Green Chemistry

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2025, **27**, 3627

Received 6th January 2025,
Accepted 1st March 2025

DOI: 10.1039/d5gc00057b

rsc.li/greenchem

CO_2-Promoted photoredox-catalyzed hydrosulfonylation of alkenes with sulfinates†

Wanhui Huang,[a,b] Ge Liu,[b,c] Fangyuanhang Yang,[b] Yuxi Ren,[b] Yuzhen Gao *[a,b,c] and Weiping Su *[a,b,c]

Herein, we report a CO_2-promoted strategy for the photoredox-catalyzed hydrosulfonylation of alkenes with sulfinates under metal-, acid-, and exogenous reagent-free conditions. This method was compatible with a wide range of functional groups, including complex drug derivatives, making it a versatile and straightforward approach for synthesizing valuable sulfonyl compounds. Notably, CO_2, which is an environmentally friendly additive, played an essential role in achieving the products, demonstrating a novel role of CO_2 in sulfonylation reactions.

Green foundation

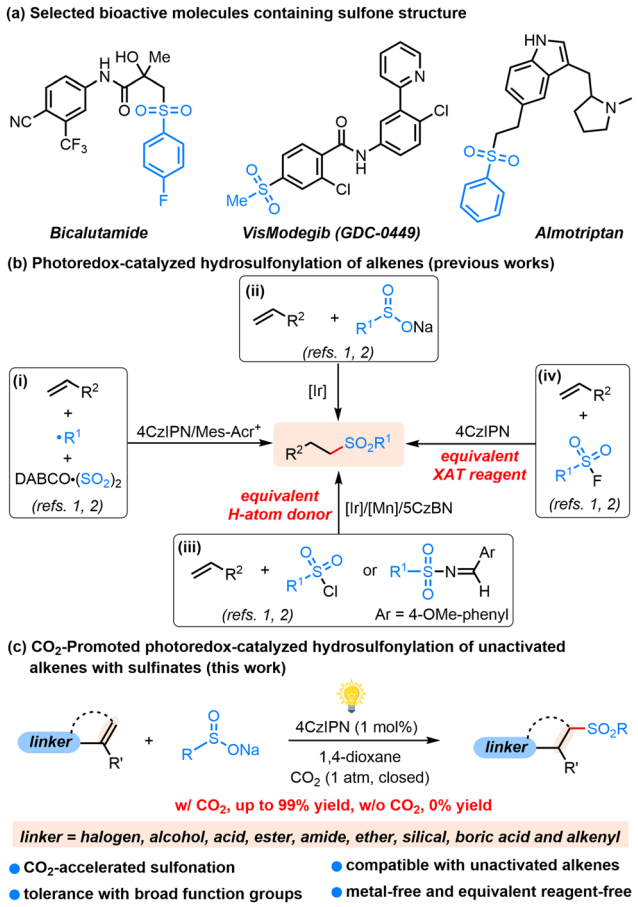
1. Carbon dioxide (CO_2) is a non-toxic, naturally abundant, stable and low-cost chemical. We demonstrated an approach for the synthesis of highly valuable sulfonyl compounds *via* CO_2-promoted photoredox-catalyzed reactions of alkenes with sodium sulfinates. This method employed low-cost reagents that are readily available and proceeded under metal-, acid- and additional reagent-free conditions. This transformation was significantly influenced by CO_2 as no target product was observed when the reaction occurred in the absence of CO_2, highlighting the essential role of CO_2 in this transformation.
2. CO_2 is usually used as a versatile C1 synthon for synthesizing valuable chemicals in organic synthesis. Besides, CO_2 has proven its remarkable ability to determine the selectivity and reactivity of certain reactions. We presented a "green" concept using CO_2 as an essential additive and low-cost reagents that are readily available, and the reaction proceeded under metal-, acid- and additional reagent-free conditions.
3. Unactivated alkenes with a broad range of functional groups (such as hydroxyl, carboxyl, ester, acylamino, ether, silicyl, boryl, terminal halogen, and alkenyl), electron-deficient styrenes, and complex drug derivatives were found to be compatible with the reaction, which will benefit organic chemists to synthesize pharmaceuticals and natural products containing sulfonyl scaffolds and other specific functional groups.

Organosulfonyl compounds exhibit excellent biological activities and distinct chemical properties, making them extensively utilized in medicine, agriculture, and materials science.[1] Compounds with C–sulfonyl bonds are particularly prevalent in drugs and natural products and exhibit antibacterial, anti-inflammatory, antiviral, and anticancer properties (Scheme 1a).[1] Consequently, incorporating sulfonyl groups into small molecules is an attractive strategy for drug molecule modifications. Additionally, organosulfonyl compounds can serve as versatile intermediates in organic synthesis to facilitate novel organic transformations.[2] Therefore, efficient synthesis of organosulfonyl compounds is of great interest to chemists. Traditional methods for constructing C–sulfonyl bonds, such as sulfonylation with highly reactive nucleophilic reagents[3] and Friedel–Crafts-type reactions with sulfonyl halides,[4] often require pre-installation of leaving groups, use of strong acids or oxidants and high temperature, which pose challenges related to regioselectivity and functional group compatibility. As a result, developing environmentally friendly and practical methods to synthesize organosulfonyl compounds has become a research hotspot in the fields of organic synthesis and medicinal chemistry.

In organic synthesis, olefin is one of the most abundant and easily accessible feedstock chemicals. Consequently,

[a]*College of Chemistry & Materials Science, Fujian Normal University, Fuzhou 350007, P. R. China*
[b]*State Key Laboratory of Structural Chemistry, Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian College, University of Chinese Academy of Sciences, Fuzhou, 350002, P. R. China. E-mail: gyz@fjirsm.ac.cn, wpsu@fjirsm.ac.cn*
[c]*University of Chinese Academy of Sciences, Beijing, 100049, China*

†Electronic supplementary information (ESI) available. CCDC 2367386 and 2367416. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d5gc00057b



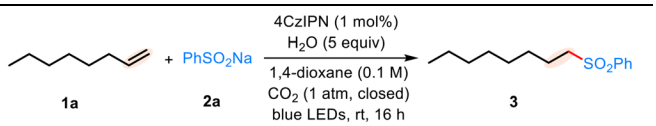
Scheme 1 (a) Selected bioactive molecules containing sulfone structure. (b) and (c) Photoredox-catalyzed hydrosulfonylation of alkenes.

photo-catalyzed reactions involving olefins and sulfonyl radicals generated from various sulfonyl reagents have emerged as a significant alternative, providing a concise approach for direct sulfonylation to obtain highly valuable sulfonyl compounds.[5–11] In 2018, Wu's group achieved photo-induced hydrosulfonylation of alkenes by generating sulfonyl radicals using [DABCO·$(SO_2)_2$] (an equivalent SO_2 surrogate) with a radical precursor (Scheme 1b, i).[7] However, this multicomponent hydrosulfonylation method was only compatible with electron-deficient alkenes. Alternatively, photoredox hydrosulfonylation of alkenes using sulfinates as the radical sources provides a straightforward method to synthesize organosulfonyl compounds (Scheme 1b, ii); however, a noble metal [Ir] and/or excess acid is essential as the catalytic system of this reaction.[8] As an important alternative to radical sulfonylation, photoredox-catalyzed hydrosulfonylation of alkenes *via* hydrogen-atom transfer (HAT)[9] (Scheme 1b, iii) or halogen-atom transfer (XAT)[10] (Scheme 1b, iv) mechanisms using sulfonyl halides[9a–c,10] or sulfonamides[9d] has also been reported. Notably, an equivalent H-atom donor reagent or XAT reagent is essential for the successful implementation of these transformations. Reactions *via* an electron donor–acceptor (EDA) pathway without an external photocatalyst have also been demonstrated as efficient protocols for hydrosulfonylation,[11] in which a photochemically active EDA complex is generally required. Despite these significant progresses, a general and facile procedure for photoredox radical hydrosulfonylation of alkenes to prepare sulfonyl compounds under metal-, acid- and additional reagent-free conditions is still not achieved.

Carbon dioxide (CO_2), which is a non-toxic, naturally abundant, stable and low-cost chemical, can be used as a versatile C1 synthon for synthesizing valuable chemicals in organic synthesis.[12,13] Beyond its potential to get converted into value-added products, CO_2 has proven its remarkable ability to determine the selectivity and reactivity of certain reactions.[14,15] Consequently, in recent years, CO_2-promoted reactions are regarded representatives of sustainable approaches and green catalytic chemistry, which is a prosperously developing concept in organic synthesis and has attracted wide attention.

Herein, we demonstrated an approach for the synthesis of highly valuable sulfonyl compounds *via* a CO_2-promoted photoredox-catalyzed reaction of alkenes with sodium sulfinates (Scheme 1c). This method employed low-cost reagents that are readily available and proceeded under metal-, acid- and additional reagent-free conditions. Notably, unactivated alkenes with a broad range of functional groups, electron-deficient styrenes, and complex drug derivatives were compatible with the reaction. As a result, this approach provides a general and straightforward procedure for the synthesis of highly valuable sulfonyl compounds. Notably, consistent with our previous reports,[1] this transformation was significantly influenced by CO_2 as no target product was observed when the reaction occurred in the absence of CO_2, highlighting the essential role of CO_2 in sulfonyl radical-involved reactions.

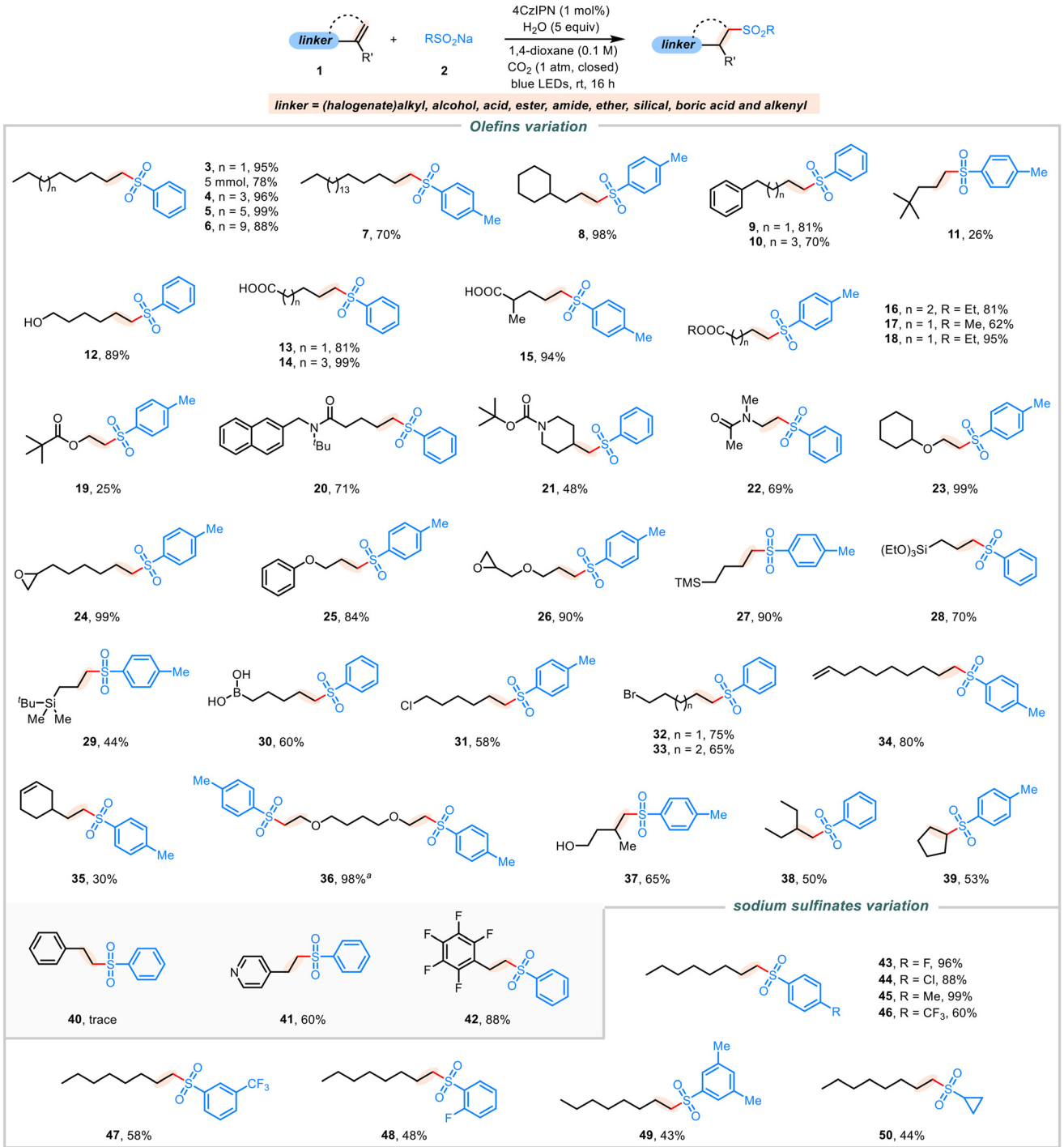
Table 1 Optimization of reaction conditions[a]



Entry	Deviation from standard conditions	Yield (%)
1	None (standard conditions)	99 (95)[b]
2	Under N_2 atmosphere	0
3	w/o 4CzIPN	0
4	w/o light	0
5	w/o H_2O	21
6	$Ir(ppy)_2(dtbbpy)\cdot PF_6$ as PC	20
7	$Ru(bpy)_3Cl_2$ as PC	42
8	Eosin Y as PC	0
9	CH_3CN as solvent	13
10	DMF as solvent	0
11	MeOH as solvent	0
12	DMSO as solvent	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv.), 4CzIPN (1 mol%), H_2O (5.0 equiv.), 1,4-dioxane (2 mL, 0.1 M), CO_2 (1 atm, closed), 5 W × 8 blue LEDs, rt, 16 h. Yield was determined using ^1H NMR with $CHCl_2CHCl_2$ as the internal standard. [b] Yield of isolated product shown in parentheses. 4CzIPN: 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile; ppy: 2-phenylpyridine; dtbbpy: 4,4-di-*tert*-butyl-2,2′-bipyridine; bpy: 2,2′-bipyridine.

For our investigation, commercially available oct-1-ene (**1a**) and sodium benzenesulfinate (**2a**) were chosen as model substrates. As shown in Table 1, the desired sulfonated product **3a** was isolated in 95% yield when the reaction was performed under a CO_2 atmosphere and catalyzed by 4CzIPN after irradiation using blue LEDs at room temperature (entry 1). Interestingly, the transformation was totally restrained when the reaction was conducted under N_2 atmosphere, and most of the substrates remained unreacted, indicating the essential role of CO_2 in this reaction (entry 2). Subsequently, control experiments were conducted, and results revealed that both light and photocatalyst (PC) were vital for this transformation (entries 3 and 4), suggesting that the reaction is light-facilitated. A low yield of **3a** was afforded when the reaction was



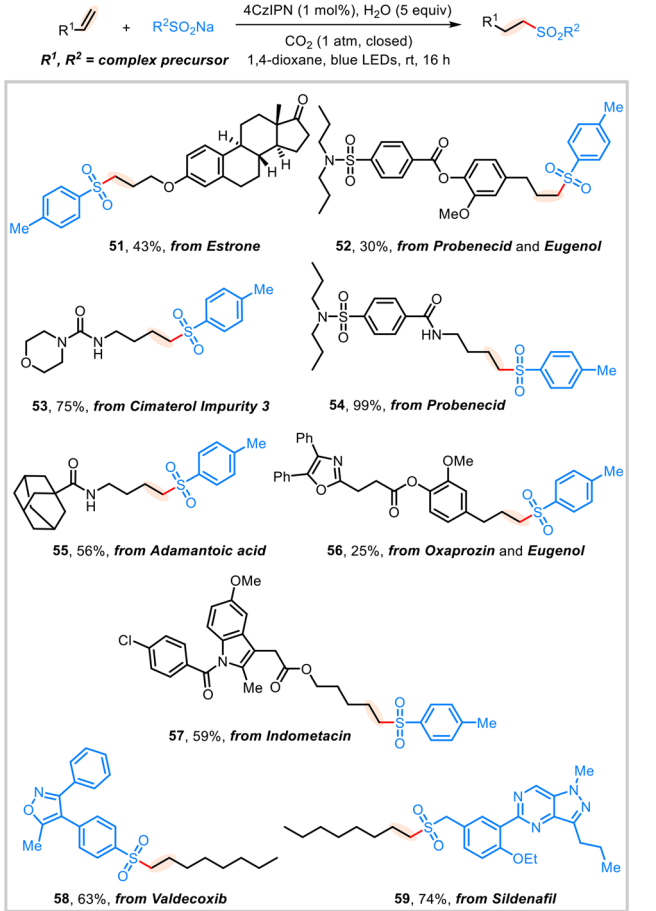
Scheme 2 Substrate scope. Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.), 4CzIPN (1 mol%), H_2O (5.0 equiv.), 1,4-dioxane (2 mL, 0.1 M), CO_2 (1 atm, closed), 5 W × 8 blue LEDs, rt, 16 h, isolated yields. [a] Sodium 4-methylbenzenesulfinate (0.5 mmol, 2.5 equiv.).

carried out in the absence of H_2O (entry 5), demonstrating that H_2O likely acted as the proton source. Notably, residual crystalline water in substrate **2a** might have served as the proton source in this water-free system. Other PCs, such as Ir(ppy)$_2$(dtbbpy)·PF$_6$, Ru(bpy)$_3$Cl$_2$ and Eosin Y, were also tested, and all of them were inferior to 4CzIPN (entries 6–8). After solvent screening, it was found that the choice of solvent played a crucial role in the success of this reaction because the target product **3a** could not be obtained or the yield was very low when the reaction was conducted in other solvents, such as CH_3CN, DMF, MeOH and DMSO (entries 9–12). This might be attributed to the poor water solubility in other solvents (*vs.* 1,4-dioxane), limiting efficient protonation, and/or the insufficient redox capability of the excited PCs in other solvents, reducing the single-electron transfer efficiency.

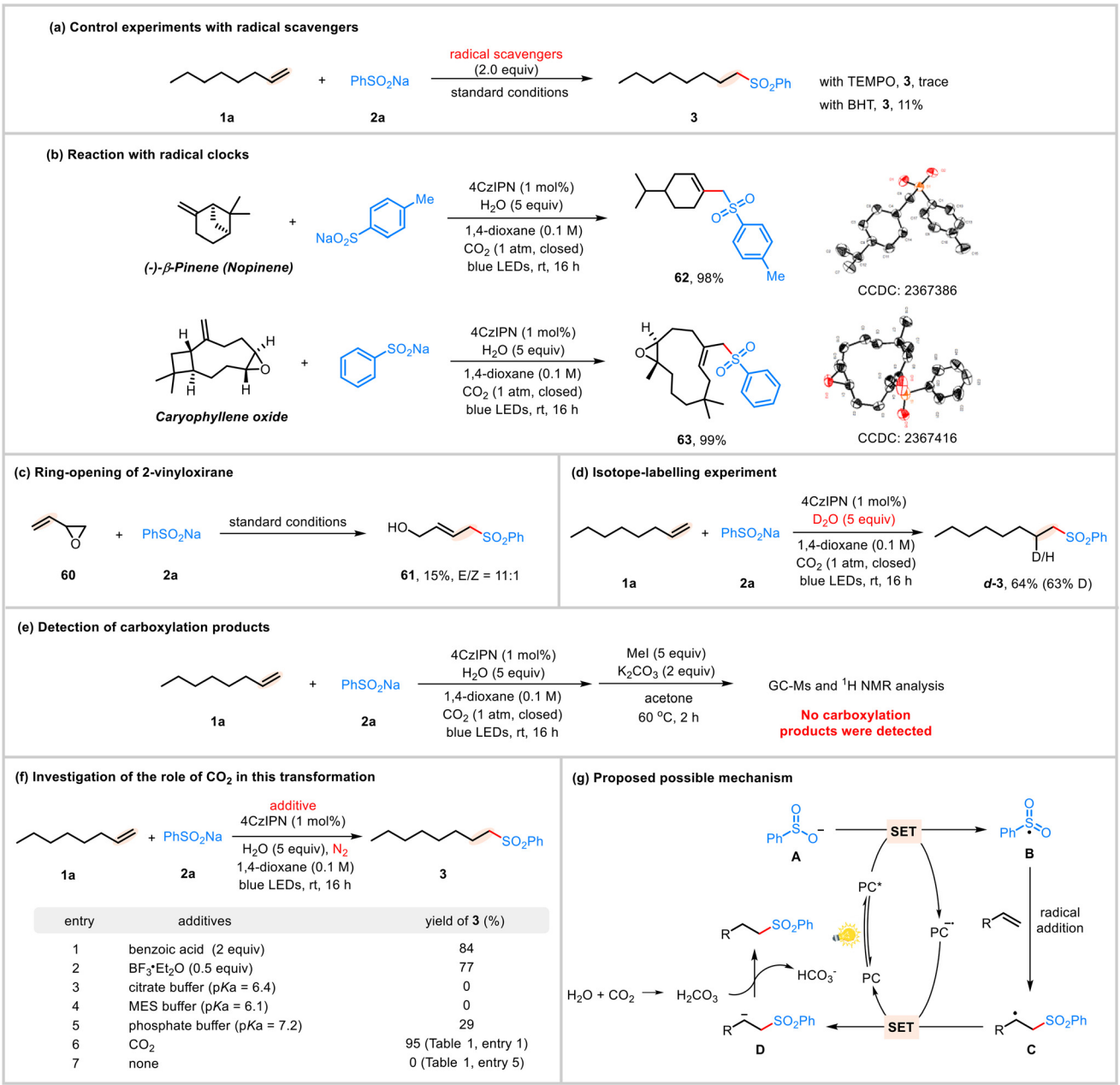
With the optimal reaction conditions in hand, the generality of this transformation was examined. As shown in Scheme 2, a broad range of unactivated alkenes with diverse functional groups were compatible with the reaction. In this transformation, the length of the alkene chain had no significant influence on the yields of products (**3**–**7**). All the cyclic (**8**), phenyl (**9**, **10**) and branched (**11**) substituents linked to the alkenes were successfully subjected to this reaction, furnishing the desired products in reasonable yields. Active hydrogen did not affect the reaction as all the alkenes containing hydroxyl (**12**, **37**) and carboxyl (**13**–**18**) groups efficiently underwent the desired transformation to yield target products in good yields. Furthermore, all the alkenes bearing ester (**19**), acylamino (**20**–**22**) and ether (**23**–**26**) groups were proved to be viable substrates to produce corresponding products in moderate to excellent yields. Notably, some sensitive functional groups, such as silicyl (**27**–**29**) and boryl (**30**) remained intact under the standard reaction conditions. Alkenes with terminal chloro (**31**) or bromo (**32**, **33**) groups also readily accommodated sulfonyl groups in acceptable yields. Substrates with two double bonds were further explored, and the target products (**34**, **35**) were obtained with good selectivity. Notably, the di-sulfonated product **36** was produced in excellent yield when the amount of sulfonate was increased to 2.5 equivalents. β,β-Disubstituted alkenes (**37**, **38**) and an internal alkene (**39**) were also proved to be suitable substrates. Moreover, alkyl olefins and aryl olefins were examined (**40**–**42**). Styrene was incompatible with this reaction (**40**), but sulfonyl groups were easily introduced in electron-deficient aryl olefins, such as 4-vinylpyridine and *penta*-fluorovinylbenzene, in good yields (**41**, **42**), indicating that a carbanion intermediate might be involved in this transformation. Subsequently, the scope of sulfinates was also examined. Aryl sulfinates with diverse functional groups (such as fluoro, chloro, methyl and trifluoromethyl) were compatible with this reaction to produce the corresponding products (**43**–**49**) in general to good yields. In addition, aliphatic sulfinates, such as sodium cyclopropanesulfinate, readily accommodated sulfonyl groups to deliver the target product **50** in an acceptable yield.

Subsequently, we explored the synthetic potential of this protocol in the late-stage modification of more complex motifs. Both alkenes and sodium sulfinates containing biologically active functional groups were evaluated and proven to be feasible (Scheme 3). Initially, alkenes containing estrone, probenecid, eugenol, cimaterol impurity 3, adamantoic acid, oxaprozin and indomethacin derivatives were examined, and all of them efficiently delivered the desired products (**51**–**57**) in moderate to good yields. Furthermore, sulfinates derived from valdecoxib and sildenafil successfully yielded the target products (**58** and **59**) in acceptable yields.

Several control experiments were performed to investigate the mechanism of this CO_2-promoted hydrosulfonylation of unactivated alkenes (Scheme 4). Initially, some radical scavengers, such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) or butylated hydroxytoluene (BHT), were added to the reaction mixture under standard reaction conditions, and the reaction was observed to be almost restrained, indicating that a radical pathway might be involved in this reaction (Scheme 4a). Subsequently, ring-opening sulfonated products (**62**, **63**) were isolated in excellent yields when medicinally relevant alkenes, such as nopinene and caryophyllene oxide, were used in this reaction (Scheme 4b). These transformations not only provide an efficient protocol for hydrosulfonylation of medicinally rele-



Scheme 3 Late-stage modification of drug derivatives and natural products.



entry	additives	yield of **3** (%)
1	benzoic acid (2 equiv)	84
2	$BF_3{\cdot}Et_2O$ (0.5 equiv)	77
3	citrate buffer (p*K*a = 6.4)	0
4	MES buffer (p*K*a = 6.1)	0
5	phosphate buffer (p*K*a = 7.2)	29
6	CO_2	95 (Table 1, entry 1)
7	none	0 (Table 1, entry 5)

Scheme 4 Mechanistic studies. MES: 2-(*N*-Morpholino)ethanesulfonic acid.

vant alkenes but also demonstrate that the reaction follows a radical process. The generation of ring-opening product **61** further supported this inference (Scheme 4c). Furthermore, when the reaction was carried out in the presence of D_2O under standard reaction conditions, deuterium product *d*-**3** was obtained with a reasonable D/H ratio (Scheme 4d), indicating that a carbanion intermediate might be generated in this reaction. In the methylated reaction system, no carboxylation products were detected during GC-MS and ^{1}H NMR analyses (Scheme 4e), indicating that CO_2 did not directly participate as a C1 synthon in this transformation. To further elucidate the role of CO_2 in the reaction, additional control experiments were conducted under an N_2 atmosphere using alternative acids and buffers (Scheme 4f). When benzoic acid or $BF_3{\cdot}Et_2O$ was added, the target product **3** was obtained in acceptable yields (Scheme 4f, entries 1 and 2). To investigate whether CO_2 functioned solely *via* its acidity (*via* H_2CO_3 formation, $pK_{a1} \approx 6.4$),[16] buffers with comparable pK_a values, such as citrate buffer ($pK_a = 6.4$), MES buffer ($pK_a = 6.1$) and phosphate buffer ($pK_a = 7.2$), were employed. Notably, the citrate- and MES-buffer systems did not yield **3** (Scheme 4f, entries 3 and 4), while the phosphate buffer achieved a modest 29% yield (Scheme 4f, entry 5), which was significantly lower than the 95% yield achieved under standard CO_2 conditions. These results indicate

that CO_2 not only generates a weakly acidic microenvironment to facilitate protonation but also potentially modulates the redox properties of the photocatalytic system without being converted into C1-products. Furthermore, light-on–off experiments were carried out to demonstrate that this reaction follows a photoredox-catalyzed radical catalytic pathway instead of a radical chain pathway (details in ESI Fig. 4†).

Based on these mechanistic studies and our previous works, a possible mechanism is proposed (Scheme 4g). Initially, excited PC* is produced upon light irradiation on the PC. Subsequently, a single-electron transfer (SET) process occurred between PC* [$E_{1/2}^{red}$ ($PC^*/PC^{\bullet-}$) = 1.43 V *vs.* SCE in MeCN for 4CzIPN][17] and phenylsulfinate **A** (−0.37 V *vs.* SCE in MeCN for $PhSO_2Na$)[18], generating a sulfonyl radical (**B**) and reduced $PC^{\bullet-}$ species. Thereafter, the addition of radical **B** to the C=C double bond generated a carbon radical intermediate **C**, which is further reduced by $PC^{\bullet-}$ to produce the carbanion intermediate **D** and ground-state PC. Finally, the desired sulfonated products are obtained after protonation from **D**. It is supposed that CO_2 serves a dual role in this transformation, namely, (i) to generate a weakly acidic microenvironment to facilitate protonation and (ii) to potentially modulate the redox properties of the photocatalytic system, ultimately enhancing the reactivity of the sulfonyl radical to ensure efficient electron transfer during the SET process.

Conclusions

In conclusion, we developed a CO_2-promoted strategy for photoredox-catalyzed hydrosulfonylation of unactivated alkenes with sulfinates to synthesize highly valuable sulfonyl compounds. A broad range of functional groups, including hydroxyl, carboxyl, ester, acylamino, ether, silicyl, boryl, terminal halogen, and alkenyl, were compatible with this sulfonated transformation, offering a straightforward and clean procedure for the synthesis of sulfonyl products. Notably, the crucial role of CO_2 in this transformation highlighted its multifunctional nature *via* which its acid-promoting and substrate-specific interactions were combined to enable high reactivity under mild conditions. Further CO_2-promoted transformations are currently being investigated in our laboratory.

Author contributions

Y. Gao conceived and designed the experiments. W. Huang performed the experiments and analysed the data. G. Liu helped analyse the data. F. Yang conducted the X-ray analysis. Y. Gao and W. Su wrote the manuscript, and all authors revised the manuscript.

Data availability

All experimental data associated with this study are provided in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (grant no. 22271285, 21931011), the National Key Research and Development Program of China (2018FYA0704502), the Self-deployment Project Research Program of Haixi Institutes, Chinese Academy of Sciences (CXZX-2022-GH04), and Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China (2021ZZ105).

References

1 (*a*) S. Patai, Z. Rappoport and C. J. M. Stirling, *The Chemistryof Sulphones and Sulfoxides*, Wiley, New York, 1988; (*b*) N. A. McGrath, M. Brichacek and J. T. Njardarson, *J. Chem. Ed.*, 2010, **87**, 1348; (*c*) C. L. Percicot, C. R. Schnell, C. Debon and C. Hariton, *J. Pharmacol. Toxicol. Methods*, 1996, **36**, 223; (*d*) M. Feng, B. Tang, S. H. Liang and X. Jiang, *Curr. Top. Med. Chem.*, 2016, **16**, 1200; (*e*) F. Zhao, J. Wang, X. Ding, S. J. Shu and H. Liu, *Chin. J. Org. Chem.*, 2016, **36**, 490; (*f*) K. A. Scott and J. T. Njardarson, *Top. Curr. Chem.*, 2018, **376**, 5.

2 (*a*) B. M. Trost and C. A. Kalnmals, *Chem. – Eur. J.*, 2019, **25**, 11193; (*b*) X.-Q. Chu, D. Ge, Y.-Y. Cui, Z.-L. Shen and C.-J. Li, *Chem. Rev.*, 2021, **121**, 12548; (*c*) M. Nambo, Y. Maekawa and C. M. Crudden, *ACS Catal.*, 2022, **12**, 3013.

3 (*a*) B. P. Bandgar, S. V. Bettigeri and J. Phopase, *Org. Lett.*, 2004, **6**, 2105; (*b*) Y. Fu, W. Zhu, X. Zhao, H. Hügel, Z. Wu, Y. Su, Z. Du, D. Huang and Y. Hu, *Org. Biomol. Chem.*, 2014, **12**, 4295; (*c*) A. G. Tathe and N. T. Patil, *Org. Lett.*, 2022, **24**, 4459.

4 (*a*) S. Répichet, C. Le Roux, P. Hernandez, J. Dubac and J.-R. Desmurs, *J. Org. Chem.*, 1999, **64**, 6479; (*b*) D. O. Jang, K. S. Moon, D. H. Cho and J.-G. Kim, *Tetrahedron Lett.*, 2006, **47**, 6063; (*c*) N.-W. Liu, S. Liang and G. Manolikakes, *Synthesis*, 2016, 1939.

5 For selected reviews, see: (*a*) S. Ye, G. Qiu and J. Wu, *Chem. Commun.*, 2019, **55**, 1013; (*b*) S. Zhao, K. Chen, L. Zhang, W. Yang and D. Huang, *Adv. Synth. Catal.*, 2020, **362**, 3516; (*c*) D. Zeng, M. Wang, W.-P. Deng and X. Jiang, *Org. Chem. Front.*, 2020, **7**, 3956; (*d*) D.-Q. Dong, Q.-Q. Han, S.-H. Yang, J.-C. Song, N. Li, Z.-L. Wang and X.-M. Xu, *ChemistrySelect*, 2020, **5**, 13103; (*e*) D. Joseph, M. A. Idris, J. Chen and S. Lee, *ACS Catal.*, 2021, **11**, 4169; (*f*) S. Liang, K. Hofman, M. Friedrich, J. Keller and G. Manolikakes, *ChemSusChem*, 2021, **14**, 4878.

6 Y. Chen, N. McNamara, O. May, T. Pillaiyar, D. C. Blakemore and S. V. Ley, *Org. Lett.*, 2020, **22**, 5746.

7 (*a*) T. Liu, Y. Li, L. Lai, J. Cheng, J. Sun and J. Wu, *Org. Lett.*, 2018, **20**, 3605; (*b*) X. Wang, M. Yang, W. Xie, X. Fan and J. Wu, *Chem. Commun.*, 2019, **55**, 6010.

8 (*a*) J.-J. Wang and W. Yu, *Org. Lett.*, 2019, **21**, 9236; (*b*) Y. Zheng, Y. You, Q. Shen, J. Zhang, L. Liu and X.-H. Duan, *Org. Chem. Front.*, 2020, **7**, 2069.

9 (*a*) S. M. Hell, C. F. Meyer, A. Misale, J. B. I. Sap, K. E. Christensen, M. C. Willis, A. A. Trabanco and V. Gouverneur, *Angew. Chem., Int. Ed.*, 2020, **59**, 11620–11626; (*b*) S. T. Shreiber and G. A. Molander, *Org. Lett.*, 2023, **25**, 2084; (*c*) C.-M. Li, X.-X. Dong, Z. Wang and B. Zhang, *Green Chem.*, 2023, **25**, 4122; (*d*) M. J. Tilby, D. F. Dewez, L. R. E. Pantaine, A. Hall, C. Martínez-Lamenca and M. C. Willis, *ACS Catal.*, 2022, **12**, 6060.

10 X. Wu and B. Gao, *Org. Lett.*, 2023, **25**, 8722.

11 (*a*) M. Kim, E. You, S. Park and S. Hong, *Chem. Sci.*, 2021, **12**, 6629; (*b*) P. Renzi, E. Azzi, S. Ascensio, S. Parisotto, F. Sordello, F. Pellegrino, G. Ghigo and A. Deagostino, *Chem. Sci.*, 2023, **14**, 2721; (*c*) Y. Song, C. Li, X. Hu, H. Zhang, Y. Mao, X. Wang, C. Wang, L. Hu and J. Yan, *Green Chem.*, 2024, **26**, 6578; (*d*) J. D. Lasso, D. J. Castillo-Pazos, J. M. Salgado, C. Ruchlin, L. Lefebvre, D. Farajat, D. F. Perepichka and C.-J. Li, *J. Am. Chem. Soc.*, 2024, **146**, 2583.

12 For selected reviews, see: (*a*) K. Huang, C.-L. Sun and Z.-J. Shi, *Chem. Soc. Rev.*, 2011, **40**, 2435; (*b*) Y. Yang and J.-W. Lee, *Chem. Sci.*, 2019, **10**, 3905; (*c*) C. S. Yeung, *Angew. Chem., Int. Ed.*, 2019, **58**, 5492; (*d*) Z. Fan, Z. Zhang and C. Xi, *ChemSusChem*, 2020, **13**, 6201; (*e*) X. He, L.-Q. Qiu, W.-J. Wang, K.-H. Chen and L.-N. He, *Green Chem.*, 2020, **22**, 7301; (*f*) J. H. Ye, T. Ju, H. Huang, L. L. Liao and D.-G. Yu, *Acc. Chem. Res.*, 2021, **54**, 2518; (*g*) L. Guo, K. J. Lamb and M. North, *Green Chem.*, 2021, **23**, 77; (*h*) A. J. Davida and A. Das, *Green Chem.*, 2025, **27**, 851.

13 For recent selected examples, see: (*a*) W. Li, B. Sun, L. Zhang and F. Mo, *Green Chem.*, 2023, **25**, 5030; (*b*) H. Huang, X. Lin, F. Yang, Y. Ren, Y. Gao and W. Su, *Org. Lett.*, 2024, **26**, 11195; (*c*) F. Zhang, X.-Y. Wu, P.-P. Gao, H. Zhang, Z. Li, S. Ai and G. Li, *Chem. Sci.*, 2024, **15**, 6178; (*d*) Y. Liu, G.-H. Xue, Z. He, J.-P. Yue, M. Pan, L. Song, W. Zhang, J.-H. Ye and D.-G. Yu, *J. Am. Chem. Soc.*, 2024, **146**, 28350; (*e*) Y. Yia and C. Xi, *Green Synth. Catal.*, 2024, DOI: 10.1016/j.gresc.2024.09.003.

14 For selected reviews, see: (*a*) P. K. Sahoo, Y. Zhang and S. Das, *ACS Catal.*, 2021, **11**, 3414; (*b*) Z. Zhang and C. Xi, *ChemCatChem*, 2025, **17**, e202401834; (*c*) W. Schilling and S. Das, *Tetrahedron Lett.*, 2018, **59**, 3821.

15 For selected examples, see: (*a*) G. Pupo, R. Properzi and B. List, *Angew. Chem., Int. Ed.*, 2016, **55**, 6099; (*b*) J. Ye, I. Kalvet, F. Schoenebeck and T. Rovis, *Nat. Chem.*, 2018, **10**, 1037; (*c*) D. Riemer, W. Schilling, A. G. Götz, Y. Zhang, S. Gehrke, I. Tkach, O. Hollóczki and S. Das, *ACS Catal.*, 2018, **8**, 11679; (*d*) M. Kapoor, P. Chand-Thakuri and M. C. Young, *J. Am. Chem. Soc.*, 2019, **141**, 7980; (*e*) Y. Zhao, X. Guo, S. Li, Y. Fan, G.-C. Ji, M. Jiang, Y. Yang and Y.-Y. Jiang, *Angew. Chem., Int. Ed.*, 2022, **61**, e202213636; (*f*) Z. Fan, S. Chen, S. Zou and C. Xi, *ACS Catal.*, 2022, **12**, 2781; (*g*) S. Chen and C. Xi, *Green Chem.*, 2023, **25**, 7978; (*h*) Z. Zhang, D. Li and C. Xi, *Org. Lett.*, 2023, **25**, 698; (*i*) Y. Gao, S. Liu and W. Su, *Green Chem.*, 2023, **25**, 7335; (*j*) G. Archer, R. Meyrelles, I. Eder, N. Kovács, B. Maryasin, M. Médebielle and J. Merad, *Angew. Chem., Int. Ed.*, 2023, e202315329; (*k*) G. Liu, D. Ma, J. Zhang, F. Yang, Y. Gao and W. Su, *Nat. Commun.*, 2024, **15**, 10153; (*l*) S. Dotzauer, G. B. Hadaf, F. S. Kamounah, A. Kadziola and J.-W. Lee, *Catalysts*, 2020, **10**, 1481.

16 A. P. Miller, Lange's Handbook of Chemistry, in *Am J Public Health N*, 4th edn, 1941, vol. 31, p. 1324.

17 E. Speckmeier, T. G. Fischer and K. Zeitler, *J. Am. Chem. Soc.*, 2018, **140**, 15353.

18 A. U. Meyer, S. Jäger, D. P. Hari and B. König, *Adv. Synth. Catal.*, 2015, **357**, 2050.