Tetrahedron 68 (2012) 5234–5240

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Rh(II)-catalyzed [2,3]-sigmatropic rearrangement of sulfur ylides derived from *N*-tosylhydrazones and sulfides

Yuye Li [a,b], Zhongxing Huang [a], Xinhu Wu [a,b], Peng-Fei Xu [b,*], Jing Jin [b], Yan Zhang [a,b,*], Jianbo Wang [a,*]

[a] Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China
[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

ARTICLE INFO

Article history:
Received 3 February 2012
Received in revised form 3 March 2012
Accepted 9 March 2012
Available online 23 March 2012

Keywords:
[2,3]-Sigmatropic rearrangement
Sulfur ylides
N-Tosylhydrazone
Allylic phenyl sulfides
Propargyl phenyl sulfides

ABSTRACT

In this paper, $Rh_2(OAc)_4$-catalyzed [2,3]-sigmatropic rearrangement of sulfur ylides derived from *N*-tosylhydrazones and sulfides is reported. A series of tosylhydrazones derived from aldehydes were successfully used for [2,3]-sigmatropic rearrangement by reaction with either allylic phenyl sulfides or propargyl phenyl sulfides. The reaction conditions were optimized and afforded the products in moderate to good yields. In addition, a novel and convenient approach for the synthesis of cyclobutenones and cyclopropanes has been developed through direct oxidation of the rearrangement products.

1. Introduction

[2,3]-Sigmatropic rearrangement of sulfur ylides is one of the most versatile bond reorganization processes in organic chemistry, which offers a platform for the formation of C–C and C–S bonds.[1] Sulfur ylides, the key intermediates in the rearrangement, can be obtained through various transformations, of which the most traditional one is the deprotonation of sulfonium salts promoted by base.[2] Although this method has been widely utilized in the [2,3]-sigmatropic rearrangement of sulfur ylides, it suffers from certain disadvantages, such as the necessity of prior preparation of sulfonium salts and inevitable use of stoichiometric strong base.

The transition-metal-catalyzed reaction of diazo compounds with allylic sulfides, known as Doyle–Kirmse reaction, provides an alternative approach to generate sulfur ylides and to have subsequent [2,3]-sigmatropic rearrangement.[3,4] In these processes, the electron-deficient metal carbenes derived from diazo compounds react readily with sulfides to afford sulfur ylides, which avoids the use of stoichiomeric strong base. A plethora of examples utilizing this method have been reported in recent literature,[5] in which copper and rhodium complexes appear to be the most efficient catalysts.

The introduction of diazo compounds has many advantages over the traditional deprotonation and renders the sulfur ylides more accessible for the rearrangement. However, due to the problem of stability, the electron-withdrawing substituent is generally required in the α-position of isolable diazo compounds.[4b,6] This limitation narrows the application of diazo compounds to considerable extent in this kind of catalytic rearrangement of sulfur ylides.

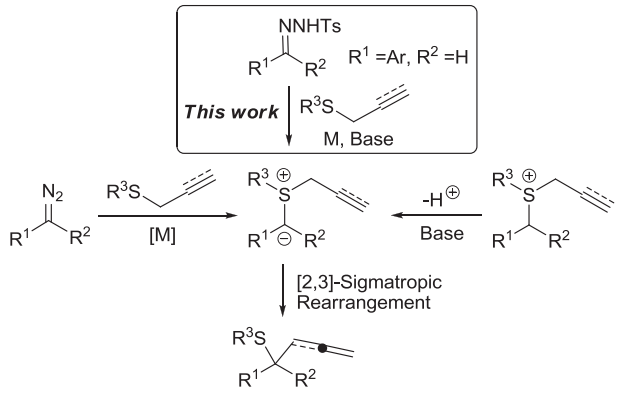
The fact that diazo compounds can be generated in situ from *N*-tosylhydrazones through Bamford–Stevens–Shapiro reaction has long been established.[7] *N*-Tosylhydrazones have been used as the source of unstable diazo compounds in various transition-metal-catalyzed transformations.[8–10] Metal carbene species were involved as vital intermediates in these reactions. Inspired by these facts and as a continuation of our previous work on the [2,3]-sigmatropic rearrangement of sulfur ylides,[5a,b,d,h] we conceived to introduce *N*-tosylhydrazones to the typical reaction system of Doyle–Kirmse reaction. Herein, we report the Rh(II)-catalyzed [2,3]-sigmatropic rearrangement of sulfur ylides derived from *N*-tosylhydrazones and sulfides (Scheme 1).

2. Results and discussion

Initially, we explored a series of catalysts for the reaction of **1a** and **2** (Table 1). Both traditional Cu(I) and Rh(II) catalysts were observed to work for the reaction and led to rearrangement products. When 1.0 equiv of *N*-tosylhydrazone **1a** and 1.0 equiv of allylic phenyl sulfide **2** were stirred in 1,4-dioxane at 90 °C, using LiO^{t}Bu as base, catalytic $Rh_2(OAc)_4$ afforded the desired product **3a** in 53%

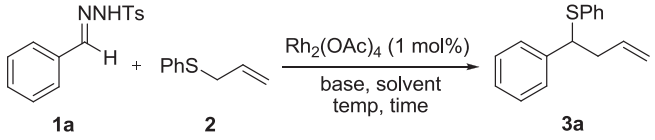
* Corresponding authors. Tel./fax: +86 10 6275 7248; e-mail address: wangjb@pku.edu.cn (J. Wang).

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2012.03.032



Scheme 1. [2,3]-Sigmatropic rearrangement of sulfur ylides.

Table 1
Optimization of reaction conditions[a]



Entry	Solvent	Base	Temp (°C)	Time (h)	Yield[b] (%)
1	1,4-Dioxane	LiO^{t}Bu	90	3	53
2	$ClCH_2CH_2Cl$	LiO^{t}Bu	90	3	46
3	CH_3CN	LiO^{t}Bu	90	3	40
4	THF	LiO^{t}Bu	90	3	50
5	Toluene	LiO^{t}Bu	90	3	38
6	1,4-Dioxane	NaO^{t}Bu	90	3	43
7	1,4-Dioxane	KO^{t}Bu	90	3	46
8	1,4-Dioxane	K_2CO_3	90	3	30
9	1,4-Dioxane	K_3PO_4	90	3	27
10	1,4-Dioxane	Cs_2CO_3	90	3	58
11	1,4-Dioxane	Cs_2CO_3	90	3	81
12	1,4-Dioxane	Cs_2CO_3	90	2	78
13	1,4-Dioxane	Cs_2CO_3	90	1	72
14	1,4-Dioxane	Cs_2CO_3	90	12	75
15	1,4-Dioxane	Cs_2CO_3	110	3	62
16	1,4-Dioxane	Cs_2CO_3	100	3	73
17	1,4-Dioxane	Cs_2CO_3	80	3	75
18	1,4-Dioxane	Cs_2CO_3	70	3	74
19	1,4-Dioxane	Cs_2CO_3	50	3	43

[a] From entry 1 to 10: the reaction was carried out with 1.0 equiv of *N*-tosylhydrazone **1a** and 1.0 equiv of sulfides **2**. From entry 11 to 19: the reaction was carried out with 1.0 equiv of *N*-tosylhydrazone **1a** and 2.5 equiv of sulfides **2**.
[b] Isolated yields after column chromatography.

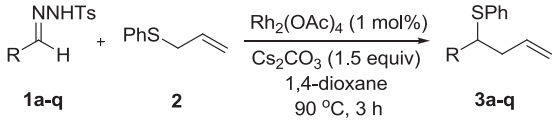
yield (Table 1, entry 1), while the performance of copper catalyst was rather poor. $Rh_2(OAc)_4$ was consequently chosen as the catalyst for the reaction.

The reaction condition was subsequently optimized (Table 1). Firstly, it turned out that the reaction could be carried out in various solvents. The reaction in THF and 1,4-dioxane afforded the desired product in similar yield (entries 1 and 4). While 1,2-dichloroethane (DCE) gave the product in lower yield (entry 2). Both polar solvent CH_3CN and apolar solvent toluene led to lower yields (entries 3 and 5). It was observed that the effect of solvent was indistinctive when LiO^{t}Bu was used as the base. Secondly, we explored the effect of base. On one hand, the reactions with NaO^{t}Bu and KO^{t}Bu afforded the product in moderate yields similar to that with LiO^{t}Bu (entries 6 and 7), while Cs_2CO_3 was found to be the optimal base (entry 10). On the other hand, the reactions with K_2CO_3 and K_3PO_4 were proved to be disfavored (entries 8 and 9). Finally, we attempted to examine the effect of the ratio of the two substrates on the reaction. It turned out that the yield of the reaction was not satisfactory when allylic phenyl sulfide reacted with the same equivalent of *N*-tosylhydrazones. The yield could be improved significantly when sulfide was used in excess. Further experiments showed that the mixture of sulfides and *N*-tosylhydrazones with 2.5:1 ratio gave the best result (entry 11). Finally, it was noted that no obvious enantioselectivity was observed even the reaction was carried out by either chiral dirhodium catalysts or copper(I) salts with chiral ligands.

With the above results in hand, we further proceeded to examine the reaction time. It was observed that the product could be obtained in 81% yield when the reaction was worked up after 3 h. A little improvement could be observed with longer reaction time when the reaction was carried out overnight (entry 14). The yields were decreased to certain extents with shorter reaction time (entries 12 and 13). A wide range of temperatures were further screened for the reaction. The temperature of 90 °C was found to be appropriate for this reaction, while the yield became lower whenever the temperature was increased (entries 15 and 16) or decreased (entries 17–19).

After acquiring the optimized conditions of the reaction, we started to explore the scope of the *N*-tosylhydrazones for the reaction (Tables 2 and 3). Generally, both allyl and propargyl sulfides underwent the rearrangement reaction smoothly and so were the substituted *N*-tosylhydrazones, all affording the rearrangement products in good to excellent yields.

Table 2
Reaction of *N*-tosylhydrazones **1a–q** with allyl phenyl sulfide **2**[a]

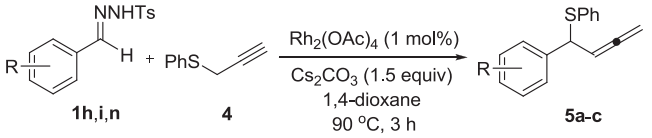


Entry	R	Product **3**	Yield[b] (%)
1	Ph	**3a**	81
2	*p*-$NO_2C_6H_4$	**3b**	75
3	*o*-BrC_6H_4	**3c**	76
4	*m*-BrC_6H_4	**3d**	65
5	*p*-BrC_6H_4	**3e**	78
6	*p*-ClC_6H_4	**3f**	74
7	3,4-$Cl_2C_6H_3$	**3g**	74
8	*p*-$MeO_2CC_6H_4$	**3h**	71
9	*p*-PhC_6H_4	**3i**	81
10	*o*-$CH_3C_6H_4$	**3j**	85
11	*m*-$CH_3C_6H_4$	**3k**	66
12	*p*-$CH_3OC_6H_4$	**3l**	18
13	2,6-$(CH_3)_2C_6H_3$	**3m**	88
14	3,5-$(CH_3O)_2C_6H_3$	**3n**	74
15	2-Naphthyl	**3o**	84
16	2-Furyl	**3p**	18
17	(*E*)-PhCH=CH	**3q**	48

[a] All reactions were performed with *N*-tosylhydrazones **1a–q** (0.5 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (0.005 mmol, 1 mol %), and Cs_2CO_3 (0.75 mmol, 1.5 equiv) in 5 mL of 1,4-dioxane, with addition of allyl phenyl sulfide **2** (1.25 mmol, 2.5 equiv), followed by stirring 3 h at 90 °C.
[b] Isolated yields after column chromatography.

The results of reaction between *N*-tosylhydrazones **1a–q** and allylic phenyl sulfide **2** under optimized conditions were summarized in Table 2. The electronic effects of the substituents on α carbon of *N*-tosylhydrazones were investigated. To our delight, most substrates bearing either electron-rich or electron-deficient substituents afforded the rearrangement products in excellent yields. For the *N*-tosylhydrazones containing *p*-$NO_2C_6H_4$, *p*-BrC_6H_4, *p*-ClC_6H_4, 3,4-$Cl_2C_6H_3$ or *p*-$MeO_2CC_6H_4$, relatively high yield of the rearrangement products were obtained (entries 2, 5, and 6–8). The reaction of substrates possessing *o*-BrC_6H_4 and *p*-PhC_6H_4 also proceeded smoothly (entries 3 and 9). However, when the substituent was *m*-BrC_6H_4, the expected product was isolated in a little lower yield (entry 4).

Table 3
Reaction of *N*-tosylhydrazones **1** with propargyl phenyl sulfide **4**[a]



1h,i,n 4 5a-c

Entry	R	Product **5**	Yield[b] (%)
1	3,5-$(CH_3O)_2C_6H_3$	**5a**	70
2	*p*-PhC_6H_4	**5b**	40
3	*p*-$MeO_2CC_6H_4$	**5c**	26

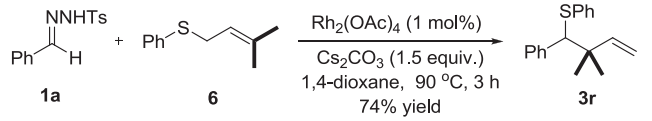
[a] All reactions were carried out with *N*-tosylhydrazones **1** (0.5 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (0.005 mmol, 1 mol %), and Cs_2CO_3 (0.75 mmol, 1.5 equiv) in 5 mL of 1,4-dioxane, with addition of propargyl phenyl sulfide **4** (1.25 mmol, 2.5 equiv), followed by stirring for 3 h at 90 °C.
[b] Isolated yields after column chromatography.

As for the electron-donating substituents on aromatic ring, such as methyl and methoxy groups, the outcomes were satisfactory regardless of the relative position and the number of the substituents on the aromatic ring (entries 10, 11, 13, and 14). However, it was rather surprising to note that the reaction with *p*-$CH_3OC_6H_4$ substituent gave low yield (entry 12), presumably due to the extremely electron-rich feature of the substrate. Substrates bearing naphthyl (entry 15) and furyl groups (entry 16) were also examined. And the former gave the product in excellent yield while the result of the latter was poor. Finally, it is noteworthy that the substrate possessing cinnamenyl also undergoes the rearrangement smoothly with moderate yield (entry 17).

In addition, we have examined the [2,3]-sigmatropic rearrangement between ketone *N*-tosylhydrazones and allyl phenyl sulfide. However, no expected products could be detected and both reactants remained intact. This may be due to the fact that the [2,3]-sigmatropic rearrangement is sensitive to the steric interaction of carbon anion on sulfur ylide.

Subsequently, the reaction condition was applied to the reaction between *N*-tosylhydrazones and propargyl phenyl sulfide. For various substituted *N*-tosylhydrazones, the reaction went smoothly and afforded the corresponding products in moderate yields as determined by the GC–MS. However, only three examples of this reaction have been shown in Table 3 due to the difficulties in separation. Nevertheless, these few examples provide proof that this kind of [2,3]-sigmatropic rearrangement of sulfur ylides is applicable for propargyl sulfide. Among these three examples, the reaction of *N*-tosylhydrazone containing 3,5-$(CH_3O)_2C_6H_3$ underwent efficiently and afforded the allene product **5a** in good yield (entry 1). The substrate bearing *p*-PhC_6H_4 could also react but gave the product in moderate yield (entry 2). However, the yield decreases considerably when the substituent is electron-withdrawing (entry 3).

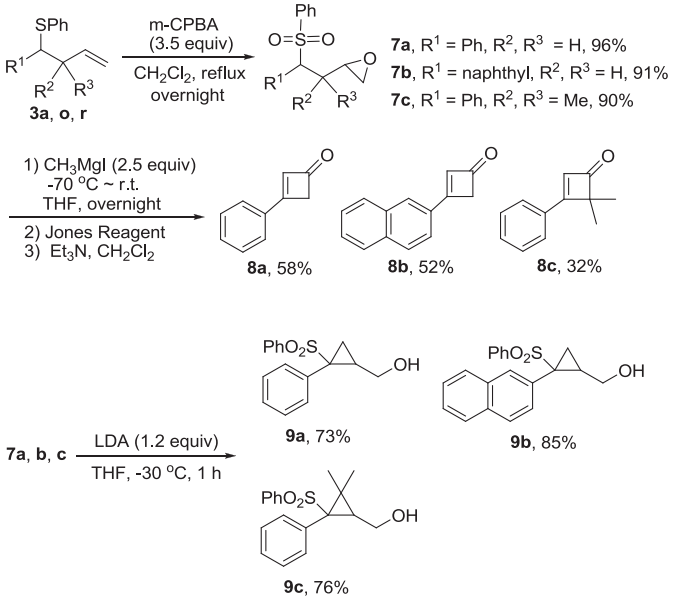
In order to further explore the scope of the rearrangement reaction we have prepared the allylic sulfide **6**, of which the terminal olefin is blocked by two methyl groups. Then its reactivity in the rearrangement was tested. To our delight, the sulfide reacted readily with *N*-tosylhydrazones **1a** and afforded the expected product **3r** (Scheme 2).



1a 6 3r

Scheme 2. Reaction of sulfide **6** with *N*-tosylhydrazones **1a**.

Finally, we proceeded to explore the utility of the rearrangement products. Through a survey of the literature we noted that the rearrangement products **3a**–**r** are useful intermediates in organic synthesis. For example, in 1970s Durst and co-worker developed a novel approach for the synthesis of cyclobutenones, which contains three highly efficient steps.[11a] Although this method demonstrates potential in organic synthesis, the starting materials, such as γ-epoxy sulfones, are not easily available through traditional methods. The preparation usually takes several steps and involves hazardous reagents.[11b] With the products of [2,3]-sigmatropic rearrangement of sulfur ylide, we developed an alternative synthesis of γ-epoxy sulfones by the direct oxidation of some of the rearrangement products by *m*-CPBA. To our delight, the reaction of the selected compounds (**3a**, **o**, **r**) proceeded smoothly to give the corresponding γ-epoxy sulfones in excellent yields. Subsequently, the synthesis of the corresponding cyclobutenones **8a**–**c** was successfully achieved by Durst's methods. Moreover, the γ-epoxy sulfones could be transformed into cyclopropanes with the aid of LDA as base by only one step with Durst's protocol, as exemplified by the synthesis of **9a**–**c** (Scheme 3).



Scheme 3. The synthesis of γ-epoxy sulfones, cyclobutenones, and cyclopropanes based on the rearrangement products.

3. Summary

In summary, we have successfully introduced *N*-tosylhydrazones into the catalytic [2,3]-sigmatropic rearrangement of sulfur ylides. To the best of our knowledge, this is the first report on the application of *N*-tosylhydrazones in Doyle–Kirmse reaction. The catalytic reaction is highly efficient and affords the products in moderate to good yields. The reaction has excellent functional group compatibility and can be applied to both allylic and propargyl sulfides. In addition, the direct oxidation of the rearrangement products, combined with Durst's methodology, offers a novel and convenient approach to the synthesis of cyclobutenones and cyclopropanes.

4. Experimental section

4.1. General

All reactions with moisture and air sensitive components are performed under a nitrogen atmosphere. 1,4-Dioxane, pentane, and ether were distilled from Na before use. 200–300 mesh silica gel was employed for the column chromatography. The boiling point of petroleum ether was between 60 and 90 °C. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker-400 ARX spectrometer. Chemical shifts were reported in parts per million

relative to the internal standard tetramethylsilane (δ=0 ppm) for ^{1}H NMR and deuteriochloroform (δ=77.00 ppm) for ^{13}C NMR spectroscopy. Mass spectra were determined on a VG ZAB-HS mass spectrometer. IR was recorded with a Nicolet Avatar 330 FT-IR infrared spectrometer.

N-Tosylhydrazones and sulfides were prepared according to literature procedure.[8,10b,12] Materials obtained from commercial suppliers were used without further purification unless otherwise noted. The syntheses of cyclobutenones and cyclopropane from γ-epoxy sulfones have been referred to the procedures reported in the literature.[11a,c]

4.2. Experimental procedure for the preparation of allyl phenyl sulfides or propargyl phenyl sulfides

To a flame-dried flask, a suspension of 80% NaH (0.1 mol) in THF (100 mL) was added and stirred at 0 °C under water-ice bath. The thiophenol (6.8 mL, 0.067 mol) was then added dropwise to the mixture over 20 min. After completion of the addition, the water-ice bath was removed and the mixture was allowed to warm to room temperature and stirred for 0.5 h. Subsequently, the mixture was again cooled to 0 °C and allyl bromide or propargyl bromide (0.1 mol) was added dropwise while stirring. After addition, the mixture was warmed to room temperature and then stirred for 2 h.

Finally, 50 mL of satd NH_4Cl solution was added to quench the reaction. The organic layer was washed with water (2×30 mL), extracted with Et_2O (2×10 mL). The organic layers were combined and concentrated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether) to afford the allyl phenyl sulfide as colorless oil.

4.3. Typical procedure for the $Rh_2(OAc)_4$-catalyzed [2,3]-sigmatropic rearrangement

A 50 mL flame-dried Schlenk flask was evacuated and backfilled with N_2 for three times, *N*-Tosylhydrazones (0.5 mmol), $Rh_2(OAc)_4$ (0.005 mmol), and 1,4-dioxane (5 mL) were charged followed by addition of the sulfide (1.25 mmol). The mixture was heated to 90 °C and stirred for 3 h. The mixture was then cooled down to room temperature and the reaction mixture was allowed to pass through a silica plug (washed with petroleum ether/ethyl acetate=3:1). The resulting filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography (petroleum ether) to give the product.

*4.3.1. Phenyl(1-phenylbut-3-enyl)sulfane (**3a**).*[12] Yield 81%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67–2.71 (m, 2H), 4.19 (t, *J*=7.6 Hz, 1H), 4.98–5.05 (m, 2H), 5.68–5.75 (m, 1H), 7.17–7.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4, 53.3, 117.2, 127.1, 127.2, 127.8, 128.3, 128.6, 132.5, 134.8, 135.2, 141.5.

*4.3.2. (1-(4-Nitrophenyl)but-3-enyl)(phenyl)sulfane (**3b**).* Yield 75%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54–2.72 (m, 2H), 4.15–4.19 (m, 1H), 4.93–4.98 (m, 2H), 5.58–5.65 (m, 1H), 7.08–7.17 (m, 5H), 7.24–7.27 (m, 2H), 7.98–8.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.8, 52.8, 118.1, 123.5, 127.9, 128.6, 128.9, 133.1, 134.0, 146.8, 149.3; IR (film) 692, 747, 1346, 1519, 2925 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 285 (M^+, 10), 244 (100), 197 (10), 130 (33), 115 (18); HRMS (ESI) calcd for $C_{16}H_{15}NNaO_2S$ $[M+Na]^+$: 308.0721, found: 308.0719.

*4.3.3. (1-(2-Bromophenyl)but-3-enyl)(phenyl)sulfane (**3c**).* Yield 76%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (t, *J*=7.2 Hz, 2H), 4.86 (t, *J*=7.6 Hz, 1H), 5.00–5.06 (m, 2H), 5.70–5.80 (m, 1H), 7.02–7.06 (m, 1H), 7.14–7.28 (m, 6H), 7.47–7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 50.7, 117.6, 124.6, 127.0, 127.6, 128.5, 128.7, 129.1, 131.9, 132.7, 134.3, 134.5, 140.3; IR (film) 661, 737, 912, 1024, 3074 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 318 (M^+, 11), 277 (95), 197 (39), 130 (100), 115 (25); HRMS (ESI) calcd for $C_{16}H_{15}BrNaS$ $[M+Na]^+$: 340.9976, found: 340.9971.

*4.3.4. (1-(3-Bromophenyl)but-3-enyl)(phenyl)sulfane (**3d**).* Yield 65%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59–2.72 (m, 2H), 4.11 (t, *J*=8.0 Hz, 1H), 5.00–5.05 (m, 2H), 5.64–5.74 (m, 1H), 7.06–7.24 (m, 7H), 7.31 (d, *J*=7.6 Hz, 1H), 7.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.1, 52.7, 117.6, 122.3, 126.5, 127.4, 128.7, 129.7, 130.2, 130.8, 132.7, 133.9, 134.6, 143.8; IR (film) 668, 690, 909, 1072, 3075 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 318 (M^+, 9), 277 (78), 197 (22), 130 (100), 115 (23); HRMS (ESI) calcd for $C_{16}H_{15}^{79}BrNaS$ $[M+Na]^+$: 340.9976, found: 340.9975.

*4.3.5. (1-(4-Bromophenyl)but-3-enyl)(phenyl)sulfane (**3e**).* Yield 78%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58–2.73 (m, 2H), 4.12–4.15 (m, 1H), 5.00–5.04 (m, 2H), 5.63–5.74 (m, 1H), 7.09 (d, *J*=8.4 Hz, 2H), 7.18–7.24 (m, 5H), 7.36 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.2, 52.6, 117.6, 120.8, 127.4, 128.7, 129.5, 131.3, 132.7, 134.1, 134.7, 140.5; IR (film) 691, 833, 909, 1010, 3075 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 318 (M^+, 7), 277 (46), 209 (30), 130 (100), 115 (22); HRMS (EI) calcd for $C_{16}H_{15}^{79}BrS$ $[M]^+$: 318.0078, found: 318.0082; $C_{16}H_{15}^{81}BrS$ $[M]^+$: 320.0057, found: 320.0062.

*4.3.6. (1-(4-Chlorophenyl)but-3-enyl)(phenyl)sulfane (**3f**).* Yield 74%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59–2.73 (m, 2H), 4.13–4.17 (m, 1H), 5.00–5.05 (m, 2H), 5.64–5.74 (m, 1H), 7.14–7.25 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 52.6, 117.5, 127.4, 128.4, 128.7, 129.2, 132.7, 134.1, 134.7, 140.0; IR (film) 691, 835, 917, 1025, 3076 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 274 (M^+, 7), 233 (61), 165 (100), 129 (57), 109 (16); HRMS (EI) calcd for $C_{16}H_{15}^{35}ClS$ $[M]^+$: 274.0583, found: 274.0586.

*4.3.7. (1-(3,4-Dichlorophenyl)but-3-enyl)(phenyl)sulfane (**3g**).* Yield 71%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59–2.68 (m, 2H), 4.08–4.12 (m, 1H), 5.01 (s, 1H), 5.04 (d, *J*=6.0 Hz, 1H), 5.64–5.69 (m, 1H), 7.03 (dd, *J*=2.0, 8.2 Hz, 1H), 7.19–7.25 (m, 5H), 7.28–7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 52.3, 117.9, 127.2, 127.6, 128.8, 129.7, 130.1, 130.9, 132.2, 132.8, 133.6, 134.3, 141.9; IR (film) 691, 823, 910, 1030, 3076 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 308 (M^+, 17), 267 (100), 199 (63), 164 (53), 129 (42); HRMS (EI) calcd for $C_{16}H_{14}^{35}Cl_2S$ $[M]^+$: 308.0193, found: 308.0197.

*4.3.8. Methyl 4-(1-(phenylthio)but-3-enyl)benzoate (**3h**).* Yield 71%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63–2.77 (m, 2H), 3.87 (s, 3H, OCH_3), 4.19–4.23 (m, 1H), 5.00–5.05 (m, 2H), 5.66–5.73 (m, 1H), 7.16–7.22 (m, 5H), 7.27 (d, *J*=8.4 Hz, 2H), 7.92 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 52.0, 53.0, 117.6, 127.4, 127.8, 128.7, 128.8, 129.5, 132.8, 133.8, 134.5, 146.8, 166.7; IR (film) 692, 732, 909, 1436, 1720 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 298 (M^+, 13), 257 (100), 189 (25), 129 (58), 115 (19), 59 (20); HRMS (ESI) calcd for $C_{18}H_{19}O_2S$ $[M+H]^+$: 299.1106, found: 299.1100; $C_{18}H_{18}NaO_2S$ $[M+Na]^+$: 321.0925, found: 321.0923.

*4.3.9. (1-(Biphenyl-4-yl)but-3-enyl)(phenyl)sulfane (**3i**).* Yield 81%; white solid; mp 60–62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71–2.75 (m, 2H), 4.22–4.26 (m, 1H), 5.01–5.08 (m, 2H), 5.70–5.81 (m, 1H), 7.11–7.22 (m, 3H), 7.28–7.34 (m, 5H), 7.39–7.43 (m, 2H), 7.48–7.50 (m, 2H), 7.56–7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 52.9, 117.3, 126.9, 127.0, 127.1, 127.2, 128.2, 128.7, 132.5, 135.1, 139.9, 140.5, 140.7; IR (film) 695, 843, 908, 1485, 3028 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 316 (M^+, 6), 275 (18), 207 (100), 179 (40), 165 (94); HRMS (ESI) calcd for $C_{22}H_{20}NaS$ $[M+Na]^+$: 339.1183, found: 339.1181.

*4.3.10. Phenyl(1-o-tolylbut-3-enyl)sulfane (**3j**).* Yield 85%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H, $ArCH_3$), 2.70 (t,

J=8.0 Hz, 2H), 4.45 (t, J=7.6 Hz, 1H), 4.96–5.04 (m, 2H), 5.65–5.75 (m, 1H), 7.10–7.28 (m, 8H), 7.34 (d, J=7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 39.8, 48.5, 117.1, 126.2, 126.9, 127.0, 127.3, 128.7, 130.2, 132.8, 134.6, 135.3, 135.8, 139.0; IR (film) 692, 740, 915, 1025, 3074 cm^{-1}; EI-MS (m/z, relative intensity): 254 (M^+, 5), 213 (54), 145 (100), 129 (23), 115 (18), 105 (23), 91 (18); HRMS (ESI) calcd for $C_{17}H_{18}NaS$ $[M+Na]^+$: 277.1027, found: 277.1022.

*4.3.11. Phenyl(1-m-tolylbut-3-enyl)sulfane (**3k**).* Yield 66%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H, $ArCH_3$), 2.68 (t, J=7.2 Hz, 2H), 4.15 (t, J=7.6 Hz, 1H), 4.97–5.04 (m, 2H), 5.67–5.74 (m, 1H), 6.99–7.05 (m, 3H), 7.12–7.19 (m, 4H), 7.25–7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 40.4, 53.1, 117.1, 124.8, 127.0, 127.9, 128.1, 128.5, 128.6, 132.3, 134.9, 135.2, 137.8, 141.2; IR (film) 692, 913, 1025, 1438, 3075 cm^{-1}; EI-MS (m/z, relative intensity): 254 (M^+, 9), 213 (60), 145 (100), 129 (27), 115 (18), 105 (27); HRMS (ESI) calcd for $C_{17}H_{18}NaS$ $[M+Na]^+$: 277.1027, found: 277.1021.

*4.3.12. (1-(4-Methoxyphenyl)but-3-enyl)(phenyl)sulfane (**3l**).*[12] Yield 18%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64–2.67 (m, 2H), 3.77 (s, 3H, OCH_3), 4.16–4.19 (m, 1H), 4.98–5.04 (m, 2H), 5.67–5.71 (m, 1H), 6.78–6.80 (m, 2H), 7.15–7.27 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.5, 52.5, 55.2, 113.6, 117.1, 127.0, 128.6, 128.9, 132.4, 133.3, 134.8, 135.2, 158.6; IR (film) 692, 732, 909, 1436, 1720 cm^{-1}; EI-MS (m/z, relative intensity): 270 (M^+, 3), 229 (5), 161 (100), 146 (11), 91 (15); HRMS (ESI) calcd for $C_{17}H_{18}NaOS$ $[M+Na]^+$: 293.0976, found: 293.0972.

*4.3.13. (1-(2,6-Dimethylphenyl)but-3-enyl)(phenyl)sulfane (**3m**).* Yield 88%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09 (s, 3H, $ArCH_3$), 2.62 (s, 3H, $ArCH_3$), 2.74–2.92 (m, 2H), 4.63–4.68 (m, 1H), 4.91–5.05 (m, 2H), 5.59–5.69 (m, 1H), 6.89 (d, J=4.4 Hz, 1H), 7.01 (d, J=4.8 Hz, 2H), 7.21–7.23 (m, 3H), 7.33–7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.5, 38.8, 49.8, 116.6, 126.8, 127.4, 128.0, 128.7, 130.4, 133.2, 135.7, 135.8, 136.2, 137.2, 137.4; IR (film) 692, 769, 909, 1025, 2976 cm^{-1}; EI-MS (m/z, relative intensity): 268 (M^+, 5), 227 (55), 159 (100), 144 (25), 129 (22); HRMS (ESI) calcd for $C_{18}H_{20}NaS$ $[M+Na]^+$: 291.1183, found: 291.1179.

*4.3.14. (1-(3,5-Dimethoxyphenyl)but-3-enyl)(phenyl)sulfane (**3n**).* Yield 74%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (t, J=7.2 Hz, 2H), 3.73 (s, 6H, OCH_3), 4.11 (t, J=7.6 Hz, 1H), 5.00–5.07 (m, 2H), 5.70–5.77 (m, 1H), 6.31 (t, J=2.4 Hz, 1H), 6.41 (d, J=2.0 Hz, 2H), 7.19–7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4, 53.4, 55.2, 99.2, 105.8, 117.2, 127.1, 128.7, 132.3, 135.1, 143.8, 160.6; IR (film) 691, 733, 909, 1065, 2936 cm^{-1}; EI-MS (m/z, relative intensity): 300 (M^+, 22), 259 (50), 191 (100), 176 (9), 160 (10); HRMS (ESI) calcd for $C_{18}H_{20}NaO_2S$ $[M+Na]^+$: 323.1082, found: 323.1081.

*4.3.15. (1-(Naphthalen-2-yl)but-3-enyl)(phenyl)sulfane (**3o**).* Yield 84%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76–2.80 (m, 2H), 4.33–4.36 (t, J=7.6 Hz, 1H), 4.96–5.07 (m, 2H), 5.68–5.78 (m, 1H), 7.12–7.16 (m, 3H), 7.23–7.26 (m, 2H), 7.40–7.42 (m, 2H), 7.48 (dd, J=1.6, 8.8 Hz, 1H), 7.55 (s, 1H), 7.69–7.71 (m, 1H), 7.76–7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 53.4, 125.7, 125.8, 126.0, 126.7, 127.1, 127.6, 127.7, 128.2, 128.6, 132.5, 132.6, 133.1, 134.6, 135.0, 138.7; IR (film) 691, 737, 911, 1438, 3057 cm^{-1}; EI-MS (m/z, relative intensity): 290 (M^+, 8), 249 (15), 181 (100), 165 (38), 153 (9); HRMS (ESI) calcd for $C_{20}H_{18}NaS$ $[M+Na]^+$: 313.1027, found: 313.1026.

*4.3.16. 2-(1-(Phenylthio)but-3-enyl)furan (**3p**).* Yield 18%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62–2.77 (m, 2H), 4.22–4.26 (m, 1H), 5.03–5.11 (m, 2H), 5.74–5.84 (m, 1H), 5.98 (d, J=3.2 Hz, 1H), 6.23 (q, J=1.6 Hz, 1H), 7.23–7.30 (m, 5H), 7.35 (q, J=0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.8, 46.2, 107.5, 110.1, 117.4, 127.6, 128.7, 133.4, 134.8, 141.8, 153.7; IR (film) 692, 733, 909, 1010, 1439 cm^{-1}; EI-MS (m/z, relative intensity): 230 (M^+, 13), 121 (100), 103 (44), 91 (37), 77 (34); HRMS (ESI) calcd for $C_{14}H_{15}OS$ $[M+H]^+$: 231.0844, found: 231.0834.

*4.3.17. (E)-Phenyl(1-phenylhexa-1,5-dien-3-yl)sulfane (**3q**).* Yield 48%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46–2.59 (m, 2H), 3.75–3.81 (m, 1H), 5.07–5.14 (m, 2H), 5.82–5.93 (m, 1H), 6.04–6.18 (m, 2H), 7.17–7.26 (m, 8H), 7.41 (dd, J=1.6, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.0, 51.8, 117.3, 126.3, 127.4, 128.4, 128.7, 129.8, 131.1, 133.5, 134.1, 134.9, 136.7; IR (film) 691, 748, 909, 1025, 3026 cm^{-1}; EI-MS (m/z, relative intensity): 266 (M^+, 3), 225 (38), 157 (14), 115 (100), 91 (28); HRMS (ESI) calcd for $C_{18}H_{19}S$ $[M+H]^+$: 267.1208, found: 267.1206.

*4.3.18. (2,2-Dimethyl-1-phenylbut-3-enyl)(phenyl)sulfane (**3r**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 3H), 1.20 (s, 3H), 4.04 (s, 1H), 4.97–5.07 (m, 2H), 5.99–6.06 (dd, J=6.4, 10.8 Hz, 1H), 7.03–7.11 (m, 3H), 7.15–7.23 (m, 5H), 7.32 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 26.8, 41.6, 65.1, 112.5, 126.2, 126.8, 127.4, 128.5, 129.8, 130.9, 136.5, 140.4, 145.3; IR (film) 690, 737, 915, 1480, 2965 cm^{-1}; EI-MS (m/z, relative intensity): 268 (M^+, 2), 199 (100), 165 (12), 117 (17), 91 (13); HRMS (ESI) calcd for $C_{18}H_{19}S$ $[M-H]^+$: 267.1207, found: 267.1202.

*4.3.19. (1-(3,5-Dimethoxyphenyl)buta-2,3-dienyl)(phenyl)sulfane (**5a**).* Yield 70%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 6H, OCH_3), 4.60–4.64 (m, 1H), 4.71–4.76 (m, 2H), 5.43–5.49 (m, 1H), 6.35 (t, J=2.4 Hz, 1H), 6.52 (d, J=2.4 Hz, 2H), 7.24–7.26 (m, 3H), 7.37–7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.1, 55.3, 92.1, 100.0, 105.7, 127.4, 128.6, 132.9, 134.8, 142.4, 160.7, 208.4; IR (film) 692, 909, 1066, 1461, 2560 cm^{-1}; EI-MS (m/z, relative intensity): 298 (M^+, 98), 283 (100), 267 (19), 207 (38), 189 (21), 161 (33); HRMS (ESI) calcd for $C_{18}H_{19}O_2S$ $[M+H]^+$: 299.1106, found: 299.1100.

*4.3.20. (1-(Biphenyl-4-yl)buta-2,3-dienyl)(phenyl)sulfane (**5b**).* Yield 40%; yellow solid; mp 52–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61–4.65 (m, 1H), 4.72–4.77 (m, 1H), 4.86 (d, J=8.4 Hz, 1H), 5.53 (dd, J=6.8, 8.0 Hz, 1H), 7.21–7.25 (m, 3H), 7.32 (t, J=7.2 Hz, 1H), 7.38–7.43 (m, 6H), 7.52–7.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 92.2, 127.0, 127.2, 127.3, 127.4, 128.2, 128.6, 128.7, 133.0, 134.9, 139.2, 140.4, 140.7, 208.6; IR (film) 752, 1240, 1486, 1738, 1952 cm^{-1}; EI-MS (m/z, relative intensity): 314 (M^+, 6), 258 (94), 205 (100), 155 (36), 127 (67), 77 (44); HRMS (ESI) calcd for $C_{22}H_{19}S$ $[M+H]^+$: 315.1207, found: 315.1202.

*4.3.21. Methyl 4-(1-(phenylthio)buta-2,3-dienyl)benzoate (**5c**).* Yield 26%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H, OCH_3), 4.63–4.68 (m, 1H), 4.74–4.79 (m, 1H), 4.83 (d, J=8.4 Hz, 1H), 5.49 (dd, J=6.4, 8.4 Hz, 1H), 7.23–7.25 (m, 3H), 7.32–7.34 (m, 2H), 7.39 (d, J=8.0 Hz, 2H), 7.96 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.0, 52.6, 91.7, 127.7, 127.9, 128.7, 129.3, 129.7, 133.2, 134.2, 145.5, 166.7, 208.6; IR (film) 749, 1111, 1279, 1721, 1952 cm^{-1}; EI-MS (m/z, relative intensity): 296 (M^+, 100), 265 (74), 205 (11), 178 (65), 117 (18); HRMS (ESI) calcd for $C_{18}H_{16}NaO_2S$ $[M+Na]^+$: 319.0769, found: 319.0757.

4.4. Typical procedure for the oxidation of rearrangement products 3a, o, r to γ-epoxy sulfones

To a flask were added phenyl(1-phenylbut-3-enyl)sulfane (240 mg, 1.0 mmol) and dichloromethane (10 mL). After the sulfane was fully dissolved, *m*-CPBA (90%, 0.67 g, 3.5 mmol) was slowly added to the flask. The solution was then heated and refluxed overnight. After the completion of the oxidation as monitored by

TLC, the solution was first allowed to cool down to room temperature and washed with 10% NaOH (aq) (2×10 mL) and H_2O (2×10 mL). The organic layer of the mixture was subsequently dried with Na_2SO_4 and concentrated under vacuum. The residue was finally purified by silica gel column chromatography (petroleum ether/ethyl acetate=5:1) to give the γ-epoxy sulfone.

*4.4.1. 2-(2-Phenyl-2-(phenylsulfonyl)ethyl)oxirane (**7a**).*[11c] Yield 96%; white solid; mp 108–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32–2.43 (m, 1H), 2.47–2.52 (m, 1H), 2.56–2.63(m, 1H), 2.67–2.73(m, 1H), 4.30–4.34(m, 2H), 7.09–7.30 (m, 5H), 7.35–7.40 (m, 2H), 7.49–7.56 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 47.9, 50.3, 68.5, 128.4, 128.5, 128.6, 128.9, 129.0, 129.6, 129.8, 131.5, 132.3, 133.6, 136.8.

*4.4.2. 2-(2-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)oxirane (**7b**).* Yield 91%; white solid; mp 92–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37–2.44 (m, 1H), 2.51–2.53 (m, 1H), 2.64–2.66 (m, 1H), 2.68–2.76 (m, 2H), 4.47–4.50 (m, 1H), 7.30–7.34 (m, 3H), 7.48–7.55 (m, 5H), 7.60 (s, 1H), 7.69–7.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 47.9, 49.2, 68.7, 126.4, 126.4, 126.7, 127.6, 128.0, 128.4, 128.6, 128.9, 129.9, 132.9, 133.3, 133.6, 136.9; IR (film) 699, 738, 1025, 1480, 2931 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 338 (M^+, 30), 196 (40), 153 (100), 128 (48), 77 (80); HRMS (ESI) calcd for $C_{20}H_{19}O_3S$ $[M+H]^+$: 339.1055, found: 339.1048, $C_{20}H_{18}NaO_3S$ $[M+Na]^+$: 361.0874, Found: 361.0876.

*4.4.3. 2-(2-Methyl-1-phenyl-1-(phenylsulfonyl)propan-2-yl)oxirane (**7c**).* Yield 90%; white solid; mp 75–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (m, 3H), 1.33 (m, 3H), 2.62–2.69 (m, 2H), 3.16–3.17 (m, 1H), 4.08 (s, 1H), 6.51 (d, *J*=7.6 Hz, 1H), 6.96 (t, *J*=7.6 Hz, 1H) 7.19–7.27 (m, 4H), 7.34–7.47 (m, 3H), 8.01 (d, *J*=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 24.2, 40.1, 44.8, 57.5, 128.1, 128.2, 128.3, 128.4, 129.7, 130.8, 132.2, 132.7, 132.9, 140.0; IR (film) 669, 743, 1144, 1308, 2924 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 316 (M^+, 17), 298 (23), 175 (6), 129 (76), 77 (100); HRMS (ESI) calcd for $C_{18}H_{21}O_3S$ $[M+H]^+$: 317.1211, found: 317.1206, $C_{18}H_{20}NaO_3S$ $[M+Na]^+$: 339.1031, found: 339.1028.

4.5. Typical procedure for the synthesis of cyclobutenones 8

To a 50 mL flame-dried Schlenk flask were added γ-epoxy sulfone **7** (1.0 mmol) and 15 mL THF. The flask was evacuated and backfilled with N_2 for three times and cooled to −78 °C. After the γ-epoxy sulfone was dissolved, methylmagnesium iodide (2.5 mmol, 2.5 M in ether) was added via syringe dropwise under stirring. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was then quenched with satd NH_4Cl (aq) and the mixture was extracted with Et_2O (3×30 mL). The organic layer was collected and concentrated under vacuum. The crude product obtained was further purified by silica gel flash chromatography (petroleum ether/ethyl acetate=2:1) to give cyclobutanol as white solid.

To a 50 mL round-bottom flask were added cyclobutanol (1.0 mmol) and 5 mL acetone. After the solid was dissolved, 1.1 equiv of Jones' reagent was added dropwise. The oxidation was monitored by TLC. Upon completion, excess amount of oxidizing reagent was destroyed by addition of 10% Na_2SO_3 solution. The reaction mixture was then poured into satd NH_4Cl (aq) and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum to a few milliliters. Et_3N (0.5 mL) was added to the residue and the mixture was stirred at room temperature. The reaction was monitored by TLC. After completion, the resulting mixture was washed with 5% HCl solution (2×10 mL) and the organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The product **8** was further purified by silica gel flash chromatography (petroleum ether/ethyl acetate=4:1) to give a colorless oil.

*4.5.1. 3-Phenylcyclobut-2-enone (**8a**).*[11a] Yield 58%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (s, 2H), 6.38 (s, 1H), 7.50–7.52 (m, 3H), 7.62–7.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.5, 128.8, 128.9, 129.7, 131.3, 131.9, 171.0, 187.4.

*4.5.2. 3-(Naphthalen-2-yl)cyclobut-2-enone (**8b**).* Yield 52%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 2H), 6.46 (s, 1H), 7.57–7.63 (m, 2H), 7.71–7.73 (m, 1H), 7.87–7.94 (m, 3H), 7.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.6, 124.3, 127.1, 127.9, 128.4, 128.8, 128.9, 129.1, 130.0, 130.2, 132.8, 134.6, 170.7, 187.5; IR (film) 750, 817, 1051, 1553, 1750 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 194 (M^+, 72), 165 (100), 127 (10), 115 (10), 39 (12); HRMS (ESI) calcd for $C_{14}H_{11}O$ $[M+H]^+$: 195.0810, found: 195.0805, $C_{14}H_{10}NaO$ $[M+Na]^+$: 217.0629, found: 217.0624.

*4.5.3. 4,4-Dimethyl-3-phenylcyclobut-2-enone (**8c**).* Yield 32%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 6H), 6.18 (s, 1H), 7.41–7.43 (m, 3H), 7.54–7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 62.2, 126.3, 128.7, 129.1, 130.6, 131.8, 180.9, 196.4; IR (film) 689, 771, 1150, 1558, 1754 cm^{-1}. EI-MS (*m*/*z*, relative intensity): 172 (M^+, 75), 157 (43), 143 (22), 129 (100), 77 (38); HRMS (ESI) calcd for $C_{12}H_{13}O$ $[M+H]^+$: 173.0966, found: 173.0961, $C_{12}H_{12}NaO$ $[M+Na]^+$: 195.0786, found: 195.0780.

4.6. Typical procedure for the synthesis of cyclopropanes 9

To a 25 mL flame-dried Schlenk tube were added γ-epoxy sulfone **7** (1.0 mmol) and 2 mL THF. The flask was evacuated and backfilled with N_2 for three times and cooled to −30 °C. LDA (1.2 mmol, 2.0 M in THF) was added dropwise via syringe under stirring. The reaction mixture was kept at −30 °C for 0.5 h, allowed to warm to room temperature and then stirred for an additional 0.5 h. Satd NH_4Cl solution was added to quench the reaction. The mixture was extracted with CH_2Cl_2 (3×10 mL) and the organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. Subsequent silica gel flash chromatography (petroleum ether/ethyl acetate=2:1) gives the product **9** as a white solid.

*4.6.1. (2-Phenyl-2-(phenylsulfonyl)cyclopropyl)methanol (**9a**).*[11c] Yield 73%; white solid; mp 131–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58–1.61 (m, 1H), 2.03–2.11 (m, 2H), 2.86 (s, 1H), 4.30–4.35 (m, 2H), 7.11–7.12 (m, 4H), 7.18–7.19 (m, 1H), 7.30–7.49 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 32.3, 52.9, 60.4, 128.1, 128.4, 128.6, 128.7, 131.2, 133.3, 135.3, 138.5.

*4.6.2. (2-(Naphthalen-2-yl)-2-(phenylsulfonyl)cyclopropyl)methanol (**9b**).* Yield 85%; white solid; mp 133–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67–1.70 (m, 1H), 2.12–2.18 (m, 2H), 2.89 (s, 1H), 4.30–4.43 (m, 2H), 7.18–7.26 (m, 3H), 7.41–7.48 (m, 5H), 7.58–7.64 (m, 3H), 7.73–7.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 32.4, 52.9, 60.4, 126.3, 126.8, 127.5, 127.8, 127.9, 128.4, 128.6, 128.7, 131.8, 132.6, 132.8, 133.4, 138.2; IR (film) 688, 741, 1147, 1303, 3058 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 338 (M^+, 15), 197 (99), 154 (40), 141 (100), 77 (68); HRMS (ESI) calcd for $C_{20}H_{19}O_3S$ $[M+H]^+$: 339.1055, found: 339.1040.

*4.6.3. (2,2-Dimethyl-3-phenyl-3-(phenylsulfonyl)cyclopropyl)methanol (**9c**).* Yield 76%, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (s, 3H), 1.26 (s, 1H), 1.88 (s, 3H), 2.57–2.61 (m, 1H), 3.58–3.73 (m, 2H), 6.59 (d, *J*=7.6 Hz, 1H), 6.88–6.91 (m, 1H), 7.25–7.30 (m, 4H), 7.36–7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 22.2, 29.4, 36.8, 59.8, 127.7, 128.1, 128.2, 128.3, 128.7, 130.9, 132.7, 132.9, 134.5, 139.6; IR (film) 688, 705, 1145, 1300, 2927 cm^{-1}; EI-MS (*m*/*z*,

relative intensity): 175 (14), 157 (46), 105 (48), 91 (100), 77 (87); HRMS (ESI) calcd for $C_{18}H_{20}NaO_3S$ $[M+Na]^+$: 339.1031, found: 339.1025.

Acknowledgements

The project is supported by 973 Program (No. 2009CB825300) NSFC and SRF for ROCS, MOE.

Supplementary data

^1H and ^{13}C NMR spectra for all the products are provided. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.03.032.

References and notes

1. For selected reviews, see: (a) Vedejs, E. *Acc. Chem. Res.* **1984**, *17*, 358; (b) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341.
2. (a) Mitani, M.; Tsuchida, M. T.; Koyama, K. *J. Chem. Soc., Chem. Commun.* **1974**, 869; (b) Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylides*; Academic: New York, NY, 1975, Chapter 7; (c) Berger, R.; Ziller, J. W.; Van Vranken, D. L. *J. Am. Chem. Soc.* **1998**, *120*, 841; (d) Padwa, A.; Gasdaska, J. R. *J. Org. Chem.* **1986**, *51*, 2857.
3. (a) Kirmse, W.; Kapps, M. *Chem. Ber.* **1968**, *101*, 994; (b) Doyle, M. P.; Tamblyn, W. H.; Bagheri, V. *J. Org. Chem.* **1981**, *46*, 5094; (c) Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; van Leusen, D. *J. Org. Chem.* **1984**, *49*, 1917.
4. For reviews, see: (a) Hodgson, D. M.; Pierard, T. M.; Stupple, P. A. *Chem. Soc. Rev.* **2001**, *30*, 50; (b) Mehta, G.; Muthusamy, S. *Tetrahedron* **2002**, *58*, 9477; (c) Ando, W.; Matsuyama, H. *Nitrogen, Oxygen Sulfur Ylide Chem.* **2002**, 163; (d) Braverman, S.; Cherkinsky, M. *Top. Curr. Chem.* **2007**, *275*, 67; (e) Reggelin, M. *Top. Curr. Chem.* **2007**, *275*, 1; (f) Wang, J. In; Mingos, D. M. P., Crabtree, R. H., Eds. *Applications II: Transition Metal Compounds in Organic Synthesis 2*; Elsevier: Oxford, 2007; Vol. 11, p 151; (g) Zhang, Y.; Wang, J. *Coord. Chem. Rev.* **2010**, *254*, 941.
5. For selected recent reports on transition-metal-catalyzed sulfur ylides, see: (a) Zhang, X.; Ma, M.; Wang, J. *Tetrahedron: Asymmetry* **2003**, *14*, 891; (b) Zhang, X.; Ma, M.; Wang, J. *Chin. J. Chem.* **2003**, *21*, 878; (c) Kato, Y.; Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *Org. Lett.* **2003**, *5*, 2619; (d) Ma, M.; Peng, L.; Li, C.; Zhang, X.; Wang, J. *J. Am. Chem. Soc.* **2005**, *127*, 15016; (e) Crich, D.; Zou, Y.; Brebion, F. *J. Org. Chem.* **2006**, *71*, 9172; (f) Stepakov, A. V.; Molchanov, A. P.; Magull, J.; Vidovic, D.; Starova, G. L.; Kopf, J.; Kostikov, R. R. *Tetrahedron* **2006**, *62*, 3610; (g) Pang, W.; Zhu, S.; Jiang, H.; Zhu, S. *Tetrahedron* **2007**, *63*, 4543; (h) Liao, M.; Wang, J. *Green Chem.* **2007**, *9*, 184; (i) Peng, L.; Zhang, X.; Ma, M.; Wang, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1905; (j) Liao, M.; Peng, L.; Wang, J. *Org. Lett.* **2008**, *10*, 693; (k) Li, Y.; Shi, Y.; Huang, Z.; Wu, X.; Xu, P.; Wang, J.; Zhang, Y. *Org. Lett.* **2011**, *13*, 1210.
6. For selected reviews, see: (a) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091; (b) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223; (c) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley-Interscience: New York, NY, 1998; (d) Padwa, A. *Chem. Commun.* **1998**, 1417; (e) Padwa, A. *J. Organomet. Chem.* **2001**, *617–618*, 3; (f) Aggarwal, V. K.; Winn, C. L. *Acc. Chem. Res.* **2004**, *37*, 611; (g) Wee, A. G. H. *Curr. Org. Synth.* **2006**, *3*, 499.
7. (a) Bamford, W. R.; Stevens, T. S. M. *J. Chem. Soc.* **1952**, 4735; (b) Shapiro, R. H. *Org. React.* **1976**, *23*, 405; (c) Adlington, R. M.; Barrett, A. G. M. *Acc. Chem. Res.* **1983**, *16*, 55.
8. Fulton, J. R.; Aggarwal, V. K.; de Vicente, J. *Eur. J. Org. Chem.* **2005**, 1479.
9. (a) Zhang, J. L.; Chan, P. W. H.; Che, C. M. *Tetrahedron Lett.* **2003**, *44*, 8733; (b) Doyle, M. P.; Yan, M. *J. Org. Chem.* **2002**, *67*, 602.
10. For selected reports and reviews on coupling reactions involving *N*-tosylhydrazones, see: (a) Barluenga, J.; Moriel, P.; Valdés, C.; Aznar, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 5587; (b) Xiao, Q.; Ma, J.; Yang, Y.; Zhang, Y.; Wang, J. *Org. Lett.* **2009**, *11*, 4732; (c) Barluenga, J.; Escribano, M.; Moriel, P.; Aznar, F.; Valdés, C. *Chem.—Eur. J.* **2009**, *15*, 13291; (d) Zhou, L.; Ye, F.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2010**, *132*, 13590; (e) Xiao, Q.; Xia, Y.; Li, H.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 1114; (f) Zhou, L.; Ye, F.; Ma, J.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 3510; (g) Barluenga, J.; Valdés, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 7486; (h) Shao, Z.; Zhang, H. *Chem. Soc. Rev.* **2012**, *41*, 560.
11. (a) Corbel, B.; Decesare, J.; Durst, T. *Can. J. Chem.* **1978**, *56*, 505; (b) Decesare, J.; Corbel, B.; Durst, T. *Can. J. Chem.* **1981**, *59*, 1415; (c) Corbel, B.; Durst, T. *J. Org. Chem.* **1976**, *41*, 3648.
12. Chiba, K.; Uchiyama, R.; Kim, S.; Kitano, Y.; Tada, M. *Org. Lett.* **2001**, *3*, 1245.