New Synthetic Methodologies for the C-C/C-X Bond Forming Reactions

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

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Tag der mündlichen Prüfung: 08th December 2022

The work reported in this thesis was performed at the Institute of Organic Chemistry at the RWTH Aachen University in Aachen from May 2019 until June 2022 under the supervision of Prof. Dr. Rene M. Koenigs.

Acknowledgement

First of all, I would like to thank my esteemed supervisor, Prof. Dr. Rene M. Koenigs, for his incredibly helpful guidance, patience, and support during my doctoral studies. When I first came to this group, he patiently guided me to start my project. When I encountered setbacks in the project, he always encouraged me with his enthusiasm. When my child was born in Germany, he also enthusiastically helped me with many life matters, such as helping me apply for kindergarten, and apply for child allowance and so on. Thanks to his help, my family and I live very comfortably in Germany.

Moreover, I would like to thank all group members of the Koenigs group. In particular, I would like to express my appreciation to Chao, Sripati and Claire, they selflessly gave me unlimited support during my PhD studies, very grateful for their help. Furthermore, I also want to thank all other kind group members: Yujing Guo, Feife He, Zhen Yang, Dr. Sourav Sekhar Bera, Hao and Yun, they also helped me a lot.

Additionally, I am grateful that I have met many friendly people from other groups in IOC. Congjun Yu, Yu Zhao, Bo Li, Raolin Huang, Wenjing liang, Wei Wang, Xinbeng Wang, Dr. Ragaa Benchouaia, Calogero Quaranta and others. Thank you so much for their presence in my life, they enrich my life.

Finally, and most importantly, I would like to express my special gratitude to my parents and my family, whose encouragement and support make my accomplishments possible.

The following parts of this work have already been published:

Catalyst-free [2, 3]-sigmatropic rearrangement reactions of photochemically generated ammonium ylides

F. Li, F. He, R. M. Koenigs, *Synthesis* **2019**, *51*, 4348–4358.

Metal-free insertion reactions of silanes with aryldiazoacetates

F. He, F. Li, R. M. Koenigs, *J. Org. Chem.* **2020**, *85*, 1240–1246.

Stoichiometric photochemical carbene transfer by bamford–stevens reaction

S. Jana, F. Li, C. Empel, D. Verspeek, P. Aseeva and R. M. Koenigs, *Chem. Eur. J.* **2020**, *26*, 2586–2591.

Photoinduced proton-transfer reactions of mild O-H functionalization of unreactive alcohols

S. Jana[+], Z. Yang[+], F. Li, C. Empel, J. Ho, R. M. Koenigs, *Angew. Chem. Int. Ed*. **2020**, *59*, 5562-5566.

Rhodium-catalyzed enamine homologation of sulfides with triazoles as carbene precursor

F. Li, C. Pei and R. M. Koenigs, *Org. Lett.*, **2020**, *22*, 6816– 6821.

Rhodium-catalyzed cascade reactions of triazoles with organoselenium compounds–a combined experimental and mechanistic study

F. Li, C. Pei and R. M. Koenigs, *Chem. Sci.*, **2021**, *12*, 6362–6369.

1, 3-Difunctionalization of imino-carbenes via rhodium-catalyzed reactions of triazoles with acyl selenides

F. Li, C. Pei, C. Quaranta, R. M. Koenigs, *Adv. Synth.Catal.* **2021**, *363*, 4365–4370.

Photocatalytic *gem*-difluoroolefination reactions by a formal C–C coupling/defluorination reaction with diazoacetates

F. Li, C. Pei and R. M. Koenigs, *Angew. Chem., Int. Ed.*, **2022**, 61, e202111892.

Photocatalytic 1, 2-oxo-alkylation reaction of styrenes with diazoacetates

F. Li, S. Zhu and R. M. Koenigs, *Chem. Commun.*, **2022**, *58*, 7526–7529.

Furan synthesis via triplet sensitization of acceptor/acceptor diazoalkanes

S. Zhu, F. Li and R. M. Koenigs, *Adv. Synth.Catal.* **2022**, *364*, 3149–3154.

The following parts of this work have been presented in poster presentations on international conferences:

Photochemical Stoichiometric Carbene Transfer Reactions via Bamford-Stevens Rearrangement

S. Jana, C. Empel, F. Li, R. M. Koenigs, 12nd *New Years' Symposium*, Aachen/D., 10. January 2020

Blue light induced C-N bond insertion and cyclopropenation reactions

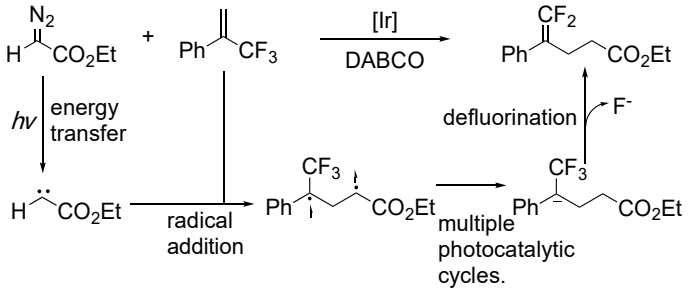
F. Li, F. He, R. M. Koenigs, *GDCh-Wissenschaftsforum Chemie*, Aachen/D., 19. September 2019

Contents

Summary

This PhD thesis explored novel C-C or C-X (X = S, N, Se) bond forming reactions using a variety of methods. Simultaneously, this thesis has expanded and enriched the carbene transfer reactions. Specifically, we investigated photocatalytic *gem*-difluoroolefination reactions with diazoacetates in the presence of the tertiary amines, which provided various useful *gem*-difluoroolefins. Furthermore, transition-metal catalyzed 1,3-difunctionalization of imino-carbenes were studied. Triazole were used as a safe and non-diazo containing precursor of carbenes. These reacted with different Lewis bases to generate the corresponding 1,3-difunctionalization products. Finally, metal-free [2,3]-sigmatropic rearrangement reactions of ammonium ylides were also discussed, to provide a various of amino esters.

In the first part, we realized the unique photocatalytic *gem*-difluoroolefination reaction using ethyl diazoacetate and α-trifluoromethyl styrenes. In this reaction, a tertiary amine played an important role, which inhibited undesirable cyclopropanation pathways and further supported the final abstraction of fluoride to produce *gem*-difluoroolefins. Furthermore, contrasting the reaction processes described by other groups, in this project, ethyl diazoacetate forms a triplet carbene intermediate via an energy transfer process in the presence of a photocatalyst. Different α-trifluoromethyl styrenes and diazoacetates were tolerated in this strategy, and various *gem*-difluoroolefins were obtained, including biologically relevant products (Scheme **1**).

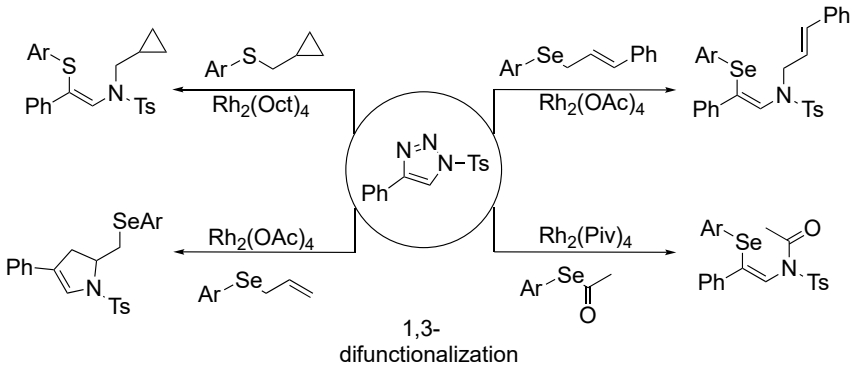


Scheme 1: Photocatalytic *gem*-difluoroolefination reactions

Next, we investigated various 1,3-difunctionalization reactions of 1-sulfonyl-1,2,3-triazoles with different substrates under transition metal-catalyzed conditions. According to the substitution patterns, different 1,3-difunctionalization products could be generated. Firstly, we studied the rhodium-catalyzed homologation reaction of alkyl aryl sulfides with triazoles via an imino carbene intermediate. In this reaction, cyclopropylmethyl sulfides were chosen as the nucleophilic reaction partner. DFT calculations revealed that the sulfur ylide intermediate was created via Dimroth rearrangement of triazoles. Subsequently, this ylide underwent a selective, intramolecular alkylation reaction to yield cyclopropylmethyl-substituted enamides instead of a classic rearrangement reaction.

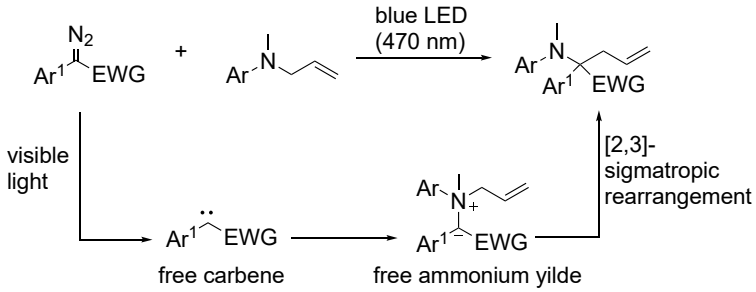
Secondly, we utilized organoselenium compounds as nucleophilic reaction partners, with which different novel carbene transfer reactions were achieved. When allyl selenides reacted with triazoles in the presence of Rh(II) catalysts, a special dihydropyrrole product was obtained via a consecutive sigmatropic rearrangement and selenium-mediated radical cyclization processes. In this process, the allyl selenide acts as both nucleophilic reagent and radical source. In contrast, cinnamyl selenide produced 1,3-difunctionalized products in a cascade reaction of sigmatropic rearrangement and aza-Cope rearrangement. Through theoretical and experimental studies, we learned that these reactions go through free ylide intermediates.

Furthermore, we expanded our strategy towards the rhodium-catalyzed 1,3-difunctionalization of triazoles with acyl selenides. A variety of α-seleno enamides were obtained with high stereoselectivity and yield. An asynchronous concerted reaction process was supported by calculations, without intermittent production of metal bound or free ylide intermediates (Scheme **2**).



Scheme 2: 1,3-Difunctionalization of imino-carbenes via rhodium catalyzed reactions of triazoles

With our ongoing interest in sigmatropic rearrangement and photochemical reactions of diazo compounds, we started our investigations on [2,3]-sigmatropic rearrangement of ammonium ylides. Under photochemical reaction conditions, aryldiazoacetates reacted with tertiary amines to form free ammonium ylides, which underwent [2,3]-sigmatropic rearrangement to furnish different α,α-disubstituted amino esters. Various amines and diazoalkanes were tolerated in the optimized conditions, and the corresponding products were generated in moderate to good yields. This simple visible-light-mediated reaction of ammonium ylide further enriches the variety of carbene transfer reactions (Scheme **3**).



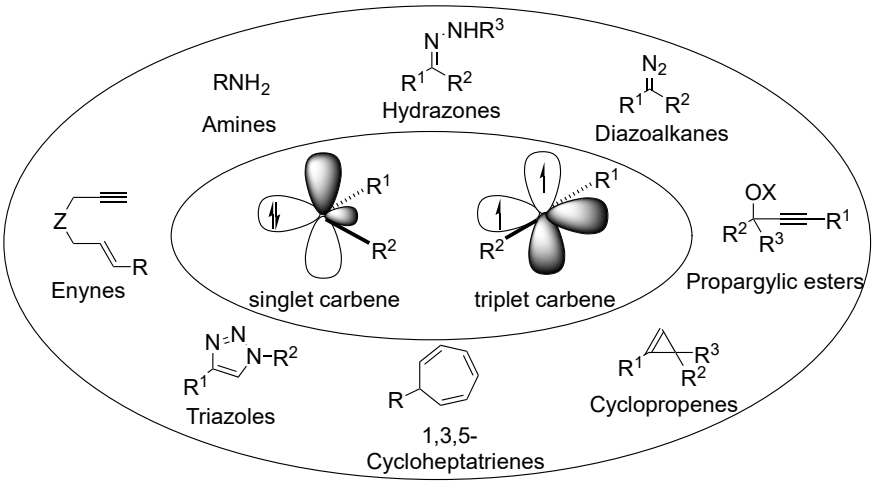
Scheme 3: Photochemical [2,3]-sigmatropic rearrangement reactions of ammonium ylide

1. Carbene

1.1 Introduction of Carbene

Dumas *et al.* proposed the generation of carbenes in the mid-19th century.[1, 2] Carbenes as highly reactive intermediates have been one of the most important reactive substances in organic chemistry in the past decades. The multifarious transformations of carbenes provided new methods to construct various chemical bonds.[3, 4] At the same time, these reactions involve carbene intermediates and were also widely used in the synthesis of natural products and pharmaceutically important molecules.[5-9]

Typically, carbene intermediates are formed from the decomposition of carbene precursors. Studies of carbene precursors have received significant attention from numerous groups. And during the past few decades, a variety of carbene precursors have been investigated,[10] such as hydrazones, amines, triazoles, 1,3,5-cycloheptatrienes, cyclopropenes, enynes, etc. Due to their distinct and high chemical reactivity, these reactions of carbene precursor are frequently employed in organic chemistry (Scheme **4**).

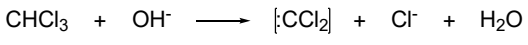


Scheme 4: Different carbene precursors

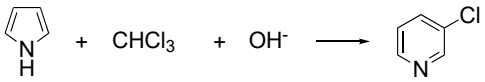
Since Dumas made the initial contributions to the study of carbenes in 1835,[1] it has been progressively come to light. Then later, in 1855, Geuther and Hermann first proposed a dichlorocarbene intermediate, which was generated by alkaline hydrolysis of chloroform (Scheme **5a**).[2] This same group also reported that chloroform reacted with potassium ethoxide to produce dichlorocarbene via elimination of hydrogen chloride in 1862. Potassium chloride and ethanol were the by-products in this reaction.[11] A similar intermediate was proposed to undergo the Ciamician-Dennstedt rearrangement by Nef in 1897 (Scheme **5b**). He asserted that mass production of methylene was possible. Unfortunately, these theories could not be translated into reality.[12] Additionally, Curtius[13] and Staudinger[14] also did groundbreaking work on the discovery of carbenes. Regrettably,

there were only insufficient analytical methods at that time, therefore the actual preparation of the dichlorocarbene remained hidden.

a), Geuther and Hermann's work

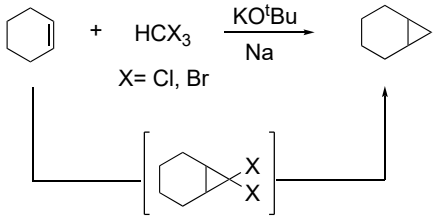


b), Nef's work



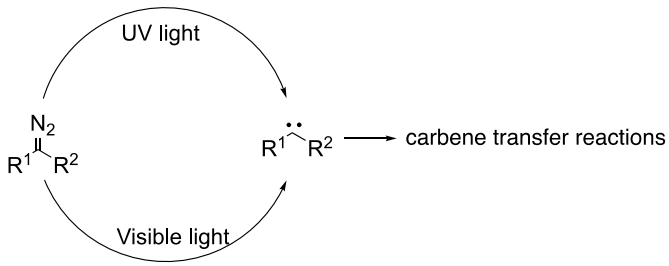
Scheme 5: Earlier pioneering work of carbene

In the early 1950s, studies on the physical and chemical properties of carbene species have attracted a lot of attention. In 1954, Doering demonstrated the synthetic utility of dihalogencarbenes. [15] The first cyclopropanation reaction of free carbene was discovered by him, and provided the initial proof that dichlorocarbene could be produced from chloroform (Scheme **6**). This species was dubbed "*the most indiscriminate reagent in organic chemistry*" by Doering.[16] Since then, chemists have conducted significant studies on it, and these highly reactive intermediates have been more and more clearly displayed in organic synthesis.



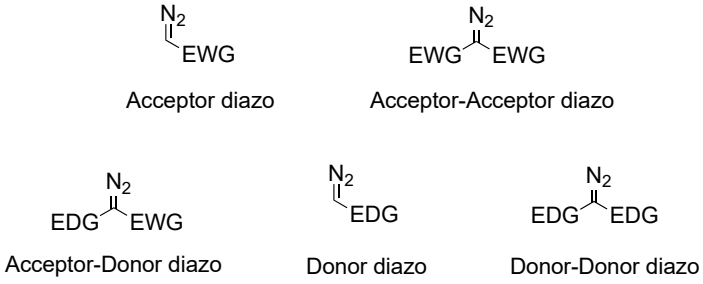
Scheme 6: The addition of dihalogencarbenes to olefins

Carbenes intermediates can be commonly classified as free carbenes and metal carbene complexes. Among them, free carbenes were first studied. The first example of photo-promoted free carbene transfer reaction was reported by Meerwein in 1942. In that experiment, diazomethane underwent UV photolysis to form methylene, which underwent unselective C−H functionalization reaction with diethyl ether solvent.[17] Subsequently, various applications of UV light-promoted carbene transfer reactions were reported.[18] However, due to the poor selectivity and high-energy light source, the utility of this approach was hampered. On the other hand, recently, visible light as a low-energy light source, has been widely applied in organic synthesis.[19-24] Since Davies, He, Zhou, and Koenigs published on the applications of carbene transfer reactions mediated by visible light in 2018, this field is developing rapidly (Scheme **7**).



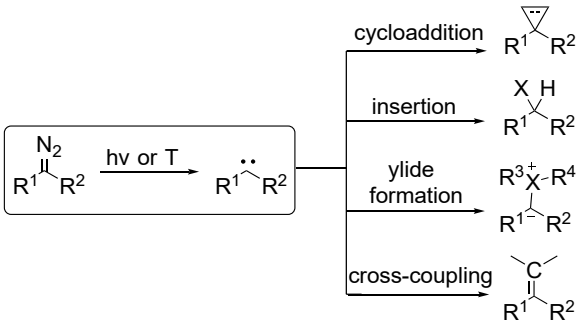
Scheme 7: Different lights promoted carbene generation

Diazo compounds, one of the carbene precursors, are the most common and widely utilized precursor to study the properties and applications of carbene.[3, 4, 6-9] Based on the substituents adjacent to the carbene center, Diazo compounds are divided into five categories: acceptor carbene, acceptor–acceptor carbene, donor–acceptor carbene, donor carbene and donor–donor carbene (Scheme **8**).[6]



Scheme 8: Different diazo compounds

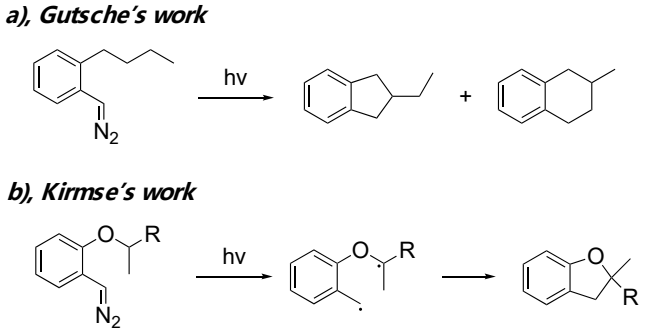
The diazo compounds can be decomposed into free carbenes under thermolysis and photolysis conditions, which can then undergo a variety of carbene transfer reactions, including cyclopropanation, C−H insertion, X−H insertion, sigmatropic rearrangement reaction and cross-coupling reaction. Therefore, these carbene transfer reactions from diazo compounds have been provided as one of the efficient classic synthesis tools for building different chemical bonds in organic synthetic methodology (Scheme **9**).[20, 24-26]



Scheme 9: Free carbenes transfer reactions

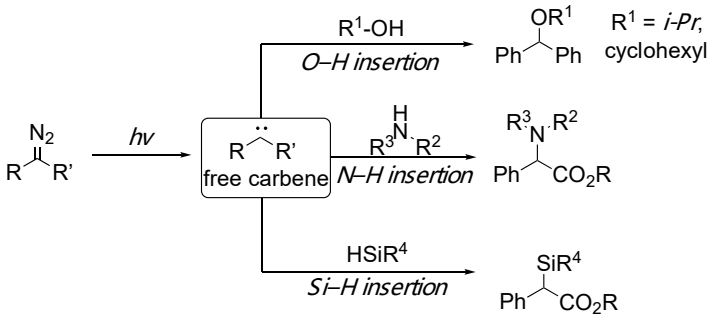
A common method for the synthesis of a wide range of small organic molecules is the free carbene C−H insertion approach. In the early studies, photolysis and thermolysis were the main approaches to generate free carbene intermediates, which have achieved C−H functionalization reactions with different reaction partners. Early work in this field was discovered by Meerwein, Rathjen, and Werner.[17] The intermolecular or intramolecular C−H

insertion process could be achieved. Due to its limited selectivity and competition from intramolecular reactions, intermolecular C−H insertion was generally not a viable tool when compared to intramolecular procedures. Early in 1958, an intramolecular C−H insertion of 2-phenyl-phenyldiazomethane was reported by Klemchuk.[27] The mechanistic investigation indicated that a free arylcarbene was formed by light irradiation. A few years later, Gutsche and co-workers disclosed an intramolecular C−H functionalization of arylcarbenes under light irradiation conditions.[28] Photolysis of the 2-*n*-butylphenyldiazomethane generated five- and six-membered rings as the major products, and an equilibrium between singlet and triplet species of the arylcarbene species was proposed as the explanation for this special result (Scheme **10a**). Later, according to the report of Kirmse and co-workers,[29] it has been shown that a triplet carbene rather than a singlet carbene was the mechanism for intramolecular C-H insertion processes (Scheme **10b)**. In recent years, different novel blue LED-mediated free carbene C–H insertion reactions were developed by Gevorgyan,[30, 31] Sen,[32, 33] Davies[20] and Koenigs groups.[25]



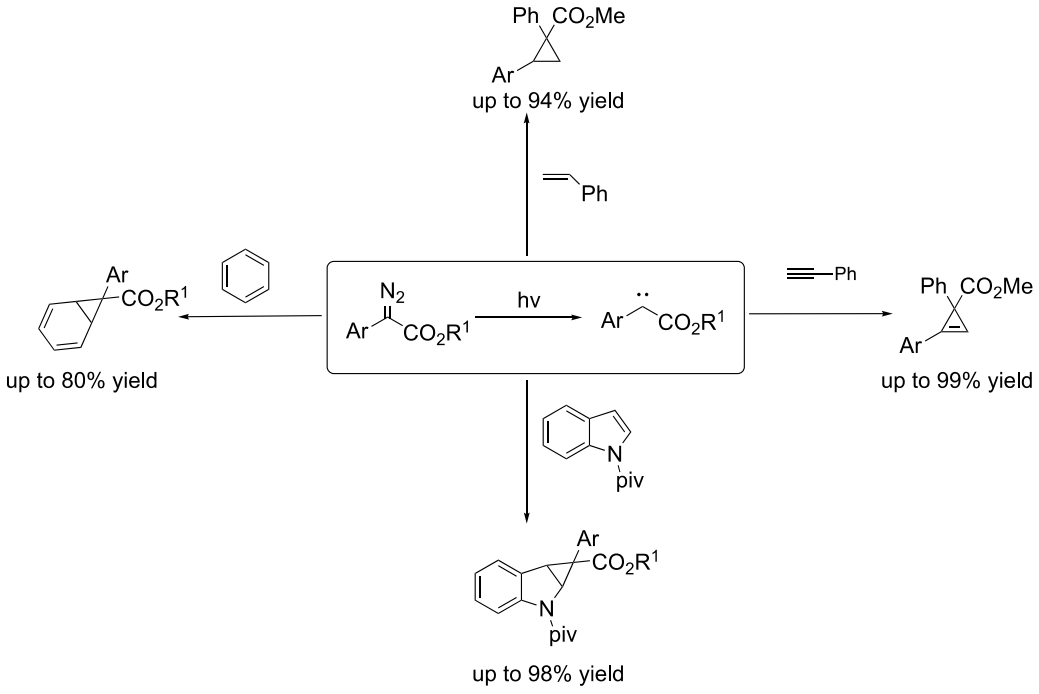
Scheme 10: Free carbene-mediated C-H insertion reaction via photolysis of diazo compounds

The X−H (X=Si, N, O, etc.) functionalization reaction via photochemical carbene transfer reactions is an important synthetic method for the formation of new C−X bonds. Early work on X−H functionalization via carbene intermediates were also carried out under photolysis conditions. In 1979, Tomioka and co-workers reported a light-promoted intermolecular O−H insertion reaction between diphenyldiazomethane and 2-propanol solvent to afford formal O−H inserted ether in quantitative yield,[34] in which the diphenylcarbene was released by the mercury lamp irradiation. However, the exact details of the reaction mechanism remained unclear. In recent years, the visible light-promoted X−H functionalization has been greatly advanced, various novel reaction pathways were developed under light irradiation conditions. Jurberg,[20, 35] Davies and Koenigs[36] have reported different blue light-promoted N−H insertion protocols of amines with aryldiazoacetates. In addition, Jurberg and Davies developed a procedure for O−H insertion using carboxylic acids with aryldiazoacetates, which allowed the synthesis of O−H insertion products in high yield (Scheme **11**). The method of Si−H insertion of silanes with aryldiazoacetates was also reported by the Koenigs group.[37]



Scheme 11: Photochemical carbene-emdiate X-H insertion reactions

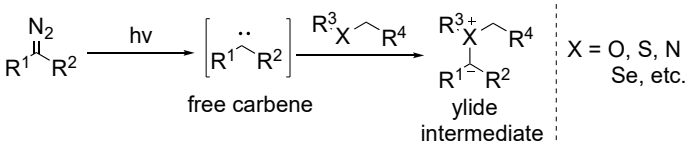
Cyclopropanes are the smallest cycloalkanes, which play an important role in organic synthesis.[38, 39] One of the most general approaches for synthesizing these compounds is the cyclopropanation of alkenes with diazo compounds. As early as 1985, Tolbert and co-workers have described a visible light-promoted cyclopropanation strategy employing diaryldiazomethane and fumarate esters as substrates. The triplet free carbene was produced by the diaryldiazomethane under photocatalytic conditions. In recent years, different groups have revealed their efforts in the development of cyclopropanation using diazo compounds. Numerous studies have been conducted on this aspect by Jurberg,[20] Koenigs[24, 40] and Niu[41] *et al.* (Scheme **12**).



Scheme 12: Light-promoted cyclopropanation reactions

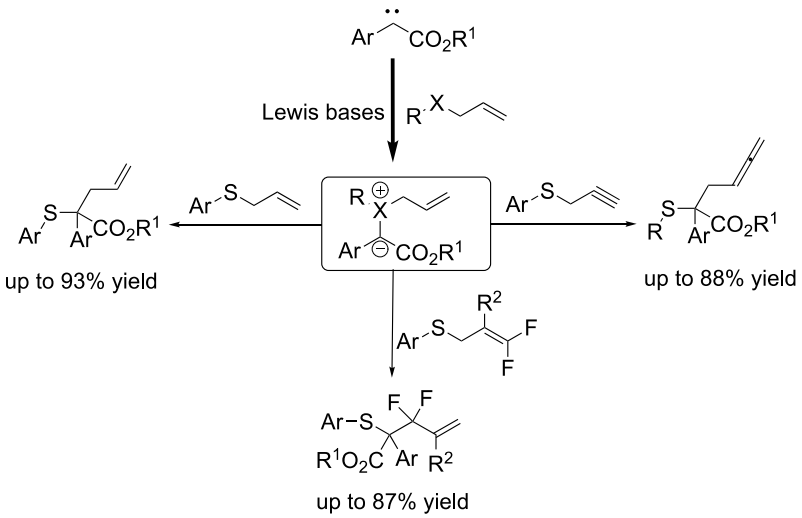
Sigmatropic rearrangements of ylide intermediates are important transformation methods allowing the synthesis of new C–C bonds.[42-45] Owing to the electrophilic properties, diazo compounds with electron-withdrawing groups can be easily converted into ylide intermediates with heteroatom Lewis bases. Under visible-light photolysis conditions, the free carbene derived from the reaction of a carbene with ethers, sulfides or amines can be used to form the corresponding ylides intermediates. These ylides are usually reactive and

readily react in further sigmatropic rearrangements transformations, such as Doyle–Kirmse rearrangement, [1,2]-sigmatropic rearrangement. Among these different sigmatropic rearrangement reactions, the [2,3]-sigmatropic rearrangement of ylides is one of the most useful transformations in synthetic chemistry and has received a great deal of attention (Scheme **13**).



Scheme 13: Formation of ylide with diazo compounds.

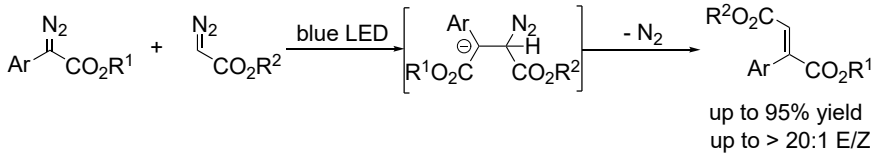
The blue light-promoted Doyle−Kirmse reactions of diazoalkanes with heteroatom Lewis bases were widely examined by various groups. In 2019, our group reported the blue-light-mediated [2,3]-sigmatropic rearrangement reaction of aryldiazoacetates with allyl sulfides, and the homoallylic sulfides were generated in good yields.[24] Subsequently, Gryko[46] and Xiao[47] further illustrated the usefulness of this strategy. Gryko revealed the efficient synthesis of allene products from propargyl sulfides and donor–acceptor diazoalkanes in high yields. Xiao and co-workers developed a unique approach toward the *gem*-difluoroallylation under visible light irradiation conditions, and this is the first example of C–CF_2 bond formation based on a [2,3]-sigmatropic rearrangement strategy (Scheme **14**).



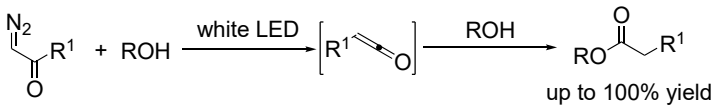
Scheme 14: Blue light-promoted [2,3]-sigmatropic rearrangement reactions

In addition, there are still a lot of different visible light-promoted carbene transfer reactions, which have been investigated extensively. The typical examples are cross-coupling reactions and Wolff rearrangement. In 2018, Zhou and co-workers described a photochemical cross-coupling reaction of aryldiazoacetates with diazocarbonyl compounds, various trisubstituted olefins were obtained with high selectivity.[22] Burtoloso and co-workers have shown that a white light-promoted Wolff rearrangement of α-diazoketones and alcohols,[48] providing the desired Arndt–Eistert homologation products in moderate to excellent yields (Scheme **15**).

a), Zhou's work

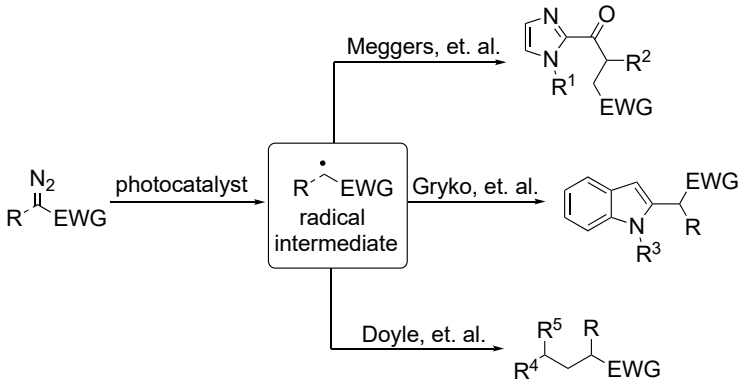


b), Burtoloso's work



Scheme 15: Visible light-promoted others carbene transfer reactions

In recent years, photoredox catalysis emerged as a facile synthetic tool for the formation of different radicals and has been widely used in the construction of new C–C bonds.[49-51] In the presence of a photosensitizer, the strategy that diazoalkanes reacts to various reactive intermediates via photoredox processes has been investigated. In this field, Meggers,[52] Gryko[53] and Doyle[54] have developed pioneering work (Scheme **16**).

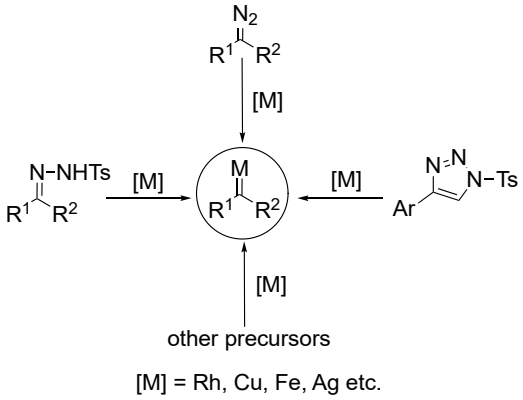


Scheme 16: Photocatalytic reactions of diazoalkanes

Although metal-free, photochemical-promoted carbene transfer reactions have many advantages and were developed early, they were still limited by some drawbacks, such as uncontrollable reactivity and poor levels of selectivity. Thanks to the emergence of metal-catalyzed carbene transfer reaction, these could be used to efficiently address these shortcomings. Metal carbenes have been extensively investigated over the past few decades and were also frequently employed in the synthesis of natural products and pharmaceutical molecules.[7, 8, 55-58] Metal carbene complexes can be classified into two categories: Fischer and Schrock carbene complexes. Fischer carbene complexes, which were first reported in 1964,[59] have been developed into powerful reagents in organic synthesis. Schrock carbene complexes were crucial to olefin metathesis and were initially identified in the early 1970s.[60, 61] In order to praise their contribution to olefin metathesis reaction, in 2005, the Nobel Prize was awarded to Richard R. Schrock, Yves Chauvin and Robert H. Grubbs.[62-64]

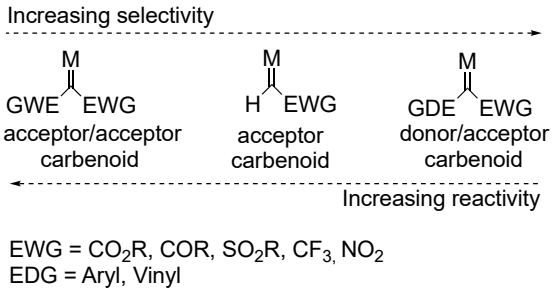
In the presence of a transition-metal catalyst, the metal carbenes intermediates are usually generated in situ by the interaction of carbene precursor compounds and the transition-

metal. Regarding those carbenes, there are several general categories, into which precursor compounds can be divided: diazo compounds, *N*-tosylhydrazones, *N*-sulfonyl-1,2,3-triazoles and other precursors (Scheme **17**).[6, 9, 10, 65, 66]



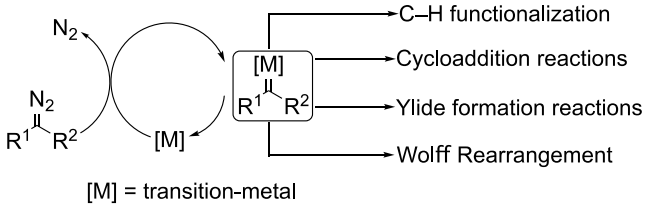
Scheme 17: Major categories of carbene precursors

Diazo compounds are adaptable organic chemicals that have become increasingly important in organic synthesis and many other fields. Particularly, diazo compounds have been frequently utilized as metal carbene precursors. According to the substituents adjacent to the carbene center, metal carbenes can be classified as follows: acceptor/acceptor- metal carbenes, acceptor- metal carbenes and donor/acceptor metal carbenes (Scheme **18**).[26, 65]



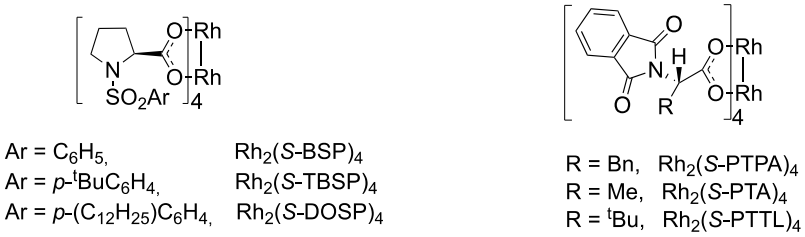
Scheme 18: Types and reactivity of metal carbenes

Over the past few decades, many practical reactions of diazo compounds have been developed, including C–H functionalization, cycloaddition reactions, ylide forming reactions, etc. These reactions can be utilized to rapidly transform simple building blocks into complex natural products and pharmaceutical targets (Scheme **19**).[6, 9, 26]



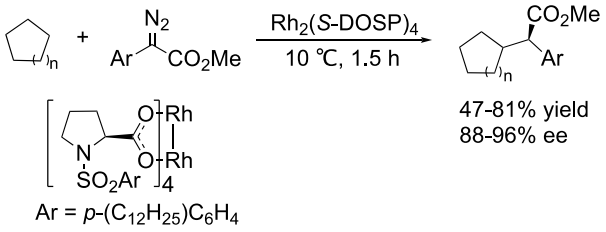
Scheme 19: Typical reactions of metal carbenes

A variety of catalysts have been described for the carbene transfer reaction, many of them consisting of transition metal complexes based on, e.g. Fe, Ru, Rh, Cu, Ag, Au, Co and Zn, and bearing predominantly elaborated ligands.[9, 67, 68] Among them, rhodium complexes, which belong to the most popular catalysts, have been proven to be a powerful and effective class of catalysts for C−C and C−X bond construction. In these rhodium-catalyzed carbene transfer reactions, a Rh-carbene is the key intermediate, which is generated from the interaction between a dirhodium(II) complex and a diazo compound undergoing the loss of dinitrogen.[56, 69-72]



Scheme 20: Typical rhodium(II) catalysts

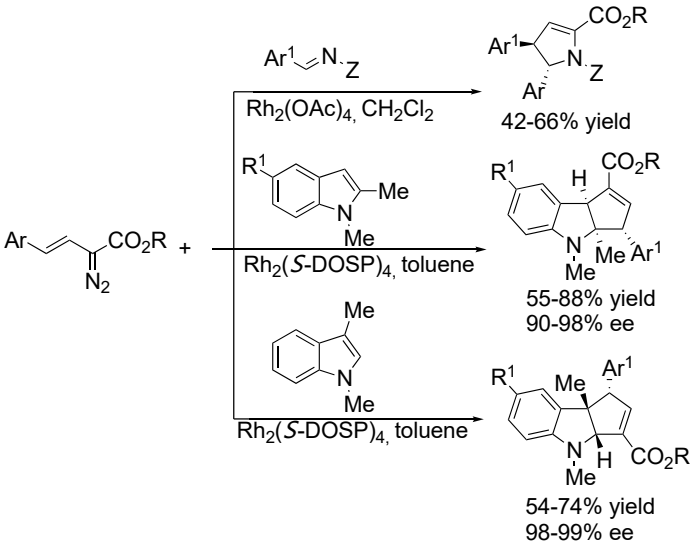
Rhodium(II) acetate derivatives, launched by Teyssie and colleagues,[73, 74] have become ascendant catalysts in the carbene transfer reactions since the 1970s. Various examples of Rh-catalyzed reactions of diazo compounds were reported by Doyle,[75] Davies[76] and other groups. In 1997, Davies and Hansen reported the first example of an asymmetric intermolecular C−H insertion reactions, where they utilized the aryldiazoacetates as the carbene precursor to react with cycloalkane solvents in the presence of Rh_2(*S*-DOSP)$_4$, providing the C−H activation products in 53% to 96% yields and with 60–89% ee.[77] When the reactions were carried out at 10 °C, the enantioselectivity could be dramatically raised to 88–96% ee (Scheme **21**).[78] In 2011, Fox demonstrated rhodium(II)-catalyzed enantioselective C−H functionalization of *N*-protected indoles and ethyl alkyldiazoacetates with Rh_2(*S*-NTTL)$_4$ catalyst in toluene at -78 °C. The chiral 3-alkylated indole derivatives were afforded in 82–96% yields with good to excellent levels of asymmetric induction (79–99% ee).[79]



Scheme 21: Asymmetric intermolecular C-H insertion reactions

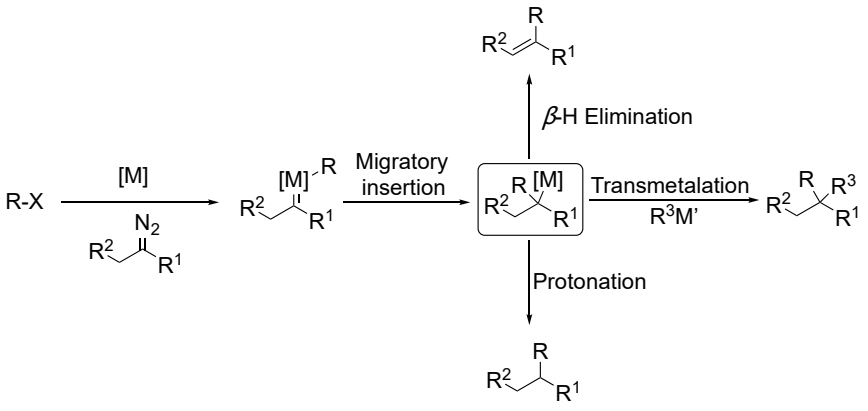
In addition, the Doyle group developed a number of [3+n]-cycloaddition with electrophilic metallo-vinylcarbenes.[76, 80] The metallo-vinylcarbenes were formed by diazoacetates with dirhodium(II) carboxylates. Subsequent cycloaddition reactions were normally characterized by high enantioselectivity. In the presence of Rh_2(*S*-DOSP)$_4$, imines and *N*-methylindole as nucleophiles interacted with vinyl diazoacetates to form dihydropyrroles

and corresponding indolines in good to excellent yields with 42-99% ee. Mechanistic studies showed that 1,2-dimethylindole and 1,3-dimethylindole should react with *s-trans* and *s-cis* styrylcarbene, respectively (Scheme **22**).



Scheme 22: [3+2]-Cycloaddition reactions of imines and indoles with styrydiazoacetates

Transition-metal-catalyzed cross−coupling reactions and ylide formation reactions have been well-established as essential tools in organic synthesis.[66, 81, 82] In 2001, van Vranken and colleagues published the first catalytic cross-coupling procedure that utilized a diazo molecule as the carbene precursor.[83] Subsequently, the transition-metal-catalyzed carbene coupling reactions have been used widely in organic synthesis, in which the diazo compounds as nucleophilic cross-coupling partners in C−C bond or C=C double bond formations have been extensively explored.[58] Rhodium is an effective catalyst in these reactions,[84] which interact with electrophiles or nucleophiles to form organometallic species via various typical processes of cross coupling. This species then reacts with carbene precursor to generate the metal carbene intermediate, which is followed by migratory insertion to produce corresponding C−C or C−X bond formation products (Scheme **23**).



Scheme 23: Carbene-mediated cross-coupling reactions

In addition, ylides can be easily prepared by reacting metal carbenes with heteroatom nucleophiles, based on sulfur, oxygen and nitrogen, and these ylides readily underwent further transformations, including [2,3]-sigmatropic rearrangement. A typical example was an asymmetric trifluoromethylthiolation of donor–acceptor diazo compounds with allyl trifluoromethyl sulfide to produce the SCF_3 -containing compounds in the present of Rh_2(*S*-DOSP)$_4$. This process underwent the enantioselective [2,3]-sigmatropic rearrangement of a sulfonium ylide that was generated from a metal carbene and sulfide.[85]

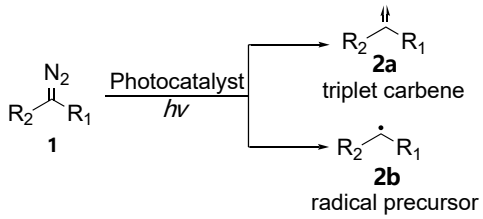
1.2 Research Objective

This thesis mainly focuses on the development of new strategies by using different aspects of carbene transfer reactions. Diazo compounds and *N*-sulfonyl-1,2,3-triazoles were used as the main carbene precursors, and studied in this thesis. Firstly, we promoted the development of rhodium-catalyzed 1,3-difunctionalization reactions of *N*-sulfonyl-1,2,3-triazoles with different substrates. For example, the rhodium-catalyzed enamine homologation reactions of triazoles with cyclopropylmethyl sulfides. Secondly, we further studied the metal-free photoinduced carbene transfer reaction, which was [2,3]-sigmatropic rearrangement reactions of ammonium ylides under blue light irradiation. Furthermore, in the field of photocatalysis, we carefully investigated the *gem*-difluoroolefination reactions with diazoacetates in the presence of photoredox catalysts. The control experiments and theoretical mechanistic studies proved that a tertiary amine takes up an important role in this photoredox reaction.

2. Photocatalytic C–C Bond Formation Reactions with Diazoalkanes

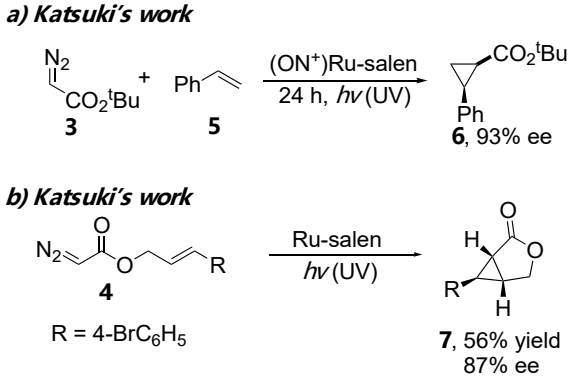
2.1 Brief Introduction: Photocatalytic reactions with diazoacetates

Diazo compounds are among the most important building blocks in organic synthesis due to their high reactivity and diverse applications. Traditionally, they likely form metal carbene intermediates with different transition metal catalysts and undergo various transformations, such as, C–H insertion, X–H insertion, cycloaddition, cyclopropanation, etc.[26, 65, 68] In recent years, photocatalysis has emerged as an important part of organic chemistry to leverage the synthesis of small molecules, which has also been applied for the decomposition and conversion of diazo compounds. In the presence of photocatalysts, diazo compounds can be used to generate new C–C and C–X bonds and undergo triplet carbenes or free radical reactions (Scheme **24**).



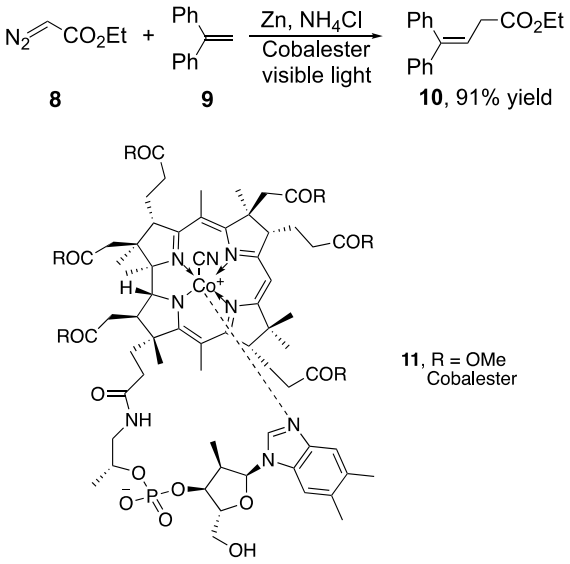
Scheme 24: Photocatalytic reactions with diazo compound

In 2000, the Katsuki group reported an example of chiral (ON^+)Ru-salen complex that catalyzed the asymmetric cyclopropanation of styrenes with α-diazoacetate under UV light irradiation. This catalyst has a vacant coordination site on the ruthenium ion that can be used to bind a diazo compound, which can achieve highly enantioselective cyclopropanation. However, The scope of the reaction is limited, and the mechanism of stereoselectivity by the (ON^+)Ru-salen complex remains unknown.[86] In 2001, Katsuki further proved that Ru-salen complexes as good catalysts can be used in asymmetric cyclopropanation reactions when exposed to light, they used *trans*-substituted allyl α-diazoacetate to achieve the intramolecular asymmetric cyclopropanation (Scheme **25**).[87]



Scheme 25: Asymmetric cyclopropanation reactions

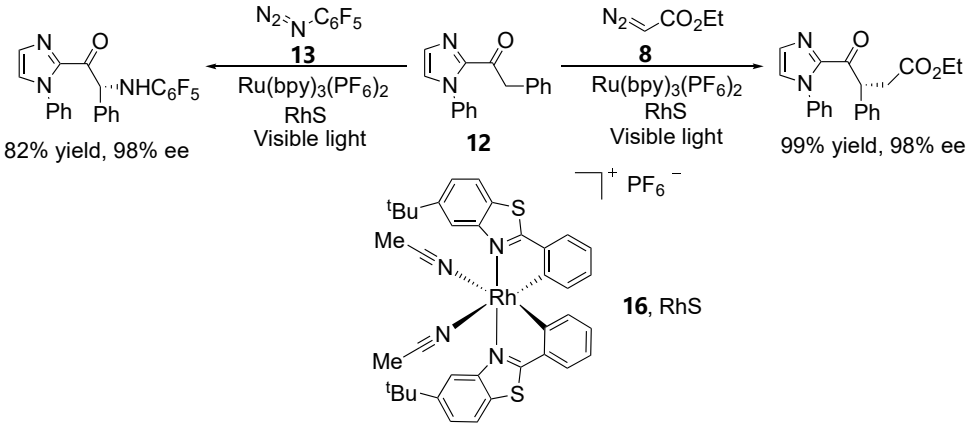
With the development of the theory about photocatalysis, a wide range of photocatalysts have been applied to the reactions of diazo compounds, which can convert diazo compounds into radical intermediates. The photocatalytic strategy, compared to previous carbene chemistry, opens up a new area. In 2004, Zhang and co-workers reported that vitamin B_{12} derivatives catalyzed asymmetric cyclopropanation of alkenes with ethyl diazoacetate (EDA) at the 80 °C.[88] Compared to this traditional thermal method, in 2016, Gryko described a cobalester-catalyzed C–H insertion reaction with ethyl diazoacetate (EDA) in the presence of LED light.[89] This work was likely to proceed *via* a radical pathway involving an ester radical species. Finally, C–C bond-formation underwent the radical addition to the electron-rich olefin (Scheme **26**).



Scheme 26: C–H functionalization of olefins with diazo esters

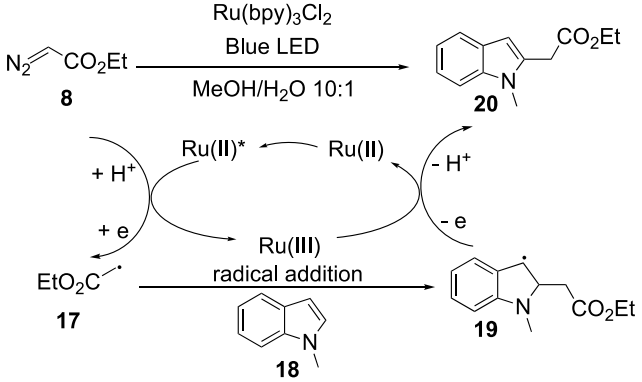
In the same year, the Meggers group published the first report on asymmetric amination and alkylation under photoredox conditions using aryl azides and *α*-diazo carboxylic esters as substrates. Up to 99% yield and 99.6% ee were obtained. In this case, the reaction underwent multiple catalytic cycles: photoredox and asymmetric catalytic cycles. Here, a rhodium-based Lewis acid was the chiral catalyst, and $Ru(bpy)_3(PF_6)_2$ acted as the

photoredox sensitizer. Same as in previous works, the diazoesters can react in a radical fashion (Scheme **27**).[52]



Scheme 27: Visible-light-activated asymmetric alkylation/amination of ketones

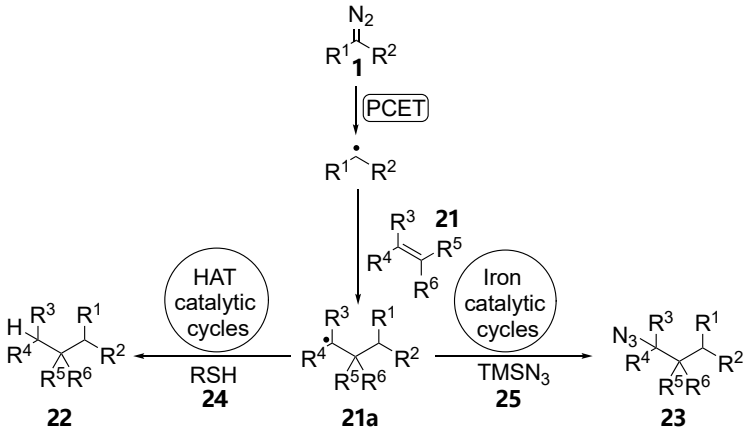
To investigate how the use of photoredox catalysts affects the reactivity of diazo reagents towards electron-rich heteroarenes, Gryko and co-workers reported an example of visible light induced C2 alkylation of indoles and pyrroles with diazo esters in 2019. This new photocatalytic method could realize a radical pathway instead of a classic carbene intermediate. After careful mechanistic research, a possible mechanism was proposed by the Gryko group: in the presence of protic solvents and photocatalyst, the ester radical species was generated and underwent radical addition with indoles to form the radical intermediate. After oxidation with $Ru(bpy)_3^{3+}$ and deprotonation, the desired alkylated product was obtained (Scheme **28**).[53]



Scheme 28: Photocatalytic alkylation of indoles with *α*-diazo esters

With the report of the carbon-centered radicals from diazo compounds in the presence of photoredox sensitizer, several research groups have focused on these special reactions of diazo compounds. In 2020, different from the two-component addition of alkenes with diazo compounds, Doyle and co-workers carefully investigated a novel strategy of diazo compounds that utilized a radical-mediated addition method to achieve difunctionalization of diverse alkenes. Under the photocatalytic condition, diazo compounds are converted to carbon-centered radicals via a proton-coupled electron transfer (PCET) processes, after

which the radical can add to a variety of alkenes with high regioselectivity. Finally, the products are generated through either hydrogen atom transfer (HAT) with a thiol catalyst or a radical trapping process with an iron catalyst. Furthermore, these novel strategies open new opportunities for addition reactions using diazo compounds (Scheme **29**).[54]



Scheme 29: Difunctionalization of alkenes with diazo compound

2.2 Photocatalytic *gem*-difluoroolefination reactions with diazoacetates

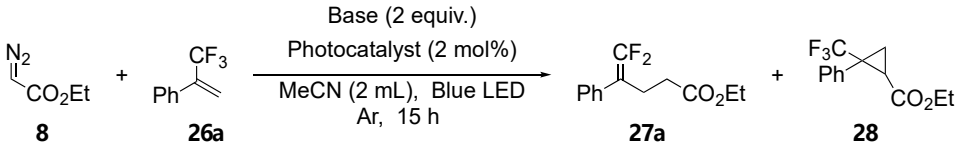
Inspired by these previous reports, we attempted the reactions of *α*-trifluoromethyl styrenes as radical acceptors with diazoalkanes, which could form the desired *gem*-difluoro olefin products in the presence of photoredox catalyst through multiple photocatalytic cycles.

We started our investigations by studying the reaction of *α*-trifluoromethyl styrenes **26a** with ethyl diazoacetate **8** using different photoredox catalysts under visible light irradiation. The screening of $(Ir[dF(CF_3)ppy]_2(bpy))PF_6$, $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$, $Ir(ppy)_3$, 4CzIPN, Rose Bengal, Eosin Y, and $Ru(bpy)_3Cl_2\ 6H_2O$ revealed that only $(Ir[dF(CF_3)ppy]_2(bpy))PF_6$ and $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ can afford the desired *gem*-difluoro olefin **27a** in the good yields (Table **1**, entry 1-7). To our delight, $(Ir[dF(CF_3)ppy]_2(bpy))PF_6$ was found to be the optimal candidate with 83% isolated yield of **27a** and 6 % cyclopropane **28** (Table **1**, entry 7)**.** Different bases were also tested (Table **1**, entry 8-13) including different inorganic or organic bases. When $KHCO_3$ or Cs_2CO_3 was used in this reaction, the cyclopropane was formed in high yield, yet the desired *gem*-difluoroolefin **27a** was not formed (Table **1**, entry 8-9). Whereas the use of other organic bases such as Et_3N, DIPEA and Piperazine resulted in a considerable increase of *gem*-difluoroolefin **27a** in the yield (Table **1**, entry 10-13). When using DABCO, the *gem*-difluoroolefin product **27a** was obtained in 83% yield, and a trace amount of cyclopropane **28** was obtained (Table **1**, entry 7).

Next, various solvents were investigated, including THF, DCM, 1,4-Dioxane and DMSO. The results revealed that the *gem*-difluoro product **27a** could be obtained in high yield only in MeCN. Other solvents proved far less efficient (Table **2**, entry 1-6). Next, we studied the stoichiometry of our reaction. When 1 equiv. *α*-trifluoromethyl styrene **26a,** and 2 equiv.

ethyl diazoacetate **8** were added in MeCN solvent under blue LED irradiation, the yield could be improved to 83%.

Table 1: Optimization of *gem*-difluoroolefination with ethyl diazoacetate



8 **26a** **27a** **28**

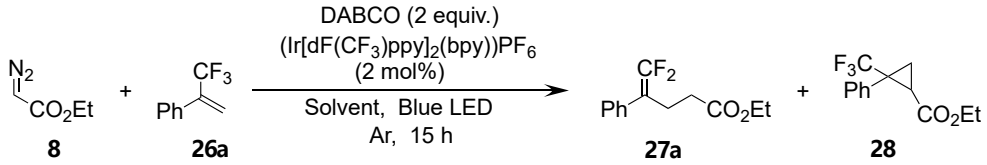
Entry[a]	photo cat.	Base	Solvent	Yield 27a (%)[b]	Yield 28 (%)[b]
1	4-CzIPN	DABCO	MeCN	28	trace
2	$Ir(ppy)_3$	DABCO	MeCN	trace	26
3	Rose Bengal	DABCO	MeCN	7	5
4	EosinY	DABCO	MeCN	trace	trace
5	$Ru(bpy)_3Cl_2$	DABCO	MeCN	trace	trace
6	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	DABCO	MeCN	53	12
7	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	DABCO	MeCN	83	6
8	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	$KHCO_3$	MeCN	trace	90
9	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	Cs_2CO_3	MeCN	trace	18
10	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	DBU	MeCN	15	trace
11	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	Et_3N	MeCN	50	trace
12	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	DIPEA	MeCN	70	trace
13	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	Piperazine	MeCN	50	21

[a]Reaction conditions: reactions were carried out (**8**/**26a**/photocat./base = 0.4/0.2/0.004/0.4 mmol) in 2.0 mL MeCN under argon at 25 °C under blue light (25 W). [b]Yields of **27a** and **28** were determined by ^1H NMR spectroscopic analyses of the reaction mixture using 4-fluorotoluene as the internal standard.

However, the further change of the equivalent of *α*-trifluoromethyl styrene **26a** or ethyl diazoacetate **8** could not provide better results (Table **2**, entry 7-10). Moreover, we improved the amount of DABCO to 1.0 or 5.0 equivalent and just obtained the desired product **27a** in moderate yield (Table **2**, entry 11-13).

To further improve the yield, we screened different concentrations of the reaction mixture. Gratifyingly, we observed that when the reaction was carried out in 2 mL of MeCN, the desired *gem*-difluoro product **27a** formed in excellent yield, and other reaction concentrations provided unsatisfying results (Table **3**, entry 1-3). At the same time, in order to inspect the necessity of each reaction parameter, several control experiments were conducted. No corresponding *gem*-difluoroolefin product **27a** was formed when the blue LED was removed at room temperature (Table **3**, entry 7). In the absence of DABCO, we just observed the cyclopropane **28** in the high yield, which proved the importance of tertiary amine base (Table **3**, entry 5). Removal of photocatalyst suppresses the *gem*-difluoroolefination reaction (Table **3**, entry 4). When the reaction was conducted in air, the desired product **27a** was obtained in moderate yield. This showed that air has a detrimental effect on this reaction (Table **3**, entry 6). Thus, we obtained the optimal condition, $(Ir[dF(CF_3)ppy]_2(bpy))PF_6$ as the photoredox catalyst, DABCO as base and MeCN as solvent under blue LED irradiation to yield the *gem*-difluoroolefin product **27a** with good efficiency.

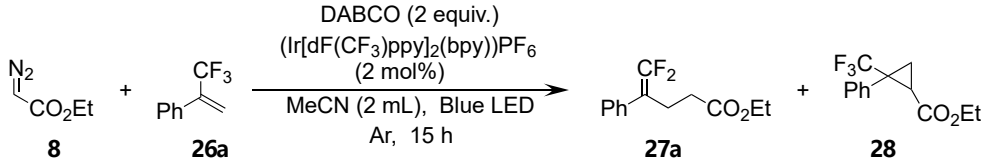
Table 2: Optimization of *gem*-difluoroolefination with ethyl diazoacetate



Entry[a]	photo cat.	8/26a/DABCO	Solvent	Yield 27a (%)[b]	Yield 28 (%)[b]
1	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	2/1/2	MeCN	83	6
2	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	2/1/2	THF	13	trace
3	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	2/1/2	DCM	7	39
4	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	2/1/2	Dioxane	10	trace
5	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	2/1/2	acetone	12	15
6	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	2/1/2	DMSO	34	trace
7	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	3/1/2	MeCN	51	20
8	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	1/1/2	MeCN	29	10
9	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	1/2/2	MeCN	22	25
10	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	1/3/2	MeCN	19	25
11	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	2/1/1	MeCN	31	40
12	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	2/1/3	MeCN	65	14
13	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	2/1/5	MeCN	40	7

[a]Reaction conditions: reactions were carried out in 2.0 mL solvent under argon at 25 °C under blue light (25 W). [b]Yields of **27a** and **28** were determined by ^{1}H NMR spectroscopic analyses of the reaction mixture using 4-fluorotoluene as the internal standard.

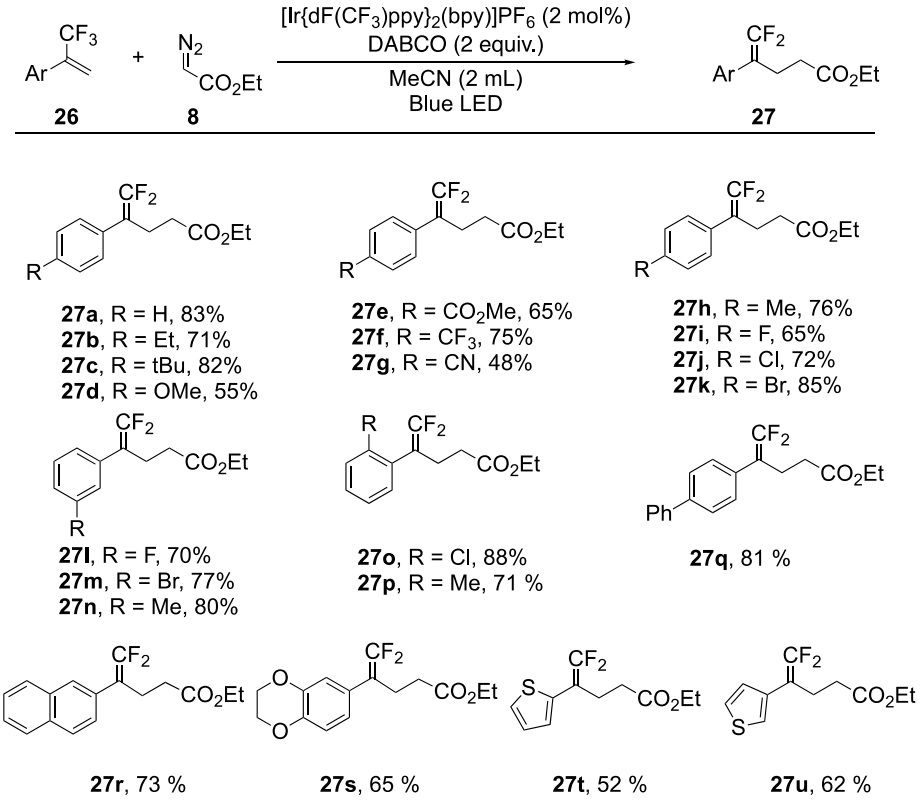
Table 3: Optimization of *gem*-difluoroolefination with ethyl diazoacetate



Entry[a]	photo cat.	Concentration(M)	Solvent	Yield 27a (%)[b]	Yield 28 (%)[b]
1	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	0.05	MeCN	50	17
2	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	0.1	MeCN	83	6
3	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	0.2	MeCN	33	16
4	No photocatalyst	0.1	MeCN	ND	ND
5[c]	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	0.1	MeCN	trace	95
6[d]	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	0.1	MeCN	55	9
7[e]	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	0.1	MeCN	NR	NR

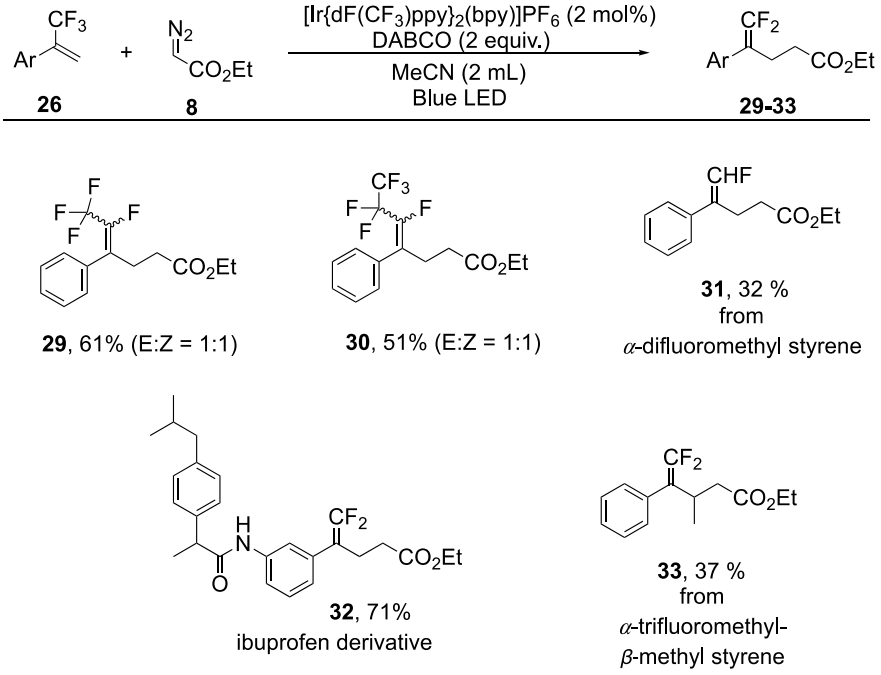
[a]Reaction conditions: reactions were carried out (**8**/**26a**/photocat./base = 0.4/0.2/0.004/0.4 mmol) in MeCN under argon at 25 °C under blue light (25 W). [b]Yields of **27a** and **28** were determined by ^{1}H NMR spectroscopic analyses of the reaction mixture using 4-fluorotoluene as the internal standard. [c]No DABCO. [d]In the air atmosphere. [e]No light. NR = no reaction. ND = not detected.

With the optimal reaction conditions in hand, we next started to investigate the scope of these reactions. First, we studied the scope of the different substitution patterns of the *α*-trifluoromethyl (Scheme **31**). To our delight, the *α*-trifluoromethyl styrene containing either an electron-donating or an electron-withdrawing groups at the *para*-, *meta*- or *ortho*-position of the phenyl ring were well tolerated, including halogens, giving the corresponding *gem*-difluoroolefin products (**27a**–**27p**) in moderate yield to good yields. Next, the naphthalene- or biphenyl-derived *α*-trifluoromethyl styrenes were also investigated, which could undergo desired *gem*-difluoroolefination reaction smoothly to give the desired products (Scheme **31**, **27q**–**27r**) in good yields. Further, the heterocyclic *α*-trifluoromethyl styrenes such as 1,4-benzodioxane and thiophene were also compatible, providing moderate yields of the corresponding products **27s**–**27u** (52–65%).



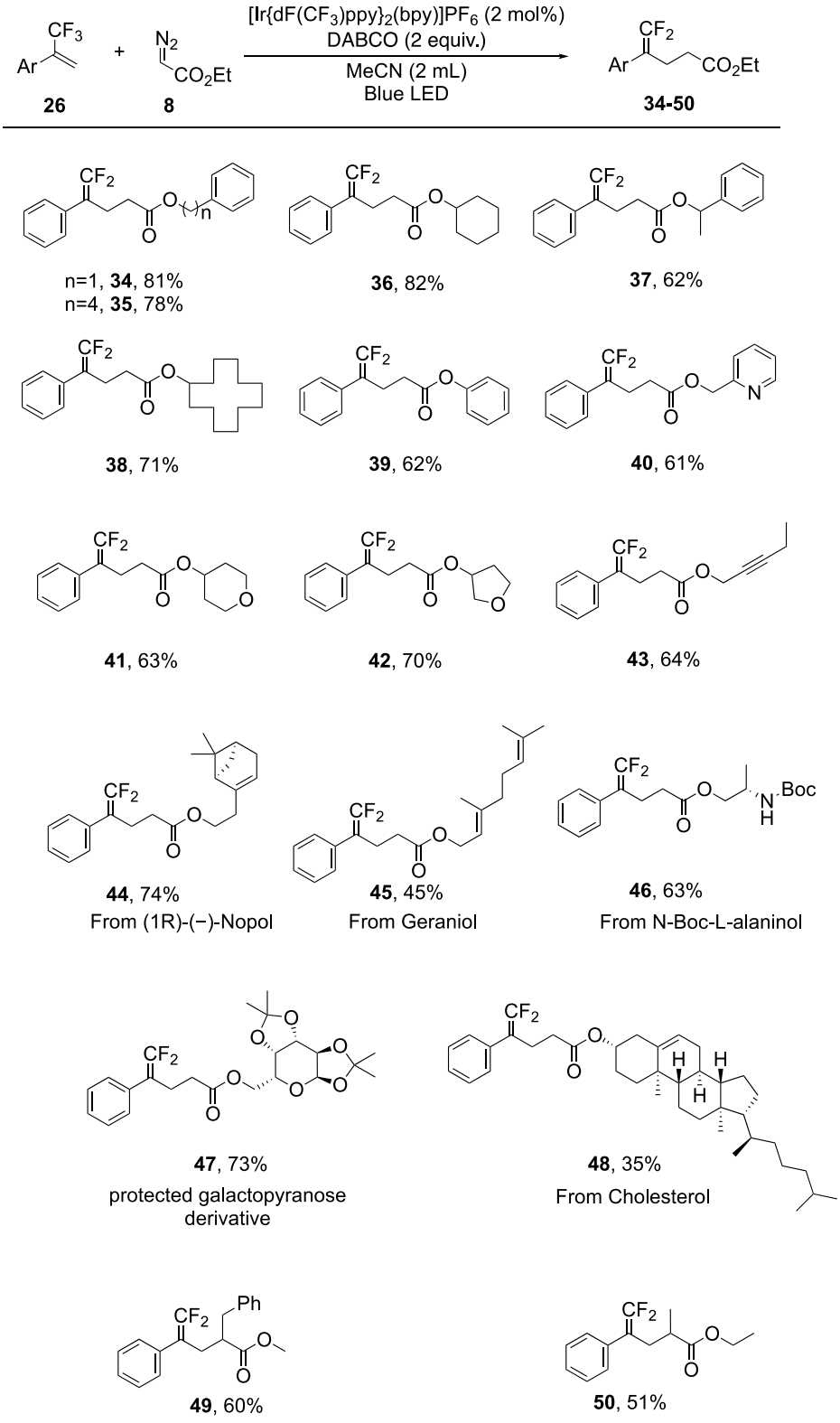
Scheme 31: Substrate scopes of different *α*-trifluoromethyl styrenes

Next, different *α*-perfluorinated styrenes were also explored, in this case, perfluorinated styrenes smoothly reacted with ethyl diazoacetate could under the optimal reaction conditions and the corresponding 1-perfluoroalkyl-1-fluoro olefins products could be isolated with moderate efficiency (Scheme **32**, **29**–**30**). We further studied the *α*-difluoromethyl styrene and *α* -trifluoromethyl-*β*-methyl styrene, and to our delight, both styrenes also were well tolerated in this *gem*-difluoroolefination reaction, and a moderate yield of the corresponding products was obtained (Scheme **32**, **31, 33**). An important result of the reaction of *α* -difluoromethyl styrene was the formation of an alkenyl fluoride **31** and no *gem*-difluoroolefin product was observed. Later, the ibuprofen-derived styrene was also employed, giving the corresponding products (Scheme **32**, **32**) in 71% yield.



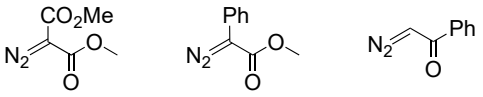
Scheme 32: Substrate scopes of different *α*-trifluoromethyl styrenes

Next, we further assessed the generality of diazo compounds, in this part, we investigated the reaction of *α*-trifluoromethyl styrene with various diazoacetates in the presence of a photocatalyst. First, different primary, secondary esters reacted smoothly to deliver the desired *gem*-difluoroolefin products in moderate to good yields (Scheme **33**, **34**–**39**), such as the 1-phenylethanol, cyclohexanol and phenylmethanol. A diverse array of heterocyclic diazo compounds (e.g., pyran, pyridine and furan) were fully compatible with the present protocol, providing the corresponding products in 61−70% yields (Scheme **33**, **40**–**42**). Furthermore, even the diazoacetate including a triple bonds also reacted well under the same reaction conditions, the *gem*-difluoroolefin product was formed in 64% yield (Scheme **33**, **43**). In addition, it is worth noting that this strategy was successful with various biologically relevant alcohol-derived diazoacetates. The derivative (-)-Nopol or Geraniol was well-tolerated. Similarly, the galactopyranose, N-Boc-L-alanine derivatives or cholesterol derivative also worked, providing the desired products in moderate to good yields (Scheme **33**, **46**–**48**). We then studied various other diazoalkanes in detail. An array of donor/acceptor disubstituted diazo compounds were also suitable with this protocol, affording the desired products in good yields (Scheme **33**, **49**–**50**).



Scheme 33: Substrate scopes of different diazoacetates

The aromatic donor/acceptor diazoalkanes **52**, acceptor-acceptor diazoalkanes **51**, and diazoketones **53** were also investigated, yet the product of *gem*-difluoroolefination could not be obtained in this case and only the decomposition of the diazoalkane was found (Scheme **34**).



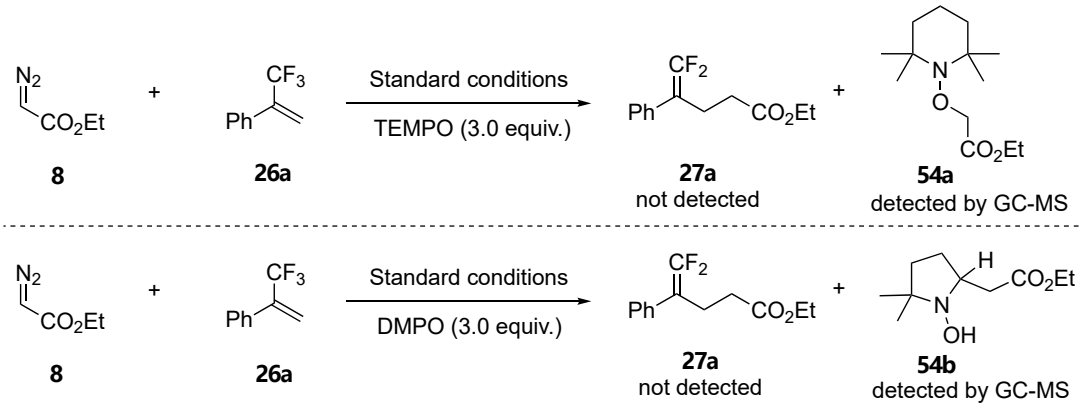
51 **52** **53**

Scheme 34: Substrate scopes of different unreactive diazoacetates

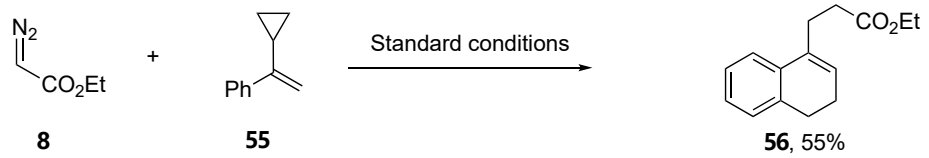
After finishing the optimization and substrate scope, we next started studying the mechanism. A series of control experiments were performed. First, related radical control experiments were conducted. When the radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was added to the reaction, we found that the reaction was completely inhibited, and the *gem*-difluoroolefin product **27a** was not found. At the same time, the radical trapping products **54a** could be observed by GCMS. Similarly, when another radical scavenger 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was added to the model reaction, the reaction was also terminated, and radical-trapping product **54b** was confirmed through GCMS, which indicated the intermediate with unpaired electrons was formed (Scheme **35**).

To further prove the radical mechanism, a radical clock experiment was studied with *α*-cyclopropyl-styrene **55**, and a 55% yield of the ring opening product **56** was obtained after chromatography (Scheme **35b**). The radical mechanism was further supported by this observation.

a) radical trapping experiments



b) radical clocks experiment

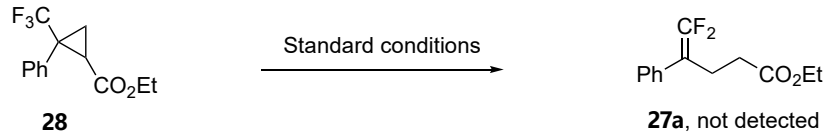


Scheme 35: Radical control experiments

In order to gain further mechanistic information about these *gem*-difluoroolefination reactions, potential ring opening reaction experiments were investigated. Trifluoromethylated cyclopropane **28** was used as substrate under the standard reaction conditions, as a result, *gem*-difluoroolefin **27a** was not generated in the reaction and **28** remained the same, disproving that *gem*-difluoroefination proceeds via cyclopropane

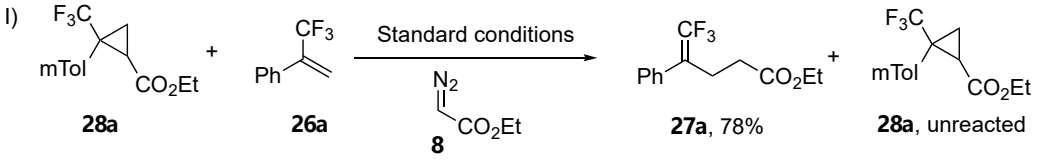
intermediates (Scheme **36a**). Next, under the present reaction conditions, a set of crossover experiments in the presence of pre-synthesized trifluoromethyl substituted cyclopropane revealed that no scrambling in the reaction product and at the same time cyclopropane remained unreacted. Thus, based on these results we can rule out the intermediate formation of cyclopropane **28** (Scheme **36b**).

a) studying the ring-opening of the cyclopropane

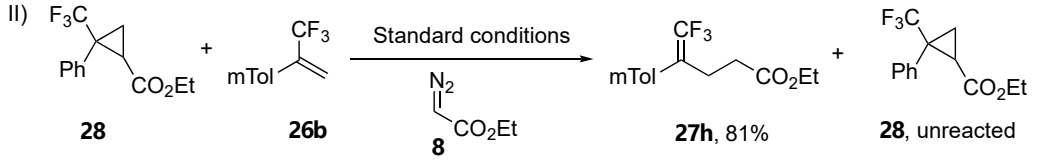


28 **27a**, not detected

b) cross-over experiments



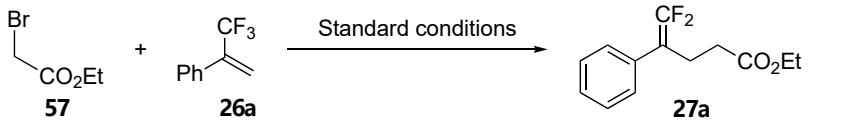
28a **26a** **8** **27a**, 78% **28a**, unreacted



28 **26b** **8** **27h**, 81% **28**, unreacted

Scheme 36: Potential cyclopropane ring opening experiment

After getting the insight into the first step, we next aimed at investigating the alternative radical sources. Under photoredox conditions, 2-bromo ethyl acetate **57** can easily undergo debromination and form a carbon-centered radical, but no *gem*-difluoroolefin product **27a** was detected in the absence of reductive quencher. Yet when 2 equiv. DABCO or Hantzsch ester **58** was added to these reactions under standard conditions, trace amount of *gem*-difluoro olefin **27a** could be observed. The result showed that the direct addition of a carbon-centered radical to α-trifluoromethyl styrene seems improbable. Therefore, as can be seen above, the *gem*-difluoroolefination reaction involves intermediates with unpaired electrons (Scheme **37**).



57 **26a** **27a**

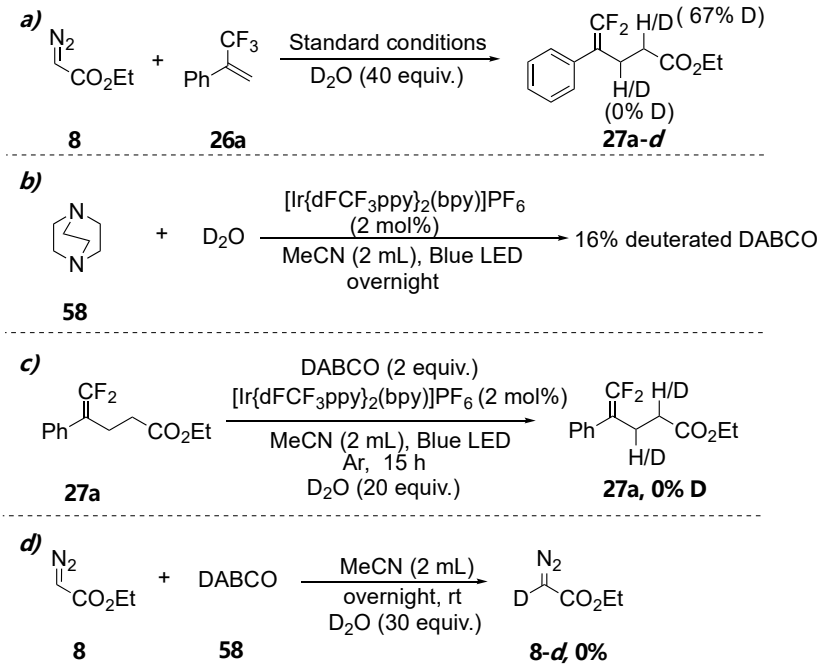
with 2 equiv. DABCO: traces
with 2 equiv. **58**: traces
without quencher: not detected

58 = Di-(tert.-butyl) 1,4-dihydro-2,6-dimethyl-3,5-pyridine-dicarboxylate.

Scheme 37: Experiments involving alternative radical sources

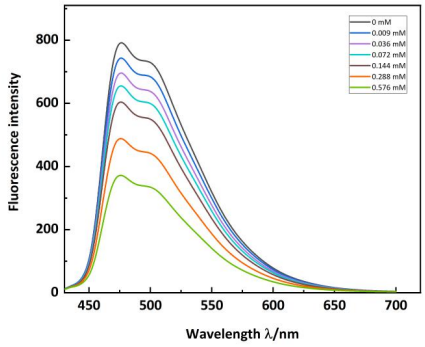
We further examined the isotopic-labeling experiments, which explored the hydrogen source of the product. First, we studied the model *gem*-difluoroolefination reaction in the presence of 40 equiv.D_2O, and 67% deuterium label was detected in the α-position to the

carbonyl group of *gem*-difluoroolefin **27a**. Next, In the presence of photocatalyst and D_2O, we investigated a potential deuteration of DABCO, and 16% DABCO of deuterium was found, which indicated reductive quenching of DABCO and subsequent proton/deuterium exchange reactions through a putative radical cation of DABCO. Furthermore, the *gem*-difluoroolefin was investigated under standard reaction conditions with 20 equiv. D_2O. The result showed no deuterium was incorporated. Finally, under catalyst-free conditions, we explored the potential proton exchange reaction between DABCO, EDA and D_2O, however, the deuterated product was not found. As can be seen above, in the photocatalytic reaction system the deuterium label is incorporated (Scheme **38**).

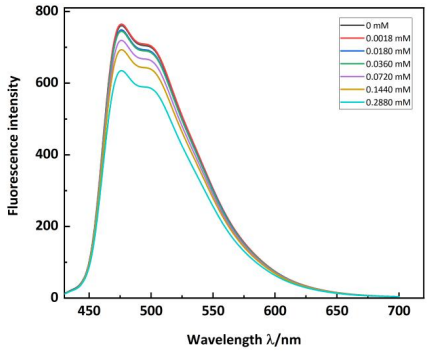


Scheme 38: Isotopic-labeling experiments

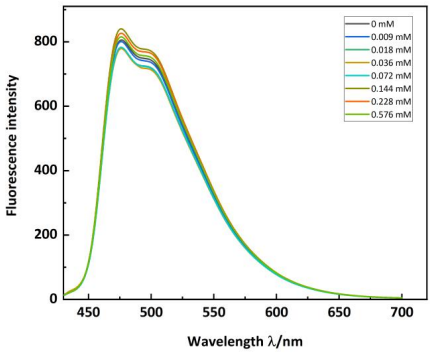
To gain further insight into the mechanism of *gem*-difluoroolefination reactions, Stern-Volmer experiments were performed. The fluorescence quenching experiment showed that the excited-state photocatalyst was quenched by the DABCO and EDA. The fluorescence quenching constant of DABCO was $k_q = 8.2 \times 10^8\ M^{-1}\ s^{-1}$; and k_q for EDA was $3.0 \times 10^8\ M^{-1}\ s^{-1}$. However, no quenching was detected in the presence of trifluoromethyl styrene **26a**. This result further supports the single electron transfer (SET) step between the excited-state photocatalyst and DABCO (Scheme **39**).



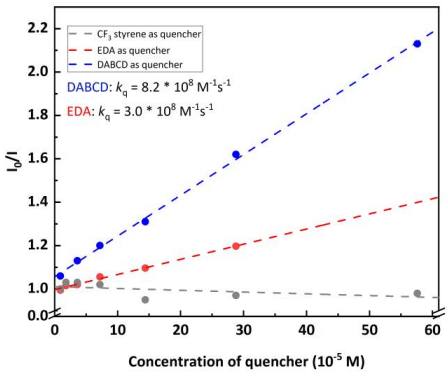
i) Fluorescence quenching of DABCO



ii) Fluorescence quenching of EDA



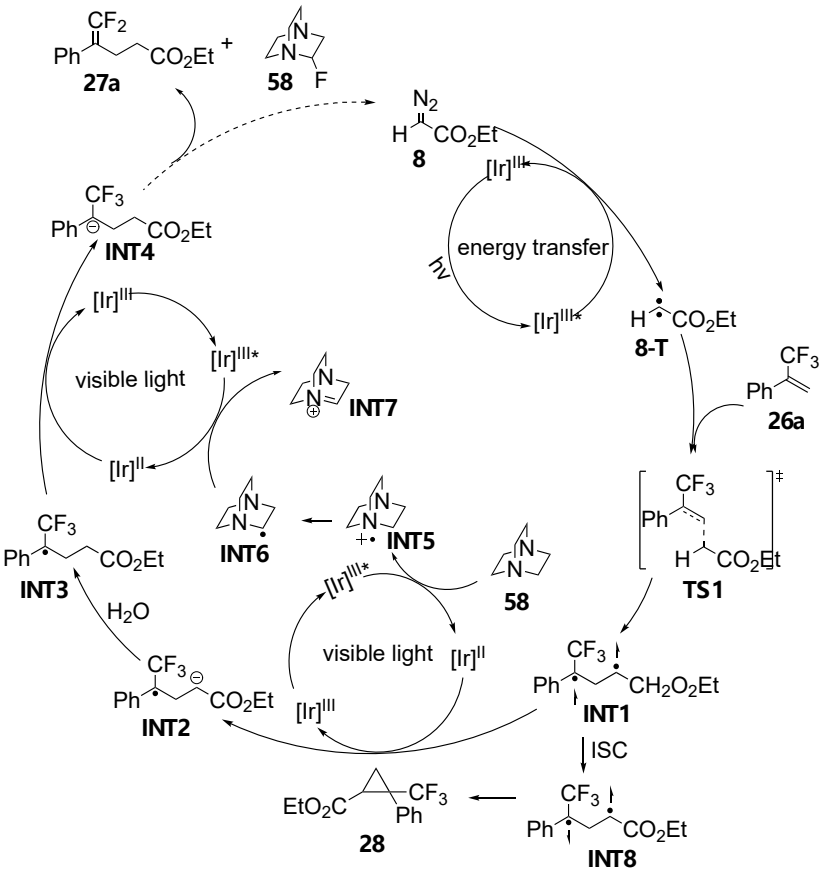
iii) Fluorescence quenching of *a*-CF_3 styrene



iv) Stern-Volmer plot of [Ir] photocatalyst

Scheme 39: Stern Volmer plots experiments

Based on the above control experiments and DFT calculations, we proposed the following possible mechanism (Scheme **40**): First, in the presence of $(Ir[dF(CF_3)ppy]_2(bpy))PF_6$, triplet carbene intermediate **8-T** was formed undergoing the energy transfer process, which conducted radical addition to the *α*-trifluoromethyl alkene to form the CF_3-triplet intermediate **INT1**. Next, the reductive quencher DABCO had participated in the second photocatalytic cycle. The photoexcited $*[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$[$E_{1/2}^{red}$ ($*Ir^{III}/Ir^{II}$) = +1.32 V vs SCE][90] through a single electron transfer (SET) was quenched by DABCO ($E_{1/2}^{ox}$ = +0.69 V vs SCE)[91] to form DABCO+ radical and an Ir^{II} species. At this stage, Ir^{II} reduced this CF_3-triplet intermediate **INT1**, affording the radical anion **INT2** intermediate. Cyclopropane **28** will receive in the absence of DABCO yet. Subsequently, passing a protonation process in the presence of water molecules, the radical intermediate **INT3** was formed. In the last photocatalytic cycle, the DABCO radical **INT6** was oxidized by photoexcited $*Ir^{III}$ to generate the iminium ion **INT7** and Ir^{II} species, then this species reduced the intermediate **INT3 to** carbanion intermediate **INT4.** Finally, a *β*-fluoride elimination reaction of intermediate **INT4** afforded the *gem*-difluoroolefin product. At this step, the iminiumion **INT7** promoted the ultimate defluorination step to yield **58** as by-product.



Scheme 40: Proposed mechanism

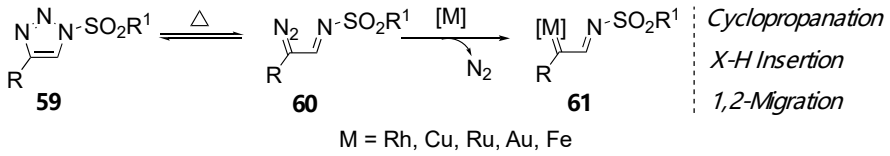
2.3 Conclusion

In summary, in this chapter, we reported a photocatalytic protocol to realize *gem*-difluoroolefination reactions with *α*-trifluoromethyl styrenes and diazoacetates. In this reaction, a triplet carbene was formed, which undergoes energy transfer in the presence of the photocatalyst. The tertiary amine acted as an important role to enable this unusual reaction pathway and avoided forming undesired cyclopropanation product. Various simple olefins, heterocyclic olefins and diazoacetates were employed in good to excellent yields. Several experimental and theoretical studies have been performed to support the proposed mechanism for this *gem*-difluorolefination reaction.

3. Transition-metal Catalyzed Reactions of *N*-Sulfonyl-1,2,3-triazoles

3.1 Brief Introduction: Reactions of *N*-sulfonyl-1,2,3-triazoles

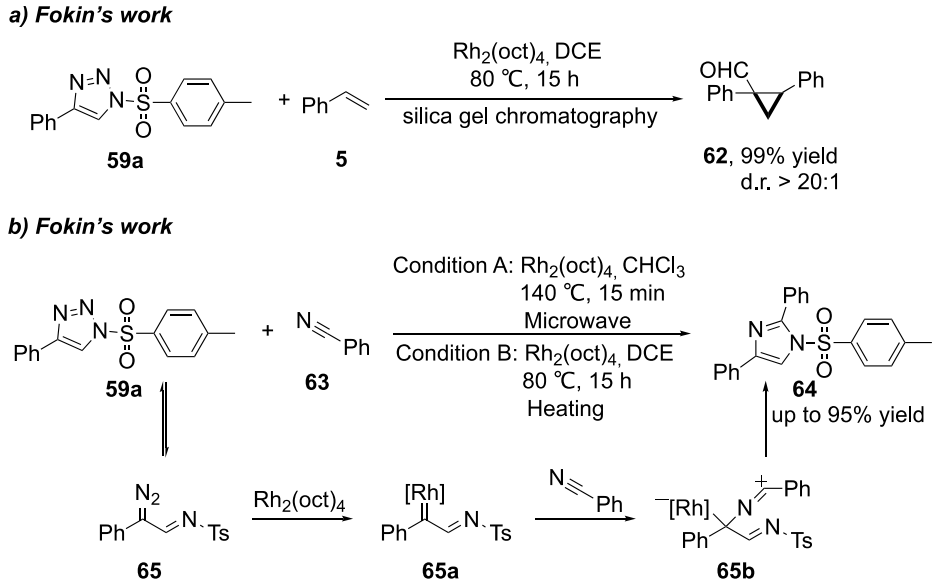
N-sulfonyl-1,2,3-triazoles are an important class of carbene precursors, which have attracted much attention in the synthetic community as safe alternatives to access carbene intermediates.[92] They can be easily prepared by copper[93, 94] or ruthenium-catalyzed[95-97] azide-alkyne cycloaddition reactions. These triazoles can easily undergo ring-opening to generate diazo imines **60** and in turn, be converted into α-imino metal carbenes **61** in the presence of metal catalysts, which then undergo a wide range of typical carbene transfer reactions, such as C−H, O−H or N−H insertion, cyclopropanation, 1,2-shifts and other types of carbene transfer reactions (Scheme **41**).[98-101]



Scheme 41: The formation of imino metal carbenes

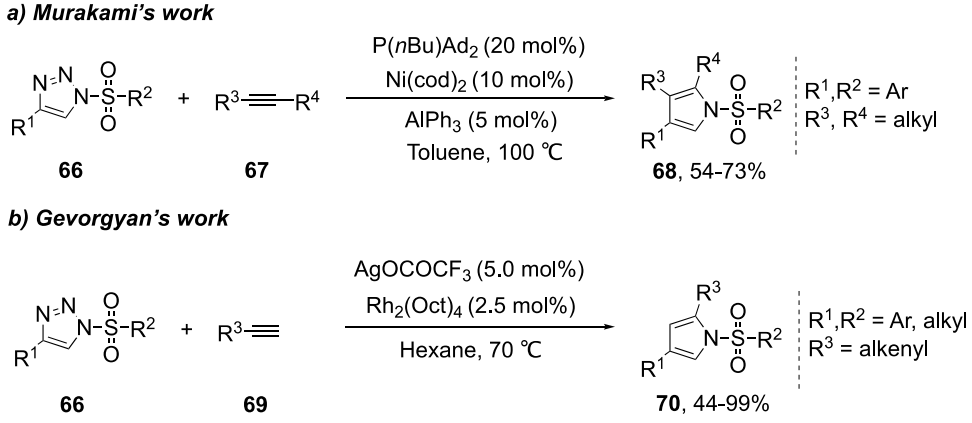
Compared to traditional donor/acceptor carbenes, this α-imino metal carbene has a distinctive feature, which includes a pendant sulfonyl-protected imine group, and the nitrogen atom exhibits a high nucleophilicity. Because of its increased nucleophilicity, the α-imino group has the ability to allow transannulation reaction with many other compounds, such as nitriles, alkynes, allenes and others, to produce various useful heterocycles.[10]

In 2008, the Fokin and Gevorgyan group reported on the carbene transfer reactions of *N*-sulfonyl-1,2,3-triazoles **59a** in the presence of a rhodium(II) catalyst. The triazole reacted with styrene to quantitatively produce the *trans*-cyclopropane carboxaldehyde **62** after silica gel chromatography (Scheme **42a**).[102] Inspired by this discovery, these groups carefully investigated transannulation reactions of the *N*-sulfonyl-1,2,3-triazoles **59a** with benzonitrile and obtained the corresponding imidazole products in up to 94% yield. In this case, the triazole was converted to a diazoimine species **65,** which in turn converted into the corresponding metal carbenoid **65a** in the presence of $Rh_2(Oct)_4$. Following [3+2] cyclization with styrene to form the zwitterion **65b**, which then smoothly converted into substituted imidazole **64** in high yield (Scheme **42b**).



Scheme 42: Transannulation of *N*-sulfonyl-1,2,3-triazole with styrene or benzonitrile

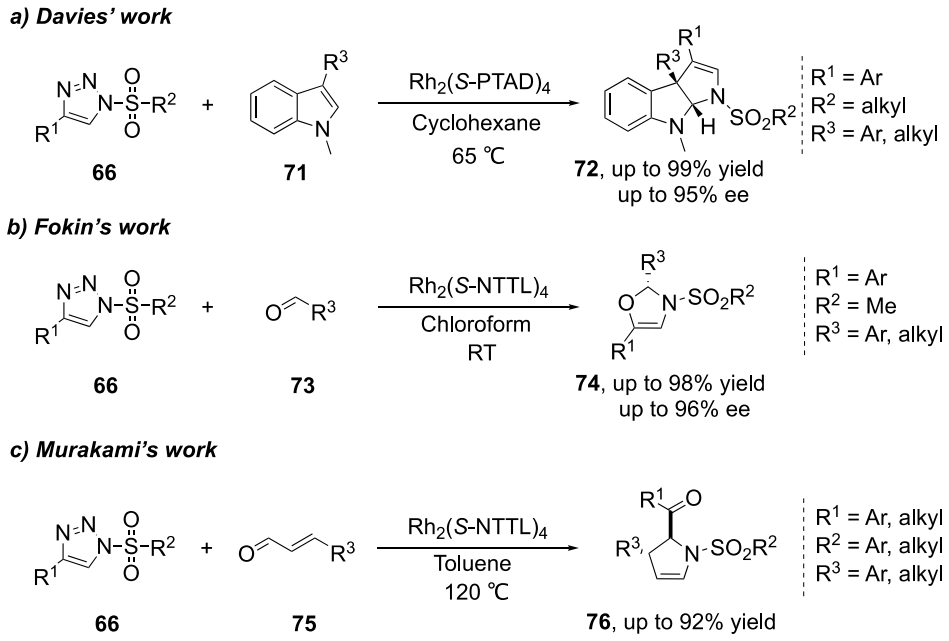
Shortly thereafter, Murakami and co-workers reported nickel-catalyzed transannulations of *N*-sulfonyl-1,2,3-triazoles with internal alkynes to synthesize various tetrasubstituted pyrroles in moderate yields in 2009.[103] In this reaction, they found that the transannulation of triazoles could be efficiently conducted by the combination of $Ni(cod)_2$ catalyst, phosphine ligand $P(nBu)Ad_2$ and $AlPh_3$, among them, the $AlPh_3$ as a Lewis acid additive. However, the reactions were not successful when the terminal alkynes were used. In 2011, Gevorgyan and co-workers overcame this challenge.[104] They disclosed a binary catalyst system approach, in which $[Rh_2(Oct)_4]$ and $AgOCOCF_3$ were employed as catalysts. With this catalyst system, *N*-sulfonyl-1,2,3-triazoles **66** worked with electron-rich terminal alkynes to afford the corresponding pyrrole products **70** in good to excellent yields. However, electron-poor terminal alkynes did not undergo this transformation (Scheme **43**).



Scheme 43: Transannulation of *N*-sulfonyl-1,2,3-triazole with alkynes

Following that, several new transannulation reactions were further disclosed. Particularly enantioselective cycloaddition reactions have been reported, which increased the diversity of transformations of *N*-sulfonyl-1,2,3-triazoles. In 2013, the Davies group uncovered an enantioselective formal [3+2] cycloaddition of *N*-sulfonyl-1,2,3-triazoles with C-3

substituted indoles, which underwent a rhodium(II)-catalyzed process to form pyrroloindolines **72**. The reaction scope was broad, and various triazoles and substituted indoles participated in this reaction, providing good yields of **72** with high enantioselectivity when Rh_2(*S*-PTAD)$_4$ was chosen as catalyst. This methodology was limited when the substrates had bulky sulfonyl groups or bulky groups at the indolic nitrogen (Scheme **44a**).[105] Shortly thereafter, Fokin's group realized an efficient synthesis of 3-sulfonyl-4-oxazolines **74** with high excellent enantioselectivity in 2013, up to 96% ee value.[106] This reaction featured general substrate scope, and a variety of aryl and alkyl aldehydes were tolerated. In all cases, the corresponding products were isolated in good to excellent yields (Scheme **44b**). Meanwhile, Murakami and Miura extended this reaction, they reported rhodium(II)-catalyzed annulation of *N*-sulfonyl-1,2,3-triazoles with *α*, *β*-unsaturated aldehydes, which afforded 2,3-dihydropyrroles with high levels of stereoselectivity. In this reaction, the chiral catalyst was similar to that reported by the Fokin group. Mechanistic investigations supported that the products were obtained through zwitterionic intermediates and intramolecular coupling (Scheme **44c**).[107]

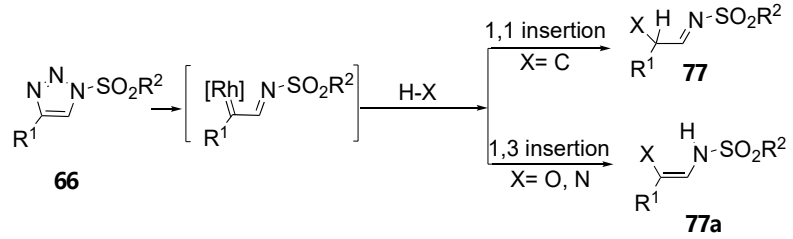


Scheme 44: Transannulation reactions of *N*-sulfonyl-triazoles

Since these initial studies, *N*-sulfonyl-triazoles have been widely applied in many different powerful synthetic methods. A large amount of transformations involve α-imino metal carbene species. Murakami and Miura, for example, have reported a nickel(0)-catalyzed transannulation of *N*-sulfonyl triazoles with allenes to provide pyrroles.[108] Davies and co-workers reported that 2,3-fused pyrroles could be synthesized from 4-alkenyl-*N*-sulfonyl triazoles via rhodium(II)-catalyzed electrocyclization in good to excellent yields.[109] Tang and co-workers have reported the rhodium-catalyzed reaction of *N*-sulfonyl-triazoles with 1,3-dienes to synthesize 2,5-dihydroazepines or 2,3-dihydropyrroles through formal [4+3] or [3+2] cycloadditions.[110] Simultaneously, the Fokin group and Davies group have also described different cycloaddition reactions involving *N*-sulfonyl-triazoles.[111, 112] Tang first

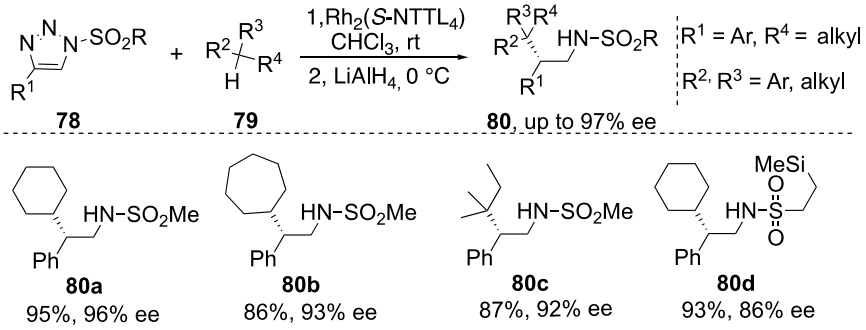
reported the silver-catalyzed ring expansion of cyclopropyl-substituted sulfonyl triazoles.[113] Murakami and Fokin further expanded on this ring expansion/rearrangement reaction.[114, 115]

Traditional diazoacetates, as far as we know, can undergo various 1,1-insertion reactions into X−H or C−X bonds, but the products are typically obtained as a racemic mixture. Similar reactions can be implemented with *N*-sulfonyl-triazoles, however, the final products of O−H and N–H insertions are enamines (Scheme **45**).



Scheme 45: Rhodium-catalyzed different insertion pathways

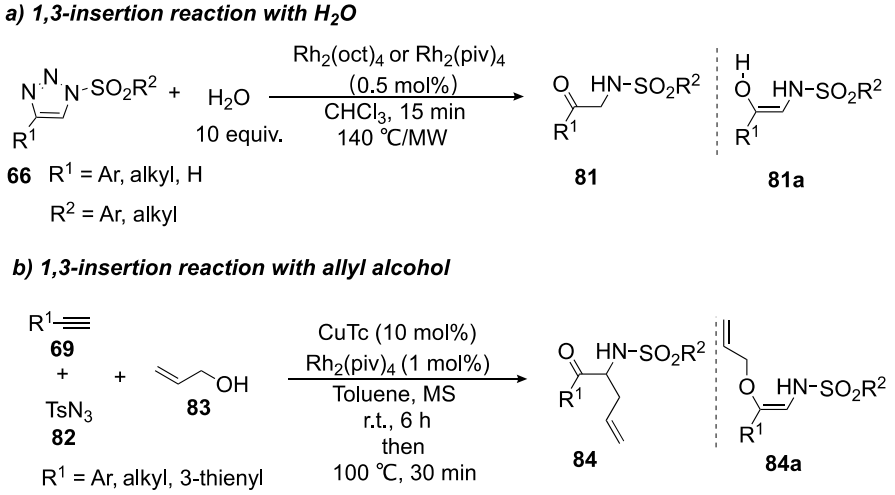
In 2011, Fokin and co-workers have reported that *N*-sulfonyl triazoles can undergo an enantioselective C−H insertion into unactivated alkanes in the presence of chiral Rh(II) catalyst. A variety of chiral *N*-sulfonylamines **80** were formed in excellent yield and high enantioselectivity. In this reaction, various substituted triazoles and alkanes were tolerated. Compared to diazoacetates, the azavinyl carbenes derived from *N*-sulfonyl-1,2,3-triazoles are more chemoselective towards insertion into tertiary C−H bonds than secondary C−H bonds (Scheme **46**).[116]



Scheme 46: Rhodium-catalyzed enantioselective C–H insertion

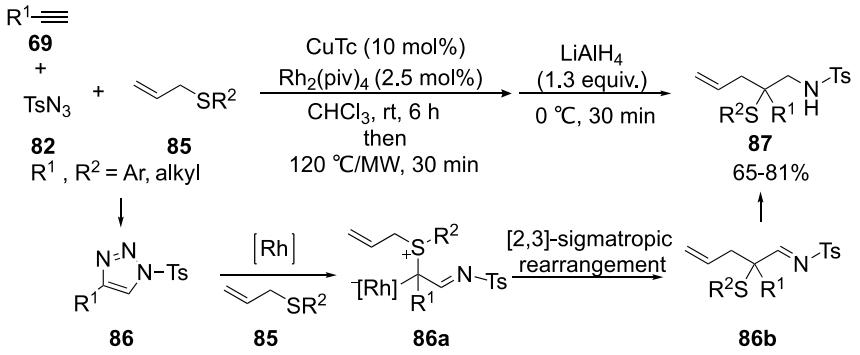
Subsequently, a few X–H insertion reactions have been developed. In 2012, Murakami and co-workers reported that α-amino ketones could be synthesized from *N*-sulfonyl triazoles and water. In this report, the insertion of rhodium carbenes into the O-H bond of water generated α-imino enols, followed by a tautomerization to produce α-amino ketones.[101] Further, the same research group developed a one pot insertion reaction of *N*-sulfonyl-1,2,3-triazole with allyl alcohols, which resulted in a [3,3]-sigmatropic rearrangement to give α-allyl-α-amino ketones. In this reaction, the *N*-sulfonyl-1,2,3-triazole was first formed by conversion of a terminal alkyne and sulfonyl azide at room temperature in the presence of a copper catalyst. The α-imino enols were then generated by introducing the rhodium-

catalyzed imino carbenes into the O–H bond of allyl alcohols, followed by a subsequent [3,3]-sigmatropic rearrangement to obtained corresponding ketones (Scheme **47**).[117]



Scheme 47: Rhodium-catalyzed O–H insertion

In addition, there has also been a report on the insertion of rhodium azavinyl carbenes into C–S bonds. Murakami and co-workers developed a useful one-pot reaction of a terminal alkyne, a tosyl azide, and an allyl sulfide to furnish α-allyl-α-sulfanyl imines via a Doyle−Kirmse reaction, the resultant sulfonyl imines can be reduced in situ with lithium aluminum hydride to formed the corresponding sulfonamides.[118] In this case, the electrophilic metallocarbene was attacked by allyl sulfides, resulting in ylide Intermediate, which then underwent a [2,3]-sigmatropic rearrangement to give an α-allyl-α-sulfanyl imine product. Later Yadagiri and Anbarasan described similar results with allyl sulfides (Scheme **48**).[119]



Scheme 48: Rhodium-catalyzed [2,3]-sigmatropic rearrangement

In 2014, Fokin and co-workers reported highly efficient O−H and N−H insertion reactions with 1-sulfonyl-1,2,3-triazoles. In this work, different primary and secondary amides, various alcohols, and carboxylic acids were used to afford a wide range of bisfunctionalized *(Z)*-enamide products with perfect regio- and stereoselectivity. Unlike traditional 1,1-insertion reactions with conventional donor− acceptor carbenes, the reaction of rhodium azavinyl carbenes derived from *N*-sulfonyl-1,2,3-triazoles employs an unusual formal 1,3-

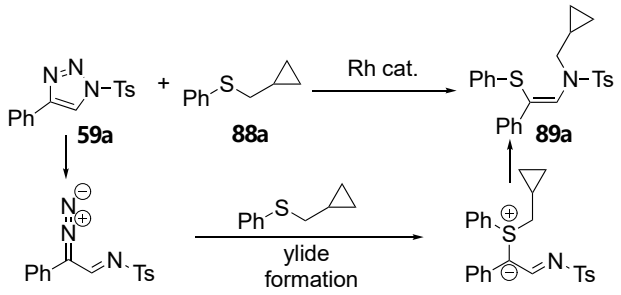
insertion approach to give highly functionalized enamide products as single geometrical isomers.[120]

Our group is always pushing for more research into carbene transfer reactions, and developing new sigmatropic rearrangement reactions with various diazoacetates.[121, 122] However, we desired to contribute more to the aspect of carbene transfer reactions of α-imino metallocarbenes derived from *N*-sulfonyl-1,2,3-triazoles. Here, in this chapter, we have researched 1,3-difunctionalization reactions of *N*-sulfonyl-1,2,3-triazoles with different substrates.

3.2 Rhodium-catalyzed enamine homologation reactions of triazoles with cyclopropylmethyl sulfides

Sigmatropic rearrangements have become a powerful method in organic synthesis for creating densely functionalized molecules, including biologically active products.[43 123, 124] Based on those rearrangements, triazoles can react with different nucleophilic sulfide reaction partners to access the corresponding rearrangement products. Anbarasan and Yadagiri have reported the sigmatropic rearrangement reactions of triazoles with benzyl sulfides, which formed α-sulfenylated imines, yet the result was that an inseparable mixture of enamine insertion and [1,2]-sigmatropic rearrangement was generated.[119] Another similar reaction was reported by Murakami and coworkers,[125] when thioesters reacted with *N*-sulfonyl-1,2,3-triazoles in the presence of rhodium(II) catalyst, the β-sulfanyl enamides with a Z configuration were obtained. However, this reaction is only limited to the transfer of acyl groups.

In order to break through the above limitations, we predicted that the cyclopropane ring could be a useful structural element, which could hinder the radical pathway of [1,2]-sigmatropic rearrangements. We thus studied the reaction of cyclopropylmethyl thioether with *N*-sulfonyl-1,2,3-triazoles. To our delight, we observed the formation of the enamine homologation product in moderate yield without accompanying [1,2]-sigmatropic rearrangement products (Scheme **49**).



Scheme 49: Rhodium-catalyzed enamine homologation reactions of triazoles

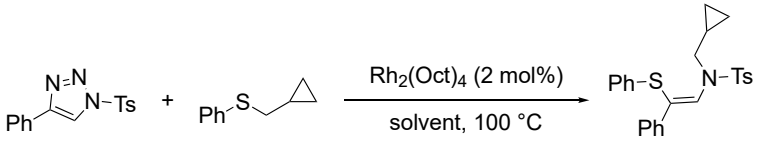
At the outset of this investigation, we examined the reaction of *N*-sulfonyl-1,2,3-triazoles **59a** and cyclopropylmethyl thioether **88a** with transition metal catalysts. First, different solvents were tested. When $CHCl_3$, DCE, or xylene was used as the solvent, the enamine homologation product **89a** could be obtained with 50% or 56% or 55% yield (Table **4**, entry 2-4). The product **89a** was also obtained with relatively high yields, if toluene was used as solvent (Table **4**, entry 1). Then, different equivalents of *N*-sulfonyl-1,2,3-triazoles and cyclopropylmethyl thioether were studied in the presence of $Rh_2(OAc)_4$ as the catalyst and toluene as the solvent. When 2 equiv. triazole and 1 equiv. thioether were used, the enamine homologation product **89a** was obtained with high efficiency (Table **4**, entry 1), However, increasing the amount of **59a** and **88a** would reduce the yield of the product **89a** (Table **4**, entry 6-8).

Following that, we set out to further optimize other reaction parameters. When the temperature of 100 °C was replaced by 80 °C or 110 °C, no further improvement in yield

was obtained and corresponding product **89a** was obtained with 51% or 60% yield (Table **4**, entry 9-10). The effect of concentration was then studied (Table **4**, entry 11-12): 4 mL toluene gave the product in approximately the same yield, but 1 mL toluene reduced the yield to 43%.

To our surprise, the reaction yield could be improved further when molecular sieves were added (Table **4**, entry 13) and the yield was increased to 76%. Furthermore, a series of Rh(II) catalysts were then investigated in order to optimize the reaction conditions. $Rh_2(Piv)_4$ was discovered to be ineffective (Table **4**, entry 15). $Rh_2(esp)_2$ and $Rh_2(Oct)_4$ gave the enamine reaction product **89a** with relatively high yields (Table **4**, entry 14,16). Among, $Rh_2(Oct)_4$ gave the optimal yield, up to 81%. Finally, we got the optimal conditions, under which 2 equiv. triazole and 1 equiv. thioether was reacted with $Rh_2(Oct)_4$ in toluene at 100 °C with molecular sieves. The enamine reaction product **89a** could be formed with 81% yield without accompanying byproducts arising from the [1,2]-sigmatropic rearrangement reaction.

Table 4: Optimization of enamine homologation reactions



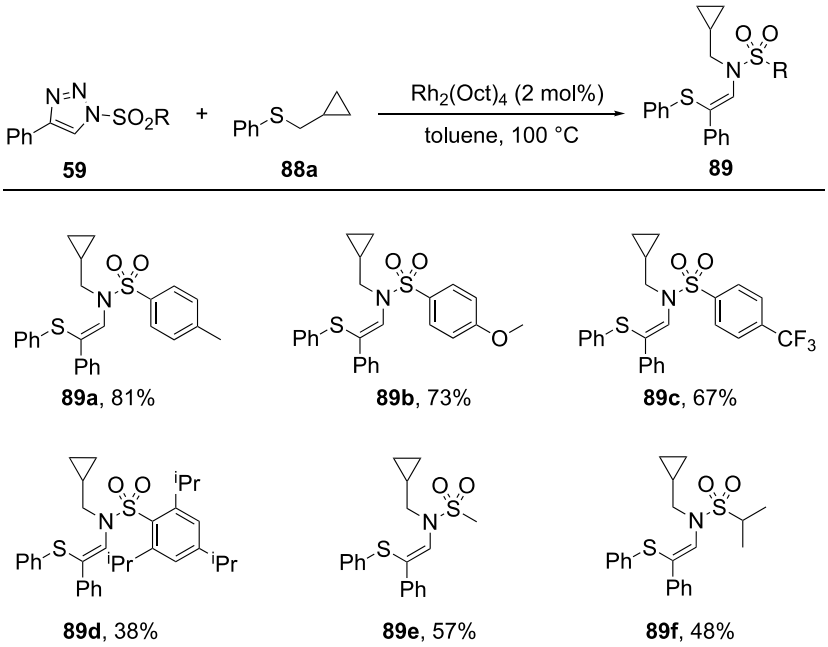
59a **88a** **89a**

Entry[a]	TM cat.	Solvent	59a/88a	Yield 89a (%)
1	$Rh_2(OAc)_4$	Toluene	1:2	65
2	$Rh_2(OAc)_4$	$CHCl_3$	1:2	50
3	$Rh_2(OAc)_4$	1,2-DCE	1:2	56
4	$Rh_2(OAc)_4$	*m*-xylene	1:2	55
5	$Rh_2(OAc)_4$	dioxane	1:2	54
6	$Rh_2(OAc)_4$	Toluene	1:1	39
7	$Rh_2(OAc)_4$	Toluene	1:3	59
8	$Rh_2(OAc)_4$	Toluene	2:1	40
9[b]	$Rh_2(OAc)_4$	Toluene	1:2	51
10[c]	$Rh_2(OAc)_4$	Toluene	1:2	60
11[d]	$Rh_2(OAc)_4$	Toluene	1:2	62
12[e]	$Rh_2(OAc)_4$	Toluene	1:2	43
13[f]	$Rh_2(OAc)_4$	Toluene	1:2	76
14[f]	$Rh_2(Oct)_4$	Toluene	1:2	81
15[f]	$Rh_2(Piv)_4$	Toluene	1:2	56
16[f]	$Rh_2(esp)_2$	Toluene	1:2	75

[a]Reaction conditions: to a solution of the **59a** (0.2 mmol, 1.0 eq.) and **88a** (2.0 eq.) and transition-metal catalyst (2 mol%) were dissolved in dry solvent. The reaction mixture was stirred at 100 °C for 12 h under argon atmosphere. [b]80 °C reaction temperature. [c]110 °C reaction temperature. [d] 4 mL of solvent. [e]1 mL of solvent. [f]with 4Å molecular sieves.

With the optimized reaction conditions in hand, we then explored the scope of a series of triazoles and sulfides. Firstly, we studied the influence of the N-protecting group of the triazoles under optimal reaction conditions. The reaction with the triazoles containing

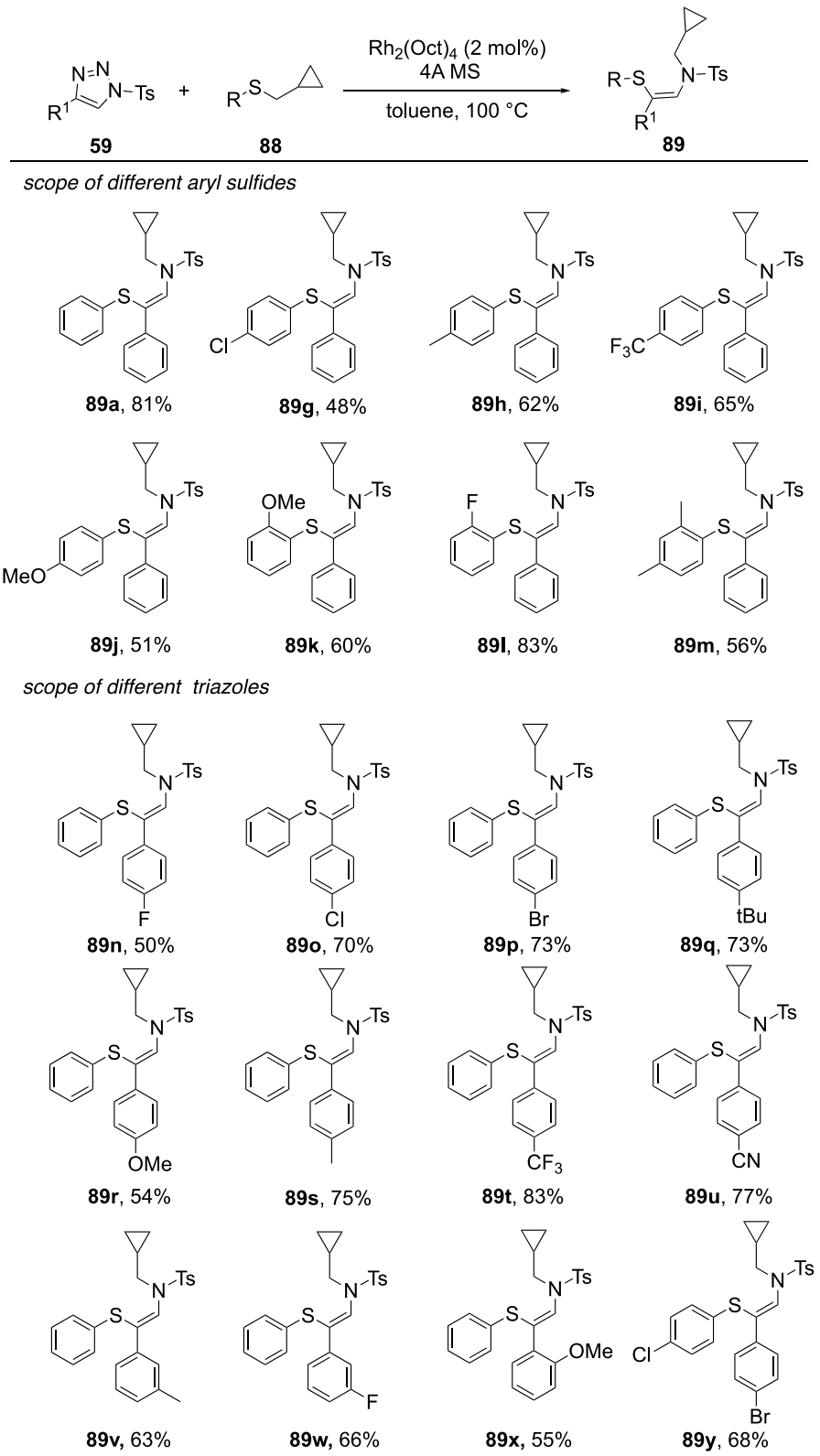
arylsulfonyl protecting groups worked well to afford the corresponding products in high yields (Scheme **50**, **89a**–**89c**). The triisopropyl phenyl group substituted triazole also worked in this reaction (**89d**), yet the yield of the product was low. In addition, alkylsulfonyl protecting groups were also compatible, and the enamine homologation products can be isolated in moderate yields (**89e, 89f**).



Scheme 50: Scope of a series of triazoles

We next investigated the influence of different substituents in all positions of the aromatic ring of sulfide. Sulfides bearing a halogen substituent in the para position were tolerated to provide the corresponding products. Electron-withdrawing trifluoro-methyl and electron-donating methoxy substituted sulfides were both compatible under optimal conditions, giving the desired homologation products in moderate yields (Scheme **51**, **89i**–**89j**). When the substituents were *o*-OMe or *o*-F, the reaction also proceeded smoothly and gave the corresponding products in good to excellent yields without observation of [1,2]-sigmatropic rearrangement products (Scheme **51, 89k**–**89m**).

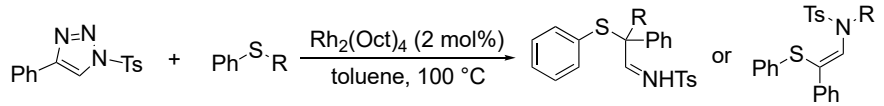
To further explore the scope of this homologation reaction, we examined the reactions with different triazoles. In these cases, substitution of the triazole with halogens or electron-withdrawing or electron-donating groups in the para position were well tolerated, giving the corresponding products in good yield (Scheme **51, 89n**–**89u**). The reactions also proceeded well under the optimal reaction conditions, forming the enamine homologation products in moderate yields when the substituents were *m*-Me, *o*-F and *o*-OMe (Scheme **51, 89v**–**89x**).



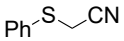
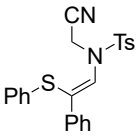
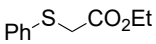
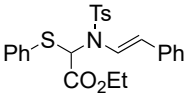
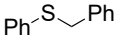
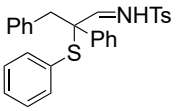
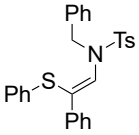
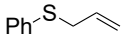
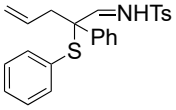
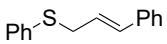
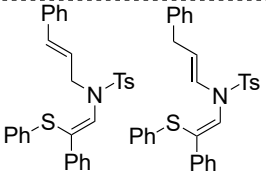
Scheme 51: Rhodium-catalyzed homologation reaction of triazoles and sulfides

Next, we investigated various sulfides with different aliphatic groups. Under the optimal reaction conditions, first, when the sulfide comprised an electron-withdrawing nitrile group, the enamine insertion product **92a** could be isolated in good yield, and no other rearrangement products were observed by ^{1}H NMR of the crude reaction mixture. Then

nitrile group was replaced by electron- withdrawing ester group, no desired enamine insertion product was observed, and only the [2,3]-sigmatropic rearrangement product **91a** was obtained. When benzyl phenyl sulfide **90c** was used, an inseparable mixture of [1,2]-sigmatropic rearrangement **91b** and enamine insertion **92b** was obtained, and this result was similar to previous reports from Anbarasan and coworkers.[119] Next, allyl sulfide **90d** with *N*-sulfonyl-1,2,3-triazole also smoothly reacted under the optimal reaction conditions and the corresponding [2,3]-sigmatropic rearrangement product was isolated in 64% yield (Scheme **52**) and we did not observe the enamine insertion product. Finally, to further diversify the methodology, cinnamyl-substituted sulfide was employed. In this case, the reaction of **90e** with *N*-sulfonyl-1,2,3-triazole formed an inseparable mixture of products **92c** and **92d** in an overall yield of 68% under the optimal reaction conditions, and no classic rearrangement product was found. The mixture of double-bond isomers likely occurred by high reaction temperature.

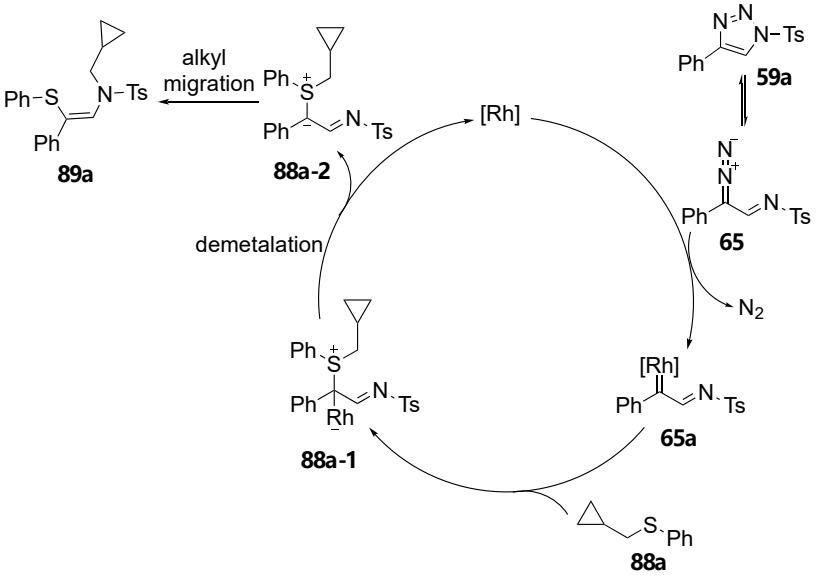


59a (1 equiv.) + **90** (2 equiv.) → **91** 1,2-sigmatropic rearrangement or **92** enamine insertion

starting material	rearrangement product	enamine insertion product	
 **90a**	not observed	 **92a**, 65%	
 **90b**	 **91a**, 48%	not observed	
 **90c**	 **91b**	 **92b**	**91b** + **92b** 84% (1 : 0.9) inseparable mixture
 **90d**	 **91c**, 64%	not observed	
 **90e**	not observed	 **92c** **92d**	**92c** + **92d**, 68% (5 : 1) inseparable mixture

Scheme 52: Scope of sulfides with different aliphatic groups

Based on previous reports, we proposed a possible mechanism. First, the α-diazoimine was generated to undergo the ring-chain isomerization of *N*-sulfonyl-1,2,3-triazole. Following the rhodium carbenoid **65a** would be formed with the extrusion of nitrogen in the presence of Rh catalyst, then it would undergo an additional reaction with cyclopropylmethyl sulfide **88a** and formed a metal-bound ylide intermediate **88a-1**. After the demetalation process, the free ylide intermediate **88a-2** was generated. Subsequently, it underwent alkyl migration to form the product of a formal enamine homologation product **89a** (Scheme **53**).



Scheme 53: Proposed mechanism

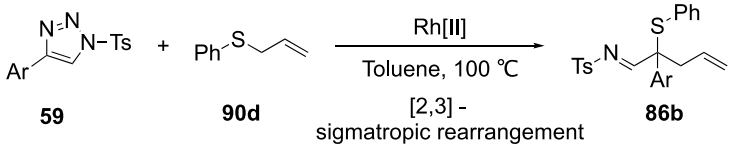
In this work, we displayed an unusual rhodium-catalyzed enamine homologation reaction of triazoles with alkyl aryl sulfides. In contrast to classic rearrangement pathways, this reaction underwent a selective 1.3-insertion strategy to form enamine homologation products in moderate to high yield. Various triazoles and sulfides were well tolerated in this way, and cyclopropylmethyl sulfides exhibited unusual reactivity. In addition, this work first reported that the migration of an alkyl group was included in enamine homologation reactions of triazoles.

3.3 Rhodium-catalyzed cascade reactions of triazoles with organoselenium compounds

N-sulfonyl-1,2,3-triazoles have proven to be an efficient source of for in situ generation of α-diazoimines, which can afford α-imino metal carbenoids with suitable transition metal catalysts. These reactive intermediates can then be used for the synthesis of various heterocycles.[104, 126] In addition, sigmatropic rearrangement reactions can be used to construct C−C or C−heteroatom bonds via ylide intermediates.[66, 82] Especially, in triazole chemistry, sigmatropic rearrangements of α-imino metal carbenoids are an important class of reactions. The groups of Murakami[101] and Fokin[120] have extensively examined the utility of azavinyl carbenes for formal 1,3-insertion of O−H and N−H bonds.

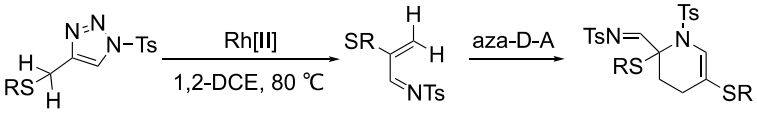
Over the past few decades, ylides intermediate have been increasingly used in organic synthesis that have emerged as versatile methods for the synthesis of heteroatom building blocks and bioactive molecules.[127-129] The Anbarasan and Murakami groups first reported that the rhodium catalyzed [2,3]-rearrangement with *N*-sulfonyl-1,2,3-triazoles and allyl thioethers proceeds via a sulfur ylide intermediate (Scheme **54a**).[118, 119] Subsequently, other sigmatropic rearrangements of sulfur ylides derived from *N*-sulfonyl-1,2,3-triazoles have been extensively studied (Scheme **54b**).[130] Our group also reported on rhodium catalyzed enamine homologation reactions of triazoles with cyclopropylmethyl sulfides via sulfur ylide (Scheme **54c**).[131] The reaction of triazoles with organoselenium compounds and formation of intermediate selenium ylides, has however not yet been exploited.

a) [2,3]-Sigmatropic rearrangement of triazole with phenylallyl sulfide



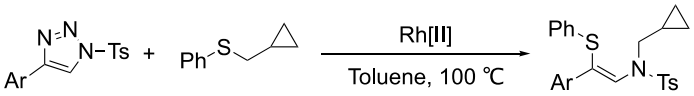
59 **90d** **86b**

b) Rhodium-catalyzed cascade reaction



93 **94** **95**

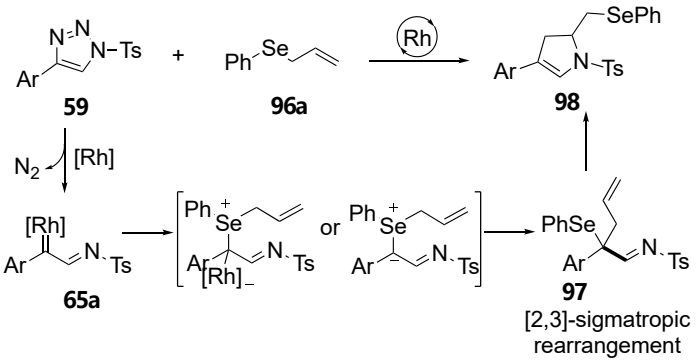
c) Rhodium-catalyzed enamine homologation reactions of triazoles



59 **88a** **89**

Scheme 54: Sigmatropic rearrangement reactions of sulfides with triazole

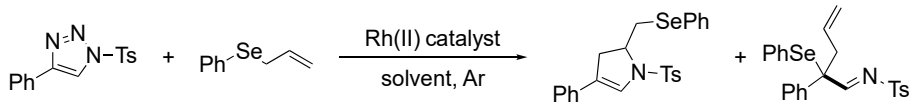
Inspired by these previous reports, we assumed that allylic selenides **96a** could interact with highly a electrophilic α-imino Rh-carbenoid, giving a selenium ylide, which can further undergo [2,3]-sigmatropic rearrangement to provide **97** (Scheme **55**). Surprisingly, we found the dihydropyrrole product **98** after the reaction instead of the rearrangement product **97**.



Scheme 55: Cascade reaction of imino-carbenes with organoselenium compounds

Intrigued by this result, we decided to optimize the reaction conditions by employing allylic selenides **96a** and phenyl triazole **59a** as the model substrates (Table **5**). In a preliminary investigation, different reactions stoichiometries were tested first. It was found that the reaction of one equivalent of triazole with one equivalent of allylic selenides in toluene at 100 °C afforded the desired dihydropyrrole product **98a** in 48% yield (Table **5**, entry 4) and no sigmatropic rearrangement product was observed. Further changes to the amount of **59a** and **96a** reduces the yield of product **98a** (Table **5**, entry 1-5). When the equivalent of allylic selenide was increased to 2 equiv. or 3 equiv., the sigmatropic rearrangement product was obtained in 55% and 61% yield, respectively. Various reaction concentrations were tested next to improve the yield of dihydropyrrole product. Interestingly, increasing the concentration to 0.2 M furnished dihydropyrrole product **98a** in 86% yield, without sigmatropic rearrangement product in the reaction mixture (entry 7). With a further increase of reaction concentration to 0.4 M, the yield decreases to 47% (entry 8). After this observation, we next investigated different reaction parameters, including temperature, solvents and rhodium catalysts.

Table 5: Optimization of cascade reaction of allyl selenide with triazole



Entry[a]	TM cat.	Conc. (M)	59a/96a	Yield 98a/97a (%)[b]
1	$Rh_2(OAc)_4$	0.1	3:1	27/-
2	$Rh_2(OAc)_4$	0.1	2:1	32/-
3	$Rh_2(OAc)_4$	0.1	1:1	48/-
4	$Rh_2(OAc)_4$	0.1	1:2	33/55
5	$Rh_2(OAc)_4$	0.1	1:3	10/61
6	$Rh_2(OAc)_4$	0.05	1:1	31/40
7	$Rh_2(OAc)_4$	0.2	1:1	86/-
8	$Rh_2(OAc)_4$	0.4	1:1	47/-

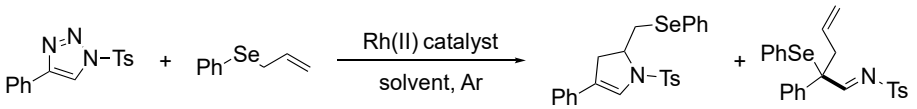
[a]Reaction condition: In an oven dried test tube, **59a**, **96a** and catalyst (2 mol%) were dissolved in toluene and heated to 100 °C for 15 hours. [b]Isolated yields.

Several solvents were investigated, such as 1,2-DCE, 1,4-dioxane, MeCN and *m*-xylene. Changing the solvent system from toluene to 1,2-DCE and 1,4-dioxane led to the formation of **98a** in diminished yields (Table **6**, entry 3-4). However, when the MeCN was used as the solvent in the presence of $Rh_2(OAc)_4$, no desired dihydropyrrole product was detected (Table **6**, entry 5) and only the decomposition of triazole was observed. If the high-boiling solvent *m*-xylene was used, no noticeable change in yield was observed (Table **6**, entry 2). Next, different normal carbene transfer Rh-catalysts were utilized. When $Rh_2(OAc)_4$ was changed to $Rh_2(piv)_4$ or $Rh_2(esp)_2$, 72% and 66% yield of the dihydropyrrole product was isolated. The yield dropped significantly to 21%, if the $Rh_2(Oct)_4$ was selected as catalyst (Table **6**, entry 6-8). Regrettably, further increase of the temperature to 120 °C with $Rh_2(OAc)_4$ gave the dihydropyrrole product **98a** only in 58% yield. A reduction of the reaction temperature also did not further improve the reaction yield (Table **6**, entry 9-10).

Furthermore, we also screened the chiral rhodium catalysts, Rh_2(*S*-BTPCP)$_4$ and Rh_2(*S*-DOSP)$_4$, under similar conditions, which yielded **98a** in lower yield (Table **6**, entries 11–12). Unfortunately, no noticeable enantioselectivity was found.

Based on these optimization results, the following conditions were chosen for further exploration of substrates: 2 mol% of $Rh_2(OAc)_4$, 1 equivalent of triazoles and 1 equivalent of organoselenium compound, 1 mL of toluene, 100°C.

Table 6: Optimization of cascade reaction of allyl selenide with triazole



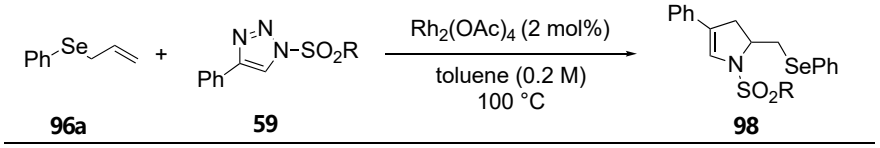
59a **96a** **98a** **97a**

Entry[a]	TM cat.	Solvent	Temperature	Yield 98a/97a (%)[b]
1	$Rh_2(OAc)_4$	Toluene	100 °C	86/-
2	$Rh_2(OAc)_4$	*m*-xylene	100 °C	83/-
3	$Rh_2(OAc)_4$	1,2-DCE	100 °C	65/-
4	$Rh_2(OAc)_4$	1,4-dioxane	100 °C	42/-
5	$Rh_2(OAc)_4$	MeCN	100 °C	*Dec.*[c]
6	$Rh_2(Oct)_4$	Toluene	100 °C	21/-
7	$Rh_2(esp)_2$	Toluene	100 °C	66/-
8	$Rh_2(Piv)_4$	Toluene	100 °C	72/-
9	$Rh_2(OAc)_4$	Toluene	80 °C	22/-
10	$Rh_2(OAc)_4$	Toluene	120 °C	58/-
11	Rh_2(*S*-BTPCP)$_4$	Toluene	100 °C	36(rac)/-
12	Rh_2(*S*-DOSP)$_4$	Toluene	100 °C	62(rac)/-

[a]Reaction condition: in an oven dried test tube, **59a**, **96a** and catalyst (2 mol%) were dissolved in toluene and heated to 100 °C for 15 hours. [b]Isolated yields. c) Decomposition of **59a**.

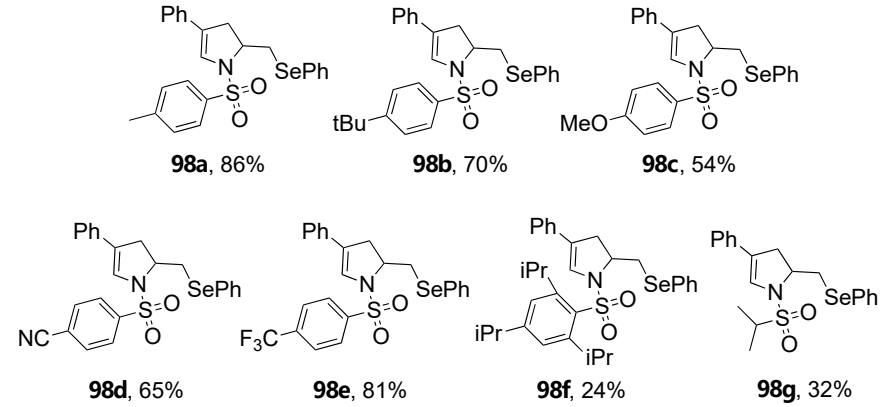
With the optimized conditions in hand, we investigated the scope of this reaction for different triazoles and alkyl allyl selenides. Under the standard conditions, first, we examined the influence of the *N*-protecting group of the triazole. 4-Methylphenyl and 4-

tert-butylphenyl sulfonyl protecting groups were well tolerated to furnish the dihydro pyrrole products in good to excellent yields (Scheme **56**, **98a**–**98c**). Electron-withdrawing substituents like cyano group and trifluoromethyl at the aryl sulfonyl group also reacted smoothly under the reaction conditions and the corresponding dihydropyrrole products were obtained with good yield (Scheme **56**, **98d**–**98e**). Moreover, 2,4,6-tri-isopropyl phenyl protecting group gave product **98f** only in 24% yield, probably because of the increased steric hindrance. Alkyl sulfonyl protecting dihydropyrrole was successfully obtained from the corresponding triazoles in low yield (Scheme **56, 98g**). In all cases, no product of [2,3]-sigmatropic rearrangement was observed.



96a **59** **98**

scope of different N-protecting groups



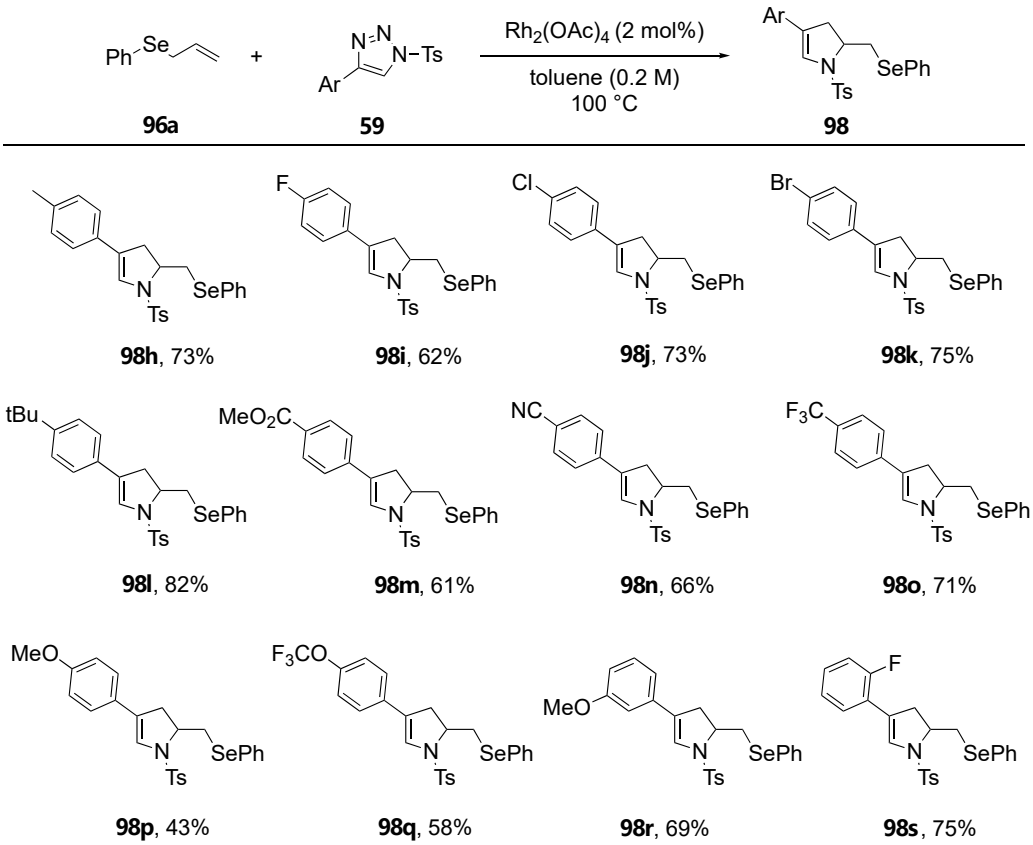
98a, 86% **98b**, 70% **98c**, 54%

98d, 65% **98e**, 81% **98f**, 24% **98g**, 32%

Scheme 56: Scope of allyl selenides with N-protecting triazoles

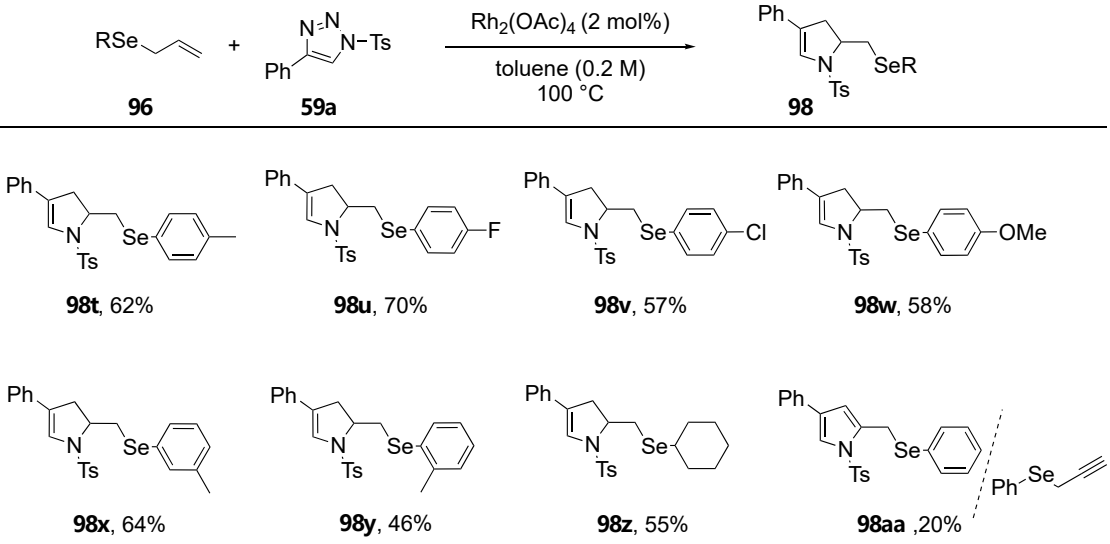
Next, we investigated various substituted triazoles. An alkyl-substituted aryl containing 1,2,3-triazole was readily converted to the corresponding dihydropyrrole **98h** in excellent yields. Similarly, different halogen (F, Cl and Br) substituted triazoles were also well employed and the corresponding products were obtained in moderate yields (Scheme **57, 98i**–**98k**). Both electron-donating and withdrawing groups in the *para*-position of the benzene ring were also well-suited and gave the corresponding products **98m–98q** in moderate to good yields (43–71%). The strongly electron-donating methoxy group had a significant impact on the yield under the standard conditions, yet when this group was in the *meta*-position, no such influence was observed, and the product **98r** was obtained in 69% yield. In addition, 2-fluorine substituted triazoles underwent the reaction smoothly to provide the dihydropyrrole **98s** in good yield (Scheme **57**).

The substrate scope of this cascade reaction of triazoles with different aryl and alkyl allyl selenides was also investigated. Methyl and halogen-substituted allyl selenides can react with *N*-sulfonyl-1,2,3-triazole smoothly to generate the corresponding dihydropyrrole in moderate to good yields (Scheme **58**, **98t–98v)**. The electron-donating group methoxy also



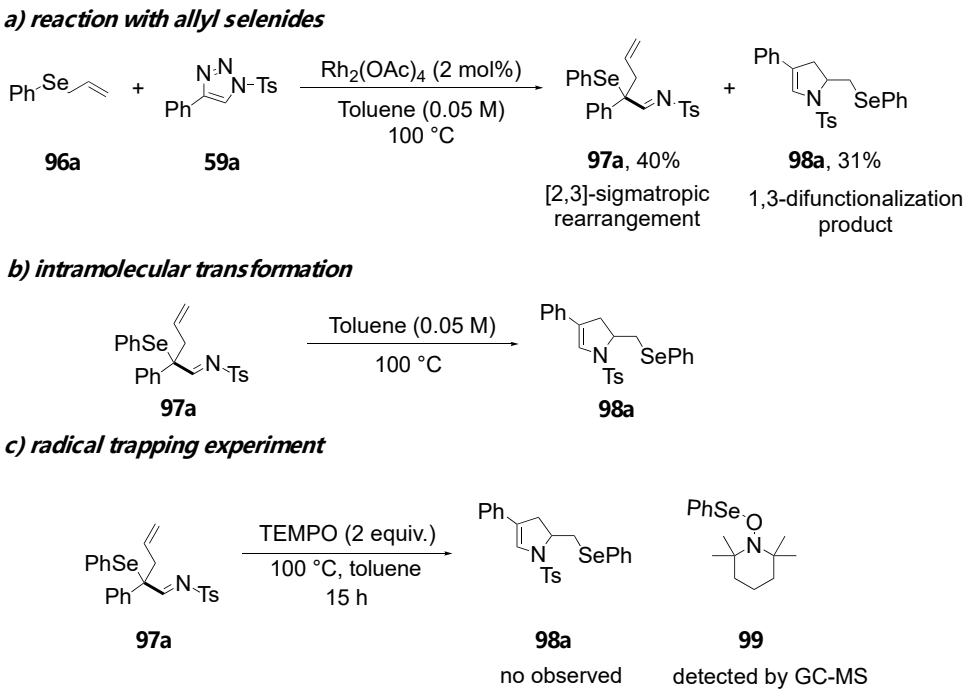
Scheme 57: Scope of allyl selenides with different aryl groups of the triazoles

was compatible under the optimal reaction conditions to provide the corresponding dihydropyrrole **98w** in 58% yield. Furthermore, 2-methyl and 3-methyl substituted allyl selenides followed a similar pathway and afforded the desired products **98x** and **98y** in 46% and 64% yield. Also, when we studied allyl(cyclohexyl)selane, to our delight, the desired dihydropyrrole product **98z** was obtained in moderate yield. Finally, the propargyl selenide was tested with *N*-sulfonyl-1,2,3-triazole under the optimal reaction conditions, and the pyrrole product **98aa** was isolated in low yield.



Scheme 58: Scope of different aryl selenides with triazole

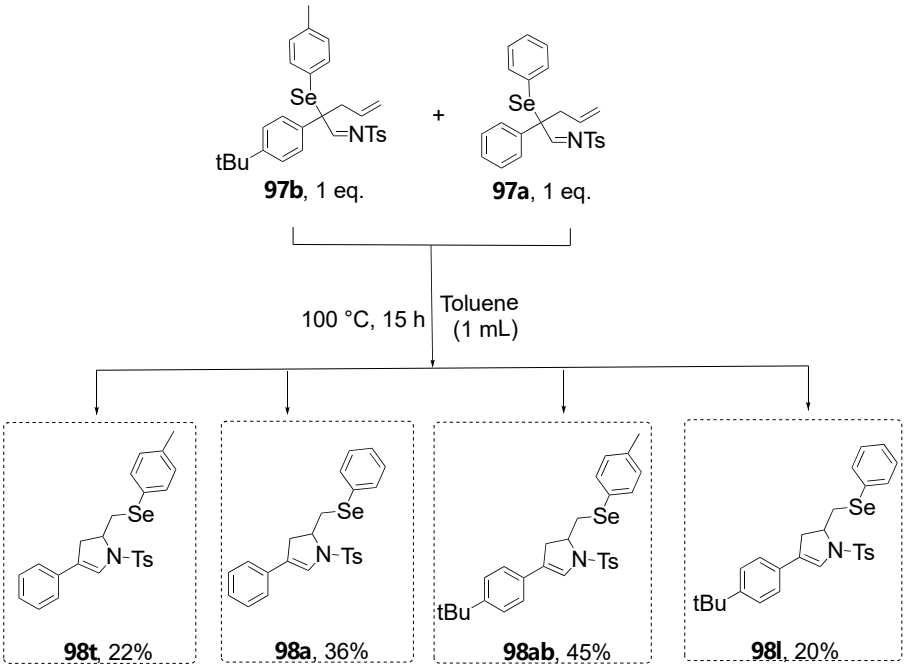
In order to get detail understanding of the reaction mechanism, a set of control experiments were conducted. The reaction of allyl selenide with triazole with lower concentration (0.05 M) furnished a mixture of [2,3]-sigmatropic rearrangement product and 1,3-difunctionalization product. To confirm the formation of intermediate [2,3]-sigmatropic rearrangement product, we carried out a control experiment where the [2,3]-sigmatropic rearrangement product **97a** was heated up at 100 °C in toluene, and after overnight reaction time a complete conversion to 1,3-difunctionlzation product was observed. This result indicates that a [2,3]-sigmatropic rearrangement occurs before the formation of the dihydropyrrole product. Furthermore, to confirm radical versus ionic pathways, we conducted a reaction in the presence of 2 equiv. of radical trap TEMPO, yet we observed complete inhibition of the reaction, and from the GC-MS we could detect the formation of adduct **99**. Therefore, based on these observations we can conclude that this cyclization process occurs from the rearrangement product via a step-wise radical pathway.



Scheme 59: Control experiments

Next, we checked if this cyclization reaction occurs via a stepwise pathway or concerted manner. The reaction in the presence of two different [2,3]-sigmatropic rearrangement products **97b** and **97a** unveiled the scrambling of the reaction products thus a stepwise pathway was the key process in this intramolecular cyclization reaction (Scheme **60**).

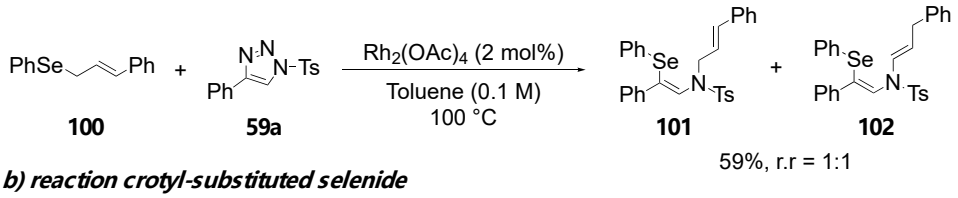
In additional experiments, we conducted the reaction of crotyl and cinnamyl substituted selenides under the optimized reaction conditions. Surprisingly, we observed that reaction of cinnamyl selenide gave the exclusive formation of 1,3-difunctionalization product as a 1:1 mixture of two different regioisomers, while crotyl substituted selenide only gave the radical cyclization product as 1:1 mixture of both diastereomers. Detailed computational investigations revealed that for the cinnamyl substituted substrate the intermediate [2,3]-



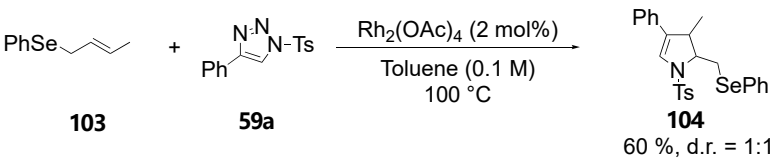
Scheme 60: Cross-over experiment

sigmatropic rearrangement product underwent aza-cope rearrangement via a favorable transition state, where the transition state is stabilized by the π-interaction of the phenyl ring in the close proximity. Contrarily, for the crotyl substituted selenide the intermediate [2,3]-sigmatropic product could not undergo aza-cope rearrangement reaction because of the less stabilization of corresponding transition state; therefore, standard radical cyclization product was formed exclusively.

a) reaction with cinnamyl selenide



b) reaction crotyl-substituted selenide

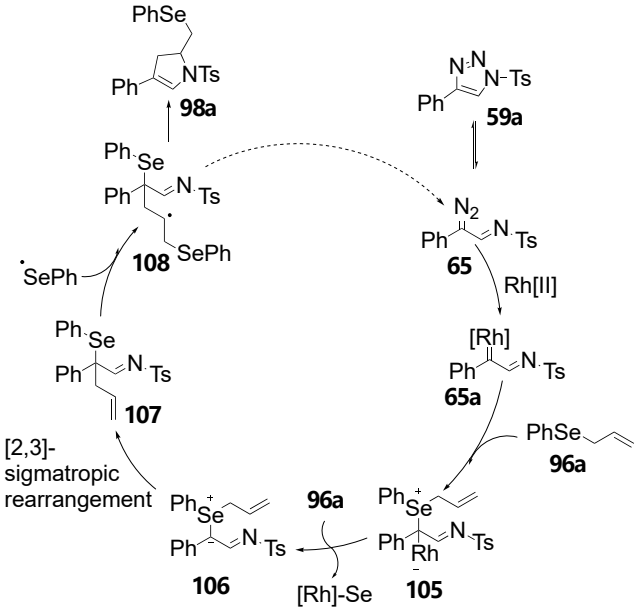


Scheme 61: Control experiments with different selenides

Based on our observation and DFT calculation, we proposed a pathway for the formation of dihydropyrrole product. This mechanism starts with an initial formation of Rh(II)–azavinyl carbene species via extrusion of dinitrogen from *N*-sulfonyl-1,2,3-triazole **59a** and $Rh_2(OAc)_4$. Following this, a metal-bound selenium ylide was generated *in situ* from the reaction of rhodium imino carbene intermediate **65a** with allyl selenides **96a**. Then, surprisingly, in the presence of allyl selenides, the formation of free ylide was promoted in this reaction. It underwent the coordination of one allyl selenide molecule to the backside

of the rhodium dimer and Rh-Se was formed as a by-product. From the calculation, we know the free ylide had the same energy as the metal-bound ylide, so it could readily undergo the back reaction to form the metal-bound ylide. Next, the free ylide then underwent a [2,3]-sigmatropic rearrangement reaction to afford the product **107**.

The sigmatropic rearrangement product was not the final product of the reaction. Subsequently, a secondary alkyl radical **108** was generated via a radical addition of selenium radical with a double bond of sigmatropic rearrangement product **107**. Next, the following cyclization of radical species **108** would furnish the final dihydropyrrole product, this process accompanied the cleavage of new selenium radical.



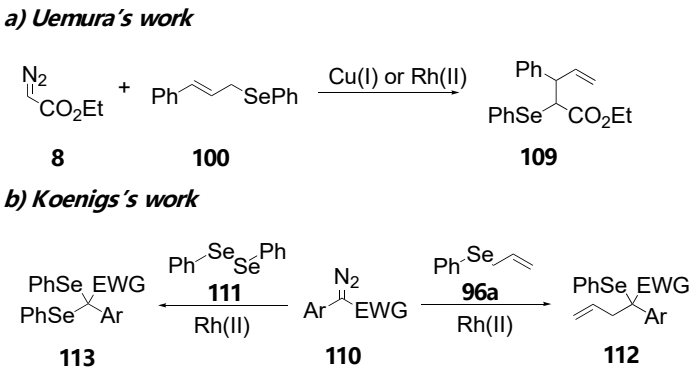
Scheme 62: Plausible mechanism

In this work, we presented a novel rhodium-catalyzed cascade reaction of triazoles with organoselenium compounds in the presence of Rh(II) catalysts. Different from classic rearrangement reactions, these dihydropyrrole products were formed via [2,3]-sigmatropic rearrangement and selenium-mediated radical cyclization. In addition, when cinnamoyl selenides were reacted with triazoles, the 1,3-difunctionalized product was obtained by a double rearrangement reaction. Mechanism experiments and DFT calculations revealed that the organoselenium compound constitutes an important role in these cascade reactions.

3.4 Rhodium-catalyzed 1,3-difunctionalization of triazoles with acyl selenides

Because of their widespread use in the synthesis of complex natural products, drugs, and materials, organoselenium compounds have attracted a great deal of attention. At the same time, they are critical tools for the efficient introduction of new functional groups.[132-134] However, the reactions of organoselenium compounds with carbenes have received far less attention, and no sufficient study of selenium ylides has previously been reported.

There are only a few examples that described the reactions of organoselenium compounds with diazoalkanes via selenium ylides intermediate. In 1995, Uemura's group reported the first example of an enantioselective addition reaction of ethyl diazoacetate with the organoselenium compound in the presence of chiral copper(I) (Scheme **63a**).[135] Following that, Koenigs and co-workers reported the rhodium catalyzed carbene transfer reactions of diazoalkanes with organoselenium compound via the formation of an intermediate selenium ylide (Scheme **63b**).[136, 137]

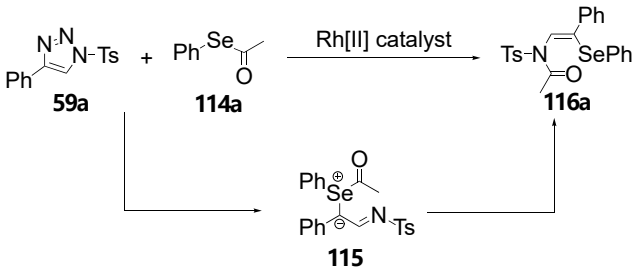


Scheme 63: Previous work of organoselenium compounds with diazoalkanes

In addition, to our knowledge, there were only rare examples for the reaction of organoselenium compounds with triazoles as carbene precursors. As previously described, our group revealed a formal 1,3-difunctionalization reaction of allyl selenides and triazoles. This reaction proceeds to form the unusual dihydropyrrole products via sigmatropic rearrangement and selenium-mediated radical cyclization. There is no further research on carbene transfer reactions of triazoles with organoselenium compounds.

We've been focused on the research of reactivity of triazoles, so we were interested in studying the preferential migration reaction of selenium ylides derived from triazoles with organoselenium compounds (Scheme **64**).

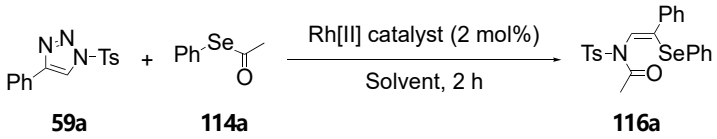
First, we decided to optimize the reaction conditions by employing acyl selenide **114a** and 1,2,3-triazole **59a** as the model substrates. The reaction of *N*-sulfonyl 1,2,3-triazole with acyl selenide in the presence of 2 mol% $Rh_2(OAc)_4$ in toluene at 100 °C gave the *Z* isomer of α-seleno enamide as the product in 70% yield (Table **7**, entry 1). Then, different Rh(II) catalysts were investigated to improve the yield of enamide **116a**, such as $Rh_2(Piv)_4$, $Rh_2(Oct)_4$ and $Rh_2(esp)_2$. Among all the catalysts under investigation, the yield of **116a** incr-



Scheme 64: Rhodium(II)-catalyzed 1,3-difunctionalization reaction

eased to 95% in the presence of $Rh_2(Piv)_4$ (Table **7**, entry 2). Next, a further optimization study was conducted with $Rh_2(Piv)_4$ as the catalyst. Changing the solvent from toluene to chloroform and 1,2-DCE led to the formation of enamide **116a** in diminished yields (Table **7**, entry 5-6). When using the 1,4-dioxane as the solvent, a significantly reduced yield of the **116a** was obtained and only 19% 1,3-difunctionalization product was detected in the reaction (Table **7**, entry 8). The effect of *m*-xylene was similar to that of toluene, and **116a** was obtained in 92% yield (Table **7**, entry 7). Then, a decrease in the temperature from 100 °C to 80 °C furnished the enamide **116a** with 76% yield (Table **7**, entry 9).

Table 7: Optimization of 1,3-Difunctionalization of triazoles with acyl selenides



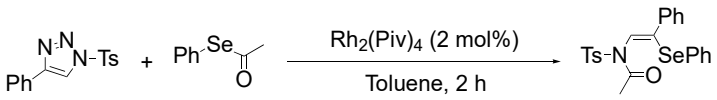
Entry[a]	TM cat.	Solvent	Temperature	Yield 116a (%)[b]
1	$Rh_2(OAc)_4$	Toluene	100 °C	70
2	$Rh_2(Piv)_4$	Toluene	100 °C	95
3	$Rh_2(Oct)_4$	Toluene	100 °C	81
4	$Rh_2(esp)_2$	Toluene	100 °C	92
5	$Rh_2(Piv)_4$	$CHCl_3$	100 °C	71
6	$Rh_2(Piv)_4$	1,2-DCE	100 °C	58
7	$Rh_2(Piv)_4$	*m*-xylene	100 °C	92
8	$Rh_2(Piv)_4$	1,4-dioxane	100 °C	19
9	$Rh_2(Piv)_4$	Toluene	80 °C	76

[a]Reaction condition: in an oven dried test tube, **59a** (0.2 mmol, 1.0 equiv.), **114a** (0.2 mmol, 1.0 equiv.) and catalyst (2 mol%) were dissolved in 1 mL toluene and heated to 100 °C for 2 hours. [b]Isolated yields.

In addition, to further improve the yield, we next studied the influence of stoichiometry, concentration, and reaction time. When the amount of *N*-sulfonyl 1,2,3-triazole was increased to 2 equiv., the yield of **116a** was reduced significantly. Similarly, when changing the amount of acyl selenide **114a**, the yield of **116a** also decreased. Furthermore, increasing or decreasing the concentrations of the reaction mixture was tested, and the result showed that no further improvement in the yield of the product enamide **116a** was realized. Further screening of the reaction time was subsequently performed. When the reaction reacted for 1 h, the product **116a** was successfully produced in 81% yield.

Extending the reaction time to 4 h had little effect on the yield. Therefore, the optimum reaction conditions are as follows: *N*-sulfonyl 1,2,3-triazole **59a** (1 equiv.), acyl selenide **114a** (1 equiv.), $Rh_2(Piv)_4$ (2 mol%), in 1 mL toluene at 100 °C for 2 h (Table **8**).

Table 8: Optimization of 1,3-Difunctionalization of triazoles with acyl selenides



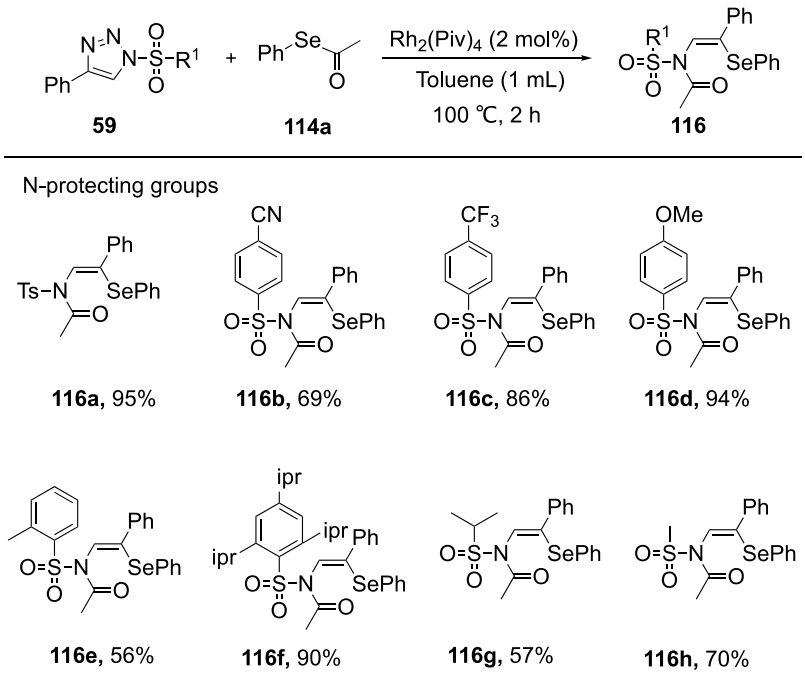
59a **114a** **116a**

Entry[a]	TM cat.	Conc. (M)	59a/114a	Yield 116a (%)[b]
1	$Rh_2(Piv)_4$	0.2	2:1	78
2	$Rh_2(Piv)_4$	0.2	1:2	87
3	$Rh_2(Piv)_4$	0.1	1:1	75
4	$Rh_2(Piv)_4$	0.4	1:1	66
5	$Rh_2(Piv)_4$	0.05	1:1	67
6[c]	$Rh_2(Piv)_4$	0.2	1:1	81
7[d]	$Rh_2(Piv)_4$	0.2	1:1	91

[a]Reaction condition: in an oven dried test tube **59a** (0.2 mmol, 1.0 equiv.), **114a** (0.2 mmol, 1.0 equiv.) and catalyst (2 mol%) were dissolved in toluene and heated to 100 °C for 2 hours. [b]Isolated yields. [c]1 h Reaction time. [d]4 h Reaction time.

After determining the optimized reaction conditions, we initially explored different triazole substrates. First, various *N*-substituted 1,2,3-triazoles were examined. Methoxy in the *para*-position of the N aryl sulfonyl group reacted well to afford the corresponding product **116d** in high yields (Scheme **65**). Notably, the Z isomers were exclusively obtained. Next, the *p*-trifluoromethyl benzene sulfonyl or *p*-nitrile benzenesulfonyl derivatives also successfully participated in the reaction, and afforded the corresponding 1,3-difunctionalization products in 86% and 69% yield. However, the *ortho*- methyl group substituted triazole derivative furnished the product **116e** in only moderate yield (Scheme **65**). The 2,4,6-tri-isopropyl phenyl substituted triazole was well compatible and afforded the product **116f** in excellent yield (Scheme **65**). To our surprise, methyl or an iso-propyl group substituted triazoles were also tolerated and the 1,3-difunctionalization product **116g** and **116h** were obtained in moderate to good yield (Scheme **65**).

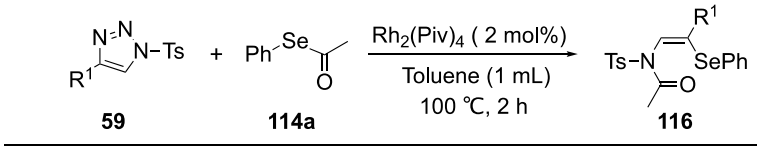
We next studied the influence of different substitutions in all positions on the aromatic ring of the 1,2,3-triazoles. When triazoles with either *para*-methyl or *tert*-butyl were used, the corresponding products **(116i, 116m)** were isolated in slightly excellent yields. Different halogen groups like fluoro, chloro and bromo were compatible under the optimized reaction conditions **(116j–116l)**, and the corresponding 1,3-difunctionalization products were obtained in good to excellent yields. Only in the case of a *para*-bromo substituent,

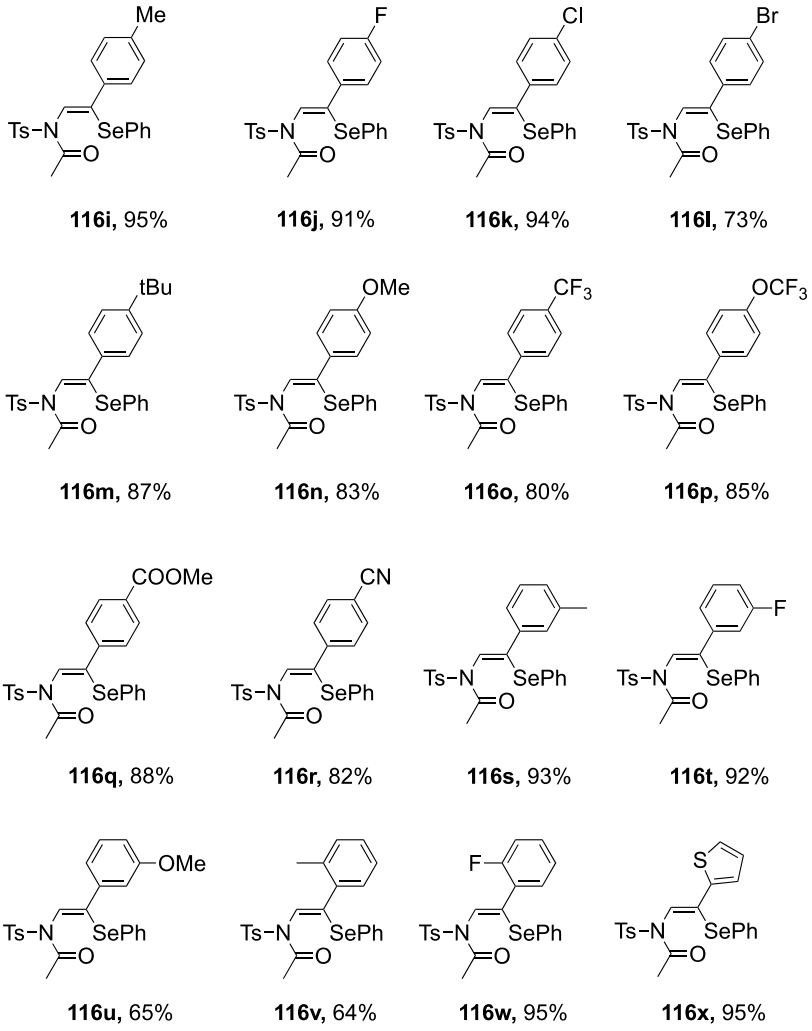


Scheme 65: Scope of different N-protecting groups

the product was obtained in a slightly reduced yield. The electron-donating methoxy group was also tolerated and formed the desired product in 83% yield. To our delight, different electron withdrawing groups in the *papa* position of aryl of 1,2,3-triazoles were completely compatible under optimal conditions, such as trifluoromethyl, nitrile or ester, and the 1,3-difunctionalization products were afforded in good yield **(116o–116r)**. In addition, different substituents at the *ortho*- or *meta*-position of the triazoles were well tolerated and the corresponding products were obtained in good to excellent yield **(116s–116w)**. Only when the methyl group in the *meta*-position of the triazole in this case, the yield of the 1,3-difunctionalization product was only 64%. Surprisingly, heteroaryl-substituted triazoles were found to be suitable substrates and provided the corresponding products in excellent yields (Scheme **66, 116x**).

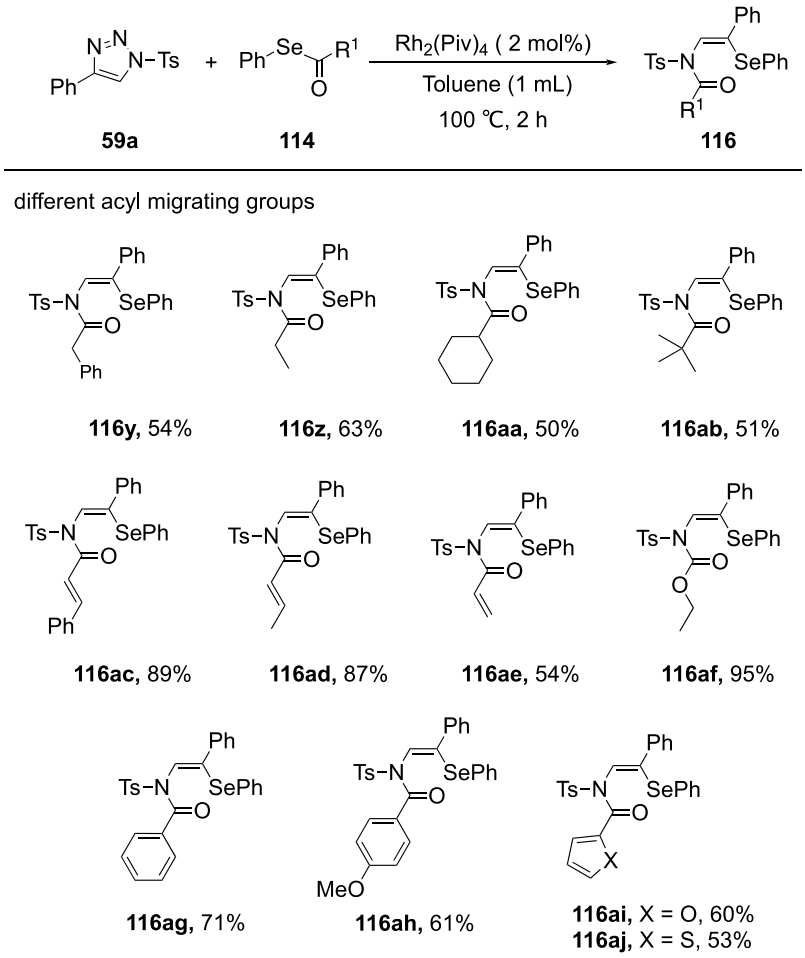
Next, we explored the scope of our protocol by employing differently substituted aliphatic acyl selenides. First, the different primary, secondary, and tertiary hydrocarbon substituted acyl selenides also were well tolerated under the standard conditions, affording the corresponding products in moderate yields (Scheme **67**). The ester group substituted acyl selenides was also converted into the corresponding 1,3-difunctionalization product in 95% yield. Then benzoyl selenides and methoxy substituted aryl substituent of acyl selenides were also investigated, which underwent smooth reactions to afford product **116ag–116ah** in good yields. Various heteroaryl-substituted acyl selenides **116ai** and **116aj** were also providing the corresponding 1,3-difunctionalization product in 60% and 53% yield. Subsequently, unsaturated acyl selenides were well-tolerated under the optimized condition and the 1,3-difunctionalization products were isolated in good to excellent yields (Scheme **67**).



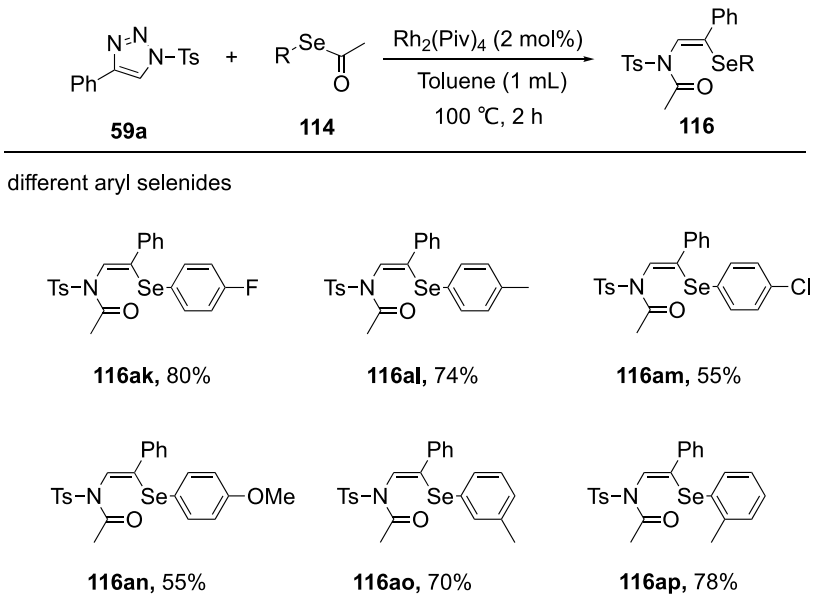


Scheme 66: Scope of different triazoles

We next studied the reaction of different substitution patterns on the aromatic ring of the acyl selenide with *N*-sulfonyl 1,2,3-triazole, such as *para*-methoxy, *para*-methyl and *para*-halogen substituents, and the corresponding 1,3-difunctionalization product were isolated in moderate to high yields (Scheme **68**, **116ak–116an**). When the methyl group in the *ortho*- or *meta*-position of the aromatic ring of the acyl selenide were used, the reactions also worked smoothly and gave moderate yields (Scheme **68, 116ao–116ap**).



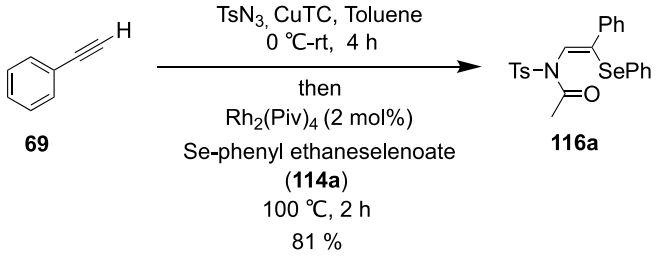
Scheme 67: Scope of different acyl selenides



Scheme 68: Scope of different acyl selenides

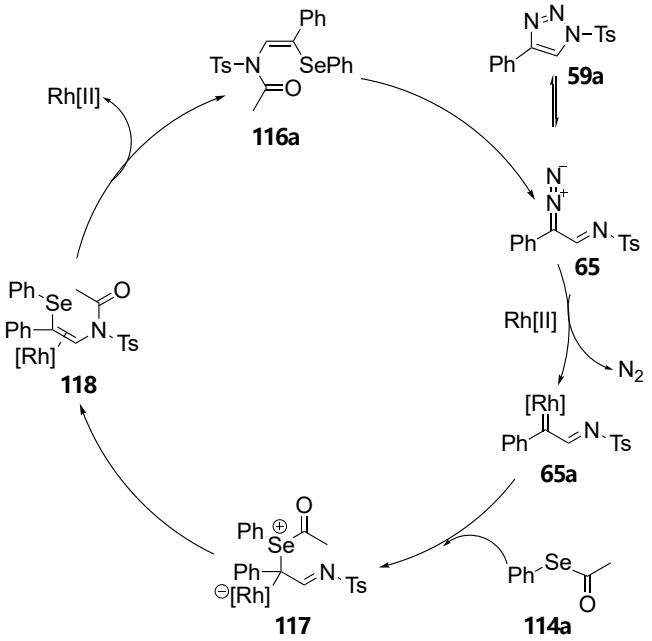
Furthermore, we also studied the one-pot conversion of alkyne to 1,3-difunctionalization enamide product **116a**. As far as we know, triazoles can be synthesized from alkyne **69** and

azide in the presence of copper catalyst. Here, we used phenylacetylene and tosyl azide to react with CuTC in toluene for 4 h at 0 °C-rt. Then, $Rh_2(Piv)_4$ and acyl selenide were added to the reaction mixture and, after heating the reaction mixture to 100 °C for 2 h, the product **116a** was obtained in 81% yield (Scheme **69**).



Scheme 69: One-pot experiment

From DFT calculations, we propose a possible mechanism. The α-diazoimine was first produced through the rearrangement of *N*-sulfonyl-1,2,3-triazole, followed by the formation of the rhodium carbenoid **65a** via the extrusion of nitrogen in the presence of Rh(II) catalyst. Further, an additional reaction had occurred with acyl selenide **114a**, and formed the metal-bound ylide intermediate **117**. The rhodium catalyst then disengages from its initial binding location and participates in an η^2-coordination to the electron-rich double bond. Finally, the Rh(II) catalyst was released, generating the 1,3-difunctionalization product **116a** (Scheme **70**).



Scheme 70: A plausible mechanism

3.5 Conclusion

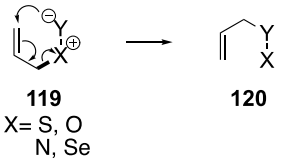
In summary, in this chapter, we revealed the rhodium-catalyzed reaction of triazoles with different sulfides or selenides under thermal conditions. Firstly, we exhibited the rhodium-catalyzed enamine homologation reactions of triazoles with cyclopropylmethyl sulfides, which underwent the intramolecular alkylation reaction to form cyclopropylmethyl-

substituted enamides. Secondly, in the presence of a rhodium catalyst, cascade reactions of triazoles with organoselenium compounds were reported. These reactions proceed via a free ylide intermediate, which underwent the [2,3]-sigmatropic rearrangement and selenium-mediated radical cyclization reaction to generate the final dihydropyrroles. However, the cinnamyl selenides will form the 1,3-difunctionalization product via cascade rearrangement reactions. In the third chapter, the synthesis of highly stereoselective α-seleno enamides in the presence of triazoles and acyl selenides was reported. By DFT calculations, this reaction went through a direct 1,3-difunctionalization process without the formation of metal-bound or free ylide intermediates.

4. Metal-Free Sigmatropic Rearrangement

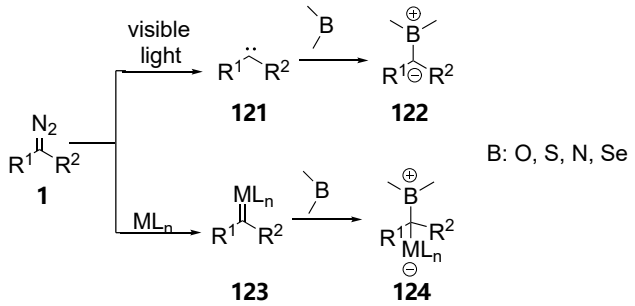
4.1 Brief Introduction: [2,3]-Sigmatropic rearrangement

[2,3]-sigmatropic rearrangement reactions were first discovered in the middle of 20th century.[138-140] Since then, this type of rearrangement reactions has been studied widely, and has been extensively used in the synthesis of various functional molecules and natural products.[77, 141-145] Typically, these reactions occur with charged or neutral substrates undergoing a 6π-electrocyclic transition state, and in this process, two adjacent σ-bonds are broken and a new bond is formed (Scheme **71**).



Scheme 71: [2,3]-Sigmatropic rearrangement of ylide

The ylides for the sigmatropic rearrangement reactions can be accessed by the reaction of electrophilic metal carbene with nucleophile, this strategy was used to develop catalytic reactions, which has been the focus of research in the past two decades. The metal complex-associated ylide or a free ylide was formed by the electron-deficient carbenic carbon of the carbene intermediate with a pair of non-bonding electrons. Generally, the non-bonding electrons come from Lewis base, such as sulfides, amines or ethers. Then, a variety of transformations have been performed on these ylide intermediates, among them, [2,3]-sigmatropic rearrangement reaction is a common type (Scheme **72**).

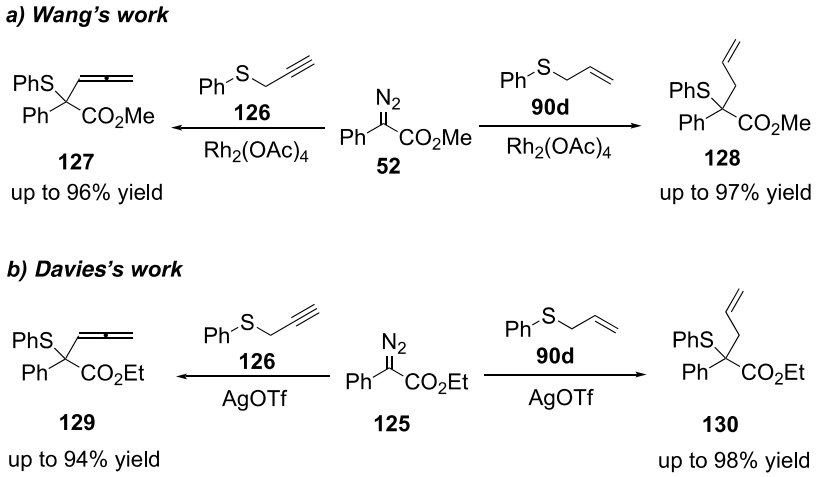


Scheme 72: Formation of ylides

[2,3]-Sigmatropic rearrangement of sulfonium ylides generated from carbene species is an effective strategy for the construction of C-S bonds. Early examples were reported by the group of Kelley and Sutherland.[139] Subsequently, in 1981, Doyle's group reported a C-C bond forming reaction under Rh(II) catalysis via intermolecular formation of a sulfonium

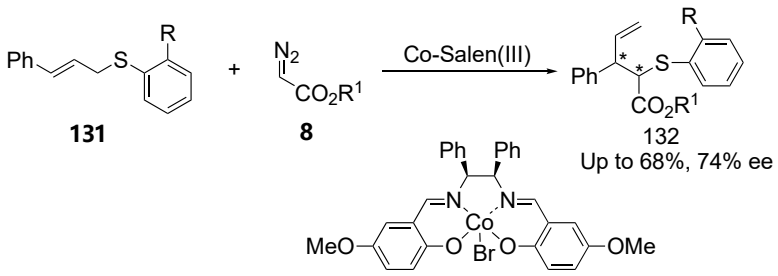
ylide. This yield was formed by [2,3]-sigmatropic rearrangements between ethyl diazoacetate and allyl sulfides[45].

Over the previous three decades, this strategy has received considerable attention and has been developed very quickly. In 2007, Wang's group first reported the [2,3]-sigmatropic rearrangement reaction of sulfur ylides generated from the reaction of aryl diazo acetate and allyl and propargyl sulphide, this reaction can be efficiently carried out in water in the presence of rhodium(II) catalysts.[146] This environmentally friendly approach afforded the corresponding rearrangement products in good to excellent yields. In 2010, the Davies group first developed a silver-catalyzed [2,3]-sigmatropic rearrangement reaction of allyl and propargyl sulfides with diazo compounds.[147] In this report, the new carbon-carbon bond was constructed via sulfonium ylide intermediates with high efficiency (Scheme **73**).



Scheme 73: Metal-catalyzed [2,3]-sigmatropic rearrangement of sulfur ylides

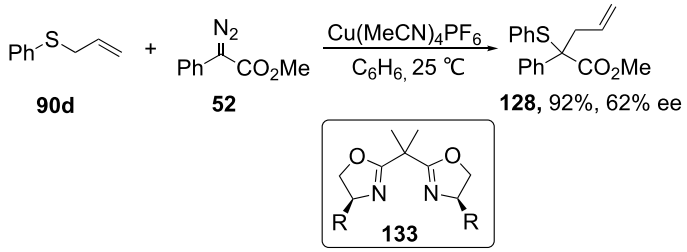
In addition, Uemura's group revealed the pioneering work about the enantioselective catalytic [2,3]-sigmatropic rearrangement of sulfur ylides in 1995.[135] Since then, the symmetric catalysis in [2,3]-sigmatropic rearrangement of sulfur ylides has attracted considerable attention.[148-152] In 1997, Katsuki and co-worker[153] reported the stereoselective [2,3]-sigmatropic rearrangement of sulfur ylides that was prepared via the reaction of cinnamyl phenyl sulfide with diazoacetate using Co-salen complex as a catalyst (Scheme **74**). These reactions proceeded with good enantioselectivity (up to 74% ee).



Scheme 74: Co-salen catalyzed asymmetric [2,3]-sigmatropic rearrangement.

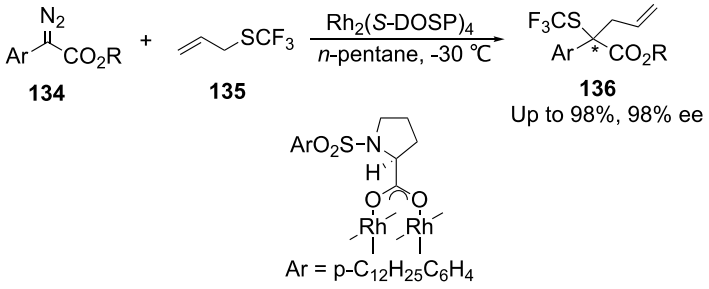
In a related study, Wang and co-worker explored some works on highly enantioselectivities [2,3]-sigmatropic rearrangement of sulfur ylides. In 2002, they reported a catalytic

asymmetric [2,3]-sigmatropic rearrangement reactions of aryldiazoacetates with allyl sulfides in the presence of chiral Rh(II) and Cu(I) catalysts.[150] This method employed sulfur ylides intermediates to obtain the sigmatropic rearrangement products with moderate to good enantioselectivity (52-78% ee). After this time and in order to improve the level of enantioselectivity, they explored a double asymmetric induction approach, by combining a chiral camphor sultam auxiliary and Cu(I) catalyst with chiral ligands.[152]



Scheme 75: Copper catalyzed [2,3]-sigmatropic rearrangement of sulfur ylides

Subsequently, in 2017, Wang and co-worker reported a chiral Rh(II)- and Cu(I)-catalyzed highly enantioselective trifluoromethylthiolation reactions.[85] In this process a chiral C(sp^3)–SCF_3 bond was formed via asymmetric [2,3]-sigmatropic rearrangements of sulfonium ylides generated from metal carbenes and sulfides. Up to 98% yield and 98% ee were achieved (Scheme **76**).

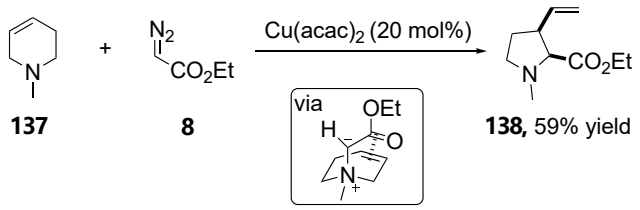


Scheme 76: Catalytic asymmetric trifluoromethylthiolation

Compared to sulfur ylides, [2,3]-sigmatropic rearrangements of oxonium ylides and ammonium ylides also have received much attention.[154, 155] Seminal works forming oxonium ylides to construct new C-C bonds were conducted by Davies,[156] Boyer[157, 158] and Yakura.[159] [2,3]-sigmatropic rearrangements of ammonium ylides were less common as compared with the corresponding sulfonium and oxonium ylides. However, [2,3]-rearrangements of ammonium ylides have great synthetic potential, because they could serve as a versatile process for the synthesis of α-amino acid derivatives.[160-162]

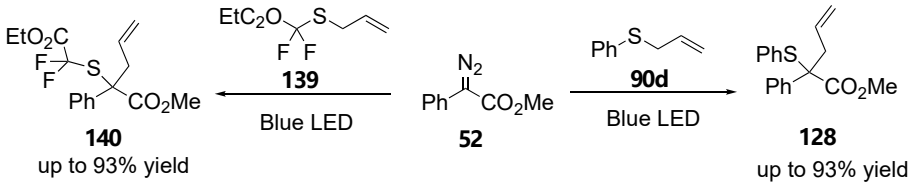
In 2003, Workman and co-workers reported the copper-catalyzed [2,3]-sigmatropic rearrangement of ammonium ylides.[163] The reaction afforded ethyl *cis*-*N*-methyl-3-ethenyl proline from *N*-methyltetrahydropyridine and diazo ethyl diazoacetate in 59% yield, which proceded through an ammonium ylide intermediate (Scheme **77**). The same group had also developed a high-yielding copper-catalyzed [2,3]-sigmatropic rearrangement of ammonium ylides derived from *N*-methyltetrahydropyridines and diazoesters.[164] In the presence of

$Cu(acac)_2$, a range of diazo and amine components were tolerated and the functionalized pyrrolidines were generated in 98% yield.



Scheme 77: Copper-Catalyzed [2,3]-Rearrangement of ammonium ylides

Recent years, photochemical metal-free sigmatropic rearrangements of ylides with diazo compounds had received much more attention. A series of examples have been explored.[20, 22, 30 165] As the strategy contains many advantages, such as, no need expensive, precious metal catalysts, mild reaction conditions and simple operation. Our group has been reported some examples about the [2,3]-sigmatropic rearrangement reaction with diazo in the visible light conditions. In 2018, we described an efficient method to synthesize homoallylic sulfides in the presence of donor–acceptor diazoalkanes, the synthesis involved a free ylide intermediate and gave the product in high yield.[24] Subsequently, we reported the synthesis of valuable fluorinated homoallylic sulfides under metal-free conditions.[166] This reaction proceded via a free ylide intermediate, which was derived from fluorinated allylic sulfides and donor–acceptor diazoalkanes (Scheme **78**).



Scheme 78: Sigmatropic rearrangement under metal-free conditions

4.2 Metel-free [2,3]-sigmatropic rearrangement reactions of ammonium ylides

This part of this thesis was done in collaboration with Feifei He. All experiments done by Feifei He are highlighted in Italic.

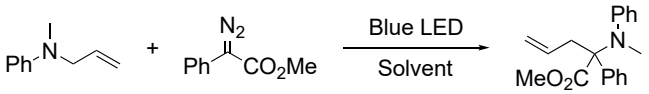
Even though there are numerous studies about on [2,3]-sigmatropic rearrangements of ammonium ylides with diazo compounds, the rearrangements of ammonium ylides under visible light conditions remains blank. Hence, we were attracted to investigate [2,3]-sigmatropic rearrangement processes of ammonium ylides under irradiation with blue LEDs.

We hypothesized that the ammonium ylides would be formed from diazoacetate and amines under photochemical conditions. We thus set out our investigations by studying the reaction of methyl phenyldiazoacetate **52** with *N*-allyl-*N*-methylaniline **141a** under irradiation with blue LEDs (470 nm) as a model reaction. First, several solvents were investigated. When MeCN was used as the solvent, 42% yield of disubstituted amino ester product **142a** was isolated (Table **9**, entry 1). Later, different polar and apolar solvents were

used, such as THF, cyclohexane or DCE, and the corresponding products amino ester **142a** were received in moderate yields (Table **9**, entry 2-7), among them, DCM turned out to be the most suitable reaction solvent (Table **9**, entry 7).

In order to improve the yield, different factors were screened. When 2.0 equivalent of *N*-allyl-*N*-methylaniline was added in DCM solvent under blue LED irradiation, no improvement was observed. Further, when increasing the equivalent of **141a** to 5.0 equivalent, the product was obtained only in reduced yield (Table **9**, entry 8-9). Similarly, the concentration of reactions was also tested. Whether to increase the concentration of the reaction solution or decrease it, no further improvements in the yield of product **142a** were found (Table **9**, entry 10-11). Next, a syringe pump was used to add methyl phenyldiazoacetate over five hours, and the yield of **142a** decreased to 59% (Table **9**, entry 12). No desired product was observed without irradiation of light, indicating irradiation was essential to this rearrangement reaction (Table **9**, entry 13).

Table 9: Optimization of metal-free photochemical rearrangement reactions



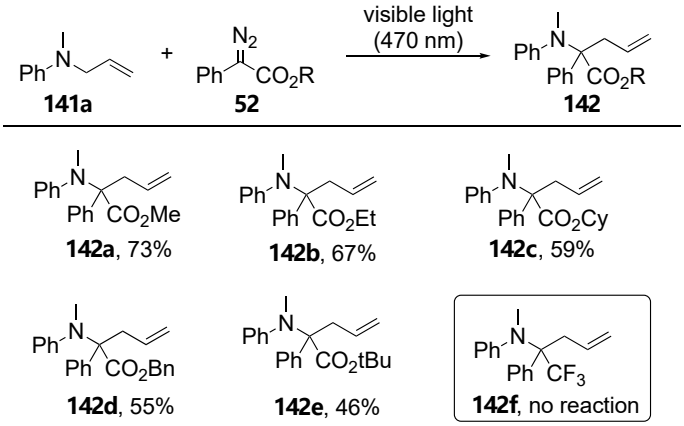
141a **52** **142a**

Entry[a]	Ratio 141a/52	Solvent	Conc.(M)	Yield 142a (%)[b]
1	1:5	MeCN	0.2	42
2	1:5	THF	0.2	22
3	1:5	EtOAc	0.2	60
4	1:5	cyclohexane	0.2	59
5	1:5	1,2-DCE	0.2	47
6	1:5	$CHCl_3$	0.2	47
7	1:5	DCM	0.2	73
8	5:1	DCM	0.2	59
9	2:1	DCM	0.2	70
10	1:5	DCM	0.4	60
11	1:5	DCM	0.1	53
12[c]	1:5	DCM	0.2	59
13[d]	1:5	DCM	0.2	NR

[a]*Reaction conditions*: **141a** and **52** were dissolved in the solvent indicated and stirred at room temperature under irradiation with blue LEDs (470 nm, 3 W) overnight. [b]Isolated yields isolated. [c]Addition of the diazo ester over a period of 5 hours. [d]In the dark condition

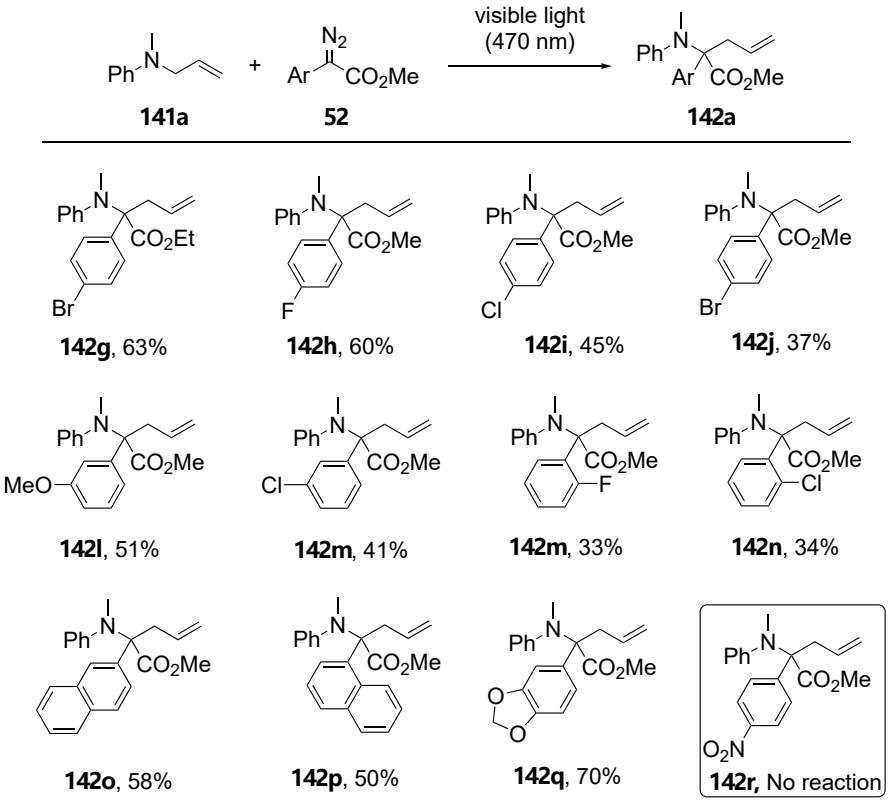
With the optimized reaction conditions in hand, the substrate scope of this reaction was then investigated. First, a series of phenyldiazoacetates were studied. As shown in scheme **79**, various phenyldiazoacetates **142a–142e** reacted smoothly with *N*-allyl-*N*-methylaniline **141a** to afford the corresponding α,α-disubstituted amino ester in moderate to good yields. Not only primary esters, secondary and tertiary hydrocarbon substituted esters were also compatible under the visible light conditions. Among these substrates, phenyldiazoacetate

bearing a benzyl ester group afforded the corresponding benzyl-producted α, α-disubstituted amino ester in 55% yield (Scheme **79**). However, the phenyldiazoacetate including an electron-withdrawing trifluoromethyl group was not tolerated in the standard conditions, and the decomposition of diazo was observed (Scheme **79, 142f**).



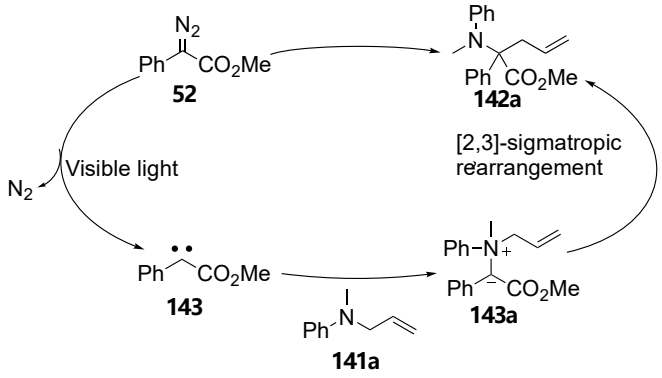
Scheme 79: Scope of different phenyldiazoacetates

Next, we investigated the reaction scope with respect to the substitution pattern of the aryldiazoacetate. As shown in Scheme **80**, various functional-group-substituted aryl diazoacetates were recognized as effective carbene precursors for this sigmatropic rearrangement reactions. The halogen groups at the *para* position of the aryl ring were well tolerated, and the corresponding rearrangement products were obtained in moderate yields (Scheme **80**, **142g–142j**). When halogen groups were at the *ortho* or *meta* position, the expected products **142m–142n** were obtained with 33%-41% yield. Furthermore, the electron-donating methoxy group was also tolerated under the standard reaction conditions, which provided the corresponding rearrangement product in 51% yield. To our surprise, the naphthalene-substituted and benzodioxole-substituted diazoacetates were also compatible in this system, affording the products in moderate to good yields (Scheme **80**, **142o–142p**). When using the strongly electron-withdrawing nitro group in the *para* position of the aromatic ring, this reaction did not work and only decomposition of the diazoacetate was noticed (Scheme **80**, **142r**).



Scheme 80: Scope of different aryl diazoacetates

On the basis of our previous reports and literature reports, we proposed a similar mechanism of this [2,3]-sigmatropic rearrangements. The initial diazoacetates **52** generated an electrophilic free carbene intermediate **143** under photochemical conditions, which underwent a nucleophilic addition reaction with allylamine **141a** to form an ammonium ylide **143a.** Finally, the α, α-disubstituted amino esters **142a** was generated by the [2,3]-sigmatropic rearrangement of ammonium ylide (Scheme **81**).



Scheme 81: Proposed mechanism of the photochemical [2,3]-sigmatropic rearrangement reaction

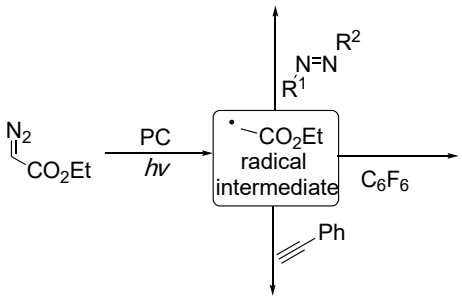
4.3 Conclusion

In conclusion, in this chapter, we presented a practical method for rearrangement of ammonium ylides with donor-acceptor diazoalkanes under visible-light photolysis

conditions. A variety of aryl diazoacetates and amines were tolerated in this method. offering a range of amino esters in moderate to excellent yields.

5. Outlook

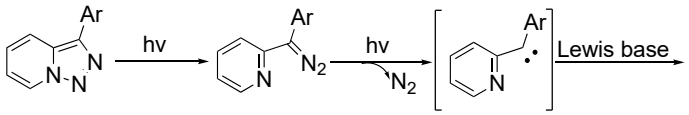
Despite diazo compounds have been studied for many years, and many carbene transfer reactions, such as cyclopropanation, C−H insertion and X−H insertion have been established, the reactions of radical addition that divide from diazo compounds in the presence of photocatalyst have rarely been undertaken. Current reports primarily focus on the radical addition reaction of ethyl diazoacetate with double bonds. Various radical acceptors should be used in this type of reaction. For example, ethyl diazoacetate could release one molecule of nitrogen with protonation to generate a carbon-centered radical, which reacts with phenylacetylene, hexafluorobenzene, or N=N bonds, to furnish final corresponding products (Scheme **82**).



Scheme 82: Potential radical addition

Furthermore, the asymmetric photoredox reactions of diazo compounds have limited examples. The development of new chiral metal catalyst in combination with photoredox catalysts for the effective asymmetric construction of C−N or C−C bond is still highly desirable.

Regarding the transfer reactions of triazoles, pyridotriazoles as hidden carbene precursors, have been developed in transition metal-catalyzed denitrogenative transformations. However, the reports of novel metal-free transformations of pyridotriazoles are limited, and just Gevorgyan's group developed the light-induced X–H insertion and cyclopropanation reactions of pyridotriazoles. Various other denitrogenative transformation of pyridotriazoles can also be achieved, such as, forming the free ylide with Lewis bases to obtain the rearrangement product (Scheme **83**).



Scheme 83: Denitrogenative transformations of pyridotriazoles

In addition, no one has studied photochemical carbene transfer reaction of *N*-sulfonyl-1,2,3-triazoles, whether we can realize that these triazole can form a carbene intermediate under visible light conditions by introducing different substituents?

6. Experimental Data

6.1 General Information

NMR spectroscopy

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

IR spectra

IR spectra were recorded on a Jasco FT/IR-420 and a Perkin Elmer Spectrum 100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

HRMS spectra

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

GC/MS spectra

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

HPLC spectra

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

Thin layer chromatography

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

Solvents

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

UV-Vis spectra

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

LEDs

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

Reagents

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

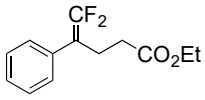
6.2 Experimental Data

6.2.1 Photocatalytic gem-Difluoroolefination Reactions

General procedure of Photocatalytic gem-Difluoroolefination Reactions with Diazoacetates

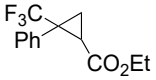
Typical experimental procedure: DABCO (45.0 mg, 0.4 mmol, 2.0 equiv.) and $(Ir[dF(CF_3)ppy]_2(bpy))PF_6$ (4.0 mg, 2.0 mol%) were added to a reaction tube with magnetic stir bar. The tube was capped. After evacuation and backfilling with argon three times, anhydrous MeCN (2.0 mL, 0.1 M) was added via a syringe, followed by the addition of trifluoromethyl alkene (0.2 mmol, 1.0 equiv.), and the corresponding diazo compound (0.4 mmol, 2.0 equiv.). The resulting solution was irradiated by a 25 W blue LED with stirring at a distance of ~1.5 cm (with cooling by the fan) at 25 °C for about 15 h. The crude mixture was purified by column chromatography on silica gel with hexanes/ethyl acetate mixtures as eluent to give the corresponding products.

Ethyl 5,5-difluoro-4-phenylpent-4-enoate **(27a)**



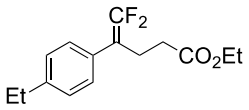
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 4.01 (q, *J* = 7.2 Hz, 2H), 2.74 – 2.61 (m, 2H), 2.33 – 2.23 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.4, 152.6 (d, *J* = 290.2 Hz), 132.8 (t, *J* = 3.0 Hz), 128.5, 128.3 (t, *J* = 3.3 Hz), 127.5, 91.2 (dd, *J* = 20.7, 15.6 Hz), 60.4, 32.6 (t, *J* = 2.8 Hz), 23.4, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.65 (d, *J* = 41.2 Hz, 1F), -90.78 (d, *J* = 41.0 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{14}O_2F_2Na^+$: 263.0854; Found: 263.0861.

Ethyl 2-phenyl-2-(trifluoromethyl)cyclopropane-1-carboxylate **(28)**



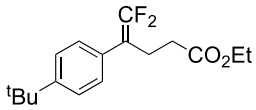
colorless oil ; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.52 (dd, *J* = 7.3, 2.2 Hz, 2.6H), 7.42 – 7.37 (m, 6H), 7.37 – 7.33 (m, 3H), 4.38 – 4.19 (m, 2.7H), 4.02 – 3.90 (m, 2H), 2.51 (dd, *J* = 8.7, 6.3 Hz, 1H), 2.32 – 2.25 (m, 1.3H), 2.07 (dd, *J* = 7.3, 5.8 Hz, 1.4H), 1.93 – 1.86 (m, 1H), 1.74 (dd, *J* = 8.7, 5.5 Hz, 1H), 1.55 – 1.49 (m, 1.4H), 1.35 (t, *J* = 7.1 Hz, 4H), 1.05 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 168.6, 168.06, 135.8, 131.4, 131.1, 130.7, 128.8, 128.7, 128.5, 128.3, 125.1 (q, *J* = 275.4 Hz), 25.03 (q, *J* = 274.8 Hz), 61.4, 61.04, 35.7 (q, *J* = 33.6 Hz).35.6 (q, *J* = 34.1 Hz), 27.2, 23.6, 14.3 (q, *J* = 2.3 Hz), 14.2 (q, *J* = 2.4 Hz), 14.08, 13.8 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -65.28, -70.48 ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{13}O_2F_3Na^+$: 281.0759; Found: 281.0759.

Ethyl 4-(4-ethylphenyl)-5,5-difluoropent-4-enoate (**27b**)



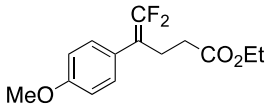
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.15 – 7.09 (m, 4H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.70 – 2.62 (m, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.33 – 2.20 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.14 (t, *J* = 6.5 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.5, 153.5 (t, *J* = 288.9 Hz), 143.6, 129.9, 128.2 (t, *J* = 3.2 Hz), 128.0, 91.0 (dd, *J* = 19.5, 16.6 Hz), 60.4, 32.6 (t, *J* = 2.9 Hz), 28.5, 23.4, 15.4, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -91.03 (d, *J* = 42 Hz, 1F), -91.12 (d, *J* = 48 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{18}O_2F_2Na^+$: 291.1167; Found: 291.1165.

Ethyl 4-(4-(*tert*-butyl)phenyl)-5,5-difluoropent-4-enoate (**27c**)



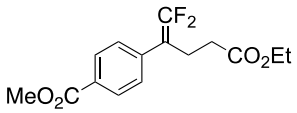
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = δ 7.32 – 7.28 (m, 2H), 7.18 – 7.14 (m, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.70 – 2.61 (m, 2H), 2.29 (dd, *J* = 8.6, 7.1 Hz, 2H), 1.25 (s, 9H), 1.14 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.5, 153.5 (dd, *J* = 290.1, 288.0 Hz), 150.4, 129.6 (t, *J* = 3.2 Hz), 127.8 (t, *J* = 3.3 Hz), 125.4, 90.9 (dd, *J* = 20.7, 15.2 Hz), 60.4, 34.5, 32.7 (t, *J* = 2.8 Hz), 31.2, 23.3, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.83 (d, *J* = 42.3 Hz, 1F), -90.96 (d, *J* = 42.1 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{22}O_2F_2Na^+$: 319.1480; Found: 319.1480.

Ethyl 5,5-difluoro-4-(4-methoxyphenyl)pent-4-enoate (**27d**)



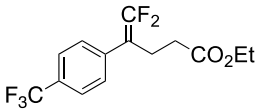
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.26 – 7.19 (m, 2H), 6.94 – 6.90 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.80 – 2.67 (m, 2H), 2.41 – 2.30 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.5, 158.8, 152.4 (dd, *J* = 288.7 Hz), 129.4 (t, *J* = 3.1 Hz), 124.8, 114.0, 90.6 (dd, *J* = 20.5, 16.2 Hz), 60.4, 55.2, 32.5 (t, *J* = 2.9 Hz), 23.5, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -91.56 (d, *J* = 43.9 Hz, 1F), -91.67 (d, *J* = 43.6 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{16}O_3F_2Na^+$: 293.0959; Found: 293.0953.

Methyl 4-(5-ethoxy-1,1-difluoro-5-oxopent-1-en-2-yl)benzoate (**27e**)



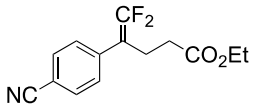
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.28 (m, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 2.70 (tt, *J* = 8.0, 2.3 Hz, 2H), 2.28 (t, *J* = 7.7 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.1, 166.6, 153.8 (dd, *J* = 292.7, 289.7 Hz), 137.6 (t, *J* = 4.0 Hz), 129.8, 129.2, 128.2 (t, *J* = 3.4 Hz), 90.9 (dd, *J* = 22.1, 14.2 Hz), 60.5, 52.1, 32.6 – 32.4 (m), 23.09, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -88.18 (dd, *J* = 36.1, 2.5 Hz, 1F), -88.52 (d, *J* = 36.2 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M + Na]^+$ Calcd. for $C_{15}H_{16}O_4F_2Na^+$: 321.0908; Found: 321.0903.

Ethyl 5,5-difluoro-4-(4-(trifluoromethyl)phenyl)pent-4-enoate (**27f**)



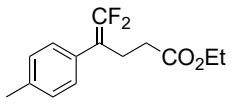
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.55 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.74 – 2.62 (m, 2H), 2.28 (t, *J* = 7.7 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.1, 153.8 (dd, *J* = 289.8, 289.9 Hz), 136.6, 129.7 (d, *J* = 32.8 Hz), 128.6 (t, *J* = 3.3 Hz), 125.5 (q, *J* = 3.8 Hz), 123.9 (d, *J* = 271.9 Hz), 90.6 (dd, *J* = 23.3, 14.3 Hz), 60.6, 32.4 (t, *J* = 2.9 Hz), 23.1, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -62.75(3F), -87.17 – -91.96 (m, 2F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{13}O_2F_5Na^+$: 331.0727; Found: 331.0728.

Ethyl 4-(4-cyanophenyl)-5,5-difluoropent-4-enoate (**27g**)



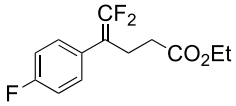
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.61 – 7.57 (m, 2H), 7.38 – 7.34 (m, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.74 – 2.63 (m, 2H), 2.28 (t, *J* = 7.7 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 171.9, 154.02 (dd, *J* = 291.0 Hz, 290.7 Hz), 137.9(t, *J* = 4.3 Hz), 132.3, 128.9 (t, *J* = 3.5 Hz), 118.4, 111.3, 90.6 (dd, *J* = 22.8, 13.7 Hz), 60.6, 32.4 (d, *J* = 2.7 Hz), 22.9, 14.1.ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -86.36 – -87.08 (m, 1F), -87.45 (d, *J* = 33.7 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{13}O_2NF_2Na^+$: 288.0806; Found: 288.0805.

Ethyl 5,5-difluoro-4-(*p*-tolyl)pent-4-enoate (**27h**)



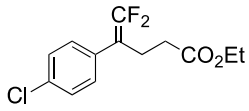
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.16 – 7.01 (m, 4H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.73 – 2.57 (m, 2H), 2.35 – 2.15 (m, 5H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.5, 153.5 (t, *J* = 288.8 Hz), 137.3, 129.7, 129.2, 128.1 (t, *J* = 3.2 Hz), 90.9 (t, *J* = 18.2 Hz), 60.4, 32.6 (t, *J* = 2.7 Hz), 23.4, 21.1, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -91.12 (2F) ppm. **HRMS** (APCI): *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_2F_2^+$: 255.1190; Found: 255.1191.

Ethyl 5,5-difluoro-4-(4-fluorophenyl)pent-4-enoate (**27i**)



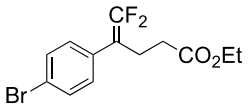
colorless oil ; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.21 – 7.16 (m, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.72 – 2.56 (m, 2H), 2.26 (t, *J* = 7.7 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.3, 162.03 (d, *J* = 247.4 Hz), 130.2 – 129.6 (m), 128.8 – 128.3 (m), 115.6, 115.5, 90.4 (dd, *J* = 21.7, 15.4 Hz), 60.5, 32.4 (t, *J* = 2.9 Hz), 23.5, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.58 (d, *J* = 41.2 Hz, 1F), -90.76 (d, *J* = 41.2 Hz, 1F), -110.99 – -117.56 (m, 1F) ppm. **HRMS** (APCI): *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{14}O_2F_3^+$: 259.0940; Found: 259.0941.

Ethyl 4-(4-chlorophenyl)-5,5-difluoropent-4-enoate (**27j**)



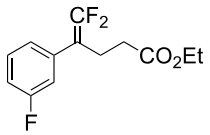
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.29 – 7.24 (m, 2H), 7.18 – 7.13 (m, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.71 – 2.59 (m, 2H), 2.31 – 2.16 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.2, 153.6 (dd, *J* = 290.8, 288.9 Hz), 133.4, 131.2 (t, *J* = 3.1 Hz), 129.6 (t, *J* = 3.1 Hz), 128.8, 90.4 (dd, *J* = 21.8, 15.0 Hz), 60.5, 32.4 (t, *J* = 3.0 Hz), 23.2, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -89.67 (dt, *J* = 38.7, 1.8 Hz, 1F), -89.89 (d, *J* = 39.9 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{13}O_2F_2ClNa^+$:297.0464; Found: 297.0464.

Ethyl 4-(4-bromophenyl)-5,5-difluoropent-4-enoate (**27k**)



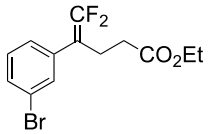
colorless oil ; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.42 (d, *J* = 8.5 Hz, 2H), 7.10 (m, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.70 – 2.58 (m, 2H), 2.31 – 2.19 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.2, 152.5 (d, *J* = 288.5 Hz), 131.7, 129.9 (t, *J* = 3.3 Hz), 121.5, 90.0 (dd, *J* = 23.4, 16.0 Hz), 60.5, 32.4 (t, *J* = 2.8 Hz), 23.2, 14.1 ppm. one carbon is missing **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -89.51 (d, *J* = 39.7 Hz, 1F), -89.75 (d, *J* = 39.0 Hz, 1F) ppm. **HRMS** (APCI): *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{14}O_2F_2BrNa^+$: 319.0139; Found: 319.0139.

Ethyl 5,5-difluoro-4-(3-fluorophenyl)pent-4-enoate (**27l**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.29 – 7.23 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.97 – 6.88 (m, 2H), 4.10 – 3.94 (m, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.28 (t, *J* = 7.7 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.2, 158.7 (dd, *J* = 246.0, 290.0 Hz), 134.9 (d, *J* = 8.3 Hz), 130.0 (d, *J* = 8.5 Hz), 123.9 (t, *J* = 3.2 Hz), 115.4 (t, *J* = 3.4 Hz), 115.2 (t, *J* = 3.6 Hz), 114.5 (d, *J* = 21.1 Hz), 90.5 (dd, *J* = 18.5, 2.5 Hz), 60.5, 32.5 (t, *J* = 2.9 Hz), 23.2, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -89.21 (2F), -112.79 (d, *J* = 6.5 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{14}O_2F_3Na^+$: 259.0940; Found: 259.0937.

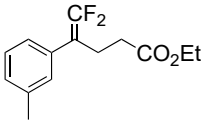
Ethyl 4-(3-bromophenyl)-5,5-difluoropent-4-enoate (**27m**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.38 – 7.36 (m, 1H), 7.36 – 7.34 (m, 1H), 7.17 – 7.15 (m, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.69 – 2.58 (m, 2H), 2.32 – 2.18 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.2, 153.7 (t, *J* = 290.4 Hz), 134.9, 131.3 (t, *J* = 3.4 Hz), 130.6, 130.0, 127.0 (t, *J* = 3.1 Hz), 122.6, 90.4 (t, *J* = 18.5 Hz), 60.6, 32.4 (t, *J* = 2.9 Hz), 23.2, 14.1 ppm.

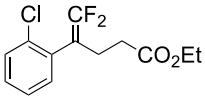
^{19}F NMR (565 MHz, Chloroform-*d*): δ = -89.24 (2F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{13}O_2F_2BrNa^+$: 340.9959; Found: 340.9957.

Ethyl 5,5-difluoro-4-(*m*-tolyl)pent-4-enoate (**27n**)



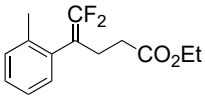
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.19 – 7.15 (m, 1H), 7.04 – 7.00 (m, 3H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.65 (tt, *J* = 7.9, 2.3 Hz, 2H), 2.32 – 2.21 (m, 5H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.5, 153.5 (dd, *J* = 289.8, 288.0 Hz), 138.1, 132.7 (t, *J* = 3.2 Hz), 129.0 (t, *J* = 3.0 Hz), 128.4, 128.3, 125.4 (t, *J* = 3.0 Hz), 91.2 (dd, *J* = 20.8, 15.3 Hz), 60.4, 32.6 (t, *J* = 3.0 Hz), 23.4, 21.4, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.82 (d, *J* = 42.1 Hz, 1F), -90.90 – -91.03 (m, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_2F_2^+$: 255.1191; Found: 255.1189.

Ethyl 4-(2-chlorophenyl)-5,5-difluoropent-4-enoate (**27o**)



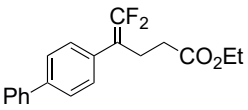
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.37 – 7.33 (m, 1H), 7.23 – 7.17 (m, 2H), 7.16 – 7.11 (m, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.70 – 2.59 (m, 2H), 2.26 (t, *J* = 7.7 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.3, 153.3 (dd, *J* = 289.8, 287.5 Hz), 134.4 (d, *J* = 3.6 Hz), 131.8 (d, *J* = 6.4 Hz), 131.5 (dd, *J* = 2.7, 1.5 Hz), 129.8, 129.4, 126.8, 89.1 (dd, *J* = 24.2, 18.5 Hz), 60.5, 32.0 (t, *J* = 2.9 Hz), 23.7 (d, *J* = 2.1 Hz), 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -87.22 (d, *J* = 38.1 Hz, 1F), -91.67 – -92.82 (m, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{13}O_2F_2ClNa^+$: 297.0464; Found: 297.0462.

Ethyl 5,5-difluoro-4-(*o*-tolyl)pent-4-enoate (**27p**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.17 – 7.13 (m, 2H), 7.13 – 7.08 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.58 (tt, *J* = 7.9, 2.2 Hz, 2H), 2.24 (t, *J* = 7.7 Hz, 2H), 2.19 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.4, 152.6 (dd, *J* = 289.3, 285.6 Hz), 137.0 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 4.2 Hz), 130.3, 129.7 (d, *J* = 3.6 Hz), 128.0, 125.8, 89.7 (dd, *J* = 20.9, 19.5 Hz), 60.5, 32.0 (t, *J* = 3.0 Hz), 24.3 (d, *J* = 2.0 Hz), 19.3, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -88.80 (d, *J* = 42.4 Hz, 1F), -93.17 – -93.81 (m, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{16}O_2F_2Na^+$: 227.1010; Found: 227.1010.

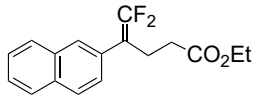
Ethyl 4-([1,1'-biphenyl]-4-yl)-5,5-difluoropent-4-enoate (**27q**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.55 – 7.48 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.26 (m, 3H), 4.10 – 3.89 (m, 2H), 2.77 – 2.66 (m, 2H), 2.32 (t, *J* = 7.8 Hz, 2H), 1.15 (m, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.4, 153.6 (dd, *J* = 288.5, 288.7 Hz), 140.4, 140.3, 131.7 (t, *J* =

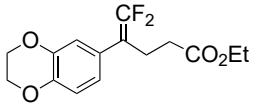
3.6 Hz), 128.8, 128.6 (t, *J* = 3.3 Hz), 127.4, 127.2, 127.0, 90.9 (dd, *J* = 21.4, 14.9 Hz), 60.5, 32.6 (t, *J* = 2.8 Hz), 23.3, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -89.98 (d, *J* = 40.2 Hz, 1F), -90.19 (d, *J* = 40.1 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{18}O_2F_2Na^+$: 339.1167; Found: 339.1173.

Ethyl 5,5-difluoro-4-(naphthalen-2-yl)pent-4-enoate (**27r**)



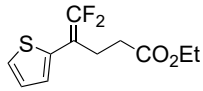
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.79 – 7.72 (m, 3H), 7.70 – 7.66 (m, 1H), 7.44 – 7.39 (m, 2H), 7.36 – 7.31 (m, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.82 – 2.73 (m, 2H), 2.36 – 2.25 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.4, 153.8 (dd, *J* = 290.5, 288.4 Hz), 133.2, 132.5, 130.1 (t, *J* = 3.7 Hz), 128.2, 127.9, 127.6, 127.4 (t, *J* = 3.3 Hz), 126.3, 126.2, 126.0 (t, *J* = 3.2 Hz), 91.3 (dd, *J* = 21.5, 14.8 Hz), 60.5, 32.6 (t, *J* = 2.8 Hz), 23.4, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -89.94 – -90.17 (m, 1F), -90.40 (d, *J* = 40.2 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{16}O_2F_2Na^+$: 313.1010; Found: 313.1013.

Ethyl 4-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-5,5-difluoropent-4-enoate (**27s**)



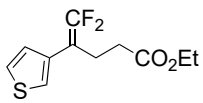
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 6.93 – 6.72 (m, 3H), 4.28 (s, 4H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.75 – 2.62 (m, 2H), 2.42 – 2.27 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.4, 153.4 (dd, *J* = 289.5, 287.6 Hz), 143.4, 142.9, 125.8 (t, *J* = 3.6 Hz), 121.4 (t, *J* = 3.3 Hz), 117.3, 117.2 (t, *J* = 3.3 Hz), 90.5 (dd, *J* = 21.7, 15.1 Hz), 64.39, 64.37, 60.4, 32.5 (t, *J* = 2.9 Hz), 23.4, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.98 (d, *J* = 42.3 Hz, 1F), -91.08 – -91.32 (m, 1F) ppm. **HRMS** (APCI): *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{17}O_4F_2^+$: 299.1089; Found:299.1081.

Ethyl 5,5-difluoro-4-(thiophen-2-yl)pent-4-enoate (**27t**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.25 – 7.20 (m, 1H), 6.99 – 6.91 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.92 – 2.63 (m, 2H), 2.57 – 2.24 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.3, 154.3 (dd, *J* = 289.0, 289.2 Hz), 134.9 (d, *J* = 6.6 Hz), 127.1, 125.4 (t, *J* = 5.0 Hz), 125.1 (dd, *J* = 5.9, 2.7 Hz), 87.3 (dd, *J* = 26.1, 14.1 Hz), 60.6, 32.8 (t, *J* = 2.7 Hz), 23.5 (d, *J* = 2.4 Hz), 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -84.22 (d, *J* = 32.3 Hz, 1F), -90.06 – -90.16 (m, 1F) ppm. **HRMS** (APCI): *m/z*: $[M+H]^+$ Calcd. for $C_{11}H_{13}O_2F_2{}^{32}S^+$: 247.0598; Found: 247.0600.

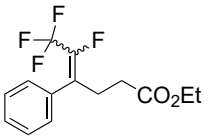
Ethyl 5,5-difluoro-4-(thiophen-3-yl)pent-4-enoate (**27u**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.26 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.16 – 7.13 (m, 1H), 7.10 – 7.06 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.77 – 2.56 (m, 2H), 2.45 – 2.20 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.5, 153.9 (dd, *J* = 293.2, 287.3 Hz), 132.8 (t, *J* =

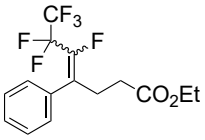
4.3 Hz), 126.8 (dd, *J* = 6.1, 2.4 Hz), 125.8, 122.0 (t, *J* = 5.2 Hz), 87.4 (dd, *J* = 23.4, 13.8 Hz), 60.5, 32.9 (d, *J* = 2.8 Hz), 22.9 (d, *J* = 2.9 Hz), 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -86.77 (d, *J* = 39.1 Hz, 1F), -90.36 – -91.65 (m, 1F) ppm. **HRMS** (APCI): *m/z*: $[M+H]^+$ Calcd. for $C_{11}H_{13}O_2F_2S^+$: 247.0598; Found: 247.0603.

Ethyl -5,6,6,6-tetrafluoro-4-phenylhex-4-enoate (**29**)



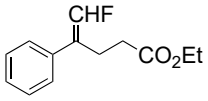
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.37 – 7.32 (m, 1H), 7.31 – 7.28 (m, 2H), 7.24 – 7.20 (m, 1H), 7.11 – 7.07 (m, 1H), 4.00 (dq, *J* = 14.3, 7.1 Hz, 2H), 2.86 – 2.79 (m, 1H), 2.79 – 2.73 (m, 1H), 2.24 (q, *J* = 7.6 Hz, 2H), 1.15 (dt, *J* = 8.5, 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 171.9, 171.8, 133.5 – 133.1 (m), 128.8, 128.6, 128.57, 128.4, 128.2, 128.1 (d, *J* = 2.9 Hz), 127.3 – 126.4 (m), 60.6, 32.5 (d, *J* = 3.9 Hz), 31.2, 27.02 (d, *J* = 5.3 Hz), 25.29 – 25.22 (m), 14.09 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -64.90 (d, *J* = 8.3 Hz, 3F), -65.06 (d, *J* = 9.4 Hz, 3F), -127.86 (q, *J* = 8.5 Hz, 1F), -129.33 (q, *J* = 9.6, 9.0 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{14}O_2F_4Na^+$:313.0822; Found:313.0819.

Ethyl -5,6,6,7,7,7-hexafluoro-4-phenylhept-4-enoate (**30**)



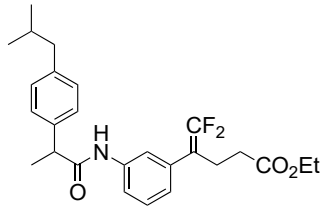
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.34 (dd, *J* = 8.1, 6.4 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.23 – 7.20 (m, 1H), 7.07 (dd, *J* = 6.7, 2.8 Hz, 1H), 4.10 – 3.94 (m, 2H), 2.85 – 2.79 (m, 1H), 2.79 – 2.74 (m, 1H), 2.30 – 2.16 (m, 2H), 1.18 – 1.06 (m, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 171.89, 171.81, 134.1 – 132.5 (m), 131.4 – 129.9 (m), 128.8, 128.6, 128.4, 128.2, 128.15, 128.11 (d, *J* = 3.2 Hz), 110.6 – 116.7 (m), 111.67 – 103.03 (m), 60.7, 60.6, 32.6 (d, *J* = 3.8 Hz), 31.1, 27.7 (d, *J* = 6.3 Hz), 25.2 (t, *J* = 4.5 Hz), 14.08 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -83.44 – -83.65 (m, 3F), -84.09 – -84.35 (m, 3F), -114.30 – -114.81 (m, 2F), -115.30 – -115.89 (m, 2F), -125.04 – -125.27 (m, 1F), -126.66 – -126.88 (m, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{14}O_2F_6Na^+$: 363.0790; Found: 363.0791.

Ethyl (*Z*)-5-fluoro-4-phenylpent-4-enoate (**31**)



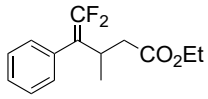
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.29 – 7.26 (m, 1H), 7.24 – 7.21 (m, 1H), 7.21 – 7.18 (m, 3H), 6.70 (d, *J* = 84.6 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.85 – 2.75 (m, 2H), 2.31 (dd, *J* = 8.7, 7.2 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.7, 146.3 (d, *J* = 261.4 Hz), 135.6 (d, *J* = 8.5 Hz), 128.6, 127.7, 126.9 (d, *J* = 3.0 Hz), 123.5 (d, *J* = 8.6 Hz), 60.4, 32.6 (d, *J* = 2.5 Hz), 22.3 (d, *J* = 4.8 Hz), 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -129.34 (dt, *J* = 84.4, 3.0 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{15}O_2FNa^+$:245.0948; Found:245.0947.

Ethyl 5,5-difluoro-4-(3-(2-(4-isobutylphenyl)propanamido)phenyl)pent-4-enoate (**32**)



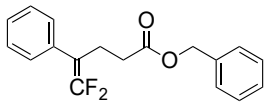
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.31 (s, 1H), 7.28 – 7.24 (m, 1H), 7.19 (d, *J* = 1.9 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.97 (s, 1H), 6.94 – 6.89 (m, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.62 (q, *J* = 7.1 Hz, 1H), 2.62 (tt, *J* = 8.0, 2.3 Hz, 2H), 2.41 (d, *J* = 7.2 Hz, 2H), 2.29 – 2.21 (m, 2H), 1.86 – 1.71 (m, 1H), 1.53 (d, *J* = 3.4 Hz, 3H), 1.51 (s, 1H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.84 (s, 3H), 0.83 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.5, 172.4, 154.5 (dd, *J* = 288.5, 288.4 Hz), 141.1, 138.2, 137.9, 133.6 (t, *J* = 3.7 Hz), 129.9, 129.0, 127.4, 124.1 (d, *J* = 3.6 Hz), 119.4 (d, *J* = 3.1 Hz), 118.8, 90.9 (dd, *J* = 21.7, 14.9 Hz), 60.4, 47.8, 45.0, 32.5 (t, *J* = 2.7 Hz), 30.1, 23.3, 22.3, 18.4, 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.08 (d, *J* = 40.0 Hz, 1F), -90.39 (d, *J* = 40.2 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{26}H_{31}O_3F_2NNa^+$: 466.2164; Found:466.2162.

Ethyl (*R*)-5,5-difluoro-3-methyl-4-phenylpent-4-enoate (**33**)



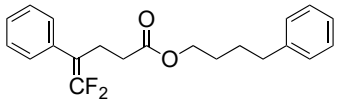
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.41 – 7.32 (m, 3H), 7.26 – 7.22 (m, 2H), 4.19 – 4.13 (m, 2H), 3.33 – 3.18 (m, 1H), 2.54 – 2.42 (m, 1H), 2.40 – 2.25 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.0, 153.4 (dd, *J* = 287.2, 287.4 Hz), 132.2 (d, *J* = 5.4 Hz), 129.8 (t, *J* = 2.6 Hz), 128.3, 127.7, 95.7 (dd, *J* = 19.2, 15.4 Hz), 60.4, 39.7 (t, *J* = 2.9 Hz), 30.4, 19.2 (t, *J* = 2.6 Hz), 14.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -89.44 (d, *J* = 44.3 Hz, 1F), -91.55 (d, *J* = 44.3 Hz,1F) ppm. **HRMS** (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_2F_2^+$: 255.1191; Found:255.1189.

Benzyl 5,5-difluoro-4-phenylpent-4-enoate (**34**)



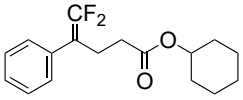
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.31 – 7.21 (m, 7H), 7.21 – 7.16 (m, 3H), 4.99 (s, 2H), 2.72 – 2.66 (m, 2H), 2.49 – 2.14 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.2, 153.5 (dd, *J* = 288.3, 288.4 Hz), 135.7, 132.6 (d, *J* = 3.9 Hz), 128.57, 128.56, 128.3 (d, *J* = 3.2 Hz), 128.29, 128.28, 127.5, 91.0 (dd, *J* = 20.7, 15.7 Hz), 66.3, 32.5 (t, *J* = 3.0 Hz), 23.3 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.54 (d, *J* = 40.9 Hz, 1F), -90.68 (d, *J* = 41.2 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{18}H_{16}O_2F_2Na^+$:325.1010; Found: 325.1010.

4-Phenylbutyl 5,5-difluoro-4-phenylpent-4-enoate (**35**)



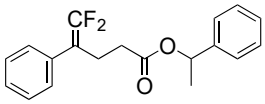
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.30 – 7.25 (m, 2H), 7.23 – 7.19 (m, 5H), 7.14 – 7.05 (m, 3H), 3.97 (t, *J* = 6.2 Hz, 2H), 2.69 – 2.62 (m, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.31 – 2.22 (m, 2H), 1.64 – 1.51 (m, 4H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.5, 153.5 (dd, *J* = 290.1, 288.4 Hz), 141.9, 132.7 (d, *J* = 3.3 Hz), 131.0, 128.5, 128.37, 128.33 (d, *J* = 4.2 Hz), 127.5, 125.8, 91.1 (dd, *J* = 20.8, 15.5 Hz), 64.4, 35.4, 32.5 (t, *J* = 2.9 Hz), 28.1, 27.6, 23.4 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.60 (d, *J* = 41.4 Hz, 1F), -90.75 (d, *J* = 41.4 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{21}H_{22}O_2F_2Na^+$: 367.1480; Found: 367.1480.

Cyclohexyl 5,5-difluoro-4-phenylpent-4-enoate (**36**)



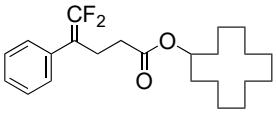
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.19 (m, 3H), 4.65 (dt, *J* = 9.0, 4.7 Hz, 1H), 2.74 – 2.58 (m, 2H), 2.26 (t, *J* = 7.8 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.66 – 1.58 (m, 2H), 1.47 – 1.43 (m, 1H), 1.34 – 1.23 (m, 4H), 1.22 – 1.12 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 171.9, 153.5 (dd, *J* = 288.1, 288.2 Hz), 132.8 (t, *J* = 3.5 Hz), 128.5, 128.3 (t, *J* = 3.0 Hz), 127.5, 91.2 (dd, *J* = 21.2, 15.1 Hz), 72.8, 32.8 (t, *J* = 2.8 Hz), 31.5, 25.3, 23.7, 23.4 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.66 (d, *J* = 41.9 Hz, 1F), -90.87 (d, *J* = 41.3 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{17}H_{20}O_2F_2Na^+$: 317.1323; Found: 317.1314.

1-Phenylethyl 5,5-difluoro-4-phenylpent-4-enoate (**37**)



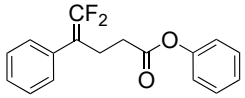
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.30 – 7.26 (m, 5H), 7.23 – 7.16 (m, 5H), 5.79 (q, *J* = 6.6 Hz, 1H), 2.78 – 2.61 (m, 2H), 2.30 (q, *J* = 7.9 Hz, 2H), 1.43 (dd, *J* = 6.7, 1.0 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 171.6, 153.5 (dd, *J* = 290.4, 288.2 Hz), 141.5, 132.7 (d, *J* = 4.2 Hz), 128.5, 128.4, 128.3 (t, *J* = 3.2 Hz), 127.9, 127.5, 126.1, 91.1 (dd, *J* = 21.2, 15.1 Hz), 72.5, 32.7 (t, *J* = 2.6 Hz), 23.3, 22.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.41 – -90.57 (m, 1F), -90.74 (d, *J* = 41.0 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{18}O_2F_2Na^+$: 339.1167; Found: 339.1162.

Cyclododecyl 5,5-difluoro-4-phenylpent-4-enoate (**38**)



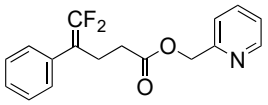
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.41 – 7.36 (m, 2H), 7.34 – 7.29 (m, 3H), 5.19 – 4.81 (m, 1H), 2.85 – 2.66 (m, 2H), 2.43 – 2.22 (m, 2H), 1.74 – 1.65 (m, 2H), 1.53 – 1.21 (m, 20H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.1, 153.5 (dd, *J* = 290.1, 288.1 Hz), 132.8 (t, *J* = 3.1 Hz), 128.5, 128.3 (t, *J* = 3.2 Hz), 127.5, 91.2 (dd, *J* = 21.2, 15.0 Hz), 72.4, 32.8 (t, *J* = 2.9 Hz), 29.0, 24.1, 23.8, 23.4, 23.3, 23.2, 20.8 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.50 – -90.67 (m, 1F), -90.84 (d, *J* = 42.0 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{23}H_{32}O_2F_2Na^+$:401.2262; Found: 401.2258.

Phenyl 5,5-difluoro-4-phenylpent-4-enoate (**39**)



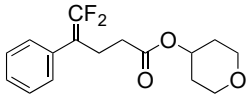
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.44 – 7.32 (m, 7H), 7.26 – 7.23 (m, 1H), 7.06 – 6.99 (m, 2H), 2.97 – 2.82 (m, 2H), 2.64 (t, *J* = 7.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 170.9, 153.6 (dd, *J* = 288.2, 288.4 Hz), 150.5, 132.6, 129.4, 128.6, 128.4 (t, *J* = 3.2 Hz), 127.7, 125.8, 121.4, 90.9 (d, *J* = 20.8 Hz), 32.6 (t, *J* = 2.9 Hz), 23.4 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.17 – -90.30 (m, 1F), -90.40 (d, *J* = 40.8 Hz, 1F) ppm. **HRMS** (APCI): *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{15}O_2F_2^+$: 289.1034; Found: 289.1026.

Pyridin-2-ylmethyl 5,5-difluoro-4-phenylpent-4-enoate (**40**)



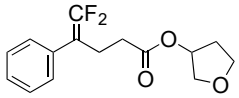
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.61 (d, *J* = 4.8 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.40 – 7.35 (m, 2H), 7.33 – 7.29 (m, 4H), 7.27 – 7.23 (m, 1H), 5.21 (s, 2H), 3.01 – 2.72 (m, 2H), 2.69 – 2.31 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.0, 155.6, 155.5, 153.5 (d, *J* = 290.3, 288.4 Hz), 149.5, 136.7, 132.6 (d, *J* = 3.5 Hz), 128.5, 128.3 (t, *J* = 3.1 Hz), 127.6, 122.9, 121.8, 91.1 (d, *J* = 15.7 Hz), 66.9, 32.4 (d, *J* = 2.7 Hz), 23.3 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.35 – -90.48 (m, 1F), -90.56 (d, *J* = 40.9 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{16}O_2F_2^+$: 304.1143; Found: 304.1141.

Tetrahydro-2*H*-pyran-4-yl 5,5-difluoro-4-phenylpent-4-enoate (**63**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.39 – 7.30 (m, 2H), 7.30 – 7.23 (m, 3H), 4.96 – 4.78 (m, 1H), 3.95 – 3.81 (m, 2H), 3.58 – 3.38 (m, 2H), 2.83 – 2.58 (m, 2H), 2.35 (t, *J* = 7.7 Hz, 2H), 1.98 – 1.79 (m, 2H), 1.69 – 1.45 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 171.8, 153.6 (dd, *J* = 290.3, 288.2 Hz), 132.7 (dd, *J* = 4.0, 2.6 Hz), 128.6, 128.3 (t, *J* = 3.1 Hz), 127.6, 91.1 (dd, *J* = 21.0, 15.5 Hz), 69.3, 65.3, 32.7 (t, *J* = 2.9 Hz), 31.7, 23.4 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.53 (dd, *J* = 41.0, 3.1 Hz, 1F), -90.70 (d, *J* = 41.1 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{19}O_3F_2^+$: 297.1296; Found: 297.1295.

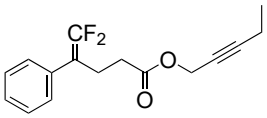
Tetrahydrofuran-3-yl 5,5-difluoro-4-phenylpent-4-enoate (**42**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.43 – 7.36 (m, 2H), 7.35 – 7.29 (m, 3H), 5.31 – 5.11 (m, 1H), 3.92 – 3.87 (m, 2H), 3.87 – 3.82 (m, 1H), 3.78 – 3.73 (m, 1H), 2.84 – 2.66 (m, 2H), 2.39 (t, *J* = 7.7 Hz, 2H), 2.22 – 2.11 (m, 1H), 1.99 – 1.90 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.2, 153.5 (dd, *J* = 288.4, 288.4 Hz), 132.6 (t, *J* = 2.9 Hz), 128.6, 128.3 (t, *J* = 3.2 Hz), 127.6, 91.0 (dd, *J* = 20.6, 16.1 Hz), 74.9, 73.0, 66.9, 32.6, 32.5 (t, *J* = 2.9 Hz), 23.3 ppm. **^{19}F NMR** (565 MHz,

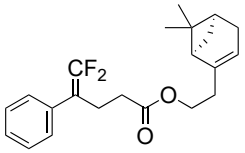
Chloroform-*d*): δ = -90.47 – -90.58 (m, 1F), -90.65 (d, *J* = 41.1 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{17}O_3F_2^+$: 283.1140; Found: 283.1141.

Pent-2-yn-1-yl 5,5-difluoro-4-phenylpent-4-enoate (**43**)



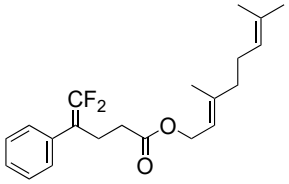
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.38 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 3H), 4.64 (t, *J* = 2.2 Hz, 2H), 2.83 – 2.71 (m, 2H), 2.42 (t, *J* = 7.8 Hz, 2H), 2.30 – 2.21 (m, 2H), 1.16 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 171.8, 153.6 (dd, *J* = 290.0, 288.6 Hz), 132.6 (t, *J* = 3.0 Hz), 128.5, 128.3 (t, *J* = 3.1 Hz), 127.5, 91.0 (dd, *J* = 20.6, 15.8 Hz), 89.0, 73.1, 52.8, 32.3 (t, *J* = 2.9 Hz), 23.3, 13.5, 12.4 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.48 (d, *J* = 41.7 Hz, 1F), -90.60 (d, *J* = 41.0 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{17}O_2F_2^+$: 279.1191; Found: 279.1203.

2-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 5,5-difluoro-4-phenylpent-4-enoate (**44**)



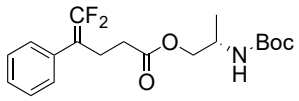
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.38 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.34 – 7.29 (m, 3H), 5.33 – 5.24 (m, 1H), 4.12 – 4.00 (m, 2H), 2.75 (tt, *J* = 8.2, 2.3 Hz, 2H), 2.37 (dt, *J* = 15.7, 6.7 Hz, 3H), 2.31 – 2.24 (m, 3H), 2.20 (dt, *J* = 18.0, 2.6 Hz, 1H), 2.14 – 2.08 (m, 1H), 2.04 (td, *J* = 5.6, 1.4 Hz, 1H), 1.28 (s, 3H), 1.15 (d, *J* = 8.6 Hz, 1H), 0.83 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.4, 153.5 (dd, *J* = 290.2, 288.0 Hz), 144.0, 132.7 (d, *J* = 3.0 Hz), 128.5, 128.2 (t, *J* = 3.2 Hz), 127.5, 118.7, 91.1 (dd, *J* = 20.9, 15.4 Hz), 62.8, 45.6, 40.7, 37.9, 35.8, 32.5 (t, *J* = 2.9 Hz), 31.6, 31.3, 26.2, 23.3, 21.0 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.44 – -90.57 (m, 1F), -90.66 (d, *J* = 41.1 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{22}H_{26}O_2F_2Na^+$: 383.1793; Found: 383.1806.

(*E*)-3,7-Dimethylocta-2,6-dien-1-yl 5,5-difluoro-4-phenylpent-4-enoate (**45**)



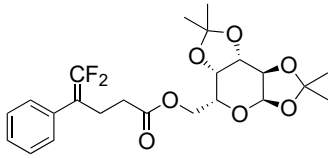
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.28 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.21 (dd, *J* = 7.9, 1.7 Hz, 3H), 5.26 – 5.18 (m, 1H), 5.03 – 4.97 (m, 1H), 4.48 (d, *J* = 7.1 Hz, 2H), 2.70 – 2.62 (m, 2H), 2.31 – 2.25 (m, 2H), 2.02 (q, *J* = 7.5 Hz, 2H), 1.99 – 1.92 (m, 2H), 1.61 (s, 3H), 1.61 (s, 3H), 1.53 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.4, 153.5 (dd, *J* = 288.4, 288.3 Hz), 142.3, 132.7 (d, *J* = 3.0 Hz), 131.8, 128.5, 128.3 (t, *J* = 3.0 Hz), 127.5, 123.7, 118.1, 91.1 (dd, *J* = 20.7, 15.8 Hz), 61.4, 39.5, 32.5 (t, *J* = 2.9 Hz), 26.2, 25.6, 23.4, 17.6, 16.4 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.62 (d, *J* = 41.2 Hz, 1F), -90.74 (d, *J* = 41.1 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+H]^+$ Calcd. for $C_{21}H_{27}O_2F_2^+$: 349.1973; Found: 349.1972.

(*S*)-2-((*tert*-Butoxycarbonyl)amino)propyl 5,5-difluoro-4-phenylpent-4-enoate (**46**)



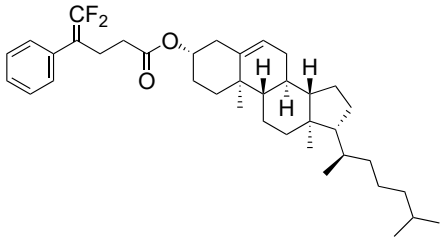
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.39 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.34 – 7.29 (m, 3H), 4.51 (s, 1H), 4.06 – 3.90 (m, 3H), 2.77 (tt, *J* = 8.1, 2.3 Hz, 2H), 2.41 (dd, *J* = 8.6, 7.0 Hz, 2H), 1.45 (s, 9H), 1.14 (d, *J* = 6.7 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.3, 153.6 (d, *J* = 289.8 Hz), 132.6, 128.6, 128.3 (t, *J* = 3.3 Hz), 127.6, 91.1 (dd, *J* = 19.9, 16.7 Hz), 67.4, 45.3, 32.3 (t, *J* = 2.8 Hz), 28.3, 23.3, 17.6 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.49 (d, *J* = 39.5 Hz, 1F), -90.58 (d, *J* = 45.2 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{25}O_4F_2NNa^+$: 392.1643; Found: 392.1639.

((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 5,5-difluoro-4-phenylpent-4-enoate (**47**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.40 – 7.36 (m, 2H), 7.33 – 7.28 (m, 3H), 5.55 (d, *J* = 5.0 Hz, 1H), 4.63 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.34 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.28 – 4.17 (m, 3H), 4.01 (dd, *J* = 6.8, 4.5 Hz, 1H), 2.81 – 2.71 (m, 2H), 2.42 (dd, *J* = 8.8, 6.9 Hz, 2H), 1.52 (s, 3H), 1.46 (s, 3H), 1.35 (d, *J* = 1.7 Hz, 6H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.3, 154.5 (dd, *J* = 288.9 Hz), 132.7 (t, *J* = 2.3 Hz), 128.5, 128.3 (t, *J* = 3.1 Hz), 127.5, 109.6, 108.7, 96.2, 91.1 (dd, *J* = 19.8, 16.4 Hz), 71.0, 70.7, 70.4, 65.8, 63.5, 32.4 (t, *J* = 2.7 Hz), 25.98, 25.94, 24.9, 24.4, 23.3 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.57 (d, *J* = 45 Hz, 1F), -90.66 (d, *J* = 45 Hz, 1F), ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{23}H_{28}O_7F_2Na^+$: 477.1695; Found: 477.1696.

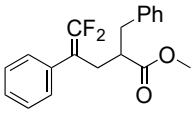
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-(cyclohexa-2,4-dien-1-yl)-5,5-difluoropent-4-enoate (**48**) (1:10 dr)



white solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 5.32 (d, *J* = 5.1 Hz, 0.09H), 5.29 (dt, *J* = 4.9, 1.7 Hz, 1H), 4.69 – 4.60 (m, 0.12H), 4.55 – 4.41 (m, 1H), 2.66 (tt, *J* = 7.9, 2.3 Hz, 2H), 2.29 – 2.23 (m, 2H), 2.23 – 2.16 (m, 2H), 1.98 – 1.86 (m, 2H), 1.82 – 1.68 (m, 3H), 1.57 – 1.33 (m, 8H), 1.33 – 1.15 (m, 5H), 1.13 – 0.97 (m, 8H), 0.93 (s, 3H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.80 (d, *J* = 2.7 Hz, 3H), 0.79 (d, *J* = 2.7 Hz, 3H), 0.60 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 171.8, 164.4, 153.5 (dd, *J* = 290.2, 288.0 Hz), 139.5, 139.3, 132.8 (t, *J* = 3.6 Hz), 128.5, 128.3, 127.5, 123.0, 122.6, 91.2 (dd, *J* = 21.3, 14.9 Hz), 74.1, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.05, 36.9, 36.5, 36.2, 35.8, 32.8 (t, *J* = 2.7 Hz), 31.8 (d, *J* = 6.3 Hz), 28.2, 28.0, 27.7, 24.2, 23.8, 23.4 (d, *J* = 2.0 Hz), 22.8, 22.5, 21.04, 19.3, 18.7, 11.8 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.57 (d, *J* = 41.4 Hz, 1F), -

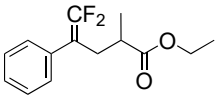
90.81 (d, *J* = 41.3 Hz, 1F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{38}H_{54}O_2F_2Na^+$: 603.3984; Found:603.3978.

Methyl (*R*)-2-benzyl-5,5-difluoro-4-phenylpent-4-enoate (**49**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.29 – 7.24 (m, 2H), 7.22 – 7.20 (m, 1H), 7.18 – 7.15 (m, 2H), 7.14 – 7.09 (m, 3H), 6.98 (dd, *J* = 7.0, 1.7 Hz, 2H), 3.41 (s, 3H), 2.86 (dd, *J* = 13.7, 8.5 Hz, 1H), 2.75 – 2.66 (m, 2H), 2.64 – 2.57 (m, 1H), 2.55 – 2.49 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 174.8, 154.02 (q, *J* = 288.4, 290.9 Hz), 138.6, 132.6 (t, *J* = 3.3 Hz), 128.8, 128.5, 128.4, 128.3, 127.5, 126.4, 90.3 (dd, *J* = 20.9, 15.5 Hz), 51.5, 45.6 (t, *J* = 2.5 Hz), 37.8, 30.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.01 – -90.32 (m, 2F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{18}O_2F_2Na^+$: 339.1167; Found: 339.1165.

Ethyl (*R*)-5,5-difluoro-2-methyl-4-phenylpent-4-enoate (**50**)



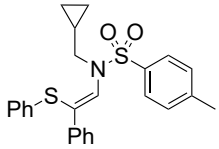
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.31 – 7.26 (m, 2H), 7.24 – 7.20 (m, 3H), 4.02 – 3.91 (m, 2H), 2.79 – 2.68 (m, 1H), 2.49 – 2.41 (m, 1H), 2.36 – 2.30 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 175.5, 154.1 (dd, *J* = 286.1, 288.1 Hz), 132.9 – 132.8 (m), 128.5, 128.4 (t, *J* = 3.1 Hz), 127.5, 90.3 (dd, *J* = 20.7, 15.5 Hz), 60.4, 37.7 (t, *J* = 2.9 Hz), 31.6, 16.3, 14.1. ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -90.46 – -90.70 (m, 2F) ppm. **HRMS** (ESI): *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{16}O_2F_2Na^+$: 277.1010; Found: 277.1002.

6.2.2 Transition-metal Catalyzed Reactions of N-Sulfonyl-1,2,3-triazoles

General procedure of rhodium-catalyzed enamine homologation reactions of triazoles with cyclopropylmethyl sulfides.

Typical experimental procedure: the sulfide (0.2 mmol, 1.0 equiv.), triazole (2.0 equiv.) and $Rh_2(Oct)_4$ (2 mol%) with 4 Å molecular sieves (60 mg) were added in a test tube with stir bar. The tube was charged with argon (repeated three times), and then the solvent (toluene, 2.0 mL) was injected. Then the reaction stirred at the 100 °C in a preheated aluminum block for 12 h. The crude reaction mixture was purified by column chromatography using hexane : ethyl acetate as eluent to afford the final product.

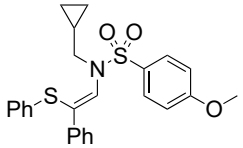
(*Z*)-*N*-(cyclopropylmethyl)-4-methyl-*N*-(2-phenyl-2-(phenylthio)vinyl)benzenesulfonamide (**89a**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.72 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.42 (m, 2H), 7.27 – 7.25 (m, 2H), 7.22 – 7.17 (m, 3H), 7.06 – 6.96 (m, 5H), 6.44 (s, 1H), 3.42 (d, *J* = 7.1 Hz, 2H), 2.41 (s,

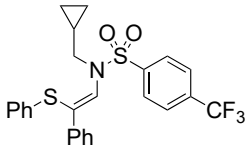
3H), 1.15 – 1.10 (m, 1H), 0.57 – 0.54 (m, 2H), 0.28 – 0.25 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.5, 137.4, 136.9, 136.1, 134.1, 130.0, 129.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.4, 126.1, 54.5, 21.5, 10.3, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{25}O_2NS_2Na^+$: 458.1215; Found: 458.1218.

(*Z*)-*N*-(cyclopropylmethyl)-4-methoxy-*N*-(2-phenyl-2-(phenylthio)vinyl)benzenesulfonamide (**89b**)



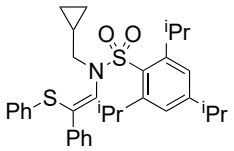
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.80 (d, *J* = 8.9 Hz, 2H), 7.46 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.09 – 7.02 (m, 5H), 6.98 – 6.94 (m, 2H), 6.50 (s, 1H), 3.87 (s, 3H), 3.46 (d, *J* = 7.0 Hz, 2H), 1.18 – 1.12 (m, 1H), 0.63 – 0.52 (m, 2H), 0.32 – 0.26 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 163.0, 137.4, 136.6, 134.2, 130.8, 130.0, 129.5, 128.7, 128.5, 128.3, 128.2, 128.1, 126.1, 114.1, 55.5, 54.5, 10.3, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{25}NO_3S_2Na^+$: 474.1168; Found: 474.1166.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-phenyl-2-(phenylthio)vinyl)-4-(trifluoromethyl)benzenesulfonamide (**89c**)



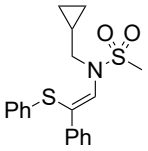
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.00 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.45 – 7.42 (m, 2H), 7.24 – 7.22 (m, 3H), 7.08 – 7.04 (m, 3H), 6.99 – 6.97 (m, 2H), 6.48 (s, 1H), 3.52 (d, J = 7.1 Hz, 2H), 1.21 – 1.17 (m, 1H), 0.68 – 0.57 (m, 2H), 0.33 (dt, J = 6.1, 4.8 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 142.8, 139.1, 136.8, 134.3 (d, *J* = 32.8 Hz), 133.4, 130.2, 128.62, 128.60, 128.3, 128.2, 127.8, 127.1, 126.5, 126.1 (q, *J* = 3.8 Hz), 123.2 (d, *J* = 272.7 Hz), 55.0, 10.5, 4.3 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -63.07 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{22}NF_3O_2S_2Na^+$: 512.0936; Found: 512.0927.

(*Z*)-*N*-(cyclopropylmethyl)-2,4,6-triisopropyl-*N*-(2-phenyl-2-(phenylthio)vinyl)benzenesulfonamide (**89d**)



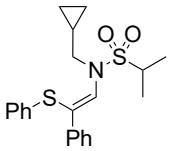
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.37 – 7.33 (m, 2H), 7.13 – 7.08 (m, 5H), 6.94 – 6.88 (m, 3H), 6.81 – 6.79 (m, 2H), 6.78 (s, 1H), 4.10 – 4.13 (m, 2H), 3.62 (d, *J* = 7.0 Hz, 2H), 2.83 – 0.85 (m, 1H), 1.19 – 1.23 (m, 18H), 0.87 – 0.72 (m, 1H), 0.52 – 0.56 (m, 2H), 0.35 – 0.19 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 153.1, 151.4, 137.3, 134.3, 133.9, 132.1, 129.8, 129.5, 128.4, 128.1, 126.1, 123.8, 54.2, 34.1, 29.9, 25.0, 23.5, 10.4, 4.4 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{41}NO_2S_2Na^+$: 570.2470; Found: 570.2463.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-phenyl-2-(phenylthio)vinyl)methanesulfonamide (**89e**)



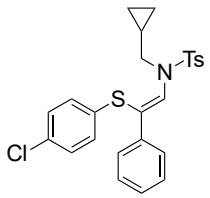
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.47 – 7.42 (m, 2H), 7.22 – 7.16 (m, 3H), 7.12 (d, *J* = 7.4 Hz, 2H), 7.08 – 7.06 (m, 2H), 7.03 – 6.99 (m, 1H), 6.70 (s, 1H), 3.58 (d, *J* = 7.0 Hz, 2H), 2.83 (s, 3H), 1.17 – 1.12 (m, 1H), 0.61 – 0.46 (m, 2H), 0.29 (dt, *J* = 6.1, 4.6 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 137.5, 134.2, 133.9, 129.8, 129.2, 128.8, 128.4, 128.3, 128.2, 126.5, 53.8, 40.1, 10.7, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{21}NO_2S_2Na^+$: 382.0904; Found: 382.0904.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-phenyl-2-(phenylthio)vinyl)propane-2-sulfonamide (**89f**)



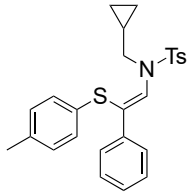
colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.52 – 7.44 (m, 2H), 7.23 – 7.17 (m, 3H), 7.12 – 7.02 (m, 5H), 7.00 (s, 1H), 3.75 (d, *J* = 7.1 Hz, 2H), 3.23 – 3.16 (m, 1H), 1.32 (d, *J* = 6.8 Hz, 6H), 1.27 – 1.19 (m, 1H), 0.57 – 0.52 (m, 2H), 0.34 – 0.30 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 137.7, 134.3, 131.3, 128.9, 128.8, 128.4, 128.2, 128.1, 127.9, 126.2, 55.0, 54.3, 16.4, 11.2, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{25}O_2NS_2Na^+$: 410.1218; Found: 410.1215.

(*Z*)-*N*-(2-((4-chlorophenyl)thio)-2-phenylvinyl)-*N*-(cyclopropylmethyl)-4-methylbenzenesulfonamide (**89g**)



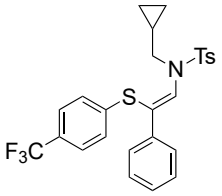
colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.27 – 7.24 (m, 2H), 7.23 – 7.18 (m, 3H), 7.01 – 6.96 (m, 2H), 6.96 – 6.92 (m, 2H), 6.40 (s, 1H), 3.37 (d, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.14 – 1.02 (m, 1H), 0.57 – 0.50 (m, 2H), 0.28 – 0.20 (m, 2H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 143.6, 137.1, 136.6, 135.9, 132.9, 132.1, 131.1, 129.6, 128.8, 128.6, 128.4, 128.3, 128.2, 127.4, 54.5, 21.5, 10.2, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}NClO_2S_2Na^+$: 492.0829; Found: 492.0823.

(*Z*)-*N*-(cyclopropylmethyl)-4-methyl-*N*-(2-phenyl-2-(*p*-tolylthio)vinyl)benzenesulfonamide (**89h**)



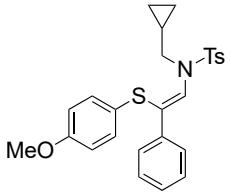
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.80 – 7.72 (m, 2H), 7.49 – 7.42 (m, 2H), 7.33 – 7.27 (m, 2H), 7.27 – 7.19 (m, 3H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.90 – 6.83 (m, 2H), 6.45 (s, 1H), 3.48 (d, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 2.22 (s, 3H), 1.21 – 1.14 (m, 1H), 0.66 – 0.54 (m, 2H), 0.31 (dt, *J* = 6.0, 4.7 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.4, 137.55, 137.52, 136.2, 136.1, 130.37, 130.36, 129.5, 129.3, 128.3, 128.16, 128.12, 127.9, 127.4, 54.5, 21.5, 20.9, 10.3, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}NO_2S_2Na^+$: 472.1375; Found: 472.1371.

Z)-*N*-(cyclopropylmethyl)-4-methyl-*N*-(2-phenyl-2-((4-(trifluoromethyl)phenyl)thio)vinyl) benzenesulfonamide (**89i**)



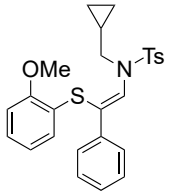
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.49 – 7.44 (m, 2H), 7.27 – 7.25 (m, 2H), 7.05 – 7.02 (m, 7H), 6.88 – 6.85 (m, 2H), 6.39 (s, 1H), 3.19 (d, *J* = 7.0 Hz, 2H), 2.18 (s, 3H), 0.92 – 0.79 (m, 1H), 0.42 – 0.23 (m, 2H), 0.04 (dt, *J* = 6.1, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.8, 140.0, 137.2, 136.0, 133.6, 130.7, 129.8, 129.7, 128.6, 128.5, 128.0, 127.7 (d, *J* = 32.7 Hz), 127.3, 125.3 (q, *J* = 3.8 Hz), 123.9 (d, *J* = 272.1 Hz), 54.4, 21.5, 10.3, 4.3 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$): δ= -62.55 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{24}NO_2F_3S_2Na^+$: 526.1092; Found: 526.1084.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-((4-methoxyphenyl)thio)-2-phenylvinyl)-4-methylbenzenesulfonamide (**89j**)



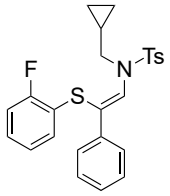
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.80 – 7.74 (m, 2H), 7.42 – 7.36 (m, 2H), 7.33 – 7.30 (m, 2H), 7.25 – 7.17 (m, 3H), 7.06 – 6.97 (m, 2H), 6.66 – 6.59 (m, 2H), 6.27 (s, 1H), 3.72 (s, 3H), 3.44 (d, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 1.21 – 1.11 (m, 1H), 0.67 – 0.55 (m, 2H), 0.33 – 0.30 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 158.6, 143.4, 139.9, 137.3, 136.1, 133.0, 129.5, 128.5, 128.1, 128.0, 127.5, 126.5, 124.1, 114.1, 55.1, 54.7, 21.5, 10.3, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}NO_3S_2Na^+$: 488.1324; Found: 488.1318.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-((2-methoxyphenyl)thio)-2-phenylvinyl)-4-methylbenzenesulfonamide (**89k**)



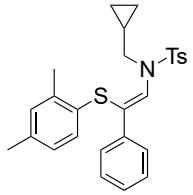
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.78 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.32 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 7.07 – 7.02 (m, 1H), 6.93 – 6.89 (m, 1H), 6.70 – 6.63 (m, 2H), 6.60 (s, 1H), 3.79 (s, 3H), 3.58 (d, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 1.25 – 1.18 (m, 1H), 0.61 – 0.54 (m, 2H), 0.35 – 0.28 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 157.3, 143.3, 137.6, 136.6, 135.7, 131.7, 129.5, 128.1, 128.09, 128.06, 127.9, 127.8, 127.4, 121.9, 120.6, 110.4, 55.5, 54.2, 21.5, 10.6, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}NO_3S_2Na^+$: 488.1324; Found: 488.1317.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-((2-fluorophenyl)thio)-2-phenylvinyl)-4-methylbenzenesulfonamide (**89l**)



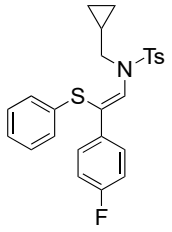
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.76 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.19 (m, 3H), 7.11 – 7.03 (m, 2H), 6.86 – 6.83 (m, 2H), 6.34 (s, 1H), 3.44 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 1.18 (m, 1H), 0.65 – 0.53 (m, 2H), 0.32 – 0.29 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 161.1 (d, *J* = 246.5 Hz), 143.5, 138.0, 136.9, 136.1, 133.5, 129.6, 128.9 (d, *J* = 7.8 Hz), 128.3, 128.0, 127.5, 127.49 (d, *J* = 32.1 Hz), 127.48, 124.0 (d, *J* = 3.9 Hz), 120.8 (d, *J* = 17.5 Hz), 115.3 (d, *J* = 22.3 Hz), 54.7, 21.5, 10.3, 4.2 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$): δ = -109.0 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}NO_2S_2FNa^+$: 476.1124; Found: 476.1117.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-((2,4-dimethylphenyl)thio)-2-phenylvinyl)-4-methylbenzenesulfonamide (**89m**)



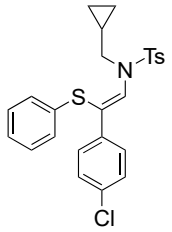
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.77 (d, *J* = 7.9 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 6.83 (s, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.69 – 6.62 (m, 1H), 6.42 (s, 1H), 3.44 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H), 2.17 (s, 3H), 1.19 – 1.14 (m, 1H), 0.64 – 0.53 (m, 2H), 0.31 – 0.28 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.4, 138.0, 137.9, 137.6, 136.3, 136.2, 131.4, 130.8, 129.5, 129.2, 128.18, 128.10, 128.04, 127.7, 127.5, 126.7, 54.7, 21.5, 20.8, 20.4, 10.4, 4.3 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{29}NO_2S_2Na^+$: 486.1531; Found: 486.1524.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-(4-fluorophenyl)-2-(phenylthio)vinyl)-4-methylbenzenesulfonamide (**89r**)



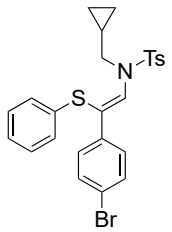
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.66 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.23 – 7.21 (m, 2H), 7.02 – 6.92 (m, 5H), 6.85 – 6.80 (m, 2H), 6.31 (s, 1H), 3.35 (d, *J* = 7.0 Hz, 2H), 2.36 (s, 3H), 1.10 – 1.00 (m, 1H), 0.55 – 0.43 (m, 2H), 0.20 (dt, *J* = 6.0, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 162.6 (d, *J* = 248.2 Hz), 143.6, 136.4, 136.1, 133.8, 133.4 (d, *J* = 3.1 Hz), 130.3, 129.9 (d, *J* = 8.1 Hz), 129.6, 128.6, 128.2, 127.4, 126.4, 115.1 (d, *J* = 21.8 Hz), 54.6, 21.5, 10.3, 4.2 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -113.24 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}NO_2S_2FNa^+$: 476.1124; Found: 476.1113.

(*Z*)-*N*-(2-(4-chlorophenyl)-2-(phenylthio)vinyl)-*N*-(cyclopropylmethyl)-4-methylbenzenesulfonamide (**89o**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 3.8 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.08 – 7.03 (m, 3H), 7.03 – 6.99 (m, 2H), 6.46 (s, 1H), 3.43 (d, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.17 – 1.05 (m, 1H), 0.61 – 0.50 (m, 2H), 0.26 (dt, *J* = 6.1, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.6, 136.13, 136.11, 135.2, 134.1, 133.8, 130.0, 129.6, 129.4, 129.0, 128.6, 128.4, 127.4, 126.4, 54.5, 21.5, 10.3, 4.3 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}O_2NClS_2Na^+$: 492.0829; Found: 492.0826.

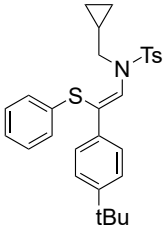
(*Z*)-*N*-(2-(4-bromophenyl)-2-(phenylthio)vinyl)-*N*-(cyclopropylmethyl)-4-methylbenzenesulfonamide (**89p**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.31 – 7.29 (m, 2H), 7.28 – 7.26 (m, 2H), 7.08 – 7.03 (m, 3H), 7.02 – 6.99 (m, 2H), 6.47 (s, 1H), 3.43 (d, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.16 – 1.06 (m, 1H), 0.58 – 0.48 (m, 2H), 0.26 (dt, *J* = 5.9, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.6, 136.6, 136.1, 135.0, 133.8, 131.3, 129.9, 129.7, 129.6,

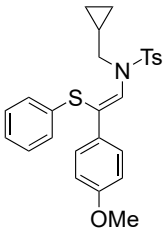
129.1, 128.7, 127.4, 126.4, 122.3, 54.4, 21.5, 10.3, 4.3 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}O_2NBrS_2Na^+$: 536.0324; Found: 536.0320.

(*Z*)-*N*-(2-(4-(*tert*-butyl)phenyl)-2-(phenylthio)vinyl)-*N*-(cyclopropylmethyl)-4-methylbenzenesulfonamide (**89q**)



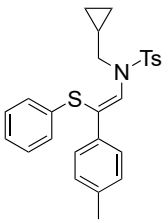
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.11 – 7.00 (m, 5H), 6.57 (s, 1H), 3.48 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 1.29 (s, 9H), 1.17 – 1.10 (m, 1H), 0.62 – 0.49 (m, 2H), 0.29 (dt, *J* = 6.0, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 151.4, 143.4, 136.3, 135.4, 134.65, 134.60, 129.58, 129.52, 128.5, 127.8, 127.4, 125.8, 125.1, 54.4, 34.5, 31.2, 21.5, 10.4, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{33}O_2NS_2Na^+$: 514.1844; Found: 514.1844.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-(4-methoxyphenyl)-2-(phenylthio)vinyl)-4-methylbenzenesulfonamide (**89r**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.30 – 7.27 (m, 2H), 7.09 – 7.05 (m, 2H), 7.05 – 7.01 (m, 3H), 6.78 – 6.70 (m, 2H), 6.35 (s, 1H), 3.76 (s, 3H), 3.41 (d, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 1.18 – 1.07 (m, 1H), 0.64 – 0.48 (m, 2H), 0.28 (dt, *J* = 6.1, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 159.7, 143.4, 137.6, 136.2, 134.3, 130.0, 129.6, 129.57, 129.52, 128.5, 127.4, 127.1, 126.0, 113.6, 55.2, 54.8, 21.5, 10.3, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}O_3NS_2Na^+$: 488.1324; Found: 488.1323.

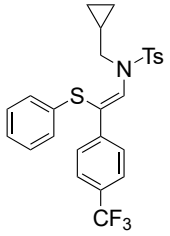
(*Z*)-*N*-(cyclopropylmethyl)-4-methyl-*N*-(2-(phenylthio)-2-(*p*-tolyl)vinyl)benzenesulfonamide (**89s**)



colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.69 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.02 – 7.01 (m, 2H), 6.99 – 9.97 (m, 5H), 6.38 (s, 1H), 3.38 (d, *J* = 7.0 Hz, 2H), 2.38 (s, 3H), 2.24 (s, 3H), 1.13 – 1.06 (m, 1H), 0.61 – 0.38 (m, 2H), 0.24 (dt, *J* = 6.1, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.4, 138.2, 137.2, 136.2, 134.49, 134.43, 129.9, 129.5, 128.9,

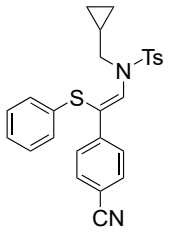
128.5, 128.1, 128.0, 127.4, 126.0, 54.7, 21.5, 21.1, 10.3, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}NO_2S_2Na^+$: 472.1375; Found: 472.1374.

(*Z*)-*N*-(cyclopropylmethyl)-4-methyl-*N*-(2-phenyl-2-((4-(trifluoromethyl)phenyl)thio)vinyl) benzenesulfonamide (**89t**)



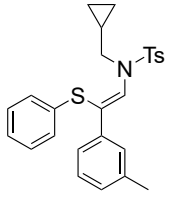
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.08 – 7.03 (m, 3H), 7.01 (dd, *J* = 8.0, 1.8 Hz, 2H), 6.63 (s, 1H), 3.49 (d, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.17 – 1.04 (m, 1H), 0.59 – 0.47 (m, 2H), 0.27 (dt, *J* = 6.0, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.8, 141.5, 136.1, 133.7, 132.8, 130.6, 130.0 (q, *J* = 32.4 Hz), 129.75, 129.73, 128.8, 128.3, 127.3, 126.5, 125.2 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.1 Hz), 54.1, 21.5, 10.4, 4.3 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -62.60 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{24}NF_3S_2O_2Na^+$: 526.1092; Found: 526.1089.

(*Z*)-*N*-(2-(4-cyanophenyl)-2-(phenylthio)vinyl)-*N*-(cyclopropylmethyl)-4-methylbenzenesulfonamide (**89u**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.67 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.08 – 7.01 (m, 3H), 6.99 – 6.98 (m, 2H), 6.71 (s, 1H), 3.51 (d, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.13 – 1.08 (m, 1H), 0.61 – 0.45 (m, 2H), 0.27 – 0.24 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.9, 142.9, 136.0, 133.5, 132.0, 131.5, 130.9, 129.8, 129.6, 128.9, 128.6, 127.3, 126.6, 118.5, 111.5, 53.9, 21.5, 10.4, 4.3 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{24}N_2O_2S_2Na^+$: 483.1171; Found: 483.1171.

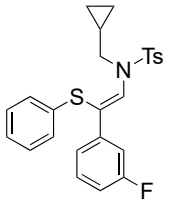
(*Z*)-*N*-(cyclopropylmethyl)-4-methyl-*N*-(2-(phenylthio)-2-(*m*-tolyl)vinyl)benzenesulfonamide (**89v**)



colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.74 – 7.63 (m, 2H), 7.25 (s, 1H), 7.25 – 7.19 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.05 – 6.95 (m, 6H), 6.44 (s, 1H), 3.41 (d, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 2.24 (s, 3H), 1.16 – 1.04 (m, 1H), 0.58 – 0.49 (m, 2H), 0.25 (dt, *J* = 6.1, 4.7 Hz, 2H) ppm. **^{13}C NMR** (101 MHz,

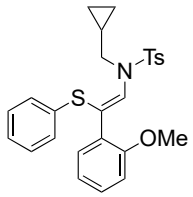
Chloroform-*d*): δ = 143.4, 137.7, 137.3, 136.7, 136.1, 134.3, 129.9, 129.5, 129.0, 128.8, 128.4, 128.3, 128.0, 127.4, 126.0, 125.4, 54.5, 21.5, 21.3, 10.3, 4.2 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}O_2NS_2Na^+$: 472.1375; Found: 472.1372.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-(3-fluorophenyl)-2-(phenylthio)vinyl)-4-methylbenzenesulfonamide (**89w**)



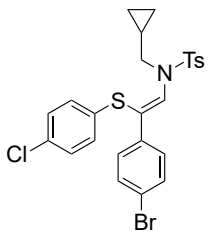
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.70 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.22 (m, 1H), 7.19 – 7.12 (m, 2H), 7.08 – 7.03 (m, 2H), 7.02 (m, 3H), 6.91 – 6.84 (m, 1H), 6.54 (s, 1H), 3.45 (d, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.16 – 1.05 (m,1 H), 0.60 – 0.48 (m, 2H), 0.27 – 0.24 (dt, *J* = 6.2, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 162.5 (d, *J* = 245.9 Hz), 143.7, 140.1 (d, *J* = 7.5 Hz), 136.1, 134.3, 133.8, 129.9, 129.7, 129.64, 129.63, 128.6, 127.4, 126.4, 123.9 (d, *J* = 2.8 Hz), 115.1 (d, *J* = 22.8 Hz), 115.0 (d, *J* = 21.3 Hz), 54.3, 21.5, 10.3, 4.3 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -113.27 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}NFO_2S_2Na^+$: 476.1124; Found: 476.1122.

(*Z*)-*N*-(cyclopropylmethyl)-*N*-(2-(2-methoxyphenyl)-2-(phenylthio)vinyl)-4-methylbenzenesulfonamide (**89x**)



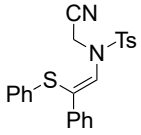
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.70 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.04 – 6.97 (m, 3H), 6.95 – 6.91 (m, 3H), 6.70 – 6.66 (m, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 6.07 (s, 1H), 3.64 (s, 3H), 3.30 (d, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 1.14 – 1.09 (m 1H), 0.56 – 0.38 (m, 2H), 0.24 (q, *J* = 5.2 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 157.0, 143.2, 136.3, 135.9, 133.3, 132.1, 131.2, 129.4, 129.2, 128.0, 127.6, 127.5, 126.7, 126.1, 120.0, 110.6, 55.3, 54.7, 21.5, 10.2, 4.1 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}O_3NS_2Na^+$: 488.1324; Found: 488.1320.

(*Z*)-*N*-(2-(4-bromophenyl)-2-((4-chlorophenyl)thio)vinyl)-*N*-(cyclopropylmethyl)-4-methylbenzenesulfonamide (**89y**)



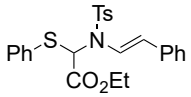
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6, Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.44 (s, 1H), 3.39 (d, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 1.09 – 1.01 (m, 1H), 0.56 – 0.53 (m, 2H), 0.26 – 0.23 (dt, *J* = 6.0, 4.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ =143.8, 136.3, 135.9, 134.7, 132.57, 132.52, 131.5, 131.1, 129.7, 129.6, 129.5, 128.9, 127.3, 122.5, 54.4, 21.5, 10.3, 4.3 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{23}NO_2BrClS_2Na^+$: 569.9934; Found: 567.9925.

(*Z*)-*N*-(cyanomethyl)-4-methyl-*N*-(2-phenyl-2-(phenylthio)vinyl)benzenesulfonamide (**92a**)



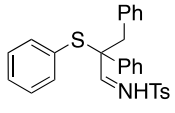
white solid; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.79 – 7.76 (m, 2H), 7.44 – 7.38 (m, 2H), 7.38 – 7.33 (m, 2H), 7.23 – 7.17 (m, 3H), 7.12 – 7.02 (m, 5H), 6.61 (s, 1H), 4.78 (s, 2H), 2.45 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 145.2, 136.6, 135.1, 134.2, 132.6, 130.2, 129.94, 128.90, 128.9, 128.4, 128.3, 127.7, 126.8, 126.1, 114.3, 36.1, 21.7 ppm. **HRMS** (ESI): m/z: $[M+H]^+$ Calcd. for $C_{23}H_{21}N_2O_2S_2^+$: 421.1039; Found: 421.1036.

Ethyl (*E*)-2-((4-methyl-*N*-styrylphenyl)sulfonamido)-2-(phenylthio)acetate (**91a**)

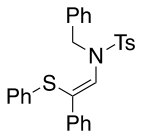


colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.59 – 7.57 (m, 2H), 7.54 – 7.49 (m, 2H), 7.38 – 7.32 (m, 3H), 7.30 – 7.26 (m, 4H), 7.22 – 7.17 (m, 3H), 6.93 (d, *J* = 14.6 Hz, 1H), 6.35 – 6.24 (m, 2H), 4.18 – 4.00 (m, 2H), 2.38 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 67.0, 144.1, 136.0, 135.9, 134.5, 133.1, 131.6, 129.5, 129.2, 129.0, 128.6, 127.7, 127.0, 125.9, 122.9, 119.1, 67.2, 62.6, 21.5, 13.9 ppm.

Synthesis of rhodium-catalyzed Stevens rearrangement of 4-phenyl-N-tosyl-1,2,3-triazole with benzylphenyl sulfides, products **91a** and **92b**



91b

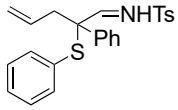


92b

4-Phenyl-*N*-sulfonyl-1,2,3-triazoles (0.2 mmol) and $Rh_2(OAc)_4$ (1.6 mg, 2 mol%) were added under argon atmosphere to an over dried 10 mL reaction tube equipped with stir bar. Subsequently, solution of benzylphenyl sulfides (0.4 mmol) in toluene (2 mL) was introduced through syringe. The reaction tube was sealed and stirred at 100 °C for 16 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using hexanes/ethyl acetate mixture as eluent to afford a inseparable mixture of *α*-sulfenylated imines and enamide through Stevens rearrangement and intramolecular trapping of the fromed sulfonium ylide with nitrogen in 5:4.5 ratio, respectively, in 84% yield.

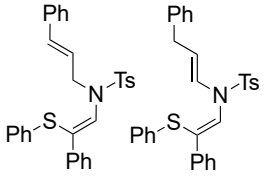
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 8.68 (s, 1H), 7.77 – 7.77 (m, 4H), 7.39 – 7.12 (m, 18H), 7.11 – 7.04 (m, 4H), 7.01 – 6.82 (m, 8H), 6.70 – 6.64 (m, 2H), 6.63 – 6.56 (m, 2H), 6.24 (s, 0.9H), 4.71 (s, 2H), 3.42 (d, *J* = 13.7 Hz, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 2.9H) ppm.

2-Phenyl-2-(phenylthio)-1-(tolylsulfonylimino)pent-4-ene (**91c**)



white solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.71 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.46 – 7.32 (m, 7H), 7.31 – 7.26 (m, 3H), 7.14 – 7.12 (m, 2H), 5.63 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 4.99 – 4.89 (m, 1H), 4.90 – 4.74 (m, 1H), 2.79 (dd, *J* = 14.9, 6.5 Hz, 1H), 2.68 (dd, *J* = 14.9, 7.3 Hz, 1H), 2.49 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.9, 144.6, 137.5, 136.7, 135.0, 132.3, 129.8, 129.7, 128.9, 128.8, 128.4, 128.3, 128.1, 127.8, 118.9, 61.1, 39.8, 21.6 ppm.

N-cinnamyl-4-methyl-*N*-((*Z*)-2-phenyl-2-(phenylthio)vinyl)benzenesulfonamide (**92c**+**92d**)

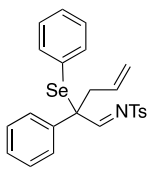


light red solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): 7.69 – 7.65 (m, 2.4H), 7.34 – 7.25 (m, 2.6H), 7.23 – 7.13 (m, 8.2H), 7.13 – 7.03 (m, 5.2H), 7.02 – 6.96 (m, 0.8H), 6.93 – 6.84 (m, 5.2H), 6.77 (s, 0.2H), 6.48 (s, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 6.4 Hz, 1H), 5.83 (d, *J* = 15.8 Hz, 0.2H), 5.51 (dt, *J* = 15.7, 6.6 Hz, 0.2H), 4.35 (dd, *J* = 6.5, 1.4 Hz, 2H), 3.82 – 3.60 (m, 0.4H), 2.38 (s, 6H), 2.34 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 144.1, 143.8, 137.6, 136.5, 136.0, 135.7, 134.8, 134.1, 134.0, 133.8, 133.7, 129.9, 129.8, 129.7, 129.6, 129.4, 128.7, 128.6, 128.5, 128.54, 128.51, 128.3, 128.25, 128.22, 128.1, 128.06, 128.00, 127.8, 127.5, 127.4, 126.57, 126.53, 126.4, 126.0, 124.1, 123.2, 51.3, 50.4, 21.5 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{27}NO_2S_2Na^+$: 520.1375; Found: 520.1370.

General procedure of rhodium-catalyzed cascade reactions of triazoles with organoselenium compounds

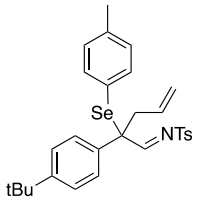
Typical experimental procedure: In a test tube and under Argon, the selenide (0.2 mmol, 1.0 equiv.), triazole (1.0 equiv.) and $Rh_2(OAc)_4$ (2 mol%) were dissolved in 1.0 mL toluene and stirred at the 100 °C in a preheated aluminum block for 15 h. Solvent was removed under reduced pressure, the crude reaction mixture was purified by column chromatography using *n*-hexane : ethyl acetate as eluent to afford the final product.

(*E*)-4-methyl-*N*-(2-phenyl-2-(phenylselanyl)pent-4-en-1-ylidene)benzenesulfonamide (**97a**)



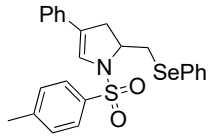
colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 8.81 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.20 (m, 10H), 7.14 – 6.97 (m, 2H), 5.55 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 4.95 – 4.67 (m, 2H), 2.77 (dt, *J* = 7.0, 1.3 Hz, 2H), 2.45 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 171.5, 144.3, 138.3, 137.0, 135.3, 132.7, 129.7, 129.6, 129.0, 128.8, 128.3, 128.1, 127.9, 125.5, 118.8, 58.7, 40.2, 21.6 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 503.20 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}NSO_2SeNa^+$: 492.0506; Found: 492.0510.

(*E*)-*N*-(2-(4-(*tert*-butyl)phenyl)-2-(*p*-tolylselanyl)pent-4-en-1-ylidene)-4-methylbenzenesulfonamide (**97b**)



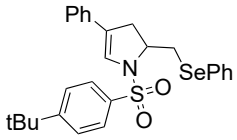
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.84 (s, 1H), 7.85 – 7.75 (m, 2H), 7.40 – 7.37 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.25 – 7.20 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 5.68 – 5.54 (m, 1H), 5.00 – 4.77 (m, 2H), 2.79 (d, *J* = 6.9 Hz, 2H), 2.50 (s, 3H), 2.29 (s, 3H), 1.34 (s, 9H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 171.7, 151.4, 144.2, 139.9, 138.3, 135.6, 133.8, 133.2, 129.8, 129.6, 127.9, 127.8, 125.8, 122.4, 118.5, 58.5, 39.6, 34.6, 31.2, 21.6, 21.3 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 489.68 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{23}NSO_2SeNa^+$: 562.1289; Found: 562.1269.

4-Phenyl-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98a**)



colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.62 – 7.56 (m, 2H), 7.46 – 7.39 (m, 2H), 7.32 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.29 – 7.24 (m, 2H), 7.23 – 7.18 (m, 3H), 7.18 – 7.13 (m, 2H), 6.81 (t, *J* = 1.8 Hz, 1H), 3.89 – 3.76 (m, 1H), 3.71 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.08 – 2.87 (m, 2H), 2.77 – 2.58 (m, 1H), 2.35 (s, 2H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 143.8, 133.4, 132.99, 132.94, 129.7, 129.2, 128.57, 128.50, 127.4, 127.24, 127.22, 124.7, 123.6, 59.6, 37.3, 33.1, 21.5 ppm. Due to the overlap of aromatic carbon peaks, one carbon signal is missing. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 261.07 (d, *J* = 24.7 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}NSO_2SeNa^+$: 492.0506; Found: 492.0493.

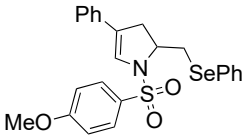
1-((4-(*tert*-Butyl)phenyl)sulfonyl)-4-phenyl-2-((phenylselanyl)methyl)-2,3-dihydro-1*H*-pyrrole (**98b**)



yellow solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.65 – 7.61 (m, 2H), 7.56 – 7.50 (m, 2H), 7.44 – 7.40 (m, 2H), 7.38 – 7.35 (m, 3H), 7.33 (m, 2H), 7.28 – 7.22 (m, 3H), 6.90 (t, *J* = 1.8 Hz, 1H), 3.91 (m, 1H), 3.76 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.09 – 2.94 (m, 2H), 2.75 (m, 1H), 1.32 (s, 9H) ppm. **^{13}C NMR** (151

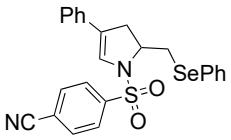
MHz, Chloroform-*d*): δ = 156.7, 133.5, 133.1, 132.9, 129.3, 128.67, 128.63, 127.29, 127.26, 127.23, 126.1, 124.8, 124.7, 123.3, 59.7, 37.4, 35.1, 33.1, 31.0 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 259.91 ppm. **HRMS** (ESI): m/z: $[M+H]^+$ Calcd. for $C_{27}H_{30}NSO_2Se^+$: 512.1157; Found: 512.1144.

1-((4-Methoxyphenyl)sulfonyl)-4-phenyl-2-((phenylselanyl)methyl)-2,3-dihydro-1*H*-pyrrole (**98c**)



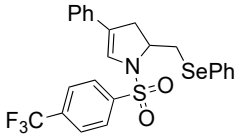
yellow solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.66 – 7.61 (m, 2H), 7.53 – 7.48 (m, 2H), 7.38 – 7.34 (m, 3H), 7.32 (m, 2H), 7.27 – 7.21 (m, 3H), 6.87 (m, 1H), 6.85 (m, 2H), 3.84 (m, 4H), 3.74 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.08 – 2.93 (m, 1H), 2.73 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 163.1, 133.5, 133.0, 129.5, 129.3, 128.6, 128.5, 127.6, 127.28, 127.24, 124.8, 124.7, 123.7, 114.3, 59.7, 55.5, 37.3, 33.2 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 261.39 (d, *J* = 24.9 Hz). **HRMS** (ESI): m/z: $[M]^+$ Calcd. for $C_{24}H_{23}NSO_3Se^+$: 485.0558; Found: 485.0551.

4-((4-Phenyl-2-((phenylselanyl)methyl)-2,3-dihydro-1*H*-pyrrol-1-yl)sulfonyl)benzonitrile (**98d**)



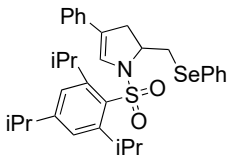
yellow solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.62 – 7.57 (m, 2H), 7.55 – 7.48 (m, 4H), 7.32 – 7.25 (m, 3H), 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 3H), 6.73 (t, *J* = 1.8 Hz, 1H), 3.75 – 3.66 (m, 1H), 3.62 (dd, *J* = 12.6, 3.0 Hz, 1H), 2.97 – 2.81 (m, 2H), 2.73 – 2.59 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 140.1, 133.4, 132.87, 132.83, 129.4, 128.7, 128.1, 127.9, 127.7, 127.6, 125.0, 124.8, 123.5, 117.1, 116.7, 59.9, 37.3, 33.0 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 265.52 (d, *J* = 25.6 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{20}N_2SO_2SeNa^+$: 503.0302; Found: 503.0278.

4-Phenyl-2-((phenylselanyl)methyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)-2,3-dihydro-1*H*-pyrrole (**98e**)



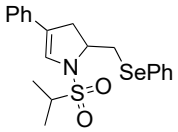
white solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.67 (s, 4H), 7.66 – 7.62 (m, 2H), 7.38 (m, 3H), 7.34 – 7.31 (m, 2H), 7.28 – 7.23 (m, 3H), 6.86 (t, *J* = 1.8 Hz, 1H), 3.83 (m, 1H), 3.74 (dd, *J* = 12.5, 3.0 Hz, 1H), 3.07 – 2.96 (m, 2H), 2.78 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 139.5, 134.6 (q, *J* = 33.1 Hz), 133.3, 132.9, 129.3, 128.6, 128.2, 127.8, 127.6, 127.5, 126.2 (q, *J* = 3.6 Hz), 124.8, 124.6, 123.8, 123.0 (q, *J* = 273.0 Hz), 59.8, 37.3, 33.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -63.17 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 264.14 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{20}NF_3SO_2SeNa^+$: 546.0224; Found: 546.0210.

4-Phenyl-2-((phenylselanyl)methyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-2,3-dihydro-1*H*-pyrrole (**98f**)



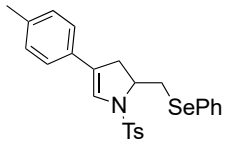
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.45 – 7.40 (m, 2H), 7.25 – 7.22 (m, 2H), 7.22 – 7.19 (m, 3H), 7.18 – 7.13 (m, 3H), 7.12 (m, 2H), 6.66 (t, *J* = 1.8 Hz, 1H), 4.51 – 4.38 (m, 1H), 4.12 (p, *J* = 6.7 Hz, 2H), 3.33 (dd, *J* = 12.2, 3.3 Hz, 1H), 3.16 (m, 1H), 3.00 (dd, *J* = 12.2, 10.4 Hz, 1H), 2.85 (p, *J* = 6.9 Hz, 1H), 2.77 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.18 (d, *J* = 6.8 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 153.6, 151.4, 133.7, 132.3, 131.0, 129.25, 129.23, 128.5, 127.1, 126.9, 124.6, 124.2, 122.5, 59.3, 37.3, 34.1, 32.9, 29.8, 25.0, 24.7, 23.5 ppm. Due to the overlap of aromatic carbon peaks, one carbon signal is missing. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 254.11 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{32}H_{39}NSO_2SeNa^+$: 604.1758; Found: 604.1750.

1-(Isopropylsulfonyl)-4-phenyl-2-((phenylselanyl)methyl)-2,3-dihydro-1*H*-pyrrole (**98g**)



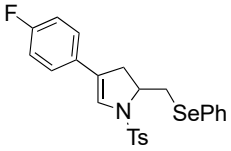
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.61 – 7.54 (m, 2H), 7.34 (m, 2H), 7.32 – 7.28 (m, 5H), 7.26 – 7.22 (m, 1H), 6.78 (t, *J* = 2.3 Hz, 1H), 4.44 (tt, *J* = 10.2, 3.7 Hz, 1H), 3.60 (dd, *J* = 12.5, 3.2 Hz, 1H), 3.38 – 3.24 (m, 2H), 3.06 (dd, *J* = 12.5, 10.3 Hz, 1H), 2.94 (m, 1H), 1.39 (d, *J* = 2.6 Hz, 3H), 1.37 (d, *J* = 2.7 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 133.6, 132.0, 129.3, 128.9, 128.6, 127.02, 127.01, 125.0, 124.5, 120.6, 60.5, 54.2, 36.8, 32.8, 16.8 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 251.53 (d, *J* = 21.5 Hz) ppm. **HRMS** (ESI): m/z: $[M+H]^+$ Calcd. for $C_{20}H_{24}NSO_2Se^+$: 422.0687; Found: 422.0676.

2-((Phenylselanyl)methyl)-4-(*p*-tolyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98h**)



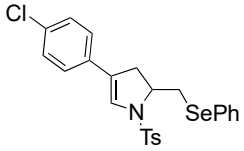
white solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.65 – 7.58 (m, 2H), 7.49 – 7.43 (m, 2H), 7.39 – 7.33 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.09 (m, 4H), 6.85 (t, *J* = 1.8 Hz, 1H), 3.89 – 3.82 (m, 1H), 3.74 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.00 (dd, *J* = 12.5, 10.8 Hz, 1H), 2.97 – 2.90 (m, 1H), 2.74 – 2.67 (m, 1H), 2.38 (s, 3H), 2.35 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.8, 137.1, 133.0, 132.9, 130.5, 129.7, 129.28, 129.26, 128.6, 127.4, 127.2, 124.7, 123.9, 123.8, 59.6, 37.3, 33.2, 21.5, 21.1 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 260.76 (d, *J* = 24.8 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{25}NSO_2SeNa^+$: 506.0663; Found: 506.0649.

4-(4-Fluorophenyl)-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98i**)



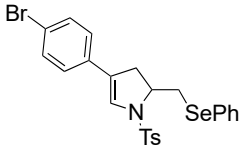
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.64 – 7.60 (m, 2H), 7.48 – 7.44 (m, 2H), 7.38 – 7.32 (m, 3H), 7.23 – 7.17 (m, 4H), 7.04 – 6.97 (m, 2H), 6.78 (t, *J* = 1.9 Hz, 1H), 3.93 – 3.83 (m, 1H), 3.74 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.00 (dd, *J* = 12.5, 10.8 Hz, 1H), 2.97 – 2.90 (m, 1H), 2.76 – 2.64 (m, 1H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 161.9 (d, *J* = 247.5 Hz), 143.9, 133.0, 129.7, 129.6 (d, *J* = 3.5 Hz), 129.3, 128.4, 127.4, 127.3, 126.3 (d, *J* = 7.9 Hz), 124.48, 124.47, 122.6, 115.5 (d, *J* = 21.7 Hz), 59.7, 37.5, 33.1, 21.5 ppm. **^{19}F NMR** (376 MHz, Chloroform-*d*): δ = -114.31 (t, *J* = 5.0 Hz) ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 260.96 (d, *J* = 24.2 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{22}NFSO_2SeNa^+$: 510.0412; Found: 510.0398.

4-(4-Chlorophenyl)-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98j**)



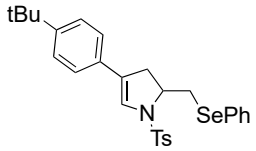
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.65 – 7.59 (m, 2H), 7.47 – 7.42 (m, 2H), 7.38 – 7.33 (m, 3H), 7.31 – 7.25 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.14 (m, 2H), 6.84 (t, *J* = 1.8 Hz, 1H), 3.92 – 3.82 (m, 1H), 3.74 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.07 – 2.90 (m, 2H), 2.77 – 2.61 (m, 1H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 144.0, 133.04, 133.02, 132.8, 131.9, 129.7, 129.3, 128.7, 128.4, 127.4, 127.3, 125.9, 125.3, 122.4, 59.7, 37.3, 33.1, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 261.23 (d, *J* = 24.9 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{22}NSClO_2SeNa^+$: 526.0117; Found: 526.0098.

4-(4-Bromophenyl)-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98k**)



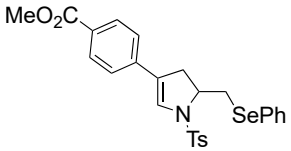
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.68 – 7.57 (m, 2H), 7.50 – 7.39 (m, 4H), 7.39 – 7.32 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.06 (m, 2H), 6.86 (t, *J* = 1.8 Hz, 1H), 3.92 – 3.81 (m, 1H), 3.74 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.06 – 2.88 (m, 2H), 2.76 – 2.63 (m, 1H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 144.0, 133.05, 133.01, 132.4, 131.6, 129.7, 129.3, 128.4, 127.4, 127.3, 126.2, 125.4, 122.4, 120.8, 59.7, 37.2, 33.1, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 261.30 (d, *J* = 24.6 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{22}NSO_2BrSeNa^+$: 569.9612; Found: 569.9595.

4-(4-(*tert*-Butyl)phenyl)-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98l**)



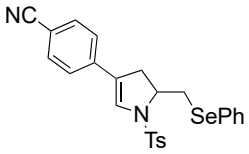
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.66 – 7.59 (m, 2H), 7.50 – 7.45 (m, 2H), 7.40 – 7.32 (m, 5H), 7.20 (dd, *J* = 8.4, 7.1 Hz, 4H), 6.83 (t, *J* = 1.9 Hz, 1H), 3.93 – 3.83 (m, 1H), 3.73 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.07 – 2.88 (m, 2H), 2.77 – 2.66 (m, 1H), 2.39 (s, 3H), 1.33 (s, 9H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 150.5, 143.8, 133.0, 132.9, 130.6, 129.7, 129.3, 128.6, 127.4, 127.2, 125.5, 124.5, 124.0, 123.7, 59.6, 37.3, 34.6, 33.2, 31.2, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 260.22 (d, *J* = 24.7 Hz) ppm. **HRMS** (ESI): m/z: $[M+H]^+$ Calcd. for $C_{28}H_{32}NSO_2Se^+$: 526.1313; Found: 526.1302.

Methyl 4-(5-((phenylselanyl)methyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)benzoate (**98m**)



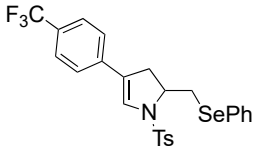
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.87 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.58 – 7.47 (m, 2H), 7.42 – 7.33 (m, 2H), 7.30 – 7.22 (m, 2H), 7.23 – 7.15 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.89 (t, *J* = 1.7 Hz, 1H), 3.83 (s, 3H), 3.82 – 3.77 (m, 1H), 3.65 (dd, *J* = 12.6, 3.0 Hz, 1H), 2.97 – 2.83 (m, 2H), 2.71 – 2.61 (m, 1H), 2.30 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 166.6, 144.1, 138.0, 133.12, 133.10, 129.89, 129.84, 129.3, 128.42, 128.40, 127.38, 127.37, 127.2, 124.4, 122.2, 59.8, 52.1, 37.2, 33.1, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 261.76 (d, *J* = 24.6 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{25}NSO_4SeNa^+$: 550.0561; Found: 526.0551.

4-(4-Isocyanophenyl)-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98n**)



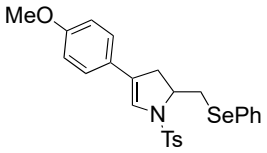
yellow solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.57 – 7.50 (m, 2H), 7.50 – 7.46 (m, 2H), 7.39 – 7.32 (m, 2H), 7.28 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 1.7 Hz, 1H), 3.87 – 3.76 (m, 1H), 3.65 (dd, *J* = 12.6, 2.9 Hz, 1H), 2.98 – 2.84 (m, 2H), 2.72 – 2.59 (m, 1H), 2.31 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 144.2, 138.1, 133.1, 133.0, 132.3, 129.9, 129.3, 128.3, 128.2, 127.4, 127.3, 124.9, 121.2, 118.8, 110.0, 59.9, 37.1, 33.0, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 261.69 (d, *J* = 25.3 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{22}N_2SO_2SeNa^+$: 517.0459; Found: 517.0449.

2-((Phenylselanyl)methyl)-1-tosyl-4-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-pyrrole (**98o**)



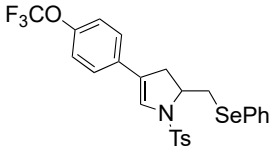
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.64 – 7.61 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.39 – 7.35 (m, 3H), 7.34 – 7.31 (m, 2H), 7.23 – 7.19 (m, 2H), 6.97 (t, *J* = 1.8 Hz, 1H), 3.90 (m, 1H), 3.75 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.08 – 2.92 (m, 2H), 2.74 (m, 1H), 2.40 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 144.1, 137.0, 133.1, 133.0, 129.8, 129.3, 128.8 (d, *J* = 32.6 Hz), 128.3, 127.4, 127.3, 127.0, 125.5 (q, *J* = 3.8 Hz), 124.7, 124.0 (d, *J* = 271.9 Hz), 121.9, 59.8, 37.2, 33.1, 21.5 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -62.54 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 261.50 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{22}NF_3SO_2SeNa^+$: 560.0380; Found: 560.0367

4-(4-Methoxyphenyl)-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98p**)



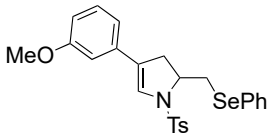
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.56 – 7.50 (m, 2H), 7.40 – 7.35 (m, 2H), 7.30 – 7.24 (m, 3H), 7.12 – 7.02 (m, 4H), 6.79 – 6.70 (m, 2H), 6.62 (t, *J* = 1.8 Hz, 1H), 3.79 – 3.74 (m, 1H), 3.72 (s, 3H), 3.64 (dd, *J* = 12.5, 3.1 Hz, 1H), 2.91 (dd, *J* = 12.5, 10.8 Hz, 1H), 2.86 – 2.78 (m, 1H), 2.63 – 2.56 (m, 1H), 2.29 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 158.9, 143.7, 133.0, 132.9, 129.6, 129.2, 128.6, 127.4, 127.2, 126.1, 126.0, 123.6, 122.9, 114.0, 59.6, 55.3, 37.4, 33.2, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 260.62 (d, *J* = 26.2 Hz) ppm. **HRMS** (ESI): m/z: $[M]^+$ Calcd. for $C_{25}H_{25}NSO_3^+$: 499.0714; Found: 499.0720.

2-((Phenylselanyl)methyl)-1-tosyl-4-(4-(trifluoromethoxy)phenyl)-2,3-dihydro-1*H*-pyrrole (**98q**)



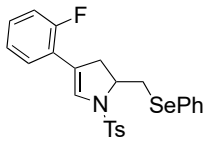
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.67 – 7.56 (m, 2H), 7.49 – 7.41 (m, 2H), 7.40 – 7.33 (m, 3H), 7.27 – 7.23 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.85 (t, *J* = 1.8 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.74 (dd, *J* = 12.5, 3.0 Hz, 1H), 3.07 – 2.90 (m, 2H), 2.76 – 2.66 (m, 1H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 148.08, 148.07, 144.0, 133.0, 132.3, 129.7, 129.3, 128.4, 127.4, 127.3, 125.9, 125.5, 122.1, 121.1, 120.4 (q, *J* = 257.3 Hz), 59.7, 37.4, 33.1, 21.5 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ = -57.92 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 260.94 (d, *J* = 24.1 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{22}NF_3SO_3SeNa^+$: 576.0329; Found: 576.0317.

4-(3-Methoxyphenyl)-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98r**)



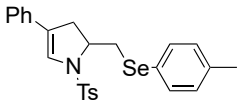
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.56 – 7.48 (m, 2H), 7.39 – 7.34 (m, 2H), 7.30 – 7.22 (m, 3H), 7.16 – 7.07 (m, 3H), 6.78 – 6.73 (m, 2H), 6.69 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.67 – 6.65 (m, 1H), 3.82 – 3.73 (m, 1H), 3.73 (s, 3H), 3.64 (dd, *J* = 12.5, 3.0 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.67 – 2.57 (m, 1H), 2.29 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 159.7, 143.9, 134.8, 133.0, 132.9, 129.7, 129.5, 129.2, 128.5, 127.4, 127.2, 125.1, 123.5, 117.3, 112.6, 110.4, 59.7, 55.2, 37.4, 33.2, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 260.94 (d, *J* = 24.6 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{25}NSO_3SeNa^+$: 522.0612; Found: 522.0601.

4-(2-Fluorophenyl)-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98s**)



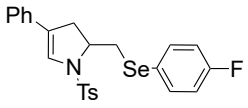
light yellow solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.56 – 7.51 (m, 2H), 7.41 – 7.37 (m, 2H), 7.30 – 7.23 (m, 3H), 7.14 – 7.05 (m, 3H), 7.02 – 6.91 (m, 4H), 3.77 – 3.70 (m, 1H), 3.68 (dd, *J* = 12.5, 3.0 Hz, 1H), 2.96 – 2.85 (m, 2H), 2.72 – 2.63 (m, 1H), 2.29 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 160.2 (d, *J* = 250.8 Hz), 143.9, 133.05, 133.02, 129.7, 129.3, 129.2, 128.5, 127.9 (d, *J* = 8.5 Hz), 127.4, 127.3, 127.2, 124.1 (d, *J* = 3.3 Hz), 121.7 (d, *J* = 13.2 Hz), 117.2 (d, *J* = 3.2 Hz), 115.7 (d, *J* = 22.4 Hz), 58.7, 38.1, 33.2, 21.5 ppm. **^{19}F** NMR (565 MHz, Chloroform-*d*) δ = -110.08 (dd, *J* = 12.3, 6.2 Hz) ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 261.03 (d, *J* = 25.0 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{22}NFSO_2SeNa^+$: 510.0412; Found: 510.0402.

4-Phenyl-2-((*p*-tolylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98t**)



white solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.54 – 7.50 (m, 2H), 7.47 – 7.43 (m, 2H), 7.34 – 7.29 (m, 2H), 7.26 – 7.21 (m, 3H), 7.20 – 7.15 (m, 4H), 6.85 (t, *J* = 1.8 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.69 (dd, *J* = 12.4, 3.1 Hz, 1H), 3.02 – 2.89 (m, 2H), 2.78 – 2.67 (m, 1H), 2.42 (s, 3H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.8, 137.3, 133.5, 133.0, 130.0, 129.6, 128.5, 127.4, 127.2, 124.8, 124.7, 124.6, 123.6, 59.7, 37.3, 33.4, 21.5, 21.1 ppm. Due to the overlap of aromatic carbon peaks, one carbon signal is missing. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 253.76 (d, *J* = 24.3 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{25}NSO_2SeNa^+$: 506.0663; Found: 506.0662.

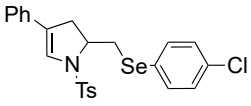
2-(((4-Fluorophenyl)selanyl)methyl)-4-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98u**)



white solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.53 – 7.48 (m, 2H), 7.38 – 7.33 (m, 2H), 7.25 – 7.20 (m, 2H), 7.17 – 7.10 (m, 5H), 7.00 – 6.94 (m, 2H), 6.76 (t, *J* = 1.8 Hz, 1H), 3.75 – 3.66 (m, 1H),

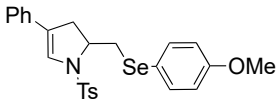
3.56 (dd, *J* = 12.5, 3.1 Hz, 1H), 2.97 – 2.83 (m, 2H), 2.68 – 2.57 (m, 1H), 2.30 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 162.6 (d, *J* = 247.5 Hz), 144.0, 135.6 (d, *J* = 7.8 Hz), 133.4, 133.0, 129.7, 128.6, 127.3, 127.2, 124.8, 124.7, 123.6, 122.8 (d, *J* = 3.4 Hz), 116.4 (d, *J* = 21.4 Hz), 59.6, 37.3, 34.0, 21.5 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -114.20 (d, *J* = 5.0 Hz) ppm. **^{77}Se** NMR (115 MHz, Chloroform-*d*): δ = 257.54 (d, *J* = 25.6 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{22}NFSO_2SeNa^+$: 510.0412; Found: 510.0392.

2-(((4-Chlorophenyl)selanyl)methyl)-4-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98v**)



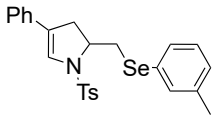
white solid; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.53 – 7.48 (m, 2H), 7.44 – 7.39 (m, 2H), 7.31 – 7.26 (m, 4H), 7.23 – 7.16 (m, 5H), 6.82 (t, *J* = 1.9 Hz, 1H), 3.81 – 3.70 (m, 1H), 3.66 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.03 – 2.85 (m, 2H), 2.72 – 2.62 (m, 1H), 2.36 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 144.0, 134.5, 133.6, 133.3, 132.9, 129.8, 129.4, 128.6, 127.38, 127.31, 126.6, 124.8, 124.7, 123.6, 59.5, 37.3, 33.6, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 260.59 (d, *J* = 25.3 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{22}NClSO_2SeNa^+$: 526.0117; Found: 526.0114.

2-(((4-Methoxyphenyl)selanyl)methyl)-4-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98w**)



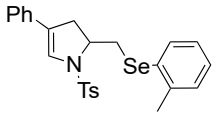
white solid; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.58 – 7.54 (m, 2H), 7.43 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.21 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.94 – 6.89 (m, 2H), 6.85 (t, *J* = 1.8 Hz, 1H), 3.88 (s, 3H), 3.82 – 3.73 (m, 1H), 3.64 (dd, *J* = 12.3, 3.1 Hz, 1H), 3.04 – 2.87 (m, 2H), 2.77 – 2.68 (m, 1H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 159.6, 143.8, 135.9, 133.5, 132.9, 129.6, 128.5, 127.4, 127.2, 124.9, 124.7, 123.5, 118.1, 114.9, 59.8, 55.3, 37.3, 34.1, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 251.59 (d, *J* = 25.4 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{25}NSO_3SeNa^+$: 522.0612; Found: 522.0603.

4-Phenyl-2-((*m*-tolylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98x**)



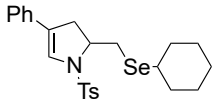
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.50 – 7.47 (m, 2H), 7.45 (s, 1H), 7.43 – 7.39 (m, 1H), 7.34 – 7.29 (m, 2H), 7.27 – 7.23 (m, 4H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.17 – 7.13 (m, 1H), 6.86 (t, *J* = 1.8 Hz, 1H), 3.94 – 3.83 (m, 1H), 3.74 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.05 – 2.88 (m, 2H), 2.79 – 2.66 (m, 1H), 2.40 (s, 3H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.8, 139.1, 133.4, 133.2, 133.1, 129.76, 129.72, 129.0, 128.5, 128.3, 128.0, 127.4, 127.2, 124.7, 123.7, 59.7, 37.3, 33.0, 21.5, 21.2 ppm. Due to the overlap of aromatic carbon peaks, one carbon signal is missing. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 257.92 (d, *J* = 25.3 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{25}NSO_2SeNa^+$: 506.0663; Found: 506.0655.

4-Phenyl-2-((*o*-tolylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98y**)



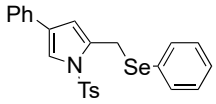
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.70 – 7.61 (m, 1H), 7.53 – 7.44 (m, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.19 (m, 8H), 6.86 (t, *J* = 1.9 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.71 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.05 – 2.91 (m, 2H), 2.79 – 2.70 (m, 1H), 2.47 (s, 3H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.8, 139.9, 133.4, 133.1, 132.3, 130.2, 129.7, 129.4, 128.5, 127.4, 127.26, 127.24, 126.6, 124.76, 124.72, 123.6, 59.5, 37.4, 32.0, 22.3, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 213.99 (d, *J* = 24.1 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{25}NSO_2SeNa^+$: 506.0663; Found: 506.0655.

2-((Cyclohexylselanyl)methyl)-4-phenyl-1-tosyl-2,3-dihydro-1H-pyrrole (**98z**)



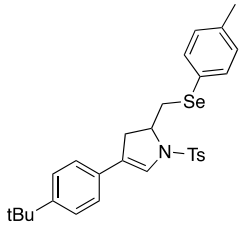
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): 7.63 – 7.53 (m, 2H), 7.26 – 7.20 (m, 4H), 7.19 – 7.17 (m, 2H), 7.16 – 7.11 (m, 1H), 6.78 (t, *J* = 1.9 Hz, 1H), 3.98 – 3.86 (m, 1H), 3.14 (dd, *J* = 12.2, 3.3 Hz, 1H), 3.01 – 2.93 (m, 1H), 2.91 – 2.84 (m, 1H), 2.78 (dd, *J* = 12.2, 10.5 Hz, 1H), 2.63 – 2.57 (m, 1H), 2.34 (s, 3H), 2.08 – 1.92 (m, 2H), 1.78 – 1.65 (m, 2H), 1.62 – 1.56 (m, 1H), 1.47 – 1.40 (m, 2H), 1.35 – 1.21 (m, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-d): δ = 144.01, 133.6, 133.5, 129.8, 128.6, 127.4, 127.2, 124.7, 124.6, 123.7, 60.6, 39.4, 37.4, 34.7, 34.6, 28.6, 26.9, 25.8, 21.5 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{29}NSO_2SeNa^+$: 498.09764; Found: 498.09796.

4-Phenyl-2-((phenylselanyl)methyl)-1-tosyl-1*H*-pyrrole (**98aa**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.65 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.38 – 7.29 (m, 10H), 6.99 (s, 1H), 6.51 (s, 1H), 4.28 (d, *J* = 1.5 Hz, 2H), 2.46 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 144.1, 136.6, 134.9, 133.4, 129.8, 129.5, 128.7, 128.0, 127.4, 127.3, 127.2, 127.01, 124.9, 122.3, 122.2, 120.1, 48.8, 21.6 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 428.85 ppm. **HRMS** (ESI): m/z: $[M-C_7H_8O_2S]^+$ Calcd. for $C_{17}H_{14}NSe^+$: 312.02860 ; Found: 312.02911.

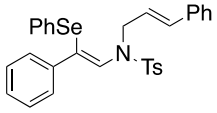
4-(4-(*tert*-Butyl)phenyl)-2-((*p*-tolylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (**98ab**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.51 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.36 – 7.32 (m, 2H), 7.22 – 7.15 (m, 6H), 6.82 – 6.79 (m, 1H), 3.83 (tdd, *J* = 10.5, 5.6, 3.1 Hz, 1H), 3.68 (dd,

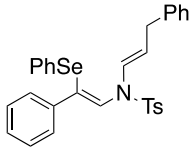
J = 12.4, 3.1 Hz, 1H), 3.02 – 2.85 (m, 2H), 2.76 – 2.60 (m, 1H), 2.41 (s, 3H), 2.39 (s, 3H), 1.32 (s, 9H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ =150.4, 143.7, 137.3, 133.4, 133.0, 130.6, 130.0, 129.6, 127.4, 125.5, 124.6, 124.5, 124.0, 123.7, 59.7, 37.2, 34.5, 33.5, 31.2, 21.5, 21.1 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 253.08 (d, *J* = 25.3 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{33}NSO_2SeNa^+$: 562.1289; Found: 562.1268.

N-cinnamyl-4-methyl-*N*-((*Z*)-2-phenyl-2-(phenylselanyl)vinyl)benzenesulfonamide (**101**)



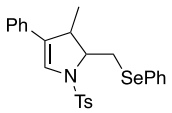
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.24 (m, 9H), 7.15 – 7.06 (m, 5H), 7.05 – 6.98 (m, 1H), 6.90 (t, *J* = 7.7 Hz, 2H), 6.64 – 6.54 (m, 1H), 6.29 (dt, *J* = 15.8, 6.7 Hz, 1H), 6.14 (s, 1H), 4.23 (dd, *J* = 6.7, 1.4 Hz, 2H), 2.45 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.8, 141.0, 138.0, 136.3, 135.4, 134.0, 133.3, 129.7, 129.5, 128.9, 128.6, 128.5, 128.1, 127.93, 127.90, 127.7, 126.88, 126.87, 126.5, 123.8, 52.4, 21.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 411.11 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{27}NSO_2SeNa^+$: 568.0819; Found: 568.0812.

4-Methyl-*N*-((*Z*)-2-phenyl-2-(phenylselanyl)vinyl)-*N*-((*E*)-3-phenylprop-1-en-1-yl)benzenesulfonamide (**102**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.77 – 7.62 (m, 2H), 7.34 – 7.25 (m, 6H), 7.24 – 7.21 (m, 1H), 7.16 – 6.98 (m, 10H), 6.89 (s, 1H), 5.89 (d, *J* = 15.8 Hz, 1H), 5.56 (dt, *J* = 15.9, 6.5 Hz, 1H), 3.76 (dd, *J* = 6.6, 1.4 Hz, 2H), 2.44 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 144.0, 137.9, 136.2, 135.9, 133.5, 132.4, 130.5, 129.8, 129.4, 128.9, 128.7, 128.5, 128.1, 127.9, 127.8, 127.4, 127.1, 126.4, 125.0, 123.3, 50.0, 21.6 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 482.05 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{27}NSO_2SeNa^+$: 568.0819; Found: 568.0810.

3-Methyl-4-phenyl-2-((phenylselanyl)methyl)-1-tosyl-2,3-dihydro-1*H*-pyrrole (104, d.r. = 1:1)



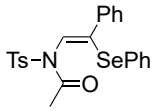
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.69 – 7.64 (m, 2H), 7.63 – 7.59 (m, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.38 – 7.33 (m, 5H), 7.32 – 7.22 (m, 10H), 7.22 – 7.17 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 6.73 (s, 1H), 3.99 – 3.90 (m, 1H), 3.59 – 3.54 (m, 1H), 3.52 – 3.45 (m, 2H), 3.43 – 3.37 (m, 1H), 3.26 – 3.17 (m, 1H), 3.13 – 3.06 (m, 1H), 2.92 (dd, *J* = 12.6, 11.2 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 1.12 (d, *J* = 6.0 Hz, 3H), 0.43 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 143.8, 134.2, 133.2, 132.7, 132.7, 131.3, 129.6, 129.5, 129.4, 129.2, 129.2, 128.8, 128.6, 127.76, 127.73, 127.3, 127.15, 127.11, 127.0, 125.5, 125.3, 125.1, 123.3, 66.7, 64.7, 43.7, 40.1,

32.2, 26.5, 21.53, 21.50, 21.0, 13.6 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 288.93 (d, *J* = 26.1 Hz), 247.12 (d, *J* = 25.8 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{25}NSO_2SeNa^+$: 506.0663; Found: 506.0652.

General procedure of rhodium-catalyzed 1,3-difunctionalization of triazoles with acyl selenides.

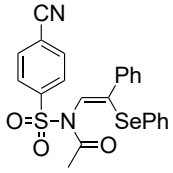
Typical experimental procedure: the acyl selenide (0.2 mmol, 1.0 equiv.), triazole (1.0 equiv.) and $Rh_2(Piv)_4$ (2 mol%) were added in a tube with stir bar. The tube was charged with argon (repeated three times), and then the solvent (toluene, 1.0 mL) was injected, and stirred at the 100 °C in a preheated aluminum block for 2 h. After cooling down to room temperature, solvent was removed under reduced pressure, the crude reaction mixture was purified by column chromatography using *n*-hexane : ethyl acetate as eluent to afford the final product.

(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116a**)



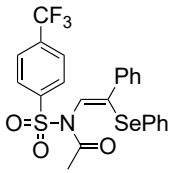
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.04 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.37 – 7.32 (m, 2H), 7.25 – 7.21 (m, 3H), 7.20 – 7.16 (m, 2H), 7.14 – 7.08 (m, 1H), 7.08 – 7.02 (m, 2H), 6.66 (s, 1H), 2.45 (s, 3H), 2.34 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.4, 146.5, 145.1, 136.7, 136.1, 133.8, 129.4, 129.0, 128.99, 128.96, 128.8, 128.2, 127.9, 127.6, 123.2, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 409.54 (d, *J* = 6.1 Hz) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{21}O_3NSSeNa^+$: 494.0299; Found: 494.0292.

(*Z*)-*N*-((4-nitrophenyl)sulfonyl)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)acetamide (**116b**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.26 – 8.17 (m, 2H), 7.76 – 7.66 (m, 2H), 7.36 – 7.29 (m, 2H), 7.17 – 7.12 (m, 3H), 7.09 – 7.02 (m, 3H), 7.02 – 6.95 (m, 2H), 6.59 (s, 1H), 2.23 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.6, 147.9, 143.1, 136.2, 133.7, 132.4, 129.8, 129.3, 129.1, 128.9, 128.3, 127.9, 127.3, 122.3, 117.5, 117.2, 24.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 407.87 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{18}O_3N_2SSeNa^+$: 505.0095; Found: 505.0073.

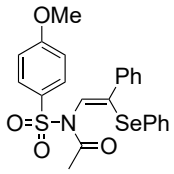
(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-((4-(trifluoromethyl)phenyl)sulfonyl)acetamide (**116c**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.22 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.16 – 7.12 (m, 3H), 7.10 – 7.06 (m, 2H), 7.05 – 7.01 (m, 1H), 6.99 – 6.93 (m, 2H), 6.58 (s, 1H), 2.23 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.6, 147.7, 142.5, 136.3,

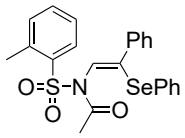
135.4 (q, *J* = 33.2 Hz), 133.8, 129.7, 129.2, 129.0, 128.9, 128.3, 127.8, 127.4, 125.8 (q, *J* = 3.7 Hz), 122.4, 122.2 (q, *J* = 273.1 Hz), 24.5 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -63.20 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 409.66 – 409.32 (m) ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{18}O_3NF_3SSeNa^+$: 548.0016; Found: 548.0023.

(*Z*)-*N*-((4-methoxyphenyl)sulfonyl)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)acetamide (**116d**)



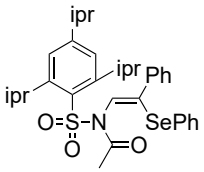
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.02 – 7.96 (m, 2H), 7.34 – 7.29 (m, 2H), 7.14 – 7.10 (m, 3H), 7.10 – 7.05 (m, 2H), 7.04 – 6.98 (m, 1H), 6.98 – 6.94 (m, 2H), 6.92 – 6.86 (m, 2H), 6.56 (s, 1H), 3.79 (s, 3H), 2.24 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.4, 164.0, 146.3, 136.7, 133.8, 131.4, 130.5, 128.96, 128.94, 128.8, 128.2, 127.9, 127.6, 123.3, 113.9, 55.7, 24.6 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 408.72 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{21}O_4NSSeNa^+$: 510.0248; Found: 510.0246.

(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-(*o*-tolylsulfonyl)acetamide (**116e**)



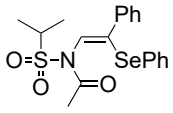
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.13 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.13 – 7.06 (m, 5H), 7.04 – 6.99 (m, 1H), 6.97 – 6.93 (m, 2H), 6.51 (s, 1H), 2.64 (s, 3H), 2.29 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.4, 147.3, 138.2, 137.5, 136.8, 134.1, 133.8, 132.6, 131.5, 128.9, 128.87, 128.82, 128.1, 127.8, 127.6, 126.3, 122.5, 24.7, 20.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 417.09 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{21}O_3NSSeNa^+$: 494.0299; Found: 494.0272.

(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-((2,4,6-triisopropylphenyl)sulfonyl)acetamide (**116f**)



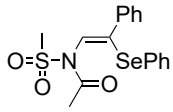
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.41 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.23 (d, *J* = 2.6 Hz, 5H), 7.15 – 7.09 (m, 1H), 7.09 – 7.03 (m, 2H), 6.49 (s, 1H), 4.25 (p, *J* = 6.8 Hz, 2H), 2.94 (p, *J* = 6.9 Hz, 1H), 2.34 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 12H), 1.29 (d, *J* = 6.9 Hz, 6H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.5, 153.8, 151.6, 149.5, 136.9, 134.5, 132.6, 129.0, 128.9, 128.8, 128.1, 127.88, 127.80, 123.9, 121.1, 34.2, 29.2, 24.6, 24.3, 23.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 430.21 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{31}H_{37}O_3NSSeNa^+$: 606.1551; Found: 606.1544.

(*Z*)-*N*-(isopropylsulfonyl)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)acetamide (**116g**)



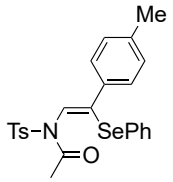
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.32 – 7.29 (m, 2H), 7.18 – 7.15 (m, 2H), 7.13 – 7.10 (m, 3H), 7.05 – 7.00 (m, 1H), 7.00 – 6.95 (m, 2H), 6.45 (s, 1H), 4.12 – 3.97 (m, 1H), 2.31 (s, 3H), 1.42 (d, *J* = 6.9 Hz, 6H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 170.9, 146.2, 136.7, 134.1, 129.0, 128.93, 128.91, 128.1, 127.7, 127.6, 123.3, 55.9, 24.6, 16.2 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 407.54 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{21}O_3NSSeNa^+$: 446.0299; Found: 446.0277.

(*Z*)-*N*-(methylsulfonyl)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)acetamide (**116h**)



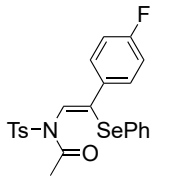
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.44 – 7.40 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.18 – 7.13 (m, 1H), 7.13 – 7.08 (m, 2H), 6.64 (s, 1H), 3.55 (s, 3H), 2.36 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 170.9, 146.6, 136.3, 133.8, 129.18, 129.13, 128.9, 128.2, 127.9, 127.3, 123.0, 43.5, 24.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 401.79 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{17}O_3NSSeNa^+$: 417.9986; Found: 417.9982.

(*Z*)-*N*-(2-(phenylselanyl)-2-(*p*-tolyl)vinyl)-*N*-tosylacetamide (**116i**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.03 (dd, *J* = 8.3, 3.4 Hz, 2H), 7.39 – 7.28 (m, 4H), 7.22 – 7.16 (m, 2H), 7.14 – 7.10 (m, 1H), 7.09 – 7.00 (m, 4H), 6.65 (d, *J* = 3.5 Hz, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 2.29 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.5, 146.3, 145.0, 139.1, 136.1, 133.9, 133.5, 129.4, 129.0, 128.9, 128.86, 128.82, 128.2, 127.4, 122.9, 24.7, 21.7, 21.2 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 401.40 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_3NSSeNa^+$: 508.0456; Found: 508.0435.

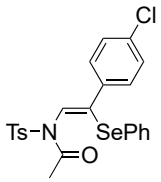
(*Z*)-*N*-(2-(4-fluorophenyl)-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116j**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.06 – 7.98 (m, 2H), 7.44 – 7.38 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.16 – 7.12 (m, 1H), 7.10 – 7.05 (m, 2H), 6.95 – 6.84 (m, 2H), 6.62 (s, 1H), 2.45 (s, 3H), 2.34 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.4, 162.9 (d, *J* = 249.4 Hz), 145.5, 145.2, 136.1, 134.0, 132.8 (d, *J* = 3.4 Hz), 130.7 (d, *J* = 8.4 Hz), 129.4, 128.97, 128.96, 127.8, 127.6, 123.2, 115.2 (d, *J* = 21.8 Hz), 24.7, 21.7 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -

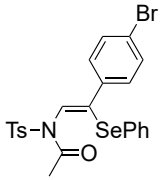
111.92 (tt, *J* = 9.1, 5.1 Hz) ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 412.23 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{20}O_3NSFSeNa^+$: 512.0205; Found:512.0194.

(*Z*)-*N*-(2-(4-chlorophenyl)-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116k**)



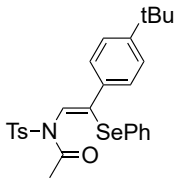
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.02 – 7.95 (m, 2H), 7.37 – 7.27 (m, 4H), 7.19 – 7.13 (m, 4H), 7.12 – 7.08 (m, 1H), 7.08 – 6.99 (m, 2H), 6.60 (s, 1H), 2.41 (s, 3H), 2.29 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.3, 145.3, 145.2, 136.1, 135.3, 134.9, 133.9, 130.2, 129.4, 129.0, 128.9, 128.4, 127.9, 127.6, 123.7, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 408.82 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{20}O_3NSClSeNa^+$: 527.9909; Found: 527.9900.

(*Z*)-*N*-(2-(4-bromophenyl)-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (116l)



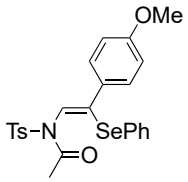
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.92 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.22 – 7.17 (m, 2H), 7.11 – 7.03 (m, 3H), 7.01 – 6.96 (m, 2H), 6.53 (s, 1H), 2.36 (s, 3H), 2.24 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.3, 145.28, 145.26, 136.0, 135.8, 133.8, 131.4, 130.4, 129.5, 129.0, 128.9, 127.9, 127.5, 123.7, 123.1, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 410.15 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{20}O_3NBrSSeNa^+$: 571.9404; Found: 571.9397.

(*Z*)-*N*-(2-(4-(*tert*-butyl)phenyl)-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116m**)



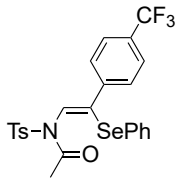
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.03 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 2H), 7.18 – 7.14 (m, 2H), 7.12 – 7.08 (m, 1H), 7.07 – 7.03 (m, 2H), 6.67 (s, 1H), 2.45 (s, 3H), 2.31 (s, 3H), 1.27 (s, 9H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.5, 152.3, 146.2, 145.0, 136.1, 133.7, 133.5, 129.3, 129.0, 128.7, 128.6, 128.2, 127.3, 125.1, 122.9, 34.6, 31.1, 24.6, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 403.69 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{29}O_3NSSeNa^+$: 550.0925; Found: 550.0920.

(*Z*)-*N*-(2-(4-methoxyphenyl)-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116n**)



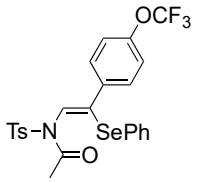
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.03 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.20 – 7.16 (m, 2H), 7.14 – 7.10 (m, 1H), 7.09 – 7.05 (m, 2H), 6.81 – 6.72 (m, 2H), 6.61 (s, 1H), 3.77 (s, 3H), 2.45 (s, 3H), 2.31 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.6, 160.2, 146.0, 145.0, 136.1, 133.4, 130.2, 129.4, 129.1, 129.0, 128.8, 128.3, 127.4, 122.2, 113.6, 55.2, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 399.94 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_4NSSeNa^+$: 524.0405; Found: 524.0394.

(*Z*)-*N*-(2-(phenylselanyl)-2-(4-(trifluoromethyl)phenyl)vinyl)-*N*-tosylacetamide (**116o**)



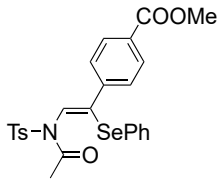
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = δ = 8.05 – 7.97 (m, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.16 (m, 2H), 7.16 – 7.11 (m, 1H), 7.10 – 7.05 (m, 2H), 6.67 (s, 1H), 2.47 (s, 3H), 2.37 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.2, 145.3, 144.9, 140.5, 136.0, 134.0, 130.7 (d, *J* = 32.7 Hz), 129.5, 129.2, 129.0, 128.8, 128.0, 127.2, 125.5 (d, *J* = 263.6 Hz), 125.1 (q, *J* = 3.6 Hz), 124.5, 24.7, 21.7 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -62.78 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 416.92 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{20}O_3F_3NSSeNa^+$: 562.0173; Found: 562.0152.

(*Z*)-*N*-(2-(phenylselanyl)-2-(4-(trifluoromethoxy)phenyl)vinyl)-*N*-tosylacetamide (**116p**)



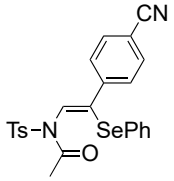
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.03 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.16 (m, 2H), 7.16 – 7.11 (m, 1H), 7.09 – 7.03 (m, 4H), 6.63 (s, 1H), 2.46 (s, 3H), 2.35 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.3, 149.3, 145.28, 145.25, 136.0, 135.4, 134.1, 130.4, 129.5, 128.99, 128.94, 127.9, 127.3, 123.6, 120.5, 120.2 (q, *J* = 257.7 Hz), 24.7, 21.7 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -57.90 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 417.56 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{20}O_4NF_3SSeNa^+$: 578.0122; Found: 578.0107.

Methyl (*Z*)-4-(1-(phenylselanyl)-2-(*N*-tosylacetamido)vinyl)benzoate (**116q**)



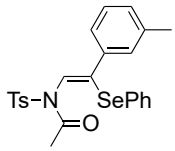
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.02 (d, *J* = 8.4 Hz, 2H), 7.91 – 7.82 (m, 2H), 7.50 – 7.45 (m, 2H), 7.37 – 7.32 (m, 2H), 7.20 – 7.15 (m, 2H), 7.13 – 7.08 (m, 1H), 7.07 – 7.00 (m, 2H), 6.69 (s, 1H), 3.89 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.2, 166.4, 145.4, 145.3, 141.3, 136.0, 133.9, 130.3, 129.5, 129.4, 129.0, 128.95, 128.92, 127.9, 127.3, 124.3, 52.2, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 414.85 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{23}O_5NSSeNa^+$: 552.0354; Found: 552.0337.

(*Z*)-*N*-(2-(4-cyanophenyl)-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116r**)



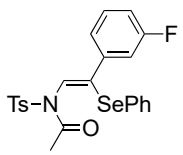
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.05 – 7.97 (m, 2H), 7.54 – 7.46 (m, 4H), 7.39 – 7.33 (m, 2H), 7.19 – 7.13 (m, 3H), 7.10 – 7.06 (m, 2H), 6.67 (s, 1H), 2.46 (s, 3H), 2.37 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.0, 145.4, 144.5, 141.6, 135.9, 134.1, 131.9, 129.64, 129.60, 129.1, 128.8, 128.2, 126.9, 125.0, 118.2, 112.4, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 419.72 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{20}O_3N_2SSeNa^+$: 519.0252; Found: 519.0236.

(*Z*)-*N*-(2-(phenylselanyl)-2-(*m*-tolyl)vinyl)-*N*-tosylacetamide (**116s**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.04 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.17 (m, 4H), 7.14 – 7.09 (m, 2H), 7.08 – 7.00 (m, 3H), 6.64 (s, 1H), 2.45 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.5, 146.6, 145.0, 137.8, 136.6, 136.2, 133.8, 129.6, 129.5, 129.4, 129.0, 128.7, 128.0, 127.9, 127.6, 126.1, 122.9, 24.6, 21.7, 21.1 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 407.61 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_3NSSeNa^+$: 508.0456; Found: 508.0446.

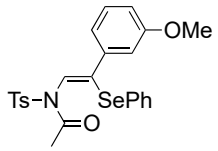
(*Z*)-*N*-(2-(3-fluorophenyl)-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116t**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.04 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.21 – 7.17 (m, 1H), 7.17 – 7.12 (m, 2H), 7.11 – 7.06 (m, 2H), 6.96 – 6.86 (m, 1H), 6.68 (s, 1H), 2.45 (s, 3H), 2.34 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.3, 162.3 (d, *J* =

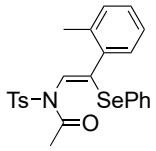
247.0 Hz), 145.26, 145.21, 139.0 (d, *J* = 7.9 Hz), 136.0, 133.9, 129.7 (d, *J* = 8.4 Hz), 129.5, 128.98, 128.95, 127.9, 127.5, 124.7 (d, *J* = 2.9 Hz), 124.1, 116.0 (d, *J* = 22.8 Hz), 115.8 (d, *J* = 21.3 Hz), 24.7, 21.7 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -108.11 – -124.48 (m) ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 411.53 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{20}O_3NFSSeNa^+$: 512.0205; Found: 512.0198.

(*Z*)-*N*-(2-(3-methoxyphenyl)-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116u**)



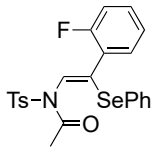
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.07 – 7.97 (m, 2H), 7.36 – 7.31 (m, 2H), 7.21 – 7.18 (m, 2H), 7.16 – 7.10 (m, 2H), 7.10 – 7.05 (m, 2H), 7.04 – 6.99 (m, 1H), 6.94 (dd, *J* = 2.6, 1.7 Hz, 1H), 6.80 – 6.74 (m, 1H), 6.67 (s, 1H), 3.73 (s, 3H), 2.45 (s, 3H), 2.34 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.4, 159.2, 146.3, 145.1, 138.0, 136.1, 133.8, 129.4, 129.2, 129.0, 128.8, 127.9, 127.6, 123.2, 121.3, 114.8, 114.4, 55.3, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 409.32 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_4NSSeNa^+$: 524.0405; Found: 524.0393.

(*Z*)-*N*-(2-(phenylselanyl)-2-(*o*-tolyl)vinyl)-*N*-tosylacetamide (**116v**)



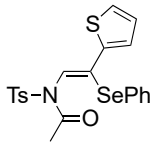
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.14 – 7.97 (m, 2H), 7.41 – 7.33 (m, 2H), 7.20 – 7.13 (m, 3H), 7.08 – 7.04 (m, 1H), 7.04 – 6.98 (m, 3H), 6.98 – 6.93 (m, 1H), 6.91 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.39 (s, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 2.33 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.5, 148.0, 145.1, 136.5, 136.38, 136.32, 135.5, 129.8, 129.6, 129.3, 129.1, 128.6, 128.49, 128.40, 125.7, 124.9, 121.2, 24.7, 21.7, 19.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 451.26 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_3NSSeNa^+$: 508.0456; Found: 508.0440.

(*Z*)-*N*-(2-(2-fluorophenyl)-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116w**)



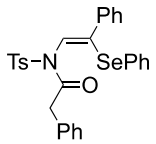
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.11 – 7.93 (m, 2H), 7.42 – 7.33 (m, 2H), 7.28 – 7.21 (m, 3H), 7.18 – 7.11 (m, 2H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.99 – 6.92 (m, 1H), 6.89 – 6.82 (m, 1H), 6.60 (s, 1H), 2.47 (s, 3H), 2.41 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.4, 159.4 (d, *J* = 248.6 Hz), 145.1, 140.9, 136.1, 135.4, 131.5 (d, *J* = 2.3 Hz), 130.3 (d, *J* = 8.0 Hz), 129.4, 129.1, 128.7, 128.3, 126.5, 124.4 (d, *J* = 14.4 Hz), 124.1 (d, *J* = 2.3 Hz), 123.6 (d, *J* = 3.6 Hz), 115.3 (d, *J* = 21.9 Hz), 24.5, 24.1 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -114.55 (dt, *J* = 11.3, 6.2 Hz) ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 449.59 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{20}O_3NFSSeNa^+$: 512.0205; Found: 512.0192.

(*Z*)-*N*-(2-(phenylselanyl)-2-(thiophen-2-yl)vinyl)-*N*-tosylacetamide (**116x**)



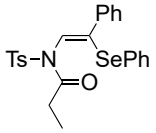
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.01 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.20 – 7.18 (m, 1H), 7.17 – 7.14 (m, 2H), 7.14 – 7.10 (m, 2H), 6.84 (s, 1H), 2.43 (s, 3H), 2.28 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.5, 145.1, 139.1, 137.9, 136.1, 132.8, 129.4, 129.0, 128.9, 128.7, 127.4, 127.2, 126.2, 125.9, 123.4, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 396.53 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{19}O_3NS_2SeNa^+$: 499.9863; Found: 499.9850.

(*Z*)-2-phenyl-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylacetamide (**116y**)



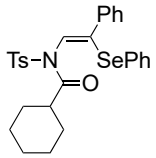
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.07 – 7.95 (m, 2H), 7.41 – 7.37 (m, 2H), 7.34 – 7.30 (m, 3H), 7.30 – 7.27 (m, 2H), 7.25 – 7.19 (m, 5H), 7.17 – 7.11 (m, 3H), 7.09 – 7.04 (m, 2H), 6.55 (s, 1H), 3.92 (s, 2H), 2.46 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 170.2, 146.7, 145.0, 136.6, 136.0, 133.9, 132.7, 129.4, 129.3, 129.1, 128.95, 128.93, 128.92, 128.7, 128.2, 127.8, 127.6, 127.3, 122.9, 43.3, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 409.68 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{25}O_3NSSeNa^+$: 570.0612; Found: 570.0605.

(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylpropionamide (**116z**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.06 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.21 – 7.17 (m, 2H), 7.14 – 7.09 (m, 1H), 7.08 – 7.02 (m, 2H), 6.64 (s, 1H), 2.61 (q, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 1.15 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 173.0, 146.8, 144.9, 136.7, 136.3, 133.9, 129.3, 129.0, 128.98, 128.93, 128.8, 128.2, 127.8, 127.6, 122.6, 29.9, 21.7, 8.5 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 410.14 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_3NSSeNa^+$: 508.0456; Found: 508.0443.

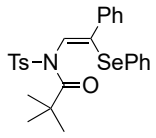
(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylcyclohexanecarboxamide (**116aa**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.07 – 7.96 (m, 2H), 7.44 – 7.38 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.16 – 7.13 (m, 2H), 7.12 – 7.08 (m, 1H), 7.07 – 7.03 (m, 2H), 6.73 (s, 1H), 2.77 (tt, *J* = 11.5, 3.4 Hz, 1H), 2.45 (s, 3H), 1.91 – 1.85 (m, 2H), 1.84 – 1.78 (m, 2H), 1.72 – 1.57 (m, 2H), 1.52 – 1.42 (m, 2H), 1.25 – 1.16 (m, 2H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 175.6,

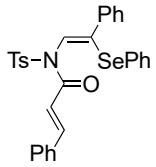
145.7, 144.8, 136.9, 136.4, 133.6, 129.4, 128.93, 128.93, 128.9, 128.8, 128.2, 128.0, 127.5, 123.1, 44.0, 28.7, 25.64, 25.62, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 404.79 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{29}O_3NSSeNa^+$: 562.0925; Found: 562.0919.

(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylpivalamide (**116ab**)



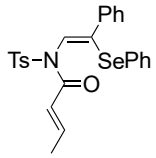
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.08 – 8.00 (m, 2H), 7.43 – 7.37 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.16 – 7.12 (m, 2H), 7.11 – 7.06 (m, 1H), 7.05 – 6.98 (m, 2H), 6.73 (s, 1H), 2.43 (s, 3H), 1.35 (s, 9H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 178.8, 146.5, 144.5, 137.1, 136.7, 133.8, 129.2, 129.1, 128.8, 128.7, 128.6, 128.24, 128.21, 127.4, 123.4, 42.6, 27.7, 21.6 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 416.57 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}O_3NSSeNa^+$: 536.0769; Found: 536.0748.

N-((*Z*)-2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylcinnamamide (**116ac**)



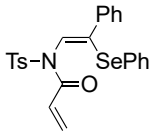
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.12 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 15.5 Hz, 1H), 7.54 – 7.46 (m, 4H), 7.44 – 7.37 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.22 (m, 3H), 7.10 – 7.04 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.94 (s, 1H), 6.93 – 6.84 (m, 3H), 2.45 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 164.9, 146.3, 145.0, 144.9, 137.1, 136.2, 134.3, 133.5, 130.7, 129.4, 129.06, 129.03, 128.99, 128.96, 128.7, 128.4, 128.3, 128.1, 127.4, 123.8, 117.9, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 402.28 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{25}O_3NSSeNa^+$: 582.0612; Found: 582.0606.

(*E*)-*N*-((*Z*)-2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylbut-2-enamide (**116ad**)



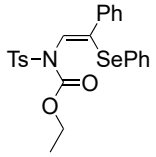
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.07 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.45 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.22 (m, 3H), 7.14 – 7.06 (m, 4H), 7.05 – 7.00 (m, 2H), 6.85 (s, 1H), 6.28 (dd, *J* = 15.1, 1.8 Hz, 1H), 2.43 (s, 3H), 1.88 (dd, *J* = 7.0, 1.6 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 164.6, 146.7, 144.9, 144.3, 137.0, 136.3, 133.2, 129.4, 128.99, 128.94, 128.7, 128.4, 128.3, 127.3, 123.9, 122.7, 21.7, 18.4 ppm. Due to the overlap of aromatic carbon peaks, one carbon signal is missing. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 399.83 ppm. **HRMS** (ESI): m/z: $[M]^+$ Calcd. for $C_{25}H_{23}O_3NSSe^+$: 497.0558; Found: 497.0558.

(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylacrylamide (**116ae**)



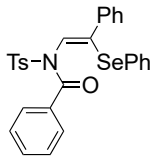
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.04 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.38 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.16 (m, 3H), 7.09 – 7.02 (m, 3H), 7.01 – 6.95 (m, 2H), 6.80 (s, 1H), 6.63 – 6.44 (m, 2H), 5.85 – 5.75 (m, 1H), 2.40 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 164.4, 145.18, 145.13, 136.8, 136.0, 133.4, 132.0, 129.4, 129.04, 129.01, 128.9, 128.7, 128.3, 128.2, 128.1, 127.4, 123.2, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 403.47 ppm. **HRMS** (ESI): m/z: $[M]^+$ Calcd. for $C_{24}H_{21}O_3NSSeNa^+$: 483.0401; Found: 483.0388.

Ethyl (*Z*)-(2-phenyl-2-(phenylselanyl)vinyl)(tosyl)carbamate (**116af**)



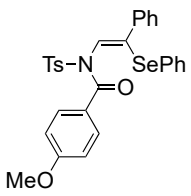
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.08 – 7.87 (m, 2H), 7.58 – 7.49 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.16 (m, 5H), 7.12 – 6.99 (m, 3H), 6.69 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 151.3, 144.9, 142.7, 137.3, 136.2, 132.9, 129.3, 129.0, 128.8, 128.7, 128.1, 127.1, 123.7, 63.7, 21.7, 14.1 ppm. Due to the overlap of aromatic carbon peaks, two carbon signals are missing. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 391.31 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_4NSSeNa^+$: 524.0405; Found: 524.0387.

(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylbenzamide (**116ag**)



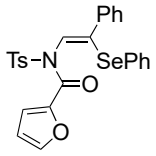
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.13 – 8.00 (m, 2H), 7.79 – 7.69 (m, 2H), 7.53 – 7.45 (m, 1H), 7.42 – 7.32 (m, 4H), 7.16 – 7.12 (m, 2H), 7.11 – 7.07 (m, 3H), 7.03 (s, 1H), 6.91 – 6.83 (m, 1H), 6.77 – 6.69 (m, 2H), 6.30 – 6.12 (m, 2H), 2.48 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 168.4, 145.2, 141.3, 137.0, 135.4, 133.6, 132.22, 132.21, 129.8, 129.6, 129.2, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 126.8, 126.4, 21.8 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 392.31 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{23}O_3NSSeNa^+$: 556.0456; Found: 556.0451.

(*Z*)-4-methoxy-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylbenzamide (**116ah**)



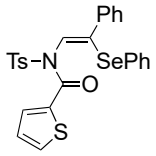
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.11 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.18 – 7.14 (m, 3H), 7.12 (s, 1H), 6.97 – 6.89 (m, 1H), 6.89 – 6.84 (m, 2H), 6.82 – 6.73 (m, 2H), 6.38 – 6.28 (m, 2H), 3.86 (s, 3H), 2.51 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 167.9, 162.9, 145.0, 140.2, 137.2, 135.5, 132.1, 132.0, 129.6, 129.1, 128.7, 128.58, 128.54, 128.3, 128.1, 127.1, 126.7, 125.6, 113.3, 55.5, 21.8 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 388.49 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{25}O_4NSSeNa^+$: 586.0561; Found: 586.0538.

(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylfuran-2-carboxamide (**116ai**)



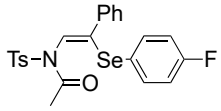
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.03 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.42 (m, 1H), 7.34 – 7.30 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.09 (m, 4H), 7.00 (s, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 2H), 6.53 (d, *J* = 7.8 Hz, 2H), 6.47 – 6.39 (m, 1H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 157.4, 146.4, 145.7, 145.2, 141.5, 137.3, 135.4, 132.6, 129.6, 129.2, 128.8, 128.7, 128.5, 128.3, 128.2, 127.0, 125.7, 119.9, 112.2, 21.8 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 387.58 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{21}O_4NSSeNa^+$: 546.0248; Found: 546.0245.

(*Z*)-*N*-(2-phenyl-2-(phenylselanyl)vinyl)-*N*-tosylthiophene-2-carboxamide (**116aj**)



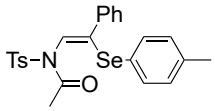
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.17 – 8.03 (m, 2H), 7.87 – 7.77 (m, 1H), 7.63 – 7.55 (m, 1H), 7.44 – 7.33 (m, 4H), 7.25 – 7.20 (m, 3H), 7.11 (s, 1H), 7.11 – 7.05 (m, 1H), 7.01 – 6.94 (m, 1H), 6.86 (t, *J* = 7.7 Hz, 2H), 6.64 – 6.51 (m, 2H), 2.49 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 161.4, 145.2, 143.1, 137.1, 136.0, 135.5, 134.6, 132.9, 132.6, 129.6, 129.2, 128.9, 128.6, 128.5, 128.37, 128.31, 127.1, 127.0, 125.7, 21.8 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 393.86 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{21}O_3NS_2SeNa^+$: 562.0020; Found: 562.0013.

(*Z*)-*N*-(2-((4-fluorophenyl)selanyl)-2-phenylvinyl)-*N*-tosylacetamide (**116ak**)



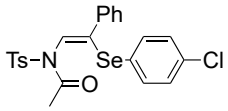
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.08 – 7.97 (m, 2H), 7.39 – 7.31 (m, 4H), 7.26 – 7.21 (m, 3H), 7.20 – 7.14 (m, 2H), 6.81 – 6.71 (m, 2H), 6.58 (s, 1H), 2.47 (s, 3H), 2.35 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.4, 162.5 (d, *J* = 248.4 Hz), 146.9, 145.2, 136.5, 136.3 (d, *J* = 7.9 Hz), 136.1, 129.5, 129.0, 128.96, 128.95, 128.2, 122.7, 122.2 (d, *J* = 3.6 Hz), 116.0 (d, *J* = 21.8 Hz), 24.7, 21.7 ppm. **^{19}F NMR** (565 MHz, Chloroform-*d*): δ = -113.13 – -113.17 (m) ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 409.21 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{20}O_3NSFSeNa^+$: 512.0205; Found: 512.0189.

(*Z*)-*N*-(2-phenyl-2-(*p*-tolylselanyl)vinyl)-*N*-tosylacetamide (**116al**)



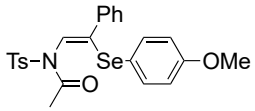
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.09 – 7.93 (m, 2H), 7.45 – 7.39 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.11 – 7.02 (m, 2H), 6.88 – 6.82 (m, 2H), 6.62 (s, 1H), 2.46 (s, 3H), 2.34 (s, 3H), 2.20 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.5, 146.9, 145.0, 137.7, 136.8, 136.2, 134.0, 129.6, 129.4, 129.0, 128.9, 128.8, 128.1, 123.9, 122.8, 24.7, 21.7, 21.0 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 402.37 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_3NSSeNa^+$: 508.0456; Found: 508.0441.

(Z)-*N*-(2-((4-chlorophenyl)selanyl)-2-phenylvinyl)-*N*-tosylacetamide (**116am**)



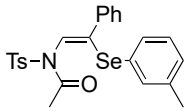
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.05 – 7.95 (m, 2H), 7.44 – 7.37 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.11 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.03 (dd, *J* = 8.3, 1.4 Hz, 2H), 6.63 (s, 1H), 2.46 (s, 3H), 2.34 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.4, 146.0, 145.2, 136.5, 136.0, 135.0, 133.9, 129.5, 129.2, 129.0, 128.93, 128.90, 128.3, 126.1, 123.6, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 405.99 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{20}O_3NClSSeNa^+$: 527.9909; Found: 527.9909.

(*Z*)-*N*-(2-((4-methoxyphenyl)selanyl)-2-phenylvinyl)-*N*-tosylacetamide (**116an**)



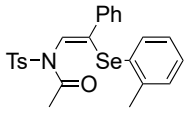
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.98 – 7.94 (m, 2H), 7.28 – 7.23 (m, 4H), 7.14 – 7.09 (m, 3H), 7.05 – 7.01 (m, 2H), 6.52 – 6.48 (m, 2H), 6.46 (s, 1H), 3.60 (s, 3H), 2.36 (s, 3H), 2.24 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.5, 159.5, 147.6, 145.0, 136.8, 136.3, 136.2, 129.4, 129.0, 128.9, 128.7, 128.1, 122.0, 117.5, 114.5, 55.1, 24.7, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 404.05 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_4NSSeNa^+$: 524.0405; Found: 524.0385.

(*Z*)-*N*-(2-phenyl-2-(*m*-tolylselanyl)vinyl)-*N*-tosylacetamide (**116ao**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.05 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.21 (m, 3H), 7.00 – 6.98 (m, 1H), 6.97 – 6.89 (m, 3H), 6.65 (s, 1H), 2.45 (s, 3H), 2.34 (s, 3H), 2.16 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.5, 146.6, 145.0, 138.6, 136.8, 136.1, 134.4, 130.8, 129.4, 129.0, 128.97, 128.90, 128.6, 128.4, 128.1, 127.5, 123.1, 24.6, 21.7, 21.0 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 408.82 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_3NSSeNa^+$: 508.0456; Found: 508.0449.

(*Z*)-*N*-(2-phenyl-2-(*o*-tolylselanyl)vinyl)-*N*-tosylacetamide (**116ap**)



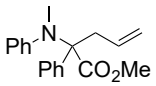
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.07 – 7.99 (m, 2H), 7.42 – 7.38 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.03 (dd, *J* = 4.1, 0.9 Hz, 2H), 6.90 – 6.81 (m, 1H), 6.69 (s, 1H), 2.44 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 169.6, 146.6, 145.0, 140.0, 136.8, 136.2, 134.8, 129.9, 129.3, 129.0, 128.92, 128.92, 128.7, 128.1, 127.9, 126.2, 123.3, 24.6, 22.5, 21.7 ppm. **^{77}Se NMR** (115 MHz, Chloroform-*d*): δ = 366.21 ppm. **HRMS** (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{23}O_3NSSeNa^+$: 508.0456; Found: 508.0442.

6.2.3 Metal-Free Sigmatropic Rearrangement

General procedure of metal-free sigmatropic rearrangement

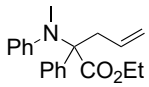
In a reaction tube and under air, the substrate (0.2 mmol, 1.0 eq.) and the diazoalkane (5.0 eq.) was dissolved in 1.0 mL DCM and irradiated with one 3 W LED (distance 1.5 cm, cooling of the setup from the outside with a fan) and stirred overnight. The crude reaction mixture was purified by column chromatography using pentane: Et_2O as eluent to afford the final product.

Methyl 2-(methyl(phenyl)amino)-2-phenylpent-4-enoate (**142a**)



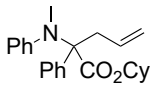
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.49 – 7.42 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.02 – 6.96 (m, 3H), 5.61 – 5.51 (m, 1H), 4.90 – 4.84 (m, 1H), 4.81 – 4.73 (m, 1H), 3.76 (s, 3H), 2.91 (s, 3H), 2.88 – 2.82 (m, 1H), 2.80 – 2.74 (m, 1H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 173.4, 149.6, 140.0, 133.6, 128.4, 128.1, 127.7, 127.2, 123.7, 122.3, 118.1, 73.1, 51.6, 44.1, 40.2 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{21}NNaO_2^+$: 318.14645; found: 318.14587. **IR** (KBr): 3449, 3063, 3023, 2946, 2657, 2327, 2090, 1995, 1912, 1727, 1596 1494, 1441, 1313, 1215, 1115, 998, 916, 828, 753, 698 cm^{-1}.

Ethyl 2-(methyl(phenyl)amino)-2-phenylpent-4-enoate (**142b**)



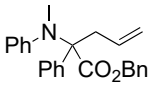
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.50 – 7.45 (m, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 7.23 – 7.18 (m, 2H), 7.02 – 6.92 (m, 3H), 5.60 – 5.53 (m, 1H), 4.89 – 4.85 (m, 1H), 4.80 – 4.74 (m, 1H), 4.28 – 4.19 (m, 2H), 2.92 (s, 3H), 2.88 – 2.83 (m, 1H), 2.81 – 2.75 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.8, 149.7, 140.3, 133.7, 128.3, 128.1, 127.7, 127.1, 123.4, 122.0, 118.1, 72.9, 60.8, 44.1, 40.1, 14.1 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{23}NNaO_2^+$: 332.16210; found: 332.16156. **IR** (KBr): 3438, 3064, 2979, 2328, 2100, 1897, 1724, 1595, 1493, 1446, 1371, 1306, 1211, 1110, 1026, 917, 860, 816, 754, 698 cm^{-1}.

Cyclohexyl 2-(methyl(phenyl)amino)-2-phenylpent-4-enoate (**142c**)



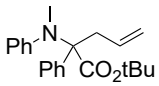
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.51 – 7.46 (m, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.21 – 7.16 (m, 2H), 6.97 (d, J = 8.1 Hz, 2H), 6.92 (t, J = 7.3 Hz, 1H), 5.63 – 5.54 (m, 1H), 4.95 – 4.89 (m, 1H), 4.88 – 4.84 (m, 1H), 4.80 – 4.74 (m, 1H), 2.96 (s, 3H), 2.90 – 2.85 (m, 1H), 2.84 – 2.76 (m, 1H), 1.87 – 1.80 (m, 1H), 1.74 – 1.56 (m, 3H), 1.52 – 1.40 (m, 3H), 1.41 – 1.28 (m, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.4, 149.8, 140.6, 133.8, 128.3, 128.1, 127.6, 127.0, 122.7, 121.5, 118.0, 73.4, 72.7, 44.1, 40.2, 31.6, 31.2, 25.3, 23.5, 23.4 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{24}H_{29}NNaO_2^+$: 386.20905; found: 386.20810. **IR** (KBr): 3877, 3426, 3188, 3068, 2933, 2859, 2663, 2328, 2109, 1997, 1890, 1719, 1640, 1595, 1494, 1446, 1317, 1214, 1115, 1015, 913, 823, 755, 697 cm^{-1}.

Benzyl 2-(methyl(phenyl)amino)-2-phenylpent-4-enoate (**142d**)



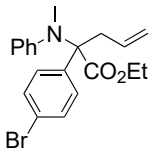
colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.50 – 7.42 (m, 2H), 7.34 – 7.25 (m, 6H), 7.24 – 7.20 (m, 2H), 7.19 – 7.12 (m, 2H), 6.97 – 6.88 (m, 3H), 5.62 – 5.46 (m, 1H), 5.20 (s, 2H), 4.87 – 4.81 (m, 1H), 4.78 – 4.59 (m, 1H), 2.90 (s, 3H), 2.87 – 2.81 (m, 1H), 2.82 – 2.72 (m, 1H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 172.7, 149.6, 140.1, 135.5, 133.5, 128.5, 128.42, 128.41, 128.18, 128.15, 127.7, 127.2, 123.4, 122.0, 118.2, 73.0, 66.8, 44.1, 40.2 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_2^+$: 394.17775; found: 394.17679. **IR** (KBr): 3442, 3192, 3066, 2938, 2809, 2667, 2332, 2094, 1954, 1886, 1726, 1595, 1494, 1448, 1374, 1312, 1202, 1113, 991, 913, 824, 745, 697 cm^{-1}.

tert-Butyl 2-(methyl(phenyl)amino)-2-phenylpent-4-enoate (**142e**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.54 – 7.47 (m, 2H), 7.35 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 7.20 – 7.14 (m, 2H), 6.98 – 6.92 (m, 2H), 6.91 – 6.85 (m, 1H), 5.69 – 5.47 (m, 1H), 4.96 – 4.70 (m, 2H), 2.97 (s, 3H), 2.90 – 2.76 (m, 2H), 1.39 (s, 9H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.1, 150.0, 140.8, 133.9, 128.2, 128.1, 127.6, 126.9, 122.0, 120.9, 117.9, 81.6, 72.9, 44.2, 39.8, 27.9 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{22}H_{27}NNaO_2^+$: 360.19340; found: 360.19370. **IR** (KBr): 3425, 3062, 2976, 2930, 2817, 2326, 2182, 2101, 1916, 1720, 1639, 1597, 1496, 1448, 1391, 1366, 1314, 1243, 1155, 1033, 991, 915, 845, 804, 752, 698 cm^{-1}.

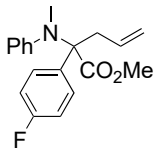
Ethyl 2-(4-bromophenyl)-2-(methyl(phenyl)amino)pent-4-enoate (**142g**)



colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ =7.48 – 7.41 (m, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.23 – 7.14 (m, 2H), 7.02 – 6.89 (m, 3H), 5.60 – 5.39 (m, 1H), 4.95 – 4.82 (m, 1H), 4.83 – 4.67 (m, 1H), 4.34 – 4.10 (m, 2H), 2.89 (s, 3H), 2.84 – 2.73 (m, 1H), 2.73 – 2.59 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 172.2, 149.3, 139.5, 133.1, 130.7, 130.0, 128.3, 123.4, 122.3, 121.1, 118.7, 72.6, 61.0, 44.3, 39.7, 14.1 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{22}BrNNaO_2^+$: 410.07261; found: 410.07230. **IR** (KBr): 3849, 3408, 3071, 2980, 2933, 2326, 2158, 2078, 1994, 1914,

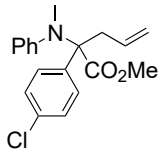
1724, 1640, 1596, 1490, 1446, 1392, 1366, 1299, 1212, 1109, 1075, 1008, 919, 860, 829, 753, 698 cm^{-1}.

Methyl 2-(4-fluorophenyl)-2-(methyl(phenyl)amino)pent-4-enoate (**142h**)



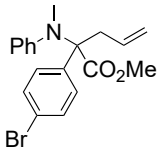
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.47 – 7.42 (m, 2H), 7.24 – 7.19 (m, 2H), 7.04 – 6.98 (m, 3H), 6.98 – 6.94 (m, 2H), 5.57 – 5.47 (m, 1H), 4.93 – 4.85 (m, 1H), 4.80 – 4.73 (m, 1H), 3.75 (s, 3H), 2.88 (s, 3H), 2.83 – 2.78 (m, 1H), 2.75 – 2.65 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 173.1, 161.8 (d, *J* = 246.5 Hz), 149.4, 135.8 (d, *J* = 3.5 Hz), 133.2, 129.8 (d, *J* = 7.9 Hz), 128.4, 123.7, 122.5, 118.5, 114.5 (d, *J* = 21.2 Hz), 72.7, 51.7, 44.4, 39.9 ppm. **^{19}F NMR** (282 MHz, Chloroform-*d*): = -115.5 ppm. HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{20}FNNaO_2^+$: 336.13703; found: 336.13623. **IR** (KBr): 3882, 3446, 3196, 3075, 2947, 2659, 2329, 2104, 1991, 1908, 1728, 1597, 1500, 1439, 1307, 1219, 1165, 1111, 1002, 918, 836, 756, 697 cm^{-1}.

Methyl 2-(4-chlorophenyl)-2-(methyl(phenyl)amino)pent-4-enoate (**142i**)



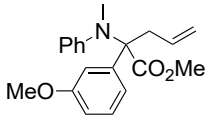
colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.43 – 7.38 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.19 (m, 2H), 7.02 – 6.98 (m, 1H), 6.98 – 6.93 (m, 2H), 5.50 (m, 1H), 4.88 (m, 1H), 4.76 (m, 1H), 3.75 (s, 3H), 2.87 (s, 3H), 2.82 – 2.73 (m, 1H), 2.73 – 2.62 (m, 1H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 172.8, 149.2, 138.7, 133.0, 132.9, 129.6, 128.4, 127.8, 123.8, 122.6, 118.7, 72.8, 51.7, 44.4, 39.9 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{20}ClNNaO_2^+$: 352.10748; found: 352.10675. **IR** (KBr): 3446, 3070, 2948, 2590, 2158, 2030, 1907, 1729, 1641, 1595, 1491, 1439, 1305, 1214, 1097, 1004, 918, 830, 760, 698 cm^{-1}.

Methyl 2-(4-bromophenyl)-2-(methyl(phenyl)amino)pent-4-enoate (**142j**)



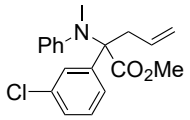
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.46 – 7.42 (m, 2H), 7.37 – 7.33 (m, 2H), 7.24 – 7.19 (m, 2H), 7.02 – 6.98 (m, 1H), 6.97 – 6.93 (m, 2H), 5.54 – 5.43 (m, 1H), 4.91 – 4.86 (m, 1H), 4.80 – 4.72 (m, 1H), 3.75 (s, 3H), 2.87 (s, 3H), 2.81 – 2.75 (m, 1H), 2.71 – 2.64 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.8, 149.2, 139.3, 133.0, 130.8, 130.0, 128.4, 123.8, 122.6, 121.2, 118.7, 72.8, 51.8, 44.3, 39.9 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{20}BrNNaO_2^+$: 396.05696; found: 396.05627. **IR** (KBr): 3447, 3071, 2948, 2327, 2158, 2088, 2012, 1913, 1727, 1639, 1596, 1490, 1436, 1395, 1303, 1215, 1175, 1111, 1074, 1003, 917, 828, 774, 754, 698 cm^{-1}.

Methyl 2-(3-chlorophenyl)-2-(methyl(phenyl)amino)pent-4-enoate (**142l**)



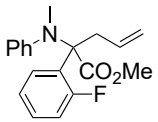
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.55 – 7.48 (m, 1H), 7.38 – 7.32 (m, 1H), 7.28 – 7.21 (m, 4H), 7.04 – 7.00 (m, 1H), 7.00 – 6.97 (m, 2H), 5.56 – 5.41 (m, 1H), 4.91 – 4.84 (m, 1H), 4.78 – 4.70 (m, 1H), 3.77 (s, 3H), 2.87 (s, 3H), 2.80 – 2.74 (m, 1H), 2.69 – 2.63 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.6, 149.2, 142.5, 133.8, 133.0, 128.9, 128.5, 128.2, 127.4, 126.4, 124.2, 123.0, 118.7, 73.0, 51.8, 44.5, 40.0 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{20}NClNaO_2^+$: 352.10748; found: 352.10718. **IR** (KBr): 3448, 3069, 2946, 2332, 2082, 1937, 1729, 1591, 1489, 1431, 1302, 1212, 1115, 999, 916, 768, 697 cm^{-1}.

Methyl 2-(3-methoxyphenyl)-2-(methyl(phenyl)amino)pent-4-enoate (**142m**)



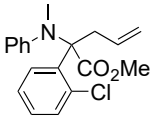
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.26 – 7.18 (m, 3H), 7.08 – 7.06 (m, 1H), 7.04 – 7.01 (m, 1H), 7.00 – 6.97 (m, 3H), 6.83 – 6.79 (m, 1H), 5.60 – 5.51 (m, 1H), 4.89 – 4.85 (m, 1H), 4.81 – 4.75 (m, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 2.90 (s, 3H), 2.85 – 2.79 (m, 1H), 2.78 – 2.71 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 173.3, 159.1, 149.6, 141.8, 133.6, 128.6, 128.4, 123.8, 122.4, 120.6, 118.0, 114.4, 112.2, 73.1, 55.2, 51.7, 44.1, 40.3 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{23}NNaO_3^+$: 348.15701; found: 348.15601. **IR** (KBr): 3444, 3193, 3078, 2945, 2837, 2660, 2334, 2251, 2090, 1925, 1727, 1595, 1489, 1436, 1290, 1225, 1113, 1037, 909, 728 cm^{-1}.

Methyl 2-(2-fluorophenyl)-2-(methyl(phenyl)amino)pent-4-enoate (**142m**)



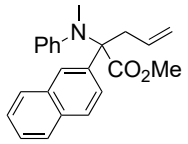
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.65 – 7.58 (m, 1H), 7.30 – 7.24 (m, 3H), 7.19 – 7.16 (m, 3H), 7.16 – 7.12 (m, 1H), 7.05 – 7.00 (m, 1H), 5.69 – 5.47 (m, 1H), 4.78 – 4.74 (m, 1H), 4.62 – 4.55 (m, 1H), 3.82 (s, 3H), 2.81 (s, 3H), 2.73 – 2.65 (m, 1H), 2.63 – 2.56 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.2, 160.5 (d, *J* = 246.5 Hz), 149.2, 133.3, 129.67, 129.64, 128.9 (d, *J* = 9.0 Hz), 128.6, 127.7, 125.0, 123.4 (d, *J* = 3.1 Hz), 117.7, 115.8 (d, *J* = 23.9 Hz), 69.6 (d, *J* = 2.5 Hz), 51.7, 42.2, 41.2 ppm. **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = -110.2 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{20}FNNaO_2^+$: 336.13703; found: 336.13724. **IR** (KBr): 3449, 3074, 2989, 2948, 2809, 2325, 2184, 2102, 1986, 1930, 1730, 1639, 1593, 1487, 1444, 1294, 1223, 1113, 992, 914, 832, 804, 760, 733, 700 cm^{-1}.

Methyl 2-(2-chlorophenyl)-2-(methyl(phenyl)amino)pent-4-enoate (**142n**)



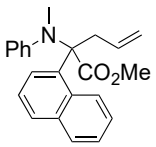
colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.88 – 7.83 (m, 1H), 7.36 – 7.33 (m, 1H), 7.33 – 7.27 (m, 5H), 7.24 – 7.20 (m, 1H), 7.19 – 7.15 (m, 1H), 5.43 – 5.35 (m, 1H), 4.66 – 4.61 (m, 1H), 4.49 – 4.45 (m, 1H), 3.84 (s, 3H), 2.89 – 2.84 (m, 1H), 2.81 – 2.76 (m, 1H), 2.76 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 172.0, 149.3, 137.9, 133.1, 130.8, 130.7, 128.6, 128.5, 128.4, 126.0, 125.4, 117.4, 71.5, 51.6, 42.1, 38.7 ppm. **HRMS** (ESI): *m/z* [M+Na]$^+$ calcd for $C_{19}H_{20}ClNNaO_2^+$: 352.10748; found: 352.10730. **IR** (KBr): 3445, 3067, 2941, 2328, 2099, 1990, 1901, 1727, 1640, 1592, 1489, 1436, 1290, 1220, 1113, 1032, 995, 913, 818, 755, 697 cm^{-1}.

Methyl 2-(methyl(phenyl)amino)-2-(naphthalen-2-yl)pent-4-enoate (**142o**)



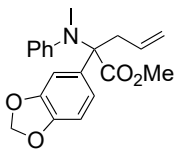
colorless oil; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 8.84 (d, J = 8.7 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.40 (t, J = 7.7 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.24 – 7.20 (m, 2H), 7.11 – 7.04 (m, 1H), 5.35 – 5.25 (m, 1H), 4.49 – 4.44 (m, 1H), 4.41 – 4.35 (m, 1H), 3.87 (s, 3H), 3.25 – 3.18 (m, 1H), 3.09 – 3.03 (m, 1H), 2.88 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 173.3, 149.6, 137.8, 133.5, 132.8, 132.6, 128.4, 128.3, 127.39, 127.36, 127.0, 126.3, 126.0, 125.9, 123.6, 122.3, 118.2, 73.3, 51.7, 43.9, 40.3 ppm. **HRMS** (ESI): *m/z* [M+Na]$^+$ calcd for $C_{23}H_{23}NNaO_2^+$: 368.16210; found: 368.16141. **IR** (KBr): 3862, 3446, 3056, 2942, 2326, 2091, 1913, 1727, 1595, 1497, 1434, 1311, 1215, 1163, 1118, 1000, 916, 860, 819, 750, 697 cm^{-1}.

Methyl 2-(methyl(phenyl)amino)-2-(naphthalen-1-yl)pent-4-enoate (**142p**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.84 (d, *J* = 8.7 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.24 – 7.20 (m, 2H), 7.11 – 7.04 (m, 1H), 5.35 – 5.25 (m, 1H), 4.49 – 4.44 (m, 1H), 4.41 – 4.35 (m, 1H), 3.87 (s, 3H), 3.25 – 3.18 (m, 1H), 3.09 – 3.03 (m, 1H), 2.88 (s, 3H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 174.0, 149.4, 135.2, 134.5, 134.2, 131.8, 129.0, 128.9, 128.6, 126.9, 125.9, 125.6, 125.3, 125.1, 124.4, 123.3, 116.5, 74.7, 51.5, 41.6, 41.5 ppm. **HRMS** (ESI): *m/z* [M+Na]$^+$ calcd for $C_{23}H_{23}NNaO_2^+$: 368.16210; found: 368.16150. **IR** (KBr): 3442, 3053, 2935, 2852, 2324, 2163, 2034, 1937, 1842, 1724, 1595, 1495, 1438, 1322, 1272, 1210, 1120, 1048, 989, 913, 776, 698 cm^1.

methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(methyl(phenyl)amino)pent-4-enoate (**142q**)



colorless oil; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.24 – 7.19 (m, 2H), 7.03 (d, *J* = 1.9 Hz, 1H), 7.00 – 6.97 (m, 1H), 6.97 – 6.94 (m, 2H), 6.90 – 6.87 (m, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 5.96 (s, 2H), 5.59 – 5.50 (m, 1H), 4.91 – 4.85 (m, 1H), 4.82 – 4.76 (m, 1H), 3.74 (s, 3H), 2.88 (s, 3H), 2.84 – 2.77 (m, 1H), 2.75 – 2.60 (m, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): δ = 173.3, 149.5, 147.3, 146.5, 134.1,

133.6, 128.4, 123.6, 122.3, 121.4, 118.2, 108.8, 107.3, 101.0, 72.9, 51.7, 44.2, 40.1 ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{21}NNaO_4^+$: 362.13628; found: 362.13565. **IR** (KBr): 3445, 3076, 2946, 2895, 2583, 2321, 2175, 2067, 1986, 1852, 1726, 1597, 1488, 1435, 1311, 1228, 1118, 1035, 926, 815, 755, 698 cm^1.

7. Abbreviations

Ad	Adamantly
Ar	Aryl
$AlPh_3$	Aluminium phosphide
aq.	Aqueous
Bn	Benzyl
B_2pin_2	Bis(pinacolato)diboron
Bu	Butyl
2,2'-bpy	2,2'-Bipyridine
cat.	Catalyst
Cy	Cyclohexyl
Co(salen)	(*N*,*N*'-Ethylenebis(salicylideniminato))cobalt
4CzIPN	1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene
CuOAc	Copper(I)acetate
CuOTf	Copper(I)triflate
CuTC	Copper(I) thiophene-2-carboxylate hydrate
DABCO	1,4-Diazabicyclo[2.2.2]octane
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DMA	*N,N*-Dimethylacetamide
DMAP	Dimethylaminopyridine
DMF	Dimethylformamide
dppb	1,4-Bis(diphenylphosphino)butane
dtbbpy	4,4′-Di-tert.-butyl-2,2′-dipyridyl
d.r	Diastereoselective ratio
EDG	Electron-donating group
Ee	Enantioselective excess
eq.	Equivalent
Et	Ethyl
EDA	Ethyl diazoacetate
Et_2OAc	Ethyl acetate
EWG	Electron-withdrawing group
FeTPPCl	5,10,15,20-Tetraphenyl-21H, 23H-prophine iron(III) chloride
GC	Gas chromatography
1,5-HAT	1,5-Hydrogen atom transfer
iPr	*iso*-Propyl
LED	Light emitting diode
Me	Methyl
MeCN	Acetonitrile
MS	Mass spectrometry
Mw	Micro wave
n.d	Not detected
n.r	No reaction
NMR	Nuclear Magnetic Resonance
Nu	Nucleophile
$Pd(OAc)_2$	Palladium (II) acetate
Piv	Pivaloyl
PTSA	*p*-Toluenesulfonic acid
PCET	Proton-coupled electron transfer
$P(nBu)Ad_2$	Di-(1-adamantyl)-n-butylphosphin

rac	Racemic
$Rh_2(piv)_4$	Rhodium (II) pivalate
$Rh_2(oct)_4$	Rhodium(II) octanoate dimer
Rh_2esp_2	Bis[rhodium(α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid)
$Rh_2(OAc)_4$	Rhodium (II) acetate
RuPhos	Dicyclohexyl-[2-[2,6-di(propan-2-yloxy)phenyl]phenyl]phosphane
rt	Room temperature
SET	Single electron transfer
TBAB	Tetrabutylaminium bromide
*t*Bu	*tert*. Butyl
TEMPO	2,2,6,6-Tetramethyl-piperidine-*N*-oxide
TFE	Trifluoroethanol
THF	Tetrahydrofuran
TM	Transition metal
UV	Ultraviolet
Vis	Visible

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