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One-Pot Synthesis of Cyclopropanes from Methylene Azabicyclo[3.1.0]hexanes Obtained by Formal Sequential [1+2]- and [2+3]-Cycloaddition Reaction of Prop-2-ynylsulfonium Salts and Tosylaminomethyl Enones

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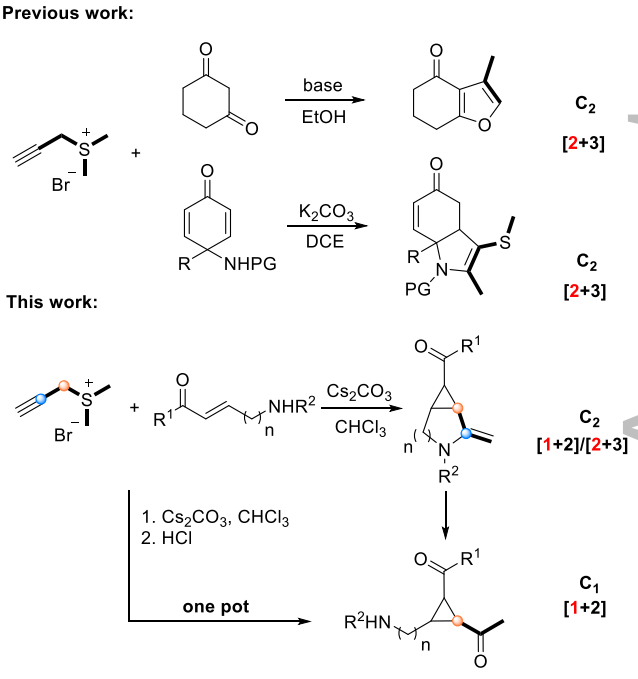
Abstract. A formal sequential [1+2]- and [2+3]-annulation of prop-2-ynylsulfonium salts and tosylaminomethyl enones was developed, constructing a series of methylene azabicyclo[3.1.0]hexane derivatives. A one-pot procedure was established via hydration of an enamine intermediate to afford substituted cyclopropanes. Prop-2-ynylsulfonium salts acted as both C_2 and C_1 synthons in these two processes.

Keywords: azabicyclo[3.1.0]hexanes; cyclopropanes; one-pot reaction; prop-2-ynylsulfonium salts; sequential annulation

First introduced in the 1960s, sulfur ylides have become powerful tools in the construction of three-membered rings such as epoxides, aziridines and cyclopropanes.[1] In recent years, different types of reactions with sulfur ylides have been developed, and novel cascade transformations have afforded a diverse range of chemical structures.[2] Beyond the traditional application of C_1 synthons, the groups of Aggarwal, Xiao and others have also made great advances using vinylsulfonium salts as C_2 synthons.[3] Important heterocyclic and fused-heterocyclic skeletons can be efficiently and conveniently constructed using vinylsulfonium salts. To further explore the chemistry of sulfur ylides, the development of different kinds of sulfur ylides and their application in more reaction types is highly desirable.

Prop-2-ynylsulfonium salts can isomerize to give allenic sulfonium salts, which can be attacked by enolate anions of *β*-diketones to afford substituted furans via [2+3]-cycloaddition (Scheme 1).[4] Recently, we developed another [2+3]-annulation of prop-2-ynylsulfonium salts and *p*-quinamines, generating a series of hydroindol-5-ones with a methylthio group.[5] As potential C_2 synthons, we were keen to investigate whether prop-2-ynylsulfonium salts could display different reactivity. Herein, we report a formal sequential [1+2]- and [2+3]-annulation of prop-2-ynylsulfonium salts and tosylaminomethyl enones[6] to afford substituted methylene azabicyclo[3.1.0]hexanes. The enamine units of the methylene azabicyclo[3.1.0]hexanes easily underwent hydration under acidic conditions to generate substituted cyclopropanes in a one-pot procedure. Prop-2-ynylsulfonium salts can behave as both a C_2 and a C_1 synthon in the construction of methylene azabicyclo[3.1.0]hexanes and cyclopropanes, which display unique reactivity.



Scheme 1. Reactions of prop-2-ynylsulfonium salts.

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Azabicyclo[3.1.0]hexane scaffolds are found in many biologically-active natural products, pharmaceuticals and agrochemicals. Molecules such as amitifadine, alatrofloxacin, victrelis and procymidone are typical examples with significant biological activity (Figure 1).[7] Although numerous methods for the synthesis of azabicyclo[3.1.0]hexane scaffolds have been developed,[3m,3o,8] a general strategy with readily accessible starting materials, mild reaction conditions and excellent functional group compatibility has been elusive.

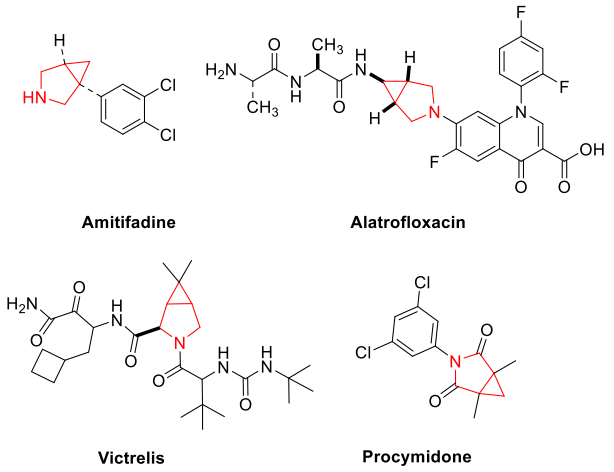
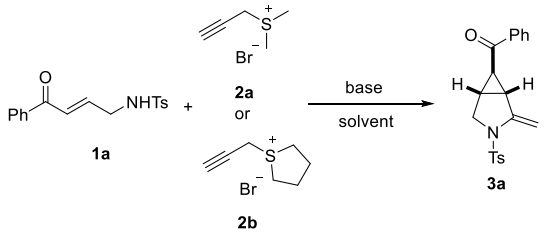


Figure 1. Representative pharmaceuticals containing azabicyclo[3.1.0]hexane scaffolds.

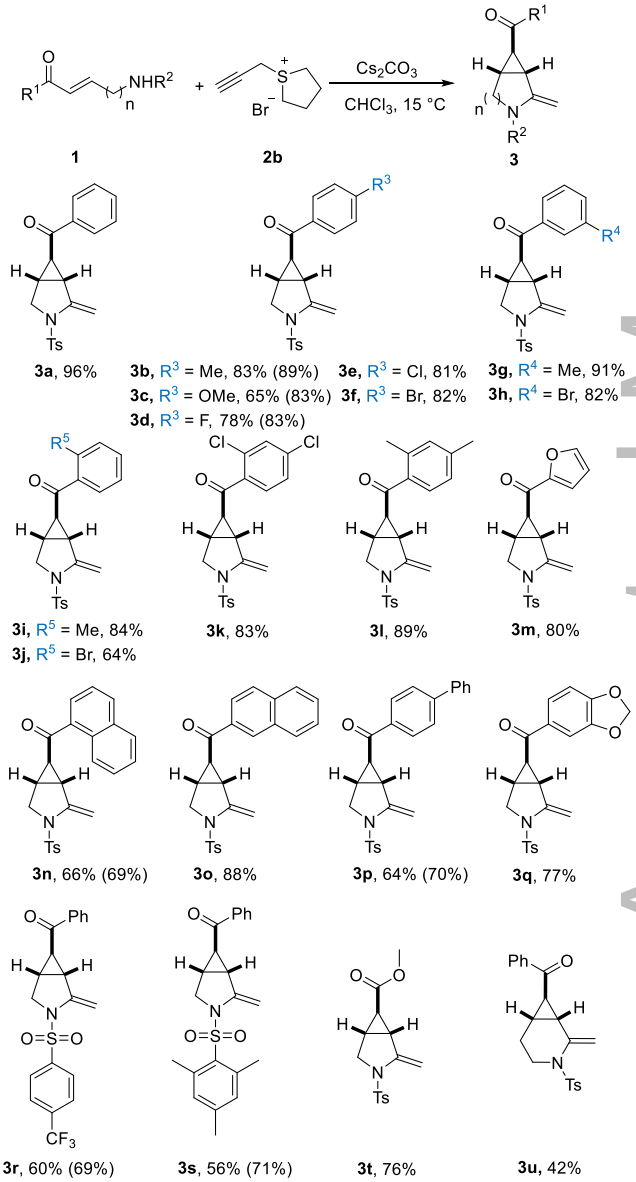
Initially, the sequential annulation of *N*-tosyl aminomethyl enone **1a** and prop-2-ynylsulfonium salt **2a** was investigated in the presence of 2.0 equivalents of Cs_2CO_3 as base in CH_3CN at 20 °C (Table 1, entry 1). Pleasingly, product **3a** was obtained in 69% yield. A range of bases and solvents were then screened to optimize the yield (Table 1, entries 2–8). The reaction conducted in $CHCl_3$ gave a better yield of 73% (Table 1, entry 7). Changing the loading of the base revealed that 3.0 equivalents of Cs_2CO_3 had a small improvement on the yield (Table 1, entry 10). Evaluation of the reaction temperature indicated that 15 °C was optimal, affording a 78% yield (Table 1, entry 13). Using distilled $CHCl_3$ as the solvent further improved the yield to 84% (Table 1, entry 14). To our delight, when tetrahydrothiophene sulfonium salt **2b** was used in the reaction, 96% yield of **3a** was obtained (Table 1, entry 15).

Table 1. Optimization of the reaction conditions.[a]



Entry	Base	Solvent	T (°C)	Ratio (**1**:**2**:base)	Yield [%][b]
1	Cs_2CO_3	CH_3CN	20	1:2:2	69
2	Et_3N	CH_3CN	20	1:2:2	64
3	DABCO	CH_3CN	20	1:2:2	23
4	K_3PO_4	CH_3CN	20	1:2:2	50
5	NaOH	CH_3CN	20	1:2:2	48
6	Cs_2CO_3	DCM	20	1:2:2	47
7	Cs_2CO_3	$CHCl_3$	20	1:2:2	73
8	Cs_2CO_3	DCE	20	1:2:2	34
9	Cs_2CO_3	$CHCl_3$	20	1:2:1.5	69
10	Cs_2CO_3	$CHCl_3$	20	1:2:3	75
11	Cs_2CO_3	$CHCl_3$	10	1:2:3	40
12	Cs_2CO_3	$CHCl_3$	30	1:2:3	50
13	Cs_2CO_3	$CHCl_3$	15	1:2:3	78
14[c]	Cs_2CO_3	$CHCl_3$	15	1:2:3	84
15[c,d]	Cs_2CO_3	$CHCl_3$	15	1:2:3	96

[a] Unless otherwise noted, reactions of **1a** (0.20 mmol) and **2a** were carried out in 4 mL of the solvent for 18 h.
[b] Isolated yields.
[c] Distilled $CHCl_3$ was used.
[d] **2b** was used instead of **2a**.

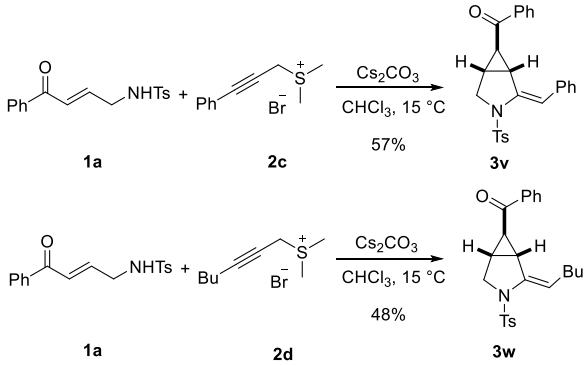


Scheme 2. Scope with respect to *N*-protected aminomethyl enones. *Conditions:* **1** (0.20 mmol), **2b** (0.40 mmol),

Cs_2CO_3 (0.60 mmol), distilled $CHCl_3$ (4 mL), 15 °C. Isolated yields. Yields of reactions using **2a** instead of **2b** are given in parentheses.

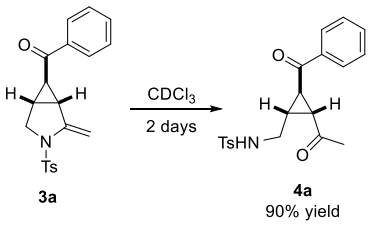
Having identified the optimal reaction conditions, the reaction scope was investigated next (Scheme 2). *N*-Tosylaminomethyl enones **1** bearing either electron-rich or electron-deficient substituents at the *para*-, *meta*- and *ortho*-positions of the phenyl ring were well-tolerated, affording the desired products in good yields (**3b–j**). Substrates **1** with 2,4-dichloro- and 2,4-dimethyl-substituted phenyl rings also generated the corresponding products in good yields (**3k** and **3l**). Further investigation showed that an enone **1** bearing a furyl group was also a suitable substrate for this conversion to give the desired product **3m**. Bicyclic substituents could also be introduced into the enone and the desired products were isolated in moderate to good yields (**3n–q**). Substrate containing a methyl group as the R^1 substituent resulted in trace amount of the product. Changing the protecting group led to a decrease in the yield (**3r** and **3s**). Methyl (*E*)-4-tosylamino but-2-enoate **1t** was also evaluated, giving product **3t** in 76% yield. Methyl (*E*)-5-tosylamino pent-2-enoate **1u** was synthesized and reacted with **2b** under our optimal reaction conditions. Azabicyclo[4.1.0]heptane skeleton **3u** was isolated in lower yield of 42% with unidentified by-products. No reaction took place when (*E*)-*N*-(4-oxo-4-phenylbut-2-en-1-yl)benzamide was used as the substrate under the standard conditions. With some moderate yields in hand, we conducted the reaction using prop-2-ynylsulfonium salts **2a** instead of **2b**. The yields were improved for **3b–d**, **3n**, **3p** and **3r**, **3s** (Scheme 2).

To further broaden the scope of the reaction, phenyl-substituted sulfonium salt **2c** and *n*-butyl-substituted sulfonium salt **2d** were used in the reaction (Scheme 3). Substituted methylene azabicyclo[3.1.0]hexanes **3v** and **3w** were synthetized in moderate yields. The stereochemistry of **3v** and **3w** was determined by NOESY spectroscopy.



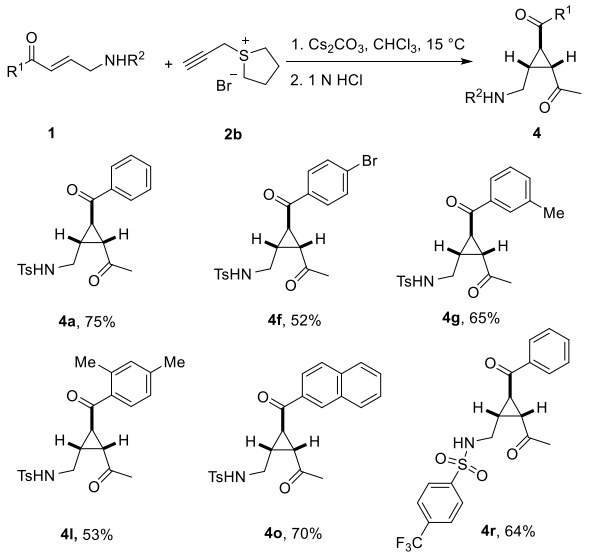
Scheme 3. Scope with respect to the sulfonium salt. *Conditions:* **1a** (0.20 mmol), **2** (0.40 mmol), Cs_2CO_3 (0.60 mmol), distilled $CHCl_3$ (4 mL), 15 °C. Isolated yields.

The obtained methylene azabicyclo[3.1.0]hexanes contain enamine units in their skeletons, which may be unstable under acidic conditions.[9] In fact, product **3a** had begun decomposing after several minutes in $CDCl_3$, and slowly decomposed at room temperature even in the pure state (Scheme 4). The hydrolyzed product was analyzed and found to be **4a**, a substituted cyclopropane derivative. Encouraged by this result, we moved to establish a one-pot procedure to synthesize substituted cyclopropanes using tosylaminomethyl enones and prop-2-ynylsulfonium salts.



Scheme 4. Hydration of **3a**.

Using the established reaction system, we added 1 N HCl solution after the completion of reactions to promote the hydration of the methylene azabicyclo[3.1.0]hexanes (Scheme 5). Substituted cyclopropanes were afforded in moderate to good yields with good functional group compatibility. The structure and stereochemistry of **4r** were characterized by single-crystal X-ray analysis (Figure 2).[10] It should be noted that the formal sequential [1+2]- and [2+3]-cycloaddition reaction is completely diastereoselective, and only one isomer was detected in all the reactions. The resulting cyclopropanes were obtained in excellent diastereoselectivity, which has provided a solution for controlling the diastereoselectivity in the construction of cyclopropanes using sulfur ylides.[11]



Scheme 5. One-pot synthesis of cyclopropanes; 2 mL of 1 N HCl was added after the completion of reactions at 15 °C for 0.5 h. Isolated yields.

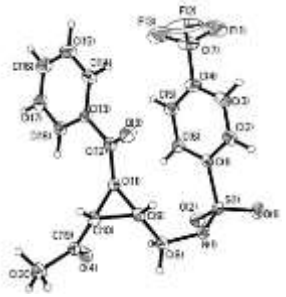
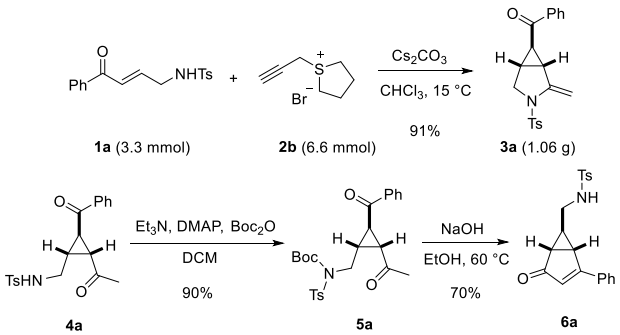


Figure 2. X-ray structure of **4r**. The ellipsoid contour percent probability level is 30%.

To explore the synthetic potential of the reaction, a gram-scale version of the reaction using substrates **1a** and **2b** was conducted and compound **3a** was obtained in 91% yield (Scheme 6). Protecting the N-H of **4a** with a *t*-butyloxy carbonyl group afforded **5a** in 90% yield. Removal of the protecting group and recyclization of **5a** under basic conditions generated bicyclo[3.1.0]hex-2-ene derivative **6a** in 70% yield. The structure and stereochemistry of **6a** were characterized by single-crystal X-ray analysis (Figure 3).[12]



Scheme 6. Gram-scale synthesis and further transformation of **4a**.

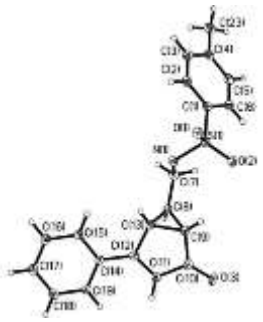
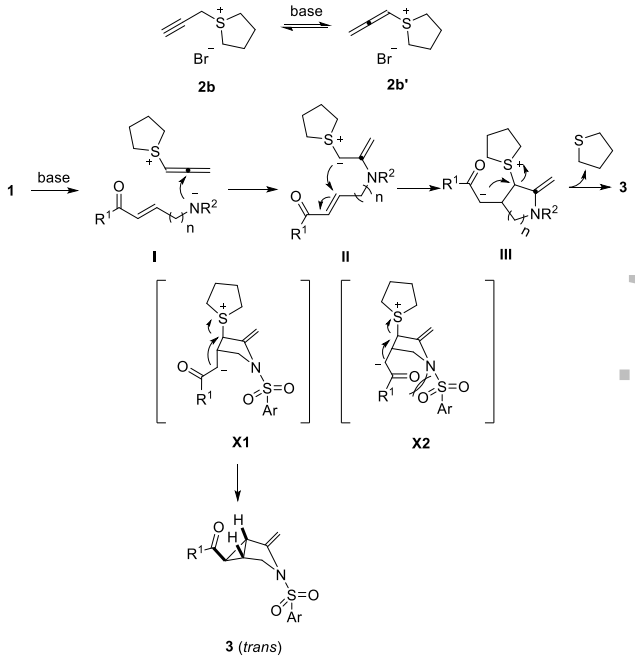


Figure 3. X-ray structure of **6a**. The ellipsoid contour percent probability level is 30%.

A postulated reaction mechanism is shown in Scheme 7. Under basic conditions, prop-2-ynylsulfonium salt **2b** isomerizes to allenic sulfonium salt **2b'**, which is attacked by the N anion of **1** to form intermediate **II**. Then, intramolecular nucleophilic addition of **II** leads to the formation of intermediate **III**. An intramolecular S_N2 reaction and elimination of tetrahydrothiophene affords product **3**. The diastereoselectivity of **3** can be rationalized by considering the steric interaction in the TSs. Because the less hindered X1 is favored over X2, the final product **3** is isolated as the *trans* isomer.



Scheme 7. Postulated reaction mechanism.

In conclusion, we have developed a prop-2-ynylsulfonium salt-based cycloaddition with tosylaminomethyl enones. Formal sequential [1+2] and [2+3]-annulation afforded various methylene azabicyclo[3.1.0]hexanes with good to high yields and excellent diastereoselectivity. A one-pot procedure was established based on the hydration of the enamine in the methylene azabicyclo[3.1.0]hexanes to construct substituted cyclopropane derivatives. Prop-2-ynylsulfonium salts acted as both C_2 and C_1 synthons in these two processes, which further broadens the application of sulfur ylides. Further work will focus on the synthetic application of this method to the synthesis of biologically-active natural products.

Experimental Section

General procedure for the synthesis of methylene azabicyclo[3.1.0]hexanes: Cs_2CO_3 (3.0 equiv.) was added to a mixture of tosylaminomethyl enones **1** (1.0 equiv., 0.20 mmol) and prop-2-ynylsulfonium salt **2a** or **2b** (2.0 equiv.) in distilled $CHCl_3$ (4.0 mL). The resulting suspension was stirred at 15 °C. After 18 h, the reaction mixture was passed through a short silica gel column and eluted with ethyl acetate. The filtrate was concentrated and the residue was purified by flash column chromatography to afford methylene azabicyclo[3.1.0]hexanes **3**.

Acknowledgements

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