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$FeCl_3$-Catalyzed Regio-Divergent Carbosulfenylation of Unactivated Alkenes: Construction of Medium-Sized Ring

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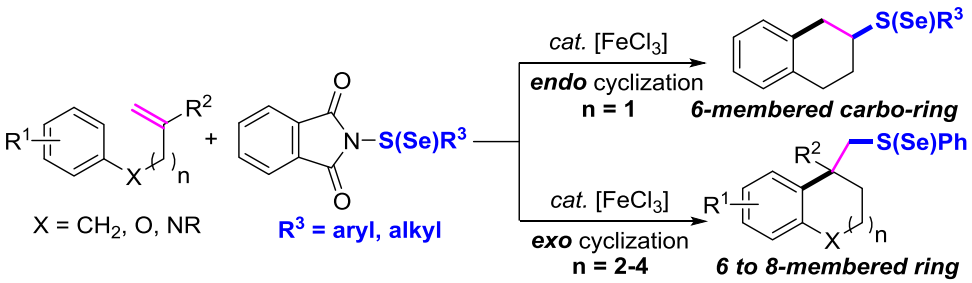
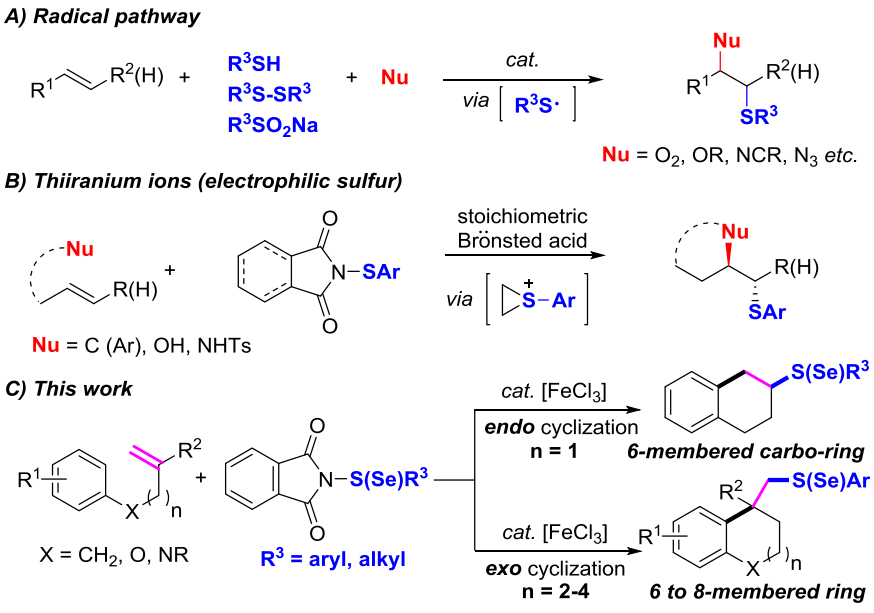


Abstract: A $FeCl_3$-catalyzed regio-divergent carbosulfenylation of unactivated alkenes with electrophilic *N*-sulfenophthalimides has been developed. This protocol provides a straightforward and efficient access to various medium-sized rings, especially strained 7-and 8-membered carborings with sulfur atom attached. The endo/exo selectivity in the reaction depends on the atom number of the chain between arene and alkene. Broad substrate scope, high yields and gram-scale synthesis exemplified the utility and practicability of this protocol. In addition, this methodology can be extended to the carboselenylation of isolated alkenes.

INTRODUCTION

Organosulfur plays a vital role in many significant biological activities, such as regulating hormone release, improving immune resistance and maintaining human's healthy metabolism. Sulfur-containing motifs also widely exists in numerous natural products,[1] pharmaceuticals and agricultures,[2] as well as functional materials[3]. Therefore,

C−S bond formation has gained much attention in the past decades and encouraged the chemists to develop new and efficient synthetic strategies.[4] Among various reported transformations, the difunctionalization of olefins has been proved to be one of the most efficient and powerful methods to incorporate sulfur-containing functional groups into target molecules.[5] In this context, the thiyl radical addition to the activated alkenes has emerged as a convenient route, and a variety of synthetically useful β-functionalized sulfides were prepared selectively and efficiently (Scheme 1A).[6-8] Notably, a breakthrough has been made by Denmark and his coworkers in 2011. They first reported stoichiometric Brönsted acid catalyzed asymmetric carbo-sulfenylation of electron-rich olefinic aryls with an electrophilic thiolating reagent by using a chiral Lewis base (Scheme 1B)[9] In addition, they also extended their protocol to realize enantioselective polyene cyclization, as well as efficient oxy-and amino-sulfenylation of double bonds.[10] Of particular note, Shaw and his coworkers reported an artistically $Sc(OTf)_3$-catalyzed alkene cyclizations for the stereoselective synthesis of complex "terpenoid-like" heterocycles with phenyl selenium/sulfur chlorides.[11] Control experiments revealed that $Sc(OTf)_3$ served as a precatalyst, and the active catalyst was protic acid produced by adventitious moisture. However, to the best of our knowledge, an efficient approach regarding sulfeno-functionalization of alkenes to build strained 7-and 8-membered carbo-rings has not been explored.



Scheme 1. Strategies for Sulfeno-Functionalization of Alkenes

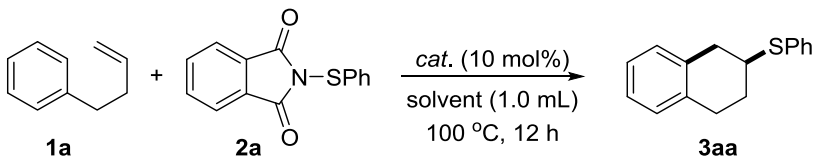
Iron is notably attractive element in the life and synthetic chemistry due to its natural abundance, low cost, versatile oxidation state and environmentally benign character.[12] It also displayed Lewis acid interactions with a variety of functional groups. To demonstrate the powerful flexibility of iron catalyst in the construction of C-S bond, herein, we wish to report a $FeCl_3$-catalyzed regio-divergent carbosulfenylation of unactivated alkenes with electrophilic *N*-sulfenophthalimide (Scheme 1C). With this method, various medium-sized rings, especially strained 7-and 8-membered carborings with sulfur atom attached, were constructed selectively and efficiently. The endo/exo selectivity in the reaction depends on the atom number of the chain between arene and alkene. Broad substrate scope, high yields, gram-scale synthesis and application to the carboselenylations exemplified the utility and practicability of this protocol.

RESULTS AND DISCUSSION

We commenced the studies by exploring the reactions of but-3-en-1-ylbenzene **1a** with *N*-phenylsulfenylimide **2a** for reaction condition optimization (Table 1). Catalytic amount (10 mol%) of Brönsted acid, such as *p*-toluenesulfonic acid (PTSA) and methanesulfonic acid (MsOH), does not work well for this reaction (entries 1 and 2). The 6-endo-trig cyclization product **3aa** was not observed in the presence of $AlCl_3$, $InCl_3$ and $ZnCl_2$ (entries 3-5). In these cases, the competitive sulfenylation-chlorination product (ca. 10-20%) was obtained and more than 60% of **1a** was remained. To our delight, **3aa** was obtained exclusively[13] in 95% yield when $FeCl_3$ as the catalyst (entry 6), and $FeCl_2$ gave a slightly decreased yield (entry 7). Other iron catalysts, such as $Fe(OTf)_2$ and $Fe(acac)_3$, were totally inactive with most starting meterial **1a** (>85%) remianed, yet without dectection of any sulfenylation-chlorination byproduct (entries 8 and 9). Although other Lewis acids, such as $SnCl_4$, TMSOTf and BF_3•OEt_2, also facilitated the 6-endo-trig cyclization (entries 10-12), they were less effective in the latter construction of strained 7-and 8-memered rings. These results indicated that $FeCl_3$ presented unique Lewis acid

character, which was beneficial for the catalytic feasibility of this intramolecular carbosulfenylation. The survey of solvents showed that other halogenated solvents, such as $CHCl_3$, CCl_4 and PhCl, were also effective for this transformation (entries 13-15). However, the formation of **3aa** was completely inhibited in non-halogenated solvents due to the decomposation of *N*-sulfenylating agent **2a** to disulfide (entries 16-20). The striking effect of halogenated solvents on reaction efficiency might be attributed to its halogen bond interactions with **2a**, which greatly suppressed the undesired disulfide formation.[14] The efficiency of this reaction was not affected when 20 mol% of $NaHCO_3$ was added (entry 21). In addition, when HCl was utilized instead of iron catalyst, **3aa** was not detected with most alkene **1a** remained (entry 22). These control experiments demonstrated that $FeCl_3$ played the role of Lewis acid, rather than the precursor of protic acid produced by adventitious moisture. The desired product **3aa** was obtained in 76% yield alone with some uncharacterized by-products when the reaction was performed at 50 ^oC (entry 23). Furthermore, **3aa** was not detected when the reaction was carried out at room temperature with **1a** recovered quantitatively (entry 24). These results indicated that the nucleophilic annulation step was most likely the rate-determinating step of the transformation, and higher temperature was necessary to overcome the energy barrier. It is noteworthy that the carbosulfenylation reaction did not occur in the absence of $FeCl_3$ catalyst (entry 25).

Table 1. Optimization of the Reaction Conditions[a]



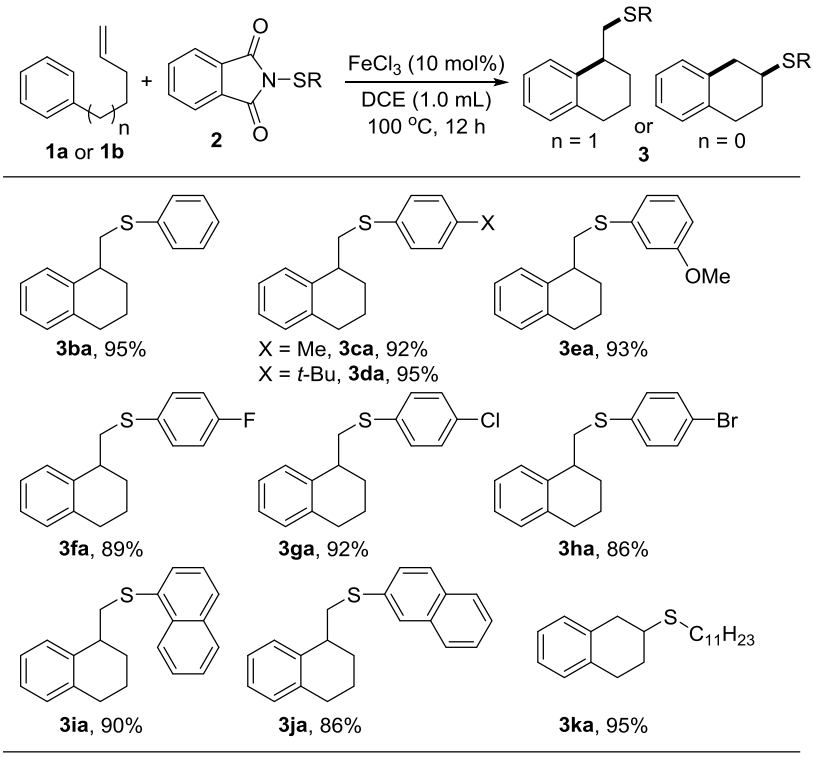
entry	catalyst	solvent	**3aa** (%)[b]
1	PTSA•H_2O	DCE	N.D.
2	MsOH	DCE	8
3	$AlCl_3$	DCE	N.D.
4	$InCl_3$	DCE	N.D.
5	$ZnCl_2$	DCE	N.D.
6	$FeCl_3$	DCE	95 (91)
7	$FeCl_2$	DCE	81
8	$Fe(OTf)_2$	DCE	N.D.
9	$Fe(acac)_3$	DCE	N.D.
10	$SnCl_4$	DCE	93
11	TMSOTf	DCE	72
12	BF_3•OEt_2	DCE	92
13	$FeCl_3$	$CHCl_3$	83
14	$FeCl_3$	CCl_4	89
15	$FeCl_3$	PhCl	91
16	$FeCl_3$	PhMe	N.D.
17	$FeCl_3$	MeCN	N.D.
18	$FeCl_3$	THF	N.D.
19	$FeCl_3$	1,4-dioxane	N.D.
20	$FeCl_3$	DMF	N.D.
21[c]	$FeCl_3$	DCE	95
22	HCl	DCE	N.D.
23[d]	$FeCl_3$	DCE	76
24[e]	$FeCl_3$	DCE	N.D.
25	-	DCE	N.D.

[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.12 mmol), catalyst (10 mol%), solvent (1.0 mL), 100 °C, 12 h, under N_2 unless otherwise noted. [b]Reported yields were based on **1a** and determined by ^{1}H NMR using mesitylene as an internal standard (isolated yield in parenthesis). [c]$NaHCO_3$ (20 mol%) was added. [d]The reaction was performed at 50 °C. [e]The reaction was performed at room temperature. N. D.= not detected.

With the optimal reaction conditions established, we turned our attention to investigate the scope of *N*-sulfenylating agents (Table 2). In general, *N*-phenylsulfenyl phthalimides bearing both electron-donating and

–withdrawing substituents on the aromatic ring were all suitable for this transformation, and the 6-exo-trig cyclization products **3ba-ha** were produced in 86-95% yields. The halogen groups, such as F, Cl, and Br, were all well tolerated, thus allowing further manipulation of these structures. Additionally, *N*-sulfenylphthalimides derived from both α-and β-naphthalenethiol served as suitable reaction partners to react with **1b**, giving the sulfenylated products **3ia** and **3ja** in good yields. To our delight, the S-alkyl thiophthalimide **2k** was also applicable with **1a** in this sulfenylation-cyclization reaction, delivering the endo cyclized product **3ka** in 95% yield.

Table 2. Scope of *N*-Sulfenylphthalimides[a]

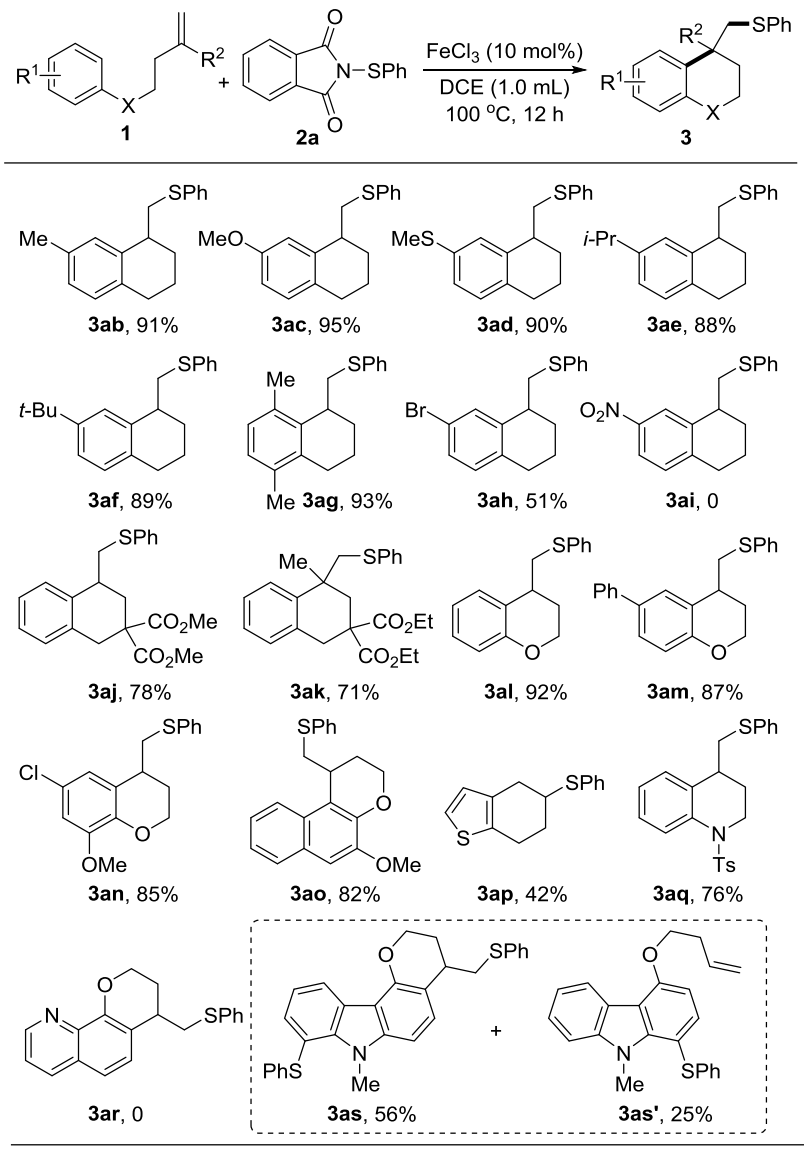


[a]Reaction conditions: **1a** or **1b** (0.1 mmol), **2** (0.12 mmol), $FeCl_3$ (10 mol %), DCE (1.0 mL), 100 °C, 12 h, under N_2; Reported yields were isolated ones based on **1a** or **1b**.

Next, the substrate scope of unactivated alkenes was explored (Table 3). The alkenes with electron-donating groups, such as Me, OMe, SMe, *i*-Pr and *t*-Bu, attached to the aromatic ring reacted smoothly with **2a** under the optimized conditions, giving the corresponding products **3ab-af** in excellent yields. Besides, the sterically hindered

product **3ag** could also be obtained in 95% yield. When electron-withdrawing groups, such as Br and NO_2, attached to the aryl moiety of alkene were tested, **3ah** was obtained in moderate yield, while **3ai** was not detected, possibly due to the strong electron-withdrawing character of -NO_2 decreased the nucleophilic property of phenyl ring. Moreover, the desired **3aj** and **3ak** were obtained in good yields with the ester groups untouched. To our delight, heterocyclic skeletons, such as chromane, cyclopenta[*b*]-thiophene, tetrahydroquinoline, were efficiently constructed when *O*-or *N*-tethered alkenes applied under the optimized conditions (**3al-aq**). The coordination of iron catalyst with substrate **1r**, which was derived from 8-hydroxyquinoline, resulted in no formation of **3ar**. It is worth noting that double sulfeno-functionalization product **3as** was obtained in 56% yield, accompanied by aryl-sulfenylated **3as´** when electron-rich carbazole derived substrate was applied.

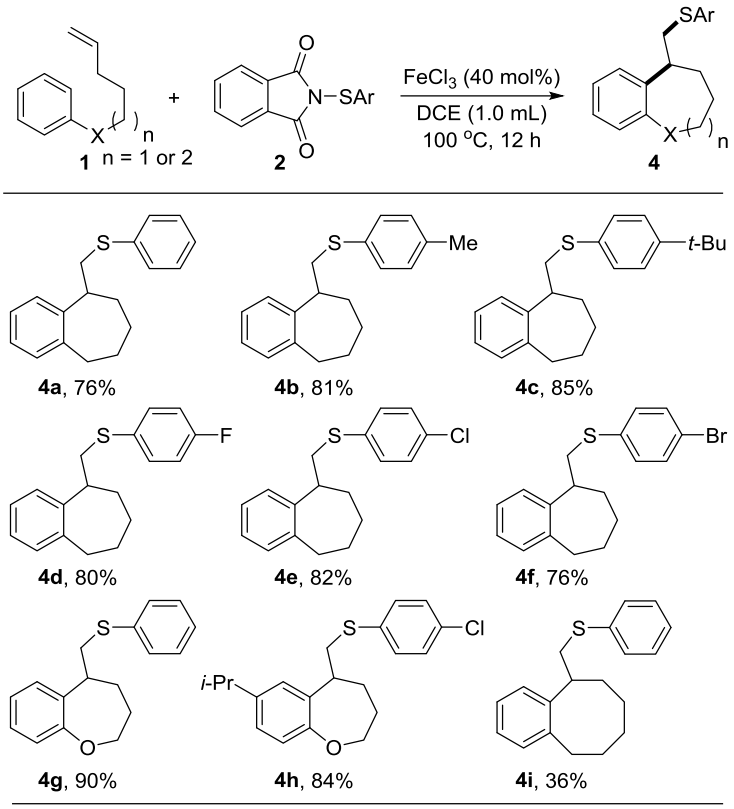
Table 3. Scope of Unactivated Alkenes[a]



[a]Reaction conditions: **1** (0.1 mmol), **2a** (0.12 mmol), $FeCl_3$ (10 mol %), DCE (1.0 mL), 100 °C, 12 h, under N_2; Reported yields were isolated yields and based on **1**.

Given the success of the carbosulfenylation to construct 6-memered ring, we turned our attention to the synthesis of more challenging medium-sized ring (Table 4).[15] To our delight, the 7-membered benzocarbo-rings, which are hard to access due to its constrained configuration, were efficiently constructed with loading of 40 mol% $FeCl_3$ (**4a-f**). Besides, tetrahydrobenzo[*b*]oxepine skeletons were also constructed with this method in excellent yields (**4g-h**). Furthermore, even 8-memered benzo-ring **4i** was accessed in 36% yield under this condition.

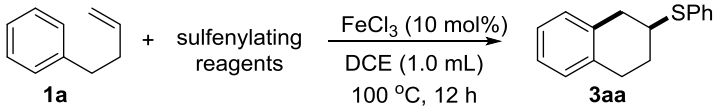
Table 4. Synthesis of 7-and 8-Membered Ring [a]



[a]Reaction conditions:**1** (0.1 mmol), **2** (0.12 mmol), $FeCl_3$ (40 mol %), DCE (1.0 mL), 100 °C, 12 h, under N_2; Reported yields were isolated ones based on **1**.

In addition, other commonly used sulfenylating reagents, such as thiol, disulfides and sulfonothioate, were also tested with **1a** under the standard conditions (Scheme 2). Gratifyingly, benzenesulfenyl chloride **8** was also identified as an efficient sulfenylating reagent, delivering the desired product **3aa** in 93% yield. .

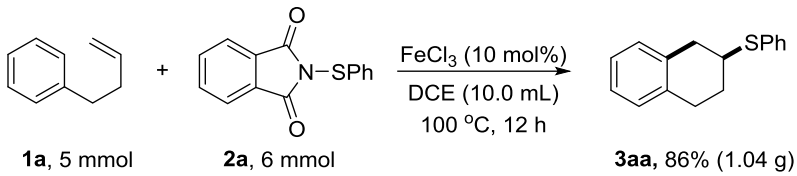
Scheme 2. Testing Other Sulfenylating Reagents.



	3aa	1a (recovered)
PhS−H (**5**)	0	96%
PhS−SPh (**6**)	10%	76%
Ph−S(=O)(=O)−SPh (**7**)	47%	38%
PhS−Cl (**8**)	93%	0

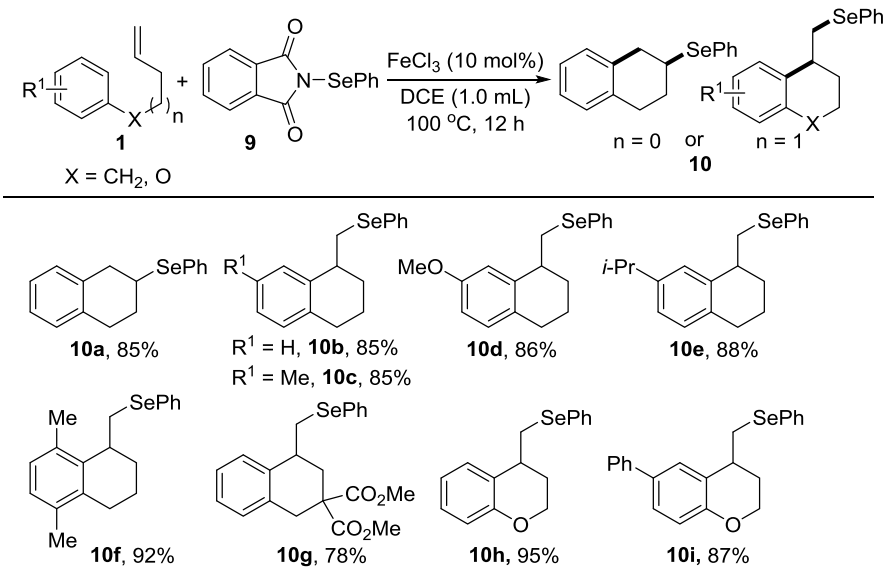
Gram-scale experiment was then performed for the model reaction, and the desired product **3aa** was obtained in 86% yield, which showed practicability of this reaction (Scheme 3).

Scheme 3. Gram-Scale Synthesis.



Organoselenium compounds have manifested potential applications in organic chemistry.[16,17] As early as 1986, Livinghouse reported the stoichiometric Lewis acid mediated selenylative carboannulations of electron-rich olefinic arenes with *N*-(phenylseleno) succinimide.[18] To further explore the potential of our catalytic methodology, the reaction of substrate **1a** with *N*-(phenylseleno)phthalimide (N-PSP) **9** was tested under the optimal conditions (Table 5). Satisfyingly, the selenylated product **10a** was obtained in 94% yield via endo-trig cyclization. When the alkenes with one more atom added on the alkyl chain were applied, the 6-exo-trig carboselenylations underwent smoothly to give the desired products **10b-i** in excellent yields, which demonstrated the general and powerful features of this $FeCl_3$-catalyzed transformation.

Table 5. Carboselenylation of Unactivated Alkenes [a]

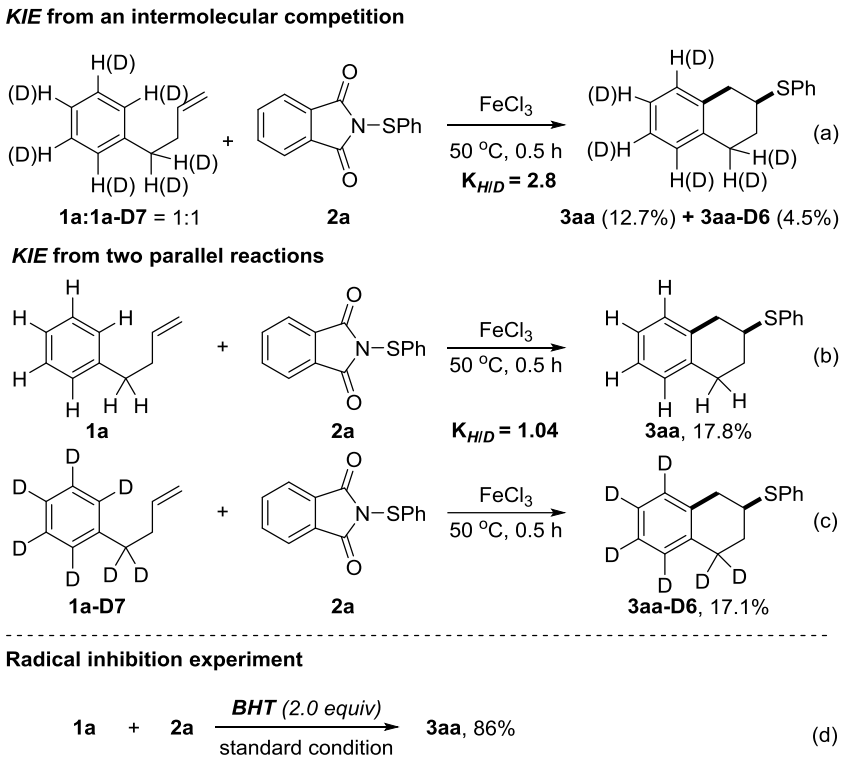


[a]Reaction conditions:**1** (0.1 mmol), **9** (0.12 mmol), $FeCl_3$ (10 mol %), DCE (1.0 mL), 100 °C, 12 h, under N_2; Reported yields were isolated ones based on **1**.

In order to gain the mechanism of this transformation, several control experiments were carried out (Scheme 4).

Obvious kinetic isotope effect ($k_{H/D}$ = 2.8) was observed from inter-molecular competition (Scheme 4a). However, two parallel reactions displayed no kinetic isotope effect ($k_{H/D}$ = 1.04) (Scheme 4b and 4c). These results indicated that the cleavage of aromatic C-H bond may be not involved in the rate-determining step.[19] Besides，the reaction was almost unaffected in the presence of radical inhibitor butylated hydroxytoluene (BHT), which suggested that a radical pathway might be excluded in this process. In addition, combined with the obvious electronic effects on the phenyl ring of alkenes observed in the experiment (Table 3, **3ah** and **3ai**), we speculated that the reaction may proceed through a Friedel–Crafts pathway, and nucleophilic attack of aryl ring to the thiiranium ion may be the key step.[9,10]

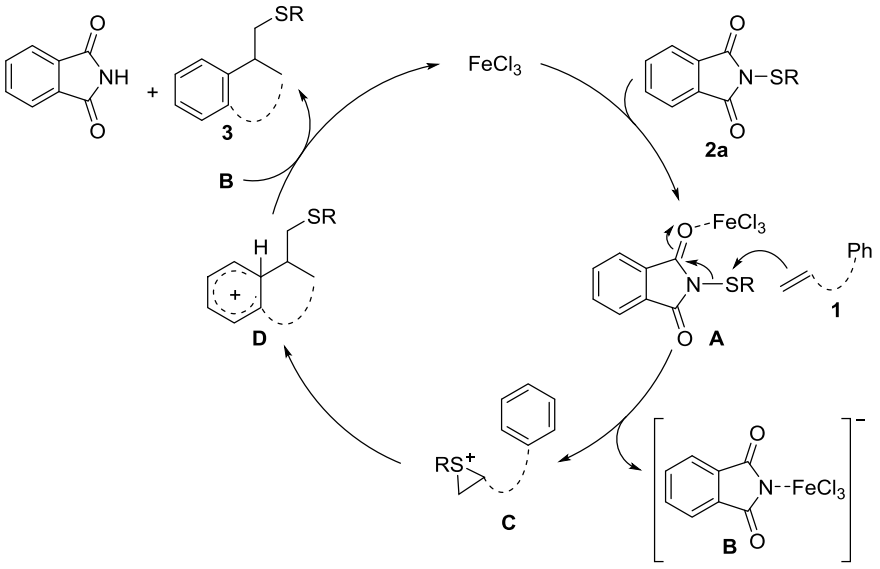
Scheme 4. Control Experiments



Based on the above investigations and reported literature,[9-12] a plausible reaction mechanism was proposed in Scheme 5. Activation of sulfenylating reagent **2a** with $FeCl_3$ gives the intermediate **A**, subsequent addition of C=C bond of **1** to the sulfenyl group forms anion **B** and thiiranium ion species **C**, which undergoes ring-opening by the intramolecular nucleophilic attack of the aryl group to give dearomatic cation **D**. The endo/exo selectivity of the

ring-opening depends on the atom number of the chain between arene and alkene. The need of higher iron catalyst loading in the formation of strained 7-and 8-membered ring suggested that $FeCl_3$ played vital role in the intermolecular nucleophilic capture process.[12,20] Finally, deprotonation of intermediate **D** by anion **B** gives the desired product **3** with release of $FeCl_3$. The similar process is engaged in the carboselenylation reactions.

Scheme 5. Proposed Mechanism for Intramolecular Carbosulfenylation of Unactivated Alkenes.



CONCLUSION

In summary, we have demonstrated a $FeCl_3$-catalyzed regio-divergent carbosulfenylation of unactivated alkenes with electrophilic *N*-sulfenophthalimides. With this method, a variety of medium-sized rings, especially strained 7-and 8-membered carborings with sulfur atom attached were constructed selectively and efficiently. The endo/exo selectivity in the reaction depends on the atom number of the chain between arene and alkene. Preliminary mechanistic studies suggested that a Friedel-Crafts pathway was involved in this transformation. Broad substrate scope, high yields and gram-scale experiment exemplified the utility and practicability of this protocol. In addition, this methodology could also be extended to the carboselenylation of isolated alkenes.

Experimental Section

General Information. ^{1}H NMR spectra were recorded on 500 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal solvent signal (7.28 ppm in $CDCl_3$). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at 125 MHz and referenced to the internal solvent signal (central peak is 77.0 ppm in $CDCl_3$). $CDCl_3$ was used as the NMR solvent. Flash column chromatography was performed over silica gel 200-300. All reagents were weighed and handled in air at room temperature. All reagents were purchased from commercial source and used without further purification. The HRMS measurements were recorded on a TOF analyzer using an ESI or APCI source in the positive mode. The substrate **1** was synthesized according to the reported literatures[21].

General procedure and characterization data for products 3 and **4.** To a mixture of alkene **1** (0.1 mmol), *N*-sulfenylimide **2** (0.12 mmol) and $FeCl_3$ (1.6 mg, 10 mol %), 1,2-dichloroethane (1.0 mL) was added under nitrogen at room temperature. Then the resulting mixture was sealed and stirred at 100 ℃ for 12 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of celite by dichloromethane. The solvent was evaporated in vacuo to give the crude product. The residue was purified by preparative chromatography on silica gel (ethyl acetate/hexane) to give the pure product **3**. In the case of synthesis of 7-and 8-membered product **4**, $FeCl_3$ (6.4 mg, 40 mol %) was added instead.

Phenyl(1,2,3,4-tetrahydronaphthalen-2-yl)sulfane (3aa). (22 mg, 91%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2H), 7.38-7.35 (m, 2H), 7.32-7.28 (m, 1H), 7.17-7.12 (m, 3H), 7.09-7.07 (m, 1H), 3.63-3.57 (m, 1H), 3.22-3.17 (m, 1H), 3.04-2.98 (m, 1H), 2.92-2.86 (m, 2H), 2.30-2.24 (m, 1H), 1.92-1.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 135.1, 134.6, 132.1, 129.0, 128.9, 128.8, 127.0, 126.1, 125.9, 43.2, 36.1, 29.5, 28.6; HRMS (ESI) calcd for $C_{16}H_{16}NaS$ [M + Na^+], 263.0865; found: 263.0871.

Phenyl((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)sulfane (3ba). (24 mg, 95%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.35-7.32 (m, 2H), 7.24-7.18 (m, 2H), 7.17-7.10 (m, 3H), 3.38-3.35 (m, 1H), 3.12-3.03 (m, 2H), 2.86-2.74 (m, 2H), 2.14-2.08 (m, 1H), 1.96-1.90 (m, 1H), 1.89-1.83 (m, 1H), 1.82-1.75 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 137.3, 136.9, 129.3, 129.0, 128.9, 126.2, 125.9, 125.8, 40.8, 37.1, 29.6, 26.5, 19.1; HRMS (ESI) calcd for $C_{17}H_{18}NaS$ [M + Na^+], 277.1021; found: 277.1019.

((1,2,3,4-Tetrahydronaphthalen-1-yl)methyl)(p-tolyl)sulfane (3ca). (25 mg, 92%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 8.2 Hz, 2H), 7.17-7.10 (m, 6H), 3.34-3.32 (m, 1H), 3.08-3.00 (m, 2H), 2.86-2.74 (m, 2H), 2.37 (s, 3H), 2.15-2.10 (m, 1H), 1.96-1.88 (m, 1H), 1.87-1.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 137.3, 136.1, 133.1, 130.1, 129.8, 129.3, 128.9, 126.1, 125.8, 41.5, 37.1, 29.6, 26.4, 21.0, 19.1; HRMS (APCI) calcd for $C_{18}H_{19}S$ [M - H^+], 267.1202; found: 267.1190.

(4-(*Tert*-butyl)phenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)sulfane (3da). (29 mg, 95%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.35 (m, 4H), 7.21-7.18 (m, 1H), 7.17-7.14 (m, 2H), 7.13-7.10 (m, 1H), 3.39-3.33 (m, 1H), 3.10-3.03 (m, 2H), 2.86-2.75 (m, 2H), 2.15-2.10 (m, 1H), 1.97-1.91 (m, 1H), 1.90-1.83 (m, 1H), 1.81-1.75 (m, 1H), 1.35 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 139.2, 137.3, 133.3, 129.4, 129.3, 128.9, 126.1, 126.0, 125.8, 41.2, 37.2, 34.5, 31.3, 29.6, 26.5, 19.2; HRMS (ESI) calcd for $C_{21}H_{26}NaS$ [M + Na^+], 333.1647; found: 333.1643.

(3-Methoxyphenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)sulfane (3ea). (26 mg, 93%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:50, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, J = 8.0 Hz, 1H), 7.24-7.21 (m, 1H), 7.20-7.15 (m, 2H), 7.14-7.11 (m, 1H), 7.03-7.01 (m, 1H), 6.98 (t, J = 2.0 Hz, 1H),

6.77 (dd, J = 8.2, 2.0 Hz, 1H), 3.85 (s, 3H), 3.41-3.36 (m, 1H), 3.14-3.07 (m, 2H), 2.87-2.76 (m, 2H), 2.14-2.10 (m, 1H), 1.98-1.92 (m, 1H), 1.90-1.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 139.1, 138.3, 137.3, 129.8, 129.3, 128.9, 126.3, 125.8, 121.2, 114.5, 111.6, 55.3, 40.5, 37.1, 29.6, 26.6, 19.2; HRMS (APCI) calcd for $C_{18}H_{21}OS$ [M + H^+], 285.1308; found: 285.1294.

(4-Fluorophenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)sulfane (3fa). (24 mg, 65%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.16-7.10 (m, 4H), 7.07-7.03 (m, 2H), 3.29 (dd, J = 12.2, 3.0 Hz, 1H), 3.08-2.98 (m, 2H), 2.86-2.74 (m, 2H), 2.13-2.08 (m, 1H), 1.96-1.89 (m, 1H), 1.88-1.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 246.1 Hz), 138.9, 137.3, 132.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 131.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 129.3, 128.8, 126.2, 125.8, 116.1 (d, $J_{C\text{-}F}$ = 22.0 Hz), 42.3, 37.2, 29.6, 26.4, 19.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.7; HRMS (ESI) calcd for $C_{17}H_{17}FNaS$ [M + Na^+], 295.0927; found: 295.0913.

(4-Chlorophenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)sulfane (3ga). (26 mg, 92%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.34 (m, 2H), 7.31-7.29 (m, 2H), 7.18-7.15 (m, 3H), 7.13-7.11 (m, 1H), 3.34-3.31 (m, 1H), 3.11-3.02 (m, 2H), 2.86-2.75 (m, 2H), 2.11-2.06 (m, 1H), 1.96-1.90 (m, 1H), 1.89-1.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 137.3, 135.5, 131.9, 130.6, 129.3, 129.1, 128.8, 126.3, 125.8, 41.1, 37.1, 29.6, 26.5, 19.1; HRMS (APCI) calcd for $C_{17}H_{16}ClS$ [M - H^+], 287.0656; found: 287.0645.

(4-Bromophenyl)((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)sulfane (3ha). (28 mg, 86%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.29-7.27 (m, 2H), 7.17-7.15 (m, 3H), 7.12-7.10 (m, 1H); 3.34-3.31 (m, 1H), 3.11-3.02 (m, 2H), 2.86-2.75 (m, 2H), 2.11-2.05 (m, 1H), 1.96-1.90 (m, 1H), 1.89-1.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 137.3, 136.2,

132.0, 130.8, 129.3, 128.8, 126.3, 125.8, 119.7, 40.9, 37.1, 29.6, 26.5, 19.1; HRMS (APCI) calcd for $C_{17}H_{16}BrS$ [M - H^+], 331.0151; found: 331.0137.

Naphthalen-1-yl((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)sulfane (3ia). (27 mg, 90%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 8.4, 1.0 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.68 (dd, J = 7.2, 1.0 Hz, 1H), 7.61 (td, J = 7.6, 1.4 Hz, 1H), 7.56 (td, J = 7.6, 1.4 Hz, 1H), 7.48-7.44 (m, 1H), 7.16-7.10 (m, 4H), 3.41 (dd, J = 12.6, 3.6 Hz, 1H), 3.21-3.17 (m, 1H), 3.12-3.07 (m, 1H), 2.87-2.75 (m, 2H), 2.24-2.19 (m, 1H), 2.01-1.95 (m, 1H), 1.93-1.85 (m, 1H), 1.84-1.77 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 137.3, 134.2, 134.0, 133.0, 129.3, 128.9, 128.6, 128.1, 127.2, 126.4, 126.3, 126.2, 125.8, 125.6, 125.1, 41.5, 37.3, 29.6, 26.7, 19.2; HRMS (ESI) calcd for $C_{21}H_{20}NaS$ [M + Na^+], 327.1178; found: 327.1178.

Naphthalen-2-yl((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)sulfane (3ja). (26 mg, 86%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.82-7,79 (m, 2H), 7.78-7.76 (m, 1H), 7.52-7.48 (m, 2H), 7.47-7.44 (m, 1H), 7.24-7.22 (m, 1H), 7.19-7.14 (m, 2H), 7.13-7.11 (m, 1H), 3.47 (dd, J = 12.6, 3.6 Hz, 1H), 3.22-3.17 (m, 1H), 3.14-3.09 (m, 1H), 2.87-2.75 (m, 2H), 2.17-2.12 (m, 1H), 1.99-1.92 (m, 1H), 1.91-1.85 (m, 1H), 1.84-1.76 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 137.3, 134.5, 133.8, 131.7, 129.3, 128.9, 128.4, 127.7, 127.4, 127.0 126.8, 126.6, 126.2, 125.8, 125.6, 40.6, 37.1, 29.6, 26.6, 19.1; HRMS (ESI) calcd for $C_{21}H_{20}NaS$ [M + Na^+], 327.1178; found: 327.1178.

(1,2,3,4-Tetrahydronaphthalen-2-yl)(undecyl)sulfane (3ka). (30 mg, 95%). Isolated by flash column chromatography (hexane, R_f = 0.8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15-7.08 (m, 4H), 3.18-3.14 (m, 1H), 3.12-3.06 (m, 1H), 3.00-2.95 (m, 1H), 2.90-2.79 (m, 2H), 2.65 (t, J = 7.5 Hz, 2H), 2.26-2.20 (m, 1H), 1.84-1.76 (m, 1H), 1.68-1.62 (m, 2H), 1.44-1.40 (m, 2H), 1.34-1.29 (m, 14H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 135.8, 135.4, 128.9, 128.8, 126.0, 125.8, 40.1, 36.7, 31.9, 30.4, 30.0, 29.9, 29.6, 29.5, 29.4, 29.3, 29.1, 28.8, 22.7, 14.1; HRMS (ESI) calcd for $C_{21}H_{34}NaS$ [M + Na^+], 341.2273; found: 341.2270.

((7-Methyl-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)sulfane (3ab). (24 mg, 91%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.35-7.32 (m, 2H), 7.24-7.21 (m, 1H), 7.02-6.97 (m, 3H), 3.39-3.35 (m, 1H), 3.12-3.07 (m, 1H), 3.06-3.01 (m, 1H), 2.82-2.70 (m, 2H), 2.33 (s, 3H), 2.12-2.07 (m, 1H), 1.95-1.89 (m, 1H), 1.88-1.80 (m, 1H), 1.80-1.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 137.1, 135.2, 134.2, 129.4, 129.2, 129.1, 128.9, 127.1, 125.9, 40.8, 37.1, 29.2, 26.6, 21.1, 19.2; HRMS (APCI) calcd for $C_{18}H_{21}S$ [M +H^+], 269.1358; found: 269.1355.

((7-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)sulfane (3ac). (27 mg, 95%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:40, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.35-7.32 (m, 2H), 7.24-7.20 (m, 1H), 7.03 (d, J = 8.8 Hz, 1H), 7.75-6.73 (m, 2H), 3.80 (s, 3H), 3.38-3.35 (m, 1H), 3.13-3.08 (m, 1H), 3.05-3.00 (m, 1H), 2.79-2.68 (m, 2H), 2.08-2.05 (m, 1H), 1.95-1.88 (m, 1H), 1.87-1.81 (m, 1H), 1.80-1.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 140.2, 136.9, 130.1, 129.4, 129.3, 129.0, 126.0, 113.9, 112.2, 55.3, 40.8, 37.5, 28.8, 26.6, 19.4; HRMS (APCI) calcd for $C_{18}H_{19}OS$ [M - H^+], 283.1151; found: 283.1147.

Methyl(8-((phenylthio)methyl)-5,6,7,8-tetrahydronaphthalen-2-yl)sulfane (3ad). (27 mg, 90%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.35-7.32 (m, 2H), 7.24-7.21 (m, 1H), 7.10-7.07 (m, 2H), 7.05-7.03 (m, 1H), 3.35-3.32 (m, 1H), 3.11-3.06 (m, 1H), 3.04-2.99 (m, 1H), 2.81-2.69 (m, 2H), 2.48 (s, 3H), 2.12-2.07 (m, 1H), 1.93-1.87 (m, 1H), 1.86-1.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 136.8, 135.0, 134.6, 129.8, 129.4, 129.0, 127.7, 126.1, 125.3, 40.8, 37.2, 29.1, 26.5, 19.1, 16.5; HRMS (ESI) calcd for $C_{18}H_{20}NaS_2$ [M + Na^+], 323.0899; found: 323.0887.

((7-*Iso*propyl-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)sulfane (3ae). (26 mg, 88%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.35-7.33 (m, 2H), 7.24-7.21 (m, 1H), 7.07-7.03 (m, 3H), 3.39-3.36 (m, 1H), 3.14-3.10 (m, 1H), 3.07-3.03 (m, 1H), 2.92-2.86 (m, 1H), 2.83-2.72 (m, 2H), 2.13-2.08 (m, 1H), 1.95-1.88 (m, 1H), 1.87-1.74 (m, 2H), 1.27 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 138.9, 137.1, 134.6, 129.2, 128.9, 126.9, 125.9, 124.4, 40.8, 37.3, 33.8, 29.2, 26.6, 24.2, 24.1, 19.2; HRMS (ESI) calcd for $C_{20}H_{24}NaS$ [M + Na^+], 319.1491; found: 319.1489.

((7-(*Tert*-butyl)-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)sulfane (3af). (28 mg, 89%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.35-7.32 (m, 2H), 7.24-7.20 (m, 3H), 7.07-7.05 (m, 1H), 3.37-3.34 (m, 1H), 3.15-3.10 (m, 1H), 3.07-3.03 (m, 1H), 2.83-2.71 (m, 2H), 2.13-2.08 (m, 1H), 1.95-1.88 (m, 1H), 1.87-1.75 (m, 2H), 1.33 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 138.5, 137.2, 134.2, 129.2, 129.0, 128.9, 125.9, 125.7, 123.4, 41.0, 37.5, 34.4, 31.4, 29.1, 26.6, 19.1; HRMS (ESI) calcd for $C_{21}H_{26}NaS$ [M + Na^+], 333.1647; found: 333.1644.

((5,8-Dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)sulfane (3ag). (26 mg, 93%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.34-7.31 (m, 2H), 7.25-7.22 (m, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 3.15-3.11 (m, 2H), 3.03-2.98 (m, 1H), 2.80-2.76 (m, 1H), 2.60-2.53 (m, 1H), 2.41-2.38 (m, 1H), 2.21 (s, 3H), 2.18 (s, 3H), 1.93-1.85 (m, 2H), 1.71-1.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 136.6, 135.1, 134.4, 133.6, 130.4, 128.9, 127.7, 126.3, 37.8, 34.5, 26.7, 24.2, 19.7, 18.7, 17.1; HRMS (ESI) calcd for $C_{19}H_{22}NaS$ [M + Na^+], 305.1334; found: 305.1334.

((7-Bromo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)sulfane (3ah). (16 mg, 51%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H),

7.36-7.33 (m, 2H), 7.30-7.29 (m, 1H), 7.26-7.22 (m, 2H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.33-3.30 (m, 1H), 3.09-3.04 (m, 1H), 3.03-2.98 (m, 1H), 2.79-2.66 (m, 2H), 2.11-2.06 (m, 1H), 1.92-1.86 (m, 1H), 1.85-1.73 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 136.5, 136.2, 131.6, 130.9, 129.6, 129.2, 129.0, 126.2, 119.2, 40.8, 37.1, 29.1, 26.2, 18.9; HRMS (APCI) calcd for $C_{17}H_{16}BrS$ [M - H^+], 331.0151; found: 331.0134.

Dimethyl 4-((phenylthio)methyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate (3aj). (29 mg, 78%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:10, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 2H), 7.20-7.15 (m, 3H), 3.78 (s, 3H), 3.61 (s, 3H), 3.54 (dd, *J* = 12.8, 3.8 Hz, 1H), 3.36 (dd, *J* = 16.0, 1.6 Hz, 1H), 3.27-3.22 (m, 2H), 3.08 (dd, *J* = 12.8, 9.2 Hz, 1H), 2.93-2.88 (m, 1H), 2.13 (dd, *J* = 12.8, 9.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 171.0, 136.7, 136.4, 134.0, 130.0, 129.1, 129.0, 127.1, 126.7, 126.6, 126.3, 53.9, 52.9, 52.6, 41.3, 35.4, 35.0, 34.1; HRMS (ESI) calcd for $C_{21}H_{22}NaO_4S$ [M + Na^+], 393.1131; found: 393.1128.

Diethyl 4-methyl-4-((phenylthio)methyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate (3ak). (29 mg, 71%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:10, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.27-7.23 (m, 3H), 7.20-7.15 (m, 4H), 4.25-4.09 (m, 4H), 3.30 (d, *J* = 16.0 Hz, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 3.22 (d, *J* = 15.6 Hz, 1H), 3.20 (d, *J* = 15.6 Hz, 1H), 2.80 (d, *J* = 14.4 Hz, 1H), 2.39 (dd, *J* = 14.4, 1.2 Hz, 1H), 1.41 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 171.4, 140.7, 137.8, 133.7, 129.5, 128.9, 128.8, 126.8, 126.6, 126.2, 125.9, 61.6, 61.4, 52.7, 49.1, 38.9, 38.4, 35.5, 29.9, 14.0, 13.9; HRMS (ESI) calcd for $C_{24}H_{28}NaO_4S$ [M + Na^+], 435.1601; found: 435.1591.

4-((Phenylthio)methyl)chromane (3al). (24 mg, 92%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:50, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.37-7.33 (m, 2H), 7.27-7.22 (m, 1H), 7.17-7.12 (m, 2H), 6.90 (td, *J* = 7.6, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.4, 1.2 Hz, 1H), 4.26-4.13 (m, 2H),

3.50-3.43 (m, 1H), 3.07-3.00 (m, 2H), 2.24-2.12 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 136.2, 129.6, 129.2, 129.1, 128.0, 126.3, 124.5, 120.4, 117.1, 62.9, 40.3, 33.1, 25.7; HRMS (ESI) calcd for $C_{16}H_{16}NaOS$ [M + Na^+], 279.0814; found: 279.0815.

6-Phenyl-4-((phenylthio)methyl)chromane (3am). (29 mg, 87%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:50, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.47-7.44 (m, 4H), 7.40 (dd, J = 8.4, 2.4 Hz, 1H), 7.38-7.32 (m, 4H), 7.27-7.24 (tt, J = 7.4, 1.2 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 4.30-4.26 (m, 1H), 4.24-4.19 (m, 1H), 3.56-3.50 (m, 1H), 3.14-3.08 (m, 2H), 2.27-2.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 140.9, 136.1, 133.6, 129.7, 129.1, 128.8, 127.9, 126.9, 126.8, 126.7, 126.4, 124.7, 117.4, 63.0, 40.4, 33.3, 25.8; HRMS (ESI) calcd for $C_{22}H_{20}NaOS$ [M + Na^+], 355.1127; found: 355.1120.

6-Chloro-8-methoxy-4-((phenylthio)methyl)chromane (3an). (27 mg, 85%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:50, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.36-7.33 (m, 2H), 7.27-7.23 (m, 1H), 6.72 (s, 2H), 4.34-4.30 (m, 1H), 4.22-4.17 (m, 1H), 3.87 (s, 3H), 3.44-3.38 (m, 1H), 3.00-2.93 (m, 2H), 2.24-2.19 (m, 1H), 2.16-2.09 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 142.8, 135.7, 130.0, 129.2, 126.6, 126.0, 124.6, 120.4, 110.3, 63.4, 56.1, 40.2, 33.0, 25.2; HRMS (ESI) calcd for $C_{17}H_{17}ClNaO_2S$ [M + Na^+], 343.0530; found: 343.0532.

5-methoxy-1-((phenylthio)methyl)-2,3-dihydro-1H-benzo[f]chromene (3ao). (25 mg, 82%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:50, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 7.8 Hz, 1H), 7.57-7.55 (m, 2H), 7.41-7.38 (m, 2H), 7.36-7.33 (m, 2H), 7.32-7.29 (m, 1H), 7.26-7.22 (m, 1H), 7.05 (s, 1H), 4.58-4.55 (m, 1H), 4.33-4.28 (m, 1H), 4.00 (s, 3H), 3.57 (d, J = 13.6 Hz, 1H), 3.52-3.49 (m, 1H), 3.03-2.98 (m, 1H), 2.54 (dq, J = 14.2, 2.0 Hz, 1H), 2.20-2.13 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 144.0, 135.5, 131.7,

129.1, 129.0, 127.4, 127.2, 124.4, 123.8, 121.1, 116.7, 105.6, 62.1, 55.8, 39.3, 29.8, 23.4; HRMS (ESI) calcd for $C_{21}H_{21}O_2S$ [M + H^+], 337.1257; found: 337.1262.

5-(Phenylthio)-4,5,6,7-tetrahydrobenzo[b]thiophene (3ap). (10 mg, 42%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.36-7.32 (m, 2H), 7.30-7.28 (m, 1H), 7.09 (d, *J* = 5.0 Hz, 1H), 6.74 (d, *J* = 5.0 Hz, 1H), 3.60-3.55 (m, 1H), 3.08 (dd, *J* = 15.6, 4.8 Hz, 1H), 2.99 (dt, *J* = 16.4, 4.8 Hz, 1H), 2.87-2.81 (m, 1H), 2.72-2.67 (m, 1H), 2.30-2.25 (m, 1H), 1.96-1.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.5, 134.4, 132.2, 128.9, 127.2, 127.1, 122.6, 43.2, 32.5, 30.0, 24.3; HRMS (APCI) calcd for $C_{14}H_{13}S_2$ [M - H^+], 245.0453; found: 245.0444.

4-((Phenylthio)methyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (3aq). (31 mg, 76%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:10, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.33-7.28 (m, 4H), 7.27-7.22 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.13 (td, *J* = 7.6, 1.2 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.89-3.84 (m, 1H), 3.81-3.75 (m, 1H), 3.04 (dd, *J* = 13.0, 4.4 Hz, 1H), 2.82-2.77 (m, 1H), 2.40-2.37 (m, 1H), 2.35 (s, 3H), 1.88-1.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.6, 136.4, 135.9, 132.1, 129.6, 129.5, 129.0, 128.8, 127.3, 127.2, 126.4, 125.0, 124.8, 44.0, 40.0, 35.1, 25.3, 21.5; HRMS (ESI) calcd for $C_{23}H_{23}NNaO_2S_2$ [M + Na^+], 432.1062; found: 432.1054.

7-Methyl-8-(phenylthio)-4-((phenylthio)methyl)-2,3,4,7-tetrahydropyrano[3,2-c]carbazole (3as). (26 mg, 56%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:10, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 1.6 Hz, 1H), 7.61 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.48-7.46 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.16-7.14 (m, 2H), 7.12-7.09 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 4.51-4.47 (m, 1H), 4.37 (td, *J* = 10.6, 3.0 Hz, 1H), 3.85 (s, 3H), 3.52 (dd, *J* = 12.8, 3.4 Hz, 1H), 3.21-3.16 (m, 1H), 3.13-3.09 (m, 1H), 2.36-2.24 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 141.7, 140.6,

140.5, 136.4, 131.7, 130.1, 129.6, 129.1, 128.8, 127.5, 126.9, 126.3, 125.0, 123.1, 121.1, 114.6, 111.0, 109.0, 101.1, 63.0, 40.7, 32.8, 29.4, 25.7; HRMS (ESI) calcd for $C_{29}H_{25}NNaOS_2$ [M + Na^+], 490.1270; found: 490.1263.

4-(But-3-en-1-yloxy)-9-methyl-1-(phenylthio)-9H-carbazole (3as'). (9 mg, 25%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:10, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 1.5 Hz, 1H), 7.61 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.26-7.20 (m, 4H), 7.15-7.12 (m, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.01-5.93 (m, 1H), 5.25 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.11-5.08 (m, 1H), 4.29 (t, *J* = 6.4 Hz, 2H), 3.87 (s, 3H), 2.73-2.69 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 142.8, 140.2, 140.0, 134.6, 131.1, 129.7, 128.8, 127.6, 127.1, 125.2, 123.3, 121.9, 117.3, 111.6, 108.8, 101.5, 101.2, 67.3, 34.0, 29.5; HRMS (ESI) calcd for $C_{23}H_{22}NOS$ [M + H^+], 360.1417; found: 360.1426.

Phenyl((6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)methyl)sulfane (4a). (20 mg, 76%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:120, R_f = 0.8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.23-7.19 (m, 1H), 7.18-7.11 (m, 4H), 3.45 (dd, *J* = 12.6, 6.2 Hz, 1H), 3.30 (dd, *J* = 12.6, 9.2 Hz, 1H), 3.17-3.12 (m, 1H), 2.88-2.80 (m, 2H), 1.99-1.87 (m, 2H), 1.81-1.74 (br, 2H), 1.73-1.64 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 142.5, 136.8, 130.0, 129.3, 128.9, 126.4, 126.1, 125.9, 44.0, 37.4, 36.2, 32.0, 28.3, 27.9; HRMS (ESI) calcd for $C_{18}H_{21}S$ [M + H^+], 269.1358; found: 269.1346.

((6,7,8,9-Tetrahydro-5H-benzo[7]annulen-5-yl)methyl)(p-tolyl)sulfane (4b). (23 mg, 81%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:120, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.18-7.10 (m, 6H), 3.42-3.38 (m, 1H), 3.27-3.23 (m, 1H), 3.13-3.09 (m, 1H), 2.88-2.79 (m, 2H), 2.35 (s, 3H), 1.99-1.89 (m, 2H), 1.81-1,73 (br, 2H), 1.70-1.62 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 142.5, 136.1, 132.9, 130.2, 129.9, 129.7, 126.4, 126.1, 43.9, 38.1, 36.2, 31.9, 28.4, 27.9, 21.0; HRMS (ESI) calcd for $C_{19}H_{23}S$ [M + H^+], 283.1515; found:283.1501.

(4-(*Tert*-butyl)phenyl)((6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)methyl)sulfane (4c). (27 mg, 85%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:120, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.32 (m, 4H), 7.19-7.11 (m, 4H), 3.42 (dd, J = 12.4, 6.0 Hz, 1H), 3.27 (dd, J = 12.4, 9.2 Hz, 1H), 3.17-3.12 (m, 1H), 2.89-2.80 (m, 2H), 2.00-1.91 (m, 2H), 1.82-1.73 (br, 2H), 1.72-1.64 (br, 2H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 144.0, 142.5, 133.1, 129.9, 129.6, 126.4, 126.1, 126.0, 44.0, 37.9, 36.2, 34.5, 32.0, 31.3, 28.4, 27.9; HRMS (ESI) calcd for $C_{22}H_{28}NaS$ [M + Na^+], 347.1804; found: 347.1800.

(4-Fluorophenyl)((6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)methyl)sulfane (4d). (23 mg, 80%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:120, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.18-7.14 (m, 2H), 7.13-7.10 (m, 2H), 7.04-7.00 (m, 2H), 3.40-3.36 (m, 1H), 3.26-3.22 (m, 1H), 3.10-3.06 (m, 1H), 2.88-2.78 (m, 2H), 1.98-1.89 (m, 2H), 1.81-1.74 (br, 2H), 1.71-1.64 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8 (d, $J_{C\text{-}F}$ = 246.2 Hz), 143.6, 142.5, 132.4 (d, $J_{C\text{-}F}$ = 7.8 Hz), 131.5 (d, $J_{C\text{-}F}$ = 3.4 Hz), 130.0, 126.5, 126.1, 116.0 (d, $J_{C\text{-}F}$ = 21.8 Hz), 44.0, 38.8, 36.1, 31.9, 28.3, 27.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.7; HRMS (ESI) calcd for $C_{18}H_{20}FS$ [M + H^+], 287.1264; found: 287.1260.

(4-Chlorophenyl)((6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)methyl)sulfane (4e). (25 mg, 65%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:120, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 4H), 7.19-7.11 (m, 4H), 3.43-3.39 (m, 1H), 3.29-3.25 (m, 1H), 3.14-3.10 (m, 1H), 2.89-2.79 (m, 2H), 1.97-1.89 (m, 2H), 1.81-1.74 (br, 2H), 1.71-1.64 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 142.4, 135.3, 131.9, 130.6, 130.0, 129.0, 126.5, 126.2, 44.0, 37.6, 36.2, 32.0, 28.2, 27.8; HRMS (ESI) calcd for $C_{18}H_{20}ClS$ [M + H^+], 303.0969; found: 303.0974.

(4-Bromophenyl)((6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)methyl)sulfane (4f). (26 mg, 76%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:120, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.40

(m, 2H), 7.24-7.21 (m, 2H), 7.17-7.13 (m, 2H), 7.13-7.11 (m, 2H), 3.43-3.39 (m, 1H), 3.29-3.24 (m, 1H), 3.14-3.10 (m, 1H), 2.89-2.79 (m, 2H), 1.97-1.87 (br, 2H), 1.83-1.74 (br, 2H), 1.72-1.63 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 142.4, 136.0, 131.9, 130.7, 130.0, 126.5, 126.2, 119.7, 44.0, 37.4, 36.2, 32.0, 28.3, 27.8; HRMS (ESI) calcd for $C_{18}H_{19}BrNaS$ [M + Na^+], 369.0283; found: 369.0273.

5-((Phenylthio)methyl)-2,3,4,5-tetrahydrobenzo[b]oxepine (4g). (24 mg, 90%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:50, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.32-7.29 (m, 2H), 7.22-7.17 (m, 2H), 7.12 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.05-7.01 (m, 2H), 4.38-4.34 (m, 1H), 3.69 (td, *J* = 11.8, 1.8 Hz, 1H), 3.46-3.41 (m, 1H), 3.38-3.34 (m, 1H), 3.13-3.08 (m, 1H), 2.30-2.16 (m, 2H), 1.86-1.79 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 136.9, 130.2, 129.2, 128.9, 128.1, 125.9, 123.8, 122.2, 73.7, 43.7, 36.0, 28.9, 27.1; HRMS (ESI) calcd for $C_{17}H_{18}NaOS$ [M + Na^+], 293.0971; found: 293.0961.

5-(((4-Chlorophenyl)thio)methyl)-7-isopropyl-2,3,4,5-tetrahydrobenzo[b]oxepine (4h). (29 mg, 84%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:50, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.24 (m, 4H), 7.04-7.01 (m, 1H), 6.92-6.90 (m, 2H), 4.36-4.32 (m, 1H), 3.64 (td, *J* = 12.0, 1.8 Hz, 1H), 3.43-3.38 (m, 1H), 3.35-3.30 (m, 1H), 3.07-2.99 (m, 1H), 2.90-2.81 (m, 1H), 2.28-2.11 (m, 2H), 1.84-1.76 (m, 2H), 1.25 (s, 3H), 1,23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 144.2, 136.2, 135.2, 131.7, 130.5, 128.9, 128.3, 125.8, 121.8, 73.5, 44.1, 36.2, 33.4, 29.0, 27.0, 24.2, 24.1; HRMS (APCI) calcd for $C_{20}H_{24}OClS$ [M + H^+], 347.1231; found: 347.1215.

((5,6,7,8,9,10-Hexahydrobenzo[8]annulen-5-yl)methyl)(phenyl)sulfane (4i). (10 mg, 36%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:150, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.22-7.18 (m, 3H), 7.13-7.11 (m, 1H), 7.09-7.06 (m, 1H), 7.04-7.01 (m, 1H), 7.01-6.98 (m, 1H), 3.19-3.14 (m, 1H), 2.94-2.90 (m, 1H), 2.85-2.80 (m, 1H), 2.66-2.63 (m, 2H), 2.19-2.14 (m, 1H), 2.00-1.94 (m, 1H), 1.71-1.38 (m, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 137.8, 132.2, 129.9, 128.4, 128.3, 126.6, 126.5, 125.7, 123.6, 37.6, 35.9, 34.1, 31.5, 26.7, 25.9, 22.8; HRMS (ESI) calcd for $C_{19}H_{22}NaS$ [M + Na^+], 305.1334; found: 305.1336.

General procedure and characterization data for product 10. To a mixture of alkene **1** (0.1 mmol), *N*-(phenylseleno)phthalimide (N-PSP) **9** (0.12 mmol) and $FeCl_3$ (1.6 mg, 10 mol %), 1,2-dichloroethane (1.0 mL) was added under nitrogen at room temperature. Then the resulting mixture was sealed and stirred at 100 ℃ for 12 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of celite by dichloromethane. The solvent was evaporated in vacuo to give the crude product. The residue was purified by preparative chromatography on silica gel (ethyl acetate/hexane) to give the pure product **10**.

Phenyl(1,2,3,4-tetrahydronaphthalen-2-yl)selane (10a). (27 mg, 94%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.35-7.30 (m, 3H), 7.16-7.09 (m, 3H), 7.05-7.03 (m, 1H), 3.70-3.64 (m, 1H), 3.24 (dd, *J* = 16.6, 5.0 Hz, 1H), 3.02-2.94 (m, 2H), 2.90-2.84 (m, 1H), 2.32-2.27 (m, 1H), 2.00-1.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 135.5, 134.9, 129.0, 128.9, 128.8, 128.7, 127.6, 126.0, 125.8, 39.0, 36.9, 30.3, 29.2; HRMS (ESI) calcd for $C_{16}H_{17}Se$ [M + H^+], 289.0490; found: 289.0479.

Phenyl((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)selane (10b). (26 mg, 85%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.56 (m, 2H), 7.32-7.26 (m, 3H), 7.15-7.10 (m, 4H), 3.35 (dd, *J* = 11.8, 3.2 Hz, 1H), 3.17-3.13 (m, 1H), 3.11-3.06 (m, 1H), 2.84-2.73 (m, 2H), 2.08-2.03 (m, 1H), 1.98-1.91 (m, 1H), 1.88-1.81 (m, 1H), 1.79-1.72 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 137.2, 132.7, 130.9, 129.2, 129.1, 128.8, 126.8, 126.1, 125.8, 37.9, 35.6, 29.7, 27.4, 19.2; HRMS (ESI) calcd for $C_{17}H_{18}NaSe$ [M + Na^+], 325.0466; found: 325.0453.

((7-Methyl-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)selane (10c). (27 mg, 85%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.33-7.26 (m, 3H), 7.01-7.00 (m, 1H), 6.98-6.95 (m, 2H), 3.36 (dd, *J* = 11.8, 3.3 Hz, 1H), 3.18-3.13 (m, 1H), 3.09-3.04 (m, 1H), 2.81-2.69 (m, 2H), 2.31 (s, 3H), 2.07-2.02 (m, 1H), 1.97-1.91 (m, 1H), 1.88-1.80 (m, 1H), 1.78-1.71 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 135.2, 134.1, 132.7, 131.0, 129.4, 129.1, 129.0, 127.1, 126.8, 38.0, 35.6, 29.3, 27.5, 21.1, 19.4; HRMS (APCI) calcd for $C_{18}H_{19}Se$ [M - H^+], 315.0647; found: 315.0631.

((7-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)selane (10d). (28 mg, 65%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:40, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.56 (m, 2H), 7.32-7.27 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 3.78 (s, 3H), 3.35 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.17-3.13 (m, 1H), 3.08-3.03 (m, 1H), 2.78-2.66 (m, 2H), 2.05-2.00 (m, 1H), 1.96-1.90 (m, 1H), 1.87-1.79 (m, 1H), 1.77-1.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 140.5, 132.7, 130.9, 130.1, 129.3, 129.1, 126.9, 113.9, 112.2, 55.3, 38.3, 35.6, 28.9, 27.5, 19.5; HRMS (APCI) calcd for $C_{18}H_{19}OSe$ [M - H^+], 331.0596; found: 331.0582.

((7-*Iso*propyl-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)selane (10e). (30 mg, 88%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.33-7.26 (m, 3H), 7.05-7.01 (m, 2H), 7.00 (s, 1H), 3.36 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.19-3.14 (m, 1H), 3.10-3.05 (m, 1H), 2.89-2.83 (m, 1H), 2.81-2.69 (m, 2H), 2.07-2.02 (m, 1H), 1.97-1.90 (m, 1H), 1.87-1.79 (m, 1H), 1.78-1.71 (m, 1H), 1.26 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 139.3, 134.5, 132.6, 131.0, 129.2, 129.1, 126.9, 126.8, 124.3, 38.1, 35.7, 33.8, 29.3, 27.5, 24.1, 24.0, 19.3; HRMS (ESI) calcd for $C_{20}H_{24}NaSe$ [M + Na^+], 367.0935; found: 367.0925.

((5,8-Dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)(phenyl)selane (10f). (30 mg, 92%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:100, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.33-7.29 (m, 3H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 3.17-3.12 (m, 2H), 3.05-3.00 (m, 1H), 2.78-2.73 (m, 1H), 2.59-2.51 (m, 1H), 2.38-2.35 (m, 1H), 2.21 (s, 3H), 2.12 (s, 3H), 1.91-1.81 (m, 2H), 1.74-1.67 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 135.0, 134.4, 133.8, 133.6, 130.3, 129.0, 127.8, 127.7, 127.2, 35.2, 32.4, 26.8, 25.0, 19.7, 18.6, 17.0; HRMS (APCI) calcd for $C_{19}H_{21}Se$ [M - H^+], 329.0803; found: 329.0787.

Dimethyl 4-((phenylselanyl)methyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate (10g). (32 mg, 78%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:10, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.33-7.24 (m, 3H), 7.21-7.15 (m, 4H), 3.79 (s, 3H), 3.62 (s, 3H), 3.48 (dd, *J* = 12.0, 3.4 Hz, 1H), 3.37 (dd, *J* = 16.0, 2.1 Hz, 1H), 3.32-3.26 (m, 2H), 3.20-3.16 (m, 1H), 2.91-2.86 (m, 1H), 2.15-2.10 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 171.0, 137.0, 133.9, 133.1, 130.3, 129.0, 128.9, 127.1, 127.0, 126.6, 126.5, 53.9, 52.8, 52.6, 35.6, 35.5, 35.4, 34.7; HRMS (ESI) calcd for $C_{21}H_{22}NaO_4Se$ [M + Na^+], 441.0576; found: 441.0581.

4-((Phenylselanyl)methyl)chromane (10h). (29 mg, 95%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:60, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.35-7.28 (m, 3H), 7.14 (td, *J* = 15.4, 1.6 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.89 (td, *J* = 7.6, 1.2 Hz, 1H), 6.85 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.24-4.20 (m, 1H), 4.17-4.13 (m, 1H), 3.48-3.42 (m, 1H), 3.11-3.02 (m, 2H), 2.19-2.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 132.9, 130.2, 129.3, 129.2, 128.0, 125.0, 120.4, 117.0, 62.9, 34.7, 33.9, 26.5; HRMS (ESI) calcd for $C_{16}H_{16}NaOSe$ [M + Na^+], 327.0259; found: 327.0268.

6-Phenyl-4-((phenylselanyl)methyl)chromane (10i). (33 mg, 87%). Isolated by flash column chromatography (ethyl acetate/hexane = 1:60, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H), 7.55-7.53 (m, 2H), 7.46-7.43 (m, 2H), 7.39 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.35-7.30 (m, 5H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.28-4.24 (m, 1H),

4.22-4.17 (m, 1H), 3.53-3.48 (m ,1H), 3.16-3.10 (m, 2H), 2.25-2.17 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 140.9, 133.6, 133.0, 130.2, 129.3, 128.7, 127.9, 127.2, 126.8, 126.7, 126.6, 125.2, 117.4, 63.1, 34.7, 34.1, 26.7; HRMS (ESI) calcd for $C_{22}H_{20}NaOSe$ [M + Na^+], 403.0572; found: 403.0570.

Kinetic isotope effect experiment. Intermolecular competition: To a mixture of alkene **1a** (0.05 mmol) and **1a-D7** (0.05 mmol) in the same tube, *N*-phenylsulfenylimide **2a** (0.12 mmol), $FeCl_3$ (1.6 mg, 10 mol %) and 1,2-dichloroethane (1.0 mL) was added sequentially under nitrogen at room temperature. Then the resulting mixture was sealed and stirred at 50 ℃ for 0.5 h. Then the mixture was immediately cooled to 0 ºC with ice-water. The ^{1}H NMR was carried out to determine the yields of **3aa** and **3aa-D6** using mesitylene as an internal standard. **Two parallel reactions:** To a mixture of alkene **1a** (0.1 mmol), *N*-phenylsulfenylimide **2a** (0.12 mmol), $FeCl_3$ (1.6 mg, 10 mol %) and 1,2-dichloroethane (1.0 mL) was added sequentially under nitrogen at room temperature. In another tube, **1a-D7** (0.1 mmol) was added, and the other conditions are the same. Then the two tubes were sealed and simultaneously stirred at 50 ℃ for 0.5 h. Then the mixtures were immediately cooled to 0 ºC with ice-water. The ^{1}H NMR was separately carried out to determine the yields of **3aa** and **3aa-D6** using mesitylene as an internal standard. **1-(But-3-en-1-yl-1,1-d2)benzene-2,3,4,5,6-d5 (1a-D7)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94-5.85 (m, 1H), 5.07 (dq, J = 17.2, 1.6 Hz, 1H), 5.02-5.00 (m, 1H), 2.40 (d, J = 6.6 Hz, 1H); EI-MS (m/z) = 139.1. **3aa-D6**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.35-7.33 (m, 2H), 7.29-7.26 (m, 1H), 3.60-3.54 (m, 1H), 3.19-3.15 (m, 1H), 3.89-2.84 (m, 1H), 2.24-2.22 (m, 1H), 1.86-1.81 (m, 1H); EI-MS (m/z) = 246.4.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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