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Visible light-induced Co or Cu-catalyzed selenosulfonylation of alkynes: synthesis of *β*-(seleno)vinyl sulfones

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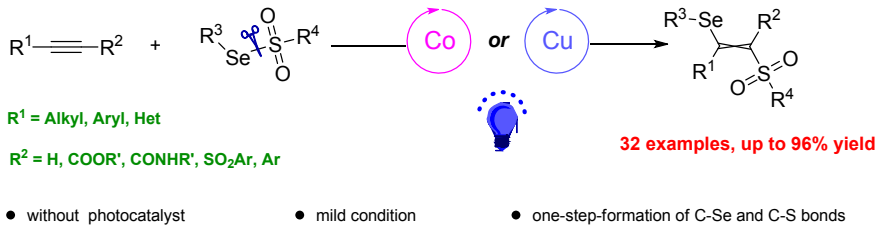


ABSTRACT. A visible light-induced Co or Cu-catalzyed selenosulfonylation of alkynes for the synthesis of *β*-(seleno) vinyl sulfones is demonstrated. This method utilizes a low-costcobalt salt or metal copper as the catalysts. The reaction goes through a photoinduced free radical addition of selenosulfonates to alkynes for the 1,2-selenosulfonylation of alkynes under mild conditions.

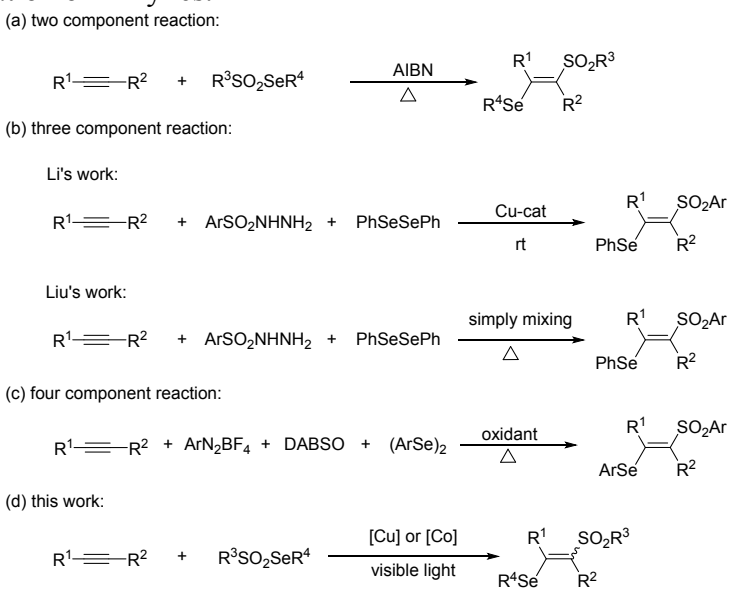
1. INTRODUCTION

Organic selenium compounds have been widely used in organic synthesis. Among them, vinyl selenides are valuable synthetic intermediates and therapeutic entities, which have a wide range of biological activities. Therefore, a plethara of synthetic strategies have been developed for the construction of vinyl selenide.[1] Selenium in organic compounds can be introduced, converted and removed using a variety of simple ways, which makes the selenization reaction essential.[2] Alkynes play a critical role in organic synthesis due to their easyavailability and accessibility. In 1983, Back *et al*. first used azobisisobutyronitrile (AIBN) as a free radical initiator to promote the cleavage of the pre-prepared $PhSeSO_2Ph$ reagent to construct *β*-(seleno) vinyl sulfone compounds (Scheme 1a).[3a] In recent years, it has been reported that multi-component reaction of benzenesulfonyl hydrazide, diselenide and alkyne can successfully affords *β*-(seleno) vinyl sulfone compounds under mild conditions through difunctionalization of alkyne (Scheme 1b).[3b,3c] Recently, a four-component reaction has been developed

for the preparation of a broad range of β-(seleno) vinyl sulfones with high levels of regioselectivity and stereoselectivity through sulfur dioxide insertion utilizing DABSO (Scheme 1c).[3d]

Visible light-induced chemical transformations have gained increasing attentions for their crucial importance in synthetic chemistry. Photoreduction-activated photo-oxidation-reduction catalysis (Ru or Ir) have been shown to involve the design and development of valuable reactions through a unique single-electron transfer pathway.[4] Nevertheless, the relatively expensive cost of Ru or Ir based photocatalysts necessitates the development of reactions utilizing inexpensive metals such as copper, cobalt, nickel, *etc.* as photocatalysts.[5] Selenosulfonates are useful synthons for the construction of organic selenium compounds. More recently, we have developed a Nickel-catalyzed reductive selenylation of alkyl bromides with selenosulfonates for the preparation of selenides. As a continuation study on selenosulfonates and C-S bond formation reactions,[6] we herein describe a visible light-induced Co or Cu-catalzyed of selenosulfonylation of alkynes for the synthesis of β-(seleno) vinyl sulfones (Scheme 1d).

Scheme 1. Selenosulfonation of Alkynes.

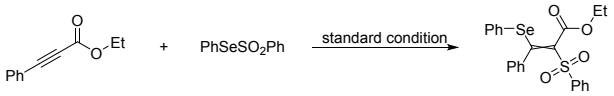


2. RESULTS AND DISCUSSION

We initially selected ethyl 3-phenylpropiolate **1a** and $PhSeSO_2Ph$ **2a** as model substrates for the optimization of the reaction conditions (Table 1). Gratifyingly, the transformation proceeded smoothly in the presence of 5 mol% $CoCl_2$ in MeCN under Ar atmosphere irradiated by blue light for 4 hours, giving ethyl 3-phenyl-3-(phenylselanyl) -2-(phenylsulfonyl)acrylate **3aa** in 83% yield (Table 1, entry 1), and the structure of compound **3aa** was unambiguously confirmed by single crystal diffraction(see Supporting Imformation (SI) for more details). We found the reaction failed to give the desired product **3aa** in the absence of $CoCl_2$ or blue LED (Table 1, entries 2-3). Next, we screened the reaction solvents. The reaction could give **3aa** in a high LC yield of 82% when using THF as the solvent (Table 1, entry 4). Subsequently,

we found that the yield of reaction was not changed when reaction time prolonged from 4 hours to 8 hours, even 12 hours (Table 1, entries 5-6). Next, we explored the effects of different transition metal-catalysts on the reaction. Surprisingly, metal copper could also promote the reaction to furnish **3aa** in 50% yield (Table 1, entry 7). The optimal result was obsreved when CoC_2O_4 was empolyed as the catalyst, furnishing **3aa** in 86% yield (Table 1. entry 8). Therefore, we established the optimum conditions for the reaction of **1a** and **2a** under the catalysis of 5 mol% CoC_2O_4, acetonitrile as solvent, under Ar atmosphere irradiated by blue LED for 4 hours.

Table 1. Optimization of the reaction conditions[a]



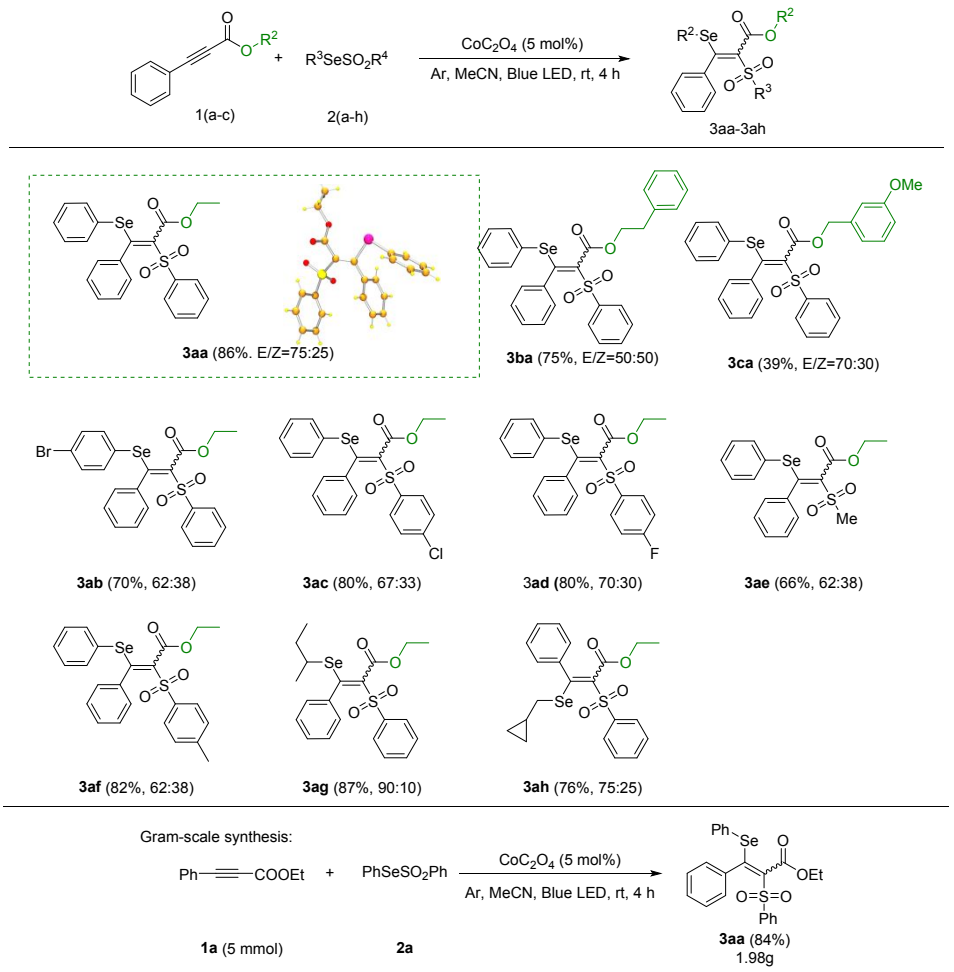
1a 2a 3aa

entry	conditions	yield (%)[b]
1	standard condition[a]	83
2	in the absence of $CoCl_2$	0
3	without blue LED	0
4	THF instead of MeCN	82[c]
5	8 h instead of 4 h	83
6	12 h instead of 4 h	83
7	Cu instead of $CoCl_2$	50
8	CoC_2O_4 instead of $CoCl_2$	86

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $CoCl_2$ (5 mol%), MeCN (1.0 mL), room temperature, under Ar and with blue LED, 4 h. [b]Isolated yield. [c] LC yield.

With the optimized reaction conditions in hand, we set out to explore the substrate scope of this reaction using a variety of different reagents, and the results are summarized in Tables 2 (Table 2). We examined the reactions of various types of alkyne esters react with **2a**, under the catalysis of CoC_2O_4. When using alkyne esters with less steric hindrance (**1a**-**1b**), the desired products **3aa** and **3ab** were obtained in 86% and 75% yields, respectively. And the sterically hindered alkyne ester (**1c**) gave **3ca** only in a yield of 39%. Then we investigated the scope of selenosulfonates. When the aryl selenosulfonates were employed, the target products could be obtained in good yields. When using **2e** as raw material, both stereoisomers of the target product can be isolated and the overall yield can reach 66%. When alkyl selenosulfonates (**2g**-**2h**) were used, the desired products 3ag and 3ah could be afforded in 87% and 76% yields, respectively. In order to test the large-scale application of the reaction, we conducted the reaction **1a** with **2a** on 5 mmol scale under standard conditions, the desired product **3aa** could also be isolated in 84% yield.

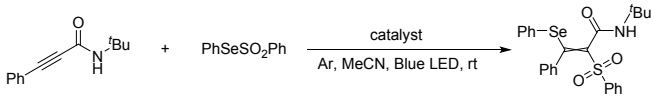
Table 2. Scope of selenosulfonates with alkyne esters [a,b]



[a]Reaction conditions: alkyne **1** (0.2 mmol), **2** (0.2 mmol), CoC_2O_4 (5.0 mol%), in MeCN (1.0 mL) at room temperature, under Ar and with blue LED,4 h. [b]Isolated yield.

After the exploration of the reaction to alkyne esters, we hope to further expand the application of the reaction. Considering the alkynamides as important functional alkyne, we tried to achieve this reaction using alkynamide compounds. Therefore, we using alkynamide compounds as the source of alkyne, and

Table 3. Optimization of the reaction conditions.[a, b]



1e **2a** **3ea**

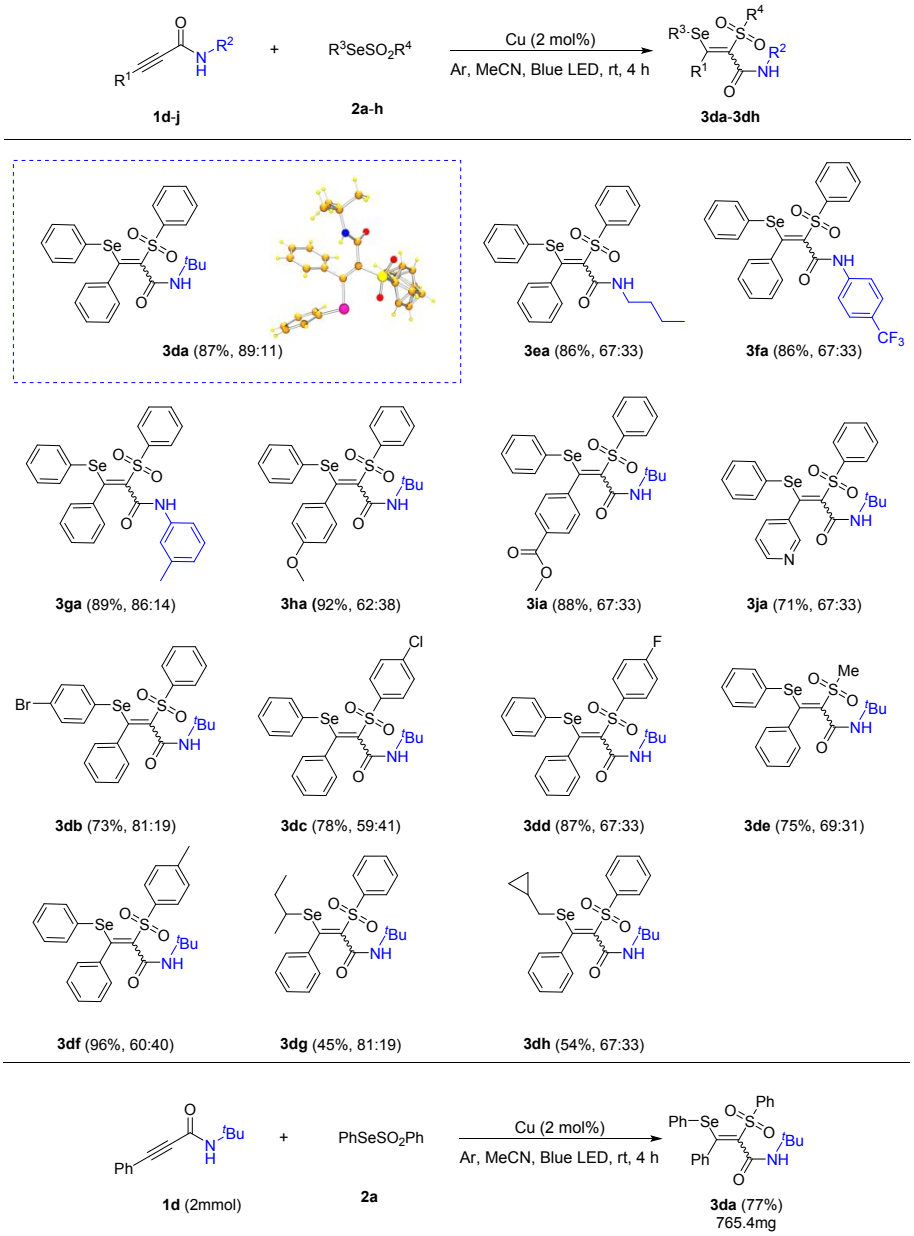
entry	catalysts (mol%)	yield (%)[b]
1	$CoCl_2$ (5)	55
2	CuI (5)	68
3	CuCl (5)	56
4	$CuCl_2$ (5)	44
5	$Cu(OAc)_2$ (5)	66
6	Cu (5)	85
7	Cu (2)	87
8	Cu (1)	72

[a]Reaction conditions: **1e** (0.2 mmol), **2a** (0.2 mmol), catalyst, MeCN (1.0 mL), room temperature, under Ar and with blue LED, 4 h. [b]Isolated yield.

react under the best condition we mentioned above. Unfortunately, under this reaction condition, the corresponding target product can only be obtained with an isolated yield of 55% (Table 3. entry 1). Then,

we explored the reaction conditions and the results are summarized in Table 3. We tried a series of copper catalysts: including CuI, CuCl, $CuCl_2$, $Cu(OAc)_2$ and Cu, and experimental results shown that the reaction using copper is the best, the target product can be obtained in an isolated yield of 85% in the presence of 5 mol% copper (Table 3. entries 2-6). Besides, the results shows that higher the valence state, the worse the catalytic effect. Next, we found that the amount of Cu(0) could be reduced from 5 mol% to 1 mol% without deteriorate the catalytic effect (Table 3. entry 6-8). After exploring the reaction conditions, we established that the **1e** and **2a** were catalyzed by 2 mol% Cu(0) in MeCN, under Ar atmosphere and blue LED for 4 hours.

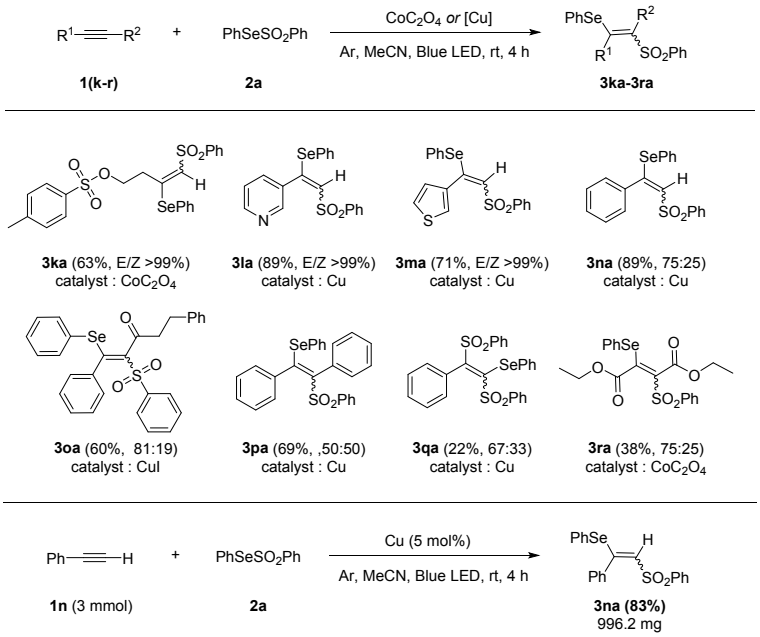
Table 4. Scope of selenosulfonates with alkynamides [a,b]



[a]Reaction conditions: alkyne **1** (0.2 mmol), **2** (0.2 mmol), Cu (2.0 mol%), in MeCN (1.0 mL) at room temperature, under Ar and with blue LED,4 h. [b]Isolated yield.

Under optimal conditions, we explored the scope of the substrate (Table 4). By comparing **3da** and **3ea**, we found that the steric hindrance and electronic effect of the group attached to the amide group has no effect on the reaction. A series of alkynamides bearing both electron-withdrawing groups (R = CF_3, COOMe) and electron-donating groups (R = Me, OMe) reacted smoothly to give the corresponding *β*-(seleno)vinyl sulfones in high yields (**3fa**-**3ia**). When pyridinamide is used, the reaction shows excellent heterocyclic tolerance, and the desired product is obtained in 71% yield. Then, we used **1d** as a reaction substrate to expand various selenosulfonates. The halogen-substituted (R = F, Cl, Br) aryl selenate sulfonate and **1d** can obtain the corresponding target product in a higher yield. Besides, the reaction with a weak electron-donating group (R = Me) could give **3df** in a yield of 96%. However, compared to aryl selenate sulfonate, alkyl selenate sulfonate does not show the excellent reaction effect. When an alkyl group is bonded to selenium, the reaction can only obtain the corresponding target product in a moderate yield, and when the sulfonyl group is an alkyl group, the reaction is relatively better. In order to test the large-scale application of the reaction, we conducted the reaction of 2 mmol **1d** with **2a** under standard conditions. The desired product **3da** could be observed in 77% yield.

Table 5. Scope of alkynes with 2a[a,b]



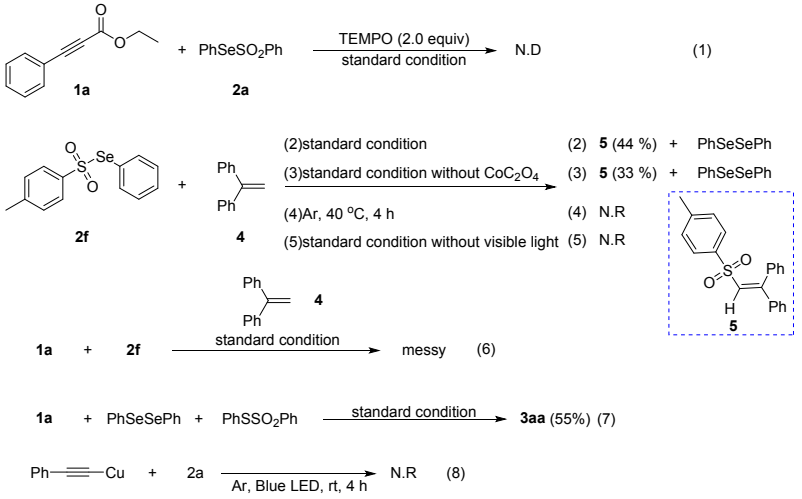
[a]Reaction conditions: alkyne 1 (0.2 mmol), 2 (0.2 mmol), CoC_2O_4 (5.0 mol%) or [Cu] (2.0 mol%), in MeCN (1.0 mL) at room temperature, under Ar and with blue LED,4 h. [b]Isolated yield.

In addition, we tried different types of alkynes, which were carried out under the conditions of cobalt oxalate and copper catalysis. The experimental results show that the reaction can be carried out and most of the corresponding target products can be obtained in modorate to good yields (Table 5). Surprisingly, but-3-yn-1-yl 4-methylbenzenesulfonate (**1k**) and the terminal alkyne bearing a heterocyclic ring (**1l, 1m**) proceeded with high levels of regio- and stereoselectivity. In order to test the large-scale application of

the reaction, we conducted the reaction of 3 mmol **1n** with **2a** under standard conditions. The desired product **3na** could be observed in 83% yield.

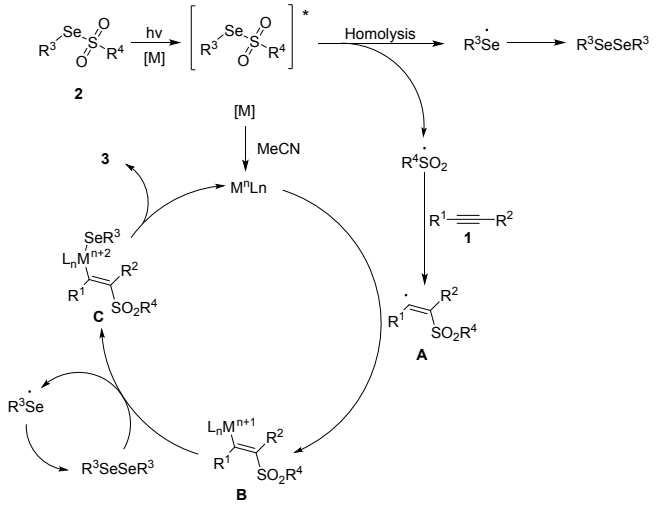
To gain some insight into the mechanism of this reaction, we conducted several control experiments. When TEMPO (2.0 equiv.) or ethene-1,1-diyldibenzene **4** (2.0 equiv.) was added to the reaction as a free radical quenching agent, we can observed that reaction was totally suppressed (Scheme 2, eq. 1 and eq. 6). After that, we try to add **4** when only **2f** exists, and 33% yield of compound **5** was obtained (Scheme 2, eq. 2). Based on this, we added CoC_2O_4 and found that the yield of the compound **5** was increased to 44% (Scheme 2, eq. 3). In order to explore the role of irradation, we perform the reaction in dark. After eq. 4 and eq. 5 reacted at 40 °C, no reaction was observed. These results indicated that light irradiation plays a crucial role in Se-S bond cleavage. It was also found that **2** easily splits to generate free radicals under light conditions, and the metal catalyst has a certain influence on the generation of free radicals. Then, we tried the reaction of **2a** with PhSeSePh and $PhSSO_2Ph$. It was found that **3aa** was observed in 55% yield, which indicated that PhSeSePh is an plausible intermediate in the reaction (Scheme 2, eq. 7). Finally, we desired to figure out if the formation of Cu-alkyne complex activates the alkyne. And result shows that Cu-alkyne complex is not reaction intermediate (Scheme 2, eq. 8).

Scheme 2. Control Experiments



Based on the reported literatures[3,7] and our experimental results, a plausible mechanisms was proposed in Scheme 3. Firstly, homolysis of **2** generates sulfonyl radical and seleno radical in the presence of metal catalyst irradiated by light. The homocoupling of seleno radical gives R^3SeSeR^3. The sulfonyl radical reacts with alkynes to form intermediates **A**. Then intermediate **A** and metal coordination to form intermediate **B**, which in turn interacts with the R^3SeSeR^3 to form intermediate **C** and regenerates a seleno radical. The reductive elimination of intermediate **C** furnishes product **3** and regenerates the catalyst.

Scheme 3. Plausible Mechanism.



3. CONCLUSION

In summary, we reports a new method for the synthesis of β-(seleno)vinyl sulfone by generating free radicals under light-induced, followed by metal-catalyzed addition to alkyne. Key features of the reaction include extensive substrate universality, readily available reagents, amenability to gram scale synthesis, excellent functional group tolerance and heterocyclic tolerance. In addition, the use of inexpensive transition metals as catalysts in photoreaction is an innovation and breakthrough in a series of previous experiments which using precious metal catalyzed visible light catalysis.

4. EXPERIMENTAL SECTION

General Experimental Information. Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were analytical grade and used without further purification. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by irradiation with UV light. For column chromatography, 200-300 mesh silica gel was used. ^{1}H-NMR and ^{13}C-NMR were recorded on a BRUKER 400 MHz spectrometer in $CDCl_3$. Chemical shifts (δ) were reported referenced to an internal tetramethylsilane standard or the $CDCl_3$ residual peak (δ 7.26) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.16). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS spectra were obtained by using BRUKER MICROTOF-Q III instrument with ESI source.

Information for LED Photoreactor. (1)Blue LEDs: 200 cm strips, 470 nm blue light, 32918 mcd ft-1; (2) Power Supply: 12V DC CPS series Power Supply - 20 Watt; (3) Connectors: LC2 Locking Male Connector CPS Adapter Cable.

General procedure for the synthesis of reactants

Procedure 1a-1c. A mixture of (0.4 mmol), phenylpropiolic acid (0.6 mmol, 87.6 mg), Cs_2CO_3 (2 equiv, 260.7 mg), CuI (10 mol%, 7.6 mg), and CH_3CN (2 mL) in a tube was stirred in air at 60 °C oil bath for 24 h. After that the mixture was poured into ethyl acetate, then washed with water, extracted with ethyl acetate, dried by anhydrous Na_2SO_4, then filtered and evaporated under vacuum, the residue was purified by flash column chromatography (petroleum ether or petroleum ether/ethyl acetate) to afford the corresponding coupling products.

Procedure 1d-1j. An oven dried round-bottom flask was charged with phenylpropiolic acid (1 mmol, 146.1 mg) and DMAP (10 mol%, 12.2 mg) and purged with argon for 10 minutes. The contents were dissolved in distilled DCM (0.25 M), and the amine was added (1.1 equiv). The mixture was cooled to 0 °C and a DCM solution (0.4 M) of DCC (1.0 mmol, 206.3 mg) was added dropwise and the reaction was warmed to room temperature and stirred overnight (approximately 12 hours). The contents of the flask were filtered through a plug of Celite® eluting with DCM. The filtrate was concentrated in vacuo while adsorbing onto silica gel and the crude material was purified by flash column silica gel chromatography using the indicated solvent system.

Procedure 1o. Ethynylbenzene (0.88 mL, 8.0 mmol, 816 mg) was dissolved into THF (8 mL), and the solution was cooled to -78 ºC. To the solution, *n*-BuLi (5.0 mL, 8.0 mmol, 1.6 M in hexane) was added. After being stirred for 1 h at -78 ºC, ethyl 3-phenylpropanoate (0.46 mL, 4.0 mmol) and $BF_3{\cdot}OEt_2$ (1.2 mL, 9.6 mmol) were added successively. The reaction was quenched by sat. NH_4Cl aq., and extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, and the solvent was removed under a reduced pressure. The residue was purified by column chromatography (SiO_2, eluent: hexane/EtOAc) to afford the desired ynones 1a in the yield of 62%.

Procedure 1q. A mixture of phenylpropiolic acid (0.5 mmol, 73 mg), $PhSO_2Na$ (2 equiv, 164 mg), I_2 (0.5 equiv, 63.3 mg), and 70% TBHP in H_2O (3 equiv, 148.5 mg) in THF (2 mL) was stirred at room temperature (30-32 °C), 16 h. 1q was obtained in the isolated yield of 83%, after chromatographic purification.

Procedure 2a-2h. A mixture of sulfinic acid sodium salt (4 mmol), diselenide (1 mmol,) and NBS (2 mmol, 356 mg) in MeCN was stirred

at room temperature. After the completion of the reaction, as monitored by TLC, the reaction mixture was washed with water and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography to provide the desired aryl-thiosulfonates.

^1H, ^{13}C spectra data of **1b-1c** can refer to published document[8a, 8b].

^1H, ^{13}C spectra data of **1d-1j** can refer to published document[8c, 8d].

^1H, ^{13}C spectra data of **1o** can refer to published document[8e, 8f].

^1H, ^{13}C spectra data of **1q** can refer to published document[8g].

^1H, ^{13}C spectra data of **2a-2h** can refer to published document[6a, 8h].

General procedure for the synthesis of products 3. Ethyl 3-phenylpropiolate **1a** (0.20 mmol, 34.8 mg), $PhSeSO_2Ph$ (0.20 mmol, 1.0 equiv, 59.4 mg) CoC_2O_4 (0.05 mmol, 1.5 mg) were added to an oven-dried schlenk reaction tube with a magnetic stir bar. The tube was sealed with a rubber cap and pumping gas three times under argon. Then MeCN (3.0 mL) were added and resulting mixture was stirred at room temperature for 4 h. After completion of the reaction, as indicated by TLC, the pure product was obtained by flash column chromatography using n-hexane on silica gel to afford **3aa** in 86% yield. All remaining β-(seleno) vinyl sulfones were prepared using a procedure similar to that used to synthesize **3aa**.

ethyl 3-phenyl-3-(phenylselanyl)-2-(phenylsulfonyl)acrylate (3aa) Yield = 86% (81.1 mg, 75 : 25). White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, J = 8.4, 1.3 Hz, 1H), 7.61 (dd, J = 14.9, 7.6 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.14 – 7.01 (m, 3H), 6.95 (dd, J = 7.8, 2.2 Hz, 5H), 6.78 (d, J = 6.8 Hz, 1H), 4.39 (q, J = 7.1 Hz, 1H), 3.84 (q, J = 7.1 Hz, 1H), 1.37 (t, J = 7.1 Hz, 2H), 0.74 (t, J = 7.1 Hz, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 165.4, 163.5, 141.7, 137.0, 136.7, 134.4, 134.0, 133.0, 128.9, 128.9, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 127.8, 127.5, 127.1, 62.8, 62.0, 14.14, 13.3. IR (ATR): ν = 1718, 1559, 1440, 1310, 1250, 1149, 1085, 1041, 998, 743, 686, 556 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{20}O_4SSeNa$ 495.0135 ; Found 495.0127.

phenethyl 3-phenyl-3-(phenylselanyl)-2-(phenylsulfonyl)acrylate (3ba) Yield =75.3% (82.5 mg, 50 : 50). White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 7.7 Hz, 1H), 7.66 (dt, J = 43.4, 7.5 Hz, 2H), 7.48 (dd, J = 25.1, 7.4 Hz, 1H), 7.28 (ddd, J = 29.8, 13.7, 7.2 Hz, 5H), 7.11 – 7.01 (m, 3H), 6.99 – 6.89 (m, 6H), 6.85 – 6.80 (m, 1H), 6.75 (d, J = 7.0 Hz, 1H), 4.54 (t, J = 7.4 Hz, 1H), 3.97 (t, J = 7.4 Hz, 1H), 3.07 (t, J = 7.4 Hz, 1H), 2.41 (t, J = 7.4 Hz, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 141.6, 136.9, 136.7, 136.5, 134.3, 134.0, 133.0, 129.1, 129.0, 128.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 127.6, 127.1, 126.8, 126.6, 67.0, 66.4, 34.9, 34.2. IR (ATR): ν = 1704, 1547, 1477, 1444, 1319, 1253,1238, 1202, 1149, 1084, 1049, 975, 807, 743, 699, 685, 597, 566, 544 cm^{-1}; HRMS (ESI): $[M+H]^+$ Calcd. for $C_{29}H_{25}O_4SSe$ $[M+H]^+$: 549.0634; Found 549.0629.

3-methoxybenzyl 3-phenyl-3-(phenylselanyl)-2-(phenylsulfonyl)acrylate (3ca) Yield =39.4% (44.4 mg, 70 : 30). White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 26.3, 7.7 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.31 – 6.72 (m, 16H), 5.54 – 4.76 (m, 2H), 3.88 – 3.66 (m, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 166.2, 163.2, 159.7, 141.2, 136.8, 136.4, 136.0, 134.1, 132.9, 130.0, 129.5, 129.2, 128.8, 128.7, 128.4, 128.4, 128.3, 128.2, 128.2, 127.9, 127.9, 127.5, 127.4, 126.9, 120.7, 120.6, 114.4, 114.0, 113.6, 68.1, 67.6, 55.2, 55.1. IR (ATR): ν = 3054, 2924, 1716, 1541, 1476, 1445, 1319, 1235, 1148, 1085, 1020, 965, 738, 685, 566 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{24}O_5SSeNa$ 587.0402; Found 587.0410.

N-(tert-butyl)-3-phenyl-3-(phenylselanyl)-2-(phenylsulfonyl)acrylamide (3da) Yield =87.3% (87.1 mg, 89 : 11). White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.34 (m, 5H), 7.14 – 7.05 (m, 4H), 6.99 – 6.90 (m, 5H), 6.76 (dd, J = 7.9, 1.5 Hz, 2H), 1.42 (s, 8H), 0.93 (s, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 161.7, 141.2, 137.1, 136.7, 134.8, 133.1, 131.8, 128.9, 128.8, 128.6, 128.5, 128.4, 128.0, 127.5, 126.9, 52.4, 28.6, 27.9. IR (ATR): ν = 3349, 2965, 1659, 1532, 1446, 1310, 1220, 1147, 1086, 739, 686, 619, 556 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{26}NO_3SSe$ 500.0793; Found 500.0811.

N-butyl-3-phenyl-3-(phenylselanyl)-2-(phenylsulfonyl)acrylamide (3ea) Yield = 86.0% (85.8 mg, 67 : 33). Yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, J = 7.4 Hz, 3H), 7.33 (t, J = 7.8 Hz, 2H), 7.07 (t, J = 8.7 Hz, 3H), 6.90 (dt, J = 21.7, 7.3 Hz, 5H), 6.67 (d, J = 7.1 Hz, 2H), 3.43 (q, J = 6.9 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.42 (q, J = 7.4 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 162.8, 137.1, 134.9, 133.1, 130.2, 129.5, 128.8, 128.6, 128.3, 127.9, 127.2, 126.8, 40.2, 31.4, 20.3, 13.9. IR (ATR): ν = 3368, 2361, 1672, 1526, 1446, 1322, 1285, 1218, 1152, 1081, 809, 686, 548 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{26}NO_3SSe$ 500.0799; Found 500.0810.

3-phenyl-3-(phenylselanyl)-2-(phenylsulfonyl)-N-(4-(trifluoromethyl)phenyl)acrylamide (3fa) Yield =86.3% (101.2 mg, 67 : 33). White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 7.7 Hz, 1H), 7.92 – 7.60 (m, 4H), 7.51 – 7.30 (m, 4H), 7.23 – 7.02 (m, 4H), 6.89 (dt, J = 28.6, 7.3 Hz, 5H), 6.69 (d, J = 7.3 Hz, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 172.2, 161.4, 141.3, 140.6, 140.2(d, J_{F-C} = 22.7 Hz) 137.1, 137.1, 136.7, 134.62, 133.49, 130.06, 129.13, 129.07, 128.90, 128.84, 128.74, 128.65, 128.53, 128.32, 128.20, 128.00, 127.32, 126.92, 126.5(q, J_{F-C} = 3.6 Hz), 126.0 (d, J_{F-C} = 3.6 Hz), 120.4, 119.8. IR (ATR): ν = 3334, 3062, 2358, 1668, 1538, 1305, 1255, 1145, 1119, 1067, 840, 741, 682, 542 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{20}F_3NO_3SSeNa$ 610.0174; Found 610.0134.

3-phenyl-3-(phenylselanyl)-2-(phenylsulfonyl)-N-(m-tolyl)acrylamide (3ga) Yield = 89.6% (95.4 mg, 86 : 14). White solid. ^1H NMR (400 MHz, $CDCl_3$)) δ 9.63 (s, 1H), 7.54 – 7.44 (m, 5H), 7.36 – 7.26 (m, 3H), 7.11 – 7.00 (m, 4H), 6.92 (dt, J = 14.5, 6.4 Hz, 6H), 6.71 (d, J = 6.8 Hz, 2H), 2.39 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 170.7, 160.8, 141.3, 139.1, 137.1, 134.9, 133.3, 129.3, 129.0, 128.9, 128.9, 128.7, 128.5, 128.4, 128.0, 127.3, 126.8, 126.0, 121.3, 117.8, 21.6. IR (ATR): ν = 3335, 3057, 1668, 1544, 1488, 1439, 1304, 1145, 1082, 730, 683, 610, 538 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{24}NO_3SSe$ 534.0637; Found 534.0611.

N-(tert-butyl)-3-(4-methoxyphenyl)-3-(phenylselanyl)-2-(phenylsulfonyl)acrylamide (3ha) Yield = 92.3% (97.6 mg, 62 : 38). White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.26 (m, 1H), 7.62 – 7.23 (m, 4H), 7.08 – 6.81 (m, 7H), 6.64 (d, J = 8.7 Hz, 1H), 6.40 (dd, J = 24.5, 8.7 Hz, 2H), 3.57 (s, 3H), 1.33 (s, 6H), 0.92 (s, 4H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 161.8, 159.5, 141.3, 136.7, 136.3, 133.6, 133.0, 130.3, 130.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.4, 127.4, 127.1, 113.1, 112.4, 55.3, 55.2, 52.3, 51.9, 28.5, 28.0. IR (ATR): ν = 3352, 2967, 1659, 1532, 1505, 1308, 1290, 1248, 1221, 1147, 1087, 735, 686, 542 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{28}NO_4SSe$ 530.0889; Found 530.0871.

methyl 4-(3-(tert-butylamino)-3-oxo-1-(phenylselanyl)-2-(phenylsulfonyl)prop-1-en-1-yl)benzoate (3ia) Yield =88.0% (97.9 mg, 67 : 33). White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 7.4 Hz, 1H), 7.73 – 7.51 (m, 5H), 7.41 (t, J = 7.7 Hz, 1H), 7.20 (s, 1H), 7.13 – 6.84 (m, 7H), 3.84 (s, 3H), 1.42 (s, 6H), 0.95 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 166.4, 161.3, 140.8, 139.7, 137.0, 136.6, 133.9, 133.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 128.1, 127.4, 52.4, 52.1, 28.5, 27.8. IR (ATR): ν = 3354, 2968, 1722, 1657, 1532, 1447, 1310, 1273, 1218, 1148, 1087, 741, 685, 566 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{27}NO_5SSeNa$ 580.0668; found 580.0634.

N-(tert-butyl)-3-(phenylselanyl)-2-(phenylsulfonyl)-3-(pyridin-3-yl)acrylamide (3ja) Yield = 71.1% (71.0 mg, 67 : 33). White solid. ^{1}H NMR (400 MHz, $CDCl_3$)) δ 8.32 (d, *J* = 7.5 Hz, 3H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.24 (s, 1H), 7.13 – 6.84 (m, 7H), 5.64 (s, 1H), 1.00 (s, 9H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 161.2, 140.0, 138.5, 136.9, 135.7, 134.1, 129.1, 129.1, 129.0, 128.8, 127.5, 52.2, 28.0. IR (ATR): ν= 3229, 2988, 1666, 1544, 1291, 1220, 1145, 1083, 823, 743, 728, 690, 597, 549, 469 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{25}N_2O_3SSe$ 501.0747; Found 501.0743.

3-(phenylselanyl)-4-(phenylsulfonyl)but-3-en-1-yl 4-methylbenzenesulfonate (3ka) Yield = 56.9% (59.3 mg, E/Z >99%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$). δ 7.78 (dd, *J* = 15.0, 7.8 Hz, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 8.6 Hz, 3H), 7.35 (d, *J* = 7.6 Hz, 4H), 5.91 (s, 1H), 4.27 (t, *J* = 6.7 Hz, 2H), 3.26 (t, *J* = 6.7 Hz, 2H), 2.45 (s, 3H).$^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 154.2, 145.0, 141.4, 136.5, 133.4, 132.7, 130.3, 130.2, 129.9, 129.4, 128.1, 127.0, 126.1, 125.6, 68.6, 32.4, 21.7. IR (ATR): ν = 3058, 2924, 1596, 1359, 1306, 1173, 1144, 1082, 973, 894, 741, 686, 658, 551, 473 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{22}O_5S_2SeNa$ 544.9967; Found 544.9970.

3-(1-(phenylselanyl)-2-(phenylsulfonyl)vinyl)pyridine (3la) Yield = 88.5% (70.9 mg, E/Z >99%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 6.4 Hz, 1H), 8.34 (d, *J* = 1.7 Hz, 1H), 7.57 (dd, *J* = 7.2, 1.5 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.48 – 7.42 (m, 3H), 7.40 – 7.35 (m, 4H), 7.22 (dd, *J* = 7.8, 4.9 Hz, 1H), 6.29 (s, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 153.7, 150.2, 148.2, 141.5, 136.6, 136.1, 133.2, 131.1, 130.4, 130.3, 129.0, 127.3, 127.2, 126.2, 122.7. IR (ATR): ν = 3052, 2924, 1719, 1571, 1445, 1320, 1233, 1147, 1083, 936, 741, 684, 567, 532 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{16}NO_2SSe$ 402.0062; Found 402.0066.

3-(1-(phenylselanyl)-2-(phenylsulfonyl)vinyl)thiophene (3ma) Yield = 70.9% (57.5 mg, E/Z >99%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.48 – 7.40 (m, 5H), 7.38 (dd, *J* = 3.4, 1.5 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.18 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.97 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.21 (s, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 152.0, 141.6, 136.5, 134.3, 132.8, 130.3, 130.2, 128.7, 128.3, 127.3, 127.2, 126.9, 126.2, 125.4. IR (ATR): ν = 2361, 1571, 1445, 1304, 1262, 1145, 1123, 1079, 848, 811, 740, 684, 550 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{14}O_2S_2SeNa$ 428.9493; Found 428.9469.

phenyl(1-phenyl-2-(phenylsulfonyl)vinyl)selane (3na) Yield = 89.1% (71.1 mg, 75: 25). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 7.41 (dq, *J* = 14.7, 6.7 Hz, 5H), 7.31 – 7.23 (m, 4H), 7.19 – 7.16 (m, 1H), 7.09 – 7.00 (m, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.17 (s, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 157.9, 141.7, 136.6, 135.8, 134.5, 133.6, 132.7, 130.3, 130.2, 129.4, 129.1, 128.7, 128.7, 128.6, 128.5, 127.9, 127.8, 127.6, 127.4, 126.8, 125.6. IR (ATR): ν = 3050, 2958, 2923, 2853, 1574, 1443, 1317, 1142, 1081, 874, 794, 740, 688, 562, 530 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{17}O_2SSe$ 401.0109; Found 401.0113.

1,5-diphenyl-1-(phenylselanyl)-2-(phenylsulfonyl)pent-1-en-3-one (3oa) Yield = 60.2% (640.0 mg, 81: 19). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.8 Hz, 2H), 7.44 – 7.24 (m, 11H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 3H), 7.05 – 6.93 (m, 1H), 6.16 (s, 1H), 2.47 (s, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 157.2, 143.6, 138.9, 136.7, 135.9, 134.7, 130.3, 130.2, 129.4, 129.3, 128.6, 128.6, 127.9, 127.9, 127.5, 126.9, 125.9, 21.6. IR (ATR): ν = 1606, 1574, 1438, 1318, 1274, 1139, 1081, 1022, 875, 801, 778, 741, 690, 649 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{25}O_3SSe$ 533.0685; Found 533.0690.

(1,2-diphenyl-2-(phenylsulfonyl)vinyl)(phenyl)selane (3pa) Yield =68.7 % (65.3 mg, 50: 50). White solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 5H), 7.32 – 7.16 (m, 2H), 7.08 – 6.98 (m, 4H), 6.95 – 6.88 (m, 3H), 6.84 – 6.59 (m, 1H). $^{13}C\{^1H\}$NMR(100 MHz, $CDCl_3$) δ 141.0, 137.3, 137.2, 135.2, 132.8, 131.1, 129.5, 128.9, 128.9, 128.8, 128.8, 128.7, 128.5, 128.4, 128.3, 128.3, 127.7, 127.7, 127.5, 127.1. IR (ATR): ν = 3050, 2923, 1721, 1574, 1475, 1438, 1317, 1275, 1142, 1081, 874, 794, 740, 680, 587, 562, 530 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{21}O_2SSe$ 477.0427; Found 477.0452.

phenyl(1-phenyl-2,2-bis(phenylsulfonyl)vinyl)selane (3qa) Yield =22.3 % (24.0 mg, 67: 33). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.4 Hz, 2H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 2H), 7.46 (dd, *J* = 12.1, 7.5 Hz, 3H), 7.31 – 7.25 (m, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.0 Hz, 2H), 6.95 – 6.86 (m, 3H), 6.79 (t, *J* = 7.5 Hz, 2H), 6.48 (d, *J* = 7.3 Hz, 2H). $^{13}C\{^1H\}$NMR(100 MHz, $CDCl_3$)) δ 176.1, 141.8, 141.5, 137.5, 134.2, 134.0, 133.2, 129.2, 129.0, 128.6, 128.5, 128.5, 128.1, 128.1, 128.0, 126.7. IR (ATR): ν = 2359, 1502, 1469, 1442, 1313, 1150, 1080, 970, 823, 785, 744, 690, 550 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{21}O_4S_2Se$ 541.0041; Found 541.0052.

diethyl 2-(phenylselanyl)-3-(phenylsulfonyl)fumarate (3ra) Yield = 36.0% (33.7 mg, 75: 25). White solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.80 (m, 3H), 7.69 – 7.35 (m, 9H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.60 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$NMR(100 MHz, $CDCl_3$) δ 166.2, 162.7, 162.6, 140.6, 138.0, 136.5, 133.5, 131.6, 130.6, 129.8, 129.0, 128.7, 128.7, 127.3, 62.7, 62.4, 13.9, 13.6. IR (ATR): ν = 2975, 1740, 1714, 1685, 1526, 1476, 1443, 1325, 1308, 1260, 1204, 1151, 1087, 1062, 1049, 1023, 1006, 803, 748, 701, 684,622 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{20}O_6SSeNa$ 491.0038; Found 491.0037.

ethyl 3-((4-bromophenyl)selanyl)-3-phenyl-2-(phenylsulfonyl)acrylate (3ab) Yield = 69.8% (76.8 mg, 62: 38). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.4 Hz, 1H), 7.62 (dd, *J* = 11.6, 7.7 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.11 – 6.76 (m, 9H), 4.38 (q, *J* = 7.2 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 2H), 0.74 (t, *J* = 7.1 Hz, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$)) δ 163.5, 141.5, 138.4, 138.1, 134.4, 134.1, 133.1, 131.8, 131.8, 129.0, 128.7, 128.7, 128.6, 128.4, 128.2, 127.8, 127.3, 126.7, 124.0, 62.9, 62.1, 14.1, 13.3. IR (ATR): ν = 1714, 1682, 1564, 1524, 1466, 1443, 1380, 1308, 1253, 1204, 1151, 1087, 1048, 1006, 803, 749, 702, 683, 622 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{25}H_{25}BrNO_3SSe$ 577.9899; Found 577.9888.

ethyl 2-((4-chlorophenyl)sulfonyl)-3-phenyl-3-(phenylselanyl)acrylate (3ac) Yield = 79.9% (80.9 mg, 67: 33). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.13 – 6.92 (m, 9H), 6.87 – 6.83 (m, 1H), 6.75 (d, *J* = 6.8 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 2H), 0.73 (t, *J* = 7.1 Hz, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 165.9, 140.2, 139.7, 137.0, 136.7, 130.1, 129.7, 129.3, 129.1, 128.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.5, 128.2, 127.6, 127.6, 127.2, 62.9, 62.1, 14.2, 13.3. IR (ATR): ν = 2987, 2361, 1712, 1576, 1475, 1329, 1248, 1150, 1085, 1040, 756, 689, 581, 552, 467 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{19}ClO_4SSeNa$ 528.9750; Found 528.9736.

ethyl 2-((4-fluorophenyl)sulfonyl)-3-phenyl-3-(phenylselanyl)acrylate (3ad) Yield = 80.2% (78.5 mg, 70: 30). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.33 (m, 1H), 7.61 – 7.54 (m, 1H), 7.29 (t, *J* = 8.6 Hz, 1H), 7.13 – 6.91 (m, 9H), 6.87 – 6.83 (m, 1H), 6.78 – 6.74 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 2H), 0.73 (t, *J* = 7.1 Hz, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 165.4(d, J_{F-C} = 254.2 Hz), 165.2, 163.5, 137.0(d, J_{F-C} = 3.1 Hz), 136.8, 134.3, 131.6(d, J_{F-C} = 9.5 Hz), 131.(d, J_{F-C} = 9.6 Hz), 129.1, 128.9, 128.7, 128.7, 128.6, 128.5, 128.2, 127.7, 127.6, 127.2, 116.3(d, J_{F-C} = 22.6 Hz), 115.8 (d, J_{F-C} = 22.4 Hz) 62.9, 62.1, 14.2, 13.4. IR (ATR): ν = 3354, 2977, 2363, 1684, 1587, 1525, 1490, 1319, 1261, 1224, 1145, 1085, 844, 818, 739, 691, 578 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{19}FO_4SSeNa$ 513.0046; Found 513.0038.

ethyl 2-(methylsulfonyl)-3-phenyl-3-(phenylselanyl)acrylate (3ae) Yield = 65.8% (53.9 mg, 62: 38). White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 6.9 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.04 – 6.96 (m, 5H), 6.95 – 6.90 (m, 2H), 3.87 (q, *J* = 7.1 Hz, 2H), 3.39 (s, 3H), 0.76 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.5, 162.3, 137.0, 136.3, 131.5, 128.9, 128.7, 128.6, 128.0, 127.8, 127.6, 62.1, 42.0, 13.4. IR (ATR): ν = 2984, 2357, 1706, 1535, 1438, 1315, 1237, 1201, 1143, 1043, 960, 765, 744, 688, 533, 473 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}O_4SSe$ 411.0164; Found 411.0162.

ethyl 3-phenyl-3-(phenylselanyl)-2-tosylacrylate (3af) Yield = 81.8% (79.5 mg, 62: 39). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.44 (dd, *J* = 25.0, 8.2 Hz, 2H), 7.17 – 6.74 (m, 11H), 4.39 (q, *J* = 7.1 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 1H), 2.49 (s, 1H), 2.37 (s, 2H), 1.39 (t, *J* = 7.1 Hz, 2H), 0.74 (t, *J* = 7.1 Hz, 1H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.6, 144.0, 138.7, 136.9, 136.7, 134.4, 129.5, 129.1, 128.9, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 127.8, 127.5, 127.0, 62.7, 61.9, 21.8, 21.6, 14.1, 13.3. IR (ATR): ν = 2339, 1715, 1441, 1324, 1245, 1148, 1085, 748, 690, 553 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{23}O_4SSe$ 487.0477; Found 487.0460.

ethyl 3-(sec-butylselanyl)-3-phenyl-2-(phenylsulfonyl)acrylate (3ag) Yield = 86.8% (78.4 mg, 90: 10). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.3 Hz, 2H), 7.61 (dt, *J* = 38.7, 7.4 Hz, 3H), 7.35 – 7.27 (m, 3H), 7.26 – 7.17 (m, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 2.24 (h, *J* = 6.9 Hz, 1H), 1.58 (s, 1H), 1.40 – 1.22 (m, 2H), 1.17 – 0.98 (m, 3H), 0.81 (t, *J* = 7.1 Hz, 2H), 0.62 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 159.9, 140.6, 137.5, 133.6, 129.4, 128.6, 128.5, 128.2, 127.8, 61.9, 42.7, 30.4, 21.4, 13.3, 11.8. IR (ATR): ν = 2962, 1719, 1542, 1445, 1320, 1238, 1204, 1148, 1085, 1041, 998, 857, 743, 685, 547 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}O_4SSe$ 453.0634; Found 453.0635.

ethyl 3-((cyclopropylmethyl)selanyl)-3-phenyl-2-(phenylsulfonyl)acrylate (3ah) Yield =76.1% (68.5 mg, 75: 25). White oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.28 (m, 8H), 7.19 – 7.03 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.03 (dd, *J* = 13.6, 7.5 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 2H), 0.86 – 0.45 (m, 4H), 0.04 (p, *J* = 5.8, 5.3 Hz, 2H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.4, 163.6, 141.8, 135.4, 133.7, 132.9, 131.8, 129.3, 129.0, 128.7, 128.5, 128.5, 128.4, 128.0, 128.0, 127.8, 127.5, 62.5, 61.9, 34.8, 14.0, 13.4, 9.8, 6.9, 6.8. IR (ATR): ν = 3333, 2975, 2361, 1708, 1529, 1313, 1246, 1147, 1084, 1044, 751, 691, 596, 553cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{22}O_4SSeNa$ 473.0297; Found 473.0283.

3-((4-bromophenyl)selanyl)-N-(tert-butyl)-3-phenyl-2-(phenylsulfonyl)acrylamide (3db) Yield =73.2% (84.5 mg, 81: 19). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.48 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.08 – 6.93 (m, 7H), 6.75 (d, *J* = 6.8 Hz, 2H), 1.41 (s, 7H), 0.94 (s, 2H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 161.7, 141.1, 138.5, 138.1, 134.9, 133.3, 131.8, 131.5, 128.94, 128.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.4, 127.1, 123.6, 52.5, 28.6, 27.9. IR (ATR): ν = 1714, 1682, 1524, 1477, 1443, 1380, 1308, 1253, 1204, 1151, 1087, 1048, 1006, 803, 749, 702, 683, 622 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{25}BrNO_3SSe$ 577.9899; Found 577.9888.

N-(tert-butyl)-2-((4-chlorophenyl)sulfonyl)-3-phenyl-3-(phenylselanyl)acrylamide (3dc) Yield = 78.2% (83.4 mg, 59: 41). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 7.12 – 6.90 (m, 10H), 6.72 (d, *J* = 8.2 Hz, 1H), 1.46 (s, 5H), 0.94 (s, 4H). ^{13}C{^{1}H}NMR(100 MHz, $CDCl_3$) δ 164.4, 161.6, 139.8, 139.7, 139.0, 137.0, 136.6, 134.5, 130.4, 129.1, 129.0, 129.0, 128.7, 128.7, 128.6, 128.6, 128.4, 128.4, 128.1, 127.8, 127.0, 52.6, 52.0, 28.6, 27.9. IR (ATR): ν = 3335, 2361, 1661, 1525, 1314, 1146, 1084, 752, 744, 688, 555, 742 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}ClNO_3SSeNa$ 556.0223; Found 556.0193.

N-(tert-butyl)-2-((4-fluorophenyl)sulfonyl)-3-phenyl-3-(phenylselanyl)acrylamide (3dd) Yield = 87.5% (90.4 mg, 67: 33). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.9, 5.1 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.12 – 6.90 (m, 11H), 6.74 – 6.72 (m, 1H), 1.46 (s, 6H), 0.94 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ164.9 (d, J_{F-C} = 6.5 Hz), 164.0 (d, J_{F-C} = 6.8 Hz), 161.9, 161.8, 137.4 (d, J_{F-C} = 3.0 Hz), 137.1, 136.7, 134.7, 132.6 (d, J_{F-C} = 3.6 Hz), 131.9 (d, J_{F-C} = 9.4 Hz), 130.5 (d, J_{F-C} = 9.9 Hz), 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.0, 116.1(d, J_{F-C} = 22.4 Hz), 116.1(d, J_{F-C} = 22.8 Hz), 115.9, 52.7, 52.0, 28.7, 27.9. IR (ATR): ν = 3352, 2967, 1656, 1531, 1493, 1316, 1292, 1218, 1144, 1086, 841, 732, 691, 551, 507 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{25}FNO_3SSe$ 518.0669; Found 518.0669.

N-(tert-butyl)-2-(methylsulfonyl)-3-phenyl-3-(phenylselanyl)acrylamide (3de) Yield =74.7% (65.2 mg, 69: 31). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (ddd, *J* = 21.1, 15.2, 7.2 Hz, 3H), 7.05 – 6.96 (m, 6H), 6.93 – 6.91 (m, 1H), 3.40 (s, 1H), 2.89 (s, 2H), 1.52 (s, 6H), 0.94 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 162.2, 137.1, 137.0, 134.8, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.0, 127.2, 52.7, 52.0, 44.2, 42.3, 28.7, 27.9. IR (ATR): ν = 3333, 2975, 2364, 1659, 1532, 1307, 1140, 746,521 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{23}NO_3SSeNa$ 460.0457; Found 460.0456.

N-(tert-butyl)-3-phenyl-3-(phenylselanyl)-2-tosylacrylamide (3df) Yield =95.9 % (98.3 mg, 60: 40). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.2 Hz, 1H), 7.43 (dd, *J* = 31.5, 8.2 Hz, 2H), 7.17 – 6.75 (m, 12H), 2.47 (s, 1H), 2.36 (s, 2H), 1.43 (s, 5H), 0.93 (s, 4H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 161.8, 161.8, 144.1, 138.2, 137.0, 136.7, 134.9, 129.4, 129.4, 128.8, 128.5, 128.5, 128.4, 128.4, 128.3, 127.9, 127.6, 127.6, 126.8, 52.3, 51.8, 28.5, 27.8, 21.8, 21.6. IR (ATR): ν = 3332, 2974, 2358, 1660, 1526, 1304, 1218, 1143, 1086, 689, 554 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}NO_3SSeNa$ 536.0769; Found 536.0783.

N-(tert-butyl)-3-(sec-butylselanyl)-3-phenyl-2-(phenylsulfonyl)acrylamide (3dg) Yield =44.9 % (43.0 mg, 81: 19). White solid. . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.56 – 7.53 (m, 3H), 7.36 (dt, *J* = 15.6, 7.9 Hz, 5H), 5.95 (s, 1H), 1.56 (s, 3H), 1.49 (d, *J* = 2.6 Hz, 9H), 1.43 – 0.83 (m, 6H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 159.3, 149.0, 147.3, 139.4, 136.7, 134.5, 134.1, 129.7, 129.6, 129.0, 128.9, 128.8, 128.8, 128.4, 128.0, 127.9, 125.4, 53.4, 28.5, 28.4. IR (ATR): ν = 3368, 2975, 2361, 1672, 1526, 1446, 1322, 1152, 1081, 809, 686, 548 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{30}NO_3SSe$ 480.1107; Found 480.1118.

N-(tert-butyl)-3-((cyclopropylmethyl)selanyl)-3-phenyl-2-(phenylsulfonyl)acrylamide (3dh) Yield =53.8% (51.3 mg, 67: 33). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.4 Hz, 1H), 7.72 – 7.55 (m, 3H), 7.49 – 7.35 (m, 5H), 7.29 (d, *J* = 5.6 Hz, 1H), 7.12 (d, *J* = 9.3 Hz, 1H), 6.85 (s, 1H), 2.02 (dd, *J* = 25.3, 7.4 Hz, 2H), 1.46 (s, 6H), 1.05 (s, 3H), 0.72 (dt, *J* = 38.1, 7.7 Hz, 1H), 0.50 (dd, *J* = 34.9, 6.9 Hz, 2H), 0.04 (dd, *J* = 27.0, 4.8 Hz, 2H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 161.8, 141.4, 135.9, 133.5, 133.1, 129.2, 128.8, 128.8, 128.7, 128.6, 128.6, 127.9, 127.8, 127.8, 127.5, 52.3, 51.9, 34.4, 28.5, 28.0, 10.3, 9.7, 6.8, 6.8. IR (ATR): ν = 3354, 2358, 1656, 1529, 1309, 1222, 1150, 1088, 736, 685, 551 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{28}NO_3SSe$ 478.0950; Found 478.0944.

(2-(p-tolyl)ethene-1,1-diyl)dibenzene (5) Yield =53.8% (51.3 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.27 (m, 6H), 7.20 (d, *J* = 7.3 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 7.1 Hz, 2H), 6.99 (s, 1H), 2.37 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 154.8, 143.8, 139.3, 138.7, 135.6, 130.3, 129.8, 129.4, 129.0, 128.9, 128.6, 128.3, 127.9, 127.8, 21.6. IR (ATR): ν = 3037, 2358, 1591, 1443, 1299, 1134, 1084, 804, 759, 694, 579, 536 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{19}O_2S$ 335.1101; Found 335.1089.

ASSOCIATED CONTENT

Supporting Information Available.

The copies of ^{1}H and ^{13}C NMR spectra of the products and crystallographic data of **3aa**, **3da**.

This material is available free of charge *via* the Internet at http://pubs.acs.org.

The syntheses and characterization of compounds **3aa, 3ah, 3da, and 3df** were repeated and checked by Jing-Hao Li in our group.

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