New methods for the synthesis of sulfur functional groups



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A thesis submitted for the degree of Doctor of Philosophy

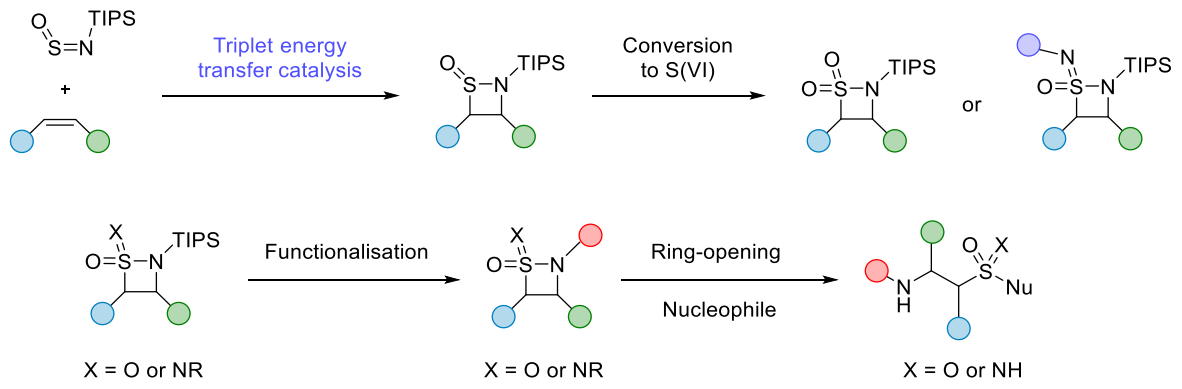
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Abstract

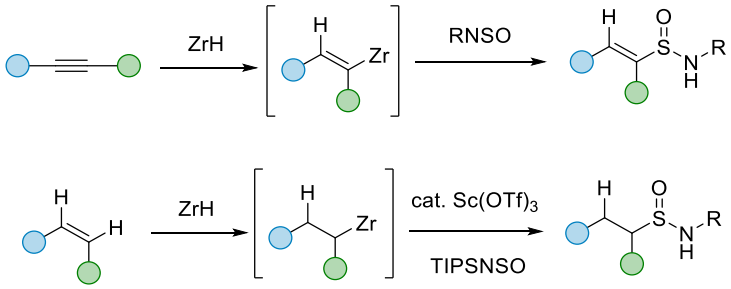
In this thesis, novel methods using different kinds of sulfinylamine reagents to synthesize different sulfinamides are described. The use of sulfinylamines in both photochemistry and organometallic chemistry provides access to a broad range of *β*-cyclicsulfinamides, alkenyl sulfinamides, and alkyl sulfinamides.

Chapter 1 is a literature review introducing the properties, applications and the reported synthetic strategies towards *β*-sultam. A brief introduction of aza-sulfur functionalities is included. Sufinylamines, especially silyl-sulfinylamines are also introduced. The physical principles of photochemistry and recent advances in energy transfer in photocycloaddition are also highlighted.

Chapter 2 describes the development of a [2+2] photocycloaddition reaction between the sulfinylamine TIPSNSO and alkenes to generate *β*-cyclicsufinamides. The reaction proceeds using energy transfer catalysis and visible light. The scope of this transformation tolerates both activated alkenes and unactivated alkenes. The formed *β*-cyclicsufinamides can be converted to *β*-sultams or aza-*β*-sultams by subsequent oxidation or imination. Both *β*-sultams and aza-*β*-sultams undergo efficient ring-opening reactions, yielding taurine analogues and aza-taurine analogues. A brief mechanistic study is then described to support our mechanistic hypothesis that the reaction proceeds via a triplet state of TIPSNSO.



Chapter 3 provides a brief review of traditional methods to synthesize sulfinamides and their associated drawbacks, followed by the discovery of the reaction between sulfinylamines and *in situ* formed zirconium reagents. Both alkynes and alkenes are capable of undergoing the hydrometalation reaction to form alkenyl or alkyl zirconium reagents and subsequent addition to sulfinylamine to generate sulfinamides.



Chapter 4 discusses the conclusions of these projects and provides potential future work.

Chapter 5 provides the experimental data and procedures used.

Declaration

I declare that the work in this thesis had not been previously submitted for a degree at the university of Oxford or any other higher education institution.

The experimental work in Chapter 2 was carried out in collaboration with Dr. Benedict A. Williams, a former DPhil student in the Willis group. The x-ray experiments discussed in this thesis were carried out by Dr. Benedict A. Williams. Other work described in this thesis is entirely the work of the author.

The work in both Chapters 2 and 3 has been prepared for publication.

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First and foremost, I would like to express my deepest gratitude to Professor Michael Willis. It is under Mike's guidance over the past few years that I was able to complete these research projects and grow into a capable DPhil student. I joined the Willis group in 2020, but the journey was far from smooth at the beginning. My early attempts at the synthesis of aminosulfonimidamides and catalytic hydrometalation of unsaturated carbon-carbon bonds followed by insertion to sulfinylamines met with numerous failures. Nevertheless, Mike never lost confidence in me. On the contrary, he recognized some of the ideas I proposed and encouraged me to start with the zirconium project. This allowed me to gain a deeper understanding of sulfur chemistry, which helped me a lot in further more complicated projects in sulfur chemistry.

Later, I encountered significant difficulties again while working on the imination of *β*-cyclicsulfinamides. At one point, I was unable to get any product, and given that the target compound was a never reported novel scaffold, it was hard to determine why the reactions failed. Even then, Mike trusted me and supported the continuation of this research. His valuable advice enabled me to eventually succeed in both the imination and subsequent ring-opening of *β*-cyclicsulfinamides. It is also notable that despite the inherent challenges associated with sulfinyl nitrene chemistry, Mike consistently supported my enthusiasm for this field. This encouragement kept my spark in sulfinyl nitrene chemistry, ultimately enabled me to design and accomplish the novel ring-opening transformation of aza-*β*-sultams. I am sincerely grateful to him for his unwavering support and encouragement.

I would also like to express my thanks to my master's supervisor, Professor Shengming Ma and Professor Minqiang Jia. Without a doubt, the training I got from Professor Shengming Ma,

especially in designing research projects and maintaining a good research mindset, had a critical impact on my ability to tackle more complex and challenging projects during my PhD. Notably, both Professor Ma and Mike's emphasis on carefully examining side-products was fundamental in my discovery and design of more ambitious photochemical reactions.

My appreciation also goes to all the members of the Willis group, who made my last five years an unforgettable and enriching experience. I am particularly grateful to my collaborator Ben for his contributions to X-ray crystallography and computational studies, as well as for our insightful discussions on organic chemistry. I would also like to thank Minyan, who generously offered support in both substrate synthesis and daily life. My sincere thanks to Charlie for our conversations on research ideas, and for your contributions to the Willis group throughout your time as a PhD student and postdoc. Special thanks to Mingkai, it has been an honor to work alongside such a talented colleague for four years. I will always remember the literature collection project we cooperated, and I am grateful for your passion and thoughtful insights on organic chemistry, which inspired me to make breakthroughs in my projects many times. I also thank May and Katherine for bringing joy to the lab and assisting me in experiments.

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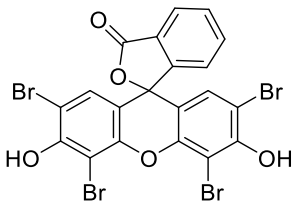
Abbreviations and Acronyms

HOAc	Acetic acid
MeCN	Acetonitrile
R	alkyl
aq.	Aqueous
Ar	aryl
Bz	Benzoyl group
Bn	Benzyl group
t-Bu	*tert*-Butyl
Boc	tert-Butyloxycarbonyl
m-CPBA	*meta*-Chloroperoxybenzoic acid
conc.	Concentrated
CN	Cyano group
DABSO	1,4-Diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DCC	*N*, *N*'-Dicyclohexylcarbodiimide
DMF	Dimethylformamide
equiv.	Equivalent(s)
ESI	Electrospray Ionisation

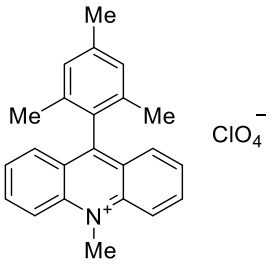
Et	Ethyl
FCC	Flash Column Chromatography
M. p.	Melting point
Ms	Methanesulfonyl group
MTBE	Methyl *tert*-butyl ether
PMP	4-Methoxyphenyl
PIDA	(Diacetoxyiodo)benzene
EWG	Electron withdraw group
ee	Enantiomeric excess
HRMS	High Resolution Mass Spectrometry
IR	Infrared Radiation
Ph	Phenyl group
PyOx	Pyridine-oxazoline-type ligands
SCE	Saturated calomel electrode
biPhONSO	*N*-Sulfinyl-([1,1'-biphenyl]-4-yloxy)amine
TBDPSNSO	*N*-Sulfinyl-*tert*-butyldiphenylsilylamine
TDSNSO	*N*-Sulfinyl-(dimethyl)thexylsilylamine
TNBSNSO	*N*-Sulfinyl-tri(*n*-butyl)silylamine
TIPSNSO	*N*-Sulfinyl-triisopropylsilylamine
TrNSO	*N*-Sulfinyltritylamine

t-OctNSO	*N*-Sulfinyl-*tert*-octylamine
TBAF	Tetra-*n*-butylammonium fluoride
THF	Tetrahydrofuran
TLC	Thin-Layer Chromatography
TFE	Trifluoroethanol
UV	Ultraviolet
λ	Wavelength

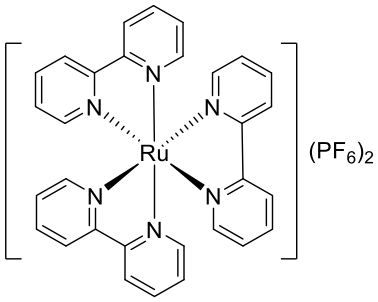
Photocatalyst Structure Index



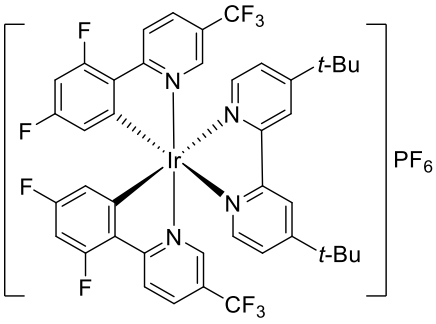
Eosin Y



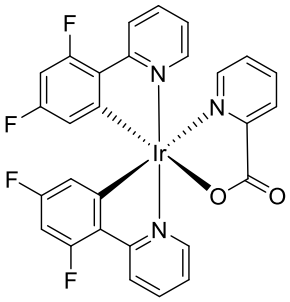
[Mes-Acr]ClO_4



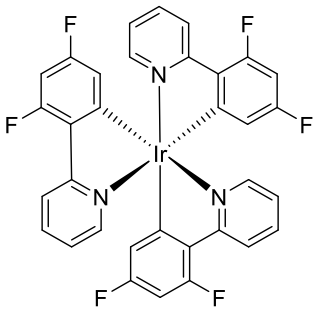
$Ru(bpy)_3(PF_6)_2$



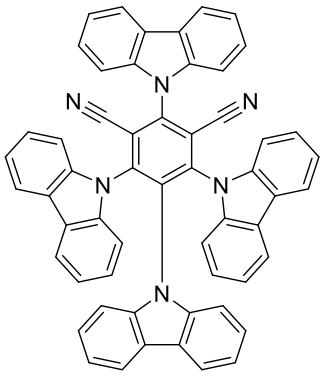
$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$



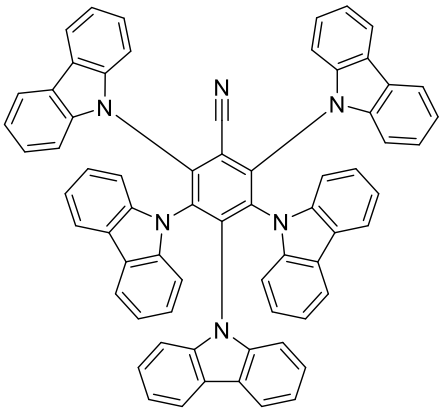
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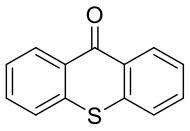
$Ir(dFppy)_3$



4CzIPN



5CzBN



Thioxanthen-9-one

Chapter 1 -Introduction

My research centers on the synthesis of *β*-sultams and aza-*β*-sultams. **Chapter 1.1** provides a concise overview of *β*-sultams, including their structural significance and relationship with *β*-lactams, while **Chapter 1.2** delves into specific strategies for their preparation. As aza-*β*-sultams represent a new class of aza analogues of *β*-sultams, **Chapter 1.3** introduces the broader context of aza-sulfur functionalities to establish their relevance. **Chapter 1.4** examines sulfinylamines, particularly silyl sulfinylamines, which serve as crucial linchpins in our synthetic approaches. Finally, given the foundational role of energy transfer catalysis in this work, **Chapter 1.5** explores key principles of photochemistry, with emphasis on energy transfer catalysis and its application in photocycloaddition reactions.

1.1 Importance of *β*-Lactams and *β*-Sultams

The *β*-lactam scaffold, a privileged four-membered cyclic framework, occupies a pivotal position across organic synthesis, the pharmaceutical chemistry, and clinical therapeutic applications (**Figure 1-1**). In particular, *β*-lactam antibiotics (such as penicillins, cephalosporins, and carbapenems) are historically significant for their bioactivity against bacterial infections (**Figure 1-1 B**). They work by acylating a key serine residue in bacterial transpeptidase enzymes, to halt the cell wall synthesis. The impact of this class of scaffolds is immense, as *β*-lactams remain the most widely used antibiotics today, accounting for roughly 65% of all injectable antibiotic prescriptions.[1]

Industrial-scale production processes for these compounds have been well-established to meet global demands. However, the escalating prevalence of bacterial resistance mechanisms, particularly through the enzymatic action of *β*-lactamases that hydrolyse the four-membered ring scaffold, rendering them inactive, poses significant therapeutic challenges. This

antimicrobial resistance crisis has inspired the development of novel *β*-lactamase inhibitors to preserve existing antibiotic efficiency and the exploration of alternative structural scaffolds retaining the privileged pharmacophore characteristics.

β-Lactam scaffolds continue to inspire synthetic innovation, particularly in design of heterocyclic bioisosteres. Among emerging candidates, *β*-sultam rings (sulfonamide analogues) represent a rational chemical extension of *β*-lactam chemistry, demonstrating comparable synthetic accessibility while potentially circumventing existing resistance mechanisms through structural diversification. In recent years, an increasing number of *β*-sultams have demonstrated promising bioactivities as enzyme inhibitors (**Figure 1-1 B)**.[2] These sulfur containing bioisosteres have displayed increased reactivity compared to their *β*-lactam counterparts, attributed to the increased ring strain relief when the sulfur centre gets attacked by nucleophiles (**Figure 1-1 A**).[3]

β-Sultams offer additional distinct advantages: (i) retaining the strained configuration of privileged *β*-lactam pharmacophores, and (ii) introducing sulfonic acid/sulfonamide moieties that enhance water solubility and target engagement. The inherent reactivity of *β*-sultams as sulfonyl electrophiles enables ring-opening reactions with nucleophiles, such as amines, generating taurine analogues (*β*-amino sulfonyl compounds, **Figure 1-1 C**).[4] Taurine analogues are an important class of therapeutics for oncology and neurological disorders, with recent examples including Lapatinib (HER2/EGFR tyrosine kinase inhibitor for breast cancer),[5] Litronesib (KSP inhibitor targeting mitotic machinery in solid tumors),[6] and Tauromustine (investigational taurine-conjugated alkylating agent for glioblastoma).[7]

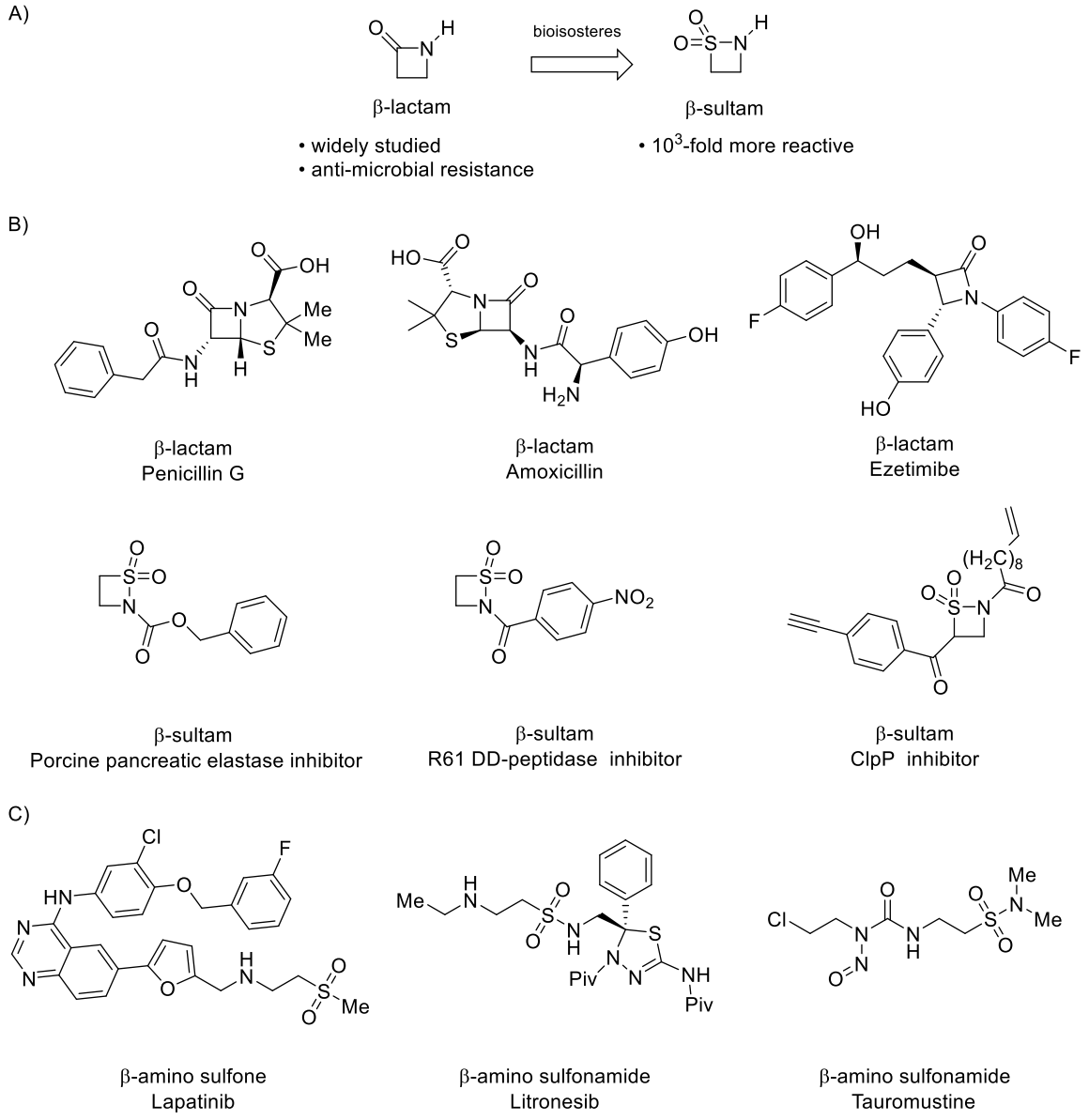


Figure 1-1(A) Relationship between *β*-lactam and *β*-sultam scaffold. (B) Examples of pharmaceutically relevant *β*-lactams and *β*-sultams. (C) Pharmaceutical taurine analogues.

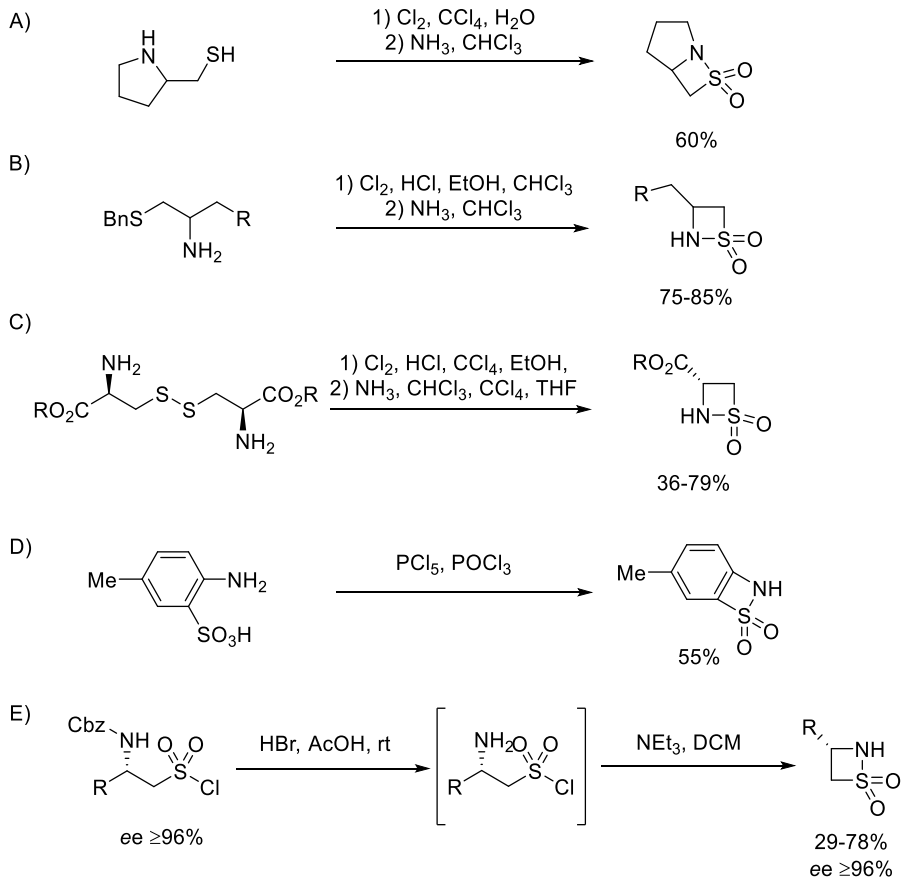
1.2 Synthesis of *β*-Sultams

The synthesis of *β*-sultams, four-membered cyclic sulfonamides, primarily relies on constructing the strained ring system while incorporating sulfonyl functional groups.[8] The most widely used approach is via cyclization reactions, where *β*-amino sulfonic acid derivatives undergo intramolecular nucleophilic displacement to form the *β*-sultam core (**Chapter 1.2.1**). Another strategy includes the intramolecular alkylation of *β*-amino sulfonic acid esters, providing an alternative route to the strained ring system (**Chapter 1.2.2**). Additionally, [2+2] cycloaddition reactions between alkyl sulfonyl chlorides and imines offer a direct approach to *β*-sultams (**Chapter 1.2.3**).

1.2.1 Synthesis of *β*-Sultams via Intramolecular Sulfonylation

The formation of acyclic sulfonamides predominantly relies on reactions between sulfonyl chlorides and amines, a strategy widely used due to its simplicity and efficiency. However, applying this methodology to synthesize *β*-sultams presents significant challenges due to the inherent incompatibility of sulfonyl chloride and amine functionalities in the same molecule. Despite these limitations, there are still some examples following this strategy. In 1982, the Otto group developed a method to generate *β*-sultams from *β*-aminothiols (**Scheme 1-1 A**).[9] The reaction was conducted using chlorine to give the *β*-aminosulfonyl chlorides, followed by cyclization with the addition of ammonia. *β*-Aminosulfides and disulfides could also be used to afford the corresponding *β*-sultams, using similar conditions (**Scheme 1-1 B-C**).[10] It is noteworthy that the use of enantioenriched *β*-aminodisulfides in these reactions leads to formation of the corresponding *β*-sultams in high optical purity.[11] In 1998, the Wu group found that S(VI)-reagents could be utilised directly; *β*-aminosulfonic acids can undergo chlorination and amination to form the corresponding *β*-sultams (**Scheme 1-1 D**).[12] This has been expanded to chiral *β*-amino sulfonyl chlorides,[13] which affords the corresponding

enantioenriched *β*-sultams from benzyl carbamate protected acyclic *β*-amino sulfonyl chlorides in a similar manner (**Scheme 1-1 E**).

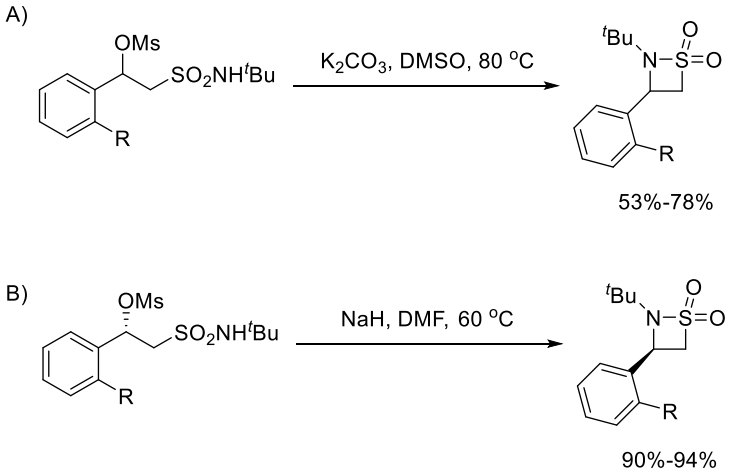


Scheme 1-1 Synthesis of *β*-sultams via nucleophilic cyclization.

1.2.2 Synthesis of *β*-Sultams via Intramolecular Alkylation

The intramolecular cyclisation of acyclic sulfonamides with a *β*-leaving group has been explored to a lesser extent, with sulfonates predominantly used as the leaving group. However, this method is not of prevalence since the *β*-functionalised sulfonamides usually take several steps to make, and the substituted group on the nitrogen of sulfonamides also needs to be electron-donating to maintain the nucleophilicity of nitrogen. Meanwhile, because of the weak

nucleophilicity of sulfonamides, the cyclization needed to be conducted at high temperatures. In 1984, Thompson developed an intramolecular *N*-alkylation to form the corresponding *β*-sultam with potassium carbonate in DMSO, using methanesulfonate ester as the leaving group (**Scheme 1-2 A**).[14] In 1999, the Buttero group applied this intramolecular *N*-alkylation to enantioenriched sulfonamides to generate enantiomerically pure *β*-sultams in a stereospecific manner, under the treatment of sodium hydride in dimethylformamide (**Scheme 1-2 B**).[15]

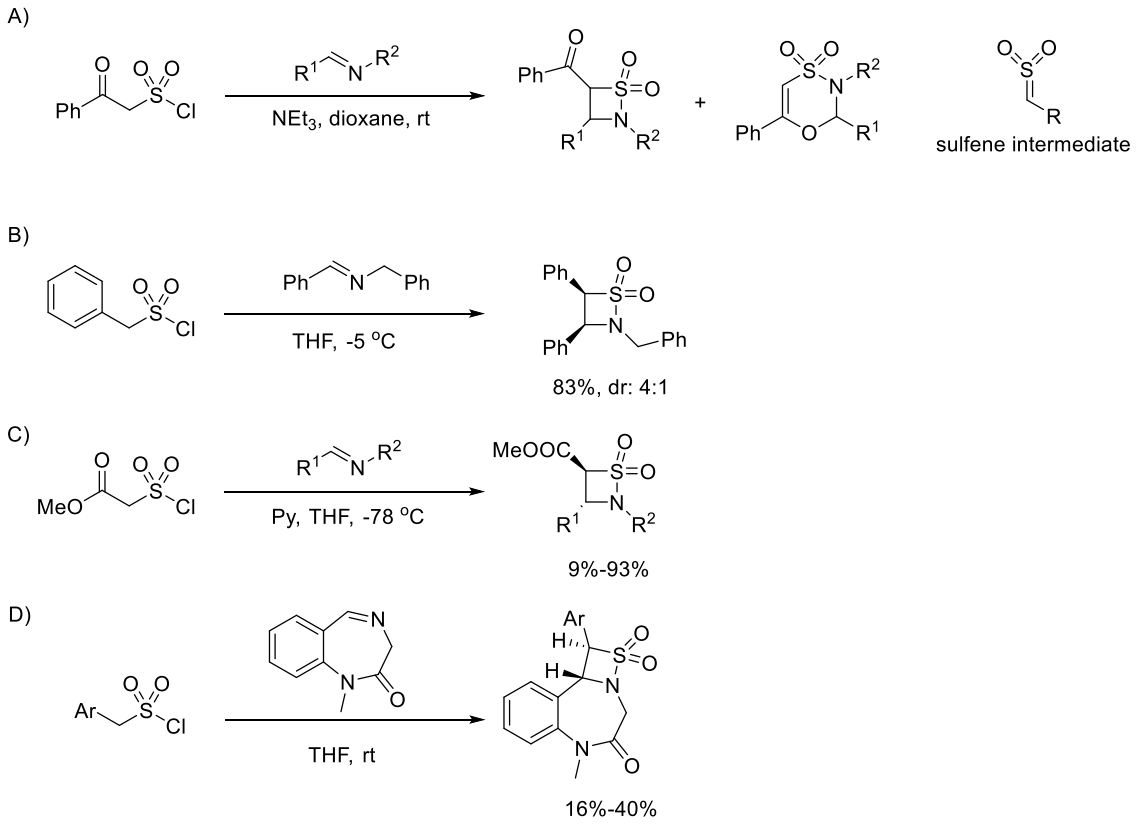


Scheme 1-2 Synthesis of *β*-sultams via intramolecular *N*-alkylation.

1.2.3 Synthesis of *β*-Sultams via [2+2] Cycloaddition

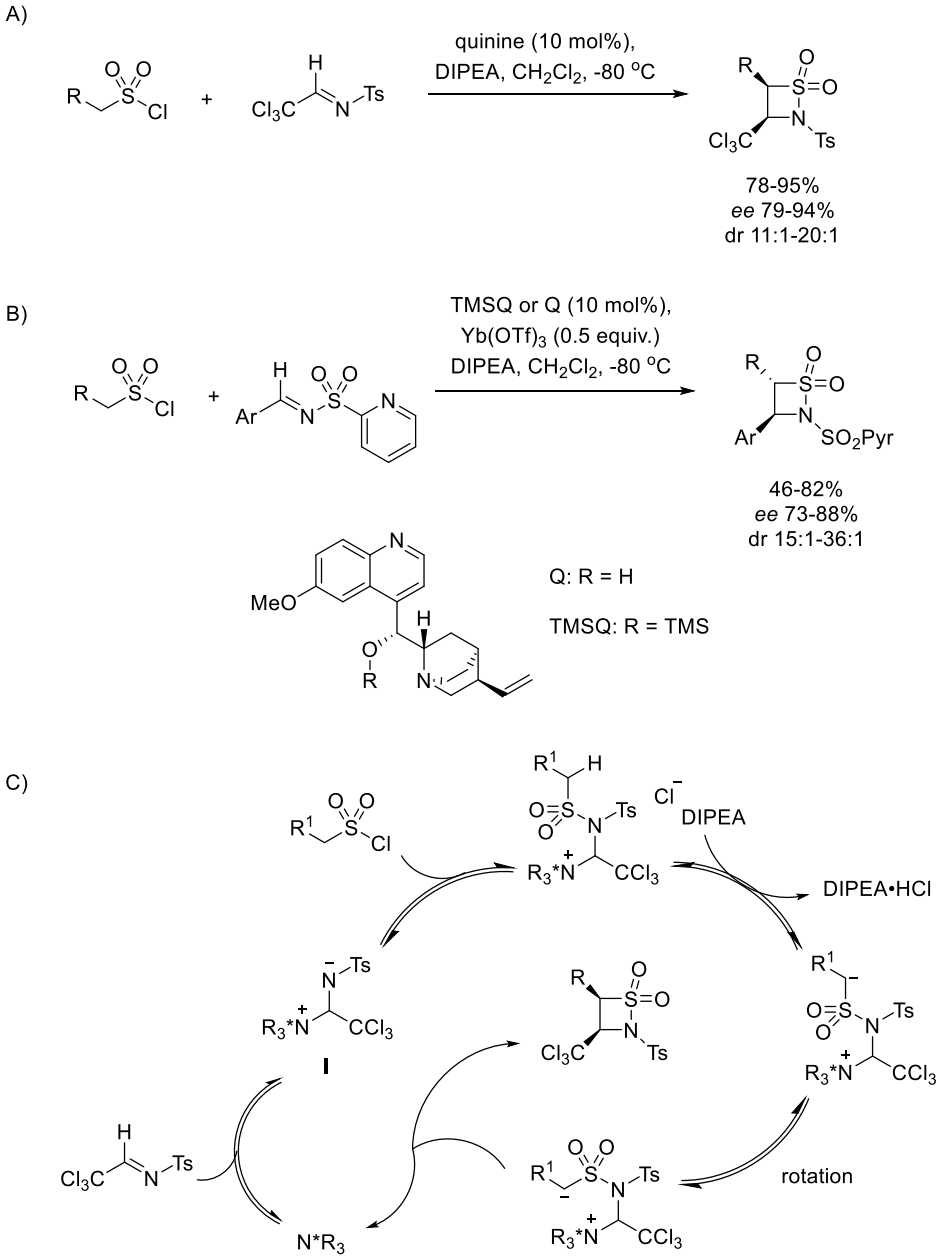
[2+2] Cycloaddition reactions are also a well-known method to build *β*-sultam scaffolds and can be categorised into two distinct classes. The most common route is the reaction between alkyl sulfonyl chlorides (which generate sulfenes *in situ*) and Schiff bases, known as the sulfur-Staudinger reaction. The first report of such a reaction was from Tsuge and co-workers, using *β*-ketosulfonyl chlorides with aryl imines to form *β*-sultams in the presence of triethylamine (**Scheme 1-3 A**).[16] However, both [2+2] and [4+2] reaction products are afforded in the reaction, resulting in the desired *β*-sultam in poor yield. It should be noted that benzylsulfonyl chlorides can react with benzyl substituted Schiff bases to form a mixture of *cis* and *trans β*-

sultam isomers (**Scheme 1-3 B**).[17] Reaction between *β*-ester containing sulfonyl chlorides with imines also affords the corresponding *β*-sultams with a preference for the *trans* isomers (**Scheme 1-3 C**).[18] The authors noted that the reactions usually performed better for the imines unable to be converted to enamines, showing less sensitivity to temperature and the order of addition of imines and sulfonyl chlorides. In 2014, the Xu group found cyclic imines can also react with alkyl sulfonyl chlorides to afford *β*-sultams (**Scheme 1-3 D**).[19] This [2+2] cycloaddition protocol was limited to α-aryl or α electron-withdrawing group substituted sulfonyl chlorides.



Scheme 1-3 Synthesis *β*-sultams via [2+2] cycloaddition

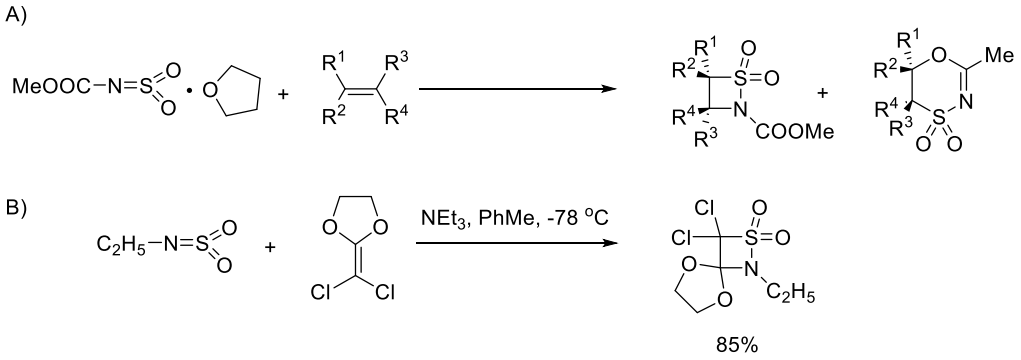
The asymmetric synthesis of substituted *β*-sultams has been highlighted in **Scheme 1-1** and **Scheme 1-2**, from enantioenriched acyclic alcohol and amino derivatives. The first catalytic asymmetric approach to enantioenriched *β*-sultams was reported by the Peters group in 2007, wherein activated *N*-tosyl imines react with alkyl sulfonyl chlorides to rapidly access enantioenriched *β*-sultams using quinine as an organocatalyst (**Scheme 1-4 A**).[20] Later, the same group extended the methodology to 2-pyridylsulfonyl imines derived from non-activated aromatic aldehydes, catalyzed by a combination of quinine or TMS-quinine and $Yb(OTf)_3$ (**Scheme 1-4 B**).[4] The mechanism was first hypothesized to proceed through a sulfene intermediate. However, deuteration experiments, whereby deuterated methanol was added to sulfonyl chloride solution under the reaction conditions, showed no incorporation of deuterium at the α-position, demonstrating sulfene intermediates are not generated in significant quantities. An alternative mechanism involving zwitterionic aminal intermediate **I** has instead been proposed. This intermediate with negatively charged nitrogen can subsequently react with sulfonyl chlorides prior to the generation of sulfenes, which then undergo deprotonation and an intramolecular substitution reaction to afford *β*-sultams and regenerate the cinchona alkaloid catalyst (**Scheme 1-4 C**).



Scheme 1-4 Synthesis of enantioenriched *β*-sultams via [2+2] cycloaddition and proposed mechanism.

Due to the extreme instability of *N*-sulfonylamines, [2+2] cycloaddition between alkenes and *N*-sulfonylamines have been rarely reported. In 1972, Burgess and Williams reported the first example using sulfonylamines (formed *in situ* from sulfamoyl chlorides) in THF as substrates to react with alkenes to afford the corresponding *β*-sultam, although the [4+2] six-membered ring side-product usually predominated (**Scheme 1-5 A**).[21] In the same year, Burgess and

Atkins demonstrated that when ethyl-*N*-sulfonylamine was treated with 2-(dichloromethylidene)-1,3-dioxolane at -78 °C, the corresponding sultam can be afforded in 85% yield (**Scheme 1-5 B**).[22]



Scheme 1-5 Synthesis of *β*-sultams via [2+2] cycloaddition between sulfonylamines formed *in situ* and alkenes.

1.3 Aza-Sulfur Functionalities

1.3.1 Importance of Aza-Sulfur Functionalities

Sulfur(VI)-containing motifs play a central role in modern pharmaceutical and agrochemical research due to their structural versatility and functional adaptability. Among these, sulfonamides and sulfones represent the most extensively utilized scaffolds, with their prevalence evidenced by the inclusion in over 150 FDA-approved therapeutic agents.[23] In recent years, more attention has shifted towards aza-analogues of these traditional sulfur(VI) functionalities, including sulfonimidamides, sulfoximines, sulfondiimines, and sulfondiimidamides, as innovative tools for drug discovery. This strategic isosteric replacement of oxygen with nitrogen has multiple advantages: (i) introduction of nitrogen-bond substituents expands molecular diversity; (ii) tuneable physicochemical properties via modulation of nitrogen electronic and substituent effects; and (iii) potential generation of stereogenic sulfur centres enabling precise optimization of target engagement.[24] While no marketed pharmaceuticals currently incorporate imidic S=N bonds, the commercial insecticide Sulfoxaflor (**Figure 1-2**), a sulfoximine-based compound, exemplifies the practical utility of such modifications in bioactive enhancement.

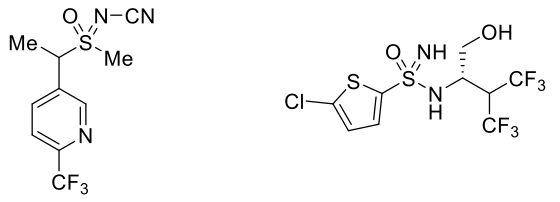
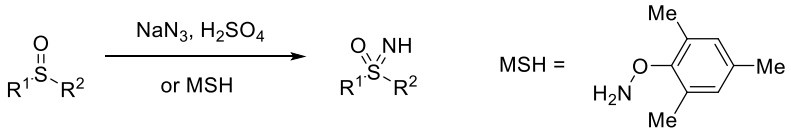


Figure 1-2 Pharmaceutical aza-sulfur functionalities

1.3.2 Imination to Synthesize Aza-Sulfur (VI) Functionalities

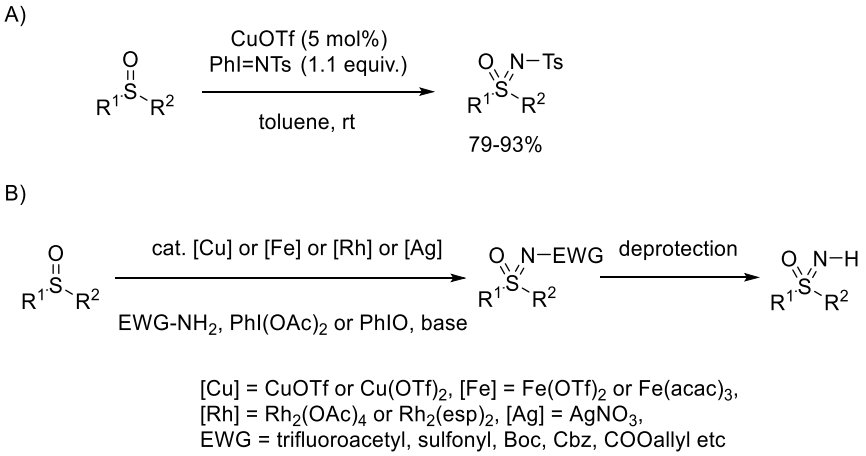
The imination of sulfur(IV) species with nitrene or nitrene precursors is a predominant strategy for synthesizing various aza-sulfur(VI) derivatives. In recent years, researchers have developed both transition metal-mediated or metal-free imination methodologies to transfer sulfur(IV) to sulfur(VI) compounds. Conventional protocols typically employ azides as the nitrene source, where active hydrazoic acid intermediates can be generated in acidic conditions.[25] *O*-Mesitylenesulfonylhydroxylamine (MSH), although an highly energetic and potentially hazardous reagent, has emerged as an alternative reagent for imination processes, demonstrating particular efficacy in constructing aza-sulfur structures (**Scheme 1-6**).[26]



Scheme 1-6 Imination with azide or MSH as nitrene sources.

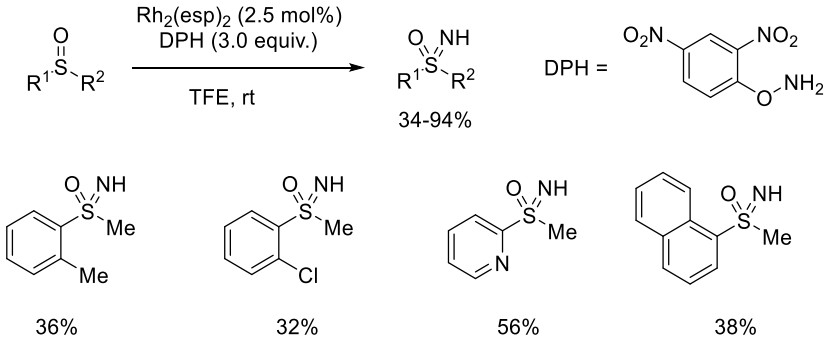
In response to the inherent safety concerns associated with azides and MSH due to their toxicity and explosive nature, iminoiodinanes (PhI=NR), and its precursors, have emerged as safer electrophilic imination reagents for sulfur(VI) imination. These reagents are stable to isolation or can be generated *in situ*, readily used under ambient conditions, and exhibit compatibility with both catalytic and non-catalytic systems.

The catalytic potential of transition metals in this domain was first disclosed in 1998, through copper-catalyzed sulfoximine synthesis using iminoiodinanes (**Scheme 1-7 A**).[27] Subsequent methodologies have been established by employing Cu(II),[28] Rh(II),[29] Fe(II),[30] Ag(I),[31] and Fe(III)[32] catalysts to generate different transient metal-nitrene intermediates from iminoiodinanes (**Scheme 1-7 B**).[33] Notably, systematic investigations by the Bolm research group have driven significant progress in this field, particularly in mechanistic elucidation and catalyst scope expansion.



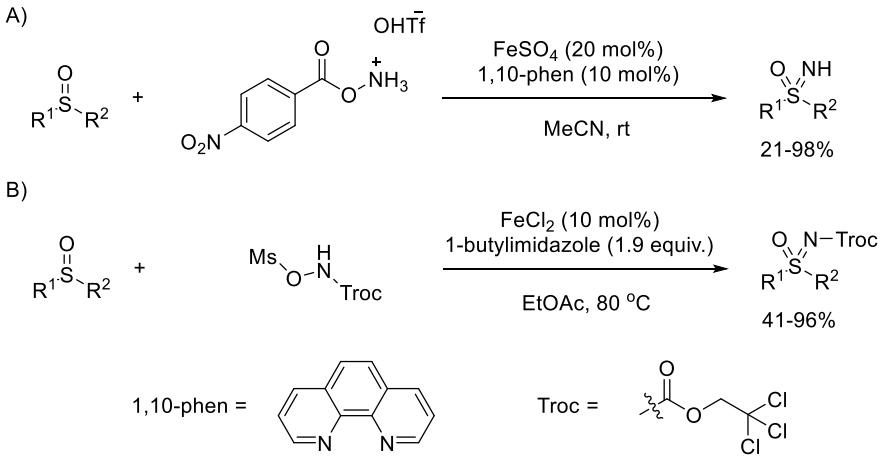
Scheme 1-7 Transition metal catalyzed iminations of sulfoxides.

Compared to substituted nitrenes engaged imination reactions, direct N-H imination is of great significance due to broad substrate scope and the potential for further derivatization of the imidic nitrogen. A breakthrough in direct N–H imination was achieved in 2014, through Ge's pioneering catalytic protocol. This methodology employed $Rh_2(esp)_2$ as a catalyst in conjunction with *O*-(2,4-dinitrophenyl)hydroxylamine (DPH) to generate transient rhodium-nitrene species, facilitating subsequent nucleophilic attack on metal-coordinated sulfoxide substrates. While demonstrating remarkable functional group tolerance, the system exhibited two principal constraints: (1) significantly diminished reaction efficiency (≤40% yield) with sterically hindered sulfoxides, and (2) requirement for excess DPH loading (3.0 equiv.) to maintain turnover of the catalytic cycle (**Scheme 1-8**).[34]



Scheme 1-8 Rhodium-catalysed imination for synthesis of N-H sulfoximines.

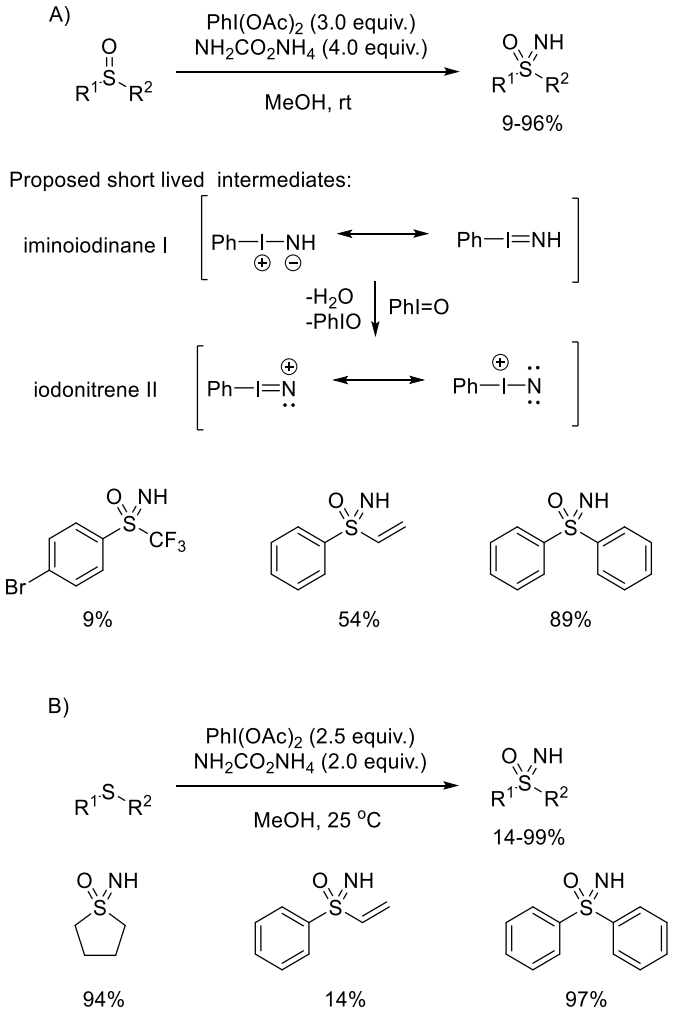
In 2018, the Bolm group introduced another transition metal-catalyzed imination to synthesize N-H sulfoximines (**Scheme 1-9 A**).[35] Their approach utilized a Fe(II) catalyst in conjunction with an *O*-acylhydroxylammonium salt as the nitrene source, enabling the efficient formation of N-H sulfoximines in high yields. However, a notable drawback of this method was the requirement for an excess of *O*-acylhydroxylammonium salt, which itself necessitates a two-step synthesis. Inspired by the hydroxylamine triflic acid nitrene precursor, the Lebel group developed a similar Fe(II) chloride system using 2,2,2-trichloroethyl-*N*-mesyloxycarbamate (Troc-NHOMs) to realize the *N*-Troc imination of sulfoxides (**Scheme 1-9 B**).[36]



Scheme 1-9 Iron catalyzed imination to synthesize aza-sulfur (VI) structures.

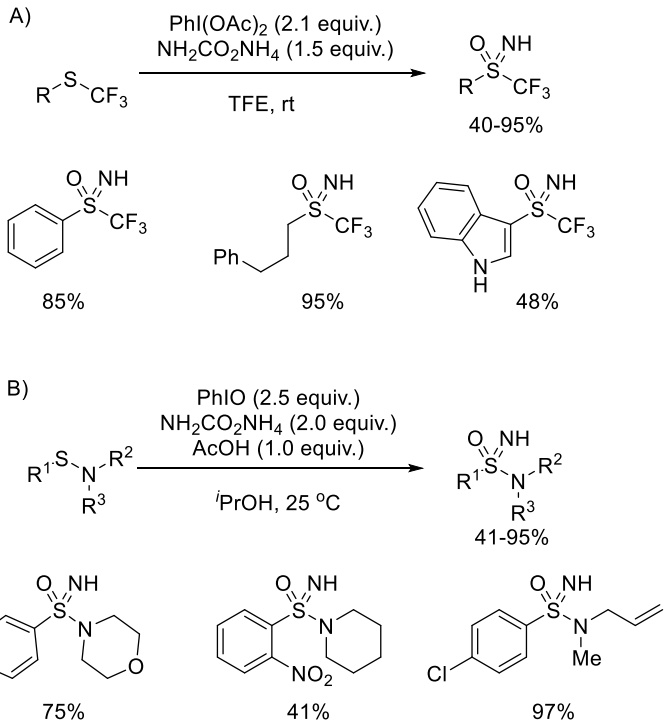
The discussed methods require the use of transition metal catalysts, which potentially increases the cost and sustainability impact of the processes. The Bull and Luisi groups pioneered a transition metal-free approach for NH-sulfoximine synthesis in 2016, utilizing a hypervalent I(III) reagent ($PhI(OAc)_2$) in conjunction with ammonium carbamate. Their catalytic system demonstrated broad substrate tolerance, successfully converting various substituted sulfoxides into target sulfoximines in moderate to good yields (54-96%) (**Scheme 1-10 A**).[37] The reaction has also been demonstrated on larger scales (10 mmol), and on enantioenriched sulfoxides with the reaction occurring in a stereospecific manner with retention of the configuration of the

sulfur centre. Notably, spectroscopic evidence via flow HRMS revealed two postulated intermediates - iminoiodinane **I** and iodonitrene **II** - during the reaction process. While exhibiting remarkable functional group compatibility, the methodology showed decreased efficiency (<30% yield) with electron-deficient arene substrates. In 2017, the Luisi and Bull groups extended this protocol to employ sulfides as substrates, using slightly modified conditions, providing sulfoximines in generally high yields (**Scheme 1-10 B**).[38] Vinyl sulfides used under these conditions displayed low yield (14%), suggesting inherent electronic constraints in this imination protocol. When ^{15}N-labelled ammonium carbamate was used, ^{15}N-labelled sulfoximines were generated, proving the nitrogen transfer from ammonium carbamate to sulfoximines.



Scheme 1-10 Metal-free imination to synthesize N-H sulfoximines.

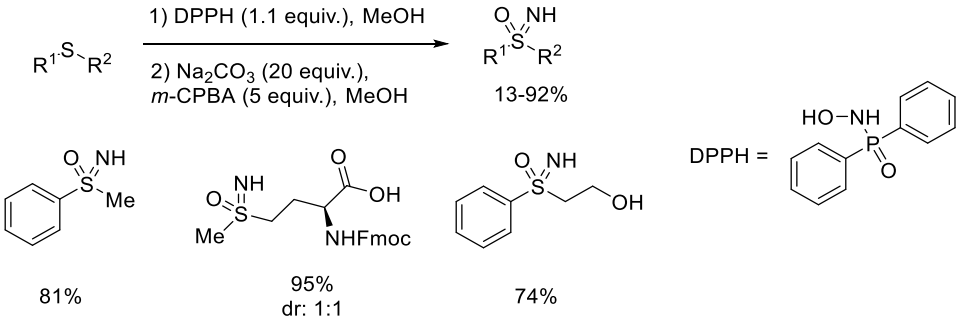
In 2018, the Reboul and Magnier group found that by modifying the solvent from methanol to trifluoroethanol using Bull's metal-free imination conditions, perfluorinated N-H sulfoximines could be obtained in up to 95% yield, while there is no product detected in the methanol system (**Scheme 1-11 A**).[39] In 2019, the Bull and Luisi groups extended their metal-free imination to sulfenamide substrates, employing iodosobenzene (PhIO) in combination with AcOH and ammonium carbamate, to successfully afford the corresponding sulfoimidamides in moderate to good yields (41 to 94%, **Scheme 1-11 B**).[40]



Scheme 1-11 Metal-free imination to other aza-sulfur(VI) functionalities.

Due to the mild reaction conditions and functional group compatibility, the discussed combination of iodine(III) reagents with ammonium carbamate is commonly employed, with application in unprecedented glycosyl[41] and bicyclo[1.1.1]pentyl (BCP)[42] sulfoximines from the respective sulfides. In 2024, the Perrin group found an alternative reagent,

diphenylphosphinylhydroxylamine (DPPH), could be employed to access sulfilimines from sulfides, followed by oxidation with *m*-CPBA to give N-H sulfoximines in 13-92% yield (**Scheme 1-12**).[43]



Scheme 1-12 Metal-free imination using DPPH as nitrene precursor.

1.4 Sulfinylamines

1.4.1 Introduction of Sulfinylamines

Sulfinylamines are a distinctive class of sulfur-containing compounds that have been recognized in chemistry for over a century. Their history dates back to 1878 when Böttinger first observed their formation,[44] and their structure was later confirmed by Michaelis and Herz in 1890.[45] These compounds, considered mono aza analogues of sulfur dioxide, exhibit unique electrophilic properties due to the presence of an electrophilic sulfur(IV) atom. This electrophilicity, while enabling diverse chemical transformations, also makes sulfinylamines highly sensitive to moisture, which has historically limited their practical applications. Chemists have explored different strategies to enhance the stability and reactivity of sulfinylamines, with the nature of the nitrogen substituent playing a crucial role in determining their electrophilicity (**Figure 1-3**). For example, sulfinylamines bearing electron-withdrawing groups such as sulfonyl or carbamate functionalities exhibit dramatically decreased stability, while others, derived from anilines, tend to degrade slowly and can be handled under air for short periods, but still require to be stored under inert atmosphere at low temperatures.[46] In 2017, the Willis group rediscovered a moisture-stable sulfinylamine, *N*-sulfinyltritylamine (TrNSO), which can be stored for at least a year under air in the freezer (-20 °C) without decomposition.[47] This enhanced stability is attributed to the steric hindrance of the trityl group. They also found trityl substituted sulfonimidamides synthesized form TrNSO can be deprotected with methanesulfonic acid to access unprotected sulfonimidamides.

Sulfinylamines predominantly adopt the (*Z*)-configuration, where the oxygen atom is positioned on the same side as the nitrogen substituent.[48] This structural preference, despite potential steric hindrance, has been confirmed by the X-ray crystal structure of TrNSO.[49] Computational investigations, specifically Natural Bond Orbital (NBO) analysis, conducted by the Willis group on Ph–O–N=S=O revealed that the (*Z*)-isomer is stabilized by the interaction

between the nitrogen lone pair and the S–O σ* orbital, as well as the sulfur lone pair's donation into the N–O σ* orbital (when present).[50] These electronic effects contribute significantly to the stability of the (*Z*)-configuration over the (*E*)-form.

Despite their long-standing presence in organic chemistry, sulfinylamines have seen only sporadic use in synthesis. However, recent advancements have renewed interest in their potential in organic synthesis, particularly in the development of medicinally relevant aza-sulfur compounds and heterocyclic scaffolds.

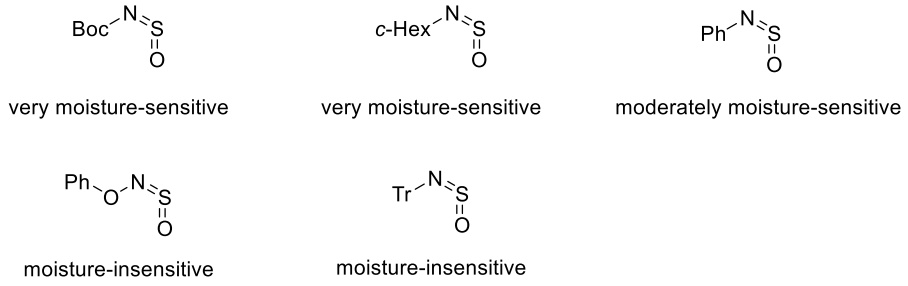
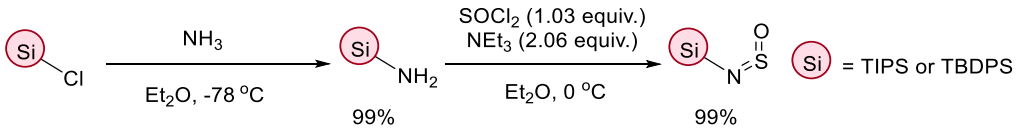


Figure 1-3 Stability of different substituted sulfinylamines.

1.4.2 Reactions with Silyl-Sulfinylamines

As mentioned above, TrNSO exhibits a significant improvement in stability towards moisture, owing to its bulky and electron-donating N-trityl substituent. However, it is noteworthy that the removal of trityl group requires strong acid (methanesulfonic acid), which can result in the decomposition of acid-sensitive functional groups in aza-sulfur structures. To tackle this problem, *N*-silyl sulfinylamines were considered due to the excellent efficiency in fluoride mediated silyl deprotection. A previous DPhil student in the Willis group, Mingyan Ding, developed a series of sulfinylamines with electron-donating silyl groups, including TIPS-NSO and TBDPS-NSO (**Scheme 1-13**). Reaction of a chlorosilane and ammonia gas in Et_2O at -78 °C provides the respective silylamines, which when combined with triethylamine and

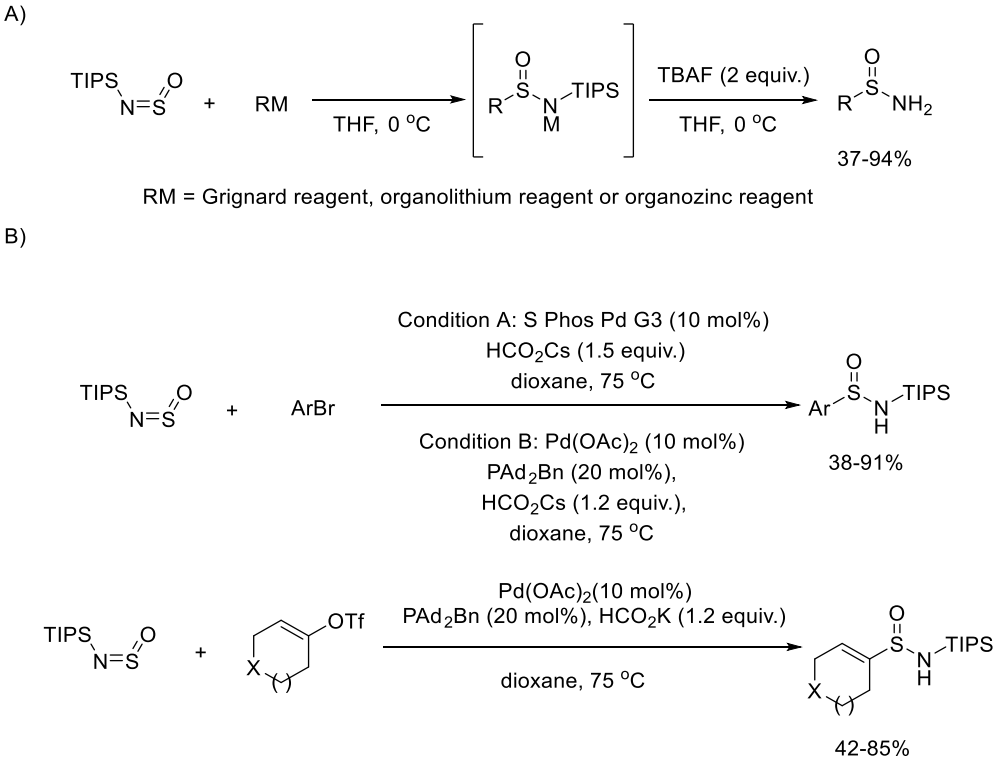
thionyl chloride provides the desired silyl sulfinylamines. Both steps can be conducted on gram scale with excellent yields and no chromatography required.[51]



Scheme 1-13 Synthesis of silyl-sulfinylamines.

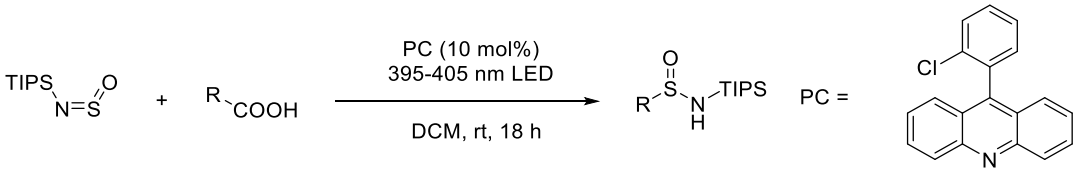
In a similar manner to TrNSO, it was found TIPS-NSO can react with Grignard, organolithium or organozinc reagents effectively to generate different silyl sulfinamides. Significantly, these intermediates could be efficiently transformed to primary sulfinamides in one-pot, through treatment with tetrabutyl ammonium fluoride (TBAF) (**Scheme 1-14 A**). The primary sulfinamides generated can be directly converted to NH-sulfonimidamides, using $PhI(OAc)_2$ in the presence of amines.

It was later discovered by Mingkai Wei and Dr. Daniel Moseley within the Willis group, that TIPS-NSO can react with aryl bromides to form aryl TIPS substituted sulfinamides, enabled by palladium catalysis (**Scheme 1-14 B**).[52] The use of electron-rich aryl halides requires switching to an alternative catalyst, and reducing the equivalents of HCO_2Cs. This method was extended to cyclic alkenyl triflates, employing HCO_2K as the reductant, to give corresponding TIPS substituted alkenyl sulfinamides in moderate to good yields. The versatility of TIPS-sulfinamides was demonstrated by derivatisation to a variety of S(IV) and S(VI)-functionalities.



Scheme 1-14 Reactions with TIPSNSO with organometallic reagents and aryl halides.

Owing to the electron-deficient property of the sulfur centre in sulfinylamines, nucleophilic radical addition to sulfinylamines to form sulfinamides has inspired the interest of researchers. Radical additions to sulfinylamines have been developed using aryl diazonium salts, 1,4-dihydropyridines, aryl trifluoroborate salts and simple hydrocarbons as radical precursors. In 2023, the Willis[53] and Larionov[54] groups independently developed methodologies to synthesize sulfinamides via acridine-catalyzed visible-light-mediated, decarboxylative radical addition to various sulfinylamines. In both cases, TIPS-NSO was used as a substrate to give the corresponding alkyl sulfinamide (**Scheme 1-15**).



Scheme 1-15 Nucleophilic radical addition to silyl sulfinylamines.

1.5 Principles of Photochemistry

The initiation of photochemical reactions involves light-induced electronic excitation governed by two fundamental principles, the Grotthuss-Draper principle and the Stark-Einstein principle. The Grotthuss-Draper principle establishes that molecular light absorption is the essential first step in photochemical activation. While the Stark-Einstein principle dictates that individual photon absorption events activate only one single molecule for photochemical transformation, while the efficiency of this process is defined as the quantum yield (φ).

When ground-state molecules (S_0) absorb radiation, electrons transit to higher-energy orbitals while maintaining spin multiplicity according to angular momentum conservation laws. Excitation typically involves electron promotion from the highest occupied molecular orbitals (HOMO) to lowest unoccupied orbitals (LUMO), creating various singlet excited states (S_1, S_2, etc.). However, Kasha's rule observes that higher singlet states (S_2, S_3, etc.) rapidly lose energy through internal conversion into the lowest singlet state (S_1).[55]

The S_1 state exhibits multiple decay pathways: radiative return to S_0 (fluorescence), or non-radiative transitions. The S_1 state can undergo spin-altering intersystem crossing to produce triplet states (T_1). The T_1 to S_0 transition (phosphorescence) becomes partially allowed through spin-orbit coupling enhancements, either through electronic configuration changes (El-Sayed's rule) or heavy atom proximity effects, though remains relatively slow compared to fluorescence.[56] Non-radiative decay pathways may involve intramolecular relaxation or intermolecular energy transfer. Collisional deactivation of excited species through intermolecular interactions represents quenching, while intentional energy transfer to acceptor molecules represents sensitization.[57] Such triplet-state energy transfer mechanisms have gained significant utility in synthetic chemistry in the form of energy transfer catalysis, enabling novel reaction pathways through controlled triplet-state manipulation.[58]

These photophysical processes are commonly visualized through Jablonski diagrams, which show electronic state transitions and energy transfer pathways (**Figure 1-4**). The interplay between radiative/non-radiative decay and intersystem crossing dictates the relative populations of excited states available for photochemical transformations. This energy exchange principle has become a cornerstone in synthetic methodologies through triplet-triplet energy transfer processes.

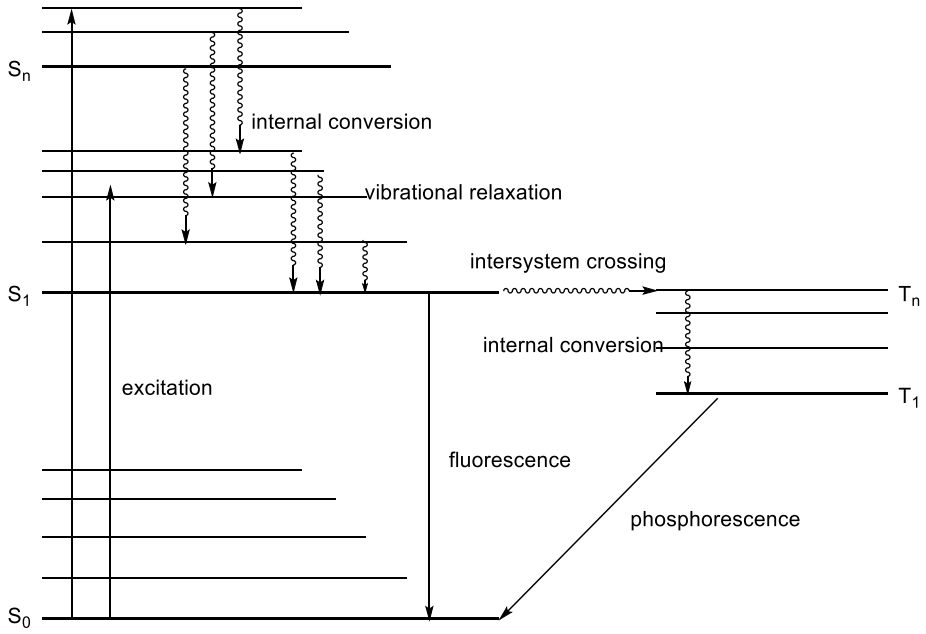


Figure 1-4 The Jablonski diagram showing fluorescence and phosphorescence.

1.5.1 Energy Transfer Catalysis

Excited triplet states unlock reaction pathways that are comparatively challenging in ground-state. Their distinct reactivity arises from their biradical electronic configuration and extended lifetimes in solution, a consequence of spin-forbidden relaxation to the ground state, which facilitates intermolecular interactions. Generation of the T_1 state via photoexcitation and intersystem crossing (ISC) faces inherent limitations for many organic substrates due to weak

light absorption, inefficient ISC rates, and competing radiative decay pathways, collectively resulting in low triplet quantum yields and decreased reaction efficiency. In addition to these challenges, the photon absorption at the UV wavelength of organic molecules and the operational hazards of UV irradiation make this direct excitation strategy impractical.[57]

In contrast, triplet-triplet energy transfer catalysis offers a more reliable approach. This methodology employs photosensitizers designed and optimized for visible-light absorption and high triplet-state quantum yields. Enhanced triplet generation is achieved through two strategies: (1) heavy-atom-induced spin-orbit coupling in polypyridyl metal complexes or (2) electronic configuration engineering in aromatic carbonyl systems. These photosensitizers avoid the conventional excitation-relaxation-ISC cascade by directly transferring energy to substrates via intermolecular triplet-triplet energy transfer, thereby generating the T_1 state without requiring direct photon absorption (**Figure 1-5**).[58]

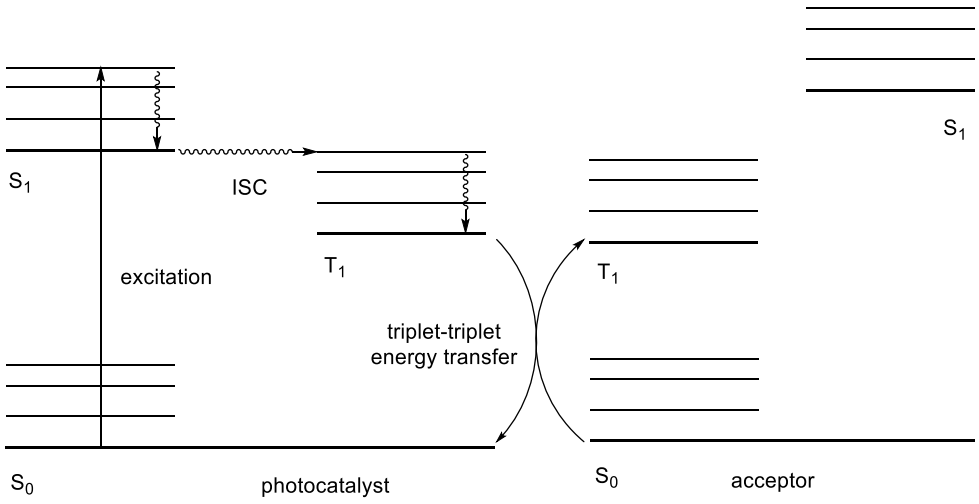


Figure 1-5 Jablonski diagram for triplet-triplet energy transfer.

The operative mechanism for triplet-triplet energy transfer typically follows a Dexter electron-exchange model. This process involves simultaneous bidirectional electron transfer between the donor's HSOMO and the acceptor's LUMO, coupled with electron migration from the

acceptor's HOMO to the donor's LSOMO (**Figure 1-6**). This exchange mechanism exhibits strict dependence on orbital overlap between donor and acceptor species, with efficiency decaying exponentially with increasing intermolecular distance. Consequently, the formation of solvent-caged encounter complexes is significant to triplet-triplet energy transfer catalysis and the reactions operate under diffusion-controlled kinetics.[57]

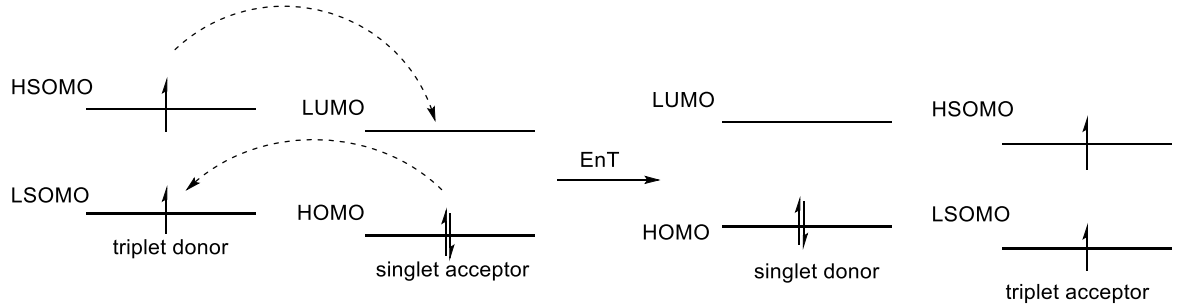
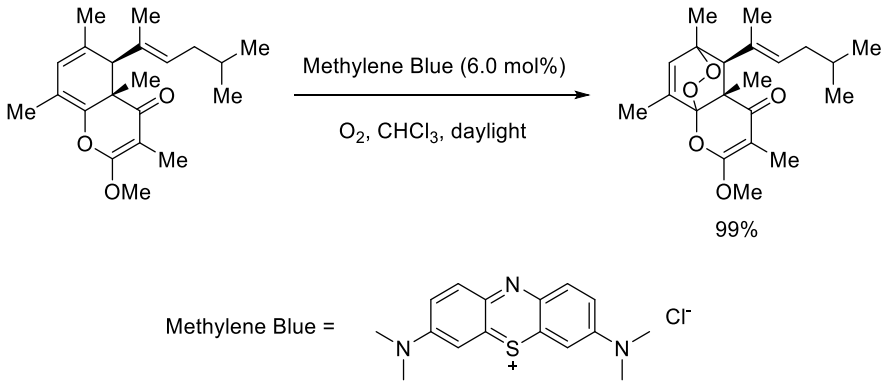


Figure 1-6 Dexter energy transfer process.

1.5.2 Energy Transfer in Photocycloaddition Reactions

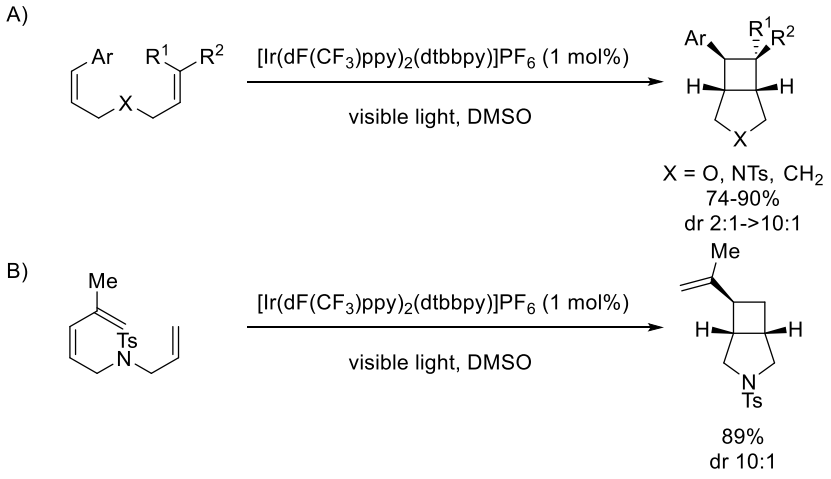
Photocycloaddition reactions provide versatile approaches for establishing covalent linkages between carbon atoms and heteroatoms to form diverse, cyclic structures. These transformations have been extensively utilized in assembling complicated frameworks with bioactivities. Conventional protocols employing UV excitation to initiate these processes frequently encounter limitations due to safety implications and competing, unmanageable side processes, thereby restricting their general application in organic synthesis. These limitations have inspired the development of advanced catalytic systems where energy transfer (EnT) processes are utilised, activated by visible light, which can circumvent previous restrictions while reserving reactivity under ambient conditions. Such approaches address the inherent drawbacks of classical methods, thereby unlocking pathways for controlled bond formation in synthetically challenging frameworks.

The initial developments of energy transfer catalysis for organic synthesis largely focused on photoinduced singlet oxygen generation and its application in diverse pericyclic transformations.[59] A notable work is by the Moses' research group, where the authors utilized methylene blue, a common visible-light-absorbing organic dye exhibiting an energy transfer capacity (E_T = 32.0 kcalmol^{-1}), to facilitate a singlet oxygen enabled [4+2] photocycloaddition. This strategy played a critical role in structural investigations of tridachiahydropyrones (**Scheme 1-16**).[60]



Scheme 1-16 Energy transfer catalysis with singlet oxygen in [4+2] photocycloaddition.

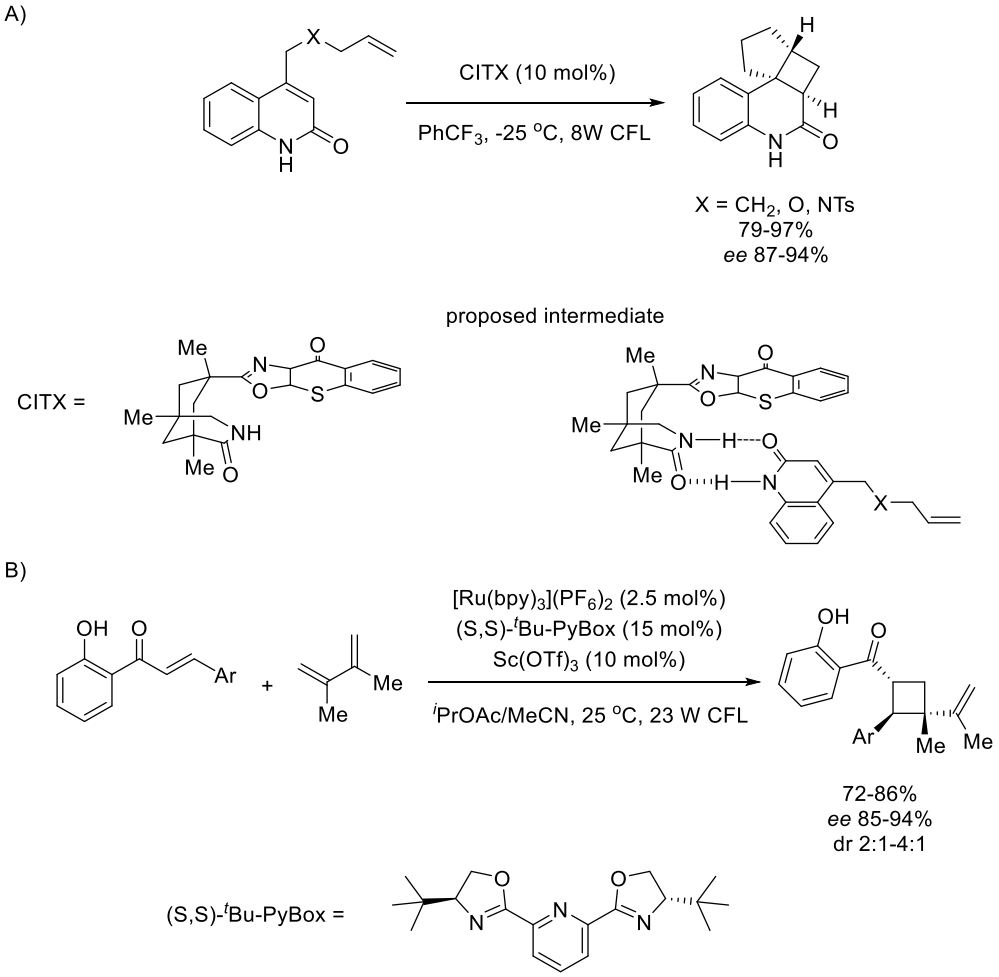
To overcome the low triplet state of Ru(II) photosensitizer[61], which resulted in limited application in energy transfer catalysis, a pivotal breakthrough in energy transfer catalysis was reported by Yoon and colleagues, who developed intramolecular [2+2] photocycloaddition reactions of alkene-linked styrene substrates. Their approach utilized an Ir(III) complex photosensitizer, $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$, characterized by a high triplet-state energy (E_T = 61.8 kcal/mol), to sensitize styrene derivatives ($E_T \approx$ 55-60 kcal/mol) into their triplet states. This energy transfer enabled efficient intramolecular cyclization, yielding fused cyclobutane scaffolds with high efficiency (**Scheme 1-17 A**).[62] Later advancements by the group extended this strategy to 1,3-diene systems (**Scheme 1-17 B**).[63]



Scheme 1-17 Energy transfer catalysis with styrene or dienes in intramolecular [2+2] photocycloaddition reactions.

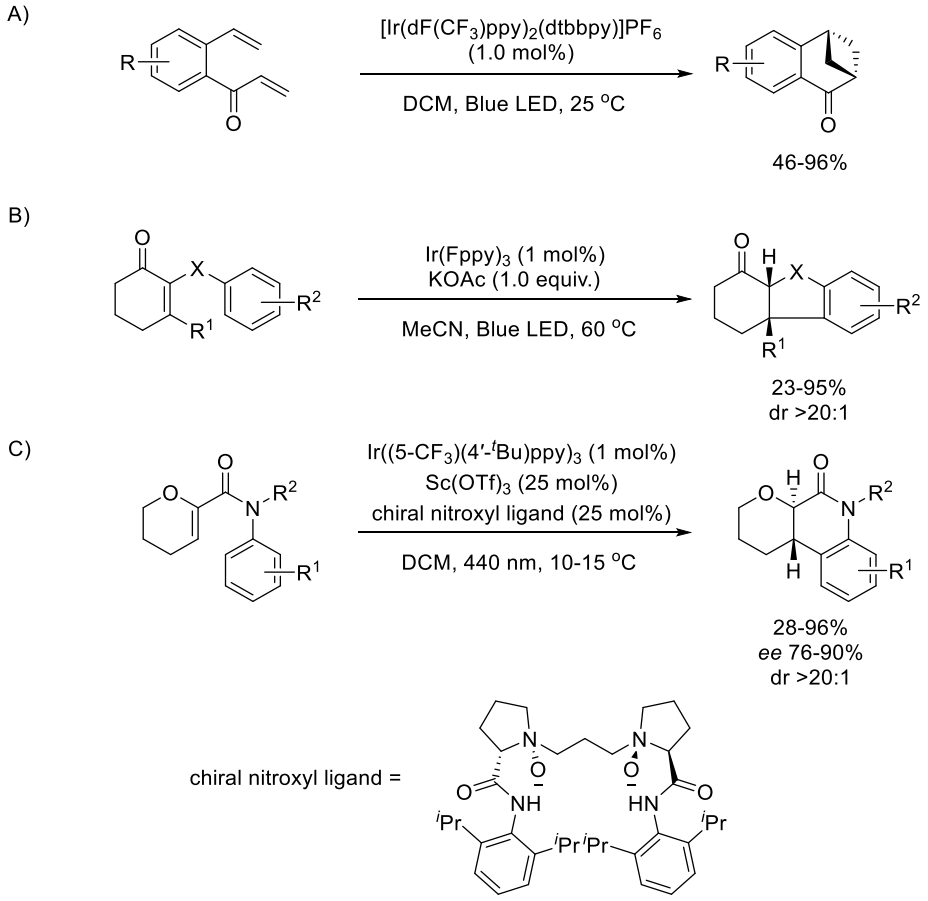
In 2014, Bach and colleagues achieved the first enantioselective [2+2] photocycloaddition via energy transfer (EnT) catalysis. The key innovation in this methodology was a chiral thioxanthone-derived photocatalyst, designed to form a hydrogen-bonding assembly with quinolone derivatives. Upon visible-light irradiation, the thioxanthone catalyst transfers energy to the substrate, populating its triplet state and inducing an asymmetric [2+2] photocycloaddition. Crucially, the chiral environment created by H-bond interactions between

photosensitizer and substrate directs preferable reactivity to the sterically unhindered face of the quinolone, enabling the formation of cyclobutane adducts with exceptional yields (up to 98%) and remarkable enantioselectivity (up to 98% *ee*) (**Scheme 1-18 A**).[64] In 2016, another strategy in enantioselective energy transfer (EnT) catalysis was achieved by Yoon and collaborators, using chiral Lewis acid coordination to enable asymmetric [2+2] photocycloaddition. Their strategy employed 2'-hydroxychalcone derivatives with inherent triplet energy (E_T = 54 kcal/mol), which, upon binding to a chiral scandium Lewis acid catalyst, formed coordination complexes exhibiting drastically reduced triplet energy levels ($E_T \approx 33$ kcal/mol). This energy gap allowed the ruthenium photocatalyst $Ru(bpy)_3PF_6$ (E_T = 49.0 kcal/mol) to selectively excite the scandium complex via a rapid, thermodynamically favourable energy transfer process. The resulting triplet intermediates underwent stereoselective [2+2] photocycloaddition with diene partners, yielding alkenylcyclobutane products with exceptional enantiocontrol (up to 97% *ee,* **Scheme 1-18 B**).[65]



Scheme 1-18 Enantioselective energy transfer catalysis in [2+2] photocycloadditions.

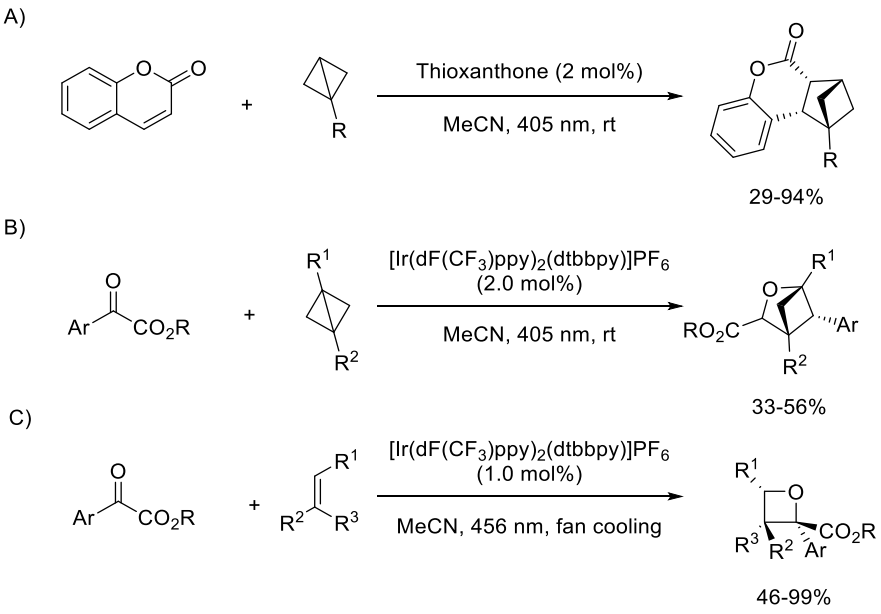
In 2017, the Kwon group reported an intramolecular crossed [2+2] photocycloaddition methodology, taking advantage of the constrained property of the dienones to generate bridged cyclobutanes (**Scheme 1-19 A**).[66] Other than conventional direct [2+2] photocycloadditions, additional applications of energy transfer catalysed photocycloadditions have been developed, proceeding *via* alternative pathways. In 2017, Smith and co-workers developed the application of energy transfer catalysis in 6π photocycloaddition reactions, utilizing a [1,4]-H shift to construct fused dihydrobenzofurans, dihydroindoles and dihydrothiophenes (**Scheme 1-19 B**).[67] By modifying the conditions and substrate, a Lewis acid-mediated, enantioselective, energy transfer catalysed synthesis of pyrones was developed (**Scheme 1-19 C**).[68]



Scheme 1-19 Energy transfer catalysis beyond [2+2] photocycloaddition.

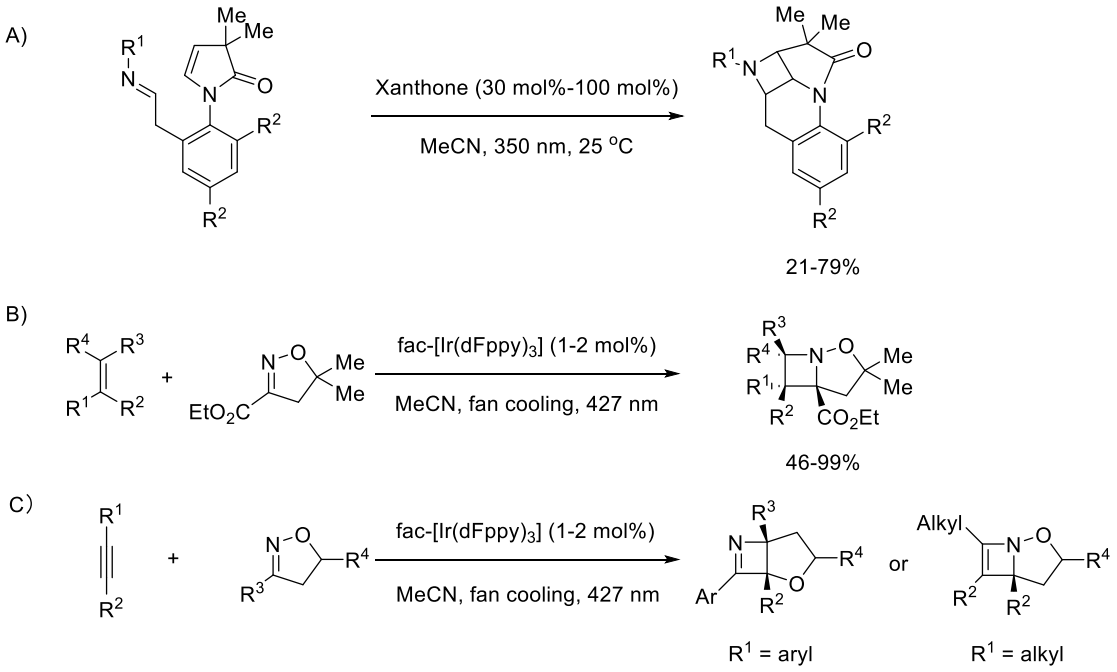
Photocycloaddition reactions, both through direct excitation and energy transfer catalysis pathways, normally utilize two olefinic components wherein the formation of two new σ-bonds occurs. In 2022, the Glorius group first introduced bicyclo[1.1.0]butanes as non-traditional 2σ-electron donors, generating complex bicyclic bioactive scaffolds via energy transfer catalysis [2π+2σ] photocycloaddition (**Scheme 1-20 A**).[69] They also found that not only sensitizable carbon-carbon double bonds can be utilized as the 2π component, but that the carbon-oxygen bond in benzoylformate esters can be utilized to generate polysubstituted 2-oxabicyclo[2.1.1]hexanes via energy transfer catalysed [2π+2σ] cyclization and subsequent aryl group migration (**Scheme 1-20 B**).[70] It is noteworthy that energy transfer catalysis [2π+2π] photocycloadditions between carbon-oxygen double bonds and alkenes, known as Paternò-

Büchi reactions, is also efficient and commonly employed in related Ir photocatalyst systems for the synthesis of oxetanes (**Scheme 1-20 C**).[71]



Scheme 1-20 Energy transfer catalysis [2+2] photocycloaddition.

As discussed above, energy transfer mediated [2+2] photocycloadditions derived from excitation of carbon-carbon and carbon-oxygen double bonds have been extensively studied. However, the related excitation of carbon-nitrogen double bonds and subsequent coupling with alkenes to form azetidines, known as aza-Paternò-Büchi reactions, is receiving increased interest in recent years. In 2017, the Sivaguru group reported an intramolecular aza Paternò-Büchi reaction via energy transfer of enamine carbon-carbon double bondto react with imines carbon-nitrogen double bond to form fused cyclic systems (**Scheme 1-21 A**).[72] In 2020, the Schindler group disclosed a significant intermolecular [2+2] photocycloaddition methodology. An activated cyclic oxime was used as the imine component, providing a long lifetime triplet state imine intermediate by preventing rotation around the C-N bond (**Scheme 1-21 B**).[73] This was extended to the energy transfer catalysed photocycloaddition of cyclic oximes with alkynes (**Scheme 1-21 C**).[74]



Scheme 1-21 Energy transfer catalysis in aza-Paternò-Büchi reaction.

Chapter 2 - Energy Transfer of Silyl-substituted Sulfinylamines and Subsequent Transformation to *β*-Sultam and aza-*β*-Sultam Scaffold

2.1 Synthetic Strategy

As discussed in **Chapter 1**, *β*-sultams and aza-*β*-sultams are important bioisosteres of *β*-lactams. While they have promising bioactive nature in bacterial infections, the methods to synthesize these two scaffolds are limited, and to the best of our knowledge, there are no reports of the synthesis of aza-*β*-sultams. For the more widely studied *β*-sultam scaffold, the reported intramolecular nucleophilic addition sequence is lengthy and complex, which greatly restricts the functional group diversity. Other methods including the [2+2] cycloaddition between sulfenes and imines, or sulfonylamines and alkenes also show strict requirements of the substituents to make the protocols efficient, resulting in limited substrate scope. To solve the above problems and to develop a modular synthetic protocol to both *β*-sultams and aza-*β*-sultams, we aimed to create an efficient methodology to generate *β*-cyclicsulfinamides, and then to form *β*-sultams and aza-*β*-sultams via subsequent oxidation or imination. This methodology has been shown to be efficient and of broad scope in the transformation of acyclic sulfur(IV) to acyclic sulfur(VI) functionalities. We envisioned that *β*-cyclicsulfinamides could be generated from the [2+2] cycloaddition between sulfinylamines and alkenes (**Figure 2-1**).

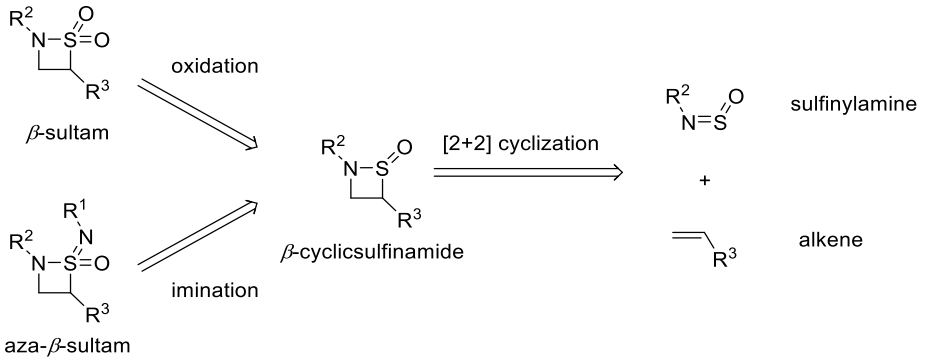
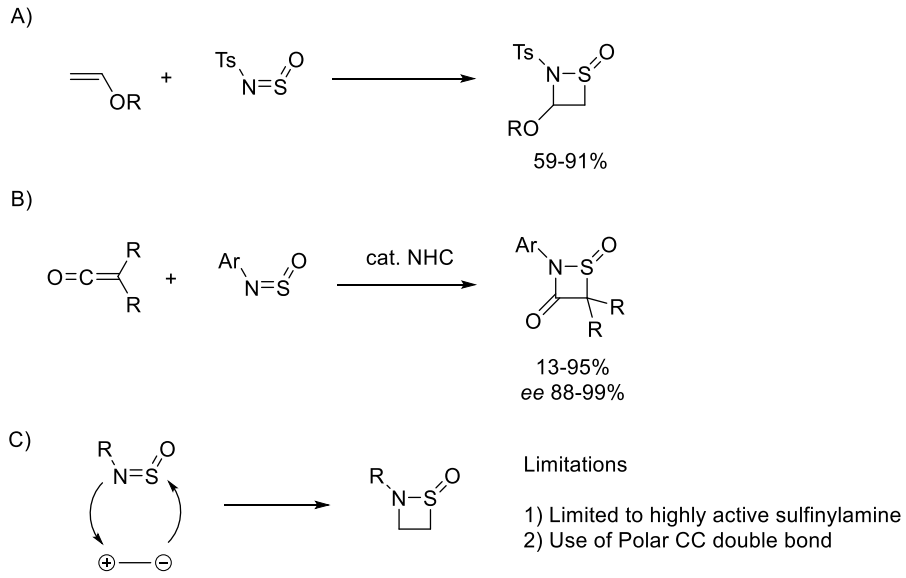


Figure 2-1 Retrosynthesis of *β*-sultams and aza-*β*-sultams

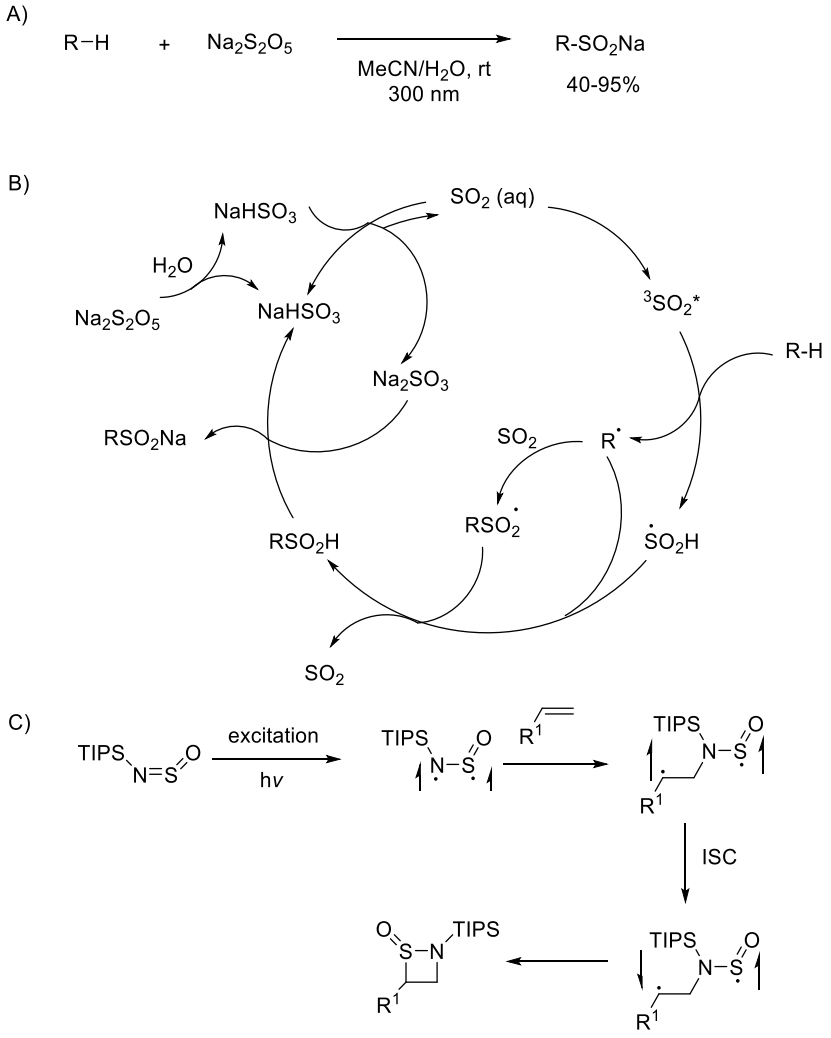
There are very limited reports of [2+2] reactions between sulfinylamines and alkenes. In 1967, Effenberger and Gleiter first reported the reaction between vinylethers and highly-active *N*-sulfonylsufinylamines at 0 °C in absence of light (**Scheme 2-1 A**).[75] In 2011, the Ye group developed a methodology which used ketenes and arylsulfinylamines to generate 3-oxo-*β*-cyclicsulfinamides *via N*-heterocyclic carbene (NHC) catalysis (**Scheme 2-1 B**).[76] The basic principle of these reported [2+2] reactions is to use the inherent polar carbon-carbon double bonds to initially generate a temporary carbanion, which could then attack the highly-reactive sulfur centre to form the four-membered ring. This mechanism has strict electronic requirements to both carbon-carbon coupling partners and sulfinylamines, limiting the functional groups on the sultam ring (**Scheme 2-1 C**). The highly activated sulfinylamines have also been shown to be unstable, as was discussed in **Chapter 1.4.1**. We hypothesized that changing the traditional intramolecular nucleophilic [2+2] cycloaddition to a novel radical promoted [2+2] cycloaddition would facilitate the reaction and would provide *β*-cyclicsulfinamides from more stable sulfinylamines under mild reaction conditions.



Scheme 2-1 Reported [2+2] cycloadditions between alkenes and sulfinylamines

As discussed in **Chapter 1.5.2**, the excitation of carbon-carbon bonds, carbon-oxygen bonds and carbon-nitrogen bonds are widely reported and utilized in the construction of complex strained rings. However, the excitation of sulfur-nitrogen bonds has generally only been exploited in fragmentation processes, with the direct use of their excited states in synthetic applications not reported.[77] In 2021, the Larionov group reported a methodology that used alkanes to generate sodium sulfinates under irradiation of UV light (**Scheme 2-2 A**).[78] The sulfur source in the reaction system was sodium metabisulfite, which is a widely used sulfur dioxide precursor. In the paper, they carried out computational studies to provide evidence for the formation of triplet-state sulfur dioxide. The triplet-state sulfur dioxide generated under UV light would undergo a hydrogen atom abstraction with alkanes to form an alkyl radical, which could then attack another molecule of sulfur dioxide to provide a sulfinate radical (**Scheme 2-2 B**). This sulfinate radical could then undergo a back-HAT reaction to give an unstable sulfinic acid, which could be converted to the corresponding stable sodium sulfinate.

This UV direct excitation of sulfur dioxide inspired us as it suggested that sulfinylamines, as an analogue of sulfur dioxide, might also be excited to the triplet state under radiation, and then undergo a [2+2] photocycloaddition with alkenes to afford *β*-cyclicsulfinamides (**Scheme 2-2 C**).



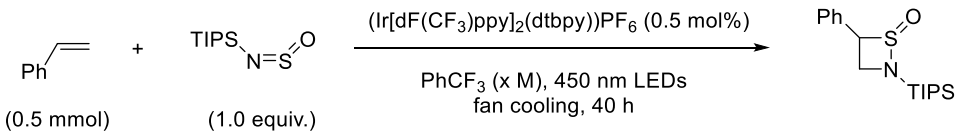
Scheme 2-2 (A) Larionov's protocol to synthesise sodium sulfinates under UV radiation. (B) Mechanism of the excitation of sulfur dioxide and subsequent hydrogen atom abstraction with alkanes. (C) Synthetic strategy for [2+2] photocycloaddition between sulfinylamines and alkenes.

2.2 Optimisation of [2+2] Photocycloaddition between TIPSNSO and Styrene

As UV radiation is of great harm to humans and it also brings potential challenges in functional group tolerance in a substrate scope, we attempted the targeted [2+2] photocycloaddition using a triplet-triplet energy transfer process instead of direct UV excitation. We started the optimisation of the [2+2] photocycloaddition between TIPSNSO and styrene, using $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ as an organic photocatalyst, which is a widely used photocatalyst in energy transfer triggered [2+2] photocycloaddition reactions.[79] The diastereomeric ratio (dr) and yield were detected using quantitive ^1H NMR spectroscopy. The yields discussed below are all a combined yield of both diastereomers.

First, we started the investigation of reaction concentration (**Table 2-1**). We observed that the reaction performed well at 1.0 M concentration, providing the corresponding *β*-cyclicsulfinamide in 49% yield with a diastereomeric ratio of 3:1. Longer reaction times didn't provide higher yields, and reducing the concentration to 0.5 M and 0.25 M didn't show significant change to either yield or diastereomeric ratio.

Table 2-1 Screening of reaction concentration of [2+2] photocycloaddition between TIPSNSO and styrene.

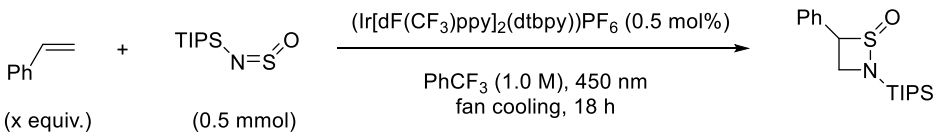


Entry	Concentration (M)	Yield[a]	d.r.[a]
1	1.0	49%	3:1
2[b]	1.0	49%	3:1
3	0.5	38%	4:1
4	0.25	42%	4:1

Reaction conditions: TIPSNSO (1.0 mmol, 1.0 equiv.), styrene (0.5 mmol, 1.0 equiv.) and (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (0.5 mol%), $PhCF_3$ (x M), 450 nm LEDs, fan cooling, 40 h. (a) Determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. (b) 18 h.

After screening the concentration, we then moved to an investigation of the styrene loading (**Table 2-2**). We started the investigation with 0.5 mmol TIPSNSO, 0.5 mmol (1 equiv.) styrene and 0.5 mol% (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6, under irradiation of 450 nm LEDs in 0.5 mL trifluorotoluene with fan cooling. We were delighted that when the loading of styrene was increased to 2 equivalents, the corresponding *β*-cyclicsulfinamide could be obtained in 72% yield with a dr of 4:1. The yield increased to 75% with a dr of 4:1 when 3 equivalents styrene was applied, while it did not improve either in yield or diastereomeric ratio when we contiuously increased the loading of styrene to 4 equivalents. Other variation in temperature and the loading of photocatalyst also did not show great improvement in either yield or diastereomeric ratio.

Table 2-2 Screening of alkene loading of [2+2] photocycloaddition between TIPSNSO and styrene.

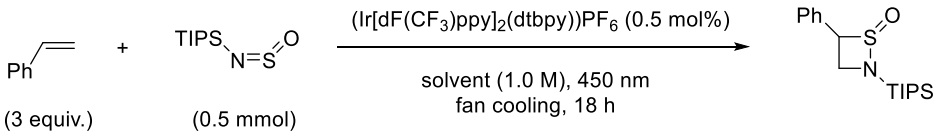


Entry	x	Yield[a]	d.r.[a]
1	1.0	49%	3:1
2	2.0	72%	4:1
3	3.0	75%	4:1
4	4.0	76%	4:1
5[b]	3.0	69%	3:1
6[b,c]	3.0	72%	3:1
7[d]	3.0	71%	3:1

Reaction conditions: TIPSNSO (0.5 mmol, 1.0 equiv.), styrene (x equiv.) and (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (0.5 mol%), $PhCF_3$ (0.5 ml, 1.0 M), 450 nm LEDs, fan cooling, 18 h. (a) Determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. (b) fan off. (c) 1 mol% photocatalyst was used. (d) 50 ˚C oil bath used.

The next parameter we investigated was the solvent, which is a significant parameter in organic photochemistry reactions (**Table 2-3**). We found that except benzene which gave no desired *β*-cyclicsulfinamide product, all other solvents screened gave the desired *β*-cyclicsulfinamide. Among them, MeCN and CH_2Cl_2 gave the highest yield, while CH_2Cl_2 gave a higher diastereomeric ratio of 6:1. THF and Et_2O gave decreased yields of only 30% and 11%, respectively, potentially due to the hydrogen atom abstraction (HAT) reaction between the triplet-state TIPSNSO and the solvent, following a similar pathway of Larionov's HAT reaction.

Table 2-3 Screening of solvent of [2+2] photocycloaddition between TIPSNSO and styrene.

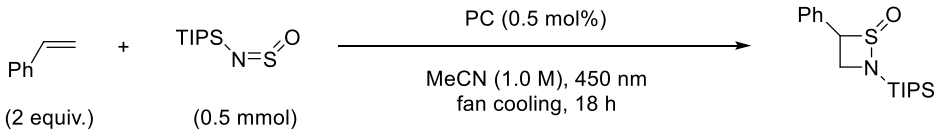


Entry	Solvent	Yield[a]	d.r.[a]
1	$PhCF_3$	75%	4:1
2	MeCN	86%	5:1
3[b]	MeCN	82%	5:1
4	THF	30%	2:1
5	Et_2O	11%	4.5:1
6	CH_2Cl_2	84%	5:1
7[b]	**CH_2Cl_2**	**83%**	**6:1**
8	EtOAc	54%	4:1
9	DMF	59%	4:1
10	Benzene	trace	-

Reaction conditions: TIPSNSO (0.5 mmol, 1.0 equiv.), styrene (1.5 mmol, 3 equiv.) and $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (0.5 mol%), solvent (0.5 ml, 1.0 M), 450 nm LEDs, fan cooling, 18 h. (a) Determined by ^{1}HNMR spectroscopy using dibromomethane as an internal standard. (b) 2 equivalents of styrene were used.

The next parameter we examined was the photocatalyst (**Table 2-4**). When we used lower triplet energy photocatalysts including Eosin Y (43.5 kcal/mol), $[Mes\text{-}Acr]ClO_4$ (44.7 kcal/mol) and $Ru(bpy)_3PF_6$ (49.0 kcal/mol), we could not generate any *β*-cyclicsulfinamide product. However, once higher triplet energy level photocatalysts were applied in the reaction, including 4CzIPN (58.3 kcal/mol), FIrPic (61.1 kcal/mol), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (61.8 kcal/mol), $Ir(dFppy)_3$ (63.5 kcal/mol) and 5CzBN (64.1 kcal/mol), the desired *β*-cyclicsulfinamide was generated in 78% to 85% yield. Among them, when 4CzIPN was used as the photocatalyst, the yield was improved to 83% with a highest dr of 6:1. Thioxanthone did not perform well in the reaction potentially due to weak absorption at 450 nm, as when repeated at 405 nm LEDs, the yield increased compared to the 450 nm result. 4CzIPN was selected as the optimal catalyst. The mechanism of the reactions will be discussed in **Chapter 2.6**.

Table 2-4 Screening of photocatalyst in the [2+2] photocycloaddition between TIPSNSO and styrene.



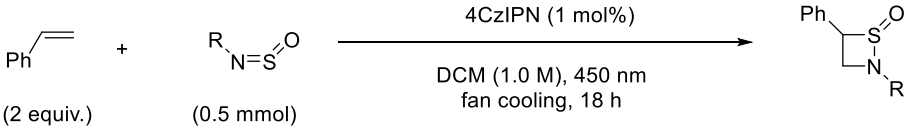
Entry	Photocatalyst	E_T (kcal/mol)	$E(M^*/M^{\bullet-})$ (V)	$E(M^{\bullet+}/M^*)$ (V)	Yield[a]	d.r.[a]
1	Eosin Y	43.5	+0.83	-1.11	0	-
2	[Mes-Acr] ClO_4	44.7	+2.18	-0.57	0	-
3	$Ru(bpy)_3PF_6$	49.0	+0.77	-0.81	0	-
4	**4CzIPN**	**58.3**	**+1.43**	**-1.18**	**83%**	**6:1**
5	FIrPic	61.1	+1.40	-1.88	85%	5:1
6	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	61.8	+1.21	-0.89	82%	5:1
7	$Ir(dFppy)_3$	63.5	+0.34	-1.44	84%	5:1
8	5CzBN	64.1	+1.31	-1.42	78%	6:1
9[b,c]	Thioxanthen-9-One	65.5	+1.18	-1.11	45%	5:1
10[b]	Thioxanthen-9-One	65.5	+1.18	-1.11	7%	6:1

Reaction conditions: TIPSNSO (0.5 mmol, 1.0 equiv.), styrene (1.0 mmol, 2 equiv.) and photocatalyst (0.5 mol%), MeCN (1.0 M), 450 nm LEDs, fan cooling, 18 h. (a) Determined by ^{1}HNMR spectroscopy using dibromomethane as an internal standard. (b) 5 mol% photocatalyst was used. (c) 405 nm.

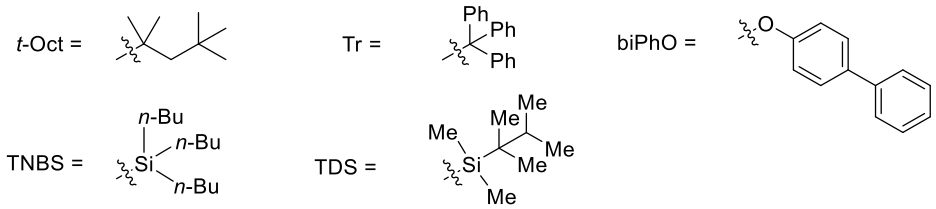
Having already investigated many other parameters in this [2+2] photocycloaddition reaction, we decided to modify the protecting group on the sulfinylamine to see its effect (**Table 2-5**). Alkyl substituted sulfinylamines, including *t*-OctNSO and TrNSO did not give the desired *β*-cyclicsulfinamide product. Another bench-stable sulfinylamine, biPhONSO, also did not give the desired product. Later screening of other silyl-substituted sulfinylamines suggested that the silyl group is essential for the [2+2] photocycloaddition to proceed as all silyl-substituted sulfinylamines tried gave the desired *β*-cyclicsulfinamides. It is surprising that larger silyl groups like TIPS and TBDPS substituted sulfinylamines gave 83% and 73% combined yield of both diastereomers, while less hindered silyl group including TNBS (tri(*n*-butyl)silyl) and TDS (Thexyldimethylsilyl) substituted sulfinylamines could only afford the corresponding *β*-

cyclicsulfinamide in 32% and 23% yield, respectively. This is potentially because a more-hindered silyl group could result in a longer lifetime triplet-state sulfinylamine, as this strategy to improve lifetime by control of configuration has been utilized in the excitation and utilization of triplet-state imines.[73]

Table 2-5 Screening of protecting groups on sulfinylamines.



Entry	R	Yield[a]	d.r.[a]
1	*t*-Oct	0[b]	-
2	Tr	0	-
3	biPhONSO	0	-
4	TBDPS	73%	4:1
5	TNBS	32%	2:1
6	TDS	23%	6:1
7	**TIPS**	**83%**	**6:1**



Reaction conditions: TIPSNSO (0.5 mmol, 1.0 equiv.), styrene (1.0 mmol, 2 equiv.) and 4CzIPN (1 mol%), DCM (1.0 M), 450 nm LEDs, fan cooling, 18 h. (a) Determined by ^{1}HNMR spectroscopy using dibromomethane as an internal standard. (b) 64% *t*-OctNSO recovery.

2.3 Scope of [2+2] Photocycloaddition between TIPSNSO and Alkenes

With the optimal conditions for the [2+2] photocycloaddition between TIPSNSO and alkenes in hand, we then turned to study the scope of the alkene coupling partner in the [2+2] photocycloaddition reaction. The reaction demonstrated high efficiency across various aryl-substituted alkenes, including Br- and Cl-substituted examples, achieving diastereomeric ratios (dr) ranging from 2:1 to 10:1 (**1a** to **1h**) (**Figure 2-2**). We were delighted that we could scale the reaction up to 5 mmol scale, with **1a** afforded in 77% yield and a diastereomeric ratio of 5:1. Hindered biaryl-substituted alkenes also afforded the desired β-cylicsulfinamide **1i** in 77% yield. Notably, α-NH-substituted alkenes also produced the corresponding products **1j** to **1n** in 47% to 90% yield with excellent diastereomeric ratios (dr > 20:1). Further control experiments, wherein the NH functionality was removed, for the synthesis of **1o** and **1p**, gave moderate diastereomeric ratios (2:1 to 4:1). X-ray analysis of product **1k** revealed that the NH bond and SO double bond are on the same side of the four-membered ring product, suggesting that the excellent diastereoselectivity may result from hydrogen bonding between the NH bond and SO double bond.

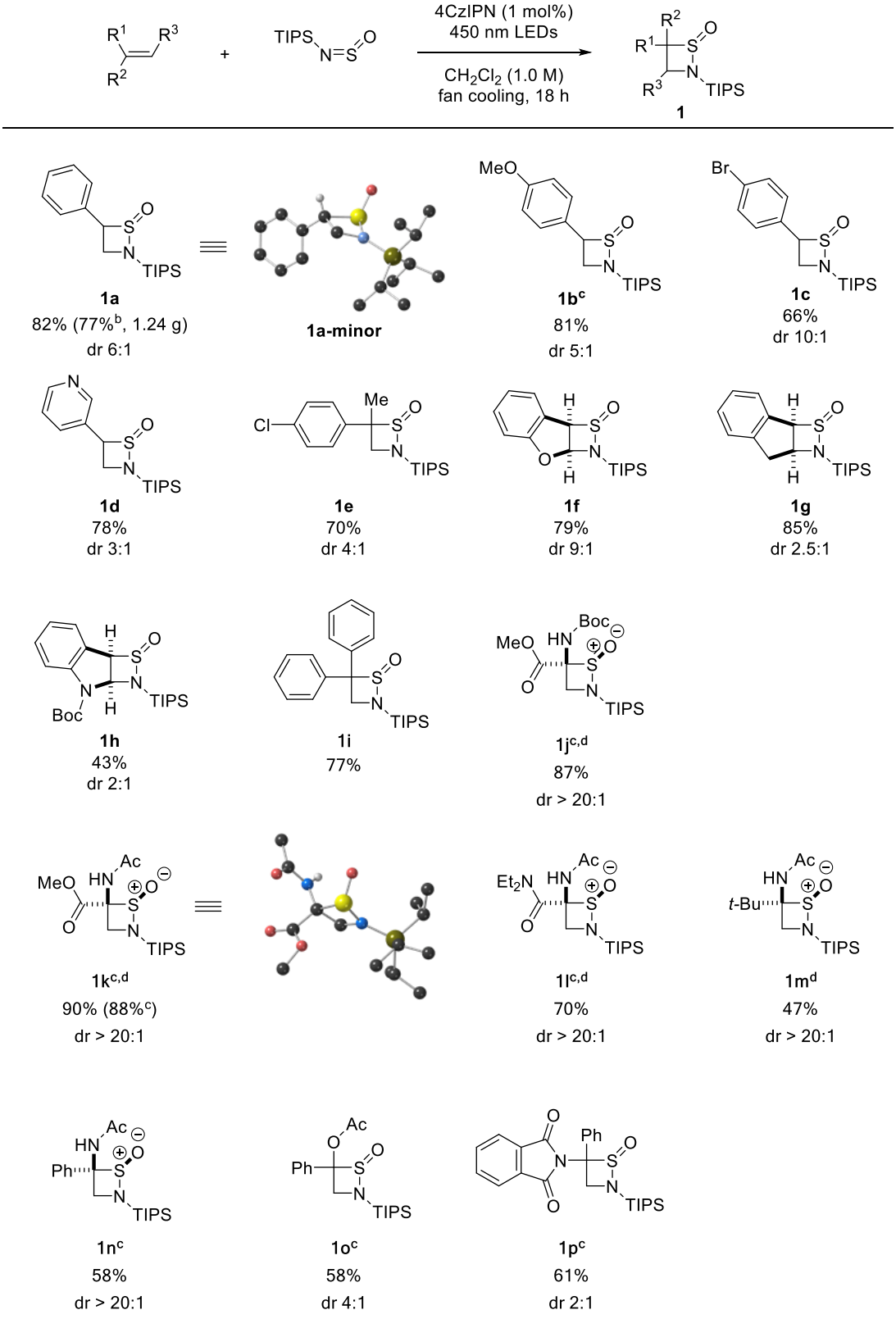


Figure 2-2 Scope of activated alkenes in the [2+2] photocycloaddition.[a]

Reaction conditions for activated alkenes: (a) TIPSNSO (0.5 mmol, 1.0 equiv.), alkene (1.0 mmol, 2.0 equiv.), 4CzIPN (0.05 mmol, 1.0 mol%), CH_2Cl_2 (0.5 mL, 1.0 M), 450 nm

irradiation, 18 h. Isolated yields. (b) The reaction was conducted on 5 mmol scale. (c) $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ used as photosensitizer. (d) 4 equiv. alkene used.

Next, we investigated the reactivity of alkyl substituted alkenes, as unactivated alkenes are generally challenging in photochemical reactions (**Figure 2-3**). Due to lower efficiency in these reactions, increased equivalents of alkyl substituted alkenes were required (4 equiv.). Mono-substituted products were obtained in moderate yields (**1q-1v**, 32-68%). More hindered 1,1-disubstituted alkenes also afforded the corresponding products **1w** to **1z** in 42% to 66% yield. Cyclooctene and methyl-2-butene were competent coupling partners providing **1aa** and **1ab** in 77% yield and 54% yield, respectively, showcasing the application of this [2+2] photocycloaddition reaction for cyclic alkenes and trisubstituted alkenes. As 4CzIPN has the similar polarity with *β*-cylicsulfinamide containing alkyloxyl group or ester group, iridium photocatalysts with similar triplet energy were used in some of the reactions for better separation (**1b**, **1j**, **1k**, **1l**, **1n**, **1o**, **1p**, **1r**, **1s**, **1v** and **1z**).

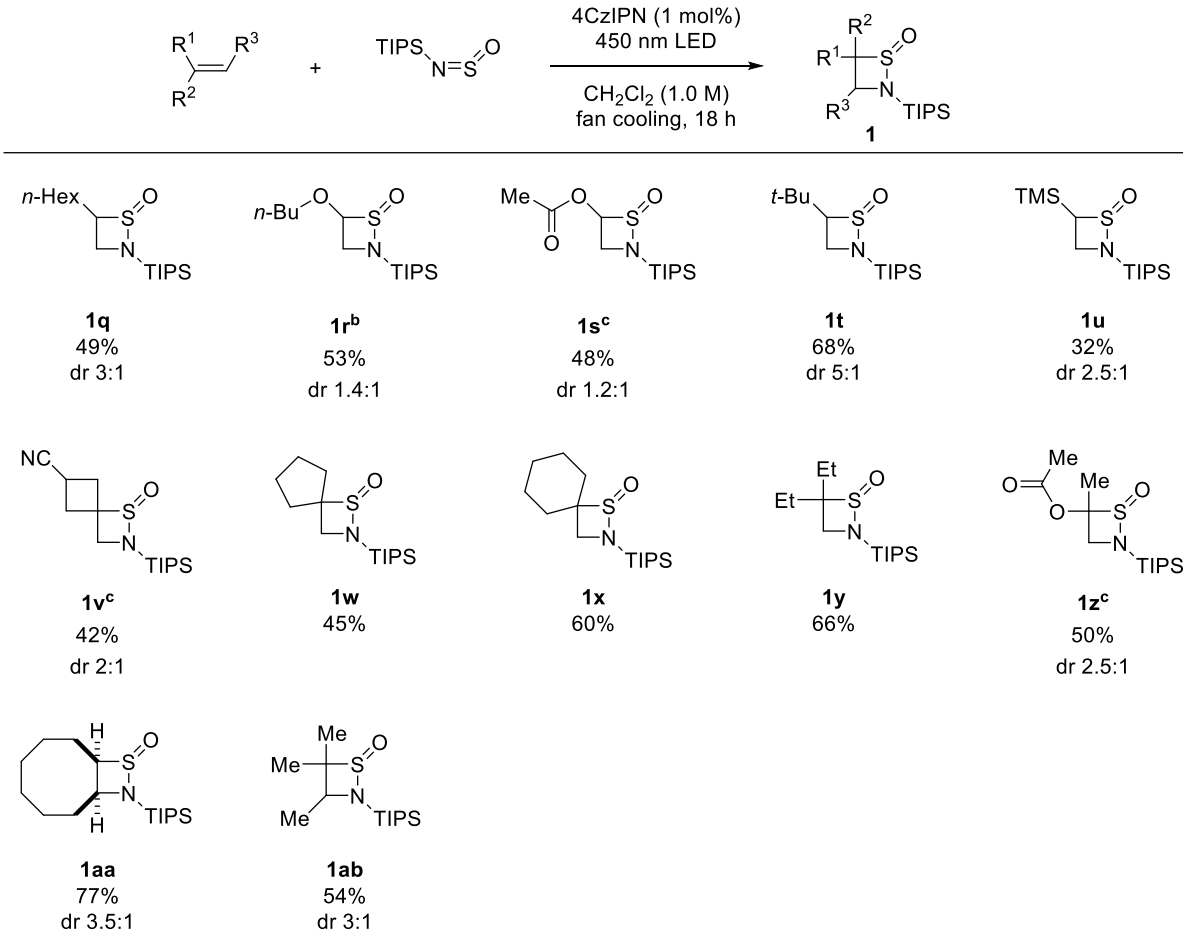


Figure 2-3 Scope of unactivated alkenes in [2+2] photocycloaddition.[a]

Reaction conditions for unactivated alkenes: (a) TIPSNSO (0.5 mmol, 1.0 eq.), alkene (2.0 mmol, 4.0 eq.), 4CzIPN (0.05 mmol, 1.0 mol%), CH_2Cl_2 (0.5 mL, 1.0 M), 450 nm irradiation, 18 h. Isolated yields. (b) $Ir(dFppy)_3$ used as photosensitizer. (c) $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ used as photosensitizer.

However, when we applied the conditions to other unsaturated carbon-carbon bond motifs, including aryl substituted alkyne (**A**), alkyl substituted alkyne (**B**) and an allene (**C**), the reaction did not afford the corresponding cyclic sulfur(IV) structure we desired. The system became very complex, potentially because the formed unsaturated cyclic sulfur(IV) structures can still be excited to undergo other side reactions. Alkenes attached to strong electron-withdrawing groups (**D**, **E**, **F**, **G** and **H**) gave no cycloaddition product, potentially due to the instability of electron-withdrawing group substituted radical intermediates. 1,2-Disubstituted

alkenes (**I**, **J** and **K**) gave *β*-cyclicsulfinamides in very low combined NMR yield of both diastereomers due to HAT side reactions. Alkene (**L**) didn't afford the corresponding *β*-cyclicsulfinamide potentially due to the interaction between the phosphine and the sulfinylamine (**Figure 2-4**).

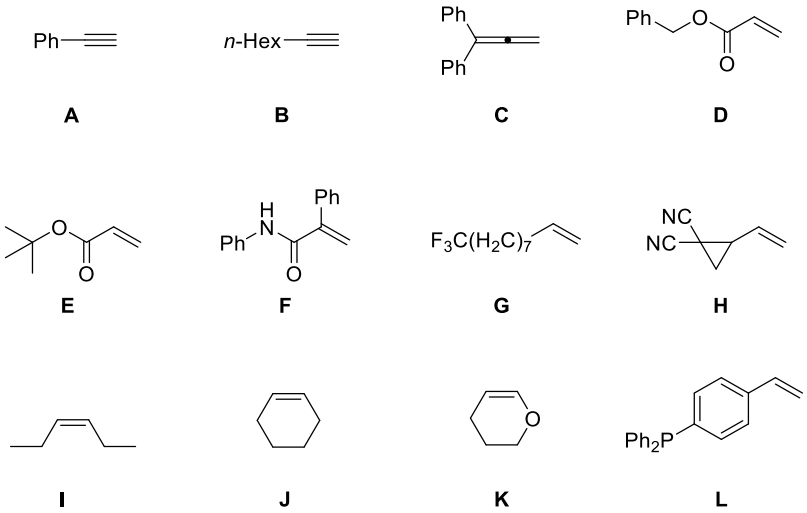
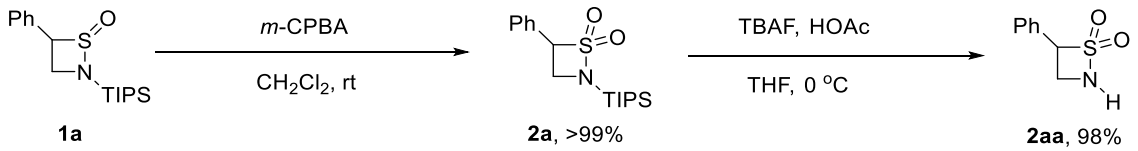


Figure 2-4 Failed carbon-carbon bond coupling partners

2.4 Derivatisation of *β*-Sultams

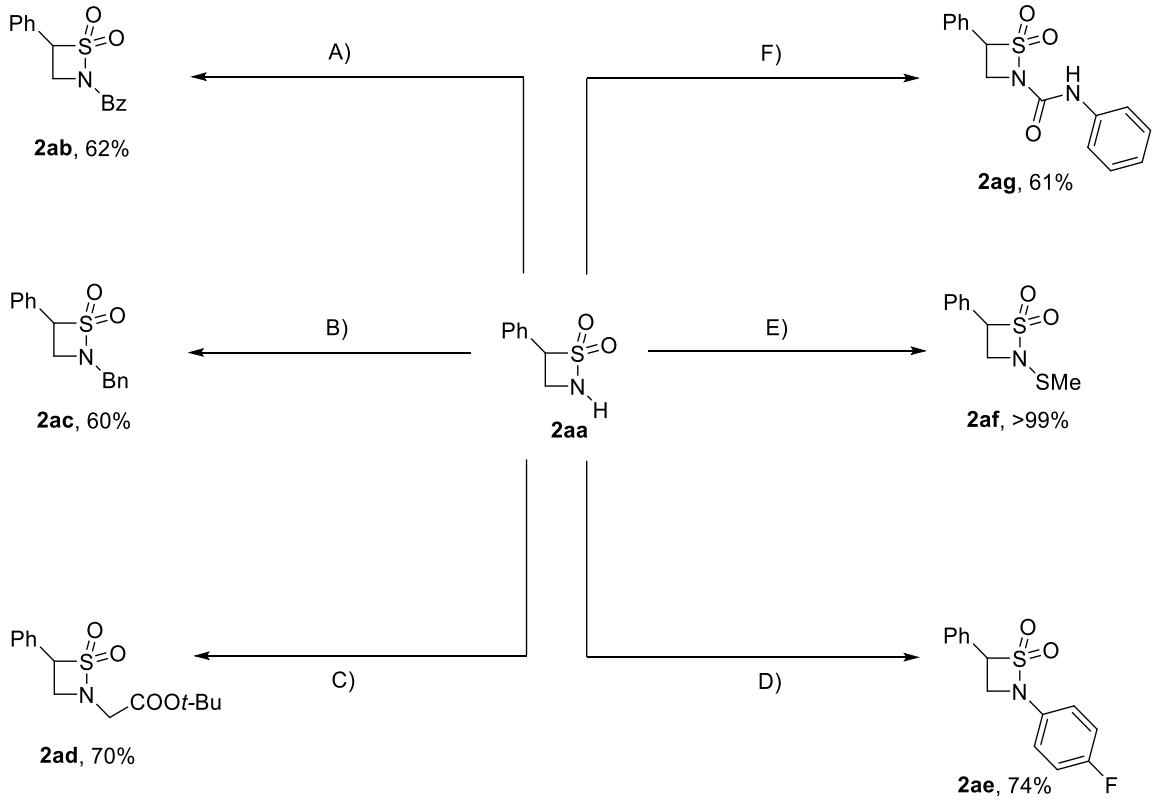
2.4.1 Synthesis of *β*-Sultams

As various substituted *β*-cyclicsulfinamides could be generated in moderate to good yield, we started to study the derivatisation to *β*-sultams. First, we treated *β*-cyclicsulfinamide **1a** with *m*-CPBA to oxidise it to the corresponding *β*-sultam **2a**, which allowed us to obtain the product in >99% yield. The TIPS protected *β*-sultam **2a** was further transformed into unprotected *β*-sultam **2aa** in 98% yield under buffered desilylation conditions (**Scheme 2-3**).[80]



Scheme 2-3 Oxidation and subsequent deprotection to form *β*-sultam **2aa**

With unprotected *β*-sultam **2aa** in hand, we reacted it with different electrophiles to produce *β*-sultams with electron-withdrawing or electron-donating substituents (**2ab** to **2af**). *β*-sultam **2aa** can be used as nucleophile to react with benzoyl chloride or phenyl isocyanate to afford electron-withdrawing group substituted *β*-sultam **2ab** (in 62% yield) or *β*-sultam **2ag** (in 61% yield) (**Scheme 2-4 A** and **F**). Benzyl bromide or *tert*-butyl bromoacetate can also react with deprotonated *β*-sultam **2aa** with TBAB as phase transfer catalyst to afford the corresponding *β*-sultam **2ac** (in 60% yield) and *β*-sultam **2ad** (in 70% yield) (**Scheme 2-4 B** and **C**).[81] We were delighted to find that *β*-sultam **2aa** could tolerate a Chan-Lam coupling reaction using copper catalysis to afford aryl-substituted *β*-sultam **2ae** in 74% yield (**Scheme 2-4 D**).[82] As methylthio-substituted lactams have been shown to be bioactive, we also treated deprotonated *β*-sultam **2aa** with S-methyl methanethiosulfonate, affording methylthio-substituted *β*-sultam **2af** in >99% yield (**Scheme 2-3 E**).[83]



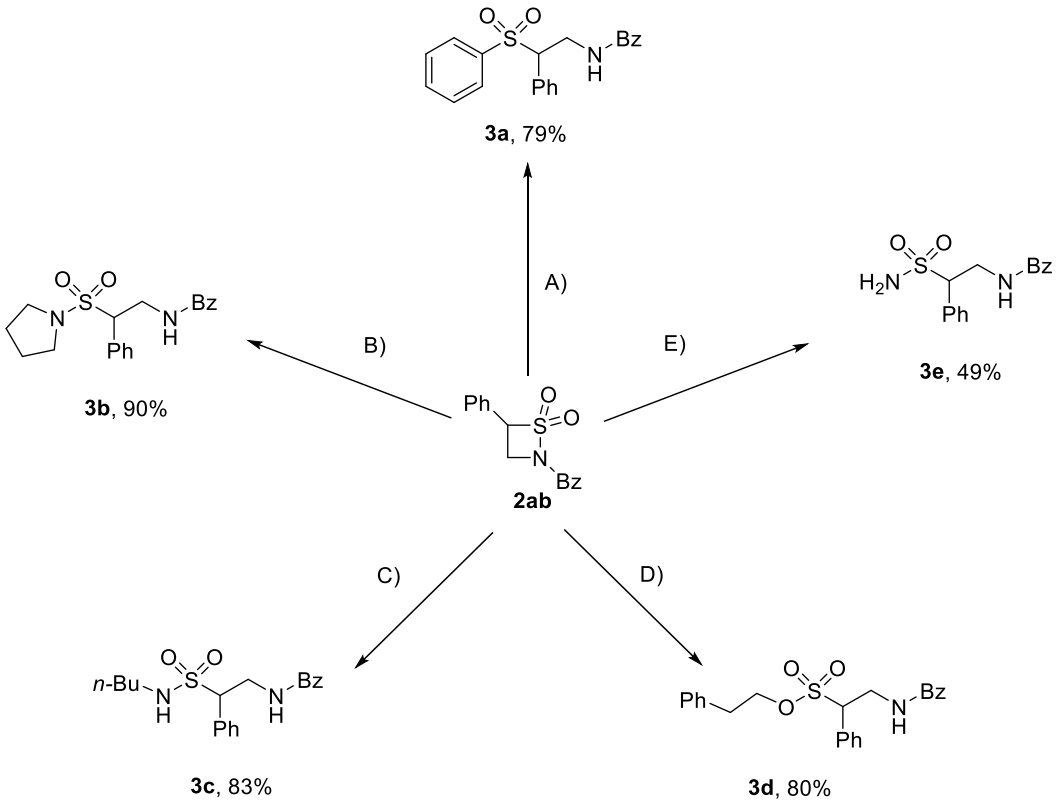
Scheme 2-3 Functionalization of *β*-sultam **2aa**.

Reaction conditions: (A) BzCl, DMAP, CH_2Cl_2, 0 °C. (B) BnBr, KOH, TBAB, THF, rt. (C) $BrCH_2COO^tBu$, KOH, TBAB, THF, rt. (D) $Cu(MeCN)_4PF_6$, *p*-Fluorophenylboronic acid, N-methylpiperidine, oxygen, MeCN, rt. (E) LiHMDS, $MeSO_2SMe$, THF, -78 °C to rt. (F) PhNCO, NEt_3, CH_2Cl_2, rt.

2.4.2 Ring-Opening of *β*-Sultams

As introduced in **Chapter 1.1**, *β*-lactams and *β*-sultams can undergo nucleophilic ring-opening reactions, showing its bioactivity towards biological nucleophiles. To demonstrate the potential reactivity of functionalised *β*-sultams, we reacted *β*-sultam **2ab** with various nucleophiles, including Grignard reagents, primary amines, secondary amines, aqueous ammonia, and alcohols, achieving acyclic *β*-amino S(VI) products in 49% to 90% yields (**Scheme 2-4**).[4] Notably, acyclic *β*-amino S(VI) compounds, known as taurine analogues, are of great interest

in medicinal chemistry, and our protocol offers an efficient alternative to traditional cyclic and acyclic *β*-amino S(IV) compounds synthesis.



Scheme 2-4 Ring-open of *β*-sultam **2aa**.

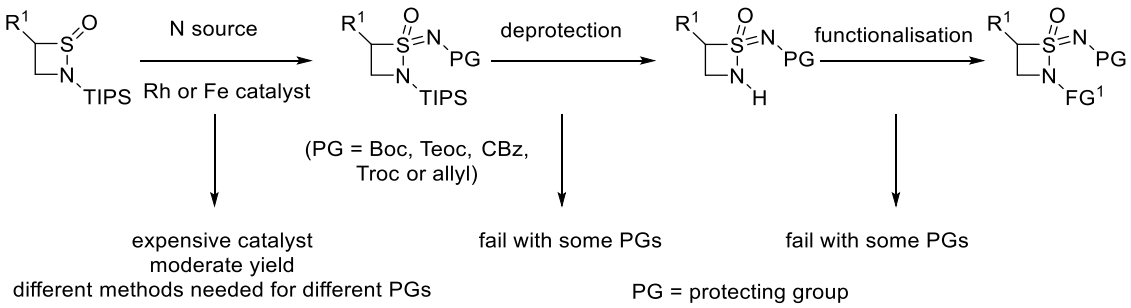
Reaction conditions: (A) PhMgBr, Et_2O,0 °C to rt. (B) Pyrrolidine, CH_2Cl_2, rt. (C) *n*-Butylamine, CH_2Cl_2, 40 °C. (D) 2-Phenylethanol, NEt_3, CH_2Cl_2, rt. (E) NH_4OH, MeCN, rt.

2.5 Derivatisation of Aza-*β*-Sultams

As discussed in **Chapter 1.3**, interest in aza-sulfur(VI) compounds has grown rapidly in recent years due to the bioactivity of acyclic aza-sulfur(VI) compounds. The development of an efficient method to synthesize aza-*β*-sultams introducing a new scaffold class, which would offer two nitrogen atoms that can be functionalised, greatly inspired our interest.

2.5.1 Synthesis of Aza-*β*-Sultams

As we can generate different substituted *β*-cyclicsulfinamides with our developed procedure, we started to establish an appropriate protocol to generate biofunctionalised aza-*β*-sultams by the imination of *β*-cyclicsulfinamides. The first protocol we tried was a transition-metal catalysed imination reaction (**Scheme 2-5**). Unfortunately, this protocol has two drawbacks: i) an expensive transition-metal catalyst is used to carry out the imination, significantly increasing the cost of the reaction; ii) for some of the aza-*β*-sultams formed after imination, the subsequent TIPS deprotection of aza-*β*-sultams resulted in decomposition, or other unknown side reactions. Lastly, we found that imination with differently substituted nitrenes usually needed completely different catalyst systems, which made the optimization complicated and time-consuming.

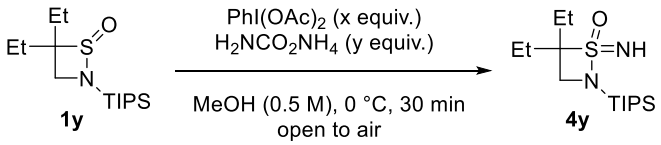


Scheme 2-5 Transition-metal catalyzed imination to synthesize bifunctionalised aza-*β*-sultams and its drawbacks.

We started the investigation into direct N-H imination, adapted from the ambient imination methodology developed by the Bull group discussed in **Chapter 1.3.2**.[37] We used *β*-cyclicsulfinamide **1y** as the substrate with $PhI(OAc)_2$ (PIDA) and ammonium carbamate as the nitrene source in methanol to start the optimization.

First, we screened the stoichiometries of the imination reagents. When 3 equivalents of $PhI(OAc)_2$ was used and 4 equivalents ammonium carbamate was, the NH aza-*β*-sultam **4y** could be generated in 59% yield and 69% mass balance (recovery of *β*-sultam **1y** plus NMR yield of aza-*β*-sultam **4y**). Reducing the $PhI(OAc)_2$ to 1.5 equivalents and the ammonium carbamate to 2.5 equivalents resulted in lower yield while the mass balance is higher (**Table 2-6**).

Table 2-6 Screening of stoichiometries of imination reagents



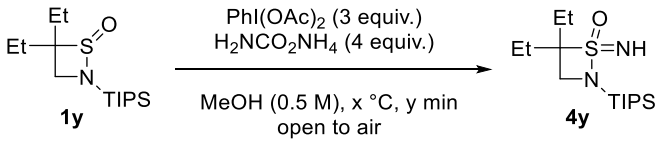
Entry	x	y	Mass balance[a,b]	Yield[b]
1	1.5	2.5	73%	47%
2	**3**	**4**	**69%**	**59%**

Reaction conditions: *β*-sultam **1y** (0.30 mmol, 1.0 equiv.), $PhI(OAc)_2$ (x equiv.) and $H_2NCO_2NH_4$ (ammonium carbamate) (y equiv.), MeOH (0.6 mL, 0.5 M), 0 °C, 30 min. (a) Recovery of *β*-sultam **1y** plus NMR yield of aza-*β*-sultam **4y**. (b) Determined by ^1H NMR spectroscopy using dibromomethane as an internal standard.

The next parameters we examined were reaction time and temperature (**Table 2-7**). When we conducted the reaction at room temperature instead of 0 °C, both mass balance and yield decreased dramatically. When the reactions were conducted at 0 °C, longer reaction time resulted in lower mass balance, while aza-*β*-sultam **4y** can be generated in highest 59% yield

after 30 minutes. This decline in mass balance can also be observed at -10 ^{o}C, as at this temperature the conversion become much lower compared to the reactions at 0 ^{o}C.

Table 2-7 Screening of reaction time and temperature

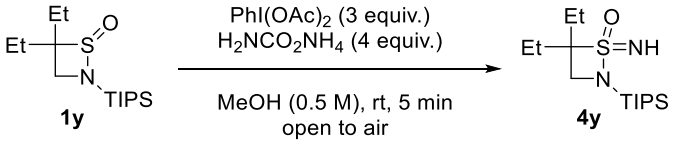


Entry	Temperature (°C)	Time (min)	Mass balance[a,b]	Yield[b]
1	0	15	77%	53%
2	rt	30	10%	0%
3	**0**	**30**	**69%**	**59%**
4	0	45	55%	49%
5	-10	30	90%	10%
6	-10	60	84%	34%
7	-10	120	80%	27%

Reaction conditions: *β*-sultam **1y** (0.30 mmol, 1.0 equiv.), $PhI(OAc)_2$ (0.9 mmol, 3.0 equiv.) and $H_2NCO_2NH_4$ (ammonium carbamate) (1.2 mmol, 4.0 equiv.), MeOH (0.6 mL, 0.5 M), -10 °C to rt, 15 to 120 min. (a) Recovery of *β*-sultam **1y** plus ^{1}H NMR yield of aza-*β*-sultam **4y**. (b) Determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard.

When we carried out NMR characterisation of aza-*β*-sultam **4y**, we found that basified deuterated chloroform needed to be used, otherwise the aza-*β*-sultam **4y** would partly decompose during NMR characterisation. This made us aware that the work up and isolation conditions could also result in the low yield of aza-*β*-sultam **4y**, so we then moved to the screening of the work up conditions. We were delighted to find that aza-*β*-sultam **4y** can be generated in much higher yield when a basic aluminium oxide plug was used instead of a silica plug for a short column, which further demonstrated that exposure to acidic environments would result in the decomposition of the aza-*β*-sultams (**Table 2-8**).

Table 2-8 Screening of work-up conditions

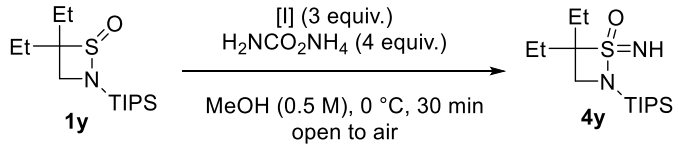


Entry	Work up condition	Mass balance[a,b]	Yield[b]
1	Short silica plug	17%	17%
2	**Basic Al_2O_3 plug**	**39%**	**39%**

Reaction conditions: *β*-sultam **1y** (0.30 mmol, 1.0 equiv.), $PhI(OAc)_2$ (0.9 mmol, 3.0 equiv.) and $H_2NCO_2NH_4$ (ammonium carbamate) (1.2 mmol, 4.0 equiv.), MeOH (0.6 mL, 0.5 M), rt, 5 min. (a) Recovery of *β*-sultam **1** plus NMR yield of aza-*β*-sultam **4y**. (b) Determined by ^1H NMR spectroscopy using dibromomethane as an internal standard.

Inspired by the effect of the acidic environment on the stability of aza-*β*-sultams, we envisioned that using a less acidic hypervalent iodine reagent would afford aza-*β*-sultams in higher yield. We replaced the $PhI(OAc)_2$ with PhIO, which can be thought of as $PhI(OAc)_2$ with 1 equivalent of carboxylic acid removed. We were delighted to find that when PhIO was used in combination with ammonium carbamate, both the yield of aza-*β*-sultam **4y** and the mass balance increased dramatically (**Table 2-9**).

Table 2-9 Screening of oxidants



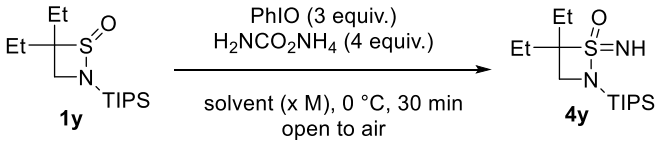
Entry	[I]	Mass balance[a,b]	Yield[b]
1	$PhI(OAc)_2$	69%	59%
2	**PhIO**	**86%**	**76%**

Reaction conditions: *β*-sultam **1y** (0.30 mmol, 1.0 equiv.), oxidant (0.9 mmol, 3.0 equiv.) and $H_2NCO_2NH_4$ (ammonium carbamate) (1.2 mmol, 4.0 equiv.), MeOH (0.6 mL, 0.5 M), 0 °C,

30 min. (a) Recovery of *β*-sultam **1y** plus NMR yield of aza-*β*-sultam **4y**. (b) Determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard.

We then moved to screen reaction concentration and solvent (**Table 2-10**). Reducing the concentration of the reaction from 0.5 M to 0.25 M or 0.125 M did not significantly affect the reaction. When we conducted the reaction in trifluoroethanol instead of methanol with PhIO, aza-*β*-sultam **4y** could be generated in the highest NMR yield of 91% with 86% isolated yield.[39] Reducing the loading of PhIO slightly reduced the conversion of *β*-cyclicsulfinamide.

Table 2-10 Screening of solvent and concentration of **1y**



Entry	Solvent	Concentration (M)	Mass balance[a,b]	Yield[b]
1	MeOH	0.5	86%	76%
2	MeOH	0.25	88%	71%
3	MeOH	0.125	83%	57%
4[c]	**TFE**	**0.5**	**91%**	**91% (86%)**
5[d]	TFE	0.5	97%	87%

Reaction conditions: *β*-sultam **1y** (0.30 mmol, 1.0 equiv.), PhIO (0.9 mmol, 3.0 equiv.) and $H_2NCO_2NH_4$ (ammonium carbamate) (1.2 mmol, 4.0 equiv.), solvent (0.6-2.4 mL, 0.125 M-0.5 M), 0 °C, 30 min. (a) Recovery of *β*-sultam **1y** plus NMR yield of aza-*β*-sultam **4y**. (b) Determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. (c) Isolated yield in parenthesis. (d) 2.0 equiv. PhIO was used.

With the optimal imination conditions in hand, we then moved to study the substrate scope of different aza-*β*-sultams. Disubstituted aza-*β*-sultams were isolated in good yields (**4i** to **4y**). Although monosubstituted aza-*β*-sultams were found to be unstable in isolation, they were directly transformed into bifunctionalised products **4aa** in two steps for both *cis* and *trans β*-cyclicsulfinamides (**Figure 2-5**).

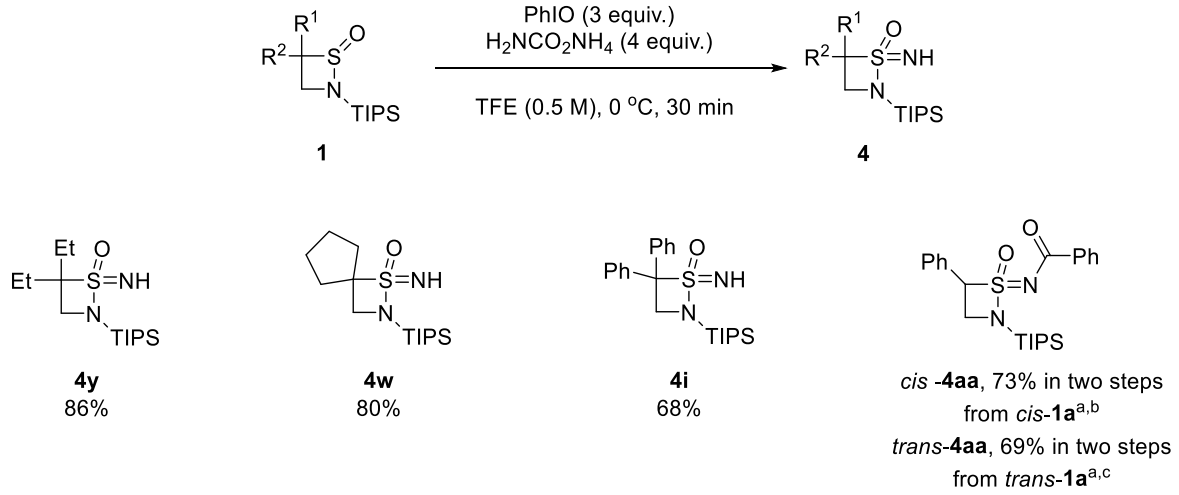
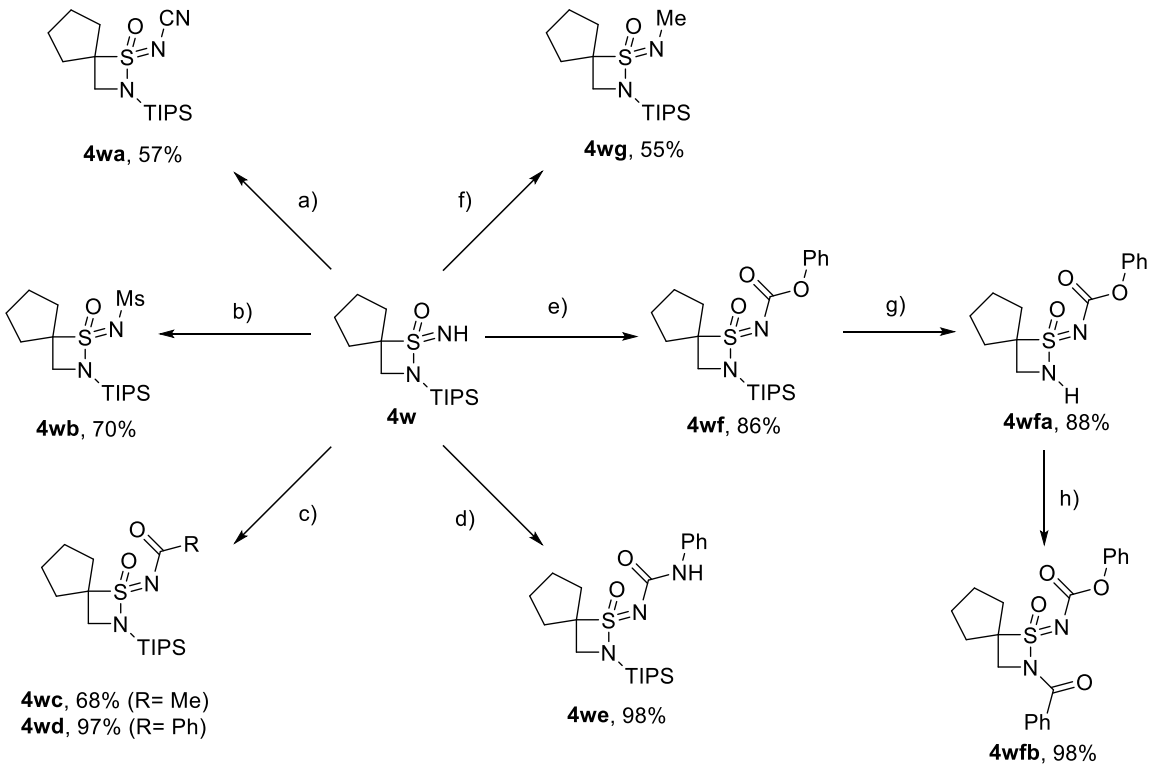


Figure 2-5 Synthesis of aza-*β*-sultams

Reaction conditions: *β*-sultam **1** (0.30 mmol, 1.0 equiv.), PhIO (0.9 mmol, 3.0 equiv.) and $H_2NCO_2NH_4$ (ammonium carbamate) (1.2 mmol, 4.0 equiv.), trifluoroethanol (0.6 mL, 0.5 M), 0 °C, 30 min. (a) React with BzCl in two steps. (b) From *cis*-**1a**. (c) From *trans*-**1a**.

2.5.2 Functionalization of Aza-*β*-Sultams

With the NH aza-*β*-sultams in hand, we then moved to functionalisation studies on the imidic nitrogen (**Scheme 2-6**). Treating aza-*β*-sultam **4w** with different electrophiles including cyanogen bromide, methanesulfonyl chloride, acetyl chloride, benzoyl chloride and phenyl isocyanate could afford the corresponding electron-withdrawing group substituted aza-*β*-sultams in moderate to good yields (**4wa** to **4wf**). Deprotonated aza-*β*-sultam **4w** can also react with methyl iodide to afford aza-*β*-sultam **4wg** in 55% yield. With the aza-*β*-sultam **4wf** in hand, monofunctionalised aza-*β*-sultam **4wfa** can be generated after TBAF-mediated silyl deprotection in 88% yield, and subsequent benzoyl functionalisation can afford bifunctionalised aza-*β*-sultam **4wfb** in 98% yield.



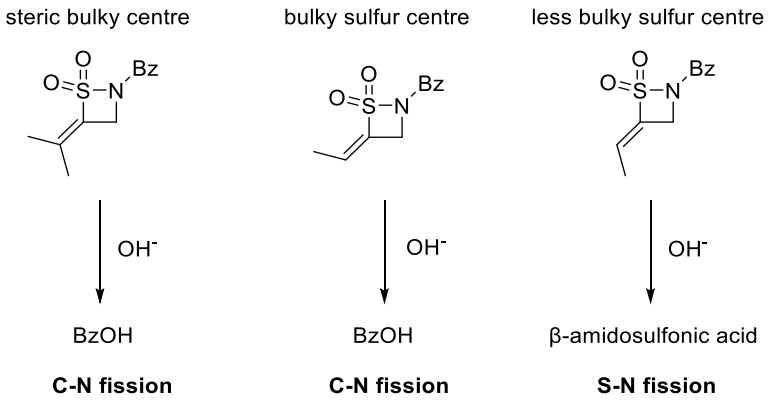
Scheme 2-6 Functionalisation and bifunctionalisation of aza-*β*-sultams.

Reaction conditions: (a) BrCN, DMAP, CH_2Cl_2, rt. (b) MsCl, NEt_3, DMAP, CH_2Cl_2, rt. (c) AcCl or BzCl, NEt_3, DMAP, CH_2Cl_2, rt. (d) PhNCO, NEt_3, CH_2Cl_2, rt. (e) PhOCOCl, NEt_3, DMAP, CH_2Cl_2, rt. (f) NaH, MeI, THF, 0 ^{o}C to rt. (g) TBAF, THF, 0 ^{o}C. (h) BzCl, DMAP, CH_2Cl_2, rt.

2.5.3 Ring-Opening of Aza-β-Sultams

As *β*-sultams can be transformed into taurine analogues under ring-opening conditions, and are important in medical and pharmaceutical fields, the ring-opening of aza-*β*-sultams deserved further exploration as this would produce aza-taurine analogues, previously challenging to synthesize. Previous studies by the Page group of the ring-opening of *β*-sultams revealed that steric effects play a vital role in the four-membered ring influenced S-N and C-N bond fission competition (**Scheme 2-7**).[84] In their paper, they found that while *β*-sultams with a less hindered sulfur centre would undergo normal S-N fission to generate *β*-aminosulfonic acid, *β*-sultams with bulky substituted groups would have an unusual C-N fission. This S-N and C-N

bond fission competition was also found for bifunctionalised aza-*β*-sultams, posing challenges for sterically hindered functionalised aza-*β*-sultams.



Scheme 2-7 Reported C-N and S-N fission competition in the ring-open of *β*-sultam scaffolds.

When we treated aza-*β*-sultam **4w** with caesium carbonate in toluene at 100 °C, we found an unusual silyl-transfer reaction, giving rearranged aza-*β*-sultam **4wh** in 79% yield; further functionalisation with different electrophiles gave complementary bifunctional aza-*β*-sultams in good yields (**4wha** and **4whb**) (**Scheme 2-8 A**). We envisioned that deprotection of the silyl group could happen under acidic fluoride conditions, resulting in the subsequent ring-open reaction to release the ring strain, forming *β*-amino sulfinyl nitrenes. Previous studies in our group revealed that sulfinyl nitrenes are a class of very active electrophiles, which can react rapdily with nucleophiles to generate *β*-amino sulfur(VI) compounds (**Scheme 2-7 B**).[50]

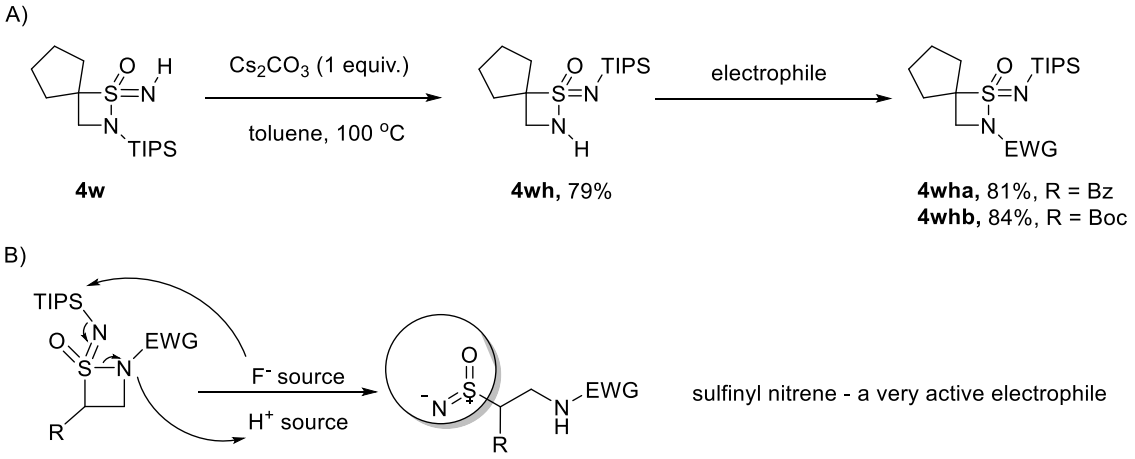
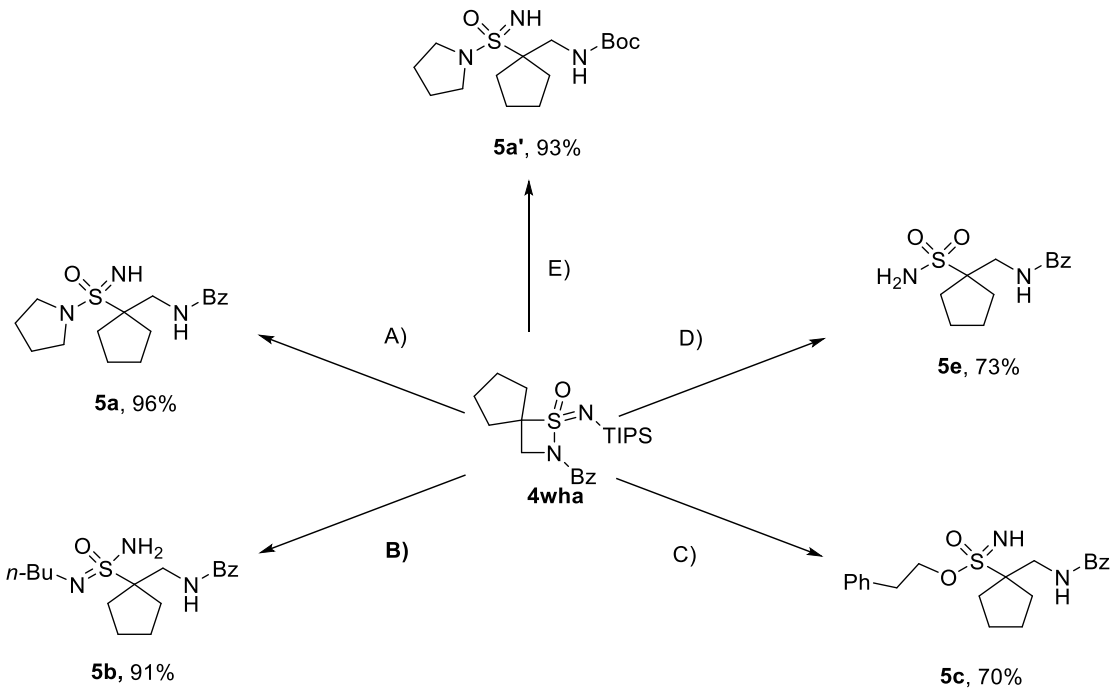


Figure 2-8 (A) unusual silyl-transfer reaction and subsequent functionalisation; (B) Proposed mechanism of the desilylative ring-opening reaction to synthesize *β*-amino sulfur(VI) compounds.

Based on the proposed mechanism of the desilylative ring-opening reaction, we utilized potassium bifluoride as the fluoride source because it is of weak acidity and its easier handling compared to other hydrofluoric acid sources. Treating aza-*β*-sultams **4wha** with pyrrolidine and potassium bifluoride yielded *β*-amino-sulfonimidamide **5a** in 96% yield (**Scheme 2-9 A**). Other nucleophiles, including acyclic amines and alcohols, produced **5b** and **5c** in 91% and 70% yields, respectively (**Scheme 2-9 B** and **C**). Direct deprotection with TBAF yielded *β*-amino sulfonamide **5d** in 73% yield (**Scheme 2-9 D**). Notably, Boc-functionalised aza-*β*-sultam **4whb** reacted with pyrrolidine and potassium bifluoride to produce Boc-substituted *β*-amino-sulfonimidamide **5a'** in 93% yield, paving the way for selective functionalisation of both nitrogen atoms in this scaffold (**Scheme 2-9 E**). In this case, we are able to access diverse *β*-amino sulfur(VI) functionalities by ring-opening of aza-*β*-sultam, which used to be quite hard to generate by nucleophilic reaction with acyclic *β*-amino sulfonimidoyl chloride or fluoride.[85]

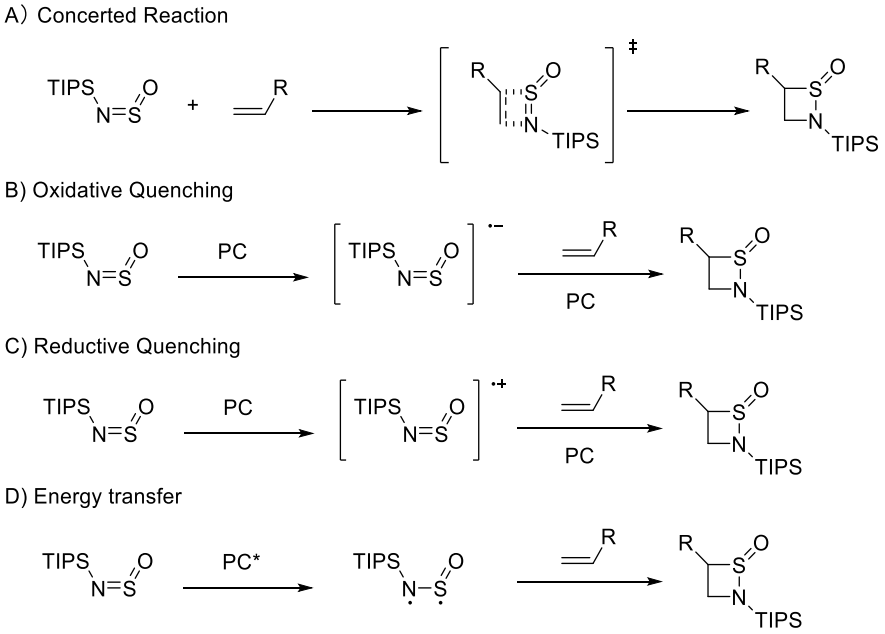


Scheme 2-9 Ring-open of aza-*β*-sultams to afford *β*-amino sulfur (VI) compounds

Reaction conditions: (A) KHF_2, pyrrolidine, MeCN, 40 °C. (B) KHF_2, *n*-butylamine, MeCN, 40 °C. (C) KHF_2, 2-phenylethanol, MeCN, 40 °C. (D) TBAF, AcOH, THF, 0 °C. (E) **4whb** was used instead of **4wha**, KHF_2, pyrrolidine, MeCN, 40 °C.

2.6 Mechanistic Studies of the [2+2] Photocycloaddition between TIPSNSO and Styrene

After the study in the substrate scope of [2+2] photocycloaddition and the derivatisation of both *β*-sultams and aza-*β*-sultams, we then moved to mechanistic studies of the [2+2] photocycloaddition reaction. Although in **Chapter 2.1**, a diradical proceeding [2+2] photocycloaddition pathway was envisioned, other mechanistic hypotheses can still be postulated for the initiation of the reaction, including i) concerted reaction; ii) oxidative quenching; iii) reductive quenching. In this section, several control experiments and photophysics studies were conducted to support the proposed energy transfer pathway (**Scheme 2-10**).

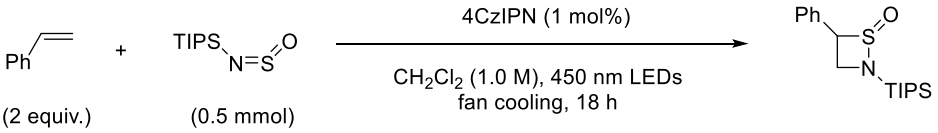


Scheme 2-10 Possible pathways for the [2+2] reaction between TIPSNSO and alkenes.

2.6.1 Control Experiments

First, we did a series of control experiments to demonstrate the significance of light and photocatalyst for this [2+2] photocycloaddition reaction (**Table 2-11**). When catalysts were removed from the reaction, the direct excitation still happened but in a much less efficient process (**Table 2-11, entry 2-entry 5**). This change between energy transfer and direct excitation process became much more obvious when acetonitrile was used as the solvent (**Table 2-11**, **entry 9** and **entry 10**). It is notable that heating can not trigger the [2+2] cycloaddition reaction (**Table 11**, **entry 6** and **entry 7**). The need for light was also confirmed (**Table 11**, **entry 8**).

Table 2-11 Control experiment for [2+2] photocycloaddition

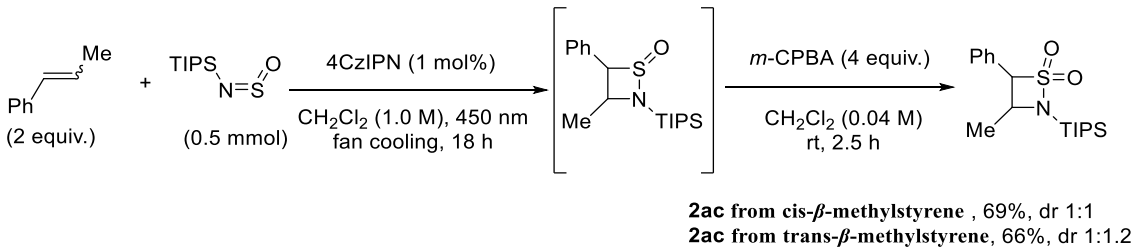


Entry	Variations from standard	Yield[a]
1	none	83%
2	No photocatalyst, 450 nm, 40 h	25%
3	No photocatalyst, 390 nm, 40 h	64%
4	No photocatalyst, 390 nm, 18 h	40%
5	No photocatalyst, 370 nm, 18 h	20%
6	No photocatalyst, No light, 40 ^{o}C, 18 h	0%
7	No photocatalyst, No light, 60 ^{o}C, 18 h, in DCE	0%
8	4CzIPN, No light, rt. 18 h	0%
9	in MeCN	83%
10	No photocatalyst, 450 nm, in MeCN	6%

Reaction conditions: TIPSNSO (0.5 mmol, 1.0 equiv.), styrene (1.0 mmol, 2 equiv.), 4CzIPN (1 mol%), CH_2Cl_2 (0.5 ml, 1.0 M), fan cooling, 18 h. (a) Combined yield for both diastereomers determined by ^{1}HNMR spectroscopy using dibromomethane as an internal standard.

Given light is fundamental to the reaction and the photocatalyst dramatically increases the efficiency of the cycloaddition, it is unlikely for the reaction proceed through a concerted

pathway. We then found when *cis*-*β*-methylstyrene and *trans*-*β*-methylstyrene were used with the optimal conditions, followed by oxidation to *β*-sultams, the corresponding *β*-sultams were afforded in a nearly identical diastereoselectivity (**Scheme 2-11**). This result is consistent with the reaction proceeding through the triplet state while the formed diradical intermediate is capable of free rotation to give similar results from alkenes with different configurations.



2ac from cis-*β*-methylstyrene , 69%, dr 1:1
2ac from trans-*β*-methylstyrene, 66%, dr 1:1.2

Scheme 2-11 Control experiment with *β*-methylstyrenes[a]

Reaction conditions: TIPSNSO (0.5 mmol, 1.0 equiv.), *β*-methylstyrenes (1.0 mmol, 2 equiv.) and 4CzIPN (1 mol%), CH_2Cl_2 (0.5 ml, 1.0 M), fan cooling, 18 h; then *m*-CPBA (2.0 mmol, 4.0 equiv.), CH_2Cl_2 (12.0 mL, 0.04 M). (a) The diastereomeric ratio determined by ^{1}HNMR spectroscopy using dibromomethane as an internal standard.

2.6.2 Stern-Volmer Quenching

In order to demonstrate the proposed mechanism, we then examined the emission spectra of 4CzIPN photocatalyst, in the presence of different concentrations of TIPSNSO or styrene in CH_2Cl_2. This allowed us to demonstrate which compound in the catalytic system quenches the excited state of 4CzIPN, as the better quencher would have a trendline of higher slope in the Stern-Volmer plot (**Figure 2-6**).

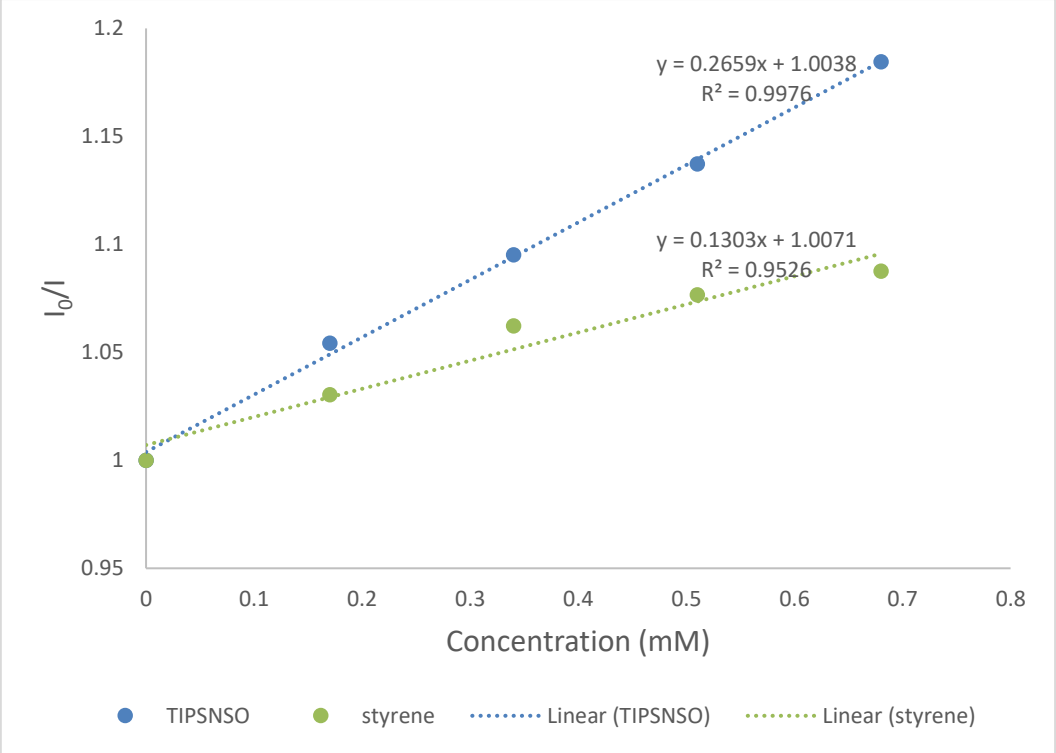


Figure 2-6 Stern-Volmer plot for the solution of photocatalyst with varying concentration of styrene and TIPSNSO at 25 °C in CH_2Cl_2 at λ_{max} = 540 nm.

The trendline of styrene has a lower slope compare to the trendline of TIPSNSO, suggesting it is not likely for the styrene to initiate the reaction. Meanwhile, it is reported that the addition of alkyl radicals to sulfinylamines is kinetically favorable.[54] This implies that the less substituted carbon radical would be more likely to attack the sulfinylamine if the diradical species was generated from the alkene, which contradicts the regioselectivity we observe for the [2+2] photocycloaddition reaction. The result of Stern-Volmer plot further enforces that the interaction between TIPSNSO and 4CzIPN is fundamental to the reaction, although the reductive quenching or oxidative quenching pathways still can't be excluded.

2.6.3 UV Absorption Spectra

The UV absorption spectrum of 4CzIPN exhibits an obvious absorption band at 450 nm, confirming its role as the predominant photoactive species during irradiation. In contrast, TIPSNSO exhibits negligible absorption above 400 nm, which strongly suggests that energy transfer pathway rather than direct excitation pathway should be dominant in the [2+2] photocycloaddition process (**Figure 2-7**). It is notable that there is negligible overlap between the absorption of TIPSNSO and the emission of 4CzIPN, suggesting it is not likely to proceed via a Forster energy transfer pathway (**Figure 2-7** and **Figure 2-8**).

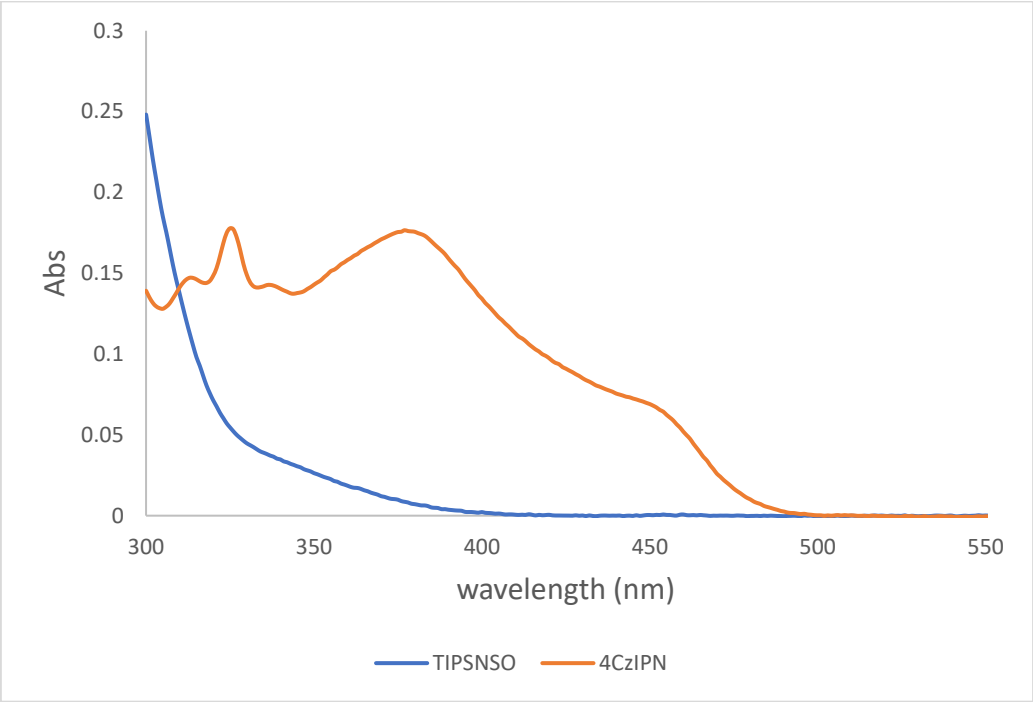


Figure 2-7 UV absorption of TIPSNSO and 4CzIPN at 25 ºC in CH_2Cl_2.

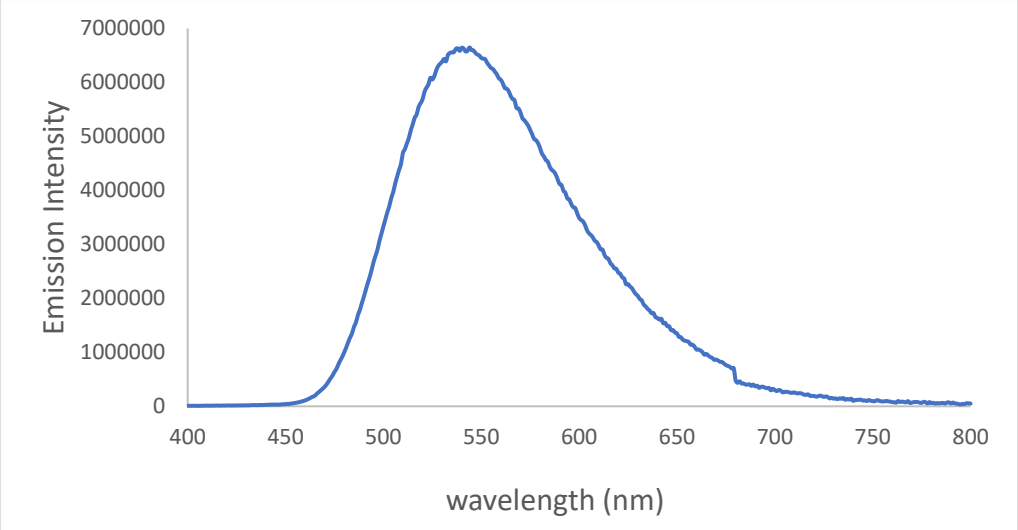


Figure 2-8 UV Emission of 4CzIPN at 25 °C in CH_2Cl_2 at $\lambda_{excitation}$ = 350 nm.

2.6.4 Cyclic Voltammetry

To determine whether the quenching of 4CzIPN with TIPSNSO proceeds via a redox pathway or an energy transfer pathway, we recorded cyclic voltammetry spectra of TIPSNSO in acetonitrile, and compared it with the reported redox potential of 4CzIPN. Cyclic voltammetry (CV) measurements in acetonitrile were conducted, while ferrocene was added after the experiment. The reduction potential of TIPSNSO ($E(TIPSNSO/TIPSNSO^{\bullet-})$ = -1.40 V (vs SCE)) was obtained. It's notable that both 4CzIPN ($E(4CzIPN^*/4CzIPN^{\bullet+})$ = -1.18 V (vs SCE)) and $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ ($E(Ir\text{-}F^*/ Ir\text{-}F^{\bullet+})$ = -0.89 V (vs SCE)) were unable to reduce TIPSNSO, indicating the reaction is not likely to proceed via a photoredox pathway (**Figure 2-8 B)**.

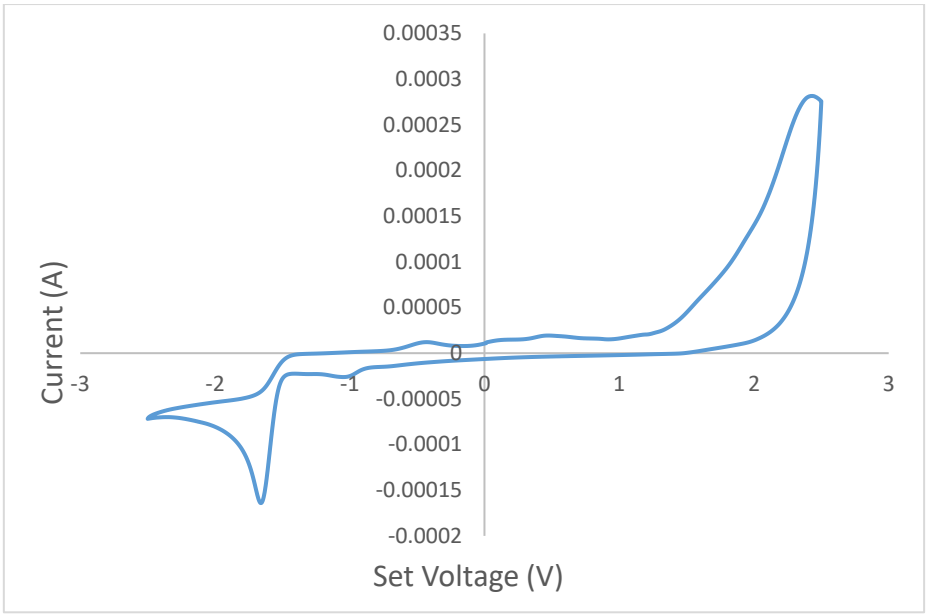


Figure 2-8 A Cyclic voltammetry of TIPSNSO for reduction without ferrocene.

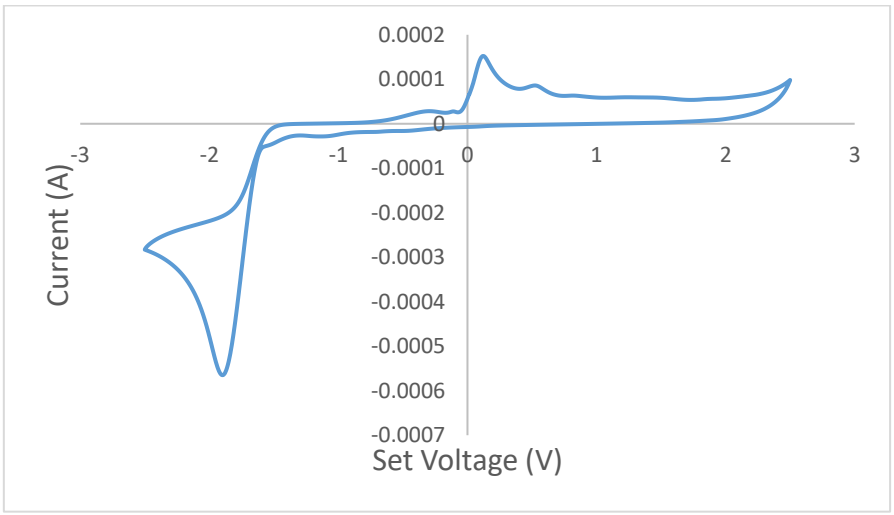
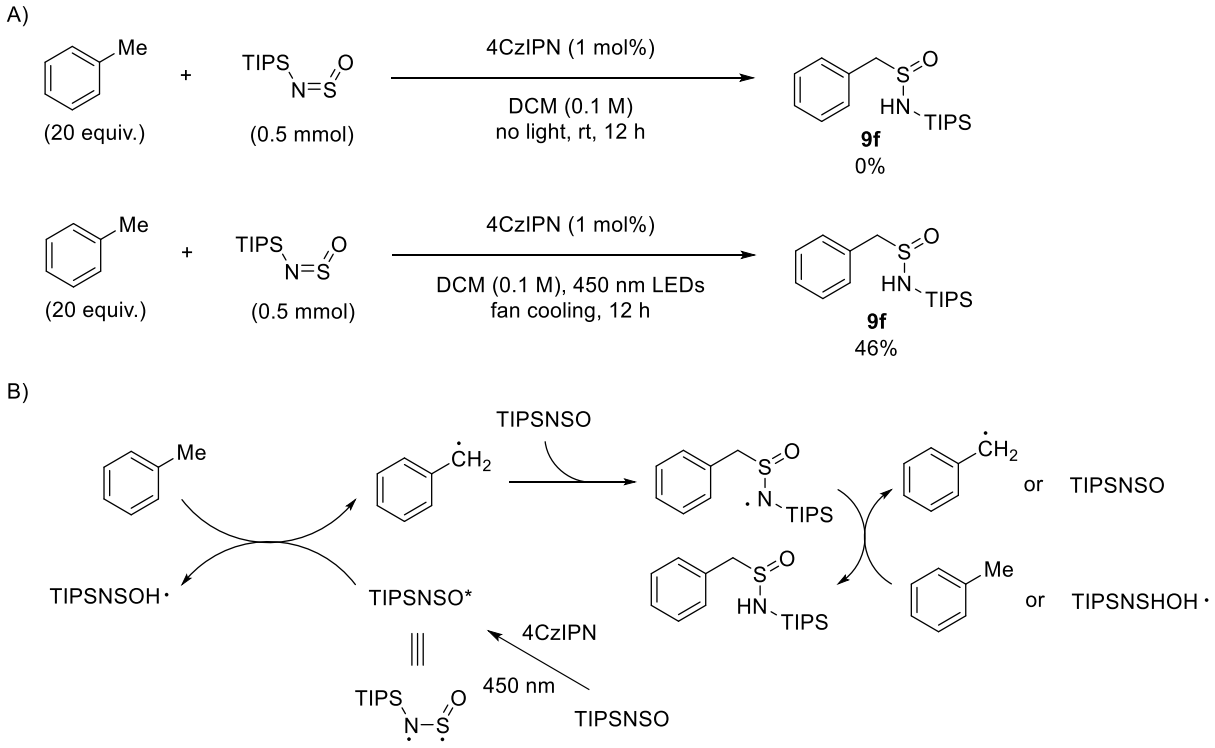


Figure 2-8 B Cyclic voltammetry of TIPSNSO for reduction in the presence of ferrocene.

2.6.5 HAT Reaction

Another convincing piece of evidence for the excitation of TIPSNSO is the hydrogen atom transfer reaction, as the excitation of TIPSNSO would provide a nitrogen radical and sulfur radical pair, which could be used in HAT reactions. We were delighted to find that when irradiating the mixture of TIPSNSO and toluene with 4CzIPN at 450 nm, the corresponding

toluene-derived sulfinamide could be isolated in decent yield (**Scheme 2-12 A**). As we have confirmed 4CzIPN is not likely to reduce TIPSNSO to TIPSNSO$^{\bullet-}$, and that toluene has an oxidation potential of E(toluene/toluene$^{\bullet+}$) = +2.26 V (vs SCE) which indicates that it can't be oxidized by 4CzIPN to provide a benzyl radical, we hypothesized that the benzyl radical should be generated by the HAT reaction with triplet TIPSNSO. First, the TIPSNSO gets excited to provide a diradical species, which then undergoes a hydrogen atom transfer reaction with toluene to form a benzyl radical. The benzyl radical then subsequently attacks another molecular of TIPNSO to afford a sulfinamide radical. The formed sulfinamide radical undergoes a HAT reaction with another molecular of toluene or TIPSNSOH radical to generate the corresponding sulfinamide (**Scheme 2-12 B**).



Scheme 2-12 (A) HAT reaction between toluene and TIPSNSO (B) Proposed mechanism for HAT reaction.

2.7 Summary

In conclusion, we have established a pioneering methodology for the modular synthesis of *β*-sultams and aza-*β*-sultams via energy transfer catalysis of silyl-substituted sulfinylamines and subsequent oxidation or imidation. The approach relies on bench-stable TIPSNSO and readily available alkenes, streamlining the synthetic pathway significantly. This versatile method tolerates diverse functional groups, empowering researchers to explore bioactivities of these cyclic S(VI) compounds. Both *β*-sultams and aza-*β*-sultams undergo efficient ring-opening reactions, yielding taurine analogues and related bioactive targets. Further mechanistic studies demonstrate the reaction likely undergoes an energy transfer pathway rather than single electron transfer or concerted process. These findings represent a significant advancement in accessing novel sulfur scaffolds with broad applicability in medicinal chemistry and pharmaceutical development.

Chapter 3 - Addition to Sulfinylamine with Zirconium Reagent *in situ* Formed from Schwartz Reagent

3.1 Introduction

3.1.1 Importance of Sulfinamides

Sulfinamides represent a versatile class of sulfur(IV) compound characterized by a stereogenic sulfur center, which have garnered considerable attention for their role in the divergent synthesis of sulfur(VI) functional bioisosteres (**Figure 3-1**). These compounds serve as pivotal precursors in accessing different sulfur(VI) architectures; mild oxidative transformations of sulfinamides yield sulfonamides, while imination strategies enable the construction of sulfonimidamides, the mono-aza analogue of sulfinamides.[86] Notably, sulfonimidoyl fluorides, aza-isosteres of sulfonyl fluorides, can also be prepared from sulfinamides, emerging as prominent sulfur(VI) electrophiles, and finding utility as robust SuFEx (Sulfur Fluoride Exchange) click reagents for modular assembly of sulfur-functionalized scaffolds.[87] Beyond these, other sulfur(VI) derivatives of broad applicability in medicinal and synthetic chemistry, including sulfones,[88] sulfonediimines,[89] and sulfonimidates,[90] can also be synthesized from sulfinamides.

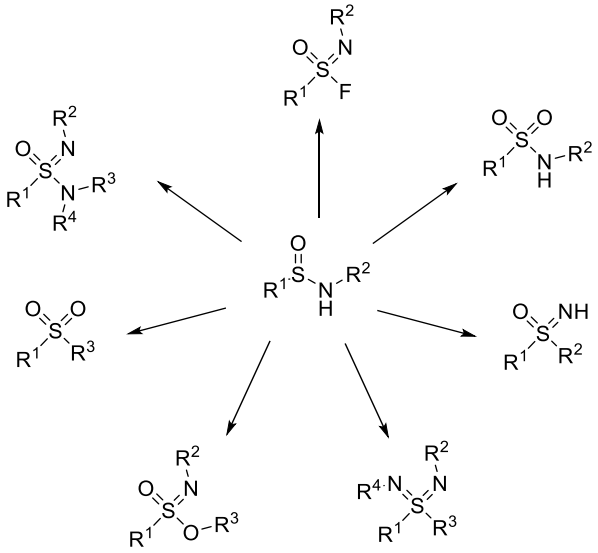
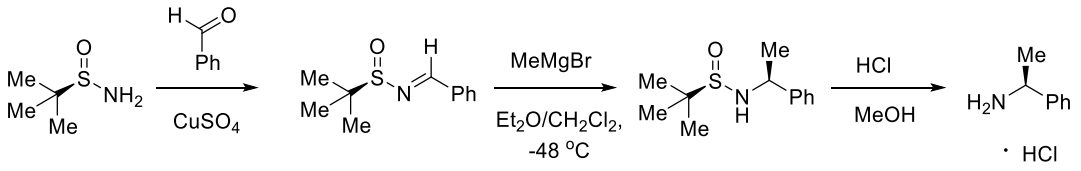


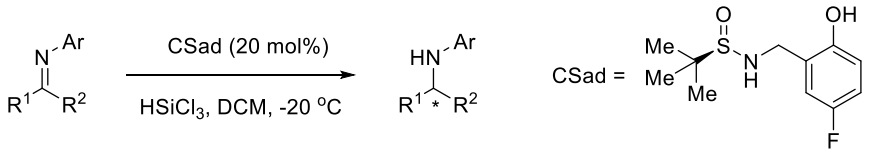
Figure 3-1 Synthesis of sulfur(VI) functionalities from sulfinamides.

In addition to their synthetic versatility, sulfinamides are distinguished by their capacity to serve as enantioenriched sulfur-based chiral motifs. Their applications include transition metal catalysis, as stereodirecting ligands, and organocatalysis. Since Ellman's report on their application in the asymmetric synthesis of enantiomerically enriched amines in 1997, enantiopure sulfinamides have been established as privileged chiral auxiliaries in academia and industry.[91] Their condensations with aldehydes or ketones proceeds efficiently under mild conditions, generating sulfinyl imines in high yields. The sulfinyl group not only activates these imines toward nucleophilic addition but also imposes precise stereochemical control, typically delivering products with exceptional diastereoselectivity. Subsequent cleavage of the sulfinyl directing group under mild acidic conditions affords enantiopure amine derivatives, underscoring the practicality of this methodology (**Scheme 3-1**).



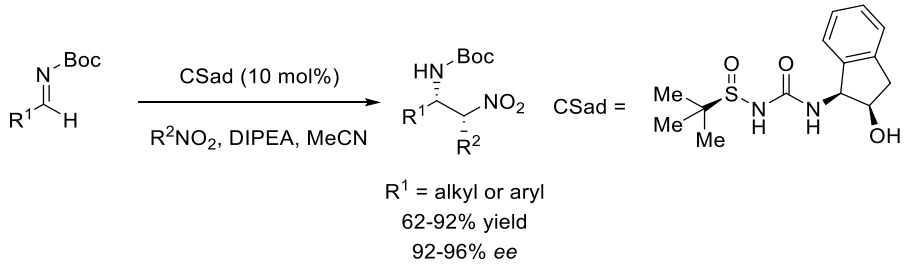
Scheme 3-1 Synthesis of chiral amines from the Ellman's auxiliary.

Since sulfinamides have a SO double bond as a good hydrogen bond acceptor and Lewis base, and a NH bond as a good hydrogen bond donor, over the last years, more and more examples of *tert*-butylsulfinamide-based organocatalysts have emerged. The first report is from Sun and and co-workers, reducing prochiral aromatic imines to chiral amines using trichlorosilane as the hydrogen source, with *tert*-butylsulfinamide as the organocatalyst.[92] Amines substituted with different functional groups can be generated in high yield and excellent enantioselectivity (**Scheme 3-2**).



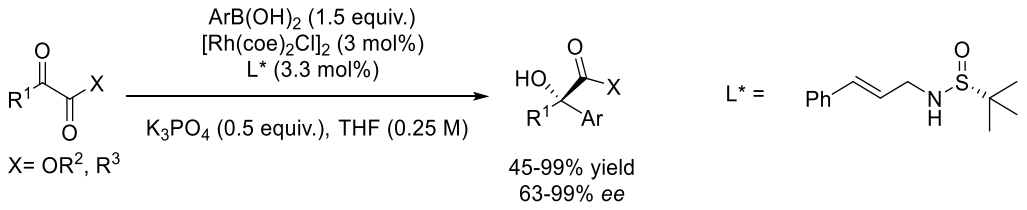
Scheme 3-2 Chiral sulfinamides as highly enantioselective organocatalysts in asymmetric hydrogenation.

In 2007, the Ellman group developed a new class of *N*-sulfinyl urea organocatalyst.[93] They took advantage of sulfinyl group as both chiral directing group and electron-withdrawing substituent on the urea motif, to make urea motif a better hydrogen-bond donor. Then, they found these catalysts can successfully catalyse aza-Henry reactions with *N*-Boc imine substrates. Both alkyl imines and aryl imines afforded the chiral amine products in high yields and excellent selectivities (**Scheme 3-3**).



Scheme 3-3 Asymmetric aza-Henry reaction with *N*-sulfinyl urea organocatalyst.

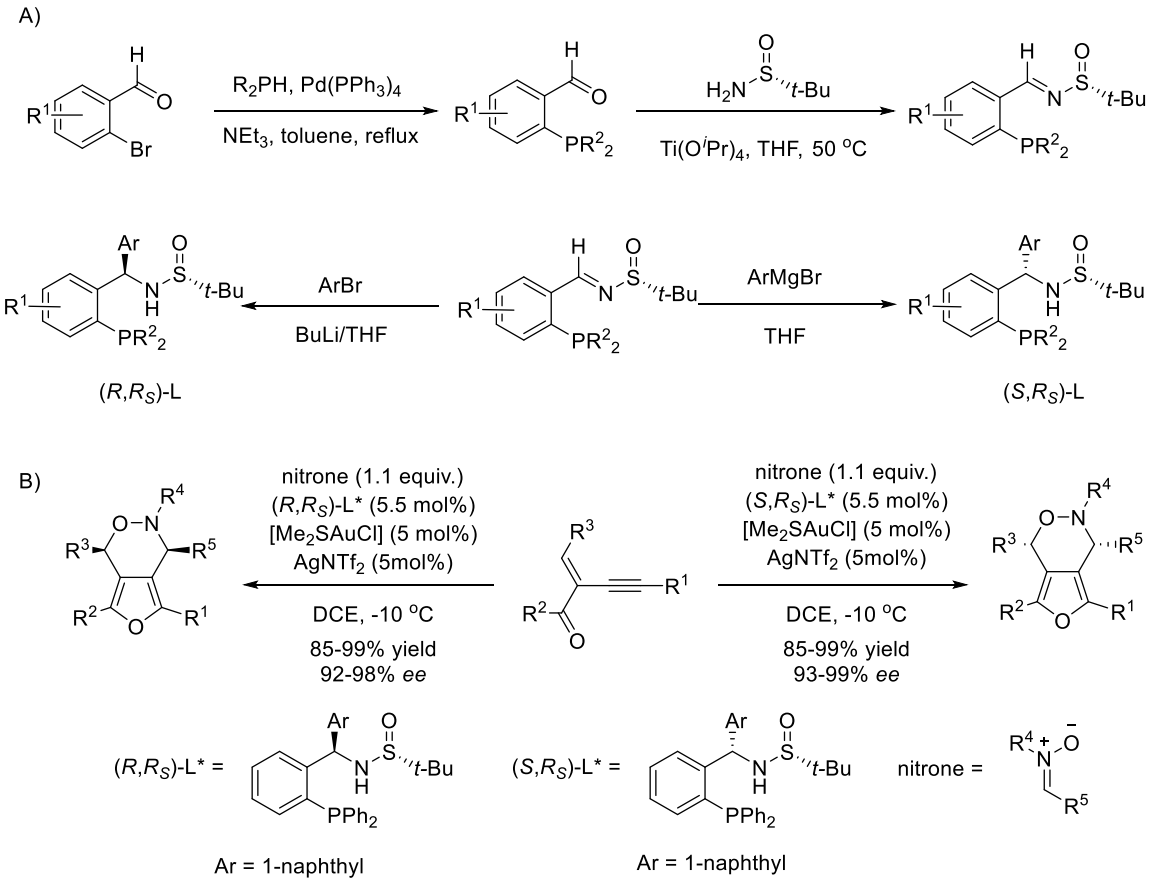
Despite unique reactivity as organocatalysts, sulfinamides also work as highly efficient ligands in transition-metal catalysts. In 2011, the Xu group developed a rhodium catalysed asymmetric synthesis of α-hydroxyl esters or α-hydroxyl ketones.[94] Chiral sulfur-olefin ligands were used in this rhodium-catalysed reaction, affording the products with moderate yields and excellent enantioselectivities (**Scheme 3-4**).



Scheme 3-4 Chiral sulfinamides used as ligand with rhodium catalyst.

The integration of phosphine and chiral sulfinamide motifs into a unified ligand architecture, named as Sadphos, has emerged as a highly effective ligand class for palladium, copper, and other transition-metal catalysts.[95] These ligands exhibit a versatile structural framework characterized by several advantages: (i) simultaneous enantioenrichment at both carbon and sulfur stereogenic centers; (ii) synthetic accessibility to all enantiomeric configurations; (iii) tunable electronic properties at the phosphine moiety *via* modification of benzaldehyde-derived starting materials; (iv) a multidentate coordination environment comprising phosphorus, oxygen, sulfur, and nitrogen donor atoms, enabling diverse binding modes with transition metals. Additionally, the retention of hydrogen-bonding capability within the sulfinamide moiety enhances substrate-ligand interactions, while the modular synthesis of Sadphos derivatives, achieved within four steps from commercially available precursors, ensures broad structural diversity (**Scheme 3-5 A**). The application of these ligands was exemplified in 2014 by Zhang and colleagues, who utilized a Sadphos ligand to enable a gold-catalysed

cycloaddition reaction, delivering asymmetric oxazinane scaffolds with exceptional yields (up to 98%) and enantioselectivities (up to 99% *ee*).[96] This work underscores the potential of Sadphos to address challenges in stereoselective catalysis through rational ligand design, combining electronic flexibility, stereochemical control, and synthetic efficiency (**Scheme 3-5 B**).



Scheme 3-5 A) General procedure to synthesize Sadphos. B) Enantioselective gold(I)-catalysed cycloaddition reactions with Sadphos as the ligand.

In summary, the dual role of sulfinamides, as linchpins for constructing sulfur(VI) architectures and as enantioselective tools, highlights their potential in organic synthesis, bridging the gap between functional group diversification and enantioenriched compounds formation.

3.1.2 Synthesis of Sulfinamides

In retrosynthetic analysis, sulfinamide scaffolds are predominantly constructed through strategic formation of C–S, N–S, or S–O bonds, employing different sulfur-containing starting materials. A prominent approach involves C–S bond formation *via* reacting organometallic reagents, including organolithium reagents, Grignard reagents or organozinc reagents, which act as carbon nucleophiles, with sulfur-based electrophiles such as *N*-sulfinylamines. This methodology has been established as an efficient route to diverse sulfinamides. Alternatively, selective S–N bond formation strategies using sulfur building blocks, including thiols, disulfides, sulfinyl chlorides, and sulfinate derivatives, have also emerged as powerful protocols for synthesizing sulfinamides. Furthermore, oxidation of sulfenamides under controlled conditions offers a complementary pathway to access sulfinamides, underscoring the synthetic flexibility of sulfur redox chemistry in generating sulfinamides (**Figure 3-1**).

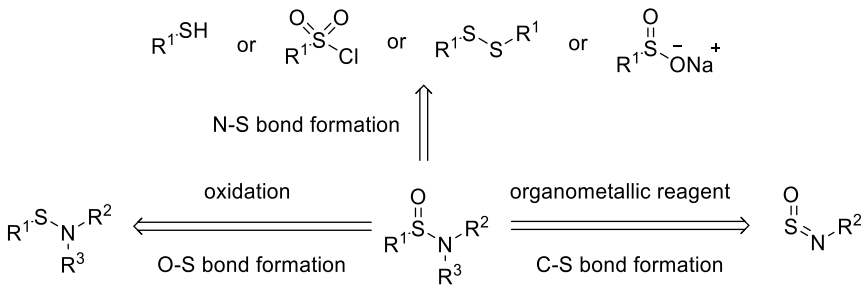
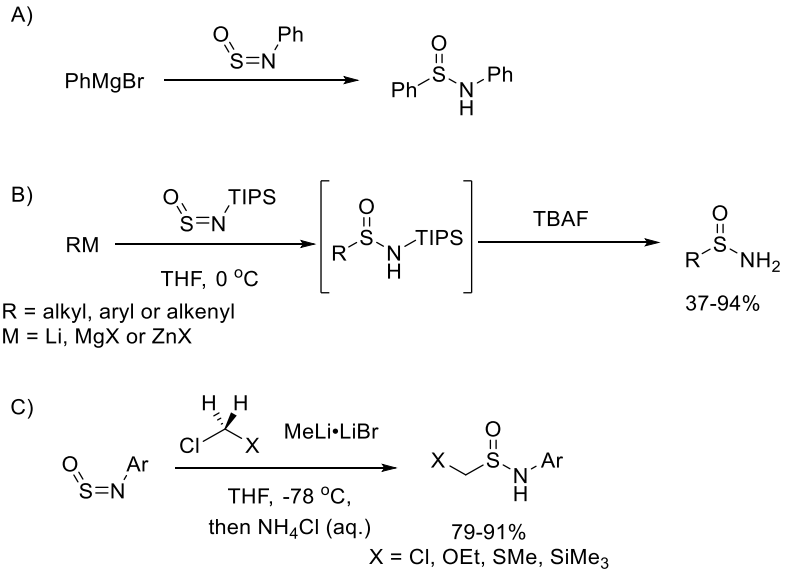


Figure 3-1 Retrosynthesis analysis for the synthesis of sulfinamides.

The reaction of sulfinylamines with organometallic reagents traces its origins to the discovery by Gilman and Morris in 1926, who demonstrated that phenylsulfinylamine undergoes C–S bond formation with Grignard reagents to yield phenylsulfinamide (**Scheme 3-6 A**).[97] In 2022, Minyan Ding in our group developed a bench-stable sulfinylamine, TIPSNSO. Minyan utilized this stable silyl-sulfinylamine to react with Grignard reagents, lithium reagents, and organozinc reagents, followed by *in situ* TBAF-mediated desilylation, enabling the synthesis of primary sulfinamides in yields ranging from 37% to 94% yield (**Scheme 3-6 B**).[51] Further progress

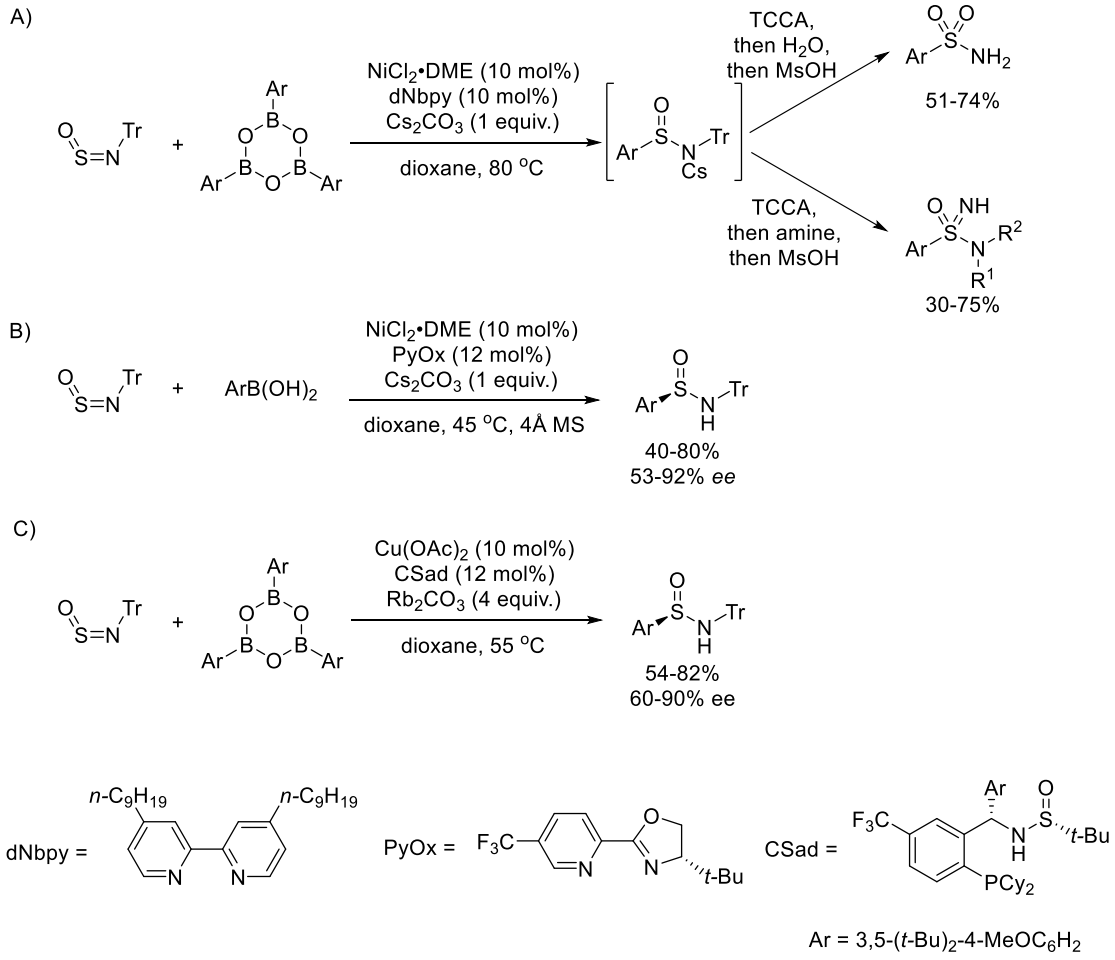
was achieved in 2023 by the Pace group, who disclosed a methodology employing α-substituted lithium reagents (*in situ* formed from chlorine-lithium exchange between substituted alkyl chloride with MeLi•LiBr) to access α-functionalized sulfinamides (79% to 91% yield) *via* reaction with aryl-sulfinylamines.[98] While this approach permits the installation of α-chloro, α-ethoxy, α-methylthio, and α-silyl substituents, it necessitates excessive amount of the organolithium reagent to suppress the formation of methyl sulfinamide byproduct. Additionally, the inherent instability of the lithium carbenoid intermediates mandates strict reaction conditions, requiring temperatures of −78 °C to suppress decomposition (**Scheme 3-6 C**).



Scheme 3-6 Reactions between sulfinylamines and organometallic reagents.

Transition-metal catalysed reactions to access sulfinamides have also been studied in the recent years. In 2021, the Willis group reported nickel-catalysed aryl and alkenyl boroxine addition to TrNSO to form sulfinamides. The formed sulfinamides can be *in situ* converted to sulfonamides and sulfonimidamides in decent yields (**Scheme 3-7 A**).[86] In 2024, the Shi group pioneered the enantioselective adaptation of this transformation, employing aryl boronic acids as starting materials to achieve stereocontrolled synthesis of sulfinamides in good yields and

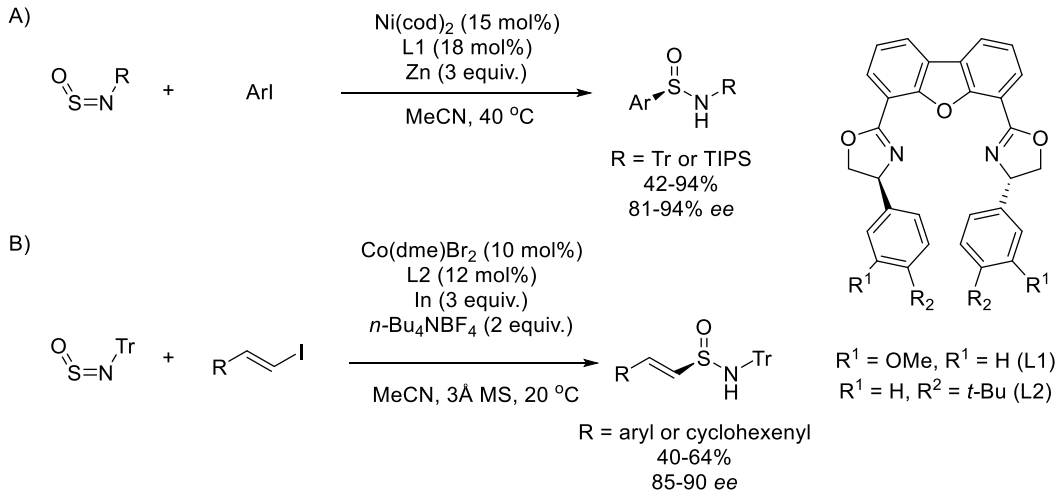
high enantioselectivities (**Scheme 3-7 B**).[99] At the same time, the Zhang group also succeed in generating enantioenriched sulfinamides with a copper-catalysed system with Sadphos as chiral ligand (**Scheme 3-7 C**).[100]



Scheme 3-7 A) Nickel-catalysed one pot synthesis of sulfonamides and sulfonimidamides via sulfinamide intermediates. B) Enantioselective synthesis of sulfinamides with nickel catalyst and chiral PyOx ligands. C) Enantioselective synthesis of sulfinamides with copper catalyst and chiral sulfinamide ligands.

In addition to the conventional aryl boronic acids or aryl boroxines as starting materials, Shi and Willis demonstrated that aryl iodides can undergo insertion into sulfinylamines to yield enantioenriched sulfinamides (**Scheme 3-8 A**).[101] Notably, by replacing the nickel catalyst with a cobalt catalyst, they enabled the reaction of TrNSO with *E*-styrenyl iodide (synthesized

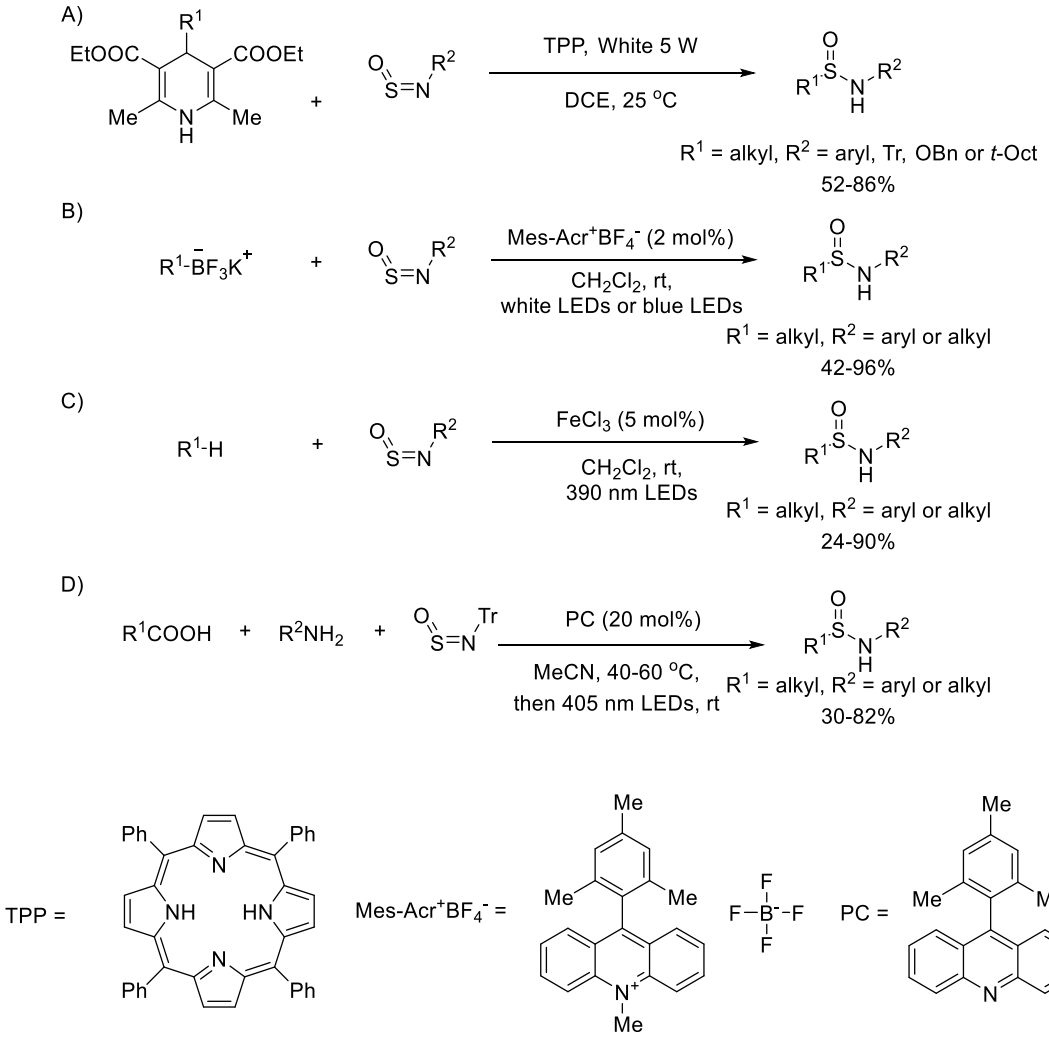
from *E*-cinnamic acid) to afford styrenyl sulfinamides in moderate yields with high enantioselectivity (**Scheme 3-8 B**). In 2024, the Willis group employed aryl bromides and alkenyl triflates as alternative substrates in a palladium-catalysed system for sulfinamide synthesis, a strategy previously outlined in **Chapter 1** (**Scheme 1-14 B**).



Scheme 3-8 Enantioselective synthesis of chiral sulfinamides from aryl iodides or alkenyl iodides.

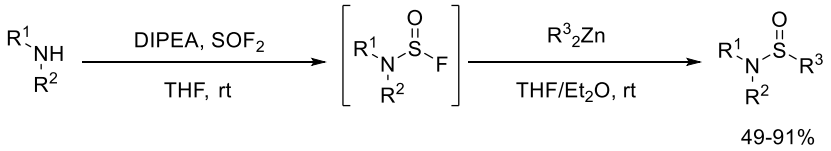
As outlined in **Chapter 1** (**Scheme 1-15**), alkyl carboxylic acids serve as viable alkyl radical precursors for sulfinamide synthesis. Recent advancements in photochemical methodologies have expanded the scope of alkyl radical precursors compatible with sulfinylamines. In 2022, the Li group demonstrated that 4-alkyl-1,4-dihydropyridines (DHPs), in the presence of tetraphenylporphyrin (TPP) as a photocatalyst, efficiently generate alkyl sulfinamides under visible-light irradiation, achieving moderate to good yields (**Scheme 3-9 A**).[102] Subsequently, both the Li[103] and Sahoo[104] groups independently reported the utility of potassium alkyltrifluoroborates as robust alkyl radical precursors, employing acridinium tetrafluoroborate as a photocatalyst to afford alkyl sulfinamides with high functional group tolerance (**Scheme 3-9 B**). More recently, the Hu group, in 2024, disclosed an iron-catalysed hydrogen atom transfer (HAT) strategy, utilizing iron(III) chloride under photochemical conditions to directly convert alkanes into alkyl sulfinamides, avoiding the need for prefunctionalized substrates (**Scheme 3-9 C**).[105] In 2024, the Willis group introduced a novel trans-sulfinylation

methodology for the synthesis of sulfinamides, employing bench-stable TrNSO, primary amines, and carboxylic acids.[106] This strategy generated alkyl/aryl sulfinylamine intermediates through the reaction equilibrium between TrNSO with primary amines, circumventing the need for isolation and preparation of unstable sulfinylamines. Subsequently, the *in situ* formed sulfinylamines undergo a decarboxylative alkylation with carboxylic acids, enabling efficient and modular access to diverse *N*-alkyl or aryl sulfinamides (**Scheme 3-9 D**). While photochemical protocols offer milder reaction conditions compared to traditional organometallic approaches, current methodologies remain predominantly limited to the synthesis of alkyl sulfinamides, highlighting a need for further exploration into diversifying substrate scope.



Scheme 3-9 Visible-light-mediated alkyl sulfinamide synthesis.

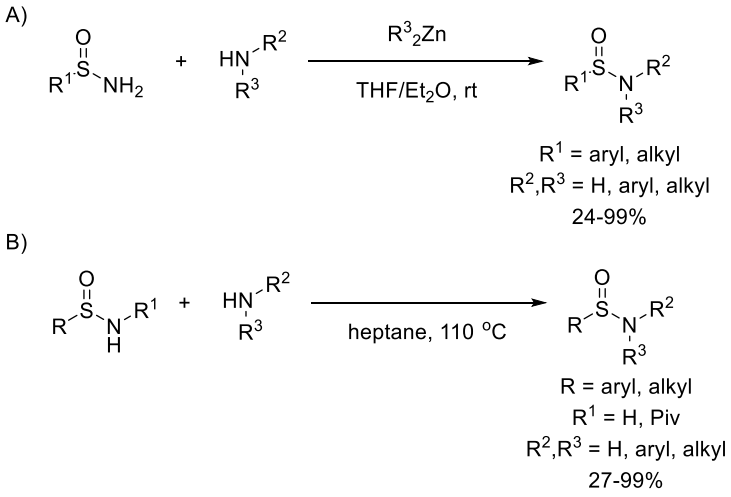
In 2024, Sammis and colleagues developed a novel rapid and efficient methodology for synthesizing sulfinamides *via* sulfur(VI) fluoride exchange (SuFEx) chemistry.[107] The protocol employs readily available secondary amines, thionyl fluoride (SOF_2), and organozinc reagents under ambient conditions, demonstrating exceptional efficiency and broad functional group tolerance. The reaction proceeds through the initial formation of an amino sulfinyl fluoride intermediate, generated *via* the reaction of SOF_2 with a secondary amine. This reactive intermediate is subsequently *in situ* captured by an organozinc nucleophile, ultimately yielding the desired sulfinamide product. This approach offers a synthetic route to sulfinamides, avoiding traditional multistep procedures while maintaining high atom economy. However, only secondary amines can be used as the starting materials, and the reaction is also restricted in using zinc reagent and highly toxic thionyl fluoride gas (**Scheme 3-10**).



Scheme 3-10 Synthesis sulfinamides from thionyl fluoride, secondary amines and organozinc reagents.

Despite the amino group's conventional classification as a poor leaving group in nucleophilic substitution reactions, recent studies have documented successful trans-sulfinamidation processes with sulfinamides. Notably, in 2021, the Tu group demonstrated a catalytic strategy employing europium(III) trifluoromethanesulfonate to facilitate the conversion of primary sulfinamides into either monosubstituted or disubstituted analogues through reaction with primary or secondary amines (**Scheme 3-11 A**).[108] In 2023, the Kano group reported a metal-free trans-sulfinamidation strategy, representing a notable advancement in sulfinamide

functionalization. However, the methodology necessitates high temperatures (70 °C to 110 °C), which may limit its applicability to thermally sensitive sulfinamides (**Scheme 3-11 B**).[109]

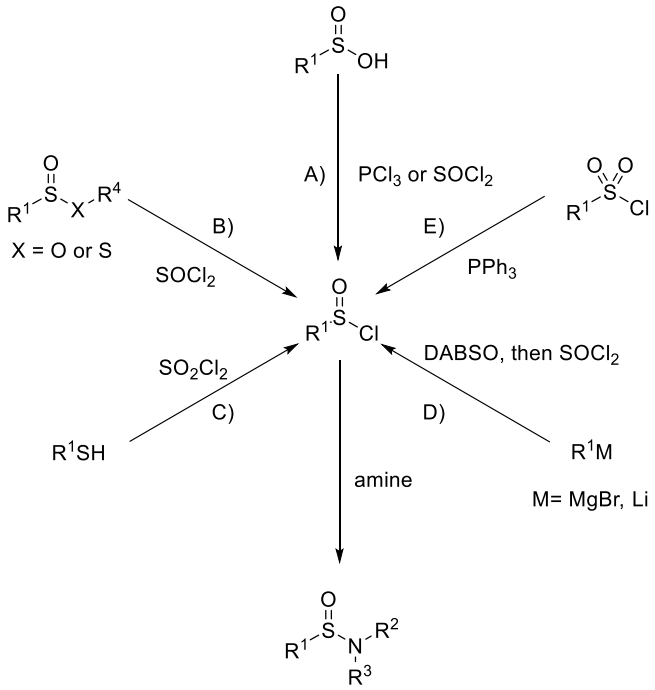


Scheme 3-11 Trans-sulfinamidation to synthesize sulfinamides.

Sulfinamides are traditionally synthesized *via* the amination of sulfinyl chlorides, a class of intermediate notorious for their inherent instability. To circumvent this limitation, researchers have developed alternative precursors to access sulfinyl chloride intermediates, enabling sulfinamide formation through sequential amination. Common strategies include treating sulfinic acids with chlorinating agents such as PCl_3,[110] $SOCl_2$[111] or condensation reagents such as DCC,[112] followed by amine coupling (**Scheme 3-12 A**). Alternative routes involve the amination of sulfinate esters[113] or thiosulfinate esters,[114] which are derived from sulfinic acids or disulfides(**Scheme 3-12 B**). Additionally, thiols have been utilized as starting materials, undergoing either one-pot oxidative chlorination[115] and subsequent amination (**Scheme 3-12 C**).

In 2020, the Willis group employed Grignard or lithium reagents in conjunction with DABSO to generate sulfinate intermediates, subsequently subjected to chlorination and amination to generate aryl and alkyl sulfinamides (**Scheme 3-12 D**).[116] In 2007, the Harmata group

demonstrated the access of sulfinyl chlorides *via* the reaction of sulfonyl chlorides with triphenylphosphine (**Scheme 3-12 E**).[117] Despite these innovations, conventional approaches remain constrained by several critical drawbacks: i) reliance on highly reactive reagents (e.g., Grignard or organolithium species), which narrows substrate compatibility; ii) dependence on sulfinates, thiols, or disulfides, often commercially inaccessible, particularly for complex architectures; iii) a predominant focus on aryl and alkyl sulfinamides, with alkenyl derivatives remaining underexplored. These limitations underscore the need for versatile, substrate-tolerant methodologies to expand the structural and functional diversity of sulfinamides available from commercially available starting materials.



Scheme 3-12 Conventional protocols to synthesize sulfinamides via sulfinyl chlorides.

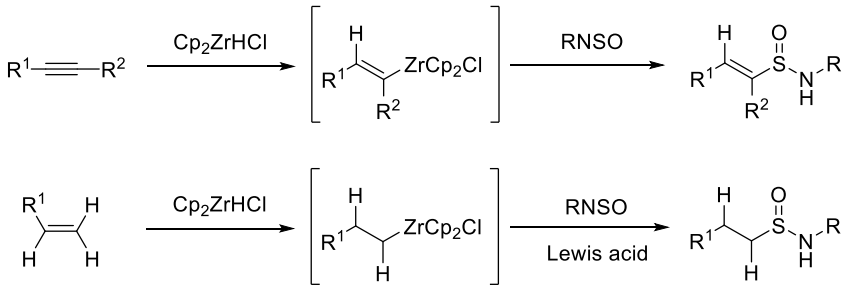
3.2 Synthetic Strategy

As discussed in **Chapter 3.1.2**, conventional synthetic routes to sulfinamides predominantly rely on highly reactive Grignard or organolithium reagents, which impose significant limitations on substrate scope. Meanwhile, reported methodologies with thiols, sulfinic acids or disulfides are restricted to aryl and alkyl sulfinamides, while alkenyl sulfinamides remain underexplored. Consequently, the development of an efficient strategy for alkenyl sulfinamide synthesis from commercially available starting materials inspired our interest.

Recent advances in transition metal hydride chemistry, including CuH,[118] NiH[119] and CoH,[120] involving the insertion of metal hydride into alkynes or alkenes followed by electrophilic trapping, have emerged as a promising protocol for constructing versatile functionalities from alkynes and alkenes. Inspired by these methodologies, we envisioned a one-pot, two-step approach where metal hydride inserts into unsaturated carbon-carbon bonds to *in situ* generate alkenyl or alkyl organometallic intermediates, which could subsequently react with sulfinylamines to afford alkenyl or alkyl sulfinamides.

Despite the potential of this strategy, the key challenge arises from the inherent redox sensitivity of sulfinylamines, which can be reduced under metal hydride-mediated conditions. Furthermore, conventional catalytic systems often necessitate strongly basic additives (e.g., potassium *tert*-butoxide) to facilitate ligand exchange and protic additive (e.g., isopropyl alcohol) for regeneration of transition metal catalyst, risking the decomposition of electrophilic sulfinylamines. To circumvent these limitations, we proposed a stoichiometric protocol by employing a bench-stable metal hydride to prepare the organometallic species prior to sulfinylamine coupling. This work introduces the application of Schwartz's reagent (Cp_2ZrHCl), a well-established zirconium hydride,[121] to generate hydrozirconation of alkynes or alkenes. The resultant alkenyl or alkyl zirconium intermediates exhibit remarkable

compatibility with sulfinylamines, enabling efficient formation of sulfinamides (**Scheme 3-13**). This methodology provides direct access to structurally diverse alkenyl and alkyl sulfinamides with enhanced functional group tolerance and improved yields, addressing longstanding gaps in alkenyl sulfinamide synthetic strategies.

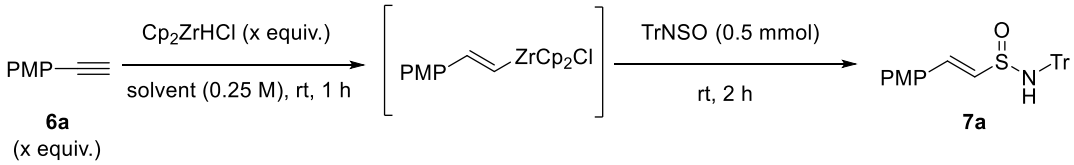


Scheme 3-13 Synthesis of alkenyl and alkyl sulfinamides with *in situ* formed zirconium reagent from Schwartz reagent.

3.3 Synthesis of Alkenyl Sulfinamides with *in situ* Formed Zirconium Reagent

As discussed in the previous chapter, we selected TrNSO as the model starting material to investigate its reactivity with Schwartz reagents and alkyne **6a** (**Table 3-1**). We found that, after optimization, when Schwartz reagent (1.5 equiv.) and 4-methoxyphenylacetylene (1.5 equiv.) were used, the corresponding sulfinamide was obtained in 84% isolated yield at room temperature (**Table 3-1**, **entry 9**). Other solvents including CH_2Cl_2, DCE and dioxane are also compatible with the reaction. Reducing the amount of Schwartz reagent (1.0 equiv.) resulted in a dramatic decline to 48% yield (**Table 3-1**, **entry 10**). When increasing the amount of Schwartz reagent to 2.0 equivalent, a 95% yield of the sulfinamide was achieved (**Table 3-1**, **entry 11**).

Table 3-1 Optimised reaction conditions for the synthesis of alkenyl sulfinamide **7a**.



Entry	X	Solvent	Yield[a,b]
1	1.5	Et_2O	trace
2	1.5	toluene	78%
3	1.5	DCM	83%
4	1.5	dioxane	86%
5	1.5	MTBE	trace
6	1.5	$CHCl_3$	72%
7	1.5	DCE	85%
8	1.5	THF	85%
9[c]	1.5	THF	91% (84%)
10[c]	1.0	THF	47% (48%)
11[c]	**2.0**	**THF**	**98% (95%)**

Reaction conditions: 4-methoxyphenyl acetylene (x equiv.), Cp_2ZrHCl (x equiv.), solvent (2 mL, 0.25 M), rt, 1 h; then TrNSO (0.5 mmol, 1.0 equiv.), rt, 2 h. (a) Determined by ^1H NMR spectra of crude mixtures using dibromomethane as an internal standard. (b) The number in parentheses is isolated yield. (c) 4 hours.

With the optimal conditions in hand, we investigated the scope of the reaction (**Figure 3-2**). This process tolerates a wide range of alkynes with different functional groups (**Figure 3-2**, **7a**-**7t**). Aryl alkynes substituted with both electron-donating and electron-withdrawing groups (**Figure 3-2**, **7a**-**7g** and **7o**) gave the corresponding sulfinamides in moderate to good yields. It is delighted we can scale the reaction up to 3 mmol scale, with **7a** afforded in 82% yield. Functional groups such as chloro-, iodo-, silyl-, and benzoyloxy-groups (**Figure 3-2**, **7h**-**7j** and **7r**) can also be tolerated. Different alkyl-substituted alkynes, including *tert*-butyl, cyclohexyl and *n*-hexyl, as well as internal alkynes can also be used (**Figure 3-2**, **7k**-**7n**). It is worth noting that when using thienyl substituted alkyne and naphthyl substituted alkyne (**Figure 3-2**, **7p** and **7q**), the corresponding sulfinamides can be isolated in 80% yield and 72% yield, respectively.

Meanwhile, changing sulfinylamine from TrNSO to *t*-OctNSO and TIPSNSO also afforded the sulfinamides in excellent yields (**Figure 3-2**, **7s** and **7t**).

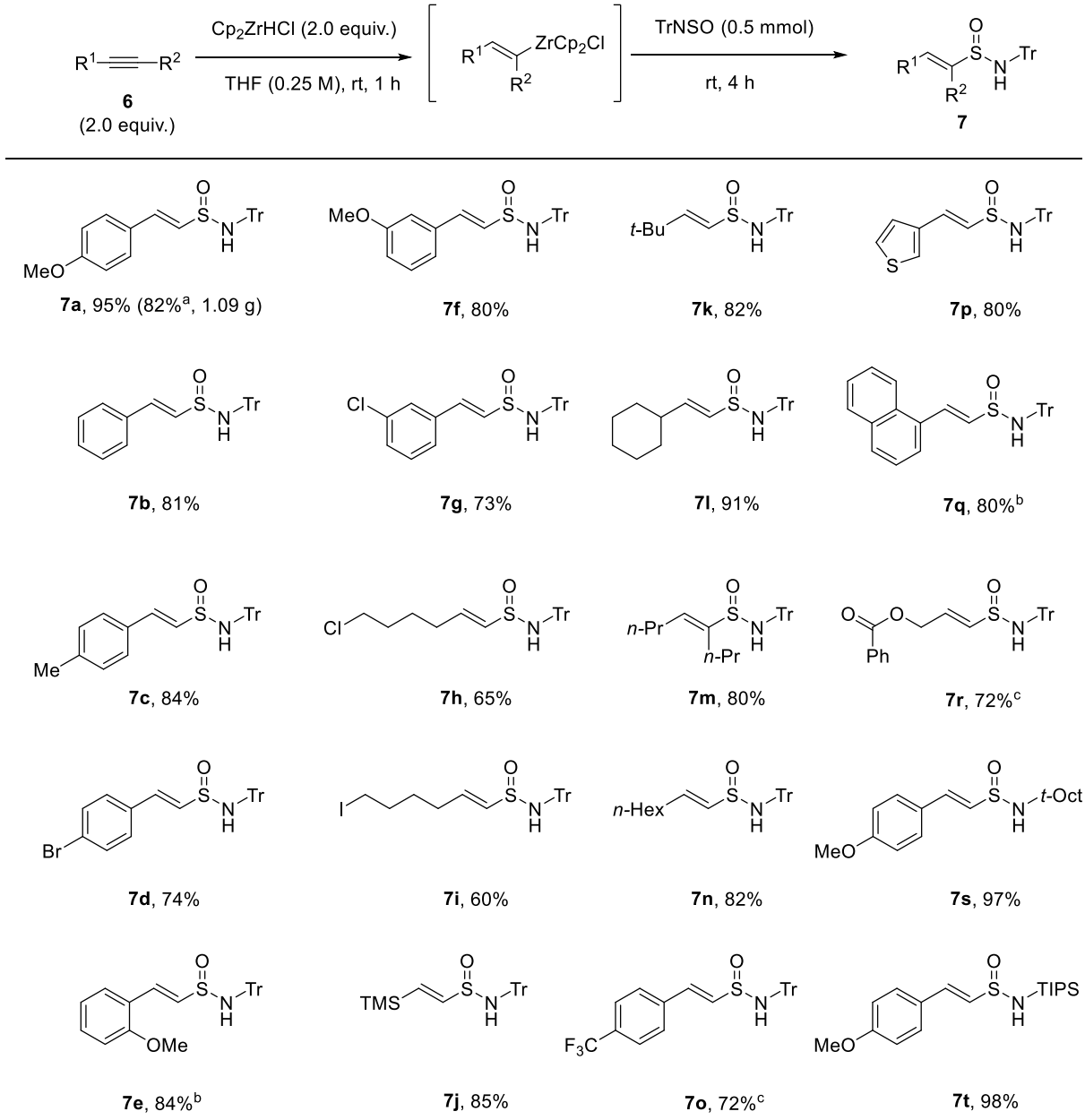


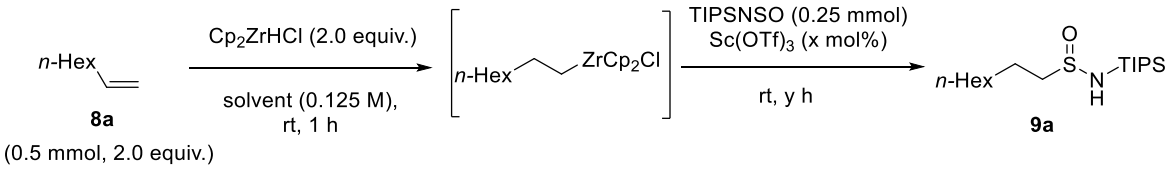
Figure 3-2 The substrate scope of alkenyl sulfinamides.

Reaction conditions: alkyne (1.0 mmol, 2.0 equiv.), Cp_2ZrHCl (1.0 mmol. 2.0 equiv.), THF (2 mL, 0.25 M), rt, 1 h; then sulfinylamine (0.5 mmol, 1.0 equiv.), rt, 4 h. (a) The reaction was conducted on 3 mmol scale. (b) Alkynes were purified by FCC before use. (c) The second step reaction between alkenyl zirconium reagent and TrNSO conducted at 40 °C.

3.4 Synthesis of Alkyl Sulfinamides with *in situ* Formed Zirconium Reagent

Next, we investigated the reactivity of alkyl zirconium reagent generated from alkenes (**Scheme 3-15**). We selected TIPSNSO as the model starting material to investigate its reactivity with Schwartz reagents and alkene **8a** (**Table 3-2**). Although alkyl zirconium reagents have much lower reactivity than alkenyl zirconium reagents, we were delighted to find the addition of scandium triflate in the second step greatly improved the yield of sulfinamide **9a** (**Table 3-2, entry 2**). Further optimization in reaction time and solvent gave sulfinamide **9a** in 89% isolated yield (**Table 3-2, entry 4**).

Table 3-2 Optimised reaction conditions for the synthesis of alkyl sulfinamide **8a**



Entry	X (cat. loading)	Y (time)	Solvent	Yield[a]
1	0	2	THF	0%
2	10	2	THF	64%
3	10	6	THF	83%
4	**10**	**6**	**DCM**	**88% (89%)[b]**

Reaction conditions: *n*-octene (0.5 mmol, 2.0 equiv.), Cp_2ZrHCl (0.5 mmol. 2.0 equiv.), THF (2 mL, 0.125 M), rt, 1 h; then $Sc(OTf)_3$ (x mol%), TIPSNSO (0.25 mmol, 1.0 equiv.), rt, y h. (a) Determined by ^1H NMR spectra of crude mixtures using dibromomethane as an internal standard. (b) The number in parentheses is the isolated yield.

With the optimal conditions in hand, we then investigated the scope of the reaction between *in situ* formed alkyl zirconium reagents and TIPSNSO (**Figure 3-3**). This protocol tolerates a range of terminal alkenes (**Figure 3-3**, **9a-9e**). It is notable that a bromo-substituted alkene can also be tolerated in this reaction (**Figure 3-3**, **9c**). The hindered alkene 3,3-dimethyl-1-butene gave the corresponding sulfinamide in lower yield (**Figure 3-3**, **9d**). When styrene

was used as the starting material, the corresponding sulfinamide was generated in 43% yield due to the formation of anti-Markovnikov hydrozirconation side products (**Figure 3-3**, **9e**).

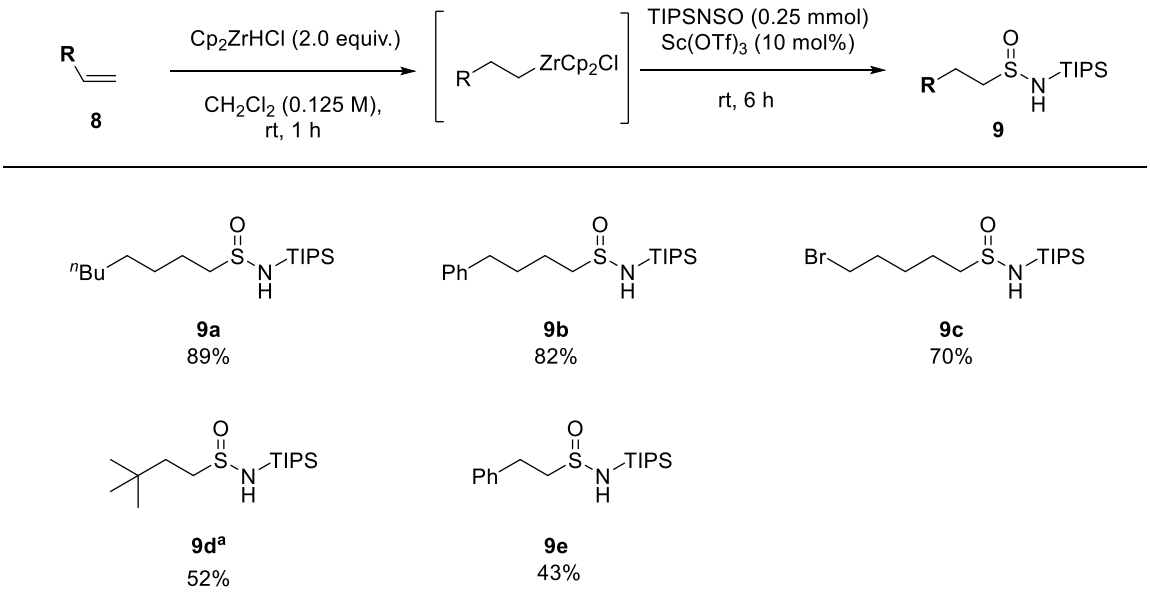
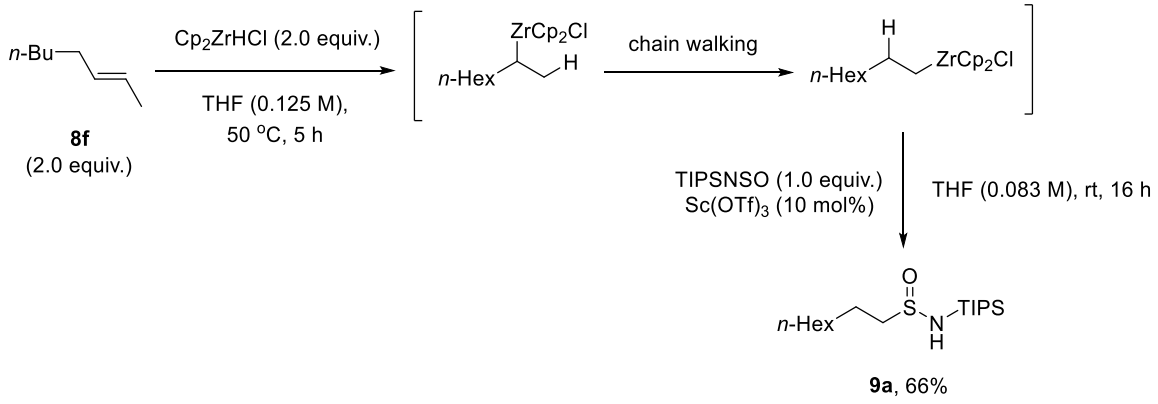


Figure 3-3 The substrate scope of alkyl sulfinamides

Reaction conditions: alkene (0.5 mmol, 2.0 equiv.), Cp_2ZrHCl (0.5 mmol. 2.0 equiv.), CH_2Cl_2 (2 mL, 0.125 M), rt, 1 h; then $Sc(OTf)_3$ (10 mol%), TIPSNSO (0.25 mmol, 1.0 equiv.), rt, 6 h. (a) the hydrozirconation step took 1.5 h.

Notably, we also found when internal alkene **8f** was used as the starting material, "chain-walking" occurs after the insertion of the Schwartz reagent, providing the linear sulfinamide **9a** in decent yield (**Scheme 3-14**).

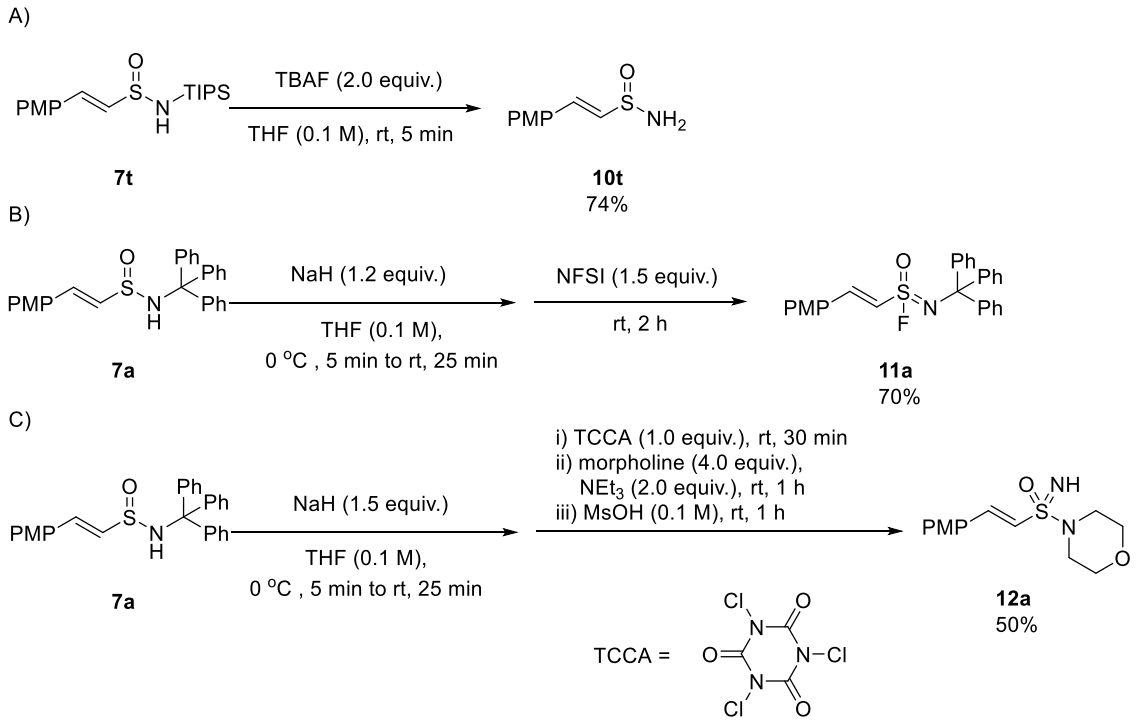


Scheme 3-14 Chain walking of alkyl zirconium reagent and subsequent insertion to TIPSNSO.

Reaction conditions: alkene (0.5 mmol, 2.0 equiv.), Cp_2ZrHCl (0.5 mmol. 2.0 equiv.), THF (2 mL, 0.125 M), 50 ^oC, 5 h; then $Sc(OTf)_3$ (10 mol%), TIPSNSO (0.25 mmol, 1.0 equiv.), rt, 16 h.

3.5 Derivatisation of Alkenyl Sulfinamides

To underscore on the potential application of the generated alkenyl sulfinamides, we have established reaction conditions to convert the alkenyl sulfinamides into other sulfur functional groups (**Scheme 3-14**). The one pot synthesis of alkenyl sulfinamides can be followed with desilylation with TBAF to afford primary alkenyl sulfinamide **10t** (**Scheme 3-15 A**). Alkenyl sulfinamide **7a** can also undergo deprotonation and subsequent fluorination to generate sulfonimidoyl fluoride **11a** (**Scheme 3-15 B**). We also developed the one pot synthesis of sulfonimidamides, using the sequence of chlorination, amination and deprotection of trityl group with methanesulfonic acid, to afford alkenyl sulfonimidamide **12a** in moderate yield (**Scheme 3-15 C**).



Scheme 3-15 Derivatisation of alkenyl sulfinamides.

3.6 Summary

In summary, this work establishes a robust and versatile one-pot methodology for the synthesis of alkenyl and alkyl sulfinamides, using Schwartz reagent in combination with commercially

accessible alkynes or alkenes, and sulfinylamines. The protocol demonstrates exceptional functional group tolerance, accommodating halides (including chloride, iodide), esters, and other sensitive motifs. A range of bench-stable sulfinylamines, including TrNSO, *t*-OctNSO, and TIPSNSO, were successfully employed, enabling tailored protection strategies for diverse synthetic needs. Scalability was confirmed through gram-scale reactions, underscoring the practicality of this approach. Furthermore, the alkenyl sulfinamide products serve as modular precursors for derivatisation into different sulfur(VI) functionalities, thereby unlocking avenues for systematic exploration of their bioactivity and potential applications in medicinal chemistry and pharmaceutical development.

Chapter 4 – Conclusions and Future Work

This thesis began by highlighting the importance and synthetic challenges associated with *β*-sultams and their aza analogues, which are predominantly accessed by lengthy intramolecular cyclization protocols, resulting in restricted substrate scopes, and limitations imposed by the sulfonyl group's inherent reactivity. To overcome these barriers, we developed a versatile strategy leveraging the photochemical reactivity of bench-stable silyl-sulfinylamines. Unlike traditional methods reliant on nucleophilic addition and subsequent cyclisation, our approach employs a triplet energy transfer mechanism, enabling [2+2] photocycloaddition of silyl-sulfinylamines with diverse alkenes (both activated and unactivated) to furnish *β*-cyclicsulfinamides with excellent chemoselectivity and regioselectivity. This method circumvents the strict requirement for a highly-active electrophilic sulfur centre, allowing gram-scale synthesis of *β*-cyclicsulfinamides and broadening functional group compatibility through the use of mild conditions. Subsequent derivatizations of the formed *β*-cyclicsulfinamides yielded *β*-sultams and taurine analogues via ring-opening reactions with biologically relevant nucleophiles. Notably, we achieved the first modular synthesis of aza-*β*-sultams through imination of *β*-cyclicsulfinamides, unlocking access to mono- and bis-functionalised aza-*β*-sultams. A unique silyl-rearrangement of aza-*β*-sultams was then utilised, followed by subsequent ring-opening reactions with nucleophiles in the presence of potassium bifluoride, providing an efficient route to aza-taurine analogues, previously difficult to access through conventional methods.

Complementary to this work, we developed a protocol using *in situ* formed zirconium reagents to synthesize alkenyl or alkyl sulfinamides from commercially available alkynes or alkenes, circumventing limitations of traditional organometallic reagents. This method tolerates

sensitive substituents and paves the way to further transformations to alkenyl sulfonimidoyl fluorides and sulfonimidamides, expanding the synthetic utility of sulfur(VI) compounds.

Future investigations following on from this thesis could focus on four aspects. First of all, exploring the reactivity of formed triplet sulfinylamines with other coupling partners such as strained bicyclobutanes or azidoalkenes to construct novel sulfur-containing scaffolds. Secondly, extending this photocycloaddition strategy to silyl-sulfurdiimides may yield *β*-cyclicsulfinamidines, which might be of great interest in pharmaceutical research field given sulfinamidines and sulfondiimidamides are emerging field of aza-sulfur chemistry. Furthermore, the desilylative ring-opening conditions utilised for aza-*β*-sultams may be applicable to acyclic substrates, which can be transformed more broadly to other useful sulfur functionalities. Additionally, the alkenyl sulfinamide synthesized from insertion of sulfinylamine by zirconium reagents may undergo an intramolecular cyclization in certain conditions, potentially yielding *β*-cyclicsulfinamides with inverted regioselectivity relative to the [2+2] photocycloaddition strategy. Such variants might exhibit distinct reactivity profiles after oxidation or imination to *β*-sultams or aza-*β*-sultams, broadening the structural diversity of *β*-sultam architectures. In conclusion, these methodologies establish a foundation for innovative sulfur(VI) chemistry, with implications for medicinal chemistry and pharmaceutical chemistry research field.

Chapter 5 Experimental Procedures and Data

5.1 General Information

Unless otherwise stated, all reactions were performed under an atmosphere of nitrogen with constant magnetic stirring, using clean, oven dried glassware. Nitrogen was sourced from the University of Oxford's internal supplies. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} pre-coated aluminium backed TLC sheets with a visualisation under a UV lamp (λmax = 254 nm) and/ or staining using $KMnO_4$, or ninhydrin stain. All chemicals used were obtained from commercial sources, unless otherwise stated, including Sigma Aldrich, Fluorochem and Alfa Aesar. Dry solvents were obtained from the University of Oxford internal solvent drying system (Innovative Technology Inc. PS-400-7), wherein they are purified through dried alumina columns. Trifluoroethanol used as solvent in imination of β-cyclicsulfinamides was obtained from Sigma Aldrich or Fluorochem, without further purification. Solvents used for isolation, were HPLC grade purchased from either Alfa Aesar or Sigma Aldrich. When referring to the solvent 'Petrol', what is meant is the fractions of petroleum ether which boil within the range 40 to 60 ^{o}C. Silica column chromatography was performed by loading the compound as an oil or concentrated solution onto a column, using Geduran® Si 60, 40–63-micron silica gel, and then run with the indicated eluent system. Basic Al_2O_3 column chromatography and basic Al_2O_3 plug were performed by loading the compound or reaction mixture, using aluminium oxide, for chromatography, basic, Brockmann I, 40-300 μm, 60 A from thermo scientific.

^{1}H NMR spectra were recorded on a Bruker AVIII HD 400 (400 MHz), AVIII 500 (500 MHz),

NEO 400 (400 MHz) spectrometer using the residual solvent as an internal standard. ^{13}C NMR spectra (proton decoupled) were recorded on a Bruker AVIII HD 400 (400 MHz),

AVIII 500 (500 MHz), NEO 400 (400 MHz) spectrometer spectrometer at 101 MHz. ^{19}F NMR spectra were recorded on a Bruker AVIII400 spectrometer at 377 MHz. All reported ^{1}H and ^{13}C chemical shifts (δ_H, δ_C) are referenced to the residual signal of deuterated solvents ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; Chemical shifts (δ) are reported in parts per million (ppm) to the nearest 0.01 ppm for ^{1}H NMR, and 0.1 ppm for ^{13}C and ^{19}F NMR. Coupling constants (*J*) are reported in Hertz (Hz) and rounded to the nearest 0.5 Hz.

Multiplicities are reported as followings: s (singlet), d (doublet), t (triplet), q (quartet), m

(multiplet), br. (broad signal). Assignments were made using the help of a variety of 2D NMR experiments (COSY, HSQC, HMBC and NOESY).

Infrared spectra were recorded on a Bruker Tensor 27 Fourier Transform spectrometer with an internal range 600-4000 cm^{-1} and all absorption maximum (ν_{max}) are given in wavenumbers (cm^{-1}).

Melting points were recorded in degrees Celsius (^{o}C) using a STUART scientific hotstage-microscope apparatus SMP1 or a Reichert melting point apparatus and are reported uncorrected. Low resolution mass spectra (LRMS) were recorded on a Waters LCT Premier mass spectrometer. High resolution mass spectra (HRMS) were obtained on an ACQUITY I-Class PLUS UPLC system (Waters, Milford, MA, USA) coupled to an ACQUITY RDa mass spectrometer (Waters, Milford, MA, USA) equipped with an ESI probe, in positive ion mode with a TOF mass analyzer. Values quoted are a ratio of mass to charge in Daltons to four decimal places. The mass found was compared to the mass calculated from the monoisotopic molecular formula, and all results were found to be within a 5 ppm error of the calculated values. Samples for mass spectra were prepared in 1 mg/mL solution in CH_2Cl_2 or EtOAc.

5.2 Photochemical Reaction Setup

450 nm LEDs refers to a 18W HepatoChem non-dimmable 450 nm light (HCK1012-01-002). 390 nm LEDs refers to a 52W Kessil PR160L-390 nm lamp. 370 nm LEDs refers to a 40W Kessil PR160L-370 nm lamp. The light was mounted in an EvoluChem™ PhotoRedOx Box device. The reactions were run at 100% percent light intensity with the built-in fans on unless otherwise specified. Reactions were carried out in microwave vials, fitted with a PTFE septum.

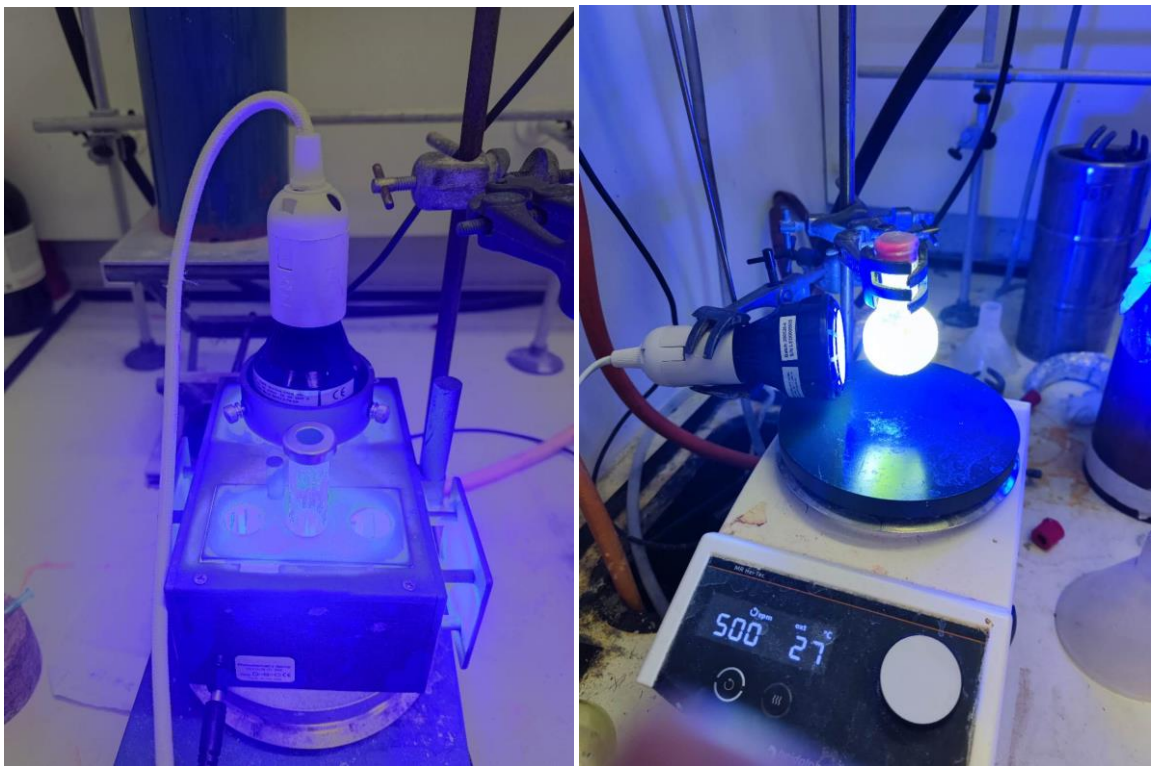
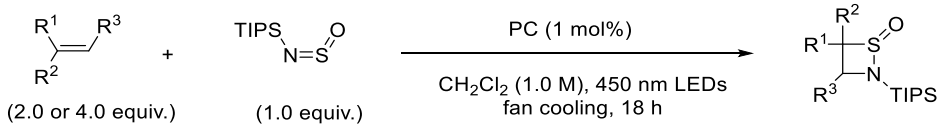


Figure 5-1 Left: Set-up for 0.5 mmol photochemical reactions. Right: Set-up for 5.0 mmol photochemical reactions.

5.3 Experimental Data for Chapter 2

5.3.1 General Procedures

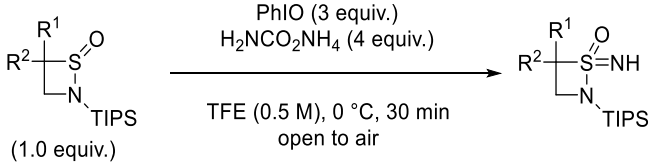
Energy-transfer mediated synthesis of *β*-cyclicsulfinamides (General Procedure A)



General Procedure A: To a 10 mL microwave vial charged with photocatalyst (1 mol%), alkene (if solid) (2 equiv. or 4 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. Alkene (if liquid) (2 equiv. or 4 equiv.) and CH_2Cl_2 (1.0 M) was added. The resulting mixture then underwent freeze pump thaw for 3 times in liquid nitrogen bath, followed by refilled with nitrogen at room temperature. Then TIPSNSO (1 equiv.) was added. The mixture was allowed to stir at 450 nm at room temperature with fan cooling.

After 18 h, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography to afford the desired product.

Synthesis of aza-*β*-sultams via imination of *β*-cyclicsulfinamides (General Procedure B)



General Procedure B: TFE (trifluoroethanol) (0.5 M) was added to a 10 mL microwave vial charged with *β*-sultam (1.0 equiv.). The mixture was stirred until dissolution before cooling to 0 °C. $H_2NCO_2NH_4$ (ammonium carbamate) (4.0 equiv.) and PhIO (3.0 equiv.) were added quickly into the vial. The resulting mixture was then stirred for 30 min at 0 °C.

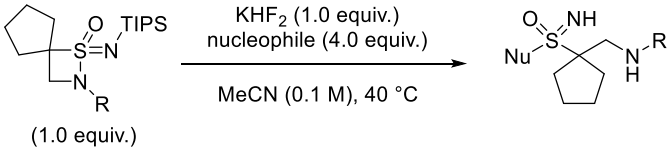
The mixture was quickly filtered through a pad of basic Al_2O_3 (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by flash column chromatography (basic Al_2O_3) to afford the desired product.

Note:

1. Aza-*β*-sultams gradually decompose in the reaction system, especially at elevated temperatures, so the reaction time and temperature should be followed.

2. Aza-*β*-sultams are very sensitive to acidic environment, so basic Al_2O_3 must be used for isolation and deuterated solvents should be basified (stored over anhydrous K_2CO_3) for characterization purposes to avoid decomposition.

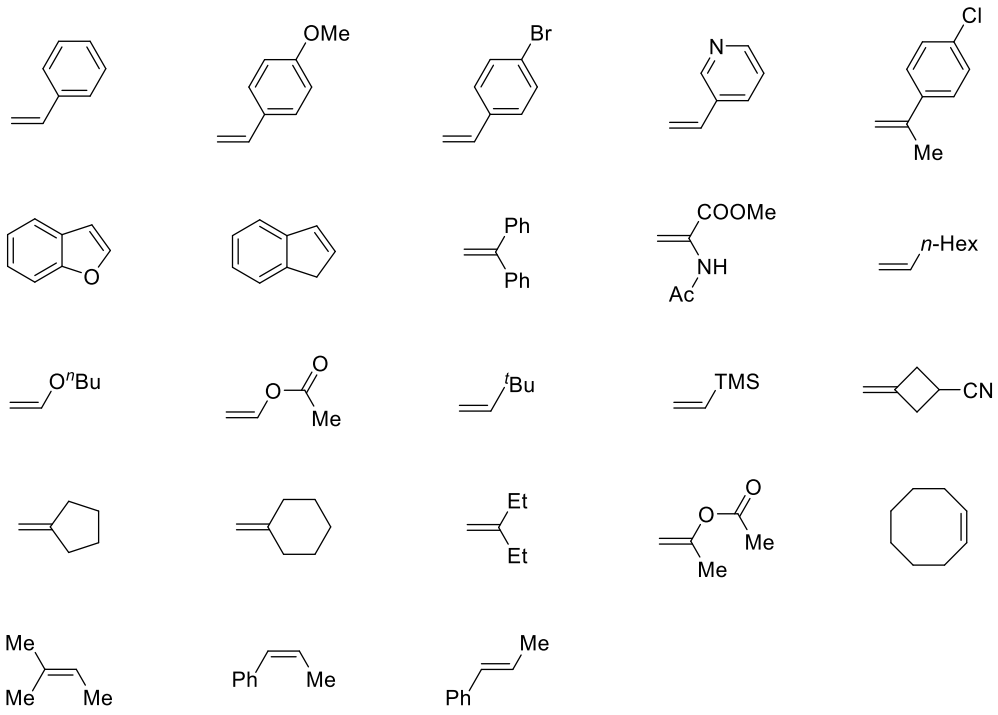
Ring opening reactions of aza-*β*-sultams with potassium bifluoride (General Procedure C)



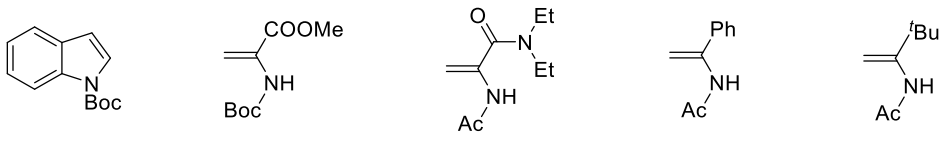
General Procedure C: To a 10 mL microwave vial, *β*-cyclicsulfonimidamide (if solid) (1.0 equiv.) and potassium bifluoride (1.0 equiv.) were added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. MeCN (0.1 M) or Sulfonimidamide (if liquid) (1.0 equiv.) in MeCN (0.1 M) solution was added, followed by the addition of nucleophile (4.0 equiv.). The resulting mixture was then heated to 40 °C and stirred for 24 h or 48 h. The mixture was cooled to room temperature and filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography to afford the desired product.

5.3.2 Preparation of Starting Materials

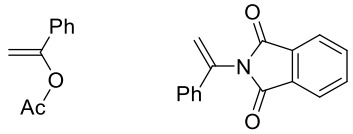
Commercially available alkenes used as received



Alkenes **A**[122], **B**[123], **C**[124], **D**[125], **E**[126], **F**[127], **G**[128] were prepared according to reference



A **B** **C** **D** **E**

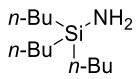


F **G**

Synthesis of sulfinylamines

TrNSO[47], *t*-OctNSO[89], biPhONSO[50], TIPSNSO[51] and TBDPSNSO[129] were synthesized according to reported procedure.

Synthesis of tri(*n*-butyl)silylamine (TNBSNH$_2$)



To an oven-dried 250 mL round-bottom flask was dissolved tri(*n*-butyl)chlorosilane (2.35 g, 10 mmol, 1.0 equiv.) in anhydrous Et_2O (60 mL). The reaction mixture was cooled to -78 °C. Anhydrous ammonia gas was bubbled through this solution for 1 hour, resulting in the immediate formation of a white precipitate. The reaction was then warmed to 0 °C and stirred for another 2 hours open to air to remove excess ammonia. When bubbling stopped, the reaction slurry was filtered through a pad of anhydrous Na_2SO_4 (3-4 cm), washed with Et_2O (20 mL), and concentrated in vacuo to afford TNBSNH$_2$ as a colourless oil (2.10 g, 9.77 mmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 – 1.22 (m, 12H), 0.93 – 0.85 (m, 9H), 0.56 – 0.46 (m, 6H), 0.30 (bs, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 26.8, 25.9, 15.0, 14.0.

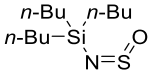
IR (ATR) (ν_{max} cm $^{-1}$) = 3401, 2956, 2919, 2872, 1548, 1464, 1193, 1081, 888, 824, 732.

Notes:

(1) The product may be slightly volatile. For this reason, when removing solvent on a rotary evaporator, the bath temperature should be set to 30 ^{o}C or lower.

(2) $TNBSNH_2$ is stored in the freezer (-20 ^oC) and can be taken out and used regularly without loss of performance for at least one month.

Synthesis of *N*-sulfinyl-tri(*n*-butyl)silylamine (TNBSNSO)



To an oven-dried 250 mL round-bottom flask was added tri(*n*-butyl)silylamine (1.64 g, 7.61 mmol, 1.00 equiv.). The vessel was sealed and subjected to three N_2 evacuation/refill cycles before anhydrous Et_2O (60 mL) was added. The solution was cooled to 0 °C and anhydrous triethylamine (2.19 mL, 15.7 mmol, 2.06 equiv.) was added. Freshly distilled thionyl chloride (0.57 mL, 7.81 mmol, 1.03 equiv.) was then added dropwise. The reaction slurry was then stirred vigorously at 0 °C for 2 hours. Upon completion, the reaction slurry was filtered through a pad of anhydrous Na_2SO_4 (3-4 cm), washed with Et_2O (20 mL), and concentrated in vacuo to afford TNBSNSO as a yellow oil (1.95 g, 7.46 mmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 – 1.23 (m, 6H), 0.92 – 0.87 (m, 9H), 0.85 – 0.76 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 26.5, 25.5, 13.9. (note: 2 peaks overlap to show 1 peak found in 13.9 ppm)

IR (ATR) (ν_{max} cm $^{-1}$) = 2960, 2926, 2873, 1463, 1303, 1197, 1129, 1082, 886, 712.

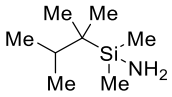
Notes:

(1) The product may be slightly volatile. For this reason, when removing solvent on a rotary evaporator, the bath temperature should be set to 30 °C or lower.

(2) TNBSNSO is stored in the freezer (-20 °C) and can be taken out and used regularly without loss of performance for several weeks.

(3) **CAUTION: Hydrolysis of sulfinylamines results in the formation of toxic sulfur dioxide gas.** Evolution of SO_2 from TNBSNSO has not been observed in the normal course of use. But avoidance of contact with water or prolonged storage at room temperature is advised.

Synthesis of (dimethyl)thexylsilylamine (TDSNH$_2$)



To an oven-dried 250 mL round-bottom flask was dissolved chloro(dimethyl)thexylsilane (3.71 g, 20.8 mmol, 1.0 equiv.) in anhydrous Et_2O (60 mL). The reaction mixture was cooled to -78 °C. Anhydrous ammonia gas was bubbled through this solution for 1 hour, resulting in the immediate formation of a white precipitate. The reaction was then warmed to 0 °C and stirred for another 2 hours open to air to remove excess ammonia. When bubbling stopped, the reaction slurry was filtered through a pad of anhydrous Na_2SO_4 (3-4 cm), washed with Et_2O (20 mL), and concentrated in vacuo to afford TDSNH$_2$ as a colourless oil (3.19 g, 20.0 mmol, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 – 1.57 (m, 1H), 0.88 (d, *J* = 6.9 Hz, 6H), 0.83 (s, 6H), 0.36 (bs, 2H), 0.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 34.5, 24.4, 20.5, 18.8, -1.2.

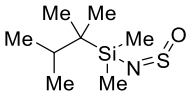
IR (ATR) (ν_{max} cm $^{-1}$) = 3350, 2959, 2868, 1466, 1253, 831, 774.

Notes:

(1) The product may be slightly volatile. For this reason, when removing solvent on a rotary evaporator, the bath temperature should be set to 30 ^{o}C or lower.

(2) $TNBSNH_2$ is stored in the freezer (-20 ^oC) and can be taken out and used regularly without loss of performance for at least one month.

Synthesis of *N*-sulfinyl-(dimethyl)thexylsilylamine (TDSNSO)



To an oven-dried 250 mL round-bottom flask was added (dimethyl)thexylsilylamine (2.53 g, 15.9 mmol, 1.00 equiv.). The vessel was sealed and subjected to three N_2 evacuation/refill cycles before anhydrous Et_2O (60 mL) was added. The solution was cooled to 0 °C and anhydrous triethylamine (4.57 mL, 32.8 mmol, 2.06 equiv.) was added. Freshly distilled thionyl chloride (1.20 mL, 16.5 mmol, 1.04 equiv.) was then added dropwise. The reaction slurry was then stirred vigorously at 0 °C for 2 hours. Upon completion, the reaction slurry was filtered through a pad of anhydrous Na_2SO_4 (3-4 cm), washed with Et_2O (20 mL), and concentrated in vacuo to afford TNBSNSO as a yellow oil (3.06 g, 14.9 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 – 1.60 (m, 1H), 0.93 (s, 6H), 0.90 (d, *J* = 6.9 Hz, 6H), 0.38 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 34.2, 24.9, 20.2, 18.7, -1.3.

IR (ATR) (ν_{max} cm $^{-1}$) = 2962, 2873, 1466, 1301, 1257, 1129, 842, 819, 786, 684.

Notes:

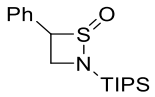
(1) The product may be slightly volatile. For this reason, when removing solvent on a rotary evaporator, the bath temperature should be set to 30 °C or lower.

(2) TDSNSO is stored in the freezer (-20 °C) and can be taken out and used regularly without loss of performance for several weeks.

(3) **CAUTION: Hydrolysis of sulfinylamines results in the formation of toxic sulfur dioxide gas.** Evolution of SO_2 from TDSNSO has not been observed in the normal course of use. But avoidance of contact with water or prolonged storage at room temperature is advised.

5.3.3 Synthesis of *β*-cyclicsulfinamides

4-Phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1a**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), styrene (115 μL, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 6:1. Purification by flash silica column chromatography (30:1 to 20:1 Petrol: EtOAc) afforded the title compound **1a**-major (113.6 mg, 70%) and **1a**-minor (19.4 mg, 12%) as separable products.

1a-major (pale-yellow solid)

Rf = 0.5 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.32 (m, 5H), 5.01 (dd, *J* = 7.7, 7.7 Hz, 1H), 4.78 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.70 (dd, *J* = 8.0, 8.0 Hz, 1H), 1.29 – 1.13 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.2, 130.0, 128.8, 128.5, 61.2, 57.9, 18.3, 18.2, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{17}H_{30}NOSSi^+$ $[M+H]^+$: 324.1812; found: 324.1807.

IR (ATR) (ν_{max} cm $^{-1}$) = 2946, 2868, 1462, 1095, 932, 912, 884.

M. p. 83-85 ^{o}C (CH_2Cl_2)

1a-minor (pale-yellow solid)

Rf = 0.2 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.29 (m, 5H), 4.96 (dd, *J* = 9.4, 9.4 Hz, 1H), 4.47 – 4.20 (m, 2H), 1.38 – 1.08 (m, 21H).

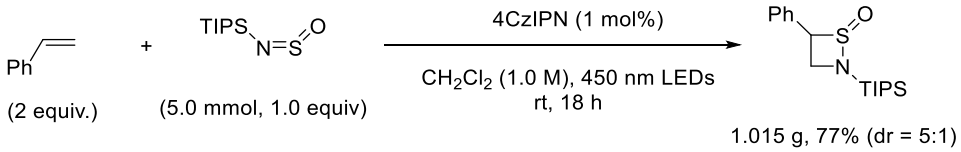
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 129.2, 128.6, 127.4, 70.3, 54.4, 18.3, 18.2, 11.5.

HRMS $(ESI)^+$ calcd. for $C_{17}H_{30}NOSSi^+$ $[M+H]^+$: 324.1812; found: 324.1825.

IR (ATR) (ν_{max} cm $^{-1}$) = 2944, 2869, 1490, 1466, 1133, 1088, 1013, 916, 881, 739.

M. p. 84-86 ^{o}C (CH_2Cl_2)

Gram scale synthesis of 4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1a**)

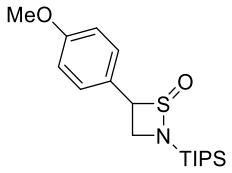


4CzIPN (39.4 mg, 0.05 mmol, 1 mol%) was added to a 25 mL RBF. The RBF was then sealed with suba-seal and subjected to three evacuation/argon refill cycles. Styrene (1.2 mL, 10.0 mmol, 2.0 equiv.), and CH_2Cl_2 (5.0 mL, 1.0 M) was added. The resulting mixture was then freeze pump thaw for 3 times in liquid nitrogen bath, followed by refilled with nitrogen at room temperature. Then TIPSNSO (1.1 g, 5.0 mmol, 1 equiv.) was added. The mixture was allowed to stir in 450nm at room temperature.

After 18 h, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc. The resultant crude solution was concentrated *in vacuo*. Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 5:1. The crude mixture was purified by silica column chromatography (30:1 to 20:1 Petrol: EtOAc) to afford the title compound **1a**-major (1.015 g, 63%) and **1a**-minor (228.0 mg, 14%) as separable products.

The data is consistent with the above reports.

4-(4-Methoxyphenyl)-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1b**)



Prepared according to **General Procedure A** using (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5.6 mg, 0.005 mmol, 1 mol%), 4-methoxystyrene (134 μL, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 5:1. Purification by flash silica column chromatography (10:1 to 5:1 Petrol: EtOAc) afforded the title compound **1b**-major (119.3 mg, 67%) and **1b**-minor (23.7 mg, 13%) as separable products.

1b-major (yellow solid)

Rf = 0.5 (5:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.33 (m, 2H), 7.02 – 6.90 (m, 2H), 4.98 (dd, *J* = 7.7, 7.7 Hz, 1H), 4.79 – 4.62 (m, 2H), 3.81 (s, 3H), 1.42 – 1.04 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 131.2, 124.4, 114.0, 60.9, 58.5, 55.4, 18.3, 18.2, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{18}H_{32}NO_2SSi^+$ $[M+H]^+$: 354.1918; found: 354.1920.

IR (ATR) (ν_{max} cm $^{-1}$) = 2986, 2944, 2870, 1743, 1515, 1375, 1247, 1098, 1050, 929, 822.

M. p. 64-68 ^{o}C (CH_2Cl_2)

1b-minor (yellow oil)

Rf = 0.3 (5:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 4.93 (dd, *J* = 9.4, 9.4 Hz, 1H), 4.48 – 4.25 (m, 2H), 3.82 (s, 3H), 1.32 – 1.08 (m, 21H).

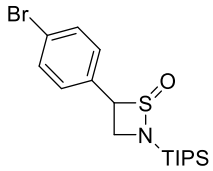
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 128.7, 127.1, 114.6, 69.9, 55.5, 54.7, 18.3, 18.2, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{18}H_{32}NO_2SSi^+$ $[M+H]^+$: 354.1918; found: 354.1934.

IR (ATR) (ν_{max} cm $^{-1}$) = 2949, 2870, 2838, 1612, 1515, 1466, 1253, 1087, 922.

M. p. 42-44 ^oC (CH_2Cl_2)

4-(4-Bromophenyl)-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1c**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), 4-bromostyrene (131 μL, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 10:1. Purification by flash silica column chromatography (20:1 to 10:1 Petrol: EtOAc) afforded the title compound **1c**-major (120.1 mg, 60%) and **1c**-minor (12.0 mg, 6%) as separable products.

1c-major (white solid)

Rf = 0.5 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.38 – 7.30 (m, 2H), 4.96 (dd, *J* = 7.7, 7.7 Hz, 1H), 4.73 – 4.66 (m, 2H), 1.27 – 1.13 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 131.5, 131.2, 123.3, 60.4, 57.8, 18.3, 18.2, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{17}H_{29}{}^{79}BrNOSSi^+$ $[M+H]^+$: 402.0917; found: 402.0914.

IR (ATR) (ν_{max} cm $^{-1}$) = 2947, 2869, 1490, 1466, 1092, 929, 914, 736.

M. p. 82-84 ^oC (CH_2Cl_2)

1c-minor (white solid)

Rf = 0.2 (10:1 Petrol: EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.96 (dd, *J* = 9.4, 9.1 Hz, 1H), 4.33 – 4.26 (m, 2H), 1.27 – 1.13 (m, 21H).

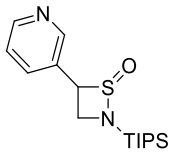
^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1, 132.4, 129.0, 122.5, 69.4, 54.3, 18.3, 18.2, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{17}H_{29}{}^{79}BrNOSSi^+$ $[M+H]^+$: 402.0917; found: 402.0927.

IR (ATR) (ν_{max} cm $^{-1}$) = 2947, 2869, 1490, 1466, 1092, 929, 914, 736.

M. p. 78-80 ^oC (CH_2Cl_2)

4-(Pyridin-3-yl)-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1d**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), 3-vinylpyridine (purified by FCC before using, 105.1 mg, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 3:1. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the title compound **1d**-major (95.6 mg, 59%) and **1d**-minor (30.8 mg, 19%) as separable products.

1d-major (yellow oil)

Rf = 0.4 (1:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.68 (td, *J* = 7.7, 1.8 Hz, 1H), 7.29 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.23 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 4.80 (dd, *J* = 8.1,

7.2 Hz, 1H), 4.74 (dd, *J* = 7.1, 4.6 Hz, 1H), 4.47 (dd, *J* = 8.1, 4.5 Hz, 1H), 1.44 – 1.02 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 150.3, 136.8, 123.1, 123.0, 71.0, 51.6, 18.2, 18.1, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{16}H_{29}N_2OSSi^+$ $[M+H]^+$: 325.1764; found: 325.1759.

IR (ATR) (ν_{max} cm $^{-1}$) = 2946, 2868, 1590, 1468, 1438, 1085, 996, 923, 884, 733.

1d-minor (pale-yellow solid)

Rf = 0.2 (1:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.60 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.37 – 7.13 (m, 1H), 5.21 (dd, *J* = 7.7, 7.7 Hz, 1H), 4.98 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.69 (dd, *J* = 8.0, 8.0 Hz, 1H), 1.27 – 1.13 (m, 21H).

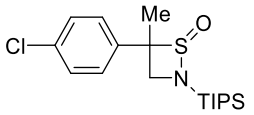
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 149.7, 136.4, 124.7, 123.2, 62.2, 55.7, 18.2, 18.1, 11.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{16}H_{29}N_2OSSi^+$ $[M+H]^+$: 325.1764; found: 354.1764.

IR (ATR) (ν_{max} cm $^{-1}$) = 2945, 2888, 1590, 1468, 1438, 1091, 996, 933, 884, 808, 695.

M. p. 40-42 ^oC (CH_2Cl_2)

4-(4-Chlorophenyl)-4-methyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1e**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), 1-chloro-4-(1-methylethenyl)-benzene (152.6 mg, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 4:1. Purification by flash silica

column chromatography (40:1 to 20:1 Petrol: EtOAc) afforded the title compound **1e**-major (105.6 mg, 57%) and **1e**-minor (25.1 mg, 13%) as separable products.

1e-major (yellow oil)

Rf = 0.3 (20:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.30 (m, 4H), 4.76 (d, *J* = 8.0 Hz, 1H), 4.20 (d, *J* = 8.0 Hz, 1H), 2.04 (s, 3H), 1.30 – 1.12 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 134.3, 129.4, 128.5, 63.4, 63.3, 21.9, 18.2, 18.1, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{18}H_{31}ClNOSSi^+$ $[M+H]^+$: 372.1579; found: 372.1589.

IR (ATR) (ν_{max} cm $^{-1}$) = 2946, 2868, 1687, 1493, 1464, 1095, 911, 734.

1e-minor (yellow oil)

Rf = 0.2 (20:1 Petrol: EtOAc)

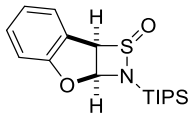
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.32 (m, 4H), 4.47 (d, *J* = 7.6 Hz, 1H), 4.39 (d, *J* = 7.6 Hz, 1H), 1.75 (s, 3H), 1.23 – 1.08 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 133.7, 129.2, 127.2, 64.6, 62.4, 20.2, 18.3, 18.1, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{18}H_{31}ClNOSSi^+$ $[M+H]^+$: 372.1579; found: 372.1574.

IR (ATR) (ν_{max} cm $^{-1}$) = 2946, 2868, 1493, 1464, 1100, 1012, 920, 885, 829, 734.

2-(Triisopropylsilyl)-2a,7b-dihydro-2H-benzofuro[2,3-c][1,2]thiazete 1-oxide (**1f**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), 2,3-benzofuran (110 μL, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 9:1. Purification by flash silica column chromatography (20:1 to 10:1 Petrol: EtOAc) afforded the title compound **1f** (132.9 mg, 79%) as an inseparable mixture.

1f-major (white solid)

Rf = 0.6 (5:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.04 – 6.99 (m, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 4.62 (d, *J* = 4.6 Hz, 1H), 1.28 – 1.18 (m, 3H), 1.14 – 1.06 (m, 18H).

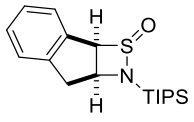
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 131.3, 125.8, 122.2, 120.4, 111.7, 100.4, 71.3, 18.2, 17.9, 11.8. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{17}H_{28}NO_2SSi^+$ $[M+H]^+$: 338.1605; found: 338.1610.

IR (ATR) (ν_{max} cm $^{-1}$) = 2948, 2869, 1723, 1595, 1467, 1388, 1235, 1131, 1087, 967, 932, 752.

M. p. 56-58 ^{o}C (CH_2Cl_2)

2-(Triisopropylsilyl)-2,2a,3,7b-tetrahydroindeno[2,1-c][1,2]thiazete 1-oxide (**1g**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), indan (112 μL, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 2.5:1. Purification by flash silica column chromatography

(20:1 to 10:1 Petrol: EtOAc) afforded the title compound **1g**-major (102.2 mg, 61%) and **1g**-minor (40.1 mg, 24%) as separable products.

1g-major (white solid)

Rf = 0.5 (5:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.19 (m, 4H), 5.14 – 5.04 (m, 2H), 3.36 – 3.18 (m, 2H), 1.41 – 0.98 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 133.6, 129.0, 127.2, 126.8, 125.7, 66.7, 61.6, 44.3, 18.2, 11.6.

HRMS $(ESI)^+$ calcd. for $C_{17}H_{28}NO_2SSi^+$ $[M+H]^+$: 336.1812; found: 336.1816.

IR (ATR) (ν_{max} cm $^{-1}$) = 2944, 2892, 1464, 1099, 973, 911, 882, 764, 738, 681.

M. p. 72-74 ^{o}C (CH_2Cl_2)

1g-minor (yellow solid)

Rf = 0.2 (5:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.06 (m, 4H), 5.88 (td, *J* = 5.2, 1.6 Hz, 1H), 4.44 (d, *J* = 5.1 Hz, 1H), 3.40 – 3.01 (m, 2H), 1.27 – 0.98 (m, 21H).

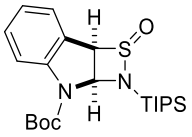
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 135.6, 129.4, 127.7, 126.0, 125.7, 72.8, 68.1, 40.5, 18.3, 18.1, 12.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{17}H_{28}NO_2SSi^+$ $[M+H]^+$: 336.1812; found: 336.1806.

IR (ATR) (ν_{max} cm $^{-1}$) = 2945, 2868, 1742, 1465, 1374, 1242, 1122, 1081, 961, 883, 813, 780, 744.

M. p. 66-68 ^{o}C (CH_2Cl_2)

***tert*-Butyl 2-(triisopropylsilyl)-2a,7b-dihydro-[1,2]thiazeto[3,4-b]indole-3(2H)-carboxylate 1-oxide (1h**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), indole-1-carboxylic acid *tert*-butyl ester (217.3 mg, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 2:1. Purification by flash silica column chromatography (20:1 to 10:1 Petrol: EtOAc) afforded the title compound **1h**-major (63.7 mg, 29%) and **1h**-minor (30.2 mg, 14%) as separable products.

1h-major (yellow oil)

Rf = 0.3 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (bs, 1H), 7.44 – 7.30 (m, 1H), 7.20 – 7.06 (m, 2H), 6.32 (bs, 1H), 5.29 (d, *J* = 5.5 Hz, 1H), 1.56 (s, 9H), 1.45 – 1.28 (m, 3H), 1.11 (d, *J* = 7.6 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 145.0, 130.1, 127.4, 123.6, 123.1, 117.6, 82.6, 73.0, 64.1, 28.4, 18.2, 11.3.

HRMS $(ESI)^+$ calcd. for $C_{22}H_{37}N_2O_3SSi^+$ $[M+H]^+$: 437.2289; found: 437.2301.

IR (ATR) (ν_{max} cm $^{-1}$) = 2947, 2868, 1703, 1480, 1377, 1346, 1164, 1064, 911, 734.

1h-minor (yellow oil)

Rf = 0.2 (10:1 Petrol: EtOAc)

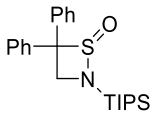
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (bs, 1H), 7.44 (dq, *J* = 7.5, 1.0 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.16 – 7.08 (m, 2H), 4.60 (d, *J* = 5.1 Hz, 1H), 1.56 (s, 9H), 1.35 – 1.20 (m, 3H), 1.11 – 1.02 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 142.6, 130.3, 125.8, 124.9, 124.1, 118.1, 83.0, 81.9, 69.4, 28.4, 18.3, 18.0, 11.7. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{22}H_{37}N_2O_3SSi^+$ $[M+H]^+$: 437.2289; found: 437.2284.

IR (ATR) (ν_{max} cm $^{-1}$) = 2947, 2869, 1708, 1480, 1378, 1340, 1256, 1165, 1130, 1055, 1018, 909, 752.

4,4-Diphenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1i**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), 1,1-diphenylethylene (176 μL, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Purification by flash silica column chromatography (20:1 Petrol: EtOAc) afforded the title compound **1i** (153.7 mg, 77%) as a white solid.

Rf = 0.4 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.31 (m, 10 H), 5.21 (d, *J* = 8.1 Hz, 1H), 4.90 (d, *J* = 8.1 Hz, 1H), 1.37 – 1.14 (m, 21H).

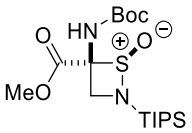
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 136.7, 129.6, 128.9, 128.3, 128.2, 128.1, 127.9, 72.9, 63.4, 18.2, 18.1, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{23}H_{34}NOSSi^+$ $[M+H]^+$: 400.2125; found: 400.2125.

IR (ATR) (ν_{max} cm $^{-1}$) = 2945, 2888, 1465, 1114, 945, 912, 884, 739, 696.

M. p. 70-72 ^{o}C (CH_2Cl_2)

Methyl 4-((*tert*-butoxycarbonyl)amino)-2-(triisopropylsilyl)-1,2-thiazetidine-4-carboxylate 1-oxide (1j)



Prepared according to **General Procedure A** using (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5.6 mg, 0.005 mmol, 1 mol%), methyl 2-[(*tert*-butoxycarbonyl)amino]acrylate (402.4 mg, 2 mmol, 4 equiv.) , TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio > 20:1. Purification by flash silica column chromatography (10:10:1 to 5:5:1 Petrol: CH_2Cl_2: EtOAc) afforded the title compound **1j** (183.0 mg, 87%) as a yellow oil.

Rf = 0.5 (1:2 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (bs, 1H), 4.82 – 4.34 (m, 2H), 3.82 (s, 3H), 1.38 (s, 9H), 1.18 – 0.95 (m, 21H).

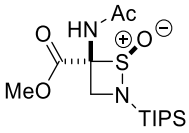
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.39, 154.2, 81.6, 72.2, 59.6, 53.1, 28.0, 17.9, 17.8, 11.2. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS (ESI)$^+$ calcd. for C18H37N2O5SSi [M+H]+: 421.2187; found: 421.2194.

IR (ATR) (ν_{max} cm $^{-1}$) = 3242, 2949, 2872, 1741, 1369, 1245, 1166, 1117, 1053, 919.

M. p. 116-118 ^{o}C (CH_2Cl_2)

Methyl 4-acetamido-2-(triisopropylsilyl)-1,2-thiazetidine-4-carboxylate 1-oxide (**1k**)



Prepared according to **General Procedure A** using (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5.6 mg, 0.005 mmol, 1 mol%), methyl 2-acetamidoacrylate (286.3 mg, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio > 20:1. Purification by flash silica column chromatography (1:2 Petrol: EtOAc) afforded the title compound **1k** (162.5 mg, 90%) as a pale-yellow solid.

Rf = 0.5 (1:2 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (bs, 1H), 4.90 – 4.67 (m, 1H), 4.46 (d, *J* = 8.6 Hz, 1H), 3.81 (s, 3H), 2.08 (s, 3H), 1.16 – 1.04 (m, 21H).

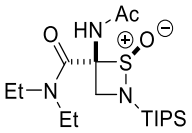
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 167.6, 71.3, 60.3, 53.3, 22.6, 17.9, 17.8, 11.2. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS (ESI)$^+$ calcd. for $C_{15}H_{31}N_2O_4SSi^+$ $[M+H]^+$: 363.1768; found: 363.1786.

IR (ATR) (ν_{max} cm $^{-1}$) = 3280, 2988, 2947, 2871, 1745, 1376, 1245, 1050.

M. p. 120-122 ^{o}C (CH_2Cl_2)

4-Acetamido-*N*,*N*-diethyl-2-(triisopropylsilyl)-1,2-thiazetidine-4-carboxamide 1-oxide (1l)



Prepared according to **General Procedure A** using (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5.6 mg, 0.005 mmol, 1 mol%), 2-acetylamino-*N*,*N*-diethylacrylamide (368.4 mg, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M).

Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio > 20:1. Purification by flash silica column chromatography (40:1 to 30:1 CH_2Cl_2: MeOH) afforded the title compound **1l** (141.3 mg, 70%) as a white solid.

Rf = 0.3 (30:1 CH_2Cl_2: MeOH)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (bs, 1H), 5.19 (d, *J* = 8.2 Hz, 1H), 4.45 (d, *J* = 8.2 Hz, 1H), 3.42 (q, *J* = 7.0 Hz, 2H), 3.15 (q, *J* = 7.0 Hz, 2H), 2.10 (s, 3H), 1.23 – 1.01 (m, 30H).

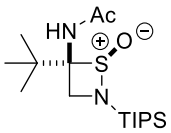
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 164.5, 72.6, 63.4, 41.9, 41.0, 23.3, 18.0, 17.9, 13.6, 12.4, 11.3. (note: for two ethyl groups, 4 peaks were found instead of 2, for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{18}H_{38}N_3O_3SSi^+$ $[M+H]^+$: 404.2398; found: 404.2400.

IR (ATR) (ν_{max} cm $^{-1}$) = 3252, 3209, 3043, 2945, 2870, 1687, 1642, 1622, 1538, 1464, 1442, 1367, 1303, 1096, 886.

M. p. 146-148 ^{o}C (CH_2Cl_2)

***N*-(4-(tert-Butyl)-1-oxido-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl)acetamide** (**1m**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), 2-acetamido-3,3-dimethyl-1-butene (282.4 mg, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio > 20:1. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the title compound **1m** (111.6 mg, 62%) as a pale-yellow solid.

Rf = 0.6 (1:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (bs, 1H), 4.60 (d, *J* = 9.1 Hz, 1H), 4.41 (d, *J* = 9.1 Hz, 1H), 2.13 (s, 3H), 1.25 – 0.92 (m, 30H).

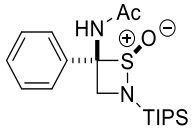
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 78.5, 54.2, 37.5, 25.0, 24.3, 18.2, 18.0, 11.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{17}H_{37}N_2O_2SSi^+$ $[M+H]^+$: 361.2340; found: 361.2347.

IR (ATR) (ν_{max} cm^{-1}) = 3277, 2957, 2870, 1677, 1540, 1469, 1372, 1282, 1093. 914.

M. p. 72-74 °C (CH_2Cl_2)

***N*-(1-Oxido-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl)acetamide (1n)**



Prepared according to **General Procedure A** using $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5.6 mg, 0.005 mmol, 1 mol%), *N*-(1-phenylvinyl)acetamide (161.2 mg, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio > 20:1. Purification by flash silica column chromatography (2:1 to 1:1 Petrol: EtOAc) afforded the title compound **1n** (110.8 mg, 58%) as a yellow solid.

Rf = 0.2 (1:1 Petrol: EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 4.93 (d, *J* = 8.9 Hz, 1H), 4.74 (d, *J* = 8.8 Hz, 1H), 2.17 (s, 3H), 1.22 – 1.10 (m, 21H).

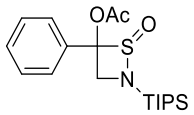
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 136.9, 129.1, 128.7, 125.5, 71.9, 64.4, 23.6, 18.2, 18.0, 11.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{19}H_{32}N_2O_2SSi^+$ $[M+Na]^+$: 403.1846; found: 403.1863.

IR (ATR) (ν_{max} cm $^{-1}$) = 3374, 2949, 2869, 1666, 1530, 1467, 1376, 1292, 1092, 1092, 913, 734, 694.

M. p. 112-114 ^{o}C (CH_2Cl_2)

1-Oxido-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl acetate (**1o**)



Prepared according to **General Procedure A** using (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5.6 mg, 0.005 mmol, 1 mol%), 1-acetoxy-1-phenylethene (162.2 mg, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 4:1. Purification by flash silica column chromatography (20:1 to 10:1 to 5:1 Petrol: EtOAc) afforded the title compound **1o**-major (89.4 mg, 47%) and **1o**-minor (21.0 mg, 11%) as separable products.

1o-major (yellow oil)

Rf = 0.3 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.30 (m, 5H), 4.84 (d, *J* = 9.8 Hz, 1H), 4.56 (d, *J* = 9.8 Hz, 1H), 2.29 (s, 3H), 1.39 – 1.10 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 131.7, 129.3, 128.4, 126.6, 96.5, 59.8, 21.3, 18.2, 18.1, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS (ESI)$^+$ calcd. for $C_{19}H_{32}NO_3SSi^+$ $[M+H]^+$: 382.1867; found: 382.1863.

IR (ATR) (ν_{max} cm $^{-1}$) = 2948, 2870, 1759, 1462, 1373, 1220, 1116, 914, 734.

1o-minor (yellow oil)

Rf = 0.1 (10:1 Petrol: EtOAc)

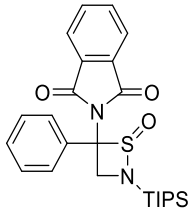
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.49 – 7.37 (m, 3H), 5.15 (d, *J* = 8.5 Hz, 1H), 4.66 (d, *J* = 8.5 Hz, 1H), 2.21 (s, 3H), 1.26 – 1.03 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 136.8, 129.1, 129.0, 125.5, 88.6, 65.6, 21.2, 18.2, 18.0, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{19}H_{32}NO_3SSi^+$ $[M+H]^+$: 382.1867; found: 382.1862.

IR (ATR) (ν_{max} cm $^{-1}$) = 2949, 2870, 1762, 1461, 1372, 1220, 1167, 1106, 1015, 915, 879, 736.

2-(1-Oxido-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl)isoindoline-1,3-dione (1p)



Prepared according to **General Procedure A** using (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5.6 mg, 0.005 mmol, 1 mol%), 2-(1-phenyl-vinyl)-isoindole-1,3-dione (249.3 mg, 1.0 mmol, 2.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 2:1. Purification by flash silica column chromatography (20:20:1 Petrol: CH_2Cl_2: EtOAc) afforded the title compound **1p**-major (90.4 mg, 39%) and **1p**-minor (52.1 mg, 22%) as separable products.

1p-major (colourless oil)

Rf = 0.3 (5:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.51 – 7.35 (m, 5H), 5.08 (d, *J* = 9.7 Hz, 1H), 4.79 (d, *J* = 9.7 Hz, 1H), 1.32 – 1.11 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 134.9, 132.0, 131.7, 129.4, 128.5, 127.0, 124.1, 78.7, 57.2, 18.3, 18.2, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{25}H_{33}N_2O_3SSi^+$ $[M+H]^+$: 469.1976; found: 469.1977.

IR (ATR) (ν_{max} cm $^{-1}$) = 2947, 2868, 1722, 1466, 1371, 1314, 1117, 1084, 883, 719.

M. p. 108-110 ^oC (CH_2Cl_2)

1p-minor (white solid)

Rf = 0.1 (5:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.65 (m, 6H), 7.47 – 7.32 (m, 3H), 5.99 (d, *J* = 9.0 Hz, 1H), 4.78 (d, *J* = 9.0 Hz, 1H), 1.26 – 0.99 (m, 21H).

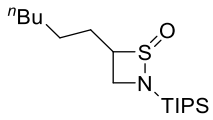
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 137.9, 134.5, 131.9, 129.0, 129.0, 126.6, 123.6, 74.6, 62.5, 18.1, 17.9, 11.3. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{25}H_{33}N_2O_3SSi^+$ $[M+H]^+$: 469.1976; found: 469.1991.

IR (ATR) (ν_{max} cm $^{-1}$) = 2947, 2868, 1722, 1466, 1371, 1114, 1086, 883, 718, 695.

M. p. 132-134 ^oC (CH_2Cl_2)

4-Hexyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1q**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), 1-octene (314 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 3:1. Purification by flash silica column chromatography

(30:1 to 15:1 Petrol: EtOAc) afforded the title compound **1q**-major (61.8 mg, 37%) and **1q**-minor (20.0 mg, 12%) as separable products.

1q-major (yellow oil)

Rf = 0.6 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.32 (dd, *J* = 7.4, 7.4 Hz, 1H), 2.07 – 1.94 (m, 1H), 1.63 – 1.53 (m, 1H), 1.32 – 0.99 (m, 29H), 0.84 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 57.5, 56.8, 31.7, 29.1, 26.3, 26.2, 22.6, 18.2, 18.1, 14.1, 11.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{17}H_{38}NOSSi^+$ $[M+H]^+$: 332.2438; found: 332.2453.

IR (ATR) (ν_{max} cm $^{-1}$) = 2932, 2867, 1465, 1101, 944, 882, 691.

1q-minor (yellow oil)

Rf = 0.3 (10:1 Petrol: EtOAc)

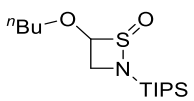
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.85 (dd, *J* = 7.5, 3.9 Hz, 1H), 3.27 – 3.12 (m, 1H), 2.04 – 1.90 (m, 1H), 1.84 – 1.70 (m, 1H), 1.47 – 1.25 (m, 8H), 1.19 – 1.09 (m, 21H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 65.8, 53.9, 31.7, 30.5, 29.1, 26.6, 22.6, 18.2, 18.1, 14.2, 11.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{17}H_{38}NOSSi^+$ $[M+H]^+$: 332.2438; found: 332.2450.

IR (ATR) (ν_{max} cm $^{-1}$) = 2929, 2867, 1464, 1109, 925, 884, 690.

4-Butoxy-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1r**)



Prepared according to **General Procedure A** using $Ir(dFppy)_3$ (3.8 mg, 0.005 mmol, 1 mol%), butyl vinyl ether (258 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^1H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 1.4:1. Purification by flash silica column chromatography (7:1 to 5:1 Petrol: EtOAc) afforded the title compound **1r**-major and **1r**-minor as an inseparable yellow oil (85.0 mg, 53%).

Rf = 0.4 (5:1 Petrol: EtOAc)

1r-major

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 – 4.78 (m, 2H), 4.73 – 4.62 (m, 1H), 3.76 – 3.61 (m, 1H), 3.60 – 3.49 (m, 1H), 1.70 – 1.57 (m, 2H), 1.46 – 1.35 (m, 2H), 1.21 – 1.06 (m, 21H), 0.97 – 0.88 (m, 3H).

1r-minor

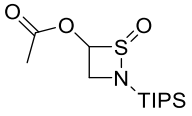
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 – 4.62 (m, 1H), 4.51 – 4.46 (m, 1H), 4.11 – 4.03 (m, 1H), 3.88 – 3.79 (m, 1H), 3.76 – 3.61 (m, 1H), 1.70 – 1.57 (m, 2H), 1.46 – 1.35 (m, 2H), 1.21 – 1.06 (m, 21H), 0.97 – 0.88 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 100.4, 85.8, 71.6, 71.0, 62.4, 54.8, 31.5, 31.4, 19.17, 19.16, 18.2, 18.12, 18.10, 18.06, 13.9, 13.8, 11.52, 11.49. (note: the signals of two diastereomers can't be distinguished in the mix ^{13}C NMR, for methyl groups in TIPS groups in both diastereomers, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{15}H_{34}NO_2SSi^+$ $[M+H]^+$: 320.2074; found: 320.2083.

IR (ATR) (ν_{max} cm $^{-1}$) = 2945, 2869, 1465, 1214, 1138, 1094, 883, 692.

1-Oxido-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl acetate (**1s**)



Prepared according to **General Procedure A** using (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5.6 mg, 0.005 mmol, 1 mol%), vinyl acetate (184 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 1.2:1. Purification by flash silica column chromatography (6:1 Petrol: EtOAc) afforded the title compound **1s**-major and **1s**-minor as an inseparable white solid (73.3 mg, 48%).

Rf = 0.4 (6:1 Petrol: EtOAc)

1s-major

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (dd, *J* = 6.6, 6.6 Hz, 1H), 4.89 (dd, *J* = 8.3, 6.3 Hz, 1H), 4.68 (dd, *J* = 8.3, 6.8 Hz, 1H), 2.22 (s, 3H), 1.23 – 1.09 (m, 21H).

1s-minor

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (dd, *J* = 6.8, 3.5 Hz, 1H), 4.80 (dd, *J* = 8.7, 6.8 Hz, 1H), 4.16 (dd, *J* = 8.7, 3.5 Hz, 1H), 2.19 (s, 3H), 1.23 – 1.09 (m, 21H).

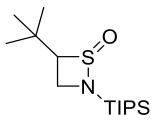
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.34, 169.30, 88.6, 75.4, 59.6, 53.4, 20.6, 20.5, 18.14, 18.08, 18.04, 18.01, 11.4. (note: the signals of two diastereomers can't be distinguished in the mix 13C NMR, for methyl groups in TIPS groups in both diastereomers, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{13}H_{28}NO_3SSi^+$ $[M+H]^+$: 306.1554; found: 306.1559.

IR (ATR) (ν_{max} cm $^{-1}$) = 2946, 2868, 1760, 1465, 1374, 1216, 1118, 1070, 883, 860, 676.

M. p. 36-38 ^{o}C (Petrol & EtOAc)

4-(*tert*-Butyl)-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1t**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), 3,3-dimethyl-1-butene (258 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 6:1. Purification by flash silica column chromatography (20:1 to 10:1 Petrol: EtOAc) afforded the title compound **1t**-major (84.5 mg, 56%) and **1t**-minor (18.2 mg, 12%) as separable products.

1t-major (yellow oil)

Rf = 0.5 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.30 (dd, *J* = 7.6, 7.6 Hz, 1H), 3.40 (dd, *J* = 7.8, 7.8 Hz, 1H), 1.25 – 1.05 (m, 30H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 64.7, 54.0, 33.2, 26.8, 18.2, 18.1, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS (ESI)$^+$ calcd. for $C_{15}H_{34}NOSSi^+$ $[M+H]^+$: 304.2125; found: 304.2123.

IR (ATR) (ν_{max} cm $^{-1}$) = 2949, 2868, 1465, 1366, 1098, 950, 883, 868, 693.

1t-minor (yellow oil)

Rf = 0.2 (10:1 Petrol: EtOAc)

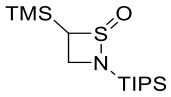
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (dd, *J* = 8.5, 7.5 Hz, 1H), 4.06 (dd, *J* = 7.5, 4.8 Hz, 1H), 3.13 (dd, *J* = 8.5, 4.8 Hz, 1H), 1.20 – 1.09 (m, 21H), 1.07 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 77.4, 48.5, 31.6, 26.3, 18.2, 18.1, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS (ESI)$^+$ calcd. for $C_{15}H_{34}NOSSi^+$ $[M+H]^+$: 304.2125; found: 304.2124.

IR (ATR) (ν_{max} cm $^{-1}$) = 2957, 2868, 1465, 1368, 1141, 1090, 924, 883, 735.

2-(Triisopropylsilyl)-4-(trimethylsilyl)-1,2-thiazetidine 1-oxide (**1u**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), vinyltrimethylsilane (294 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 2.5:1. Purification by flash silica column chromatography (20:1 to 10:1 Petrol: EtOAc) afforded the title compound **1u**-major (36.2 mg, 23%) and **1u**-minor (14.0 mg, 9%) as separable products.

1u-major (yellow oil)

Rf = 0.5 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 – 4.28 (m, 2H), 3.47 (dd, *J* = 8.4, 6.6 Hz, 1H), 1.22 – 1.04 (m, 21H), 0.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 50.0, 48.5, 18.3, 18.2, 11.4, -2.2. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{14}H_{34}NOSSi_2^+$ $[M+H]^+$: 320.1894; found: 320.1907.

IR (ATR) (ν_{max} cm $^{-1}$) = 2950, 2868, 1465, 1251, 1087, 934, 850, 749, 684.

1u-minor (yellow oil)

Rf = 0.3 (10:1 Petrol: EtOAc)

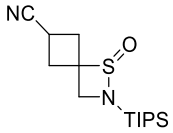
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (dd, *J* = 8.8, 7.0 Hz, 1H), 4.23 (dd, *J* = 7.0, 4.3 Hz, 1H), 2.89 (dd, *J* = 8.8, 4.4 Hz, 1H), 1.22 – 1.05 (m, 21H), 0.19 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 55.5, 50.7, 18.3, 18.1, 11.5, -3.0. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS (ESI) calcd. for $C_{14}H_{34}NOSSi_2^+$ $[M+H]^+$: 320.1894; found: 320.1908.

IR (ATR) (ν_{max} cm $^{-1}$) = 2953, 2872, 1466, 1254, 1116, 919, 849, 740, 681.

2-(Triisopropylsilyl)-1-thia-2-azaspiro[3.3]heptane-6-carbonitrile 1-oxide (**1v**)



Prepared according to **General Procedure A** using (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5.6 mg, 0.005 mmol, 1 mol%), 3-methylenecyclobutanecarbonitrile (204 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 2:1. Purification by flash silica column chromatography (5:1 to 2:1 Petrol: EtOAc) afforded the title compound **1v**-major (38.7 mg, 25%) and **1v**-minor (27.0 mg, 17%) as separable products.

1v-major (white solid)

Rf = 0.5 (5:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (d, *J* = 8.4 Hz, 1H), 4.25 (d, *J* = 8.3 Hz, 1H), 3.29 – 3.20 (m, 1H), 3.08 – 2.97 (m, 2H), 2.87 – 2.73 (m, 1H), 2.50 – 2.37 (m, 1H), 1.22 – 1.03 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 121.0, 61.1, 60.9, 34.4, 31.2, 18.1, 18.0, 16.9, 11.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for two CH_2 groups in four-membered ring, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{15}H_{29}N_2OSSi^+$ $[M+H]^+$: 313.1764; found: 313.1778.

IR (ATR) (ν_{max} cm $^{-1}$) = 2943, 2867, 1463, 1106, 1063, 937, 882, 776, 694.

M. p. 66-68 ^{o}C (Petrol & EtOAc)

1v-minor (yellow oil)

Rf = 0.3 (5:1 Petrol: EtOAc)

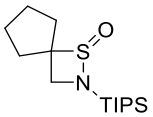
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 (d, *J* = 8.1 Hz, 1H), 4.27 (d, *J* = 8.1 Hz, 1H), 3.25 – 3.06 (m, 2H), 3.00 – 2.91 (m, 1H), 2.89 – 2.76 (m, 1H), 2.56 – 2.44 (m, 1H), 1.27 – 1.01 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 120.9, 61.9, 60.4, 34.1, 31.1, 18.1, 18.0, 17.2, 11.3. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for two CH_2 groups in cyclicbutane, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{15}H_{29}N_2OSSi^+$ $[M+H]^+$: 313.1764; found: 313.1764.

IR (ATR) (ν_{max} cm $^{-1}$) = 2945, 2868, 1464, 1099, 938, 883, 736, 689.

2-(Triisopropylsilyl)-1-thia-2-azaspiro[3.4]octane 1-oxide (1w)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), methylenecyclopentane (210 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Purification by flash silica column chromatography (20:1 Petrol: EtOAc) afforded the title compound **1w** (68.2 mg, 45%) as a yellow soild.

Rf = 0.5 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (d, *J* = 7.5 Hz, 1H), 4.13 (d, *J* = 7.5 Hz, 1H), 2.74 – 2.54 (m, 1H), 2.54 – 2.37 (m, 1H), 2.00 – 1.86 (m, 1H), 1.75 – 1.51 (m, 4H), 1.50 – 1.37 (m, 1H), 1.22 – 1.05 (m, 21H).

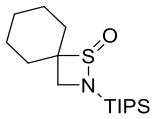
^{13}C NMR (101 MHz, $CDCl_3$) δ 69.8, 61.8, 35.9, 29.8, 25.4, 25.1, 18.2, 18.1, 11.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{15}H_{32}NOSSi^+$ $[M+H]^+$: 302.1968; found: 302.1974.

IR (ATR) (ν_{max} cm $^{-1}$) = 2947, 2867, 1464, 1100, 1069, 921, 885, 692.

M. p. 34-36 °C (CH_2Cl_2)

2-(Triisopropylsilyl)-1-thia-2-azaspiro[3.5]nonane 1-oxide (**1x**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), methylenecyclohexane (240 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Purification by flash silica column chromatography (20:1 Petrol: EtOAc) afforded the title compound **1x** (95.0 mg, 60%) as a yellow oil.

Rf = 0.5 (10:1 Petrol: EtOAc)

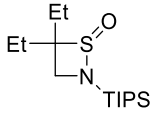
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (d, *J* = 7.3 Hz, 1H), 3.81 (d, *J* = 7.3 Hz, 1H), 2.21 – 2.03 (m, 2H), 1.88 – 1.75 (m, 1H), 1.58 – 1.40 (m, 6H), 1.33 – 1.25 (m, 1H), 1.17 – 0.98 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 62.7, 62.1, 33.0, 29.4, 25.0, 23.0, 22.4, 18.2, 18.0, 11.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for five CH_2 groups in six-membered ring, 5 peaks were found instead of 3)

HRMS $(ESI)^+$ calcd. for $C_{16}H_{34}NOSSi^+$ $[M+H]^+$: 316.2125; found: 316.2125.

IR (ATR) (ν_{max} cm $^{-1}$) = 2939, 2866, 1463, 1093, 937, 881, 672.

4,4-Diethyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1y**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), methylenecyclohexane (244 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0

equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Purification by flash silica column chromatography (20:1 Petrol: EtOAc) afforded the title compound **1y** (100.2 mg, 66%) as a yellow oil.

Rf = 0.5 (10:1 Petrol: EtOAc)

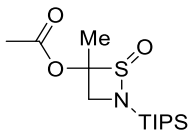
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (d, *J* = 7.4 Hz, 1H), 3.83 (d, *J* = 7.4 Hz, 1H), 2.03 – 1.78 (m, 4H), 1.21 – 1.04 (m, 21H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 65.6, 60.2, 25.4, 21.5, 18.2, 18.1, 11.5, 8.5, 6.9. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for two ethyl groups, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{15}H_{34}NOSSi^+$ $[M+H]^+$: 304.2125; found: 304.2138.

IR (ATR) (ν_{max} cm $^{-1}$) = 2956, 2868, 1461, 1097, 1001, 937, 886, 687.

4-Methyl-1-oxido-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl acetate (1z)



Prepared according to **General Procedure A** using $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5.6 mg, 0.005 mmol, 1 mol%), isopropenyl acetate (220 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 2.5:1. Purification by flash silica column (20:1 to 10:1 to 5:1 Petrol: EtOAc) afforded the title compound **1z**-major (56.0 mg, 35%) and **1z**-minor (24.0 mg, 15%) as separable products.

1z-major (colourless oil)

Rf = 0.3 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29 (d, *J* = 8.5 Hz, 1H), 4.24 (d, *J* = 8.5 Hz, 1H), 2.12 (s, 3H), 1.73 (s, 3H), 1.22 – 1.04 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 94.5, 60.0, 21.3, 18.1, 18.0, 17.5, 11.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{14}H_{30}NO_3SSi^+$ $[M+H]^+$: 320.1710; found: 320.1704.

IR (ATR) (ν_{max} cm $^{-1}$) = 2946, 2868, 1752, 1465, 1372, 1219, 1191, 1020, 930, 885.

1z-minor (colourless oil)

Rf = 0.2 (10:1 Petrol: EtOAc)

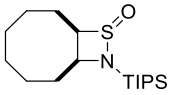
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (d, *J* = 8.1 Hz, 1H), 4.23 (d, *J* = 8.1 Hz, 1H), 2.16 (s, 3H), 1.99 (s, 3H), 1.22 – 1.02 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 86.7, 65.9, 21.2, 19.9, 18.1, 18.0, 11.4. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{14}H_{30}NO_3SSi^+$ $[M+H]^+$: 320.1710; found: 320.1704.

IR (ATR) (ν_{max} cm $^{-1}$) = 2945, 2869, 1756, 1464, 1371, 1237, 1197, 1118, 1091, 1016, 914, 881, 855.

10-(Triisopropylsilyl)-9-thia-10-azabicyclo[6.2.0]decane 9-oxide (1aa)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), *cis*-cyclooctene (260 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 3.5:1. Purification by flash silica column chromatography (15:1 Petrol: EtOAc) afforded the title compound **1aa**-major and **1aa** -minor as an inseparable yellow oil (127.0 mg, 77%).

Rf = 0.6 (10:1 Petrol: EtOAc)

1aa-major

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 – 4.42 (m, 1H), 3.74 – 3.63 (m, 1H), 2.45 – 0.98 (m, 33H).

1aa-minor

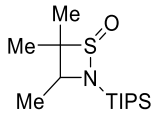
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 – 5.00 (m, 1H), 3.15 – 3.02 (m, 1H), 2.45 – 0.98 (m, 33H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 69.8, 69.4, 65.7, 59.2, 35.7, 29.7, 29.2, 28.5, 27.9, 27.2, 26.4, 25.73, 25.6, 25.1, 24.2, 20.3, 18.4, 18.3, 18.2, 12.4, 11.8. (note: the signals of two diastereomers can't be distinguished in the mix ^{13}C NMR, for methyl groups in TIPS groups in both diastereomers, 3 peaks were found instead of 2)

HRMS (ESI) calcd. for $C_{17}H_{36}NOSSi^+$ $[M+H]^+$: 330.2281; found: 330.2280.

IR (ATR) (ν_{max} cm $^{-1}$) = 2931, 2866, 1464, 1074, 920, 883, 732.

3,4,4-Trimethyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (**1ab**)



Prepared according to **General Procedure A** using 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%), *cis*-cyclooctene (212 μL, 2.0 mmol, 4.0 equiv.), TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M). Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 3:1. Purification by flash silica column chromatography (20:1 to 10:1 Petrol: EtOAc) afforded the title compound **1ab**-major and **1ab**-minor as inseparable yellow oil (78.2 mg, 77%).

Rf = 0.5 (5:1 Petrol: EtOAc)

1ab-major

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (q, *J* = 6.6 Hz, 1H), 1.56 (s, 3H), 1.36 (d, *J* = 6.6 Hz, 3H), 1.23 (s, 3H), 1.21 – 1.05 (m, 21H)

1ab-minor

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (q, *J* = 6.6 Hz, 1H), 1.41 (s, 3H), 1.25 (s, 3H), 1.21 – 1.05 (m, 24H)

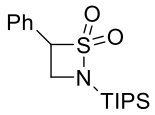
^{13}C NMR (101 MHz, $CDCl_3$) δ 68.54, 68.47, 60.3, 59.8, 24.9, 22.9, 19.3, 18.4, 18.3, 18.2, 17.3, 14.9, 12.3, 11.7. (note: the signals of two diastereomers can't be distinguished in the mix ^{13}C NMR, for methyl groups in TIPS groups in both diastereomers, 3 peaks were found instead of 2, for CH groups in TIPS groups in both diastereomers, 2 peaks overlap to show just 1 peak)

HRMS $(ESI)^+$ calcd. for $C_{14}H_{32}NOSSi^+$ $[M+H]^+$: 290.1968; found: 290.1967.

IR (ATR) (ν_{max} cm $^{-1}$) = 2947, 2868, 1464, 1373, 1092, 998, 883, 855, 686.

5.3.4 Derivatization of *β*-sultams

4-Phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1,1-dioxide (2a)



To a 10 mL microwave vial, **1a** (5:1 **1a**-major: **1a**-minor) (48.5 mg, 0.15 mmol, 1 equiv.) was added. The vial was then capped with suba-seal and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (1 mL, 0.15 M) was added, followed by *m*-CPBA (≤77%, 67.2 mg, 0.3 mmol, 2 equiv.). The mixture was allowed to stirred at room temperature.

After 2 h, the mixture was transferred to a 50 mL RBF with EtOAc (20 mL), then quenched with aqueous $Na_2S_2O_3$ solution (10 mL), washed with aqueous $NaHCO_3$ solution (10 mL). The mixture was then extracted with EtOAc (2×10 mL). The organic layer was combined and dried with anhydrous Na_2SO_4. The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (20:1 Petrol: EtOAc) to afford title compound **2a** (50.7 mg, >99%) as a white solid.

Rf = 0.5 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46– 7.36 (m, 5H), 5.59 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.81 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.47 (dd, *J* = 5.8, 5.8 Hz, 1H), 1.41 – 1.30 (m, 3H), 1.27 – 1.18 (m, 18H).

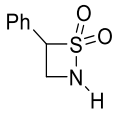
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.2, 129.5, 129.1, 128.9, 77.7, 40.3, 18.2, 12.0.

HRMS $(ESI)^+$ calcd. for $C_{17}H_{30}NO_2SSi^+$ $[M+H]^+$: 340.1761; found: 340.1769.

IR (ATR) (ν_{max} cm $^{-1}$) = 2951, 2870, 1466, 1309, 1177, 1063, 912, 737.

M. p. 72-74 ^oC (CH_2Cl_2)

4-Phenyl-1,2-thiazetidine 1,1-dioxide (2aa)



To a 10 mL microwave vial, **2a** (67.9 mg, 0.2 mmol, 1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. THF (0.8 mL, 0.25 M) was then added. The mixture was placed in 0 ^{o}C ice water bath, followed by addition of acetate acid (24 μL, 0.4 mmol, 2 equiv.). TBAF (1M in THF, 0.2 mL, 0.2 mmol, 1 equiv.) was then added, the reaction was allowed to stirred in 0 ^{o}C ice water bath.

After 5 min, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (2:1 Petrol: EtOAc) to afford the title compound **2aa** (33.7 mg, 92%) as a white solid.

Rf = 0.5 (1:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.59 – 7.50 (m, 2H), 7.49 – 7.36 (m, 3H), 6.93 (s, 1H), 5.77 (dd, *J* = 8.6, 6.5 Hz, 1H), 3.84 – 3.75 (m, 1H), 3.54 – 3.45 (m, 1H).

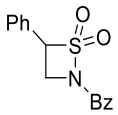
^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 132.4, 129.9, 129.8, 129.6, 78.8, 37.0.

HRMS $(ESI)^+$ calcd. for $C_8H_9NO_2SNa^+$ $[M+Na]^+$: 206.0246; found: 206.0247.

IR (ATR) (ν_{max} cm $^{-1}$) = 3332, 1499, 1311, 1157, 773, 700.

M. p. 102-104 ^{o}C (CH_2Cl_2)

(1,1-Dioxido-4-phenyl-1,2-thiazetidin-2-yl)(phenyl)methanone (2ab)



To a 25 mL oven dried RBF charged with **2aa** (91.6 mg, 0.5 mmol, 1 equiv.), DMAP (91.7 mg, 0.75 mmol, 1.5 equiv.) was added. The vial was then capped with suba-seal and

subjected to three evacuation/argon refill cycles. CH_2Cl_2 (5 mL, 0.1 M) was added, followed by addition of benzoyl chloride (88 μL, 0.75 mmol, 1.5 equiv.). The reaction was allowed to stirred at room temperature.

After 2 h, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (8:1 Petrol: EtOAc) to afford the title compound **2ab** (114.4 mg, 80%) as a white solid.

Rf = 0.5 (3:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.44 (m, 7H), 5.61 (dd, *J* = 9.3, 6.4 Hz, 1H), 4.33 (dd, *J* = 8.9, 8.9 Hz, 1H), 4.03 (dd, *J* = 8.5, 6.4 Hz, 1H).

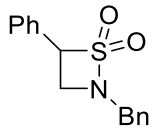
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 133.8, 132.4, 130.3, 129.4, 129.2, 129.1, 129.0, 128.7, 74.8, 39.8.

HRMS $(ESI)^+$ calcd. for $C_{15}H_{13}NO_3SNa^+$ $[M+Na]^+$: 310.0508; found: 310.0504.

IR (ATR) (ν_{max} cm $^{-1}$) = 3066, 1677, 1452, 1349, 1322, 1184,1030, 912, 733, 696.

M. p. 114-116 ^oC (CH_2Cl_2)

2-Benzyl-4-phenyl-1,2-thiazetidine 1,1-dioxide (2ac)



To a 10 mL microwave vial charged with **2aa** (36.6 mg, 0.2 mmol, 1 equiv.), TBAB (6.4 mg, 0.02 mmol, 10 mol%) and KOH powder (12.3 mg, 0.22 mmol, 1.1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill

cycles. THF (2 mL, 0.1 M) was added, followed by addition of benzyl bromide (0.22 mmol, 26 μL, 1.1 equiv.). The reaction was then allowed to stirred at room temperature.

After 16 h, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (5:1 Petrol: EtOAc) to afford the title compound **2ac** (33.0 mg, 60%) as a yellow oil.

Rf = 0.4 (5:1 Petrol: EtOAc)

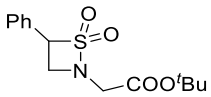
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 10H), 5.43 (dd, *J* = 8.2, 5.8 Hz, 1H), 4.37 – 4.29 (m, 2H), 3.55 (dd, *J* = 8.2, 6.1 Hz, 1H), 3.22 (dd, *J* = 6.0, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 130.1, 129.7, 129.2, 128.93, 128.90, 128.7, 128.2, 75.1, 50.5, 44.1.

HRMS $(ESI)^+$ calcd. for $C_{15}H_{15}NO_2SNa^+$ $[M+Na]^+$: 296.0716; found: 296.0709.

IR (ATR) (ν_{max} cm $^{-1}$) = 2993, 1743, 1377, 1244, 1180, 1044, 941, 809, 768.

***tert*-Butyl 2-(1,1-dioxido-4-phenyl-1,2-thiazetidin-2-yl)acetate (2ad)**



To a 10 mL microwave vial charged with **2aa** (36.6 mg, 0.2 mmol, 1 equiv.), TBAB (6.4 mg, 0.02 mmol, 10 mol%) and KOH powder (12.3 mg, 0.22 mmol, 1.1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. THF (2 mL, 0.1 M) was added, followed by addition of *tert*-butyl bromoacetate (0.3 mmol, 46 μL, 1.5 equiv.). The reaction was then allowed to stirred at room temperature.

After 16 h, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was

purified by silica column chromatography (5:1 Petrol: EtOAc) to afford the title compound **2ad** (41.6 mg, 70%) as a yellow oil.

Rf = 0.4 (5:1 Petrol: EtOAc)

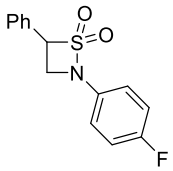
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 5H), 5.49 (dd, *J* = 8.3, 5.8 Hz, 1H), 3.85 – 3.77 (m, 3H), 3.49 (dd, *J* = 6.0, 6.0 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 129.9, 129.7, 129.1, 129.0, 82.8, 76.1, 48.0, 44.7, 28.1.

HRMS $(ESI)^+$ calcd. for $C_{14}H_{19}NO_4SNa^+$ $[M+Na]^+$: 320.0927; found: 320.0927.

IR (ATR) (ν_{max} cm $^{-1}$) = 2981, 1742, 1370, 1325, 1236, 1163.

2-(4-Fluorophenyl)-4-phenyl-1,2-thiazetidine 1,1-dioxide (2ae)



To a 10 mL microwave vial charged with **2aa** (73.3 mg, 0.4 mmol, 1 equiv.), 4-Fluorophenylboronic acid (112.0 mg, 0.8 mmol, 2 equiv.) and $Cu(CH_3CN)_4PF_6$ (74.0 mg, 0.2 mmol, 0.5 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/oxygen refill cycles. MeCN (1.5 mL, 0.27 M) was added, followed by addition of *N*-methylpiperidine (388 μL, 3.2 mmol, 8 equiv.). The reaction was then allowed to stirred at room temperature.

After 16 h, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (20:20:1 Petrol: CH_2Cl_2: EtOAc) to afford the title compound **2ae** (82.0 mg, 74%) as a pale-yellow solid.

Rf = 0.8 (20:20:1 Petrol: CH_2Cl_2: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.38 (m, 5H), 7.13 – 6.97 (m, 4H), 5.60 (dd, *J* = 8.2, 5.4 Hz, 1H), 4.09 (dd, *J* = 8.2, 5.7 Hz, 1H), 3.76 (dd, *J* = 5.6, 5.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 (d, *J* = 243.0 Hz), 134.5 (d, *J* = 2.6 Hz), 130.1, 129.6, 129.3, 129.1, 117.7 (d, *J* = 8.1 Hz), 116.6 (d, *J* = 23.0 Hz), 75.3, 42.6.

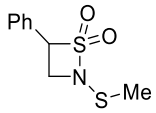
^{19}F NMR (377 MHz, $CDCl_3$) δ -118.96 (s).

HRMS $(ESI)^+$ calcd. for $C_{14}H_{12}FNO_2SNa^+$ $[M+Na]^+$: 300.0465; found: 300.0476.

IR (ATR) (ν_{max} cm $^{-1}$) = 1512, 1327, 1234, 1179, 826, 739.

M. p. 116-118 ^oC (CH_2Cl_2)

2-(Methylthio)-4-phenyl-1,2-thiazetidine 1,1-dioxide (2af)



To a 10 mL microwave vial, **2aa** (36.6 mg, 0.2 mmol, 1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/nitrogen refill cycles. THF (2 mL, 0.1 M) was added. The mixture was then placed in 78 ^oC dry ice acetone bath, followed by addition of LiHMDS solution (1 M in THF, 0.22 mL, 0.22 mmol, 1.1 equiv.). After the reaction mixture was stirred for 5 min, S-methylmethanethiosulfonate (48 μL, 0.5 mmol, 2.5 equiv.) was added. The solution was allowed to warm to room temperature.

After 3 h, the reaction was quenched with aqueous NH_4Cl solution (1.5 mL) and extracted with EtOAc (3×10 mL). The organic layer was combined and dried with anhydrous Na_2SO_4. The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (3:1 Petrol: EtOAc) to afford title compound **2af** (45.7 mg, >99%) as a colourless oil.

Rf = 0.4 (3:1 Petrol: EtOAc)

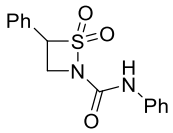
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 5H), 5.49 (dd, *J* = 8.4, 5.8 Hz, 1H), 3.89 (dd, *J* = 8.4, 6.1 Hz, 1H), 3.59 (dd, *J* = 5.9, 5.9 Hz, 1H), 2.61 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.0, 129.9, 129.3, 128.7, 76.9, 46.3, 20.0.

HRMS $(ESI)^+$ calcd. for $C_{14}H_{12}FNO_2SNa^+$ $[M+Na]^+$: 300.0465; found: 300.0476.

IR (ATR) (ν_{max} cm $^{-1}$) = 1512, 1327, 1234, 1179, 826, 739.

***N*,4-Diphenyl-1,2-thiazetidine-2-carboxamide 1,1-dioxide (2ag)**



To a 10 mL microwave vial, **2aa** (36.6 mg, 0.2 mmol, 1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (2 mL, 0.1 M) was added, followed by addition of phenyl isocyanate (34 μL, 0.3 mmol, 1.5 equiv.) and triethylamine (42 μL, 0.3 mmol, 1.5 equiv.). The reaction was then allowed to stirred at room temperature.

After 4 h, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (16:16:1 Petrol: CH_2Cl_2: EtOAc) to afford the title compound **2ag** (37.0 mg, 61%) as a white solid.

Rf = 0.3 (16:16:1 Petrol: CH_2Cl_2: EtOAc)

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.52 (s, 1H), 7.65 – 7.59 (m, 4H), 7.56 – 7.41 (m, 3H), 7.38 – 7.28 (m, 2H), 7.15 – 7.06 (m, 1H), 5.89 (dd, *J* = 8.9, 6.1 Hz, 1H), 4.40 (dd, *J* = 8.9, 7.0 Hz, 1H), 4.08 (dd, *J* = 6.5, 6.5 Hz, 1H).

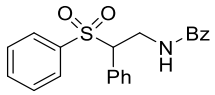
^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 149.4, 138.0, 129.59, 129.57, 129.4, 128.9, 128.7, 123.7, 120.3, 74.6, 41.2.

HRMS (ESI)$^+$ calcd. for $C_{15}H_{15}N_2O_3S^+$ [M+H]$^+$: 303.0798; found: 303.0784.

IR (ATR) (ν_{max} cm $^{-1}$) = 3368, 1680, 1600, 1544, 1446, 1343, 1156, 911, 741.

M. p. 166-168 ^{o}C (CH_2Cl_2)

***N*-(2-Phenyl-2-(phenylsulfonyl)ethyl)benzamide (3a)**



To a 10 mL microwave vial, **2ab** (28.7 mg, 0.1 mmol, 1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/nitrogen refill cycles. Et_2O (2 mL, 0.05 M) was added. The mixture was then placed in 0 ^{o}C ice water bath, followed by addition of PhMgBr (3 M in Et_2O, 0.1 mL, 0.3 mmol, 3 equiv.). After the reaction mixture was stirred for 20 min, the solution was allowed to warm to room temperature and stirred for additional 5 min.

Then, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (16:4:1 to 8:4:1 hexane: CH_2Cl_2: EtOAc) to afford the title compound **3a** (29.0 mg, 79%) as a colourless oil.

Rf = 0.4 (2:1 hexane: EtOAc)

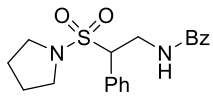
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.58 – 7.47 (m, 4H), 7.44 – 7.34 (m, 4H), 7.32 – 7.19 (m, 4H), 7.13 – 7.05 (m, 2H), 4.47 (dd, *J* = 9.0, 4.8 Hz, 1H), 4.36 (ddd, *J* = 14.5, 7.8, 4.8 Hz, 1H), 4.23 (ddd, *J* = 14.5, 9.0, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 136.8, 134.1, 134.0, 131.9, 131.5, 129.6, 129.3, 129.1, 128.9, 128.8, 128.7, 127.1, 70.2, 39.3.

HRMS (ESI)$^+$ calcd. for $C_{21}H_{20}NO_3S^+$ [M+H]$^+$: 366.1158; found: 366.1163.

IR (ATR) (ν_{max} cm $^{-1}$) = 3369, 3065, 1649, 1536, 1307, 1146, 1084, 911, 732, 694.

***N*-(2-Phenyl-2-(pyrrolidin-1-ylsulfonyl)ethyl)benzamide (3b)**



To a 10 mL microwave vial, **2ab** (28.7 mg, 0.1 mmol, 1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/nitrogen refill cycles. CH_2Cl_2 (1 mL, 0.1 M) was added, followed by addition of pyrrolidine (16 μL, 0.2 mmol, 2 equiv.). The reaction mixture was then stirred at room temperature.

After 4 h, the reaction mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (2:1 hexane: EtOAc) to afford the title compound **3b** (32.3 mg, 90%) as a colourless oil.

Rf = 0.3 (2:1 hexane: EtOAc)

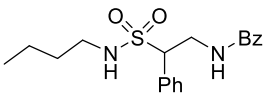
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.52 – 7.33 (m, 8H), 7.15 (s, 1H), 4.47 (dd, *J* = 9.0, 4.9 Hz, 1H), 4.28 (ddd, *J* = 14.4, 7.9, 4.9 Hz, 1H), 4.15 (ddd, *J* = 14.3, 9.0, 4.1 Hz, 1H), 3.25 – 3.15 (m, 2H), 2.95 – 2.81 (m, 2H), 1.82 – 1.59 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 134.1, 132.8, 131.8, 129.4, 129.3, 128.9, 128.7, 127.1, 66.2, 48.4, 40.4, 25.9.

HRMS $(ESI)^+$ calcd. for $C_{19}H_{23}N_2O_3S^+$ $[M+H]^+$: 359.1424; found: 359.1431.

IR (ATR) (ν_{max} cm $^{-1}$) = 3393, 2981, 2887, 1650, 1540, 1490, 1299, 1200, 1144, 1078, 1016, 914.

***N*-(2-(*N*-Butylsulfamoyl)-2-phenylethyl)benzamide (3c)**



To a 10 mL microwave vial, **2ab** (28.7 mg, 0.1 mmol, 1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/nitrogen refill cycles. CH_2Cl_2 (1 mL, 0.1 M) was added, followed by addition of *n*-butylamine (40 μL, 0.4 mmol, 4 equiv.). The reaction mixture was then stirred at 40 ^oC.

After 16 h, the reaction mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (2:1 hexane: EtOAc) to afford the title compound **3c** (29.9 mg, 83%) as a colourless oil.

Rf = 0.3 (2:1 hexane: EtOAc)

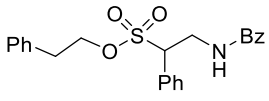
^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.87 (s, 1H), 7.78 – 7.69 (m, 2H), 7.55 – 7.44 (m, 3H), 7.43 – 7.30 (m, 5H), 6.15 (t, *J* = 5.9 Hz, 1H), 4.70 (dd, *J* = 8.6, 6.0 Hz, 1H), 4.28 (ddd, *J* = 13.8, 6.0, 5.1 Hz, 1H), 4.05 (ddd, *J* = 13.8, 8.6, 6.7 Hz, 1H), 2.93 (dt, *J* = 7.0, 5.9 Hz, 2H), 1.52 – 1.37 (m, 2H), 1.35 – 1.21 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 167.6, 135.5, 134.3, 132.1, 130.8, 129.2, 129.2, 129.1, 127.9, 66.8, 44.0, 41.1, 33.2, 20.3, 13.9.

HRMS $(ESI)^+$ calcd. for $C_{19}H_{25}N_2O_3S^+$ $[M+H]^+$: 361.1580; found: 361.1587.

IR (ATR) (ν_{max} cm $^{-1}$) = 3296, 2959, 1699, 1648, 1539, 1319, 1144, 704.

Phenethyl 2-benzamido-1-phenylethane-1-sulfonate (3d)



To a 10 mL microwave vial, **2ab** (28.7 mg, 0.1 mmol, 1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/nitrogen refill cycles. CH_2Cl_2 (1 mL, 0.1 M) was added, followed by addition of 2-phenylethanol (24 μL, 0.2 mmol,

2 equiv.) and triethylamine (14 μL, 0.1 mmol, 1 equiv.). The reaction mixture was then stirred at room temperature.

After 20 h, the reaction mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (5:1 to 2:1 hexane: EtOAc) to afford the title compound **3d** (32.8 mg, 80%) as a colourless oil.

Rf = 0.3 (2:1 hexane: EtOAc)

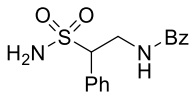
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.57 – 7.48 (m, 1H), 7.47 – 7.34 (m, 7H), 7.34 – 7.24 (m, 3H), 7.15 – 7.07 (m, 2H), 6.88 (s, 1H), 4.60 (dd, *J* = 8.6, 5.4 Hz, 1H), 4.30 – 4.20 (m, 2H), 4.20 – 4.07 (m, 2H), 2.90 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 136.1, 133.9, 132.0, 131.1, 129.6, 129.4, 129.2, 129.1, 128.8, 127.1, 127.1, 72.0, 66.1, 40.6, 35.7. (note: 2 peaks overlap to give 1 peak found in 128.8 ppm)

HRMS $(ESI)^+$ calcd. for $C_{23}H_{24}NO_4S^+$ $[M+H]^+$: 410.1421; found: 410.1420.

IR (ATR) (ν_{max} cm $^{-1}$) = 3334, 2876, 1651, 1536, 1491, 1353, 1315, 1168, 956, 913, 736, 699.

***N*-(2-Phenyl-2-sulfamoylethyl)benzamide (3e)**



To a 10 mL microwave vial, **2ab** (28.7 mg, 0.1 mmol, 1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/nitrogen refill cycles. MeCN (1 mL, 0.1 M) was added, followed by addition of aqueous ammonia (35%, 0.1 mL). The reaction mixture was then stirred at room temperature.

After 20 h, the reaction mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (1:1 hexane: EtOAc) to afford the title compound **3e** (14.9 mg, 49%) as a white solid.

Rf = 0.3 (1:1 hexane: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.50 – 7.29 (m, 8H), 7.09 (t, *J* = 6.0 Hz, 1H), 5.07 (s, 2H), 4.57 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.28 – 4.13 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 133.9, 132.6, 132.0, 129.54, 129.45, 129.2, 128.8, 127.2, 68.7, 40.6.

HRMS $(ESI)^+$ calcd. for $C_{15}H_{17}N_2O_3S^+$ $[M+H]^+$: 305.0954; found: 305.0954.

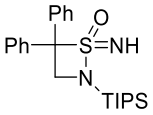
IR (ATR) (ν_{max} cm $^{-1}$) = 3375, 1710, 1647, 1540, 1331, 1150, 914, 735.

M. p. 78-80 ^{o}C (CH_2Cl_2)

5.3.5 Derivatization of aza-*β*-sultams

5.3.5.1 Synthesis of aza-*β*-sultams

1-Imino-4,4-diphenyl-2-(triisopropylsilyl)-1λ^6,2-thiazetidine 1-oxide (**4i**)



Prepared according to **General Procedure B**, using sulfinamide **1i** (119.9 mg, 0.30 mmol, 1.0 equiv.), $H_2NCO_2NH_4$ (93.7 mg, 1.20 mmol, 4.0 equiv.) and PhIO (198.0 mg, 0.90 mmol, 3.0 equiv.) and TFE (0.5 M). Purification by basic Al_2O_3 column chromatography (4:1 Petrol: EtOAc) afforded title compound **4i** (84.6 mg, 68%) as a white solid.

Rf = 0.5 (5:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.27 (m, 10H), 4.14 (d, *J* = 6.3 Hz, 1H), 4.04 (d, *J* = 6.4 Hz, 1H), 3.28 (bs, 1H), 1.46 – 1.32 (m, 3H), 1.30 – 1.15 (m, 18H).

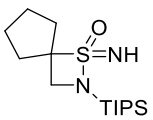
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.1, 128.9, 128.7, 128.4, 128.14, 128.07, 127.9, 92.5, 47.9, 18.32, 18.26, 12.3. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{23}H_{35}N_2OSSi^+$ $[M+H]^+$: 415.2234; found: 415.2249.

IR (ATR) (ν_{max} cm^{-1}) = 3329, 2949, 2870, 1459, 1250, 1064, 912, 738.

M.p. 106-108 °C (CH_2Cl_2).

1-Imino-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octane 1-oxide (**4w**)



Prepared according to **General Procedure B**, using sulfinamide **1w** (90.5 mg, 0.30 mmol, 1.0 equiv.), $H_2NCO_2NH_4$ (93.7 mg, 1.20 mmol, 4.0 equiv.) and PhIO (198.0 mg, 0.90 mmol,

3.0 equiv.) and TFE (0.5 M). Purification by basic Al_2O_3 column chromatography (4:1 Petrol: EtOAc) afforded title compound **4w** (75.9 mg, 80%) as a yellow solid.

Rf = 0.4 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (d, *J* = 5.6 Hz, 1H), 3.18 (d, *J* = 5.5 Hz, 1H), 2.89 (bs, 1H), 2.74 – 2.60 (m, 2H), 1.94 – 1.83 (m, 2H), 1.80 – 1.65 (m, 4H), 1.37 – 1.21 (m, 3H), 1.18 – 1.08 (m, 18H).

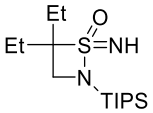
^{13}C NMR (101 MHz, $CDCl_3$) δ 87.1, 48.1, 36.1, 33.7, 25.8, 25.6, 18.31, 18.29, 12.2. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{15}H_{33}N_2OSSi^+$ $[M+H]^+$: 317.2077; found: 317.2087.

IR (ATR) (ν_{max} cm^{-1}) = 3276, 2848, 2871, 1465, 1212, 1051, 1004, 922, 689.

M.p. 60-62 °C (CH_2Cl_2).

4,4-Diethyl-1-imino-2-(triisopropylsilyl)-1λ^6,2-thiazetidine 1-oxide (**4y**)



Prepared according to **General Procedure B**, using sulfinamide **1y** (91.1 mg, 0.30 mmol, 1.0 equiv.), $H_2NCO_2NH_4$ (93.7 mg, 1.2 mmol, 4.0 equiv.) and PhIO (198.0 mg, 0.90 mmol, 3.0 equiv.) and TFE (0.5 M). Purification by basic Al_2O_3 column chromatography (6:1 Petrol: EtOAc) afforded title compound **4y** (82.2 mg, 86%) as a yellow oil.

Rf = 0.5 (4:1 Petrol: EtOAc).

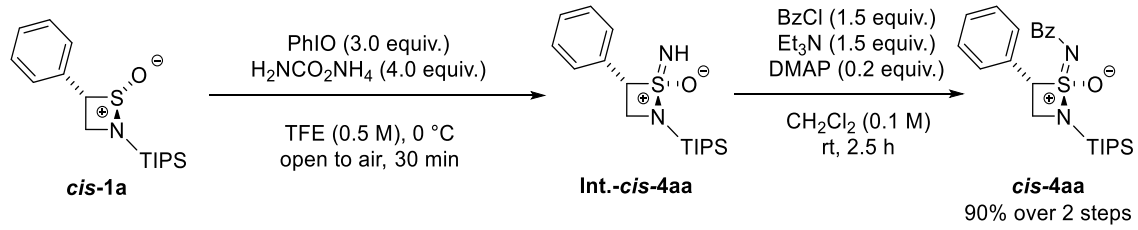
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 – 2.86 (m, 3H), 2.21 – 2.07 (m, 2H), 1.97 – 1.82 (m, 2H), 1.32 – 1.17 (m, 3H), 1.14 – 1.07 (m, 18H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 84.6, 46.5, 25.3, 24.2, 18.19, 18.16, 12.0, 9.0, 8.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for two ethyl groups, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{15}H_{35}N_2OSSi^+$ $[M+H]^+$: 319.2234; found: 319.2241.

IR (ATR) (ν_{max} cm^{-1}) = 3341, 2947, 2873, 1463, 1215, 1065, 1025, 960, 888, 689.

***cis*-*N*-(1-Oxido-4-phenyl-2-(triisopropylsilyl)-1λ^6,2-thiazetidin-1-ylidene)benzamide (*cis*-4aa)**



Synthesis of Int.-*cis*-4aa

Prepared according to **General Procedure B**, using *cis*-**1a** (**1a**-major) (97.1 mg, 0.30 mmol, 1.0 equiv.), ammonium carbamate (93.7 mg, 1.20 mmol, 4.0 equiv.) and PhIO (198.0 mg, 0.90 mmol, 3.0 equiv.) and TFE (0.5 M). The mixture was quickly filtered through a pad of basic Al_2O_3 (2 cm), washing with EtOAc (70 mL) and concentrated *in vacuo* to give **Int.-4aa**, which was used directly in the next step without further purification.

Synthesis of *cis*-4aa

To a 50 mL oven-dried round bottom flask, DMAP (7.3 mg, 0.06 mmol, 0.20 equiv.) was added. The round bottom flask was then capped with a suba-seal and subjected to three evacuation/argon refill cycles. **Int.-*cis*-4aa** was dissolved in CH_2Cl_2 (3 mL) and transferred to the flask, followed by addition of Et_3N (62 μL, 0.45 mmol, 1.5 equiv.) and benzoyl chloride (52 μL, 0.45 mmol, 1.5 equiv.), The resulting mixture was then stirred for 2.5 h, filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude

solution was concentrated *in vacuo* and purified by silica column chromatography (15:1 Petrol: EtOAc) to afford the desired product *cis*-**4aa** (119.3 mg, 90% over 2 steps) as a white solid.

Rf = 0.5 (8:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 2H), 7.54 – 7.37 (m, 8H), 6.41 (dd, *J* = 8.3, 5.0 Hz, 1H), 4.33 (dd, *J* = 8.3, 5.4 Hz, 1H), 3.70 (dd, *J* = 5.2, 5.2 Hz, 1H), 1.40 – 1.27 (m, 3H), 1.25 – 1.15 (m, 18H).

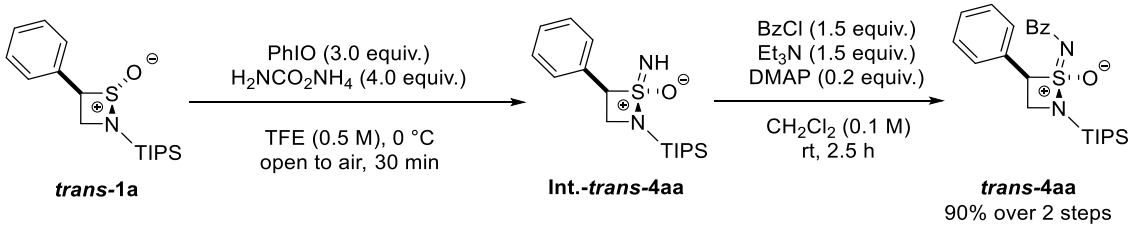
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 136.0, 132.1, 130.3, 129.7, 129.6, 129.4, 129.0, 128.0, 75.3, 43.5, 18.1, 18.0, 12.0. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{24}H_{35}N_2O_2SSi^+$ $[M+H]^+$: 443.2183; found: 443.2191.

IR (ATR) (ν_{max} cm^{-1}) = 2986, 1743, 1375, 1284, 1245, 152.

M.p. 64-66 °C (CH_2Cl_2).

***Trans*-*N*-(1-Oxido-4-phenyl-2-(triisopropylsilyl)-1λ^6,2-thiazetidin-1-ylidene)benzamide (*trans*-4aa)**



Synthesis of Int.-*trans*-4aa

Prepared according to **General Procedure B**, using *trans*-**1a** (**1a**-minor) (97.1 mg, 0.30 mmol, 1.0 equiv.), $H_2NCO_2NH_4$ (93.7 mg, 1.20 mmol, 4.0 equiv.) and PhIO (198.0 mg, 0.90 mmol, 3.0 equiv.) and TFE (0.5 M). The mixture was quickly filtered through a pad of basic

Al_2O_3 (2 cm), washing with EtOAc (70 mL) and concentrated *in vacuo* to give **Int.-4aa**, which was used directly in the next step without further purification.

Synthesis of *trans*-4aa

To a 50 mL oven-dried round bottom flask, DMAP (7.3 mg, 0.06 mmol, 0.20 equiv.) was added. The round bottom flask was then capped with a suba-seal and subjected to three evacuation/argon refill cycles. **Int.-*trans*-4aa** was dissolved in CH_2Cl_2 (3 mL) and transferred to the flask, followed by addition of Et_3N (62 μL, 0.45 mmol, 1.5 equiv.) and benzoyl chloride (52 μL, 0.45 mmol, 1.5 equiv.), The resulting mixture was then stirred for 2.5 h, filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (4:1 Petrol: EtOAc) to afford the desired product *trans*-**4aa** (119.0 mg, 90%) as a colourless oil.

Rf = 0.4 (4:1 Petrol:EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.39 (t, *J* = 7.1 Hz, 1H), 7.34 – 7.26 (m, 5H), 5.85 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.09 (dd, *J* = 5.9, 5.9 Hz, 1H), 4.02 (dd, *J* = 8.4, 5.7 Hz, 1H), 1.50 – 1.34 (m, 3H), 1.28 – 1.22 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 135.8, 131.6, 130.8, 129.3, 129.2, 128.8, 128.5, 127.8, 79.0, 42.6, 18.24, 18.15, 12.1. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

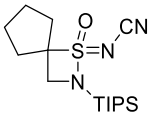
HRMS $(ESI)^+$ calcd. for $C_{24}H_{35}N_2O_2SSi^+$ $[M+H]^+$: 443.2183; found: 443.2184.

IR (ATR) (ν_{max} cm^{-1}) = 2950, 2871, 1632, 1284, 1245, 1058, 969, 732.

M.p. 88-90 °C (CH_2Cl_2).

5.3.5.2 Functionalization of aza-*β*-sultams

_N_-(1-Oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)cyanamide (4wa)



To a 10 mL microwave vial, sulfonimidamide **4w** (63.3 mg, 0.20 mmol, 1.0 equiv.) and DMAP (48.9 mg, 0.40 mmol, 2.0 equiv.) were added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (2 mL, 0.1 M) was added, followed by BrCN solution (0.10 mL, 3.0 M solution in CH_2Cl_2, 0.3 mmol, 1.5 equiv.). The resulting mixture was then stirred at room temperature for 1 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (3:1 Petrol: EtOAc) to afford the desired product **4wa** (39.0 mg, 57%) as a yellow oil.

Rf = 0.3 (2:1 Petrol: EtOAc).

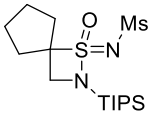
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (d, *J* = 5.3 Hz, 1H), 3.41 (d, *J* = 5.3 Hz, 1H), 2.86 – 2.71 (m, 2H), 2.19 – 2.08 (m, 1H), 2.06 – 1.94 (m, 1H), 1.88 – 1.72 (m, 4H), 1.40 – 1.22 (m, 3H), 1.20 – 1.12 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 112.6, 89.5, 50.1, 35.1, 34.8, 25.6, 25.3, 18.04, 17.99, 11.9. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{16}H_{32}N_3OSSi^+$ $[M+H]^+$: 342.2030; found: 342.2041.

IR (ATR) (ν_{max} cm^{-1}) = 2954, 2872, 2197, 1466, 1255, 1209, 1042, 860.

_N_-(1-Oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)methanesulfonamide (4wb)



To a 10 mL microwave vial, sulfonimidamide **4w** (63.3 mg, 0.20 mmol, 1.0 equiv.) and DMAP (4.9 mg, 0.04 mmol, 0.2 equiv.) were added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (2 mL, 0.1 M) was added, followed by Et_3N (42 μL, 0.30 mmol, 1.5 equiv.) and methanesulfonyl chloride (20 μL, 0.24 mmol, 1.2 equiv.). The resulting mixture was then stirred at room temperature for 1 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (4:1 Petrol: EtOAc) to afford the desired product **4wb** (55.6 mg, 70%) as a pale-yellow solid.

Rf = 0.4 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47 (d, *J* = 5.2 Hz, 1H), 3.40 (d, *J* = 5.3 Hz, 1H), 3.05 (s, 3H), 3.03 – 2.92 (m, 1H), 2.79 – 2.66 (m, 1H), 2.06 – 1.62 (m, 6H), 1.36 – 1.20 (m, 3H), 1.17 – 1.10 (m, 18H).

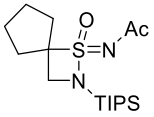
^{13}C NMR (101 MHz, $CDCl_3$) δ 88.8, 50.8, 43.3, 36.1, 35.2, 26.0, 25.2, 18.1, 18.0, 11.9. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{16}H_{35}N_2O_3S_2Si^+$ $[M+H]^+$: 395.1853; found: 395.1871.

IR (ATR) (ν_{max} cm^{-1}) = 2954, 2872, 1466, 1311, 1231, 1143, 1053, 913, 736.

M.p. 50-52 °C (CH_2Cl_2).

***N*-(1-Oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)acetamide (4wc)**



To a 10 mL microwave vial, sulfonimidamide **4w** (63.3 mg, 0.20 mmol, 1.0 equiv.) and DMAP (4.9 mg, 0.04 mmol, 0.2 equiv.) were added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (2 mL, 0.1 M) was added, followed by Et_3N (42 μL, 0.30 mmol, 1.5 equiv.) and acetyl chloride (22 μL, 0.30 mmol, 1.5 equiv.). The resulting mixture was then stirred at room temperature for 3 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (4:1 Petrol: EtOAc) to afford the desired product **4wc** (48.8 mg, 68%) as a yellow solid.

Rf = 0.2 (5:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (d, *J* = 4.7 Hz, 1H), 3.37 (d, *J* = 4.7 Hz, 1H), 2.89 – 2.78 (m, 1H), 2.53 – 2.42 (m, 1H), 2.08 (s, 3H), 2.06 – 1.88 (m, 2H), 1.83 – 1.60 (m, 4H), 1.33 – 1.19 (m, 3H), 1.18 – 1.11 (m, 18H).

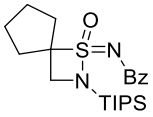
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 86.3, 51.6, 36.3, 34.3, 26.8, 25.90, 25.88, 18.10, 18.05, 12.1. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{17}H_{35}N_2O_2SSi^+$ $[M+H]^+$: 359.2183; found: 359.2191.

IR (ATR) (ν_{max} cm^{-1}) = 2953, 2872, 1639, 1465, 1362, 1268, 1234, 1046, 915, 846, 737.

M.p. 38-40 °C (CH_2Cl_2).

***N*-(1-Oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)benzamide (4wd)**



To a 10 mL microwave vial, sulfonimidamide **4w** (63.3 mg, 0.20 mmol, 1.0 equiv.) and DMAP (4.9 mg, 0.04 mmol, 0.2 equiv.) were added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (2 mL, 0.1 M) was added, followed by Et_3N (42 μL, 0.30 mmol, 1.5 equiv.) and benzoyl chloride (34 μL, 0.30 mmol, 1.5 equiv.). The resulting mixture was then stirred at room temperature for 3 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (10:1 Petrol: EtOAc) to afford the desired product **4wd** (81.6 mg, 97%) as a yellow oil.

Rf = 0.5 (5:1 Petrol: EtOAc).

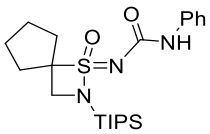
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.0 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 3.85 (d, *J* = 4.9 Hz, 1H), 3.47 (d, *J* = 4.9 Hz, 1H), 2.96 – 2.85 (m, 1H), 2.62 – 2.50 (m, 1H), 2.10 – 1.57 (m, 6H), 1.40 – 1.20 (m, 3H), 1.20 – 1.13 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 136.1, 131.7, 129.4, 128.0, 86.6, 52.0, 36.1, 34.7, 26.0, 25.9, 18.14, 18.07, 12.1. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{22}H_{36}N_2O_2SSiNa^+$ $[M+Na]^+$: 443.2159; found: 443.2170.

IR (ATR) (ν_{max} cm^{-1}) = 2953, 2872, 1625, 1285, 1235, 1134, 1045, 932, 721.

1-(1-Oxido-2-(triisopropylsilyl)- 1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)-3-phenylurea (**4we**)



To a 10 mL microwave vial, sulfonimidamide **4w** (63.3 mg, 0.20 mmol, 1.0 equiv.) and DMAP (4.9 mg, 0.04 mmol, 0.2 equiv.) were added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (2 mL, 0.1 M) was added, followed by Et_3N (42 μL, 0.30 mmol, 1.5 equiv.) and phenyl isocyanate (32 μL, 0.30 mmol, 1.5 equiv.). The resulting mixture was then stirred at room temperature for 4.5 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (6:1 Petrol: EtOAc) to afford the desired product **4we** (85.0 mg, 98%) as a yellow solid.

R_f = 0.4 (6:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.00 – 6.90 (m, 2H), 3.84 (d, *J* = 4.5 Hz, 1H), 3.27 (d, *J* = 4.5 Hz, 1H), 2.85 – 2.74 (m, 1H), 2.62 – 2.47 (m, 1H), 2.13 – 2.02 (m, 1H), 1.95 – 1.85 (m, 1H), 1.78 – 1.55 (m, 4H), 1.30 – 1.18 (m, 3H), 1.16 – 1.00 (m, 18H).

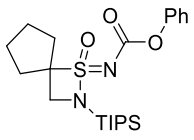
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 139.4, 128.9, 122.7, 118.9, 86.9, 50.6, 36.7, 33.8, 25.8, 25.7, 18.1, 18.0, 12.0. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{22}H_{38}N_3O_2SSi^+$ $[M+H]^+$: 436.2449; found: 436.2463.

IR (ATR) (ν_{max} cm^{-1}) = 3272, 2953, 2872, 1654, 1514, 1438, 1220, 1043, 916, 737.

M.p. 68-70 °C (CH_2Cl_2).

Phenyl (1-oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)carbamate (**4wf**)



To a 10 mL microwave vial, sulfonimidamide **4w** (63.3 mg, 0.20 mmol, 1.0 equiv.) and DMAP (4.9 mg, 0.04 mmol, 0.2 equiv.) were added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (2 mL, 0.1 M) was added, followed by Et_3N (42 μL, 0.30 mmol, 1.5 equiv.) and phenyl chloroformate (38 μL, 0.30 mmol, 1.5 equiv.). The resulting mixture was then stirred at room temperature for 1 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (8:1 Petrol: EtOAc) to afford the desired product **4wf** (75.0 mg, 68%) as a pale-yellow solid.

Rf = 0.5 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.20 – 7.09 (m, 3H), 3.78 (d, *J* = 4.8 Hz, 1H), 3.35 (d, *J* = 4.8 Hz, 1H), 2.90 – 2.78 (m, 1H), 2.66 – 2.54 (m, 1H), 2.15 – 2.03 (m, 1H), 2.02 – 1.90 (m, 1H), 1.87 – 1.62 (m, 4H), 1.33 – 1.20 (m, 3H), 1.16 – 1.11 (m, 18H).

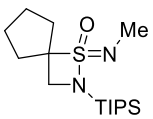
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 152.0, 129.2, 125.2, 121.9, 86.9, 51.2, 36.5, 34.0, 25.8, 25.7, 18.1, 18.0, 12.0. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{22}H_{37}N_2O_3SSi^+$ $[M+H]^+$: 437.2289; found: 437.2294.

IR (ATR) (ν_{max} cm^{-1}) = 2956, 2872, 1688, 1466, 1264, 1194, 1046, 914, 734.

M.p. 76-78 °C (CH_2Cl_2).

1-(Methylimino)-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octane 1-oxide (**4wg**)



To a 10 mL microwave vial, sulfonimidamide **4w** (63.3 mg, 0.20 mmol, 1.0 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three

evacuation/argon refill cycles. THF (1 mL, 0.2 M) was added, and the reaction mixture cooled to 0 °C. NaH (60 % dispersion in mineral oil, 24 mg, 0.60 mmol, 3.0 equiv.) was added and the resulting mixture stirred at 0 °C for 30 min. Iodomethane (124 μL, 2.0 mmol, 10 equiv.) was added and the reaction mixture warmed to room temperature and stirred for 16 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (60:1:1 Petrol: EtOAc: Et_3N) to afford the desired product **4wg** (36.6 mg, 55%) as a yellow oil.

Rf = 0.4 (30:1 Petrol: EtOAc).

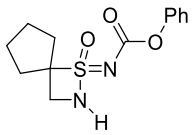
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (d, *J* = 5.4 Hz, 1H), 3.11 (d, *J* = 5.4 Hz, 1H), 2.79 (s, 3H), 2.69 – 2.52 (m, 2H), 1.91 – 1.76 (m, 2H), 1.73 – 1.57 (m, 4H), 1.30 – 1.17 (m, 3H), 1.16 – 1.07 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 88.4, 47.5, 35.2, 34.2 32.2, 25.7, 25.4, 18.3, 18.2, 12.1. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{16}H_{35}N_2OSSi^+$ $[M+H]^+$: 331.2234; found: 331.2232.

IR (ATR) (ν_{max} cm^{-1}) = 2948, 2869, 1464, 1246, 1157, 1049, 917, 883, 736, 679.

Phenyl (1-oxido-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)carbamate (**4wfa**)



To a 10 mL microwave vial, sulfonimidamide **4wf** (436.7 mg, 1.00 mmol, 1.0 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. THF (10 mL, 0.1 M) was then added. The mixture was cooled to 0 °C, followed by addition of TBAF (1.0 mL, 1.0 M in THF, 1.00 mmol, 1.0 equiv.). The

reaction mixture was stirred for 5 min at 0 °C, filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (1:1 Petrol: EtOAc) to afford the title compound **4wfa** (247.3 mg, 88%) as a white solid.

Rf = 0.5 (1:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 2H), 7.24 – 7.12 (m, 3H), 6.12 (bs, 1H), 3.64 (d, *J* = 5.7 Hz, 1H), 3.36 (d, *J* = 5.6 Hz, 1H), 2.92 – 2.81 (m, 1H), 2.78 – 2.66 (m, 1H), 2.08 – 1.95 (m, 2H), 1.88 – 1.69 (m, 4H).

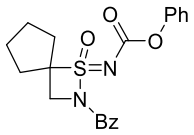
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 151.5, 129.5, 125.7, 121.8, 88.3, 46.5, 35.4, 34.0, 25.9, 25.3. (note: for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{13}H_{17}N_2O_3S^+$ $[M+H]^+$: 281.0954; found: 281.0959.

IR (ATR) (ν_{max} cm^{-1}) = 3273, 2969, 1686, 1270, 1194, 913, 735.

M.p. 88-90 °C (CH_2Cl_2).

Phenyl (2-benzoyl-1-oxido-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)carbamate (**4wfb**)



To a 10 mL microwave vial, sulfonimidamide **4wfa** (56.1 mg, 0.20 mmol, 1.0 equiv.) and DMAP (36.7 mg, 0.30 mmol, 1.5 equiv.) were added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (2 mL, 0.1 M) was added, followed by the addition of benzoyl chloride (0.3 mmol, 34 μL, 1.5 equiv.). The resulting mixture was stirred at room temperature for 4 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was

concentrated *in vacuo* and purified by silica column chromatography (5:1 Petrol: EtOAc) to afford the desired product **4wfb** (75.4 mg, 98%) as white solid.

Rf = 0.1 (5:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 2H), 4.23 (d, *J* = 7.1 Hz, 1H), 3.74 (d, *J* = 7.1 Hz, 1H), 3.01 – 2.89 (m, 1H), 2.64 – 2.51 (m, 1H), 2.22 – 2.07 (m, 2H), 1.91 – 1.74 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 155.4, 151.1, 133.7, 132.2, 129.4, 129.0, 128.6, 125.8, 121.4, 84.6, 49.7, 36.5, 33.8, 25.9, 25.7. (note: for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

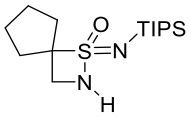
HRMS $(ESI)^+$ calcd. for $C_{20}H_{21}N_2O_4S^+$ $[M+H]^+$: 385.1217; found: 385.1232.

IR (ATR) (ν_{max} cm^{-1}) = 2969, 1697, 1310, 1282, 1195, 918, 727.

M.p. 86-88 °C (CH_2Cl_2).

5.3.5.3 Rearrangement and functionalization of aza-*β*-sultams

1-((Triisopropylsilyl)imino)- 1λ^6-thia-2-azaspiro[3.4]octane 1-oxide (**4wh**)



To a 100 mL round bottom flask, sulfonimidamide **4w** (569.9 mg, 1.8 mmol, 1.0 equiv.) and Cs_2CO_3 (586.4 mg,1.8 mmol, 1.0 equiv.) were added. The round bottom flask was then capped with a suba-seal and subjected to three evacuation/argon refill cycles. Toluene (18 mL, 0.1 M) was added and the resulting mixture was stirred at 100 °C for 24 h. On cooling, the mixture was filtered through a pad of basic Al_2O_3 (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by basic Al_2O_3 column chromatography (8:1 to 4:1 Petrol: EtOAc) to afford the desired product **4wh** (452.0 mg, 79%) as a yellow solid.

Rf = 0.5 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (bs, 1H), 3.19 (dd, *J* = 6.8, 5.6 Hz, 1H), 3.14 (dd, *J* = 6.7, 5.1 Hz, 1H), 2.82 – 2.68 (m, 2H), 1.95 – 1.82 (m, 2H), 1.79 – 1.63 (m, 4H), 1.16 – 0.99 (m, 21H).

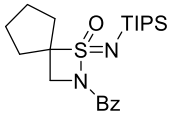
^{13}C NMR (101 MHz, $CDCl_3$) δ 89.8, 44.1, 35.7, 34.5, 25.9, 25.8, 18.4, 12.9. (note: for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{15}H_{33}N_2OSSi^+$ $[M+H]^+$: 317.2077; found: 317.2075.

IR (ATR) (ν_{max} cm^{-1}) = 3265, 2951, 2866, 1465, 1342, 1155, 886, 680.

M.p. 46-48 °C (CH_2Cl_2).

(1-Oxido-1-((triisopropylsilyl)imino)-1λ^6-thia-2-azaspiro[3.4]octan-2-yl)(phenyl)methanone (**4wha**)



To a 50 mL round bottom flask, sulfonimidamide **4wh** (316.6 mg, 1.00 mmol, 1.0 equiv.) and DMAP (183.3 mg, 1.50 mmol, 1.5 equiv.) were added. The round bottom flask was then sealed with a suba-seal and subjected to three evacuation/argon refill cycles. CH_2Cl_2 (10 mL, 0.1 M) was added, followed by the addition of benzoyl chloride (174 μL, 1.5 mmol, 1.5 equiv.). The resulting mixture was then stirred at room temperature for 2 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (20:1 to 10:1 Petrol: EtOAc) to afford the desired product **4wha** (341.7 mg, 81%) as a white solid.

Rf = 0.4 (10:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.57 – 7.50 (m, 1H), 7.45 – 7.40 (m, 2H), 3.83 (d, *J* = 8.3 Hz, 1H), 3.57 (d, *J* = 8.3 Hz, 1H), 2.91 – 2.79 (m, 1H), 2.73 – 2.63 (m, 1H), 2.09 – 1.89 (m, 2H), 1.89 – 1.65 (m, 4H), 0.95 – 0.78 (m, 18H), 0.69 – 0.55 (m, 3H).

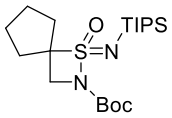
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 134.1, 132.7, 129.2, 128.6, 86.9, 47.1, 36.0, 34.8, 26.3, 25.5, 18.1, 12.9. (note: for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{22}H_{37}N_2O_2SSi^+$ $[M+H]^+$: 421.2340; found: 421.2339.

IR (ATR) (ν_{max} cm^{-1}) = 2950, 2867, 1664, 1459, 1374, 1328, 1166, 714.

M.p. 56-58 °C (CH_2Cl_2).

***tert*-Butyl 1-((triisopropylsilyl)imino)-1λ^6-thia-2-azaspiro[3.4]octane-2-carboxylate 1-oxide** (**4whb**)



To a 10 mL microwave vial, sulfonimidamide **4wh** (63.3 mg, 0.20 mmol, 1.0 equiv.) and DMAP (36.7 mg, 0.30 mmol, 1.5 equiv.) were added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. Di-*tert*-butyl dicarbonate (131.0 mg, 0.60 mmol, 3.0 equiv.) in CH_2Cl_2 (4 mL, 0.05 M) was added. The resulting mixture was then stirred at room temperature for 8 h. The mixture was filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (20:1 to 10:1 Petrol: EtOAc) to afford the desired product **4whb** (70.0 mg, 84%) as a colourless oil.

Rf = 0.5 (10:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.45 (d, *J* = 7.1 Hz, 1H), 3.39 (d, *J* = 7.1 Hz, 1H), 2.78 – 2.66 (m, 2H), 1.93 – 1.81 (m, 2H), 1.80 – 1.63 (m, 4H), 1.48 (s, 9H), 1.18 – 0.99 (m, 21H).

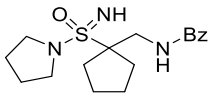
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 86.1, 82.8, 47.7, 35.2, 34.8, 28.4, 26.1, 25.8, 18.33, 18.25, 13.0. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1, for four CH_2 groups in five-membered ring, 4 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{20}H_{40}N_2O_3SSiNa^+$ $[M+Na]^+$: 439.2421; found: 439.2431.

IR (ATR) (ν_{max} cm^{-1}) = 2950, 2868, 1718, 1468, 1370, 1175, 1138, 1049.

5.3.5.4 Ring opening reactions of aza-*β*-sultams with potassium bifluoride

***N*-((1-(Pyrrolidine-1-sulfonimidoyl)cyclopentyl)methyl)benzamide** (**5a**)



Prepared according to **General Procedure C**, using sulfonimidamide **4wha** (42.0 mg, 0.10 mmol, 1.0 equiv.), potassium bifluoride (7.8 mg, 0.10 mmol, 1.0 equiv.), pyrrolidine (34 μL, 0.40 mmol, 4.0 equiv.) and MeCN (1 mL, 0.1 M). The resulting mixture was then heated to 40 °C and stirred for 24 h. Purification by silica column chromatography (1:1 to 1:2 hexane: EtOAc) afforded the desired product **5a** (32.3 mg, 96%) as a colourless oil.

Rf = 0.3 (1:2 hexane: EtOAc).

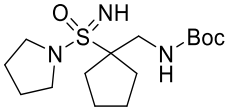
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (bs, 1H), 7.87 – 7.81 (m, 2H), 7.51 – 7.36 (m, 3H), 3.87 (dd, *J* = 14.7, 6.2 Hz, 1H), 3.58 (dd, *J* = 14.7, 3.8 Hz, 1H), 3.53 – 3.34 (m, 4H), 2.63 (bs, 1H), 2.36 – 2.20 (m, 2H), 1.94 – 1.85 (m, 4H), 1.83 – 1.63 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 134.3, 131.5, 128.6, 127.1, 73.6, 50.1, 44.4, 33.0, 32.5, 26.4, 25.6, 25.5.

HRMS $(ESI)^+$ calcd. for $C_{17}H_{25}N_3O_2SNa^+$ $[M+Na]^+$: 358.1560; found: 358.1561.

IR (ATR) (ν_{max} cm^{-1}) = 3261, 2965, 2876, 1655, 1533, 1486, 1292, 1230, 1062, 1007, 916, 735.

***tert*-Butyl ((1-(pyrrolidine-1-sulfonimidoyl)cyclopentyl)methyl)carbamate** (**5a'**)



Prepared according to **General Procedure C**, using sulfonimidamide**4whb** (66.7 mg, 0.16 mmol, 1.0 equiv.), potassium bifluoride (12.5 mg, 0.16 mmol, 1.0 equiv.), pyrrolidine (54 μL, 0.60 mmol, 4.0 equiv.) and MeCN (1.6 mL, 0.1 M). The resulting mixture was then

heated to 40 °C and stirred for 24 h. Purification by silica column chromatography (2:1 to 1:1 hexane: EtOAc) afforded the desired product **5a'** (49.3 mg, 93%) as a colourless oil.

Rf = 0.5 (1:1 hexane: EtOAc).

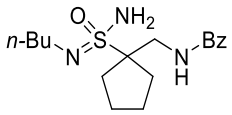
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (bs, 1H), 3.53 – 3.29 (m, 6H), 2.38 (bs, 1H), 2.25 – 2.10 (m, 2H), 1.93 – 1.80 (m, 4H), 1.80 – 1.57 (m, 6H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 79.2, 74.0, 50.0, 45.3, 32.7, 32.2, 28.5, 26.4, 25.54, 25.50.

HRMS $(ESI)^+$ calcd. for $C_{15}H_{29}N_3O_3SNa^+$ $[M+Na]^+$: 354.1822; found: 354.1819.

IR (ATR) (ν_{max} cm^{-1}) = 3483, 3343, 2972, 2877, 1704, 1505, 1452, 1368, 1254, 1171, 1060, 1001, 915, 734.

***N*-((1-(*N'*-Butylsulfamidimidoyl)cyclopentyl)methyl)benzamide (5b)**



Prepared according to **General Procedure C**, using sulfonimidamide **4wha** (42.0 mg, 0.10 mmol, 1.0 equiv.), potassium bifluoride (7.8 mg, 0.10 mmol, 1.0 equiv.), *n*-butylamine (40 μL, 0.40 mmol, 4.0 equiv.) and MeCN (1 mL, 0.1 M). The resulting mixture was then heated to 40 °C and stirred for 24 h. Purification by silica column chromatography (1:1 to 1:2 hexane: EtOAc) afforded the desired product **5b** (30.7 mg, 91%) as a colourless oil.

Rf = 0.3 (1:2 hexane: EtOAc).

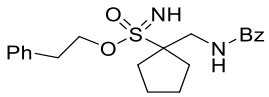
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (bs, 1H), 7.84 – 7.76 (m, 2H), 7.51 – 7.35 (m, 3H), 3.86 (dd, *J* = 14.7, 6.2 Hz, 1H), 3.64 (dd, *J* = 14.7, 4.1 Hz, 1H), 3.25 – 3.10 (m, 2H), 2.27 – 2.11 (m, 2H), 1.86 – 1.64 (m, 6H), 1.57 – 1.43 (m, 2H), 1.41 – 1.28 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 134.2, 131.6, 128.6, 127.1, 72.1, 45.0, 44.3, 33.5, 32.9, 32.4, 25.63, 25.55, 19.9, 13.8.

HRMS $(ESI)^+$ calcd. for $C_{17}H_{27}N_3O_2SNa^+$ $[M+Na]^+$: 360.1716; found: 360.1725.

IR (ATR) (ν_{max} cm^{-1}) = 3483, 3343, 2872, 2877, 1704, 1506, 1453, 1368, 1254, 1171, 1060, 1001, 915, 734.

Phenethyl 1-(benzamidomethyl)cyclopentane-1-sulfonimidate (**5c**)



Prepared according to **General Procedure C**, using sulfonimidamide **4wha** (42.0 mg, 0.10 mmol, 1.0 equiv.), potassium bifluoride (7.8 mg, 0.10 mmol, 1.0 equiv.), 2-phenylethanol (48 μL, 0.40 mmol, 4.0 equiv.) MeCN (1 mL, 0.1 M). The resulting mixture was then heated to 40 °C and stirred for 48 h. Purification by silica column chromatography (3:1 to 2:1 hexane: EtOAc) afforded the desired product **5c** (27.0 mg, 70%) as a colourless oil.

Rf = 0.5 (1:1 hexane: EtOAc).

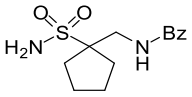
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (bs, 1H), 7.83 – 7.75 (m, 2H), 7.53 – 7.39 (m, 3H), 7.34 – 7.18 (m, 5H), 4.47 – 4.31 (m, 2H), 3.90 (dd, *J* = 14.7, 7.0 Hz, 1H), 3.61 (dd, *J* = 14.7, 4.2 Hz, 1H), 3.10 (s, 1H), 3.02 (t, *J* = 6.8 Hz, 2H), 2.28 – 2.12 (m, 2H), 1.86 – 1.62 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 136.9, 134.2, 131.7, 129.1, 128.8, 128.7, 127.1, 72.1, 67.5, 44.0, 36.0, 32.9, 32.2, 25.7. (note: 2 peaks overlap to show 1 peak found in 127.1 ppm, for four CH_2 groups in five-membered ring, 3 peaks were found instead of 2)

HRMS $(ESI)^+$ calcd. for $C_{21}H_{26}N_2O_3SNa^+$ $[M+Na]^+$: 409.1556; found: 409.1572.

IR (ATR) (ν_{max} cm^{-1}) = 3297, 2960, 1655, 1533, 1291, 1250, 957, 914, 738.

***N*-((1-Sulfamoylcyclopentyl)methyl)benzamide (5d)**



To a 10 mL microwave vial, sulfonimidamide **4wha** (42.0 mg, 0.10 mmol, 1.0 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. THF (1 mL, 0.1 M) was added and the reaction mixture was cooled to 0 °C. Acetic acid (6 μL, 0.10 mmol, 1.0 equiv.) was added, followed by TBAF (0.10 mL, 1.0 M in THF, 0.10 mmol, 1.0 equiv.). The reaction mixture was stirred for 10 min at 0 °C, filtered through a pad of silica (2 cm), washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (1:1 hexane: EtOAc) to afford the title compound **5d** (20.6 mg, 73%) as a white solid.

Rf = 0.2 (1:1 hexane: EtOAc).

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.87 – 7.79 (m, 2H), 7.75 (bs, 1H), 7.59 – 7.43 (m, 3H), 6.40 (s, 2H), 3.86 (d, *J* = 6.1 Hz, 2H), 2.29 – 2.13 (m, 2H), 1.92 – 1.66 (m, 4H).

^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 167.8, 135.6, 132.3, 129.4, 127.8, 71.8, 44.8, 33.0, 26.7.

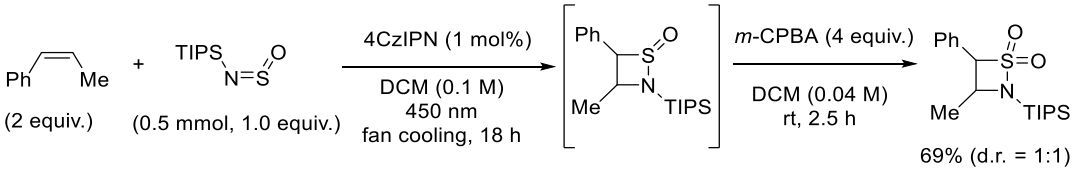
HRMS $(ESI)^+$ calcd. for $C_{13}H_{19}N_2O_3S^+$ $[M+H]^+$: 283.1111; found: 283.1100.

IR (ATR) (ν_{max} cm^{-1}) = 3333, 1697, 1647, 1541, 1317, 1141, 716.

M.p. 118-120 °C (CH_2Cl_2).

5.3.6 Control Experiments with *cis*-*β*-methylstyrene and *trans*-*β*-methylstyrene

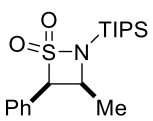
Synthesis from *cis*-*β*-methylstyrene



Prepared according to **General Procedure A** using 4CzIPN (0.005 mmol, 3.9 mg, 1 mol%), *cis*-*β*-methylstyrene (1.0 mmol, 236.4 mg, 2 equiv.), TIPSNSO (0.5 mmol, 109.7 mg, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1 M). After 18 h, a 25 mL round-bottom flask containing a magnetic stirring bar was charged with *m*-CPBA (≤77%) (2.0 mmol, 448.0 mg, 4.0 equiv.) and CH_2Cl_2 (10 mL). The flask was cooled to 0 ˚C using an ice-water bath, the photochemistry reaction mixture then was syringed out and slowly added to the flask. Then, the vial was rinsed with CH_2Cl_2 (2 mL). The ice-water bath was then removed and the reaction mixture was allowed to stirred at room temperature for 2.5 h. Then, the reaction mixture was quenched with 10 mL aqueous $Na_2S_2O_3$ solution and washed with 10 mL $NaHCO_3$ solution. After collecting the organic phase, the aqueous phase was then extracted with CH_2Cl_2 (2×10 mL). The organic layer was combined and dried with anhydrous Na_2SO_4. The resultant crude solution was concentrated *in vacuo*. Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 1:1. Purification by flash silica column chromatography (40:1 to 20:1 Petrol: EtOAc) afforded title compound *cis*-**2ac** (60.2 mg, 34%) and *trans*-**2ac** (61.5 mg, 35%) as separable products.

***cis*-3-Methyl-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1,1-dioxide**

cis-**2ac** (white solid)



Rf = 0.3 (20:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.44 – 7.32 (m, 3H), 5.70 (d, *J* = 8.5 Hz, 1H), 4.17 (qd, *J* = 8.6, 6.5 Hz, 1H), 1.43 – 1.28 (m, 3H), 1.28 – 1.15 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.0, 129.7, 129.2, 128.6, 79.1, 46.7, 18.9, 18.32, 18.25, 12.5. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

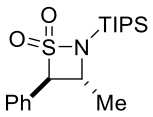
HRMS (ESI) calcd. for $C_{18}H_{32}NO_2SSi^+$ $[M+H]^+$: 354.1918; found: 354.1924.

IR (ATR) (ν_{max} cm $^{-1}$) = 2949, 2873, 1461, 1301, 1165, 1073, 1009, 868, 749, 693.

M. p. 50-52 ^{o}C (CH_2Cl_2)

***trans*-3-Methyl-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1,1-dioxide**

trans-**2ac** (white solid)



Rf = 0.2 (20:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.34 (m, 5H), 5.00 (d, *J* = 5.2 Hz, 1H), 3.89 (qd, *J* = 6.1, 5.2 Hz, 1H), 1.58 (d, *J* = 6.0 Hz, 3H), 1.40 – 1.30 (m, 3H), 1.27 – 1.20 (m, 18H).

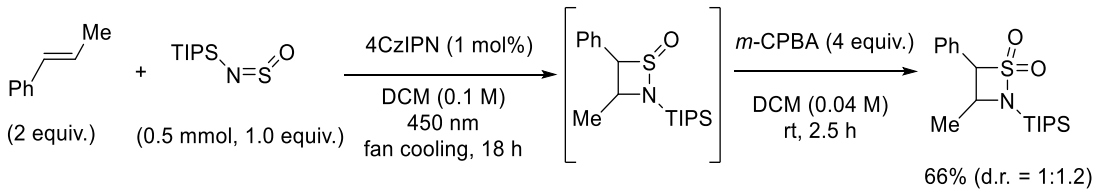
^{13}C NMR (101 MHz, $CDCl_3$) δ 130.89, 129.46, 129.07, 129.05, 83.94, 49.80, 22.63, 18.35, 18.32, 12.47. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{18}H_{32}NO_2SSi^+$ $[M+H]^+$: 354.1918; found: 354.1926.

IR (ATR) (ν_{max} cm $^{-1}$) = 2950, 2873, 1462, 1308, 1178, 1063, 1006, 874, 740, 691.

M. p. 62-64 ^{o}C (CH_2Cl_2)

Synthesis from *trans*-*β*-methylstyrene



Prepared according to **General Procedure A** using 4CzIPN (0.005 mmol, 3.9 mg, 1 mol%), *trans-β*-methylstyrene (1.0 mmol, 236.4 mg, 2 equiv.), TIPSNSO (0.5 mmol, 109.7 mg, 1.0 equiv.) and CH_2Cl_2 (0.5 mL, 1 M). After 18 h, a 25 mL round-bottom flask containing a magnetic stirring bar was charged with *m*-CPBA (≤77%) (2.0 mmol, 448.0 mg, 4.0 equiv.) and CH_2Cl_2 (10 mL). The flask was cooled to 0 ˚C using an ice-water bath, the photochemistry reaction mixture then was syringed out and slowly added to the flask. Then, the vial was rinsed with CH_2Cl_2 (2 mL). The ice-water bath was then removed and the reaction mixture was allowed to stirred at room temperature for 2.5 h. Then, the reaction mixture was quenched with 10 mL aqueous $Na_2S_2O_3$ solution and washed with 10 mL $NaHCO_3$ solution. After collecting the organic phase, the aqueous phase was then extracted with CH_2Cl_2 (2×10 mL). The organic layer was combined and dried with anhydrous Na_2SO_4. The resultant crude solution was concentrated *in vacuo*. Quantitative ^{1}H NMR analysis of the crude reaction mixture revealed a diastereomer ratio = 1:1.2. Purification by flash silica column chromatography (40:1 to 20:1 Petrol: EtOAc) afforded title compound *cis*-**2ac** (54.2 mg, 31%) and *trans*-**2ac** (61.5 mg, 35%) as separable products. The data is consistent with the above reports.

5.3.7 Stern-Volmer Data

Fluorescence spectra were acquired at 298 K using an Edinburgh Instruments FS5 spectrofluorometer operating Fluoracle® software, and equipped with a xenon arc lamp (providing 230–1000 nm excitation range), a thermostatic sample holder (SC-20) and an R13456 PMT detector (200–950 nm spectral coverage, Hamamatsu). Spectroscopic measurements were conducted using quartz cuvettes (10 mm path length, Starna Scientific Ltd).

Fluorescence quenching of 4CzIPN was investigated by measuring the emission spectrum of 4CzIPN in the presence of the reaction components and varying the concentration under an atmosphere of N_2. A solution of 4CzIPN (0.01 mM) in degassed CH_2Cl_2 was treated with (0.17 – 0.68 mM) of styrene solution in degassed CH_2Cl_2 or (0.17 – 0.68 mM) of TIPSNSO solution in degassed CH_2Cl_2. The samples were irradiated at 450 nm and luminescence was measured over a range of 460 - 750 nm (at λmax = 540 nm). I_0/I in the range of 0.17 – 0.68 mM was plotted against the concentration of styrene or TIPSNSO.

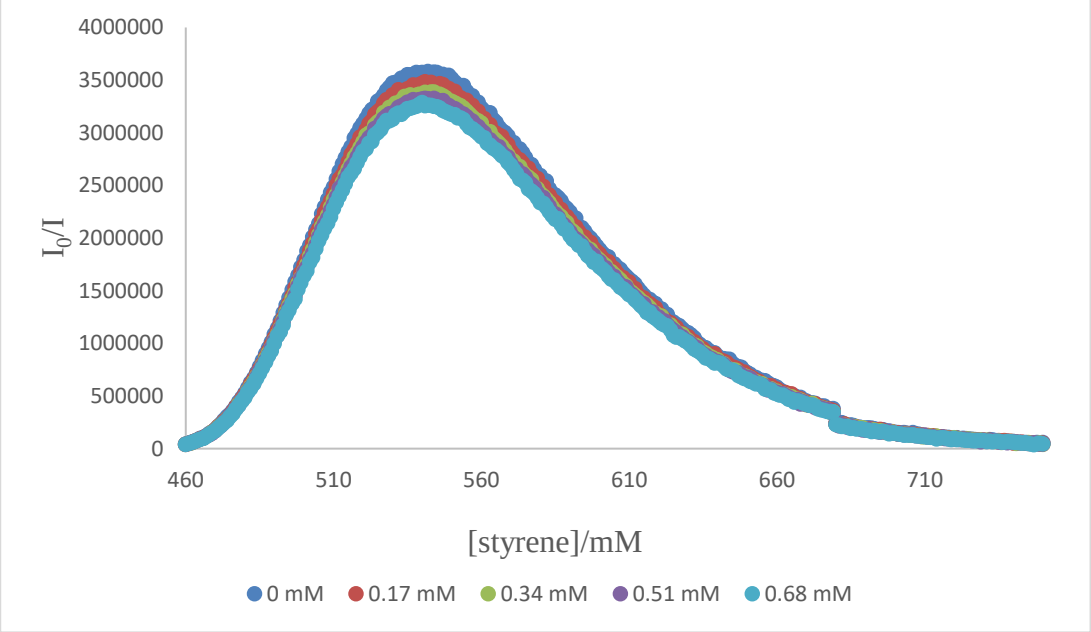


Figure 5-2 Stern-Volmer quenching of 4CzIPN by styrene.

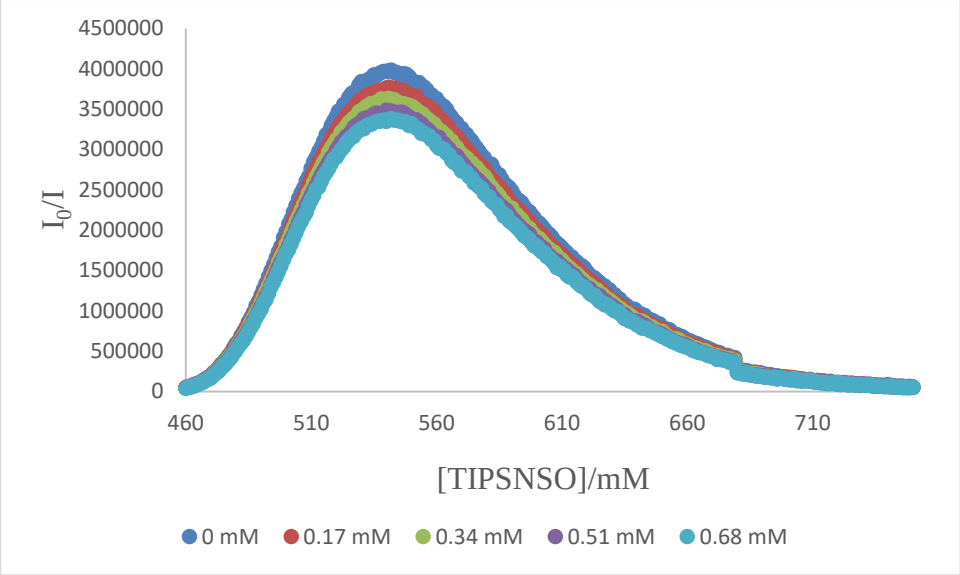


Figure 5-3 Stern-Volmer quenching of 4CzIPN by TIPSNSO.

	I_0/I	
mM	**TIPSNSO**	**Sytrene**
0.00	1.00	1.00
0.17	1.05	1.03
0.34	1.10	1.06
0.51	1.14	1.08
0.68	1.18	1.09

Table 5-1 Fluorescence quenching of 4CzIPN.

5.3.8 UV absorption spectra

UV absorption spectra was acquired at 298 K using an Agilent Cary 60 ultraviolet–visible (UV–vis) spectrophotometer, with baseline correction. The emission spectra was conducted at 298 K using an Edinburgh Instruments FS5 spectrofluorometer operating Fluoracle® software, and equipped with a xenon arc lamp (providing 230–1000 nm excitation range), a thermostatic sample holder (SC-20) and an R13456 PMT detector (200–950 nm spectral coverage, Hamamatsu). Spectroscopic measurements were conducted using quartz cuvettes (10 mm path length, Starna Scientific Ltd). A solution of 4CzIPN (0.01 mM) in degassed CH_2Cl_2 was irradiated at 350 nm and luminescence was measured over a range of 400 - 800 nm.

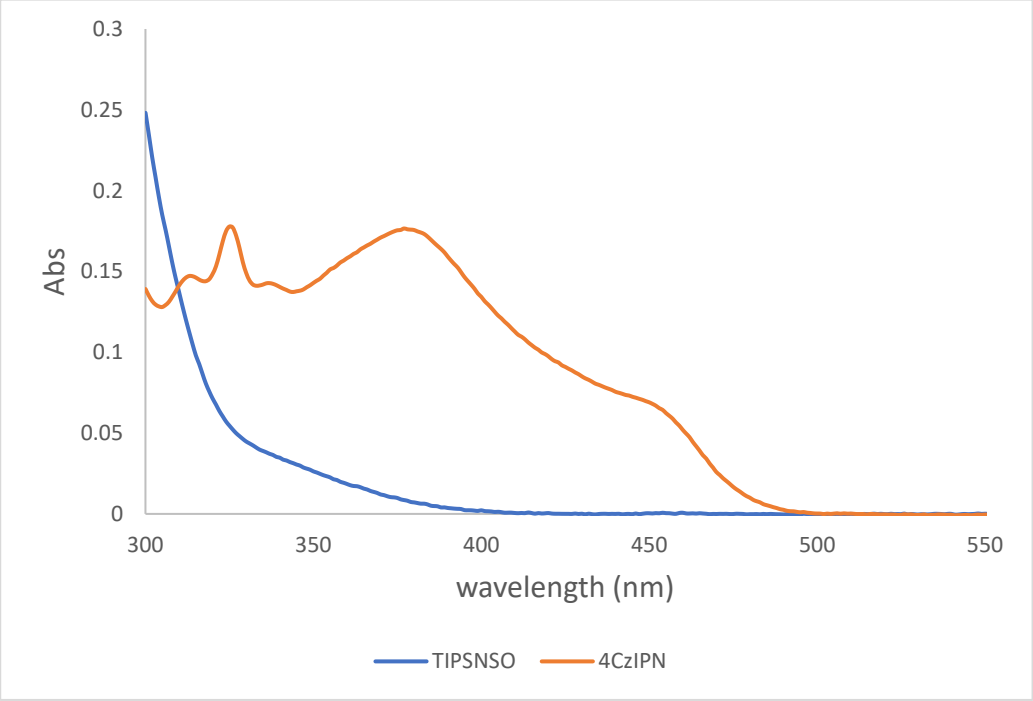


Figure 5-4 UV absorption of TIPSNSO and 4CzIPN at 25 °C in CH_2Cl_2.

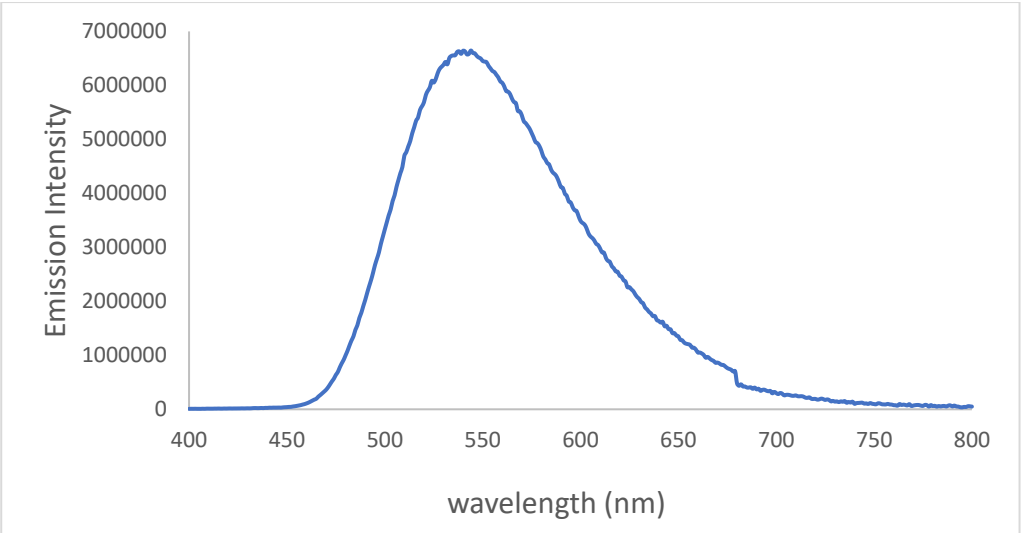


Figure 5-5 UV Emission of 4CzIPN at 25 ºC in CH_2Cl_2 at $\lambda_{exciation}$ = 350 nm.

5.3.9 Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were recorded on a Autolab Electrochemical System, using a 3-electrode setup: a glassy carbon working electrode, a platinum wire counter electrode and a $Ag|AgNO_3$ (100 mM in MeCN) reference electrode. Parameters for CV: 50 mVs^{-1} scan rate. Measurements at a concentration of 0.05 M and were performed in MeCN with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as the electrolyte. Sample solutions were deoxygenated by purging with N2 for 2 - 3 minutes before the measurements. Ferrocene was added after the experiment and the peaks reported are reference to the Fc^+ /Fc peak. The reported potentials were taken at the half-height of the cathodic peak of the compounds as all redox processes were irreversible.

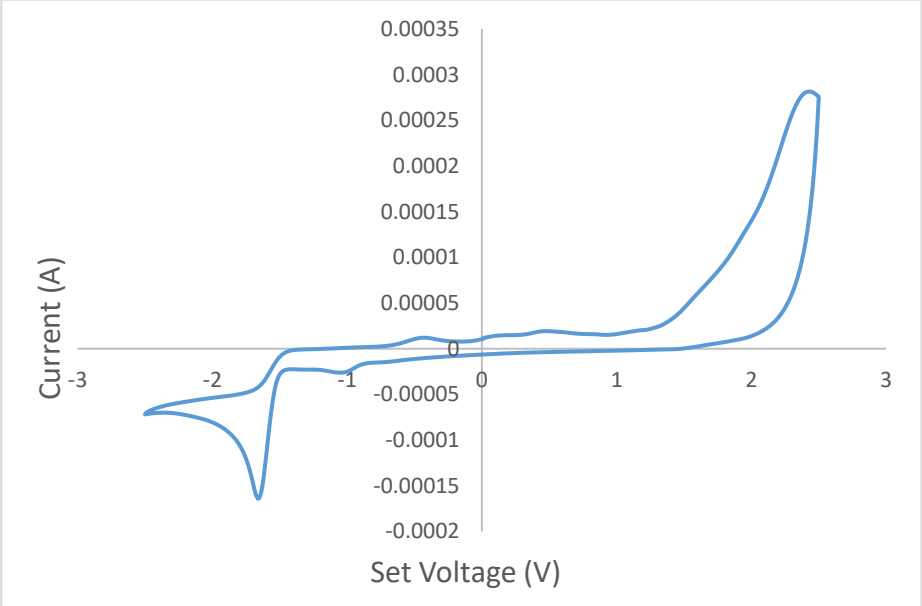


Figure 5-6 Cyclic voltammetry of TIPSNSO for reduction without ferrocene.

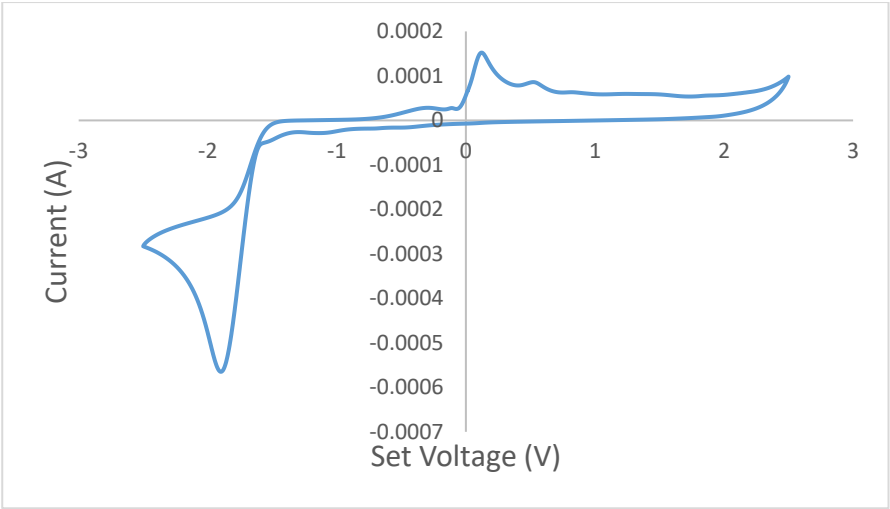
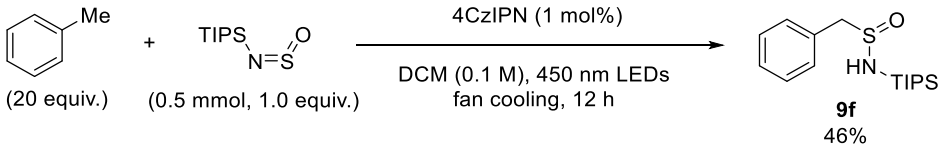


Figure 5-7 Cyclic voltammetry of TIPSNSO for reduction in the presence of ferrocene.

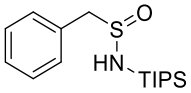
5.3.10 HAT reaction



To a 10 mL microwave vial was added 4CzIPN (3.9 mg, 0.005 mmol, 1 mol%). The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. Toluene (1.06 mL, 10 mmol, 20 equiv.) and CH_2Cl_2 (0.5 mL, 1.0 M) was added. The resulting mixture was then freeze pump thaw for 3 times in liquid nitrogen bath, followed by refilled with nitrogen at room temperature. Then TIPSNSO (109.7 mg, 0.5 mmol, 1.0 equiv.) was added. The mixture was allowed to stir in 450nm at room temperature with fan cooling.

After 12 h, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (2:1 Petrol: EtOAc) to afford title compound **9f** (72.1 mg, 46%) as white solid.

1-Phenyl-*N*-(triisopropylsilyl)methanesulfinamide (**9f**)



Rf = 0.3 (2:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 5H), 3.99 (d, *J* = 12.6 Hz, 1H), 3.86 (d, *J* = 12.6 Hz, 1H), 3.23 (s, 1H), 1.39 – 0.88 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.0, 128.8, 128.4, 64.4, 17.9, 17.8, 11.8. (note: 2 peaks overlap to show 1 peak found in 128.8 ppm, for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS $(ESI)^+$ calcd. for $C_{16}H_{29}NOSSiNa^+$ $[M+H]^+$: 334.1631; found: 334.1626.

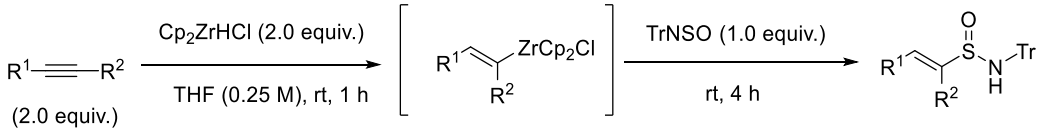
IR (ν_{max}) 3224, 2943, 2866, 1703, 1457, 1097, 882, 750, 676 cm^{-1}.

M. p. 68-70 ^oC (CH_2Cl_2)

5.4 Experimental Data for Chapter 3

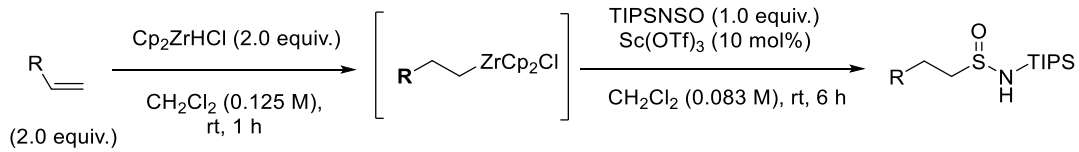
5.4.1 General Procedures

Synthesis of alkenyl sulfinamides (General procedure D)



An oven-dried 10 mL microwave vial containing a magnetic stirring bar was charged with Schwartz reagent (2.0 equiv.) and alkyne (if solid) (2.0 equiv.). The vial was sealed and subjected to three N_2 evacuation/refill cycles before THF (0.25 M) was added. Alkyne (if liquid) (2.0 equiv.) was then added. The reaction mixture was stirred at room temperature for 1 hour. Then, the vial was open followed by the addition of *N*-trityl sulfinylamine (1 equiv.). The reaction mixture was resealed and stirred at the appropriate temperature for 4 hours. Then, silica gel (200 mg for 0.5 mmol scale reaction) and ethyl ether (2 mL for 0.5 mmol scale reaction) were added to the reaction mixture and stirred for 10 mins. the mixture was filtered through a pad of silica (2 cm for 0.5 mmol scale reaction) washing with EtOAc (70 mL for 0.5 mmol scale reaction). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography to afford the desired product.

Synthesis of alkyl sulfinamides (General procedure E)

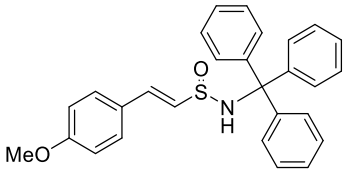


An oven-dried 10 mL microwave vial containing a magnetic stirring bar was charged with Schwartz reagent (2.0 equiv.) and alkene (if solid) (2.0 equiv.). was sealed and subjected to three N_2 evacuation/refill cycles before CH_2Cl_2 (TIPSNSO conc. 0.125 M) was added. Alkene (if liquid) (2.0 equiv.) was then added. The reaction mixture was stirred at room temperature for 1 hour. Then, the reaction mixture was transferred using a syringe to another

oven-dried 10 mL microwave vial containing a magnetic stirring bar and scandium(III) triflate (10 mol%) under N_2 atmosphere. Additional CH_2Cl_2 (1 mL for 0.25 mmol scale reaction) was used to rinse the first microwave vial. Then, TIPSNSO (1.0 equiv.) was added to the reaction mixture. The reaction mixture (TIPSNSO conc. 0.083 M) stirred at the room temperature for 6 hours. Then, silica gel (100 mg for 0.25 mmol scale reaction) and ethyl ether (2 mL for 0.25 mmol scale reaction) were added to the reaction mixture and stirred for 10 mins. the mixture was filtered through a pad of silica (2 cm for 0.25 mmol scale reaction) washing with EtOAc (70 mL for 0.25 mmol scale reaction). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography to afford the desired product.

5.4.2 Synthesis of alkenyl sulfinamides

(*E*)-2-(4-Methoxyphenyl)-*N*-tritylethene-1-sulfinamide (7a)



Prepared according to **General Procedure D** using Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2.0 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 4-ethynylanisole (132.0 mg, 1.0 mmol, 2.0 equiv.). The reaction was stirred at room temperature for 4 hours. Purification by flash silica column chromatography (3:1 Petrol: EtOAc) afforded the desired sulfinamide **7a** as a white solid (209.2 mg, 95%).

Rf = 0.3 (3:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.12 (m, 17H), 7.07 (d, *J* = 15.2 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 15.2, 1H), 4.99 (s, 1H), 3.72 (s, 3H).

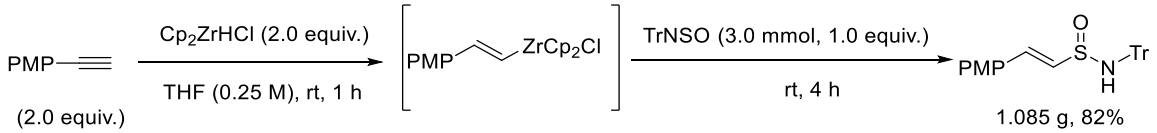
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 144.9, 136.1, 130.0, 129.4, 129.3, 128.2, 127.5, 126.7, 114.4, 73.0, 55.4.

HRMS(ESI^+) calcd. for $C_{28}H_{25}NNaO_2S^+$ $[M+Na]^+$: 462.1498; found: 462.1497.

IR (ν_{max}) 1603, 1510, 1446, 1255, 1174, 1032, 910, 757, 732, 701 cm^{-1}.

M.p. 144-146 °C (CH_2Cl_2).

Gram scale synthesis of (*E*)-2-(4-methoxyphenyl)-*N*-tritylethene-1-sulfinamide (7a)

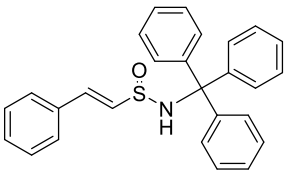


An oven-dried 50 mL round-bottom flask containing a magnetic stirring bar was charged with Schwartz reagent (1.547 g, 6.0 mmol, 2.0 equiv.). The flask was then sealed and subjected to three N_2 evacuation/refill cycles before THF (12 mL, 0.25 M) was added,

followed by the addition of 4-ethynylanisole (793 mg, 6.0 mmol, 2.0 equiv.). The reaction mixture was stirred at room temperature for 1 hour. Then, TrNSO (916 mg, 3.0 mmol, 1.0 equiv.) was added under N_2 atmosphere. The reaction mixture was stirred at the room temperature for 4 hours. Then, silica gel (1.2 g) and ethyl ether (12 mL) were added to the reaction mixture and stirred for 10 mins. Then, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc. The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (3:1 Petrol: EtOAc) to afford the desired sulfinamide **7a** (1.085 g, 82%).

The data is consistent with the above reports.

(*E*)-2-Phenyl-*N*-tritylethene-1-sulfinamide (7b)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and phenylacetylene (103.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (6:1 Petrol: EtOAc) afforded the desired sulfinamide **7b** as a white solid (166.5 mg, 81%).

Rf = 0.3 (6:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.25 (m, 21H), 6.75 (d, *J* = 15.2 Hz, 1H), 5.09 (s, 1H).

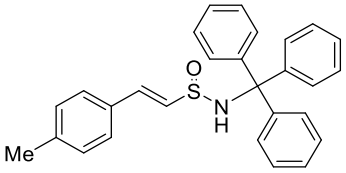
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 136.6, 134.0, 132.7, 129.7, 129.4, 129.00, 128.2, 128.0, 127.6, 73.1.

HRMS(ESI^+) calcd. for $C_{27}H_{23}NNaOS^+$ $[M+Na]^+$: 432.1393; found: 432.1389.

IR (ν_{max}) 1492, 1446, 1069, 1018, 962, 743, 700 cm^{-1}.

M.p. 154-158 °C (CH_2Cl_2).

(*E*)-2-(*p*-Tolyl)-*N*-tritylethene-1-sulfinamide (7c)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 4-ethynyltoluene (116.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (5:1 Petrol: EtOAc) afforded the desired sulfinamide **7c** as a white solid (177.5 mg, 84%).

Rf = 0.3 (5:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.07 (m, 21H), 6.69 (d, *J* = 15.3 Hz, 1H), 5.08 (s, 1H), 2.39 (s, 3H).

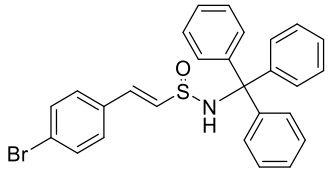
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.0, 136.6, 131.6, 131.3, 129.7, 129.4, 128.2, 127.9, 127.6, 73.1, 21.5.

HRMS(ESI^+) calcd. for $C_{27}H_{23}NNaOS^+$ $[M+Na]^+$: 446.1549; found: 446.1546.

IR (ν_{max}) 1492, 1446, 1070, 1017, 963, 791, 748, 700 cm^{-1}.

M.p. 134-136 °C (CH_2Cl_2).

(*E*)-2-(4-Bromophenyl)-*N*-tritylethene-1-sulfinamide (7d)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 1-bromo-4-ethynylbenzene

(186.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (5:1 Petrol: EtOAc) afforded the desired sulfinamide **7d** as a white solid (177.5 mg, 74%).

Rf = 0.3 (5:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.44-7.23 (m, 17H), 7.18 (d, *J* = 15.3 Hz, 1H), 6.71 (d, *J* = 15.2 Hz, 1H), 5.07 (s, 1H).

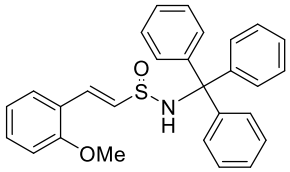
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 135.4, 133.6, 132.9, 132.2, 129.4, 129.4, 128.3, 127.6, 123.9, 73.2.

HRMS(ESI^+) calcd. for $C_{27}H_{22}BrNNaOS^+$ $[M+Na]^+$: 510.0498; found: 510.0500.

IR (ν_{max}) 1487, 1446, 1070, 1009, 962, 794, 755, 700 cm^{-1}.

M.p. 66-70 ^oC (CH_2Cl_2).

(*E*)-2-(2-Methoxyphenyl)-*N*-tritylethene-1-sulfinamide (7e)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 2-ethynylanisole (purified by FCC before using, 1.0 mmol, 132.0 mg, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (3:1 Petrol: EtOAc) afforded the desired sulfinamide **7e** as a white solid (185.2 mg, 84%).

Rf = 0.3 (3:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.23 (m, 18H), 7.01-6.86 (m, 3H), 5.06 (s, 1H), 3.87 (s, 3H).

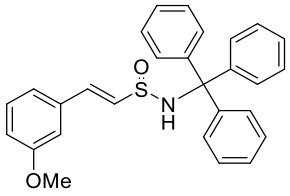
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 145.0, 133.7, 132.2, 130.9, 129.9, 129.4, 128.2, 127.5, 122.9, 120.8, 111.2, 73.0, 55.5.

HRMS(ESI^+) calcd. for $C_{28}H_{25}NNaO_2S^+$ $[M+Na]^+$: 462.1498; found: 462.1495.

IR (ν_{max}) 1575, 1489, 1463, 1447, 1249, 1072, 1021, 752, 701 cm^{-1}.

M.p. 148-152 °C (CH_2Cl_2).

(*E*)-2-(3-Methoxyphenyl)-*N*-tritylethene-1-sulfinamide (7f)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 3-ethynylanisole (132.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (3:1 Petrol: EtOAc) afforded the desired sulfinamide **7f** as a pale-yellow solid (176.3 mg, 84%).

Rf = 0.3 (3:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.14 (m, 17H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 2.1 Hz, 1H), 6.87 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.67 (d, *J* = 15.2 Hz, 1H), 5.05 (s, 1H), 3.80 (s, 3H).

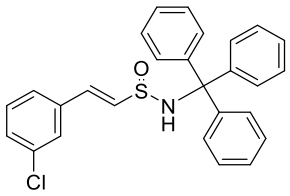
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 144.8, 136.5, 135.3, 133.1, 130.0, 129.4, 128.2, 127.6, 120.5, 115.5, 113.1, 73.1, 55.4.

HRMS(ESI^+) calcd. for $C_{28}H_{25}NNaO_2S^+$ $[M+Na]^+$: 462.1498; found: 462.1498.

IR (ν_{max}) 1597, 1578, 1491, 1447, 1266, 1071, 1038, 1018, 773, 700 cm^{-1}.

M.p. 100-104 °C (CH_2Cl_2).

(*E*)-2-(3-Chlorophenyl)-*N*-tritylethene-1-sulfinamide (7g)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 3-chloro-1-ethynylbenzene (137.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the desired sulfinamide **7g** as a white solid (162.8 mg, 73%).

Rf = 0.3 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.06 (m, 21H), 6.65 (d, *J* = 15.2 Hz, 1H), 4.99 (s, 1H).

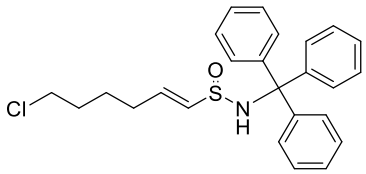
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 135.8, 135.2, 135.0, 134.4, 130.3, 129.6, 129.4, 128.3, 127.7, 127.6, 126.3, 73.2.

HRMS(ESI^+) calcd. for $C_{27}H_{22}ClNNaOS^+$ $[M+Na]^+$: 466.1003; found: 466.1003.

IR (ν_{max}) 1594, 1562, 1492, 1447, 1072, 908, 772, 732, 700 cm^{-1}.

M.p. 64-68 ^{o}C (CH_2Cl_2).

(*E*)-6-Chloro-*N*-tritylhex-1-ene-1-sulfinamide (7h)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 6-chloro-1-hexyne (117.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the desired sulfinamide **7h** as a white solid (137.5 mg, 65%).

Rf = 0.3 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.21 (m, 15H), 6.44 (dt, *J* = 14.9, 6.8 Hz, 1H), 6.16 (dt, *J* = 14.9, 1.5 Hz, 1H), 4.90 (s, 1H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.29-2.19 (m, 2H), 1.85-1.73 (m, 2H), 1.66-1.54 (m, 2H).

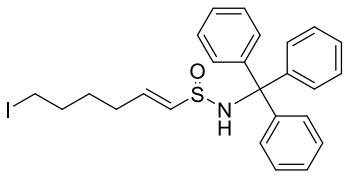
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 139.1, 135.0, 129.3, 128.1, 127.5, 73.0, 44.7, 31.9, 30 8, 25.5.

HRMS(ESI^+) calcd. for $C_{25}H_{26}ClNNaOS^+$ $[M+Na]^+$: 446.1316; found: 446.1316.

IR (ν_{max}) 1596, 1492, 1446, 1066, 1020, 960, 755, 701 cm^{-1}.

M.p. 124-128 ^{o}C (CH_2Cl_2).

(*E*)-6-Iodo-*N*-tritylhex-1-ene-1-sulfinamide (7i)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 6-iodo-1-hexyne (208.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the desired sulfinamide **7i** as a white solid (154.0 mg, 60%).

Rf = 0.3 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.25 (m, 15H), 6.45 (dt, *J* = 14.7, 6.8 Hz, 1H), 6.18 (d, *J* = 14.9 Hz, 1H), 4.94 (s, 1H), 3.19 (t, *J* = 6.9 Hz, 2H), 2.29-2.20 (m, 2H), 1.90-1.80 (m, 2H), 1.63-1.53 (m, 2H).

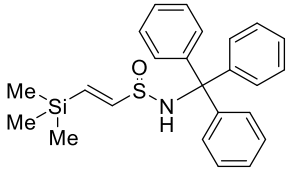
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 139.2, 135.0, 129.4, 128.2, 127.5, 73.0, 32.9, 30.5, 29.2, 6.2.

HRMS(ESI$^+$) calcd. for $C_{25}H_{26}INNaOS^+$ [M+Na]$^+$: 538.0672; found: 538.0667.

IR (ν_{max}) 1492, 1446, 1209, 1039, 909, 731, 700 cm^{-1}.

M.p. 124-128 ^{o}C (CH_2Cl_2).

(*E*)-2-(Trimethylsilyl)-*N*-tritylethene-1-sulfinamide (7j)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and ethynyltrimethylsilane (99.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the desired sulfinamide **7j** as a white solid (170.8 mg, 84%).

Rf = 0.3 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 15H), 6.88 (d, *J* = 17.6 Hz, 1H), 6.48 (d, *J* = 17.5 Hz, 1H), 4.85 (s, 1H), 0.13 (s, 9H).

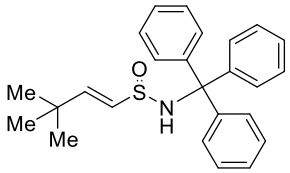
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 144.8, 138.5, 129.3, 128.1, 127.4, 73.0, -1.5.

HRMS(ESI$^+$) calcd. for $C_{24}H_{28}NOSSi^+$ [M+H]$^+$: 406.1655; found: 406.1653.

IR (ν_{max}) 1492, 1447, 1249, 1076, 862, 840, 737, 700 cm^{-1}.

M.p. 122-126 ^{o}C (CH_2Cl_2).

(*E*)-3,3-Dimethyl-*N*-tritylbut-1-ene-1-sulfinamide (7k)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 3,3-dimethyl-1-butyne (83.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the desired sulfinamide **7k** as a white solid (159 mg, 84%).

Rf = 0.3 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-6.79 (m, 15H), 6.42 (d, *J* = 15.1 Hz, 1H), 5.96 (d, *J* = 15.1 Hz, 1H), 4.86 (s, 1H), 1.06 (s, 9H).

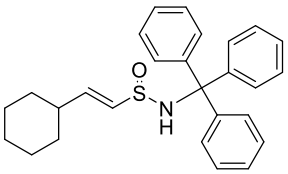
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 144.9, 130.4, 129.2, 128.0, 127.3, 72.8, 33.8, 29.0.

HRMS(ESI^+) calcd. for $C_{25}H_{27}NNaOS^+$ $[M+Na]^+$: 412.1706; found: 412.1706.

IR (ν_{max}) 1492, 1447, 1364, 1266, 1072, 1020, 745, 700 cm^{-1}.

M.p. 140-144 ^{o}C (CH_2Cl_2).

(*E*)-2-Cyclohexyl-*N*-tritylethene-1-sulfinamide (7l)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and cyclohexylacetylene (108.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the desired sulfinamide **7l** as a white solid (188.6 mg, 91%).

Rf = 0.3 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-6.98 (m, 15H), 6.32 (dd, *J* = 15.0, 6.5 Hz, 1H), 5.98 (d, *J* = 15.1 Hz, 1H), 4.80 (s, 1H), 2.24-1.89 (m, 1H), 1.79-1.46 (m, 5H), 1.32-0.85 (m, 5H).

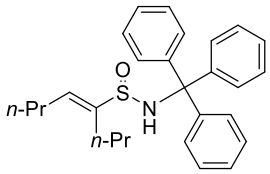
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 145.0, 132.4, 129.4, 128.2, 127.5, 73.0, 40.1, 32.1, 26.0, 25.9.

HRMS(ESI^+) calcd. for $C_{27}H_{30}NOS^+$ $[M+H]^+$: 416.2043; found: 416.2041.

IR (ν_{max}) 2924, 2851, 1492, 1447, 1071, 1020, 962, 753, 700 cm^{-1}.

M.p. 138-142 °C (CH_2Cl_2).

(*E*)-*N*-Trityloct-4-ene-4-sulfinamide (7m)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 4-octyne (110.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (4:1:1 Petrol: CH_2Cl_2: Et_2O) afforded the desired sulfinamide **7m** as colourless oil (166.4 mg, 80%).

Rf = 0.3 (4:1:1 Petrol: CH_2Cl_2: Et_2O).

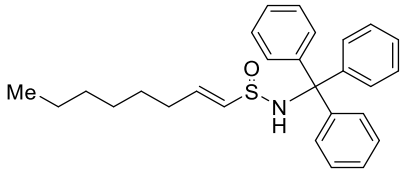
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.13 (m, 15H), 6.35 (t, *J* = 7.5 Hz, 1H), 4.72 (s, 1H), 2.43-2.13 (m, 4H), 1.55-1.33 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 145.0, 133.0, 129.7, 128.0, 127.5, 73.3, 30.2, 28.7, 22.7, 22.4, 14.11, 14.06.

HRMS(ESI^+) calcd. for $C_{27}H_{32}NOS^+$ $[M+H]^+$: 418.2199; found: 418.2198.

IR (ν_{max}) 2958, 2930, 1493, 1446, 1075, 1017, 912, 754, 700 cm^{-1}.

(*E*)-*N*-Trityloct-1-ene-1-sulfinamide (7n)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 1-octyne (110.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (6:1 Petrol: EtOAc) afforded the desired sulfinamide **7n** a white solid (171.0 mg, 82%).

Rf = 0.3 (6:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.05 (m, 15H), 6.44 (dt, *J* = 14.9, 6.9 Hz, 1H), 6.13 (d, *J* = 14.9 Hz, 1H), 4.88 (s, 1H), 2.34-2.04 (m, 2H), 1.48-1.37 (m, 2H), 1.33-1.23 (m, 6H), 0.88 (t, *J* = 8.0 Hz, 3H).

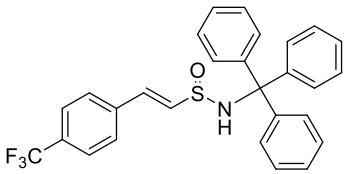
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 140.3, 134.3, 129.4, 128.2, 127.5, 73.0, 31.71, 31.69, 28.9, 28.3, 22.7, 14.2.

HRMS(ESI^+) calcd. for $C_{27}H_{32}NOS^+$ $[M+H]^+$: 418.2199; found: 418.2198.

IR (ν_{max}) 2926, 1629, 1596, 1492, 1446, 1070, 1020, 754, 700 cm^{-1}.

M.p. 64-68 ^{o}C (CH_2Cl_2).

(*E*)-2-(4-(Trifluoromethyl)phenyl)-N-tritylethene-1-sulfinamide (7o)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 4-ethynyl-α,α,α-

trifluorotoluene (170.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 1 h then 40 °C for 4 h. Purification by flash silica column chromatography (6:1:1 Petrol: CH_2Cl_2: EtOAc) afforded the desired sulfinamide **7o** a pale-yellow solid (172.1 mg, 72%).

Rf = 0.3 (6:1:1 Petrol: CH_2Cl_2: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.16 (m, 16H), 6.71 (d, *J* = 15.3 Hz, 1H), 5.02 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 137.3, 135.6, 135.0, 131.2 (q, *J* = 32.7 Hz), 129.3, 128.3, 128.1, 127.6, 125.9 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.2 Hz), 73.2.

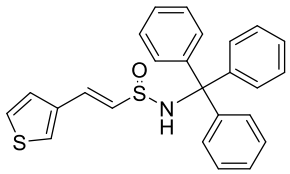
^{19}F NMR (377 MHz, $CDCl_3$) δ -62.68 (s).

HRMS(ESI^+) calcd. for $C_{28}H_{22}F_3NNaOS^+$ $[M+Na]^+$: 500.1266; found: 500.1260.

IR (ν_{max}) 1492, 1447, 1323, 1167, 1126, 1066, 1016, 909, 731, 701 cm^{-1}.

M.p. 156-160 °C (CH_2Cl_2).

(*E*)-2-(Thiophen-3-yl)-*N*-tritylethene-1-sulfinamide (7p)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 3-ethynylthiophene (109.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (3:1 Petrol: EtOAc) afforded the desired sulfinamide **7p** a white solid (166.0 mg, 80%).

Rf = 0.3 (3:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.02 (m, 19H), 6.55 (d, *J* = 15.2 Hz, 1H), 5.08 (s, 1H).

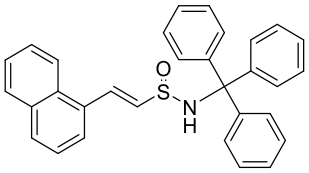
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 136.6, 132.2, 130.4, 129.4, 128.2, 127.6, 127.0, 126.8, 125.4, 73.1.

HRMS(ESI^+) calcd. for $C_{25}H_{21}NNaOS_2^+$ $[M+Na]^+$: 438.0957; found: 438.0951.

IR (ν_{max}) 1614, 1597, 1492, 1446, 1066, 1018, 959, 769, 700 cm^{-1}.

M.p. 148-152 °C (CH_2Cl_2).

(*E*)-2-(Naphthalen-1-yl)-*N*-tritylethene-1-sulfinamide (7q)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and 1-ethynylnaphthalene (purified by FCC before using, 152.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (6:1 Petrol: EtOAc) afforded the desired sulfinamide **7q** a pale-yellow solid (182.6 mg, 80%).

Rf = 0.3 (6:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.6 Hz, 1H), 8.07 (d, *J* = 15.0 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.59-7.26 (m, 18H), 6.85 (d, *J* = 15.0 Hz, 1H), 5.15 (s, 1H).

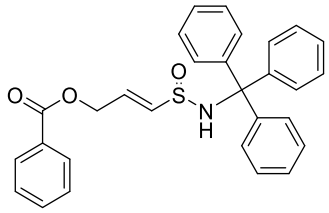
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 135.5, 134.1, 133.8, 131.4, 131.3, 130.1, 129.4, 128.7, 128.3, 127.6, 126.9, 126.4, 125.5, 125.1, 123.7, 73.2.

HRMS(ESI^+) calcd. for $C_{31}H_{25}NNaOS^+$ $[M+Na]^+$: 482.1549; found: 482.1549.

IR (ν_{max}) 1596, 1492, 1447, 1069, 1036, 1016, 909, 791, 769, 731, 700 cm^{-1}.

M.p. 74-78 °C (CH_2Cl_2).

(*E*)-3-((Tritylamino)sulfinyl)allyl benzoate (7r)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TrNSO (153.0 mg, 0.5 mmol, 1 equiv.) and propargyl benzoate (160.0 mg, 1.0 mmol, 2.0 equiv.) were combined at 40 ^{o}C for 4 hours. Purification by flash silica column chromatography (3:1 Petrol: EtOAc) afforded the desired sulfinamide **7r** a white solid (168.2 mg, 72%).

Rf = 0.3 (3:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.9 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.22 (m, 15H), 6.65 (dt, *J* = 15.0, 4.6 Hz, 1H), 6.39 (dt, *J* = 14.9, 1.8 Hz, 1H), 5.05 (s, 1H), 5.01 (dd, *J* = 4.5, 1.8 Hz, 2H).

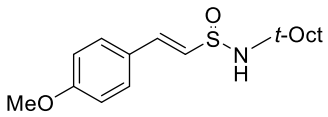
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 144.7, 136.3, 133.5, 133.1, 129.9, 129.7, 129.2, 128.6, 128.2, 127.6, 73.0, 63.0.

HRMS(ESI^+) calcd. for $C_{29}H_{25}NNaO_3S^+$ $[M+Na]^+$: 490.1447; found: 490.1444.

IR (ν_{max}) 1720, 1599, 1492, 1448, 1270, 1116, 1070, 1021, 703 cm^{-1}.

M.p. 58-62 ^{o}C (CH_2Cl_2).

(*E*)-2-(4-Methoxyphenyl)-N-(2,4,4-trimethylpentan-2-yl)ethene-1-sulfinamide (7s)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), *t*-Oct-NSO (88.0 mg, 0.5 mmol, 1 equiv.) and 4-ethynylanisole (132.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by

flash silica column chromatography (4:1 Petrol: EtOAc) afforded the desired sulfinamide **7s** a white solid (150.5 mg, 97%).

Rf = 0.3 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 15.3 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.63 (d, *J* = 15.2 Hz, 1H), 3.83 (s, 3H), 3.73 (s, 1H), 1.75-1.52 (m, 2H), 1.47 (s, 3H), 1.42 (s, 3H), 1.03 (s, 9H).

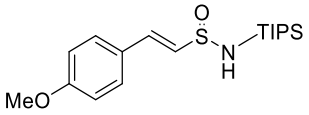
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 136.1, 129.9, 129.4, 126.9, 114.3, 58.0, 55.9, 55.4, 32.3, 31.91, 31.86, 29.7. (note: for methyl groups in *t*-Oct group, 2 peaks were found instead of 1)

HRMS(ESI^+) calcd. for $C_{17}H_{28}NO_2S^+$ $[M+H]^+$: 310.1835; found: 310.1838.

IR (ν_{max}) 2953, 1605, 1511, 1463, 1366, 1304, 1253, 1059, 1034, 967, 836, 798 cm^{-1}.

M.p. 84-88 °C (CH_2Cl_2).

(*E*)-2-(4-Methoxyphenyl)-*N*-(triisopropylsilyl)ethene-1-sulfinamide (7t)



Prepared according to **General Procedure D**, Schwartz reagent (257.0 mg, 1.0 mmol, 2.0 equiv.), THF (2 mL), TIPS-NSO (110.0 mg, 0.5 mmol, 1 equiv.) and 4-ethynylanisole (132.0 mg, 1.0 mmol, 2.0 equiv.) were combined at room temperature for 4 hours. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the desired sulfinamide **7t** a white solid (172.2 mg, 98%)

Rf = 0.3 (4:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7 Hz, 1H), 7.18 (d, *J* = 15.2 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.74 (d, *J* = 15.2 Hz, 1H), 3.83 (s, 3H), 3.61 (s, 1H), 1.30-1.16 (m, 2H), 1.16-1.03 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 135.0, 133.5, 129.4, 126.7, 114.4, 55.44, 18.01, 17.95, 11.8. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

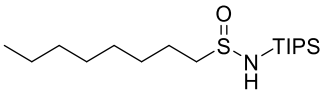
HRMS(ESI^+) calcd. for $C_{18}H_{32}NO_2SSi^+$ $[M+H]^+$: 354.1918; found: 354.1918.

IR (ν_{max}) 2943, 2866, 1605, 1511, 1442, 1253, 1055, 1035, 840, 799, 744, 677 cm^{-1}.

M.p. 82-86 ^oC (CH_2Cl_2).

5.4.3 Synthesis of alkyl sulfinamides

_N_-(Triisopropylsilyl)octane-1-sulfinamide (9a)



Prepared according to **General Procedure E**, Schwartz reagent (128.9 mg, 0.5 mmol, 2.0 equiv.), CH_2Cl_2 (2 mL) and 1-octene (56.1 mg, 0.5 mmol, 2.0 equiv.) were combined at room temperature for 1 hour. Then, the above reaction mixture was transferred to another microwave vial contained scandium triflate (12.3 mg, 0.025 mmol, 10 mol%), rinsed with CH_2Cl_2 (1 mL). TIPSNSO (54.9 mg, 0.25 mmol, 1 equiv.) was then added and the reaction mixture was stirred for 6 h. Purification by flash silica column chromatography (2:1 Petrol: EtOAc) afforded the desired sulfinamide **9a** as a colourless oil (74.1 mg, 89%).

Rf = 0.5 (1:1 Petrol: EtOAc).

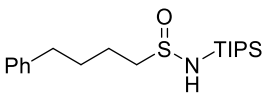
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.49 (s, 1H), 2.70 (t, *J* = 7.7 Hz, 2H), 1.73 – 1.59 (m, 2H), 1.44 – 1.33 (m, 2H), 1.30 – 1.21 (m, 8H), 1.18 – 1.10 (m, 3H), 1.09 – 1.02 (m, 18H), 0.84 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 61.2, 31.8, 29.3, 29.1, 28.8, 23.4, 22.7, 18.0, 17.9, 14.1, 11.8. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS(ESI^+) calcd. for $C_{17}H_{40}NOSSi^+$ $[M+H]^+$: 334.2594; found: 334.2591.

IR (ν_{max}) 3199, 2927, 2866, 1464, 1054, 881, 733, 677 cm^{-1}.

4-Phenyl-_N_-(triisopropylsilyl)butane-1-sulfinamide (9b)



Prepared according to **General Procedure E**, Schwartz reagent (128.9 mg, 0.5 mmol, 2.0 equiv.), CH_2Cl_2 (2 mL) and 4-phenyl-1-butene (66.1 mg, 0.5 mmol, 2.0 equiv.) were combined at room temperature for 1 hour. Then, the above reaction mixture was transferred to another microwave vial contained scandium triflate (12.3 mg, 0.025 mmol, 10 mol%), rinsed with CH_2Cl_2 (1 mL). TIPSNSO (54.9 mg, 0.25 mmol, 1 equiv.) was then added and the reaction mixture was stirred for 6 h. Purification by flash silica column chromatography (2:1 Petrol: EtOAc) afforded the desired sulfinamide **9b** as a white solid (72.3 mg, 82%).

Rf = 0.3 (2:1 Petrol: EtOAc).

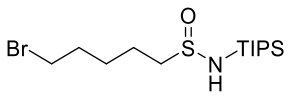
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 7.21 – 7.12 (m, 3H), 3.41 (s, 1H), 2.77 – 2.70 (m, 2H), 2.68 – 2.61 (m, 2H), 1.78 – 1.69 (m, 4H), 1.20 – 1.10 (m, 3H), 1.11 – 1.03 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 128.5, 126.0, 61.1, 35.7, 30.6, 23.2, 18.0, 17.9, 11.8. (note: for phenyl group, 4 peaks overlap to show 3 peaks; for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS(ESI^+) calcd. for $C_{19}H_{36}NOSSi^+$ $[M+H]^+$: 354.2281; found: 354.2280.
IR (ν_{max}) 3186, 2943, 2867, 1462, 1058, 907, 881, 732 cm^{-1}.

M.p. 76-78 °C (CH_2Cl_2).

5-Bromo-*N*-(triisopropylsilyl)pentane-1-sulfinamide (9c)



Prepared according to **General Procedure E**, Schwartz reagent (128.9 mg, 0.5 mmol, 2.0 equiv.), CH_2Cl_2 (2 mL) and 5-bromo-1-pentene (74.5 mg, 0.5 mmol, 2.0 equiv.) were combined at room temperature for 1 hour. Then, the above reaction mixture was transferred to another microwave vial contained scandium triflate (12.3 mg, 0.025 mmol, 10 mol%), rinsed

with CH_2Cl_2 (1 mL). TIPSNSO (54.9 mg, 0.25 mmol, 1 equiv.) was then added and the reaction mixture was stirred for 6 h. Purification by flash silica column chromatography (2:1 Petrol: EtOAc) afforded the desired sulfinamide **9c** as a colourless oil (65.2 mg, 70%).

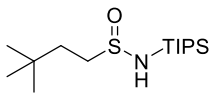
Rf = 0.5 (1:1 Petrol: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (s, 1H), 3.38 (t, *J* = 6.7 Hz, 2H), 2.74 – 2.68 (m, 2H), 1.92 – 1.81 (m, 2H), 1.75 – 1.67 (m, 2H), 1.60 – 1.51 (m, 2H), 1.19 – 1.09 (m, 3H), 1.08 – 1.01 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 60.7, 33.3, 32.4, 27.3, 22.8, 17.94, 17.87, 11.8. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS(ESI^+) calcd. for $C_{14}H_{33}{}^{79}BrNOSSi^+$ $[M+H]^+$: 370.1230; found: 370.1222.
IR (ν_{max}) 3187, 2943, 2867, 1463, 881, 755, 677 cm^{-1}.

3,3-Dimethyl-*N*-(triisopropylsilyl)butane-1-sulfinamide (9d)



Prepared according to **General Procedure E**, Schwartz reagent (128.9 mg, 0.5 mmol, 2.0 equiv.), CH_2Cl_2 (2 mL) and 3,3-dimethyl-1-butene (42.1 mg, 0.5 mmol, 2.0 equiv.) were combined at room temperature for 1 hour. Then, the above reaction mixture was transferred to another microwave vial contained scandium triflate (12.3 mg, 0.025 mmol, 10 mol%), rinsed with CH_2Cl_2 (1 mL). TIPSNSO (54.9 mg, 0.25 mmol, 1 equiv.) was then added and the reaction mixture was stirred for 6 h. Purification by flash silica column chromatography (2:1 Petrol: EtOAc) afforded the desired sulfinamide **9d** as a colourless oil (40.0 mg, 52%).

Rf = 0.4 (2:1 Petrol: EtOAc).

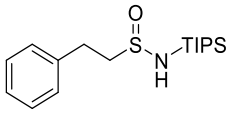
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (s, 1H), 2.74 – 2.63 (m, 2H), 1.58 – 1.49 (m, 2H), 1.21 – 1.01 (m, 21H), 0.91 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 57.2, 36.5, 30.3, 29.3, 18.0, 17.9, 11.8. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS(ESI^+) calcd. for $C_{15}H_{35}NOSSiNa^+$ $[M+Na]^+$: 328.2101; found: 328.2095.

IR (ν_{max}) 3167, 2947, 2868, 1466, 1061, 907, 880, 733 cm^{-1}.

2-Phenyl-*N*-(triisopropylsilyl)ethane-1-sulfinamide (9e)



Prepared according to **General Procedure E**, Schwartz reagent (128.9 mg, 0.5 mmol, 2.0 equiv.), CH_2Cl_2 (2 mL) and styrene (52.1 mg, 0.5 mmol, 2.0 equiv.) were combined at room temperature for 1 hour. Then, the above reaction mixture was transferred to another microwave vial contained scandium triflate (12.3 mg, 0.025 mmol, 10 mol%), rinsed with CH_2Cl_2 (1 mL). TIPSNSO (54.9 mg, 0.25 mmol, 1 equiv.) was then added and the reaction mixture was stirred for 6 h. Purification by flash silica column chromatography (4:1 Petrol: EtOAc) afforded the desired sulfinamide **9e** as a white solid (35.0 mg, 43%).

Rf = 0.2 (4:1 Petrol: EtOAc).

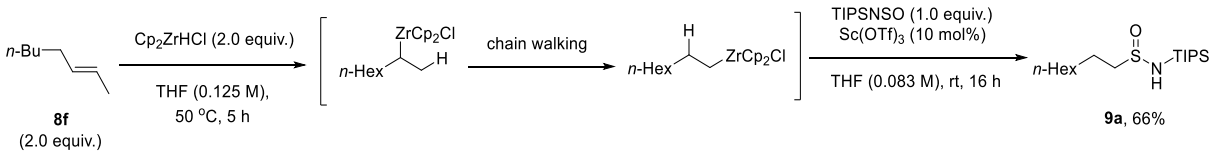
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.11 (m, 5H), 3.47 (s, 1H), 3.06 – 2.88 (m, 4H), 1.14 – 0.90 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 128.85, 128.6, 126.7, 61.8, 29.4, 18.0, 17.9, 11.8. (note: for methyl groups in TIPS group, 2 peaks were found instead of 1)

HRMS(ESI^+) calcd. for $C_{17}H_{31}NOSSiNa^+$ $[M+Na]^+$: 348.1788; found: 348.1784.

IR (ν_{max}) 3168, 2944, 2867, 1463, 1056, 906, 880, 731 cm^{-1}.

Synthesis *N*-(Triisopropylsilyl)octane-1-sulfinamide (9a) from *trans*-2-octene (8f)

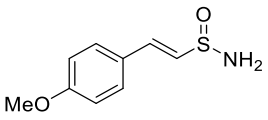


An oven-dried 10 mL microwave vial containing Schwartz reagent (128.9 mg, 0.5 mmol, 2.0 equiv.) was sealed and subjected to three N_2 evacuation/refill cycles before THF (2 mL, 0.25 M) was added. *trans*-2-Octene (56.1 mg, 0.5 mmol, 2.0 equiv.) was then added by a micro syringe. The reaction mixture was stirred at 50 ^oC for 5 hours. Then, the reaction mixture was cooled to room temperature and transferred to another oven-dried 10 mL microwave vial in N_2 atmosphere, which contained scandium(III) triflate (12.3 mg, 0.025 mmol, 10 mol%). Additional THF (1 mL) was used to rinse the first microwave vial. Then, TIPNSO (54.9 mg, 0.25 mmol, 1 equiv.) was added. The reaction mixture was sealed and stirred at the appropriate temperature for 16 hours. Then, silica gel (200 mg) and ethyl ether (2 mL) were added to the reaction mixture and stirred for 10 mins. the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo* and purified by silica column chromatography (2:1 Petrol: EtOAc) to afford the desired sulfinamide **9a** (55 mg, 66%) as a colourless oil.

The data is consistent with the above reports.

5.4.4 Derivatization of alkenyl sulfinamides

(*E*)-2-(4-Methoxyphenyl)ethene-1-sulfinamide (10t)



To a 10 mL microwave vial, (*E*)-2-(4-methoxyphenyl)-*N*-(triisopropylsilyl)ethene-1-sulfinamide **7t** (70.8 mg, 0.2 mmol, 1 equiv.) was added. The vial was then sealed with a microwave cap and subjected to three evacuation/argon refill cycles. THF (2.0 mL, 0.1 M) was then added, followed by addition of TBAF (1M in THF, 0.4 mL, 0.4 mmol, 2 equiv.), the reaction was allowed to stirred at room temperature.

After 5 min, the mixture was quenched with aqueous saturated NH_4Cl solution (5 mL). The mixture was then extracted with EtOAc (2×10 mL). The organic layer was combined and dried with anhydrous Na_2SO_4. The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (1:1:3 to 1:1:6 Petrol: CH_2Cl_2: EtOAc) to afford title compound **10t** (29.1 mg, 74%) as a white solid.

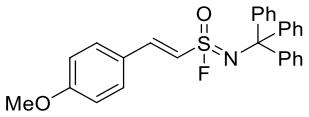
Rf = 0.3 (1:3 Petrol: EtOAc)

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.55 (d, *J* = 8.7 Hz, 2H), 7.09 – 6.92 (m, 4H), 5.97 (s, 2H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 160.1, 134.1, 133.1, 129.3, 126.7, 114.3, 55.2.

HRMS(ESI^+) calcd. for $C_9H_{12}NO_2S^+$ $[M+H]^+$: 198.0583; found: 198.0583.
IR (ν_{max}) 3192, 3063, 1605, 1512, 1254, 1178, 1058, 1029, 798, 753 cm^{-1}.

(*E*)-2-(4-methoxyphenyl)-N-tritylethene-1-sulfonimidoyl fluoride (11a)



An oven-dried 10 mL microwave vial containing (*E*)-2-(4-methoxyphenyl)-*N*-tritylethene-1-sulfinamide **7a** (87.9 mg, 0.2 mmol, 1.0 equiv.) was sealed and subjected to three N_2 evacuation/refill cycles before THF (2 mL, 0.1 M) was added. NaH (60% dispersion in mineral oil, 9.6 mg, 0.24 mmol, 1.2 equiv.) was added to the solution. The reaction was stirred in 0 ^oC ice water bath for 5 min, and then at room temperature for another 25 min, followed by the addition of NFSI (94.6 mg, 0.3 mmol, 1.5 equiv.) under N_2 atmosphere. The reaction mixture was then stirred at room temperature for another 2 h. Then, the mixture was filtered through a pad of silica (2 cm) washing with EtOAc (70 mL). The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (10:1 Petrol: EtOAc) to afford the desired sulfonimidoyl fluoride **11a** (64.2 mg, 70%) as a white solid.

Rf = 0.5 (10:1 Petrol: EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 15.4 Hz, 1H), 7.44 – 7.36 (m, 8H), 7.27 – 7.14 (m, 9H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.80 (dd, *J* = 15.3, 2.4 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 146.44 (d, *J* = 4.2 Hz), 143.0, 130.6, 128.9, 127.9, 127.1, 124.5, 121.07 (d, *J* = 32.2 Hz), 114.74, 73.96 (d, *J* = 4.4 Hz), 55.60.

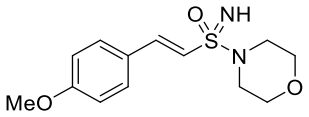
^{19}F NMR (377 MHz, $CDCl_3$) δ 89.40 (s).

HRMS(ESI^+) calcd. for $C_{28}H_{24}FNO_2SNa^+$ $[M+Na]^+$: 480.1404; found: 480.1405.

IR (ν_{max}) 1603, 1513 1260, 1174, 909, 732, 702 cm^{-1}.

M.p. 134-136 °C (CH_2Cl_2).

(*E*)-4-(2-(4-methoxyphenyl)vinylsulfonimidoyl)morpholine (12a)



An oven-dried 25 mL round-bottom flask containing (*E*)-2-(4-methoxyphenyl)-*N*-tritylethene-1-sulfinamide **7a** (175.8 mg, 0.4 mmol, 1.0 equiv.) was sealed and subjected to three N_2 evacuation/refill cycles before THF (4 mL, 0.1 M) was added. NaH (60% dispersion in mineral oil, 24.0 mg, 0.6 mmol, 1.5 equiv.) was added to the solution. The reaction was stirred in 0 ^oC ice water bath for 5 min, and then at room temperature for another 25 min, followed by the addition of TCCA (trichloroisocyanuric acid) (102.6 mg, 0.4 mmol, 1.0 equiv.) under N_2 atmosphere at room temperature. The reaction mixture was stirred at room temperature for 30 min, then triethylamine (0.8 mmol, 2.0 equiv.) was added, followed by the addition of morpholine (1.6 mmol, 4.0 equiv.). The reaction was stirred at room temperature for 1 h, then MsOH (methanesulfonic acid) (0.4 mL, 0.1 M) was added dropwise, and the reaction mixture was stirred for another 1 h. The mixture was diluted with CH_2Cl_2 (10 mL) and transferred to a 50 mL separating funnel, before neutralizing with saturated aqueous $NaHCO_3$ solution (10 mL). The aqueous layer was then extracted with CH_2Cl_2 (2×10 mL). The organic layer was combined and dried with anhydrous Na_2SO_4. The resultant crude solution was concentrated *in vacuo*. The crude mixture was purified by silica column chromatography (1:3 Petrol: EtOAc) to afford title compound **12a** (56.3 mg, 50%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.33 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 15.4 Hz, 1H), 3.82 (s, 3H), 3.75 – 3.68 (m, 4H), 3.21 – 3.04 (m, 4H), 2.44 (bs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 143.4, 130.1, 125.3, 118.2, 114.6, 66.6, 55.5, 47.0.

HRMS(ESI^+) calcd. for $C_{13}H_{19}N_2O_3S^+$ $[M+H]^+$: 283.1111; found: 283.1121.**IR** (ν_{max}) 3252, 2858, 1604, 1512, 1257, 1112, 929, 730 cm^{-1}.

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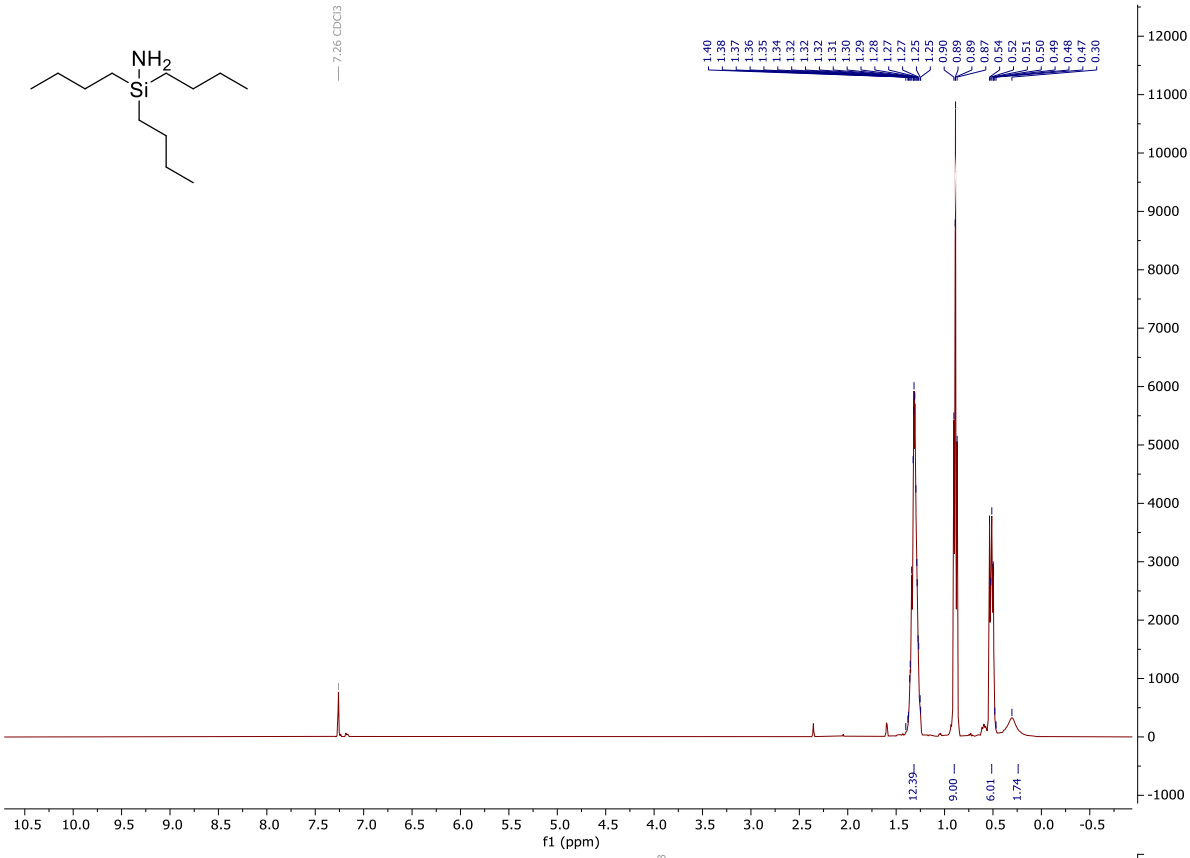
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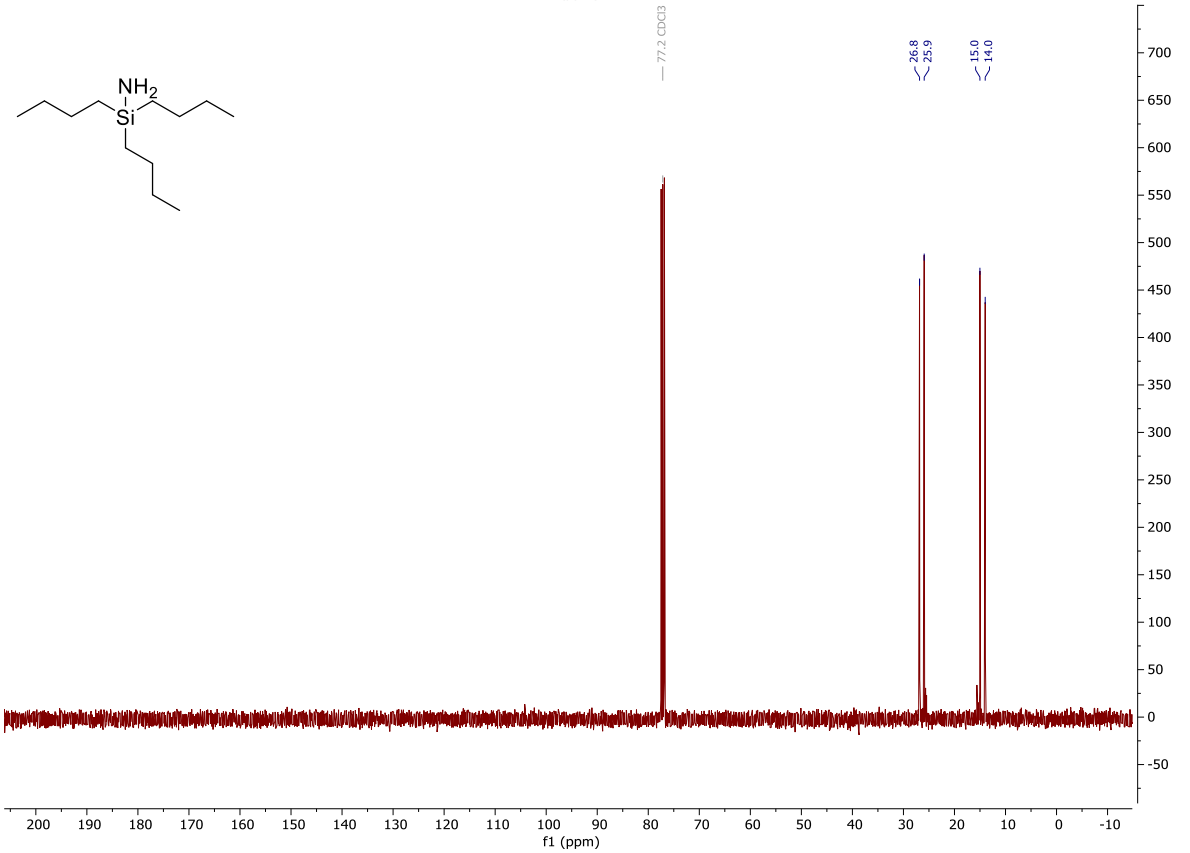
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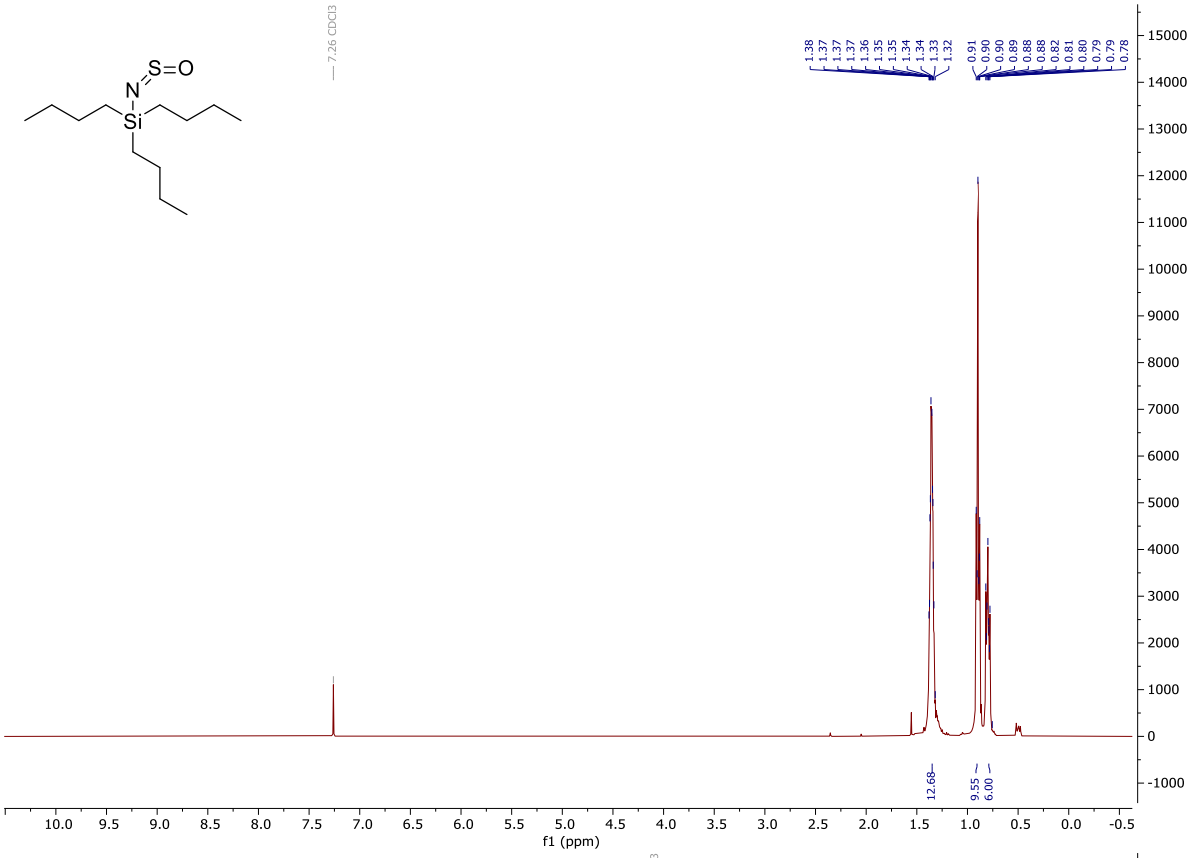
Appendix I-NMR Spectra of Chapter 2

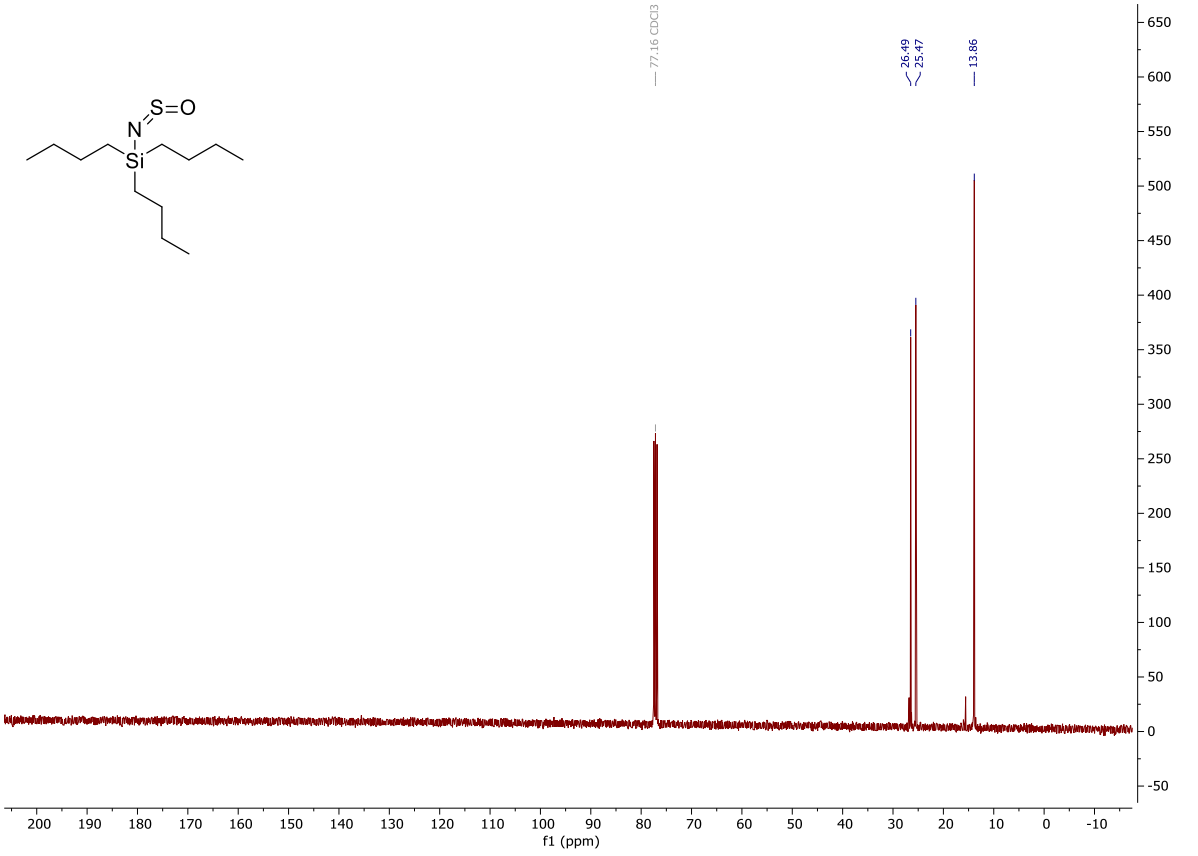
tri(*n*-Butyl)silylamine ($TNBSNH_2$)



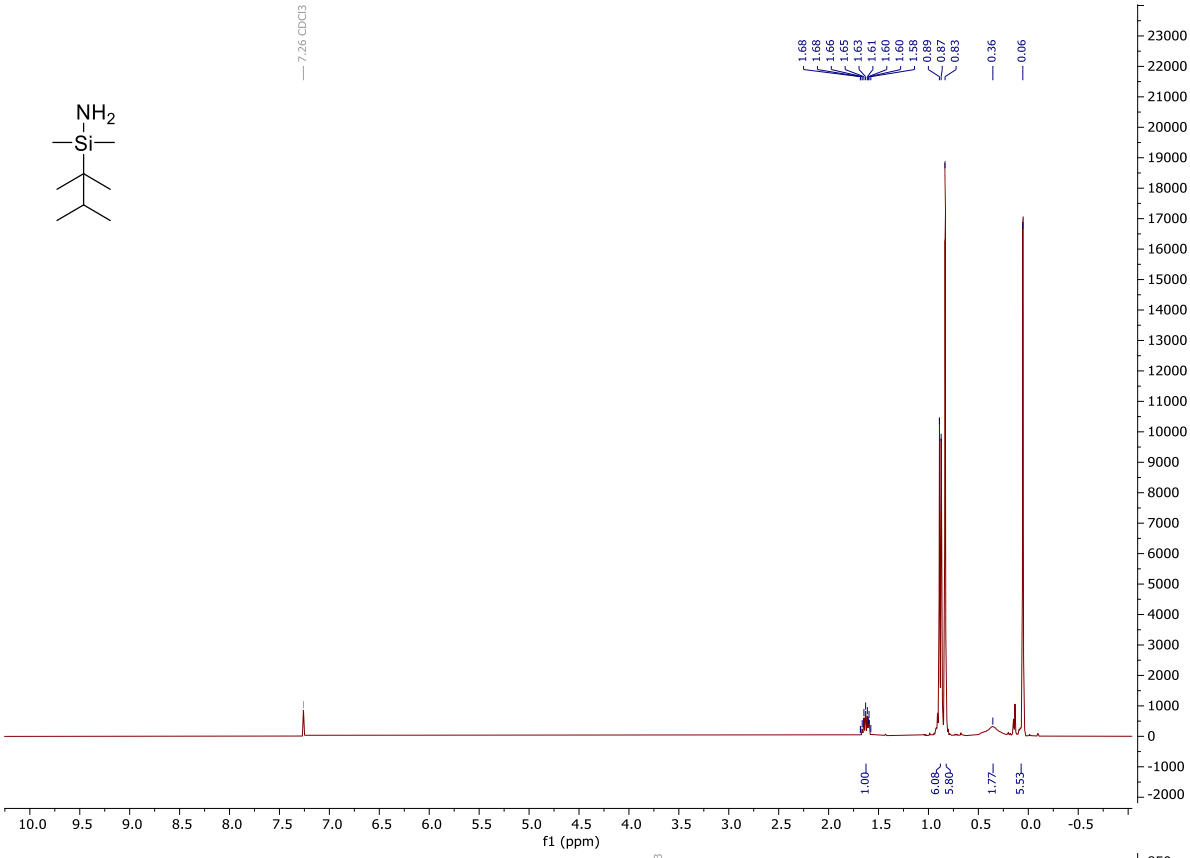


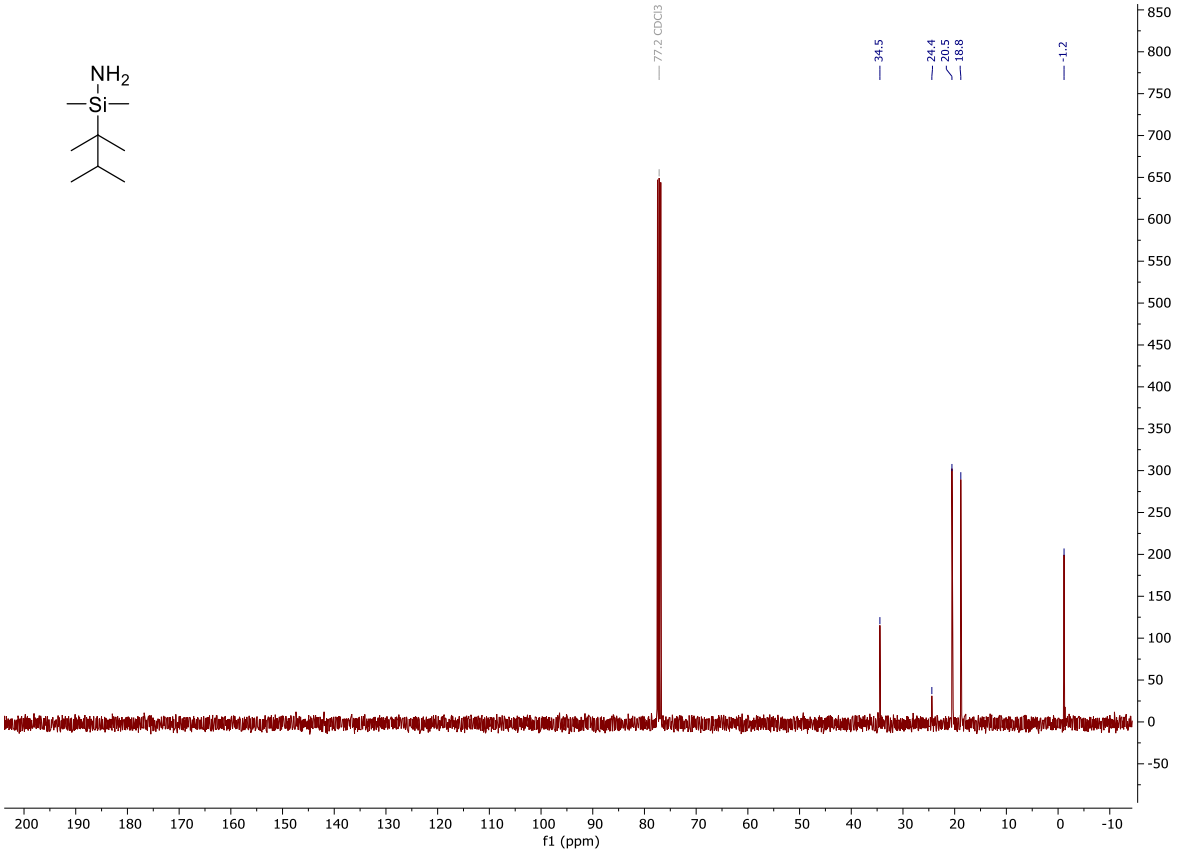
N-Sulfinyl-tri(*n*-butyl)silylamine (TNBSNSO)



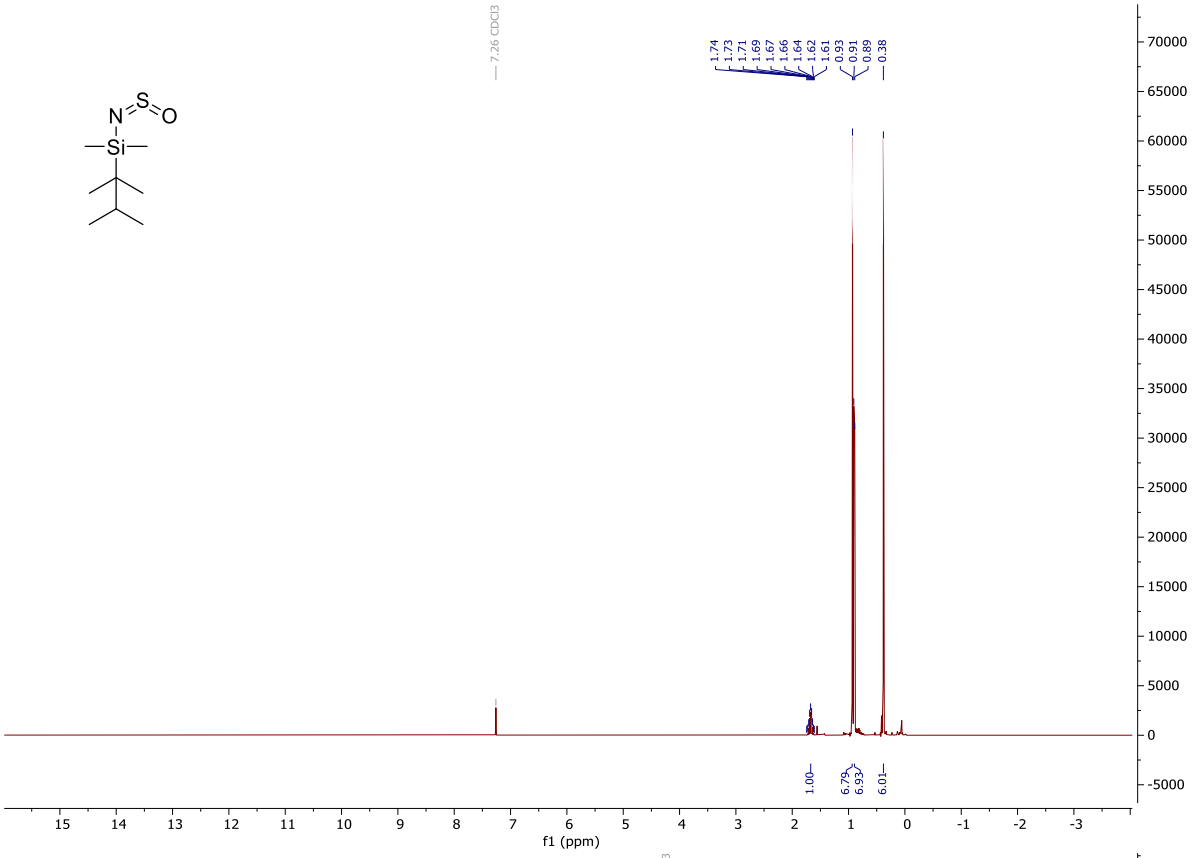


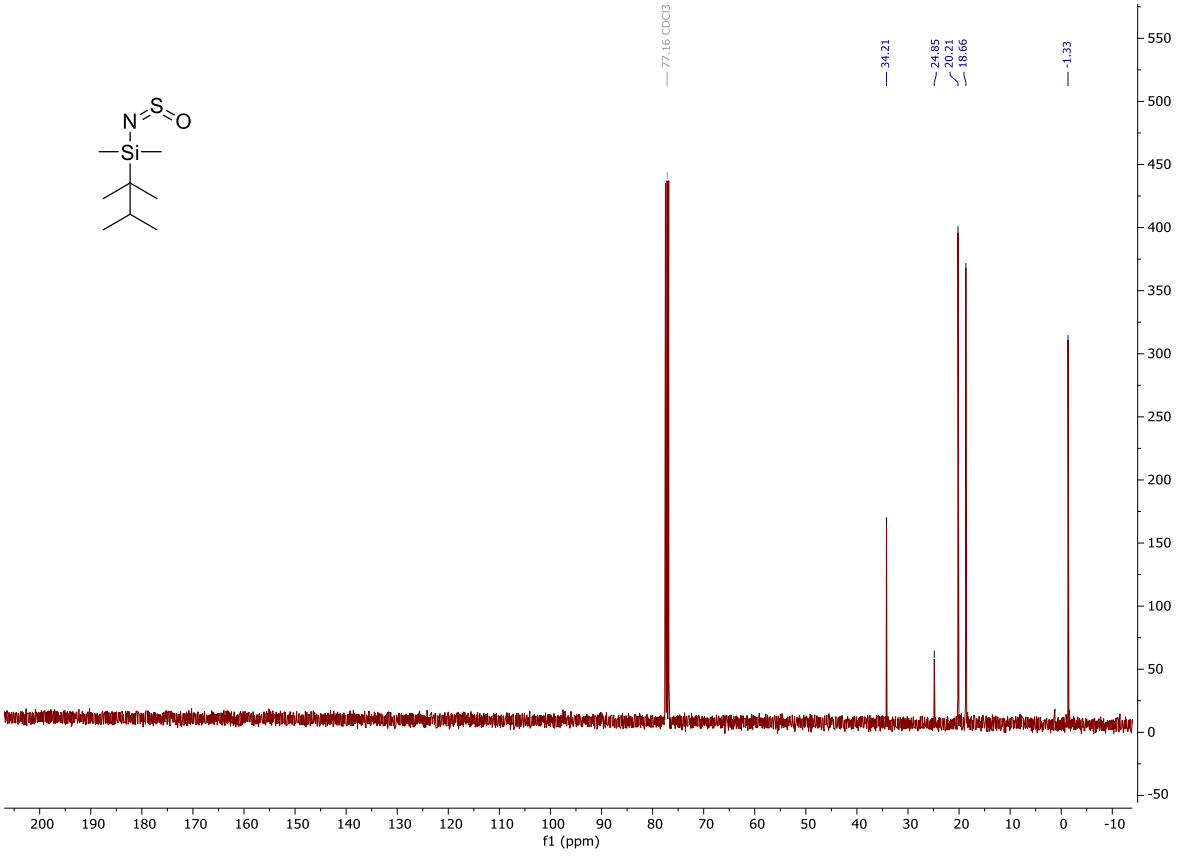
(Dimethyl)thexylsilylamine ($TDSNH_2$)



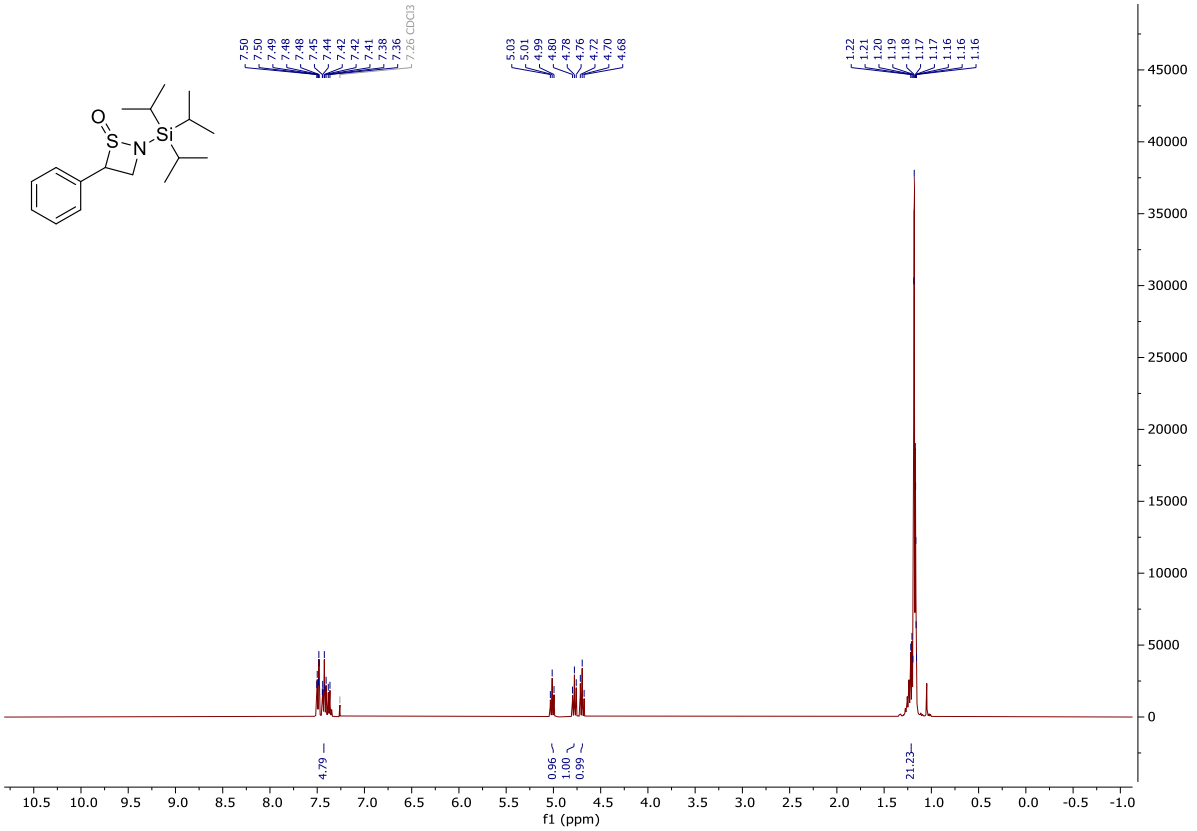


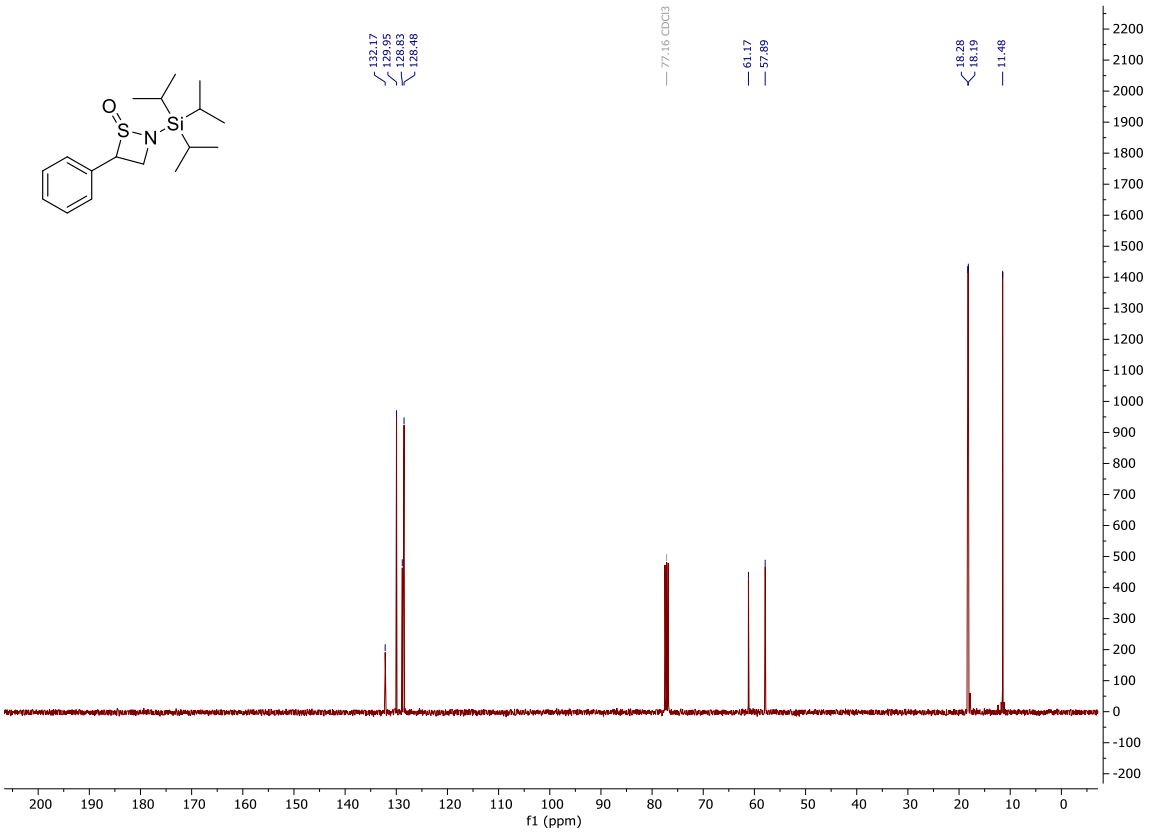
N-sulfinyl-(dimethyl)thexylsilylamine (TDSNSO)



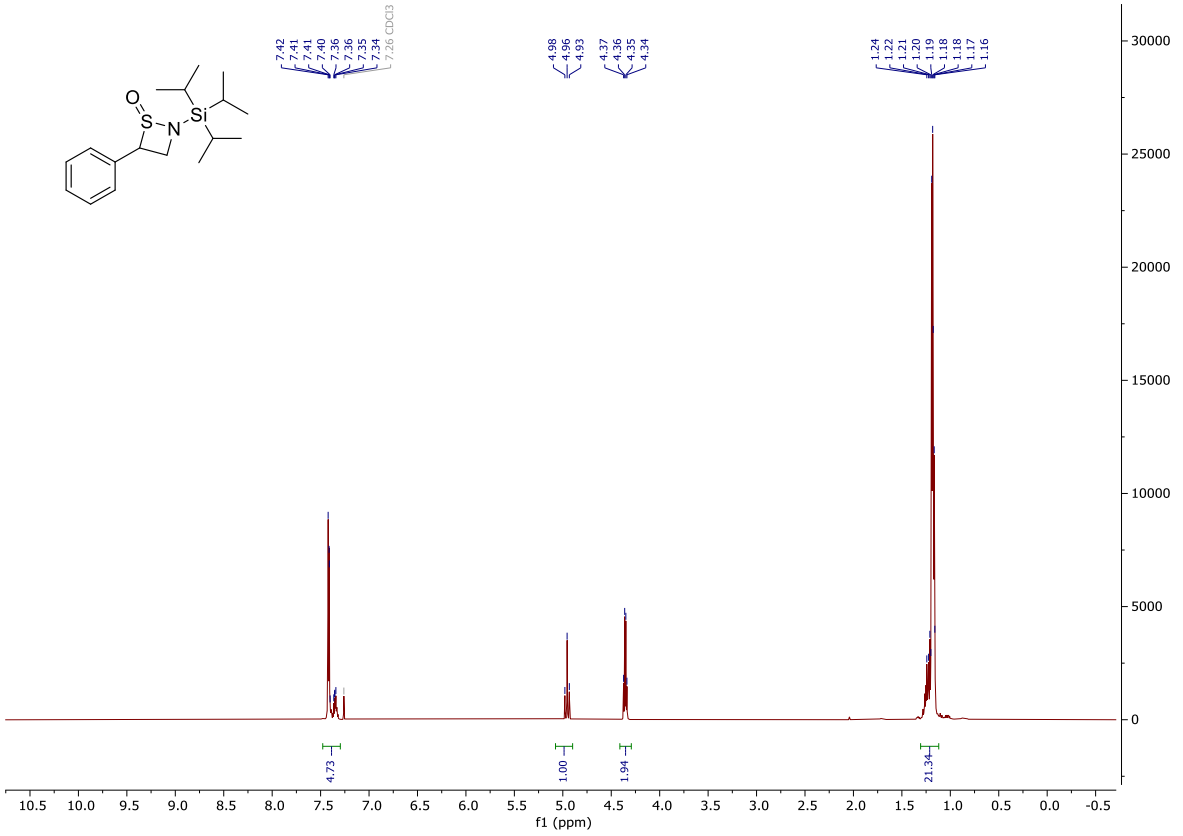


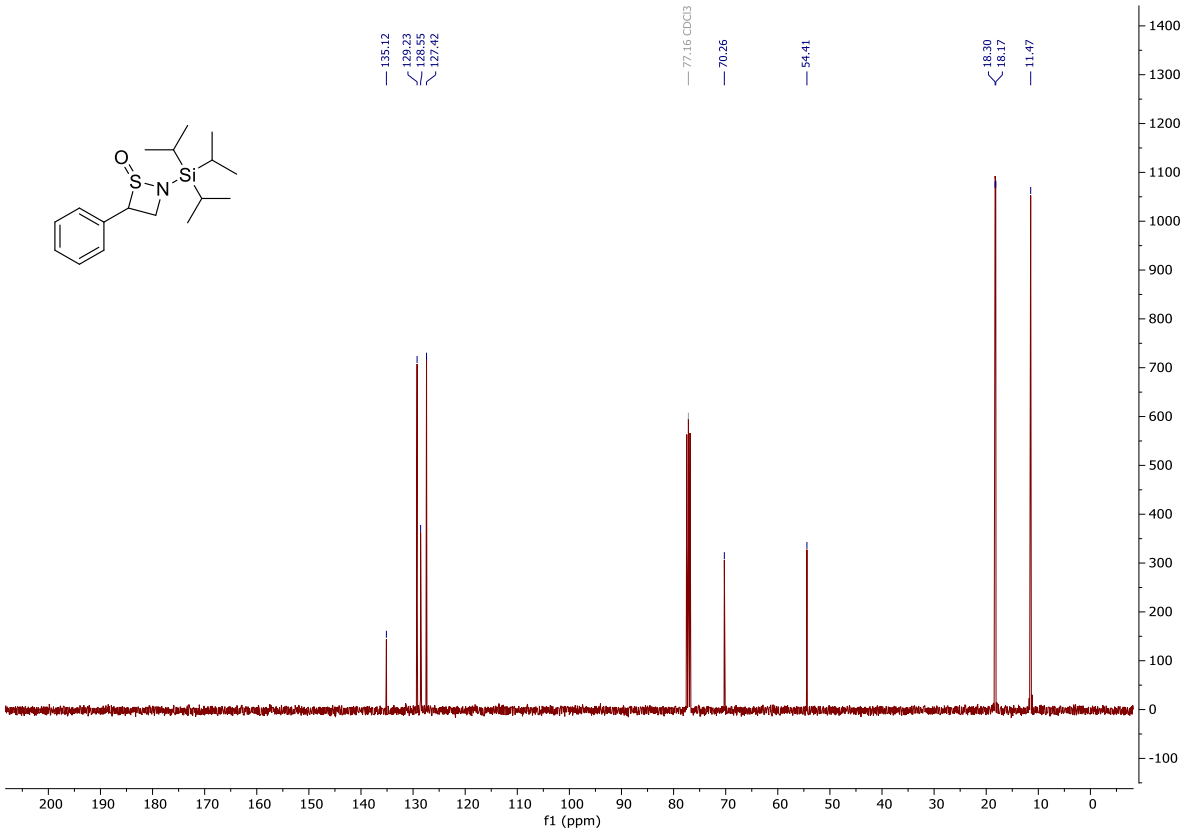
4-Phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1a-major)



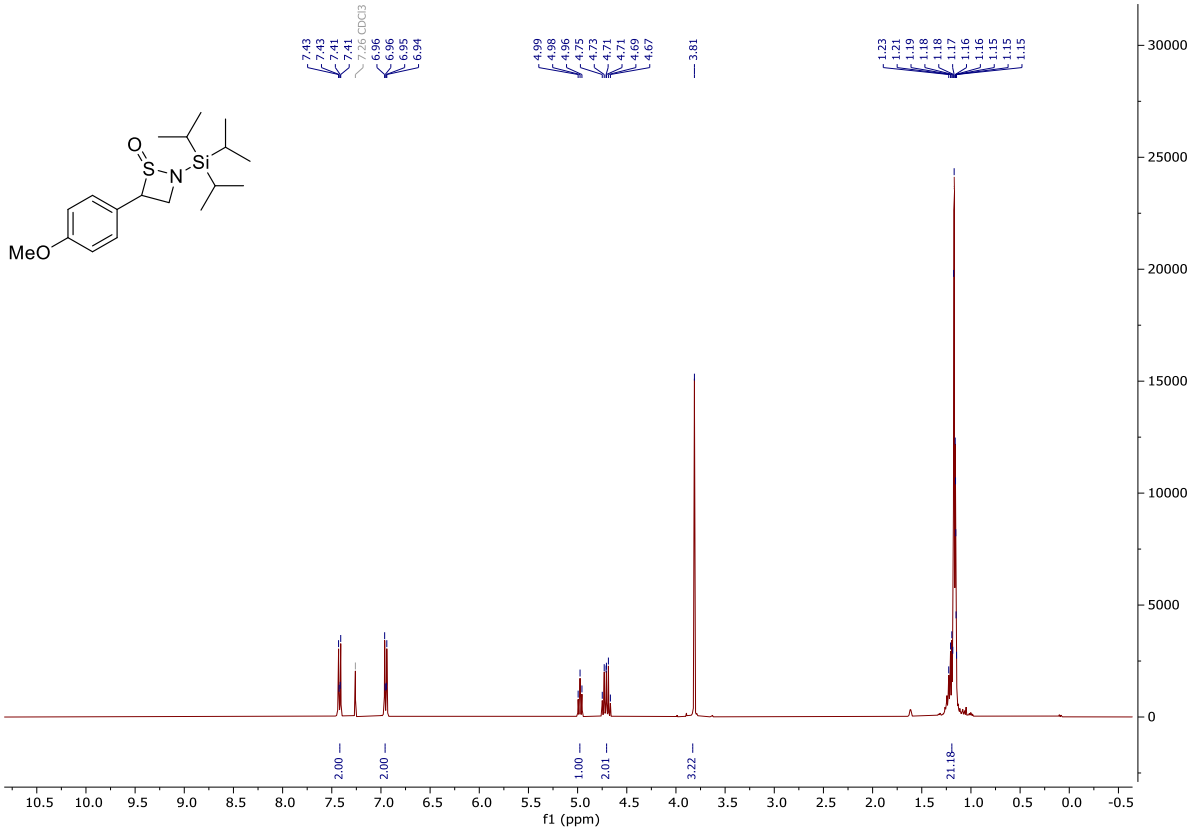


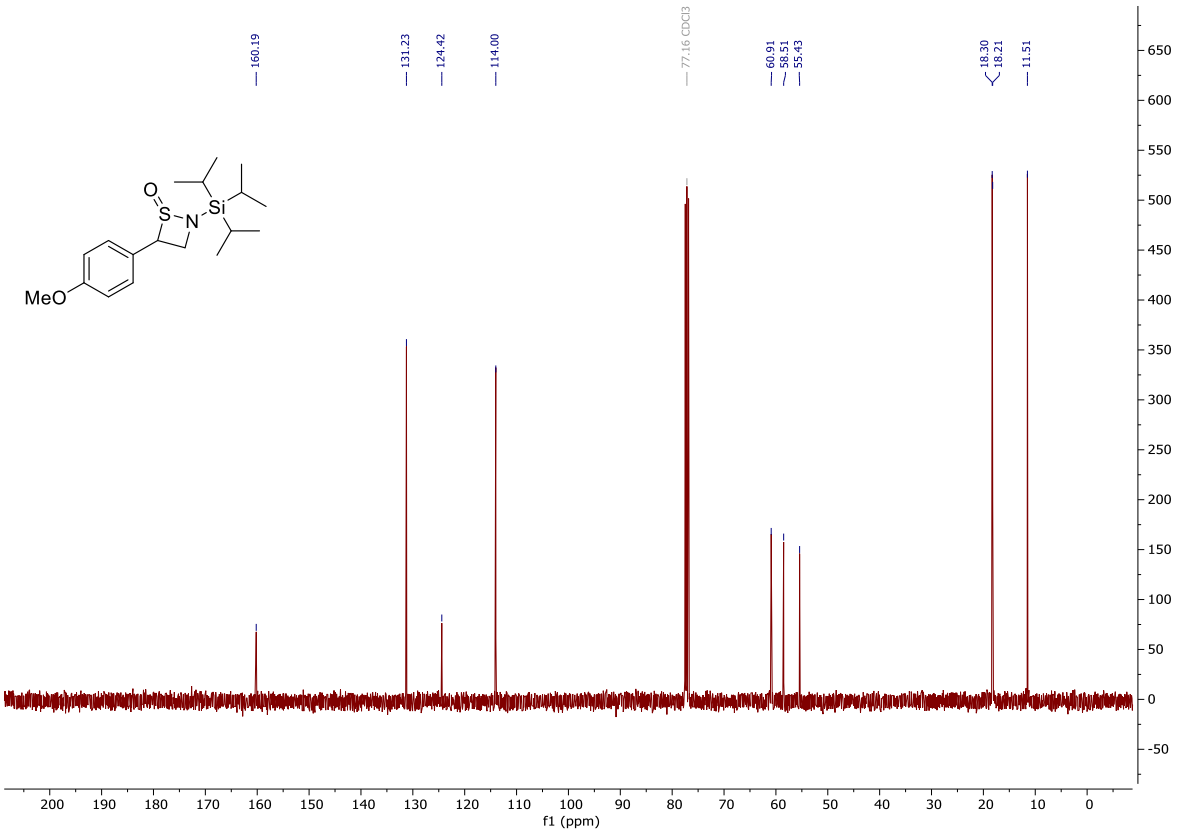
4-Phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1a-minor)



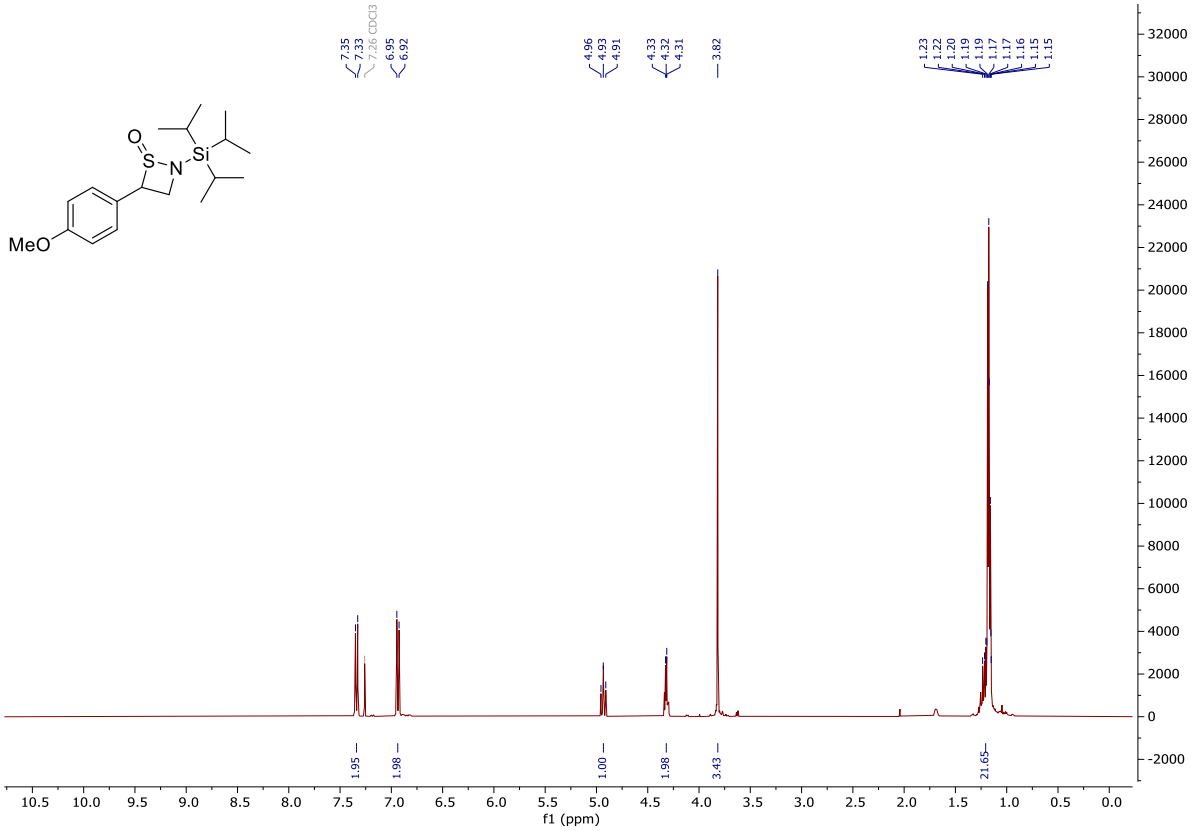


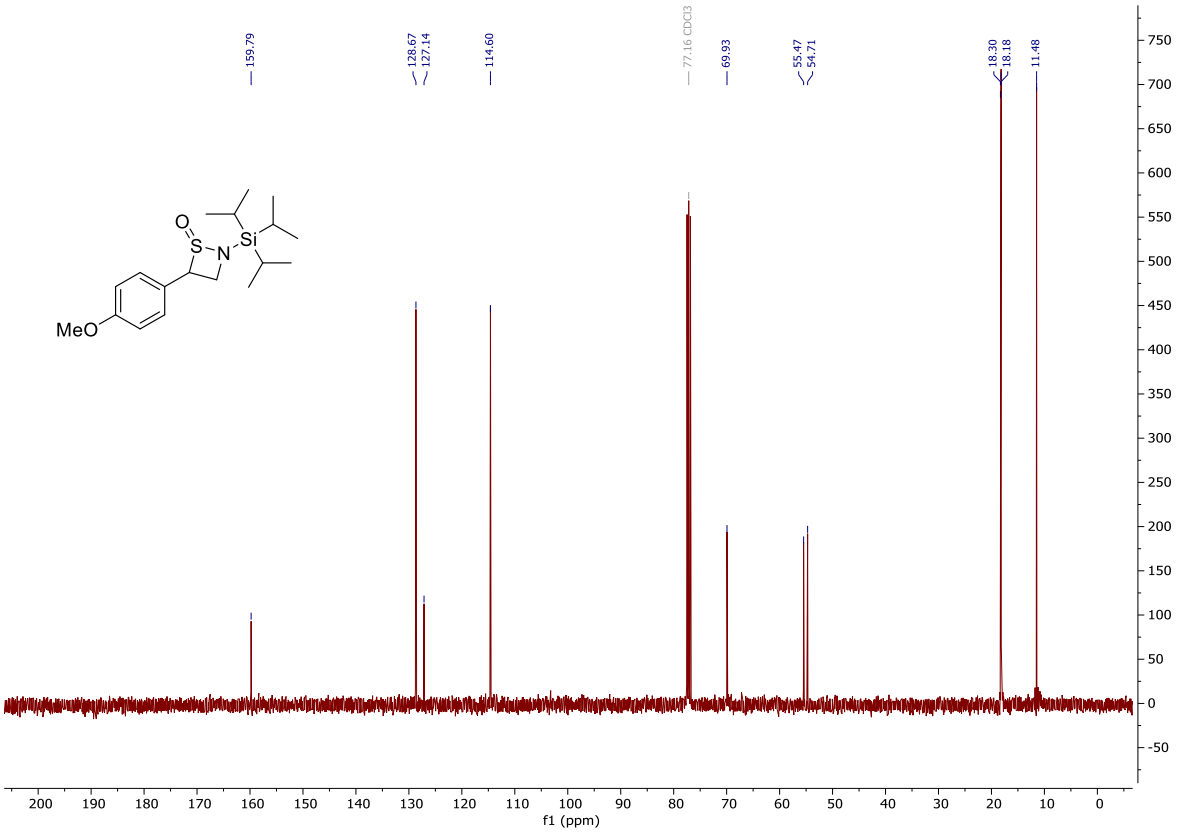
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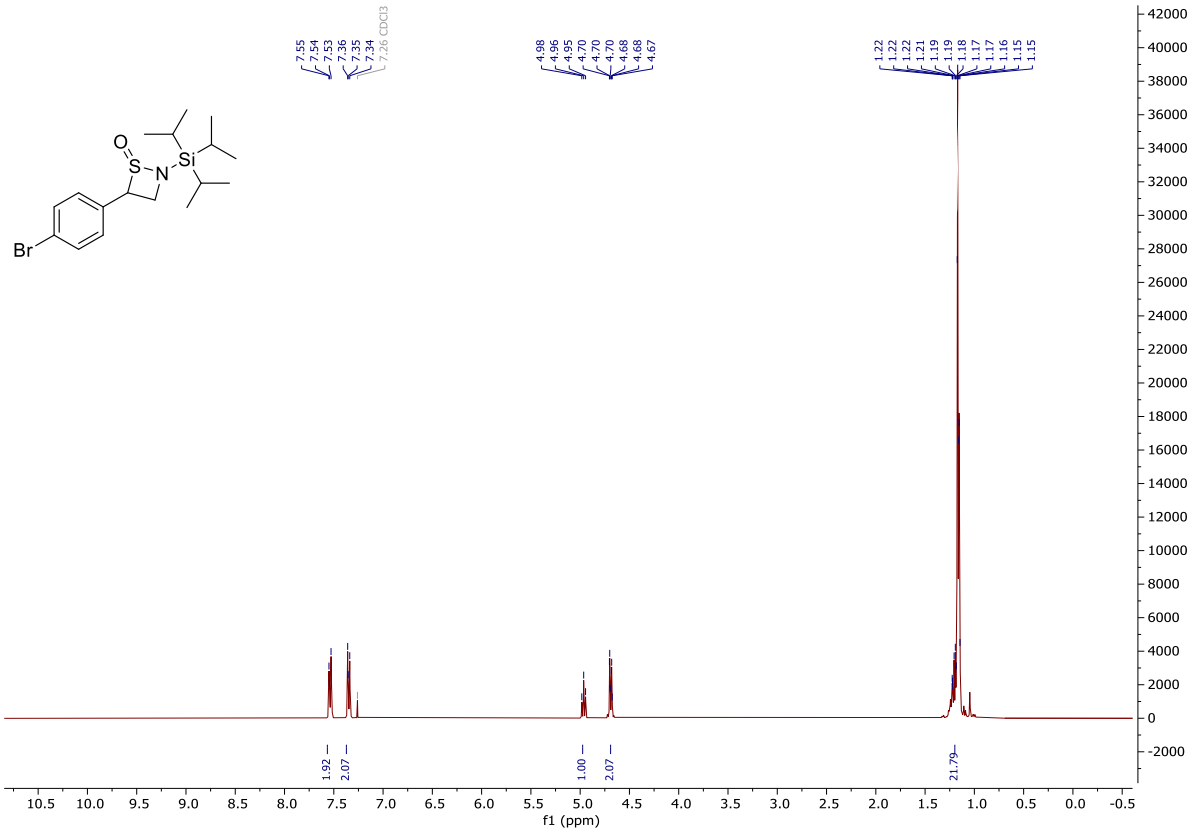


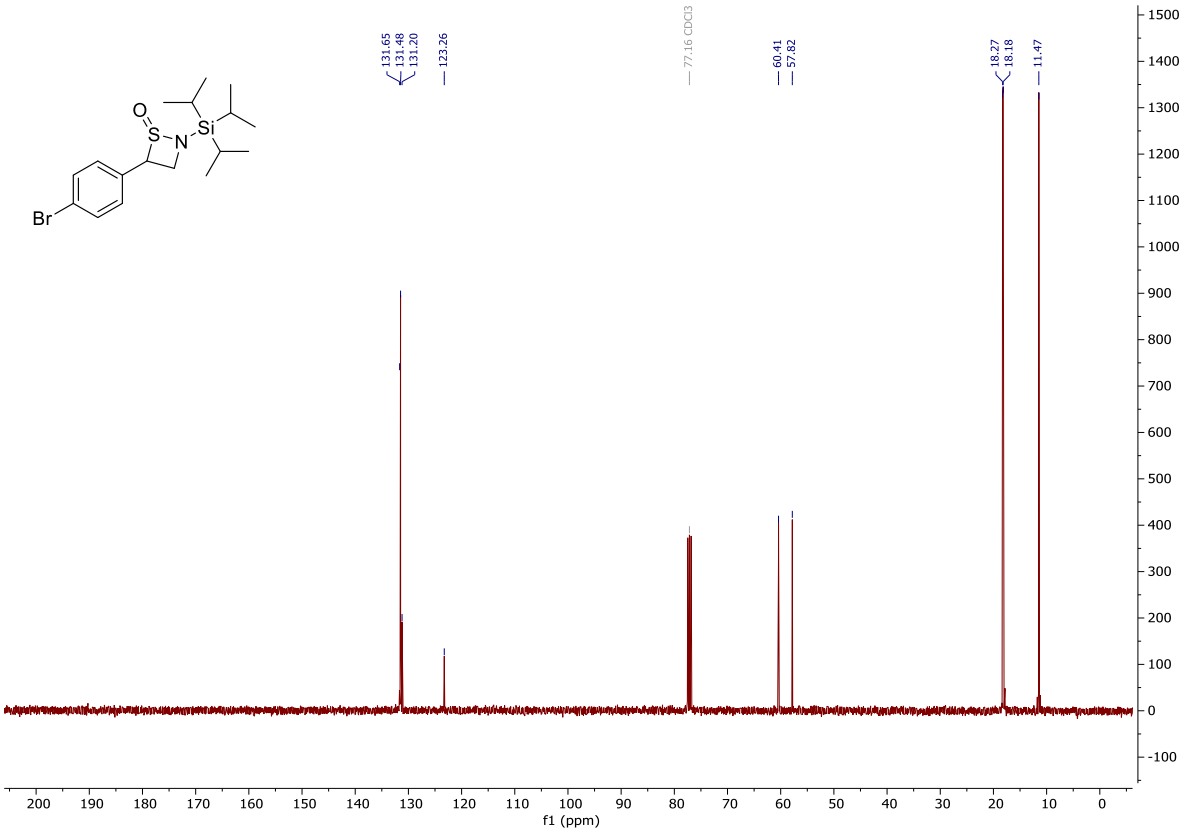
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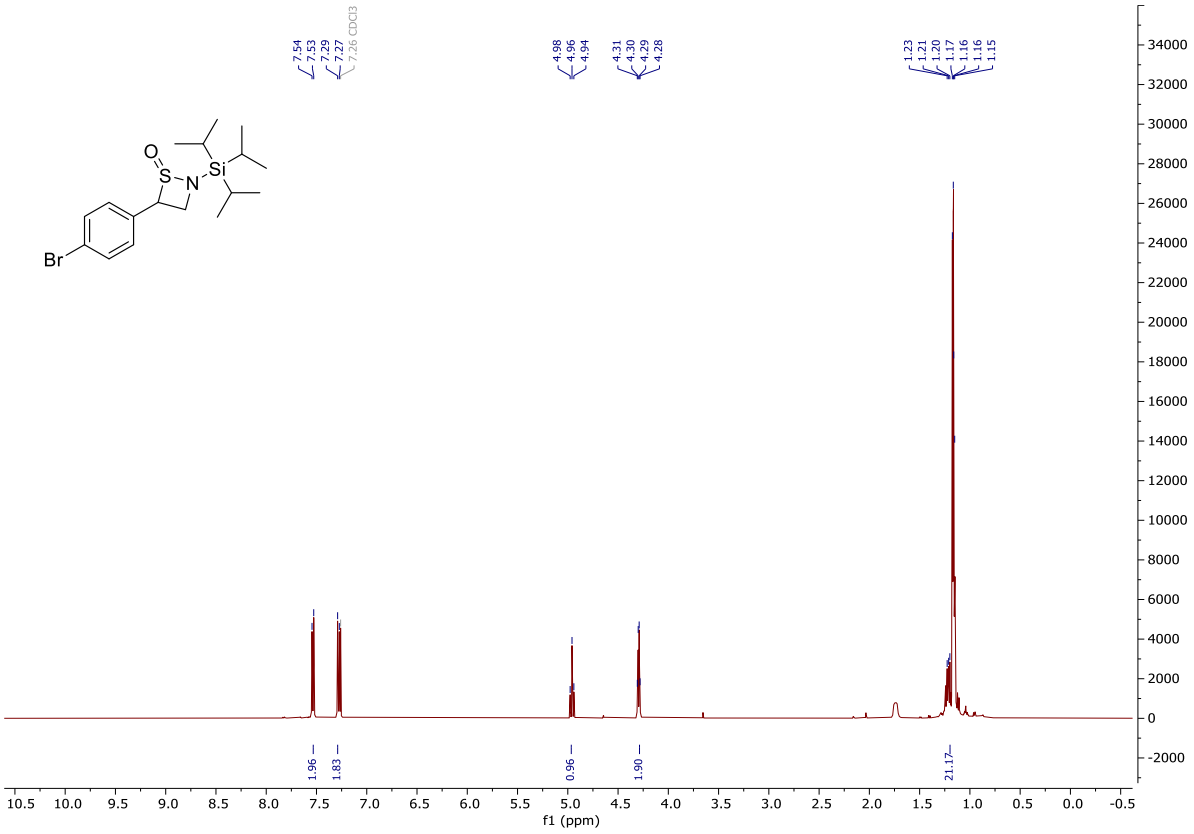


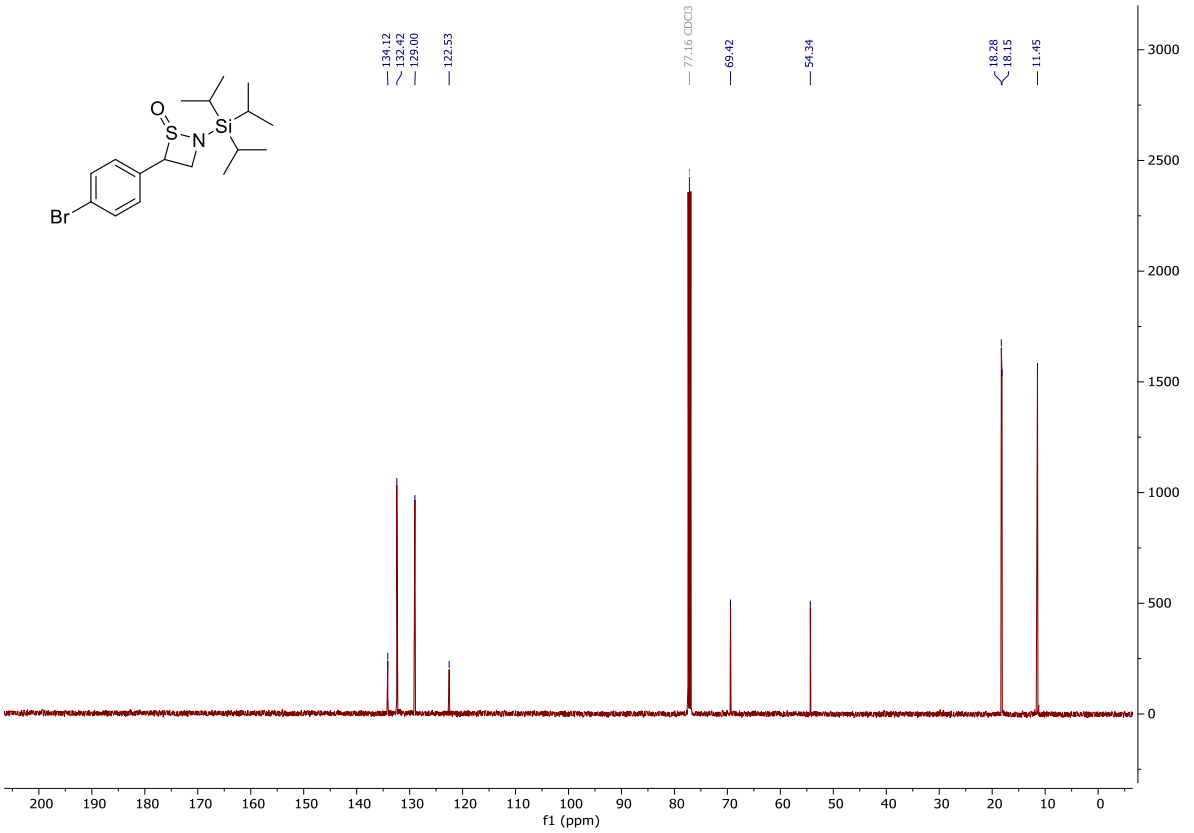
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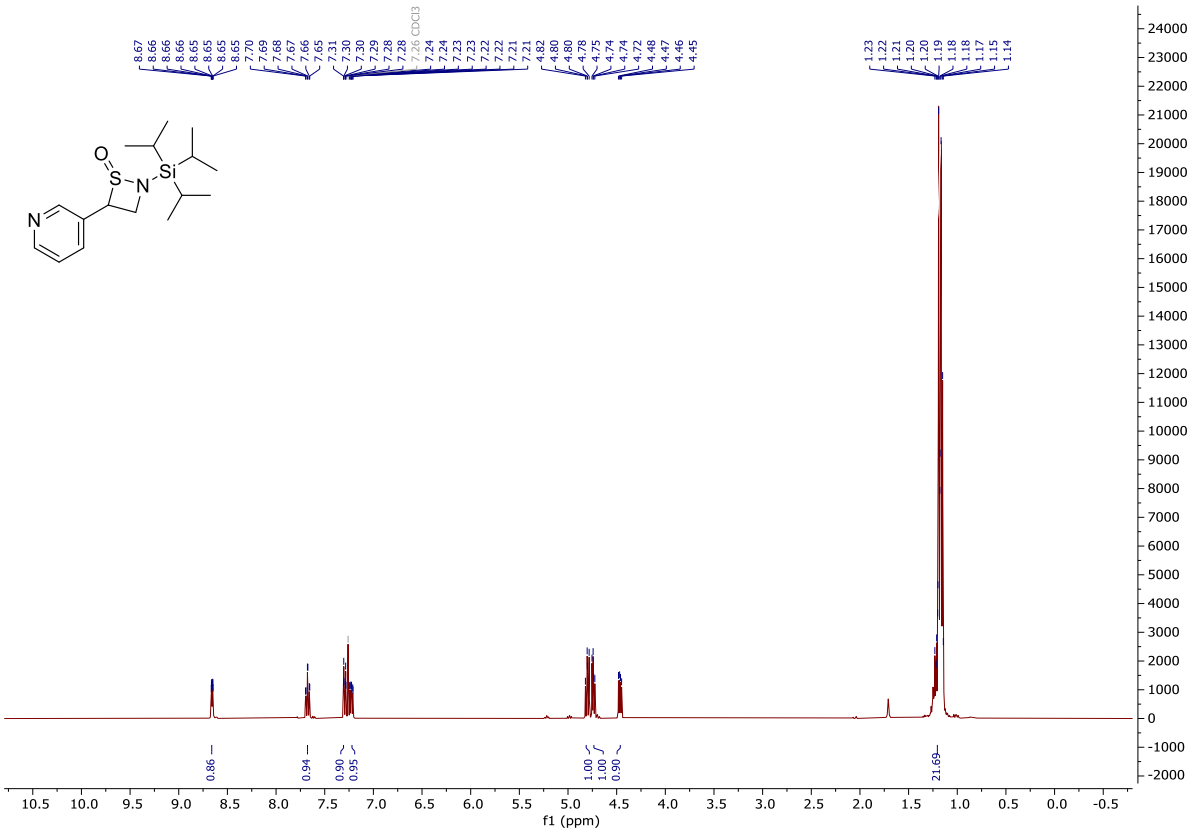


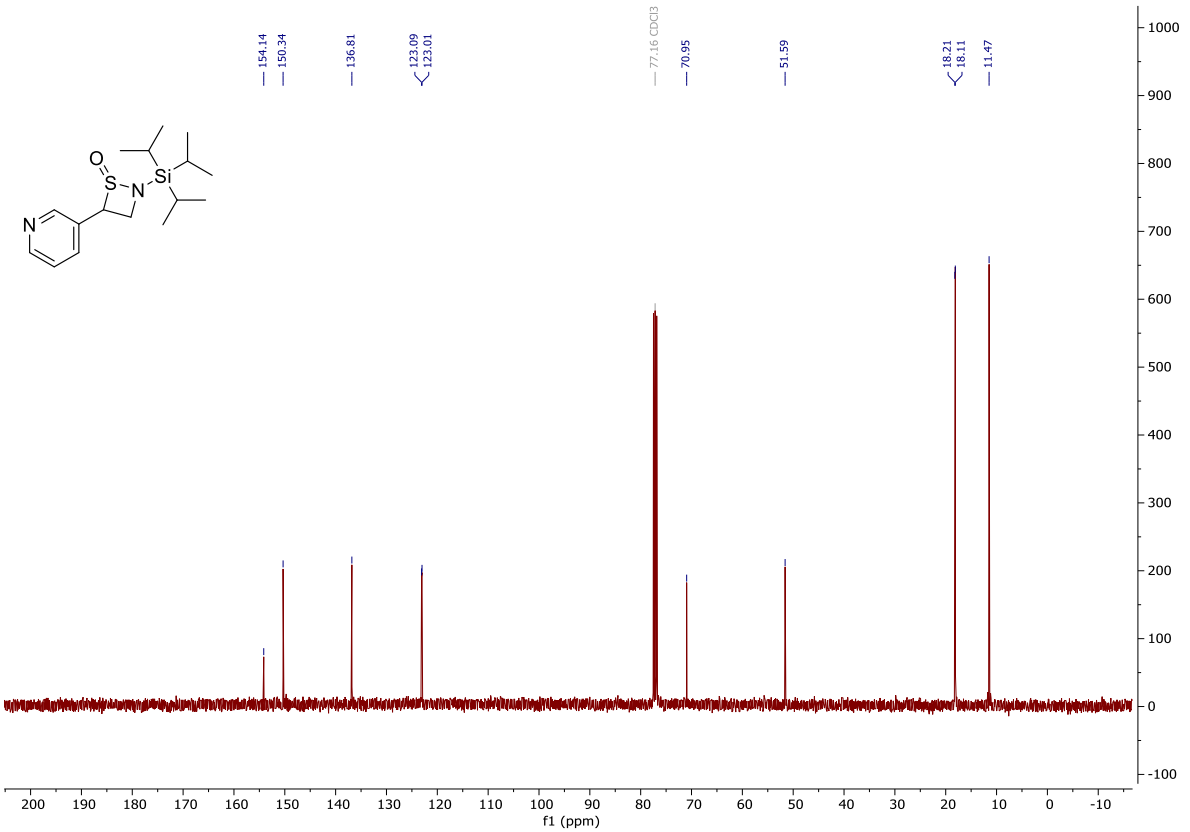
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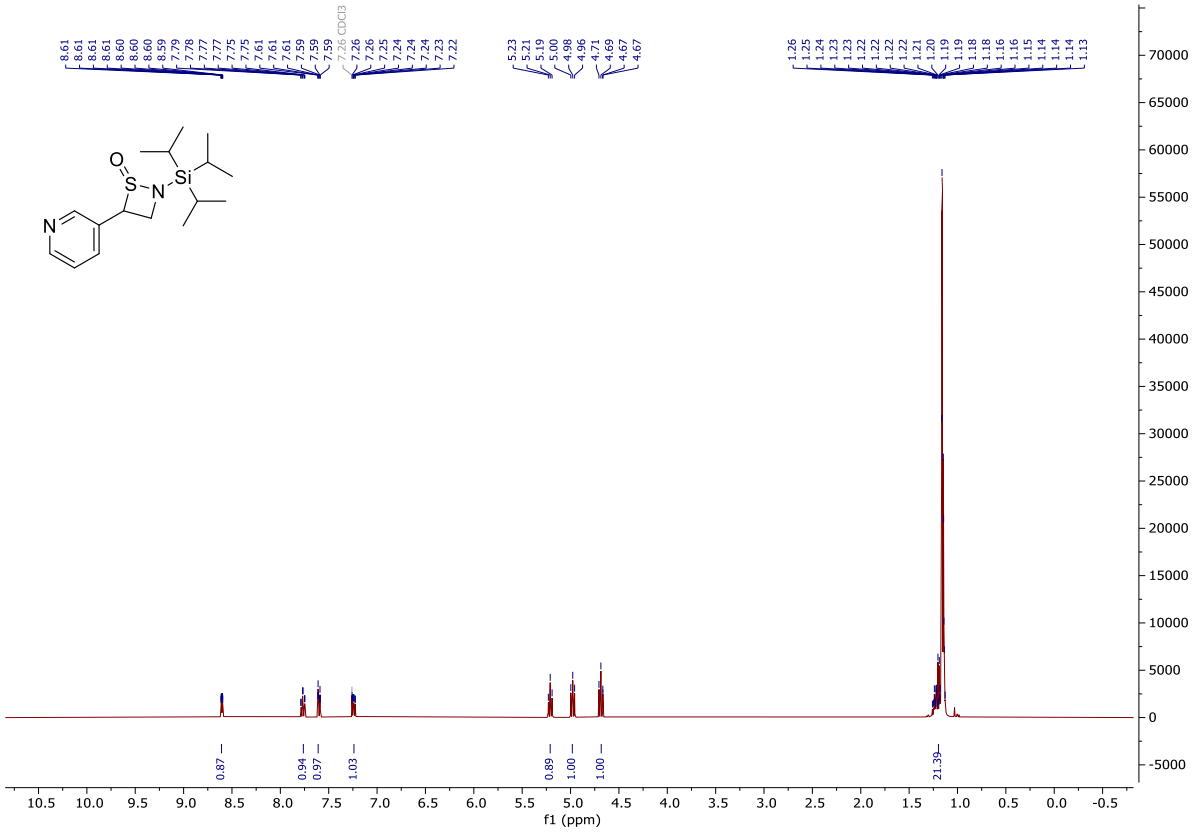


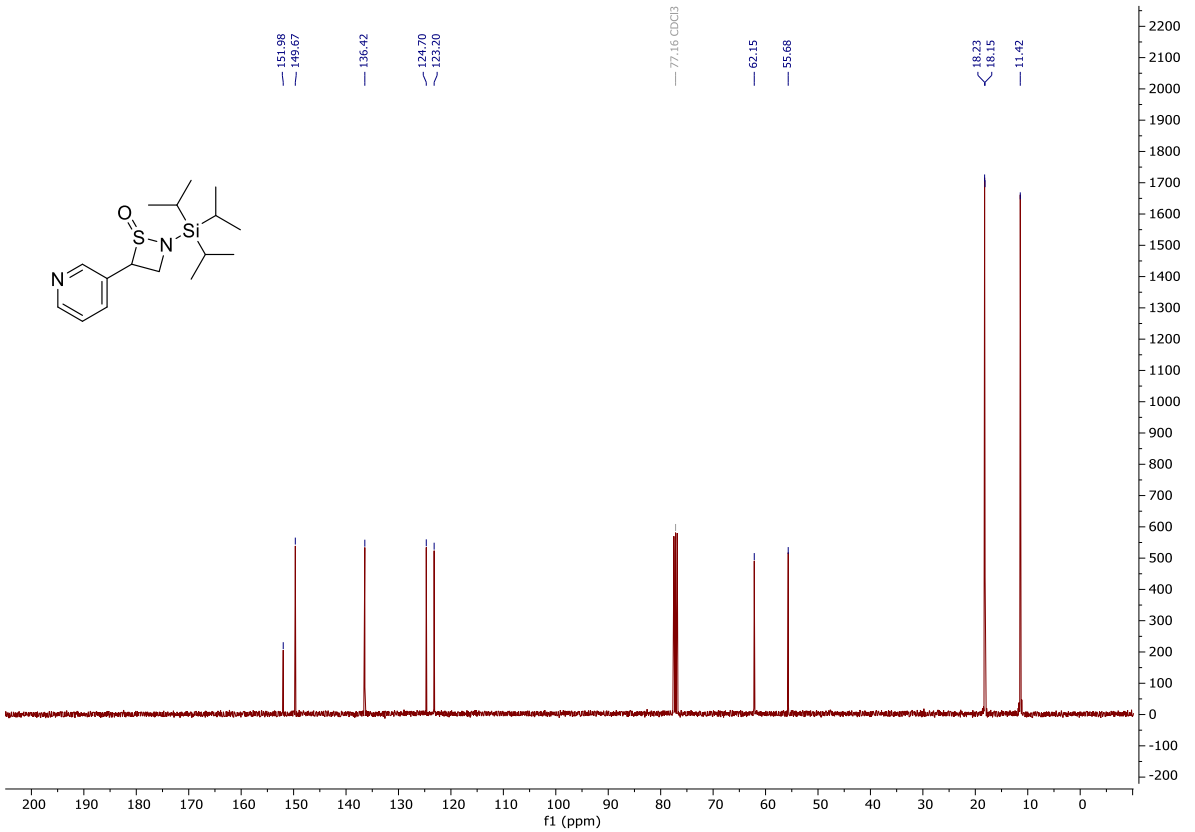
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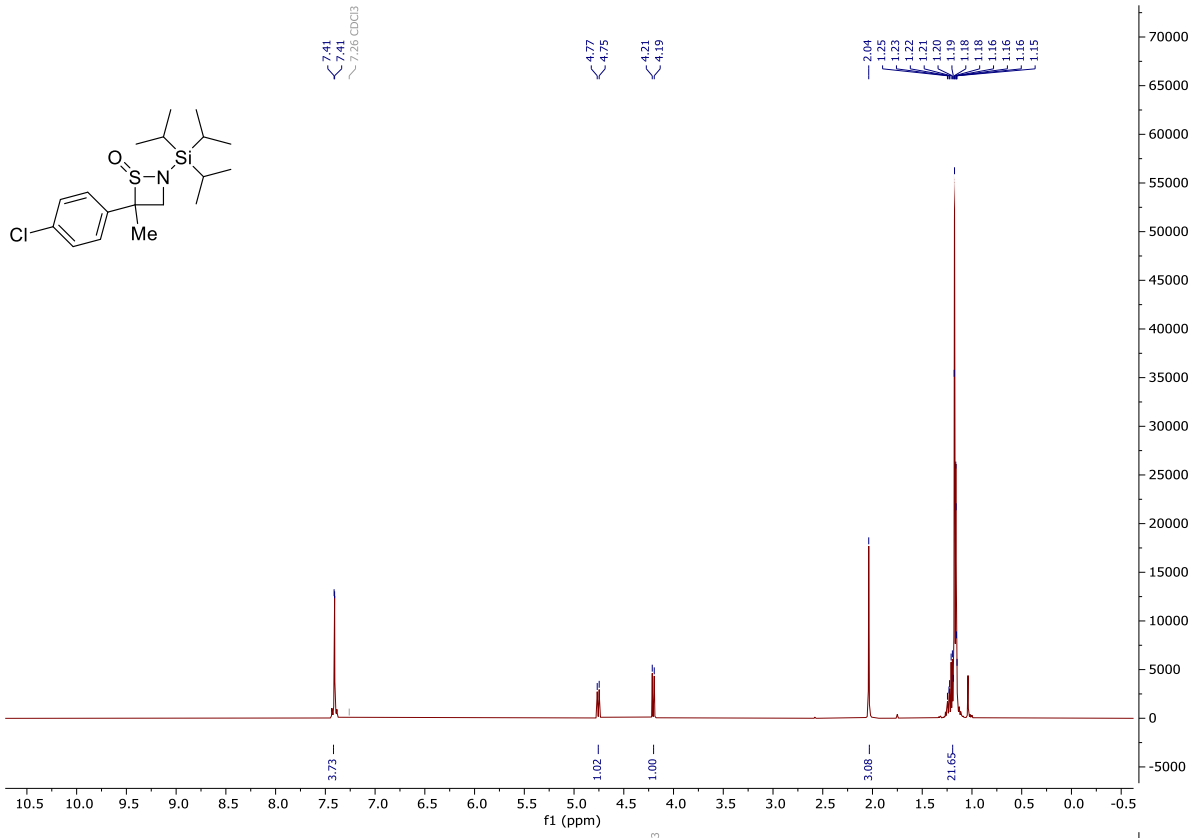


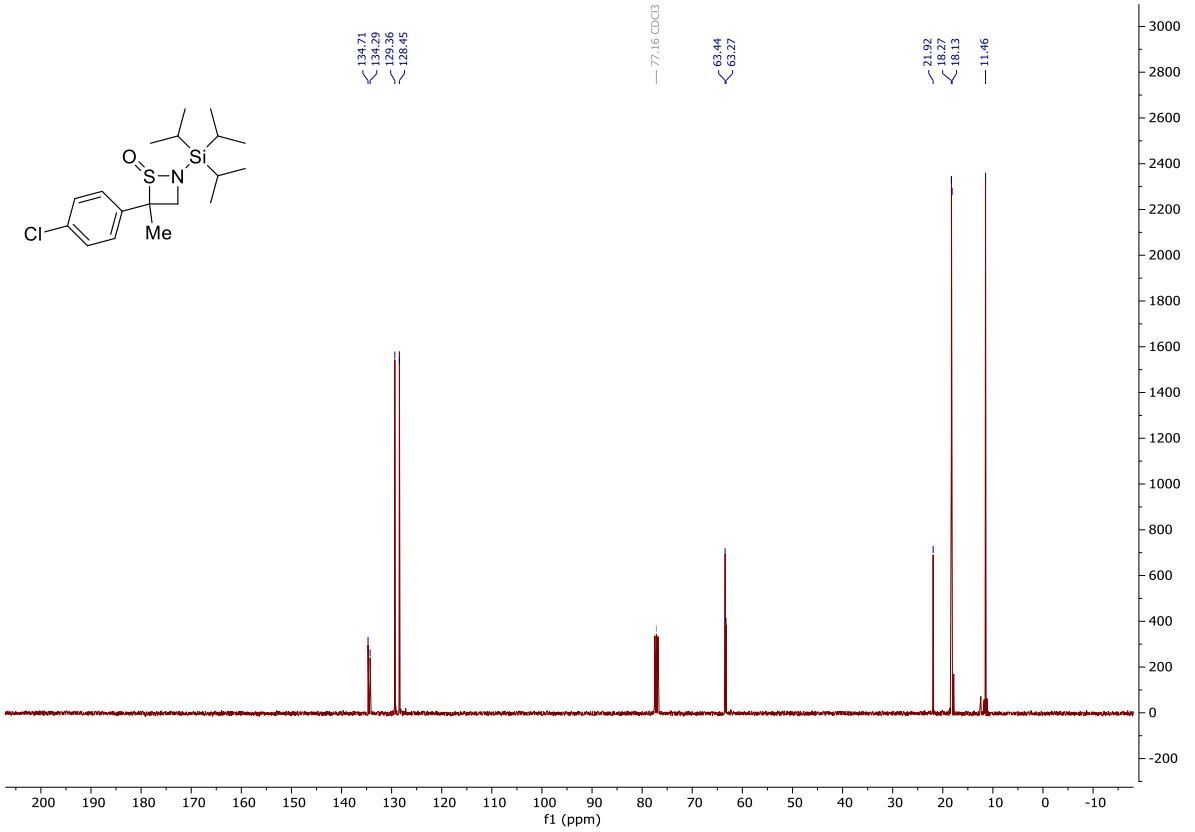
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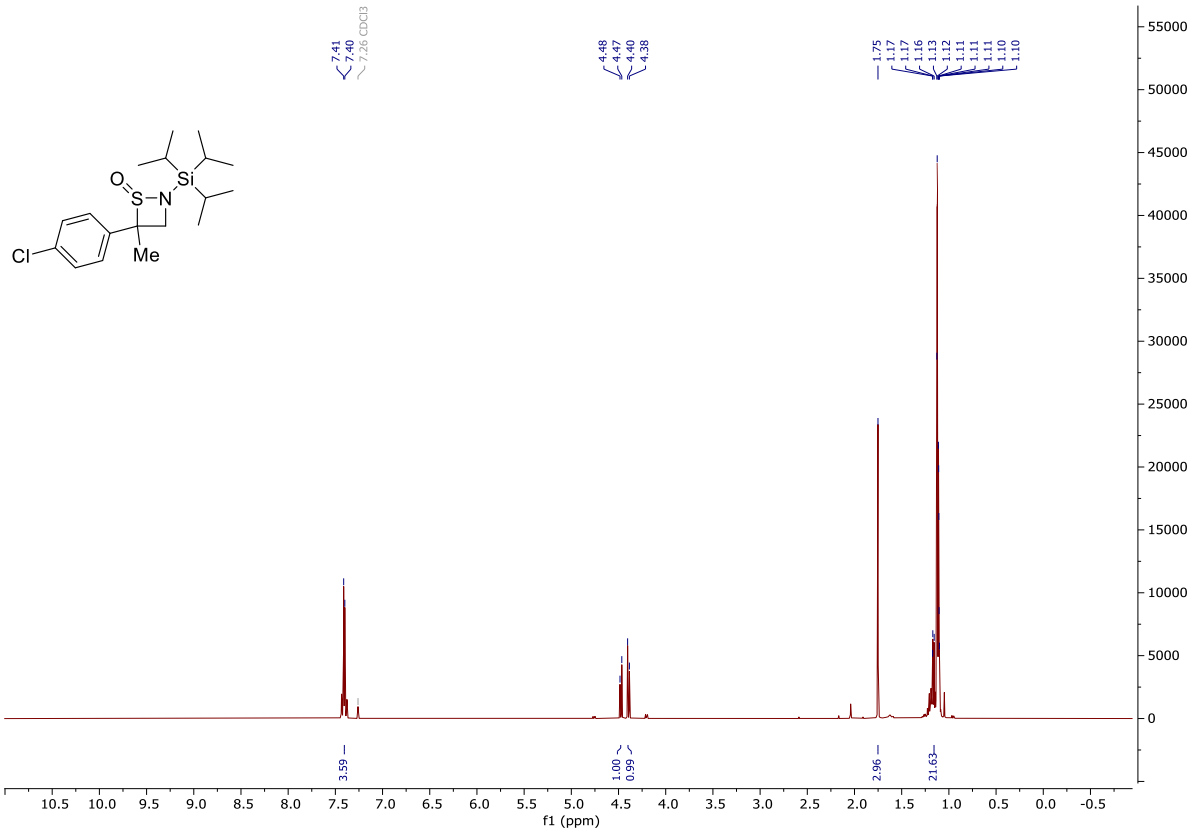


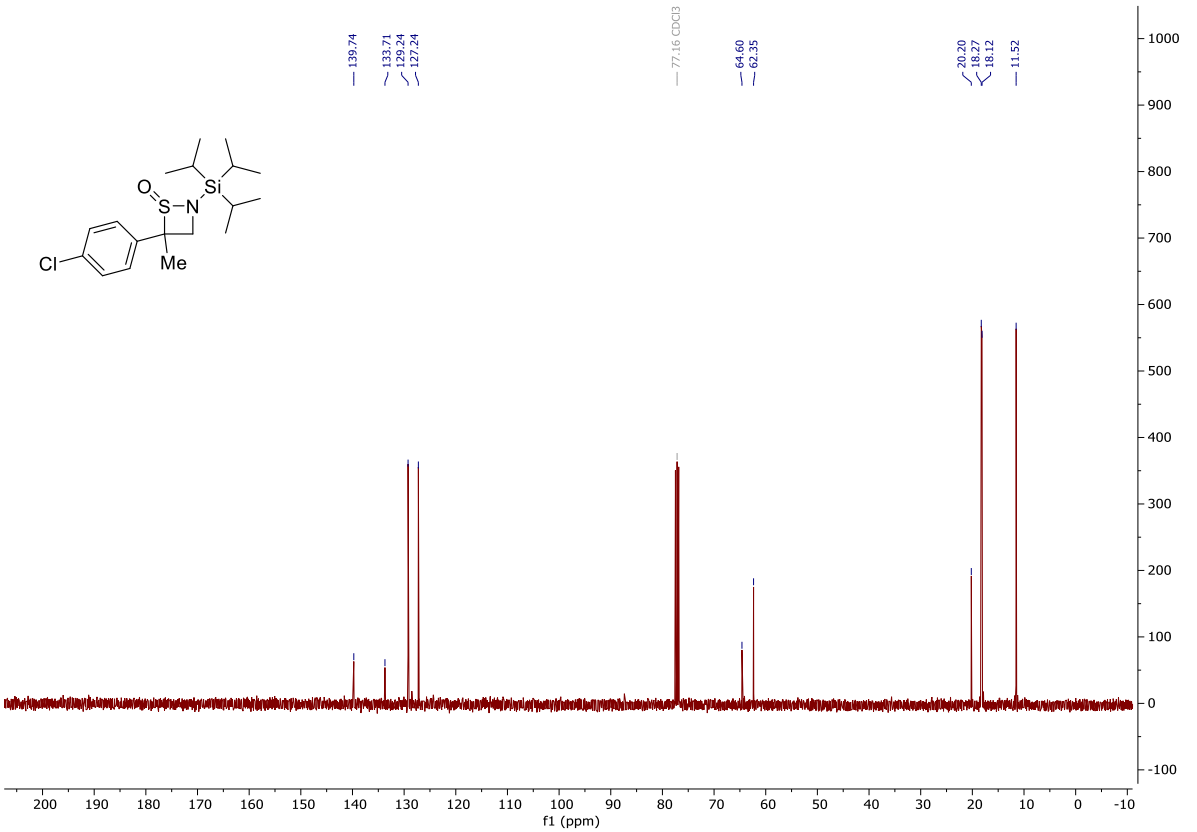
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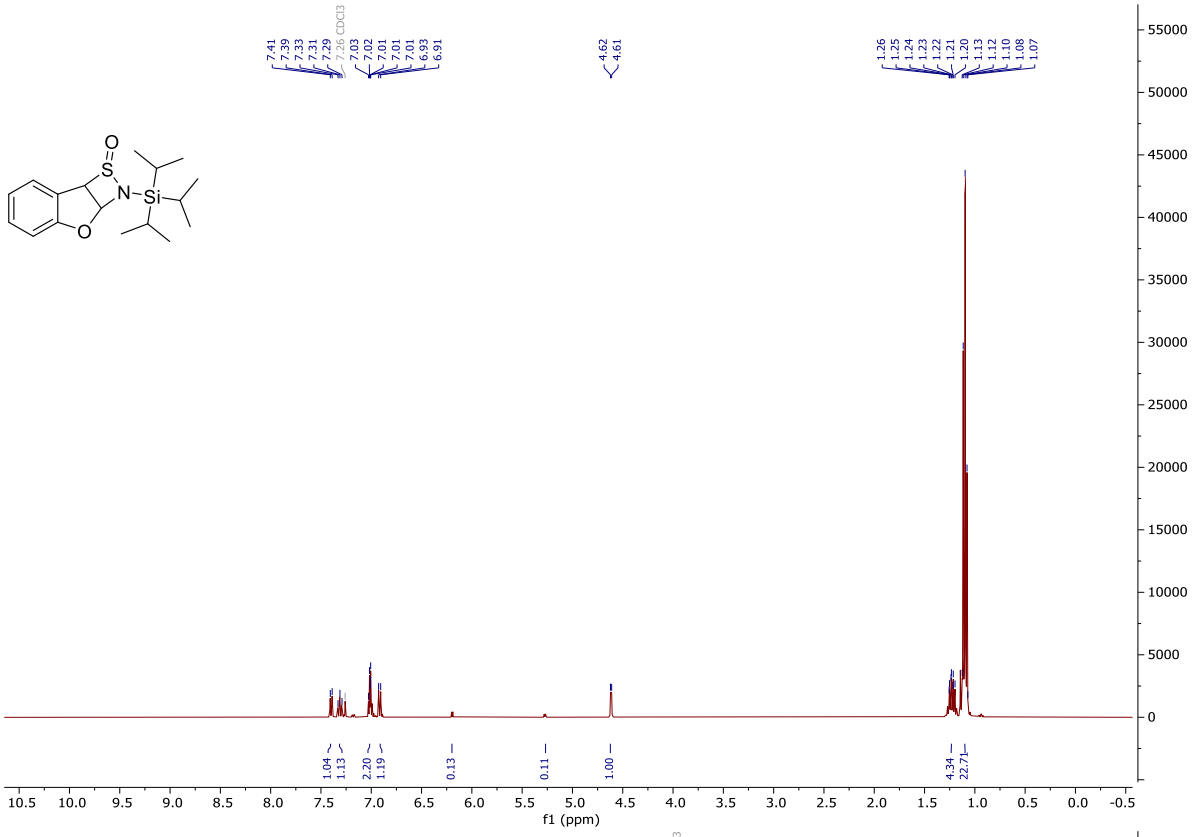


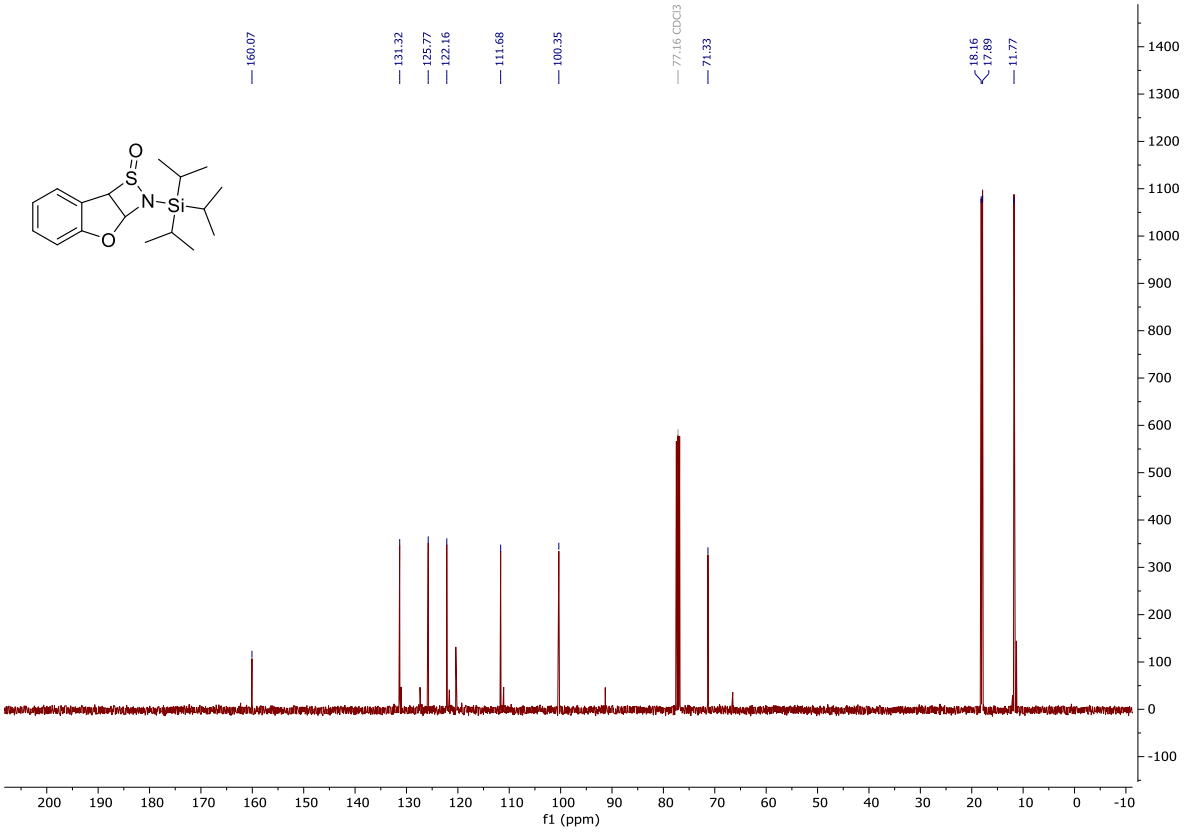
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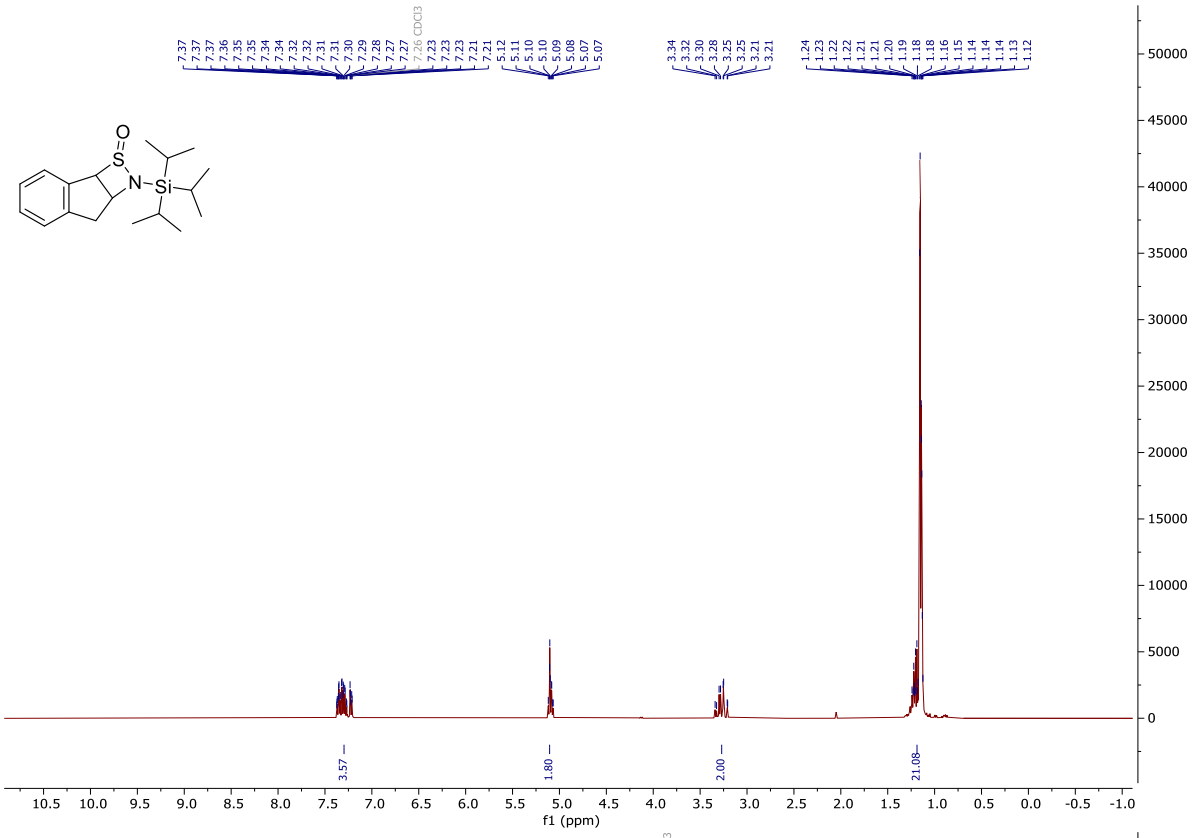


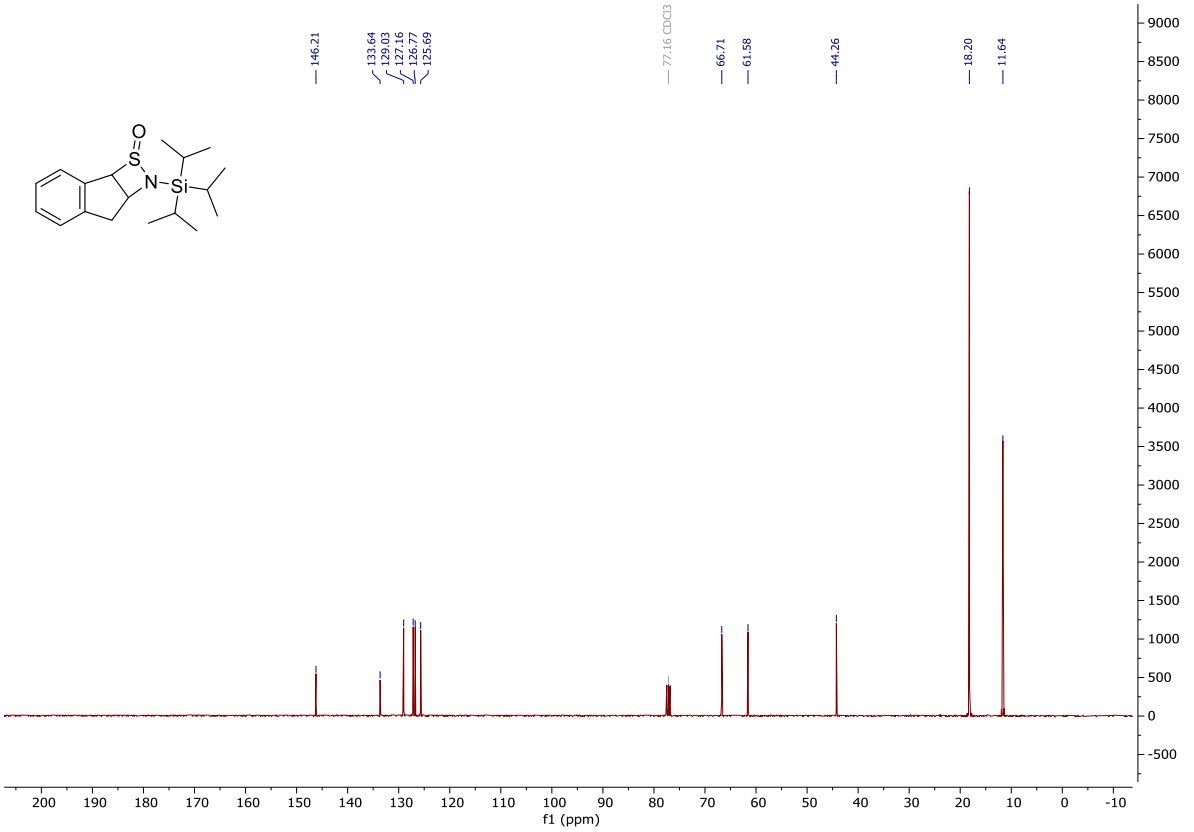
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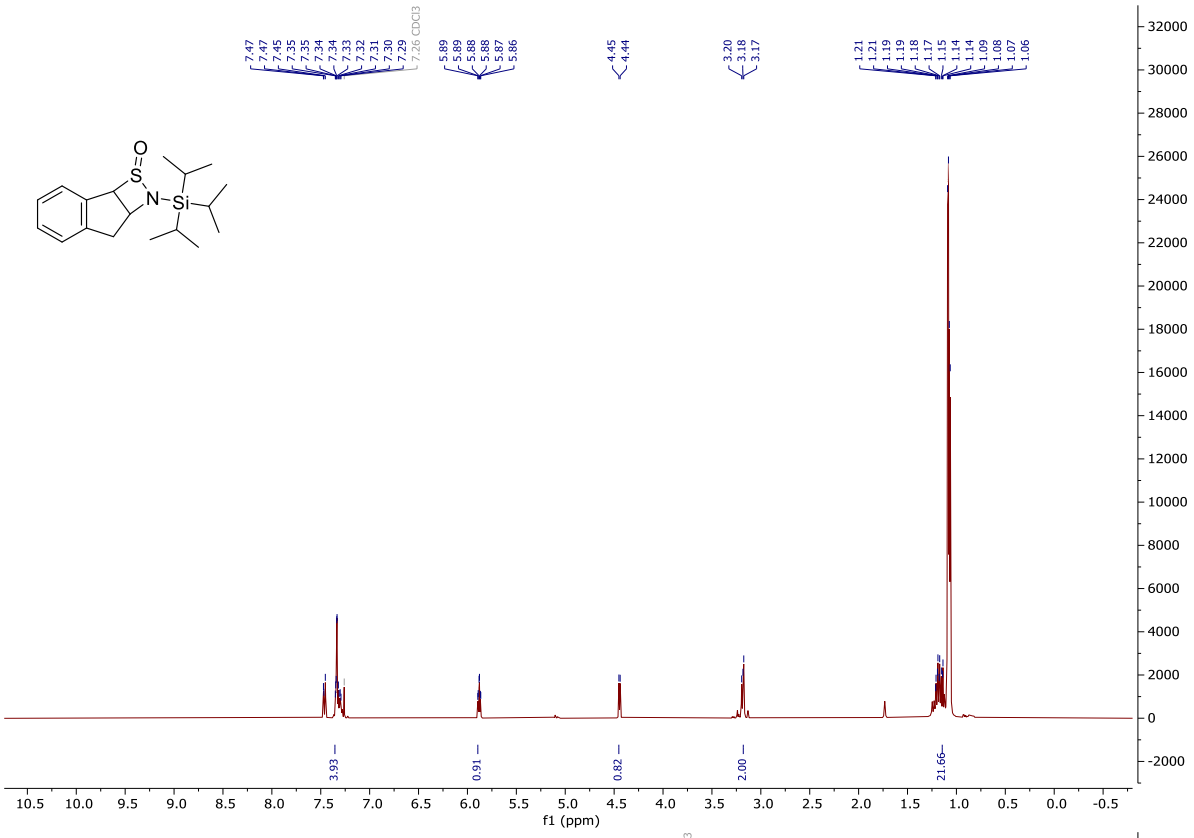


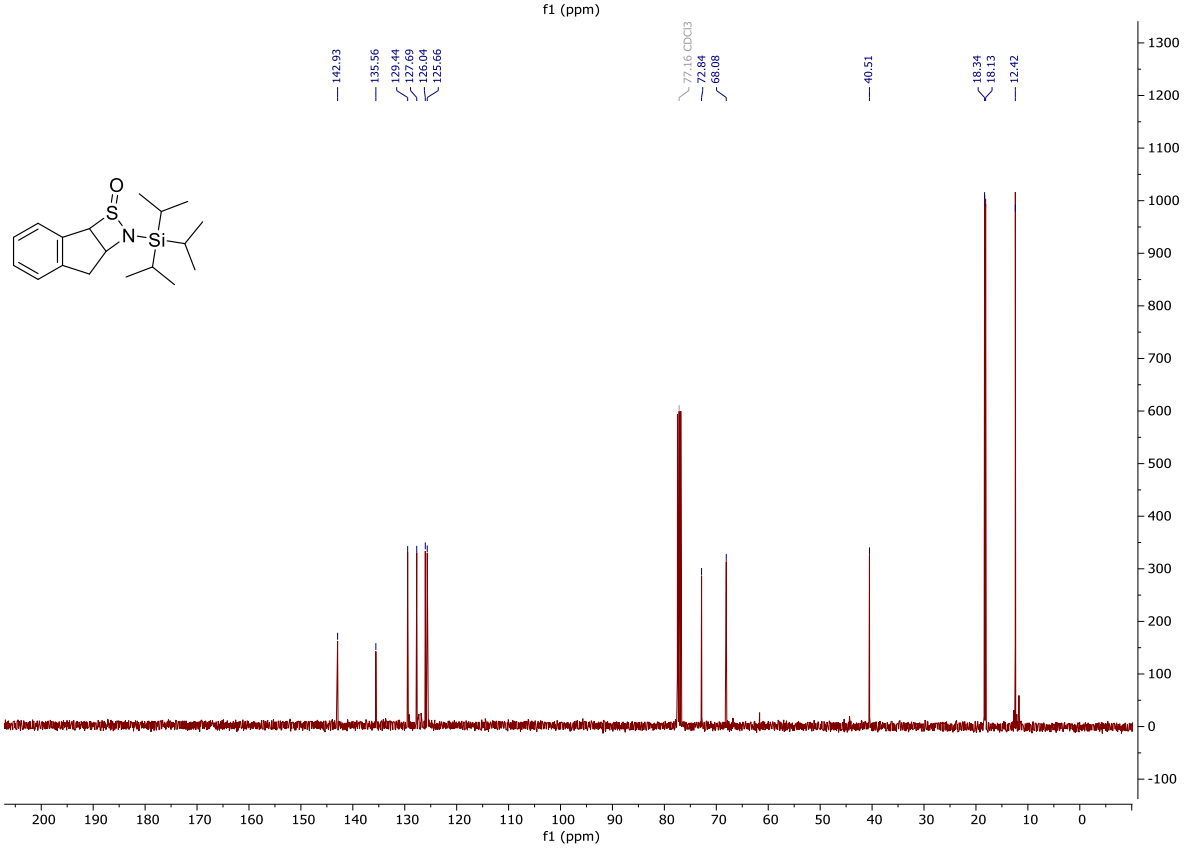
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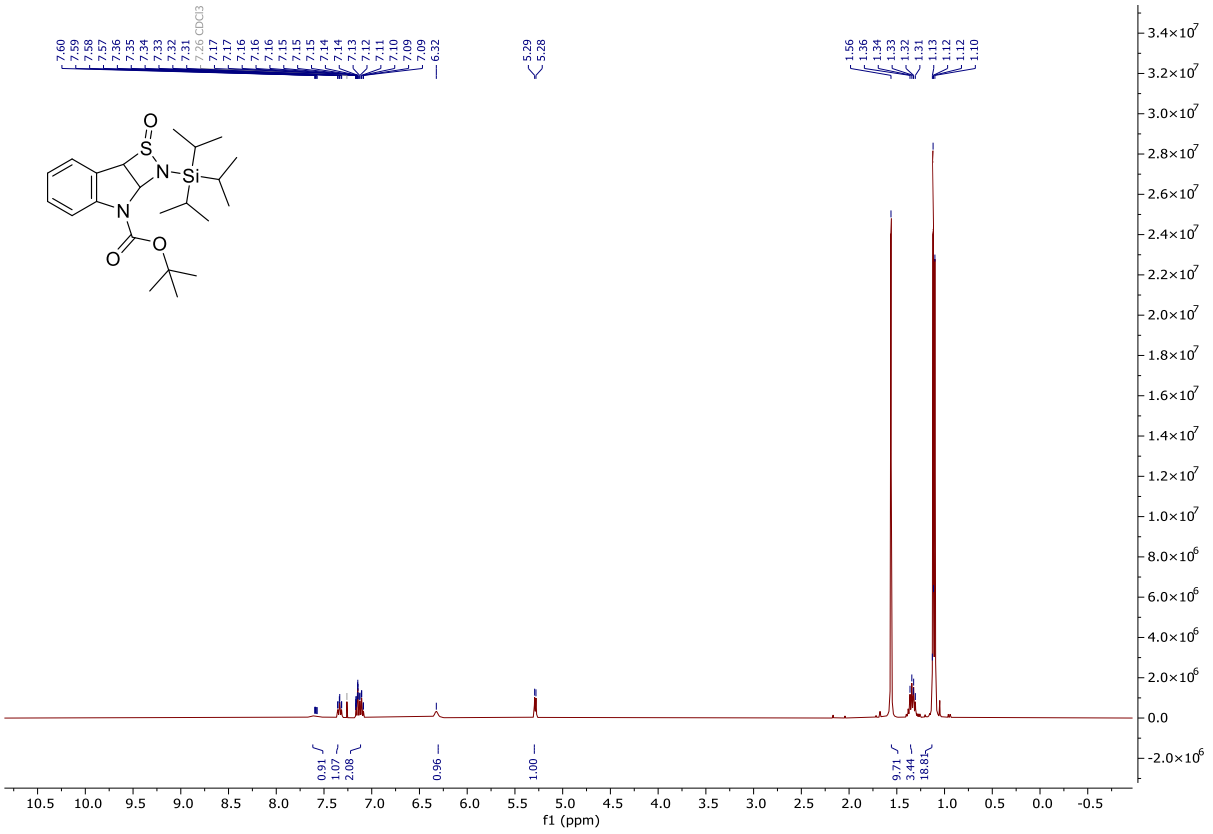


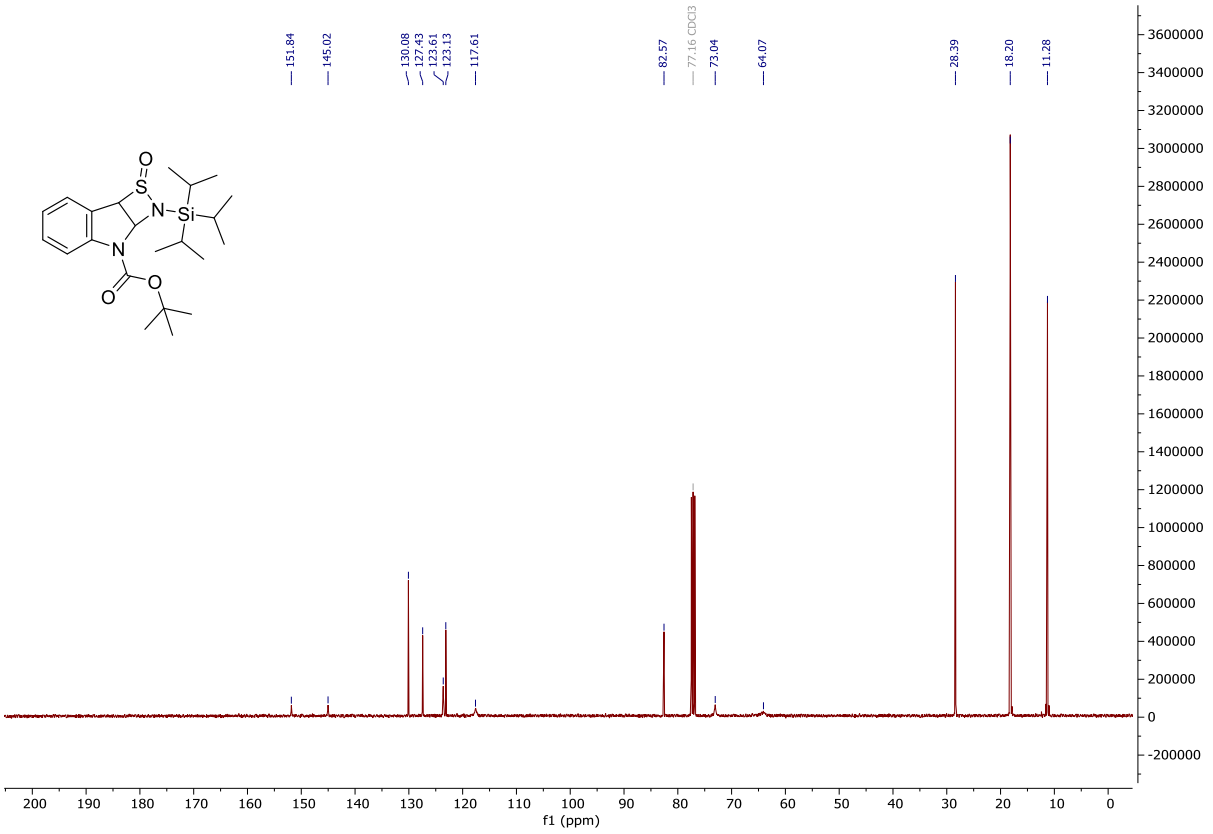
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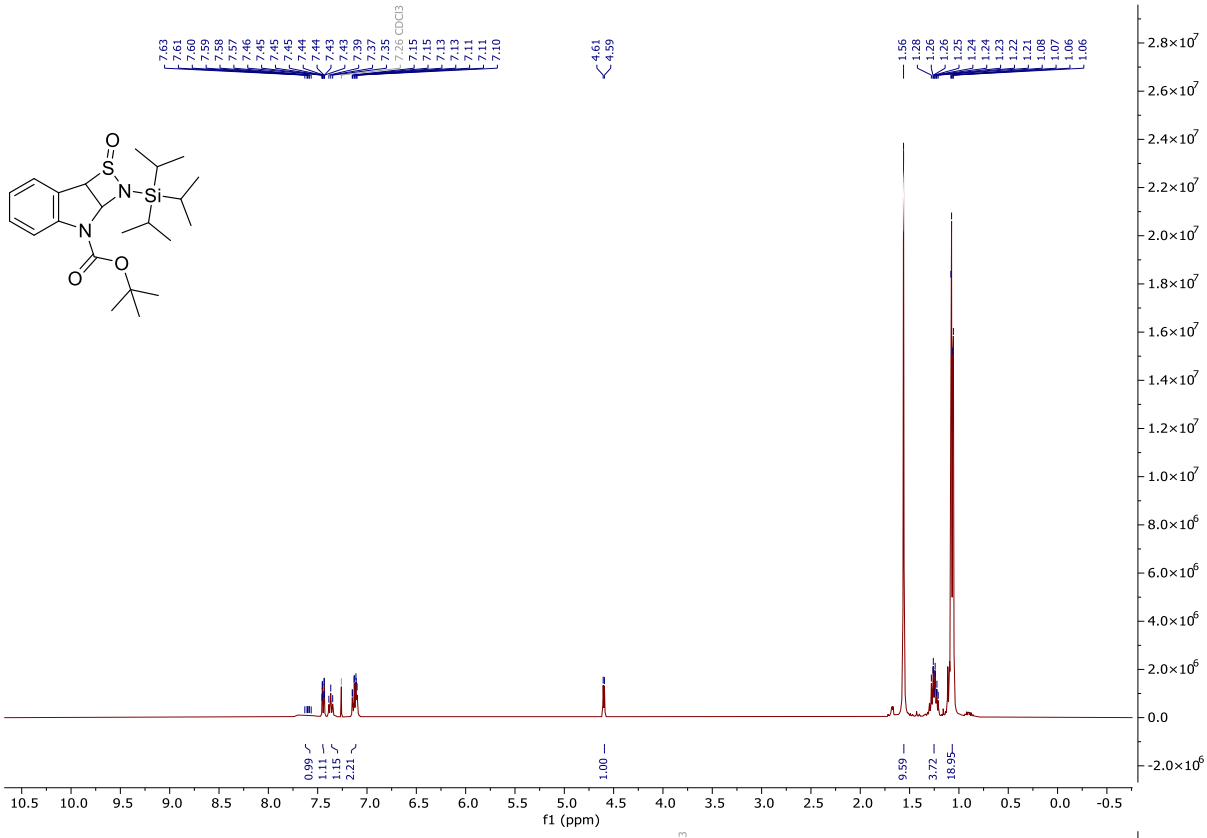


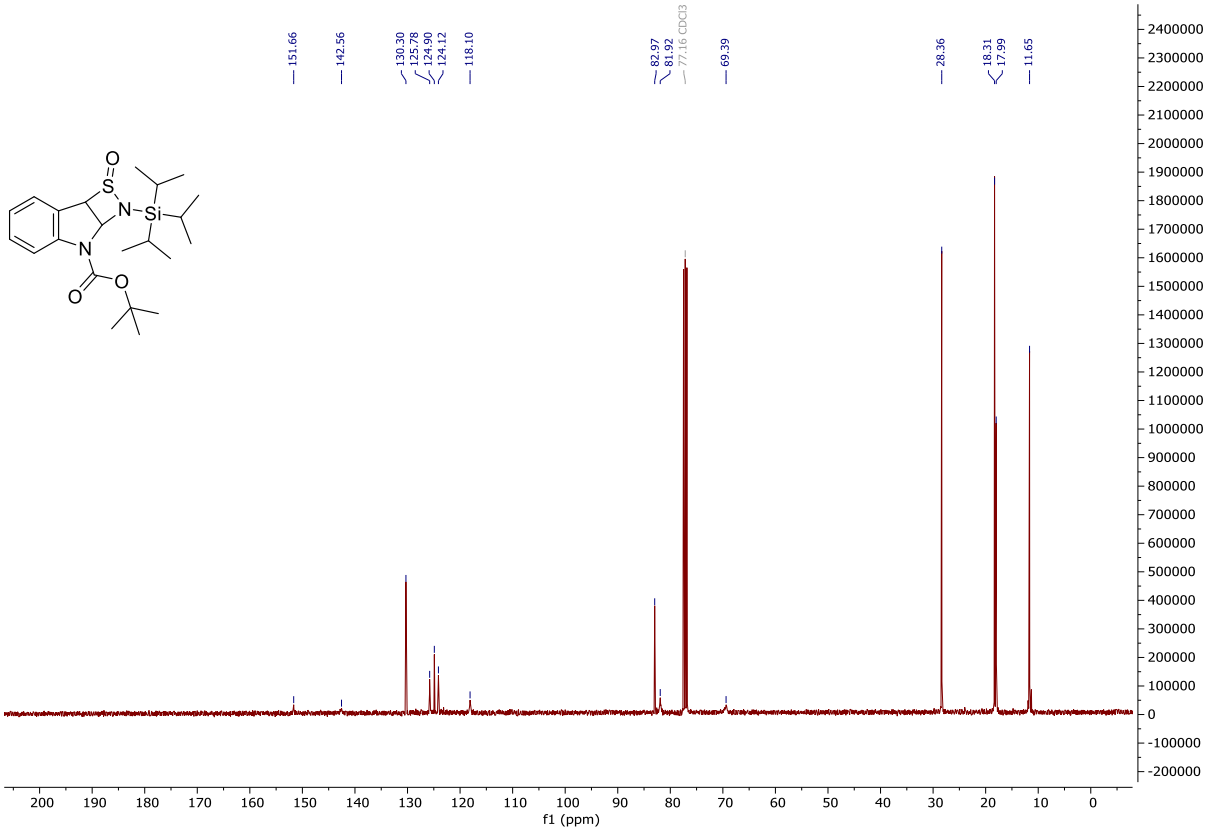
tert-Butyl 2-(triisopropylsilyl)-2a,7b-dihydro-[1,2]thiazeto[3,4-b]indole-3(2H)-carboxylate 1-oxide (1h-major)



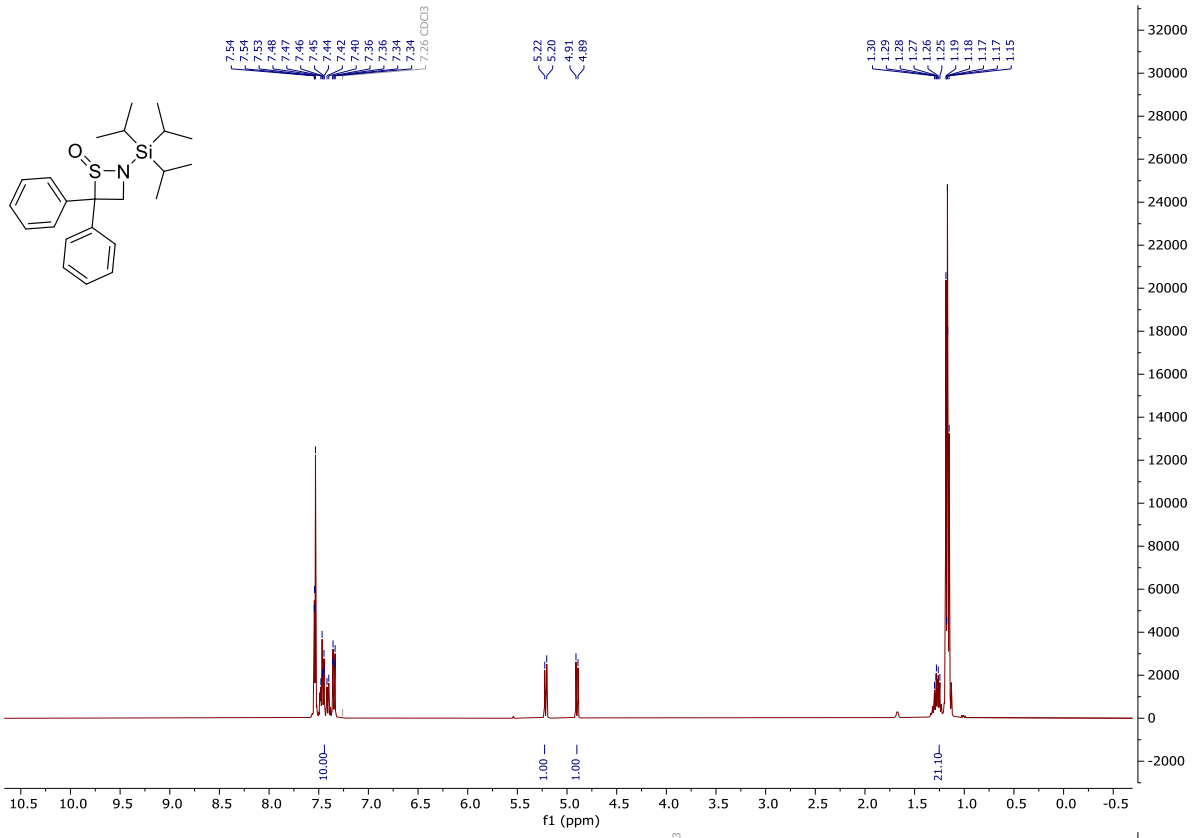


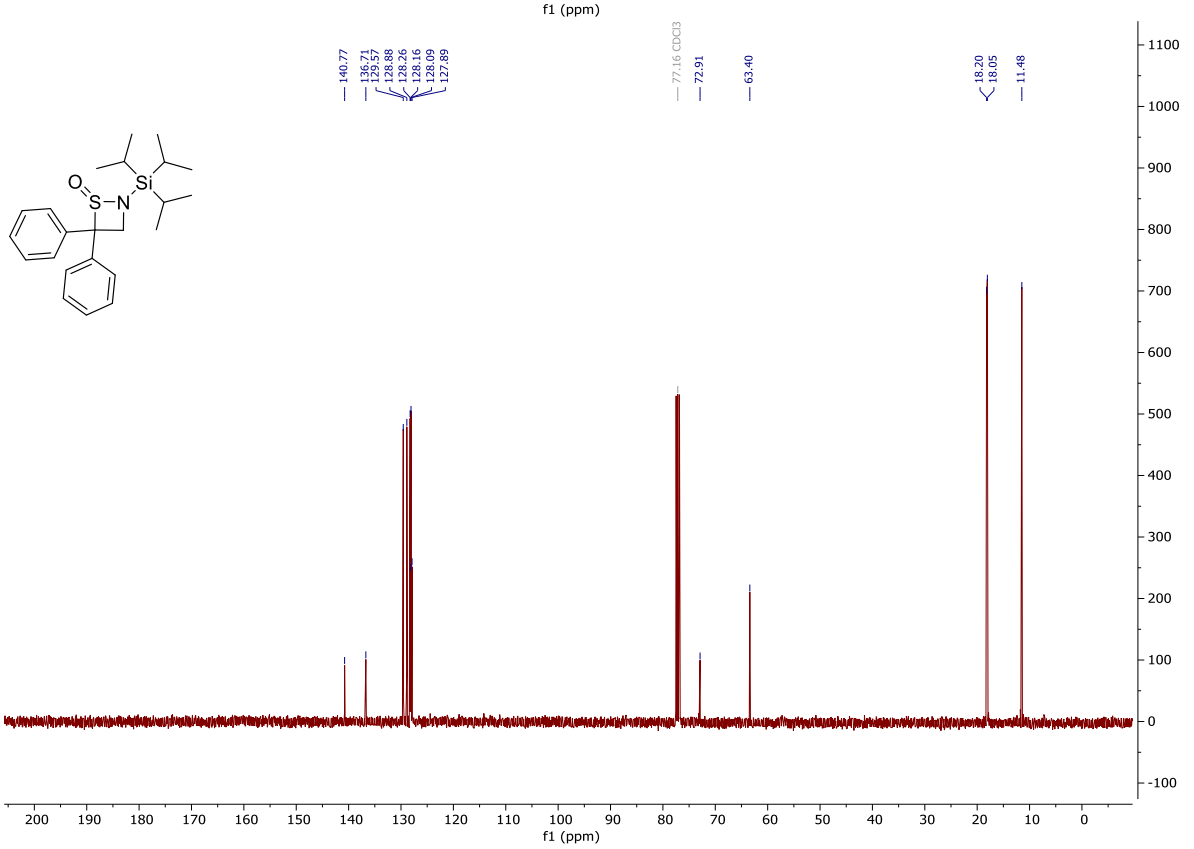
tert-Butyl 2-(triisopropylsilyl)-2a,7b-dihydro-[1,2]thiazeto[3,4-b]indole-3(2H)-carboxylate 1-oxide (1h-minor)



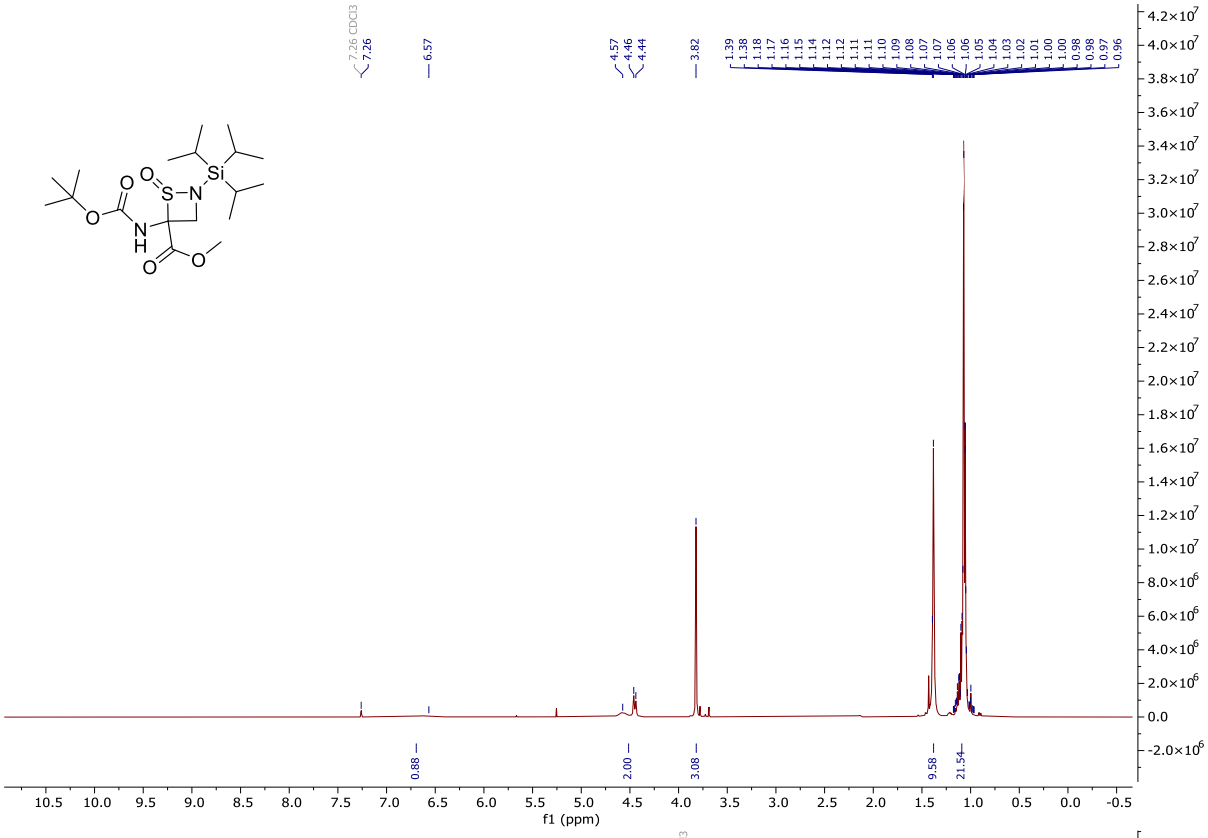


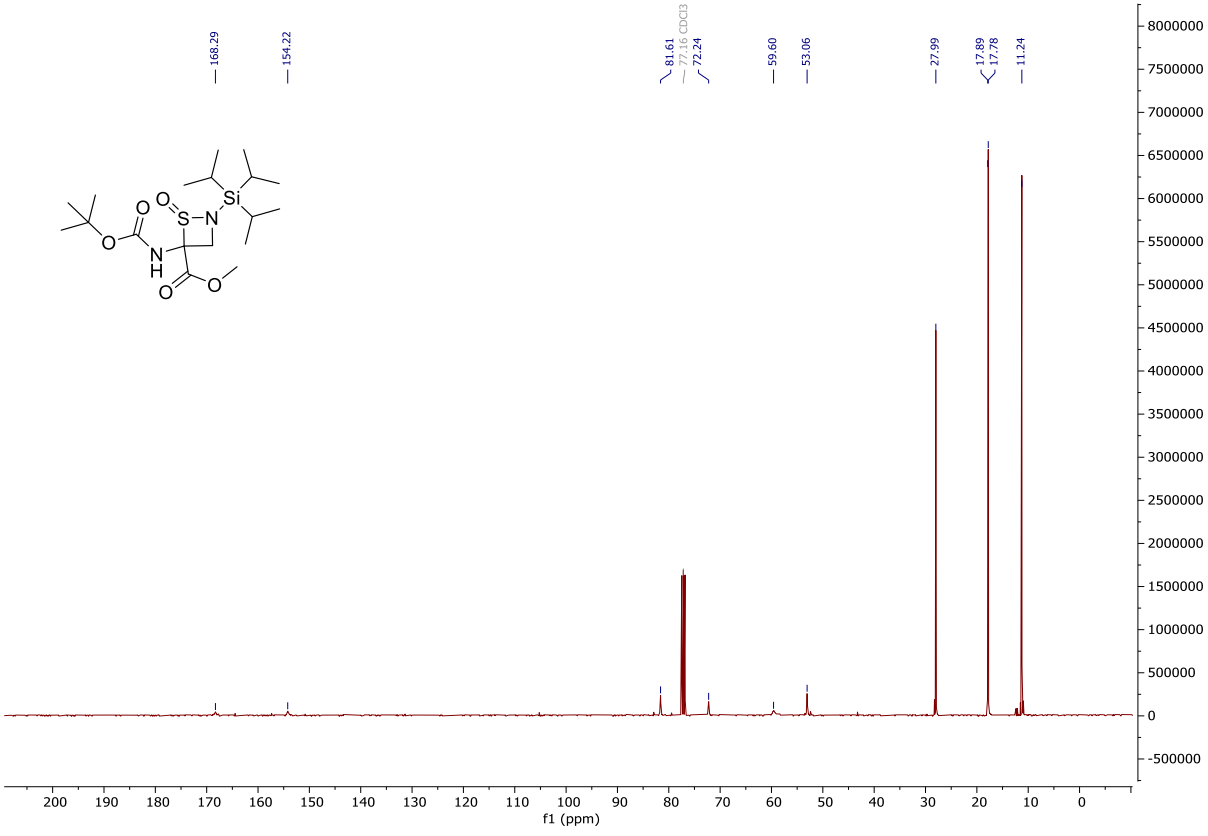
4,4-Diphenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1i)



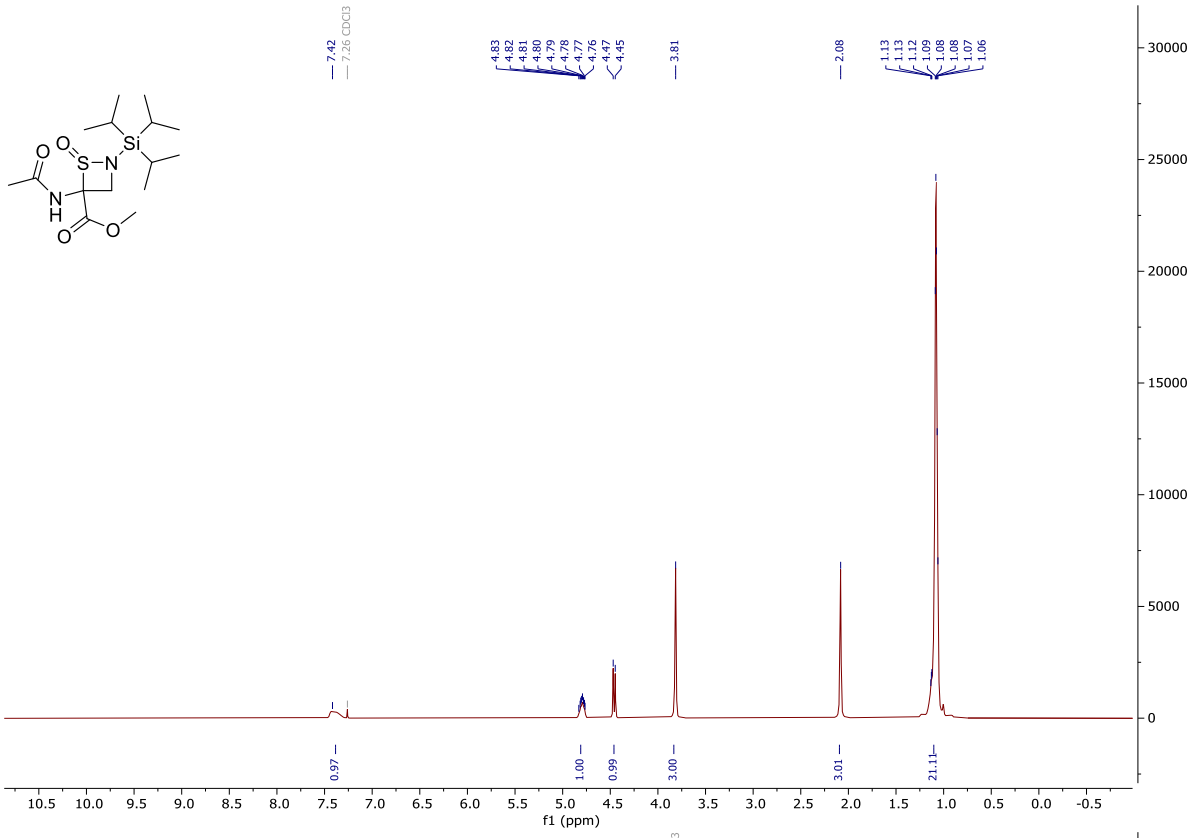


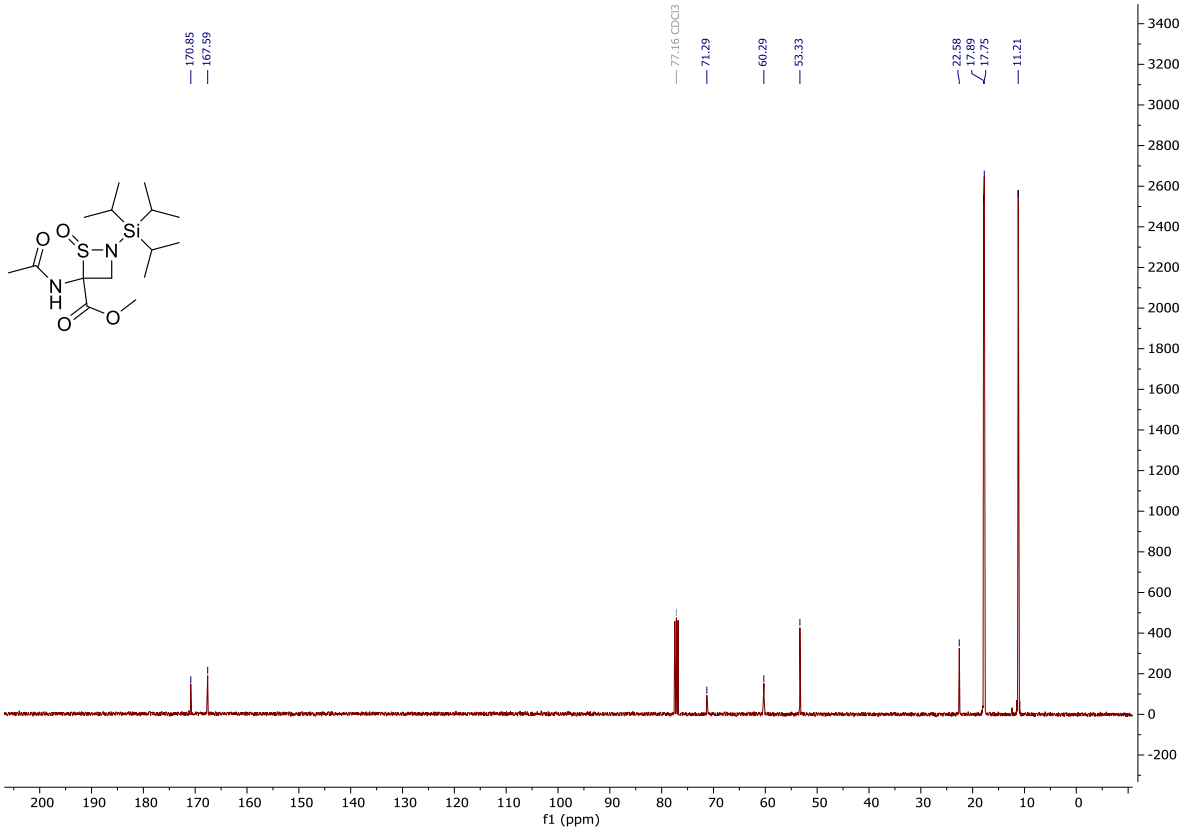
Methyl 4-((*tert*-butoxycarbonyl)amino)-2-(triisopropylsilyl)-1,2-thiazetidine-4-carboxylate 1-oxide (1j)



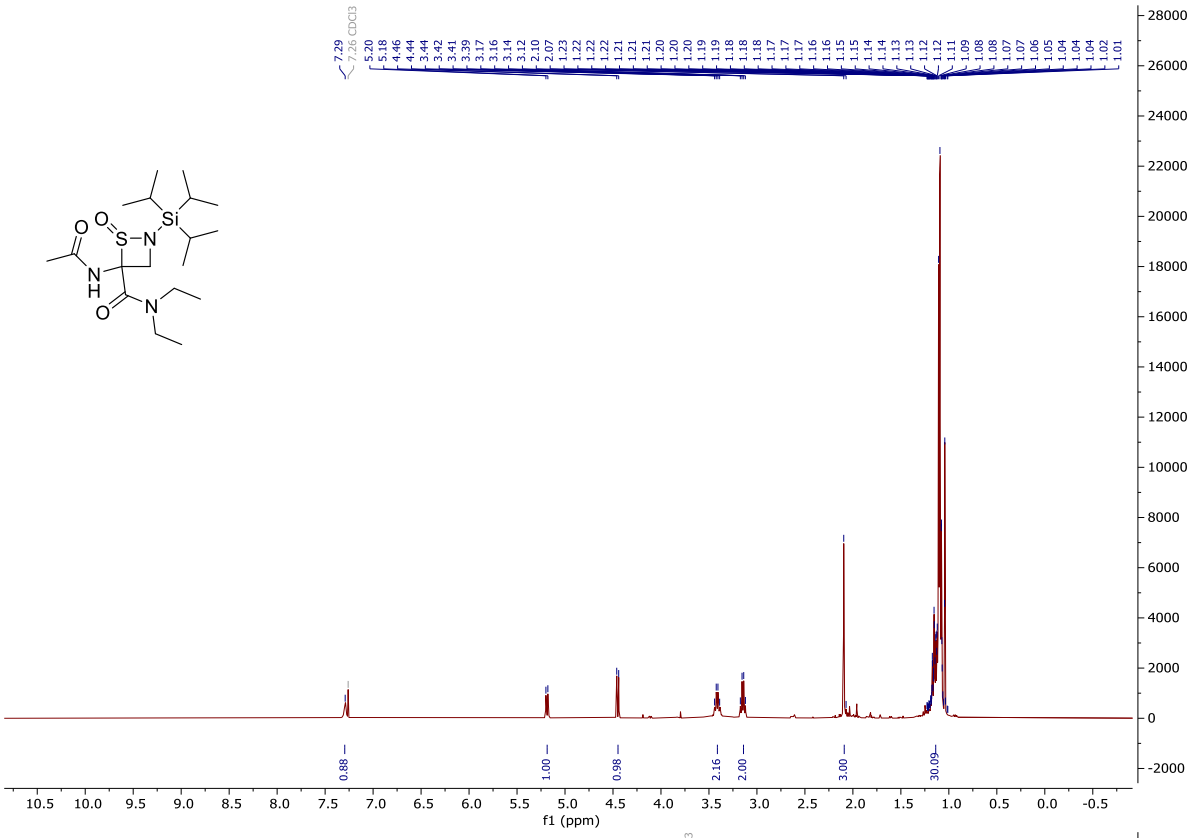


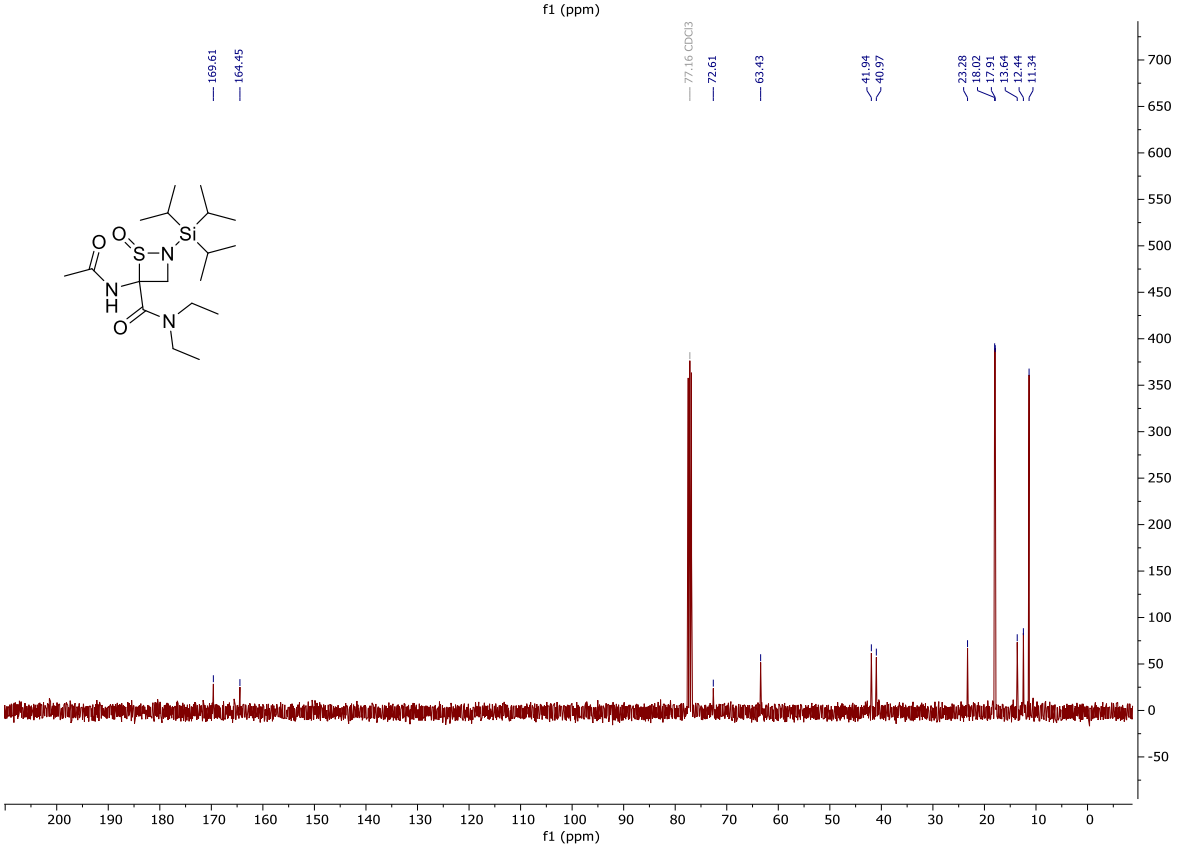
Methyl 4-acetamido-2-(triisopropylsilyl)-1,2-thiazetidine-4-carboxylate 1-oxide (1k)



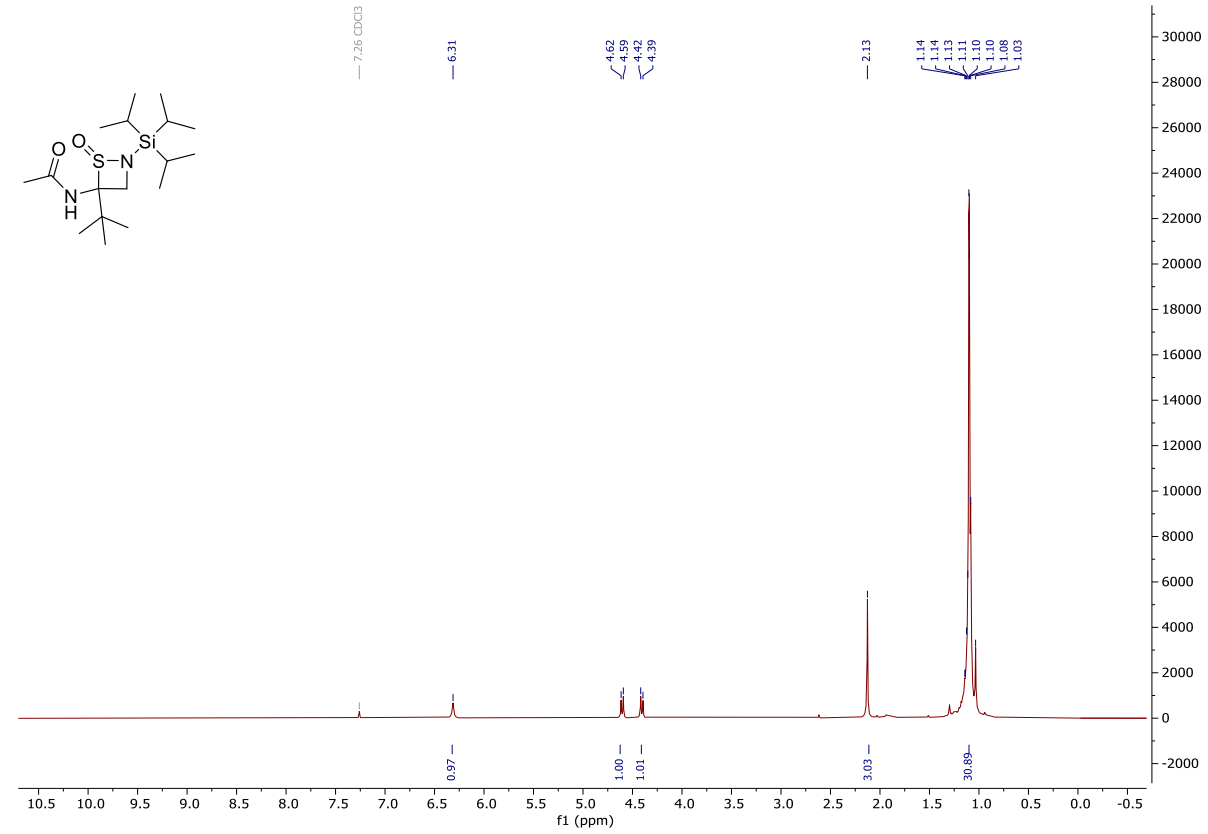


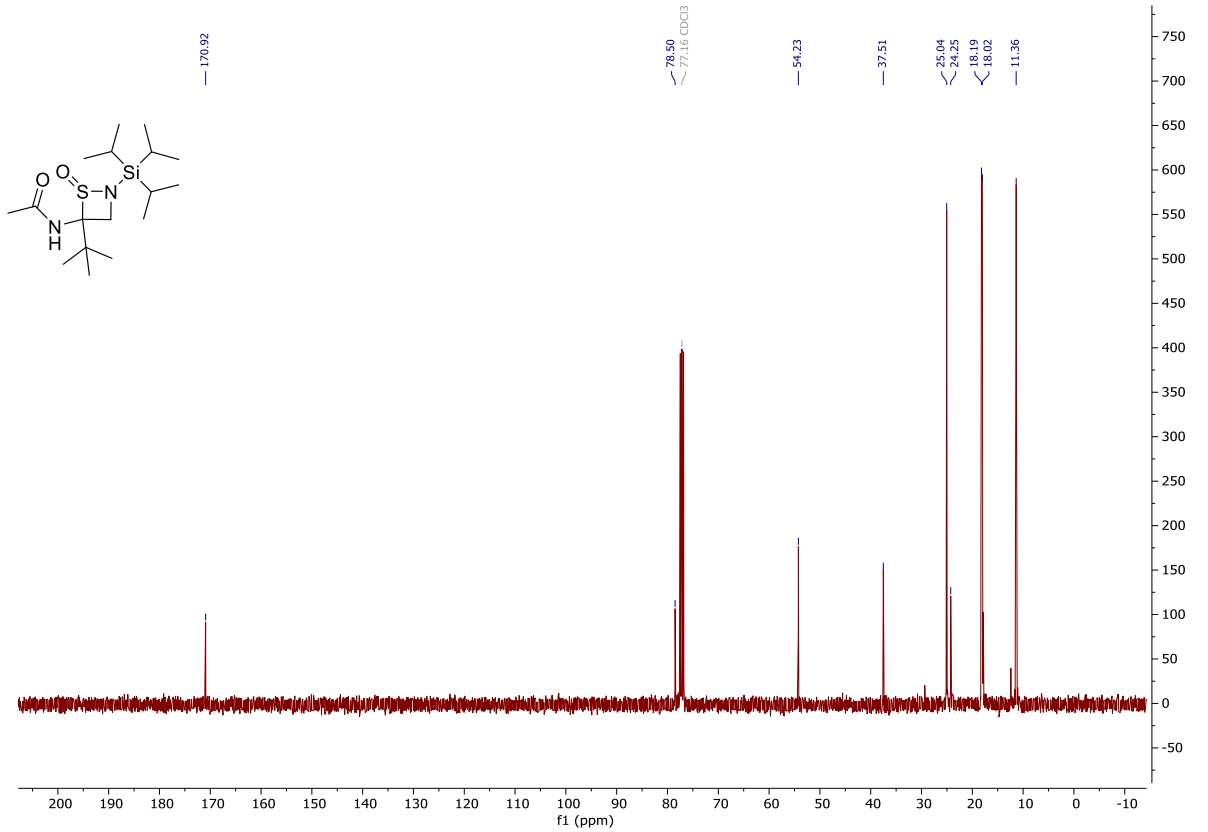
4-Acetamido-*N*,*N*-diethyl-2-(triisopropylsilyl)-1,2-thiazetidine-4-carboxamide 1-oxide (1l)



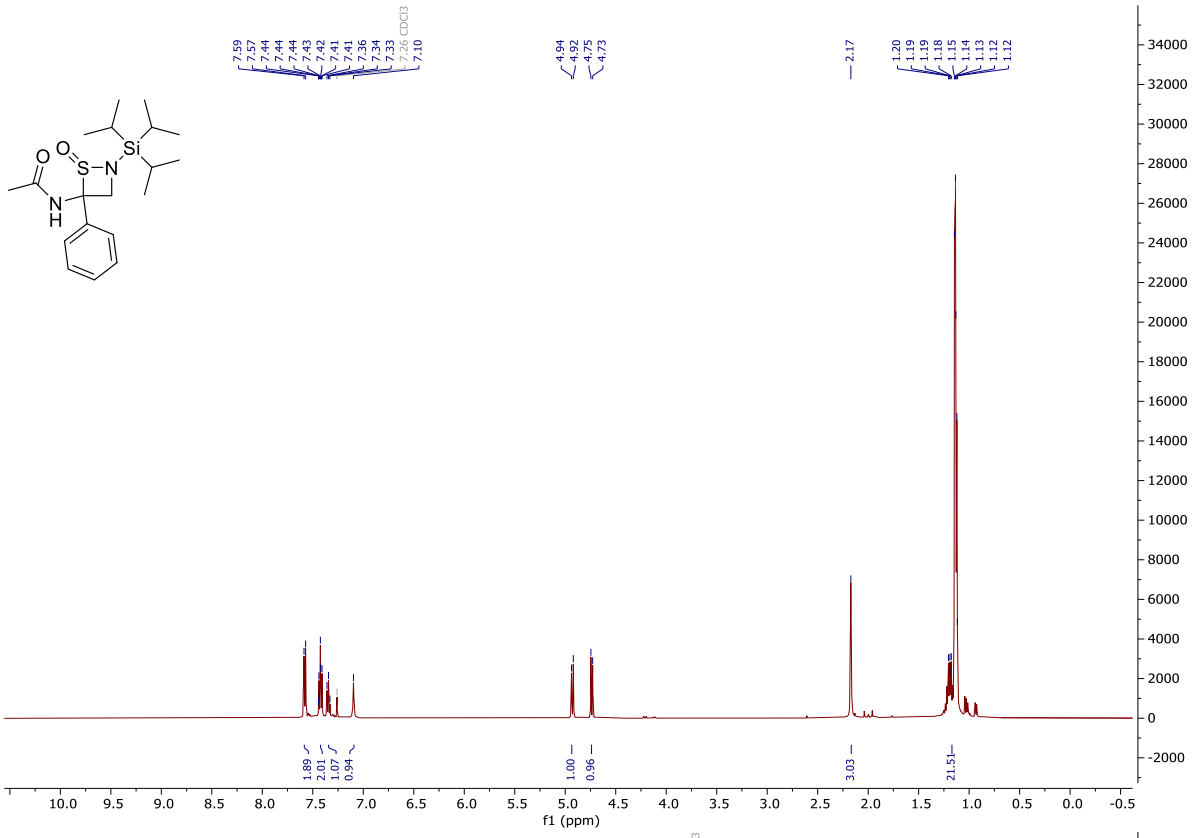


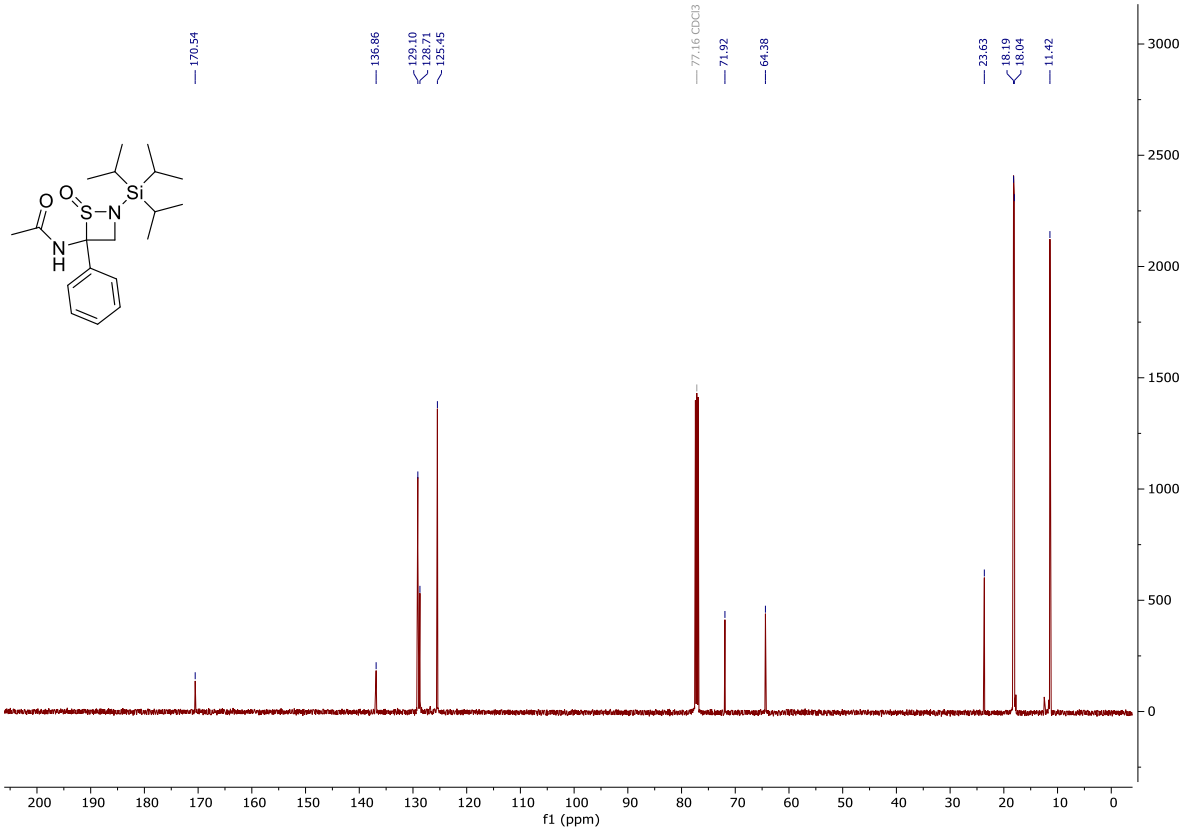
N-(4-(*tert*-Butyl)-1-oxido-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl)acetamide (1m)



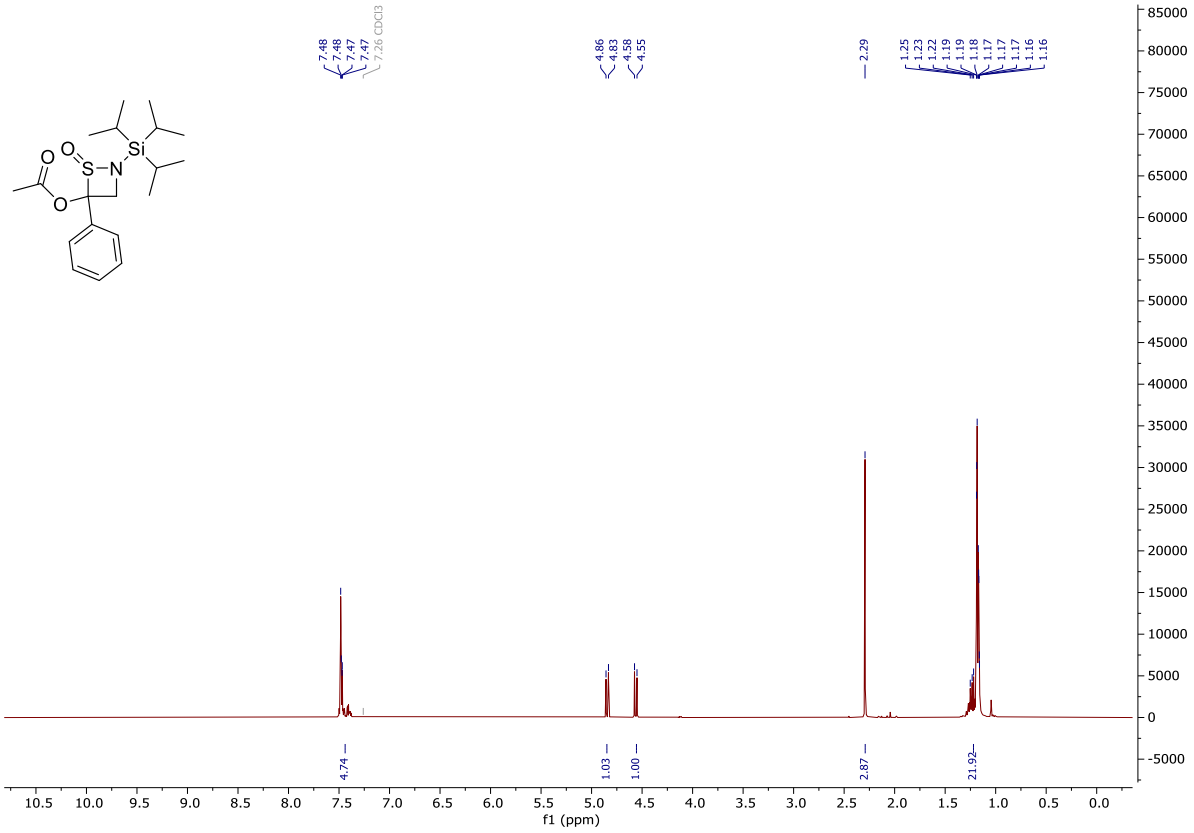


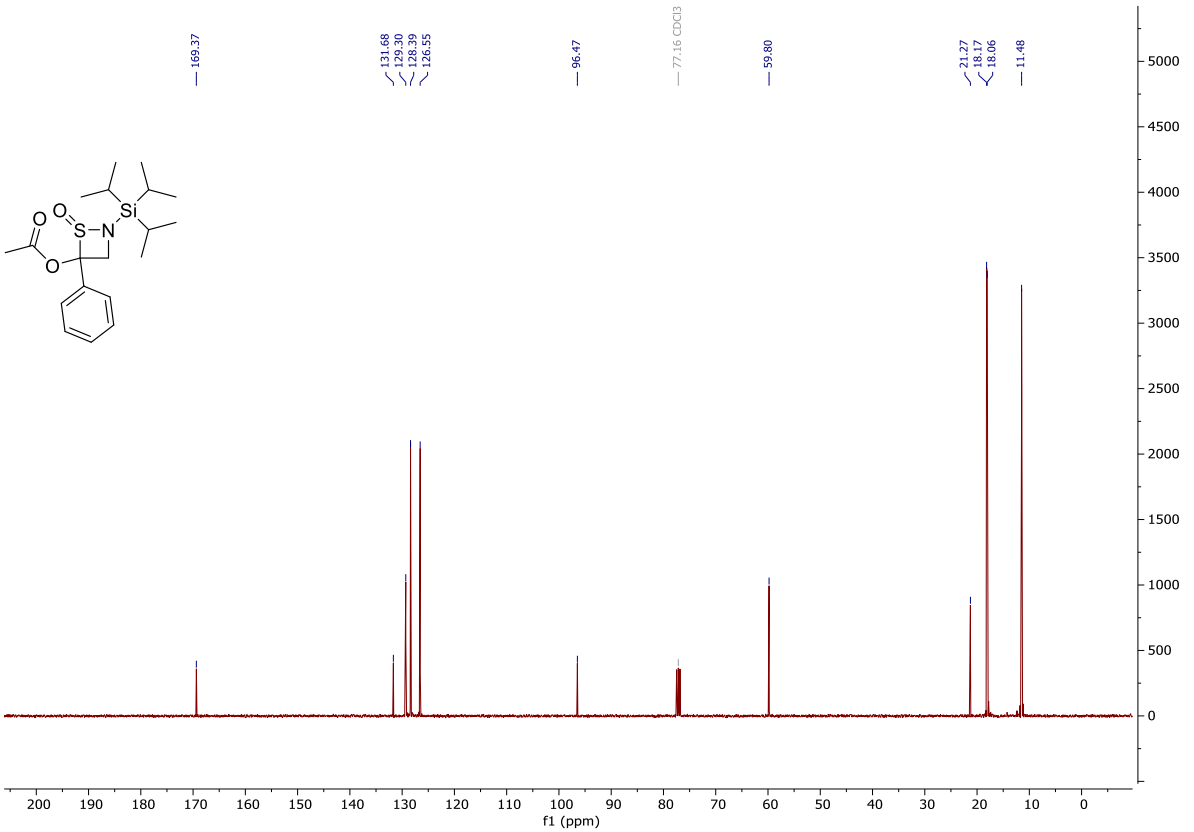
N-(1-Oxido-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl)acetamide (1n)



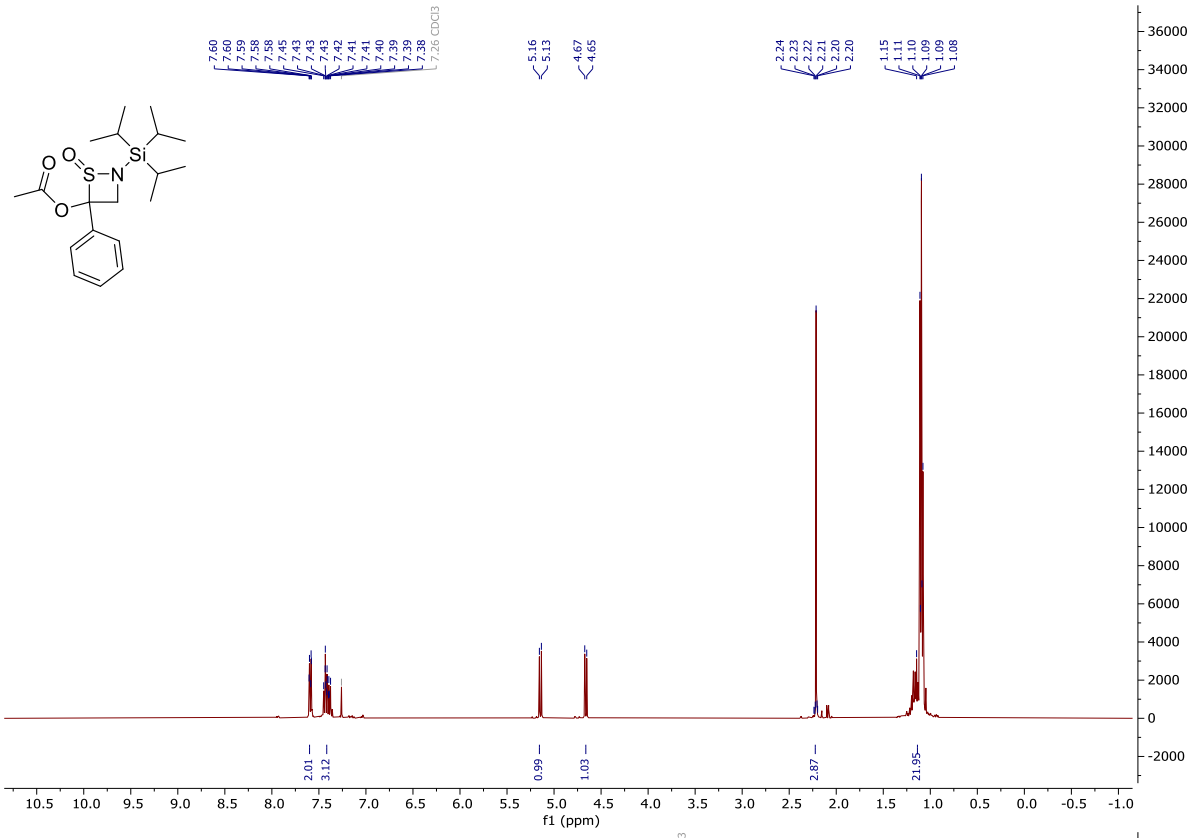


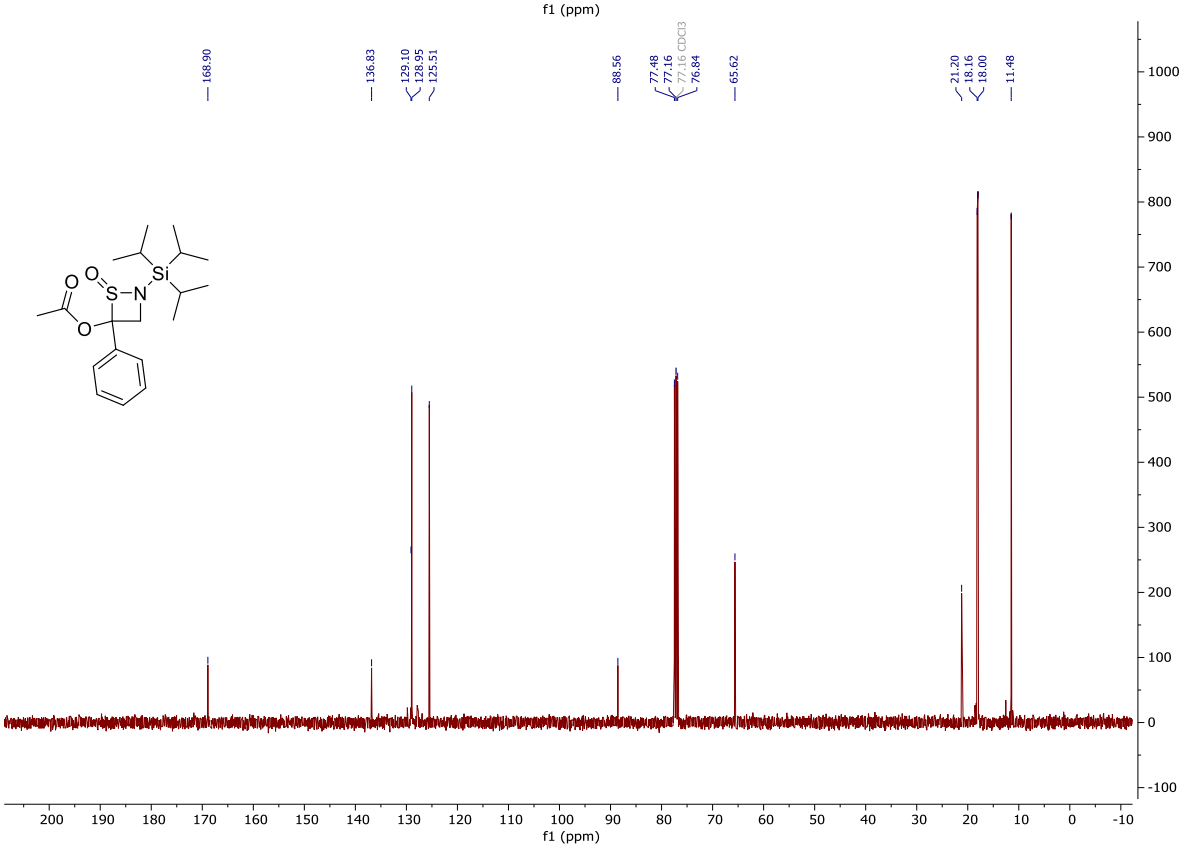
1-Oxido-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl acetate (1o-major)



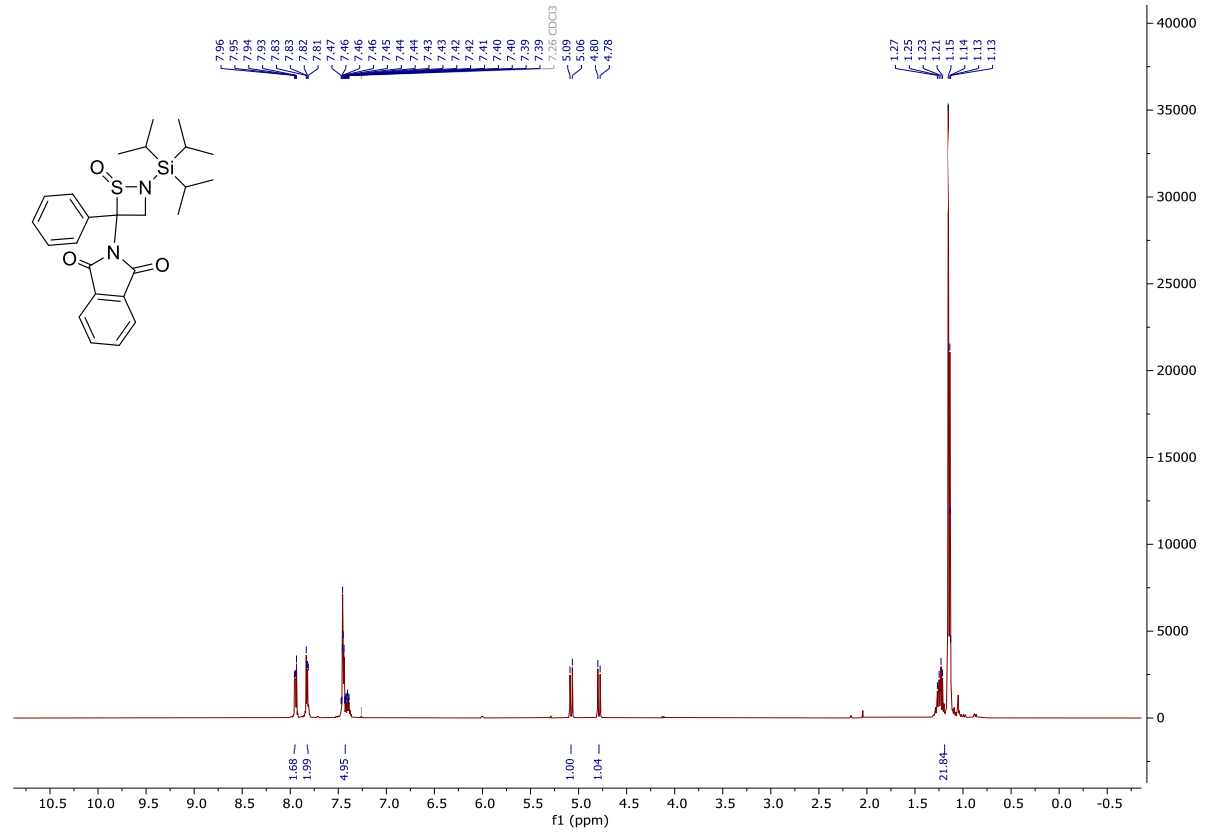


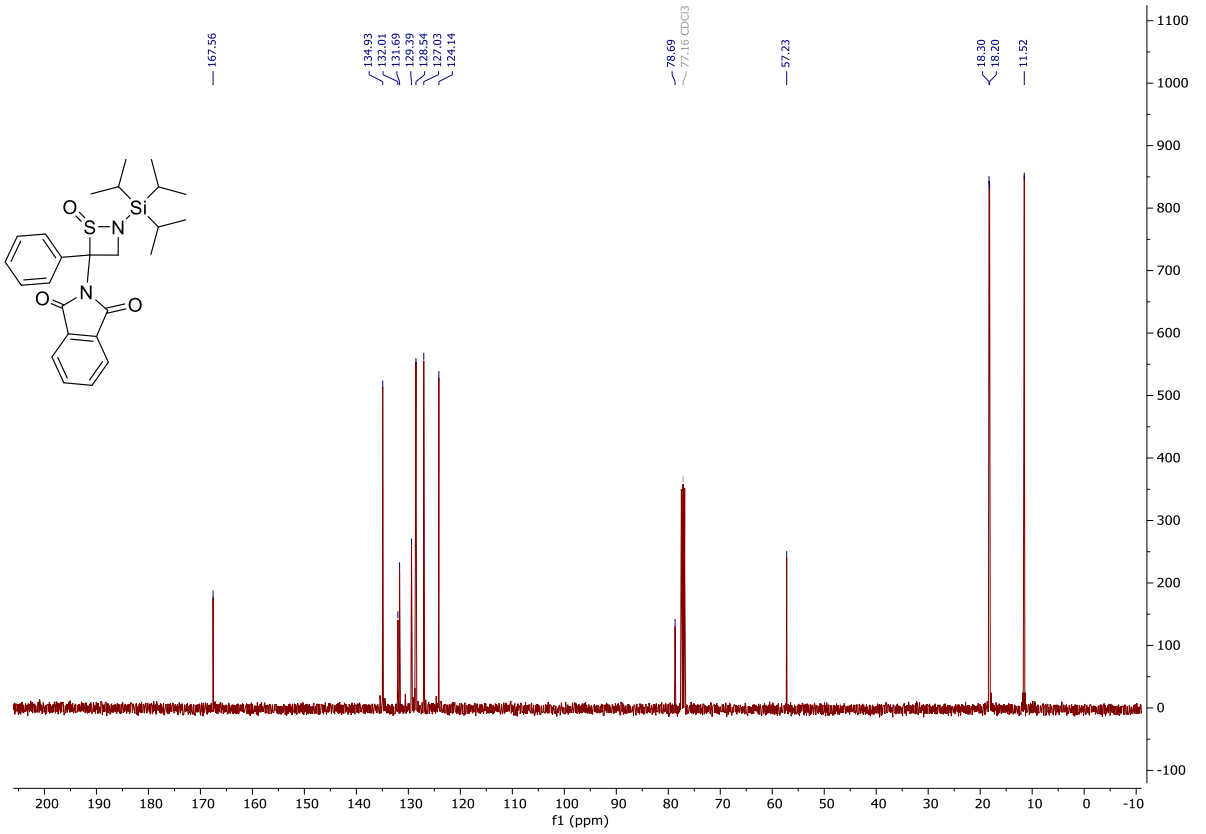
1-Oxido-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl acetate (1o-minor)



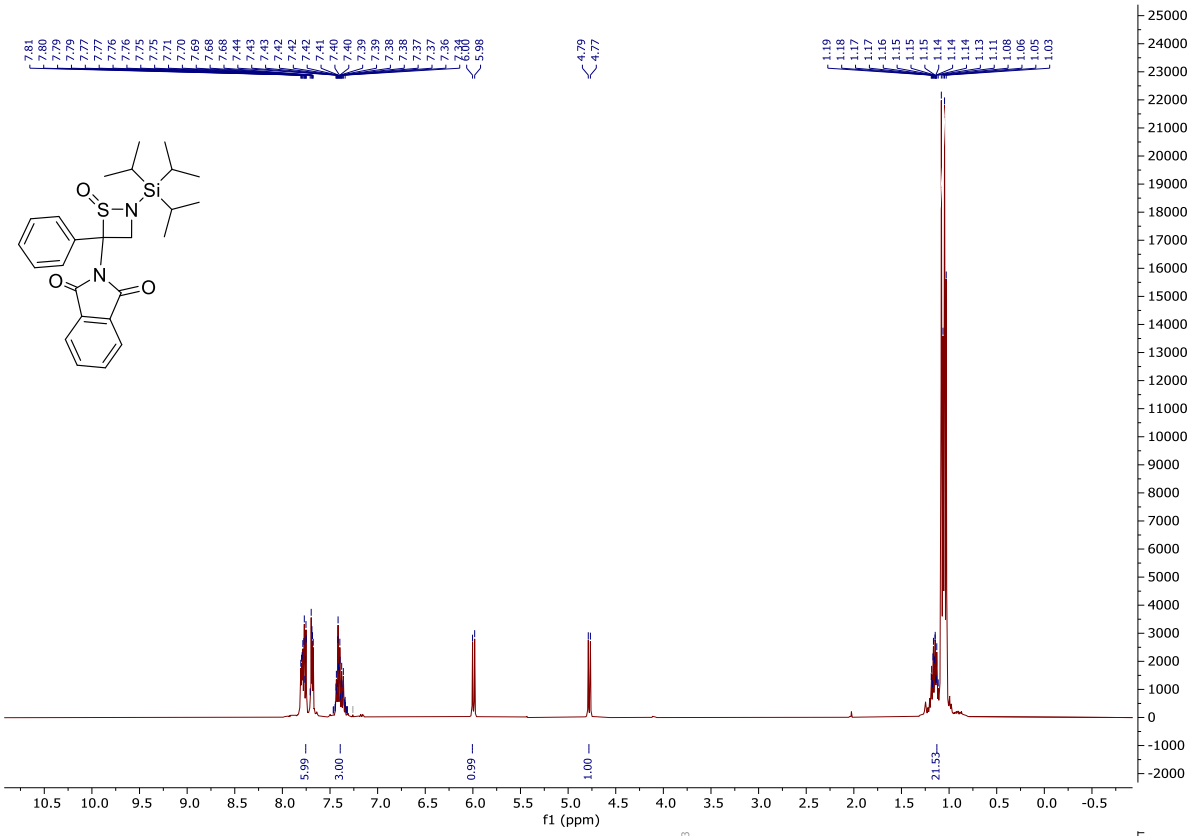


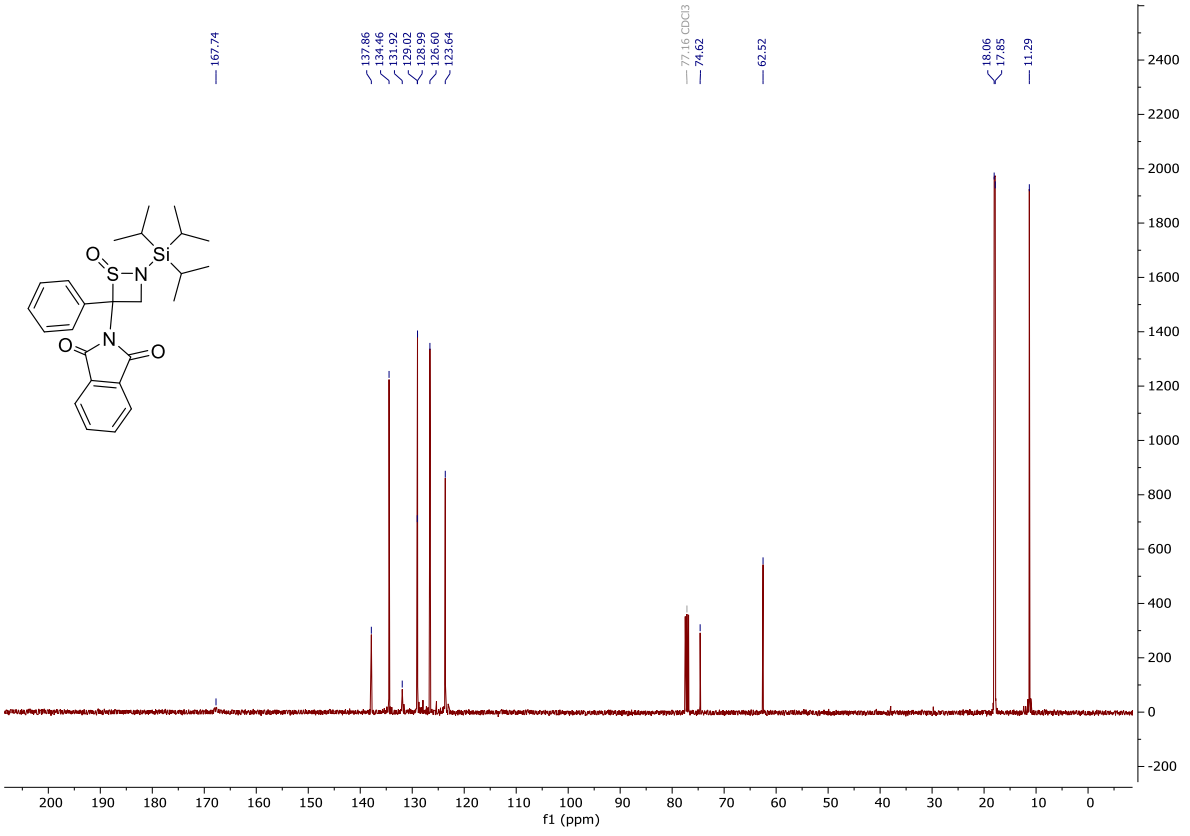
2-(1-Oxido-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl)isoindoline-1,3-dione (1p-major)



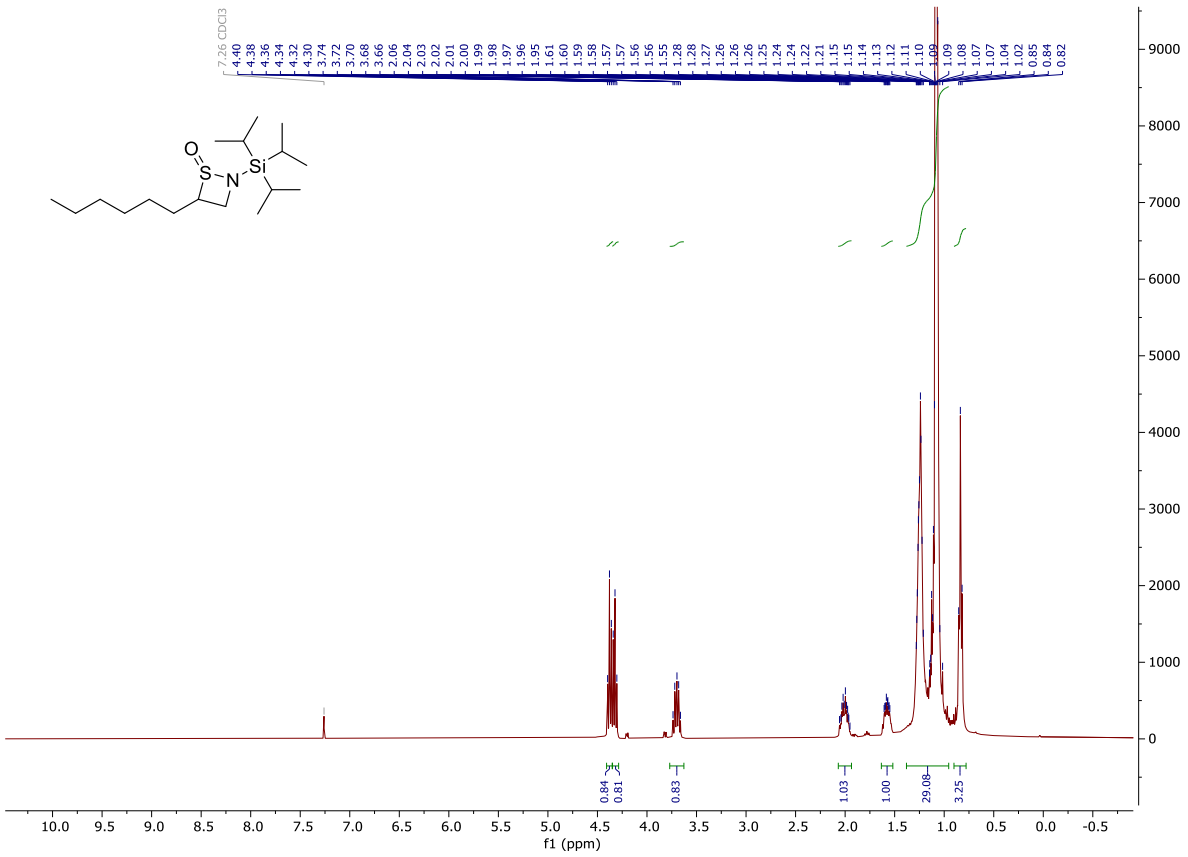


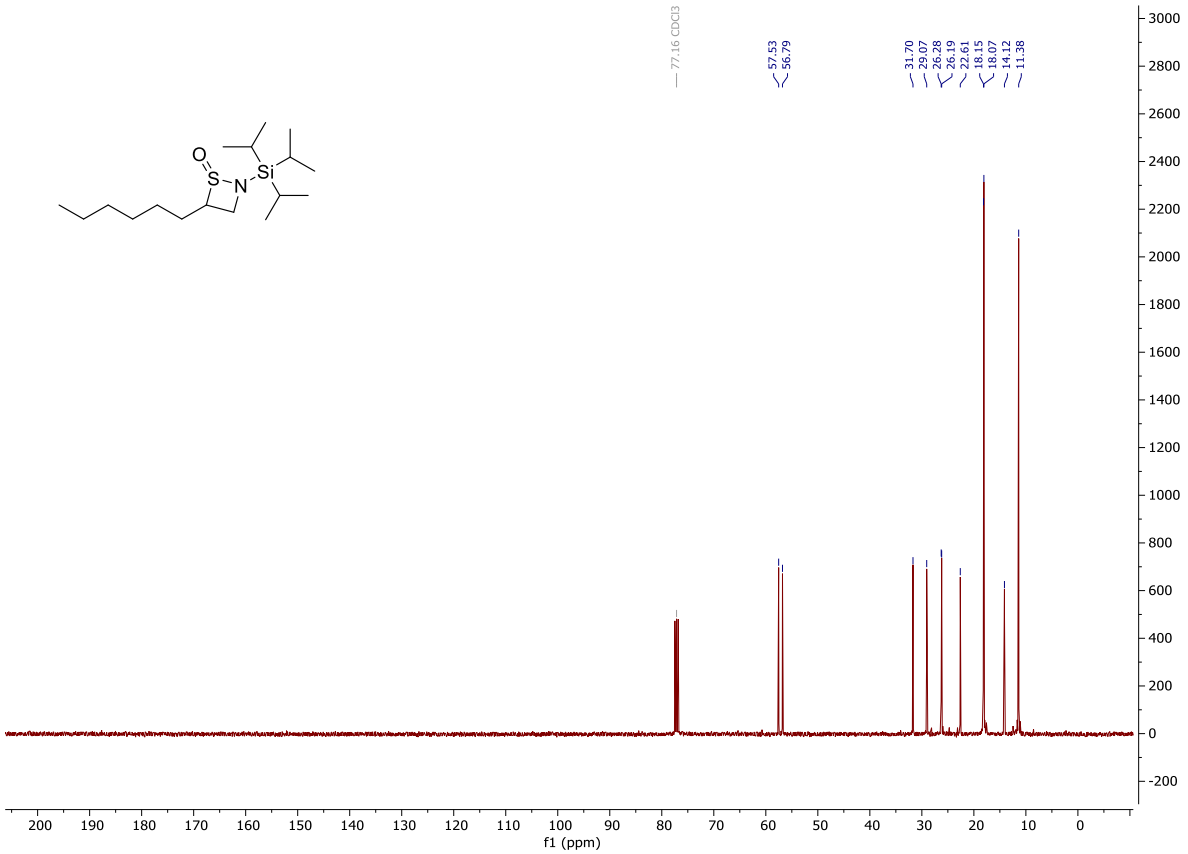
2-(1-Oxido-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl)isoindoline-1,3-dione (1p-minor)



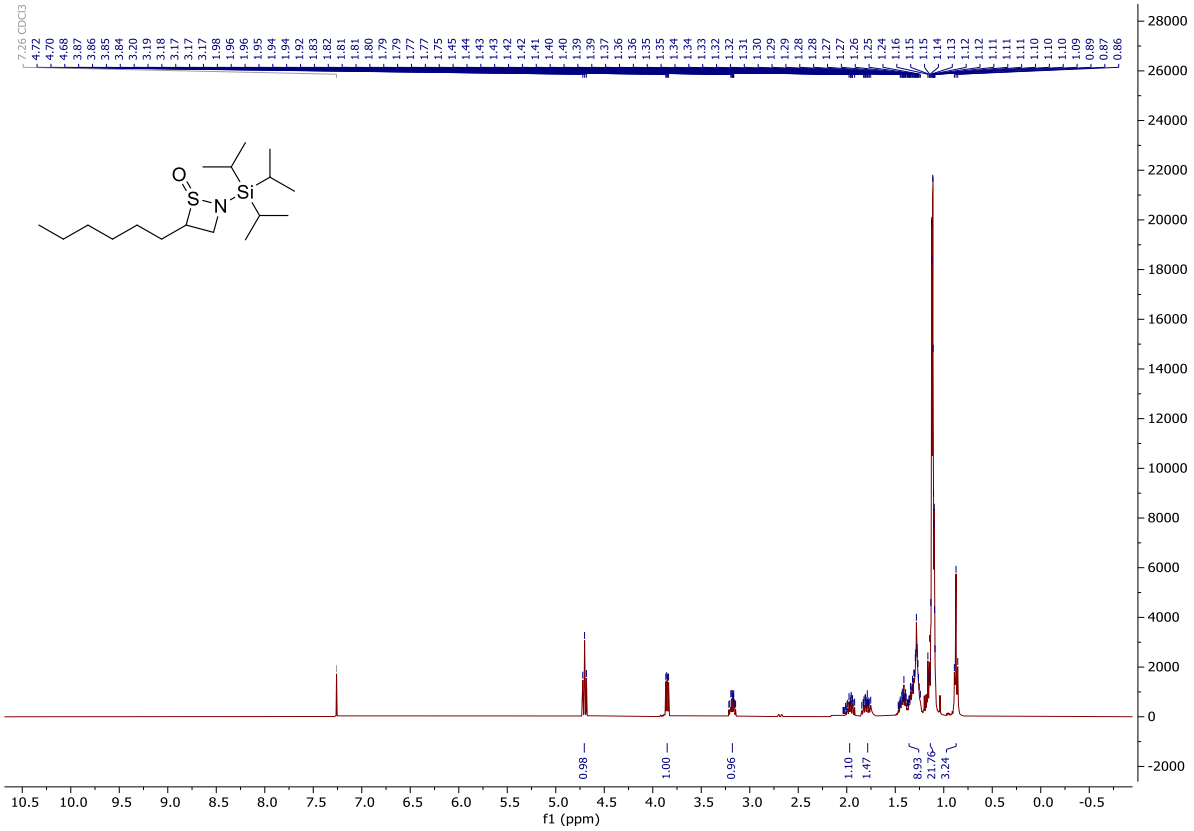


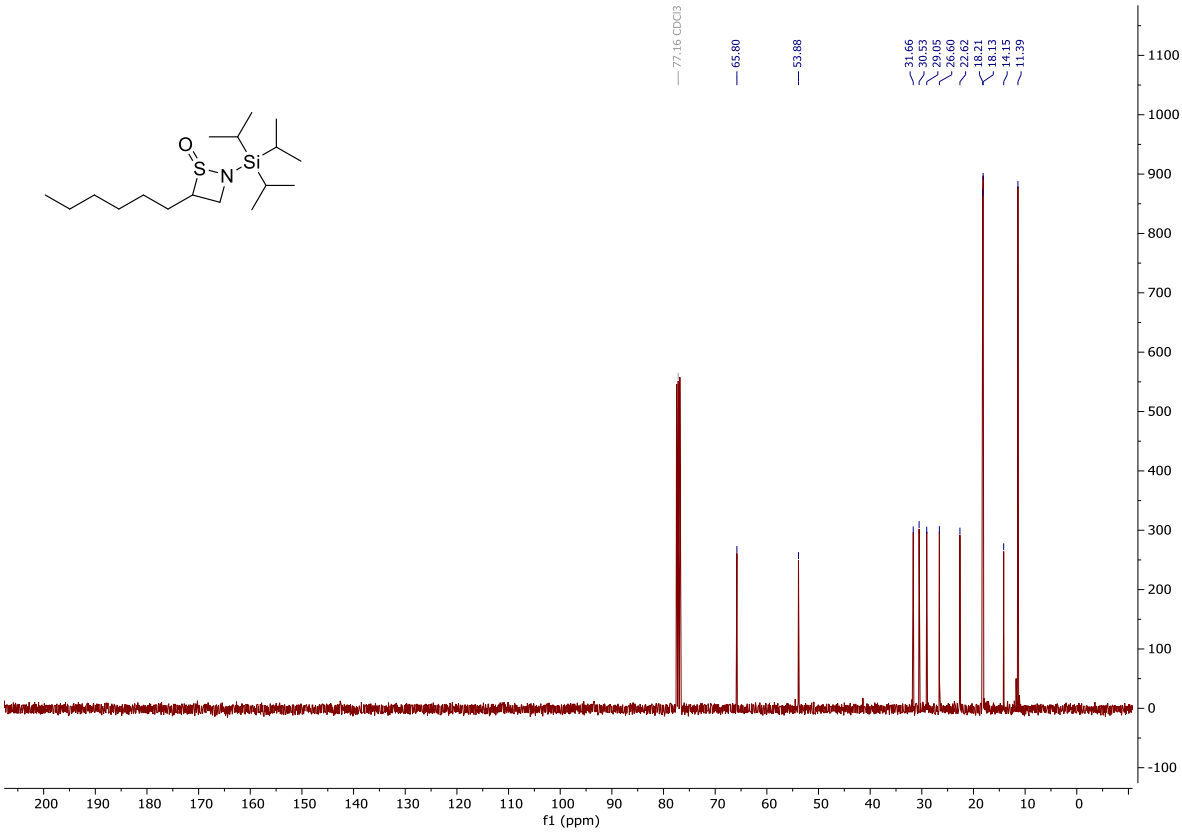
4-Hexyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1q-major)



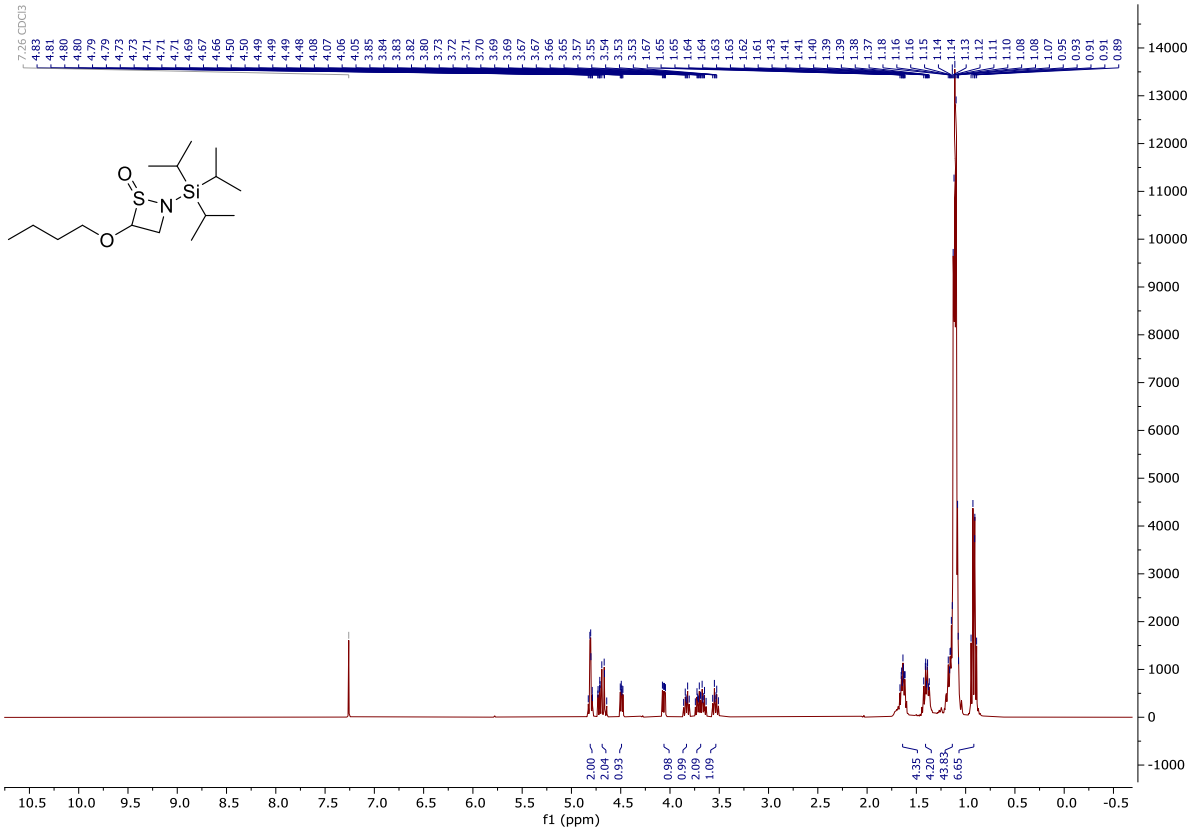


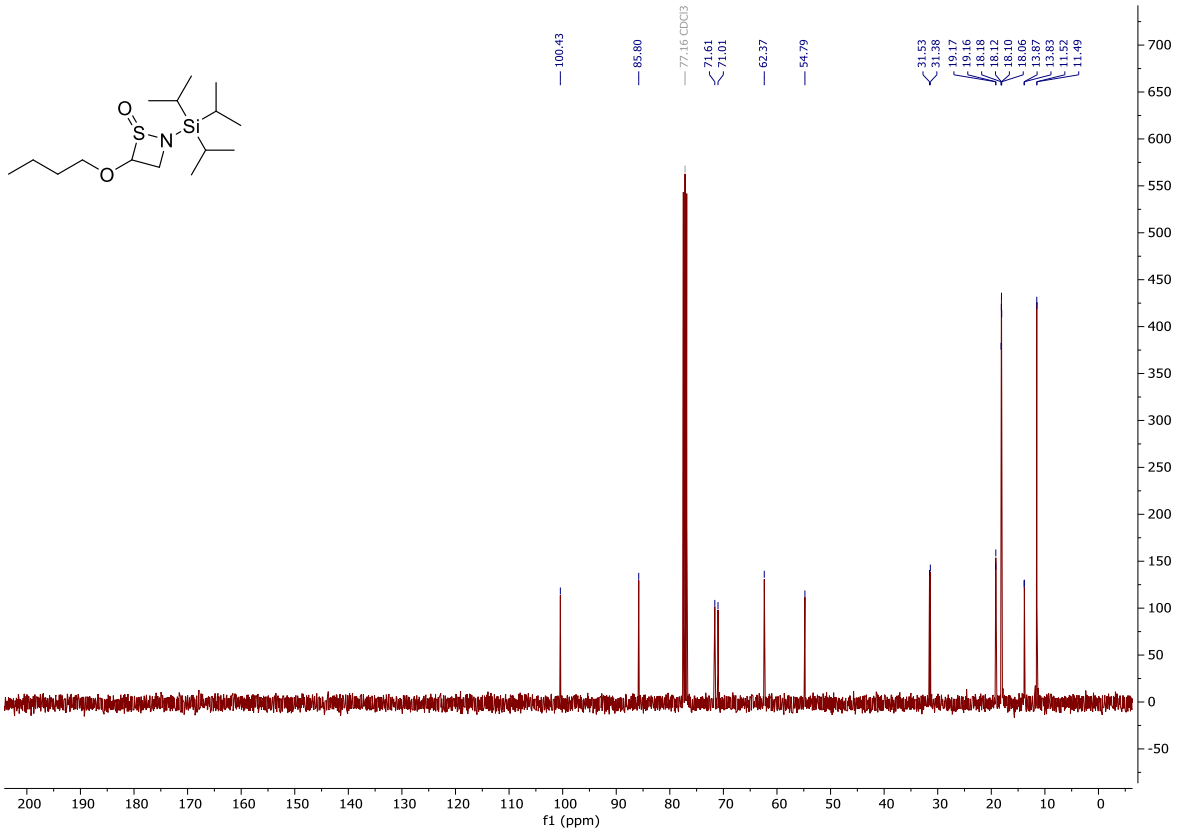
4-Hexyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1q-minor)



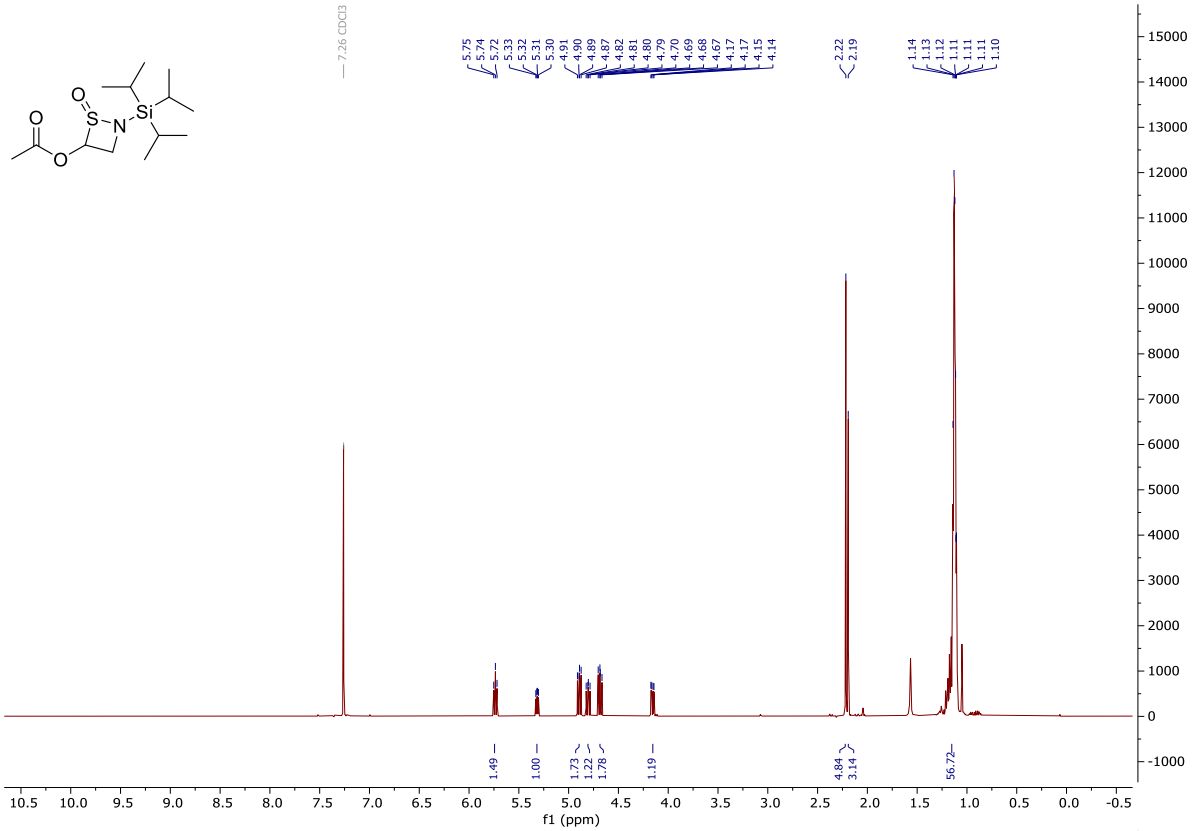


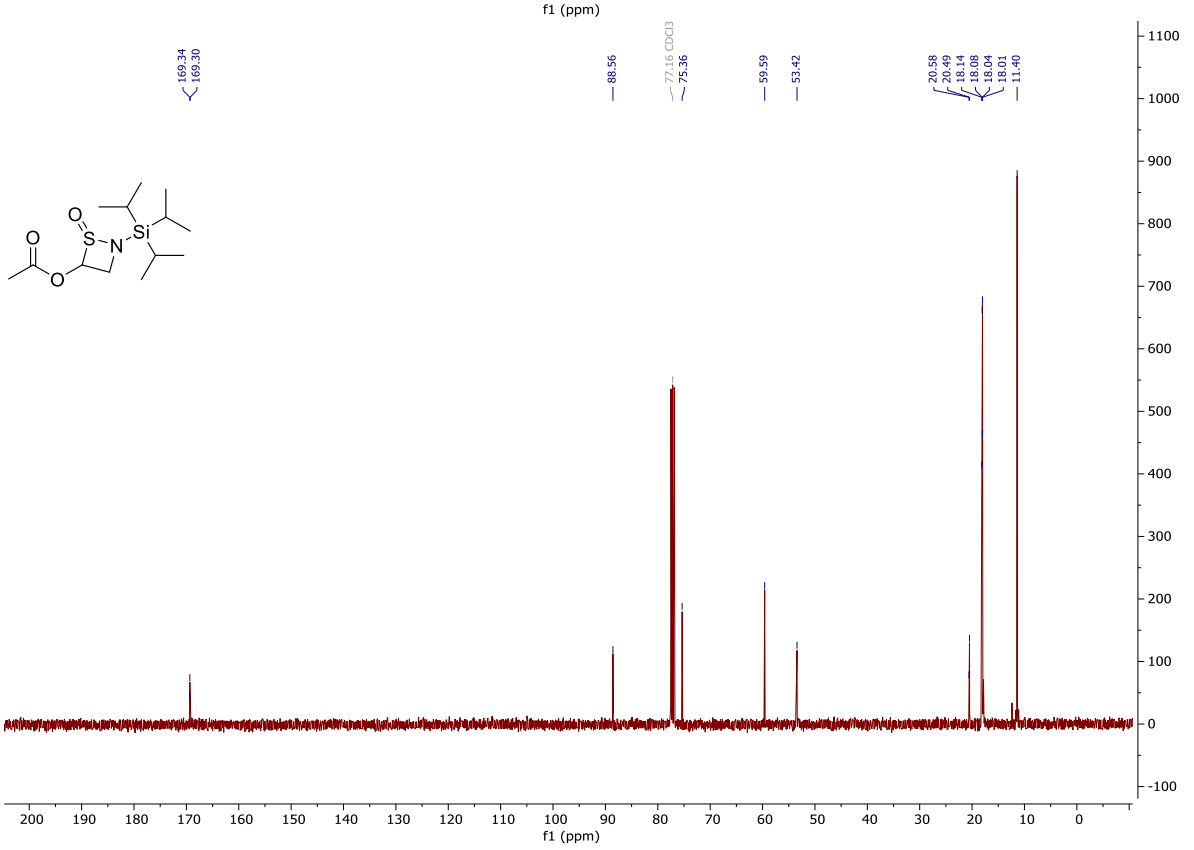
4-Butoxy-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1r)



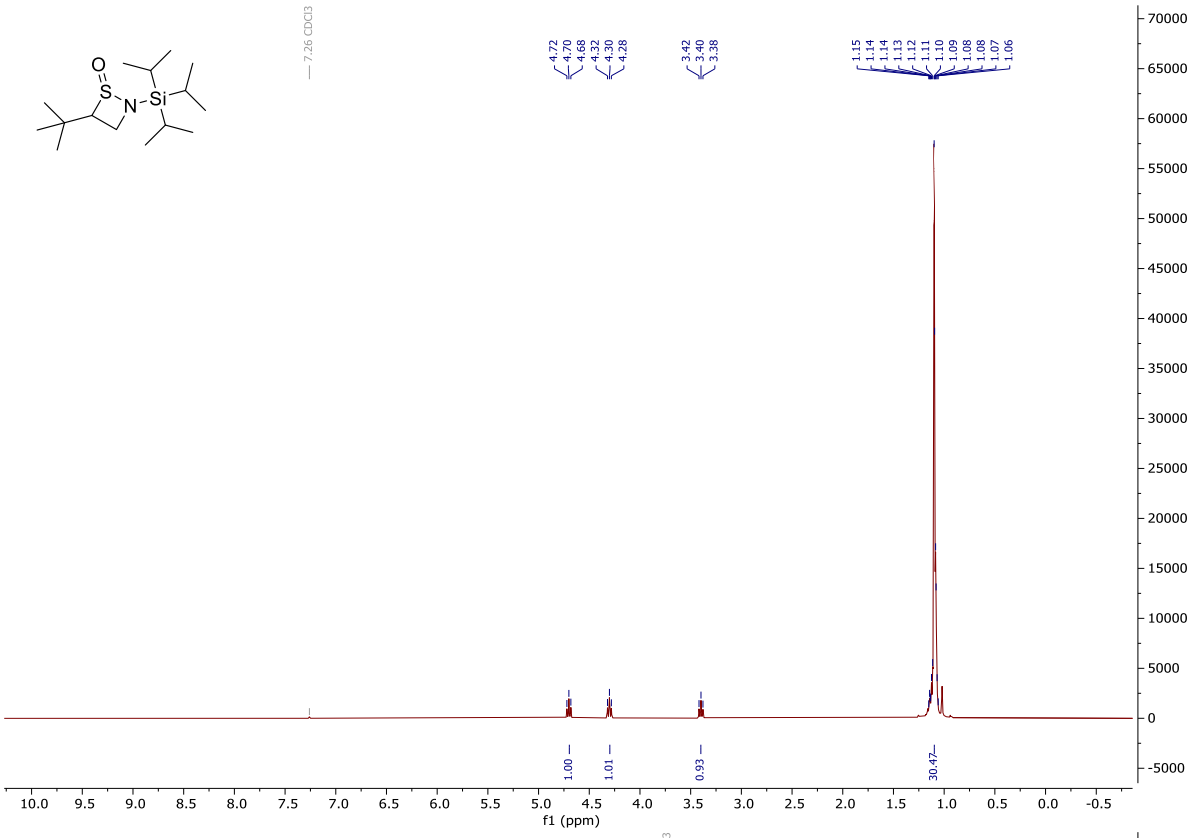


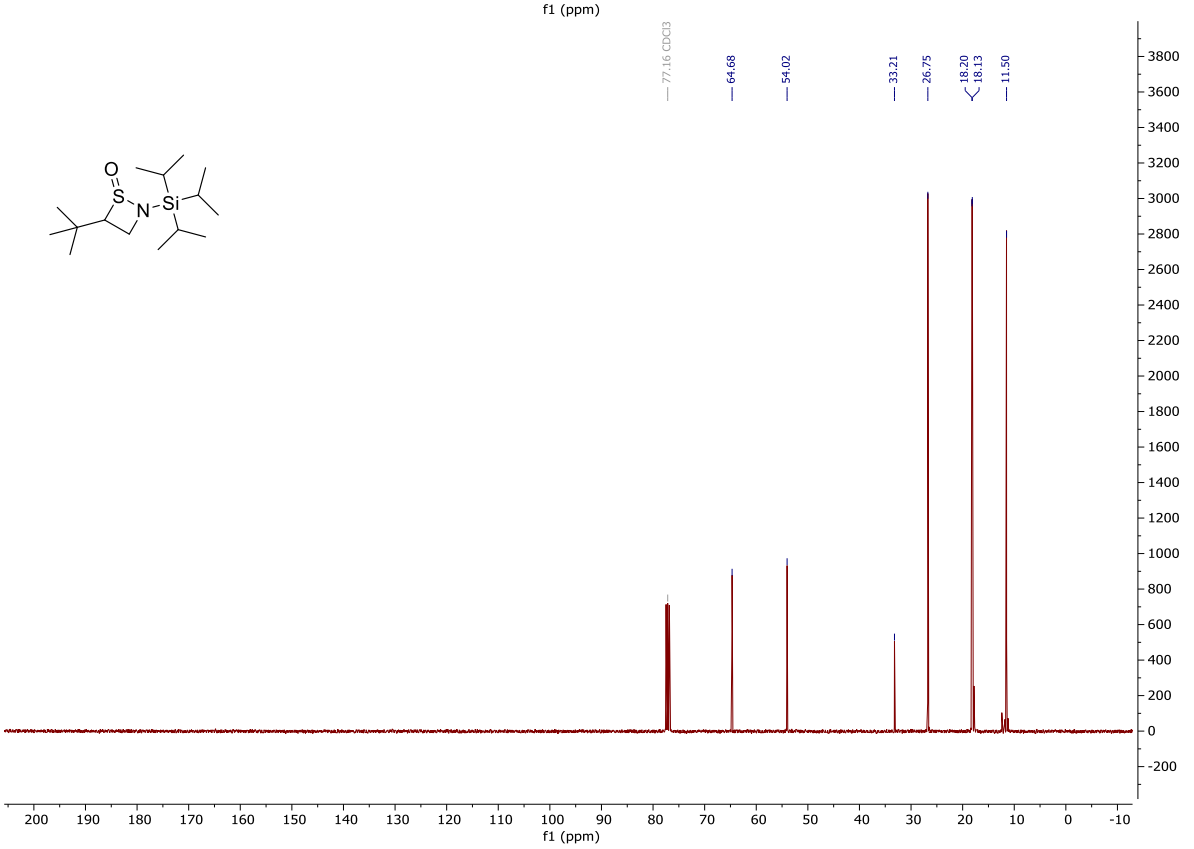
1-Oxido-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl acetate (1s)



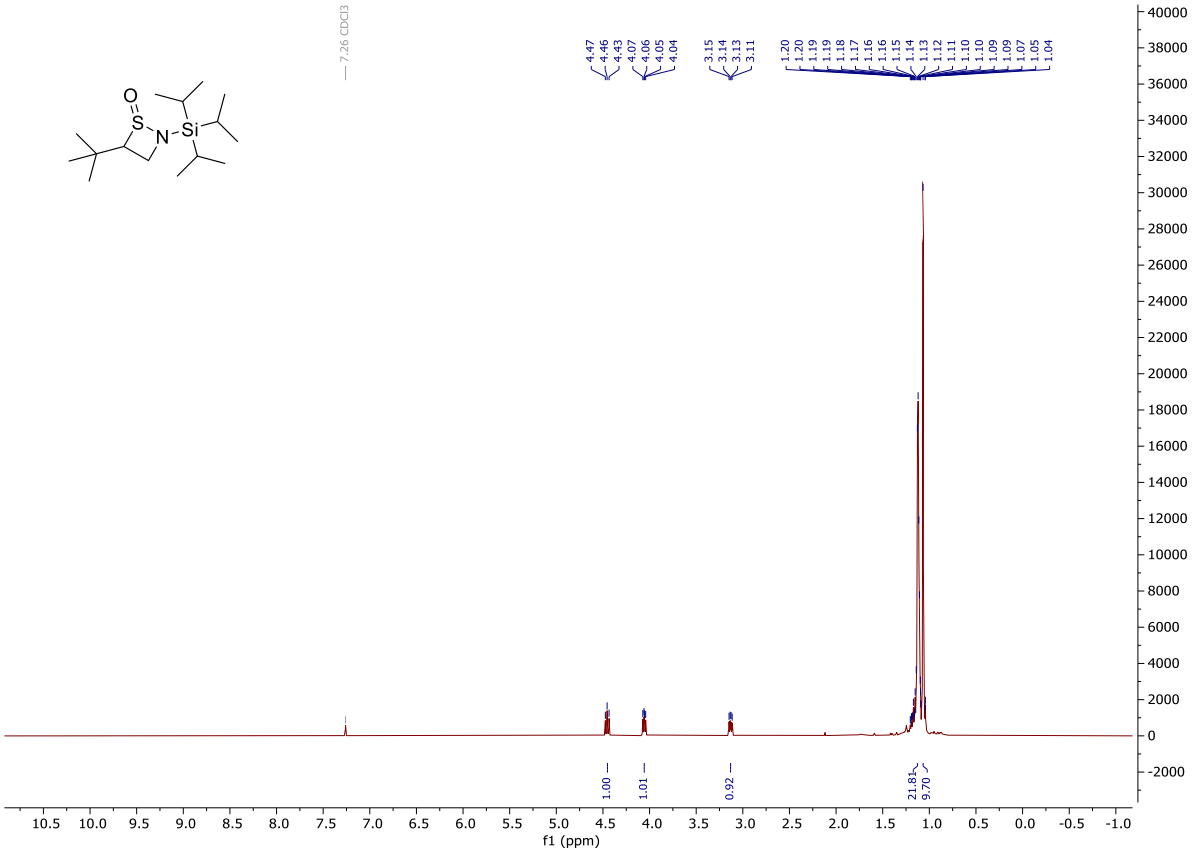


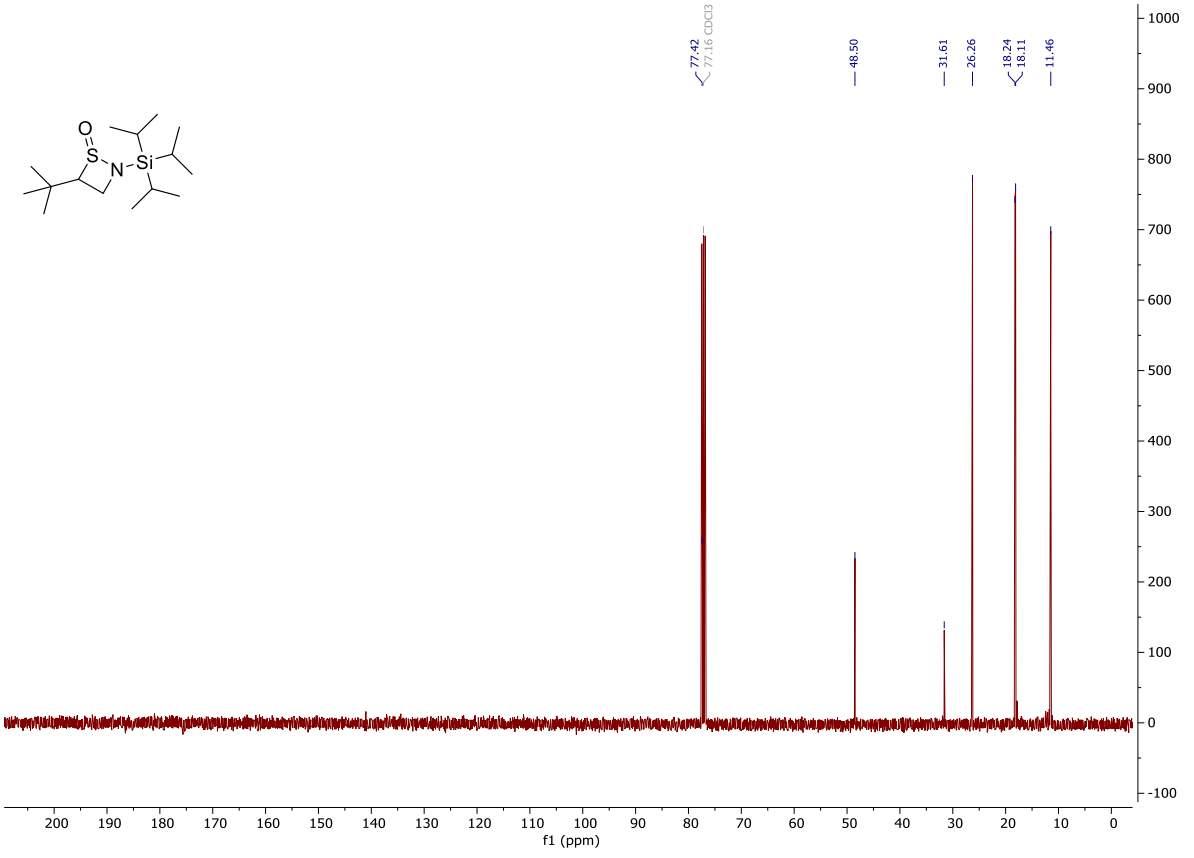
4-(*tert*-Butyl)-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1t-major)



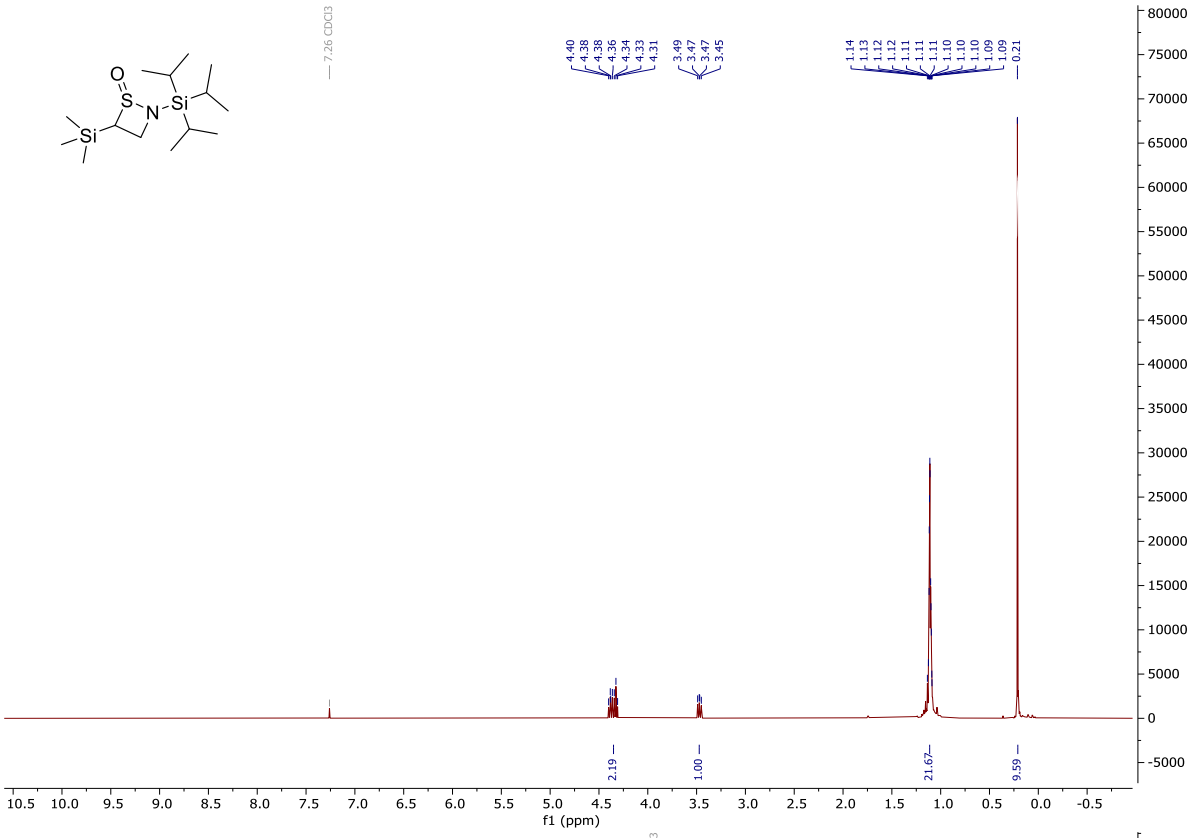


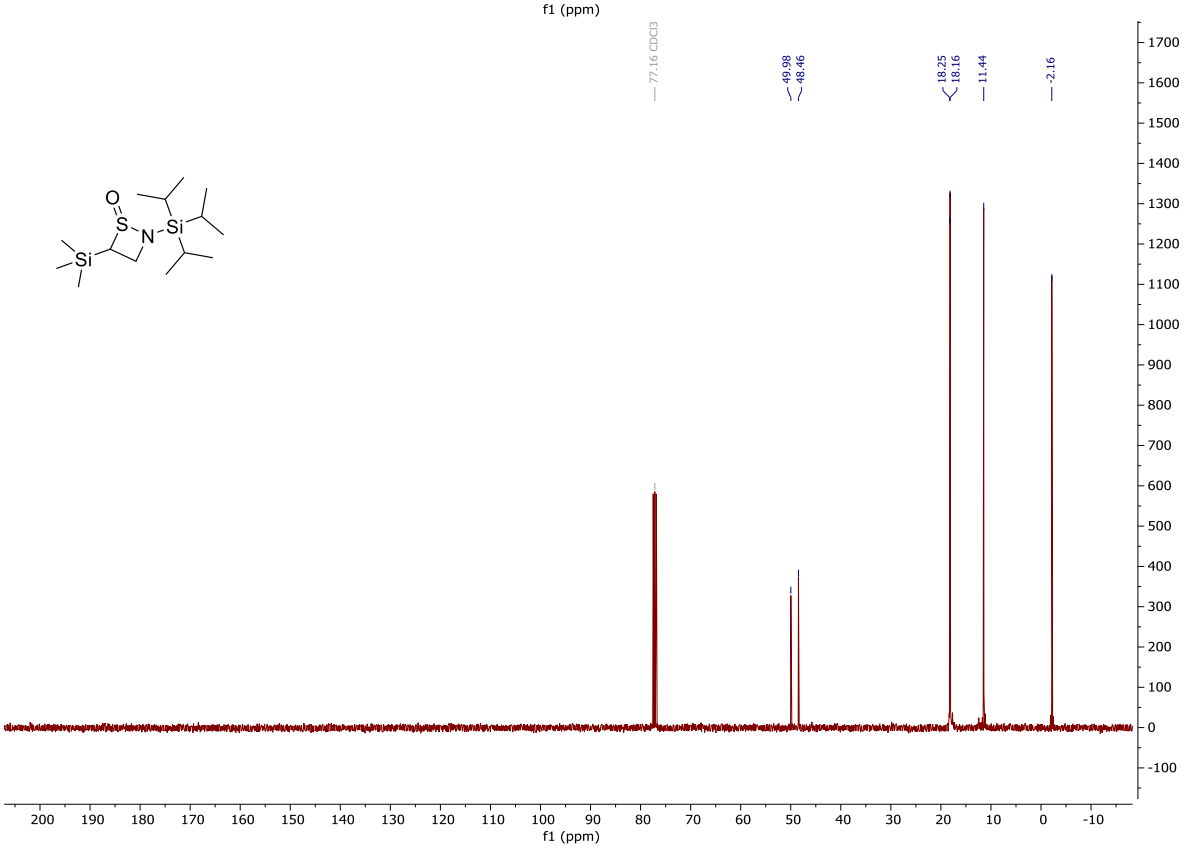
4-(*tert*-Butyl)-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1t-minor)



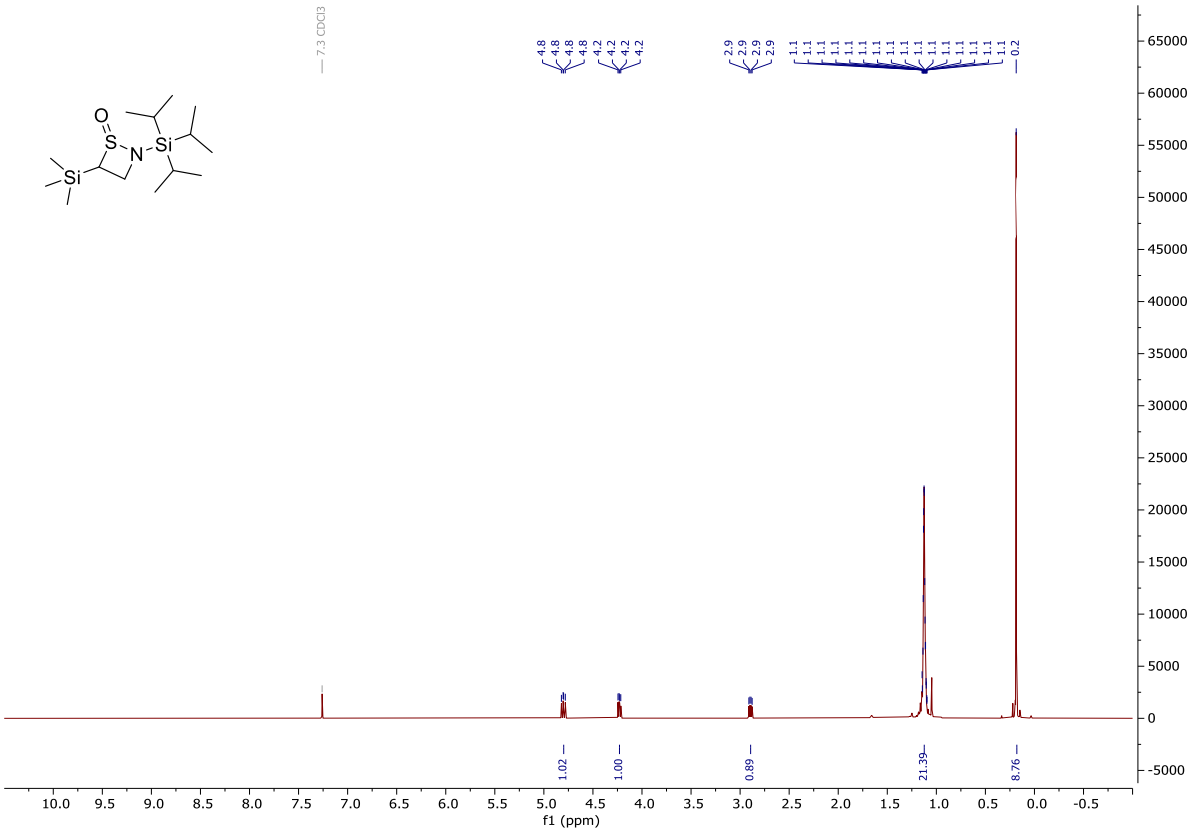


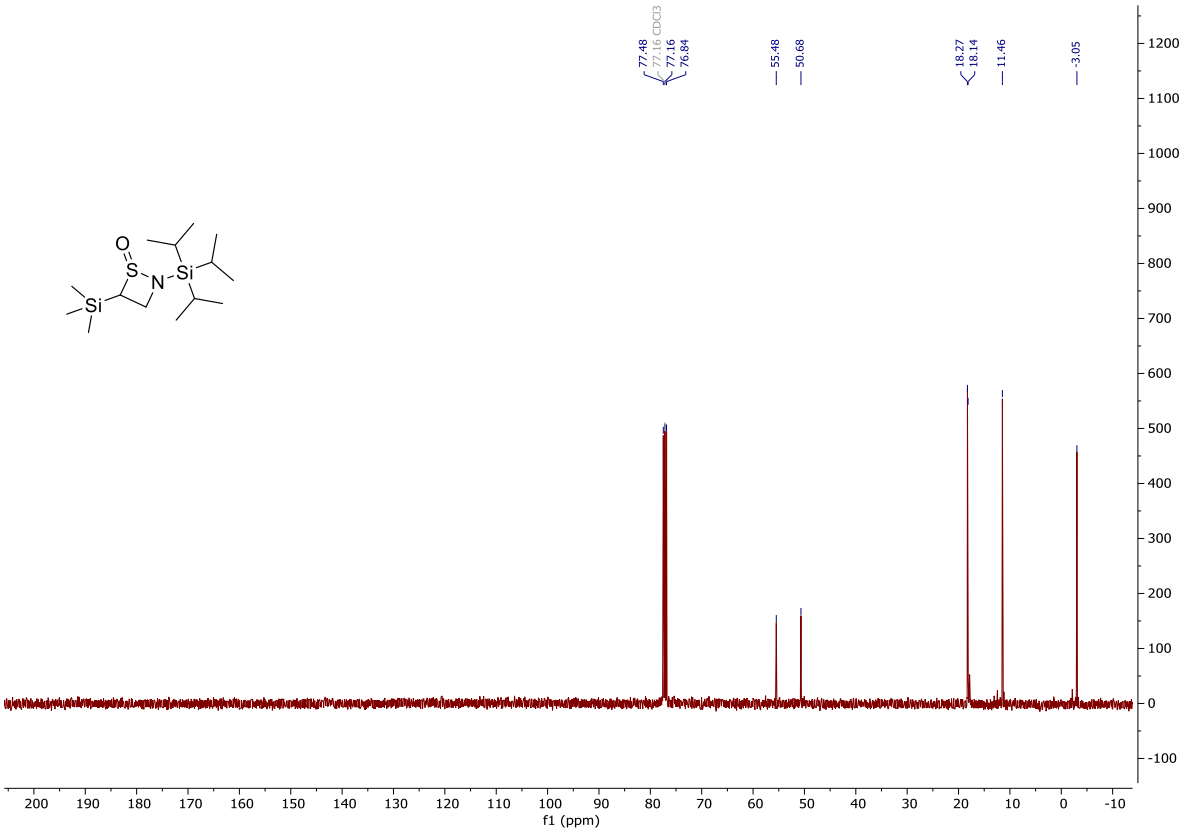
2-(Triisopropylsilyl)-4-(trimethylsilyl)-1,2-thiazetidine 1-oxide (1u-major)



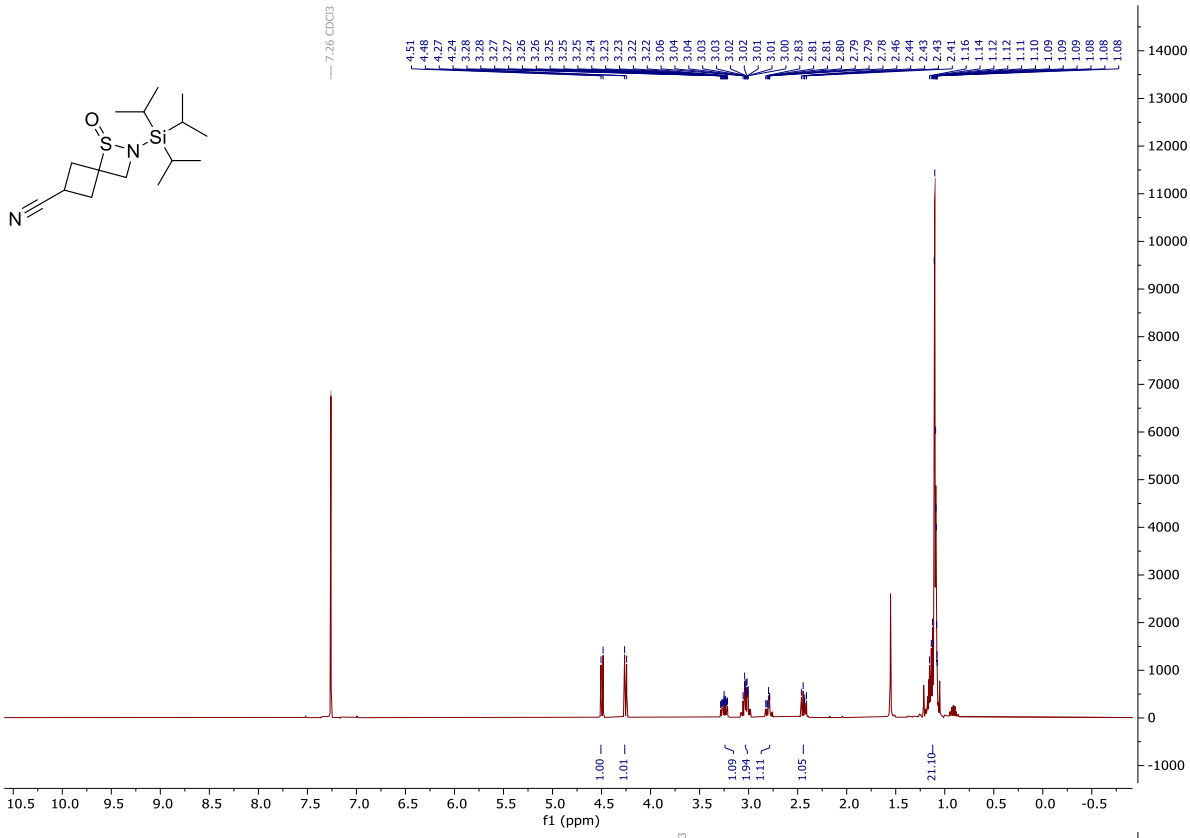


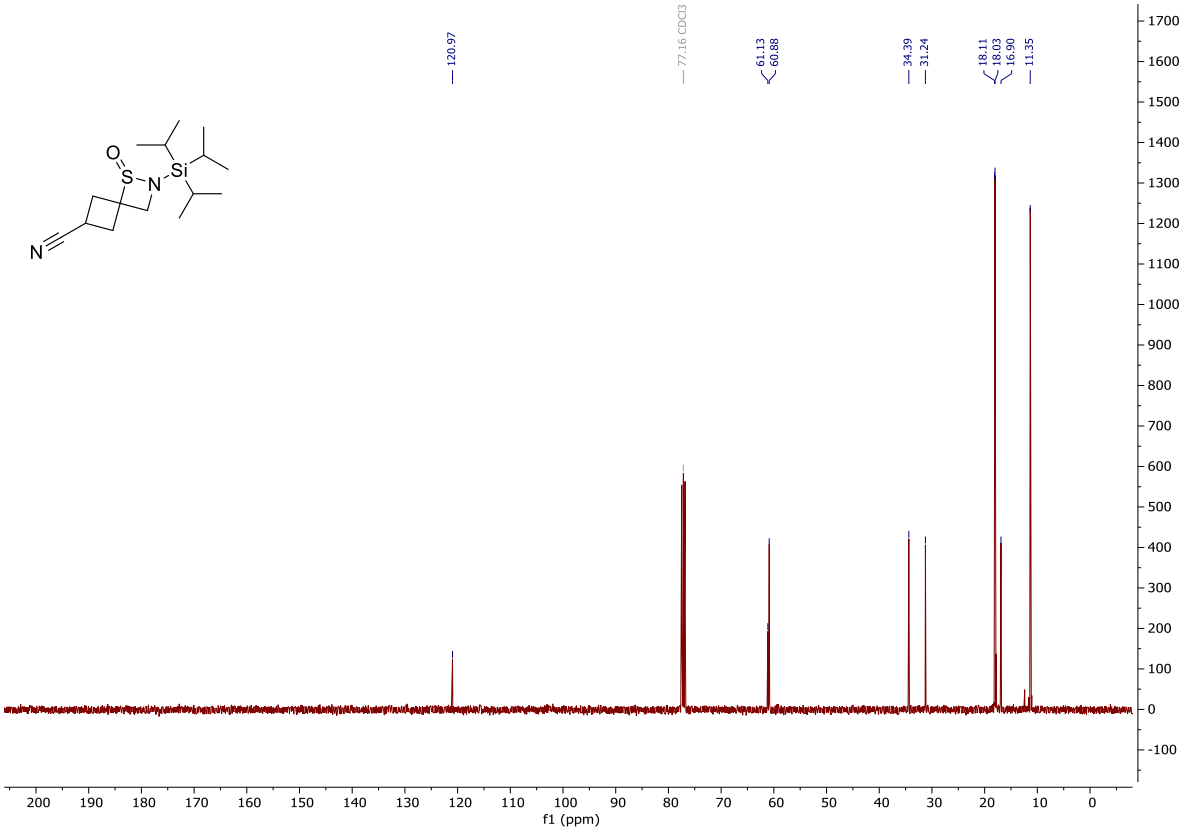
2-(Triisopropylsilyl)-4-(trimethylsilyl)-1,2-thiazetidine 1-oxide (1u-minor)



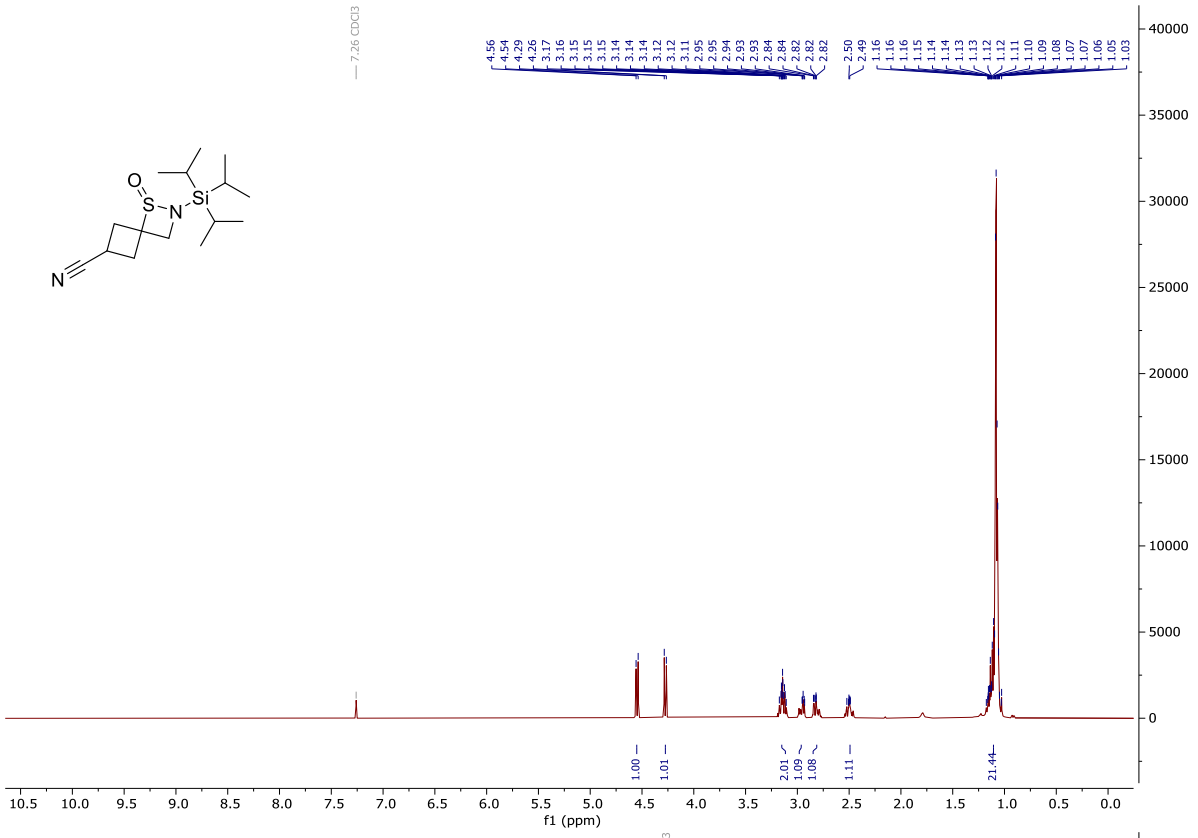


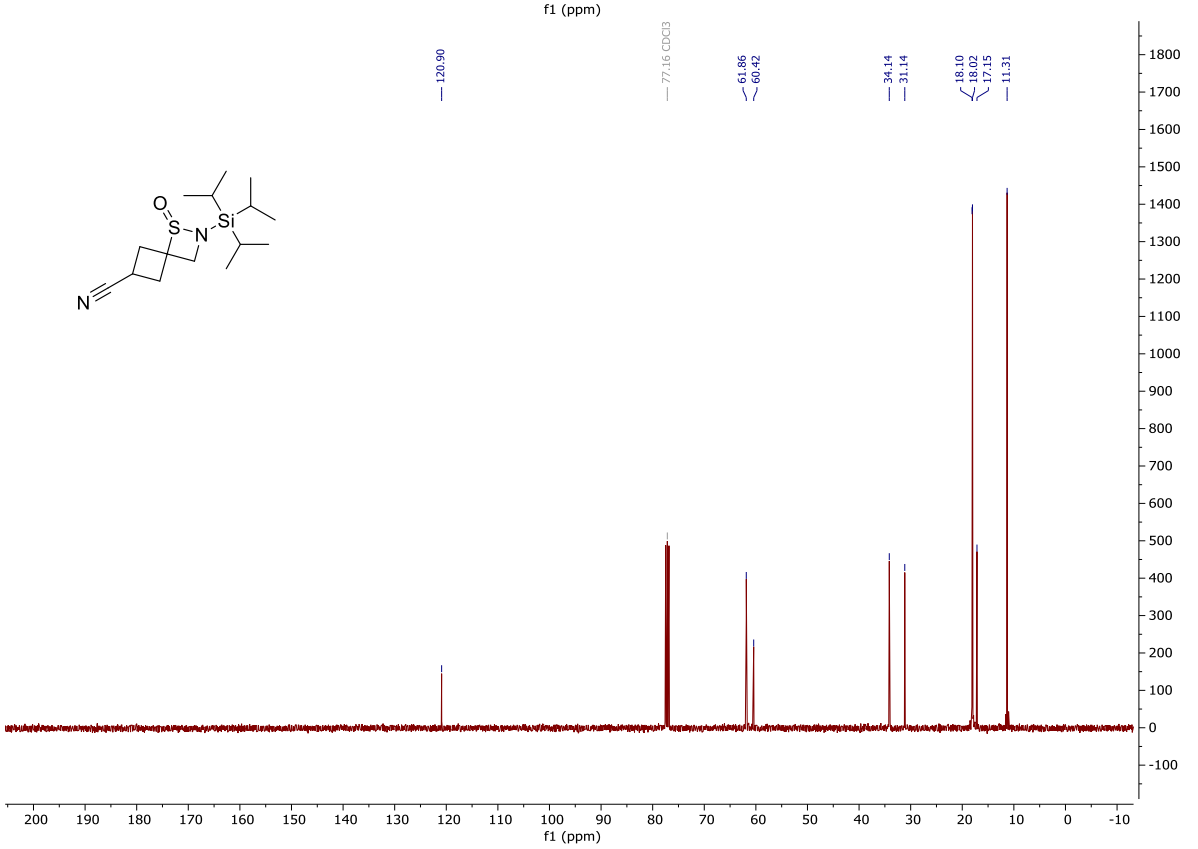
2-(Triisopropylsilyl)-1-thia-2-azaspiro[3.3]heptane-6-carbonitrile 1-oxide (1v-major)



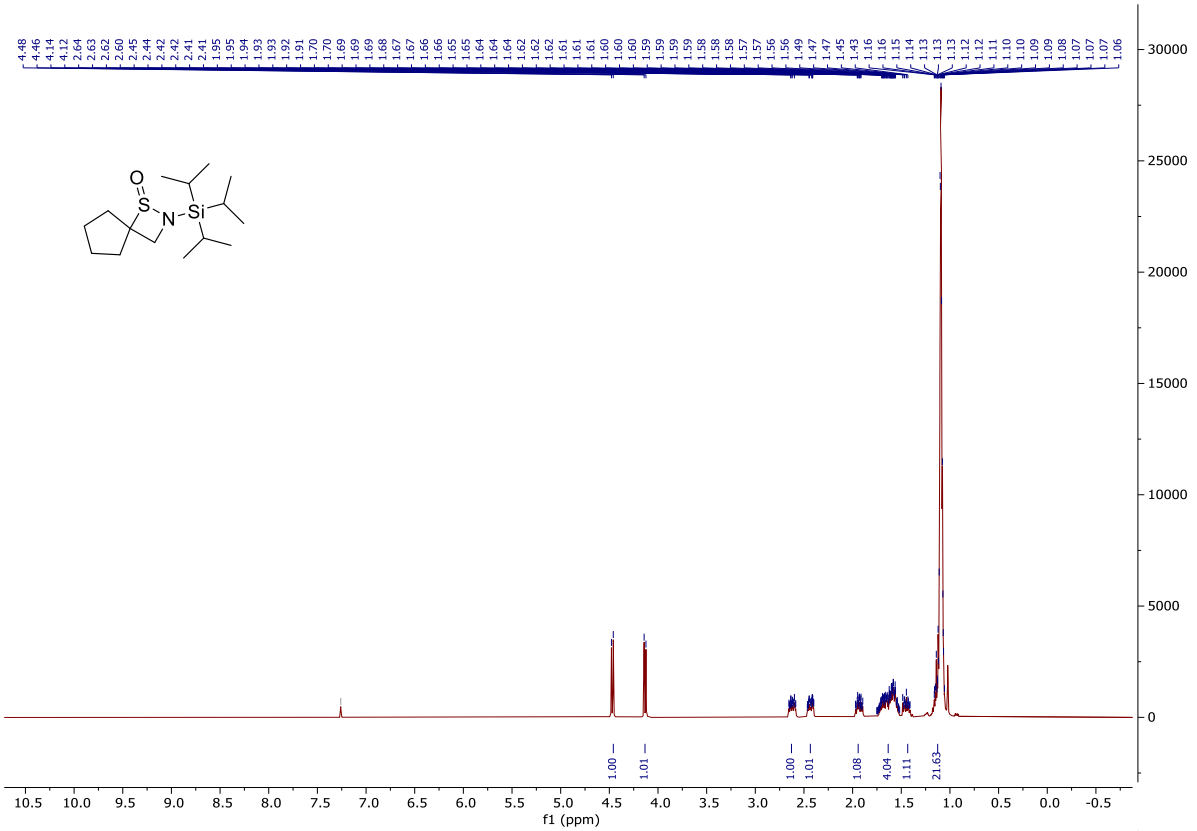


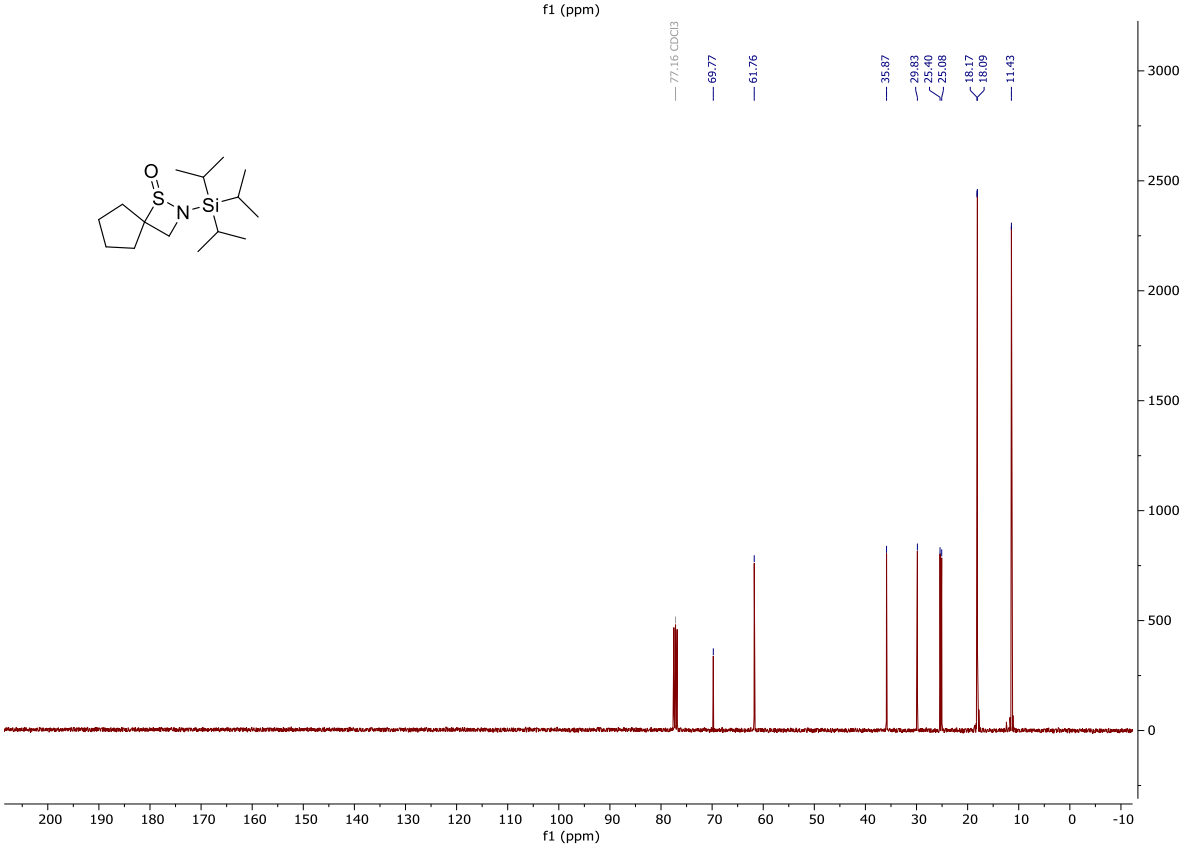
2-(Triisopropylsilyl)-1-thia-2-azaspiro[3.3]heptane-6-carbonitrile 1-oxide (1v-minor)



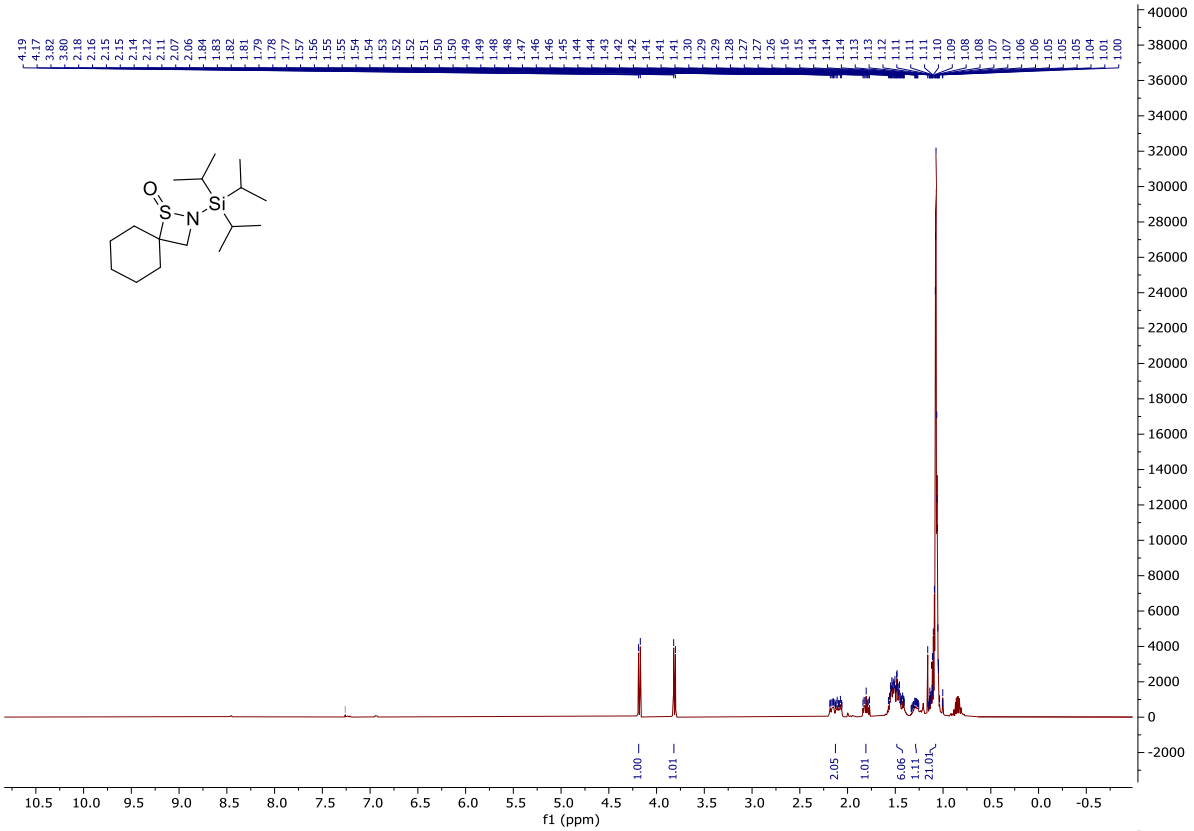


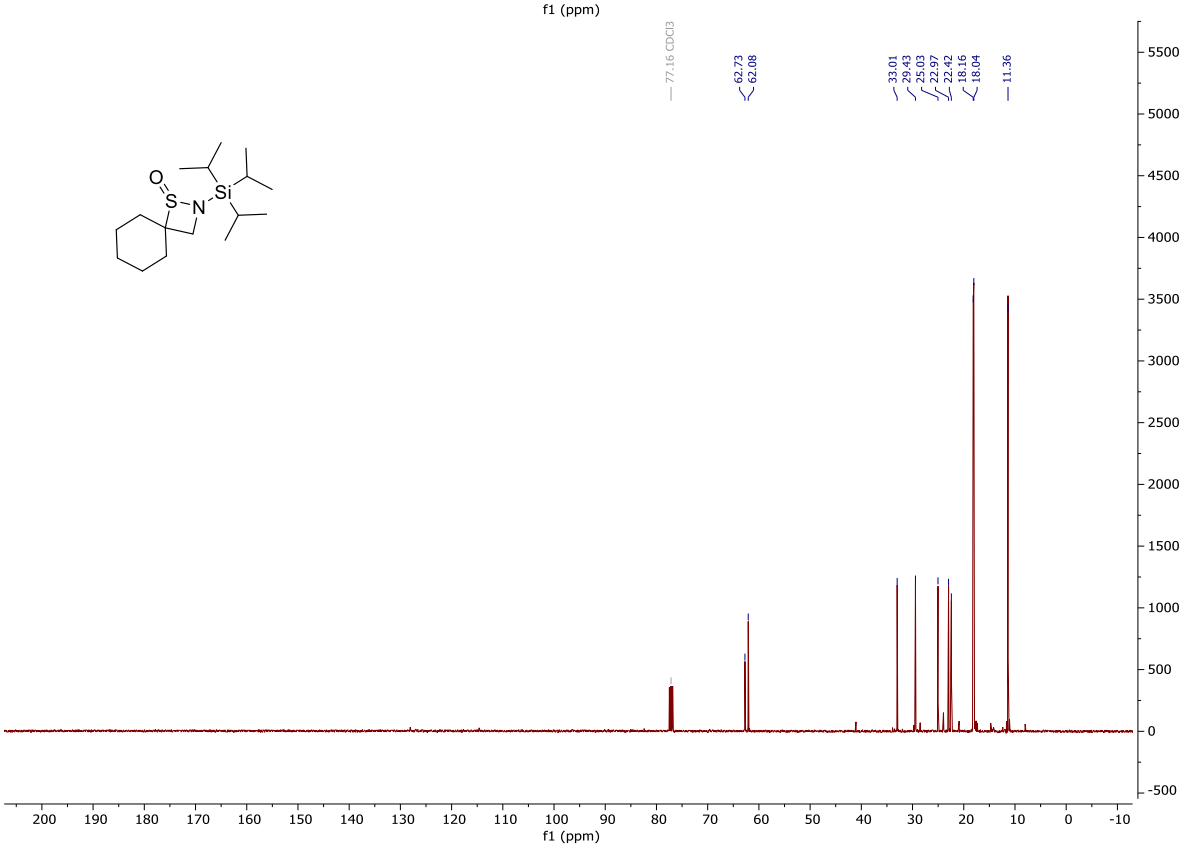
2-(Triisopropylsilyl)-1-thia-2-azaspiro[3.4]octane 1-oxide (1w)



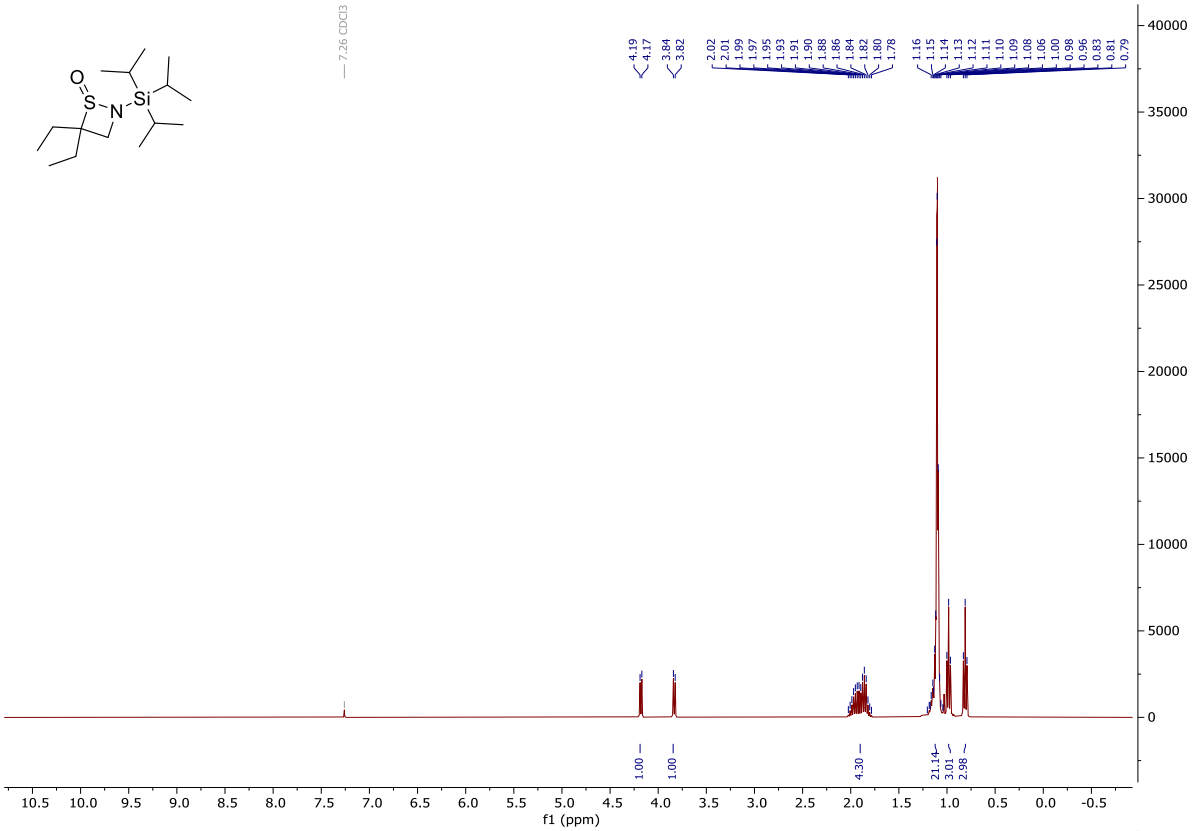


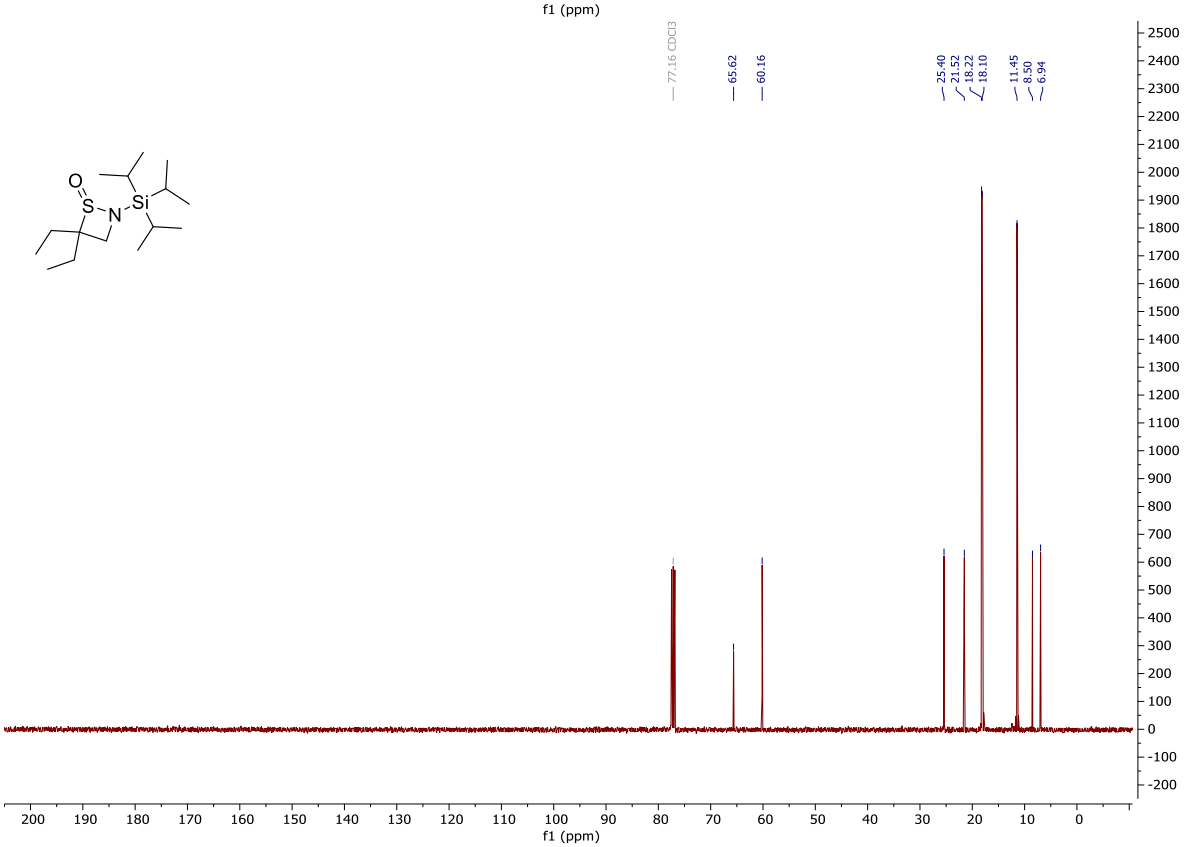
2-(Triisopropylsilyl)-1-thia-2-azaspiro[3.5]nonane 1-oxide (1x)



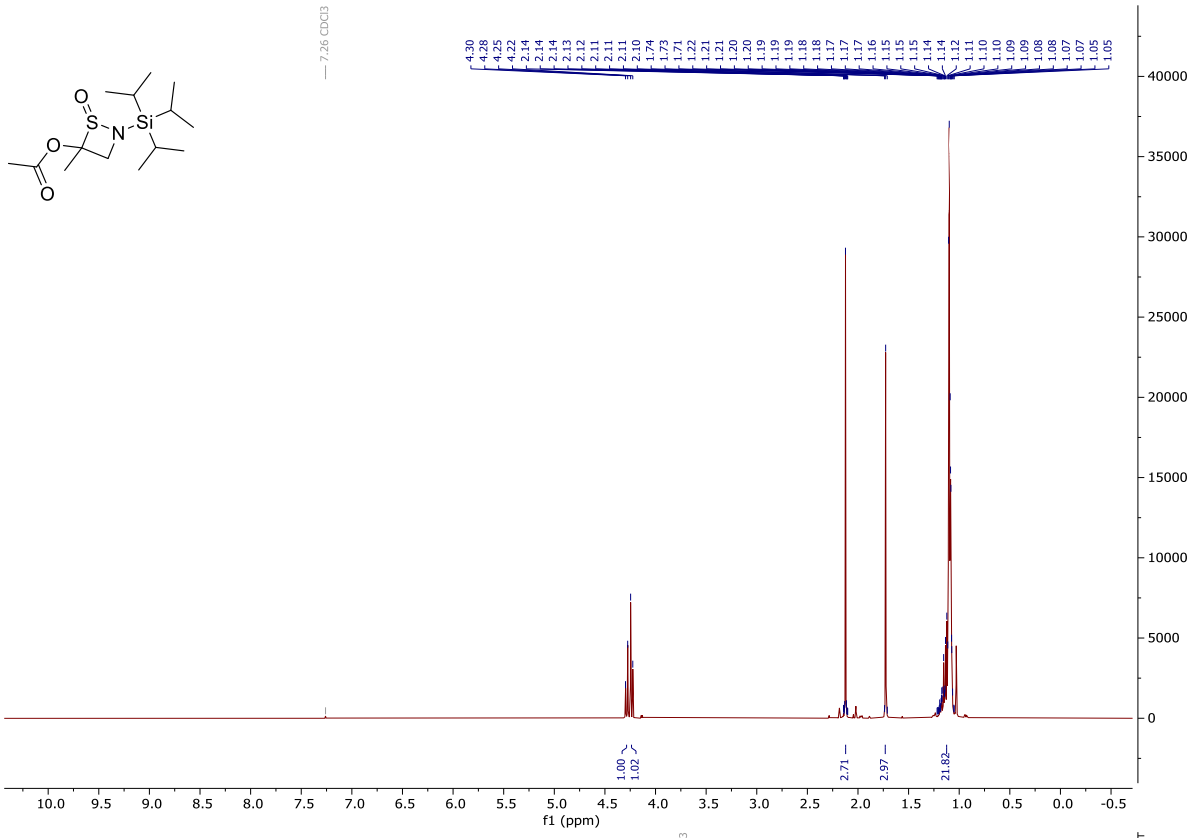


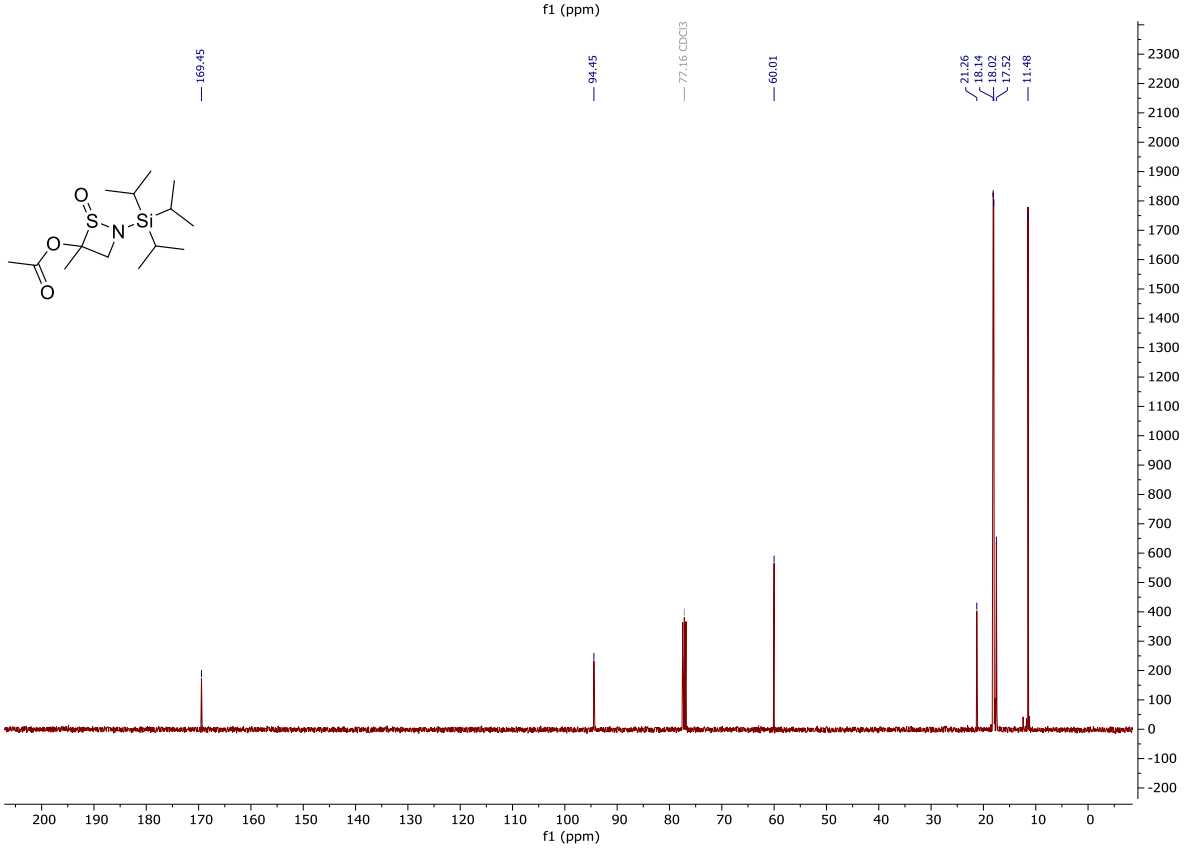
4,4-Diethyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1y)



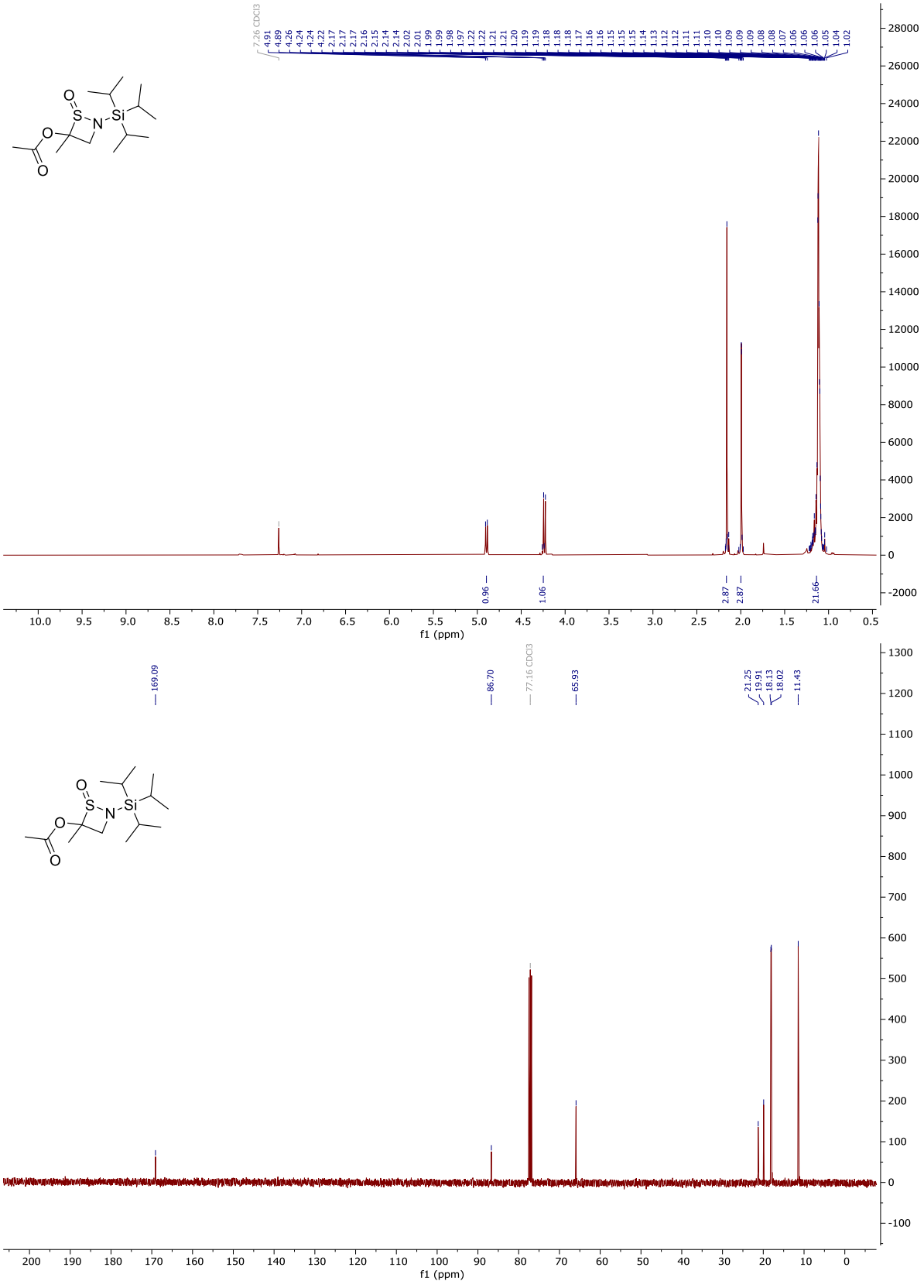


4-Methyl-1-oxido-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl acetate (1z-major)

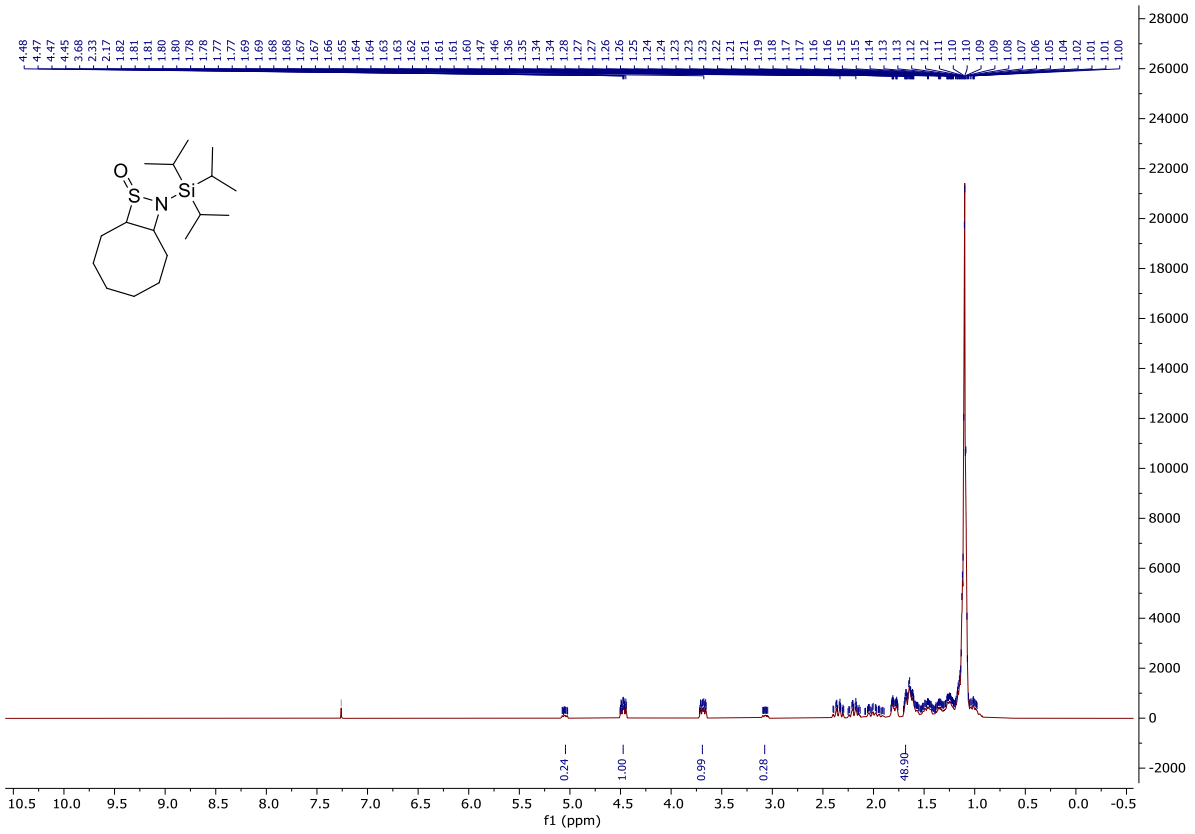


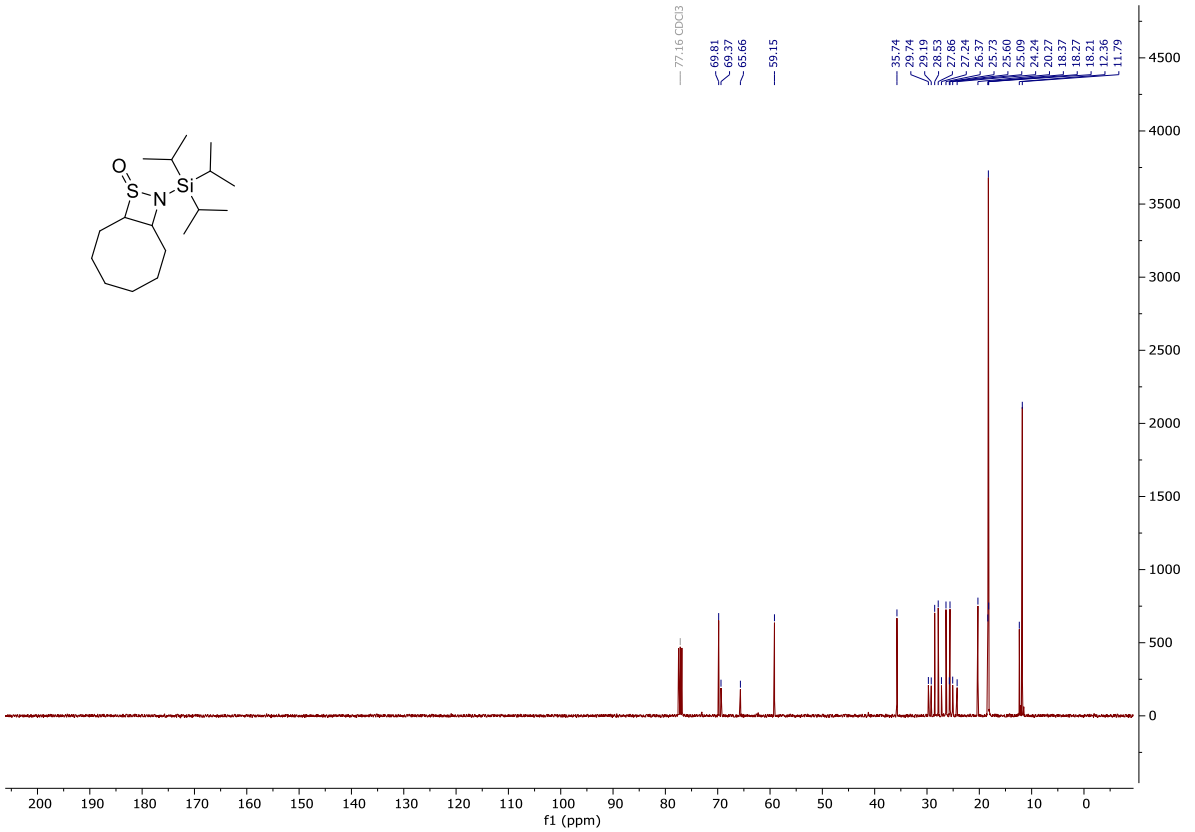


4-Methyl-1-oxido-2-(triisopropylsilyl)-1,2-thiazetidin-4-yl acetate (1z-minor)

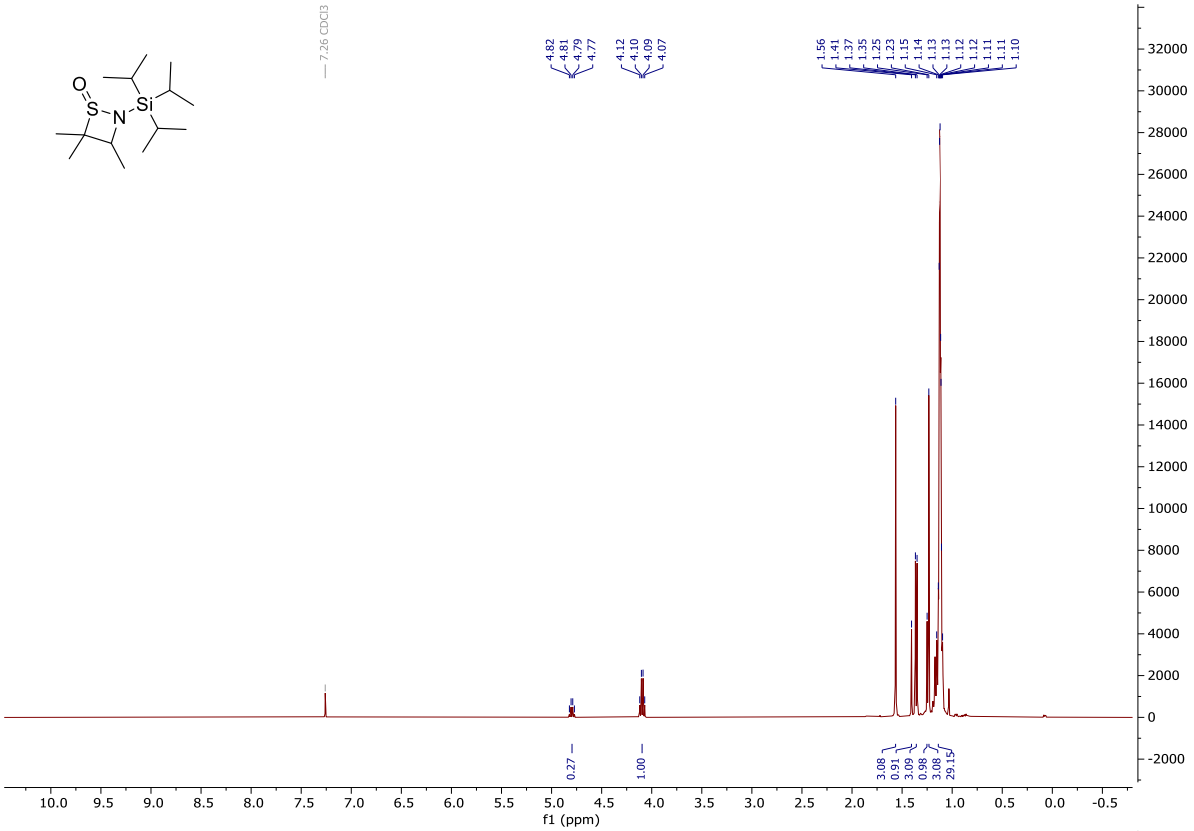


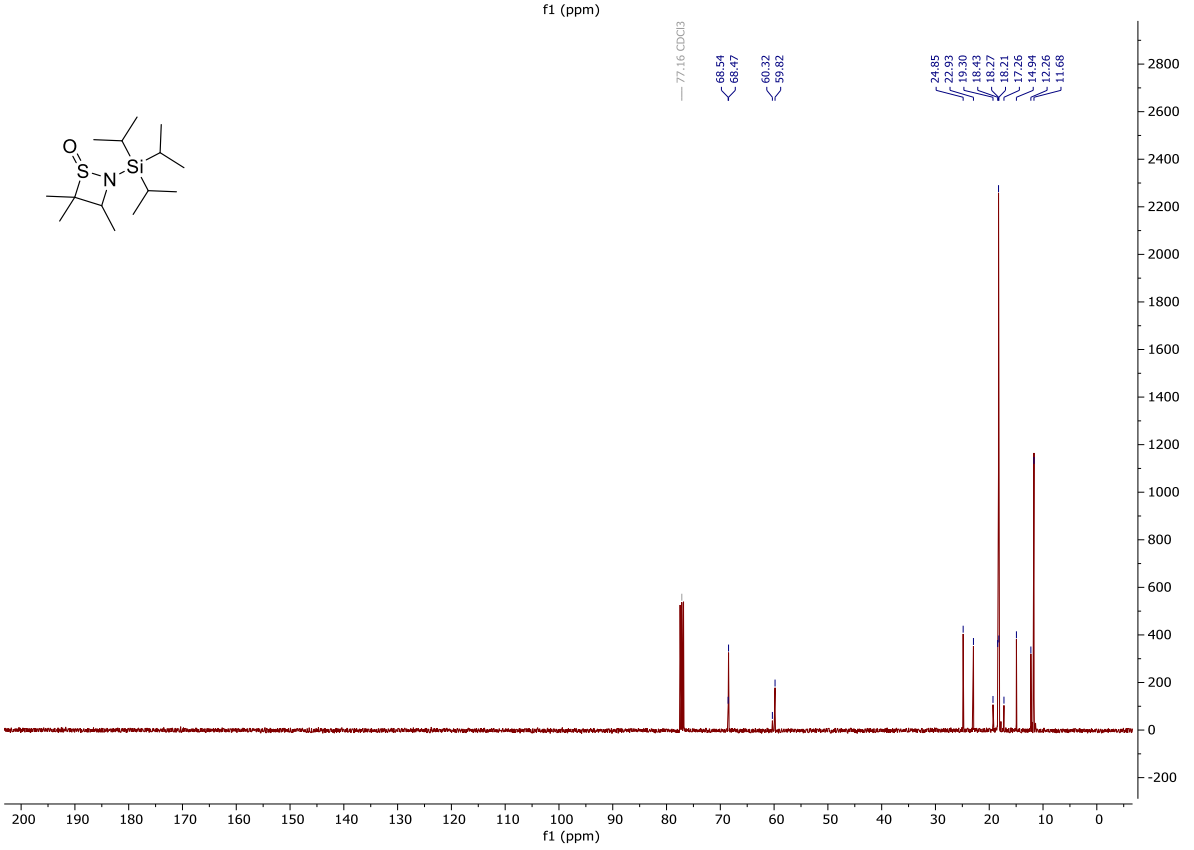
10-(Triisopropylsilyl)-9-thia-10-azabicyclo[6.2.0]decane 9-oxide (1aa)



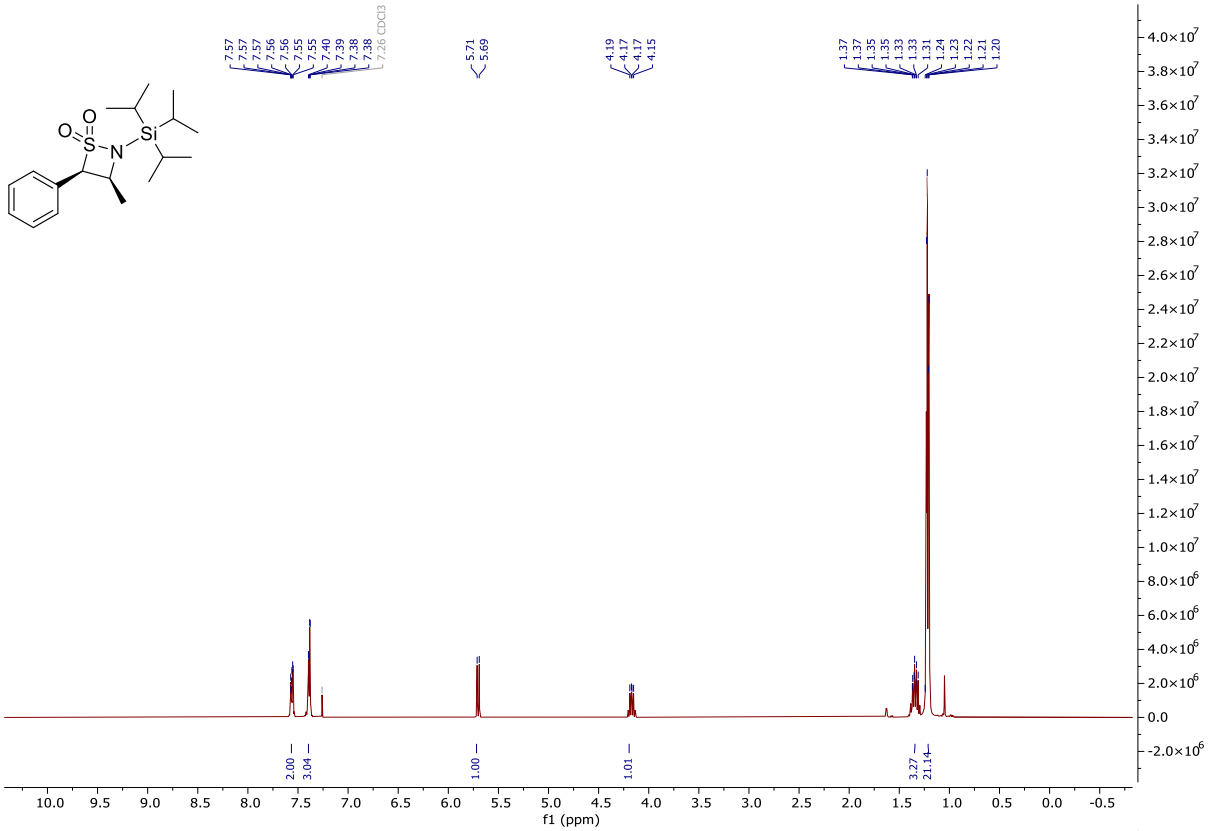


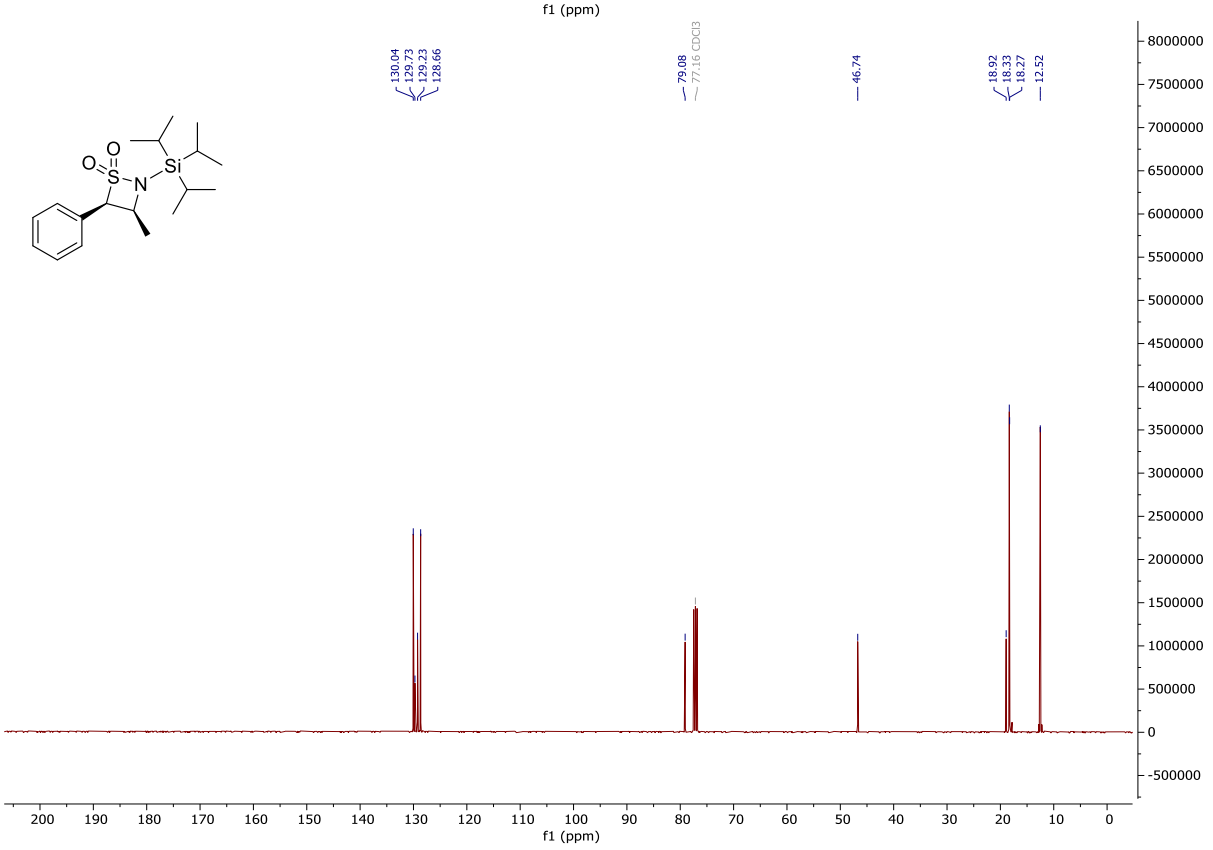
3,4,4-Trimethyl-2-(triisopropylsilyl)-1,2-thiazetidine 1-oxide (1ab)



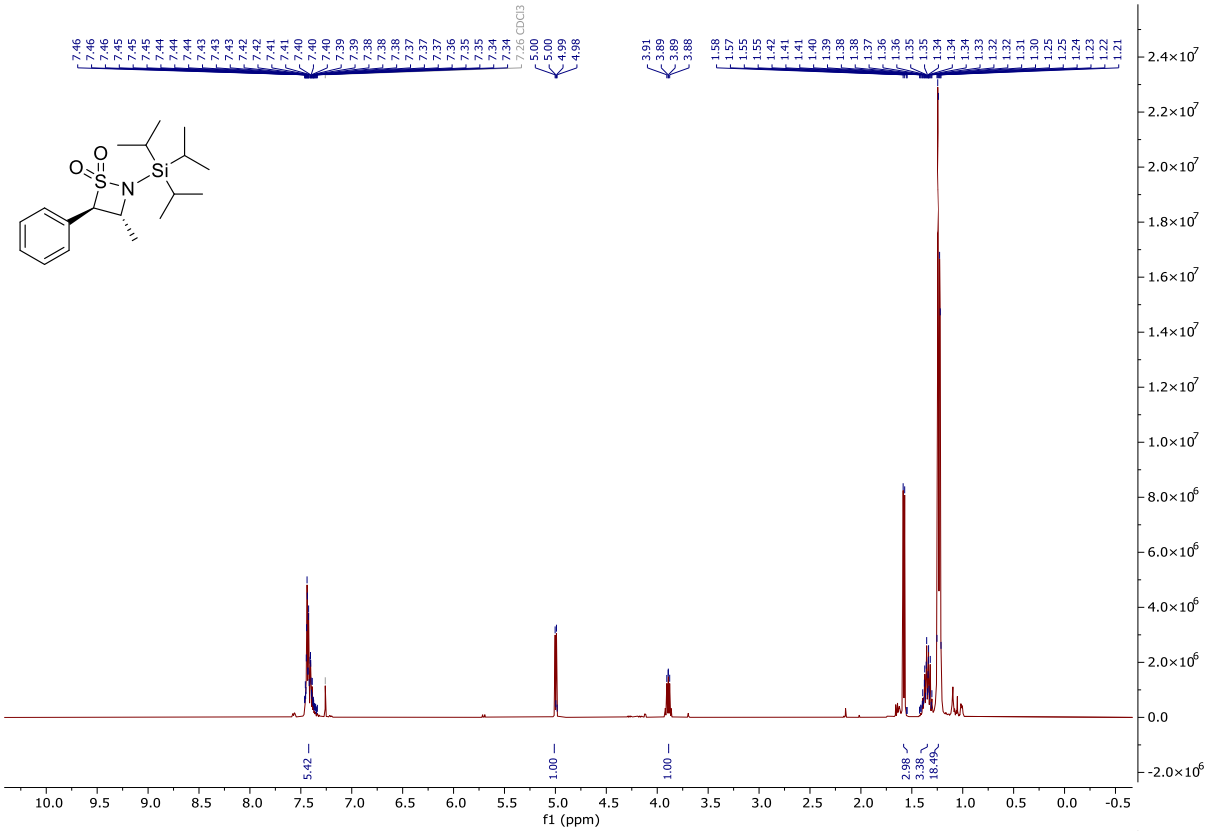


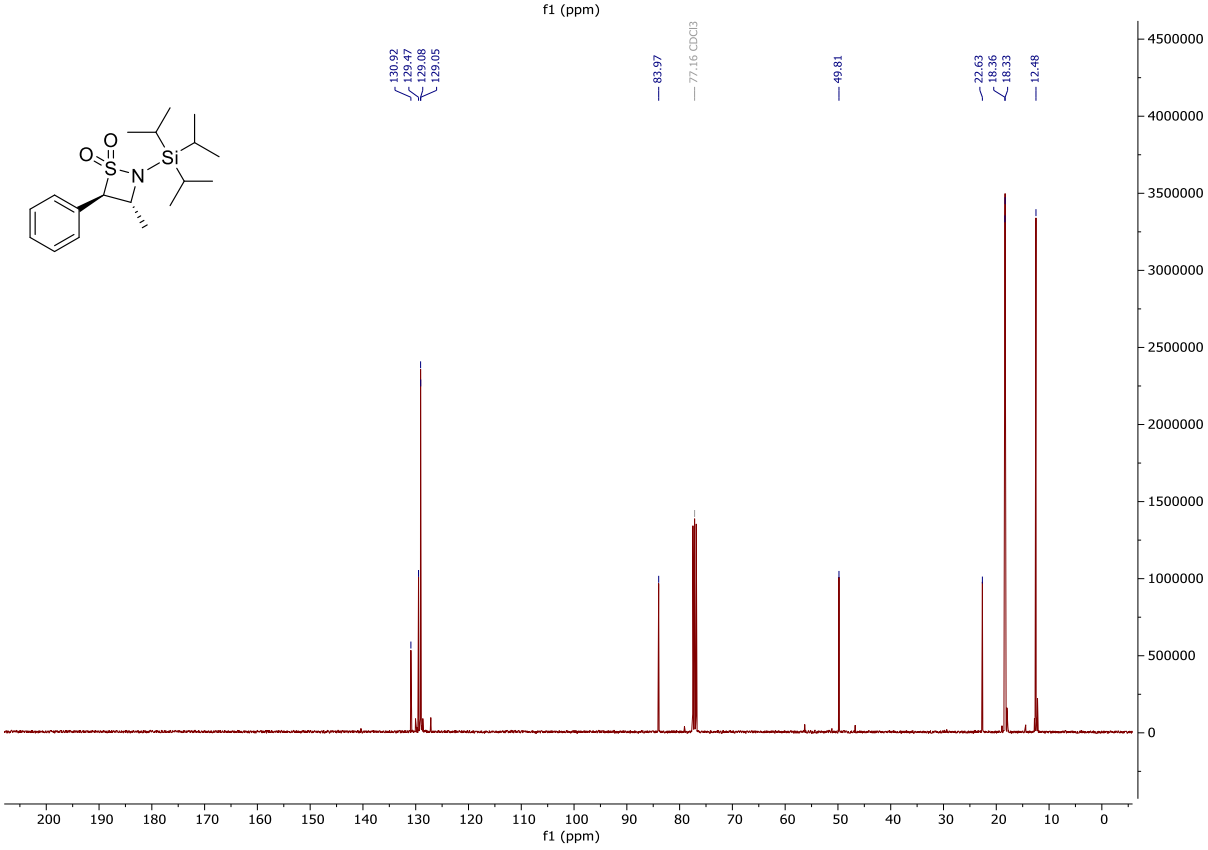
cis-3-Methyl-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1,1-dioxide (*cis*-2ω)



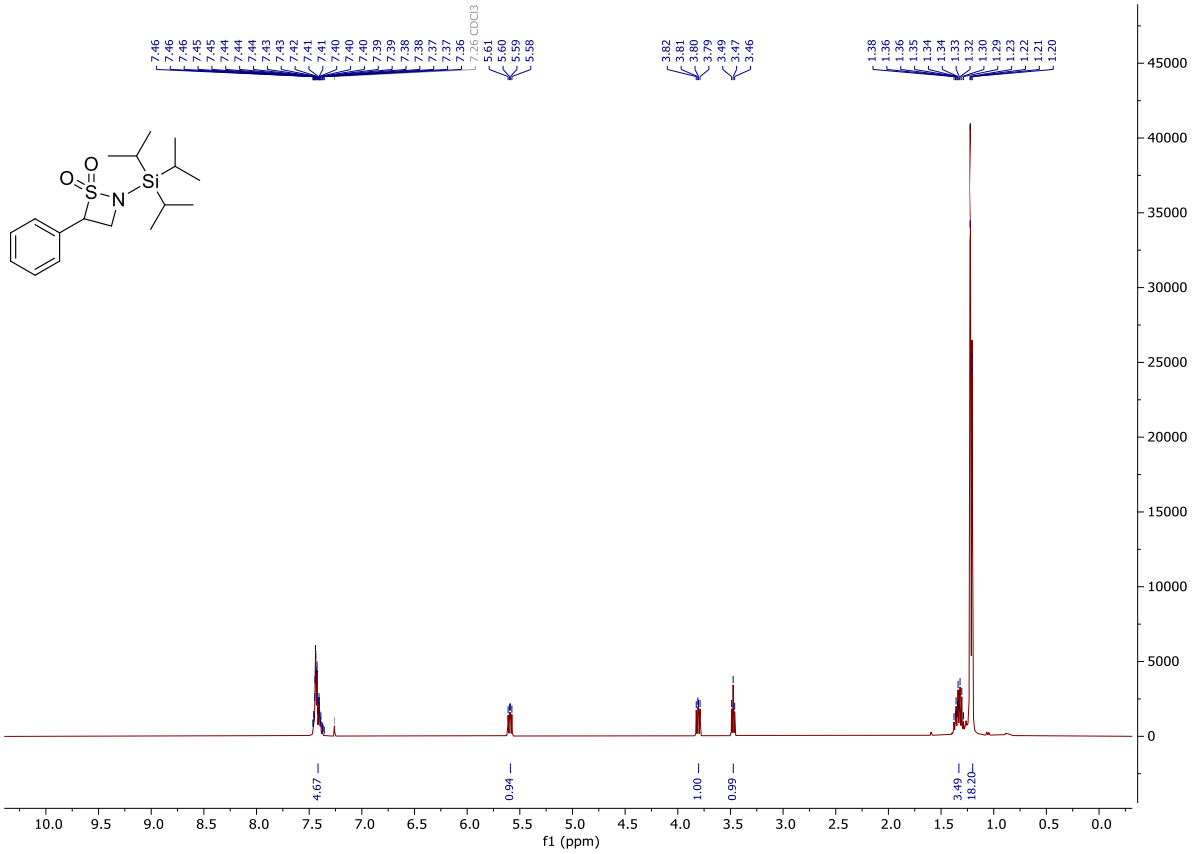


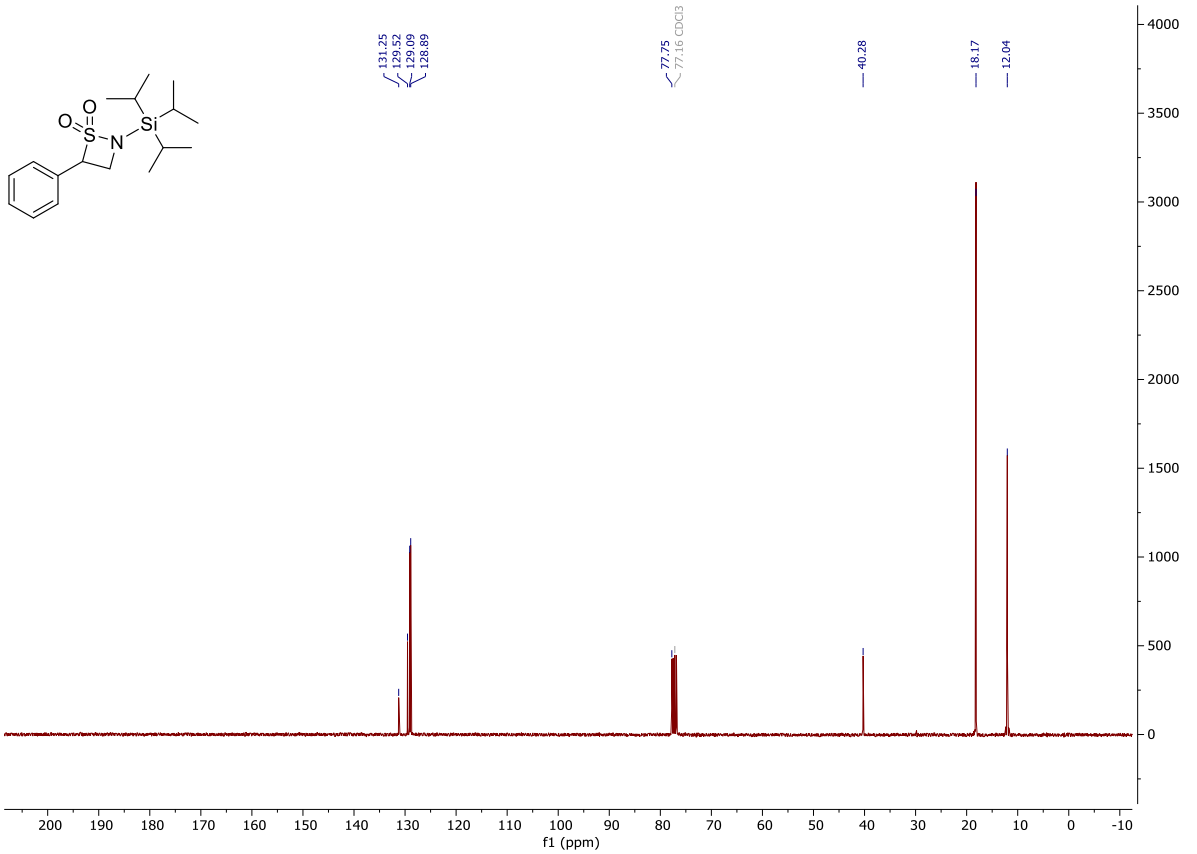
trans-3-Methyl-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1,1-dioxide (*trans*-2ω)



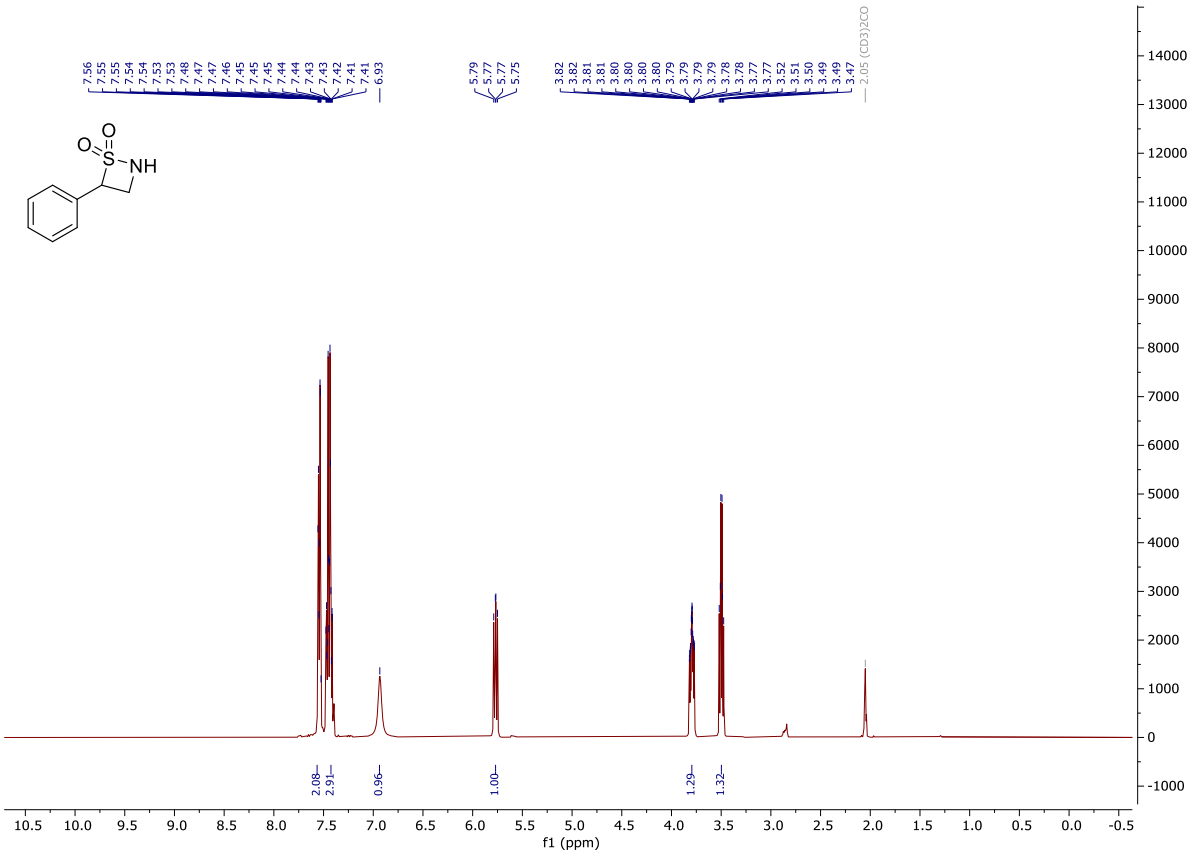


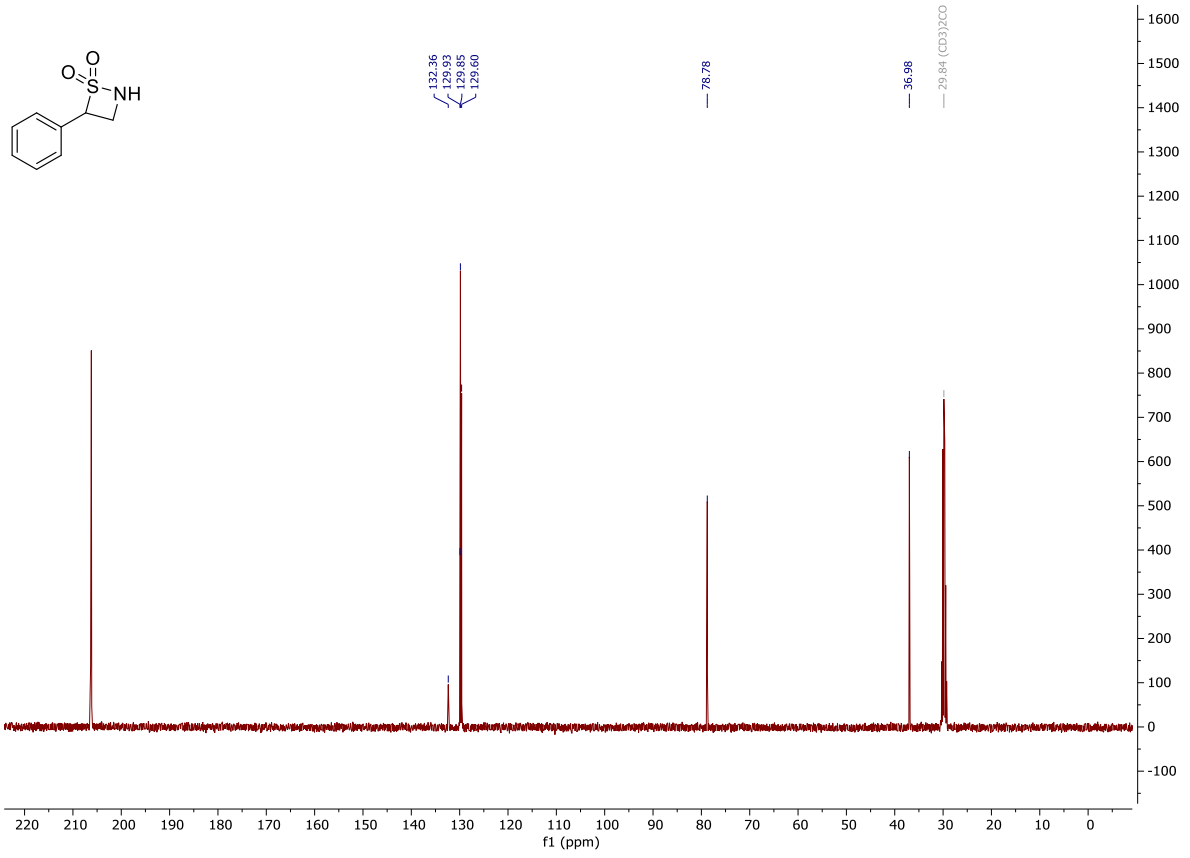
4-Phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1,1-dioxide (2a)


7.46
7.46
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3.46
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1.35
1.34
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1.33
1.32
1.30
1.29
1.23
1.22
1.21
1.20
O
O
S
N
Si
4.67
0.94
1.00
0.99
3.49
18.20
f1 (ppm)

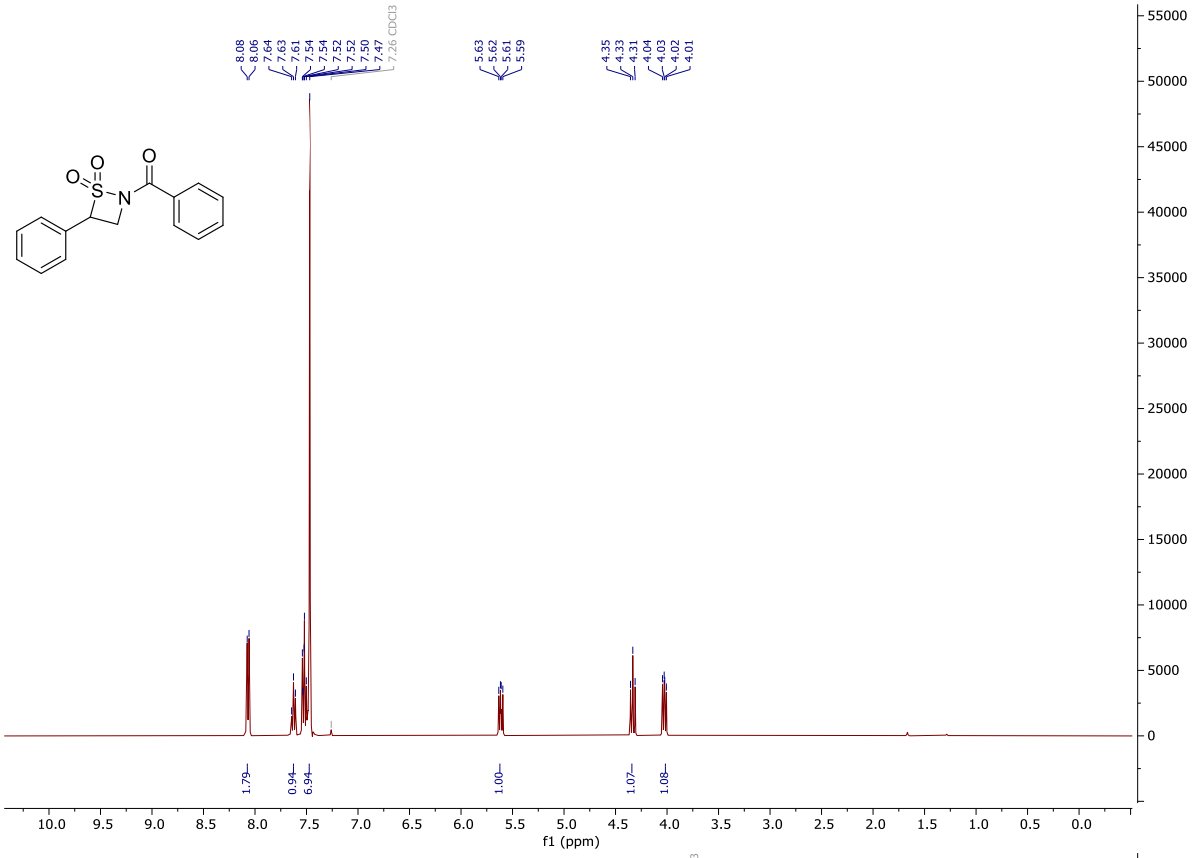

131.25
129.52
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77.75
77.16 CDCl3
40.28
18.17
12.04
O
O
S
N
Si
f1 (ppm)

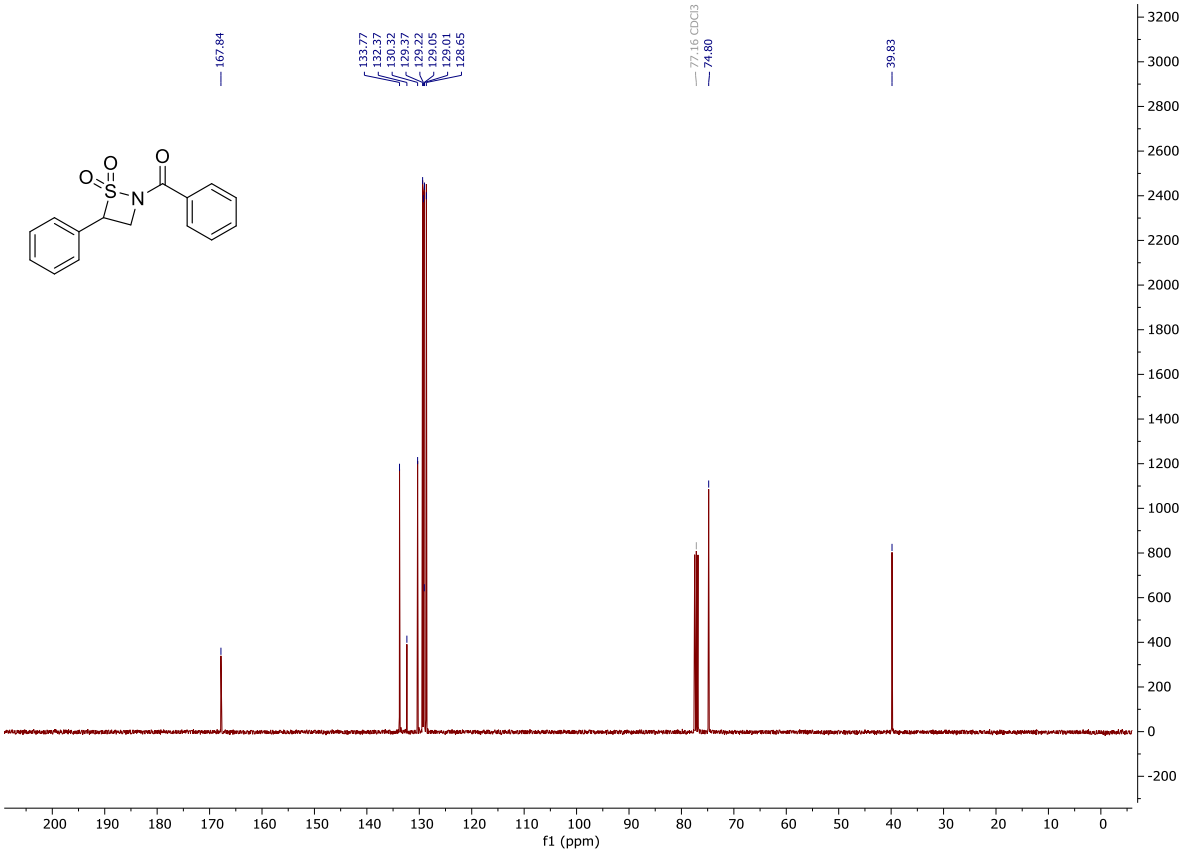
4-Phenyl-1,2-thiazetidine 1,1-dioxide (2aa)



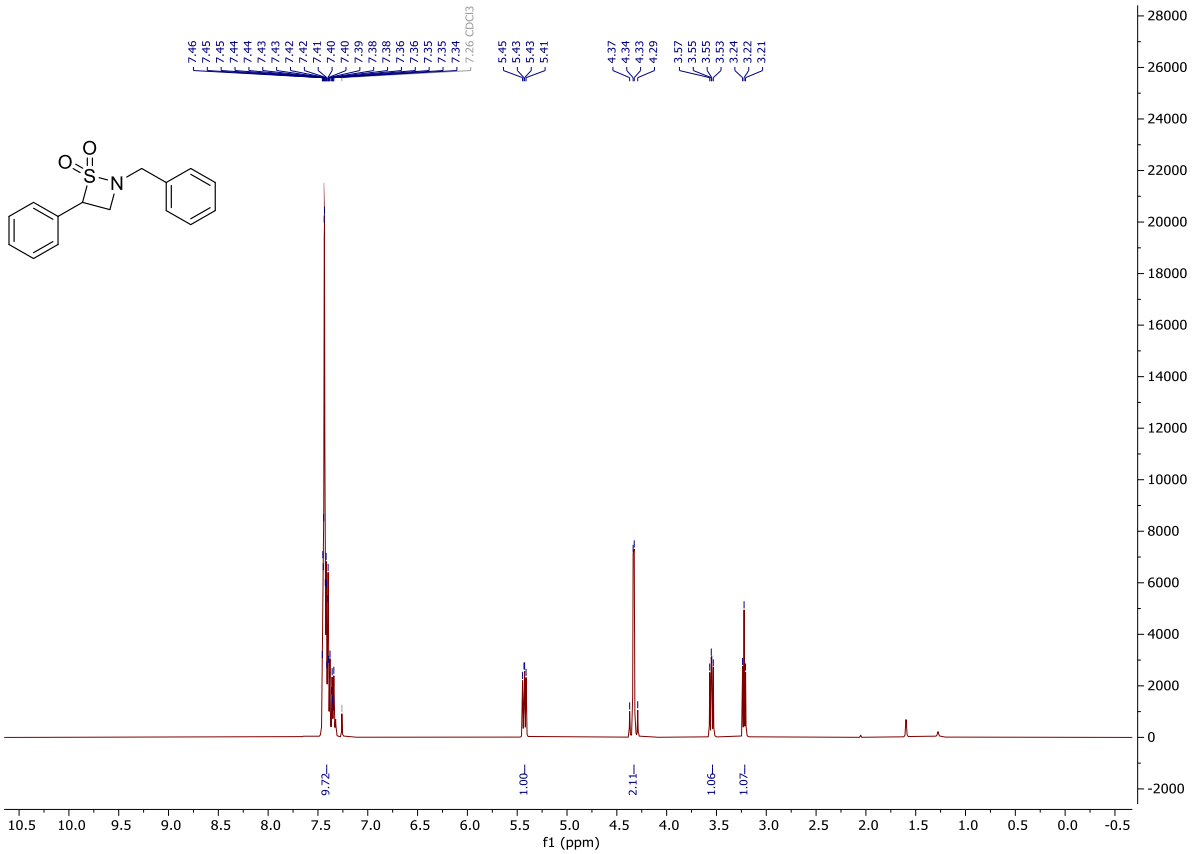


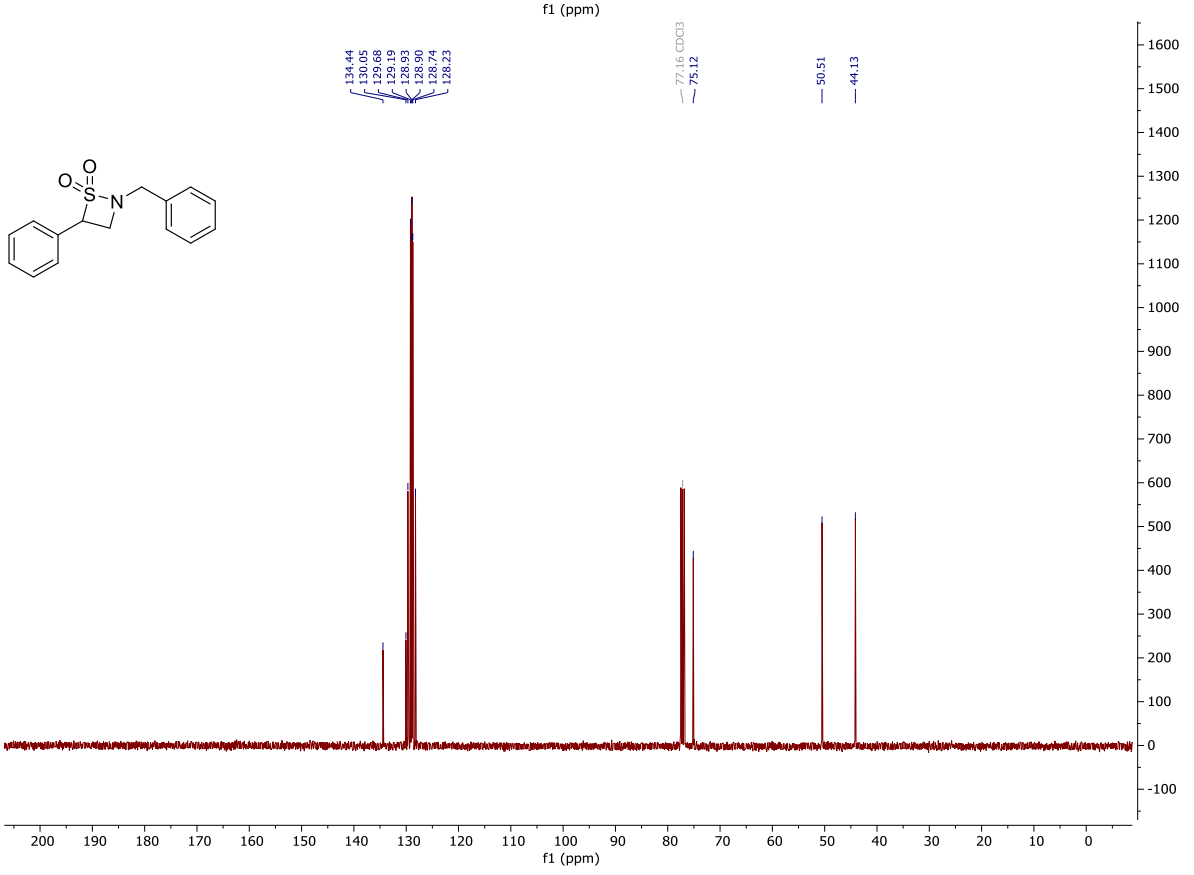
(1,1-Dioxido-4-phenyl-1,2-thiazetidin-2-yl)(phenyl)methanone (2ab)



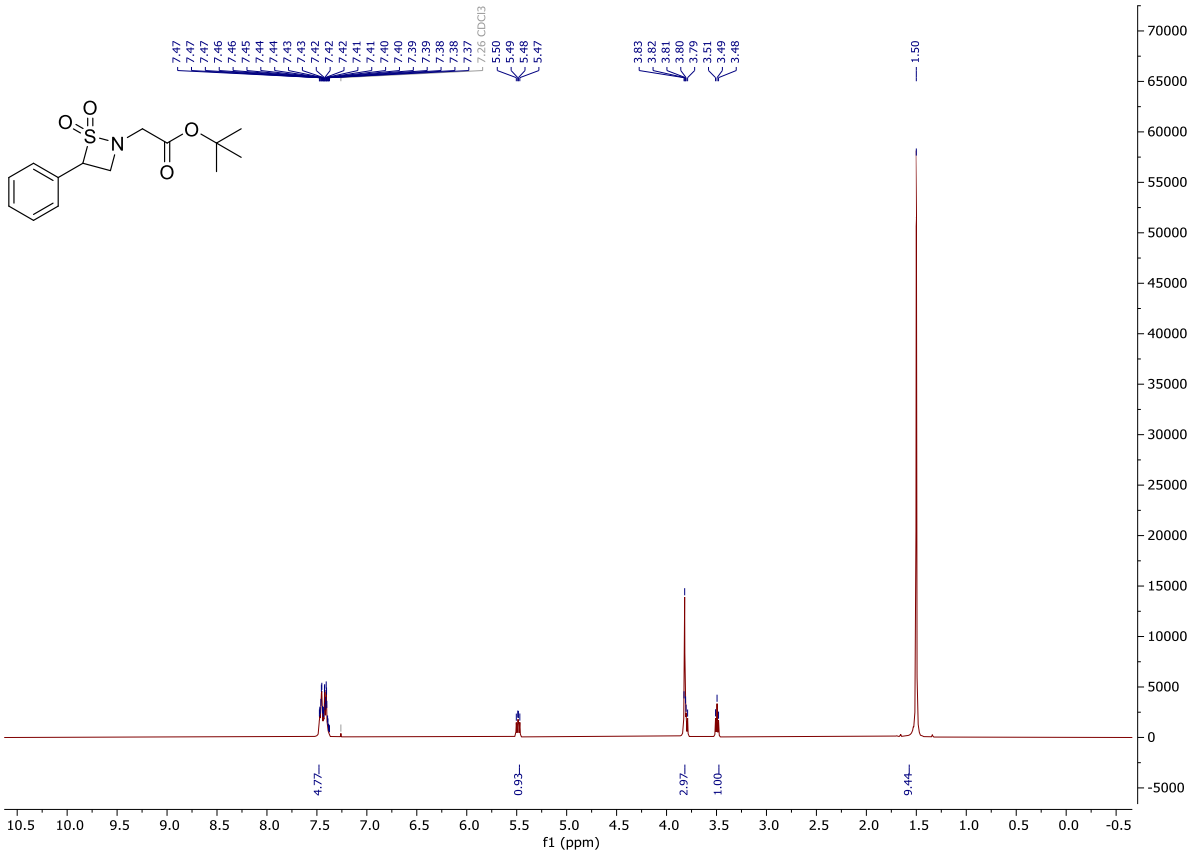


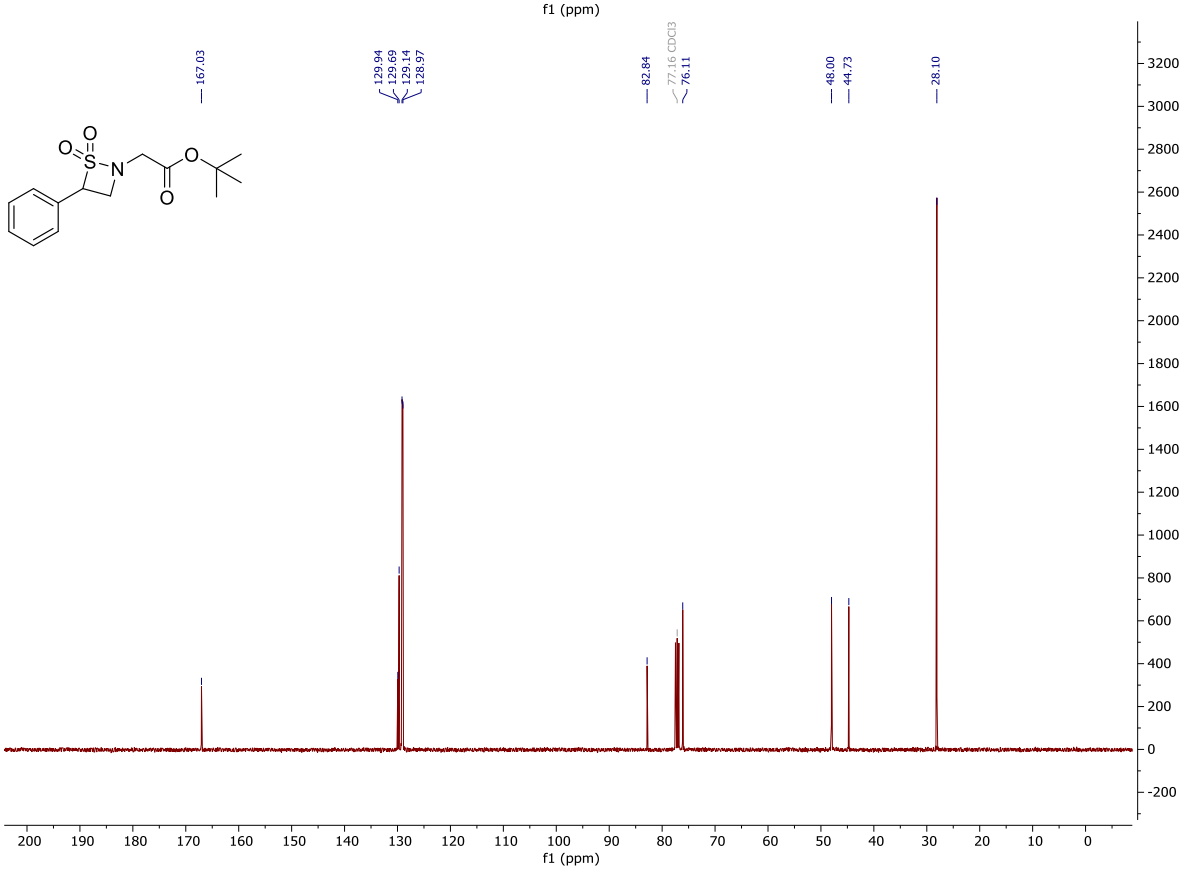
2-Benzyl-4-phenyl-1,2-thiazetidine 1,1-dioxide (2ac)



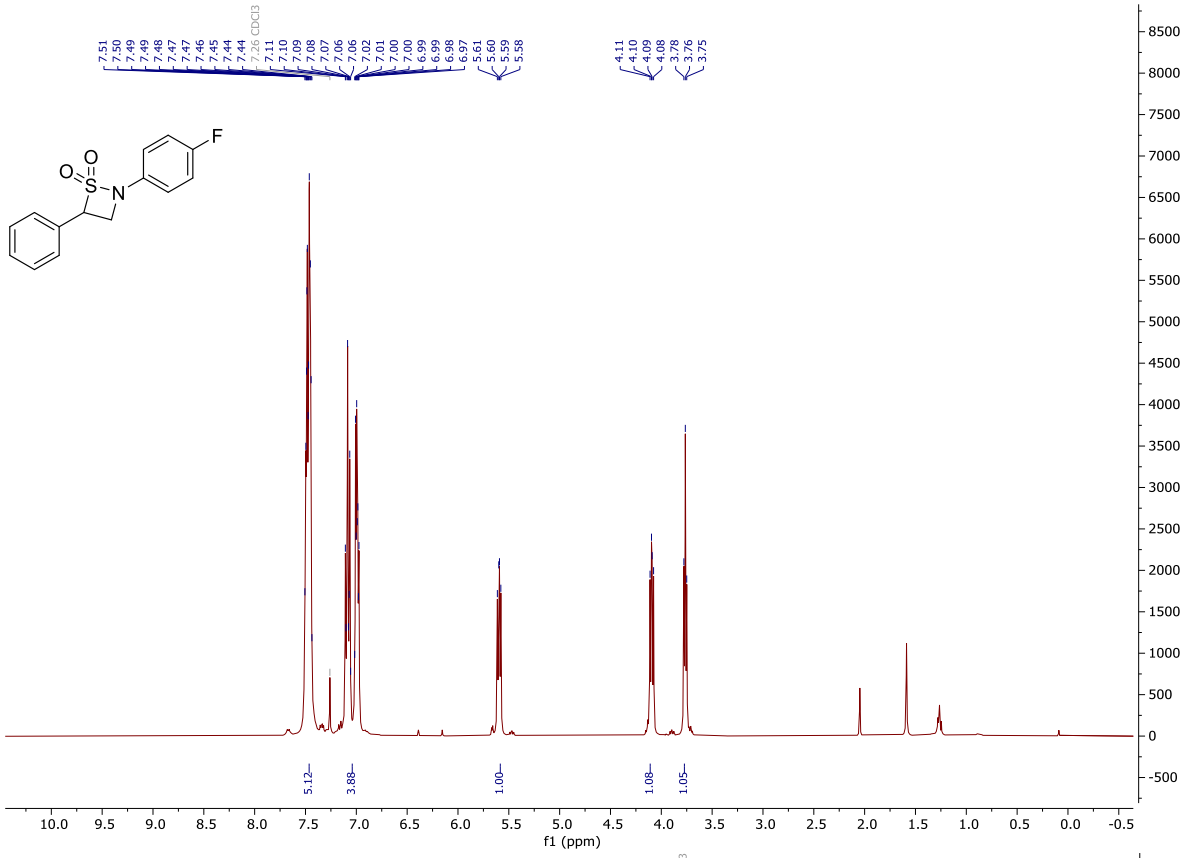


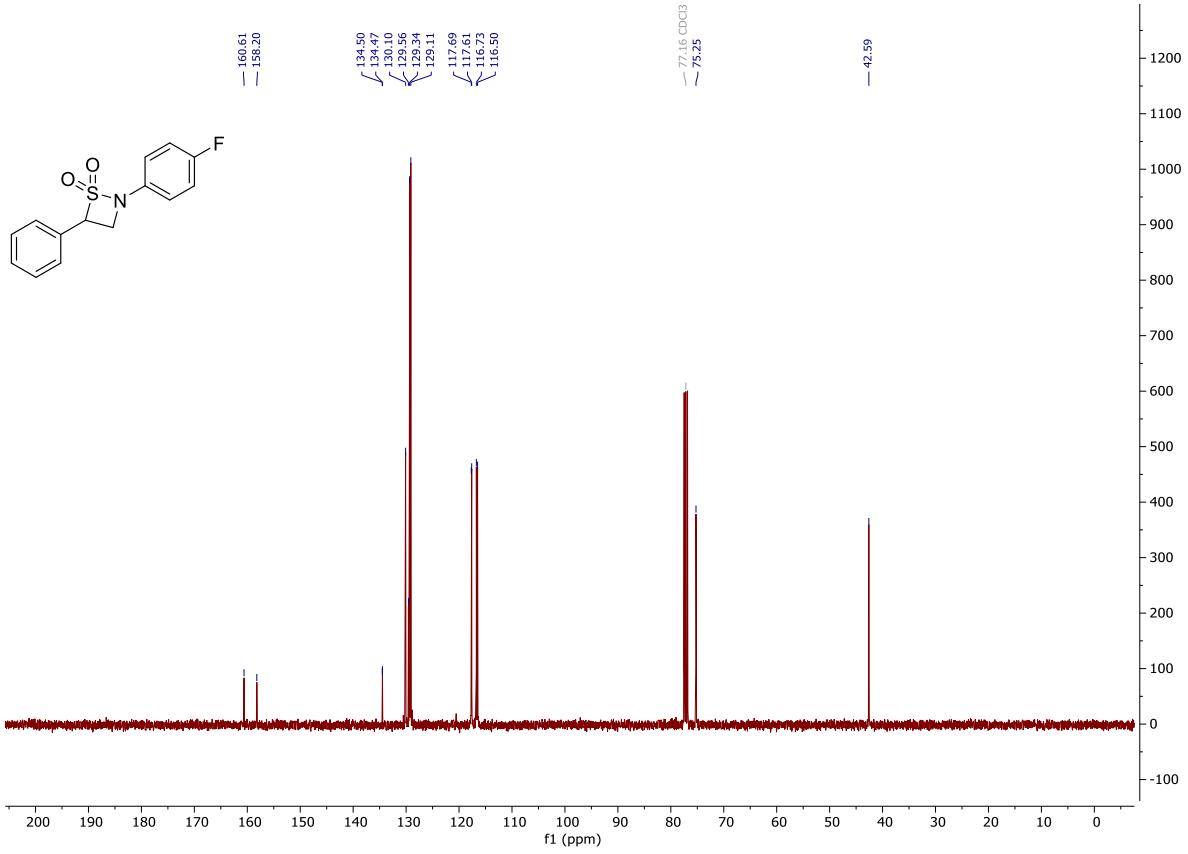
tert-Butyl 2-(1,1-dioxido-4-phenyl-1,2-thiazetidin-2-yl)acetate (2ad)

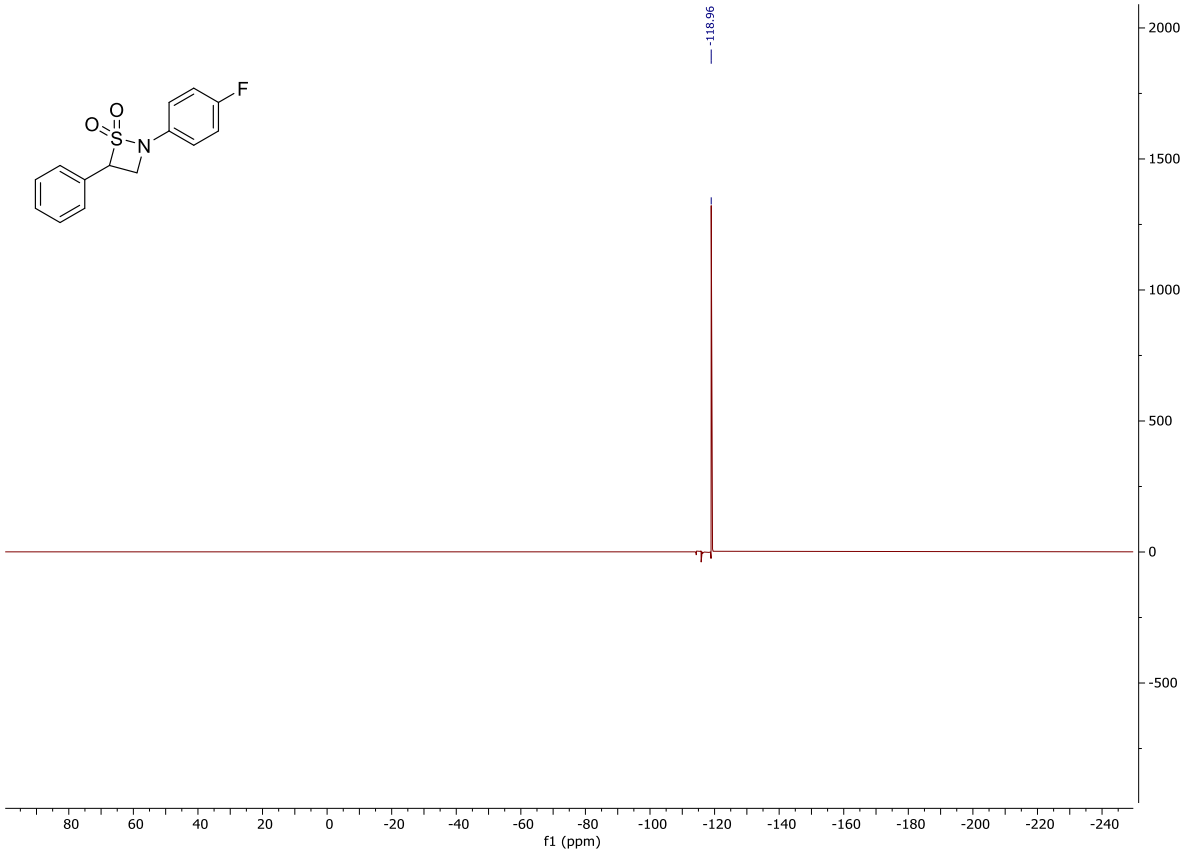




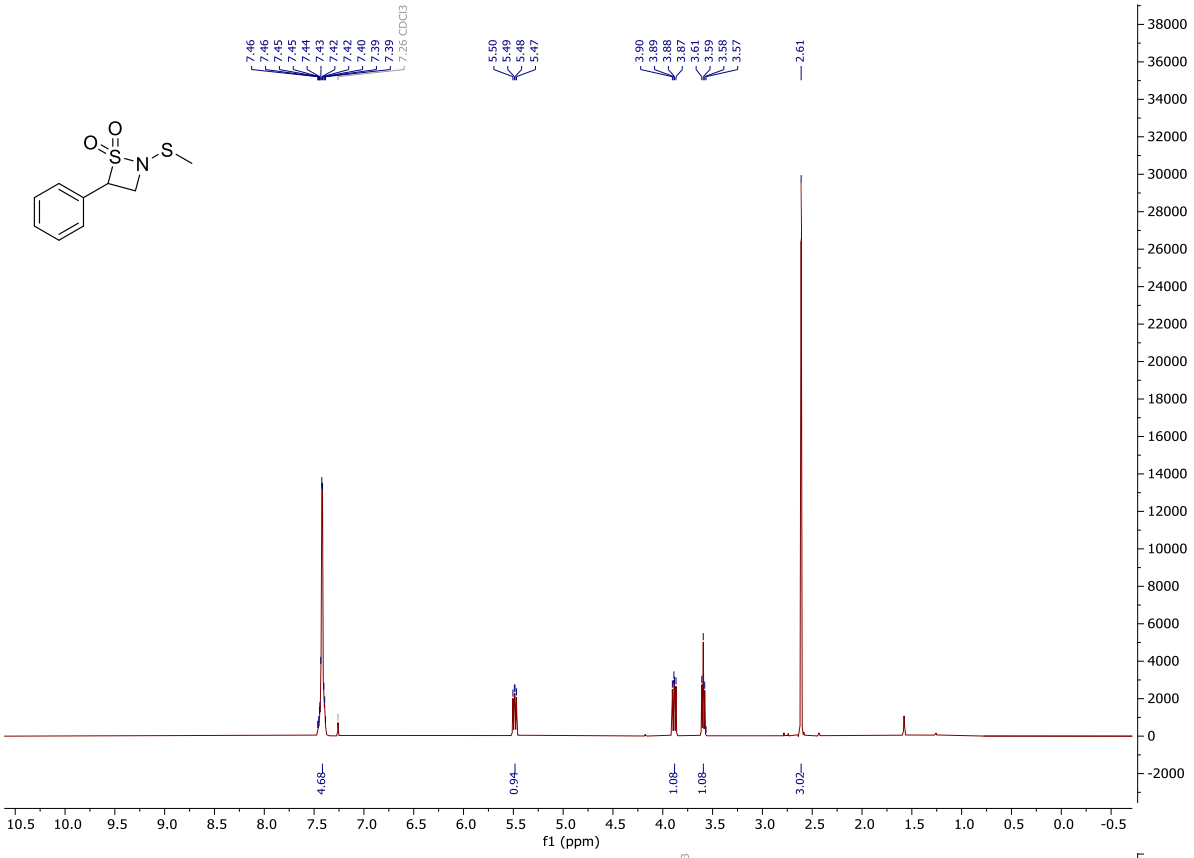
2-(4-Fluorophenyl)-4-phenyl-1,2-thiazetidine 1,1-dioxide (2ae)

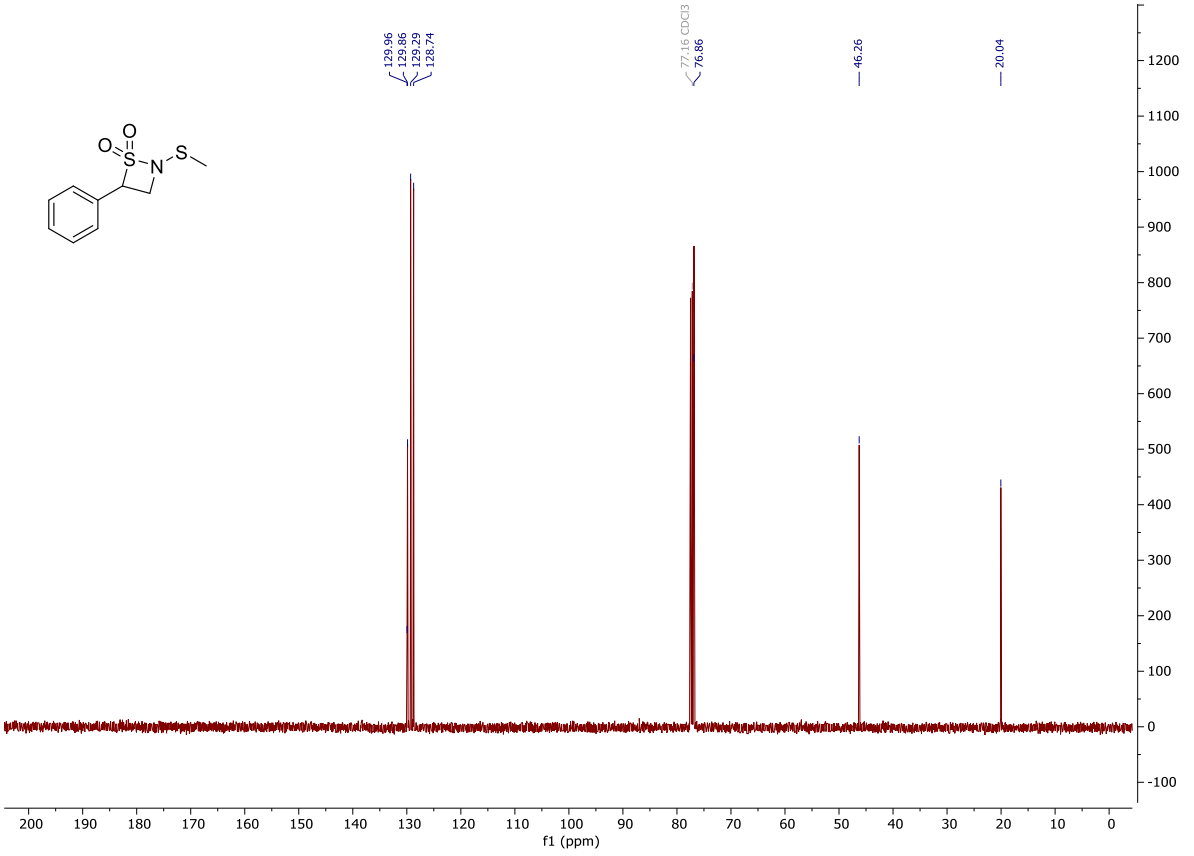




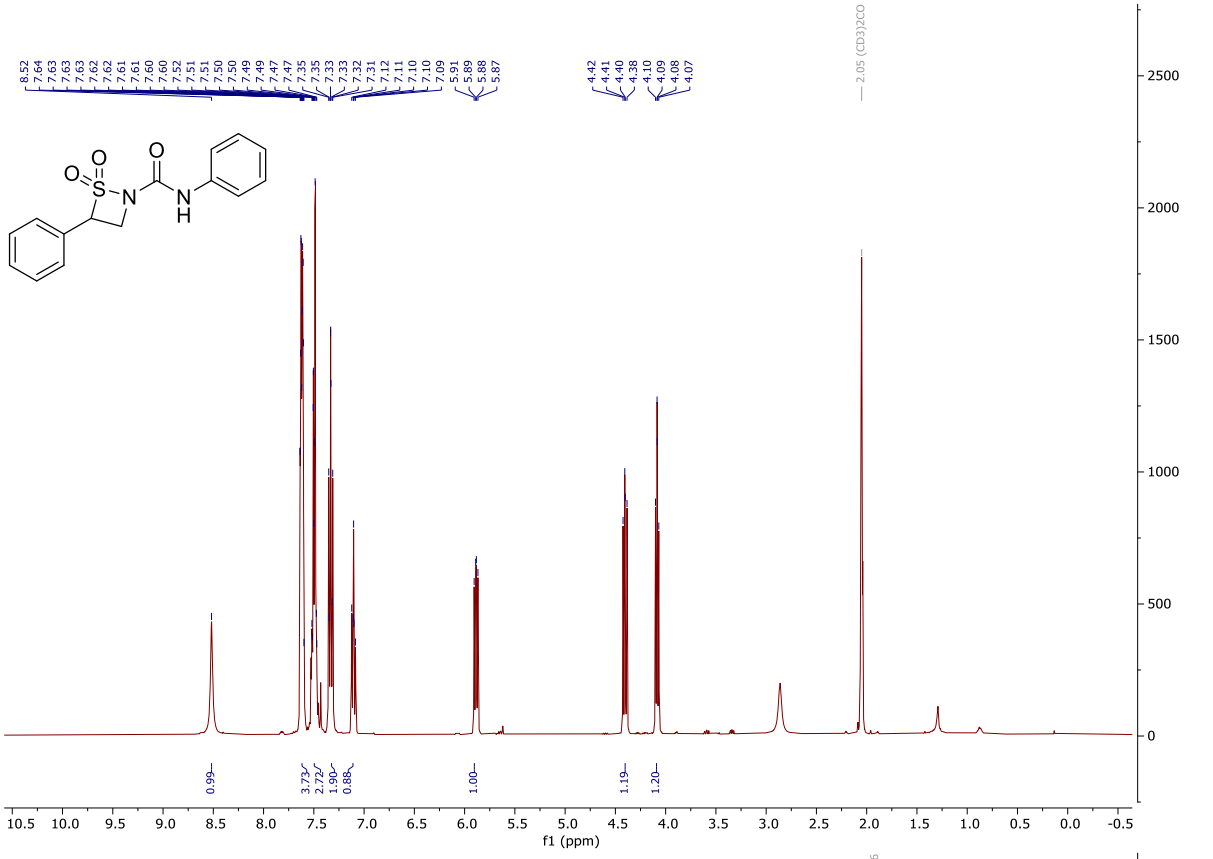

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1000
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0
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-40
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O
O
S
N
F

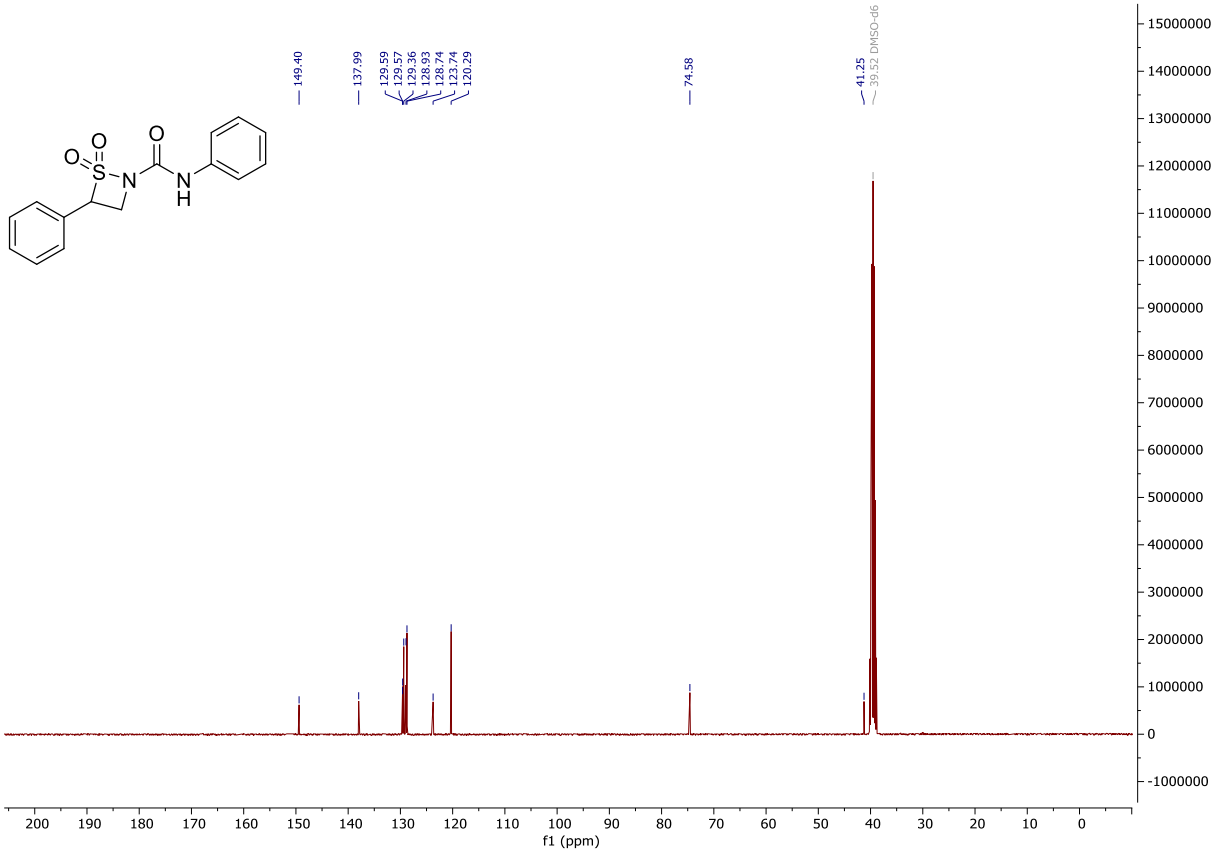
2-(Methylthio)-4-phenyl-1,2-thiazetidine 1,1-dioxide (2af)



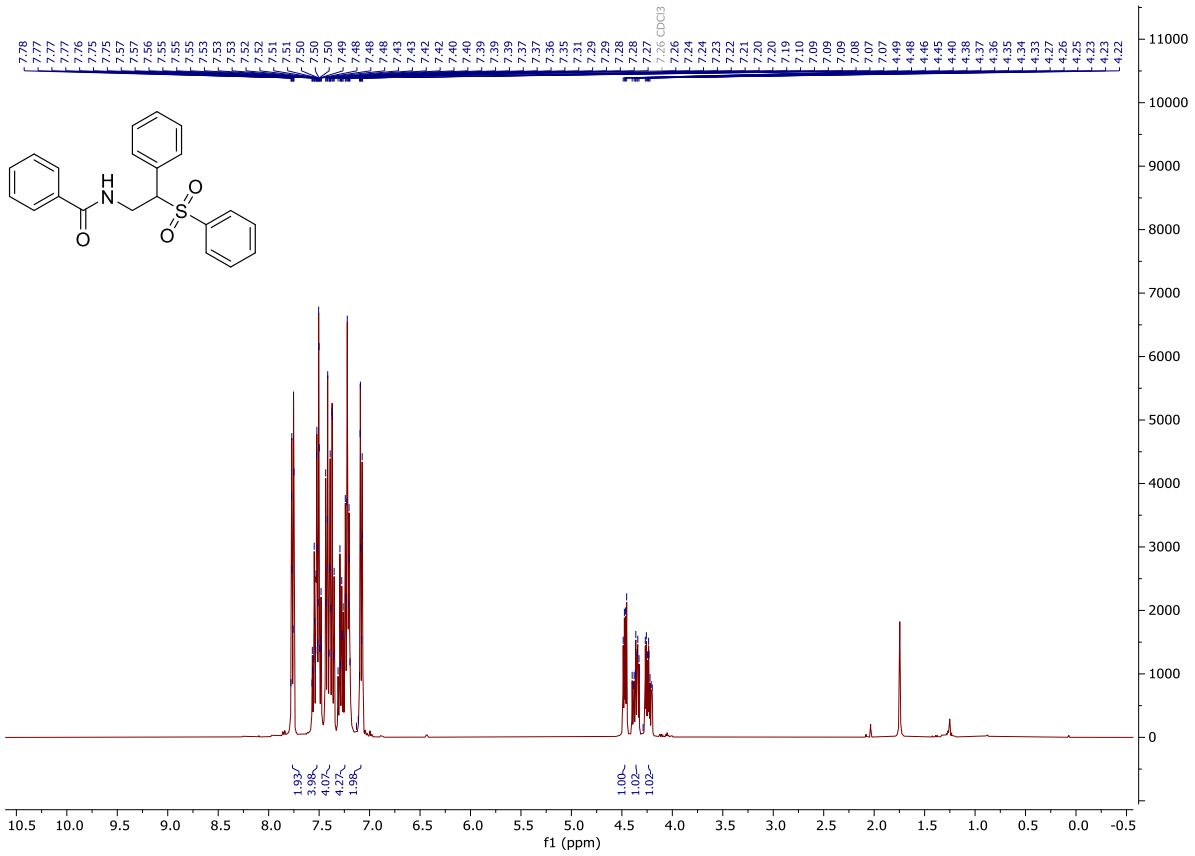


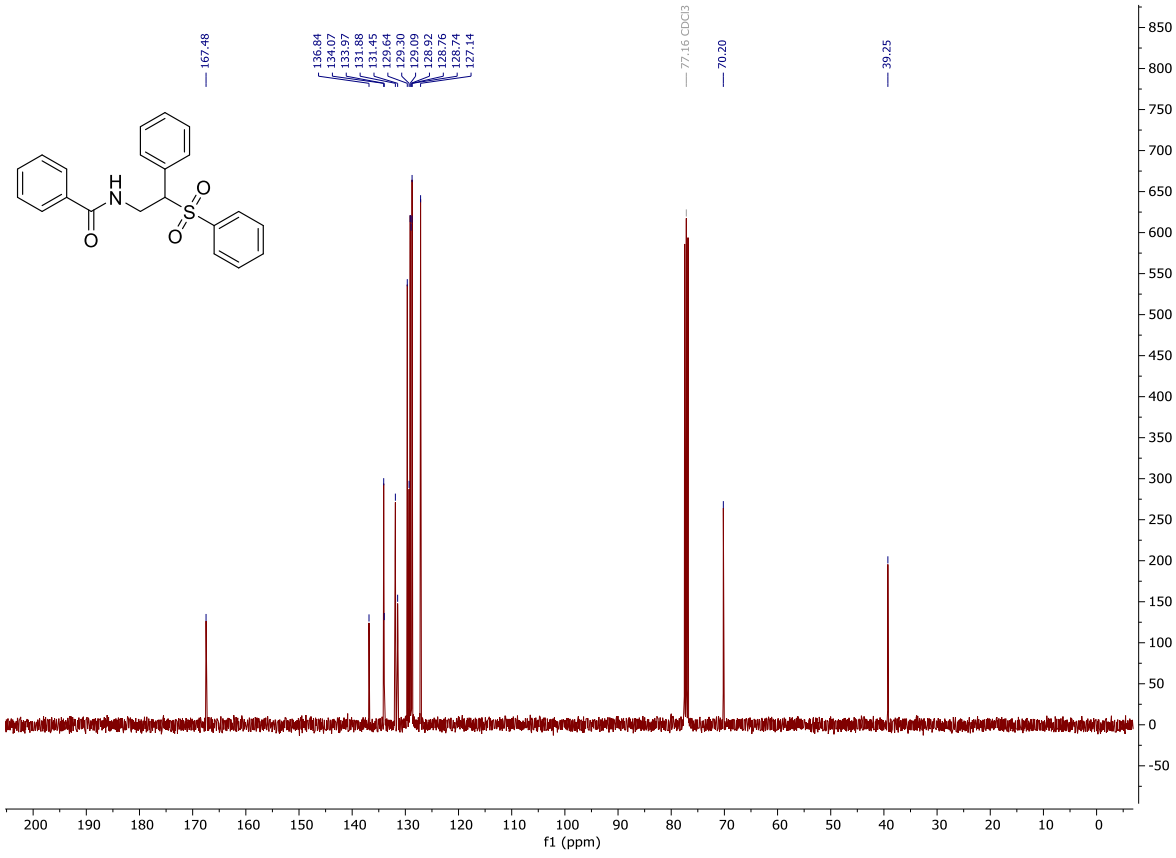
N,4-Diphenyl-1,2-thiazetidine-2-carboxamide 1,1-dioxide (2ag)



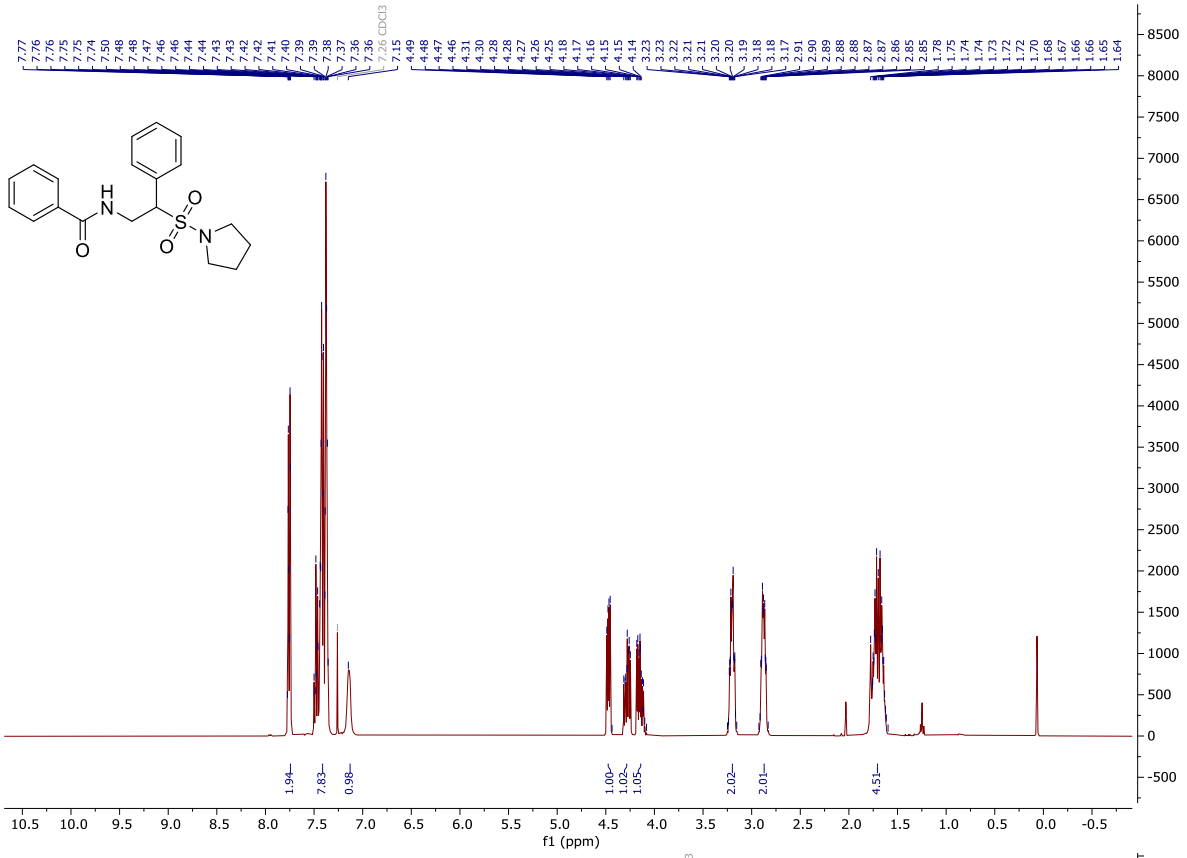


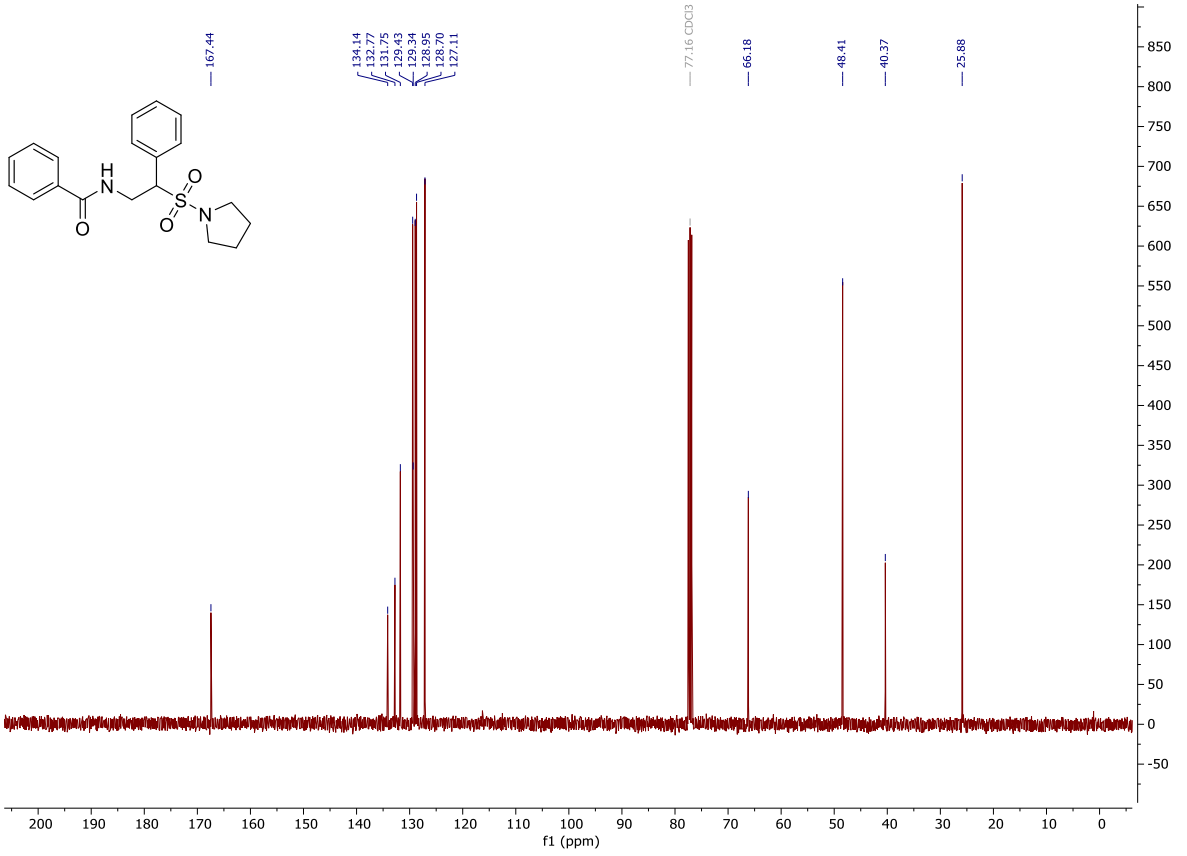
N-(2-Phenyl-2-(phenylsulfonyl)ethyl)benzamide (3a)



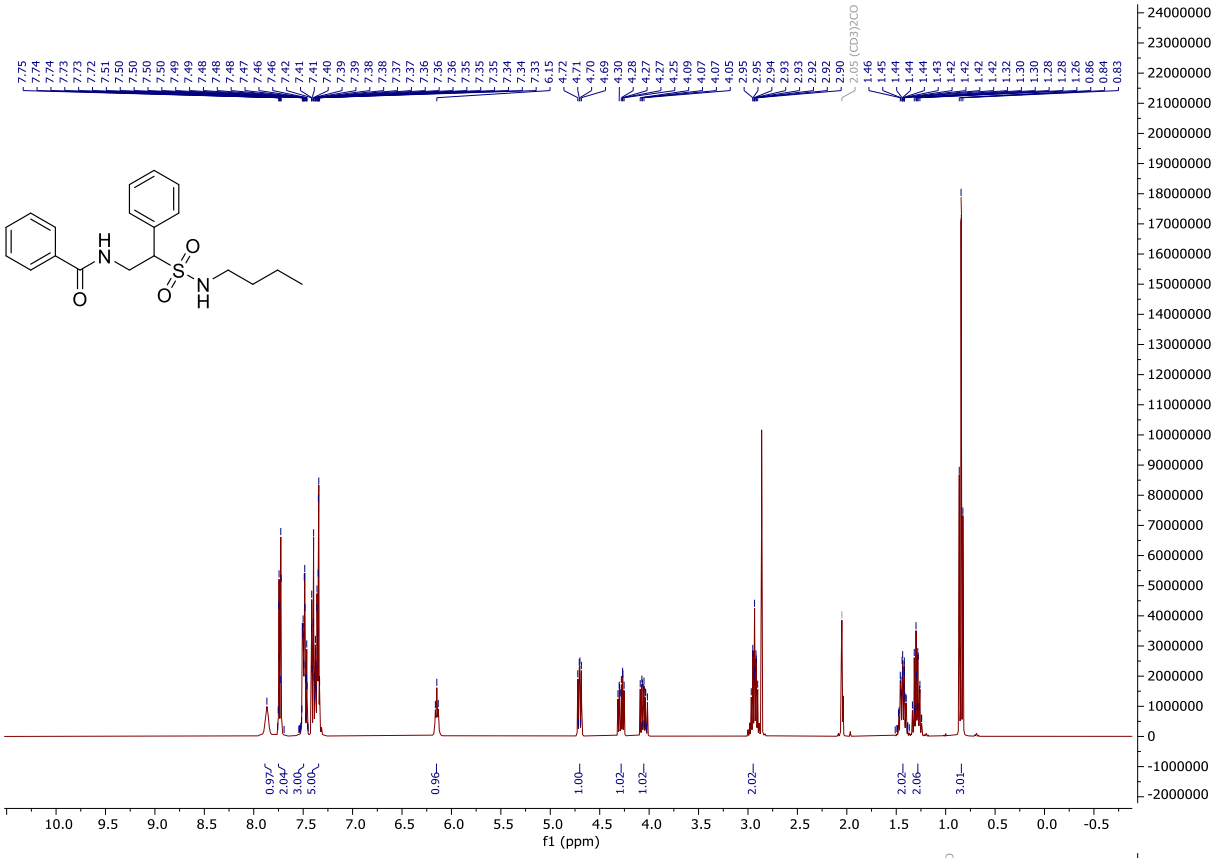


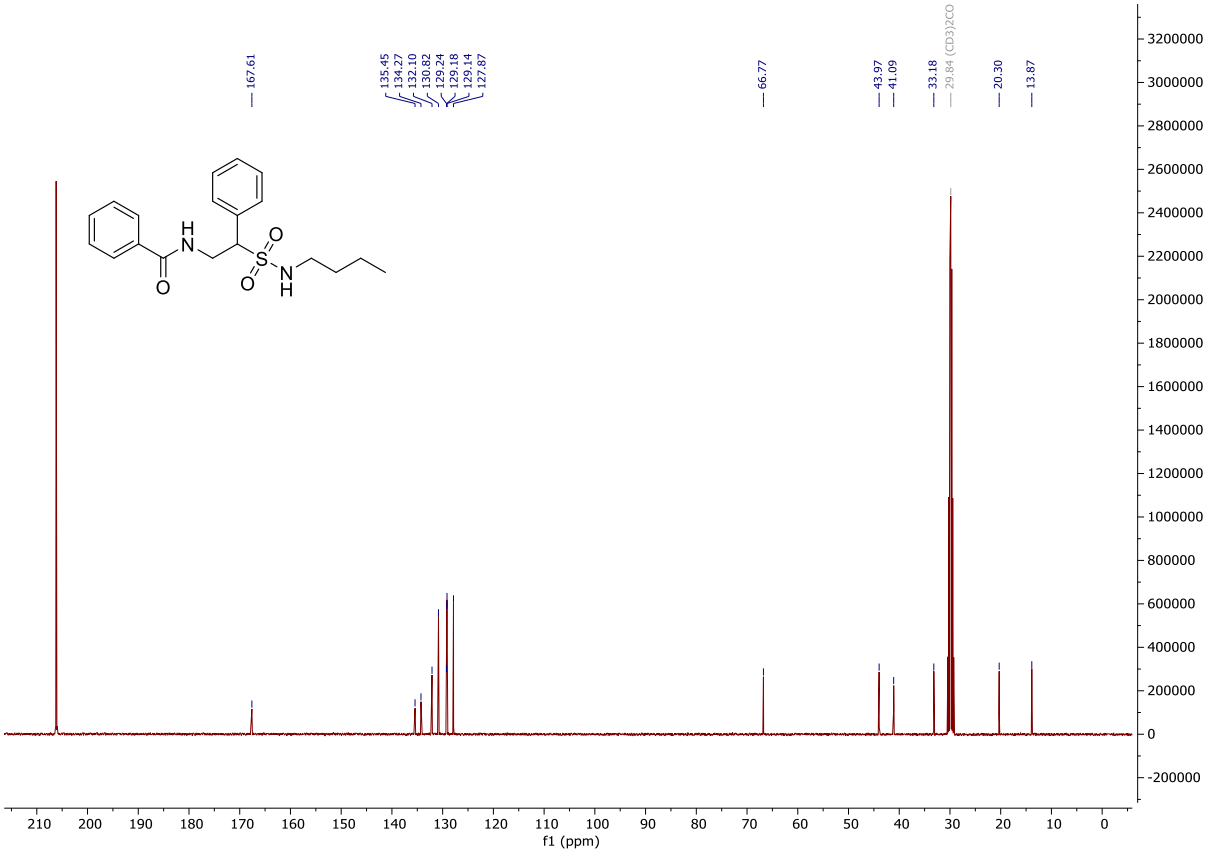
N-(2-Phenyl-2-(pyrrolidin-1-ylsulfonyl)ethyl)benzamide (3b)



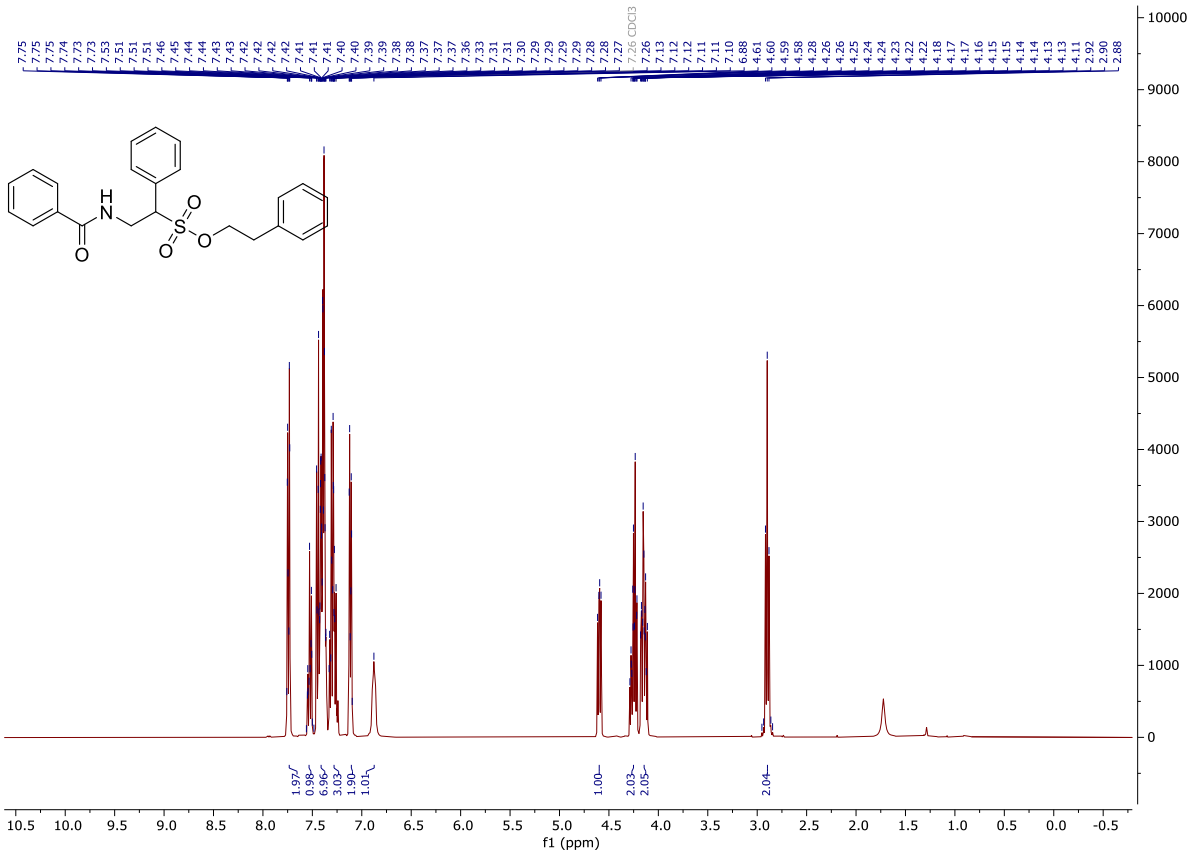


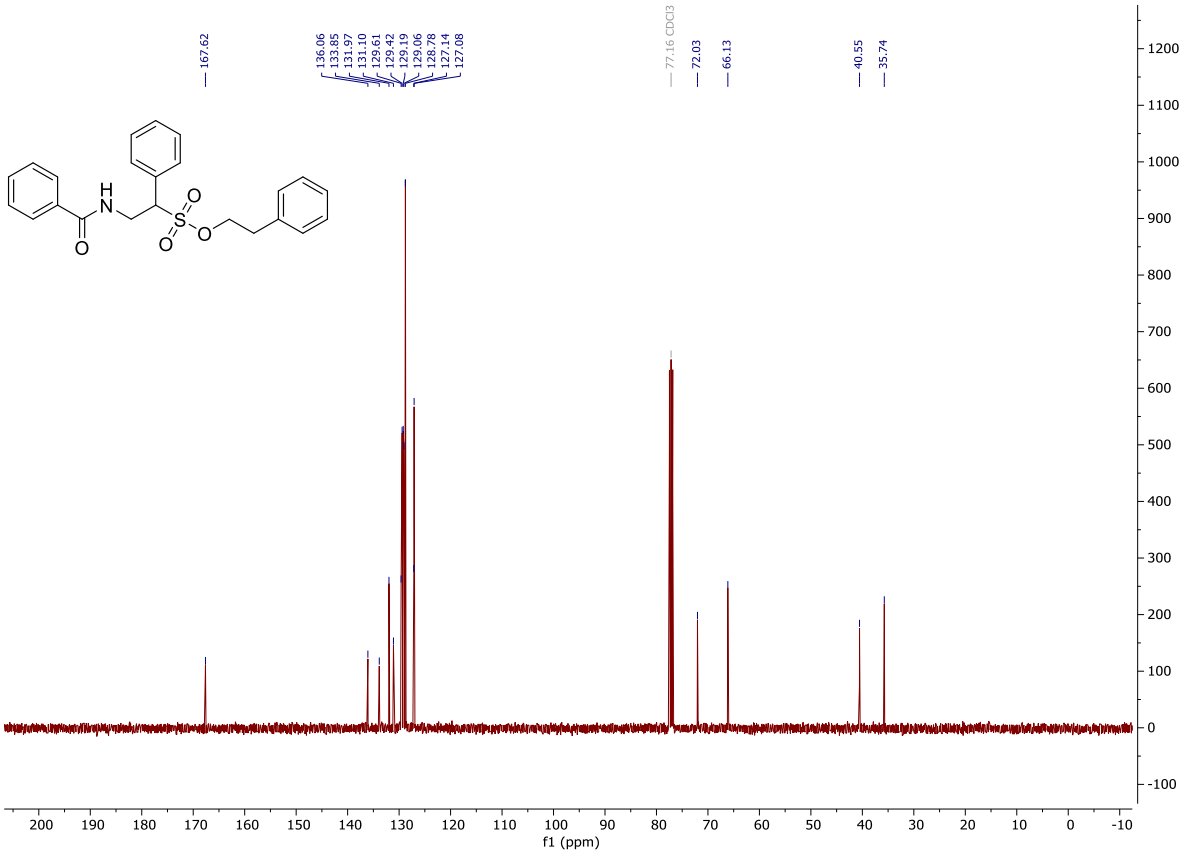
N-(2-(*N*-Butylsulfamoyl)-2-phenylethyl)benzamide (3c)



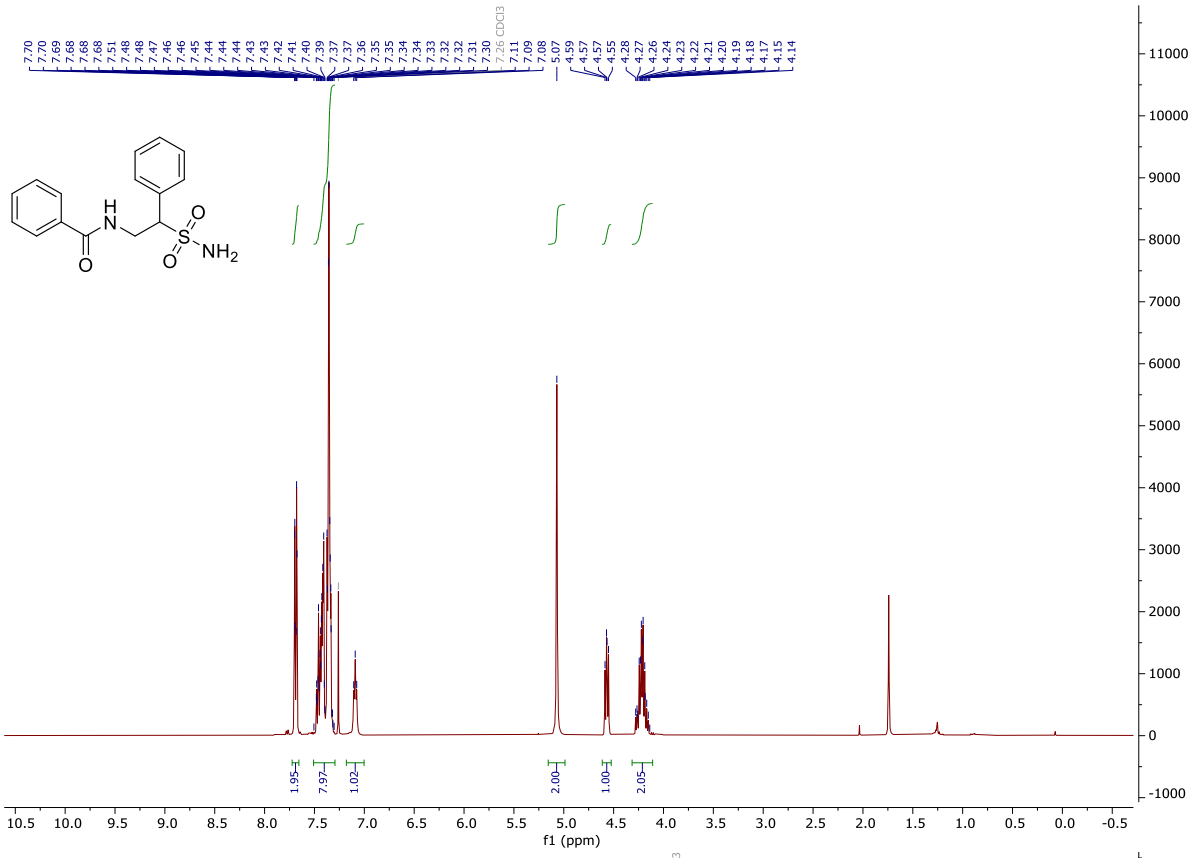


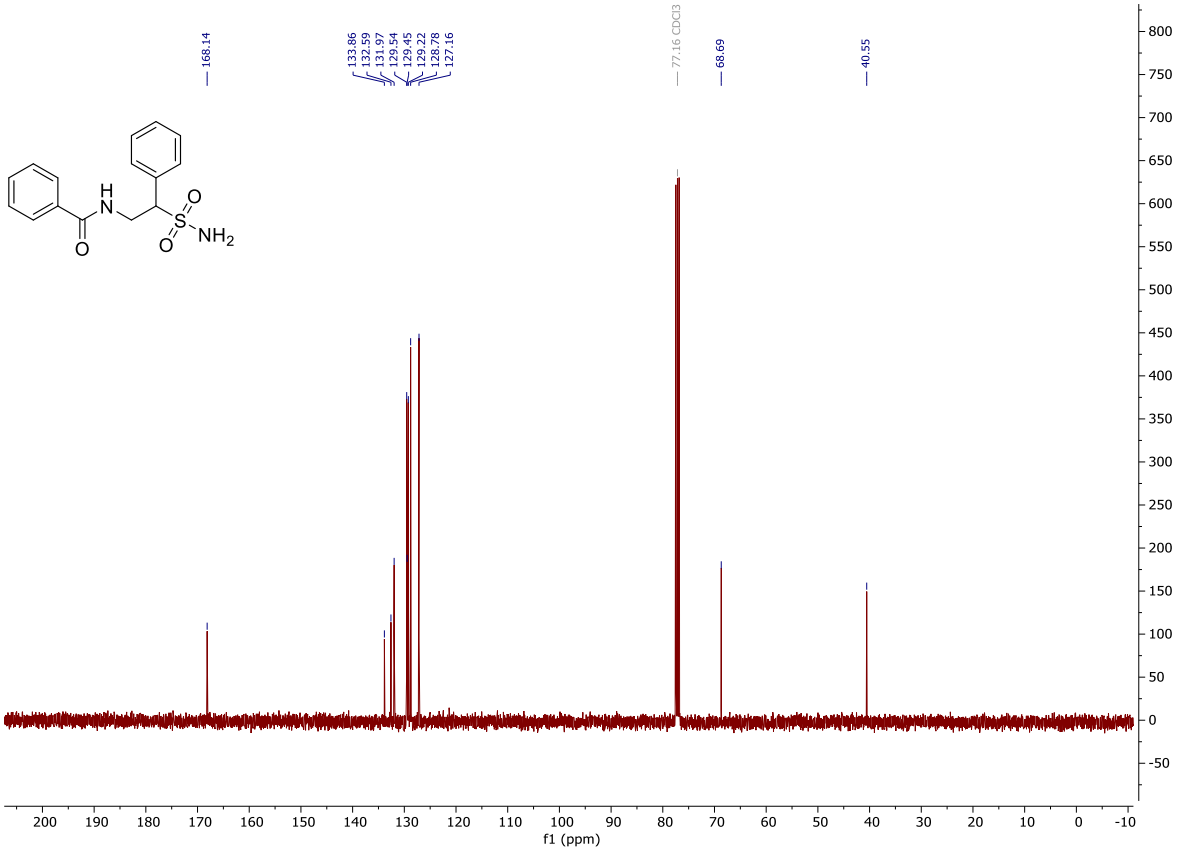
Phenethyl 2-benzamido-1-phenylethane-1-sulfonate (3d)



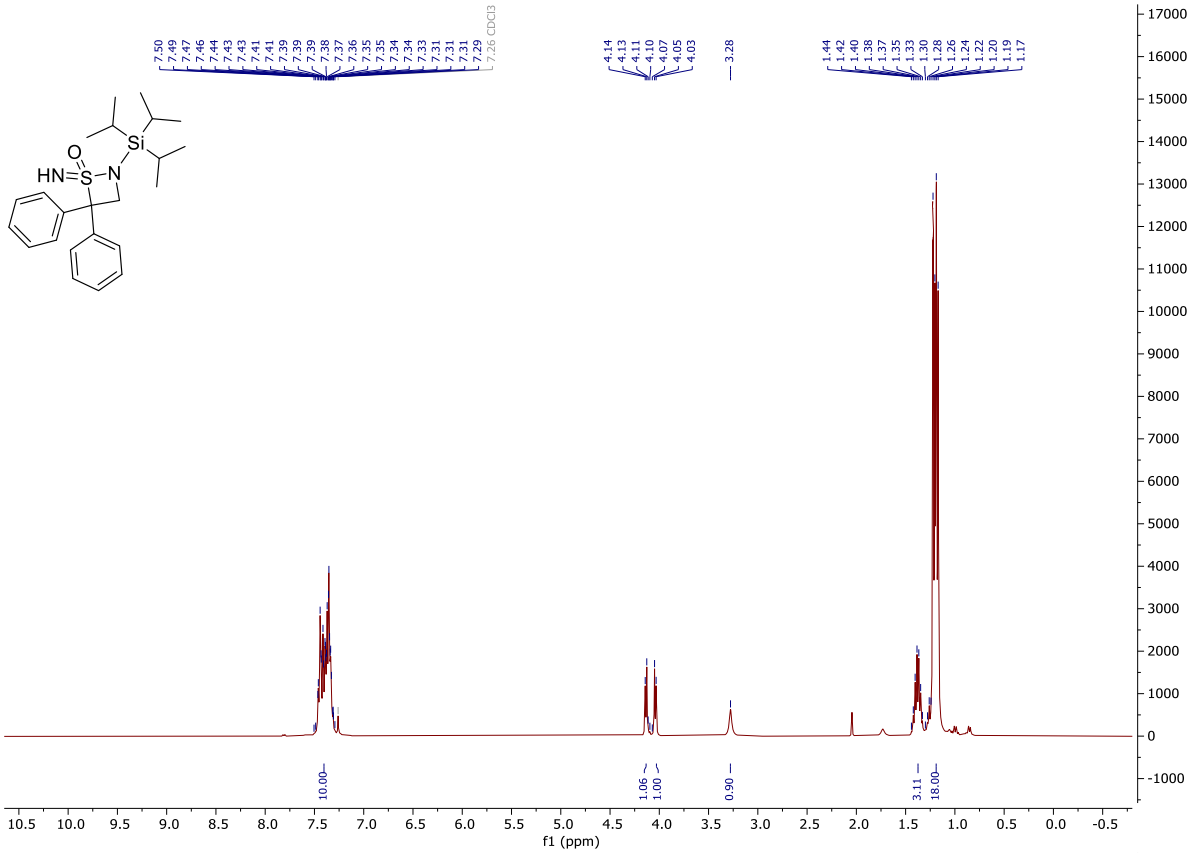


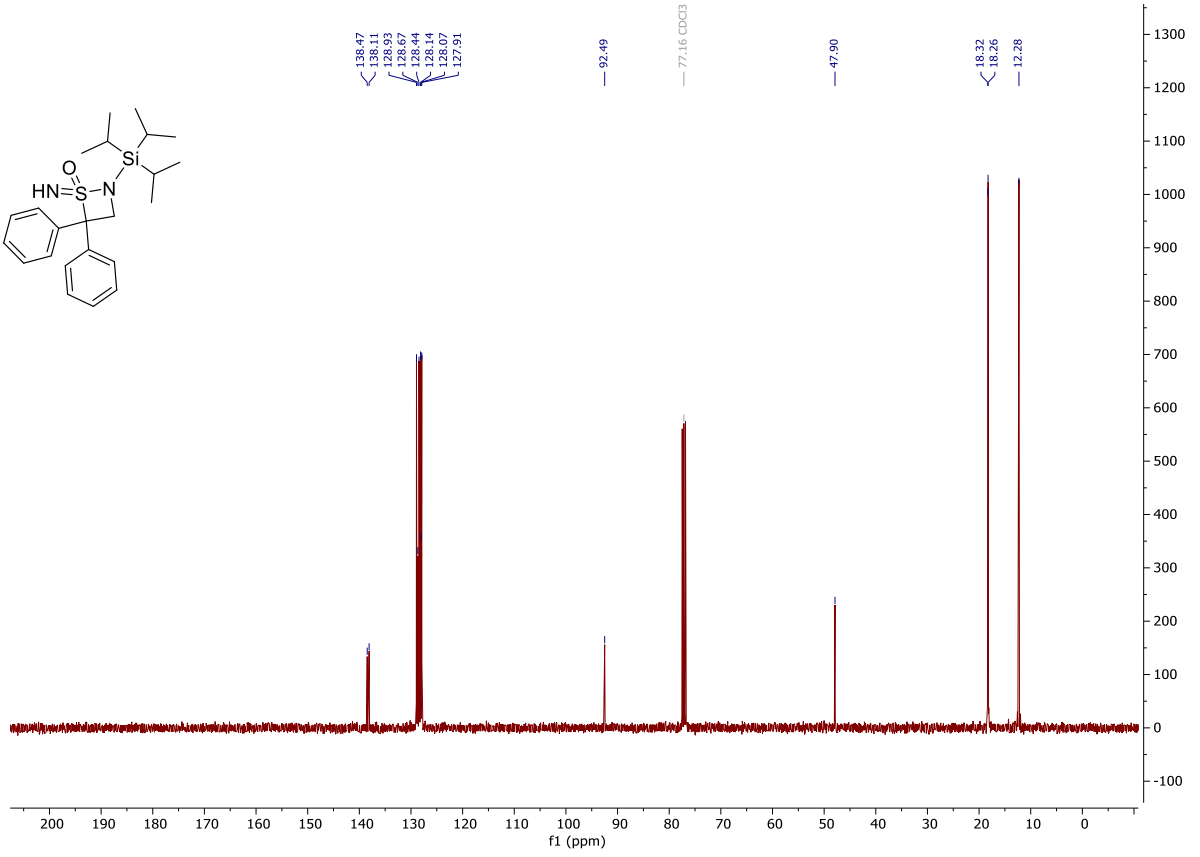
N-(2-Phenyl-2-sulfamoylethyl)benzamide (3e)



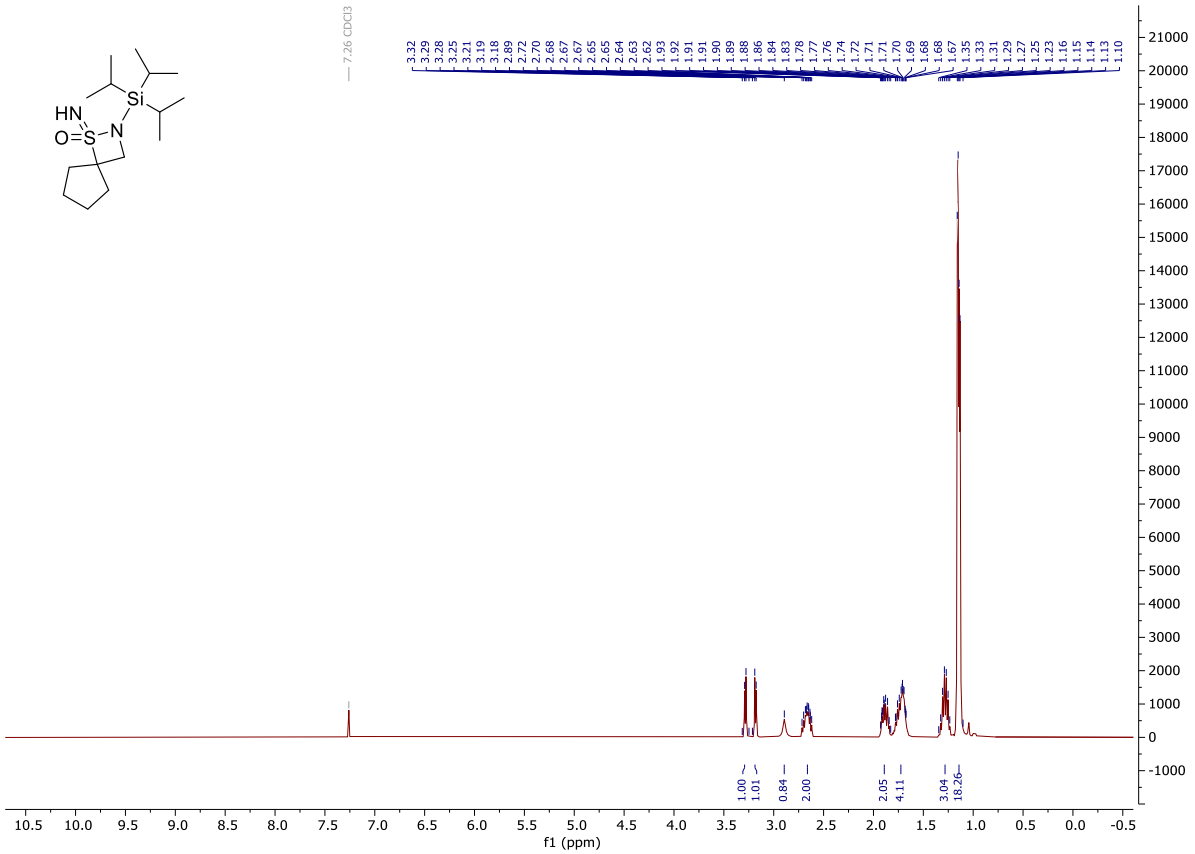


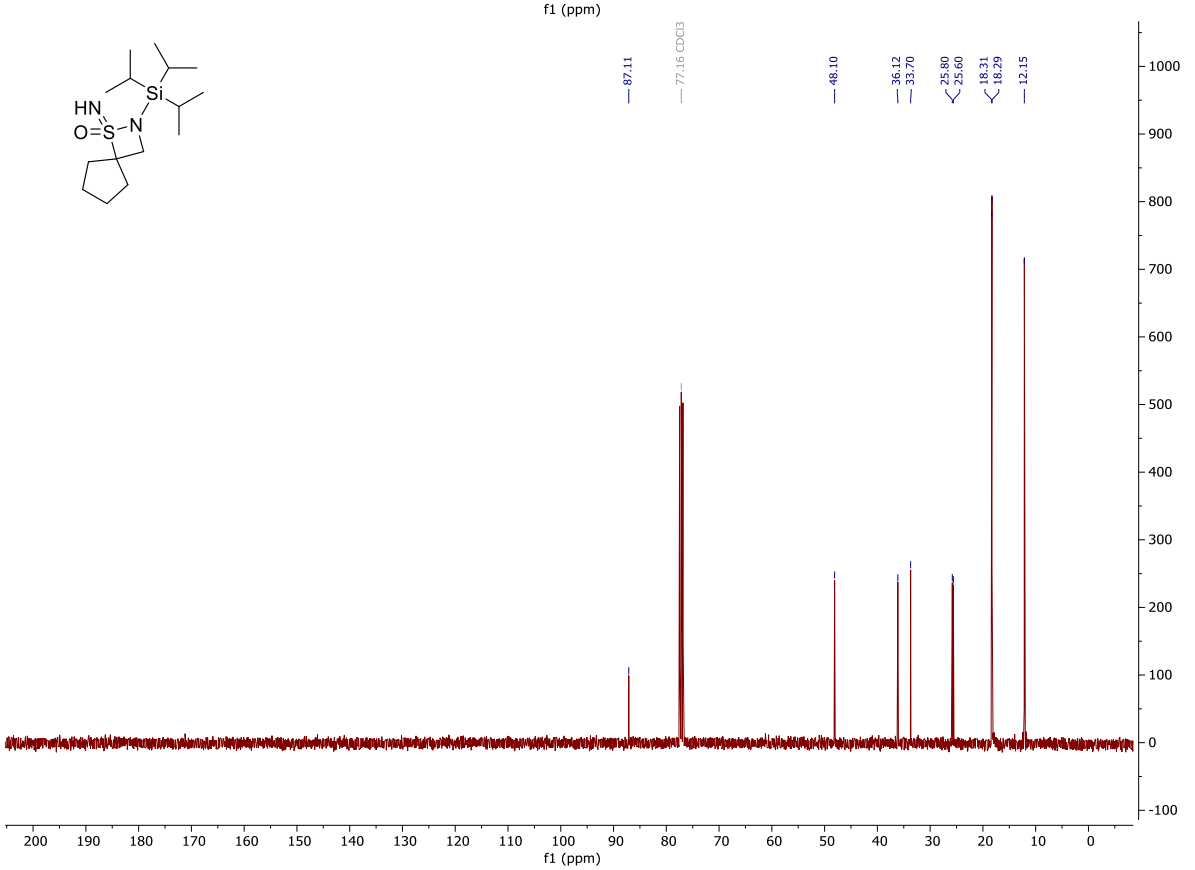
1-Imino-4,4-diphenyl-2-(triisopropylsilyl)- 1λ⁶,2-thiazetidine 1-oxide (4i)



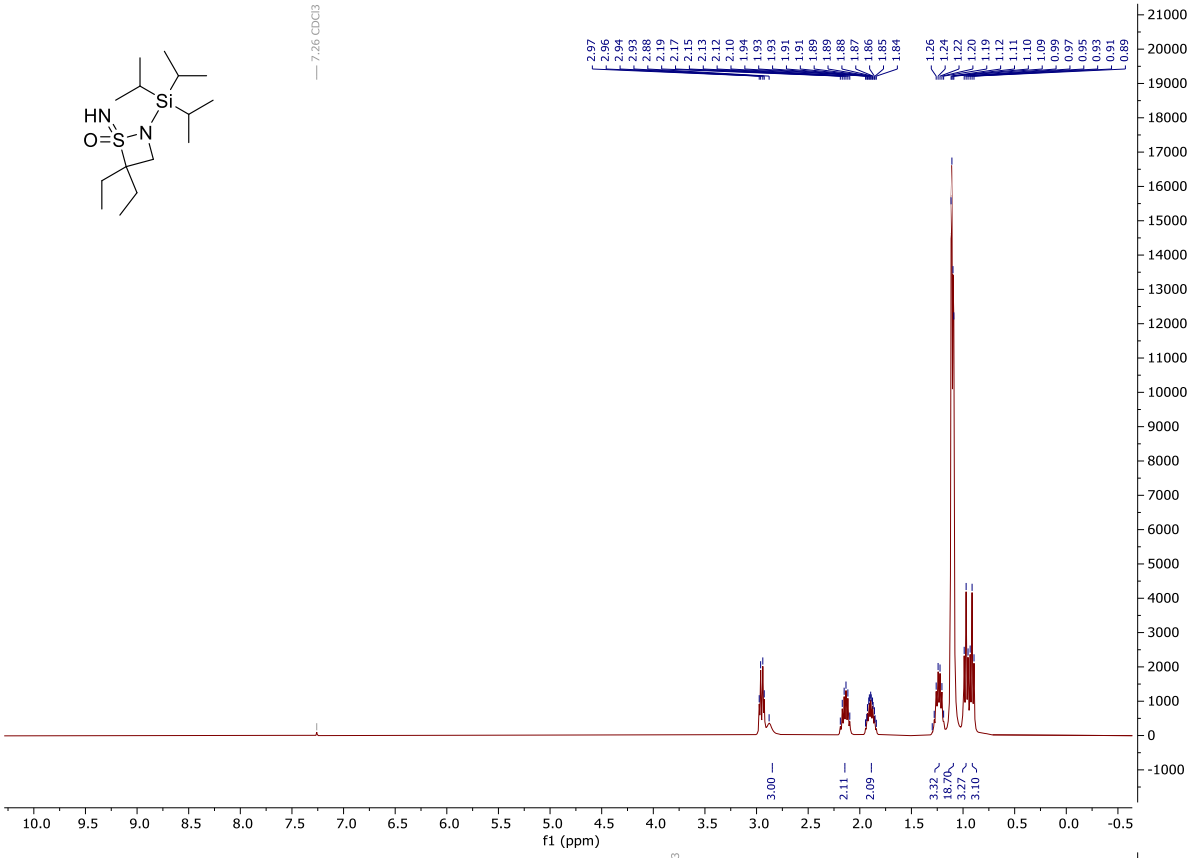


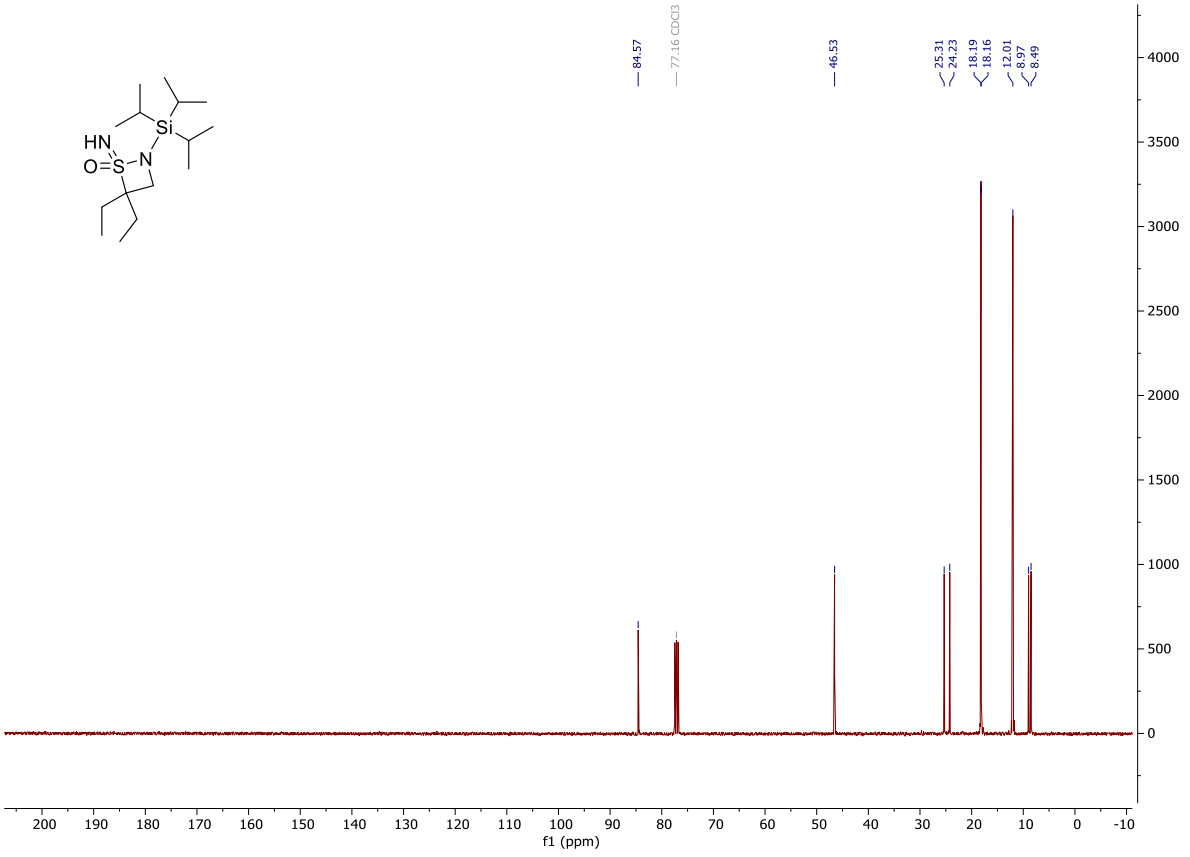
1-Imino-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octane 1-oxide (4w)



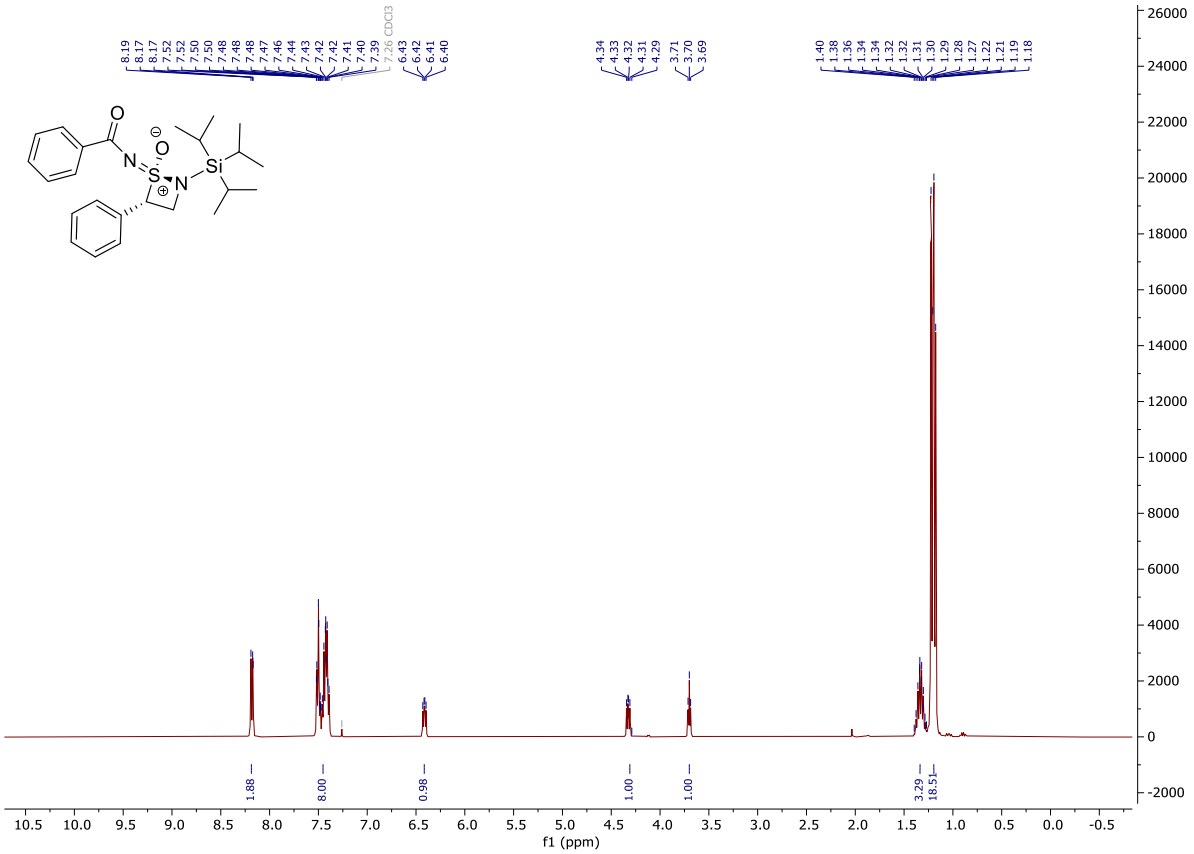


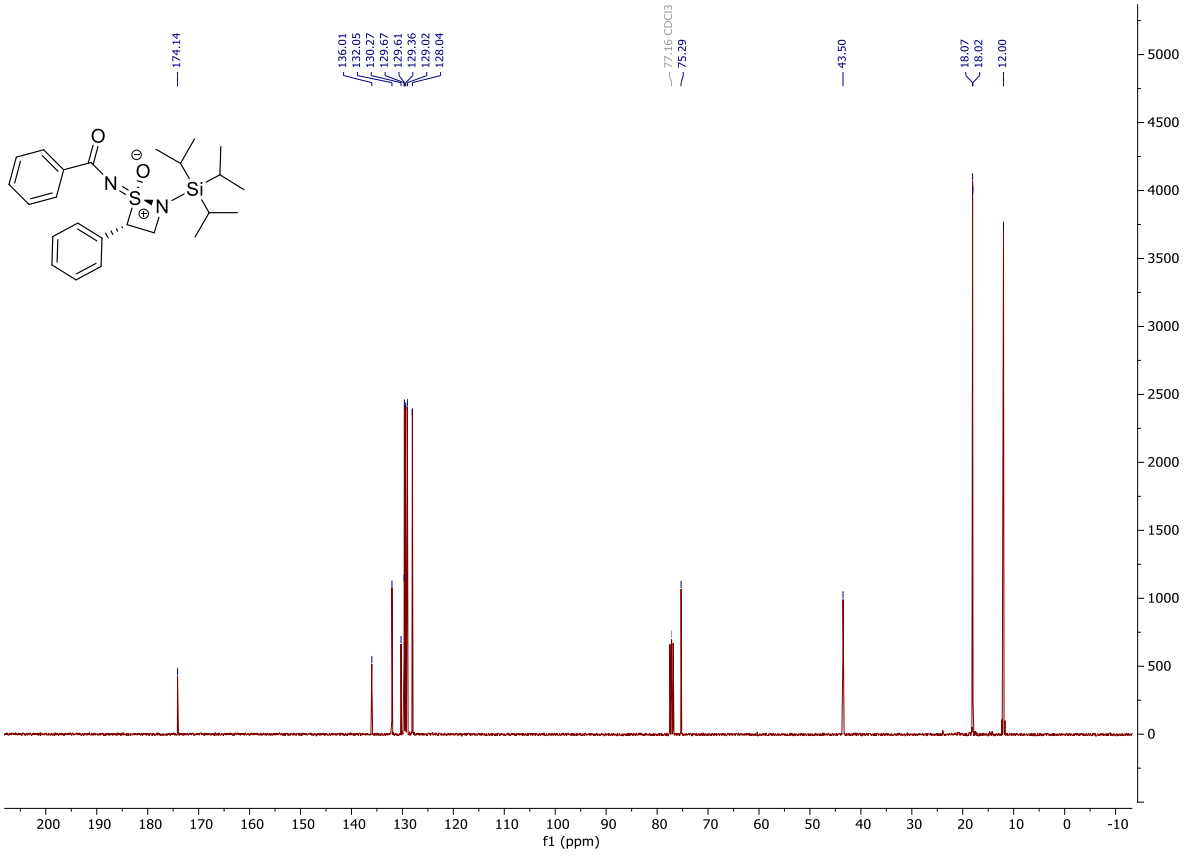
4,4-Diethyl-1-imino-2-(triisopropylsilyl)-1λ^6,2-thiazetidine 1-oxide (4y)



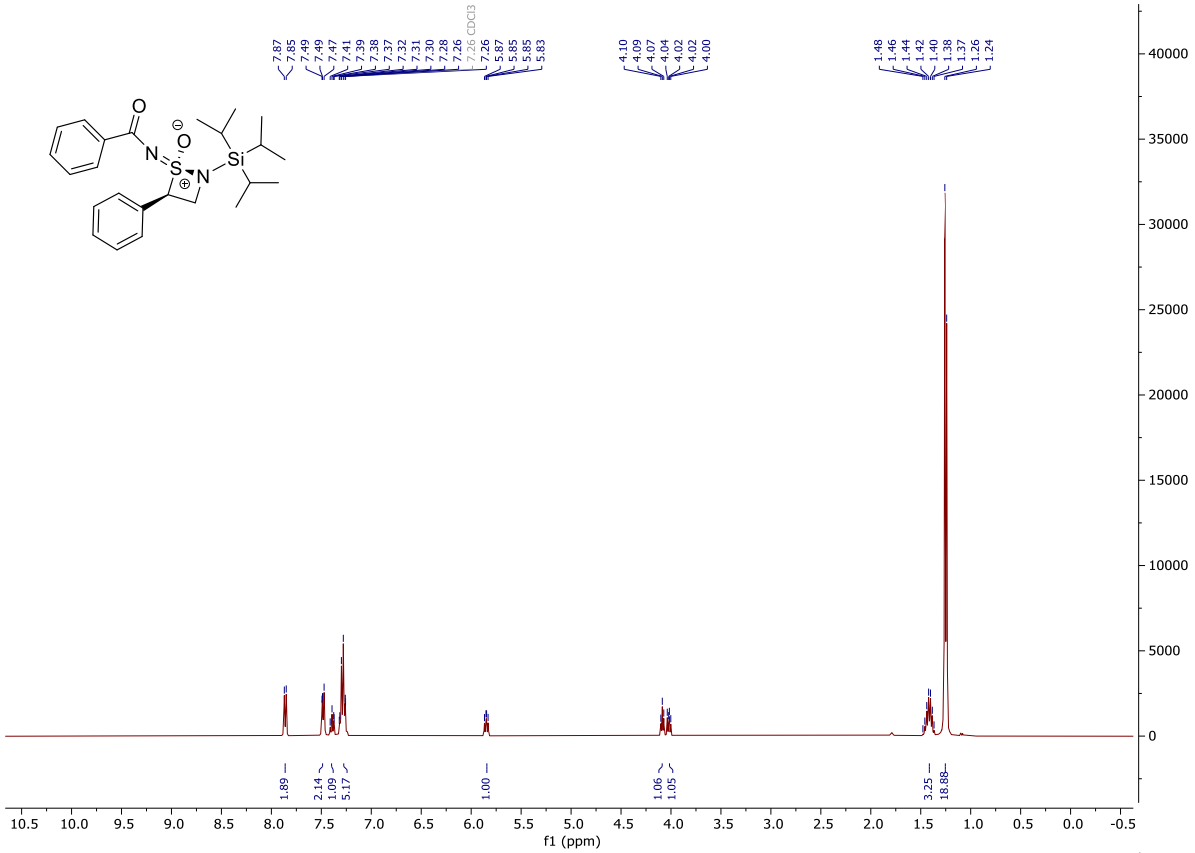


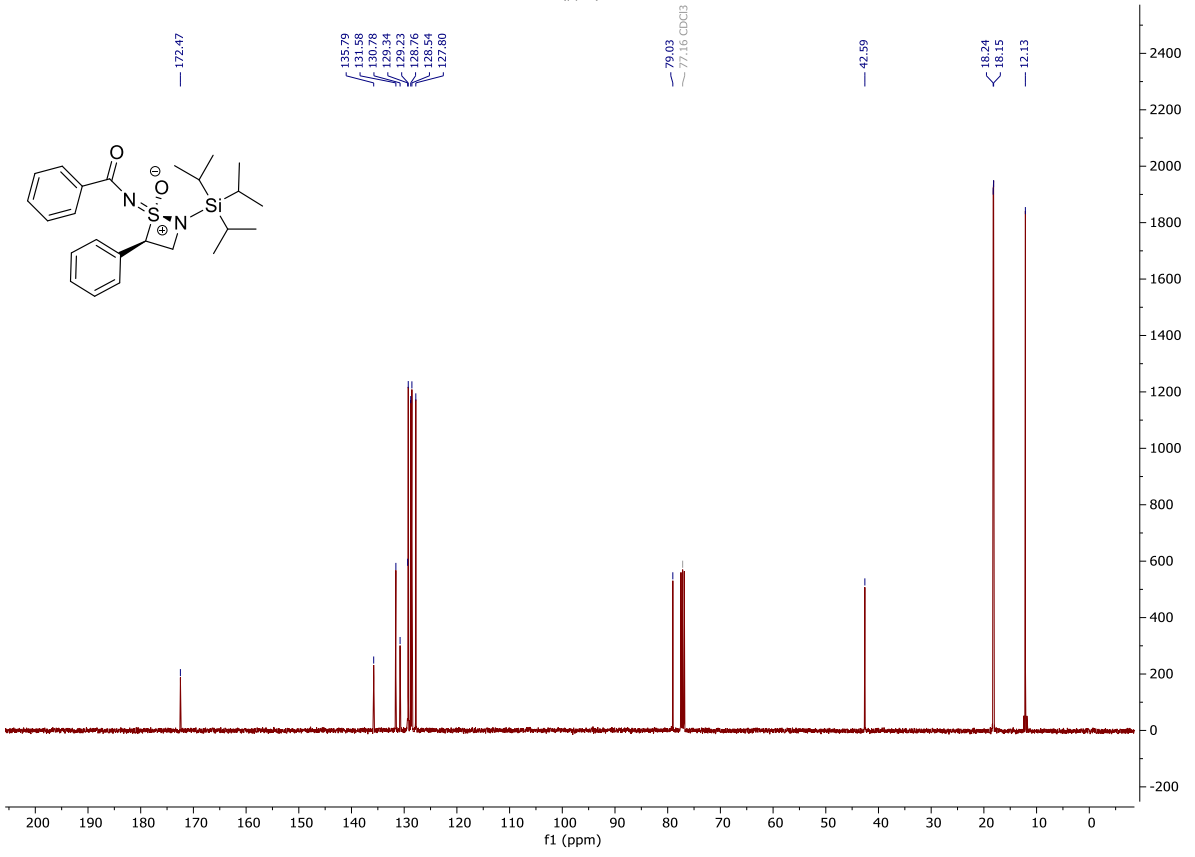
cis-_N_-(1-Oxido-4-phenyl-2-(triisopropylsilyl)-1λ^6,2-thiazetidin-1-ylidene)benzamide (_cis_-4aa)



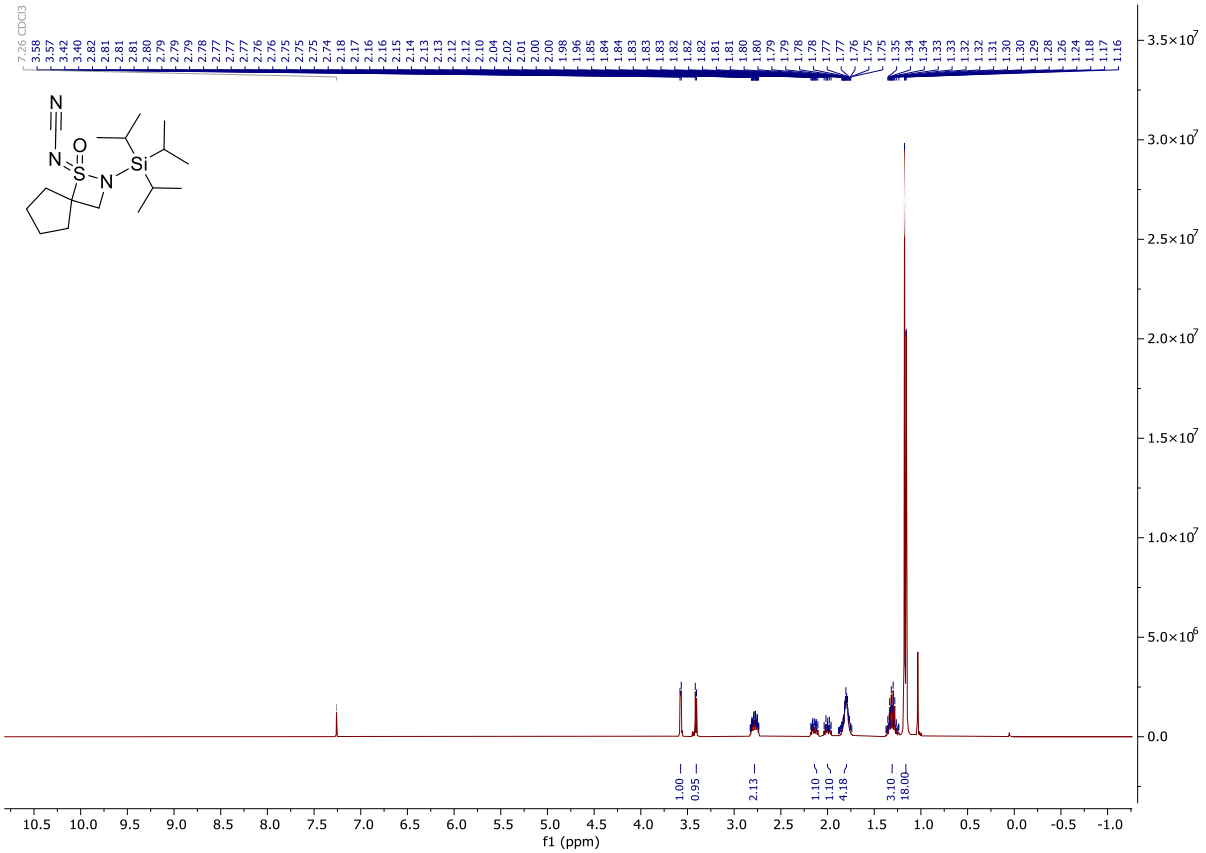


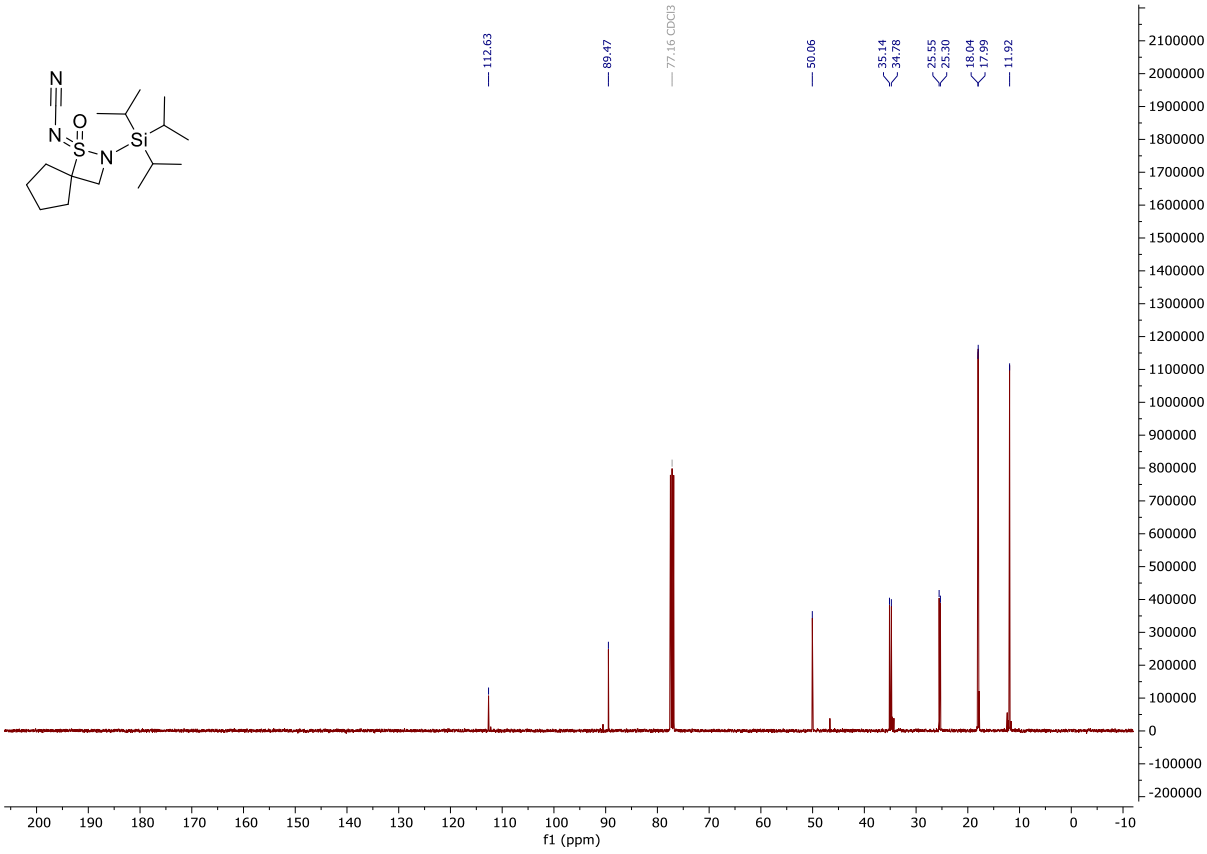
trans-_N_-(1-Oxido-4-phenyl-2-(triisopropylsilyl)-1λ^6,2-thiazetidin-1-ylidene)benzamide (_trans_-4aa)



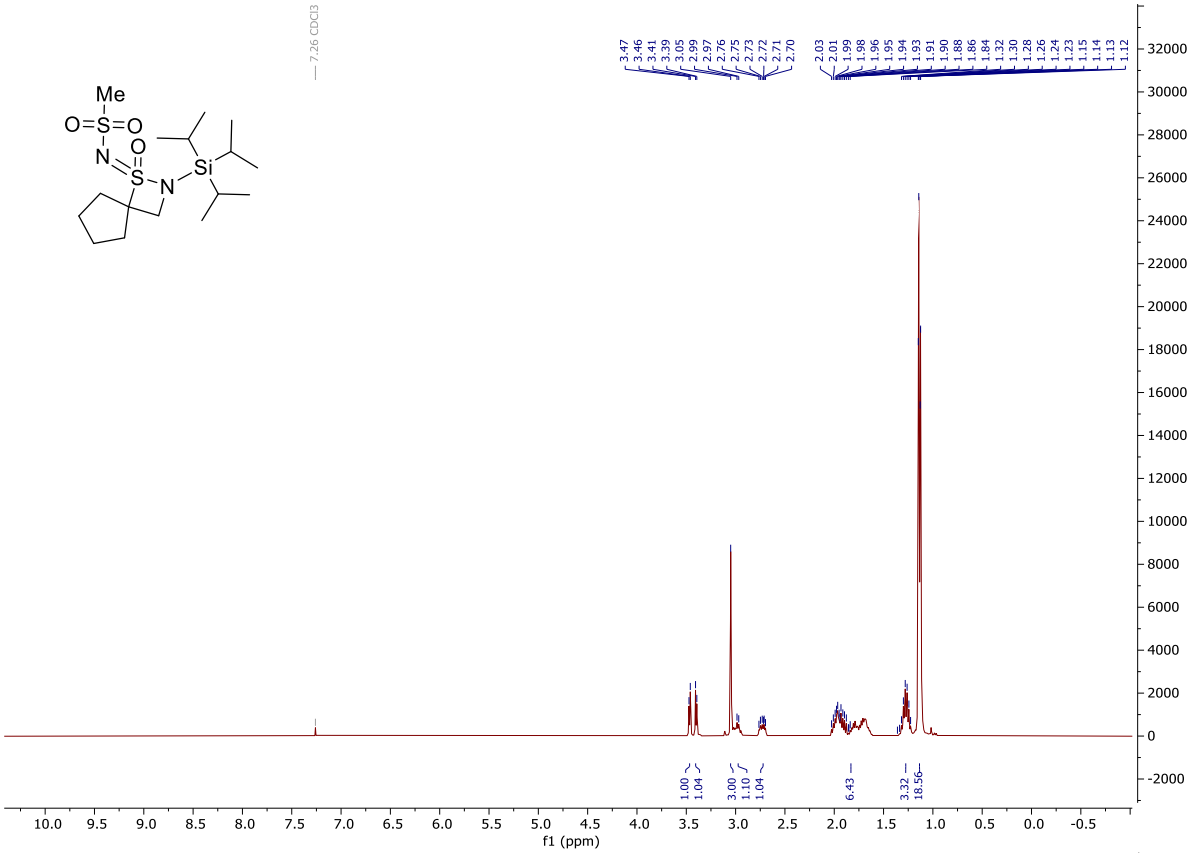


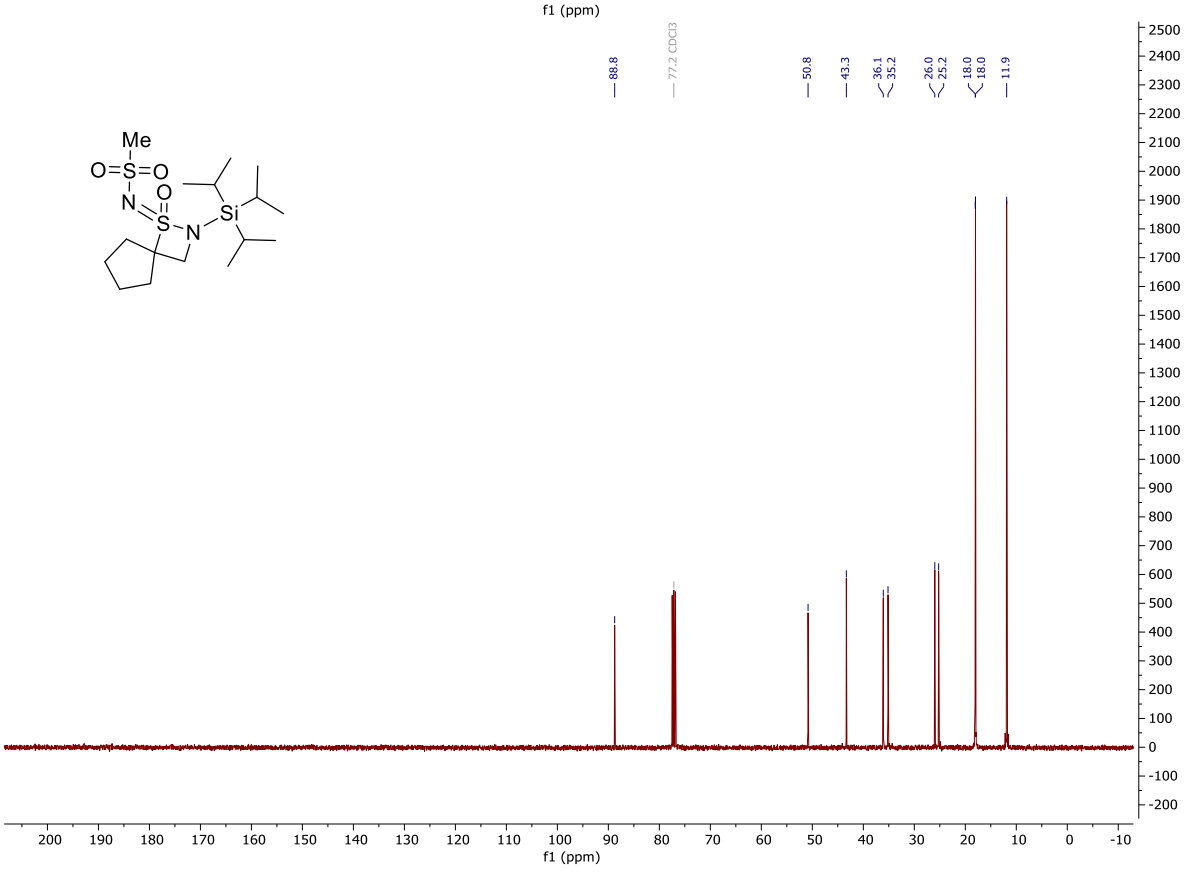
N-(1-Oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)cyanamide (4wa)



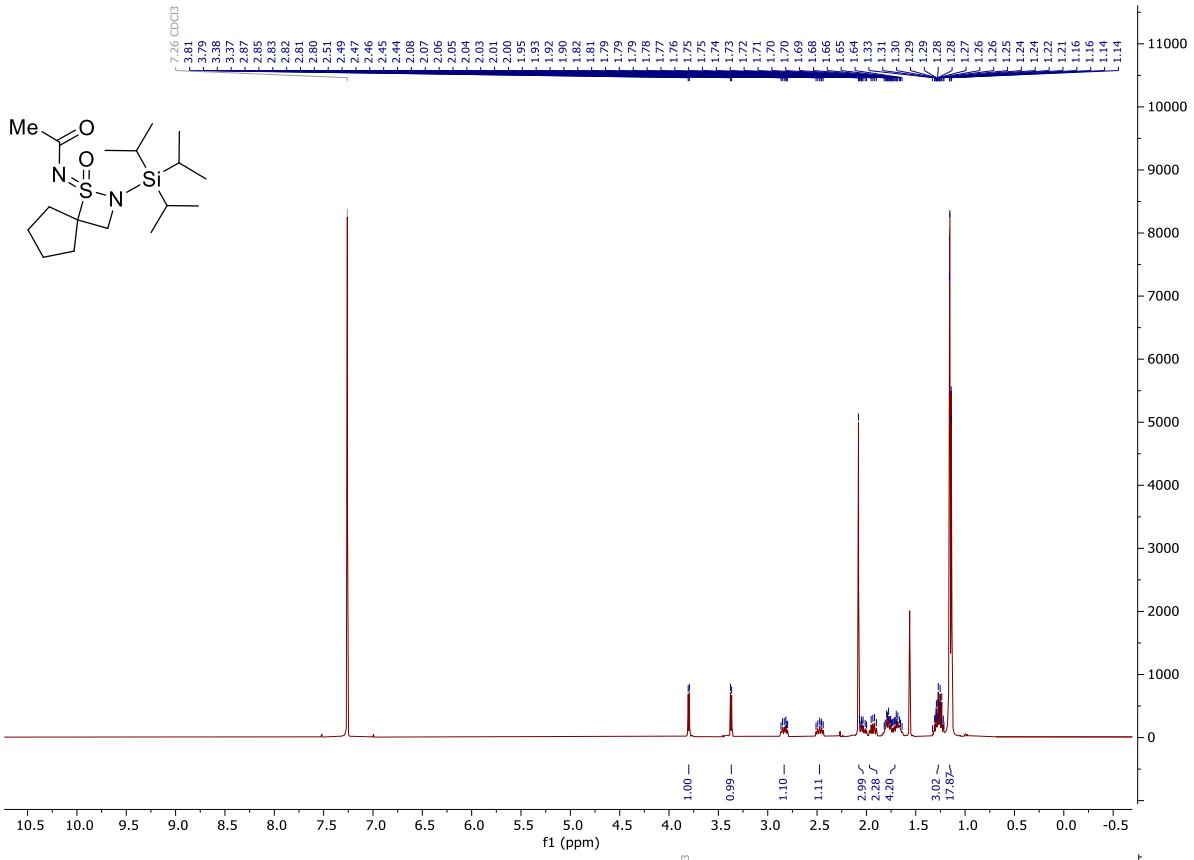


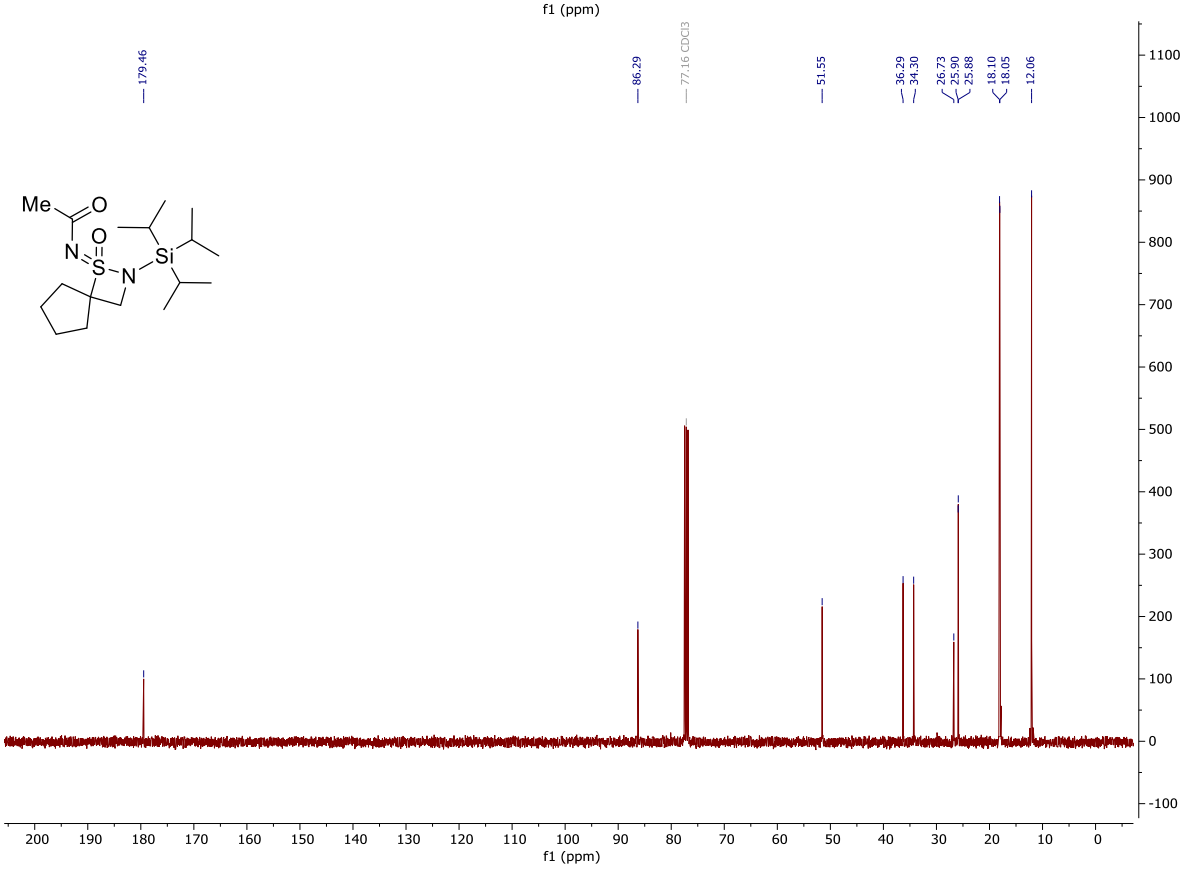
N-(1-Oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)methanesulfonamide (4wb)



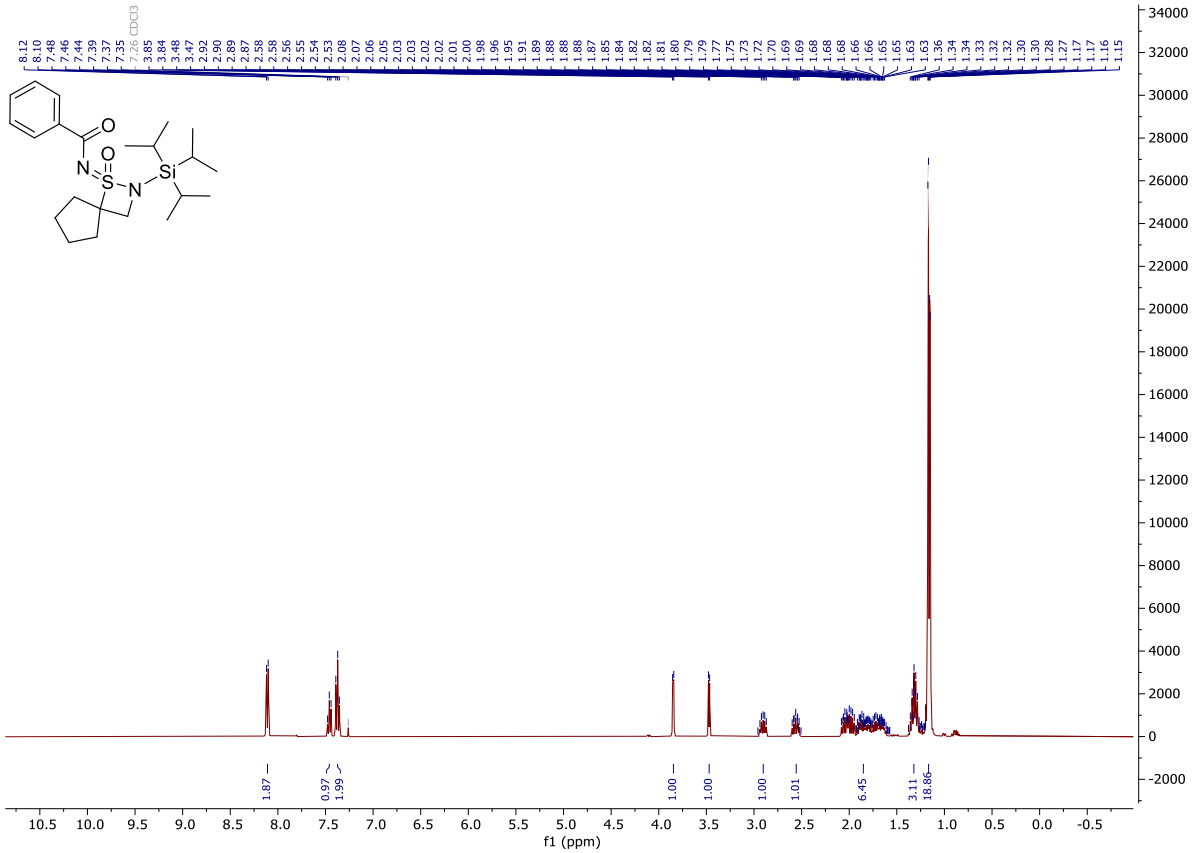


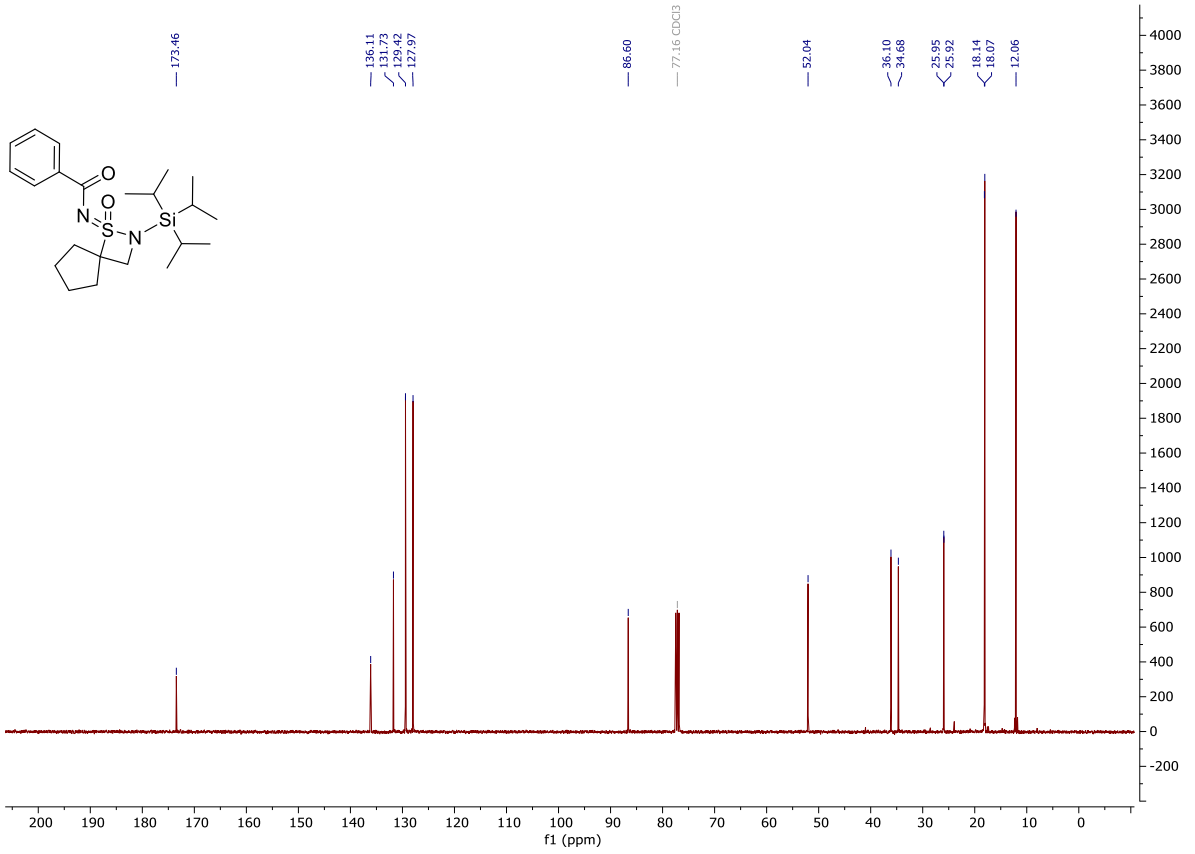
N-(1-Oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)acetamide (4wc)



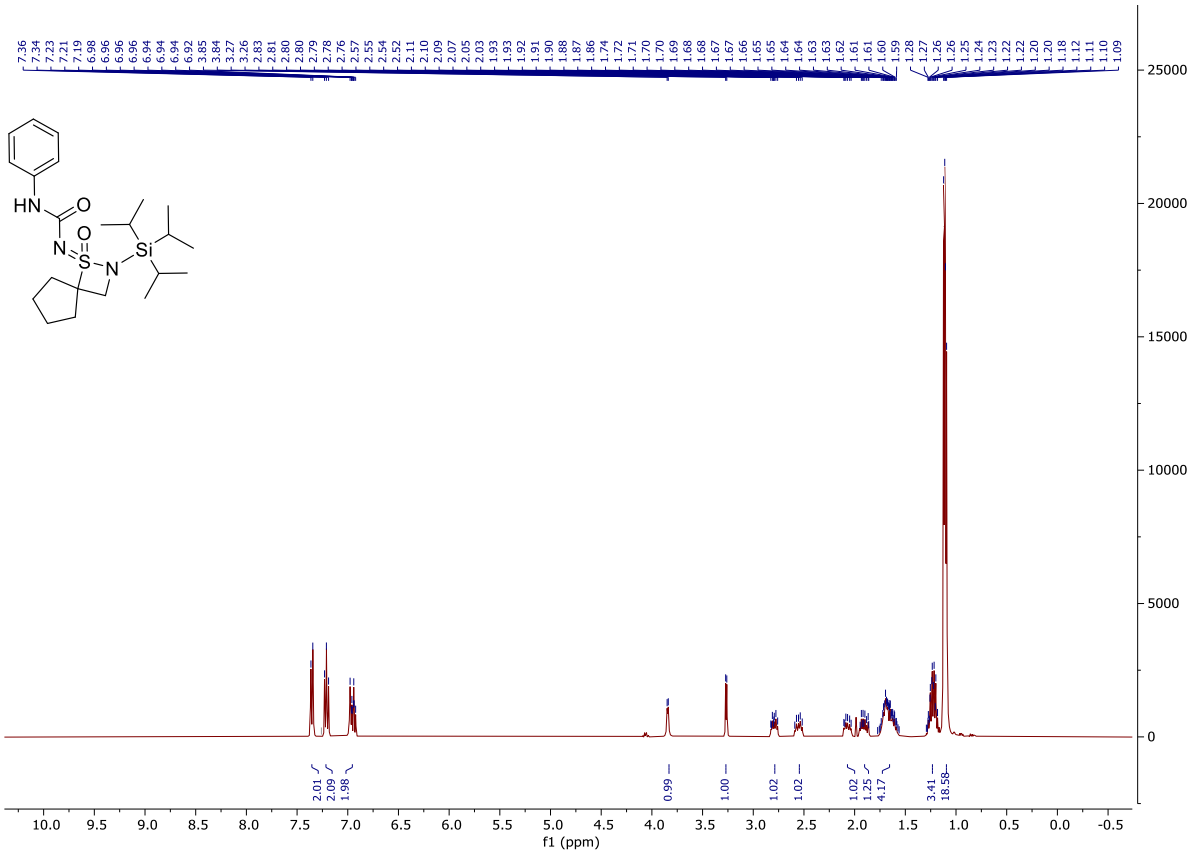


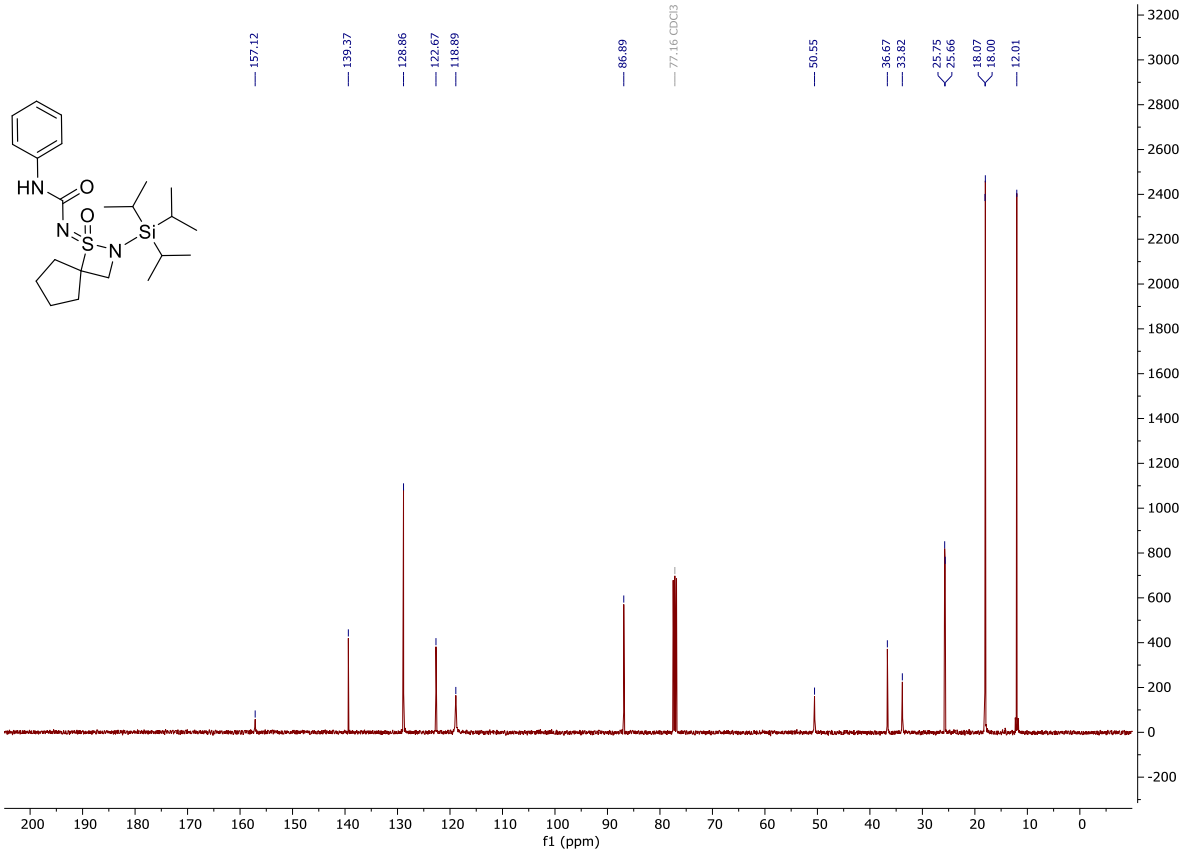
_N_-(1-Oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)benzamide (4wd)



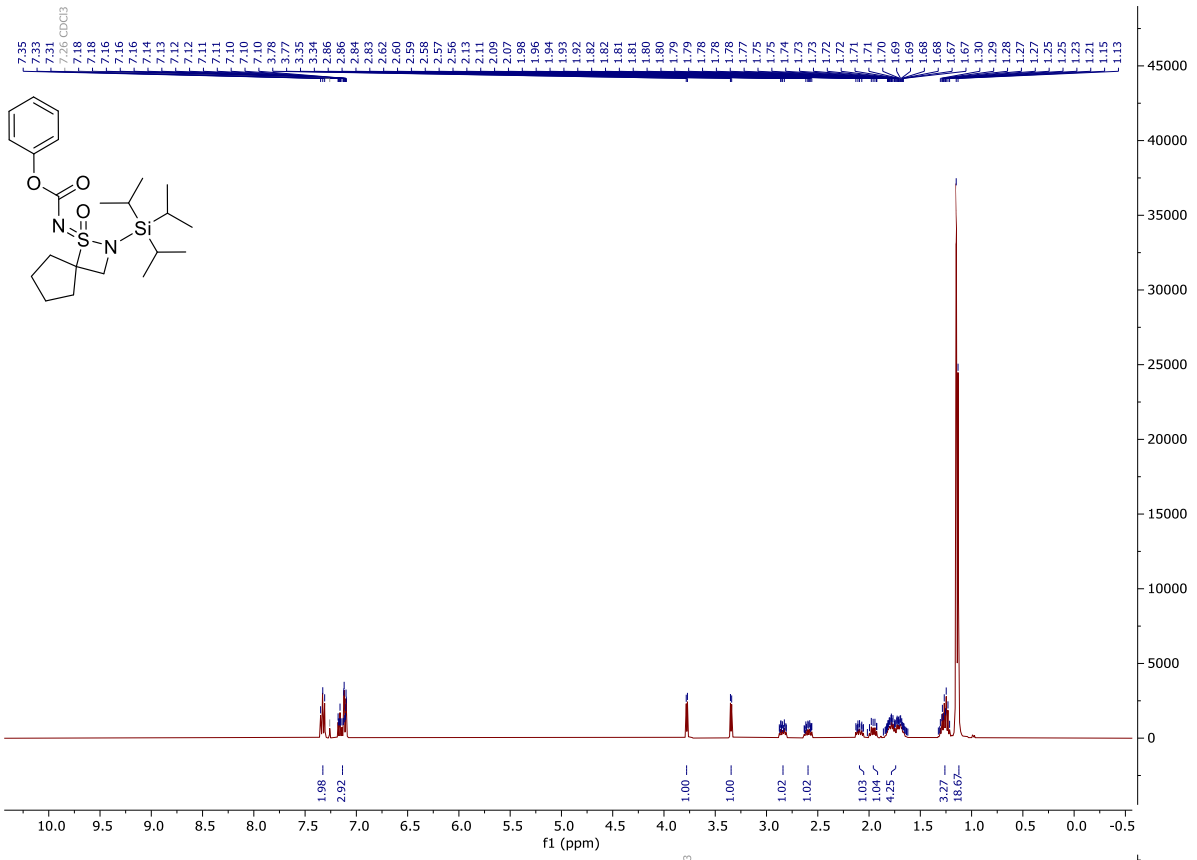


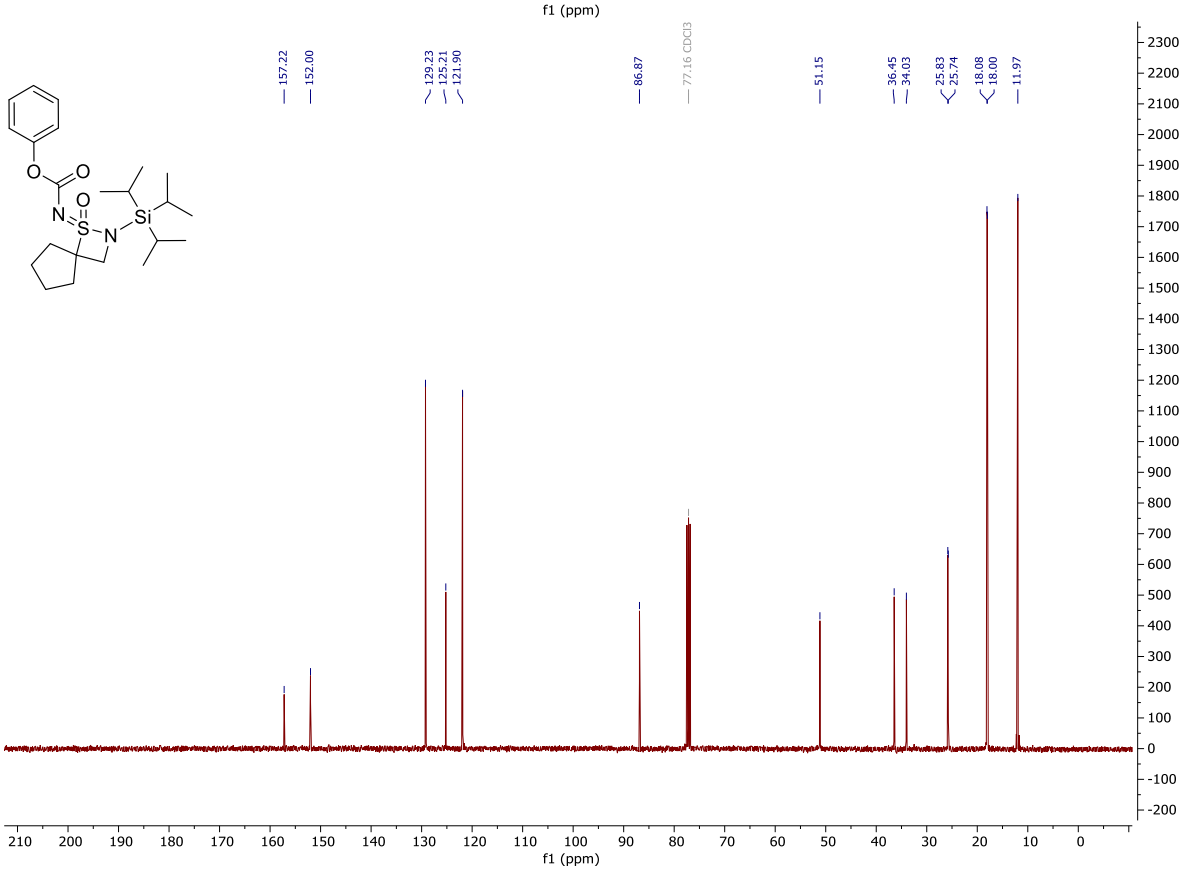
1-(1-Oxido-2-(triisopropylsilyl)- 1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)-3-phenylurea (4we)



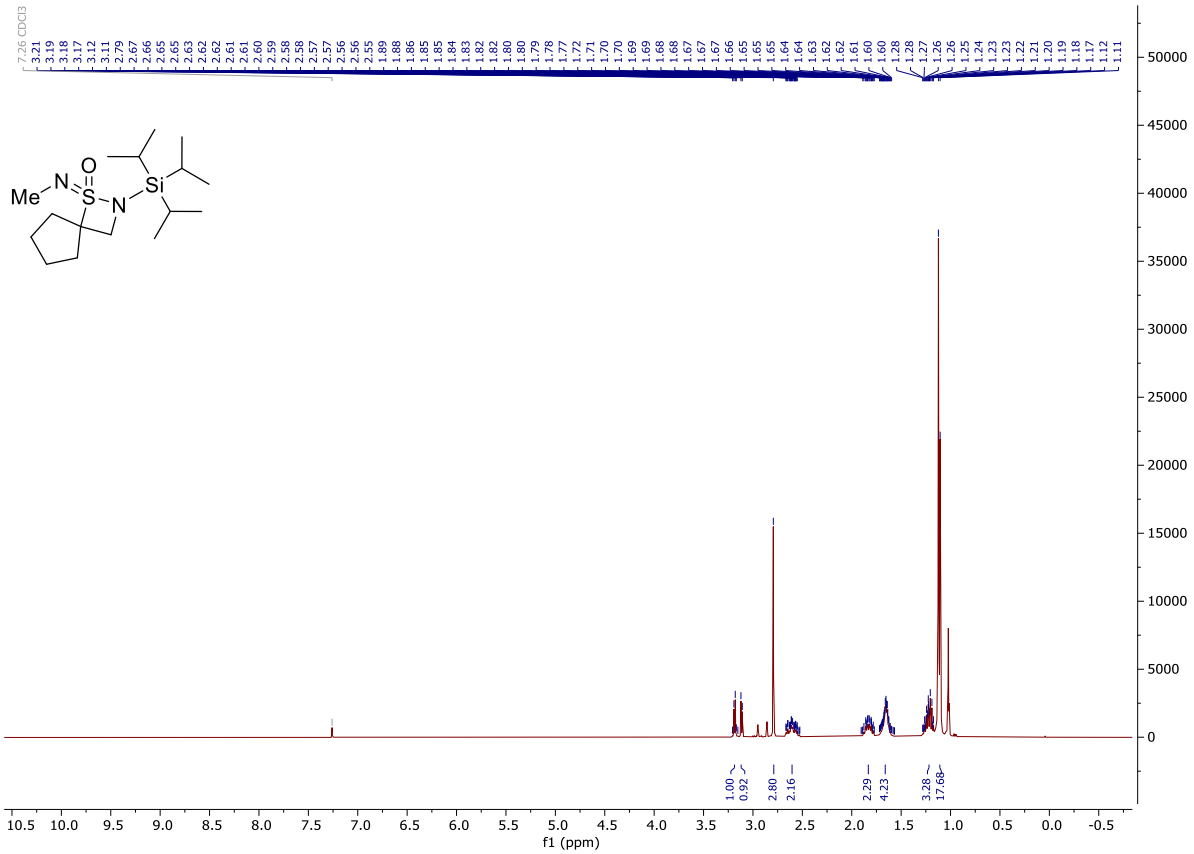


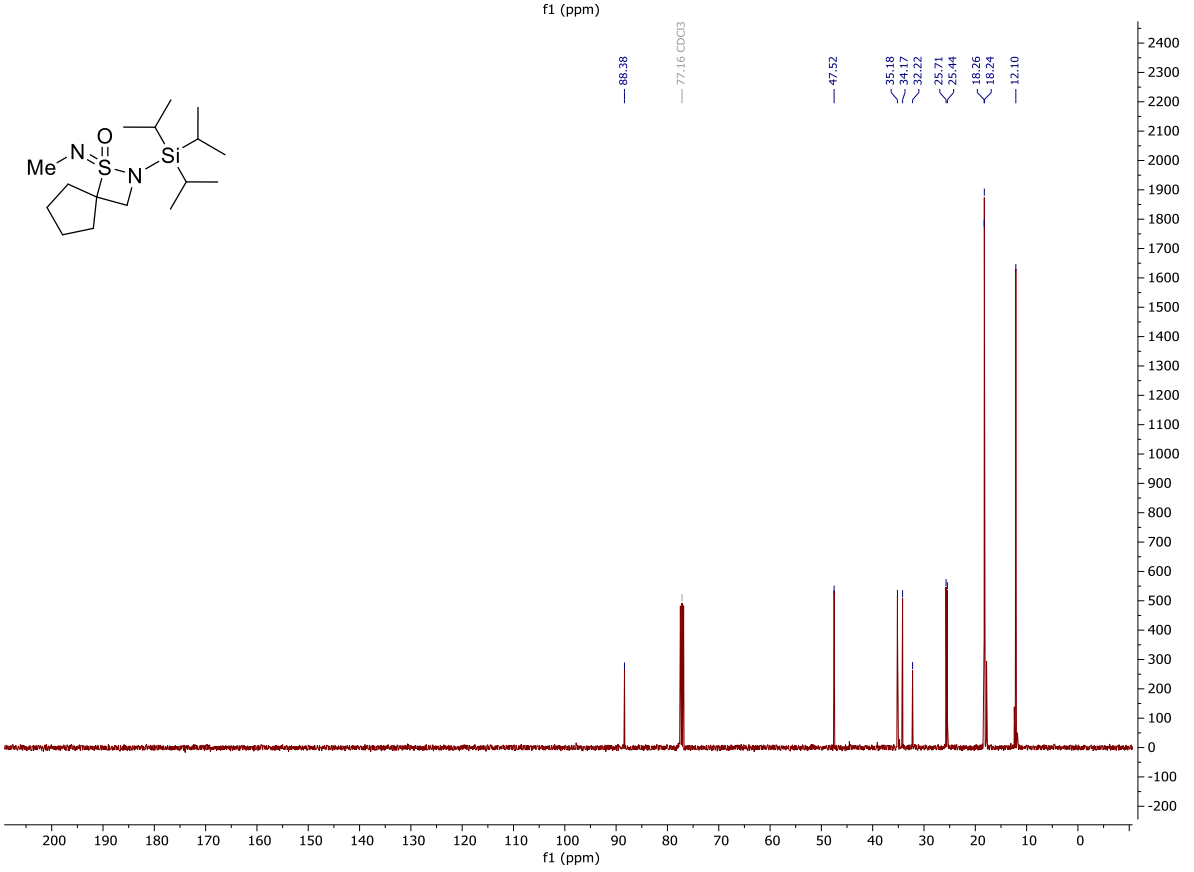
Phenyl (1-oxido-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)carbamate (4wf)



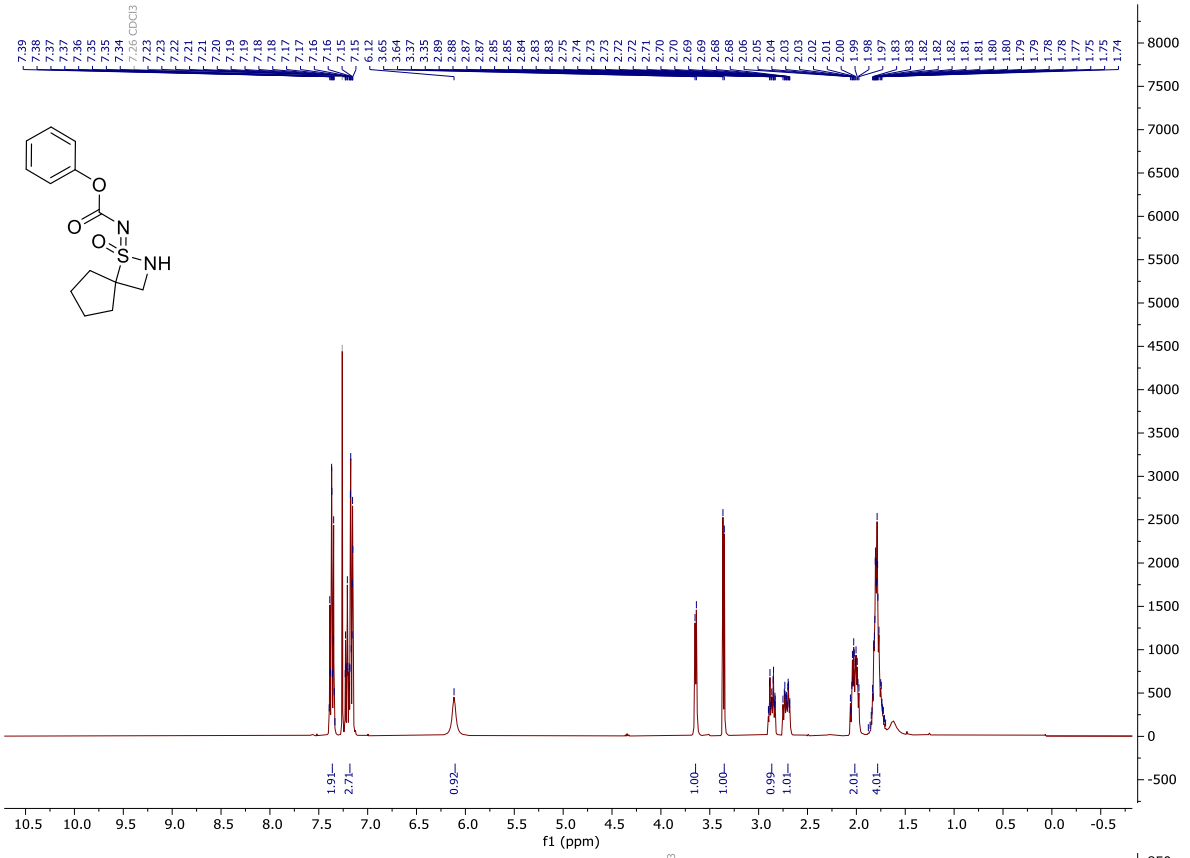


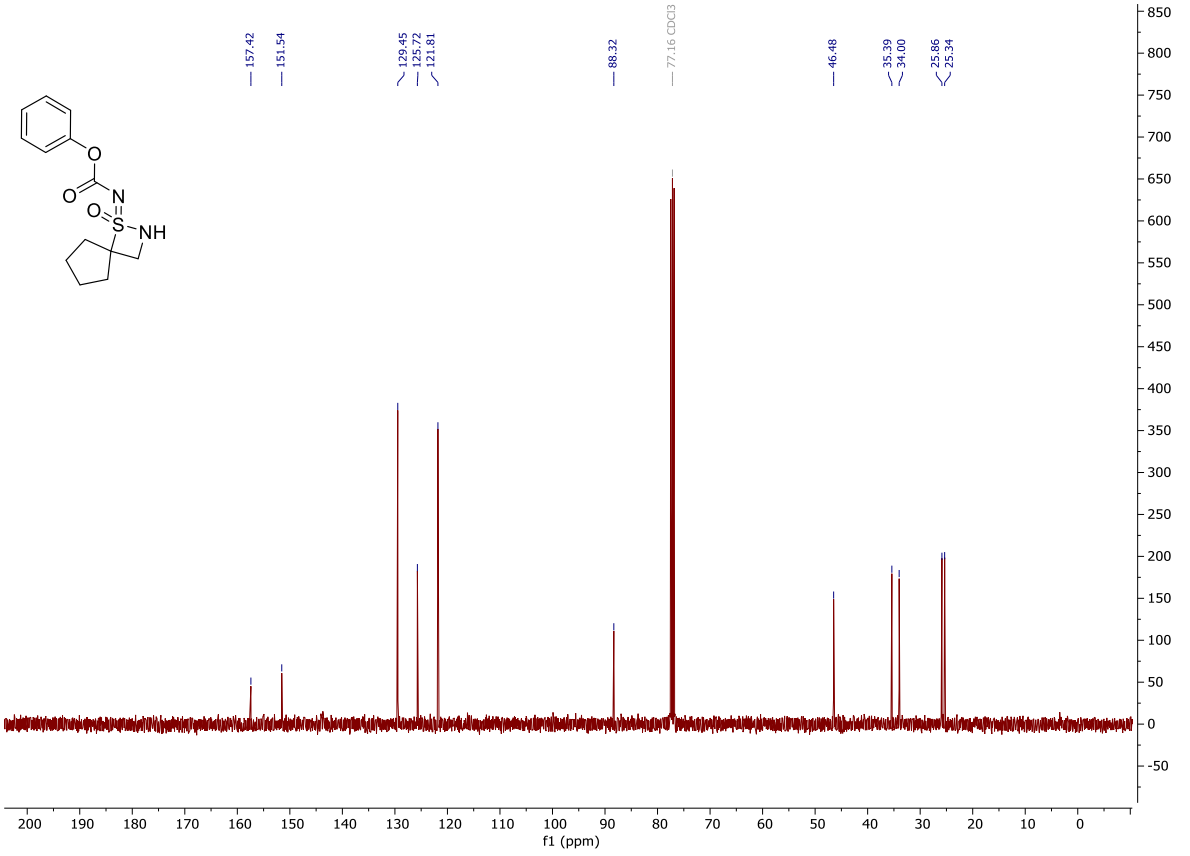
1-(Methylimino)-2-(triisopropylsilyl)-1λ^6-thia-2-azaspiro[3.4]octane 1-oxide (4wg)



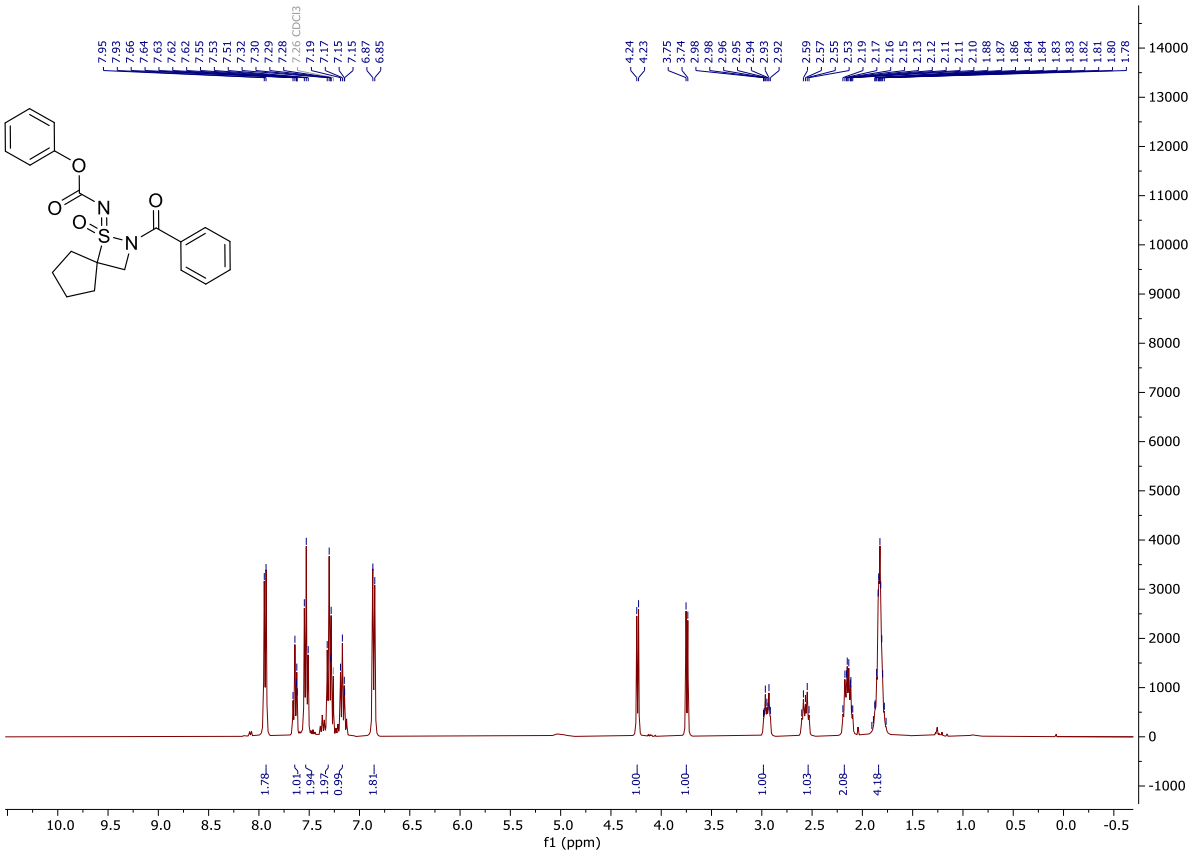


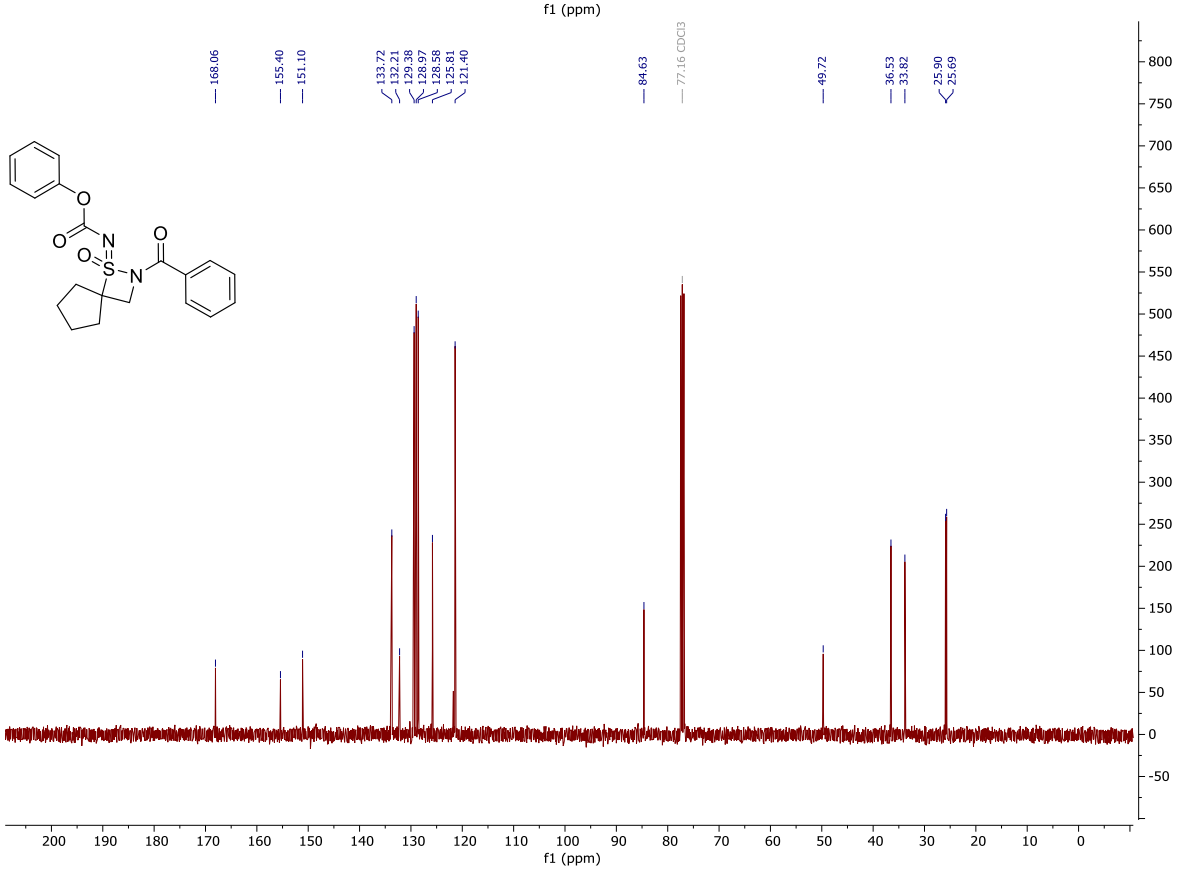
Phenyl (1-oxido-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)carbamate (4wfa)



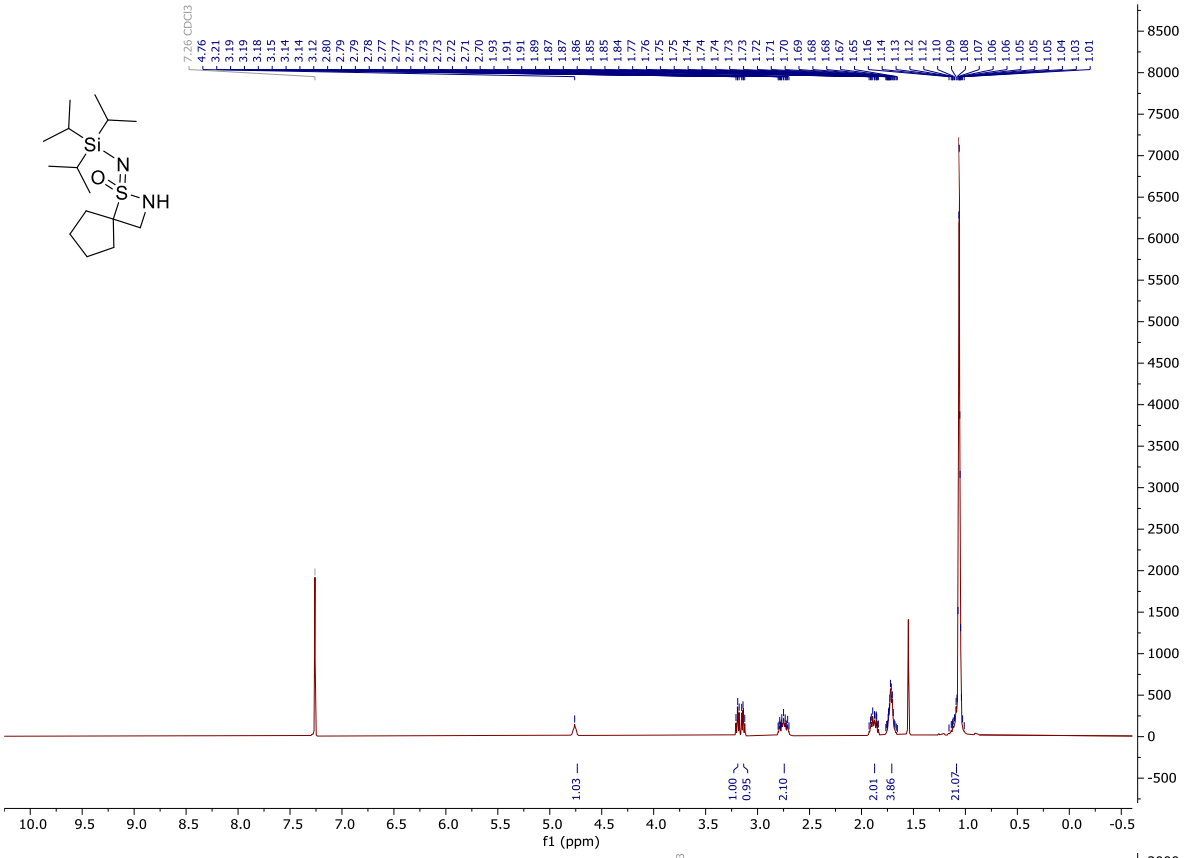


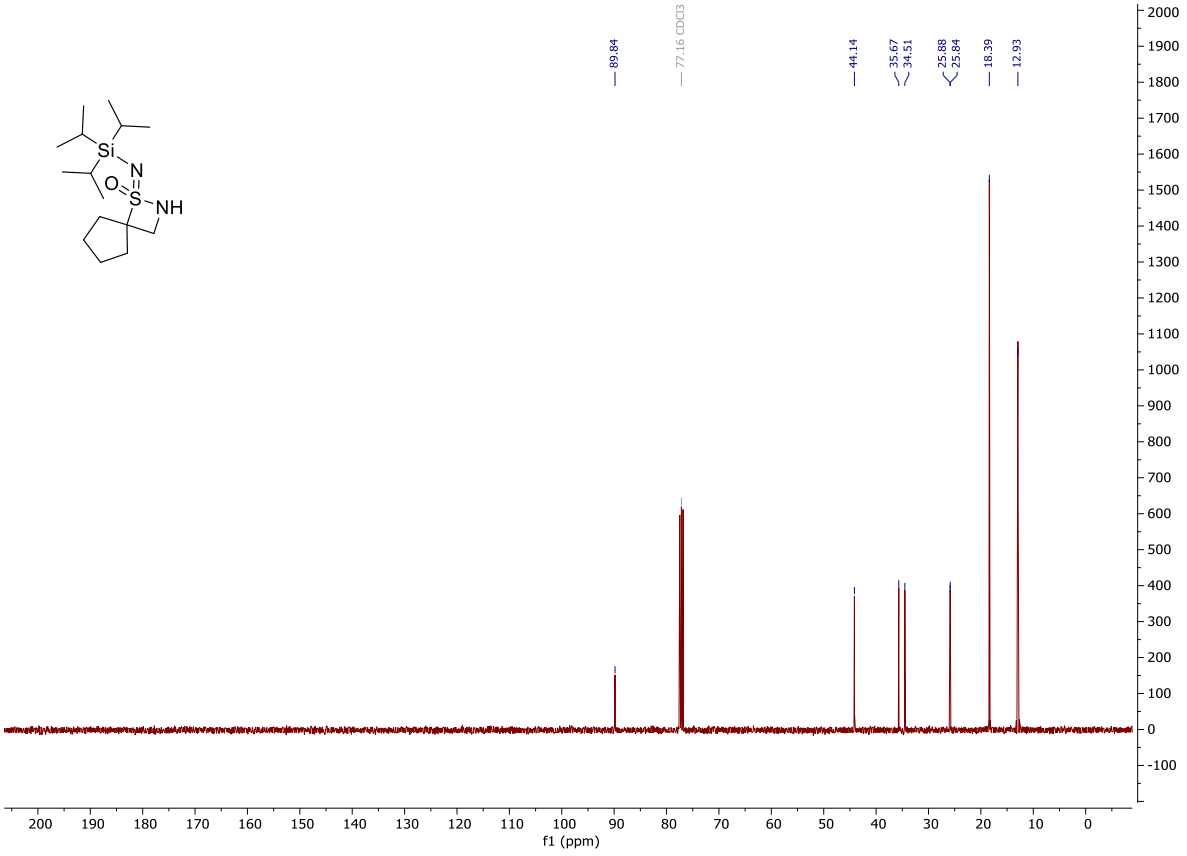
Phenyl (2-benzoyl-1-oxido-1λ^6-thia-2-azaspiro[3.4]octan-1-ylidene)carbamate (4wfb)



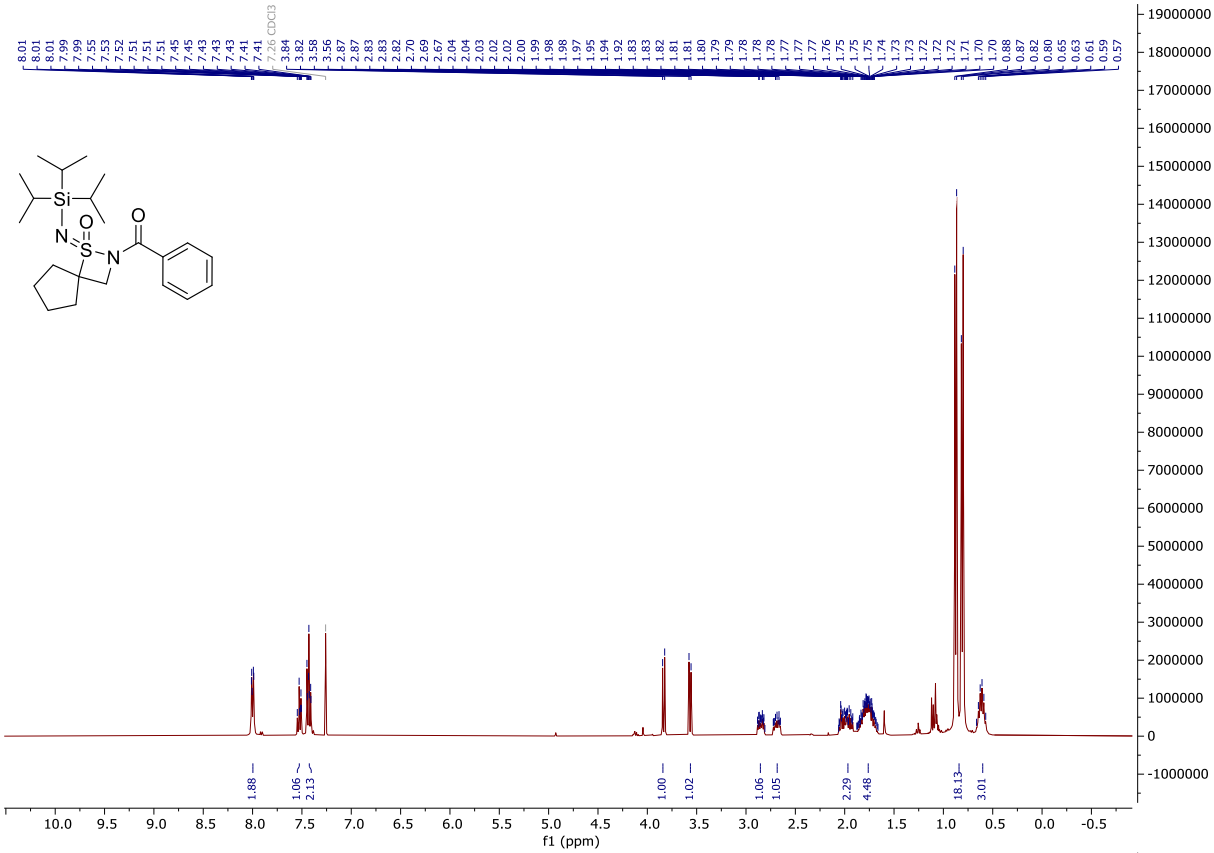


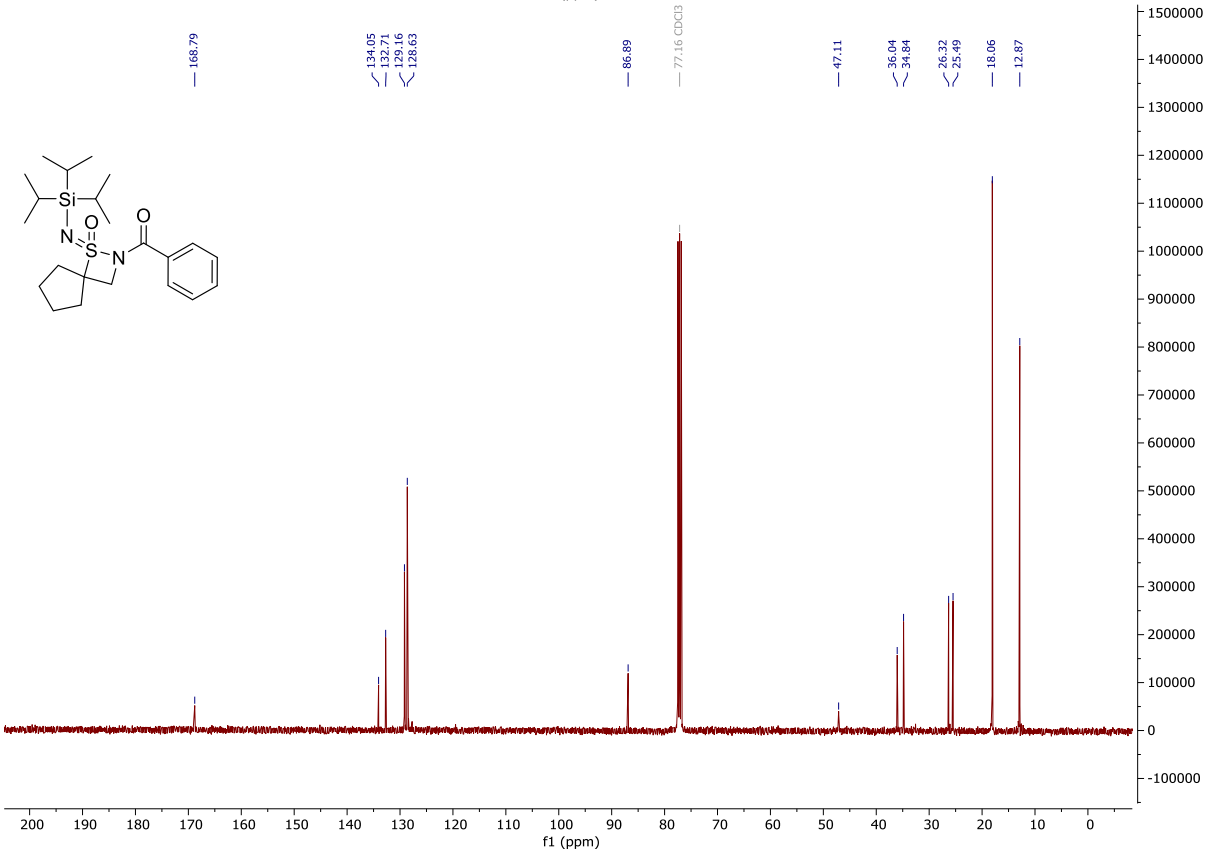
1-((Triisopropylsilyl)imino)- 1λ^6-thia-2-azaspiro[3.4]octane 1-oxide (4wh)



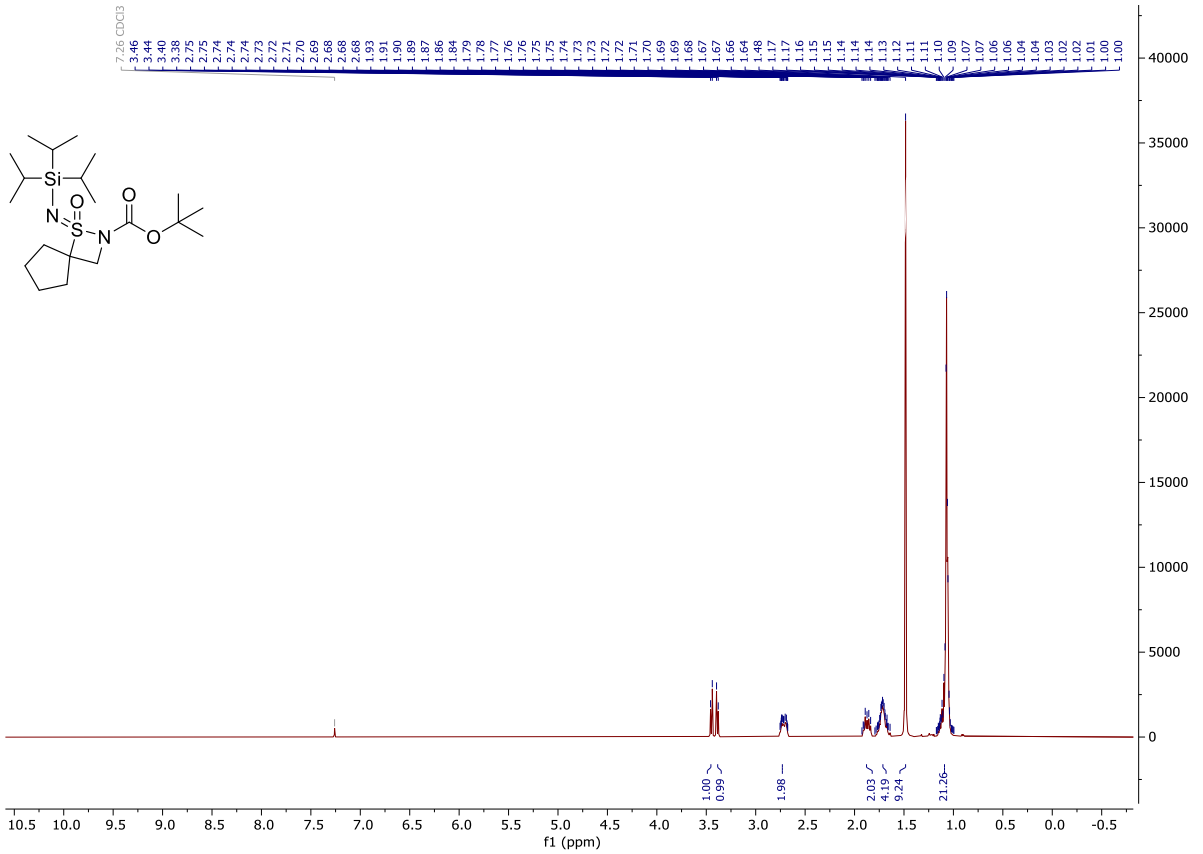


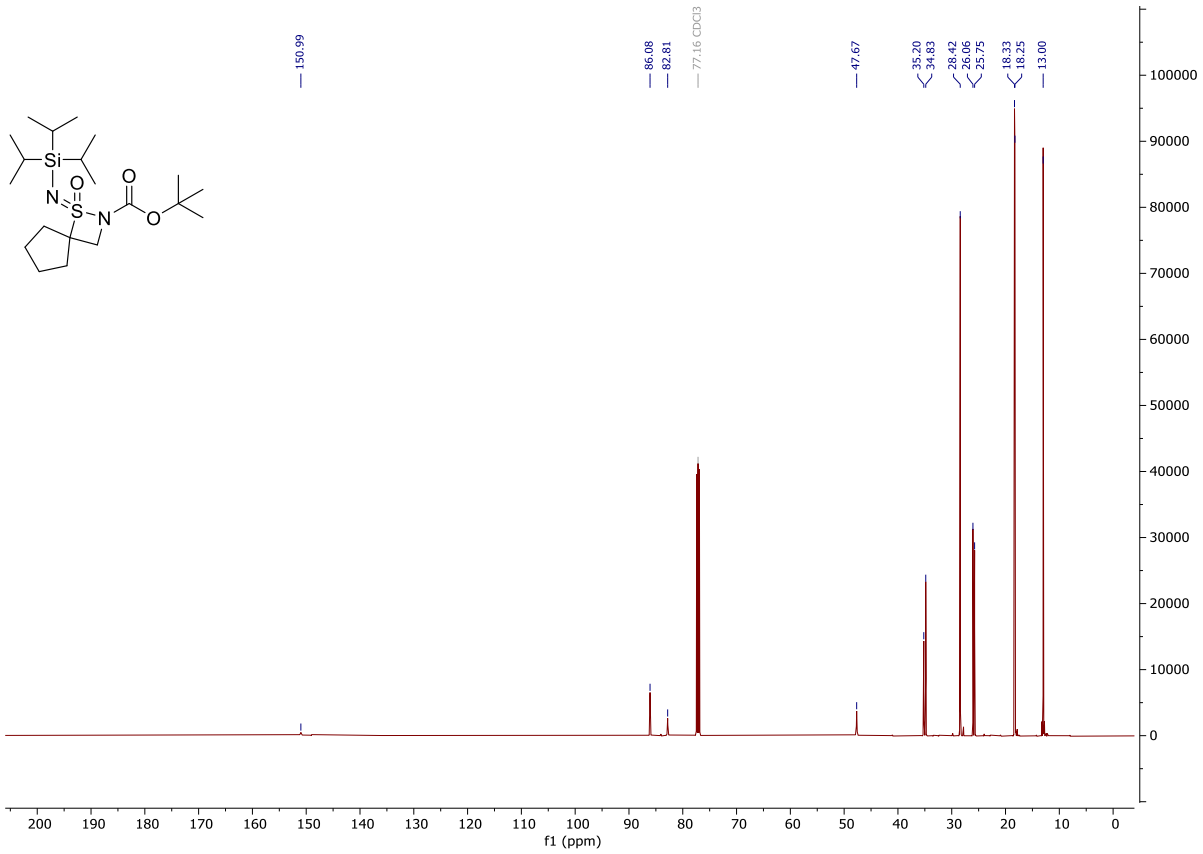
(1-Oxido-1-((triisopropylsilyl)imino)-1λ^6-thia-2-azaspiro[3.4]octan-2-yl)(phenyl)methanone (4wha)



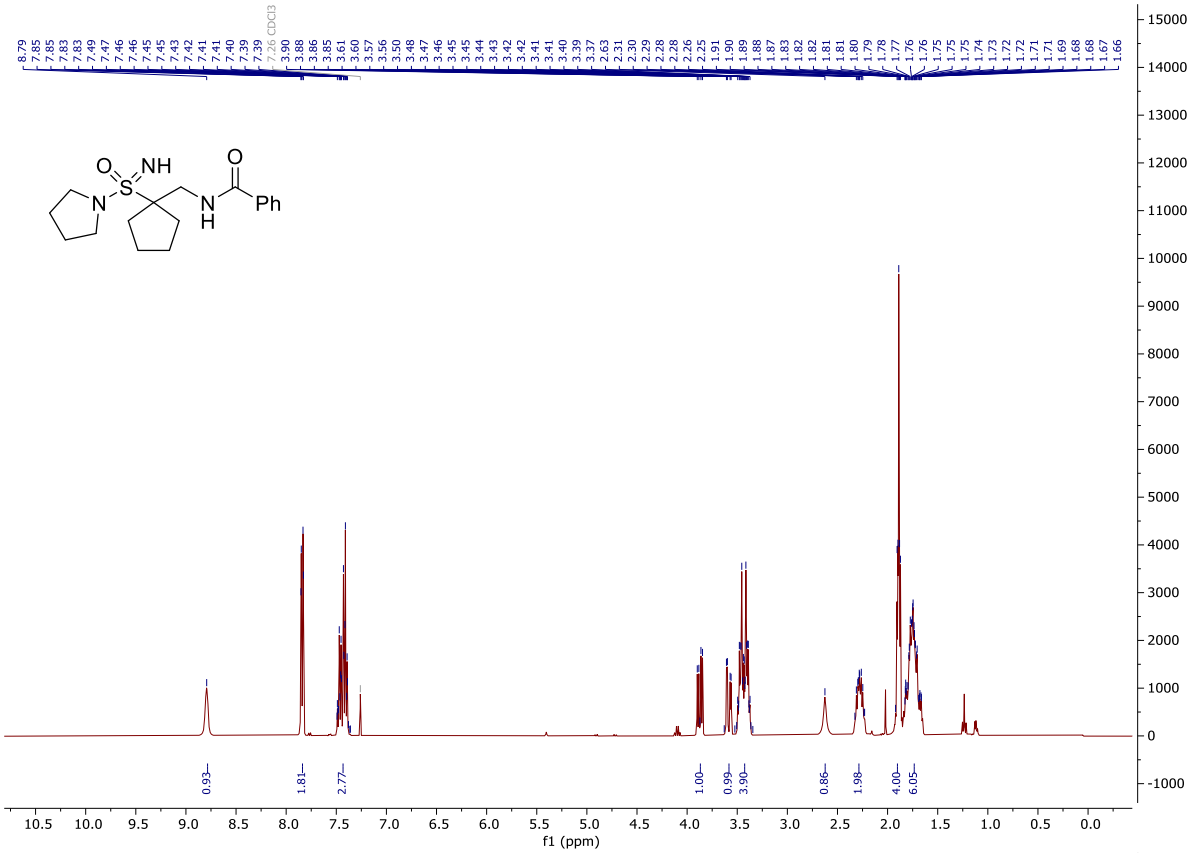


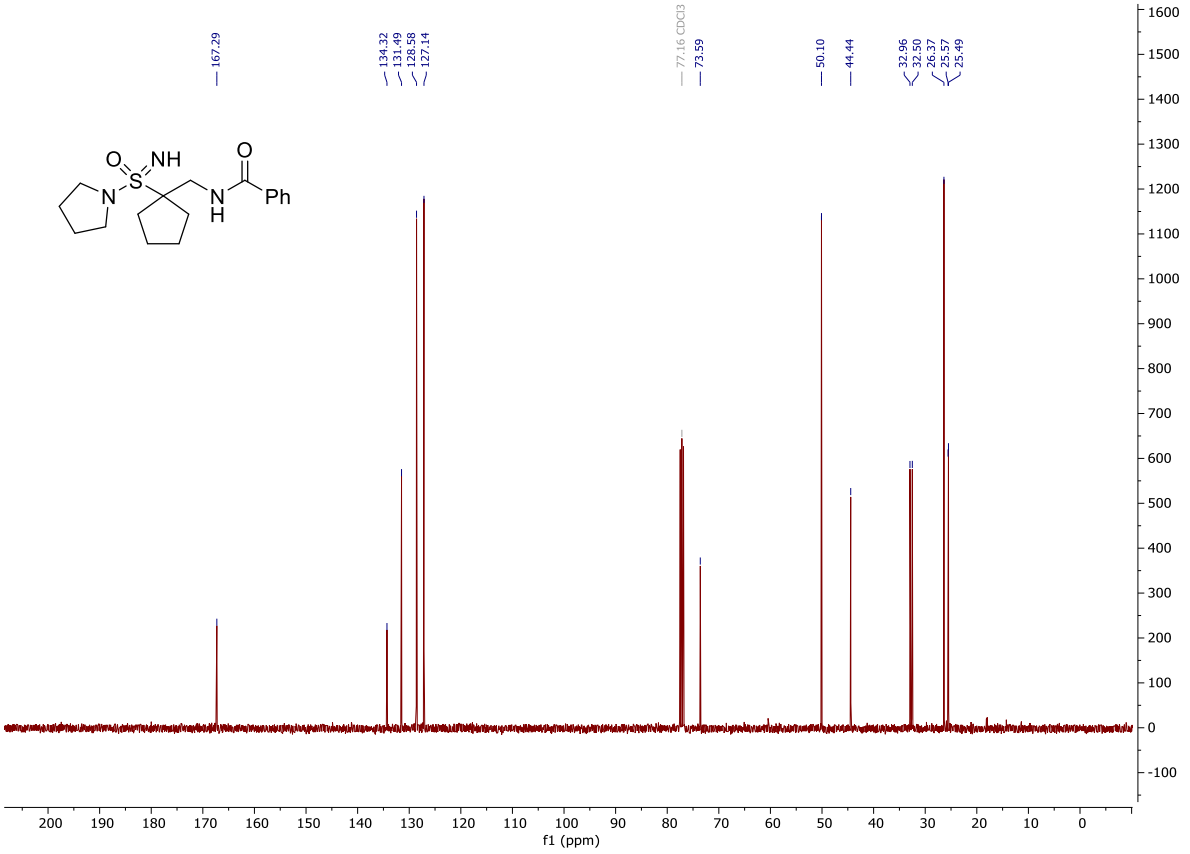
tert-Butyl 1-((triisopropylsilyl)imino)-1λ^6-thia-2-azaspiro[3.4]octane-2-carboxylate 1-oxide (4whb)



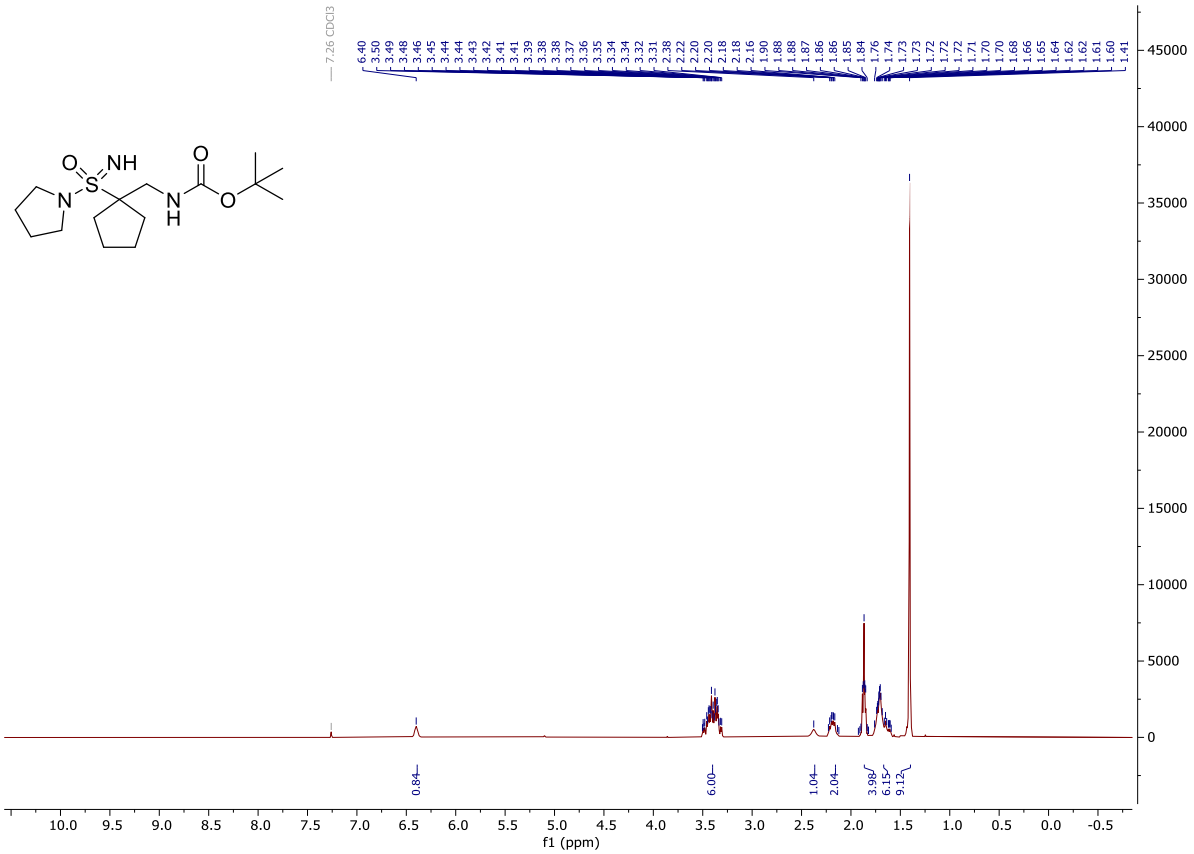


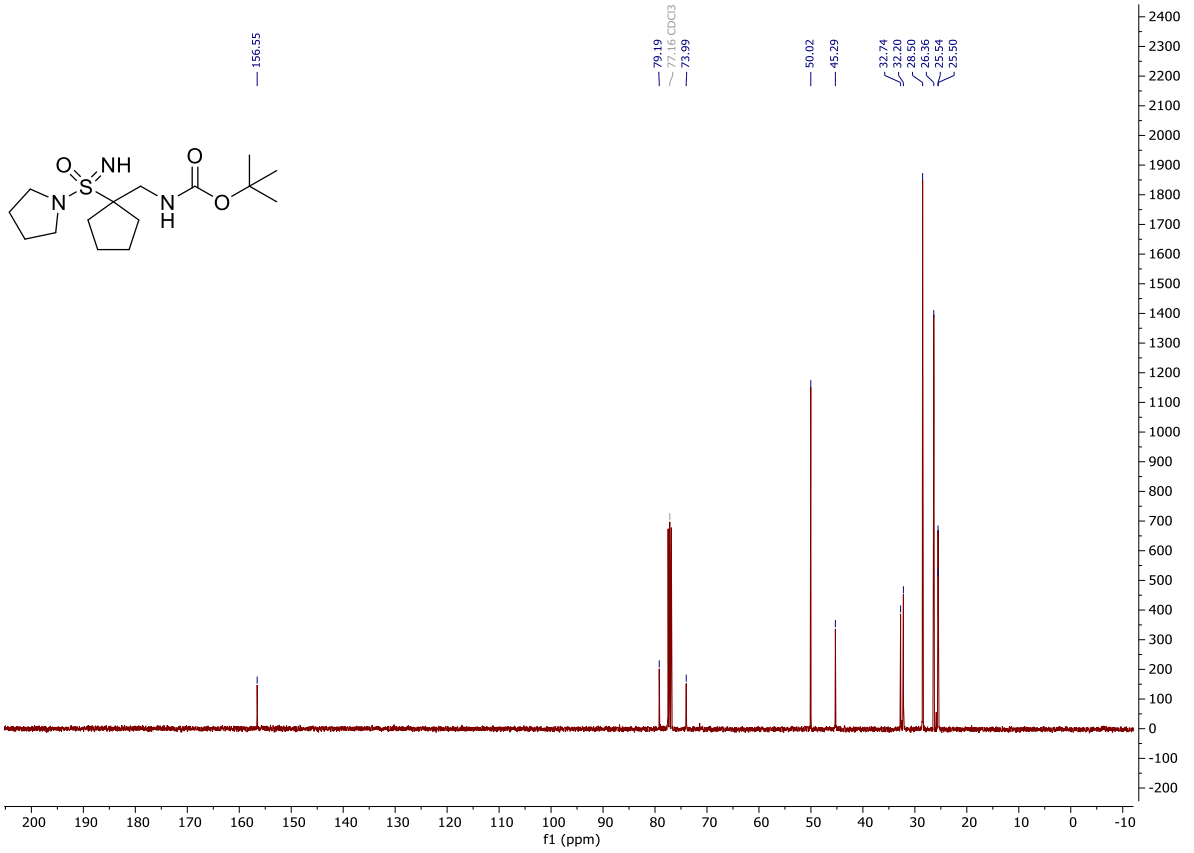
N-((1-(Pyrrolidine-1-sulfonimidoyl)cyclopentyl)methyl)benzamide (5a)



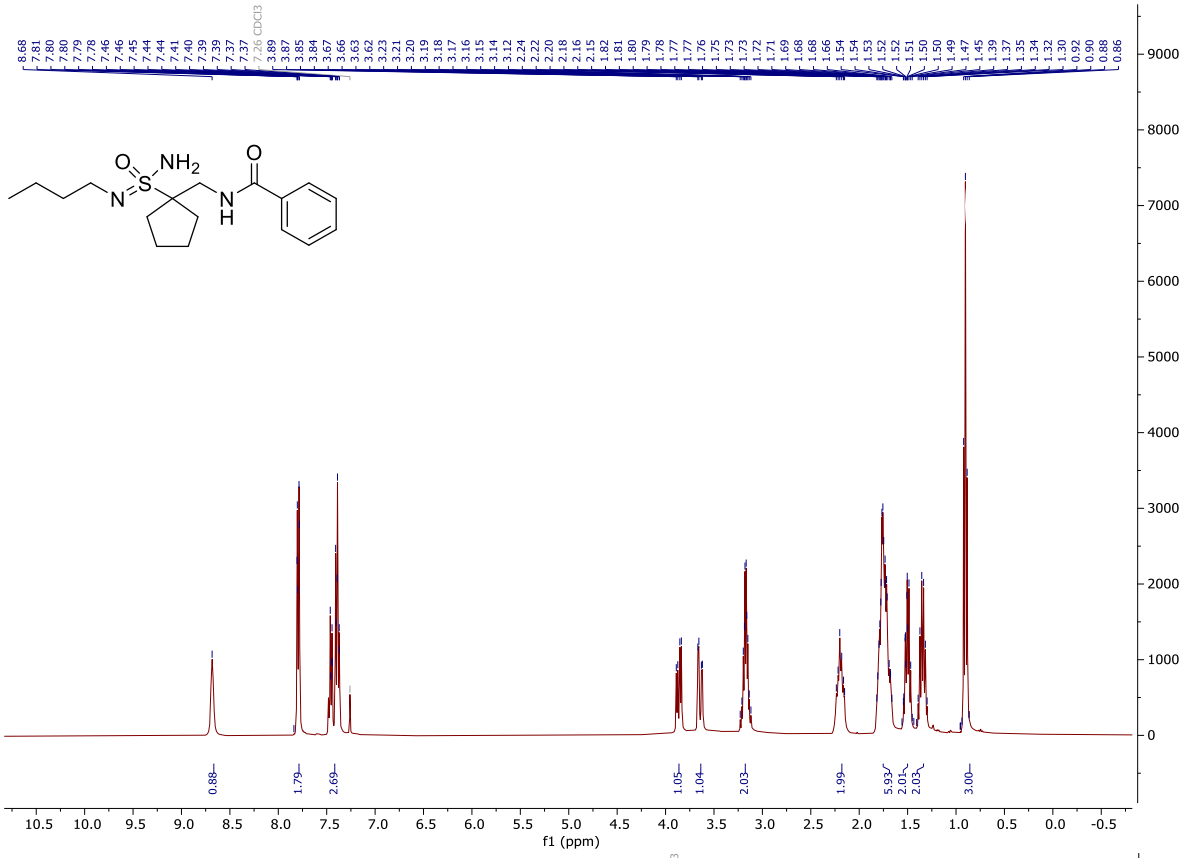


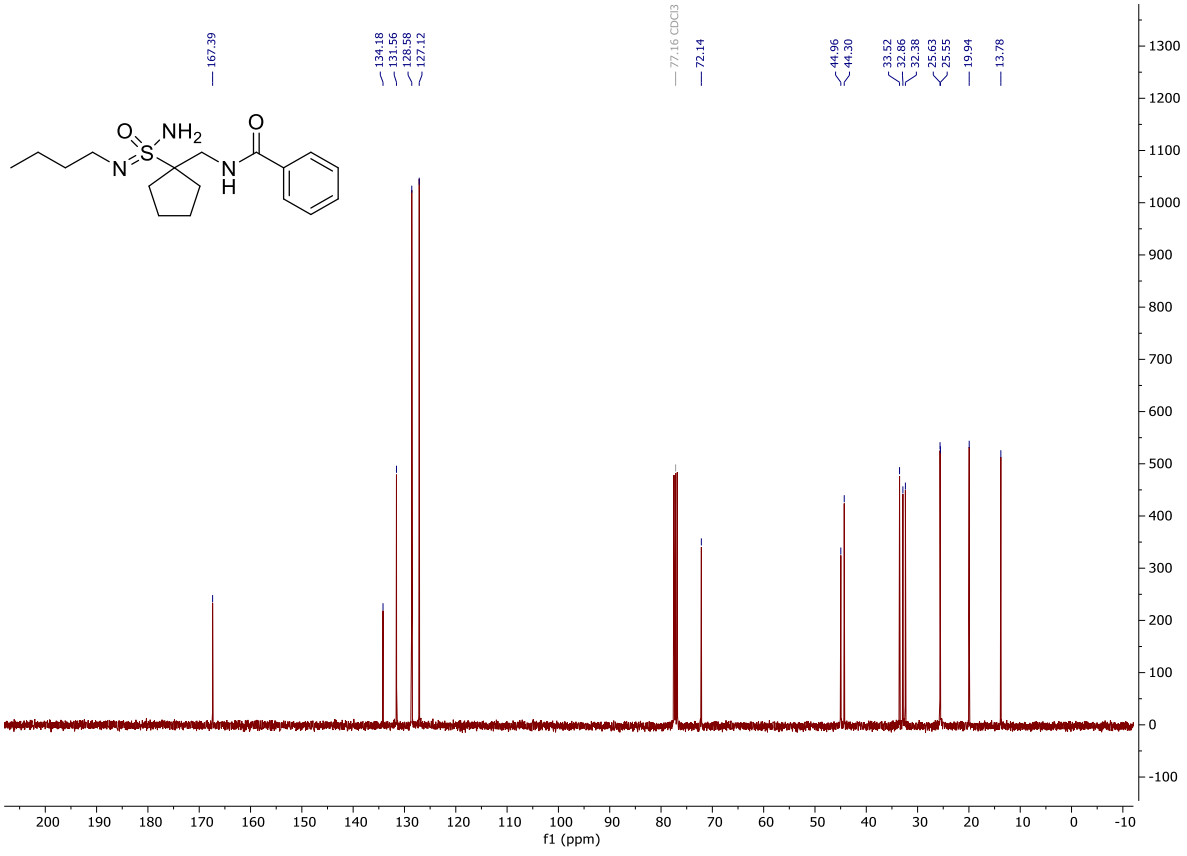
tert-Butyl ((1-(pyrrolidine-1-sulfonimidoyl)cyclopentyl)methyl)carbamate (5a')



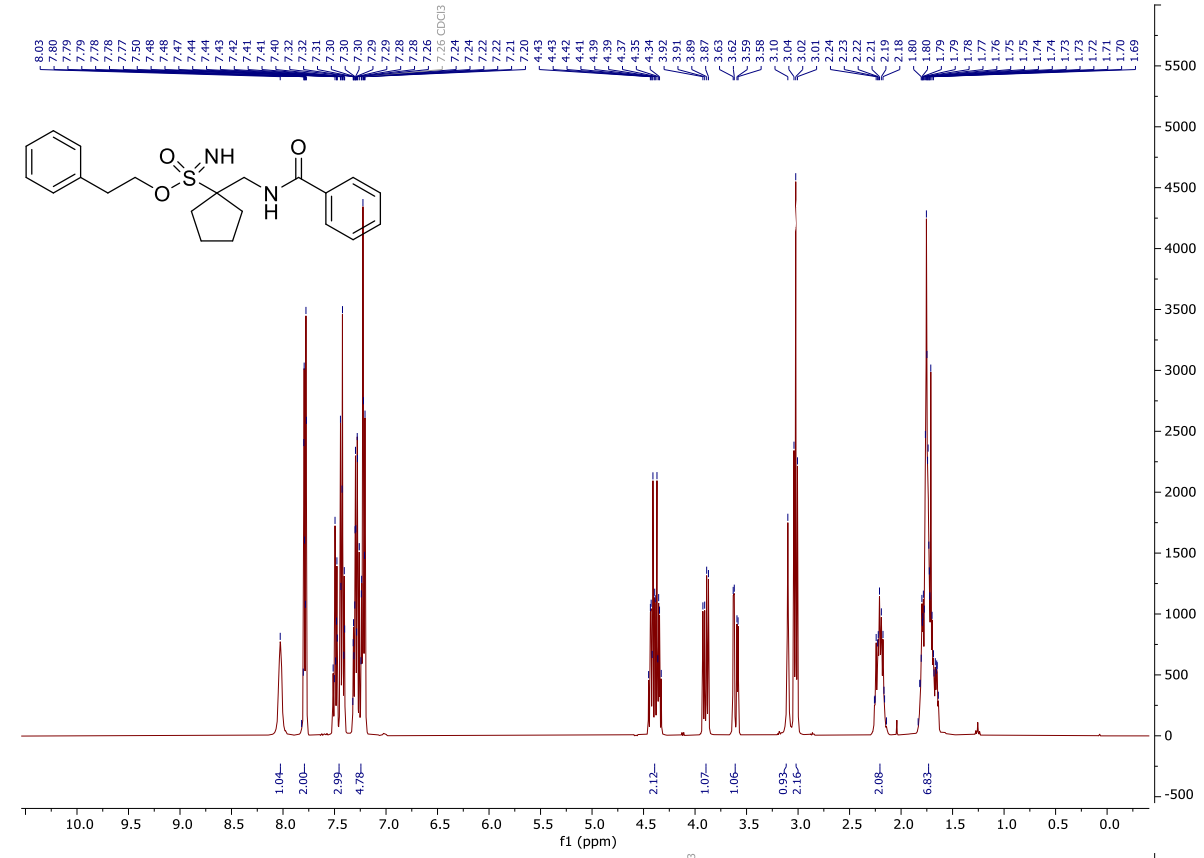


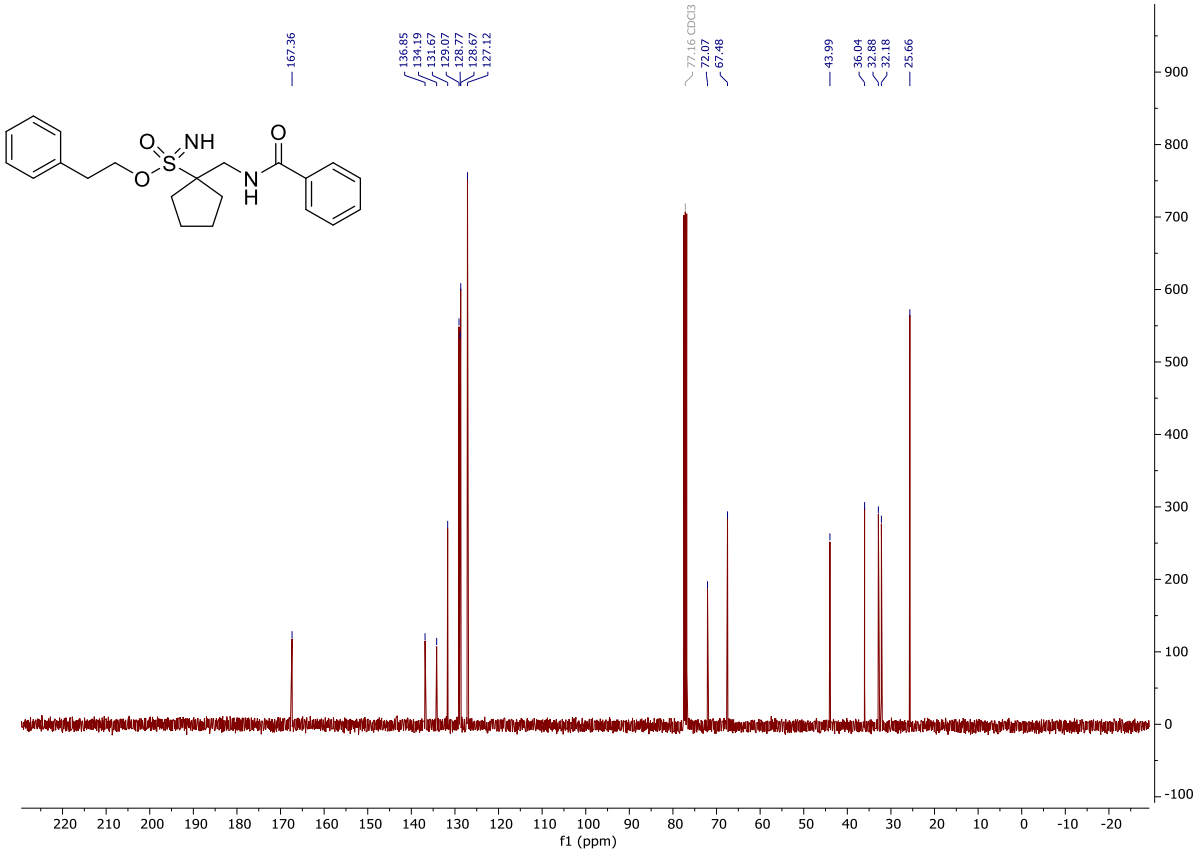
N-((1-(*N*'-Butylsulfamidimidoyl)cyclopentyl)methyl)benzamide (5b)



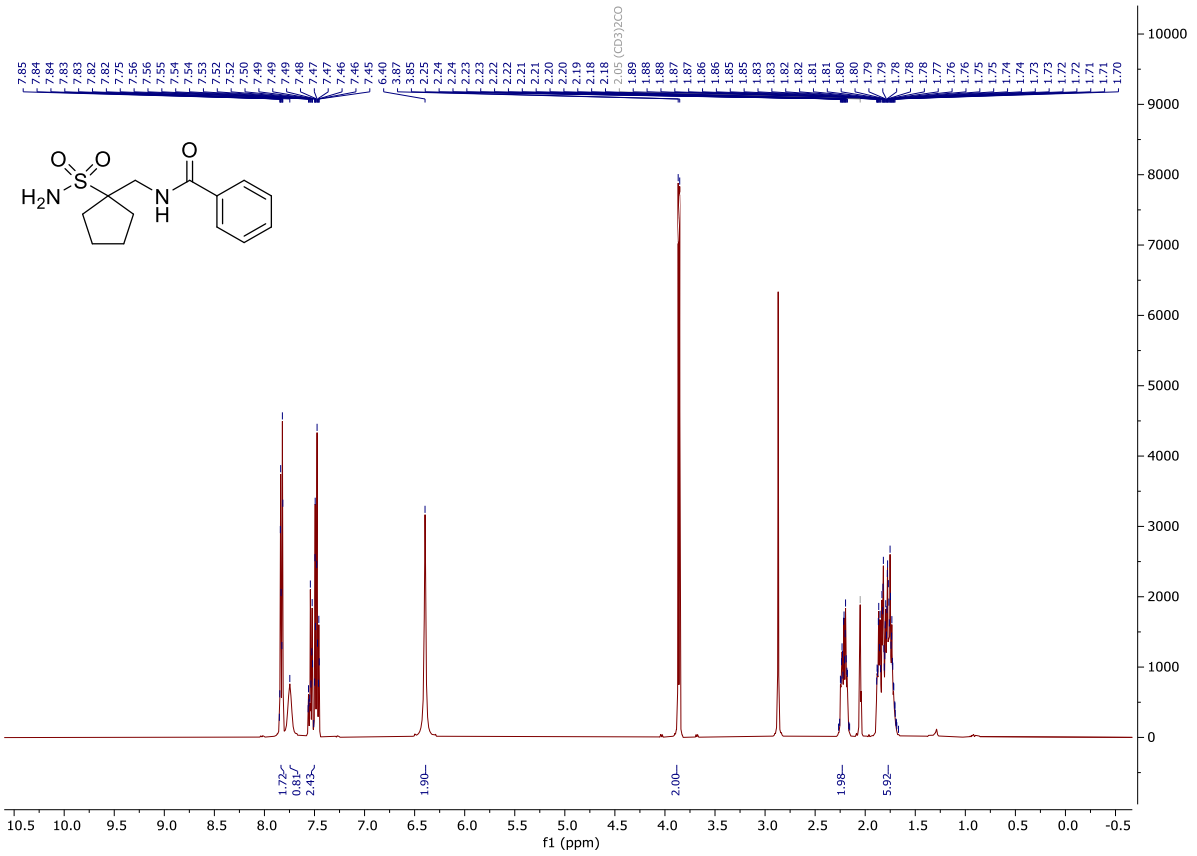


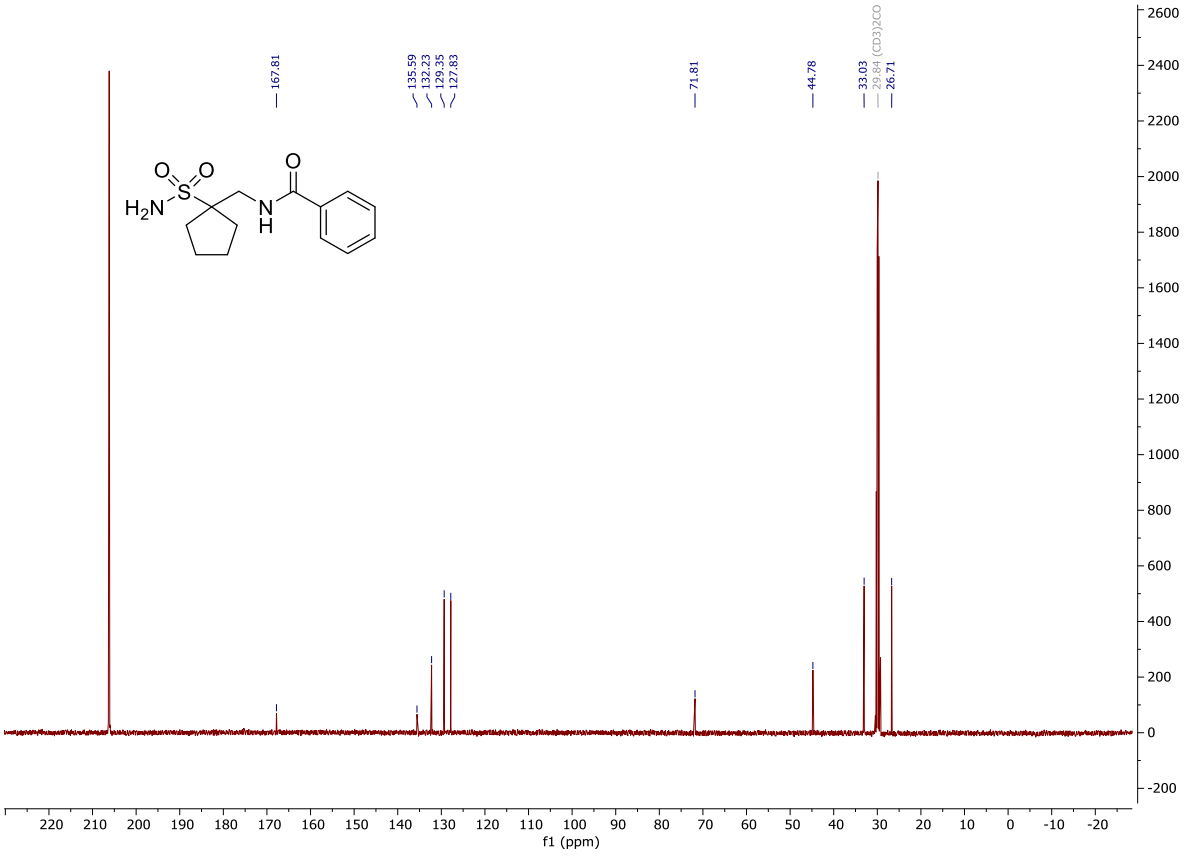
Phenethyl 1-(benzamidomethyl)cyclopentane-1-sulfonimidate (5c)



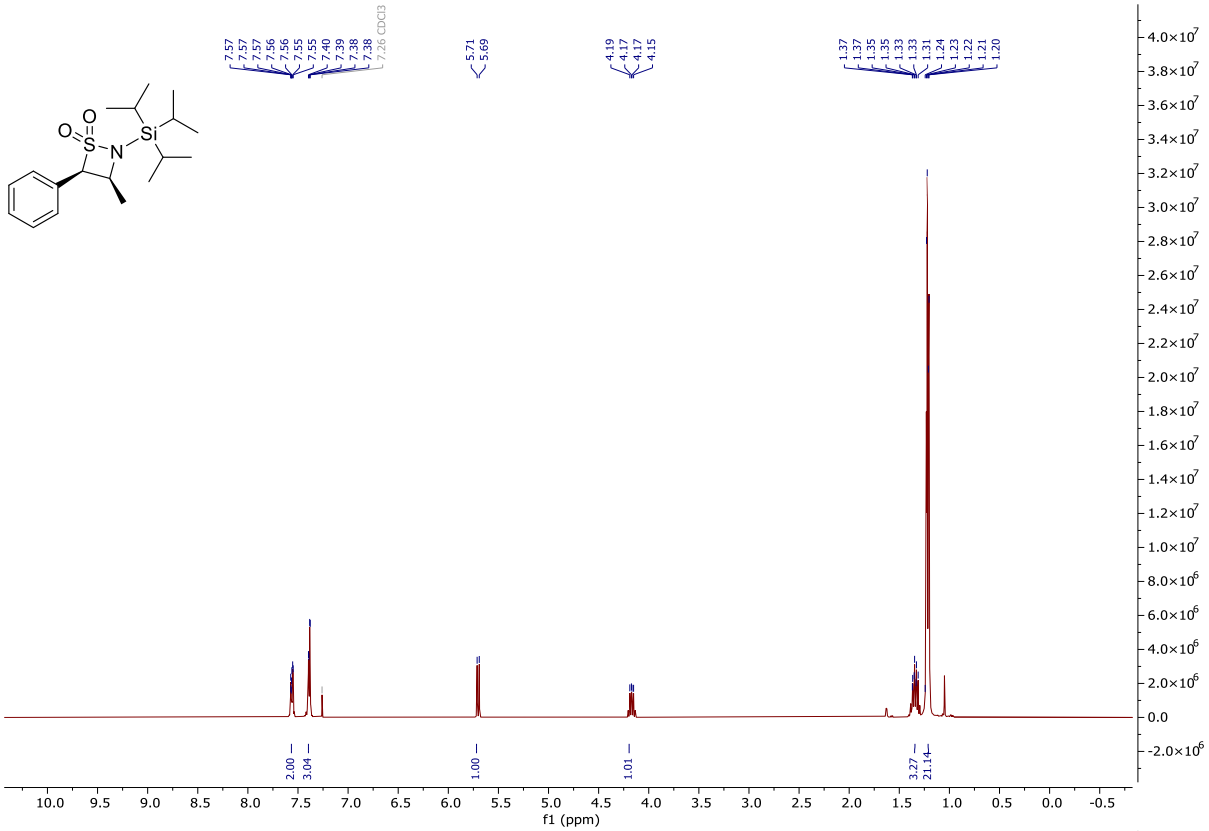


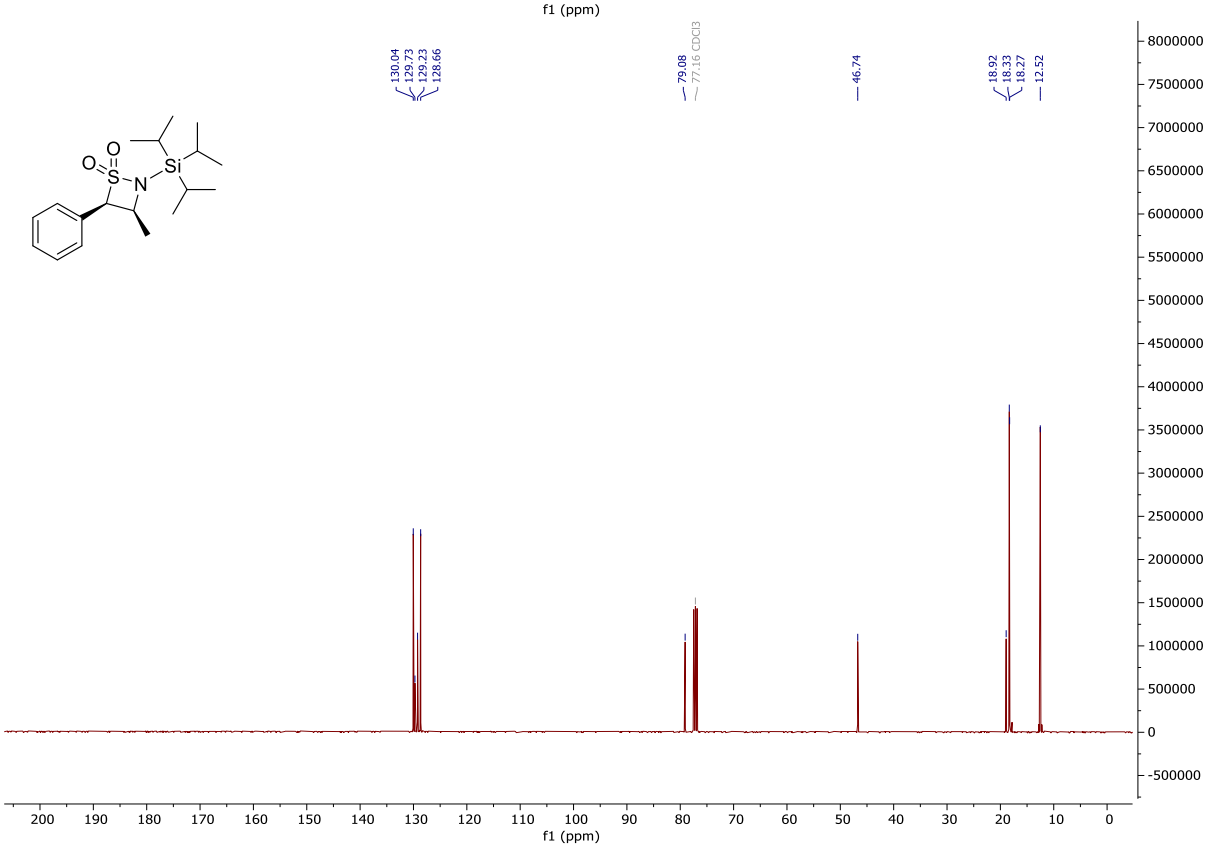
N-((1-Sulfamoylcyclopentyl)methyl)benzamide (5d)



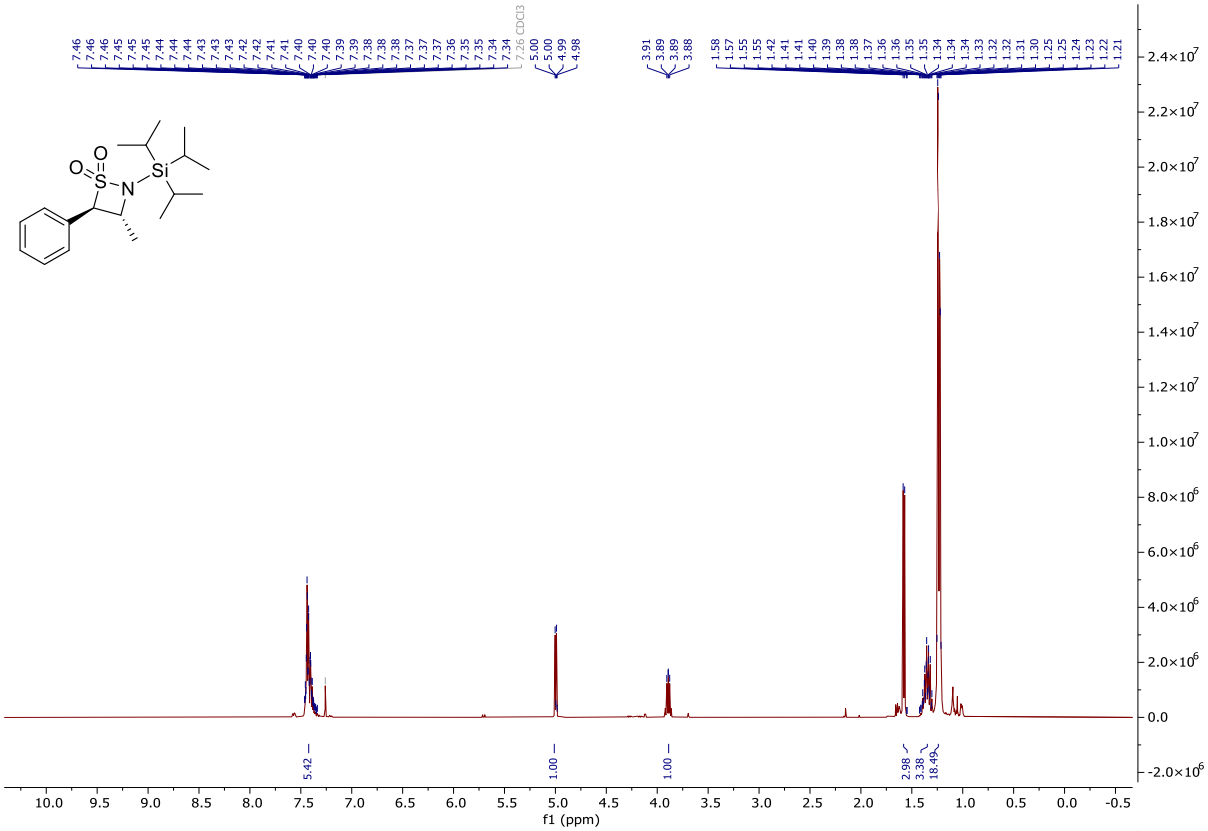


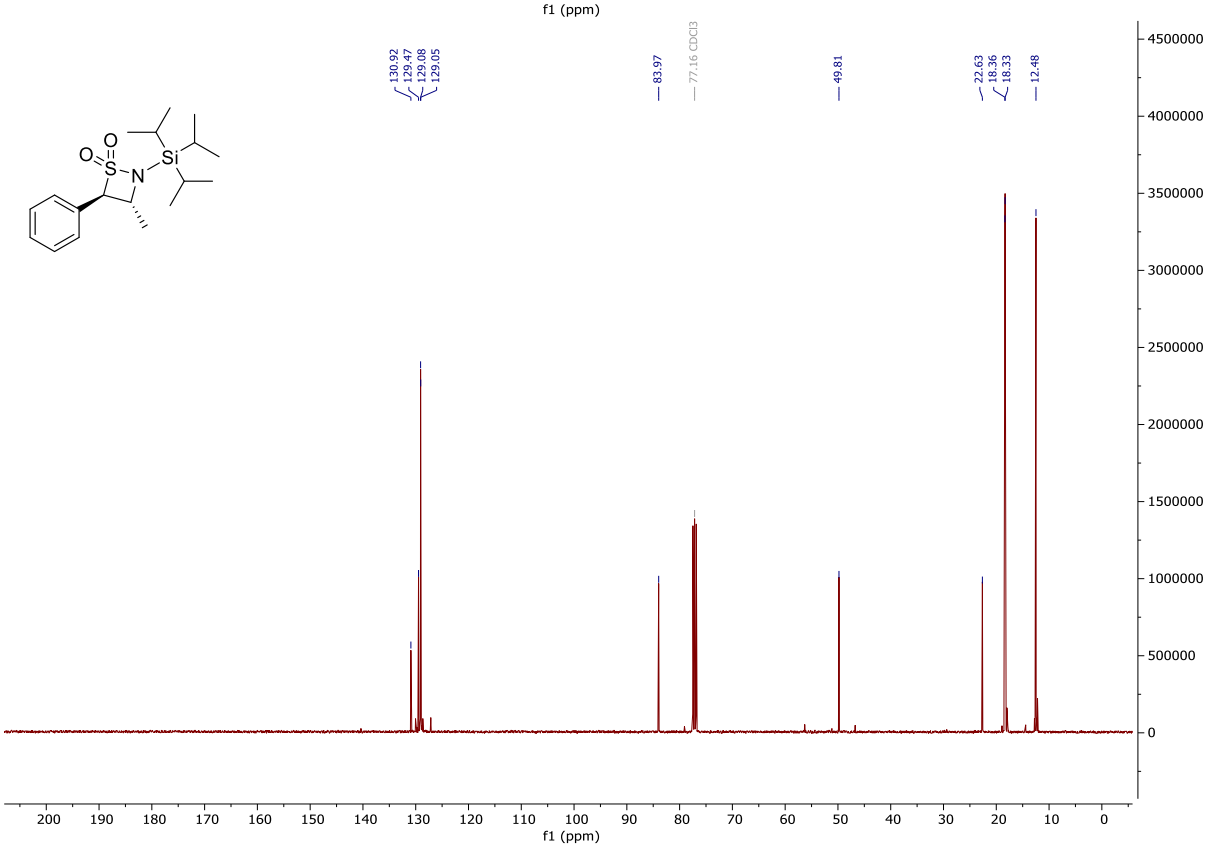
cis-3-Methyl-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1,1-dioxide (*cis*-2ac)



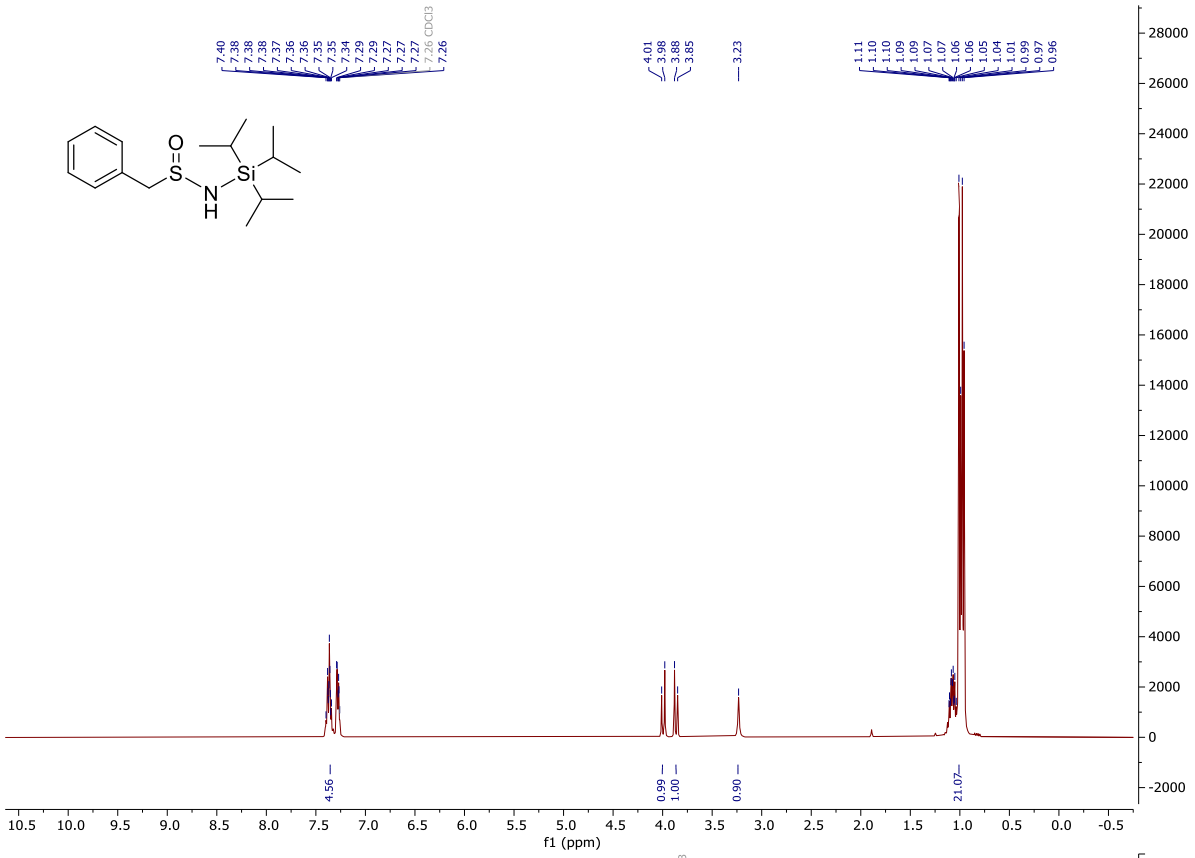


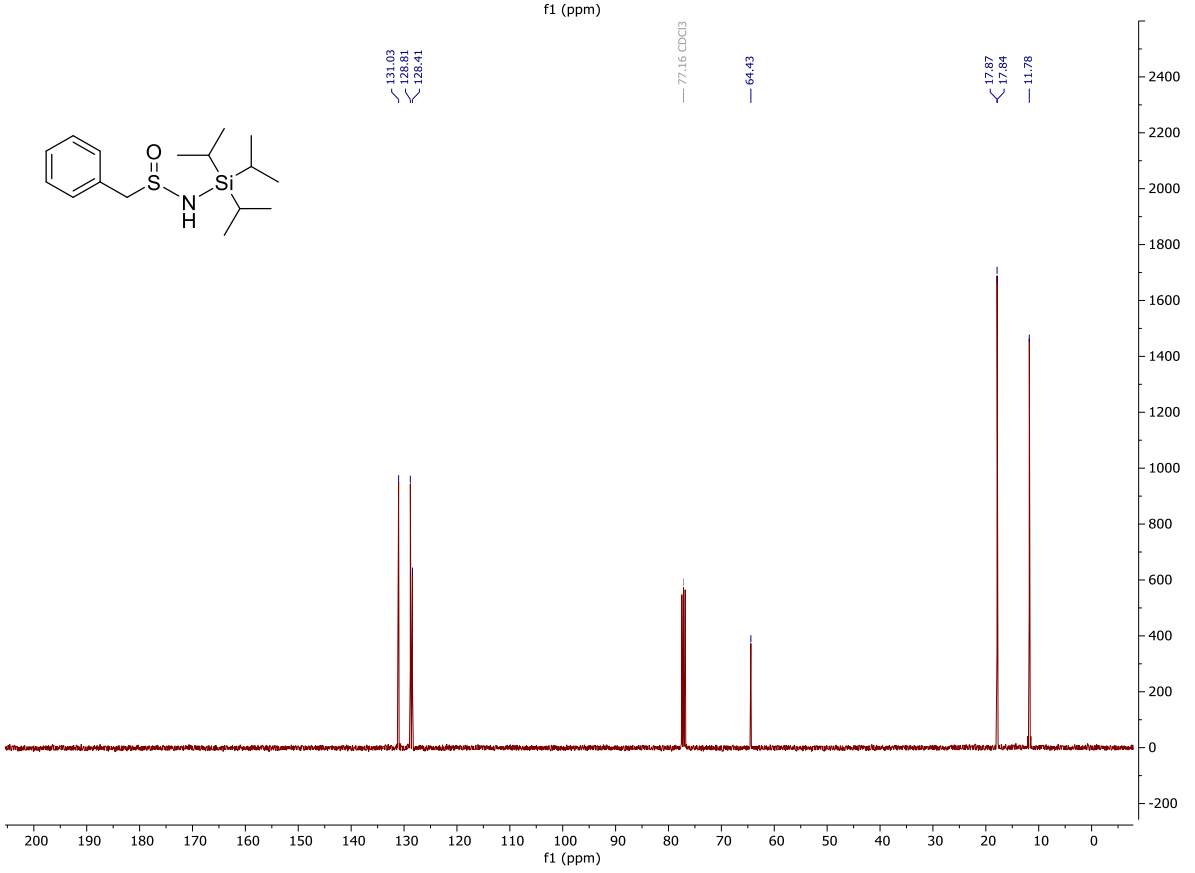
trans-3-Methyl-4-phenyl-2-(triisopropylsilyl)-1,2-thiazetidine 1,1-dioxide (_trans_-2ac)





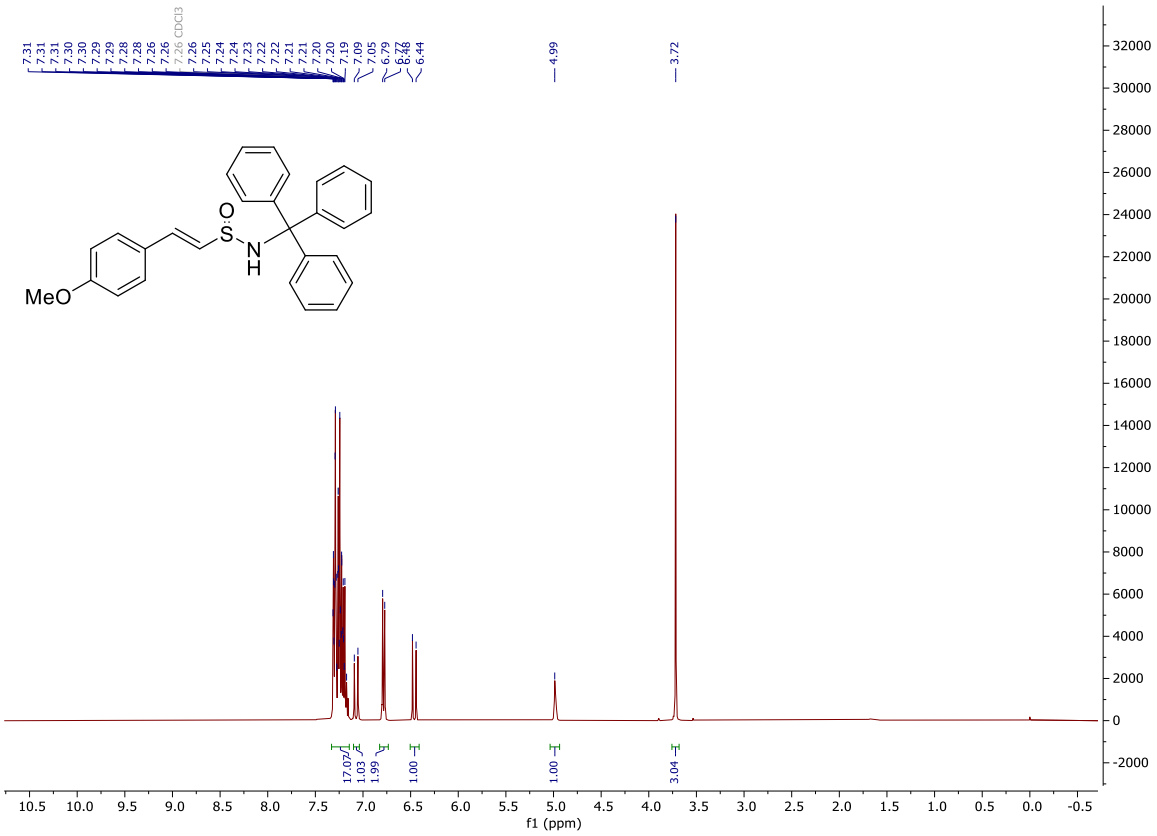
1-Phenyl-*N*-(triisopropylsilyl)methanesulfinamide (9f)

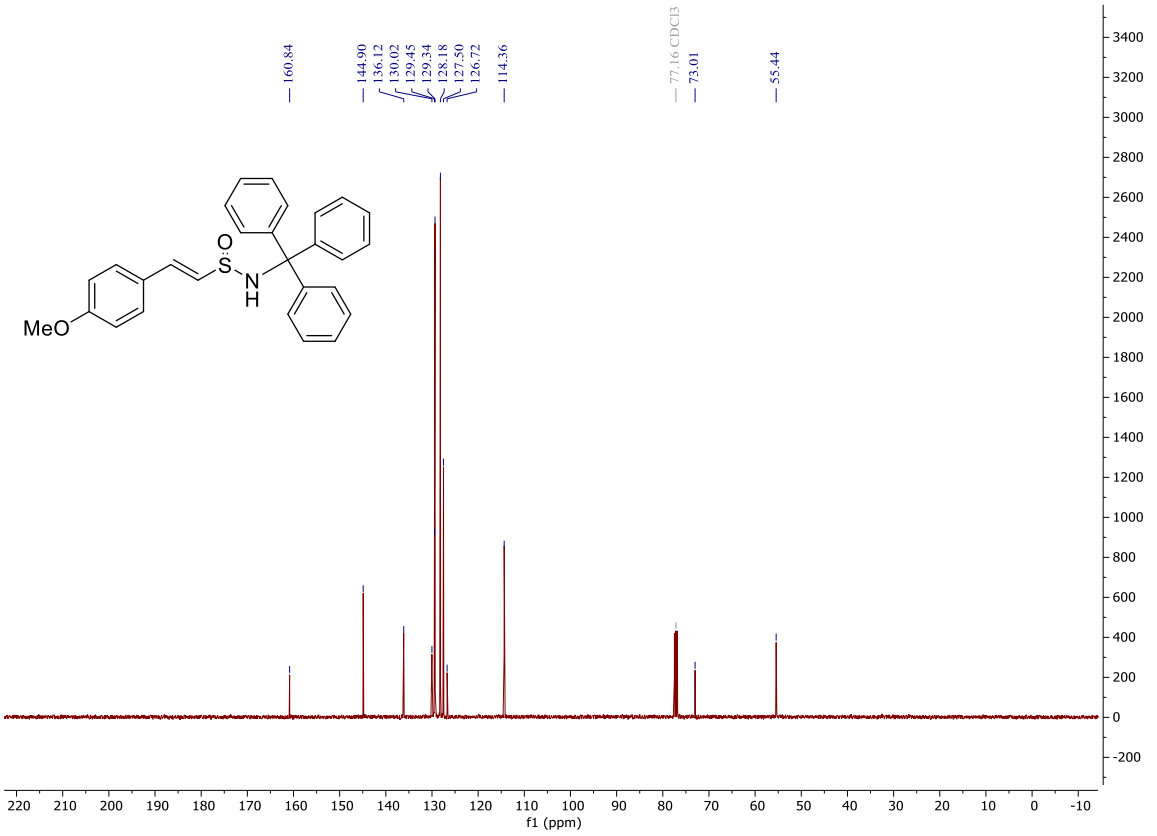




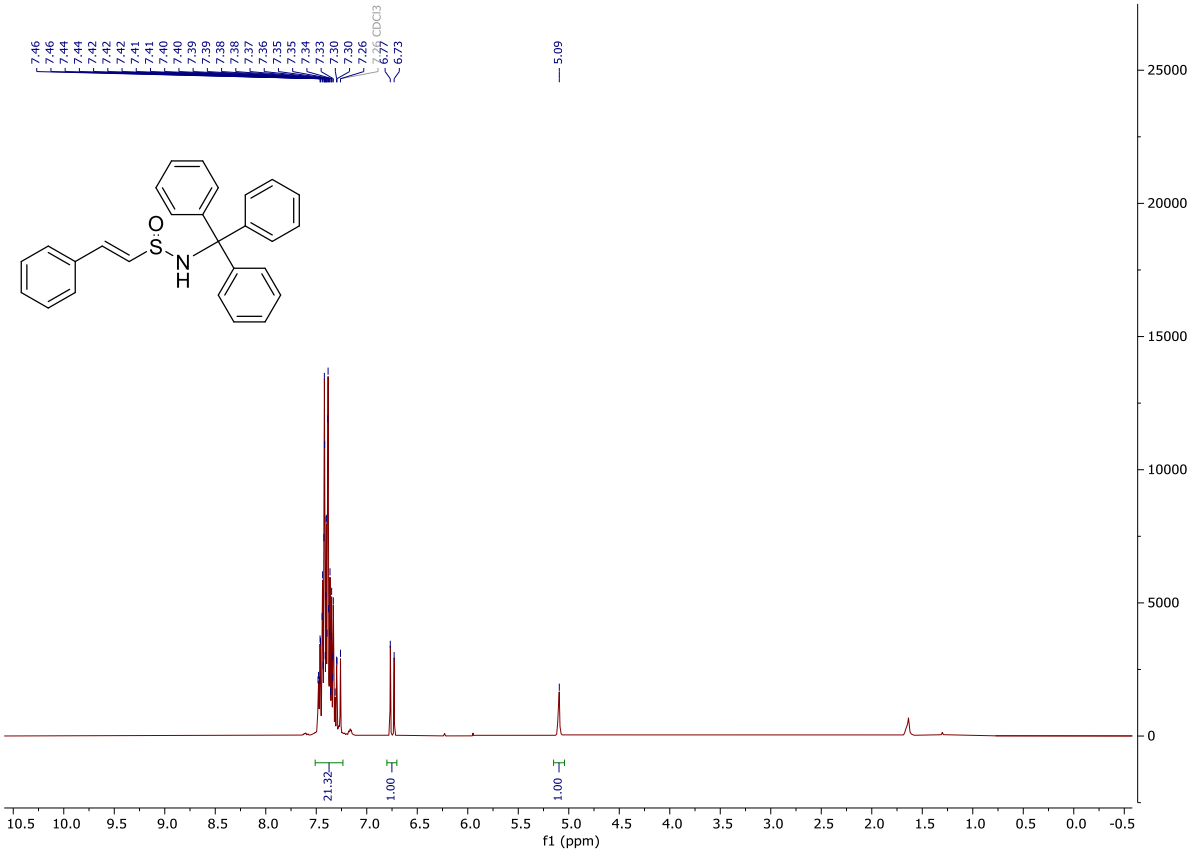
Appendix II-NMR Spectra of Chapter 3

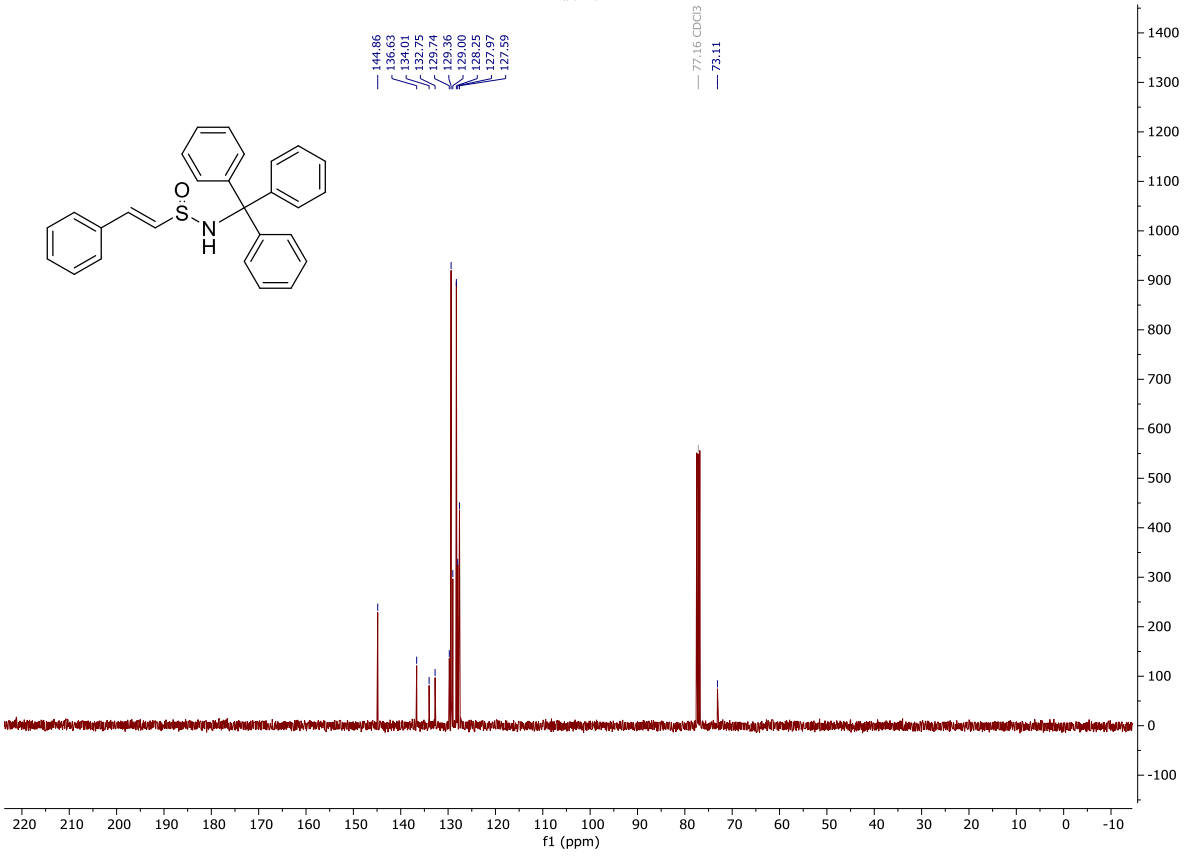
(*E*)-2-(4-Methoxyphenyl)-*N*-tritylethene-1-sulfinamide (7a)



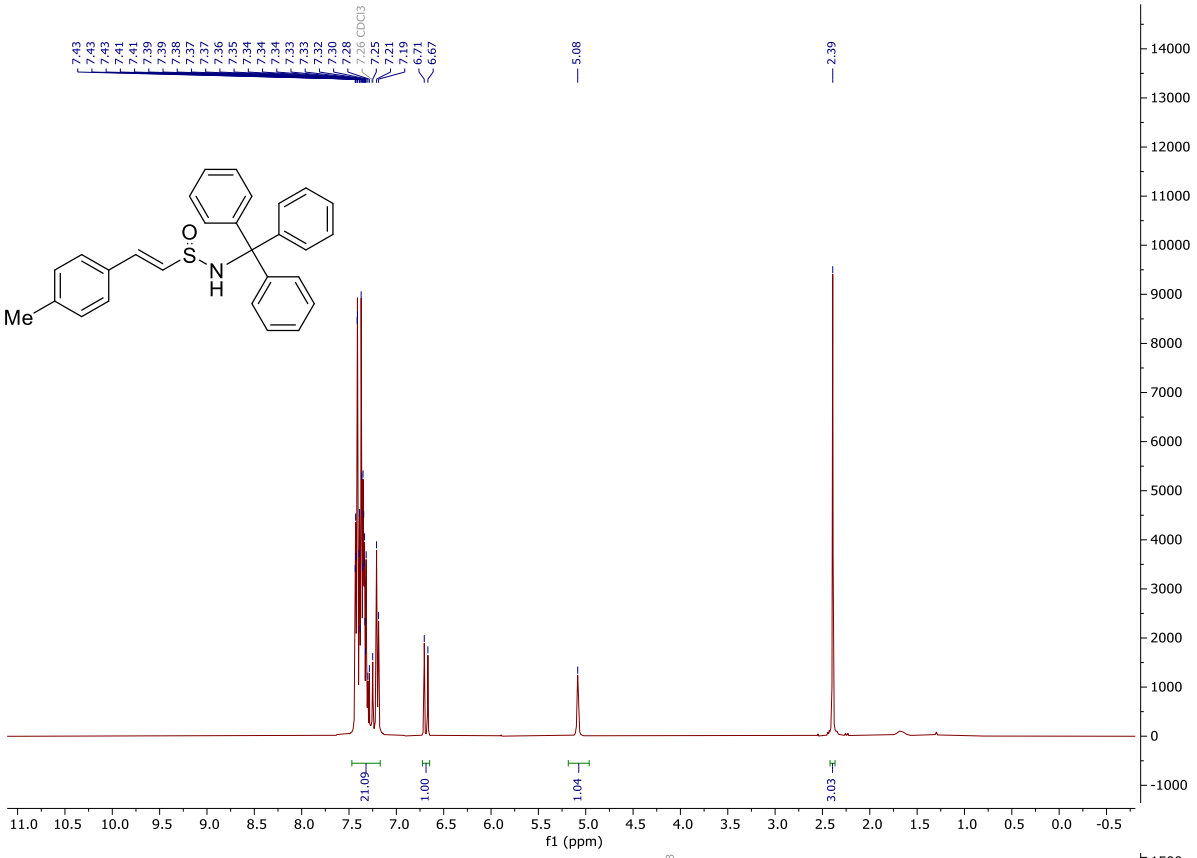


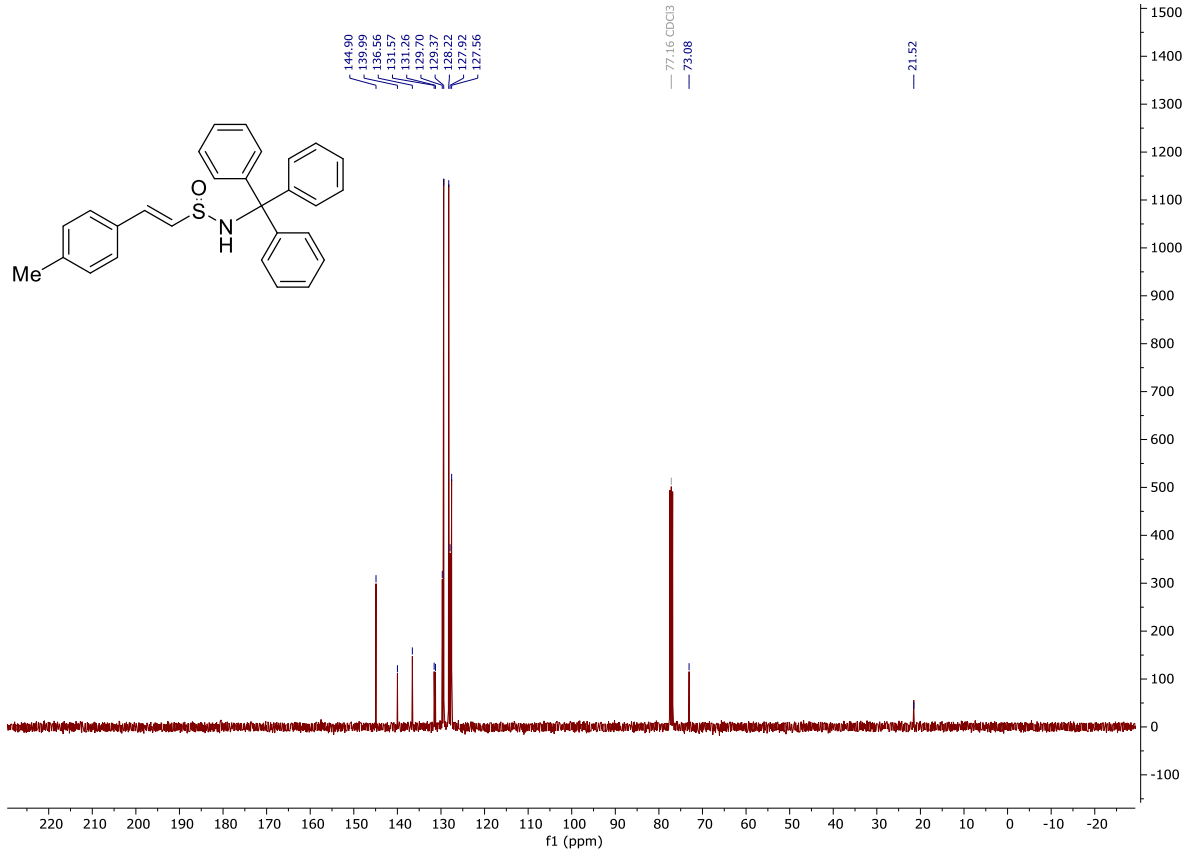
(*E*)-2-Phenyl-*N*-tritylethene-1-sulfinamide (7b)



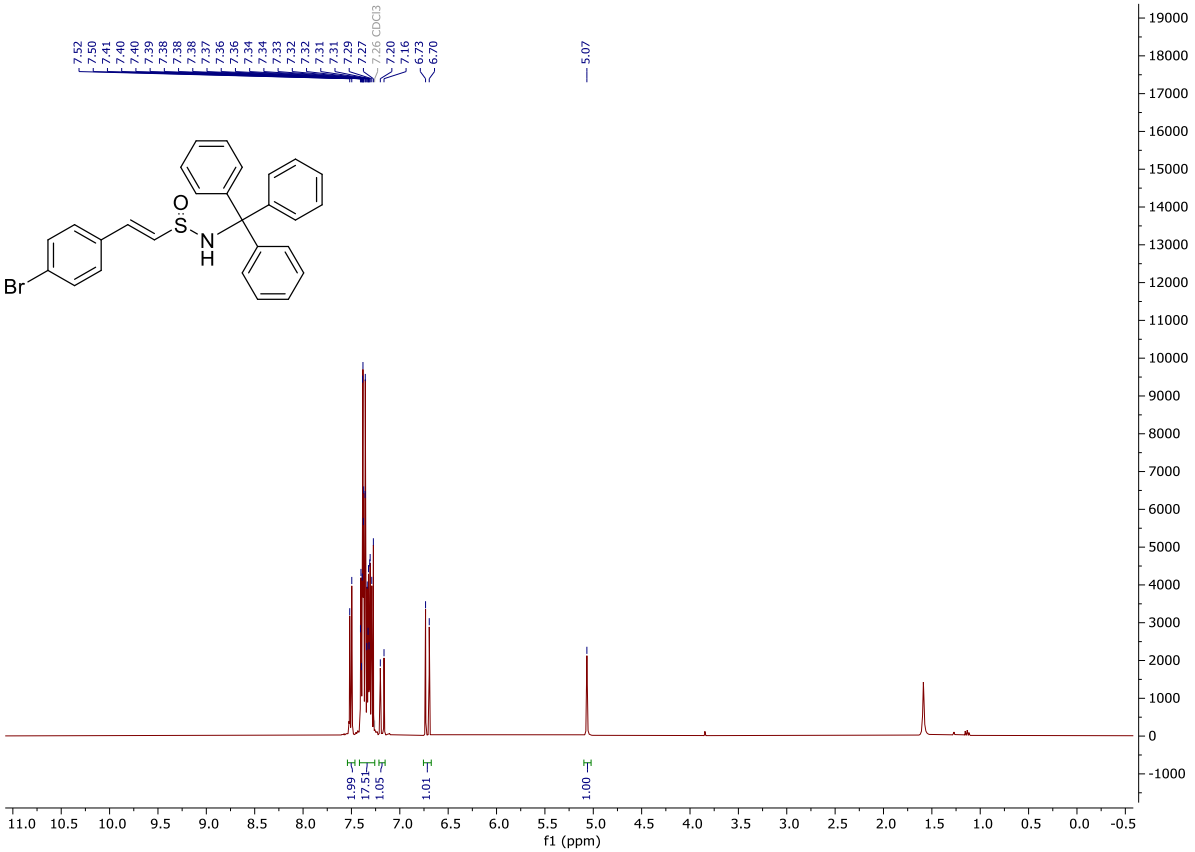


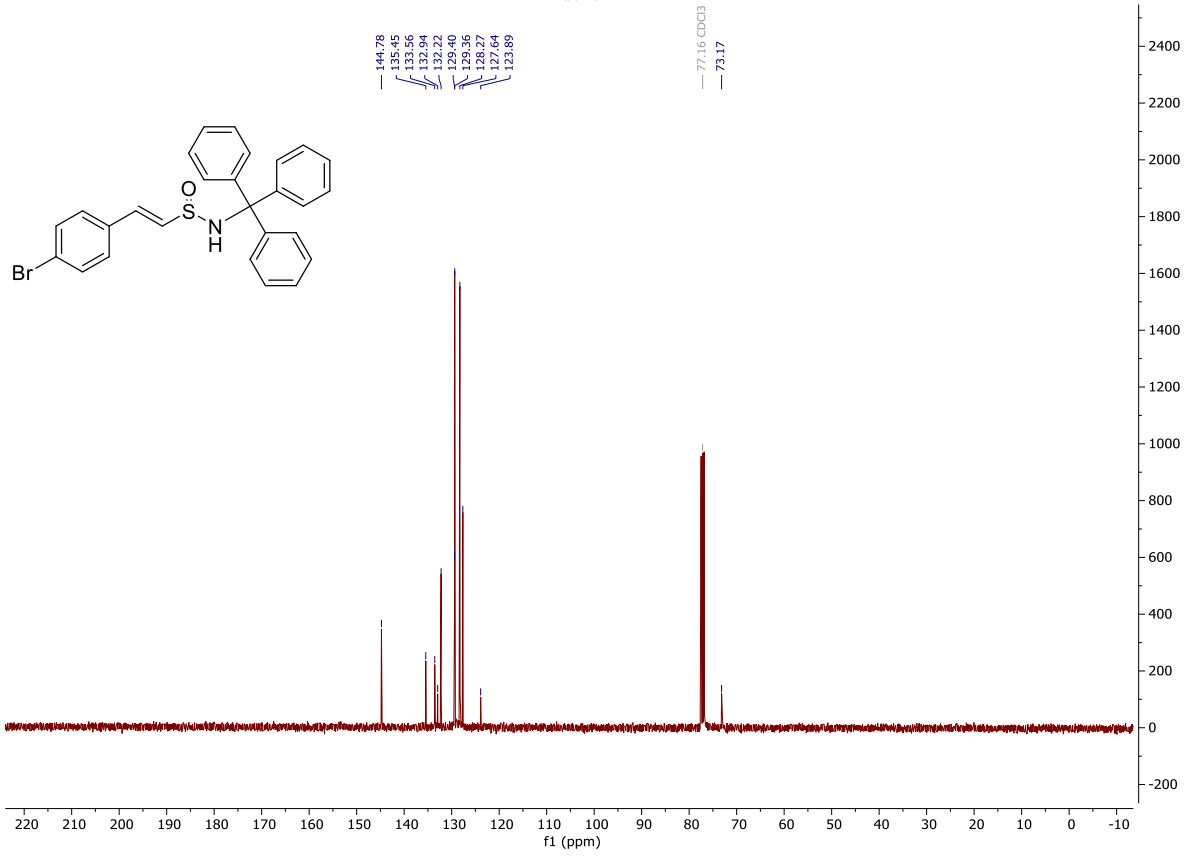
(*E*)-2-(*p*-Tolyl)-*N*-tritylethene-1-sulfinamide (7c)



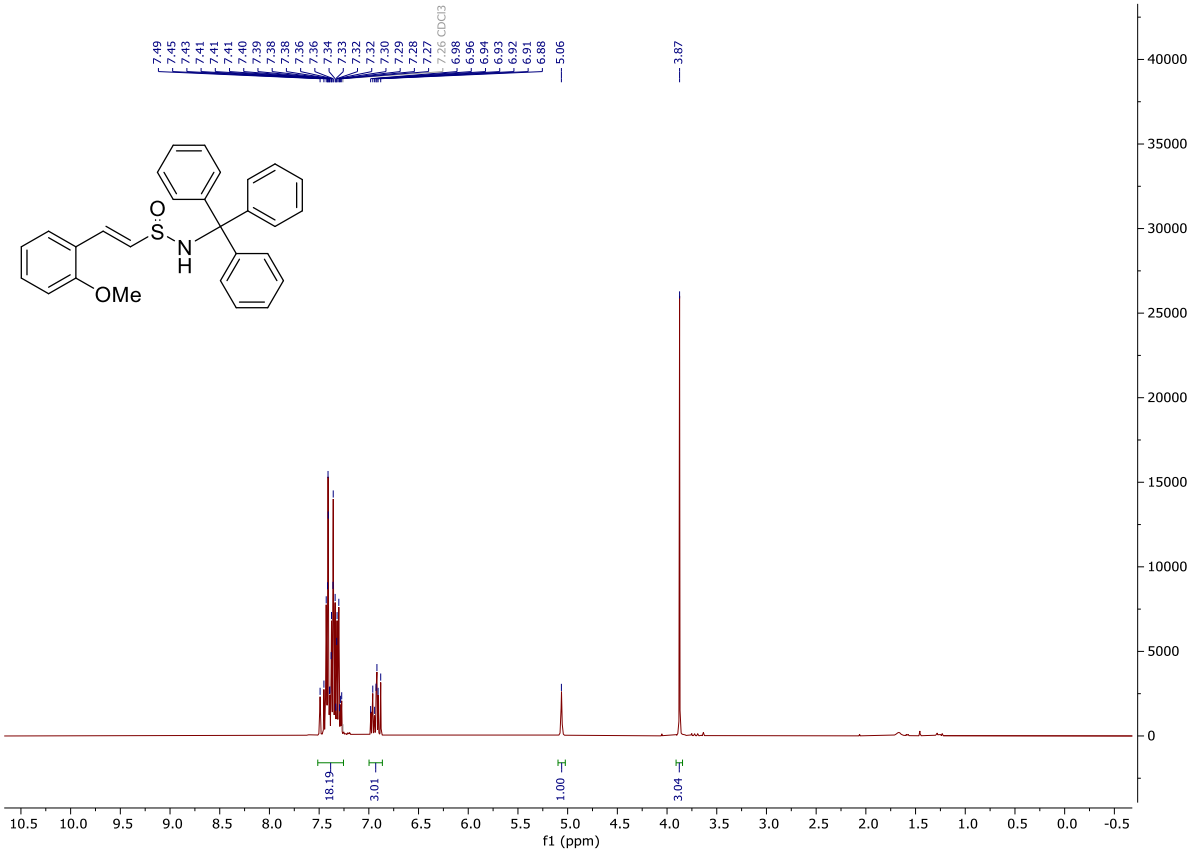


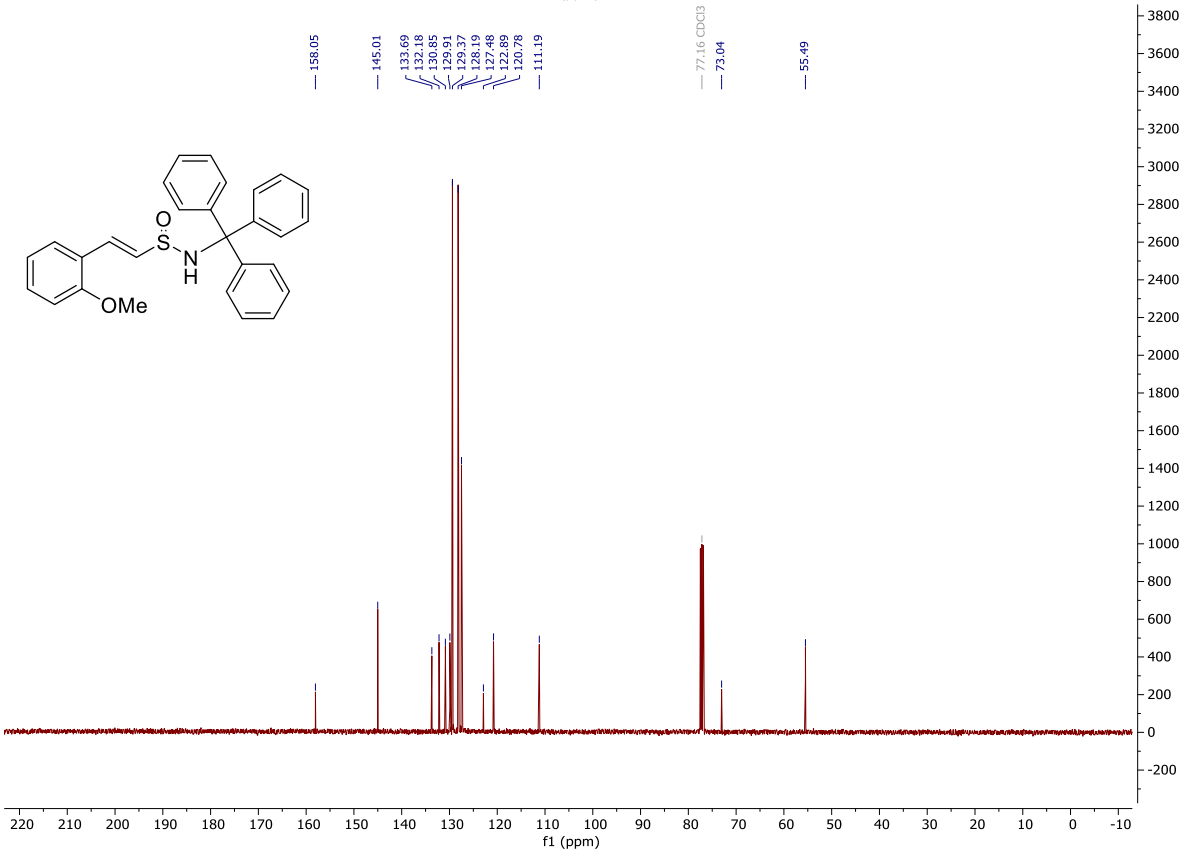
(*E*)-2-(4-Bromophenyl)-*N*-tritylethene-1-sulfinamide (7d)



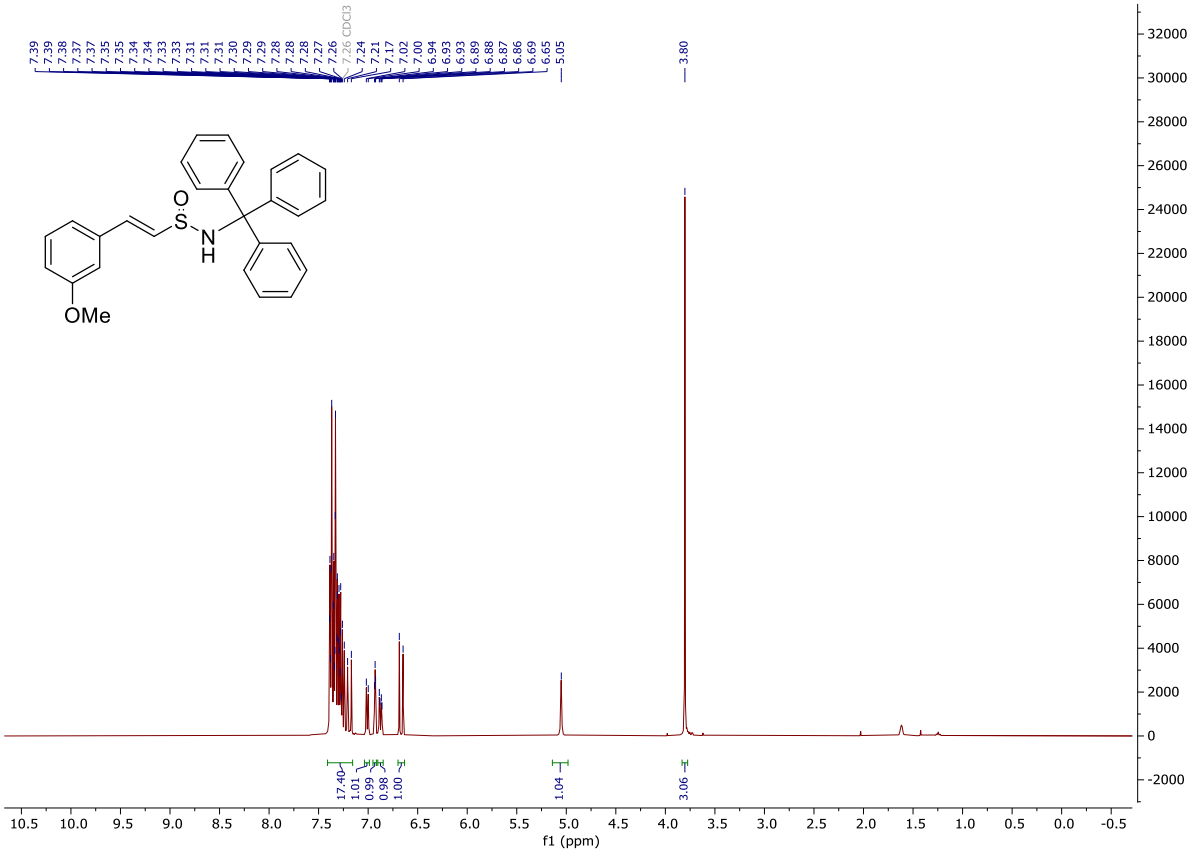


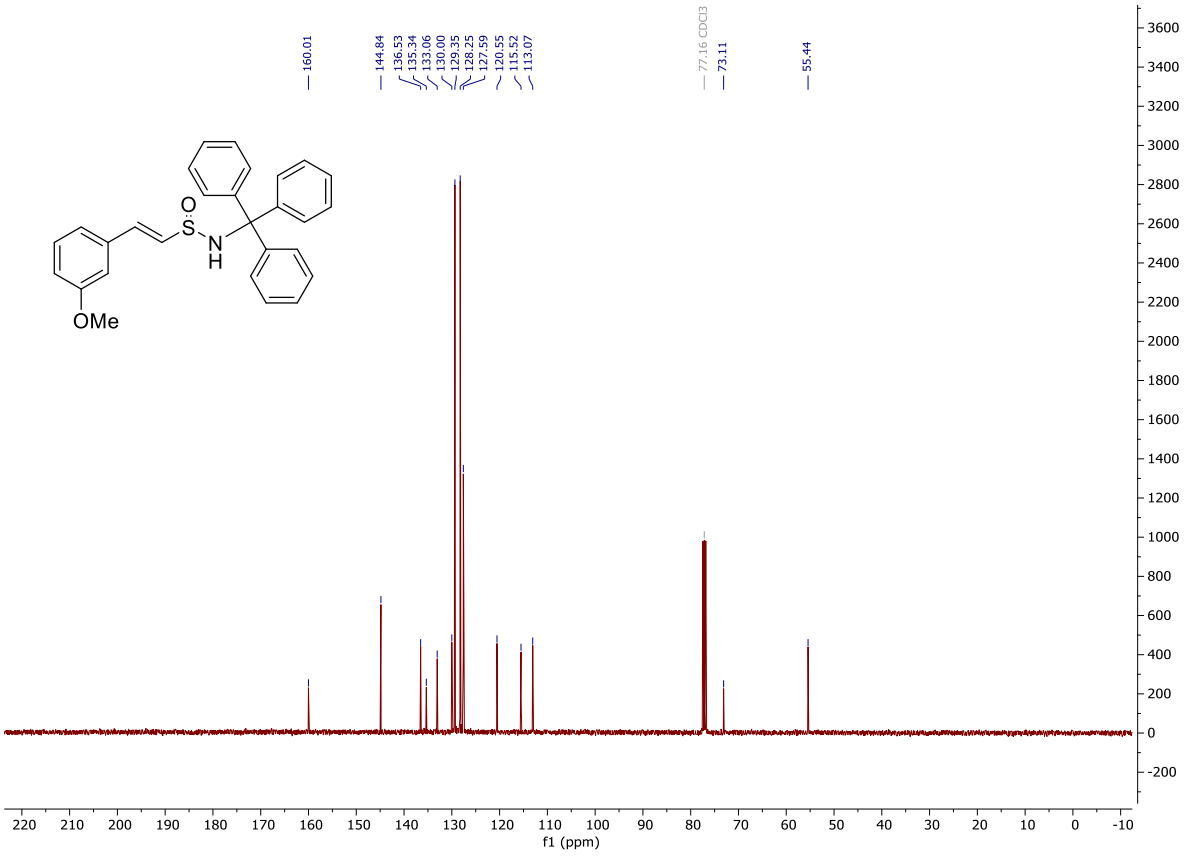
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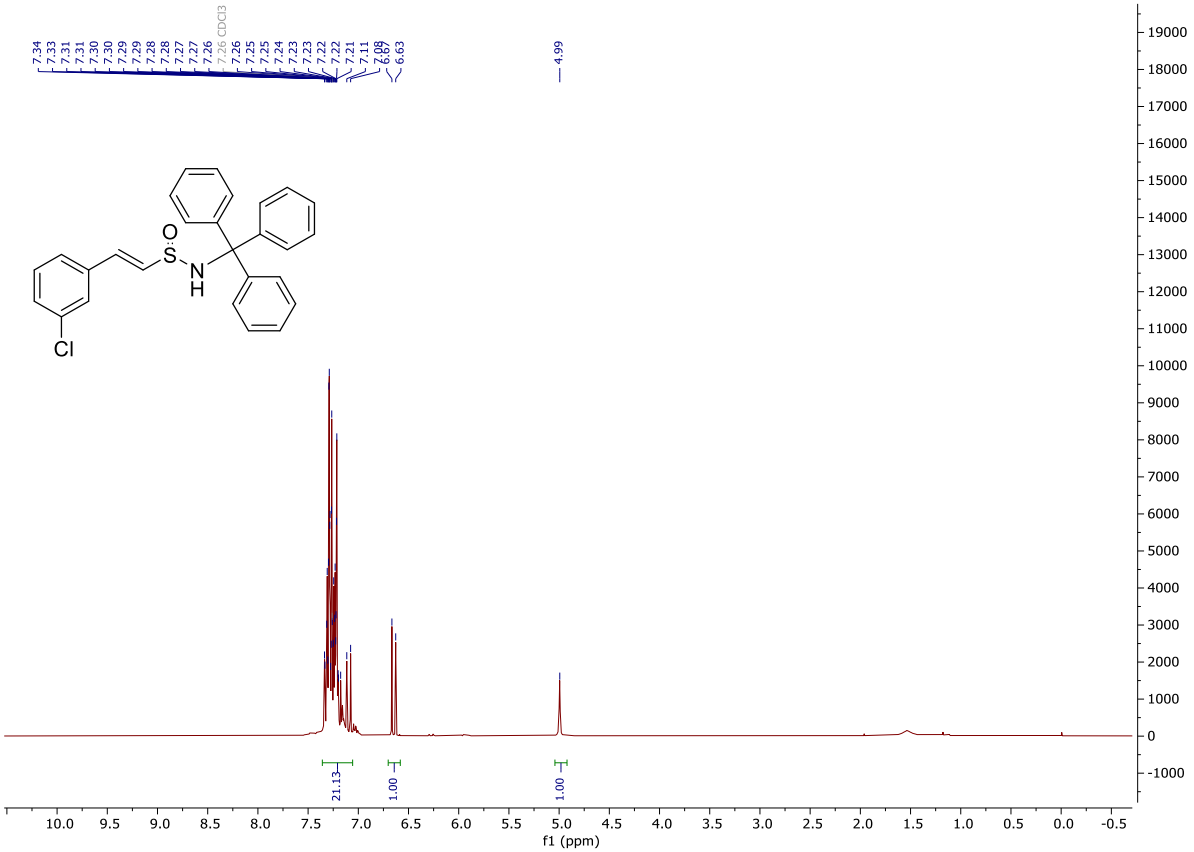


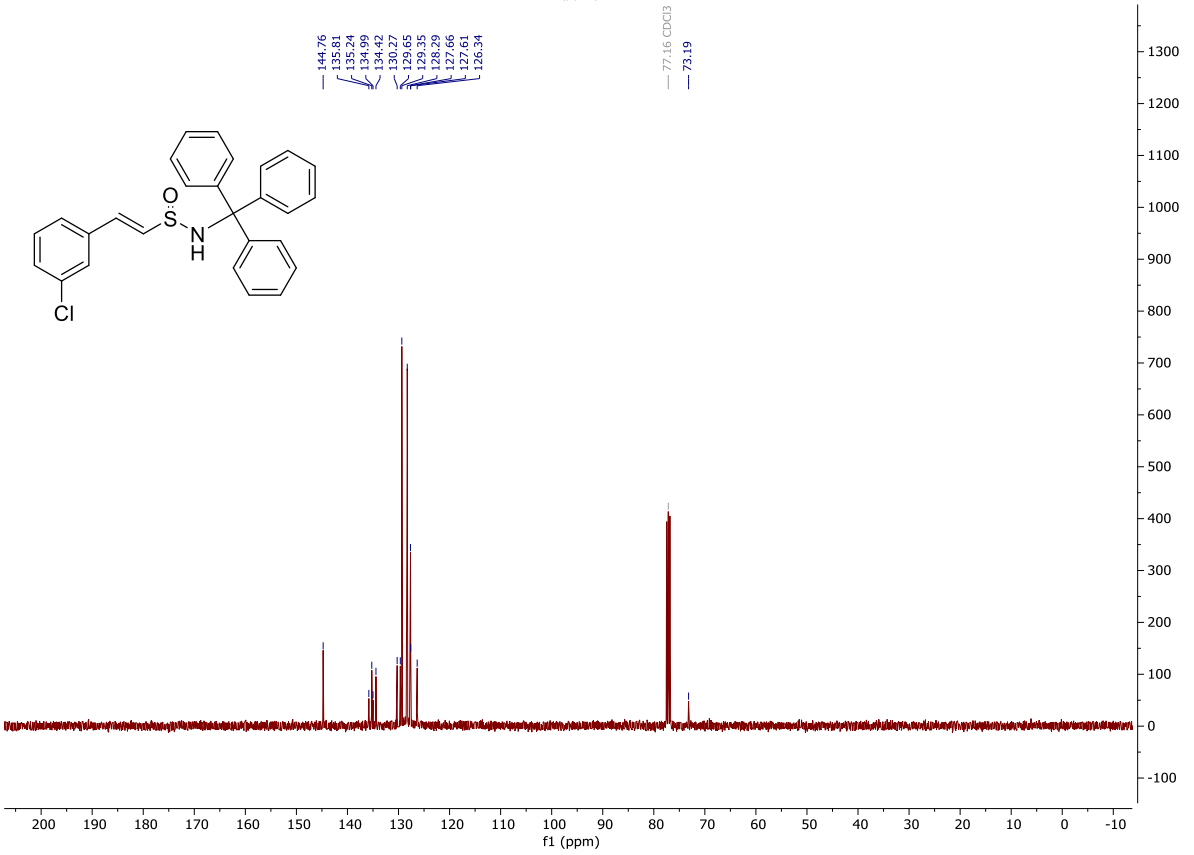
(*E*)-2-(3-Methoxyphenyl)-*N*-tritylethene-1-sulfinamide (7f)



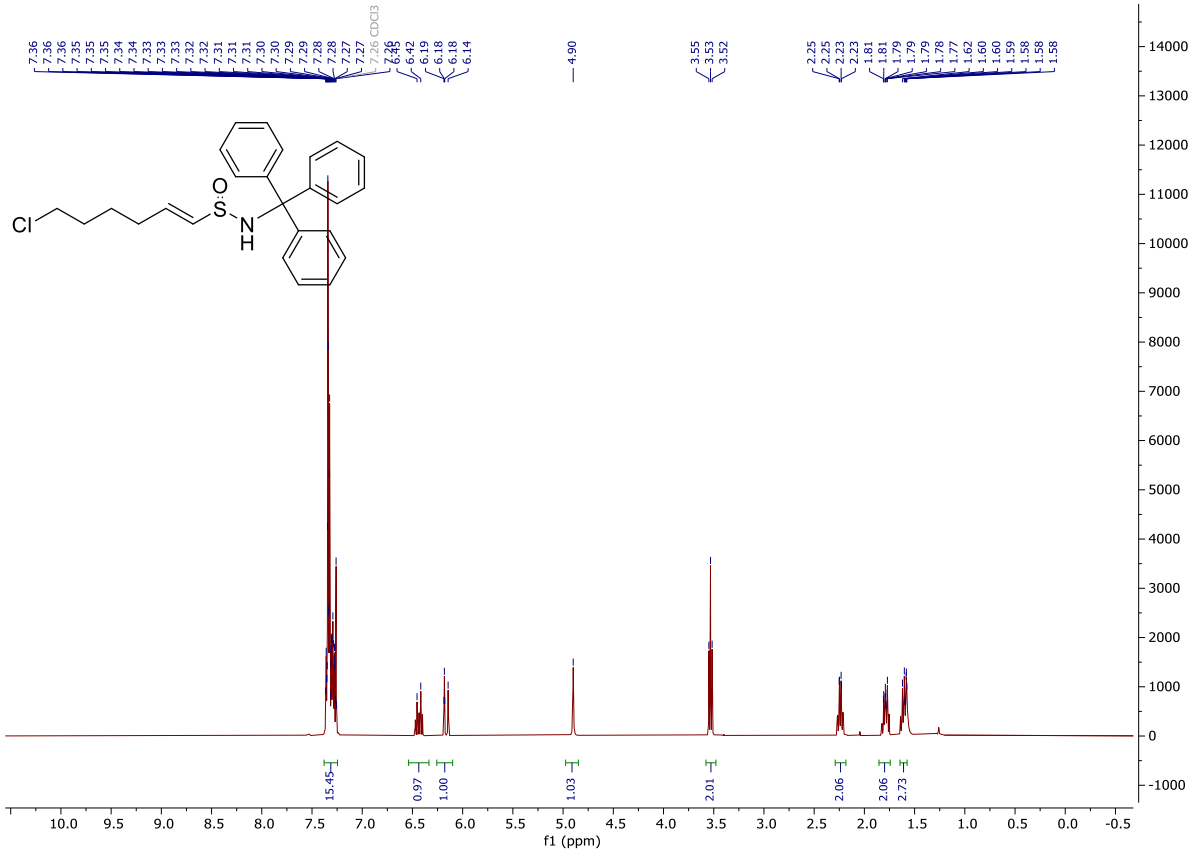


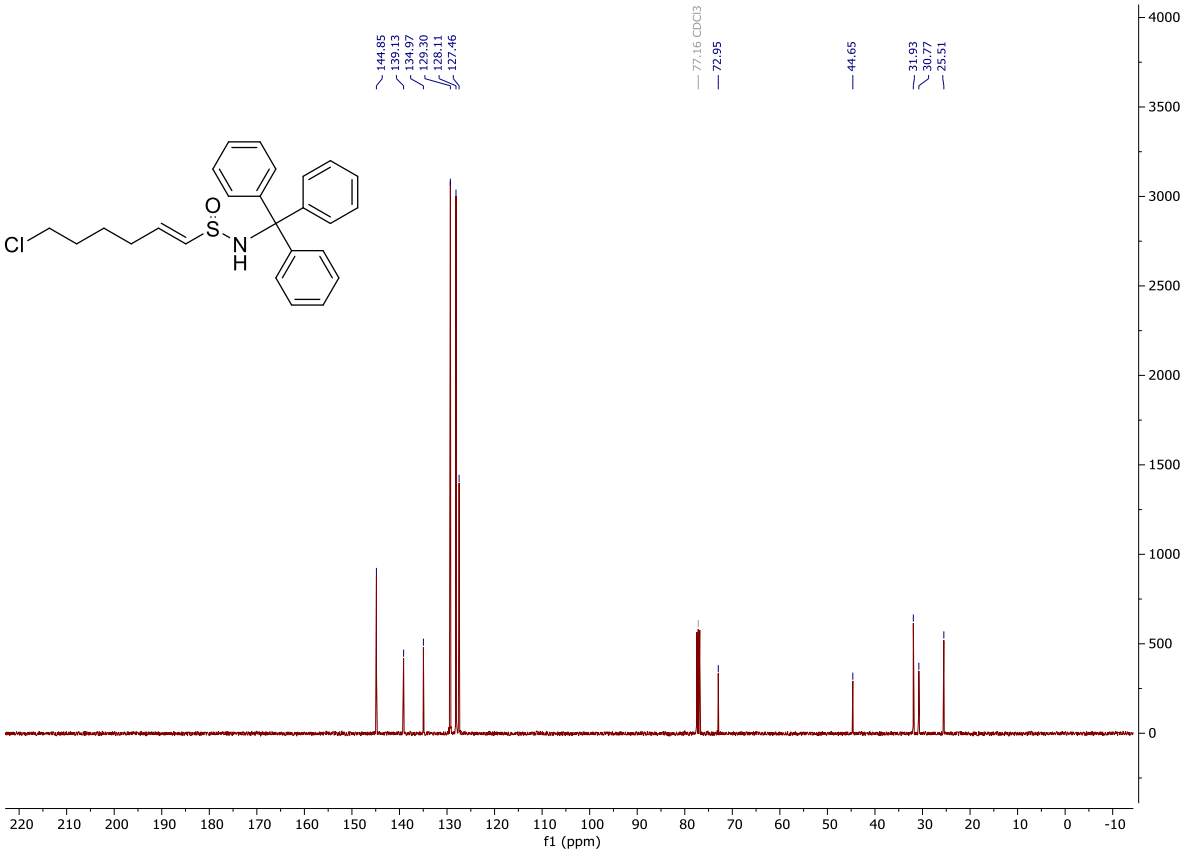
(*E*)-2-(3-Chlorophenyl)-*N*-tritylethene-1-sulfinamide (7g)



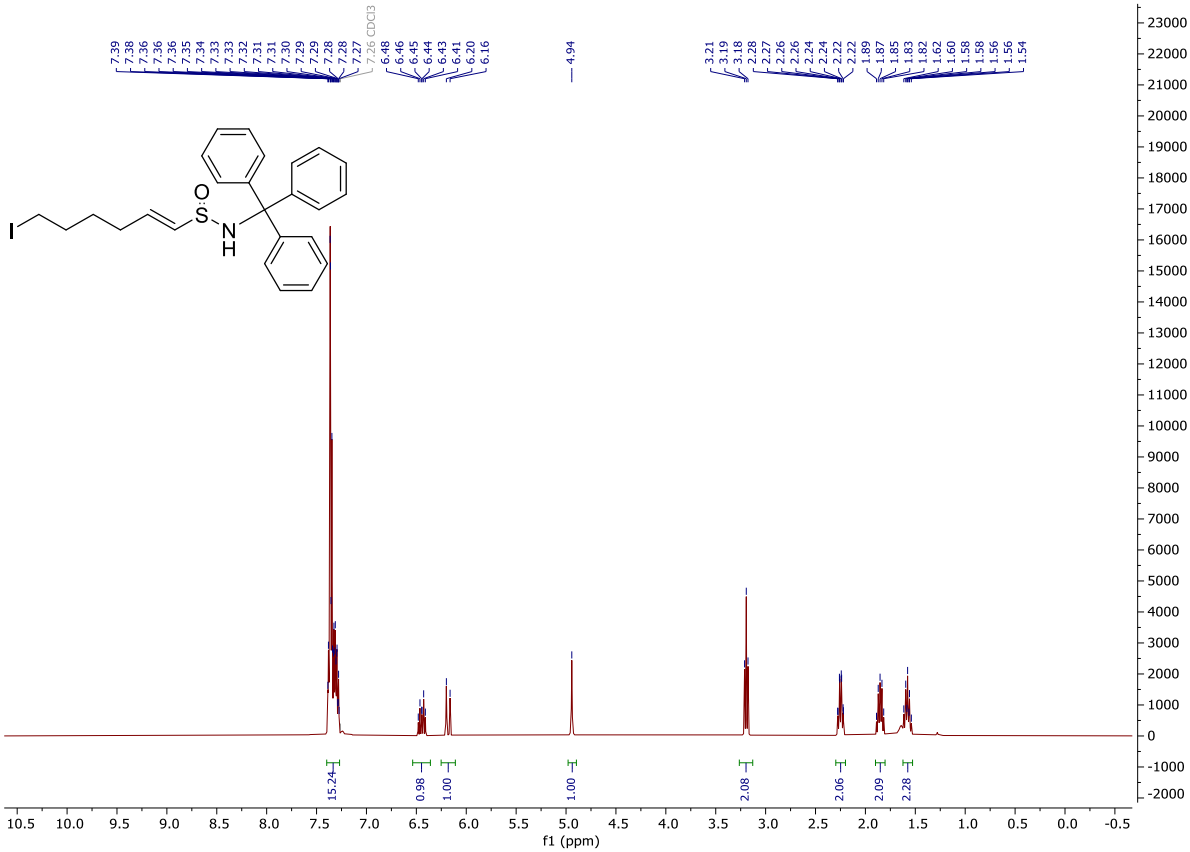


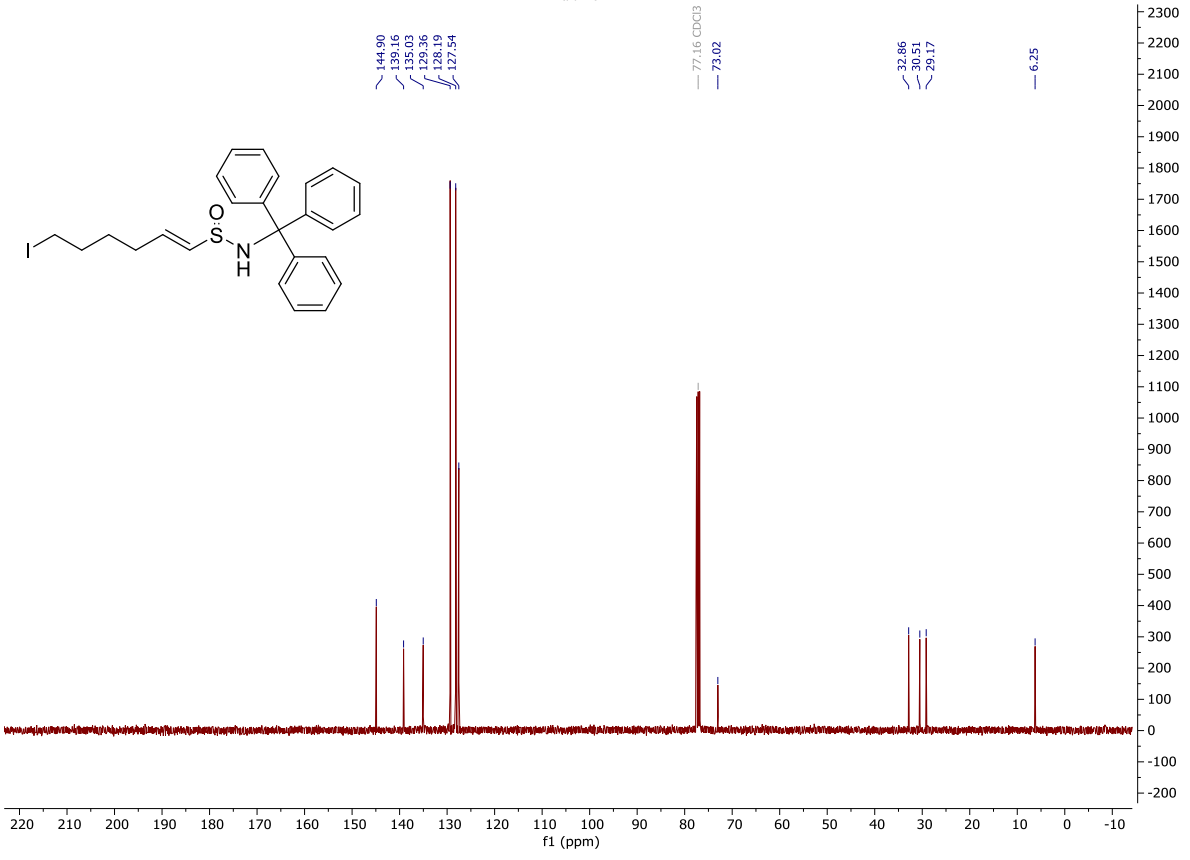
(*E*)-6-Chloro-*N*-tritylhex-1-ene-1-sulfinamide (7h)



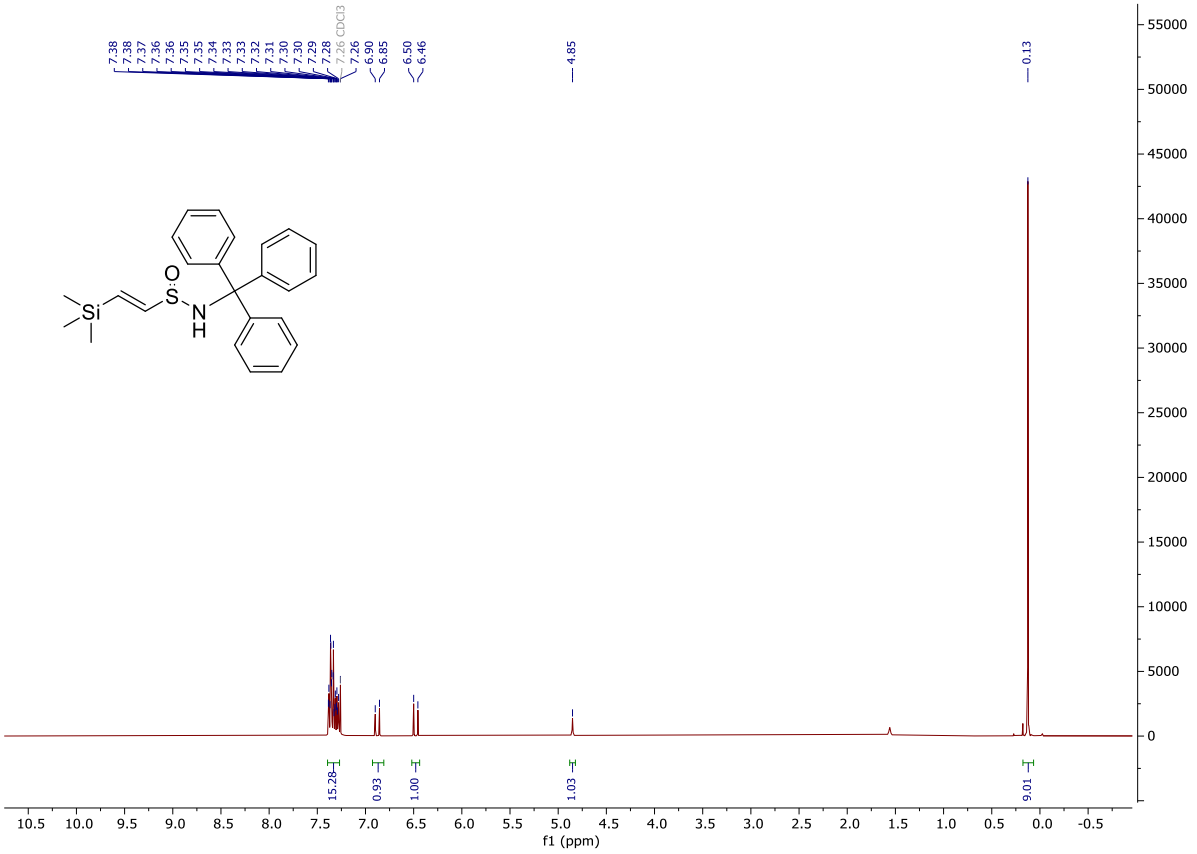


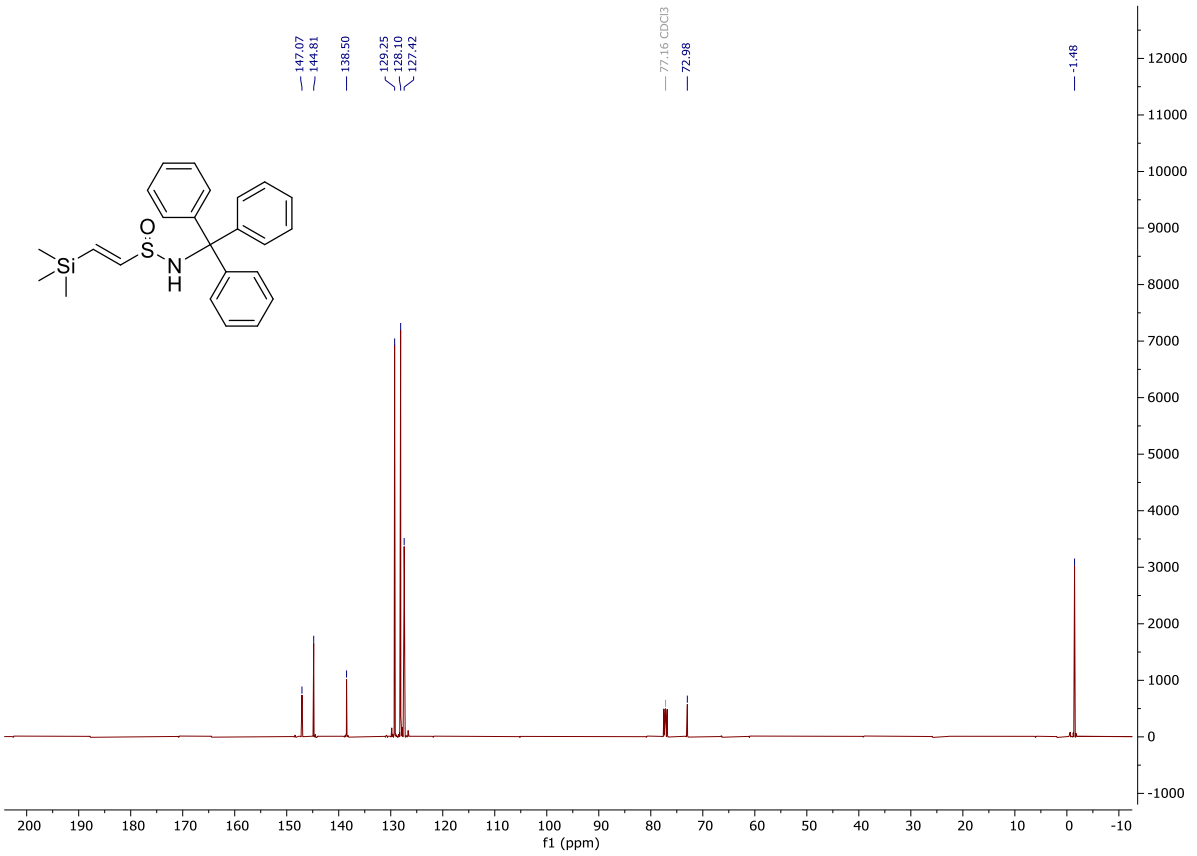
(*E*)-6-Iodo-*N*-tritylhex-1-ene-1-sulfinamide (7i)



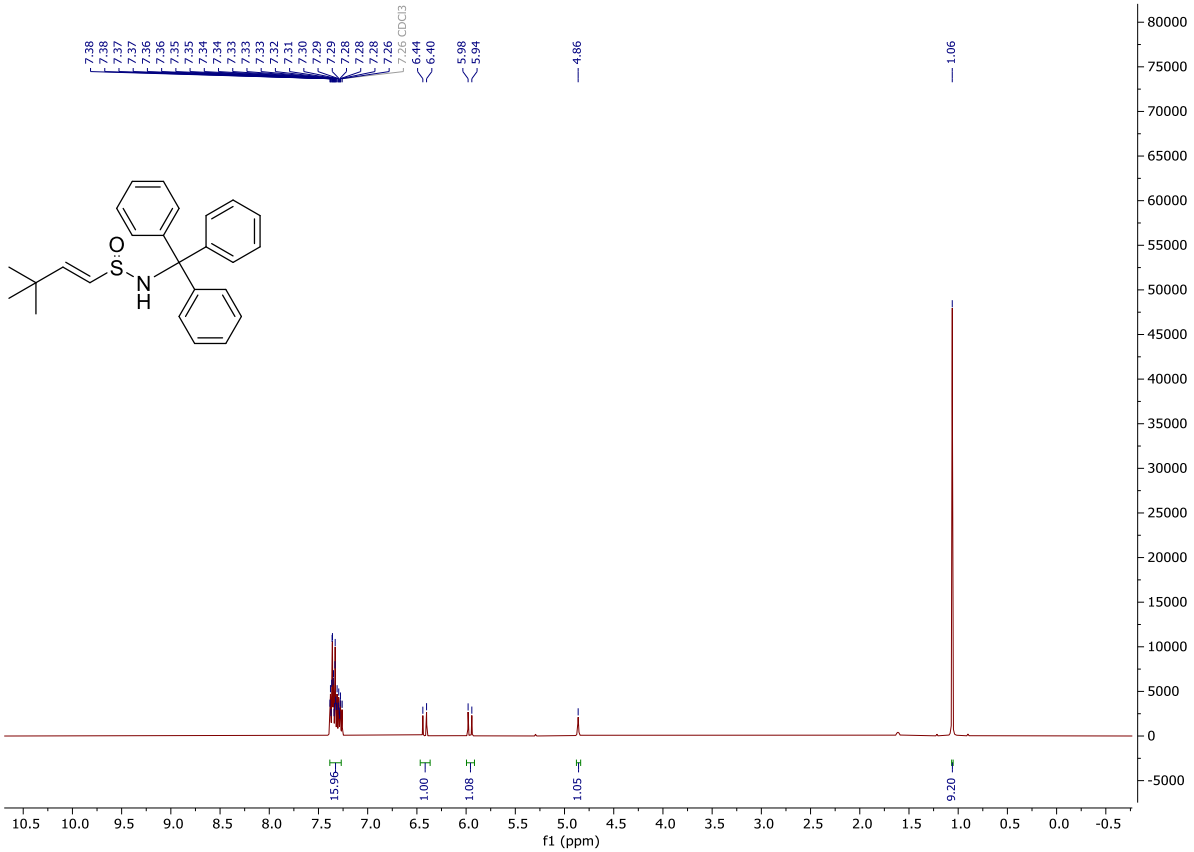


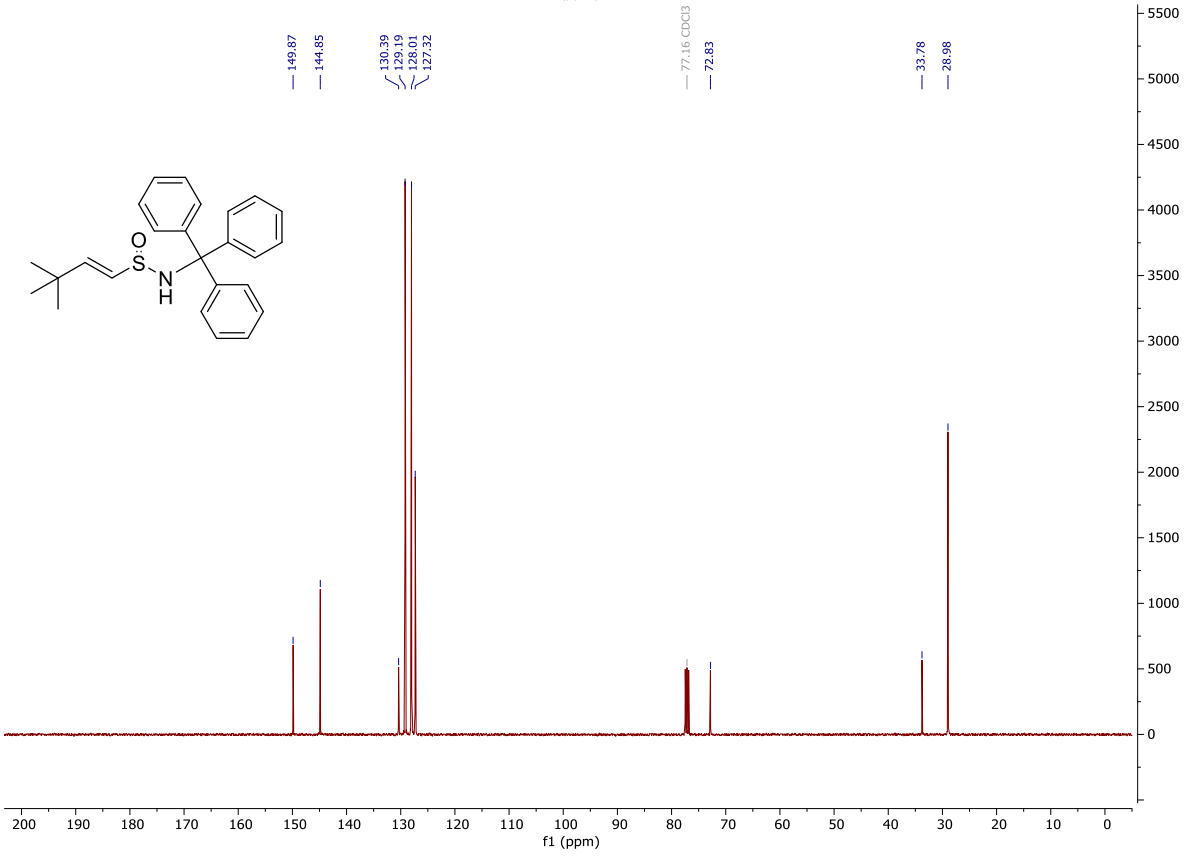
(*E*)-2-(Trimethylsilyl)-*N*-tritylethene-1-sulfinamide (7j)



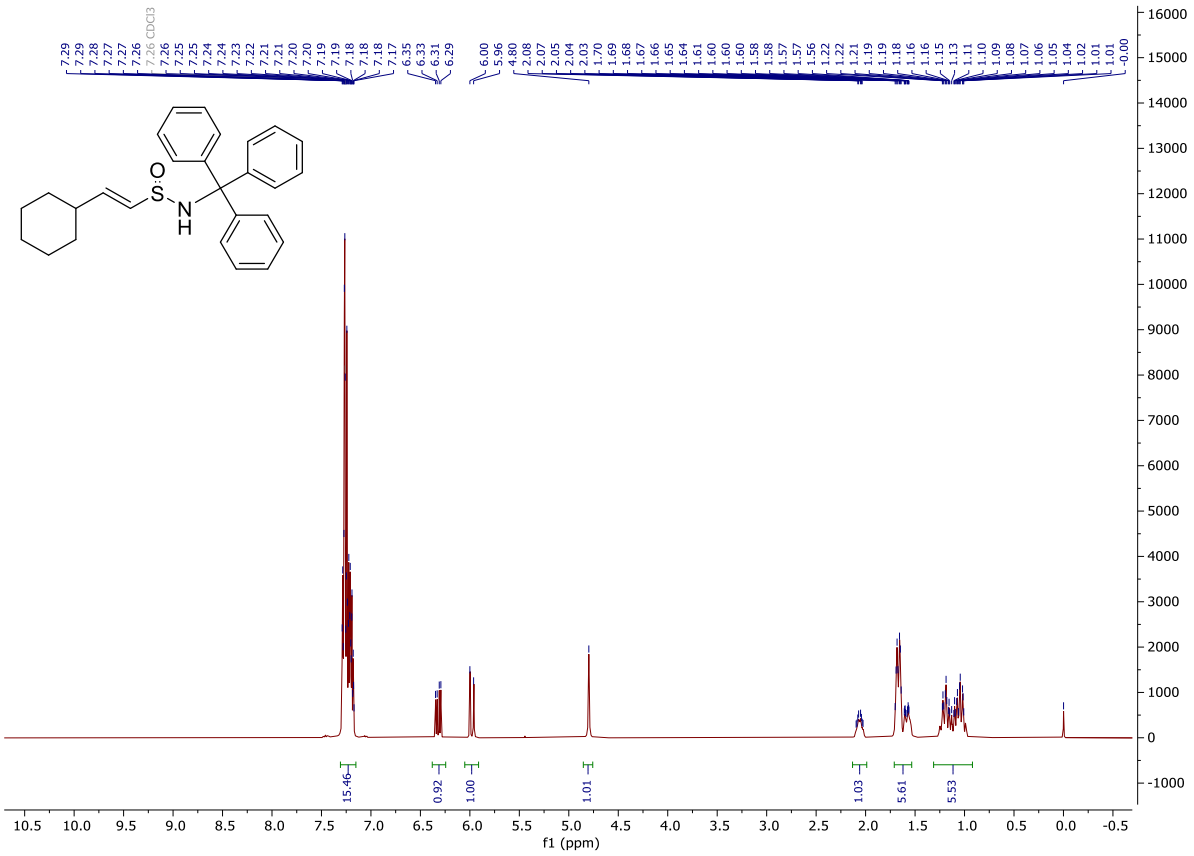


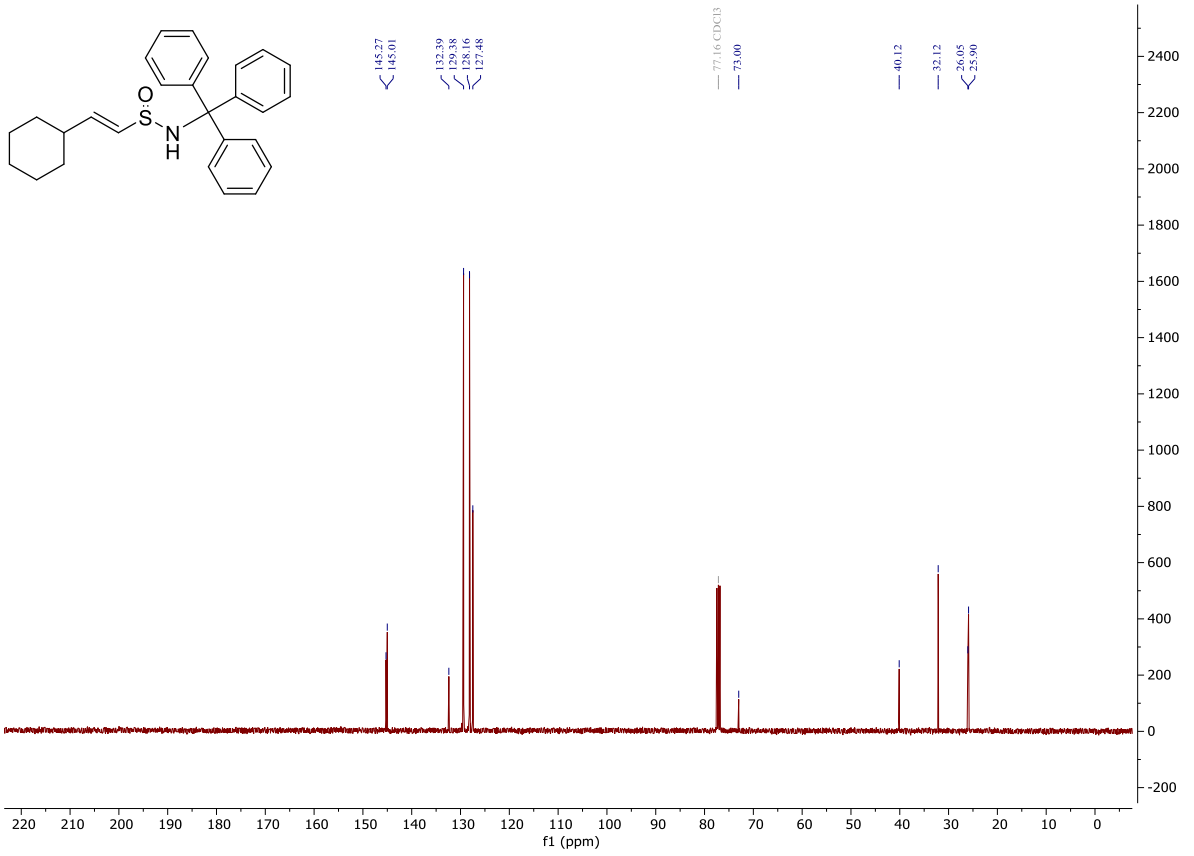
(*E*)-3,3-Dimethyl-*N*-tritylbut-1-ene-1-sulfinamide (7k)



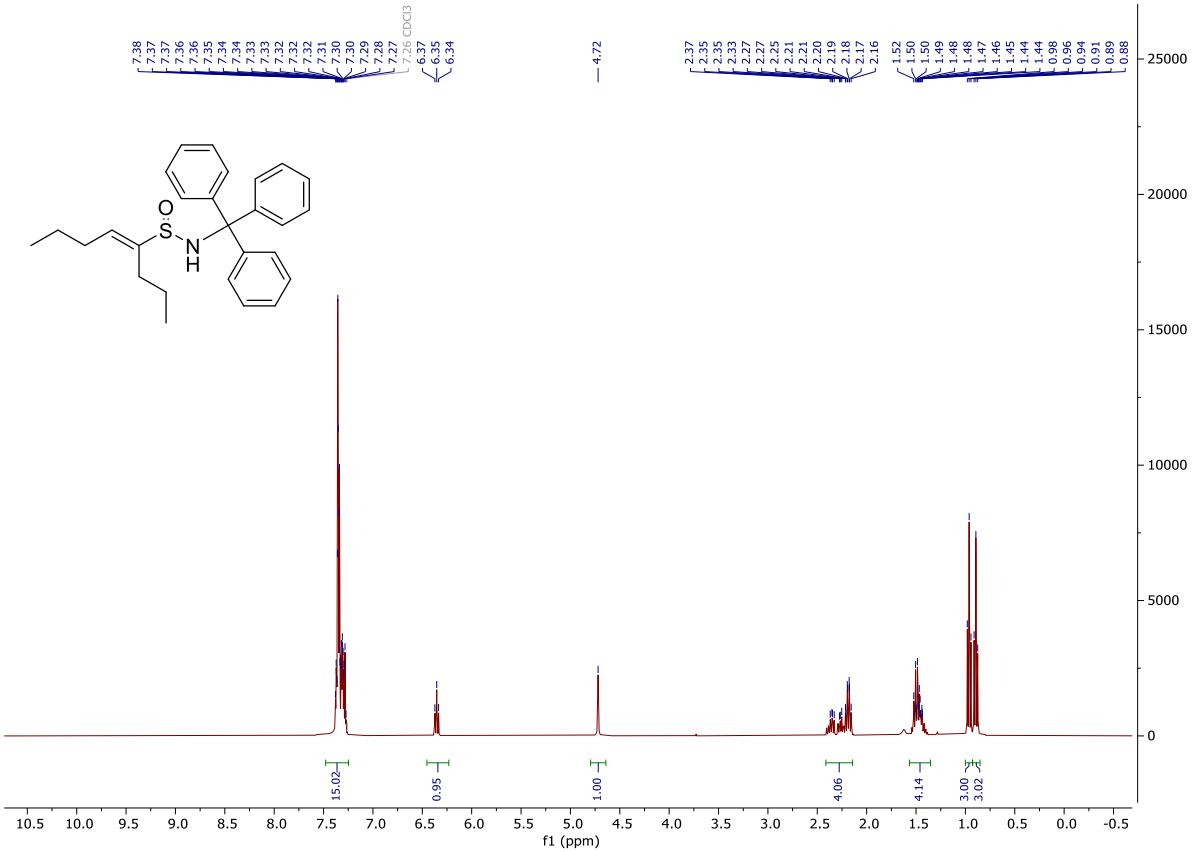


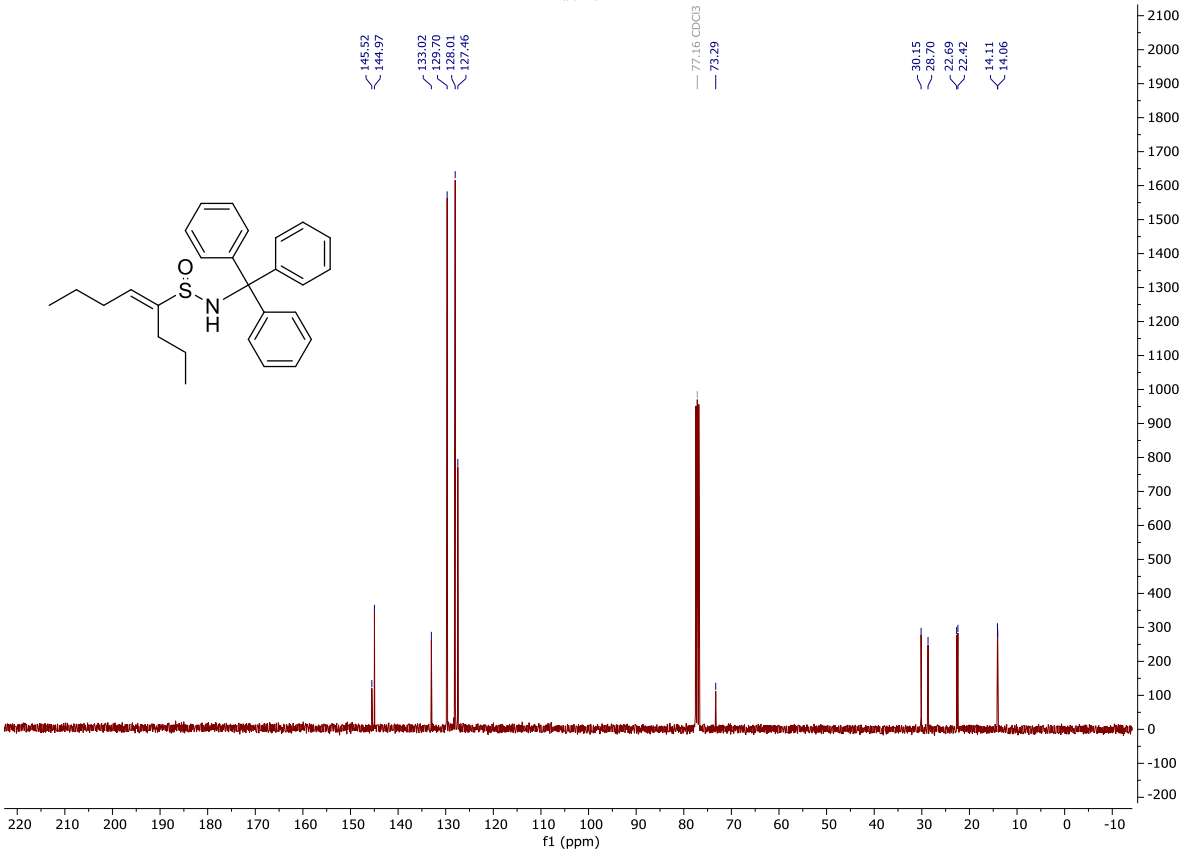
(*E*)-2-Cyclohexyl-*N*-tritylethene-1-sulfinamide (7l)



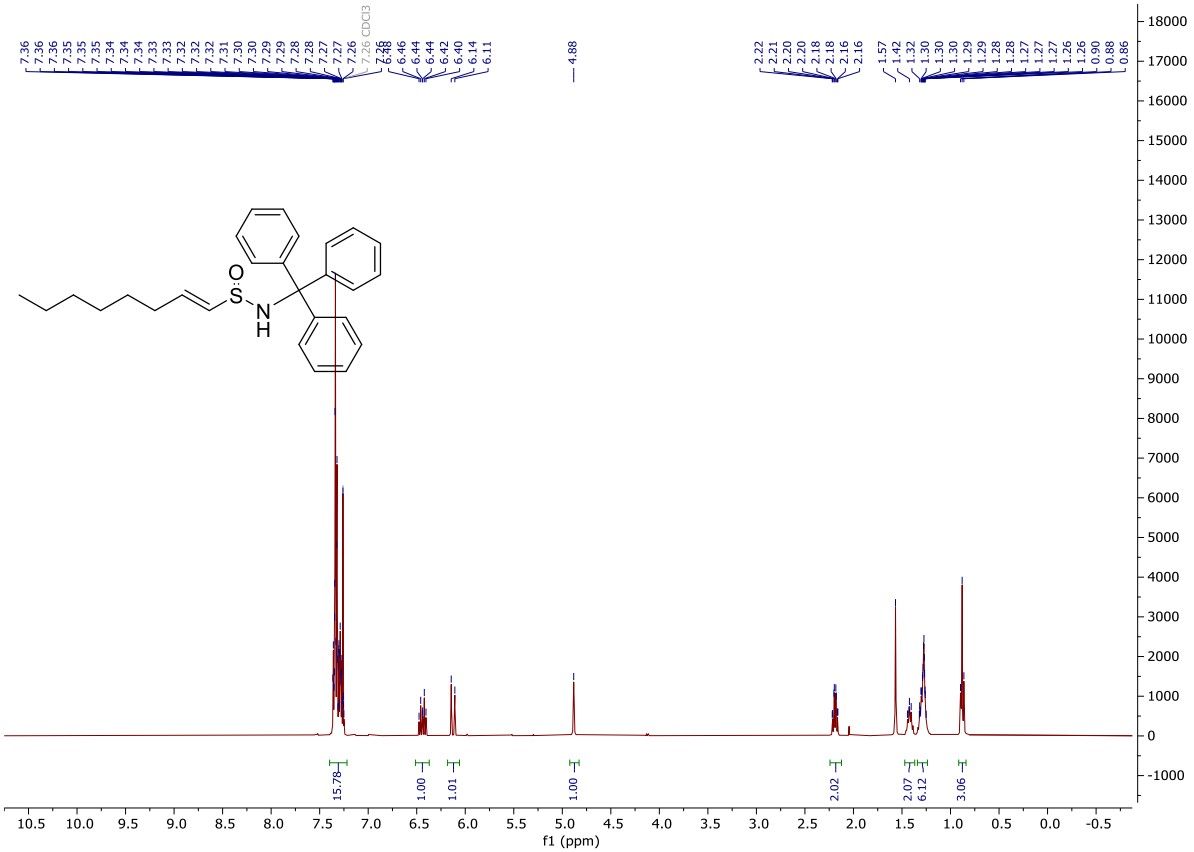


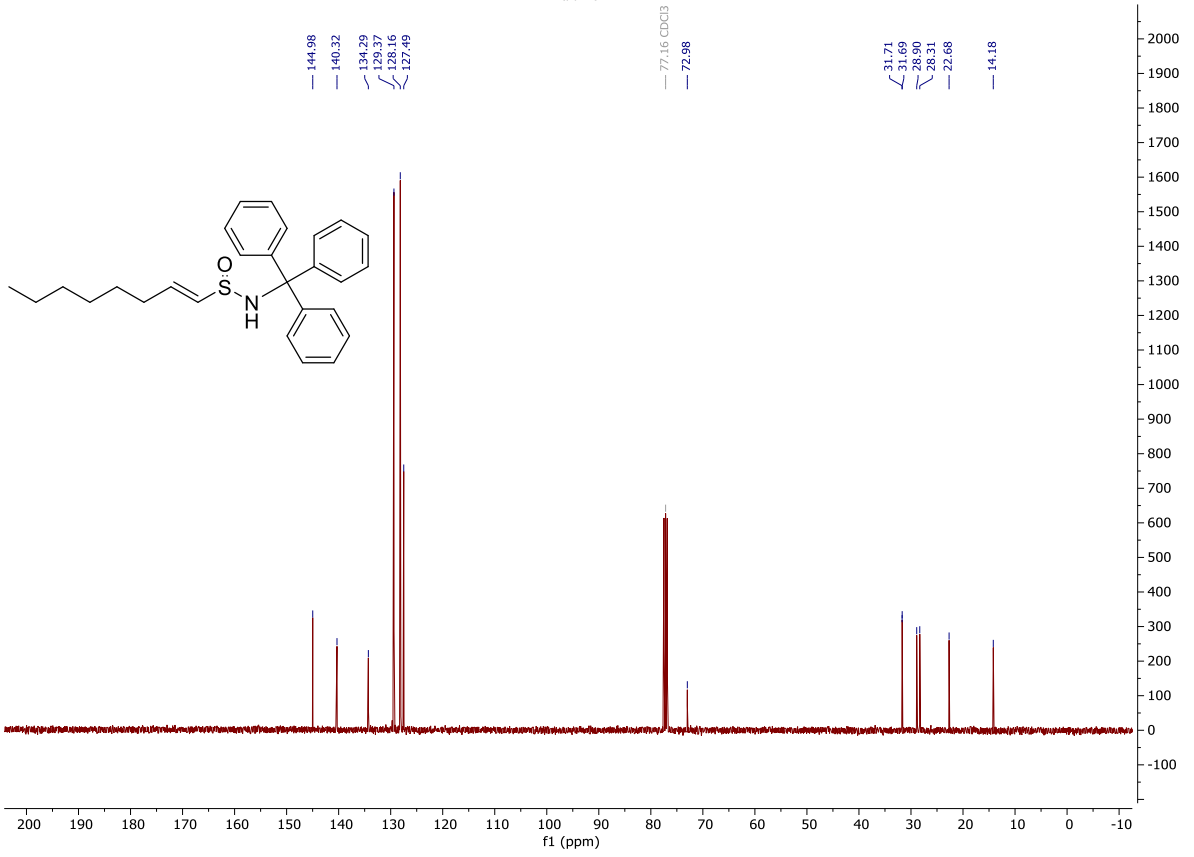
(*E*)-*N*-Trityloct-4-ene-4-sulfinamide (7m)



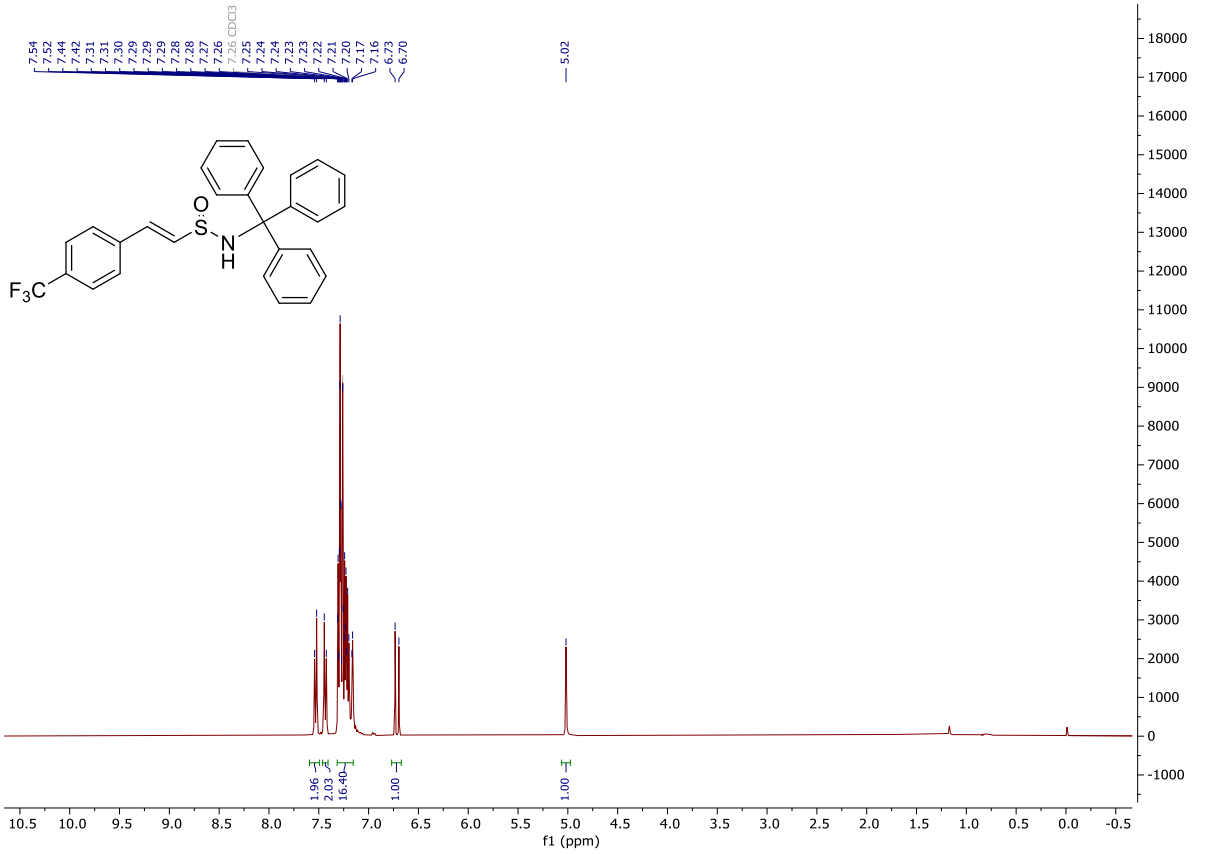


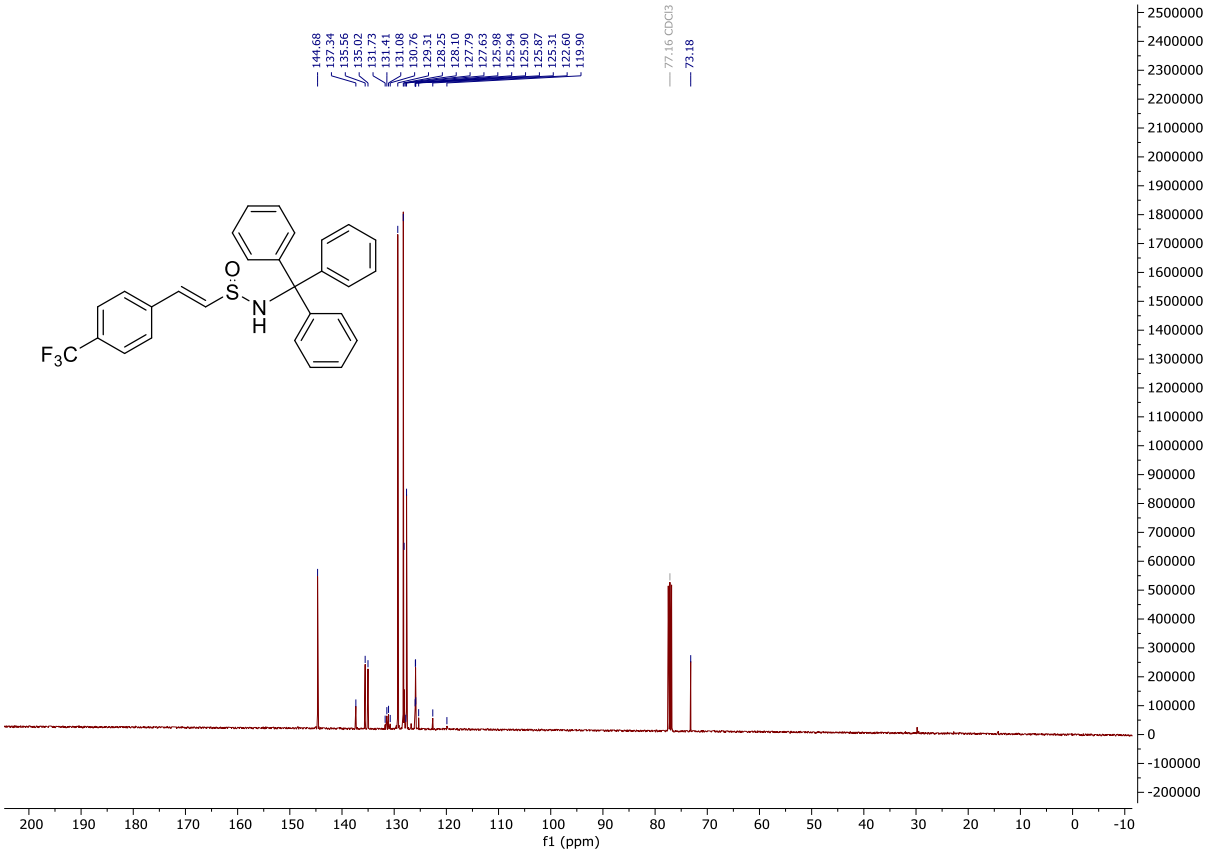
(*E*)-*N*-Trityloct-1-ene-1-sulfinamide (7n)

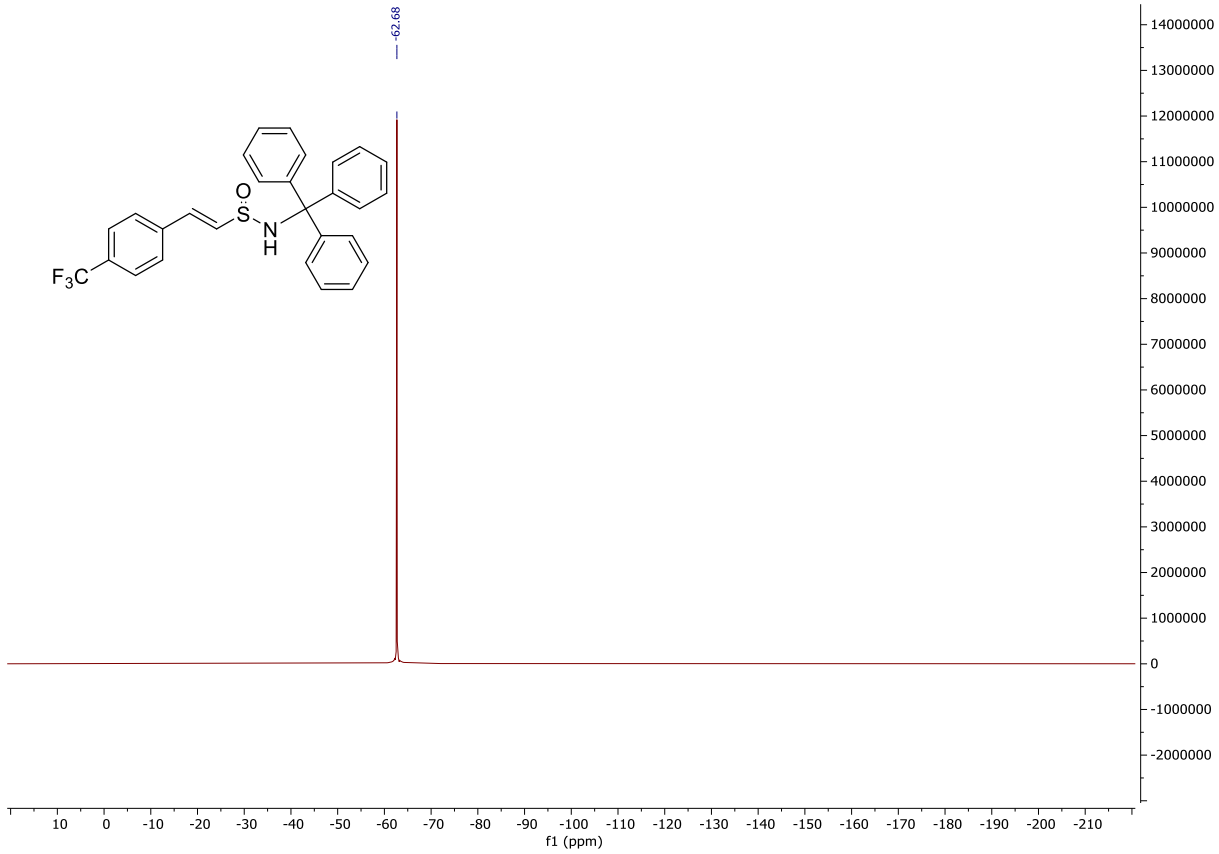




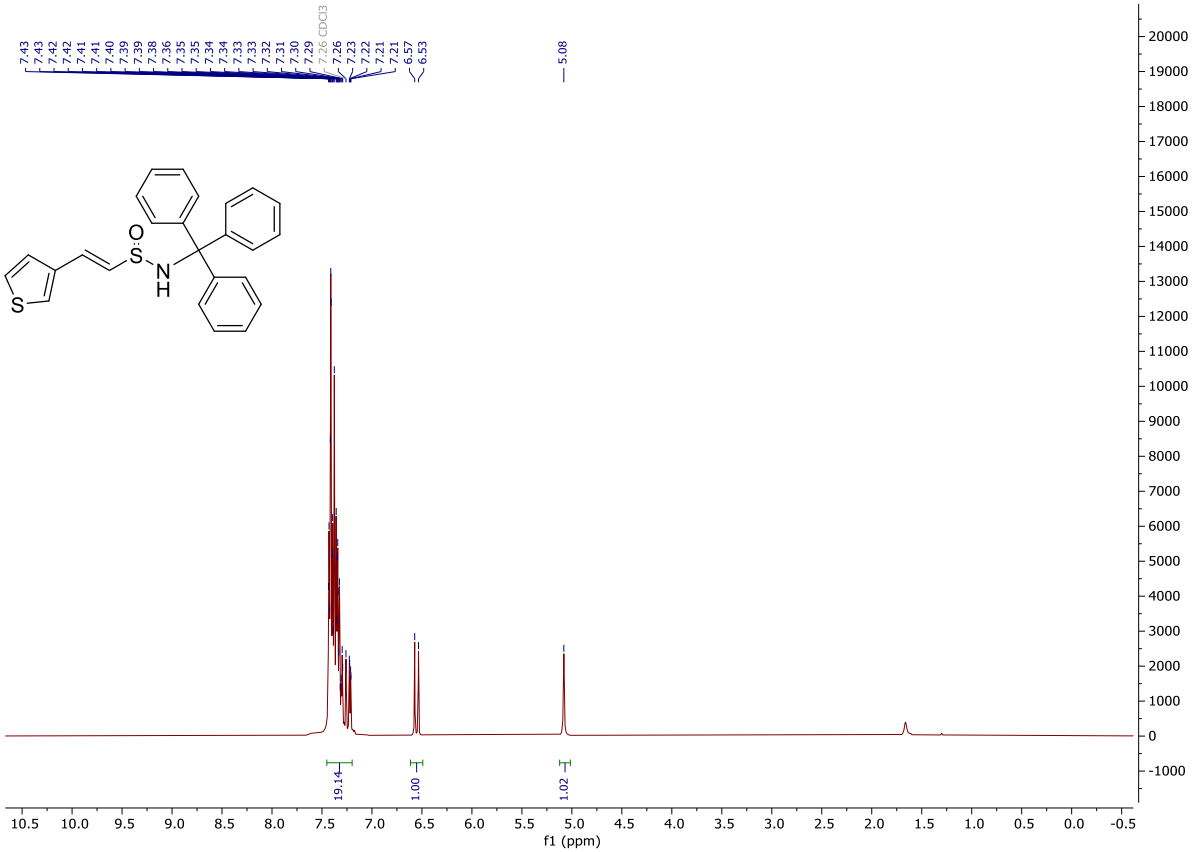
(*E*)-2-(4-(Trifluoromethyl)phenyl)-N-tritylethene-1-sulfinamide (7o)

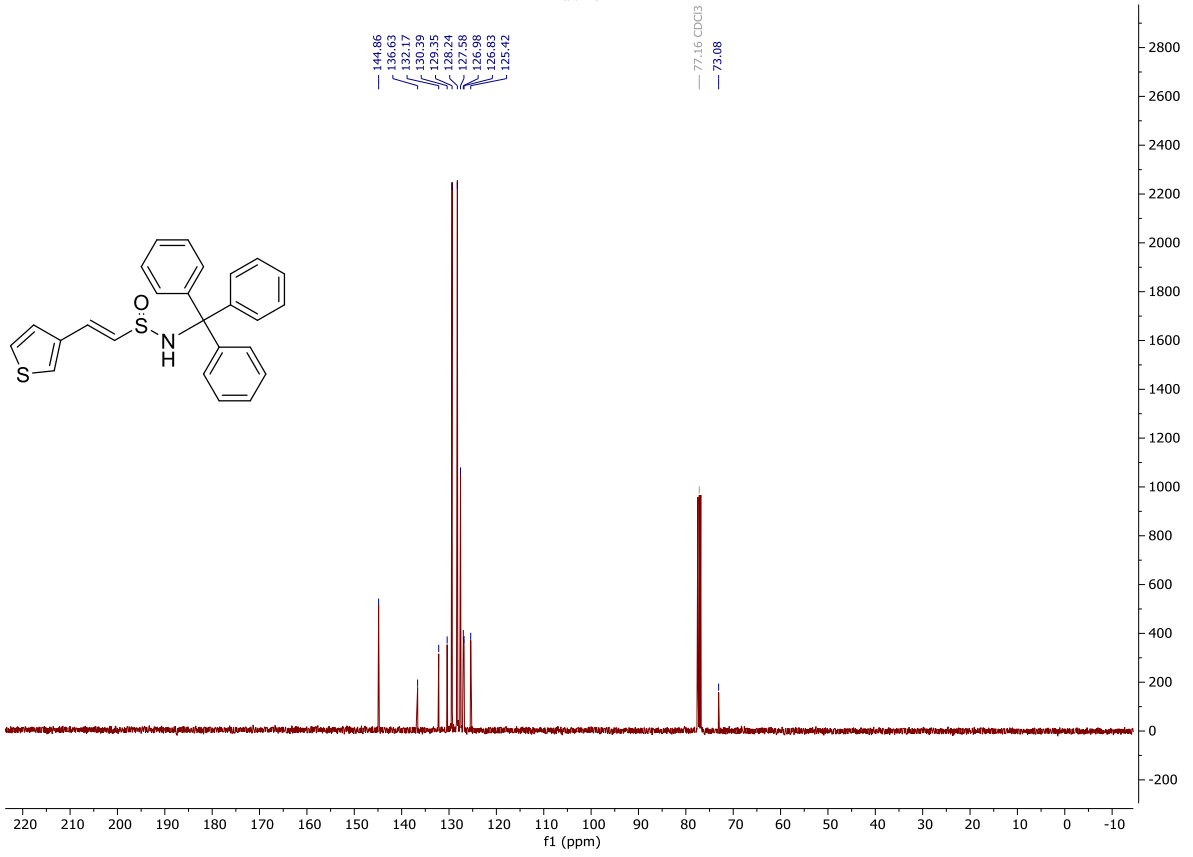




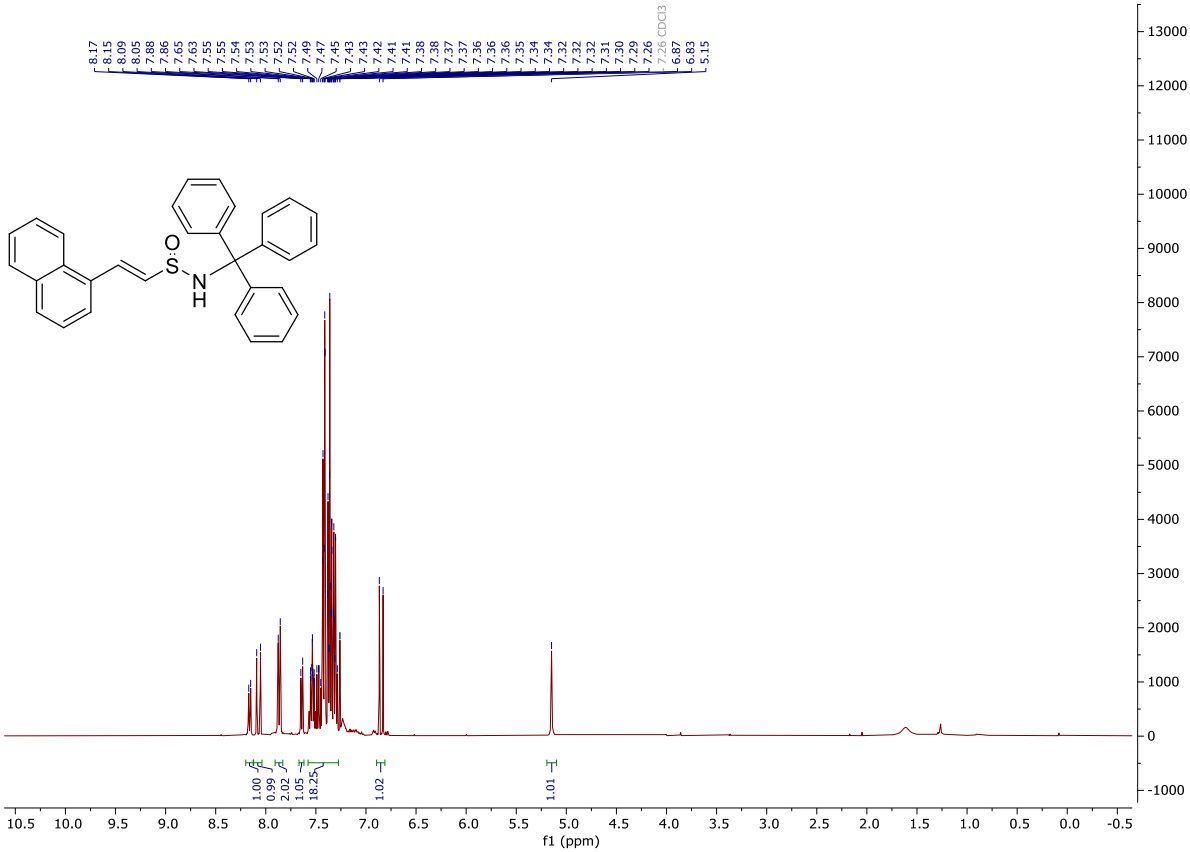

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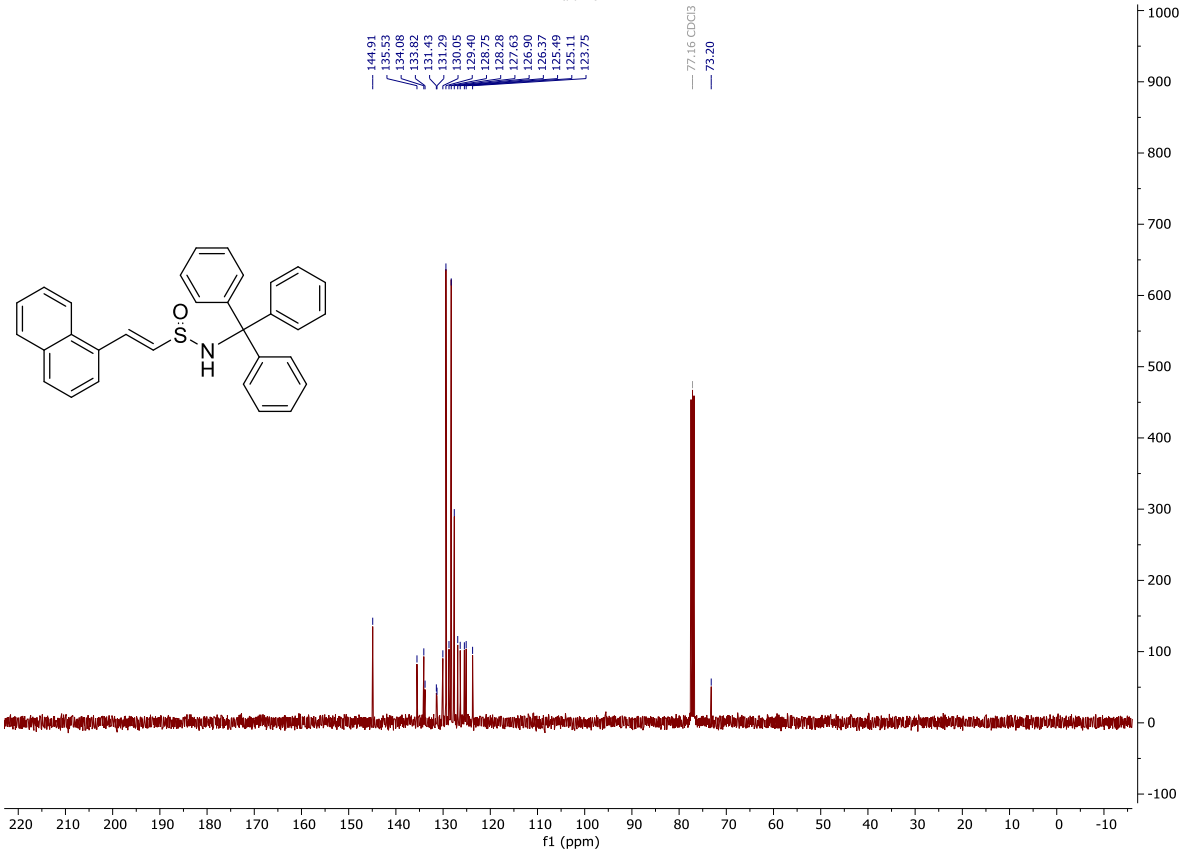
(*E*)-2-(Thiophen-3-yl)-*N*-tritylethene-1-sulfinamide (7p)



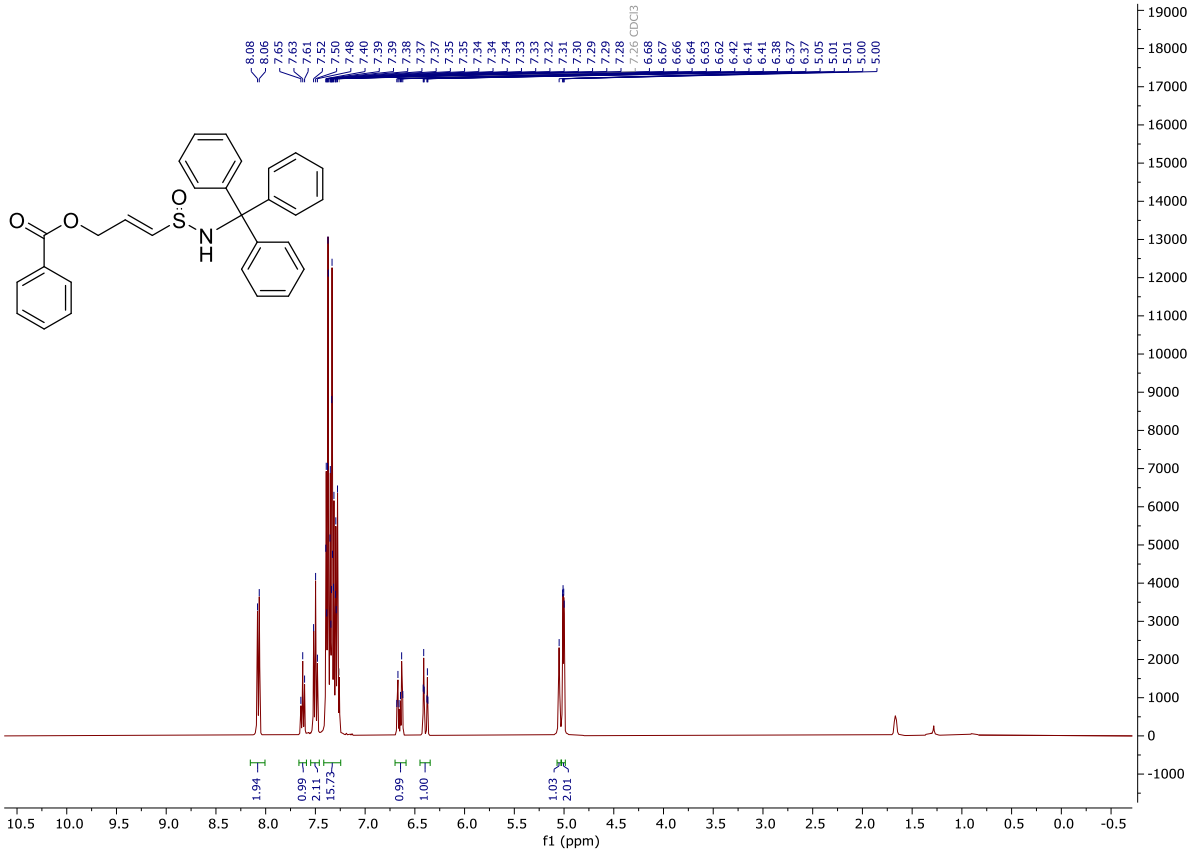


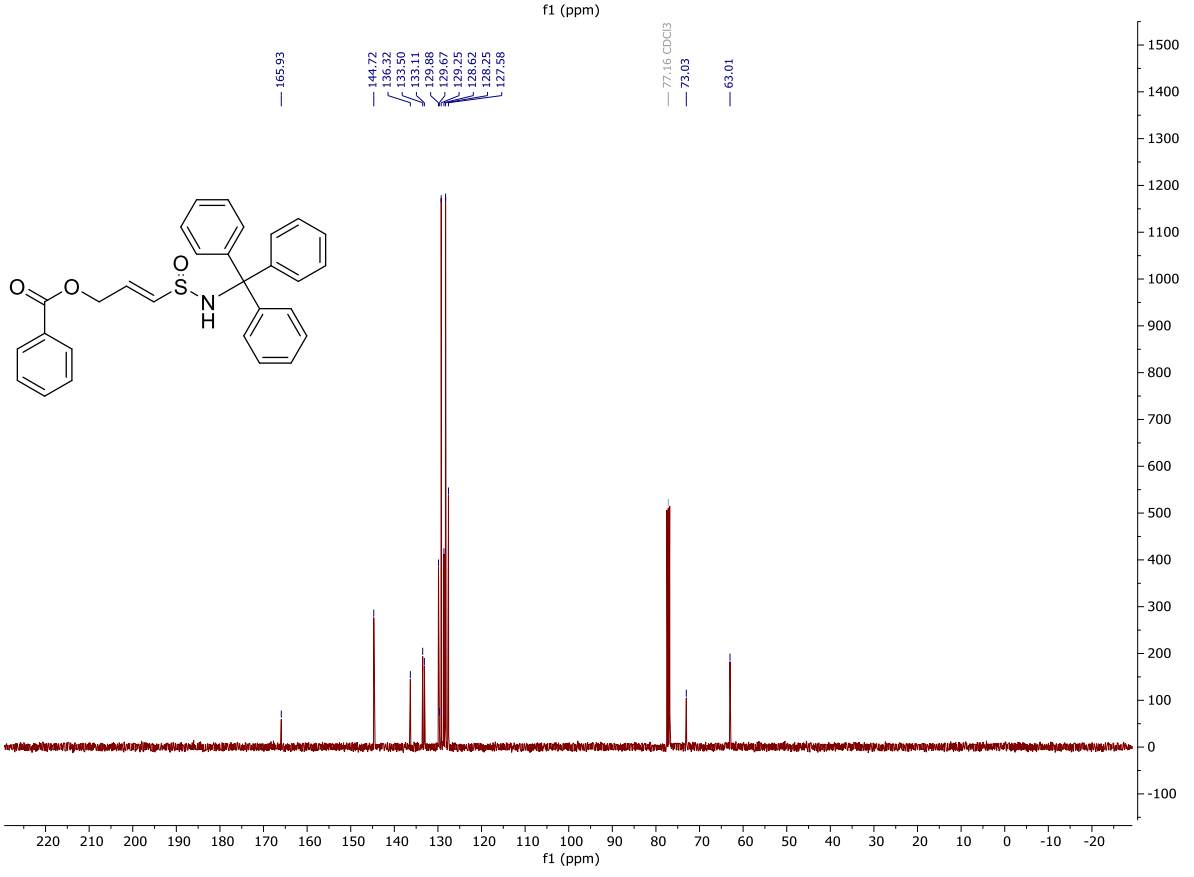
(*E*)-2-(Naphthalen-1-yl)-*N*-tritylethene-1-sulfinamide (7q)



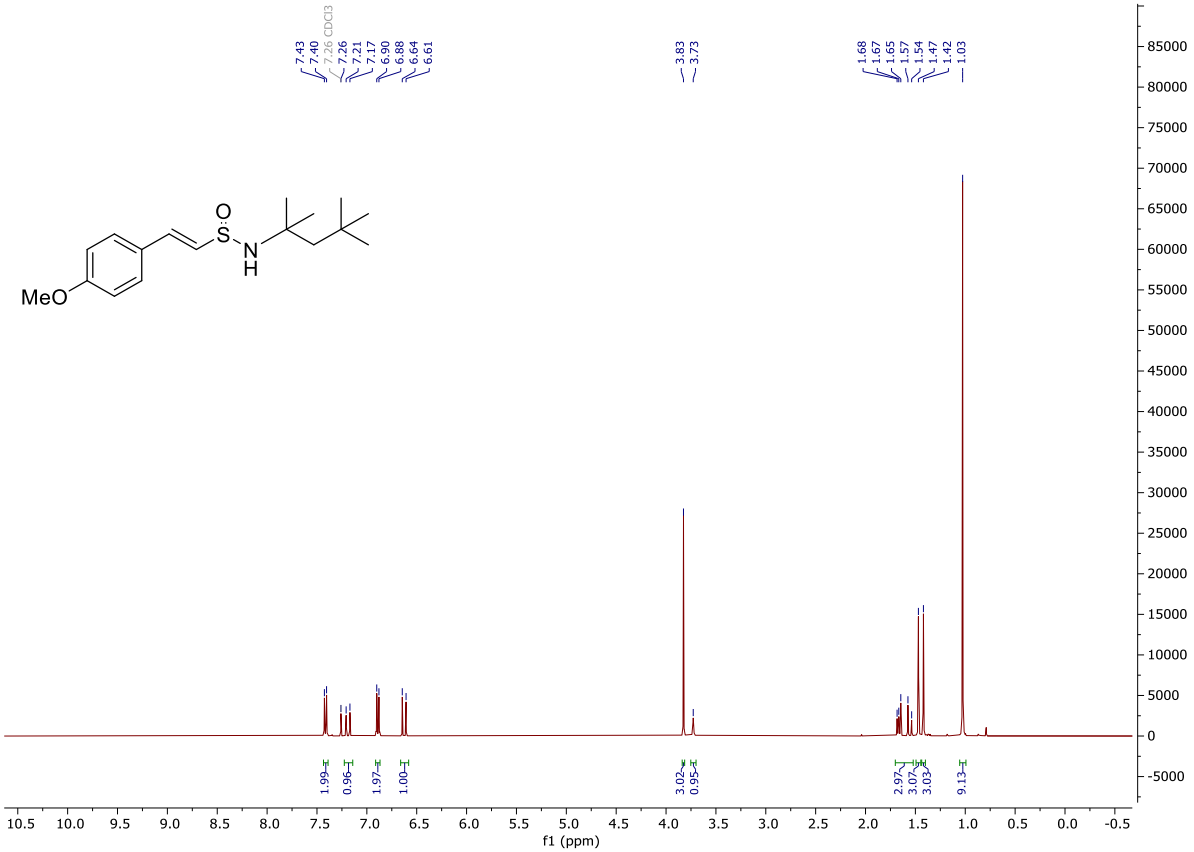


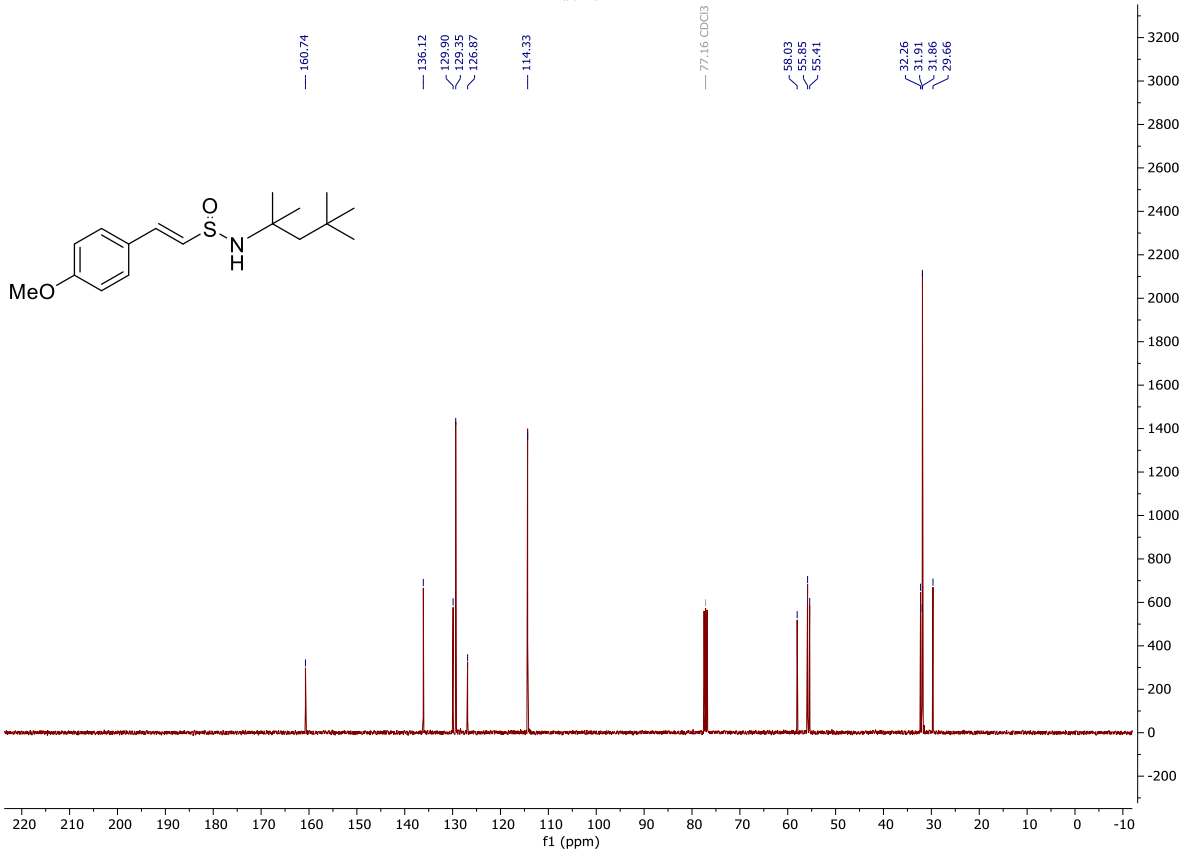
(*E*)-3-((Tritylamino)sulfinyl)allyl benzoate (7r)



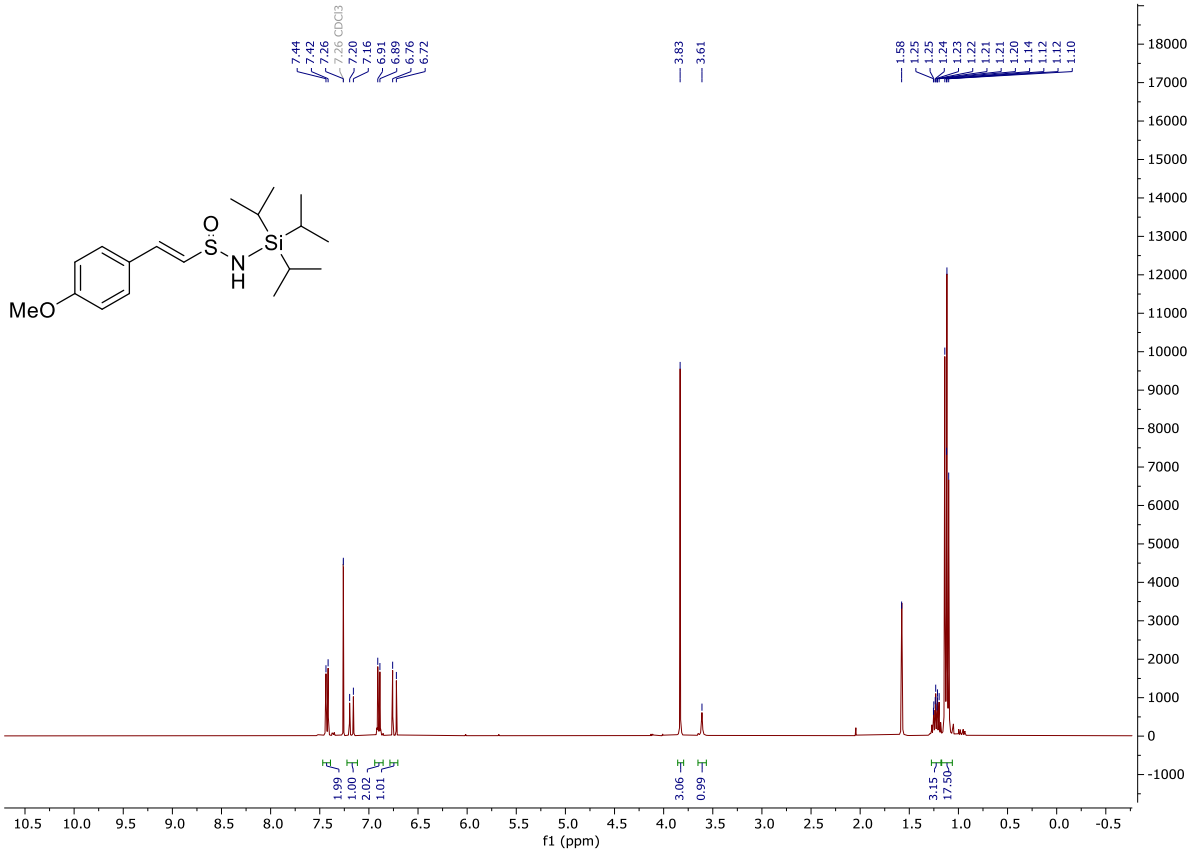


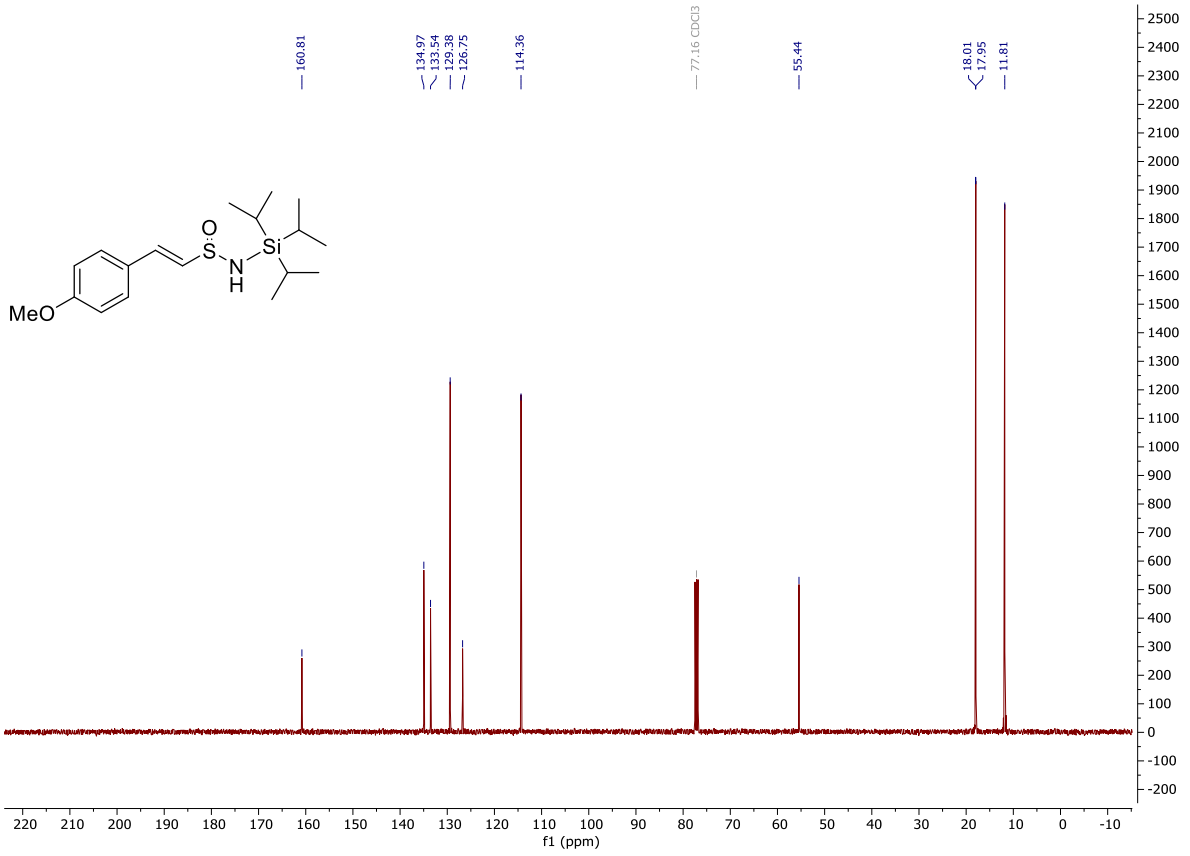
(*E*)-2-(4-Methoxyphenyl)-N-(2,4,4-trimethylpentan-2-yl)ethene-1-sulfinamide (7s)



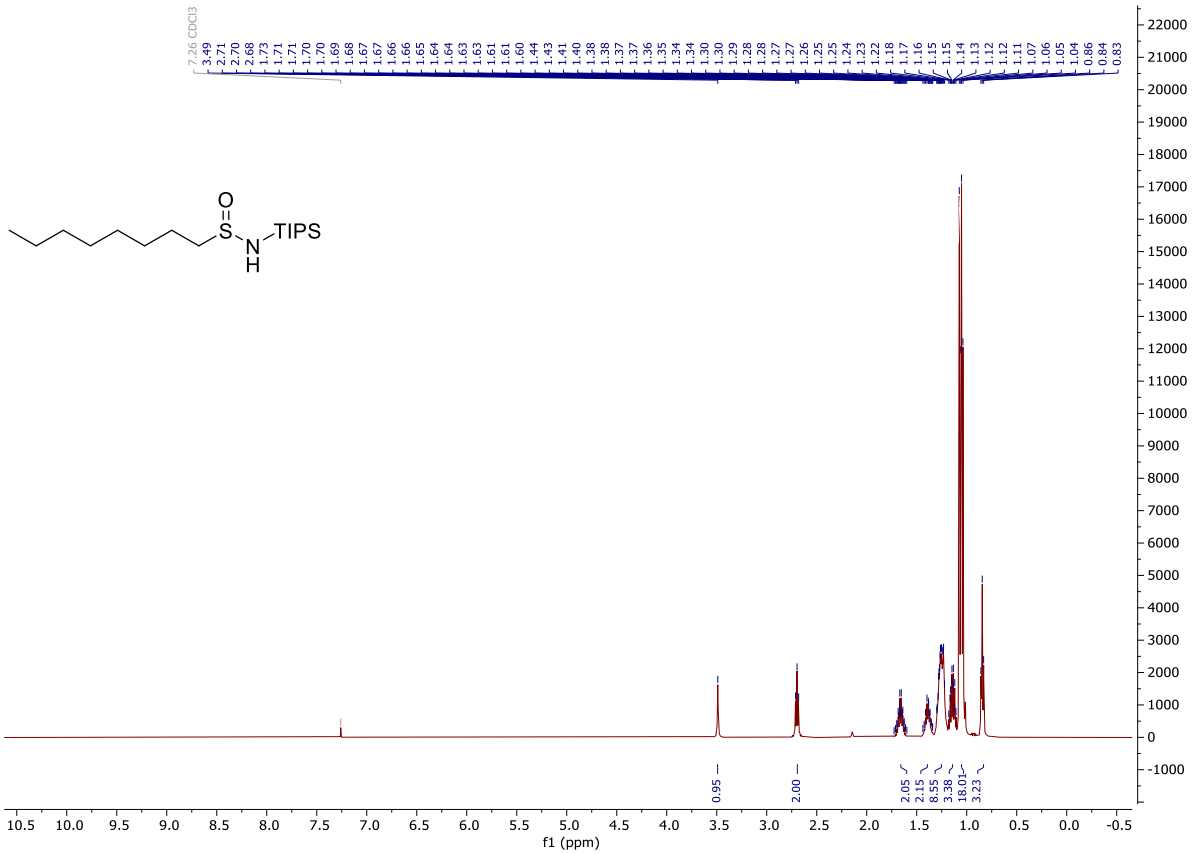


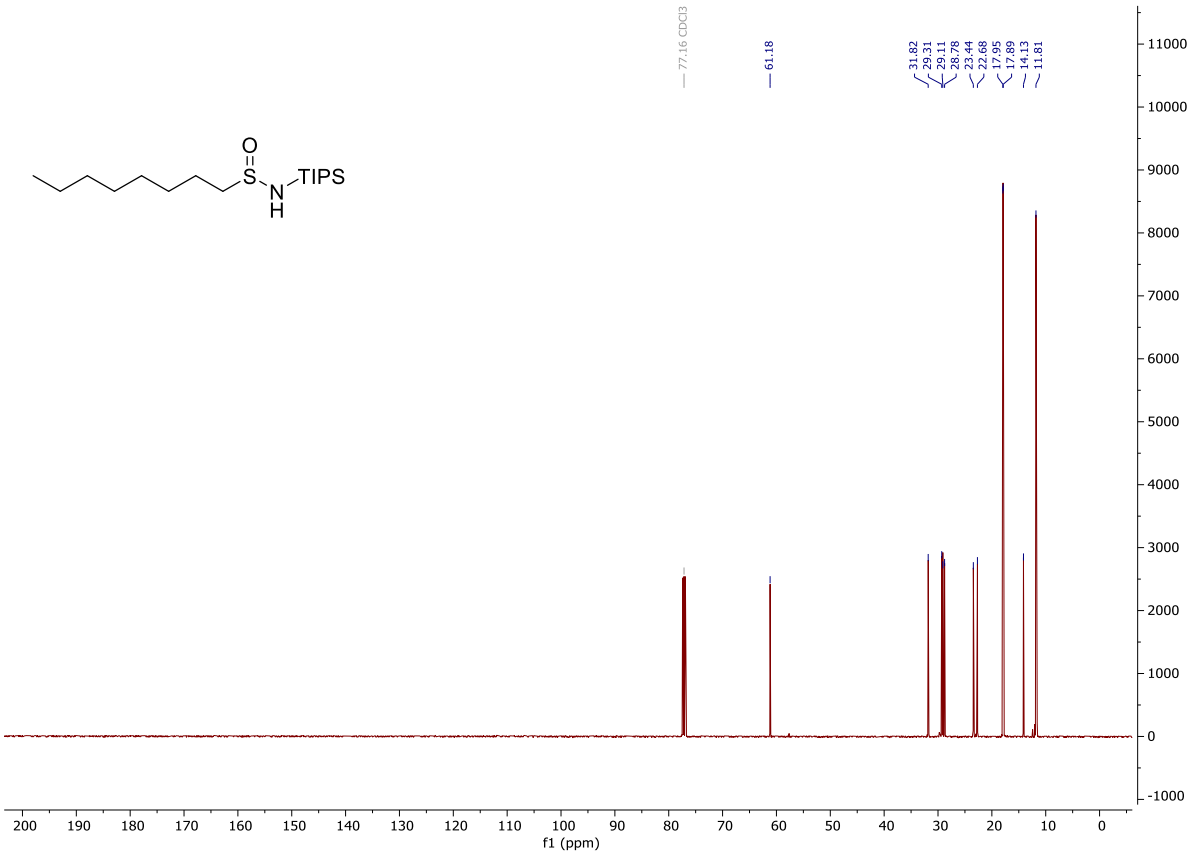
(*E*)-2-(4-Methoxyphenyl)-*N*-(triisopropylsilyl)ethene-1-sulfinamide (7t)



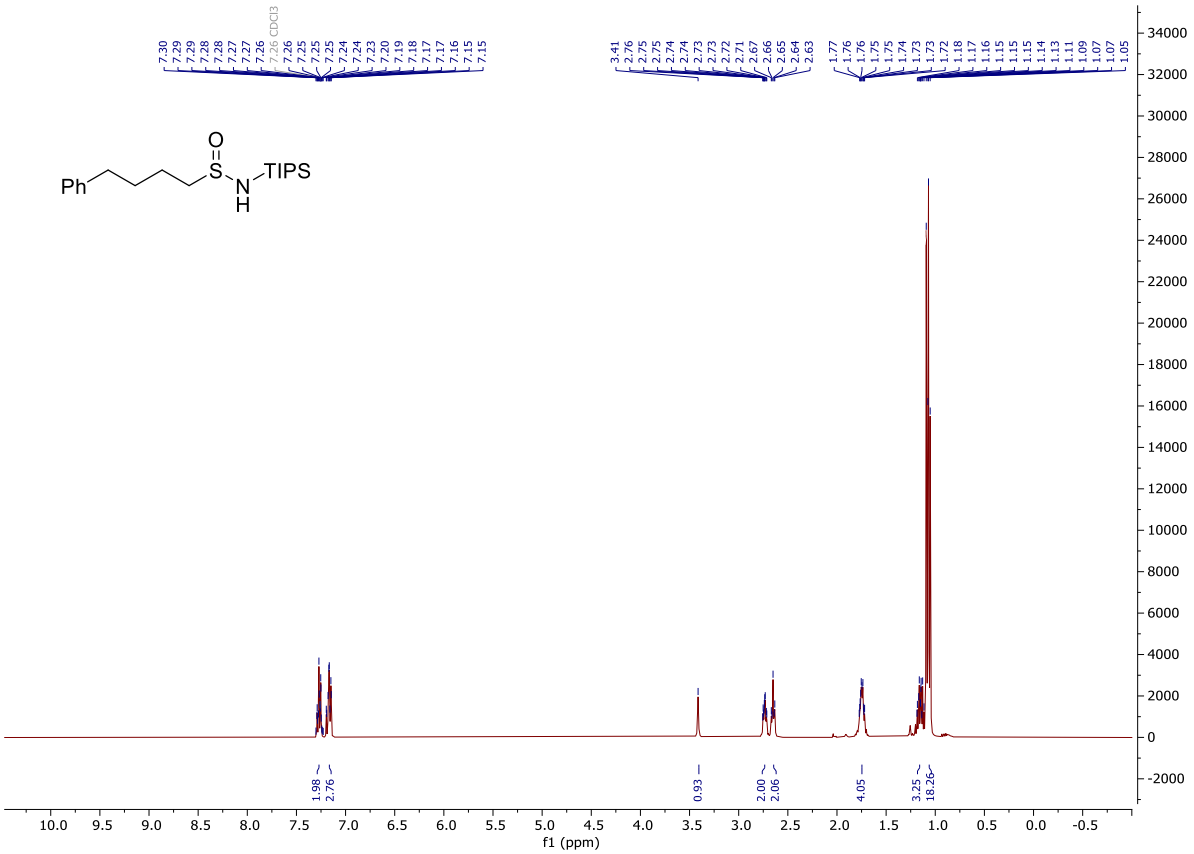


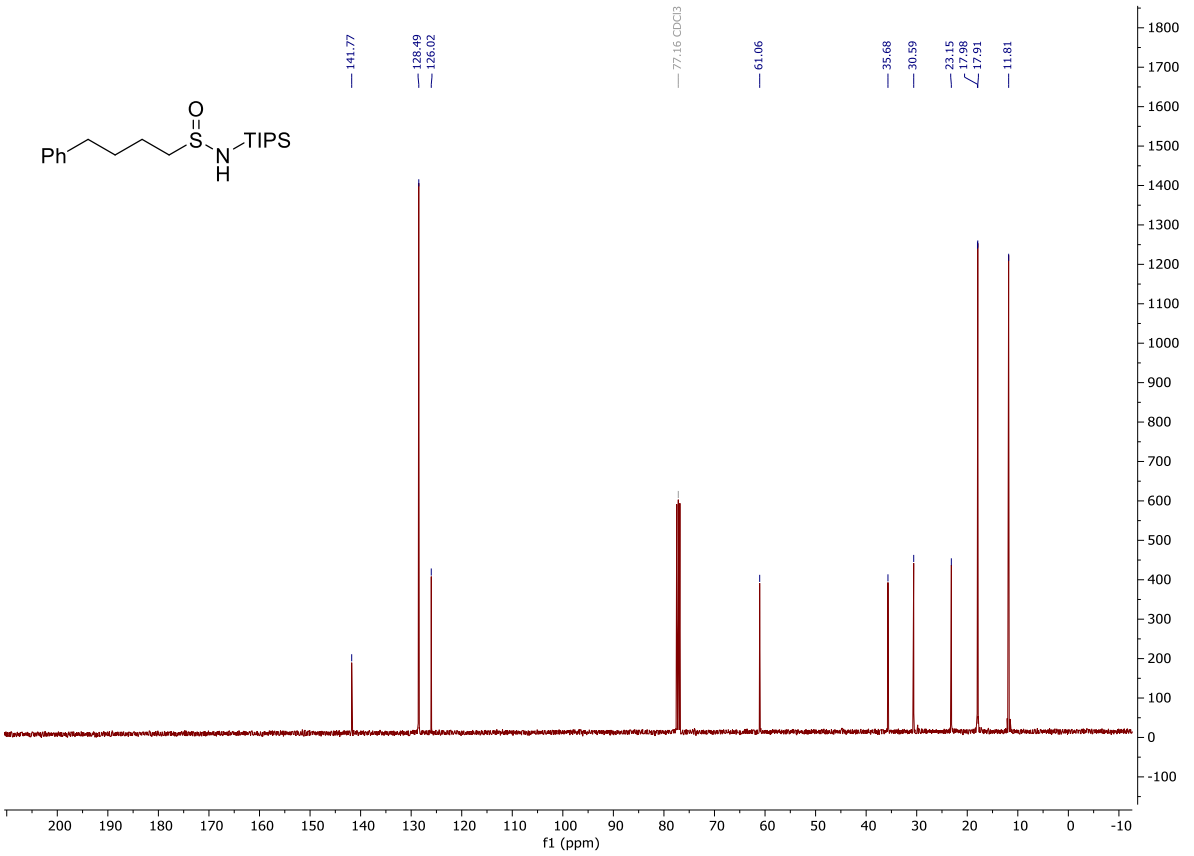
N-(Triisopropylsilyl)octane-1-sulfinamide (9a)



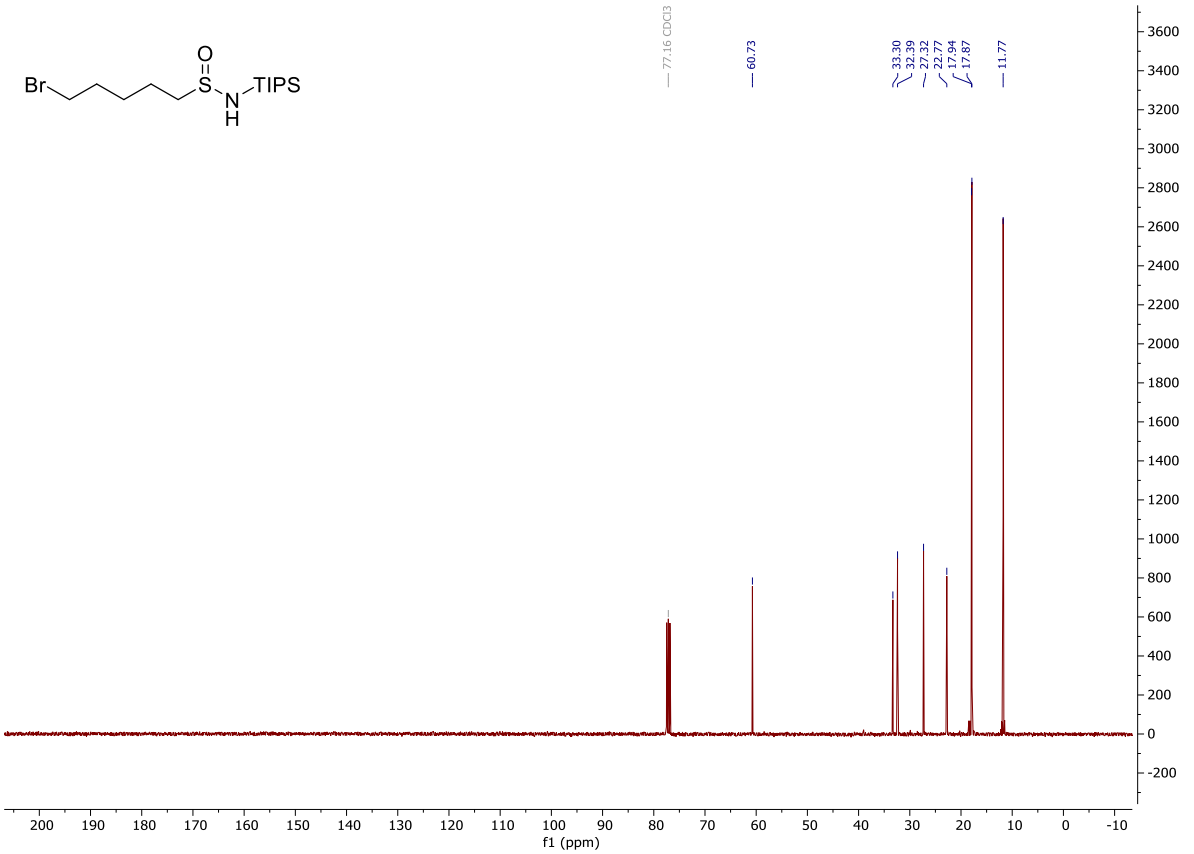


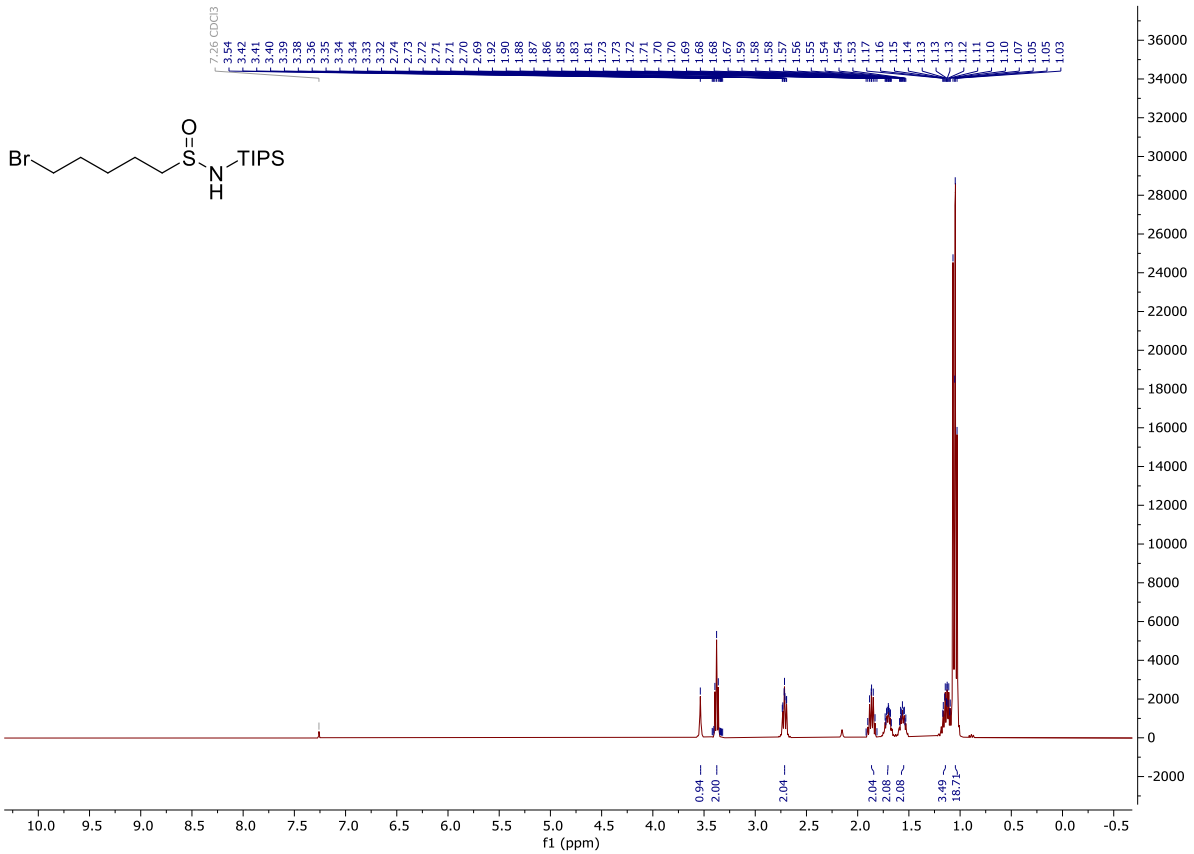
4-Phenyl-*N*-(triisopropylsilyl)butane-1-sulfinamide (9b)



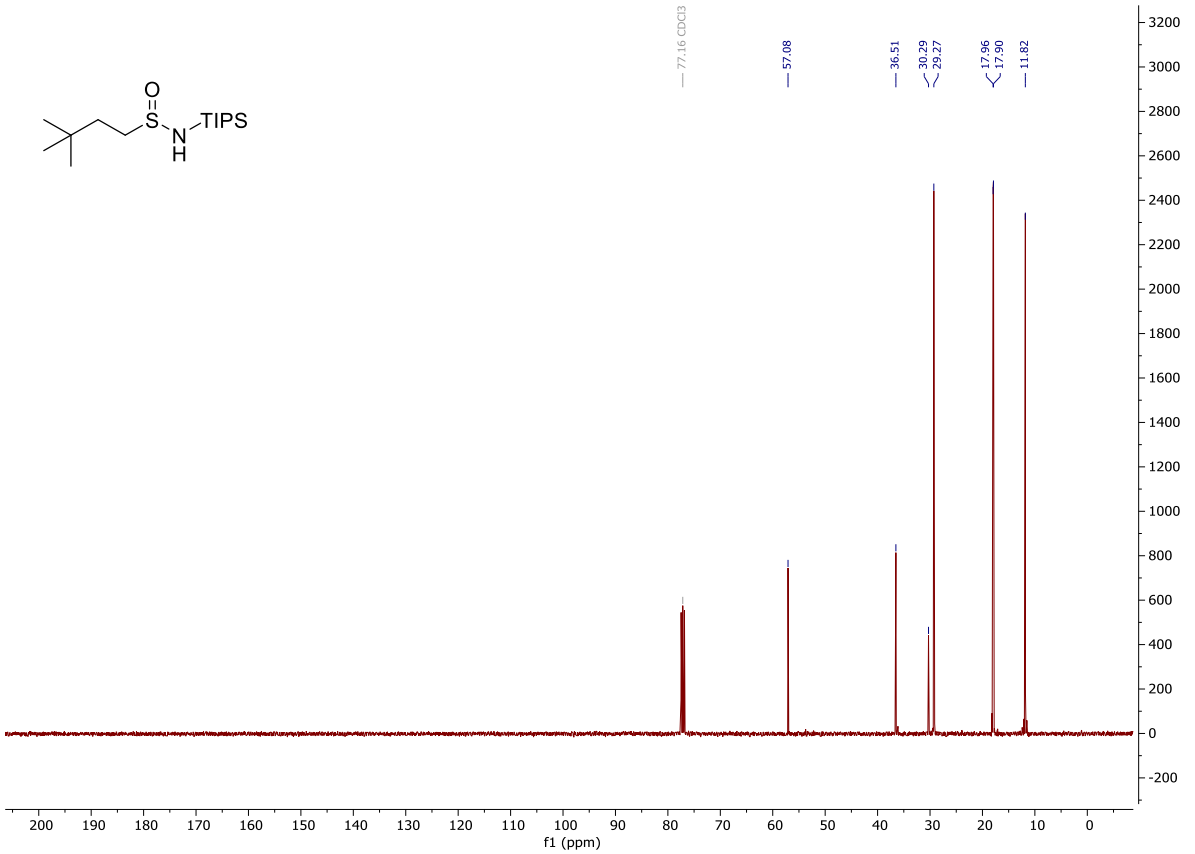


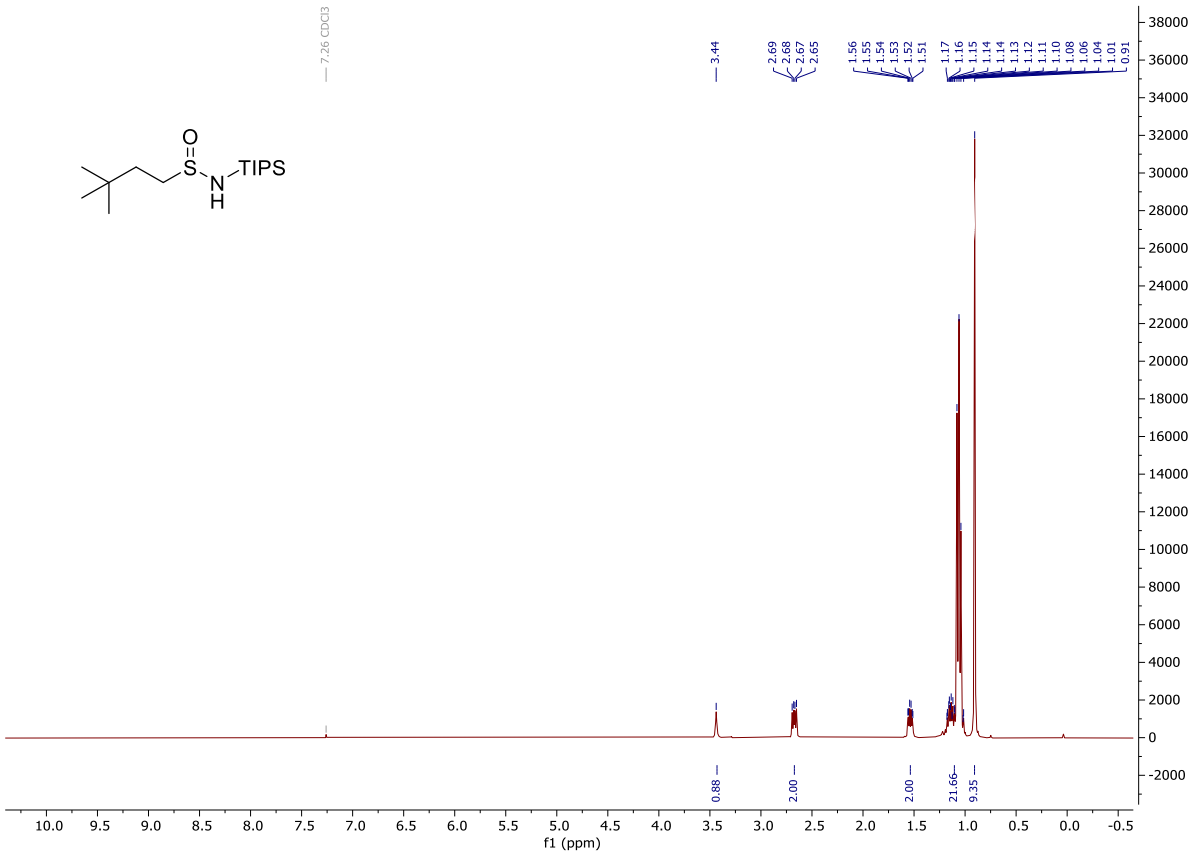
5-Bromo-*N*-(triisopropylsilyl)pentane-1-sulfinamide (9c)



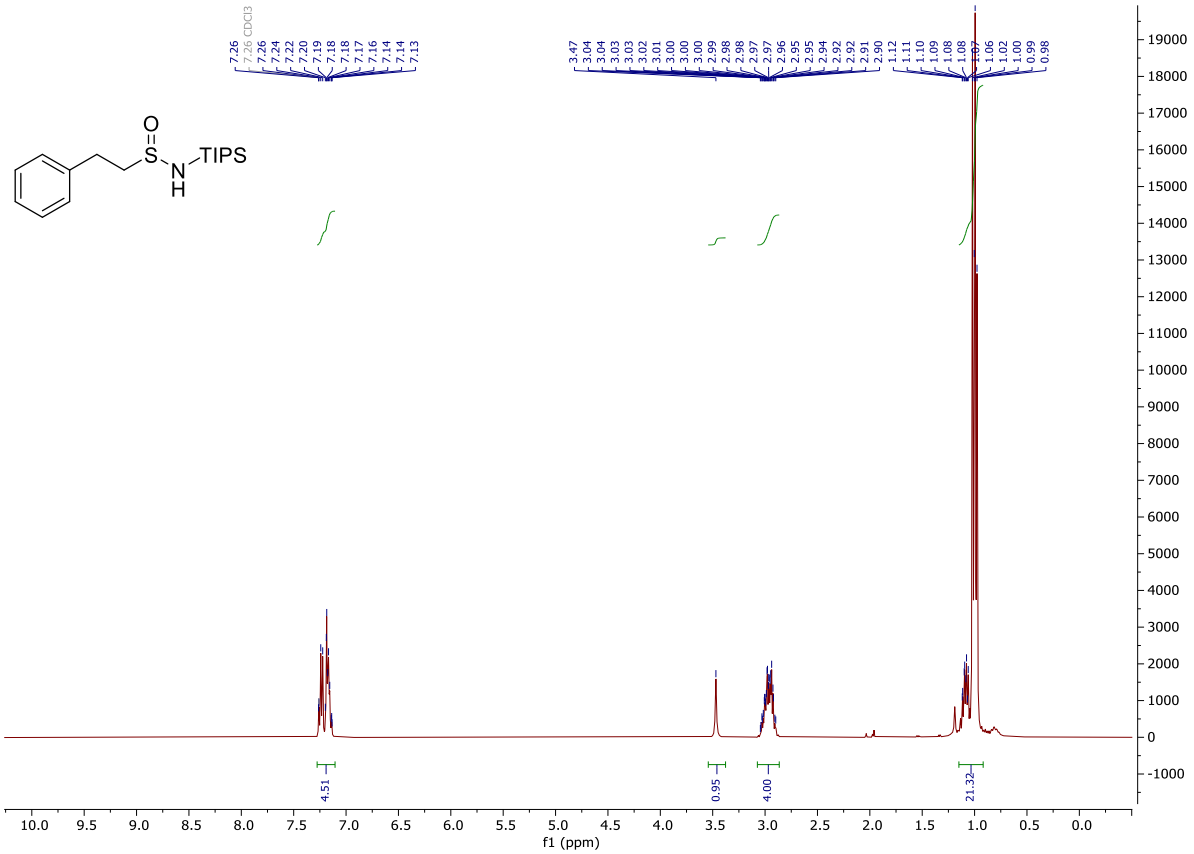


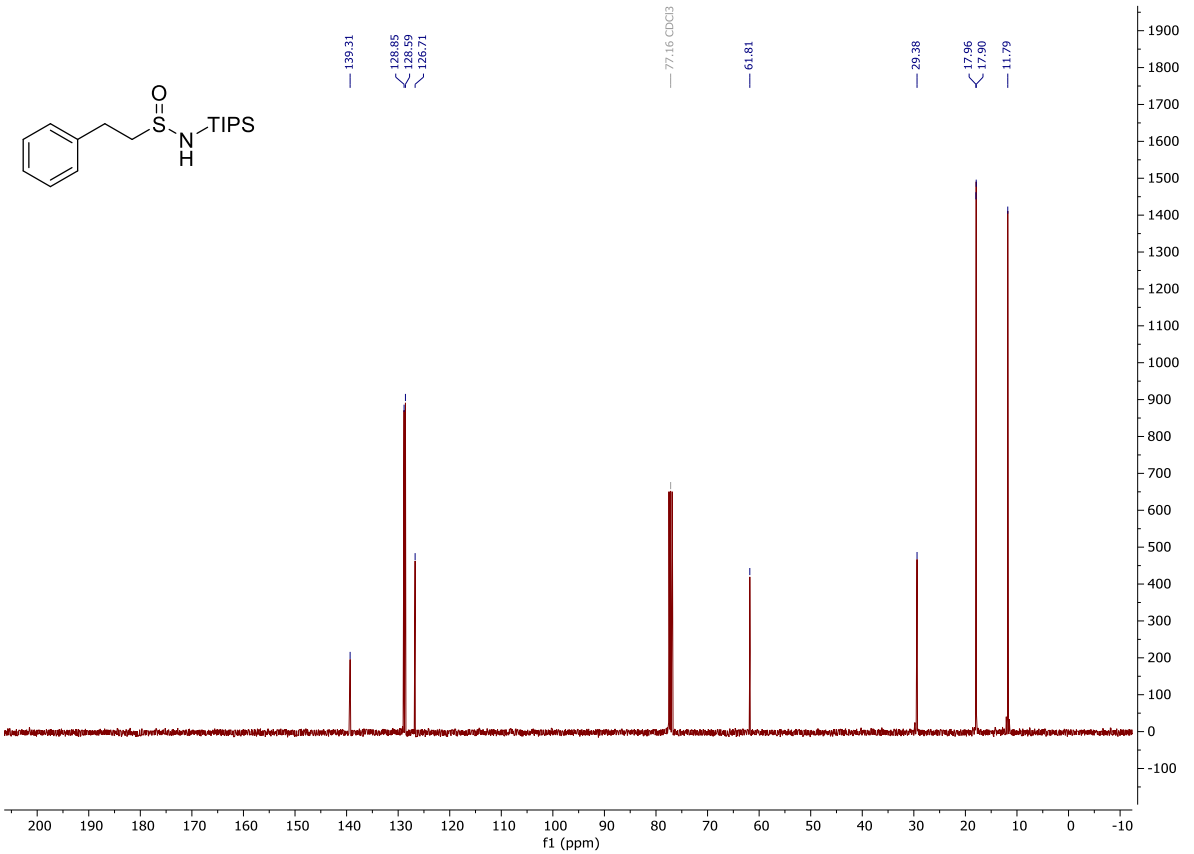
3,3-Dimethyl-*N*-(triisopropylsilyl)butane-1-sulfinamide (9d)



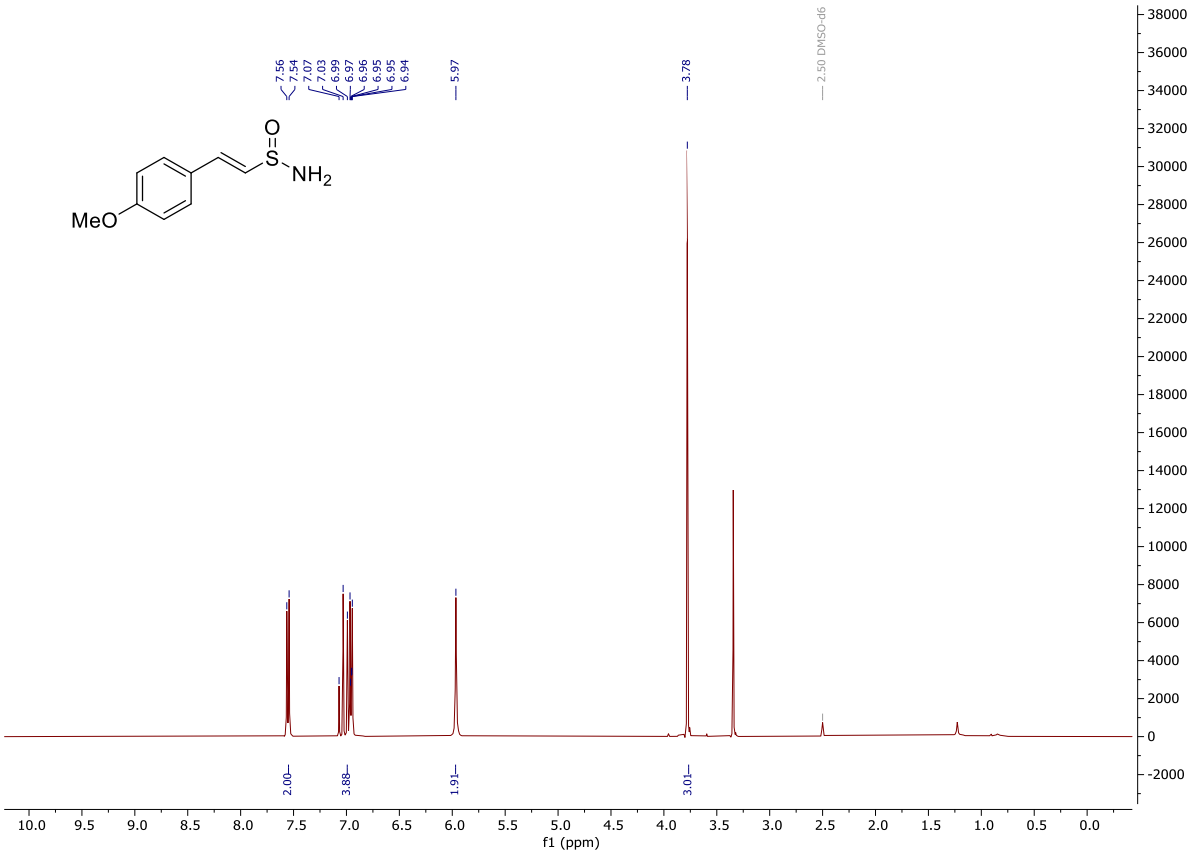


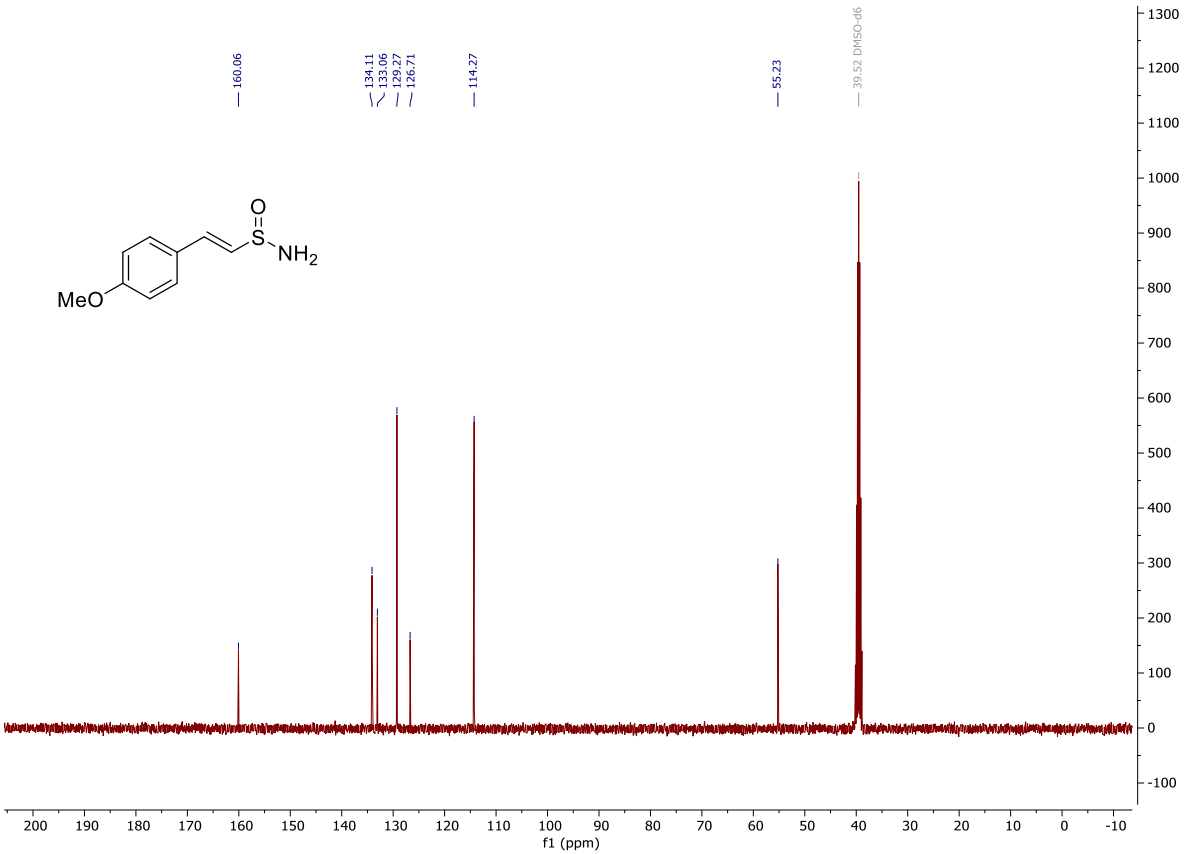
2-Phenyl-*N*-(triisopropylsilyl)ethane-1-sulfinamide (9e)



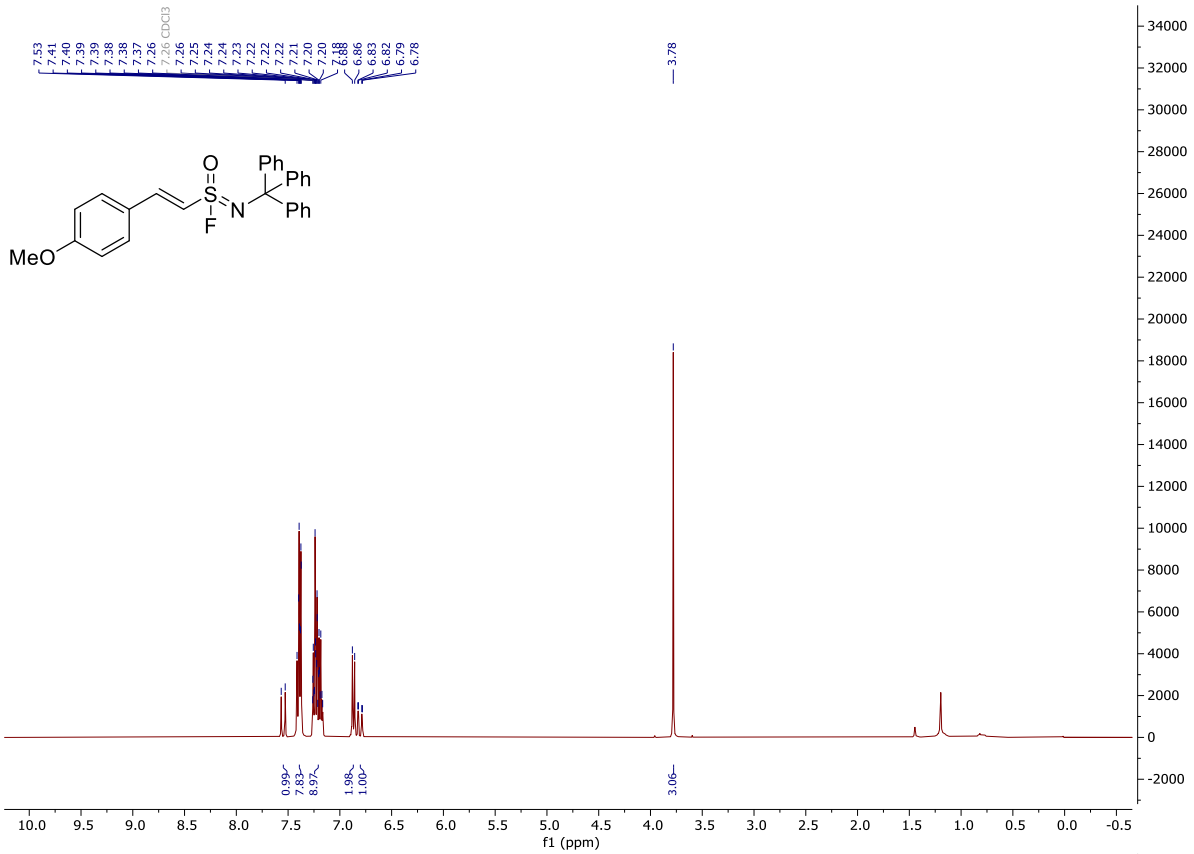


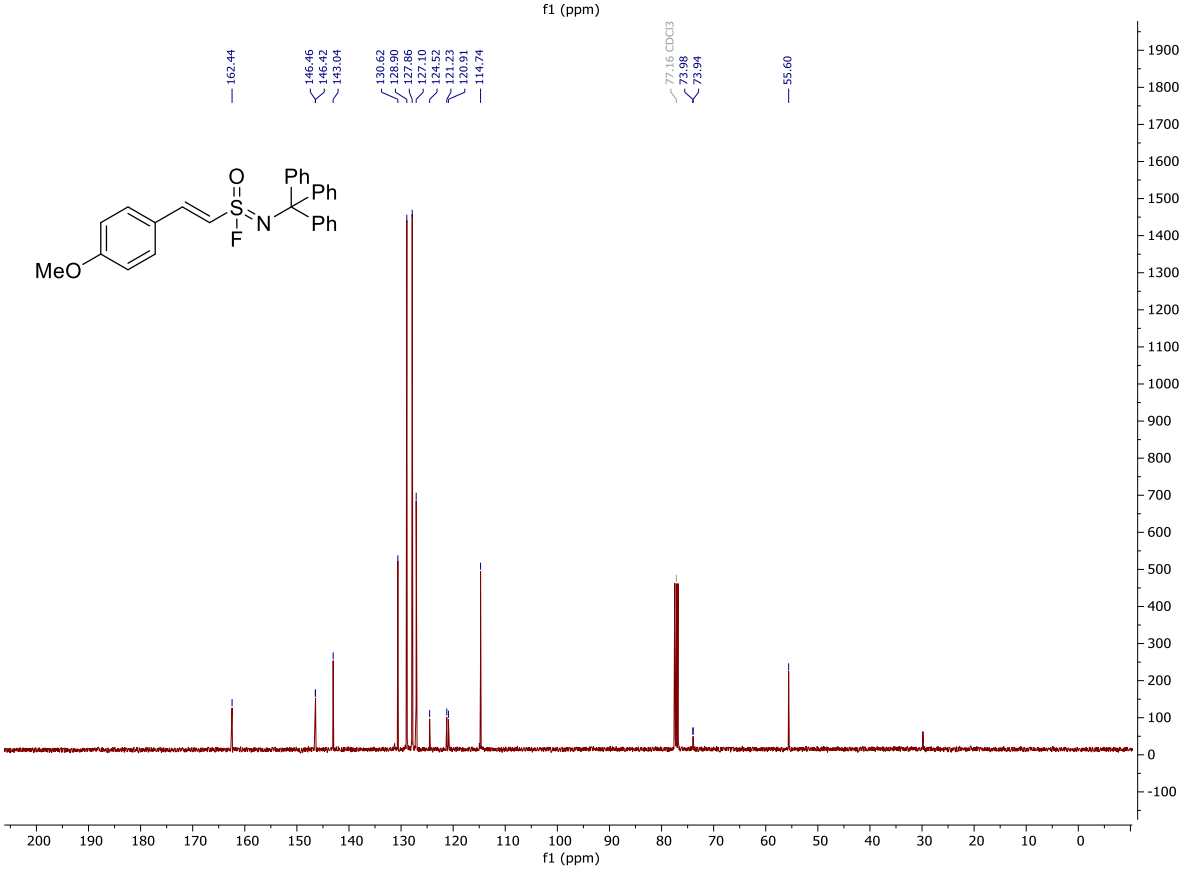
(*E*)-2-(4-Methoxyphenyl)ethene-1-sulfinamide (10t)

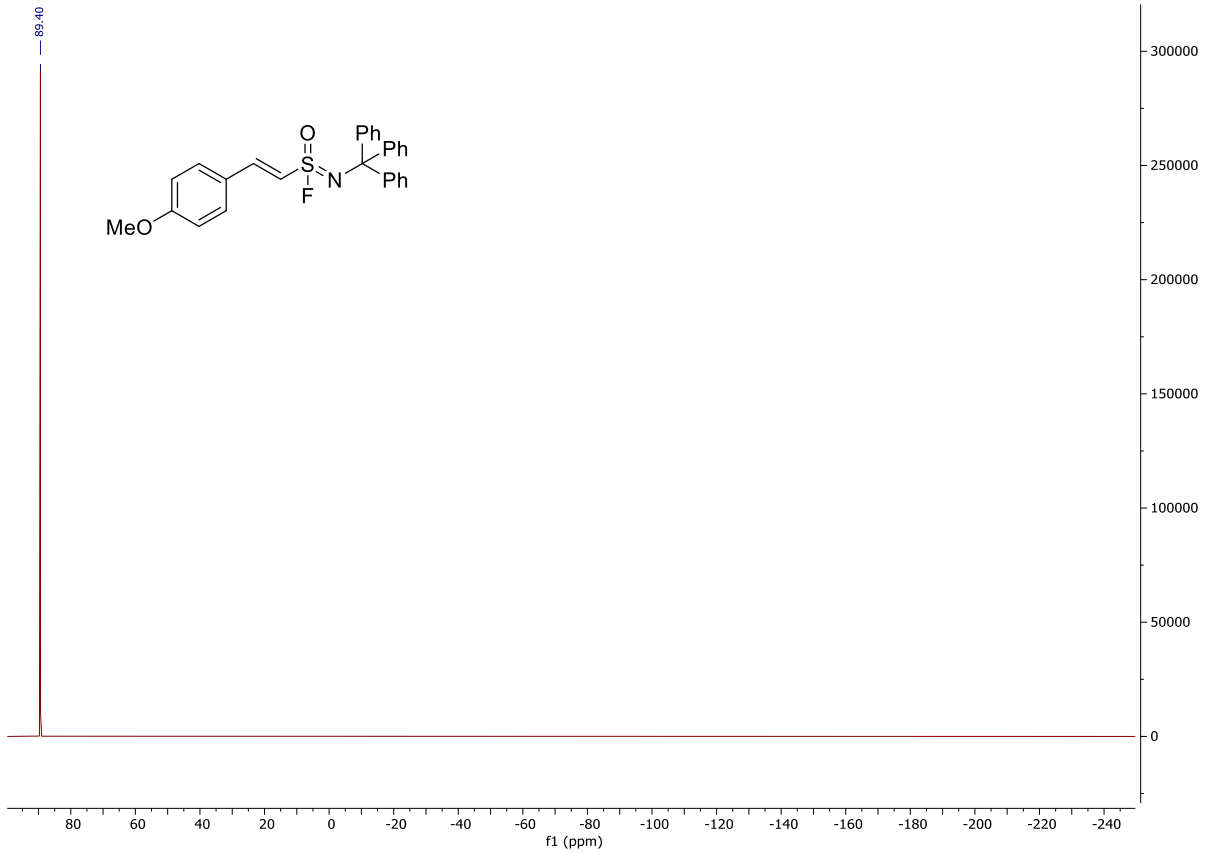




(*E*)-2-(4-methoxyphenyl)-N-tritylethene-1-sulfonimidoyl fluoride (11a)






89.40
O
S
F
N
Ph
Ph
Ph
MeO
300000
250000
200000
150000
100000
50000
0
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

(*E*)-4-(2-(4-methoxyphenyl)vinylsulfonimidoyl)morpholine (12a)

