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The effects of C–S and C–Se bonds on torquoselectivity: stereoselective olefination of α-thio and α-selenoketones with ynolates

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ABSTRACT

Highly *Z*-selective olefination of acyclic α-thio and α-selenoketones with ynolates has been achieved, and the theoretical calculations of the transition states in the ring-opening of the intermediates, the β-lactone enolates, revealed that the torquoselectivity was controlled by the secondary orbital interactions between the σ orbital of the C–S bond or a lone pair orbital on the S and σ* orbitals of the breaking C–O bond, and the σ orbital of the breaking C–O bond or a lone pair orbital on the O on the ring and the σ* orbitals of the C–S bond. The synthetic applications of the resulting olefins are also shown.

1. Introduction

Torquoselectivity is a fundamental concept for the control of stereoselectivity in the thermal electrocyclic ring-opening reaction of unsaturated four-membered rings such as cyclobutenes and oxetenes.[1] According to Houk, the geometry of the alkenyl products is controlled by the torquoselectivity wherein the electron donating groups rotate outward and the electron withdrawing groups inward, via the orbital interactions between the breaking C–C σ or σ* orbitals and the appropriate bonding and/or antibonding orbitals of the substituents on the ring (Fig. 1).[1,2] On the other hand, Inagaki et al. propose the geminal bond participation.[3] However, experimental studies on the effects of the substituents as well as their synthetic applications have not been as thoroughly reported, probably due to difficulties in the preparation of the corresponding four-membered rings.[2]

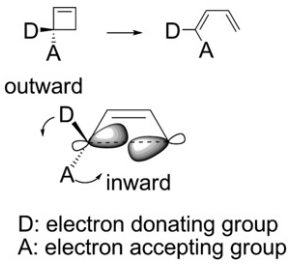
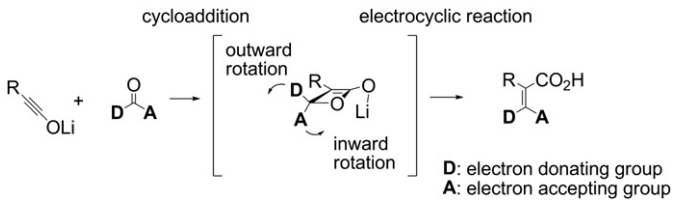


Figure 1. Torquoselectivity.

Recently, we developed a novel olefination methodology for carbonyl compounds with ynolates providing tetrasubstituted olefins with high stereoselectivities in which the β-lactone enolate intermediates (oxetenes) are ring-opened with high torquoselectivity (Scheme 1).[4] Olefinations of acylsilanes,[5] acylgermanes,[6] esters,[7] and alkynyl ketones[8] are based on the effect of controlling groups directly attached to the carbonyl group. In the course of this study, we have achieved a highly *Z*-selective olefination of α-alkoxy and α-aminoketones providing tetrasubstituted olefins where one carbon was inserted between the carbonyl group and the directing group, like the alkoxy group (Scheme 2).[9] In other words, the alkoxymethyl and aminomethyl groups rotate inward exclusively in



Scheme 1. Torquoselective olefination with ynolates.

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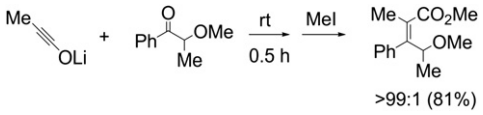


Scheme 2. Torquoselective olefination of α-oxyketones.

the ring-opening of the oxetenes, while an alkoxy group rotates outward exclusively in the olefination of esters.[6] Initially we had considered the chelation control by the ethereal alkoxy and the amino groups as hard Lewis bases; however, the secondary orbital interactions turned out to be critical for the torquoselectivity rather than chelation. Theoretical calculations and experimental evidence revealed that, in the transition states of the conrotatory ring-opening, the secondary orbital interactions between the breaking C–O σ* orbital and the C–H σ orbital (TSZ1), and partially between the breaking C–O σ orbital and the C–O σ* orbital (TSZ2), determined the torquoselectivity (Fig. 2). These results demonstrate the importance of the σ orbital as an electron donating group and the σ* orbital as an electron accepting group rather than chelation.[10] Based on this information, we decided to examine the olefination of thiomethyl and selenomethyl ketones since these substituents would work as electron accepting groups to give *Z*-olefins, even though sulfur and selenium atoms are softer Lewis bases than oxygen atoms. Theory indicates that the antibonding orbitals of C–S and C–Se bonds have potent electron accepting ability[11] but there has been no experimental evidence to support this indication. In this paper, we describe the effects of C–S and C–Se bonds on the torquoselectivity and the *Z*-selective olefination of α-thio and α-selenoketones.

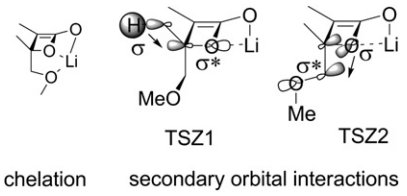


Figure 2. Torquoselectivity controlled by chelation or the secondary orbital interaction.

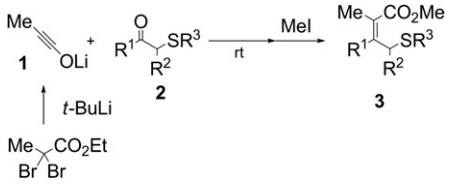
2. Results and discussion

2.1. Olefination of α-thioketones

We began our study on the olefination of α-dodecylthioketones (**2a**–**2c**) with ynolates. The lithium ynolate, prepared from ethyl 2,2-dibromopropionate with *t*-BuLi,[12] reacted with the ketones in THF at room temperature to afford the desired tetrasubstituted alkenes (**3a**–**3c**) with excellent *Z*-selectivity in good to moderate yields (Table 1, entries 1–3). The olefination of α-phenylthioketones (**2d**–**2f**) furnished the tetrasubstituted alkenes (**3d**–**3f**) with acceptable high *Z*-selectivity (Table 1, entries 4–6). When the substrates of **2b** and **2e** were used, the yields were low, and the α-methylated ketones were isolated, due to the partial enolization of the ketones.

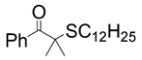
In contrast to the acyclic ketones, 2-phenylthiocycloalkanones induced no torquoselectivity (Scheme 3), although α-siloxycyclohexanone was olefinated to give an alkene in a *Z*/*E* ratio of 83:17.[9] If this reaction was controlled by the secondary orbital interactions, as was seen in the case of α-siloxycyclohexanone, the conformation of the directing group (RS–) might be more strongly fixed in the equatorial position (Fig. 3). Our previous work demonstrated that high torquoselectivity required the alkoxy-directing group to be in the axial orientation in the lactone enolate intermediate, but in the equatorial position it induced no selectivity.

Table 1
Olefination of α-thioketones with ynolates



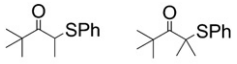
Entry	2	R^1	R^2	R^3	3	Yield (%)	*Z*:*E*
1	**2a**	Ph	Me	$C_{12}H_{25}$	**3a**	77	>99:1
2	**2b**	Ph	H	$C_{12}H_{25}$	**3b**	32[a]	>99:1
3	**2c**	Pr	Et	$C_{12}H_{25}$	**3c**	76	>99:1
4	**2d**	Ph	Me	Ph	**3d**	82	95:5
5	**2e**	*t*-Bu	H	Ph	**3e**	19[b]	83:17
6	**2f**	Pr	Et	Ph	**3f**	81	97:3

[a] A methylated ketone was generated

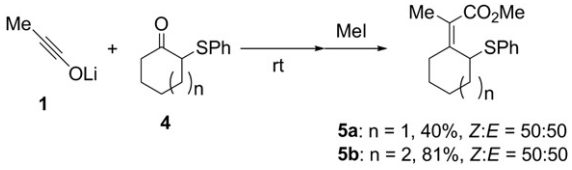


10%

[b] The methylated ketones were generated



36% 16%



Scheme 3. Olefination of cyclic α-thioketones.

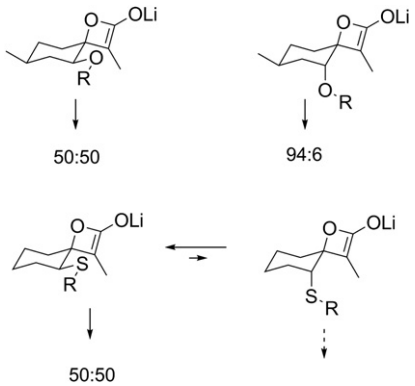
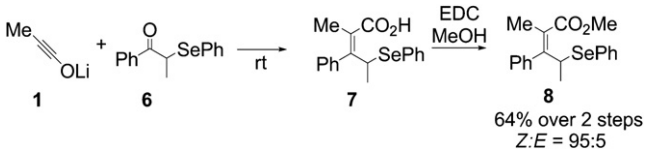


Figure 3. Possible conformation of the intermediates.

The fact that the A-value of CH_3S– (4.35 kJ/mol) is much larger than that of CH_3O– (2.30–3.14 kJ/mol) would support this hypothesis.[13]

2.2. Olefination of α-selenoketones

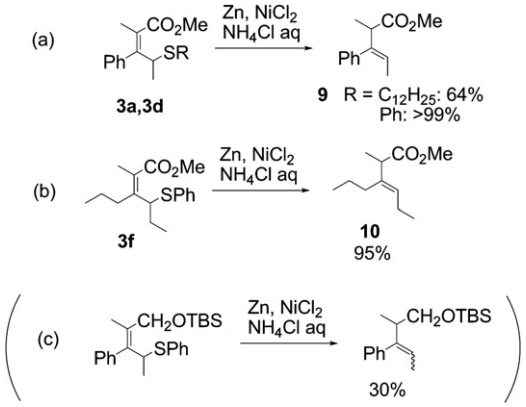
The olefination of the α-phenylselenoketone **6** provided the alkenes **8** with high *Z*-selectivity after methyl esterification (Scheme 4). From this result, acyclic α-seleno functionalities as well as α-oxy and α-amino groups were found to be good directing groups in the torquoselective olefination with ynolates.



Scheme 4. Olefination of α-selenoketone.

2.3. Synthetic utility

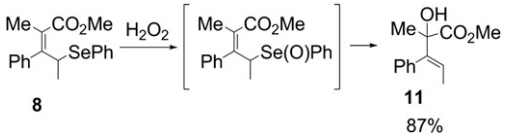
In order to show the synthetic utility of the olefination, several reactions of the sulfur and selenium functionalities were examined. Attempts at desulfurization of the olefins with activated Zn–$NiCl_2$–NH_4Cl aq[14] provided the unconjugated β,γ-unsaturated esters in only the *Z*-form (Scheme 5). Since, even in the absence of a conjugated phenyl group (Scheme 5b) or a conjugated carbonyl group (Scheme 5c), the double bond was isomerized by the



Scheme 5. Stereoselective synthesis of β,γ-unsaturated esters by desulfurization.

desulfurization, the trisubstituted olefins are therefore preferable to the tetrasubstituted olefins, probably due to the steric strain in the transition states of the protonation of the allylic radical or anion species. This represents a stereoselective synthesis of multi-substituted β,γ-unsaturated esters.

The seleno product **8** was converted into the *E*-allylic alcohol **11** via oxidation of the selenide followed by a [2,3]-sigmatropic rearrangement (Scheme 6).[15]



Scheme 6. [2,3]-Sigmatropic rearrangement.

2.4. Theoretical studies

B3LYP hybrid density functional calculations[16] were carried out for the olefination of α-methylthioacetone as a model compound. Since the C–S σ* orbital is expected to be more electron accepting than the C–O σ* orbital (Table 2), this torquoselectivity should also be controlled by the secondary orbital interactions. We obtained ten transition states leading to the *Z*-alkene (TSZ1-TSZ10), and eight transition states (TSE1-TSE8) leading to the *E*-alkene in the ring-opening of the β-lactone enolates. The chelated transition structure

Table 2
NBO energies of C–X σ- and σ*-orbitals in Hartrees at the B3LYP/6–31G* level

$H_3C{-}X{-}CH_3$ X = CH_2, O, S

	C–H	C–C	C–O	C–S
E_σ (au)	−0.51	−0.58	−0.79	−0.58
E_{σ^*} (au)	0.43	0.40	0.32	0.17

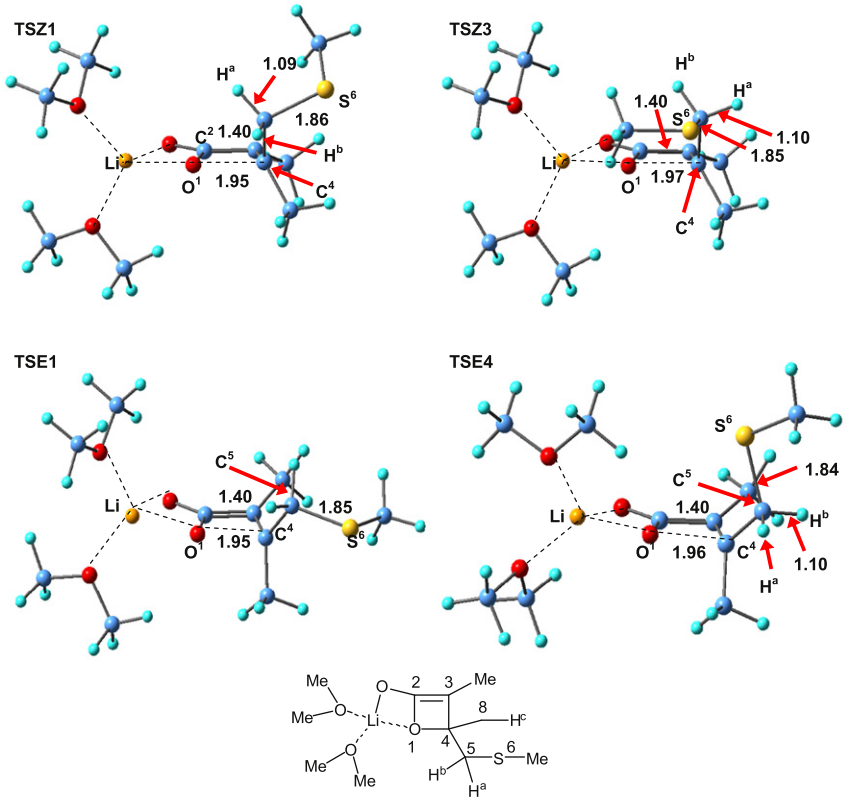


Figure 4. Structures of the transition states leading to the *E*- and *Z*-forms.

for the methylthio case (see Fig. 2) could not be located as for the methoxy analogue.[9] Representative structures are shown in Figure 4, with their relative energies listed in Table 3. Since the structure of TSZ2 was quite similar to that of TSZ1, and those of TSE2 and TSE3 likewise similar to that of TSE1, except for the arrangements of the coordinating ether, TSZ2, TSE2, and TSE3 are not shown in this table (see Supplementary data). TSZ1 and TSE1 were the most stable in energy, leading to the *Z*- and *E*-alkenes, respectively, and TSZ1 was more stable in enthalpy by 12.4 kJ/mol and in Gibbs energy by 12.3 kJ/mol, which is fairly consistent with the experimental results. In the most stable transition state for the methylthio case, TSZ1, the C^5–S^6 bond was nearly anti-periplanar to the breaking $C^4\cdots O^1$ bond (the dihedral angle of O^1–C^4–C^5–S^6 is −164°). In TSZ3, which was higher in enthalpy by 4.7 kJ/mol and in Gibbs energy by 4.3 kJ/mol, the S–Me bond in the methylthio group was almost perpendicular to the breaking $C^4\cdots O^1$ bond (the dihedral angle of O^1–C^4–C^5–S^6 is −79°), and the C^5–H^a bond was anti-periplanar to the breaking $C^4\cdots O^1$ bond (the dihedral angle of O^1–C^4–C^5–H^a is −165°) (Table 4). The other TSZs were much higher in energy than TSZ1 and TSZ3.

Table 3
Relative activation energies ($\Delta\Delta E^{\ddagger}$), activation enthalpies ($\Delta\Delta H^{\ddagger}$), and Gibbs free energies of activation ($\Delta\Delta G^{\ddagger}$) at 298.15 K of TSs relative to TSZ1 in kJ/mol

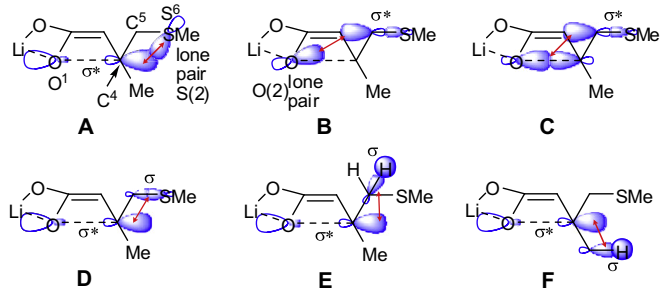
	$\Delta\Delta E$	$\Delta\Delta H$	$\Delta\Delta G$
TSZ1	0.0	0.0	0.0
TSZ3	5.6	4.7	4.3
TSE1	12.8	12.4	12.3
TSE4	16.8	16.0	16.8

Table 4
Representative bond angles in degrees

	(O^1–C^4–C^8)	(O^1–C^4–C^5)	(O^1–C^4–C^8–H^c)	(O^1–C^4–C^5–S^6)	(O^1–C^4–C^5–H^a)
TSZ1	117	93	−179	−164	78
TSZ3	119	95	−179	−79	−165
TSE1	94	115	170	151	−82
TSE4	93	121	172	−46	−165

NBO (natural bond orbital) analyses[17] were carried out to examine the differences in the stability with respect to the secondary orbital interactions (Table 5). The largest energy preference of TSZ1 over TSE1 was the interaction between a lone pair on S^6 and the σ* orbital of the breaking C^4–O^1 bond (**A**) by −11.9 kJ/mol. In TSZ1, there were other important interactions between the lone pair on O^1 and the σ* orbital of the anti-periplanar C^5–S^6 bond (**B**), the σ orbital of the C^4–O^1 bond and the σ* orbital of the anti-periplanar C^5–S^6 bond (**C**), the σ orbital of C^5–S^6 bond and the σ* orbital of C^4–O^1 bond (**D**), and the σ orbital of C^8–H^c bond and the σ* orbital of the anti-periplanar C^4–O^1 bond (**F**). These results show that 1) the thiomethyl substituent works both as an electron-donor and an electron-acceptor since the energy of the C–S σ bond was higher than that of the oxymethyl substituent while the energy of the C–S σ* bond was lower (see Table 2), and that 2) the orbital overlaps were larger in TSZ than in TSE. Although the interactions between the σ* orbital of C^4–O^1 bond and the σ orbitals of the anti-periplanar C^5–H^a and C^5–H^b bonds (**E**) exclusively stabilized TSZ3 and TSE4, no definitive differences were observed. On the other hand, only small differences among TSs were observed in the geminal bond participation[3] (see Table in Supplementary data). Consequently, these orbital interactions dominate the torquoselectivity.

Table 5
Second-order interaction energies between NBOs of the transition states in kJ/mol



TSs	A	B	C	D	E	F
TSZ1	−16.0	−6.8	−16.3	−22.6	−3.8	−35.5
TSZ3	−0.4	>−0.4	−0.8	−3.5	−30.2	−39.0
TSE1	−4.1	−0.5	−8.1	−14.4	>−0.4	−27.4
TSE4	>−0.4	>−0.4	−0.7	−3.9	−36.4	−25.9

3. Conclusion

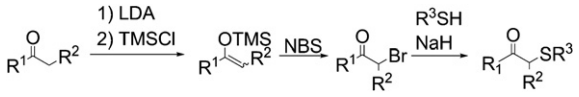
We have found a highly *Z*-selective olefination of α-thio and α-selenoketones with ynolates. Theoretical calculations revealed that the torquoselectivity was controlled by the secondary orbital interactions between the σ orbital of the C–S bond or a lone pair orbital on the S and σ* orbital of the breaking C–O bond and the interactions between the σ orbital of the breaking C–O bond or a lone pair orbital on the O and the σ* orbital of the C–S bond. These are the first experimental examples of the effects of sulfur and selenium on the torquoselectivity. This work not only contributes to a practical application of olefination but also provides new insights into torquoselectivity.

4. Experimental

4.1. General procedures

^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ solution and referenced to TMS (0.00 ppm) and $CDCl_3$ (77.0 ppm), respectively. All reactions were performed in oven-dried glassware under positive pressure of argon, unless otherwise noted. HPLC was performed using a Mightysil Si 60 column (10 mm×25 cm). The stereochemistry was determined by NOE experiments, unless otherwise indicated.

4.2. General procedure for the preparation of α-thioketones



To a solution of diisopropylamine (1.28 mL, 9.10 mmol) in THF (14 mL), cooled to −78 °C under argon, was added dropwise a solution of *n*-butyllithium (3.44 mL, 8.75 mmol, 2.54 M in hexane). The solution was stirred for 20 min at −78 °C and then trimethylsilyl chloride (freshly distilled from calcium hydride, 4.44 mL, 35 mmol) and a solution of the ketone (7.0 mmol) in THF (3 mL) were added. After 1 h, to the resulting reaction mixture was added triethylamine (4.88 mL, 35 mmol) and a saturated $NaHCO_3$ solution (14 mL), and the mixture was allowed to warm to room temperature. The resulting mixture was filtered with aspirator and separated. The water phase was extracted with hexane. The organic phase was washed with water, a saturated $NaHCO_3$ solution, and brine. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated to afford the silyl enol ether.

To a solution of silyl enol ether in THF (105 mL) was added *N*-bromosuccinimide (1.87 g, 10.5 mmol) at 0 °C. After being stirred at

0 °C for 30 min, the reaction mixture was poured into a saturated $NaHCO_3$ solution and extracted with Et_2O. The organic phase was dried over $MgSO_4$, filtered, and concentrated to afford a residue. Hexane was added to the residue, which then was filtered. The filtrate was concentrated to give the α-bromoketone.

To a solution of sodium hydride (NaH, 252 mg, 6.6 mmol, 62.7% in oil) in THF (24 mL) was added the thiol (6.6 mmol) at 0 °C. After 30 min, to the resulting mixture was added dropwise a solution of α-bromoketone (6.0 mmol) in THF (6 mL) at 0 °C. After being stirred at room temperature for 1.5 h, the reaction mixture was quenched with a saturated NH_4Cl solution at 0 °C and extracted with Et_2O. The organic phase was washed with water, brine, dried over $MgSO_4$, filtered, and concentrated to give a residue, which was purified by column chromatography to afford the α-thio ketone.

*4.2.1. 2-(Dodecylthio)-1-phenylpropan-1-one (**2a**).* Yield 91%. Pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, J=6.8 Hz, 3H), 1.21–1.32 (m, 18H), 1.43–1.52 (m, 2H), 1.56 (d, J=6.8 Hz, 3H), 2.37 (dt, J=7.2, 12.0 Hz, 1H), 2.53 (dt, J=7.6, 12.0 Hz, 1H), 4.32 (q, J=7.2 Hz, 1H), 7.46 (tt, J=1.6, 7.6 Hz, 2H), 7.56 (tt, J=1.6, 7.2 Hz, 1H), 8.01 (dd, J=1.2, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2 (q), 16.4 (q), 22.7(t), 28.7 (t), 28.9 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t), 29.6 (t×2), 31.9 (t), 41.5 (d), 128.4 (d), 128.4 (d), 132.8 (d), 135.6 (s), 195.8 (s); IR ($CHCl_3$): 1676 cm^{-1}; MS (EI) m/z 334 (M^+), 229 (100%). Anal. Calcd for $C_{21}H_{34}OS$: C, 75.39; H, 10.24. Found: C, 75.48; H, 10.17.

*4.2.2. 2-(Dodecylthio)-1-phenylethanone (**2b**).* Yield 93%. Yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, J=6.8 Hz, 3H), 1.24–1.37 (m, 18H), 1.54–1.62 (m, 2H), 2.56 (dd, J=7.2, 7.2 Hz, 2H), 3.78 (s, 2H), 7.47 (t, J=8.0 Hz, 2H), 7.58 (tt, J=1.6, 7.2 Hz, 1H), 7.98 (dd, J=2.0, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2 (q), 22.7 (t), 28.8 (t), 29.0 (t), 29.2 (t), 29.4 (t), 29.5 (t), 29.6 (t), 29.7 (t), 29.7 (t), 31.9 (t), 32.4 (t), 37.1 (t), 128.5 (d), 128.7 (d), 133.2 (d), 135.2 (s), 194.4 (s); IR ($CHCl_3$): 1674 cm^{-1}; MS (EI) m/z 320 (M^+), 105 (100%). Anal. Calcd for $C_{20}H_{32}OS$: C, 74.94; H, 10.06. Found: C, 74.84; H, 10.00.

*4.2.3. 3-(Dodecylthio)heptan-4-one (**2c**).* Yield 95% over 3 steps. Yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, J=6.8 Hz, 3H), 0.94 (t, J=7.2 Hz, 3H), 0.97 (J=7.2 Hz, 3H), 1.25–1.35 (m, 18H), 1.47–1.91 (m, 6H), 2.31–2.45 (m, 2H), 2.58 (dd, J=6.8, 7.6 Hz, 2H), 3.10 (dd, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.1 (q), 13.8 (q), 14.1 (q), 17.6 (t), 22.7 (t), 23.2 (t), 28.9 (t), 29.2 (t), 29.4 (t×2), 29.5 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.8 (t), 31.9 (t), 40.6 (t), 55.0 (d), 206.8 (s); IR (Neat): 1704 cm^{-1}; MS (EI) m/z 314 (M^+), 243 (100%); HRMS (EI) calcd for $C_{19}H_{38}OS$: 314.2643, found: 314.2667.

*4.2.4. 1-Phenyl-2-(phenylthio)propan-1-one (**2d**).* Yield 89%. Pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.54 (d, J=6.8 Hz, 3H), 4.63 (q, J=6.8 Hz, 1H), 7.26–7.36 (m, 5H), 7.45 (t, J=8.0 Hz, 2H), 7.56 (tt, J=1.2, 7.6 Hz, 1H), 7.95 (dd, J=1.2, 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.0 (q), 46.1 (d), 128.4 (d×2), 128.7 (d), 131.6 (s), 132.8 (d), 134.3 (d), 135.5 (s), 195.9 (s); IR (Neat): 1682 cm^{-1}; MS (EI) m/z 242 (M^+), 137 (100%); HRMS (EI) calcd for $C_{15}H_{14}OS$: 242.0765, found: 242.0771.

*4.2.5. 3,3-Dimethyl-1-(phenylthio)butan-2-one (**2e**).* Yield 84%. Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (s, 9H), 3.96 (s, 2H), 7.21 (tt, J=1.6, 7.2 Hz, 1H), 7.29 (tt, J=1.6, 7.2 Hz, 2H), 7.38 (dd, J=1.6, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.5 (q×3), 40.5 (t), 44.2 (s), 126.5 (d), 128.7 (d), 129.9 (d), 135.3 (s), 209.1 (s); IR (Neat): 1707 cm^{-1}; MS (EI) m/z 208 (M^+), 57 (100%).

*4.2.6. 3-(Phenylthio)heptan-4-one (**2f**).* Yield 70% over 3 steps. Pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, J=7.2 Hz, 3H), 1.02 (t, J=7.2 Hz, 3H), 1.54–1.63 (m, 4H), 1.70 (dd, J=7.2, 7.2 Hz, 2H), 3.55 (dd, J=7.2, 7.2 Hz, 1H), 7.25–7.31 (m, 3H), 7.36 (dd, J=1.6, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.9 (q), 13.7 (q), 17.2 (t), 23.7 (t), 41.3 (t), 58.5 (d), 127.5 (d), 128.8 (d), 132.2 (d), 133.0 (s), 207.0 (s); IR (Neat): 1707 cm^{-1}; MS (EI) m/z 222 (M^+), 151 (100%); HRMS (EI) calcd for $C_{13}H_{18}OS$: 222.1078, found: 222.1059.

*4.2.7. 2-(Phenylthio)cyclohexanone (**4a**).* Yield 86% . Pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.65–2.33 (m, 7H), 2.88–2.96 (m, 1H), 3.83 (ddd, J=1.6, 5.2, 6.0 Hz, 1H), 7.24 (tt, J=1.6, 7.2 Hz, 1H), 7.29 (tt, J=1.6, 6.8 Hz, 2H), 7.40 (dd, J=1.6, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.6 (t), 27.2 (t), 33.9 (t), 39.0 (t), 56.3 (d), 127.2 (d), 128.8 (d), 131.6 (d), 133.6 (s), 207.2 (s); IR (Neat): 1713 cm^{-1}; MS (EI) m/z 206 (M^+, 100%).

*4.2.8. 2-(Phenylthio)cycloheptanone (**4b**).* Yield 87% over 3 steps. Pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.28–2.28 (m, 8H), 2.39 (ddd, J=2.8, 7.2, 13.2 Hz, 1H), 2.78 (ddd, J=3.6, 11.6, 13.2 Hz, 1H), 3.78 (dd, J=5.6, 10.4 Hz, 1H), 7.21–7.31 (m, 3H), 7.40 (dd, J=1.2, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.3 (t), 27.0 (t), 29.8 (t), 30.3 (t), 39.8 (t), 57.2 (d), 127.2 (d), 128.7 (d), 131.6 (d), 133.6 (s), 208.5 (s); IR (Neat): 1699 cm^{-1}; MS (EI) m/z 220 (M^+), 110 (100%).

4.3. General procedure for the olefination of α-thio ketone

To a solution of ethyl 2,2-dibromopropionate (312 mg, 1.2 mmol) in THF (6 mL), cooled to −78 °C under argon, was added dropwise a solution of *tert*-butyllithium (3.58 mL, 4.8 mmol, 1.34 M in pentane). The yellow solution was stirred for 3 h at −78 °C and allowed to warm to 0 °C. After 30 min, the resulting pale yellow reaction mixture was warmed to room temperature, and a solution of thioketone **2** (1.0 mmol) in THF (2 mL) was added. After 0.5 h, methyl iodide (0.62 mL, 10 mmol) and HMPA (1.7 mL, 10 mmol) were added. After 18 h, a saturated NH_4Cl solution (10 mL) was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with water, a saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, filtered, and concentrated to give a residue, which was purified by column chromatography followed by preparative HPLC to afford the ester **3**.

*4.3.1. (Z)-Methyl 4-dodecylthio-2-methyl-3-phenyl-2-pentenoate (**3a**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, J=7.2 Hz, 3H), 1.16 (d, J=6.8 Hz, 3H), 1.20–1.41 (m, 18H), 1.55–1.62 (m, 1H), 1.63 (s, 3H), 2.45–2.59 (m, 2H), 3.80 (s, 3H), 4.62 (q, J=6.8 Hz, 1H), 7.15 (d, J=6.4 Hz, 2H), 7.29–7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2 (q), 17.9 (q), 19.8 (q), 22.7 (t), 29.2 (t), 29.4 (t), 29.4 (t), 29.6 (t), 29.7 (t×2), 29.7 (t), 29.7 (t), 31.6(t), 31.9 (t), 41.2 (d), 51.7 (q), 126.7 (s), 127.1 (d), 127.5 (d), 129.2 (d), 137.0 (s), 148.1 (s), 169.9 (s); IR (Neat): 1716 cm^{-1}; MS (EI) m/z 404 (M^+), 203 (100%); HRMS (EI) calcd for $C_{25}H_{40}O_2S$: 404.2749, found: 404.2761.

*4.3.2. (Z)-Methyl 4-dodecylthio-2-methyl-3-phenyl-2-butenoate (**3b**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, J=7.2 Hz, 3H), 1.20–1.32 (m, 18H), 1.43–1.50 (m, 2H), 1.76 (s, 3H), 2.39 (dd, J=7.2, 7.6 Hz, 2H), 3.78 (s, 2H), 3.81 (s, 3H), 7.19 (dd, J=1.2, 8.4 Hz, 2H), 7.30 (tt, J=1.2, 7.6 Hz, 1H), 7.37 (tt, J=1.2, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2 (q), 17.7 (q), 22.7 (t), 28.9 (t), 29.3 (t), 29.4 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.7 (t), 29.7 (t), 31.9 (t), 32.2 (t), 36.2 (t), 51.7 (q), 126.6 (s), 127.4 (d), 128.0 (d), 128.1 (d), 140.6 (s), 146.1 (s), 169.5 (s); IR (Neat): 1717 cm^{-1}; MS (EI) m/z 390 (M^+), 190 (100%); HRMS (EI) calcd for $C_{24}H_{38}O_2S$: 390.2593, found: 390.2556.

*4.3.3. (Z)-Methyl 4-dodecylthio-2-methyl-3-propyl-2-hexenoate (**3c**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, J=6.4 Hz, 3H), 0.93 (t, J=7.2 Hz, 3H), 1.20–1.35 (m, 18H), 1.40–1.61 (m, 6H), 1.92 (s, 3H), 2.02 (dt, J=4.4, 12.4 Hz, 1H), 2.20–2.40 (m, 3H), 3.71 (s, 3H), 4.16 (dd, J=6.8, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.4 (q), 14.1 (q), 14.9 (q), 16.3 (q), 22.7 (t), 23.0 (t), 26.4 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.6 (t), 29.6 (t), 29.7 (t), 29.9 (t), 31.4 (t), 31.4 (t), 31.9 (t),

49.9 (q), 51.4 (d), 126.3 (s), 147.1 (s), 170.3 (s); IR (Neat): 1717 cm^{-1}; MS (EI) *m*/*z* 384 (M^+), 55 (100%); HRMS (EI) calcd for $C_{23}H_{44}O_2S$: 384.3062, found: 384.3077.

*4.3.4. (Z)-Methyl 2-methyl-3-phenyl-4-phenylthio-2-pentenoate (**3d**).* Colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ: 1.28 (d, *J*=7.2 Hz, 3H), 1.56 (s, 3H), 3.65 (s, 3H), 5.23 (q, *J*=6.8 Hz, 1H), 7.16 (dd, *J*=1.6, 8.0 Hz, 2H), 7.22–7.39 (m, 6H), 7.44 (dd, *J*=1.6, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.9 (q), 19.9 (q), 45.4 (d), 51.7 (q), 127.0 (d), 127.1 (s), 127.2 (d), 127.8 (d), 128.7 (d), 128.9 (d), 132.4 (d), 135.3 (s), 137.4 (s), 148.5 (s), 169.4 (s); IR (Neat): 1714 cm^{-1}; MS (EI) *m*/*z* 312 (M^+), 203 (100%); HRMS (EI) calcd for $C_{19}H_{20}O_2S$: 312.1184, found: 312.1185.

*4.3.5. (Z)-Methyl 2,4,4-trimethyl-3-phenylthiomethyl-2-pentenoate (**3e**).* Pale yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ: 1.32 (s, 9H), 2.05 (s, 3H), 3.61 (s, 3H), 3.80 (s, 2H), 7.18 (tt, *J*=1.2, 7.6 Hz, 1H), 7.25–7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.8 (q), 30.3 (q×3), 35.9 (s), 37.0 (t), 51.7 (q), 126.1 (d), 128.7 (d), 129.9 (d), 130.1 (s), 137.2 (s), 144.3 (s), 171.8 (s); IR (Neat): 1716 cm^{-1}; MS (EI) *m*/*z* 278 (M^+), 57 (100%); HRMS (EI) calcd for $C_{16}H_{22}O_2S$: 278.1341, found: 278.1324.

*4.3.6. (Z)-Methyl 2-methyl-4-phenylthio-3-propyl-2-hexenoate (**3f**).* Pale yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ: 0.97 (t, *J*=7.2 Hz, 3H), 1.01 (t, *J*=7.2 Hz, 3H), 1.13–1.57 (m, 2H), 1.67–1.81 (m, 2H), 1.79 (s, 3H), 2.07 (dt, *J*=4.8, 13.2 Hz, 1H), 3.56 (s, 3H), 4.80 (dd, *J*=7.2, 8.0 Hz, 1H), 7.16–7.25 (m, 3H), 7.32 (dd, *J*=1.2, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.4 (q), 14.9 (q), 16.2 (q), 22.7 (t), 26.5 (t), 32.1 (t), 51.2 (q), 54.0 (d), 126.3 (s), 126.7 (d), 128.4 (d), 132.2 (d), 135.5 (s), 147.8 (s), 169.6 (s); IR (Neat): 1713 cm^{-1}; MS (EI) *m*/*z* 292 (M^+), 183 (100%); HRMS (EI) calcd for $C_{17}H_{24}O_2S$: 292.1497, found: 292.1488.

*4.3.7. (Z)-Methyl 2-(2-phenylthiocyclohexylidene)propionate (**5aZ**).* Pale yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ: 1.28–1.42 (m, 1H), 1.55–1.63 (m, 1H), 1.78–1.96 (m, 3H), 1.81 (s, 3H), 2.02–2.08 (m, 1H), 2.48–2.52 (m, 2H), 3.51 (s, 3H), 5.04 (t, *J*=3.2 Hz, 1H), 7.23–7.29 (m, 3H), 7.39 (dd, *J*=1.6, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.6 (q), 21.3 (t), 26.6 (t), 27.4 (t), 32.6 (t), 49.6 (d), 51.4 (q), 121.9 (s), 127.3 (d), 128.5 (d), 133.4 (d), 135.0 (s), 146.8 (s), 169.4 (s); IR (Neat): 1713 cm^{-1}; MS (EI) *m*/*z* 276 (M^+), 167 (100%); HRMS (EI) calcd for $C_{16}H_{20}O_2S$: 276.1184, found: 276.1159.

*4.3.8. (Z)-Methyl 2-(2-phenylthiocycloheptylidene)propionate (**5bZ**).* Pale yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ: 1.14–1.55 (m, 4H), 1.70–1.82 (m, 2H), 1.81 (s, 3H), 1.84–1.92 (m, 1H), 2.24–2.32 (m, 2H), 2.46 (dd, *J*=6.0, 13.6 Hz, 1H), 3.44 (s, 3H), 5.09 (dd, *J*=7.6, 10.0 Hz, 1H), 7.23–7.27 (m, 3H), 7.35–7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.7 (q), 25.7 (t), 27.6 (t), 28.0 (t), 30.7 (t), 33.0 (t), 49.9 (d), 51.2 (q), 125.3 (s), 127.6 (d), 128.4 (d), 134.1 (s), 134.7 (d), 149.5 (s), 169.4 (s); IR (Neat): 1712 cm^{-1}; MS (EI) *m*/*z* 290 (M^+), 181 (100%); HRMS (EI) calcd for $C_{17}H_{22}O_2S$: 290.1341, found: 290.1326.

4.4. 2-(Phenylseleno)-1-phenylpropan-1-one (6)

To a solution of diisopropylamine (0.547 mL, 3.9 mmol) in THF (12 mL), cooled to −78 °C under argon, was added dropwise a solution of *n*-butyllithium (2.62 mL, 3.75 mmol, 1.43 M in hexane). The solution was stirred for 20 min at −78 °C. A solution of propiophenone (403 mg, 3.0 mmol) in THF (3 mL) was then added. After 1 h, phenylselenyl chloride (1.15 mg, 6.0 mmol) was added to the reaction mixture at −78 °C. After 1.5 h, a saturated $NaHCO_3$ solution was added and the mixture was allowed to warm to room temperature. The water phase was extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to give a residue, which was purified by column chromatography to afford the α-selenoketone (782 mg, 90%) as a yellow oil: ^1H NMR (270 MHz, $CDCl_3$) δ: 1.65 (d, *J*=6.8 Hz, 3H), 4.69 (q, *J*=6.8 Hz, 1H), 7.23–7.57 (m, 8H), 7.89 (dd, *J*=1.6, 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.2 (q), 39.7 (d), 126.9 (s), 128.3 (d), 128.4 (d), 128.9 (d), 129.0 (d), 132.8 (d), 135.8 (s), 136.6 (d), 196.3 (s); IR (Neat): 1672 cm^{-1}; MS (EI) *m*/*z* 242 (M^+), 137 (100%); HRMS (EI) calcd for $C_{15}H_{14}OS$: 242.0765, found: 242.0771.

4.5. (*Z*)-Methyl 2-methyl-3-phenyl-4-(phenylseleno)pent-2-enoate (8)

To a solution of ethyl 2,2-dibromopropionate (468 mg, 1.8 mmol) in THF (9 ml), cooled to −78 °C under argon, was added dropwise a solution of *tert*-butyllithium (4.59 mL, 7.2 mmol, 1.57 M in pentane). The yellow solution was stirred for 10 min at −78 °C and allowed to warm to 0 °C. After 30 min, a solution of α-phenylselenylpropiophenone (434 mg, 1.5 mmol) in THF (3 mL) was added at room temperature. After 1 h, the mixture was concentrated in vacuo, and then diluted with hexane. The resulting solution was washed with water. The combined water phase was acidified with 1 M HCl solution and extracted with CH_2Cl_2. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to give the carboxylic acid. To a solution of the carboxylic acid (150 mg, 0.434 mmol) and MeOH (0.035 ml, 0.868 mmol) in CH_2Cl_2 was added EDC·HCl (91.6 mg, 0.478 mmol) and DMAP (2.4 mg, 0.0199 mmol) at room temperature. After 4 h, a saturated NH_4Cl solution was added and the mixture was extracted with CH_2Cl_2. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to give a residue, which was purified by column chromatography followed by HPLC to afford the methyl ester (117.5 mg, 64% over 2 steps) as a pale yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ: 1.33 (d, *J*=7.2 Hz, 3H), 1.56 (s, 3H), 3.61 (s, 3H), 5.40 (q, *J*=7.2 Hz, 1H), 7.22–7.41 (m, 8H), 7.58 (dd, *J*=1.6, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.9 (q), 20.5 (q), 41.1 (d), 51.6 (q), 126.0 (s), 127.3 (d), 127.7 (d), 127.8 (d), 127.9 (d), 128.9 (d), 130.0 (s), 135.5 (d), 138.0 (s), 149.8 (s), 169.4 (s); IR (Neat): 1709 cm^{-1}; MS (EI) *m*/*z* 360 (M^+), 203 (100%); HRMS (EI) calcd for $C_{19}H_{20}O_2Se$: 360.0629, found: 360.0633.

4.6. Representative procedure for desulfurization

To a solution of (*Z*)-methyl 2-methyl-3-phenyl-4-phenythio-2-pentenoate (**3d**, 10 mg, 0.032 mmol) in THF (2.5 ml) was added activated zinc (250 mg), a saturated NH_4Cl solution (0.5 ml) and $NiCl_2$ (50 mg, anhydrous), and the mixture was vigorously stirred at room temperature for 11 h. The mixture then was filtered and washed with a saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, filtered, and concentrated to give a residue, which was purified by preparative TLC (silica gel, hexane/AcOEt=75:25) to afford (*Z*)-methyl 2-methyl-3-phenyl-3-pentenoate (**9**, 6.7 mg, quant.) as a pale yellow oil.

*4.6.1. (Z)-Methyl 2-methyl-3-phenyl-3-pentenoate (**9**).* ^1H NMR (400 MHz, $CDCl_3$) δ: 1.26 (d, *J*=7.2 Hz, 3H), 1.53 (d, *J*=6.8 Hz, 3H), 3.43 (q, *J*=7.2 Hz, 1H), 3.64 (s, 3H), 5.69 (q, *J*=6.8 Hz, 1H), 7.11 (dd, *J*=1.6, 8.8 Hz, 2H), 7.25 (t, *J*=7.2 Hz, 1H), 7.33 (t, *J*=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.9 (q), 16.7 (q), 47.6 (d), 51.8 (q), 123.4 (d), 126.7 (d), 127.9 (d), 128.7 (d), 139.4 (s), 140.4 (s), 174.8 (s); IR (Neat): 1739 cm^{-1}; MS (EI) *m*/*z* 204 (M^+), 189 (100%, M^+-Me); HRMS (EI) calcd for $C_{13}H_{16}O_2$: 204.1150, found: 204.1142.

*4.6.2. (E)-Methyl 2-methyl-3-propyl-3-hexenoate (**10**).* Colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, *J*=7.2 Hz, 3H), 0.95 (t, *J*=7.2 Hz, 3H), 1.24 (d, *J*=7.2 Hz, 3H), 1.32–1.42 (m, 2H), 3.07 (q, *J*=6.8 Hz, 1H), 3.66 (s, 3H), 5.29 (t, *J*=7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3 (q), 14.5 (q), 16.9 (q), 21.3 (t), 22.2 (t), 32.1 (t), 45.8 (d), 51.7 (q), 128.9 (d), 137.4 (s), 175.5 (s); IR (Neat):

1739 cm^{-1}; MS (EI) *m*/*z* 184 (M^+), 55 (100%); HRMS (EI) calcd for $C_{11}H_{20}O_2$: 184.1463, found: 184.1461.

*4.6.3. (E)-Methyl 2-hydroxy-2-methyl-3-phenylpent-3-enoate (**11**).* To a solution of the γ-seleno ester (10 mg, 0.0278 mmol) in CH_2Cl_2 (0.3 ml) was added H_2O_2 (0.1 ml) slowly at 0 °C. The reaction mixture was stirred for 20 min at room temperature before a saturated Na_2SO_3 solution was added. The resulting mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated to give the residue, which was purified by preparative TLC to afford the trisubstituted olefin (5.3 mg, 87%) as a colorless oil: ^1H NMR (270 MHz, $CDCl_3$) δ: 1.45 (d, *J*=6.8 Hz, 3H), 1.57 (s, 3H), 3.25 (s, 1H), 3.69 (s, 3H), 6.00 (q, *J*=6.8 Hz, 1H), 7.06 (dd, *J*=1.6, 7.6 Hz, 2H), 7.24–7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.7 (s), 23.9 (q), 52.7 (q), 123.9 (d), 127.2 (d), 128.0 (d), 129.6 (d), 137.4 (s), 143.1 (s), 176.2 (s); IR (Neat): 3539 cm^{-1}, 1732 cm^{-1}; MS (EI) *m*/*z* 220 (M^+), 161 (100%); HRMS (EI) calcd for $C_{13}H_{16}O_3$: 220.1099, found: 220.1097.

4.7. Computational details

All calculations in the present study were performed with the Gaussian 03 program (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*, revision E.01; Gaussian Inc.: Wallingford, CT, 2004.). We employed the B3LYP hybrid functional with the 6-31G(d) basis sets for the transition states of the ring-opening process of a β-lactone enolate intermediate, the lithium 4-methylthiomethyl-3,4-dimethyloxet-2-enoxide, in which two Me_2O molecules are solvated to the lithium atom. The normal coordination analyses were performed for stationary points. One imaginary frequency was confirmed at each optimized TS structure. The origin of the stereoelectronic effects of the ring-opening of the β-lactone enolate derivative was examined with the aid of NBO analysis. The transition states of the ring-opening are reactant-like rather than product-like by optimal Lewis structure search. Second-order perturbation analysis of bonding NBOs and antibonding NBOs was carried out for these transition states. The second-order interaction energy is expressed as follows.

$$E^{(2)}_{\phi\phi^*} = -2\frac{\langle\phi|F|\phi^*\rangle^2}{\varepsilon_{\phi^*}-\varepsilon_{\phi}} = -2\frac{F^2_{ij}}{\Delta\varepsilon} \quad (1)$$

The ϕ/ϕ^* and *F* refer to the filled/vacant NBO and Fock matrices, respectively. The ε_ϕ and ε_{ϕ^*} refer to the NBO energies of the bonding/lone pair and those of antibonding/Rydberg, respectively. NBOs are mutually orthogonal. Boys and the natural localized MO analysis[18] gave essentially the same conclusion.

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Supplementary data

NOE experiments and Cartesian coordinates of transition states can be found in the online version, at doi:10.1016/j.tet.2009.08.060.

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