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Additive-free four-component radical selenosulfonylation of alkenes†

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While multicomponent tandem reactions offer an efficient platform for the difunctionalization of alkenes, the precise regulation of component ordering in reaction systems remains a persistent challenge. Herein, we present an additive-free method to achieve the radical selenosulfonylation of alkenes through four-component sequential participation, enabled by the precise regulation of equilibria among multiple components and the ingenious utilization of radical-polarity matching effects between the intermediates and alkenes. Moreover, this strategy overcomes the limitations of the cumbersome presynthesis of selenosulfonates and successfully extends the substrate scope to unactivated alkenes. Simultaneously, C–S and C–Se bonds can be constructed under mild conditions without any additives, achieving the highly selective conversion of difunctionalized alkenes with the introduction of bis-heteroatoms. Through systematic controlled experiments and mechanistic studies, the radical tandem reaction pathway and polarity matching regulation mechanism were revealed.

The intermolecular difunctionalization of alkenes has attracted significant interest from synthetic chemists, as it facilitates the efficient, ordered modular assembly of complex molecules.[1] Although there have been numerous reports of 1,2-difunctionalization in recent years,[2] studies on the introduction of 1,2-bis-heteroatoms remain scant due to the intricate challenges faced in reconciling conflicting electronic effects and matching steric hindrance. The current advances in this field have predominantly focused on the construction of C–O/C–N/C–X (X = F, Cl, Br, I)/C–S bonds, exemplified by *O*,*N*-oxyamination,[3] X,*N*-haloamination,[4] X,*S*-halosulfonation,[5] *O*,*O*-dioxygenation,[6] *N*,*N*-diamination,[7] and *S*,*S*-disulfonation[8] (Scheme 1A). Despite these advancements, there are few reports on radical 1,2-difunctionalization of alkenes for the simultaneous construction of C–S and C–Se bonds. The following three critical bottlenecks have been identified: (1) persistent reliance on metal catalysts, stoichiometric reagents (*e.g.*, oxidants/bases), and high temperature to overcome the activation energy barrier; (2) compromised regioselectivity arising from competing electronic effects and steric hindrance at sulfur/selenium–carbon coupling sites; and (3) uncontrollable radical generation and transformation pathways, where the chain propagation of selenide/sulfur-centered radicals is readily quenched by oxygen or impurities, resulting in diminished efficiency or the formation of radical coupling and β-H elimination byproducts (Scheme 1B). Accordingly, the pursuit of an efficient and selective methodology for the concurrent construction of C–S and C–Se bonds is of utmost importance to advance intermolecular 1,2-difunctionalization of alkenes to access architecturally complex molecules.

Sulfonyl and selenyl groups are highly valued for their ease of conversion and ability to actively participate in subsequent synthetic reactions.[9] Additionally, they can be conveniently introduced and flexibly modulated through a variety of synthetic routes. The combination of these merits endows selenosulfonylation of alkenes with unique potential for application in organic synthesis. At present, radical selenosulfonylation of alkenes primarily involves two-component radical addition systems that rely on organocatalysts, elevated temperatures or photoexcitation.[10] Nevertheless, these methods face inherent obstacles due to the cumbersome selenosulfonate presynthesis, multi-step synthetic procedures, and limited substituent tolerance. Therefore, it is imperative to develop a new strategy for efficient and speedy selenosulfonylation of alkenes. In this

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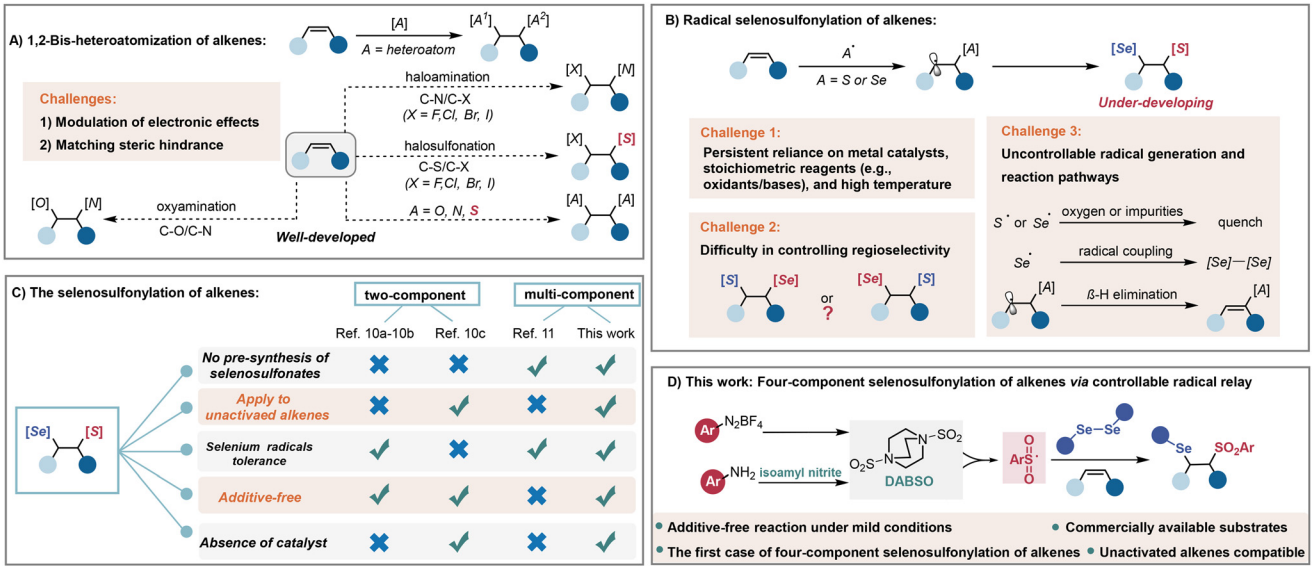


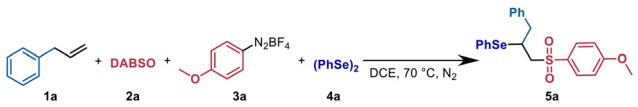
Scheme 1 1,2-Bis-heteroatomization and selenosulfonylation of alkenes.

regard, chemists envision a multi-component (three or more components) radical tandem strategy to bypass the laborious presynthesis of selenosulfonates. To date, this method has primarily exploited sulfonohydrazides/diselenides as dual radical precursors. In 2022, Zhao demonstrated a copper-catalyzed system utilizing *tert*-butyl hydroperoxide (TBHP) as the oxidant to induce the three-component radical selenosulfonylation of sulfonyl hydrazides/diselenides/maleimides.[11] Yet, the practical scalability of this methodology is impacted by the mandatory use of metal-based catalytic systems and stoichiometric oxidative reagents, introducing challenges in terms of cost efficiency and environmental compatibility. In addition, this protocol remains confined to activated alkenes with low reactivity and faces challenges in modulating the regioselectivity toward unactivated alkenes (Scheme 1C). Meanwhile, competitive radical quenching (*e.g.*, Se–Se coupling) and deactivation of the selenyl group *via* over-oxidation lead to unsatisfactory results (β-H elimination). Hence, developing additive-free strategies for the selenosulfonylation of alkenes with broad substrate scopes and controllable selectivity mechanisms continues to be a pivotal scientific challenge in this field.

Herein, we disclose an additive-free four-component controllable radical relay strategy to achieve 1,2-selenosulfonylation of alkenes. The method not only obviates the necessity for pre-preparation of selenosulfonates, but also demonstrates compatibility with unactivated alkenes. It can efficiently construct both C–S and C–Se bonds under mild conditions (Scheme 1D). Specifically, the reaction employs aryldiazonium tetrafluoroborates/aniline derivatives for *in situ* generation of aryl radicals, with the solid-state sulfur dioxide surrogate 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO) as the sulfonyl source and diselenides as the selenium radical source. The produced aryl radical inserts into a sulfur dioxide surrogate to first generate a highly electrophilic sulfonyl radical *in situ*, and then rapidly adds to the alkene to form a more reactive alkyl radical intermediate, with the regioselectivity controlled by strategic installation of electron-donating/withdrawing groups on alkenes. Subsequently, this intermediate selectively couples with diphenyldiselenide to achieve four-component 1,2-selenosulfonylation. This mechanism orchestrates the sequential generation of radical species, enabling polarity-matched installation of functional groups while addressing regioselectivity challenges inherent to multi-component radical cascades. Collectively, this strategy manifests four salient merits: (1) metal-catalyst- and additive-free reaction under mild conditions; (2) use of commercial feedstocks to achieve the step-economical construction of C–S and C–Se bonds in one pot, avoiding cumbersome preparations; (3) the first example of four-component selenosulfonylation of alkenes; and (4) enhanced substrate generality and compatibility with low-activity unactivated alkenes.

We initiated our optimization by investigating the reaction of allylbenzene (**1a**), DABSO (**2a**), 4-methoxybenzenediazonium tetrafluoroborate (**3a**), and diphenyl diselenide (**4a**) as model substrates (Table 1). The reaction proceeded efficiently in the presence of dichloroethane (DCE) under a nitrogen atmosphere at 70 °C for 12 h, affording the desired product **5a** with a yield of 78% (entry 1). Encouraged by this result, the performance of different solvents was examined to improve the chemoselectivity of this transformation. We conducted a brief screening of different solvents, including dichloromethane (DCM), $CHCl_3$, tetrahydrofuran (THF), acetonitrile (MeCN), ethyl acetate (EtOAc), EtOH, *N*,*N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), and toluene (entries 2–10). Comparative analyses showed that DCE was the most efficient solvent. With DCE as the solvent, additional parameters were screened to maximize the efficiency of this reaction. Next the effect of reaction temperature on the yield was assessed; the

Table 1 Screening of optimal reaction conditions[a]



Entry	Variation from the standard reaction conditions	Yield of **5a** [b] (%)
1	None	78
2	DCM instead of DCE	49
3	$CHCl_3$ instead of DCE	45
4	THF instead of DCE	42
5	MeCN instead of DCE	47
6	EtOAc instead of DCE	21
7	EtOH instead of DCE	15
8	DMA instead of DCE	67
9	DMSO instead of DCE	35
10	Toluene instead of DCE	37
11	60 °C	71
12	80 °C	73
13	90 °C	29
14	$Na_2S_2O_5$ instead of **2a**	54
15	$K_2S_2O_5$ instead of **2a**	47
16	**1a** (1.0 mmol) for 36 h	74

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv.), **3a** (2.0 equiv.), **4a** (1.5 equiv.) in DCE (2.0 mL) under N_2 at 70 °C for 12 h. [b] Isolated yields based on **1a**.

temperature initially exerted a marginal influence on the yield (entries 11 and 12). Interestingly, a remarkable decrease in yield was observed at 90 °C compared to that at 70 °C (entry 13), which can be attributed to the accelerated side reactions that compromise both the reaction selectivity and product yield. Moreover, replacement of DABSO with either $Na_2S_2O_5$ or $K_2S_2O_5$ did not result in an enhancement of the yield (entries 14 and 15). To further investigate the practicality of this reaction, a scale-up experiment was carried out using **1a** on a reaction scale of 1.0 mmol. A 74% yield of product **5a** was obtained after the reaction time was extended to 36 h (entry 16).

To highlight the reproducibility, robustness and practicality of the experimentation, a sensitivity assessment based on reaction conditions was conducted (Fig. 1).[12] To this end, the assessment focused on five critical parameters: evaluated-concentration, water level, oxygen level, temperature and scale. These were selected for different potential error types.

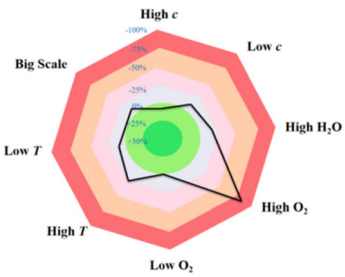
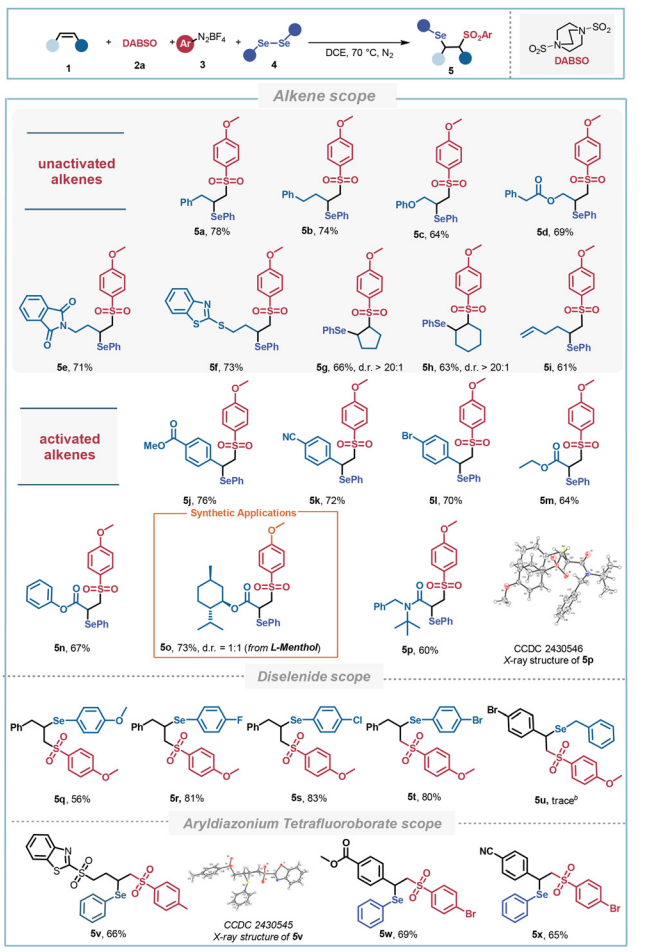


Fig. 1 Sensitivity assessment.

Variations in oxygen level exerted a decisive influence on the efficiency of this selenosulfonylation. In contrast, the concentration and temperature exhibited only marginal effects, suggesting outstanding reproducibility under various conditions.

With the optimized reaction conditions in hand, the generality of this selenosulfonylation was then investigated (Table 2). First, different substituted alkenes were evaluated. To our delight, the system exhibited broad functional group tolerance across a spectrum of unactivated alkenes, successfully delivering the target products. Comparatively, all-carbon chain alkenes exhibited superior synthetic yields relative to heteroatom-containing alkenes. Both allylbenzene and 4-phenyl-1-butene easily underwent selenosulfonylation, with products (**5a** and **5b**) being isolated in 78% and 74% yields. Besides, heteroatom-containing alkenes, such as ether (**5c**), ester (**5d**), imide (**5e**) and benzothiazole (**5f**), were also well tolerated, generating the corresponding products in 64–73%

Table 2 Aryldiazonium tetrafluoroborates as aryl radical precursors[a]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (2.0 equiv.), **3** (2.0 equiv.), **4** (1.5 equiv.) in DCE (2.0 mL) under N_2 at 70 °C for 12 h. [b] 46% of the by-product 1-bromo-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene was detected.

yields. Gratifyingly, cyclic alkenes were amenable to this reaction, as exemplified by the reaction of cyclopentene and cyclohexene under standard conditions, which furnished the products **5g** and **5h** in 66% and 63% yields, respectively. Furthermore, the methodology proved effective for dienes, such as the successful conversion of 1,5-hexadiene to the product (**5i**) with a yield of 61%. The result clearly establishes the preferential occurrence of 1,2-addition over 4-*exo-trig* cyclization in 1,5-diene systems. In addition, a series of activated alkenes including *para*-substituted aryl- (**5j–5l**), ester- (**5m–5o**), and amide- (**5p**) alkenes were also investigated, and these substrates were found to be viable, yielding the target products in good to moderate yields (60–76%). Notably, we found that this strategy can serve as a tool for late-stage functionalization, with alkenes derived from pharmaceutically active compounds, such as L-menthol (**5o**), exhibiting satisfactory performance under the reaction conditions. This remarkable substrate generality reflects that the method retains sufficient electrophilicity to engage in selenosulfonylation of activated alkenes, while simultaneously remaining well suited for unactivated alkenes.

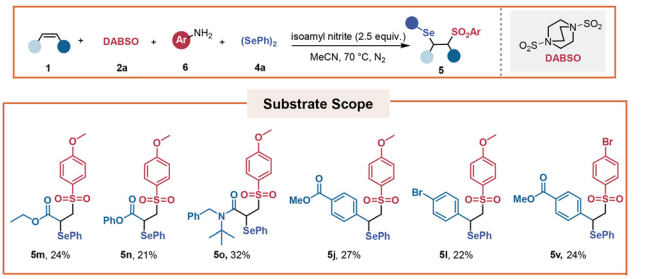
Given the versatile reactivity of alkenes, we then embarked on experiments to assess the reactivity of diselenides. The result revealed that diaryl diselenides exhibited better tolerance with an electron-withdrawing group on the aromatic ring than those with an electron-donating group. For instance, substrates bearing 4-F, 4-Cl and 4-Br successfully produced the desired target products (**5r–5t**) in 80–83% yields under the standard conditions. In order to further exemplify the applicability of the protocol to dialkyl diselenides, we explored the reactions with more challenging dibenzyl diselenide. Unfortunately, it only yielded traces of the target product (**5u**).

To expand the scope of coupling partners, we systematically evaluated substituted aryldiazonium tetrafluoroborates. Pleasingly, both electron-donating (4-OMe, 4-Me) and moderately electron-withdrawing (4-Br) substituents demonstrated excellent compatibility with the selenosulfonylation process, affording products in 65–69% yields. This broad functional group tolerance serves to emphasize the robustness of the mechanism in accommodating diverse electronic environments.

In the pursuit of feasible alternatives to aryldiazonium salts as aryl radical precursors, we developed a streamlined protocol that generates aryldiazonium intermediates *in situ* through diazotization of aniline derivatives with isoamyl nitrite. The initial experiment revealed exceptional functional group tolerance across structurally diverse alkenes when employing aniline as the aryl radical precursor (Table 3). Building on this foundation, we systematically benchmarked substituted anilines, encompassing –OMe and –Br. Encouragingly, these substituted anilines underwent transformation into the targeted products, with yields ranging from 21% to 32%.

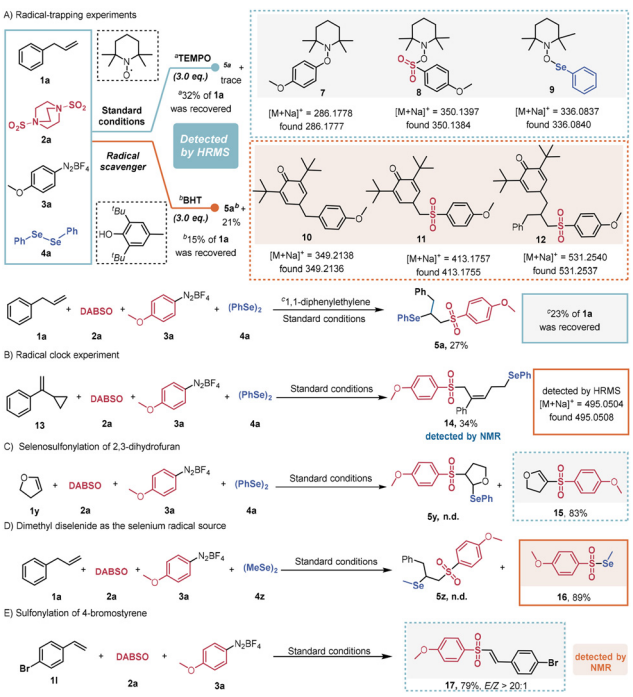
To gain further insights into the mechanism of this selenosulfonylation of alkenes, several control experiments were meticulously conducted under the standard conditions. It is worth pointing out that the radical nature of the reaction was

Table 3 Aniline derivatives as aryl radical precursors[a]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (2.0 equiv.), **6** (2.0 equiv.), **4a** (1.5 equiv.), isoamyl nitrite (2.5 equiv.) in MeCN (2.0 mL) under N_2 at 70 °C for 12 h.

confirmed by the addition of radical inhibitors to the model reaction. Specifically, introducing radical scavengers such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 1,1-diphenylethylene into the model reaction under the standard conditions resulted in marked inhibition of the formation of **5a** (Scheme 2A). Notably, high-resolution mass spectrometry (HRMS) successfully identified the adducts formed between these radical scavengers and the pivotal radical intermediates (aryl radicals, arylsulfonyl radicals, selenium radicals, and sulfonylation-derived alkyl radicals), thereby providing compelling evidence for the proposed mechanism. Subsequently, in the radical clock experiment utilizing (1-cyclopropylvinyl)benzene (**13**) under the standard conditions, the ring-opened product **14**



Scheme 2 Control experiments and mechanistic studies.

was successfully obtained (Scheme 2B). This observation underscores the heightened reactivity of the arylsulfonyl radical in comparison with the selenyl radical within this competitive reaction mechanism. However, in the case of 2,3-dihydrofuran as an alternative alkene or dimethyldienyl as a selenium radical precursor, neither of the selenosulfonylation products could be obtained (Scheme 2C and D). Conversely, these afforded β-H elimination product **15** devoid of diselenide, along with product **16** arising from the interaction between the arylsulfonyl radical and dimethyl diselenide. This result shows the vital role of polarity matching between substituted alkenes and radicals in this multicomponent reaction, wherein the aryl radical in conjunction with DABSO forms the arylsulfonyl radical with a superior generation rate and reactivity compared to the selenyl radical. Lastly, when 4-bromostyrene (**1l**), DABSO (**2a**) and 4-methoxybenzenediazonium tetrafluoroborate (**3a**) were reacted under the standard reaction conditions in the absence of diselenide, the sulfonylation product was observed, fully in accordance with the theoretical result (Scheme 2E).

Based on the above-mentioned experimental results and literature precedents,[13,14] the proposed mechanism proceeds through an additive-free radical relay process, as shown in Fig. 2. Initially, the reaction proceeds through a metal-free activation pathway where aryldiazonium salt **3** and DABSO **2a** form an electrostatic complex **A** under mild conditions,[13a,b,e] and then this complex **A** undergoes spontaneous N–S bond cleavage *via* single electron transfer (SET),[14b,c] generating an aryl radical, sulfur dioxide, tertiary amine radical cation **B**, and nitrogen gas. Subsequently, the produced aryl radical rapidly undergoes SO_2 insertion to form a highly electrophilic arylsulfonyl radical intermediate **C**.[13c,d,14a] Then intermediate **C** engages in radical addition to the alkene and forms a carbon-centered radical intermediate **D**.[14e] Finally, homolytic cleavage of the diselenide bond generates a selenium-centered radical,[14d] which participates in radical–radical coupling with intermediate **D**. This step efficiently terminates the radical chain and delivers the final selenosulfonylation product **5**.

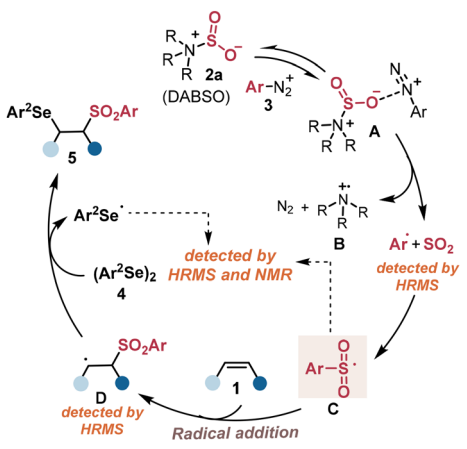


Fig. 2 Plausible reaction mechanism.

Conclusions

In summary, we have established a mild, efficient and practical four-component controllable radical tandem strategy for the selenosulfonylation of alkenes that enables the step-economical construction of C–S and C–Se bonds. This method represents the first instance of four-component radical selenosulfonylation of alkenes, effectively tackling obstacles related to polarity alignment between radical intermediates and alkenes, as well as managing regioselectivity issues encountered with multicomponent tandem reactions. Notably, the developed reaction is additive-free and overcomes the limitations of the cumbersome presynthesis of selenosulfonates, while exhibiting good functional group tolerance across a broad range of unactivated alkenes. The remarkable generality and sustainability of this method underscore its potential as a versatile platform for functionalization of alkenes.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

Acknowledgements

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