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Synthesis of enantiomerically pure substituted tetrahydrofurans from epoxides and phenylselenium reagents

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Abstract—Starting from commercially available enantiomerically pure epoxides, enantiomerically pure substituted tetrahydrofurans were prepared using simple conversions promoted by organoselenium reagents. The first step consisted in the opening of the epoxides with phenylselenolate anions to afford hydroxyalkyl phenyl selenides. The PhSe group was then substituted by an allyl group by treatment with allyltributyltin and AIBN. The reaction of these allylic derivatives with electrophilic phenylselenium reagents afforded selenium containing tetrahydrofurans as the result of a stereospecific 5-*exo*-*trig* cyclization. The tetrahydrofuran derivatives thus obtained were finally deselenenylated with triphenyltin hydride and AIBN.

1. Introduction

Owing to the great importance of heterocyclic compounds as final products or as reaction intermediates several methods have been described for their construction. Among these, the use of selenium reagents to effect ring closure reactions has recently gained increasing popularity. This is due to the ready availability of the reagents, the numerous chemical manipulations, which can be effected on the selenium moiety before or during its removal and to the mild reaction conditions required in the various steps. Selenium promoted cyclization reactions thus provide an easy access to a wide variety of heterocyclic compounds in general and to those containing oxygen and/or nitrogen heteroatoms in particular.[1–3]

An important new finding is that optically active heterocyclic compounds can be prepared using electrophilic selenium reagents RSeX in which R is a chiral group. Several enantiomerically pure diselenides have been employed as precursor to promote the cyclization of alkenes containing internal nucleophiles.[4–13] Satisfactory diastereoselectivities were observed in most cases. Recently, two new enantiomerically pure diselenides, the di-2-[(1*S*)-1-(methylthio)ethyl]phenyl diselenide and the di-2-methoxy-6-[(1*S*)-1-methylthio)ethyl]phenyl diselenide, have been prepared.[14,15] The electrophilic reagents produced from them have been employed to effect asymmetric selenocyclization reactions. Thus, tetrahydrofurans,[16] lactones, lactams, N-protected pyrrolidines,[16] 1,2-oxazines, and cyclic nitrones have been prepared.[17] The transfer of chirality was very efficient and the diastereoselectivities observed are comparable or better than those obtained with the most efficient diselenides previously described in the literature. The efficiency of these reagents has been attributed to the presence of a sulfur atom linked to the stereogenic center and close to the selenium atom.

We now report that the versatile chemical behavior of organoselenium compounds allows the preparation of enantiomerically pure heterocyclic compounds to be effected using an alternative approach. This consists in the reaction of the achiral phenylselenium reagent with an enantiomerically pure easily available substrate. As a first example we describe the synthesis of substituted tetrahydrofurans starting from enantiomerically pure epoxides. The stereoselective synthesis[18,19] of substituted cyclic ether is important since cyclic ether units are frequently found in polyether antibiotics, C-glycosides, and other biologically active natural products.[20]

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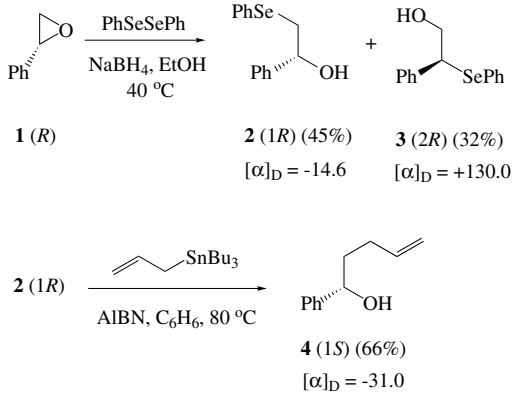
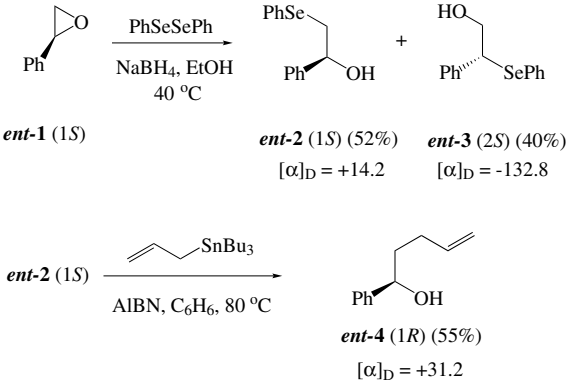
2. Results and discussion

As illustrated in Scheme 1, the opening of the epoxide (*R*)-phenyloxirane **1** (ee equal or greater than 98%) with the phenylselenolate anions, produced in situ by diphenyl diselenide and sodium borohydride in ethanol, was not regiospecific and the two enantiomerically pure β-hydroxyalkyl phenyl selenides **2** and **3** were obtained. The two regioisomers were easily separated by column chromatography and the β-hydroxy selenide **2** was treated with allyltributyltin and AIBN.[21] The enantiomerically pure alkenol **4** was formed in reasonably good yields. Its absolute configuration was confirmed by comparison of its specific rotation with that reported in the literature.[22]



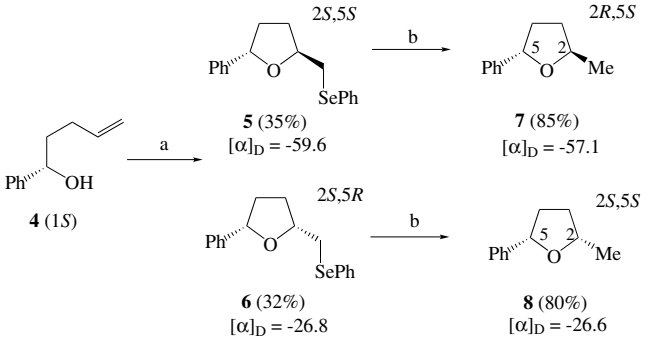
Scheme 1.

Following the same procedures (Scheme 2), the (*S*)-phenyloxirane ***ent*-1** (ee equal or greater than 98%) gave a mixture of the two regioisomers ***ent*-2** and ***ent*-3**. Compound ***ent*-2** was then converted into the enantiomerically pure alkenol ***ent*-4**.



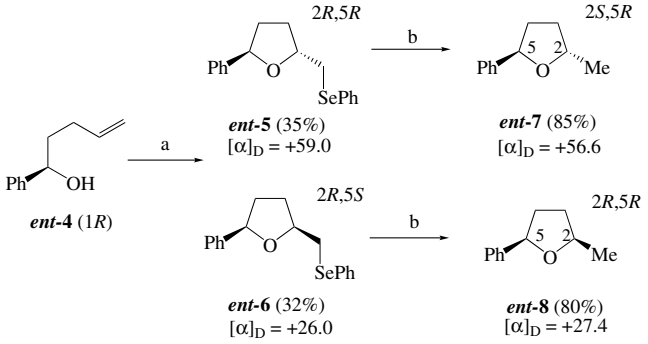
Scheme 2.

The following step of the sequence was the 5-*exo*-*trig* cyclization reaction promoted by the electrophilic phenylselenenyl sulfate, generated by the reaction of the diphenyl diselenide with ammonium persulfate in the presence of trifluoromethanesulfonic acid (Scheme 3).[23] This ring closure reaction was not stereoselective. Thus, starting from the alkenol **4** an almost equimolar mixture of the two enantiomerically pure diastereoisomeric 2,5-disubstituted tetrahydrofurans **5** and **6** was formed. These were separated by column chromatography. Finally, **5** and **6** were deselenenylated with triphenyltin hydride and AIBN and afforded the enantiomerically pure 2-methyl-5-phenyl tetrahydrofurans **7** and **8**, respectively.



Scheme 3. Reagents and conditions: (a) PhSeSePh, $(NH_4)_2S_2O_8$, CF_3SO_3H, MeCN, rt; (b) Ph_3SnH, AIBN, C_6H_6, 80 °C.

The same cyclization procedure applied to the alkenol ***ent*-4**, gave rise to the two diastereoisomeric tetrahydrofurans ***ent*-5** and ***ent*-6** and, after deselenylation, the two enantiomerically pure 2-methyl-5-phenyl tetrahydrofurans ***ent*-7** and ***ent*-8** were obtained (Scheme 4).

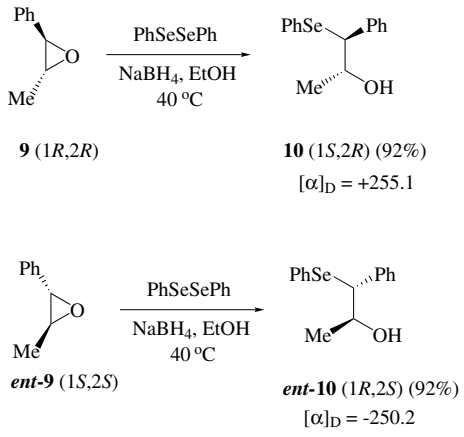


Scheme 4. Reagents and conditions: (a) PhSeSePh, $(NH_4)_2S_2O_8$, CF_3SO_3H, MeCN, rt; (b) Ph_3SnH, AIBN, C_6H_6, 80 °C.

The relative configurations within 2-methyl-5-phenyl tetrahydrofurans **7** (2*R*,5*S*) and **8** (2*S*,5*S*), ***ent*-7** (2*S*,5*R*) and ***ent*-8** (2*R*,5*R*) were determined by NMR spectroscopy on the basis of the results of NOESY experiments. In compounds **7** and ***ent*-7** a strong dipolar interaction was observed between the methyl in the 2-position and the proton in the 5-position whereas in compounds **8** and ***ent*-8** the NOE effect was observed between the proton in the 2- and the proton in the 5-positions. The relative configurations within the selenides **5**, **6**, ***ent*-5**, and ***ent*-6** were deduced from those of the corresponding deselenenylated compounds. The enantiomeric excess of the tetrahydrofurans **7**, **8**, ***ent*-7**, ***ent*-8** was confirmed by GC–MS experiments using a Chirasildex column.

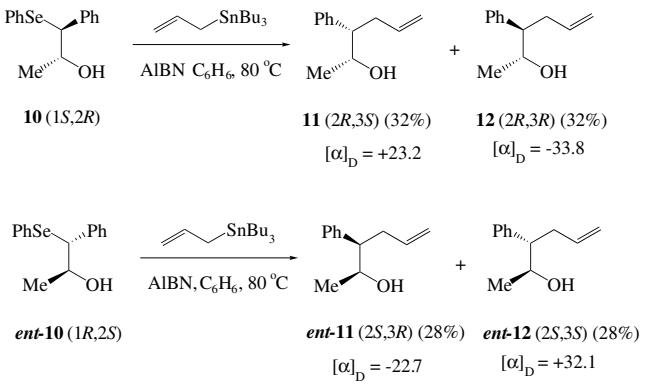
Thus, starting from the (*R*)-phenyloxirane **1** and the (*S*)-phenyloxirane ***ent*-1** and using the simple reaction sequence described above, all the four 2-methyl-5-phenyl tetrahydrofurans **7**, **8**, ***ent*-7**, and ***ent*-8** could be obtained in an enantiomerically pure form.

The same synthetic sequence described above for (*R*) and (*S*)-phenyloxirane was then applied to the commercially available (1*R*,2*R*)-1-phenylpropylene oxide **9** (99% ee) and (1*S*,2*S*)-1-phenylpropylene oxide ***ent*-9** (99% ee). In the present case the stereospecific opening of the chiral epoxides **9** and ***ent*-9** by sodium phenylselenolate was regiospecific and afforded exclusively the enantiomerically pure 1-phenyl-1-(phenylseleno)propan-2-ols **10** and ***ent*-10**, respectively, in high yields (Scheme 5).[24]

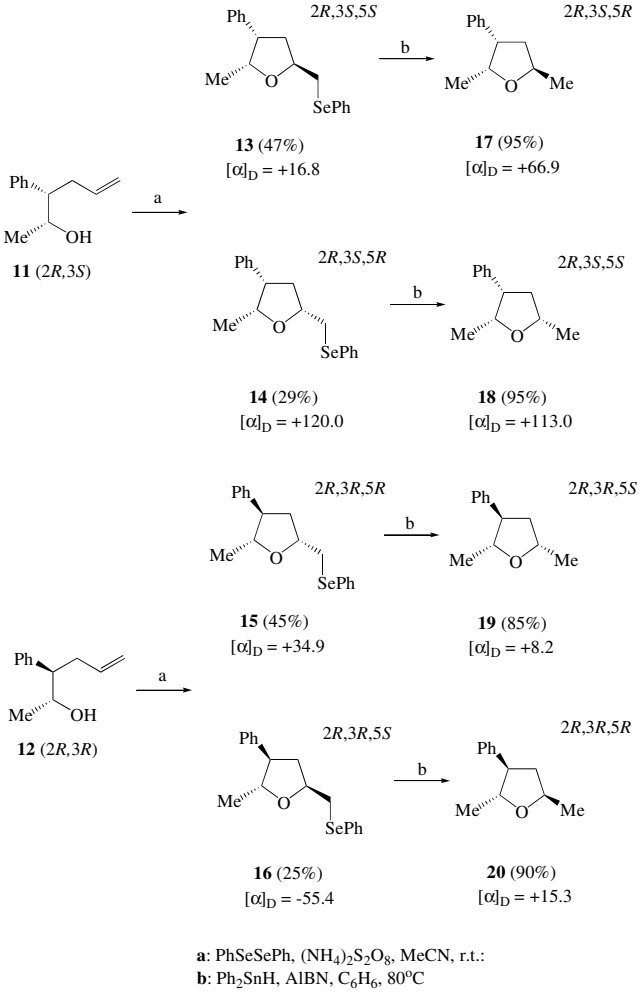


Scheme 5.

Owing to its radical nature, the substitution of the PhSe with the allyl group produced the epimerization of the stereogenic center at the 1-position and gave rise to the diasteroisomeric mixtures of the alkenols **11**, **12** and ***ent*-11**, ***ent*-12** (Scheme 6). These could be easily separated by column chromatography and hence obtained in an enantiomerically pure form. The absolute configurations of the alkenols **11** and **12** were established by comparison of their specific rotations with those reported in the literature.[25]



Scheme 6.



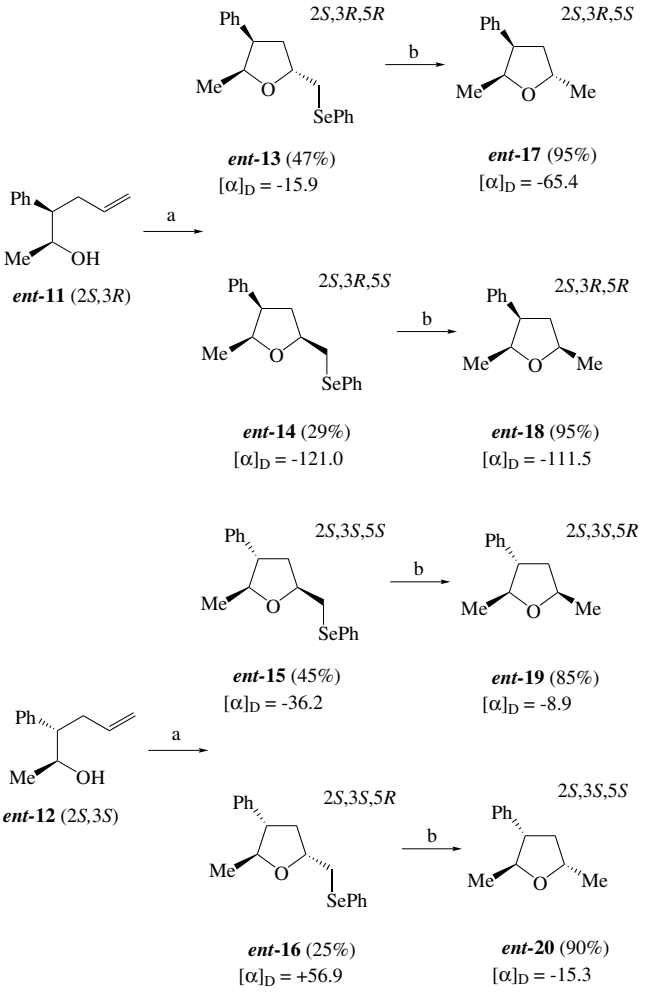
Scheme 7. Reagents and conditions: (a) PhSeSePh, $(NH_4)_2S_2O_8$, CF_3SO_3H, MeCN, rt; (b) Ph_3SnH, AIBN, C_6H_6, 80 °C.

As indicated in Scheme 7, by cyclization with phenylselenenyl sulfate, the alkenol **11** afforded a mixture of the two diastereoisomers **13** and **14** and the alkenol **12** gave a mixture of **15** and **16**. In both cases the two diastereoisomers could be easily separated by column chromatography and hence obtained in an enantiomerically pure form. Their deselenenylations eventually afforded the four enantiomerically pure 2,5-dimethyl-3-phenyltetrahydrofurans **17**, **18**, **19**, and **20**.

In the same way, the cyclization (Scheme 8) of the alkenols ***ent*-11** and ***ent*-12** gave rise to the enantiomeric tetrahydrofurans ***ent*-13**–***ent*-16**. These were then deselenenylated and afforded the four enantiomeric 2,3,5-trisubstituted tetrahydrofurans ***ent*-17**–***ent*-20**.

In this case also, using the simple reaction sequence described herein, all the eight 2,5-dimethyl-3-phenyltetrahydrofurans could be obtained in an enantiomerically pure form.

The relative configurations indicated in the Schemes 7 and 8 for the tetrahydrofurans **17**–**20** and ***ent*-17**–***ent*-20** were determined by NMR on the basis of the results of NOESY experiments.The configurations of the carbon



Scheme 8. Reagents and conditions: (a) PhSeSePh, $(NH_4)_2S_2O_8$, CF_3SO_3H, MeCN, rt; (b) Ph_3SnH, AIBN, C_6H_6, 80 °C.

atoms in the 2- and 3-positions were obviously unchanged in respect to those of the starting alkenols **11**–**12**. This was also confirmed by the strong dipolar interactions observed between the protons in the 2- and in the 3-positions in compounds **17**–**18** and ***ent*-17**–***ent*-18** and between the methyl in the 2- and the proton in the 3-position in the cases of compounds **19**–**20** and ***ent*-19**–***ent*-20**. Further support was obtained by the observation of the chemical shift of the methyl group in the ^1H NMR spectrum. In fact, in compounds **17**–**18** and ***ent*-17**–***ent*-18**, the methyl in the 2-position and the phenyl group have a *cis* relationship and the methyl group lies in the shielding cone of the aromatic ring. In these compounds, the absorption due to the methyl group was observed at 0.8 ppm whereas in compounds **19**–**20** and ***ent*-19**–***ent*-20** this absorption occurred at 1.2 ppm. NOE experiments allowed the relative configuration of the carbon atom in the 5-position to be determined. In fact, in compounds **17**, **20**, ***ent*-17**, ***ent*-20** a dipolar interaction between the proton at 2 and methyl at 5 was observed. In compounds **18**, **19**, ***ent*-18**, ***ent*-19** instead the interaction occurred between the methyls as well as between the protons at the 2- and in the 5-positions. The relative configurations of the selenides **13**–**16** and ***ent*-13**–***ent*-16** were deduced from those of the corresponding deselenenylated compounds. The enantiomeric excess of the 2,5-dimethyl-3-phenyltetrahydrofurans was determined by GC–MS experiments using a Chirasildex column.

3. Conclusions

Starting from commercially available chiral epoxides, all the possible isomers of 2-methyl-5-phenyl tetrahydrofurans and of 2,5-dimethyl-3-phenyltetrahydrofurans were synthesized in an enantiomerically pure form, using simple conversions promoted by the versatile organoselenium reagents. All the steps of the synthetic sequence occurred with satisfactory to good chemical yields. The present procedure seems to be of general application and favorably compares with other methods described in the literature. Further experiments are now in progress in order to find useful applications of this new methodology for the preparation of more complex tetrahydrofurans as well as of other type of heterocyclic compounds.

4. Experimental

All new compounds were characterized by MS, ^1H, and ^{13}C NMR spectroscopy. GC 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. GC chiral analyses and MS spectra were carried out with an HP 5890 gas chromatograph (25 m Chirasildex capillary column) 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 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. Starting products

The starting epoxides **1**, ***ent*-1**, **9**, and ***ent*-9** were commercial products and were used without further purification.

4.2. Conversion of epoxides into β-hydroxyalkyl phenyl selenides. General procedure

Sodium borohydride (6 mmol) was added to a solution of diphenyl diselenide (3 mmol) in ethanol (8 mL) at 40 °C. After 45 min a solution of the epoxides **1**, ***ent*-1**, **9**, ***ent*-9** (4 mmol) in ethanol (8 mL) was added. The pro-

gress of the reaction was monitored by TLC and by GC–MS. After 2 h the reaction mixture was poured into aqueous NH_4Cl solution and extracted with diethyl ether. The organic layer was dried over Na_2SO_4, filtered, and evaporated under vacuum. Reaction products were obtained in a pure form after column chromatography of the residue on silica gel with a 3:7 mixture of diethyl ether and light petroleum as eluant. The products obtained and the reaction yields are reported in Schemes 1, 2, and 5. Physical and spectral data are reported below.

4.2.1. (1*R*)-1-Phenyl-2-(phenylseleno)ethanol, 2. Oil; $[\alpha]_D^{24} = -14.6$ (*c* 1.70, $CHCl_3$). ^1H NMR: δ 7.65–7.55 (m, 2H), 7.45–7.20 (m, 8H), 4.75 (dd, 1H, $J = 3.7$, 9.3 Hz), 3.35 (dd, 1H, $J = 3.7$, 12.8 Hz), 3.17 (dd, 1H, $J = 9.3$, 12.8 Hz), 2.91 (br s, 1H); ^{13}C NMR: δ 142.5, 133.0 (two carbons), 129.3, 129.2 (two carbons), 128.5 (two carbons), 127.9, 127.3, 125.8 (two carbons), 72.3, 38.4; MS *m/z* (rel int): 278 (37), 172 (100), 157 (38), 121 (53), 107 (48), 103 (54), 91 (67), 77 (92), 51 (32). Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.73; H, 5.19.

4.2.2. (1*S*)-1-Phenyl-2-(phenylseleno)ethanol, *ent*-2. $[\alpha]_D^{25} = +14.2$ (*c* 1.02, $CHCl_3$). Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.81; H, 5.17.

4.2.3. (2*R*)-2-Phenyl-2-(phenylseleno)ethanol, 3. Oil; $[\alpha]_D^{26} = +130.0$ (*c* 2.20, $CHCl_3$). ^1H NMR: δ 7.60–7.45 (m, 2H), 7.38–7.20 (m, 8H), 4.41 (dd, 1H, $J = 6.5$, 7.7 Hz), 4.03 (dd, 1H, $J = 7.7$, 11.6 Hz), 3.94 (dd, 1H, $J = 6.5$, 11.6 Hz), 2.20 (br s, 1H); ^{13}C NMR: δ 139.3, 135.3 (two carbons), 129.0 (two carbons), 128.8, 128.7 (two carbons), 128.1, 127.9 (two carbons), 127.5, 65.0, 50.8; MS *m/z* (rel int): 278 (33), 158 (40), 121 (100), 103 (73), 91 (40), 77 (38), 51 (10). Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.70; H, 5.11.

4.2.4. (2*S*)-2-Phenyl-2-(phenylseleno)ethanol, *ent*-3. Oil; $[\alpha]_D^{25} = -132.8$ (*c* 1.35, $CHCl_3$). Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.69; H, 5.00.

4.2.5. (1*S*,2*R*)-1-Phenyl-1-(phenylseleno)propan-2-ol, 10. Oil; $[\alpha]_D^{20} = +255.1$ (*c* 1.96, $CHCl_3$). ^1H NMR: δ 7.58–7.48 (m, 2H), 7.30–7.24 (m, 8H), 4.26 (d, 1H, $J = 5.6$ Hz), 4.19 (ddq, 1H, $J = 3.4$, 5.6, 6.0 Hz), 2.35 (d, 1H, $J = 3.4$ Hz), 1.26 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR: δ 140.4, 134.7 (two carbons), 129.0, 128.6 (two carbons), 128.5 (two carbons), 128.1 (two carbons), 127.6, 127.0, 68.9, 56.9, 20.4; MS *m/z* (rel int): 292 (25), 248 (7), 167 (26), 135 (100), 115 (14), 91 (38), 77 (19), 57 (17). Anal. Calcd for $C_{15}H_{16}OSe$: C, 61.86; H, 5.54. Found: C, 61.80; H, 5.33.

4.2.6. (1*R*,2*S*)-1-Phenyl-1-(phenylseleno)propan-2-ol, *ent*-10. Oil; $[\alpha]_D^{22} = -250.2$ (*c* 1.57, $CHCl_3$). Anal. Calcd for $C_{15}H_{16}OSe$: C, 61.86; H, 5.54. Found: C, 61.70; H, 5.32.

4.3. Conversion of β-hydroxyalkyl phenyl selenides into alkenols. General procedure

A catalytic amount of AIBN and allyltributylstannane (7 mmol) were added to a solution of β-hydroxyalkyl phenyl selenide **2**, ***ent*-2**, **10**, and ***ent*-10** (1 mmol) in refluxing dry benzene (8 mL) under nitrogen. A second portion of allyltributylstannane (7 mmol) and a catalytic amount of AIBN was then added after 1 h. The progress of the reaction was monitored by TLC and ^1H NMR. In the case of compounds **4** and ***ent*-4** the reactions were stirred for 5 h and then directly evaporated under vacuum. The reaction products were obtained in a pure form after column chromatography of the residue on silica gel using dichloromethane as eluant. In the case of compounds **11**, **12**, ***ent*-11**, ***ent*-12** the reactions were stirred for 23 h, and the purification of the products required a first column chromatography on silica gel using dichloromethane as eluant and a second medium pressure chromatography on a silica gel column (Merck, LiChroprep® Si60, 40–63 μm) using a 1:9 mixture of diethyl ether and light petroleum as eluant. The products obtained and the reaction yields are reported in Schemes 1, 2, and 6. Physical and spectral data are reported below.

4.3.1. (1*S*)-1-Phenylpent-4-en-1-ol, 4. Oil; $[\alpha]_D^{24} = -31.0$ (*c* 3.37, $CHCl_3$).[22] ^1H NMR: δ 7.48–7.15 (m, 5H), 5.89 (ddt, 1H, $J = 6.4$, 10.1, 16.6 Hz), 5.24–4.97 (m, 2H), 4.73 (dd, 1H, $J = 5.8$, 7.4 Hz), 2.50 (br s, 1H), 2.23–2.15 (m, 2H), 2.0–1.80 (m, 2H); ^{13}C NMR: δ 144.6, 138.2, 128.4 (two carbons), 127.5, 125.9 (two carbons), 114.9, 73.9, 38.0, 30.0; MS *m/z* (rel int): 162 (1), 144 (7), 120 (33), 107 (100), 105 (16), 79 (70), 77 (40), 55 (3), 51(9). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.32; H, 8.63.

4.3.2. (1*R*)-1-Phenylpent-4-en-1-ol, *ent*-4. $[\alpha]_D^{23} = +31.2$ (*c* 2.86, $CHCl_3$). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.51; H, 8.75.

4.3.3. (2*R*,3*S*)-3-Phenylhex-5-en-2-ol, 11. Oil; $[\alpha]_D^{21} = +23.2$ (*c* 2.05, $CHCl_3$).[25] ^1H NMR: δ 7.40–7.25 (m, 2H), 7.24–7.17 (m, 3H), 5.66 (dddd, 1H, $J = 6.5$, 7.2, 10.1, 16.8 Hz), 5.08–4.85 (m, 2H), 3.98 (ddq, 1H, $J = 3.8$, 5.8, 6.2 Hz), 2.66 (ddd, 1H $J = 5.6$, 5.8, 9.3 Hz), 2.57 (dddt, 1H, $J = 1.2$, 5.6, 7.2, 12.5 Hz), 2.47 (dddt, 1H, $J = 1.3$, 6.5, 9.3, 12.5 Hz), 1.39 (d, 1H, $J = 3.8$ Hz), 1.21 (d, 3H, $J = 6.2$ Hz); ^{13}C NMR: δ 140.7, 136.6, 128.9 (two carbons), 128.5 (two carbons), 126.8, 116.2, 69.2, 53.4, 36.7, 21.2; MS *m/z* (rel int): 176 (1), 132 (87), 117 (81), 91 (100), 78 (26), 65 (8), 54 (13). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.67; H, 9.20.

4.3.4. (2*S*,3*R*)-3-Phenylhex-5-en-2-ol, *ent*-11. Oil; $[\alpha]_D^{19} = -22.7$ (*c* 1.51, $CHCl_3$). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.85; H, 9.06.

4.3.5. (2*R*,3*R*)-3-Phenylhex-5-en-2-ol, 12. Oil; $[\alpha]_D^{21} = -33.8$ (*c* 2.0, $CHCl_3$). ^1H NMR: δ 7.40–7.20 (m, 5H), 5.68 (dddd, 1H, $J = 6.2$, 6.6, 10.1, 16.9 Hz), 5.10–4.78 (m, 2H), 3.96 (dq, 1H, $J = 6.2$, 6.4 Hz), 2.75–2.67 (m, 2H), 2.49 (dddt, 1H, $J = 1.3$, 6.2, 9.6, 12.5 Hz), 1.60 (br s, 1H), 1.07 (d, 3H, $J = 6.2$ Hz); ^{13}C NMR: δ 141.5, 136.8, 128.8 (two carbons), 128.4 (two carbons), 126.4, 115.8, 71.3, 53.3, 35.7, 21.0; MS *m*/*z* (rel int): 176 (1), 132 (89), 117 (82), 91 (100), 78 (24), 54 (12). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.81; H, 9.23.

4.3.6. (2*S*,3*S*)-3-Phenylhex-5-en-2-ol, *ent*-12. Oil; $[\alpha]_D^{23} = +32.1$ (*c* 1.13, $CHCl_3$). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.66; H, 9.22.

4.4. Synthesis of tetrahydrofurans. General procedure for the cyclofunctionalization reactions

A mixture of diphenyl diselenide (0.5 mmol), ammonium persulfate (0.5 mmol), and trifluoromethanesulfonic acid (1 mmol) in acetonitrile (5 mL) was stirred at room temperature for 15 min. The solution of an alkenol (1 mmol) was then added and the mixture was stirred for 2 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 dichloromethane. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and evaporated. The reaction products were separated by medium pressure chromatography on a silica gel column (Merck, LiChroprep® Si60, 40–63 μm) using a 1:9 mixture of diethyl ether and light petroleum as eluant. The products obtained and the reaction yields are reported in Schemes 3, 4, 7, and 8. Physical and spectral data are reported below.

4.4.1. (2*S*,5*S*)-2-Phenyl-5-[(phenylseleno)methyl]tetrahydrofuran, 5. Oil; $[\alpha]_D^{25} = -59.6$ (*c* 0.69, $CHCl_3$). ^1H NMR: δ 7.60–7.50 (m, 2H), 7.40–7.10 (m, 8H), 5.07 (dd, 1H, $J = 6.0$, 7.9 Hz), 4.50–4.43 (m, 1H), 3.26 (dd, 1H, $J = 5.1$, 12.1 Hz), 3.06 (dd, 1H, $J = 7.6$, 12.1 Hz), 2.43–2.35 (m, 1H), 2.28–2.20 (m, 1H), 1.93–1.77 (m, 2H); ^{13}C NMR: δ 144.0, 133.5 (two carbons), 130.1, 129.9 (two carbons), 129.2 (two carbons), 128.1, 127.7, 126.5 (two carbons), 81.8, 79.9, 36.2, 34.2, 33.2; MS *m*/*z* (rel int): 318 (33), 281 (10), 207 (30), 171 (15), 161 (42), 147 (66), 129 (37), 117 (51), 91 (100), 77 (35), 55 (19). Anal. Calcd for $C_{17}H_{18}OSe$: C, 64.35; H, 5.72. Found: C, 64.30; H, 5.59.

4.4.2. (2*R*,5*R*)-2-Phenyl-5-[(phenylseleno)methyl]tetrahydrofuran, *ent*-5. $[\alpha]_D^{22} = +59.0$ (*c* 5.11, $CHCl_3$). Anal. Calcd for $C_{17}H_{18}OSe$: C, 64.35; H, 5.72. Found: C, 64.28; H, 5.63.

4.4.3. (2*S*,5*R*)-2-Phenyl-5-[(phenylseleno)methyl]]tetrahydrofuran, 6. Oil; $[\alpha]_D^{26} = -26.8$ (*c* 1.51, $CHCl_3$). ^1H NMR: δ 7.61–7.50 (m, 2H), 7.40–7.10 (m, 8H), 4.92 (dd, 1H, $J = 6.2$, 7.4 Hz), 4.37–4.28 (m, 1H), 3.28 (dd, 1H, $J = 5.1$, 12.2 Hz), 3.12 (dd, 1H, $J = 7.2$, 12.2 Hz), 2.40–2.25 (m, 1H), 2.18–2.08 (m, 1H), 1.90–1.71 (m, 2H); ^{13}C NMR: δ 142.7, 132.5 (two carbons), 130.3, 129.0 (two carbons), 128.2 (two carbons), 127.2, 126.8, 125.7 (two carbons), 81.5, 78.9, 34.4, 33.1, 31.4; MS *m*/*z* (rel int): 318 (69), 171 (20), 161 (30), 147 (100), 129 (47), 117 (42), 105 (27), 91 (96), 77 (29), 55 (10). Anal. Calcd for $C_{17}H_{18}OSe$: C, 64.35; H, 5.72. Found: C, 64.21; H, 5.69.

4.4.4. (2*R*,5*S*)-2-Phenyl-5-[(phenylseleno)methyl]tetrahydrofuran, *ent*-6. Oil; $[\alpha]_D^{25} = +26.0$ (*c* 0.99, $CHCl_3$). Anal. Calcd for $C_{17}H_{18}OSe$: C, 64.35; H, 5.72. Found: C, 64.40; H, 5.80.

4.4.5. (2*R*,3*S*,5*S*)-2-Methyl-3-phenyl-5-[(phenylseleno)-methyl]tetrahydrofuran, 13. Oil; $[\alpha]_D^{24} = +16.8$ (*c* 1.61, $CHCl_3$). ^1H NMR: δ 7.52–7.50 (m, 2H), 7.32–7.10 (m, 8H), 4.60–4.54 (m, 1H), 4.42 (dq, 1H, $J = 6.2$, 6.4 Hz), 3.43 (ddd, 1H, $J = 5.2$, 6.2, 8.0 Hz), 3.24 (dd, 1H, $J = 5.5$, 12.1 Hz), 3.05 (dd, 1H, $J = 7.4$, 12.1 Hz), 2.41 (ddd, 1H, $J = 5.2$, 7.8, 12.8 Hz), 2.20 (ddd, 1H, $J = 5.6$, 8.0, 12.8 Hz), 0.84 (d, 3H, $J = 6.4$ Hz); ^{13}C NMR: δ 140.7, 132.5 (two carbons), 130.1, 129.0 (two carbons), 128.2 (four carbons), 126.8, 126.4, 77.8, 77.0, 48.9, 37.9, 34.2, 16.7; MS *m*/*z* (rel int): 332 (26), 330 (14), 157 (25), 143 (18), 131 (100), 117 (23), 91 (62), 77 (14), 55 (6). Anal. Calcd for $C_{18}H_{20}OSe$: C, 65.25; H, 6.08. Found: C, 65.12; H, 6.18.

4.4.6. (2*S*,3*R*,5*R*)-2-Methyl-3-phenyl-5-[(phenylseleno)-methyl]tetrahydrofuran, *ent*-13. Oil; $[\alpha]_D^{25} = -15.9$ (*c* 2.40, $CHCl_3$). Anal. Calcd for $C_{18}H_{20}OSe$: C, 65.25; H, 6.08. Found: C, 65.07; H, 6.14.

4.4.7. (2*R*,3*S*,5*R*)-2-Methyl-3-phenyl-5-[(phenylseleno)-methyl]tetrahydrofuran, 14. Oil; $[\alpha]_D^{25} = +120.0$ (*c* 2.37, $CHCl_3$). ^1H NMR: δ 7.60–7.50 (m, 2H), 7.30–7.10 (m, 8H), 4.30 (dq, 1H, $J = 6.4$, 7.2 Hz), 4.24–4.16 (m, 1H), 3.51 (ddd, 1H, $J = 7.2$, 7.9, 8.3 Hz), 3.33 (dd, 1H, $J = 5.6$, 12.1 Hz), 3.15 (dd, 1H, $J = 7.0$, 12.1 Hz), 2.51 (ddd, 1H, $J = 6.1$, 7.9, 12.7 Hz), 1.97 (ddd, 1H, $J = 8.3$, 9.3, 12.7 Hz), 0.84 (d, 3H, $J = 6.4$ Hz); ^{13}C NMR: δ 141.0, 132.5 (two carbons), 130.3, 129.0 (two carbons), 128.4 (two carbons), 128.2 (two carbons), 126.9, 126.4, 78.5, 78.0, 48.6, 38.3, 32.8, 18.0; MS *m*/*z* (rel int): 332 (17), 157 (10), 131 (100), 117 (12), 91 (38), 77 (9). Anal. Calcd for $C_{18}H_{20}OSe$: C, 65.25; H, 6.08. Found: C, 65.31; H, 6.15.

4.4.8. (2*S*,3*R*,5*S*)-2-Methyl-3-phenyl-5-[(phenylseleno)-methyl]tetrahydrofuran, *ent*-14. Oil; $[\alpha]_D^{20} = -121.0$ (*c* 2.25, $CHCl_3$). Anal. Calcd for $C_{18}H_{20}OSe$: C, 65.25; H, 6.08. Found: C, 65.19; H, 6.21.

4.4.9. (2*R*,3*R*,5*R*)-2-Methyl-3-phenyl-5-[(phenylseleno)-methyl]tetrahydrofuran, 15. Oil; $[\alpha]_D^{22} = +34.9$ (*c* 1.33,

$CHCl_3$). ^1H NMR: δ 7.55–7.50 (m, 2H), 7.35–7.15 (m, 8H), 4.43–4.37 (m, 1H), 3.92 (dq, 1H, $J = 6.0$, 8.9 Hz), 3.21 (dd, 1H, $J = 5.2$, 12.2 Hz), 3.09 (dd, 1H, $J = 7.1$, 12.2 Hz), 2.90 (q, 1H, $J = 8.9$ Hz), 2.32–2.20 (m, 2H), 1.23 (d, 3H, $J = 6.0$); ^{13}C NMR: δ 141.1, 132.5 (two carbons), 130.3, 129.0 (two carbons), 128.6 (two carbons), 127.6 (two carbons), 126.8, 126.7, 82.9, 77.6, 52.4, 40.5, 33.7, 19.0; MS *m/z* (rel int): 332 (30), 161 (37), 143 (25), 131 (100), 117 (30), 105 (10), 91 (70), 77 (15), 55 (7). Anal. Calcd for $C_{18}H_{20}OSe$: C, 65.25; H, 6.08. Found: C, 65.09; H, 6.10.

4.4.10. (2*S*,3*S*,5*S*)-2-Methyl-3-phenyl-5-[(phenylseleno)-methyl]tetrahydrofuran, *ent*-15. Oil; $[\alpha]_D^{18} = -36.2$ (*c* 1.02, $CHCl_3$). Anal. Calcd for $C_{18}H_{20}OSe$: C, 65.25; H, 6.08. Found: C, 65.11; H, 6.17.

4.4.11. (2*R*,3*R*,5*S*)-2-Methyl-3-phenyl-5-[(phenylseleno)-methyl]tetrahydrofuran, 16. Oil; $[\alpha]_D^{24} = -55.4$ (*c* 2.45, $CHCl_3$). ^1H NMR: δ 7.54–7.50 (m, 2H), 7.38–7.10 (m, 8H), 4.44–4.37 (m, 1H), 4.09 (dq, 1H, $J = 5.9$, 9.4 Hz), 3.27 (dd, 1H, $J = 5.1$, 12.2 Hz), 3.13 (dd, 1H, $J = 7.2$, 12.2 Hz), 2.90 (ddd, 1H, $J = 7.1$, 9.4, 11.7 Hz), 2.54 (ddd, 1H, $J = 6.7$, 7.1, 12.3 Hz), 2.01 (ddd, 1H, $J = 9.1$, 11.7, 12.3 Hz), 1.19 (d, 3H, $J = 5.9$ Hz); ^{13}C NMR: δ 140.1, 132.5 (two carbons), 130.2, 129.0 (two carbons), 128.6 (two carbons), 127.5 (two carbons), 126.8 (two carbons), 81.6, 77.4, 54.0, 41.7, 33.7, 19.1; MS *m/z* (rel int): 332 (42), 161 (43), 143 (27), 131 (100), 117 (31), 105 (10), 91 (69), 77 (15), 55 (7). Anal. Calcd for $C_{18}H_{20}OSe$: C, 65.25; H, 6.08. Found: C, 65.22; H, 6.13.

4.4.12. (2*S*,3*S*,5*R*)-2-Methyl-3-phenyl-5-[(phenylseleno)-methyl]tetrahydrofuran, *ent*-16. Oil; $[\alpha]_D^{22} = +56.9$ (*c* 0.94, $CHCl_3$). Anal. Calcd for $C_{18}H_{20}OSe$: C, 65.25; H, 6.08. Found: C, 65.19; H, 6.01.

4.5. Reductive deselenenylation. General procedure

A catalytic amount of AIBN and triphenyltin hydride (0.5 mmol) were added to a solution of the tetrahydrofurans (0.3 mmol) in dry benzene (3 mL) and the mixture refluxed under nitrogen. The reaction was stirred and refluxed for 2 h and, after removal of the solvent under reduced pressure, the residue was purified by chromatography on silica gel with a 1:9 mixture of diethyl ether and light petroleum as eluant. The products obtained and the reaction yields are reported in Schemes 3, 4, 7, and 8. Physical and spectral data are reported below.

4.5.1. (2*R*,5*S*)-2-Methyl-5-phenyltetrahydrofuran, 7. Oil; $[\alpha]_D^{25} = -57.1$ (*c* 1.87, $CHCl_3$). ^1H NMR: δ 7.50–7.05 (m, 5H), 5.07 (dd, 1H, $J = 6.5$, 8.0 Hz,), 4.38 (ddq, 1H, $J = 5.9$, 6.0, 8.0 Hz), 2.42 (dddd, 1H, $J = 3.2$, 6.5, 7.3, 12.3 Hz), 2.18 (dddd, 1H, $J = 3.2$, 5.9, 7.8, 12.0 Hz), 1.91 (dddd, 1H, $J = 7.8$, 8.0, 9.9, 12.3 Hz), 1.65 (dddd, 1H, $J = 7.3$, 8.0, 9.9, 12.0 Hz), 1.35 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR: δ 143.9, 128.0 (two carbons), 126.9, 125.4 (two carbons), 80.1, 75.8, 35.5, 34.1, 21.4; MS *m/z* (rel int): 162 (100), 161 (70), 147 (9), 117 (54), 105 (80), 91 (35), 77 (34), 56 (40). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.37; H, 8.60.

4.5.2. (2*S*,5*R*)-2-Methyl-5-phenyltetrahydrofuran, *ent*-7. Oil; $[\alpha]_D^{24} = +56.6$ (*c* 1.04, $CHCl_3$). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.59; H, 8.65.

4.5.3. (2*S*,5*S*)-2-Methyl-5-phenyltetrahydrofuran, 8. Oil; $[\alpha]_D^{23} = -26.6$ (*c* 0.57, $CHCl_3$). ^1H NMR: δ 7.45–7.15 (m, 5H), 4.91 (dd, 1H, $J = 7.1$, 7.4 Hz), 4.20 (ddq, 1H, $J = 6.0$, 6.2, 7.4 Hz), 2.34 (dddd, 1H, $J = 6.4$, 7.1, 8.2, 12.3 Hz), 2.12 (dddd, 1H, $J = 6.1$, 6.2, 8.2, 12.0 Hz), 1.88 (dddd, 1H, $J = 6.1$, 7.4, 9.1, 12.3 Hz), 1.64 (dddd, 1H, $J = 6.4$, 7.4, 9.1, 12.0 Hz), 1.41 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR: δ 143.4, 128.1 (two carbons), 127.0, 125.7 (two carbons), 80.9, 75.9, 34.5, 33.0, 21.2; MS *m/z* (rel int): 162 (100), 161 (77), 147 (10), 117 (49), 107 (45), 105 (77), 91 (29), 77 (32), 56 (36). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.29; H, 8.78.

4.5.4. (2*R*,5*R*)-2-Methyl-5-phenyltetrahydrofuran, *ent*-8. Oil; $[\alpha]_D^{21} = +27.4$ (*c* 1.62, $CHCl_3$). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.43; H, 8.72.

4.5.5. (2*R*,3*S*,5*R*)-2,5-Dimethyl-3-phenyltetrahydrofuran, 17. Oil; $[\alpha]_D^{26} = +66.9$ (*c* 1.29, $CHCl_3$). ^1H NMR: δ 7.30–7.15 (m, 5H), 4.51 (ddq, 1H, $J = 5.7$, 6.2, 7.7 Hz), 4.38 (dq, 1H, $J = 6.3$, 6.4 Hz), 3.41 (ddd, 1H, $J = 5.2$, 6.3, 8.1 Hz), 2.37 (ddd, 1H, $J = 5.2$, 7.7, 12.8 Hz), 1.98 (ddd, 1H, $J = 5.7$, 8.1, 12.8 Hz), 1.31 (d, 3H, $J = 6.2$ Hz), 0.85 (d, 3H, $J = 6.4$ Hz); ^{13}C NMR: δ 141.1, 128.3 (two carbons), 128.2 (two carbons), 126.2, 76.9, 73.6, 48.9, 39.5, 22.7, 16.8; MS *m/z* (rel int): 176 (1), 132 (52), 117 (100), 91 (17), 77 (5). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.67; H, 9.10.

4.5.6. (2*S*,3*R*,5*S*)-2,5-Dimethyl-3-phenyltetrahydrofuran, *ent*-17. Oil; $[\alpha]_D^{24} = -65.4$ (*c* 0.56, $CHCl_3$). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.71; H, 9.21.

4.5.7. (2*R*,3*S*,5*S*)-2,5-Dimethyl-3-phenyltetrahydrofuran, 18. Oil; $[\alpha]_D^{24} = +113.0$ (*c* 0.76, $CHCl_3$). ^1H NMR: δ 7.32–7.15 (m, 5H), 4.20 (dq, 1H, $J = 6.4$, 7.2 Hz), 4.06 (ddq, 1H, $J = 6.1$, 6.2, 9.3 Hz), 3.44 (ddd, 1H, $J = 7.2$, 7.7, 8.4 Hz), 2.47 (ddd, 1H, $J = 6.2$, 8.4, 12.7 Hz), 1.77 (ddd, 1H, $J = 7.7$, 9.3, 12.7 Hz), 1.42 (d, 3H, $J = 6.1$ Hz), 0.83 (d, 3H, $J = 6.4$); ^{13}C NMR: δ 142.1, 128.5 (two carbons), 128.1 (two carbons), 126.2, 78.1, 74.7, 49.0, 40.9, 20.8, 17.7; MS *m/z* (rel int): 176 (2), 132 (54), 117 (100), 91 (18), 77 (5). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.70; H, 9.23.

4.5.8. (2*S*,3*R*,5*R*)-2,5-Dimethyl-3-phenyltetrahydrofuran, *ent*-18. Oil; $[\alpha]_D^{24} = -111.5$ (*c* 0.76, $CHCl_3$). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.07.

4.5.9. (2*R*,3*R*,5*S*)-2,5-Dimethyl-3-phenyltetrahydrofuran, 19. Oil; $[\alpha]_D^{22} = +8.2$ (*c* 1.03, $CHCl_3$). ^{1}H NMR: δ 7.30–7.15 (m, 5H), 4.32–4.24 (m, 1H), 3.85 (dq, 1H, $J = 5.9$, 8.8 Hz), 2.86 (ddd, 1H, $J = 8.0$, 8.8, 9.7 Hz), 2.21 (ddd, 1H, $J = 7.8$, 8.0, 12.7 Hz), 2.01 (ddd, 1H, $J = 6.5$, 9.7, 12.7 Hz), 1.32 (d, 3H, $J = 6.1$ Hz), 1.23 (d, 3H, $J = 5.9$ Hz); ^{13}C NMR: δ 142.0, 128.5 (two carbons), 127.6 (two carbons), 126.4, 82.7, 74.6, 52.6, 42.4, 21.9, 19.0; MS *m*/*z* (rel int): 176 (3), 132 (63), 117 (100), 91 (19), 77 (5). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.14.

4.5.10. (2*S*,3*S*,5*R*)-2,5-Dimethyl-3-phenyltetrahydrofuran, *ent*-19. Oil; $[\alpha]_D^{20} = -8.9$ (*c* 1.76, $CHCl_3$). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.68; H, 9.11.

4.5.11. (2*R*,3*R*,5*R*)-2,5-Dimethyl-3-phenyltetrahydrofuran, 20. Oil; $[\alpha]_D^{23} = +15.3$ (*c* 1.0, $CHCl_3$). ^{1}H NMR: δ 7.34–7.15 (m, 5H), 4.30 (ddq, 1H, $J = 5.5$, 6.0, 9.4 Hz), 4.04 (dq, 1H, $J = 6.0$, 9.0 Hz), 2.91 (ddd, 1H, $J = 7.0$, 9.0, 11.7 Hz), 2.43 (ddd, 1H, $J = 5.5$, 7.0, 12.2 Hz), 1.76 (ddd, 1H, $J = 9.4$, 11.7, 12.2 Hz), 1.35 (d, 3H, $J = 6.0$ Hz), 1.21 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR: δ 140.4, 128.1 (two carbons), 127.1 (two carbons), 126.2, 80.6, 74.0, 54.0, 43.3, 21.2, 19.0; MS *m*/*z* (rel int): 176 (1), 132 (53), 117 (100), 91 (17), 77 (5). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.66; H, 9.16.

4.5.12. (2*S*,3*S*,5*S*)-2,5-Dimethyl-3-phenyltetrahydrofuran, *ent*-20. Oil; $[\alpha]_D^{22} = -15.3$ (*c* 0.86, $CHCl_3$). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.64; H, 9.12.

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