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Asymmetric synthesis of thioamido selenides. A simple synthetic route to enantiopure thiazolines

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Abstract—The mixtures of two enantiomerically pure diastereoisomeric amido selenides, obtained from the reactions of alkenes with camphorselenyl sulfate in a mixture of water and a nitrile, were treated with Lawesson's reagent to afford a mixture of the two corresponding thioamido derivatives. The two diastereoisomeric thioamido selenides could be easily separated by flash chromatography. The thioamido selenides, after activation with PhSeCl, underwent deselenylation by a stereospecific intramolecular substitution. Thus both enantiomeric thiazolines could be obtained in enantiomerically pure form.

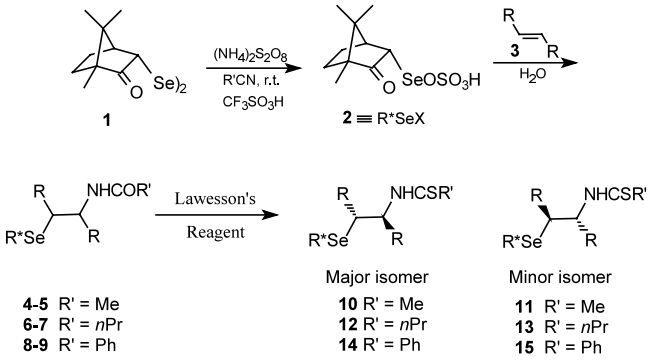
1. Introduction

Chiral non-racemic organoselenium compounds have been recently employed to effect successful asymmetric syntheses.[1] Several research groups have developed simple and efficient procedures to prepare a number of optically active diselenides which can be transformed in situ into efficient electrophilic selenylating agents to introduce new functional groups into unsaturated organic substrates under very mild conditions. Using different chiral diselenides good asymmetric inductions were obtained in the selenomethoxylation and selenohydroxylation as well as in the selenium induced cyclofunctionalization of alkenes.[1–11]

In recent years we described some asymmetric syntheses promoted by the camphorselenyl sulfate **2**, which is produced in situ by treating readily available camphor diselenide **1**, introduced by Back,[7] with ammonium persulfate (Scheme 1). Reagent **2** gave rise to selenomethoxylation[12] and selenohydroxylation[13] of alkenes with good facial selectivity. A great advantage of this reagent is that the addition reactions can be carried out at room temperature or even at 40°C as in the case of the hydroxylation reactions. Furthermore, using an excess of ammonium persulfate, it was also possible to effect in one-pot the selenylation and deselenylation of alkenes.[14] Good results were also obtained by Back using camphorselenyl triflate at −78°C.[15] Very recently we also reported that camphorselenyl sulfate **2** can be successfully employed to effect the asymmetric amidoselenylation of alkenes (Scheme 1).

In the case of the acetamido derivatives, column chromatography of the reaction mixtures afforded the two enantiomerically pure diastereoisomeric acetamido selenides **4** and **5**. On the contrary, the selenides **6** and **7** and **8** and **9** could not be separated. All these selenides were easily transformed into the corresponding oxazolines.[16]

We now report that the treatment of the diastereomeric mixtures of the acetamido **4**+**5**, butyramido **6**+**7** and benzamido **8**+**9** selenides with the Lawesson's reagent



Scheme 1. Synthesis of amido and thioamido selenides.

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easily produces the corresponding mixtures of thioamido selenides **10**+**11**, **12**+**13** and **14**+**15**. In this case the mixtures of the two diastereoisomers could be separated in every case and diastereomerically pure thioamido selenides could thus be obtained (Scheme 1).

We also report that upon treatment with PhSeCl these thioamido selenides can be efficiently converted into the corresponding enantiomerically pure thiazolines.

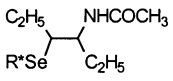
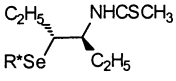
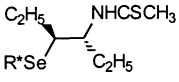
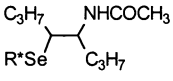
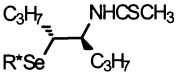
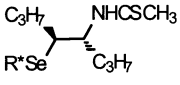
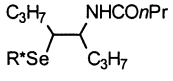
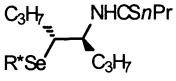
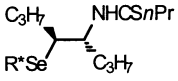
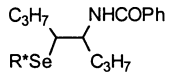
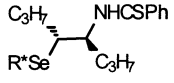
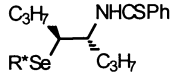
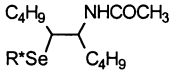
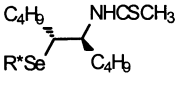
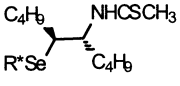
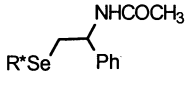
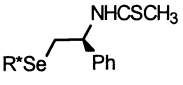
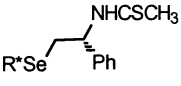
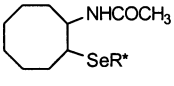
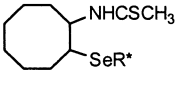
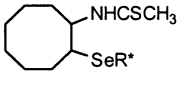
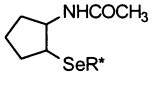
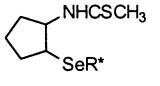
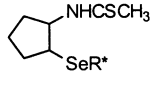
2. Results and discussion

The mixtures of the amido selenides **4a–f**+**5a–f**, **6**+**7** and **8**+**9**, necessary for the present investigation, were prepared as described in our previous work.[16] Thus, as indicated in Scheme 1, the commercially available alkenes **3** were treated with the camphorselenyl sulfate **2** in a mixture of water and acetonitrile, butyronitrile or benzonitrile, in the presence of a stoichiometric amount of CF_3SO_3H. The two diastereomeric addition products were not separated and the mixtures were directly treated with the Lawesson's reagent. Thus, 1 mmol of a mixture of the amido selenides **4**+**5**, **6**+**7** or **8**+**9** was heated under reflux in THF in the presence of 1.5 mmol of Lawesson's reagent for the time indicated in Table 1. ^{1}H NMR analyses of the reaction mixtures indicated that in every case the diastereomeric ratios of the two thioamides corresponded to those of the starting amides. The two diastereoisomeric thioamido selenides were easily separated by flash chromatography of the reaction mixtures.

In this way, as indicated in Scheme 1 and in Table 1, both the major **10a–f**, **12**, **14** and the minor **11a–f**, **13**, **15** stereoisomer could be obtained in enantiomerically pure form. The absolute configurations of the major and the minor thioamido selenides indicated in Table 1 have been assigned on the basis of those of the corresponding amido selenides, which were determined in our previous work.[16]

Removal of the selenium-containing moiety from a dialkyl selenide can be easily effected by reductive or oxidative elimination. Alternatively, the deselenylation can be effected by nucleophilic substitution. In this

Table 1. Synthesis of thioamido selenides

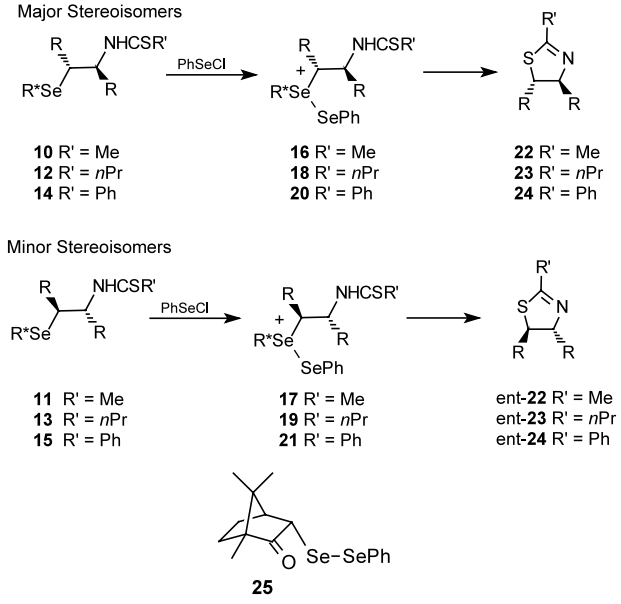
Entry	Amido Selenide		Reaction Time (h)	Thioamido selenide Major Stereoisomers		Yield (%)	Thioamido selenide Minor Stereoisomers		Yield (%)
1		**4a+5a**	1,5		**10a**	72		**11a**	26
2		**4b+5b**	3		**10b**	69		**11b**	23
3		**6+7**	4		**12**	62		**13**	18
4		**8+9**	4		**14**	49		**15**	31
5		**4c+5c**	2		**10c**	67		**11c**	17
6		**4d+5d**	3		**10d**	48		**11d**	42
7		**4e+5e**	2		**10e**	54		**11e**	36
8		**4f+5f**	6		**10f**	40		**11f**	30

case, however, the selenium-containing group must first be transformed into a good leaving group. This can be effected by treating the selenide with an electrophilic selenylating agent which converts the selenide into a selenonium ion. In this way the leaving group is a diselenide molecule. In recent papers we have described a series of these displacement reactions and we have also observed that, in the case of substrates containing suitably positioned internal nucleophilic substituents, an intramolecular displacement readily takes place and several heterocyclic compounds can be produced.[17] An important characteristic of these substitution reactions is that they are stereospecific and occur with inversion of configuration at the carbon atom bearing the selenium atom.[17] Recently, we have applied this simple procedure to the amido selenides **4a–e** and **5a–e** and we have obtained the corresponding optically pure oxazolines.[16] In the hope that the sulfur atom of the thioamides can act as a good nucleophile, we now applied this procedure to the thioamido selenides in order to obtain optically pure thiazolines.

For this purpose we have treated the major stereoisomers of the camphorselenyl thioamides **10a–f**, **12**, and **14** with phenylselenyl chloride at room temperature in CH_2Cl_2 for 3 h. Under these conditions, the initially formed selenonium ion intermediates **16**, **18** and **20** were easily converted into the corresponding enantiomerically pure thiazolines **22–24**. These conversions are illustrated in Scheme 2. In a similar way the minor stereoisomers **11a–f**, **13**, and **15** were converted into the intermediates **17**, **19** and **21** and then into the enantiomeric thiazolines *ent*-**22–24** (Scheme 2). The diselenide **25** was isolated only in the case of deselenylation of **14** and **15**. In all other cases, during the workup, it gave rise to a mixture of diphenyl diselenide and camphor diselenide **1**. The chemical yields and specific rotation values of the thiazolines **22–24** are reported in Table 2.

The cyclization reaction failed in the case of thioamido selenides derived from cyclopentene. The absolute configurations of the thiazolines indicated in Table 2 were assigned on the basis of those of the corresponding thioamido selenides assuming that the deselenylation processes occur with inversion of configuration at the carbon bearing the selenium atom, as has been observed in all the previously studied cases.[16,17] A further indication that the displacement of the selenium moiety occurs with inversion of configuration was obtained in the case of the thioamido selenides **10e** and **11e**. NOE experiments carried out on these two compounds confirmed the expected *trans* relationship between the camphorselenyl and the thioamido groups. A strong NOE effect between the two vicinal protons was observed in the corresponding cyclization products, the thiazolines (−)-**22e** and (+)-**22e**, clearly indicating a *cis* fusion of the two rings.

In conclusion this work describes an efficient synthesis of several new enantiomerically pure thioamido selenides and their use as starting products for an easy conversion into optically pure thiazolines. All the reactions described above occur with good chemical yields and are effected using readily available starting material. The compounds here reported can find useful applications in asymmetric synthesis and as chiral complexing agents. Thiazoline derivatives have recently attracted much attention because the thiazoline ring is present in many biologically active compounds[18] including natural products[19] and drugs such as antibiotic,[20] antihelmintic and antifungal agents.[21]



Scheme 2. Synthesis of thiazolines.

Table 2. Yields and specific optical rotations of thiazolines

Thioamido selenides	Thiazolines	$[\alpha]_D$	Yield (%)
(3*R*,4*S*)-(−)-**10a**	(4*S*,5*S*)-(−)-**22a**	−76.4	85
(3*S*,4*R*)-(+)-**11a**	(4*R*,5*R*)-(+)-**22a**	+76.1	99
(4*R*,5*S*)-(−)-**10b**	(4*S*,5*S*)-(−)-**22b**	−258.0	84
(4*S*,5*R*)-(+)-**11b**	(4*R*,5*R*)-(+)-**22b**	+257.5	92
(4*R*,5*S*)-(−)-**12**	(4*S*,5*S*)-(−)-**23**	−59.0	70
(4*S*,5*R*)-(−)-**13**	(4*R*,5*R*)-(+)-**23**	+59.2	70
(4*R*,5*S*)-(+)-**14**	(4*S*,5*S*)-(−)-**24**	−127.0	72
(4*S*,5*R*)-(+)-**15**	(4*R*,5*R*)-(+)-**24**	+126.8	70
(5*R*,6*S*)-(−)-**10c**	(4*S*,5*S*)-(−)-**22c**	−62.1	83
(5*S*,6*R*)-(+)-**11c**	(4*R*,5*R*)-(+)-**22c**	+62.7	95
(2*S*)-(−)-**10d**	(4*S*)-(−)-**22d**	−21.2	35
(2*R*)-(+)-**11d**	(4*R*)-(+)-**22d**	+21.1	30
(−)-**10e**	(−)-**22e**	−5.2	50
(+)-**11e**	(+)-**22e**	+5.5	45
(−)-**10f**	None		
(−)-**11f**	None		

3. Experimental

New compounds were characterized by mass, ^1H and ^{13}C NMR spectra. GC–MS analyses were carried out with an HP-5890 gas chromatograph (dimethyl silicone column, 12.5 m) equipped with an HP-5971 mass selective detector. ^1H and ^{13}C NMR spectra were recorded

at 400 and 100.62 MHz, respectively, on a Bruker Avance-DRX 400 instrument; unless otherwise specified $CDCl_3$ was used as the solvent and TMS as internal standard. Optical rotations were measured with a JASCO DIP-1000 digital polarimeter. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer.

3.1. Synthesis of thioamido selenides. General procedure

To a solution of a diastereomeric mixture of the amido selenides **4**+**5**, **6**+**7** or **8**+**9**[16] (1 mmol), in freshly distilled THF (1 mL), was added Lawesson's reagent (1.5 mmol) and the reaction mixture was heated under reflux for the time indicated in Table 1. The progress of the reaction was monitored by TLC and GC–MS. The reaction mixture was cooled to 20°C and the solvent evaporated under reduced pressure. The major, **10**, **12** and **14**, and the minor, **11**, **13** and **15** stereoisomers were obtained in pure form by silica gel column chromatography of the reaction mixtures using a mixture of light petroleum and diethyl ether (80:20) as eluant. The products obtained and the reaction yields are collected in Table 1. Physical and spectral data are reported below.

3.1.1. (3*R*,4*S*)-3-(Camphorseleno)-4-(thioacetamido)-hexane 10a. Oil: $[\alpha]_D^{20}=-97.2$ ($c=3.0$, $CHCl_3$); ^{1}H NMR δ 9.35 (d, 1H, $J=8.5$ Hz), 4.7 (tt, 1H, $J=2.8$, 8.5 Hz), 3.38 (dd, 1H, $J=2.1$, 4.8 Hz), 3.2 (ddd, 1H, $J=2.8$, 6.0, 8.7 Hz), 2.45 (s, 3H), 2.21 (t, 1H, $J=4.8$ Hz), 1.8–1.2 (m, 8H), 1.05 (t, 3H, $J=7.2$ Hz), 0.95 (s, 3H), 0.94 (t, 3H, $J=7.2$ Hz), 0.88 (s, 3H), 0.80 (s, 3H); ^{13}C NMR δ 222.2, 209.6, 60.6, 58.5, 53.9, 49.7, 49.5, 47.0, 33.6, 30.4, 27.8, 23.4, 23.3, 19.6, 19.1, 13.1, 10.6, 9.7. MS m/z (rel. int.) 389 (1), 238 (25), 158 (100), 152 (8), 128 (9), 109 (9), 100 (77), 95 (11), 83 (32), 68 (9), 59 (12), 55 (26), 41 (14). Anal. calcd for $C_{18}H_{31}NOSSe$: C, 55.66; H, 8.04; N, 3.61; found: C, 55.75; H, 8.00; N, 3.67%.

3.1.2. (3*S*,4*R*)-3-(Camphorseleno)-4-(thioacetamido)-hexane 11a. Oil: $[\alpha]_D^{21.6}=+87.9$ ($c=1.5$, $CHCl_3$); ^{1}H NMR δ 7.47 (d, 1H, $J=8.0$ Hz), 4.65 (ddt, 1H, $J=3.8$, 8.0, 9.5 Hz), 3.7 (dd, 1H, $J=1.6$, 4.8 Hz), 3.25 (dt, 1H, $J=3.8$, 7.6 Hz), 2.51 (s, 3H), 2.05 (t, 1H, $J=4.8$ Hz), 1.8–1.2 (m, 8H), 1.06 (t, 3H, $J=7.3$ Hz), 0.95 (s, 3H), 0.5 (t, 3H, $J=7.3$ Hz), 0.85 (s, 3H), 0.80 (s, 3H); ^{13}C NMR δ 217.7, 200.3, 59.7, 58.5, 49.4, 48.9, 48.0, 34.6, 30.5, 27.5, 23.3, 22.8, 19.7, 19.6, 13.0, 10.9, 9.7. MS m/z (rel. int.) 389 (1), 238 (100), 158 (70), 152 (14), 128 (8), 109 (9), 100 (62), 95 (6), 83 (21), 68 (4), 59 (13), 55 (25). Anal. calcd for $C_{18}H_{31}NOSSe$: C, 55.66; H, 8.04; N, 3.61; found: C, 55.54; H, 7.95; N, 3.73%.

3.1.3. (4*R*,5*S*)-4-(Camphorseleno)-5-(thioacetamido)-octane 10b. Oil: $[\alpha]_D^{22.7}=-122.1$ ($c=4.65$, $CHCl_3$); ^{1}H NMR δ 9.3 (d, 1H, $J=8.5$ Hz), 4.81 (tt, 1H, $J=2.4$, 8.5 Hz), 3.41 (dd, 1H, $J=2.1$, 4.8 Hz), 3.33 (ddd, 1H, $J=2.4$, 7.6, 7.9 Hz), 2.45 (s, 3H), 2.26 (t, 1H, $J=4.16$ Hz), 1.9–1.3 (m, 12H), 0.98 (s, 3H), 0.92 (t, 3H, $J=7.0$ Hz), 0.92 (t, 3H, $J=7.1$ Hz), 0.91 (s, 3H), 0.83 (s, 3H); ^{13}C NMR δ 222.2, 200.2, 58.8, 58.4, 51.5, 49.7, 49.3, 46.9, 36.6, 33.5, 32.3, 30.3, 23.2, 21.4, 19.6, 19.2, 19.1, 14.2, 13.8, 9.7. MS m/z (rel. int.) 417 (1), 266 (39), 232 (3), 186 (100), 142 (9), 128 (65), 95 (4), 81 (6), 55 (10). Anal. calcd for $C_{20}H_{35}NOSSe$: C, 57.68; H, 8.47; N, 3.36; found: C, 57.55; H, 8.51; N, 3.35%.

3.1.4. (4*S*,5*R*)-4-(Camphorseleno)-5-(thioacetamido)-octane 11b. Oil: $[\alpha]_D^{23.0}=+113.2$ ($c=4.05$, $CHCl_3$); ^{1}H NMR δ 7.64 (d, 1H, $J=9.0$ Hz), 4.8 (tt, 1H, $J=3.6$, 9.0 Hz), 3.75 (dd, 1H, $J=1.6$, 4.8 Hz), 3.47 (dt, 1H, $J=3.6$, 7.24 Hz), 2.5 (s, 3H), 2.13 (t, 1H, $J=4.1$ Hz), 1.8–1.2 (m, 12H), 1.0 (s, 3H), 0.98 (t, 3H, $J=7.2$ Hz), 0.945 (t, 3H, $J=7.0$ Hz), 0.94 (s, 3H), 0.91 (s, 3H); ^{13}C NMR δ 217.6, 200.0, 58.2, 57.9, 48.8, 48.2, 47.2, 46.8, 36.6, 34.5, 31.8, 30.4, 23.3, 21.3, 19.7, 19.6, 19.4, 14.0, 13.9, 9.7. MS m/z (rel. int.) 417 (1), 266 (55), 233 (6), 186 (42), 142 (40), 128 (36), 109 (35), 95 (61), 81 (48), 69 (100), 55 (66). Anal. calcd for $C_{20}H_{35}NOSSe$: C, 57.68; H, 8.47; N, 3.36; found: C, 57.70; H, 8.80; N, 3.31%.

3.1.5. (4*R*,5*S*)-4-(Camphorseleno)-5-(thiobutyrramido)-octane 12. Oil: $[\alpha]_D^{20.2}=-109.9$ ($c=1.1$, $CHCl_3$); ^{1}H NMR δ 9.33 (d, 1H, $J=7.5$ Hz), 4.8 (tdd, 1H, $J=2.8$, 7.5, 8.6 Hz), 3.42 (dd, 1H, $J=1.6$, 4.6 Hz), 3.2 (ddd, 1H, $J=2.3$, 5.8, 8.6 Hz), 2.6 (m, 2H), 2.27 (t, 1H, $J=4.6$ Hz), 2.0–1.3 (m, 14H), 1.1 (t, 3H, $J=7.2$ Hz), 1.0 (s, 3H), 0.98 (t, 3H, $J=7.4$ Hz), 0.96 (t, 3H, $J=7.5$ Hz), 0.93 (s, 3H), 0.84 (s, 3H); ^{13}C NMR δ 221.9, 205.4, 60.2, 58.4, 54.0, 49.6, 49.5, 48.4, 46.9, 30.4, 30.3, 27.8, 23.4, 23.2, 23.1, 23.0, 19.5, 19.1, 13.4, 13.0, 10.6, 9.7. Anal. calcd for $C_{22}H_{39}NOSSe$: C, 59.44; H, 8.84; N, 3.15; found: C, 59.60; H, 8.80; N, 3.23%.

3.1.6. (4*S*,5*R*)-4-(Camphorseleno)-5-(thiobutyrramido)-octane 13. Oil: $[\alpha]_D^{24.4}=-51.4$ ($c=0.59$, $CHCl_3$); ^{1}H NMR δ 9.35 (d, 1H, $J=8.3$ Hz), 4.71 (tdd, 1H, $J=2.1$, 6.6, 8.8 Hz), 3.41 (dd, 1H, $J=2.1$, 4.6 Hz) 3.31 (ddd, 1H, $J=2.1$, 5.8, 8.3 Hz), 2.5 (dt, 2H, $J=6.1$, 8.5 Hz), 2.3 (dd, 1H, $J=4.3$, 4.6 Hz), 1.8–1.2 (m, 14H), 1.0 (s, 3H), 0.97 (t, 3H, $J=7.2$ Hz), 0.95 (t, 3H, $J=7.1$ Hz), 0.94 (s, 3H), 0.93 (t, 3H, $J=7.0$ Hz), 0.85 (s, 3H); ^{13}C NMR δ 221.9, 205.0, 58.3, 58.2, 51.7, 49.6, 49.3, 48.2, 46.8, 36.6, 32.3, 30.2, 23.1, 23.0, 21.3, 19.4, 19.1, 19.0, 14.1, 13.7, 13.2, 9.6. Anal. calcd for $C_{22}H_{39}NOSSe$: C, 59.44; H, 8.84; N, 3.15; found: C, 59.48; H, 8.78; N, 3.20%.

3.1.7. (4*R*,5*S*)-4-(Camphorseleno)-5-(thiobenzamido)-octane 14. Oil: $[\alpha]_D^{24.3}=+82.0$ ($c=1.4$, $CHCl_3$); ^{1}H NMR δ 9.75 (d, 1H, $J=8.5$ Hz), 7.8–7.7 (m, 2H), 7.4–7.2 (m, 3H), 4.85 (ddt, 1H, $J=2.5$, 8.5, 11.1 Hz), 3.65 (dt, 1H, $J=2.5$, 7.7 Hz), 3.22 (dd, 1H, $J=2.1$, 4.7 Hz), 2.1 (dd, 1H, $J=4.5$, 4.7 Hz), 1.7–1.2 (m, 12H), 0.97 (t, 3H, $J=7.0$ Hz), 0.94 (t, 3H, $J=7.1$ Hz), 0.80 (s, 3H), 0.60 (s, 3H), 0.1 (s, 3H); ^{13}C NMR δ 221.6, 198.2, 140.8, 130.8, 127.8 (two carbons), 127.4 (two carbons), 59.3, 58.0, 49.5, 49.4, 48.1, 46.4, 35.9, 31.6, 30.1, 22.8, 21.3, 19.5, 18.9, 18.6, 14.1, 13.8, 9.3. Anal. calcd for $C_{25}H_{37}NOSSe$: C, 62.74; H, 7.79; N, 2.93; found: C, 62.60; H, 7.58; N, 3.01%.

3.1.8. (4*S*,5*R*)-4-(Camphorseleno)-5-(thiobenzamido)-octane 15. Oil: $[\alpha]_D^{24.9}=+3.0$ ($c=1.0$, $CHCl_3$); ^1H NMR δ 7.85 (d, 1H, $J=8.8$ Hz), 7.78–7.72 (m, 2H), 7.5–7.3 (m, 3H), 4.96 (tt, 1H, $J=3.8$, 8.8 Hz), 3.65 (dd, 1H, $J=1.5$, 4.7 Hz), 3.6 (dt, 1H, $J=3.8$, 7.5 Hz), 2.1–2.2 (m, 1H), 2.0–1.4 (m 12H) 1.1 (s, 3H), 0.98 (t, 3H, $J=7.0$ Hz), 0.91 (t, 3H, $J=7.1$ Hz), 0.86 (s, 3H), 0.77 (s, 3H); ^{13}C NMR δ 217.4, 198.1, 141.9, 131.1, 128.5 (two carbons), 126.7 (two carbons), 58.1, 58.0, 48.8, 48.6, 47.8, 46.7, 36.6, 31.9, 30.4, 23.2, 22.3, 21.3, 19.6, 19.5, 14.0, 13.9, 9.7. Anal. calcd for $C_{25}H_{37}NOSSe$: C, 62.74; H, 7.79; N, 2.93; found: C, 61.99; H, 8.01; N, 3.00%.

3.1.9. (5*R*,6*S*)-5-(Camphorseleno)-6-(thioacetamido)-decane 10c. Oil: $[\alpha]_D^{21.3}=-46.6$ ($c=5.0$, $CHCl_3$); ^1H NMR δ 9.41 (d, 1H, $J=8.1$ Hz), 4.8 (tt, 1H, $J=2.1$, 8.1 Hz), 3.43 (dd, 1H, $J=2.1$, 4.6 Hz), 3.33 (ddd, 1H, $J=2.3$, 5.5, 8.1 Hz), 2.5 (s, 3H), 2.25 (t, 1H, $J=4.6$ Hz), 1.9–1.3 (m, 16H), 1.01 (s, 3H), 0.93 (s, 3H), 0.90 (t, 3H, $J=7.4$ Hz), 0.89 (t, 3H, $J=7.4$ Hz), 0.82 (s, 3H); ^{13}C NMR δ 222.4, 200.1, 59.1, 58.4, 51.8, 49.6, 49.3, 46.9, 34.1, 33.6, 30.3, 30.2, 29.8, 28.1, 23.2, 22.8, 22.3, 19.6, 19.0, 14.0, 13.9, 9.7. MS m/z (rel. int.) 445 (1), 294 (31), 214 (100), 156 (73), 95 (10), 83 (14), 69 (10), 55 (17). Anal. calcd for $C_{22}H_{39}NOSSe$: C, 59.44; H, 8.84; N, 3.15; found: C, 59.86; H, 8.65; N, 3.21%.

3.1.10. (5*S*,6*R*)-5-(Camphorseleno)-6-(thioacetamido)-decane 11c. Oil: $[\alpha]_D^{22.9}=+66.2$ ($c=4.0$, $CHCl_3$); ^1H NMR δ 7.50 (d, 1H, $J=8.6$ Hz), 4.68 (ddt, 1H, $J=$ 3.45, 8.6, 10.36 Hz), 3.68 (dd, 1H, $J=2.4$, 4.6 Hz), 3.34 (dt, 1H, $J=3.6$, 7.2 Hz), 2.5 (s, 3H), 2.0 (t, 1H, $J=4.6$ Hz), 1.75–1.25 (m, 16H), 0.93 (s, 3H), 0.88 (t, 3H, $J=7.8$ Hz), 0.84 (t, 3H, $J=7.4$ Hz), 0.84 (s, 3H), 0.82 (s, 3H); ^{13}C NMR δ 218.0, 200.3, 58.6, 58.5, 49.3, 48.5, 47.8, 47.2, 34.9, 34.5, 30.9, 30.6, 29.7, 28.7, 23.7, 23.0, 22.8, 20.1, 20.0, 14.4, 14.3, 10.1. MS m/z (rel. int.) 445 (1), 294 (7), 214 (9), 180 (21), 156 (100), 110 (21), 100 (15), 95 (25), 83 (51), 69 (33), 55 (50), 41 (31). Anal. calcd for $C_{22}H_{39}NOSSe$: C, 59.44; H, 8.84; N, 3.15; found: C, 58.97; H, 8.54; N, 3.18%.

3.1.11. (2*S*)-1-(Camphorseleno)-2-(thioacetamido)-2-phenylethane 10d. Oil: $[\alpha]_D^{22.6}=-39.0$ ($c=2.7$, $CHCl_3$); ^1H NMR δ 9.77 (d, 1H, $J=8.0$ Hz), 7.5–7.4 (m, 5H), 6.15 (dt, 1H, $J=4.1$, 8.0 Hz), 3.58 (dd, 1H, $J=2.2$, 4.6 Hz), 3.49 (dd, 1H, $J=4.1$, 13.7 Hz), 3.25 (dd, 1H, $J=4.1$, 13.7 Hz), 2.68 (s, 3H), 2.26 (dd, 1H, $J=4.4$, 4.6 Hz), 1.9–1.8 (m, 1H), 1.7 (dt, 1H, $J=3.2$, 13.4 Hz), 1.55 (ddd, 1H, $J=3.2$, 9.0, 12.7 Hz), 1.45 (ddd, 1H, $J=4.6$, 9.0, 13.4 Hz), 1.02 (s, 3H), 0.97 (s, 3H), 0.89 (s, 3H); ^{13}C NMR δ 221.4, 201.1, 139.1, 128.5 (two carbons), 127.6, 126.7 (two carbons), 58.4, 58.1, 49.3, 49.2, 47.0, 33.6, 32.9, 30.5, 23.3, 19.7, 19.1, 9.6. Anal. calcd for $C_{20}H_{27}NOSSe$: C, 58.82; H, 6.66; N, 3.43; found: C, 57.91; H, 6.65; N, 3.48%.

3.1.12. (2*R*)-1-(Camphorseleno)-2-thioacetamido-2-phenylethane 11d. Oil: $[\alpha]_D^{21.8}=+30.6$ ($c=2.1$, $CHCl_3$); ^1H NMR δ 8.9 (d, 1H, $J=7.3$ Hz), 7.5–7.4 (m, 5H), 5.66 (ddd, 1H, $J=5.7$, 7.3, 9.1 Hz), 3.6 (dd, 1H, $J=$ 2.1, 4.6 Hz), 3.38 (dd, 1H, $J=5.7$, 13.2 Hz), 3.27 (dd, 1H, $J=9.1$, 13.2 Hz), 2.63 (s, 3H), 2.18 (dd, 1H, $J=4.2$, 4.6 Hz), 1.9–1.8 (m, 1H), 1.72 (dt, 1H, $J=3.2$, 13.6 Hz), 1.60 (ddd, 1H, $J=3.2$, 9.1, 12.6 Hz), 1.45 (ddd, 1H, $J=4.7$, 9.1, 13.6 Hz), 1.0 (s, 3H), 0.95 (s, 3H), 0.84 (s, 3H); ^{13}C NMR δ 220.6, 200.9, 140.0, 128.8 (two carbons), 127.8, 126.7 (two carbons), 59.4, 58.5, 48.5, 47.5, 46.9, 33.9, 30.7, 29.6, 23.4, 19.6, 19.3, 9.5. Anal. calcd for $C_{20}H_{27}NOSSe$: C, 58.82; H, 6.66; N, 3.43; found: C, 59.59; H, 6.59; N, 3.40%.

3.1.13. 1-(Camphorseleno)-2-(thioacetamido)cycloctane 10e. Oil: $[\alpha]_D^{24.0}=-1.0$ ($c=3.0$, $CHCl_3$); ^1H NMR δ 8.8 (d, 1H, $J=6.8$ Hz), 4.37 (ddt, 1H, $J=1.8$, 11.5, 6.8 Hz), 3.50 (dd, 1H, $J=1.4$, 4.7 Hz), 3.49 (ddd, 1H, $J=3.0$, 6.8, 11.5 Hz), 2.45 (s, 3H), 2.2 (t, 1H, $J=4.7$ Hz), 2.0–1.2 (m, 16H), 0.95 (s, 3H), 0.87 (s, 3H), 0.86 (s, 3H); ^{13}C NMR δ 222.8, 198.7, 60.0, 58.6, 48.6, 47.3, 47.0, 46.3, 33.6, 32.0, 31.3, 30.9, 26.8, 25.8, 25.5, 25.4, 23.7, 19.6, 19.1, 9.5. MS m/z (rel. int.) 415 (1), 264 (100), 207 (4), 184 (73), 152 (9), 126 (38), 109 (49), 95 (14), 81 (19), 67 (40), 59 (12), 55 (17). Anal. calcd for $C_{20}H_{33}NOSSe$: C, 57.96; H, 8.03; N, 3.38; found: C, 58.21; H, 7.96; N, 3.41%.

3.1.14. 1-(Camphorseleno)-2-(thioacetamido)cycloctane 11e. Oil: $[\alpha]_D^{21.0}=-5.3$ ($c=2.0$, $CHCl_3$); ^1H NMR δ 8.6 (d, 1H, $J=7.4$ Hz), 4.62 (ddt, 1H, $J=2.9$, 7.4, 10.2 Hz), 3.94 (d, 1H, $J=4.5$ Hz), 3.43 (ddd, 1H, $J=2.7$, 6.6, 10.2 Hz), 2.4 (s, 3H), 2.09 (t, 1H, $J=4.5$ Hz), 1.8–1.2 (m, 16H), 0.97 (s, 3H), 0.87 (s, 3H), 0.83 (s, 3H); ^{13}C NMR δ 220.1, 198.5, 62.4, 58.4, 48.7, 47.3, 44.8, 43.0, 34.0, 30.9, 30.6, 30.1, 26.5, 25.9, 25.8, 25.4, 23.0, 19.7, 19.5, 9.6. MS m/z (rel. int.) 415 (1), 264 (100), 207 (11), 184 (58), 152 (14), 126 (35), 110 (10), 109 (54), 81 (24), 67 (45), 55 (22). Anal. calcd for $C_{20}H_{33}NOSSe$: C, 57.96; H, 8.03; N, 3.38; found: C, 57.99; H, 8.23; N, 3.21%.

3.1.15. 1-(Camphorseleno)-2-(thioacetamido)cyclopentane 10f. Oil: $[\alpha]_D^{24.6}=+3.2$ ($c=4.5$, $CHCl_3$). ^1H NMR δ 8.7 (m, 1H), 4.45 (ddd, 1H, $J=7.6$, 8.0, 14.2 Hz), 3.9 (dd, 1H, $J=1.9$, 4.5 Hz), 3.53 (dt, 1H, $J=8.0$, 8.5 Hz), 2.62 (s, 3H), 2.31 (t, 1H, $J=4.5$ Hz), 1.9–1.4 (m, 10H), 1.03 (s, 3H), 0.95 (s, 3H), 0.94 (s, 3H); ^{13}C NMR δ 221.3, 201.6, 64.3, 58.9, 49.1, 47.8, 47.5, 43.9, 34.4, 32.8, 31.0, 29.9, 24.1, 22.6, 20.1, 19.8, 10.0. MS m/z (rel. int.) 373 (2), 298 (10), 222 (100), 142 (33), 123 (11), 84 (25), 67 (21), 59 (12), 55 (8). Anal. calcd for $C_{17}H_{27}NOSSe$: C, 54.84; H, 7.31; N, 3.76; found: C, 55.02; H, 7.00; N, 3.59%.

3.1.16. 1-(Camphorseleno)-2-(thioacetamido)cyclopentane 11f. Oil: $[\alpha]_D^{24.8}=-101.3$ ($c=3$, $CHCl_3$); ^1H NMR δ 8.3 (m, 1H), 4.75 (quint, 1H, $J=6.9$ Hz), 4.12 (dd, 1H, $J=1.7$, 4.6 Hz), 3.75 (dt, 1H, $J=6.9$, 7.5 Hz), 2.47 (s, 3H), 2.24 (t, 1H, $J=4.6$ Hz), 1.9–1.4 (m, 10H), 1.0 (s, 3H), 0.9 (s, 3H), 0.89 (s, 3H); ^{13}C NMR δ 220.3, 199.6, 65.5, 58.2, 48.2, 47.2, 44.8, 41.1, 33.9, 31.3, 30.9, 30.2, 23.3, 23.0, 19.5, 19.4, 9.5. MS m/z (rel. int.) 373 (2), 298 (9), 222 (100), 142 (27), 123 (9), 84 (23), 67 (23), 55 (8). Anal. calcd for $C_{17}H_{27}NOSSe$: C, 54.84; H, 7.31; N, 3.76; found: C, 54.81; H, 7.43; N, 3.69%.

3.2. Conversion of thioamides into thiazolines

To a solution of the thioamido selenides **10a**–**f**, **11a**–**f**, **12**, **13**, **14** or **15** (1 mmol) in dichloromethane (2 mL), PhSeCl (1.2 mmol) was added and the reaction mixtures were stirred at room temperature for 3 h. The progress of the reaction was monitored by TLC and GC–MS. The reaction mixtures were poured into a 10% solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layers were washed with brine, dried over sodium sulfate and evaporated under pressure. The residue was chromatographed on a silica gel column using a mixture of light petroleum and diethyl ether (85:15) as eluant. The reaction yields and the specific rotations of the thiazolines thus obtained are collected in Table 2. Physical and spectral data are reported below.

3.2.1. (4*S*,5*S*)-4,5-Diethyl-2-methyl-4,5-dihydro-1,3-thiazole (−)-22a. Oil: $[\alpha]_D^{15.4}=-76.4$ ($c=0.4$, $CHCl_3$); ^1H NMR δ 3.98 (ddt, 1H, $J=1.2$, 5.6, 5.8 Hz), 3.4 (ddd, 1H, $J=4.2$, 5.6, 8.4 Hz), 2.13 (d, 3H, $J=1.2$ Hz), 1.6–1.4 (m, 4H), 0.91 (t, 3H, $J=7.4$ Hz), 0.82 (t, 3H, $J=7.2$ Hz); ^{13}C NMR δ 155.2, 83.6, 58.6, 29.7, 26.6, 20.9, 12.5, 10.7. MS m/z (rel. int.) 159 (29), 128 (28), 116 (25), 100 (3), 83 (100), 68 (48), 55 (14). Anal. calcd for $C_8H_{15}NS$: C, 61.10; H, 9.61; N, 8.91; found: C, 61.21; H, 9.45; N, 8.77%.

3.2.2. (4*R*,5*R*)-4,5-Diethyl-2-methyl-4,5-dihydro-1,3-thiazole (+)-22a. Oil: $[\alpha]_D^{16.4}=+76.1$ ($c=0.38$, $CHCl_3$). Anal. calcd for $C_8H_{15}NS$: C, 61.10; H, 9.61; N, 8.91; found: C, 61.23; H, 9.55; N, 9.00%.

3.2.3. (4*S*,5*S*)-2-Methyl-4,5-dipropyl-4,5-dihydro-1,3-thiazole (−)-22b. Oil: $[\alpha]_D^{27.0}=-258.0$ ($c=0.9$, $CHCl_3$); ^1H NMR δ 4.14 (m, 1H), 3.58 (ddd, 1H, $J=2.8$, 3.3, 4.6 Hz), 2.24 (d, 3H, $J=1.3$ Hz), 1.75–1.3 (m, 8H), 1.0 (t, 3H, $J=7.3$ Hz), 0.9 (t, 3H, $J=7.2$ Hz); ^{13}C NMR δ 165.3, 81.8, 57.2, 39.3, 36.5, 21.3, 20.4, 19.7, 14.1, 13.8. MS m/z (rel. int.) 185 (10), 152 (12), 142 (100), 97 (45), 68 (44), 59 (14), 55 (12). Anal. calcd for $C_{10}H_{19}NS$: C, 64.81; H, 10.33; N, 7.56; found: C, 65.21; H, 10.21; N, 7.77%.

3.2.4. (4*R*,5*R*)-2-Methyl-4,5-dipropyl-4,5-dihydro-1,3-thiazole (+)-(22b). Oil: $[\alpha]_D^{26.5}=+257.5$ ($c=0.5$, $CHCl_3$). Anal. calcd for $C_{10}H_{19}NS$: C, 64.81; H, 10.33; N, 7.56; found: C, 64.73; H, 10.22; N, 7.74%.

3.2.5. (4*S*,5*S*)-2,4,5-Tripropyl-4,5-dihydro-1,3-thiazole (−)-23. Oil: $[\alpha]_D^{21.3}=-59.0$ ($c=0.35$, $CHCl_3$); ^1H NMR δ 4.21 (dt, 1H, $J=4.2$, 6.2 Hz), 3.56 (ddd, 1H, $J=4.2$, 4.5, 9.0 Hz), 2.8–2.7 (m, 2H), 2.1–1.9 (m, 2H), 1.8–1.6 (m, 8H), 1.06 (t, 3H, $J=7.1$ Hz), 1.03 (t, 3H, $J=7.0$ Hz), 1.0 (t, 3H, $J=7.1$ Hz); ^{13}C NMR δ 154.0, 71.7, 56.6, 35.0, 31.9, 30.0, 29.4, 26.5, 21.5, 13.5, 11.5, 10.0. MS m/z (rel. int.) 213 (11), 185 (26), 170 (100), 142 (16), 128 (24), 125 (26), 111 (8), 101 (14), 96 (64), 69 (17), 55 (18). Anal. calcd for $C_{12}H_{23}NS$: C, 67.55; H, 10.86; N, 6.56; found: C, 67.75; H, 10.50; N, 6.35%.

3.2.6. (4*R*,5*R*)-2,4,5-Tripropyl-4,5-dihydro-1,3-thiazole (+)-23. Oil: $[\alpha]_D^{20.0}=+59.2$ ($c=0.5$, $CHCl_3$). Anal. calcd for $C_{12}H_{23}NS$: C, 67.55; H, 10.86; N, 6.56; found: C, 67.80; H, 10.68; N, 6.63%.

3.2.7. (4*S*,5*S*)-2-Phenyl-4,5-dipropyl-4,5-dihydro-1,3-thiazole (−)-24. Oil: $[\alpha]_D^{24.7}=-127.0$ ($c=0.35$, $CHCl_3$) ^1H NMR δ 8.1–7.9 (m, 2H), 7.5–7.1 (m, 3H), 4.45 (dt, 1H, $J=4.0$, 6.0 Hz), 3.65 (ddd, 1H, $J=4.0$, 6.0, 8.2 Hz), 1.8–1.3 (m, 8H), 1.0 (t, 3H, $J=7.2$ Hz), 0.98 (t, 3H, $J=7.1$ Hz); ^{13}C NMR δ 166.5, 133.1, 131.2, 128.4 (two carbons), 128.3 (two carbons), 81.9, 55.7, 39.3, 36.2, 21.1, 19.7, 14.1, 13.8. MS m/z (rel. int.) 247 (5), 204 (100), 162 (19), 159 (14), 130 (39), 104 (16), 77 (7), 69 (5), 55 (6). Anal. calcd for $C_{15}H_{21}NS$: C, 72.82; H, 8.56; N, 5.66; found: C, 72.98; H, 8.21; N, 5.18%.

3.2.8. (4*R*,5*R*)-2-Phenyl-4,5-dipropyl-4,5-dihydro-1,3-thiazole (+)-24. Oil: $[\alpha]_D^{25.0}=+126.8$ ($c=1.0$, $CHCl_3$). Anal. calcd for $C_{15}H_{21}NS$: C, 72.82; H, 8.56; N, 5.66; found: C, 72.56; H, 8.36; N, 5.97%.

3.2.9. (4*S*,5*S*)-4,5-Dibutyl-2-methyl-4,5-dihydro-1,3-thiazole (−)-22c. Oil: $[\alpha]_D^{20.5}=-62.1$ ($c=3.8$, $CHCl_3$); ^1H NMR δ 4.14 (qdt, 1H, $J=1.4$, 4.8, 4.8 Hz), 3.48 (dt, 1H, $J=4.8$, 9.2 Hz), 2.18 (d, 3H, $J=1.4$ Hz), 1.7–1.3 (m, 12H), 0.91 (t, 3H, $J=6.9$ Hz), 0.89 (t, 3H, $J=7.2$ Hz); ^{13}C NMR δ 164.5, 83.0, 57.9, 37.4, 34.6, 30.8, 29.1, 23.2, 22.8, 21.0 14.4, 14.3. MS m/z (rel. int.) 213 (7), 180 (22), 156 (100), 111 (11), 100 (18), 81 (10), 68 (22), 55 (16), 41 (14). Anal. calcd for $C_{12}H_{23}NS$: C, 67.55; H, 10.86; N, 6.56; found: C, 67.63; H, 10.91; N, 6.49%.

3.2.10. (4*R*,5*R*)-4,5-Dibutyl-2-methyl-4,5-dihydro-1,3-thiazole (+)-22c. Oil: $[\alpha]_D^{16.3}=+62.7$ ($c=2.0$, $CHCl_3$). Anal. calcd for $C_{12}H_{23}NS$: C, 67.55; H, 10.86; N, 6.56; found: C, 66.98; H, 10.88; N, 6.49%.

3.2.11. (4*S*)-2-Methyl-4-phenyl-4,5-dihydro-1,3-thiazole (−)-22d. Oil: $[\alpha]_D^{21.3}=-21.2$ ($c=1.0$, $CHCl_3$); ^1H NMR δ 7.3 (m, 5H), 5.57 (tdd, 1H, $J=1.5$, 8.6, 9.2 Hz), 3.8 (dd, 1H, $J=8.6$, 11.1 Hz), 3.35 (dd, 1H, $J=9.2$, 11.1 Hz), 1.26 (d, 3H, $J=1.5$ Hz); ^{13}C NMR δ 168.2, 139.0, 128.8 (two carbons), 127.9, 126.5 (two carbons), 80.3, 41.5, 22.7. MS m/z (rel. int.) 177 (5), 165 (16), 135 (100), 91 (34), 77 (15), 51 (8). Anal. calcd for $C_{10}H_{11}NS$: C, 67.76; H, 6.25; N, 7.90; found: C, 67.92; H, 6.22; N, 7.85%.

3.2.12. (4*R*)-2-Methyl-4-phenyl-4,5-dihydro-1,3-thiazole (+)-22d. Oil: $[\alpha]_D^{20.0}=+21.1$ ($c=1.0$, $CHCl_3$). Anal. calcd for $C_{10}H_{11}NS$: C, 67.76; H, 6.25; N, 7.90; found: C, 67.21; H, 6.33; N, 7.54%.

3.2.13. (−)-2-Methyl-3a,4,5,6,7,8,9,9a-octahydrocycloocta[*d*][1,3]-thiazole (−)-22e. Oil: $[\alpha]_D^{21.3}=-5.2$ ($c=0.3$, $CHCl_3$); ^1H NMR δ 4.15 (m, 1H), 3.88 (ddd, 1H, $J=1.5$, 7.9, 10.9 Hz), 2.12 (d, 3H, $J=1.5$ Hz), 2.1–1.3 (m, 12H); ^{13}C NMR δ 167.5, 71.8, 49.3, 31.8, 30.4, 27.0, 25.1, 24.3, 24.2, 20.3. MS m/z (rel. int.) 183 (69), 150 (100), 126 (40), 109 (71), 67 (96), 59 (33). Anal. calcd for $C_{10}H_{17}NS$: C, 65.52; H, 9.35; N, 7.65; found: C, 66.01; H, 9.38; N, 7.64%.

3.2.14. (+)-2-Methyl-3a,4,5,6,7,8,9,9a-octahydrocycloocta[*d*][1,3]-thiazole (+)-22e. Oil: $[\alpha]_D^{20.0} = +5.5$ ($c = 0.1$, $CHCl_3$). Anal. calcd for $C_{10}H_{17}NS$: C, 65.52; H, 9.35; N, 7.65; found: C, 64.21; H, 9.21; N, 7.55%.

Diselenide **25** was obtained in 30% yields as a by-product in the deselenylations of **14** and **15**.

3.2.15. Camphor-phenyl diselenide 25. Oil: ^{1}H NMR δ 7.8–7.7 (m, 2H), 7.4–7.2 (m, 3H), 4.37 (dd, 1H, $J = 1.9$, 4.4 Hz), 2.29 (t, 1H, $J = 4.4$ Hz), 2.0–1.0 (m, 4H), 1.04 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H); ^{13}C NMR δ 215.9, 132.1, 130.9, 129.6, 128.0, 58.7, 55.8, 49.0, 47.0, 30.7, 30.1, 23.3, 20.1, 10.1. Anal. calcd for $C_{16}H_{20}Se_2$: C, 49.75; H, 5.22; found: C, 49.81; H, 5.38%.

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