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Stereoselective Synthesis of Polysubstituted Tetrahydropyrans by Radical Cyclization of Epoxides using a Transition-Metal Radical Source

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Keywords: Tetrahydropyrans / Radical cyclization / Epoxides / Transition metals

Epoxyalkyl propargyl ethers **3a–f** and allyl epoxyalkyl ethers **6a–c** smoothly undergo radical cyclization reactions using a titanium(III) species (Cp_2TiCl) as the radical initiator to form polysubstituted tetrahydropyrans **4a–f** and **7a–c** in good yields and with high diastreoselectivity. The titanium(III) species was prepared in situ from commercially available titanocene dichloride and Zn dust in THF. On the other hand, the epoxyalkyl propargyl ethers **3g** and **3h** furnished the spirocyclic ethers **4g** and **4h**, respectively, on radical cyclization reaction as the sole products.

Introduction

Six-membered saturated oxygen heterocycles are structural features of a variety of biologically important natural products[1] such as polyether antibiotics, marine toxins, pheromones, and pharmaceutical agents. The tetrahydropyran ring is part of the backbone of various important carbohydrates, as well as their oligomers and polymers, which are the most abundant biological molecules[2] on earth and play several crucial roles in living organisms.

Considerable efforts have been made toward the synthesis of tetrahydropyran-type compounds,[3] for example by hetero Diels–Alder reactions, via oxiranyl anions, carbonyl ylides, by Claisen rearrangements, ring opening of epoxides, iodocyclizations, olefin metathesis, and many others.[4] Recently, there has been an increasing interest in using the Prins cyclization[4,5] to generate tetrahydropyran derivatives in a stereocontrolled manner, with potential applications to the synthesis of polyether antibiotics and other complex natural products. The ubiquitous presence of polysubstituted tetrahydropyrans, associated with the challenge offered by the total synthesis of some of these tetrahydropyran-containing natural products, requires the development of efficient methodologies to synthesize tetrahydropyran derivatives. Therefore, good and efficient methodologies for the stereocontrolled synthesis of polysubstituted tetrahydropyrans are still needed.

The explosive growth in free radical chemistry in recent years reflects its significance as powerful tool in modern synthetic chemistry.[6] Radicals are frequently employed as reactive intermediates in organic synthesis because of the mildness of their generation, their high functional group tolerance, and the useful possibilities for the formation of C–C bonds. A limitation of the classical free radical chemistry lies in the substrate-controlled course of the reaction. An interesting alternative is represented by reagent-controlled transformations.[7] Epoxides are vastly used as building blocks for organic synthesis due to their ready availability and facile substitution reactions with predictable stereochemistry.[8] Our earlier investigations[9] towards the stereoselective radical cyclization of epoxy ethers using Cp_2TiCl[10] as the radical initiator have opened the door to utilize this methodology for the synthesis of complex natural products. Herein, in continuation to our earlier work related to 5-*exo-dig* and 5-*exo-trig* radical cyclizations,[9] we wish to report the 6-*exo-dig* cyclization of epoxyalkyl propargyl ethers and the 6-*exo-trig* cyclization of allyl epoxyalkyl ethers using a titanium(III) species as the radical initiator to synthesize tetrahydropyran derivatives in a stereocontrolled manner.

Results and Discussion

Preparation of Epoxides and Propargylation and Allylation of Epoxy Alcohols

Epoxy alcohols **2** were prepared from the corresponding homoallyl alcohols **1** (prepared from the corresponding aldehyde and allyl bromide using Cp_2TiCl in THF)[11a] by treatment with *m*-CPBA in $CHCl_3$ (Scheme 1).

The epoxides **2a–e** were found to be a mixture of two isomers in a ratio of 1:1. This isomeric ratio was determined from the ^1H NMR signals for the epoxide methine proton, e.g., for **2b** the particular signals appeared as two multiplets centered at δ = 3.16 ppm for one isomer and at δ = 3.00 ppm for the other. In case of epoxides **2f** and **2h** the

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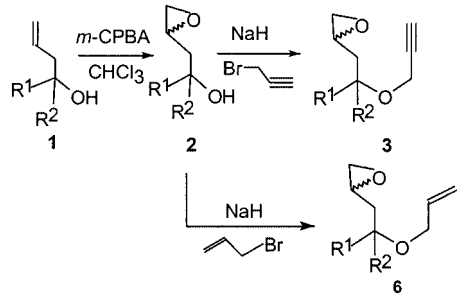
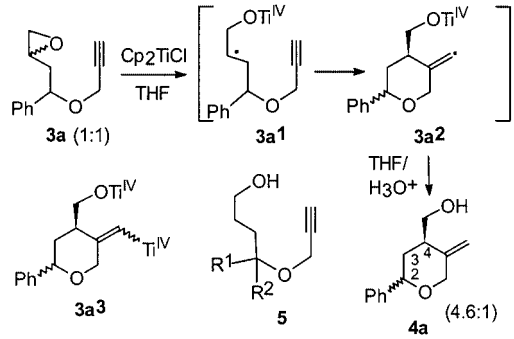


Scheme 1. Preparation of epoxyalkyl ethers.



Scheme 2. Radical cyclization of epoxides.

isomeric ratio was found to be 1.5:1. For epoxide **2g**, no distinguishable signals were found to determine the ratio of the isomers. It might be a single isomer (only one chiral carbon atom) or a mixture of two diastereomers as we have observed for **2h** (no shift reagent was used). The ratio of isomers in **2f** was determined from the ^{1}H NMR signals for the methyl protons, which appeared as two singlets at δ = 1.65 ppm for one isomer and at δ = 1.59 ppm for the other. Since the isomers in **2a**–**h** could not be separated by usual chromatographic methods, the mixture of isomers was used for the next step. Thus, compounds **2a**,**d**,**e**, on treatment with propargyl bromide, and compounds **2a**,**d**,**e**, on treatment with allyl bromide in the presence of NaH in THF/DMSO (10:1), furnished **3a**–**h** and **6a**–**c** as an inseparable mixture of two isomers in the same ratio as observed for **2a**–**h**. This isomeric ratio was determined from the ^{1}H NMR signals for the epoxide methine proton, e.g., for **3a**, the particular signals appeared as two multiplets centered at δ = 2.88 ppm for one isomer and at δ = 3.18 ppm for the other. Since the isomers could not be separated by usual chromatographic methods, the crude isomeric mixtures were used for the radical cyclization reactions.

Radical Cyclization of Epoxy Ethers using Cp_2TiCl

For the homolytic cleavage of epoxides, a titanium(III) reagent (Cp_2TiCl) was used at room temperature. A satisfactory reagent was prepared[10] by stirring a red THF solution of Cp_2TiCl_2 with activated Zn dust [Equation (1)]. After 15 min, the solution turned lime-green and the formation of Cp_2TiCl was completed.

$$2\ Cp_2TiCl_2 + Zn \rightarrow 2\ Cp_2TiCl + ZnCl_2 \quad (1)$$

In a preliminary experiment, 2.1 mol-equiv. of Cp_2TiCl in THF was added dropwise to a THF solution of epoxyalkyl propargyl ether **3a**. The initial green color of the titanium(III) species instantly discharged to red upon exposure to the epoxide. Quenching of the mixture with 10% H_2SO_4 (15 mL) in H_2O afforded the tetrahydropyran derivative **4a** as a mixture of two isomers in 78% yield (Scheme 2).

Thus, the radical cyclization reaction was applied to a series of substituted epoxy alkynes and the results are summarized in Table 1. The epoxyalkyl ethers **3a**–**f**, upon radical cyclization reaction, afforded a mixture of two isomeric products as indicated in Table 1, whereas **3g** and **3h** furnished the spiro ethers **4g** and **4h**, respectively, as the only isolated product.

The ratio of the two isomers in the cyclized products was determined from the two distinguishable multiplets in the ^{1}H NMR spectra for 4-H, e.g., for **4a**, two multiplets centered at δ = 2.61 ppm for the major isomer and at δ = 2.73 ppm for the minor isomer. For **4f** the ratio of isomers was determined from the two distinguishable singlets of the methyl protons in the ^{1}H NMR spectra which appeared at δ = 1.40 ppm for the major isomer and at δ = 1.54 ppm for the minor isomer. The major isomer in **4a**–**e** was partly separated by preparative TLC (15% ethyl acetate in light petroleum ether), but the minor isomer could not be separated in pure form, and was always contaminated with the major isomer. In analogy to the deuteriolysis experiment reported by RajanBabu and Nugent,[10] presumably, the highly reactive vinyl radical **3a^2**, which is formed initially, abstracts a hydrogen atom from the THF solvent before it has a chance to encounter any reducing titanium species **3a^3**. In the case of **4f**, the isomers could not be separated by usual chromatographic methods, and for **4a**,**c**,**g** the corresponding reduced products **5** were obtained in 16, 15, and 35% yield, respectively.

The *cis* orientation of the C-2 and C-4 substituents in the major isomer of cyclized products **4a^1**–**e^1** was established by NOE analysis (Figure 1) of the major isomer, e.g., **4b^1** in which an enhancement (1.5 %) between the signals of 2-H to 4-H was observed.

This *cis* relationship between two substituents at C-2 and C-4 may also be rationalized by invoking well-known conformational effects in the intermediates by using models for selectivities in radical reactions proposed by Beckwith,[12a] Houk[12b] and RajanBabu.[12c] Four transition complexes are possible of the intermediate radical before cyclization. Here the transition complexes **B** and **D** are of higher energy than **A** or **C**, where a bulky group (phenyl) is in axial position (Figure 2). Between complexes **A** and **C**, complex **A** should have a lower energy compared to **C**, because both the phenyl and the CH_2OTi^{IV} moieties in **A** are in equato-

Table 1. Radical cyclization of epoxyalkyl propargyl ethers using Cp_2TiCl.

Entry	Epoxy alcohol (Yield %, ratio of isomers)	Epoxy ether (Yield %, ratio of isomers)	Cyclized product (Yield %, ratio of isomers)	Isolated pure isomer (Yield %) [a]
1	**2a** (90, 1:1)	**3a** (82, 1:1)	**4a** (78, 4.6:1)	**4a¹** (55)
2	**2b** (86, 1:1)	**3b** (80, 1:1)	**4b** (73, 4.7:1)	**4b¹** (51)
3	**2c** (84, 1:1)	**3c** (81, 1:1)	**4c** (82, 5:1)	**4c¹** (57)
4	**2d** (85, 1:1)	**3d** (84, 1:1)	**4d** (72, 4:1)	**4d¹** (50)
5	**2e** (88, 1:1)	**3e** (78, 1:1)	**4e** (74, 5:1)	**4e¹** (53)
6	**2f** (86, 1.5:1)	**3f** (88, 1.5:1)	**4f** (85, 2:1)	Two isomers could not be separated
7	**2g** (91)	**3g** (85)	**4g** (56)	–
8	**2h** (89, 1.5:1)	**3h** (80, 1.5:1)	**4h** (70)	–

[a] Yields refer to pure isolated products.

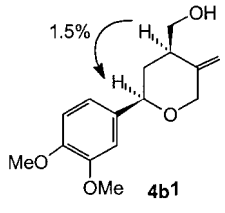


Figure 1. NOE analysis of **4b¹**.

rial position whereas in **C**, one is equatorial and the other is axial. Thus, the transition complex **A** lies on the pathway to the more stable product. Therefore, preferential formation of *cis* products **4a**–**e** derived from **A** should occur. In the case of **4f**, where the benzylic hydrogen atom is replaced by a methyl group, the selectivity decreases. Since the minor isomer in **4a**–**f** could not be separated by usual chromatographic methods in pure form, the stereochemistry of the minor isomer remained uncertain.

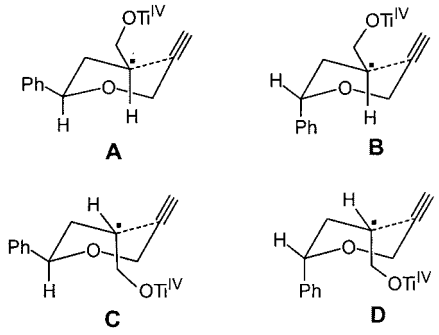


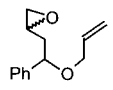
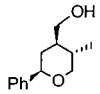
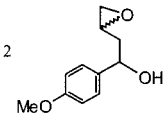
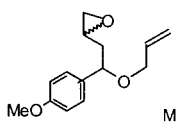
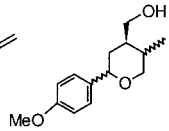
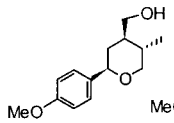
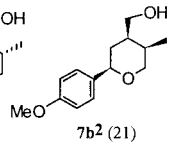
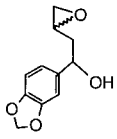
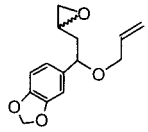
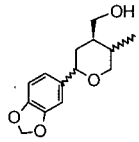
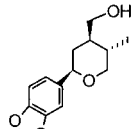
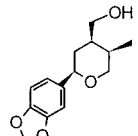
Figure 2. Transition complexes of the intermediate radical.

On the other hand, similar radical cyclization reactions were performed on allyl epoxyalkyl ethers **6a**–**c** and the results are summarized in Table 2. Although theoretically four isomers are expected in the radical cyclization reaction, three isomeric products were actually obtained in each case. The ratio of the three isomers in the cyclized products was determined from the three distinguishable doublets of methyl protons in the ^1H NMR spectra, e.g., for **7a**, two doublets at δ = 0.90 and 1.07 ppm for the two major isomers and another doublet at δ = 0.93 ppm for the third minor isomer. The major two isomers in **7a**–**c** were separated by preparative TLC (20% ethyl acetate in light petroleum ether), but the third minor isomer could not be isolated in pure form as it was produced in very minute quantity. In the case of **6a** and **6c**, the corresponding reduced products **8** were also obtained in 8% and 10% yield, respectively.

Comparing with the mode of epoxy/alkyne cyclizations (Table 1), it may be concluded that the substituents at C-2 (Ar) and C-4 (CH_2OH) in the two major isolated isomers in the cyclized products **7a**–**c** (Table 2) will be in *cis* (equatorial-equatorial) configuration with respect to each other. The third substituent (Me) at C-5 might be *trans*, e.g. in **7a¹** (equatorial-equatorial, lower energy) or *cis*, e.g. in **7a²** (equatorial-axial, higher energy) with respect to that at C-4 as shown in Figure 3.

This can also be rationalized by analogy with the work reported in the literature[10] for the higher chemical shift values of the carbon signals, in general, for *trans*-1,2-dialkylcycloalkanes. In our case the isolated major isomer, e.g., **7a¹** showed signals at δ = 31.9 (C-5), 44.5 (C-4) ppm and the corresponding signals in the isolated minor isomer, e.g., **7a²** appeared at δ = 29.2 and 41.1 ppm, respectively. Hence, it is reasonable to assume that the isolated major isomer should be **7a¹** which possesses all the substituents in the equatorial orientation and in **7a²** the substituents at C-2

Table 2. Radical cyclization of allyl epoxyalkyl ethers using Cp_2TiCl.

Entry	Epoxy alcohol (Yield %, ratio of isomers)	Epoxy-allylic ether (Yield %, ratio of isomers)	Cyclized product (Yield %, ratio of isomers)	Isolated pure isomers (Yield %)[a]	
1	 **2a** (90, 1:1)	 **6a** (89, 1:1)	 **7a** (83, 2.6:1:0.2)	 **7a1** (49)	 **7a2** (19)
2	 **2d** (85, 1:1)	 **6b** (86, 1:1)	 **7b** (87, 2.4:1:0.22)	 **7b1** (52)	 **7b2** (21)
3	 **2e** (88, 1:1)	 **6c** (88, 1:1)	 **7c** (81, 2.5:1:0.2)	 **7c1** (49)	 **7c2** (20)

[a] Yields refer to pure isolated procucts.

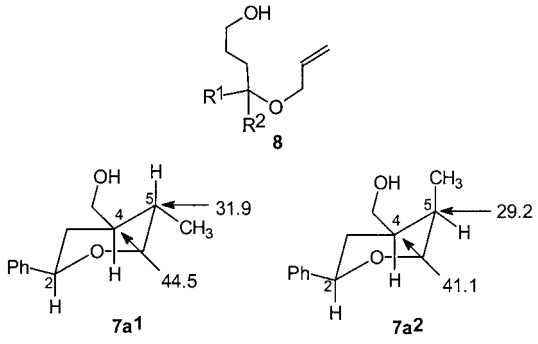


Figure 3. Comparison of ^{13}C NMR data for **7a1** and **7a2**.

and C-4 are equatorial and at C-5 axial. As the minor isolated isomer **7a2** was a crystalline solid, the stereochemistry was finally proved by an X-ray crystallographic study of **7a2** (Figure 4).

In the radical cyclization reaction of substituted epoxy alkynes and epoxy olefins using stoichiometric titanocene chloride as reducing agent, the real nature of the titanium(III) species[13] in THF solution is the symmetric dimeric complex **I** having no free coordination site (known from the solid phase) and there is even the possibility that the dimeric structure **II** in THF solution from the very beginning is of the half-open type (Figure 5), thereby leaving room for an easily accessible coordination site. Both the dimeric

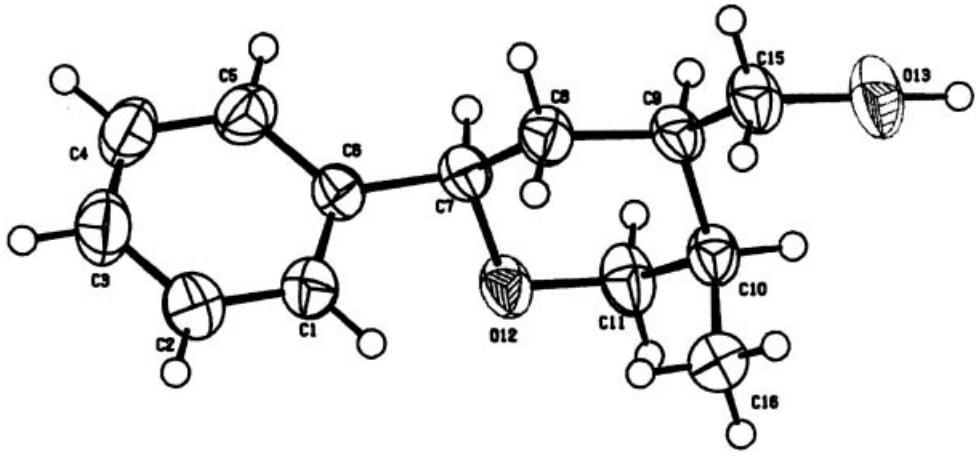


Figure 4. X-ray picture of **7a2**.

complex **I** and **II** should exhibit the same reactivity as Cp_2TiCl.

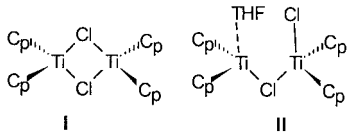


Figure 5. Dimeric complexes of Cp_2TiCl.

In this titenium(III)-mediated radical cyclization, reduced products **5** and **8** probably derived from adventitious water in the reaction medium, thereby forming a water-solvated Cp_2TiCl complex and a hydrogen atom transfer process occurs from water to a carbon-centered free radical forming the reduced products.[14] In the absence of water only allylic alcohols can be expected.[15] Although in this paper a stoichiometric amount of titanium(III) reagent is used, an alternative approach using a catalytic[16] amount of the reagent with different additives has also been reported in the literature.

Conclusions

In summary, we have demonstrated the stereoselective synthesis of important polysubstituted tetrahydropyran derivatives by radical cyclization of epoxides using a transition metal radical source. Synthetically versatile substituted spiro ethers have also been synthesized according to the same strategy.

Experimental Section

General: The compounds described are all racemates. The homoallyl alcohols **1** were prepared[11a] from the corresponding aldehydes or ketones and allyl bromide using Cp_2TiCl in THF and their spectroscopic data were compared to those of authentic samples.[11,17] ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with 300 and 75 MHz NMR spectrometers (Bruker), respectively, using tetramethylsilane as the internal standard and FT-IR spectra were recorded with a Shimadzu FT IR-8300. Column chromatography was performed on silica gel (60–120 mesh) and preparative TLC was performed using Merck pre-coated silica 60 F 254 plates (0.2 mm). Diethyl ether and tetrahydrofuran were freshly distilled from sodium. Dimethyl sulfoxide was freshly distilled from calcium hydride. Petroleum ether of boiling range 60–80 °C was used for chromatography. Elemental analyses were performed with an analytical instrument (Dr. Hans Hosli, 0A1, 468) in our analytical laboratories.

2-Oxiranyl-1-phenylethanol (2a): A mixture of homoallyl alcohol **1a** (R^1, R^2 = Ph, H) (1 g, 6.75 mmol) and *m*-CPBA (2.8 g, 55% dispersion, 8 mmol) in $CHCl_3$ (100 mL) was stirred at room temperature for 60 h. After that, the reaction mixture was further stirred with a saturated Na_2SO_3 solution (30 mL) for 0.5 h and then the reaction mixture was transfered to a separating funnel and the chloroform layer was successively washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (15 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue obtained was purified by column chromatography on silica gel (40% ethyl acetate in light petroleum ether) to furnish epoxy alcohol **2a**[18] (0.99 g, 90%) as a viscous liquid as an inseparable mixture of two isomers in a ratio of 1:1. IR (neat): $\tilde{\nu}$ = 3388 (br), 2920, 1602, 1494, 1454, 1056 cm^{-1}. ^1H NMR: δ = 1.81–1.94 (m, 1 H), 1.99–2.12 (m, 1 H), 2.49 (dd, J = 2.7, 4.9 Hz, 0.5 H), 2.59 (dd, J = 2.8, 4.8 Hz, 0.5 H), 2.74 (t app, J = 4.6 Hz, 0.5 H), 2.81 (t app, J = 4.5 Hz, 0.5 H), 2.99–3.01 (m, 0.5 H), 3.15–3.18 (m, 0.5 H), 4.90–4.95 (m, 1 H), 7.26–7.39 (m, 5 H). ^{13}C NMR: δ = 41.9, 42.1, 47.2, 47.6, 50.4, 50.6, 72.0, 72.8, 126.0, 126.2, 127.9, 128.1, 128.8, 128.9, 144.3, 144.6 ppm. $C_{10}H_{12}O_2$ (164.20): calcd. C 73.15, H 7.37; found C 73.10, H 7.33.

1-(3,4-Dimethoxyphenyl)-2-oxiranylethanol (2b): Compound **2b** was prepared according to the same procedure as described for **2a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3363 (br), 2922, 2839, 1606, 1593, 1525, 1421, 1263 cm^{-1}. ^1H NMR: δ = 1.72–1.92 (m, 1 H), 1.98–2.17 (m, 1 H), 2.50 (dd, J = 2.5, 4.8 Hz, 0.5 H), 2.60 (dd, J = 2.6, 4.8 Hz, 0.5 H), 2.74 (t app, J = 4.2 Hz, 0.5 H), 2.82 (t app, J = 4.5 Hz, 0.5 H), 2.96–2.99 (m, 0.5 H), 3.15–3.18 (m, 0.5 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 4.84–4.90 (m, 1 H), 6.81–6.98 (m, 3 H) ppm. ^{13}C NMR: δ = 41.9, 42.1, 47.1, 47.5, 50.3, 50.6, 56.2, 56.3, 71.7, 72.7, 109.2, 109.3, 111.4, 111.5, 118.1, 118.4, 137.0, 137.3, 148.7, 148.8, 149.3, 149.4 ppm. $C_{12}H_{16}O_4$ (224.25): calcd. C 64.27, H 7.19; found C 64.12, H 7.11.

1-(4-Benzyloxy-3-methoxyphenyl)-2-oxiranylethanol (2c): Compound **2c** was prepared according to the same procedure as described for **2a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3404 (br), 3068, 1658, 1583, 1259 cm^{-1}. ^1H NMR: δ = 1.76–2.11 (m, 2 H), 2.47 (dd, J = 2.7, 4.8 Hz, 0.5 H), 2.56 (dd, J = 2.7, 4.7 Hz, 0.5 H), 2.72 (t app, J = 4.5 Hz, 0.5 H), 2.80 (t app, J = 4.4 Hz, 0.5 H), 2.95–2.98 (m, 0.5 H), 3.13–3.16 (m, 0.5 H), 3.86 (s, 3 H), 4.81–4.86 (m, 1 H), 5.11(s, 2 H), 6.77–6.94 (m, 3 H), 7.26–7.42 (m, 5 H) ppm. ^{13}C NMR: δ = 41.4, 41.6, 46.6, 46.8, 49.9, 50.1, 55.8, 56.9, 71.3, 71.7, 102.8, 103.9, 109.2, 109.3, 113.7, 113.8, 117.6, 117.9, 127.0, 127.1, 127.6, 128.3, 128.4, 128.5, 128.7, 128.8, 137.0, 137.2, 147.4, 147.5, 149.6, 149.7 ppm. $C_{18}H_{20}O_4$ (300.34): calcd. C 71.98, H 6.71; found C 71.95, H 6.70.

1-(4-Methoxyphenyl)-2-oxiranylethanol (2d): Compound **2d** was prepared according to the same procedure as described for **2a**. IR (neat): $\tilde{\nu}$ = 3400 (br), 2916, 1612, 1514, 1247 cm^{-1}. ^1H NMR: δ = 1.70–2.12 (m, 2 H), 2.45 (dd, J = 2.7, 4.8 Hz, 0.5 H), 2.55 (dd, J = 2.7, 4.8 Hz, 0.5 H), 2.70 (t app, J = 4.2 Hz, 0.5 H), 2.78 (t app, J = 4.3 Hz, 0.5 H), 2.91–2.95 (m, 0.5 H), 3.10–3.13 (m, 0.5 H), 3.78 (s, 3 H), 4.82–4.86 (m, 1 H), 6.85, 6.87 (2 d, J = 8.5 Hz each, total 2 H), 7.24–7.28 (m, 2 H) ppm. ^{13}C NMR: δ = 41.7, 42.1, 47.2, 47.5, 50.4, 50.6, 55.6, 55.6, 71.7, 72.6, 114.1, 114.2, 127.2, 127.4, 136.3, 136.6, 159.4, 159.5 ppm. $C_{11}H_{14}O_3$ (194.22): calcd. C 68.02, H 7.27; found C 67.98, H 7.21.

1-(Benzo[1,3]dioxol-5-yl)-2-oxiranylethanol (2e): Compound **2e** was prepared according to the same procedure as described for **2a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3367 (br), 2902, 1610, 1504, 1487, 1444, 1247 cm^{-1}. ^1H NMR: δ = 1.70–1.90 (m, 1 H), 1.95–2.13 (m, 1 H), 2.49 (dd, J = 2.6, 4.8 Hz, 0.5 H), 2.59 (dd, J = 2.6, 4.8 Hz, 0.5 H), 2.74 (t app, J = 4.2 Hz, 0.5 H), 2.82 (t app, J = 4.1 Hz, 0.5 H), 2.95–2.99 (m, 0.5 H), 3.12–3.17 (m, 0.5 H), 4.81–4.87 (m, 1 H), 5.94 (s, 2 H), 6.75–6.88 (m, 3 H) ppm. ^{13}C NMR: δ = 41.2, 41.6, 46.6, 46.9, 49.8, 50.1, 71.4, 72.4, 100.9, 100.9, 106.0, 106.1, 108.0, 108.0, 118.8, 119.1, 137.7, 138.0, 147.7 ppm. $C_{11}H_{12}O_4$ (208.21): calcd. C 63.45, H 5.81; found C 63.32, H 5.78.

1-Oxiranyl-2-phenylpropan-2-ol (2f): Compound **2f** was prepared according to the same procedure as described for **2a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3433 (br), 2976, 1602, 1494, 1446, 1134 cm^{-1}. ^1H NMR: δ = 1.59 (s, 9/5 H), 1.65 (s, 6/5 H), 1.76 (dd, J = 8.0, 14.5 Hz, 6/5 H), 2.01–2.03 (m, 4/5 H), 2.25 (dd, J = 3.6, 14.4 Hz,

2/5 H), 2.39 (ddd, J = 2.7, 4.8, 15.5 Hz, 3/5 H), 2.62 (t app, J = 4.6 Hz, 3/5 H), 2.69 (t app, J = 4.6 Hz, 2/5 H), 2.83–2.88 (m, 3/5 H), 2.91–2.98 (m, 2/5 H), 7.21–7.49 (m, 5 H) ppm. ^{13}C NMR: δ = 29.5, 30.6, 46.0, 46.2, 46.4, 46.8, 49.2, 49.4, 73.9, 74.5, 124.5, 124.6, 126.6, 126.8, 128.1, 128.2, 147.3, 147.4 ppm. $C_{11}H_{14}O_2$ (178.22): calcd. C 74.13, H 7.92; found C 74.01, H 7.88.

1-(Oxiranylmethyl)cyclohexanol (2g): Compound **2g** was prepared according to the same procedure as described for **2a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3396 (br), 2929, 2856, 1651, 1446, 1257 cm^{-1}. ^{1}H NMR: δ = 1.19–1.61 (m, 10 H), 1.75 (dd, J = 4.4, 14.4 Hz, 2 H), 2.08 (br. s, OH), 2.43 (dd, J = 2.7, 4.9 Hz, 1 H), 2.74 (t app, J = 4.6 Hz, 1 H), 3.08–3.14 (m, 1 H) ppm. ^{13}C NMR: δ = 21.9, 22.0, 25.5, 37.5, 37.8, 44.4, 46.6, 48.8, 71.3 ppm. $C_9H_{16}O_2$ (156.22): calcd. C 69.19, H 10.32; found C 69.04, H 10.28.

1-(Oxiranylmethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (2h): Compound **2h** was prepared according to the same procedure as described for **2a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3417 (br), 2937, 1487, 1454, 1257, 1101 cm^{-1}. ^{1}H NMR: δ = 1.76–2.25 (m, 6 H), 2.42 (dd, J = 2.7, 4.9 Hz, 2/5 H), 2.48 (dd, J = 2.5, 5.2 Hz, 3/5 H), 2.70–2.87 (m, 3 H), 2.97–3.02 (m, 3/5 H), 3.12–3.16 (m, 2/5 H), 7.07 (d, J = 7.3 Hz, 1 H), 7.14–7.26 (m, 2 H), 7.51–7.57 (m, 1 H) ppm. ^{13}C NMR: δ = 19.6, 19.8, 29.4, 29.6, 36.6, 36.8, 44.7, 44.9, 46.4, 46.9, 49.0, 49.2, 72.1, 72.2, 125.8, 126.0, 126.1, 126.3, 127.1, 127.2, 128.8, 128.9, 136.3, 136.6, 141.3, 141.9 ppm. $C_{13}H_{16}O_2$ (204.26): calcd. C 76.44, H 7.90; found C 76.29, H 7.85.

2-[2-Phenyl-2-(prop-2-ynyloxy)ethyl]oxirane (3a): To a stirred suspension of NaH (0.36 g, 60% dispersion, 9 mmol) in dry THF/DMSO (10:1) (5 mL) was added dropwise a solution of epoxy alcohol **2a** (1 g, 6 mmol) in dry THF (10 mL) at 0 °C under nitrogen. After the evolution of hydrogen had ceased, a solution of propargyl bromide (0.94 g, 7.8 mmol) in dry THF (10 mL) was added dropwise at 0 °C over 30 min. The reaction mixture was then stirred at room temperature for 8 h and carefully quenched with ice/water. After removal of most of the THF under reduced pressure, the resulting residue was extracted with diethyl ether (3 × 30 mL). The combined ether extracts were washed with saturated brine (25 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue obtained was purified by column chromatography on silica gel (10% ethyl acetate in light petroleum ether) to furnish the epoxy ether **3a** (1.1 g, 82%) as a viscous liquid as an inseparable mixture of two isomers in a ratio of 1:1. IR (neat): $\tilde{\nu}$ = 3286, 3030, 2920, 2858, 1494, 1454, 1350, 1089 cm^{-1}. ^{1}H NMR: δ = 1.64–1.73 (m, 0.5 H), 1.86–1.94 (m, 0.5 H), 2.08–2.20 (m, 1 H), 2.44 (dd, J = 2.6, 5.4 Hz, 0.5 H), 2.46–2.49 (m, 10.5 H), 2.69 (t app, J = 4.5 Hz, 0.5 H), 2.79 (t app, J = 4.5 Hz, 0.5 H), 2.85–2.90 (m, 0.5H), 3.16–3.20 (m, 0.5 H), 3.88 (t app, J = 15.5 Hz, each peak split into doublet, J = 2.2 Hz, 1 H), 4.13 (ddd, J = 2.3, 6.6, 15.7 Hz, 1 H), 4.67–4.77 (m, 1 H), 7.27–7.43 (m, 5 H) ppm. ^{13}C NMR: δ = 40.9, 41.8, 47.3, 47.8, 49.8, 49.9, 55.8, 56.1, 74.7, 74.8, 78.5, 78.6, 80.0, 80.1, 127.1, 127.3, 128.5, 128.6, 129.0, 129.1, 140.5, 141.0 ppm. $C_{13}H_{14}O_2$ (202.24): calcd. C 77.21, H 6.97; found C 77.09, H 6.92.

2-[2-(3,4-Dimethoxyphenyl)-2-(prop-2-ynyloxy)ethyl]oxirane (3b): Compound **3b** was prepared according to the same procedure as described for **3a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3263, 2999, 2937, 2837, 1606, 1593, 1515, 1463, 1263, 1026 cm^{-1}. ^{1}H NMR: δ = 1.59–1.70 (m, 0.5 H), 1.87–1.95 (m, 0.5 H), 2.06–2.17 (m, 1 H), 2.41 (dd, J = 2.4, 6.1 Hz, 0.5H), 2.48–2.50 (m, 10.5H), 2.70 (t app, J = 4.3 Hz, 0.5 H), 2.80 (t app, J = 4.4 Hz, 0.5 H), 2.83–2.89 (m, 0.5 H), 3.13–3.19 (m, 0.5 H), 3.82–3.93 (m, 1 H), 3.87 (s, 3 H), 3.88 (s, 3 H), 4.11 (ddd, J = 2.3, 6.1, 15.6 Hz, 1 H), 4.59–4.69 (m, 1 H), 6.81–6.91 (m, 3 H) ppm. ^{13}C NMR: δ = 40.8, 41.8, 47.2, 47.8, 49.8, 50.0, 55.6, 55.9, 56.2, 56.2, 56.3, 56.3, 74.6, 74.7, 78.3, 78.5, 80.1, 80.2, 109.6, 109.8, 111.3, 111.4, 119.6, 120.1, 132.9, 133.4, 149.2, 149.3, 149.6, 149.7 ppm. $C_{15}H_{18}O_4$ (262.29): calcd. C 68.69, H 6.91; found C 68.56, H 6.88.

2-[2-[4-(Benzyloxy)-3-methoxyphenyl]-2-(prop-2-ynyloxy)ethyl]oxirane (3c): Compound **3c** was prepared according to the same procedure as described for **3a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3284, 2999, 2920, 2871, 1604, 1593, 1514, 1454, 1261, 1139 cm^{-1}. ^{1}H NMR: δ = 1.57–1.65 (m, 0.5 H), 1.80–1.89 (m, 0.5 H), 2.01–2.11 (m, 1 H), 2.36 (dd, J = 2.3, 5.3 Hz, 0.5H) 2.42–2.44 (m, 10.5H), 2.64 (t app, J = 4.3 Hz, 0.5 H), 2.75 (t app, J = 4.2 Hz, 0.5 H), 2.78–2.84 (m, 0.5 H), 3.08–3.14 (m, 0.5 H), 3.75–3.91 (m, 1 H), 3.84 (s, 3 H), 4.05 (ddd, J = 2.3, 6.2, 15.6 Hz, 1 H), 4.51–4.64 (m, 1 H), 5.09 (s, 2 H), 6.72–6.86 (m, 3 H) 7.21–7.40 (m, 5 H) ppm. ^{13}C NMR: δ = 40.8, 41.8, 47.3, 47.9, 49.8, 50.0, 55.7, 56.0, 56.4, 56.4, 71.4, 71.4, 74.6, 74.7, 78.4, 78.5, 80.1, 80.2, 110.2, 110.3, 114.1, 114.2, 119.5, 120.0, 127.6, 127.7, 128.2, 128.3, 128.9, 128.9, 133.5, 134.0, 137.4, 137.5, 148.4, 148.5, 150.3, 150.4 ppm. $C_{21}H_{22}O_4$ (338.39): calcd. C 74.54, H 6.54; found C 74.41, H 6.50.

2-[2-(4-Methoxyphenyl)-2-(prop-2-ynyloxy)ethyl]oxirane (3d): Compound **3d** was prepared according to the same procedure as described for **3a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3286, 2999, 2918, 2837, 1612, 1512, 1247, 1174, 1076 cm^{-1}. ^{1}H NMR: δ = 1.61–1.70 (m, 0.5 H), 1.83–1.92 (m, 0.5 H), 2.06–2.16 (m, 1 H), 2.41 (dd, J = 2.3, 5.5 Hz, 0.5H), 2.45–2.48 (m, 10.5H), 2.68 (t app, J = 4.3 Hz, 0.5 H), 2.78 (t app, J = 4.3 Hz, 0.5 H), 2.83–2.86 (m, 0.5 H), 3.12–3.16 (m, 0.5 H), 3.71–3.89 (m, 1 H), 3.79 (s, 3 H), 4.08 (ddd, J = 2.3, 5.4, 15.6 Hz, 1 H), 4.60–4.70 (m, 1 H), 6.88, 6.89 (2 d, J = 8.7 Hz each, total 2 H), 7.24, 7.26 (2d, J = 8.7 Hz each, total 2 H) ppm. ^{13}C NMR: δ = 40.3, 41.2, 46.8, 47.3, 49.3, 49.5, 55.0, 55.1, 55.3, 55.3, 74.1, 74.2, 77.5, 77.6, 79.6, 79.7, 113.9, 114.0, 127.8, 128.1, 131.9, 132.4, 159.3, 159.4 ppm. $C_{14}H_{16}O_3$ (232.27): calcd. C 72.40, H 6.93; found C 72.28, H 6.89.

2-[2-(Benzo[1,3]dioxol-5-yl)-2-(prop-2-ynyloxy)ethyl]oxirane (3e): Compound **3e** was prepared according to the same procedure as described for **3a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3288, 2995, 2898, 1487, 1504, 1442, 1244, 1039 cm^{-1}. ^{1}H NMR: δ = 1.59–1.67 (m, 0.5 H), 1.81–1.89 (m, 0.5 H), 2.03–2.12 (m, 1 H), 2.41 (dd, J = 2.7, 5.5 Hz, 0.5H), 2.45–2.49 (m, 10.5H), 2.69 (t app, J = 4.3 Hz, 0.5H), 2.78 (t app, J = 4.3 Hz, 0.5H), 2.82–2.88 (m, 0.5 H), 3.10–3.15 (m, 0.5H), 3.80–3.90 (m, 1 H), 4.09 (ddd, J = 2.2, 5.4, 15.7 Hz, 1 H), 4.57–4.66 (m, 1 H), 5.95 (s, 2 H), 6.74–6.84 (m, 3 H) ppm. ^{13}C NMR: δ = 40.3, 41.2, 46.8, 47.3, 49.2, 49.4, 55.1, 55.3, 74.1, 74.2, 77.7, 77.8, 79.5, 79.6, 100.9, 101.0, 106.6, 106.7, 108.0, 108.1, 120.3, 120.7, 133.8, 134.4, 147.3, 147.4, 147.9, 148.0 ppm. $C_{14}H_{14}O_4$ (246.25): calcd. C 68.29, H 5.72; found C 68.15, H 5.66.

2-[2-Phenyl-2-(prop-2-ynyloxy)propyl]oxirane (3f): Compound **3f** was prepared according to the same procedure as described for **3a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3288, 3055, 2983, 2920, 1685, 1494, 1446, 1380, 1068 cm^{-1}. ^{1}H NMR: δ = 1.71–1.85 (m, 1 H), 1.71 (s, 6/5 H), 1.73 (s, 9/5 H), 2.01–2.12 (m, 1 H), 2.29–2.37 (m, 7/5 H), 2.39 (dd, J = 2.4, 4.7 Hz, 3/5 H), 2.60–2.70 (m, 1 H), 2.75–2.79 (m, 2/5 H), 3.12–3.17 (m, 3/5 H), 3.81–3.99 (m, 2 H), 7.25–7.45 (m, 5 H) ppm. ^{13}C NMR: δ = 23.6, 23.7, 46.7, 46.8, 47.0, 47.0, 49.1, 49.2, 51.6, 51.8, 73.8, 73.8, 80.1, 81.3, 81.3, 80.3, 126.2, 126.6, 127.9, 128.0, 128.8, 128.9, 143.6, 144.4 ppm. $C_{14}H_{16}O_2$ (216.27): calcd. C 77.75, H 7.45; found C 77.66, H 7.40.

2-{[1-(Prop-2-ynyloxy)cyclohexyl]methyl}oxirane (3g): Compound **3g** was prepared according to the same procedure as described for **3a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3288, 2933, 2858, 1450, 1062 cm^{-1}. ^{1}H NMR: δ = 1.20–1.90 (m, 12 H), 2.37 (dd, J = 2.2, 4.6 Hz, 1 H), 2.44 (dd, J = 2.7, 5.0 Hz, 1 H), 2.76 (t app, J =

4.7 Hz, 1 H), 3.05–3.11 (m, 1 H), 4.03, 4.10 (ABq, J = 15.2 Hz, each peak split into doublet, J = 2.3 Hz, 2 H) ppm. ^{13}C NMR: δ = 21.7, 21.8, 25.5, 34.6, 34.7, 39.9, 46.8, 48.4, 49.3, 73.1, 76.6, 81.1 ppm. $C_{12}H_{18}O_2$ (194.26): calcd. C 74.20, H 9.33; found C 74.10, H 9.31.

2-{[1-(Prop-2-ynyloxy)-1,2,3,4-tetrahydronaphthalen-1-yl]methyl}-oxirane (3h): Compound **3h** was prepared according to the same procedure as described for **3a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3286, 2941, 2868, 1487, 1450, 1058 cm^{-1}. ^{1}H NMR: δ = 1.74–2.15 (m, 6 H), 2.28 (t app, J = 2.2 Hz, 1 H), 2.36 (dd, J = 2.6, 4.9 Hz, 1 H), 2.60–2.77 (m, 3 H), 2.88–2.94 (m, 1 H), 3.75, 3.84 (ABq, J = 15.2 Hz, each peak split into doublet, J = 2.6 Hz, 2 H), 7.02 (d, J = 6.8 Hz, 1 H), 7.09–7.18 (m, 2 H), 7.41 (d, J = 7.9 Hz, 1 H) ppm. ^{13}C NMR: δ = 20.4, 29.5, 31.7, 45.6, 46.9, 48.7, 51.2, 73.0, 78.7, 81.1, 126.2, 126.7, 127.5, 128.9, 137.3, 138.7 ppm. $C_{16}H_{18}O_2$ (242.30): calcd. C 79.31, H 7.48; found C 79.20, H 7.44.

2-(2-Allyloxy-2-phenylethyl)oxirane (6a): To a stirred suspension of NaH (77 mg, 60% dispersion, 1.92 mmol) in dry THF/DMSO (10:1) (5 mL) was added dropwise a solution of epoxy alcohol **2a** (210 mg, 1.28 mmol) in dry THF (5 mL) at 0 °C under nitrogen. After the evolution of hydrogen had ceased, a solution of allyl bromide (232 mg, 1.92 mmol) in dry THF (5 mL) was added dropwise at 0 °C over 30 min. The reaction mixture was then stirred at room temperature for 8 h and carefully quenched with ice/water. After removal of most of the THF under reduced pressure, the resulting residue was extracted with diethyl ether (3 × 30 mL). The combined ether extracts were washed with saturated brine (25 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue obtained was purified by column chromatography on silica gel (10% ethyl acetate in light petroleum ether) to furnish the epoxy ether **6a** (232 mg, 89%) as a viscous liquid as an inseparable mixture of two isomers in a ratio of 1:1. IR (neat): $\tilde{\nu}$ = 3028, 2918, 2860, 1647, 1454, 1091 cm^{-1}. ^{1}H NMR: δ = 1.63–1.70 (m, 0.5 H), 1.86–1.94 (m, 0.5 H), 2.08–2.18 (m, 1 H), 2.46–2.50 (m, 1 H), 2.71 (t app, J = 4.4 Hz, 0.5 H), 2.81(t app, J = 4.4 Hz, 0.5 H), 2.85–2.91 (m, 0.5 H), 3.19–3.25 (m, 0.5 H), 3.76–4.00 (m, 2 H), 4.48–4.60 (m, 1 H), 5.16–5.30 (m, 2 H), 5.85–6.00 (m, 1 H), 7.28–7.38 (m, 5 H) ppm. ^{13}C NMR: δ = 40.7, 41.7, 46.8, 47.4, 49.3, 49.5, 69.2, 69.4, 78.6, 78.7, 116.6, 116.7, 126.2, 126.6, 127.5, 127.7, 128.3, 128.4, 134.5, 134.6, 141.2, 141.7 ppm. $C_{13}H_{16}O_2$ (204.26): calcd. C 76.44, H 7.90; found C 76.38, H 7.87.

2-[2-(Allyloxy)-2-(4-methoxyphenyl)ethyl]oxirane (6b): Compound **6b** was prepared from **2d** according to the same procedure as described for **6a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 2999, 2837, 1612, 1512, 1247, 1033 cm^{-1}. ^{1}H NMR: δ = 1.60–1.70 (m, 0.5 H), 1.84–1.92 (m, 0.5 H), 2.06–2.16 (m, 1 H), 2.45–2.50 (m, 1 H), 2.70 (t app, J = 4.5 Hz, 0.5 H), 2.80 (t app, J = 4.5 Hz, 0.5 H), 2.84–2.89 (m, 0.5 H), 3.15–3.21 (m, 0.5 H), 3.72–3.97 (m, 2 H), 3.82 (s, 3 H), 4.43–4.54 (m, 1 H), 5.15–5.29 (m, 2 H), 5.83–5.98 (m, 1 H), 6.90, 6.91 (2d, J = 8.6 Hz each, 2 H), 7.23–7.29 (m, 2 H) ppm. ^{13}C NMR: δ = 40.8, 41.8, 47.0, 47.5, 49.5, 49.7, 55.2, 55.2, 69.1, 69.3, 78.3, 78.4, 113.8, 113.9, 116.6, 116.7, 127.6, 127.9, 133.3, 133.8, 134.7, 134.8, 159.1, 159.2 ppm. $C_{14}H_{18}O_3$ (234.28): calcd. C 71.77, H 7.74; found C 71.70, H 7.71.

5-[1-(Allyloxy)-2-oxiranylethyl]benzo[1,3]dioxole (6c): Compound **6c** was prepared from **2e** according to the same procedure as described for **6a** as a viscous liquid. IR (neat): $\tilde{\nu}$ = 3016, 2887, 1504, 1487, 1442, 1217, 1041 cm^{-1}. ^{1}H NMR: δ = 1.54–1.63 (m, 0.5 H), 1.79–1.88 (m, 0.5 H), 2.00–2.11 (m, 1 H), 2.43–2.47 (m, 1 H), 2.68 (t app, J = 4.3 Hz, 0.5 H), 2.78 (t app, J = 4.3 Hz, 0.5 H), 2.81–2.86 (m, 0.5 H), 3.11–3.17 (m, 0.5 H), 3.71–3.96 (m, 2 H), 4.36–4.48 (m, 1 H), 5.13–5.27 (m, 2 H), 5.80–5.94 (m, 1 H), 5.94 (s, 2 H), 6.75–6.85 (m, 3 H) ppm. ^{13}C NMR: δ = 40.9, 41.8, 46.9, 47.4, 49.4, 49.6, 69.1, 69.3, 78.5, 78.6, 100.9, 101.0, 106.5, 106.7, 108.0, 108.0, 116.7, 116.8, 119.9, 120.4, 134.6, 134.7, 135.3, 135.9, 147.1, 147.2, 147.9, 148.0 ppm. $C_{14}H_{16}O_4$ (248.27): calcd. C 67.73, H 6.50; found C 67.64, H 6.46.

[(2*R*,4*R*)-5-Methylene-2-phenyltetrahydro-2*H*-pyran-4-yl]methanol (4a^1): A solution of titanocene dichloride (0.65 g, 2.6 mmol) in dry THF (35 mL) was stirred with activated zinc dust (0.482 g, 7.2 mmol) under argon for 1 h (activated zinc dust was prepared by washing 20 g of commercially available zinc dust with 60 mL of 4 N HCl and thorough washing with water and finally with dry acetone and then drying in vacuo). The resulting green solution was then transferred through a cannula to a dropping funnel and was added dropwise to a magnetically stirred solution of the epoxyalkyl propargyl ether **3a** (250 mg, 1.2 mmol) in dry THF (30 mL) at room temperature under argon during 40 min. The reaction mixture was stirred for an additional 1.5 h and decomposed with 10% H_2SO_4 (15 mL). Most of the solvent was removed under reduced pressure, and the residue obtained was extracted with diethyl ether (4 × 30 mL). The combined ether layers were washed with saturated $NaHCO_3$ (2 × 20 mL), brine (20 mL) and then dried (Na_2SO_4). Removal of the solvent under reduced pressure afforded a viscous mass which was chromatographed on silica gel (20% ethyl acetate in light petroleum ether) to yield the cyclized product **4a** (196 mg, 78%) as a mixture of two isomers in a ratio of 4.6:1 and the reduced product **5a** (40 mg, 16%). The major isomer was separated by preparative TLC (15% ethyl acetate in light petroleum ether) of the cyclized crude product to obtain the major isomer **4a^1** (139 mg, 55%) as a viscous oil. IR (neat): $\tilde{\nu}$ = 3420 (br), 2918, 2848, 1652, 1450, 1028 cm^{-1}. ^{1}H NMR: δ = 1.45–1.57 (m, 1 H), 1.53 (br. s, OH), 2.14 (ddd, J = 2.1, 4.3, 13.0 Hz, 1 H), 2.61–2.65 (m, 1 H), 3.74 (dd, J = 6.1, 10.6 Hz, 1 H), 3.96 (dd, J = 5.6, 10.5 Hz, 1 H), 4.15, 4.36 (AB q, J = 12.3 Hz, 2 H), 4.57 (dd, J = 2.1, 11.3 Hz, 1 H), 4.89 (s, 1 H), 5.03 (s, 1 H), 7.24–7.37 (m, 5 H) ppm. ^{13}C NMR: δ = 38.9, 42.7, 64.4, 74.1, 80.1, 108.6, 126.2, 127.9, 128.7, 142.4, 144.7 ppm. $C_{13}H_{16}O_2$ (204.26): calcd. C 76.45, H 7.88; found C 76.31, H 7.85. The minor isomer could not be separated in pure form and was always contaminated with the major isomer.

Compounds **4b**–**h** were prepared according to the same procedure as described for **4a**. The major isomers **4b^1**–**4e^1** were separated by preparative TLC (15% ethyl acetate in light petroleum ether) but the minor isomer in each case could not be separated in pure form an was always contaminated with the major isomer.

[(2*R*,4*R*)-2-(3,4-Dimethoxyphenyl)-5-methylenetetrahydro-2*H*-pyran-4-yl]methanol (4b^1): Viscous oil. IR (neat): $\tilde{\nu}$ = 3417(br), 2937, 2837, 1651, 1593, 1517, 1263 cm^{-1}. ^{1}H NMR: δ = 1.40–1.52 (m, 1 H), 1.52 (br. s, OH), 2.05 (ddd, J = 2.0, 4.4, 12.9 Hz, 1 H), 2.51–2.57 (m, 1 H), 3.69 (dd, J = 6.0, 10.6 Hz 1 H), 3.79 (s, 3 H), 3.82 (s, 3 H), 3.90 (dd, J = 5.8, 10.7 Hz, 1 H), 4.07, 4.28 (ABq, J = 12.3 Hz, 2 H), 4.45 (dd, J = 2.0, 11.3 Hz, 1 H), 4.82 (s, 1 H), 4.96 (s, 1 H), 6.74–6.85 (m, 3 H) ppm. ^{13}C NMR: δ = 38.8, 42.7, 56.2, 56.3, 64.4, 74.1, 79.9, 108.5, 109.5, 111.3, 118.5, 135.1, 144.7, 148.8, 149.3 ppm. $C_{15}H_{20}O_4$ (264.31): calcd. C 68.17, H 7.62; found C 68.09, H 7.58.

{(2*R*,4*R*)-2-[4-(Benzyloxy)-3-methoxyphenyl]-5-methylenetetrahydro-2*H*-pyran-4-yl}methanol (4c^1): Viscous oil. IR (neat): $\tilde{\nu}$ = 3390 (br), 2848, 1651, 1593, 1463, 1031 cm^{-1}. ^{1}H NMR: δ = 1.45–1.64 (m, 1 H), 1.56 (br. s, OH), 2.10 (ddd, J = 2.0, 4.3, 12.9 Hz, 1 H), 2.57–2.61 (m, 1 H), 3.75 (dd, J = 6.0, 10.6 Hz, 1 H), 3.89 (s, 3 H), 3.96 (dd, J = 5.6, 10.4 Hz, 1 H), 4.13, 4.34 (ABq, J = 12.3 Hz, 2 H), 4.50 (dd, J = 2.0, 11.3 Hz, 1 H), 4.89 (s, 1 H), 5.02 (s, 1 H), 5.13 (s, 2 H), 6.77–6.94 (m, 3 H), 7.25–7.43 (m, 5 H) ppm. ^{13}C

NMR: δ = 38.2, 42.2, 55.9, 63.9, 70.9, 73.6, 79.4, 108.0, 109.6, 113.8, 118.0, 127.6, 127.7, 128.4, 135.2, 137.1, 144.2, 147.4, 149.6 ppm. $C_{21}H_{24}O_4$ (340.40): calcd. C 74.10, H 7.10; found C 73.99, H 7.07.

[(2*R*,4*R*)-2-(4-Methoxyphenyl)-5-methylenetetrahydro-2*H*-pyran-4-yl-]methanol (4d[1]): Viscous oil. IR (neat): ṽ = 3417 (br), 2916, 2848, 1612, 1514, 1247, 1031 cm^{-1}. ^{1}H NMR: δ = 1.45–1.58 (m, 1 H), 1.57 (br. s, OH), 2.10 (ddd, *J* = 2.1, 4.4, 12.0 Hz, 1 H), 2.58–2.63 (m, 1 H), 3.74 (dd, *J* = 6.0, 10.6 Hz, 1 H), 3.79 (s, 3 H), 3.95 (dd, *J* = 5.8, 10.6 Hz, 1 H), 4.13, 4.33 (ABq, *J* = 12.3 Hz, 2 H), 4.52 (dd, *J* = 2.1, 11.3 Hz, 1 H), 4.89 (s, 1 H), 5.02 (s, 1 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 7.28 (d, *J* = 9.1 Hz, 2 H) ppm. ^{13}C NMR: δ = 38.2, 42.2, 55.1, 63.9, 73.6, 79.2, 107.9, 113.6, 127.0, 134.1, 144.3, 158.9 ppm. $C_{14}H_{18}O_3$ (234.28): calcd. C 71.78, H 7.73; found C 71.70, H 7.71.

[(2*R*,4*R*)-2-(1,3-Benzodioxol-5-yl)-5-methylenetetrahydro-2*H*-pyran-4-yl]methanol (4e[1]): Viscous oil. IR (neat): ṽ = 3417 (br), 2916, 2848, 1504, 1488, 1444, 1251 cm^{-1}. ^{1}H NMR: δ = 1.42–1.62 (m, 1 H), 1.62 (br. s, OH), 2.09 (ddd, *J* = 2.1, 4.4, 13.0 Hz, 1 H), 2.56–2.62 (m, 1 H), 3.74 (dd, *J* = 6.1, 10.6 Hz, 1 H), 3.95 (dd, *J* = 5.7, 10.6 Hz, 1 H), 4.12, 4.33 (ABq, *J* = 12.2 Hz, 2 H), 4.48 (dd, *J* = 2.0, 11.3 Hz, 1 H), 4.88 (s, 1 H), 5.02 (s, 1 H), 5.93 (s, 2 H), 6.77–6.87 (m, 3 H) ppm. ^{13}C NMR: δ = 38.3, 42.1, 63.9, 73.6, 79.4, 100.8, 106.5, 108.0, 119.1, 136.0, 144.1, 146.7, 146.8 ppm. $C_{14}H_{16}O_4$ (248.27): calcd. C 67.74, H 6.49; found C 67.63, H 6.45.

[(4*R*)-2-Methyl-5-methylene-2-phenyltetrahydro-2*H*-pyran-4-yl]-methanol (4f): Viscous oil. IR (neat): ṽ = 3396 (br), 2972, 2925, 1651, 1494, 1446, 1060 cm^{-1}. ^{1}H NMR: δ = 1.40 (s, 6/3 H), 1.54 (s, 3/3 H), 2.15–2.39 (m, 2 H), 2.71 (dd, *J* = 3.8, 13.5 Hz, 1 H), 3.52–3.74 (m, 1 H), 3.86–3.94 (m, 1 H), 3.94 (s, 1 H), 4.16, 4.27 (AB_q, *J* = 13.2 Hz, 1 H), 4.70 (s, 2/3 H), 4.83 (s, 1/3 H), 4.87 (s, 2/3 H), 4.96 (s, 1/3 H), 7.22–7.46 (m, 5 H) ppm. ^{13}C NMR: δ = 26.7, 33.6, 38.5, 39.1, 39.5, 63.9, 66.1, 68.0, 75.3, 76.9, 106.9, 108.2, 124.3, 124.6, 125.9, 126.5, 126.7, 128.1, 128.2, 128.6, 143.6, 144.7, 145.0, 147.7 ppm. $C_{14}H_{18}O_2$ (218.28): calcd. C 77.04, H 8.30; found C 76.90, H 8.25.

(3-Methylene-1-oxaspiro[5.5]undec-4-yl)methanol (4g): Viscous oil. IR (neat): ṽ = 3390 (br), 2931, 2856, 1651, 1444, 1062 cm^{-1}. ^{1}H NMR: δ = 1.13–1.74 (m, 10 H), 1.79 (dd, *J* = 4.7, 13.0 Hz, 1 H), 1.81 (br. s, OH), 2.03–2.07 (m, 1 H), 2.53–2.59 (m, 1 H), 3.62 (dd, *J* = 5.9, 10.4 Hz, 1 H), 3.85 (dd, *J* = 5.9, 10.4 Hz, 1 H), 3.94, 4.11 (ABq, *J* = 13.0 Hz, 2 H), 4.77 (s, 1 H), 4.91 (s, 1 H) ppm. ^{13}C NMR: δ = 21.5, 21.7, 25.9, 26.0, 30.3, 37.6, 39.2, 64.3, 65.9, 72.5, 107.0, 145.6 ppm. $C_{12}H_{20}O_2$ (196.28): calcd. C 73.44, H 10.26; found C 73.36, H 10.23.

(5′-Methylene-3,3′,4,4′,5′,6′-hexahydro-2*H*-spiro[naphthalene-1,2′-pyran]-4′-yl)methanol (4h): Viscous oil. IR (neat): ṽ = 3400 (br), 2933, 2866, 1649, 1488, 1448, 1047 cm^{-1}. ^{1}H NMR: δ = 1.56 (br. s, OH), 1.66–1.84 (m, 2 H), 1.90–2.08 (m, 3 H), 2.37–2.45 (m, 1 H), 2.68–2.75 (m, 1 H), 2.77–2.89 (m, 2 H), 3.69 (dd, *J* = 5.7, 10.6 Hz, 1 H), 3.91 (dd, *J* = 5.9, 10.6 Hz, 1 H), 4.13, 4.36 (AB q, *J* = 12.9 Hz, 2 H), 4.89 (s, 1 H), 5.03 (s, 1 H), 7.04 (d, *J* = 7.2 Hz, 1 H), 7.11–7.20 (m, 2 H), 7.55 (d, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR: δ = 20.4, 30.0, 30.1, 38.8, 40.8, 64.8, 67.6, 74.9, 108.0, 126.6, 127.3, 127.4, 128.9, 137.0, 141.8, 145.5 ppm. $C_{16}H_{20}O_2$ (244.32): calcd. C 78.66, H 8.24; found C 78.52, H 8.20.

[(2*R*,4*R*,5*S*)-5-Methyl-2-phenyltetrahydro-2*H*-pyran-4-yl]methanol (7a[1]) and [(2*R*,4*R*,5*R*)-5-Methyl-2-phenyltetrahydro-2*H*-pyran-4-yl]-methanol (7a[2]): A solution of titanocene dichloride (0.57 g, 2.24 mmol) in dry THF (28 mL) was stirred with activated zinc dust (0.4 g, 6.12 mmol) under argon for 1 h (activated zinc dust was prepared by washing 20 g of commercially available zinc dust with 60 mL of 4 N HCl and thorough washing with water and finally with dry acetone and then drying in vacuo). The resulting green solution was then transferred through a cannula to a dropping funnel and was added dropwise to a magnetically stirred solution of the allyl epoxyalkyl ether **6a** (210 mg, 1.03 mmol) in dry THF (25 mL) at room temperature under argon during 40 min. The reaction mixture was stirred for an additional 1.5 h and decomposed with 10% H_2SO_4 (15 mL). Most of the solvent was removed under reduced pressure, and the residue obtained was extracted with diethyl ether (4 × 30 mL). The combined ether layers were washed with saturated $NaHCO_3$ (2 × 20 mL), brine (20 mL) and then dried (Na_2SO_4). Removal of the solvent under reduced pressure afforded a viscous mass which was chromatographed on silica gel (30% ethyl acetate in light petroleum ether) to yield the cyclized product **7a** (176 mg, 83%) as a mixture of three isomers in a ratio of 2.6:1:0.2 and the reduced product **8a** (17 mg, 8%). The crude **7a** was subjected to preparative TLC (20% ethyl acetate in light petroleum ether) to furnish **7a[1]** (105 mg, 49%) as a viscous oil and **7a[2]** (40 mg, 19%) as a crystalline solid, m.p. 138–140 °C. Spectral data of the major isomer **7a[1]**: IR (neat): ṽ = 3390 (br), 3030, 2916, 2873, 1600, 1454, 1085 cm^{-1}. ^{1}H NMR: δ = 0.90 (d, *J* = 6.4 Hz, 3 H), 1.40–1.75 (m, 4 H including OH), 1.98–2.03 (m, 1 H), 3.24 (t app, *J* = 11.0 Hz, 1 H), 3.56 (dd, *J* = 10.7, 6.2 Hz, 1 H), 3.80 (dd, *J* = 10.7, 3.2 Hz, 1 H), 4.01 (dd, *J* = 11.4, 4.4 Hz, 1 H), 4.38 (dd, *J* = 11.0, 2.2 Hz, 1 H), 7.24–7.37 (m, 5 H) ppm. ^{13}C NMR: δ = 14.1, 31.9, 36.8, 44.5, 64.9, 74.2, 79.7, 125.6, 127.2, 128.2, 142.6 ppm. $C_{13}H_{18}O_2$ (206.27): calcd. C 75.69, H 8.80; found C 75.61, H 8.77. Spectral data of the minor isomer **7a[2]**: IR (neat): ṽ = 3433 (br), 2931, 2848, 1454, 1371, 1099 cm^{-1}. ^{1}H NMR: δ = 1.07 (d, *J* = 7.1 Hz, 3 H), 1.40–1.73 (m, 3 H including OH), 1.87–1.92 (m, 1 H), 2.09–2.18 (m, 1 H), 3.48–3.61 (m, 2 H), 3.77, 3.96 (ABq, *J* = 11.3 Hz, each peak split into doublet, *J* = 2.3 Hz, 2 H), 4.34 (dd, *J* = 11.3, 2.5 Hz, 1 H), 7.23–7.38 (m, 5 H) ppm. ^{13}C NMR: δ = 11.1, 29.2, 31.8, 41.1, 65.5, 74.6, 79.9, 125.7, 127.8, 128.4, 142.9 ppm. $C_{13}H_{18}O_2$ (206.27): calcd. C 75.69, H 8.80; found C 75.60, H 8.76. The other third isomer could not be isolated in pure form as it was produced in minute quantity.

[(2*R*,4*R*,5*S*)-2-(4-Methoxyphenyl)-5-methyltetrahydro-2*H*-pyran-4-yl]methanol (7b[1]) and [(2*R*,4*R*,5*R*)-2-(4-Methoxyphenyl)-5-methyltetrahydro-2*H*-pyran-4-yl]methanol (7b[2]): Compounds **7b[1]** and **7b[2]** were prepared from **6b** in 52% and 21% yield, respectively, as viscous oils according to the same procedure as described for **7a[1]** and **7a[2]**. Spectral data of the major isomer **7b[1]**: IR (neat): ṽ = 3410 (br), 2950, 2837, 1612, 1514, 1247, 1033 cm^{-1}. ^{1}H NMR: δ = 0.88 (d, *J* = 6.1 Hz, 3 H), 1.40–1.72 (m, 4 H including OH), 1.95–1.99 (m, 1 H), 3.22 (t app, *J* = 11.2 Hz, 1 H), 3.56 (dd, *J* = 10.6, 5.2 Hz, 1 H), 3.73–3.86 (m, 1 H), 3.79 (s, 3 H), 3.99 (dd, *J* = 11.4, 4.3 Hz, 1 H), 4.30–4.34 (m, 1 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 7.28 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR: δ = 14.2, 32.0, 36.7, 44.6, 55.2, 65.1, 74.4, 79.5, 113.6, 127.0, 135.0, 158.9 ppm. $C_{14}H_{20}O_3$ (236.30): calcd. C 71.16, H 8.53; found C 71.06, H 8.49. Spectral data of the minor isomer **7b[2]**: IR (neat): ṽ = 3398, 2935, 2875, 1614, 1514, 1247, 1035 cm^{-1}. ^{1}H NMR δ: 1.06 (d, *J* = 7.0 Hz, 3 H), 1.40–1.81 (m, 3 H including OH), 1.83–1.96 (m, 1 H), 1.99–2.16 (m, 1 H), 3.45–3.69 (m, 2 H), 3.71–3.92 (m, 2 H), 3.79 (s, 3 H), 4.28 (dd, *J* = 11.3, 2.2 Hz, 1 H), 6.87 (d, *J* = 8.1 Hz, 2 H), 7.28 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR: δ = 11.0, 27.0, 31.8, 40.9, 55.1, 65.3, 74.5, 79.5, 113.5, 126.8, 135.1, 158.7 ppm. $C_{14}H_{20}O_3$ (236.30): calcd. C 71.16, H 8.53; found C 71.12, H 8.50. The other third isomer could not be isolated in pure form as it was produced in minute quantity.

[(2*R*,4*R*,5*S*)-2-(1,3-Benzodioxol-5-yl)-5-methyltetrahydro-2*H*-pyran-4-yl]methanol (7c[1]) and [(2*R*,4*R*,5*R*)-2-(1,3-Benzodioxol-5-yl)-5-

methyltetrahydro-2*H*-pyran-4-yl]methanol (7c²): Compounds **7c¹** and **7c²** were prepared from **6c** in 49% and 20% yield, respectively, as viscous oils according to the same procedure as described for **7a¹** and **7a²**. Spectral data of the major isomer **7c¹**: IR (neat): $\tilde{\nu}$ = 3417 (br), 3010, 2954, 2879, 1504, 1488, 1442, 1251, 1039 cm^{-1}. ^1H NMR: δ = 0.88 (d, J = 6.4 Hz, 3 H), 1.37–1.81 (m, 4 H including OH), 1.93–1.98 (m, 1 H), 3.20 (t app, J = 11.0 Hz, 1 H), 3.55 (dd, J = 10.6, 6.0 Hz, 1 H), 3.78 (dd, J = 10.7, 3.2 Hz, 1 H), 3.98 (dd, J = 11.4, 4.4 Hz, 1 H), 4.28 (dd, J = 10.9, 2.1 Hz, 1 H), 5.92 (s, 2 H), 6.74–6.89 (m, 3 H) ppm. ^{13}C NMR: δ = 14.1, 31.8, 36.8, 44.4, 64.9, 74.2, 79.6, 100.7, 106.5, 107.8, 118.9, 136.7, 146.6, 147.4 ppm. $C_{14}H_{18}O_4$ (250.28): calcd. C 67.18, H 7.25; found C 67.10, H 7.22. Spectral data of the minor isomer **7c²**: IR (neat): $\tilde{\nu}$ = 3419 (br), 3016, 2881, 1504, 1488, 1442, 1215, 1041 cm^{-1}. ^1H NMR: δ = 1.06 (d, J = 7.1 Hz, 3 H), 1.38–1.78 (m, 3 H including OH), 1.81–1.98 (m, 1 H), 2.02–2.16 (m, 1 H), 3.46–3.61 (m, 2 H), 3.74, 3.93 (ABq, J = 11.3 Hz, each peak split into doublet, J = 2.0 Hz, 2 H), 4.25 (dd, J = 11.3, 2.4 Hz, 1 H), 5.93 (s, 2 H), 6.74–6.82 (m, 2 H), 6.88 (s, 1 H) ppm. ^{13}C NMR: δ = 11.0, 29.0, 31.7, 40.9, 65.3, 74.4, 79.6, 100.8, 106.5, 107.8, 119.0, 136.9, 146.6, 147.4 ppm. $C_{14}H_{18}O_4$ (250.28): calcd. C 67.18, H 7.25; found C 67.06, H 7.20. The other third isomer could not be isolated in pure form as it was produced in minute quantity.

X-ray Crystallographic Structure Determination of 7a²: A colourless single crystal was analyzed with a DIPLABO Kappa image plate diffractometer using the oscillation method at 293 K. Crystal size: 0.25 × 0.25 × 0.30 mm^3. Crystal system: monoclinic, space group $P2_1/c$ (No. 14) with cell parameters a = 9.7060(8) Å, b = 7.9000(6) Å, c = 17.0040(11) Å, β = 119.301(3)°, V = 1137.0(2) $Å^3$, $\rho_{calcd.}$ = 1.205 gcm^{-3}, Z = 4. 6233 reflections were collected, resulting in 3593 independent and 3568 observed [$I > 2\sigma(I)$] reflections. Absorption coefficient μ = 0.079 mm^{-1}, no absorption correction, 136 refined parameters. Non-hydrogen atoms were refined anisotropically and H atoms were added at the calculated positions. $R1$ = 0.1367, w$R2$ = 0.4104 for data [$I > 2\sigma(I)$].

CCDC-278957 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra of compounds **2a**, **2d**, **3a**, **3d**, **4a¹**, **4d¹**, **6a**, **7a¹** and **7a²**.

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