Chalcogeno Morita−Baylis−Hillman Reaction of 2-(Methylchalcogeno)phenyl Vinyl Ketones with Aldehydes, Ketones, and α-Dicarbonyl Compounds

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Reactions of 2-(methylchalcogeno)phenyl vinyl ketones **1** and **4** with aldehydes **5** were conducted in the presence of $BF_3{\cdot}Et_2O$. The reaction was quenched by addition of Et_3N and gave the Morita–Baylis–Hillman adducts **6**–**7** in good yields. When the reaction mixture of **1** with **5a** was worked up with saturated aqueous $NaHCO_3$, the sulfonium salt **8a** was obtained together with **6**. Ketones **10**, α-diketones, and α-oxo esters **13**, which hardly react in the traditional Morita–Baylis–Hillman reaction, similarly reacted with 2-(methylchalcogeno)phenyl vinyl ketones **1** and **4** to give the Morita–Baylis–Hillman adducts **11**–**12** and **14**–**15**. Selenochromanones **9** and **16** were obtained together with **7** and **15** from reactions of seleno derivative **4**, with **5** and **13** as by-products. The formation mechanism for the sulfonium salt *syn-trans*-**8a** is discussed.

Introduction

The Morita−Baylis−Hillman reaction is well known as a coupling reaction of aldehydes and activated alkenes catalyzed by tertiary amines or phosphanes to produce α-hydroxyalkylated alkenes and is widely used because it provides densely functionalized alkenes.[1] However, this reaction traditionally suffers from a low reaction rate and limited substrate scope. Therefore, we devised a tandem Michael aldol reaction using chalcogenide/$TiCl_4$.[2] This reaction is much faster than the original reaction and has a wide application to the reactions of acrylthioesters[3a][3b] and electron-deficient alkynes,[3c][3d] which cannot undergo the traditional Morita−Baylis−Hillman reaction, with aldehydes. However, this reaction starts with the Michael addition of a chloride ion of the $TiCl_4$ to an activated alkene and not with the Michael addition of a chalcogeno ether.[2d,3b] Balenkova et al. have shown that thio derivatives undergo cyclization in the presence of a Lewis acid.[4] This implies that the intramolecular Michael addition is more efficient than the intermolecular one. On the basis of these data, we have developed a tandem intramolecular Michael aldol reaction which starts with the Michael addition of a chalcogeno ether to the activated alkene (the chalcogeno Morita−Baylis−Hillman reaction).[5] The chalcogeno Morita−Baylis−Hillman reaction of 2-(methylchalcogeno)-phenyl vinyl ketones with carbonyl compounds is described in detail in this paper.

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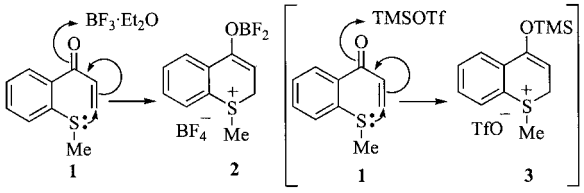
Results and Discussion

Reaction of 2-(Methylchalcogeno)phenyl Vinyl Ketones with Carbonyl Compounds

First of all, we investigated the chemical behavior of thio derivative **1** with a Lewis acid by NMR spectroscopy. As Lewis acids containing nucleophilic substituents cannot be used in order to avoid the Michael addition of the substituent to the enone moiety, $BF_3{\cdot}Et_2O$ was used for the reaction. The ^1H NMR spectrum of the reaction mixture of 1-[2-(methylthio)phenyl]propenone (**1**) and $BF_3{\cdot}Et_2O$ in CD_3CN (Scheme 1) exhibits signals at δ_H = 3.90 (dd, J = 5.0, 18.0 Hz, 1 H, 2-H), 4.39 (dd, J = 2.0, 18.0 Hz, 1 H, 2-H), and 5.27 (dd, J = 2.0, 5.0 Hz, 1 H, 3-H) ppm. This spectrum agrees closely with that of the corresponding TMS enol ether **3**, which was generated from the reaction of **1** with TMSOTf, showing signals at δ_H = 3.93 (dd, J = 2.0, 17.0 Hz, 1 H, 2-H), 4.37 (dd, J = 3.5, 17.0 Hz, 1 H, 2-H), and 5.27 (dd, J = 2.0, 3.5 Hz, 1 H, 3-H) ppm. From



Scheme 1. Formation of the boron γ-(sulfonio)enolate **2**

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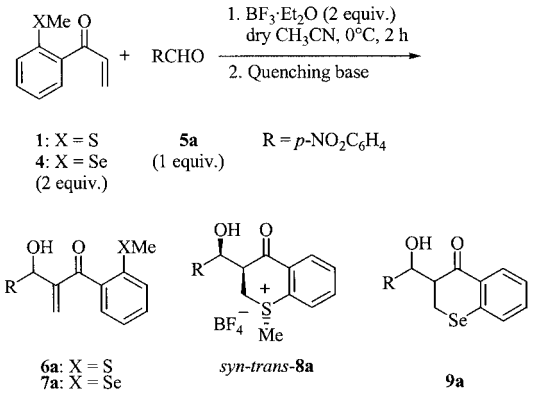
these spectroscopic data, we confirmed the formation of boron enolate **2** from the reaction of **1** with $BF_3{\cdot}Et_2O$.

We next examined the reaction of thio derivative **1** with *p*-nitrobenzaldehyde (**5a**) in the presence of 2 equiv. of $BF_3{\cdot}Et_2O$[5] and the influence of the quenching method of this reaction (Table 1).

Table 1. Examination of quenching reagents



Entry	Chalcogeno ether	Quenching base	Products (yield [%])
1	1	satd. aq. $NaHCO_3$	**6a** (45), **8a** (26)
2	1	satd. aq. $NaHCO_3$[a]	**6a** (52)
3	1	Et_3N (2 equiv.)	**6a** (75)
4	4	Et_3N (2 equiv.)	**7a** (75)/**9a** (16), 95:5[b]

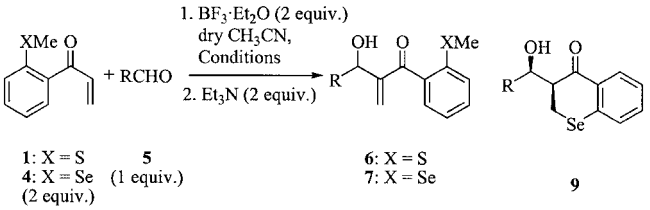
[a] The reaction mixture was poured into an excess of an $NaHCO_3$ solution. [b] Diastereoisomer ratio (*syn*/*anti* isomer).

Treatment of the reaction mixture with saturated aqueous $NaHCO_3$ gave the Morita−Baylis−Hillman adduct **6a** (45%) and the sulfonium salt *syn-trans*-**8a** (26%); the stereostructure of **8a** will be discussed below (Table 1, Entry 1). When the reaction mixture was poured into an excess of saturated aqueous $NaHCO_3$, the adduct **6a** was obtained in 52% yield (Entry 2). The yield of **6a** was increased up to 75% by treatment of the reaction mixture with triethylamine (Entry 3). The reaction of the seleno congener **4** gave the adduct **7a** (75%) and selenochromanone **9a** (*syn*/*anti* = 95:5, 16%) after treatment with triethylamine (Entry 4). The product *syn*-**9a** was isomerized to the *anti* isomer *anti*-**9a** during separation of the raw product by preparative TLC on silica gel.[6] The stereochemical assignment for **9a** was determined from the coupling constant between the methine proton at the 3-position and the benzylic proton in comparison with those of the isomers of 2-(α-hydroxybenzyl)cyclohexanone, showing J = 2.5 Hz for the *syn* isomer and J = 8.3 Hz for the *anti* isomer.[7] One of the isomers of **9a** with J = 3.2 Hz and another one with J = 7.8 Hz were assigned to be the *syn* and the *anti* isomers, respectively. We further examined the reactions of various aldehydes with 2-(methylchalcogeno)phenyl vinyl ketones **1** and **4** under similar conditions to those in Entries 3 and 4 in Table 1 (see Table 2).

The reactions of benzaldehyde (**5d**) and hydrocinnamaldehyde (**5e**) were continued until the aldehydes had disappeared according to TLC. The reactions of thio derivative **1** with both aromatic and aliphatic aldehydes **5b**−**5e** gave the adducts **6b**−**6e** in good yields (Table 2, Entries 1, 3−5). The reaction of seleno derivative **4** with *p*-chlorobenzaldehyde (**5b**) gave adduct **7b** (69%) and selenochromanone **9b** (*syn* only, 20%) (Table 2, Entry 2).

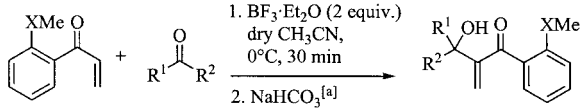
In addition to aldehydes, various carbonyl compounds, such as highly fluorinated ketones and non-enolizable α-dicarbonyl compounds, have been used as electrophiles in the Morita−Baylis−Hillman reaction.[1] However, the Morita−Baylis−Hillman reaction does not occur with ketones and enolizable α-dicarbonyl compounds under normal conditions.[8] The intermediate of the chalcogeno Morita−Baylis−Hillman reaction described above is a boron enolate and can be expected to react with these carbonyl compounds under mild conditions.[9] These results encouraged us to conduct the reactions of 2-(methylchalcogeno)phenyl vinyl ketones **1** and **4** with various carbonyl compounds that do not react under traditional Morita−Baylis−Hillman conditions.

Table 2. Reaction of 1-[2-(methylchalcogeno)phenyl]propenones **1** and **4** with aldehydes **5**



Entry	Chalcogeno ether	Aldehyde **5**	Conditions	Products (yield [%])
1	**1**	R = *p*-ClC_6H_4 (**5b**)	0 °C, 2 h	**6b** (73)
2	**4**	R = *p*-ClC_6H_4 (**5b**)	0 °C, 2 h	**7b** (69), **9b** (20), *syn* only
3	**1**	R = *p*-$CF_3C_6H_4$ (**5c**)	0 °C, 2 h	**6c** (75)
4	**1**	R = Ph (**5d**)	0 °C, 2 h then room temp., 3 h	**6d** (60)
5	**1**	R = PhC_2H_4 (**5e**)	0 °C, 2 h then room temp., 3 h	**6e** (70)

Table 3. Reaction of 1-[2-(methylchalcogeno)phenyl]propenones **1** and **4** with ketones **10**



1: X = S
4: X = Se
(2 equiv.)

10
(1 equiv.)

11: X = S
12: X = Se

Entry	Chalcogeno ether	Ketone **10**	Product (yield [%])
1[b]	**1**	R^1 = *p*-$NO_2C_6H_4$, R^2 = Me (**10a**)	**11a** (47)
2	**1**	**10a**	**11a** (47)
3	**4**	**10a**	**12a** (50)
4	**1**	R^1 = Ph, R^2 = Me (**10b**)	**11b** (19)
5	**4**	**10b**	**12b** (26)
6	**1**	R^1 = R^2 = $(CH_2)_5$ (**10c**)	**11c** (56)
7	**4**	**10c**	**12c** (53)

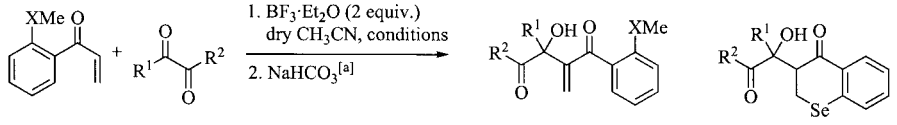
[a] The reaction mixture was poured into an $NaHCO_3$ solution. [b] Et_3N (2 equiv.) was used instead of an $NaHCO_3$ solution.

We first carried out the reaction of *p*-nitroacetophenone (**10a**) with thio derivative **1** in dry CH_3CN at 0 °C for 30 min, quenched the reaction with triethylamine, and obtained adduct **11a** (47%; Table 3, Entry 1).

When the reaction mixture was poured into an excess of saturated aqueous $NaHCO_3$, the adduct **11a** was obtained in 47% yield (Entry 2). Since the quenching methods did not cause a difference in yield, the reaction mixtures of various ketones were worked up by pouring the mixture into an excess of saturated aqueous $NaHCO_3$. Acetophenone (**10b**), without an electron-withdrawing group on the benzene ring, gave **11b** and **12b** in low yields (Entries 4 and 5), and cyclohexanone **10c** afforded **11c** and **12c** in moderate yields (Entries 6 and 7). Next, the reactions of α-diketones **13a**−**b** or α-oxo esters **13c**−**d** as electrophiles were studied. The results are shown in Table 4.

The reactions of α-diketones **13a** and **13b** gave the adducts **14a**, **15a** and **14b**, **15b** in low yields. However, this is the first example of an enolizable α-diketone reacting as an electrophile under mild conditions in the Morita−Baylis−Hillman reaction.[5b] The reaction of ethyl pyruvate (**13c**) with 3-buten-2-one did not give the expected adduct under various Morita−Baylis−Hillman reaction conditions,[10] while the reaction of **1** and **4** with **13c** gave **14c** and **15c** in 70 and 74% yield, respectively (Entries 5 and 6). Reactions with methyl benzoylformate (**13d**) gave the products in low yields. The reaction of seleno derivative **4** with oxo esters **13c**−**d** gave trace amounts of selenochromanones

Table 4. Reaction of 1-[2-(methylchalcogeno)phenyl]propenones **1** and **4** with α-dicarbonyl compounds **13**



1: X = S
4: X = Se
(2 equiv.)

13
(1 equiv.)

14: X = S
15: X = Se

16

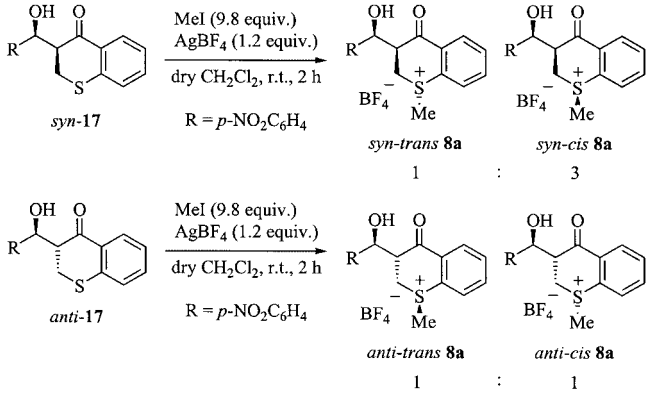
Entry	Chalcogeno ether	α-Dicarbonyl compound **13**	Conditions	Products (yield [%])
1[a]	**1**	R^1 = R^2 = Ph (**13a**)	0 °C, 2 h	**14a** (41)
2[b]	**4**	**13a**	0 °C, 2 h	**15a** (4)
3	**1**	R^1 = R^2 = Me (**13b**)	0 °C, 1 h	**14b** (29)
4	**4**	**13b**	0 °C, 1 h	**15b** (24)
5	**1**	R^1 = Me, R^2 = OEt (**13c**)	room temp., 2 h	**14c** (70)
6	**4**	**13c**	room temp., 2 h	**15c** (74), **16c** (2)[c]
7	**1**	R^1 = Ph, R^2 = OMe (**13d**)	room temp., 2 h	**14d** (37)
8	**4**	**13d**	room temp., 2 h	**15d** (29), **16d** (6)[c]

[a] The reaction mixture was poured into an excess of an $NaHCO_3$ solution. [b] BF_3·Et_2O (3 equiv.) was used. [c] Only one diastereoisomer was obtained, but the stereostructure was not determined.

16c−d as by-products. These compounds are only one isomer, but their amounts were so small that their stereostructures could not be determined.

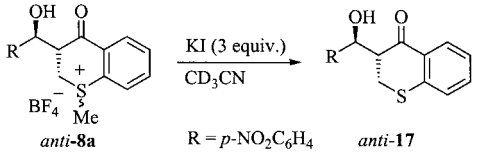
Structural Investigations

To clarify the stereochemistry of sulfonium salt **8a**, we synthesized authentic samples of the stereosiomers of **8a** (Scheme 2). 3-(α-Hydroxybenzyl)thiochromanone (**17**) was prepared as a mixture of *syn* and *anti* isomers (*syn*/*anti* = 4:1) from thiochroman-4-one by silylation of the enolate and the aldol reaction with *p*-nitrobenzaldehyde (**5a**). The *syn* and *anti* isomers were separated by recycling preparative HPLC. The stereochemistry of the isomers **17** was assigned by comparison of the coupling constants of *syn*-**17** (3.2 Hz) and *anti*-**17** (8.3 Hz) with those of the cyclohexanone derivatives (2.5 Hz for the *syn* isomer and 8.3 Hz for the *anti* isomer).[7] The methylation of *syn*-**17** with MeI and $AgBF_4$ gave two stereoisomers of **8a** (*syn-cis*-**8a**/*syn-trans*-**8a** = 3:1).



Scheme 2. Synthesis of sulfonium salts **8a**

Their stereostructures were determined from the NOEs between the methyl group and the 3-proton. *syn-trans*-**8a** shows a 6% NOE enhancement each between the methyl group and the 3-proton and between the methyl group and one of the 2-protons, while *syn-cis*-**8a** shows no NOE enhancement between the methyl group and the 3-proton, although it does show a 5% NOE enhancement between the methyl group and one of the 2-protons. The ^1H NMR spectrum (CD_3CN) of *syn-trans*-**8a** exhibits the signals at δ_H = 3.10 (s, 3 H, SMe) and 5.79 (dd, J = 3.0, 4.0 Hz, 1 H, benzylic H) ppm, and that of *syn-cis*-**8a** shows signals at δ_H = 3.29 (s, 3 H, SMe) and 5.95 (d, J = 2.0 Hz, 1 H, benzylic H) ppm. According to the ^1H NMR spectroscopic data, the methyl group of *syn-trans*-**8a** occupies the axial position and that of *syn-cis*-**8a** the equatorial position. This stereochemistry agrees with the conformation of the *syn*,*anti* isomer of 3-(α-methoxybenzyl)-1-(methylseleno)-chromanium salt, which was determined by X-ray analysis.[6] The methylation of *anti*-**17** similarly gave two kinds of sulfonium salts, *anti-cis*-**8a** and *anti-trans*-**8a**, in a ratio of 1:1 (Scheme 2). Neither isomers showed an NOE enhancement between the methyl group and the 3-proton, although the spectral pattern is very similar to that of the *syn* isomers. Therefore, an isomer showing the signals (CD_3CN) at δ_H = 3.23 (s, 3 H, SMe) and 5.56 (d, J = 2.4 Hz, 1 H, benzylic H) ppm was assigned to be *anti-trans*-**8a**, and the other, exhibiting the signals (CD_3CN) at δ_H = 3.29 (s, 3 H, SMe) and 5.68 (d, J = 3.9 Hz, 1 H, benzylic H) ppm, was assigned as *anti-cis*-**8a**. Surprisingly, the coupling constants of the benzylic protons of the sulfonium salts **8a** are small (2.4, 3.9 Hz), and are close to those of the *syn* isomers. The demethylation of a mixture of *cis* and *trans* isomers of *anti*-**8a** with potassium iodide was carried out to confirm that no isomerization of the *anti* isomer to the *syn* isomer had occurred during the methylation of the *anti* isomer (Scheme 3).



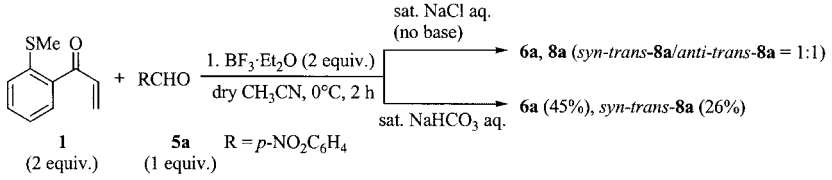
Scheme 3. Demethylation of *anti*-sulfonium salt **8a**

The product shows a large coupling constant for the benzylic proton (J = 8.3 Hz in $CDCl_3$), which is consistent with that of an authentic sample of *anti*-**17**. The ^1H NMR spectra of *syn*- and *anti*-**17** in CD_3CN were measured just to be certain of the solvent effect of CD_3CN. Surprisingly, the chemical shifts and coupling constants changed: ^1H NMR (CD_3Cl): *syn*-**17**: δ = 5.83 (d, J = 3.4 Hz, 1 H, benzylic H); *anti*-**17**: δ = 5.25 (d, J = 8.3 Hz, 1 H, benzylic H) ppm; (CD_3CN): *syn*-**17**: δ = 5.68 (t, J = 4.0 Hz, 1 H, benzylic H); *anti*-**17**: δ = 5.3 (dd, J = 4.0, 6.0 Hz, 1 H, benzylic H) ppm.

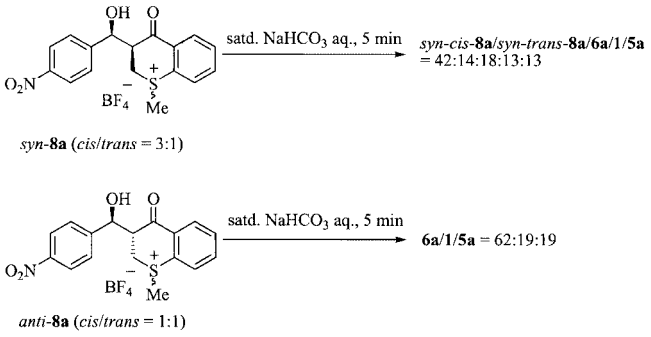
Reaction Mechanism

In order to elucidate the reaction mechanism, we conducted several experiments on sulfonium salt **8a**. The workup of the reaction mixture of **1** and **5a** with saturated aqueous $NaHCO_3$ gave **6a** (45%) and *syn-trans*-**8a** (26%), while the workup with saturated aqueous NaCl (without base) produced **6a** and a mixture of *syn-trans*-**8a** and *anti-trans*-**8a** in a ratio of 1:1 (Scheme 4).

We next conducted the reactions of **8a** with saturated aqueous $NaHCO_3$ in order to investigate this difference further (Scheme 5). Treatment of the *syn*-sulfonium salt **8a** (*syn-cis*-**8a**/*syn-trans*-**8a** = 3:1) with saturated aqueous $NaHCO_3$ gave the Morita−Baylis−Hillman adduct **6a**, sulfonium salts **8a**, *p*-nitrobenzaldehyde (**5a**), and thio derivative **1**. On the other hand, treatment of the *anti*-sulfonium salts **8a** (*anti-cis*-**8a**/*anti-trans*-**8a** = 1:1) with saturated aqueous $NaHCO_3$ gave the Morita−Baylis−Hillman adduct **6a**, *p*-nitrobenzaldehyde (**5a**), and thio derivative **1**; the starting material **8a** was not recovered. These results indicate that *anti*-**8a** undergoes β-elimination more easily than the *syn* isomer and that the retro-aldol reaction of **8a** also



Scheme 4. Isomer ratio of sulfonium salts **8a** by different quenching methods

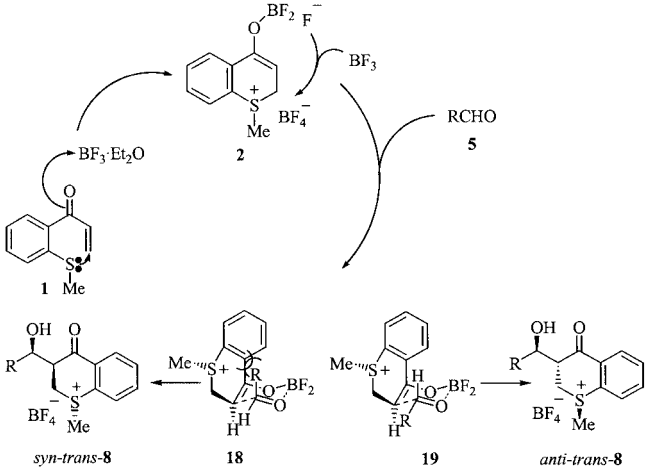


Scheme 5. Reaction of sulfonium salts **8a** with saturated aqueous $NaHCO_3$

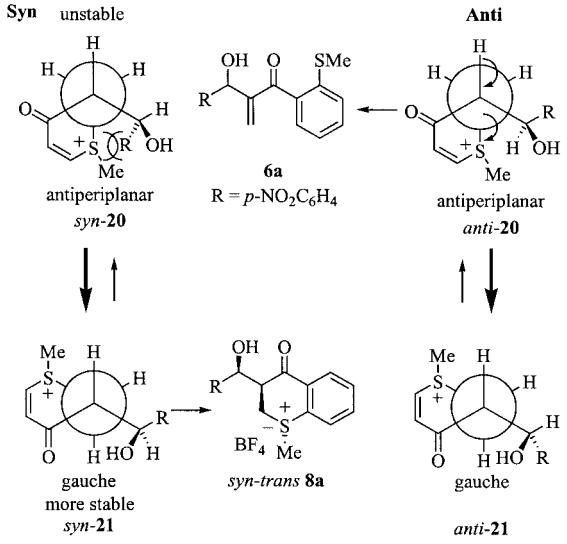
occurs in competition with β-elimination upon treatment with a base.

On the basis of these results, a possible mechanism for the chalcogeno Morita−Baylis−Hillman reaction is shown in Scheme 6. The activation of the enone by BF_3·Et_2O allows a chalcogeno ether to add to the β-carbon atom of an enone moiety.

Diastereoselectivity would be induced in the reaction step of boron enolate **2** with aldehyde **5**. The transition state **19** with an equatorial R group is favored over the other transition state **18** with an axial R group, and the *anti* isomer **8** is preferably formed. When aldehyde **5** approaches enolate **2**, the methyl group on the chalcogen atom takes the opposite position to the aldehyde, i.e. the *trans* configuration. The difference of reactivity between *syn*- and *anti*-**8** and a base is shown in Scheme 7. In both isomers, the *gauche* conformation **21**, in which the hydroxybenzyl group is in the equatorial position, is more stable than the antiperiplanar conformation **20** with an axial hydroxybenzyl group. β-Elimination occurs via the antiperiplanar conformation **20**. Steric repulsion between the lone pair of electrons and the benzylic hydrogen atom in *anti*-**20** is much less than that between the lone pair of electrons and the R group in *syn*-**20**. Therefore, *anti*-**20** undergoes β-elimination easier than *syn*-**20**, which is why *anti*-**8a** was not obtained from the reaction of **1** and **5a** after working up the reaction mixture with a base.



Scheme 6. Mechanism for the formation of α-hydroxyalkylated compounds



Scheme 7. Structure and reactivity of sulfonium salts **8a**

Conclusion

The chalcogeno Morita−Baylis−Hillman reaction of 2-(methylchalcogeno)phenyl vinyl ketones with carbonyl compounds has been discussed in detail. The reaction could be applied to non-activated ketones, such as acetophenone and cyclohexanone, and enolizable α-dicarbonyl compounds, such as diacetyl and ethyl pyruvate, under mild conditions. Further development of the tandem intramolecular Michael aldol reaction is now in progress.

Experimental Section

General: Melting points were obtained with a Yanagimoto micro-melting-point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (NaCl) were recorded with a JASCO FT/IR-230 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL EX-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained with a JEOL EX-400 (100 MHz) spectrometer with $CDCl_3$ (δ = 77.0 ppm) or CD_3CN (δ = 1.3 ppm) as an internal standard. The degree of substitution of the carbon atoms was determined by DEPT. Mass spectra were recorded with a JEOL JMS-SX102A spectrometer with a direct-insertion probe at 70 eV. Elemental analyses of new compounds were performed with a Yanaco CHN Corder MT-5. All chromatographic isolations were accomplished with BW-350 (Fuji Silysia) for column chromatography or with Kieselgel 60 PF_{254} containing gypsum (Merck) for preparative TLC. CH_2Cl_2, MeCN, ethanol, and THF were purified and dried by standard procedures and freshly distilled prior to use. The recycling preparative HPLC was performed with an LC-918 liquid chromatography (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL-1H and -2H columns (polystyrene gels).

3-(Phenylseleno)propionic Acid: $NaBH_4$ (about 16 g) was slowly added to a solution of diphenyl diselenide (36.7 g, 0.117 mol) in dry ethanol (600 mL) until the solution became colorless. An aqueous solution of sodium 3-chloropropionate, prepared from Na_2CO_3 (15.3 g, 0.144 mol) and 3-chloropropionic acid (31.4 g, 0.289 mol) in H_2O (60 mL), was added to the resulting solution. The mixture was heated at reflux for 2.5 h and was then allowed to cool to room temperature. H_2O (600 mL) was added and extracted with benzene (200 mL, twice). The aqueous layer was acidified with concentrated hydrochloric acid and extracted with benzene (300 mL, three times). The extracts were washed with water, dried with $MgSO_4$, and filtered. The solvent was removed in vacuo to give the crude product as a white powder (52 g, 96%), which was used without further purification. The spectroscopic data are identical to those cited in the literature.[11]

Selenochroman-4-one: 3-(Phenylseleno)propionic acid (20 g, 0.087 mol) was heated in polyphosphoric acid (160 g) at 100 °C for 1 h and was then allowed to cool to room temperature. The mixture was poured into ice-cold water (500 mL), stirred for 1 h, and extracted with CH_2Cl_2 (150 mL, four times). The combined extracts were washed with brine (150 mL, twice) and then with saturated aqueous $NaHCO_3$, dried with $MgSO_4$, and filtered. After evaporation of the solvent, the product was purified by distillation (150 °C, 8 Torr) to yield an orange solid (15.6 g, 80%). The spectroscopic data are identical to those cited in the literature.[11] Thiochroman-4-one was similarly synthesized from 3-(phenylthio)propionic acid.[12]

1-Methyl-4-oxoselenochromanium Tetrafluoroborate: A solution of $BF_3{\cdot}Et_2O$ (38 mL, 0.3 mol) in dry CH_2Cl_2 (60 mL) was slowly added to trimethyl orthoformate (32 g, 0.3 mol) at −30 °C.[13] The solution was stirred at that temperature for 1 h and then at 0 °C for 15 min. The solution was cooled to −30 °C again, and a solution of selenochroman-4-one (32 g, 0.15 mol) in dry CH_2Cl_2 (200 mL) was slowly added. The resulting mixture was stirred at 0 °C for 12 h, and the precipitate was collected and washed with diethyl ether to yield the product (38 g, 80%). Brown crystals (from acetone/diethyl ether), m.p. 133−136 °C (dec.). ^{1}H NMR (400 MHz, CD_3CN): δ = 3.04 (s, 3 H, $SeCH_3$), 3.19−3.33 (m, 2 H, 2-CH_2), 3.79 (ddd, *J* = 4.5, 6.4, 11.2 Hz, 1 H, 3-CH_2), 4.06 (ddd, *J* = 2.0, 4.5, 11.2 Hz, 1 H, 3-CH_2), 7.78−7.88 (m, 3 H, ArH), 8.28 (dd, *J* = 2.4, 6.4 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 24.2 (q), 33.1 (t), 33.3 (t), 127.9 (s), 131.4 (d), 132.9 (d), 134.36 (d), 134.42 (s), 136.4 (d), 191.6 (s) ppm. IR (KBr): $\tilde{\nu}$ = 1690 (C=O), 1064 cm^{-1} (BF_4^-). MS (EI or FAB): no [M^+] or [M^+ + H] peak. $C_{10}H_{11}BF_4OSe$ (312.96): calcd. C 38.38, H 3.54; found C 38.49, H 3.58.

1-Methyl-4-oxothiochromanium Tetrafluoroborate: This compound was similarly prepared according to the procedure for 1-methyl-4-oxoselenochromanium tetrafluoroborate. The physicochemical data and spectroscopic data are identical with those of an authentic sample.[14]

1-[2-(Methylseleno)phenyl]propenone (4): A solution of NaOH (6.75 g, 169 mmol) in H_2O (135 mL) was slowly added to a solution of 1-methyl-4-oxoselenochromanium tetrafluoroborate (25.8 g, 82.4 mmol) in a mixture of CH_2Cl_2 (300 mL) and H_2O (600 mL). The mixture was stirred at room temperature for 20 min and then extracted with CH_2Cl_2 (200 mL, three times). The combined extracts were dried with $MgSO_4$, filtered, and concentrated to dryness. The residue was purified by column chromatography (hexane/CH_2Cl_2, 3:1) to yield **4** (17.4 g, 94%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, $SeCH_3$), 5.94 (dd, *J* = 1.5, 10.5 Hz, 1 H, 3-H), 6.42 (dd, *J* = 1.5, 17.0 Hz, 1 H, 3-H), 7.14 (dd, *J* = 10.5, 17.0 Hz, 1 H, 2-H), 7.26 (dt, *J* = 1.5, 7.8 Hz, 1 H, ArH), 7.45 (dt, *J* = 1.5, 7.8 Hz, 1 H, ArH), 7.50 (dd, *J* = 1.5, 7.8 Hz, 1 H, ArH), 7.87 (dd, *J* = 1.5, 7.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.6 (q), 124.2 (d), 128.3 (d), 130.2 (t), 130.9 (d), 132.2 (d), 132.8 (d), 135.4 (s), 138.8 (s), 191.3 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 1651 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 226 (45) [M^+], 211 (100). $C_{10}H_{10}OSe$ (225.15): calcd. C 53.35, H 4.48; found C 53.18, H 4.52.

1-[2-(Methylthio)phenyl]propenone (1): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, SCH_3), 5.96 (dd, *J* = 1.4, 10.8 Hz, 1 H, 3-H), 6.31 (dd, *J* = 1.4, 17.6 Hz, 1 H, 3-H), 6.98 (dd, *J* = 10.8, 17.6 Hz, 1 H, 2-H), 7.21 (dt, *J* = 1.0, 7.3 Hz, 1 H, ArH), 7.37 (dd, *J* = 1.0, 7.3 Hz, 1 H, ArH), 7.47 (dt, *J* = 1.0, 7.3 Hz, 1 H, ArH), 7.66 (dd, *J* = 1.0, 7.3 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2 (q), 123.8 (d), 125.9 (d), 129.9 (d), 130.5 (t), 131.8 (d), 134.4 (d), 135.5 (s), 141.3 (s), 192.7 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 1653 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 178 (55) [M^+], 150 (100). $C_{10}H_{10}OS$ (178.25): calcd. C 67.38, H 5.66; found C 67.16, H 5.74.

Generation of Boron Enolate 2: $BF_3{\cdot}Et_2O$ (32 μL, 0.25 mmol) was added to a solution of thio derivative **1** (45 mg, 0.25 mmol) in CD_3CN (1 mL) at 0 °C. The solution was stirred at the same temperature for 15 min and then submitted to ^{1}H NMR spectroscopy.

Generation of Boron Enolate 3: The reaction was similarly conducted on the same scale using TMSOTf (56 mg, 0.25 mmol) instead of $BF_3{\cdot}Et_2O$.

General Procedure for Reactions of 2-(Methylchalcogeno)phenyl Vinyl Ketone 1 or 4 with Aldehyde 5: $BF_3{\cdot}Et_2O$ (127 mL, 1.0 mmol) was added dropwise at 0 °C to a stirred solution of 1-[2-(methylthio)-phenyl]propenone (**1**; 178 mg, 1.0 mmol) and *p*-nitrobenzaldehyde (**5a**; 76 mg, 0.5 mmol) in dry CH_3CN (1.5 mL). The mixture was stirred at the same temperature for 2 h and then quenched by addition of Et_3N (140 mL, 1.0 mmol). After stirring the mixture at the same temperature for 10 min, it was poured into saturated aqueous NaCl (10 mL) and extracted with CH_2Cl_2 (5 mL, three times). The combined extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative TLC eluting with hexane/EtOAc (3:1) to give **6a**.

2-[1-Hydroxy-1-(4-nitrophenyl)methyl]-1-[2-(methylthio)phenyl]-propenone (6a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, SCH_3), 3.55 (d, *J* = 5.4 Hz, 1 H, OH), 5.79 (s, 1 H, olefinic H), 6.09 (s, 1 H, olefinic H), 5.91 (d, *J* = 5.4 Hz, 1 H, benzylic H), 7.17 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.43 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.26 (dd, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.35 (dd, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.66 (d *J* = 8.8 Hz, 2 H, ArH), 8.21 (d *J* = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.0 (q), 72.4 (d), 123.8 (d), 124.6 (d), 127.4 (d), 127.7 (d), 129.7 (d), 130.1 (t), 131.7 (d), 136.9 (s), 139.3 (s), 147.5 (s), 149.1 (s), 149.2 (s), 198.2 (s) ppm. IR (NaCl): ṽ = 3423 (OH), 1651 (C=O), 1517 (NO_2), 1343 cm^{-1} (NO_2). MS (EI): *m*/*z* (%) = 329 (10) [M$^+$], 177 (100). $C_{17}H_{15}NO_4S$ (329.37): calcd. C 61.99, H 4.59, N 4.25; found C 61.93, H 4.94, N 3.99.

2-[1-(4-Chlorophenyl)-1-hydroxymethyl]-1-[2-(methylthio)phenyl]-propenone (6b): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, SCH_3), 3.28 (d, *J* = 4.9 Hz, 1 H, OH), 5.72 (s, 1 H, olefinic H), 5.80 (d, *J* = 4.9 Hz, 1 H, benzylic H), 6.03 (s, 1 H, olefinic H), 7.14−7.18 (m, 1 H, ArH), 7.27−7.44 (m, 7 H, ArH) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 16.8 (q), 72.5 (d), 124.4 (d), 127.2 (d), 128.1 (d), 128.6 (d), 129.1 (t), 129.6 (d), 131.3 (d), 133.5 (s), 137.1 (s), 139.1 (s), 139.8 (s). 149.7 (s), 198.3 (s) ppm. IR (NaCl): ṽ = 3453 (OH), 1651 cm^{-1} (C=O). MS (FAB, NBA): *m*/*z* (%) = 319 (25) [M$^+$ + H], 154 (100). $C_{17}H_{15}ClO_2S$ (318.82): calcd. C 64.04, H 4.74; found C 64.07, H 4.97.

2-{1-Hydroxy-1-[4-(trifluoromethyl)phenyl]methyl}-1-[2-(methylthio)phenyl]propenone (6c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, SCH_3), 3.46 (d, *J* = 5.0 Hz, 1 H, OH), 5.75 (s, 1 H, olefinic H), 5.87 (d, *J* = 5.0 Hz, 1 H, benzylic H), 6.05 (s, 1 H, olefinic H), 7.16 (t, *J* = 7.5 Hz, 1 H, ArH), 7.28 (d, *J* = 7.5 Hz, 1 H, ArH), 7.34 (d, *J* = 7.5 Hz, 1 H, ArH), 7.42 (t, *J* = 7.5 Hz, 1 H, ArH), 7.57−7.62 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8 (q), 72.6 (d), 122.8 (s), 124.5 (d), 125.3 (d), 125.4 (d), 127.0 (d), 129.4 (t), 129.6 (d), 129.7 (s), 131.4 (d), 137.1 (s), 139.1 (s), 145.3 (s), 149.4 (s), 198.3 (s) ppm. IR (NaCl): ṽ = 3452 (OH), 1651 (C=O), 1121 cm^{-1} (CF_3). MS (EI): *m*/*z* (%) = 352 (7) [M$^+$], 177 (100). $C_{18}H_{15}F_3O_2S$ (352.37): calcd. C 61.35, H 4.29; found C 61.13, H 4.28.

2-(1-Hydroxy-1-phenylmethyl)-1-[2-(methylthio)phenyl]propenone (6d): Yellow prisms (from CH_2Cl_2/hexane), m.p. 88−89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, SCH_3), 3.23 (d, *J* = 4.5 Hz, 1 H, OH), 5.71 (s, 1 H, olefinic H), 5.84 (d, *J* = 4.5 Hz, 1 H, benzylic H), 6.02 (s, 1 H, olefinic H), 7.13 −7.17 (m, 1 H, ArH), 7.27−7.47 (m, 8 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.1 (q), 73.4 (d), 124.6 (d), 127.0 (d), 127.5 (d), 128.0 (d), 128.7 (d), 129.0 (t), 129.9 (d), 131.5 (d), 137.7 (s), 139.4 (s), 141.5 (s), 150.4 (s), 198.7 (s) ppm. IR (KBr): ṽ = 3503 (OH), 1631 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 284 (6) [M$^+$], 237 (100). $C_{17}H_{16}O_2S$ (284.37): calcd. C 71.80, H 5.67; found C 71.59, H 5.72.

2-(1-Hydroxy-3-phenylpropyl)-1-[2-(methylthio)phenyl]propenone (6e): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03−2.11 (m, 2 H, 2′-H), 2.43 (s, 3 H, SCH_3), 2.74−2.81 (m, 2 H, 3′-H and OH), 2.86−2.94 (m, 1 H, 3′-H), 4.67 (dd, *J* = 4.9, 7.8 Hz, 1 H, 1′-H), 5.67 (s, 1 H, olefinic H), 6.12 (s, 1 H, olefinic H), 7.17−7.45 (m, 9 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8 (q), 32.0 (t), 37.7 (t), 70.9 (d), 124.4 (d), 125.8 (d), 127.3 (d), 128.3 (t), 128.4 (d), 128.5 (d), 129.3 (d), 131.0 (d), 137.8 (s), 138.5 (s), 141.7 (s), 150.2 (s), 198.8 (s) ppm. IR (NaCl): ṽ = 3451 (OH), 1651 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 312 (7) [M$^+$], 91 (100). $C_{19}H_{20}O_2S$ (312.43): calcd. C 73.04, H 6.45; found C 72.76, H 6.55.

2-[1-Hydroxy-1-(4-nitrophenyl)methyl]-1-[2-(methylseleno)phenyl]-propenone (7a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, $SeCH_3$), 3.48 (d, *J* = 5.4 Hz, 1 H, OH), 5.77 (s, 1 H, olefinic H), 5.91 (d, *J* = 5.4 Hz, 1 H, benzylic H), 6.05 (s, 1 H, olefinic H), 7.21 (t, *J* = 7.3 Hz, 1 H, ArH), 7.41 (t, *J* = 7.3 Hz, 1 H, ArH), 7.42 (d, *J* = 7.3 Hz, 1 H, ArH), 7.49 (d, *J* = 7.3 Hz, 1 H, ArH), 7.66 (d, *J* = 8.3 Hz, 2 H, ArH), 8.21 (d, *J* = 8.3 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.6 (q), 72.9 (d), 123.7 (d), 124.8 (d), 127.4 (d), 128.7 (t), 129.9 (d), 130.9 (d), 132.1 (d), 135.8 (s), 137.1 (s), 147.5 (s), 148.5 (s), 148.6 (s), 198.0 (s) ppm. IR (NaCl): ṽ = 3440 (OH), 1640 (C=O), 1520 (NO_2), 1350 cm^{-1} (NO_2). MS (EI): *m*/*z* (%) = 377 (25) [M$^+$], 282 (100). $C_{17}H_{15}NO_4Se$ (376.27): calcd. C 54.27, H 4.02, N 3.72; found C 54.09, H 4.19, N 3.64.

2-[1-(4-Chlorophenyl)-1-hydroxymethyl]-1-[2-(methylseleno)-phenyl]propenone (7b): Yellow plates (CH_2Cl_2/hexane), m.p. 97−98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, $SeCH_3$), 3.29 (br. s, 1 H, OH), 5.69 (s, 1 H, olefinic H), 5.81 (s, 1 H, benzylic H), 6.00 (s, 1 H, olefinic H), 7.19 (t, *J* = 7.3 Hz, 1 H, ArH), 7.32 (d, *J* = 8.3 Hz, 2 H, ArH), 7.39−7.48 (m, 5 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.7 (q), 73.3 (d), 125.0 (d), 127.9 (t), 128.3 (d), 128.9 (d), 129.9 (d), 131.4 (d), 132.2 (d), 133.9 (s), 136.2 (s), 137.6 (s), 140.0 (s), 149.6 (s), 198.5 (s) ppm. IR (KBr): ṽ = 3444 (OH), 1644 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 366 (20) [M$^+$], 271 (100). $C_{17}H_{15}ClO_2Se$ (365.71): calcd. C 55.83, H 4.13; found C 55.70, H 4.16.

(1*R,1′*S**,3*S**)-3-[1-Hydroxy-1-(4-nitrophenyl)methyl]-1-methyl-4-oxothiochromanium Tetrafluoroborate (8a):** Colorless needles (acetone/CH_2Cl_2), m.p. 199−201 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.10 (s, 3 H, SCH_3), 3.60 (dd, *J* = 4.9, 15.1 Hz, 1 H, -CH_2S), 3.61 (ddd, *J* = 2.9, 4.9, 10.3 Hz, 1 H, CHCO), 4.02 (dd, *J* = 10.3, 15.1 Hz, 1 H, -CH_2S), 4.36 (d, *J* = 4.4 Hz, 1 H, OH), 5.79 (dd, *J* = 2.9, 4.4 Hz, 1 H, benzylic H), 7.71 (d, *J* = 8.8 Hz, 2 H, ArH), 7.93 (m, 3 H, ArH), 8.28 (d, *J* = 8.8 Hz, 2 H, ArH), 8.38 (dd, *J* = 2.2, 7.1 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.6 (q), 38.0 (t), 51.3 (d), 70.1 (d), 124.5 (d), 128.2 (d), 128.8 (s), 129.1 (d), 131.4 (d), 131.7 (s), 134.1 (d), 136.6 (d), 148.6 (s), 149.7 (s), 189.8 (s) ppm. IR (KBr): ṽ = 3414 (OH), 1618 (C=O), 1521 (NO_2), 1306 (NO_2), 1084 cm^{-1} (BF_4^-). MS (EI or FAB): no [M$^+$] or [M$^+$ +1] peak. $C_{17}H_{16}BF_4NO_4S$ (417.18): calcd. C 48.94, H 3.87, N 3.36; found C 49.06, H 3.90, N 3.18.

(1′*R,3*R**)-3-[1-Hydroxy-1-(4-nitrophenyl)methyl]selenochroman-4-one (*syn*-9a):** Yellow needles (CH_2Cl_2/hexane), m.p. 129−130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (dd, *J* = 3.2, 12.2 Hz, 1 H, CH_2Se), 3.15 (br. s, 1 H, OH), 3.32 (dt, *J* = 3.2, 13.2 Hz, 1 H, -CHCO), 3.48 (dd, *J* = 12.2, 13.2 Hz, 1 H, CH_2Se), 5.78 (d, *J* = 3.2 Hz, 1 H, benzylic H), 7.24 (dd, *J* = 3.4, 7.8 Hz, 1 H, ArH), 7.36 (d, *J* = 3.4 Hz, 2 H, ArH), 7.57 (d, *J* = 8.8 Hz, 2 H, ArH), 8.11 (d, *J* = 7.8 Hz, 1 H, ArH), 8.25 (d, *J* = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.9 (t), 54.7 (d), 70.8 (d), 123.7 (d), 125.7 (d), 126.8 (d), 129.9 (d), 130.4 (d), 133.2 (s), 133.7 (d), 136.4 (s), 147.3 (s), 148.5 (s), 196.8 (s) ppm. IR (KBr): ṽ = 3503 (OH), 1668 (C=O), 1518 (NO_2), 1346 cm^{-1} (NO_2). MS (EI): *m*/*z* (%) = 363 (8) [M$^+$], 184 (100). $C_{16}H_{13}NO_4Se$ (362.24): calcd. C 53.05, H 3.62, N 3.87; found C 53.17, H 3.60, N 3.90.

(1′*R,3*S**)-3-[1-Hydroxy-1-(4-nitrophenyl)methyl]selenochroman-4-one (*anti*-9a):** Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (dd, *J* = 3.4, 12.2 Hz, 1 H, CH_2Se), 2.98 (t, *J* = 12.2 Hz, 1 H, CH_2Se), 3.27 (ddd, *J* = 3.4, 7.8, 12.2 Hz, 1 H, -CHCO), 4.01 (br. s, 1 H, OH), 5.25 (d, *J* = 7.8 Hz, 1 H, benzylic H), 7.26 (dd, *J* = 3.4, 7.8 Hz, 1 H, ArH), 7.36−7.39 (m, 2 H, ArH), 7.65 (d, *J* = 8.8 Hz, 2 H, ArH), 8.14 (d, *J* = 7.8 Hz, 1 H, ArH), 8.25 (d, *J* = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4

(t), 54.2 (d), 73.9 (d), 123.8 (d), 125.9 (d), 128.1 (d), 129.9 (d), 130.7 (d), 132.9 (s), 133.8 (d), 136.3 (s), 147.7 (s), 147.8 (s), 197.9 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3503 (OH), 1669 (C=O), 1518 (NO_2), 1345 cm^{-1} (NO_2). MS (FAB, Gly): *m/z* (%) = 364 (2) [M^+ + H], 185 (100). HRMS (FAB, Gly): calcd. for $C_{16}H_{14}NO_4Se$ [M^+ + H]: 364.0010, found 364.0085.

(1′*R,3*R**)-3-[1-Hydroxy-1-(4-chlorophenyl)methyl]selenochroman-4-one (*syn*-9b):** Light yellow powder, m.p. 90−90.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.73 (dd, *J* = 2.9, 12.5 Hz, 1 H, CH_2Se), 2.99 (br. s, 1 H, OH), 3.24 (dt, *J* = 2.9, 12.5 Hz, 1 H, -CHCO), 3.45 (t, *J* = 12.5 Hz, 1 H, CH_2Se), 5.65 (t, *J* = 2.9 Hz, 1 H, benzylic H), 7.21−7.37 (m, 7 H, ArH), 8.10 (d, *J* = 7.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2 (t), 54.8 (d), 70.9 (d), 125.6 (d), 127.3 (d), 128.7 (d), 129.9 (d), 130.3 (d), 133.3 (s), 133.5 (d), 136.5 (s), 139.4 (s), 197.3 (s) ppm. One quaternary carbon is overlapped. IR (KBr): $\tilde{\nu}$ = 3745 (OH), 1665 cm^{-1} (C=O). MS (EI): *m/z* (%) = 352 (3) [M^+], 184 (100). $C_{16}H_{13}ClO_2Se$ (351.69): calcd. C 54.64, H 3.73; found C 54.86, H 3.77.

General Procedure for Reactions of 2-(Methylchalcogeno)phenyl Vinyl Ketone 1 or 4 with Ketone 10 or α-Dicarbonyl Compound 13: $BF_3{\cdot}Et_2O$ (127 mL, 1.0 mmol) was added dropwise at 0 °C to a stirred solution of 1-[2-(methylthio)phenyl]propenone (**1**; 178 mg, 1.0 mmol) and *p*-nitroacetophenone (**10a**; 83 mg, 0.5 mmol) in dry CH_3CN (1.5 mL). The mixture was stirred at the same temperature for 30 min, then poured into an $NaHCO_3$ solution (10 mL), and extracted with CH_2Cl_2 (5 mL, three times). The combined extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative TLC eluting with hexane/EtOAc (3:1) to give **11a**.

3-Hydroxy-2-methylene-1-[2-(methylthio)phenyl]-3-(4-nitrophenyl)-butan-1-one (11a): Yellow needles (EtOAc/hexane), m.p. 100−101 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.76 (s, 3 H, CH_3), 2.40 (s, 3 H, SCH_3), 4.98 (s, 1 H, OH), 5.90 (s, 1 H, olefinic H), 6.31 (s, 1 H, olefinic H), 7.19 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.31 (dd, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.33 (d, *J* = 7.5 Hz, 1 H, ArH), 7.44 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.71 (d, *J* = 8.8 Hz, 2 H, ArH), 8.19 (d, *J* = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8 (q), 29.0 (q), 76.1 (s), 123.5 (d), 124.4 (d), 126.0 (d), 127.2 (d), 129.7 (d), 130.1 (t), 131.6 (d), 136.8 (s), 139.6 (s), 147.0 (s), 150.5 (s), 154.1 (s), 200.0 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3448 (OH), 1631 (C=O), 1509 (NO_2), 1347 cm^{-1} (NO_2). MS (EI): *m/z* (%) = 343 (2) [M^+], 177 (100). $C_{18}H_{17}NO_4S$ (343.40): calcd. C 62.96, H 4.99, N 4.08; found C 63.08, H 5.10, N 3.98.

3-Hydroxy-2-methylene-1-[2-(methylthio)phenyl]-3-phenylbutan-1-one (11b): Yellow powder (EtOAc/hexane), m.p. 82−85 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, CH_3), 2.40 (s, 3 H, SCH_3), 5.00 (s, 1 H, OH), 5.76 (s, 1 H, olefinic H), 6.19 (s, 1 H, olefinic H), 7.15 (t, *J* = 7.8 Hz, 1 H, ArH), 7.22 (dt, *J* = 1.3, 7.8 Hz, 1 H, ArH), 7.31−7.35 (m, 4 H, ArH), 7.41 (t, *J* = 7.8 Hz, 1 H, ArH), 7.53 (d, *J* = 7.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7 (q), 29.2 (q), 76.3 (s), 124.1 (d), 124.9 (d), 126.90 (d), 126.95 (d), 128.2 (d), 128.7 (t), 130.0 (d), 131.4 (d), 137.1 (s), 139.8 (s), 146.3 (s), 151.6 (s), 200.3 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3445 (OH), 1626 cm^{-1} (C=O). MS (EI): *m/z* (%) = 298 (2) [M^+], 177 (100). HRMS (EI): calcd. for $C_{18}H_{18}O_2S$ [M^+]: 298.1027; found 298.1041.

2-(1-Hydroxycyclohexyl)-1-[2-(methylthio)phenyl]propenone (11c): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23−1.32 (m, 1 H), 1.55−1.62 (m, 2 H), 1.65−1.83 (m, 5 H), 1.84−1.95 (m, 2 H), 2.44 (s, 3 H, SCH_3), 3.81 (s, 1 H, OH), 5.54 (s, 1 H, olefinic H), 6.05 (s, 1 H, olefinic H), 7.18 (dt, *J* = 1.3, 7.3 Hz, 1 H, ArH), 7.34 (dd, *J* = 1.3, 7.3 Hz, 1 H, ArH), 7.42−7.46 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.5 (q), 21.6 (t), 25.6 (t), 36.3 (t), 72.9 (s), 124.0 (d), 126.1 (t), 126.6 (d), 130.5 (d), 131.3 (d), 137.4 (s), 139.8 (s), 153.7 (s), 200.8 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3484 (OH), 1651 cm^{-1} (C=O). MS (EI): *m/z* (%) = 276 (20) [M^+], 261 (100). $C_{16}H_{20}O_2S$ (276.39): calcd. C 69.53, H 7.29; found C 69.25, H 7.31.

3-Hydroxy-2-methylene-1-[2-(methylseleno)phenyl]-3-(4-nitrophenyl)butan-1-one (12a): Yellow needles (from $CHCl_3$), m.p. 170−171.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, CH_3), 2.24 (s, 3 H, $SeCH_3$), 5.06 (br. s, 1 H, OH), 5.84 (s, 1 H, olefinic H), 6.26 (s, 1 H, olefinic H), 7.22 (dt, *J* = 1.5, 7.8 Hz, 1 H, ArH), 7.41 (dt, *J* = 1.5, 7.8 Hz, 1 H, ArH), 7.46 (dd, *J* = 1.5, 7.8 Hz, 1 H, ArH), 7.49 (dd, *J* = 1.5, 7.8 Hz, 1 H, ArH), 7.70 (d, *J* = 8.8 Hz, 2 H, ArH), 8.18 (d, *J* = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.3 (q), 28.9 (q), 76.2 (s), 123.6 (d), 124.6 (d), 126.0 (d), 128.4 (t), 129.6 (d), 131.4 (d), 132.2 (d), 136.7 (s), 136.8 (s), 147.0 (s), 150.0 (s), 153.9 (s), 199.8 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3446 (OH), 1604 (C=O), 1519 (NO_2), 1347 cm^{-1} (NO_2). MS (EI): *m/z* (%) = 391 (15) [M^+], 225 (100). $C_{18}H_{17}NO_4Se$ (390.29): calcd. C 55.39, H 4.39, N 3.59; found C 55.13, H 4.44, N 3.52.

3-Hydroxy-2-methylene-1-[2-(methylseleno)phenyl]-3-phenylbutan-1-one (12b): Yellow plates (from CH_2Cl_2/hexane), m.p. 94−94.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, CH_3), 2.22 (s, 3 H, SeMe), 5.02 (s, 1 H, OH), 5.70 (s, 1 H, olefinic H), 6.15 (s, 1 H, olefinic H), 7.16−7.22 (m, 2 H, ArH), 7.31 (t, *J* = 7.8 Hz, 2 H, ArH), 7.38 (dt, *J* = 1.4, 7.3 Hz, 1 H, ArH), 7.44 (dd, *J* = 1.4, 7.3 Hz, 1 H, ArH), 7.52−7.53 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.2 (q), 29.1 (q), 76.4 (s), 124.3 (d), 125.0 (d), 126.96 (d), 127.04 (t), 128.2(d), 129.2 (d), 131.7 (d), 132.0 (d), 136.8 (s), 137.2 (s), 146.2 (s), 151.2 (s), 200.3 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3451 (OH), 1638 cm^{-1} (C=O). MS (EI): *m/z* (%) = 346 (15) [M^+], 225 (100). $C_{18}H_{18}O_2Se$ (345.29): calcd. C 62.61, H 5.25; found C 62.41, H 5.28.

2-(1-Hydroxycyclohexyl)-1-[2-(methylseleno)phenyl]propenone (12c): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24−1.32 (m, 1 H, cyclohexy H), 1.53−1.60 (m, 2 H, cyclohexyl H), 1.63−1.91 (m, 7 H, cyclohexyl H), 2.27 (s, 3 H, SeMe), 3.60 (s, 1 H, OH), 5.46 (s, 1 H, olefinic H), 5.99 (s, 1 H, olefinic H), 7.21 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.42 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.48 (dd, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.65 (dd, *J* = 1.3, 7.5 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.0 (q), 21.8 (t), 26.0 (t), 36.5 (t), 73.1 (s), 123.7 (t), 124.3 (d), 128.8 (d), 132.1 (d), 132.6 (d), 137.1 (s), 137.3 (s), 153.4 (s), 200.8 (s) ppm. IR (NaCl): $\tilde{\nu}$ = 3472 (OH), 1641 cm^{-1} (C=O). MS (EI): *m/z* (%) = 324 (45) [M^+], 309 (100). $C_{16}H_{12}O_2Se$ (323.29): calcd. C 59.44, H 6.24; found C 59.16, H 6.38.

2-Hydroxy-3-methylene-4-[2-(methylthio)phenyl]-1,2-diphenylbutane-1,4-dione (14a): Yellow powder (from EtOAc/hexane), m.p. 130−133 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, SCH_3), 5.39 (s, 1 H, olefinic H), 5.70 (s, 1 H, olefinic H), 5.90 (s, 1 H, OH), 7.23−7.31 (m, 3 H, ArH), 7.36 (dt, *J* = 1.3, 7.5 Hz, 2 H, ArH), 7.40−7.51 (m, 4 H, ArH), 7.68 (dd, *J* = 1.3, 7.5 Hz, 2 H, ArH), 7.94 (dd, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.95 (dt, *J* = 1.3, 7.5 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2 (q), 86.5 (s), 123.7 (d), 125.9 (d), 126.6 (d), 127.8 (d), 128.3 (d), 128.7 (d), 130.8 (d), 130.9 (t), 132.0 (d), 132.4 (d), 132.7 (d), 134.8 (s), 135.5 (s), 137.7 (s), 141.1 (s), 152.2 (s), 201.2 (s), 201.3 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3412 (OH), 1669 (C=O), 1613 cm^{-1} (C=O). MS (EI): *m/z* (%) = 388 (1) [M^+], 105 (100). HRMS (EI): calcd. for $C_{24}H_{20}O_3S$ [M^+]: 388.1133; found 388.1126.

3-Hydroxy-3-methyl-2-methylene-1-[2-(methylthio)phenyl]pentane-1,4-dione (14b): Yellow prisms (from EtOAc/hexane), m.p. 130−131

°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 2.44 (s, 3 H, SCH_3), 4.55 (s, 1 H, OH), 5.72 (s, 1 H, olefinic H), 6.17 (s, 1 H, olefinic H), 7.18 (dt, *J* = 1.3, 7.8 Hz, 1 H, ArH), 7.33 (dd, *J* = 1.3, 7.8 Hz, 1 H, ArH), 7.45 (dt, *J* = 1.3, 7.8 Hz, 1 H, ArH), 7.57 (dd, *J* = 1.3, 7.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.3 (q), 22.9 (q), 23.5 (q), 79.1 (s), 123.9 (d), 126.2 (d), 126.9 (t), 131.4 (d), 131.8 (d), 135.6 (s), 140.7 (s), 150.3 (s), 198.3 (s), 209.4 (s) ppm. IR (KBr): ν̃ = 3467 (OH), 1717 (C=O), 1651 cm^{-1} (C=O). MS (FAB, Gly): *m*/*z* (%) = 265 (12) [M$^+$ + H], 185 (100). $C_{14}H_{16}O_3S$ (264.34): calcd. C 63.61, H 6.10; found C 63.40, H 5.92.

Ethyl 2-Hydroxy-2-methyl-3-[2-(methylthio)benzoyl]but-3-enoate (14c): Colorless prisms (from EtOAc/hexane), m.p. 56−59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 2.44 (s, 3 H, SCH_3), 4.11 (s, 1 H, OH), 4.22−4.28 (m, 2 H, CH_2), 5.76 (s, 1 H, olefinic H), 6.24 (s, 1 H, olefinic H), 7.17 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.34 (dd, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.42 (dd, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.43 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (q), 16.4 (q), 23.8 (q), 62.0 (t), 74.2 (s), 124.0 (d), 126.5 (d), 127.9 (t), 130.3 (d), 131.4 (d), 136.4 (s), 139.8 (s), 149.5 (s), 174.8 (s), 198.0 (s) ppm. IR (KBr): ν̃ = 3464 (OH), 1722 (C=O), 1658 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 294 (2) [M$^+$], 221 (100). $C_{15}H_{18}O_4S$ (297.37): calcd. C 61.20, H 6.16; found C 61.20, H 6.20.

Methyl 2-Hydroxy-3-[2-(methylthio)benzoyl]-2-phenylbut-3-enoate (14d): Light yellow crystal (from CH_2Cl_2/hexane), m.p. 109−111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, SCH_3), 3.81 (s, 3 H, OCH_3), 4.75 (s, 1 H, OH), 5.64 (s, 1 H, olefinic H), 5.78 (s, 1 H, olefinic H), 7.20 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.35−7.44 (m, 5 H, ArH), 7.58 (dd, *J* = 1.3, 7.5 Hz, 1 H, ArH), 7.70 (dd, *J* = 1.3, 7.5 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.4 (q), 53.2 (q), 79.5 (s), 124.0 (d), 126.5 (d), 126.7 (d), 128.2 (d), 128.3 (d), 130.6 (d), 131.6 (d), 132.0 (t), 136.2 (s), 137.8 (s), 140.0 (s), 150.8 (s), 174.0 (s), 198.7 (s) ppm. IR (KBr): ν̃ = 3448 (OH), 1728 (C=O), 1656 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 342 (3) [M$^+$], 177 (100). HRMS (EI): calcd. for $C_{19}H_{18}O_4S$ [M$^+$]: 342.0926; found 342.0934.

2-Hydroxy-3-methylene-4-[2-(methylseleno)phenyl]-1,2-diphenylbutane-1,4-dione (15a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, $SeCH_3$), 5.35 (s, 1 H, OH), 5.67 (s, 1 H, olefinic H), 6.03 (s, 1 H, olefinic H), 7.26−7.48 (m, 9 H, ArH), 7.67 (dd, *J* = 1.3, 7.6 Hz, 2 H, ArH), 7.95 (dd, *J* = 1.3, 7.6 Hz, 2 H, ArH), 8.08 (dd, *J* = 1.3, 7.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.8 (q), 86.9 (s), 124.3 (d), 126.5 (d), 127.8 (d), 128.3 (d), 128.5 (d), 128.6 (d), 130.0 (t), 130.9 (d), 132.4 (d), 132.7 (d), 133.7 (d), 134.6 (s), 136.0 (s), 137.6 (s), 137.8 (s), 151.5 (s), 201.0 (s), 201.6 (s) ppm. IR (NaCl): ν̃ = 3439 (OH), 1672 (C=O), 1631 cm^{-1} (C=O). MS (FAB, NBA): *m*/*z* (%) = 437 (10) [M$^+$ + H], 154 (100). HRMS (FAB, NBA): calcd. for $C_{24}H_{21}O_3Se$ [M$^+$ + H]: 437.0578; found 437.0646.

3-Hydroxy-3-methyl-2-methylene-1-[2-(methylseleno)phenyl]-pentane-1,4-dione (15b): Yellow powder, m.p. 117.5−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 3 H, Me), 2.26 (s, 3 H, SeMe), 2.34 (s, 3 H, COMe), 4.56 (s, 1 H, OH), 5.67 (s, 1 H, olefinic H), 6.11 (s, 1 H, olefinic H), 7.22 (dt, *J* = 1.0, 7.5 Hz, 1 H, ArH), 7.43 (dt, *J* = 1.0, 7.5 Hz, 1 H, ArH), 7.46 (dd, *J* = 1.0, 7.5 Hz, 1 H, ArH), 7.74 (dd, *J* = 1.0, 7.5 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.8 (q), 22.9 (q), 23.3 (q), 79.3 (s), 124.3 (d), 125.0 (t), 128.6 (d), 132.4 (d), 132.9 (d), 135.9 (s), 137.6 (s), 149.9 (s), 198.1 (s), 209.1 (s) ppm. IR (NaCl): ν̃ = 3440 (OH), 1714 (C=O), 1645 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 312 (2) [M$^+$], 269 (100). $C_{14}H_{10}O_3Se$ (311.24): calcd. C 54.03, H 5.18; found C 53.92, H 5.21.

Ethyl 2-Hydroxy-2-methyl-3-[2-(methylseleno)benzoyl]but-3-enoate (15c): Pale yellow cubic (diethyl ether), m.p. 53−54.5 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 6.8 Hz, 3 H, CH_2CH_3), 1.69 (s, 3 H, CH_3), 2.26 (s, 3 H, $SeCH_3$), 4.10 (br. s, 1 H, OH), 4.25 (m, 2 H, CH_2CH_3), 5.69 (s, 1 H, olefinic H), 6.18 (s, 1 H, olefinic H), 7.21 (dt, *J* = 1.3, 7.8 Hz, 1 H, ArH), 7.41 (dt, *J* = 1.3, 7.8 Hz, 1 H, ArH), 7.47 (dd, *J* = 1.3, 7.8 Hz, 1 H, ArH), 7.63 (dd, *J* = 1.3, 7.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.9 (q), 14.0 (q), 24.0 (q), 62.2 (t), 74.6 (s), 124.3 (d), 126.1 (t), 129.0 (d), 132.0 (d), 132.2 (d), 136.6 (s), 136.7 (s), 149.1 (s), 174.9 (s), 197.9 (s) ppm. IR (KBr): ν̃ = 3493 (OH), 1731 (C=O), 1651 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 342 (29) [M$^+$], 269 (100). $C_{15}H_{18}O_4Se$ (341.26): calcd. C 52.79, H 5.32; found C 52.77, H 5.44.

Methyl 2-Hydroxy-3-[2-(methylseleno)benzoyl]-2-phenylbut-3-enoate (15d): Yellow prisms (EtOAc/hexane), m.p. 139.5−140.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, $SeCH_3$), 3.80 (s, 3 H, CO_2CH_3), 4.83 (br. s, 1 H, OH), 5.60 (s, 1 H, olefinic H), 5.75 (s, 1 H, olefinic H), 7.24 (dt, *J* = 1.2, 7.8 Hz, 1 H, ArH), 7.35−7.45 (m, 4 H, ArH), 7.49 (d, *J* = 7.8 Hz, 1 H, ArH), 7.69 (dd, *J* = 1.2, 7.8 Hz, 2 H, ArH), 7.73 (dd, *J* = 1.2, 7.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.0 (q), 53.2 (q), 80.0 (s), 124.4 (d), 126.7 (d), 128.3 (d), 128.4 (d), 129.1 (d), 130.8 (t), 132.1 (d), 136.5 (s), 136.7 (s), 137.9 (s), 150.3 (s), 174.0 (s), 198.9 (s) ppm. IR (KBr): ν̃ = 3480 (OH), 1732 (C=O), 1651 (C=O). MS (EI): *m*/*z* (%) = 390 (17) [M$^+$], 105 (100). $C_{19}H_{18}O_4Se$ (389.30): calcd. C 58.62, H 4.66; found C 58.46, H 4.76.

Ethyl 2-Hydroxy-2-(4-oxoselenochroman-3-yl)propionate (16c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3), 1.48 (s, 3 H, CH_3), 3.10 (dd, *J* = 3.4, 12.2 Hz, 1 H, CH_2Se), 3.49 (dd, *J* = 12.2, 13.7 Hz, 1 H, CH_2Se), 3.62 (dd, *J* = 3.4, 13.7 Hz, 1 H, CHC=O), 4.26 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 7.20 (dt, *J* = 1.5, 7.8 Hz, 1 H, ArH), 7.34 (dt, *J* = 1.5, 7.8 Hz, 1 H, ArH), 7.39 (dd, *J* = 1.5, 7.8 Hz, 1 H, ArH), 8.06 (dd, *J* = 1.5, 7.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (q), 17.9 (t), 24.2 (q), 55.7 (d), 61.9 (t), 73.9 (s), 125.7 (d), 129.8 (d), 130.5 (d), 133.3 (d), 133.5 (s), 136.1 (s), 176.5 (s), 195.6 (s) ppm. IR (NaCl): ν̃ = 3490 (OH), 1734 (C=O), 1672 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 328 (15) [M$^+$], 49 (100). HRMS (EI) calcd. for $C_{14}H_{16}O_4Se$ [M$^+$]: 328.0214; found 328.0207.

Methyl 1-Hydroxy-1-(4-oxoselenochroman-3-yl)-1-phenylacetate (16d): Pale yellow prisms (diethyl ether), m.p. 114−114.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (dd, *J* = 3.4, 12.7 Hz, 1 H, -CH_2Se), 3.38 (dd, *J* = 12.7, 13.7 Hz, 1 H, -CH_2Se), 3.78 (s, 3 H, OCH_3), 4.03 (br. s, 1 H, OH), 4.15 (dd, *J* = 3.4, 13.7 Hz, 1 H, CHC=O), 7.21 (dt, *J* = 1.5, 7.3 Hz, 1 H, ArH), 7.31−7.42 (m, 5 H, ArH), 7.70 (dd, *J* = 1.5, 7.3 Hz, 2 H, ArH), 8.13 (dd, *J* = 1.5, 7.3 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1 (t), 53.2 (q), 57.0 (d), 78.4 (s), 125.6 (d), 125.7 (d), 128.2 (d), 128.7 (d), 129.9 (d), 130.1 (s), 130.6 (d), 133.4 (d), 136.5 (s), 138.5 (s), 174.6 (s), 195.8 (s) ppm. IR (KBr): ν̃ = 3498 (OH), 1734 (C=O), 1672 cm^{-1} (C=O). MS (EI): *m*/*z* (%) = 376 (10) [M$^+$], 105 (100). $C_{18}H_{16}O_4Se$ (375.28): calcd. C 57.61, H 4.30; found C 57.56, H 4.40.

Synthesis of 17: A solution of *p*-nitrobenzaldehyde (**5a**; 6.25 g, 41.4 mmol) and 4-(trimethylsilyloxy)thiochrom-3-ene[15] (7.74 g, 45.5 mmol) in dry THF (50 mL) was added to a suspension of TBAF (540 mg, 2.1 mmol) in THF (5 mL) at −78 °C. After stirring at that temperature for 3 h and at −40 °C for 1 h, the reaction

mixture was quenched by adding AcOH/H_2O (40 mL) and stirred at room temperature overnight. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (100 mL, three times). The combined extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc, 3:1) to yield **17** as a yellow powder (*syn*/*anti* = 4:1, 7.84 g, 60%). The mixture of diastereomers **17** was separated into *syn* and *anti* isomers by recycling preparative HPLC with $CHCl_3$.

(1′*R,3*R**)-3-[1-Hydroxy-1-(4-nitrophenyl)methyl]thiochroman-4-one (*syn*-17):** Yellow needles (from CH_2Cl_2/hexane), m.p. 130−131.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (dd, *J* = 3.2, 13.4 Hz, 1 H, SCH_2), 2.97 (br. s, 1 H, OH), 3.19 (dt, *J* = 3.2, 13.4 Hz, 1 H, COCH), 3.48 (t, *J* = 13.4 Hz, 1 H, SCH_2), 5.84 (d, *J* = 3.2 Hz, 1 H, benzylic H), 7.19−7.30 (m, 2 H, ArH), 7.42 (dt, *J* = 1.2, 7.8 Hz, 1 H, ArH), 7.58 (d, *J* = 8.3 Hz, 2 H, ArH), 8.12 (dd, *J* = 1.2, 7.8 Hz, 1 H, ArH), 8.27 (d, *J* = 8.3 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3 (t), 54.4 (d), 69.9 (d), 123.7 (d), 125.0 (d), 126.7 (d), 127.4 (d), 129.5 (d), 130.7 (s), 133.7 (d), 142.0 (s), 147.3 (s), 148.5 (s), 195.2 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3414 (OH), 1671 (C=O), 1518 (NO_2), 1345 cm^{-1} (NO_2). MS (EI): *m*/*z* (%) = 315 (2) [M^+], 136 (100). $C_{16}H_{12}NO_4S$ (315.34): calcd. C 60.94, H 4.16, N 4.44; found C 60.72, H 4.25, N 4.32.

(1′*R,3*S**)-3-[1-Hydroxy-1-(4-nitrophenyl)methyl]thiochroman-4-one (*anti*-17):** Yellow solid, m.p. 133−133.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.72 (dd, *J* = 3.4, 13.4 Hz, 1 H, SCH_2), 2.97 (dd, *J* = 12.2, 13.4 Hz, 1 H, SCH_2), 3.14 (ddd, *J* = 3.4, 8.3, 12.2 Hz, 1 H, COCH), 4.17 (br. s, 1 H, OH), 5.25 (d, *J* = 8.3 Hz, 1 H, benzylic H), 7.19−7.26 (m, 2 H, ArH), 7.43 (dt, *J* = 1.2, 7.6 Hz, 1 H, ArH), 7.65 (d, *J* = 8.8 Hz, 1 H, ArH), 8.13 (dd, *J* = 1.2, 7.6 Hz, 1 H, ArH), 8.26 (d, *J* = 7.6 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7 (t), 53.4 (d), 72.8 (d), 123.5 (d), 124.9 (d), 127.1 (d), 127.7 (d), 129.5 (d), 130.0 (s), 133.7 (d), 141.5 (s), 147.2 (s), 147.6 (s), 196.3 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3391 (OH), 1674 (C=O), 1518 (NO_2), 1346 cm^{-1} (NO_2). MS (EI): *m*/*z* (%) = 315 (1) [M^+], 136 (100). $C_{16}H_{12}NO_4S$ (315.34): calcd. C 60.94, H 4.16, N 4.44; found C 60.81, H 4.22, N 4.37.

Preparation and Reactivity of Sulfonium Salt 8a: $AgBF_4$ (15 mg, 0.08 mmol) was slowly added to a stirred mixture of **17** (22 mg, 0.07 mmol) and MeI (102 mg, 0.69 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature, stirred for 3 h, and then concentrated under reduced pressure. The residue was dissolved in CH_3CN (0.5 mL), and then saturated aqueous $NaHCO_3$ (0.5 mL) was added. The mixture was stirred at room temperature for 5 min and concentrated to dryness under reduced pressure. The residue was dissolved in CD_3CN and submitted to ^{1}H NMR spectroscopy.

Demethylation of *anti*-Sulfonium Salt 8: KI (25 mg, 0.15 mmol) was added to a solution of *anti*-sulfonium salt **8** (21 mg, 0.05 mmol) in CH_3CN (1 mL). The reaction mixture was stirred at room temperature for 1 h, concentrated under reduced pressure, and submitted to ^{1}H NMR spectroscopy in $CDCl_3$.

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