General and Practical Metal-Free Aziridination and Cyclopropanation of XH_2 (X = N, C) with Alkenes by Thianthrenation

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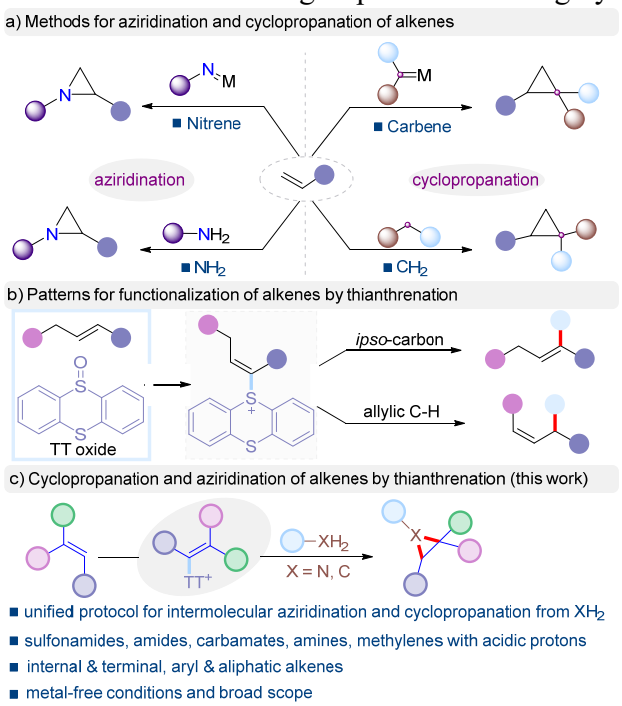
Abstract: Three-membered cyclic structures are widely existing in natural products and serve as enabling intermediates in organic synthesis. However, the efficient and straightforward access to such structures with diversity remains a formidable challenge. Herein, a general and practical protocol to aziridines and cyclopropanes synthesis using free XH_2 (X = C or N) with alkenes by thianthrenation is presented. This metal-free protocol features the direct aziridination and cyclopropanation of unprotected NH_2 under mild conditions. Free sulfonamides, amides, carbamates, amines, and methylene with acidic protons, are good precursors for three-membered ring formation, providing an attractive alternative for straightforward synthesis of aziridines and cyclopropanes from easily available starting materials.

Three-membered cycles, particularly cyclopropanes and aziridines, are prevalent structural units in natural products and bioactive molecules.[1,2] Due to the intrinsic substantial ring-strain of three-membered ring systems, ring-opening reactions render cyclopropanes and aziridines versatile building blocks for organic synthesis.[3,4] Consequently, the development of efficient methods to build aziridines and cyclopropanes is one of the contemporary subjects in synthetic chemistry.[1,5-8] Among various efforts, transforming of readily-available and cost-effective alkenes into aziridines and cyclopropanes is the most attractive synthetic strategy. Most classical and reliable methods to cyclopropanes and aziridines rely on the transition-metal catalyzed cyclopropanation and aziridination of alkenes from carbene and nitrene precursors have been extensively explored (Scheme 1a, top).[6-13] Metal-catalyzed cyclopropanations of alkenes generally use metal carbene species generated from α-diazocarbonyl compounds.[6,10,14,15] Aziridinations of alkenes require the use of suitable and activated nitrene precursors, such as iminoiodinanes and azides in the presence of a transition-metal (Cu, Rh, Co, Fe, Pd, Au).[9,12,16-19] These methods are limited to the use of hazardous and explosive carbene and nitrene precursors as well as additional steps for diazo synthesis and transition-metal residue removal. These limitations stimulated the development of more efficient and sustainable alternatives to access cyclopropanes and aziridines from free XH_2 (X = C, N). To this end, new methods utilizing electrochemical activation to undergo oxidative cyclization have been devised (Scheme 1a, bottom).[20] In 2022, Xu developed an electrochemistry enabled intramolecular cyclopropanation of aliphatic alkenes with active methylene compounds.[21] Intermolecular cyclopropanations of alkenes from active methylenes is unsuccessful and remains unknown. Yudin,[22] Little,[23] and Cheng[24] developed electrochemical aziridination of alkenes using *N*-amino-phthalimide ($PhtNH_2$) and trifluoromethylated sulfamate ($HfsNH_2$) as the source of electrophilic nitrogen source. In 2021, Noël developed an elegant example of electrochemical aziridination of internal styrenes with primary amines.[25] Terminal alkenes, aliphatic alkenes, amides, carbamates, sulfonamides remain problematic. In the same year, Wickens reported electrochemical aziridination of terminal aliphatic alkenes with aliphatic primary amines.[26] Overall, existing protocols for cyclopropanations and

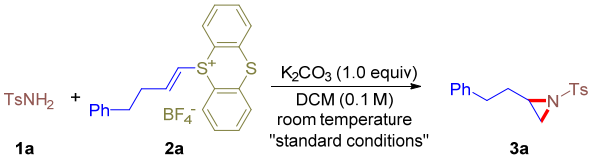
aziridinations of alkenes suffer from significant limitations and challenges from different aspects. Thus, a general, straightforward, and metal-free method to access cyclopropanes and aziridines from free XH_2 (X = C or N) and diverse alkenes with broad functional group tolerance is highly desirable.



Scheme 1. Impetus for Metal-Free Aziridination and Cyclopropanation of Free XH_2 with Alkenyl Thianthrenium Salts.

On the other hand, synthesis of aryl thianthrenium salts from arenes was first developed by Shine in 1965.[27,28] Over the past years, Ritter flourishes the direct functionalization of arene C-H bonds via the formation of aryl thianthrenium salts.[29-36] Recently, Ritter and others developed the *ipso*-functionalization of aryl and alkenyl thianthrenium salts via metal-catalyzed cross-coupling and radical reactions (Scheme 1b, top).[37-52] In 2021, Wickens and our group independently reported the functionalization of alkenes by thianthrenation to formally transform allylic C-H bond to form C-C, C-O, and C-N bonds with C-, O-, and N-based nucleophiles (Scheme 1b, bottom).[53,54] Herein, a general and practical protocol for cyclopropanation and aziridination using free XH_2 (X = C and N) with alkenes by thianthrenation was developed (Scheme 1c). Notably, free amides, sulfonamides, amines, carbamates, and methylenes with acidic protons are used as the precursors. The metal-free condition allows for the direct cyclopropanation and aziridination of terminal and internal alkenes as well as aromatic and aliphatic alkenes.

Table 1. Condition development of the reaction.



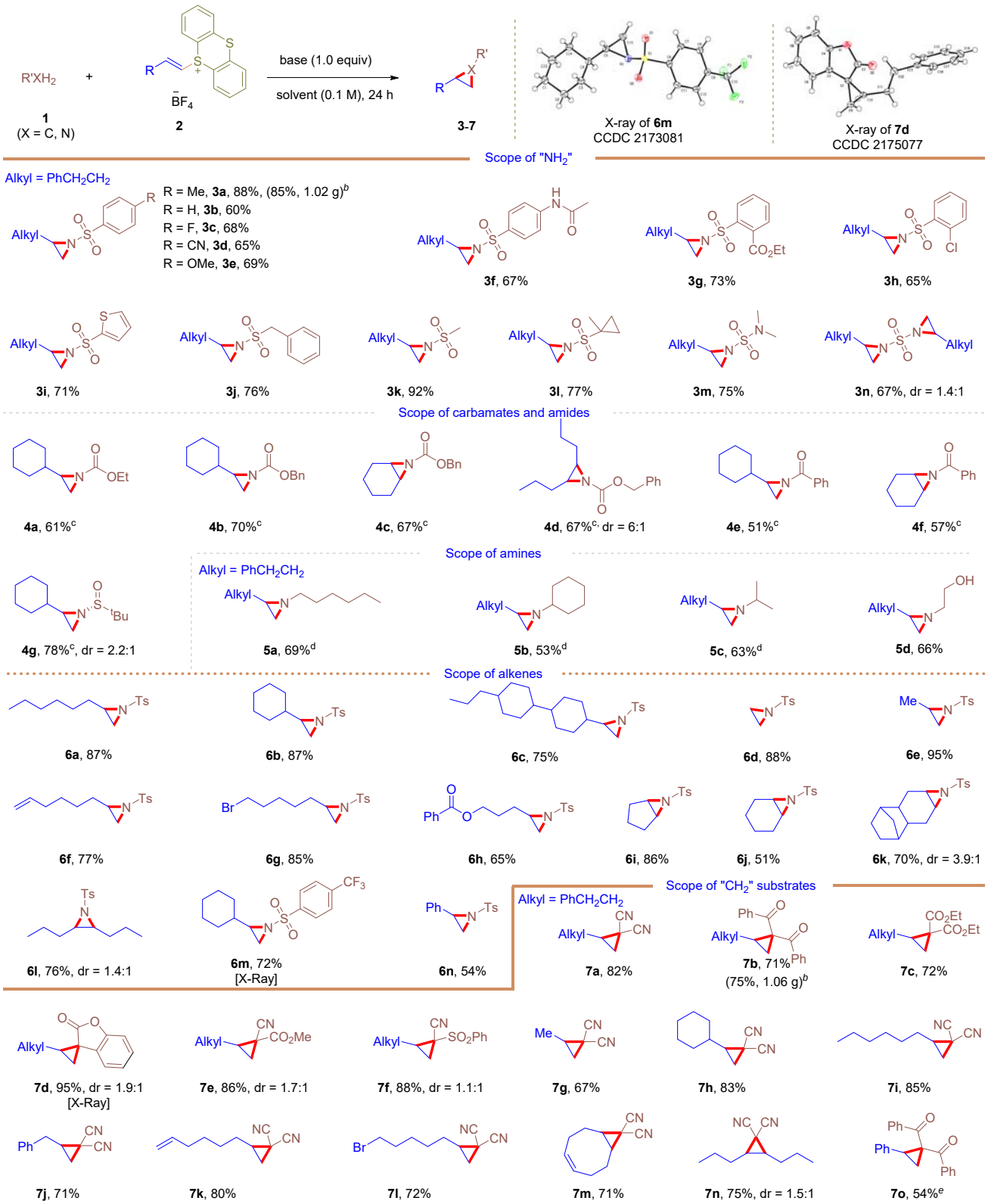
entry	variation from "standard conditions"	yield of **3a**
1	none	94% (88%)[b]
2	Na_2CO_3 as base	90% (85%)[b]
3	NaO^{t}Bu as base	78%
4	Cs_2CO_3 as base	86%
5	KOH as base	70%
6	DCE as solvent	83%
7	CH_3CN as solvent	25%

8	THF as solvent	63%
9	DMSO as solvent	N.D.

[a] The reaction was conducted using **1a** (0.12 mmol) and **2a** (0.10 mmol) at room temperature for 24 h. Yield was determined by ^{1}H NMR of the crude mixture using mesitylene as internal standard. N.D. = not detected. [b] Isolated yield after flash chromatography.

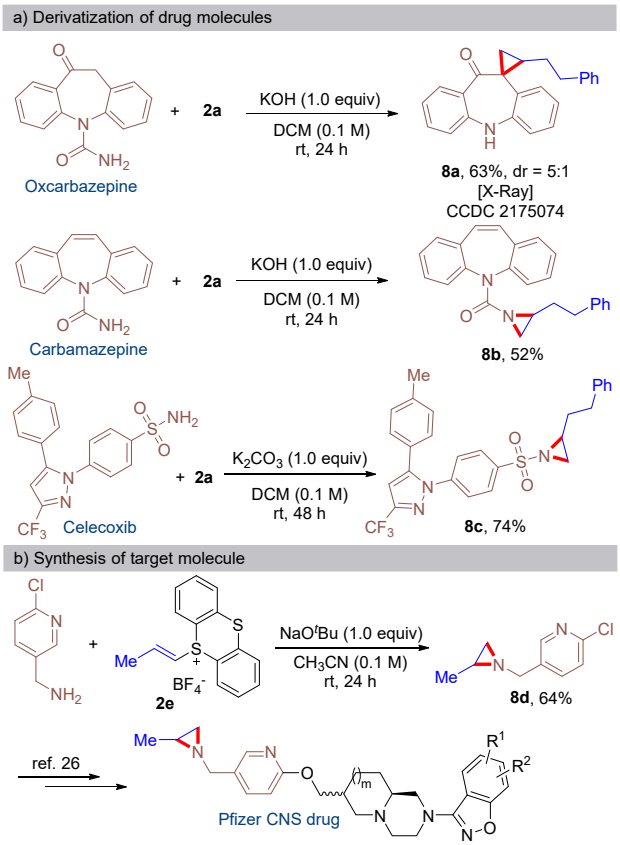
We started our investigation by employing *p*-toluene sulfonamide **1a** with 4-phenylbut-1-vinylthianthrenium salt **2a** as model substrates (Table 1). To our delight, *N*-tosyl aziridination of the C=C bond of vinyl thianthrenium salt was exclusively formed, without formation of previously reported allylic C-H nitrogenation product.[54] After evaluation of various reaction parameters, we define the use of potassium carbonate (1.0 equiv) as base in DCM (0.1 M) at room temperature as standard conditions, delivering the desired *N*-tosylaziridine **3a** in 88% isolated yield (Table 1, entry 1). Using sodium carbonate (1.0 equiv) instead of potassium carbonate as base delivered **3a** in comparable yield (Table 1, entry 2). Additionally, the use of stronger base, such as sodium *tert*-butoxide, cesium carbonate, or potassium hydroxide as base delivered **3a** in 70%-86% yields (Table 1, entries 3-5). Evaluation of solvent effect revealed that the reaction proceeded smoothly in most tested solvents, affording the desired product **3a** in 25%-83% yields (Table 1, entries 6-8). However, no desired product **3a** was detected in DMSO (Table 1, entry 9).

With the optimized conditions established, we turned to evaluate the scope of the aziridination and cyclopropanation of alkenes with free XH_2 (X= N, C) by thianthrenation (Scheme 2). Impressively, this protocol tolerates a wide range of free amides, amines, and active methylenes to form strained three-membered cycles with a variety of alkenyl thianthrenium salts, with broad functional group tolerance and substitution pattern compatibility. First, the scope of aziridination reaction with free NH_2 was examined. A wide range of sulfonamides are suitable for this reaction, delivering corresponding aziridines in good yields (**3a**-**3n**). *para*-Substituted aryl sulfonamides with electron-withdrawing (**3c** and **3d**) or electron-donating (**3e** and **3f**) groups were all well-tolerated in the reaction to give corresponding aziridination products in good yields. Aryl sulfonamides with other substitution patterns are also good substrates for this reaction (**3g** and **3h**). Heteroaryl sulfonamides underwent aziridination to give **3i** in 71% yield. Moreover, aliphatic free sulfonamides with acidic protons worked well for this metal-free aziridination process, furnishing corresponding aziridines (**3j** and **3l**) in 76% and 92% yields, respectively. Sterically congested α-tertiary sulfonamides proceeded smoothly to deliver corresponding aziridine **3l** in 77% yield. Impressively, sulfuric diamides could undergo mono- and bis-aziridination with alkenyl thianthrenium salt **2a** to deliver corresponding products (**3m** and **3n**) in 75% and 67% yields. Notably, free carbamates and amides could react with diverse alkenyl thianthrenium salts to form corresponding aziridines (**4a**-**4f**) in 51%-70% yields. Interestingly, enantioenriched aziridines could be obtained by the aziridination reaction of commercially available (*R*)-2-methyl-2-propanesulfinamide with alkenyl thianthrenium salt, affording **4g** in 78% yield with 2.2:1 dr. Additionally, aliphatic primary amines, are good substrates for this cyclization process, giving corresponding aziridines (**5a**-**5d**) in 53%-69% yields. Next, the scope of alkenyl thianthrenium salts was investigated (**6a**-**6n**). Linear and α-branched terminal alkene based thianthrenium salts are all compatible in this reaction, generating the corresponding aziridination products in 75%-87% yields (**6a**-**6c**). It is noteworthy that gaseous alkenes could be efficiently involved in the aziridination process by thianthrenation, giving **6d** and **6e** in 88% and 95% yields, respectively. Moreover, aliphatic alkenyl thianthrenium salts with pendant alkenes, bromides, esters were all compatible in the reaction, delivering the desired aziridines (**6f**-**6h**) in 65-85% yields with chemical space for further elaboration. Both cyclic and acyclic internal aliphatic alkenes derived thianthrenium salts were amenable to the reaction, affording diverse aziridines 51%-86% yields (**6i**-**6l**). Notably, fused cyclic systems were obtained using cyclic alkenes (**6i**-**6k**). The structure of the aziridines was confirmed unambiguously by X-ray diffraction of **6m**. Additionally, styrenes also worked for the reaction to afford **6n** in 54% yield. Next, we turned to test the scope of cyclopropanation reaction using methylenes with alkenyl thianthrenium salts. Disubstituted methylenes with different electron-withdrawing groups are good



Scheme 2. Scope of Metal-Free Aziridination and Cyclopropanation of Alkenyl Thianthrenium Salts[a]
[a] Standard conditions, see Table 1 for details. [b] 4.0 mmol scale reaction. [c] KOH (1.0 equiv) was used as the base. [d] NaO^{t}Bu (1.0 equiv) was used as the base in CH_3CN (0.1 M). [e] Nucleophile (1.0 equiv) and thianthrenium salt (2.0 equiv) were used.

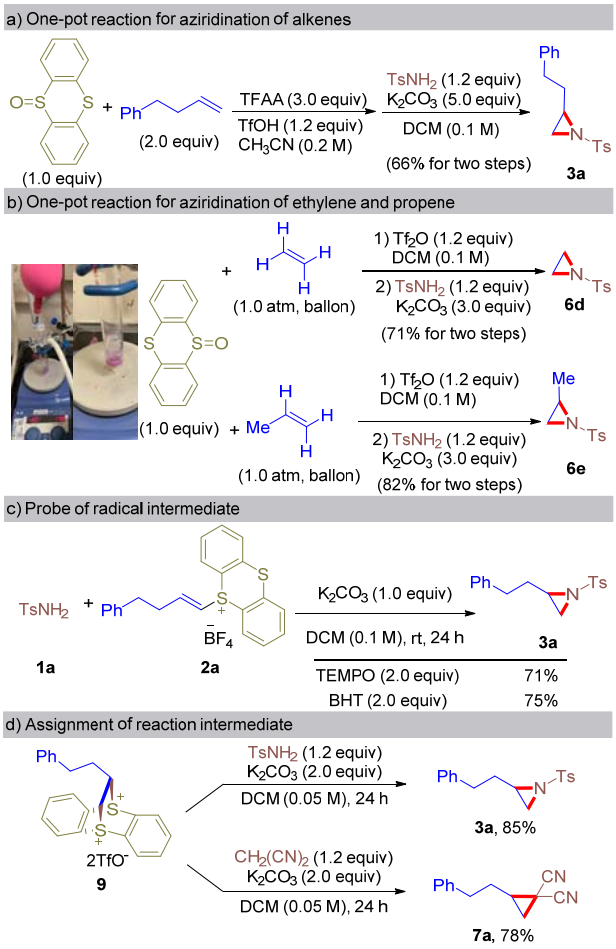
substrates for this metal-free cyclopropanation reaction, giving corresponding cyclopropanes with diverse substitution patterns (**7a-7f**) in good to excellent yields (71%-95%). Linear and α-branched alkenes were all compatible with this cyclopropanation, generating corresponding cyclopropanes (**7g-7j**) in 67%- 85% yields. Isolated alkenes and bromides were tolerated in the reaction, leading to the cyclopropanes (**7k** and **7l**) in 80% and 72% yields. Cyclic and acyclic internal alkenes were successfully transformed into cyclopropanes (**7m** and **7n**) in 71% and 53% yields. Styrenes were able to undergo cyclopropanation under the conditions to afford **7o** in synthetic useful yield. The structure of the cyclopropanes was confirmed unambiguously by X-ray diffraction of **7d**. In addition, the mild conditions are amenable to large-scale synthesis of aziridines and cyclopropanes without diminishing the efficiency. The reaction of sulfonamide **1a** with alkenyl thianthrenium salt **2a** (4.0 mmol) under standard conditions afforded 1.02 g of aziridine **3a** in 85% yield. The use of dibenzoylmethane with **2a** (4.0 mmol) furnished **7b** (1.05 g) in 75% yield.



Scheme 3. Target Molecule Derivatization and Synthesis.

To further prove the usefulness of this protocol, drug molecules and target synthesis have been demonstrated (Scheme 3). It is noteworthy that Oxcarbazepine underwent chemoselective cyclopropanation reaction of methylene instead of the aziridination urea with **2a** to give cyclopropane product **8a** in 63% yield under standard conditions. The structure of **8a** was confirmed by the X-ray diffraction analysis. Interestingly, the reaction of Carbamazepine with **2a** underwent the aziridination of NH_2 of urea to form the aziridine **8b** in 52% yield. In addition, Celecoxib was tolerated under the reaction

conditions, delivering Celecoxib derived aziridine **8c** in 74% yield. Furthermore, this strategy was successfully applied to the synthesis of aziridine **8d** in 64% yield from the reaction of (6-chloropyridin-3-yl)methanamine with **2e**, which serves as a common intermediate for the synthesis of patented agonists of the dopamine D2 and 5-hydroxytryptamine (5-HT) 1B and 2A receptors.[26]

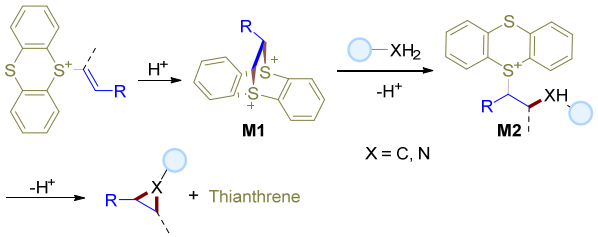


Scheme 4. One-Pot Procedure and Control Experiments.

To improve the practicality of this method, a one-pot procedure to access aziridine from alkenes, thianthrene *S*-oxide, and amides was demonstrated (Scheme 4a). The one-pot reaction of 4-phenyl-1-butene and thianthrene *S*-oxide, followed by addition of *p*-toluene sulfonamide afforded the desired aziridine product **3a** in 66% yield without any workup or intermediate purification. Notably, the one-pot reaction is also amenable to aziridination of gaseous feedstock alkenes, such as ethylene and propene, furnishing corresponding aziridines (**6d** and **6e**) in 71% and 82% yields, respectively (Scheme 4b). Next, a series of control experiments were conducted to probe the mechanism of the reaction. The reaction of **1a** with **2a** in the presence of a radical scavenger (TEMPO or BHT) was conducted under otherwise identical to standard conditions, furnishing the desired aziridine **3a** in 71% and 75% yields (Scheme 4c). The results showed that the presence of TEMPO or BHT did not affect he efficiency of this reaction, ruling out the radical pathway of this reaction. To further probe the mechanism of the reaction, a

dithianthrenium salt **9** was subjected to the reaction with *p*-toluenesulfonamide or malononitrile under standard conditions (Scheme 4d). Corresponding aziridine **3a** and cyclopropane **7a** were obtained in 85% and 78% yield, suggesting dithianthrenium salt might serve as the intermediate for this three-membered ring-forming process.

Based on the experimental results and literature,[26,53,54] a plausible mechanism is proposed and depicted in Scheme 5. First, the dithianthrenium salt **M1** was formed by intramolecular attack of sulfur on the olefinic moiety of the vinyl thianthrenium salt. Then, **M1** could undergo site-selective ring-opening by intermolecular attack of C- or N-nucleophile in the presence of a base to give the alkyl thianthrenium salt intermediate **M2**. Under the basic conditions, **M2** could selectively undergo intramolecular nucleophilic substitution to afford aziridines and cyclopropanes by releasing the thianthrene.



Scheme 5. Proposed Mechanism for the Reaction.

In summary, a unified protocol for intermolecular aziridination and cyclopropanation of alkenes was achieved by thianthrenation under transition-metal-free conditions for the first time. This operationally simple protocol features: 1) Aziridination and cyclopropanation of alkenes with free XH_2 (X = N, C) without protection or pre-functionalization. 2) A variety of nucleophiles, including free amides, sulfonamides, amines, carbamates, and active methylenes are directely used as the precursors. 3) Styrenes and aliphatic alkenes as well as terminal and internal alkenes are tolerated. Notably, gaseous alkenes, such as ethylene, propene are also tolerated in the reaction. Moreover, one-pot procedure renders further practicality of this method. The operationally simple conditions tolerate broad functional groups, providing a direct and general access to aziridines and cyclopropanes from readily available starting materials.

Acknowledgements

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