# 117. A New Approach to the Synthesis of Long-Chain Polypropionates Based on the *Diels-Alder* Monoadditions of 2,2′-Ethylidenebis[3,5-dimethylfuran][1])

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Acidic condensation of 2,4-dimethylfuran with acetaldehyde provided 2,2′-ethylidenebis[3,5-dimethylfuran] (**7**) which added 1 equiv. of methyl bromopropynoate to give a major adduct **8**. Regio- and stereoselective hydroboration of the latter 7-oxanorbornadiene derivative followed by alcohol protection and methanolysis of its β-bromoacrylate moiety gave (1*RS*,2*RS*,4*RS*,5*SR*,6*SR*,1′*RS*)-methyl 4-[1′-(3″,5″-dimethylfuran-2″-yl)ethyl]-3,3-dimethoxy-6-*exo*-[(2-methoxy)ethoxy]-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptane-2-*endo*-carboxylate (**24**) (*Schemes 2* and *3*). Reduction of **24** with $LiAlH_4$, followed by $H_2O$ and MeOH elimination gave the 3-methylidene-7-oxanorbornan-2-one derivative **26** which underwent 7-oxa ring opening through a $S_N2'$ type of reaction with $Me_2CuLi$ (*Scheme 4*). Stereoselective hydrogenation and ketone reduction provided (1*RS*,2*SR*,3*RS*,4*RS*,5*SR*,6*RS*,1′*SR*)-1-[1′-(3″,5″-dimethylfuran-2″-yl)]-*c*-3-ethyl-*c*-5-[(2-methoxyethoxy)methoxy]-*t*-4,*t*-6-dimethylcyclohexane-*r*-1,*c*-2-diol (**32**), the oxidative cleavage of which with $Pb(OAc)_4$ generated a 6-oxo-aldehyde **33** (*Schemes 4* and *5*). Chemoselective protection of **33** and chemo- and stereoselective reductions generated (2*RS*,3*RS*,4*SR*,5*SR*,6*SR*,7*RS*)-7-(3′,5′-dimethylfuran-2′-yl)-2-ethyl-6-hydroxy-4-[(2-methoxyethoxy)methoxy]-3,5-dimethyloct-1-yl pivaloate (**36**) and its 4-hydroxy 6-epimer **40** (12 and 13 steps, resp., from adduct **8**; *Scheme 5*). Oxidation of the furan ring of **36** led to a (2*RS*,3*SR*,4*RS*,5*SR*,6*RS*,7*RS*)-7-ethyl-3,5,8-trihydroxy-2,4,6-trimethyloctanoic acid derivative **44**, a polypropionate fragment with six contiguous stereogenic centres (*Scheme 6*).

**Introduction.** – A great number of natural products of biological interest contain polypropionate fragments (chain with alternating OH and Me substituents) [1] [2] (see also ref. 2 in [2]). In 1956, *Woodward* [3] described these compounds as 'hopelessly complex' for synthesis. Since then, several methods and strategies have been developed to provide access to these systems which possess a large number of stereogenic centres [4] (see also ref. 4–16 in [2]). During the seventies and eighties, the carbohydrate approach was the most popular to construct these acyclic chains. More recently, the advent of new chiral auxiliaries [5] and chirons [6], as well as the development of new techniques to control the diastereoselectivity of aldehyde nucleophilic additions [7] and cross-aldolization [8], made possible the total, asymmetric synthesis of a large number of polypropionate natural products and analogues [9]. Other approaches imply two-directional chain elongation and a 'desymmetrization' process [10]. Bicyclic alkenes and ketones that display high facial selectivity in their reactions for steric reasons have also been used as starting materials [11–18]. We have shown [19] that the $ZnI_2$-catalyzed *Diels-Alder* addition of 2,4-dimethylfuran to 1-cyanovinyl (1*R*)-camphanate leads to optically pure adduct (+)-**1** in high yield, the saponification of which furnishes enone (+)-**2** and allows one

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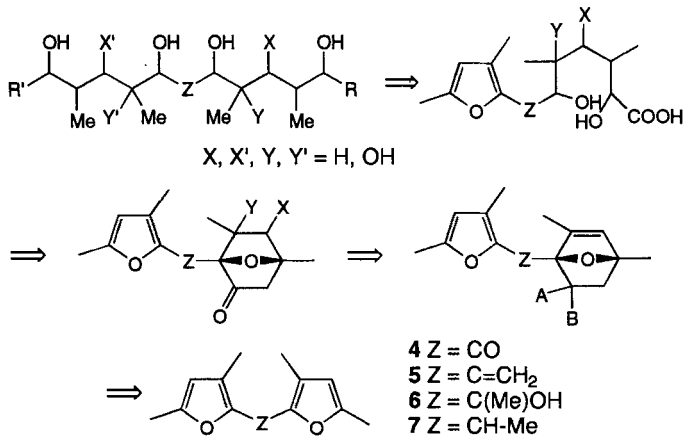
to recover the chiral auxiliary ((1*R*)-camphanic acid). Starting with 1-cyanovinyl (1*S*)-camphanate leads to the diastereoisomeric adduct (−)-**3** and enantiomeric enone (−)-**2** with the same ease ('naked sugars of the second generation' [20]). The *Diels-Alder* approach to the synthesis of polypropionates had been applied earlier by *Danishefsky* and coworkers [21] to prepare a racemic precursor of 6-deoxyerytrothonolide B. Recently, *Yamamoto* and coworkers [22] have shown that the hetero-*Diels-Alder* additions of furan-2-carboxaldehyde to (*E*)-1-methoxy-2-methyl-3-(trimethylsilyloxy)penta-1,3-diene used by *Danishefsky* [21] can now be carried out with excellent asymmetric induction with a homochiral *Lewis*-acid catalyst. The bicyclic alkenes (+)-**1**, (+)-**2**, (−)-**3**, and (−)-**2** have been converted into all kinds of polypropionate fragments [19] [20] [23] [24] including long-chain derivatives containing up to eleven contiguous stereogenic centres and tertiary-alcohol moieties [2]. The method is highly convergent, it involves cross-aldolizations of lithium enolates of 7-oxabicyclo[2.2.1]heptan-2-ones with α-methyl aldehydes, reactions that can be highly stereoselective.


(+)-**1** (+)-**2** (-)-**2** (-)-**3**

R* = (1*R*)-camphanoyl R' = (1*S*)-camphanoyl

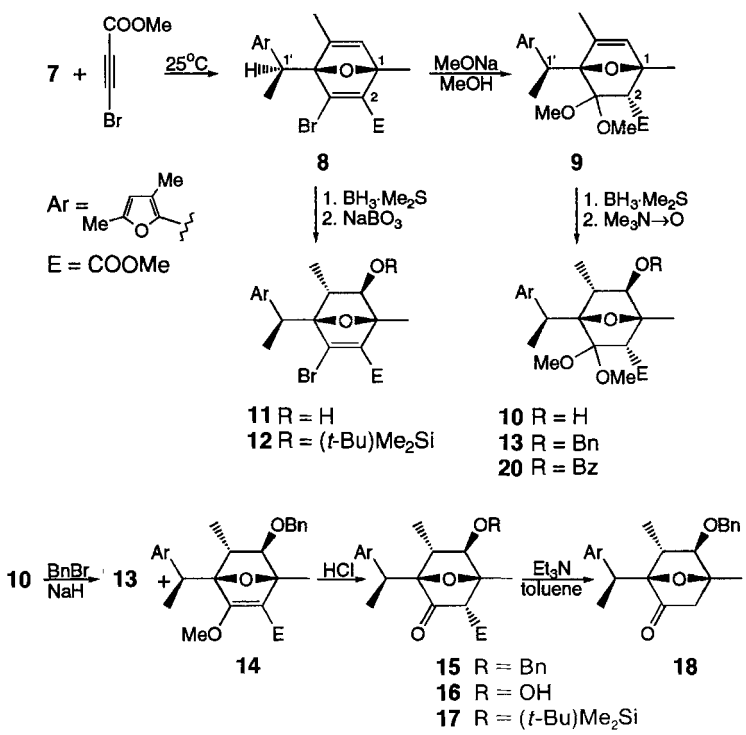
In all the methods already established, the construction of a long-chain polypropionate requires, at certain stages, the joining through C–C bonds of two, or more than two, shorter chains. In this report we wish to present a completely new strategy (*Scheme 1*) which uses an achiral starting material having a polyunsaturated long C-chain with Me substituents onto which OH groups or other groups should be introduced chemoselectively and stereoselectively. Since 2,4-dimethylfuran is a compound readily available from acetone [25], we wondered whether it could not be used to construct such a backbone. We explored first the possibility to use the bisfuran derivative **4**, obtained by condensation of the lithium conjugate base of 2,4-dimethylfuran to methyl *N*,*N*-dimethylcarbamate. This compound refused to undergo *Diels-Alder* additions [26], a reaction which we chose as a mean to desymmetrize the backbone and to generate 7-oxabicyclo[2.2.1]heptene derivatives that would allow one to carry out highly regio- and stereoselective hydroborations [20], hydrogenations [27], double hydroxylations [19], and other reactions [23]. We then converted **4** into alkene **5** through a *Wittig* reaction. Unfortunately, most dienophiles refused to engender 7-oxabicyclo[2.2.1]heptenes with **5**; they preferred to give [4 + 2] or/and [2 + 2] adducts involving the exocyclic double bond of **5**. The tertiary alcohol **6** obtained by MeLi addition to **4** was a very sensitive compound which led only to polymers when submitted to the conditions of thermal or *Lewis*-acid-catalyzed *Diels-Alder* additions [26]. We have found now that the condensation of 2,4-dimethylfuran with acetaldehyde under acidic conditions generates 2,2′-ethylidene-bis[3,5-dimethylfuran] (**7**) in 80% yield. This bisfuran gives unseparable mixture of adducts with simple dienophiles such as methyl acrylate, maleic anhydride, and methyl allene-1,3-dicarboxylate [28]. However, a major mono-adduct was obtained in the reaction of **7** with methyl bromopropynoate. We report here our preliminary work which intends to convert this mono-adduct into long-chain polyproniate fragments.

*Scheme 1*




**Results and Discussion.** – When a 1:1 mixture of **7** and methyl bromopropynoate was stirred for 3 days at −2°, a black mixture was obtained from which adduct **8** was isolated in 55% yield after flash chromatography on silica gel (*Scheme 2*). The relative configuration of this adduct was established by $^1$H-NMR of a product of transformation (see

*Scheme 2*



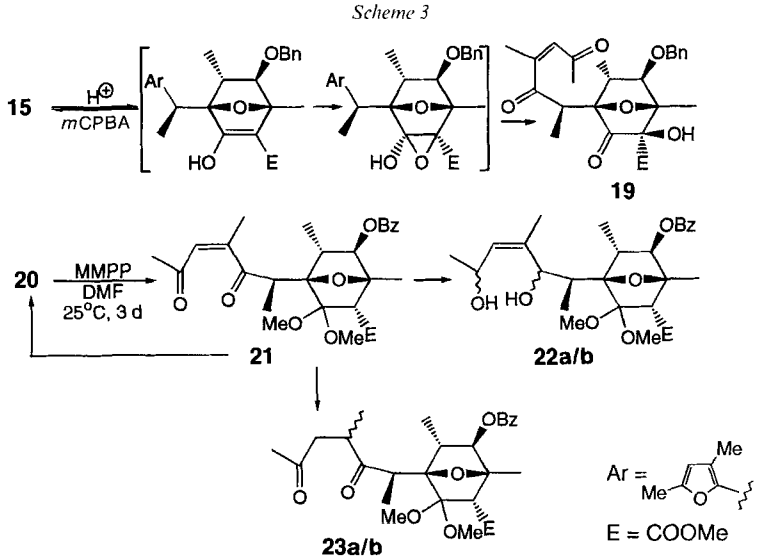
below). At this stage of this work, we do not know yet whether **8** corresponds to a product of kinetic or thermodynamic control. Treatment of **8** with 30% MeONa in MeOH (25°, 3 h) provided the dimethyl acetal **9** as unique product isolated in 65% yield. Regio- and stereoselective hydroboration of **9** with $BH_3 \cdot Me_2S$ (25°, $Et_2O$, 6 h), followed by oxidative workup ($Me_3NO$, *o*-xylene, 110°, 12 h) gave alcohol **10** (82%). No other stereoisomer was detected by 400-MHz $^1$H-NMR of the crude reaction mixture. Selective hydroboration of the *Diels-Alder* adduct **8** ($BH_3 \cdot Me_2S$, $Et_2O$, 25°; then $NaBO_3$) furnished the expected alcohol **11** which was silylated with (*t*-Bu)$Me_2SiOSO_2CF_3$ and 2,6-lutidine into **12** (80%).

Acidic hydrolysis of the dimethyl-acetal moiety of **10** (*Nafion NR50*, $H^+$ form, acetone/$H_2O$, reflux, 12 h) refused to deliver the expected ketone **16**. The same was observed when using *Amberlyst 15*. However, with *Amberlite IR 120* in acetone, the corresponding methyl enol ether was obtained. Finally, we found that 2M HCl in aqueous acetone did liberate the desired ketone **16** that was treated directly with (*t*-Bu)$Me_2SiOSO_2OCF_3$ and 2,6-lutidine (25°) to afford **17** (80%).

Protection of alcohol **10** as its benzyl ether **13** (NaH, BnBr, $Bu_4NI$, 25°, 3 d) was accompanied by the formation of enol methyl ether **14**. Treatment of the crude mixture **13**/**14** with 2M HCl in 1:1 acetone/$H_2O$ provided the desired benzylated ketone **15** (85% based on **10**).

Attempts to induce the 7-oxa-bridge opening through a $E_{1cb}$-like type of process under strongly basic conditions using bases such as NaH, KH, $(i\text{-Pr})_2NLi$, $(Me_3Si)_2NLi$, or $(Me_3Si)_2NK$ in THF failed to isomerize the 7-oxanorbornanone **15**. With $Et_3N$ in boiling toluene, the product of saponification and decarboxylation **18** was obtained in moderate yield (47%; *Scheme 2*). Under conditions of the *Baeyer-Villiger* oxidation [29], no trace of any lactone could be seen, product **19** was formed instead (*Scheme 3*). Using 2 equiv. of *meta*-chloroperbenzoic acid (*m*CPBA) in $CH_2Cl_2$ or 2 equiv. of magnesium monoperoxyphthalate (MMPP) in DMF, 80–90% conversion of **15** was observed, and **19** was isolated in 60–70% yield. This transformation follows probably the path depicted in *Scheme 3*. When the benzoate **20** (derived from alcohol **10** on treatment with BzCl/$Et_3N$, $CH_2Cl_2$, 25°, 4 days, 95%) was oxidized with 1.5 equiv. of MMPP in DMF (25°), enedione **21** was obtained quantitatively. Reduction of **21** with $Zn(BH_4)_2$ furnished **20** nearly quantitatively. With $NaBH_4/CeCl_3$ [30] in MeOH, a 1:1 mixture **22a**/**22b** was

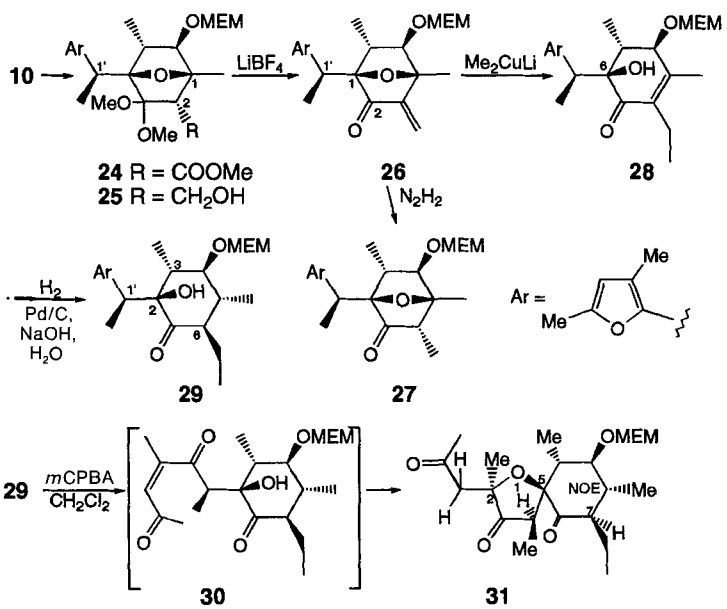
*Scheme 3*



formed from **21**, together with **20**. In the presence of 2 equiv. of 9-borabicyclo[3.3.1]nonane (9-BBN), a 4:1 mixture of the two diastereoisomeric diones **23a** and **23b** was obtained, together with **20**. The relative configurations of the isomeric product pairs **22a**/**22b** and **23a**/**23b** were not established.

Protection of alcohol **10** as a (2-methoxyethoxy)methyl ether **24** (86%) and reduction of its ester moiety with $LiAlH_4$ in THF (25°) afforded **25** (90%) (*Scheme 4*). Treatment of **25** with $LiBF_4$ (1 equiv., 2% $H_2O$ in MeCN, 25°) induced acetal hydrolysis and $H_2O$ elimination, giving the exocyclic enone **26** (83%). Reduction of the methylidene group of **26** with diimide generated by acidic decomposition of potassium azodicarboxylate [31] provided the 7-oxanorbornanone derivative **27** stereoselectively in 70% yield, the *exo* relative configuration of $H_{exo}$–C(3) being confirmed by NOE measurements in its 400-MHz $^1$H-NMR spectrum. The same compound **27** was obtained from **26** in 90% yield through 1,4-addition of hydride using $[(Ph_3P)CuH]_6$ [32]. To our surprise, treatment of enone **26** with $Me_2CuLi$ ($Et_2O$, 25°) did not give the corresponding product of 1,4-addition, but led to an $S_N2'$ oxa-ring opening of the 7-oxanorbornanone [33] with the formation of the cyclohexenone derivative **28** (60%). Being a tetrasubstituted alkene, **28** was not reduced with hydrides such as $LiAlH_4$/CuI in THF [34] or $[(Ph_3P)CuH]_6$ in degassed toluene. Hydrogenation in the presence of Rh/C in light petroleum [35] also failed to reduce the alkenone. Finally, hydrogenation (40 bar of $H_2$) over 40% Pd/C in the presence of 0.1N aqueous NaOH solution (20 mol-%) led to cyclohexanone **29** (85%). This product arises probably from *cis*-addition of $H_2$ to the face of the alkene moiety '*syn*' with respect to the OH group at C(6) giving an unstable α-ethylcyclohexanone that undergoes isomerization *via* the corresponding enol under the reaction conditions

*Scheme 4*



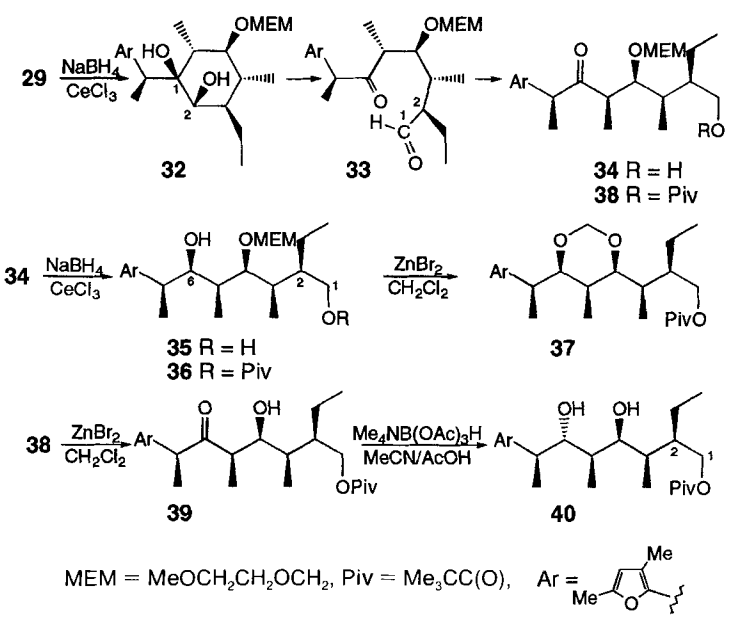
(NaOH). The oxaspiro compound **31** was obtained in 81% yield on treatment of **29** with *m*CPBA in $CH_2Cl_2$. Contrary to our expectations, the α-hydroxy-ketone moiety of **29** did not undergo *Baeyer-Villiger* oxidation with *m*CPBA; it was its dimethylfuran unit which was oxidized rapidly, generating the hypothetical [36] enetrione intermediate **30** which underwent an intramolecular conjugate addition with the tertiary alcohol with high face selectivity [37]. NOE Measurements in the $^1$H-NMR spectrum (360 MHz) of **31** allowed one to establish its structure and concomitantly the relative configuration of the ethylidene link connecting the 7-oxanorbornadiene unit and the 3,5-dimethylfuryl moiety of the *Diels-Alder* adduct **8** (see *Scheme* 2).

The *trans* relative configuration of Et–C(6) and Me–C(5) of **29** was given by the large coupling constants $^3J$(H–C(5),H–C(6)) = 11.2 Hz (coupling between two vicinal axial protons) in the $^1$H-NMR spectrum (400 MHz). Because of signal overlaps, $J$(H–C(4),H–C(5)) could not be measured, but the *trans* relative configuration between MEMO–C(4) and Me–C(5) was established by the $^1$H-NMR spectrum (250 MHz) of derivative **31** which displays two large coupling constants (10.0 and 12.0 Hz) for its H–C(9) (3.31 ppm; see *Exper. Part*).

Strong NOE effects were observed for **31** between the signals attributed to Me–C(4) (1.23 ppm, *d*, $^3J$ = 7.2 Hz) and H–C(7) (1.98 ppm, *m*) on one hand, and between the signals of H–C(4) (2.86 ppm, *q*, $^3J$ = 7.2 Hz) and Me–C(10) (1.19 ppm, *d*, $^3J$ = 6.5 Hz) on the other hand. A strong NOE effect between H–C(7) (1.98 ppm, *m*) and Me–C(8) (1.13 ppm, *d*, $^3J$ = 7.1 Hz) confirmed the *trans* relationship between Et–C(7) and Me–C(8) of **31**.

Attempts to cleave the α-hydroxycyclohexanone unit of **29** with $H_2O_2$/NaOH in MeOH [38], $H_2O_2$/NaOCl [39], or $Pb(OAc)_4$ in $CH_2Cl_2$ were not met with success. Under *Malaprade* conditions [40] and using $NaIO_4$ in aqueous THF, only slow decomposition of **29** was observed. Attempts to induce α-acyl cleavage of **29** under UV photochemical condition [41] as well as photo-iodination [42] ($I_2$, $PhI(OAc)O_2$, 40°, visible light) led to complex mixtures of products. These failures led us to reduce first the cyclohexanone

*Scheme 5*



moiety of **29** with $NaBH_4/CeCl_3$ in EtOH. The reaction was highly diastereoselective giving the *cis*-diol **32** in 81% yield (*Scheme 5*). Oxidative cleavage of **32** with $Pb(OAc)_4$ in $CH_2Cl_2$ furnished the keto aldehyde **33** (90%), the chemoselective reduction of which with $LiAl(t\text{-}BuO)_3H$ in THF provided hydroxy ketone **34** (96%). Reduction of the ketone function of **34** with $NaBH_4/CeCl_3$ in EtOH [30] was highly diastereoselective giving diol **35** (84%), the primary-alcohol moiety of which could be protected selectively through esterification with pivaloyl chloride in pyridine/$CH_2Cl_2$ leading to the pivalate **36** (96%; 5.5% based on the *Diels-Alder* adduct **8**, 12 steps, 78.5% per step). The relative configuration at C(6) of diol **35** was established by the NOESY 2D $^1$H-NMR spectrum (360 MHz) of 1,3-dioxane derivative **37**, obtained on treatment of **35** with $ZnBr_2$ in $CH_2Cl_2$, as well as by the coupling constants of **37** ($^3J$(H–C(4),H–C(5)) $\approx$ $^3J$(H–C(5),H–C(6)) $\approx$ 0 Hz, $^3J$(H–C(3),H–C(4)) = 10.1 Hz, $^3J$(H–C(6),H–C(7)) = 10.8 Hz). These data are consistent with the conformation depicted in *Fig. 1* for **37** (substituents at C(4), C(5), C(6) are all *syn*, *i.e.*, 4,5-*syn*,4,6-*syn*).

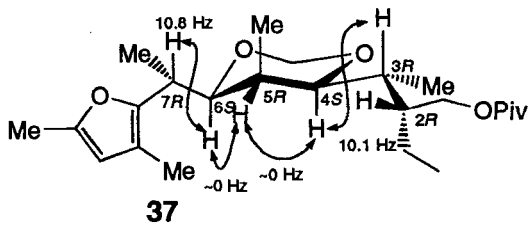
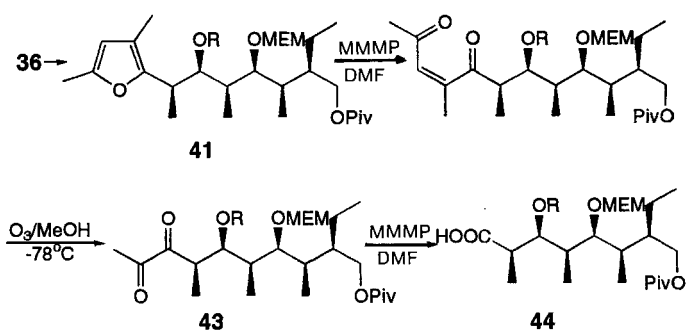



Fig. 1. *Conformation of 1,3-dioxane derivative* **37**

To obtain the 6-epimer of **36** (with 4,5-*syn*,4,6-*anti*-configurated substituents at C(4), C(5) and C(6)), we deprotected the secondary-alcohol moiety of **38** with $ZnBr_2$ in $CH_2Cl_2$ (25°), and reduced the obtained aldol **39** (80%) with $Me_4NB(AcO)_3H$ in AcOH/MeCN [43] diastereoselectively into diol **40** (88%; *Scheme 5*).

A polypropionate fragment containing six contiguous stereogenic centres was prepared upon oxidation of the 3,5-dimethylfuran moiety of **36** (*Scheme 6*). Silylation of its

*Scheme 6*



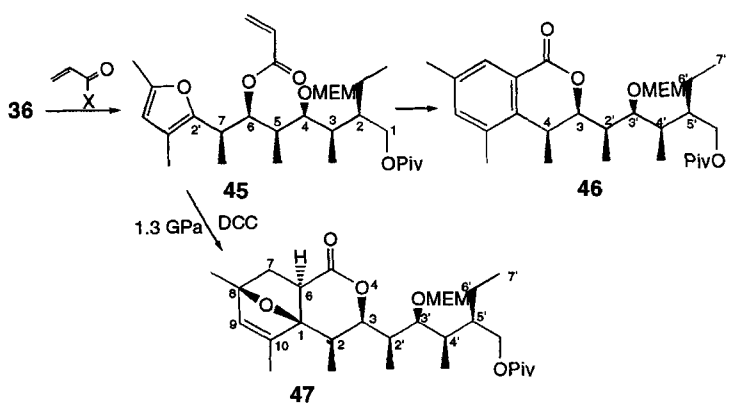

R = (*t*-Bu)$Me_2Si$ **42** MEM = $MeOCH_2CH_2OCH_2$, Piv = $Me_3CC(O)$

unprotected OH group with (*t*-Bu)$Me_2SiOSO_2CF_3$ in 2,6-lutidine (0°) afforded **41** (96%). Treatment with magnesium monoperoxyphthalate (MMPP) in DMF (25°) yielded the corresponding enedione **42** which was directly ozonolyzed into dione **43** and further oxidized with MMPP in DMF to give the carboxylic acid **44** (70% based on **41**).

Longer polypropionate fragments should be attained through *Diels-Alder* additions of the furan unit of intermediate **36** and related systems. Work with this goal in mind will be reported in the future. Preliminary experiments were carried out with acrylic acid, acryloyl chloride, and methyl bromopropynoate as dienophiles (*Scheme 7*). In the presence of $Me_3Al$, the latter did not add to **36** between −78 and 25° after 5 days, but generated the 1,3-dioxane **37** (50%). Under high pressure (1.3 GPa, 50°, 24 h), only decomposition was observed! Under a pressure of 1.3 GPa and in the presence of $Et_3N$ and 4-(dimethylamino)pyridine (50°, 24 h), acryloyl chloride reacted with **36** giving polymers and the benzopyranone **46** (isolated in 35% yield). The latter was probably formed *via* the intermediate acrylate **45** which underwent intramolecular *Diels-Alder* addition giving **47** which eliminated 1 equiv. of $H_2O$ (→ **46**). When **36** was reacted with acrylic acid in $CH_2Cl_2$ in the presence of dicyclohexylcarbodiimide (50°, 1.3 GPa, 24 h), adduct **47** was obtained in 28% yield. Product **47** also arose from acrylate **45** which was prepared independently by esterification of **36** with acryloyl chloride ($CH_2Cl_2$, $(i\text{-Pr})_2NEt$, 25°, 2 h). The best yield of **45** (40%) was obtained when the esterification was done in an ultrasound bath.

The structures of all the new compounds described in this report were established by their mode of formation and their spectral data. $^1$H-NMR Signal assignments relied on double-irradiation experiments including 2D-COSY or/and NOESY spectra. The relative configuration at C(7) of **45** and of the related precursors was further confirmed by the vicinal coupling constant $^3J$(H–C(3),H–C(4)) ≈ 0 Hz measured for **46**, the benzopyranone moiety of which adopts probably the conformation shown in *Fig. 2*. Furthermore, in the $^1$H-NMR spectrum of adduct **47**, the coupling constants $^3J$(H–C(2),H–C(3)) = 6.6 Hz and $^3J$(H–C(2′),H–C(3)) = 10.3 Hz were observed, suggesting the average conformation shown in *Fig. 2*.

*Scheme 7*




MEM = $MeOCH_2CH_2OCH_2$, Piv = $Me_3CC(O)$

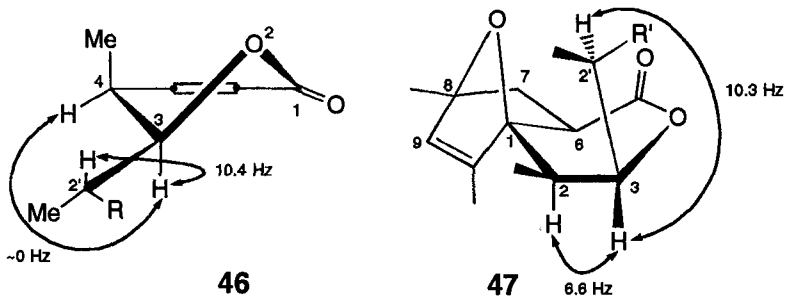



Fig. 2. *Conformation of dihydrobenzopyranone* **46** *and adduct* **47**

**Conclusion.** – The 2,2′-ethylidenebis[3,5-dimethylfuran] (**7**) obtained in three steps from mesityl oxide ( = 4-methylpent-3-en-2-one) and acetaldehyde can be converted into polypropionate fragments through *Diels-Alder* mono-addition to methyl bromopropynoate. One major adduct is formed which can be transformed into (2*RS*,3*RS*,4*SR*,5*SR*,6*SR*,7*RS*)-7-(3,5-dimethylfuran-2-yl)-2-ethyl-6-hydroxy-4-[(2-methoxyethoxy)-methoxy]-3,5-dimethyloct-1-yl pivaloate **36** and its 4-hydroxy 6-epimer **40** in 12 and 13 steps, respectively. Oxidation of the furan ring of **36** allows one to generate a (2*RS*,3*SR*,4*RS*,5*SR*,6*RS*,7*RS*)-7-ethyl-3,5,8-trihydroxy-2,4,6-trimethyloctanoic-acid derivative **44**, a polypropionate fragment containing six contiguous stereogenic centres, in 15 steps from **7**. All the reactions are highly stereoselective. The full power of the new strategy disclosed here will be attained when asymmetry will be induced, *e.g.*, with the initial *Diels-Alder* cycloadditions of **7**, and when the second 3,5-dimethylfuran-2-yl moiety of the polypropionate fragments already obtained will be converted into a polysubstituted chain with more than one stereogenic centre.

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## Experimental Part

*General.* See [19] [20] [44]. None of the procedures were optimized. All solvents were distilled prior to use, THF and $Et_2O$ from Na and benzophenone, DMF, $CH_2Cl_2$, and toluene from $P_2O_5$, $Et_3N$ and pyridine from $CaH_2$. TLC: for reaction monitoring, *Merck* silica gel *60* $F_{254}$ plates, detection by UV light or phosphomolybdic acid and heat. Flash column chromatography (FC): *Merck* silica gel *60* (63–200 μm).

*2,4-Dimethylfuran* [25]. To $Ac_2O$ (480 g, 4.7 mol) at −10°, $H_2SO_4$ (206 g, 2 mol) was added dropwise under vigorous mechanical stirring, taking care that the temp. of the viscous mixture which formed remained below 0°. Then the mixture was cooled again to −10°, and mesityl oxide (196 g, 2 mol) was added dropwise while maintaining the temp. below −5°. The resulting dark orange-red mixture was stirred for 24 h at −5° and then for the next 24 h at 20°. The mixture was poured into 2 l of ice-water under vigorous stirring, the crystals were filtered off, washed carefully with ice-water, and dried *in vacuo*. The sand-colored crude sultone (141 g, 45%), freshly ignited calcium oxide powder (140 g), and quinoline (5.5 g) were intimately mixed, transferred to a distilling flask (1 l, 2-necked,

thermometer), and heated to 230°. A regular and not too rapid development of $SO_2$ took place, and 2,4-dimethylfuran distilled slowly as a yellow liquid which was collected in an ice-cooled flask containing KOH (56 g) in $H_2O$ (300 ml). When the distillation began to subside, the temp. was raised to 250° and maintained at 250° until no more product distilled over. The crude 2,4-dimethylfuran was washed successively with aq. KOH soln., $H_2O$, ice-cold dil. $H_2SO_4$ soln., dil. $KHCO_3$ soln., and $H_2O$, dried ($MgSO_4$), and distilled: 37 g (47%) of colorless liquid. B.p. 94–96°. $^1$H-NMR (250 MHz, $CDCl_3$): 7.08 (*q*, $^4J$ = 1.1); 5.87 (*q*, $^4J$ = 1.1); 2.27 (*d*, $^4J$ = 1.1); 2.01 (*d*, $^4J$ = 1.1).

*2,2′-Ethylidenebis[3,5-dimethylfuran]* (**7**). To EtOH (95%; 3 ml), 35% HCl soln. (2 ml), and 2,4-dimethylfuran (10 ml, 9.6 g, 0.1 mol) at −5°, acetaldehyde (2.8 ml, 0.05 mol) was added dropwise (temp. < +5°; → orange) and the mixture stirred for 24 h at 20°. The brownish black mixture was diluted with $Et_2O$, the aq. phase basified with sat. aq. $Na_2CO_3$ soln. and then extracted with $Et_2O$, the $Et_2O$ extract dried ($MgSO_4$) and evaporated, and the residue distilled: 8.85 g (80%) of **7**. Colorless oil. B.p. 94°/10 Torr. IR ($CH_2Cl_2$): 3100, 2975, 2920, 2870, 2740, 1770, 1710, 1630, 1605, 1570, 1450, 1400, 1380, 1360, 1240, 1215, 1150, 1120, 1050, 1000, 980, 950. $^1$H-NMR (250 MHz, $CDCl_3$): 5.73 (*d*, $^4J$ = 1.0, 2 H, H–C(4)); 4.14 (*q*, $^3J$ = 7.3, MeC*H*); 2.23 (*d*, $^4J$ = 1.0, 6 H, Me–C(5)); 2.21 (*s*, 6 H, Me–C(3)); 1.58 (*d*, $^3J$ = 7.3, *Me*CH). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 149.4 (*s*, C(2)); 149.0 (*s*, C(5)); 114.0 (*s*, C(3)); 109.1 (*d*, C(4)); 29.7 (*d*, MeCH); 17.8, 13.5, 9.6 (3*q*, Me). EI-MS (70 eV): 218 (24, $M^+$), 203 (100), 155 (5), 123 (17), 115 (5), 109 (7), 105 (6), 97 (6), 95 (9), 81 (9), 79 (7), 71 (16).

*(1RS,4SR,1′SR)-Methyl 3-Bromo-4-[1′-(3″,5″-dimethylfuran-2″-yl)ethyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate* (**8**). At 20°, **7** (8.24 g, 37.8 mmol) and methyl bromopropynoate (6.16 g, 37.8 mmol) were stirred for 3 days (→ black). FC (*in the fume-hood, since the dienophile is strongly lacrymogenic*; 860 g of $SiO_2$, AcOEt/light petroleum ether 1:24, $R_f$ 0.24) gave a yellow oil that was crystallized from light petroleum ether: 8 g (55.5%) of **8**. The product decomposed while storing at −20° in a few days. Colorless crystals. M.p. 79–80°. UV (MeCN): 220 (17000), 297 (3300). IR ($CH_2Cl_2$): 3000, 2940, 2880, 2200, 1700, 1640, 1590, 1380, 1310, 1140, 1070, 940, 870, 850. $^1$H-NMR (250 MHz, $CDCl_3$): 6.34 (*q*, $^4J$ = 1.9, H–C(6″)); 5.73 (br. *s*, H–C(4″)); 3.80 (*s*, MeO); 3.75 (*q*, $^3J$ = 7.2, H–C(1′)); 2.21 (br. *s*, Me–C(5″)); 1.99 (*s*, Me–C(3″)); 1.85 (*s*, Me–C(1)); 1.57 (*d*, $^4J$ = 1.9, Me–C(5)); 1.33 (*d*, $^3J$ = 7.2, Me(2′)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 163.8 (*s*, $CO_2$); 154.9, 152.7 (2*s*, C(2), C(3)); 149.7 (*s*, C(5)); 148.3, 148.1 (2*s*, C(2″), C(5″)); 140.3 (*d*, C(6)); 115.7 (*s*, C(3″)); 109.7 (*d*, C(4″)); 99.7, 91.9 (2*s*, C(1), C(4)); 51.5 (*q*, MeO); 30.3 (*d*, C(1′)); 16.6, 15.8, 13.9, 12.8, 10.3 (5*q*, 5 Me). CI-MS ($NH_3$): 381 (4, $M^+$), 325 (34), 301 (7), 269 (22), 203 (38), 123 (100), 96 (17).

*(1RS,2SR,4SR,1′SR)-Methyl 4-[1′-(3″,5″-Dimethylfuran-2″-yl)ethyl]-3,3-dimethoxy-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-ene-2-*endo-*carboxylate* (**9**). To a stirred soln. of **8** (0.600 g, 15.7 mmol) in anh. MeOH (2.5 ml) at −5°, *ca.* 5.4M NaOMe in MeOH (2.1 ml) was added dropwise within 30 min. After addition, the cooling bath was removed and the mixture stirred at 20° for 3 h. The solvent was evaporated, AcOEt (10 ml) added, the mixture filtered, the white solid dissolved in $H_2O$ (10 ml), and the aq. soln. extracted with AcOEt (10 ml, 3 times). The combined org. layers were dried ($MgSO_4$) and evaporated. The semisolid was filtered through silica gel giving a white solid that was crystallized from $Et_2O$/light petroleum ether: 0.319 g (55%) of **9**. Colorless crystals. M.p. 114–116°. UV (MeCN): 218 (16500). IR (KBr): 2990, 2940, 1730, 1630, 1450, 1430, 1380, 1350, 1310, 1250, 1230, 1190, 1130, 1060, 1000, 980, 940, 900, 830, 800, 770. $^1$H-NMR (250 MHz, $CDCl_3$): 6.21 (br. *q*, $^4J$ = 1.6, H–C(6)); 5.71 (br. *s*, H–C(4″)); 3.65 (*s*, MeO); 3.49 (*q*, $^3J$ = 7.3, H–C(1′)); 3.42 (*s*, MeO); 2.99 (*s*, $H_{exo}$–C(2)); 2.20 (*s*, Me–C(5″)); 1.98 (*d*, $^4J$ = 1.6, Me–C(5)); 1.96 (*s*, Me–C(3″)); 1.48 (*s*, Me–C(1)); 1.35 (*d*, $^3J$ = 7.3, Me(2′)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 170.1 (*s*, $CO_2$); 148.7, 148.5 (2*s*, C(2″), C(5″)); 143.5, 136.0 (2*s*, C(5), C(6)); 116.7 (*s*, C(3″)); 113.4 (*s*, C(3)); 108.9 (*d*, C(4″)); 97.8, 83.1 (2*s*, C(1), C(4)); 61.8 (*d*, C(2)); 51.5, 51.4 (2*q*, 2 MeO); 50.3 (*q*, MeO); 31.5 (*d*, C(1′)); 18.6, 16.5, 14.4, 13.3, 10.1 (5*q*, 5 Me). EI-MS (70 eV): 364 (0.1, $M^+$), 218 (18), 203 (100), 161 (8), 123 (20), 77 (3), 69 (9). Anal. calc. for $C_{20}H_{28}O_6$ (364.44): C 65.92, H 7.74; found: C 65.80, H 7.85.

*(1RS,2RS,4SR,5SR,6SR,1′RS)-Methyl 4-[1′-(3″,5″-Dimethylfuran-2″-yl)ethyl]-6-*exo-*hydroxy-3,3-dimethoxy-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptane-2-*endo-*carboxylate* (**10**). To the stirred soln. of **9** (1.984 g, 5.45 mmol) in anh. $Et_2O$ (15 ml), 10M $BH_3 \cdot Me_2S$ (0.36 ml, 1.98 equiv. of H) was added at 25°, and the mixture was stirred for 6 h. Then *o*-xylene (7 ml) was added and the $Et_2O$ evaporated. To the resulting soln., trimethylamine *N*-oxide (1.2 g, 1.98 equiv.) was added and the mixture heated at 120° overnight and then filtrated through a thin layer of silica gel which was washed with AcOEt. The solvents were evaporated. FC (50 g $SiO_2$, AcOEt/light petroleum ether 1:6, $R_f$ 0.06) gave a white powder which was crystallized from light petroleum ether/AcOEt: 1.71 g (82%) of **10**. Colorless crystals. M.p. 127–128°. UV (MeCN): 218 (11500). IR (KBr): 3500, 2980, 2940, 2880, 1710, 1570, 1450, 1430, 1350, 1290, 1240, 1230, 1190, 1140, 1090, 1060, 1030, 990, 810. $^1$H-NMR (250 MHz, $CDCl_3$): 5.68 (br. *s*, H–C(4″)); 4.65 (*d*, $^3J$ = 4.4, H–C(6)); 3.68 (*s*, MeO); 3.63 (*q*, $^3J$ = 7.3, H–C(1′)); 3.33 (*s*, MeO); 2.99 (*s*, H–C(2)); 2.56 (*s*, MeO); 2.20 (br. *s*, Me–C(5″)); 2.11 (*qd*, $^3J$ = 7.3, 4.4, H–C(5)); 1.91 (*s*, Me–C(3″)); 1.39 (*s*, Me–C(1)); 1.30 (*d*, $^3J$ = 7.3, Me–C(1′), Me–C(5)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 169.3 (*s*, $CO_2$); 149.2, 148.8 (2*s*,

C(2″), C(5″)); 116.5 (*s*, C(3″)); 110.2 (*s*, C(3)); 108.7 (*d*, C(4″)); 94.3, 84.6 (2*s*, C(1), C(4)); 79.8 (*d*, C(6)); 61.1 (*d*, C(2)); 51.6, 50.0, 49.1 (3*q*, 3 MeO); 48.6 (*d*, C(5)); 31.1 (*d*, C(1′)); 16.9, 15.8, 13.5, 12.0, 10.1 (5*q*, 5 Me). CI-MS ($NH_3$): 400 (5, $[M + 18]^+$), 382 ($M^+$), 368 (12), 351 (54), 319 (8), 171 (3), 123 (100), 91 (2). Anal. calc. for $C_{20}H_{30}O_7$ (382.45): C 62.81, H 7.91; found: C 62.72, H 7.85.

*(1*RS,*4*SR,*5*SR,*6*SR,*1′*RS*)-Methyl 3-Bromo-4-[1′-(3″,5″-dimethylfuran-2″-yl)ethyl]-6-*exo-*hydroxy-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]hept-2-ene-2-carboxylate* (**11**). To a soln. of **8** (2.57 g, 6.75 mmol) in $Et_2O$ (10 ml) at −20°, 10M $BH_3 \cdot Me_2S$ (0.34 ml, 1.5 equiv.) was added. The mixture was allowed to warm up to 25° and stirring continued for 5 h. Another 0.1 ml of $BH_3 \cdot Me_2S$ was added and stirring continued for 3 h. After addition of $H_2O$ (10 ml) and $NaBO_3$ (2.72 g), the mixture was stirred overnight and then worked up as usual. FC (100 g of $SiO_2$, AcOEt/light petroleum ether 1:6, $R_f$ 0.11) gave a colorless oil that crystallized from light petroleum ether/AcOEt: 1.456 g (54%) of **11**. Colorless crystals. M.p. 131–133°. UV (MeCN): 223 (19800). IR ($CH_2Cl_2$): 3600–3550, 2950, 2880, 1705, 1605, 1570, 1370, 1150, 1070, 1040, 1000, 950. $^1$H-NMR (250 MHz, $CDCl_3$): 5.76 (br. *s*, H−C(4″)); 3.83 (*s*, MeO); 3.54 (*q*, $^3J$ = 7.2, H−C(1′)); 3.49 (*d*, $^3J$ = 2.5, H−C(6)); 2.22 (br. *s*, Me−C(5″)); 1.98 (*s*, Me−C(3″)); 1.64 (*s*, Me−C(1)); 1.45 (*qd*, $^3J$ = 7.3, 2.5, H−C(5)); 1.35 (*d*, $^3J$ = 7.3, Me−C(5)); 1.04 (*d*, $^3J$ = 7.2, Me(2′)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 163.1 (*s*, $CO_2$); 149.9, 147.2 (2*s*, C(2″), C(5″)); 140.4, 139.2 (2*s*, C(2), C(3)); 116.2 (*s*, C(3″)); 108.8 (*d*, C(4″)); 94.6, 90.4 (2*s*, C(1), C(4)); 81.4 (*d*, C(6)); 51.5 (*q*, MeO); 48.1 (*d*, C(5)); 30.1 (*d*, C(1′)); 14.3, 13.8, 13.5, 13.4, 10.1 (5*q*, 5 Me). CI-MS ($NH_3$): 417 ($[M + 18]^+$), 401 (12), 399 (13), 342 (40), 340 (36), 327 (99), 325 (100), 247 (11), 123 (33), 77 (13). Anal. calc. for $C_{18}H_{23}BrO_5$ (399.28): C 54.15, H 5.89, Br 20.4; found: C 54.17, H 5.72, Br 20.11.

*(1*RS,*4*SR,*5*SR,*6*SR,*1′*RS*)-Methyl 3-Bromo-6-*exo-*[(*tert*-butyl)dimethylsilyloxy]-4-[1′-(3″,5″-dimethylfuran-2″-yl)ethyl]-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]hept-2-ene-2-carboxylate* (**12**). To the soln. of **11** (1.40 g, 3.5 mmol) in $CH_2Cl_2$ (10 ml) and 2,6-dimethylpyridine (1.5 g, 4 equiv.), (*t*-Bu)$Me_2SiOSO_2CF_3$ (3.21 ml, 3.69 g, 4 equiv.) was added dropwise under stirring at −30°. The mixture was allowed to warm up to 20° and stirring continued for 3.5 h. Solvents were evaporated, and FC (90 g of $SiO_2$, AcOEt/light petroleum ether 1:6, $R_f$ 0.63) gave 1.44 g (80%) of **12**. Colorless oil. UV (MeCN): 220 (20500). IR ($CH_2Cl_2$): 2940, 2920, 2880, 2840, 1710, 1600, 1320, 1150, 1110, 1070, 1040, 1000, 850, 830. $^1$H-NMR (250 MHz, $CDCl_3$): 5.75 (br. *s*, H−C(4″)); 3.83 (*s*, MeO); 3.55 (*q*, $^3J$ = 7.2, H−C(1′)); 3.49 (*d*, $^3J$ = 2.3, H−C(6)); 2.21 (br. *s*, Me−C(5″)); 1.97 (*s*, Me−C(3″)); 1.58 (*s*, Me−C(1)); 1.47 (*qd*, $^3J$ = 7.3, 2.3, H−C(5)); 1.33 (*d*, $^3J$ = 7.2, Me(2′)); 0.94 (*d*, $^3J$ = 7.3, Me−C(5)); 0.83 (*s*, *t*-BuSi); 0.21, −0.07 (2*s*, $Me_2Si$). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 163.5 (*s*, $CO_2$); 150.1, 147.8 (2*s*, C(2″), C(5″)); 140.9, 139.7 (2*s*, C(2), C(3)); 116.1 (*s*, C(3″)); 108.5 (*d*, C(4″)); 94.8, 91.2 (2*s*, C(1), C(4)); 81.6 (*d*, C(6)); 51.6 (*q*, MeO); 47.3 (*d*, C(5)); 30.2 (*d*, C(1′)); 25.6 (*q*, *Me*$_3$CSi); 17.8 (*s*, $Me_3$*C*Si); 14.6, 14.0, 13.7, 13.4, 10.1 (5*q*, 5 Me); −4.6, −5.0 (2*q*, $Me_2Si$). CI-MS ($NH_3$): 530 (6, $[M + 17]^+$), 515 (8), 513 (7, $M^+$), 342 (100), 340 (89), 327 (89), 325 (88), 247 (10), 123 (27), 73 (60).

*(1*RS,*4*SR,*5*SR,*6*SR,*1′*RS*)-Methyl 6-*exo-*(Benzyloxy)-4-[1′-(3″,5″-dimethylfuran-2″-yl)ethyl]-1,5-*endo-*dimethyl-3-methoxy-7-oxabicyclo[2.2.1]hept-2-ene-2-carboxylate* (**14**). On protection of alcohol **10** under basic conditions (see preparation of **15**), **14** was obtained besides **13**. The same product **14** was obtained from **13** on treatment with LHMDS in THF (90%) or with *Amberlite IR120* in acetone (75%). FC ($SiO_2$, AcOEt/light petroleum ether 1:12, $R_f$ 0.14) gave pure **14**. White solid. M.p. 139–141°. UV (MeCN): 209 (19000). IR (KBr): 3040, 2980, 2940, 2880, 1690, 1630, 1570, 1440, 1350, 1330, 1190, 1170, 1100, 1040, 950, 790. $^1$H-NMR (250 MHz, $CDCl_3$): 7.32–7.20 (*m*, 5 H); 5.76 (*s*, H−C(4″)); 4.51 (*s*, 2 H); 4.00, 3.73 (2*s*, 2 MeO); 3.45 (*d*, $^3J$ = 2.3, H−C(6)); 3.38 (*q*, $^3J$ = 7.2, H−C(1′)); 2.24 (*s*, Me−C(5″)); 1.98 (*s*, Me−C(3″)); 1.70 (*qd*, $^3J$ = 7.2, 2.3, H−C(5)); 1.66 (*s*, Me−C(1)); 1.35 (*d*, $^3J$ = 7.2, Me(2′)); 0.91 (*d*, $^3J$ = 7.2, Me−C(6)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 171.2 (*s*, $CO_2$); 165.1 (*s*, C(3)); 149.6, 148.1 (2*s*, C(2″), C(5″)); 139.8, 128.0, 127.5, 127.1, 127.0 (arom. C); 115.8 (*s*, C(3″)); 108.7 (*d*, C(4″)); 108.5 (*s*, C(2)); 92.04, 88.3 (2*s*, C(1), C(4)); 89.8 (*d*, C(6)); 70.9 (*t*, $CH_2O$); 60.2 (*q*, MeO); 50.9 (*q*, MeO); 44.0 (*d*, C(5)); 28.8 (*d*, C(1′)); 15.6, 14.8, 14.4, 13.4, 10.1 (5*q*, 5 Me). CI-MS ($NH_3$): 458 (1, $[M + 18]^+$), 441 (1, $M^+$), 293 (13), 277 (100), 197 (5), 123 (24), 91 (54). Anal. calc. for $C_{26}H_{32}O_6$ (440.53): C 70.89, H 7.32; found: C 70.67, H 7.24.

*(1*RS,*2*RS,*4*SR,*5*SR,*6*SR,*1′*RS*)-Methyl 6-*exo-*(Benzyloxy)-4-[1′-(3″,5″-dimethylfuran-2″-yl)ethyl]-1,5-*endo-*dimethyl-3-oxo-7-oxabicyclo[2.2.1]heptane-2-*endo-*carboxylate* (**15**). To a soln. of **10** (4.2 g, 11 mmol) in 60 ml of anh. THF, NaH (80% in white oil; 1.63 g, 5 equiv.) was added and the mixture stirred at 25° for 40 min. Then $Bu_4NI$ (0.05 g, 1 mol-%) was added, followed by $PhCH_2Br$ (6.5 ml, 9.386 g, 0.055 mol, 5 equiv.). The mixture was stirred at 25° until **10** had disappeared (4 days; TLC monitoring: two new spots). Then the mixture was filtered through *Celite*, the filtrate washed carefully with $H_2O$ (20 ml), the aq. phase extracted with $Et_2O$ (3 × 20 ml), and the combined org. phase dried ($MgSO_4$) and evaporated: 11.54 g of slightly yellow oil (mixture of dimethyl acetal **13** and methyl enol ether **14**). Without purification, **13**/**14** was dissolved in acetone (200 ml) and 2M HCl (100 ml) added. After stirring at 25° for 24 h, the mixture was poured into sat. aq. $NaHCO_3$ soln. and then extracted with $Et_2O$ (5 × 100 ml). After drying ($MgSO_4$) and solvent evaporation, FC (45 g $SiO_2$, AcOEt/light petroleum ether

1:24 then 1:12, $R_f$ 0.17) gave a slightly yellow oil that crystallized from light petroleum ether/AcOEt: 3.98 g (85%) of **15**. Colorless crystals. M.p. 96–97°. UV (MeCN): 208 (21000). IR (film): 3050, 2980, 2960, 2880, 1760, 1730, 1630, 1570, 1490, 1440, 1430, 1380, 1330, 1250, 1200, 1100, 1000, 960, 950, 930, 890, 800, 750, 730, 700. $^1$H-NMR (250 MHz, $CDCl_3$): 7.35–7.29 (*m*, 5 H); 5.76 (*s*, $^4J$ = 0.5, H–C(4″)); 4.48 (br. *s*, 2 H); 3.79 (*d*, $^3J$ = 3.5, H–C(6)); 3.75 (*s*, MeO); 3.40 (*q*, $^3J$ = 7.2, H–C(1′)); 3.24 (*s*, H–C(2)); 2.23 (*s*, $^4J$ = 0.5, Me–C(3″)); 1.96 (*s*, Me–C(5″)); 1.82 (*qd*, $^3J$ = 7.5, 3.5, H–C(5)); 1.69 (*s*, Me–C(1)); 1.22 (*d*, $^3J$ = 7.2, Me(2′)); 0.88 (*d*, $^3J$ = 7.5, Me–C(5)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 205.7 (*s*, C=O); 167.0 (*s*, $CO_2$); 150.2, 147.4 (2*s*, C(2″), C(5″)); 138.3, 128.4, 128.3, 127.7 (arom. C); 116.4 (*s*, C(3″)); 108.8 (*d*, C(4″)); 95.1, 89.5 (2*s*, C(1), C(4)); 85.1 (*d*, C(6)); 71.1 (*t*, Ph$CH_2$); 62.0 (*d*, C(2)); 52.4 (*q*, MeO); 45.1 (*d*, C(5)); 29.1 (*d*, C(1′)); 17.1, 14.7, 13.6, 12.1, 10.2 (5*q*, 5 Me). EI-MS (70 eV): 426 (3, $M^+$), 308 (1), 275 (6), 197 (2), 123 (91), 91 (100), 77 (6). Anal. calc. for $C_{25}H_{30}O_6$ (426.50): C 70.39, H 7.09; found: C 70.46, H 7.15.

*(1*RS,*2*RS,*4*SR,*5*SR,*6*SR,*1′*RS*)-Methyl* 6-exo-*[(*tert-*Butyl)dimethylsilyloxy]-4-[1′-(3″,5″-dimethylfuran-2″-yl)ethyl]-1,5-*endo-*dimethyl-3-oxo-7-oxabicyclo[2.2.1]heptane-2-*endo-*carboxylate* (**17**). To a soln. of **10** (0.74 g, 2.2 mmol) in acetone (25 ml), 2N HCl (15 ml) was added. After stirring at 25° for 24 h, the mixture was poured into sat. aq. $NaHCO_3$ soln. and then extracted with $Et_2O$ (20 ml, 5 times). The org. phase was dried ($MgSO_4$) and evaporated and the yellowish oil dissolved in anh. $CH_2Cl_2$ (5 ml) and cooled to 0°. Then 2,6-dimethylpyridine (0.77 ml, 3 equiv.) was added, followed by (*t*-Bu)$Me_2SiOSO_2CF_3$ (1.51 ml, 3 equiv.). The cooling bath was removed and the mixture stirred at 25° for 3 h. Sat. aq. $NaHCO_3$ soln. (5 ml) was added at 0° and, after a short stirring, the layers were separated. The aq. layer was extracted with $CHCl_3$ (3 × 5 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. FC (40 g $SiO_2$, AcOEt/light petroleum ether 1:24, $R_f$ 0.11) gave 0.848 g (85.6%) of **17**. Colorless oil. UV (MeCN): 217 (12000). IR (film): 2960, 2940, 2850, 1770, 1730, 1630, 1570, 1450, 1380, 1330, 1250, 1200, 1120, 1080, 1000, 890, 860, 830, 770. $^1$H-NMR (250 MHz, $CDCl_3$): 5.70 (*s*, H–C(4″)); 3.96 (*d*, $^3J$ = 3.0, H–C(6)); 3.74 (*s*, MeO); 3.40 (*q*, $^3J$ = 7.2, H–C(1′)); 3.22 (*s*, H–C(2)); 2.19 (br. *s*, Me–C(5″)); 1.92 (*s*, Me–C(3″)); 1.55 (*qd*, $^3J$ = 7.3, 3.0, H–C(5)); 1.54 (*s*, Me–C(1)); 1.19 (*d*, $^3J$ = 7.2, Me(2′)); 0.83 (*d*, $^3J$ = 7.3, Me–C(5)); 0.81 (*s*, *t*-BuSi); −0.02, −0.07 (2*s*, $Me_2Si$). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 205.6 (*s*, C=O); 167.0 (*s*, $CO_2$); 150.1, 147.5 (2*s*, C(2″), C(5″)); 116.1 (*s*, C(3″)); 108.5 (*d*, C(4″)); 95.0, 86.3 (2*s*, C(1), C(4)); 83.7 (*d*, C(6)); 61.3 (*d*, C(2)); 52.3 (*q*, MeO); 47.4 (*d*, C(5)); 28.7 (*d*, C(1′)); 25.5 (*q*, *Me*$_3$CSi); 17.7 (*s*, $Me_3C$Si); 17.2, 14.7, 13.4, 11.2, 10.1 (5*q*, 5 Me); −4.2, −4.4 (2*q*, $Me_2$Si). EI-MS (70 eV): 451 (11, $M^+$), 450 (6), 366 (4), 299 (11), 237 (8), 179 (4), 123 (100), 73 (33). Anal. calc. for $C_{24}H_{38}O_6Si$ (450.64): C 63.97, H 8.50; found: C 62.86, H 8.31.

*(1*RS,*4*SR,*5*RS,*6*RS,*1′*SR*)-5-*exo-*(Benzyloxy)-4,6-*endo-*dimethyl-1-[1′-(3″,5″-dimethylfuran-2″-yl)ethyl]-7-oxabicyclo[2.2.1]heptan-2-one* (**18**). To the soln. of **15** (0.32 g, 0.75 mmol) in toluene (5 ml), $Et_3N$ (0.48 ml) was added and the soln. heated under reflux for 3 days. After evaporation, the yellow oil was purified by FC (12 g $SiO_2$, AcOEt/light petroleum ether 1:6, $R_f$ 0.35): 0.13 g (47%) of **18** and 0.12 g of **15**. **18**: Colorless oil. $^1$H-NMR (250 MHz, $CDCl_3$): 7.34–7.29 (*m*, 5 H); 5.76 (br. *s*, H–C(4″)); 4.50, 4.41 (2*d*, $^2J$ = 12.2); 3.40 (*q*, $^3J$ = 7.2, H–C(1′)); 3.24 (*d*, $^3J$ = 3.0, H–C(5)); 2.26 (*d*, $^2J$ = 17.6, $H_{exo}$–C(3)); 2.24 (br. *s*, Me–C(5″)); 2.04 (*d*, $^2J$ = 17.6, $H_{endo}$–C(3)); 1.97 (*s*, Me–C(3″)); 1.80 (*qd*, $^3J$ = 7.5, 3.0, H–C(6)); 1.60 (*s*, Me–C(4)); 1.26 (*d*, $^3J$ = 7.2, H–C(2′)); 0.85 (*d*, $^3J$ = 7.5, Me–C(6)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 212.4 (*s*, C=O); 150.0, 147.9 (2*s*, C(2″), C(5″)); 138.2, 128.2, 127.5, 127.2 (arom. C); 115.9 (*s*, C(3″)); 108.7 (*d*, C(4″)); 93.7, 83.3 (2*s*, C(1), C(4)); 89.0 (*d*, C(5)); 70.4 (*t*, Ph$CH_2$); 47.6 (*t*, C(3)); 43.5 (*d*, C(6)); 28.5 (*d*, C(1′)); 17.2, 14.7, 13.6, 13.5, 10.1 (5*q*, 5 Me).

*(1*RS,*2*RS,*4*RS,*5*RS,*6*RS,*1′*RS*)-Methyl 6-*exo-*(Benzoyloxy)-4-(1′,3′-dimethyl-2′,5′-dioxohex-3′-en-1′-yl)-1,5-*endo-*dimethyl-3-oxo-7-oxabicyclo[2.2.1]heptane-2-*endo-*carboxylate* (**19**). To the soln. of **15** (0.32 g, 0.75 mmol) in anh. DMF (5 ml), MMPP (85%; 0.873 g, 2 equiv.) was added and the resulting soln. stirred at 25° for 2 days. The mixture was washed with sat. aq. $NaHCO_3$ soln. (10 ml), the aq. phase extracted with $Et_2O$ (3 × 10 ml), and the combined org. phase washed with 5% aq. HCl and sat. aq. $NaHCO_3$ soln., dried ($MgSO_4$), and evaporated. FC (15 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.16) gave 210 mg (61%) of **19**. Colorless oil. IR (film): 3550–3350 (OH), 3050, 3000, 2960, 2880, 1770, 1730, 1680, 1605, 1440, 1360, 1260, 1250, 1160, 1070, 980, 750, 700. $^1$H-NMR (400 MHz, $CDCl_3$): 7.34–7.28 (*m*, 5 H); 6.14 (*q*, $^4J$ = 1.6, H–C(4′)); 4.58, 4.48 (2*d*, $^2J$ = 11.5); 3.80 (*d*, $^3J$ = 3.3, H–C(6)); 3.74 (*s*, MeO); 3.34 (*q*, $^3J$ = 7.5, H–C(1′)); 2.54 (*qd*, $^3J$ = 7.4, 3.3, H–C(5)); 2.19 (*s*, H–C(6′)); 2.02 (*d*, $^4J$ = 1.6, Me–C(3′)); 1.50 (*s*, Me–C(1)); 1.28 (*d*, $^3J$ = 7.5, Me–C(1′)); 1.13 (*d*, $^3J$ = 7.4, Me–C(5)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 208.6, 204.8, 196.8 (3*s*, 3 C=O); 168.6 (*s*, $CO_2$Me); 154.6 (*s*, C(3′)); 137.6, 128.2, 127.6, 127.5 (arom. C); 126.0 (*d*, C(4′)); 91.7, 90.0 (2*s*, C(1), C(4)); 83.6 (*d*, C(6)); 79.7 (*s*, C(2)); 71.2 (*t*, Ph$CH_2$); 52.8 (*q*, MeO); 46.2, 43.7 (2*d*, C(1′), C(5)); 29.7 (*q*, C(6′)); 20.3, 12.5, 11.8, 10.8 (4*q*, 4 Me). CI-MS ($NH_3$): 476 (1, $[M + 18]^+$), 459 (39, $M^+$), 235 (15), 196 (8), 139 (8), 91 (100), 74 (30).

*(1*RS,*2*RS,*4*SR,*5*SR,*6*SR,*1′*RS*)-Methyl* 6-exo-*(Benzoyloxy)-4-[1′-(3″,5″-dimethylfuran-2″-yl)ethyl]-3,3-dimethoxy-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptane-2-*endo-*carboxylate* (**20**). To a soln. of **10** (1.00 g, 2.6 mmol) in $CH_2Cl_2$ (5 ml) at 0°, $Et_3N$ (1.46 ml, 4 equiv.) was added, followed by benzoyl chloride (1.22 ml, 4 equiv.).

The cooling bath was removed and the soln. stirred at 25° for 4 days. The mixture was washed with sat. aq. $NaHCO_3$ soln., dried ($MgSO_4$), and filtrated through silica gel. Crystallization from AcOEt/light petroleum ether gave 1.2 g (94%) of **20**. Colorless crystals. M.p. 157–159°. UV (MeCN): 226 (22000), 272 (2600). IR (KBr): 3050, 2980, 2960, 2840, 1770, 1740, 1730, 1710, 1595, 1570, 1450, 1380, 1350, 1310, 1280, 1250, 1220, 1140, 1110, 1060, 980, 780, 710. $^1$H-NMR (400 MHz, $CDCl_3$): 8.14–8.11 (*m*, 2 H); 7.56–7.41 (*m*, 3 H); 6.27 (*d*, $^3J$ = 4.3, H–C(6)); 5.68 (*q*, $^4J$ = 0.5, H–C(4″)); 3.72 (*s*, MeO); 3.69 (*q*, $^3J$ = 7.5, H–C(1′)); 3.37 (*s*, MeO); 3.06 (*s*, H–C(2)); 2.64 (*s*, MeO); 2.50 (*qd*, $^3J$ = 7.2, 4.3, H–C(5)); 2.19 (*d*, $^4J$ = 0.5, Me–C(5″)); 1.94 (*s*, Me–C(3″)); 1.41 (*s*, Me–C(1)); 1.38 (*d*, $^3J$ = 7.2, Me–C(5)); 1.36 (*d*, $^3J$ = 7.5, Me(2′)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 168.6, 165.9 (2*s*, 2 $CO_2$); 149.3, 148.7 (2*s*, C(2″), C(5″)); 134.5, 132.8, 130.5, 129.6, 128.8 (arom. C); 116.5 (*s*, C(3″)); 109.9 (*s*, C(3)); 108.8 (*d*, C(4″)); 94.6, 84.1 (2*s*, C(1), C(4)); 84.1 (*d*, C(6)); 61.6 (*d*, C(2)); 51.7, 50.1, 49.1 (3*q*, 3 MeO); 45.8 (*d*, C(5)); 31.1 (*d*, C(1′)); 17.2, 15.8, 13.4, 11.9, 10.1 (5*q*, 5 Me). CI-MS ($NH_3$): 504 (2, $[M + 18]^+$), 486 (15, $M^+$), 455 (54), 427 (9), 349 (16), 253 (7), 213 (15), 169 (12), 123 (100), 105 (94), 77 (28). Anal. calc. for $C_{27}H_{34}O_8$ (486.56): C 66.65, H 7.04; found: C 66.62, H 7.02.

*(1*RS,*2*RS,*4*SR,*5*SR,*6*SR,*1′*SR*)-Methyl* 6-exo-*(Benzoyloxy)-4-(1′,3′-dimethyl-2′,5′-dioxohex-3′-en-1′-yl)-3,3-dimethoxy-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptane-2-*endo-*carboxylate* (**21**). To the soln. of **20** (0.472 g, 0.97 mmol) in anh. DMF (10 ml), MMPP (85%; 0.719 g, 1.5 equiv.) was added, and the resulting soln. was stirred at 25° for 3 days. After the usual workup and without purification by chromatography, 0.487 g (100%) of pure **21** was obtained. Colorless oil. IR (film): 3050, 2980, 2960, 2940, 2840, 1780, 1730–1680, 1590, 1450, 1430, 1380, 1350, 1310, 1270, 1230, 1150, 1120, 1060, 980, 950, 920, 750, 730, 710. $^1$H-NMR (400 MHz, $CDCl_3$): 8.03–8.00 (*m*, 2 H); 7.52 (*m*, 1 H); 7.42 (*m*, 2 H); 6.15 (*d*, $^3J$ = 4.5, H–C(6)); 6.04 (*q*, $^4J$ = 1.5, H–C(4′)); 3.71 (*s*, MeO); 3.36 (*q*, $^3J$ = 7.3, H–C(1′)); 3.28, 3.20 (2*s*, 2 MeO); 2.96 (*s*, H–C(2)); 2.18 (*qd*, $^3J$ = 7.4, 4.5, H–C(6)); 2.17 (*s*, H–C(6′)); 2.04 (*d*, $^4J$ = 1.5, Me–C(3′)); 1.48 (*d*, $^3J$ = 7.4, Me–C(5)); 1.40 (*d*, $^3J$ = 7.3, Me–C(1′)); 1.35 (*s*, Me–C(1)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 208.2, 197.8 (2*s*, 2 C=O); 168.2, 165.8 (2*s*, 2 $CO_2$); 155.5 (*s*, C(3′)); 134.7, 129.6, 128.3 (arom. C); 126.8 (*d*, C(4′)); 110.12 (*s*, C(3)); 93.7, 84.7 (2*s*, C(1), C(4)); 81.6 (*d*, C(6)); 60.8 (*d*, C(2)); 51.8, 51.5 (2*q*, 2 MeO); 51.6 (*d*, C(1′)); 49.2 (*q*, MeO); 47.8 (*d*, C(6)); 30.2 (*q*, C(6′)); 21.4, 17.1, 13.0, 12.5 (4 *q*, 4 Me). CI-MS ($NH_3$): 520 (2, $[M + 18]^+$), 502 (2, $M^+$), 471 (27), 443 (9), 365 (5), 307 (6), 245 (8), 182 (8), 123 (42), 105 (100), 77 (25).

*(1*RS,*2*RS,*4*RS,*5*SR,*6*SR,*1′*RS,*2′*SR *or* RS,*5′*SR *or* RS*)-Methyl* 6-exo-*(Benzoyloxy)-4-(2′,5′-dihydroxy-1′,4′-dimethylhex-3′-en-1′-yl)-3,3-dimethoxy-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptane-2-*endo-*carboxylate* (**22a**/**22b**). $CeCl_3 \cdot 7\ H_2O$ (22.8 mg) was added to a soln. of **21** (30.8 mg, 0.061 mmol) in EtOH (0.5 ml), and the mixture was cooled to −78°. $NaBH_4$ (4 mg) was added and the mixture stirred for 3 h, allowing the temp. to rise up to −5°. The mixture was filtered through silica gel and the filtrate evaporated. FC (1.5 g of $SiO_2$, AcOEt/light petroleum ether 1:2) gave 7 mg of **22a** ($R_f$ 0.13), 7 mg of **22b** ($R_f$ 0.05), and 5 mg of **20b** ($R_f$ 0.60).

*Data of* **22a**: $^1$H-NMR (250 MHz, $CDCl_3$): 8.12–8.03 (*m*, 2 H); 7.59–7.55 (*m*, 1 H); 7.50–7.43 (*m*, 2 H); 6.09 (*d*, $^3J$ = 4.9, H–C(6)); 5.40 (*qd*, $^3J$ = 8.6, $^4J$ = 1.4, H–C(4′)); 5.01 (*d*, $^3J$ = 9.1, H–C(2′)); 4.71 (*dq*, $^3J$ = 8.6, 7.2, H–C(5′)); 3.79, 3.56, 3.30 (3*s*, 3 MeO); 3.16 (*s*, H–C(2)); 2.35 (*qd*, $^3J$ = 7.4, 9.1, H–C(1′)); 2.21 (*qd*, $^3J$ = 7.5, 4.9, H–C(5)); 1.75 (*d*, $^4J$ = 1.4, Me–C(3′)); 1.49 (*d*, $^3J$ = 7.5, Me–C(5)); 1.44 (*s*, Me–C(1)); 1.27 (*d*, $^3J$ = 7.2, H–C(6′)); 1.06 (*d*, $^3J$ = 7.4, Me–C(1′)).

*Data of* **22b**: $^1$H-NMR (250 MHz, $CDCl_3$): 8.08–8.04 (*m*, 2 H); 7.56–7.53 (*m*, 1 H); 7.47–7.41 (*m*, 2 H); 6.21 (*d*, $^3J$ = 4.7, H–C(6)); 5.37 (br. *d*, $^3J$ = 7.6, H–C(4′)); 4.97 (br. *s*, H–C(2′)); 4.80 (*m*, H–C(5′)); 3.78, 3.48, 3.28 (3*s*, 3 MeO); 3.06 (*s*, H–C(2), 1 H); 2.30 (br. *q*, $^3J$ = 6.7, H–C(1′)); 2.26 (*qd*, $^3J$ = 6.8, 4.7, H–C(5)); 1.74 (br. *s*, Me–C(3′)); 1.51 (*d*, $^3J$ = 7.6, H–C(6′)); 1.43 (*s*, Me–C(1)); 1.27 (*d*, $^3J$ = 6.7, Me–C(1′)); 1.24 (*d*, $^3J$ = 6.8, Me–C(5)).

*(1*RS,*2*RS,*4*SR,*5*SR,*6*SR,*1′*SR,*3′*SR *and 3′*RS*)-Methyl* 6-exo-*(Benzoyloxy)-4-(1′,3′-dimethyl-2′,5′-dioxohex-1′-yl)-3,3-dimethoxy-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptane-2-*endo-*carboxylate* (**23a**/**23b**). To the soln. of **21** (0.101 g, 0.2 mmol) in anh. THF (3 ml), 9-BBN (0.049 g, 0.40 mmol, 2 equiv.) in anh. THF (2 ml) was added dropwise at −40°. The soln. was stirred at 0° for 5 h. $H_2O$ (2 ml) was added, the aq. phase extracted with $Et_2O$ (3 × 5 ml), and the extract dried ($MgSO_4$) and evaporated. FC (6 g of $SiO_2$, AcOEt/light petroleum ether 1:6, $R_f$ 0.06) gave 0.090 g of **23a**/**23b**, *ca.* 4:1 which could not be separated by crystallization. White solid. UV (MeCN): 228 (18000), 279 (2800). IR (KBr): 2990, 2980, 2920, 1730, 1700, 1590, 1450, 1350, 1270, 1150, 1100, 1060, 1020, 980, 720. $^1$H-NMR (400 MHz, $CDCl_3$): 8.10–8.08 (*m*, 2 H); 7.57–7.54 (*m*, 1 H); 7.47–7.43 (*m*, 2 H); 6.20 (*d*, $^3J$ = 4.8, H–C(6)); 3.75 (*s*, MeO); 3.56 (*q*, $^3J$ = 7.3, H–C(1′)); 3.37 (*s*, MeO); 3.37 (*m*, H–C(3′)); 3.06 (*s*, MeO); 3.01 (*s*, H–C(2)); 2.92 (*dd*, $^2J$ = 17.6, $^3J$ = 7.5, H–C(4′)); 2.42 (*qd*, $^3J$ = 7.5, 4.8, H–C(5)); 2.31 (*dd*, $^2J$ = 17.6, $^3J$ = 5.8, H–C(4′)); 2.15 (*s*, H–C(6′)); 1.48 (*d*, $^3J$ = 7.5, Me–C(5)); 1.39 (*s*, Me–C(1)); 1.36 (*d*, $^3J$ = 7.3, Me–C(1′)); 1.15 (*d*, $^3J$ = 7.2, Me–C(4′)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 213.6, 206.8 (2*s*, 2 C=O); 168.4, 165.8 (2*s*, 2 COO); 132.8, 130.2, 129.6, 128.3 (arom. C); 110.2 (*s*, C(3)); 93.6, 84.4 (2*s*, C(1), C(4)); 81.7 (*d*, C(6)); 61.3 (*d*,

C(2)); 51.8, 51.4, 49.6 (3*q*, 3 MeO); 46.7, 46.0, 45.9 (C(5), C(5'), C(4')); 41.1 (*d*, C(1')); 30.3 (*q*, C(6')); 17.0, 16.3, 14.7, 12.0 (4*q*, 4 Me). CI-MS ($NH_3$): 505 (4), 474 (10), 446 (18), 367 (9), 307 (7), 213 (14), 123 (42), 105 (100), 77 (41).

*(1*RS,*2*RS,*4*SR,*5*SR,*6*SR,*1'*RS*)-Methyl 4-[1'-(3'',5''-Dimethylfuran-2''-yl)ethyl]-3,3-dimethoxy-6-*exo*-[(2-methoxyethoxy)methoxy]-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptane-2-*endo*-carboxylate* (**24**). To the soln. of **10** (2.3 g, 6 mmol) in anh. $CH_2Cl_2$ (10 ml), $(i\text{-}Pr)_2EtN$ (10.3 ml, 10 equiv.) was added at 0°, followed by (2-methoxyethoxy)methyl chloride (6.8 ml, 10 equiv.). The soln. was stirred at 25° for 17 h. After solvent evaporation, FC (90 g $SiO_2$, AcOEt/light petroleum ether 1:4, $R_f$ 0.17) gave a colorless oil that was crystallized from AcOEt/light petroleum ether: 2.38 g (84%) of **24**. Colorless crystals. M.p. 83–84°. UV (MeCN): 220 (12000). IR (KBr): 2970, 2870, 1730, 1630, 1570, 1450, 1360, 1340, 1290, 1240, 1150, 1100, 1050, 980, 940, 920, 900, 840, 790. $^1$H-NMR (400 MHz, $CDCl_3$): 5.68 (*s*, H–C(4'')); 4.84, 4.80 (2*d*, $^2J$ = 6.8, $OCH_2O$); 4.65 (*d*, $^3J$ = 4.7, H–C(6)); 3.87–3.58 (*m*, $OCH_2CH_2O$, H–C(1')); 3.67, 3.40, 3.32 (3*s*, 3 MeO); 2.95 (*s*, H–C(2)); 2.52 (*s*, MeO); 2.31 (*qd*, $^3J$ = 7.4, 4.7, H–C(5)); 2.20 (*s*, Me–C(5'')); 1.91 (*s*, Me–C(3'')); 1.38 (*s*, Me–C(1)); 1.31 (*d*, $^3J$ = 7.4, Me–C(5)); 1.30 (*d*, $^3J$ = 7.2, Me–C(1')). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 169.0 (*s*, C=O); 149.1, 148.8 (2*s*, C(2''), C(5'')); 116.5 (*s*, C(3'')); 109.9 (*s*, C(3)); 108.7 (*d*, C(4'')); 95.4 (*t*, $OCH_2O$); 94.4, 84.3 (2*s*, C(1), C(4)); 85.7 (*d*, C(6)); 71.7, 66.9 (2*t*, 2 $OCH_2$); 61.2 (*d*, C(2)); 59.0 (*q*, COO*Me*); 51.5, 50.0, 49.2 (3*q*, 3 MeO); 46.1 (*d*, C(5)); 31.1 (*d*, C(1')); 17.1, 15.7, 13.4, 11.9, 10.1 (5*q*, 5 Me). EI-MS (70 eV): 471 (7, $M^+$), 349 (18), 291 (8), 218 (15), 123 (100), 89 (19). Anal. calc. for $C_{24}H_{38}O_9$ (470.56): C 61.26, H 8.14; found: C 61.31, H 8.15.

*(1*RS,*2*RS,*4*SR,*5*SR,*6*SR,*1'*RS*)-4-[1'-(3'',5''-Dimethylfuran-2''-yl)ethyl]-3,3-dimethoxy-6-*exo*-[(2-methoxyethoxy)methoxy]-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptane-2-methanol* (**25**). At −70°, 1.0M $LiAlH_4$ in anh. THF (8.5 ml, 2 equiv.) was added dropwise to a soln. of **24** (2.0 g) in anh. THF. The cooling bath was removed and the soln. stirred for 6 h at 25°. The soln. was poured into $H_2O$ (20 ml) mixed with ice. The aq. layer was extracted with $Et_2O$ (4 × 20 ml) and the combined org. phase dried ($MgSO_4$) and evaporated: 1.95 g of oil used in the next step without further purification. An anal. sample of **25** was obtained by crystallization from light petroleum ether/$Et_2O$: colorless crystals. M.p. 84–86°. IR (KBr): 3500 (br.), 3000–2880, 2820, 1630, 1570, 1450, 1370, 1310, 1200, 1170–1130, 1090, 1070–1010, 970, 930, 880, 840, 820, 740, 670. $^1$H-NMR (400 MHz, $CDCl_3$): 5.69 (br. *s*, H–C(4'')); 4.83, 4.70 (2*d*, $OCH_2O$); 3.96–3.49 (*m*, $OCH_2CH_2O$, $OCH_2$–C(2), H–C(5)); 3.41 (*s*, MeO); 3.22 (*s*, MeO); 2.62 (*s*, MeO); 2.37 (*dq*, H–C(5)); 2.25 (*m*, H–C(2)); 2.21 (br. *s*, Me–C(5'')); 1.93 (*s*, Me–C(3'')); 1.40 (*s*, Me–C(1)); 1.32 (*d*, $^3J$ = 7.2, Me(2')); 1.31 (*d*, $^3J$ = 7.6, Me–C(5)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 149.2, 149.1 (2*s*, C(5''), C(2'')); 116.4 (*s*, C(3'')); 109.7 (*s*, C(3)); 108.8 (*d*, C(3'')); 94.7 (*t*, $OCH_2O$); 93.1, 84.0 (2*s*, C(1), C(4)); 85.3 (*d*, C(6)); 71.6, 66.8 (2*t*, $OCH_2CH_2O$); 59.7 (*t*, $CH_2$–C(2)); 59.0 (*q*, MeO); 56.6, 45.9 (*d*, C(2), C(5)); 49.7, 47.9 (2*q*, 2 MeO); 30.7 (*d*, C(1')); 17.2, 15.9, 13.5, 12.2, 10.0 (5*q*, 5 Me). CI-MS ($NH_3$): 442 (1, $M^+$), 412 (5), 321 (10), 217 (18), 123 (100), 89 (11). Anal. calc. for $C_{23}H_{38}O_8$ (442.54): C 62.42, H 8.65; found: C 62.90, H 8.71.

*(1*RS,*4*SR,*5*RS,*6*RS,*1'*SR*)-1-[1'-(3'',5''-Dimethylfuran-2''-yl)ethyl]-5-*exo*-[(2-methoxyethoxy)methoxy]-4,6-*endo*-dimethyl-3-methylidene-7-oxabicyclo[2.2.1]heptan-2-one* (**26**). $LiBF_4$ (0.070 g, 1 equiv.) in MeCN (1 ml) was added at 25° to a soln. of **25** (0.398 g, 0.75 mmol) in MeCN (0.5 ml) containing 2% of $H_2O$. After 20 h, the mixture was diluted with $Et_2O$ (4 ml) and sat. aq. $NaHCO_3$ soln. (2 ml). The aq. layer was extracted with $Et_2O$ (5 ml, 4 times) and the combined org. phase dried ($MgSO_4$) and evaporated. FC (18 g of $SiO_2$, AcOEt/light petroleum ether 1:4) gave 0.234 g (83%) of **26**. Colorless oil ($R_f$ 0.18). UV (MeCN): 223 (17200). IR (film): 3020, 2935, 2870, 1745, 1660, 1580, 1455, 1385, 1250, 1115, 1040, 875, 805, 735. $^1$H-NMR (400 MHz, $CDCl_3$): 5.95 (*s*, 1 H, $CH_2$=C(3)); 5.72 (*s*, H–C(4'')); 5.30 (*s*, 1 H, $CH_2$=C(3)); 4.71, 4.64 (2*d*, $^2J$ = 7.1, $OCH_2O$); 3.57–3.42, 3.35 (2*m*, $OCH_2CH_2O$, H–C(5), H–C(1')); 3.33 (*s*, MeO); 2.21 (*s*, Me–C(5'')); 1.96 (*s*, Me–C(3'')); 1.76 (*qd*, $^3J$ = 7.5, 2.6, H–C(6)); 1.56 (*s*, Me–C(4)); 1.23 (*d*, $^3J$ = 7.3, Me(2')); 0.82 (*d*, $^3J$ = 7.5, Me–C(6)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 201.0 (*s*, CO); 149.9, 148.0 (2*s*, C(5''), C(2'')); 147.3 (*s*, C(3)); 116.1 (*s*, C(3'')); 113.6 (*t*, $CH_2$=C(3)); 108.7 (*d*, C(4'')); 95.0 (*t*, $OCH_2O$); 93.0, 85.5 (2*s*, C(1), C(4)); 88.3 (*d*, C(5)); 71.5, 66.8 (2*t*, $OCH_2CH_2O$); 58.9 (*q*, MeO); 45.1 (*d*, C(6)); 28.9 (*d*, C(1')); 14.6, 14.5, 13.5, 13.0, 10.1 (5*q*, 5 Me). CI-MS ($NH_3$): 378 (3, $M^+$), 303 (3), 274 (3), 123 (100), 89 (12), 77 (2).

*(1*RS,*3*SR,*4*SR,*5*RS,*6*RS,*1'*SR*)-1-[1'-(3'',5''-Dimethylfuran-2''-yl)ethyl]-5-*exo*-[(2-methoxyethoxy)methoxy]-3-*endo*,4,6-*endo*-trimethyl-7-oxabicyclo[2.2.1]heptan-2-one* (**27**). A soln. of **26** (0.505 g, 1.33 mmol) was added at 25° to a suspension of potassium azodicarboxylate (0.648 g, 3.34 mmol) in dry dioxine. AcOH (0.95 ml, 12.5 equiv.) in dioxane (1 ml) was added dropwise within 70 min. The mixture was stirred for 4 h at 25° and then filtered. The white solid was washed with $CH_2Cl_2$, and 2M aq. HCl (1.5 ml) was added to the filtrate. The mixture was stirred for another 4 h at 25°. The aq. phase was neutralized with sat. aq. $NaHCO_3$ soln. After extraction with $CH_2Cl_2$ (10 ml, 3 times), the combined org. layers were dried ($MgSO_4$) and evaporated. FC (25 g of $SiO_2$, AcOEt/light petroleum ether 1:4) gave 0.360 g (71%) of **27**. Colorless oil ($R_f$ 0.18). The same product was obtained when **26** was treated with 0.4 equiv. of (triphenylphosphine)copper hydride hexamer in degassed toluene for 5 h at

25° (yield 90%). UV (MeCN): 212 (11 200). IR (film): 3020, 2935, 2880, 1755, 1580, 1455, 1385, 1250, 1115, 1045, 865. $^1$H-NMR (400 MHz, $CDCl_3$): 5.74 (*s*, H–C(3″)); 4.71, 4.61 (2*d*, $^2J$ = 7.1, $OCH_2O$); 3.59–3.53, 3.49–3.33 (2*m*, $OCH_2CH_2O$, H–C(5), H–C(1′)); 3.36 (*s*, MeO); 2.23 (*q*, H–C(3)); 2.22 (*s*, Me–C(5″)); 1.96 (*s*, Me–C(3″)); 1.70 (*m*, H–C(6)); 1.48 (*s*, Me–C(4)); 1.23 (*d*, $^3J$ = 7.2, Me(2′)); 1.02 (*d*, $^3J$ = 7.4, Me–C(3)); 0.84 (*d*, $^3J$ = 7.5, Me–C(6)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 215.3 (*s*, C(2)); 150.0, 147.9 (2*s*, C(5″), C(2″)); 116.1 (*s*, C(3″)); 108.7 (*d*, C(4″)); 94.9 (*t*, $OCH_2O$); 94.0, 86.1 (2*s*, C(1), C(4)); 83.7 (*d*, C(5)); 71.5, 66.8 (2*t*, $OCH_2CH_2O$); 58.9 (*q*, MeO); 52.2 (*d*, C(3)); 45.9 (*d*, C(6)); 28.8 (*d*, C(1′)); 16.2, 14.7, 13.6, 12.0, 10.2, 8.9 (6*q*, 6 Me). CI-MS ($NH_3$): 380 (4, $M^+$), 305 (6), 263 (1), 199 (3), 136 (5), 123 (100), 89 (8). CI-MS ($NH_3$): 380 (4, $M^+$), 305 (7), 263 (1), 199 (3), 123 (100), 89 (8), 77 (1).

*(4*RS,*5*RS,*6*RS,*1′*SR*)*-*t-*6-*[1′-(3″,5″-Dimethylfuran-2″-yl)ethyl]-2-ethyl-*c-*6-hydroxy-*r-*4-[(2-methoxyethoxy)methoxy]-3,*t-*5-dimethylcyclohex-2-en-1-one* (**28**). MeLi (1.6M in hexane, 13.2 ml, 0.0212 mol) was added at 0° to the suspension of 2.015 g of CuI (0.0106 mol) in 30 ml of anh. $Et_2O$. After stirring at 0° for 15 min, the soln. became colorless. At −20°, **26** (2.00 g, 5.29 mmol) in anh. $Et_2O$ (20 ml) was added under vigorous stirring (→ yellow). The mixture was then stirred at 0° for 5 h. Sat. aq. $NH_4Cl$ soln. (20 ml), then $Et_2O$ (20 ml) were added. The aq. phase was extracted with $Et_2O$ (3 × 50 ml) and the combined org. phase dried ($MgSO_4$) and evaporated giving a yellow oil. FC (100 g of $SiO_2$, AcOEt/light petroleum ether 1:2) gave 1.269 g (60.8%) of **28**. Colorless oil ($R_f$ 0.48). A 2nd fraction gave 0.60 g of a mixture of other products. UV (MeCN): 228 (15 850). IR (film): 3465, 3030, 2935, 2880, 1665, 1605, 1560, 1455, 1370, 1300, 1260, 1100, 1030, 850, 800. $^1$H-NMR (400 MHz, $CDCl_3$): 5.74 (*s*, H–C(4″)); 4.82, 4.80 (2*d*, $^2J$ = 6.9, $OCH_2O$); 4.17 (*d*, $^3J$ = 8.9, H–C(4)); 4.13 (*s*, OH); 3.86–3.82, 3.71–3.66, 3.58–3.53 (3*m*, $OCH_2CH_2O$); 3.39 (*s*, MeO); 2.99 (*q*, $^3J$ = 7.2, H–C(1′)); 2.48 (*m*, 1 H, $CH_2$–C(2)); 2.29 (*m*, 1 H, $CH_2$–C(2)); 2.23 (br. *s*, Me–C(5″)); 2.05 (*m*, H–C(5)); 2.03 (*s*, Me–C(3)); 1.97 (*s*, Me–C(3″)); 1.06 (*d*, $^3J$ = 7.2, Me–C(1′)); 1.00 (*t*, $^3J$ = 7.5, *Me*$CH_2$–C(2)); 0.73 (*d*, $^3J$ = 7.0, Me–C(5)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 201.7 (*s*, C=O); 152.8 (*s*, C(3)); 148.9, 148.6 (2*s*, C(2″), C(5″)); 135.8 (*s*, C(2)); 116.0 (*s*, C(3″)); 109.7 (*d*, C(4″)); 97.0 (*t*, $OCH_2O$); 82.1 (*d*, C(4)); 78.2 (*s*, C(6)); 71.6, 68.1 (2*t*, $OCH_2CH_2O$); 59.0 (*q*, MeO); 46.8 (*d*, C(5)); 35.3 (*d*, C(1′)); 19.8 (*t*, Me*C*$H_2$–C(2)); 16.7, 14.4, 13.4, 12.9, 10.4, 10.1 (6*q*, 6 Me). CI-MS ($NH_3$): 413 (1, $[M + 18]^+$), 395 (7, $M^+$), 319 (3), 289 (17), 167 (1), 123 (100), 94 (14), 79 (1).

*(2*RS,*3*RS,*4*SR,*5*RS,*6*RS,*1′*SR*)*-2-[1′-(3″,5″-Dimethylfuran-2″-yl)ethyl]-*c-*6-ethyl-*r-*2-hydroxy-*c-*4-[(2-methoxyethoxy)methoxy]-*t-*3,*t-*5-dimethylcyclohexan-1-one* (**29**). To a soln. of **28** (950 mg, 2.4 mmol) in EtOH (15 ml), 0.1N NaOH (4.8 ml, 20 mol-%) was added, followed by 10% Pd/C (285 mg). The mixture was degassed in an autoclave, and $H_2$ was introduced under a pressure of 40 bar. The mixture was stirred for 2 h and then filtered through *Celite* (washing with $CHCl_3$) and evaporated. FC (42 g of $SiO_2$, AcOEt/light petroleum ether 1:6, $R_f$ 0.57 in 1:2) gave 812 mg (85%) of **29**. Colorless oil. UV (MeCN): 219 (9500). IR (film): 3470, 2935, 3020, 1710, 1575, 1455, 1380, 1250, 1100, 1040. $^1$H-NMR (400 MHz, $CDCl_3$): 5.74 (*s*, H–C(4″)); 4.80, 4.77 (2*d*, $^2J$ = 7.0, $OCH_2O$); 4.16 (*s*, OH–C(2)); 3.83–3.53 (3*m*, $OCH_2CH_2O$, H–C(4)); 3.39 (*s*, MeO); 3.23 (*q*, $^3J$ = 7.2, H–C(1′)); 2.37 (*m*, $^3J$(5,6) = 11.2, H–C(6)); 2.23 (br. *s*, Me–C(5″)); 2.01 (*s*, Me–C(3″)); 1.73–1.57 (*m*, Me*CH*$_2$–C(6), H–C(5), H–C(3)); 1.24 (*d*, $^3J$ = 6.4, Me–C(5)); 1.05 (*d*, $^3J$ = 7.2, Me(2′)); 0.94 (*t*, $^3J$ = 7.3, *Me*$CH_2$–C(6)); 0.68 (*d*, $^3J$ = 7.0, Me–C(3)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 212.8 (*s*, C=O); 149.3, 148.3 (2*s*, C(2″), C(5″)); 116.2 (*s*, C(3″)); 109.7 (*d*, C(4″)); 97.6 (*t*, $OCH_2O$); 83.8 (*d*, C(4)); 82.1 (*s*, C(2)); 77.0 (*d*, C(6)); 71.7, 68.0 (2*t*, $OCH_2CH_2O$); 59.1 (*q*, MeO); 50.7, 44.2, 35.4 (3*d*, C(3), C(5), C(2′)); 19.4 (*t*, *C*$H_2$–C(6)); 17.3, 14.6, 13.5, 11.6, 10.6, 10.3 (6*q*, 6 Me). CI-MS ($NH_3$): 321 (2, $[M - 75]^+$), 291 (1), 123 (100), 89 (3), 75 (0.2). Anal. calc. for $C_{22}H_{36}O_6$ (396.52): C 66.62, H 9.16; found: C 66.53, H 9.25.

*(2*RS,*4*RS,*5*RS,*7*RS,*8*RS,*9*SR,*10*RS*)*-7-Ethyl-9-[(2-methoxyethoxy)methoxy]-2,4,8,10-tetramethyl-2-(2-oxopropyl)-1-oxaspiro[4.5]decane-3,6-dione* (**31**). *m*CPBA (90%; 3.2 mg, 1.1 equiv.) was added to a stirred soln. of **29** (6 mg) in $CH_2Cl_2$ (0.2 ml) at 25°. After stirring for 3 h at 25°, the solvent was evaporated. FC (0.5 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.20) gave 5 mg (80%) of **31**. Colorless oil. IR (film): 2975, 2920, 2870, 1760, 1710, 1450, 1360, 1105, 1035. $^1$H-NMR (250 MHz, $CDCl_3$): 4.86 (*s*, $OCH_2O$); 3.84–3.79, 3.58–3.53 (2*m*, $OCH_2CH_2O$); 3.40 (*s*, MeO); 3.31 (*dd*, $^3J$ = 12.0, 10.0, H–C(9)); 3.25 (*d*, $^2J$ = 15.0, 1 H, $CH_2$–C(2)); 2.86 (*q*, $^3J$ = 7.2, H–C(4)); 2.81 (*d*, $^2J$ = 15.0, 1 H, $CH_2$–C(2)); 2.22 (*s*, Ac); 2.21 (*m*, H–C(10)); 1.98 (*m*, H–C(7)); 1.90–1.50 (*m*, H–C(8), $CH_2$–C(7)); 1.38 (*s*, Me–C(2)); 1.23 (*d*, $^3J$ = 7.2, Me–C(4)); 1.19 (*d*, $^3J$ = 6.5, Me–C(10)); 1.13 (*d*, $^3J$ = 7.1, Me–C(8)); 0.84 (*t*, $^3J$ = 7.5, *Me*$CH_2$). $^{13}$C-NMR (69.3 MHz, $CDCl_3$): 209.2, 206.9, 198.3 (3*s*, 3 C=O); 97.5 (*t*, $OCH_2O$); 90.3, 80.0 (2*s*, C(2), C(5)); 83.3 (*d*, C(9)); 71.7, 68.3 (2*t*, $OCH_2CH_2O$); 59.1 (*q*, MeO); 54.2, 47.0, 41.6, 40.9 (4*d*, C(4), C(7), C(10), C(9)); 50.4 (*t*, *C*$H_2$–C(2)); 31.5 (*q*, *Me*–C=O); 19.1 (*t*, *C*$H_2$–C(7)); 17.0, 13.2, 12.4, 10.5 (4*q*, 5 Me). CI-MS ($NH_3$): 430 (2, $[M + 18]^+$), 413 (1, $[M + 1]^+$), 337 (16), 313 (36), 279 (33), 237 (15), 179 (5), 89 (100).

*(1*RS,*2*SR,*3*RS,*4*RS,*5*SR,*6*RS,*1′*SR*)*-1-[1′-(3″,5″-Dimethylfuran-2″-yl)ethyl]-*c-*3-ethyl-*c-*5-[(2-methoxyethoxy)methoxy]-*t-*4,*t-*6-dimethylcyclohexane-*r-*1,*c-*2-diol* (**32**). $CeCl_3 \cdot 7\,H_2O$ (93.6 mg, 1 equiv.) was added into a

soln. of **29** (99 mg, 0.25 mmol). The mixture was stirred for 5 min and cooled to −78°. $NaBH_4$ (38 mg, 4 equiv.) was added and the suspension stirred overnight, allowing the temp. to rise to 25°. After filtration through *Celite*, the solvent was evaporated and the oil purified by FC (5 g of $SiO_2$, AcOEt/light petroleum ether 1:2) giving 0.088 g (88.5%) of **32**. Colorless oil ($R_f$ 0.30). UV (MeCN): 220 (10000). IR (film): 3485, 2925, 2880, 1460, 1375, 1240, 1120, 1040. $^1$H-NMR (250 MHz, $CDCl_3$): 5.74 (*s*, H–C(4″)); 4.69, 4.67 (2*d*, $^2J$ = 7.0, $OCH_2O$); 3.74–3.47 (*m*, $OCH_2CH_2O$, H–C(5)); 3.38 (*s*, MeO); 3.19 (*q*, $^3J$ = 7.1, H–C(1′)); 3.17 (br. *s*, H–C(2)); 3.03 (*dd*, $^3J$ = 9.0, 10.0, H–C(5)); 2.22 (*s*, Me–C(5″)); 1.93 (*s*, Me–C(3″)); 1.85–1.43 (*m*, H–C(4), H–C(3), H–C(6), $CH_2$–C(3)); 1.35 (*d*, $^3J$ = 7.1, H–C(2′)); 1.04 (*d*, $^3J$ = 6.3, Me–C(6)); 0.88 (*t*, $^3J$ = 7.4, *Me*$CH_2$–C(3)); 0.69 (*d*, $^3J$ = 6.9, Me–C(4)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 151.7, 149.3 (2*s*, C(2″), C(5″)); 114.2 (*s*, C(3″)); 108.9 (*d*, C(4″)); 96.9 (*t*, $OCH_2O$); 86.6 (*d*, C(5)); 78.1 (*s*, C(1)); 71.6, 67.5 (2*t*, $OCH_2CH_2O$); 59.0 (*q*, MeO); 47.2, 43.3, 38.5, 32.9 (4*d*, C(2), C(5), C(4), C(3)); 20.6 (*t*, $CH_2$–C(3)); 16.6, 13.5, 10.2, 7.9 (4*q*, 6 Me). CI-MS ($NH_3$): 417 (0.1, $[M + 18]^+$), 394 (0.1, $M^+$), 381 (7), 323 (13), 275 (8), 241 (1), 199 (4), 169 (21), 124 (100), 109 (42), 89 (24). Anal. calc. for $C_{22}H_{38}O_6$ (398.54): C 66.30, H 9.61; found: C 66.33, H 9.52.

*(2*RS*,3*RS*,4*SR*,5*RS*,7*SR*)-7-(3′,5′-Dimethylfuran-2′-yl)-2-ethyl-4-[(2-methoxyethoxy)methoxy]-3,5-dimethyl-6-oxooctanal* (**33**). $Pb(OAc)_4$ (276 mg, 1.1 equiv.) was added at 25° into a soln. of **32** (0.225 g, 0.56 mmol) in $CH_2Cl_2$ (5 ml). After stirring for 10 min, the mixture was washed with a sat. aq. $NH_4Cl$ soln. (3 ml, 3 times) and a sat. aq. $NaHCO_3$ soln. (2 ml), dried ($MgSO_4$), and evaporated. FC (11 g $SiO_2$, AcOEt/light petroleum ether 1:4, $R_f$ 0.41) gave 0.201 g (90%) of **33**. Colorless oil. UV (MeCN): 222 (7600). IR (film): 2970, 2935, 2875, 1715, 1575, 1455, 1370, 1120, 1035. $^1$H-NMR (400 MHz, $CDCl_3$): 9.52 (*d*, $^3J$ = 4.0, H–C(1)); 5.80 (*s*, H–C(4′)); 4.69, 4.66 (2*d*, $^2J$ = 6.4, $OCH_2O$); 3.90 (*q*, $^3J$ = 7.0, H–C(7)); 3.72–3.67 (*m*, $OCH_2CH_2O$, H–C(4)); 3.54–3.52 (*m*, $OCH_2CH_2O$); 3.37 (*s*, MeO); 2.90 (*qd*, $^3J$ = 7.2, 9.1, H–C(5)); 2.19 (*s*, Me–C(5′)); 2.00 (*s*, Me–C(3′)); 2.00 (*m*, H–C(2)); 1.60–1.46 (*m*, H–C(3), $MeCH_2$–C(2)); 1.34 (*d*, $^3J$ = 7.0, H–C(8)); 1.14 (*d*, $^3J$ = 7.2, Me–C(5)); 0.82 (*t*, $^3J$ = 7.4, *Me*$CH_2$–C(2)); 0.57 (*d*, $^3J$ = 7.0, Me–C(3)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 210.4 (*s*, HC=O); 205.6 (*s*, C=O); 150.4, 145.7 (2*s*, C(2′), C(5′)); 117.9 (*s*, C(3′)); 109.6 (*d*, C(4′)); 97.5 (*t*, $OCH_2O$); 80.8 (*d*, C(4)); 71.7, 68.3 (2*t*, $OCH_2CH_2O$); 59.2 (*q*, MeO); 56.3, 47.8, 43.3, 36.6 (4*d*, C(7), C(5), C(2), C(3)); 19.9 (*t*, $CH_2$–C(2)); 15.4, 13.6, 13.4, 11.7, 10.8, 9.9 (6*q*, 6 Me). CI-MS ($NH_3$): 396 (0.1, $M^+$), 321 (5), 291 (10), 243 (2), 167 (1), 123 (100), 89 (14). Anal. calc. for $C_{22}H_{36}O_6$ (396.52): C 66.62, H 9.02; found: C 66.51, H 9.02.

*(2*RS*,4*SR*,5*RS*,6*SR*,7*SR*)-3-(3′,5′-Dimethylfuran-2′-yl)-7-(hydroxymethyl)-5-[(2-methoxyethoxy)methoxy]-4,6-dimethylnonan-3-one* (**34**). LiAl(*t*-BuO)$_3$H (1M in THF; 0.5 ml, 1.2 equiv.) was added at −78° to the soln. of **33** (0.164 g, 0.4 mmol) in THF (5 ml). The mixture was then allowed to warm up to 25° and stirred for 4.5 h. Sat. aq. $NaHCO_3$ soln. (2 ml) was added and, after short stirring, the aq. phase was extracted with $Et_2O$ (3 × 5 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. FC (8 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.24) gave 0.155 g (94%) of **34**. Colorless oil. UV (MeCN): 222 (7600). IR (film): 3505, 2980, 2935, 2880, 1715, 1575, 1455, 1380, 1100, 1040, 850, 800. $^1$H-NMR (400 MHz, $CDCl_3$): 5.77 (*s*, H–C(4′)); 4.74, 4.72 (2*d*, $^2J$ = 6.9, $OCH_2O$); 4.00 (*dd*, $^3J$ = 9.6, 0.9, H–C(5)); 3.89 (*q*, $^3J$ = 7.0, H–C(2)); 3.79–3.74 (*m*, 1 H, $OCH_2CH_2O$); 3.79 (*dd*, $^2J$ = 11.9, $^3J$ = 3.8, 1 H, $CH_2$–C(7)); 3.63 (br. *dd*, $^2J$ = 11.9, $^3J$ = 2.8, 1 H, $CH_2$–C(7)); 3.60–3.50 (*m*, 3 H, $OCH_2CH_2O$); 3.36 (*s*, MeO); 2.93 (*qd*, $^3J$ = 7.2, 9.6, H–C(4)); 2.30 (*m*, H–C(7)); 2.17 (*s*, Me–C(5′)); 1.97 (*s*, Me–C(3′)); 1.41–1.32, 1.26–1.21 (2*m*, $CH_2$(8)); 1.32 (*d*, $^3J$ = 7.0, H–C(1)); 1.13 (*d*, $^3J$ = 7.2, Me–C(4)); 0.85 (*t*, $^3J$ = 7.2, H–C(9)); 0.54 (*d*, $^3J$ = 6.9, Me–C(6)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 211.7 (*s*, C=O); 151.0, 144.9 (2*s*, C(2′), C(5′)); 117.6 (*s*, C(3′)); 109.4 (*d*, C(4′)); 97.4 (*t*, $OCH_2O$); 80.4 (*d*, C(5)); 71.7, 67.7, 61.9 (3*t*, $OCH_2CH_2O$, $CH_2OH$); 59.0 (*q*, MeO); 47.7, 44.1, 43.5, 36.6 (4*d*, C(2), C(4), C(7), C(6)); 21.1 (*t*, C(8)); 15.3, 13.7, 13.4, 11.2, 9.9 (5*q*, 6 Me, superposed). CI-MS ($NH_3$): 417 (3, $[M + 18]^+$), 399 (1, $M^+$), 323 (100), 293 (24), 170 (28), 123 (19), 94 (15), 89 (2). Anal. calc. for $C_{22}H_{38}O_6$ (398.54): C 66.30, H 9.61; found: C 66.25, H 9.56.

*(2*RS*,3*RS*,4*SR*,5*SR*,6*SR*,7*RS*)-7-(3′,5′-Dimethylfuran-2′-yl)-2-ethyl-4-[(2-methoxyethoxy)methoxy]-3,5-dimethyloctane-1,6-diol* (**35**). $CeCl_3 \cdot 7\,H_2O$ (0.139 g, 1 equiv.) was added to a soln. of **34** (0.149 g, 0.37 mmol) in EtOH (5 ml). $NaBH_4$ (0.142 g, 10 equiv.) was added and the suspension stirred at 25° for 16 h. After filtration through *Celite* and solvent evaporation, FC (7 g $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.12) gave 0.124 g (84%) of **35**. Colorless oil. UV (MeCN): 219 (11100). IR (film): 3475, 2970, 2930, 2880, 1580, 1455, 1380, 1245, 1100, 1040, 850, 800. $^1$H-NMR (400 MHz, $CDCl_3$): 5.74 (*s*, H–C(4′)); 4.86, 4.77 (2*d*, $^2J$ = 6.6, $OCH_2O$); 3.90 (*dd*, $^3J$ = 8.9, 1.8, H–C(4)); 3.81–3.77 (*m*, 1 H, $OCH_2CH_2O$); 3.73–3.69 (*m*, 1 H, $OCH_2CH_2O$); 3.64 (*dd*, $^2J$ = 10.9, $^3J$ = 4.9, 1 H–C(1)); 3.60 (*m*, $OCH_2CH_2O$); 3.51 (*m*, H–C(6)); 3.46 (*dd*, $^2J$ = 10.9, $^3J$ = 8.5, 1 H–C(1)); 3.08 (*qd*, $^3J$ = 7.2, 3.1, H–C(7)); 2.20 (*s*, Me–C(5′)); 1.94 (*s*, Me–C(3′)); 1.91 (*m*, H–C(3)); 1.41 (*m*, H–C(5)); 1.35 (*d*, $^3J$ = 7.2, H–C(8)); 1.31 (*m*, H–C(2)); 1.20, 1.01 (2*m*, $MeCH_2$–C(2)); 0.87 (*d*, $^3J$ = 6.9, Me–C(3)); 0.83 (*d*, $^3J$ = 6.8, Me–C(5)); 0.76 (*t*, $^3J$ = 7.4, *Me*$CH_2$–C(2)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 150.0, 149.7 (2*s*, C(2′), C(5′)); 115.7 (*s*, C(3′)); 108.7 (*d*, C(4′)); 97.8 (*t*, $OCH_2O$); 82.4 (*d*, C(4)); 71.7, 67.8, 63.8 (3*t*, $OCH_2CH_2O$, $CH_2OH$); 59.0 (*q*, MeO); 43.4, 38.9, 35.8, 33.3 (4*d*, C(6), C(2), C(3), C(5)); 18.8 (*t*, $CH_2$–C(2)); 17.5, 13.5, 12.6, 11.2, 10.2 (5*q*,

6 Me). CI-MS ($NH_3$): 419 (0.2, $[M+18]^+$), 401 (0.6, $M^+$), 342 (2), 325 (100), 295 (6), 201 (2), 153 (3), 123 (23), 89 (3). Anal. calc. for $C_{22}H_{40}O_6$ (400.56): C 65.97, H 10.07; found: C 65.94, H 10.06.

*(2RS,3RS,4SR,5SR,6SR,7RS)-7-(3′,5′-Dimethylfuran-2′-yl)-2-ethyl-6-hydroxy-4-[(methoxyethoxy)-methoxy]-3,5-dimethyloct-1-yl 2,2-Dimethylpropanoate* (**36**). Pivaloyl chloride (= 2,2-dimethylpropanoyl chloride; 8.7 mg, 1.5 equiv.) was added to a soln. of **35** (19.3 mg, 0.048 mmol) in 0.7 ml of pyridine at 0°. The mixture was stirred at 0° for 5 h. $CHCl_3$ (1 ml) and then sat. aq. $NaHCO_3$ soln. (1 ml) were added. The aq. phase was extracted with $CHCl_3$ (3 × 5 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. FC (1.5 g of $SiO_2$, light petroleum ether/AcOEt 1:4, $R_f$ 0.3) gave 13.4 mg (96%) of **36**. Colorless oil. UV (MeCN): 220 (11200). IR (film): 3510, 2965, 2930, 2880, 1730, 1575, 1480, 1460, 1400, 1285, 1160, 1100, 1040, 855, 795. $^1$H-NMR (400 MHz, $CDCl_3$): 5.73 (*s*, H–C(4′)); 4.85, 4.76 (2*d*, $^2J$ = 6.7, $OCH_2O$); 4.02 (*dd*, $^3J$ = 4.5, 11.0, H–C(4)); 3.88–3.79 (*m*, 2 H–C(1), 1 H of $OCH_2CH_2O$); 3.70–3.65, 3.56 (2*m*, 3 H, $OCH_2CH_2O$); 3.50 (*ddd*, $^3J$ = 10.0, 8.2, 2.5, H–C(6)); 3.39 (*s*, MeO); 3.11 (*d*, $^3J$ = 8.2, OH); 3.06 (*qd*, $^3J$ = 7.0, 2.5, H–C(7)); 2.20 (*s*, Me–C(5′)); 1.93 (*s*, Me–C(3′)); 1.85 (*m*, H–C(3)); 1.43 (*m*, H–C(2)); 1.36 (*d*, $^3J$ = 7.2, Me–C(7)); 1.33 (*m*, H–C(5)); 1.19, 1.01 (2*m*, $CH_2$–C(2)); 1.17 (*s*, $Me_3CCO$); 0.85 (*d*, $^3J$ = 6.8, Me–C(3)); 0.80 (*d*, $^3J$ = 6.7, Me–C(5)); 2.21 (*t*, $^3J$ = 7.4, $MeCH_2$). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 178.5 (*s*, COO); 150.0, 149.6 (2*s*, C(2′), C(5′)); 115.6 (*s*, C(3′)); 108.6 (*d*, C(4′)); 97.9 (*t*, $OCH_2O$); 82.3 (*d*, C(4)); 76.2 (*d*, C(6)); 71.6, 67.8, 65.2 (3*t*, $OCH_2CH_2O$, C(1)); 59.1 (*q*, MeO); 39.9, 38.7, 35.9, 33.3 (4*d*, C(7), C(5), C(3), C(2)); 38.7 (*s*, $Me_3C$); 27.2 (*q*, $Me_3C$); 18.3 (*t*, $MeCH_2$); 17.5, 13.5, 12.5, 10.8, 10.1, 9.8 (6*q*, 6 Me). CI-MS ($NH_3$): 485 (0.2, $M^+$), 410 (2), 256 (7), 183 (4), 153 (10), 123 (100), 89 (46).

*(2RS,3RS,4SR,5RS,6SR,7RS)-7-(3′,5′-Dimethylfuran-2′-yl)-2-ethyl-4,6-(methylenedioxy)-3,5-dimethyloct-1-yl 2,2-Dimethylpropanoate* (= *3-{6-[1-(3,5-Dimethylfuran-2-yl)ethyl]-5-methyl-1,3-dioxan-4-yl}-2-ethylbutyl 2,2-Dimethylpropanoate*; **37**). To a soln. of **36** (18 mg, 0.037 mmol) in $CH_2Cl_2$ (1 ml), $ZnBr_2$ (41.3 mg, 5 equiv.) was added. The mixture was stirred at 25° for 24 h and then evaporated. FC (1 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.8) gave 10.3 mg (66%) of **37**. Colorless solid. M.p. 83–86°. UV (MeCN): 219 (11000). IR (film): 2970, 1730, 1590, 1460, 1290, 1175, 1090, 1050, 1005. $^1$H-NMR (400 MHz, $CDCl_3$): 5.74 (*s*, H–C(4′)); 4.88 (2*d*, $^3J$ = 6.3, $OCH_2O$); 4.15 (*dd*, $^3J$ = 4.4, $^2J$ = 11.0, 1 H–C(1)); 3.91 (*dd*, $^3J$ = 10.2, $^2J$ = 11.0, 1 H–C(1)); 3.85 (*d*, $^3J$ = 10.8, H–C(6)); 3.60 (*d*, $^3J$ = 10.1, H–C(4)); 3.54 (*qd*, $^3J$ = 6.9, 10.8, H–C(7)); 2.21 (*s*, Me–C(5′)); 1.96 (*s*, Me–C(3′)); 1.92 (*m*, H–C(3)); 1.84 (*m*, H–C(5)); 1.75 (*m*, H–C(2)); 1.30 (*m*, $CH_2$–C(2)); 1.22 (*d*, Me–C(5)); 1.21 (*s*, $Me_3C$); 1.18 (*d*, $^3J$ = 6.9, Me–C(7)); 0.99 (*t*, $^3J$ = 7.4, $MeCH_2$–C(2)); 0.90 (*d*, $^3J$ = 6.7, Me–C(3)). NOESY (360 MHz, $CDCl_3$): NOE between H–C(6)/H–C(7), H–C(5); H–C(7)/H–C(6), H–C(5); H–C(5)/H–C(6), H–C(7), H–C(4). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 177.0 (*s*, C=O); 149.6, 149.4 (2*s*, C(2′), C(5′)); 114.6 (*s*, C(3′)); 108.6 (*d*, C(4′)); 88.9 (*t*, $OCH_2O$); 81.4 (*d*, C(4)); 76.9 (*t*, C(1)); 64.9 (*d*, C(6)); 37.7, 33.9, 29.8 (3*d*, C(2), C(3), C(7)); 29.4 (*t*, $CH_2$–C(2)); 27.3 (*q*, $Me_3C$); 18.6, 16.6, 13.5, 13.1, 12.9, 10.0 (6*q*, 6 Me). CI-MS ($NH_3$): 426 (2, $[M+NH_3]^+$), 407 (0.3, $M^+$), 307 (1), 235 (2), 183 (1), 123 (100), 96 (25), 70 (2). Anal. calc. for $C_{24}H_{40}O_5$ (408.58): C 70.55, H 9.87; found: C 70.53, H 9.92.

*(2RS,3RS,4SR,5RS,7SR)-7-(3′,5′-Dimethylfuran-2′-yl)-2-ethyl-4-[(2-methoxyethoxy)methoxy]-3,5-dimethyl-6-oxooct-1-yl 2,2-Dimethylpropanoate* (**38**). To a soln. of **34** (87 mg, 0.022 mmol) in pyridine (3 ml), pivaloyl chloride (0.04 ml, 1.5 equiv.) was added at −10°. The mixture was stirred at 0° for 2.5 h. $CHCl_3$ (4.5 ml) was added and then sat. aq. $NaHCO_3$ soln. (3 ml). The aq. phase was extracted with $CHCl_3$ (3 × 5 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. FC (5 g of $SiO_2$, AcOEt/light petroleum ether 1:4, $R_f$ 0.37) gave 84 mg (80%) of **38**. Colorless oil. UV (MeCN): 223 (7500). IR (film): 2970, 2920, 2860, 1720, 1575, 1460, 1365, 1285, 1160, 1035, 945. $^1$H-NMR (250 MHz, $CDCl_3$): 5.78 (br. *s*, H–C(4′)); 4.74 (*s*, $OCH_2O$); 4.06 (*m*, 2 H); 3.85 (*q*, $^3J$ = 6.9, H–C(7)); 3.82 (*dd*, $^3J$ = 8.8, 2.9, H–C(4)); 3.78–3.50 (2*m*, $OCH_2CH_2O$); 3.37 (*s*, MeO); 2.88 (*qd*, $^3J$ = 8.0, 7.0, H–C(5)); 2.17 (br. *s*, Me–C(5′)); 1.97 (*s*, Me–C(3′)); 1.54–1.40 (*m*, H–C(2)); 1.31 (*d*, $^3J$ = 7.0, Me–C(5)); 1.40 (*m*, $CH_2$–C(2)); 1.22 (*s*, $Me_3C$); 1.20 (*m*, H–C(3)); 1.12 (*d*, $^3J$ = 7.1, Me–C(7)); 0.83 (*t*, $^3J$ = 7.4, $MeCH_2$–C(2)); 0.57 (*d*, $^3J$ = 6.9, Me–C(3)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 209.8, 178.5 (*s*, 2 C=O); 150.6, 145.6 (2*s*, C(5′), C(2′)); 117.1 (*s*, C(3′)); 109.2 (*d*, C(4′)); 97.6 (*t*, $OCH_2O$); 81.2 (*d*, C(4)); 71.6, 67.7, 64.2 (3*t*, $OCH_2CH_2O$, $CH_2OPiv$); 58.9 (*q*, MeO); 46.9, 43.2, 40.8, 36.3 (4*d*, C(2), C(3), C(5), C(7)); 27.1 (*q*, $Me_3C$); 20.2 (*t*, $CH_2$–C(2)); 14.5, 13.9, 13.3, 11.2, 10.3, 9.9 (6*q*, 6 Me). CI-MS ($NH_3$): 500 (3, $[M+NH_3]^+$), 483 (0.2, $M^+$), 407 (8), 377 (3), 329 (1), 227 (3), 123 (100), 89 (12). Anal. calc. for $C_{27}H_{46}O_7$ (482.66): C 67.19, H 9.61; found: C 67.14, H 9.63.

*(2RS,3RS,4SR,5RS,7SR)-7-(3′,5′-Dimethylfuran-2′-yl)-2-ethyl-4-hydroxy-3,5-dimethyl-6-oxooct-1-yl 2,2-Dimethylpropanoate* (**39**). To a soln. of **38** (67 mg, 0.018 mmol) in anh. $CH_2Cl_2$ (2 ml), $ZnBr_2$ (310 mg, 10 equiv.) was added at 25°. The mixture was stirred for 24 h and then evaporated. FC (4 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.37) gave 34 mg (63%) of **39**. Colorless oil. UV (MeCN): 219 (10100), 294 (2240). IR (film): 3520, 2965, 2930, 2880, 1725, 1715, 1575, 1455, 1400, 1285, 1165, 1045, 970. $^1$H-NMR (400 MHz, $CDCl_3$): 5.78 (br. *s*, H–C(4′)); 4.04 (*dd*, $^3J$ = 11.2, 4.7, 1 H–C(1)); 3.95–3.85 (*m*, 1 H–C(1), H–C(7)); 3.65 (*m*, H–C(4)); 3.08 (br. *s*, OH–C(4)); 2.75 (*qd*, $^3J$ = 7.2, 3.9, H–C(5)); 2.17 (br. *s*, Me–C(5′)); 1.96 (*s*, Me–C(3′)); 1.61–1.56 (*m*, H–C(3));

1.43–1.37 (*m*, H–C(2)); 1.32 (*d*, $^3J$ = 7.0, Me–C(7)); 1.19 (*s*, $Me_3C$); 1.09 (*d*, $^3J$ = 7.2, Me–C(5)); 1.08–1.01 (*m*, $CH_2$–C(2)); 0.78 (*t*, $^3J$ = 7.3, *Me*$CH_2$–C(2)); 0.75 (*d*, $^3J$ = 6.8, Me–C(3)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 215.1, 180.0 (2*s*, 2 C=O); 152.2, 147.1 (2*s*, C(2'), C(5')); 118.6 (*s*, C(3')); 110.8 (*d*, C(4')); 73.7 (*d*, C(4)); 66.4 (*t*, PivO*C*$H_2$); 45.7, 45.0, 41.9, 36.9 (4*d*, C(2), C(3), C(5), C(7)); 40.2 (*s*, $Me_3C$); 28.6 (*q*, $Me_3$C); 20.7 (*t*, $CH_2$–C(2)); 15.4, 14.8, 13.6, 12.6, 11.6, 11.3 (6*q*, 6 Me). CI-MS ($NH_3$): 395 (2, $M^+$), 394 (1), 293 (2), 181 (3), 123 (100), 85 (3).

*(2*RS,*3*RS,*4*SR,*5*RS,*6*RS,*7*RS*)-7-(3',5'-Dimethylfuran-2'-yl)-2-ethyl-4,6-dihydroxy-3,5-dimethyloct-1-yl 2,2-Dimethylpropanoate* (**40**). AcOH (0.5 ml) was added to a soln. of tetramethylammonium triacetoxyborohydride (181 mg, 8 equiv.) in anh. MeCN (0.5 ml). The mixture was stirred at 25° for 30 min and then cooled to −30°. The soln. of **39** (34 mg, 0.086 mmol) in MeCN (0.3 ml) was added, the mixture stirred at −30° for 17 h, then the temp. raised to 0°, the mixture stirred at 0° for 24 h, the temp. raised to 25°, and the mixture stirred at 25° for 24 h. After dilution with $CHCl_3$ (5 ml) and quenching with sat. aq. $NaHCO_3$ soln. (3 ml), the aq. phase was extracted with $CHCl_3$ (3 × 5 ml), and the combined org. phase dried ($MgSO_4$) and evaporated. FC (2 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.59) gave 30 mg (88%) of **40**. Colorless oil. UV (MeCN): 219 (10 500). IR (film): 3475, 2965, 2935, 2875, 1730, 1580, 1480, 1455, 1400, 1285, 1160, 1035, 970. $^1$H-NMR (400 MHz, $CDCl_3$): 5.77 (*s*, H–C(4')); 4.12 (*dd*, $^2J$ = 11.1, $^3J$ = 4.4, H–C(1)); 3.93–3.88 (*m*, H–C(1), H–C(4)); 3.72 (*m*, H–C(6)); 3.09 (*m*, H–C(7)); 2.21 (br. *s*, Me–C(5')); 1.95 (*s*, Me–C(3')); 1.89–1.61 (3*m*, H–C(2), H–C(3), H–C(5)); 1.34–1.11 (*m*, $CH_2$–C(2)); 1.22 (*d*, $^3J$ = 7.1, Me–C(7)); 1.21 (*s*, $Me_3$C); 1.03 (*d*, $^3J$ = 7.0, Me–C(5)); 0.95 (*d*, $^3J$ = 6.8, Me–C(3)); 0.91 (*t*, $^3J$ = 7.7, *Me*$CH_2$–C(2)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 178.6 (*s*, C=O); 150.3, 148.9 (2*s*, C(2'), C(5')); 116.9 (*s*, C(3')); 108.8 (*d*, C(4')); 79.4 (*d*, C(4)); 72.3 (*d*, C(6)); 65.2 (*t*, O*C*$H_2$–C(2)); 39.7, 35.9, 35.2, 34.6 (4*d*, C(2), C(3), C(5), C(7)); 38.8 (*s*, $Me_3C$); 27.2 (*q*, $Me_3$C); 18.6 (*t*, $CH_2$–C(2)); 16.0, 13.4, 12.7, 10.7, 10.3, 9.9 (6*q*, 6 Me). CI-MS ($NH_3$): 397 (1, $M^+$), 277 (2), 211 (2), 164 (10), 123 (100), 113 (91), 85 (10), 70 (4).

*(2*RS,*3*RS,*4*SR,*5*RS,*6*SR,*7*RS*)-6-[(*tert*-Butyl)dimethylsilyloxy]-7-(3',5'-dimethylfuran-2'-yl)-2-ethyl-4-[(2-methoxyethoxy)methoxy]-3,5-dimethyloct-1-yl 2,2-Dimethylpropanoate* (**41**). To a soln. of **36** (103 mg, 0.21 mmol) in $CH_2Cl_2$ (3 ml), 2,6-dimethylpyridine (0.1 ml, 4 equiv.) followed by (*t*-Bu)$Me_2SiOSO_2CF_3$ (0.19 ml, 4 equiv.) were added at 0°. After stirring for 2 h, the mixture was quenched with sat. aq. $NaHCO_3$ soln. (3 ml). The aq. phase was extracted with $CHCl_3$ (3 × 5 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. FC (6 g of $SiO_2$, AcOEt/light petroleum ether 1:24, $R_f$ 0.78 (1:2)) gave 122 mg (96%) of **41**. Colorless oil. UV (MeCN): 220 (11 100). IR (film): 2960, 2930, 2880, 1730, 1630, 1575, 1460, 1395, 1380, 1360, 1285, 1255, 1160, 1040, 940, 835, 775. $^1$H-NMR (400 MHz, $CDCl_3$): 5.69 (*s*, H–C(4')); 4.79, 4.73 (2*d*, $^2J$ = 6.8, $OCH_2O$); 4.13–4.03 (*m*, $CH_2$(1)); 3.90 (*dd*, $^3J$ = 5.3, 3.9, H–C(6)); 3.73–3.69, 3.56–3.54 (2*m*, H–C(4), $OCH_2CH_2O$, 5 H); 3.38 (*s*, MeO); 3.02 (*qd*, $^3J$ = 7.2, 3.9, H–C(7)); 2.18 (*s*, Me–C(5')); 1.92 (*s*, Me–C(3')); 1.88–1.80 (*m*, H–C(5)); 1.69–1.63 (*m*, H–C(2)); 1.53–1.49 (*m*, H–C(3)); 1.23 (*d*, $^3J$ = 7.2, Me–C(7)); 1.19 (*m*, $CH_2$–C(2)); 1.19 (*s*, $Me_3$C); 0.93–0.88 (*m*, Me–C(3), *Me*$CH_2$–C(2)); 0.89 (*s*, $Me_3$C); 0.68 (*d*, $^3J$ = 7.0, Me–C(5)); 0.10, 0.03 (2*s*, $Me_2$Si). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 178.6 (*s*, C=O); 149.9, 148.5 (2*s*, C(2'), C(5')); 114.4 (*s*, C(3')); 109.1 (*d*, C(4')); 97.5 (*t*, $OCH_2O$); 82.4 (*d*, C(4)); 75.9 (*d*, C(6)); 71.7, 67.6, 64.5 (3*t*, $OCH_2CH_2O$, *C*$H_2$OPiv); 59.0 (*q*, MeO); 40.4, 40.0 (2*d*, C(7), C(5)); 38.8 (*s*, $Me_3C$); 36.2, 36.1 (2*d*, C(2), C(3)); 27.7, 26.0 (2*q*, 2 $Me_3$C); 19.3 (*t*, *C*$H_2$–C(2)); 14.6, 13.4, 12.1, 10.9, 10.5, 10.0 (6*q*, 6 Me); −3.8, −4.8 (2*q*, $Me_2$Si). CI-MS ($NH_3$): 616 (2, $[M + NH_3]^+$), 523 (7), 413 (2), 369 (12), 303 (7), 185 (20), 123 (50), 89 (100). Anal. calc. for $C_{33}H_{62}O_7Si$ (598.94): C 66.18, H 10.4, Si 4.69; found: C 66.90, H 10.32, Si 4.61.

*(2*RS,*3*RS,*4*SR,*5*RS,*6*SR,*7*RS*)-6-[(*tert*-Butyl)dimethylsilyloxy]-2-ethyl-4-[(2-methoxyethoxy)methoxy]-3,5,7-trimethyl-8,9-dioxodec-1-yl 2,2-Dimethylpropanoate* (**43**). MMPP (85%; 119 mg, 0.16 mmol) was added to a soln. of **41** (66 mg, 0.11 mmol) in anh. DMF (2 ml). After stirring at 25° for 8 h, a sat. aq. $NaHCO_3$ soln. (2 ml) was added. The mixture was extracted with $Et_2O$ (7 × 5 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. The resulting oil was dissolved in MeOH (3 ml), and after cooling to −78°, $O_3$ was bubbled through the mixture (2 g of $O_3$ per h) for 40 min. After additional stirring for 20 min, $Me_2S$ was added (1 ml) and the mixture allowed to warm up to 25°. After a negative test for ozonides (KI paper), the solvents were evaporated, and FC (2 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.76) gave 45 mg (71%) of **43**. Yellow oil. IR (film): 2960, 2930, 2880, 1730, 1715, 1460, 1380, 1360, 1285, 1260, 1155, 1080, 1040, 930, 835, 775. $^1$H-NMR (400 MHz, $CDCl_3$): 4.77, 4.68 (2*d*, $^2J$ = 6.7, $OCH_2O$); 4.26 (*dd*, $^3J$ = 8.8, 3.4, H–C(6)); 4.08 (*dd*, $^2J$ = 11.1, $^3J$ = 6.7, 1 H–C(1)); 3.92 (*dd*, $^2J$ = 11.1, $^3J$ = 8.9, 1 H–C(1)); 3.71–3.55 (*m*, $OCH_2CH_2O$, H–C(4)); 3.49 (*qd*, $^3J$ = 6.8, 3.4, H–C(7)); 3.40 (*s*, MeO); 2.34 (*s*, Me–C(9)); 1.87–1.73 (*m*, H–C(5), H–C(3)); 1.62–1.54 (*m*, H–C(2)); 1.48–1.38 (*m*, 1 H, $CH_2$–C(2)); 1.18 (*s*, $Me_3$C); 1.18–1.10 (*m*, 1 H, $CH_2$–C(2)); 1.13 (*d*, $^3J$ = 6.8, Me–C(7)); 0.91 (*t*, $^3J$ = 7.3, *Me*$CH_2$–C(2)); 0.89 (*s*, $Me_3$C); 0.83 (*d*, $^3J$ = 7.0, Me–C(3)); 0.58 (*d*, $^3J$ = 7.1, Me–C(5)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 201.7, 198.4 (2*s*, 2 CO); 178.5 (*s*, COO); 97.8 (*t*, $OCH_2O$); 82.3 (*d*, C(4)); 73.3 (*d*, C(6)); 71.7, 64.7, 65.0 (3*t*, $OCH_2CH_2O$, *C*$H_2$OPiv); 59.0 (*q*, MeO); 46.6 (*d*, C(7)); 40.2, 39.5, 36.4 (3*d*, C(5), C(3), C(2)); 38.8 (*s*, $Me_3C$); 27.2, 25.9, 24.6 (3*q*, 2 $Me_3$C, *Me*CO); 18.7 (*t*, *C*$H_2$–C(7)); 18.2 (*s*, $Me_3C$); 12.4, 10.9, 10.2, 8.0 (4*q*, 4 Me); −4.0, −4.4 (2*q*, $Me_2$Si). CI-MS ($NH_3$): 592 (12, $[M + NH_3]^+$), 575 (0.2, $M^+$), 469 (1), 402 (2), 337 (3), 243 (9), 133 (100), 89 (66).

*(2*RS,*3*SR,*4*RS,*5*SR,*6*RS,*7*RS*)-3-[(*tert*-*Butyl)dimethylsilyloxy]-5-[(2-methoxyethoxy)methoxy]-2,4,6-trimethyl-7-[(2,2-dimethyl-1-oxopropyloxy)methyl]nonanoic Acid* (**44**). MMPP (85%; 56 mg, 0.096 mmol), **43** (37 mg, 0.064 mmol), and DMF (1 ml) were stirred at 25° for 6 h. A sat. aq. $NaHCO_3$ soln. (5 ml) and $Et_2O$ (5 ml) were added. The aq. phase was acidified and extracted with $Et_2O$ (5 × 5 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. FC (1.5 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.13) gave 35 mg (99%; 70% based on **41**) of **44**. Colorless oil. UV (MeCN): transparent > 210. IR (film): 3400–3100, 2960, 2935, 2880, 1730, 1705, 1460, 1385, 1285, 1160, 1065, 1045, 940, 855, 835. $^1$H-NMR (400 MHz, $CDCl_3$): 4.80, 4.72 (*d*, $^2J$ = 7.0, $OCH_2O$); 4.24 (*dd*, $^3J$ = 7.9, 2.3, H–C(3)); 4.10 (*dd*, $^2J$ = 11.4, $^3J$ = 4.4, $CH_3$–C(7)); 3.94 (*dd*, $^2J$ = 11.4, $^3J$ = 8.8, $CH_2$–C(7)); 3.89–3.84, 3.66–3.54 (2*m*, $OCH_2CH_2O$, H–C(5)); 3.39 (*s*, MeO); 2.77 (*qd*, $^3J$ = 7.2, 2.7, H–C(2)); 1.86–1.80 (*m*, H–C(4), H–C(6)); 1.64–1.58 (*m*, H–C(7)); 1.43–1.38 (*m*, H–C(8)); 1.20 (*d*, $^3J$ = 7.2, Me–C(2)); 1.19 (*s*, $Me_3C$); 1.18–1.09 (*m*, H–C(8)); 0.92 (*t*, $^3J$ = 7.4, *Me*–C(8)); 0.91 (*s*, $Me_3C$); 0.85, 0.82 (2*d*, $^3J$ = 7.0, 7.1, Me–C(4), Me–C(6)); 0.18, 0.17 (2*s*, $Me_2Si$). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 178.8, 178.6 (2*s*, 2 COO); 97.6 (*t*, $OCH_2O$); 83.0 (*d*, C(5)); 74.7 (*d*, C(3)); 71.7, 67.6, 65.0 (3*t*, $OCH_2CH_2O$, $CH_2OPiv$); 58.9 (*q*, MeO); 44.0, 40.2, 39.6, 36.4 (4*d*, C(2), C(4), C(6), C(7)); 38.7 (*s*, $Me_3C$); 27.2, 25.8 (2*q*, 2 $Me_3C$); 18.7 (*t*, C(8)); 18.1 (*s*, $Me_3C$); 12.4, 10.9, 10.8, 8.8 (4*q*, 4 Me); −4.0, −5.1 (2*q*, $Me_2Si$). CI-MS ($NH_3$): 567 (0.8, $[M + NH_3]^+$), 549 (0.5, $M^+$), 473 (7), 443 (3), 369 (3), 283 (6), 244 (12), 173 (41), 133 (100), 89 (95). Anal. calc. for $C_{28}H_{56}O_8Si$ (548.83): C 61.28, H 10.28, Si 5.12; found: C 61.25, H 10.24, Si 5.13.

*(2*RS,*3*RS,*4*SR,*5*RS,*6*SR,*7*RS*)-7-(3′,5′-Dimethylfuran-2′-yl)-2-ethyl-4-[(2-methoxyethoxy)methoxy]-3,5-dimethyl-6-(1-oxoprop-2-enyloxy)oct-1-yl 2,2-Dimethylpropanoate* (**45**). (i-Pr)$_2$EtN (0.042 ml, 0.25 mmol) and acryloyl chloride (0.02 ml) were added to a stirred soln. of **36** (11.9 mg, 0.0245 mmol) in $CH_2Cl_2$ (0.1 ml) at −10°. The cooling bath was removed and the mixture left in an ultra-sound bath at 25° for 12 h. After solvent evaporation, FC (1 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.64) gave 5.2 mg (40%) of **45**, along with 2 mg (17%) of **36**. **45**: Colorless oil. UV MeCN): 219 (13000). IR (film): 2970, 1725, 1630, 1460, 1405, 1265, 1195, 1155, 1040, 805. $^1$H-NMR (400 MHz, $CDCl_3$): 6.45 (*dd*, $^3J$ = 17.2, $^2J$ = 1.5, 1 H); 6.13 (*dd*, $^3J$ = 17.2, 10.4, 1 H); 5.86 (*dd*, $^2J$ = 1.5, $^3J$ = 10.4, 1 H); 5.71 (*s*, H–C(4′)); 5.09 (*dd*, $^3J$ = 9.5, 3.8, H–C(6)); 4.70, 4.68 (2*d*, $^2J$ = 6.4, $OCH_2O$); 4.04, 3.90 (2*dd*, each with $^2J$ = 11.0, $^3J$ = 2.2, $CH_2$(1)); 3.88–3.54 (3*m*, $OCH_2CH_2O$); 3.38 (*s*, MeO); 3.37 (*dd*, $^3J$ = 9.7, 8.4, H–C(4)); 3.19 (*qd*, $^3J$ = 7.2, 3.8, H–C(7)); 2.18 (*s*, Me–C(5′)); 1.94 (*s*, Me–C(3′)); 1.81 (*m*, H–C(3), H–C(5)); 1.47 (*m*, H–C(2)); 1.30–1.20 (*m*, 1 H, $CH_2$–C(2)); 1.22 (*d*, $^3J$ = 7.2, Me(8)); 1.16 (*s*, $Me_3C$); 1.10–1.04 (*m*, 1 H, $CH_2$–C(2)); 0.87 (*d*, $^3J$ = 6.7, Me–C(5)); 0.86 (*d*, $^3J$ = 6.9, Me–C(3)); 0.86 (*t*, $^3J$ = 7.0, *Me*$CH_2$). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 165.6 (*s*, $CO_2$); 149.5, 148.3 (2*s*, C(2′), C(5′)); 131.0 (*t*, $CH_2$=CHCO); 127.4 (*d*, $CH_2$=*C*HCO); 115.8 (*s*, C(3′)); 110.6 (*d*, C(4′)); 98.6 (*t*, $OCH_2O$); 80.1 (*d*, C(4)); 76.3 (*d*, C(6)); 71.9, 66.7, 60.8 (3*t*, $OCH_2CH_2O$, C(1)); 58.6 (*q*, MeO); 41.2, 37.6, 36.4, 33.5 (4*d*, C(2), C(3), C(5), C(7)); 38.7 (*s*, $Me_3C$); 27.0 (*q*, $Me_3C$); 18.6 (*t*, $CH_2$–C(2)); 16.4, 13.5, 12.7, 10.7, 10.0, 9.9 (6*q*, 6 Me). CI-MS ($NH_3$): 555 (5, $[M + NH_3]^+$), 464 (8), 392 (3), 253 (13), 163 (67), 123 (100), 89 (88). Anal. calc. for $C_{30}H_{50}O_8$ (538.72): C 66.89, H 9.35; found: C 66.99, H 9.33.

*(2′*RS,*3*RS,*3′*SR,*4*SR,*4′*RS,*5′*RS*)-3-{5′-[(2″,2″-Dimethyl-1″-oxopropyloxy)methyl]-3′-[(2-methoxyethoxy)methoxy]-4′-methylheptan-2′-yl}-3,4-dihydro-4,5,7-trimethyl-1*H*-2-benzopyran-1-one* (**46**). A soln. of **36** (16 mg, 0.033 mmol), $Et_3N$ (0.02 mg), acryloyl chloride (0.011 ml), and a catalytic amount of 4-(dimethylamino)-pyridine in $CH_2Cl_2$ (2.5 ml) was exposed at 50° to a pressure of 1.3 GPa for 24 h. After evaporation, FC (0.8 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.42) gave 6 mg (35%) of **46**. Colorless oil. IR (film): 2970, 2930, 2875, 1725, 1615, 1480, 1460, 1380, 1330, 1285, 1235, 1170, 1040, 970. $^1$H-NMR (400 MHz, $CDCl_3$): 7.72 (br. *s*, 1 arom. H); 7.22 (br. *s*, 1 arom. H); 4.92, 4.83 (2*d*, $^2J$ = 6.3, $OCH_2O$); 4.53 (*d*, $^3J$ = 10.4, H–C(3)); 4.00 (*dd*, $^2J$ = 11.0, $^3J$ = 4.3, 1 H, $CH_2$–C(5′)); 3.83–3.72, 3.62–3.59 (2*m*, $OCH_2CH_2O$, H–C(3′), 1 H of $CH_2$–C(5′)); 3.43 (*s*, MeO); 3.17 (*q*, $^3J$ = 7.0, H–C(4)); 2.33 (br. *s*, Me–C(5), Me–C(7)); 1.80–1.75 (*m*, H–C(2′)); 1.69–1.60 (*m*, H–C(4′)); 1.36 (*d*, $^3J$ = 7.0, Me–C(4)); 1.25–1.12 (*m*, $CH_2$(6′)); 1.08 (*s*, $Me_3C$); 0.86 (*d*, $^3J$ = 6.9, Me–C(4′)); 0.75 (*d*, $^3J$ = 6.9, Me–C(2′)); 0.69 (*t*, $^3J$ = 7.4, Me(7′)). CI-MS ($NH_3$): 539 (0.1, $[M + NH_3]^+$), 521 (1, $M^+$), 415 (7), 335 (23), 306 (7), 261 (8), 189 (16), 117 (11), 89 (100).

*(1*RS,*2*SR,*2′*SR,*3*RS,*3′*RS,*4′*SR,*5′*SR,*6*SR,*8*RS*)-3-{5′-[(2″,2″-Dimethyl-1″-oxopropyloxy)methyl]-3′-[(2-methoxyethoxy)methoxy]-4′-methylheptan-2′-yl}-2,8,10-trimethyl-4,11-dioxatricyclo[6.2.1.0$^{1,6}$]undec-9-en-5-one* (*= 3-{5′-[(2″,2″-Dimethyl-1″-oxopropyloxy)methyl]-3′-[(2-methoxyethoxy)methoxy]-4′-methylheptan-2′-yl}-3,4,8,8a-tetrahydro-4,5,7-trimethyl-4a,7-epoxy-4a*H*-2-benzopyran-1(7*H*)-one*; **47**). A soln. of **36** (21.8 mg, 0.045 mmol), dicyclohexylcarbodiimide (18.5 mg), and acrylic acid (0.1 ml) in $CH_2Cl_2$ (4.5 ml) was heated to 50° under a pressure of 1.3 GPa for 24 h. Solvent evaporation and FC (1 g of $SiO_2$, AcOEt/light petroleum ether 1:2, $R_f$ 0.47) gave 7 mg (28%) of **47**. Colorless oil. A 2nd fraction (13 mg, $R_f$ 0.26) contained a mixture of two unidentified compounds, being possibly other *Diels-Alder* adducts. IR (film): 2970, 2930, 2875, 1755, 1725, 1665, 1460, 1385, 1360, 1280, 1160, 1105, 1045. $^1$H-NMR (400 MHz, $CDCl_3$): 6.06 (br. *s*, H–C(9)); 4.89, 4.80 (2*d*, $^2J$ = 6.4, $OCH_2O$);

4.44 (*dd*, $^3J$ = 10.3, 6.6, H–C(3)); 4.10 (*dd*, $^2J$ = 11.1, $^3J$ = 4.6), 3.92 (*dd*, $^2J$ = 11.1, $^3J$ = 9.1, $CH_2$(5′)); 3.81 (br. *d*, $^3J$ = 10.1, H–C(3′)); 3.92–3.79, 3.74–3.69, 3.58–3.55 (3*m*, $OCH_2CH_2O$); 3.37 (*s*, MeO); 2.59 (*dd*, $^3J$ = 8.6, 4.5, $H_{endo}$–C(6)); 2.48 (*qd*, $^3J$ = 7.5, 6.6, H–C(2)); 1.93 (*dd*, $^2J$ = 11.5, $^3J$ = 8.6, $H_{endo}$–C(7)); 1.88 (*d*, $^4J$ = 1.6, Me–C(10)); 1.88 (*m*, H–C(2′)); 1.84 (*dd*, $^2J$ = 11.5, $^3J$ = 4.5, $H_{exo}$–C(7)); 1.60 (*s*, Me–C(8)); 1.36 (*d*, $^3J$ = 6.8, Me–C(2)); 1.33–1.10 (*m*, $CH_2$(6′), H–C(4′)); 1.20 (*s*, $Me_3C$); 1.58 (*m*, H–C(5′)); 1.02 (*d*, $^3J$ = 7.0, Me–C(2′)); 0.91–0.86 (*m*, Me–C(4′), Me(7′)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 178.5, 170.1 (2*s*, 2 CO); 141.3 (*s*, C(10)); 139.2 (*d*, C(9)); 98.4 (*t*, $OCH_2O$); 90.0, 87.1 (2*s*, C(1), C(9)); 86.0, 81.5 (2*d*, C(3), C(3′)); 71.8, 68.1, 65.3 (3*t*, $OCH_2CH_2O$, $CH_2OPiv$); 59.0 (*q*, MeO); 47.9, 40.1, 39.4, 36.5, 36.0 (5*d*, C(2), C(2′), C(4′), C(4′), C(6)); 44.1 (*t*, C(7)); 38.8 (*s*, $Me_3C$); 27.2 (*q*, $Me_3C$); 18.7 (*t*, $CH_2$(6′)); 18.6, 16.4, 14.7, 12.7, 10.8, 9.2 (6*q*, 6 Me). CI-MS ($NH_3$): 556 (6.0, $[M + NH_3]^+$), 538 (0.2, $M^+$), 463 (5), 391 (2), 353 (6), 252 (8), 197 (13), 123 (100), 89 (86).

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