RSC Advances

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *RSC Adv.*, 2022, **12**, 16745

Metal- and base-free tandem sulfonylation/cyclization of 1,5-dienes with aryldiazonium salts *via* the insertion of sulfur dioxide†

Xiaohong Wang,‡ Fengzhi You,‡ Baojian Xiong, Lei Chen, Xuemei Zhang*
and Zhong Lian *

Received 13th May 2022
Accepted 31st May 2022

DOI: 10.1039/d2ra03034a

rsc.li/rsc-advances

A metal- and base-free 5-*endo*-trig sulfonylative cyclization between 1,5-dienes, aryldiazonium salts and SO_2 (from SOgen) is presented. This method could successfully produce sulfonylated pyrrolin-2-ones in one pot with excellent regioselectivity and good-to-excellent yields. This strategy features mild reaction conditions and broad substrate scope. Moreover, a scale-up reaction and three synthetic applications demonstrate the practicality of this method. Lastly, control experiments indicate that the 5-*endo*-trig sulfonylative cyclization may proceed in a radical pathway.

Introduction

Pyrrolin-2-ones and their N-heterocyclic compound derivatives, widely exist in natural plants,[1] pharmaceuticals[2] and bioactive molecules.[3] Similarly, sulfonyl groups are frequently found in pharmaceuticals[4] and photoelectric materials[5] due to their unique chemical properties. Numerous studies have indicated that the incorporation of sulfonyl groups into heterocycles could enhance their pharmacological activity.[6] Therefore, great efforts have been devoted to explore efficient and straightforward methods to build sulfone-containing N-heterocyclic frameworks.

Radical cascade cyclization reactions represent a powerful strategy for the synthesis of functionalized cyclic structure, characterized by multiple C–C/C–X bond-forming in one step.[7] The incorporation of sulfonyl group into heterocycles by radical cascade cyclization reactions has aroused extensive interest among scientists.[8] In recent years, many sulfone-containing heterocyclic frameworks have been constructed by radical cascade cyclization reactions, such as sulfonylindoles,[9] sulfonylindolins,[10] sulfonylated pyrrolidines,[11] sulfonylated phenanthridines,[12] sulfonylated benzofurans,[13] sulfonated oxazolines,[14] sulfonylated spirocycles[15] and others.[16] In 2021, sulfonylated pyrrolinones were synthesized *via* sulfonylation/cyclization of 1,5-dienes with sulfonyl chlorides or sodium sulfinates by Wang and co-workers (Fig. 1a and b).[17] However, due to the limited accessibility of sulfonyl chlorides and sodium sulfinates, these two methods suffered from a narrow range of substrates. Besides, transition metal (Cu and Ag), base and elevated temperature were essential in these transformations.

On the other hand, direct insertion of sulfur dioxide (SO_2) provides an alternative and efficient approach to introduce sulfonyl moiety into molecules.[18,19] Recently, a cheap and bench-stable SO_2 surrogate (SOgen) has been developed by our group, which has been successfully applied in several sulfonylation reactions.[20] Inspired by Wang's work and our continuous

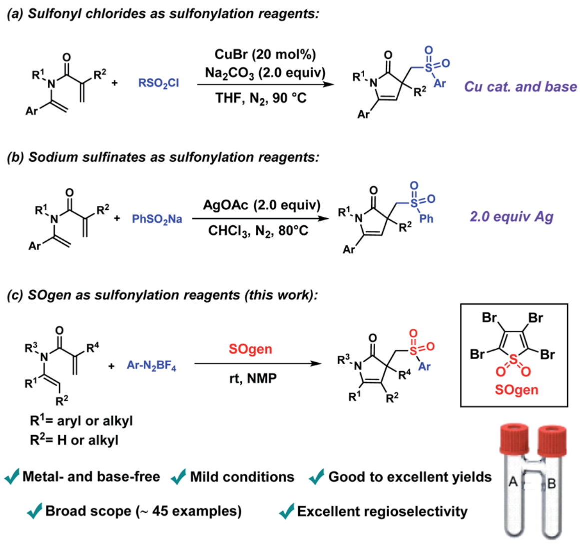


Fig. 1 Overview of tandem sulfonylative cyclization of 1,5-dienes: (a) sulfonyl chlorides as sulfonylation reagents; (b) sodium sulfinates as sulfonylation reagents; (c) SOgen as sulfonylation reagents (this work).

Department of Dermatology, State Key Laboratory of Biotherapy and Cancer Center, National Clinical Research Center for Geriatrics, West China Hospital, West China School of Pharmacy, Sichuan University, Chengdu 610041, China. E-mail: xuemeizhang@scu.edu.cn; lianzhong@scu.edu.cn

† Electronic supplementary information (ESI) available: Experimental procedures, characterization data of products, and NMR spectra, and X-ray crystallographic data. CCDC 2131001 (**3ah**). For ESI and crystallographic data in CIF or other electronic format see https://doi.org/10.1039/d2ra03034a

‡ These authors contributed equally.

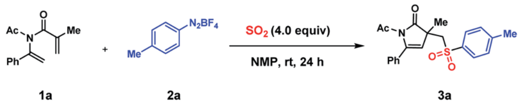
interests in SO_2 chemistry, we herein attempt to construct sulfonylated pyrrolinones using SOgen as SO_2 surrogate (Fig. 1c). This transformation features metal- and base-free conditions and could proceed smoothly at room temperature to form sulfonylated pyrrolinones with excellent regioselectivity and good to excellent yields.

Results and discussion

We started the studies by evaluating the reaction between 1,5-diene (**1a**), 4-methylbenzenediazonium tetrafluoroborate (**2a**) and SO_2 gas (from SOgen) under metal- and base-free conditions. Pleasingly, when the reaction was carried out in NMP at room temperature for 24 h, desired product **3a** was successfully obtained in 91% yield with excellent regioselectivity (Table 1, entry 1).

Then we explored the influence of other solvents on this reaction, the target product (**3a**) was not obtained in most solvents, such as THF, MeCN, DCM, toluene and MeOH (Table 1, entries 2–6). When the solvent was DMA, DMF and DMSO, **3a** was formed in only poor yields (Table 1, entries 7–9). Next, the amount of SO_2 (from 2.5 equiv. to 4.0 equiv.) was investigated, and the results indicated that 4.0 equiv. was the best choice (Table 1, entries 10–12). Although this reaction could work under an air atmosphere, argon atmosphere proved to be more beneficial for the transformation (Table 1, entry 13). Finally, other sulfur dioxide surrogates were examined. The use of DABSO and inorganic SO_2 surrogates ($Na_2S_2O_5$ and $K_2S_2O_5$) could both lead to the formation of product **3a** but with lower yields (Table 1, entries 14–16). Unfortunately, rongalite reagent ($HOCH_2SO_2Na \cdot H_2O$) would hamper the reaction (Table 1, entry 17).

Table 1 Optimization of reaction conditions[a]



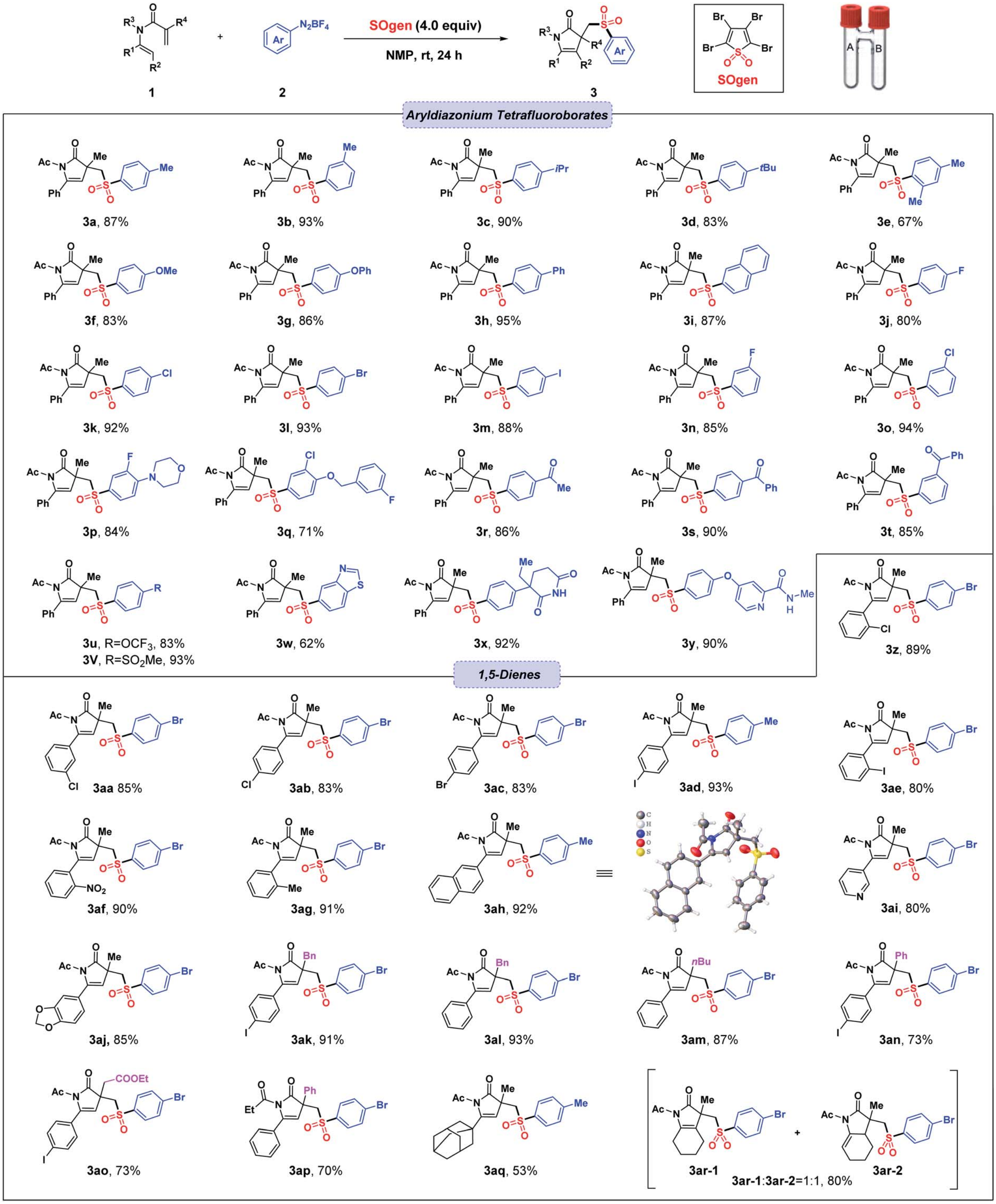
Entry	Variation from std conditions	Yield of **3a**[b] (%)
1	None	91 (87)[c]
2	THF instead of NMP	0
3	MeCN instead of NMP	0
4	DCM instead of NMP	0
5	Toluene instead of NMP	0
6	MeOH instead of NMP	0
7	DMSO instead of NMP	21
8	DMF instead of NMP	20
9	DMA instead of NMP	56
10	3.5 equiv. of SO_2	86
11	3.0 equiv. of SO_2	80
12	2.5 equiv. of SO_2	74
13	Air instead of Ar	54
14[d]	DABSO as SO_2 surrogate	71
15[d]	$Na_2S_2O_5$ as SO_2 surrogate	53
16[d]	$K_2S_2O_5$ as SO_2 surrogate	52
17[d]	$HOCH_2SO_2Na \cdot H_2O$ as SO_2 surrogate	0

[a] Standard conditions: chamber A, SOgen (0.80 mmol), 1-methyl-4-vinylbenzene (0.81 mmol), tetradecane (1.0 mL), at 100 °C for 10 min; chamber B, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.44 mmol, 2.2 equiv.), NMP (1.0 mL), at room temperature for 24 h under argon atmosphere. [b] Yields were determined by ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield in the parentheses. [d] The reaction was set up in a 4 mL vial.

After determining the optimal reaction conditions, we began to explore the substrate scope of this reaction, and the results are summarized in Scheme 1. We first investigated the functional group compatibility of aryldiazonium tetrafluoroborates in the transformation. Alkyl substituted aryldiazonium tetrafluoroborates at the *meta*- or *para*-position of the phenyl ring proceeded well and afforded corresponding products **3b–3d** in good yields (83–93%). While a methyl substituent at the *ortho*-position could lead to a lower yield (67%, **3e**), possibly due to the steric hindrance. In addition, substrates with methoxy or phenoxy group delivered desired products **3f** and **3g** in 83% and 86% yield, respectively. Substrates bearing a biphenyl or 2-naphthyl group showed good reactivity, producing expected products (**3h** and **3i**) in excellent yields. Notably, halogen groups were found to be well tolerated under the standard conditions (**3j–3q**). Moreover, substrates with electron-withdrawing groups such as MeCO–, PhCO–, CF_3O–, $MeSO_2$– were subject to the reaction conditions, and gave corresponding products (**3r–3v**) in good yields. In addition, heterocyclic diazonium salt was found to be compatible in the transformation (**3w**). Finally, aryldiazonium tetrafluoroborates with complicated substituent structures could also work smoothly to afford **3x** and **3y** in 92% and 90% yield, respectively.

Next, the substrate scope of 1,5-dienes was investigated. The results showed that halogen groups (–Cl, –Br and –I) on 1,5-dienes had little effect on the reaction, and the corresponding products **3z–3ae** were formed in 80–93% yields. Notably, 1,5-diene with a strongly electron-withdrawing group (–NO_2) could deliver desired products **3af** in an excellent yield (90%). Meanwhile, the one with an electron-donating group (–Me) could also give products **3ag** in a similar yield (91%). Naphthalene ring was well tolerated, achieving **3ah** in 92% yield and the configuration of compound **3ah** was confirmed by X-ray crystallography. Pyridine moiety was also adapted to the reaction conditions and generated **3ai** in 80% yield. In addition, it was found that benzodioxole moiety (**3aj**) could be well tolerated under the standard conditions. When R^4 group was replaced by other substituents, such as benzyl, phenyl, *n*-butyl and –CH_2COOEt, desired products (**3ak–3ap**) could still be made in good-to-excellent yields. When R^1 group was alkyl, the sulfonylation reaction could still proceed, demonstrated by two successful examples (**3aq** and **3ar**). It was worth noting that compound **3ar** contained two isomers (**3ar-1** : **3ar-1** = 1 : 1).

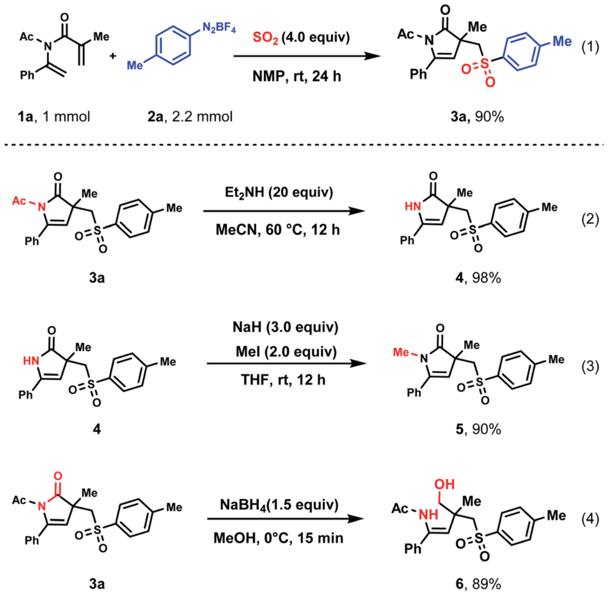
The practicality of this methodology was successfully illustrated by the production of **3a** with 90% yield in a scale-up reaction (Scheme 2(1)). To further demonstrate the synthetic utility of this method, **3a** was then applied in subsequent transformations. In the presence of diethylamine, the acetyl group on the nitrogen atom could be easily removed in a quantitative yield (Scheme 2(2)). Then, different substituents could be introduced on the N atom. For example, N–H could be



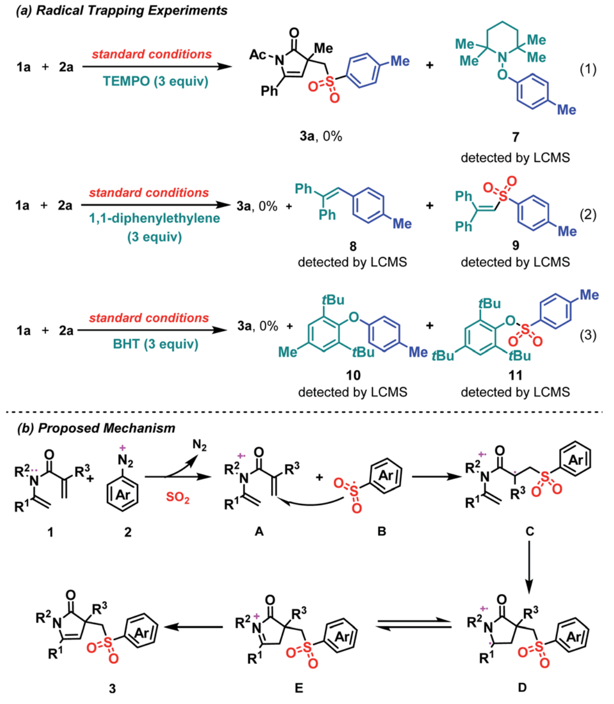
Scheme 1 Substrate scope[a]. [a]Reaction conditions: chamber A, SOgen (0.80 mmol), 1-methyl-4-vinylbenzene (0.81 mmol), tetradecane (1.0 mL), at 100 °C for 10 min; chamber B, **1** (0.2 mmol, 1.0 equiv.), **2** (0.44 mmol, 2.2 equiv.), NMP (1.0 mL), at rt for 24 h under argon atmosphere. All yields are isolated yields.

transferred to N–Me (**5**) in 90% yield in a mixture of sodium hydride and iodomethane (Scheme 2(3)). In addition, the amide moiety of **3a** could be reduced to hydroxy amine (**6**) *via* ring-opening by $NaBH_4$ in excellent yield (Scheme 2(4)).

In order to understand the mechanism of this reaction, three control experiments with radical scavengers were carried out. Firstly, in the presence of radical scavenger (TEMPO), the desired product (**3a**) was totally quenched and TEMPO adduct **7**



Scheme 2 Scale-up reaction and synthetic applications.



Scheme 3 (a) Control experiments and (b) proposed mechanism.

was identified by LC-MS (Scheme 3a(1)). Secondly, when 1,1-diphenylethylene or BHT was added, the reaction showed similar result and corresponding aryl radicals adduct (**8** or **10**) sulfonyl radicals adduct (**9** or **11**) were identified, respectively (Scheme 3(2) and (3)). These results indicated that this transformation might proceed through a radical pathway.

Base on the control experiments and literature,[20c] a plausible reaction mechanism is proposed herein (Scheme 3b). One of lone-pair electrons on the N atom of 1,5-diene is transferred to aryldiazonium tetrafluoroborate, which leads to the formation of nitrogen radical cation species (**A**) and aryl radical. Then aryl radical is trapped by sulfur dioxide and gives aryl sulfone radical (**B**). Sulfonyl radical **B** selectively adds to the double bond of 1,5-diene and produces alkyl radical species **C**. Subsequently, intramolecular 5-*endo*-trig cyclization produces intermediate **D**, which has an equilibrium with **E**. Finally, the desired product (**3**) is produced *via* tautomerization from **E**.

Conclusions

In conclusion, a metal- and base-free sulfonylative cyclization of 1,5-dienes with aryldiazonium salts *via* the insertion of SO_2 (from SOgen) has been developed. This method can work under mild conditions and provide the desired products in good yields with excellent regioselectivity. In addition, this approach greatly expands the substrates scope compared with previous reported work. Preliminary mechanism studies indicate that this 5-*endo*-trig sulfonylative cyclization may proceed in a radical pathway.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by National Natural Science Foundation of China (21901168), "1000-Youth Talents Plan", Sichuan Science and Technology Program (2021YJ0395) and "1.3.5 Project for Disciplines of Excellence, West China Hospital, Sichuan University". We also thank Jing Li from the Comprehensive Training Platform of Specialized Laboratory in College of Chemistry at Sichuan University for sample analysis.

Notes and references

1 For selected examples, see: (*a*) N. Dev, A. K. Das, M. A. Hossain and S. M. M. Rahman, Chemical Compositions of Different Extracts of Ocimum Basilicum Leaves, *J. Sci. Res.*, 2011, **3**, 197–206; (*b*) S. Chu, S. Liu, W. Duan, Y. Cheng, X. Jiang, C. Zhu, K. Tang, R. Wang, L. Xu, X. Wang, X. Yu, K. Wu, Y. Wang, M. Wang, H. Huang and J. Zhang, The Anti-Dementia Drug Candidate, (−)-Clausenamide, Improves Memory Impairment Through Its Multi-target Effect, *Pharmacol. Ther.*, 2016, **162**, 179–187.

2 For selected examples, see: (*a*) R. Kontnik and J. Clardy, Codinaeopsin, an Antimalarial Fungal Polyketide, *Org. Lett.*, 2008, **10**, 4149–4151; (*b*) S. Castellano, H. D. G. S. Fiji, S. S. Kinderman, M. Watanabe, P. deLeon, F. Tamanoi and O. Kwon, Small-Molecule Inhibitors of Protein Geranylgeranyltransferase Type I, *J. Am. Chem. Soc.*, 2007, **129**, 5843–5845.

3 For selected examples, see: (*a*) S. S. Ariya, J. Baby, V. Santhanam and H. Waheeta, Computational Analysis of Compounds form Ocimum Sanctum for Anticancer Activity Against Oral Squamous Cell Carcinoma, *Asian J. Pharm.*

Clin. Res., 2019, **12**, 168–172; (*b*) V. R. Macherla, S. S. Mitchell, R. R. Manam, K. A. Reed, T. H. Chao, B. Nicholson, G. Deyanat-Yazdi, B. Mai, P. R. Jensen, W. F. Fenical, S. T. C. Neuteboom, K. S. Lam, M. A. Palladino and B. C. M. Potts, Structure–Activity Relationship Studies of Salinosporamide A (NPI-0052), a Novel Marine Derived Proteasome Inhibitor, *J. Med. Chem.*, 2005, **48**, 3684–3687.

4 For selected examples, see: (*a*) A. Guerrini, A. Tesei, C. Ferroni, G. Paganelli, A. Zamagni, S. Carloni, M. D. Donato, G. Castoria, C. Leonetti, M. Porru, M. De Cesare, N. Zaffaroni, G. Luca Beretta, A. Del Rio and G. Varchi, A New Avenue toward Androgen Receptor Pan-antagonists: C_2 Sterically Hindered Substitution of Hydroxy-propanamides, *J. Med. Chem.*, 2014, **57**, 7263–7279; (*b*) K. G. Liu, A. J. Robichaud, R. C. Bernotas, Y. Yan, J. R. Lo, M. Y. Zhang, Z. A. Hughes, C. Huselton, G. M. Zhang, J. Y. Zhang, D. M. Kowal, D. L. Smith, L. E. Schechter and T. A. Comery, 5-Piperazinyl-3-Sulfonylindazoles as Potent and Selective 5-Hydroxytryptamine-6 Antagonists, *J. Med. Chem.*, 2010, **53**, 7639–7646.

5 (*a*) A. Ulman, C. S. Willand, W. Kohler, D. R. Robello, D. J. Williams and L. Handley, New Sulfonyl-containing Materials for Nonlinear Optics: Semiempirical Calculations, Synthesis, and Properties, *J. Am. Chem. Soc.*, 1990, **112**, 7083–7090; (*b*) Y. Huang, L. j. Huo, S. Q. Zhang, X. Guo, C. C. Han, Y. F. Li and J. H. Hou, Sulfonyl: a New Application of Electron-Withdrawing Substituent in Highly Efficient Photovoltaic Polymer, *Chem. Commun.*, 2011, **47**, 8904–906.

6 For selected examples, see: (*a*) W. Grell, R. Hurnaus, G. Griss, R. Sauter, E. Rupprecht, M. Mark, P. Luger, H. Nar, H. Wittneben and P. Müller, Repaglinide and Related Hypoglycemic Benzoic Acid Derivatives, *J. Med. Chem.*, 1998, **41**, 5219–5246; (*b*) T. Uchida, K. Hayashi, H. Kido and M. Watanabe, Diuretic Action of the Novel Loop Diuretic Torasemide in the Presence of Angiotensin II or Endothelin-1 in Anaesthetized Dogs, *J. Pharm. Pharmacol.*, 2011, **44**, 39–43.

7 For selected examples, see: (*a*) N. Fuentes, W. Kong, L. Fernandez-Sanchez, E. Merino and C. Nevado, Cyclization Cascades *via* N-Amidyl Radicals toward Highly Functionalized Heterocyclic Scaffolds, *J. Am. Chem. Soc.*, 2015, **137**, 964–973; (*b*) J. Xuan and A. Studer, Radical Cascade Cyclization of 1,n-enynes and Diynes for the Synthesis of Carbocycles and Heterocycles, *Chem. Soc. Rev.*, 2017, **46**, 4329–4346; (*c*) H. M. Huang, J. J. W. McDouall and D. J. Procter, SmI_2-catalysed cyclization cascades by radical relay, *Nat. Catal.*, 2019, **2**, 211–218; (*d*) C. Z. Zhang, D. S. Wang, W. C. C. Lee, A. M. McKillop and X. P. Zhang, Controlling Enantioselectivity and Diastereoselectivity in Radical Cascade Cyclization for Construction of Bicyclic Structures, *J. Am. Chem. Soc.*, 2021, **143**, 11130–11140; (*e*) Y. Liu, J. L. Zhang, R. J. Song, P. C. Qian and J. H. Li, Cascade Nitration/Cyclization of 1,7-Enynes with *t*BuONO and H_2O: One-Pot Self-Assembly of Pyrrolo[4,3,2-de] quinolinones, *Angew. Chem., Int. Ed.*, 2014, **53**, 9017–9022.

8 For selected examples, see: (*a*) W. T. Wei, M. B. Zhou, J. H. Fan, W. Liu, R. J. Song, Y. Liu, M. Hu, P. Xie and J. H. Li, Synthesis of Oxindoles by Iron-Catalyzed Oxidative 1,2-Alkylarylation of Activated Alkenes with an Aryl C(sp^2)–H Bond and a C(sp^3)–H Bond Adjacent to a Heteroatom, *Angew. Chem., Int. Ed.*, 2013, **52**, 1–5; (*b*) N. Fuentes, W. Kong, L. Fernandez-Sanchez, E. Merino and C. Nevado, Cyclization Cascades *via* N-Amidyl Radicals toward Highly Functionalized Heterocyclic Scaffolds, *J. Am. Chem. Soc.*, 2015, **137**, 964–973; (*c*) M. Hu, R. J. Song and J. H. Li, Metal-Free Radical 5-*exo*-dig Cyclizations of Phenol-Linked 1,6-Enynes for the Synthesis of Carbonylated Benzofurans, *Angew. Chem., Int. Ed.*, 2014, **53**, 608–613; (*d*) Z. Z. Chen, S. Liu, W. J. Hao, G. Xu, S. Wu, J. N. Miao, B. Jiang, S. L. Wang, S. J. Tu and G. Li, Catalytic Arylsulfonyl Radical-Triggered 1,5-Enyne-Bicyclizations and Hydrosulfonylation of *α,ß*-Conjugates, *Chem. Sci.*, 2015, **6**, 6654–6658; (*e*) B. Huang, L. Zeng, Y. Shen and S. Cui, Nickel-Catalyzed Acetamidation and Lactamization of Arylboronic Acids, *Chem. Commun.*, 2017, **53**, 11996–11999; (*f*) C. Z. Zhang, D. S. Wang, W. C. Cindy Lee, A. M. McKillop and X. P. Zhang, Controlling Enantioselectivity and Diastereoselectivity in Radical Cascade Cyclization for Construction of Bicyclic Structures, *J. Am. Chem. Soc.*, 2021, **143**, 11130–11140; (*g*) D. M. Zeng, M. Wang, W. P. Deng and X. F. Jiang, The Same Oxygenation-State Introduction of Hypervalent Sulfur under Transition-metal-free Conditions, *Org. Chem. Front.*, 2020, **7**, 3956–3966.

9 H. J. Chen, M. L. Liu, G. Y. S. Qiu and J. Wu, A Three-Component Reaction of Aryldiazonium Tetrafluoroborates, Sulfur Dioxide, and 1-(Prop-2-yn-1-yl)Indoles under Catalyst-Free Conditions, *Adv. Synth. Catal.*, 2019, **361**, 146–150.

10 T. Liu, D. Q. Zheng and J. Wu, Synthesis of 3-((Arylsulfonyl) methyl)Indolin-2-Ones *via* Insertion of Sulfur Dioxide using Anilines as the Aryl Source, *Org. Chem. Front.*, 2017, **4**, 1079–1083.

11 L. Zheng, Z. Z. Zhou, Y. T. He, L. H. Li, J. W. Ma, Y. F. Qiu, P. X. Zhou, X. Y. Liu, P. F. Xu and Y. M. Liang, Iodine-Promoted Radical Cyclization in Water: A Selective Reaction of 1,6-Enynes with Sulfonyl Hydrazides, *J. Org. Chem.*, 2016, **81**, 66–76.

12 X. F. Wang, Y. W. Li, G. Y. S. Qiu and J. Wu, Synthesis of 6-(Sulfonylmethyl)Phenanthridines through a Reaction of Aryldiazonium Tetrafluoroborates, Sulfur Dioxide, and Vinyl Azides, *Org. Chem. Front.*, 2018, **5**, 2555–2559.

13 J. Xu, X. Yu, J. Yan and Q. Song, Synthesis of 3-(Arylsulfonyl) benzothiophenes and Benzoselenophenes *via* TBHP-Initiated Radical Cyclization of 2-Alkynylthioanisoles or -selenoanisoles with Sulfinic Acid, *Org. Lett.*, 2017, **19**, 6292–6295.

14 Z. C. Chen, H. Zhang, S. F. Zhou and X. L. Cui, Photoredox-Catalyzed Synthesis of Sulfonated Oxazolines from N-

allylamides through the Insertion of Sulfur Dioxide, *Org. Chem. Front.*, 2022, **9**, 364–369.

15 W. Dong, L. Qi, J. Y. Song, J. M. Chen, J. X. Guo, S. Shen, L. J. Li, W. Li and L. J. Wang, Direct Synthesis of Sulfonylated Spiro[indole-3,3'-pyrrolidines] by Silver-Mediated Sulfonylation of Acrylamides Coupled with Indole Dearomatization, *Org. Lett.*, 2020, **22**, 1830–1835.

16 (*a*) Z. C. Chen, H. Zhang, S. F. Zhou and X. L. Cui, $K_2S_2O_8$-Initiated Cascade Cyclization of 2-Alkynylnitriles with Sodium Sulfinates: Access to Fused Cyclopenta[gh] phenanthridines, *Chin. J. Org. Chem.*, 2020, **40**, 3866–3872; (*b*) Z. Cao, Q. Zhu, Y. W. Lin and W. M. He, The Concept of Dual Roles Design in Clean Organic Preparation, *Chin. Chem. Lett.*, 2019, **30**, 2132–2144; (*c*) K. D. Zhou, J. Zhang, G. Y. S. Qiu and J. Wu, Copper(II)-Catalyzed Reaction of 2,3-Allenoic Acids, Sulfur Dioxide, and Aryldiazonium Tetrafluoroborates: Route to 4-Sulfonylated Furan-2(5H)-ones, *Org. Lett.*, 2019, **21**, 275–278; (*d*) F. Herrera, P. Esteban, A. Luna and P. Almendros, Metal-Catalyzed Reactivity Reversal in the Sulfonylation Reaction of α-Allenols: Controlled Synthesis of 4-(Arylsulfonyl)-2,5-Dihydrofurans, *Adv. Synth. Catal.*, 2021, **363**, 3952–3956.

17 (*a*) R. Ding, M. H. Mao, W. Z. Jia, J. M. Fu, L. Liu, Y. Y. Mao, Y. Guo and P. L. Wang, Synthesis of Sulfonylated Pyrrolines and Pyrrolinones *via* Ag-Mediated Radical Cyclization of Olefinic Enamides with Sodium Sulfinates, *Asian J. Org. Chem.*, 2021, **10**, 366–370; (*b*) R. Ding, Y. L. Liu, H. Hao, C. Y. Chen, L. Liu, N. S. Chen, Y. Guo and P. L. Wang, Regioselective, Copper(I)-Catalyzed, Tandem Sulfonylation-Cyclization of 1,5-Dienes with Sulfonyl Chlorides, *Org. Chem. Front.*, 2021, **8**, 3123–3127.

18 For selected reviews, see: (*a*) E. J. Emmett and M. C. Willis, The Development and Application of Sulfur Dioxide Surrogates in Synthetic Organic Chemistry, *Asian J. Org. Chem.*, 2015, **4**, 602–611; (*b*) G. S. Qiu, K. D. Zhou, L. Gao and J. Wu, Insertion of Sulfur Dioxide Via a Radical Process: An Efficient Route to Sulfonyl Compounds, *Org. Chem. Front.*, 2018, **5**, 691–705; (*c*) K. Hofman, N. W. Liu and G. Manolikakes, Radicals and Sulfur Dioxide: A Versatile Combination for the Construction of Sulfonyl-Containing Molecules, *Chem.–Eur. J.*, 2018, **24**, 11852–11863; (*d*) D. Joseph, M. A. Idris, J. Chen and S. Lee, Recent Advances in the Catalytic Synthesis of Arylsulfonyl Compounds, *ACS Catal.*, 2021, **11**, 4169–4204.

19 For selected examples, see: (*a*) D. Q. Zheng, Y. Y. An, Z. H. Li and J. Wu, Metal-Free Aminosulfonylation of Aryldiazonium Tetrafluoroborates with $DABCO\cdot(SO_2)_2$ and Hydrazines, *Angew. Chem., Int. Ed.*, 2014, **53**, 2451–2454; (*b*) B. Nguyen, E. J. Emmett and M. C. Willis, Palladium-Catalyzed Aminosulfonylation of Aryl Halides, *J. Am. Chem. Soc.*, 2010, **132**, 16372–16373; (*c*) Y. Meng, M. Wang and X. Jiang, Multicomponent Reductive Cross-Coupling of an Inorganic Sulfur Dioxide Surrogate: Straightforward Construction of Diversely Functionalized Sulfones, *Angew. Chem., Int. Ed.*, 2020, **59**, 1346–1353; (*d*) W. Li, H. Li, P. Langer, M. Beller and X. F. Wu, Palladium-Catalyzed Aminosulfonylation of Aryl Iodides by using Na_2SO_3 as the SO_2 Source, *Eur. J. Org. Chem.*, 2014, 3101–3103; (*e*) H. B. Zhu, Y. J. Shen, D. H. Wen, Z. G. Le and T. Tu, Selective Synthesis of *ortho*-Substituted Diarylsulfones by Using NHC-Au Catalysts under Mild Conditions, *Org. Lett.*, 2019, **21**, 974–979; (*f*) Y. Wang, L. L. Deng, J. Zhou, X. C. Wang, H. B. Mei, J. L. Han and Y. Pan, Synthesis of Chiral Sulfonyl Lactones via Copper-Catalyzed Asymmetric Radical Reaction of $DABCO\cdot(SO_2)$, *Adv. Synth. Catal.*, 2018, **360**, 1060–1065; (*g*) A. Shavnya, K. D. Hesp, V. Mascitti and A. C. Smith, Palladium-Catalyzed Synthesis of (Hetero)Aryl Alkyl Sulfones from (Hetero)Aryl Boronic Acids, Unactivated Alkyl Halides, and Potassium Metabisulfite, *Angew. Chem., Int. Ed.*, 2015, **54**, 13571–13575; (*h*) N. von Wolff, J. Char, X. Frogneux and T. Cantat, Synthesis of Aromatic Sulfones from SO_2 and Organosilanes Under Metal-free Conditions, *Angew. Chem., Int. Ed.*, 2017, **56**, 5616–5619.

20 (*a*) X. W. Jia, S. Kramer, T. Skrydstrup and Z. Lian, Design and Applications of a SO_2 Surrogate in Palladium-Catalyzed Direct Aminosulfonylation between Aryl Iodides and Amines, *Angew. Chem., Int. Ed.*, 2021, **60**, 7353–7359; (*b*) Y. Li, L. Shen, M. Zhou, B. J. Xiong, X. M. Zhang and Z. Lian, Copper-Catalyzed Chloro-Arylsulfonylation of Styrene Derivatives *via* the Insertion of Sulfur Dioxide, *Org. Lett.*, 2021, **23**, 5880–5884; (*c*) L. Chen, M. Zhou, L. Shen, X. C. He, X. Li, X. M. Zhang and Z. Lian, Metal- and Base-Free $C(sp^2)$–H Arylsulfonylation of Enamides for Synthesis of (*E*)-*ß*-Amidovinyl Sulfones *via* the Insertion of Sulfur Dioxide, *Org. Lett.*, 2021, **23**, 4991–4996; (*d*) G. Chen, J. Xu, B. J. Xiong, H. Z. Song, X. M. Zhang, X. L. Ma and Z. Lian, Copper-Catalyzed Trifluoromethylthio-arylsulfonylation of Styrene Derivatives *via* the Insertion of Sulfur Dioxide, *Org. Lett.*, 2022, **24**(5), 1207–1212; (*e*) X. W. Jia, C. X. Huang, X. M. Zhang and Z. Lian, Metal-free Sulfonylative Annulations of Alkyl Diiodides with Sulfur Dioxide: Synthesis of Cyclic Aliphatic Sulfones, *Org. Chem. Front.*, 2021, **8**, 5310–5315.