NJC

Regiodivergent Sulfonylation of Terminal Olefins via Dearomative Rearrangement

Journal:	*New Journal of Chemistry*
Manuscript ID	NJ-ART-08-2023-003595
Article Type:	Paper
Date Submitted by the Author:	01-Aug-2023
Complete List of Authors:	Blé González, Ever; Florida Gulf Coast University Isbel, Stephen; Florida Gulf Coast University Ojo, Olatunji; University of Texas at Arlington, Department of Chemistry & Biochemistry Hillesheim, Patrick; Ave Maria University, Zeller, Matthias; Youngstown State University, Department of Chemistry Bugarin, Alejandro; Florida Gulf Coast University, Chemistry & Physics

ARTICLE

Regiodivergent Sulfonylation of Terminal Olefins via Dearomative Rearrangement

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

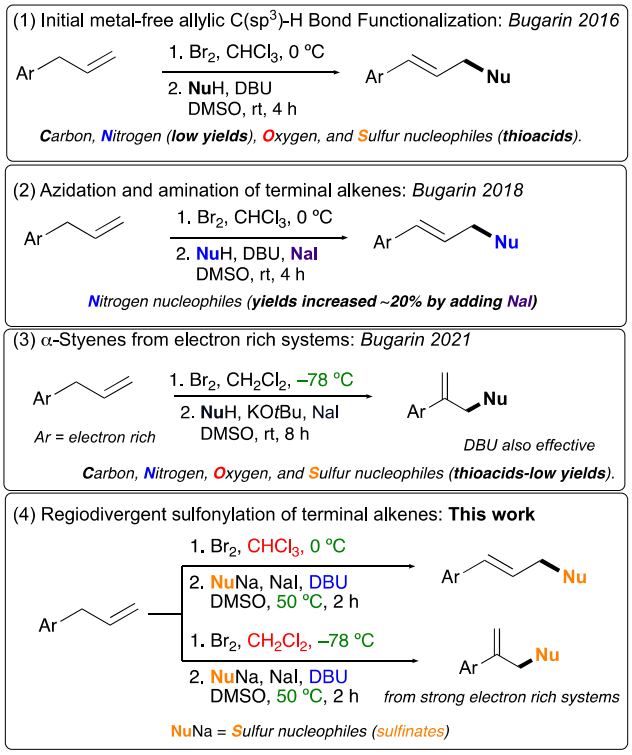
Ever A. Blé-González,[a] Stephen R. Isbel,[a] Olatunji S. Ojo,[b] Patrick C. Hillesheim,[c] Matthias Zeller,[d] and Alejandro Bugarin*[a]

Sulfones are fascinating and highly used functional groups, but current syntheses still have limitations. Here, a regiodivergent transition metal-free approach towards sulfones [(*E*)-allylic sulfones and α-sulfonylmethyl styrenes] is reported. The method employs commercially available olefins, bases, additives, solvents, and sodium sulfinates (RSO_2Na) and produces adducts in good yields. Considering that up to 4 reactions (bromination, dearomative rearrangement, E2, and S_N2) are happening, this approach is very efficient. The structures of key adducts were confirmed by X-ray crystallography.

Introduction

Sulfones are an important class of organosulfur compounds because of their vast applications in the synthetic, medical, and material fields.[1,2] Among sulfones, allylsulfone derivatives[3] are one of the most exploited intermediates in organic synthesis, as they are found in numerous bioactive molecules.[4,5,6] For example, allylsulfones can be antibacterial agents,[6a] TSH receptor antagonist, [6b] cysteine protease inhibitors,[6c-d] anticancer agents,[6e] etc.[6f-k] Currently, there are several synthetic approaches to prepare allylsulfones. The traditional approaches are to either use the Tsuji-Trost reaction (Pd[7] or Ir[8])[9] for allylsulfones[10] or sulfonyl radical additions to prepare α-sulfonylmethyl styrenes.[11,12,13] Alternatively, the stoichiometric oxidation[14] of sulfides with strong oxidants has also provided allylsulfones.[1] Other alternatives from alkenes include metal catalyzed (e.g., Pd[7,15,16], Ni, & Cu[17]) and substitutions[18,19,20] reactions. Couplings of allylic alcohols with sulfinyl chlorides,[21] activated by NBS,[22] or catalyzed by Pd[3,23] have afforded allylsulfone . Similarly, allylic amines using Pd,[24] allenes using Pd,[25] activated alcohols using W[26] or Ir,[27] alkynes with Rh,[28] dienes with Pd,[29] and allyl halides[30] have been reported to produce allylsulfones; whereas, α-sulfonylmethyl styrenes have been mainly prepared by radical reactions[13,31,32,33,34,35] or using stoichiometric ZnI_2.[36]

Despite progress, we sought to develop a complementary and tunable synthetic approach (regiodivergent sulfonylation) that utilizes inexpensive and readily available starting materials and reagent under transition metal-free conditions.



Scheme 1 Evolution of our allylic C(sp^3)-H bond functionalization.

In 2016, we developed a transition metal-free method towards allylic functionalization of terminal alkenes (Scheme 1, eq 1).[37] It was found that a variety of olefins could serve as starting materials, except allylaryl systems bearing strong electron donating groups (e.g., MeO). During the same study, it was found that the reaction tolerated an assortment of carbon, nitrogen, oxygen, and sulfur nucleophiles. However, two things were noted; first that only thioacids were effective for the sulfur nucleophiles and second that nitrogen adducts were obtained in modest yields. In 2018, we discovered that using NaI as an

[a] Department of Chemistry and Physics, Florida Gulf Coast University, Fort Myers, Florida, 33965, United States of America. E-mail: abugarin@fgcu.edu.
[b] Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, Texas 76019, United States of America.
[c] Department of Chemistry and Physics, Ave Maria University, Ave Maria, Florida, 34142, United States of America.
[d] Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907, United States of America

†Electronic Supplementary Information (ESI) available: Experimental details, procedures, ^1H NMR & ^{13}C NMR spectra, and X-Ray acquisition data and structures of **3b** & **4c**. See DOI: 10.1039/x0xx00000x

additive increased the yields *ca.* 20% across the board (Scheme 1, eq 2).[38] Then, we turned our attention to electron rich allylaryl systems. In 2021, we reported a straightforward protocol for the synthesis of α-alkyl styrenes (Scheme 1, eq 3).[39] It was observed that the bromination step plays a decisive role in determining the adduct regioselectivity and yield. Specifically, the bromination solvent and temperature. It was also observed that DBU was the most effective base for sulfur nucleophiles.

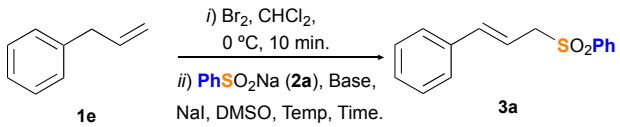
With the above information on hand and in our continued effort to develop a facile protocol for the functionalization of terminal alkenes, we focused on the development of a regiodivergent method for the synthesis of allylsulfones [(*E*)-allylic and α-methyl styrenes] (Scheme 1, eq 4).

Results and discussion

Although there was strong evidence for the best bromination conditions, we conducted additional ^{1}H NMR studies to further confirm the optimal bromination conditions (see ESI, Table S1)† and its effects on the second step (see ESI, Table S2).† It was confirmed that using chloroform ($CHCl_3$) at 0 °C for 10 min were the optimal conditions for the synthesis of (*E*)-allylic sulfones (**3**), whereas using dichloromethane (CH_2Cl_2) at –78 °C for 30 min were the best conditions for the synthesis of α-sulfonylmethyl styrenes (**4**).

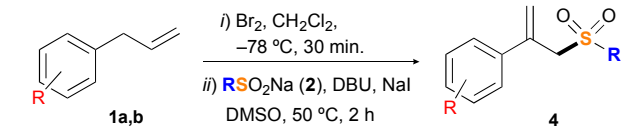
After the optimal bromination conditions were set, allylbenzene (**1e**) and the sulfinate salt[40] sodium benzenesulfinate (**2a**) were selected as model substrates to attempt the two-step protocol (Table 1). In order to establish the best reaction conditions for the second step, different bases and temperatures were studied. From these experiments, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was identified as the superior base over other bases such as: Li_2CO_3, Na_2CO_3, K_2CO_3, Cs_2CO_3, and KO^{t}Bu (Table 1, entries 2-7). It is important to note that in the absence of base the reaction did not proceed (Table 1, entry 1) and adding more than 1.2 equivalents of base did not increase the yield (not shown). Further control experiments revealed that slightly higher temperatures can increase yield. For instance, by using DBU at room temperature (22 °C) a 49% yield was observed after 4 hours (entry 7). When the temperature was increased to 35 °C, the yield increased to 55% (entry 8) and at 50 °C the reaction reached its maximum yield (65%) in only 2 hours (entry 9). Although the reaction was completed faster at higher temperatures, the yields were diminished, perhaps due to the decomposition of the intermediates and products (entries 10 & 11). Other solvents were also screened (e.g., DMA, DMF, THF, toluene, etc.) but none were as effective as DMSO.

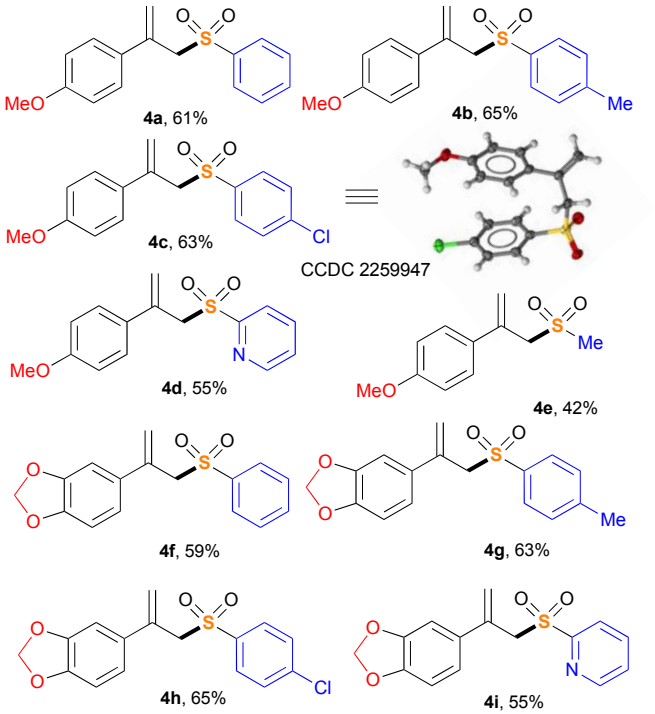
Table 1 Optimization of reaction conditions[a]



Entry	Base	Temp (°C)	Time (h)	Yield (%)[b]
1	none	22 = rt	4	0
2	Li_2CO_3	22	4	22
3	Na_2CO_3	22	4	23
4	K_2CO_3	22	4	27
5	Cs_2CO_3	22	4	38
6	KO^{t}Bu	22	4	46
7	DBU	22	4	49
8	DBU	35	4	55
9	**DBU**	**50**	**2[c]**	**65**
10	DBU	80	1[c]	48
11	DBU	100	0.5[c]	45

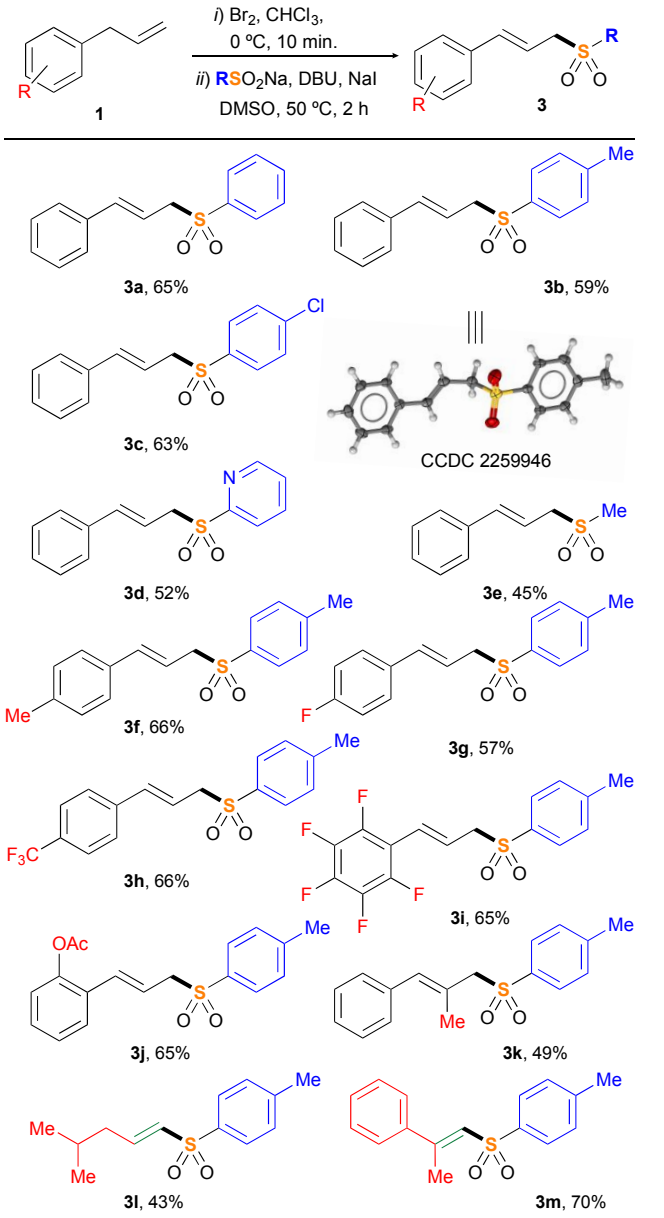
[a] Reactions were carried out with allylbenzene **1e** (0.4 mmol, 1 equiv) Br_2 (0.44 mmol, 1.1 equiv), in 1.0 mL of $CHCl_3$ at 0 °C for 10 min. Then, the volatiles were removed. To the crude reaction mixture was added 1.0 mL of DMSO, $PhSO_2Na$ **2a** (0.60 mmol, 1.5 equiv), NaI (0.40 mmol, 1.0 equiv), and base (0.48 mmol, 1.2 equiv). Then, the reaction flask was capped and stirred. [b] Isolated yields by silica gel flash column chromatography. [c] The reaction mixture was monitored by TLC and stopped after the dibromide intermediate was deemed consumed.





Scheme 2 Synthesis of α-sulfonylmethyl styrenes. Reactions conditions: allylaryl **1** (0.4 mmol, 1 equiv) Br_2 (0.44 mmol, 1.1 equiv), in 1.0 mL of CH_2Cl_2 at –78 °C for 30 min. Then, the volatiles were removed. To the crude reaction mixture was added 1.0 mL of DMSO, sodium sulfinate **2** (0.60 mmol, 1.5 equiv), NaI (0.40 mmol, 1.0 equiv), and DBU (0.48 mmol, 1.20 equiv). Then, the reaction was stirred at 50 °C for 2 h. All yields are from Isolated materials.

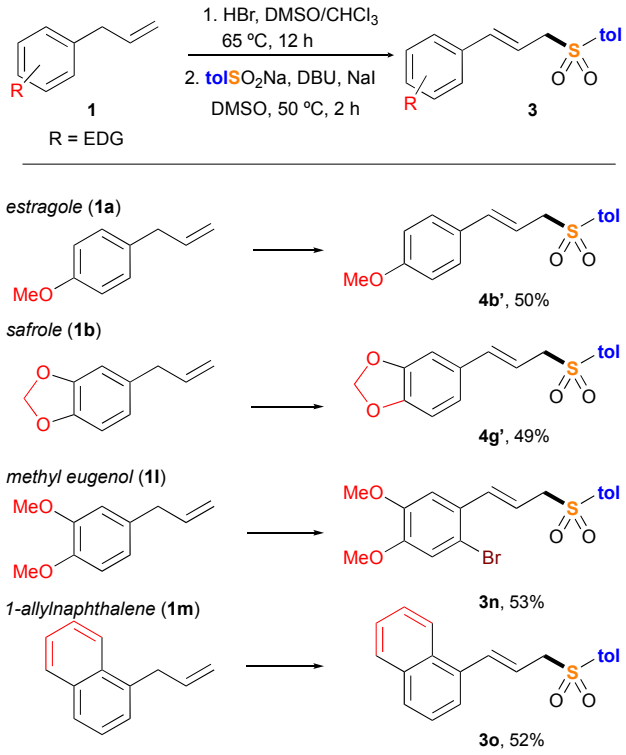
Having identified the optimal conditions for the conversion of terminal olefins to allylsulfones, we then examined the scope of the two-step synthetic approach, as depicted in Scheme 2. The electron rich estragole **1a** or safrole **1b** were treated with 1.1 equiv of bromine at −78 °C in DCM and stirred for 30 min. Then, the volatiles were removed under reduced pressure. To the crude dibrominated intermediates, DMSO, the respective sodium sulfinate (**2**), NaI, and DBU were added and the reaction mixture was stirred for 2 h, at 50 °C (Scheme 2). For comparative purposes, all reactions were quenched after 2 h. Estragole **1a** was the first allylaryl starting material used for this scheme, in combination with miscellaneous sodium sulfinates (e.g., aromatic, heteroaromatic, and aliphatic sulfinates). To our delight, when sodium benzenesulfinate **2a** was used as the nucleophile, the reaction afforded the expected α-sulfonylmethyl styrenes **4a**, in 61% yield. Similarly, sodium 4-methylbenzenesulfinate **2b** produced adduct **4b** in 65% yield. The halogenated derivative, sodium 4-chlorobenzenesulfinate **2c** was also effective and delivered product **4c** in 63% yield. Single crystal X-ray diffraction of **4c** (CCDC 2259947) unambiguously confirmed its structure. In addition, the heterocycle derivative, sodium pyridine-2-sulfinate **2d** was tolerated to produce **4d** in 55% yield. Besides aromatic sulfinates, we also investigated the aliphatic derivative sodium methanesulfinate **2e**. To our satisfaction, the reaction produced its respective α-sulfonylmethyl styrene **4e** in 42% yield. Scheme 2 also includes the yields of the adducts when safrole **1b** and different sodium sulfinates were used. For instance, when sodium benzenesulfinate **2a** was used a 59% isolated yield of **4f** was obtained, sodium 4-methylbenzenesulfinate **2b** gave **4g** in 63% yield, sodium 4-chlorobenzenesulfinate **2c** delivered **4h** in 65% yield, and sodium pyridine-2-sulfinate **2d** produced **4i** in 55% yield (Scheme 2).



Scheme 3 Synthesis of (*E*)-allylic sulfones. Reactions conditions: allylaryl **1** (0.4 mmol, 1 equiv) Br_2 (0.44 mmol, 1.1 equiv), in 1.0 mL of $CHCl_3$ at 0 °C for 10 min. Then, the volatiles were removed. To the crude reaction mixture was added 1.0 mL of DMSO, sodium sulfinate **2** (0.60 mmol, 1.5 equiv), NaI (0.40 mmol, 1.0 equiv), and DBU (0.48 mmol, 1.20 equiv). Then, the reaction was stirred at 50 °C for 2 h. All yields are from Isolated materials.

In our search to expand our protocol to other allylaryls, we then utilized our complementary bromination conditions ($CHCl_3$ at 0 °C for 10 min), which favor the formation of (*E*)-allylic sulfones **3**. The synthetic utility and scope of the DBU-mediated regiodivergent sulfonylation of terminal olefins was evaluated as follows. Allylbenzene **1e** was dibrominated and then reacted with sodium benzenesulfinate **2a** in the presence of DBU and NaI, which delivered 3a in 65% isolated yield (Scheme 3). Likewise, sodium 4-methylbenzenesulfinate **2b** gave **3b** in 59% yield. Single crystal X-ray diffraction of **3b** (CCDC 2259946) unambiguously confirmed its structure. Sodium 4-chlorobenzenesulfinate **2c** produced **3c** in 63% yield, sodium pyridine-2-sulfinate **2d** afforded **3d** in 52% yield, and the

aliphatic sodium methanesulfinate **2e** also delivered its respective (*E*)-allylic sulfones **3e** in 45% yield (Scheme 3). Then, we focused our attention on exploring different allylic compounds with sodium 4-methylbenzenesulfinate **2b** as the nucleophile. The *para* substituted 4-allyl toluene **1c** was an effective substrate delivering adduct **3f** in 66% isolated yield (Scheme 3). Fluorinated starting materials such as: 1-allyl-4-fluorobenzene **1d**, 1-allyl-4-(trifluoromethyl)benzene **1f**, and 1-allyl-2,3,4,5,6-pentafluorobenzene **1g**, produced their corresponding sulfones in 57% (**3g**), 66% (**3h**), and 65% yield (**3i**), respectively. The *ortho* substituted 2-allylphenyl acetate **1h** also reacted well and produced its corresponding allylsulfone **3j** in 65% yield. Furthermore, the presence of an alkyl group in position 2 of the propene was investigated, this time using (2-methyl-2-propenyl)benzene **1i** as the starting material. To our satisfaction, the adduct **3k** was obtained in yield 49%. In addition, the unactivated alkenes 4-methyl-1-pentene **1j** was compatible with the reaction conditions. Vinyl sulfone **3l** was obtained in 43% yield instead of the expected allylic sulfone, this to favor conjugation with the sulfonyl group.[41] Nonetheless, this represents a breakthrough in that aliphatic substrates (unactivated alkenes) are also effective under our new method. Furthermore, when α-methyl styrene **1k** was used as starting material, it also produced vinyl sulfone **3m** in 70% isolated yield after double bond isomerization driven by the formation of a conjugated system (Scheme 3).[42]



Scheme 4 Synthesis of (*E*)-allylic sulfones from electron rich systems. Reactions conditions: allylaryl **1** (0.4 mmol, 1 equiv) HBr (48%aq, 5 equiv), in 0.5 mL of DMSO and 0.5 mL of $CHCl_3$ at 65 °C for 12 h. Then, the mixture was extracted and the volatiles removed. To the crude mixture was added 1.0 mL of DMSO, sodium sulfinate **2b** (0.60 mmol, 1.5 equiv), NaI (0.40 mmol, 1.0 equiv), and DBU (0.48 mmol, 1.20 equiv). Then, the reaction was stirred at 50 °C for 2 h. All yields are from Isolated materials. tol = toluene

After analyzing all the previous results and to further expand the scope of our protocol, we proceeded to search for a modification to our protocol aiming to eliminate one of the major limitations. Therefore, we focused our attention to the fact that electron rich systems produce almost exclusively α-sulfonylmethyl styrenes (Scheme 2). Nonetheless, (*E*)-allylic sulfones from electron rich systems are highly desirable building blocks as well. In order to access (*E*)-allylic sulfones from electron rich systems, we hypothesized that using Magolan's dibromination of olefins protocol should work.[43] The protocol utilizes HBr and DMSO to produce bromodimethylsulfonium bromide *in situ*, a well-known electrophilic bromination agent.[44] Although our bromination protocol and Magolan's bromination gave access to dibromo adducts, the key difference is the presence of acid on Magolan's method. Under acidic conditions, electron rich systems such as estragole **1a** and safrole **1b**, having electron donating groups (i.e., OMe, OCH_2O) will be protonated. Thus, deactivating the aryl group to form now an electron-poor system and as established above, electron-poor systems gave almost exclusively (*E*)-allylic sulfones (Scheme 3). To test our hypothesis, we reacted estragole **1a** under Magolan's dibromination conditions followed by our standard second-step utilizing sodium 4-methylbenzenesulfinate **2b** as the nucleophilic partner. To our gratification, the (*E*)-allylic sulfone **4b'** was obtained in 50% isolated yield and 40:1 ratio (Scheme 4). Treatment of safrole **1b** under the same protocol was also effective and delivered allylsulfone **4g'** in 49% yield and >50:1 ratio. Furthermore, methyl eugenol **1l** was also tolerated presenting its corresponding allylsulfone **3n** 53% yield and >50:1 ratio. It is important to note that bromo was also installed *ortho* to the allylic system. This due to the excess of HBr used during the bromination step, an observation previously documented.[37] Finally, 1-allylnaphtalene **1m** was also examined. Although this allylaryl compound doesn't have EDGs bearing heteroatoms, its electron density caused a 4:1 ratio using our standard bromination conditions ($CHCl_3$ at 0 °C) towards (*E*)-allylic sulfones. Favorably, using Magolan's dibromination conditions, adduct **3o** was successfully synthesized in 52% yield and >50:1 ratio. These excellent results allow the conversion of electron rich systems to (*E*)-allylic sulfones even with or without heteroatoms bearing electron donating groups (Scheme 4).

It is worth noting that proposed mechanisms for the formation of (*E*)-allylic compounds and α-alkyl styrenes have been reported previously. However, a unified mechanism that encompasses the three different protocols is depicted in the ESI (Scheme ESI-1).† In summary, terminal olefins undergo a bromination, followed by a dearomative rearrangement (mainly for styrene derivatives). Then, an E2 followed by an S_N2 will construct the expected adducts.

Conclusions

This manuscript documents a practical synthetic approach to (*E*)-allylic sulfones and α-sulfonylmethyl styrenes from terminal olefins. The method is effective across the board, from electron rich to electron poor aryl systems, and aliphatic alkenes. The approach tolerates aryl, heteroaryl, and alkyl sulfinates. In addition, by simple bromination under acidic conditions the electron-rich systems can be tuned toward formation of (*E*)-allylic sulfones. The reaction yields although modest to good, they are the sum-up of 3-4 consecutive chemical reactions. Overall, the data presented in this manuscript provides solid evidence for the generality of our regiodivergent approach towards (*E*)-allylic sulfones and α-sulfonylmethyl styrenes. This methodology should be considered as an excellent option for the rapid generation of allylsulfones scaffolds, a significant building block in the synthesis of useful molecules.[45]

Author Contributions

E. Ble-González, O. Ojo, and S. Isbel performed the experiments. M. Zeller and P. Hillesheim acquired and processed the X-ray data. A. Bugarin conceived and designed the study, secured the funds, and wrote the paper.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the National Institute of General Medical Sciences of the National Institutes of Health (NIH) under award number 1R15GM141726-01. A. B. is also thankful to Florida Gulf Coast University. P. C. H gratefully acknowledges the donors of the American Chemical Society Petroleum Research Fund for partial support of this research (66195-UNI10). M.Z. acknowledges National Science Foundation under Grant number CHE-1625543 (MRI).

References

1 N.-W. Liu, S. Liang and G. Manolikakes, Recent Advances in the Synthesis of Sulfones, *Synthesis*, 2016, **48**, 1939–1973.

2 X. Liang and Y. Shen, Advances in Synthesis of Enantioenriched Chiral Sulfones by Enantioselective Conjugate Addition Reactions, *Asian J. Org. Chem.*, 2022, **11**, e202100598.

3 B. M. Trost and M. R. Chadiri, Sulfones as chemical chameleons. Cyclization via 1,1-dipole synthons, *J. Am. Chem. Soc.*, 1984, **106**, 7260–7261.

4 M. Feng, B. Tang, H. S. Liang and X. Jiang, Sulfur Containing Scaffolds in Drugs: Synthesis and Application in Medicinal Chemistry, *Curr. Top. Med. Chem.*, 2016, **16**, 1200–1216.

5 K. A. Scott and J. T. Njardarson, Analysis of US FDA-Approved Drugs Containing Sulfur Atoms, *Top. Curr. Chem.*, 2018, **376**, 5.

6 (*a*) F. Reck, F. Zhou, M. Girardot, G. Kern, C. J. Eyermann, N. J. Hales, R. R. Ramsay, M. B. Gravestock, Identification of 4-Substituted 1,2,3-Triazoles as Novel Oxazolidinone Antibacterial Agents with Reduced Activity against Monoamine Oxidase, *J. Med. Chem.* 2005, **48**, 499−506; (*b*) M. C. Gershengorn, S. Neumann, C. J. Thomas, H. Jaeschke, S. Moore, G. Krause, B. Raaka, R. Paschke, G. Kleinau, US2009203716 (A1), 2009; (*c*) J. C. Powers, G. M Gotz, U.S. Patent 0241057, 2006; (*d*) M. G. Götz, C. R. Caffrey, E. Hansell, J. H. McKerrow and J. C. Powers, Peptidyl allyl sulfones: a new class of inhibitors for clan CA cysteine proteases, *Bioorg. Med. Chem.*, 2004, **12**, 5203–5211; (*e*) N. Neamati, G. W. Kabalka, B. Venkataiah, R. Dayam, U.S. Patent 0203224, 2007; (*f*) X. Chen, S. Hussain, S. Parveen, S. Zhang, Y. Yang, C. Zhu, Sulfonyl Group-Containing Compounds in the Design of Potential Drugs for the Treatment of Diabetes and Its Complications, *Curr. Med. Chem.* 2012, **19**, 3578−3604; (*g*) T. G. Back, K. N. Clary, D. Gao, Cycloadditions and Cyclizations of Acetylenic, Allenic, and Conjugated Dienyl Sulfones, *Chem. Rev.* 2010, **110**, 4498−4553; (*h*) N. Neamati, G. W. Kabalka, B. Venkataiah, R. Dayam, WO2007081966 (A2), 2007; (*i*) (*h*) N. Neamati, G. W. Kabalka, B. Venkataiah, R. Dayam, WO2007081966 (A3), 2007; (*j*) J. C. Powers, G. M. Gotz, US200601729529 (A1), 2006; (*k*) F. G. Pilkiewicz, L. Boni, C. Mackinson, J. B. Portnoff, A. Scotto, WO20030758899 (A1), 2003.

7 T. Chen, J. Lahbi, G. Broggini, A. Pradal and G. Poli, Allylsulfones through Palladium-Catalyzed Allylic C–H Sulfonylation of Terminal Alkenes, *Eur. J. Org. Chem.*, 2023, **26**, e202201493.

8 M. Bellido, C. Riego-Mejías, A. Diaz-Moreno, X. Verdaguer and A. Riera, Enantioselective Ir-Catalyzed Hydrogenation of Terminal Homoallyl Sulfones: Total Synthesis of (−)-Curcumene, *Org. Lett.*, 2023, **25**, 1453–1457.

9 For reviews of Tsuji-Trost reactions, see: (*a*) J. Tsuji Palladium *Reagents and Catalysts: New Perspectives for the 21st Century*; John Wiley & Sons, Ltd.: Chichester, U.K., 2004; Chapter 4, p 431; (*b*) B. M. Trost and D. L. Van Vranken, Asymmetric Transition Metal-Catalyzed Allylic Alkylations, *Chem. Rev*. 1996, **96**, 395-422; (*c*) E.-I. Negishi, Ed. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley-Interscience: New York, 2002.

10 J. Yu, X. Chang, R. Ma, Q. Zhou, M. Wei, X. Cao and X. Ma, Water-Promoted Dehydrative Tsuji–Trost Reaction of Non-Derivatized Allylic Alcohols with Sulfinic Acids, *Eur. J. Org. Chem.*, 2020, **2020**, 7238–7242.

11 Y. Lou, J. Qiu, K. Yang, F. Zhang, C. Wang and Q. Song, Ni-Catalyzed Reductive Allylation of α-Chloroboronates to Access Homoallylic Boronates, *Org. Lett.*, 2021, **23**, 4564–4569.

12 M.-M. Zhang and F. Liu, Visible-light-mediated allylation of alkyl radicals with allylic sulfones via a deaminative strategy, *Org. Chem. Front.*, 2018, **5**, 3443–3446.

13 H. Xu, H. Zhang, Q.-X. Tong and J.-J. Zhong, Photoredox/cobaloxime co-catalyzed allylation of amines and sulfonyl hydrazines with olefins to access α-allylic amines and allylic sulfones, *Org. Biomol. Chem.*, 2021, **19**, 8227–8231.

14 X. Li, X. Xu and C. Zhou, Tetrabutylammonium iodide catalyzed allylic sulfonylation of α-methyl styrene derivatives with sulfonylhydrazides, *Chem. Commun.*, 2012, **48**, 12240–12242.

15 N. Taniguchi, Aerobic Palladium-Catalyzed Arylation of Alkenes Using Sodium Sulfinates, *Synlett*, 2013, 2571–2574.

16 Q. Zhang, D. Dong and W. Zi, Palladium-Catalyzed Regio- and Enantioselective Hydrosulfonylation of 1,3-Dienes with Sulfinic Acids: Scope, Mechanism, and Origin of Selectivity, *J. Am. Chem. Soc.*, 2020, **142**, 15860–15869.

17 V. V. Ermolaeva, N. P. Gerasimova, N. A. Nozhnin, Y. A. Moskvichev, E. M. Alov, A. S. Danilova, I. V. Shutova and O. S. Kozlova, Reaction of α-methylstyrene with arylsulfonyl

chlorides: spontaneous dehydrochlorination against the Zaitsev rule, *Mendeleev Commun.*, 2005, **15**, 84–86.
18 A. Shankar, Md. Waheed and R. J. Reddy, Simple and Efficient Synthesis of Allyl Sulfones through Cs2CO3-Mediated Radical Sulfonylation of Morita–Baylis–Hillman Adducts with Thiosulfonates, *SynOpen*, 2021, **05**, 91–99.
19 A. S. Deeming, C. J. Russell, A. J. Hennessy and M. C. Willis, DABSO-Based, Three-Component, One-Pot Sulfone Synthesis, *Org. Lett.*, 2014, **16**, 150–153.
20 S. Jin, G. C. Haug, R. Trevino, V. D. Nguyen, H. D. Arman and O. V. Larionov, Photoinduced C(sp^3)–H sulfination empowers the direct and chemoselective introduction of the sulfonyl group, *Chem. Sci.*, 2021, **12**, 13914–13921.
21 H.-H. Li, D.-J. Dong, Y.-H. Jin and S.-K. Tian, An Expeditious Entry to Benzylic and Allylic Sulfones through Byproduct-Catalyzed Reaction of Alcohols with Sulfinyl Chlorides, *J. Org. Chem.*, 2009, **74**, 9501–9504.
22 T. Murakami and K. Furusawa, One-pot Synthesis of Aryl Sulfones from Alcohols, *Synthesis*, 2002, **2002**, 479–482.
23 S. Chandrasekhar, V. Jagadeshwar, B. Saritha and C. Narsihmulu, Palladium−Triethylborane-Triggered Direct and Regioselective Conversion of Allylic Alcohols to Allyl Phenyl Sulfones, *J. Org. Chem.*, 2005, **70**, 6506–6507.
24 X.-S. Wu, Y. Chen, M.-B. Li, M.-G. Zhou and S.-K. Tian, Direct Substitution of Primary Allylic Amines with Sulfinate Salts, *J. Am. Chem. Soc.*, 2012, **134**, 14694–14697.
25 J.-H. Zeng, D.-C. Li, S. Zhang and Z.-P. Zhan, Chemodivergent Synthesis of Allylic Sulfones via Ligand-Controlled Coupling of Allenes with Sulfinic Acids, *Org. Lett.*, 2022, **24**, 1195–1200.
26 Y. Xu, M. Salman, S. Khan, J. Zhang and A. Khan, Tungsten-Catalyzed Allylic Substitution with a Heteroatom Nucleophile: Reaction Development and Synthetic Applications, *J. Org. Chem.*, 2020, **85**, 11501–11510.
27 M. Ueda and J. F. Hartwig, Iridium-Catalyzed, Regio- and Enantioselective Allylic Substitution with Aromatic and Aliphatic Sulfinates, *Org. Lett.*, 2010, **12**, 92–94.
28 K. Xu, V. Khakyzadeh, T. Bury and B. Breit, Direct Transformation of Terminal Alkynes to Branched Allylic Sulfones, *J. Am. Chem. Soc.*, 2014, **136**, 16124–16127.
29 H.-M. Huang, P. Bellotti, P. M. Pflüger, J. L. Schwarz, B. Heidrich and F. Glorius, Three-Component, Interrupted Radical Heck/Allylic Substitution Cascade Involving Unactivated Alkyl Bromides, *J. Am. Chem. Soc.*, 2020, **142**, 10173–10183.
30 P. K. Shyam and H.-Y. Jang, Synthesis of Sulfones and Sulfonamides via Sulfinate Anions: Revisiting the Utility of Thiosulfonates, *J. Org. Chem.*, 2017, **82**, 1761–1767.
31 X. Lei, L. Zheng, C. Zhang, X. Shi and Y. Chen, Allylic C–S Bond Construction through Metal-Free Direct Nitroalkene Sulfonation, *J. Org. Chem.*, 2018, **83**, 1772–1778.
32 G. Zhang, L. Zhang, H. Yi, Y. Luo, X. Qi, C.-H. Tung, L.-Z. Wu and A. Lei, Visible-light induced oxidant-free oxidative cross-coupling for constructing allylic sulfones from olefins and sulfinic acids, *Chem. Commun.*, 2016, **52**, 10407–10410.
33 Y. Wang, G. Xiong, C. Zhang and Y. Chen, Controllable Activation of β-Alkyl Nitroalkenes: Regioselective Synthesis of Allyl and Vinyl Sulfones, *J. Org. Chem.*, 2021, **86**, 4018–4026.
34 R. Mao, Z. Yuan, R. Zhang, Y. Ding, X. Fan and J. Wu, A copper(II)-catalyzed three-component reaction of aryldiazonium tetrafluoroborates, sulfur dioxide, with alkenes, *Org. Chem. Front.*, 2016, **3**, 1498–1502.
35 L. Kadari, R. K. Palakodety and L. P. Yallapragada, Iodine-Catalyzed Facile Approach to Sulfones Employing TosMIC as a Sulfonylating Agent, *Org. Lett.*, 2017, **19**, 2580–2583.
36 M.-Y. Chang, H.-Y. Chen and H.-S. Wang, Regiocontrolled Synthesis of α-Sulfonylmethyl *o* -Nitrostyrenes via ZnI_2-Mediated Sulfonylation and $AgNO_2$/Pd(PPh_3)$_4$-Promoted *o* -Nitration, *J. Org. Chem.*, 2017, **82**, 10601–10610.
37 X. Huang, B. Fulton, K. White and A. Bugarin, Metal-Free, Regio- and Stereoselective Synthesis of Linear (E)-Allylic Compounds Using C, N, O, and S Nucleophiles, *Org. Lett.*, 2015, **17**, 2594–2597.
38 O. S. Ojo, O. Miranda, K. C. Baumgardner and A. Bugarin, Practical regio- and stereoselective azidation and amination of terminal alkenes, *Org. Biomol. Chem.*, 2018, **16**, 9354–9358.
39 O. S. Ojo and A. Bugarin, One-Pot Synthesis of α-Alkyl Styrene Derivatives, *ACS Omega*, 2021, **6**, 20619–20628.
40 S. Liang, K. Hofman, M. Friedrich and G. Manolikakes, Recent Advances in the Synthesis and Direct Application of Sulfinate Salts, *Eur. J. Org. Chem.*, 2020, **2020**, 4664–4676.
41 A. O. Terent'ev, O. M. Mulina, D. A. Pirgach, A. I. Ilovaisky, M. A. Syroeshkin, N. I. Kapustina and G. I. Nikishin, Electrosynthesis of vinyl sulfones from alkenes and sulfonyl hydrazides mediated by KI: An electrochemical mechanistic study, *Tetrahedron*, 2017, **73**, 6871–6879.
42 T. Hirata, Y. Sasada, T. Ohtani, T. Asada, H. Kinoshita, H. Senda and K. Inomata, "Syn-Effect" in the Conversion of (E)-Vinylic Sulfones to the Corresponding Allylic Sulfones, *BCSJ*, 1992, **65**, 75–96.
43 M. Karki and J. Magolan, Bromination of Olefins with HBr and DMSO, *J. Org. Chem.*, 2015, **80**, 3701–3707.
44 L. H. Choudhury, T. Parvin and A. T. Khan, Recent advances in the application of bromodimethylsulfonium bromide (BDMS) in organic synthesis, *Tetrahedron*, 2009, **65**, 9513–9526.
45 W. Chen, S. Ni, Y. Wang and Y. Pan, Electrochemical-Promoted Nickel-Catalyzed Reductive Allylation of Aryl Halides, *Org. Lett.*, 2022, **24**, 3647–3651.

