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# Asymmetric aldol reactions from titanium enolates of α-seleno ketones and esters

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**Abstract**—Asymmetric aldol condensations using titanium enolates of (*R*)-camphorselenoacetone and of methyl (*R*)-camphorselenoacetate are reported. The reactions with aromatic, α,β-unsaturated or aliphatic aldehydes proceed with good chemical yields giving a mixture of the *syn* and *anti* aldols. These diastereoisomers were easily separated by column chromatography. The two *syn* diastereoisomers were obtained in enantiomerically pure form.

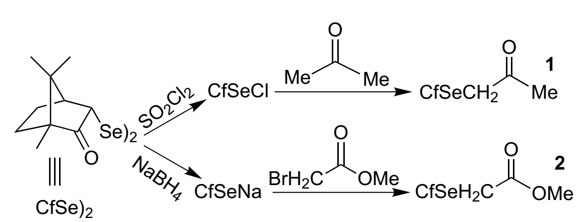

## 1. Introduction

Organoselenium reagents have been widely employed in organic synthesis to effect nonconventional conversions of functional groups. In recent years, several research groups have been involved in the preparation of optically active diselenides, which have found extensive application in electrophilic addition reactions. Depending on the efficiency of the chiral diselenide asymmetric inductions from good to excellent have been observed. Thus, highly diastereoselective seleno-alkoxylation, seleno-hydroxylation,[1] selenoazidation reactions of alkenes,[2] as well as cyclofunctionalization reactions,[1] have been recently reported.

On the other hand, asymmetric additions of selenium-containing nucleophiles are still poorly explored.[3] Stereoselective aldol reactions between enolates of α-phenylseleno substituted carbonyl compounds and various aldehydes have recently appeared in the literature.[4] These reactions allow *syn* aldols to be formed as racemates with high diastereoselectivity. The use of enolates generated from enantiomerically pure selenium-containing carbonyl compounds may be a useful elaboration of this methodology and an interesting alternative to the more classical chiral auxiliary mediated aldol condensations, which are still the subject of intense synthetic and mechanistic studies.[5] Moreover, these reactions can be synthetically important because the optically active selenoaldols so formed may be converted into several other derivatives taking advantage of the versatile chemistry of the organoselenium compounds.[1,3] The only previous example of stereoselective aldol reactions using selenium reagents is the recently reported reaction of titanium enolates of chiral *N*-acyl selones with aldehydes.[6]

## 2. Results and discussion

On the basis of the results of some preliminary experiments we observed that, in the present case, the most convenient chiral diselenide was the (*R*,*R*)-camphor diselenide introduced by Back et al.[7] Thus, starting from this diselenide and using standard procedures we have prepared two new camphor derivatives: (*R*)-camphorselenoacetone **1** and methyl (*R*)-camphorselenoacetate **2**. As shown in Scheme 1, (*R*)-camphorselenoacetone **1** was prepared from acetone and camphorselenenyl chloride




**Scheme 1.** Synthesis of the (*R*)-camphorseleno acetone **1** and the methyl (*R*)-camphorseleno acetate.

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generated in situ from camphor diselenide and $SO_2Cl_2$ in dichloromethane at 0 °C (55% yield).[8] Methyl (*R*)-camphorselenoacetate **2** was synthesized by nucleophilic substitution starting from methyl bromoacetate and sodium camphorselenolate, generated in situ by treatment of the camphor diselenide with sodium borohydride in methanol (97% yield).[9] Compounds **1** and **2** were used as precursors of chiral titanium enolates in aldol condensations, according to the following protocol.

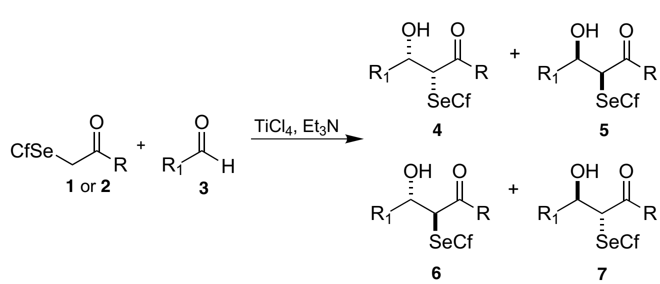
A solution of the α-seleno carbonyl compound **1** or **2** in $CH_2Cl_2$ was treated with 1.1 equiv of $TiCl_4$ at −78 °C under nitrogen. After 5 min 2 equiv of $Et_3N$ were added and the resulting yellow mixture turned immediately dark.[10] After 1 h 1.1 equiv of an aromatic, α,β-unsaturated or aliphatic aldehyde **3** were added dropwise and the reaction mixture was stirred at the same temperature for about 6 h. In the cases of the aldehydes **3c**, **3g**, and **3h** at the end of the addition the reaction temperature was slowly allowed to raise to −30 °C. The reaction was then quenched with a saturated solution of $NH_4Cl$ and extracted with $CH_2Cl_2$. The crude mixtures were purified by flash chromatography using mixtures of diethyl ether and light petroleum (40–60 °C) as the eluant.

The condensation reactions generated the four possible enantiomerically pure diasteroisomers. The reaction products, the yields and the diastereomeric ratios, measured by $^1$H NMR on the crude mixtures and confirmed after column chromatography purification, are collected in Table 1. Good yields and good or moderate selectivities in favor of the *syn* products (*syn*:*anti* ratio up to 81:19) were observed in every case. Starting from the α-selenoketone **1** the *syn*:*anti* ratios were higher than those obtained from the α-selenoester **2**. Different *syn* (**4**:**5**) and *anti* selectivities (**6**:**7**) were observed in the various cases. The two enantiomerically pure *syn* aldols **4** and **5** could be easily separated by flash chromatography, whereas the *anti* isomers, with the exception of **6a** and **7a**, were obtained as mixtures, which could not be separated.

The structural determination of the β-hydroxy carbonyl compounds **4**, **5**, **6**, and **7** was not straightforward. The relative configuration of aldol-type products is generally assigned on the basis of the values of the $^1$H NMR coupling constants of the vicinal protons.[5c,11] In fact, the *anti* aldols show larger $^3J_{AB}$ values (7–10 Hz) than the *syn* aldols ($^3J_{AB}$ = 2–5 Hz) as a consequence of the preferentially assumed chair-like conformations in which hydrogen bonds exist between the hydroxy and the carbonyl groups. This seems not to be valid in the present case since all the $^3J_{AB}$ coupling constants of the β-hydroxyketones and of the β-hydroxyesters **4**, **5**, **6**, and **7** are large. As an example, the values of the coupling constants observed for **4a**, **5a**, **6a**, and **7a** are $J_{AB}$ = 8.5, 7.9, 7.7, and 9.5, respectively. These large $^3J_{AB}$ values are consistent with an antiperiplanar orientation of $H_A$ and $H_B$ protons, in both the *syn* and the *anti* adducts, as indicated in the proposed preferentially adopted conformation reported in Figure 1. These conformations also explain the shielding effects observed in the chemical shifts of the methyl group in the *syn* products **4a** and **5a** and in the chemical shifts of the proton $H_X$ in the *anti* adducts **6a** and **7a**. These effects are due to the presence of the methyl or of the $H_X$ in the shielding cone of the phenyl group.[12]

The proposed absolute configurations of **4a**, **5a**, **6a**, and **7a** were confirmed by the results of the simple reactions indicated in Scheme 2 and in Scheme 3. Scheme 2 refers

**Table 1.** $TiCl_4$-mediated aldol condensation between **1** and **2** and various aldehydes




| | R | $R_1$ | *syn*:*anti*[a] | *syn* **4**[b] | *syn* **5**[b] | **4**:**5**[a] | *anti* **6+7**[b] | **6**:**7**[c] |
|---|---|---|---|---|---|---|---|---|
| a | Me | Ph | 76:24 | 41 | 9 | 82:18 | 16 | 58:42 |
| b | Me | $PhCH_2CH_2$ | 81:19 | 33 | 28 | 54:46 | 14[c] | 70:30 |
| c | Me | $PhCH_2OCH_2$ | 73:27 | 27 | 20 | 57:43 | 17[c] | 56:44 |
| d | OMe | Ph | 61:39 | 35 | 17 | 68:32 | 33[c] | 80:20 |
| e | OMe | *p*-OMe-$C_6H_4$ | 65:35 | 28 | 15 | 65:35 | 23[c] | 80:20 |
| f | OMe | PhCH=CH | 60:40 | 12 | 24 | 33:67 | 24[c] | 67:33 |
| g | OMe | $PhCH_2CH_2$ | 65:35 | 24 | 11 | 69:31 | 19[c] | 70:30 |
| h | OMe | $PhCH_2OCH_2$ | 63:37 | 18 | 6 | 75:25 | 14[c] | 19:81 |

[a] The diastereomeric ratios were determined by $^1$H NMR on the crude mixtures and confirmed after chromatographic separation.
[b] Percentage yields of the isolated products.
[c] With the exception of **6a** and **7a**, all the other couples of diastereoisomers could not be separated. The ratios were determined by $^1$H NMR of the mixtures.

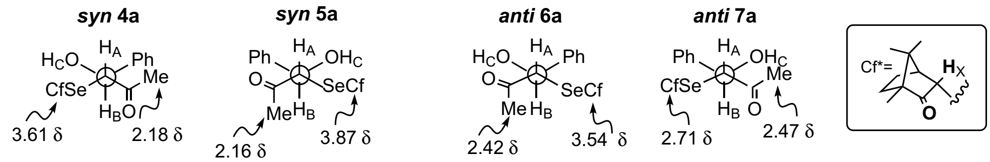
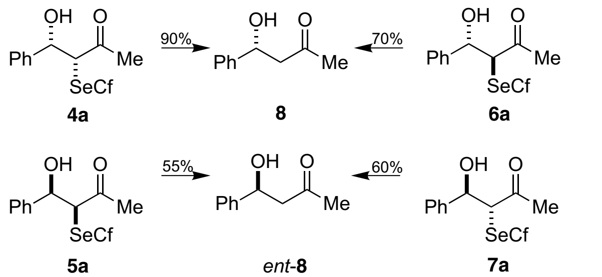
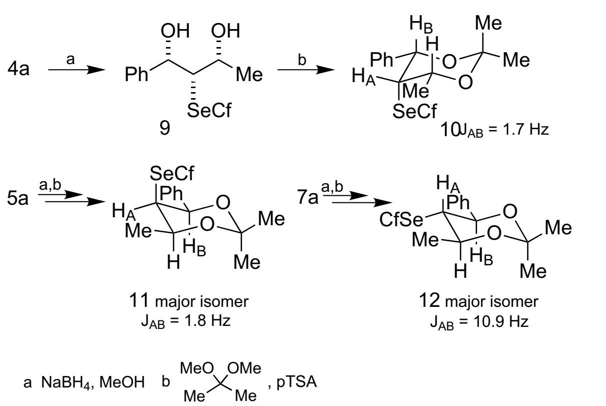


**Figure 1.** Proposed preferred conformations for **4a**, **5a**, **6a**, and **7a**.



**Scheme 2.** Reductive deselenenylations of **4a**, **5a**, **6a**, and **7a** with $Ph_3SnH$ and catalytic AIBN in refluxing $C_6H_6$.



**Scheme 3.** Formation of the acetonides of compounds **4a**, **5a**, and **7a**.

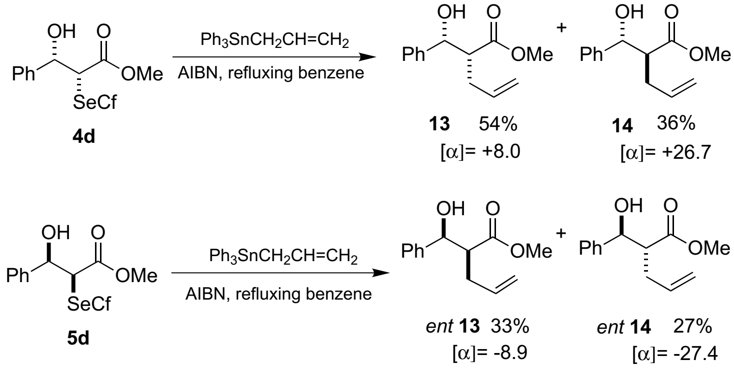
to the reductive deselenenylations of **4a**, **5a**, **6a**, and **7a**. These reactions allow the absolute configuration at the benzylic carbon to be assigned by comparison of the specific rotations of the two enantiomers of 4-hydroxy-4-phenylbutan-2-one **8** and *ent*-**8** with those reported in the literature.

As indicated in Scheme 2, **4a** and **6a** gave the (4*R*)-isomer **8**, while **5a** and **7a** gave the (4*S*)-isomer *ent*-**8**.[13]

Scheme 3 describes the conversions of **4a**, **5a**, and **7a** into the corresponding acetonides **10**, **11**, and **12**. For this purpose the α-selenoaldols were reduced with $NaBH_4$ in MeOH and the resulting 1,3-diols were treated with 2,2-dimethoxypropane in acetone in the presence of catalytic amounts of *p*-toluensulphonic acid.[4a] Only the reduction of **4a** was completely stereoselective, giving the indicated diol **9** as a single isomer. On the contrary, the reductions of **5a** and **7a** gave mixtures of the two possible diastereomeric diols. For the sake of simplicity, Scheme 3 reports only the acetonides **11** and **12**, deriving from the major isomers of the diols. The observed $^1$H NMR vicinal coupling constants of the acetonides and the results of some NOESY experiments fully confirm the indicated configurations. In particular the $^3J_{AB}$ values, clearly indicate the relative stereochemistry of the -Ph and the -SeCf substituents: *syn* in **10** and **11** and *anti* in **12**.[14]

The absolute configuration of the carbon bearing the hydroxy group in compounds **4b–d**,**f**,**h**, **5b–d**,**f**,**h**, **6b**,**d**,**f**,**h**, and **7b–d**,**f**,**h** was determined by reductive deselenenylation.[15] The stereochemistry of all the aldols was assigned by comparison of the $^1$H, $^{13}$C and $^{77}$Se spectra with those of **4a**, **5a**, **6a**, and **7a**.[16]

In order to test their potential use as chiral building blocks some simple manipulations of the aldols, produced as described above, were effected. Scheme 4 shows the radical allylation of the *syn* β-hydroxy-α-camphorseleno esters, **4d** and **5d**, effected with allyltriphenyltin in



**Scheme 4.** Radical allylation of the β-hydroxy-α-camphorseleno esters **4d** and **5d**.

the presence of AIBN in refluxing benzene. In both cases the substitution products **13** and **14** or their enantiomers *ent*-**13** and *ent*-**14** were isolated by column chromatography in good yields. Thus, all the four possible enantiomerically pure isomers of the methyl 2-[hydroxy(phenyl)methyl]pent-4-enoate were obtained. These unsaturated hydroxyesters may be used as starting materials for further stereospecific transformations. For example, they may be easily converted into enantiomerically pure trisubstituted tetrahydrofurans by ring closure reactions promoted by electrophilic reagents.[1]

## 3. Conclusion

In conclusion, we have reported that the titanium enolates deriving from (*R*)-camphorselenoacetone **1** and methyl (*R*)-camphorselenoacetate **2** can be successfully employed as chiral nucleophiles in asymmetric crossed aldol reactions in the presence of aromatic, conjugated or aliphatic aldehydes. Enantiomerically pure *syn* and *anti* aldols have been separated in good yields and with moderate selectivities. Several simple manipulations of the β-hydroxy-α-camphorseleno ketones or esters were carried out in order to determine their structures and to study their potential application as intermediates in asymmetric synthesis.

## 4. Experimental

New compounds were characterized by MS, $^{1}$H, $^{77}$Se and $^{13}$C NMR spectroscopy. GLC analyses and MS spectra were carried out with an HP 6890 gas chromatograph (25 m dimethyl silicone capillary column) equipped with an HP 5973 Mass Selective Detector; for the ions containing selenium only the peaks arising from the selenium-80 isotope is given. $^{1}$H, $^{77}$Se and $^{13}$C NMR spectra were recorded at 400, 76.27 and 100.62 MHz, respectively, on a Bruker DRX 400 instrument; unless otherwise specified, $CDCl_3$ was used as solvent and TMS as standard. Optical rotations were measured with a Jasco DIP-1000 digital polarimeter. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer.

### 4.1. Syntheses of the (*R*)-camphorselenoacetone 1 and of the methyl (*R*)-camphorselenoacetate 2

The α-selenoketone **1** and the α-selenoester **2** have been prepared starting from the (*R*,*R*)-camphor diselenide using standard procedures.[8,9]

### 4.2. (*R*)-Camphorselenoacetone 1

Oil; $[\alpha]_D^{20} = +18.3$ (*c* 1.2, $CHCl_3$). $^{1}$H NMR: δ 3.76 (dd, 1H, $J = 2.0$, 4.6 Hz), 3.55 (d, 1H, $J = 12.0$ Hz), 3.37 (d, 1H, $J = 12.0$ Hz), 2.34 (s, 3H), 2.20 (t, 1H, $J = 4.2$ Hz), 1.85–1.50 (m, 3H), 1.45–1.20 (m, 1H), 0.99 (s, 3H), 0.90 (s, 3H), 0.89 (s, 3H). $^{13}$C NMR: δ 217.3, 203.8, 58.1, 47.7, 47.4, 46.7, 32.2, 30.5, 27.8, 23.2, 19.5, 19.4, 9.5. MS *m*/*z* (rel. int.) 288 (100), 231 (44), 202 (42), 177 (13), 152 (15), 121 (54), 109 (21), 93 (16), 83 (44), 79 (15), 67 (13), 55 (24). Anal. Calcd for $C_{13}H_{20}O_2Se$: C, 54.36; H, 7.02. Found: C, 54.01; H, 6.98.

### 4.3. Methyl (*R*)-camphorselenoacetate 2

Oil; $[\alpha]_D^{25} = -23.9$ (*c* 3.2, $CHCl_3$). $^{1}$H NMR: δ 3.99 (dd, 1H, $J = 2.0$, 4.7 Hz), 3.75 (s, 3H), 3.55 (d, 1H, $J = 12.7$ Hz), 3.27 (d, 1H, $J = 12.7$ Hz), 2.24 (t, 1H, $J = 4.3$ Hz), 1.80–1.60 (m, 3H), 1.58–1.30 (m, 1H), 1.03 (s, 3H), 0.95 (s, 6H). $^{13}$C NMR: δ 217.4, 171.7, 58.1, 52.4, 47.8, 47.2, 46.8, 30.5, 23.3, 22.3, 19.6, 19.4, 9.5. MS *m*/*z* (rel. int.) 304 (100), 276 (18), 244 (9), 231 (91), 203 (15), 193 (26), 151 (45), 137 (10), 123 (81), 109 (30), 107 (32), 95 (28), 93 (28), 91 (29), 83 (69), 81 (46), 79 (29), 67 (20), 55 (50). Anal. Calcd for $C_{13}H_{20}O_3Se$: C, 51.49; H, 6.65. Found: C, 51.92; H, 6.21.

### 4.4. Aldol reactions: general procedure

A solution of the α-seleno carbonyl compound **1** or **2** in $CH_2Cl_2$ was treated with 1.1 equiv of $TiCl_4$ at −78 °C under nitrogen. After 5 min 2 equiv of $Et_3N$ were added and immediately the yellow mixture turned dark. After 1 h 1.1 equiv of an aromatic, α,β-unsaturated or aliphatic aldehyde **3** were added dropwise and the reaction mixture was stirred at the same temperature for about 6 h. In the cases of the aldehydes **3c**, **3g**, and **3h**, at the end of the addition, the reaction temperature was slowly allowed to rise to −30 °C. The reaction was then quenched with a saturated solution of $NH_4Cl$ and extracted with $CH_2Cl_2$. The crude mixture was purified by flash chromatography using mixtures of diethyl ether and light petroleum (40–60 °C) as the eluant. The compounds **4a–g**, **5a–g**, **6a**, **7a**, and the mixtures of **4h**/**5h** and **6b–h**/**7b–h** were separated and characterized. Physical and spectral data of these products are reported below.

### 4.5. (3*R*,4*S*)-3-(camphorseleno)-4-hydroxy-4-phenyl butan-2-one 4a

Oil; $[\alpha]_D^{20} = +70.0$ (*c* 2.4, $CHCl_3$). $^{1}$H NMR: δ 7.40–7.15 (m, 5H), 4.97 (d, 1H, $J = 8.5$ Hz), 4.60 (br s, 1H), 3.96 (d, 1H, $J = 8.5$ Hz), 3.61 (dd, 1H, $J = 1.8$, 4.8 Hz), 2.18 (s, 3H), 2.11 (t, 1H, $J = 4.2$ Hz), 1.92–1.30 (m, 4H), 0.98 (s, 3H), 0.95 (s, 3H), 0.89 (s, 3H). $^{13}$C NMR: δ 220.9, 204.5, 146.0, 128.3 (two carbons), 127.8, 126.7 (two carbons), 71.0, 58.6, 55.7, 48.6, 46.0, 41.7, 30.8, 29.1, 23.7, 19.7, 19.0, 9.5. $^{77}$Se NMR: δ 480.3. Anal. Calcd for $C_{20}H_{26}O_3Se$: C, 61.06; H, 6.66. Found: C, 61.60; H, 6.75.

### 4.6. (3*R*,4*S*)-3-(camphorseleno)-4-hydroxy-6-phenyl hexan-2-one 4b

Oil; $[\alpha]_D^{21} = +47.3$ (*c* 2.7, $CHCl_3$). $^{1}$H NMR: δ 7.35–7.15 (m, 5H), 4.37 (d, 1H, $J = 3.7$ Hz), 3.88–3.80 (m, 1H), 3.71 (dd, 1H, $J = 2.3$–4.5 Hz), 3.51 (d, 1H, $J = 9.5$ Hz), 3.04–2.95 (ddd, 1H, $J = 5.5, 8.2, 13.8$ Hz), 2.69 (dt, 1H, $J = 8.2, 13.8$ Hz), 2.31 (s, 3H), 2.15 (t, 1H, $J = 4.4$ Hz), 1.92–1.65 (m, 4H), 1.52–1.38 (m, 2H), 1.0 (s, 3H), 0.98 (s, 3H), 0.95 (s, 3H). $^{13}$C NMR: $\delta$ 221.2, 203.8, 142.1, 128.4 (two carbons), 128.2 (two carbons), 125.6, 68.2, 58.6, 54.6, 48.7, 47.2, 45.8, 36.9, 32.7, 30.7, 29.0, 23.9, 19.7, 19.0, 9.5. $^{77}$Se NMR: $\delta$ 481.4. Anal. Calcd for $C_{22}H_{30}O_3Se$: C, 62.70; H, 7.18. Found: C, 62.39; H, 7.40.

### 4.7. (3*R*,4*S*)-5-(benzyloxy)-3-(camphorseleno)-4-hydroxy pentan-2-one 4c

Oil; $[\alpha]_D^{22} = +49.3$ ($c$ 1.4, $CHCl_3$). $^1$H NMR: $\delta$ 7.47–7.28 (m, 5H), 4.57 (d, 1H, $J = 11.9$ Hz), 4.50 (d, 1H, $J = 11.9$ Hz), 4.49 (br s, 1H), 4.18–4.03 (m, 1H), 3.84 (dd, 1H, $J = 2.5, 4.7$ Hz), 3.81 (d, 1H, $J = 9.3$ Hz), 3.68 (dd, 1H, $J = 4.6, 10.0$ Hz), 3.64 (dd, 1H, $J = 5.2, 10.0$ Hz), 2.31 (s, 3H), 2.19 (t, 1H, $J = 4.4$ Hz), 1.98–1.65 (m, 2H), 1.52–1.30 (m, 2H), 1.0 (s, 3H), 0.97 (s, 3H), 0.95 (s, 3H). $^{13}$C NMR: $\delta$ 221.2, 204.0, 135.0, 128.3 (two carbons), 127.7 (two carbons), 127.6, 73.4, 71.7, 68.0, 58.5, 51.5, 48.8, 46.8, 45.9, 30.7, 28.6, 23.9, 19.7, 19.0, 9.5. $^{77}$Se NMR: $\delta$ 468.4. Anal. Calcd for $C_{22}H_{30}O_4Se$: C, 60.41; H, 6.91. Found: C, 60.19; H, 6.99.

### 4.8. Methyl (2*R*,3*S*)-2-(camphorseleno)-3-hydroxy-3-phenylpropanoate 4d

Oil; $[\alpha]_D^{25} = -41.2$ ($c$ 1.5, $CHCl_3$). $^1$H NMR: $\delta$ 7.49–7.35 (m, 2H), 7.35–7.20 (m, 3H), 4.88 (dd, 1H, $J = 3.9, 9.0$ Hz), 4.75 (d, 1H, $J = 3.9$ Hz), 4.19 (dd, 1H, $J = 2.3, 4.6$ Hz), 3.69 (d, 1H, $J = 9.0$ Hz), 3.55 (s, 3H), 2.20 (t, 1H, $J = 4.3$ Hz), 1.90–1.68 (m, 3H), 1.50–1.40 (m, 1H), 1.0 (s, 3H), 0.96 (s, 6H). $^{13}$C NMR: $\delta$ 220.8, 172.3, 140.1, 128.2 (two carbons), 127.9, 126.4 (two carbons), 72.0, 58.5, 52.0, 48.6, 47.7, 47.1, 45.6, 30.6, 23.4, 19.6, 19.0, 9.4. $^{77}$Se NMR: $\delta$ 505.2. Anal. Calcd for $C_{20}H_{26}O_4Se$: C, 58.68; H, 6.40. Found: C, 58.80; H, 6.46.

### 4.9. Methyl (2*R*,3*S*)-2-(camphorseleno)-3-hydroxy-3-(4-methoxyphenyl)propanoate 4e

Oil; $[\alpha]_D^{26} = -40.4$ ($c$ 2.0, $CHCl_3$). $^1$H NMR: $\delta$ 7.30 ($A_2B_2$ system, 2H), 6.83 ($A_2B_2$ system, 2H), 4.83 (dd, 1H, $J = 3.9, 9.3$ Hz), 4.67 (d, 1H, $J = 3.9$ Hz), 4.17 (dd, 1H, $J = 2.3, 4.6$ Hz), 3.80 (s, 3H), 3.67 (d, 1H, $J = 9.3$ Hz), 3.54 (s, 3H), 2.21 (t, 1H, $J = 4.3$ Hz), 1.80–1.30 (m, 4H), 1.0 (s, 3H), 0.93 (s, 6H). $^{13}$C NMR: $\delta$ 221.3, 172.8, 159.7, 132.8, 128.3 (two carbons), 114.2 (two carbons), 72.3, 59.1, 55.6, 52.6, 49.2, 48.3, 47.7, 46.2, 31.3, 24.1, 20.2, 19.6, 10.0. $^{77}$Se NMR: $\delta$ 505.6. Anal. Calcd for $C_{21}H_{28}O_5Se$: C, 57.40; H, 6.42. Found: C, 57.73; H, 6.19.

### 4.10. Methyl (2*R*,3*S*,4*E*)-2-(camphorseleno)-3-hydroxy-5-phenylpent-4-enoate 4f

Oil; $[\alpha]_D^{23} = -58.1$ ($c$ 1.6, $CHCl_3$). $^1$H NMR: $\delta$ 7.50–7.25 (m, 5H), 6.73 (d, 1H, $J = 15.9$ Hz), 6.20 (dd, 1H, $J = 6.5, 15.9$ Hz), 4.73 (d, 1H, $J = 4.0$ Hz), 4.52 (ddd, 1H, $J = 4.0, 6.5, 9.3$ Hz), 4.27 (dd, 1H, $J = 2.3, 4.6$ Hz), 3.71 (s, 3H), 3.52 (d, 1H, $J = 9.3$ Hz), 2.29 (t, 1H, $J = 4.4$ Hz), 1.95–1.83 (m, 1H), 1.81–1.75 (m, 1H), 1.58–1.40 (m, 2H), 1.04 (s, 3H), 0.99 (s, 3H), 0.98 (s, 3H). $^{13}$C NMR: $\delta$ 221.1, 172.4, 136.5, 132.4, 128.5 (two carbons), 127.8, 127.2, 126.6 (two carbons), 70.8, 58.7, 52.3, 48.8, 47.3, 46.1, 45.7, 30.8, 23.7, 19.7, 19.1, 9.6. $^{77}$Se NMR: $\delta$ 503.0. Anal. Calcd for $C_{22}H_{28}O_4Se$: C, 60.69; H, 6.48. Found: C, 60.99; H, 6.60.

### 4.11. Methyl (2*R*,3*S*)-2-(camphorseleno)-3-hydroxy-5-phenylpentanoate 4g

Oil; $[\alpha]_D^{17} = -41.6$ ($c$ 3.5, $CHCl_3$). $^1$H NMR: $\delta$ 7.30–7.08 (m, 5H), 4.50 (br s, 1H), 4.14 (dd, 1H, $J = 2.3, 4.6$ Hz), 3.80 (dt, 1H, $J = 2.9, 9.0$ Hz), 3.70 (s, 3H), 3.35 (d, 1H, $J = 9.0$ Hz), 2.99 (ddd, 1H, $J = 5.0, 10.5, 13.8$ Hz), 2.70 (ddd, 1H, $J = 6.4, 11.0, 13.8$ Hz), 2.22 (t, 1H, $J = 4.4$ Hz), 1.98–1.70 (m, 4H), 1.65–1.35 (m, 2H), 1.0 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H). $^{13}$C NMR: $\delta$ 221.1, 173.0, 142.0, 128.5 (two carbons), 128.3 (two carbons), 125.7, 69.1, 58.7, 52.3, 48.8, 47.2, 46.4, 45.6, 36.7, 32.5, 30.7, 24.3, 19.7, 19.1, 9.6. $^{77}$Se NMR: $\delta$ 505.3. Anal. Calcd for $C_{22}H_{30}O_4Se$: C, 60.41; H, 6.91. Found: C, 60.73; H, 6.98.

### 4.12. Methyl (2*R*,3*S*) and (2*S*,3*R*)-4-(benzyloxy)-2-(camphorseleno)-3-hydroxybutanoate 4h and 5h

Major diastereoisomer (2*R*,3*S*): $^1$H NMR $\delta$ 7.38–7.30 (m, 5H), 4.61 (d, 1H, $J = 11.8$ Hz), 4.54 (d, 1H, $J = 11.8$ Hz), 4.28–4.22 (m, 1H), 3.98 (d, 1H, $J = 6.2$ Hz), 3.97 (dd, 1H, $J = 2.6, 5.0$ Hz), 3.77 (d, 1H, $J = 2.9$ Hz), 3.72 (s, 3H), 3.70–3.67 (m, 2H), 2.30 (t, 1H, $J = 4.3$ Hz), 1.95–1.80 (m, 1H), 1.78–1.60 (m, 2H), 1.58–1.40 (m, 1H), 1.03 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H). $^{13}$C NMR: $\delta$ 218.7, 173.2, 138.3, 128.8 (two carbons), 128.3 (two carbons), 128.1, 73.9, 72.0, 70.8, 58.6, 52.9, 49.2, 48.3, 47.3, 45.2, 31.0, 23.9, 20.0, 19.7, 10.1. $^{77}$Se NMR: $\delta$ 501.3. Anal. Calcd for $C_{22}H_{30}O_5Se$: C, 58.28; H, 6.67. Found: C, 58.43; H, 6.70. Minor diastereoisomer (2*S*,3*R*) (distinct signals): $^1$H NMR: $\delta$ 4.64 (d, 1H, $J = 4.7$ Hz), 4.58 (d, 1H, $J = 11.8$ Hz), 4.53 (d, 1H, $J = 11.8$ Hz), 4.25–4.21 (m, 1H), 4.14–4.07 (m, 1H), 3.63 (s, 3H), 2.25 (t, 1H, $J = 4.3$ Hz), 1.02 (s, 3H), 0.98 (s, 3H), 0.97 (s, 3H). $^{13}$C NMR: $\delta$ 221.6, 128.7, 128.2, 128.0, 72.2, 69.2, 59.1, 52.6, 49.3, 47.7, 46.2, 44.3, 31.2, 24.1, 20.1. $^{77}$Se NMR: $\delta$ 496.7.

### 4.13. (3*S*,4*R*)-3-(camphorseleno)-4-hydroxy-4-phenyl butan-2-one 5a

Oil; $[\alpha]_D^{22} = -125.0$ ($c$ 0.4, $CHCl_3$). $^1$H NMR: $\delta$ 7.35–7.01 (m, 5H), 5.08 (dd, 1H, $J = 2.2, 7.9$ Hz), 4.13 (d, 1H, $J = 2.2$ Hz), 3.99 (d, 1H, $J = 7.9$ Hz), 3.87 (dd, 1H, $J = 2.2, 4.6$ Hz), 2.32 (t, 1H, $J = 4.4$ Hz), 2.16 (s, 3H), 1.92–1.50 (m, 4H), 1.04 (s, 3H), 0.95 (s, 6H). $^{13}$C NMR: $\delta$ 217.9, 204.7, 140.5, 128.3 (two carbons), 128.0, 127.4 (two carbons), 73.1, 58.2, 57.7, 49.0, 48.8, 47.0, 30.4, 29.3, 23.5, 19.7, 19.4, 9.5. $^{77}$Se NMR: $\delta$ 478.0. Anal. Calcd for $C_{20}H_{26}O_3Se$: C, 61.06; H, 6.66. Found: C, 61.22; H, 6.79.

### 4.14. (3*S*,4*R*)-3-(camphorseleno)-4-hydroxy-6-phenyl hexan-2-one 5b

Oil; $[\alpha]_D^{24} = -105.7$ ($c$ 0.4, $CHCl_3$). $^1$H NMR: $\delta$ 7.30–7.18 (m, 5H), 4.04-3.97 (m, 1H), 3.83 (dd, 1H, $J = 2.4$, 4.5 Hz), 3.76 (d, 1H, $J = 6.4$ Hz), 3.63 (br s, 1H), 2.90 (ddd, 1H, $J = 5.3$, 9.6, 13.6 Hz), 2.75 (ddd, 1H, $J = 7.1$, 9.2, 13.6), 2.39 (s, 3H), 2.29 (t, 1H, $J = 4.4$ Hz), 1.99–1.40 (m, 6H), 1.05 (s, 3H), 0.96 (s, 3H) 0.90 (s, 3H). $^{13}$C NMR: $\delta$ 217.6, 206.1, 142.2, 129.0 (two carbons), 128.8 (two carbons), 126.3, 70.1, 58.6, 56.1, 49.4, 49.3, 48.5, 36.9, 32.3, 30.9, 29.3, 24.0, 20.1, 19.8, 10.0. $^{77}$Se NMR: $\delta$ 473.6. Anal. Calcd for $C_{22}H_{30}O_3Se$: C, 62.70; H, 7.18. Found: C, 62.99; H, 7.30.

### 4.15. (3*S*,4*R*)-5-(benzyloxy)-3-(camphorseleno)-4-hydroxypentan-2-one 5c

Oil; $[\alpha]_D^{24} = -64.9$ ($c$ 0.5, $CHCl_3$). $^1$H NMR: $\delta$ 7.48–7.28 (m, 5H), 4.56 (d, 1H $J = 11.9$ Hz), 4.49 (d, 1H, $J = 11.9$ Hz), 4.20 (dt, 1H, $J = 5.0$, 6.5 Hz), 3.91 (d, 1H, $J = 6.5$ Hz), 3.79 (dd, 1H, $J = 2.7$, 4.7 Hz), 3.66 (dd, 1H, $J = 5.0$, 9.7 Hz), 3.62 (dd, 1H, $J = 5.0$, 9.7 Hz), 3.50 (br s, 1H), 2.40 (s, 3H), 2.26 (t, 1H, $J = 4.4$ Hz), 1.98–1.50 (m, 4H), 1.0 (s, 3H), 0.98 (s, 3H) 0.95 (s, 3H). $^{13}$C NMR: $\delta$ 217.7, 205.2, 137.6, 128.4 (two carbons), 127.9 (two carbons), 127.8, 73.5, 71.5, 69.6, 58.2, 52.6, 49.0, 48.4, 46.9, 30.5, 28.6, 23.6, 19.7, 19.3, 9.6. $^{77}$Se NMR: $\delta$ 467.5. Anal. Calcd for $C_{22}H_{30}O_4Se$: C, 60.41; H, 6.91. Found: C, 60.93; H, 6.72.

### 4.16. Methyl (2*S*,3*R*)-2-(camphorseleno)-3-hydroxy-3-phenylpropanoate 5d

Oil; $[\alpha]_D^{26} = -86.4$ ($c$ 2.5, $CHCl_3$). $^1$H NMR: $\delta$ 7.40–7.35 (m, 2H), 7.35–7.20 (m, 3H), 5.05 (dd, 1H, $J = 1.8$, 8.3 Hz), 4.48 (d, 1H, $J = 1.8$ Hz), 3.93 (dd, 1H, $J = 2.2$, 4.6 Hz), 3.91 (d, 1H, $J = 8.3$ Hz), 3.55 (s, 3H), 2.29 (t, 1H, $J = 4.4$ Hz), 1.92–1.81 (m, 1H), 1.75–1.66 (m, 1H), 1.61 (ddd, 1H, $J = 3.7$, 9.2, 13.1 Hz), 1.50–1.36 (m, 1H), 1.01 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H). $^{13}$C NMR: $\delta$ 218.8, 171.6, 140.2, 128.3 (two carbons), 128.2, 126.6 (two carbons), 74.3, 58.3, 52.3, 50.6, 49.0, 48.8, 47.0, 30.6, 23.4, 19.7, 19.3, 9.6. $^{77}$Se NMR: $\delta$ 509.4. Anal. Calcd for $C_{20}H_{26}O_4Se$: C, 58.68; H, 6.40. Found: C, 58.89; H, 6.49.

### 4.17. Methyl (2*S*,3*R*)-2-(camphorseleno)-3-hydroxy-3-(4-methoxyphenyl)propanoate 5e

Oil; $[\alpha]_D^{26} = -51.3$ ($c$ 1.3, $CHCl_3$). $^1$H NMR: $\delta$ 7.31 ($A_2B_2$ system, 2H), 6.85 ($A_2B_2$ system, 2H), 5.0 (dd, 1H, $J = 2.4$, 8.3 Hz), 4.39 (d, 1H, $J = 2.4$ Hz), 3.94 (dd, 1H, $J = 2.3$, 4.3 Hz), 3.87 (d, 1H, $J = 8.3$ Hz), 3.80 (s, 3H), 3.54 (s, 3H), 2.30 (t, 1H, $J = 4.5$ Hz), 1.98–1.80 (m, 1H), 1.77–1.52 (m, 2H), 1.48–1.30 (m, 1H), 1.13 (s, 3H), 0.98 (s, 3H), 0.97 (s, 3H). $^{13}$C NMR: $\delta$ 219.4, 172.0, 159.8, 132.7, 128.8 (two carbons), 114.1 (two carbons), 74.4, 58.7, 55.6, 52.7, 51.2, 49.4, 49.3, 47.4, 31.0, 23.8, 20.1, 19.7, 10.0. $^{77}$Se NMR: $\delta$ 510.0. Anal. Calcd for $C_{21}H_{28}O_5Se$: C, 57.40; H, 6.42. Found: C, 57.85; H, 6.20.

### 4.18. Methyl (2*S*,3*R*,4*E*)-2-(camphorseleno)-3-hydroxy-5-phenylpent-4-enoate 5f

Oil; $[\alpha]_D^{24} = -50.4$ ($c$ 2.5, $CHCl_3$). $^1$H NMR: $\delta$ 7.42–7.23 (m, 5H), 6.74 (d, 1H, $J = 15.9$ Hz), 6.26 (d, 1H, $J = 6.4$, 15.9 Hz), 4.72 (ddd, 1H, $J = 2.7$, 6.4, 7.2 Hz), 4.15 (d, 1H, $J = 2.7$ Hz) 3.97 (dd, 1H, $J = 2.3$, 4.6 Hz), 3.91 (d, 1H, $J = 7.2$ Hz), 3.75 (s, 3H), 2.27 (t, 1H, $J = 4.4$ Hz), 1.90–1.80 (m, 1H), 1.75–1.53 (m, 2H), 1.50–1.35 (m, 1H), 1.02 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H). $^{13}$C NMR: $\delta$ 218.8, 172.2, 136.5, 132.6, 128.5 (two carbons), 127.8, 127.4, 126.7 (two carbons), 72.7, 58.2, 52.5, 48.8, 48.1, 48.0, 47.0, 30.5, 23.4, 19.7, 19.2, 9.6. $^{77}$Se NMR: $\delta$ 507.8. Anal. Calcd for $C_{22}H_{28}O_4Se$: C, 60.69; H, 6.48. Found: C, 60.99; H, 6.50.

### 4.19. Methyl (2*S*,3*R*)-2-(camphorseleno)-3-hydroxy-5-phenylpentanoate 5g

Oil; $[\alpha]_D^{19} = -79.5$ ($c$ 1.7, $CHCl_3$). $^1$H NMR: $\delta$ 7.27–7.08 (m, 5H), 4.50 (br s, 1H), 3.99 (ddd, 1H, $J = 3.8$, 5.3, 9.0 Hz), 3.91 (dd, 1H, $J = 2.2$, 4.6 Hz), 3.88 (d, 1H, $J = 5.3$ Hz), 3.74 (s, 3H), 2.87 (ddd, 1H, $J = 5.4$, 9.7, 13.8 Hz), 2.74 (ddd, 1H, $J = 7.1$, 9.2, 13.8 Hz), 2.27 (t, 1H, $J = 4.4$ Hz), 2.02–1.91 (m, 1H), 1.91–1.79 (m, 2H), 1.78–1.68 (m, 1H), 1.64–1.55 (m, 1H), 1.51–1.41 (m, 1H), 1.01 (s, 3H), 0.97 (s, 3H), 0.96 (s, 3H). $^{13}$C NMR: $\delta$ 218.8, 173.6, 141.8, 128.6 (two carbons), 128.3 (two carbons), 125.8, 70.4, 58.2, 52.4, 48.7, 47.3, 47.0, 46.9, 36.1, 31.7, 30.5, 23.5, 19.6, 19.2, 9.6. $^{77}$Se NMR: $\delta$ 505.5. Anal. Calcd for $C_{22}H_{30}O_4Se$: C, 60.41; H, 6.91. Found: C, 60.58; H, 6.99.

### 4.20. (3*S*,4*S*)-3-(camphorseleno)-4-hydroxy-4-phenyl butan-2-one 6a

Oil (purity about 90%, [α] not determined); $^1$H NMR: $\delta$ 7.50–7.20 (m, 5H), 5.50 (dd, 1H, $J = 3.4$, 7.7 Hz), 4.08 (d, 1H, $J = 7.7$ Hz), 3.54 (dd, 1H, $J = 2.1$, 4.6 Hz), 3.44 (d, 1H, $J = 3.4$ Hz), 2.42 (s, 3H), 2.19 (t, 1H, $J = 4.0$ Hz), 1.98–1.30 (m, 4H), 1.02 (s, 3H), 0.91 (s, 3H), 0.85 (s, 3H). $^{13}$C NMR: $\delta$ 216.8, 206.5, 140.9, 128.4 (two carbons), 128.1, 126.7 (two carbons), 75.2, 58.1, 52.6, 48.5, 47.9, 46.8, 30.4, 29.2, 23.5, 19.6, 19.5, 9.6.

### 4.21. (3*S*,4*S*)- and (3*S*,4*R*)-3-(camphorseleno)-4-hydroxy-6-phenylhexan-2-one 6b and 7b

Oil; Major diastereoisomer (3*S*,4*S*): $^1$H NMR: $\delta$ 7.30–7.20 (m, 5H), 3.92–3.84 (m, 1H), 3.72 (d, 1H, $J = 8.0$ Hz), 3.56 (dd, 1H, $J = 2.9$, 3.9 Hz), 3.11 (d, 1H, $J = 5.5$ Hz), 2.97–2.85 (m, 1H), 2.85–2.70 (m, 1H), 2.45 (s, 3H), 2.16 (t, 1H, $J = 4.3$ Hz), 1.98–1.52 (m, 6H), 0.97

(s, 3H), 0.91 (s, 3H) 0.84 (s, 3H). $^{13}$C NMR: δ 217.5, 206.6, 142.1, 129.2 (two carbons), 128.8 (two carbons), 126.3, 70.7, 58.4, 53.6, 49.4, 48.3, 47.2, 36.2, 32.1, 30.8, 29.3, 24.1, 20.0, 19.8, 10.0. $^{77}$Se NMR: δ 492.8. Anal. Calcd for $C_{22}H_{30}O_3Se$: C, 62.70; H, 7.18. Found: C, 62.85; H, 7.28. Minor diastereoisomer (3*R*,4*R*) (distinct signals): $^1$H NMR: δ 4.12–4.06 (m, 1H), 3.71 (dd, 1H, $J = 2.1$, 4.9 Hz), 3.66 (d, 1H, $J = 8.2$ Hz), 2.99 (d, 1H, $J = 7.2$ Hz), 2.43 (s, 3H), 1.01 (s, 3H), 0.96 (s, 3H). $^{13}$C NMR: δ 217.7, 206.4, 142.4, 129.0 (two carbons), 126.2, 72.1, 58.6, 51.9, 48.8, 47.5, 47.3, 32.5, 30.1, 29.4, 23.9, 10.1. $^{77}$Se NMR: δ 500.6.

### 4.22. (3*S*,4*S*) and (3*S*,4*R*)-5-(benzyloxy)-3-(camphorseleno)-4-hydroxypentan-2-one 6c and 7c

Oil; $^1$H NMR: δ 7.46–7.25 (m, 10H), 4.64–4.55 (m, 4H), 4.29–4.20 (m, 1H), 4.19–4.10 (m, 1H), 4.02 (dd, 1H, $J = 4.0$, 10.1 Hz), 3.94 (d, 1H, $J = 9.3$ Hz), 3.91 (d, 1H, $J = 8.6$ Hz), 3.84 (dd, 1H, $J = 3.3$, 10.1 Hz), 3.83–3.79 (m, 2H), 3.78–3.74 (m, 2H), 3.20 (br s, 1H), 2.99 (br s, 1H), 2.45 (s, 6H), 2.20–2.10 (m, 2H), 1.98–1.50 (m, 8H), 1.0 (s, 3H), 0.98 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H), 0.88 (s, 3H), 0.87 (s, 3H). $^{13}$C NMR: δ 217.6 (two carbons), 205.2, 204.9, 137.9 (two carbons), 128.4 (four carbons), 127.8 (six carbons), 73.5 (two carbons), 71.6, 71.3, 71.2, 71.0, 58.2, 58.0, 49.0, 48.8, 48.5 (two carbons), 47.3, 47.0, 46.9, 46.8, 30.4 (two carbons), 28.7, 28.2, 23.6, 23.5, 19.6, 19.5, 19.4, 19.3, 9.6 (two carbons). $^{77}$Se NMR: δ 492.8 and 490.3. Anal. Calcd for $C_{22}H_{30}O_4Se$: C, 60.41; H, 6.91. Found: C, 60.75; H, 6.70.

### 4.23. Methyl (2*S*,3*S*)- and (2*R*,3*R*)-2-(camphorseleno)-3-hydroxy-3-phenylpropanoate 6d and 7d

Oil; Major diastereoisomer (2*S*,3*S*): $^1$H NMR: δ 7.48–7.25 (m, 5H), 5.12 (dd, 1H, $J = 6.2$, 7.9 Hz), 4.22 (d, 1H, $J = 6.2$ Hz), 3.80 (d, 1H, $J = 7.9$ Hz), 3.70 (dd, 1H, $J = 2.2$, 4.7 Hz), 3.68 (s, 3H), 2.16 (t, 1H, $J = 4.3$ Hz), 1.88–1.76 (m, 1H), 1.72–1.60 (m, 2H), 1.45–1.35 (m, 1H), 0.99 (s, 3H), 0.89 (s, 3H) 0.83 (s, 3H). $^{13}$C NMR: δ 217.6, 173.1, 140.7, 128.2 (two carbons), 127.8, 126.1 (two carbons), 75.0, 58.0, 52.3, 48.0, 46.9, 46.7, 44.3, 30.3, 23.2, 19.4, 19.3, 9.4. $^{77}$Se NMR: δ 539.8. Anal. Calcd for $C_{20}H_{26}O_4Se$: C, 58.68; H, 6.40. Found: C, 58.77; H, 6.31. Minor diastereoisomer (2*R*,3*R*) (distinct signals): $^1$H NMR: δ 5.07 (dd, 1H, $J = 1.2$, 8.3 Hz), 4.0 (d, 1H, $J = 8.3$ Hz), 3.72 (s, 3H), 3.50 (d, 1H, $J = 1.2$ Hz), 3.44 (dd, 1H, $J = 1.9$, 4.6 Hz), 1.90 (t, 1H, $J = 4.3$ Hz), 0.92 (s, 3H), 0.86 (s, 3H) 0.73 (s, 3H). $^{13}$C NMR: δ 172.7, 128.1, 126.7, 75.3, 52.4, 46.8, 44.9, 30.1, 23.0, 19.1. $^{77}$Se NMR: δ 527.9.

### 4.24. Methyl (2*S*,3*S*)- and (2*R*,3*R*)-2-(camphorseleno)-3-hydroxy-3-(4-methoxyphenyl) propanoate 6e and 7e

Oil; Major diastereoisomer (2*S*,3*S*): $^1$H NMR: δ 7.30 ($A_2B_2$ system, 2H), 6.60 ($A_2B_2$ system, 2H), 5.06 (dd, 1H, $J = 5.7$, 6.5 Hz), 4.16 (d, 1H, $J = 6.5$ Hz), 3.79 (s, 3H), 3.73 (dd, 1H, $J = 2.2$, 4.7 Hz), 3.71 (s, 3H), 3.63 (d, 1H, $J = 5.7$ Hz), 2.14 (t, 1H, $J = 4.3$ Hz), 1.95–1.55 (m, 3H), 1.50–1.28 (m, 1H), 1.0 (s, 3H), 0.90 (s, 3H) 0.80 (s, 3H). $^{13}$C NMR: δ 218.0, 173.7, 159.7, 133.3, 128.0 (two carbons), 114.2 (two carbons), 75.2, 58.6, 55.6, 52.8, 48.6, 47.6, 47.2, 45.2, 30.9, 23.8, 20.0, 19.9, 10.0. $^{77}$Se NMR: δ 535.6. Anal. Calcd for $C_{21}H_{28}O_5Se$: C, 57.40; H, 6.42. Found: C, 57.71; H, 6.55. Minor diastereoisomer (2*R*,3*R*) (distinct signals): $^1$H NMR: δ 7.36 ($A_2B_2$ system, 2H), 5.04 (d, 1H, $J = 8.5$ Hz), 3.98 (d, 1H, $J = 8.5$ Hz), 3.74 (s, 3H), 3.45 (dd, 1H, $J = 1.9$, 4.6 Hz), 3.30 (br s, 1H), 1.98 (t, 1H, $J = 4.3$ Hz), 0.95 (s, 3H), 0.87 (s, 3H), 0.75 (s, 3H). $^{13}$C NMR: δ 173.2, 128.5, 75.5, 53.0, 45.8, 30.8, 23.6, 19.7. $^{77}$Se NMR: δ 526.7.

### 4.25. Methyl (2*S*,3*S*,4*E*)- and (2*R*,3*R*,4*E*)-2-(camphorseleno)-3-hydroxy-5-phenylpent-4-enoate 6f and 7f

Oil; Major diastereoisomer (2*S*,3*S*): $^1$H NMR: δ 7.45–7.20 (m, 5H), 6.77 (dd, 1H, $J = 1.1$, 15.9 Hz), 6.37 (dd, 1H, $J = 6.0$, 15.9 Hz), 4.80–4.70 (m, 1H), 4.15 (d, 1H, $J = 5.3$ Hz) 3.96 (dd, 1H, $J = 2.2$, 4.7 Hz), 3.79 (s, 3H), 3.69 (d, 1H, $J = 8.9$ Hz), 2.28 (t, 1H, $J = 4.6$ Hz), 1.95–1.55 (m, 3H), 1.52–1.40 (m, 1H), 1.03 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H). $^{13}$C NMR: δ 218.4, 173.0, 136.4, 132.2, 128.5 (three carbons), 127.8, 126.7 (two carbons), 73.0, 58.2, 52.5, 48.5, 47.2, 46.9, 45.1, 30.5, 23.4, 19.6, 19.3, 9.6. $^{77}$Se NMR: δ 521.7. Anal. Calcd for $C_{22}H_{28}O_4Se$: C, 60.69; H, 6.48. Found: C, 60.79; H, 6.23. Minor diastereoisomer (2*R*,3*R*) (distinct signals): $^1$H NMR: δ 6.73 (dd, 1H, $J = 1.1$, 15.9 Hz), 6.36 (dd, 1H, $J = 6.2$, 15.9 Hz), 4.17 (dd, 1H, $J = 2.2$, 4.6 Hz), 3.76 (d, 1H, $J = 6.9$ Hz), 3.43 (d, 1H, $J = 6.6$ Hz), 2.47 (t, 1H, $J = 4.4$ Hz), 1.2 (s, 3H), 0.95 (s, 3H), 0.91 (s, 3H). $^{13}$C NMR: δ 217.4, 172.5, 136.3, 132.3, 128.2, 127.9, 73.2, 58.2, 48.4, 47.7, 43.9, 23.3, 19.4.

### 4.26. Methyl (2*S*,3*S*)- and (2*R*,3*R*)-2-(camphorseleno)-3-hydroxy-5-phenylpentanoate 6g and 7g

Oil; Major diastereoisomer (2*S*,3*S*): $^1$H NMR: δ 7.35–7.15 (m, 5H), 4.50 (br s, 1H), 3.93 (d, 1H, $J = 5.7$ Hz), 3.91 (dt, 1H, $J = 3.5$, 5.7 Hz), 3.85 (dd, 1H, $J = 2.1$, 4.6 Hz), 3.76 (s, 3H), 2.95–2.88 (m, 1H), 2.80–2.69 (m, 1H), 2.11 (t, 1H, $J = 4.4$ Hz), 2.15–2.01 (m, 1H), 1.94–1.77 (m, 2H), 1.74–1.64 (m, 1H), 1.61–1.53 (m, 1H), 1.48–1.38 (m, 1H), 0.99 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H). $^{13}$C NMR: δ 218.2, 173.4, 141.6, 128.5 (two carbons), 128.3 (two carbons), 125.8, 71.5, 58.1, 52.4, 48.6, 47.0, 46.8, 44.9, 36.6, 31.9, 30.4, 23.5, 19.6, 19.3, 9.5. $^{77}$Se NMR: δ 526.2. Anal. Calcd for $C_{22}H_{30}O_4Se$: C, 60.41; H, 6.91. Found: C, 60.60; H, 6.99. Minor diastereoisomer (2*R*,3*R*) (distinct signals): $^1$H NMR: δ 4.14 (dd, 1H, $J = 2.3$, 4.5 Hz), 4.0 (ddd, 1H, $J = 3.2$, 6.3, 9.4 Hz), 3.52 (d, 1H, $J = 6.3$ Hz), 2.20 (t, 1H, $J = 4.4$ Hz), 1.1 (s, 3H), 0.93 (s, 3H), 0.81 (s, 3H). $^{13}$C NMR: δ 217.0, 173.2, 71.9, 48.5, 47.3, 43.7, 32.0, 23.3, 19.4, 9.6.

### 4.27. Methyl (2*S*,3*S*)- and (2*R*,3*R*)-4-(benzyloxy)-2-(camphorseleno)-3-hydroxybutanoate 6h and 7h

Major diastereoisomer (2*R*,3*R*): $^1$H NMR δ 7.40–7.25 (m, 5H), 4.59 (d, 1H, $J = 11.8$ Hz), 4.56 (d, 1H, $J = 11.8$

Hz), 4.20 (ddt, 1H, $J = 5.1, 7.1, 8.3$ Hz), 3.99 (dd, 1H, $J = 2.2, 4.6$ Hz), 3.98 (d, 1H, $J = 7.1$ Hz), 3.84 (dd, 1H, $J = 5.0, 9.8$ Hz), 3.76 (dd, 1H, $J = 5.0, 9.8$ Hz), 3.74 (s, 3H), 3.37 (d, 1H, $J = 8.3$ Hz), 2.25 (t, 1H, $J = 4.4$ Hz), 1.95–1.80 (m, 1H), 1.75–1.50 (m, 2H), 1.50–1.35 (m, 1H), 1.03 (s, 3H), 0.95 (s, 3H), 0.91 (s, 3H). $^{13}$C NMR: $\delta$ 217.9, 173.3, 138.2, 128.8 (two carbons), 128.2 (three carbons), 73.9, 72.1, 72.0, 58.5, 52.9, 49.1, 48.5, 47.3, 42.1, 30.9, 23.8, 20.0, 19.9, 10.0. $^{77}$Se NMR: $\delta$ 520.0. Anal. Calcd for $C_{22}H_{30}O_5Se$: C, 58.28; H, 6.67. Found: C, 58.51; H, 6.49. Minor diastereoisomer (2*S*,3*S*) (distinct signals): $^1$H NMR: $\delta$ 4.61 (d, 1H, $J = 11.6$ Hz), 4.54 (d, 1H, $J = 11.6$ Hz), 3.81 (dd, 1H, $J = 5.7, 9.7$ Hz), 3.72 (s, 3H), 3.19 (d, 1H, $J = 7.7$ Hz), 2.30 (t, 1H, $J = 4.3$ Hz), 1.03 (s, 3H), 0.94 (s, 3H), 0.93 (s, 3H). $^{13}$C NMR: $\delta$ 218.7, 173.1, 138.3, 128.7, 128.3, 128.1, 71.4, 58.6, 49.0, 47.6, 40.3, 20.1, 19.8. $^{77}$Se NMR: $\delta$ 519.6.

### 4.28. (3*R*,4*R*)-3-(camphorseleno)-4-hydroxy-4-phenyl butan-2-one 7a

Oil; $[\alpha]_D^{24} = +56.1$ (*c* 0.9, $CHCl_3$). $^1$H NMR: $\delta$ 7.52–7.15 (m, 5H), 5.14 (dd, 1H, $J = 3.6, 9.5$ Hz), 4.31 (d, 1H, $J = 9.5$ Hz), 3.13 (d, 1H, $J = 3.6$ Hz), 2.71 (dd, 1H, $J = 1.9, 4.6$ Hz), 2.47 (s, 3H), 1.79 (t, 1H, $J = 4.0$ Hz), 1.95–1.30 (m, 4H), 0.92 (s, 3H), 0.89 (s, 3H), 0.63 (s, 3H). $^{13}$C NMR: $\delta$ 218.3, 206.9, 140.7, 128.2 (three carbons), 127.4 (two carbons), 75.2, 58.1, 53.4, 48.1, 46.7, 46.4, 30.4, 29.3, 23.4, 19.5, 19.1, 9.5. $^{77}$Se NMR: $\delta$ 513.7. Anal. Calcd for $C_{20}H_{26}O_3Se$: C, 61.06; H, 6.66. Found: C, 61.00; H, 6.42.

### 4.29. Radical deselenenylations of the α-camphorseleno-β-hydroxyketones and of the α-camphorseleno-β-hydroxyesters. General procedure

To a solution of the α-camphorseleno-β-hydroxyketone or ester (0.2 mmol) in benzene under nitrogen triphenyltin hydride (0.6 mmol) and a catalytic amount of AIBN were added and the reaction was refluxed for 2 h. The residue obtained after removal of the solvent under reduced pressure was purified by column chromatography on silica gel. Physical and spectral data of the obtained β-hydroxy ketones and esters are in good agreement with those already described in the literature.[13,15]

### 4.30. Synthesis of the acetonides 10, 11 and 12. General procedure

To a 0 °C cooled solution of **4a**, **5a** or **7a** (0.15 mmol) in methanol (5 mL) $NaBH_4$ (0.17 mmol) was added and the resulting mixture was stirred for 1 h. The reaction mixture was poured into water and extracted with diethyl ether. The organic layers were dried with $Na_2SO_4$ and evaporated. The resulting crude diols were obtained in virtually quantitative yields and were used for the next step without any purification. The diols were dissolved in 2,2-dimethoxypropane (3 mL) and acetone (1 mL) and a catalytic amount of *p*-toluensulphonic acid was added. The reactions were stirred at room temperature for 2 h, then a 10% aqueous solution of NaOH and diethyl ether were added and the mixtures were left under stirring for 10 min. The organic layers were dried with $Na_2SO_4$ and evaporated under reduced pressure. The pure acetonides were separated by column chromatography on florisil.

### 4.31. (4*R*,5*S*,6*S*)-5-(camphorseleno)-2,2,4-trimethyl-6-phenyl-1,3-dioxane 10

M.p. 90–91 °C; $[\alpha]_D^{26} = -113.5$ (*c* 1.4, $CHCl_3$). $^1$H NMR: $\delta$ 7.50–7.40 (m, 2H), 7.35–7.15 (m, 3H), 5.23 (d, 1H, $J = 1.7$ Hz), 4.38 (dq, 1H, $J = 1.7, 6.2$ Hz), 3.77 (t, 1H, $J = 1.7$ Hz), 2.02 (dd, 1H, $J = 1.3, 4.5$ Hz), 1.80–1.40 (m, 5H), 1.55 (s, 3H), 1.53 (s, 3H), 1.44 (d, 3H, $J = 6.2$ Hz), 0.82 (s, 3H), 0.78 (s, 3H), 0.41 (s, 3H). Anal. Calcd for $C_{23}H_{32}O_3Se$: C, 63.44; H, 7.41. Found: C, 63.39; H, 7.30.

### 4.32. (4*S*,5*R*,6*R*)-5-(camphorseleno)-2,2,4-trimethyl-6-phenyl-1,3-dioxane 11

$^1$H NMR $\delta$ 7.55–7.15 (m, 5H), 5.24 (d, 1H, $J = 1.8$ Hz), 4.35 (dq, 1H, $J = 1.8, 5.9$ Hz), 3.21 (t, 1H, $J = 1.8$ Hz), 2.80 (dd, 1H, $J = 1.7, 4.5$ Hz), 1.78 (t, 1H, $J = 4.3$ Hz), 1.70–1.30 (m, 4H), 1.55 (s, 3H), 1.54 (s, 3H), 1.43 (d, 3H, $J = 5.9$ Hz), 1.26 (s, 3H), 0.92 (s, 3H), 0.77 (s, 3H). Anal. Calcd for $C_{23}H_{32}O_3Se$: C, 63.44; H, 7.41. Found: C, 63.60; H, 7.52. The acetonide is impure of the (4*R*,5*R*,6*R*)-isomer (distinct signals): $^1$H NMR: $\delta$ 4.38 (dq, 1H, $J = 1.7, 6.2$ Hz), 3.78 (t, 1H, $J = 1.7$ Hz), 2.03 (dd, 1H, $J = 1.5, 4.5$ Hz), 1.56 (s, 3H), 1.53 (s, 3H), 1.41 (d, 3H, $J = 6.1$ Hz), 0.82 (s, 3H), 0.79 (s, 3H).

### 4.33. (4*S*,5*S*,6*R*)-5-(camphorseleno)-2,2,4-trimethyl-6-phenyl-1,3-dioxane 12

Oil; $^1$H NMR: $\delta$ 7.52–7.40 (m, 2H), 7.35–7.18 (m, 3H), 4.80 (d, 1H, $J = 10.9$ Hz), 3.92 (dq, 1H, $J = 6.0, 11.2$ Hz), 3.12 (dd, 1H, $J = 10.9, 11.2$ Hz), 2.27 (dd, 1H, $J = 1.5, 4.4$ Hz), 1.75–1.25 (m, 5H), 1.54 (s, 3H), 1.50 (d, 3H, $J = 6.0$ Hz), 1.44 (s, 3H), 1.21 (s, 3H), 0.78 (s, 3H), 0.76 (s, 3H). Anal. Calcd for $C_{23}H_{32}O_3Se$: C, 63.44; H, 7.41. Found: C, 63.12; H, 7.49. The (4*R*,5*S*,6*R*)-isomer was also present. Oil; $^1$H NMR: $\delta$ 7.70–7.52 (m, 2H), 7.48–7.25 (m, 3H), 5.26 (d, 1H, $J = 9.2$ Hz), 4.54 (dq, 1H, $J = 5.5, 6.4$ Hz), 3.81 (dd, 1H, $J = 1.7, 4.5$ Hz), 3.40 (dd, 1H, $J = 5.5, 9.2$ Hz), 2.10 (t, 1H, $J = 4.3$ Hz), 1.85–1.40 (m, 4H), 1.44 (s, 3H), 1.43 (s, 3H), 1.38 (d, 3H, $J = 6.6$ Hz), 0.97 (s, 3H), 0.92 (s, 3H), 0.74 (s, 3H).

### 4.34. General procedure for the radical allylation of the camphorselenoesters 4d and 5d

To a solution of **4d** or **5d** (0.15 mmol) in dry benzene (3 mL) allyltributylstannane (1.5 mmol) and a catalytic amount of AIBN were added in three portions over a period of 3 h and the reaction was stirred for 4 h. The crude mixture obtained after evaporation of the solvent under reduced pressure was filtered through florisil and then purified by chromatography on a silica gel column. Physical and spectral data of the resulting products **13**, *ent*-**13**, **14**, and *ent*-**14** were reported below. The ee was >98% in every case.

### 4.35. Methyl (2*R*)-2-[(*R*)-hydroxy(phenyl)methyl] pent-4-enoate 13

Oil; $[\alpha]_D^{24} = +8.0$ (*c* 0.8, $CHCl_3$). $^1H$ NMR: $\delta$ 7.48–7.30 (m, 5H), 5.75 (dddd, 1H, $J = 6.5$, 7.6, 10.3, 17.1 Hz), 5.15–5.0 (m, 3H), 3.61 (s, 3H), 2.86 (ddd, 1H, $J = 4.5$, 5.5, 10.0 Hz), 2.84 (d, 1H, $J = 3.0$ Hz), 2.51 (dddt, 1H, $J = 1.0$, 7.6, 10.0, 14.0 Hz), 2.41 (dddt, 1H, $J = 1.4$, 4.5, 6.5, 14.0 Hz). $^{13}C$ NMR: $\delta$ 174.6, 141.3, 135.3, 128.4 (two carbons), 127.8, 126.1 (two carbons), 116.8, 73.8, 52.7, 51.6, 31.4. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.73; H, 7.42.

### 4.36. Methyl (2*S*)-2-[(*S*)-hydroxy(phenyl)methyl] pent-4-enoate ent-13

$[\alpha]_D^{25} = -8.9$ (*c* 0.8, $CHCl_3$).

### 4.37. Methyl (2*S*)-2-[(*R*)-hydroxy(phenyl)methyl] pent-4-enoate 14

Oil; $[\alpha]_D^{25} = +26.7$ (*c* 0.5, $CHCl_3$). $^1H$ NMR: $\delta$ 7.50–7.15 (m, 5H), 5.70 (dddd, 1H, $J = 6.5$, 7.7, 10.4, 17.0 Hz), 5.15–5.0 (m, 2H), 4.84 (dd, 1H, $J = 5.3$, 7.8 Hz), 3.70 (s, 3H), 2.94 (d, 1H, $J = 5.3$ Hz), 2.88 (ddd, 1H, $J = 5.1$, 7.8, 9.2 Hz), 2.35–2.25 (m, 1H), 2.20–2.10 (m, 1H). $^{13}C$ NMR: $\delta$ 175.0, 141.7, 134.3, 128.6 (two carbons), 128.1, 126.4 (two carbons), 117.3, 74.9, 52.8, 51.7, 33.8. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.92; H, 7.18.

### 4.38. Methyl (2*R*)-2-[(*S*)-hydroxy(phenyl)methyl] pent-4-enoate ent-14

$[\alpha]_D^{25} = -27.4$ (*c* 0.5, $CHCl_3$).

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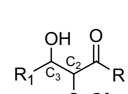
16. For the assignment of the configurations the following trends in $^{13}C$ and $^{77}Se$ NMR spectra were particularly useful:




| | | | |
|---|---|---|---|
| $^{13}C$ | $C_3$ | *syn* < *anti* | $\Delta\delta$ 0.3–3.9 ppm |
| | $C_2$ | *syn* > *anti* | $\Delta\delta$ 1.0–4.2 ppm |
| $^{77}Se$ | | *syn* ≪ *anti* | $\Delta\delta$ 10–35 ppm. |