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Diastereoselective Synthesis of Functionalized 9-Ring Ethers (Oxonins).

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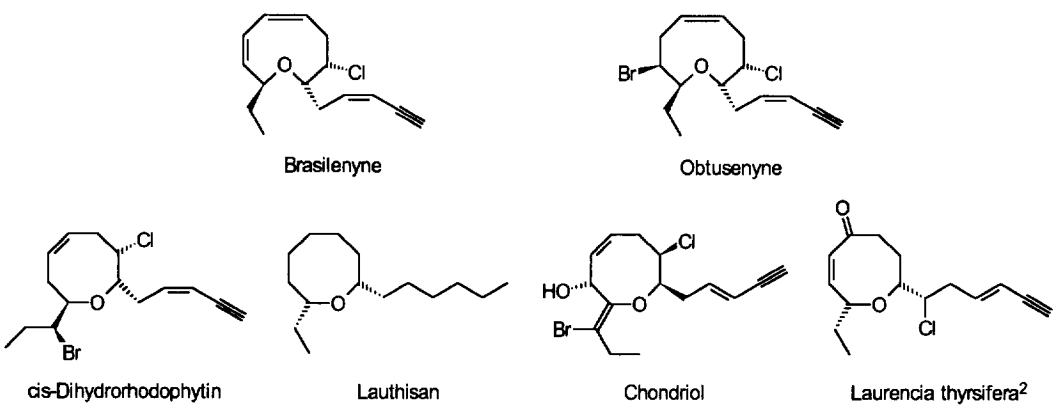
Abstract: In response to the challenge of preparing medium ring ethers of the *Laurencia* class, a simple synthesis of functionalized, acyclic α,α′-chiral disecondary ethers has been developed. Stereocontrolled cyclization to 9-membered rings was effected in overall high yield by Pd(0) catalyzed allylic alkylation.

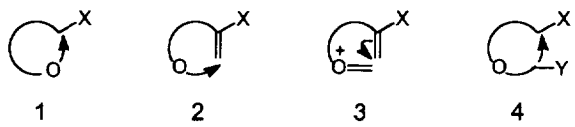
Medium ring ethers, especially 8- and 9-membered rings of the genus *Laurencia* (Scheme 1) have been investigated increasingly in the last few years.[§] Following their isolation, mainly from marine sources[1,2] several total syntheses were reported, including the early work of Masamune,[3] Nicolaou,[4] Overman,[5] Holmes,[6] Paquette,[7] Kotsuki,[8] and Murai.[9] However, neither 9-membered brasilenyne nor obtusenyne have yielded to synthesis at present.



Scheme 1. Medium Ring Ethers from Red Algae

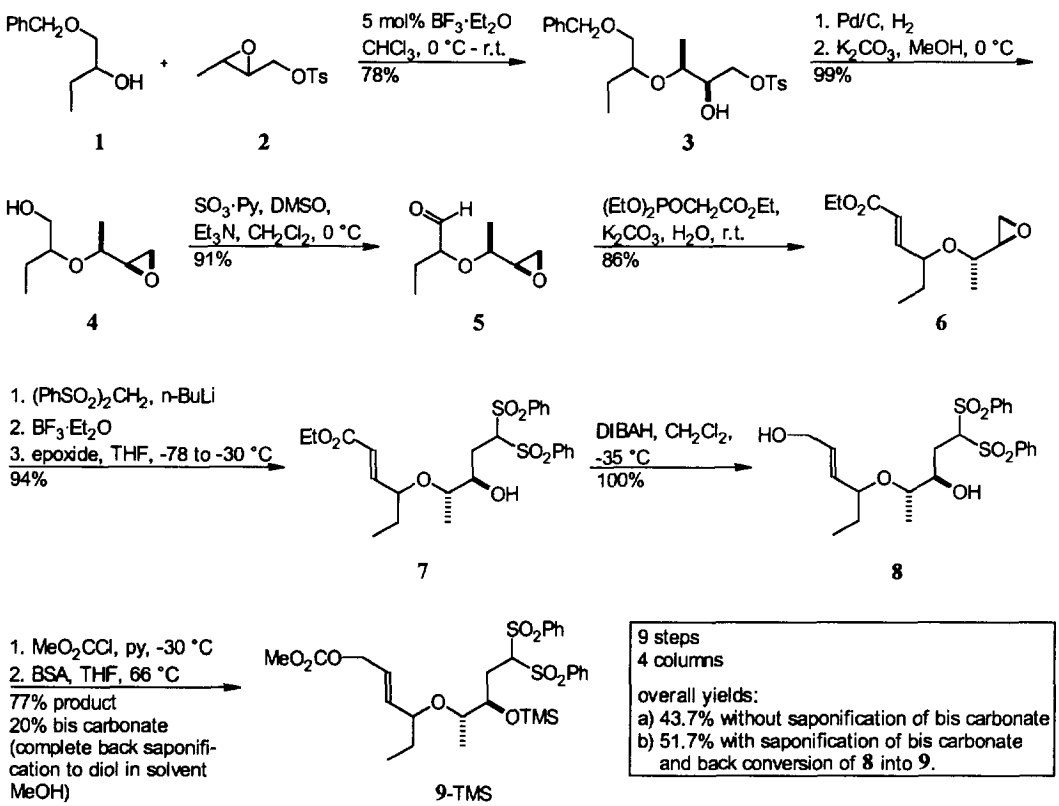
Obstacles to medium ring synthesis are well known and include unfavourable transannular interactions, torsional strain and angle deformations in transition states and products, entropy loss, centres of chirality and additional substituents attached to the ring. Four modes of cyclization can be envisaged (Scheme 2),[10] of which

mode 4 has, to our knowledge, not yet been realized. A prerequisite of mode 4 is the synthesis of acyclic, multifunctionalized, α,α′-disecondary ethers (cf. Scheme 1), which we have accomplished recently.[11]



Scheme 2. Cyclization Modes for Medium Ring Ethers

Starting from simple, racemic model compounds we have developed a flexible route to potential cyclization precursors. Specifically, under BF_3 catalysis epoxy tosylate **2**, readily available from *trans*-crotyl alcohol, and monoprotected butane-1,2-diol **1** combined to hydroxy tosylate **3** in satisfactory yield. Deprotection followed by treatment with base delivered epoxy alcohol **4** in nearly quantitative yield (99%) under mild conditions.



Scheme 3. Synthesis of an Acyclic 9-Ring Precursor (Racemic Starting Materials).

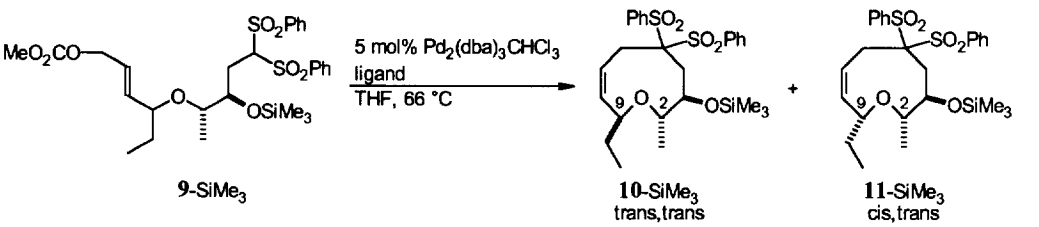
Oxidation of **4** succeeded with SO_3·pyridine in the presence of dimethyl sulfoxide, giving sensitive α-alkoxy aldehyde **5**, which was converted without delay and further purification into α,β-unsaturated ester **6**, using triethyl phosphonoacetate in an aqueous medium.[12] The acyclic ether chain of **6** was extended by one carbon atom, using deprotonated bis(phenylsulfonyl)methane in the presence of BF_3 at low temperature. BF_3 directs the nucleophile regioselectively towards the methylene terminus of the epoxide, in the presence of the Michael acceptor in **6**, which remains unscathed under these conditions. Reduction of the unsaturated ester in **7** with an excess of diisobutylaluminium hydride afforded the acyclic allylic alcohol **8**. Conversion into the carbonate and protection of the secondary alcohol by silylation delivered **9**-TMS.

After a total of 9 steps and only 4 chromatographic separations it was possible to isolate **9**-TMS in multigram quantities (5 g) and excellent overall yield (Scheme 3).

Classical methods for making carbon-carbon bonds (mode 4) are generally ineffective for preparing medium rings.[13] However, Trost has shown[14a] that the minimum in yield, encountered for the formation of medium ring lactones[14b] and medium ring carbocycles,[14c] can be overcome by a palladium(0) catalyzed allylic cyclization.

Starting from bisallylic substrate **9**-TMS, in which the better leaving group, i. e. carbonate, is attached to the primary terminus, we obtained the 9-membered ring in 71 - 88% yield. Best results were obtained by adding **9**-TMS in THF by syringe pump over a period of 8 h to a solution of $Pd_2(dba)_3CHCl_3$ (5 mol%) and ligand in refluxing THF (final concentration of substrate 0.02 M).

Table 1. Intramolecular Allylic Alkylation. Diastereoselective Cyclization *via* Pd(0) Catalyzed Alkylation with a Carbon Nucleophile. Generation of a Cleavable Cyclic Allyl Ether as an Intermediate?



Entry	SiR_3	Solvent	Temp [°C]	Ligand	Yield [%] **10**-SiR_3 + **11**-SiR_3	Ratio **10**-SiR_3/**11**-SiR_3
1	$SiMe_3$	THF	66	dppe, 21 mol%	72 + 16 = 88	4.5 : 1
2	$SiMe_3$	THF	66	$P(OEt)_3$, 50 mol%	66 + 5 = 71	14.3 : 1
3	$SiBu^tMe_2$	THF	66	dppe, 21 mol%	25 + 63 = 88	1 : 2.5
4	$SiBu^tPh_2$	THF	66	dppe, 21 mol%	52 + 32 = 84	1.6 : 1

Formation of 7-membered ring was not observed. The two 9-membered rings **10**-TMS and **11**-TMS are diastereomeric at C(9) and were separated by conventional column chromatography. The relative configuration of the 3 chiral centres in **10**-TMS and **11**-TMS was established spectroscopically by NOE and in light of the Holmes[6d]-Kotsuki[8] correlations, referring to the ^{13}C chemical shifts of the α,α′-disecondary ether carbons (Table 2).

Table 2. ^{13}C NMR Chemical Shifts of Diastereomeric Cyclic 9-Membered Ethers**10**-SiR_3 and **11**-SiR_3.

SiR_3	C(2)/C(9) *trans* **10**	C(2)/C(9) *cis* **11**
$SiMe_3$	73.84/74.95	80.53/81.50
$SiBu^tMe_2$	74.32/75.72	80.13/81.21
$SiBu^tPh_2$	74.11/75.19	79.70/80.39

In the *trans* series **10**-SiR_3 ^{13}C shifts are upfield with respect to the *cis* series **11**-SiR_3.

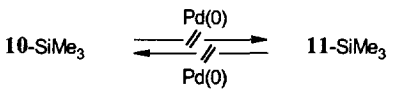
Diastereomeric control was accomplished by the type of ligand and of silyl protecting group. We were surprised to find that epimerization at carbon C(9), which is attached to the ethyl group, was feasible on cyclization (cf. following paper).

In view of the synthesis of natural products (Scheme 1) it is important that the desired *trans* configuration [with respect to C(2) and C(9)] as in series **10** is tunable by proper choice of ligand and protecting group.

Although the **10** : **11** selectivity is somewhat lower for ligand dppe (4.5 : 1) than for ligand $P(OEt)_3$ (14.3 : 1), the overall chemical yield (88%) for dppe is higher than for $P(OEt)_3$ (71%). Thus, the absolute yield of isolated, desired **10**-TMS is highest for dppe.

With TBDMS (≡ $SiBu^tMe_2$) protection of acyclic **9** the diastereomeric ratio of **10**-TBDMS : **11**-TBDMS (1 : 2.5) was reversed in favour of *cis*-2,9-disubstituted cyclic ether. Protection of starting material by highly bulky TBDPS (≡ $SiBu^tPh_2$) continued to provide a good chemical yield of cyclization product (84%), but the diastereoselectivity (1.6 : 1) was low (Table 1).

Control experiments showed that epimerization of diastereomerically pure **10**-TMS as well as **11**-TMS with Pd(0) under cyclizing conditions did not occur. A new diastereomer was not detected (cf. Scheme 4 and following paper).



Scheme 4. *No* Epimerization or Equilibration at C(9) under Cyclization Conditions.

We calculate (MMX) that diastereomers **10** are less stable than diastereomers **11** by ca. 4 kcal mol^{-1}. This result is in agreement with equilibration experiments by Holmes[6d] on 8- and 9-membered ring ethers.

In summary, starting from inexpensive materials we have developed a high yielding, reliable sequence, with a potential for scale up, to functionalized unsaturated nine-membered allylic ethers (oxonins). Stereocontrol of all three chiral centres has been accomplished in the key steps. The less stable diastereomer, as it occurs in brasilenyne and obtusenyne, can be accumulated at the expense of the more stable diastereomer by proper choice of palladium ligand and siloxy group.

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EXPERIMENTAL

General. Melting points: uncorrected, Büchi apparatus. — Infrared spectra: Perkin-Elmer 1710 spectrometer. — ^{1}H NMR spectra: At 80, 90 and 200 MHz, Bruker WP 80, WH 90 or WP 200 SY spectrometer, solvent $CDCl_3$ unless stated otherwise. — ^{13}C NMR spectra: Bruker WP 200 SY at 50 MHz. APT (attached proton test): spin echo base selection of multiplicities of ^{13}C signals. Quaternary C and CH_2 carbon atoms give positive signals (+), while CH and CH_3 give negative signals (-). — MS: Low and high resolution electron impact mass spectra, Finnigan MAT 312 spectrometer, 70 eV, room temperature, unless otherwise stated. Relative intensities in parentheses. — Microanalysis: Department of Organic Chemistry of the University of Hannover. — Preparative column chromatography: J. T. Baker silica gel (particle size 30 - 60 µm). — Analytical TLC: Aluminium-backed 0.2 mm silica gel 60 F_{254} plates (E. Merck). — THF and diethyl ether (E) were distilled from sodium benzophenone ketyl prior to use, CH_2Cl_2 from CaH_2. PE refers to light petroleum, bp 30 - 60 °C, redistilled prior to use.

1-Benzyloxy-2-butanol (**1**). To a solution of 1,2-butanediol (59.8 mL, 667 mmol) in DMF (140 mL) and THF (130 mL) was added NaH (9.59 g, 400 mmol) portionwise at 0 °C. The mixture was stirred for 1 h at r.t., then cooled to ca. -25 °C and benzyl chloride (38.93 g, 308 mmol) in THF (190 mL) was added. The temperature of the solution should be kept below -10 °C. After 2 h the mixture was allowed to reach r.t. and stirred for further 40 h. Then sat. aq. NH_4Cl solution was added and the aqueous layer was extracted with E. The organic phase was dried ($MgSO_4$) and evaporated. The resulting crude product was purified by chromatography (E/PE, 1 : 3) to give **1** (40.2 g, 67%) as a colourless oil. IR ($CHCl_3$) ν 3440, 3424, 3088 - 2876, 1452, 1204, 1028, 992 cm^{-1}; ^{1}H NMR δ 0.95 (t, ^3J = 7 Hz, 3 H, CH_3), 1.49 (dq, ^3J = 1, 7 Hz, C*H*$_2$CH$_3$), 2.36 (d, , ^3J = 3.6 Hz, 1 H, OH), 3.33 (dd, ^3J = 7.5 Hz, ^2J = 9.5 Hz, 1 H, OC*H*HCHOH), 3.53 (dd, ^3J = 3 Hz, ^2J = 9.5 Hz, 1 H, OCH*H*CHOH), 3.76 (m, 1 H, C*H*OH), 4.56 (s, 2 H, PhC*H*$_2$O), 7.36 (m, 5 H, arom. H); ^{13}C NMR (APT) δ 9.93 (-, CH_3), 26.18 (+, C*H*$_2$CH$_3$), 71.61 (-, CHOH), 73.21 (+, OC*H*$_2$CHOH), 74.38 (+, PhC*H*$_2$O), 127.66 (-, arom. C), 128.37 (-, arom. C), 138.09 (+, arom. C); MS *m/z* 180 (M^+, 5), 122 (5), 107 (20), 91 (100).

trans-*2,3-Epoxy-butyl tosylate* (**2**). A flame-dried flask was charged with *trans*-crotyl alcohol (13.58 mL, 160 mmol) in CH_2Cl_2 (400 mL) and *m*-CPBA (43.3 g, 176 mmol, 70%) was added in portions at 0 °C. After 1.5 h $Ca(OH)_2$ (40 g) was added and the mixture was stirred for a further 1 h. The suspension was suction-filtered and the residue was washed with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and evaporated carefully at reduced pressure to afford the epoxy alcohol, 13.48 g (86%, GC-purity: 90%). To a solution of the epoxy alcohol (13.48 g) and NEt_3 (23.14 mL, 166 mmol) in CH_2Cl_2 (100 mL) tosyl chloride (27.63 g, 168 mmol) in CH_2Cl_2 (100 mL) was added dropwise at 0 °C. After 1 h at 0 °C the mixture was allowed to reach r.t and stirred for further 19 h. The organic layer was extracted with aq. H_2SO_4 (5%), aq. $NaHCO_3$ solution, aq. NaCl solution and dried ($MgSO_4$),. The solvent was removed to give a green oil, which was crystallized from PE to afford crystalline **2**, 27.10 g, 79%. IR (KBr) ν 3005 - 2931, 1595, 1494, 1455, 1362, 1307, 1252, 1189, 1173, 1123, 1096, 1019, 968 cm^{-1}; ^{1}H NMR δ 1.30 (d, ^3J = 5 Hz, 3 H, CH_3), 2.46 (s, 3 H, arom. CH_3), 2.90 (m, 2 H, OCH), 3.98 (dd, ^3J = 5.5 Hz, ^2J = 11 Hz, 1 H, OC*H*H), 4.19 (dd, ^3J = 3.8 Hz, ^2J = 11 Hz, 1 H, OCH*H*), 7.37 (d, ^3J = 8 Hz, 2 H, arom. H), 7.81 (d, ^3J = 8 Hz, 2 H, arom. H); MS *m/z* 243 (2), 242 (M^+, 8), 199 (9), 155 (100).

3-[1-(Benzyloxy-2-butoxy]-2-hydroxy-butyl tosylate (**3**). A flame-dried flask was charged with epoxy tosylate **2** (4.07 g, 16.8 mmol) and alcohol **1** (4.84 g, 26.9 mmol) under N_2. CH_2Cl_2 (12.6 mL) was added and the mixture was cooled to 0 °C. $BF_3{\cdot}Et_2O$ (0.21 mL, 1.7 mmol) was added and the reaction mixture was allowed to reach r.t. After stirring for 20 h the solvent was removed and the crude product was purified by chromatography to afford **3**, 5.17 g (78%), viscous oil. The pair of diastereomers could be separated by chromatography (E/PE, 1 : 3) to give non-polar diastereomer (35%, isolated yield) and polar diastereomer (30%, isolated yield). IR ($CHCl_3$) ν 3436, 3065 - 2878, 1455, 1361, 1309, 1211, 1190, 1177, 1097, 1020, 968 cm^{-1}; ^{1}H NMR, non-polar diastereomer: δ 0.83 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 1.13 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.49 (m, 2 H, CH_2CH_3), 2.43 (s, 3 H, arom. CH_3), 3.37 - 3.70 (m, 4 H, $PhCH_2OCH_2$, CHOH, $OCHCH_3$), 3.78 (m, 1 H, $OCHCH_2$), 4.05 (dd, ^3J = 6 Hz, ^2J = 10 Hz, 1 H, TsOC*H*H), 4.14 (dd, ^3J = 4 Hz, ^2J = 10 Hz, 1 H, TsOCH*H*), 4.51 (s, 2 H, $PhCH_2$), 7.32 (m, 7 H, arom. H), 7.80 (d, ^3J = 8 Hz, 2 H, arom. H); ^{1}H NMR (DMSO-D_6) δ 5.24 (d, ^3J = 5.8 Hz, 1 H, OH); ^{1}H NMR, polar diastereomer: δ 0.88 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 1.10 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.41 (m, 2 H, CH_2CH_3), 1.63 (br. s, 1 H, OH), 2.43 (s, 3 H, arom. CH_3), 3.32 - 3.71 (m, 4

H, $PhCH_2OCH_2$, $CHOH$, $OCHCH_3$), 3.80 (m, 1 H, $OCHCH_2$), 4.03 (dd, ^3J = 6.5 Hz, ^2J = 10 Hz, 1 H, $TsOCHH$), 4.17 (dd, ^3J = 4 Hz, ^2J = 10 Hz, 1 H, $TsOCHH$), 4.49 (d, J = 3 Hz, 2 H, $PhCH_2$), 7.33 (m, 7 H, arom. H), 7.80 (d, ^3J = 8 Hz, 2 H, arom. H); ^{1}H NMR (DMSO-D_6) δ 5.26 (d, ^3J = 6 Hz, 1 H, OH); ^{13}C NMR (APT), diastereomeric mixture δ 9.63/9.84 (-, CH_2CH_3), 16.28/16.41 (-, CH_3), 24.48 (-, arom. CH_3), 24.52/25.42 (+, CH_2CH_3), 71.02/71.20 (+, $PhCH_2OCH_2$), 71.69/72.17 (-, CHOH or OCH), 72.35/72.97 (+, $PhCH_2$), 73.18/73.23 (+, $TsOCH_2$), 74.21/76.11 (-, CHOH or OCH), 78.41/79.17 (-, CHOH or OCH), 127.52 (-, arom. C), 127.74 (-, arom. C), 127.90 (-, arom. C), 128.29/128.41 (-, arom. C), 129.81/129.87 (-, arom. C), 132.69/132.90 (+, arom. C), 137.55/138.24 (+, arom. C), 144.72/144.88 (+, arom. C); MS *m/z* 422 (M^+, 0), 301 (1), 244 (5), 155 (24), 91 (100).

2-(1,2-Epoxy-3-butoxy)-butanol (**4**). To a solution of **3** (115 mg, 0.27 mmol) in THF (3 mL) was added Pd/C (5%, cat.). The flask was evacuated, refilled with H_2 and the mixture was hydrogenated for 18 h with vigorous stirring. The suspension was suction-filtered through silica gel and the residue washed with E, to give after removal of the solvent a highly viscous oil (91 mg, 100%). The oil was dissolved in MeOH (2 mL) and treated with K_2CO_3 (75 mg, 0.54 mmol). After 2 h at r.t. water was added and the aqueous layer was extracted with E. The organic phase was dried ($MgSO_4$) and evaporated to afford **4**, 43 mg (99%). IR (film) ν 3436, 2973 - 2879, 1462, 1373, 1291, 1259, 1178, 1079, 999 cm^{-1}; ^{1}H NMR δ 0.92 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 1.25, 1.29 (2 x d, J = 3 Hz, 3 H, $CHCH_3$), 1.38 - 1.62 (m, 2 H, CH_2CH_3), 1.81 (br. s, 1 H, OH), 2.77 (m, 2 H, CH_2OCH), 2.98 (m, 1 H, CH_2OCH), 3.30 - 3.90 (m, 4 H, $HOCH_2CHOCH$); MS *m/z* 160 (M^+, 0), 129 (22), 117 (7), 87 (7), 73 (20), 71 (100).

2(-1,2-Epoxy-3-butoxy)-butanal (**5**). To a solution of **4** (5.5 g, 34.4 mmol) and NEt_3 (24 mL, 172 mmol) in DMSO (40.7 mL) and CH_2Cl_2 (165 mL) was added SO_3·py (21.6 g, 138 mmol) in portions within 15 min at 0 °C. After 3.5 h at 0 °C the mixture was worked up extractively (E/H_2SO_4 (1 N)/$NaHCO_3$). The organic layer was dried ($MgSO_4$) and the solvent removed. The sensitive crude product was stored at -20 °C without further purification. IR ($CHCl_3$) ν 3060 - 2719, 1733, 1456, 1377, 1311, 1290, 1259, 1127, 1098 cm^{-1}; ^{1}H NMR, diastereomeric mixture δ 0.98 (t, ^3J = 7 Hz,, 3 H, CH_2CH_3), 1.31 (2 x d, ^3J = 3.5 Hz, 3 H, $CHCH_3$), 1.69 (m, 2 H, CH_2CH_3), 2.76 (m, 2 H, OCH_2), 2.93 (m, 1H, $CHOCH_2$), 3.48 (2 x dq, ^3J = 4.5, 11 Hz, 1 H, CH_3CH), 3.67, 3.82 (ddd, ^3J = 2, 5.5, 8 Hz, 1 H, $OCHCHO$), 9.61 (2 x d, ^3J = 2 Hz, 1 H, CHO); MS *m/z* 158 (M^+, 1), 129 (13), 87 (6).

4-(1,2-Epoxy-3-butoxy)-(E)-2-hexenoic acid, ethyl ester (**6**). To a solution of K_2CO_3 (13.2 g, 93.9 mmol) in H_2O (14.7 mL) was added triethyl phosphonoacetate (6.54 mL, 32.9 mmol) followed after 15 min by **5** (4.96 g, 31.3 mmol). The mixture was stirred for 23 h. The aqueous layer was extracted with E, the organic layer dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography (E/PE, 1 : 2) to afford **6**, colourless liquid, 6.1 g (86%). IR (film) ν 2979 - 2878, 1719, 1658, 1451, 1370, 1304, 1272, 1243, 1179, 1124, 1097, 1040 cm^{-1}; ^{1}H NMR, diastereomeric mixture δ 0.93 (t, ^3J = 7 Hz, 3 H, $CHCH_2CH_3$), 1.24 (d, ^3J = 7 Hz, 3 H, $CHCH_3$), 1.32 (2 x d, ^3J = 7 Hz, 3 H, $CO_2CH_2CH_3$), 1.58 (m, 2 H, $CHCH_2CH_3$), 2.74 (m, 2 H, $CHOCH_2$), 2.89 (m, 1 H, $CHOCH_2$), 3.38 (m, 1 H, $OCHCH_3$), 3.96 (2 x ddd, ^4J = 1 Hz, ^3J = 6, 13 Hz, 1 H, CH_3CH_2CH), 4.21 (2 x q, ^3J = 7 Hz, 2 H, $CO_2CH_2CH_3$), 5.97 (2 x dd, ^4J = 1 Hz, ^3J = 16 Hz, 1 H, $CHCO_2Et$), 6.80 (2 x dd, ^3J = 6, 16 Hz, 1 H, CH=$CHCO_2Et$); ^{13}C NMR (APT), diastereomeric mixture δ 9.57/9.61 (-, $CHCH_2CH_3$), 14.25 (-, $CO_2CH_2CH_3$), 17.27/18.46 (-, $CHCH_3$), 28.01/28.19 (+, $CHCH_2CH_3$), 45.24/45.91 (+, $CHOCH_2$), 60.45 (+, $CO_2CH_2CH_3$), 72.33/73.55 (-, $CHCH_3$), 78.35/79.11 (-, $CHCH_2CH_3$), 121.58/121.81 (-, $CHCO_2Et$), 148.65 (-, CH=$CHCO_2Et$), 166.24/166.31 (+, CO_2Et); MS *m/z* 228 (M^+, 1), 199 (11), 180 (4), 157 (15), 141 (17), 129 (31), 113 (28), 107 (27).

4-[1,1-Bis-(phenylsulfonyl)-3-hydroxy-4-pentoxy]-(E)-2-hexenoic acid, ethyl ester (**7**). Bis(phenylsulfonyl)methane (8.92 g, 30 mmol) in THF (92 mL) was deprotonated with *n*-BuLi (19.1 mL, 30.8 mmol, 1.6 M solution in hexane) at -78 °C. BF_3·Et_2O (3.3 mL, 27 mmol) was added dropwise at the same temperature followed by **6** (3.42 g, 15 mmol). After 15 min the cooling bath was removed and the mixture quenched by addition of sat. aq. NH_4Cl/NaCl solution. The aqueous phase was extracted with E, the organic layer dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography (CH_2Cl_2/E, 19 : 1) to yield **7**, viscous oil, 7.36 g (94%). IR ($CHCl_3$) ν 3556, 3400, 3364, 3072 - 2876, 1712, 1448, 1332, 1276, 1240, 1152, 1080, 1036cm^{-1}; ^{1}H NMR, diastereomeric mixture δ 0.88 (t, ^3J = 7 Hz, 3 H, $CHCH_2CH_3$), 1.04 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.30 (2 x t, ^3J = 7 Hz, 3 H, $CO_2CH_2CH_3$), 1.57 (m, 2 H, $CHCH_2CH_3$), 2.11 (2 x d, ^3J = 8.5 Hz, 1 H, OH), 2.33 (dd, ^3J = 4, 7 Hz, 2 H, $CH_2CH(SO_2Ph)_2$), 3.53 (m, 1 H, OCH), 3.84 (br. m, 2 H, OCH), 4.21 (2 x q, ^3J = 7 Hz, 2 H, $CO_2CH_2CH_3$), 4.96 (dt, ^3J = 1.5, 4 Hz, 1 H, $CH(SO_2Ph)_2$), 5.92 (2 x dd, ^4J = 1.5

Hz, ^3J = 16 Hz, 1 H, C*H*CO_2Et), 6.75 (2 x dd, ^3J = 6, 16 Hz, 1 H, C*H*=CHCO$_2$Et), 7.51 - 8.01 (m, 10 H, arom. H); ^{13}C NMR (APT), diastereomeric mixture δ 9.30/9.53 (-, $CHCH_2CH_3$), 14.24/14.69 (-, $CHCH_3$), 15.98 (-, $CO_2CH_2CH_3$), 27.53/27.71 (+, $CHCH_2CH_3$), 27.64/28.17 (+, $CH_2CH(SO_2Ph)_2$), 60.51/60.57 (+, CO_2CH_2-CH_3), 71.14/71.35, 7470/77.20, 78.71/79.82 (-, OCH), 76.70 (-, $CH(SO_2Ph)_2$), 122.77 (-, $CHCO_2Et$), 129.12/129.56, 134.52/134.62, 137.66/137.69 (-, arom. C), 138.01(138.11 (+, arom. C), 147.63/148.59 (-, *C*H=CH-CO$_2$Et), 166.25 (+, *C*O$_2$Et); MS: not informative, M$^+$-fragment PhSO$_2$ = 141 was found.

1,1-Bis-(phenylsulfonyl)-4-[1-hydroxy-(E)-2-hexen-4-oxy]-3-pentanol (**8**). To a solution of **7** (7.3 g, 13.9 mmol) in CH_2Cl_2 (75 mL) was added diisobutylaluminium hydride (58 mL, 69.5 mmol, 1.2 M solution in toluene) dropwise at -35 °C. After 0.5 h at -20 °C the rection mixture was hydrolyzed carefully with aq. 2 N HCl solution and allowed to reach r.t. The organic layer was extracted with aq. 2 N HCl solution, sat. aq. $NaHCO_3$ solution and brine. The organic layer was dried ($MgSO_4$) and the solvent was removed to afford **8**, highly viscous oil, 6.6 g (100%). IR ($CHCl_3$) ν 3608, 3552, 3068 - 2876, 1448, 1332, 1228, 1152, 1080, 1024, 976, 908 cm^{-1}; ^{1}H NMR, diastereomeric mixture δ 0.86 (m, 3 H, CH_2CH_3), 1.04 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.30 (2 x t, ^3J = 7 Hz, 3 H, $CO_2CH_2CH_3$), 1.57 (m, 2 H, $CHCH_2CH_3$), 2.11 (2 x d, ^3J = 8.5 Hz, 1 H, OH), 2.33 (dd, ^3J = 4, 7 Hz, 2 H, $CH_2CH(SO_2Ph)_2$), 3.53 (m, 1 H, OCH), 3.84 (br. m, 2 H, OCH), 4.21 (2 x q, ^3J = 7 Hz, 2 H, $CO_2CH_2CH_3$), 4.96 (dt, ^3J = 1.5, 4 Hz, 1 H, $CH(SO_2Ph)_2$), 5.92 (2 x dd, ^4J = 1.5 Hz, ^3J = 16 Hz, 1 H, C*H*CO$_2$Et), 6.75 (2 x dd, ^3J = 6, 16 Hz, 1 H, C*H*=CHCO$_2$Et), 7.51 - 8.01 (m, 10 H, arom. H); MS (140 °C) *m/z* 483 (M$^+$, 0), 454 (1), 368 (7), 226 (10), 169 (23), 125 (100).

4-[1,1-Bis-(phenylsulfonyl)-3-hydroxy-4-pentoxy]-(E)-2-hexenyl methyl carbonate (**9**-H). To a solution of **8** (4.00g, 8.58 mmol) and pyridine (0.89 mL, 16.3 mmol) in CH_2Cl_2 (17 mL) was added ethyl chloroformate (0.90 mL, 16.3 mmol) dropwise at -35 °C. The mixture was stirred for 8 h at -30 °C. The organic layer was extracted with aq. 1 N HCl, sat. aq. $NaHCO_3$ solution and brine, dried ($MgSO_4$) and evaporated. The crude product, which contains bis carbonate, was used in the next step without further purification. A small sample was purified for spectral data. IR ($CHCl_3$) ν 3428, 3368, 3068 - 2876, 1748, 1448, 1332, 1272, 1228, 1104, 1080, 976 cm^{-1}; ^{1}H NMR, diastereomeric mixture δ 0.85 (2 x t, ^3J = 7 Hz, 3 H, CH_2CH_3), 1.00/1.03 (2 x d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.50 (m, 2 H, CH_2CH_3), 2.07/2.12 (2 x d, ^3J = 8 Hz, 1 H, OH), 2.32 (m, 2 H, $CH_2CH(SO_2Ph)_2$), 3.52 (m, 1 H, OCH), 3.71 (m, 2 H, OCH), 3.80 (2 x s, 3 H, OMe), 4.62 (t, ^3J = 4 Hz, 2 H, OCH_2), 4.95 (2 x t, ^3J = 5 Hz, 1 H, $CH(SO_2Ph)_2$), 5.44 - 5.80 (m, 2 H, HC=CH), 7.51 - 8.02 (m, 10 H, arom. H); ^{13}C NMR ($CDCl_3$) δ 9.69/9.90 (-, CH_2CH_3), 16.83 (-, $CHCH_3$), 28.60/28.89 (+, CH_2CH_3), 29.15/29.90 (+, CH_2CH-$(SO_2Ph)_2$), 55.00 (OMe), 65.94/67.78 (+, OCH_2), 75.01/76.28, 78.52/80.11 (-, OCH), 81.02 (-, $CH(SO_2Ph)_2$), 125.47/126.08 (-, HC=CH), 129.17, 129.30, 129.31, 130.02, 134.51, 134.95 (-, arom. C), 136.06/136.91 (-, HC=CH), 138.32, 138.40 (+, arom. C), 155.70 (+, *C*O$_2$Me). FAB-MS *m/z* 541 (M$^+$, 27), 425 (32), 367 (100).

4-[1,1-Bis-(phenylsulfonyl)-3-trimethylsiloxy-4-pentoxy]-(E)-2-hexenyl methyl carbonate (**9**-TMS). To a solution of **9**-H (crude product, 8.58 mmol) in THF (50 mL) was added BSA (6.36 mL, 41.7 mmol) and the mixture was heated to reflux for 3 h. After removal of the solvent the crude product was purified by column chromatography (E/PE, 2 : 1) to give **9**-TMS (4.06 g, 77%, highly viscous oil) and bis carbonate (1 g, 20 %), which was formed in the experiment above. The bis carbonate can be saponified quantitatively by addition of K_2CO_3 (2 eq) in MeOH. IR ($CHCl_3$) ν 3688, 3420, 3396, 3192 - 2724, 2396, 2336, 1588, 1472, 1396, 1100, 1048, 980 cm^{-1}; ^{1}H NMR (CD_2Cl_2), diastereomeric mixture δ 0.09 (s, 9 H, $SiMe_3$), 0.78/0.86 (2 x t, ^3J = 7 Hz, 3 H, CH_2CH_3), 0.97 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.43 (m, 2 H, CH_2CH_3), 2.24 (m, 2 H, $CH_2CH(SO_2Ph)_2$), 3.40 (m, 2 H, OCH), 3.74 (s, 3 H, OMe), 3.99 (m, 1 H, OCH), 4.56 - 4.73 (m, 3 H, OCH_2, $CH(SO_2Ph)_2$), 5.47 - 5.78 (m, 2 H, HC=CH), 7.50 - 8.04 (m, 10 H, arom. H); ^{13}C NMR (CD_2Cl_2) δ 0.63/0.70 (-, $SiMe_3$), 9.72/9.93 (-, CH_2CH_3), 14.35 (-, $CHCH_3$), 28.65/28.92 (+, CH_2CH_3), 29.20/29.92 (+, $CH_2CH(SO_2Ph)_2$), 55.04 (OMe), 66.03/67.98 (+, OCH_2), 73.53/73.69, 75.26/76.59, 78.73/80.47 (-, OCH), 81.13 (-, $CH(SO_2Ph)_2$), 125.87/126.48 (-, HC=CH), 129.47/129.51, 129.60/130.21, 134.80/135.07 (-, arom. C), 136.36/137.01 (-, HC=CH), 138.35/138.47, 138.52/138.64 (+, arom. C), 155.91 (+, *C*O$_2$Me). FAB-MS *m/z* 613 (M$^+$, 2), 457 (6), 439 (44), 297 (41), 157 (100).

*4-[1,1-Bis-(phenylsulfonyl)-3-*tert.*-butyldimethylsiloxy-4-pentoxy]-(E)-2-hexenyl methyl carbonate* (**9**-TBDMS). To imidazol (502 mg, 7.38 mmol) and TBDMS-Cl (556 mg, 3.69 mmol) was added a solution of **9**-H (797 mg, 1.48 mmol) in DMF (2 mL). The reaction mixture was stirred for 24 h at. r.t. and 1 h at 60 °C (incomplete reaction!). CH_2Cl_2 was added and the organic layer was washed with sat. aq. NH_4Cl solution, H_2O and brine, dried ($MgSO_4$) and evaporated. Purification by column chromatography afforded **9**-TBDMS, highly viscous oil, 665 mg (69%). IR ($CHCl_3$) ν 3688, 3396, 3191 - 2724, 2395, 1588, 1470, 1392, 1100, 1048, 982

cm^{-1}; ^1H NMR δ 0.08 (s, 6 H, $SiMe_3$), 0.88 (m, 12 H, $SiMe_3$, $SiC(CH_3)_3$, CH_2CH_3), 0.98 (2 x d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.48 (br. m, 2 H, CH_2CH_3), 2.08 - 2.39 (m, 2 H, $CH_2CH(SO_2Ph)_2$), 3.40 (m, 2 H, *H*COTBDMS, $CHCH_3$), 3.75 (2 x s, 3 H, OMe), 4.07 (m, 1 H, $OCHCH_2CH_3$), 4.61 (d, ^3J = 5 Hz, 2 H, OCH_2), 4.79 (2 x d, ^3J = 3 Hz, 1 H, $CH(SO_2Ph)_2$), 5.50 - 5.80 (m, 2 H, HC=CH), 7.52 - 8.01 (m, 10 H, arom. H); FAB-MS *m/z* 655 (M^+, 3), 481 (25), 339 (36), 157 (100).

*4-[1,1-Bis-(phenylsulfonyl)-3-*tert.*-butyldiphenylsiloxy-4-pentoxy]-(E)-2-hexenyl methyl carbonate* (**9**-TBDPS). To imidazol (108 mg, 1.58 mmol), DMAP (10 mg) and TBDPS-Cl (274 µL, 10.6 mmol) was added a solution of **9**-H (285 mg, 0.528 mmol) in DMF (0.9 mL). The reaction mixture was stirred for 24 h at. r.t. and 24 h at 85 °C. CH_2Cl_2 was added and the organic layer was washed with 2 N HCl and brine, dried ($MgSO_4$) and evaporated. Purification by column chromatography afforded **9**-TBDPS, viscous oil, 280 mg (68%), and starting material, 57 mg (20 mg). IR ($CHCl_3$) ν 3072 - 2860, 1748, 1448, 1332, 1272, 1156, 1112, 1080, 976, 908 cm^{-1}; ^1H NMR δ 0.79 (m, 6 H, CH_2CH_3, $CHCH_3$), 1.02 (s, 9 H, $C(CH_3)_3$), 1.34 (br. m, 2 H, CH_2CH_3), 2.22 (2 x br. m, 2 H, $CH_2CH(SO_2Ph)_2$), 3.32 (m, 1 H, *H*COCH), 3.52 (m, 1 H, HCOC*H*), 3.78 (2 x s, 3 H, OMe), 4.34 (*H*COTBDPS), 4.52 (d, ^3J = 5 Hz, 2 H, OCH_2), 4.70/4.89 (2 x dd, ^3J = 3, 9 Hz, 1 H, $CH(SO_2Ph)_2$), 5.30 - 5.58 (m, 2 H, HC=CH), 7.32 - 7.86 (m, 20 H, arom. H); FAB-MS *m/z* 779 (M^+, 4).

General Procedure for the Pd(0) Catalyzed Cyclization. A flame-dried two-necked flask was charged with $Pd_2(dba)_3CHCl_3$ (5 mol%) and ligand (21 mol%). The apparatus was evacuated and refilled with N_2 (3x), to exclude any oxygen during reaction. Solvent (THF) was added, the solution should be 0.02 M with respect to starting material. After 10 min the colour of the dark violet solution turns to yellow. The colour indicates the formation of the desired Pd(0) complex. The reaction mixture was heated to reflux and the cyclization precursor (0.02 M in THF) was added *via* syringe drive within 8 h. After complete addition the reaction mixture was heated to reflux for a further 0.5 - 18 h. The solvent was removed and the crude product was purified by chromatography.

Unsaturated 9-ring ether **10**-TMS *and unsaturated ring ether* **11**-TMS. Approach 1. **9**-TMS (2.12 g, 3.47 mmol) in THF (42 mL) and dppe (290 mg, 21 mol%) in THF (100 mL) were allowed to react according to the general procedure to afford **10**-TMS and **11**-TMS (4.5 : 1). Reaction temperature: reflux. Addition time: 8 h. Reaction time: 16 h. Yield: **10**-TMS, 1.34 g (72%), white solid, m. p. 69 - 71 °C; **11**-TMS, 0.30 g (16%), light yellow semi-solid compound. Approach 2. **9**-TMS (436 mg, 0.711 mmol) in dioxane (8 mL) and dppe (59.5 mg, 21 mol%) in dioxane (15 mL) were allowed to react according to the general procedure to afford **10**-TMS and **11**-TMS (4 : 1). Reaction temperature: 102 °C. Addition time: 8 h. Reaction time: 16 h. Yield: 322 mg (84%); after separation **10**-TMS, (171 mg, 0.92 mmol) and **11**-TMS (43 mg, 0.08 mmol). Approach 3. **9**-TMS (300 mg, 0.49 mmol) in THF (5 mL) and $P(OEt)_3$ (42 µL, 50 mol%) in THF (5 mL) were allowed to react according to the general procedure to afford **10**-TMS and **11**-TMS (14.3 : 1). Reaction temperature: reflux. Addition time: 6 h. Reaction time: 0.5 h. Yield: **10**-TMS, 172 mg (66%), **11**-TMS, 12 mg (5%).

Spectroscopic data for **10**-TMS. IR ($CHCl_3$) ν 3000, 2964, 2932, 2876, 1448, 1328,1308, 1252, 1144, 1076, 876 cm^{-1}; ^1H NMR δ -0.4 - -0.24 (m, 9 H, $SiMe_3$), 0.98 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 1.18 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.58 (m, 1 H, $CHHCH_3$), 1.79 (m, 1 H, $CHHCH_3$), 2.42 - 2.69 (m, 2 H, $CH_2CHOTMS$), 2.88 (br. dd, ^3J = 5 Hz, ^2J = 13 Hz, 1 H, $=CHCHHC(SO_2Ph)_2$), 3.50 (m, 1 H, $CHCH_3$), 2.88 (br. dd, ^3J = 11 Hz, ^2J = 13 Hz, 1 H, $=CHCHHC(SO_2Ph)_2$), 4.28 - 4.48 (m, 2 H, $CHCH_2CH_3$, *CH*OTMS), 5.72 (br. dd, ^3J = 3, 11 Hz, 1 H, $OCHCH{=}CH$), 6.03 (m, 1 H, $OCHCH{=}CH$), 7.50 - 8.23 (m, 10 H, arom. H); NOE experiment: 1.18 ppm, ($CHCH_3$) strong with ($CHCH_3$), strong with ($CHCH_2CH_3$) and/or ($CHOTMS$); 3.50 ppm, ($CHCH_3$) strong with ($CHCH_3$), medium with ($CH_2CHOTMS$); ^{13}C NMR δ -0.09 (-, $SiMe_3$), 10.50 (-, CH_2CH_3), 21.42 (-, $CHCH_3$), 27.23 (+, CH_2CH_3), 30.03 (+, $CH_2CHOTMS$), 38.80 (+, $=CHCH_2C(SO_2Ph)_2$), 72.18 (-, *C*HOTMS), 73.84 (-, OCH), 74.97 (-, OCH), 93.30 (+, $C(SO_2Ph)_2$), 128.28, 128.40 (-, arom. C), 129.97 (-, $OCHCH{=}CH$), 130.97, 131.46, 134.23 (-, arom. C), 136.35 (+, arom. C), 136.50 (-, $OCHCH{=}CH$), 138.12 (+, arom. C); FAB-MS *m/z* 537 (M^+, 20), 391 (14), 307 (25), 253 (100), 154 (97). Anal. Calcd. for $C_{26}H_{36}O_6S_2Si$: C, 58.21; H, 6.72. Found: C, 58.12; H, 6.72.

Spectroscopic data for **11**-TMS. IR ($CHCl_3$) ν 3068, 3000, 2964, 2936, 2876, 1584, 1448, 1328, 1308, 1228, 1144, 1076, 928, 880, 844 cm^{-1}; ^1H NMR δ 0.03 (s, 9 H, $SiMe_3$), 0.93 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 1.10 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.57 (m, 2 H, CH_2CH_3), 2.65 (m, 2 H, $CH_2CHOTMS$), 2.82 (m, 1 H, $=CHCHH$-$C(SO_2Ph)_2$), 3.18 (m, 1 H, $CHCH_3$), 3.73 (br. dt, ^3J = 3,5, 6 Hz, 1 H, $CHCH_2CH_3$), 4.23 (m, 1 H, $=CHCHH$-$C(SO_2Ph)_2$), 4.40 (dt, ^3J = 3.6, 8 Hz, 1 H, *CH*OTMS), 5.76 (m, 2 H, CH=CH), 7.52 - 8.08 (m, 10 H, arom. H); ^1H NMR (C_6D_6) δ 0.18 (s, 9 H, $SiMe_3$), 0.88 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 1.20 (d, ^3J = 6 Hz, 3 H, $CHCH_3$),

1.45 (m, 2 H, CH_2CH_3), 3.01 (m, 2 H, CH_2CHOTMS), 3.10 (dd, ^3J = 6, 13.5 Hz, 1 H, =CHC*H*HC$(SO_2Ph)_2$), 3.22 (dd, ^3J = 6,9 Hz, 1 H, C*H*CH_3), 3.38 (dt, ^3J = 4.5, 7:5 Hz, 1 H, C*H*OTMS), 4.50 (dd, ^3J = 11, 13.5 Hz, 1 H, =CHCH*H*C$(SO_2Ph)_2$), 4.82 (m, 1 H, C*H*CH_2CH_3), 5.49 (dd, ^3J = 4.5, 11 Hz, 1 H, OCHC*H*=CH), 6.07 (dt, ^3J = 6, 11 Hz, 1 H, OCHCH=C*H*), aromatic signals are not useful (C_6D_6 solvent); NOE experiment: 1.10 ppm, ($CHCH_3$) strong with (C*H*CH_3), weak with (C*H*CH_2CH_3), medium with (C*H*OTMS); 3.18 ppm, (C*H*CH_3) strong with ($CHCH_3$), medium with (CH_2CHOTMS), strong with (C*H*CH_2CH_3), medium with (=CHCH_2-C$(SO_2Ph)_2$), weak with (HC=CH); ^{13}C NMR (CD_2Cl_2) δ 0.03 (-, $SiMe_3$), 11.03 (-, CH_2CH_3), 18.79 (-, $CHCH_3$), 29.53 (+, CH_2CH_3), 30.55 (+, CH_2CHOTMS), 40.02 (+, =CHCH_2C$(SO_2Ph)_2$), 71.82 (-, CHO-TMS), 80.53 (-, OCH), 81.50 (-, OCH), 94.44 (+, C$(SO_2Ph)_2$), 125.09 (-, OCHCH=CH), 128.95, 131.47, 131.90, 134.76 (-, arom. C), 137.31 (-, OCHCH=CH), 137.61, 138.82 (+, arom. C); FAB-MS *m/z* 537 (M^+, 19), 307 (24), 253 (100), 154 (97). Anal. Calcd. for $C_{26}H_{36}O_6S_2Si$: C, 58.21; H, 6.72. Found: C, 58.28; H, 6.68.

Unsaturated 9-ring ether **10**-TBDMS *and unsaturated* **11**-TBDMS. **9**-TBDMS (600 mg, 0.916 mmol) in THF (13 mL) and dppe (79 mg, 21 mol%) in THF (20 mL) were allowed to react according to the general procedure to afford **10**-TBDMS and **11**-TBDMS (1 : 2.5). Reaction temperature: reflux. Addition time: 8 h. Reaction time: 17 h. Yield: 464 mg (88%) of **10**-TBDMS, semi-solid compound, and **11**-TBDMS, white solid, m. p. 153 °C.

Spectroscopic data for **10**-TBDMS. IR ($CHCl_3$) ν 3068 - 2856, 1448, 1328, 1252, 1144, 1040, 864, 836 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ -0.2 (m, 2 H, $SiCH_3$), 0.05 (m, 4 H, $SiCH_3$), 0.87 (br. s, 9 H, C$(CH_3)_3$), 1.02 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 1.20 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.62 (br. m, 1 H, C*H*HCH_3), 1.82 (br. m, 1 H, CH*H*CH_3), 2.42 - 2.70 (m, 2 H, CH_2CHOTMS), 2.85 (br. d, ^3J = 4.5 Hz, ^2J = 13 Hz, 1 H, =CHC*H*HC$(SO_2Ph)_2$), 3.51 (m, 1 H, C*H*CH_3), 3.97 (dd, ^3J = 12 Hz, ^2J = 13 Hz, 1 H, =CHCH*H*C$(SO_2Ph)_2$), 4.25 - 4.46 (m, 2 H, C*H*CH_2CH_3, C*H*OTBDMS), 5.79 (dd, ^3J = 3, 11 Hz, 1 H, OCHC*H*=CH), 6.08 (m, 1 H, OCHCH=C*H*), 7.58 - 8.18 (m, 10 H, arom. H); NOE experiment: 4.08 ppm, (=CHC*H*HC$(SO_2Ph)_2$) weak with (OCHC*H*=CH), strong with (=CH-CH*H*C$(SO_2Ph)_2$), medium with (C*H*CH_3) or (C*H*CH_2CH_3), medium with arom. H; 3.64 pmm, (C*H*CH_3) strong with ($CHCH_3$), strong with (=CHC*H*HC$(SO_2Ph)_2$), medium with (CH_2CHOTBDMS), weak with (=CHCH*H*-C$(SO_2Ph)_2$); ^{13}C NMR δ -4.71 - -4.56 (-, $SiCH_3$), 10.97 (-, CH_2CH_3), 18.07 (+, C$(CH_3)_3$), 23.14 (-, $CHCH_3$), 26.08(-, C$(CH_3)_3$), 30.14 (+, CH_2CH_3), 30.80 (+, CH_2CHOTBDMS), 39.31 (+, =CHCH_2C$(SO_2Ph)_2$), 72.84, 74.32, 75,72 (-, CHOTBDMS, OCH), 94.04 (+, C$(SO_2Ph)_2$), 128.88, 129.05 (-, arom. C), 130.55 (-, OCHCH=CH), 131.59, 132.12, 134.74, 134.84 (-, arom. C), 137.04 (+, arom. C), 137.33 (-, OCHCH=CH), 138.83 (+, arom. C); FAB-MS *m/z* 579 (M^+, 10), 447 (27), 295 (98).

Spectroscopic data for **11**-TBDMS. IR ($CHCl_3$) ν 3068 - 2856, 1448, 1328, 1308, 1144, 1092, 1040, 864, 836 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ -0.06 (s, 3 H, $SiCH_3$), 0.10 (s, 3 H, $SiCH_3$), 0.90 (s, 9 H, C$(CH_3)_3$), 0.98 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 1.18 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.62 (m, 2 H, CH_2CH_3), 2.68 (m, 2 H, CH_2CHO-TBDMS), 2.82 (m, 1 H, =CHC*H*HC$(SO_2Ph)_2$), 3.25 (m, 1 H, C*H*CH_3), 3.80 (m, 1 H, C*H*CH_2CH_3), 4.25 (m, 1 H, =CHCH*H*C$(SO_2Ph)_2$), 4.39 (dt, ^3J = 3, 8 Hz, 1 H, C*H*OTBDMS), 5.86 (m, 2 H, CH=CH), 7.58 - 8.12 (m, 10 H, arom. H); ^{1}H NMR (C_6D_6) δ 0.10 (2 x s, 6 H, $SiCH_3$), 0.90 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 0.97 (s, 9 H, C$(CH_3)_3$), 1.22 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 1.50 (br. m, 2 H, CH_2CH_3), 2.94 (m, 2 H, CH_2CHOTMS), 3.04 (dd, ^3J = 6, ^2J = 13 Hz, 1 H, =CHC*H*HC$(SO_2Ph)_2$), 3.23 (m, 1 H, C*H*CH_3), 3.40 (dt, ^3J = 4.5, 9 Hz, 1 H, C*H*CH_2CH_3), 4.50 (dd, ^3J = 11, ^2J = 13 Hz, 1 H, =CHCH*H*C$(SO_2Ph)_2$), 4.84 (m, 1 H, C*H*OTBDMS), 5.52 (dd, ^3J = 4.5, 11 Hz, 1 H, OCHC*H*=CH), 6.15 (dt, ^3J = 6, 11 Hz, 1 H, OCHCH=C*H*), aromatic signals not diagnostic (C_6D_6 solvent); NOE experiment: 3.21 ppm, (C*H*CH_3), strong with ($CHCH_3$), strong with (=CHCH_2C$(SO_2Ph)_2$), strong with (C*H*CH_2CH_3); 3.75 ppm (C*H*CH_2CH_3), strong with (CH_2CH_3), strong with (OCHC*H*=CH), strong with ($CHCH_3$); 4.23 ppm (=CHC*H*HC$(SO_2Ph)_2$), strong with (=CHCH*H*C$(SO_2Ph)_2$), weak with (OCHCH=C*H*), weak with arom. H; 4.38 ppm, (C*H*OTBDMS), strong with (CH_2CHOTMS), medium with (C*H*CH_3); ^{13}C NMR (CD_2Cl_2) δ -4.52 - -4.41 (-, $SiCH_3$), 11.09 (-, CH_2CH_3), 18.11 (+, C$(CH_3)_3$), 18.97 (-, $CHCH_3$), 26.10 (-, C$(CH_3)_3$), 29.50 (+, CH_2CH_3), 30.49 (+, CH_2CHOTBDMS), 40.00 (+, =CHCH_2-C$(SO_2Ph)_2$), 71.91 (-, CHOTBDMS), 80.13 (-, OCH), 81.21 (-, OCH), 94.32 (+, C$(SO_2Ph)_2$), 125.45 (-, OCHCH=CH), 128.90, 128.96, 131.57, 132.03, 134.74 (-, arom. C), 137.17 (-, OCHCH=CH), 137.49, 138.70 (+, arom. C); FAB-MS *m/z* 579 (M^+, 12), 521 (27), 447 (28), 295 (97), 125 (100). Anal. Calcd. for $C_{29}H_{42}O_6S_2Si$: C, 60.21; H, 7.27. Found: C, 60.22; H, 7.29.

Unsaturated 9-ring ether (**10**-TBDPS) *and unsaturated* **11**-TBDPS. **9**-TBDPS (270 mg, 0.346 mmol) in THF (6.5 mL) and dppe (31.1 mg, 21 mol%) in THF (12 mL) were allowed to react according to the general procedure to afford **10**-TBDPS and **11**-TBDPS (1.6 : 1). Reaction temperature: reflux. Addition time: 8 h.

Reaction time: 16 h. Yield: 205 mg (84%) of **10**-TBDPS, 114 mg, white solid, m. p. 94 °C, and **11**-TBDPS, white solid, m. p. 170 °C.

Spectroscopic data for **10**-TBDPS. IR ($CHCl_3$) ν 3072 - 2856, 1448, 1308, 1144, 1076, 908 cm^{-1}; ^1H NMR δ 0.75 (m, 15 H, $C(CH_3)_3$, CH_2CH_3, $CHCH_3$), 1.60 (br. m, 2 H, CH_2CH_3), 2.68 - 2.93 (m, 3 H, $CH_2CHOTPS$, $=CHCHHC(SO_2Ph)_2$), 3.46 (m, 1 H, $CHCH_3$), 3.72 (dd, ^3J = 10 Hz, ^2J = 13 Hz, 1 H, $=CHCHHC(SO_2Ph)_2$), 4.12 (br. m, 1 H, $CHCH_2CH_3$), 4.44 (m, 1 H, CHOTBDPS), 5.72 (dd, ^3J = 3, 11 Hz, 1 H, $OCHCH=CH$), 6.04 (m, 1 H, $OCHCH=CH$), 7.28 - 7.95 (m, 20 H, arom. H); ^{13}C NMR δ 10.61 (-, CH_2CH_3), 19.72 (+, $C(CH_3)_3$), 22.34 (-, $CHCH_3$), 26.89 (+, CH_2CH_3), 27.06 (-, $C(CH_3)_3$), 30.37 (+, $CH_2CHOTBDPS$), 38.52 (+, $=CHCH_2C(SO_2Ph)_2$), 73.63 (-, CHOTBDPS), 74.11 (-, OCH), 93.82 (+, $C(SO_2Ph)_2$), 129.46 - 138.10 (11 signals, HC=CH, arom. C); FAB-MS *m/z* 703 (M^+, 9), 645 (57), 419 (100). Anal. Calcd for $C_{39}H_{46}O_6S_2Si$: C, 66.68; H, 6.55. Found: C, 66.20; H, 6.77.

Spectrosopic data for **11**-TBDPS. IR ($CHCl_3$) ν 3072 - 2856, 1428, 1328, 1144, 1092, 908 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 0.82 (d, ^3J = 6 Hz, 3 H, $CHCH_3$), 0.93 (s, 9 H, $C(CH_3)_3$), 1.30 (m, 2 H, CH_2CH_3), 2.83 (br. m, 3 H, $CH_2CHOTBDPS$, $=CHCHHC(SO_2Ph)_2$), 3.18 (m, 1 H, $CHCH_3$), 3.56 (m, 1 H, $CHCH_2CH_3$), 3.90 (br. m, 1 H, $=CHCHHC(SO_2Ph)_2$), 4.25 (dt, ^3J = 3, 8 Hz, 1 H, CHOTBDPS), 5.81 (m, 2 H, CH=CH), 7.29 - 7.98 (m, 20 H, arom. H); ^{13}C NMR δ 10.60 (-, CH_2CH_3), 18.99 (-, $CHCH_3$), 19.68 (+, CH_2CH_3), 27.12 (-, $C(CH_3)_3$), 28.84 (+, $C(CH_3)_3$), 29.68 (+, $CH_2CHOTBDPS$), 39.25 (+, $=CHCH_2C(SO_2Ph)_2$), 73.11 (-, CHOTBDPS), 79.70 (-, OCH), 80.38 (-, OCH), 94.19 (+, $C(SO_2Ph)_2$), 125.29 (-, $OCHCH=CH$), 136.02 (-, $OCHCH=CH$), 128.46 - 138.05 (12 signals, arom. C); FAB-MS *m/z* 703 (M^+, 9), 645 (50), 419 (100). Anal. Calcd. for $C_{39}H_{46}O_6S_2Si$: C, 66.68; H, 6.55. Found: C, 66.37; H, 6.60.

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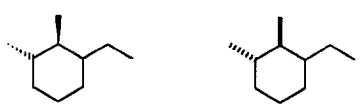
§ Throughout this paper the Maehr convention is used (Maehr, H. *J. Chem. Ed.* **1985**, *62*, 114). Solid and broken *lines* refer to racemic materials and *relative* configuration, whereas solid and broken *wedges* are used to indicate *absolute* configuration.



2 stereoisomers 4 stereoisomers

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