Metal-Free Z-Selective Allylic C-H Nitrogenation, Oxygenation, and Carbonation of Alkenes by Thianthrenation

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Abstract: Selective functionalization of allylic C-H bonds into other chemical bonds with Z-selectivity are 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 thiathrenium salts. Notably, the reaction preferably provides multialkyl substituted allylic amines, esters, and ethers with Z-selectivity. 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.

Methods for direct allylic C-H functionalizations are among the most attractive transformations to streamline organic synthesis as it maximizes the step- and atom-economy to generate stereodefined allylic species amenable to further chemical transformations, thus minimizing the cost and waste.1-8 Traditional allylic C-H functionalization reactions generally require the catalysis of transition-metals such as Pd, Cu, and Ir, in which involve the formation of an allyl-metal complex via C-H activation followed by being attacked by an intra- or intermolecular nucleometallation (Fig. 1a).9-28 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.21,29-35 These two strategies proved to be powerful for organic synthesis and extensively investigated. The stereochemistry outcomes heavily rely on the property of transition-metals and anchoring ligands and are mostly dominated by thermodynamic control, leading to the formation of C-H functionalizaiton products with more stable E-selectivity.9,24,36-44 On the contrast, the realization of Z-selective allylic C-H functionalizations is more challenging and remains elusive.45-47 On the other hands, organothiathrenium 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 precesses.48,49 This two-step strategy arises potential chemical space for
manipulating C-H bond of arenes and alkenes. Recently, 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 (Fig. 1b).\cite{50-57} Wang group developed the Pd-catalyzed site-selective C-H borylation and arylation of arenes by employing the same strategy (Fig. 1b).\cite{58-60} Recently, Shi group developed the utilization of alkyl thianthrenium salts for C-B and C-C bond formation.\cite{61,62} 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.\cite{63} In 2020, Ritter group developed elegant examples of C-H functionalizations of alkenes via the isolated vinyl thianthrenium salts, giving alkylation, alkynylation, arylation, halogenation, and trifluorosulfonylation of alkenes (Fig. 1b).\cite{64,65} Despite the promising progress, all the above-mentioned C-H functionalization reactions are restricted to \textit{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 reported the metal-free selective allylic C-H functionalizations of alkenes via thianthrenation (Fig. 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, arylation of allylic C-H bonds.\cite{66} Notably, the metal-free C-H functionalizations deliver allylic esters, ethers, amines, ammonium salts, and amides with preferred Z-selectivity.

![Fig. 1](image.png)

**Fig. 1** Impetus for metal-free Z-selective allylic C-H functionalizations of thianthrenium salts

We started to investigate the reaction by using cyclohexylvinylthiathiarenium salt \textbf{1a} with benzoic acid \textbf{2a}. Interestingly, translocation of alkene by allylic C-H functionalization was observed, affording 1,1,2-trialkyl substituted alkene \textbf{3a} instead of \textit{ipso}-vinyl substitution of vinylthiathrenium. After evaluation of a variety of reaction conditions.
parameters, we defined the use of potassium carbonate (1.0 equiv) as 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).

**Table 1.** Condition development of the reaction.

| entries[a] | Variation from “standard conditions” | yield of 3a |
|------------|--------------------------------------|-------------|
| 1          | none                                 | 92% (91%)b  |
| 2          | Cs2CO3 as base                       | 85%         |
| 3          | K3PO4 as base                        | 72%         |
| 4          | Li2CO3 as base                       | N.D.        |
| 5          | DCE as solvent                       | 88%         |
| 6          | CH3CN 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 1H NMR of the crude mixture using mesitylene as 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 vinylthiophenium salts and different nucleophiles with broad functional group and substitution pattern compatibility (Fig. 2). First, the scope for 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, 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 to corresponding allylic ester 3p in 84% yield without erasing 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 benzylenicillin was compatible in the reaction, delivering the esterification product 3w in 92% yield in high chemoselectivity, without detecting 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 vinylthiathrenium salts was investigated. Five, six, seven-membered cyclic alkenes could be involved to undergo allylic C-H oxygenation with benzoic acid to furnish cyclic allylic esters (4a-4e) 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 thiathrenium 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 thiathrenium salts were converted to allylic esterification products smoothly. Surprisingly, the reaction delivered 1,2-substituted alkenes favored Z-selectivity. Alkenes with pendant bromides, alkenes, alcohols, esters were all compatible in the reaction, delivering the esterification of allylic C-H bonds in 56-95% yields with 2.0:1-3.8:1 ratios of Z-selectivity (4f-4m). Notably, the Z-selectivity could be further improved up to 9.0:1 (4g, 4h, 4k, and 4m) using pentamethyldiethylenetriamine (PMDTA) as the base. The configuration of the major product was confirmed unambiguously by X-ray diffraction of 4m. Moreover, the reaction could be easily scaled up. The reaction on 4.0 mmol scale afforded 1.19 g of 4m in 83% yield. Next, the application of allylic C-H functionalization was extended 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 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, aliphatic amines were all well tolerated, delivering allylic secondary amines (6a-6c) in 55-72% 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 thiathrenium salts were converted to Z-selective 1,2-disubstituted allylic amines in 47-75% yields with 1.9:1-4.9:1 ratio (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 allylic C-H amination reaction to afford allylic trialkyl ammonium salts in 70-76% yields (6k-6m). When 4-phenyl-1-butene derived thiathrenium salt was exposed in 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 in 4.4:1. Notably, allylic C-H sulfonyl amidation of vinyl thiathrenium salts were also successful, affording corresponding allylic sulfonyl amides in 73% and 75% yields (6n and 6o), respectively.
Fig. 2 Scope for the metal-free allylic C-H functionalizations of vinyl thianthrenium salts.  

The reaction was conducted on 0.2 mmol scale. Standard conditions, see Table 1 for detail.  

PMDTA (pentamethyldiethylenetriamine, 1.0 equiv) was used as base with nucleophile (2.0 equiv) in DCE (0.05 M).  

Potassium thioacetate and H2O (0.2 μL) were used.  

The reaction was conducted using amine (2.0 equiv), H2O (0.2 μL).  

KOH (1.0 equiv) was used as base.
To demonstrate the practicality of this reaction, a one-pot operation from an alkene and thianthreneoxide, followed by a nucleophile was demonstrated (Fig. 3a). The one pot reaction from 3-phenyl-1-propene, followed by N-methylaniline could afford the desired allylic amine \(6d\) in 63% yield without any workup or intermediate purification, which is comparable to previous result. Next, the reaction of \(1a\) with \(2a\) was conducted in the presence of a radical scavenger under otherwise identical to standard conditions (Fig. 3b). It is shown that the reaction proceeded smoothly in the presence of TEMPO, BHT or 9,10-dihydroanthracene, affording the desired product \(3a\) without erasing the efficacy. These results exclude the involving of radical intermediates in this reaction.

To further probe the mechanism of the reaction, a dithianthrenium salt \(7\) was submitted to the reaction with benzoic acid or N-methylaniline, corresponding allylic C-H esterification product \(4g\) and amination product \(6d\) were obtained in 72% and 71% yield, respectively (Fig. 3c). The yield and stereoselectivity are comparable to the results of using corresponding vinylthianthrenium. These results indicated dithianthrenium salt could serve as the reactive intermediate for this reaction.

Based on literature and the experimental results, a plausible mechanism is described in Fig. 4. First, intramolecular attack of sulfur on 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.
Fig. 4 Proposed mechanism for the reaction.

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. One-pot procedure proved efficient to access direct allylic C-H functionalizations from 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.

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Selective functionalization of allylic C-H bonds into other chemical bonds with Z-selectivity are 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 thianthrene was developed. This operationally simple protocol allows for the unified allylic C-H amination, esterification, etherification, and arylation of vinyl thianthrene salts. Notably, the reaction preferably provides multi-alkyl substituted allylic amines, esters, and ethers with Z-selectivity. 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.