


 Cite this: *RSC Adv.*, 2021, **11**, 33447

 Received 2nd May 2021
 Accepted 30th September 2021

DOI: 10.1039/d1ra03443j

rsc.li/rsc-advances

Direct halosulfonylation of alkynes: an overview

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The difunctionalization reactions of easily available and inexpensive alkynes have emerged as a reliable, powerful, and step-economical approach for the construction of highly substituted complex alkenes in a one-pot manner, without the need for isolation of intermediates. A wide variety of transformations based on this concept have been successfully achieved for the preparation of synthetically and biologically important β -halovinyl sulfone scaffolds. In this Review, we summarize the recent advances and developments in this field and present a comprehensive overview of halosulfonylation of alkyne substrates with emphasis on the mechanistic features of the reactions.

1. Introduction

Sulfones ($\text{RSO}_2\text{R}'$) appeared as a useful and important class of organosulfur compounds due to the prevalence of this moiety in a great number of biologically active compounds¹ as well as commercialized drugs, including apremilast, ceritinib, chlor-zemanone, dapsone, eletriptan, lifitegrast, tinidazole, and vismodegib.² In addition, these compounds are very versatile synthetic intermediates and can function as suitable building blocks to synthesize various biologically active compounds or functional materials.³ In this family of compounds, β -halovinyl sulfones have attracted significant attention from the synthetic community because of their diverse reaction patterns and application in the assembly of various sulfonyl-substituted heterocycles⁴ and other value-added chemicals such as β -keto sulfones,^{5a,b} β -amino sulfones,⁶ sulfonyl-substituted 1,3-enynes,⁷ acetylene sulfonyl compounds,⁸ 1,3-bis(arylsulfonyl) allenes⁹ and many more. Therefore, it is always interesting to develop cost-effective facile synthesis strategies to prepare this special class of organosulfur compounds from easily available and inexpensive starting materials.

Recently, the direct halosulfonylation of easily accessible alkynes has emerged as an ideal strategy for the construction of the titled compounds which makes the synthetic route cleaner, greener, and faster than traditional methods that rely on the three-step sulfonation–zirconation–halogenation sequence.¹⁰ Although no reporting guideline exists for the direct fluoro-sulfonylation of alkynes and only a handful of methodologies have been reported for bromo-sulfonylation of alkynes, synthesis of β -chloro- and β -iodo-vinyl sulfones through the direct chloro- and iodo-sulfonylation of alkynes has been the subject of intense research efforts in recent years. In 2016, Luo

and co-workers published an interesting review paper entitled “recent advances in the synthesis of vinyl sulfones” that covers most of the advances in the preparation of vinyl sulfone derivatives.¹¹ However, synthesis of β -halovinyl sulfones through the direct halosulfonylation of simple and easily accessible alkynes was almost omitted, while this procedure has recently attracted a lot of attention because of its operational simplicity and high atom and step economy. In connection with our recent reviews on the synthesis of organosulfur compounds¹² and new methodologies in modern organic synthesis,^{13–20} herein, we provide an overview of the direct halosulfonylation of C–C triple bonds (Fig. 1), with special emphasis on the mechanistic aspect of the reactions. For clarity, the reactions will be classified by the type of halogen atoms and sulfonylating agents.

2. Chlorosulfonylation

In this section, the attention is paid to the synthesis of β -chlorovinyl sulfones from the corresponding alkynes by means of the concomitant formation of C–S and C–Cl bonds. The section is divided into two parts according to chlorosulfonylating reagents. The first includes the chlorosulfonylation of alkynes using bifunctional reagents, while the second contains the three-component reactions.

2.1. Two-component reactions

The reported examples of the chlorosulfonylation of alkynes are mainly rely on the use of sulfonyl chlorides as the both sulfonylating and chlorinating agents. As early as 1971, the first

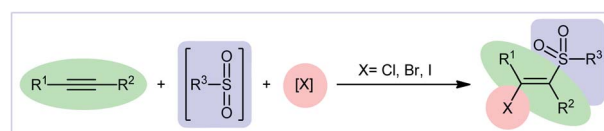
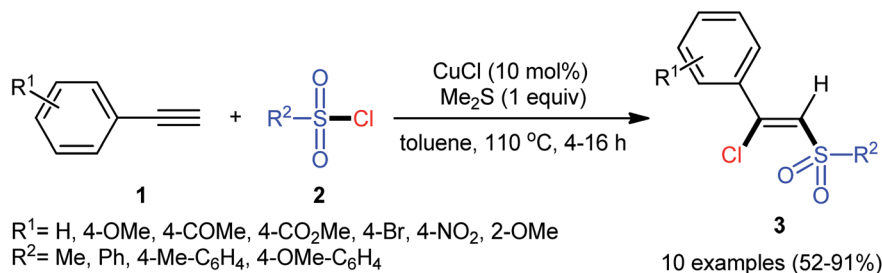


Fig. 1 Direct halosulfonylation of alkynes.

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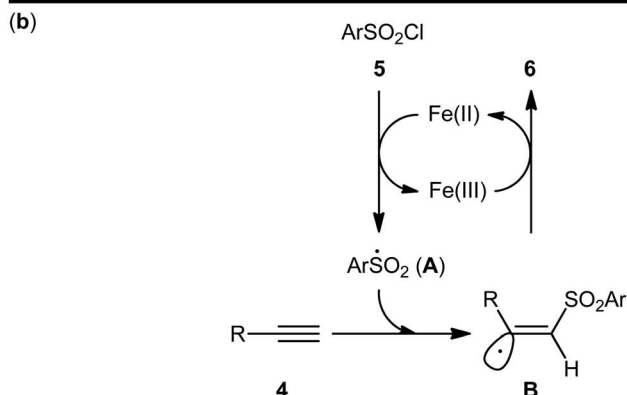
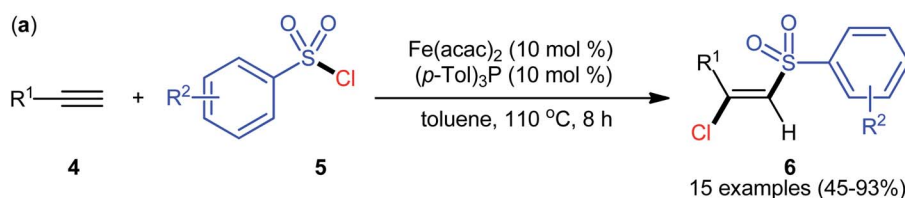


Scheme 1 Cu-catalyzed chlorosulfonylation of alkynes 1 with sulfonyl chlorides 2.

synthesis of β -chlorovinyl sulfones *via* the direct chlorosulfonylation of the corresponding alkynes with sulfonyl chlorides was realized by Amiel *et al.*^{21,22} However, since then, this synthetic strategy did not attract the attention of chemists for nearly 35 years. Since last three decades, several research groups investigated the scope and limitation of this transformation. In 2005, Liang and co-workers studied the possibility of stereoselective synthesis of β -chlorovinyl sulfones through the direct Cu-catalyzed chlorosulfonylation of phenylacetylene derivatives.²³ By employing phenylacetylene and *p*-toluenesulfonyl chloride as the model substrates, the reaction variables such as catalysts, additives, and solvents were attentively screened. The results indicated that the merge of 10 mol% of CuCl with 1 equiv. of Me₂S was the most appropriate catalytic system for this conversion and among the various aprotic solvents (*e.g.*, THF, DMF, DCM, MeCN, toluene, dioxane); toluene was found to be the most suitable solvent. Under the optimized conditions, a diverse array of (*Z*)- β -chlorovinyl sulfones 3 were selectively obtained in good to excellent yields

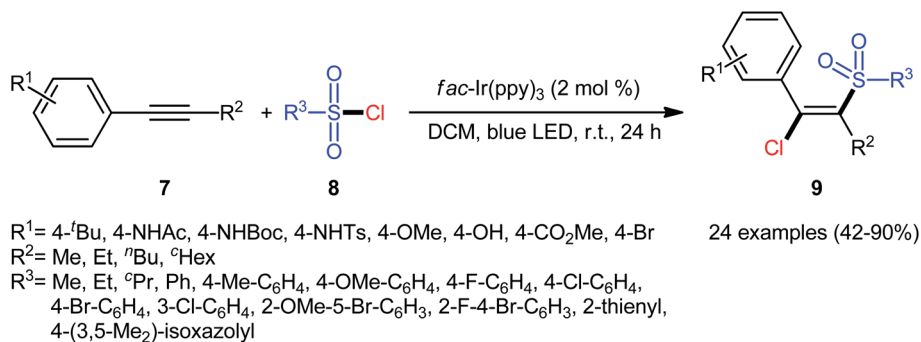
by reaction of various phenylacetylene derivatives 1 with sulfonyl chlorides 2 under an atmosphere of air at 110 °C (Scheme 1). An internal aryl-alkyl alkyne was also tested and gave the desired product but in moderate yield. The system was also amenable to the chlorosulfonylation of vinyl alkynes as exemplified by synthesis of (*Z*)-((2-chloro-2-(cyclohex-1-en-1-yl)vinyl)sulfonyl)benzene using 1-cyclohexeneacetylene as the reactant. However, diphenylacetylene, propargyl alkyl ether, and propiolate failed to participate in this transformation. The authors assumed that the Me₂S is probably involved in stabilizing the intermediate A. Nevertheless, no comment was made by them regarding the plausible mechanistic pathway of this transformation.

Seven years later, the iron-catalyzed version of this difunctionalization reaction was disclosed by Nakamura and colleagues,²⁴ who revealed that the treatment of various aromatic and aliphatic terminal alkynes 4 with aromatic sulfonyl chlorides 5 in the presence of a combination of Fe(acac)₂ (10 mol%) and (*p*-Tol)₃P (10 mol%) in refluxing



Scheme 2 (a) Fe-catalyzed chlorosulfonylation of terminal alkynes 4 with arylsulfonyl chlorides 5; (b) proposed mechanism for the formation of (*E*)- β -chlorovinyl sulfones 6.





Scheme 3 Visible-light-mediated chlorosulfonylation of internal aryl-alkyl alkynes **7** with sulfonyl chlorides **8**.

toluene afforded the corresponding β -chlorovinyl sulfones **6** in moderate to high yields and complete (*E*)-selectivities (Scheme 2a). According to authors proposed mechanistic pathways (Scheme 2b), this reaction proceeds through an electron transfer between iron(II) catalyst and sulfonyl chloride **5**, following the radical addition of the resulting sulfonyl radical **A** to the alkyne **4** to give vinyl radical intermediate **B**, which could be trapped by *in situ* generated iron(III) chloride to yield (*E*)- β -chlorovinyl sulfone derivatives **6**. According to the authors, the iron(III) chloride species acts as a bulky chlorine donor and is responsible for the excellent (*E*)-selectivity for the desired products. Subsequently, a similar reaction conditions were applied by Yang and Zhu along with their colleagues to chlorosulfonylation of a diverse array of alkynyl chlorides and the desired *cis*-1,2-dichlorovinylsulfones were obtained in good to excellent yields, ranging from 55% to 91%.²⁵

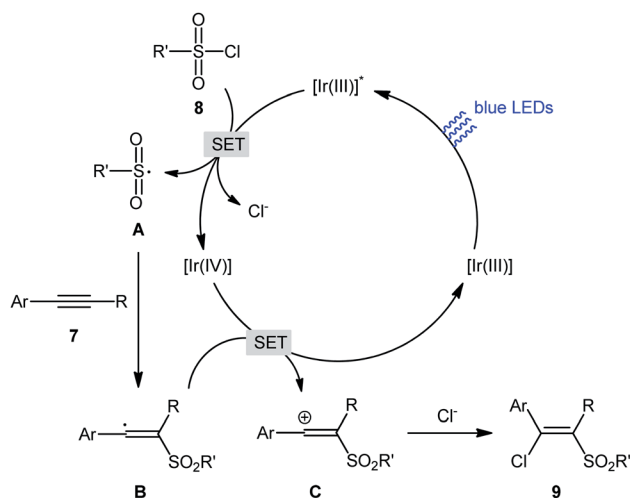
In 2018, Kim-Han's research group described a visible-light-mediated, *fac*-Ir(ppy)₃-catalyzed regio- and stereo-selective chlorosulfonylation of internal aryl-alkyl alkynes **7** with various aliphatic, aromatic, and heteroaromatic sulfonyl chlorides **8**.²⁶ This synthetic transformation exhibited an efficient and attractive method for the high yielding synthesis of (*E*)- β -chlorovinyl sulfone derivatives **9** at room temperature under

additive-free conditions (Scheme 3). Noteworthy, the reaction exhibited high degree of regioselectivity, in which the sulfonyl group is predominantly placed on the carbon atom adjacent to the alkyl group and Cl group added to the carbon atom near the aryl group. Interestingly, the reaction could be conducted on gram quantities without any difficulty. This procedure was also compatible with a variety of common functional groups including fluoro, chloro, bromo, hydroxy, methoxy, amide, sulfonamide, and ester functionalities, which are useful for further functionalization. According to the authors, this transformation involves a radical mechanism as shown in Scheme 4. In a related investigation, Reiser and co-workers reported the usefulness of well-established [Cu(dap)₂]Cl photoredox catalyst for the direct chlorosulfonation of unsaturated hydrocarbons with sulfonyl chloride under green light irradiation.²⁷ Thus, a small library of alkynes (terminal and internal) reacted with *p*-toluenesulfonyl chloride to give the respective β -chlorovinyl sulfone in moderate to almost quantitative yields. However, the regioselectivity of products was modest at best.

A similar strategy was then extended to a heteroleptic copper(I)-mediated chlorosulfonylation of terminal aryl alkynes **10** with *para*-fluorobenzylsulfonyl chloride **11** by the Hu group.²⁸ As shown in Scheme 5, thirteen (*E*)-chlorosulfonylvinylbenzenes **12** were efficiently produced with excellent (*E*)-selectivity. However, internal aryl alkynes and aliphatic alkynes failed to undergo the reaction. It should be mentioned that the synthetic concept could also be extended to terminal alkene substrates. The authors stated that the outstanding (*E*)-selectivity in this difunctionalization reaction may originated from an outer-sphere mechanism where the radical termination step proceeds through the thermodynamically favored configuration.

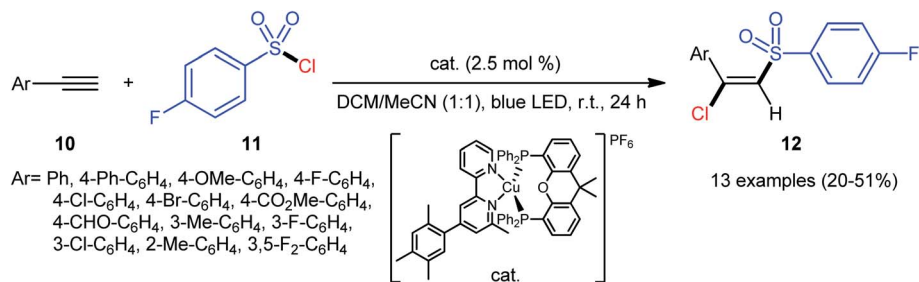
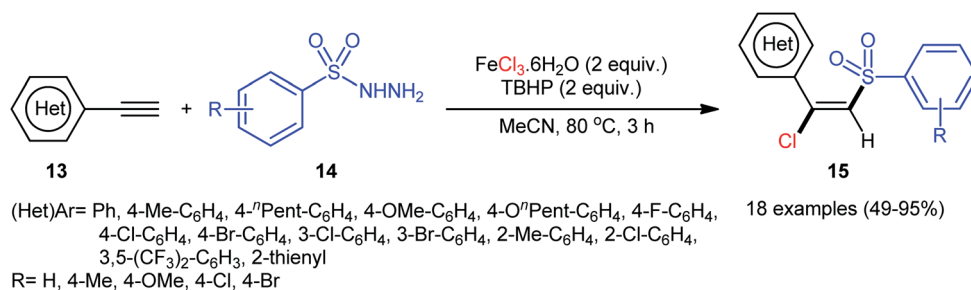
2.2. Three-component reactions

In 2013, Xu, Li, and colleagues disclosed the preparation of (*E*)-chlorosulfonylvinylarenes **15** with moderate to excellent yield (up to 95%) through iron-mediated regio- and stereo-selective chlorosulfonylation of terminal (hetero)aromatic alkynes **13** with arylsulfonyl hydrazides **14** (Scheme 6).²⁹ The protocol uses iron(III) chloride hexahydrate as Cl source as well as mediator and *tert*-butyl hydroperoxide (^tBuOOH; TBHP) as the oxidant. A series of important functional groups such as F, Cl, Br, CF₃, and



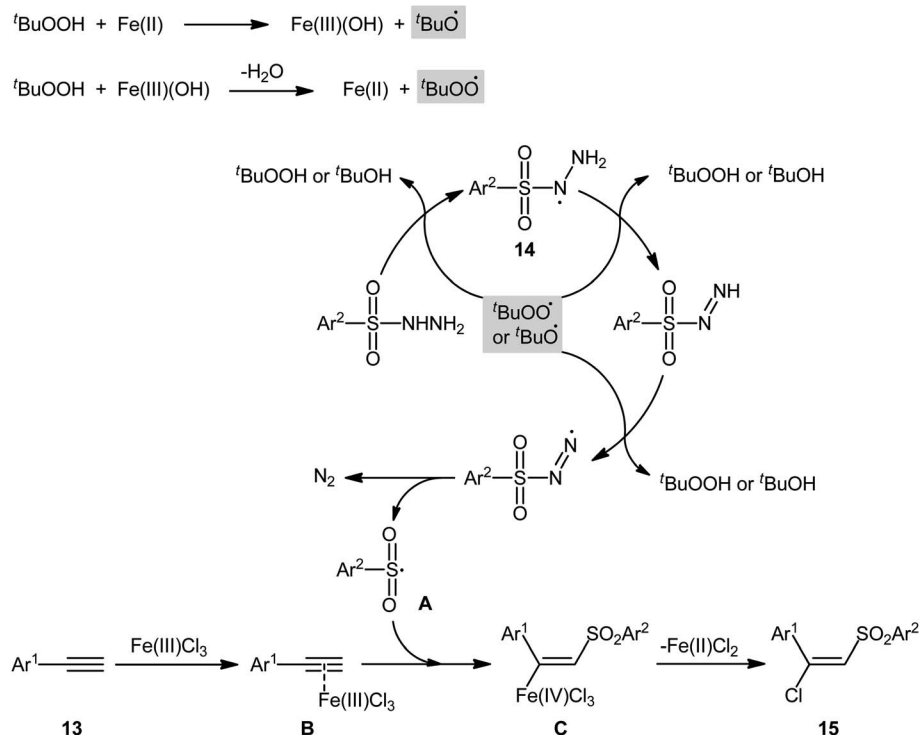
Scheme 4 Mechanistic explanation for the reaction in Scheme 3.



Scheme 5 Hu's synthesis of (*E*)-chlorosulfonylvinylbenzenes 12.Scheme 6 Chlorosulfonylation of terminal (hetero)aromatic alkynes 13 with arylsulfonyl hydrazides 14 and FeCl₃.

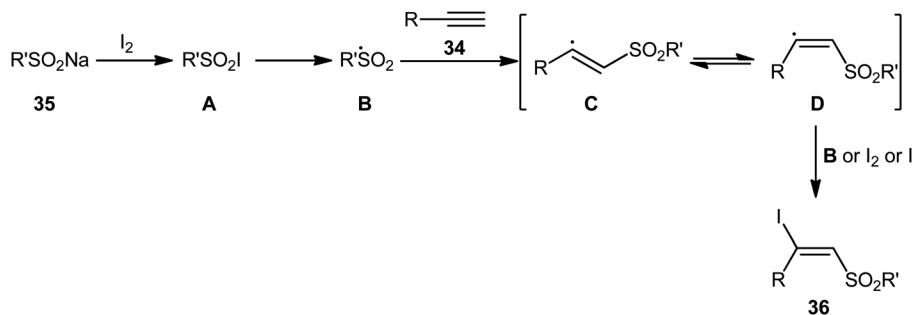
ether functionalities are found to be compatible under the reaction conditions. However, internal aryl alkynes were not effective in this system and applicability of alkylsulfonyl hydrazides did not investigated in this synthetic strategy. Hept-1-yne did not work well in the reaction and therefore no other

aliphatic alkynes were examined in the protocol. Interestingly, by replacing FeCl₃ with FeBr₃, β-bromovinyl sulfones were afforded in high yields under the identical conditions. According to the control experiments and literature reports, the authors assumed that the reaction may starts with the



Scheme 7 Proposed Mechanism for the reaction in Scheme 6.





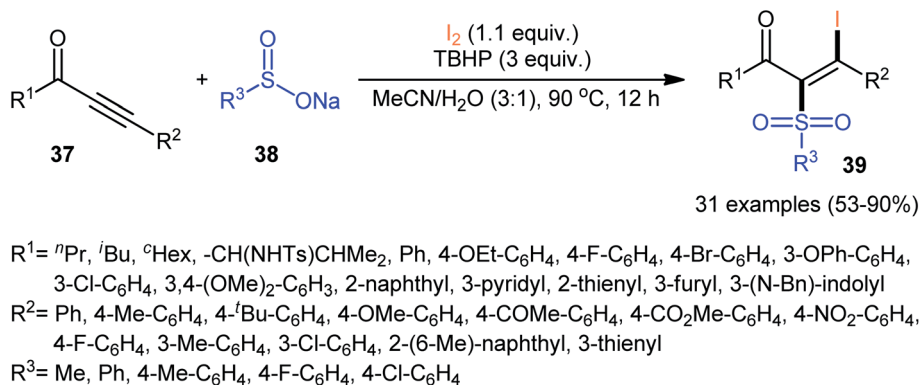
Scheme 16 A proposed pathway for the formation of (*E*)-β-iodovinyl sulfones **36**.

were able to demonstrated that a diverse range of (*E*)-β-iodovinyl sulfones **36** could be obtained in moderate to excellent yields from the reaction of alkynes **34** (terminal and internal) with sodium sulfinates **35** (aromatic and aliphatic) and molecular iodine in the most environmentally friendly solvent, water, at room temperature under catalyst- and additive-free conditions (Scheme 15).⁴⁰ In addition, a scale-up experiment (20 mmol scale) and a few synthetic applications based on the known cross-coupling reactions highlighted the usefulness of this methodology. A few control experiments were carried out to gain mechanistic insights for this appealing reaction. With the use of the radical scavenger butylated hydroxytoluene (BHT), no prohibition of the reaction was occurred. However, the reaction was completely inhibited in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), which indicated that the reaction presumably underwent a radical pathway (Scheme 16). Initially, a sulfonyl iodide intermediate **A** was formed *via* the reaction of sulfinate sodium salt **35** with iodine. In the next step, this intermediate **A** underwent homolytic cleavage and a sulfonyl radical **B** along with an iodine radical was generated. Thereafter, the newly formed radical **B** was added chemoselectively to the alkyne **34** and provided the vinyl sulfone radicals **C** and **D**. Finally, electrophilic addition of I^\bullet the vinyl sulfone radical **D** gave the desired product **36**. Subsequently, Bi and co-workers slightly improved the efficiency of this reaction in the term of product yields by performing the process in the presence of 2 equiv. of di-*tert*-butyl peroxide (DTBP) as an

oxidant in the binary solvent EtOH/H₂O with ratio 1 : 1 at 60 °C.⁴¹

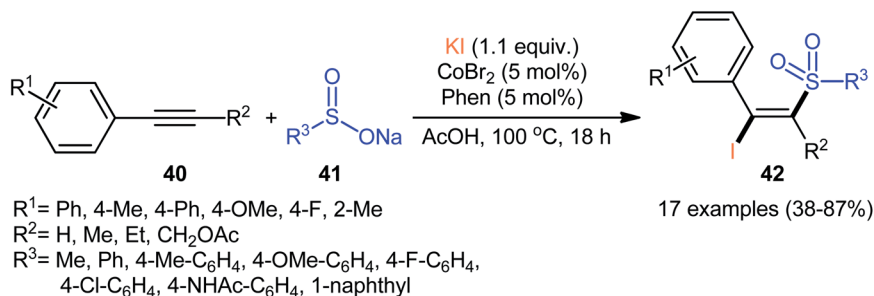
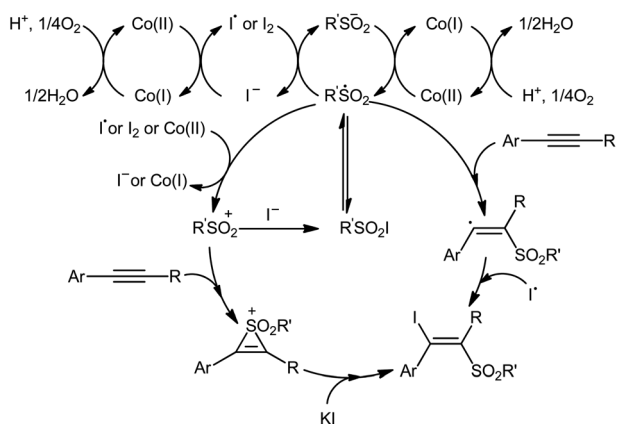
Based on these developments, Reddy and co-workers developed a metal-free iododisulfonylation reaction of acetylenic ketones **37** using sodium sulfinates **38** and molecular iodine as the sulfonyl and iodine sources, respectively.⁴² In the presence of TBHP as oxidant, a wide range of internal acetylenic ketones successfully underwent the reaction to generate polyfunctional tetrasubstituted olefins **39** in moderate to excellent yields with complete regio- and stereoselectivity (Scheme 17). Regarding the regioselectivity of this transformation, in all examples the sulfonyl group selectively attacked to the carbon atom adjacent to the carbonyl group and iodine placed on the carbon atom near the aryl/alkyl substituents. A wide range of functionalities both in the acetylenic ketones and sodium sulfinates were well tolerated with these reaction conditions. However, nitro-substituted sodium arylsulfinates did not respond this reaction. Recently, the Zhang–Xie group successfully extended this chemistry to propargyl alcohols using a 1 : 2 mixture of ClCH₂CH₂Cl : H₂O as the reaction medium.⁴³ Noteworthy, the reaction proceeded effectively without addition of any catalyst or oxidant, ultimately minimizing the production of waste streams.

In 2018, Taniguchi reported that cobalt salts could act as efficient catalysts for iododisulfonylation reactions of alkynes with sodium sulfinates in which potassium iodide (KI) was used as iodination reagent.⁴⁴ Among the various cobalt catalysts like



Scheme 17 Metal-free direct iododisulfonylation of acetylenic ketones **37** with sodium sulfinates **38** and I₂ developed by Reddy.



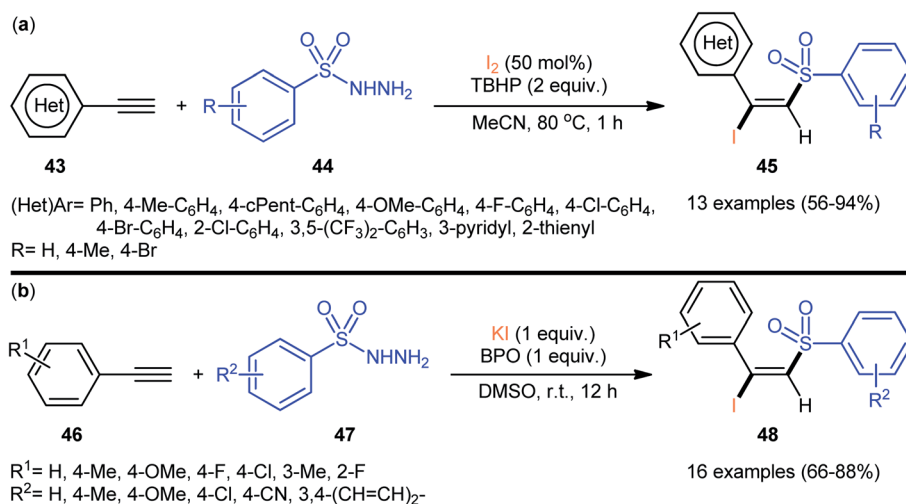
Scheme 18 Co-catalyzed iododisulfonation of alkynes **40** with sodium sulfinates **41** and KI.

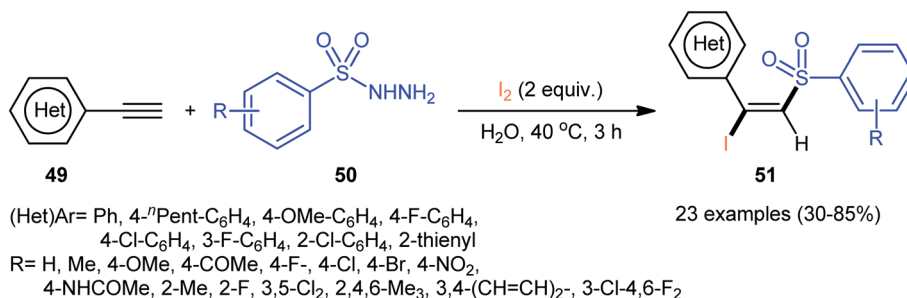
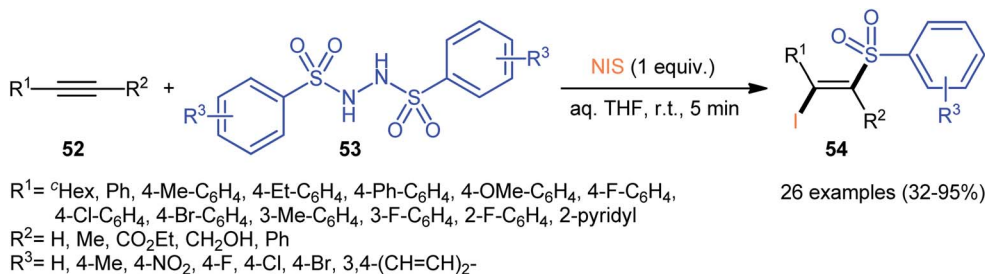
Scheme 19 The proposed mechanism for the reaction in Scheme 18.

CoCl₂, CoBr₂, Co(OAc)₂; low-cost CoBr₂ was the most efficient for the transformation. In the presence of 5 mol% of CoBr₂ and 5 mol% of Phen·H₂O (Phen = phenanthroline) in AcOH under air, a library of aromatic terminal and aryl-alkyl internal alkynes **40** smoothly underwent iododisulfonation with sodium aryl/alkyl-sulfinates **41** and KI to give structurally diverse (*E*)-β-iodovinyl sulfones **42** in modestly to high yields (Scheme 18). It

should be mentioned that iododisulfonation of a vinylacetylene was also achieved with use of similar reaction conditions. However, this synthetic strategy was found not to be applicable to terminal alkyl and internal aryl-aryl alkynes. Interestingly, when the reaction was performed in the absence of sodium sulfinates, the corresponding diiodoalkenes were obtained in high yields. The mechanism proposed for the formation of β-iodovinyl sulfones is depicted in Scheme 19.

4.2.2. Sulfonyl hydrazides as sulfonation agents. In 2013, Li-Xu's group reported the first iododisulfonation of alkynes with sulfonyl hydrazides and molecular iodine.⁴⁵ In this work, a regio- and stereoselective iododisulfonation reaction occurs in the presence of TBHP as the oxidant. A wide range of (hetero) aromatic terminal alkynes **43** could be reacted with arylsulfonyl hydrazides **44** under the optimized conditions to give the (*E*)-β-iodovinyl sulfone products **45** in moderate to almost quantitative yields (Scheme 20a). Aliphatic terminal alkynes, such as hept-1-yne, could also be reacted under the identical conditions. However, the desired products were obtained in poor yields. The authors proposed a mechanism analogous to that of their chlorosulfonylation strategy. Drawing inspiration from this work, Yang and co-workers reported the synthesis of a library of (*E*)-β-iodovinyl sulfone products **48** shown in

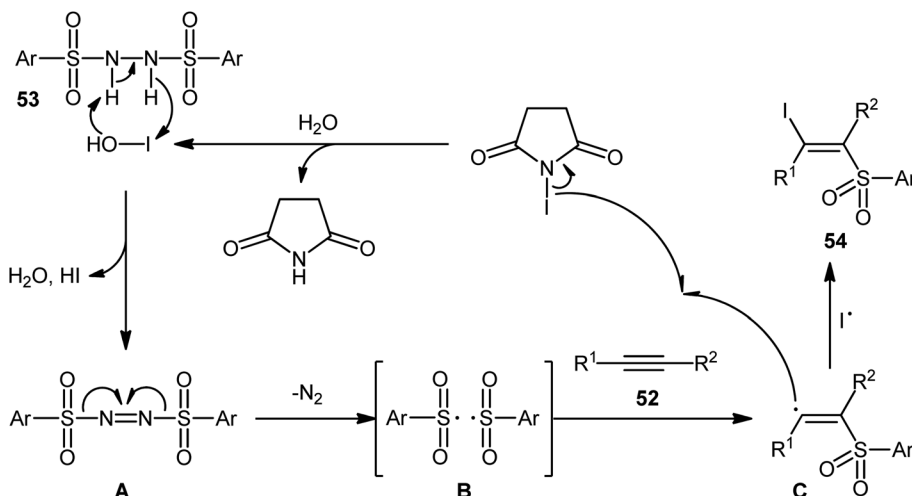
Scheme 20 (a) TBHP-mediated iododisulfonation of terminal alkynes **43** with arylsulfonyl hydrazides **44** and I₂; (b) BPO-mediated three-component reaction between alkynes **46**, arylsulfonyl hydrazides **47**, and KI.

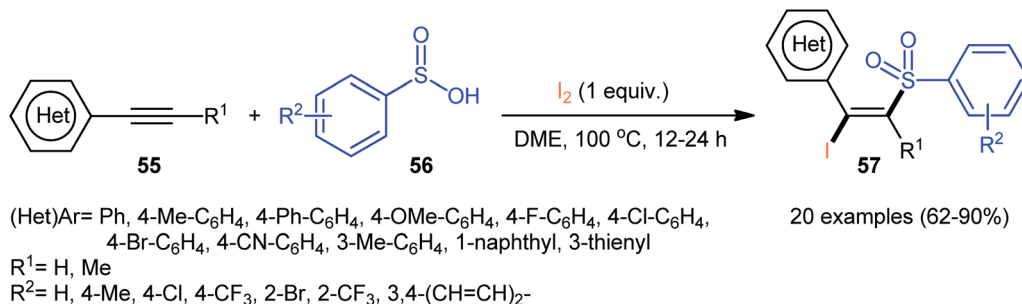
Scheme 21 Catalyst-free iododisulfonation of alkynes **49** with arylsulfonyl hydrazides **50** and I₂ in water.Scheme 22 Synthesis of (*E*)-β-iodovinyl sulfones **54** via the reaction of alkynes **52** with *N,N'*-disulfonylhydrazides **53** and NIS.

Scheme 20b.⁴⁶ These compounds were formed by reaction of the corresponding alkynes **46** with arylsulfonyl hydrazides **47** using KI as iodine source and benzoic peroxyanhydride (BPO) as an oxidant. Subsequently, Tong *et al.* utilized TBAI as iodine source, and developed a K₂S₂O₈-mediated reaction of alkynes with sulfonyl hydrazides for the stereoselective synthesis of (*E*)-β-iodovinyl sulfones.⁴⁷

Following these works, an elegant catalyst- and additive-free reaction of preparing (*E*)-β-iodovinyl sulfone scaffolds **51** from terminal aromatic alkynes **49**, arylsulfonyl hydrazides **50**, and molecular iodine using environmentally benign water as the solvent under room temperature was demonstrated by Wang

and Yan (Scheme 21).³⁷ The results indicated that the phenyl-acetylenes with electron-donating substituents gave higher yields compared to the electron-withdrawing group containing phenylacetylenes. Unfortunately, the alkynes bearing nitro-substitution were incompatible in this transformation. Intriguingly, the electronic character of the substituents on the arylsulfonyl hydrazides had a little impact on the rate of this reaction. However, nitro-substituted arylsulfonyl hydrazides did not work well in the methodology. The mechanism investigation of the reaction using the radical scavengers indicated that a radical pathway could be involved. Shortly afterwards, Sun and co-workers extended the substrate scope of this

Scheme 23 Mechanism that accounts for the generation of (*E*)-β-iodovinyl sulfones **54**.

Scheme 24 Wang's synthesis of (*E*)-β-iodovinyl sulfones 57.

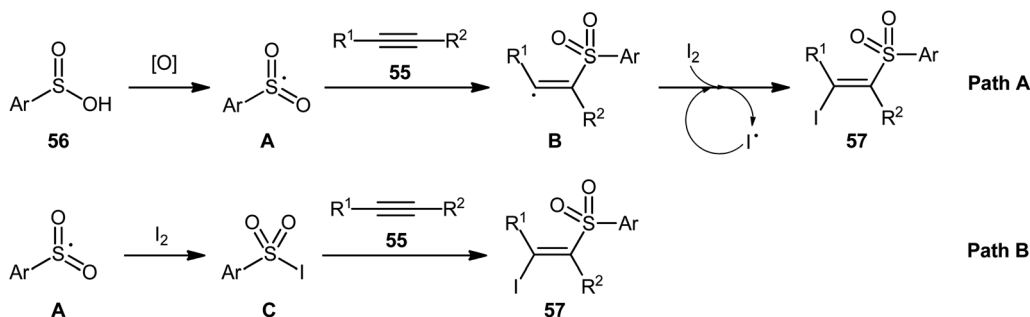
iodosulfonylation reaction to internal alkynes by preforming the process in the presence of over-stoichiometric amounts of H₂O₂ using KI as iodine source.⁴⁸ Interestingly, when the same reaction was performed in 2,2,2-trifluoroethanol (TFE), aggregation induced-emission (AIE)-active benzo[*b*]thiophene-1,1-dioxides were obtained instead of the desired iodovinyl sulfones through intra-molecular cyclization of the vinyl radical intermediate (generated from the addition of sulfonyl radical to alkyne). Along this line, Wei and Wang along with their colleagues demonstrated the synthesis of multisubstituted α,β-enones through the direct selective iodosulfonylation of alkynones with arylsulfonyl hydrazides and iodine pentoxide (I₂O₅).⁴⁹

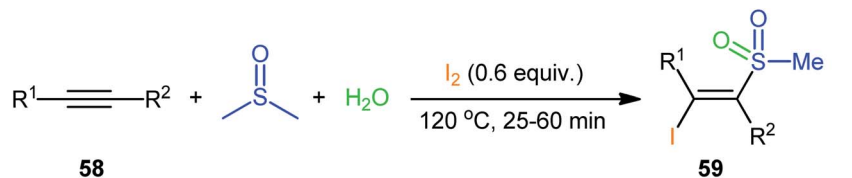
Very recently, the group of Wang and Hu informed for the first time the usefulness of *N,N'*-disulfonylhydrazines as novel sulfonylating reagents for halosulfonylation reactions.⁵⁰ Thus, in the absence of any catalyst or additive in aqueous THF at room temperature, the reaction of various terminal and internal alkynes 52 with *N,N'*-disulfonylhydrazines 53 and NIS furnished the corresponding (*E*)-β-iodovinyl sulfones 54 in moderate to excellent yields within only 5 min (Scheme 22). Indeed, NIS played a dual role in this transformation; the iodine source and the oxidant. Mechanistically, the reaction starts with the formation of HOI oxidant through the hydrolysis of NIS by H₂O, which subsequently oxidizes *N,N'*-disulfonyl-hydrazine 53 into the corresponding azo-intermediate A. Next, this intermediate undergoes a spontaneous decomposition to give two sulfonyl radicals B. Thereafter, the newly formed radical selectively attacks to the less hindered end of alkyne 52 to yield a vinyl

radical C that, after getting an iodine radical from NIS affords the expected products 54 (Scheme 23).

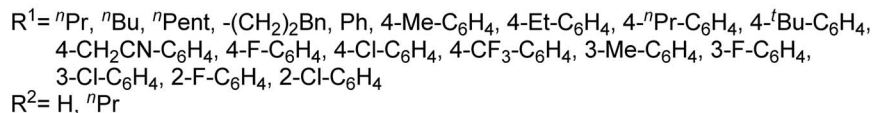
4.2.3. Miscellaneous reactions. In 2015, the Wang group realized that sulfinic acids could serve as good sulfonyl sources in halosulfonylation reactions of alkynes.⁵¹ They showed that three-component reaction between aromatic alkynes 55, sulfinic acids 56, and molecular iodine in the absence of any catalyst or additive formed a series corresponding (*E*)-β-iodovinyl sulfones 57 in good to excellent yields with outstanding stereo- and regio-selectivities (Scheme 24). Of note, propiolates could also be participated in this reaction, albeit with lower efficiencies. However, when 1-hexyne (an aliphatic alkyne) was employed under the identical reaction conditions, the desired product was isolated obtained in only 12% yield. Interestingly, when the reactions were performed in the presence of stoichiometric amounts of K₂CO₃, the corresponding acetylenic sulfones were obtained in high yields. Based on a series of control experiments, a plausible mechanism was suggested for the formation of (*E*)-β-iodovinyl sulfones, as depicted in Scheme 25. Initially, the sulfinic acid 56 was oxidized by air oxygen to form the sulfonyl radical A, followed by addition to alkyne 55 to generate the alkenyl radical B. Finally, the interaction of intermediate B with molecular iodine delivered the desired β-iodovinyl sulfone 57 (Scheme 25, path a). In another possibility, the direct iodosulfonylation of alkyne 55 with *in situ* generated sulfonyl iodides C (from sulfinic acid 56 and molecular iodine) led to the formation of the target products 57 (Scheme 25, path b).

Recently, in a significant contribution in this field, Pan and Liu developed an efficient four-component synthesis of (*E*)-α-

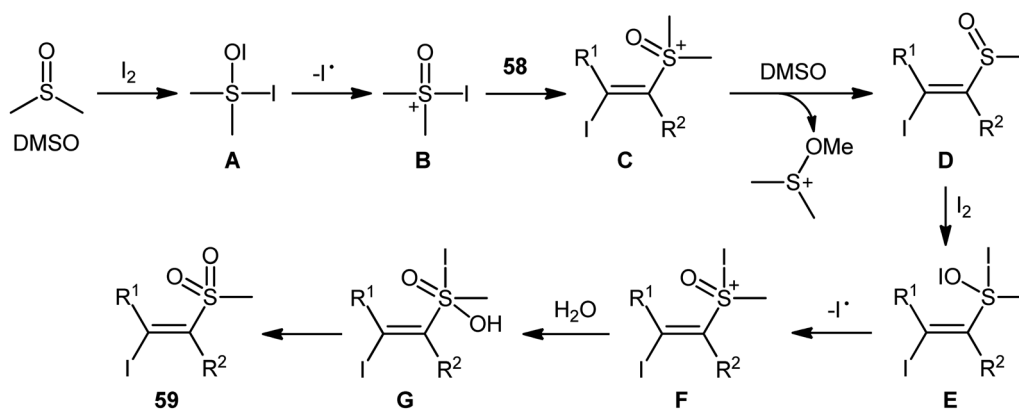
Scheme 25 Possible reaction pathway for the formation (*E*)-β-iodovinyl sulfones 57.



18 examples (53-81%)



Scheme 26 Catalyst-free four-component synthesis of (*E*)- α -iodo- β -methylsulfonylalkenes **59** from alkynes **58**, DMSO, I₂, and H₂O.



Scheme 27 Possible pathway of (*E*)- α -iodo- β -methylsulfonylalkenes **59** formation.

iodo- β -methylsulfonylalkenes **59** from alkynes **58**, dimethyl sulfoxide (DMSO), molecular iodine and water without any added catalyst and solvent (Scheme 26).⁵² This eco-friendly synthetic strategy is distinguished by its generality, accommodating aliphatic and aromatic terminal alkynes, and even internal alkyl-alkyl alkynes in the presence of various sensitive functional groups (*e.g.*, F, Cl, CF₃, CN). A possible mechanism for this transformation was proposed by the authors, as shown in Scheme 27.

Finally, it should be noted that transition metals play main role in direct halosulfonylation of alkynes.⁵³⁻⁶¹

5. Conclusion

Difunctionalization of alkyne feedstocks is a specific class of important synthetic transformations that allow for the buildup of molecular complexity within a single click.⁶² In this context, the direct halosulfonylation of alkynes which provide a powerful strategy for the preparation of β -halovinyl sulfone derivatives has devoted a great deal of attention. As illustrated, most of the halosulfonylation reaction of alkynes were performed under catalyst- and additive-free conditions. Despite the remarkable progress that has been achieved in this interesting research arena, some challenging problems remain unsolved yet. For example: (i) generally, the regioselectivity of reactions is dominated by the Markovnikov-type products. Thus, many more

studies are further needed to development of efficient procedures that allow halosulfonylation reactions in an anti-Markovnikov-type manner; (ii) the number of reported examples in bromosulfonylation reactions are very narrow and, of course, there is a need to study the scope and limitations of these reactions; and (iii) fluorosulfonylation of alkynes should be explored.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was sponsored by Hanshan Normal University.

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