Regioselective Epoxide Ring Opening. Stereoselective Synthesis of a Tetrahydropyran Ring.

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The stereoselective synthesis of a 2-substituted tetrahydropyran with adjacent alkoxy-bearing stereogenic centre is described. The key steps of this synthesis were the stereoselective epoxidation of an allylic alcohol and the regioselective epoxide ring opening by lithium aluminum hydride. The regio and stereoselective synthesis of a trihydroxyselenide and a trihydroxysulfide is also described. The latter compounds are not suitable for cyclization to tetrahydrofuran ring.

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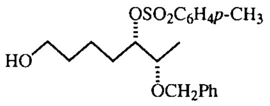

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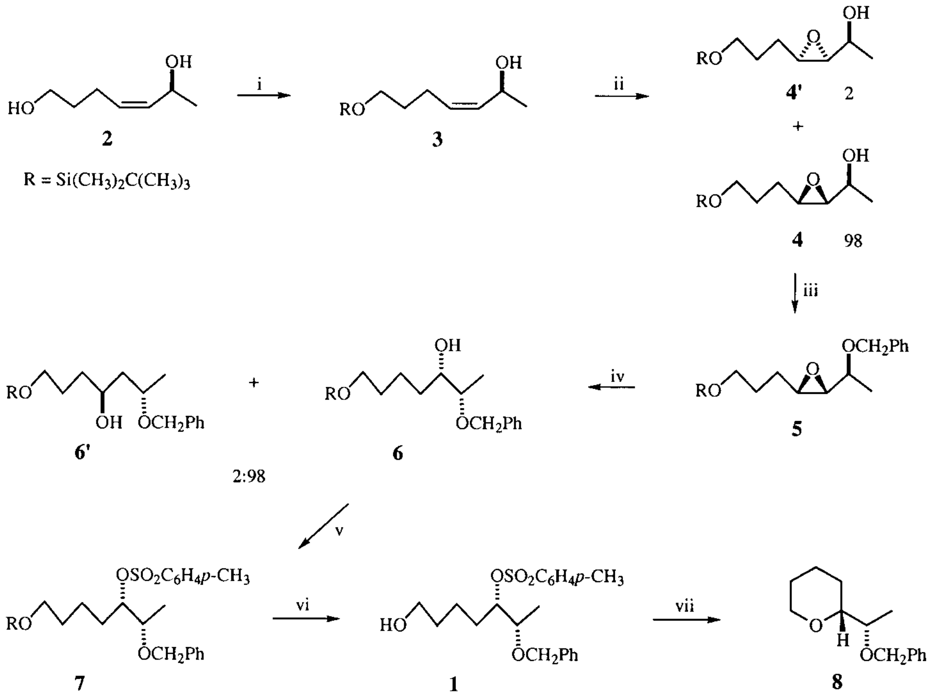
Figure 1.

The stereoselective synthesis of tetrahydrofuran and tetrahydropyran rings is of current interest owing to their occurence in biologically active natural products such as polyether antibiotics. The framework of these molecules is dominated by the presence of 2,5-disubstituted tetrahydrofurans, substituted tetrahydropyrans and spiroketal systems [1,2]. Hence, considerable attention has been focused on development of efficient and stereocontrolled routes to these key structural fragments. We have recently carried out studies on stereoselective synthesis of 2,5-*cis*-disubstituted tetrahydrofurans with adjacent alkyl-bearing stereogenic centres [3]. Now we report preliminary results on a stereoselective synthesis of a tetrahydropyran ring with adjacent alkoxy-bearing stereogenic centre. We were interested in constructing such a tetrahydropyran ring

Scheme 1

Reagents and conditions; i, imidazole, *tert*-butyldimethylsilyl chloride, dichloromethane, -10°-rt (84%); ii, *m*-chloroperbenzoic acid, dichloromethane, 0° (90%); iii, sodium hydride, benzyl bromide, tetrabutylammonium iodide, tetrahydrofuran, 0° -rt (91%); iv, lithium aluminum hydride, diethyl ether, reflux (76%); v, toluene-*p*-sulfonyl chloride, pyridine, 4-dimethylaminopyridine, dichloromethane, 0° -rt (84%); vi, tetrabutylammonium fluoride, tetrahydrofuran, rt (80%); vii, sodium hydride, tetrahydrofuran, reflux (38%).



using an intramolecular cyclization by nucleophilic attack on C-5 by an alkoxide at C-1 of a 1,5-diol system. This methodology has been employed in various approaches to polyether antibiotics [2]. Here we report a reliable method for the stereoselective synthesis of the 1,5(*S*),6(*S*)-triol **1** that then can be cyclized to tetrahydropyran ring. The synthesis of the ring precursor **1** was accomplished in six steps from the known diol **2** [4] as outlined in Scheme 1.

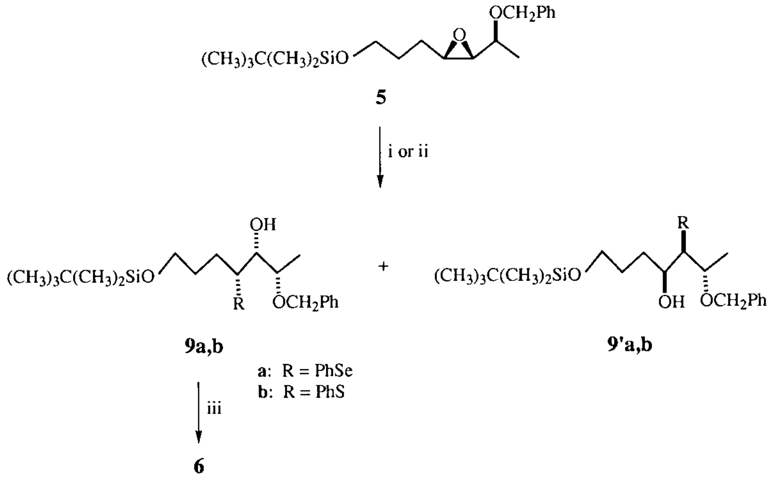
After protection of the primary alcohol as its *tert*-butyldimethylsilyl ether, the allylic alcohol **3** was epoxidated with *m*-chloroperbenzoic acid to provide the epoxide with excellent yield and diasteromeric ratio (98:2) being the *threo*-epoxy alcohol **4** the major isomer. The high stereoselectivity observed is due to the steric interactions in the *erythro* transition state between the methyl and the *tert*-butyldimethylsilyl protected propyloxy groups [5]. The secondary alcohol function was then protected as its benzyl ether. The epoxide ring opening was carried out with lithium aluminum hydride in refluxing ether. The regioselectivity of hydride reduction was high giving predominantly (98:2) the 1,5(*S*),6(*S*)-triol **6**. The structure of the major regioisomer was established by means of the COSY spectrum of compound **6**. It showed that the H-6 proton is coupled with the deshielded H-5 proton, not with the shielded H-5 protons as should be for compound **6'**. Treatment of compound **6** with pyridine and toluene-*p*-sulfonyl chloride gave the tosylate that was finally treated with tetrabutylammonium fluoride to furnish the 1,5(*S*),6(*S*)-triol **1**.

Compound **1** was then allowed to react in refluxing tetrahydrofuran with sodium hydride to give the expected tetrahydropyran ring **8** *via* an intramolecular attack of the alkoxide on the C-5 carbon atom. The yield of the cyclization step was modest, however it was higher than the cyclization of the corresponding mesylate [6] prepared, as for the tosylate, from the alcohol **6**. The structure of the tetrahydropyran **8** was consistent with its spectroscopic data and mode of synthesis from the epoxide **4**.

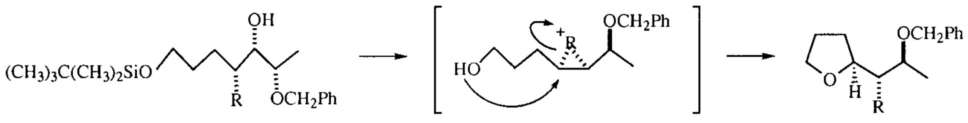
As a further developing of this strategy we decided to perform the epoxide ring opening with different nucleophiles. In the previous paper [3] we realized the stereoselective synthesis of tetrahydrofuran rings by hydroxyl capture of a selenonium ion during acid-catalyzed cyclization of trihydroxyselenides. Moreover the acid-catalyzed cyclization of diols with suitably placed phenylthio (PhS) groups to yield cyclic ethers is also an important method [7]. For these reasons we have chosen as nucleophiles the sodium phenyl selenide and the sodium phenyl thiolate. The epoxide **5** was treated with diphenyl diselenide and sodium borohydride in ethanol at room temperature. After 24 hours the reaction was not complete, however carrying out the reaction in refluxing ethanol it was possible to get in high yield the opened product. The ^{1}H-nmr and ^{13}C-nmr spectra showed a quite clean product (regioisomeric ratio 97/3), but it was not possible to determine which regioisomer was predominant. Whichever temperature was used, the regioisomeric ratio did not change. By comparison of the spectroscopic data of compound **6** with the product obtained by reduction of compound **9a** with tributyltin hydride and 2,2'-azobisisobutyronitrile in refluxing toluene that removed the phenylselenenyl residue, we found that the major regioisomer was **6**. Finally the epoxide **5** was treated with sodium thiophenate in refluxing methanol. Also in this case the yield and regioselectivity were high, the major regioisomer being assigned by analogy. With the trihydroxyselenide **9a** and the trihydroxysulfide **9b** in our hands we hoped to be able to realize the cyclization to tetrahydrofurans *via* the intermediate **10**.

Scheme 2

Reagents and conditions: i, diphenyl diselenide, sodium borohydride, ethanol, reflux (88%); ii, thiophenol, sodium thiophenate, methanol, reflux (98%); iii, tributyltin hydride, 2,2'-azobisisobutyronitrile, toluene, reflux (74%).



Scheme 3



9a,b **10** **11**

The rearrangement of phenylselenyl or phenylthio substituted diols in acid solution could give the same type of intermediate and similar tetrahydrofurans **11**. The two stereogenic centres present in compound **11** (when R = H) have the right configuration of (-)-nonactic acid [3]. As a first attempt we reacted **9a** with a few drops of perchloric acid in dichloromethane solution at room temperature, but we mainly obtained the deprotected diol. However, when we tried the reactions of the deprotected diols of **9a** and **9b** with different acids (perchloric, *p*-toluensulfonic, triflic) in different solvents (dichloromethane, benzene) we obtained a complex mixture of products.

In conclusion it has been shown that the alkoxy substituent in the α position to the epoxide ring is determinant for the regioselective epoxide ring opening. This ring opening has allowed the synthesis of the interesting building block **1** and the following ring closure has allowed the synthesis of a tetrahydropyran ring that cannot be obtained by direct electrophilic ring closure of the diol **2**. The unsuccessful attempts of cyclizing the trihydroxyselenide and the trihydroxysulfide seem to demonstrate that the relative positions of the R (PhSe or PhS) and OH groups towards the terminal OH group play an important role in this cyclization. In all the cases examined before [7] these positions had not been examined.

EXPERIMENTAL

Anhydrous solvents were distilled as follows: Tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium benzophenone immediately prior to use. Dichloromethane was distilled under nitrogen from calcium hydride and used immediately. Toluene was distilled under argon from phosphorus pentoxide. The ^{1}H-nmr and ^{13}C-nmr spectra were recorded as deuteriochloroform solutions on a Bruker AC-E series 250 MHz spectrometer. Flash chromatography was carried out using Macherey-Nagel silica gel (0.04-0.063 mm). Light petroleum refers to the fraction boiling in the range 40-60°. Optical rotations were measured at 25° as dichloromethane solutions on a Jasco DIP-370 polarimeter.

(5*S*,6*S*)-6-Benzyloxy-5-[(toluene-*p*-sulfonyl)oxy]heptan-1-ol (**1**).

A solution of tetrabutylammonium fluoride (392 mg, 1.20 mmoles) in anhydrous tetrahydrofuran (2 ml) was added to a stirred solution of **7** (420 mg, 0.83 mmole) in anhydrous tetrahydrofuran (2 ml) *via* cannula at 0° under argon and the reaction mixture was stirred for 24 hours at room temperature. Water was added followed by diethyl ether. The aqueous solution was extracted with diethyl ether and the combined organic extracts dried over magnesium sulfate and concentrated under reduced pressure. The residue was chromatographed with light petroleum-diethyl ether (1:1) to give **1** (260 mg, 80%) as a colorless oil; $[\alpha]_D^{25}$ + 3.6° (c 0.552); ^{1}H nmr : δ 1.12 (d, 3H, J = 6.5 Hz), 1.16-1.81 (m, 7H), 2.41 (s, 3H), 3.52 (t, 2H, J = 6.4 Hz), 3.60-3.69 (m, 1H), 4.38 and 4.52 (d, each 1H, J = 11.7 Hz), 4.54-4.60 (m, 1H), 7.23-7.37 (m, 7H), 7.76 (d, 2H, J = 8.3 Hz); ^{13}C nmr: 14.4, 21.2, 21.5, 28.6, 32.1, 62.3, 71.2, 74.3, 83.9, 127.6, 127.6, 127.7, 128.3, 129.6, 134.2, 138.1, 144.5.

Anal. Calcd. for $C_{21}H_{28}O_5S$: C, 64.26; H, 7.19. Found: C, 64.30; H, 7.22.

(4*Z*,6*S*)-1-[(*tert*-Butyldimethylsilyl)oxy]hept-4-en-6-ol (**3**).

Imidazole (1.05 g, 15.42 mmoles) was added to a solution of **2** in anhydrous dichloromethane (50 ml) under argon at -10°. After 10 minutes, a solution of *tert*-butyldimethylsilyl chloride (1.62 g, 10.76 mmoles) in anhydrous dichloromethane (40 ml) was slowly added, *via* cannula, and the mixture was stirred at room temperature for 14 hours. The organic layer was washed with brine, dried over magnesium sulfate and evaporated under reduced pressure. The residue was chromatographed with light petroleum-diethyl ether (1:1) to give **3** (2.11 g, 84%) as a colorless oil; $[\alpha]_D^{25}$ +8.4° (c 0.155); ^{1}H nmr: δ 0.04 (s, 6H), 0.87 (s, 9H), 1.21 (d, 3H, J = 6.2 Hz), 1.48-1.61 (m, 2H), 2.03-2.14 (m, 1H), 2.19-2.29 (m, 2H), 3.61 (t, 2H, J = 6.2 Hz), 4.58-4.64 (m, 1H), 5.27-5.44 (m, 2H); ^{13}C nmr: -4.58, 19.0, 23.9, 24.2, 26.6, 32.9, 62.6, 63.9, 130.9, 135.5.

Anal. Calcd. for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55. Found: C, 63.79; H, 11.60.

(4*S*,5*R*,6*S*)-1-[(*tert*-Butyldimethylsilyl)oxy]-4,5-epoxyheptan-6-ol (**4**).

To a solution of **3** (530 mg, 2.17 mmoles) in anhydrous dichloromethane (5 ml), *m*-chloroperbenzoic acid (70%, 535 mg, 2.17 mmoles) was added at 0° under argon. The resultant pink suspension was stirred for 2 hours at 0° then dichloromethane was added. The organic layer was washed with sodium hydroxide solution (0.5 *N*), dried over magnesium sulfate and evaporated under reduced pressure. The residue was chromatographed with light petroleum-diethyl ether (1:1) to give **4** (504 mg, 90%) as a colorless oil; $[\alpha]_D^{25}$ -11.6° (c 0.129); ^{1}H nmr: δ 0.03 (s, 6H), 0.87 (s, 9H), 1.24 (d, 3H, J = 6.4 Hz), 1.58-1.69 (m, 4H), 2.50 (s, 1H), 2.87 (dd, 1H, J = 4.4, 8.1 Hz), 3.04-3.06 (m, 1H), 3.61-3.68 (m, 3H); ^{13}C nmr: -4.67, 18.9, 19.9, 25.4, 26.5, 30.5, 58.4, 62.3, 63.1, 67.0.

Anal. Calcd. for $C_{13}H_{28}O_3Si$: C, 59.95; H, 10.84. Found: C, 59.87; H, 10.88.

(4*S*,5*R*,6*S*)-6-Benzyloxy-1-[(*tert*-butyldimethylsilyl)oxy]-4,5-epoxyheptane (**5**).

A solution of **4** (800 mg, 3.07 mmoles) in anhydrous tetrahydrofuran (4 ml) was added dropwise to sodium hydride (60% suspension in oil, 160 mg, 3.99 mmoles) suspended in anhydrous tetrahydrofuran (4 ml) at 0° under argon and the mixture allowed to warm to room temperature and stirred for 15 minutes. The mixture was cooled to 0° and benzyl bromide (475 µl, 3.99 mmoles) was added to it followed by tetrabutylammonium iodide (catalyst). The reaction mixture was stirred for 3 hours at room temperature, then diethyl ether was added and extracted with water and brine. The organic layer was dried over magnesium sulfate and evaporated under reduced pressure. The residue was chromatographed with light petroleum-diethyl ether (7:1) to give **5** (985 mg, 91%) as a colorless oil; $[\alpha]_D^{25}$ -3.3° (c 0.362); ^{1}H nmr: δ 0.12 (s, 6H), 0.85 (s, 9H), 1.22 (d, 3H, J = 6.6 Hz), 1.36-1.44 (m, 1H), 1.56-1.73 (m, 3H), 2.88-2.98 (m, 2H), 3.35-3.42 (m, 1H), 3.57-3.68 (m, 2H), 4.56 and 4.77 (d, each 1H, J = 11.8 Hz), 7.22-7.36 (m, 5H); ^{13}C nmr: -4.63, 18.3, 19.0, 25.5, 26.6, 30.7, 55.1, 61.4, 63.1, 71.9, 74.7, 128.1, 128.4, 129.0, 139.4.

Anal. Calcd. for $C_{20}H_{34}O_3Si$: C, 68.52; H, 9.78. Found: C, 68.71; H, 9.81.

(5*S*,6*S*)-6-Benzyloxy-1-[(*tert*-butyldimediylsilyl)oxy]heptan-5-ol (**6**).

To a solution of **5** (458 mg, 1.31 mmoles) in anhydrous diethyl ether (9 ml) was carefully added lithium aluminum hydride (95%, 52 mg, 1.31 mmoles). The reaction mixture was refluxed for 3 hours then water was carefully added until complete destruction of unreacted lithium aluminum hydride. The organic mixture was extracted with dichloromethane, washed with brine, dried over magnesium sulfate and evaporated under reduced pressure. The residue was chromatographed with light petroleum-diethyl ether (5:1) to give **6** (350 mg, 76%) as a colorless oil; $[\alpha]_D^{25}$ +26.7° (c 0.125); ^{1}H nmr: δ 0.06 (s, 6H), 0.91 (s, 9H), 1.20 (d, 3H, J = 5.9 Hz), 1.39-1.54 (m, 6H), 2.63 (d, 1H, J = 2.6 Hz), 3.33-3.43 (m, 2H), 3.59-3.64 (m, 2H), 4.44 and 4.67 (d, each 1H, J = 11.5 Hz), 7.26-7.39 (m, 5H); ^{13}C nmr: -5.27, 15.6, 18.3, 21.9, 26.0, 32.7, 32.9, 63.2, 71.0, 74.9, 78.4, 127.7, 127.8, 128.4, 138.4.

Anal. Calcd. for $C_{20}H_{36}O_3Si$: C, 68.13; H, 10.29. Found: C, 68.22; H, 10.20.

(5*S*,6*S*)-6-Benzyloxy-1-[(*tert*-butyldimethylsilyl)oxy]-5-[(toluene-*p*-sulfonyl)oxy]heptane (**7**).

A solution of toluene-*p*-sulfonyl chloride (432 mg, 2.27 mmoles), pyridine (274 µl, 3.39 mmoles) and a catalytic amount of 4-dimethylaminopyridine in anhydrous dichloromethane (3 ml) was added dropwise to a stirred solution of the alcohol **6** (400 mg, 1.13 mmoles) in anhydrous dichloromethane (3 ml) at 0° under argon and the mixture stirred for 12 hours at room temperature. The organic phase was washed with water, dried over magnesium sulfate and evaporated under reduced pressure. The residue was chromatographed with light petroleum-diethyl ether (5:1) to give **7** (481 mg, 84%) as a colorless oil; $[\alpha]_D^{25}$ -3.9° (c 0.333); ^{1}H nmr: δ 0.04 (s, 6H), 0.89 (s, 9H), 1.14 (d, 3H, J = 6.4 Hz), 1.18-1.75 (m, 6H), 2.41 (s, 3H), 3.50 (t, 2H, J = 6.4 Hz), 3.67-3.71 (m, 1H), 4.41 and 4.53 (d, each 1H, J = 12 Hz), 4.51-4.60 (m, 1H), 7.25-7.33 (m, 7H), 7.76 (d, 2H, J = 8.3 Hz); ^{13}C nmr: -5.32, 14.4, 18.3, 21.4, 21.6, 25.9, 28.7, 32.4, 62.7, 71.3, 74.4, 84.1, 127.6, 127.6, 127.7, 128.3, 129.6, 134.4, 138.3, 144.4.

Anal. Calcd. for $C_{27}H_{42}O_5SSi$: C, 63.99; H, 8.35; S, 6.33. Found: C, 64.08; H, 8.30; S, 6.26.

(2*R*,1'*S*)-2-[1'-(Benzyloxy)ethyl]tetrahydropyran (**8**).

A solution of **1** (163 mg, 0.42 mmole) in anhydrous tetrahydrofuran (2 ml) was added *via* cannula to a suspension of sodium hydride (60% suspension in oil, 31 mg, 0.84 mmole) in anhydrous tetrahydrofuran (2 ml) under argon. The reaction mixture was refluxed for 24 hours, poured into water and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and evaporated under reduced pressure. The residue was chromatographed with light petroleum-diethyl ether (5:1) to give **8** (35 mg, 38%) as a colorless oil; $[\alpha]_D^{25}$ +9.0° (c 0.210); ^{1}H nmr: δ 1.22 (d, 3H, J = 6.3 Hz), 1.26-1.89 (m, 6H), 3.27 (ddd, 1H, J = 7.2, 5.0, 2.1 Hz), 3.38-3.48 (m, 2H), 3.99-4.06 (m, 1H), 4.56 and 4.63 (d, each 1H, J = 11.9 Hz), 7.25-7.38 (m, 5H); ^{13}C nmr: 15.9, 23.3, 26.2, 27.6, 68.7, 71.1, 77.5, 81.0, 127.4, 127.6, 128.2, 138.9.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.99; H, 9.64.

(4*R*,5*S*,6*S*)-6-Benzyloxy-1-[(*tert*-butyldimethylsilyl)oxy]-4-phenylselenylheptan-5-ol (**9a**).

Diphenyl diselenide (134 mg, 0.43 mmole) was dissolved in absolute ethanol (5 ml), sodium borohydride (95%, 34.10 mg, 0.86 mmole) was added in batches and the mixture was stirred until the bright yellow solution turned colorless. Compound **5** (200 mg, 0.57 mmole) was dissolved in absolute ethanol (5 ml) and added *via* cannula. The reaction mixture was refluxed for 2 hours then water was added and extracted with dichloromethane. The organic phase was washed with brine, dried over magnesium sulfate and evaporated under reduced pressure. The residue was chromatographed with light petroleum-ethyl acetate (9:1) to give **9a** (254 mg, 88%) as a colorless oil; $[\alpha]_D^{25}$ +31.6° (c 0.05); ^{1}H nmr: δ 0.03 (s, 6H), 0.87 (s, 9H), 1.18 (d, 3H, J = 6.2 Hz), 1.63-1.94 (m, 4H), 3.08 (br s, 1H), 3.21 (dt, 1H, J = 6.8 and 3.5 Hz), 3.52-3.61 (m, 3H), 3.90 (quint, 1H, J = 6.2 Hz), 4.47 and 4.69 (d, each 1H, J = 11.4 Hz), 7.23-7.37 (m, 8H), 7.54-7.58 (m, 2H); ^{13}C nmr: -5.37, 15.6, 18.3, 25.9, 29.6, 30.4, 31.3, 50.1, 62.9, 71.1, 77.1, 127.3, 127.7, 127.8, 128.4, 129.0, 134.5, 138.2.

Anal. Calcd. for $C_{26}H_{40}O_3SeSi$: C, 61.52; H, 7.94. Found: C, 61.60; H, 8.01.

(4*R*,5*S*,6*S*)-6-Benzyloxy-1-[(*tert*-butyldimethylsilyl)oxy]-4-phenylthioheptan-5-ol (**9b**).

To a solution of **5** (327 mg, 0.93 mmole) in anhydrous methanol (2 ml) was added *via* cannula a solution of thiophenol/sodium thiophenate (1:1, 1.86 mmoles) in anhydrous methanol (2 ml). The reaction mixture was refluxed for 24 hours then water was added followed by dichloromethane. The aqueous solution was extracted with dichloromethane, washed with brine, dried over magnesium sulfate and evaporated under reduced pressure. The residue was chromatographed with light petroleum-diethyl ether (10:1) to give **9b** (282 mg, 98%) as a colorless oil; $[\alpha]_D^{25}$ +34.4° (c 0.137); ^{1}H nmr: δ 0.06 (s, 6H), 0.90 (s, 9H), 1.23 (d, 3H, J = 6.3 Hz), 1.65-1.90 (m, 4H), 3.10 (d, 1H, J = 2.6 Hz), 3.20-3.24 (m, 1H), 3.56-3.63 (m, 3H), 3.90 (quint, 1H, J = 6.3 Hz), 4.48 and 4.70 (d, each 1H, J = 11.3 Hz), 7.23-7.46 (m, 10H); ^{13}C nmr: -5.37, 15.7, 18.2, 25.9, 28.8, 30.5, 52.5, 62.8, 71.0, 75.9, 76.0, 126.8, 127.7, 127.8, 128.4, 128.8, 131.9, 135.1, 138.1.

Anal. Calcd. for $C_{26}H_{40}O_3SSi$: C, 67.78; H, 8.75; S, 6.96. Found: C, 67.66; H, 8.79; S, 7.02.

Reduction of (4*R*,5*S*,6*S*)-6-Benzyloxy-1-[(*tert*-butyldimethylsilyl)oxy]-4-phenylselenylheptan-5-ol (**9a**) with Tributyltin Hydride.

A solution of compound **9a** (559 mg, 1.10 mmoles) dissolved in anhydrous toluene (4.5 ml) was degassed for 15 minutes with argon then tributyltin hydride (641 mg, 2.20 mmoles) and 2,2'-azobisisobutyronitrile (9 mg, 0.055 mmole) were added and the mixture heated under reflux for 1 hour before being cooled and concentrated under reduced pressure. The residue was chromatographed with light petroleum-ethyl acetate (9:1 plus 1% of triethylamine) to give **6** (286 mg, 74%).

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[6] Mesylate $[\alpha]_D^{25}$ +16.3° (c 0.122); ^{1}H-nmr: δ 1.23 (d, 3H, J = 6.3 Hz), 1.43-1.82 (m, 7H), 2.94 (s, 3H), 3.64 (t, 2H, J = 6.0 Hz), 3.73 (quint, 1H, J = 6.3 Hz), 4.47 and 4.66 (d, each 1H, J = 11.5 Hz), 4.58-4.65 (m, 1H), 7.26-7.36 (m, 5H).

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