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Metal-free allylic C–H nitrogenation, oxygenation, and carbonation of alkenes by thianthrenation†

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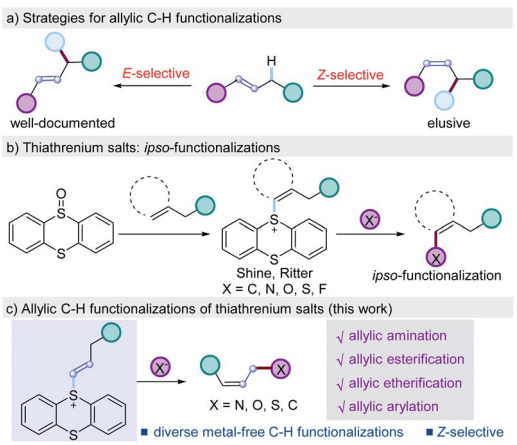
Selective functionalization of allylic C–H bonds into other chemical bonds is among the most straightforward and attractive, yet challenging transformations. Herein, a transition-metal-free protocol for direct allylic C–H nitrogenation, oxygenation, and carbonation of alkenes by thianthrenation was developed. This operationally simple protocol allows for the unified allylic C–H amination, esterification, etherification, and arylation of vinyl thianthrenium salts. Notably, the reaction furnishes multialkyl substituted allylic amines, ammonium salts, sulfonyl amides, esters, and ethers in good yields. The reaction proceeds under mild conditions with excellent functional group tolerance and could be applied to late-stage allylation of natural products, drug molecules and peptides with excellent chemoselectivity.

Introduction

Methods for direct allylic C–H functionalizations are among the most attractive transformations to streamline organic synthesis as they maximize the step- and atom-economy to generate stereodefined allylic species amenable to further chemical transformations, thus minimizing the cost and waste.[1,2] Traditional allylic C–H functionalization reactions generally require the catalysis of transition-metals such as Pd, Cu, and Ir, which involves the formation of an allyl–metal complex *via* C–H activation followed by an intra- or intermolecular nucleometallation (Scheme 1a).[3,4] Recently, the radical cleavage of an allylic C–H bond *via* hydrogen atom transfer is also developed to generate carbon-centered radical intermediates, which could be involved in following radical processes or transition-metal catalysis.[3m,5] These two strategies proved to be powerful for organic synthesis and extensively investigated. The stereochemical outcomes heavily rely on the properties of transition-metals and anchoring ligands and are mostly dominated by thermodynamic control, leading to the formation of C–H functionalization products with more stable *E*-selectivity.[3,6,7] On the contrast, the realization of *Z*-selective allylic C–H functionalizations is more challenging and remains elusive.[8] On the other hand, organothianthrenium salts could be easily prepared from arenes and alkenes by thianthrenation using stoichiometric thianthrene S-oxide or phenoxathiine 10-oxide as the mediators, which could serve as the precursors for both cross-coupling reactions and radical processes.[9] This two-step strategy creates potential chemical space for manipulating the C–H bond of arenes and alkenes. Recently, the Ritter group reported seminal work on selective C–H functionalizations of arenes *via* thianthrenation, providing access to diverse chemical bonds from aryl C–H bonds (Scheme 1b).[10] The Wang group developed the Pd-catalyzed site-selective C–H borylation and arylation of arenes by employing the same strategy (Scheme 1b).[11] Recently, the Shi group developed the utilization of alkyl thianthrenium salts for C–B and C–C bond formation.[12] The Wickens group reported the electrochemical synthesis of 1,2-disubstituted thianthrenium salts from alkenes and thianthrene, which were used as the key intermediates to produce aziridines by C–N formation.[13] In 2020, the Ritter group developed elegant examples of C–H functionalizations of alkenes *via* the isolated vinyl thianthrenium salts, leading to alkylation, alkynylation, arylation, halogenation, and trifluorosulfinylation



Scheme 1 Impetus for metal-free allylic C–H functionalizations using thianthrenium salts.

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of alkenes (Scheme 1b).[14] Despite the promising progress, all the above-mentioned C–H functionalization reactions are restricted to *ipso*-functionalizations of arenes or alkenes *via* thianthrenation by replacing the C–S bond in the thianthrenium salts. Yet, no example of C–H functionalization at the allylic position of alkenes was reported. Herein, we report the metal-free selective allylic C–H functionalizations of alkenes *via* thianthrenation (Scheme 1c). The mild conditions allow for the allylic C–H nitrogenation, oxygenation, and carbonation of alkenes at room temperature by the formation of C–O, C–C, and C–N bonds, affording diverse esterifications, thioesterifications, etherifications, aminations, and arylations of allylic C–H bonds.[15] Notably, the metal-free C–H functionalizations deliver allylic esters, ethers, amines, ammonium salts, and amides with preferred *Z*-selectivity.[16]

Results and discussion

We started to investigate the reaction of cyclohexylvinylthianthrenium salt **1a** with benzoic acid **2a**. Interestingly, translocation of the alkene by allylic C–H functionalization was observed, affording 1,1,2-trialkyl substituted alkene **3a** instead of *ipso*-vinyl substitution of vinylthianthrenium. After evaluation of a variety of reaction parameters, we defined the use of potassium carbonate (1.0 equiv.) as the base in DCM (0.1 M) at room temperature as standard conditions, delivering the desired product **3a** in 91% isolated yield (Table 1, entry 1). The use of other bases could also mediate the reaction. Cesium carbonate and potassium phosphate tribasic delivered **3a** in 85% and 72% yields, respectively (Table 1, entries 2 and 3). Lithium carbonate led to no formation of **3a** (Table 1, entry 4). The reaction proceeded in most tested solvents, including polar and nonpolar solvents, furnishing the desired product **3a** in 47–88% yields (Table 1, entries 5–9).[17]

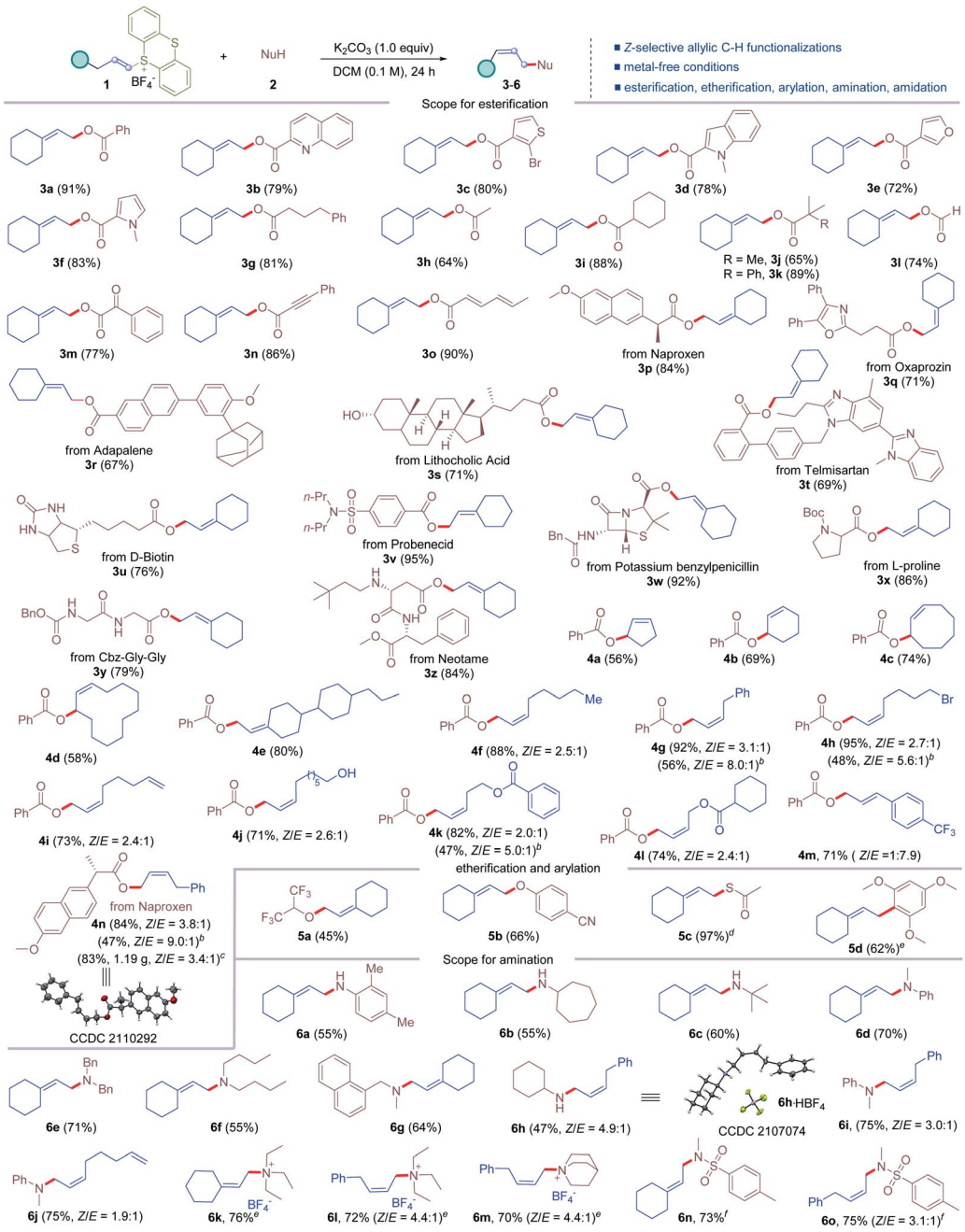
Table 1 Condition development of the reaction[a]

Entries	Variations as shown	Yield of **3a**
1	None	92% (91%)[b]
2	Cs_2CO_3 as base	85%
3	K_3PO_4 as base	72%
4	Li_2CO_3 as base	N.D.
5	DCE as solvent	88%
6	CH_3CN as solvent	82%
7	Acetone as solvent	69%
8	THF as solvent	47%
9	Toluene as solvent	81%

[a] The reaction was conducted using **1a** (0.1 mmol) and **2a** (0.12 mmol) at room temperature for 24 h. Yield was determined by ^{1}H NMR of the crude mixture using mesitylene as the internal standard. [b] Isolated yield after flash chromatography.

With the optimized conditions established, we turned to evaluate the scope of this reaction. It is found that the reaction conditions tolerate a variety of vinylthianthrenium salts and different nucleophiles with broad functional group and substitution pattern compatibility (Table 2). First, the scope of allylic C–H esterification was examined. A surprisingly wide range of carboxylic acids were tolerated (**3a–3o**). Aromatic and heteroaromatic carboxylic acids, such as quinoline carboxylic acid, thiophene carboxylic acid, indole carboxylic acid, furan carboxylic acid, and pyrrole carboxylic acid, could be involved in the reaction to deliver the allylic C–H esterification products (**3b–3f**) in 72–83% yields. Aliphatic acids, including α-linear, α-branched and α-tertiary carboxylic acids, are good substrates for this metal-free C–H functionalization process, giving corresponding esters (**3g–3k**) in 64–89% yields. Formic acid could form allylic formic ester **3l** in 74% yield. Benzoylformic acid could form corresponding ester **3m** in 77% yield *via* allylic C–H functionalization. Propiolic acid was tolerated to give corresponding allylic ester **3n** in 86% yield. Conjugated dienoic acid was converted to **3o** in 90% yield, leaving the conjugated diene intact. Moreover, this protocol was applicable to late-stage functionalization of complex molecules. Naproxen was transformed into corresponding allylic ester **3p** in 84% yield without affecting the stereogenic center. Oxaprozin, adapalene, lithocholic acid, telmisartan, D-biotin, and probenecid were all good substrates for this allylic C–H esterification reaction, furnishing corresponding esters (**3q–3v**) in 67–95% yields. Potassium benzylpenicillin was compatible in the reaction, delivering the esterification product **3w** in 92% yield in high chemoselectivity, without the formation of the *N*-allylation product. Notably, the reaction tolerated a wide range of natural and unnatural amino acids and peptides. *N*-Boc protected L-proline was successfully converted to allylic ester **3x** in 86% yield. Peptides, such as CBz-Gly-Gly and neotame underwent allylic C–H esterification selectively to leave free amide and amine unreactive, affording **3y** and **3z** in 79% and 84% yields, respectively. Next, the scope of vinylthianthrenium salts was investigated. Five, six, and eight-membered cyclic alkenes could be involved to undergo allylic C–H oxygenation with benzoic acid to furnish cyclic allylic esters (**4a–4c**) in 56–74% yields. Cyclododecene was converted to corresponding allylic ester **4d** in 58% yield with exclusive *Z*-selectivity. A mixture of isomers of alkene-derived thianthrenium salt delivered a single isomer of the corresponding allylic C–H oxygenation product **4e** in 80% yield. It is noteworthy that 1-substituted alkene based thianthrenium salts were converted to allylic esterification products smoothly. Surprisingly, the reaction delivered 1,2-substituted alkenes favoring *Z*-selectivity. Alkenes with pendant bromides, alkenes, alcohols, and esters were all compatible in the reaction, leading to the esterification of allylic C–H bonds in 56–95% yields with 2.0 : 1–3.1 : 1 ratios of *Z*-selectivity (**4f–4l**). Additionally, 3-phenyl-1-propene derived thianthrenium salt furnished styrene type allylic ester **4m** in 71% yield with E/Z = 7.9 : 1. Moreover, the reaction could be easily scaled up. The reaction on a 4.0 mmol scale afforded 1.19 g of **4n** in 83% yield. Notably, the *Z*-selectivity could be further improved up to 9.0 : 1 (**4g**, **4h**, **4k**, and **4n**) using pentamethyldiethylenetriamine

Table 2 Scope of the metal-free allylic C–H functionalizations using vinyl thianthrenium salts[a]

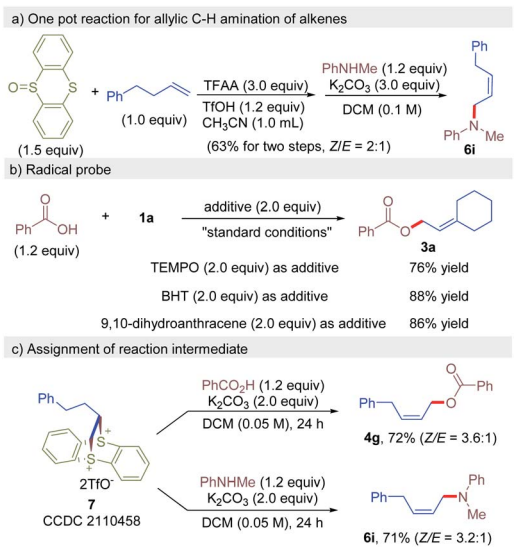


[a] The reaction was conducted on a 0.2 mmol scale. Standard conditions, see Table 1 for details. [b] PMDTA (pentamethyldiethylenetriamine, 1.0 equiv.) was used as the base with a nucleophile (2.0 equiv.) in DCE (0.05 M). [c] 4.0 mmol scale reaction. [d] Potassium thioacetate and H_2O (0.2 μL) were used. [e] The reaction was conducted using amine (2.0 equiv.) and H_2O (0.2 μL). [f] KOH (1.0 equiv.) was used as the base.

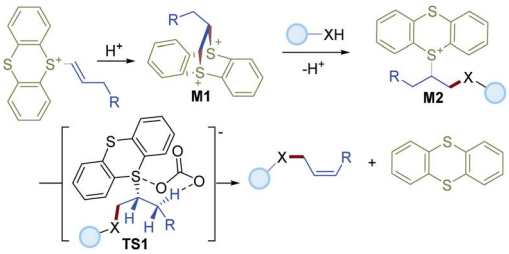
(PMDTA) as the base, probably due to the rigid configuration with a more sterically hindered base. The configuration of the major product was confirmed unambiguously by X-ray diffraction of **4n**. Next, the application of allylic C–H functionalization to other nucleophiles was examined. Allylic C–H etherification was successful using both alcohols and phenols as the nucleophile, furnishing alkyl and phenyl allylic ethers (**5a** and **5b**) in 45% and 66% yields. Thioesterification of the allylic C–H bond was achieved in 97% yield (**5c**) using potassium thioacetate. Allylic C–H arylation was also accomplished in 62% yield (**5d**) with trimethoxybenzene as the nucleophile. Moreover, allylic C–H amination was also demonstrated. Primary anilines and aliphatic amines were all well tolerated, delivering allylic secondary amines (**6a–6c**) in 55–60% yields. Secondary amines with different substitution patterns were all good substrates for this reaction, giving diverse allylic tertiary amines (**6d–6g**) in 55–

71% yields. Monosubstituted alkene based thianthrenium salts were converted to *Z*-selective 1,2-disubstituted allylic amines in 47–75% yields with 1.9 : 1–4.9 : 1 ratios (**6h–6j**). The configuration of the major isomer of allylic amines was further confirmed by the X-ray diffraction of the salt of **6h**. Impressively, tertiary amines were also compatible in the allylic C–H amination reaction to afford allylic trialkyl ammonium salts in 70–76% yields (**6k–6m**). When 4-phenyl-1-butene derived thianthrenium salt was exposed to the reaction conditions with triethyl amine and quinuclidine, the desired allylic ammonium salts were obtained in 72% and 70% yields (**6l** and **6m**), favoring *Z*-selectivity of 4.4 : 1. Notably, allylic C–H sulfonyl amidation of vinyl thianthrenium salts was also successful, affording corresponding allylic sulfonyl amides in 73% and 75% yields (**6n** and **6o**), respectively.

Next, a one-pot operation from an alkene and thianthrene-oxide, followed by a nucleophile was demonstrated to prove the practicality of this reaction (Scheme 2a). The one pot reaction of 4-phenyl-1-butene with thianthrene *S*-oxide, followed by *N*-methylaniline afforded the desired allylic amine **6i** in 63% yield without any workup or intermediate purification, which is comparable to previous results of step-wise procedure. Next, the reaction of **1a** with **2a** was conducted in the presence of a radical scavenger under otherwise identical to standard conditions (Scheme 2b). It is shown that the reaction proceeded smoothly in the presence of TEMPO, BHT or 9,10-dihydroanthracene, affording the desired product **3a** without affecting the efficacy. These results exclude the involvement of radical intermediates in this reaction. To further probe the mechanism of the reaction, a dithianthrenium salt **7** was subjected to the reaction with benzoic acid or *N*-methylaniline, and corresponding allylic C–H esterification product **4g** and amination product **6i** were obtained in 72% and 71% yield, respectively (Scheme 2c). The yield and stereoselectivity are comparable to the results obtained using corresponding vinylthianthrenium. These results



Scheme 2 One-pot synthesis and control experiments.



Scheme 3 Proposed mechanism for the reaction.

indicate that dithianthrenium salt could serve as the reactive intermediate for this reaction.

Based on the literature and the experimental results, a plausible mechanism is described in Scheme 3. First, intramolecular attack of sulfur on the alkene moiety of vinylthianthrenium salt could deliver the dithianthrenium salt **M1**, which could further undergo site-selective ring-opening by intermolecular attack by a nucleophile to give an alkylthianthrenium salt intermediate **M2**. In the presence of a base, **M2** would undergo a *syn*-elimination *via* **TS1** to give the final allylic C–H functionalization product in favor of *Z*-selectivity.

Conclusions

In summary, a unified transition-metal-free protocol for diverse functionalizations of allylic C–H bonds of alkenes by thianthrenation under mild conditions has been demonstrated for the first time. Notably, the reaction features *Z*-selectivity to afford multi-alkyl substituted allylic esters, thioesters, ethers, primary, secondary, tertiary amines, amides, and arenes in good yields without incorporation of any transition-metals. The one-pot procedure proved efficient to access direct allylic C–H functionalizations of alkenes. The reaction tolerates a wide range of O-, N-nucleophiles with excellent functional group tolerance, and could be applied to late-stage functionalizations of natural products, amino acids, and drug-like molecules with excellent chemoselectivity.

Data availability

Experimental data has been provided as ESI.†

Author contributions

M. S. L. discovered the reactions. W. S. and M. S. L. designed the experiments. M. S. L. and H. W. D performed and analysed the experiments. W. S. and M. S. L. wrote the manuscript. All authors discussed the experimental results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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17 For more details on the condition optimization, see ESI.†