New Nonhydrolyzable Mimetics of Sialyl Lewis X and Their Binding Affinity to P-Selectin

by **Frédéric Carrel**[a]), **Sylvain Giraud**[b]), **Olivier Spertini**[b]), and **Pierre Vogel***[a])

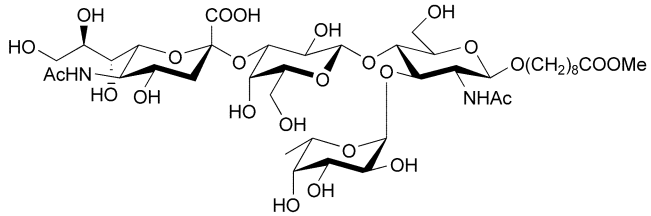
[a]) Institut des sciences et ingénerie chimiques, Ecole Polytechnique Fédérale de Lausanne, BCH, CH-1015 Lausanne-Dorigny

[b]) Institut d'hématologie, Centre hospitalier universitaire vaudois, CH-1011 Lausanne

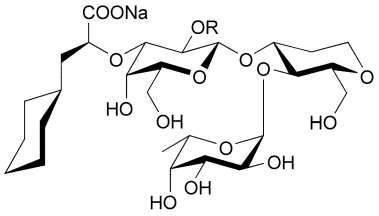
Wittig olefination of (2*S*,3*R*,5*S*,6*R*)-5-(acetyloxy)-tetrahydro-6-[(methoxymethoxy)methyl]-3-(phenylthio)-2*H*-pyran-2-acetaldehyde ((+)-**10**) with {2-[(2*S*,3*R*,4*R*,5*R*,6*S*)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]ethyl}triphenylphosphonium iodide ((−)-**11**) gave a (*Z*)-alkene derivative (+)-**12** that was converted into (α*R*,2*R*,3*S*,4*R*,5*R*,6*S*)-tetrahydro-α,3-dihydroxy-2-(hydroxymethyl)-5-(phenylthio)-6-{(2*Z*)-4-[(2*S*,3*S*,4*R*,5*S*,6*S*)-tetrahydro-3,4,5-trihydroxy-6-methyl-2*H*-pyran-2-yl]but-2-enyl}2*H*-pyran-4-acetic acid (**8**), (α*R*,2*R*,3*S*,4*R*,6*S*)-tetrahydro-α,3-dihydroxy-2-(hydroxymethyl)-6-{4-[(2*S*,3*S*,4*R*,5*S*,6*S*)-tetrahydro-3,4,5-trihydroxy-6-methyl-2*H*-pyran-2-yl]butyl}-2*H*-pyran-4-acetic acid (**9**), and simpler analogues without the hydroxyacetic side chain such as (2*S*,3*S*,4*R*,5*S*,6*S*)-tetrahydro-6-methyl-2-{(2*Z*)-4-[(2*S*,3*R*,5*S*,6*R*)-tetrahydro-5-hydroxy-6-(hydroxymethyl)-3-(phenylthio)-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-3,4,5-triol (**30**), (2*S*,3*S*,4*R*,5*S*,6*S*)-tetrahydro-6-methyl-2-{[(2*S*,5*S*,6*R*)-tetrahydro-5-hydroxy-6-(hydroxymethyl)-2*H*-pyran-2-yl]butyl}-2*H*-pyran-3,4,5-triol ((−)-**41**) and (2*S*,3*S*,4*R*,5*S*,6*S*)-tetrahydro-6-methyl-2-{(2*Z*/*E*))-4-[(2*R*,5*S*,6*R*)-tetrahydro-5-hydroxy-6-(hydroxymethyl)-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-3,4,5-triol (**43**). The key intermediates (+)-**10** and (−)-**11** were derived from isolevoglucosenone and from L-fucose, respectively. The following IC_{50} values were measured in a ELISA test for the affinities of sialyl Lewis x tetrasaccharide, **8**, **9**, **30**, (−)-**41**, and **43** toward P-selectin: 0.7, 2.5–2.8, 7.3–8.0, 5.3–5.9, 5.0–5.2, and 3.4–4.1 mM, respectively.

Introduction. – The selectins are a family of cell-adhesion proteins that mediate the tethering and the rolling of leucocyte endothelial cells through the recognition of the tetrasaccharide epitope sialyl Lewis x (sLe^x) [1]. Control of the leucocyte endothelial cell adhesion process may prove useful in cases where excess recruitment of leucocytes can contribute to acute diseases such as stroke and reperfusion injury and chronic diseases such as psoriasis and rheumatoid arthritis. The development of molecules that block the interactions between sLe^x and the selectins has become an active area of research [2–13]. Among the most promising sialyl Lewis x mimetics are compounds **2** and **3** [3] that are more potent than sLe^x-glycoside **1** in a E-selectin binding assay. They can be prepared from commercially available starting materials in good yield [3]. These systems contain two glycosidic acetal moieties that are readily hydrolyzed by the stomach acidity and by ubiquitous glycosidases of the blood stream. This has stimulated synthetic efforts to generate nonhydrolyzable mimetics of the sialyl Lewis x epitope, in particular compounds containing α-*C*-fucopyranoside [2][4][5][7] or β-*C*-mannoside moieties [2][5][6]. *Wong* and co-workers have found that compound **4**, which contains the most essential functions of sLe^x necessary in the selectin recognition (the carboxylic group of sialic acid, the 4-OH and 6-OH groups of the galactopyranosyl unit, the three OH groups of the α-L-fucopyranosyl moiety [2]) is *ca.* 30 times less potent than sLe^x in binding E-selectin [4]. Our studies on the synthesis of *C*-linked oligosaccharides (see,

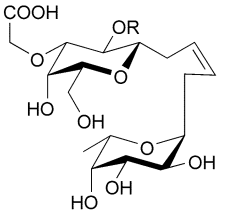
e.g., [14]) prompted us to prepare analogues of **4**. In particular, ketones of type **5** were targeted as potential partners in cross-aldol reactions with sialic acid mimics such as **6** [15] with the hope to be able to generate yet unknown C,C,C-linked tetrasaccharides of type **7** that can be seen as mimics of sLe^x (**1**). This goal has not been reached yet. In the meantime, our exploratory synthetic studies incited us to prepare compounds **8** and **9** that are mimics of **4**. These compounds, and simpler derivatives, were assayed for their binding of P-selectin. We found that **8**, which contains a 2-deoxy-2-(phenylthio)-β-D-glucopyranosyl moiety instead of a β-D-galactopyranosyl unit, is almost as potent as the sLe^x tetrasaccharide in its binding with P-selectin. Simpler analogs without any substituents at C(2) and C(3) of the β-D-glucopyranosyl moiety of **9** are also recognized by P-selectin. This work suggests that sLe^x mimics with their β-galactopyranosyl moiety modified widely may retain good P-selectin affinity.



1 (rel. IC_{50} (E-Sel) = 1.0)



2 R = H (rel. IC_{50} = 0.030)
3 R = Bz (rel. IC_{50} = 0.010)



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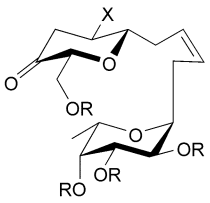

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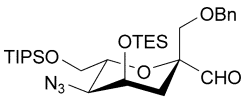
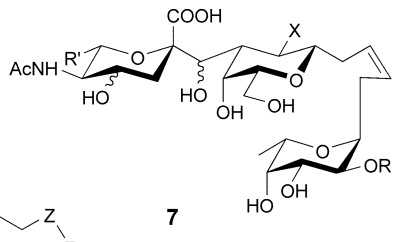


6
TIPS = $^i Pr_3Si$, TES = Et_3Si



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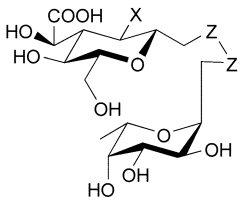


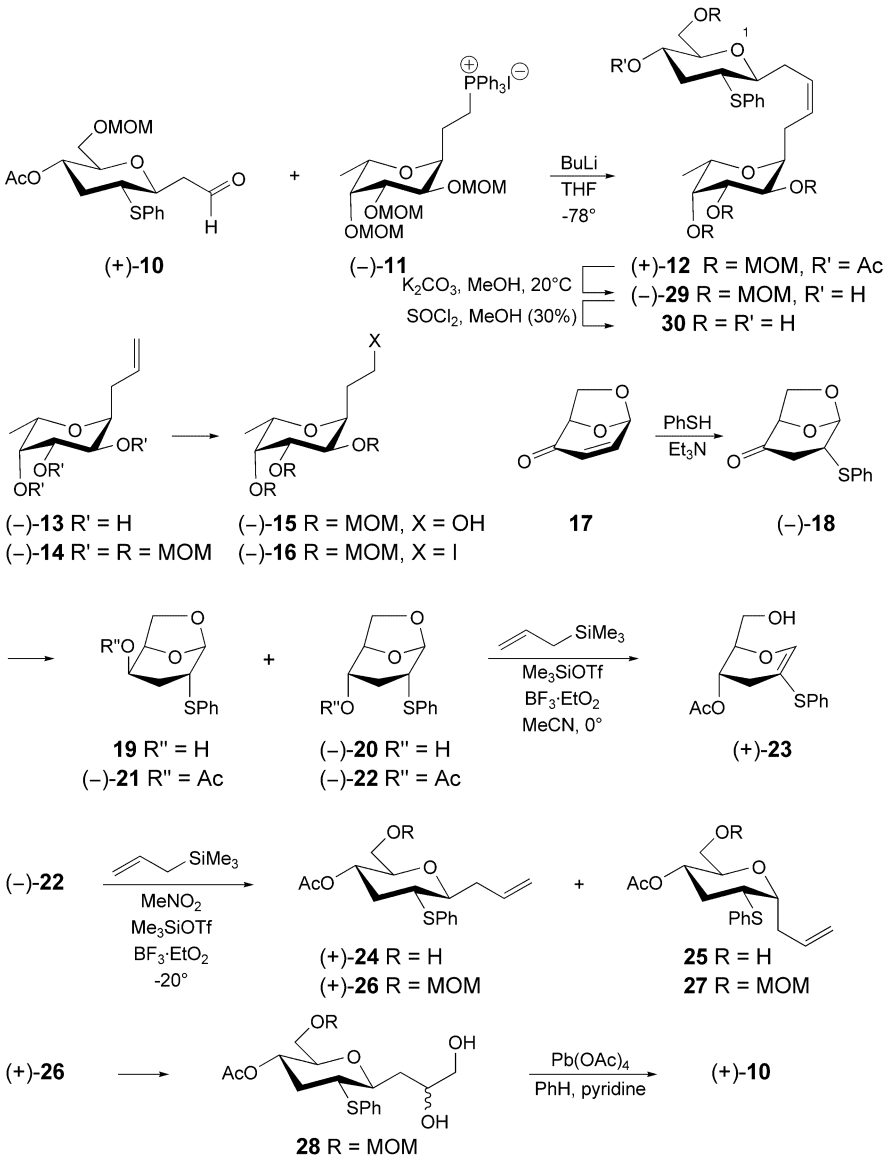
8 X = SPh, Z-Z = CH=CH
9 X = H, Z-Z = CH_2-CH_2

Synthesis of the New sLe^x Mimics. – Following the pioneering work of *Wong* and coworkers [2][4], we coupled (2*S*,3*R*,5*S*,6*R*)-5-(acetyloxy)-tetrahydro-6-[(methoxymethoxy)methyl]-3-(phenylthio)-2*H*-pyran-2-acetaldehyde ((+)-**10**) with the L-fucose-derived phosphonium iodide (−)-**11** *via* a *Wittig* olefination that gave the (*Z*)-alkene derivative (+)-**12**, the precursor of the sLe^x mimics prepared in this work (*Scheme 1*). The salt (−)-**11** was derived from the known '3-(α-L-fucopyranosyl)prop-1-ene' (−)-**13** [4]. Its OH groups were protected as methoxymethyl (MOM = $MeOCH_2$) ethers (Bu_4NI, $^iPr_2NEt$, $MeOCH_2Cl$, 0–20°) giving (−)-**14** (96%). Ozonolysis of (−)-**14** and subsequent treatment with Me_2S and $NaBH_4$ in CH_2Cl_2/MeOH provided alcohol (−)-**15** (99%). It was converted into iodide (−)-**16** on treatment with Ph_3P/1*H*-imidazole and I_2 (79%) and then into the phosphonium iodide (−)-**11** (Ph_3P, benzene; 64% overall yield based on L-fucose) applying classical procedures.

Aldehyde (+)-**10** was derived from isolevoglucosenone (**17**) [16] in 52% overall yield (*Scheme 1*). Conjugated addition of PhSH to **17** (Et_3N as catalyst) afforded (−)-**18** quantitatively. The high *exo* stereoselectivity of this addition was expected for both kinetic and thermodynamic reasons (steric factor) [17]. The 2-(phenylthio) substituent was introduced to insure stereoselective β-*C*-glycosidation (see below). The *C*-glycosidation of allyltrimethylsilane with ketone (−)-**18** failed as treatment of (−)-**18** under *Lewis* acid conditions led to the bis-allylated product. Ketone (−)-**18** was thus reduced into a mixture of alcohols **19** and **20**. The diastereoselectivity (product ratio **19**/**20**) was poor with $NaBH_4$ in MeOH at 0° (1:1), with $LiBH_4$ in THF at −78° (1:2), and with $LiAlH(O^tBu)_3$ in THF at −78° (1:1.2). With *K-Selectride* (K^sBu_3BH), *L-Selectride* (Li^sBu_3BH), and *Super-H* ($LiEt_3BH$) in THF at −78°, **20** was the major product of reduction, with diastereoselectivities of 1:5, <1:10, and <1:10, respectively. In contrast, with DIBAL-H ($^iBu_2AlH$) in THF at −78°, reduction of (−)-**18** gave alcohol **19** predominantly with a diastereoselectivity better than 7:1. Alcohols **19** and **20** were acetylated separately under standard conditions, giving acetate (−)-**21** (56%) and (−)-**22** (88%), respectively.

Attempts to promote the *C*-glycosidation of (−)-**22** with allyltrimethylsilane in CH_2Cl_2 by $Me_3SiOSO_2CF_3$ alone, by $BF_3 \cdot OEt_2$ alone, or by both *Lewis* acids simultaneously led only to products of decomposition (0°). When CH_2Cl_2 was exchanged for MeCN as solvent, traces of *C*-glycosides (+)-**24** and **25** were formed besides glycal (+)-**23** that was isolated in 70% yield (*Scheme 1*). To our delight, we found that, when nitromethane was used as solvent and in the presence of a large amount of allyltrimethylsilane, a 10:1 mixture of (+)-**24** and **25** could be isolated in 81% yield. For success, both *Lewis* acid $Me_3SiOSO_2CF_3$ and $BF_3 \cdot OEt_2$ were necessary in equimolar ratio (−20°). Pure (+)-**24** was obtained by flash chromatography (FC; silica gel). Its structure was deduced from its ^{1}H-NMR spectrum that showed typically large ^3J(H,H) (axial/axial H) coupling constants of a β-D-glucopyranosyl system. The 6-OH group of crude (+)-**24** was protected as a MOM ether, giving (+)-**26** (82%, based on (−)-**22**; <10% of **27**). Dihydroxylation of (+)-**26** with *N*-methylmorpholine *N*-oxide (NMO) and a catalytical amount of OsO_4 yielded a mixture **28** of diols that was oxidized by $Pb(OAc)_4$ in benzene/pyridine to furnish aldehyde (+)-**10** (96%). Treatment of phosphonium salt (−)-**11** with BuLi in THF (−78°) followed by addition of aldehyde (+)-**10** led to a mixture of (+)-**12** and its product of saponification (−)-**29**.

Scheme 1

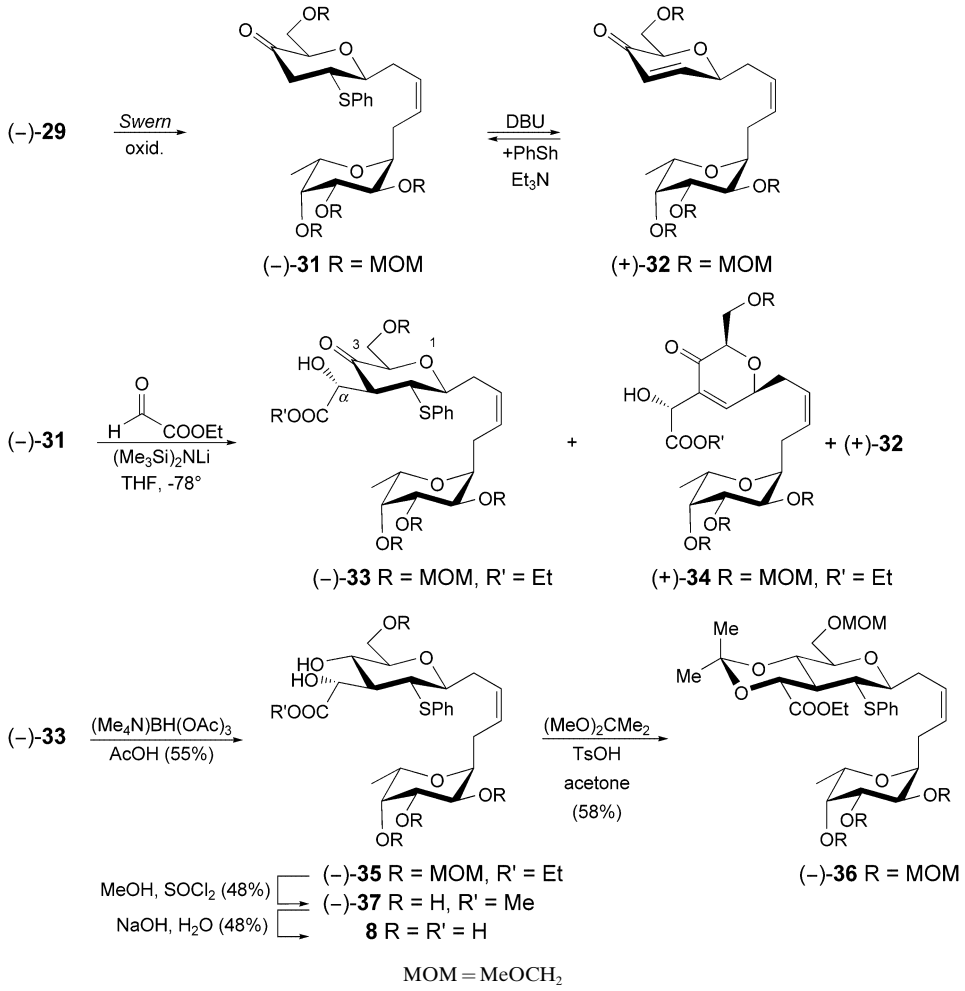


This crude mixture, upon treatment with K_2CO_3/MeOH at 20°, produced pure (–)-**29** in 63–76% yield after FC (silica gel; removal of Ph_3PO).

Cleavage of the MOM protective group of (–)-**29** was realized by treatment with MeOH and thionyl chloride (20 equiv.) at 0°. This gave **30** in 30% yield only (*Scheme 1*). *Swern* oxidation of (–)-**29** ($(COCl)_2$, DMSO, CH_2Cl_2, –78°, then Et_3N)

furnished ketone (−)-**31**, (*Scheme 2*), an unstable compound that eliminated PhSH on storing at room temperature under diluted conditions. Treatment of crude (−)-**31** with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) at 0° provided enone (+)-**32** (89%, based on (−)-**29**). Reaction of 0.1M (+)-**32** with 2 equiv. of PhSH in CH_2Cl_2 at 20° (Et_3N as catalyst promoted) equilibration with (−)-**31**, which could be isolated by low-temperature FC in 65% yield. Crude (−)-**31** (obtained by *Swern* oxidation) was used directly in its cross-aldol condensation with ethyl glyoxylate. This led to a complex mixture of products from which pure aldol (−)-**33** and enones (+)-**34** and (+)-**32** could be isolated in 29%, 32%, and 22% yield, respectively. Reduction of aldol (−)-**33** with $(Me_4N)BH(OAc)_3$ [18] in AcOH (20°) provided the glucopyranosyl derivative (−)-**35**. Its structure was established by its ^{1}H-NMR spectrum (typical vicinal coupling constants $^3J(2,3) = 9.6$ Hz and $^3J(3,4) = 9.9$ Hz). The configuration of the secondary-

Scheme 2



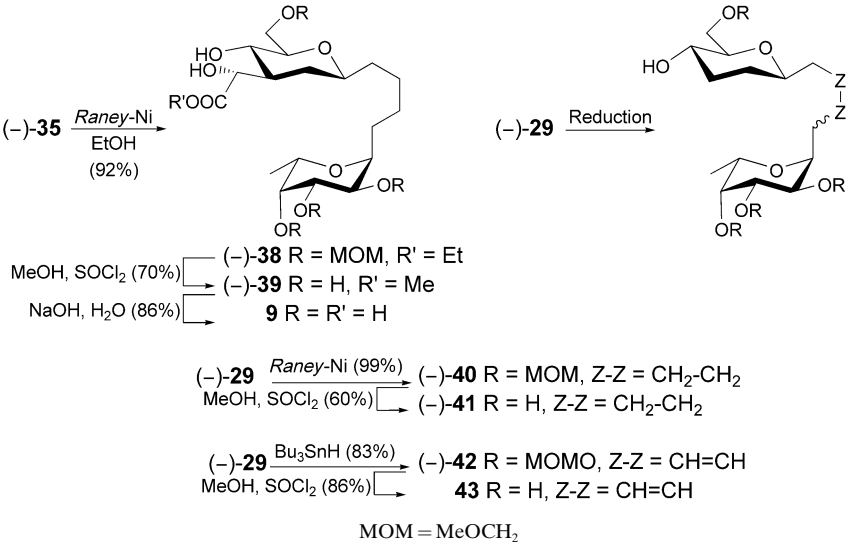
MOM = $MeOCH_2$

alcohol moiety of the 3-(hydroxyacetate) group was determined by the NMR data (^3J(H,H) and 2D-NOESY ^{1}H-NMR) of acetonide (−)-**36**, obtained by treatment of (−)-**35** with acetone and $(MeO)_2CMe_2$ under acidic conditions (TsOH) [19]. The ^{13}C-NMR spectrum for the *gem*-dimethyl moiety of (−)-**36** (δ(C) 19.8 and 29.7) is typical of the chair conformation imposed by the substitution of the 1,3-dioxane system [20]. This result confirmed that the aldol condensation (−)-**31** + EtOCOCHO follows the *Zimmerman–Traxler* model [21]. Attemps to obtain the β-D-galactopyranoside analogue of (−)-**35** all failed. Reductions of (−)-**33** with $NaBH_4$ in excess, ^{i}Bu$_2$AlH, *L-Selectride*, *K-Selectride*, or $Et_2BOMe/NaBH_4$ [22] all gave (−)-**35** and by-products containing alcohol (−)-**29** resulting from a *retro*-aldol reaction of (−)-**33** with formation of ketone (−)-**31** and subsequent reduction.

Treatment of (−)-**35** with MeOH and $SOCl_2$ (0°) gave hexahydroxy ester (−)-**37** (48%). Saponification of (−)-**37** (0.1M NaOH/H_2O) furnished the sialyl Lewis x mimetic **8** that was isolated in 48% yield (*Scheme 2*).

Reductive desulfurization of (−)-**35** with *Raney*-Ni in EtOH afforded (−)-**38** (63%, based on (−)-**33**) (*Scheme 3*). Hydrogenation of the alkene moiety could not be avoided. Acidic methanolysis of (−)-**38** with $SOCl_2$/MeOH gave hexahydroxy ester (−)-**39** (70%). Saponification of (−)-**39** produced **9** in 86% yield. In a similar way, (−)-**29** was converted into (−)-**40** (99%) and then deprotected into (−)-**41** (60%). To avoid hydrogenation of the C=C bond of (−)-**29**, we carried out the desulfurization of (−)-**29** with Bu_3SnH and AIBN (2,2′-azabis[2-methylpropanenitrile]) (toluene, 80°). This led to a 1:2 mixture of (*Z*)- and (*E*)-alkene derivatives (−)-**42** (83%). Deprotection ($SOCl_2$, MeOH, 0°) provided **43** ((*Z*)/(*E*) 1:2). All the new substances described here were characterized by the spectral data (see *Exper. Part*).

Scheme 3



Affinity of the New sLe^x Mimetics toward P-Selectin by an ELISA Test. – Evaluation of the affinity for P-selectin of **8**, **9**, **30**, (−)-**41**, and **43** relative to sLe^x were carried out following a protocol already described [23], which implied solutions of the ligands with a concentration varying between 1 μM to 10 mM. The results are given in the *Table*. The *Figure* displays the fitted curve for each product used in the biological testing.

Table. IC_{50} [mM] *Values for Some Synthesized Products Obtained as Described in the* Exper. Part. The IC_{50} values are given as 90% confidence intervals, obtained from the curve fitting, and with the R^2 for each curve fitting.

	8	**9**	**30**	(−)-**41**	**43**	sLe^x[a])
IC_{50}	2.4–2.8	7.3–8.0	5.3–5.9	5.0–5.2	3.3–4.1	0.7
R^2	0.9954	0.9874	0.9903	0.9968	0.9890	–

[a]) IC_{50} = 8 mM for a P-selectin ELISA-based assay by *Kaila* and co-workers [6].

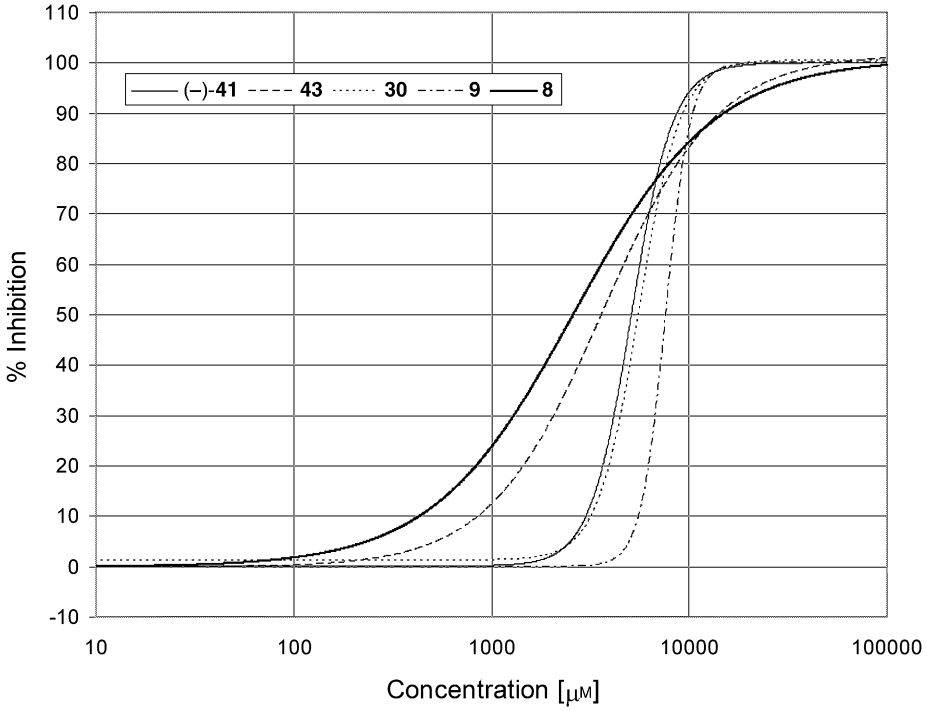


Figure. *Curve fitting from the measurements obtained in the ELISA test with* **8**, **9**, **30**, *(−)*-**41**, *and* **43**. For each product, every set of concentration was tested between two and six times. All inhibitions were calculated as described in the *Exper. Part*.

Discussion. – All new sialyl Lewis x mimetics **8**, **9**, **30**, (−)-**41**, and **43** are recognized by P-selectin at low mM concentration. The best ligand is **8**, which is only four times weaker than sLe^x itself. Removal of the 2-(phenylthio) substituent group in **8** and

reducing its alkene moiety gives ligand **9**, which shows a diminished (by a factor of 3) binding affinity. Recent results by *Thoma* and *Schwarzenbach* [3] with mimetics **2** and **3** have shown that the 2-OH group of the β-D-galactopyranosyl moiety of **2** can be esterified without loss of the binding affinity. In fact, the 2-(benzoyloxy) derivative **3** is three times better than **2** for binding E-selectin. Thus, our observations made with **8** and **9**, are parallel to those made with **2** and **3**. It is surprising that our mimetics **8** and **9**, which have a β-D-glucopyranosyl moiety instead of the β-D-galactopyranoside unit of sLe^x, and analogues such as **2** and **3** should maintain a binding affinity almost as good as sLe^x assays with P-selectin. This might not be the case with E-selectin. A second surprise is the observation that the simpler analogues of **8** and **9**, which are devoid of any carboxylic moiety, are in fact as active as **9**. As expected for entropy reasons, mimetics with the (*Z*)-alkene moiety that imitates the GlcNAc unit of sLe^x should be better ligands than the correponding alkanes. The greater binding activity of **43** (IC_{50} 3.7 mM) compared with that of (−)-**41** (IC_{50} 5.1 mM) is in agreement with this hypothesis, although the difference in binding affinity is relatively small!

Conclusion. – Compound (−)-**41**, which links a 2,3-dideoxy-β-D-*erythro*-hexopyranosyl moiety with an α-L-fucopyranosyl moiety through a butane-1,4-diyl spacer, realizes a simple nonhydrolyzable mimetic of sLe^x as it binds to P-selectin with an affinity only eight times lower than that of sLe^x! If the butane-1,4-diyl spacer is replaced by a less flexible (2*Z*)-but-2-en-1,4-diyl moiety, as in **43**, the binding affinity is slightly improved. Decoration of the 2,3-dideoxy-β-D-*erythro*-hexopyranosyl unit with a 2-(phenylthio) substituent or/and a 3-(2-hydroxyacetic acid) group might enhance the binding affinity to P-selectin. We suggest that other simple analogues (other stereoisomers) of (−)-**41** and **43** with further substituents that could vary widely should be made and tested for their binding affinity to the selectins.

We are grateful to the *Swiss National Science Foundation* and the *Office Fédéral de l'Education et de la Science* (Bern, COST D13/0001/99) for financial support. We thank also Mr. *Martial Rey* and Mr. *Francisco Sepulveda* for their technical help, and Prof. *Inmaculada Robina*, University of Seville (*SOCRATES* EPFL-Seville), for helpful discussions and assistance in the high-resolution mass spectroscopy.

Experimental Part

General. See [24].

Antibodies and Chimeric Proteins. The anti-P-selectin antibody able to block almost all P-selectin interactions (WAPS 12.2) is produced from hybridoma-cell (ATCC number HB-299) culture medium and purified by using the MAPP II kit (*Bio-Rad Laboratories*, Glattbrugg, Switzerland) or are from private industries (*Dako*, Glostrup, Danemark, and *Amersham Pharmacia Biotech*, Dübendorf, Switzerland). The P-selectin/μ chimera is obtained from the culture medium of CHO cells transfected with a plasmid containing the corresponding DNA as described previously [23].

Determination of Products Concentration Giving 50% of Inhibition (IC_{50}) *by ELISA*. At 37°, 0.15 μg of sLe^x-BSA (*Oxford GlycoSystems*, Oxford, United Kingdom) diluted in carbonate buffer (pH 9.4) is coated overnight in a 96-well high-binding ELISA plate (*Costar*, Cambridge, MA). The plate is then washed (3 times with 200 μl of PBS + 0.1% BSA + 0.05% *Tween-20*) and blocked (200 μl of PBS + 1% BSA) for 2 h at 37°. P-Selectin/μ chimera is diluted to a final concentration of 2 μg/ml with or without inhibitor, then preincubated for 1 h at 20° with a biotin-labeled anti-human IgM antibody (goat anti-human IgM biotin; *Catlag*, Bulingame, CA) and peroxydase-linked streptavidin (*Amersham Bioscience*, Uppsala, Sweden). The inhibitors are diluted from 1 mM to 10 nM. All these mixtures are then incubated for 4 h at 20° in the wells of the ELISA plate. The plate revelation is made with OPD (0.67 mg/ml; *Sigma*, Steinheim, Germany) in a citrate/phosphate buffer (pH

5.0) + 0.16 (*v*/*v*) H_2O_2, and the reaction is blocked with 50 µl of 3M H_2SO_4. The absorbance for each plate well is read at 490 nm with a plate reader (model *MR-500*; *Dynatech*, *Microtec Produkte*, Embrach-Embraport, Switzerland). The noise corresponding to the absorbances from the detection complex is subtracted from all absorbances of the plates. For each concentration and all products, relative inhibitions are calculated by *Eqn. 1* and the absorbances obtained without inhibitors and the one obtained with the anti-P-selectin antibody WAPS. Then, for each product, the inhibitions are plotted against the concentrations, and the IC_{50} is calculated with the *GraphPad*® program from *Prism*, following the manual instructions.

$$\text{Inhibition}[\%] = \frac{(\text{Abs(w/o inhib)} - \text{Abs(product)})}{(\text{Abs(w/o inhib)}\text{Abs(WAPS)})} \cdot 100 \quad (1)$$

*(*α*R,2R,3S,4R,5R,6S)-Tetrahydro-α,3-dihydroxy-2-(hydroxymethyl)-5-(phenylthio)-6-[(2Z)-4-[(2S,3S,4R,5S,6S)-tetrahydro-3,4,5-trihydroxy-6-methyl-2*H*-pyran-2-yl]but-2-enyl]-2*H*-pyran-4-acetic Acid* (**8**). A mixture of (−)-**37** (15 mg, 0.028 mmol) and 0.1M aq. NaOH (1 ml, 0.1 mmol) was stirred at 20° for 6 h. The mixture was neutralized with 0.1M aq. HCl (1.2 ml) and the solvent evaporated. The residue was purified by reversed-phase HPLC (*Vydac Protein C4*, 15 → 45% MeCN/H_2O): 7 mg (48%) of pure **8**. White powder. IR (film): 3420, 2925, 1720, 1635, 1440, 1385, 1240, 1125, 1070, 875, 840, 750, 690, 660. ^{1}H-NMR (400 MHz, CD_3OD): 7.57–7.53, 7.36–7.26 (2*m*, 5 arom. H); 5.60 (*ddd*, $^3J(2',3') = 10.8$, $^3J(2',1') = 6.8$, 6.8, H−C(2′)); 5.46 (*ddd*, $^3J(3',2') = 10.8$, $^3J(3',4') = 6.8$, 6.8, H−C(3′)); 5.04 (*s*, H−C(α)); 3.92 (*ddd*, $^3J(2'',4'') = 10.5$, $^3J(2'',3'') = 5.4$, $^3J(2'',4') = 5.4$, H−C(2″)); 3.89 (*dd*, $^3J(3'',4'') = 8.6$, $^3J(3'',2'') = 5.4$, H−C(3″)); 3.80 (*qd*, $^3J(6'', \text{Me}-C(6'')) = 6.5$, $^3J(6'',5'') = 1.9$, H−C(6″)); 3.77 (*dd*, $^2J = 11.9$, $^3J(CH_2-C(2),2) = 1.9$, 1 H, CH_2−C(2)); 3.73 (*dd*, $^3J(3,4) = 10.8$, $^3J(3,2) = 9.7$, H−C(3)); 3.71–3.69 (*m*, H−C(5″)); 3.66 (*dd*, $^3J(4'',3'') = 8.6$, $^3J(4'',5'') = 3.5$, H−C(4″)); 3.58 (*dd*, $^2J = 11.9$, $^3J(CH_2-C(2),2) = 6.0$, 1 H, CH_2−C(2)); 3.36–3.28 (*m*, H−C(6), overlapped by solvent); 3.10 (*ddd*, $^3J(2,3) = 9.7$, $^3J(2, CH_2-C(2)) = 6.0$, $^3J(2, CH_2-C(2)) = 1.9$, H−C(2)); 3.01 (*dd*, $^3J(5,4) = 11.8$, $^3J(5,6) = 10.6$, H−C(5)); 2.85 (*ddm*, $^2J = 14.8$, $^3J(1',2') = 6.8$, 1 H−C(1′)); 2.45–2.23 (*m*, 2 H−C(4′), 1 H−C(1′)); 2.18 (*dd*, $^3J(4,5) = 11.9$, $^3J(4,3) = 10.8$, H−C(4)); 1.20 (*d*, $^3J(\text{Me}-C(6''),6'') = 6.5$, Me−C(6″)). ^{13}C-NMR (100.6 MHz, CD_3OD): 178.7 (*s*, COOH); 135.1 (*s*, arom. C), 133.9 (2 arom. C); 130.2 (2 arom. C); 129.1 (C(3′)); 128.7 (arom. C); 128.4 (C(2′)); 82.7 (C(2)); 82.5 (C(6)); 76.3 (C(2″)); 72.6 (C(5″)); 72.2 (C(4″)); 69.9 (C(3″)); 69.0 (C(6″)); 69.0 (C(α)); 65.9 (C(3)); 63.1 (CH_2−C(2)); 52.0 (C(4)); 52.0 (C(5)); 32.5 (C(1′)); 24.5 (C(4′)); 16.7 (Me−C(6″)). ESI-MS: 1029.34 (92, $[2M]^+$), 536.83 (6, $[M + Na]^+$), 532.32 (12, $[M + H_2O]^+$), 515.32 (100, $[M + H]^+$). FAB-MS: 537 (30, $[M + Na]^+$), 237 (100). HR-FAB-MS: 537.1768 ($C_{24}H_{34}NaO_{10}S^+$, $[M + Na]^+$; calc. 537.1770).

*(*α*R,2R,3S,4R,6S)-Tetrahydro-α,3-dihydroxy-2-(hydroxymethyl)-6-[4-[(2S,3S,4R,5S,6S)-tetrahydro-3,4,5-trihydroxy-6-methyl-2*H*-pyran-2-yl]butyl]-2*H*-pyran-4-acetic Acid* (**9**). As described for **8**, with (−)-**39** (50 mg, 0.118 mmoles): 41 mg (86%) of pure **9**. White powder. IR (film): *ca.* 3500, 2935, 1720, 1640, 1385, 1230, 1080. ^{1}H-NMR (CD_3OD, 400 MHz): 4.26 (*d*, $^3J(\alpha,4) = 2.6$, H−C(α)); 3.95–3.88 (*m*, H−C(2″), H−C(3″)); 3.84 (*dd*, $^2J = 12.0$, $^3J(CH_2-C(2),2) = 2.2$, 1 H, CH_2−C(2)); 3.80 (*qd*, $^3J(6'', \text{Me}-C(6'')) = 6.5$, $^3J(6'',5'') = 1.8$, H−C(6″)); 3.74–3.69 (*m*, H−C(5″), H−C(4″)); 3.64 (*dd*, $^2J = 12.0$, $^3J(CH_2-C(2),2) = 6.0$, 1 H, CH_2−C(2)); 3.55 (*dd*, $^3J(3,4) = 10.0$, $^3J(3,2) = 9.5$, H−C(3)); 3.50–3.42 (*m*, H−C(6)); 3.24 (*ddd*, $^3J(2,3) = 9.5$, $^3J(2, CH_2-C(2)) = 6.0$, 2.2, H−C(2)); 2.15 (*dddd*, $^3J(4,5\text{ax}) = 11.8$, $^3J(4,3) = 10.0$, $^3J(4,\alpha) = 2.6$, $^3J(4,5\text{eq}) = 2.4$, H−C(4)); 1.82 (*dm*, H_{eq}−C(5)); 1.75–1.24 (*m*, 2 H−C(1′), 2 H−C(2′), 2 H−C(3′), 2 H−C(4′), H_{ax}−C(5)); 1.20 (*d*, $^3J(\text{Me}-C(6''),6'') = 6.5$, Me−C(6″)). ^{13}C-NMR (100.6 MHz, CD_3OD): 177.7 (*s*, COOH); 82.9 (*d*, $^1J(C,H) = 141$, C(2)); 78.2 (*d*, $^1J(C,H) = 139$, C(6)); 76.5 (*d*, $^1J(C,H) = 148$, C(2″)); 72.8 (*d*, $^1J(C,H) = 145$, C(5″) or C(4″)); 71.7 (*d*, $^1J(C,H) = 145$, C(α)); 71.5 (*d*, $^1J(C,H) = 140$, C(4″) or C(5″)); 69.5 (*d*, $^1J(C,H) = 142$, C(3″)); 68.1 (*d*, $^1J(C,H) = 129$, C(6″)); 66.8 (*d*, $^1J(C,H) = 135$, C(3)); 62.9 (*t*, $^1J(C,H) = 143$, CH_2−C(2)); 47.5 (*t*, $^1J(C,H) = 129$, C(4)); 36.3 (*t*, $^1J(C,H) = 125$, C(1′)); 34.4 (*t*, $^1J(C,H) = 129$, C(5)); 26.7 (*t*, $^1J(C,H) = 129$, C(2′) or C(3′)); 26.1 (*t*, $^1J(C,H) = 128$, C(3′) or C(2′)); 24.8 (*t*, $^1J(C,H) = 125$, C(4′)); 16.7 (*q*, $^1J(C,H) = 127$, Me−C(6″)). ES: 839.3 (36, $[2M + Na]^+$), 430.86 (100, $[M + Na]^+$), 356.87 (34, product of *retro*-ene reaction). HR-FAB-MS: 431.1883 ($C_{18}H_{32}NaO_{10}^+$, $[M + Na]^+$; calc. 431.1893).

*(2S,3R,5S,6R)-5-(Acetyloxy)-tetrahydro-6-[(methoxymethoxy)methyl]-3-(phenylthio)-2*H*-pyran-2-acetaldehyde* ((+)-**10**). A mixture of crude diol (+)-**28** (8.05 g, 20.1 mmol) and $Pb(OAc)_4$ (10.1 g, 22.8 mmol) in benzene (200 ml) and anh. pyridine (200 ml) was stirred at 20° for 40 min. After evaporation, the residue was purified by FC (silica gel, AcOEt): 7.114 g (96%) of (+)-**10**. Colorless oil. $[\alpha]_{589}^{25} = +31$, $[\alpha]_{577}^{25} = +32$, $[\alpha]_{546}^{25} = +34$, $[\alpha]_{435}^{25} = +53$, $[\alpha]_{405}^{25} = +60$ ($c = 1.0$, $CHCl_3$). UV (MeCN): 254 (5000), 221 (4900). IR (film): 2940, 2885, 1735, 1580, 1475, 1440, 1375, 1235, 1150, 1090, 1040, 920, 805, 750. ^{1}H-NMR (400 MHz, CD_2Cl_2): 9.76 (*dd*, $^3J(\text{CH=O},\alpha) = 2.7$, $^3J(\text{CH=O},\alpha) = 1.1$, CH=O); 7.50–7.30 (*m*, 5 arom. H); 4.75 (*ddd*, $^3J(5,4\text{ax}) = 11.0$, $^3J(5,6) = 9.8$, $^3J(5,4\text{eq}) = 4.8$, H−C(5)); 4.57, 4.54 (2*d*, $^2J = 6.5$, MeOCH_2); 3.88 (*ddd*, $^3J(2,3) = 10.2$,

$^3J(2,\alpha) = 9.2$, $^3J(2,\alpha) = 2.8$, H–C(2)); 3.57–3.55 (*m*, CH_2–C(6)); 3.88 (*ddd*, $^3J(6,5) = 9.8$, $^3J(6,CH_2$–C(6)) = 7.3, 3.8, H–C(6)); 3.28 (*s*, *Me*OCH_2); 3.08 (*ddd*, $^2J = 16.7$, $^3J(\alpha,2) = 2.8$, $^3J(\alpha,CH{=}O) = 1.1$, 1 H–C(α)); 3.03 (*ddd*, $^3J(3,4ax) = 12.4$, $^3J(3,2) = 10.2$, $^3J(3,4eq) = 4.1$, H–C(3)); 2.58 (*ddd*, $^2J = 16.7$, $^3J(\alpha,2) = 9.2$, $^3J(\alpha,CH{=}O) = 2.7$, 1 H–C(α)); 2.58 (*ddd*, $^2J = 12.4$, $^3J(4eq,5) = 4.8$, $^3J(4eq,3) = 4.1$, H_{eq}–C(4)); 2.02 (*s*, *Me*CO); 1.60 (*ddd*, $^2J = 12.4$, $^3J(4ax,3) = 12.4$, $^3J(4ax,5) = 11.0$, H_{ax}–C(4)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2): 200.5 (*d*, $^1J(C,H) = 175$, CH=O); 170.0 (*s*, *Me*CO); 133.7 (*d*, $^1J(C,H) = 161$, 2 arom. C); 132.5 (*s*, arom. C); 129.6 (*d*, $^1J(C,H) = 161$, 2 arom. C); 128.5 (*d*, $^1J(C,H) = 161$, arom. C); 96.9 (*t*, $^1J(C,H) = 163$, MeOCH_2); 79.0 (*d*, $^1J(C,H) = 141$, C(6)); 77.1 (*d*, $^1J(C,H) = 144$, C(2)); 67.8 (*d*, $^1J(C,H) = 152$, C(5); 66.6 (*t*, $^1J(C,H) = 142$, CH_2–C(6)); 55.2 (*q*, $^1J(C,H) = 142$, *Me*OCH_2; 47.3 (*d*, $^1J(C,H) = 141$, C(3)); 47.3 (*td*, $^1J(C,H) = 128$, $J = 25$, C(α)); 37.1 (*t*, $^1J(C,H) = 133$, C(4)); 21.2 (*q*, $^1J(C,H) = 130$, *Me*CO). CI-MS (NH_3): 386 (100, $[M + NH_4]^+$), 369 (37, $[M + H]^+$), 368 (34, M^+), 337 (39, $[M - OMe]^+$), 324 (8, $[M + H - MeOCH_2]^+$), 307 (4, $[M - MeOCH_2O]^+$), 276 (11, $[M - Ph - Me]^+$). Anal. calc. for $C_{18}H_{24}O_6S$ (368.35): C 58.68, H 6.57, S 8.70; found: C 58.62, H 6.49, S 8.69.

*{2-[(2*S*,3*R*,4*R*,5*R*,6*S*)-Tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]ethyl}triphenylphosphonium Iodide* ((–)-**11**). A mixture of iodide (–)-**16** (5 g, 11.5 mmol) and PPh_3 (6.38 g, 23.0 mmol) in benzene (50 ml) was stirred at 20° for 10 min and then heated under reflux for 24 h. After evaporation, the residue was taken up in CH_2Cl_2 (10 ml), and this soln. was poured dropwise into Et_2O (200 ml). The precipitate was recovered. The filtrate was evaporated and the residue dissolved in CH_2Cl_2 (10 ml). This soln. was added dropwise to Et_2O (200 ml) giving a second fraction of crude (–)-**11**. Both precipitates were dissolved in CH_2Cl_2 (8 ml), and the soln. was poured into Et_2O (200 ml) (elimination of residual PPh_3). The precipitate was collected and dissolved in CH_2Cl_2 (20 ml) and the soln. evaporated again: 7.73 g of (–)-**11** (containing 10% of PPh_3; converted mass (yield), 7.67 g (96%). White foam. $[\alpha]_{589}^{25} = -1.1$, $[\alpha]_{577}^{25} = -0.8$, $[\alpha]_{546}^{25} = -0.8$, $[\alpha]_{435}^{25} = -0.7$, $[\alpha]_{405}^{25} = -1.1$ ($c = 1.0$, $CHCl_3$). UV (MeCN): 231 (17400). IR (film): 2895, 1630, 1585, 1480, 1440, 1365, 1320, 1215, 1150, 1110, 1030, 990, 915, 810, 750, 690. ^{1}H-NMR (400 MHz, CD_2Cl_2): 7.92–7.73 (*m*, 15 arom. H); 4.78, 4.64 (2*d*, $^2J = 6.8$, 1 MeOCH_2); 4.71, 4.67 (2*d*, $^2J = 6.8$, 1 MeOCH_2); 4.64, 4.58 (2*d*, $^2J = 6.8$, 1 MeOCH_2); 4.14 (br. *ddd*, $^3J(2',2) = 9.7$, $^3J(2',2) = 3.0$, $^3J(2',3') = 3.0$, H–C(2')); 3.90–3.81 (*m*, H–C(3'), H–C(4'), H–C(5'), H–C(6')); 3.66–3.43 (*m*, 2 H–C(1)); 3.38, 3.36, 3.19 (3*s*, 3 *Me*OCH_2); 2.11–1.92 (*m*, 2 H–C(2)); 1.33 (*d*, ^3J(Me–C(6'),6') = 6.5, Me–C(6')). ^{13}C-NMR ((100.6 MHz, CD_2Cl_2): 135.7, 135.7 (2*d*, $^1J(C,H) = 166–163$, 3 arom. C); 134.0, 133.9, 131.0, 130.8 (4*d*, $^1J(C,H) = 166–163$, 12 arom. C); 118.6, 117.8 (2*s*, 3 arom. C); 97.7, 97.0, 96.7 (3*t*, $^1J(C,H) = 162$, 3 MeOCH_2); 75.9 (*d*, $^1J(C,H) = 147$, C(3', 4', 5', or 6')); 74.7 (*d*, $^1J(C,H) = 145$, C(3', 4', 5', or 6')); 73.8 (*d*, $^1J(C,H) = 142$, C(3', 4', 5', or 6')); 70.7 (*d*, $^1J(C,H) = 143$, C(2')); 69.7 (*d*, $^1J(C,H) = 141$, C(3', 4', 5', or 6')); 56.1, 56.0, 55.9 (3*q*, $^1J(C,H) = 143$, 3 *Me*OCH_2); 21.7 (*t*, $^1J(C,H) = 130$, C(2)); 20.2 (*t*, $^1J(C,H) = 135$, C(1)); 15.6 (*q*, $^1J(C,H) = 127$, *Me*–C(6')). CI-MS (NH_3): 570 (7, $[M - I + H]^+$), 569 (8, $[M - I]^+$), 279 (44, $[PPh_3 + NH_3]^+$), 263 (77, $[PPh_3 + H]^+$), 183 (26), 83 (100).

*(2*R*,3*S*,5*R*,6*S*)-Tetrahydro-2-[(methoxymethoxy)methyl]-5-(phenylthio)-6-{(2*Z*)-4-[(2*S*,3*R*,4*R*,5*R*,6*S*)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-3-ol Acetate* ((+)-**12**). At –78°, 1.6M BuLi in hexane (1.05 ml, 1.68 mmol) was added dropwise to a stirred soln. of (–)-**11** (1.033 g, 1.48 mmol) in anh. THF (15 ml). After 20 min at –78°, a soln. of (+)-**10** (364 mg, 0.99 mmol) in anh. THF (5 ml) was added dropwise under stirring at –78°. After stirring at –78° for another 20 min, solvents were evaporated at –20°. The residue was purified by FC (silica gel, Et_2O): *Fr. 1* containing 341 mg (53%) of (+)-**12**, 39 mg (6%) of *Fr. 2* containing (+)-**12** and (–)-**29**, and *Fr. 3* of (–)-**29** (100 mg, 17%), all as colorless oils.

Data of (+)-**12**: $[\alpha]_{589}^{25} = +16$, $[\alpha]_{577}^{25} = +17$, $[\alpha]_{546}^{25} = +19$, $[\alpha]_{435}^{25} = +33$, $[\alpha]_{405}^{25} = +42$ ($c = 1.0$, $CHCl_3$). UV (MeCN): 256 (5900), 205 (9500). IR (film): 2935, 1740, 1440, 1375, 1235, 1150, 1110, 1035, 990, 805, 740, 695. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42–7.28 (*m*, 5 arom. H); 5.65 (*ddd*, $^3J(2'',3') = 10.9$, $^3J(2',1') = 6.8, 6.8$, H–C(2')); 5.54 (*ddd*, $^3J(3',2') = 10.9$, $^3J(3',4') = 6.8, 6.8$, H–C(3')); 4.87, 4.67 (2*d*, $^2J = 6.9$, 1 MeOCH_2); 4.74, 4.64 (2*d*, $^2J = 6.9$, 1 MeOCH_2); 4.78–4.71 (*m*, H–C(3), 1 MeOCH_2); 4.63, 4.60 (2*d*, $^2J = 6.9$, 1 MeOCH_2); 4.09–4.03 (*m*, H–C(2'')); 3.96–3.89 (*m*, H–C(3''), H–C(4''), H–C(5''), H–C(6'')); 3.60–3.58 (*m*, CH_2–C(2)); 3.46–3.30 (*m*, H–C(2), H–C(6)); 3.42, 3.39, 3.35, 3.22 (4*s*, 4 *Me*OCH_2); 3.03 (*ddd*, $^3J(5,4ax) = 12.5$, $^3J(5,6) = 10.2$, $^3J(5,4eq) = 4.3$, H–C(5)); 2.78 (*ddm*, $^2J = 14.6$, $^3J(1',2') = 6.8$, H–C(1')); 2.51 (*ddd*, $^2J = 12.5$, $^3J(4eq,3) = 4.5$, $^3J(4eq,5) = 4.5$, H_{eq}–C(4)); 2.48 (*m*, 2 H–C(4'), 1 H–C(1')); 2.02 (*s*, *Me*CO); 1.54 (*ddd*, $^2J = 12.5$, $^3J(4ax,5) = 12.5$, $^3J(4ax,3) = 11.1$, H_{ax}–C(4)); 1.31 (*d*, ^3J(Me–C(6''),6'') = 6.4, Me–C(6'')). ^{13}C-NMR (100.6 MHz, CD_2Cl_2): 169.8 (*s*, MeCO); 133.1 (*d*, $^1J(C,H) = 162$, 2 arom. C); 132.7 (*s*, arom. C); 129.1 (*d*, $^1J(C,H) = 162$, 2 arom. C); 127.9 (*d*, $^1J(C,H) = 162$, C(3')); 127.8 (*d*, $^1J(C,H) = 161$, arom. C); 126.9 (*d*, $^1J(C,H) = 155$, C(2')); 97.5, 96.9, 96.8, 96.5 (4*t*, $^1J(C,H) = 167$, 4 MeOCH_2); 81.0 (*d*, $^1J(C,H) = 140$, C(6)); 78.7 (*d*, $^1J(C,H) = 142$, C(2)); 75.6 (*d*, $^1J(C,H) = 141$, C(3'', 4'', 5'', or 6'')); 75.2 (*d*, $^1J(C,H) = 144$, C(3'', 4'', 5'', or 6'')); 74.4 (*d*, $^1J(C,H) = 145$, C(3'', 4'', 5'', or 6'')); 71.6 (*d*, C(2'')); 68.4 (*d*, $^1J(C,H) = 140$, C(3'', 4'', 5'', or 6'')); 68.0 (*d*, $^1J(C,H) = 152$, C(3));

66.6 (*t*, ^1J(C,H) = 142, CH_2–C(2)); 55.8, 55.8, 55.6, 55.2 (4*q*, ^1J(C,H) = 143, 4 *Me*OCHH$_2$); 46.5 (*d*, ^1J(C,H) = 139, C(5)); 37.0 (*t*, ^1J(C,H) = 131, C(4)); 30.9 (*t*, ^1J(C,H) = 125, C(1′)); 25.5 (br. *t*, ^1J(C,H) ≈ 120, C(4′)); 21.0 (*q*, ^1J(C,H) = 129, *Me*CO); 15.7 (*q*, ^1J(C,H) = 129, *Me*–C(6″)). CI-MS(NH_3): 678 (75), 677 (100), 676 (76, $[M+NH_4]^+$), 659 (1.5, $[M+H]^+$), 658 (1.3, M^+), 644 (1, $[M+H-Me]^+$), 627 (12, $[M-OMe]^+$), 600 (5, $[M+H-OAc]^+$), 551 (13), 365 (13). Anal. calc. for $C_{32}H_{50}O_{12}S$ (658.81): C 58.34, H 7.54; found: C 58.08, H 7.72.

*(2S,3R,4R,5R,6S)-Tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2-(prop-2-enyl)-2*H*-pyran* ((−)-**14**). Bu_4NI (500 mg) was added to a stirred soln. of (−)-**13** [4] (4.43 g, 23.5 mmol) in CH_2Cl_2 (235 ml). After cooling at 0°, $^i Pr_2NEt$ (24.2 ml, 141 mmol) and $MeOCH_2Cl$ (7.15 ml, 94.2 mmol) were added successively. The mixture was stirred at 20° for 2 h, and more $^i Pr_2NEt$ (24.2 ml) and $MeOCH_2Cl$ (7.15 ml) were added successively. After stirring at 20° for 3 h, more $^i Pr_2NEt$ (24.2 ml) and $MeOCH_2Cl$ (7.15 ml) were added. After stirring at 20° for 69 h, the mixture was poured into a vigourously stirred mixture of CH_2Cl_2 (200 ml) and sat. aq. $NaHCO_3$ soln. (50 ml). If the pH was lower than 7, solid $NaHCO_3$ was added until the aq. layer became basic. The aq. phase was extracted with CH_2Cl_2 (300 ml, 4 ×), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (50 ml), dried ($MgSO_4$), and evaporated, and the residue subjected to fast FC (silica gel (height 5 cm), light petroleum ether/AcOEt 1:1): 7.24 g (96%) of (−)-**14**. Colorless oil. $[\alpha]_{589}^{25} = -20$, $[\alpha]_{577}^{25} = -24$, $[\alpha]_{546}^{25} = -26$, $[\alpha]_{435}^{25} = -42$, $[\alpha]_{405}^{25} = -50$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 295 (100), 194 (1000). IR (film): 2935, 2895, 2825, 1640, 1465, 1445, 1380, 1360, 1300, 1215, 1150, 915. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.87 (*dddd*, ^3J(2′,3′trans) = 17.0, ^3J(2′,3′cis) = 10.1, ^3J(2′,1′) = 6.9, 6.9, H–C(2′)); 5.09 (*ddd*, ^3J(3′trans,2′) = 17.0, ^4J(3′trans,1′) = 3.2, 1.4, Htrans–C(3′)); 5.05 (*dm*, ^3J(3′cis,2′) = 10.1, H_{cis}–C(3′)); 4.83, 4.64 (2*d*, ^2J = 6.6, 1 MeOCH_2); 4.74, 4.64 (2*d*, ^2J = 6.6, 1 MeOCH_2); 4.73, 4.70 (2*d*, ^2J = 6.6, 1 MeOCH_2); 4.07 (*ddd*, ^3J(2,3) = 5.2, ^3J(2,1′) = 8.9, 3.5, H–C(2)); 3.97–3.87 (*m*, H–C(3), H–C(4), H–C(5), H–C(6)); 3.39, 3.38, 3.37 (3*s*, 3 *Me*OCH$_2$); 2.47–2.30 (*m*, 2 H–C(1′)); 1.29 (*d*, ^3J(Me–C(6),6) = 6.3, Me–C(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 135.1 (*d*, ^1J(C,H) = 153, C(2′)); 116.6 (*t*, ^1J(C,H) = 156, C(3′)); 97.5, 96.7, 96.5 (3*t*, ^1J(C,H) = 163, 3 MeO*C*H$_2$); 75.6 (*d*, ^1J(C,H) = 144, C(3, 4, 5, or 6)); 75.1 (*d*, ^1J(C,H) = 145, C(3, 4, 5, or 6)); 74.2 (*d*, ^1J(C,H) = 141, C(3, 4, 5, or 6)); 71.0 (*d*, ^1J(C,H) = 151, C(2)); 68.4 (*d*, ^1J(C,H) = 141, C(3, 4, 5, or 6)); 55.8, 55.7, 55.5 (3*q*, ^1J(C,H) = 142, 3 *Me*OCH$_2$); 31.9 (*t*, ^1J(C,H) = 126, C(1′)); 15.4 (*q*, ^1J(C,H) = 127, Me–C(6)). CI-MS (NH_3): 338 (100, $[M+NH_4]^+$), 321 (1.4, $[M+H]^+$), 289 (32, $[M-OMe]^+$), 245 (20), 243 (22), 213 (39), 203 (43), 161 (52). Anal. calc. for $C_{15}H_{28}O_7$ (320.38): C 56.23, H 8.81; found: C 56.21, H 8.74.

*(2S,3R,4R,5R,6S)-Tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-ethanol* ((−)-**15**). Ozone (3% O_3 in O_2) was bubbled through a soln. of (−)-**14** (4.37 g, 13.6 mmol) in CH_2Cl_2 (40 ml) and MeOH (10 ml) cooled at −78° and containing $NaHCO_3$ (100 mg). When the blue color of O_3 persisted, O_2 was bubbled through the soln. for 10 min. Me_2S (2.5 ml, 34.1 mmol) was added, and the mixture was stirred at −78° for 30 min. Then $NaBH_4$ (1.55 g, 40.9 mmol) was added and the mixture stirred at 20° for 210 min. AcOEt (150 ml) and 1N aq. HCl (50 ml) were added. The aq. phase was extracted with AcOEt (150 ml, 3 ×), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (50 ml, 2 ×) and brine (50 ml), dried ($MgSO_4$), and evaporated: 4.36 g (99%) of (−)-**15**. Colorless oil. $[\alpha]_{589}^{25} = -0.6$, $[\alpha]_{577}^{25} = -2.1$, $[\alpha]_{546}^{25} = -1.8$, $[\alpha]_{435}^{25} = -2.4$, $[\alpha]_{405}^{25} = -1.9$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 265 (200), 223 (700), 196 (1600). IR (film): 3475, 2940, 2895, 1640, 1445, 1365, 1215, 1150, 1110, 1035, 915, 665. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.86, 4.67 (2*d*, ^2J = 6.9, 1 MeOCH_2); 4.77, 4.66 (2*d*, ^2J = 6.9, 1 MeOCH_2); 4.75, 4.72 (2*d*, ^2J = 6.9, 1 MeOCH_2); 4.26 (*dm*, ^3J(2,1′) = 10.7, H–C(2)); 4.01 (*qd*, ^3J(6,Me–C(6)) = 6.6, ^3J(6,5) = 3.2, H–C(6)); 3.95–3.90 (*m*, H–C(5), H–C(4), H–C(3)); 3.80 (*m*, 2 H–C(2′)); 3.41, 3.40, 3.38 (3*s*, 3 *Me*OCH$_2$); 2.39 (br. *s*, OH–C(2′)); 2.07–1.96 (*m*, 1 H–C(1′)); 1.82–1.70 (*m*, 1 H–C(1′)); 1.33 (*d*, ^3J(Me–C(6),6) = 6.6, Me–C(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 97.5, 96.8, 96.4 (3*t*, ^1J(C,H) = 164, 3 MeO*C*H$_2$); 75.6 (*d*, ^1J(C,H) = 149, C(3) or C(4)); 74.9 (*d*, ^1J(C,H) = 143, C(3) or C(4)); 74.0 (*d*, ^1J(C,H) = 145, C(5)); 71.3 (*d*, ^1J(C,H) = 145, C(2)); 68.8 (*d*, ^1J(C,H) = 142, C(6)); 61.5 (*d*, ^1J(C,H) = 145, C(2′)); 55.8, 55.7, 55.5 (3*q*, ^1J(C,H) = 142, 3 *Me*OCH$_2$); 29.5 (*t*, ^1J(C,H) = 125, C(1′)); 15.6 (*q*, ^1J(C,H) = 128, Me–C(6)). CI-MS (NH_3): 342 (17, $[M+NH_4]^+$), 325 (9, $[M+H]^+$), 310 (8, $[M+H-Me]^+$), 293 (26, $[M-OMe]^+$), 261 (100), 217 (49), 161 (57). Anal. calc. for $C_{14}H_{28}O_8$ (324.37): C 51.84, H 8.70; found: C 51.72, H 8.52.

*(2S,3R,4R,5R,6S)-Tetrahydro-2-(2-iodoethyl)-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran* ((−)-**16**). A mixture of (−)-**15** (5.97 g,18.4 mmol), Et_2O (45 ml), MeCN (15 ml), 1*H*-imidazole (3.76 g, 55.2 mmol), and PPh_3 (7.24 g, 27.6 mmol) was stirred at 0° for 30 min, then at 20° for 20 h. Et_2O (200 ml) was added, then 1M aq. $Na_2S_2O_3$ until complete decoloration of the soln. The aq. phase was extracted with Et_2O (100 ml, 5 ×), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (20 ml), dried ($MgSO_4$), and evaporated, and the residue subjected to FC (silica gel, Et_2O/light petroleum ether 2:1): 6.29 g (79%, based on (−)-**14**) of (−)-**16**. Colorless oil. $[\alpha]_{589}^{25} = -26$, $[\alpha]_{577}^{25} = -29$, $[\alpha]_{546}^{25} = -30$, $[\alpha]_{435}^{25} = -49$, $[\alpha]_{405}^{25} = -59$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 254 (500), 197 (1600). IR (film): 2935, 2895, 2825, 1740, 1465, 1440, 1370, 1300, 1245, 1215, 1150, 1110, 1035, 990, 920. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.82, 4.64 (2*d*, ^2J = 6.9, 1 MeOCH_2); 4.74, 4.62 (2*d*, ^2J = 6.9, 1 MeOCH_2); 4.73,

4.70 (2*d*, ^2J = 6.9, 1 MeOCH_2); 4.17 (*ddd*, ^3J(2,1′) = 10.6, 3.2, ^3J(2,3) = 3.2, H–C(2)); 3.96–3.82 (*m*, H–C(6), H–C(5), H–C(4), H–C(3)); 3.39, 3.38, 3.37 (3*s*, 3 *Me*OCH$_2$); 3.33–3.17 (*m*, 2 H–C(2′)); 2.23–2.12 (*m*, 1 H–C(1′)); 2.06–1.95 (*m*, 1 H–C(1′)); 1.32 (*d*, ^3J(Me–C(6),6) = 6.6, Me–C(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 97.3, 96.6, 96.4 (3*t*, ^1J(C,H) = 164, 3 MeO*C*H$_2$); 75.4 (*d*, ^1J(C,H) = 151, C(3, 4, 5, or 6)); 75.1 (*d*, ^1J(C,H) = 153, C(3, 4, 5, or 6)); 73.9 (*d*, ^1J(C,H) = 132, C(3, 4, 5, or 6)); 70.9 (*d*, ^1J(C,H) = 147, C(2)); 68.6 (*d*, ^1J(C,H) = 142, C(3, 4, 5, or 6)); 55.9, 55.8, 55.6 (3*q*, ^1J(C,H) = 141, 3 *Me*OCH$_2$); 31.4 (*t*, ^1J(C,H) = 127, C(1′)); 15.5 (*q*, ^1J(C,H) = 127, *Me*–C(6)); 2.9 (*t*, ^1J(C,H) = 151, C(2′)). CI-MS (NH_3): 452 (16, $[M+NH_4]^+$), 403 (4, $[M-OMe]^+$), 357 (16, $[M-2\,OMe-Me]^+$), 327 (65, $[M-3\,OMe-Me]^+$), 315 (100), 267 (68), 161 (79). Anal. calc. for $C_{14}H_{27}IO_7$ (434.27): C 38.72, H 6.27, I 29.22; found: C 38.83, H 6.30, I 29.11.

*(1*R*,4*R*,5*R*)-4-(Phenylthio)-6,8-dioxabicyclo[3.2.1]octan-2-one* ((−)-**18**). Thiophenol (5 ml, 48.97 mmol) and Et_3N (1.14 ml, 8.16 mmol) were added to a soln. of **17** (5.15 g, 40.8 mmol) in CH_2Cl_2 (125 ml). The mixture was stirred at 20° for 24 h and then evaporated: 9.99 g (quant.) of (−)-**18**. Yellow oil. An anal. sample of (−)-**18** was obtained by FC (silica gel, AcOEt/light petroleum ether 1:2). $[\alpha]^{25}_{589} = -61$, $[\alpha]^{25}_{577} = -63$, $[\alpha]^{25}_{546} = -76$, $[\alpha]^{25}_{435} = -170$, $[\alpha]^{25}_{405} = -238$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 252 (5200), 217 (5800). IR (KBr): 2990, 1735, 1585, 1480, 1440, 1240, 1120, 1010, 950, 895, 795, 745. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.48–7.41, 7.38–7.28 (2*m*, 5 arom. H); 5.69 (*s*, H–C(5)); 4.58 (*d*, ^3J(1,7exo) = 5.5, H–C(1)); 3.97 (*d*, ^2J = 8.1, H$_{endo}$–C(7)); 3.87 (*dd*, ^2J = 8.1, ^3J(7exo,1) = 5.5, H$_{exo}$–C(7)); 3.55 (*ddd*, ^3J(4,3) = 7.8, ^3J(4,3) = 4.9, ^3J(4,5) = 0.9, H–C(4)); 2.86 (*dd*, ^2J = 17.6, ^3J(3endo,4) = 7.8, H$_{endo}$–C(3)); 2.57 (*dddd*, ^2J = 17.6, ^3J(3exo,4) = 4.9, ^4J(3exo,1) = 0.9, ^4J(3exo,1) = 0.9, H$_{exo}$–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 204.3 (*s*, C(2)); 133.0 (*s*, arom. C); 132.2 (*d*, ^1J(C,H) = 161, 2 arom. C); 129.3 (*d*, ^1J(C,H) = 161, 2 arom. C); 127.9 (*d*, ^1J(C,H) = 161, arom. C); 103.0 (*d*, ^1J(C,H) = 178, C(5)); 79.2 (*d*, ^1J(C,H) = 162, C(1)); 67.2 (*t*, ^1J(C,H) = 154, C(7)); 47.3 (*d*, ^1J(C,H) = 147, C(4)); 38.7 (*t*, ^1J(C,H) = 133, C(3)). CI-MS (NH_3): 236 (21, M^+), 218 (4, $[M-O]^+$), 194 (2), 167 (2), 136 (100), 126 (6), 109 (29, PhS^+). Anal. calc. for $C_{12}H_{12}O_3S$ (236.29): C 61.00, H 5.12, S 13.57; found: C 60.92, H 5.17, S 13.65.

*(1*R*,2*R*,4*R*,5*R*)-4-(Phenylthio)-6,8-dioxabicyclo[3.2.1]octan-2-ol* (**19**). To a soln. of crude (−)-**18** (31 mg, 0.13 mmol) in anh. THF (1.3 ml) at −78°, 1M ^{i}Bu$_2$AlH in CH_2Cl_2 (0.262 ml, 0.262 mmol) was added dropwise under stirring. After 30 min at −78°, CH_2Cl_2 (10 ml) and 1M aq. HCl (3 ml) were added, and the mixture was extracted with CH_2Cl_2 (10 ml, 3×). The combined org. extract was washed with a sat. $NaHCO_3$ soln. (5 ml), dried ($MgSO_4$), and evaporated: **19**/(−)-**20** 7:1 (25 mg, 80%). An anal. sample of **19** was obtained by FC (silica gel, AcOEt/light petroleum ether 2:1). IR (film): 3420, 2960, 2900, 1745, 1585, 1480, 1440, 1345, 1300, 1215, 1125, 1070, 1025, 985, 955, 915, 850, 795, 745, 690, 670. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.43–7.22 (*m*, 5 arom. H); 5.50 (br. *s*, H–C(5)); 4.45 (br. *dd*, ^3J(1,7exo) = 4.9, ^3J(1,2) = 4.0, H–C(1)); 4.27 (*ddd*, ^3J(2,3endo) = 10.5, ^3J(2,3exo) = 5.8, ^3J(2,1) = 4.0, H–C(2)); 4.18 (*d*, ^2J = 7.7, H$_{endo}$–C(7)); 3.75 (*dd*, ^2J = 7.7, ^3J(7exo,1) = 4.9, H$_{exo}$–C(7)); 3.36 (br. *d*, ^3J(4,3endo) = 5.7, H–C(4)); 2.17 (*ddq*, ^2J = 13.9, ^3J(3exo,2) = 5.8, ^4J(3exo,5) = 0.9, ^4J(3exo,1) = 0.9, ^3J(3exo,4) = 0.9, H$_{exo}$–C(3)); 2.01 (*ddd*, ^2J = 13.9, ^3J(3endo,4) = 10.5, ^3J(3endo,2) = 5.7, H$_{endo}$–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 131.2 (*d*, ^1J(C,H) = 161, 2 arom. C); 129.1 (*d*, ^1J(C,H) = 161, 2 arom. C); 127.1 (*s*, arom. C); 127.1 (*d*, ^1J(C,H) = 162, arom. C); 101.1 (*d*, ^1J(C,H) = 178, C(5)); 76.3 (*d*, ^1J(C,H) = 156, C(1)); 63.8 (*t*, ^1J(C,H) = 153, C(7)); 63.8 (*d*, ^1J(C,H) = 143, C(2)); 48.9 (*d*, ^1J(C,H) = 144, C(4)); 31.4 (*t*, ^1J(C,H) = 132, C(3)). CI-MS (NH_3): 252 (28, $[M+NH_4]^+$), 239 (84, $[M+H]^+$), 238 (83, M^+), 221 ($[M-OH]^+$), 203 (40), 192 (26), 136 (100).

*(1*R*,2*S*,4*R*,5*R*)-4-(Phenylthio)-6,8-dioxabicyclo[3.2.1]octan-2-ol* ((−)-**20**). A mixture of isolevoglucosenone [16] (**17**; 5.15 g, 40.8 mmol), thiophenol (5 ml, 49.0 mmol), and Et_3N (1.14 ml, 8.16 mmol) in CH_2Cl_2 (125 ml) was stirred at 20° for 24 h. Evaporation gave 9.98 g of ketone (−)-**18** that was dissolved in THF (200 ml) and rapidly cooled to −78°. *Super-H* (1M $LiEt_3BH$ in THF; 61.2 ml, 61.2 mmol) was added dropwise under stirring at −78°. After 30 min at −78°, the mixture was poured into CH_2Cl_2 (300 ml) and 1M aq. HCl (200 ml). The aq. phase was extracted with CH_2Cl_2 (200 ml, 3×), the combined org. extract washed with sat. $NaHCO_3$ soln. (50 ml, 2×), dried ($MgSO_4$), and evaporated: 8.75 g (90%, based on **17**) of (−)-**20**. Colorless solid. M.p. 59–61°. $[\alpha]^{25}_{589} = -63$, $[\alpha]^{25}_{577} = -65$, $[\alpha]^{25}_{546} = -75$, $[\alpha]^{25}_{435} - 124$, $[\alpha]^{25}_{405} = -146$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 249 (3400), 221 (3000). IR (KBr): 3495, 3055, 2960, 2895, 1585, 1480, 1400, 1355, 1310, 1235, 1185, 1130, 1100, 1060, 1025, 1000, 950, 910, 865, 775, 745, 690. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.48–7.28 (*m*, 5 arom. H); 5.52 (br. *s*, H–C(5)); 4.60 (*m*, H–C(1)); 3.87, 3.86 (2*s*, 2 H–C(7)); 3.67 (br. *s*, H–C(2)); 3.29 (br. *d*, ^3J(4,3endo) = 5.9, H–C(4)); 2.26 (*ddd*, ^2J = 15.7, ^3J(3endo,4) = 5.7, ^3J(3endo,2) = 4.3, H$_{endo}$–C(3)); 1.97 (*dm*, ^2J = 15.7, H$_{exo}$–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 132.3 (*d*, ^1J(C,H) = 161, 2 arom. C); 129.3 (*d*, ^1J(C,H) = 161.4, 2 arom. C); 127.8 (*s*, arom. C); 127.8 (*d*, ^1J(C,H) = 162, arom. C); 101.5 (*d*, ^1J(C,H) = 177, C(5)); 78.1 (*d*, ^1J(C,H) = 158, C(1)); 67.3 (*d*, ^1J(C,H) = 145, C(2)); 66.4 (*t*, ^1J(C,H) = 150, C(7)); 46.1 (*d*, ^1J(C,H) = 146, C(4)); 28.0 (*t*, ^1J(C,H) = 132, C(3)). CI-MS (NH_3): 239 (19, $[M+H]^+$), 238 (42, M^+); 221

(1, $[M-OH]^+$), 203 (7), 192 (8), 136 (100). Anal. calc. for $C_{12}H_{14}O_3S$ (238.31): C 60.48, H 5.92, S 13.45; found: C 60.41, H 5.91, S 13.41.

*(1*R*,2*R*,4*R*,5*R*)-4-(Phenylthio)-6,8-dioxabicyclo[3.2.1]octan-2-ol Acetate* ((−)-**21**). *N,N*-Dimethylpyridin-4-amine (20 mg) was added to a soln. of **19** (44 mg, 0.185 mmol) in pyridine (1 ml) and Ac_2O (1 ml). After stirring at 20° for 30 min, CH_2Cl_2 (20 ml) and 1M aq. HCl (5 ml) were added. The mixture was extracted with CH_2Cl_2 (10 ml, 3 ×), the combined org. extract washed with a sat. aq. $NaHCO_3$ soln. (5 ml), dried ($MgSO_4$), and evaporated, and the residue subjected to FC (silica gel, AcOEt/light petroleum ether 1:3): 29 mg (56%) of (−)-**21**. Colorless solid. M.p. 69–70°. $[\alpha]_{589}^{25}=-87$, $[\alpha]_{577}^{25}=-92$, $[\alpha]_{546}^{25}=-105$, $[\alpha]_{435}^{25}=-187$, $[\alpha]_{405}^{25}=-230$ ($c=1.0$, $CHCl_3$). UV (MeCN): 251 (6700), 216 (6000). IR (KBr): 2965, 2900, 1730, 1585, 1485, 1400, 1370, 1315, 1240, 1210, 1130, 1090, 1045, 1025, 990, 965, 910, 875, 800, 745, 695. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.44–7.22 (*m*, 5 arom. H); 5.53 (br. *s*, H−C(5)); 5.25 (*ddd*, ^3J(2,3endo) = 10.9, ^3J(2,3exo) = 6.0, ^3J(2,1) = 3.9, H−C(2)); 4.56 (br. *dd*, ^3J(1,7) = 5.0, ^3J(1,2) = 3.9, H−C(1)); 4.13 (*d*, ^2J = 7.8, H_{endo}−C(7)); 3.76 (*dd*, ^2J = 7.8, ^3J(7exo,1) = 5.0, H_{exo}−C(7)); 4.13 (br. *d*, ^3J(4,3endo) = 5.7, H−C(4)); 2.21 (*ddddd*, ^2J = 13.7, ^3J(3exo,2) = 6.0, ^3J(3exo,4) = 1.2, ^4J(3exo,5) = 1.2, ^4J(3exo,1) = 1.2, H_{exo}−C(3)); 2.08 (*ddd*, ^2J = 13.7, ^3J(3endo,2) = 10.9, ^3J(3endo,4) = 5.7, H_{endo}−C(3)); 2.01 (*s*, *Me*CO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.7 (*s*, Me*C*O); 134.6 (*s*, arom. C); 131.6 (*d*, ^1J(C,H) = 162, 2 arom. C); 129.1 (*d*, ^1J(C,H) = 161, 2 arom. C); 127.3 (*d*, ^1J(C,H) = 161, arom. C); 101.4 (*d*, ^1J(C,H) = 177, C(5)); 73.5 (*d*, ^1J(C,H) = 154, C(1)); 66.0 (*d*, ^1J(C,H) = 154, C(2)); 64.4 (*t*, ^1J(C,H) = 149, C(7)); 49.0 (*d*, ^1J(C,H) = 146, C(4)); 28.0 (*t*, ^1J(C,H) = 136, C(3)); 20.9 (*q*, ^1J(C,H) = 130, *Me*CO). CI-MS (NH_3): 298 (55, $[M+NH_4]^+$), 281 (100, $[M+H]^+$), 280 (41, M^+), 221 (11, $[M-OAc]^+$), 203 (5, $[M-Ph]^+$), 171 (7), 136 (19). Anal. calc. for $C_{14}H_{16}O_4S$ (280.34): C 59.98, H 5.76, S 11.42; found: C 59.89, H 5.83, S 11.33.

*(1*R*,2*S*,4*R*,5*R*)-4-(Phenylthio)-6,8-dioxabicyclo[3.2.1]octan-2-ol Acetate* ((−)-**22**). A mixture of crude (−)-**20** (8.75 g, 40.8 mmol), pyridine (200 ml), Ac_2O (200 ml), *N,N*-dimethylpyridin-4-amine (500 mg) was stirred at 20° for 1 h. The mixture was poured into Et_2O (400 ml) and sat. aq. $NaHCO_3$ soln. (200 ml) under vigorous stirring. Solid $NaHCO_3$ was added until neutralization. The mixture was extracted with Et_2O (400 ml, 4 ×), then with AcOEt (300 ml, 2 ×), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (100 ml), dried ($MgSO_4$), and evaporated, and the residue recrystallized from light petroleum ether (150 ml)/Et_2O (150 ml): 4.21 g of (−)-**22**. The mother liquor was evaporated and the residue recrystallized as above: (−)-**22** (2.25 g). The mother liquor was evaporated and the residue (5.3 g) purified by FC (silica gel, AcOEt/light petroleum ether 1:2.5): (−)-**22** (1.53 g). Total yield: 7.99 g (70%, based on (−)-**18**) of (−)-**22**. White solid. M.p. 92–94°. $[\alpha]_{589}^{25}=-25$, $[\alpha]_{577}^{25}=-26$, $[\alpha]_{546}^{25}=-30$, $[\alpha]_{435}^{25}=-50$, $[\alpha]_{405}^{25}=-60$ ($c=1.0$, $CHCl_3$). UV (MeCN): 253 (6900), 213 (6500). IR (KBr): 2960, 2895, 1725, 1580, 1485, 1445, 1430, 1365, 1255, 1130, 1110, 1040, 1020, 980, 965, 935, 920, 890, 785, 750, 715, 690, 675. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.44–7.21 (*m*, 5 arom. H); 5.53 (br. *s*, H−C(5)); 4.76–4.72 (*m*, H−C(2)); 4.66–4.62 (*m*, H−C(1)); 3.91 (*dd*, ^2J = 7.9, ^3J(7endo,1) = 0.8, H_{endo}−C(7)); 3.85 (*dd*, ^2J = 7.9, ^3J(7exo,1) = 5.4, H_{exo}−C(7)); 3.25 (br. *d*, ^3J(4,3endo) = 6.8, H−C(4)); 2.52 (*ddd*, ^2J = 16.1, ^3J(3endo,4) = 6.8, ^3J(3endo,2) = 4.8, H_{endo}−C(3)); 2.21 (*s*, *Me*CO); 2.06 (*dm*, ^2J = 16.1, H_{exo}−C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.7 (*s*, Me*C*O); 135.4 (*s*, arom. C); 131.1 (*d*, ^1J(C,H) = 161, 2 arom. C); 129.1 (*d*, ^1J(C,H) = 161, 2 arom. C); 127.0 (*d*, ^1J(C,H) = 161, arom. C); 101.9 (*d*, ^1J(C,H) = 177, C(5)); 74.8 (*d*, ^1J(C,H) = 160, C(1)); 67.8 (*d*, ^1J(C,H) = 150, C(2)); 66.1 (*t*, ^1J(C,H) = 151, C(7)); 45.7 (*d*, ^1J(C,H) = 144, C(4)); 26.9 (*t*, ^1J(C,H) = 131, C(3)); 21.3 (*q*, ^1J(C,H) = 130, *Me*CO). CI-MS (NH_3): 298 (23, $[M+NH_4]^+$), 281 (100, $[M+H]^+$), 280 (55, M^+), 220 (11, $[M-H-OAc]^+$), 203 (12, $[M-Ph]^+$), 171 (11), 136 (47). Anal. calc. for $C_{14}H_{16}O_4S$ (280.34): C 59.98, H 5.76, S 11.42; found: C 59.95, H 5.87, S 11.37.

*(2*R*,3*S*)-3-(Acetyloxy)-3,4-dihydro-5-(phenylthio)-2*H*-pyran-2-methanol* ((+)-**23**). Allyltrimethylsilane (52 µl, 0.321 mmol), $BF_3\cdot OEt_2$ (41 µl, 0.321 mmol), and $Me_3SiOSO_2CF_3$ (58 µl, 0.321 mmol) were added successively to a soln. of (−)-**22** (30 mg, 0.107 mmol) in MeCN (300 µl) stirred at 0°. After 15 min at 0°, CH_2Cl_2 (5 ml) and 1M aq. HCl (1 ml) were added. The aq. phase was extracted with CH_2Cl_2 (5 ml, 3 ×), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (3 ml, 2 ×), dried ($MgSO_4$), and evaporated, and the residue subjected to FC (silica gel, AcOEt/light petroleum ether 1:1): (+)-**23** (21 mg, 70%). Colorless oil. $[\alpha]_{589}^{25}=+128$, $[\alpha]_{577}^{25}=+133$, $[\alpha]_{546}^{25}=+152$, $[\alpha]_{435}^{25}=+268$, $[\alpha]_{405}^{25}=+331$ ($c=0.5$, $CHCl_3$). IR (film): 3415, 1735, 1630, 1585, 1475, 1435, 1375, 1240, 1160, 1025, 740, 690. UV (MeCN): 245 (8900), 219 (7800). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.30–7.16 (*m*, 5 arom. H); 6.94 (br. *s*, H−C(6)); 5.16 (*ddd*, ^3J(3,2) = 7.3, ^3J(3,4) = 7.1, 5.8, H−C(3)); 3.99 (*ddd*, ^3J(2,3) = 7.3, ^3J(2,CH_2−C(2)) = 5.2, 3.3, H−C(2)); 3.82 (*ddd*, ^2J = 12.3, ^3J(CH_2−C(2),OH) = 7.9, ^3J(CH_2−C(2),2) = 3.3, 1 H, CH_2−C(2)); 3.74 (*ddd*, ^2J = 12.3, ^3J(CH_2−C(2),OH) = 5.7, ^3J(CH_2−C(2),2) = 5.2, 1 H, CH_2−C(2)); 2.54 (*ddd*, ^2J = 16.8, ^3J(4,3) = 5.8, ^4J(4,6) = 1.5, 1 H−C(4)); 2.30 (*ddd*, ^2J = 16.8, ^3J(4,3) = 7.1, ^4J(4,6) = 1.5, 1 H−C(4)); 2.19 (*dd*, ^3J(OH,CH_2−C(2)) = 5.2, 3.3, CH_2O*H*); 2.10 (*s*, *Me*CO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.3 (*s*, Me*C*O); 148.7 (*d*, C(6)); 135.8 (*s*, arom. C); 129.1 (*d*, 2 arom. C); 127.7 (*d*, 2 arom. C); 126.0 (*d*, arom. C); 102.2 (*s*, C(5)); 76.5, 65.5, 61.1 (C(2), C(3), *C*H_2−C(2)); 30.8 (*t*, C(4)); 20.9

(*q*, *Me*CO). CI-MS (NH_3): 298 (100, $[M+NH_4]^+$), 281 (88, $[M+H]^+$), 263 (5, $[M-OH]^+$), 238 (4, $[M+H-Ac]^+$), 221 (31, $[M-OAc]^+$), 220 (31, $[M-Ac-OH]^+$), 203 (25, $[M-Ph]^+$), 171 (53). Anal. calc. for $C_{14}H_{16}O_4S$ (280.34): C 59.98, H 5.76, S 11.42; found: C 59.92, H 5.85, S 11.39.

*(2*R*,3*S*,5*R*,6*S*)-3-(Acetyloxy)-tetrahydro-5-(phenylthio)-6-(prop-2-enyl)-2*H*-pyran-2-methanol* ((+)-**24**). $BF_3\cdot OEt_2$ (1.34 ml, 10.7 mmol) and $Me_3SiOSO_2CF_3$ (1.93 ml, 10.7 mmol) were added simultaneously and dropwise to a vigorously stirred mixture (two phases) of (−)-**22** (1 g, 3.57 mmol) in $MeNO_2$ (28 ml) and allyltrimethylsilane (7 ml) at −20°. After stirring at −20° for 3.5 h, the mixture was poured onto a vigorously stirred mixture of Et_2O (350 ml) and 1M aq. HCl (50 ml). The aq. phase was extracted with AcOEt (150 ml, 3 ×), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (50 ml), dried ($MgSO_4$), and evaporated, and the residue subjected to FC (silica gel, AcOEt/light petroleum ether 1:2): 531 mg (46%) of pure (+)-**24**, then 350 mg (30%) of (+)-**24**/**25** 10:1, and 55 mg (5%) of pure **25**, all as colorless oils.

*Data of (+)-***24**: $[\alpha]_{589}^{25}=+24$, $[\alpha]_{577}^{25}=+26$, $[\alpha]_{546}^{25}=+31$, $[\alpha]_{435}^{25}=+52$, $[\alpha]_{405}^{25}=+66$ ($c=0.5$, $CHCl_3$). IR (film): 3470, 3075, 2935, 2865, 1740, 1640, 1585, 1480, 1440, 1375, 1240, 1085, 1040, 1000, 915, 800, 750, 695. ^{1}H-NMR (100.6 MHz, $CDCl_3$): 7.46–7.29 (*m*, 5 arom. H); 5.87 (*dddd*, ^3J(2′,3′trans) = 16.9, ^3J(2′,3′cis) = 10.8, ^3J(2′,1′) = 10.8, 7.3, H−C(2′)); 5.12–5.05 (*m*, 2 H−C(3′)); 4.70 (*ddd*, ^3J(3,4ax) = 10.8, ^3J(3,2) = 9.7, ^3J(3,4eq) = 4.8, H−C(3)); 3.68 (br. *ddd*, ^2J = 12.1, ^3J(CH_2−C(2),OH) = 7.7, ^3J(CH_2−C(2),2) = 2.5, 1 H, CH_2−C(2)); 3.37 (br. *ddd*, ^2J = 12.1, ^3J(CH_2−C(2),2) = 5.7, ^3J(CH_2−C(2),OH) = 5.4, 1 H, CH_2−C(2)); 3.37 (*ddd*, ^3J(6,5) = 10.3, ^3J(6,1′) = 7.7, 2.8, H−C(6)); 3.31 (*ddd*, ^3J(2,3) = 9.7, ^3J(2,CH_2−C(2)) = 5.7, 2.5, H−C(2)); 2.98 (*ddd*, ^3J(5,4ax) = 12.6, ^3J(5,6) = 10.3, ^3J(5,4eq) = 4.2, H−C(5)); 2.81 (*ddddd*, ^2J = 15.0, ^3J(1′,2′) = 6.5, ^3J(1′,6) = 2.8, ^4J(1′,3′) = 1.3, 1.3, 1 H−C(1′)); 2.50 (*ddd*, ^2J = 12.5, ^3J(4eq,3) = 4.8, ^3J(4eq,5) = 4.2, H_{eq}−C(4)); 2.805 (br. *ddd*, ^2J = 15.0, ^3J(1′,6) = 7.7, ^3J(1′,2′) = 7.3, 1 H−C(1′)); 2.15 (br. *dd*, ^3J(OH,CH_2−C(2)) = 7.7, 5.4, CH_2O*H*); 2.05 (*s*, *Me*CO); 1.61 (*ddd*, ^2J = 12.5, ^3J(4ax,5) = 12.6, ^3J(4ax,3) = 10.8, H_{ax}−C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.2 (*s*, Me*C*O); 134.1 (*d*, ^1J(C,H) = 155, C(2′)); 133.5 (*d*, ^1J(C,H) = 162, 2 arom. C); 132.4 (*s*, arom. C); 129.1 (*d*, ^1J(C,H) = 161, 2 arom. C); 127.9 (*d*, ^1J(C,H) = 161, arom. C); 117.5 (*t*, ^1J(C,H) = 156, C(3′)); 80.3 (*d*, ^1J(C,H) = 145, C(6)); 79.3 (*d*, ^1J(C,H) = 144, C(2)); 67.7 (*d*, ^1J(C,H) = 152, C(3)); 62.1 (*t*, ^1J(C,H) = 142, CH_2−C(2)); 46.6 (*d*, ^1J(C,H) = 149, C(5)); 36.8 (2*t*, ^1J(C,H) = 134, C(1′), C(4)); 21.0 (*q*, ^1J(C,H) = 130, *Me*CO). CI-MS (NH_3): 323 (11, $[M+H]^+$), 281 (17, $[M-allyl]^+$), 263 (4, $[M-OAc]^+$), 203 (10), 163 (20), 135 (60), 109 (54), 81 (100). Anal. calc. for $C_{17}H_{22}O_4S$ (322.46): C 63.33, H 6.88, S 9.94; found: C 63.22, H 6.84, S 9.98.

*(2*R*,3*S*,5*R*,6*S*)-Tetrahydro-2-[(methoxymethoxy)methyl]-5-(phenylthio)-6-(prop-2-enyl)-2*H*-pyran-3-ol Acetate* ((+)-**26**). The crude reaction mixture obtained above (before chromatography; see (+)-**24**) was dissolved in CH_2Cl_2 (35 ml). After cooling at 0°, Bu_4NI (200 mg), $^iPr_2NEt$ (3.6 ml, 21.4 mmol), and $MeOCH_2Cl$ (1.35 ml, 17.9 mmol) were added successively under stirring at 0°. After stirring at 0° for 2 h, the same quantities of $^iPr_2NEt$ and $MeOCH_2Cl$ were added, and the mixture was stirred for another 2 h at 0°. Then the same amounts of $^iPr_2NEt$ and $MeOCH_2Cl$ were added again, and the mixture was stirred at 20° for 18 h. The mixture was poured into a vigorously stirred soln. of CH_2Cl_2 (100 ml) and 1M aq. HCl (30 ml). The aq. phase was extracted with CH_2Cl_2 (100 ml, 3 ×), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (25 ml), dried ($MgSO_4$), and evaporated, and the residue subjected to FC (silica gel, AcOEt/light petroleum ether 1:3): 1.075 g (82%) of (+)-**26** containing less than 10% of the anomer **27**. Colorless oil.

*Data of (+)-***26**: $[\alpha]_{589}^{25}=+27$, $[\alpha]_{577}^{25}=+29.5$, $[\alpha]_{546}^{25}=+35$, $[\alpha]_{435}^{25}=+62$, $[\alpha]_{405}^{25}=+66$ ($c=1.0$, $CHCl_3$). UV (MeCN): 251 (3200), 223 (2900). IR (film): 2945, 1740, 1640, 1585, 1480, 1440, 1375, 1235, 1150, 1110, 1045, 920, 850, 800, 750, 695. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.45-7.27 (*m*, 5 arom. H); 5.90 (*dddd*, ^3J(2′,3′trans) = 17.0, ^3J(2′,3′cis) = 10.4, ^3J(2′,1′) = 6.9, 6.9, H−C(2′)); 5.10–5.03 (*m*, 2 H−C(3′)); 4.73 (*ddd*, ^3J(3,4ax) = 10.8, ^3J(3,2) = 9.9, ^3J(3,4eq) = 4.6, H−C(3)); 4.63, 4.61 (2*d*, ^2J = 6.6, MeOCH_2); 3.61–3.58 (*m*, CH_2−C(2)); 3.43 (*ddd*, ^3J(2,3) = 9.9, ^3J(2,CH_2−C(2)) = 4.6, 3.1, H−C(2)); 3.34 (*ddd*, ^3J(6,5) = 10.3, ^3J(6,1′) = 7.4, 2.8, H−C(6)); 3.33 (*s*, *Me*CH_2O); 3.00 (*ddd*, ^3J(5,4ax) = 12.6, ^3J(5,6) = 10.3, ^3J(5,4eq) = 4.2, H−C(5)); 2.78 (*ddm*, ^2J = 14.8, ^3J(1′,2′) = 6.8, 1 H−C(1′)); 2.53 (*ddd*, ^2J = 12.4, ^3J(4eq,3) = 4.6, ^3J(4eq,5) = 4.6, H_{eq}−C(4)); 2.385 (br. *ddd*, ^2J = 14.8, ^3J(1′,6) = 7.4, ^3J(1′,2′) = 6.9, 1 H−C(1′)); 2.10 (*s*, *Me*CO); 1.55 (*ddd*, ^2J = 12.4, ^3J(4ax,5) = 12.6, ^3J(4ax,3) = 10.8, H_{ax}−C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.8 (*s*, Me*C*O); 134.3 (*d*, ^1J(C,H) = 155, C(2′)); 133.6 (*s*, arom. C); 133.4 (*d*, ^1J(C,H) = 162, 2 arom. C); 129.0 (*d*, ^1J(C,H) = 161, 2 arom. C); 127.8 (*d*, ^1J(C,H) = 161, arom. C); 117.2 (*t*, ^1J(C,H) = 156, C(3′)); 96.6 (*t*, ^1J(C,H) = 163, MeO*C*H_2); 80.6 (*d*, ^1J(C,H) = 142, C(6)); 78.6 (*d*, ^1J(C,H) = 141, C(2)); 67.9 (*d*, ^1J(C,H) = 151, C(3)); 66.4 (*t*, ^1J(C,H) = 143, *C*H_2−C(2)); 55.1 (*q*, ^1J(C,H) = 142, *Me*OCH_2); 46.4 (*d*, ^1J(C,H) = 142, C(5)); 36.9, 36.8 (2*t*, ^1J(C,H) = 133, C(1′), C(4)); 21.0 (*q*, ^1J(C,H) = 129, *Me*CO). CI-MS (NH_3): 384 (100, $[M+NH_4]^+$), 367 (52, $[M+H]^+$), 335 (73, $[M-OMe]^+$), 325 (21, $[M-CH_2CHCH_2]^+$). Anal. calc. for $C_{19}H_{26}O_5S$ (366.48): C 62.27, H 7.15, S 8.75; found: C 62.30, H 7.18, S 8.70.

*(2*R*)- and (2*S*)-3-[(2*S*,3*R*,5*S*,6*R*)-5-(Acetyloxy)-tetrahydro-6-[(methoxymethoxy)methyl]-3-(phenylthio)-2*H*-pyran-2-yl]propane-1,2-diol* (1:1 mixture; **28**). *N*-Methylmorpholine *N*-oxide (4.07 g, 30.1 mmol) was added

to a stirred soln. of (+)-**26** (7.357 g, 20.1 mmol) in acetone (178 ml) and H_2O (22 ml) at 20°. Then 0.1M OsO_4 in CCl_4 (10 ml, 1 mmol) was added dropwise. After stirring at 20° for 3 h, AcOEt (275 ml) and $Na_2S_2O_3$ (27.5 g) were added. After stirring at 20° for 1 h, the mixture was filtered through a pad of *Celite* (height 5 cm), which was washed with AcOEt (150 ml, 5 ×). The solvents were evaporated and the residue (10.5 g) purified by FC (silica gel, MeOH/CH_2Cl_2 1:9): 7.99 g (96%) of crude **28** used directly in the next step. An anal. sample was obtained after purification by a second FC (silica gel, AcOEt). $[\alpha]_{589}^{25} = +15$, $[\alpha]_{577}^{25} = +16$, $[\alpha]_{546}^{25} = +19$, $[\alpha]_{435}^{25} = +31$, $[\alpha]_{405}^{25} = +36$ ($c = 1.0$, $CHCl_3$). UV (MeCN): 255 (5500), 217 (6800). IR (film): 3445, 2930, 1740, 1440, 1375, 1235, 1150, 1040, 920, 735, 695. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.45–7.28 (*m*, 5 arom. H, 2 diast.); 4.79–4.65 (*m*, H–C(5′), 2 diast.); 4.63, 4.59 (2*d*, $^2J = 6.8$, MeOCH_2, 2 diast.); 4.02–3.87 (*m*, H–C(2), 2 diast.); 3.65–3.40 (*m*, H–C(2′), H–C(1), H–C(6′), CH_2–C(6′), OH–C(1), OH–C(2), 2 diast.); 3.33 (2*s*, *Me*OCH$_2$, 2 diast.); 3.03 (*ddd*, $^3J = 14.5$, $^3J = 10.5$, $^3J(3',4'\text{eq}) = 4.0$, H–C(3′), diast. 1); 2.96 (*ddd*, $^3J = 14.2$, $^3J = 10.2$, $^3J(3',4'\text{eq}) = 4.0$, H–C(3′), diast. 2); 2.60–2.49 (*m*, H–C(4′), 2 diast.); 2.36 (br. *d*, $^2J = 14.8$, H–C(3), diast. 2); 2.26 (*ddd*, $^2J = 14.8$, $^3J = 8.9$, $^3J = 2.5$, H–C(3), diast. 1); 2.03 (*s*, *Me*CO, 2 diast.); 1.70 (*ddd*, $^2J = 14.8$, $^3J = 8.6$, $^3J = 3.4$, H–C(3), diast. 1); 1.68–1.58 (*m*, H–C(3), diast. 2); 1.56 (*ddd*, $^2J \approx 12.3$, 12.3, 12.3, H–C(4′), 2 diast.). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.8, 169.8 (2*s*, Me*C*O); 133.5, 133.5 (2*d*, ^1J(C,H) = 162, 162, 2 arom. C); 132.3, 131.9 (2*s*, arom. C); 129.2, 129.1 (2*d*, ^1J(C,H) = 162, 162, 2 arom. C); 128.2, 128.1 (2*d*, ^1J(C,H) = 161, 161, arom. C); 96.7, 96.6 (2*t*, ^1J(C,H) = 163, 163, MeO*C*H$_2$); 81.7, 79.0 (2*d*, ^1J(C,H) = 143, 146, C(2′)); 78.4, 78.1 (2*d*, ^1J(C,H) = 142, C(6′)); 71.7, 69.0 (2*d*, ^1J(C,H) = 141, 144, C(2)); 67.8, 67.7 (2*d*, ^1J(C,H) = 130, 130, C(5′)); 67.0, 66.7, 66.6, 66.5 (4*t*, ^1J(C,H) = 142, *C*H$_2$–C(6′), C(1)); 55.4, 55.3 (2*q*, ^1J(C,H) = 142, 142, *Me*OCH$_2$); 47.3, 46.7 (2*d*, ^1J(C,H) = 141, 141, C(3′)); 36.8, 36.8 (2*t*, ^1J(C,H) = 132, 133, C(4′)); 35.7, 35.4 (2*t*, ^1J(C,H) = 125, 128, C(3)); 21.0, 21.0 (2*q*, ^1J(C,H) = 129, 129, *Me*CO). CI-MS (NH_3): 418 (95, $[M + NH_4]^+$), 401 (64, $[M + H]^+$), 386 (51, $[M + H - Me]^+$), 369 (100, $[M - OMe]^+$), 363 (59), 340 (9), 309 (14), 261 (11).

*(2*R*,3*S*,5*R*,6*S*)-Tetrahydro-2-[(methoxymethoxy)methyl]-5-(phenylthio)-6-{(2*Z*)-4-[(2*S*,3*R*,4*R*,5*R*,6*S*)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-3-ol* ((−)-**29**). Crude (−)-**12** (4.54 g, 6.89 mmol) was dissolved in MeOH (200 ml). After the addition of anh. K_2CO_3 (4.76 g, 34.5 mmol), the mixture was stirred at 20° for 1 h and then evaporated. The residue was dissolved in AcOEt (200 ml), and H_2O (50 ml) and 1M aq. HCl were added until pH 4. The aq. phase was extracted with AcOEt (200 ml, 5 ×), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (50 ml), dried ($MgSO_4$), and evaporated, and the residue subjected to FC (silica gel, AcOEt/light petroleum ether 3:1): 2.86 g (67%, based on (+)-**10**) of (−)-**29** as yellowish oil and 217 mg (5%) of (−)-**29** contaminated by Ph_3PO. $[\alpha]_{589}^{25} = -13$, $[\alpha]_{577}^{25} = -14$, $[\alpha]_{546}^{25} = -16$, $[\alpha]_{435}^{25} = -28$, $[\alpha]_{405}^{25} = -34$ ($c = 1.0$, $CHCl_3$). UV (MeCN): 256 (5400), 200 (12900). IR (film): 3455, 2935, 2890, 1650, 1585, 1475, 1440, 1405, 1360, 1320, 1305, 1270, 1215, 1150, 1110, 1030, 990, 920, 875, 850, 805, 735, 695. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.44–7.24 (*m*, 5 arom. H); 5.62 (*ddd*, $^3J(2',3') = 10.8$, $^3J(2',1') = 6.8$, 6.8, H–C(2′)); 5.53 (*ddd*, $^3J(3',2') = 10.8$, $^3J(3',4') = 6.8$, 6.8, H–C(3′)); 4.87, 4.67 (2*d*, $^2J = 6.9$, 1 MeOCH_2); 4.74, 4.72 (2*d*, $^2J = 6.9$, 1 MeOCH_2); 4.73 (*d*, $^2J = 6.9$, 1 H, MeOCH_2); 4.65–4.63 (*m*, 3 H, MeOCH_2); 4.08–4.02 (*m*, H–C(2″)); 3.95–3.88 (*m*, H–C(3″), H–C(4″), H–C(5″), H–C(6″)); 3.77 (*dd*, $^2J = 10.6$, $^3J(CH_2\text{–}C(2),2) = 4.8$, 1 H, CH_2–C(2)); 3.70 (*dd*, $^2J = 10.6$, $^3J(CH_2\text{–}C(2),2) = 5.1$, 1 H, CH_2–C(2)); 3.60 (*ddd*, $^3J(3,4\text{ax}) = 10.8$, $^3J(3,2) = 9.5$, $^3J(3,4\text{eq}) = 4.6$, H–C(3)); 3.41, 3.39, 3.36, 3.35 (4*s*, 4 *Me*OCH$_2$); 3.28 (*ddd*, $^3J(6,5) = 10.3$, $^3J(6,1') = 7.9$, 7.2, H–C(6)); 3.23 (*ddd*, $^3J(2,3) = 9.5$, $^3J(2,CH_2\text{–}C(2)) = 5.1$, 4.8, H–C(2)); 2.95 (*ddd*, $^3J(5,4\text{ax}) = 12.6$, $^3J(5,6) = 10.3$, $^3J(5,4\text{eq}) = 4.1$, H–C(5)); 2.76 (br. *dd*, $^2J = 14.8$, $^3J(1',2') = 6.8$, 1 H–C(1′)); 2.49–2.27 (*m*, H_{eq}–C(4), 1 H–C(1′), 2 H–C(4′)); 1.52 (*ddd*, $^2J = 12.6$, $^3J(4\text{ax},5) = 12.6$, $^3J(4\text{ax},3) = 10.8$, H_{ax}–C(4)); 1.30 (*d*, ^3J(Me–C(6″),6″) = 6.3, Me–C(6″)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 133.4 (*d*, ^1J(C,H) = 162, 2 arom. C); 132.7 (*s*, arom. C); 129.0 (*d*, ^1J(C,H) = 161, 2 arom. C); 127.7 (*d*, ^1J(C,H) = 161, arom. C); 127.7 (*d*, C(3′)); 127.1 (*d*, C(2′)); 97.4, 96.8, 96.8, 96.4 (4*t*, ^1J(C,H) = 167, 4 MeO*C*H$_2$); 80.7 (*d*, ^1J(C,H) = 143, C(6)); 79.6 (*d*, ^1J(C,H) = 141, C(2)); 75.5 (*d*, ^1J(C,H) = 145, C(3″, 4″, 5″, 6″, or 3)); 75.2 (*d*, ^1J(C,H) = 145, C(3″, 4″, 5″, 6″, or 3)); 74.4 (*d*, ^1J(C,H) = 141, C(3″, 4″, 5″, 6″, or 3)); 71.6 (*d*, ^1J(C,H) = 141, C(2″)); 68.7 (*t*, ^1J(C,H) = 142, *C*H$_2$–C(2)); 68.6 (*d*, ^1J(C,H) = 145, C(3″, 4″, 5″, 6″, or 3)); 68.3 (*d*, ^1J(C,H) = 141, C(3″, 4″, 5″, 6″, or 3)); 55.8, 55.8, 55.6, 55.4 (4*q*, ^1J(C,H) = 142, 4 *Me*OCH$_2$); 46.7 (*d*, ^1J(C,H) = 142, C(5)); 39.8 (*t*, ^1J(C,H) = 131, C(4)); 30.9 (*t*, ^1J(C,H) = 126, C(1′)); 25.4 (br. *t*, ^1J(C,H) = 121, C(4′)); 15.7 (*q*, ^1J(C,H) = 127, *Me*–C(6″)). CI-MS (NH_3): 635 (100), 634 (73, $[M + NH_4]^+$), 616 (2, M^+), 603 (3), 586 (16, $[M + H - OMe]^+$), 554 (9, $[M - 2\ OMe]^+$), 509 (12), 477 (12). Anal. calc. for $C_{30}H_{48}O_{11}S$ (616.77): C 58.42, H 7.84, S 5.20; found: C 58.42, H 7.89, S 5.19.

*(2*S*,3*S*,4*R*,5*S*,6*S*)-Tetrahydro-6-methyl-2-{(2*Z*)-4-[(2*S*,3*R*,5*S*,6*R*)-tetrahydro-5-hydroxy-6-(hydroxymethyl)-3-(phenylthio)-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-3,4,5-triol* (**30**). Freshly distilled $SOCl_2$ (165 µl, 2.27 mmol) was added to a stirred soln. of (−)-**29** (70 mg, 0.114 mmol) in anh. MeOH (2.25 ml) at 0°. The mixture was stirred at 0° for 5 min, then at 20° for 2 h. Evaporation gave a residue (50 mg) that was purified by HPLC (*Nucleosil 100-5* (*Macherey-Nagel*), MeOH/CH_2Cl_2 1:9, 5 ml/min, 45 bar): 15 mg (30%) of **30**. Colorless

oil. UV (MeOH): 256 (3300), 216 (5100). IR (film): 3405, 2930, 1680, 1440, 1205, 1140, 1085, 800, 725. ^{1}H-NMR (400 MHz, CD_3OD): 7.48–7.26 (*m*, 5 arom. H); 5.65 (*ddd*, $^3J(3',2')=10.8$, $^3J(3',4')=7.2$, 6.9, H–C(3')); 5.50 (*ddd*, $^3J(2',3')=10.8$, $^3J(2',1')=7.3$, 7.0, H–C(2')); 3.95 (*ddd*, $^3J(2,3)=5.5$, $^3J(2,1')=10.6$, 5.0, H–C(2)); 3.89 (*dd*, $^3J(3,4)=8.8$, $^3J(3,2)=5.5$, H–C(3)); 3.80 (*qd*, $^3J(6,Me–C(6))=6.6$, $^3J(6,5)=2.0$, H–C(6)); 3.80 (*dd*, $^2J=11.8$, $^3J(CH_2–C(6''),6'')=2.4$, 1 H, CH_2–C(6'')); 3.70 (*dd*, $^3J(5,4)=3.4$, $^3J(5,6)=2.0$, H–C(5)); 3.67 (*dd*, $^3J(4,3)=8.8$, $^3J(4,5)=3.4$, H–C(4)); 3.62 (*dd*, $^2J=11.8$, $^3J(CH_2–C(6''),6'')=5.8$, 1 H, CH_2–C(6'')); 3.45 (*ddd*, $^3J(5'',4''ax)=10.9$, $^3J(5'',6'')=9.7$, $^3J(5'',4''eq)=4.7$, H–C(5'')); 3.25 (*ddd*, $^3J(2'',3'')=10.0$, $^3J(2'',4')=8.2$, 2.4, H–C(2'')); 3.06 (*ddd*, $^3J(6'',5'')=9.7$, $^3J(6'',CH_2–C(6''))=5.8$, 2.4, H–C(6'')); 3.02 (*ddd*, $^3J(3'',4''ax)=11.8$, $^3J(3'',2'')=10.0$, $^3J(3'',4''eq)=4.0$, H–C(3'')); 2.74 (*ddm*, $^2J=14.7$, $^3J=6.5$, 1 H–C(4')); 2.44–2.25 (*m*, H_{eq}–C(4''), 1 H–C(4'), 2 H–C(1')); 1.47 (*ddd*, $^2J=12.5$, $^3J(4''ax,3'')=11.8$, $^3J(4''ax,5'')=10.9$, H_{ax}–C(4'')); 1.21 (*d*, $^3J(Me–C(6),6)=6.6$, Me–C(6)). ^{13}C-NMR (100.6 MHz, CD_3OD): 134.8 (*s*, arom. C); 133.9 (*d*, $^1J(C,H)=161$, 2 arom. C); 130.2 (*d*, $^1J(C,H)=161$, 2 arom. C); 129.2 (*d*, $^1J(C,H)=157$, C(2')); 128.6 (*d*, $^1J(C,H)=161$, arom. C); 128.3 (*d*, $^1J(C,H)=159$, C(3')); 84.0 (*d*, $^1J(C,H)=138$, C(6'')); 82.6 (*d*, $^1J(C,H)=141$, C(2'')); 76.3 (*d*, $^1J(C,H)=149$, C(2)); 72.6 (*d*, $^1J(C,H)=144$, C(4) or C(5)); 72.2 (*d*, $^1J(C,H)=141$, C(5) or C(4)); 69.9 (*d*, $^1J(C,H)=143$, C(3)); 69.0 (*d*, $^1J(C,H)=141$, C(6)); 67.2 (*d*, $^1J(C,H)=144$, C(5'')); 63.0 (*t*, $^1J(C,H)=141$, CH_2–C(6'')); 47.8 (*d*, $^1J(C,H)=142$, C(3'')); 41.6 (*t*, $^1J(C,H)=129$, C(4'')); 32.1 (*t*, $^1J(C,H)=128$, C(4')); 24.5 (*t*, $^1J(C,H)=128$, C(1')); 16.7 (*q*, $^1J(C,H)=125$, *Me*–C(6)). CI-MS (NH_3): 458 (100, $[M+NH_4]^+$), 441 (42, $[M+H]^+$), 348 (5), 279 (8), 256 (6), 206 (21), 186 (20). ESI-MS: 441.35 (100, *M*); 881 (24, 2 *M*). FAB-MS: 463 (50, $[M+Na]^+$), 150 (100). HR-FAB-MS: 441.1947 ($C_{22}H_{33}O_7S^+$, $[M+H]^+$; calc. 441.1947).

*(2*R*,5*R*,6*S*)-5,6-Dihydro-2-[(methoxymethoxy)methyl]-5-(phenylthio)-6-[(2*Z*)-4-[(2*S*,3*R*,4*R*,5*R*,6*S*)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]but-2-enyl]-2*H*-pyran-3(4*H*)-one* ((–)-**31**). A mixture of oxalyl chloride (167 µl, 1.98 mmol), DMSO (288 µl, 3.95 mmol), and CH_2Cl_2 (7 ml) was stirred at –78° for 15 min. A soln. of (–)-**29** (300 mg, 0.49 mmol) in CH_2Cl_2 (3 ml) was added dropwise under stirring at –78°. After stirring at –78° for 30 min, Et_3N (827 µl, 5.93 mmol) was added dropwise, and the mixture was stirred at –78° for 90 min. After evaporation, the residue was extracted Et_2O (10 ml, 3 ×) and the combined org. extract dried ($MgSO_4$) and evaporated: (–)-**31** (314 mg, quant.), pure enough for the next step. An anal. sample was obtained by FC (silica gel, Et_2O). Yellowish oil. $[\alpha]_{589}^{25}=-5$, $[\alpha]_{577}^{25}=-7.2$, $[\alpha]_{546}^{25}=-13$ (*c* = 0.5, $CHCl_3$). UV (MeCN): 256 (4800), 207 (10600). IR (film): 2935, 2825, 1730, 1585, 1475, 1440, 1405, 1380, 1360, 1305, 1215, 1150, 1110, 1035, 990, 920, 845, 810, 750, 695. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.44–7.30 (*m*, 5 arom. H); 5.66 (*ddd*, $^3J(2',3')=11.1$, $^3J(2',1')\approx 6.8$, 6.8, H–C(2')); 5.61 (*ddd*, $^3J(3',2')=11.1$, $^3J(3',4')\approx 6.1$, 6.1, H–C(3')); 4.87, 4.67 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.76, 4.66 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.76, 4.73 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.625, 4.605 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.11–4.01 (*m*, H–C(2'')); 4.00–3.89 (*m*, H–C(3''), H–C(4''), H–C(5''), H–C(6''), H–C(2)); 3.85 (*dd*, $^2J=11.1$, $^3J(CH_2–C(2),2)=3.1$, 1 H, CH_2–C(2)); 3.815 (*dd*, $^2J=11.1$, $^3J(CH_2–C(2),2)=4.9$, 1 H, CH_2–C(2)); 3.64 (*ddd*, $^3J(6,5)\approx 7.5$, $^3J(6,1')\approx 7.5$, 4.1, H–C(6)); 3.53 (*ddd*, $^3J(5,6)\approx 7.5$, $^3J(5,4ax)=6.9$, $^3J(5,4eq)=6.2$, H–C(5)); 3.42, 3.40, 3.37, 3.33 (4*s*, 4 *Me*OCH$_2$); 2.94 (*ddd*, $^2J=15.8$, $^3J(4eq,5)=6.2$, H_{eq}–C(4)); 2.77 (*ddd*, $^2J=14.4$, $^3J\approx 5.2$, $^3J\approx 4.1$, 1 H–C(1')); 2.48 (*ddd*, $^2J=15.8$, $^3J(4ax,5)=6.9$, H_{ax}–C(4)); 2.39 (*ddd*, $^2J=15.1$, $^3J(4',3')\approx 5.3$, $^3J(4',2'')\approx 5.3$, 1 H–C(4')); 2.57–2.35 (*m*, 1 H–C(1'), 1 H–C(4')); 1.31 (*d*, $^3J(Me–C(6''),6'')=6.2$, Me–C(6'')). ^{13}C-NMR (100.6 MHz, CD_2Cl_2): 206.5 (*s*, C(3)); 133.8 (*d*, $^1J(C,H)=161$, 2 arom. C); 131.9 (*s*, arom. C); 129.25 (*d*, $^1J(C,H)=161$, 2 arom. C); 128.9 (*d*, $^1J(C,H)=156$, C(3') or C(2')); 128.35 (*d*, $^1J(C,H)=161$, arom. C); 128.9 (*d*, $^1J(C,H)=157$, C(3') or C(2')); 97.5, 96.8, 96.6, 96.5 (4*t*, $^1J(C,H)=164$, 4 MeOCH_2); 82.4 (*d*, $^1J(C,H)=140$, C(2)); 79.7 (*d*, $^1J(C,H)=145$, C(6)); 75.7 (*d*, $^1J(C,H)=145$, C(3'', 4'', 5'', or 6'')); 75.2 (*d*, $^1J(C,H)=143$, C(3'', 4'', 5'', or 6'')); 74.4 (*d*, $^1J(C,H)=139$, C(3'', 4'', 5'', or 6'')); 71.4 (*d*, $^1J(C,H)=145$, C(2'')); 68.6 (*d*, $^1J(C,H)=141$, C(3'', 4'', 5'', or 6'')); 66.0 (*t*, $^1J(C,H)=145$, CH_2–C(2)); 55.9, 55.9, 55.6, 55.2 (4*q*, $^1J(C,H)=142$, 4 *Me*OCH$_2$); 46.95 (*d*, $^1J(C,H)=145$, C(5)); 43.5 (*t*, $^1J(C,H)=132$, C(4)); 32.1 (*t*, $^1J(C,H)=126$, C(1')); 25.7 (*t*, $^1J(C,H)=127$, C(4')); 15.6 (*q*, $^1J(C,H)=126$, *Me*–C(6'')). CI-MS (NH_3): 633 (100), 632 (79, $[M+NH_4]^+$), 587 (9), 584 (4, $[M+H-OMe]^+$), 583 (4, $[M-OMe]^+$), 523 (10). HR-FAB-MS: 637.2625 ($C_{30}H_{46}NaO_{11}S^+$, $[M+Na]^+$; calc. 637.2659). Anal. calc. for $C_{30}H_{46}O_{11}S$ (614.76): C 58.61, H 7.54; found: C 57.37, H 7.65.

*(2*R*,6*S*)-2-[(Methoxymethoxy)methyl]-6-[(2*Z*)-4-[(2*S*,3*R*,4*R*,5*R*,6*S*)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]but-2-enyl]-2*H*-pyran-3(6*H*)-one* ((+)-**32**). DBU (50 µl, 0.335 mmol) was added to a stirred soln. of crude (–)-**31** (41 mg, 0.067 mmol) maintained at 0°. After stirring at 20° for 15 min, CH_2Cl_2 (5 ml) and sat. aq. $NaHCO_3$ soln. (3 ml) were added. The aq. phase was extracted with CH_2Cl_2 (5 ml, 4 ×), the combined org. extract dried ($MgSO_4$) and evaporated and the residue subjected to FC (silica gel, Et_2O): (+)-**32** (39 mg, 89% based on (–)-**29**). Yellowish oil. $[\alpha]_{589}^{25}=+3.0$, $[\alpha]_{577}^{25}=+3.2$, $[\alpha]_{546}^{25}=+3.5$, $[\alpha]_{435}^{25}=+14.5$, $[\alpha]_{405}^{25}=+19.6$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 227 (4300). IR (film): 2935, 2835, 1745, 1695, 1440, 1385, 1260, 1215, 1150,

1110, 1030, 920, 805, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.97 (*dd*, $^3J(5,4)=10.3$, $^3J(5,6)=1.2$, H−C(5)); 6.12 (*dd*, $^3J(4,3)=10.3$, $^4J(4,6)=2.2$, H−C(4)); 5.64 (*ddd*, $^3J(3',2')=11.2$, $^3J(3',4')=7.0$, 7.0, H−C(3')); 5.56 (*ddd*, $^3J(2',3')=11.2$, $^3J(2',1')=7.2$, 7.2, H−C(2')); 4.84, 4.65 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.75, 4.65 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.74, 4.71 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.67 (*s*, 1 MeOCH_2); 4.42 (*m*, H−C(6)); 4.215 (*ddd*, ^3J(2,CH_2−C(2))=5.9, 2.6, $J=2.3$, H−C(2)); 4.08–4.03 (*m*, H−C(2'')); 4.02 (*dd*, $^2J=11.3$, ^3J(CH_2−C(2),2)=2.6, 1 H, CH_2−C(2)); 3.94–3.90 (*m*, H−C(3''), H−C(4''), H−C(5''), H−C(6'')); 3.89 (*dd*, $^2J=11.3$, ^3J(CH_2−C(2),2)=5.9, 1 H, CH_2−C(2)); 3.40, 3.39, 3.37, 3.36 (4*s*, 4 *Me*OCH_2); 2.55–2.31 (*m*, 2 H−C(1'), 2 H−C(4')); 1.31 (*d*, ^3J(Me−C(6''),6'')=6.2, Me−C(6'')). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 194.1 (*s*, C(3)); 150.9 (*d*, ^1J(C,H)=161, C(5)); 129.7 (*d*, ^1J(C,H)=154, C(3')); 127.1 (*d*, ^1J(C,H)=167, C(4)); 125.0 (*d*, ^1J(C,H)=157, C(2')); 97.5, 96.7, 96.6, 96.4 (4*t*, ^1J(C,H)=164, 4 *Me*OCH_2); 80.2 (*d*, ^1J(C,H)=137, C(2)); 75.7 (*d*, ^1J(C,H)=149, C(3'', 4'', 5'', or 6'')); 75.0 (*d*, ^1J(C,H)=140, C(3'', 4'', 5'', or 6'')); 74.1 (*d*, ^1J(C,H)=148, C(3'', 4'', 5'', or 6'')); 73.7 (*d*, ^1J(C,H)=137, C(6)); 71.4 (*d*, ^1J(C,H)=146, C(2'')); 68.5 (*d*, ^1J(C,H)=142, C(3'', 4'', 5'', or 6'')); 65.8 (*t*, ^1J(C,H)=143, *C*H_2−C(2)); 55.8, 55.8, 55.6, 55.2 (4*q*, ^1J(C,H)=142, 4 *Me*OCH_2); 32.7 (*t*, ^1J(C,H)=127, C(1')); 25.6 (*t*, ^1J(C,H)=121, C(4')); 15.5 (*q*, ^1J(C,H)=126, Me−C(6'')). CI-MS (NH_3): 522 (100, $[M+NH_4]^+$), 473 (1.1, $[M-OMe]^+$), 397 (8), 296 (28), 224 (15). HR-FAB-MS: 527.2481 ($C_{24}H_{40}O_{11}Na^+$, $[M+Na]^+$; calc. 527.2468).

*Ethyl (*α*R,2R,4S,5R,6S)-Tetrahydro-α-hydroxy-2-[(methoxymethoxy)methyl]-3-oxo-5-(phenylthio)-6-{(2Z)-4-[(2S,3R,4R,5R,6S)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-4-acetate* ((−)-**33**) *and Ethyl (*α*R,2R,6S)-3,6-Dihydro-α-hydroxy-2-[(methoxymethoxy)methyl]-3-oxo-6-{(2Z)-4-[(2S,3R,4R,5R,6S)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-4-acetate* ((+)-**34**). A 1:1 mixture of ethyl glyoxylate and toluene (4 ml, 20 mmol) was added to a soln. of crude (−)-**31** (0.615 g, 1 mmol) in anh. THF (10 ml) stirred at −78°. Then 1M $(Me_3Si)_2$NLi in THF (2 ml, 2 mmol) was added dropwise under stirring at −78°. More $(Me_3Si)_2$NLi in THF (up to 10 mmol) was added until completion of the reaction (TLC control). After stirring at −78° for 30 min, the mixture was poured into CH_2Cl_2 (50 ml) and 1N aq. HCl (10 ml), the aq. phase extracted with CH_2Cl_2 (50 ml, 4 ×), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (10 ml), dried ($MgSO_4$), and evaporated and the residue subjected to FC (silica gel, Et_2O): 208 mg (29%) of (−)-**33**, 110 mg (22%) of (+)-**32** (yellowish oil), and (eluent: MeOH/CH_2Cl_2 1:9) 193 mg (32%) of (+)-**34**).

*Data of (−)-***33**: Yellowish oil. $[\alpha]_{589}^{25}=-3.7$, $[\alpha]_{577}^{25}=-3.8$, $[\alpha]_{546}^{25}=-4.2$ ($c=1.0$, $CHCl_3$). UV (MeCN): 246 (5200), 205 (13600). IR (film): 3455, 2935, 2825, 1740, 1470, 1440, 1365, 1260, 1215, 1150, 1110, 1035, 915, 860, 805, 735, 695, 665. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55–7.30 (*m*, 5 arom. H); 5.64 (*ddd*, $^3J(2',3')=10.8$, $^3J(2',1')=6.8$, 6.8, H−C(2')); 5.56 (*ddd*, $^3J(3',2')=10.8$, $^3J(3',4')=6.8$, 6.8, H−C(3')); 4.87, 4.675 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.86 (*d*, $^3J(\alpha,4)=2.0$, H−C(α)); 4.76, 4.74 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.74, 4.64 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.60 (*s*, 1 MeOCH_2); 4.35–4.21 (*m*, MeCH_2O); 4.10–4.01 (*m*, H−C(2'')); 3.98–3.88 (*m*, H−C(3''), H−C(4''), H−C(5''), H−C(6''), H−C(2)); 3.855 (*dd*, $^2J=11.4$, ^3J(CH_2−C(2),2)=3.3, 1 H, CH_2−C(2)); 3.71 (*ddd*, $^3J(6,5)=10.8$, $^3J(6,1')=8.0$, 2.0, H−C(6)); 3.68 (*dd*, $^2J=11.4$, ^3J(CH_2−C(2),2)=5.9, 1 H, CH_2−C(2)); 3.58 (*dd*, $^3J(5,4)=11.5$, $^3J(5,6)=10.8$, H−C(5)); 3.42, 3.40, 3.36, 3.33 (4*s*, 4 *Me*OCH_2); 3.06–2.97 (*m*, 1 H−C(1')); 3.02 (*dd*, $^3J(4,5)=11.5$, $^3J(4,\alpha)=10.8$, H−C(4)); 2.50–2.30 (*m*, 1 H−C(1'), 2 H−C(4')); 1.32 (*d*, ^3J(Me−C(6''),6'')=6.8, Me−C(6'')); 1.25 (*t*, $^3J=7.1$, *Me*CH_2O). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 203.0 (*s*, C(3)); 173.4 (*s*, COO); 133.8 (*d*, ^1J(C,H)=162, 2 arom. C); 131.6 (*s*, arom. C); 129.3 (*d*, ^1J(C,H)=162, 2 arom. C); 128.5 (*d*, ^1J(C,H)=162, arom. C, C(3')); 126.4 (*d*, ^1J(C,H)=156, C(2')); 97.5, 96.7, 96.7, 96.5 (4*t*, ^1J(C,H)=164, 4 MeO*C*H_2); 81.7 (*d*, ^1J(C,H)=138, C(2)); 80.4 (*d*, ^1J(C,H)=144, C(6)); 75.6 (*d*, ^1J(C,H)=138, C(3'', 4'', 5'', or 6'')); 75.1 (*d*, ^1J(C,H)=144, C(3'', 4'', 5'', or 6'')); 74.2 (*d*, ^1J(C,H)=138, C(3'', 4'', 5'', or 6'')); 71.4 (*d*, ^1J(C,H)=148, C(2'')); 68.5 (*d*, ^1J(C,H)=139, C(3'', 4'', 5'', or 6'')); 67.8 (*d*, ^1J(C,H)=145, C(α)); 65.4 (*t*, ^1J(C,H)=147, *C*H_2−C(2)); 62.0 (*t*, ^1J(C,H)=148, Me*C*H_2O); 56.2 (*d*, ^1J(C,H)=126, C(4)); 55.8, 55.8, 55.6, 55.3 (4*q*, ^1J(C,H)=142, 4 *Me*OCH_2); 51.3 (*d*, ^1J(C,H)=141, C(5)); 32.1 (*t*, ^1J(C,H)=127, C(1')); 25.6 (*t*, ^1J(C,H)=126, C(4')); 15.6 (*q*, ^1J(C,H)=127, Me−C(6'')); 14.1 (*q*, ^1J(C,H)=127, *Me*CH_2O). CI-MS (NH_3): 716 (100, $[M+NH_4]^+$), 624 (58, $[M-PhSH]^+$).

*Data of (+)-***34**: Orange oil. $[\alpha]_{589}^{25}=+11$, $[\alpha]_{577}^{25}=+12$, $[\alpha]_{546}^{25}=+15$, $[\alpha]_{435}^{25}=+39$, $[\alpha]_{405}^{25}=+45$ ($c=0.25$, $CHCl_3$). UV (MeCN): 223 (1750), 194 (4000). IR (film): 3440, 2940, 2895, 2825, 1740, 1690, 1465, 1445, 1370, 1300, 1260, 1215, 1150, 1110, 1030, 995, 920, 870, 805. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.06 (*m*, H−C(5)); 5.71–5.62 (*dm*, $^3J(3',2')=11.0$, H−C(3')); 5.61–5.53 (*m*, H−C(2')); 4.90–4.87 (*m*, H−C(α)); 4.85, 4.67 (2*d*, $^2J=6.7$, 1 MeOCH_2); 4.76, 4.73 (2*d*, $^2J=6.7$, 1 MeOCH_2); 4.76, 4.66 (2*d*, $^2J=6.8$, 1 MeOCH_2); 4.67 (*s*, 1 MeOCH_2); 4.54–4.46 (*m*, H−C(6)); 4.26–4.18 (*m*, H−C(2)); 4.23 (*q*, $^3J=7.0$, MeCH_2O); 4.10–4.05 (*m*, H−C(2'')); 4.03 (*dd*, $^2J=11.3$, ^3J(CH_2−C(2),2)=2.6, 1 H, CH_2−C(2)); 3.97–3.84 (*m*, H−C(3''), H−C(4''), H−C(5''), H−C(6''), 1 H of CH_2−C(2)); 3.41, 3.41, 3.39, 3.37 (4*s*, 4 *Me*OCH_2); 2.62–2.30 (*m*, 2 H−C(1'), 2 H−C(4'));

1.31 (*d*, ^3J(Me–C(6″),6″) = 6.2, Me–C(6″)); 1.25 (*t*, ^3J = 7.0, *Me*CH_2O). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 192.8 (*s*, C(3)); 172.3 (*s*, COO); 148.4 (*d*, ^1J(C,H) = 159, C(5)); 135.2 (*s*, C(4)); 129.9 (*d*, ^1J(C,H) = 154, C(3′)); 124.9 (*d*, ^1J(C,H) = 155, C(2′)); 97.6, 96.7, 96.7, 96.5 (4*t*, ^1J(C,H) = 164, 4 MeO*C*H_2); 80.2 (*d*, ^1J(C,H) = 138, C(2)); 75.8 (*d*, C(3″, 4″, 5″, or 6″)); 75.1 (*d*, ^1J(C,H) = 138, C(3″, 4″, 5″, or 6″)); 74.1 (*d*, ^1J(C,H) = 146, C(3″, 4″, 5″, or 6″)); 73.7 (*d*, ^1J(C,H) = 135, C(6)); 71.1 (*d*, ^1J(C,H) = 141, C(2″)); 68.6 (*d*, ^1J(C,H) = 144, C(3″, 4″, 5″, or 6″)); 68.1 (*d*, ^1J(C,H) = 149, C(α)); 66.0 (*t*, ^1J(C,H) = 145, *C*H_2–C(2)); 62.3 (*t*, ^1J(C,H) = 148, Me*C*H_2O); 55.9, 55.8, 55.6, 55.3 (4*q*, ^1J(C,H) = 142, 4 *Me*OCH_2); 32.6 (*t*, ^1J(C,H) = 134, C(1′)); 25.8 (*t*, ^1J(C,H) = 127, C(4′)); 15.5 (*q*, ^1J(C,H) = 128, *Me*–C(6″)); 14.0 (*q*, ^1J(C,H) = 127, *Me*CH_2O). CI-MS (NH_3): 624 (100, $[M+NH_4]^+$), 608 (4, $[M+D]^+$), 578 (39, $[M+1-Et]^+$), 522 (7), 484 (12), 340 (13), 279 (11), 164 (28). HR-FAB-MS: 629.2776 ($C_{28}H_{46}O_{14}Na^+$, $[M+Na]^+$; calc. 629.2785).

Ethyl (α*R*,2*R*,3*S*,4*R*,5*R*,6*S*)*-Tetrahydro-α,3-dihydroxy-2-[(methoxymethoxy)methyl]-5-(phenylthio)-6-{(2Z)-4-[(2S,3R,4R,5R,6S)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-4-acetate* ((−)-**35**). A mixture of (−)-**33** (100 mg, 0.14 mmol), AcOH (2.8 ml), and $(Me_4N)BH(OAc)_3$ (731 mg, 2.78 mmol) was stirred at 20° for 2 h and then evaporated. The residue was taken up with CH_2Cl_2 (10 ml) and sat. aq. $NaHCO_3$ soln. (3 ml). The aq. phase was neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 (10 ml, 5 ×), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue subjected to FC (silica gel, CH_2Cl_2/MeOH 97:3): 55 mg (55%) of (−)-**35**. Colorless oil. $[\alpha]_{589}^{25} = -10$, $[\alpha]_{577}^{25} = -11$, $[\alpha]_{546}^{25} = -13$, $[\alpha]_{435}^{25} = -21$, $[\alpha]_{405}^{25} = -24$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 257 (5200), 204 (9800). IR (film): 3440, 2960, 2925, 1730, 1440, 1380, 1265, 1215, 1150, 1110, 1030, 915. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.52–7.48, 7.32–7.22 (2*m*, 5 arom. H); 5.58 (*ddd*, ^3J(2′,3′) = 11.1, ^3J(2′,1′) = 6.8, 6.8, H–C(2′)); 5.48 (*ddd*, ^3J(3′,2′) = 11.1, ^3J(3′,4′) = 6.8, 6.8, H–C(3″)); 5.09 (br. *d*, ^3J(α,OH–C(α)) = 4.0, H–C(α)); 4.87, 4.67 (2*d*, ^2J = 6.7, 1 MeOCH_2); 4.75, 4.73 (2*d*, ^2J = 6.7, 1 MeOCH_2); 4.72, 4.63 (2*d*, ^2J = 6.7, 1 MeOCH_2); 4.61 (*s*, 1 MeOCH_2); 4.31, 4.18 (2*dq*, ^2J = 10.8, ^3J = 7.1, MeCH_2O); 4.04–3.99 (*m*, H–C(2″)); 3.97–3.88 (*m*, H–C(3″), H–C(4″), H–C(5″), H–C(6″), H–C(3)); 3.76 (*dd*, ^2J = 10.8, ^3J(CH_2–C(2),2) = 4.3, 1 H, CH_2–C(2)); 3.68 (*dd*, ^2J = 10.8, ^3J(CH_2–C(2),2) = 4.6, 1 H, CH_2–C(2)); 3.41, 3.40, 3.35, 3.34 (4*s*, 4 *Me*OCH_2); 3.42–3.33 (H–C(6), overlapped by 4 *Me*OCH_2); 3.29 (*d*, ^3J(OH–C(α),α) = 4.0, OH–C(α)); 3.23 (*ddd*, ^3J(2,3) = 9.6, ^3J(2,CH_2–C(2)) = 4.6, 4.3, H–C(2)); 3.04 (*dd*, ^3J(5,4) = 11.7, ^3J(5,6) = 10.8, H–C(5)); 2.90 (br. *d*, ^3J(OH–C(3),3) = 4.3, OH–C(3)); 2.92–2.84 (*m*, 1 H–C(1′)); 2.44–2.22 (*m*, 2 H–C(4′), 1 H–C(1′)); 2.14 (*ddm*, ^3J(4,5) = 11.7, ^3J(4,3) = 9.9, H–C(4)); 1.32 (*t*, ^3J = 7.1, *Me*CH_2O); 1.29 (*d*, ^3J(Me–C(6″),6″) = 6.5, Me–C(6″)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 173.4 (*s*, COO); 133.5 (*s*, arom. C); 132.6 (*d*, ^1J(C,H) = 164, 2 arom. C); 129.0 (*d*, ^1J(C,H) = 161, 2 arom. C); 127.7 (*d*, ^1J(C,H) ≈ 152, C(3′)); 127.5 (*d*, ^1J(C,H) ≈ 160, arom. C); 127.3 (*d*, ^1J(C,H) ≈ 151, C(2′)); 97.5, 97.1, 96.8, 96.5 (4*t*, ^1J(C,H) = 162, 4 MeO*C*H_2); 81.0 (*d*, ^1J(C,H) = 145, C(6)); 78.1 (*d*, ^1J(C,H) ≈ 140, C(2)); 75.5 (*d*, ^1J(C,H) ≈ 146, C(3, 3″, 4″, 5″, or 6″)); 75.2 (*d*, ^1J(C,H) = 144, C(3, 3″, 4″, 5″, or 6″)); 74.4 (*d*, ^1J(C,H) = 141, C(3, 3″, 4″, 5″, or 6″)); 71.6 (*d*, ^1J(C,H) ≈ 152, C(2″)); 68.9 (*t*, ^1J(C,H) = 146, *C*H_2–C(2)); 68.4 (*d*, ^1J(C,H) = 142, C(3, 3″, 4″, 5″, or 6″)); 67.7 (*d*, ^1J(C,H) = 145, C(α)); 66.8 (*d*, ^1J(C,H) = 148, C(3, 3″, 4″, 5″, or 6″)); 61.8 (*t*, ^1J(C,H) = 150, Me*C*H_2O); 55.9, 55.9, 55.6, 55.6 (4*q*, ^1J(C,H) = 142, 4 *Me*OCH_2); 50.4 (*d*, ^1J(C,H) = 146, C(5)); 50.3 (*d*, ^1J(C,H) = 126, C(4)); 31.3 (*t*, ^1J(C,H) ≈ 126, C(1′)); 25.4 (*t*, ^1J(C,H) = 128, C(4′)); 15.7 (*q*, ^1J(C,H) = 124, *Me*–C(6″)); 14.1 (*q*, ^1J(C,H) = 127, *Me*CH_2O). CI-MS (NH_3): 736 (100, $[M+NH_4]^+$). HR-FAB-MS: 741.3133 ($C_{34}H_{54}NaO_{14}S^+$, $[M+Na]^+$; calc. 741.3132).

Ethyl (4*R*,4a*R*,5*R*,6*S*,8*R*,8a*S*)*-Hexahydro-8-[(methoxymethoxy)methyl]-2,2-dimethyl-5-(phenylthio)-6-{(2Z)-4-[(2S,3R,4R,5R,6S)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]but-2-enyl}pyrano[3,4-*d*][1,3]dioxin-4-carboxylate* ((−)-**36**). A mixture of (−)-**35** (51 mg, 0.071 mmol), TsOH (10 mg), acetone (0.35 ml), and 2,2-dimethoxypropane (0.35 ml) was stirred at 20° for 90 min. CH_2Cl_2 (3 ml) and sat. aq. $NaHCO_3$ soln. (1 ml) were added. The aq. phase was extracted with CH_2Cl_2 (5 ml, 4 ×), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue subjected to FC (silica gel, Et_2O/light petroleum ether 4:1): 31 mg (58%) of (−)-**36**. Colorless oil. $[\alpha]_{589}^{25} = -14$, $[\alpha]_{577}^{25} = -18$, $[\alpha]_{546}^{25} = -20$, $[\alpha]_{435}^{25} = -35$, $[\alpha]_{405}^{25} = -44$ (*c* = 0.3, $CHCl_3$). UV (MeCN): 257 (7200), 205 (12100). IR (film): 2935, 1745, 1585, 1475, 1440, 1405, 1380, 1260, 1205, 1150, 1105, 1040, 990, 920, 865, 745, 720, 695, 670. ^{1}H-NMR (400 MHz, C_6D_6): 7.62–7.59, 7.11–7.06, 7.00–6.95 (3*m*, 5 arom. H); 5.78 (*ddd*, ^3J(2′,3′) = 10.8, ^3J(2′,1′) = 6.5, 6.5, H–C(2′)); 5.71 (*ddd*, ^3J(3′,2′) = 10.8, ^3J(3′,4′) = 6.5, 6.5, H–C(3′)); 4.80, 4.53 (2*d*, ^2J = 6.8, 1 MeOCH_2); 4.70, 4.68 (2*d*, ^2J = 6.8, 1 MeOCH_2); 4.64, 4.49 (2*d*, ^2J = 6.8, 1 MeOCH_2); 4.62, 4.59 (2*d*, ^2J = 6.8, 1 MeOCH_2); 4.47 (*d*, ^3J(4,4a) = 10.0, H–C(4)); 4.25 (*ddd*, ^3J(2″,4′) = 9.6, ^3J(2″,4′) = 4.8, ^3J(2″,3″) = 4.8, H–C(2″)); 4.15 (*dd*, ^3J(3″,4″) = 7.7, ^3J(3″,2″) = 4.3, H–C(3″)); 4.09 (*dd*, ^3J(4″,3″) = 7.7, ^3J(4″,5″) = 2.7, H–C(4″)); 4.06, 3.97 (2*dq*, ^2J = 11.1, ^3J = 7.1, MeCH_2O); 3.95 (*dd*, ^3J(5″,4″) = 2.7, ^3J(5″,6″) = 2.7, H–C(5″)); 3.84 (*qd*, ^3J(6″,Me–C(6″)) = 6.5, ^3J(6″,5″) = 2.7, H–C(6″)); 3.76 (*dd*, ^3J(8a,4a) = 9.9, ^3J(8a,8) = 9.5, H–C(8a)); 3.73 (*d*, ^3J(CH_2–C(8),8) = 3.4, CH_2–C(8)); 3.35 (*ddd*, ^3J(6,5) = 9.9, ^3J(6,1′) = 8.3, 2.5, H–C(6)); 3.30 (*dt*, ^3J(8,8a) = 9.5, ^3J(8,CH_2–C(8)) = 3.4, H–C(8)); 3.25,

3.22, 3.20, 3.16 (4*s*, 4 *Me*OCH$_2$); 2.95 (*ddm*, ^2J = 14.8, ^3J(1′,2′) = 6.5, 1 H–C(1′)); 2.74 (*dd*, ^3J(5,4a) = 12.0, ^3J(5,6) = 9.9, H–C(5)); 2.62–2.45 (*m*, 2 H–C(4′)); 2.52 (*ddd*, ^3J(4a,5) = 12.0, ^3J(4a,4) = 10.0, ^3J(4a,8a) = 9.9, H–C(4a)); 2.52 (*ddd*, ^2J = 14.8, ^3J(1′,6) = 8.3, ^3J(1′,2′) = 6.5, 1 H–C(1′)); 1.46 (*s*, Me–C(2)); 1.39 (*d*, ^3J(Me–C(6″),6″) = 6.5, Me–C(6″)); 1.46 (*s*, 2 Me–C(2)); 0.93 (*t*, ^3J = 7.1, *Me*CH$_2$O). ^{13}C-NMR (100.6 MHz, C_6D_6): 169.7 (*s*, COO); 134.5 (*s*, arom. C); 132.9 (*d*, ^1J(C,H) = 161, 2 arom. C); 129.4 (*d*, ^1J(C,H) = 161, 2 arom. C); 128.7 (*d*, C(3′)); arom. C, overlapped by C_6D_6; 127.4 (*d*, C(2′)); 99.8 (*s*, C(2)); 97.5, 97.0, 96.9, 96.3 (4*t*, ^1J(C,H) = 163, 4 MeO*C*H$_2$); 82.1 (*d*, ^1J(C,H) = 145, C(6)); 78.7 (*d*, ^1J(C,H) = 140, C(8)); 75.9 (*d*, ^1J(C,H) = 147, C(3″)); 75.5 (*d*, ^1J(C,H) = 147, C(4)); 75.2 (*d*, ^1J(C,H) = 142, C(4″) or C(5″)); 75.0 (*d*, ^1J(C,H) = 140, C(5″) or C(4″)); 72.1 (*d*, ^1J(C,H) = 146, C(2″)); 69.6 (*d*, ^1J(C,H) = 144, C(8a)); 68.5 (*d*, ^1J(C,H) = 142, C(6″)); 66.0 (*t*, ^1J(C,H) = 143, CH$_2$–C(8)); 61.4 (*t*, ^1J(C,H) = 147, Me*C*H$_2$O); 55.5, 55.5, 55.3, 54.8 (4*q*, ^1J(C,H) = 141, 4 *Me*OCH$_2$); 49.6 (*d*, ^1J(C,H) = 136, C(5)); 44.8 (*d*, ^1J(C,H) = 132, C(4a)); 31.2 (*t*, ^1J(C,H) = 126, C(1′)); 29.7 (*q*, ^1J(C,H) = 128, *Me*–C(2)); 26.0 (*t*, ^1J(C,H) ≈ 126, C(4′)); 19.8 (*q*, ^1J(C,H) = 125, *Me*–C(2)); 16.2 (*q*, ^1J(C,H) = 127, *Me*–C(6″)); 13.7 (*q*, ^1J(C,H) = 127, *Me*CH$_2$O). CI-MS (NH_3): 776 (6, $[M+NH_4]^+$), 727 (2, $[M-OMe]^+$), 697 (2, $[M-MeOCH_2O]^+$), 593 (11), 335 (12), 203 (18), 110 (100, $PhSH^+$). HR-FAB-MS: 781.3436 ($C_{37}H_{58}NaO_{14}S^+$, $[M+Na]^+$; calc. 781.3435).

Methyl (α*R*,2*R*,3*S*,4*R*,5*R*,6*S*)*-Tetrahydro-α,3-dihydroxy-2-(hydroxymethyl)-5-(phenylthio)-6-[(2Z)-4-[(2S,3S,4R,5S,6S)-tetrahydro-3,4,5-trihydroxy-6-methyl-2*H*-pyran-2-yl]but-2-enyl]-2*H*-pyran-4-acetate* ((−)-**37**). A mixture of (−)-**35** (60 mg, 0.084 mmol), anh. MeOH (1.7 ml), and freshly distilled $SOCl_2$ (121 µl, 1.67 mmol) was stirred at 0° for 5 min, then at 20° for 16 h. Evaporation and FC (silica gel, CH_2Cl_2/MeOH 6 : 1) gave 21 mg (48%) of (−)-**37**. White solid. $[\alpha]_{589}^{25} = -27$, $[\alpha]_{577}^{25} = -39$, $[\alpha]_{546}^{25} = -44$, $[\alpha]_{435}^{25} = -56$, $[\alpha]_{405}^{25} = -68$ (*c* = 0.3, MeOH). IR (film): 3435, 2925, 1735, 1645, 1440, 1240, 1125, 1065, 1000, 875, 750, 695. UV (MeCN): 260 (4100), 216 (5500), 211 (5650). ^{1}H-NMR (400 MHz, CD_3OD): 7.55–7.51, 7.37–7.26 (2*m*, 5 arom. H); 5.60 (br. *ddd*, ^3J(2′,3′) = 10.8, ^3J(2′,1′) = 6.8, 6.8, H–C(2′)); 5.46 (*ddd*, ^3J(3′,2′) = 10.8, ^3J(3′,4′) = 6.8, 6.8, H–C(3′)); 5.08 (*d*, ^3J(α,4) = 1.5, H–C(α)); 3.92 (*dd*, ^3J(2″,4′) = 10.6, ^3J(2″,3″) = 5.5, H–C(2″)); 3.89 (*dd*, ^3J(3″,4″) = 8.4, ^3J(3″,2″) = 5.5, H–C(3″)); 3.81 (*qd*, ^3J(6″,Me–C(6″)) = 6.5, ^3J(6″,5″) = 1.8, H–C(6″)); 3.76 (*dd*, ^2J = 11.9, ^3J(CH$_2$–C(2),2) = 2.4, 1 H, CH$_2$–C(2)); 3.73–3.65 (*m*, MeO, H–C(3), H–C(4″), H–C(5″)); 3.58 (*dd*, ^2J = 11.9, ^3J(CH$_2$–C(2),2) = 5.8, 1 H, CH$_2$–C(2)); 3.37–3.29 (*m*, overlapped by solvent, H–C(6)); 3.08 (*ddd*, ^3J(2,3) = 9.7, ^3J(2,CH$_2$–C(2)) = 5.8, 2.4, 1 H, CH$_2$–C(2)); 3.04 (*dd*, ^3J(5,4) = 11.9, ^3J(5,6) = 10.6, H–C(5)); 2.85 (*ddm*, ^2J = 14.7, ^3J(1′,2′) = 6.8, 1 H–C(1′)); 2.44–2.22 (*m*, 2 H–C(4′), 1 H–C(1′)); 2.11 (*ddd*, ^3J(4,5) = 11.9, ^3J(4,3) = 10.1, ^3J(4,α) = 1.5, H–C(4)); 1.20 (*d*, ^3J(Me–C(6″),6″) = 6.5, Me–C(6″)). ^{13}C-NMR (100.6 MHz, CD_3OD): 177.4 (*s*, COO); 135.1 (*s*, arom. C), 133.8 (*d*, ^1J(C,H) = 164, 2 arom. C); 130.2 (*d*, ^1J(C,H) = 163, 2 arom. C); 129.1 (*d*, ^1J(C,H) = 155, C(3′)); 128.7 (*d*, ^1J(C,H) = 163, arom. C); 128.3 (*d*, ^1J(C,H) = 154, C(2′)); 82.7 (*d*, ^1J(C,H) = 139, C(6)); 82.4 (*d*, ^1J(C,H) = 141, C(2)); 76.4 (*d*, ^1J(C,H) = 147, C(2″)); 72.6 (*d*, ^1J(C,H) = 143, C(5″)); 72.1 (*d*, ^1J(C,H) = 140, C(4″)); 69.8 (*d*, ^1J(C,H) = 144, C(3″)); 68.9 (*d*, ^1J(C,H) = 143, C(6″)); 68.9 (*d*, ^1J(C,H) = 143, C(α)); 65.6 (*d*, ^1J(C,H) = 145, C(3)); 63.1 (*t*, ^1J(C,H) = 141, *C*H$_2$–C(2)); 52.4 (*q*, ^1J(C,H) = 148, *Me*OCH$_2$); 52.2 (*d*, ^1J(C,H) = 130, C(4)); 51.8 (*d*, ^1J(C,H) = 138, C(5)); 32.4 (*t*, ^1J(C,H) = 126, C(1′)); 24.5 (*t*, ^1J(C,H) = 126, C(4′)); 16.7 (*q*, ^1J(C,H) = 127, *Me*–C(6″)). ESI-MS: 529.05 (100, M^+). FAB-MS: 551 (100, $[M+Na]^+$). HR-FAB-MS: 529.2116 ($C_{25}H_{37}O_{10}S^+$, $[M+H]^+$; calc. 529.2107).

Ethyl (α*R*,2*R*,3*S*,4*R*,6*S*)*-Tetrahydro-α,3-dihydroxy-2-[(methoxymethoxy)methyl]-6-{4-[(2S,3R,4R,5R,6S)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]butyl}-2*H*-pyran-4-acetate* ((−)-**38**). A mixture of (−)-**35** (crude obtained from 166 mg (0.23 mmol) of (−)-**33**), EtOH (4.6 ml), and *Raney*-Ni (1 g) was stirred at 20° for 2 h. More *Raney*-Ni (1 g) was added and the mixture stirred at 20° for 15 h. The precipitate was filtered off over *Celite* (height 2 cm), which was washed with EtOH (5 ml, 4 ×). The filtrate was evaporated, the residue taken up in CH_2Cl_2 (10 ml), the soln. dried ($MgSO_4$) and evaporated, and the residue subjected to FC (silica gel, CH_2Cl_2/MeOH 96 : 4): 89 mg (63%, based on (−)-**33**) of pure (−)-**38**. Colorless oil. $[\alpha]_{589}^{25} = -16$, $[\alpha]_{577}^{25} = -17$, $[\alpha]_{546}^{25} = -19$, $[\alpha]_{435}^{25} = -31$, $[\alpha]_{405}^{25} = -37$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 194 (2200). IR (film): 3460, 2940, 2825, 1730, (≈1650), 1465, 1445, 1370, 1260, 1215, 1150, 1110, 1040, 920, 870, 805, 730, 665. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.87, 4.66 (2*d*, ^2J = 6.8, MeOC*H*$_2$); 4.75, 4.64 (2*d*, ^2J = 6.8, MeOC*H*$_2$); 4.75, 4.72 (2*d*, ^2J = 6.8, MeOC*H*$_2$); 4.65 (*s*, MeOC*H*$_2$); 4.29, 4.22 (2*dq*, ^2J = 10.8, ^3J = 7.1, MeC*H*$_2$O); 4.10 (*dd*, ^3J(α,OH–C(α)) = 4.6, ^3J(α,4)) = 3.7, H–C(α)); 3.98 (*ddd*, ^3J(2″,4′) = 10.2, ^3J(2″,4′) = 3.7, ^3J(2″,3″) = 3.7, H–C(2″)); 3.95–3.84 (*m*, H–C(3″), H–C(4″), H–C(5″), H–C(6″)); 3.80 (*dd*, ^2J = 10.5, ^3J(CH$_2$–C(2),2) = 4.6, 1 H, CH$_2$–C(2)); 3.74 (*dd*, ^2J = 10.5, ^3J(CH$_2$–C(2),2) = 4.3, 1 H, CH$_2$–C(2)); 3.72 (*ddd*, ^3J(3,4) = 9.9, ^3J(3,2) = 9.3, ^3J(3,OH–C(3)) = 3.7, H–C(3)); 3.41, 3.40, 3.38, 3.37 (4*s*, 4 *Me*OCH$_2$); 3.42–3.36 (H–C(6), overlapped by 4 *Me*OCH$_2$); 3.31 (*ddd*, ^3J(2,3) = 9.3, ^3J(2,CH$_2$–C(2)) = 4.6, 4.3, H–C(2)); 3.26 (*d*, ^3J(OH–C(α),α) = 4.6, OH–C(α)); 2.98 (br. *d*, ^3J(OH–C(3),3) = 3.7, OH–C(3)); 2.13 (*dddd*, ^3J(4,5ax) = 12.6, ^3J(4,3) = 9.9, ^3J(4,α) = 3.7, ^3J(4,5eq) = 3.7, H–C(4)); 1.77–1.35 (*m*, 2 H–C(1′), 2 H–C(2′), 2 H–C(3′), 2 H–C(4′), 2 H–C(5)); 1.32 (*t*, ^3J = 7.1,

MeCH_2O); 1.29 (*d*, ^3J(Me−C(6″),6″) = 6.5, Me−C(6″)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 174.8 (*s*, COO); 97.4, 97.0, 96.9, 96.4 (4*t*, ^1J(C,H) = 162, 4 MeO*C*H_2); 79.9 (*d*, ^1J(C,H) = 140, C(2)); 76.9 (*d*, C(6)); 75.7 (*d*, ^1J(C,H) ≈ 145, C(3″, 4″, 5″, or 6″)); 75.1 (*d*, ^1J(C,H) ≈ 145, C(3″, 4″, 5″, or 6″)); 74.6 (*d*, ^1J(C,H) ≈ 142, C(3″, 4″, 5″, or 6″)); 72.1 (*d*, ^1J(C,H) = 147, C(α)); 72.0 (*d*, C(2″)); 69.0 (*t*, ^1J(C,H) = 145, CH_2−C(2)); 68.3 (*d*, ^1J(C,H) = 140, C(3)); 67.9 (*d*, ^1J(C,H) = 141, C(3″, 4″, 5″, or 6″)); 61.8 (*t*, ^1J(C,H) = 148, Me*C*H_2O); 55.9, 55.8, 55.6, 55.5 (4*q*, ^1J(C,H) = 142, 4 *Me*OCH_2); 45.6 (*d*, ^1J(C,H) = 127, C(4)); 35.6 (*t*, ^1J(C,H) = 123, C(1′)); 33.7 (*d*, ^1J(C,H) = 127, C(5)); 26.6 (*t*, ^1J(C,H) = 127, C(4′)); 25.9 (*t*, ^1J(C,H) ≈ 124, C(2′) or C(3′)); 25.6 (*t*, ^1J(C,H) ≈ 127, C(3′) or C(2′)); 15.8 (*q*, ^1J(C,H) = 127, *Me*−C(6″)); 14.1 (*q*, ^1J(C,H) = 127, *Me*CH_2O). CI-MS (NH_3): 630 (1, $[M+NH_4]^+$), 473 (13), 315 (16), 244 (82), 142 (100). FAB-MS: 635 (100, $[M+Na]^+$), HR-FAB-MS: 613.3394 ($C_{28}H_{53}O_{14}^+$, $[M+H]^+$; calc. 613.3435).

*Methyl (*α*R,2R,3S,4R,6S)-Tetrahydro-*α*,3-dihydroxy-2-(hydroxymethyl)-6-[4-[(2S,3S,4R,5S,6S)-tetrahydro-3,4,5-trihydroxy-6-methyl-2*H*-pyran-2-yl]butyl]-2*H*-pyran-4-acetate* ((−)-**39**). A mixture of (−)-**38** (44 mg, 0.072 mmol), anh. MeOH (1.5 ml), and freshly distilled $SOCl_2$ (105 μl, 1.44 mmol) was stirred at 0° for 5 min, then at 20° for 16 h. Evaporation and FC (silica gel, CH_2Cl_2/MeOH 4:1) gave 21 mg (70%) of (−)-**39**. Colorless solid. $[\alpha]_{589}^{25} = -62$, $[\alpha]_{577}^{25} = -67$, $[\alpha]_{546}^{25} = -71$, $[\alpha]_{435}^{25} = -113$, $[\alpha]_{405}^{25} = -134$ (*c* = 0.3, MeOH). UV (MeOH): 209 (450). IR (film): 3420, 2935, 2860, 1735, 1635, 1440, 1385, 1230, 1120, 1085, 1015, 870, 800, 750, 670. ^{1}H-NMR (400 MHz, CD_3OD): 4.21 (*d*, ^3J(α,4) = 1.9, H−C(α)); 3.91–3.84 (*m*, H−C(2″), H−C(3″)); 3.81 (*dd*, ^2J = 11.8, ^3J(CH_2−C(2),2) = 2.4, 1 H, CH_2−C(2)); 3.78 (*qd*, ^3J(6″,Me−C(6″)) = 6.5, ^3J(6″,5″) = 1.8, H−C(6″)); 3.72 (*s*, MeO); 3.68 (*dd*, ^3J(5″,4″) = 3.3, ^3J(5″,6″) = 1.8, H−C(5″)); 3.65 (*dd*, ^3J(4″,3″) = 8.4, ^3J(4″,5″) = 3.3, H−C(4″)); 3.61 (*dd*, ^2J = 11.8, ^3J(CH_2−C(2),2) = 5.9, 1 H, CH_2−C(2)); 3.49 (*dd*, ^3J(3,4) = 10.5, ^3J(3,2) = 9.8, H−C(3)); 3.44–3.37 (*m*, H−C(6)); 3.16 (*ddd*, ^3J(2,3) = 9.8, ^3J(2,CH_2−C(2)) = 5.9, 2.4, 1 H, CH_2−C(2)); 2.11 (*dddd*, ^3J(4,5ax) = 12.7, ^3J(4,3) = 10.5, ^3J(4,5eq) = 3.9, ^3J(4,α) = 2.7, H−C(4)); 1.74 (*ddd*, ^2J = 13.2, ^3J(5eq,4) = 3.9, ^3J(5eq,6) = 1.6, H_{eq}−C(5)); 1.71–1.25 (*m*, 2 H−C(1′), 2 H−C(2′), 2 H−C(3′), 2 H−C(4′), H_{ax}−C(5)); 1.21 (*d*, ^3J(Me−C(6″),6″) = 6.5, *Me*−C(6″)). ^{13}C-NMR (100.6 MHz, CD_3OD): 176.2 (*s*, COO); 83.2 (*d*, ^1J(C,H) = 139, C(2)); 78.2 (*d*, ^1J(C,H) = 136, C(6)); 76.3 (*d*, ^1J(C,H) = 144, C(2″)); 72.7 (*d*, ^1J(C,H) = 145, C(5″)); 72.2 (*d*, ^1J(C,H) = 145, C(α)); 72.15 (*d*, ^1J(C,H) = 138, C(4″)); 70.0 (*d*, ^1J(C,H) = 145, C(3″)); 68.5 (*d*, ^1J(C,H) = 144, C(6″)); 66.8 (*d*, ^1J(C,H) = 142, C(3)); 63.4 (*t*, ^1J(C,H) = 141, *C*H_2−C(2)); 52.4 (*q*, ^1J(C,H) = 147, MeO); 47.9 (*t*, ^1J(C,H) ≈ 125, C(4)); 36.8 (*t*, ^1J(C,H) = 126, C(1′)); 34.9 (*t*, ^1J(C,H) = 126, C(5)); 27.1 (*t*, ^1J(C,H) = 125, C(2′) or C(3′)); 26.5 (*t*, ^1J(C,H) = 128, C(3′) or C(2′)); 25.4 (*t*, ^1J(C,H) = 120, C(4′)); 16.7 (*q*, ^1J(C,H) = 127, *Me*−C(6)). ESI-MS: 422.88 (100, M^+), 844.85 (100, [2 *M*]$^+$). FAB-MS: 445 (90, $[M+Na]^+$), 288 (100). HR-FAB-MS: 423.2227 ($C_{19}H_{35}O_{10}^+$, $[M+H]^+$; calc. 423.2230).

*(2R,3S,6S)-Tetrahydro-2-[(methoxymethoxy)methyl]-6-[4-[(2S,3R,4R,5R,6S)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]butyl]-2*H*-pyran-3-ol* ((−)-**40**). A mixture of (−)-**29** (200 mg, 0.32 mmol), THF (6.5 ml), and *Raney*-Ni (1 g) was stirred at 20° for 30 min. More *Raney*-Ni (1 g) was added (until disappearence of (−)-**29**, TLC control), and the mixture was stirred at 20° for 90 min. The precipitate was filtered off on a pad of *Celite* (height 3 cm), which was washed with AcOEt (25 ml, 5 ×). The soln. was dried ($MgSO_4$) and evaporated: 163 mg (99%) of (−)-**29**. Colorless oil. $[\alpha]_{589}^{25} = -3.4$, $[\alpha]_{577}^{25} = -3.6$, $[\alpha]_{546}^{25} = -4.9$, $[\alpha]_{435}^{25} = -8.1$, $[\alpha]_{405}^{25} = -8.6$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 194 (2000). IR (film): 3460, 2935, 1445, 1365, 1215, 1150, 1105, 1035, 915. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.86, 4.66 (2*d*, ^2J = 6.8, 1 MeOCH_2); 4.74, 4.64 (2*d*, ^2J = 6.8, 1 MeOCH_2); 4.74, 4.72 (2*d*, ^2J = 6.8, 1 MeOCH_2); 4.67 (*s*, 1 MeOCH_2); 3.98 (*d*, ^3J(2″,4′) = 10.2, 3.7, ^3J(2″,3″) = 3.7, H−C(2″)); 3.94–3.84 (*m*, H−C(3″), H−C(4″), H−C(5″), H−C(6″)); 3.80 (*dd*, ^2J = 10.2, ^3J(CH_2−C(2),2) = 4.8, 1 H, CH_2−C(2)); 3.73 (*dd*, ^2J = 10.2, ^3J(CH_2−C(2),2) = 5.0, 1 H, CH_2−C(2)); 3.59–3.50 (*m*, H−C(3)); 3.41, 3.39, 3.39, 3.36 (4*s*, 4 *Me*OCH_2); 3.31–3.23 (*m*, H−C(2), H−C(6)); 2.65 (*d*, ^3J(OH−C(3),3) = 2.8, OH−C(3)); 2.14–2.07 (*m*, H_{eq}−C(4)); 1.74–1.24 (*m*, 2 H−C(5), 2 H−C(1′), 2 H−C(2′), 2 H−C(3′), 2 H−C(4′), H_{ax}−C(4)); 1.28 (*d*, ^3J(Me−C(6″),6″) = 6.2, Me−C(6″)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 97.4, 96.8, 96.8, 96.4 (4*t*, ^1J(C,H) = 162, 4 MeO*C*H_2); 79.8 (*d*, ^1J(C,H) = 140, C(2) or C(6)); 77.5 (*d*, ^1J(C,H) ≈ 155, C(2) or C(6)); 75.7 (*d*, ^1J(C,H) ≈ 145, C(3″, 4″, 5″, or 6″)); 75.1 (*d*, ^1J(C,H) ≈ 143, C(3″, 4″, 5″, or 6″)); 74.7 (*d*, ^1J(C,H) ≈ 144, C(3″, 4″, 5″, or 6″)); 71.8 (*d*, ^1J ≈ 147, C(2″)); 69.2 (*t*, ^1J = 144, *C*H_2−C(2)); 68.8 (*d*, ^1J(C,H) = 143, C(3)); 67.9 (*d*, ^1J(C,H) = 139, C(3″, 4″, 5″, or 6″)); 55.9, 55.8, 55.6, 55.4 (4*q*, ^1J(C,H) = 142, 4 *Me*OCH_2); 35.6 (*t*, ^1J(C,H) = 124, C(1′)); 32.2 (*t*, ^1J(C,H) = 130, C(4)); 30.6 (*t*, ^1J(C,H) = 130, C(5)); 26.5 (*t*, ^1J(C,H) ≈ 128, C(4′)); 25.9 (*t*, ^1J(C,H) = 129, C(2′) or C(3′)); 25.6 (*t*, ^1J(C,H) = 125, C(2′) or C(3′)); 15.8 (*q*, ^1J(C,H) = 126, *Me*−C(6″)). CI-MS (NH_3): 528 (100, $[M+NH_4]^+$), 511 (1.4, $[M+H]^+$), 496 (1.2, $[M+1-Me]$), 403 (7), 341 (4), 246 (2.5), 161 (15), 83 (15). Anal. calc. for $C_{24}H_{46}O_{11}$ (510.62): C 56.45, H 9.08; found: C 56.30, H 9.04.

*(2S,3S,4R,5S,6S)-Tetrahydro-6-methyl-2-[4-[(2S,5S,6R)-tetrahydro-5-hydroxy-6-(hydroxymethyl)-2*H*-pyran-2-yl]butyl]-2*H*-pyran-3,4,5-triol* ((−)-**41**). A mixture of (−)-**40** (77 mg, 0.15 mmol), anh. MeOH (3 ml), and

freshly distilled $SOCl_2$ (0.2 ml, 3 mmol) was stirred at 0° for 5 min, then at 20° for 2 h. Evaporation and FC (silica gel, CH_2Cl_2/MeOH 4:1) gave 25 mg (60%) of (−)-**41**. Colorless oil. $[\alpha]_{589}^{25} = -58$, $[\alpha]_{577}^{25} = -61$, $[\alpha]_{546}^{25} = -68$, $[\alpha]_{435}^{25} = -102$, $[\alpha]_{405}^{25} = -118$ ($c = 0.3$, MeOH). UV (MeOH): 268 (650), 195 (600). IR (film): 3385, 2935, 2860, 1650, 1455, 1380, 1260, 1155, 1070, 985, 875, 800, 750. ^{1}H-NMR (400 MHz, CD_3OD): 3.90–3.84 (*m*, H−C(2), H−C(3)); 3.82 (*dd*, $^2J = 11.7$, $^3J(CH_2{-}C(6'),6'') = 2.7$, 1 H, $CH_2{-}C(6'')$); 3.78 (*qd*, $^3J(6,Me{-}C(6)) = 6.5$, $^3J(6,5) = 1.9$, H−C(6)); 3.68 (*dd*, $^3J(5,4) = 3.4$, $^3J(5,6) = 1.9$, H−C(5)); 3.64 (*dd*, $^3J(4,3) = 8.5$, $^3J(4,5) = 3.4$, H−C(4)); 3.62 (*dd*, $^2J = 11.7$, $^3J(CH_2{-}C(6''),6'') = 6.0$, 1 H, $CH_2{-}C(6'')$); 3.36 (*ddd*, $^3J \approx 10$, $^3J = 9.4$, $^3J(5'',4''eq) = 4.9$, H−C(5″)); 3.30–3.27 (*m*, H−C(2″)); 3.12 (*ddd*, $^3J(6'',5'') = 9.0$, $^3J(6'',CH_2{-}C(6'')) = 6.0$, 2.6, H−C(6″)); 2.05 (*dddd*, $^2J = 12.3$, $^3J \approx 4.5$, 3.8, 3.8, $H_{eq}{-}C(4'')$); 1.75–1.26 (*m*, $H_{ax}{-}C(4'')$, 2 H−C(3″), 2 H−C(1′), 2 H−C(2′), 2 H−C(3′), 2 H−C(4′)); 1.21 (*d*, $^3J(Me{-}C(6),6) = 6.5$, Me−C(6)). ^{13}C-NMR (100.6 MHz, CD_3OD): 83.9 (*d*, $^1J(C,H) = 136$, C(6″)); 78.7 (*d*, $^1J(C,H) = 137$, C(2″)); 76.2 (*d*, $^1J(C,H) = 140$, C(2)); 72.7 (*d*, $^1J(C,H) = 144$, C(5)); 72.2 (*d*, $^1J(C,H) = 140$, C(4)); 70.0 (*d*, $^1J(C,H) = 143$, C(3)); 68.5 (*d*, $^1J(C,H) = 144$, C(6)); 67.7 (*d*, $^1J(C,H) = 144$, C(5″)); 63.6 (*t*, $^1J(C,H) = 142$, $CH_2{-}C(6'')$); 36.8 (*t*, $^1J(C,H) = 129$, C(4′)); 33.7 (*t*, $^1J(C,H) = 132$, C(4″)); 32.1 (*t*, $^1J(C,H) = 131$, C(3″)); 27.2 (*t*, $^1J(C,H) = 124$, C(2′) or C(3′)); 26.6 (*t*, $^1J(C,H) = 124$, C(3′) or C(2′)); 25.4 (*t*, $^1J(C,H) = 120$, C(1′)); 16.7 (*q*, $^1J(C,H) = 127$, *Me*−C(6)). CI-MS (NH_3): 335 (19, $[M+H]^+$), 281 (11), 267 (9), 217 (44), 131 (46), 81 (100). ESI-MS: 356.85 (100, $[M+Na]^+$). FAB-MS: 357 (100, $[M+Na]^+$). HR-FAB-MS: 335.2077 ($C_{16}H_{31}O_7^+$, $[M+H]^+$; calc. 335.2070).

*(2*R*,3*S*,6*R*)-Tetrahydro-2-[(methoxymethoxy)methyl]-6-{(2*Z*/*E*)-4-[(2*S*,3*R*,4*R*,5*R*,6*S*)-tetrahydro-3,4,5-tris(methoxymethoxy)-6-methyl-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-3-ol* ((−)-**42**). A mixture of (−)-**29** (182 mg, 0.295 mmol), Bu_3SnH (15 ml), AIBN (10 mg, 0.059 mmol), and toluene (15 ml) was stirred at 80° for 2 h. More AIBN (10 mg) was added every 2 h until disappearance of (−)-**29**. After stirring at 80° for 26 h, the mixture was poured into pentane/MeCN 1:1 (40 ml). The pentane fraction was extracted with MeCN (10 ml, 5×) The combined MeCN phase was washed with pentane (10 ml, 2×) and evaporated and the residue subjected to FC (silica gel, AcOEt): 125 mg (83%; (*Z*)/(*E*) 1:2) of (−)-**42**. Colorless oil. $[\alpha]_{589}^{25} = -9.8$, $[\alpha]_{577}^{25} = -0.3$, $[\alpha]_{546}^{25} = -11.3$, $[\alpha]_{435}^{25} = -19.8$, $[\alpha]_{405}^{25} = -23.2$ ($c = 3$, $CHCl_3$). UV (MeCN): 198 (4700). IR (film): 3465, 2935, 1650, 1440, 1370, 1215, 1150, 1035, 990, 920, 810. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.55–5.42 (*m*, $J_{trans} = 15.7$, $J_{cis} = 11.7$, $J = 6.8$, $H{-}C(2')_{trans+cis}$, $H{-}C(3')_{trans+cis}$); 4.85, 4.65 (2*d*, $^2J = 6.8$, 1 MeOCH_{2cis}); 4.84, 4.65 (2*d*, $^2J = 6.8$, 1 MeOCH_{2trans}); 4.74, 4.72 (2*d*, $^2J = 6.8$, 1 MeOCH_{2cis}); 4.74, 4.71 (2*d*, $^2J = 6.8$, 1 MeOCH_{2trans}); 4.74, 4.64 (2*d*, $^2J = 6.8$, 1 MeOCH_{2cis}); 4.74, 4.64 (2*d*, $^2J = 6.8$, 1 MeOCH_{2trans}); 4.67 (*s*, MeOC$H_{2trans+cis}$); 4.05–3.98 (*m*, $H{-}C(2'')_{trans+cis}$); 3.96–3.86 (*m*, $H{-}C(3'')_{trans+cis}$, $H{-}C(4'')_{trans+cis}$, $H{-}C(5'')_{trans+cis}$, $H{-}C(6'')_{trans+cis}$); 3.79 (*dd*, $^2J = 10.5$, $^3J(CH_2{-}C(2),2) = 4.8$, 1 H of $CH_2{-}C(2)_{cis}$); 3.79 (*dd*, $^2J = 10.5$, $^3J(CH_2{-}C(2),2) = 4.8$, 1 H of $CH_2{-}C(2)_{trans}$); 3.74 (*dd*, $^2J = 10.5$, $^3J(CH_2{-}C(2),2) = 4.9$, 1 H of $CH_2{-}C(2)_{trans}$); 3.73 (*dd*, $^2J = 10.5$, $^3J(CH_2{-}C(2),2) = 4.9$, 1 H of $CH_2{-}C(2)_{cis}$); 3.55 (*ddd*, $^3J(3,4ax) = 10.5$, $^3J(3,2) = 10.5$, $^3J(3,4eq) = 5.2$, $H{-}C(3)_{cis}$); 3.54 (*ddd*, $^3J(3,4ax) = 10.5$, $^3J(3,2) = 10.5$, $^3J(3,4eq) = 5.2$, $H{-}C(3)_{trans}$); 3.40, 3.39, 3.38, 3.37 ((4*s*, 4 *Me*OCH_{2cis}); 3.40, 3.38, 3.38, 3.37 ((4*s*, 4 *Me*OCH_{2trans}); 3.34–3.24 (*m*, $H{-}C(6)_{trans+cis}$, $H{-}C(2)_{trans+cis}$); 2.64 (br. *s*, $OH{-}C(3)_{trans+cis}$); 2.44–2.06 (*m*, 2 $H{-}C(4')_{trans+cis}$, 2 $H{-}C(1')_{trans+cis}$, $H{-}C(4)_{trans+cis}$); 1.77–1.68 (*m*, $H{-}C(5)_{trans+cis}$); 1.51–1.30 (*m*, $H{-}C(4)_{trans+cis}$, $H{-}C(5)_{trans+cis}$); 1.28 (*d*, $^3J(Me{-}C(6''),6'') = 6.2$, $Me{-}C(6'')_{trans+cis}$). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 128.7 (*d*, $^1J(C,H) = 154$, C(2′ or 3′)$_{trans}$); 128.4 (*d*, $^1J(C,H) = 153$, C(3′ or 2′)$_{trans}$); 127.6 (*d*, $^1J(C,H) = 157$, C(2′ or 3′)$_{cis}$); 127.1 (*d*, $^1J(C,H) = 158$, C(3′ or 2′)$_{cis}$); 97.5, 97.4, 96.75, 96.7, 96.5, 96.4 (6*t*, $^1J(C,H) = 163$, 4 MeO$CH_{2trans+cis}$); 79.9 (*d*, $^1J(C,H) = 141$, $C(2)_{trans+cis}$); 77.4 (*d*, $^1J(C,H) \approx 143$, $C(6)_{trans}$); 77.2 (*d*, $C(6)_{cis}$); 75.5 (*d*, $^1J(C,H) = 143$, C(3″, 4″, 5″, or 6″)$_{trans+cis}$); 75.1 (*d*, $^1J(C,H) = 144$, C(3″, 4″, 5″, or 6″)$_{trans+cis}$); 74.2 (*d*, $^1J(C,H) = 145$, C(3″, 4″, 5″, or 6″)$_{trans+cis}$); 71.3 (*d*, $^1J(C,H) \approx 160$, $C(2'')_{trans+cis}$); 69.0 (*t*, $J(C,H) = 142$, $CH_2{-}C(2)_{trans+cis}$); 68.5 (*d*, $^1J(C,H) = 144$, C(4, 3″, 4″, 5″, or 6″))$_{trans+cis}$); 68.3 (*d*, C((3″, 4″, 5″, or 6″ or 4)$_{trans+cis}$); 55.8, 55.8, 55.5, 55.3 4 (4*q*, $^1J(C,H) = 142$, 4 *Me*OC$H_{2trans+cis}$); 38.9 (*t*, $^1J(C,H) = 124$, $C(1')_{trans}$); 33.8 (*t*, $^1J(C,H) = 131$, $C(1')_{cis}$); 32.05 (*t*, $^1J(C,H) = 129$, $C(4)_{trans+cis}$); 30.6 (*t*, $^1J(C,H) = 126$, $C(4')_{trans}$); 30.2 (*t*, $^1J(C,H) = 124$, $C(5)_{cis}$); 30.0 (*t*, $^1J(C,H) = 128$, $C(5)_{trans}$); 25.3 (*t*, $^1J(C,H) = 127$, $C(4')_{cis}$); 15.5 (*q*, $^1J(C,H) = 128$, $Me{-}C(6'')_{cis}$); 15.4 (*q*, $^1J(C,H) = 128$, $Me{-}C(6'')_{trans}$). CI-MS (NH_3): 526 (100, $[M+NH_4]^+$), 477 (1.4, $[M-OMe]^+$). FAB-MS: 531 (100, $[M+Na]^+$). HR-FAB-MS: 509.2943 ($C_{24}H_{45}O_{11}^+$, $[M+H]^+$; calc. 509.2962).

*(2*S*,3*S*,4*R*,5*S*,6*S*)-Tetrahydro-6-methyl-2-{(2*Z*/*E*)-4-[(2*R*,5*S*,6*R*)-tetrahydro-5-hydroxy-6-(hydroxymethyl)-2*H*-pyran-2-yl]but-2-enyl}-2*H*-pyran-3,4,5-triol* (**43**). A mixture of (−)-**42** (68 mg, 0.134 mmol), anh. MeOH (2.7 ml) and freshly distilled $SOCl_2$ (195 µl, 2.67 mmol) was stirred at 0° for 5 min, then at 20° for 2 h. Evaporation and FC (silica gel, CH_2Cl_2/MeOH 4:1) gave 38 mg (86%; (*Z*)/(*E*) 1:2) of **43**. Colorless oil. IR (film): 3380, 2935, 1650, 1445, 1245, 1155, 1070, 875, 800. UV (MeCN): 205 (800). ^{1}H-NMR (400 MHz, CD_3OD): 5.62–5.45 (*m*, $J_{trans} = 15.2$, $J_{cis} = 10.3$, $J = 6.8$, $H{-}C(2')_{trans+cis}$, $H{-}C(3')_{trans+cis}$); 3.96–3.78 (*m*, $H{-}C(2)_{trans+cis}$, $H{-}C(3)_{trans+cis}$, 1 H of $CH_2{-}C(6'')_{trans+cis}$, $H{-}C(6)_{trans+cis}$); 3.72–3.67 (*m*, $H{-}C(5)_{trans+cis}$);

3.66 (*dd*, $^3J(4,3) = 8.4$, $^3J(4,5) = 3.5$, H–C(4)$_{trans+cis}$); 3.62 (*dd*, $^2J = 11.6$, $^3J(CH_2–C(6''),6'') = 6.0$, 1 H of $CH_2–C(6'')_{trans+cis}$); 3.40–3.31 (*m*, H–C(2'')$_{trans+cis}$, H–C(5'')$_{trans+cis}$); 3.13 (*ddd*, $^3J(6'',5'') = 9.2$, $^3J(6'',CH_2–C(6'')) = 6.0$, 2.7, H–C(6'')$_{trans+cis}$); 2.45–2.01 (*m*, 2 H–C(1')$_{trans+cis}$, 2 H–C(4')$_{trans+cis}$, H–C(4'')$_{trans+cis}$); 1.78–1.70 (*m*, H–C(3'')$_{trans+cis}$); 1.51–1.26 (*m*, H–C(4'')$_{trans+cis}$, H–C(3'')$_{trans+cis}$); 1.21 (*d*, $^3J(Me–C(6),6) = 6.5$, Me–C(6)$_{cis}$); 1.20 (*d*, $^3J(Me–C(6),6) = 6.5$, Me–C(6)$_{trans}$). ^{13}C-NMR (100.6 MHz, CD_3OD): 130.4 (*d*, $^1J(C,H) = 154$, C(2' or 3')$_{trans}$); 129.4 (*d*, $^1J(C,H) = 154$, C(3' or 2')$_{trans}$); 129.1 (*d*, $^1J(C,H) = 155$, C(2' or 3')$_{cis}$); 128.2 (*d*, $^1J(C,H) = 155$, C(3' or 2')$_{cis}$); 84.0 (*d*, $^1J(C,H) = 137$, C(6'')$_{trans+cis}$); 78.6 (*d*, $^1J(C,H) = 140$, C(2'')$_{trans+cis}$); 76.2, 76.1 (2*d*, $^1J(C,H) \approx 147$, C(2)$_{trans+cis}$); 72.6, 72.5 (2*d*, $^1J(C,H) = 145$, C(4 or 5)$_{trans+cis}$); 72.2, 72.1 (2*d*, $^1J(C,H) = 140$, C(5 or 4)$_{trans+cis}$); 69.9, 69.8 (2*d*, $^1J(C,H) = 145$, C(3)$_{trans+cis}$); 68.8, 68.6 (2*d*, $^1J(C,H) = 142$, C(6)$_{trans+cis}$); 67.6 (*d*, $^1J(C,H) \approx 145$, C(5'')$_{trans}$); 67.5 (*d*, $^1J(C,H) \approx 145$, C(5'')$_{cis}$); 63.6 (*t*, $^1J(C,H) = 141$, $CH_2–C(6'')_{trans}$); 63.5 (*t*, $^1J(C,H) = 141$, $CH_2–C(6'')_{cis}$); 40.1 (*t*, $^1J(C,H) = 126$, C(4')$_{trans}$); 34.8 (*t*, $^1J(C,H) = 124$, C(4')$_{cis}$); 33.7, 33.5 (2*t*, $^1J(C,H) \approx 130$, C(4'')$_{trans+cis}$); 31.4 (*t*, $^1J(C,H) = 124$, C(3'')$_{trans+cis}$); 29.5 (*t*, $^1J(C,H) = 125$, C(1')$_{trans}$); 24.4 (*t*, $^1J(C,H) \approx 126$, C(1')$_{cis}$); 16.6, 16.5 (2*q*, $^1J(C,H) = 127$, Me–C(6)$_{trans+cis}$). ESI-MS: 354.83 (100, $[M+Na]^+$); 333.34 (*ca.* 10, $[M+H]^+$). FAB-MS: 355 (100, $[M+Na]^+$). HR-FAB-MS: 333.1911 ($C_{16}H_{29}O_7^+$, $[M+H]^+$; calc. 333.1913).

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Received August 26, 2003