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苄叉丙酮、硒粉和硼氢化钠一锅法构建四氢-2*H*-硒吡喃衍生物

陈栋栋* 杨旭锋
(吕梁学院化学化工系 山西吕梁 033001)

摘要 报道了一种以苄叉丙酮、硒粉和硼氢化钠为原料, 采用一锅法合成一系列四氢-2*H*-硒吡喃衍生物的新方法. 此反应通过形成 6 个新的化学键很好的构建一系列含硒六元环. 得到了 20 个含有四氢-2*H*-硒吡喃结构的小分子化合物, 最高产率可达 91%. X 单晶衍射分析表明四氢-2*H*-硒吡喃六元环与环己烷具有类似的空间立体结构, 呈现出稳定的椅式构象. 此反应在克量级规模下依然可以顺利进行. 可能的反应机理表明此反应为涉及双 Michael 加成/二硒键的断裂/Michael 加成/Aldol 反应的多步串级反应. 此方法具有底物适应性强、不使用过度金属催化剂以及反应条件温和的特点.
关键词 四氢-2*H*-硒吡喃; 环化; 硒; 一锅法; 苄叉丙酮

One-Pot Synthesis of Tetrahydro-2*H*-selenopyran Derivatives from Benzalacetones, Elemental Selenium, and Sodium Borohydride

Chen, Dongdong* Yang, Xufeng
(*Department of Chemistry & Chemical Engineering, Lyuliang University, Lvliang, Shanxi 033001*)

Abstract A reaction has been developed to synthesize a series of tetrahydro-2*H*-selenopyran derivatives from benzalacetones, sodium borohydride, and elemental selenium by one-pot method. The reaction proceeds well to construct a tetrahydro-2*H*-selenopyran ring and six new bonds. Twenty tetrahydro-2*H*-selenopyran derivatives were obtained, and the yield was up to 91%. The X-ray single crystal analysis showed that this selenium-containing heterocyclic ring exists as a stable chair conformation similar to cyclohexane. The reaction works well when scaled up to the gram scale. A possible mechanism was proposed, involving hydrogenation of selenium/double Michael addition/cleavage of diselenide bond/Michael addition/Aldol reaction. This reaction is characterized by high compatibility to substrates, transition-metal free, and mild reaction conditions.
Keywords tetrahydro-2*H*-selenopyran, cyclization, elemental selenium, one-pot, benzalacetones

1 Introduction

Selenium (Se), one of the essential trace elements of human body, is important for health.[1] Selenium-containing compounds are widely present in natural compounds and exhibit a variety of biological activities.[2] They play an important role in organic chemistry, food chemistry, agricultural chemistry and material chemistry.[3] Some chemicals with tetrahydro-2*H*-selenopyran moiety exhibit antifungal activity and antioxidant activity,[4-5] and used as photosensitizers for the treatment of cancers (Figure 1).[6] The fruitful application of selenium-containing compounds has attracted the interest from chemists in developing new synthetic strategies for selenium-containing compounds.[7] In the past decades, some synthetic methods for tetrahydro-2*H*-selenopyran derivatives have been reported.[8] For instance, Levanova and co-workers[9] have declared an efficient synthesis of tetrahydro-2*H*-selenopyran from 1,5-dibromopentane and K_2Se (Scheme 1a). Waldvogel and co-workers[10] reported a series of selenium heterocyclic compounds using diselenide as raw material by dehydrogenation coupling reaction (Scheme 1b). Recently, Sanz and co-workers[11] described a gold(I)-catalyzed cascade reaction for the stereoselective synthesis of selenium-containing indeno[1,2-*b*]thiophene derivatives from *o*-(alkynyl)styrenes substituted at the triple bond with the selenoaryl group (Scheme 1c). However, the involvement of transition metal catalysts and complex substrates limit the application of their strategies in the industry.

One-pot reaction can construct complex compounds efficiently from simple starting materials. Compared with traditional synthesis methods, one-pot reaction can reduce

* Corresponding author. E-mail: chenddxy@163.com
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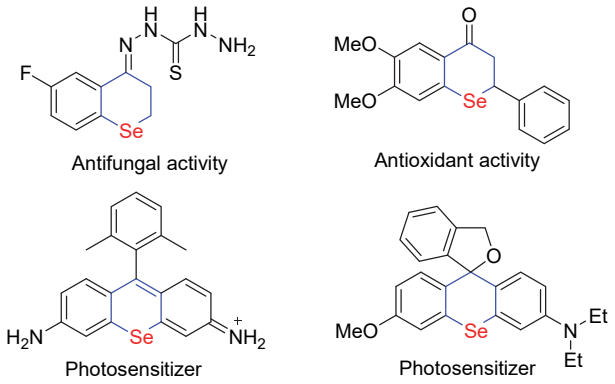
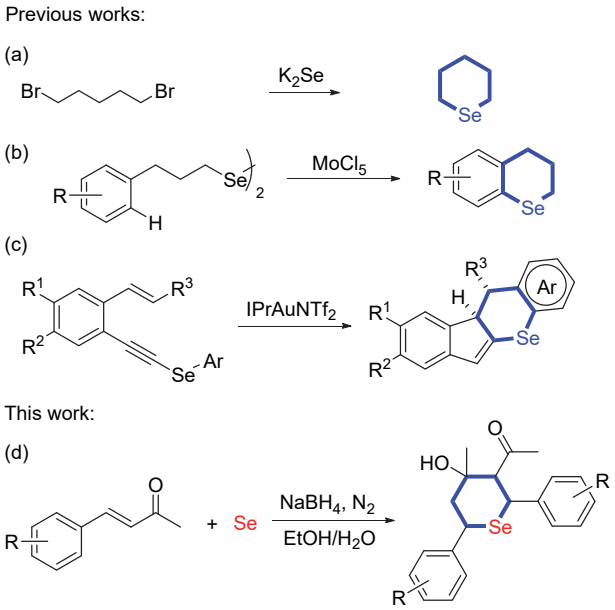


Figure 1 Biological activities from tetrahydro-2*H*-selenopyran derivatives

the reaction steps and avoid the organic waste generated in the process of intermediate separation. Therefore, one-pot reaction has the advantages of high atomic utilization, simple operation and environmental friendliness.[12] Elemental selenium is often used in the synthesis of selenium-containing compounds.[13] Based on our previous works,[14] we herein report a novel domino reaction to synthesize a series of tetrahydro-2*H*-selenopyran derivatives from benzalacetones, sodium borohydride, and elemental selenium in mild conditions (Scheme 1d).

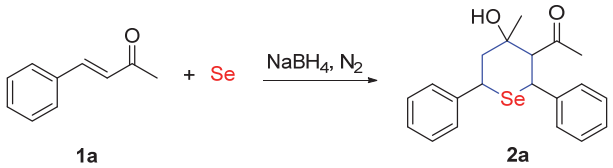


Scheme 1 Synthesis of tetrahydro-2*H*-selenopyran derivatives

2 Results and discussion

Initially, the synthesis of tetrahydro-2*H*-selenopyran derivative **2a** from benzalacetone, sodium borohydride, and elemental selenium was chosen as a model system to evaluate different reaction parameters under nitrogen. As shown in Table 1, no product was formed at room temperature for 6 h when water alone was selected as solvent (Table 1, Entry 1). Once alcohols were introduced, the reaction proceeded (Table 1, Entries 2～4). Elemental selenium existed as ions in the reaction system, so a series of co-solvent systems including acetonitrile-water, *N*,*N*-dimethylformamide-water, dimethyl sulfoxide-water, methanol-water, and ethanol-water were developed (Table 1, Entries 5～9). Encouragingly, co-solvent systems, especially ethanol-water or methanol-water, performed better than ethanol or methanol as solvent alone. Among all these co-solvent systems, the ethanol-water system afforded product **2a** with the highest yield of 88% (Table 1, Entry 9). When the reaction time was adjusted from 12 h to either 6 or 24 h, lower yields were observed (Table 1, Entries 10～11). Similarly, altering the reaction temperature from room temperature to 50 or 0 ℃ also resulted in a slight decrease in yield (Table 1, Entries 12～13). This indicates that the duration and temperature of the reaction play crucial roles, with a 12-hour reaction time and room temperature being more favorable for higher yields. Therefore, the treatment of the reaction solution of benzalacetone **1a** (1 equiv., 1 mmol), selenium powder (0.6 equiv., 0.6 mmol) and sodium borohydride (1.2 equiv., 1.2 mmol) in the co-solvent of ethanol-water (*V*∶*V*=1∶1, 4 mL) under nitrogen at room temperature for 12 h was selected as the most optimal condition.

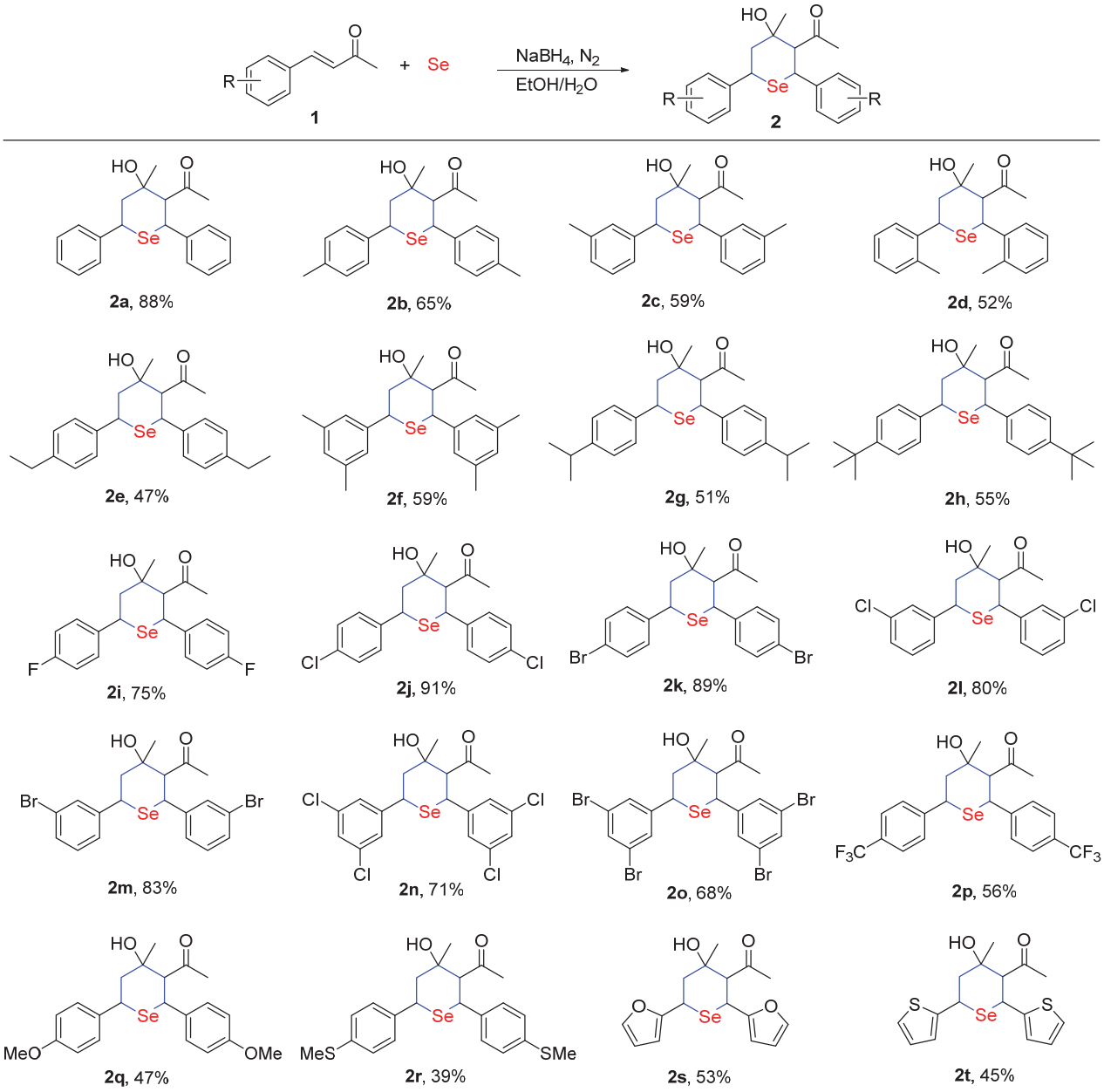
Table 1 Optimization of the reaction conditions[a]



Entry	Solvent	Time/h	*T*/℃	Yield[b]/%
1	H_2O	6	r.t.	0
2	MeOH	6	r.t.	37
3	EtOH	6	r.t.	46
4	EtOH	12	r.t.	62
5	MeCN/H_2O (*V*∶*V*=1∶1)	12	r.t.	13
6	DMF/H_2O (*V*∶*V*=1∶1)	12	r.t.	＜10
7	DMSO/H_2O (*V*∶*V*=1∶1)	12	r.t.	＜10
8	MeOH/H_2O (*V*∶*V*=1∶1)	12	r.t.	79
9	**EtOH/H_2O (*V*∶*V*=1∶1)**	**12**	r.t.	**88**
10	EtOH/H_2O (*V*∶*V*=1∶1)	6	r.t.	59
11	EtOH/H_2O (*V*∶*V*=1∶1)	24	r.t.	75
12	EtOH/H_2O (*V*∶*V*=1∶1)	12	50	71
13	EtOH/H_2O (*V*∶*V*=1∶1)	12	0	80

[a] Reaction conditions: **1a** (1.0 equiv., 1 mmol), selenium powder (0.6 equiv., 0.6 mmol) and sodium borohydride (1.2 equiv., 1.2 mmol) in solvent (4 mL) stirring under nitrogen. [b] Isolated yield based on **1a**.

With the optimized reaction condition in hand (Table 1, Entry 9), various benzalacetones were then employed to synthesize corresponding tetrahydro-2*H*-selenopyran derivatives (Scheme 2). Compared with the model substrate of benzalacetone (**2a**), the yields from alkyl substituted benzalacetones [methyl (**2b**), ethyl (**2e**), isopropyl (**2g**), and *tert*-butyl (**2h**)] decreased slightly. While, the yields of these alkyl substituents were not subjected to their positions in the benzene ring. In terms of halogenated substrates (**2i**～



Scheme 2 Synthesis of tetrahydro-2*H*-selenopyran derivatives **2**

2o), significant increase of yields was observed, especially the chloro (**2j**), or bromo (**2k**) at the 4-position of the benzene ring. After that, benzalacetones with substituents of trifluoromethyl (**2p**), methoxy (**2q**), and methylthio (**2r**) were conducted for the reaction with moderate yields. Different from benzalacetone, furfural acetone and thiophenylalacetone gave yields of 53% (**2s**) and 45% (**2t**), respectively. This be caused by the reaction involves a multi-step Michael addition (Scheme 4), and the electron-rich *β*-position hinders the smooth progress of the Michal addition. These results demonstrate the domino reaction has a wide range of compatibility to different benzalacetones with moderate to decent yields. The yields of the reaction were mainly subjected to the type of substituents rather than the position of these substituents on the benzene ring of benzalacetone **1**.

All the tetrahydro-2*H*-selenopyran derivatives **2** were characterized by ^{1}H NMR and ^{13}C NMR spectra and HRMS. To further illustrate the relative stereochemistry of these compounds, one of them **2a** was confirmed by the X-ray single crystal analysis (CCDC 2128170).[15] This selenium-containing heterocyclic ring exists as a stable chair conformation similar to cyclohexane (Figure 2). The two phenyl groups at the 2,6-position and the hydroxyl group at the 4-position are on the same side of the ring in the equatorial positions, while acetyl and methyl groups at the 4-position group direct to another side.

The reaction worked well when scaled up to the gram scale and the corresponding products **2a** was obtained in a 67% yield under the optimized conditions (Scheme 3).

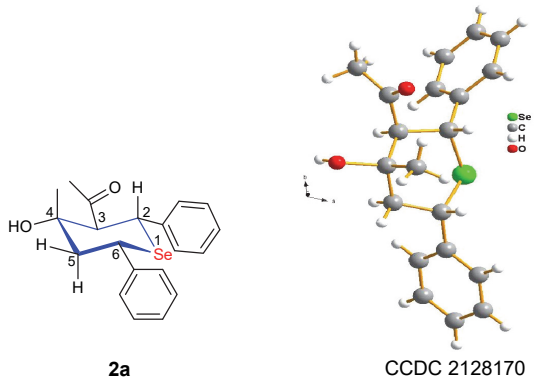
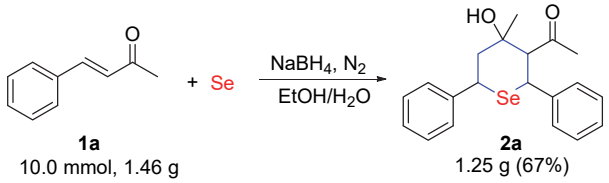


Figure 2 Relative stereochemistry and single-crystal X-ray structure of compound **2a**



Scheme 3 Gram scale reaction

A potential mechanistic pathway is outlined in Scheme 4 involving five steps: (1) sodium borohydride reduces selenium powder to form the diselenium anion; (2) the diselenium anion undergoes Michael addition with 2 equiv. of benzalacetones **1**, yielding intermediate **A** (the formation of intermediate **A** for compound **2a** was confirmed through ^{1}H NMR, ^{13}C NMR, and HRMS, as detailed in the Supporting Information). The target compound **2a** can be successfully obtained by using intermediate **A** instead of benzylideneacetone as raw material under the optimal reaction conditions); (3) the weak Se—Se bond in intermediate **A** is cleaved, leading to the formation of intermediate **B**; (4) intermediate **B**, along with 1 equiv. of benzalacetones **1**, undergoes another Michael addition to generate intermediate **C**; (5) the target product **2** is ultimately produced through an intramolecular Aldol reaction from intermediate **C**.

3 Conclusions

In summary, we have developed a novel one pot reaction to synthesize tetrahydro-2*H*-selenopyran derivatives with moderate to high yields by using benzalacetones, sodium borohydride, and selenium powder. This one-pot reaction features wide substrate scope, transition-metal free and mild reaction conditions. Further investigations and applications for this domino reaction are under study in our laboratory.

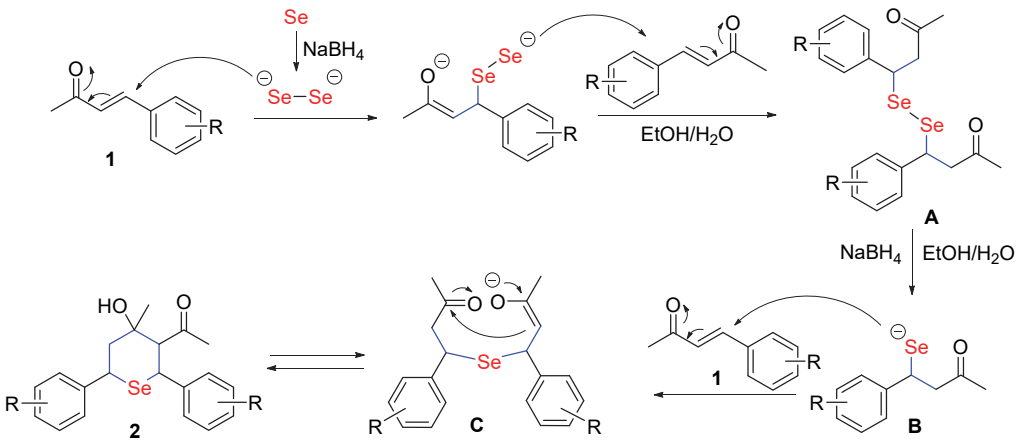
4 Experimental section

4.1 Materials

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise stated. Melting points (m.p.) were determined on an XT-4 micro-melting point apparatus and uncorrected. Nuclear magnetic resonance spectra (NMR) were recorded on a Bruker AVIII-400 (^{1}H MNR: 400 MHz, ^{13}C NMR: 100 MHz) (Bruker, Karlsruhe, Germany) instrument in $CDCl_3$ and using tetramethyl silane (TMS) as an internal standard. High resolution mass spectra (HRMS) were obtained using a Bruker micrOTOF-Q II focus spectrometer (ESI). Column chromatography was performed on silica gel (200～300 mesh).

4.2 Chemistry

A round bottom flask with selenium powder (47.4 mg, 0.6 mmol, 0.6 equiv.) was purged with nitrogen for three times, followed by the addition of sodium borohydride (45.4 mg, 1.2 mmol, 1.2 equiv.) solution in water (2 mL). The reaction mixture was then left to stir at room temperature for 15 min. Then, a solution of benzalacetones (1 mmol, 1 equiv.) in ethanol (2 mL) was added into the flask and the reaction mixture was stirred for 12 h. The resulting mixture was diluted with DCM (20 mL), filtered to get rid of solids. The organic layer washed with water (15 mL×3), brine (15 mL), dried over anhydrous Na_2SO_4, filtered, evaporated under vacuum. The evaporated residue was purified by a silica gel column using a petroleum ether/ethyl acetate (V/V=10/1) mixture to afford pure product **2**.



Scheme 4 P lausible reaction mechanism

1-(4-Hydroxy-4-methyl-2,6-diphenyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2a**): White solid; isolated yield: 164.2 mg (88%); m.p. 182～183 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V* = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.36 (m, 4H), 7.33～7.28 (m, 4H), 7.25～7.21 (m, 2H), 4.84 (dd, *J*=12.3, 2.8 Hz, 1H), 4.77 (d, *J*=11.4 Hz, 1H), 3.89 (s, 1H), 3.39 (d, *J*=11.4 Hz, 1H), 2.36 (dd, *J*=14.1, 2.8 Hz, 1H), 7.27～7.20 (m, 1H), 1.77 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.6, 141.4, 139.1, 128.9, 128.7, 128.3, 128.0, 127.7, 127.3, 71.9, 63.9, 46.7, 40.7, 37.1, 35.0, 30.5. HRMS (ESI) calcd for $C_{20}H_{23}O_2Se$ $[M+H]^+$ 375.0858, found 375.0851.

1-(4-Hydroxy-4-methyl-2,6-di-*p*-tolyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2b**): White solid; isolated yield: 130.5 mg (65%); m.p. 135～136 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V* = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28～7.27 (m, 2H), 7.27～7.25 (m, 2H), 7.11 (t, *J*=7.6 Hz, 4H), 4.79 (dd, *J*=12.2, 2.7 Hz, 1H), 4.73 (d, *J*=11.4 Hz, 1H), 3.92 (s, 1H), 3.37 (d, *J*=11.4 Hz, 1H), 2.36 (dd, *J*=13.3, 2.9 Hz, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.21 (dd, *J*=14.1, 12.2 Hz, 1H), 1.79 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.8, 138.5, 137.6, 137.0, 136.1, 129.6, 129.4, 128.2, 127.5, 71.9, 63.9, 46.9, 40.4, 36.8, 35.1, 30.5, 21.12, 21.10. HRMS (ESI) calcd for $C_{22}H_{27}O_2Se$ $[M+H]^+$ 403.1171, found 403.1162.

1-(4-Hydroxy-4-methyl-2,6-di-*m*-tolyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2c**): White solid; isolated yield: 118.0 mg (59%); m.p. 112～113 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20～7.17 (m, 6H), 7.05～7.02 (m, 2H), 4.79 (dd, *J*=12.2, 2.8 Hz, 1H), 4.73 (d, *J*=11.4 Hz, 1H), 3.91 (d, *J*=2.4 Hz, 1H), 3.39 (d, *J*=11.4 Hz, 1H), 2.36～2.29 (m, 7H), 2.26～2.19 (m, 1H), 1.79 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.7, 141.4, 139.1, 138.6, 138.3, 129.0, 128.8, 128.7, 128.6, 128.4, 128.1, 125.3, 124.7, 71.9, 63.8, 46.9, 40.7, 37.1, 35.0, 30.5, 21.41, 21.35. HRMS (ESI) calcd for $C_{22}H_{27}O_2Se$ $[M+H]^+$ 403.1171, found 403.1159.

1-(4-Hydroxy-4-methyl-2,6-di-*o*-tolyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2d**): White solid; isolated yield: 104.3 mg (52%); m.p. 148～150 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J*=7.7 Hz, 1H), 7.40 (d, *J*=7.6 Hz, 1H), 7.20～7.09 (m, 6H), 5.09 (d, *J*=11.3 Hz, 1H), 5.01 (dd, *J*=9.1, 5.7 Hz, 1H), 3.86 (s, 1H), 3.48 (d, *J*=11.3 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H), 2.32～2.30 (m, 2H), 1.85 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.8, 139.4, 137.2, 136.1, 135.9, 131.1, 130.7, 127.9, 127.6, 127.0, 126.7, 126.40, 126.37, 72.1, 63.5, 46.4, 35.1, 35.0, 33.1, 30.5, 19.6, 19.4. HRMS (ESI) calcd for $C_{22}H_{27}O_2Se$ $[M+H]^+$ 403.1171, found 403.1155.

1-(2,6-Bis(4-ethylphenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2e**): White solid; isolated yield: 101.5 mg (47%); m.p. 98～99 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31～7.27 (m, 4H), 7.13 (t, *J*=8.2 Hz, 4H), 4.80 (dd, *J*=12.3, 2.7 Hz, 1H), 4.74 (d, *J*=11.4 Hz, 1H), 3.90 (s, 1H), 3.37 (d, *J*=11.4 Hz, 1H), 2.65～2.57 (m, 4H), 2.34 (dd, *J*=14.1, 2.8 Hz, 1H), 2.21 (dd, *J*=14.1, 12.3 Hz, 1H), 1.78 (s, 3H), 1.28 (s, 3H), 1.26～1.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.9, 144.0, 143.3, 138.7, 136.3, 128.4, 128.24, 128.15, 127.6, 72.0, 63.9, 46.9, 40.4, 36.9, 35.1, 30.5, 28.51, 28.49, 15.44, 15.40. HRMS (ESI) calcd for $C_{24}H_{30}NaO_2Se$ $[M+Na]^+$ 453.1303, found 453.1307.

1-(2,6-Bis(3,5-dimethylphenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2f**): White solid; isolated yield: 127.5 mg (59%); m.p. 143～144 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V* = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.99 (d, *J*=4.5 Hz, 4H), 6.85 (d, *J*=4.5 Hz, 2H), 4.75 (dd, *J*=12.2, 2.8 Hz, 1H), 4.68 (d, *J*=11.4 Hz, 1H), 3.90 (s, 1H), 3.38 (d, *J*=11.4 Hz, 1H), 2.34～2.29 (m, 7H), 2.27～2.17 (m, 7H), 1.81 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.7, 141.4, 139.0, 138.4, 138.1, 129.6, 129.0, 126.0, 125.5, 71.9, 63.8, 47.0, 40.6, 37.1, 35.1, 30.5, 21.3, 21.2. HRMS (ESI) calcd for $C_{24}H_{31}O_2Se$ $[M+H]^+$ 431.1484, found 431.1483.

1-(4-Hydroxy-2,6-bis(4-isopropylphenyl)-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2g**): White solid; isolated yield: 116.6 mg (51%); m.p. 114～115 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V* = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31～7.27 (m, 4H), 7.17～7.13 (m, 4H), 4.80 (dd, *J*=12.3, 2.7 Hz, 1H), 4.74 (d, *J*=11.4 Hz, 1H), 3.90 (s, 1H), 3.36 (d, *J*=11.5 Hz, 1H), 2.90～2.82 (m, 2H), 2.34 (dd, *J*=14.1, 2.8 Hz, 1H), 2.24～2.17 (m, 1H), 1.75 (s, 3H), 1.27 (s, 3H), 1.23 (d, *J*=6.9 Hz, 6H), 1.20 (d, *J*=6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.9, 148.6, 147.9, 138.9, 136.4, 128.2, 127.6, 126.9, 126.7, 71.9, 64.0, 47.0, 40.4, 36.8, 34.9, 33.8, 30.5, 23.93, 23.89, 23.86. HRMS (ESI) calcd for $C_{26}H_{35}O_2Se$ $[M+H]^+$ 459.1797, found 459.1788.

1-(2,6-Bis(4-(Tert-butyl)phenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2h**): White solid; isolated yield: 134.2 mg (55%); m.p. 170～172 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V* = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.31 (m, 4H), 7.29～7.27 (m, 4H), 4.80 (dd, *J*=12.3, 2.7 Hz, 1H), 4.74 (d, *J*=11.4 Hz, 1H), 3.89 (s, 1H), 3.37 (d, *J*=11.4 Hz, 1H), 2.34 (dd, *J*=14.1, 2.7 Hz, 1H), 2.21 (dd, *J*=14.1, 12.3 Hz, 1H), 1.75 (s, 3H), 1.30 (s, 9H), 1.28 (s, 9H), 1.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 217.0, 150.9, 150.1, 138.5, 136.0, 128.0, 127.3, 125.8, 125.6, 71.9, 64.0, 46.9, 40.2, 36.7, 35.0, 34.6, 34.5, 31.33, 31.28, 30.4. HRMS (ESI) calcd for $C_{28}H_{39}O_2Se$ $[M+H]^+$ 487.2110, found 487.2111.

1-(2,6-bis(4-Fluorophenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2i**): White solid; isolated yield: 154.0 mg (75%); m.p. 175～176 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.37～7.32 (m, 4H), 7.02～6.98 (m, 4H), 4.81 (dd, *J*=12.3, 2.7 Hz, 1H), 4.75 (d, *J*=11.4 Hz, 1H), 3.82 (s, 1H), 3.33 (d, *J*=11.4 Hz, 1H), 2.34 (dd, *J*=14.1, 2.7 Hz, 1H), 2.18 (dd, *J*=14.1, 12.3 Hz, 1H), 1.81 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.4, 162.14 (d, *J*=247.6 Hz), 161.92 (d, *J*=246.1 Hz), 137.0 (d,

J=3.2 Hz), 134.85 (d, *J*=3.3 Hz), 129.9 (d, *J*=8.0 Hz), 129.21 (d, *J*=8.1 Hz), 115.95 (d, *J*=21.5 Hz), 115.60 (d, *J*=21.3 Hz), 71.9, 63.9, 46.7, 39.8, 36.3, 35.1, 30.4. HRMS (ESI) calcd for $C_{20}H_{20}ClF_2O_2Se$ $[M+Cl]^-$ 445.0291, found 445.0283.

1-(2,6-Bis(4-chlorophenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2j**): White solid; isolated yield: 200.7 mg (91%); m.p. 164～165 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.32～7.27 (m, 8H), 4.80 (dd, *J*=12.3, 2.7 Hz, 1H), 4.74 (d, *J*=11.5 Hz, 1H), 3.79 (d, *J*=2.4 Hz, 1H), 3.34 (d, *J*=11.5 Hz, 1H), 2.33 (dd, *J*=14.1, 2.7 Hz, 1H), 2.21～2.14 (m, 1H), 1.83 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 216.1, 139.7, 137.6, 133.8, 133.1, 129.6, 129.2, 129.0, 128.9, 71.8, 63.7, 46.5, 39.9, 36.4, 35.2, 30.4. HRMS (ESI) calcd for $C_{20}H_{21}Cl_2O_2Se$ $[M+H]^+$ 443.0078, found 443.0075.

1-(2,6-Bis(4-bromophenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2k**): White solid; isolated yield: 236.3 mg (89%); m.p. 173～175 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.45～7.42 (m, 4H), 7.25～7.23 (m, 4H), 4.78 (dd, *J*=12.3, 2.7 Hz, 1H), 4.73 (d, *J*=11.4 Hz, 1H), 3.73 (s, 1H), 3.34 (d, *J*=11.5 Hz, 1H), 2.33 (dd, *J*=14.1, 2.7 Hz, 1H), 2.17 (dd, *J*=14.1, 12.3 Hz, 1H), 1.84 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 216.1, 140.2, 138.0, 132.2, 131.9, 130.0, 129.4, 121.9, 121.2, 71.8, 63.5, 46.4, 40.0, 36.5, 35.2, 30.4. HRMS (ESI) calcd for $C_{21}H_{21}Br_2O_4Se$ $[M+HCOO]^-$ 576.8957, found 576.8953.

1-(2,6-Bis(3-chlorophenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2l**): White solid; isolated yield: 176.6 mg (80%); m.p. 130～131 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.39 (d, *J*=13.1, 2H), 7.25～7.21 (m, 6H), 4.80 (dd, *J*=12.3, 2.7 Hz, 1H), 4.74 (d, *J*=11.4 Hz, 1H), 3.78 (s, 1H), 3.36 (d, *J*=11.4 Hz, 1H), 2.34 (dd, *J*=14.1, 2.7 Hz, 1H), 2.19 (dd, *J*=14.1, 12.3 Hz, 1H), 1.85 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 216.0, 143.2, 141.0, 134.8, 134.5, 130.3, 130.0, 128.4, 128.3, 127.8, 127.7, 126.6, 126.0, 71.7, 63.4, 46.4, 40.1, 36.6, 35.2, 30.4. HRMS (ESI) calcd for $C_{20}H_{20}Cl_3O_2Se$ $[M+Cl]^-$ 476.9700, found 476.9679.

1-(2,6-Bis(3-bromophenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2m**): White solid; isolated yield: 220.2 mg (83%); m.p. 129～130 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.57～7.52 (m, 2H), 7.40～7.36 (m, 2H), 7.31～7.27 (m, 2H), 7.20～7.16 (m, 2H), 4.78 (dd, *J*=12.3, 2.6 Hz, 1H), 4.72 (d, *J*=11.5 Hz, 1H), 3.76 (s, 1H), 3.35 (d, *J*=11.5 Hz, 1H), 2.34 (dd, *J*=14.1, 2.6 Hz, 1H), 2.18 (dd, *J*=14.1, 12.3 Hz, 1H), 1.85 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 216.0, 143.4, 141.3, 131.3, 130.7, 130.6, 130.5, 130.3, 127.0, 126.5, 122.9, 122.7, 71.7, 63.4, 46.4, 40.0, 36.6, 35.2, 30.4. HRMS (ESI) calcd for $C_{21}H_{21}Br_2O_4Se$ $[M+HCOO]^-$ 576.8957, found 576.8957.

1-(2,6-Bis(3,5-dichlorophenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2n**): White solid; isolated yield: 181.2 mg (71%); m.p. 134～136 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.26 (d, *J*=7.2 Hz, 6H), 4.76 (dd, *J*=12.3, 2.6 Hz, 1H), 4.70 (d, *J*=11.4 Hz, 1H), 3.67 (d, *J*=2.5 Hz, 1H), 3.33 (d, *J*=11.4 Hz, 1H), 2.33 (dd, *J*=14.1, 2.7 Hz, 1H), 2.22～2.10 (m, 1H), 1.93 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 215.3, 144.2, 142.2, 135.5, 135.2, 128.5, 127.8, 126.8, 126.3, 71.6, 63.1, 46.1, 39.6, 36.2, 35.3, 30.3. HRMS (ESI) calcd for $C_{21}H_{19}Cl_4O_4Se$ $[M+HCOO]^-$ 556.9179, found 556.9160.

1-(2,6-Bis(3,5-dibromophenyl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2o**): White solid; isolated yield: 233.9 mg (68%); m.p. 196～198 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.57 (t, *J*=1.7 Hz, 1H), 7.55 (t, *J*=1.7 Hz, 1H), 7.46 (d, *J*=1.7 Hz, 2H), 7.44 (d, *J*=1.7 Hz, 2H), 4.73 (dd, *J*=12.3, 2.6 Hz, 1H), 4.67 (d, *J*=11.4 Hz, 1H), 3.64 (s, 1H), 3.32 (d, *J*=11.4 Hz, 1H), 2.32 (dd, *J*=14.1, 2.6 Hz, 1H), 2.13 (dd, *J*=14.1, 12.3 Hz, 1H), 1.93 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 215.3, 144.8, 142.7, 134.0, 133.3, 130.1, 129.7, 123.4, 123.2, 71.6, 63.0, 46.1, 39.5, 36.2, 35.4, 30.3. HRMS (ESI) calcd for $C_{20}H_{18}Br_4ClO_2Se$ $[M+Cl]^-$ 724.6859, found 724.6863.

1-(4-Hydroxy-4-methyl-2,6-bis(4-(trifluoromethyl)phenyl)tetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2p**): White solid; isolated yield: 142.6 mg (56%); m.p. 153～154 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.60～7.57 (m, 4H), 7.52～7.48 (m, 4H), 4.91 (dd, *J*=12.2, 2.7 Hz, 1H), 4.86 (d, *J*=11.4 Hz, 1H), 3.76 (s, 1H), 3.42 (d, *J*=11.5 Hz, 1H), 2.38 (dd, *J*=14.1, 2.8 Hz, 1H), 2.25 (dd, *J*=14.1, 12.2 Hz, 1H), 1.84 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 215.7, 145.0, 143.0, 130.3 (q, *J*=32.4 Hz), 129.7 (q, *J*=32.4 Hz), 128.7, 128.1, 126.0 (q, *J*=3.8 Hz), 125.8 (q, *J*=3.8 Hz), 124.0 (q, *J*=271.9 Hz), 123.8 (q, *J*=272.2 Hz), 71.7, 63.3, 46.2, 40.2, 36.7, 35.2, 30.4. HRMS (ESI) calcd for $C_{23}H_{21}F_6O_4Se$ $[M+HCOO]^-$ 555.0515, found 555.0519.

1-(4-Hydroxy-2,6-bis(4-methoxyphenyl)-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2q**): White solid; isolated yield: 102.2 mg (47%); m.p. 171～172 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.31～7.28 (m, 4H), 6.85～6.81 (m, 4H), 4.78 (dd, *J*=12.3, 2.7 Hz, 1H), 4.72 (d, *J*=11.4 Hz, 1H), 3.87 (s, 1H), 3.784 (s, 3H), 3.775 (s, 3H), 3.34 (d, *J*=11.4 Hz, 1H), 2.32 (dd, *J*=14.1, 2.7 Hz, 1H), 2.18 (dd, *J*=14.1, 12.3 Hz, 1H), 1.80 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 217.0, 159.1, 158.7, 133.6, 131.1, 129.4, 128.7, 114.3, 114.1, 72.0, 64.0, 55.28, 55.26, 46.9, 40.0, 36.5, 35.1, 30.5. HRMS (ESI) calcd for $C_{22}H_{27}O_4Se$ $[M+HCOO]^-$ 435.1069, found 435.1052.

1-(4-Hydroxy-4-methyl-2,6-bis(4-(methylthio)phenyl)-tetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2r**): White solid; isolated yield: 91.3 mg (39%); m.p. 164～165 ℃. Eluent: petroleum ether/ethyl acetate (*V*/*V*=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.30～7.28 (m, 4H), 7.20～

7.16 (m, 4H), 4.79 (dd, J=12.3, 2.7 Hz, 1H), 4.73 (d, J=11.4 Hz, 1H), 3.84 (s, 1H), 3.36 (d, J=11.4 Hz, 1H), 2.465 (s, 3H), 2.457 (s, 3H), 2.33 (dd, J=14.1, 2.7 Hz, 1H), 2.19 (dd, J=14.1, 12.3 Hz, 1H), 1.83 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.6, 138.4, 138.2, 137.4, 135.6, 128.7, 128.1, 126.9, 126.7, 71.9, 63.7, 46.6, 40.2, 36.7, 35.2, 30.4, 15.9, 15.6. HRMS (ESI) calcd for $C_{22}H_{25}O_2S_2Se$ $[M-H]^-$ 465.0467, found 465.0485.

1-(2,6-Di(furan-2-yl)-4-hydroxy-4-methyltetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2s**): White solid; isolated yield: 94.2 mg (53%); m.p. 113～114 ℃. Eluent: petroleum ether/ethyl acetate (V/V=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.33 (m, 2H), 6.31～6.29 (m, 2H), 6.21～6.19 (m, 2H), 4.98 (dd, J=12.3, 2.7 Hz, 1H), 4.93 (d, J=11.4 Hz, 1H), 3.85 (s, 1H), 3.49 (d, J=11.4 Hz, 1H), 2.38 (dd, J=14.2, 2.7 Hz, 1H), 2.21 (dd, J=14.2, 12.3 Hz, 1H), 1.91 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.5, 154.4, 151.7, 142.4, 141.9, 110.9, 110.5, 108.1, 106.1, 71.2, 61.5, 44.4, 33.6, 31.6, 30.0, 29.0. HRMS (ESI) calcd for $C_{16}H_{19}O_4Se$ $[M+H]^+$ 355.0443, found 355.0435.

1-(4-Hydroxy-4-methyl-2,6-di(thiophen-2-yl)tetrahydro-2*H*-selenopyran-3-yl)ethan-1-one (**2t**): White solid; isolated yield: 86.7 mg (45%); m.p. 144～146 ℃. Eluent: petroleum ether/ethyl acetate (V/V=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (td, J=5.4, 1.1 Hz, 2H), 7.01～7.00 (m, 1H), 6.94～6.89 (m, 3H), 5.16 (dd, J=12.3, 2.7 Hz, 1H), 5.12 (d, J=11.3 Hz, 1H), 3.86 (s, 1H), 3.34 (d, J=11.3 Hz, 1H), 2.50 (dd, J=14.1, 2.7 Hz, 1H), 2.19 (dd, J=14.1, 12.3 Hz, 1H), 1.87 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.6, 144.8, 142.4, 127.0, 126.8, 126.3, 125.2, 124.7, 124.3, 71.9, 65.5, 48.1, 35.1, 34.9, 32.1, 30.1. HRMS (ESI) calcd for $C_{16}H_{19}O_2S_2Se$ $[M+H]^+$ 386.9986, found 386.9962.

4,4'-Diselanediylbis(4-phenylbutan-2-one) (the intermediate A of compound **2a**): White solid; m.p. 164～165 ℃. Eluent: petroleum ether/ethyl acetate (V/V=10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.27 (m, 6H), 7.25～7.21 (m, 6H), 4.37 (dd, J=8.4, 6.5 Hz, 1H), 4.26 (dd, J=8.4, 6.5 Hz, 1H), 3.16～3.04 (m, 4H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.8, 205.6, 140.9, 140.8, 128.71, 128.69, 127.8, 127.7, 127.6, 49.6, 49.4, 40.3, 39.8, 30.3. HRMS (ESI) calcd for $C_{20}H_{23}O_2Se_2$ $[M+H]^+$ 455.0023, found 455.0031.

Supporting Information ^{1}H NMR and ^{13}C NMR spectra, and HRMS of all compounds and OPTEP drawing of compound **2a**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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[15] CCDC 2128170 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(Lu, Y.)