JOC The Journal of Organic Chemistry

Note

Copper-catalyzed Three Component Regio- and Stereo-specific Selenosulfonation of Alkynes: Synthesis of (E)-#-selenovinyl Sulfones

Yang Liu, Guangfan Zheng, Qian Zhang, Yan Li, and Qian Zhang

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b03049 • Publication Date (Web): 26 Jan 2017

Just Accepted

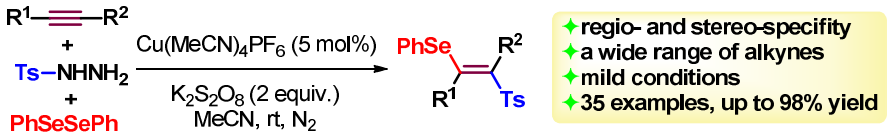
ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Copper-catalyzed Three Component Regio- and Stereo-specific Selenosulfonation of Alkynes: Synthesis of (*E*)-β-selenovinyl Sulfones

Yang Liu, Guangfan Zheng, Qian Zhang†, Yan Li*, and Qian Zhang†,*

Key Laboratory of Functional Organic Molecule Design & Synthesis of Jilin Province, Department of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun, Jilin 130024, China

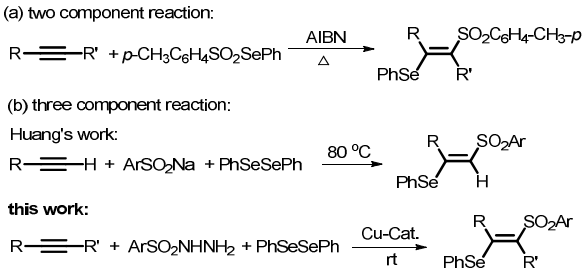


ABSTRACT: A copper-catalyzed high regio- and stereo-specific selenosulfonation of alkynes with arylsulfonohydrazides and diphenyl diselenide has been developed. This novel three component reaction proceed under very mild conditions and with a broad scope of substrates, providing a wide range of (*E*)-β-selenovinyl sulfones in good to excellent yields.

Vinyl sulfones are unique motifs in some biologically active molecules[1] and usefully synthetic intermediates in organic synthesis.[2] Accordingly, considerable effort has been devoted to develop new and efficient methods for the construction of these compounds,[3] including the oxidation of the corresponding vinyl sulides,[4] Knoevenagel condensation of aromatic aldehydes with sulfonylacetic acids,[5] Wittig reaction of α-sulfonyl phosphonium ylides,[6] β-elimination of selenosulfones or halosulfones,[7] and sulfonation of alkenes[8]/alkynes.[9-12] Among them, sulfonative functionalization of alkynes, the addition of sulfonyl and other groups across a triple bond,

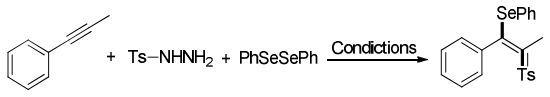
represents one of the most straightforward strategies. For example, alkynes sulfonative difunctionalization, such as halosulfonylation,[9] sulfonyloxidation,[10] sulfonamination[11] and sulfonylcarbonation,[12] has been successfully realized for the synthesis of various sulfonative difunctionalization products. Vinyl selenides[13] are useful synthetic intermediates and therapeutic entities that display a wide spectrum of biological activities, thus rendering these motifs highly important synthetic targets.[14] β-Selenovinyl sulfones could be obtained through radical selenosulfonation of alkynes and Se-phenyl *p*-tolueneselenosulfonate (Scheme 1a),[15] which usually need to be pre-pared through the reaction of sulfinates, sulfonhydrazides, or selenenyl halides with benzeneseleninic acid, or sodium sulfonates with diphenyl diselenide.[16] Therefore, the development of direct three component selenosulfonation reactions starting from readily available sulfonyl and selenyl radical sources is highly desirable. In this context, Huang and co-workers realized selenosulfonation of acetylenes with sodium arenesulfinates and diphenyl diselenide (Scheme 1b).[17] However, these reaction were performed at 80 ^{o}C and only terminal alkynes were effect. Recently, we realized copper-catalyzed radical aminative functionalizations of al-kynes.[18] As our continuous interest in radical reactions,[19] we expected to explore three component radical selenosul-fonation of alkynes. Herein, we reported a novel copper-catalyzed regio- and stereo-specific selenosulfonation of alkynes with arylsulfonohydrazides and diphenyl diselenide under very mild conditions, synthesizing a wide range of (*E*)-β-selenovinyl sulfones (Scheme 1b).

Scheme 1. Selenosulfonation of Alkynes



Initially, the reaction of prop-1-yn-1-ylbenzene (**1a**, 0.3 mmol) with *p*-toluenesulfonyl hydrazide (**2a**, 1.2 equiv.) and diphenyl diselenide (**3**, 0.5 equiv.) was chosen as model reaction to optimize the conditions. No reaction occurred at 70 ^{o}C in CH_3CN without catalyst and oxidant (Table 1, entry 1). In the presence of $K_2S_2O_8$ (2 equiv.), to our delight, the desired selenofulfonation product **4a** was obtain in 43% yield (Table 1, entry 2). Upon adding $Cu(MeCN)_4PF_6$ (5 mol%), 72% of **4a** was obtained (Table 1, entry 3). Decreasing temperature to 50 ^{o}C, a better yield (92%) of **4a** was given (Table 1, entry 4). Among CH_3CN, DCE, CH_3OH, DMF, THF and toluene, CH_3CN was the best solvent (Table 1, entries 4-9). Other oxidants, such as H_2O_2, DTBP and TBHP were also examined, but the result was not improved (Table 1, entries 10-12). Other copper-catalysts such as CuBr•Me_2S, CuBr, CuCl, CuI and $Cu(OAc)_2$ were not as efficient as $Cu(MeCN)_4PF_6$ (Table 1, entries 13-17). Finally, we tried to conduct the reaction at room temperature. Satisfactorily, the yield of **4a** was improved to 98% (Table 1, entry 18), while in absence of the catalyst no reaction was observed (Table 1, entry 19). The configurations of **4a** was further confirmed by X-ray analysis.[20]

Table 1. Optimization of Reaction Conditions[a]



1a **2a** **3** **4a**

entry	catalyst	oxidant	solvent	T (^{o}C)	yield[b] (%)

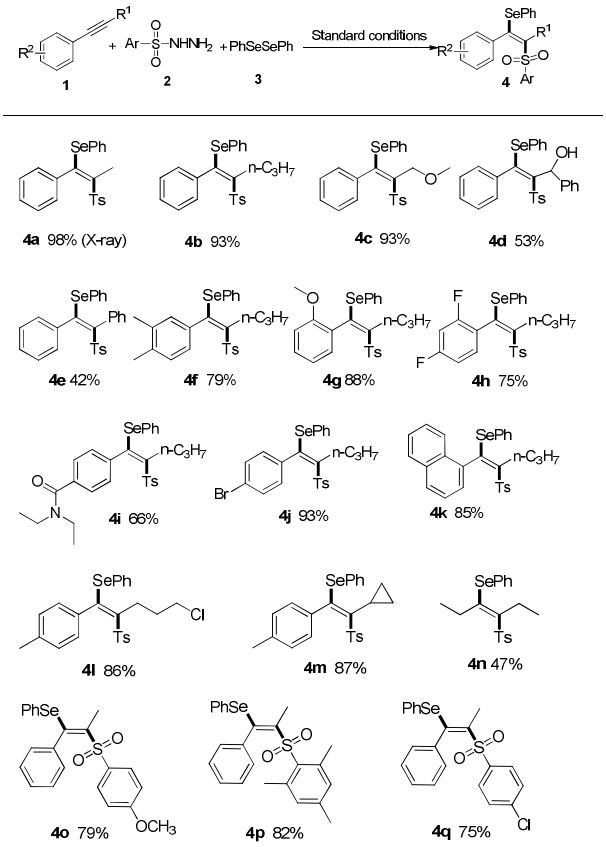
1	none	none	CH_3CN	70	0
2	none	$K_2S_2O_8$	CH_3CN	70	43
3	$Cu(MeCN)_4PF_6$	$K_2S_2O_8$	CH_3CN	70	72
4	$Cu(MeCN)_4PF_6$	$K_2S_2O_8$	CH_3CN	50	92
5	$Cu(MeCN)_4PF_6$	$K_2S_2O_8$	DCE	50	68
6	$Cu(MeCN)_4PF_6$	$K_2S_2O_8$	CH_3OH	50	35
7	$Cu(MeCN)_4PF_6$	$K_2S_2O_8$	DMF	50	27
8	$Cu(MeCN)_4PF_6$	$K_2S_2O_8$	THF	50	50
9	$Cu(MeCN)_4PF_6$	$K_2S_2O_8$	Toluene	50	43
10	$Cu(MeCN)_4PF_6$	H_2O_2	CH_3CN	50	40
11	$Cu(MeCN)_4PF_6$	DTBP	CH_3CN	50	0
12	$Cu(MeCN)_4PF_6$	TBHP	CH_3CN	50	70
13	$CuBr•Me_2S$	$K_2S_2O_8$	CH_3CN	50	75
14	CuBr	$K_2S_2O_8$	CH_3CN	50	68
15	CuCl	$K_2S_2O_8$	CH_3CN	50	78
16	CuI	$K_2S_2O_8$	CH_3CN	50	45
17	$Cu(OAc)_2$	$K_2S_2O_8$	CH_3CN	50	65
18	**$Cu(MeCN)_4PF_6$**	**$K_2S_2O_8$**	**CH_3CN**	**rt**	**98**
19	none	$K_2S_2O_8$	CH_3CN	rt	0

[a] General reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), **3** (0.15 mmol), catalyst (5 mol%), oxidant (0.6 mmol), solvent (2 mL), nitrogen atmosphere, 12 h. Ts = $-SO_2C_6H_4$-*p*-CH_3. [b] Isolated yield.

With the optimized reaction conditions (Table 1, entry 18), we next explored the scope of the selenosulfonation process with respect to internal alkyes **1** and arylsulfonyl-hydrazides **2**, the results are shown in Table 2. Delightfully, the internal alkynes with alkyl (**1a–e**) or aryl (**1e**), smoothly participated in this highly region- and stereo-selective selenosulfonation reaction to provide (*E*)-β-selenovinyl sulfones **4a–e** in moderate to excellent yields. It should be noted that a synthetically attractive hydroxyl group, which is sensitive to oxidants survived from the reaction conditions, gave the expected product **4d** in an accepted yield (53%). The substrates **1f–m**, bearing either electron-donating or electron-withdrawing groups on the benzene ring, were compatible with this reaction as well, regardless of their different electronic properties and sites,

affording desired (*E*)-β-selenovinyl sulfones **4f–m** in 53-88% yields. In addition, internal aliphatic alkyne **1n** successfully underwent selenosulfonylation to give **4n**, albeit in a low yield. Next, the scope of arylsulfonylhydrazides **2** was examined. Gratifyingly, introduction of methyoxyl, methyl and halo-gen groups into the aromatic ring of sulfonylhydrazides was well-tolerated, and the corresponding (*E*)-β-selenovinyl sulfones **4o-q** were formed in good to excellent yield. It should be noted that in all reactions, no other isomers were observed.

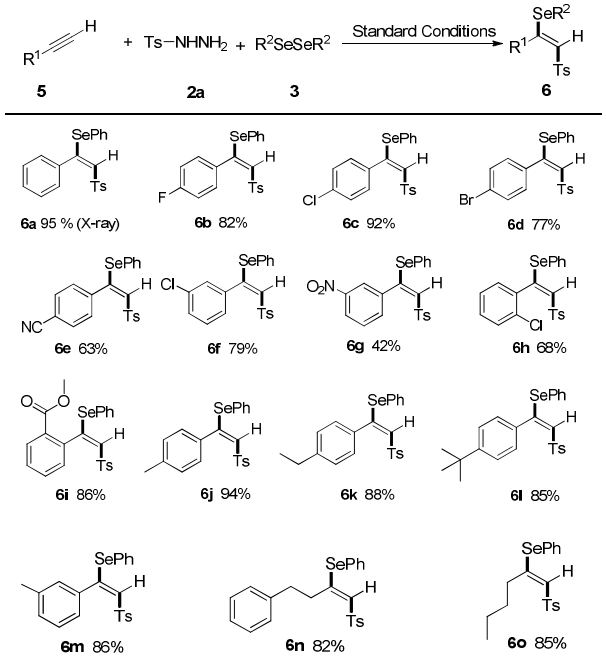
Table 2. Scope of Internal Alkynes and Arylsulfonylhydrazides[a]

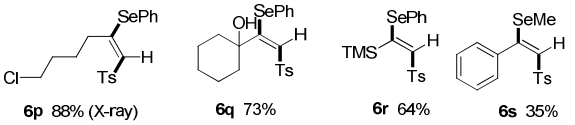


[a] Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), **3** (0.15 mmol), $Cu(MeCN)_4PF_6$ (5 mol%), $K_2S_2O_8$ (0.6 mmol), CH_3CN (2 mL), nitrogen atmosphere, room temperature, 12 h. Isolated yield. Ts = $-SO_2C_6H_4$-*p*-CH_3.

Inspired by the above excellent results, we sent to explore the selenosulfonation of terminal alkynes. As described in Table 3, aromatic terminal alkynes with a wide range of functional groups, such as F, Cl, Br, CN, NO_2, MeOCO, Me, Et and *t*-Bu, were well tolerated, producing (*E*)-β-selenovinyl sulfones **6a-m** in up to 95% yield. Gratifyingly, aliphatic alkynes **5n** and **5o** were viable substrates for the selenosulfonation, producing **6n** and **6o** with a yield of 82% and 85%, respectively. Significantly, aliphatic alkynes with Cl (**5p**), OH (**5q**) and TMS (**5r**) groups which can readily undergo further transformation were founded to be suitable for the reaction, delivering the desired (*E*)-β-selenovinyl sulfones **6p-r**. The configurations of **6a** and **6p** were further confirmed by X-ray analysis.[20] Additionally, dimethyl diselenide was efficient for this reaction, providing the corresponding selenosulfonation product **6s** in 35% yield.

Table 3. Variety of Terminal Alkynes and Disenides[a]



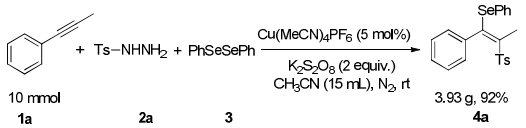


6p 88% (X-ray) **6q** 73% **6r** 64% **6s** 35%

[a] Reaction conditions: **5** (0.3 mmol), **2a** (0.36 mmol), **3** (0.15 mmol), $Cu(MeCN)_4PF_6$ (5 mol%), $K_2S_2O_8$ (0.6 mmol), CH_3CN (2 mL), nitrogen atmosphere, room temperature, 12 h. Isolated yield. Ts = $-SO_2C_6H_4$-*p*-CH_3.

In order to demonstrate the synthetic utility of the three component selenosulfonation of alkynes with aryl sulfonyhydrzides and diphenyl diselenide, we performed this three component reaction on a gram scale (Scheme 2). Pleasingly, 3.93 g (*E*)-β-selenovinyl sulfone **4a** was isolated.

Scheme 2. Gram-scale Synthesis of (*E*)-β-Selenovinyl Sulfone

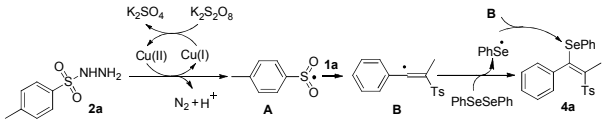


10 mmol **1a** **2a** **3** 3.93 g, 92% **4a**

To gain some insights into the reaction mechanism, some control experiments were carried out. As known, selenosulfonates might be formed from the reaction of arysulfonohydrazides with diphenyl diselenide. Thus, the reaction of prop-1-yn-1-ylbenzene (**1a**) with Se-phenyl *p*-tolueneselenosulfonate was performed under optimized conditions (Table 1, entry 18). No reaction occurred and the substrate was recovered completely. This result showed that the selenosufonation might not involve a selenosulfonate intermediate. Next, Adding 1 equiv. of BHT and TEMPO to the reaction of **1a** under standard conditions, the yield of **4a** decreased to 17% and 21%, respectively. With 2 equiv. of BHT and TEMPO, the selenosulfonation was completely suppressed and no **4a** was detected. These results suggested that this transformation might proceed via a radical pathway.

Based on the experimental results and literatures,[7b,15a,15b, 21] a proposed radical mechanism is shown in Scheme 3. Initially, the sulfonyl radical **A** was generated in the presence of copper salt and $K_2S_2O_8$ via single electron transfer and deprotonation process, along with the release of N_2.[22] Then, the sulfonyl radical **A** region-specifically added to alkynes, forming a relatively stable β-sulfonyl vinyl radical **B**. Subsequently, the phenyl selenol group transferred from diphenyl diselenide to **B** or coupled between **B** and phenyl selenol radical to afford thermodynamically stable (*E*)-β-selenovinyl sulfone **4a**. Alternatively, the phenyl selenol group transfer might be much more rapid than the inversion of **B**,[15b] thus resulting in a single isomer **4a**.

Scheme 3. Proposed Mechanism



In conclusion, we have developed a copper-catalyzed high regio- and stereo-specific selenosulfonation of alkynes with aryl sulfonohydrazides and diphenyl diselenide. This three component reaction proceed under very mild conditions and with a broad scope of substrates. With the reaction, a wide range of (*E*)-β-selenovinyl sulfones are synthesized in good to excellent yields.

EXPERIMENTAL SECTION

General Experimental Methods. All the reagents were used as purchased from commercial suppliers without further purification. Acetonitrile was distilled over calcium hydride before use. Analytical thin layer chromatography (TLC) was performed on pre-coated alumina-backed silica gel plates (0.2 mm thickness) which were developed using UV florescence. Flash chromatography

was performed on silica gel (300−400 mesh). Melting points were measured on a standard melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a 400, 500 or 600 MHz spectrometer, while ^{13}C NMR spectra were recorded on a 100, 125 and 150 MHz instrument. Chemical shifts are reported in δ ppm referenced to an internal TMS standard for ^{1}H NMR and chloroform-d (δ = 77.0 ppm) for ^{13}C NMR. HRMS spectra were recorded using FAB (TOF analyzer) or ESI (TOF analyzer). Single-crystal X-ray diffraction data were recorded at a temperature of 293(2) K on an Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å).

Characterization Data for Selenosulfonation Products. 4a, **4e** and **6a** were reported by Miura and coworkers.[15a] **4n**, **6a**, **6d** and **6j** were reported by Back and coworkers.[15b] **4b−4d**, **4f−4m**, **4o−4q**, **6b**, **6c**, **6e−6i**, and **6k−6r** were synthesized as follows.

General Procedure A for the Synthesis of Products 4 and 6. In a dried glass vial, equipped with a magnetic stir bar, charged with PhSeSePh (46.8 mg, 0.15 mmol, 0.5 equiv.), $Cu(MeCN)_4PF_6$ (5.6 mg, 5 mol%), $K_2S_2O_8$ (162.2 mg, 0.6 mmol, 2.0 equiv.) under nitrogen atmosphere, 2 mL MeCN was added next, followed by addition of alkyne **1** or **5** (0.3 mmol, 1.0 equiv.) and benzenesulfonyl hydrazide (0.36 mmol, 1.2 equiv.). After stirring for 12 h, the reaction mixture was concentrated, then the residue was subjected to column chromatography on silica gel (petroleum ether: diethyl ether = 40:1 – 12:1) to afford the desired product **4** or **6**.

*(E)-phenyl(1-phenyl-2-tosylprop-1-en-1-yl)selane (**4a**)*.[15a] Following the general procedure A, **4a** was obtained as a white solid (98% yield, 125.8 mg). mp: 93−94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.18 – 7.06 (m, 5H), 7.02 – 6.86 (m, 5H), 6.74 – 6.68 (m, 2H), 2.38 (s, 3H),

2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 143.4, 138.3, 137.0, 135.9, 129.2, 129.1, 128.6, 128.5, 127.7, 127.3, 127.0, 126.7, 21.5, 18.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{20}O_2SSe$ ([M + H]$^+$), 429.0427, found 429.0422.

*(E)-phenyl(1-phenyl-2-tosylpent-1-en-1-yl)selane (**4b**)*. Following the general procedure A, **4b** was obtained as a white solid (93% yield, 127.2 mg). mp: 102−104 °C; ^{1}H NMR (400 MHz, CDCl3) δ 7.21 (d, *J* = 8.4 Hz, 2H), 7.12 – 7.04 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.85 (m, 3H), 6.80 (t, *J* = 7.6 Hz, 2H), 6.65 – 6.54 (m, 2H), 2.96 – 2.82 (m, 2H), 2.32 (s, 3H), 1.95 – 1.78 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 150.9, 143.0, 139.2, 138.6, 136.9, 129.3, 128.9, 128.5, 128.3, 127.4, 127.1, 126.8, 126.5, 35.2, 22.4, 21.4, 14.1. HRMS (ESI-TOF) (m/z): Calcd for C24H24O2SSe ([M + Na]$^+$), 479.0566, found 479.0567.

*(E)-(3-methoxy-1-phenyl-2-tosylprop-1-en-1-yl)(phenyl)selane (**4c**)*. Following the general procedure A, **4c** was obtained as a yellow oil. (93% yield, 127.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.00 (m, 5H), 6.98 – 6.89 (m, 3H), 6.85 (t, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 7.2 Hz, 2H), 4.70 (s, 2H), 3.47 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 143.2, 138.6, 136.8, 135.4, 135.3, 129.00, 128.96, 128.6, 128.4, 127.6, 127.2, 126.6, 70.0, 58.0, 21.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{22}O_3SSe$ ([M + Na]$^+$), 481.0368, found 481.0359.

*(E)-1,3-diphenyl-3-(phenylselanyl)-2-tosylprop-2-en-1-ol (**4d**)*. Following the general procedure A, **4d** was obtained as a white solid. (53% yield, 82.7 mg). mp: 170−171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.05 (m, 3H), 7.00 – 6.81 (m, 8H), 6.75 (dd, *J* = 19.2, 7.2 Hz, 2H), 6.51 (d, *J* = 10.8 Hz, 2H), 4.71 (d, *J* = 11.2 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 143.4, 141.0, 140.7, 138.6, 137.0, 134.9, 129.8, 129.4, 128.9, 128.8, 128.6, 127.65, 127.63, 127.61, 126.82, 126.78, 126.6, 75.4, 21.5. HRMS (ESI-TOF)

(m/z): Calcd for $C_{28}H_{24}O_3SSe$ ([M + Na]$^+$), 543.0511, found 543.0515.

*(E)-(1,2-diphenyl-2-tosylvinyl)(phenyl)selane (**4e**)*.[15a] Following the general procedure A, **4e** was obtained as a white solid. (42% yield, 61.7 mg). mp: 167−168 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 3H), 7.38 – 7.34 (m, 2H), 7.27 – 7.22 (m, 2H), 7.10 – 7.03 (m, 5H), 7.03 – 6.99 (m, 3H), 6.94 – 6.89 (m, 4H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.8, 143.5, 138.0, 137.4, 137.1, 135.2, 134.7, 131.0, 129.3, 128.8, 128.5, 128.3, 127.7, 127.5, 126.9, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{22}O_2SSe$ ([M + H]$^+$), 491.0589, found 491.0586.

*(E)-(1-(3,4-dimethylphenyl)-2-tosylpent-1-en-1-yl)(phenyl)selane (**4f**)*. Following the general procedure A, **4f** was obtained as a white solid. (79% yield, 114.7 mg). mp: 89−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.10 – 7.04 (m, 3H), 7.03 – 6.89 (m, 4H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.49 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.06 (s, 1H), 2.84 – 2.95 (m, 2H), 2.33 (s, 3H), 2.03 (s, 3H), 1.82 (m, 6H), 1.61 – 1.46 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 142.7, 139.3, 138.9, 136.9, 135.5, 134.4, 133.1, 130.3, 128.6, 128.3, 128.1, 127.8, 127.6, 127.1, 33.0, 31.1, 22.9, 21.4, 19.3, 19.0, 13.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{27}O_2SSe$ ([M + Na]$^+$), 506.0795, found 506.0791.

*(E)-(1-(2-methoxyphenyl)-2-tosylpent-1-en-1-yl)(phenyl)selane (**4g**)*. Following the general procedure A, **4g** was obtained as a white solid. (88% yield, 128.3 mg). mp: 99−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.20 – 7.27 (m, 2H), 7.12 – 7.05 (m, 3H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.96 – 6.83 (m, 4H), 6.64 (t, *J* = 7.6 Hz, 1H), 5.99 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H), 2.81 (q, *J* = 4.0 Hz, 2H), 2.32 (s, 3H), 1.99 – 1.79 (m, 2H), 1.12 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 148.7, 142.6, 138.4, 137.9, 137.3, 131.4, 129.5, 128.5, 127.9, 127.7, 126.6, 124.33, 119.0, 108.9, 54.0, 34.7, 22.0, 21.4, 14.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{26}O_3SSe$ ([M + Na]$^+$), 509.0664, found

507.0661.

(E)-(1-(2,4-difluorophenyl)-2-tosylpent-1-en-1-yl)(phenyl)selane ***(4h)***. Following the general procedure A, **4h** was obtained as a white solid. (75% yield, 110.7 mg). mp: 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.11 (m, 5H), 7.07 – 6.97 (m, 2H), 6.76 (td, *J* = 8.4, 6.4 Hz, 1H), 6.58 – 6.45 (m, 1H), 6.20 (td, *J* = 9.6, 2.4 Hz, 1H), 2.87 – 2.67 (m, 2H), 2.37 (s, 3H), 1.92 – 1.70 (m, 2H), 1.09 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, CDCl3) δ 162.6 (dd, *J* = 298.6, 11.5 Hz), 157.8 (dd, *J* = 298.6, 14.7 Hz), 143.7, 140.2, 137.8, 137.3, 131.9 (dd, *J* = 9.6, 3.9 Hz), 129.2, 128.6, 127.5, 125.9, 120.4 (dd, *J* = 19.1, 3.6 Hz), 109.9 (dd, *J* = 21.4, 3.3 Hz), 102.7 (t, *J* = 25.5 Hz),102.52, 35.0, 21.8, 21.5, 14.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{22}F_2O_2SSe$ ($[M + Na]^+$), 515.0372, found 515.0377.

(E)-N,N-diethyl-4-(1-(phenylselanyl)-2-tosylbut-1-en-1-yl)benzamide ***(4i)***. Following the general procedure A, **4i** was obtained as a white solid. (66% yield, 109.9 mg). mp: 123−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.13 – 6.98 (m, 5H), 6.96 – 6.88 (m, 2H), 6.78 – 6.71 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 2H), 3.52 – 3.31 (bs, 2H), 2.97 – 2.78 (m, 4H), 2.29 (s, 3H), 1.92 – 1.77 (m, 2H), 1.19 – 1.01 (m, 6H), 1.02 – 0.85 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 149.4, 143.2, 140.0, 138.3, 137.1, 136.5, 136.0, 129.3, 129.0, 128.5, 128.4, 127.3, 126.7, 124.4, 35.1, 22.3, 21.3, 14.0. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{33}NO_3SSe$ ($[M + Na]^+$), 578.1249, found 578.1245.

(E)-(1-(4-bromophenyl)-2-tosylpent-1-en-1-yl)(phenyl)selane ***(4j)***. Following the general procedure A, **4j** was obtained as a white solid. (93% yield, 149.0 mg). mp: 132−133 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 8.4 Hz, 4H), 7.00 (t, *J* = 7.8 Hz, 2H), 6.96 – 6.90 (m, 2H), 6.47 (d, *J* = 8.4 Hz, 2H), 2.91 – 2.82 (m, 2H), 2.36 (s, 3H), 1.90 – 1.77 (m, 2H), 1.11 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.0, 143.4, 140.4, 138.5, 137.0, 135.0,

130.9, 129.9, 129.1, 128.7, 127.5, 126.6, 121.5, 35.3, 22.4, 21.5, 14.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{23}BrO_2SSe$ ($[M + H]^+$), 536.9826, found 536.9831.

(E)-(1-(naphthalen-1-yl)-2-tosylpent-1-en-1-yl)(phenyl)selane ***(4k)***. Following the general procedure A, **4k** was obtained as a white solid. (85% yield, 129.1 mg). mp: 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 3H), 7.25 – 7.18 (m, 2H), 7.04 (t, *J* = 6.8 Hz, 1H), 7.01 – 6.91 (m, 3H), 6.90 – 6.83 (m, 1H), 6.81 – 6.73 (m, 2H), 6.69 – 6.56 (m, 4H), 3.12 – 2.91 (m, 2H), 2.13 – 1.97 (m, 5H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 142.6, 140.2, 137.3, 137.1, 132.4, 132.2, 129.9, 128.5, 128.4, 128.2, 127.6, 127.5, 127.4, 126.0, 125.7, 125.13, 125.11, 123.9, 34.8, 22.3, 21.1, 14.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{26}O_2SSe$ ($[M + Na]^+$), 529.0716, found 529.0723.

(E)-(5-chloro-1-(p-tolyl)-2-tosylpent-1-en-1-yl)(phenyl)selane ***(4l)***. Following the general procedure A, **4l** was obtained as a white solid. (86% yield, 130.0 mg). mp: 108−109 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.05 (m, *J* = 14.9, 7.8 Hz, 3H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.94 (t, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 8.4 Hz, 2H), 3.72 (t, *J* = 6.6 Hz, 2H), 3.07 – 2.98 (m, 2H), 2.37 – 2.28 (m, 5H), 2.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.5, 143.2, 138.4, 137.4, 137.2, 136.9, 132.7, 129.1, 128.9, 128.5, 128.4, 127.5, 127.3, 126.8, 44.6, 31.5, 30.9, 21.4, 21.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{27}ClO_2SSe$ ($[M + Na]^+$), 541.0489, found 541.0485.

(E)-(2-cyclopropyl-1-(p-tolyl)-2-tosylvinyl)(phenyl)selane ***(4m)***. Following the general procedure A, **4m** was obtained as a white solid. (87% yield, 122.2 mg). mp: 105−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.05 (m, 5H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.77 – 6.65 (m, 4H), 2.35 (s, 3H), 2.16 (s, 3H), 1.23 – 1.15 (m, 3H), 1.03 – 0.94 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 143.0, 138.8, 137.5, 136.3, 133.1, 129.2, 128.9, 128.1, 127.7, 127.5, 21.5, 21.1, 13.6, 10.5.

HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{24}O_2SSe$ ([M + Na]$^+$), 491.0561, found 491.0569.

(E)-phenyl(4-tosylhex-3-en-3-yl)selane ***(4n)***. [15b] Following the general procedure A, **4n** was obtained as a white solid. (47% yield, 55.6 mg). mp: 56−57 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.36 – 7.29 (m, 4H), 2.74 – 2.63 (m, 4H), 2.44 (s, 3H), 1.15 (t, *J* = 7.8 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 143.9, 139.3, 137.5, 136.4, 129.7, 129.4, 129.1, 127.3, 127.0, 27.4, 26.7, 21.6, 14.6, 13.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{22}O_2SSe$ ([M + Na]$^+$), 417.0408, found 417.0410.

(E)-(2-((4-methoxyphenyl)sulfonyl)-1-phenylprop-1-en-1-yl)(phenyl)selane ***(4o)***. Following the general procedure A, **4o** was obtained as a white solid. (79% yield, 105.2 mg). mp: 87−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.14 – 7.08 (m, 3H), 7.03 – 6.87 (m, 5H), 6.79 (d, *J* = 9.2 Hz, 2H), 6.75 – 6.68 (m, 2H), 3.81 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9, 150.5, 136.9, 136.0, 132.8, 129.7, 129.1, 128.6, 128.4, 127.3, 126.7, 113.8, 55.5, 18.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{20}O_3SSe$ ([M + Na]$^+$), 467.0197, found 467.0205.

(E)-(2-(mesitylsulfonyl)-1-phenylprop-1-en-1-yl)(phenyl)selane ***(4p)***. Following the general procedure A, **4p** was obtained as a white solid. (82% yield, 112.2 mg). mp: 92−93 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 – 7.05 (m, 3H), 6.93 (t, *J* = 7.8 Hz, 2H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.70 (t, *J* = 7.8 Hz, 2H), 6.63 (s, 2H), 6.56 (d, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.29 (s, 6H), 2.17 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 142.0, 139.1, 137.0, 135.6, 135.5, 135.0, 131.5, 128.7, 128.5, 128.4, 127.1, 127.0, 126.6, 21.9, 20.8, 17.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{28}O_2SSe$ ([M + Na]$^+$), 507.0879, found 507.0871.

(E)-(2-((4-chlorophenyl)sulfonyl)-1-phenylprop-1-en-1-yl)(phenyl)selane ***(4q)***. Following the general procedure A, **4q** was obtained as a white solid. (75% yield, 100.8 mg). mp: 125−126 °C; ^{1}H

NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.99 – 6.92 (m, 3H), 6.89 (t, *J* = 7.2 Hz, 2H), 6.66 (d, *J* = 7.2 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.1, 139.9, 139.1, 137.0, 135.5, 132.5, 129.2, 129.0, 128.8, 128.7, 128.5, 127.5, 126.9, 18.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}ClO_2SSe$ ($[M + Na]^+$), 470.9705, found 470.9708.

(E)-phenyl(1-phenyl-2-tosylvinyl)selane ***(6a)***.[15a, 15b] Following the general procedure A, **6a** was obtained as a white solid. (95% yield, 118.0 mg). mp: 150−151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.46 – 7.42(m, 1H), 7.41 – 7.37 (m, 2H), 7.36 – 7.23 (m, 5H), 7.21 – 7.15 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.16 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 143.5, 136.5, 134.6, 130.12, 130.09, 129.24, 129.23, 128.4, 127.8, 127.4, 126.8, 125.8, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{18}O_2SSe$ ($[M + Na]^+$), 437.0089, found 437.0100.

(E)-(1-(4-fluorophenyl)-2-tosylprop-1-en-1-yl)(phenyl)selane ***(6b)***. Following the general procedure A, **6b** was obtained as a white solid. (82% yield, 106.3 mg). mp: 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 6.8 Hz, 2H), 7.48 – 7.29 (m, 5H), 7.7.23 – 7.12 (m, 4H), 6.96 (t, *J* = 8.8 Hz, 2H), 6.19 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2 (d, *J* = 248.0), 155.8, 143.7, 138.7, 136.5, 130.59 (d, *J* = 9.0 Hz), 130.15, (d, *J* = 5.4 Hz), 129.3, 127.3, 126.7, 126.5, 115.0 (d, *J* = 22.0), 114.9, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}FO_2SSe$ ($[M + Na]^+$), 454.9998, found 454.9998.

(E)-(1-(4-chlorophenyl)-2-tosylprop-1-en-1-yl)(phenyl)selane ***(6c)***. Following the general procedure A, **6c** was obtained as a white solid. (92% yield, 123.6 mg). mp: 122−123 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.46 – 7.41 (m, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.17 – 7.11 (m, 4H), 6.18 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 143.9, 138.7, 136.5, 135.5, 133.1, 130.2, 129.9, 129.4, 128.1, 127.4, 126.5, 21.5. HRMS

(ESI-TOF) (m/z): Calcd for $C_{21}H_{17}ClO_2SSe$ ($[M + H]^+$), 448.9877, found 448.9873.

(E)-(1-(4-bromophenyl)-2-tosylprop-1-en-1-yl)(phenyl)selane ***(6d)***.[15b] Following the general procedure A, **6d** was obtained as a white solid. (77% yield, 113.6 mg). mp: 144−145 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.0 Hz, 2H), 7.45 – 7.36 (m, 5H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.16 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 143.9, 138.6, 136.5, 133.6, 131.0, 130.2, 130.1, 129.4, 127.4, 126.5, 126.4, 123.7, 21.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}BrO_2SSe$ ($[M + Na]^+$), 514.9190, found 514.9193.

(E)-4-(1-(phenylselanyl)-2-tosylprop-1-en-1-yl)benzonitrile ***(6e)***. Following the general procedure A, **6e** was obtained as a white solid. (63% yield, 83.0 mg). mp: 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.49 (m, 4H), 7.48 – 7.42 (m, 1H), 7.41 – 7.33 (m, 4H), 7.32 – 7.25 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.23 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 144.3, 139.6, 138.4, 136.6, 131.5, 130.4, 130.3, 129.6, 129.2, 127.3, 126.9, 125.9, 118.3, 112.8, 21.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{17}NO_2SSe$ ($[M + H]^+$), 440.0224, found 440.0228.

(E)-(1-(3-chlorophenyl)-2-tosylprop-1-en-1-yl)(phenyl)selane ***(6f)***. Following the general procedure A, **6f** was obtained as a white solid. (79% yield, 106.2 mg). mp: 120−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.36 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 3H), 6.94 (s, 1H), 6.20 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 144.0, 138.5, 136.6, 136.2, 133.8, 130.3, 130.2, 129.2, 128.0, 127.4, 126.89, 126.86, 126.3, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}ClO_2SSe$ ($[M + H]^+$), 448.9887, found 448.9873.

(E)-(1-(3-nitrophenyl)-2-tosylvinyl)(phenyl)selane ***(6g)*** Following the general procedure A, **6g** was obtained as a white solid. (42% yield, 57.8 mg). mp: 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz,

1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 147.5, 144.4, 138.3, 136.6, 136.4, 134.8, 130.5, 130.3, 129.6, 129.0, 127.5, 127.3, 125.9, 123.8, 123.0, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}NO_4SSe$ ($[M + H]^+$), 460.0123, found 460.0128.

*(E)-(1-(2-chlorophenyl)-2-tosylvinyl)(phenyl)selane (**6h**)* Following the general procedure A, **6h** was obtained as a white solid. (68% yield, 91.4 mg). mp: 124−125 °C; ^{1}H NMR (400 MHz, $cdcl_3$) δ7.57 – 7.52 (m, 2H), 7.47 – 7.31 (m, 5H), 7.25 – 7.22 (m, 2H), 7.17 – 7.11 (m, 4H), 6.18 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 143.9, 138.4, 136.5, 136.2, 133.7, 130.2, 130.2, 129.3, 129.1, 127.9, 127.4, 126.8, 126.8, 126.2, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}ClO_2SSe$ ($[M + H]^+$), 448.9881, found 448.9878.

*(E)-methyl 2-(1-(phenylselanyl)-2-tosylvinyl)benzoate (**6i**)* Following the general procedure A, **6i** was obtained as a yellow oil. (86% yield, 121.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6, 1H), 7.59 – 7.53 (m, 2H), 7.46 – 7.35 (m, 3H), 7.34 – 7.27 (m, 4H), 7.12 (d, *J* = 8.8 Hz, 3H), 6.24 (s, 1H), 3.75 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 156.2, 143.6, 138.4, 136.6, 135.9, 131.5, 130.4, 130.0, 129.8, 129.8, 129.2, 128.9, 128.3, 127.5, 126.7, 124.8, 51.8, 21.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{20}O_4SSe$ ($[M + H]^+$), 473.0326, found 473.0328.

*(E)-phenyl(1-(p-tolyl)-2-tosylvinyl)selane (**6j**).*[15b] Following the general procedure A, **6j** was obtained as a white solid. (94% yield, 120.7 mg). mp: 162−163 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.574 (d, *J* = 6.6 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.14 – 7.06 (m, 6H), 6.10 (s, 1H), 2.37 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 143.5, 139.5, 139.0, 136.5, 131.7, 130.1, 130.0, 129.2, 128.5, 128.4, 127.4, 127.1, 125.4, 21.5, 21.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{20}O_2SSe$ ($[M + Na]^+$), 451.0277, found 451.0271.

*(E)-(1-(4-ethylphenyl)-2-tosylprop-1-en-1-yl)(phenyl)selane (**6k**)* Following the general procedure A, **6k** was obtained as a white solid. (88% yield, 116.7 mg). mp: 91−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.4, 2H), 7.47 – 7.35 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.03 (m, 6H), 6.12 (s, 1H), 2.64 (q, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 145.7, 143.4, 138.8, 136.5, 131.8, 130.1, 130.0, 129.1, 128.5, 127.4, 127.3, 127.0, 125.6, 28.7, 21.5, 15.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{22}O_2SSe$ ($[M + Na]^+$), 465.0406, found 465.0398.

*(E)-(1-(4-(tert-butyl)phenyl)-2-tosylprop-1-en-1-yl)(phenyl)selane (**6l**)* Following the general procedure A, **6l** was obtained as a white solid. (85% yield, 119.9 mg). mp: 121−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.8 Hz, 2H), 7.46 – 7.34 (m, 3H), 7.26 – 7.20 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.13 (s, 1H), 2.32 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 152.5, 143.2, 138.7, 136.6, 131.5, 130.2, 130.0, 129.0, 128.2, 127.5, 126.9, 125.9, 124.7, 34.7, 31.2, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{26}O_2SSe$ ($[M + H]^+$), 471.0898, found 471.0892.

*(E)-phenyl(1-(m-tolyl)-2-tosylvinyl)selane (**6m**)* Following the general procedure A, **6m** was obtained as a white solid. (86% yield, 110.4 mg). mp: 109−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.47 – 7.35 (m, 3H), 7.32 – 7.26 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 3H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.86 (s, 1H), 6.13 (s, 1H), 2.36 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 143.4, 138.9, 137.5, 136.6, 134.43, 130.2, 130.1, 130.0, 129.1, 128.7, 127.8, 127.5, 125.7, 125.6, 21.5, 21.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{20}O_2SSe$ ($[M + Na]^+$), 451.0251, found 451.0242.

*(E)-phenyl(4-phenyl-1-tosylbut-1-en-2-yl)selane (**6n**)* Following the general procedure A, **6n** was

obtained as a white solid. (82% yield, 108.7 mg). mp: 90−91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.22 (d, *J* = 7.5 Hz, 3H), 5.94 (s, 1H), 3.11 (q, *J* =5.0 Hz, 2H), 2.97 –2.89 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 144.0, 139.2, 136.6, 136.5, 130.0, 129.9, 129.8, 129.2, 128.4, 127.1, 127.0, 126.1, 124.9, 38.3, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{22}O_2SSe$ ([M + H]$^+$), 443.0586, found 443.0579.

*(E)-phenyl(1-tosylhex-1-en-2-yl)selane (**6o**)* Following the general procedure A, **6o** was obtained as a white solid. (85% yield, 100.5 mg). mp: 68−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.45 – 7.33 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.85 (s, 1H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.60 – 1.49 (m, 2H), 1.42 – 1.29 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 143.8, 139.6, 136.7, 130.0, 129.9, 129.7, 126.9, 125.9, 123.7, 33.0, 32.1, 22.5, 21.5, 13.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{22}O_2SSe$ ([M + Na]$^+$), 417.0403, found 417.0398.

*(E)-(6-chloro-1-tosylhex-1-en-2-yl)(phenyl)selane (**6p**)* Following the general procedure A, **6p** was obtained as a white solid. (88% yield, 113.0 mg). mp: 90−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.90 (s, 1H), 3.54 (t, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.87 – 1.68 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 144.01, 133.99, 139.5, 136.7, 130.1, 130.0, 129.8, 126.9, 125.8, 124.4, 44.5, 32.2, 32.0, 27.3, 21.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{21}ClO_2SSe$ ([M + H]$^+$), 429.0195, found 429.0191.

*(E)-1-(1-(phenylselanyl)-2-tosylvinyl)cyclohexanol (**6q**)* Following the general procedure A, **6q** was obtained as a white solid. (73% yield, 95.5 mg). mp: 56−58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d,

J = 8.4 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.22 (m, 2H), 5.54 (s, 1H), 4.83 (s, 1H), 2.41 (s, 3H), 2.09 – 1.90 (m, 4H), 1.87 – 1.68 (m, 3H), 1.66 – 1.55 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 143.9, 138.5, 136.6, 130.1, 129.8, 129.6, 127.6, 126.9, 122.7, 76.3, 36.2, 25.0, 21.5, 21.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{24}O_3SSe$ ($[M + Na]^+$), 459.0508, found 459.0504.

*(E)-trimethyl(1-(phenylselanyl)-2-tosylvinyl)silane (**6r**)* Following the general procedure A, **6r** was obtained as a white solid. (64% yield, 78.7 mg). mp: 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.30 (m, 5H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.04 (s, 1H), 2.40 (s, 3H), 0.49 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 143.7, 138.5, 136.8, 131.6, 130.1, 129.8, 129.7, 126.9, 126.7, 21.5, 0.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{22}O_2SSeSi$ ($[M + Na]^+$), 433.0174, found 433.0167.

*(E)-methyl(1-phenyl-2-tosylvinyl)selane (**6s**)* Following the general procedure A, **6s** was obtained as a yellow oil. (35% yield, 43.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 4H), 6.44 (s, 1H), 2.38 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.1, 143.6, 138.9, 135.2, 129.3, 129.2, 128.2, 127.8, 127.5, 124.8, 21.5, 8.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{16}O_2SSe$ ($[M + K]^+$), 390.9668 , found 390.9643.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data for **4a**, **6a** and **6p** (CIF), and spectral data for new compounds. The Supporting Information is available free of charge on the ACS Publications web-site.

AUTHOR INFORMATION

Corresponding Author

*E-mail: liy078@nenu.edu.cn

*E-mail: zhangq651@nenu.edu.cn

Notes

The authors declare no competing financial interest.

† These authors are different persons.

ACKNOWLEDGMENT

We acknowledge the financial support for this work from the National NSF of China (21172033, 21372041 and 21302017), Changbai Mountain Scholarship Program, and the Fundamental Research Funds for the Central Universities (2412016KJ006).

REFERENCES

(1) (a) Ettari, R.; Nizi, E.; Francesco, M. E. D.; Dude, M.-A.; Pradel, G.; Vicik, R.; Schirmeister, T.; Micale, N.; Grasso, S.; Zappala, M. *J. Med. Chem*. **2008**, *51*, 988–996. (b) Ni, L.; Zheng, X. S.; Somers, P. K.; Hoong, L. K.; Hill, R. R.; Marino, E. M.; Suen, K.-L.; Saxena, U.; Meng, C. Q. *Bioorg*. *Med. Chem. Lett.* **2003**, *13*, 745–748. (c) Forristal, I. J. *Sulfur Chem*. **2005**, *26*, 163–195. (d) Wang, G.; Mahesh, U.; Chen, G. Y. J.; Yao, S.-Q. *Org. Lett*. **2003**, *5*, 737–740. (e) Ni, L.; Zheng, X. S.; Somers, P. K.; Hoong, L. K.; Hill, R. R.; Marino, E. M.; Suen, K.-L.; Saxena, U.; Meng, C. Q. *Bioorg. Med. Chem. Lett*. **2003**, *13*, 745–748.

(2) (a) Pandey, G.; Tiwari, K. N.; Puranik, V. G. *Org. Lett.* **2008**, *10*, 3611–3614. (b) Oh, K. *Org. Lett*. **2007**, *9*, 2973–2975. (c) Desrosiers, J. N.; Charette, A. B. *Angew. Chem., Int. Ed*. **2007**, *46*, 5955–5957. (d) Noshi, M. N.; El-Awa, A.; Torres, E.; Fuchs, P. L. *J. Am. Chem. Soc*. **2007**, *129*, 11242–11247. (e) Mu, L.; Drandarov, K.; Bisson, W. H.; Schibig, A.; Wirz, C.; Schubiger, P. A.; Westera, G. *Eur. J. Med. Chem*. **2006**, *41*, 640–650. (f) Hof, F.; Schutz, A.; Fah, C.; Meyer, S.; Bur,

D.; Liu, J.; Goldberg, D. E.; Diederich, E. *Angew. Chem., Int. Ed*. **2006**, *45*, 2138–2141. (g) Wardrop, D. J.; Fritz, J. *Org. Lett*. **2006**, *8*, 3659–3662.

(3) A recent review, to see: Fang, Y.; Luo, Z.; Xu, X. *RSC Adv*. **2016**, *6*, 59661–59676.

(4) (a) Kirihara, M.; Yamamoto, J.; Noguchi, T.; Hirai, Y. *Tetrahedron Lett*. **2009**, *50*, 1180–1183. (b) Huang, X.; Duan, D.-H.; Zheng, W.-X. *J. Org. Chem*. **2003**, *68*, 1958–1963.

(5) (a) Balasubramanian, M.; Baliah, V. *J. Chem. Soc*. **1954**, 1844–1847. (b) Chodroff, S.; Whitmore, W. F. *J. Am. Chem. Soc*. **1950**, *72*, 1073–1076. (c) Happer, D. A. R.; Steenson, B. E. *Synthesis* **1980**, *10*, 806–807.

(6) van Steenis, J. H.; van Es, J. J. G. S.; van der Gen, A. *Eur. J. Org. Chem*. **2000**, 2787–2793.

(7) (a) Back, T. G.; Collins, S. *Tetrahedron Lett*. **1980**, *21*, 2215-2218. (b) Back, T. G.; Collins, S. *J. Org. Chem*. **1981**, 46, 3249–3256. (c) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett*. **1980**, *21*, 4155–4158. (d) Asscher, M.; Vofsi, D. *J. Chem. Soc*. **1964**, 4962–4971. (e) Asscher, M.; Vofsi, D. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1543–1545. (f) Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem*. **1978**, *43*, 1208–1217.

(8) (a) Nie, G.; Deng, X.; Lei, X.; Hu, Q.; Chen, Y. *RSC Adv*. **2016**, *6*, 75277–75281. (b) Zhang, N.; Yang, D.; Wei, W.; Yuan, L.; Cao, Y.; Wang, H. *RSC Adv*. **2015**, *5*, 37013–37017. (c) Katrun, P.; Chiampanichayakul, S.; Korworapan, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Kuhakarn, C. *Eur. J. Org. Chem.* **2010**, 5633–5641. (d) Nair, V.; Augustine, A.; Suja, T. D. *Synthesis* **2002**, 2259−2265. (e) Taniguchi, N. *Synlett* **2011**, *22*, 1308−1312. (f) Taniguchi, N. *Synlett* **2012**, *23*, 1245−1249. (g) Li, X.; Xu, Y.; Wu, W.; Jiang, C.; Qi, C.; Jiang, H. *Chem. Eur. J*. **2014**, *20*, 7911–7915.

(9) (a) Wan, J.-P.; Hu, D.; Bai, F.; Wei, L.; Liu, Y. *RSC Adv.* **2016**, *6*, 73132–73135. (b) Wei, W.; Wen,

J.; Yang, D.; Jing, H.; You, J.; Wang, H, *RSC Adv*. **2015**, *5*, 4416−4419. (c) Wei, W.; Li, J.; Yang, D.; Wen, J.; Jiao, Y.; You J.; Wang, H. *Org. Biomol. Chem.* **2014**, *12*, 1861−1864. And references cited therein.

(10) (a) Lai, C.; Xi, C.; Jiang, Y.; Hua, R. *Tetrahedron Lett*. **2015**, *46*, 513–515. (b) Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, A. *J. Am. Chem. Soc*. **2013**, *135*, 11481−11484.

(11) Chen, F.; Meng, Q.; Han, S.-Q.; Han, B. *Org. Lett*. **2016**, *18*, 3330−3333.

(12) (a) Wen, J.; Wei, W.; Xue, S.; Yang, D.; Lou, Y.; Gao, C.; Wang, H. *J. Org. Chem*. **2015**, *80*, 4966−4972. (b) Senadi, G. C.; Guo, B.-C.; Hub, W.-P.; Wang, J.-J. *Chem. Commun*. **2016**, *52*, 11410–11413. (c) Hao, W.-J.; Du, Y.; Wang, D.; Jiang, B.; Gao, Q.; Tu, S.-J.; Li, G. *Org. Lett*. **2016**, *18*, 1884−1887.

(13) Mugesh, G.; Mont, W.-W. d.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125−2180.

(14) Recent reviews, to see: a) Beletskaya, I. P.; Ananikov, V. P.; *Chem. Rev.* **2011**, *111*, 1596−1636. (b) Orlov, N. V. *Chemistry Open* **2015**, *4*, 682–697.

(15) (a) Back, T. G.; Collins, S. *Tetrahedron Lett*. **1981**, *22*, 5111–5114. (b) Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438−439. (c) Back, T.G.; Collins, S.; Kerr, R.G. *J. Org. Chem*. **1983**, *48*, 3077−3084. (d) Back, T.G.; Collins, S.; Gokhale, U.; Law, K.-W. *J. Org. Chem*. **1983**, *48*, 4776−4779. (e) Back, T.G.; Collins, S.; Krishna, M.V.; Law, K.-W. *J. Org. Chem.* **1987**, *52*, 4258−4264. (f) Back, T.G.; Krishna, M.V.; Muralidharan, K.R. *J. Org. Chem.* **1989**, *54*, 4146−4153. (g) Back, T. G. Nakajima, K. *J. Org. Chem*. **1998**, *63*, 6566−6571.

(16) (a) Gancarz, R.A.; Kice, J. L. *Tetrahedron Lett*. **1980**, *21*, 1697−1700. (b) Back, T. G.; Collins, S. *Can. J. Chem.* **1987**, *65*, 38−42. (c) Wang, L.; Huang, X. *Synth. Commun.* **1993**, *23*, 2817−2820. (d) Chen, D.-W.; Chen, Z.-C. *Tetrahedron Lett*. **1994**, *35*, 7637−7638.

(17) Huang, X.; Xu, Q.; Liang, C.-G.; He, Q.-W. *Syn. Comm.* **2002**, *32*, 1243−1249.

(18) (a) Zheng, G.; Li, Y.; Han, J.; Xiong, T.; Zhang, Q. *Nat. Commun*. **2015**, 6:7011 doi: 10.1038/ncomms8011. (b) Sun, J.; Zheng, G.; Xiong, T.; Zhang, Q.; Zhao, J.; Li, Y.; Zhang, Q.; *ACS Catal.* **2016**, *6*, 3674−3678.

(19) (a) Ni, Z.; Zhang, Q.; Xiong, T.; Zheng, Y.; Li, Y.; Zhang, H.; Zhang, J.; Liu, Q. *Angew. Chem. Int. Ed.* **2012**, *51*, 1244−1247. (b) Zhang, Q.; Lv, Y.; Li, Y.; Xiong, T.; Zhang, Q. *Acta Chim. Sinica*. **2014**, *72*, 1139−1143. (c) Sun, K.; Li, Y.; Zhang, Q.; *Sci. China Chem.* **2015**, *58*, 1354−1358. (d) Zhang, G.; Xiong, T.; Wang, Z.; Xu, G.; Wang, X.; Zhang, Q. *Angew. Chem. Int. Ed.* **2015**, *54*, 12649−12653. (e) Li, Y.; Zhou, X.; Zheng, G.; Zhang, Q. *Beilstein J. Org. Chem*. **2015**, *11*, 2721−2726.

(20) For the crystal structure of **4a** to see CCDC 1517579, **6a** to see CCDC 1517580 and **6p** to see 1517581. And the corresponding figures and tables to see Figure S1, S2, S3 and Table S1, S2, S3 in Supporting Information.

(21) (a) Zhang, M.; Xie, P.; Zhao, W.; Niu, B.; Wu, W.; Bian, Z.; Pittman, C. U., Jr.; Zhou, A. *J. Org. Chem.* **2015**, *80*, 4176−4183. (b) Taniguchi, T.; Idota, A.; Ishibashi, H. *Org. Biomol. Chem*. **2011**, *9*, 3151−3153. (c) Li, X.; Xu, X.; Hu, P.; Xiao, X.; Zhou, C. *J. Org. Chem*. **2013**, *78*, 7343. (d) Wei, W.; Wen, J.; Yang, D.; Guo, M.; Wang, Y.; You, J.; Wang, H. *Chem. Commun*. **2015**, *51*, 768−778. (e) Li, X.; Xu, X.; Tang, Y. *Org. Biomol. Chem*. **2013**, *11*, 1739−1742. (f) Li, X.; Xu, X.; Zhou, C. *Chem. Commun.* **2012**, *48*, 12240−11242. (g) Chen, Z.; Liu, S.; Hao, W.; Xu, G.; Wu, S.; Miao, J.; Jiang, B.; Wang, S.; Tu, S.; Li, G. *Chem. Sci*. **2015**, *6*, 6654−6658. (h) Barton, D. H.R.; Csiba, M. A.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1994**, *35*, 2869−2872.

(22) (a) Taniguchi, T.; Sugiura, Y.; Zaimoku, H.; Ishibashi, H. *Angew. Chem., Int. Ed*. **2010**, *49*,

10154−10355. (b) Taniguchi, T.; Zaimoku, H.; Ishibashi, H. *Chem. Eur. J.* **2011**, *17*, 4307−4312. (c) Taniguchi, T.; Idota, A.; Ishibashi, H. *Org. Biomol. Chem*. **2011**, *9*, 3151−3153. (d) Wei, W.; Liu, C.; Yang, D.; Wen, J.; You, J.; Suoc, Y.; Wang, H. *Chem. Commun*. **2013**, *49*, 10239−10241.