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Synthetic studies toward miroestrols: trials for elongation of the methyl group of 5-substituted 2-methyl-2-cyclohexanone to 3-methyl-2-butenyl function

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ABSTRACT

Toward total synthesis of miroestrols (miroestrol and deoxymiroestrol), 3-methyl-2-butenyl function (*endo*-C5 unit) on D ring as a carbon chain for C and E rings was prepared by elongation of the methyl group in α-methyl-α,β-unsaturated ketone unit, and 3,5-dinitrobenzoyl group was introduced as a potential leaving group for the construction of B ring. The former was accomplished through a sequence of epoxide ring-opening, microwave-irradiated siloxy-Cope rearrangement, and isomerization of 3-methyl-3-butenyl function (*exo*-C5 unit) to *endo*-C5 unit.

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1. Introduction

A medicinal plant ‘kwao keur’ has been locally considered to be a rejuvenating drug in Thailand and was identified as *Pueraria mirifica* (Leguminosae).[1] The relationship between the chemical constituents and estrogenic activity has been widely studied and (+)-miroestrol (**1**) was isolated as an active principle.[2] We have independently investigated the analysis and the total synthesis of chemical components of *P. mirifica*[3] and (+)-deoxymiroestrol (**2**) was successfully isolated as a new active component, which possesses ten times stronger activity than miroestrol (**1**).[4] Therefore, even though the first total synthesis of (+)-miroestrol (**1**) had already been achieved by Corey and Wu,[5] synthetic studies of these strong phytoestrogens via new strategy is much valuable for further pharmacological studies. We have reported synthetic approaches toward these compounds, in which A ring was introduced via boron trichloride-mediated regioselective Claisen rearrangement of resorcinol carvonyl ether **7**, derived from (*R*)-(−)-carvone (**4b**), to phenol **6**[6] and the synthesis of methoxyethoxymethyl (MEM) ether **4a** was achieved via oxygenative isomerization of allylbenzene **5**.[7] As next stages, the following reactions have been studied toward the synthesis of key diol **3**: (1) conversion of methyl group of **4a** to 3-methyl-2-butenyl (*endo*-C5) unit as a carbon chain for the construction of C and E rings, (2) introduction of oxygen functionality at positions 15 and 17,[8] and (3) displacement of the MEM function to leaving group for B ring formation. In this study, we achieved the preparation of key intermediate **8**, which possesses an *endo*-C5 unit, an oxygen functionality on position 17, and 3,5-dinitrobenzoyl (DNB) group as a potential leaving group (Scheme 1).

2. Results and discussion

For the construction of *endo*- or 3-methyl-3-butenyl (*exo*-C5) unit on D ring, we planned three routes as follows; (1) siloxy-Cope rearrangement of diene **9a** followed by Cope rearrangement of **11**, after oxidative dehydrosilylation of **10a**, to enone **12** (rearrangement route), (2) double epoxidation—ring-opening sequence from **4a** to dihydroxy ketone **16** through epoxides **13c** and **15** (ring-opening route), and (3) a combination of ring-opening of epoxide **17** and siloxy-Cope rearrangement of **18** to enone **12** via **19** (combination route) (Scheme 2).

2.1. Rearrangement route

At first, rearrangement route was examined with (*R*)-(−)-carvone (**4b**) as a model substrate. Grignard reaction of **4b** with 2-methylallylmagnesium chloride afforded carbinol (18*S*)-**20b**[9] in 77% as a 95:5 diastereomeric mixture. Next, the carbinol **20b** and the corresponding TMS ether **9b** were subjected to oxy- and siloxy-Cope rearrangements.[10] Under conventional thermal conditions with **20b**, no reaction occurred in the case of without solvent and decomposition to (*R*)-(−)-carvone (**4b**) (10%) was observed via retro-oxy-ene (retro-allyl-Grignard) type reaction[11] when *N*,*N*-diethylaniline ($PhNEt_2$) was used as a solvent. On the other hand, microwave (MW) irradiation[12] of silyl ether **9b** without solvent gave the desired **10b** (31%) (Scheme 3). However, application of this reaction condition to a fully functionalized silyl ether **9a**, derived

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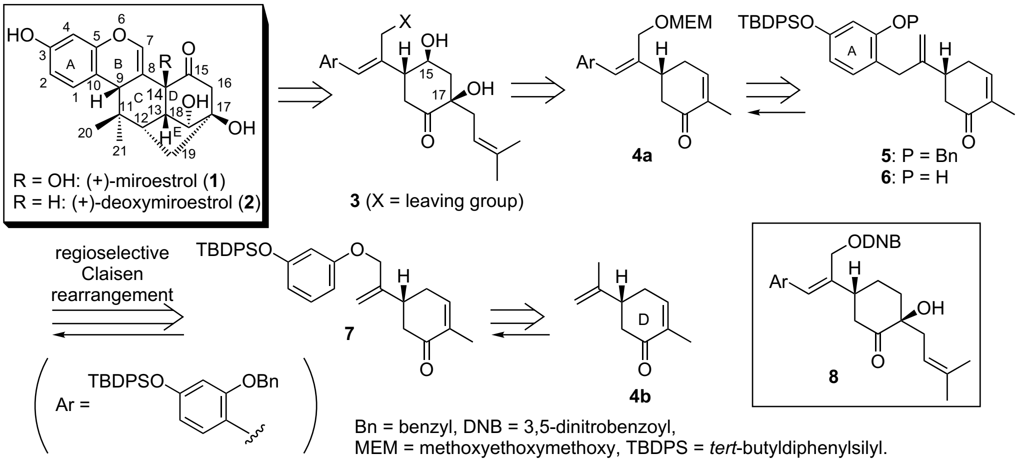


Bn = benzyl, DNB = 3,5-dinitrobenzoyl,
MEM = methoxyethoxymethoxy, TBDPS = *tert*-butyldiphenylsilyl.

Scheme 1. Retrosynthesis of miroestrols (**1** and **2**).

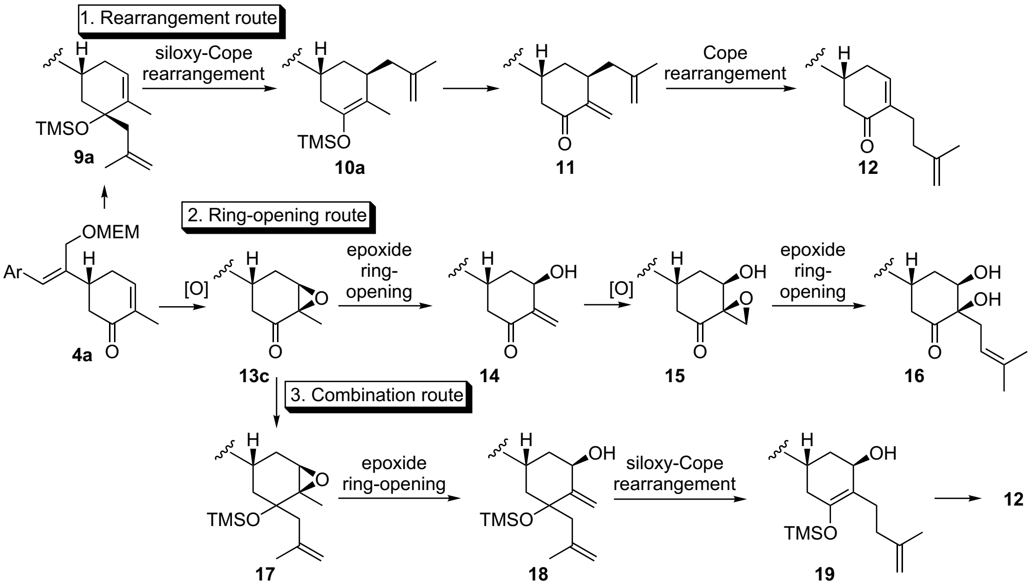
from **4a**, gave a complex mixture. Anionic oxy-Cope rearrangement[13] of carbinol **20a** led to the formation of only desilylated product **21** in 26% yield.

2.2. Ring-opening route

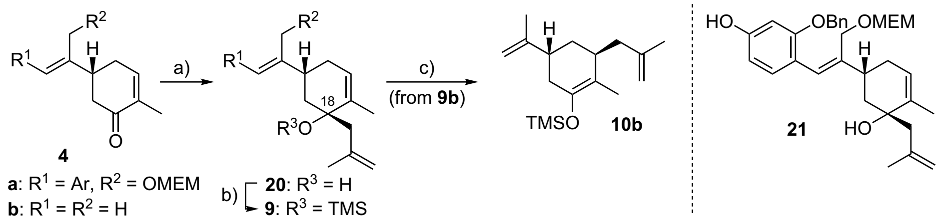
Next, ring-opening route was attempted (Scheme 4). Stereoselective epoxidation[14] of enone **4a** with cumene hydroperoxide (CHP) in the presence of Triton® B afforded epoxy ketone **13c** in 87% yield as a single diastereoisomer. Ring-opening of epoxide **13c** did not proceed with lithium diisopropylamide (LDA) even under refluxed condition, and reaction with boron trifluoride etherate gave a complex mixture. Treatment with trimethylsilyl trifluoromethanesulfonate in the presence of 2,6-lutidine[15] gave enone **22** in 34%, which was supposed to be formed by Favorskii-type reaction of the silyl ether **23** followed by cyclization of **24** (Scheme 5), and that with aluminum triisopropoxide [Al(O*i*-Pr)$_3$][16] afforded diol **25**[17] in 19% via ring-opening of epoxide followed by undesired Meerwein–Ponndorf–Verley reduction of ketone. Use of diethylaluminum amide **26**,[14] instead of Al(O*i*-Pr)$_3$, afforded a complex mixture.

2.3. Combination route

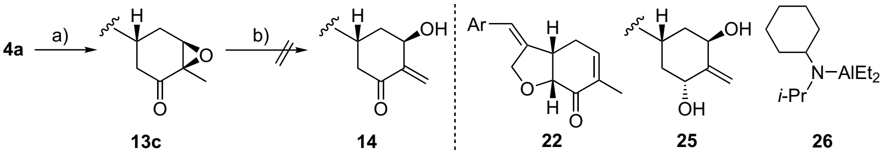
Finally, combination route was examined (Scheme 6). Dienes **28** and **18** were prepared as substrates for oxy- and siloxy-Cope rearrangement. Grignard reaction of **13c** with 2-methylallylmagnesium chloride afforded homoallyl alcohol **27** as a 1:1 mixture of diastereoisomers. Next, the carbinol **27** and the corresponding TMS ether **17** were subjected to ring-opening reaction (Table 1). Treatment of **27** with Al(O*i*-Pr)$_3$ in refluxed xylenes gave desired allylic alcohol **28** (9%) together with small amount of cyclohexene **29** (6%) (run 1, Table 1). NOE enhancements of **28** and **29** (Fig. 1a) showed that these were derived from (18*S*)- and (18*R*)-**27**, respectively. Reaction of siloxy epoxide **17** under the same reaction conditions as run 1 afforded desired silyl ether **18** in better yield (27%) and undesired isopropyl ether **30** (13%) (run 2), and the latter was supposed to be formed by S$_N$2′ type reaction of **18** with isopropoxide anion. Absolute configurations of position 18 of **18** obtained above



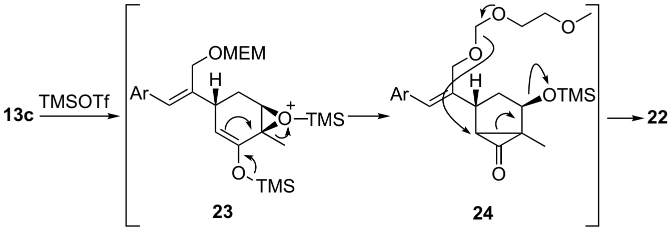
Scheme 2. Plans for introduction of *endo*- and *exo*-C5 units as a carbon chain for C and E rings.



Scheme 3. Synthesis and trials for the Cope rearrangement carbinols **20** and TMS ethers **9** on the rearrangement route. Reagents and conditions: (a) 2-methylallylmagnesium chloride, −78 °C, 75% for **20a**, 77% for **20b**; (b) TMSCl, imidazole, DMF, rt, 83% for **9a**, 98% for **9b**; (c) MW, 250 °C, 5 min, 31%.



Scheme 4. Trials for ring-opening of epoxide **13c** on the ring-opening route. Reagents and conditions: (a) CHP, Triton® B, toluene, 0 °C, 87%; (b) see text.



Scheme 5. Supposed mechanism for the formation of enone **22**.

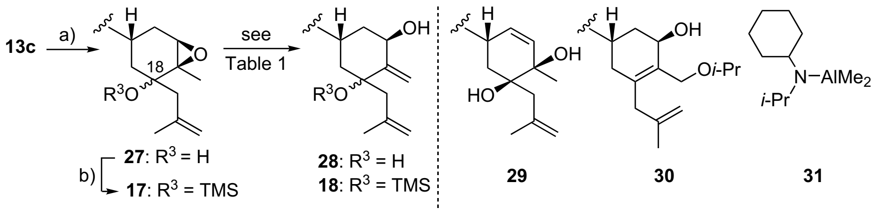
was determined as *S* by NOE enhancements (Fig. 1b). Utilization of aluminum amide reagents **26** and **31** improved the yield of **18**: the reaction with dimethylaluminum amide **31** afforded **18** in 50% yield as a 1:3 mixture of diastereoisomers together with a small amount of TMS-deprotected (18*R*)-**28** (run 3). When diethylaluminum reagent **26** was used, the yield of **18** was greatly improved up to 74% from **13c**, obtained as a 1:2 mixture of diastereoisomers (run 4).

Siloxy-Cope rearrangement of **18** was examined (Table 2). The rearrangement of diastereomerically pure (18*S*)- and (18*R*)-**18** under conventional thermal condition without solvent gave desired enone **12** in 24–28% yields after dehydrosilylation of intermediate **19** (runs 1 and 2). Similar result was obtained when a diastereomeric mixture of **18** was used (run 3). The reaction was accelerated by MW irradiation and completed within 6 min in neat condition; however, yield of **12** was still low (22%) (run 4). Yield was not improved with using $PhNEt_2$ (28%) (run 5) and a complex mixture was obtained in dimethylsulfoxide (DMSO) (run 6). Product was increased (56%) when xylenes were used (run 7). Reaction in *N*,*N*-dimethylformamide (DMF) gave the best result with shorter reaction period (run 8).

Siloxy-Cope rearrangement of **18** with an activated allylic hydroxyl group as **32** (X=leaving group) was also examined (Table 3). Rearrangement of **18** in the presence of methanesulfonyl chloride (MsCl) in refluxed dichloromethane (CH_2Cl_2) gave desired **12** (25%) and a bicyclic byproduct **34** (16%) (run 1). The use of Burgess reagent[18] afforded an aromatized byproduct **35** (13%) without improvement of the formation of **12** (26%) (run 2). Although yields in these trials were still low, the acceleration of reaction was observed.

2.4. Trials for the introduction of oxygen functionality at positions 15 and 17

Toward the introduction of oxygen functionality at positions 15 and 17 on enone **12**, model reactions using the methyl epoxide **13c** were examined. After the stereoselective reduction[14] of epoxide **13c**, ring-opening of **36c** with Al(O*i*-Pr)$_3$ gave allylic alcohol **37c**. Hydrogen bond-directed epoxidation[19] of **37c** with *m*-chloroperbenzoic acid (*m*-CPBA) gave smoothly epoxide **38c** even contamination with diepoxide **38c′**. Reductive ring-opening of the epoxide **38c** and the corresponding TBS ether **39c** under several conditions were examined; however, the desired 15-OH isomer **40** was not produced in all cases: only regioisomeric 16-OH derivative **41** was obtained when alcohol **38c** was treated with lithium aluminum hydride ($LiAlH_4$). Similar transformation of epoxide **13d** with *exo*-C5 unit, prepared by epoxidation and simultaneous desilylation of **12** to **13d′** followed by re-silylation, gave key allylic alcohol **37d** in moderate yield; however, epoxidation of this compound to the corresponding epoxide **38d** was low yield (13%) (Scheme 7). Thus, we gave up to introduce oxygen functionality on position 15 in this strategy, and decided to proceed our synthetic study with 15-deoxygenated compounds.



Scheme 6. Preparation of allyl alcohols **28** and **18** as substrates for oxy-Cope rearrangement. Reagents and conditions: (a) 2-methylallylmagnesium chloride, THF, −78 °C; (b) TMSCl, imidazole, DMF, rt, 92% from **13c**, dr=1:1.

Table 1
Ring-opening of epoxides **27** and **17**

Run	Substrate[a]	R^3	Reagent	Solvents	Conditions	Results
1	**27**	H	$Al(Oi\text{-}Pr)_3$	Xylenes	115 °C to reflux, 9 h	(18*S*)-**28** (9%), **29** (6%)
2	**17**	TMS	$Al(Oi\text{-}Pr)_3$	Xylenes	Reflux, 7 h	(18*S*)-**18** (27%), **30** (13%), (18*R*)-**17** recovery (27%)
3	**17**	TMS	**31**	Benzene	rt, 22 h	**18**[b] (50%), (18*R*)-**28** (7%), **17**[a] recovery (23%)
4	**17**	TMS	**26**	Benzene	30 °C, 4 h	**18**[c] (74%)[d]

[a] dr=1:1.
[b] Ratio: (18*R*)-**18**/(18*S*)-**18**=1:3.
[c] Ratio: (18*R*)-**18**/(18*S*)-**18**=1:2.
[d] From **13c**.

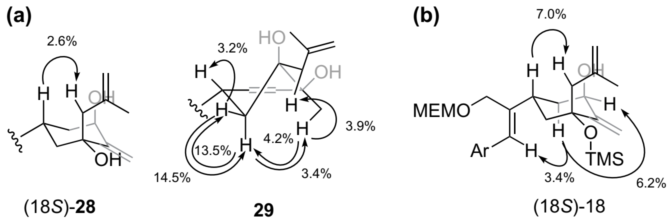


Figure 1. Selected NOE enhancements of (18*S*)-**28**, **29**, and (18*S*)-**18**.

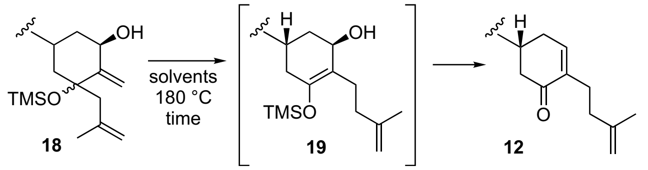
As a model substrate for the removal of MEM group, α-hydroxy ketone **42** was synthesized by regioselective reduction of epoxide **36c** followed by *o*-iodoxybenzoic acid (IBX)[20] oxidation of secondary alcohol. Unfortunately, trials for the removal of MEM group of α-hydroxyl ketone **42** under reported conditions (10% HCl aq,[3c] $TiCl_4$,[21] $CeCl_3$,[22] CBr_4[23]) gave no desired allylic alcohol **43**. Only in the case when pyridinium *p*-toluenesulfonate (PPTS) in *tert*-butyl alcohol[24] was used, **43** was obtained in 21% yield. Replacement of the solvent to methyl ethyl ketone (MEK)[25] slightly increased the yield [31%: recovery of **42** (18%)]. Irradiation of MW effectively accelerated the reaction and gave better yield (**43**: 42%), in which **42** was recovered in 32% (Scheme 7).

2.5. Isomerization of *exo*- to *endo*-C5 unit

Next, we tried isomerization of the *exo*-C5 unit to the *endo* one in **36d**. The substrate **45** for the isomerization was prepared via reductive ring-opening of epoxide **36d** and ketalization of 1,2-diol **44**. Initial trials for isomerization of **45** under reported conditions, such as iodine,[26] *p*-toluenesulfonic acid,[27] and rhodium chloride (III),[28] resulted in the formation of complex mixtures. Only in the case when Wilkinson's catalyst $[ClRh(PPh_3)_3]$[27] was applied, desired **46** was obtained in 88% yield as a 10:1 inseparable mixture with **45**. Deprotection of the acetonide function[29] in **46** followed by IBX oxidation of diol **47** gave ketone **48**, MEM group of which was removed with PPTS under MW condition to afford diol **49** (30%) together with recovery of **48** (48%).

Finally, DNB group was smoothly introduced at allylic hydroxyl group to give desired **8** (Scheme 8).

Table 2
Construction of *exo*-C5 unit by siloxy-Cope rearrangement of **18**



Run	**18**	Solvent	Time		**12** (%)
			Conventional (h)	MW (min)	
1	*S* only	None	1.5	—	24
2	*R* only	None	1.5	—	28
3	[a]	None	2.0	—	22
4	[a]	None	—	6	22
5	[a]	$PhNEt_2$	—	6	28
6	[a]	DMSO	—	5	CM[b]
7	[a]	Xylenes	—	16	56
8	[a]	DMF	—	4	69

[a] Ratio: (18*R*)-**18**/(18*S*)-**18**=1:2.
[b] A complex mixture.

3. Conclusion

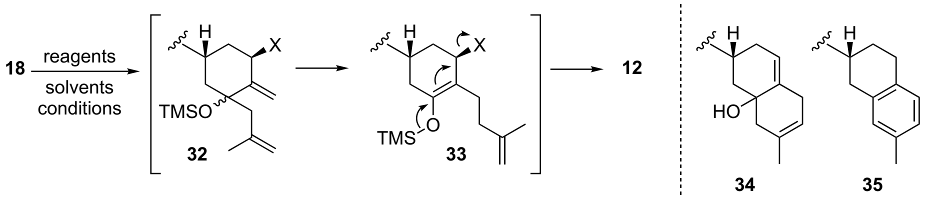
In conclusion, toward total synthesis of strongly phytoestrogenic miroestrols we accomplished the synthesis of key intermediate **8**, which possesses *endo*-C5 unit as a side chain which will constitute the C and E rings, one hydroxyl group at position 17, and DNB group as a potential leaving group. On the construction of *exo*-C5 unit by siloxy-Cope rearrangement of allylic alcohol **18**, MW irradiation was effective to give key enone **12**. Oxygen functionality at position 17 was introduced via epoxidation and reductive ring-opening of **12**. Isomerization of *exo*-C5 unit by Wilkinson catalyst was successful to give desired *endo* one. Removal of MEM group with PPTS gave low yield; however, the yield was slightly improved by MW irradiation. Further approaches to the construction of C and E rings and total synthesis of miroestrols are under investigation.

4. Experimental section

4.1. General

IR spectra were recorded on a JASCO FT/IR-300E and FT/IR-6300 spectrophotometer; ATR=attenuated total reflectance system. ^1H NMR spectra were recorded in $CDCl_3$ on JEOL JNM-GSX400A (400 MHz), JNM-ECP400 (400 MHz), JNM-ECX400 (400 MHz), JNM-GSX500A (500 MHz), JNM-ECP600 (600 MHz) or Bruker Biospin-AVANCE 400 (400 MHz) using tetramethylsilane (0.00 ppm) or residual chloroform ($CHCl_3$) (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ on JEOL JNM-ECP400 (100 MHz), JNM-ECX400 (100 MHz), JNM-GSX500A (125 MHz), JNM-ECP600 (150 MHz) or Bruker Biospin-AVANCE 400 (100 MHz) using the middle resonance of $CDCl_3$ (77.0 ppm) as an internal standard; δ in parts per million, J in hertz, dif.=diffused. Optical rotations were measured with a Jasco DIP-140 or P-1030 polarimeter as a chloroform solution. EIMS were recorded on a JEOL GC-Mate with direct inlet. FABMS were recorded on a JEOL JMS-HX110 with *m*-nitrobenzyl alcohol as a matrix. FT-ICR-MS were recorded on a Bruker Daltonics apex-Qe 9.4 T with direct inlet. For TLC was used TLC plates Silica gel 60 F_{254} (Merck No. 5715) and for column chromatography Silica gel 60, spherical, particle size 63–210 μm (Kanto Chemical No. 37564-85 for normal, No. 37565-84 for neutral). Microwave (MW) irradiation was done in a CEM Discover system in a sealed tube. Biotage Horizon system was used for flash chromatography. Anhydrous dichloromethane (CH_2Cl_2) and diethyl

Table 3
Trials for Cope rearrangement of **18** under dehydration condition[a]



Run	Reagents	Solvent	Conditions	Results
1	MsCl, Et_3N, DMAP	CH_2Cl_2	−20 °C to reflux, 6 h	**12** (25%), **34** (16%)
2	Burgess reagent	Benzene	rt, 18 h	**12** (26%), **35** (13%)

[a] A diastereomeric mixture of **18** (18*R*/18*S*=1:2) was used as a substrate.

ether (Et_2O) were purchased from Kanto Chemicals and Wako Pure Chemical. Anhydrous tetrahydrofuran (THF) was purchased from Wako Pure Chemical. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from Kanto Chemicals. Burgess reagent [$(C_2H_5)_3N^+SO_2N^-CO_2CH_3$], a THF solution of 2-methylallylmagnesium chloride, a hexane solution of potassium bis(trimethylsilyl)amide (KHMDS), a THF solution of lithium triethylborohydride ($LiEt_3BH$), and a heptane solution of diethylaluminum chloride (Et_2AlCl) were purchased from Aldrich. A hexane solution of dimethylaluminum chloride (Me_2AlCl) was purchased from Kanto Chemicals.

4.1.1. *(1S,5R)-5-Isopropenyl-2-methyl-1-(2-methyl-2-propen-1-yl)-2-cyclohexen-1-ol (**20b**)*

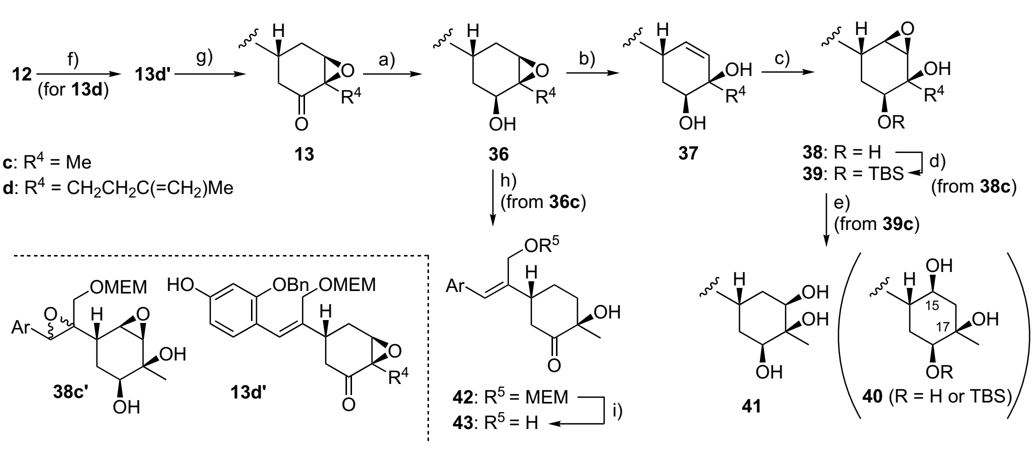
2-Methylallylmagnesium chloride (0.5 M solution in THF, 8.90 mL, 4.45 mmol) was added to a solution of (*R*)-carvone (**4b**, 556 mg, 4.70 mmol) in THF (2 mL) at −78 °C and the whole was stirred at −78 °C for 30 min. Satd aq NH_4Cl and H_2O were added and the whole was extracted with Et_2O. The organic layer was washed with H_2O and brine, successively, and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by column chromatography (CC, *n*-hexane/AcOEt=11:1) to give **20b** as a colorless oil (586 mg, 77%) and the corresponding diastereoisomer (32 mg, 4%).

$[\alpha]_D^{23}$ −59.6 (*c* 1.0). IR (neat, cm^{-1}): 3452. ^1H NMR (400 MHz) δ: 1.48 (1H, ddd, *J*=12.5, 12.5, 1.1 Hz, H-6), 1.68 (1H, s, OH, exchangeable with D_2O), 1.73 (3H, br s, Me), 1.75 (3H, ddd, *J*=2.6, 1.4, 1.4 Hz, Me), 1.85 (3H, br s, Me), 1.97 (1H, dddq, *J*=17.8, 10.7, 2.6, 2.6 Hz, H-4), 2.05–2.14 (2H, m, H-4 and 6), 2.31 (1H, d, *J*=13.7 Hz, one of CH_2), 2.33–2.40 (1H, m, H-5), 2.45 (1H, d, *J*=13.7 Hz, one of CH_2), 4.73 (2H, br s, $=CH_2$), 4.77 (1H, br s, one of $=CH_2$), 4.94 (1H, dq, *J*=2.4, 1.5 Hz, one of $=CH_2$), 5.44 (1H, ddq, *J*=5.1, 2.6, 1.4 Hz, H-3). ^{13}C NMR (100 MHz) δ: 17.0, 20.4, 24.7, 30.9, 39.5, 40.3, 45.7, 73.9, 109.1, 114.9, 123.2, 138.7, 142.6, 148.7. LRFABMS *m*/*z*:205 [$(M-H)^+$].

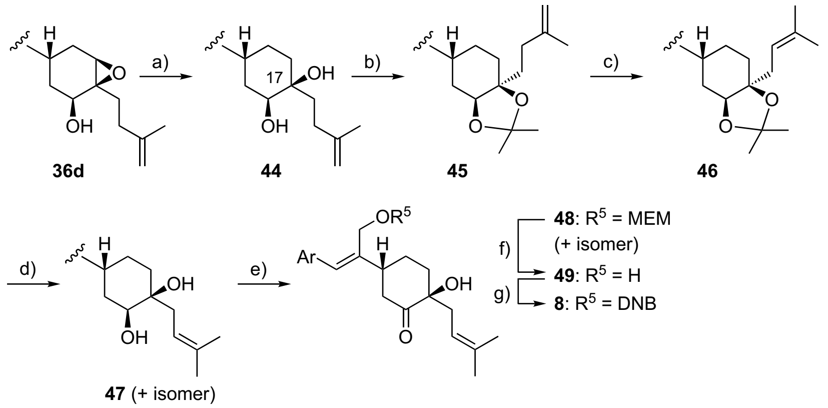
4.1.2. *(4S,6R)-4-Isopropenyl-1-methyl-6-(2-methyl-2-propen-1-yl)-6-trimethylsilanlyloxycyclohexene (**9b**)*

Chlorotrimethylsilane (TMSCl) (0.27 mL, 2.13 mmol) was added to a solution of **20b** (293 mg, 1.42 mmol) and imidazole (192 mg, 2.82 mmol) in DMF (1 mL) and the whole was stirred at rt for 1 h. Satd aq NH_4Cl was added and the whole was extracted with Et_2O. The organic layer was washed with H_2O and brine, successively, and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by CC (neutral SiO_2, hexane/Et_2O=20:1) to give **9b** as a colorless oil (388 mg, 98%).

$[\alpha]_D^{23}$ −45.5 (*c* 1.1). IR (neat, cm^{-1}): 1645. ^1H NMR (400 MHz) δ: 0.09 (9H, s, TMS), 1.53 (1H, ddd, *J*=12.7, 12.7, 1.3 Hz, H-5), 1.71 (3H, ddd, *J*=2.5, 1.6, 1.6 Hz, Me), 1.72 (3H, br s, Me), 1.82 (3H, br s, Me), 1.92 (1H, dddq, *J*=17.2, 12.7, 2.5, 2.5 Hz, H-3), 2.05 (1H, ddddq, *J*=17.2, 5.1, 5.1, 1.6, 1.6 Hz, H-3), 2.15 (1H, ddd, *J*=12.7, 2.1, 2.1 Hz, H-5), 2.24 (1H, d, *J*=13.6 Hz, one of CH_2), 2.27–2.35 (1H, m, H-4), 2.44 (1H, d, *J*=13.6 Hz, one of CH_2), 4.66 (1H, m, one of $=CH_2$), 4.70–4.72 (2H, m, $=CH_2$), 4.85 (1H, dq, *J*=2.8, 1.4 Hz, one of $=CH_2$), 5.36 (1H, ddq, *J*=5.1, 3.4, 1.6 Hz, H-2). ^{13}C NMR (100 MHz) δ: 2.05, 17.5, 20.9, 24.3, 31.1, 39.9 (overlapped), 47.6, 77.7, 108.7, 114.3, 122.1, 140.0, 143.8, 149.1. LREIMS *m*/*z*: 279 [$(M+H)^+$], 277 [$(M-H)^+$].



Scheme 7. Trials of introduction of oxygen functionality on positions 15 and 17 and removal of MEM group of **42**. Reagents and conditions: (a) $LiBEt_3H$, THF, 0 °C, 30 min, 90% for **36c**, 93% for **36d**; (b) Al(O*i*-Pr)$_3$, toluene, reflux, 1.5 h, 86% for **37c**, 66% for **37d**; (c) *m*-CPBA, CH_2Cl_2, −30 °C, 16 h, 90% (as a 5:1 mixture of **38c** and **38c′**), 13% for **38d**; (d) TBSOTf, 2,6-lutidine, CH_2Cl_2, −78 °C, 30 min, 60%; (e) $LiAlH_4$, THF, rt, 5 h, 31% for **41c**; (f) TBHP, Triton® B, toluene, rt; (g) TBDPSCl, imidazole, DMF, rt, two steps 90%; (h) (1) $LiAlH_4$, THF, rt, 92%, (2) IBX, DMSO, 60 °C, 90%; (i) PPTS, MEK, MW, 90 °C, 20 min, 42% for **43**, recovery of **42** (32%).



Scheme 8. Isomerization of *exo* **45** to *endo* olefin **46** and introduction of DNB group. Reagents and conditions: (a) $LiAlH_4$, THF, rt, 89%; (b) 2,2-dimethoxypropane, $TsOH\cdot H_2O$, CH_2Cl_2, rt, 97%; (c) $ClRh(PPh_3)_3$, 10% aq EtOH, reflux, 24 h, 88%, **46**/**45**=10:1; (d) $AcOH/H_2O/THF$ (4:1:1), rt, 92%; (e) IBX, DMSO, 60 °C, 90%; (f) PPTS, MEK, MW, 90 °C, 30% for **49**; recovery for **48** (48%); (g) DNBCl, NEt_3, CH_2Cl_2, 0 °C, 96%.

*4.1.3. (3S,5R)-5-Isopropenyl-2-methyl-3-(2-methyl-2-propen-1-yl)-1-trimethylsilanyloxycyclohexene (**10b**)*

Compound **9b** (120 mg, 0.43 mmol) was irradiated under MW condition (300 W) at 250 °C for 5 min. The residue was purified by CC (neutral SiO_2, *n*-hexane/benzene=20:1) to give **10b** as a colorless oil (38 mg, 31%).

$[\alpha]_D^{21}$ +31.1 (*c* 1.3). IR (ATR, cm^{-1}): 1648. ^1H NMR (400 MHz) δ: 0.18 (9H, s, TMS), 1.32 (1H, dddd, *J*=12.8, 12.8, 5.5, 0.8 Hz, H-4), 1.61 (3H, dif. dd, *J*=1.9, 1.6 Hz, Me), 1.68–1.73 (1H, m, H-4), 1.71–1.73 (6H, m, 2×Me), 1.94 (1H, dd, *J*=13.7, 11.1 Hz, one of CH_2), 2.02 (2H, dif. d, *J*=8.1 Hz, H-6), 2.16–2.23 (1H, m, H-3), 2.28 (1H, dif. dd, *J*=13.7, 2.8 Hz, one of CH_2), 2.32–2.40 (1H, m, H-5), 4.67–4.69 (1H, m, one of $=CH_2$), 4.70–4.73 (2H, m, $=CH_2$), 4.76–4.78 (1H, m, one of $=CH_2$). ^{13}C NMR (100 MHz) δ: 0.7, 14.9, 20.8, 22.1, 30.4, 35.5, 36.9 (overlapped), 41.4, 108.7, 112.0, 114.8, 143.4, 144.9, 149.4. LRFABMS *m*/*z*: 277 $[(M-H)^+]$.

*4.1.4. (1S,5R,Z)-5-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-2-methyl-1-(2-methyl-2-propen-1-yl)-2-cyclohexenol (**20a**)*

To a solution of **4a** (1.86 g, 2.70 mmol) in Et_2O (20 mL), 2-methylallylmagnesium chloride[30] (0.9 M solution in Et_2O, 9.00 mL, 8.10 mmol) was added at −78 °C under Ar and the mixture was stirred at −78 °C for 30 min. After the mixture was poured into satd aq NH_4Cl, the whole was diluted with H_2O and extracted with Et_2O. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=3:1) to give **20a** as a colorless oil (1.51 g, 75%).

$[\alpha]_D^{21}$ −34.1 (*c* 1.0). IR (ATR, cm^{-1}): 3485. ^1H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.64 (1H, dd, *J*=12.4, 12.4 Hz, H-6), 1.74 (3H, ddd, *J*=2.2, 2.2, 1.4 Hz, Me), 1.80 (3H, br s, Me), 1.82 (1H, s, OH, exchangeable with D_2O), 2.03–2.23 (3H, m, 2×H-4 and −6), 2.31, 2.44 (each 1H, d, *J*=13.7 Hz, CH_2), 2.64–2.71 (1H, m, H-5), 3.34 (3H, s, OMe), 3.45–3.47 (2H, m, OCH_2CH_2OMe), 3.63–3.66 (2H, m, OCH_2CH_2OMe), 4.06, 4.10 (each 1H, d, *J*=10.5 Hz, CH_2OMEM), 4.66 (2H, s, OCH_2O or CH_2Ph), 4.67 (2H, s, CH_2Ph or OCH_2O), 4.75 (1H, br s, one of $=CH_2$), 4.85 (1H, dq, *J*=2.6, 1.3 Hz, one of $=CH_2$), 5.44 (1H, dq, *J*=4.6, 1.4 Hz, H-3), 6.29 (1H, d, *J*=2.4 Hz, Ar H-3), 6.34 (1H, dd, *J*=8.2, 2.4 Hz, Ar H-5), 6.55 (1H, s, $=CH$), 7.04 (1H, d, *J*=8.2 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=8.1 Hz, Ph), 7.30 (3H, dif. t, *J*=8.0 Hz, Ph), 7.37 (4H, dif. t, *J*=7.2 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.69 (4H, dif. d, *J*=8.1 Hz, Ph). ^{13}C NMR (100 MHz) δ: 17.1, 19.5, 24.7, 26.6, 31.9, 37.8, 40.6, 45.8, 59.0, 65.7, 67.1, 69.8, 71.7, 73.8, 95.4, 104.5, 111.5, 114.9, 119.4, 123.5, 124.8, 127.0, 127.6, 127.8, 128.4, 129.9, 130.4, 132.9, 135.5, 137.0, 138.7, 140.0, 142.8, 156.0, 156.7. HRFABMS: *m*/*z* 785.3627 (calcd for $C_{47}H_{58}KO_6Si$: 785.3640).

*4.1.5. (4R,6S,Z)-4-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-1-methyl-6-(2-methyl-2-propen-1-yl)-6-trimethylsilanyloxycyclohexene (**9a**)*

Compound **9a** was prepared from **20a** by the same procedure for **9b** and was obtained as a colorless oil in 83%.

$[\alpha]_D^{20}$ −29.6 (*c* 1.0). IR (ATR, cm^{-1}): 1603. ^1H NMR (400 MHz) δ: 0.06 (9H, s, TMS), 1.10 (9H, s, *t*-Bu), 1.66 (1H, m, H-5), 1.70 (3H, br s, Me), 1.78 (3H, s, Me), 1.98 (1H, dddq, *J*=17.0, 11.5, 2.9, 2.9 Hz, H-3), 2.14–2.23 (2H, m, H-3 and 5), 2.24, 2.42 (each 1H, d, *J*=13.4 Hz, CH_2), 2.61 (1H, dif. ddd, *J*=11.5, 11.5, 4.8 Hz, H-4), 3.33 (3H, s, OMe), 3.44 (2H, t, *J*=4.7 Hz, OCH_2CH_2OMe), 3.59–3.68 (2H, m, OCH_2CH_2OMe), 4.06, 4.10 (each 1H, d, *J*=10.8 Hz, CH_2OMEM), 4.63–4.66 (1H, m, one of $=CH_2$), 4.65 (2H, s, OCH_2O or CH_2Ph), 4.67, 4.69 (each 1H, d, *J*=7.0 Hz, CH_2Ph or OCH_2O), 4.75 (1H, dq, *J*=1.3, 1.3 Hz, one of $=CH_2$), 5.34–5.36 (1H, m, H-2), 6.32 (1H, d, *J*=2.3 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.2, 2.3 Hz, Ar H-5), 6.54 (1H, s, $=CH$), 7.06 (1H, d, *J*=8.2 Hz, Ar H-6), 7.23–7.32 (5H, m, Ph), 7.37 (4H, dif. t, *J*=7.2 Hz, Ph), 7.44 (2H, dif. t, *J*=7.3 Hz, Ph), 7.71 (4H, dif. d, *J*=8.1 Hz, Ph). ^{13}C NMR (100 MHz) δ: 2.0, 17.5, 19.4, 24.3, 26.5, 32.1, 38.2, 40.2, 47.5, 58.9, 65.8, 66.9, 69.7, 71.6, 77.9, 95.3, 104.3, 111.4, 114.3, 119.4, 122.2, 124.1, 126.9, 127.6, 127.8, 128.3, 129.9, 130.4, 132.9, 135.5, 136.9, 139.8, 140.2, 143.6, 155.9, 156.7. HRFABMS *m*/*z* 857.4030 (calcd for $C_{50}H_{66}KO_6Si_2$: 857.4035).

*4.1.6. Trial for the synthesis of **10a**: (1S,5R,Z)-5-{3-[2-benzyloxy-4-hydroxyphenyl]-1-[(2-methoxyethoxy)methoxy]2-propen-2-yl}-2-methyl-1-(2-methyl-2-propen-1-yl)-2-cyclohexenol (**21**)*

To a solution of **20a** (116 mg, 0.16 mmol) and 18-crown-6 (247 mg, 0.94 mmol) in toluene (1 mL), KHMDS (0.5 M in hexane, 1.00 mL, 0.50 mmol) was added and whole was stirred at −78 °C for 1 h. The temperature was gradually warmed up to refluxed condition within 5 h and the whole was refluxed for further 15.5 h. After cooling to rt, the reaction mixture was poured into satd aq NH_4Cl. The whole was diluted with H_2O and extracted with AcOEt. The organic layer was washed with satd aq NH_4Cl and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=3:2) to give **21** as a colorless oil (21 mg, 26%).

IR (ATR, cm^{-1}): 3413. ^1H NMR (400 MHz) δ: 1.70 (1H, dd, *J*=12.3, 12.3 Hz, H-6), 1.75 (3H, br s, Me), 1.81 (3H, s, Me), 1.99 (1H, br s, OH, exchangeable with D_2O), 2.09–2.24 (3H, m, 2×H-4 and H-6), 2.33, 2.45 (each 1H, d, *J*=13.7 Hz, CH_2), 2.68–2.76 (1H, m, H-5), 3.35 (3H, s, OMe), 3.52 (2H, dif. t, J=4.6 Hz, OCH$_2$C*H*$_2$OMe), 3.68 (2H, dif. t, J=4.6 Hz, OC*H*$_2$CH$_2$OMe), 4.12, 4.16 (each 1H, d, J=10.7 Hz, C*H*$_2$OMEM), 4.70 (2H, s, OCH$_2$O or C*H*$_2$Ph), 4.77, 4.87 (each 1H, s, =CH$_2$), 4.99 (2H, s, C*H*$_2$Ph or OCH$_2$O), 5.47 (2H, br s, H-3 and Ar 4-OH, exchangeable with D$_2$O), 6.35 (1H, dd, J=8.2, 2.3 Hz, Ar H-5), 6.42 (1H, d, J=2.3 Hz, Ar H-3), 6.60 (1H, s, =CH), 7.12 (1H, d, J=8.2 Hz, Ar H-6), 7.28–7.38 (5H, m, Ph). ^{13}C NMR (100 MHz) δ: 17.1, 24.7, 31.7, 37.5, 40.6, 45.9, 59.0, 65.7, 67.1, 70.0, 71.7, 74.0, 95.4, 100.3, 107.0, 115.0, 118.9, 123.6, 125.0, 127.1, 127.8, 128.5, 130.9, 137.0, 138.6, 139.9, 142.8, 156.4, 157.3. HRFABMS *m*/*z*: 531.2687 (calcd for $C_{31}H_{40}NaO_6$: 531.2723).

4.1.7. *(2R,3R,5R,Z)-5-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-2,3-epoxy-2-methylcyclohexanone (**13c**)*

A solution of **4a** (1.05 g, 1.51 mmol), CHP (3.5 M solution in toluene, 4.30 mL, 15.1 mmol), and Triton® B (40% solution in MeOH, 0.13 mL, 0.34 mmol) in toluene (2 mL) was stirred at 0 °C for 1 day. Triton® B (40% solution in MeOH, 0.10 mL, 0.26 mmol) was added at 0 °C and the mixture was stirred at 0 °C for 1 day. After the addition of 10% aq Na$_2$S$_2$O$_3$ at 0 °C, NaCl was added until the aqueous layer was saturated and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO$_4$ and evaporated in vacuo. The residue was purified by CC (*n*-hexane/acetone=8:1) to give **13c** as a colorless oil (928 mg, 87%).

$[\alpha]_D^{22}$ +14.3 (*c* 1.0). IR (ATR, cm^{-1}): 1709. ^{1}H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.39 (3H, s, Me), 2.03 (1H, ddd, J=14.8, 11.5, 1.1 Hz, H-4), 2.16 (1H, dd, J=17.8, 11.5 Hz, H-6), 2.43 (1H, dif. ddd, J=14.8, 4.5, 4.5 Hz, H-4), 2.67 (1H, ddd, J=17.8, 4.5, 1.1 Hz, H-6), 3.04 (1H, dddd, J=11.5, 11.5, 4.5, 4.5 Hz, H-5), 3.34 (3H, s, OMe), 3.43 (1H, dif. dd, J=4.5, 1.1 Hz, H-3), 3.47 (2H, m, OCH$_2$C*H*$_2$OMe), 3.64 (2H, m, OC*H*$_2$CH$_2$OMe), 4.06, 4.09 (each 1H, d, J=11.0 Hz, C*H*$_2$OMEM), 4.66 (4H, s, OCH$_2$O and C*H*$_2$Ph), 6.29 (1H, d, J=2.3 Hz, Ar H-3), 6.35 (1H, dd, J=8.2, 2.3 Hz, Ar H-5), 6.49 (1H, s, =CH), 6.96 (1H, d, J=8.2 Hz, Ar H-6), 7.20 (2H, dif. dd, J=7.8, 1.8 Hz, Ph), 7.29 (3H, dif. t, J=8.0 Hz, Ph), 7.36 (4H, dif. t, J=7.8 Hz, Ph), 7.43 (2H, dif. t, J=7.3 Hz, Ph), 7.69 (4H, dif. d, J=8.0 Hz, Ph). ^{13}C NMR (100 MHz) δ: 15.3, 19.4, 26.5, 29.3, 33.2, 42.6, 58.7, 58.9, 61.4, 65.7, 67.1, 69.8, 71.6, 95.4, 104.6, 118.7, 125.4, 126.9, 127.7, 127.8, 128.5, 129.9, 130.3, 132.8, 135.5, 136.8, 137.8, 156.2, 156.7, 205.6. HREIMS *m*/*z* 706.3263 (calcd for $C_{42}H_{50}O_7Si$: 706.3326).

4.1.8. *Trial for the ring-opening of **13c** with TMSOTf: (3aS,Z)-3-[2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)benzylidene]-6-methyl-2,3,3a,7a-tetrahydro-4H-benzo[b]furan-7-one (**22**)*

To a solution of **13c** (117 mg, 0.17 mmol) in CH$_2$Cl$_2$ (1 mL), 2,6-lutidine (0.06 mL, 0.52 mmol) and TMSOTf (0.06 mL, 0.33 mmol) were added at −78 °C under Ar and the mixture was stirred at −78 °C for 1 h, −40 °C for 1 h, and then 0 °C for 2 h. Satd aq NH$_4$Cl was added and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO$_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/acetone=8:1) to give **22** as a colorless oil (34 mg, 34%).

IR (ATR, cm^{-1}): 1676. ^{1}H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.75 (3H, dd, J=3.2, 1.7 Hz, Me), 2.61–2.79 (2H, m, H-4), 3.38 (1H, br s, H-3a), 4.37 (1H, d, J=7.0 Hz, H-7a), 4.48 (1H, ddd, J=14.0, 2.1, 2.1 Hz, H-2), 4.59 (1H, ddd, J=14.0, 2.4, 1.4 Hz, H-2), 4.67 (2H, s, C*H*$_2$Ph), 6.32 (1H, d, J=2.4 Hz, Ar H-3), 6.37 (1H, dd, J=8.4, 2.4 Hz, Ar H-5), 6.56–6.59 (2H, m, H-5 and =CH), 6.70 (1H, d, J=8.4 Hz, Ar H-6), 7.22 (2H, dif. d, J=7.8 Hz, Ph), 7.31 (3H, dif. t, J=7.5 Hz, Ph), 7.37 (2H, dif. t, J=7.1 Hz, Ph), 7.43 (2H, dif. t, J=7.3 Hz, Ph), 7.69 (4H, dif. d, J=6.6 Hz, Ph). ^{13}C NMR (100 MHz) δ: 15.9, 19.5, 25.8, 26.5, 43.6, 69.3, 70.0, 78.8, 104.8, 112.1, 114.7, 119.0, 127.0, 127.78, 127.84, 128.4, 128.6, 130.0, 132.8, 135.1, 135.5, 136.9, 138.0, 143.5, 156.0, 156.4, 196.8. HRFABMS *m*/*z* 600.2728 (calcd for $C_{39}H_{40}O_4Si$ 600.2696).

4.1.9. *Trial for the ring-opening of **13c** with Al(Oi-Pr)$_3$: (1R,3R,Z)-c-5-[3-{2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-2-methylenecyclohexane-r-1,3-diol (**25**)*

A mixture of **13c** (156 mg, 0.22 mmol) and Al(O*i*-Pr)$_3$ (100 mg, 0.49 mmol) in toluene (2 mL) was stirred at rt for 1 h, 70 °C for 1 h, and then refluxed for 6 h under Ar. After cooling to rt, 10% aq NaOH was added and the mixture was extracted with Et$_2$O. The organic layer was washed with 10% aq NaOH and brine, dried over MgSO$_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/acetone=3:1) to give **25** as a light yellow oil (30 mg, 19%).

$[\alpha]_D^{24}$ −15.5 (*c* 0.5). IR (ATR, cm^{-1}): 3415. ^{1}H NMR (500 MHz) δ: 1.09 (1H, s, *t*-Bu), 1.38 (1H, ddd, J=12.1, 12.1, 12.1 Hz, H-6), 1.53 (1H, ddd, J=13.5, 13.5, 2.8 Hz, H-4), 1.76 (1H, br d, J=5.2 Hz, OH), 1.92 (1H, br s, OH), 2.11 (1H, ddd, J=13.5, 5.3, 2.8 Hz, H-4), 2.27–2.32 (1H, m, H-6), 3.04 (1H, dddd, J=12.1, 12.1, 2.8, 2.8 Hz, H-5), 3.36 (3H, s, OMe), 3.51 (2H, t, J=4.6 Hz, OCH$_2$C*H*$_2$OMe), 3.63–3.67, 3.71–3.75 (each 1H, m, OC*H*$_2$CH$_2$OMe), 4.12 (2H, s, =CH), 4.56 (1H, dd, J=2.8, 2.8 Hz, H-1 or 3), 4.55–4.60 (1H, m, H-3 or 1), 4.67 (4H, s, OCH$_2$O and C*H*$_2$Ph), 5.02, 5.11 (each 1H, d, J=1.5, 1.5 Hz, =CH$_2$), 6.29 (1H, d, J=2.3 Hz, Ar H-3), 6.35 (1H, dd, J=8.2, 2.3 Hz, Ar H-5), 6.52 (1H, s, =CH), 6.99 (1H, d, J=8.2 Hz, Ar H-6), 7.20 (2H, dif. d, J=8.2 Hz, Ph), 7.23–7.30 (3H, m, Ph), 7.36 (4H, t, J=7.8 Hz, Ph), 7.43 (2H, dif. t, J=7.5 Hz, Ph), 7.68 (4H, dif. d, J=8.0 Hz, Ph). ^{13}C NMR (100 MHz) δ: 19.5, 26.6, 35.2, 39.8, 42.4, 59.1, 65.9, 67.2, 69.0, 69.8, 71.9, 73.5, 95.3, 104.8, 107.4, 111.7, 119.5, 124.5, 126.8, 127.6, 127.8, 128.4, 129.9, 130.4, 133.0, 135.5, 137.0, 139.4, 152.2, 156.0, 156.7. HRFABMS *m*/*z* 733.3544 (calcd for $C_{43}H_{54}O_7Si$: 733.3536).

4.1.10. *(1R,2R,3R,5R,Z)- and (1S,2R,3R,5R,Z)-5-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)-methoxy]-2-propen-2-yl}-2,3-epoxy-2-methyl-1-(2-methyl-2-propen-1-yl)cyclohexanol (**27**)*

2-Methylallylmagnesium chloride (0.5 M solution in THF, 8.90 mL, 4.45 mmol) was added to a solution of **13c** (322 mg, 0.46 mmol) in THF (1 mL) at −78 °C and the whole was stirred at −78 °C for 30 min. Satd aq NH$_4$Cl and H$_2$O were added and the whole was extracted with Et$_2$O. The organic layer was washed with H$_2$O and brine, dried over MgSO$_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/Et$_2$O=3:1) to give **27** as a colorless oil (282 mg, 81%, dr 1:1). An aliquot was further purified by CC to give (18*R*)- and (18*S*)-**27**.

Compound (18*R*)-**27**: a colorless oil. $[\alpha]_D^{24}$ +7.5 (*c* 1.1). IR (ATR, cm^{-1}): 3480. ^{1}H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.33 (1H, m H-6), 1.37 (each 3H, s, Me), 1.67–1.74 (2H, m, H-4 and 6), 1.82 (3H, s, Me), 2.20 (1H, d, J=14.1 Hz, one of CH$_2$), 2.30 (1H, br d, J=14.7 Hz, H-4), 2.47 (1H, d, J=14.1 Hz, one of CH$_2$), 2.55 (1H, br t, J=12.3 Hz, H-5), 2.87 (1H, s, OH, exchangeable with D$_2$O), 3.30 (1H, br d, J=1.8 Hz, H-3), 3.36 (3H, s, OMe), 3.48–3.50, 3.65–3.68 (each 2H, s, OC*H*$_2$-C*H*$_2$OMe), 4.04, 4.07 (each 1H, d, J=10.9 Hz, C*H*$_2$OMEM), 4.65 (1H, br s, one of =CH$_2$), 4.66, 4.67 (each 2H, s, C*H*$_2$Ph or OCH$_2$O), 4.81 (1H, br t, J=1.6 Hz, one of =CH$_2$), 6.30 (1H, d, J=2.2 Hz, Ar H-3), 6.34 (1H, dd, J=8.2, 2.2 Hz, Ar H-5), 6.48 (1H, s, =CH), 7.00 (1H, d, J=8.2 Hz, Ar H-6), 7.22 (2H, dif. d, J=7.9 Hz, Ph), 7.29 (3H, dif. t, J=7.9 Hz, Ph), 7.36 (4H, dif. t, J=7.2 Hz, Ph), 7.43 (2H, dif. t, J=7.4 Hz, Ph), 7.69 (4H, dif. d, J=8.0 Hz, Ph). ^{13}C NMR (100 MHz) δ: 19.0, 19.5, 24.4, 26.5, 30.8, 31.3, 41.2, 47.5, 59.0, 62.8, 65.0, 66.2, 67.0, 69.8, 71.2, 71.7, 95.3, 104.6, 111.6, 114.2, 119.3, 124.5, 126.9, 127.0, 127.6, 127.8, 128.4, 129.9, 130.4, 132.9, 135.5, 136.9, 139.7, 142.6, 156.0, 156.7. HRFABMS *m*/*z* 801.3622 (calcd for $C_{47}H_{58}KO_7Si$: 801.3589).

Compound (18*S*)-**27**: a colorless oil. $[\alpha]_D^{24}$ −14.6 (*c* 1.9). IR (ATR, cm^{-1}): 3480. ^{1}H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.32 (each 3H, s, Me), 1.43 (1H, dd, J=12.9, 11.9 Hz, H-6), 1.81 (1H, br d, J=12.9 Hz, H-6), 1.85 (3H, s, Me), 1.88 (1H, dif. ddd, J=14.8, 10.2, 2.0 Hz, H-4), 2.20 (1H, dif. dd, J=14.8, 4.5 Hz, H-4), 2.25 (1H, d, J=13.4 Hz, one of CH$_2$), 2.35 (1H, s, OH, exchangeable with D$_2$O), 2.42 (1H, m, H-5), 2.52 (1H, d, J=13.4 Hz, one of CH$_2$), 3.09 (1H, dd, J=2.0, 2.0 Hz, H-3), 3.34 (3H, s, OMe), 3.46–3.48, 3.64–3.66 (each 2H, m, OCH_2CH_2OMe), 4.03, 4.07 (each 1H, d, *J*=10.6 Hz, CH_2OMEM), 4.66, 4.67 (each 2H, s, CH_2Ph or OCH_2O), 4.82 (1H, br s, one of $=CH_2$), 4.95 (1H, br dd, *J*=1.3, 1.3 Hz, one of $=CH_2$), 6.29 (1H, d, *J*=2.2 Hz, Ar H-3), 6.34 (1H, dd, *J*=8.2, 2.2 Hz, Ar H-5), 6.52 (1H, s, =CH), 7.01 (1H, d, *J*=8.2 Hz, Ar H-6), 7.21 (2H, dif. d, *J*=7.9 Hz, Ph), 7.28 (3H, dif. t, *J*=7.7 Hz, Ph), 7.36 (4H, dif. t, *J*=7.9 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.69 (4H, dif. d, *J*=7.9 Hz, Ph). ^{13}C NMR (100 MHz) δ: 18.9, 19.5, 25.1, 26.5, 31.5, 33.1, 40.5, 43.9, 59.0, 61.7, 62.9, 65.9, 67.1, 69.8, 71.7, 71.9, 95.4, 104.5, 111.6, 115.7, 119.1, 125.1, 127.0, 127.7, 127.8, 128.4, 129.9, 130.3, 132.9, 135.5, 136.9, 139.6, 142.6, 156.1, 156.7. HRFABMS *m*/*z* 762.3927 (calcd for $C_{47}H_{58}O_7Si$: 762.3952).

*4.1.11. (1R,2RS,4R,6R,Z)-4-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-1,6-epoxy-1-methyl-2-(2-methyl-2-propen-1-yl)-2-trimethylsilanyloxylcyclohexane (**17**)*

To a solution of **13c** (2.55 g, 3.64 mmol) in Et_2O (30 mL), 2-methylallylmagnesium chloride (0.9 M solution in Et_2O, 16.0 mL, 14.4 mmol) was added at −78 °C under Ar and the mixture was stirred at −78 °C for 30 min. Satd aq NH_4Cl was added and the mixture was extracted with Et_2O. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated in vacuo to give a crude **27** (3.0 g). TMSCl (1.00 mL, 7.88 mmol) was added to a solution of the crude **27** and imidazole (735 mg, 10.8 mmol) in DMF (10 mL) and the whole mixture was stirred at rt for 4 h. Satd aq NH_4Cl was added and extracted with AcOEt. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=8:1) to give **17** as a colorless oil (2.76 g, 92%, dr 1:1).

IR (ATR, cm^{-1}): 1603. ^1H NMR (400 MHz) δ: 0.10, 0.15 (each 9H, s, 2×TMS), 1.10 (18H, s, 2×*t*-Bu), 1.31–1.47 (1H, m, H-5), 1.33 (6H, s, 2×Me), 1.61–1.75 (5H, m, 2×H-5 and 3×H-3), 1.77, 1.82 (each 3H, s, 2×Me), 2.03 (1H, dif. dd, *J*=12.6, 1.7, 1.7 Hz, H-5), 2.11 (1H, d, *J*=13.8 Hz, one of CH_2), 2.22 (1H, d, *J*=13.3 Hz, one of CH_2), 2.24 (1H, dif. d, *J*=14.5 Hz, H-3), 2.37 (1H, m, H-4), 2.39 (1H, d, *J*=13.8 Hz, one of CH_2), 2.45 (1H, d, *J*=13.3 Hz, one of CH_2), 2.75 (1H, dddd, *J*=12.0, 12.0, 3.2, 3.2 Hz, H-4), 3.08 (1H, dif. d, *J*=1.1 Hz, H-6), 3.09 (1H, dif. d, *J*=2.4 Hz, H-6), 3.33, 3.34 (each 3H, s, 2×OMe), 3.45–3.47 (4H, m, 2×OCH_2CH_2OMe), 3.63–3.66 (4H, m, 2×OCH_2CH_2OMe), 3.99, 4.035, 4.043, 4.07 (each 1H, d, *J*=10.7 Hz, 2×CH_2OMEM), 4.61 (1H, br s, one of $=CH_2$), 4.64, 4.67 (each 4H, m, 2×CH_2Ph and 2×OCH_2O), 4.73 (1H, dif. d, *J*=1.8 Hz, one of $=CH_2$), 4.77 (1H, dif. dd, *J*=1.9, 1.9 Hz, one of $=CH_2$), 4.85 (1H, dif. dd, *J*=2.6, 1.4 Hz, one of $=CH_2$), 6.30, 6.31 (each 1H, d, *J*=2.5 Hz, Ar H-3), 6.35, 6.34 (each 1H, dd, *J*=8.3, 2.5 Hz, 2×Ar H-5), 6.47, 6.49 (each 1H, s, 2 =CH), 7.02, 7.03 (each 1H, d, *J*=8.3 Hz, 2×Ar H-6), 7.23 (4H, dif. d, *J*=7.7 Hz, Ph), 7.25–7.30 (6H, m, Ph), 7.37 (8H, dif. t, *J*=7.2 Hz, Ph), 7.43 (4H, dif. t, *J*=7.2 Hz, Ph), 7.70 (8H, dif. d, *J*=8.0 Hz, Ph). ^{13}C NMR (100 MHz) δ: 2.5, 2.7, 19.5, 19.6, 19.9, 24.5, 25.1, 26.6, 31.2, 32.2, 32.3, 33.2, 41.2, 41.3, 44.2, 51.2, 59.0, 61.4, 61.5, 62.3, 62.6, 66.1, 66.2, 66.9, 67.0, 69.76, 69.80, 71.7, 75.8, 76.5, 95.5, 95.6, 104.4, 104.5, 111.5, 111.6, 114.3, 115.3, 119.2, 119.5, 124.5, 124.6, 127.0, 127.1, 127.6, 127.7, 127.79, 127.80, 128.35, 128.40, 130.0, 130.4, 130.5, 132.95, 132.96, 135.5, 136.9, 137.0, 139.6, 140.1, 142.8, 143.0, 156.0, 156.1, 156.69, 156.72. HRFABMS *m*/*z* 834.4418 (calcd for $C_{50}H_{66}O_7Si_2$: 834.4347).

*4.1.12. Ring-opening of **27** with Al(Oi-Pr)$_3$ (run 1 in Table 1): (1S,3R,5R,Z)-5-{3-[2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(methoxyethoxy)methoxy]-2-propen-2-yl}-2-methylene-1-(2-methyl-2-propen-1-yl)-1,3-cyclohexadiol [(18S)-**28**] and (1R,2R,5S,Z)-5-{3-[2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(methoxyethoxy)methoxy]-2-propen-2-yl}-2-methyl-1-(2-methyl-2-propen-1-yl)-3-cyclohexen-1,2-diol (**29**)*

A mixture of **27** (150 mg, 0.12 mmol) and Al(O*i*-Pr)$_3$ (241 mg, 1.18 mmol) in xylenes (2 mL) was stirred at 115 °C for 3 h and then refluxed for 6 h under Ar. After cooling to rt, 5% aq NaOH was added and the mixture was extracted with AcOEt. The organic layer was washed with 5% aq NaOH and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/acetone=4:1) to give (18*S*)-**28** (14 mg, 9%) and **29** (4 mg, 6%) as a colorless oil, respectively.

Compound (18*S*)-**28**: $[\alpha]_D^{22}$ −9.5 (*c* 1.2). IR (ATR, cm^{-1}): 3496. ^1H NMR (400 MHz) δ: 1.08 (9H, s, *t*-Bu), 1.53 (1H, dd, *J*=12.7, 12.7 Hz, H-6), 1.55–1.68 (1H, m, H-4), 1.82 (4H, s, Me and OH, exchangeable with D_2O), 2.09 (2H, m, H-4 and 6), 2.22 (1H, s, OH, exchangeable with D_2O), 2.61, 2.78 (each 1H, d, *J*=13.5 Hz, CH_2), 3.04 (1H, m, H-5), 3.35 (3H, s, OMe), 3.49–3.53, 3.64–3.74 (each 2H, m, OCH_2CH_2OMe), 4.10 (2H, s, CH_2OMEM), 4.58 (1H, br s, H-3), 4.68 (4H, s, OCH_2O and CH_2Ph), 4.82, 4.92 (each 1H, br s, $=CH_2$), 5.09, 5.29 (each 1H, d, *J*=1.4 Hz, $=CH_2$), 6.28 (1H, d, *J*=2.2 Hz, Ar H-3), 6.34 (1H, dd, *J*=8.3, 2.2 Hz, Ar H-5), 6.55 (1H, s, =CH), 7.02 (1H, d, *J*=8.3 Hz, Ar H-6), 7.19–7.30 (5H, m, Ph), 7.36 (4H, dif. t, *J*=7.3 Hz, Ph), 7.43 (2H, dif. t, *J*=7.2 Hz, Ph), 7.68 (4H, dif. d, *J*=7.3 Hz, Ph). ^{13}C NMR (100 MHz) δ: 19.5, 24.8, 26.6, 34.8, 40.1, 46.5, 48.2, 59.1, 65.8, 67.1, 69.8, 71.9, 74.0, 74.2, 95.3, 104.7, 111.6, 112.4, 115.3, 119.5, 124.8, 126.8, 127.6, 127.8, 128.4, 129.9, 130.4, 133.0, 135.5, 137.0, 139.5, 143.8, 152.9, 156.0, 156.7. HRFABMS *m*/*z* 801.3622 (calcd for $C_{47}H_{58}KO_7Si$: 801.3589).

Compound **29**: IR (ATR, cm^{-1}): 3494. ^1H NMR (400 MHz) δ: 1.10 (9H, s, *t*-Bu), 1.20 (3H, s, Me), 1.55 (1H, dd, *J*=14.0, 10.7 Hz, H-6), 1.87 (3H, s, Me), 2.07 (1H, d, *J*=13.3 Hz, one of CH_2), 2.22 (1H, dd, *J*=14.0, 5.6 Hz, H-6), 2.35 (1H, s, 1-OH, exchangeable with D_2O), 2.64 (1H, d, *J*=13.3 Hz, one of CH_2), 2.80 (1H, s, 2-OH, exchangeable with D_2O), 3.23–3.28 (1H, m, H-5), 3.34 (3H, s, OMe), 3.48, 3.66 (each 2H, dif. t, *J*=4.5 Hz, OCH_2CH_2OMe), 4.04, 4.12 (each 1H, d, *J*=10.6 Hz, CH_2OMEM), 4.65, 4.68 (2H, s, OCH_2O or CH_2Ph), 4.79, 5.01 (each 1H, s, $=CH_2$), 5.58 (1H, dd, *J*=10.2, 2.4 Hz, H-3), 5.65 (1H, br d, *J*=10.2 Hz, H-4), 6.31 (1H, d, *J*=2.2 Hz, Ar H-3), 6.36 (1H, dd, *J*=8.2, 2.2 Hz, Ar H-5), 6.55 (1H, s, =CH), 7.06 (1H, d, *J*=8.2 Hz, Ar H-6), 7.24–7.32 (5H, m, Ph), 7.37 (4H, dif. t, *J*=7.5 Hz, Ph), 7.44 (2H, dif. t, *J*=7.3 Hz, Ph), 7.71 (4H, dif. d, *J*=6.8 Hz, Ph). ^{13}C NMR (100 MHz) δ: 19.5, 24.6, 25.7, 26.5, 38.1, 38.9, 42.2, 59.0, 66.2, 67.0, 69.7, 71.7, 72.5, 74.5, 95.4, 104.4, 111.6, 116.0, 119.1, 126.1, 126.9, 127.7, 127.8, 128.3, 129.1, 129.9, 130.1, 132.9, 134.6, 135.5, 136.9, 139.6, 142.8, 156.1, 156.7. HRFABMS *m*/*z* 801.3533 (calcd for $C_{47}H_{58}KO_7Si$: 801.3589).

*4.1.13. Ring-opening of **17** with Al(Oi-Pr)$_3$ (run 2 in Table 1): (1R,3S,5R,Z)-5-{3-[2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-3-(2-methyl-2-propen-1-yl)-2-methylene-3-trimethylsilanyloxy-1-cyclohexanol [(18S)-**18**] and (1R,5S,2E,Z)-5-{3-[2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(methoxyethoxy)methoxy]-2-propen-2-yl}-2-isopropyloxymethyl-3-(2-methyl-2-propen-1-yl)-2-cyclohexen-1-ol (**30**)*

A mixture of **17** (108 mg, 0.13 mmol) and Al(O*i*-Pr)$_3$ (161 mg, 0.79 mmol) in xylenes (1 mL) was refluxed for 7 h under Ar. After cooling to rt, satd aq NH_4Cl was added and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=4:1 to 2:1) to give (18*S*)-**18** (29 mg, 27%) and **30** (13 mg, 13%) as a colorless oil, respectively, with recovery of (18*R*)-**17** (29 mg, 27%).

Compound (18*S*)-**18**: $[\alpha]_D^{20}$ −9.5 (*c* 1.3). IR (ATR, cm^{-1}): 3466. ^1H NMR (400 MHz) δ: 0.08 (9H, s, TMS), 1.09 (9H, s, *t*-Bu), 1.45 (1H, ddd, *J*=13.5, 13.5, 2.7 Hz, H-6), 1.64 (1H, dd, *J*=12.3, 12.3 Hz, H-4), 1.74 (1H, s, OH), 1.80 (3H, s, Me), 2.09 (1H, ddd, *J*=13.5, 5.3, 2.7 Hz, H-6), 2.16 (1H, ddd, *J*=12.3, 2.3, 2.3 Hz, H-4), 2.55, 2.61 (each 1H, d, *J*=13.8 Hz, CH_2), 3.00 (1H, m, H-5), 3.34 (3H, s, OMe), 3.45–3.52 (2H, m, OCH_2CH_2OMe), 3.62–3.74 (2H, m, OCH_2CH_2OMe), 4.09, 4.13 (each 1H, d, *J*=10.6 Hz, CH_2OMEM), 4.52 (1H, br d, *J*=2.7, 2.7 Hz, H-1), 4.66–4.70 (1H, m, one of $=CH_2$), 4.66 (2H, s, CH_2Ph), 4.70 (2H, s, OCH_2O), 4.79 (1H, br dd, *J*=2.7, 1.3 Hz, one of $=CH_2$), 5.08 (1H, d, *J*=2.3 Hz, one of $=CH_2$), 5.27 (1H, d, *J*=2.3 Hz, one of $=CH_2$), 6.31 (1H, d, *J*=2.3 Hz, Ar

H-3), 6.35 (1H, dd, J=8.3, 2.3 Hz, Ar H-5), 6.53 (1H, s, =CH), 7.04 (1H, d, J=8.3 Hz, Ar H-6), 7.22 (2H, dif. d, J=7.7 Hz, Ph), 7.25–7.31 (3H, m, Ph), 7.37 (4H, dif. t, J=7.4 Hz, Ph), 7.43 (2H, dif. t, J=7.3 Hz, Ph), 7.70 (4H, dif. d, J=6.4 Hz, Ph). ^{13}C NMR (100 MHz) δ: 2.7, 19.5, 24.7, 26.6, 35.0, 39.4, 45.6, 49.7, 59.0, 66.0, 67.0, 69.7, 71.8, 73.6, 79.1, 95.4, 104.5, 111.5, 113.8, 114.0, 119.4, 124.4, 127.0, 127.6, 127.8, 128.4, 129.9, 130.5, 132.9, 135.5, 136.9, 139.8, 145.0, 152.3, 156.0, 156.7. HRFABMS m/z 834.4340 (calcd for $C_{50}H_{66}O_7Si_2$: 834.4347).

Compound **30**: IR (ATR, cm^{-1}): 3471. ^{1}H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.17, 1.20 (each 3H, d, J=6.1 Hz, *Me*$_2$CH), 1.60 (1H, ddd, J=13.3, 13.3, 3.9 Hz, H-6), 1.67 (3H, s, Me), 1.94–2.08 (2H, m, H-4 and 6), 2.23 (1H, dd, J=7.4, 4.6 Hz, H-4), 2.76, 2.81 (each 1H, d, J=14.9 Hz, CH_2), 2.79–2.83 (1H, m, H-5), 3.13 (1H, br s, OH), 3.34 (3H, s, OMe), 3.44–3.51 (2H, m, OCH_2CH_2OMe), 3.60–3.67 (2H, m, OCH_2CH_2OMe), 3.94 (1H, dd, J=10.5, 2.0 Hz, one of CH_2), 4.11 (2H, s, CH_2OMEM), 4.29 (1H, d, J=10.5 Hz, one of CH_2), 4.35 (1H, br s, Me_2CH), 4.65 (1H, br s, one of =CH_2), 4.65–4.70 (1H, m, H-1), 4.67 (2H, s, CH_2Ph), 4.68 (2H, s, OCH_2O), 4.73 (1H, br s, one of =CH_2), 6.29 (1H, d, J=2.3 Hz, Ar H-3), 6.35 (1H, dd, J=8.3, 2.3 Hz, Ar H-5), 6.54 (1H, s, =CH), 7.04 (1H, d, J=8.3 Hz, Ar H-6), 7.22 (2H, m Ph), 7.25–7.30 (3H, m, Ph), 7.36 (4H, dif. t, J=7.2 Hz, Ph), 7.43 (2H, dif. t, J=6.9 Hz, Ph), 7.69 (4H, dif. d, J=6.6 Hz, Ph). ^{13}C NMR (100 MHz) δ: 19.5, 22.0, 22.2, 22.6, 26.6, 34.0, 36.3, 36.9, 41.4, 59.0, 66.3, 66.9, 67.8, 68.1, 69.8, 71.8, 71.9, 95.4, 104.7, 111.5, 111.6, 119.7, 124.2, 126.8, 127.6, 127.8, 128.3, 129.9, 130.4, 133.0, 135.6, 136.7, 137.1 (overlapped), 140.6, 142.8, 155.9, 156.7. HRFABMS m/z 843.4005 (calcd for $C_{50}H_{64}KO_7Si$: 843.4058).

4.1.14. *Ring-opening of **17** with dimethylaluminum amide **31** (run 3 in Table 1): (1R,3RS,5R,Z)-5-{3-[2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-3-(2-methyl-2-propen-1-yl)-2-methylene-3-trimethylsilanyloxy-1-cyclohexanol (**18**) and (1R,3R,5R,Z)-5-{3-[2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(methoxyethoxy)methoxy]-2-propen-2-yl}-2-methylene-1-(2-methyl-2-propen-1-yl)-1,3-cyclohexadiol [(R)-**28**]*

To a solution of *N*-cyclohexyl-*N*-isopropylamine (0.12 mL, 0.73 mmol) in benzene (0.5 mL), *n*-BuLi (1.3 M solution in *n*-hexane, 0.57 mL, 0.75 mmol) was slowly added at 0 °C under Ar and the solution was stirred at 0 °C for 10 min. Me_2AlCl (0.94 M in *n*-hexane, 0.80 mL, 0.75 mmol) was slowly added and the solution was stirred at 0 °C for 30 min. To the solution, a solution of **17** (104 mg, 0.13 mmol, dr 1:1) in benzene (1.5 mL) was slowly added at 0 °C and the mixture was stirred at rt for 22 h. Satd aq NH_4Cl was added at 0 °C and the mixture was extracted with AcOEt. The organic layer was washed with satd aq NH_4Cl and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (neutral SiO_2, *n*-hexane/AcOEt=3:1) to give **18** as a light yellow oil (52 mg, 50%, dr 1:3) and (18*R*)-**28** as a brown oil (7 mg, 7%) with recovery of **17** (24 mg, 23%, dr 1:1). An aliquot of **18** was further purified by CC to give (18*R*)-**18** as a colorless oil.

Compound (18*R*)-**18**: $[\alpha]_D^{23}$ −3.1 (*c* 1.0). IR (ATR, cm^{-1}): 3494. ^{1}H NMR (600 MHz) δ: 0.16 (9H, s, TMS), 1.10 (9H, s, *t*-Bu), 1.57 (1H, ddd, J=13.2, 13.2, 2.8 Hz, H-6), 1.64 (1H, dd, J=13.7, 12.6 Hz, H-4), 1.93 (1H, ddd, J=13.7, 2.8, 2.8 Hz, H-4), 2.16 (1H, ddd, J=13.2, 5.8, 3.6 Hz, H-6), 2.40, 2.61 (each 1H, d, J=16.7 Hz, CH_2), 3.17 (1H, dddd, J=12.6, 12.6, 3.3, 3.3 Hz, H-5), 3.33 (3H, s, OMe), 3.46 (2H, t, J=4.7 Hz, OCH_2CH_2OMe), 3.62–3.68 (2H, m, OCH_2CH_2OMe), 4.05 (1H, d, J=8.7 Hz, OH, exchangeable with D_2O), 4.08, 4.10 (each 1H, d, J=10.8 Hz, CH_2OMEM), 4.33 (1H, ddd, J=8.7, 3.3, 3.3 Hz, H-1), 4.33, 4.68 (each 2H, s, OCH_2O or CH_2Ph), 4.87, 4.90 (each 1H, s, =CH_2), 5.10 (1H, d, J=0.8 Hz, one of =CH_2), 5.13 (1H, s, one of =CH_2), 6.30 (1H, d, J=2.4 Hz, Ar H-3), 6.35 (1H, dd, J=8.3, 2.4 Hz, Ar H-5), 6.54 (1H, s, =CH), 7.02 (1H, d, J=8.3 Hz, Ar H-6), 7.22 (2H, dif. d, J=8.2 Hz, Ph), 7.26–7.30 (3H, m, Ph), 7.37 (4H, t, J=7.3 Hz, Ph), 7.43 (2H, dif. t, J=7.3 Hz, Ph), 7.70 (4H, dif. d, J=8.2 Hz, Ph). ^{13}C NMR (125 MHz) δ: 2.4, 19.5, 25.2, 26.5, 32.9, 41.1, 45.2, 47.0, 59.0, 65.9, 66.9, 69.8, 71.7, 75.0, 79.7, 95.4, 104.5, 111.6, 112.6, 115.5, 119.4, 124.9, 127.0, 127.6, 127.8, 128.3, 129.9, 130.4, 132.9, 135.5, 137.0, 139.8, 140.1, 148.2, 156.0, 156.7. HRFABMS m/z 873.3956 (calcd for $C_{50}H_{66}KO_7Si_2$: 873.3984).

Compound (18*R*)-**28**: IR (ATR, cm^{-1}): 3411. ^{1}H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.37 (1H, dd, J=13.4, 13.4 Hz, H-6), 1.52–1.58 (1H, m, H-4), 1.83 (3H, s, Me), 2.12 (1H, ddd, J=13.3, 2.8, 2.8 Hz, H-4), 2.22 (1H, dddd, J=13.4, 2.9, 2.9, 2.9 Hz, H-6), 2.32, 2.63 (each 1H, d, J=13.5 Hz, CH_2), 3.17 (1H, m, H-5), 3.36 (3H, s, OMe), 3.51 (2H, t, J=4.5 Hz, OCH_2CH_2OMe), 3.64–3.76 (2H, m, OCH_2CH_2OMe), 4.10, 4.13 (each 1H, d, J=10.5 Hz, CH_2OMEM), 4.46 (1H, br s, H-3), 4.67, 4.68 (each 2H, s, CH_2Ph or OCH_2O), 4.77 (1H, br s, one of =CH_2), 4.94 (1H, dq, J=1.4, 1.4 Hz, one of =CH_2), 5.09, 5.11 (each 1H, s, =CH_2), 6.29 (1H, d, J=2.3 Hz, Ar H-3), 6.35 (1H, dd, J=8.2, 2.3 Hz, Ar H-5), 6.52 (1H, s, =CH), 7.02 (1H, d, J=8.2 Hz, Ar H-6), 7.22 (2H, dif. d, J=7.9 Hz, Ph), 7.26–7.31 (3H, m, Ph), 7.36 (4H, dif. t, J=7.2 Hz, Ph), 7.43 (2H, dif. t, J=7.3 Hz, Ph), 7.69 (4H, dif. d, J=8.0 Hz, Ph). ^{13}C NMR (100 MHz) δ: 19.5, 25.4, 26.6, 31.9, 40.6, 43.8, 46.7, 59.1, 66.1, 67.0, 69.8, 71.9, 74.0, 75.7, 95.2, 104.7, 111.5, 111.6, 115.6, 119.5, 124.5, 126.9, 127.6, 127.8, 128.4, 129.9, 130.4, 132.9, 135.5, 137.0, 139.9, 142.0, 149.7, 156.0, 156.7. HRFABMS m/z 762.3942 (calcd for $C_{47}H_{58}O_7Si$: 762.3952).

4.1.15. *Ring-opening of **17** with diethylaluminum amide **26**: three-step procedure from **13c** (run 4 in Table 1)*

To a solution of **13c** (279 mg, 0.39 mmol) in Et_2O (3 mL), 2-methylallylmagnesium chloride (0.9 M solution in Et_2O, 1.80 mL, 1.62 mmol) was added at −78 °C under Ar and the mixture was stirred at −78 °C for 30 min. Satd aq NH_4Cl was added and the mixture was extracted with Et_2O. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated in vacuo to give crude **27** as a colorless oil (390 mg). To a solution of crude **27** and imidazole (82 mg, 1.20 mmol) in DMF (1 mL), TMSCl (0.12 mL, 0.95 mmol) was added at rt under Ar and the mixture was stirred for 4 h. Satd aq NH_4Cl was added and the whole was extracted with AcOEt. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated in vacuo to give crude **17** as a colorless oil (349 mg). To a solution of *N*-cyclohexyl-*N*-isopropylamine (0.39 mL, 2.37 mmol) in benzene (0.5 mL), *n*-BuLi (1.3 M solution in *n*-hexane, 1.8 mL, 2.36 mmol) was slowly added at 0 °C under Ar and the solution was stirred at 0 °C for 10 min. Et_2AlCl (1 M solution in heptanes, 2.4 mL, 2.40 mmol) was slowly added and the solution was stirred at 0 °C for 30 min. To the solution, a solution of crude **17** in benzene (1.5 mL) was slowly added at 0 °C and the mixture was stirred at 30 °C for 3 h. 2% Aq HCl was added at 0 °C and the mixture was extracted with AcOEt. The organic layer was washed with 2% aq HCl and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (neutral SiO_2, *n*-hexane/AcOEt=3:1) to give **18** as a light yellow oil (242 mg, 74%, dr 1:2).

4.1.16. *MW-irradiated Cope rearrangement of **18** in DMF (run 8 in Table 2): (R,Z)-5-{3-[2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)-phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-2-(3-methyl-3-buten-1-yl)-2-cyclohexen-1-one (**12**)*

5-mL portions of a solution of **18** (7.50 g, 8.97 mmol, dr 1:2) in DMF (100 mL) were irradiated under MW condition (300 W) at 180 °C for 4 min. After cooling to rt, the portions were combined. H_2O was added and the mixture was extracted with AcOEt. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (neutral SiO_2, *n*-hexane/Et_2O=2:1) to give **12** as a light yellow oil (4.60 g, 69%).

$[\alpha]_D^{22}$ −19.1 (*c* 1.0). IR (ATR, cm^{-1}): 1672. ^{1}H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.72 (3H, s, Me), 2.09–2.13 (2H, m, CH_2), 2.31–2.36 (2H, m, CH_2), 2.39–2.46 (1H, m, H-4), 2.45 (1H, dd, J=16.2, 13.8 Hz, H-6), 2.53 (1H, br ddd, J=18.0, 4.9, 4.9 Hz, H-4), 2.66 (1H, br dd, *J*=16.2, 3.1 Hz, H-6), 2.94–3.02 (1H, m, H-5), 3.31 (3H, s, OMe), 3.46 (2H, dif. t, *J*=4.6 Hz, OCH$_2$CH$_2$OMe), 3.64 (2H, dif. t, *J*=4.6 Hz, OCH$_2$CH$_2$OMe), 4.12 (2H, s, CH$_2$OMEM), 4.65 (1H, br s, one of =CH$_2$), 4.67 (4H, s, CH$_2$Ph and OCH$_2$O), 4.70 (1H, br s, one of =CH$_2$), 6.30 (1H, d, *J*=2.3 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.2, 2.3 Hz, Ar H-5), 6.55 (1H, s, =CH), 6.72 (1H, dif. d, *J*=3.8 Hz, H-3), 6.98 (1H, d, *J*=8.2 Hz, Ar H-6), 7.21 (2H, dif. d, *J*=6.4 Hz, Ph), 7.26–7.32 (3H, m, Ph), 7.37 (4H, dif. t, *J*=7.1 Hz, Ph), 7.43 (2H, dif. t, *J*=7.1 Hz, Ph), 7.69 (4H, dif. d, *J*=7.9 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.4, 22.4, 26.5, 27.5, 32.1, 36.6, 40.5, 43.9, 59.0, 65.6, 67.1, 69.8, 71.6, 95.4, 104.6, 110.2, 111.6, 118.8, 125.2, 126.8, 127.7, 127.7, 128.4, 129.9, 130.4, 132.8, 135.5, 136.8, 138.0, 138.8, 144.6, 145.3, 156.2, 156.7, 199.4. HRFABMS *m*/*z* 783.3537 (calcd for C$_{47}$H$_{56}$KO$_6$Si: 783.3483).

*4.1.17. Trial for Cope rearrangement of **18** in the presence of MsCl (run 1 in Table 3): (R,Z)-6-[3-{2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-3-methyl-1,4,4a,5,6,7-hexahydronaphthalen-4a-ol (**34**)*

To a solution of **18** (81 mg, 96 mmol, dr 1:2) in CH$_2$Cl$_2$ (1 mL), pyridine (25 μL, 0.31 mmol) and MsCl (15 μL, 0.19 mmol) were added at 0 °C under Ar and the mixture was stirred at 0 °C for 3.5 h and rt for 7 h. Pyridine (25 μL, 0.31 mmol) and MsCl (15 μL, 0.19 mmol) was added at 0 °C and the mixture was stirred at rt for 14 h. Aq CuSO$_4$ (10%) was added and the mixture was extracted with AcOEt. The organic layer was washed with 10% aq CuSO$_4$, satd aq NaHCO$_3$ and brine, dried over MgSO$_4$, and evaporated in vacuo. The residue was purified by CC (neutral SiO$_2$, *n*-hexane/AcOEt=6:1 to 4:1) to give **12** (18 mg, 25%) and **34** (12 mg, 16%) as a colorless oil, respectively.

Compound **34**: $[\alpha]_{\mathrm{D}}^{24}$ −26.5 (*c* 0.6). IR (ATR, cm^{-1}): 3477. ^{1}H NMR (500 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.68 (3H, s, Me), 1.90 (1H, dd, *J*=12.7, 12.7 Hz, H-5), 1.99–2.12 (3H, m, H-4, 5, and 7), 2.08 (1H, s, OH), 2.21 (1H, dif. ddd, *J*=16.9, 5.3, 5.3 Hz, H-7), 2.48–2.59 (3H, m, H-1, H-4 and 6), 3.07 (1H, br d, *J*=16.9 Hz, H-1), 3.34 (3H, s, OMe), 3.48 (2H, t, *J*=4.8 Hz, OCH$_2$CH$_2$OMe), 3.62–3.70 (2H, m, OCH$_2$CH$_2$OMe), 4.09, 4.13 (each 1H, d, *J*=10.7 Hz, CH$_2$OMEM), 4.69 (4H, s, CH$_2$Ph and OCH$_2$O), 5.45 (1H, br s, H-2), 5.53 (1H, ddd, *J*=5.3, 1.9, 1.9 Hz, H-8), 6.29 (1H, d, *J*=2.2 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.4, 2.2 Hz, Ar H-5), 6.56 (1H, s, =CH), 7.01 (1H, d, *J*=8.4 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=8.2 Hz, Ph), 7.25–7.31 (3H, m, Ph), 7.37 (4H, t, *J*=7.3 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.69 (4H, dif. d, *J*=7.9 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.5, 23.5, 26.5, 31.2, 32.0, 38.8, 42.5, 45.4, 59.0, 65.9, 67.1, 69.8, 71.1, 71.7, 95.5, 104.7, 111.6, 119.4, 120.4, 121.4, 124.6, 126.8, 127.6, 127.8, 128.4, 129.9, 130.4, 131.8, 132.9, 135.5, 136.96, 136.99, 139.8, 156.0, 156.7. HRFABMS *m*/*z* 783.3458 (calcd for C$_{47}$H$_{56}$KO$_6$Si: 783.3483).

*4.1.18. Trial for Cope rearrangement of **18** in the presence of Burgess reagent (run 2 in Table 3): (R,Z)-2-{3-[2-benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-7-methyl-1,2,3,4-tetrahydronaphthalene (**35**)*

A solution of **18** (90 mg, 0.11 mmol) and Burgess reagent (69 mg, 0.29 mmol) in benzene (1 mL) was stirred at rt for 17.5 h under Ar. Satd aq NH$_4$Cl was added and the mixture was extracted with AcOEt. The organic layer was washed with satd aq NH$_4$Cl, H$_2$O, and brine, dried over MgSO$_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=9:1) to give **12** (21 mg, 26%) and **35** (10 mg, 13%) as a colorless oil, respectively.

Compound **34**: $[\alpha]_{\mathrm{D}}^{24}$ −26.5 (*c* 0.6). IR (ATR, cm^{-1}): 1603. ^{1}H NMR (500 MHz) δ: 1.10 (9H, s, *t*-Bu), 1.72 (1H, dddd, *J*=11.1, 11.1, 11.1, 6.2 Hz, H-4), 2.07 (1H, m, H-3), 2.28 (3H, s, Me), 2.65 (1H, dif. t, *J*=11.6 Hz, H-2), 2.77 (1H, m, H-1), 2.80–2.87 (2H, m, H-3 and 4), 2.94 (1H, dd, *J*=16.3, 3.9 Hz, H-1), 3.32 (3H, s, OMe), 3.45 (2H, t, *J*=4.7 Hz, OCH$_2$CH$_2$OMe), 3.64 (2H, t, *J*=4.7 Hz, OCH$_2$CH$_2$OMe), 4.15, 4.17 (each 1H, d, *J*=11.2 Hz, CH$_2$OMEM), 4.67 (2H, s, CH$_2$Ph), 4.69 (2H, s, OCH$_2$O), 6.30 (1H, d, *J*=2.1 Hz, Ar H-3), 6.37 (1H, dd, *J*=8.2, 2.1 Hz, Ar H-5), 6.57 (1H, s, =CH), 6.88 (1H, s, H-8), 6.91 (1H, d, *J*=7.8 Hz, H-6), 6.97(1H, d, *J*=7.8 Hz, H-5), 7.04 (1H, d, *J*=8.2 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=8.2 Hz, Ph), 7.27–7.31 (3H, m, Ph), 7.37 (4H, t, *J*=7.3 Hz, Ph), 7.43 (2H, dif. t, *J*=7.4 Hz, Ph), 7.70 (4H, dif. d, *J*=7.9 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.5, 21.0, 26.6, 28.8, 29.3, 35.9, 39.5, 59.0, 66.2, 67.0, 69.8, 71.7, 95.5, 104.7, 111.6, 119.7, 124.1, 126.4, 126.9, 127.6, 127.8, 128.4, 128.7, 129.6, 129.9, 130.4, 133.0, 133.4, 134.9, 135.6, 136.7, 137.1, 140.9, 155.9, 156.7. HRFABMS *m*/*z* 765.3381 (calcd for C$_{47}$H$_{54}$KO$_5$Si: 765.3378).

*4.1.19. (1S,2S,3R,5S,Z)-5-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-2,3-epoxy-2-methylcyclohexanol (**36c**)*

To a solution of **13c** (535 mg, 0.76 mmol) in THF (5 mL), LiEt$_3$BH (1 M solution in THF, 1.10 mL, 1.10 mmol) was added at 0 °C under Ar and the mixture was stirred at 0 °C for 30 min. Satd aq NaHCO$_3$ was added and the mixture was extracted with CH$_2$Cl$_2$. The organic layer was washed with H$_2$O and brine, dried over MgSO$_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=3:2) to give **36c** as a colorless oil (482 mg, 90%).

$[\alpha]_{\mathrm{D}}^{24}$ −15.4 (*c* 1.0). IR (ATR, cm^{-1}): 3464. ^{1}H NMR (600 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.37 (3H, s, Me), 1.48 (1H, ddd, *J*=13.8, 11.5, 4.9 Hz, H-6), 1.76 (1H, dif. dd, *J*=15.0, 2.2 Hz, H-4), 1.77 (1H, dif. dd, *J*=13.8, 2.1 Hz, H-6), 2.24 (1H, dif. ddd, *J*=15.0, 2.2, 2.2 Hz, H-4), 2.34 (1H, d, *J*=10.4 Hz, OH, exchangeable with D$_2$O), 2.55 (1H, m, H-5), 3.26 (1H, dd, *J*=2.2, 2.2 Hz, H-3), 3.35 (3H, s, OMe), 3.49 (2H, dd, *J*=5.2, 4.1 Hz, OCH$_2$CH$_2$OMe), 3.67 (2H, m, OCH$_2$CH$_2$OMe), 3.91 (1H, ddd, *J*=10.4, 4.2, 4.2 Hz, H-1), 4.05, 4.08 (each 1H, d, *J*=10.7 Hz, CH$_2$OMEM), 4.67 (4H, s, OCH$_2$O and CH$_2$Ph), 6.30 (1H, d, *J*=2.3 Hz, Ar H-3), 6.36 (1H, dd, *J*=8.3, 2.3 Hz, Ar H-5), 6.45 (1H, s, =CH$_2$), 6.99 (1H, d, *J*=8.3 Hz, Ar H-6), 7.21 (2H, dif. d, *J*=7.2 Hz, Ph), 7.25–7.31 (3H, m, Ph), 7.36 (4H, t, *J*=7.3 Hz, Ph), 7.43 (2H, dif. t, *J*=7.4 Hz, Ph), 7.69 (4H, dif. d, *J*=8.3 Hz, Ph). ^{13}C NMR (150 MHz) δ: 19.4, 21.3, 26.5, 30.0, 30.7, 36.1, 59.0, 59.7, 63.0, 66.1, 67.0, 68.2, 69.8, 71.7, 95.3, 104.6, 111.6, 119.2, 124.5, 126.9, 127.6, 127.7, 128.3, 129.9, 130.3, 132.9, 135.5, 136.9, 139.3, 156.0, 156.6. HREIMS *m*/*z* 708.3463 (calcd for C$_{43}$H$_{52}$O$_7$Si: 708.3482).

*4.1.20. (1R,2S,4R,Z)-4-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-1-methyl-5-cyclohexen-1,2-diol (**37c**)*

A mixture of **36c** (301 mg, 0.425 mmol) and Al(O*i*-Pr)$_3$ (133 mg, 0.651 mM) in toluene (3 mL) was refluxed for 1.5 h. After cooling to rt, 10% aq HCl was added and the whole was extracted with CH$_2$Cl$_2$. The organic layer was washed with 10% aq HCl and brine, dried over Na$_2$SO$_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=2:3) to give **37c** as a colorless oil (259 mg, 86%).

$[\alpha]_{\mathrm{D}}^{24}$ −86.1 (*c* 1.0). IR (ATR, cm^{-1}): 3435. ^{1}H NMR (500 MHz) δ: 1.10 (9H, s, *t*-Bu), 1.16 (3H, s, Me), 1.77 (1H, ddd, *J*=13.4, 5.8, 2.8 Hz, H-3), 2.04 (1H, ddd, *J*=13.4, 8.2, 5.5 Hz, H-3), 2.24 (1H, s, OH, exchangeable with D$_2$O), 2.26 (1H, d, *J*=6.4 Hz, OH, exchangeable with D$_2$O), 3.31 (1H, br t, *J*=6.6 Hz, H-4), 3.35 (1H, s, OMe), 3.50 (2H, t, *J*=4.7 Hz, OCH$_2$CH$_2$OMe), 3.62–3.73 (3H, m, OCH$_2$CH$_2$OMe and H-2), 4.08, 4.17 (each 1H, d, *J*=11.9 Hz, CH$_2$OMEM), 4.61, 4.63 (each 1H, d, *J*=11.6 Hz, OCH$_2$O), 4.69, 4.70 (each 1H, d, *J*=7.0 Hz, CH$_2$Ph), 5.68 (1H, dd, *J*=10.0, 1.7 Hz, H-6), 5.72 (1H, dd, *J*=10.0, 3.4 Hz, H-5), 6.30 (1H, d, *J*=2.3 Hz, Ar H-3), 6.36 (1H, dd, *J*=8.3, 2.3 Hz, Ar H-5), 6.42 (1H, s, =CH), 7.01 (1H, d, *J*=8.3 Hz, Ar H-3), 7.23–7.33 (5H, m, Ph), 7.37 (4H, dif. t, *J*=7.2 Hz, Ph), 7.44 (2H, dif. t, *J*=7.3 Hz, Ph), 7.71 (4H, dif. d, *J*=7.9 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.4, 26.4, 26.5, 32.7, 38.0, 58.9, 65.9, 66.9, 69.5, 69.7, 71.3, 71.7, 95.3, 104.3, 111.5, 119.1, 126.2, 127.0, 127.65, 127.72, 128.3, 129.9, 130.1, 130.9, 132.79, 132.80, 135.4, 136.8, 138.2, 156.0, 156.6. HRFABMS *m*/*z*: 731.3337 (calcd for C$_{43}$H$_{52}$NaO$_7$Si: 731.3380).

*4.1.21. (1S,2R,3R,4R,6S,Z)-4-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-2,3-epoxy-1-methylcyclohexan-1,6-diol (**38c**)*

To a solution of **37c** (440 mg, 0.62 mmol) in CH_2Cl_2 (4 mL), *m*-CPBA (65%, 182 mg, 0.69 mmol) was added at −30 °C and the whole was stirred at −30 °C for 16 h. Aq $Na_2S_2O_3$ (10%) was added and the whole was extracted with CH_2Cl_2. The organic layer was washed with 10% aq $Na_2S_2O_3$, satd aq $NaHCO_3$, and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by CC (neutral SiO_2, benzene/AcOEt=3:2) to give **38c** as a colorless oil (406 mg, 90%, **38c**/**38c′**=5:1).

$[\alpha]_D^{24}$ −48.9 (*c* 1.1). IR (ATR, cm^{-1}): 3462. ^1H NMR (500 MHz) δ: 1.11 (9H, s, *t*-Bu), 1.13 (3H, s, Me), 1.65 (1H, ddd, *J*=14.0, 7.3, 3.0 Hz, H-5), 1.90 (1H, ddd, *J*=14.0, 7.0, 7.0 Hz, H-5), 2.73 (1H, d, *J*=11.0 Hz, 6-OH, exchangeable with D_2O), 3.05 (1H, s, 1-OH, exchangeable with D_2O), 3.16–3.19 (2H, m, H-2 and 4), 3.34 (3H, s, OMe), 3.43–3.47 (2H, m, H-3 and 6), 3.49 (2H, t, *J*=4.6 Hz, OCH_2CH_2OMe), 3.65–3.67 (2H, m, OCH_2CH_2OMe), 4.12, 4.21 (each 1H, d, *J*=11.3 Hz, CH_2OMEM), 4.61, 4.62 (each 1H, d, *J*=11.0 Hz, CH_2Ph), 4.70 (2H, s, OCH_2O), 6.33 (1H, d, *J*=2.2 Hz, Ar H-3), 6.38 (1H, dd, *J*=8.3, 2.2 Hz, Ar H-5), 6.47 (1H, s, =CH), 6.99 (1H, d, *J*=8.3 Hz, Ar H-6), 7.21 (2H, dif. d, *J*=7.9 Hz, Ph), 7.28–7.36 (3H, m, Ph), 7.38 (4H, dif. t, *J*=7.7 Hz, Ph), 7.44 (2H, dif. t, *J*=7.3 Hz, Ph), 7.71 (4H, dif. d, *J*=7.9 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.5, 22.9, 26.5, 30.5, 36.1, 59.0, 59.6, 61.1, 66.2, 67.1, 68.6, 70.0, 71.57, 71.64, 95.4, 104.3, 111.6, 118.3, 126.7, 127.4, 127.8, 127.9, 128.5, 130.0, 130.1, 132.8, 135.5, 136.6, 136.8, 156.4, 156.8. LREIMS 724 (M^+).

*4.1.22. (1R,2R,3R,4R,6S,Z)-4-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-6-tert-butyldimethylsilanyloxy-2,3-epoxy-1-methyl-1-cyclohexanol (**39c**)*

To a solution of **38c** (114 mg, 0.16 mmol, **38c**/**38c′**=5:1) in CH_2Cl_2 (2 mL), 2,6-lutidine (0.03 mL, 0.26 mmol) and TBSOTf (0.046 mL, 0.20 mmol) were added at −78 °C and the whole was stirred at −78 °C for 30 min. Satd aq NH_4Cl and H_2O were added and the whole was extracted with AcOEt. The organic layer was washed with satd aq NH_4Cl and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (neutral SiO_2, *n*-hexane/AcOEt=3:1) to give **39c** as a colorless oil (79 mg, 60%).

$[\alpha]_D^{25}$ −58.2 (*c* 1.0). IR (ATR, cm^{-1}): 3548. ^1H NMR (400 MHz) δ: −0.03, −0.02 (each 3H, s, Me-TBS), 0.86 (9H, s, *t*-Bu), 1.09 (9H, s, *t*-Bu), 1.10 (3H, s, Me), 1.47 (1H, ddd, *J*=13.3, 3.8, 3.8 Hz, H-5), 1.85 (1H, ddd, *J*=13.3, 10.4, 5.3 Hz, H-5), 3.04 (1H, d, *J*=3.7 Hz, H-2), 3.05 (1H, s, OH, exchangeable with D_2O), 3.19 (1H, br t, *J*=4.6 Hz, H-4), 3.30 (1H, br d, *J*=4.6 Hz, H-3), 3.35 (3H, s, OMe), 3.47–3.50 (3H, m, OCH_2CH_2OMe and H-6), 3.65–3.68 (2H, m, OCH_2CH_2OMe), 4.11, 4.20 (each 1H, d, *J*=10.8 Hz, CH_2OMEM), 4.66 (2H, s, CH_2Ph), 4.71, 4.72 (each 1H, d, *J*=7.2 Hz, OCH_2O), 6.31 (1H, d, *J*=2.3 Hz, Ar H-3), 6.38 (1H, dd, *J*=8.3, 2.3 Hz, Ar H-5), 6.46 (1H, s, =CH), 7.02 (1H, d, *J*=8.3 Hz, Ar H-6), 7.18 (2H, dif. d, *J*=7.3 Hz, Ph), 7.26–7.29 (3H, m, Ph), 7.37 (4H, dif. t, *J*=7.8 Hz, Ph), 7.44 (2H, t, *J*=7.3 Hz, Ph), 7.70 (4H, dif. d, *J*=8.1 Hz, Ph). ^{13}C NMR (100 MHz) δ: −5.0, −4.4, 17.9, 19.4, 25.7, 25.8, 26.5, 28.3, 37.6, 56.8, 58.3, 58.9, 66.5, 67.0, 68.2, 70.0, 70.8, 71.6, 95.4, 104.4, 111.6, 118.5, 126.7, 127.2, 127.8, 127.9, 128.4, 129.9, 130.2, 132.8, 135.5, 136.3, 136.6, 156.3, 156.8. HRFABMS *m*/*z* 764.4060 (calcd for $C_{47}H_{60}O_7Si$: 764.4108).

*4.1.23. (2S,6R,Z)-t-4-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-1-methylcyclohexan-r-1,c-2,c-6-triol (**41**)*

To a solution of **38c** (105 mg, 0.14 mmol, **38c**/**38c′**=5:1) in THF (1 mL), $LiAlH_4$ (29 mg, 0.70 mmol) was added and the whole was stirred at rt for 4 h. $LiAlH_4$ (29 mg, 0.70 mM) was added and the whole was stirred at rt for further 1 h. Aq HCl (10%) was added under ice-cooling and the whole was CH_2Cl_2. The organic layer was washed with 10% aq HCl and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/acetone=1:1) to give **41** as a colorless oil (32 mg, 31%).

IR (ATR, cm^{-1}): 3383. ^1H NMR (500 MHz) δ: 1.10 (9H, s, *t*-Bu), 1.19 (3H, s, Me), 1.74 (2H, br dd, *J*=12.5, 12.5 Hz, H-3 and 5), 2.11 (2H, br d, *J*=14.3 Hz, H-3 and 5), 2.99 (1H, dddd, *J*=12.5, 12.5, 3.3, 3.3 Hz, H-4), 3.36 (3H, s, OMe), 3.43 (2H, br d, *J*=4.2 Hz, 2- and 6-OH, exchangeable with D_2O), 3.52 (2H, dif. t, *J*=4.6 Hz, OCH_2CH_2OMe), 3.60 (1H, br s, 1-OH, exchangeable with D_2O), 3.69 (2H, dif. t, *J*=4.6 Hz, OCH_2CH_2OMe), 3.79 (2H, br s, H-2 and 6), 4.14 (2H, s, CH_2OMEM), 4.68 (4H, s, OCH_2O and CH_2Ph), 6.30 (1H, d, *J*=2.1 Hz, Ar H-3), 6.36 (1H, dd, *J*=8.2, 2.1 Hz, Ar H-5), 6.55 (1H, s, =CH), 6.98 (1H, d, *J*=8.2 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=7.9 Hz, Ph), 7.26–7.31 (3H, m, Ph), 7.37 (4H, t, *J*=7.2 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.70 (4H, dif. d, *J*=7.9 Hz, Ph). ^{13}C NMR (100 MHz) δ: 19.4, 23.0, 26.5, 28.9, 35.1, 59.1, 65.9, 67.1, 69.8, 71.3, 71.9, 75.8, 95.2, 104.7, 111.7, 119.3, 124.3, 126.8, 127.6, 127.8, 128.3, 129.9, 130.3, 132.9, 135.5, 137.0, 139.4, 156.0, 156.7. HRFABMS *m*/*z* 726.3599 (calcd for $C_{43}H_{54}O_8Si$: 726.3588).

*4.1.24. (2R,3R,5R,Z)-5-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-2,3-epoxy-2-(3-methyl-3-buten-1-yl)cyclohexanone (**13d**)*

A solution of **12** (845 mg, 1.13 mmol), TBHP (2.6 M solution in toluene, 3.0 mL, 7.74 mmol), and Triton® B (40% solution in MeOH, 0.95 mL, 2.27 mmol) was stirred at rt for 22 h. Aq $Na_2S_2O_3$ (10%) was added at 0 °C and the mixture was extracted with AcOEt. The organic layer was washed with 10% aq $Na_2S_2O_3$ and brine, dried over $MgSO_4$, and evaporated in vacuo to give crude **13d′** as a yellow oil (945 mg). To a solution of crude **13d′** and imidazole (243 mg, 3.6 mmol) in DMF (5 mL), TBDPSCl (0.44 mL, 1.69 mmol) was added at rt and the mixture was stirred at rt for 7 h. Satd aq NH_4Cl was added and the mixture was extracted with AcOEt. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=5:1) to give **13d** as a colorless oil (776 mg, 90%).

Compound **13d**: $[\alpha]_D^{24}$ +17.0 (*c* 1.0). IR (ATR, cm^{-1}): 1709. ^1H NMR (500 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.63 (1H, ddd, *J*=13.8, 9.4, 6.8 Hz, one of CH_2), 1.71 (3H, s, Me), 1.98 (1H, ddd, *J*=14.8, 11.7, 0.8 Hz, H-4), 2.06 (1H, dd, *J*=9.4, 6.2 Hz, one of CH_2), 2.07 (1H, dd, *J*=9.4, 6.8 Hz, one of CH_2), 2.12 (1H, dd, *J*=17.6, 12.1 Hz, H-6), 2.25 (1H, ddd, *J*=13.8, 8.7, 6.2 Hz, one of CH_2), 2.45 (1H, ddd, *J*=14.8, 3.0, 3.0 Hz, H-4), 2.66 (1H, ddd, *J*=17.6, 4.4, 1.1 Hz, H-6), 2.99 (1H, dddd, *J*=11.7, 11.7, 4.3, 4.3 Hz, H-5), 3.34 (3H, s, OMe), 3.44 (1H, d, *J*=2.5 Hz, H-3), 3.47 (2H, dif. t, *J*=4.7 Hz, OCH_2CH_2OMe), 3.64 (2H, dif. t, *J*=4.7 Hz, OCH_2CH_2OMe), 4.07, 4.10 (each 1H, d, *J*=11.0 Hz, CH_2OMEM), 4.64 (1H, br s, one of $=CH_2$), 4.66 (2H, s, OCH_2O), 4.67 (2H, s, CH_2Ph), 4.69 (1H, br s, one of $=CH_2$), 6.29 (1H, d, *J*=2.2 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.2, 2.2 Hz, Ar H-5), 6.49 (1H, s, =CH), 6.96 (1H, d, *J*=8.2 Hz, Ar H-6), 7.20 (2H, dif. d, *J*=8.2 Hz, Ph), 7.27–7.32 (3H, m, Ph), 7.37 (4H, t, *J*=7.4 Hz, Ph), 7.43 (2H, dif. t, *J*=7.4 Hz, Ph), 7.69 (4H, dif. d, *J*=8.2 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.4, 22.3, 26.5, 27.3, 29.6, 32.7, 32.9, 43.3, 59.0, 60.1, 60.8, 65.8, 67.1, 69.8, 71.6, 95.4, 104.6, 110.4, 111.6, 118.7, 125.4, 126.9, 127.7, 127.8, 128.4, 129.9, 130.3, 132.8, 135.5, 136.8, 137.7, 145.0, 156.2, 156.7, 204.9. HRFABMS *m*/*z* 799.3465 (calcd for $C_{47}H_{56}KO_7Si$: 799.3432).

*4.1.25. (1S,2S,3R,5S,Z)-5-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-2,3-epoxy-2-(3-methyl-3-buten-1-yl)cyclohexanol (**36d**)*

Compound **36d** was prepared from **13d** by the same procedure as for **36c** and was obtained as a colorless oil in 93%.

$[\alpha]_D^{24}$ −8.0 (*c* 1.0). IR (ATR, cm^{-1}): 3450. ^1H NMR (500 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.39 (1H, ddd, *J*=13.2, 13.2, 4.1 Hz, H-6), 1.65–1.74

(2H, m, H-4 and one of CH_2), 1.71 (3H, s, Me), 1.83 (1H, d, *J*=13.2 Hz, H-6), 1.94 (1H, ddd, *J*=13.8, 10.2, 5.4 Hz, H-4), 2.09–2.19 (2H, m, CH_2), 2.29 (1H, br d, *J*=14.6 Hz, one of CH_2), 2.46 (1H, d, *J*=10.4 Hz, OH, exchangeable with D_2O), 2.54 (1H, dd, *J*=11.5, 11.5 Hz, H-5), 3.30 (1H, br s, H-3), 3.36 (3H, s, OMe), 3.49 (2H, dif. t, *J*=4.5 Hz, OCH_2CH_2OMe), 3.67 (2H, dif. t, *J*=4.5 Hz, OCH_2CH_2OMe), 4.05 (1H br s, H-1), 4.07 (2H, s, CH_2OMEM), 4.67 (4H, s, OCH_2O and CH_2Ph), 4.67, 4.71 (each 1H, s, $=CH_2$), 6.29 (1H, d, *J*=2.3 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.3, 2.3 Hz, Ar H-5), 6.47 (1H, s, =CH), 6.99 (1H, d, *J*=8.3 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=7.0 Hz, Ph), 7.25–7.32 (3H, m, Ph), 7.36 (4H, t, *J*=7.3 Hz, Ph), 7.43 (2H, dif. t, *J*=7.4 Hz, Ph), 7.69 (4H, dif. d, *J*=7.6 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.4, 22.5, 26.5, 29.5, 31.1, 32.6, 33.5, 37.0, 59.0, 62.0, 66.2, 66.5, 67.0, 69.8, 71.7, 95.3, 104.6, 110.2, 111.6, 119.2, 124.5, 126.8, 127.6, 127.8, 128.3, 129.9, 130.4, 132.9, 135.5, 137.0, 139.4, 145.0, 156.0, 156.6. HRFABMS *m*/*z* 762.3939 (calcd for $C_{47}H_{58}O_7Si$: 762.3952).

*4.1.26. (1R,2S,4S,Z)-4-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-1-(3-methyl-3-buten-1-yl)-5-cyclohexen-1,2-diol (**37d**)*

Compound **37d** was prepared from **36d** by the same procedure as for **37c** and was obtained as a colorless oil in 66%.

$[\alpha]_D^{24}$ −62.6 (*c* 1.0). IR (ATR, cm^{-1}): 3417. ^{1}H NMR (500 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.66 (3H, s, Me), 1.66–1.70 (2H, m, CH_2), 1.81 (1H, ddd, *J*=13.4, 5.6, 2.8 Hz, H-3), 2.03–2.10 (3H, m, H-3 and CH_2), 2.28 (1H, d, *J*=6.2 Hz, 2-OH, exchangeable with D_2O), 2.32 (1H, s, 1-OH, exchangeable with D_2O), 3.30–3.35 (1H, m, H-4), 3.35 (3H, s, OMe), 3.49 (2H, t, *J*=4.6 Hz, OCH_2CH_2OMe), 3.60–3.65, 3.67–3.72 (each 1H, m, OCH_2CH_2OMe), 3.77 (1H, ddd, *J*=6.2, 6.2, 2.5 Hz, H-2), 4.08, 4.16 (each 1H, d, *J*=10.8 Hz, CH_2OMEM), 4.62, 4.65 (each 1H, br s, $=CH_2$), 4.65 (2H, s, CH_2Ph), 4.69 (2H, s, OCH_2O), 5.73 (1H, dd, *J*=10.1, 1.7 Hz, H-6), 5.81 (1H, dd, *J*=10.1, 3.5 Hz, H-5), 6.28 (1H, d, *J*=2.2 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.2, 2.2 Hz, Ar H-5), 6.43 (1H, s, =CH), 6.98 (1H, d, *J*=8.2 Hz, Ar H-6), 7.20 (2H, dif. d, *J*=8.1 Hz, Ph), 7.25–7.31 (3H, m, Ph), 7.36 (4H, t, *J*=7.2 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.68 (4H, dif. d, *J*=8.1 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.4, 22.5, 26.5, 31.5, 32.2, 37.2, 38.1, 59.0, 66.0, 67.0, 69.4, 69.7, 71.5, 71.7, 95.4, 104.5, 109.8, 111.6, 119.2, 126.2, 126.8, 127.6, 127.7, 128.3, 129.9, 130.2, 131.3, 132.1, 132.9, 135.5, 136.9, 138.3, 145.9, 156.0, 156.6. HRFABMS *m*/*z* 801.3570 (calcd for $C_{47}H_{58}KO_7Si$: 801.3589).

*4.1.27. (1S,2R,3R,4R,6S,Z)-4-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-2,3-epoxy-1-(3-methyl-3-buten-1-yl)cyclohexan-1,6-diol (**38d**)*

Compound **38d** was prepared from **37d** by the same procedure as for **38c** and was obtained as a colorless oil in 13%.

IR (ATR, cm^{-1}): 3485. ^{1}H NMR (500 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.66 (3H, s, Me), 1.66–1.75 (3H, m, CH_2), 1.88 (1H, ddd, *J*=14.1, 7.1, 7.1 Hz, H-5), 2.09–2.16 (2H, m, H-5 and one of CH_2), 2.73 (1H, d, *J*=11.0 Hz, 6-OH, exchangeable with D_2O), 2.97 (1H, s, 1-OH, exchangeable with D_2O), 3.21 (1H, m, H-3), 3.26 (1H, m, H-2), 3.34 (3H, s, OMe), 3.45–3.49 (3H, m, OCH_2CH_2OMe and H-6), 3.55 (1H, ddd, *J*=15.7, 7.9, 3.5 Hz, H-4), 3.63–3.66 (2H, m, OCH_2CH_2OMe), 4.14, 4.20 (each 1H, d, *J*=11.4 Hz, CH_2OMEM), 4.61, 4.65 (each 1H, br s, $=CH_2$), 4.66 (2H, s, CH_2Ph), 4.68 (2H, s, OCH_2O), 6.29 (1H, d, *J*=2.2 Hz, Ar H-3), 6.37 (1H, dd, *J*=8.2, 2.2 Hz, Ar H-5), 6.48 (1H, s, =CH), 6.95 (1H, d, *J*=8.2 Hz, Ar H-6), 7.16 (2H, dif. d, J=7.9 Hz, Ph), 7.26–7.28 (3H, m, Ph), 7.37 (4H, dif. t, *J*=7.7 Hz, Ph), 7.44 (2H, dif. t, *J*=7.3 Hz, Ph), 7.68 (4H, dif. d, *J*=8.1 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.5, 22.6, 26.6, 29.8, 30.7, 33.8, 36.3, 59.0, 59.7, 60.1, 66.3, 67.1, 69.5, 69.9, 70.1, 71.7, 95.5, 104.6, 110.0, 111.7, 118.5, 126.7, 126.9, 127.8, 127.8, 128.5, 130.0, 130.3, 132.8, 135.5, 136.8, 145.4, 156.4, 156. HRFABMS *m*/*z* 778.3930 (calcd for $C_{47}H_{58}O_8Si$: 778.3901).

*4.1.28. (2R,5R,Z)-5-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)-phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-2-hydroxy-2-methylcyclohexan-1-one (**42**)*

$LiAlH_4$ (36 mg, 0.88 mmol) was placed in a flask and a solution of **36c** (637 mg, 0.90 mmol) in THF (7 mL) was added at 0 °C under Ar. The mixture was stirred at rt for 1 h. Aq HCl (10%) was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with 10% aq HCl and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=5:12) to give diol as a colorless oil (585 mg, 92%).

$[\alpha]_D^{25}$ +8.2 (*c* 1.0). IR (ATR, cm^{-1}): 3417. ^{1}H NMR (500 MHz) δ: 1.10 (9H, s, *t*-Bu), 1.23 (3H, s, Me), 1.42 (1H, dddd, *J*=12.6, 12.6, 12.6, 3.6 Hz, H-5), 1.57 (1H, dif. dd, *J*=12.6, 2.9 Hz, H-6), 1.60 (1H, ddd, *J*=14.2, 11.9, 2.4 Hz, H-3), 1.77–1.82 (1H, m, H-5), 1.84 (1H, dif. ddd, *J*=12.6, 12.6, 3.6 Hz, H-6), 2.02 (1H, ddd, *J*=14.2, 5.7, 3.5 Hz, H-3), 2.57 (1H, br s, 1-OH or 2-OH, exchangeable with D_2O), 2.68 (1H, dddd, *J*=11.9, 11.9, 3.3, 3.3 Hz, H-4), 2.97 (1H, br s, 2-OH or 1-OH, exchangeable with D_2O), 3.35 (3H, s, OMe), 3.48–3.54 (2H, m, OCH_2CH_2OMe), 3.62–3.65 (1H, m, one of OCH_2CH_2OMe), 3.64–3.65 (1H, m, H-2), 3.71–3.75 (1H, m, one of OCH_2CH_2OMe), 4.09, 4.12 (each 1H, d, *J*=10.4 Hz, CH_2OMEM), 4.68 (4H, s, OCH_2O and, CH_2Ph), 6.30 (1H, d, *J*=2.2 Hz, Ar H-3), 6.36 (1H, dd, *J*=8.2, 2.2 Hz, Ar H-5), 6.53 (1H, s, =CH), 7.01 (1H, d, *J*=8.2 Hz, Ar H-6), 7.23 (2H, dif. d, *J*=7.0 Hz, Ph), 7.26–7.30 (3H, m, Ph), 7.36 (4H, t, *J*=7.3 Hz, Ph), 7.42 (2H, dif. t, *J*=7.3 Hz, Ph), 7.70 (4H, dif. d, *J*=7.9 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.4, 24.0, 26.5, 28.6, 34.4, 35.1, 35.4, 58.9, 65.9, 66.9, 69.7, 71.7, 71.8, 73.7, 95.2, 104.6, 111.6, 119.5, 123.9, 126.7, 127.5, 127.7, 128.3, 129.9, 130.3, 132.8, 135.5, 137.0, 140.2, 155.8, 156.6. HREIMS *m*/*z* 710.3624 (calcd for $C_{43}H_{54}O_7Si$: 710.3639).

A solution of diol (276 mg, 0.39 mmol) and IBX (162 mg, 0.58 mmol) in DMSO (3 mL) was stirred at 60 °C for 1 h. After cooling to rt, H_2O was added and the mixture was filtered. The filtrate was extracted with AcOEt. The organic layer was washed with satd aq $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=4:3) to give **42** as a colorless oil (246 mg, 90%).

$[\alpha]_D^{25}$ +8.2 (*c* 1.0). IR (ATR, cm^{-1}): 3494, 1711. ^{1}H NMR (400 MHz) δ: 1.10 (9H, s, *t*-Bu), 1.41 (3H, s, Me), 1.70–1.85 (2H, m, H-3 and 4), 1.99 (1H, dif. d, *J*=14.1 Hz, H-4), 2.17 (1H, ddd, *J*=12.4, 2.7, 2.7 Hz, H-3), 2.59–2.69 (3H, m, H-5 and 2×H-6), 3.33 (3H, s, OMe), 3.47 (2H, dif. t, *J*=4.6 Hz, OCH_2CH_2OMe), 3.64 (2H, dif. t, *J*=4.6 Hz, OCH_2CH_2OMe), 3.99 (1H, s, OH, exchangeable with D_2O), 4.13 (2H, s, CH_2OMEM), 4.67(each 2H, s, OCH_2O or CH_2Ph), 4.68 (each 2H, s, CH_2Ph or OCH_2O), 6.31 (1H, d, *J*=2.4 Hz, Ar H-3), 6.37 (1H, dd, *J*=8.2, 2.4 Hz, Ar H-5), 6.56 (1H, s, =CH), 6.97 (1H, d, *J*=8.2 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=7.5 Hz, Ph), 7.26–7.32 (3H, m, Ph), 7.37 (4H, dif. t, *J*=7.8 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.70 (4H, dif. d, *J*=8.2 Hz, Ph). ^{13}C NMR (100 MHz) δ: 19.5, 25.0, 26.5, 29.0, 40.7, 43.1, 45.1, 59.0, 65.7, 67.1, 69.8, 71.7, 76.1, 95.4, 104.7, 111.7, 118.7, 124.9, 126.8, 127.7, 127.8, 128.4, 130.0, 130.3, 132.8, 135.5, 136.9, 138.2, 156.3, 156.8, 213.7. HRFABMS *m*/*z* 708.3473 (calcd for $C_{43}H_{52}O_7Si$: 708.3482).

*4.1.29. (2R,5R,Z)-5-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)-phenyl]-1-hydroxy-2-propen-2-yl}-2-hydroxy-2-methylcyclohexan-1-one (**43**)*

5-mL portions of a mixture of **42** (2.70 g, 3.77 mmol) and PPTS (4.70 g, 18.8 mmol) in MEK (30 mL) were irradiated under MW condition (300 W) at 90 °C for 10 min. After cooling to rt, the portions were combined. Aq HCl (10%) was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with 10% aq HCl and brine, dried over $MgSO_4$, and evaporated in vacuo to give a light yellow crude oil (3.1 g). 5-mL portions of a mixture of crude oil and PPTS (4.70 g, 18.8 mmol) in MEK (30 mL) were irradiated under MW condition (300 W) at 90 °C for 10 min. After cooling to rt, the portions were combined. Aq HCl (10%) was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with 10% aq HCl and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by flash CC (*n*-hexane/Et_2O=2:3) to give **43** as a light yellow oil (973 mg, 42%) with recovery of **42** (841 mg, 32%).

$[\alpha]_D^{23}$ −0.68 (*c* 1.0). IR (ATR, cm^{-1}): 3452, 1711. ^1H NMR (400 MHz) δ: 1.11 (9H, s, *t*-Bu), 1.41 (3H, s, Me), 1.49 (1H, t, *J*=5.5 Hz, $\mathrm{CH_2O}\mathit{H}$, exchangeable with D_2O), 1.72 (1H, ddd, *J*=12.8, 12.8, 3.5 Hz, H-3), 1.80–1.87, 1.93–1.99 (each 1H, m, H-4), 2.16 (1H, ddd, *J*=12.8, 2.9, 2.9 Hz, H-3), 2.57 (1H, dd, *J*=9.0, 2.1 Hz, H-6), 2.69–2.71 (2H, m, H-5 and 6), 3.96 (1H, s, 2-OH, exchangeable with D_2O), 4.10 (2H, d, *J*=5.5 Hz, $\mathrm{C}\mathit{H}_2\mathrm{OH}$), 4.66 (2H, s, $\mathrm{C}\mathit{H}_2\mathrm{Ph}$), 6.36 (1H, d, *J*=2.3 Hz, Ar H-3), 6.38 (1H, s, =CH), 6.40 (1H, dd, *J*=8.3, 2.3 Hz, Ar H-5), 6.88 (1H, d, *J*=8.3 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=7.3 Hz, Ph), 7.30 (3H, dif. t, *J*=6.2 Hz, Ph), 7.37 (4H, dif. t, *J*=7.1 Hz, Ph), 7.44 (2H, dif. t, *J*=7.3 Hz, Ph), 7.70 (4H, dif. d, *J*=7.8 Hz, Ph). ^{13}C NMR (100 MHz) δ: 19.4, 25.0, 26.5, 29.2, 40.7, 43.2, 45.1, 60.5, 70.3, 76.1 105.1 112.1, 118.7, 123.8 126.8 127.8, 128.1 128.5, 129.98, 130.44, 132.7, 135.5, 136.4, 141.8, 156.1, 156.4, 213.7. HRFTMS *m*/*z* 643.2863 (calcd for $C_{39}H_{44}NaO_5Si$: 643.2850).

*4.1.30. (1R,2S,4S,Z)-4-{3-[2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl]-1-[(2-methoxyethoxy)methoxy]-2-propen-2-yl}-1-(3-methyl-3-buten-1-yl)-cyclohexan-1,2-diol (**44**)*

$LiAlH_4$ (76 mg, 1.84 mmol) was placed in a flask and a solution of **36d** (378 mg, 0.49 mmol) in THF (3 mL) was added at 0 °C under Ar. The mixture was stirred at rt for 1.5 h. Aq HCl (10%) was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with 10% aq HCl and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=2:3) to give **44** as a colorless oil (335 mg, 89%).

$[\alpha]_D^{22}$ +6.6 (*c* 1.0). IR (ATR, cm^{-1}): 3442. ^1H NMR (500 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.40 (1H, dif. ddd, *J*=12.8, 12.8, 12.8 Hz, H-5), 1.57–1.68 (3H, m, H-3, 6 and one of CH_2), 1.74 (3H, s, Me), 1.71–1.79 (3H, m, H-5, 6 and one of CH_2), 2.05 (1H, br d, *J*=15.1 Hz, H-3), 2.11 (2H, t, *J*=8.2 Hz, CH_2), 2.28 (1H, s, 1-OH, exchangeable with D_2O), 2.70 (1H, br t, *J*=15.1 Hz, H-4), 2.74 (1H, s, 1-OH, exchangeable with D_2O), 3.36 (3H, s, OMe), 3.48–3.55 (2H, m, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{OMe}$), 3.61–3.65 (1H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OMe}$), 3.71 (1H, br s, H-2), 3.71–3.79 (1H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OMe}$), 4.09, 4.12 (each 1H, d, *J*=10.6 Hz, $\mathrm{C}\mathit{H}_2\mathrm{OMEM}$), 4.67 (2H, s, $\mathrm{C}\mathit{H}_2\mathrm{Ph}$), 4.68 (2H, s, OCH_2O), 4.70, 4.72 (each 1H, br s, $=CH_2$), 6.30 (1H, d, *J*=2.2 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.2, 2.2 Hz, Ar H-5), 6.52 (1H, s, =CH), 6.99 (1H, d, *J*=8.2 Hz, Ar H-6), 7.23 (2H, dif. d, *J*=7.9 Hz, Ph), 7.25–7.31 (3H, m, Ph), 7.37 (4H, t, *J*=7.5 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.69 (4H, dif. d, *J*=7.3 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.4, 22.7, 26.5, 28.1, 30.7, 31.8, 33.7, 35.1 (overlapped), 59.0, 66.0, 67.0, 69.7, 71.8, 72.7, 73.3, 95.3, 104.6, 109.8, 111.6, 119.5, 124.0, 126.8, 127.6, 127.8, 128.3, 129.9, 130.3, 132.9, 135.50, 137.0, 140.2, 146.1, 155.9, 156.6. HRFABMS *m*/*z* 764.4060 (calcd for $C_{47}H_{60}O_7Si$: 764.4108).

*4.1.31. (1S,2S,4R,Z)-4-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-1,2-(dimethylmethylenedioxy)-1-(3-methyl-3-buten-1-yl)-cyclohexane (**45**)*

A mixture of **44** (1.1 g, 1.47 mmol) and $TsOH \cdot H_2O$ (86 mg, 0.45 mmol) in CH_2Cl_2 (10 mL) was stirred at rt for 30 min. Satd aq $NaHCO_3$ was added and the mixture was extracted with AcOEt. The organic layer was washed satd aq $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by CC (*n*-hexane/AcOEt=8:1) to give **45** as a colorless oil (1.10 g, 97%).

$[\alpha]_D^{18}$ −3.2 (*c* 1.0). IR (ATR, cm^{-1}): 1603. ^1H NMR (500 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.35, 1.52 (each 3H, s, $\mathrm{C}\mathit{Me}_2$), 1.54–1.83 (7H, m, 2×H-3, 2×H-5, 6 and CH_2), 1.74 (3H, s, Me), 2.10, 2.19 (each 1H, ddd, *J*=13.3, 13.3, 4.7 Hz, CH_2), 2.28 (1H, br d, *J*=15.0 Hz, H-6), 2.62 (1H, br dd, *J*=12.1, 12.1 Hz, H-4), 3.34 (3H, s, OMe), 3.47 (2H, dd, *J*=6.4, 3.7 Hz, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{OMe}$), 3.67 (2H, dd, *J*=5.8, 3.7 Hz, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OMe}$), 3.99 (1H, dd, *J*=2.7, 2.7 Hz, H-2), 4.07, 4.11 (each 1H, d, *J*=10.7 Hz, $\mathrm{C}\mathit{H}_2\mathrm{OMEM}$), 4.68 (2H, s, $\mathrm{C}\mathit{H}_2\mathrm{Ph}$), 4.69 (2H, s, OCH_2O), 4.70, 4.72 (each 1H, br s, $=CH_2$), 6.29 (1H, d, *J*=2.3 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.3, 2.3 Hz, Ar H-5), 6.53 (1H, s, =CH), 7.01 (1H, d, *J*=8.3 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=7.0 Hz, Ph), 7.24–7.35 (3H, m, Ph), 7.36 (4H, t, *J*=7.5 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.69 (4H, dif. d, *J*=6.7 Hz, Ph). ^{13}C NMR (125 MHz) δ: 19.5, 22.8, 26.5, 27.1, 28.6, 28.9, 31.6, 32.5, 33.2, 34.4, 36.9, 59.0, 66.0, 66.9, 69.8, 71.7, 77.3, 80.3, 95.3, 104.7, 106.9, 109.5, 111.6, 119.5, 124.2, 126.8, 127.6, 127.8, 128.3, 129.9, 130.4, 132.9, 135.5, 137.0, 140.5, 145.9, 155.9, 156.7. HRFABMS *m*/*z* 804.4449 (calcd for $C_{50}H_{64}O_7Si$: 804.4421).

*4.1.32. (1S,2S,4R,Z)-4-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-1,2-dimethylmethylenedioxy-1-(3-methyl-2-buten-1-yl)cyclohexane (**46**)*

A mixture of **45** (97 mg, 0.12 mmol) and $ClRh(PPh_3)_3$ (23 mg, 25 μM) in degassed 10% aq EtOH (2 mL) was refluxed for 24 h under N_2. After cooling to rt, the mixture was filtered through a Celite pad and the filtrate was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by CC (neutral SiO_2, *n*-hexane/AcOEt=6:1) to give **46** as a brown oil (85 mg, 88%, as 10:1 mixture of **46** and **45**).

$[\alpha]_D^{23}$ −4.3 (*c* 1.0). IR (ATR, cm^{-1}): 1603. ^1H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.22–1.33 (1H, m, H-5), 1.33, 1.50 (each 3H, s, $\mathrm{C}\mathit{Me}_2$), 1.56–1.60 (1H, m, H-6), 1.58 (3H, s, Me), 1.73 (3H, s, Me), 1.70–1.77 (3H, m, 2×H-3 and H-5), 2.25–2.33 (3H, m, H-6 and CH_2), 2.60 (1H, dd, *J*=12.1, 12.1 Hz, H-4), 3.34 (3H, s, OMe), 3.47 (2H, dif. t, *J*=4.7 Hz, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{OMe}$), 3.67 (2H, dif. t, *J*=4.7 Hz, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OMe}$), 3.95 (1H, br s, H-2), 4.07, 4.11 (each 1H, d, *J*=11.0 Hz, $\mathrm{C}\mathit{H}_2\mathrm{OMEM}$), 4.67 (2H, s, $\mathrm{C}\mathit{H}_2\mathrm{Ph}$), 4.68 (2H, s, OCH_2O), 5.29 (1H, t, *J*=7.3 Hz, =CH), 6.29 (1H, d, *J*=2.0 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.3, 2.0 Hz, Ar H-5), 6.52 (1H, s, =CH), 7.01 (1H, d, *J*=8.3 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=7.8 Hz, Ph), 7.26–7.31 (3H, m, Ph), 7.36 (4H, t, *J*=7.3 Hz, Ph), 7.43 (2H, t, *J*=7.3 Hz, Ph), 7.69 (4H, dif. d, *J*=7.8 Hz, Ph). ^{13}C NMR (100 MHz) δ: 18.1, 19.6, 26.0, 26.7, 27.0, 28.7, 29.2, 32.8, 33.8, 34.9, 36.9, 59.1, 66.2, 67.1, 69.9, 71.9, 77.1, 81.0, 95.4, 104.8, 107.1, 111.7, 119.5, 119.7, 124.2, 126.9, 127.7, 127.9, 128.4, 130.0, 130.5, 133.1, 134.2, 135.6, 137.2, 140.7, 156.0, 156.8. HRFTMS *m*/*z* 827.4312 (calcd for $C_{50}H_{64}NaO_7Si$: 827.4314).

*4.1.33. (1S,2S,4R,Z)-4-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-1-(3-methyl-2-buten-1-yl)-cyclohexane-1,2-diol (**47**)*

A solution of **46** (733 mg, 0.91 mmol) in a mixture of AcOH, THF, and H_2O (4:1:1, 14 mL) was stirred at 40 °C for 11 h. After cooling to rt, satd aq $NaHCO_3$ was added at 0 °C and the mixture was extracted with CH_2Cl_2. The organic layer was washed with satd aq $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by CC (neutral SiO_2, *n*-hexane/AcOEt=2:3) to give **47** as a colorless oil (639 mg, 92%).

$[\alpha]_D^{23}$ +7.9 (*c* 1.0). IR (ATR, cm^{-1}): 3428. ^1H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.42 (1H, dif. dd, *J*=11.9, 3.2 Hz, H-5), 1.59–1.65 (2H, m, H-3 and 6), 1.62 (3H, s, Me), 1.71–1.82 (2H, m, H-5 and 6), 1.74 (3H, s, Me), 2.03 (1H, dif. d, *J*=14.2 Hz, H-3), 2.12 (1H, s, 1-OH, exchangeable with D_2O), 2.24 (1H, dd, *J*=14.3, 7.3 Hz, one of CH_2), 2.29 (1H, dd, *J*=14.3, 7.6 Hz, one of CH_2), 2.67 (1H, s, 2-OH, exchangeable with D_2O), 2.70 (1H, dif. dd, *J*=12.6, 12.6 Hz, H-4), 3.35 (3H, s, OMe), 3.50 (2H, dif. t, *J*=4.4 Hz, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{OMe}$), 3.62–3.67 (1H, m, one of $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OMe}$), 3.69–3.78 (2H, m, one of $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OMe}$ and H-2), 4.09, 4.12 (each 1H, d, *J*=11.4 Hz, $\mathrm{C}\mathit{H}_2\mathrm{OMEM}$), 4.67 (2H, s, $\mathrm{C}\mathit{H}_2\mathrm{Ph}$), 4.68 (2H, s, OCH_2O), 5.25 (1H, t, *J*=7.6 Hz, =CH), 6.30 (1H, d, *J*=2.3 Hz, Ar H-3), 6.35 (1H, dd, *J*=8.2, 2.3 Hz, Ar H-5), 6.53 (1H, s, =CH), 7.00 (1H, d, *J*=8.2 Hz, Ar H-6), 7.23 (2H, dif. d, *J*=7.8 Hz, Ph), 7.25–7.31 (3H, m, Ph), 7.36 (4H, t, *J*=7.1 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.69 (4H, dif. d, *J*=8.3 Hz, Ph). ^{13}C NMR (100 MHz) δ: 18.2, 19.6, 26.2, 26.7, 28.4, 32.4, 34.6, 35.1, 35.3, 59.1, 66.2, 67.1, 69.9, 71.9, 72.5, 73.9, 95.4, 104.8, 111.7, 118.1, 119.7, 124.1, 126.9, 127.7, 127.9, 128.4, 130.0, 130.5, 133.1, 135.6, 135.9, 137.2, 140.5, 156.0, 156.8. HRFTMS *m*/*z* 787.4006 (calcd for $C_{47}H_{60}NaO_7Si$: 787.4001).

*4.1.34. (2S,5R,Z)-5-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-{(2-methoxyethoxy)methoxy}-2-propen-2-yl]-2-hydroxy-2-(3-methyl-2-buten-1-yl)-cyclohexan-1-one (**48**)*

Compound **48** was prepared from **47** by the same procedure for **42** and was obtained as a colorless oil in 90%.

$[\alpha]_D^{20}$ +19.5 (*c* 1.0). IR (ATR, cm^{-1}): 3480, 1710. ^{1}H NMR (400 MHz) δ: 1.07 (9H, s, *t*-Bu), 1.59 (3H, s, Me), 1.64 (1H, ddd, *J*=12.9, 12.9, 5.5 Hz, H-3), 1.69 (3H, s, Me), 1.82 (1H, dddd, *J*=14.3, 14.3, 14.3, 3.2 Hz, H-4), 1.96 (1H, dif. d, *J*=14.3 Hz, H-4), 2.24 (1H, ddd, *J*=12.9, 2.8, 2.8 Hz, H-3), 2.38 (1H, dd, *J*=15.6, 7.1 Hz, one of CH_2), 2.55 (1H, dd, *J*=15.6, 8.0 Hz, one of CH_2), 2.58–2.71 (3H, m, H-5 and 2×H-6), 3.33 (3H, s, OMe), 3.47 (2H, dif. t, *J*=4.7 Hz, OCH_2CH_2OMe), 3.64 (2H, dif. t, *J*=4.7 Hz, OCH_2CH_2OMe), 3.90 (1H, s, OH, exchangeable with D_2O), 4.12 (2H, s, CH_2OMEM), 4.31 (4H, s, CH_2Ph and OCH_2O), 5.02 (1H, dd, *J*=7.3, 7.3 Hz, =CH), 6.31 (1H, d, *J*=2.2 Hz, Ar H-3), 6.37 (1H, dd, *J*=8.4, 2.2 Hz, Ar H-5), 6.54 (1H, s, =CH), 6.97 (1H, d, *J*=8.4 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=7.8 Hz, Ph), 7.26–7.32 (3H, m, Ph), 7.37 (4H, t, *J*=7.3 Hz, Ph), 7.44 (2H, dif. t, *J*=7.3 Hz, Ph), 7.69 (4H, dif. d, *J*=7.8 Hz, Ph). ^{13}C NMR (100 MHz) δ: 18.3, 19.6, 26.1, 26.7, 29.0, 36.1, 39.1, 43.6, 45.1, 59.1, 66.0, 67.2, 70.0, 71.8, 78.9, 95.5, 104.8, 111.8, 116.9, 118.8, 125.0, 127.0, 127.9, 127.9, 128.5, 130.1, 130.5, 132.9, 135.6, 135.7, 137.0, 138.4, 156.4, 156.9, 213.5. HRFTMS *m*/*z* 785.3855 (calcd for $C_{47}H_{58}NaO_7Si$: 785.3844).

*4.1.35. (2S,5R,Z)-5-[3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-1-hydroxy-2-propen-2-yl]-2-hydroxy-2-(3-methyl-2-buten-1-yl) cyclohexan-1-one (**49**)*

3-mL portions of a mixture of **48** (2.1 g, 2.71 mmol) and PPTS (2.2 g, 8.79 mmol) in MEK (21 mL) were irradiated under MW condition (300 W) at 90 °C for 6 min. After cooling, the portions were combined. 10% aq HCl was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with 10% aq HCl and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by flash CC (*n*-hexane/Et_2O=2:1) to give **49** as a light yellow oil (539 mg, 30%) with recovery of **48** (1.00 g, 48%).

$[\alpha]_D^{21}$ +7.0 (*c* 1.0). IR (ATR, cm^{-1}): 3460, 1709. ^{1}H NMR (400 MHz) δ: 1.10 (9H, s, *t*-Bu), 1.47 (1H, t, *J*=5.3 Hz, CH_2OH, exchangeable with D_2O), 1.60 (3H, s, Me), 1.65 (1H, dif. ddd, *J*=13.8, 13.8, 5.4 Hz, H-3), 1.69 (3H, s, Me), 1.80–1.95 (2H, m, 2×H-4), 2.23 (1H, ddd, *J*=13.8, 3.1, 3.1 Hz, H-3), 2.39 (1H, dd, *J*=14.8, 7.5 Hz, one of CH_2), 2.54–2.73 (4H, m, H-5, 2×H-6 and one of CH_2), 3.89 (1H, s, 2-OH, exchangeable with D_2O), 4.10 (2H, br d, *J*=5.3 Hz, CH_2OMEM), 4.66 (2H, s, CH_2Ph), 5.02 (1H, dd, *J*=7.2, 7.2 Hz, =CH), 6.35 (1H, d, *J*=2.1 Hz, Ar H-3), 6.38 (1H, s, =CH), 6.40 (1H, dd, *J*=8.2, 2.1 Hz, Ar H-5), 6.88 (1H, d, *J*=8.2 Hz, Ar H-6), 7.22 (2H, dif. d, *J*=7.9 Hz, Ph), 7.28–7.34 (3H, m, Ph), 7.37 (4H, t, *J*=7.3 Hz, Ph), 7.44 (2H, dif. t, *J*=7.4 Hz, Ph), 7.70 (4H, dif. d, *J*=7.6 Hz, Ph). ^{13}C NMR (100 MHz) δ: 18.3, 19.6, 26.1, 26.6, 29.2, 36.1, 39.1, 43.7, 45.1, 60.7, 70.5, 78.9, 105.2, 112.2, 116.9, 118.9, 123.9, 127.3, 127.9, 128.2, 128.6, 130.1, 130.6, 132.9, 135.6, 135.8, 136.6, 142.0, 156.3, 156.5, 213.4. HRFTMS *m*/*z* 697.3329 (calcd for $C_{43}H_{50}NaO_5Si$: 697.3320).

*4.1.36. (1R,4S,Z)-3-{2-Benzyloxy-4-(tert-butyldiphenylsilanyloxy)phenyl}-2-{4-hydroxy-4-(3-methyl-2-buten-1-yl)-3-oxocyclohexyl}-2-propenyl 3,5-dinitrobenzoate (**8**)*

A mixture of **49** (156 mg, 0.23 mmol), 3,5-dinitrobenzoyl chloride (136 mg, 0.59 mmol), and Et_3N (0.10 mL, 0.72 mmol) in CH_2Cl_2 (1 mL) was stirred at 0 °C for 30 min under N_2. Aq HCl (10%) was added at 0 °C and the mixture was extracted with AcOEt. The organic layer was washed with 10% aq HCl, satd aq $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by CC (neutral SiO_2, *n*-hexane/AcOEt=5:1) to give **8** as yellow amorphous (193 mg, 96%).

$[\alpha]_D^{23}$ +27.3 (*c* 1.0). IR (KBr, cm^{-1}): 3494, 1732, 1712. ^{1}H NMR (400 MHz) δ: 1.09 (9H, s, *t*-Bu), 1.58 (3H, s, Me), 1.60–1.70 (1H, m, H-5), 1.68 (3H, s, Me), 1.83 (1H, dif. ddd, *J*=11.8, 11.8, 11.8 Hz, H-6), 2.03 (1H, dif. d, *J*=11.8 Hz, H-6), 2.27 (1H, ddd, *J*=13.4, 3.1, 3.1 Hz, H-5), 2.39 (1H, dd, *J*=14.8, 7.5 Hz, one of CH_2), 2.53 (1H, dd, *J*=14.8, 6.8 Hz, one of CH_2), 2.59–2.68 (3H, m, H-1 and 2×H-2), 3.84 (1H, br s, OH, exchangeable with D_2O), 4.69 (2H, s, CH_2Ph), 4.95, 5.01 (each 1H, d, *J*=12.1 Hz, CH_2ODNB), 4.97–5.02 (1H, m, =CH), 6.34 (1H, br s, Ar H-3), 6.36 (1H, dd, *J*=9.7, 2.3 Hz, Ar H-5), 6.73 (1H, s, =CH), 6.89 (1H, d, *J*=9.7 Hz, Ar H-6), 7.21 (2H, dif. d, *J*=8.2 Hz, Ph), 7.25–7.32 (3H, m, Ph), 7.36 (4H, t, *J*=7.1 Hz, Ph), 7.43 (2H, dif. t, *J*=7.3 Hz, Ph), 7.67 (4H, dif. d, *J*=7.8 Hz, Ph), 9.02 (2H, d, *J*=2.3 Hz, DNB-*ortho*), 9.20 (1H, t, *J*=2.3 Hz, DNB-*para*). ^{13}C NMR (100 MHz) δ: 18.1, 19.4, 25.9, 26.4, 28.9, 35.9, 38.7, 43.2, 44.6, 64.9, 69.9, 78.7, 104.8, 112.0, 116.4, 117.8, 122.4, 126.8, 127.8, 127.8, 128.0, 128.4, 129.2, 129.9, 130.0, 132.6, 133.4, 135.0, 135.4, 135.9, 136.6, 148.5, 156.8, 156.8, 162.3, 212.4. HRFTMS *m*/*z* 891.3271 (calcd for $C_{50}H_{52}N_2NaO_{10}Si$: 891.3283).

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