) 141.8, 134.2, 130.3, 130.0, 115.0, 43.9.

MS (EI, 70 eV): \(m/z\) (%) = 245.9 (85, M\(^+\)), 176.0 (41), 174.0 (85), 160.9 (52), 158.9 (100), 130.9 (19), 128.0 (20), 126.0 (12), 111.0 (19).

HRMS (ESI) (\(m/z\)) [M+Na]\(^+\): Calcd. [C₈H₇N₂O₂S₂ClNa]\(^+\): 252.9882, found 252.9878.

IR (ATR): \(\nu\) = 3542, 3299, 3078, 3016, 2923, 2661, 2310, 2134, 2055, 1915, 1573, 1472, 1395, 1318, 1218, 1085, 975, 829, 773, 685.

(4-Fluorophenyl)(methyl)(thiocyanatoimino)-2₆-sulfanone (279f)

![Chemical Structure]

Colourless oil, 31.1 mg, 68% yield,

\(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 7.97 – 7.92 (m, 2H), 7.34 (t, \(J\) = 8.5 Hz, 2H), 3.32 (s, 3H).

\(^{13}\)C NMR (151 MHz, CDCl₃) \(\delta\) 166.4 \(J\) = 258 Hz), 131.6 \(J\) = 10.5 Hz), 131.5 \(J\) = 3 Hz, 117.5 \(J\) = 22.5 Hz), 115.1, 44.0.

MS (EI, 70 eV): \(m/z\) (%) = 230.0 (6, M\(^+\)), 158.0 (34), 143.0 (58), 110.1 (97), 95.2 (68), 83.1 (48), 75.2 (55), 63.2 (23), 59.2 (33), 50.2 (46), 46.2 (100).

HRMS (ESI) (\(m/z\)) [M+Na]\(^+\): Calcd. [C₈H₇N₂O₂F₂Na]\(^+\): 268.9586, found 268.9581.


(3-Methoxyphenyl)(methyl)(thiocyanatoimino)-2₆-sulfanone (279g)

![Chemical Structure]

Colourless oil, 24.7 mg, 51% yield,

\(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 7.55 (td, \(J\) = 8.1, 1.9 Hz, 1H), 7.47 (d, \(J\) = 7.7 Hz, 1H), 7.39 (d, \(J\) = 1.4 Hz, 1H), 7.25 (d, \(J\) = 8.3 Hz, 1H), 3.90 (d, \(J\) = 2.0 Hz, 3H), 3.30 (d, \(J\) = 1.9 Hz, 3H).
\[ ^{13} \text{C NMR (151 MHz, CDCl}_3 \] \delta 160.5, 136.9, 131.0, 121.4, 120.6, 115.3, 112.9, 55.9, 55.9, 43.9, 43.9.

**MS (EI,70 eV): m/z (%) = 242.2 (7, M+), 155.0 (19), 124.1 (11), 95.1 (13), 92.1 (40), 78.2 (13), 77.1 (50), 64.2 (58), 63.2 (81), 46.1 (100).**

**HRMS (ESI) (m/z) [M+Na]⁺: Calcd. [C\(_{9}\)H\(_{10}\)N\(_2\)O\(_2\)S\(_2\)Na]⁺ 265.0081, found 265.0079.**

**IR (ATR): \( \nu = 3743, 3625, 3303, 3073, 3015, 2924, 2666, 2320, 2134, 1993, 1904, 1741, 1570, 1461, 1405, 1318, 1295, 977, 778, 680.**

**3-Bromophenyl)(methyl)(thiocyanatoimino)\(-\lambda^6\)-sulfanone (279h)**

Colourless oil, 40.1 mg, 69% yield,

\[ ^{1} \text{H NMR (600 MHz, CDCl}_3 \] \( \delta 8.07 \text{ (t, } J = 1.7 \text{ Hz, 1H)}, 7.90 – 7.81 \text{ (m, 2H)}, 7.54 \text{ (t, } J = 8.0 \text{ Hz, 1H)}, 3.33 \text{ (s, 3H).}

\[ ^{13} \text{C NMR (151 MHz, CDCl}_3 \] \( \delta 137.9, 137.7, 131.5, 131.4, 127.1, 124.0, 114.9, 43.8, 43.8.

**MS (EI,70 eV): m/z (%) = 289.9 (56, M⁺), 219.9 (100), 218.0 (90), 204.9 (74), 202.9 (72), 156.9 (15), 155.0 (15), 75.2 (30), 50.2 (36).**

**HRMS (ESI) (m/z) [M+Na]⁺: Calcd. [C\(_{8}\)H\(_{7}\)N\(_2\)OS\(_2\)BrNa]⁺ 312.9081, found 312.9075.**

**IR (ATR): \( \nu = 3616, 3021, 2924, 2341, 2116, 1743, 1570, 1406, 1217, 1095, 968, 776, 689.**

**3-Chlorophenyl)(methyl)(thiocyanatoimino)-\(\lambda^6\)-sulfanone (279i)**

Colourless oil, 32.4 mg, 66% yield,

\[ ^{1} \text{H NMR (400 MHz, CDCl}_3 \] \( \delta 7.90 \text{ (dd, } J = 5.5, 1.6 \text{ Hz, 1H)}, 7.79 \text{ (t, } J = 7.2 \text{ Hz, 1H)}, 7.70 \text{ (t, } J = 7.2 \text{ Hz, 1H)}, 7.65 – 7.55 \text{ (m, 1H)}, 3.31 \text{ (s, 3H).}

\[ ^{13} \text{C NMR (101 MHz, CDCl}_3 \] \( \delta 137.6, 136.3, 134.9, 131.2, 128.6, 126.6, 114.9, 43.8.

**MS (EI,70 eV): m/z (%) =176.1 (18), 174.1 (54), 161.1 (14), 159.1 (36), 131.1 (22), 128.2 (28), 126.1 (36), 113.1 (21), 111.1 (67), 99.2 (21), 45.3 (100).**

**HRMS (ESI) (m/z) [M+Na]⁺: Calcd. [C\(_{8}\)H\(_{7}\)N\(_2\)OS\(_2\)ClNa]⁺ 268.9586, found 268.9581**
IR (ATR): $\nu = 3867, 3532, 3298, 3013, 2921, 2657, 2319, 2127, 2063, 1898, 1636, 1574, 1460, 1408, 1318, 1220, 1115, 976, 788, 678.$

**(2-Bromophenyl)(methyl)(thiocyanatoimino)-$\lambda^6$-sulfanone (279j)**

![2-Bromophenyl](image)

Colourless oil, 46.4 mg, 80% yield,

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.82 (d, $J = 7.8$ Hz, 1H), 7.70 – 7.48 (m, 2H), 3.54 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 136.1, 135.8, 134.8, 133.4, 128.6, 120.7, 114.1, 41.9.

MS (EI, 70 eV): $m/z$ (%) = 289.9 (99, M$^+$), 220.0 (100), 218.0 (100), 204.9 (86), 202.9 (86), 139.1 (61), 75.2 (26).

HRMS (ESI) ($m/z$) [M+Na]$^+$: Calcd. [C$_8$H$_7$N$_2$OS$_2$BrNa]$^+$ 312.9081, found 312.9075

IR (ATR): $\nu = 3624, 3305, 3083, 3010, 2925, 2329, 2136, 2055, 1917, 1738, 1632, 1568, 1434, 1315, 1217, 1097, 1029, 975, 758, 681.$

**(2-Chlorophenyl)(methyl)(thiocyanatoimino)-$\lambda^6$-sulfanone (279k)**

![2-Chlorophenyl](image)

Colourless oil, 30.1 mg, 61% yield,

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.24 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.69 (td, $J = 7.8, 1.5$ Hz, 1H), 7.65 – 7.57 (m, 2H), 3.53 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 136.0, 133.1, 133.0, 132.5, 132.4, 128.0, 114.2, 42.2, 42.2.

MS (EI, 70 eV): $m/z$ (%) = 245.9 (8, M$^+$), 176.0 (6), 174.0 (18), 161.0 (10), 159.0 (27), 133.0 (6.2), 131.0 (18), 76.2 (12), 75.1 (64), 741.1 (19), 63.1 (34), 50.2 (68), 46.1 (100).

HRMS (ESI) ($m/z$) [M+Na]$^+$: Calcd. [C$_8$H$_7$N$_2$OS$_2$ClNa]$^+$ 268.9586, found 268.9583.

IR (ATR): $\nu = 3899, 3743, 3621, 3525, 3013, 2929, 2677, 2316, 2114, 1999, 1901, 1741, 1589, 1540, 1368, 1218, 1094, 975, 808, 763, 692.$

**(3,5-Dichlorophenyl)(methyl)(thiocyanatoimino)-$\lambda^6$-sulfanone (279l)**

![3,5-Dichlorophenyl](image)
Colourless oil, 47.0 mg, 84% yield, 
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 1.8$ Hz, 2H), 7.71 (t, $J = 1.6$ Hz, 1H), 3.35 (s, 3H).
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 138.9, 137.1, 134.8, 126.9, 114.6, 43.8, 43.8.
MS (EI,70 eV): $m/z$ (%) = 279.9 (18, M$^+$), 209.9 (25), 207.9 (37), 194.9 (30), 192.9 (44), 163.9 (17), 161.9 (28), 147.1 (12), 145.0 (23), 111.0 (16), 109.0 (38), 75.1 (68), 46.2 (100).
HRMS (ESI) (m/z) [M+Na]$^+$: Calcd. [C$_8$H$_6$N$_2$OS$_2$Cl$_2$Na]$^+$ 302.9196, found 302.9193.
IR (ATR): $\nu$ = 3893, 3742, 3614, 2961, 2334, 2098, 1897, 1722, 1532, 1360, 1247, 1118, 1001, 864, 764.

Diphenyl(thiocyanatoimino)-$\lambda^6$-sulfanone (279m)

Colourless oil, 42.2 mg, 77% yield, 
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 7.3$ Hz, 4H), 7.64 (d, $J = 6.1$ Hz, 2H), 7.58 (d, $J = 7.1$ Hz, 4H).
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 137.6, 134.2, 129.7, 128.5, 115.2.
MS (EI,70 eV): $m/z$ (%) = 274.0 (100, M$^+$), 202.0 (93), 186.1 (15), 174.0 (34), 154.1 (74), 109.1 (38), 77.2 (23).
HRMS (ESI) (m/z) [M+Na]$^+$: Calcd. [C$_{13}$H$_{10}$N$_2$OS$_2$Na]$^+$ 297.0132, found 297.0128.

Ethyl(phenyl)(thiocyanatoimino)-$\lambda^6$-sulfanone (279n)

Colourless oil, 35.3 mg, 78% yield, 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 – 7.83 (m, 2H), 7.76 – 7.69 (m, 1H), 7.67 – 7.61 (m, 2H), 3.51 – 3.28 (m, 2H), 1.28 (t, $J = 7.4$ Hz, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.7, 133.8, 129.9, 129.3, 115.4, 50.5, 71.1.
MS (EI,70 eV): $m/z$ (%) = 226.0 (73, M$^+$), 154.0 (37),126.0 (100), 125.0 (38), 78.2 (37), 77.2 (26).
HRMS (ESI) (m/z) [M+Na]$^+$: Calcd. [C$_9$H$_{10}$N$_2$OS$_2$Na]$^+$ 249.0132, found 249.0126.
IR (ATR): $\nu$ = 3854, 3745, 3462, 2930, 2314, 2061, 1901, 1741, 1547, 1450, 1365, 1218, 1099, 960, 734, 677.
Methyl(phenyl)[(2-phenyl-2-thiocyanatoethyl)imino]-λ⁶-sulfanone (280aa)

Light yellow oil, 34.2 mg, 72% yield. $dr = 1:1$.

$^1$H NMR (400 MHz, CDCl₃, mixture of diastereomers) $\delta$ 7.89 – 7.78 (m, 2H), 7.66 – 7.49 (m, 3H), 7.39 – 7.26 (m, 5H), 4.81 – 4.54 (m, 1H), 3.59 – 3.50 (m, 1H), 3.41 – 3.30 (m, 1H), 3.09 (d, $J = 8.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl₃, mixture of diastereomers) $\delta$ 138.9, 138.6, 137.4, 137.3, 133.3, 133.3, 129.6, 129.6, 128.9, 128.8, 128.5, 128.4, 128.0, 127.8, 112.3, 112.3, 56.9, 55.9, 48.5, 48.4, 45.1, 44.8.

MS (EI, 70 eV): $m/z$ (%) = 287.0 (20), 168.0 (100), 141.0 (61), 132.0 (19), 125.0 (19), 77.1 (19). MS (ESI) [M+H]$^+$: 317.08.

HRMS (ESI) ($m/z$) [C$_{16}$H$_{17}$N$_2$O$_2$]$^+$: Calcd. 317.0782, found, 317.0761.

IR (ATR): $\nu = 3522, 3011, 2926, 2838, 2607, 2337, 2143, 2092, 1907, 1785, 1607, 1510, 1448, 1238, 1139, 1029, 973, 892, 833, 743.$

Methyl(phenyl)[[2-thiocyanato-2-(o-tolyl)ethyl]imino]-λ⁶-sulfanone (280ab)

Light yellow oil, 18.8 mg, 38% yield, $dr = 1:1$.

$^1$H NMR (400 MHz, CDCl₃, mixture of diastereomers) $\delta$ 7.95 – 7.81 (m, 2H), 7.68 – 7.49 (m, 3H), 7.35 – 7.22 (m, 1H), 7.21 – 7.12 (m, 3H), 4.87 – 4.71 (m, 1H), 3.62 – 3.52 (m, 1H), 3.48 – 3.35 (m, 1H), 3.10 (d, $J = 12.5$ Hz, 3H), 2.36 (d, $J = 2.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl₃, mixture of diastereomers) $\delta$ 139.2, 138.6, 136.5, 136.3, 135.1, 133.3, 133.2, 130.8, 130.8, 129.7, 129.6, 128.6, 128.4, 126.7, 126.7, 126.6, 126.5, 112.1, 52.8, 51.5, 48.3, 48.2, 45.1, 44.8.

MS (EI, 70 eV): $m/z$ (%) = 168.0 (100), 141.0 (63), 77.1 (18). MS (ESI) [M+H]$^+$: 331.09.

HRMS (ESI) ($m/z$) [C$_{17}$H$_{19}$N$_2$O$_2$]$^+$: Calcd. 331.0939. found, 331.0936.

IR (ATR): $\nu = 3533, 3019, 2924, 2849, 2334, 2147, 1997, 1911, 1736, 1591, 1450, 1235, 1140, 1087, 973, 887, 742, 688.$

Methyl(phenyl)[[2-thiocyanato-2-(m-tolyl)ethyl]imino]-λ⁶-sulfanone (280ac)
Light yellow oil, 25.3 mg, 51% yield, $dr = 1:1$.

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.92 – 7.75 (m, 2H), 7.66 – 7.45 (m, 3H), 7.24 – 7.19 (m, 1H), 7.15 – 7.09 (m, 3H), 4.58 – 4.50 (m, 1H), 3.58 – 3.51 (m, 1H), 3.40 – 3.29 (m, 1H), 3.09 (d, $J = 9.0$ Hz, 3H), 2.31 (d, $J = 5.2$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 139.0, 138.7, 138.6, 137.2, 133.3, 133.2, 129.7, 129.6, 129.6, 128.7, 128.6, 128.5, 128.5, 128.4, 125.1, 124.8, 112.4, 57.0, 56.0, 48.6, 48.4, 45.1, 44.8, 21.4.

MS (EI,70 eV): $m/z$ (%) = 168.0 (100), 141.1 (63), 125.0 (20), 77.1 (15). MS (ESI) [M+H]$^+$: 331.09

HRMS (ESI) ($m/z$) [C$_{17}$H$_{19}$N$_2$O$_2$]$^+$: Calcd. 331.0939. found, 331.0915.


Methyl(phenyl)[(2-thiocyanato-2-(p-tolyl)ethyl]imino-$\lambda^6$-sulfanone (280ad)

Light yellow oil, 25.7 mg, 52% yield, $dr = 1:1$.

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.89 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.63 (q, $J = 7.4$ Hz, 1H), 7.56 (dt, $J = 15.2, 7.7$ Hz, 2H), 7.27 – 7.23 (m, 1H), 7.21 (d, $J = 8.1$ Hz, 1H), 7.17 – 7.12 (m, 2H), 4.57 (ddd, $J = 24.9, 8.6, 5.7$ Hz, 1H), 3.60 – 3.50 (m, 1H), 3.40 – 3.31 (m, 1H), 3.11 (d, $J = 12.9$ Hz, 3H), 2.33 (d, $J = 9.6$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 139.0, 138.8, 138.6, 134.3, 134.2, 133.3, 133.3, 129.7, 129.6, 129.6, 129.5, 128.6, 128.4, 127.9, 127.7, 112.5, 112.5, 56.9 55.9, 48.6, 48.4, 45.1, 44.8, 21.2, 21.2.

MS (EI,70 eV): $m/z$ (%) = 168.0 (100), 141.0 (46), 125.0 (11). MS (ESI) [M+H]$^+$: 331.09

HRMS (ESI) ($m/z$) [C$_{17}$H$_{19}$N$_2$O$_2$]$^+$: Calcd. 331.0939. found, 331.0934.

[(4-{(tert-butyl)phenyl}-2-thiocyanatoethyl)imino]methyl)(phenyl)-ζ6-sulfanone (280ae)

Light yellow oil, 33.5 mg, 60% yield, \( dr = 1:1 \).

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \& 7.90 – 7.86 (m, 1H), 7.86 – 7.83 (m, 1H), 7.66 – 7.60 (m, 1H), 7.58 – 7.54 (m, 2H), 7.38 – 7.32 (m, 2H), 7.29 (d, \( J = 8.4 \) Hz, 1H), 7.26 – 7.23 (m, 1H), 4.61 – 4.54 (m, 1H), 3.58 – 3.52 (m, 1H), 3.41 – 3.32 (m, 1H), 1.29 (d, \( J = 9.5 \) Hz, 3H), 1.29 (d, \( J = 11.9 \) Hz, 3H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \& 151.89, 138.94, 138.61, 134.23, 134.22, 133.31, 133.27, 129.64, 129.60, 128.61, 128.42, 127.62, 127.46, 125.81, 125.77, 112.56, 112.55, 56.78, 55.78, 48.68, 48.43, 45.08, 44.83, 34.64, 34.62, 31.24, 31.22.

MS (EI, 70 eV): \( m/z \) (%) = 168.0 (100), 141.1 (65), 125.0 (19), 117.0 (16), 91.1 (12), 77.1 (12). MS (ESI) [M+Na]^+: 395.12

HRMS (ESI) (\( m/z \)) [C\(_{20}\)H\(_{24}\)N\(_2\)O\(_2\)S\(_2\)Na]^+: Calcd. 395.1227. found, 395.1216.

IR (ATR): \( \nu = 3746, 3612, 2957, 2331, 2149, 1913, 1738, 1609, 1510, 1453, 1408, 1366, 1235, 1139, 973, 896, 836, 742, 687.

[(2-{(4-Methoxyphenyl}-2-thiocyanatoethyl)imino]methyl)\( \lambda 6 \)-sulfanone (280af)

Light yellow oil, 27.0 mg, 52% yield, \( dr = 1:1 \).

\(^1\)H NMR (400 MHz, CDCl\(_3\), mixture of diastereomers) \& 7.90 – 7.80 (m, 2H), 7.64 – 7.51 (m, 3H), 7.26 (dd, \( J = 17.6, 8.2 \) Hz, 2H), 6.84 (dd, \( J = 8.5, 6.4 \) Hz, 2H), 4.62 – 4.52 (m, 1H), 3.77 (d, \( J = 6.0 \) Hz, 3H), 3.56 – 3.49 (m, 1H), 3.40 – 3.27 (m, 1H), 3.09 (d, \( J = 8.1 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \& 159.9, 133.3, 133.2, 129.6, 129.6, 129.3, 129.1, 128.6, 128.4, 114.2, 112.5, 56.8, 55.8, 55.3, 48.6, 48.4, 45.1, 44.8.

MS (EI, 70 eV): \( m/z \) (%) = 287.0 (20), 168.0 (100), 141.0 (61), 132.0 (19), 125.0 (19), 91.1 (12), 77.1 (18). MS (ESI) [M+H]^+: 347.09

HRMS (ESI) (\( m/z \)) [C\(_{17}\)H\(_{19}\)N\(_2\)O\(_2\)S\(_2\)]^+: Calcd. 347.0888. found, 347.0882.
IR (ATR): $\nu = 3522, 3011, 2926, 2838, 2670, 2337, 2143, 2092, 1907, 1758, 1607, 1510, 1448, 1238, 1139, 1029, 973, 892, 833, 743, 687.$

$$\left[2\text{-}(4\text{-Bromophenyl})\text{-}2\text{-thiocyanatoethyl} \text{imino} \right] \text{(methyl)} \text{(phenyl)}\text{-}z^6\text{-sulfanone} \quad (280\text{ag})$$

Light yellow oil, 39.0 mg, 66% yield, $dr = 1:1$.

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.87 – 7.78 (m, 2H), 7.67 – 7.60 (m, 1H), 7.59 – 7.52 (m, 2H), 7.49 – 7.45 (m, 2H), 7.27 – 7.18 (m, 2H), 4.59 – 4.46 (m, 1H), 3.55 – 3.48 (m, 1H), 3.38 – 3.25 (m, 1H), 3.08 (d, $J = 10.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 138.8, 138.6, 136.5, 133.4, 133.3, 132.0, 129.7, 129.6, 129.5, 128.5, 128.3, 122.9, 56.0, 55.0, 48.1, 45.1, 44.9.

MS (EI, 70 eV): $m/z$ (%) = 169.0 (19), 168.0 (100), 141.0 (77), 124.9 (28), 124.0 (11), 97.0 (11). MS (ESI) [M+Na]$^+$: 416.97

HRMS (ESI) ($m/z$) [C$_{16}$H$_{15}$N$_2$O$_2$S$_2$BrNa]$^+$: Calcd. 416.9707. found, 416.9718.


$$\left[2\text{-}(4\text{-Chlorophenyl})\text{-}2\text{-thiocyanatoethyl} \text{imino} \right] \text{(methyl)} \text{(phenyl)}\text{-}z^6\text{-sulfanone} \quad (280\text{ah})$$

Light yellow oil, 27.8 mg, 53% yield, $dr = 1:1$.

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.85 (dd, $J = 17.6, 7.5$ Hz, 2H), 7.67 – 7.61 (m, 1H), 7.57 (q, $J = 7.6$ Hz, 2H), 7.33 – 7.25 (m, 4H), 4.60 – 4.52 (m, 1H), 3.56 – 3.49 (m, 1H), 3.39 – 3.28 (m, 1H), 3.10 (d, $J = 15.0$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 138.8, 138.6, 136.0, 135.9, 134.8, 133.4, 129.7, 129.7, 129.4, 129.3, 129.1, 129.1, 128.5, 128.4, 112.0, 112.0, 56.0, 55.0, 48.3, 48.2, 45.1, 44.9.

MS (EI, 70 eV): $m/z$ (%) = 168.0 (100), 141.1 (45), 125.0 (25). MS (ESI) [M+Na]$^+$: 373.02

HRMS (ESI) ($m/z$) [C$_{16}$H$_{15}$N$_2$O$_2$ClNa]$^+$: Calcd. 373.0212. found, 373.0201.
IR (ATR): \( \nu = 3461, 3021, 2923, 2319, 2147, 2057, 1907, 1737, 1590, 1485, 1235, 1135, 1088, 974, 740, 831, 740, 685 \).

\[{\{2-(4-Fluorophenyl)-2-thiocyanatoethyl]imino\}(methyl)(phenyl)-26-sulfanone \(280ai\)}

Light yellow oil, 25.0 mg, 50% yield, \( dr = 1:1 \).

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 7.89 – 7.81 \) (m, 2H), 7.68 – 7.61 (m, 1H), 7.57 (q, \( J = 7.6 \) Hz, 2H), 7.40 – 7.34 (m, 1H), 7.32 (dd, \( J = 8.6, 5.2 \) Hz, 1H), 7.03 (q, \( J = 8.5 \) Hz, 2H), 4.64 – 4.53 (m, 1H), 3.58 – 3.51 (m, 1H), 3.40 – 3.29 (m 1H), 3.11 (d, \( J = 12.9 \) Hz, 3H).

\(^13\)C NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 163.6, 163.6, 161.9, 161.9, 138.8, 138.6, 133.4, 133.4, 129.9, 129.9, 129.9, 129.7, 129.7, 128.5, 128.4, 115.9, 115.8, 112.2, 112.1, 56.1, 55.1, 48.5, 48.3, 45.1, 45.0.

MS (EI, 70 eV): \( m/z \) (%) = 168.0 (100), 141.1 (54), 125.0 (17). MS (ESI) [M+Na]\(^+\): 357.05

HRMS (ESI) \( m/z \) [C\(_{16}\)H\(_{15}\)N\(_2\)OS\(_2\)FNa]\(^+\): Calcd. 357.0508. found, 357.0492.

IR (ATR): \( \nu = 2918, 2336, 2122, 1898, 1740, 1604, 1501, 1225, 976, 741 \).

\[{\{2-[(1,1'-Biphenyl)-4-yl]-2-thiocyanatoethyl]imino\}(methyl)(phenyl)-26-sulfanone \(280aj\)}

Light yellow oil, 24.1 mg, 41% yield, \( dr = 1:1 \).

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 7.93 – 7.79 \) (m, 2H), 7.64 (dd, \( J = 14.4, 7.2 \) Hz, 1H), 7.60 – 7.52 (m, 6H), 7.47 – 7.39 (m, 4H), 7.35 (dd, \( J = 13.3, 7.1 \) Hz, 1H), 4.71 – 4.57 (m, 1H), 3.63 – 3.59 (m, 1H), 3.47 – 3.37 (m, 1H), 3.13 (d, \( J = 15.1 \) Hz, 3H).

\(^13\)C NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 141.8, 140.3, 140.3, 138.9, 138.6, 136.3, 136.3, 133.4, 133.3, 129.7, 129.7, 128.8, 128.8, 128.6, 128.5, 128.4, 128.3, 127.6, 127.6, 127.5, 127.1, 112.4, 112.3, 56.7, 55.6, 48.5, 48.4, 45.1, 44.9.

MS (EI, 70 eV): \( m/z \) (%) = 168.0 (100), 141.1 (47), 125.0 (15), 77.1 (17), 58.1 (25).

MS (ESI) [M+Na]\(^+\): 415.09
HRMS (ESI) (m/z) [C_{22}H_{20}N_{2}O_{2}S_{2}Na]^+: Calcd. 415.09147. found, 415.08948.

IR (ATR): ν = 3534, 3029, 2825, 2148, 1724, 1599, 1483, 1447, 1407, 1236, 1138, 1083, 974, 839, 738, 691.

[(2-Mesityl-2-thiocyanatoethyl)imino](methyl)(phenyl)-6-sulfanone (280ak)

Light yellow oil, 17.7 mg, 33% yield, dr = 1:1.

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) δ 7.88 (dd, J = 48.1, 7.2 Hz, 2H), 7.71 – 7.48 (m, 3H), 6.90 – 6.71 (m, 2H), 5.30 – 5.14 (m, 1H), 3.76 – 3.51 (m, 1H), 3.43 – 3.34 (m, 1H), 3.14 (d, J = 12.2 Hz, 3H), 2.47 – 2.15 (m, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$, mixture of diastereomers) δ 139.3, 138.8, 138.2, 137.4, 137.1, 137.0, 133.3, 133.2, 131.4, 131.3, 129.8, 129.6, 129.6, 129.5, 129.4, 128.6, 128.3, 113.1, 113.1, 54.0, 52.6, 47.2, 46.3, 45.0, 44.8, 21.3, 21.1, 20.8.

MS (EI, 70 eV): m/z (%) = 190.1 (10), 168.0 (79), 145.1 (16), 141.0 (100), 133.1 (26), 125.0 (67), 117.1 (32), 115.1 (33), 91.1 (47), 77.2 (67), 51.2 (54). MS (ESI) [M+Na]^+: 359.12

HRMS (ESI) (m/z) [C_{19}H_{23}N_{2}O_{2}]^+: Calcd. 359.1252. found, 359.1238.

IR (ATR): ν = 3523, 2926, 2336, 2144, 1912, 1727, 1606, 1452, 1229, 1137, 971, 858, 743, 678.

(4-Methoxyphenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)-6-sulfanone (280ba)

Light yellow oil, 42.0 mg, 81% yield, dr = 1:1.

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) δ 7.77 (dd, J = 21.5, 8.8 Hz, 2H), 7.39 – 7.29 (m, 5H), 7.01 (dd, J = 11.0, 8.8 Hz, 2H), 4.62 – 4.56 (m, 1H), 3.87 (s, 3H), 3.56 – 3.52 (m, 1H), 3.42 – 3.31 (m, 1H), 3.08 (d, J = 15.7 Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$, mixture of diastereomers) δ 163.5, 163.5, 137.5, 137.4, 130.7, 130.6, 130.0, 129.6, 128.9, 128.8, 128.0, 127.9, 114.9, 114.8, 112.4, 112.4, 57.0, 56.0, 55.8, 48.6, 48.4, 45.5, 45.2.
MS (EI, 70 eV): m/z (%) = 198.0 (90), 171.0 (96), 154.9 (100), 139.0 (13), 91.1 (41), 77.1 (18), 63.1 (11). MS (ESI) [M+H]^+: 347.09
HRMS (ESI) (m/z) [C_{17}H_{19}N_{2}O_{2}S_{2}]^+: Calcd. 347.0888, found 347.0873.
IR (ATR): ν = 3556, 3018, 2923, 2845, 2570, 2325, 2147, 1901, 1722, 1588, 1492, 1454, 1410, 1306, 1245, 1135, 1091, 1021, 973, 891, 834, 766, 699.

Methyl[(2-phenyl-2-thiocyanatoethyl)imino](p-tolyl)-\(\lambda^6\)-sulfanone (280ca)

Light yellow oil, 35.1 mg, 71% yield, \(dr = 1:1\).

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) δ 7.73 (dd, \(J = 20.3, 8.2\) Hz, 2H), 7.42 – 7.28 (m, 7H), 4.62 – 4.58 (m, 1H), 3.59 – 3.49 (m, 1H), 3.41 – 3.31 (m, 1H), 3.09 (d, \(J = 14.5\) Hz, 3H), 2.45 (d, \(J = 1.9\) Hz, 3H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) δ 144.3, 144.2, 137.4, 137.4, 135.8, 135.4, 130.3, 128.9, 128.8, 128.6, 128.5, 128.0, 127.9, 112.4, 112.4, 57.0, 56.0, 48.6, 48.4, 45.2, 45.0, 21.6.

MS (EI, 70 eV): m/z (%) = 198.0 (100), 155.0 (48), 139.0 (18), 91.1 (17). MS (ESI) [M+H]^+: 331.09
HRMS (ESI) (m/z) [C_{17}H_{19}N_{2}O_{2}S_{2}]^+: Calcd. 331.0939, found, 331.0924.

(4-Bromophenyl)(methyl)[(2-phenyl-2-thiocyanatoethyl)imino]-\(\lambda^6\)-sulfanone (280da)

Light yellow oil, 39.1 mg, 66% yield, \(dr = 1:1\).

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) δ 7.74 – 7.65 (m, 4H), 7.38 – 7.31 (m, 5H), 4.62 – 4.53 (m, 1H), 3.59 – 3.54 (m, 1H), 3.40 – 3.30 (m, 1H), 3.10 (d, \(J = 16.4\) Hz, 3H).
(4-Chlorophenyl)(methyl][(2-phenyl-2-thiocyanatoethyl)imino]-ω-sulfanone (280ea)

Light yellow oil, 34.1 mg, 65% yield, \( dr = 1:1 \).

\(^1^H\) NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 7.81 - 7.78 \) (m, 1H), 7.76 – 7.73 (m, 1H), 7.55 – 7.50 (m, 2H), 7.37 – 7.31 (m, 5H), 4.61 – 4.55 (m, 1H), 3.60 – 3.53 (m, 1H), 3.41 – 3.31 (m, 1H), 3.10 (d, \( J = 16.4 \) Hz, 3H).

\(^1^C\) NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 140.8, 140.0, 137.5, 137.2, 137.2, 130.1, 130.0, 129.9, 129.0, 128.9, 128.9, 128.0, 127.8, 112.2, 112.2, 56.68, 56.67, 55.7, 48.5, 48.4, 45.1, 44.9.

MS (EI, 70 eV): m/z (%) = 203.9 (36), 201.9 (100), 176.9 (22), 174.9 (60), 159.9 (12), 158.9 (25), 118.0 (17), 91.1 (26). MS (ESI) [M+Na]: 373.02

HRMS (ESI) (m/z) \([C_{16}H_{15}N_2OS_2ClNa]^+\): Calcd. 373.0212. found, 373.0200.

IR (ATR): \( \nu = 3543, 3067, 3027, 2923, 2844, 2563, 2324, 2149, 2055, 1925, 1811, 1728, 1576, 1466, 1393, 1238, 1141, 1082, 975, 889, 829, 769, 699.

(4-Fluorophenyl)(methyl][(2-phenyl-2-thiocyanatoethyl)imino]-ω-sulfanone (280fa)

Light yellow oil, 27.6 mg, 55% yield, \( dr = 1:1 \).
$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.91 – 7.75 (m, 2H), 7.37 – 7.29 (m, 4H), 7.25 – 7.18 (m, 2H), 4.60 – 4.53 (m, 1H), 3.60 – 3.51 (m, 1H), 3.41 – 3.29 (m, 1H), 3.08 (d, $J = 10.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 166.8, 164.3, 137.2, 137.2, 134.9, 134.6, 131.4, 131.3, 131.2, 131.1, 128.9, 128.9, 128.9, 128.0, 127.8, 117.0, 117.0, 116.8, 116.7, 112.2, 112.1, 56.7, 55.7, 48.5, 48.4, 45.3, 45.0.

MS (El, 70 eV): $m/z$ (%) = 185.9 (100), 158.9 (47), 142.9 (15). MS (ESI) [M+H]$^+$: 335.07,

HRMS (ESI) ($m/z$) [C$_{16}$H$_{16}$N$_2$OS$_2$F]$^+$: Calcd. 335.0688. found, 335.0674.


$^{3}$-[Methoxyphenyl](methyl)[(2-phenyl-2-thiocyanatoethyl)imino]-$\lambda_6$-sulfanone (280ga)

Light yellow oil, 20.8 mg, 40% yield, $dr = 1:1$.

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.50 – 7.42 (m, 2H), 7.41 – 7.30 (m, 6H), 7.16 – 7.13 (m, 1H), 4.63 – 4.56 (m, 1H), 3.86 (d, $J = 4.6$ Hz, 3H), 3.60 – 3.53 (m, 1H), 3.44 – 3.34 (m, 1H), 3.11 (d, $J = 13.3$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 160.4, 160.4, 140.2, 139.9, 137.4, 137.3, 130.7, 130.6, 128.9, 128.9, 128.9, 128.0, 127.9, 120.5, 120.3, 119.8, 119.6, 113.0, 112.3, 56.9, 55.9, 55.7, 48.6, 48.4, 45.1, 44.8.

MS (El, 70 eV): $m/z$ (%) = 198.0 (100), 171.0 (96), 155.0 (63), 148.0 (18), 121.0 (29), 108.0 (29), 91.1 (82), 77.1 (58). MS (ESI) [M+H]$^+$: 347.09

HRMS (ESI) ($m/z$) [C$_{17}$H$_{19}$N$_2$O$_2$S$_2$]$^+$: Calcd. 347.0888. found, 347.0877.

IR (ATR): $\nu = 3589, 3018, 2925, 2846, 2331, 2147, 1892, 1772, 1593, 1470, 1239, 1138, 1084, 1034, 972, 864, 767, 692.

$^{3}$-[Bromophenyl](methyl)[(2-phenyl-2-thiocyanatoethyl)imino]-$\lambda_6$-sulfanone (280ha)

(3-Methoxyphenyl)(methyl)[(2-phenyl-2-thiocyanatoethyl)imino]-$\lambda_6$-sulfanone
Light yellow oil, 26.0 mg, 44% yield, \( dr = 1:1 \).

\(^1\)H NMR (400 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.98 (dt, \( J = 16.7, 1.8 \) Hz, 1H), 7.80 – 7.70 (m, 2H), 7.41 (q, \( J = 8.0 \) Hz, 1H), 7.35 – 7.30 (m, 5H), 4.59 – 4.53 (m, 1H), 3.61 – 3.52 (m, 1H), 3.41 – 3.30 (m, 1H), 3.09 (d, \( J = 11.2 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 141.2, 141.0, 137.1, 136.4, 136.3, 131.6, 131.3, 131.1, 129.0, 128.9, 128.0, 127.8, 127.0, 126.9, 123.7, 123.6, 112.1, 112.1, 56.6, 55.6, 48.5, 48.3, 45.1, 44.9.

MS (EI, 70 eV): \( m/z \) (%) = 247.9 (100), 245.9 (99), 220.9 (40), 218.9 (41), 204.9 (10), 202.8 (9), 91.1 (13). MS (ESI) [M+Na]^+: 416.97
HRMS (ESI) (m/z) [C\(_{16}\)H\(_{15}\)N\(_2\)O\(_2\)S\(_2\)BrNa]^+: Calcd. 416.9707. found, 416.9718.

IR (ATR): \( \nu = 3063, 3027, 2925, 2845, 2328, 2149, 1889, 1737, 1568, 1493, 1454, 1404, 1366, 1235, 1140, 1098, 979, 889, 834, 774, 732, 699, 678.\n
(3-Chlorophenyl)(methyl)[(2-phenyl-2-thiocyanatoethyl)imino]-2\(^6\)-sulfanone (280ia)

Light yellow oil, 22.6 mg, 43% yield, \( dr = 1:1 \).

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.84 (dt, \( J = 28.8, 1.6 \) Hz, 1H), 7.72 (dd, \( J = 27.1, 7.8 \) Hz, 1H), 7.62 – 7.56 (m, 1H), 7.53 – 7.48 (m, 1H), 7.37 – 7.32 (m, 5H), 4.61 – 4.56 (m, 1H), 3.61 – 3.53 (m, 1H), 3.42 – 3.33 (m, 1H), 3.11 (d, \( J = 17.2 \) Hz, 3H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 141.1, 140.7, 137.1, 135.9, 135.9, 133.5, 133.5, 130.9, 129.00, 128.9, 128.9, 128.5, 128.0, 127.8, 126.7, 126.5, 112.2, 112.1, 56.6, 55.6, 48.5, 48.3, 45.1, 44.9.

MS (EI, 70 eV): \( m/z \) (%) = 222.2 (42), 204.0 (53), 202.0 (100), 177.0 (22), 175.0 (58), 159.0 (16), 118.1 (49), 104.1 (10), 91.1 (30). MS (ESI) [M+Na]^+: 373.02
HRMS (ESI) (m/z) [C\(_{16}\)H\(_{15}\)N\(_2\)O\(_2\)S\(_2\)ClNa]^+: Calcd. 373.0212. found, 373.0197.

IR (ATR): \( \nu =3525, 3065, 3028, 2923, 2849, 2688, 2339, 2149, 2061, 1887, 1731, 1577, 1454, 1408, 1241, 1139, 1077, 975, 891, 840, 758, 696.\n
(2-Bromophenyl)(methyl)[(2-phenyl-2-thiocyanatoethyl)imino]-2\(^6\)-sulfanone (280ja)
Light yellow oil, 22.5 mg, 38% yield, $dr = 1:1$.

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 8.21 – 8.17 (m, 1H), 7.81 – 7.73 (m, 1H), 7.56 – 7.50 (m, 1H), 7.48 – 7.42 (m, 1H), 7.38 – 7.30 (m, 5H), 4.62 – 4.57 (m, 1H), 3.53 – 3.44 (m, 1H), 3.36 – 3.28 (m, 4H).

$^{13}$C NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 137.7, 137.7, 137.2, 137.2, 135.8, 135.7, 134.4, 133.3, 133.2, 128.9, 128.9, 128.9, 128.5, 128.4, 128.0, 127.9, 120.7, 120.7, 112.3, 112.3, 56.5, 55.7, 48.6, 48.5, 42.7, 42.6.

MS (EI, 70 eV): $m/z$ (%) = 393.9 (2, M$^+$), 247.9 (100), 245.9 (96), 220.9 (59), 218.9 (60), 204.9 (15), 202.8 (14). MS (ESI) [M+Na]$^+$: 416.97
HRMS (ESI) ($m/z$) [C$_{16}$H$_{15}$N$_2$OS$_2$BrNa]$^+$: Calcd. 416.9707. found, 416.9712.

IR (ATR): $\nu$ = 3533, 3028, 2923, 2845, 2693, 2326, 2148, 1992, 1940, 1734, 1569, 1492, 1441, 1235, 1141, 1093, 1025, 972, 878, 832, 758, 700.

(2-Chlorophenyl)(methyl)[(2-phenyl-2-thiocyanatoethyl)imino]-$\lambda^6$-sulfanone (280ka)

Light yellow oil, 27.3 mg, 52% yield, $dr = 1:1$.

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 8.17 – 8.09 (m, 1H), 7.55 – 7.52 (m, 2H), 7.49 – 7.43 (m, 1H), 7.35 – 7.26 (m, 5H), 4.58 – 4.53 (m, 1H), 3.54 – 3.44 (m, 1H), 3.36 – 3.24 (m, 4H).

$^{13}$C NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 137.2, 136.1, 134.4, 132.9, 132.9, 132.3, 132.2, 132.1, 128.9, 127.9, 127.9, 127.8, 127.7, 112.2, 56.4, 55.7, 48.6, 48.3, 43.1, 42.3.

MS (EI, 70 eV): $m/z$ (%) = 203.9 (38), 202.0 (100), 176.9 (27), 174.9 (66), 160.0 (10), 158.9 (12), 91.1 (16). MS (ESI) [M+Na]$^+$: 373.02
HRMS (ESI) ($m/z$) [C$_{16}$H$_{15}$N$_2$OS$_2$ClNa]$^+$: Calcd. 373.0212. found, 373.0198.

IR (ATR): $\nu$ = 3836, 3508, 3065, 2922, 2845, 2681, 2328, 2145, 1882, 1739, 1573, 1493, 1445, 1243, 1142, 1029, 969, 761, 700.

(3,5-Dichlorophenyl)(methyl)[(2-phenyl-2-thiocyanatoethyl)imino]-$\lambda^6$-sulfanone (280la)

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Light yellow oil, 32.8 mg, 57% yield, $dr = 1:1$

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.72 (d, $J = 1.8$ Hz, 1H), 7.66 (d, $J = 1.8$ Hz, 1H), 7.60 – 7.56 (m, 1H), 7.39 – 7.27 (m, 5H), 4.59 – 4.50 (m, 1H), 3.61 – 3.55 (m, 1H), 3.41 – 3.31 (m, 1H), 3.09 (d, $J = 14.0$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 142.6, 142.3, 136.9, 136.9, 136.6, 136.6, 133.3, 133.3, 129.1, 129.0, 128.9, 127.9, 127.8, 126.9, 126.7, 112.0, 111.9, 56.4, 55.3, 48.5, 48.2, 45.0, 44.9.

MS (EI, 70 eV): $m/z$ (%) = 238.0 (63), 235.9 (100), 211.0 (31), 208.9 (50), 194.9 (9), 192.9 (15), 118.1 (21), 91.1 (31). MS (ESI) [M+H]$^+$: 385.00

HRMS (ESI) ($m/z$) [C$_{16}$H$_{15}$N$_2$OS$_2$Cl$_2$]$^+$: Calcd. 385.0003. found, 384.9990.

IR (ATR): $\nu$ = 3479, 3057, 2923, 2149, 1743, 1568, 1408, 1241, 1139, 980, 780, 699.

Diphenyl[2-phenyl-2-thiocyanatoethyl]imino-$\lambda^6$-sulfanone (280ma)

Ethyl(phenyl)[2-phenyl-2-thiocyanatoethyl]imin-$\lambda^6$-sulfanone (280na)

Light yellow oil, 27.2 mg, 48% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (dt, $J = 8.4$, 4.3 Hz, 4H), 7.59 – 7.42 (m, 7H), 7.40 – 7.31 (m, 6H), 4.71 (dd, $J = 8.2$, 5.7 Hz, 1H), 3.60 (qd, $J = 12.9$, 7.0 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.1, 139.8, 137.6, 132.8, 129.3, 129.3, 128.9, 128.8, 128.5, 128.3, 128.1, 128.0, 112.4, 56.8, 48.2.

MS (EI,70 eV): $m/z$ (%) = 230.1 (82), 203.1 (62), 186.1 (20), 154.1 (24), 125.0 (29), 121.0 (23), 118.1 (40), 109.0 (55), 104.1 (23), 97.1 (34), 91.1 (100), 89.1 (27), 78.2 (28), 77.2 (94), 65.2 (62). MS (ESI) [M+H]$^+$: 379.09

HRMS (ESI) ($m/z$) [C$_{21}$H$_{19}$N$_2$OS$_2$]$^+$: Calcd. 379.0939. found, 379.0920.

IR (ATR): $\nu$ = 3596, 3061, 2920, 2846, 2334, 2149, 2055, 1901, 1739, 1585, 1447, 1365, 1245, 1142, 1083, 996, 896, 835, 728.

Ethyl(phenyl)[2-phenyl-2-thiocyanatoethyl]imin-$\lambda^6$-sulfanone (280na)

Light yellow oil, 27.2 mg, 55% yield, $dr = 1:1$. 

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\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}, mixture of diastereomers) \(\delta 7.80 \) (dd, \( J = 20.3, 7.8 \) Hz, 2H), 7.65 – 7.60 (m, 1H), 7.55 (dd, \( J = 16.6, 8.1 \) Hz, 2H), 7.40 – 7.30 (m, 5H), 4.66 – 4.59 (m, 1H), 3.62 – 3.55 (m, 1H), 3.43 – 3.38 (m, 1H), 3.25 – 3.11 (m, 2H), 1.24 (dt, \( J = 12.5, 7.4 \) Hz, 3H).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}, mixture of diastereomers) \(\delta 137.5, 137.5, 137.2, 136.9, 133.3, 133.2, 129.6, 129.5, 129.3, 129.1, 128.8, 128.8, 128.1, 127.9, 112.5, 112.5, 57.3, 56.2, 51.1, 50.9, 48.4, 48.2, 7.2, 7.2.

MS (EI, 70 eV): \( m/\ell (%) = 183.0 \) (21), 182.0 (100), 155.0 (61), 125.0 (14), 109.0 (14), 91.0 (12). MS (ESI) [M+Na]+: 353.08.

HRMS (ESI) (m/\ell) [C\textsubscript{17}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2}Na]+: Calcd. 353.0758. found, 353.0746.

IR (ATR): \( \nu = 3905, 2928, 2677, 2336, 2096, 1743, 1448, 1226, 895, 725.

\textbf{Methyl(phenyl)[(2-phenyl-2-(phenylthio)ethyl)imino]-\textgreek{S}-sulfanone (282)}

Light yellow oil, 6.6 mg, 12% yield, yield, \( dr = 1:1 \).

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}, mixture of diastereomers) \(\delta 7.72 – 7.66 \) (m, 2H), 7.52 – 7.47 (m, 1H), 7.37 (t, \( J = 7.8 \) Hz, 2H), 7.27 (d, \( J = 8.1 \) Hz, 2H), 7.22 – 7.16 (m, 7H), 7.12 – 7.07 (m, 1H), 4.29 (dd, \( J = 7.5, 6.5 \) Hz, 1H), 3.52 (dd, \( J = 13.0, 6.3 \) Hz, 1H), 3.29 (dd, \( J = 9.4, 3.6 \) Hz, 1H), 3.11 (s, 3H).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}, mixture of diastereomers) \(\delta 143.5, 139.7, 136.9, 134.8, 132.7, 130.0, 129.0, 128.7, 128.6, 128.6, 128.1, 127.1, 127.1, 125.4, 58.1, 45.0, 43.5.

MS (EI, 70 eV): \( m/\ell (%) = 244.1 \) (100), 141.1 (82), 125.0 (27), 123.1 (27), 91.1 (17), 77.2 (49). MS (ESI) [M+H]+: 368.11

HRMS (ESI) (m/\ell) [C\textsubscript{21}H\textsubscript{22}NOS\textsubscript{2}]+: Calcd. 368.1143 found, 368.1127.

IR (ATR): \( \nu = 3440, 3061, 2923, 2858, 2662, 2322, 2101, 1995, 1908, 1729, 1581, 1448, 1355, 1313, 1226, 1129, 976, 847, 739, 693.

\[89\]
7. Photocatalyzed functionalizations of alkenes with $N$-Ts sulfoximidoxy chloride

There are many precursors and methods to form sulfonyl radicals. However, sulfoximidoxy radicals as analogs of sulfonyl radicals have remained unexplored. Based on the preparation of sulfoximidoxy chlorides, we wonder if sulfur-centered sulfoximidoxy radicals could participate in the ATRA reaction.

7.1 Results and discussion

7.1.1 Research objective

As shown in Scheme 45, the key step in the ATRA reaction was the generation of the sulfonyl radical by photocatalysis. Inspired by past research, we wondered if the $N$-Ts protected sulfoximidoxy chloride could be utilized to form the sulfoximidoxy radical and add to unsaturated C–C bonds, thus leading to a difunctionalized product, which would provide a sulfoximidoxy radical and undergo an addition reaction to deliver the sulfoximidoxy moieties. Elimination of the ATRA product to construct a C–C double bond by base-mediated elimination might be possible (Scheme 67).

**Scheme 67**: Possible ATRA reaction for $N$-Ts protected sulfoximidoxy chloride

7.1.2 Optimization of the reaction conditions

Using the racemic $N$-Ts protected sulfoximidoxy chloride 286a and styrene (110a) as substrates, the reaction was tested with a series of photocatalysts (Table 7). In the initial screening, various Ir-based photocatalysts were examined in DCM under irradiation with 5 W blue-LEDs at room temperature. For the formation of 287aa, Ir(ppy)$_3$ was found to be most suitable photocatalyst in the ATRA process (entries 1-5). Additionally, olefinic product 288aa was isolated in 5% yield under the same conditions (entry 1). Testing the influence of solvents indicated that DCM was superior to others (entries 6-10). Extending the reaction time to 40 h increased the yield of 287aa to 88% (entry 11). In the absence of a photocatalyst, no product could
be detected (entry 12). Thus, the optimal reaction conditions for 287aa were found to require the use of 5 W blue-LED irradiations and 1 mol% of Ir(ppy)_3 in DCM (0.1 M) for 40 h (entry 11). 288aa was obtained in 97% yield after adding K$_2$CO$_3$ (2.0 equiv) to the crude product mixture of 287aa and stirring for 16 h (entry 11).

Table 7: Optimization of reaction conditions$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)$^b$ 3a/4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ir(ppy)$_3$</td>
<td>DCM</td>
<td>15</td>
<td>72/5 (82)$^c$</td>
</tr>
<tr>
<td>2</td>
<td>Ir[dCF$_3$(ppy)$_2$]bpyPF$_6$</td>
<td>DCM</td>
<td>15</td>
<td>46/trace (54)$^c$</td>
</tr>
<tr>
<td>3</td>
<td>Ir[dF(CF$_3$)ppy]$_2$(bpy)PF$_6$</td>
<td>DCM</td>
<td>15</td>
<td>55/trace (58)$^c$</td>
</tr>
<tr>
<td>4</td>
<td>Ir[dF(CF$_3$)ppy]$_2$(dtbpy)PF$_6$</td>
<td>DCM</td>
<td>15</td>
<td>49/trace (55)$^c$</td>
</tr>
<tr>
<td>5</td>
<td>Ir(bpy)(dtppy)$_2$PF$_6$</td>
<td>DCM</td>
<td>15</td>
<td>48/trace (53)$^c$</td>
</tr>
<tr>
<td>6</td>
<td>Ir(ppy)$_3$</td>
<td>DCE</td>
<td>15</td>
<td>58/3 (62)$^c$</td>
</tr>
<tr>
<td>7</td>
<td>Ir(ppy)$_3$</td>
<td>CH$_3$CN</td>
<td>15</td>
<td>52/trace (57)$^c$</td>
</tr>
<tr>
<td>8</td>
<td>Ir(ppy)$_3$</td>
<td>CCl$_4$</td>
<td>15</td>
<td>trace/NR (3)$^c$</td>
</tr>
<tr>
<td>9</td>
<td>Ir(ppy)$_3$</td>
<td>CHCl$_3$</td>
<td>15</td>
<td>41/trace (42)$^c$</td>
</tr>
<tr>
<td>10</td>
<td>Ir(ppy)$_3$</td>
<td>CH$_2$Br$_2$</td>
<td>15</td>
<td>42/trace (45)$^c$</td>
</tr>
<tr>
<td>11</td>
<td>Ir(ppy)$_3$</td>
<td>DCM</td>
<td>40</td>
<td>88/7 (97)$^c$</td>
</tr>
<tr>
<td>12</td>
<td>--</td>
<td>DCM</td>
<td>40</td>
<td>NR</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 286a (0.1 mmol), 110a (0.5 mmol) and photocatalyst (1 mol%), in solvent (1.0 mL) under argon with 5 W blue-LEDs at room temperature for 40 h. The dr was determined by $^1$H NMR analysis. NR = no reaction. $^b$Yield of 287aa and 288aa after column chromatography. $^c$K$_2$CO$_3$ (27.6 mg, 0.2 mmol, 2.0 equiv) under air for 16 h.
7.1.3 Substrate scope of the reactions

With the optimized reaction conditions in hand, we examined the ATRA reaction with a variety of styrenes \(110\text{-}p\) and \(N\text{-}Ts\) sulfoximidoyl chloride \(286\text{a}\) (Table 8). The addition reactions of methyl-substituted styrenes proceeded well, leading to the desired products in 73-83% yields (entries 2-4). In addition, various halo-substituted styrenes resulted in the formation of products (entries 5-9). For other para-substituted styrenes, the products were obtained in good yields (entries 10-11, 13-14). When multi-substituted styrenes were used, corresponding products were obtained in high yields (entries 12 and 15). Moreover, \(\beta\)-methyl styrene \(110\text{p}\) reacted with sulfoximidoyl chloride \(286\text{a}\), affording \(287\text{ap}\) in 74% yield (entry 16). A larger scale experiment was performed (1.0 mmol), affording \(287\text{aa}\) in 85% yield.

Table 8: Scope of styrenes in 1,2-addition reaction

\[
\begin{array}{ccc}
\text{Entry} & \text{R, }110\text{-}p & \text{Products (287\text{aa-ap})} & \text{Yield (%)} \\
1 & \text{H, }110\text{a} & 287\text{aa} & 88 \\
2 & \text{o-Me, }110\text{b} & 287\text{ab} & 73 \\
3 & \text{m-Me, }110\text{c} & 287\text{ac} & 79 \\
4 & \text{p-Me, }110\text{d} & 287\text{ad} & 83 \\
\end{array}
\]
<table>
<thead>
<tr>
<th>5</th>
<th>m-F, 110k</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>p-F, 110h</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>m-Cl, 110l</td>
<td>74</td>
</tr>
<tr>
<td>8</td>
<td>p-Cl, 110m</td>
<td>80</td>
</tr>
<tr>
<td>9</td>
<td>p-Br, 110g</td>
<td>79</td>
</tr>
<tr>
<td>10</td>
<td>p-tBu, 110e</td>
<td>86</td>
</tr>
<tr>
<td>11</td>
<td>p-OMe, 110f</td>
<td>55</td>
</tr>
<tr>
<td>12</td>
<td>3,5-(CF3)2, 110n</td>
<td>92</td>
</tr>
<tr>
<td>13</td>
<td>p-Ph, 110i</td>
<td>60</td>
</tr>
</tbody>
</table>
Photocatalytic formation of addition products \( \text{287} \) starting from sulfoximidoyl chloride \( \text{286a} \) (36.3 mg, 0.1 mmol, 1.0 equiv) and styrenes \( \text{110} \) (0.5 mmol, 5.0 equiv). In parentheses: result of a 1.0 mmol scale of \( \text{286a} \) reaction in 85% yield. Yields after column chromatography.

Then, the effect of different functional groups on the sulfoximidoyl chlorides \( \text{286} \) was investigated (Table 9), and the results revealed that \( S \)-aryl substrates bearing various substitutions also worked very effectively in generating the corresponding products in high yields (entries 1-3).

<table>
<thead>
<tr>
<th>Entry</th>
<th>( R ), ( \text{286b-d} )</th>
<th>Products (( \text{287ba-da} ))</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( p-tBu ), ( \text{286b} )</td>
<td>( \text{287ba} )</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>( p-Me ), ( \text{286c} )</td>
<td>( \text{287ca} )</td>
<td>78</td>
</tr>
</tbody>
</table>
Photocatalytic formation of addition products 287 starting from sulfoximoyl chlorides 286 (0.1 mmol, 1.0 equiv) and styrene 110a (52.0 mg, 0.5 mmol, 5.0 equiv); yields after column chromatography.

When K₂CO₃ (2 equiv) was added to the reaction mixture and it was stirred for an additional 16 h, the unsaturated product 288aa was obtained in 97% yield (Table 7, entry 11). The scope of unsaturated sulfoximine 288 was explored by varying substituent of styrenes (Table 10, entries 1-22). Using those conditions, we found that the substituted styrenes gave the corresponding products 288aa-ax in the high an average yield of 95%. The used 2-methylbut-1-en-3-yne and 2-methyl-2-propenoic acid methylester, without the aryl groups, resulted in moderate yields of 288aw-ax (Table 10, entries 23-24). The formation of 288aw revealed that the C–C double bond reacted preferentially over the respective C–C triple bond. On a 1 mmol scale, the photocatalysis with 110a and 286a as starting materials gave 288aa in 99% yield.

Table 10: Conversion of styrenes to the unsaturated products

<table>
<thead>
<tr>
<th>Entry</th>
<th>110a-x</th>
<th>Products (288aa-ax)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110a</td>
<td>288aa</td>
<td>97 (99)⁵</td>
</tr>
<tr>
<td>2</td>
<td>110b</td>
<td>288ab</td>
<td>97</td>
</tr>
</tbody>
</table>

12  \( \text{110n} \)  \( \text{288an} \)  95

13  \( \text{110i} \)  \( \text{288ai} \)  80

14  \( \text{110o} \)  \( \text{288ao} \)  98

15  \( \text{110j} \)  \( \text{288aj} \)  82

16  \( \text{110p} \)  \( \text{288ap} \)  95

17  \( \text{110q} \)  \( \text{288aq} \)  95

18  \( \text{110t} \)  \( \text{288at} \)  93

19  \( \text{110r} \)  \( \text{288ar} \)  93

20  \( \text{110s} \)  \( \text{288as} \)  97
Photocatalytic formation of unsaturated products 288 by reaction of sulfoximidoyl chlorides 286a (36.3 mg, 0.1 mmol, 1.0 equiv) and styrenes 110 (0.5 mmol, 5.0 equiv) followed by treatment of the resulting crude product mixture with K₂CO₃ (27.6 mg, 0.2 mmol) for 16 h; yields after column chromatography. ⁶In parentheses: result of a 1.0 mmol scale of 286a reaction in 99% yield.

Then, reactivities of sulfoximidoyl chlorides bearing various substituents were tested (Table 11). Electron-donating and -withdrawing substituents on the phenyl group, such as tBu (286b), methyl (286c, 286f, and 286e), halogens (286d and 286g) and ethyl (286h) groups were tolerated, providing the products in yields ranging from 75% to 94% (entries 1-7). N-Ts S-methyl sulfoximidoyl chloride delivered product 288ia with 35% yield (entry 8).

Table 11: Conversion of sulfoximidoyl chlorides to the unsaturated products

<table>
<thead>
<tr>
<th>Entry</th>
<th>R, 286b-i</th>
<th>Products (288)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>110u</td>
<td>288au</td>
<td>95</td>
</tr>
<tr>
<td>22</td>
<td>110v</td>
<td>288av</td>
<td>25</td>
</tr>
<tr>
<td>23</td>
<td>110w</td>
<td>288aw</td>
<td>42</td>
</tr>
<tr>
<td>24</td>
<td>110x</td>
<td>288ax</td>
<td>41</td>
</tr>
</tbody>
</table>

[^a]: Conversion of sulfoximidoyl chlorides to the unsaturated products.
Photocatalytic formation of unsaturated products 288 by reaction of sulfoximidoxyl chlorides 286 (0.1 mmol, 1.0 equiv) and styrene 110a (54.0 mg, 0.5 mmol, 5.0 equiv) followed by treatment of the resulting crude product mixture with K$_2$CO$_3$ (27.6 mg, 0.2 mmol); yields after column
The reactions with sulfoximidoyl chlorides were unsuccessful, when the compounds shown in Scheme 68 were used as substrates.

Scheme 68: Unreacting alkenes

7.1.4 Plausible mechanism

On the basis of previous reports, an ATRA pathway could be proposed (Scheme 69). The photocatalyst (PC) accepts a photon to generate (PC*), and single electron transfer (SET) from PC* to sulfoximidoyl chloride 286 leads to PC⁺, Cl⁻ and sulfoximidoyl radical A. Then, A reacts with olefin 110 affording intermediate B, which is oxidized by PC⁺ to give intermediate C. Simultaneously, PC is regenerated to initiate a new catalytic cycle. The reaction of intermediate C with Cl⁻ provides product 287, which reacts with additional K₂CO₃ affording product 288.

Scheme 69: Proposed catalytic cycle

7.1.5 Applications

To demonstrate the potential synthetic value of the functionalization products, we investigated their properties for subsequent transformations (Scheme 70). In Scheme 70, eq 1, 288aa, 288ha, and 288fa were applied as representative starting materials in...
the deprotection of Ts with concentrated sulfuric acid. Neutralization by NaOH gave the S-styryl S-aryl sulfoximines 289a-c in excellent yields.[104] It provided a new method for the synthesis of S-styryl S-aryl sulfoximines.

![Scheme 70](image)

Scheme 70. Transformations of product 288.

In Scheme 70, eq 2, sulfoximines 289b and 289c were reacted in a HLF-type cyclization reaction,[105] leading to dihydroisothiazole oxides 290a and 290b in good yield with a $dr$ value of 1:1.

In Scheme 70, eq 3, palladium-catalyzed Suzuki coupling reactions[106] of 280ar and 280ga with boronic acid 8a under basic conditions in MeCN/H2O afforded arylated products 292a and 292b in moderate yield.

7.1.6 Summary

In summary, we have developed a new type of sulfur-centered sulfoximidoyl radical addition process by photocatalysis using N-Ts sulfoximidoyl chlorides and olefins as starting materials. The 1,2-addition products 287 and unsaturated sulfoximines 288 were obtained in high yields. A possible ATRA mechanism has been proposed and synthetic applications for the products have also explored.
7.2 Experimental

7.2.1 General information

Visible light was provided by blue-LEDs (5 W, 455 nm)

7.2.2 General procedures and characterization data

Synthesis of sulfoximidoyl chlorides 286 (as illustrated for the preparation of 286a):[107]

Thiophenol (402 mg, 3.65 mmol, 1.0 equiv) and acetic acid (220 mg, 3.65 mmol, 1.0 equiv) were placed in a 50 mL flask. Then, SO$_2$Cl$_2$ (1.04 g, 620 mL, 7.7 mmol, 2.1 equiv) was added by syringe pump over 15 min. Subsequently, the mixture was stirred at room temperature for 2 h, and then heated to 35 °C for 2 h. After removal of the volatiles, the crude product was used without further purification. Under argon, chloramine T (831.0 mg, 3.65 mmol, 1.0 equiv) was added to the sulfinic chloride (1.0 equiv) in dry toluene 20 mL at room temperature. The resulting suspension was heated to 85 °C and then stirred for 1.5 h. After cooling to room temperature, the solid was filtered off and washed with dry toluene. Purification by flash column chromatography (ethyl acetate/ n-pentane = 1/4) afforded 286a as a white solid (974 mg, 81% from thiophenol).

Synthesis of products 287 and 288

Under argon, sulfoximidoyl chloride 286 (0.1 mmol, 1.0 equiv), olefin 110 (0.5 mmol, 5.0 equiv) and Ir(ppy)$_3$ (0.7 mg, 1.0 mol %, 0.01 equiv) were added into a sealable reaction tube (5.0 mL). Then, DCM (1.0 mL) was added, and the mixture was stirred under blue LED irradiation (5 W) at room temperature for 40 h. Subsequently, 287 and 288 were obtained by the following methods:

- Product 287: Purification by flash column chromatography (ethyl acetate/ n-pentane = 1/3).
- Product 288: Addition of K$_2$CO$_3$ (0.2 mmol, 27.6 mg, 2.0 equiv) to the reaction tube at room temperature and stirring in air for 16 h; then, purification by flash column chromatography (ethyl acetate/ n-pentane = 1/2).

The diastereomeric ratios of products 287 were determined by $^1$H NMR spectroscopy of the crude product mixtures.

Synthesis of products 289.[107]
Compound 288 (0.1 mmol) and concentrated sulfuric acid (96%, 3.6 mmol, 0.2 mL) were added to a reaction tube. The mixture was stirred at room temperature for 2 h and cooled down to 0 °C. Cold water (2.0 mL) was added to quench the reaction. Then, NaOH (7.2 mmol, 280 mg) in water (2.0 mL) was added dropwise upon cooling. When the mixture became nearly neutral, Na₂CO₃ was added to adjust the pH to 9. The mixture was extracted with CH₂Cl₂ (3 × 2 mL), and the combined organic layers were concentrated to give product 289. The purification was done by flash column chromatography (ethyl acetate/ n-pentane = 1/1).

**Synthesis of products 290.**[^105]

Under argon, compound 289 (0.1 mmol, 1.0 equiv), PhI(OAc)₂ (96.9 mg, 0.3 mmol, 3.0 equiv) and iodine (25.4 mg, 0.1 mmol, 1.0 equiv) were added into a sealable reaction tube (5 mL). Then, DCE (1.0 mL) was added and the reaction was stirred for 16 h under the visible light (provided by a fluorescent lamp) at room temperature. Subsequently, the mixture was quenched by the addition of a sat. aqueous solution of Na₂S₂O₃ (2.0 mL) and extracted with DCM (3 × 5.0 mL). The solvent was removed in vacuum, and the product was purified by flash column chromatography (ethyl acetate/ n-pentane = 1/3) to give 290a and 290b. The diastereomeric ratio of 290a was determined by ¹H NMR spectroscopy of the crude product mixture.

**Synthesis of products 292.**[^106]

Under argon, compound 288 (24 mg, 0.05 mmol, 1.0 equiv), phenyl boronic acid

[^105]: Compound 289 was synthesized as described.

[^106]: Compound 292 was synthesized as described.
(12.2 mg, 0.1 mmol, 2.0 equiv), Pd(PPh₃)₄ (2.9 mg, 0.0025 mmol, 0.05 equiv), K₂CO₃ (9.7 mg, 0.07 mmol, 1.4 equiv), MeCN (0.9 mL) and H₂O (0.3 mL) were placed in a reaction tube. After stirring at 120 °C for 24 h, the reaction mixture was cooled to room temperature.

Product 292a: Purification by flash column chromatography (ethyl acetate/ n-pentane = 1/4) gave the product (starting from 288ar) as a colorless oil in 62% yield.

Product 292b: Purification by flash column chromatography (ethyl acetate/ n-pentane = 1/4) gave the product (starting from 288ga) as a colorless oil in 67% yield.

Characterization data

\[ \text{N-}\left\{2\text{-Chloro-2-phenylethyl}(\text{oxo})(\text{phenyl})-\lambda^6\text{-sulfaneylidene}\}4\text{-methylbenzenesulfonamide (287aa)} \]

\[ \begin{array}{c}
\text{Ph} \\
\text{Cl} \\
\text{O} \\
\text{S} \\
\text{N} \\
\text{Ts} \\
\text{Ph} \\
\end{array} \]

Light yellow oil, 38.1 mg, 88% yield, \( dr = 1:1 \)

\(^1\)H NMR (400 MHz, CDCl₃, mixture of diastereomers) \( \delta 7.86 – 7.78 \) (m, 3H), 7.78 – 7.72 (m, 1H), 7.61 – 7.53 (m, 1H), 7.49 – 7.38 (m, 2H), 7.24 – 7.22 (m, 5H), 7.19 – 7.13 (m, 2H), 5.44 – 5.32 (m, 1H), 4.49 – 4.38 (m, 1H), 4.28 – 4.18 (m, 1H), 2.38 (d, \( J = 3.0 \) Hz, 3H).

\(^{13}\)C\{\(^1\)H\} NMR (101 MHz, CDCl₃, mixture of diastereomers) \( \delta 143.0, 140.5, 137.7, 137.6, 136.9, 136.7, 134.3, 134.3, 129.4, 129.3, 129.3, 129.0, 128.8, 128.3, 128.3, 127.2, 126.6, 65.3, 65.0, 54.9, 54.7, 21.5. \)

MS (EI, 70 eV): \( m/z \) (%) = 154.9 (23), 140 (34), 139.0 (62), 124.9 (39), 123.9 (11), 104.1 (48), 103.0 (88), 92.1 (15), 91.0 (100), 89.1 (10), 77.1 (58), 65.1 (27). MS (ESI) [M+Na]⁺: 456.05,

HRMS (ESI) (m/z) [C₂₁H₂₂NO₃S₂Na]⁺: Calcd. 456.0471, found 456.0461.

IR (ATR): \( \nu = 3570, 3064, 2925, 2855, 2587, 2324, 2254, 2160, 2100, 1991, 1598, 1494, 1450, 1379, 1311, 1234, 1149, 1060, 1021, 901, 812, 737. \)

\[ \text{N-}\left\{2\text{-Chloro-2-(o-tolyl)ethyl}(\text{oxo})(\text{phenyl})-\lambda^6\text{-sulfaneylidene}\}4\text{-methylbenzenesulfonamide (287ab)} \]

\[ \begin{array}{c}
\text{Me} \\
\text{Cl} \\
\text{O} \\
\text{S} \\
\text{N} \\
\text{Ts} \\
\text{Ph} \\
\text{Me} \\
\end{array} \]
Light yellow oil, 32.6 mg, 73% yield, \( dr = 1:1 \)

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 7.84 - 7.80 \) (m, 3H), 7.76 - 7.73 (m, 1H), 7.62 - 7.55 (m, 1H), 7.46 (t, \( J = 7.9 \) Hz, 1H), 7.41 (t, \( J = 8.0 \) Hz, 1H), 7.26 - 7.22 (m, 2H), 7.16 - 6.93 (m, 4H), 5.70 - 5.60 (m, 1H), 4.61 - 4.46 (m, 1H), 4.33 - 4.24 (m, 1H), 2.42 - 2.32 (m, 6H).

\(^{13}\)C{\(^1\)H} NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 143.0, 143.0, 140.5, 140.5, 136.7, 136.5, 135.7, 135.7, 135.6, 135.6, 134.4, 134.3, 131.0, 130.9, 129.4, 129.3, 129.2, 129.1, 128.3, 128.1, 126.9, 126.8, 126.8, 126.7, 126.7, 126.6, 64.5, 64.1, 51.1, 50.7, 21.6, 19.1, 19.1.

MS (EI, 70 eV): \( m/z \) (%) = 295.0 (13), 155.0 (22), 152.0 (25), 140.0 (20), 139.0 (38), 124.9 (22), 118.1 (26), 117.0 (59), 115.0 (30), 91.1 (100), 77.1 (25), 65.1 (23). MS (ESI) [M+Na]\(^+\): 490.01.

HRMS (ESI) \( (m/z) \) \([C_{22}H_{22}ClNO_3S_2Na]^+\) : Calcd. 470.0627, found 470.0621.

IR (ATR): \( \nu = 3842, 3163, 3062, 2925, 2654, 2161, 1991, 1600, 1491, 1448, 1397, 1315, 1234, 1152, 1091, 998, 893, 813, 747. \)

\( N\)-\{[2-Chloro-2-(m-tolyl)ethyl]oxo(phenyl)-\( \lambda^6\)-sulfaneylidene\}-4-methylbenzenesulfonamide (287ac)

Light yellow oil, 35.3 mg, 79% yield, \( dr = 1:1 \)

\(^1\)H NMR (400 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 7.83 - 7.79 \) (m, 3H), 7.74 - 7.21 (m, 1H), 7.56 (dt, \( J = 16.0, 7.5 \) Hz, 1H), 7.46 - 7.37 (m, 2H), 7.23 (d, \( J = 8.2 \) Hz, 2H), 7.16 - 6.88 (m, 4H), 5.39 - 5.27 (m, 1H), 4.52 - 4.36 (m, 1H), 4.31 - 4.17 (m, 1H), 2.37 (s, 3H), 2.20 (d, \( J = 20.3 \) Hz, 3H).

\(^{13}\)C{\(^1\)H} NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 143.0, 140.5, 138.8, 138.6, 137.5, 137.4, 136.9, 136.6, 134.3, 134.2, 130.1, 130.0, 129.3, 129.2, 128.9, 128.7, 128.3, 128.2, 127.7, 127.7, 126.6, 124.4, 65.3, 64.9, 54.9, 54.8, 21.5, 21.2.

MS (EI, 70 eV): \( m/z \) (%) = 328.0 (12), 296.0 (15), 294.9 (15), 294.9 (15), 155.0 (32), 152.0 (43), 140.0 (27), 139.0 (64), 133.0 (16), 124.9 (31), 118.1 (38), 117.1 (79), 115.0 (37), 91.1 (100), 77.1 (26), 65.1 (25). MS (ESI) [M+Na]\(^+\): 470.06.

HRMS (ESI) \( (m/z) \) \([C_{22}H_{22}ClNO_3S_2Na]^+\) : Calcd. 470.0627, found 470.0614.

IR (ATR): \( \nu = 3664, 3064, 2923, 2467, 2168, 2040, 1597, 1448, 1381, 1312, 1223, \)
N-[[2-Chloro-2-(p-tolyl)ethyl](oxo)(phenyl)-λ₆-sulfaneylidene]-4-methylbenzenesulfonamide (287ad)

Light yellow oil, 37.1 mg, 83% yield, $dr = 1:1$

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) δ 7.85 – 7.77 (m, 3H), 7.73 (dd, $J = 8.5, 1.1$ Hz, 1H), 7.62 – 7.53 (m, 1H), 7.46 – 7.37 (m, 2H), 7.26 – 7.20 (m, 2H), 7.11 (d, $J = 8.2$ Hz, 1H), 7.03 (dd, $J = 10.0, 8.2$ Hz, 2H), 6.93 (d, $J = 7.9$ Hz, 1H), 5.40 – 5.29 (m, 1H), 4.49 – 4.36 (m, 1H), 4.28 – 4.16 (m, 1H), 2.37 (d, $J = 3.2$ Hz, 3H), 2.26 (d, $J = 11.6$ Hz, 3H).

$^{13}$C{$_{^1}$H} NMR (101 MHz, CDCl$_3$, mixture of diastereomers) δ 142.9, 140.5, 139.3, 139.3, 136.9, 136.8, 134.7, 134.6, 134.2, 134.1, 129.6, 129.4, 129.3, 129.2, 128.3, 127.1, 127.1, 126.7, 126.6, 65.4, 65.1, 54.8, 54.7, 21.5, 21.1.

MS (EI, 70 eV): $m/z$ (%) = 295.0 (13), 155.0 (22), 139.0 (38), 118.1 (26), 117.0 (59), 91.1 (100), 77.1 (25), 65.1 (23). MS (ESI) [M+Na]$^+$: 470.06, HRMS (ESI) ($m/z$) [C$_{22}$H$_{22}$ClNO$_3$S$_2$Na]$^+$: Calcd. 470.0627, found 470.0610.

IR (ATR): $\nu$ = 3842, 3163, 3062, 2925, 2858, 2654, 2330, 2161, 1991, 1897, 1806, 1600, 1491, 1448, 1397, 1315, 1234, 1152, 1091, 998, 893, 813.

N-[[2-Chloro-2-(3-fluorophenyl)ethyl](oxo)(phenyl)-λ₆-sulfaneylidene]-4-methylbenzenesulfonamide (287ak)

Light yellow oil, 33.8 mg, 75% yield, $dr = 1:1$

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) δ 7.82 – 7.78 (m, 4H), 7.60 (dd, $J = 14.5, 7.3$ Hz, 1H), 7.51 – 7.41 (m, 2H), 7.26 – 7.10 (m, 3H), 7.03 (dd, $J = 23.5, 7.8$ Hz, 1H), 6.97 – 6.83 (m, 2H), 5.40 – 5.34 (m, 1H), 4.44 – 4.37 (m, 1H), 4.25 – 4.15, (m, 1H), 2.38 (d, $J = 2.5$ Hz, 3H).

$^{13}$C{$_{^1}$H} NMR (101 MHz, CDCl$_3$, mixture of diastereomers) δ 163.9, 163.7, 161.4, 161.3, 143.1, 143.1, 140.4, 136.7, 136.6, 134.5, 130.7, 130.6, 130.5, 130.5, 129.4, 129.4, 129.3, 128.2, 126.6, 123.0, 116.5, 116.4, 116.3, 116.2, 114.4, 114.2, 114.2, 65.1,
64.7, 54.1, 53.9, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): m/z (%) = 295.0 (19), 155.0 (42), 140.1 (58), 139.1 (99), 125.0 (66), 122.1 (42), 121.1 (36), 101.1 (28), 91.1 (100), 78.2 (22), 77.2 (34), 65.2 (30). MS (ESI) [M+Na]^+: 474.04.

HRMS (ESI) (m/z) [C_{21}H_{19}FClNO_3S_2Na]^+: Calcd. 474.0352, found 474.0367.


\[ \text{N-\{} \{\text{2-Chloro-2-(4-fluorophenyl)ethyl}\} \text{(oxo)(phenyl) -}\lambda^6\text{-sulfaneylidene}\} \text{-4-methylbenzenesulfonamide (287ah)} \]

Light yellow oil, 27.0 mg, 60% yield, \( dr = 1:1 \)

\(^1\)H NMR (400 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.84 – 7.73 (m, 4H), 7.60 (dd, \( J = 13.8, 7.4 \text{ Hz, 1H} \)), 7.45 (dd, \( J = 15.6, 7.5 \text{ Hz, 2H} \)), 7.26 – 7.19 (m, 3H), 7.16 (dd, \( J = 8.7, 5.2 \text{ Hz, 1H} \)), 6.85 (dt, \( J = 23.3, 8.6 \text{ Hz, 2H} \)), 5.43 – 5.34 (m, 1H), 4.47 – 4.36 (m, 1H), 4.29 – 4.14 (m, 1H), 2.38 (d, \( J = 3.6 \text{ Hz, 3H} \)).

\(^{13}\)C\{\(^1\)H\}\} NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 164.1, 164.1, 161.6, 161.6, 143.1, 140.4, 140.4, 136.9, 136.7, 134.6, 134.5, 133.5, 133.4, 133.4, 129.4, 129.4, 129.3, 129.2, 129.2, 128.2, 126.7, 126.6, 116.0, 115.9, 115.8, 115.7, 65.3, 65.0, 54.2, 54.1, 21.1. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): m/z (%) = 295.0 (23), 157.1 (18), 156.1 (22), 155.0 (45), 140.1 (61), 139.0 (100), 125.0 (56), 122.1 (68), 121.0 (56), 101.1 (34), 91.1 (100), 77.2 (34), 65.2 (41). MS (ESI) [M+Na]^+: 474.04.

HRMS (ESI) (m/z) [C_{21}H_{19}FClNO_3S_2Na]^+: Calcd. 474.0352, found 474.0367.

IR (ATR): ν = 3067, 2987, 2929, 1602, 1510, 1448, 1400, 1312, 1230, 1150, 1062, 1023, 909, 841, 812, 738, 679.

\[ \text{N-\{} \{\text{2-Chloro-2-(3-chlorophenyl)ethyl}\} \text{(oxo)(phenyl) -}\lambda^6\text{-sulfaneylidene}\} \text{-4-methylbenzenesulfonamide (287al)} \]

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Light yellow oil, 34.5 mg, 74% yield, \(dr = 1:1\)

\(^1\)H NMR (600 MHz, CDCl₃, mixture of diastereomers) \(\delta 7.84 - 7.76\) (m, 3H), 7.78 - 7.75 (m, 1H), 7.61 (dt, \(J = 13.6, 7.5\) Hz, 1H), 7.46 (dt, \(J = 13.9, 7.9\) Hz, 2H), 7.27 - 7.24 (m, 2H), 7.23 - 7.10 (m, 4H), 5.41 - 5.32 (m, 1H), 4.50 - 4.37 (m, 1H), 4.31 - 4.19 (m, 1H), 2.39 (d, \(J = 2.3\) Hz, 3H).

\(^1^3\)C\(^{\{1\}}\)H NMR (151 MHz, CDCl₃, mixture of diastereomers) \(\delta 143.2, 143.1, 142.2, 140.4, 140.3, 139.4, 136.6, 136.4, 134.8, 134.7, 134.6, 134.5, 134.2, 131.5, 130.4, 130.3, 130.1, 129.7, 129.5, 129.4, 129.4, 129.3, 128.4, 128.2, 128.2, 127.8, 127.4, 127.4, 127.3, 127.1, 126.8, 126.6, 125.7, 125.6, 64.9, 64.6, 54.1, 53.9, 21.6.

MS (EI, 70 eV): \(m/z\) (%): 295.0 (22), 154.9 (34), 140.0 (52), 139.0 (100), 124.9 (66), 13.9 (21), 103.1 (22), 91.0 (97), 77.1 (42). MS (ESI) [M+Na]\(^+\): 490.01,

HRMS (ESI) \((m/z)\) \([\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{NO}_3\text{S}_2\text{Na}]^+\): Calcd. 490.0081, found 490.0072.

IR (ATR): \(\nu = 3064, 2926, 2316, 2168, 2033, 1736, 1595, 1446, 1400, 1309, 1235, 1148, 1059, 906, 812, 743\).

\(\text{N-\{2-Chloro-2-(4-chlorophenyl)ethyl\}(oxo)(phenyl)-}^6\text{sulfaneylidene}\)-4-methyl benzenesulfonamide (287ap)

Light yellow oil, 37.4 mg, 80% yield, \(dr = 1:1\)

\(^1\)H NMR (400 MHz, CDCl₃, mixture of diastereomers) \(\delta 7.81 - 7.73\) (M, 3H), 7.64 - 7.57 (m, 1H), 7.47 - 7.42 (m, 2H), 7.23 (dd, \(J = 7.4, 0.4\) Hz, 2H), 7.13 (d, \(J = 22.4\) Hz, 3H), 5.42 - 5.32 (m, 1H), 4.46 - 4.34 (m, 1H), 4.30 - 4.12 (m, 1H), 2.38 (d, \(J = 4.1\) Hz, 3H).

\(^1^3\)C\(^{\{1\}}\)H NMR (101 MHz, CDCl₃, mixture of diastereomers) \(\delta 143.1, 140.4, 136.8, 136.0, 135.2, 134.4, 129.4, 129.3, 129.1, 129.0, 128.7, 128.7, 128.2, 126.7, 126.6, 65.2, 64.9, 54.1, 54.0, 21.5.

MS (EI, 70 eV): \(m/z\) (%): 295.0 (23), 172.0 (12), 155.0 (35), 140.1 (66), 139.1 (100), 138.0 (55), 137.0 (19), 125.0 (56), 124.1 (22), 123.1 (11), 103.1 (32), 102.1 (18), 101.1 (15), 97.1 (13), 91.1 (79), 78.2 (22), 77.2 (50), 65.2 (27). MS (ESI) [M+Na]\(^+\): 490.01,
HRMS (ESI) ($m/z$) [C$_{21}$H$_{19}$Cl$_2$NO$_3$S$_2$Na]$^+$: Calcd. 490.0081, found 490.0077.


$N^{-}\{[2-(4-Bromophenyl)-2-chloroethyl](oxo)(phenyl)-\lambda^6$-sulfaneylidene}$-4$-methylbenzenesulfonamide (287ag)

Light yellow oil, 40.4 mg, 79% yield, $dr$ = 1:1

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.82 – 7.71 (m, 4H), 7.64 – 7.58 (m, 1H), 7.47 – 7.42 (m, 2H), 7.31 (d, $J$ = 8.4 Hz, 1H), 7.24 (t, $J$ = 7.0 Hz, 3H), 7.10 (d, $J$ = 8.3 Hz, 1H), 7.04 (d, $J$ = 8.3 Hz, 1H), 5.40 – 5.32 (m, 1H), 4.46 – 4.34 (m, 1H), 4.31 – 4.13 (m, 1H), 2.38 (d, $J$ = 4.5 Hz, 3H).

$^{13}$C ($^1$H) NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 143.1, 140.3, 136.8, 136.7, 136.4, 134.3, 132.0, 131.9, 129.4, 129.3, 129.0, 128.2, 126.7, 126.6, 123.5, 123.4, 65.1, 64.8, 54.2 54.1 21.5.

MS (EI, 70 eV): $m/z$ (%) = 295.1 (31), 184.1 (28), 182.1 (31), 155.1 (46), 140.1 (65), 139.1 (100), 138.1 (16), 125.1 (52), 124.1 (22), 103.2 (26), 102.1 (20), 91.1 (83), 77.2 (48). MS (ESI) [M+H]$^+$: 511.98,

HRMS (ESI) ($m/z$) [C$_{21}$H$_{20}$BrClNO$_3$S$_2$]$^+$: Calcd. 511.9757, found 511.9768.


$N^{-}\{[2-[4-(Tert-butyl)phenyl]-2-chloroethyl](oxo)(phenyl)-\lambda^6$-sulfaneylidene}$-4$-methylbenzenesulfonamide (287ae)

Light yellow oil, 41.9 mg, 86% yield, $dr$ = 1:1

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.86 – 7.75 (m, 3H), 7.73 – 7.67 (m, 1H), 7.58 – 7.48 (m, 1H), 7.43 – 7.34 (m, 2H), 7.26 – 7.20 (m, 3H), 7.14 (d, $J$ = 9.0 Hz, 2H), 7.06 (d, $J$ = 8.4 Hz, 1H), 5.38 (dt, $J$ = 13.9, 6.6 Hz, 1H), 4.55 – 4.37 (m, 1H), 4.32 – 4.20 (m, 1H), 2.37 (s, 3H), 1.25 (d, $J$ = 9.2 Hz, 9H).
$^{13}$C\{\textsuperscript{1}H\} NMR (101 MHz, CDCl\textsubscript{3}, mixture of diastereomers) δ 152.4, 152.3, 143.0, 140.6, 136.9, 136.6, 134.5, 134.4, 134.2, 134.1, 129.3, 129.2, 128.3, 128.2, 126.9, 126.6, 125.9, 125.7, 65.3, 64.8, 54.7, 54.7, 34.6, 34.6, 31.2, 21.5.

MS (EI, 70 eV): m/z (%) = 194.0 (38), 181.0 (22), 179.0 (44), 154.9 (26), 145.0 (58), 139.0 (39), 124.9 (23). MS (ESI [M+H]\textsuperscript{+}): 490.13.

HRMS (ESI) (m/z) \([\text{C}_{25}\text{H}_{29}\text{ClNO}_3\text{S}_2]^+\): Calcd. 490.1277, found 490.1254.


\textit{N-}{[\text{2-Chloro-2-(4-methoxyphenyl)ethyl}(oxo)(phenyl)–$\lambda^6$-sulfaneylidene]}-4-methylbenzenesulfonamide (287af)

Light yellow oil, 25.5 mg, 55% yield, $dr = 1:1$

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, mixture of diastereomers) δ 7.84 – 7.77 (m, 3H), 7.75 – 7.70 (m, 1H), 7.60 – 7.53 (m, 1H), 7.46 – 7.38 (m, 2H), 7.26 – 7.19 (m, 2H), 7.14 (d, $J = 8.7$ Hz, 1H), 7.06 (d, $J = 8.7$ Hz, 1H), 6.75 – 6.67 (m, 1H), 6.63 (d, $J = 8.8$ Hz, 1H), 5.43 – 5.29 (m, 1H), 4.51 – 4.35 (m, 1H), 4.30 – 4.15 (m, 1H), 3.74 (d, $J = 9.2$ Hz, 3H), 2.37 (d, $J = 2.8$ Hz, 3H).

\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (101 MHz, CDCl\textsubscript{3}, mixture of diastereomers) δ 160.2, 160.1, 143.0, 140.5, 136.9, 136.8, 134.2, 134.1, 129.7, 129.6, 129.4, 129.3, 129.3, 128.6, 128.3, 128.2, 126.6, 114.3, 114.1, 65.4, 65.0, 55.3, 54.8, 54.7, 21.5.

MS (EI, 70 eV): m/z (%) = 294.9 (30), 183.9 (16), 181.9 (18), 154.9 (42), 140.0 (64), 139.0 (100), 123.9 (86), 103.0 (33), 91.0 (92), 77.1 (44). MS (ESI [M+H]\textsuperscript{+}): 464.08.

HRMS (ESI) (m/z) \([\text{C}_{22}\text{H}_{22}\text{ClNO}_4\text{S}_2\text{Na}]^+\): Calcd. 486.0577, found 486.0583.

IR (ATR): $\nu$ = 3067, 2927, 2682, 2427, 2474, 2331, 2213, 2103, 1992, 1945, 1815, 1732, 1592, 1488, 1449, 1330, 1234, 1181, 1145, 1102, 1042, 1021, 996, 902, 839, 754.

\textit{N-}{[\text{2-[3,5-Bis(trifluoromethyl)phenyl]-2-chloroethyl}(oxo)(phenyl)–$\lambda^6$-sulfaneylidene]}-4-methylbenzenesulfonamide (287an)
Light yellow oil, 52.3 mg, 92% yield, \( dr = 1:1 \)

\(^1\)H NMR (400 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.83 – 7.74 (m, 3H), 7.70 (t, \( J = 9.9 \) Hz, 4H), 7.56 (dd, \( J = 8.7, 7.7 \) Hz, 1H), 7.44 – 7.37 (m, 2H), 7.28 – 7.20 (m, 2H), 5.57 – 5.47 (m, 1H), 4.62 – 4.24 (m, 2H), 2.38 (s, 3H).

\(^1^3\)C\(^{\text{\textsuperscript{1}}\text{H}}\) NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 143.3, 140.1, 140.0, 136.3, 136.1, 134.7, 134.7 132.5, 132.5, 132.2, 132.1, 129.9, 129.6, 129.5, 129.4, 128.1, 128.0, 127.7, 126.6, 124.0, 123.2, 121.3, 64.5, 64.2, 53.3, 53.2, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): \( m/z \) (%) = 294.0 (16), 219.0 (12), 155.0 (34), 140.0 (30), 139.0 (69), 124.9 (84), 97.0 (13), 91.1 (100), 78.1 (16), 77.1 (35), 65.1 (29). MS (ESI) [M+Na]^+: 592.02,

HRMS (ESI) \( m/z \) [C\(_{23}\)H\(_{18}\)ClF\(_6\)NO\(_3\)S\(_2\)Na]^+: Calcd. 592.0219, found 592.0210.


\( N-\{[2-[(1,1\textsuperscript{'})\text{Biphenyl}-4-yl]-2-chloroethyl\}(oxo)(phenyl)-\lambda\textsuperscript{6}-sulfaneylidene\}-4-methylbenzenesulfonamide (287ai) \)

Light yellow oil, 30.6 mg, 60% yield, \( dr = 1:1 \)

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.85 (dd, \( J = 8.2, 5.6 \) Hz, 2H), 7.81 (dd, \( J = 8.5, 0.9 \) Hz, 1H), 7.74 (dd, \( J = 8.5, 1.0 \) Hz, 1H), 7.60 – 7.33 (m, 10H), 7.31 (d, \( J = 8.3 \) Hz, 1H), 7.24 (dd, \( J = 8.2, 4.6 \) Hz, 3H), 5.52 – 5.40 (m, 1H), 4.60 – 4.44 (m, 1H), 4.39 – 4.26 (m, 1H), 2.38 (d, \( J = 3.7 \) Hz, 3H).

\(^1^3\)C\(^{\text{\textsuperscript{1}}\text{H}}\) NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 143.0, 142.3, 142.2, 140.5, 140.5, 140.0, 140.0, 136.9, 136.7, 136.3, 136.2, 134.2, 134.1, 129.4, 129.3, 128.9, 128.9, 128.3, 128.2, 127.8, 127.8, 127.8, 127.6, 127.5, 127.0, 127.0, 126.7, 126.7, 65.3, 64.8, 54.7, 54.6, 21.5.

MS (EI, 70 eV): \( m/z \) (%) = 214.0 (21), 195.0 (100), 180.1 (73), 179.1 (34), 178.0 (59), 177.0 (19), 167.0 (64), 165.1 (48), 155.0 (27), 139.0 (96), 125.0 (48), 123.9 (20), 91.1 (90), 71.1 (53). MS (ESI) [M+H]^+: 510.10,
HRMS (ESI) (m/z) [C_{27}H_{25}ClNO_3S_2Na]^+: Calcd. 510.0964, found 510.0942.
IR (ATR): $\nu = 3454, 3034, 2926, 2334, 2151, 2107, 1913, 1738, 1597, 1484, 1447, 1402, 1308, 1228, 1150, 1065, 906, 812, 743.$

4-[1-Chloro-2-((N-toslyphenylsulfonimidoyl)ethyl)phenylacetate (287ao)

Light yellow oil, 41.7 mg, 85% yield, $dr = 1:1$

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.82 (dd, $J = 8.3$, 1.7 Hz, 2H), 7.79 – 7.71 (m, 2H), 7.63 – 7.53 (m, 1H), 7.43 (dt, $J = 16.2$, 8.2 Hz, 2H), 7.23 (dd, $J = 8.3$, 1.8 Hz, 3H), 7.18 (d, $J = 8.6$ Hz, 1H), 6.94 (d, $J = 8.6$ Hz, 1H), 5.45 – 5.35 (m, 1H), 4.51 – 4.33 (m, 1H), 4.31 – 4.16 (m, 1H), 2.37 (d, $J = 1.9$ Hz, 3H), 2.26 (d, $J = 3.7$ Hz, 3H).

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 168.9, 168.9, 151.1, 151.1, 143.0, 140.5, 136.7, 136.5, 135.0, 135.0, 134.4, 128.5, 128.5, 128.2, 126.6, 122.1, 122.0, 65.4, 65.0, 54.3, 54.2, 21.5, 21.1.

MS (EI, 70 eV): $m/z$ (%) = 162.1 (10), 155.0 (39), 154.0 (28), 140.1 (21), 139.1 (45), 135.1 (14), 125.0 (70), 120.1 (100), 119.1 (18), 91.1 (76), 77.2 (31), 65.3 (26). MS (ESI) [M+Na]$^+$: 514.05.

HRMS (ESI) (m/z) [C_{23}H_{22}ClNO_5S_2Na]^+: Calcd. 514.0527, found 514.0514.
IR (ATR): $\nu = 3055, 2985, 2684, 2325, 2173, 2112, 1992, 1763, 1601, 1507, 1423, 1371, 1319, 1264, 1204,1155, 1092, 1066, 1017, 907, 732.$

N-[2-Chloro-2-mesitylethyl](oxo)(phenyl)-$\lambda^5$-sulfaneylidene]-4-methylbenzenesulfonyamide (287aj)

Light yellow oil, 37.1 mg, 78% yield, $dr = 1:1$

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.82 (dd, $J = 10.4$, 8.0 Hz, 3H), 7.74 – 7.71 (m, 1H), 7.65 – 7.55 (m, 1H), 7.47 (t, $J = 8.0$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 7.24 (dd, $J = 8.0$, 4.6 Hz, 2H), 6.66 (dd, $J = 109.3$, 54.2 Hz, 2H), 5.85 (dt, $J = 14.0$, 6.6 Hz, 1H), 4.66 – 4.36 (m, 2H), 2.42 – 2.16 (m, 12H).

$^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 143.0, 142.9, 140.5, 140.5, 139.0, 139.0, 137.2, 136.6, 136.4, 136.3, 136.1, 134.3, 134.1, 131.5, 131.4,

MS (EI, 70 eV): m/z (%) = 162.1 (10), 161.0 (100), 154.9 (10), 145.0 (66), 139.0 (31), 129.0 (26), 91.0 (39), 77.1 (10). MS (ESI) [M+H]+: 476.11,
HRMS (ESI) (m/z) [C24H27ClNO3S2]+: Calcd. 476.1121, found 476.1118.
IR (ATR): ν = 3885, 2925, 2325, 2176, 1993, 1741, 1606, 1449, 1382, 1317, 1233, 1152, 1091, 1066, 897, 855, 813, 741, 682.

N-[(1-Chloro-1-phenylpropan-2-yl)(oxo)(phenyl)-\(\lambda^6\)-sulfaneylidene]-4-methylbenzenesulfonamide (287ap)

Light yellow oil, 33.0 mg, 74% yield, \(dr = 1:1\)

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) δ 8.06 – 7.95 (m, 2H), 7.88 (t, \(J = 7.8 \) Hz, 2H), 7.72 – 7.67 (m, 1H), 7.60 – 7.56 (m, 2H), 7.42 – 7.38 (m, 2H), 7.37 – 7.29 (m, 3H), 7.28 – 7.23 (m, 2H), 5.98 – 5.86 (m, 1H), 4.24 – 4.08 (m, 1H), 2.39 (s, 3H), 1.46 – 1.36 (m, 3H).

\(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) δ 142.9, 142.9, 140.8, 140.8, 137.9, 137.7, 134.9, 134.7, 134.5, 134.3, 130.24, 129.8, 129.3, 129.1, 128.8, 128.8, 127.1, 127.1, 126.7, 126.6, 69.8, 68.8, 59.8, 58.8, 21.6.

MS (EI, 70 eV): m/z (%) = 155.4 (11), 139.3 (38), 133.4 (18), 125.3 (20), 116.3 (30), 115.3 (78), 105.3 (20), 91.3 (100), 77.3 (31), 65.1 (38). MS (ESI) [M+Na]+: 470.06,
HRMS (ESI) (m/z) [C\(_{22}\)H\(_{22}\)ClNO\(_3\)S\(_2\)Na]+: Calcd. 470.0627, found 470.0611.
IR (ATR): ν = 3664, 3064, 2923, 2467, 2168, 2040, 1597, 1448, 1381, 1312, 1223, 1150, 1052, 880, 839, 812, 761.

N-[(4-(Tert-butyl)phenyl)(2-chloro-2-phenylethyl)(oxo)-\(\lambda^6\)-sulfaneylidene]-4-methylbenzenesulfonamide (287ba)

Light yellow oil, 43.1 mg, 88% yield, \(dr = 1:1\)

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) δ 7.83 (dd, \(J = 10.0, 8.4 \) Hz, 2H), 7.68 (d, \(J = 8.6 \) Hz, 1H), 7.60 (d, \(J = 8.6 \) Hz, 1H), 7.41 (d, \(J = 8.6 \) Hz, 1H), 7.36
(d, J = 8.6 Hz, 1H), 7.26 – 7.16 (m, 5H), 7.13 (dd, J = 10.0, 7.0 Hz, 2H), 5.48 – 5.32 (m, 1H), 4.54 – 4.35 (m, 1H), 4.34 – 4.16 (m, 1H), 2.39 (d, J = 4.0 Hz, 3H), 1.30 (d, J = 7.0 Hz, 9H).

$^{13}$C{$_1^1$H} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) δ 158.4, 158.3, 142.9, 140.6, 140.6, 137.6, 137.4, 133.4, 133.2, 129.2, 129.2, 129.2, 128.9, 128.8, 128.1, 128.0, 127.3, 126.7, 126.7, 126.4, 126.4, 65.2, 64.7, 54.8, 35.3, 35.3, 31.0, 30.9, 215.5.

MS (EI, 70 eV): m/z (%) = 155.0 (64), 151.0 (38), 140.0 (65), 139.0 (100), 124.8 (98), 91.1 (83), 77.2 (29). MS (ESI) [M+H]$^+$: 490.13.

HRMS (ESI) (m/z) [C$_{25}$H$_{29}$ClNO$_3$S$_2$]$: Calcd. 490.1277, found 490.1266.

IR (ATR): ν = 3065, 2930, 2146, 2026, 1912, 1737, 1599, 1449, 1398, 1319, 1236, 1066, 902, 805, 743, 681.

$^{13}$C{$_1^1$H} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) δ 145.7, 145.7, 142.9, 140.6, 140.6, 137.8, 137.7, 133.6, 133.4, 130.0, 130.0, 129.3, 129.2, 129.1, 129.0, 128.8, 128.4, 128.3, 127.2, 127.2, 126.7, 126.6, 65.4, 65.2, 55.0, 54.8, 217, 217, 21.5.

MS (EI, 70 eV): m/z (%) = 155.2 (27), 139.2 (100), 104.2 (20), 103.2 (22), 91.2 (56), 65.2 (16). MS (ESI) [M+Na]$^+$: 470.06.

HRMS (ESI) (m/z) [C$_{22}$H$_{22}$ClNO$_3$S$_2$Na]$^+$: Calcd. 470.0627, found 470.0624.

IR (ATR): ν = 3747, 3040, 2928, 2676, 2327, 2255, 2158, 1915, 1804, 1735, 1595, 1494, 1453, 1396, 1310, 1233, 1150, 1066, 907, 811, 729.

$N$-[(2-Chloro-2-phenylethyl)(oxo)(p-tolyl)-$\lambda^6$-sulfaneylidene]-4-methylbenzenesulfonamide (287ca)

Light yellow oil, 34.8 mg, 78% yield, $dr = 1:1$

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) δ 7.85 – 7.80 (m, 2H), 7.71 (d, J = 8.3 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.26 – 7.21 (m, 7H), 7.19 – 7.17 (m, 2H), 5.41 – 5.33 (m, 1H), 4.44 – 4.38 (m, 1H), 4.26 – 4.19 (m, 1H), 2.43 – 2.37 (m, 6H).

$^{13}$C{$_1^1$H} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) δ 145.7, 145.7, 142.9, 140.6, 140.6, 137.8, 137.7, 133.6, 133.4, 130.0, 130.0, 129.3, 129.2, 129.1, 129.0, 128.8, 128.4, 128.3, 127.2, 127.2, 126.7, 126.6, 65.4, 65.2, 55.0, 54.8, 217, 217, 21.5.

MS (EI, 70 eV): m/z (%) = 155.2 (27), 139.2 (100), 104.2 (20), 103.2 (22), 91.2 (56), 65.2 (16). MS (ESI) [M+Na]$^+$: 470.06.

HRMS (ESI) (m/z) [C$_{22}$H$_{22}$ClNO$_3$S$_2$Na]$^+$: Calcd. 470.0627, found 470.0624.

IR (ATR): ν = 3747, 3040, 2928, 2676, 2327, 2255, 2158, 1915, 1804, 1735, 1595, 1494, 1453, 1396, 1310, 1233, 1150, 1066, 907, 811, 729.

$N$-[(2-Chloro-2-phenylethyl)(3-fluorophenyl)(oxo)-$\lambda^6$-sulfaneylidene]-4-methylbenzenesulfonamide (287da)
Light yellow oil, 13.5 mg, 30% yield, $dr = 1:1$

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.86 – 7.77 (m, 2H), 7.60 (dd, $J = 22.8$, 7.5 Hz, 1H), 7.47 – 7.33 (m, 3H), 7.24 (dd, $J = 8.4$, 5.5 Hz, 5H), 7.17 (d, $J = 3.4$ Hz, 2H), 5.47 – 5.32 (m, 1H), 4.53 – 4.17 (m, 2H), 2.39 (s, 3H).

$^{13}$C {$^1$H} NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 143.2, 137.9, 137.2, 131.1, 131.1, 129.5, 129.4, 129.3, 129.3, 129.2, 129.0, 128.9, 128.8, 127.2, 127.2, 126.7, 126.7, 124.1, 121.5, 116.0, 65.4, 65.0, 54.7, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): $m/z$ (%) = 139.1 (16), 104.1 (59), 103.1 (99), 95.1 (18), 91.1 (100), 77.2 (58), 65.3 (40). MS (ESI) [M+Na]$^+$: 474.04,

HRMS (ESI) ($m/z$) [C$_{21}$H$_{19}$ClFNO$_3$S$_2$Na]$^+$: Calcd. 474.0377, found 474.0371.

IR (ATR): $\nu = 3836$, 3648, 3073, 2925, 2857, 2692, 2470, 2164, 2044, 1911, 1732, 1594, 1473, 1314, 1226, 1150, 1070, 878, 806, 741, 688.

*(E)-4-Methyl-\text{-}N\text{-}[\text{oxo(phenyl)(styryl)-2\text{-}sulfaneylidene}]\text{benzenesulfonamide}*

(288aa)

Light yellow solid, 38.5 mg, 97% yield, melting point: 129 – 131 °C.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 7.6$ Hz, 2H), 7.86 (d, $J = 8.2$ Hz, 2H), 7.67 – 7.62 (m, 2H), 7.57 (t, $J = 7.8$ Hz, 2H), 7.46 – 7.38 (m, 5H), 7.24 (d, $J = 8.1$ Hz, 2H), 6.89 (d, $J = 15.2$ Hz, 1H), 2.37 (s, 3H).

$^{13}$C {$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 143.9, 142.8, 140.8, 134.0, 134.0, 131.8, 131.7, 129.6, 129.3, 129.1, 128.9, 127.7, 126.8, 125.5, 21.5.

MS (EI, 70 eV): $m/z$ (%) = 214.1 (11), 139.0 (100), 125.0 (29), 119.0 (24), 91.1 (71), 77.1 (22). MS (ESI) [M+H]$^+$: 398.09,

HRMS (ESI) ($m/z$) [C$_{21}$H$_{20}$NO$_3$S$_2$]$^+$: Calcd. 398.0885, found 398.0880.

(E)-4-Methyl-N-{(2-methylstyril)(oxo)(phenyl)-2\textsuperscript{5}-sulfaneylidene}benzenesulfonamide (288ab)

![Chemical structure of (E)-4-Methyl-N-{(2-methylstyril)(oxo)(phenyl)-2\textsuperscript{5}-sulfaneylidene}benzenesulfonamide (288ab)]

Light yellow solid, 39.9 mg, 97% yield, melting point: 134 – 136 °C.

\[^1\text{H} \text{NMR (600 MHz, CDCl}_3\text{)} \delta 8.04 \text{ (dd, } J = 8.4, 0.9 \text{ Hz, 2H}), 7.96 \text{ (d, } J = 15.2 \text{ Hz, 1H}), 7.87 \text{ (d, } J = 8.2 \text{ Hz, 2H}), 7.67 \text{ (dd, } J = 10.8, 4.0 \text{ Hz, 1H}), 7.60 \text{ (dt, } J = 17.3, 7.9 \text{ Hz, 3H}), 7.51 \text{ (dd, } J = 7.8, 1.3 \text{ Hz, 1H}), 7.32 \text{ (t, } J = 7.5 \text{ Hz, 1H}), 7.27 \text{ (dt, } J = 10.4, 4.6 \text{ Hz, 3H}), 6.98 \text{ (d, } J = 15.2 \text{ Hz, 1H}), 2.38 \text{ (s, 3H).}

\[^{13}\text{C}\{^1\text{H}\} \text{NMR (151 MHz, CDCl}_3\text{)} \delta 143.0, 142.2, 140.6, 138.0, 134.2, 133.6, 132.5, 132.1, 129.7, 129.3, 128.9, 128.7, 128.0, 127.9, 126.8, 125.7, 21.6.

\[\text{MS (EI, 70 eV): } m/z \text{ (%) = 382.2 (17), 155.1 (21), 139.1 (71), 133.1 (29), 125.1 (36), 116.1 \text{ (36), 105.2 (23), 91.1 (100), 77.2 (43), 65.2 (51). MS (ESI) [M+H]\text{]: 412.10,}

\text{HRMS (ESI) (m/z) [C}_{22}\text{H}_{22}\text{NO}_3\text{S}_2^+}: \text{Calcd. 412.1041, found 412.1032.}

\text{IR (ATR): } \nu = 3841, 3644, 3424, 3323, 3145, 3062, 2922, 2705, 2494, 2293, 2200, 2158, 2100, 2057, 1984, 1925, 1739, 1597, 1483, 1447, 1379, 1309, 1223, 1150, 1057, 968, 837, 811, 752.

\[\text{(E)-4-Methyl-N-{(3-methylstyril)(oxo)(phenyl)-2\textsuperscript{5}-sulfaneylidene}benzenesulfonamide (288ac)}\]

![Chemical structure of (E)-4-Methyl-N-{(3-methylstyril)(oxo)(phenyl)-2\textsuperscript{5}-sulfaneylidene}benzenesulfonamide (288ac)]

Light yellow solid, 40.2 mg, 98% yield, melting point: 155 – 157 °C.

\[^1\text{H} \text{NMR (600 MHz, CDCl}_3\text{)} \delta 8.00 \text{ (d, } J = 8.2 \text{ Hz, 2H}), 7.85 \text{ (d, } J = 8.0 \text{ Hz, 2H}), 7.66 – 7.58 \text{ (m, 2H), 7.55 \text{ (t, } J = 7.7 \text{ Hz, 2H}), 7.34 \text{ (d, } J = 7.9 \text{ Hz, 2H}), 7.23 \text{ (d, } J = 8.1 \text{ Hz, 2H}), 7.19 \text{ (d, } J = 7.9 \text{ Hz, 2H}), 6.82 \text{ (d, } J = 15.2 \text{ Hz, 1H}), 2.36 \text{ (s, 6H).}

\[^{13}\text{C}\{^1\text{H}\} \text{NMR (151 MHz, CDCl}_3\text{)} \delta 144.0, 142.8, 142.6, 140.8, 138.9, 133.9, 129.9, 129.6, 129.6, 129.1, 128.9, 127.7, 127.7, 126.8, 124.1, 21.6, 21.5.

\[\text{MS (EI, 70 eV): } m/z \text{ (%) = 382.1 (18), 139.0 (100), 133.1 (58), 125.0 (23), 115.1 (17), 91.1 \text{ (65), 77.2 (17). MS (ESI) [M+H]\text{]: 412.10,}

\text{HRMS (ESI) (m/z) [C}_{22}\text{H}_{22}\text{NO}_3\text{S}_2^+}: \text{Calcd. 412.1041, found 412.1030.}

\text{IR (ATR): } \nu = 3839, 3660, 3327, 3058, 2921, 2726, 2472, 2255, 2160, 2034, 1991, 1918, 1809, 1735, 1602, 1509, 1446, 1411, 1312, 1231, 1150, 1054, 910, 865, 821,
(E)-4-Methyl-N-[(4-methylstyrlyl)(oxo)(phenyl)-6-sulfaneylidene]benzenesulfonamide (288ad)

Light yellow solid, 39.4 mg, 96% yield, melting point: 120 – 122 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.03 – 7.99 (m, 2H), 7.86 (d, $J$ = 8.2 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.56 (t, $J$ = 7.9 Hz, 2H), 7.25 (dt, $J$ = 19.8, 7.7 Hz, 6H), 6.87 (d, $J$ = 15.2 Hz, 1H), 2.36 (d, $J$ = 16.5 Hz, 6H).

$^{13}$C $^1$H NMR (151 MHz, CDCl$_3$) δ 144.2, 142.8, 140.8, 138.9, 138.8, 134.0, 132.6, 131.7, 129.9, 129.6, 129.3, 129.3, 129.3, 128.9, 127.7, 127.7, 126.8, 126.2, 125.2, 21.5, 21.2.

MS (EI, 70 eV): $m/z$ (%) = 139.0 (100), 133.1 (43), 130.1 (16), 125.0 (26), 115.1 (24), 105.1 (23), 91.1 (64), 77.2 (20). MS (ESI) [M+H]$^+$: 412.10, HRMS (ESI) ($m/z$) [C$_{22}$H$_{22}$NO$_3$S$_2$]$^+$: Calcd. 412.1041, found 412.1031.

IR (ATR): $\nu$ = 3059, 2921, 2253, 2162, 2033, 1917, 1808, 1734, 1603, 1479, 1446, 1312, 1233, 1150, 1088, 1054, 996, 833, 742.

(E)-N-[(3-Fluorostyrlyl)(oxo)(phenyl)-6-sulfaneylidene]-4-methylbenzenesulfonamide (288ak)

Light yellow solid, 38.6 mg, 93% yield, melting point: 155 – 157 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.05 – 7.99 (m, 2H), 7.86 (d, $J$ = 8.3 Hz, 2H), 7.66 (t, $J$ = 7.4 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.41 – 7.33 (m, 1H), 7.28 – 7.22 (m, 3H), 7.13 (t, $J$ = 8.0 Hz, 2H), 6.91 (d, $J$ = 15.2 Hz, 1H), 2.38 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 162.9 (d, $J$ = 247.6 Hz), 143.0, 142.4 (d, $J$ = 3.0 Hz), 140.7, 138.2, 134.2, 133.9 (d, $J$ = 7.6 Hz), 130.8 (d, $J$ = 6.0 Hz), 129.7, 129.3, 127.8, 127.2, 126.8, 124.9 (d, $J$ = 3.0 Hz), 118.7 (d, $J$ = 21.1 Hz), 115.2 (d, $J$ = 22.7 Hz), 21.5.

MS (EI, 70 eV): $m/z$ (%) = 277.9 (21), 138.9 (100), 124.9 (35), 109.0 (16), 91.0 (64), 77.1 (18). MS (ESI) [M+Na]$^+$: 438.06,
HRMS (ESI) (m/z) [C_{21}H_{18}FNO_{3}S_{2}Na]^+: Calcd. 438.0610, found 438.0598.
IR (ATR): ν = 3844, 3313, 3063, 2922, 2856, 2690, 2472, 2318, 2170, 2047, 2013, 1957, 1904, 1773, 1729, 1609, 1580, 1486, 1446, 1376, 1311, 1264, 1234, 1149, 1054, 996, 968, 834, 746.

(E)-N-[(4-Fluorostyryl)(oxo)(phenyl)-2'-sulfaneylidene]-4-methylbenzenesulfonamide (288ah)

Light yellow solid, 37.7 mg, 91% yield, melting point: 142 – 144 °C.

^1H NMR (600 MHz, CDCl$_3$) δ 8.01 (dd, $J = 8.5, 0.9$ Hz, 2H), 7.85 (d, $J = 8.3$ Hz, 2H), 7.65 (dd, $J = 10.7, 4.1$ Hz, 1H), 7.61 (d, $J = 15.2$ Hz, 1H), 7.57 (t, $J = 7.8$ Hz, 2H), 7.46 (dd, $J = 8.7, 5.3$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.08 (t, $J = 8.5$ Hz, 2H), 6.84 (d, $J = 15.2$ Hz, 1H), 2.38 (s, 3H).

^13C NMR (151 MHz, CDCl$_3$) δ 164.6 (d, $J = 253.7$ Hz), 142.9, 142.6, 140.7, 138.6, 134.1, 131.0 (d, $J = 9.1$ Hz), 129.7, 129.3, 128.1 (d, $J = 3.0$ Hz), 127.7, 126.7, 125.3, 116.4 (d, $J = 22.7$ Hz), 21.5.

MS (EI, 70 eV): m/z (%) = 139.0 (100), 125.0 (38), 109.0 (37), 97.0 (11), 91.1 (73), 77.1 (15). MS (ESI) [M+Na]^+: 438.06,
HRMS (ESI) (m/z) [C_{21}H_{18}FNO_{3}S_{2}Na]^+: Calcd. 438.0610, found 438.0601.

(E)-N-[(3-Chlorostyryl)(oxo)(phenyl)-2'-sulfaneylidene]-4-methylbenzenesulfonamide (288al)

Light yellow solid, 38.7 mg, 90% yield, melting point: 144 – 146 °C.

^1H NMR (600 MHz, CDCl$_3$) δ 8.01 (d, $J = 7.5$ Hz, 2H), 7.86 (d, $J = 8.2$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.60 – 7.55 (m, 3H), 7.43 – 7.31 (m, 4H), 7.24 (d, $J = 8.1$ Hz, 2H), 6.91 (d, $J = 15.2$ Hz, 1H), 2.38 (s, 3H). ^13C NMR (151 MHz, CDCl$_3$) δ 143.0, 142.2, 140.7, 138.2, 135.2, 134.2, 133.5, 131.5, 130.4, 129.7, 129.3, 128.4, 127.8, 127.3, 127.1, 126.8, 21.5.
MS (EI, 70 eV): \( m/z \) (%): 278.0 (22), 139.0 (100), 124.9 (36), 91.0 (44). MS (ESI) [M+Na\(^+\)]: 454.03,

HRMS (ESI) \( m/z \) \([C_{21}H_{18}ClNO_3S_2Na]^+\): Calcd. 454.0314, found 454.0301.

IR (ATR): \( \nu = 3416, 3053, 2854, 2643, 2560, 2460, 2392, 2312, 2203, 2172, 2085, 2036, 1991, 1922, 1893, 1804, 1740, 1607, 1564, 1473, 1444, 1317, 1226, 1153, 1092, 995, 902, 828, 752.\)

\((E)\)-N-[(4-Chlorostyryl)(oxo)(phenyl)-\( \sigma^6 \)-sulfaneylidene]-4-methylbenzenesulfonamide (288am)

\[
\text{Cl} \quad \text{O} \quad \text{S} \quad \text{N} \quad \text{Ts} \quad \text{Ph}
\]

Light yellow solid, 41.4 mg, 96% yield, melting point: 170 – 172 °C.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \): 8.06 – 7.99 (m, 2H), 7.85 (d, \( J = 8.3 \) Hz, 2H), 7.65 (t, \( J = 7.4 \) Hz, 1H), 7.62 – 7.55 (m, 3H), 7.42 – 7.34 (m, 4H), 7.24 (d, \( J = 8.1 \) Hz, 2H), 6.89 (d, \( J = 15.2 \) Hz, 1H), 2.37 (s, 3H).

\(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CDCl\(_3\)) \( \delta \): 142.9, 142.4, 140.7, 138.4, 134.1, 130.3, 130.1, 129.7, 129.5, 129.3, 127.8, 126.7, 126.2, 21.5.

MS (EI, 70 eV): \( m/z \) (%): 278.0 (12), 154.9 (13), 139.0 (100), 124.9 (39), 101.0 (12), 91.1 (76), 77.1 (19), 65.1 (18). MS (ESI) [M+H\(^+\)]: 432.05,

HRMS (ESI) \( m/z \) \([C_{21}H_{19}ClNO_3S_2]^+\): Calcd. 432.0495, found 432.0477.

IR (ATR): \( \nu = 3059, 2924, 2253, 2161, 1949, 1812, 1731, 1598, 1490, 1447, 1405, 1312, 1236, 1150, 1087, 1055, 1017, 910, 858, 806, 730.\)

\((E)\)-N-[(4-Bromostyryl)(oxo)(phenyl)-\( \sigma^6 \)-sulfaneylidene]-4-methylbenzenesulfonamide (288ag)

\[
\text{Br} \quad \text{O} \quad \text{S} \quad \text{N} \quad \text{Ts} \quad \text{Ph}
\]

Light yellow solid, 42.7 mg, 90% yield, melting point: 182 – 184 °C.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \): 8.03 – 7.99 (m, 2H), 7.85 (d, \( J = 8.3 \) Hz, 2H), 7.66 (dd, \( J = 10.7, 4.2 \) Hz, 1H), 7.60 – 7.55 (m, 3H), 7.52 (d, \( J = 8.5 \) Hz, 2H), 7.32 (d, \( J = 8.5 \) Hz, 2H), 7.24 (d, \( J = 8.1 \) Hz, 2H), 6.91 (d, \( J = 15.2 \) Hz, 1H), 2.38 (s, 3H).

\(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CDCl\(_3\)) \( \delta \): 142.9, 142.5, 140.7, 138.4, 134.1, 132.4, 130.7, 130.2, 129.7, 129.3, 127.8, 126.7, 126.3, 21.5.
MS (EI, 70 eV): m/z (%) = 278.1 (22), 139.0 (100), 125.1 (24), 102.1 (11), 91.2 (28).
MS (ESI) [M+H]^+: 475.99,
HRMS (ESI) (m/z) [C_{21}H_{19}BrNO_3S_2]^+: Calcd. 475.9990, found 475.9976.

\((E)-N\)-[[4-\{(Tert-butyl)styryl\}\{oxo\}(phenyl)-\(\lambda^6\)-sulfaneylidene]-4-methylbenzenesulfonamide (288ae)

Light yellow solid, 44.8 mg, 99% yield, melting point: 187 – 189 °C.

\(^1\)H NMR (600 MHz, CDCl\textsubscript{3}) δ 8.00 (dd, \(J = 8.5, 0.8\) Hz, 2H), 7.86 (d, \(J = 8.2\) Hz, 2H), 7.66 – 7.59 (m, 2H), 7.55 (t, \(J = 7.8\) Hz, 2H), 7.43 – 7.36 (m, 4H), 7.23 (d, \(J = 8.1\) Hz, 2H), 6.84 (d, \(J = 15.2\) Hz, 1H), 2.36 (s, 3H), 1.30 (s, 9H).

\(^{13}\)C \{'\(^1\)H\} NMR (151 MHz, CDCl\textsubscript{3}) δ 155.6, 143.9, 142.8, 140.8, 139.0, 133.9, 129.6, 129.3, 129.1, 128.8, 127.6, 126.8, 126.1, 124.3, 35.1, 31.1, 21.5.

MS (EI, 70 eV): m/z (%) = 424.1 (15), 139.0 (78), 125.0 (21), 91.1 (23), 57.2 (100).
MS (ESI) [M+H]^+: 454.15,
HRMS (ESI) (m/z) [C_{25}H_{28}NO_3S_2]^+: Calcd. 454.1511, found 454.1491.

\((E)-N\)-[[4-Methoxystyryl\{oxo\}(phenyl)-\(\lambda^6\)-sulfaneylidene]-4-methylbenzenesulfonamide (288af)

Light yellow oil, 39.7 mg, 93% yield

\(^1\)H NMR (600 MHz, CDCl\textsubscript{3}) δ 8.05 – 7.97 (m, 2H), 7.85 (d, \(J = 8.2\) Hz, 2H), 7.59 (ddd, \(J = 17.8, 15.4, 7.6\) Hz, 4H), 7.41 (d, \(J = 8.8\) Hz, 2H), 7.23 (d, \(J = 8.1\) Hz, 2H), 6.89 (d, \(J = 8.7\) Hz, 2H), 6.71 (d, \(J = 15.1\) Hz, 1H), 3.84 (s, 3H), 2.37 (s, 3H).

\(^{13}\)C \{'\(^1\)H\} NMR (151 MHz, CDCl\textsubscript{3}) δ 162.5, 143.7, 142.7, 140.9, 139.3, 133.8, 130.8, 129.6, 129.2, 127.6, 126.8, 124.5, 122.3, 114.6, 55.5, 21.5.
MS (EI, 70 eV): m/z (%) = 149.1 (100), 139.1 (21), 121.2 (17), 91.2 (17). MS (ESI) [M+Na]+: 450.08,
HRMS (ESI) (m/z) [C_{22}H_{21}BrNO_4S_2Na]+: Calcd. 450.0810, found 450.0801.

(E)-N-[(3,5-Bis(trifluoromethyl)styryl)(oxo)(phenyl)-2'-sulfaneylidene)-4-methyl benzenesulfonamide (288an)

Light yellow solid, 49.0 mg, 92% yield, melting point: 182 – 183 °C.

1H NMR (600 MHz, CDCl_3) δ 8.08 – 8.02 (m, 2H), 7.89 (dd, J = 19.6, 8.3 Hz, 5H), 7.70 (dd, J = 18.3, 11.3 Hz, 2H), 7.60 (t, J = 7.9 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.14 (d, J = 15.2 Hz, 1H), 2.38 (s, 3H).

13C{^1}H NMR (151 MHz, CDCl_3) δ 143.2, 140.5, 140.0, 137.4, 134.6, 134.0, 132.7 (q, J = 33.2 Hz), 130.5, 129.9, 129.4, 128.5 (d, J = 3.0 Hz), 128.0, 126.7, 124.6, 123.6 (t, J = 3.0 Hz), 121.8, 21.5.

MS (EI, 70 eV): m/z (%) = 278.1 (27), 139.1 (100), 125.0 (77), 97.1 (17), 91.1 (76), 77.2 (26). MS (ESI) [M+H]+: 534.06,
HRMS (ESI) (m/z) [C_{23}H_{18}F_6NO_3S_2]+: Calcd. 534.0632, found 534.0607.

(E)-N-[(2-[(1,1'-Biphenyl)-4-yl]vinyl)(oxo)(phenyl)-2'-sulfaneylidene)-4-methylbenzenesulfonamide (288ai)

Light yellow oil, 37.9 mg, 80% yield

1H NMR (600 MHz, CDCl_3) δ 8.04 (d, J = 7.7 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 7.70 – 7.61 (m, 4H), 7.61 – 7.55 (m, 4H), 7.53 (d, J = 8.3 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 8.1 Hz, 2H), 6.92 (d, J = 15.2 Hz, 1H), 2.38 (s, 3H).

13C{^1}H NMR (151 MHz, CDCl_3) δ 144.5, 143.5, 142.8, 140.8, 139.6, 138.8, 134.0,
130.7, 129.7, 129.4, 129.0, 128.2, 127.7, 127.7, 127.1, 126.8, 125.1, 21.5.

MS (EI, 70 eV): m/z (%) = 358.2 (31), 196.1 (19), 195.0 (18), 167.1 (20), 139.1 (15), 125.0 (27), 111.1 (19), 97.1 (31), 77.2 (21). MS (ESI) [M+H]^+: 474.12,
HRMS (ESI) (m/z) [C_{27}H_{24}NO_{3}S_{2}]^+: Calcd. 474.1198, found 474.1179.


(E)-4-[2-(N-Tosylphenylsulfonimidoyl)vinyl]phenyl acetate (288ao)

Light yellow oil, 44.6 mg, 98% yield

{^1}H NMR (600 MHz, CDCl_3) δ 8.03 – 7.98 (m, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.67 – 7.59 (m, 2H), 7.56 (t, J = 7.9 Hz, 2H), 7.47 (t, J = 5.6 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.14 – 7.11 (m, 2H), 6.85 (d, J = 15.2 Hz, 1H), 2.37 (s, 3H), 2.30 (s, 3H).

{^{13}}C{^1}H NMR (151 MHz, CDCl_3) δ 168.9, 153.1, 142.9, 142.8, 140.7, 138.6, 134.1, 130.1, 129.7, 129.5, 129.3, 127.7, 126.7, 125.6, 122.5, 21.5, 21.1.

MS (EI, 70 eV): m/z (%) = 426.1 (20), 279.0 (69), 155.1 (16), 154.0 (34), 140.1 (19), 139.0 (100), 135.1 (56), 126.1 (31), 91.2 (35). MS (ESI) [M+H]^+: 456.09,
HRMS (ESI) (m/z) [C_{23}H_{22}NO_{5}S_{2}]^+: Calcd. 456.0939, found 456.0925.


(2S,4S)-Methyl-N-[oxo(phenyl)(2,4,6-trimethylstyryl)-2'-sulfaneylidene]benzenesulfonamide (288aj)

Light yellow solid, 36.0 mg, 82% yield, melting point: 128 – 130 °C.

{^1}H NMR (600 MHz, CDCl_3) δ 8.02 (d, J = 8.0 Hz, 2H), 7.87 (dd, J = 17.6, 11.9 Hz, 3H), 7.65 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.25 (d, J = 9.0 Hz, 2H), 6.87 (s, 2H), 6.70 (d, J = 15.5 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 6H), 2.27 (s, 3H).

{^{13}}C{^1}H NMR (151 MHz, CDCl_3) δ 142.8, 142.3, 140.9, 140.2, 138.9, 137.7, 133.9, 129.7, 129.6, 129.2, 127.8, 127.6, 126.7, 21.5, 21.1.

MS (EI, 70 eV): m/z (%) = 161.0 (100), 144.0 (30), 139.0 (33), 129.0 (25), 124.9 (14), 91.0 (31). MS (ESI) [M+Na]^+: 462.12,
HRMS (ESI) \(m/z\) \([C_{24}H_{25}NO_3S_2Na]^+\): Calcd. 462.1174, found 462.1158.

\( (E)-4\)-Methyl-\(N\)-[oxo(phenyl)(1-phenylprop-1-en-2-yl)-\(\lambda^6\)-sulfaneylidene]benzenesulfonamide (288ap) 

\[
\begin{align*}
\text{Ph} & \quad \text{O} \quad \text{N} \quad \text{Ts} \\
\text{Me} & \quad \text{Ph}
\end{align*}
\]

Light yellow oil, 39.0 mg, 95% yield

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.01 (d, \(J = 8.3\) Hz, 2H), 7.92 – 7.83 (m, 3H), 7.65 (t, \(J = 7.0\) Hz, 1H), 7.56 (t, \(J = 7.7\) Hz, 2H), 7.47 – 7.34 (m, 5H), 7.25 (dd, \(J = 10.2, 4.4\) Hz, 2H), 2.37 (s, 3H), 2.15 (s, 3H).

\(^{13}\)C\({}^{1}\)H NMR (151 MHz, CDCl\(_3\)) \(\delta\) 142.7, 141.0, 139.2, 136.8, 135.6, 134.0, 133.3, 129.8, 129.5, 128.9, 128.8, 128.3, 126.7, 21.5, 13.6.

MS (EI, 70 eV): \(m/z\) (\%) = 139.2 (43), 133.2 (21), 125.2 (21), 116.2 (29), 115.2 (69), 105.2 (25), 91.2 (100), 77.2 (32), 65.2 (38). MS (ESI) [M+ Na\(^+\)]: 434.08.

HRMS (ESI) \(m/z\) \([C_{22}H_{21}NO_3S_2Na]^+\): Calcd. 434.0861, found 434.0856.
IR (ATR): \(\nu = 3853, 3746, 3624, 3272, 3061, 2923, 2860, 2669, 2321, 2166, 2034, 1912, 1812, 1728, 1597, 1446, 1308, 1230, 1151, 1051, 813, 749\).

\( (E)-N\)-[(2-Fluorostyryl)(oxo)(phenyl)-\(\lambda^6\)-sulfaneylidene]-4-methylbenzenesulfonamide (288aq) 

\[
\begin{align*}
\text{F} & \quad \text{O} \quad \text{N} \quad \text{Ts} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

Light yellow solid, 39.4 mg, 95% yield, melting point: 153 – 155 °C.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.01 (d, \(J = 7.7\) Hz, 2H), 7.86 (d, \(J = 8.2\) Hz, 2H), 7.70 (d, \(J = 15.3\) Hz, 1H), 7.65 (t, \(J = 7.4\) Hz, 1H), 7.56 (t, \(J = 7.8\) Hz, 2H), 7.42 (dt, \(J = 22.6, 6.9\) Hz, 2H), 7.23 (d, \(J = 8.1\) Hz, 2H), 7.17 (t, \(J = 7.6\) Hz, 1H), 7.13 – 7.03 (m, 2H), 2.36 (s, 3H).

\(^{13}\)C\({}^{1}\)H NMR (151 MHz, CDCl\(_3\)) \(\delta\) 161.5 (d, \(J = 256.7\) Hz), 142.9, 140.7, 138.4, 136.9, 134.1, 133.4 (d, \(J = 9.1\) Hz), 130.7 (d, \(J = 4.5\) Hz), 129.7, 129.3, 128.4 (d, \(J = 9.1\) Hz), 127.8, 126.8, 126.4, 124.8, 124.8, 120.1, 120.0, 116.4 (d, \(J = 21.1\) Hz), 21.5.

MS (EI, 70 eV): \(m/z\) (\%) = 139.0 (100), 119.1 (30), 91.1 (89). MS (ESI) [M+H\(^+\)]: 416.08,
HRMS (ESI) (m/z) [C_{21}H_{19}FNO_3S_2]^{+}: Calcd. 416.0790, found 416.0778.

(E)-N-[(2-Chlorostyryl)(oxo)(phenyl)-2sulfaneylidene]-4-methylbenzenesulfonamide (288at)

\[
\text{Cl} \quad \text{O} \quad \text{S}^{=N}_{\text{Ts}} \quad \text{Ph}
\]

Light yellow solid, 40.1 mg, 93% yield, melting point: 178 – 180 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.04 (d, J = 7.8 Hz, 2H), 7.99 (d, J = 15.3 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.66 (dd, J = 10.7, 4.1 Hz, 1H), 7.58 (t, J = 7.3 Hz, 2H), 7.51 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.26 (dd, J = 17.6, 7.8 Hz, 3H), 7.03 (dd, J = 15.3, 1.5 Hz, 1H), 2.37 (s, 3H).

$^{13}$C{\(^1\)H} NMR (151 MHz, CDCl$_3$) δ 143.0, 140.7, 139.6, 138.1, 135.4, 134.2, 132.4, 130.4, 130.2, 129.7, 129.3, 128.7, 128.6, 127.9, 127.3, 126.8, 21.5.

MS (EI, 70 eV): m/z (%) = 278.0 (23), 155.0 (17), 139.0 (100), 125.0 (39), 101.1 (16), 91.1 (80), 77.2 (24), 65.2 (23). MS (ESI) [M+H]$^+$: 432.05,

HRMS (ESI) (m/z) [C_{21}H_{19}FNO_3S_2]^{+}: Calcd. 432.0495, found 432.0479.

IR (ATR): ν = 3882, 3358, 3260, 3059, 2923, 2705, 2488, 2298, 2161, 2052, 1977, 1925, 1822, 1728, 1601, 1528, 1471, 1445, 1383, 1309, 1223, 1153, 1062, 974, 904, 875, 810, 753.

(E)-N-[(2-Bromostyryl)(oxo)(phenyl)-2sulfaneylidene]-4-methylbenzenesulfonamide (288ar)

\[
\text{Br} \quad \text{O} \quad \text{S}^{=N}_{\text{Ts}} \quad \text{Ph}
\]

Light yellow solid, 44.1 mg, 93% yield, melting point: 179 – 180 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.05 – 7.99 (m, 2H), 7.90 (d, J = 15.1 Hz, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.9 Hz, 2H), 7.41 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 8.1 Hz, 2H), 7.20 (dd, J = 15.3, 7.6 Hz, 2H), 6.85 (d, J = 15.1 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H).

$^{13}$C{\(^1\)H} NMR (151 MHz, CDCl$_3$) δ 142.8, 141.7, 140.8, 138.7, 138.5, 134.0, 131.5, 131.1, 130.7, 129.6, 129.3, 127.7, 127.3, 126.7, 126.6, 126.4, 21.5, 19.8.

MS (EI, 70 eV): m/z (%) = 278.0 (15), 139.0 (98), 125.0 (32), 102.1 (24), 91.1 (100),
(E)-N-[(3-Bromostyryl)(oxo)(phenyl)-26-sulfaneylidene]-4-methylbenzenesulfonamide (288as)

Light yellow solid, 46.1 mg, 97% yield, melting point: 155 – 157 °C.

H NMR (600 MHz, CDCl$_3$) δ 8.01 (d, $J = 7.7$ Hz, 2H), 7.85 (d, $J = 8.2$ Hz, 2H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.60 – 7.52 (m, 5H), 7.38 (d, $J = 7.8$ Hz, 1H), 7.28 – 7.23 (m, 3H), 6.90 (d, $J = 15.2$ Hz, 1H), 2.38 (s, 3H).

C{H} NMR (151 MHz, CDCl$_3$) δ 143.0, 142.1, 140.7, 138.2, 134.4, 134.2, 133.8, 131.3, 130.6, 129.7, 127.8, 127.6, 127.3, 126.8, 123.2, 21.5.

MS (EI, 70 eV): m/z (%) = 278.0 (19), 139.0 (100), 124.9 (31), 102.0 (12), 91.0 (41).

HRMS (ESI) [M+Na]$^+$: Calcd. 497.9809, found 497.9827.


(E)-4-Methyl-N-oxo(phenyl)[3-(trifluoromethyl)styryl]-26-sulfaneylidene)benzenesulfonamide (288au)

Light yellow solid, 44.1 mg, 95% yield, melting point: 168 – 170 °C.

H NMR (600 MHz, CDCl$_3$) δ 8.03 (d, $J = 7.9$ Hz, 2H), 7.86 (d, $J = 8.2$ Hz, 2H), 7.67 (dd, $J = 14.3$, 6.5 Hz, 5H), 7.59 (t, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 8.1$ Hz, 2H), 6.99 (d, $J = 15.2$ Hz, 1H), 2.38 (s, 3H).

C{H} NMR (151 MHz, CDCl$_3$) δ 143.0, 141.9, 140.6, 138.0, 134.3, 132.6, 132.0, 131.7 (q, $J = 33.2$ Hz), 129.8, 129.8, 129.3, 128.0 (q, $J = 4.5$ Hz), 127.9, 127.9, 126.7, 125.3 (q, $J = 4.5$ Hz), 124.4, 122.5, 21.5.

MS (EI, 70 eV): m/z (%) = 278.0 (29), 155.0 (11), 139.1 (100), 125.0 (34), 91.1 (48),
(E)-4-Methyl-N-[oxo(phenyl)(2-phenylprop-1-en-1-yl)-λ6-sulfaneylidene]benzenesulfonamide (288av)

Light yellow oil, 10.3 mg, 25% yield

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 8.3$ Hz, 2H), 7.50 – 7.45 (m, 2H), 7.26 – 7.22 (m, 3H), 7.19 (d, $J = 8.1$ Hz, 3H), 7.11 (t, $J = 7.6$ Hz, 2H), 6.92 – 6.85 (m, 3H), 2.36 (s, 3H), 2.15 (d, $J = 1.4$ Hz, 3H).

$^{13}$C{ $^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ 143.7, 142.5, 140.9, 133.0, 129.9, 129.1, 128.6, 128.6, 127.9, 127.9, 126.9, 126.7, 28.0, 21.5.

MS (EI, 70 eV): $m/z$ (%) = 279.1 (72), 155.1 (24), 139.1 (75), 133.1 (18), 125.1 (31), 115.1 (48), 105.1 (31), 91.1 (100), 77.2 (37). MS (ESI) [M+H]$^+$: 412.10,

HRMS (ESI) ($m/z$) [C$_{22}$H$_{22}$NO$_3$S$_2$]$^+$: Calcd. 412.1041. found 412.1021.


(E)-4-Methyl-N-[2-methylbut-1-en-3-yn-1-yl)(oxo)(phenyl)-λ6-sulfaneylidene]benzenesulfonamide (288aw)

Light yellow oil, 15.0 mg, 42% yield

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.03 (d, $J = 7.8$ Hz, 2H), 7.85 (d, $J = 8.1$ Hz, 2H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.54 (t, $J = 7.8$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 6.90 (s, 1H), 3.69 (s, 1H), 2.38 (s, 3H), 2.06 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 142.8, 140.7, 138.6, 135.5, 135.1, 134.0, 129.2, 129.1, 128.4, 126.8, 94.1, 25.4, 21.5.

MS (EI, 70 eV): $m/z$ (%) = 155.3 (12), 139.2 (32), 125.2 (30), 97.2 (20), 91.2 (100), 77.2 (43), 65.2 (40). MS (ESI) [M+Na]$^+$: 382.05,
HRMS (ESI) (m/z) [C_{18}H_{17}NO_{3}S_{2}Na]^+: Calcd. 382.0548, found 382.0536.

IR (ATR): $\nu = 3853, 3745, 3619, 3251, 3062, 2924, 2164, 2102, 1722, 1590, 1443, 1307, 1234, 1149, 1053, 853, 808, 744$.

**Methyl (E)-2-methyl-3-(N-toslyphenylsulfonimidoyl)acrylate (288ax)**

![Methyl (E)-2-methyl-3-(N-toslyphenylsulfonimidoyl)acrylate](image)

Light yellow oil, 16.1 mg, 41% yield

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.02 $-$ 7.98 (m, 2H), 7.84 (d, $J = 8.3$ Hz, 2H), 7.71 $-$ 7.67 (m, 1H), 7.62 $-$ 7.57 (m, 2H), 7.38 (q, $J = 1.3$ Hz, 1H), 7.27 $-$ 7.24 (m, 2H), 3.78 (s, 3H), 2.39 (s, 3H), 2.22 (d, $J = 1.5$ Hz, 3H).

$^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 165.3, 143.5, 143.0, 140.5, 138.1, 136.9, 134.5, 129.7, 129.3, 129.3, 127.9, 126.7, 53.3, 21.6, 13.5.

MS (EI, 70 eV): m/z (%) = 394.0 (M$^+$, 16), 294.0 (57), 277.9 (29), 155.0 (46), 139.0 (62), 125.0 (96), 97.0 (19), 91.1 (100), 77.1 (34), 65.2 (29). MS (ESI) [M+H]$^+$: 394.08,

HRMS (ESI) (m/z) [C$_{18}$H$_{20}$NO$_5$S$_2$]$^+$: Calcd. 394.0783, found 394.0771.

IR (ATR): $\nu = 3063, 2953, 2161, 1728, 1598, 1444, 1385, 1315, 1235, 1151, 1087, 1054, 996, 846, 810, 737$.

(E)-N-{[4-(Tert-butyl)phenyl](oxo)(styryl)-2'-sulfaneylidene}-4-methylbenzenesulfonamide (288ba)

![E-N-{[4-(Tert-butyl)phenyl](oxo)(styryl)-2'-sulfaneylidene}-4-methylbenzenesulfonamide](image)

Light yellow oil, 42.6 mg, 94% yield

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J = 8.7$ Hz, 2H), 7.86 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 15.2$ Hz, 1H), 7.55 (d, $J = 8.7$ Hz, 2H), 7.46 $-$ 7.36 (m, 5H), 7.22 (d, $J = 8.2$ Hz, 2H), 6.89 (d, $J = 15.2$ Hz, 1H), 2.36 (s, 3H), 1.32 (s, 9H).

$^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 158.1, 143.4, 142.7, 140.9, 135.4, 131.9, 131.6, 129.2, 129.1, 128.8, 127.6, 126.8, 126.7, 125.8, 35.3, 31.0, 21.5.

MS (EI, 70 eV): m/z (%) = 181.0 (100), 165.9 (30), 150.0 (46), 138.9 (34), 91.1 (47), 77.1 (13). MS (ESI) [M+H]$^+$: 454.15,

HRMS (ESI) (m/z) [C$_{25}$H$_{28}$NO$_3$S$_2$]$^+$: Calcd. 454.1511, found 454.1498.
IR (ATR): \( \nu = 3632, 3058, 2925, 2163, 1913, 1815, 1732, 1604, 1454, 1310, 1231, 1148, 1073, 860, 812, 740 \). 

\((E)-4\text{-Methyl-N-}[\text{oxo(styryl)}(\alpha\text{-tolyl)}-\lambda^6\text{-sulfaneylidene}]\text{benzenesulfonamide (288ca)}\)

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{N} & \quad \text{Tb}
\end{align*}
\]

Light yellow oil, 37.9 mg, 92% yield

\(^1\)H NMR (600 MHz, CDCl\(_3\) \( \delta \) 7.89 (d, \( J = 8.4 \) Hz, 2H), 7.86 (d, \( J = 8.2 \) Hz, 2H), 7.60 (d, \( J = 15.2 \) Hz, 1H), 7.47 – 7.40 (m, 3H), 7.40 – 7.33 (m, 4H), 7.23 (d, \( J = 8.1 \) Hz, 2H), 6.88 (d, \( J = 15.2 \) Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H).

\(^{13}\)C \(^1\)H NMR (151 MHz, CDCl\(_3\) \( \delta \) 145.3, 143.4, 142.8, 140.9, 135.5, 131.9, 131.6, 130.3, 129.2, 129.1, 128.8, 127.8, 126.8, 125.8, 21.7, 21.5.

MS (EI, 70 eV): \( m/z \) (%) = 155.0 (10), 139.0 (95), 119.0 (13), 91.1 (100), 77.1 (35).

MS (ESI) \([\text{M+H}]^+\): 412.10,

HRMS (ESI) \((m/z)\) \([\text{C}_{22}\text{H}_{22}\text{NO}_3\text{S}_2]^+\): Calcd. 412.1041, found 412.1025.

IR (ATR): \( \nu = 5343, 3059, 2962, 2162, 2031, 1977, 1915, 1809, 1721, 1600, 1493, 1451, 1401, 1311, 1234, 1150, 1058, 1015, 974, 912, 853, 810, 739.

\((E)-\text{N-}[(\text{3-Fluorophenyl})(\text{oxo(styryl)}-\lambda^6\text{-sulfaneylidene})-4\text{-methylbenzenesulfonamide (288da)}\)

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{N} & \quad \text{Tb}
\end{align*}
\]

Light yellow oil, 37.6 mg, 91% yield

\(^1\)H NMR (400 MHz, CDCl\(_3\) \( \delta \) 7.82 (t, \( J = 9.2 \) Hz, 3H), 7.72 – 7.61 (m, 2H), 7.54 (td, \( J = 8.1, 5.2 \) Hz, 1H), 7.48 – 7.29 (m, 6H), 7.23 (d, \( J = 8.8 \) Hz, 2H), 6.86 (d, \( J = 15.2 \) Hz, 1H), 2.36 (s, 3H).

\(^{13}\)C \(^1\)H NMR (101 MHz, CDCl\(_3\) \( \delta \) 162.5 (d, \( J = 253.5 \) Hz), 144.8, 143.0, 141.0 (d, \( J = 7.1 \) Hz) 140.6, 132.0, 131.6, 131.4 (d, \( J = 8.1 \) Hz), 129.3, 129.2, 128.9, 126.7, 124.8, 123.6 (d, \( J = 3.0 \) Hz), 121.2 (d, \( J = 21.2 \) Hz), 115.3, 115.0 (d, \( J = 2.0 \) Hz), 21.5.

MS (EI, 70 eV): \( m/z \) (%) = 386.1 (45), 155.1 (12), 139.1 (100), 119.2 (18), 102.1 (11), 91.1 (64), 77.2 (19), 65.4 (14). MS (ESI) \([\text{M+Na}]^+\): 438.06,

HRMS (ESI) \((m/z)\) \([\text{C}_{21}\text{H}_{18}\text{FNO}_3\text{S}_2\text{Na}]^+\): Calcd. 438.0610, found 438.0589.
IR (ATR): $\nu = 3537, 3062, 2922, 2856, 2608, 2458, 2289, 2165, 2035, 1989, 1912,$
$1813, 1597, 1474, 1440, 1311, 1228, 1151, 1056, 996, 885, 810, 738, 670.$

$(E)$-4-Methyl-$N$-[oxo(styryl)(o-tolyl)-$\lambda^6$-sulfaneylidene]benzenesulfonamide

$(288ea)$

Light yellow oil, 37.0 mg, 90% yield

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.23 – 8.16 (m, 1H), 7.83 (d, $J = 8.2$ Hz, 2H), 7.63 (d, $J = 15.2$ Hz, 1H), 7.57 – 7.50 (m, 1H), 7.46 (dd, $J = 6.3, 5.1$ Hz, 2H), 7.45 – 7.38 (m, 4H), 7.30 (d, $J = 7.5$ Hz, 1H), 7.22 (d, $J = 8.1$ Hz, 2H), 6.94 (d, $J = 15.2$ Hz, 1H), 2.64 (s, 3H), 2.37 (s, 3H).

$^{13}$C{$_1^H$} NMR (151 MHz, CDCl$_3$) $\delta$ 144.6, 142.8, 140.8, 138.2, 136.3, 134.2, 133.3, 131.8, 129.6, 129.2, 129.2, 128.8, 127.0, 126.7, 124.5, 21.5, 20.6.

MS (EI, 70 eV): $m/z$ (%) = 228.1 (11), 155.0 (14), 139.0 (88), 137.0 (14), 119.0 (17), 91.1 (100), 77.1 (47). MS (ESI) [M+H]$^+$: 412.10,

HRMS (ESI) ($m/z$) [C$_{22}$H$_{22}$NO$_3$S$_2$]$^+$: Calcd. 412.1041, found 412.1043.

IR (ATR): $\nu = 3632, 3058, 2925, 2163, 1913, 1815, 1732, 1604, 1454, 1310, 1231,$
$1148, 1073, 860, 812, 740.$

$(E)$-N-[Mesityl(oxo)(styryl)-$\lambda^6$-sulfaneylidene]-4-methylbenzenesulfonamide

$(288fa)$

Light yellow oil, 32.8 mg, 75% yield

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 15.3$ Hz, 1H),
7.48 – 7.36 (m, 5H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 15.3$ Hz, 1H), 6.96 (s, 2H),
2.67 (s, 6H), 2.38 (s, 3H), 2.30 (s, 3H).

$^{13}$C{$_1^H$} NMR (151 MHz, CDCl$_3$) $\delta$ 143.8, 143.1, 142.5, 140.9, 140.0, 132.9, 132.36, 132.0, 131.6, 129.2, 129.1, 128.6, 127.0, 126.7, 23.2, 21.5, 21.0.

MS (EI, 70 eV): $m/z$ (%) = 220.2 (20), 167.2 (31), 166.1 (19), 139.2 (26), 105.2 (23),
104.2 (33), 103.1 (41), 91.2 (100), 77.2 (45). MS (ESI) [M+Na]$^+$: 462.12,

HRMS (ESI) ($m/z$) [C$_{21}$H$_{18}$FNO$_3$S$_2$Na]$^+$: Calcd. 462.1174, found 462.1150.
IR (ATR): $\nu = 3487, 3023, 2857, 2164, 1909, 1814, 1732, 1601, 1451, 1391, 1307, 1149, 1067, 907, 856, 809, 743, 663$

(E)-N-((2-bromophenyl)(oxo)(styryl)-$\lambda^6$-sulfaneylidene)-4-methylbenzenesulfonamide (288ga)

Light yellow oil, 39.8 mg, 84% yield

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 7.9$ Hz, 2H), 7.73 – 7.65 (m, 2H), 7.54 (t, $J = 7.7$ Hz, 1H), 7.49 – 7.36 (m, 6H), 7.27 – 7.19 (m, 3H), 2.36 (s, 3H).

$^{13}$C {$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ 146.5, 142.9, 140.5, 138.2, 135.9, 134.8, 131.9, 131.4, 129.2, 129.2, 128.9, 128.2, 126.8, 123.0, 120.7, 21.5.

MS (EI, 70 eV): $m/z$ (%) = 205.0 (10), 203.0 (10), 155.0 (24), 139.1 (24), 102.1 (24), 91.1 (100), 77.1 (33). MS (ESI) [M+Na]$^+$: 497.98.

HRMS (ESI) ($m/z$) [C$_{21}$H$_{18}$BrNO$_3$S$_2$Na]$^+$: Calcd. 497.9809, found 497.9807.

IR (ATR): $\nu = 3358, 3090, 2928, 2329, 2164, 1913, 1803, 1646, 1595, 1451, 1378, 1337, 1274, 1158, 1082, 995, 811, 759, 676, 655$.

(E)-N-[(2-Ethylphenyl)(oxo)(styryl)-$\lambda^6$-sulfaneylidene]-4-methylbenzenesulfonamide (288ha)

Light yellow oil, 37.0 mg, 87% yield

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 8.1$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, 2H), 7.57 (dd, $J = 18.4, 11.3$ Hz, 2H), 7.50 – 7.32 (m, 7H), 7.20 (d, $J = 7.9$ Hz, 2H), 6.98 (d, $J = 15.2$ Hz, 1H), 3.02 (q, $J = 7.4$ Hz, 2H), 2.35 (s, 3H), 1.24 (t, $J = 7.5$ Hz, 3H).

$^{13}$C {$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ 144.3, 142.7, 140.9, 136.1, 134.21, 131.9, 131.7, 131.3, 129.4, 129.2, 128.8, 126.7, 126.7, 125.4, 21.5, 15.1.

MS (EI, 70 eV): $m/z$ (%) = 396.1 (31), 272.2 (12), 242.1 (57), 238.1 (20), 237.1 (100), 206.1 (29), 204.1 (33), 155.0 (21), 139.1 (40), 135.0 (36), 91.1 (99), 77.2 (41). MS (ESI) [M+Na]$^+$: 448.10.

HRMS (ESI) ($m/z$) [C$_{23}$H$_{24}$NO$_3$S$_2$Na]$^+$: Calcd. 448.1017, found 448.1009.

IR (ATR): $\nu = 3914, 3887, 3779, 3700, 3659, 3440, 2921, 2855, 2734, 2595, 2424$,
2208, 1952, 1841, 1726, 1618, 1454, 1383, 1313, 1234, 1152, 1070, 874, 814, 741, 664, 609.

(E)-4-Methyl-N-[methyl(oxo)(styryl)-λ^6-sulfaneylidene]benzenesulfonamide

(288ia)

\[
\text{Ph} \equiv \text{S} \equiv \text{N} \equiv \text{Me} \quad \text{Ts}
\]

Light yellow solid, 11.7 mg, 35% yield, melting point: 146 – 148 °C.

\(^1\)H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta 7.87 \ (d, J = 8.2 \text{ Hz}, 2H), 7.64 \ (d, J = 15.3 \text{ Hz}, 1H), 7.49 \ (dd, J = 12.9, 7.1 \text{ Hz}, 3H), 7.44 \ (t, J = 7.3 \text{ Hz}, 2H), 7.26 \ (d, J = 5.1 \text{ Hz}, 2H), 6.92 \ (d, J = 15.3 \text{ Hz}, 1H), 3.42 \ (s, 3H), 2.38 \ (s, 3H).

\(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CDCl\textsubscript{3}) \(\delta 145.9, 143.0, 140.5, 132.0, 131.4, 129.3, 129.3, 128.9, 126.7, 123.9, 45.3, 21.5.

MS (EI, 70 eV): \(m/z \ (% = 139.0 \ (100), 119.1 \ (30), 91.1 \ (89). MS (ESI) [M+Na]^+: 358.05,

HRMS (ESI) (m/z) [C\textsubscript{16}H\textsubscript{17}NO\textsubscript{3}S\textsubscript{2}Na]^+: Calcd. 358.0548, found 358.0540.


(E)-Imino(phenyl)(styryl)-λ^6-sulfanone (289a)

\[
\text{Ph} \equiv \text{HN} \equiv \text{S} \equiv \text{Ph}
\]

Light yellow oil, 24.1 mg, 99% yield

\(^1\)H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta 8.05 – 8.01 \ (m, 2H), 7.63 \ (d, J = 15.3 \text{ Hz}, 1H), 7.58 – 7.56 \ (m, 1H), 7.55 – 7.49 \ (m, 2H), 7.49 – 7.44 \ (m, 2H), 7.40 – 7.33 \ (m, 3H), 6.94 \ (d, J = 15.2 \text{ Hz}, 1H), 2.67 \ (s, 1H).

\(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CDCl\textsubscript{3}) \(\delta 142.8, 141.6, 132.8, 132.6, 130.8, 129.5, 129.2, 129.0, 128.5, 127.9.

MS (EI, 70 eV): \(m/z \ (% = 243.4 \ (M^+, 2), 118.1 \ (44), 91.1 \ (18), 77.2 \ (9). MS (ESI) [M+Na]^+: 266.06,

HRMS (ESI) (m/z) [C\textsubscript{14}H\textsubscript{13}NOSNa]^+: Calcd. 266.0616, found 266.0612.

IR (ATR): \(\nu = 3867, 3567, 3265, 3056, 2920, 2672, 2333, 2089, 1977, 1900, 1813, 1614, 1576, 1487, 1445, 1326, 1215, 1080, 971, 855, 805, 744.

(E)-Imino(mesityl)(styryl)-λ^6-sulfanone (289b)
Light yellow oil, 28.2 mg, 99% yield

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 15.3$ Hz, 1H), 7.47 (dd, $J = 6.8$, 2.8 Hz, 2H), 7.36 (dd, $J = 4.9$, 1.7 Hz, 3H), 7.04 (d, $J = 15.3$ Hz, 1H), 6.93 (s, 2H), 2.71 (s, 6H), 2.27 (s, 3H).

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ 142.2, 140.3, 139.4, 136.9, 132.8, 132.5, 130.6, 129.7, 129.0, 128.3, 23.4, 20.8.

MS (EI, 70 eV): $m/z$ (%) = 119.1 (28), 118.1 (55), 117.1 (29), 115.1 (26), 106.1 (45), 105.1 (25), 103.1 (33), 91.1 (100), 77.2 (74), 65.3 (22). MS (ESI) [M+H]$^+$: 286.13, HRMS (ESI) ($m/z$) [C$_{17}$H$_{20}$NOS]$^+$: Calcd. 286.1266, found 286.1250.

IR (ATR): $\nu$ = 3568, 3301, 3028, 2930, 2738, 2320, 2170, 1896, 1726, 1606, 1449, 1390, 1326, 1215, 1105, 1041, 969, 853, 800, 743.

(E)-(2-Ethylphenyl)(imino)(styryl)-$\lambda^6$-sulfanone (289c)

Light yellow oil, 26.5 mg, 98% yield

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.24 – 8.15 (m, 1H), 7.64 (d, $J = 15.3$ Hz, 1H), 7.57 – 7.45 (m, 3H), 7.43 – 7.29 (m, 5H), 6.97 (d, $J = 15.4$ Hz, 1H), 3.14 (qd, $J = 7.4$, 2.7 Hz, 2H), 2.68 (s, 1H), 1.27 (t, $J = 7.5$ Hz, 3H).

$^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\delta$ 144.2, 141.6, 140.4, 133.1, 132.7, 131.0, 130.8, 129.4, 129.0, 128.4, 126.3, 25.8, 15.7.

MS (EI, 70 eV): $m/z$ (%) = 273.1 (20), 272.1 (100), 254.1 (14), 238.1 (15), 237.1 (50), 222.1 (21), 206.1 (17), 204.1 (58), 191.1 (30), 151.0 (26), 191.1 (75), 118.1 (78), 106.1 (36), 103.1 (32), 91.1 (99), 77.2 (62). MS (ESI) [M+Na]$^+$: 294.09, HRMS (ESI) ($m/z$) [C$_{16}$H$_{17}$NOSNa]$^+$: Calcd. 294.0912, found 294.09123.

IR (ATR): $\nu$ = 3547, 3269, 3057, 2968, 2931, 2873, 2656, 2331, 2163, 2107, 1954, 1821, 1719, 1615, 1453, 1375, 1324, 1216, 1104, 1062, 969, 855, 801, 747, 684.

(E)-5,7-Dimethyl-1-styryl-3H-1$\lambda^4$-benzo[d]isothiazole 1-oxide (290a)

Light yellow oil, 21.3 mg, 75% yield
$^1$H NMR (600 MHz, CDCl$_3$) δ 7.69 (d, $J = 15.0$ Hz, 1H), 7.52 (dd, $J = 7.5$, 1.7 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.12 (s, 1H), 7.04 (s, 1H), 6.87 (d, $J = 15.0$ Hz, 1H), 4.91 (d, $J = 15.7$ Hz, 1H), 4.74 (d, $J = 17.0$ Hz, 1H), 2.52 (s, 3H), 2.42 (s, 3H).

$^{13}$C ($^1$H) NMR (151 MHz, CDCl$_3$) δ 147.1, 144.8, 143.9, 134.3, 132.8, 131.1, 131.0, 129.0, 128.7, 127.4, 121.9, 57.1, 21.5, 17.1.

MS (EI, 70 eV): m/z (%) = 155.1 (11), 139.0 (19), 124.1 (16), 102.1 (17), 91.1 (100), 89.1 (16), 77.2 (51), 65.3 (32). MS (ESI) [M+H]$^+$: 284.11,

HRMS (ESI) (m/z) $[C_{17}H_{18}NOS]^+$: Calcd. 284.1109, found 284.1099.

IR (ATR): $\nu = 3626, 3059, 2923, 2856, 2462, 2166, 1910, 1813, 1731, 1605, 1447, 1399, 1311, 1235, 1150, 1055, 855, 813, 742, 670.$

(E)-3-Methyl-1-styryl-3H-1,2-benzo[d]isothiazole 1-oxide (290b)

Light yellow oil, 19.4 mg, 72% yield, $dr = 5:1$.

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers) δ 7.78 – 7.63 (m, 2H), 7.58 (td, $J = 7.2$, 4.2 Hz, 1H), 7.55 – 7.43 (m, 4H), 7.43 – 7.34 (m, 3H), 6.88 (dd, $J = 15.0$, 8.3 Hz, 1H), 5.09 (dq, $J = 67.0$, 6.7 Hz, 1H), 1.61 (dd, $J = 26.6$, 6.8 Hz, 3H).

$^{13}$C ($^1$H) NMR (101 MHz, CDCl$_3$, mixture of diastereomers) δ 150.7, 150.6, 145.5, 144.5, 137.3, 132.7, 132.6, 132.4, 132.4, 131.1, 131.0, 129.0, 128.8, 128.7, 127.1, 126.7, 123.9, 123.6, 122.3, 122.2, 65.3, 64.35, 24.9, 23.4.

MS (EI, 70 eV): m/z (%) = 269.1 (12), 255.0 (12), 254.0 (68), 152.0 (40), 151.0 (68), 137.0 (40), 136.0 (35), 135.0 (91), 134.0 (43), 103.1 (68), 102.1 (42), 91.1 (92), 77.2 (100), 51.6 (41). MS (ESI) [M+H]$^+$: 270.10,

HRMS (ESI) (m/z) $[C_{16}H_{16}NOS]^+$: Calcd. 270.0953, found 279.0942.

IR (ATR): $\nu = 3397, 3059, 2968, 2923, 2856, 2462, 2166, 1910, 1813, 1731, 1605, 1447, 1399, 1311, 1235, 1150, 1055, 855, 813, 742, 670.$

(E)-N-{{2-[(1,1'-Biphenyl)-2-yl]vinyl}(oxo)(phenyl)-2'-sulfaneylidene}-4-methylbenzenesulfonamide (292a)

Light yellow oil, 15.8 mg, 67% yield.
$^1$H NMR (600 MHz, CDCl$_3$) δ 7.94 (dd, $J = 8.5, 1.1$ Hz, 2H), 7.85 – 7.82 (m, 2H), 7.66 – 7.63 (m, 1H), 7.60 – 7.53 (m, 4H), 7.47 (td, $J = 7.5, 1.1$ Hz, 1H), 7.41 – 7.37 (m, 5H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.21 – 7.19 (m, 2H), 6.90 (d, $J = 15.2$ Hz, 1H), 2.38 (s, 3H).

$^{13}$C$^1$H NMR (151 MHz, CDCl$_3$) δ 143.5, 143.3, 142.7, 140.9, 139.1, 138.5, 135.6, 133.9, 131.1, 130.6, 130.3, 129.8, 129.6, 129.2, 128.4, 128.0, 127.8, 127.7, 127.1, 126.7, 21.5.

MS (EI, 70 eV): m/z (%) = 288.2 (12), 279.1 (41), 278.1 (23), 256.2 (53), 195.2 (26), 180.2 (15), 179.1 (53), 178.1 (100), 177.1 (25), 167.2 (30), 166.1 (30), 165.1 (92), 152.2 (27), 139.1 (63), 125.1 (41), 91.2 (64), 77.2 (23). MS (ESI) [M+Na]$^+$: 496.10, HRMS (ESI) (m/z) [C$_{27}$H$_{23}$NO$_3$S$_2$Na]$^+$: Calcd. 496.1017, found 496.0994.

IR (ATR): ν = 3516, 3257, 3059, 2922, 2855, 2654, 2326, 2168, 2071, 1915, 1816, 1729, 1597, 1447, 1311, 1235, 1151, 1056, 815, 748.

(E)-N-[(1,1'-Biphenyl)-2-yl(oxo)(styryl)-2$^6$-sulfaneylidene]-4-methylbenzenesulfonamide (292b)

Light yellow oil, 14.6 mg, 62% yield

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.41 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.81 (d, $J = 8.3$ Hz, 2H), 7.65 (td, $J = 7.4, 1.3$ Hz, 1H), 7.59 (td, $J = 7.9, 1.4$ Hz, 1H), 7.38 (s, 3H), 7.37 – 7.31 (m, 6H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 7.4$ Hz, 2H), 7.03 (d, $J = 15.3$ Hz, 1H), 6.18 (d, $J = 15.3$ Hz, 1H), 2.35 (s, 3H).

$^{13}$C$^1$H NMR (151 MHz, CDCl$_3$) δ 144.7, 142.6, 141.7, 141.0, 138.3, 138.0, 133.4, 132.9, 132.0, 131.5, 130.4, 129.2, 128.9, 128.7, 128.5, 128.1, 127.8, 126.7, 124.4, 21.5.

MS (EI, 70 eV): m/z (%) = 201.1 (18), 198.0 (12), 184.0 (23), 166.1 (21), 155.0 (16), 152.1 (47), 151.1 (15), 139.1 (21), 91.1 (100), 77.2 (24), 65.3 (26). MS (ESI) [M+Na]$^+$: 496.10, HRMS (ESI) (m/z) [C$_{27}$H$_{23}$NO$_3$S$_2$Na]$^+$: Calcd. 496.1017, found 496.1015.

8. Photocatalyzed trifluoromethylation of alkenes with N–Ts trifluoromethyl sulfoximines

The trifluoromethyl (CF$_3$) group is a useful structural motif in many biologically active molecules, due to its chemical and metabolic stability, lipophilicity, and binding selectivity.$^{[108]}$ To date, many commonly used trifluoromethylation reagents have been reported, for instance, Umemoto’s reagent,$^{[109]}$ Togni’s reagent,$^{[110]}$ Shibata’s reagent,$^{[111]}$ trifluoriodomethane,$^{[112]}$ TMSCF$_3$,$^{[113]}$ trifluoromethanesulfonyl chloride,$^{[114]}$ sodium trifluoromethanesulfinate,$^{[115]}$ sulfilimino iminiumsand,$^{[116]}$ and AgCF$_3$. $^{[113]}$ All of them have been frequently used as the CF$_3$ source in photocatalysis, metal catalysis and base-assisted reactions. The various reaction mechanisms have shown that the trifluoromethylation can be classified into nucleophilic, electrophilic, and radical trifluoromethylation.

8.1 Results and discussion

8.1.1 Research objective

In our former studies, sulfoximidoyl chloride has been used in the difunctionalization of olefins under photocatalytic conditions through ATRA reaction of the sulfoximidoyl radical. Therefore, we hypothesized that sulfoximidoyl containing N–Ts trifluoromethyl sulfoximine could serve as efficient trifluoromethylation precursors in the photocatalyzed ATRA reaction with styrenes (Scheme 71).

Scheme 71: ATRA reaction of N–Ts trifluoromethyl sulfoximine and olefins

The reduction potential of 293a was found to be $E_{p/2} = -1.62$ V v. SCE as measured on PGSTAT101. As Ir(ppy)$_3$ has the reduction potential of $E_{p/2} = -1.73$ V v. SCE, we theorized that it could be used in the photoredox reaction with the designed trifluoromethylation reagent 293a.
8.1.2 Optimization of the reaction conditions

Using 293a and 110a as the substrates, the reaction was tested with Ir(ppy)₃ to give 294a in 32% yield (Table 12, entry 1). Then, various organic dyes and ruthenium complexes were used to examine the scope of the photocatalyst, but no targeted difunctionalization product 294a was detected (Table 12, entries 2-10). Also carrying out the photocatalytic reaction with other Ir complexes as catalysts did not afford the desired product 294a (entries 11-17). With this results in hands, we further tested different solvents, light sources, and concentrations. The optimal conditions are summarized in entry 23. When Ir(ppy)₃ was used as a catalyst with 293a [0.033 M] in DCM, the 294a was obtained in 62% yield.

Table 12: Optimization of reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Solvent (mL)</th>
<th>Time (h)</th>
<th>Light source</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ir(ppy)₃</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>Ru(bpy)₃Cl₃</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>3</td>
<td>Acr-Mes⁻ClO₄⁻</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>4</td>
<td>Rhodamin B</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>5</td>
<td>Ru(bpy)₃(PF₆)₃</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>7</td>
<td>Rose Bengal</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>8</td>
<td>9-Flourenone</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
</tbody>
</table>

Table 12: Optimization of reaction conditions
<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Solvent</th>
<th>Time</th>
<th>Light Source</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Eosin Y</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>11</td>
<td>Ir[d(CF₃)ppy]₂(bpy)PF₆</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>12</td>
<td>Ir{d[d(CF₃(ppy))]₂(bpy)PF₆</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>13</td>
<td>Ir(ppy)₂(dt/bpy)PF₆</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>14</td>
<td>Ir(ppy)₂[dCF₃(bpy)]PF₆</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>15</td>
<td>Ir[dF(CF₃)(ppy)]₂(bpy)PF₆</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>16</td>
<td>Ir(dtppy)₂(dt/bpy)PF₆</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>17</td>
<td>Ir(ppy)₂(bpy)PF₆</td>
<td>DCM (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>18</td>
<td>Ir(ppy)₃</td>
<td>DCE (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>30</td>
</tr>
<tr>
<td>19</td>
<td>Ir(ppy)₃</td>
<td>CDCl₃ (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>39</td>
</tr>
<tr>
<td>20</td>
<td>Ir(ppy)₃</td>
<td>CHCN (1mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>N.R.</td>
</tr>
<tr>
<td>21</td>
<td>Ir(ppy)₃</td>
<td>DCM (3mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>40</td>
</tr>
<tr>
<td>22</td>
<td>Ir(ppy)₃</td>
<td>CDCl₃ (3mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>42</td>
</tr>
<tr>
<td>23</td>
<td>Ir(ppy)₃</td>
<td>DCM (3mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>62</td>
</tr>
<tr>
<td>25</td>
<td>Ir(ppy)₃</td>
<td>CDCl₃ (3mL)</td>
<td>40 h</td>
<td>blue LEDs</td>
<td>58</td>
</tr>
</tbody>
</table>

*R eaction conditions: 293a (0.1 mmol, 1.0 equiv), 110a (0.5 mmol, 5.0 equiv) and the photocatalyst (1 mol %) in the given solvent. The *dr* was determined by *¹*H NMR analysis, yield after column chromatography.
8.1.3 Substrate scope the reactions

After finding the optimal conditions, the scope of styrenes was examined (Table 13). First, various halo- and methyl-substituted styrenes 110 were reacted in the presence of N-Ts trifluoromethyl sulfoximine 293a obtaining the desired products in the yields from 18% to 78% (entries 1-8).

Table 13: Scope of styrenes 110 with N-Ts trifluoromethyl sulfoximine 293a

<table>
<thead>
<tr>
<th>Entry</th>
<th>R, 110</th>
<th>Products 294</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H, 110a</td>
<td>294aa</td>
<td>62</td>
</tr>
<tr>
<td>2</td>
<td>o-Cl, 110t</td>
<td>294at</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>m-Cl, 110l</td>
<td>294al</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>o-F, 110q</td>
<td>294aq</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>o-Br, 110r</td>
<td>294ar</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>m-Me, 110c</td>
<td>294ac</td>
<td>32</td>
</tr>
</tbody>
</table>
Next, methyl-substituted \( N \)-Ts trifluoromethyl sulfoximine (293b) was tested as 1,2 addition reagent, and the corresponding products (294) were obtained in an average of 50% yield (Table 14, entries 1-8).

**Table 14: Scope of styrenes 110 with 293b**

<table>
<thead>
<tr>
<th>Entry</th>
<th>R, 110</th>
<th>Products 294</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( m )-Br, 110r</td>
<td>294br</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>( o )-Br, 110s</td>
<td>294bs</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>( o )-Cl, 110t</td>
<td></td>
<td>50</td>
</tr>
</tbody>
</table>

\[ \text{Reaction conditions: 1) 293a (37.8 mg, 0.1 mmol, 36.3 mg, 1.0 equiv), 110 (54 mg, 0.5 mmol, 1.0 equiv) and photocatalyst Ir(ppy)3 (0.7 mg, 1 mol%), in DCM (1.0 mL) under argon with 24 W blue-LEDs at room temperature for 40 h, yield after column chromatography.} \]
8.1.4 Plausible mechanism

Based on our previous work, a plausible mechanism is depicted in Scheme 72. Initially, the sulfoximidoyl free radical $A$ and the anion $\text{CF}_3^-$ were generated by the PC*. Then, the resulting intermediate $A$ reacted with $\text{110}$ to give intermediate $B$, which could generate intermediate $C$ due to the oxidation by $\text{PC}^+$. Finally, a nucleophilic reaction took place affording product $\text{294}$.

---

<table>
<thead>
<tr>
<th>Reaction Condition</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 $m$-Cl, $\text{110l}$</td>
<td>$\text{294bt}$</td>
<td>53</td>
</tr>
<tr>
<td>5 $o$-F, $\text{110q}$</td>
<td>$\text{294bl}$</td>
<td>45</td>
</tr>
<tr>
<td>6 $m$-F, $\text{110k}$</td>
<td>$\text{294bk}$</td>
<td>31</td>
</tr>
<tr>
<td>7 $o$-Me, $\text{110b}$</td>
<td>$\text{294bb}$</td>
<td>44</td>
</tr>
<tr>
<td>8 2,4,6-Me$_3$, $\text{110j}$</td>
<td>$\text{294bj}$</td>
<td>74</td>
</tr>
</tbody>
</table>

*Reaction conditions: $\text{293a}$ (0.1 mmol, 37.7 mg, 1.0 equiv), $\text{110}$ (0.5 mmol, 5.0 equiv) and photocatalyst $\text{Ir}($ppy$)$; (0.7 mg, 1 mol%), in DCM (1.0 mL) under argon with 24 W blue-LEDs at room temperature for 40 h, yield after column chromatography.
Scheme 72: Proposed catalytic cycle.

8.1.5 Summary

In summary, we have developed a protocol for the trifluoromethylsulfoximidoylation of styrenes through regioselectivity of the CF₃ addition. A possible mechanism has been proposed as an ATRA reaction.

8.2 Experimental

8.2.1 General information

Visible light was provided by blue-LEDs (24 W, 455 nm). Cyclic voltammograms were taken on a PGSTAT101.

8.2.2 General procedures and characterization data

Procedure for the preparation of product 294.

Under argon, 293a (36.3 mg, 0.1 mmol, 1.0 equiv), styrene (110a, 52.0 mg, 0.5 mmol, 5.0 equiv) and [Ir(ppy)₃] (0.7 mg, 1.0 mol %, 0.01 equiv) were added into a sealable reaction tube (10.0 mL). After the addition of DCM (3.0 mL), the mixture was stirred at room temperature under blue LED irradiations (24 W) for 40 h. Subsequently, 294 was purified by flash column chromatography (with ethyl acetate/ n-pentane = 1/4 as eluent) to give 29.0 mg (62% yield) of the product as an oily liquid. The diastereomeric ratio of 294 was determined by ¹H NMR spectroscopy of the crude
product mixture.

**Reduction potential of 293a.**

Cyclic voltammograms were taken on a PGSTAT101 from Metrohm Autolab using a platinum working electrode, a Ag⁺(0.01 M AgNO₃, 0.1 M NBu₄PF₆, CH₂CN)/Ag as reference electrode, a platinum wire counter electrode and 0.1 M NBu₄PF₆ as supporting electrolyte. The solution was prepared in CH₃CN and degassed with nitrogen bubbling for 20 min prior to voltammetric studies. The scan rate was 20 mV/s. The potentials were given relative to the Fc/Fc⁺ redox couple with ferrocene as internal standard. For conversion to SCE as reference, it is known that SCE is 400 mV more negative than Fc/Fc⁺ in MeCN with NBu₄PF₆ as supporting electrolyte.¹¹⁷

![Cyclic voltammogram](image)

The irreversible peak at -1.94 V correspond to the reduction of 293a

\[
E_{1/2}(\text{Fc/Fc}^+) = +0.085 \text{ V}
\]

\[
E_{p/2} = -2.02 \text{ V v. Fc/Fc}^+
\]

\[
E_{p/2} = -1.62 \text{ V v. SCE}
\]

**Characterization date**

4-Methyl-N-[oxo(phenyl)(3,3,3-trifluoro-2-phenylpropyl)-6-sulfaneylidene|benzenesulfonamide (294aa)

![Chemical structure](image)

Light yellow oil, 29.0 mg, 62% yield, \(dr = 1:1\)
\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta \) 7.81 (dd, \(J = 14.6, 8.2\) Hz, 2H), 7.66 – 7.50 (m, 3H), 7.43 (t, \(J = 7.9\) Hz, 1H), 7.37 (dd, \(J = 16.6, 7.9\) Hz, 1H), 7.30 – 7.15 (m, 5H), 7.02 (dd, \(J = 40.1, 7.5\) Hz, 2H), 4.67 – 4.54 (m, 1H), 3.45 – 3.30 (m, 1H), 3.07 – 2.92 (m, 1H), 2.40 (d, \(J = 2.5\) Hz, 3H).

\(^13\)C\{\(^1\)H\} NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta \) 143.0, 142.9, 140.6, 140.5, 134.8, 134.5, 134.3, 133.7, 130.1, 130.1, 129.6, 129.3, 129.1, 128.9, 128.6, 126.7, 126.6, 69.1, 67.8, 33.0, 32.8, 32.3, 32.1, 31.6, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): \(m/\varepsilon\) (%) = 295.1 (31), 173.1 (80), 155.1 (16), 140.1 (19), 139.1 (24), 133.1 (21), 109.1 (100), 91.2 (25), 77.2 (26). MS (ESI) [M+Na\(^+\)]: 490.07

HRMS (ESI) (m/z) [C\(_{20}\)H\(_{20}\)F\(_3\)N\(_1\)O\(_3\)S\(_2\)Na\(^+\)]: Calcd. 490.0734, found 490.0734.


**N-[[2-(2-Chlorophenyl)-3,3,3-trifluoropropyl]oxo](phenyl)-\(\lambda^6\)-sulfaneylidene]-4-methylbenzenesulfonamide (294at)**

Light yellow oil, 15.5 mg, 31% yield, \(dr = 1:1\)

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta \) 7.80 (dd, \(J = 15.4, 8.2\) Hz, 2H), 7.74 – 7.52 (m, 4H), 7.41 – 7.34 (m, 2H), 7.32 – 7.20 (m, 4H), 7.13 (ddd, \(J = 56.9, 8.0, 1.0\) Hz, 1H), 5.40 – 5.28 (m, 1H), 3.46 – 3.27 (m, 1H), 3.11 – 2.86 (m, 1H), 2.40 (d, \(J = 12.1\) Hz, 3H).

\(^13\)C\{\(^1\)H\} NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta \) 143.1, 143.0, 140.5, 140.4, 136.3, 136.1, 134.9, 134.7, 134.6, 134.1, 131.2, 131.2, 130.2, 129.8, 129.7, 129.5, 129.4, 129.3, 129.3, 129.1, 129.0, 127.6, 127.4, 127.2, 126.7, 126.6, 126.2, 77.2, 77.0, 76.8, 63.3, 61.9, 33.3, 33.1, 32.9, 32.9, 32.7, 32.7, 32.5, 32.3, 21.5.

Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.
MS (EI, 70 eV): \( m/z \) (%) = 466.2 (32), 327.1 (34), 295.0 (79), 207.0 (51), 187.1 (30), 155.0 (65), 151.1 (52), 143.1 (79), 140.0 (89), 139.1 (100), 125.1 (33), 91.1 (77). MS (ESI) [M+Na]^+: 524.03, HRMS (ESI) \( m/z \) [C\(_{22}\)H\(_{19}\)ClNO\(_3\)S\(_2\)F\(_3\)Na]^+: Calcd. 524.0345, found 534.0338. IR (ATR): \( \nu = \) 3784, 3468, 3069, 2922, 2852, 2256, 1918, 1808, 1589, 1493, 1450, 1382, 1319, 1249, 1152, 1092, 1061, 998, 911, 850, 813, 735.

4-Methyl-N-[oxo(phenyl)(3,3,3-trifluoro-2-(m-tolyl)propyl)-\( \lambda^6 \)-sulfaneylidene]benzenesulfonamide (294al)

Light yellow oil, 9.1 mg, 18% yield, \( dr = 1:1 \)

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.82 – 7.78 (m, 2H), 7.70 – 7.66 (m, 1H), 7.59 – 7.55 (m, 2H), 7.52 – 7.42 (m, 2H), 7.35 – 7.32 (m, 1H), 7.29 (d, \( J = 6.5 \) Hz, 1H), 7.26 – 7.20 (m, 2H), 7.03 (d, \( J = 7.6 \) Hz, 1H), 6.92 (s, 1H), 4.61 (dd, \( J = 28.4, 11.1 \) Hz, 1H), 3.42 – 3.29 (m, 1H), 2.99 – 2.90 (m, 1H), 2.40 (s, 3H).

\(^{13}\)C\({ }^1\)H NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 143.1, 140.4, 135.1, 134.9, 134.5, 133.4, 130.9, 130.3, 130.1, 129.9, 129.6, 129.3, 129.3, 129.2, 128.4, 127.9, 126.7, 126.6, 126.5, 77.2, 77.0, 76.8, 68.3, 67.2, 33.3, 33.0, 32.8, 32.6, 21.6. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): \( m/z \) (%) = 295.0 (78), 207.0 (35), 155.0 (65), 143.1 (100), 140.1 (68), 139.0 (76), 125.1 (31), 91.2 (56). MS (ESI) [M+Na]^+: 524.03, HRMS (ESI) \( m/z \) [C\(_{22}\)H\(_{19}\)ClNO\(_3\)S\(_2\)F\(_3\)Na]^+: Calcd. 524.0345, found 534.0338.

IR (ATR): \( \nu = \) 3403, 3066, 2925, 2857, 2650, 2325, 2170, 2081, 2000, 1808, 1734, 1595, 1576, 1476, 1440, 1379, 1315, 1243, 1147, 1057, 998, 943, 844.

4-Methyl-N-[oxo(phenyl)(3,3,3-trifluoro-2-(2-fluorophenyl)propyl)-\( \lambda^6 \)-sulfaneylidene]benzenesulfonamide (294aq)

Light yellow oil, 15.6 mg, 32% yield, \( dr = 1:1 \)
\( ^1 H \) NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 7.81 \) (d, \( J = 8.2 \) Hz, 2H), 7.68 – 7.63 (m, 1H), 7.62 – 7.56 (m, 2H), 7.45 – 7.41 (m, 1H), 7.40 – 7.36 (m, 1H), 7.30 – 7.28 (m, 1H), 7.26 – 7.23 (m, 2H), 7.22 – 7.11 (m, 1H), 6.87 – 6.81 (m, 1H), 6.74 – 6.70 (m, 1H), 5.09 – 4.98 (m, 1H), 3.45 – 3.28 (m, 1H), 3.12 – 2.95 (m, 1H), 2.40 (s, 3H).

\( ^{13} C \{ ^1 H \} \) NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 161.8, 161.2, 160.3, 159.5, 143.1, 143.0, 142.9, 140.2, 140.2, 140.4, 136.3, 134.9, 134.7, 133.9, 132.1, 132.1, 132.0, 129.4, 129.3, 129.3, 129.2, 129.1, 129.1, 127.9, 126.7, 126.6, 126.6, 124.7, 124.6, 124.6, 123.8, 123.7, 115.7, 115.5, 115.3, 115.1, 77.2, 77.0, 76.8, 60.1, 32.7, 32.5, 32.3, 32.1, 31.9, 31.7, 31.5, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): \( m/z \) (%) = 485.2 (M\(^+\), 2), 295.0 (88), 191.0 (56), 155.0 (49), 140.1 (55), 139.0 (58), 127.0 (100), 91.2 (41). MS (ESI) [M+Na]\(^+\): 508.06

HRMS (ESI) (m/z) [C\(_{22}\)H\(_{19}\)NO\(_3\)S\(_2\)F\(_4\)Na]: Calcd. 508.0640, found 508.0634.


**N-([2-(2-Bromophenyl)-3,3,3-trifluoropropyl](oxo)(phenyl)-\( \lambda^6\)-sulfaneylidene)-4-methylbenzenesulfonamide (294as)**

Light yellow oil, 13.7 mg, 25% yield, \( dr = 1:1 \)

\( ^1 H \) NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 7.84 – 7.73 \) (m, 2H), 7.66 – 7.51 (m, 3H), 7.42 – 7.35 (M, 3H), 7.33 – 7.12 (m, 5H), 5.46 – 5.26 (m, 1H), 3.46 – 3.24 (m, 1H), 3.09 – 2.87 (M, 1H), 2.40 (d, \( J = 2.7 \) Hz, 3H).

\( ^{13} C \{ ^1 H \} \) NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta 143.0, 140.5, 140.4, 134.9, 134.8, 134.6, 134.1, 133.2, 133.0, 131.4, 131.4, 130.4, 130.0, 129.7, 129.5, 129.4, 129.3, 129.3, 129.1, 129.0, 128.0, 127.8, 127.5, 127.1, 126.7, 126.6, 126.0, 66.0, 64.7, 33.4, 33.2, 33.1, 33.0, 32.9, 32.8, 32.7, 32.5, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.
MS (EI, 70 eV): \( m/z \) (%) = 466.2 (60), 295.0 (100), 252.9 (30), 250.9 (30), 187.0 (30), 155.5 (53), 152.0 (50), 151.1 (42), 140.0 (70), 139.0 (79), 187.0 (30), 155.5 (53), 152.0 (50), 151.1 (42), 140.0 (70), 139.0 (79), 91.2 (47).

IR (ATR): \( \nu = 3933, 3783, 3467, 3066, 2921, 2852, 2588, 2254, 2096, 1916, 1808, 1730, 1581, 1469, 1442, 1382, 1320, 1244, 1151, 1092, 1060, 910, 849 \).

4-Methyl-N-{oxo(phenyl)[3,3,3-trifluoro-2-(m-tolyl)propyl]-2,6-sulfaneylidene}benzenesulfonamide (294ac)

Light yellow oil, 15.4 mg, 32% yield, \( dr = 1:1 \)

\(^1^H\) NMR (400 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.79 (dd, \( J = 11.5, 8.3 \) Hz, 2H), 7.65 – 7.48 (m, 3H), 7.45 – 7.33 (m, 2H), 7.24 – 7.20 (m, 2H), 7.13 (t, \( J = 8.5 \) Hz, 1H), 7.08 – 7.03 (m, 1H), 6.88 – 6.71 (m, 2H), 4.64 – 4.50 (m, 1H), 3.39 – 3.26 (m, 1H), 3.06 – 2.84 (m, 1H), 2.38 (s, 3H), 2.17 (d, \( J = 22.1 \) Hz, 3H).

\(^{13}^C\) NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 142.9, 142.9, 140.6, 140.5, 138.4, 138.3, 134.7, 134.4, 134.3, 133.7, 130.9, 130.8, 129.7, 129.3, 129.3, 129.2, 129.1, 129.0, 128.6, 128.4, 127.6, 127.1, 126.6, 126.5, 69.1, 67.9, 33.1, 32.8, 32.3, 32.0, 21.5, 21.2, 21.1. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): \( m/z \) (%) = 356.2 (34), 295.1 (42), 234.3 (30), 187.2 (100), 155.2 (56), 140.2 (34), 139.1 (52), 123.2 (67), 91.3 (54). MS (ESI) [M+Na]+: 504.09

HRMS (ESI) \( m/z \) [C\(_{23}\)H\(_{22}\)NO\(_3\)S\(_2\)F\(_3\)Na]+: Calcd. 504.0891, found 504.0870

IR (ATR): \( \nu = 3782, 3463, 3028, 2921, 2853, 2582, 2253, 2803, 1731, 1600, 1446, 1383, 1371, 1243, 1151, 1091, 1062, 910, 878, 850, 810, 733, 689 \).

4-Methyl-N-{oxo(phenyl)[3,3,3-trifluoro-2-(o-tolyl)propyl]-2,6-sulfaneylidene}benzenesulfonamide (294ab)

Light yellow oil, 10.6 mg, 22% yield, \( dr = 1:1 \)
1H NMR (600 MHz, CDCl₃, mixture of diastereomers) δ 7.80 (dd, J = 46.5, 8.2 Hz, 2H), 7.69 – 7.52 (m, 3H), 7.50 – 7.41 (m, 2H), 7.36 (t, J = 7.9 Hz, 1H), 7.27 – 7.17 (m, 4H), 6.97 (dd, J = 104.8, 7.4 Hz, 1H), 5.07 – 4.86 (m, 1H), 3.47 – 3.27 (m, 1H), 2.98 – 2.90 (m, 1H), 2.40 (d, J = 11.7 Hz, 3H), 1.86 (d, J = 123.8 Hz, 3H).

13C NMR (151 MHz, CDCl₃, mixture of diastereomers) δ 143.0, 142.9, 140.6, 140.6, 139.1, 138.4, 134.8, 134.6, 130.7, 130.7, 130.0, 129.9, 129.6, 129.4, 129.3, 129.2, 129.1, 129.0, 128.4, 128.4, 127.7, 126.7, 126.5, 126.5, 126.3, 63.5, 62.4, 33.8, 33.6, 33.5, 33.3, 33.2, 33.0, 32.8, 32.6, 21.6, 21.5, 19.3, 18.9. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): m/z (%) = 481.1 (M⁺, 1), 356.0 (41), 295.0 (55), 187.1 (100), 140.1 (29), 139.0 (33), 123.1 (64). MS (ESI) [M+Na]⁺: 504.09

HRMS (ESI) (m/z) [C₂₃H₂₂NO₃S₂F₃Na]⁺: Calcd. 504.0891, found 504.0888


4-Methyl-N-[oxo(p-tolyl)(3,3,3-trifluoro-2-mesitylpropyl)-26-sulfaneylidene]benzene sulsonamid (294aj)

Light yellow oil, 39.7 mg, 78% yield, dr = 1:1

1H NMR (600 MHz, CDCl₃, mixture of diastereomers) δ 7.80 (dd, J = 30.9, 8.2 Hz, 2H), 7.61 – 7.45 (m, 4H), 7.31 – 7.24 (m, 3H), 7.20 (d, J = 8.1 Hz, 1H), 6.88 – 6.80 (m, 1H), 6.14 (t, J = 6.9 Hz, 1H), 5.93 (dd, J = 8.3, 5.7 Hz, 1H), 2.68 (dd, J = 7.0, 6.0, 4.7 Hz, 2H), 2.40 – 2.14 (m, 12H).

13C NMR (151 MHz, CDCl₃, mixture of diastereomers) δ 142.7, 142.4, 140.4, 140.1, 139.0, 138.4, 136.6, 135.3, 133.3, 132.8, 131.3, 130.4, 129.5, 129.4, 129.3, 129.1, 127.4, 126.7, 126.5, 126.3, 77.2, 77.0, 76.8, 73.6, 69.5, 39.5, 39.4, 39.3, 39.2, 39.1, 39.0, 38.9, 38.8, 21.4, 21.0, 20.7, 20.3. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): m/z (%) = 342.2 (40), 309.0 (61), 273.0 (67), 155.0 (47), 129.0 (100), 109.1 (98), 91.2 (61). MS (ESI) [M+Na]⁺: 532.12

HRMS (ESI) (m/z) [C₂₅H₂₆NO₃S₂F₂Na]⁺: Calcd. 532.1204, found 532.1199
IR (ATR): $\nu = 3933, 3783, 3467, 3066, 2921, 2852, 2588, 2254, 2096, 1916, 1808, 1730, 1581, 1469, 1442, 1382, 1320, 1244, 1151, 1092, 1060, 910, 849, 811, 753$.

N-{[2-(2-Bromophenyl)-3,3,3-trifluoropropyl]oxo}(p-tolyl)-$\lambda^6$-sulfaneylidene)-4-methylbenzenesulfonamide (294br)

Light yellow oil, 26.7 mg, 48% yield, $dr = 1:1$

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.79 (dd, $J = 25.8, 8.3$ Hz, 2H), 7.72 – 7.57 (m, 1H), 7.51 (d, $J = 8.3$ Hz, 1H), 7.42 – 7.31 (m, 3H), 7.25 – 7.22 (m, 2H), 7.20 – 7.15 (m, 3H), 5.39 – 5.30 (m, 1H), 3.43 – 3.24 (m, 1H), 3.06 – 2.86 (m, 1H), 2.40 (dd, $J = 12.4, 8.2$ Hz, 6H).

$^{13}$C-$^1$H NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 146.4, 146.2, 142.9, 142.9, 140.7, 140.6, 133.2, 133.0, 131.5, 131.4, 131.3, 130.9, 130.4, 130.0, 129.8, 129.7, 129.7, 129.6, 129.5, 129.3, 129.2, 128.1, 127.9, 127.7, 127.5, 127.2, 126.7, 126.5, 65.9, 64.7, 33.3, 33.1, 33.0, 32.8, 32.6, 21.8, 21.7, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): $m/z$ (%) = 480.4 (23), 309.2 (43), 308.2 (15), 253.1 (29), 251.1 (29), 189.1 (11), 187.2 (12), 155.2 (61), 154.1 (28), 153.2 (11), 139.2 (100), 91.3 (42). MS (ESI) [M+Na]$^+$: 522.05

HRMS (ESI) ($m/z$) [C$_{23}$H$_{21}$BrNO$_3$S$_2$F$_3$Na]$^+$: Calcd. 581.9996, found 582.0018.

IR (ATR): $\nu = 3857, 3334, 3063, 2925, 2687, 2494, 2314, 2208, 2169, 2069, 2011, 1938, 1806, 1732, 1593, 1470, 1439, 1378, 1318, 1243, 1147, 1057, 932, 852.

N-{[2-(3-Bromophenyl)-3,3,3-trifluoropropyl]oxo}(p-tolyl)-$\lambda^6$-sulfaneylidene)-4-methylbenzenesulfonamide (294bs)

Light yellow oil, 28.5 mg, 51% yield, $dr = 1:1$

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.79 (dd, $J = 19.4, 8.2$ Hz, 2H), 7.54 – 7.39 (m, 3H), 7.50 – 7.42 (m, 4H), 7.18 (dd, $J = 16.6, 8.6$ Hz, 1H), 7.10
(dd, J = 12.9, 5.1 Hz, 1H), 7.02 (s, 1H), 4.74 – 4.44 (m, 1H), 3.44 – 3.22 (m, 1H), 3.03 – 2.79 (m, 1H), 2.51 – 2.37 (m, 6H).

$^{13}$C$^1$H NMR (151 MHz, CDCl$_3$, mixture of diastereomers) δ 146.7, 146.5, 143.0, 143.0, 140.5, 140.5, 133.1, 133.1, 133.0, 132.8, 131.2, 130.6, 130.4, 130.1, 130.1, 130.0, 130.0, 129.6, 129.4, 129.3, 129.2, 128.9, 126.6, 126.5, 122.4, 122.3, 77.2, 77.0, 76.8, 68.3, 67.3, 33.3, 33.1, 32.9, 32.7, 32.5, 32.3, 32.1, 21.7, 21.7, 21.6. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): m/z (%) = 309.1 (43), 189.1 (17), 187.1 (19), 155.2 (52), 154.1 (20), 139.1 (100), 91.3 (42). MS (ESI) [M+Na]$^+$: 522.05

HRMS (ESI) (m/z) [C$_{23}$H$_{21}$BrNO$_3$S$_2$F$_3$Na$^+$]: Calcd. 581.9996, found 582.0007.


$\text{N-}[(\text{2-(2-Chlorophenyl)-3,3,3-trifluoropropyl})\text{oxo}](\text{p-tolyl})\text{-}\lambda^6\text{-sulfaneylidene})\text{-4-methylbenzenesulfonamide (294bt)}$

Light yellow oil, 25.8 mg, 50% yield, $dr = 1:1$

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) δ 7.80 (dd, J = 19.1, 8.2 Hz, 2H), 7.70 – 7.57 (m, 1H), 7.46 (dd, J = 48.2, 8.3 Hz, 2H), 7.37 – 7.28 (m, 1H), 7.25 – 7.18 (m, 4H), 7.17 – 7.10 (m, 2H), 5.38 – 5.28 (m, 1H), 3.44 – 3.24 (m, 1H), 3.08 – 2.87 (m, 1H), 2.40 (dd, J = 12.5, 9.1 Hz, 6H).

$^{13}$C$^1$H NMR (151 MHz, CDCl$_3$, mixture of diastereomers) δ 146.4, 146.2, 142.9, 142.9, 140.7, 140.6, 136.4, 136.1, 131.5, 131.2, 131.1, 131.0, 130.1, 129.8, 129.8, 129.7, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 127.7, 127.3, 127.1, 126.7, 126.5, 126.3, 77.2, 77.0, 76.8, 63.2, 62.0, 33.4, 33.2, 33.0, 33.0, 32.8, 32.7, 32.6, 32.4, 21.8, 21.7, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.
MS (EI, 70 eV): m/z (%) = 309.0 (23), 207.1 (24), 206.0 (18), 187.1 (13), 155.0 (35), 154.0 (36), 153.0 (22), 151.0 (27), 143.1 (31), 139.0 (100), 108.1 (43), 91.2 (100), 108.1 (43), 91.2 (100).

HRMS (ESI) (m/z) [C_{23}H_{21}ClNO_3S_2F_3Na]^+: Calcd. 538.0501, found 538.0489.

IR (ATR): ν = 3829, 3449, 3065, 2926, 2861, 2653, 2319, 2182, 2043, 1988, 1920, 1734, 1594, 1477, 1434, 1379, 1318, 1243, 1149, 1053, 933, 855, 811.

N-[[2-(3-Chlorophenyl)-3,3,3-trifluoropropyl](oxo)(p-tolyl)-\(\lambda^6\)-sulfaneylidene]-4-methylbenzenesulfonamide (294bl)

\[
\text{Cl} \quad \text{CF}_3 \quad \text{O} \quad \text{N} \quad \text{T}s \\
\text{Me}
\]

Light yellow oil, 27.5 mg, 55% yield, dr = 1:1

\(^1\)H NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) δ 7.79 (dd, J = 19.4, 8.2 Hz, 2H), 7.44 (dd, J = 11.9, 8.3 Hz, 2H), 7.27 (d, J = 8.1 Hz, 1H), 7.24 (dd, J = 10.6, 6.5 Hz, 3H), 7.20 – 7.13 (m, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.97 (d, J = 7.2 Hz, 1H), 6.92 (s, 1H), 4.67 – 4.55 (m, 1H), 3.39 – 3.26 (m, 1H), 2.97 – 2.84 (m, 1H), 2.46 – 2.37 (m, 6H).

\(^{13}\)C\(^{\text{\textsuperscript{1}}}\)H NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) δ 146.7, 146.5, 143.0, 143.0, 140.5, 140.5, 134.5, 134.4, 131.0, 130.6, 130.2, 130.2, 130.1, 130.1, 123.0, 129.9, 129.9, 129.8, 129.8, 129.7, 129.6, 129.3, 129.3, 129.3, 129.2, 129.1, 128.5, 127.9, 127.7, 127.6, 126.6, 126.5, 68.2, 67.2, 33.1, 32.9, 32.7, 32.5, 32.3, 32.1, 21.7, 21.7, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): m/z (%) = 207.2 (15), 206.2 (15), 155.2 (47), 154.2 (28), 153.2 (11), 151.2 (12), 143.2 (44), 139.2 (100), 108.3 (28), 92.4 (25), 91.4 (93). MS (ESI) [M+Na]^+: 522.05

HRMS (ESI) (m/z) [C_{23}H_{23}ClNO_3S_2F_3Na]^+: Calcd. 538.0501, found 538.0511


4-Methyl-N-\{oxo(p-tolyl)\}[3,3,3-trifluoro-2-(2-fluorophenyl)propyl]-\(\lambda^6\)-sulfaneylidene]benzenesulfonamide (294bq)
Light yellow oil, 22.5 mg, 45% yield, $dr = 1:1$

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.82 – 7.77 (m, 2H), 7.46 (dd, $J = 18.7, 8.3$ Hz, 2H), 7.36 – 7.17 (m, 5H), 7.15 – 7.06 (m, 1H), 6.88 – 6.82 (m, 1H), 6.76 (dd, $J = 12.3, 6.0$ Hz, 1H), 5.12 – 4.95 (m, 1H), 3.46 – 3.23 (m, 1H), 3.08 – 2.90 (m, 1H), 2.43 – 2.37 (m, 6H).

$^{13}$C,$^1$H NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 161.9, 160.2, 146.4, 146.1, 142.9, 142.9, 140.6, 140.5, 132.1, 132.0, 131.9, 131.9, 129.8, 129.8, 129.7, 129.5, 129.3, 129.3, 129.2, 129.2, 127.9, 126.6, 126.6, 126.6, 124.6, 124.6, 124.5, 124.5, 115.5, 115.4, 60.4, 60.1, 32.8, 32.6, 32.4, 32.2, 32.1, 32.0, 31.8, 31.6, 21.7, 21.7, 21.5.

Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): $m/z$ (%) = 309.2 (41), 308.2 (40), 191.2 (69), 155.2 (75), 154.2 (17), 139.2 (100), 127.2 (59), 123.2 (29), 91.3 (33). MS (ESI) [M+Na]$^+$: 522.08

HRMS (ESI) ($m/z$) $[C_{23}H_{21}NO_3S_2F_4Na]^+$: Calcd. 522.0797, found 522.0808

IR (ATR): $\nu = 3060, 2933, 2167, 1923, 1808, 1731, 1594, 1492, 1453, 1383, 1316, 1247, 1146, 1060, 936, 813.$

4-Methyl-N-[oxo(p-tolyl)[3,3,3-trifluoro-2-(3-fluorophenyl)propyl]-2$^6$-sulfaneylidene]benzenesulfonamide (294bk)

Light yellow oil, 15.4 mg, 31% yield, $dr = 1:1$

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.84 – 7.74 (m, 2H), 7.49 – 7.41 (m, 2H), 7.26 (d, $J = 2.0$ Hz, 4H), 7.08 (d, $J = 8.2$ Hz, 1H), 7.00 (s, 1H), 6.90 (d, $J = 6.6$ Hz, 1H), 6.80 – 6.74 (m, 1H), 4.61 (dd, $J = 28.6, 11.9$ Hz, 1H), 3.40 – 3.24 (m, 1H), 2.90 (dd, $J = 21.0, 11.5$ Hz, 1H), 2.45 – 2.36 (m, 6H).

$^{13}$C,$^1$H NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 163.1, 161.5, 146.6, 146.3, 143.0, 143.0, 140.5, 140.5, 131.4, 131.4, 130.8, 130.5, 130.5, 130.3, 130.2, 130.2, 130.1, 129.9, 129.6, 129.3, 129.3, 128.0, 126.6, 126.6, 126.5, 126.1,
117.2, 117.1, 68.3, 67.2, 33.2, 33.0, 32.7, 32.5, 32.5, 21.7, 21.5. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): m/z (%) = 310.2 (13), 309.2 (28), 308.2 (36), 191.3 (27), 155.2 (91), 154.2 (16), 139.2 (100), 127.2 (41), 91.3 (45). MS (ESI) [M+Na]+: 522.08

HRMS (ESI) (m/z) [C_{23}H_{21}NO_{3}S_{2}F_{4}Na]$: Calcd. 522.0797, found 522.0802

IR (ATR): \( \nu = 3064, 2929, 2164, 2025, 1808, 1731, 1593, 1490, 1449, 1381, 1313, 1247, 1146, 1059, 964, 883. \)

\( \text{4-Methyl-N-[oxo(p-tolyl)(3,3,3-trifluoro-2-(o-tolyl)propyl)-}\lambda^6\text{-sulfaneylidene]benzenesulfonamide (294bb)} \)

Light yellow oil, 21.8 mg, 44% yield, \( dr = 1:1 \)

\( ^1H \text{ NMR (600 MHz, CDCl}_3, \text{ mixture of diastereomers) } \delta 7.83 (d, J = 8.2 \text{ Hz}, 1H), 7.75 (d, J = 8.2 \text{ Hz}, 1H), 7.52 – 7.38 (m, 2H), 7.26 – 7.12 (m, 6H), 7.11 – 7.04 (m, 1H), 6.95 – 6.87 (m, 1H), 5.09 – 4.85 (m, 1H), 3.41 – 3.25 (m, 1H), 2.99 – 2.82 (m, 1H), 2.40 (dd, J = 22.3, 9.6 \text{ Hz}, 6H), 1.90 (d, J = 134.7 \text{ Hz}, 3H). \)

\( ^{13}C\{^1H\} \text{ NMR (151 MHz, CDCl}_3, \text{ mixture of diastereomers) } \delta 146.3, 146.1, 142.9, 142.8, 140.8, 140.7, 139.2, 138.5, 132.0, 130.7, 130.6, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 129.2, 129.1, 128.4, 128.3, 127.8, 127.8, 127.2, 126.6, 126.6, 126.5, 126.4, 126.2, 63.3, 62.4, 33.9, 33.7, 33.5, 33.3, 33.1, 32.9, 32.7, 21.7, 21.7, 21.5, 21.5, 19.4, 19.0. \)

Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): m/z (%) = 356.0 (46), 309.0 (32), 187.1 (100), 139.0 (66), 123.1 (84), 108.1 (40, 91.2 (40). MS (ESI) [M+Na]+: 518.10

HRMS (ESI) (m/z) [C_{24}H_{24}NO_{3}S_{2}F_{3}Na]$: Calcd. 518.1047, found 518.1046

IR (ATR): \( \nu = 3029, 2926, 2648, 2293, 2190, 2075, 2039, 2009, 1922, 1809, 1733, 1595, 1492, 1453, 1377, 1317, 1241, 1148, 1090, 1055, 933, 851. \)

\( \text{4-Methyl-N-[oxo(p-tolyl)(3,3,3-trifluoro-2-mesitylpropyl)-}\lambda^6\text{-sulfaneylidene]benzenesulfonamide (294bj)} \)

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Light yellow oil, 38.7 mg, 74% yield, $dr = 1:1$

$^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.80 (dd, $J = 35.9, 8.3$ Hz, 2H), 7.47 (dd, $J = 8.2, 6.3$ Hz, 2H), 7.27 – 7.25 (m, 3H), 7.13 (dd, $J = 74.8, 8.2$ Hz, 2H), 6.83 (d, $J = 28.7$ Hz, 1H), 6.13 – 5.89 (m, 1H), 2.73 – 2.57 (m, 2H), 2.55 – 2.06 (m, 15H).

$^{13}$C NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 144.4, 144.1, 142.7, 142.3, 140.5, 140.3, 138.9, 138.3, 133.5, 132.1, 131.2, 130.6, 130.5, 130.1, 129.6, 129.4, 129.3, 127.2, 126.7, 126.6, 126.4, 126.2, 73.3, 69.2, 39.4, 39.4, 39.2, 39.2, 39.1, 39.0, 38.9, 38.8, 21.6, 21.4, 21.0, 20.8, 20.3. Note: Due to the high number of signals in close proximity, we were unable to unambiguously assign those values resulting from C–F couplings. Thus, the given numbers are only peak listings.

MS (EI, 70 eV): $m/z$ (%) = 384.3 (60), 228.1 (31), 215.1 (100), 139.1 (51), 91.2 (38).

MS (ESI) [M+Na]$^+$: 546.14

HRMS (ESI) ($m/z$) [C$_{26}$H$_{28}$NOS$_2$F$_3$Na]$^+$: Calcd. 546.1360, found 546.1359.

III. List of Abbreviations

Ac  acetyl
ACCN  1,10-azo bis(cyclohexanecarbonitrile)
AIBN  2,2-azo bisisobutyronitrile
ATE  acyl thiol-ene
ATRA  atom transfer radical addition
Ar (in conditions)  argon
Ar (in molecular structure)  aryl
ATY  acyl thiol-yne
BHT  2,4-di-tert-butyl-4-methylphenol
bpy  2,2'-bipyridine
bpz  bipyrazine
Bn  benzyl
dtbppy  4,4'-di-tert-butyl-2,2'-bipyridine
br  broad (NMR signal)
Boc  tert-butylxocarbonyl
Bu  butyl
nBu  n-butyl
tBu  t-butyl
Bz  benzoyle
Calcd.  calculated
CAN  ceric ammonium nitrate
°C  centigrade
conc.  concentrated
CPBA  benzoyl hydroperoxide
CTAB  hexadecyltrimethylammonium bromide
δ  chemical shift
d  doublet (NMR signal)
DABCO  1,4-diazabicyclo[2.2.2]octane
DBU  1,8-diazabicyclo(5.4.0)undec-7-ene
DCE  1,2-dichloroethane
DCM  dichloromethane
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<tr>
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TLC  thin layer chromatography
TMS  trimethylsilyl
Ts   toluenesulfonyl
p-Tol p-methylphenyl
tosyl toluenesulfonyl
V    Volt
vs   versus
IV. References


[87] a) P. R. Blakemore, M. S. Burge, J. Am. Chem. Soc. 2007, 129, 3068; b) M.


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VI. Curriculum Vitae

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Subject: Pd-catalyzed C-H Functionalization of Aryl Azobenzenes  
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Journal publications:  
1 Electrophilic Sulfoximidations of Thiols by Hypervalent Iodine Reagents  
2 Photocatalytic Additions of 1-Sulfoximidoyl-1,2-Benziodoxoles to Styrenes  
3 Photocatalytic difunctionalisations of alkenes with N–SCN sulfoximines  
4 Sulfoximidations of Benzylic C–H Bonds by Photocatalysis  
5 An Iodine-Mediated Hofmann-Löffler-Freytag Reaction of Sulfoximines Leading to Dihydroisothiazole Oxides  
2017, 359, 4274–4277.

6 Sulfoximidoyl-Containing Hypervalent Iodine(III) Reagents: 1-Sulfoximidoyl-1,2-benziodoxoles

7 Organocatalytic Asymmetric Synthesis of trans-γ-Lactams

8 Organocatalytic Kinetic Resolution of Sulfoximines.

9 Pd-catalyzed C-H Bond Sulfonylation of Azobenzenes with Arylsulfonyl Chlorides.

10 Palladium-Catalyzed Direct ortho C–O Bond Construction of Aromatic Azoxybenzene Compounds with Carboxylic Acids and Alcohols.

11 Direct diphosphonylation of quinolines with H-phosphonates under metal-free conditions.