Organic & Biomolecular Chemistry

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ARTICLE

Mechanistic Investigation of *Anti*-Elimination in (*Z*)-1,2-bis(arylseleno)-1-alkenes and their Sulfur Analogs

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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The oxidation of (*Z*)-1,2-bis(arylseleno)-1-alkenes is known to afford alkynyl selenoxides via a unique selenoxide *anti*-elimination mechanism; however, to date, there have been no mechanistic studies of this reaction. During our studies of this transformation, monoselenoxides **6, 7** were unexpectedly isolated as stable reaction intermediates. In addition, ^{77}Se NMR studies of the reaction mixture revealed the presence of an intramolecular Se···O interaction and the formation of alkynyl selenoxides. Meanwhile, even at higher temperature, the reaction of a (*Z*)-1,2-bis(arylsulfinyl)-1-alkene, the sulfur analog of (*Z*)-1,2-bis(arylseleninyl)-1-alkenes, did not proceed via sulfoxide elimination but proceeded via isomerization and disproportionation. Therefore, the intramolecular Se···O interaction can be concluded to play a pivotal role in the *anti*-elimination reaction.

Introduction

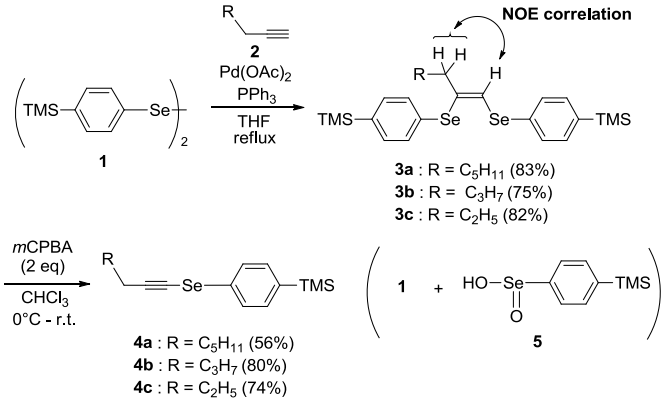
Organoselenium reagents have unique reactivity and high chemoselectivity because of the fact that selenium has both mixed metallic and non-metallic characteristics,[1)] and their synthetic utility has been confirmed as demonstrated by their growing application in organic synthesis.[1,2)] However, their toxicity and malodorous reputation have often made them unattractive to organic chemists.[3)] We previously reported bis[4-(trimethylsilyl)phenyl]diselenide (**1**)[3)] as an odorless equivalent of diphenyl diselenide, which is commonly employed for selenylation reactions because of its versatile reactivity (both nucleophilic and electrophilic). The introduction of the trimethylsilyl group on the aromatic ring was the crucial factor in achieving an odorless compound. Importantly, selenylation using **1** followed by oxidative elimination proceeds in high yield, and thus, diselenide **1** has been shown to be an odorless equivalent of malodorous diphenyl diselenide.

Selenoxide elimination is one of the useful reactions used to form carbon–carbon unsaturated bonds via *syn*-elimination at low temperature.[4)] The seleninyl group, typically generated in situ by oxidizing the corresponding selenide, is eliminated with the intramolecular β proton via a cyclic transition state.[5)] However, Ogawa and coworkers reported that the oxidation of (*Z*)-1,2-bis(phenylseleno)-1-octene resulted in the corresponding alkynyl selenoxide via a remarkable *anti*-elimination reaction.[6)] We were interested in determining whether this unique selenoxide elimination proceeds for alkenes substituted with the 4-trimethylsilylphenylseleno group and whether the *syn*-elimination reaction can afford allene derivatives. Herein, we describe the results of a mechanistic study of the selenoxide elimination in 1,2-bis[4-(trimethylsilyl)phenylseleno]-1-alkene (**3**) (prepared from diselenide **1**), including the analyses of isolated reaction intermediates and in situ ^{77}Se NMR spectroscopic data.

Results and discussion

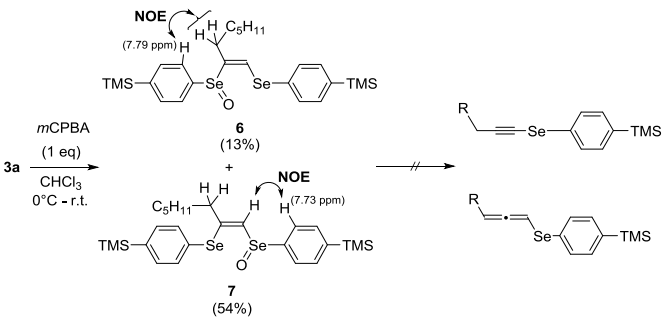
First, (*Z*)-1,2-bis(arylseleno)-1-alkene (**3**) was prepared from diselenide 1 and 1-alkynes (**2**) in 72%–83% yield via a palladium-catalyzed reaction.[7)] The stereochemistry of selenides **3** was confirmed using NOE experiments, as shown in Scheme 1. Selenoxide elimination was examined by oxidizing **3** with 2 equivalents of *meta*-chloroperbenzoic acid (*m*CPBA). The elimination occurred as expected; however, rather than the corresponding selenoxides, alkynyl selenides **4** were obtained. In addition, when **3a** was treated with hydrogen peroxide, alkynyl selenide **4a** was obtained in 32% yield. Furthermore, during the reaction of **3a** with *m*CPBA, seleninic acid **5** and diselenide **1** were isolated in 50% and 25% yield, respectively, which were certainly formed via the disproportionation of the corresponding selenenic acid (Ar-SeOH).[8)]

Ogawa reported that the *anti*-elimination of bisselenoxides led to alkynyl phenyl selenoxides, the yields of which were determined by converting them into the corresponding alkynyl phenyl selenides (the reductant was not described).[6)] In the present study, however, only the alkynyl aryl selenides **4** were obtained. Thus, the oxidation of bisselenide **3** with just 1 equivalent of *m*CPBA was performed in an attempt to obtain monoselenoxide. Rewardingly, the elimination reaction did not occur, and the monoselenoxides **6** and **7** were successfully isolated in 13% and 54% yield, respectively (Scheme 2).



Scheme 1. Preparation of bisselenide **3** and its oxidative anti-elimination

Although it is known that vinyl aryl selenoxides are relatively stable against elimination,[6,9] there are only a few examples of the isolation after the purification of vinyl selenoxides with β hydrogens that can undergo *syn*-elimination.[10] Fortunately, the monoselenoxides **6** and **7** were sufficiently stable for purification via silica gel column chromatography. An NOE correlation between the allylic proton and the most downfield (7.79 ppm) aromatic signal was observed in the NOE analysis of **6**, whereas that between the vinylic proton and the most downfield (7.73 ppm) signal was confirmed in **7**. In the spectra of our synthesized selenium compounds (**8a** and **9**), the aromatic protons of arylselenoxides have been observed at approximately 7.70 ppm. Therefore, the monoselenoxides **6** and **7** were assumed to be internal and terminal selenoxides, respectively. Notably, neither of the monoselenoxides could be converted to alkynyl selenide **4** in chloroform under reflux conditions for 7 h.



Scheme 2. Isolation of monoselenoxides **6** and **7**

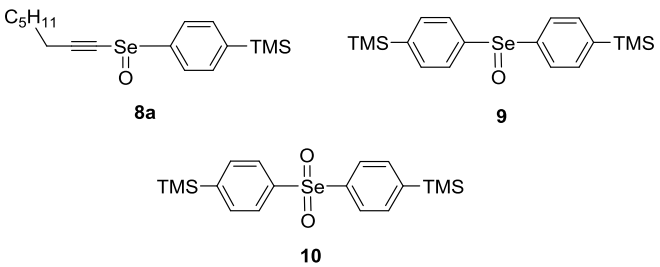
Next, the chemical shifts of the relevant reaction intermediates in the selenoxide *anti*-elimination reaction were determined using ^{77}Se NMR,[11,12] and the results are summarized in Table 1. The chemical shifts for the selenides **3a** and **4a** were between 274 and 402 ppm, those of the selenoxides **8a** and **9** were 849 and 858 ppm, respectively, that of selenone **10** was 967 ppm, and that of seleninic acid **5** was 1179 ppm. In the spectra of **6** and **7**, signals for both selenides (364 and 416 ppm) and selenoxides (868 and 865 ppm) were observed.

The reaction mixture obtained when bisselenide **3a** was treated with 2 equivalents of *m*CPBA was then observed using ^{77}Se NMR ($CDCl_3$, −20 °C). In this spectrum, two sets of two signals (924, 855 ppm and 920, 857 ppm) were observed (Figure 1a),[13] and these shifts were similar to the chemical shifts for the bisselenoxide reported by Ogawa.[6] When compared to the shifts of the related selenium compounds listed in Table 1, it is interesting to note that in each set of two signals,

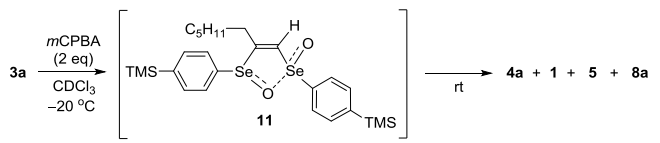
Table 1. ^{77}Se NMR shifts for selenium compounds of various oxidation states used or prepared in this study

compound	^{77}Se NMR (ppm)	compound	^{77}Se NMR (ppm)
1	455	**6**	364, 868
3a	393, 402	**7**	416, 865
4a	274	**8a**[a]	849
5	1179	**9**[a]	858
		10[a]	967

a) The selenoxide or selenone were prepared by the treatment of the corresponding selenide with *m*CPBA.



one signal had a chemical shift value similar to those of the selenoxides, whereas the other was shifted downfield and close to the chemical shift values for the selenones. These observations suggest that the electron density around one of selenium atoms in **11** was decreased because of an intramolecular nonbonded Se···O interaction.[14] Barton and co-workers have also reported the downfield shift associated with Se···O interactions in selenoiminoquinones.[14b] In addition, this phenomenon is similar to the increase in the acidity of silicon observed upon addition of a Lewis base in Lewis acid-catalyzed reactions, as described by Denmark.[15a] That is, the electron donor–acceptor interaction leads to increasing polarities of the bonds originating from the donor and acceptor atoms due to the spillover of the negative charge from the acceptor atom and the pileup of the negative charge at the donor atom.[15b] The downfield shift observed for the selenium signal is therefore believed to result because the selenium acts as an acceptor atom. When the temperature of the reaction mixture was increased to 35 °C, the signals for **11** completely disappeared, and four products were formed, *i.e.*, alkynyl selenide **4a**, alkynyl



Scheme 3. Oxidative elimination of **3a** in $CDCl_3$

selenoxide **8a**, which was observed for the first time as a product of an *anti*-elimination reaction (Figure 1b), diselenide **1**, and seleninic acid **5**. On the other hand, the ^{77}Se NMR signal for selenenic acid was not observed.[11a]

To further investigate the structural features of **11**, geometry optimizations using density functional theory (DFT) calculations were performed for the two model structures of the

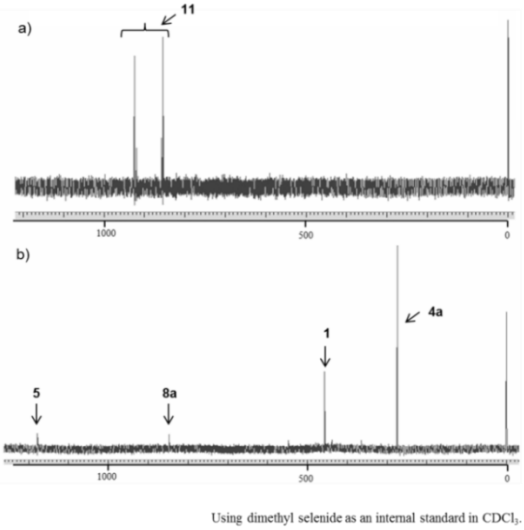


Figure 1. ^{77}Se NMR spectra of the reaction mixture containing 3a and 2 equivalents of *m*CPBA at a) −20 °C and b) room temperature.

bisselenoxide involving Se(1)···O(2) and Se(2)···O(1) interactions by respectively varying the dihedral angles θ_1 (C2-C1-Se1-O1) and θ_2 (C1-C2-Se2-O2) from +120° to +230° and −50° to −180° stepwise by 10°, as shown in Figure 2. In the presence of each Se…O interaction, these close contacts were found to be 2.873 and 2.896 Å, which are less than the sum of the Se and O van der Waals radii (3.40 Å).[16] In addition, in conformation A, which is expected to favor elimination, the distance between O(1) and the vinylic proton is 2.637 Å. Because this distance is close to the sum of the O and H van der Waals radii (2.60 Å),[16] such a geometry is believed to facilitate the abstraction of the vinylic proton.

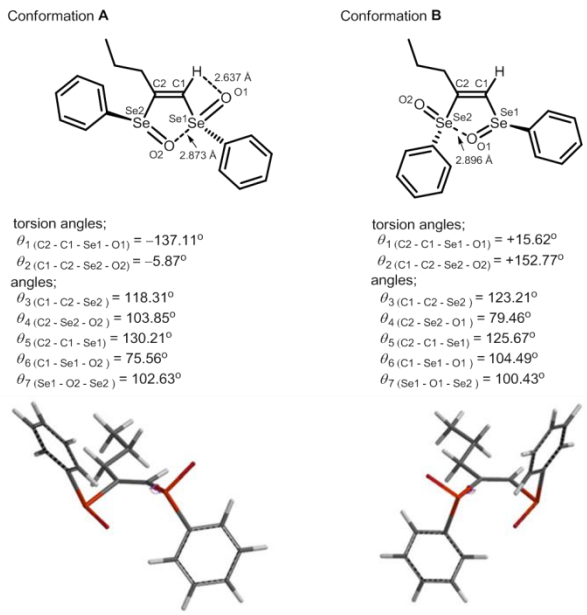
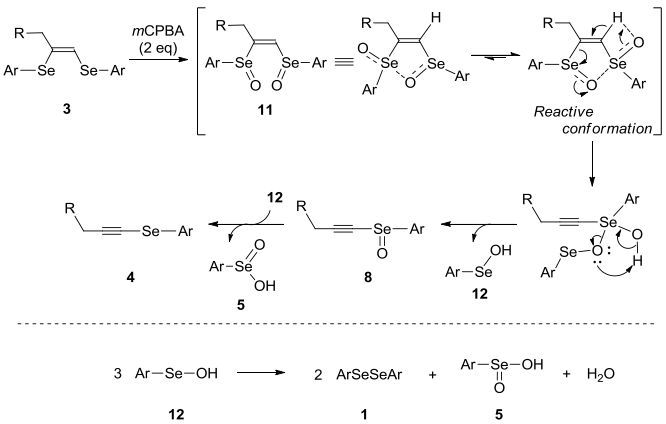


Figure 2. Geometry optimization for model structures of bisselenoxide **11** using DFT calculation

By considering the above results, a plausible reaction mechanism was proposed and is presented in Scheme 4.

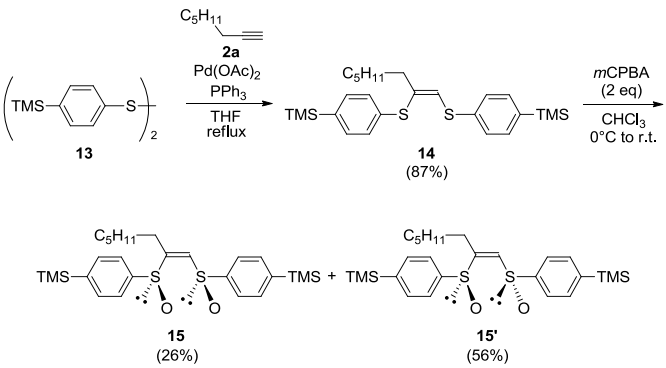
Bisselenide **3** is oxidized to bisselenoxide **11**, which on heating undergoes anti-elimination to generate both alkynyl selenoxide **8** and selenenic acid **12**. Compound **8** is then rapidly reduced by **12**, affording the alkynyl selenide **4** and seleninic acid **5**. Trace amounts of diselenide **1** are produced via the disproportion of selenenic acid **12**.[8] Furthermore, monoselenoxides **6** and **7** do not undergo *anti*-elimination.

The oxidative elimination of the corresponding sulfur derivative was also investigated. Bissulfide **14** was prepared from disulfide **13**, as reported previously,[3] and oxidation led to the desired bissulfoxides **15** and **15'** as a diastereomeric mixture (Scheme 5). Although nonbonded S···O interactions have been observed in sulfoxides,[14a,17] the oxidative elimination of **15** and **15'** did not proceed, even with sufficient heating. On the other hand, the isomerization of bissulfoxides at the sulfur atom and intermolecular disproportionation both occurred, with compound **15** affording sulfone **16** and sulfoxide **17** (Table 2). Only **16** and **17** were likely formed via



Scheme 4. Plausible reaction mechanism for oxidative elimination in bisselenide **3a**.

disproportionation because the steric hindrance of the sulfinyl group at the 1 position was less than that at the 2 position. In addition, the isomerization of bissulfoxide **15'** occurred to a greater extent than of bissulfoxide **15**. Furthermore, X-ray crystallographic analysis of a single crystal of sulfoxide **15** revealed the lack of any sulfur–oxygen interaction in this compound (Figure 3).[18] Based on these results, it was concluded that the oxidative elimination of bissulfoxides **15** and **15'** could not be facilitated by nonbonded S···O interactions.



Scheme 5. Examination of the elimination reaction of (Z)-1,2-bis(arylsulfinyl)-1-alkene

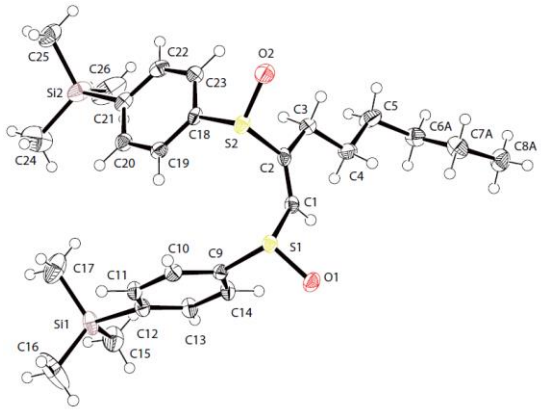
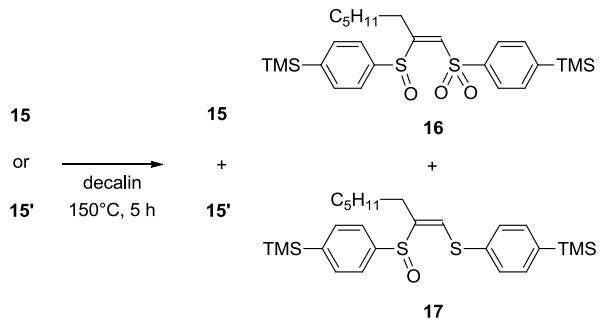


Figure 3. X-ray crystal structure of **15**.

Table 2. Isomerization and intermolecular disproportionation of bissulfoxides **15** and **15'**



entry	compound	yield (%)			
		15	**15'**	**16**	**17**
1	**15**	26	17	11	4
2	**15'**	3	55	5	trace

Conclusions

We confirmed that anti-elimination in (*Z*)-1,2-bis(arylseleno)-1-alkenes with a trimethylsilyl group at the 4 position of the aromatic ring proceeds via oxidation. Monoselenoxides **6** and **7** were isolated via silica gel column chromatography and found to be unexpectedly stable under ambient conditions. Using ^{77}Se NMR analysis of the reaction mixture and DFT calculations of possible structures for bisselenoxide **11**, a conformation involving an intramolecular Se···O interaction was proposed to exist and facilitate *anti*-elimination in the (*Z*)-1,2-bis(arylseleno)-1-alkenes. In addition, the formation of alkynyl selenoxide **8a** was observed for the first time during the in situ ^{77}Se NMR analysis of the reaction of **3a** with *m*CPBA. Furthermore, compound **8a** was found to be rapidly reduced by selenenic acid to afford **4a**. Finally, although the sulfur analog was expected to react in a manner similar to the corresponding selenium compound, elimination was not observed. This different behavior is attributed to the distinctly different nonbonded interactions in the (*Z*)-1,2-bis(arylseleninyl)-1-alkene and (*Z*)-1,2-bis(arylsulfinyl)-1-alkene.

Experimental

NMR spectra were obtained using a JEOL ECA-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{77}Se: 95 MHz) or JEOL JNM-ECP400 (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{77}Se: 76 MHz) with tetramethylsilane as the standard for the ^{1}H and ^{13}C NMR analyses and dimethyl selenide as the standard for the ^{77}Se NMR analyses. The chemical shifts are expressed in ppm. Mass spectra and FAB Mass spectra were obtained using a JEOL MStation JMS-700 spectrometer. IR spectra were obtained using an IRAffinity-1 spectrometer (Shimadzu). Elemental analyses were performed using a PERKIN ELMER series II CHNS/O Analyzer 2400. Silica gel (Merck Art. 7734) and Silica gel 60 PF_{254} (Nacalai Tesque Inc.) were used for column chromatography and preparative thin layer chromatography (PTLC). All reagents and starting materials were purchased from commercial sources and used without further purification unless otherwise indicated.

General procedure for the synthesis of bisselenyl alkenes 3

Palladium (II) acetate (5.0 mol%) and a terminal alkyne were added to a mixture of diselenide **1** (1.0 or 2.0 mmol) and triphenylphosphine (3.0 equiv.) under an argon atmosphere. The mixture was then dissolved in anhydrous tetrahydrofuran, and the solution was stirred under reflux conditions. After the completion of the reaction, the mixture was filtered, and the filtrate was concentrated under vacuum. The residue was purified via silica gel column chromatography (hexane) to afford **3**.

1,2-Bis[4-(trimethlsilyl)phenylseleno]-1-octene (3a)

The synthesis of **3a** was performed using diselenide **1** (456 mg, 1.0 mmol), 1-octyne (177 μL, 1.2 mmol), palladium (II) acetate (11.2 mg), and triphenylphosphine (790 mg, 3.0 mmol) in anhydrous tetrahydrofuran (3 mL) for 19.5 h. Additional 1-octyne (117 μL, 1.2 mmol) was then added to the mixture, which was stirred under the same conditions for 9 h, giving **3a** (473 mg, 83%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.26 (9H, s, Si-$(CH_3)_3$), 0.27 (9H, s, Si-$(CH_3)_3$), 0.84 (3H, t, J = 7.0 Hz, -CH_3), 1.13–1.28 (6H, m, -$(CH_2)_3$-), 1.44–152 (2H, m, -CH_2-), 2.29 (2H, t, J = 7.4 Hz, -CH_2-C=C), 6.97 (1H, s, -C=CH), 7.41 (2H, d, J = 8.1 Hz, Ar–H), 7.44 (2H, d, J = 8.4 Hz, Ar–H), 7.48 (2H, d, J = 8.0 Hz, Ar–H), 7.53 (2H, d, J = 8.0 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.18, −1.16, 14.0, 22.5, 28.4, 28.9, 31.5, 40.2, 128.4, 130.6, 131.7, 134.0, 134.1, 136.2, 139.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ: 393, 402; IR ($CHCl_3$): 2956, 1577, 1478, 1379, 1110, 1014, 840 cm^{-1}; MS (EI) *m/z*: 568 (M^+, 43), 363 (11), 269 (14), 214 (28), 73 (100); HR-MS (EI) *m/z*: 568.0999 (Calcd for $C_{26}H_{40}Si_2Se_2$; 568.1004).

1,2-Bis[4-(trimethlsilyl)phenylseleno]-1-hexene (3b)

The synthesis of **3b** was performed using diselenide **1** (916 mg, 2.0 mmol), 1-hexyne (344 μL, 3.0 mmol), palladium (II) acetate (22.0 mg), and triphenylphosphine (1.57 g, 6.0 mmol) in anhydrous tetrahydrofuran (2 mL) for 20 h. Additional 1-hexyne (344 μL, 3.0 mmol) was then added to the mixture, which was stirred under the same conditions for 4.5 h, giving **3b** (803 mg, 75%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.26 (9H, s, Si-$(CH_3)_3$), 0.27 (9H, s, Si-$(CH_3)_3$), 0.82 (3H, t, J = 7.3 Hz, -CH_3), 1.24 (2H, sext, J = 6.2 Hz, -CH_2-C=CH), 1.43–1.51 (2H, m, -CH_2-), 2.31 (2H, t, J = 7.5 Hz, -CH_2-), 6.98 (1H, s, -C=CH), 7.41 (2H, d, J = 8.1 Hz, Ar–H), 7.44 (2H, d, J = 8.1

Hz, Ar–H), 7.48 (2H, d, *J* = 8.0 Hz, Ar–H), 7.53 (2H, d, *J* = 7.7 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.18, −1.17, 13.8, 21.9, 31.1, 39.9, 128.5, 131.6, 131.7, 134.0, 134.1, 136.0, 139.5; IR ($CHCl_3$): 3013, 2957, 2932, 1250, 843, 810 cm^{-1}; MS (EI) *m/z*: 540 (M+, 65), 255 (18), 214 (28), 73 (100); HR-MS (EI) *m/z*: 540.0690 (Calcd for $C_{23}H_{34}Si_2Se_2$; 540.0684).

1,2-Bis[4-(trimethlsilyl)phenylseleno]-1-pentene (3c)

The synthesis of **3c** was performed using diselenide **1** (457 mg, 1.0 mmol), 1-pentyne (300 μL, 3.0 mmol), palladium (II) acetate (11.0 mg), and triphenylphosphine (787 mg, 3.0 mmol) in anhydrous tetrahydrofuran (2 mL) for 27 h. Additional 1-pentyne (300 μL, 3.0 mmol) was then added to the mixture, which was stirred under the same conditions for 23 h, giving **3c** (403 mg, 82%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.26 (9H, s, Si-$(CH_3)_3$), 0.27 (9H, s, Si-$(CH_3)_3$), 0.84 (3H, t, *J* = 7.3 Hz, -CH_3), 1.48–1.57 (2H, m, -CH_2-), 2.29 (2H, t, *J* = 7.4 Hz, -CH_2-C=C), 6.99 (1H, s, -C=CH), 7.41 (2H, d, *J* = 8.5 Hz, Ar–H), 7.44 (2H, d, *J* = 8.1 Hz, Ar–H), 7.48 (2H, d, *J* = 8.1 Hz, Ar–H), 7.54 (2H, d, *J* = 7.7 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.2, 13.3, 22.1, 42.2, 129.0, 130.6, 131.5, 131.7, 134.0, 134.1, 135.5, 139.2, 139.5.; IR ($CHCl_3$): 3011, 2959, 1574, 1250, 1206, 843, 725 cm^{-1}; MS (EI) *m/z*: 526 (M$^+$, 33), 248 (11), 214 (23), 149 (11), 73 (100); HRMS (EI) *m/z*: 526.0527 (Calcd for $C_{23}H_{34}Si_2Se_2$; 526.0534).

General procedure for oxidative elimination reactions

The oxidant *m*CPBA (70%, 2 equiv.) was added to a solution of **3** (0.25–0.50 mmol) in anhydrous chloroform at 0 °C, and the mixture was stirred at room temperature for 27 h. Next, the reaction mixture was diluted with chloroform and washed with an aqueous 5% (w/v) solution of sodium bicarbonate (10 mL × 3). The organic layer was dried over magnesium sulfate and concentrated under vacuum. The residue was purified via silica gel column chromatography (hexane) to give **4**.

1-(4-Trimethylsilylphenyl)seleno-1-octyne (4a)

The reaction was performed using **3a** (283 mg, 0.5 mmol) and *m*CPBA (70%, 271 mg, 1.1 mmol) in anhydrous chloroform (7 mL) for 24 h. A mixture of **4a** (94 mg, 56%) and diselenide **1** (19 mg, 25%) was obtained (each yield was calculated based on ^{1}H NMR integrations). The pH of the aqueous layer was lowered until a white powder precipitated. The aqueous layer was extracted with chloroform, and the organic layer was dried over magnesium sulfate and concentrated under vacuum to give a mixture of seleninic acid **5** (66 mg, 50%) and m-chlorobenzoic acid (the yield was calculated based on the ^{1}H NMR integrations).
Yellow oil (**4a**); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.25 (9H, s, Si-$(CH_3)_3$), 0.90 (3H, t, *J* = 7.0 Hz, -CH_3), 1.26–1.35 (4H, m, -$(CH_2)_2$-), 1.40–1.47 (2H, m, -CH_2-), 1.59 (2H, quint, *J* = 7.3 Hz, -CH_2-), 2.44 (2H, t, *J* = 7.2 Hz, -CH_2-C≡C), 7.43 (2H, d, *J* = 8.4 Hz, Ar-H), 7.50 (2H, d, *J* = 8.4 Hz, Ar-H); ^{13}C NMR (100MHz, $CDCl_3$) δ: −1.1, 14.1, 20.6, 22.6, 28.6, 28.7, 28.8, 31.4, 57.4, 104.8, 127.9, 128.0, 130.3, 130.6, 132.4, 134.3, 138.8.; ^{77}Se NMR (76 MHz, $CDCl_3$) δ: 271. IR ($CHCl_3$): 2957, 2932, 2859, 1576, 1252, 843 cm^{-1}; MS (EI) *m/z*: 338 (M$^+$, 69), 323 (42), 243 (14), 172 (17), 109 (18), 73 (100); HR-MS (EI) *m/z*: 338.0960 (Calcd for $C_{17}H_{26}SiSe$; 338.0969).

4-Trimethylsilylphenyl seleninic acid (5)

White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.29 (9H, s, Si-$(CH_3)_3$), 3.33 (5H, s, -OH), 7.70 (2H, d, *J* = 8.1 Hz, Ar-H), 7.78 (2H, d, *J* = 8.1 Hz, Ar-H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ: −2.0, 125.9, 134.6, 145.9, 147.4. ^{77}Se NMR (76 MHz, $CDCl_3$) δ: 1179. IR ($CHCl_3$): 3686, 2995, 2959, 1601, 1377, 1252, 889, 868, 843 cm^{-1}. Anal: Found: C, 41.60; H, 5.14 (Calcd for $C_9H_{14}O_2SeSi$: C, 41.38; H, 5.40%).

1-(4-Trimethylsilylphenyl)seleno-1-hexyne (4b)

The reaction was performed using **3b** (135 mg, 0.25 mmol) and *m*CPBA (70%, 123 mg, 0.50 mmol) in anhydrous chloroform (4 mL) for 3 h, giving **4b** (62 mg, 80%).
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.25 (9H, s, Si-$(CH_3)_3$), 0.93 (3H, t, *J* = 7.4 Hz, -CH_3), 1.44–1.51 (2H, m, -CH_2-), 1.54–1.60 (2H, m, -CH_2-), 2.45 (2H, t, *J* = 7.0 Hz, -CH_2-C≡C), 7.42 (2H, d, *J* = 8.0 Hz, Ar-H), 7.48 (2H, d, *J* = 8.0 Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.2, 13.5, 20.2, 22.0, 30.8, 57.2, 104.7, 127.8, 130.5, 134.2, 138.7; IR ($CHCl_3$): 3011, 2959, 2936, 2901, 1574, 1252, 843, 719 cm^{-1}; MS (EI) *m/z*: 310 (M$^+$, 100), 295 (86), 215 (39), 172 (19), 119 (18), 73 (90); HR-MS (EI) *m/z*: 310.0650 (Calcd for $C_{15}H_{22}SiSe$; 310.0656).

1-(4-Trimethylsilylphenyl)seleno-1-pentyne (4c)

The reaction was performed using **3c** (162 mg, 0.31 mmol) and *m*CPBA (70%, 152 mg, 0.62 mmol) in anhydrous chloroform (4 mL) for 27 h, giving **4c** (67 mg, 74%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.25 (9H, s, Si-$(CH_3)_3$), 1.03 (3H, t, *J* = 7.3 Hz, -CH_3), 1.62 (2H, sext, *J* = 7.2 Hz, -CH_2-), 2.43 (2H, t, *J* = 7.2 Hz, -CH_2-C≡C), 7.43 (2H, d, *J* = 8.1 Hz, Ar-H), 7.50 (2H, d, *J* = 8.1 Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.2, 13.5, 22.2, 22.6, 57.4, 104.6, 127.8, 130.5, 134.2, 138.8; IR ($CHCl_3$): 3017, 2961, 2936, 1574, 1252, 1223, 843, 789, 671 cm^{-1}; MS (EI) m/z: 296 (M$^+$, 100), 281 (96), 279 (46), 73 (1); HR-MS (EI) m/z: 296.0494 (Calcd for $C_{14}H_{20}SiSe$; 296.0500).

Procedure for the oxidation of 3a to generate the monoselenoxide derivatives 6 and 7

The oxidant *m*CPBA (70%, 74 mg, 0.3 mmol) was added to a solution of **3a** (170 mg, 0.3 mmol) in anhydrous chloroform (7 mL) at 0 °C, and the mixture was stirred for 2 h. The reaction mixture was then diluted with chloroform and washed with an aqueous 5% (w/v) solution of sodium bicarbonate (15 mL × 2). The organic layer was dried over magnesium sulfate and concentrated under vacuum. The residue was purified via silica gel PTLC (chloroform/ethyl acetate = 5/2) to give **6** (23 mg, 13%) and **7** (94 mg, 54%).

1-[4-(Trimethlsilyl)phenylseleno]-2-[4-(trimethlsilyl)phenyl-seleninyl]-1-octene (6)

Rf 0.5 (chloroform/ethyl acetate = 5/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.28 (9H, s, Si-$(CH_3)_3$), 0.29 (9H, s, Si-$(CH_3)_3$), 0.81 (3H, t, *J* = 7.1 Hz, -CH_3), 1.08–1.42 (8H, m, -$(CH_2)_4$-), 2.23 (1H, m, -CH_2-C=C), 2.50 (1H, m, -CH_2-C=CH), 7.01 (1H, t, *J* = 1.5Hz, -C=CH), 7.44 (2H, d, *J* = 8.4 Hz, Ar-H), 7.49 (2H, d, *J* = 8.5 Hz, Ar-H), 7.58 (2H, d, *J* = 8.1 Hz, Ar-H), 7.79 (2H, d, *J* = 8.0 Hz, Ar-H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ: −1.3, −1.2, 13.9, 22.4, 27.9, 28.5, 28.8, 31.4, 124.8, 125.2, 131.1, 131.7, 134.3, 134.5, 140.5, 142.0, 144.5, 152.7; ^{77}Se NMR (76 MHz, $CDCl_3$) δ: 362, 868. IR ($CHCl_3$): 2956, 1377, 1252, 1223, 1207, 840 cm^{-1}; MS (FAB) *m/z*: 585 (M+H$^+$, 24), 109 (14), 73 (100);

HR-MS (FAB) *m/z*: 585.1028 (Calcd for $C_{26}H_{40}OSi_2Se_2$; 585.1031).

1-[4-(Trimethlsilyl)phenylseleninyl]-2-[4-(trimethlsilyl)phenyl-seleno]-1-octene (7)

Rf 0.3 (chloroform/ethyl acetate = 5/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.26 (9H, s, Si-$(CH_3)_3$), 0.29 (9H, s, Si-$(CH_3)_3$), 0.80 (3H, t, *J* = 7.0 Hz, -CH_3), 1.11–1.26 (6H, m, -$(CH_2)_3$-), 1.45 (2H, quint, *J* = 7.3 Hz, -CH_2-), 2.28 (2H, t, *J* = 7.9 Hz, -CH_2-C=CH), 6.78 (1H, s, -C=CH), 7.42 (2H, d, *J* = 8.4 Hz, Ar-H), 7.45 (2H, d, *J* = 8.1 Hz, Ar-H), 7.65 (2H, d, *J* = 8.4 Hz, Ar-H), 7.73 (2H, d, *J* = 8.1 Hz, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: −1.23, −1.22, 13.9, 22.4, 28.16, 28.24, 31.3, 39.0, 125.6, 128.8, 132.9, 134.46, 134.48, 141.1, 141.3, 143.2, 144.6, 148.9; ^{77}Se NMR (76 MHz, $CDCl_3$) δ: 416, 865; IR($CHCl_3$): 2959, 2859, 1574, 1377, 1252, 843, 810 cm^{-1}; MS (FAB) *m/z*: 585 (M+H$^+$, 56), 568 (22), 109 (20), 73 (100); HR-MS (FAB) *m/z*: 585.1025 (Calcd for $C_{26}H_{40}OSi_2Se_2$; 585.1031).

1-(4-Trimethylsilylphenyl)seleninyl-1-octyne (8a)

The oxidant *m*CPBA (82%, 63 mg, 0.30 mmol) was added to a solution of **4a** (100 mg, 0.30 mmol) in chloroform (5 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 25 min. The mixture was then washed twice with an aqueous 5% (w/v) solution of sodium bicarbonate, dried over magnesium sulfate, and concentrated under vacuum to give **8a** (58 mg, 55%).
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.30 (9H, s, Si-$(CH_3)_3$), 0.87 (3H, t, *J* = 7.0 Hz, -CH_3), 1.20–1.39 (6H, m, -$(CH_2)_3$-), 1.55 (2H, quint, *J* = 7.3 Hz, -CH_2-), 2.38 (2H, t, *J* = 7.0 Hz, -CH_2-C≡C), 7.69 (2H, d, *J* = 8.4 Hz, Ar–H), 7.82 (2H, d, *J* = 8.4 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.4, 13.9, 19.7, 22.4, 27.5, 28.4, 31.1, 74.4, 105.7, 125.5, 134.6, 142.8, 145.5; MS (FAB) *m/z*: 355 (M+H$^+$); HR-MS (FAB) *m/z*: 355.0998 (Calcd for $C_{17}H_{27}OSeSi$: 355.0996).

Bis(4-trimethylsilylphenyl) selenoxide (9)

The oxidant *m*CPBA (70%, 64.1 mg, 0.26 mmol) was added to a solution of bis(4-trimethylsilylphenyl)selenide[19] (100 mg, 0.26 mmol) in chloroform (5 mL) at −7 °C, and the reaction mixture was stirred at room temperature for 9 h. The mixture was then washed with an aqueous 5% (w/v) solution of sodium bicarbonate (10 mL × 3) and brine (15 mL × 1), dried over magnesium sulfate, and concentrated under vacuum. The residue was purified via silica gel PTLC (hexane/ethyl acetate = 1/1) to afford **9** (62.8 mg, 61%).
White solid; Rf 0.07 (hexane/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.25 (18H, s, Si-$(CH_3)_3$), 7.63 (4H, d, *J* = 8.1 Hz, Ar–H), 7.70 (4H, d, *J* = 8.1 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.3, 125.4, 134.5, 143.5, 144.8; ^{77}Se NMR (76 MHz, $CDCl_3$) δ: 858; IR ($CHCl_3$): 3028, 2951, 2893, 1572, 1377, 1250, 1099, 831, 814 cm^{-1}; MS (FAB) *m/z*: 395 (M+H$^+$); HR-MS (FAB) *m/z*: 395.0766 (Calcd for $C_{18}H_{26}OSeSi2$: 395.0765); Anal: Found: C, 54.79; H, 6.40 (Calcd for $C_{18}H_{26}OSeSi_2$: C, 54.94; H, 6.66%).

Bis(4-trimethylsilylphenyl) selenone (10)

The oxidant *m*CPBA (70%, 259 mg, 1.05 mmol) was added to a solution of bis(4-trimethylsilylphenyl)selenide[19] (189 mg, 0.50 mmol) in chloroform (6 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 15 h. The mixture was then washed with an aqueous 5% (w/v) solution of sodium hydroxide (10 mL × 4), dried over magnesium sulfate, and concentrated under vacuum. The residue was purified via silica gel PTLC (hexane) to afford **10** (110 mg, 82%).
White crystals; mp 186.1–187.1 °C (recryst. from ethyl acetate–hexane); Rf 0.43 (hexane/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.29 (18H, s, Si-$(CH_3)_3$), 7.73 (4H, d, *J* = 8.1 Hz, Ar–H), 7.94 (4H, d, *J* = 8.1 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.4, 125.8, 134.9, 143.1, 148.9; ^{77}Se NMR (76 MHz, $CDCl_3$) δ: 967; IR ($CHCl_3$): 3048, 3034, 2955, 2895, 1379, 1250, 1101, 945, 887, 842 cm^{-1}; MS (FAB) *m/z*: 411 (M+H$^+$); HR-MS (FAB) *m/z*: 411.0715 (Calcd for $C_{18}H_{27}O_2SeSi_2$: 411.0713); Anal: Found: C, 52.60; H, 6.24 (Calcd for $C_{18}H_{26}O_2SeSi_2$: C, 52.79; H, 6.40%).

(*Z*)-1,2-Bis[4-(trimethylsilyl)phenylsulfanyl]-1-octene (14)

Palladium (II) acetate (22.4 mg, 0.10 mmol, 5.0 mol%) and 1-octyne (443 μL, 3.0 mmol) were added to a mixture of bis[(4-trimethylsilyl)phenyl]disulfide (**13**) (725 mg, 2.0 mmol) and triphenylphosphine (525 mg, 2.0 mmol) under a nitrogen atmosphere. The mixture was dissolved in anhydrous tetrahydrofuran (5 mL), and the solution was stirred under reflux conditions for 9 h. Additional 1-octyne (443 μL, 3.0 mmol) was then added to the mixture, which was stirred under the same conditions for further 15.5 h. Next, the mixture was filtered, and the filtrate was concentrated under vacuum. The residue was purified via silica gel column chromatography (hexane) to afford **14** (819 mg, 87%).
Orange oil; ^{1}H NMR (400 MHz; $CDCl_3$) δ: 0.25 (9H, s, Si-$(CH_3)_3$), 0.26 (9H, s, Si-$(CH_3)_3$), 0.85 (3H, t, *J* = 7.0 Hz, -CH_3), 1.20–1.22 (6H, m, -$(CH_2)_3$-), 1.46–1.53 (2H, m, -CH_2-), 2.27 (2H, t, *J* = 7.6Hz, -CH_2-C=C), 6.61 (1H, s, -C=CH), 7.31 (2H, d, *J* = 8.1 Hz, Ar–H), 7.38 (2H, d, *J* = 8.4 Hz, Ar–H),7.43 (2H, d, *J* = 8.0 Hz, Ar–H),7.47 (2H, d, *J* = 8.0 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.18, −1.15, 14.0, 22.5, 28.5, 28.5, 31.5, 37.4, 128.8, 129.2, 129.7, 133.9, 134.0, 134.1, 134.8, 136.7, 138.6, 138.9; IR ($CHCl_3$): 2956, 1577, 1485, 1381, 1251, 1076, 840 cm^{-1}; MS (EI) *m/z*: 472 (M$^+$, 100), 315 (36), 221 (57), 149 (43), 73 (48); HRMS (EI) *m/z*: 472.2110 (Calcd for $C_{26}H_{40}Si_2S_2$;472.2110); Anal: Found: C, 65.87; H, 8.82 (Calcd for $C_{26}H_{40}S_2Si_2$: C, 66.03; H, 8.53%).

(*Z*)-1,2-Bis[4-(trimethylsilyl)phenylsulfinyl]-1-octene (15)

The oxidant *m*CPBA (82%, 210 mg, 1.0 mmol) was added to a solution of **14** (236 mg, 0.50 mmol) in chloroform (5 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 2.5 h. The mixture was then washed with a 5% aqueous sodium bicarbonate solution (10 mL × 3) and brine, dried over magnesium sulfate, and concentrated under vacuum. The residue was purified via silica gel column chromatography (hexane/ethyl acetate = 5/1) to give **15** (66.8 mg, 26%) and **15'** (141 mg, 56%).
Colorless prisms (**15**); mp 116.8–119.1 °C (recrystallized from ethyl acetate–hexane); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.28 (9H, s, Si-$(CH_3)_3$), 0.29 (9H, s, Si-$(CH_3)_3$), 0.77 (3H, t, *J* = 7.0 Hz, -CH_3), 1.02−1.20 (6H, m, -$(CH_2)_3$-), 1.37−1.44 (2H, m, -CH_2-), 2.11−2.24 (2H, t, *J* = 7.6 Hz, -CH_2-C=C), 6.37 (1H, s, -C=CH), 7.40 (2H, d, *J* = 8.1 Hz, Ar−H), 7.49 (2H, d, *J* = 8.4 Hz, Ar−H), 7.65 (4H, d, *J* = 8.0 Hz, Ar−H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.33, −1.31, 13.9, 22.3, 25.8, 27.5, 28.5, 31.3, 124.0, 124.2, 134.2, 134.5, 140.6, 142.5, 144.5, 145.2, 145.6, 157.4; IR ($CHCl_3$): 2958, 1379, 1251, 1105, 1037, 842 cm^{-1}; MS (FAB) *m/z*: 505 (M+H$^+$); HR-MS (FAB) *m/z*: 505.2086 (Calcd for $C_{26}H_{41}S_2Si_2$; 505.2087).

Colorless oil (**15'**); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.29 (9H, s, Si-$(CH_3)_3$), 0.32 (9H, s, Si-$(CH_3)_3$), 0.77 (3H, t, J = 7.0 Hz, -CH_3), 1.03–1.20 (6H, m, -$(CH_2)_3$-), 1.26–1.31 (2H, m, -CH_2-), 2.00–2.08 (1H, m, -CH_2-C=C), 2.37–2.46 (1H, m, -CH_2-C=C), 6.59 (1H, s, -C=CH), 7.68 (2H, d, J = 8.0 Hz, Ar–H), 7.72 (4H, s, Ar–H), 7.76 (2H, d, J = 8.0 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.4, 13.8, 22.2, 25.2, 27.4, 28.3, 31.1, 123.3, 123.7, 134.1, 134.4, 140.3, 141.7, 144.5, 144.9, 145.1, 159.2.; IR ($CHCl_3$): 3012, 2958, 1251, 1105, 1037, 842 cm^{-1}; MS (FAB) *m/z*: 505 ($M+H^+$); HRMS (FAB) *m/z*: 505.2086 (Calcd for $C_{26}H_{40}Si_2S_2$; 505.2087).

Isomerization and disproportion of bissulfoxides 15 and 15'

A solution of **15** (73.3 mg, 0.15 mmol) in decalin (5 mL) was stirred at 150 °C for 5 h. The reaction mixture was then cooled to room temperature and washed with hexane on silica gel to remove decalin. After eluting with ethyl acetate and evaporation, the residue was purified using recycled high-performance liquid chromatography (JAI LC-908) on a gel permeation chromatography column (JAIGEL 1H and 2H) and silica gel PTLC (hexane/ethyl acetate = 3/1) to give a mixture of **15** (19.1 mg, 26%) and **15'** (12.3 mg, 17%), as well as **16** (8.6 mg, 11%) and **17** (3.5 mg, 5%), as disproportionation products. When **15'** (252 mg, 0.50 mmol) was used in decalin (15 mL), a mixture of 15 (8.5 mg, 3%) and **15'** (140 mg, 55%), as well as **16** (12.1 mg, 5%) and **17** (4.5 mg, 0.4%), was obtained.

(*Z*)-2-[4-(Trimethylsilyl)phenylsulfinyl]-1-[4-(trimethylsilyl)phenylsulfonyl]-1-octene (16)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.30 (9H, s, Si-$(CH_3)_3$), 0.32 (9H, s, Si-$(CH_3)_3$), 0.74 (3H, t, J = 7.0Hz, -CH_3), 1.10–1.20 (6H, m, -$(CH_2)_3$-), 1.23–1.30 (2H, m, -CH_2-), 2.08–2.16 (1H, m, -CH_2-C=C), 2.48–2.56 (1H, m, -CH_2-C=C), 6.64 (1H, s, -C=CH), 7.66 (2H, d, J = 8.0 Hz, Ar–H), 7.75 (2H, s, Ar–H),7.85 (2H, d, J = 8.0 Hz, Ar–H), 7.99 (2H, d, J = 8.0 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.4, −1.3, 13.9, 22.3, 24.5, 27.9, 28.4, 31.2, 124.0, 126.6, 132.4, 134.1, 134.5, 140.2, 142.0, 149.5, 160.4; IR ($CHCl_3$): 2958, 1379, 1319, 1251, 1149, 1105, 1037, 842 cm^{-1}; MS (FAB) *m/z*: 521 ($M+H^+$); HRMS (FAB) *m/z*: 521.2038 (Calcd for $C_{26}H_{40}Si_2S_2$; 521.2036).

(*Z*)-2-[4-(Trimethylsilyl)phenylsulfinyl]-1-[4-(trimethylsilyl)phenylthio]-1-octene (17)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.28 (9H, s, Si-$(CH_3)_3$), 0.29 (9H, s, Si-$(CH_3)_3$), 0.81 (3H, t, J = 7.0 Hz, -CH_3), 1.10–1.23 (6H, m, -$(CH_2)_3$-), 1.25–1.39 (2H, m, -CH_2-), 2.07–2.16 (1H, m, -CH_2-C=C), 2.37–2.46 (1H, m, -CH_2-C=C), 6.67 (1H, s, -C=CH), 7.39 (2H, d, J = 8.1 Hz, Ar–H), 7.52 (2H, d, J = 8.4 Hz, Ar–H),7.62 (2H, d, J = 8.0 Hz, Ar–H), 7.65 (2H, d, J = 8.0 Hz, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: −1.25, −1.22, 13.9, 22.4, 25.5, 28.2, 28.7, 31.4, 123.1, 129.1, 130.4, 133.9, 134.3, 135.6, 140.2, 143.8, 144.0, 145.9; IR ($CHCl_3$): 2956, 1573, 1462, 1379, 1251, 1107, 1029, 842 cm^{-1}; MS (FAB) *m/z*: 489 ($M+H^+$); HRMS (FAB) *m/z*: 489.2140 (Calcd for $C_{26}H_{40}Si_2Se_2$; 489.2137).

Computational studies

All calculations were performed with the Spartan'14 program (Wavefunction Inc., Irvine, CA) using DFT. The geometries of all stationary points were completely optimized using the B3LYP functional and 6-31G* basis sets, and their natures (minima) were determined via frequency analysis.

Acknowledgements

We would like to thank the staff of the Instrument Analysis Center of Mukogawa Women's University for the NMR and MS measurements and elemental analyses.

Notes and references

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18) The crystal of **15** was obtained as a cocrystal of two conformers. Crystallographic data (excluding structure factors) for the structure in this study have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1052034 for **15**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

19) Please see supplementary information.

