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Synthesis of enantiomerically pure 1,4-dioxanes from alkenes promoted by organoselenium reagents

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Abstract—An alkene can be converted into two enantiomerically pure diastereomeric selenoethers through a regio- and stereospecific *anti* addition reaction mediated by *N*-(phenylseleno)phthalimide in the presence of an enantiomerically pure 1,2-diol. This alkoxyselenylation reaction can be employed as the key step to allow the synthesis of several isomeric tetrasubstituted 1,4-dioxanes in enantiomerically pure form.

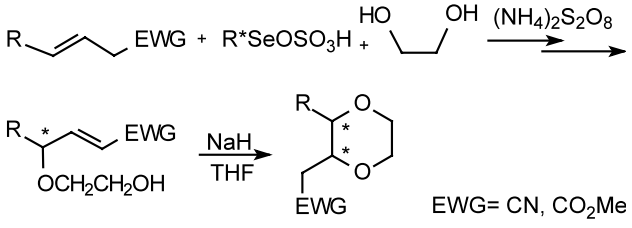
1. Introduction

An alkene can be regio- and stereospecifically converted into a selenoether, a selenoalcohol or a selenoamide through an *anti* addition reaction mediated by an electrophilic selenium reagent in the presence of the appropriate nucleophile.[1,2] These products may be further functionalized by taking advantage of the versatile chemistry of the resulting selenium compounds. Thus, for example, the selenium moiety can be directly removed by reductive deselenylation or it can be converted into other functional groups after oxidation to the corresponding selenoxide or selenone, by subsequent elimination or substitution, respectively.[2]

The alkoxyselenylation reaction of alkenes also occurs easily when diols are used as nucleophiles.[3–6] In a previous paper[4] we reported the conversion of β,γ-unsaturated esters and nitriles into enantiomerically enriched γ-hydroxy- or γ-alkoxy-α,β-unsaturated derivatives by a one-pot oxyselenylation and deselenylation sequence. The reaction was promoted by camphor diselenide and ammonium persulfate in water, methanol or ethylene glycol. Scheme 1 describes the synthetic sequence when ethylene glycol was employed as the nucleophile. Moderate to good chemical yields (from 50 to 84%) and enantiomeric excesses (from 40 to 64% ee) were obtained. In the same paper it was also demonstrated that the allylic ether products can be transformed easily into dioxanes by an intramolecular conjugate addition reaction. Unfortunately, the dioxanes were obtained as inseparable 1:1 mixtures of enantiomerically enriched *cis* and *trans* isomers.

We now report that the alkoxyselenylation reaction of alkenes in the presence of enantiomerically pure diols can be employed as the key step to prepare several isomeric tetrasubstituted 1,4-dioxanes in enantiomerically pure form.

Very few methods are reported in the literature for the synthesis of these heterocycles, particularly in enantiomerically enriched form.[5–9] Moreover, these dioxanes can be reductively cleaved to afford enantiomerically pure diols and this represents a further useful application of the procedure we describe herein.



Scheme 1.

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2. Results and discussion

The results reported in Scheme 2 refer to the first experiments carried out with nitrile **1** and (1*R*,2*R*)-1,2-diphenyl-1,2-ethanediol **2a**.

The synthetic procedure involves three steps. In the first step the regio- and stereospecific *anti* addition promoted by *N*-(phenylseleno)phthalimide on the alkene **1** in the presence of the diol **2a** generated the two enantiomerically pure diastereomeric alkoxyselenides **3a** and **7a**. The addition products were separated by column chromatography in 19 and 21% yield, respectively. It is probable that under the reaction conditions employed, i.e. in acidic medium, **3a** and **7a** are transformed into 4-hydroxy-3-(phenylseleno)pentanenitrile which was recovered as a by-product in 30% yield. It is interesting to note that **3a** and **7a** were not formed when other selenoelectrophilic reagents, such as phenylselenyltriflate and phenylselenylsulfate, were employed.

In the second step the two diastereoisomers **3a** and **7a** were subjected to oxidation with hydrogen peroxide. The elimination reactions of the corresponding selenoxides afforded the Michael acceptors **4a** and **8a** in 80 and 98% yield, respectively.

In the last step isomeric 1,4-dioxanes were formed by treatment of **4a** and **8a** with NaH in anhydrous THF at 0°C. The attack of the nucleophilic oxygen on the carbon–carbon double bond generates a new stereocentre. In both cases the attack was not stereoselective.

In fact, as indicated in Fig. 1, the *Re* or *Si* attacks of the oxygen nucleophile produce **5a** (15% yield) and **6a** (75% yield) from the alkene **4a**; and **9a** and **10a**, (isolated as an inseparable mixture in 85% yield, **9a**:**10a** = 12:88), from the alkene **8a**.

The formation of compounds **6a** and **10a** as the major products, can be explained on the basis of the higher stability of the chair transition states generated from B and D, in which all the substituents (B) or at least three substituents (D) occupy equatorial positions.

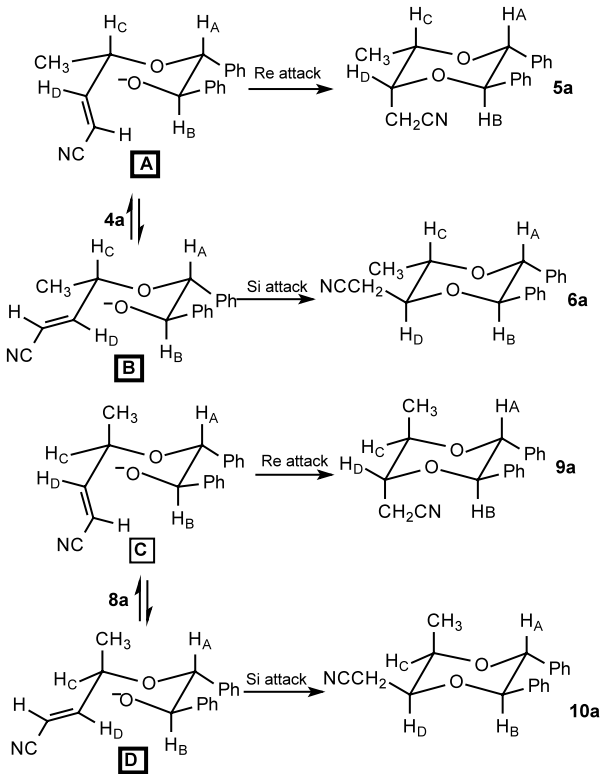
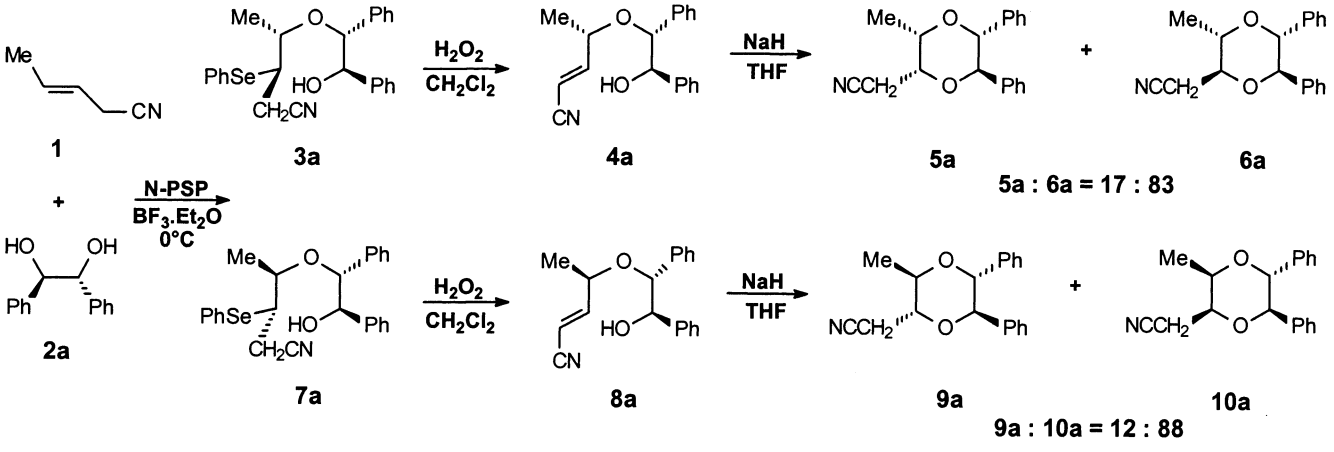


Figure 1.

The stereochemistry of each of the enantiomerically pure substituted 1,4-dioxanes was easily assigned on the basis of ^{1}H, ^{13}C NMR and NOESY experiments.

The four ring protons could be unambiguously assigned on the basis of their chemical shifts, multiplicity and coupling constant data. In compounds **5a**, **6a**, **9a** and **10a** the values of the vicinal coupling constants J_{AB} and J_{CD} (reported in the experimental), clearly suggest that the molecular geometries are those indicated in Fig. 1.[7,10]

Further support came from the results of the NOESY experiments. Strong dipolar interactions exist between



Scheme 2.

the protons H_A and H_C for both the dioxanes **5a** and **6a**, between H_B and CH_2CN for **5a** and between H_B and H_D for **6a**. Furthermore, significant NOE effects between the methyl group and H_A for both the dioxanes **9a** and **10a**, between H_B and CH_2CN for **9a** and between H_B and H_D for **10a** fully confirmed the assigned stereochemistries.

Interesting results were obtained when methyl styrylacetate **11** and three (*R*,*R*)-diols, the previously employed **2a**, (1*R*,2*R*)-1,2-cyclohexanediol **12** and (2*R*,3*R*)-2,3-butanediol **13**, were used as starting materials. The synthetic sequences were carried out as previously described. Scheme 3 shows the reaction products and yields obtained from these reactions.

Starting from methyl styrylacetate **11** the alkoxyselenylation products were formed in better overall yields, particularly when **2a** and **12** were used as the diols. In all of the cases examined the diastereoisomers **7b–d** were the major products.

After chromatographic purification **3b–d** and **7b–d** were submitted to oxidative deselenylation and then to cyclization. The so-formed isomeric 1,4-dioxanes were isolated in enantiomerically pure form after column chromatography

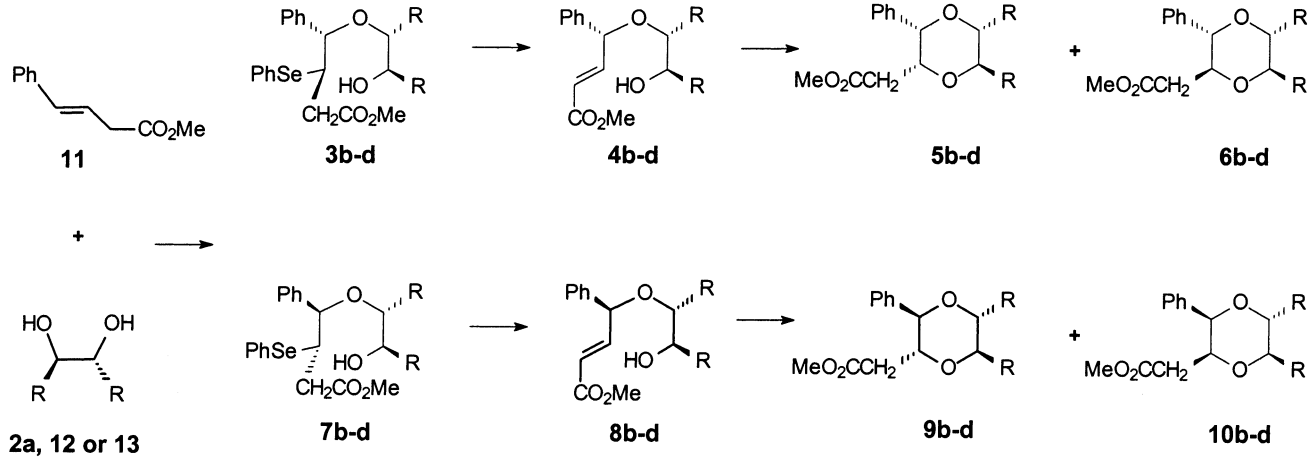
As indicated in Scheme 3, compounds **4b–d** produced the diastereomeric dioxanes **5b–d** and **6b–d**, the former being the major products. Some experiments with **4d** demonstrated that the diastereomeric ratio is influenced by the reaction temperature. TLC and GC–MS analyses after 2 and 4 h when the reaction mixture was stirred at −78°C showed the presence of the dioxanes **5d** and **6d** in a 30:70 ratio, together with a large amount of unreacted starting alkene. The reaction was then allowed to warm to room temperature and the analyses were repeated. Under these conditions the conversion of the starting alkene into the reaction products was complete. Moreover, the diastereomeric ratio was reversed (**5d**:**6d** = 68:32).

The alkenes **8b–d** behaved differently in the cyclization reactions to **8a**. In fact, compounds **8b** and **8c** did not undergo cyclization whereas **8d** generated **9d** as the sole reaction product.

Structural determination of compound **9d** was not so straightforward because of the observed values of the two vicinal coupling constants (J_{AB} = 5.4 Hz and J_{CD} = 5.2Hz). However, the NOESY spectrum indicated that strong dipolar interactions exist between Me_A and H_C and between the Me_B and H_D, which suggests that both the methyl groups occupy axial positions and that compound **9d** assumes a B conformation (see Fig. 2) in which the phenyl group occupies an equatorial position. In order to explain the observed vicinal coupling constant values it can be suggested that the molecule does not assume a perfect chair conformation, but is partially distorted.

Figure 2.

It is interesting to note that the dioxanes **9b**,**c** and **10b–d**, which, must place one or more bulky groups, such as the phenyl group[11] or the fused ring, in axial



	R	3	7	4	8	5	6	9	10
b	Ph	14%	56%	74%	90%	45%	34%	–	–
c	-$(CH_2)_4$-	29%	42%	68%	55%	50%	24%	–	–
d	Me	21%	31%	73%	90%	50%	30%	65%	–

Scheme 3.

positions in both of the possible chair conformations are not formed in this cyclization reaction.

Starting from the commercially available (*S*,*S*)-diols the enantiomers of the dioxanes described above can be obtained. This was demonstrated in the reaction with (2*S*,3*S*)-2,3-butanediol and methyl styrylacetate. Stereochemical assignment was confirmed by measuring the specific rotation values of the intermediates and the final dioxane products.

3. Conclusion

Further experiments are now in progress in order to find useful applications of this new methodology for the preparation of more complex dioxanes as well as to test the use of these heterocycles as chiral building blocks.

4. Experimental

New compounds were characterized by MS, ^{1}H 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 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 β,γ-unsaturated nitrile **1**, the ester **11** and the enantiopure diols **2a**, **12** and **13**, (ee >99%), are all commercial products.

4.2. Conversion of β,γ-unsaturated esters and nitrile into β-phenylseleno γ-alkoxy derivatives

To a solution of *N*-(phenylseleno)phthalimide (1 mmol) in dichloromethane (6 mL) at 0°C the alkene **1** or **11** (2.5 mmol) and the diol **2a**, **12** or **13** (1.3 mmol) were added. Finally, a catalytic amount of $BF_3{\cdot}Et_2O$ was added dropwise. The temperature was allowed to raise to room temperature over a 2 h period and the progress of the reaction was monitored by TLC, GC–MS and ^{1}H NMR. In the case of **12** (Scheme 3, entry c) the reaction was stirred at room temperature for 20 h. The reaction was poured into a solution of 5% aqueous NaOH and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated. Reaction products were obtained in a pure form after column chromatography of the residue on silica gel.

4.2.1. (3*R*,4*S*)-4-{[(1*R*,2*R*)-2-Hydroxy-1,2-diphenylethyl]oxy}-3-(phenylseleno)pentanenitrile, 3a. Oil; $[\alpha]_D^{24} = -45.3$ (*c* 1.68, $CHCl_3$). ^{1}H NMR: δ 7.60–7.49 (m, 2H), 7.40–7.25 (m, 3H), 7.20–7.15 (m, 6H), 7.15–7.00 (m, 4H), 4.77 (d, 1H, $J=8.2$ Hz), 4.37 (d, 1H, $J=8.2$ Hz), 3.90 (dq, 1H, $J=4.3$, 6.4 Hz), 3.75 (br s, 1H), 3.51 (ddd, 1H, $J=4.3$, 6.4, 7.0 Hz), 2.76 (dd, 1H, $J=6.4$, 17.3 Hz), 2.78 (dd, 1H, $J=7.0$, 17.3 Hz), 1.12 (d, 3H, $J=6.4$ Hz). ^{13}C NMR: δ 139.4, 138.7, 136.2 (two carbons), 130.1 (two carbons), 129.3, 128.5, 128.4 (two carbons), 128.3 (two carbons), 128.2, 128.1 (two carbons), 127.7, 127.6 (two carbons), 118.7, 88.3, 79.3, 76.5, 46.6, 21.1, 19.4. Anal. calcd for $C_{25}H_{25}NO_2Se$: C, 66.66; H, 5.59, N, 3.11. Found: C, 66.69; H, 5.51; N, 2.94%.

4.2.2. Methyl (3*R*,4*S*)-4-{[(1*R*,2*R*)-2-hydroxy-1,2-diphenylethyl]oxy}-4-phenyl-3-(phenylseleno) butanoate, 3b. Oil; $[\alpha]_D^{22} = -1.8$ (*c* 0.10, $CHCl_3$). ^{1}H NMR: δ 7.60–7.56 (m, 2H), 7.31–7.20 (m, 5H), 7.10–6.95 (m, 9H), 6.92–6.88 (m, 2H), 6.77–6.72 (m, 2H), 4.90 (d, 1H, $J=4.6$ Hz), 4.81 (dd, 1H, $J=1.8$, 8.2 Hz), 4.48 (d, 1H, $J=1.8$ Hz), 4.27 (d, 1H, $J=8.2$ Hz), 3.76 (ddd, 1H, $J=4.6$, 6.4, 7.9 Hz), 3.61 (s, 3H), 2.80 (dd, 1H, $J=7.9$, 16.3 Hz), 2.74 (dd, 1H, $J=6.4$, 16.3 Hz). ^{13}C NMR: δ 172.9, 139.8, 139.1 (two carbons), 135.4 (two carbons), 129.8 (two carbons), 129.4, 128.6, 128.3 (four carbons), 128.1 (three carbons), 128.0 (three carbons), 127.9, 127.8 (two carbons), 127.6 (two carbons), 88.0, 84.9, 80.1, 52.3, 48.6, 36.4. Anal. calcd for $C_{31}H_{30}O_4Se$: C, 68.25; H, 5.54. Found: C, 68.19; H, 6.05%.

4.2.3. Methyl (3*R*,4*S*)-4-{[(1*R*,2*R*)-2-hydroxycyclohexyl]oxy}-4-phenyl-3-(phenylseleno)butanoate, 3c. Oil; $[\alpha]_D^{20} = +17.6$ (*c* 1.47, $CHCl_3$). ^{1}H NMR: δ 7.60–7.55 (m, 2H), 7.26–7.02 (m, 8H), 4.78 (d, 1H, $J=4.4$ Hz), 4.0 (br s, 1H), 3.59 (dt, 1H, $J=4.5$, 6.9 Hz), 3.53 (s, 3H), 3.51 (ddd, 1H, $J=5.0$, 8.6, 11.0 Hz), 3.03 (ddd, 1H, $J=4.3$, 8.6, 10.8 Hz), 2.75–2.68 (m, 2H), 2.02–1.85 (m, 1H), 1.7–1.4 (m, 3H), 1.4–0.98 (m, 4H). ^{13}C NMR: δ 172.6, 140.7, 134.6 (two carbons), 134.2, 129.2 (two carbons), 128.1 (two carbons), 128.0, 127.9, 123.5 (two carbons), 85.4, 84.3, 75.0, 51.7, 48.9, 35.3, 32.4, 31.6, 24.4, 23.9. Anal. calcd for $C_{23}H_{28}O_4Se$: C, 61.74; H, 6.31. Found: C, 61.91; H, 6.39%.

4.2.4. Methyl (3*R*,4*S*)-4-{[(1*R*,2*R*)-2-hydroxy-1-methylpropyl]oxy}-4-phenyl-3-(phenylseleno)butanoate, 3d. Oil; $[\alpha]_D^{27} = +9.3$ (*c* 0.81, $CHCl_3$). ^{1}H NMR: δ 7.60–7.50 (m, 2H), 7.27–7.10 (m, 8H), 4.74 (d, 1H, $J=4.7$ Hz), 3.68–3.55 (m, 3H), 3.52 (s, 3H), 3.19 (dq, 1H, $J=6.3$, 7.4 Hz), 2.74 (dd, 1H, $J=6.2$, 16.1 Hz), 2.69 (dd, 1H, $J=7.9$, 16.1 Hz), 1.06 (d, 3H, $J=6.4$ Hz), 0.82 (d, 3H, $J=6.3$ Hz). ^{13}C NMR: δ 173.0, 140.7, 135.2 (two carbons), 129.6 (two carbons), 129.4, 128.6 (two carbons), 128.4 (two carbons), 127.7 (two carbons), 84.5, 82.3, 72.7, 52.2, 48.8, 36.0, 19.2, 18.0. MS *m*/*z* (rel. int.): 422 (3), 333 (2), 273 (3), 259 (3), 244 (3), 195 (4), 179 (76), 157 (12), 117 (35), 115 (26), 107 (100), 105 (10), 91 (17), 73 (36), 55 (9). Anal. calcd for $C_{21}H_{26}O_4Se$: C, 59.86; H, 6.22. Found: C, 59.80; H, 6.32%.

4.2.5. (3*S*,4*R*)-4-{[(1*R*,2*R*)-2-Hydroxy-1,2-diphenylethyl]oxy}-3-(phenylseleno)pentanenitrile, 7a. Oil; $[\alpha]_D^{25} = +46.3$ (*c* 2.07, $CHCl_3$). ^{1}H NMR: δ 7.60–7.55

(m, 2H), 7.30–7.03 (m, 9H), 7.02–6.98 (m, 4H), 4.71 (d, 1H, $J=8.1$ Hz), 4.33 (d, 1H, $J=8.1$ Hz), 3.63 (quint, 1H, $J=6.2$ Hz), 3.40 (br s, 1H), 3.17 (q, 1H, $J=6.2$ Hz), 2.70 (dd, 1H, $J=6.2$, 17.2 Hz), 2.64 (dd, 1H, $J=6.2$, 17.2 Hz), 1.32 (d, 3H, $J=6.2$ Hz). ^{13}C NMR: δ 139.5, 137.0, 136.0 (two carbons), 129.9 (two carbons), 129.1, 128.9, 128.7 (two carbons), 128.6 (two carbons), 128.3, 128.1 (two carbons), 127.9, 127.6 (two carbons), 119.2, 85.1, 78.5, 73.8, 46.0, 21.6, 17.7. Anal. calcd for $C_{25}H_{25}NO_2Se$: C, 66.66; H, 5.59; N, 3.11. Found: C, 66.75; H, 5.66; N, 2.96%.

4.2.6. Methyl (3*S*,4*R*)-4-{[(1*R*,2*R*)-2-hydroxy-1,2-diphenylethyl]oxy}-4-phenyl-3-(phenylseleno)butanoate, 7b. Oil; $[\alpha]_D^{26}=-99.9$ (c 1.51, $CHCl_3$). ^{1}H NMR: δ 7.40–7.05 (m, 16H), 7.05–6.95 (m, 2H), 6.95–6.85 (m, 2H), 4.72 (d, 1H, $J=8.0$ Hz), 4.34 (d, 1H, $J=8.0$ Hz), 4.06 (d, 1H, $J=8.0$ Hz), 3.87 (ddd, 1H, $J=6.6$, 7.3, 8.0 Hz), 3.72 (s, 3H), 3.46 (br s, 1H), 3.00 (dd, 1H, $J=7.3$, 16.0 Hz), 2.79 (dd, 1H, $J=6.6$, 16.0 Hz). ^{13}C NMR: δ 173.2, 139.6, 138.4, 137.1, 135.4 (two carbons), 129.3 (three carbons), 128.9, 128.8 (three carbons), 128.7 (three carbons), 128.6 (two carbons), 128.5 (two carbons), 128.2 (two carbons), 128.0, 127.5 (two carbons), 84.1, 81.3, 78.7, 52.2, 46.8, 38.7. Anal. calcd for $C_{31}H_{30}O_4Se$: C, 68.25; H, 5.54. Found: C, 68.24; H, 5.47%.

4.2.7. Methyl (3*S*,4*R*)-4-{[(1*R*,2*R*)-2-hydroxycyclohexyl]oxy}-4-phenyl-3-(phenylseleno)butanoate, 7c. Oil; $[\alpha]_D^{21}=-47.4$ (c 1.66, $CHCl_3$). ^{1}H NMR: δ 7.50–7.10 (m, 10H), 4.60 (d, 1H, $J=7.6$ Hz), 3.67 (ddd, 1H, $J=6.1$, 7.3, 7.6 Hz), 3.60 (s, 3H), 3.31 (ddd, 1H, $J=4.5$, 8.6, 10.9 Hz), 2.93–2.86 (m, 1H), 2.89 (dd, 1H, $J=6.1$, 16.1 Hz), 2.71 (dd, 1H, $J=7.3$, 16.1 Hz), 2.30 (br s, 1H), 2.10–1.99 (m, 1H), 1.99–1.75 (m, 1H), 1.73–1.48 (m, 2H), 1.25–0.99 (m, 4H). ^{13}C NMR: δ 172.5, 139.4, 134.8 (two carbons), 129.2, 128.9 (two carbons), 128.5 (two carbons), 128.3, 127.6, 127.5 (two carbons), 80.4, 80.2, 73.6, 51.6, 46.8, 37.5, 31.7, 28.4, 23.9, 23.7. Anal. calcd for $C_{23}H_{28}O_4Se$: C, 61.74; H, 6.31. Found: C, 61.61; H, 6.25%.

4.2.8. Methyl (3*S*,4*R*)-4-{[(1*R*,2*R*)-2-hydroxy-1-methylpropyl]oxy}-4-phenyl-3-(phenylseleno)butanoate, 7d. Oil; $[\alpha]_D^{24}=-74.6$ (c 1.15, $CHCl_3$). ^{1}H NMR: δ 7.40–7.18 (m, 10H), 4.61 (d, 1H, $J=7.9$ Hz), 3.79 (dt, 1H, $J=6.8$, 7.9 Hz), 3.62 (s, 3H), 3.50 (quint, 1H, $J=6.3$ Hz), 3.10 (quint, 1H, $J=6.3$ Hz), 2.93 (dd, 1H, $J=6.8$, 16.1 Hz), 2.78 (dd, 1H, $J=6.8$, 16.1 Hz), 2.50 (br s, 1H), 1.07 (d, 3H, $J=6.3$ Hz), 1.03 (d, 3H, $J=6.3$ Hz). ^{13}C NMR: δ 173.0, 139.3, 135.3 (two carbons), 129.4, 129.3 (two carbons), 128.8 (two carbons), 128.7, 128.2 (two carbons), 128.1, 81.1, 76.7, 71.6, 52.1, 46.9, 38.3, 19.1, 15.0. MS m/z (rel. int.): 422 (4), 333 (3), 273 (4), 259 (3), 244 (4), 195 (4), 179 (84), 157 (12), 117 (33), 115 (25), 107 (100), 105 (10), 91 (16), 73 (35), 55 (8). Anal. calcd for $C_{21}H_{26}O_4Se$: C, 59.86; H, 6.22. Found: C, 59.91; H, 6.35%.

4.3. Conversion of selenoesters and selenonitrile into allylic ethers

The selenonitriles **3a** and **7a** or the selenoesters **3b–d** and **7b–d** (0.5 mmol) were treated with an excess of hydrogen peroxide 30% (5 mmol) in dichloromethane at room temperature. The progress of the reactions was followed by TLC. After 1–2 h the reaction mixtures were poured into water and extracted with dichloromethane. The organic layers were dried and evaporated. The reaction products were purified by column chromatography on silica gel. Physical and spectral data of the products **4a–d** and **8a–d** are reported below.

4.3.1. (2*E*,4*S*)-4-{[(1*R*,2*R*)-2-Hydroxy-1,2-diphenylethyl]oxy}pent-2-enenitrile, 4a. Oil; $[\alpha]_D^{23}=-101.6$ (c 1.95, $CHCl_3$). ^{1}H NMR: δ 7.20–7.02 (m, 6H), 7.0–6.85 (m, 4H), 6.50 (dd, 1H, $J=5.8$, 16.4 Hz), 5.40 (dd, 1H, $J=1.2$, 16.4 Hz), 4.65 (d, 1H, $J=7.4$ Hz), 4.23(d, 1H, $J=7.4$ Hz), 3.87 (ddq, 1H, $J=1.2$, 5.8, 6.6 Hz), 3.0 (br s, 1H), 1.17 (d, 3H, $J=6.6$ Hz). ^{13}C NMR: δ 155.6, 139.7, 137.9, 128.8 (two carbons), 128.7, (two carbons), 128.4 (two carbons), 128.0 (two carbons), 127.4 (two carbons), 117.4, 100.9, 85.7, 78.8, 72.7, 21.5. MS m/z (rel. int.): 293 (1), 187 (10), 107 (100), 105 (12), 81 (10), 80 (12), 79 (28), 77 (20), 53 (6). Anal. calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.85; H, 6.60; N, 4.71%.

4.3.2. Methyl (2*E*,4*R*)-4-{[(1*R*,2*R*)-2-hydroxy-1,2-diphenylethyl]oxy}-4-phenylbut-2-enoate, 4b. Oil; $[\alpha]_D^{25}=-27.0$ (c 1.95, $CHCl_3$). ^{1}H NMR: δ 7.40–7.00 (m, 15H), 6.86 (dd, 1H, $J=7.2$, 15.8 Hz), 6.03 (dd, 1H, $J=1.1$, 15.8 Hz), 4.88 (dd, 1H, $J=1.1$, 7.2 Hz), 4.82 (d, 1H, $J=7.7$ Hz), 4.53 (d, 1H, $J=7.7$ Hz), 3.78 (s, 3H), 3.40 (br s, 1H). ^{13}C NMR: δ 166.3, 146.3, 139.1, 138.8, 137.1, 128.5 (two carbons), 128.2 (two carbons), 128.1 (two carbons), 127.9 (two carbons), 127.8 (two carbons), 127.7, 127.1 (two carbons), 126.8 (two carbons), 122.6, 85.1, 78.4, 78.0, 51.7. MS m/z (rel. int.): 388 (<1), 281 (1), 176 (100), 161 (5), 144 (41), 117 (19), 115 (73), 107 (51), 105 (14), 91 (8), 79 (19), 77 (19). Anal. calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.36; H, 6.50%.

4.3.3. Methyl (2*E*,4*R*)-4-{[(1*R*,2*R*)-2-hydroxycyclohexyl]oxy}-4-phenylbut-2-enoate, 4c. Oil; $[\alpha]_D^{23}=+7.3$ (c 2.13, $CHCl_3$). ^{1}H NMR: δ 7.45–7.25 (m, 5H), 6.98 (dd, 1H, $J=6.1$, 15.7 Hz), 6.10 (dd, 1H, $J=1.4$, 15.7 Hz), 5.17 (dd, 1H, $J=1.4$, 6.1 Hz), 3.75 (s, 3H), 3.55 (ddd, 1H, $J=4.5$, 8.6, 10.3 Hz), 3.26 (ddd, 1H, $J=4.7$, 8.6, 10.4 Hz), 2.50 (br s, 1H), 2.10–1.99 (m, 1H), 1.90–1.75 (m, 1H), 1.70–1.55 (m, 2H), 1.35–1.10 (m, 4H). ^{13}C NMR: δ 167.0, 148.3, 140.5, 129.1 (two carbons), 128.6, 127.4 (two carbons), 121.3, 83.0, 79.8, 74.5, 52.1, 32.7, 30.6, 24.5, 24.2. MS m/z (rel. int.): 290 (1), 231 (12), 191 (19), 176 (88), 174 (28), 163 (21), 161 (22), 160 (15), 144 (75), 133 (25), 131 (20), 117 (32), 116 (36), 115 (100), 107 (9), 105 (9), 91 (7), 79 (11), 77 (7), 67 (6), 55 (5). Anal. calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.26; H, 7.60%.

4.3.4. Methyl (2*E*,4*R*)-4-{[(1*R*,2*R*)-2-hydroxy-1-methylpropyl]oxy}-4-phenylbut-2-enoate, 4d. Oil; $[\alpha]_D^{29}=+5.3$ (*c* 1.18, $CHCl_3$). ^1H NMR: δ 7.40–7.20 (m, 5H), 6.97 (dd, 1H, $J=6.3$, 15.7 Hz), 6.10 (dd, 1H, $J=1.3$, 15.7 Hz), 5.09 (dd, 1H, $J=1.3$, 6.3 Hz), 3.75 (s, 3H), 3.69 (quint, 1H, $J=6.3$ Hz), 3.42 (quint, 1H, $J=6.3$ Hz), 2.50 (br s, 1H), 1.20 (d, 3H, $J=6.3$ Hz), 1.04 (d, 3H, $J=6.3$ Hz). ^{13}C NMR: δ 166.6, 147.6, 139.8, 128.7 (two carbons), 128.3, 127.1 (two carbons), 121.2, 79.6, 79.1, 71.3, 51.7, 18.8, 16.3. MS *m*/*z* (rel. int.): 264 (<1), 263 (1), 233 (1), 191 (5), 176 (51), 161 (8), 144 (45), 133 (10), 131 (13), 117 (21), 115 (100), 101 (16), 91 (6), 77 (5), 55 (4). Anal. calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.25; H, 7.70%.

4.3.5. (2*E*,4*R*)-4-{[(1*R*,2*R*)-2-Hydroxy-1,2-diphenylethyl]oxy}pent-2-enenitrile, 8a. Oil; $[\alpha]_D^{22}=+69.5$ (*c* 1.06, $CHCl_3$). ^1H NMR: δ 7.35–7.15 (m, 6H), 7.15–6.95 (m, 4H), 6.57 (dd, 1H, $J=4.5$, 16.3 Hz), 5.58 (dd, 1H, $J=1.9$, 16.3 Hz), 4.74 (d, 1H, $J=8.0$ Hz), 4.40 (d, 1H, $J=8.0$ Hz), 4.05 (ddq, 1H, $J=1.9$, 4.5, 6.6 Hz), 3.20 (br s, 1H), 1.33 (d, 3H, $J=6.6$ Hz). ^{13}C NMR: δ 155.2, 138.7, 137.0, 128.1, (two carbons), 127.8 (four carbons), 127.5 (two carbons), 127.0 (two carbons), 116.8, 98.8, 85.5, 78.0, 72.0, 18.8. MS *m*/*z* (rel. int.): 293 (1), 187 (9), 107 (100), 105 (15), 81 (8), 80 (12), 79 (27), 77 (22), 53 (7). Anal. calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.85; H, 6.60; N, 4.71%.

4.3.6. Methyl (2*E*,4*S*)-4-{[(1*R*,2*R*)-2-hydroxy-1,2-diphenylethyl]oxy}-4-phenylbut-2-enoate, 8b. Oil; $[\alpha]_D^{24}=-69.2$ (*c* 1.21, $CHCl_3$). ^1H NMR: δ 7.40–7.30 (m, 3H), 7.30–7.10 (m, 8H), 7.05–6.92 (m, 4H), 6.98 (dd, 1H, $J=4.4$, 15.7 Hz), 6.15 (dd, 1H, $J=1.8$, 15.7 Hz), 4.85 (dd, 1H, $J=1.8$, 4.4 Hz), 4.79 (d, 1H, $J=7.7$ Hz), 4.25 (d, 1H, $J=7.7$ Hz), 3.72 (s, 3H), 3.30 (br s, 1H). ^{13}C NMR: δ 166.6, 147.5, 138.9, 137.7, 136.8, 128.8 (two carbons), 128.5, 128.2 (three carbons), 127.7 (two carbons), 127.6 (two carbons), 127.5 (three carbons), 127.0 (two carbons), 119.8, 83.7, 78.2, 77.4, 51.5. MS *m*/*z* (rel. int.): 388 (<1), 281 (1), 176 (100), 161 (6), 144 (41), 117 (19), 116 (22), 115 (74), 107 (53), 105 (17), 91 (8), 79 (20), 77 (20). Anal. calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.36; H, 6.50%.

4.3.7. Methyl (2*E*,4*S*)-4-{[(1*R*,2*R*)-2-hydroxycyclohexyl]oxy}-4-phenylbut-2-enoate, 8c. Oil; $[\alpha]_D^{25}=-98.8$ (*c* 1.74, $CHCl_3$). ^1H NMR: δ 7.30–7.24 (m, 5H), 6.94 (dd, 1H, $J=4.8$, 15.6 Hz), 6.03 (dd, 1H, $J=1.7$, 15.6 Hz), 5.04 (dd, 1H, $J=1.7$, 4.8 Hz), 3.76 (s, 3H), 3.42 (ddd, 1H, $J=4.4$, 8.5, 10.3 Hz), 3.04 (ddd, 1H, $J=4.5$, 8.5, 10.3 Hz), 2.25 (br s, 1H), 2.04–1.96 (m, 1H), 1.92–1.84 (m, 1H), 1.60–1.55 (m, 2H), 1.25–1.05 (m, 4H). ^{13}C NMR: δ 166.7, 148.3, 139.1, 128.8 (two carbons), 128.3, 127.1 (two carbons), 119.9, 81.4, 78.3, 73.6, 51.5, 31.8, 29.3, 24.0, 23.6. MS *m*/*z* (rel. int.): 290 (1), 231 (9), 191 (29), 176 (53), 174 (21), 163 (19), 161 (19), 160 (14), 144 (64), 133 (23), 131 (23), 117 (28), 116 (34), 115 (100), 105 (9), 81 (11), 79 (11), 77 (7), 67 (6), 55 (5). Anal. calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.30; H, 7.65%.

4.3.8. Methyl (2*E*,4*S*)-4-{[(1*R*,2*R*)-2-hydroxy-1-methylpropyl]oxy}-4-phenylbut-2-enoate, 8d. Oil; $[\alpha]_D^{26}=-118.2$ (*c* 1.02, $CHCl_3$). ^1H NMR: δ 7.48–7.27 (m, 5H), 7.02 (dd, 1H, $J=4.9$, 15.6 Hz), 6.10 (dd, 1H, $J=1.8$, 15.6 Hz), 5.06 (dd, 1H, $J=1.8$, 4.9 Hz), 3.75 (s, 3H), 3.62 (quint, 1H, $J=6.4$ Hz), 3.25 (quint, 1H, $J=6.4$ Hz), 2.50 (br s, 1H), 1.15 (d, 3H, $J=6.4$ Hz), 1.10 (d, 3H, $J=6.4$ Hz). ^{13}C NMR: δ 166.8, 148.3, 138.8, 129.0 (two carbons), 128.6, 127.4 (two carbons), 120.1, 78.5, 77.9, 71.2, 51.7, 18.6, 14.2. MS *m*/*z* (rel. int.): 264 (<1), 263 (1), 233 (2), 191 (18), 176 (44), 161 (8), 144 (42), 131 (16), 117 (21), 115 (100), 101 (14), 91 (6), 77 (5), 55 (4). Anal. calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.11; H, 7.65%.

4.4. Conversion of allylic ethers into dioxane derivatives

The allylic ethers **4a**–**d** or **8a**–**d** (0.5 mmol) were treated with sodium hydride (0.55 mmol) in anhydrous THF (4 mL) at 0°C. After 2–3 h the reaction mixtures were worked up in the usual way. Purifications were effected by column chromatography on silica gel. Physical and spectral data of the products **5a**–**d**, **6a**–**d**, **9a**, **9d** and **10a** are reported below.

4.4.1. [(2*R*,3*S*,5*R*,6*R*)-3-Methyl-5,6-diphenyl-1,4-dioxan-2-yl]acetonitrile, 5a. Oil; $[\alpha]_D^{23}=+92.3$ (*c* 0.51, $CHCl_3$). ^1H NMR: δ 7.25–7.15 (m, 6H), 6.95–6.80 (m, 4H) 4.52 (d, 1H, $J=9.4$ Hz), 4.44 (d, 1H, $J=9.4$ Hz), 4.27 (dq, 1H, $J=2.9$, 6.6 Hz), 4.18 (ddd, 1H, $J=2.9$, 5.6, 8.2 Hz), 3.11 (dd, 1H, $J=8.2$, 17.0 Hz), 2.82 (dd, 1H, $J=5.6$, 17.0 Hz),), 1.22 (d, 3H, $J=6.6$ Hz). ^{13}C NMR: δ 137.5, 137.1, 128.7 (two carbons), 128.5 (two carbons), 128.5 (two carbons), 128.1 (two carbons), 127.8 (two carbons), 117.8, 85.4, 76.9, 73.5, 72.1, 17.3, 16.2. MS *m*/*z* (rel. int.): 293 (11), 187 (18), 180 (3), 179 (8), 178 (11), 165 (8), 152 (4), 107 (100), 106 (36), 105 (70), 82 (30), 79 (20), 77 (27), 55 (6), 51 (5). Anal. calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53, N, 4.77. Found: C, 77.72, H, 6.54, N, 4.68%.

4.4.2. Methyl [(2*R*,3*S*,5*R*,6*R*)-3,5,6-triphenyl-1,4-dioxan-2-yl]acetate, 5b. Oil; $[\alpha]_D^{24}=+60.8$ (*c* 0.76, $CHCl_3$). ^1H NMR: δ 7.45–7.25 (m, 4H), 7.30–7.10 (m, 7H), 7.10–7.00 (m, 4H), 5.28 (d, 1H, $J=3.3$ Hz), 4.78 (d, 1H, $J=9.5$ Hz), 4.68 (ddd, 1H, $J=3.3$, 4.7, 10.0 Hz), 4.64 (d, 1H, $J=9.5$ Hz), 3.51 (s, 3H), 3.11 (dd, 1H, $J=10.0$, 14.9 Hz), 2.27 (dd, 1H, $J=4.7$, 14.9 Hz). ^{13}C NMR: δ 171.9, 138.0, 137.9, 137.8, 128.9 (two carbons), 128.6, 128.5, 128.4 (two carbons), 128.3, (two carbons), 128.2 (two carbons), 128.1, 127.9 (two carbons), 125.8 (two carbons), 85.5, 79.2, 76.8, 74.1, 52.2, 32.2. MS *m*/*z* (rel. int.): 388 (1), 282 (4), 281 (1), 207 (5), 192 (3), 176 (100), 165 (5), 144 (3), 134 (8), 117 (53), 115 (14), 105 (7), 91 (8), 77 (5). Anal. calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.32, H, 6.30%.

4.4.3. Methyl [(2*R*,3*S*,4a*R*,8a*R*)-3-phenyloctahydro-1,4-benzodioxin-2-yl]acetate, 5c. Oil; $[\alpha]_D^{23}=+74.7$ (*c* 1.20, $CHCl_3$). ^1H NMR: δ 7.40–7.25 (m, 5H), 5.03 (d, 1H, $J=3.4$ Hz), 4.47 (ddd, 1H, $J=3.4$, 4.6, 10.4 Hz), 3.57

(s, 3H), 3.53 (ddd, 1H, $J=4.2$, 9.4, 10.4 Hz), 3.40 (ddd, 1H, $J=4.2$, 9.4, 11.2 Hz), 2.93 (dd, 1H, $J=10.4$, 14.9 Hz),), 2.08 (dd, 1H, $J=4.6$, 14.9 Hz), 2.02–1.9 (m, 1H), 1.80–1.74 (m, 2H), 1.52–1.25 (m, 5H). ^{13}C NMR: δ 172.2, 138.5, 128.8 (two carbons), 127.9, 125.9 (two carbons), 81.9, 79.7, 74.5, 72.4, 52.0, 32.2, 30.6, 30.5, 24.7 (two carbons). MS m/z (rel. int.): 290 (1), 216 (35), 193 (69), 192 (39), 161 (41), 160 (28), 133 (8), 117 (10), 115 (15), 107 (100), 105 (11), 103 (12), 91 (18), 82 (28), 67 (45), 54 (12). Anal. calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.30, H, 7.71%.

4.4.4. Methyl [(2*R*,3*S*,5*R*,6*R*)-5,6-dimethyl-3-phenyl-1,4-dioxan-2-yl]acetate, 5d. Oil; $[\alpha]_D^{27}=+25.3$ (c 0.26, $CHCl_3$). ^{1}H NMR: δ 7.40–7.20 (m, 5H), 4.95 (d, 1H, $J=3.4$ Hz), 4.42 (ddd, 1H, $J=3.4$, 4.4, 10.4 Hz), 3.64 (dq, 1H, $J=6.1$, 9.2 Hz), 3.57 (s, 3H), 3.50 (dq, 1H, $J=6.2$, 9.2 Hz), 2.88 (dd, 1H, $J=10.4$, 14.8 Hz), 2.05 (dd, 1H, $J=4.4$, 14.8 Hz), 1.25 (d, 3H, $J=6.2$ Hz), 1.11 (d, 3H, $J=6.1$ Hz). ^{13}C NMR: δ 172.3, 138.5, 128.8 (two carbons), 127.9, 125.8 (two carbons), 79.1, 78.8, 74.1, 69.5, 52.0, 32.0, 17.9, 17.8. MS m/z (rel. int.): 264 (1), 233 (4), 220 (5), 193 (62), 176 (13), 161 (62), 160 (28), 133 (15), 117 (39), 115 (28), 107 (100), 105 (21), 103 (13), 91 (31), 79 (20), 77 (15), 56 (45). Anal. calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.10; H, 7.61%.

4.4.5. [(2*S*,3*S*,5*R*,6*R*)-3-Methyl-5,6-diphenyl-1,4-dioxan-2-yl]acetonitrile, 6a. Oil; $[\alpha]_D^{21}=+96.0$ (c 1.67, $CHCl_3$). ^{1}H NMR: δ 7.20–7.15 (m, 6H), 6.90–6.80 (m, 4H) 4.45 (d, 1H, $J=9.1$ Hz), 4.42 (d, 1H, $J=9.1$ Hz), 3.87 (dq, 1H, $J=6.3$, 9.1 Hz), 3.69 (dt, 1H, $J=4.6$, 9.1 Hz), 2.70 (dd, 1H, $J=4.6$, 17.1 Hz), 2.57 (dd, 1H, $J=4.6$, 17.1 Hz), 1.28 (d, 3H, $J=6.3$ Hz). ^{13}C NMR: δ 137.5, 137.3, 128.6 (two carbons), 128.4 (two carbons), 128.3 (two carbons), 128.0 (two carbons), 127.9 (two carbons), 117.7, 84.7, 84.6, 76.0, 75.0, 21.0, 17.6. MS m/z (rel. int.): 293 (43), 187 (11), 180 (10), 179 (10), 178 (14), 165 (9), 152 (5), 107 (100), 106 (34), 105 (73), 82 (30), 79 (22), 77 (29), 55 (5), 51 (5). Anal. calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53, N, 4.77. Found: C, 77.83, H, 6.50, N, 4.71%.

4.4.6. Methyl [(2*S*,3*S*,5*R*,6*R*)-3,5,6-triphenyl-1,4-dioxan-2-yl]acetate, 6b. Oil; $[\alpha]_D^{21}=+31.1$ (c 0.79, $CHCl_3$). ^{1}H NMR: δ 7.50–7.45 (m, 2H), 7.35–7.25 (m, 2H), 7.20–7.08 (m, 7H), 7.03–6.98 (m, 4H), 4.65 (d, 1H, $J=9.2$ Hz), 4.64 (d, 1H, $J=9.0$ Hz), 4.53 (d, 1H, $J=9.0$ Hz), 4.28 (ddd, 1H, $J=4.1$, 7.8, 9.2 Hz), 3.50 (s, 3H), 2.48 (dd, 1H, $J=7.8$, 15.6 Hz), 2.35 (dd, 1H, $J=4.1$, 15.6 Hz). ^{13}C NMR: δ 171.4, 138.0, 137.9, 137.8, 129.1 129.0 (two carbons), 128.4, 128.3 (three carbons), 128.2 (two carbons), 128.1(two carbons), 128.0 (two carbons), 127.9 (two carbons), 84.7, 84.6, 82.7, 77.8, 52.1, 37.2. MS m/z (rel. int.): 388 (1), 282 (4), 281 (3), 207 (6), 192 (3), 176 (100), 165 (5), 144 (3), 134 (10), 117 (59), 115 (14), 105 (7), 91 (9), 77 (6). Anal. calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.23, H, 6.18%.

4.4.7. Methyl [(2*S*,3*S*,4a*R*,8a*R*)-3-phenyloctahydro-1,4-benzodioxin-2-yl]acetate, 6c. Oil; $[\alpha]_D^{23}=+22.1$ (c 0.30, $CHCl_3$). ^{1}H NMR: δ 7.40–7.25 (m, 5H), 4.36 (d, 1H, $J=8.9$ Hz), 4.07 (ddd, 1H, $J=3.8$, 8.7, 8.9 Hz), 3.49 (s, 3H), 3.45–3.32 (m, 2H), 2.39 (dd, 1H, $J=8.7$, 15.5 Hz), 2.21 (dd, 1H, $J=3.8$, 15.5 Hz), 2.0–1.82 (m, 1H), 1.80–1.70 (m, 2H), 1.52–1.25 (m, 5H). ^{13}C NMR: δ 171.5, 138.2, 129.0 (three carbons), 128.2 (two carbons), 83.3, 80.5, 80.3, 77.8, 52.0, 37.3, 30.6, 30.5, 24.6, 24.5. MS m/z (rel. int.): 290 (1), 216 (27), 193 (56), 192 (27), 161 (33), 160 (23), 133 (9), 117 (13), 115 (17), 107 (100), 105 (12), 103 (13), 91 (18), 82 (29), 67 (51), 54 (16). Anal. calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.30, H, 7.71%.

4.4.8. Methyl [(2*S*,3*S*,5*R*,6*R*)-5,6-dimethyl-3-phenyl-1,4-dioxan-2-yl]acetate, 6d. Oil; $[\alpha]_D^{30}=+26.3$ (c 0.34, $CHCl_3$). ^{1}H NMR: δ 7.35–7.20 (m, 5H), 4.29 (d, 1H, $J=9.1$ Hz), 3.99 (ddd, 1H, $J=3.8$, 8.7, 9.1 Hz), 3.57 (s, 3H), 3.51 (dq, 1H, $J=6.1$, 8.7 Hz), 3.46 (dq, 1H, $J=6.0$, 8.7 Hz), 2.37 (dd, 1H, $J=8.7$, 15.4 Hz), 2.20 (dd, 1H, $J=3.8$, 15.4 Hz), 1.19 (d, 3H, $J=6.0$ Hz), 1.17 (d, 3H, $J=6.1$ Hz). ^{13}C NMR: δ 171.6, 138.3, 129.0 (two carbons), 128.8, 128.2 (two carbons), 82.9, 77.8, 77.7, 77.6, 52.0, 37.3, 17.8, 17.7. MS m/z (rel. int.): 264 (1), 233 (12), 220 (5), 193 (63), 176 (12), 161 (54), 160 (28), 133 (18), 117 (41), 115 (28), 107 (100), 105 (22), 103 (13), 91 (26), 79 (19), 77 (15), 56 (46). Anal. calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.07; H, 7.69%.

4.4.9. (2*S*,3*R*,5*R*,6*R*)- and (2*R*,3*R*,5*R*,6*R*)-[3-Methyl-5,6-diphenyl-1,4-dioxan-2-yl]acetonitriles, 9a and 10a. Oil; (mixture of isomers **9a**:**10a** = 12:88); **10a** ^{1}H NMR: δ 7.30–7.15 (m, 6H), 7.15–7.00 (m, 4H) 4.69 (d, 1H, $J=9.4$ Hz), 4.51 (d, 1H, $J=9.4$ Hz), 4.45 (dt, 1H, $J=3.1$, 7.2 Hz), 4.28 (dq, 1H, $J=3.1$, 6.7 Hz), 2.65 (dd, 1H, $J=7.2$, 16.8 Hz), 2.52 (dd, 1H, $J=7.2$, 16.8 Hz) 1.57 (d, 3H, $J=6.7$ Hz). ^{13}C NMR: δ 137.6, 137.4, 128.7, 128.6, 128.5 (two carbons), 128.4 (two carbons), 128.0 (two carbons), 127.9 (two carbons), 116.9, 85.7, 76.1, 73.7, 70.2, 20.9, 11.9. MS m/z (rel. int.): 293 (43), 187 (11), 180 (10), 179 (10), 178 (14), 165 (9), 152 (5), 107 (100), 106 (34), 105 (73), 82 (30), 79 (22), 77 (29), 55 (5), 51 (5). Anal. calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53, N, 4.77. Found: C, 77.83, H, 6.50, N, 4.71%.

9a (distinct signals): ^{1}H NMR: δ 4.91 (d, 1H, $J=8.1$ Hz), 4.75 (d, 1H, $J=8.1$ Hz), 4.09 (dq, 1H, $J=2.3$, 6.6 Hz), 4.06 (dt, 1H, $J=2.3$, 6.8 Hz), 3.08 (dd, 1H, $J=6.8$, 16.7 Hz), 3.13 (dd, 1H, $J=6.8$, 16.7 Hz), 1.61 (d, 3H, $J=6.6$ Hz). ^{13}C NMR: δ 138.0, 137.7, 128.8, 128.2, 128.1, 76.9, 75.7, 71.6, 69.2, 20.5, 17.3.

4.4.10. Methyl [(2*R*,3*R*,5*R*,6*R*)-5,6-dimethyl-3-phenyl-1,4-dioxan-2-yl]acetate, 9d. Oil; $[\alpha]_D^{27}=+18.4$ (c 0.95, $CHCl_3$). ^{1}H NMR: δ 7.55–7.25 (m, 5H), 4.62 (d, 1H, $J=5.2$ Hz), 4.55 (dt, 1H, $J=5.2$, 8.1 Hz), 3.75 (dq, 1H, $J=5.4$, 6.4 Hz), 3.70 (s, 3H), 3.60 (dq, 1H, $J=5.4$, 6.4 Hz), 2.78 (dd, 1H, $J=8.1$, 15.1 Hz), 2.60 (dd, 1H, $J=5.2$, 15.1 Hz), 1.32 (d, 3H, $J=6.4$ Hz), 1.28 (d, 3H, $J=6.4$ Hz). ^{13}C NMR: δ 171.8, 139.0, 128.9 (two carbons), 128.6, 128.5, (two carbons), 74.9, 71.3, 71.0, 69.9, 52.2, 37.1, 17.7, 17.6. MS m/z (rel. int.): 264 (1), 233 (3), 220 (4), 193 (47), 176 (13), 161 (58), 160 (25), 133 (18), 117 (74), 115 (35), 107 (100), 105 (25), 103

(13), 91 (39), 79 (18), 77 (16), 56 (63). Anal. calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.22; H, 7.69%.

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