118. The *Diels-Alder* Reactivity of 2,2′-Ethylidenebis[3,5-dimethylfuran] and Exploratory Chemistry of the Mono-adducts

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In the presence of Me_3Al, 1-cyanovinyl acetate added to 2,2′-ethylidenebis[3,5-dimethylfuran] (**1**) to give a 20:10:1:1 mixture of mono-adducts **4**, **5**, **6**, and **7** resulting from the same regiocontrol ('*para*' orienting effect of the 5-methyl substituent in **1**). The additions of a second equiv. of dienophile to **4**–**7** were very slow reactions. The major mono-adducts **4** (solid) and **5** (liquid) have 2-*exo*-carbonitrile groups. The molecular structure of **4** ((1*RS*,1′*RS*,2*SR*,4*SR*)-2-*exo*-cyano-4-[1-(3,5-dimethylfuran-2-yl)ethyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl acetate) was determined by X-ray single-crystal radiocrystallography. Mono-adducts **4** and **5** were saponified into the corresponding 7-oxanorbornenones **8** and **9** which were converted with high stereoselectivity into (1*RS*,1′*SR*,4*RS*,5*RS*,6*RS*)-4-[1-(3,5-dimethylfuran-2-yl)ethyl]-6-*exo*-methoxy-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-one dimethyl acetal (**12**) and its (1′*RS*)-stereoisomer **12a**, respectively. Acetal hydrolysis of **12a** followed by treatment with (*t*-Bu)$Me_2SiOSO_2CF_3$ led to silylation and pinacol rearrangement with the formation of (1*RS*,1′*RS*,5*RS*,6*RS*)-4-[(*tert*-butyl)dimethylsilyloxy]-1-(3,5-dimethylfuran-2-yl)ethyl]-5-methoxy-6-methyl-3-methylidene-2-oxabicyclo[2.2.1]heptane (**16**). In the presence of Me_3Al, dimethyl acetylenedicarboxylate added to **12** giving a major adduct **19** which was hydroborated and oxidized into (1*RS*,1′*RS*,2″*RS*,3″*RS*,4*SR*,4″*RS*,5*SR*,6*SR*)-dimethyl 5-*exo*-hydroxy-4,6-*endo*-dimethyl-1-[1-(3-*exo*,5,5-trimethoxy-2-*endo*,4-dimethyl-7-oxabicyclo[2.2.1]hept-2-yl)ethyl]-7-oxabicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**20**). Acetylation of alcohol **20** followed by C=C bond cleavage afforded (1′*RS*,1″*SR*,2*RS*,2″*SR*,3*RS*,3″*SR*,4*RS*,4″*SR*,5*RS*)-dimethyl {3-acetoxy-2,3,4,5-tetrahydro-2,4-dimethyl-5-[1-(3-*exo*,5,5-trimethoxy-2-*endo*,4-dimethyl-7-oxabicyclo[2.2.1]hept-1-yl)-ethyl]furan-2,5-diyl}bis[glyoxylate] (**24**).

Introduction. – In the preceding report [1], we have disclosed a new synthetic approach to complex and long-chain polypropionates based on the *Diels-Alder* addition of 2,2′-ethylidenebis[3,5-dimethylfuran] (**1**). This bisfuran derivative adds to methyl bromopropynoate giving a 7:1 mixture of the mono-adducts **2** and **3**. Because of the concurrent decomposition of **1**–**3** under prolonged heating, it could not be established whether the regioselectivity and the face selectivity observed for the mono-cycloaddition of **1** to methyl bromopropynoate are due to a kinetic control only or/and to a thermodynamic control. Even using neat dienophile as solvent, no bis-adduct of **1** could be observed after 5 days at 25°. With the hope to learn more about the factors responsible for the selectivities mentioned here above, we studied the *Diels-Alder* additions of **1** to 1-cyanovinyl acetate, a masked ketene known to react readily with furans [2] [3]. We also explored routes to convert the mono-adducts so-obtained into polysubstituted 2,2′-ethylidenebis[7-oxabicyclo[2.2.1]heptane] derivatives in highly stereoselective fashions.

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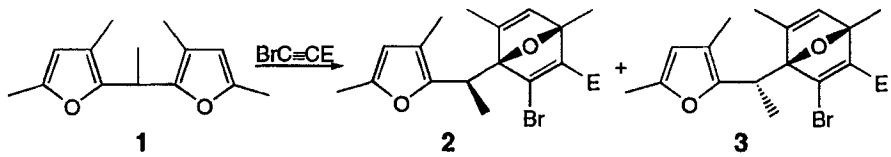
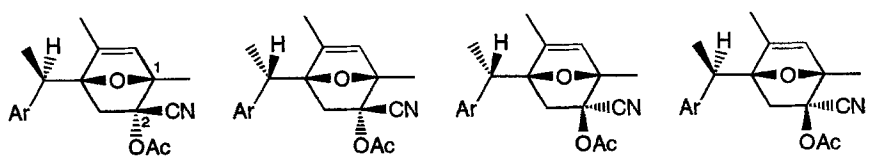
Scheme 1



1 **2** **3**

E = COOMe

***Diels-Alder* Mono-additions.** – In the absence of a *Lewis*-acid promoter, the *Diels-Alder* addition of **1** to 1-cyanovinyl acetate was a very slow reaction at 25°. For a 1:1 mixture of **1** and the dienophile (neat), a 6% yield of a 4:4:1:1 mixture of mono-adducts **4**, **5**, **6**, and **7** was obtained after 4 days at 25°. The proportion of these mono-adducts did not vary during the reaction. Heating above 25° increased the polymerization of **1** and of the dienophile (in the presence of radical scavenging agents such as hydroquinone or 2,6-bis(*tert*-butyl)-*para*-cresol). In the presence of 0.5 equiv. of ZnI_2, a 1.5:1 mixture of **1** and 1-cyanovinyl acetate generated a 4:2:3:3 mixture of **4**, **5**, **6**, and **7** after 3 days at 25° (30% yield). Because of reduced solubility of ZnI_2 at lower temperature, the reaction could not be carried out below 20°. $BF_3 \cdot Et_2O$ was quite soluble both in **1** and in the dienophile, but led to fast decomposition of a 1:1 mixture of **1** and 1-cyanovinyl acetate. *Lewis* acids such as [Eu(hfc)$_3$] [4] did not promote the cycloaddition at 25°. We finally found that the best yield and stereoselectivity were obtained when a 1:1 mixture of **1** and 1-cyanovinyl acetate was mixed with 1 equiv. of Me_3Al as 2M solution in toluene at −20° and allowed to react at 0° for 4 days. A 20:10:1:1 mixture of mono-adducts **4**, **5**, **6**, and **7** was formed (50% yield). Crystallization of this mixture from hexane (twice) provided pure **4** (31%), and flash chromatography of the mother liquor furnished **5** (15%). Changing the relative amount of $AlMe_3$ and of the temperature (−20 to +25°) affected the product ratio **4** + **5**/**6** + **7** but not that of **4**/**5**. These results demonstrate that the face selectivity of the *Diels-Alder* addition of **1** to 1-cyanovinyl acetate is bad both under the *Lewis*-acid-promoted conditions (−20°) and the thermal conditions (25°).



4 **5** **6** **7**

Ar = 3″,5″-dimethylfuran-2″-yl

No trace of the regioisomers of **4**–**7** could be detected in the crude reaction mixtures (400-MHz ^{1}H-NMR) after prolonged staying at 25°, suggesting that these adducts are significantly less stable than **4**–**7**, or that, as we believe, the energy barrier for their formation is significantly higher than that of the reactions leading to **4**–**7**. The kinetically controlled regioselectivity of the *Diels-Alder* additions of **1** to 1-cyanovinyl acetate and to methyl bromopropynoate can be attributed to the '*para*'-orienting effect of the 5-methyl group of the 3,5-dimethylfuran unit [4]. Apparently, the Br substituent in methyl bromo-

propynoate is necessary for the dienophile to feel the difference in bulk between the prochiral faces of the furan units of **1**. No double additions of 1-cyanovinyl acetate to **1** was observed in the presence of a large excess of the dienophile and after several days at 25°. This can be attributed to an increase of the steric hindrance experienced by the dienophile when attacking mono-adducts of **1** rather than **1**. Alternatively, **1** might be considered similar to 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptanes and 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene derivatives in what makes their *Diels-Alder* reactivity higher than that of their corresponding mono-adducts (changes in the exothermicity of the two successive cycloadditions [5]).

Structure of the Adducts. – Adduct **4** was submitted to single-crystal X-ray diffraction (*Table 1*) for which the molecular structure shown in the *Figure* was obtained (see *Table 2* for bond lengths and angles)[2]). As for a large number of 7-oxabicyclo[2.2.1]hept-2-ene derivatives [6], the endocyclic double bond of **4** is not planar as shown by the torsional angle C(1)–C(6)–C(5)–C(6) of −171.5°. The Me group at C(5) bends toward the *endo* face of the bicyclic olefin by *ca.* 8.5°. Furthermore, the oxa bridge in **4** is 'repelled' by the C(5)–C(6) bond as the angle between the average planes C(1)–C(6)–C(5)–C(4) and C(1)–O(7)–C(4) is 130.7° whereas angle between average planes C(1)–C(2)–C(3)–C(4) and C(1)–O(7)–C(4) is 119.1° (see *Table 2*).

Saponification of **4** and **5** followed by treatment with formaline gave the corresponding ketones **8** and **9**, respectively, which are diastereoisomeric because of the ethylidene link. Adducts **4** and **5** are similar regioisomers, since [Eu(hfc)$_3$]-induced shifts in the

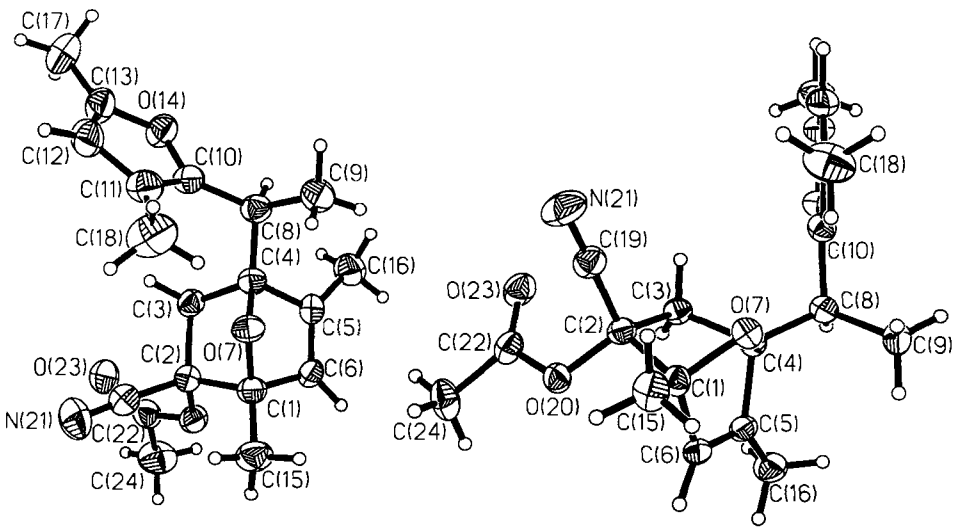


Figure. *Two representations of the molecular structure of* **4**. Arbitrary numbering.

[2]) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/5. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: teched@chemcrys. cam.ac. uk).

Table 1. *Crystal Data and Structure Refinement for (1*RS,*1'*RS,*2*SR,*4*SR*)-2-Cyano-4-[1-(3,5-dimethylfuran-2-yl)ethyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Acetate* (**4**)

Empirical formula	$C_{19}H_{23}NO_4$	Absorption coefficient	0.085 mm^{-1}
Formula weight	329.28	$F(000)$	352
Temperature	293 (2) K	θ Range for data collection	2.18 to 22.53°
Radiation	MoK_α (0.71073 Å)	Index ranges	$-8 \le h \le 8$, $-11 \le k \le 11$, $-12 \le l \le 12$
Crystal system	triclinic		
Space group	$P\bar{1}$	Reflections collected	4682
Unit cell dimension	a = 8.197 (2) Å, α = 114.72 (2)°	Independent reflections	2338 (R_{int} = 0.0237)
		Refinement method	full-matrix least-squares on F^2
	b = 10.845 (2) Å, β = 102.63 (2)°	Data/restraints/parameters	2338/0/241
	c = 11.514 (3) Å, γ = 92.46 (2)°	Weight function	$1/G^2(F^2)$
		Goodness-of-fit on F^2	4.187
Volume	896.8 (4) $Å_3$	Final R indices ($I > 2\sigma(I)$)	$R1$ = 0.0494, $wR2$ = 0.0925
Z	2	R indices (all data)	$R1$ = 0.0595, $wR2$ = 0.0932
Density (calc.)	1.220 Mg/m^3	Extinction coefficient	0.038 (3)
		Largest diff. peak and hole	0.269 and −0.275 $eÅ^{-3}$

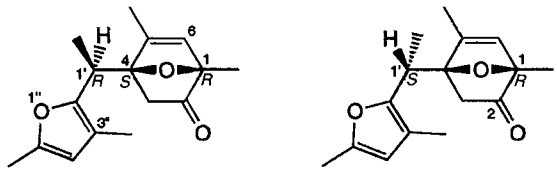
Table 2. *Selected Bond Lengths* [Å], *Bond Angles* [°], *and Torsion Angles* [°] *for* **4**[a])

O(7)–C(1)	1.433 (3)	O(14)–C(10)	1.387 (3)
O(7)–C(4)	1.451 (3)	C(1)–O(7)–C(4)	97.5 (2)
C(1)–C(6)	1.502 (3)	C(5)–C(4)–C(3)	104.6 (2)
C(1)–C(2)	1.565 (3)	C(6)–C(5)–C(4)	105.5 (2)
C(2)–C(3)	1.546 (3)	C(12)–C(13)–O(14)	108.5 (2)
C(4)–C(5)	1.529 (3)	O(14)–C(13)–C(17)	116.5 (3)
C(3)–C(4)	1.543 (3)	C(11)–C(10)–C(8)	136.3 (2)
C(5)–C(6)	1.312 (3)	C(5)–C(6)–C(1)	107.3 (2)
C(12)–C(11)	1.424 (4)	C(6)–C(5)–C(16)	130.7 (2)
C(13)–C(12)	1.331 (4)	C(16)–C(5)–C(4)	123.3 (2)
C(10)–C(11)	1.349 (3)		
Torsion angles:			
C(1)–C(6)–C(5)–C(4)	−0.1	C(11)–C(10)–C(8)–C(4)	69.9
C(1)–C(6)–C(5)–C(16)	−171.5	C(11)–C(10)–C(8)–C(9)	−57.9
C(5)–C(4)–C(8)–C(10)	169.5	C(15)–C(1)–C(6)–C(5)	−154.1
C(5)–C(4)–C(8)–C(9)	−62.4	C(8)–C(4)–C(5)–C(6)	152.3
Angles between average planes:			
plane 1: C(1)–C(2)–C(3)–C(4)		plane 2: C(1)–O(7)–C(4)	
plane 3: C(1)–C(6)–C(5)–C(4)			
< (1,2): 119.1	< (1,3): 110.2	< (2,3): 130.7	

[a]) Symmetry transformations were used to generate equivalent atoms.

^{1}H-NMR spectra of ketones **8** and **9** were very similar (the largest induced shifts being found for CH_2(3) and the Me group at the bridgehead centre C(1)). NOE Measurements in the ^{1}H-NMR spectra of **4** and **5** established the *endo* relative configuration of the acetate groups (NOE between MeCO and H–C(6); NOE between CH_2(3) and MeC(1')(ethylidene link)).

Saponification of adduct **6** and **7**, followed by treatment with formaline afforded ketones **9** and **8**, respectively. The absence of NOE between proton signals of the acetate moieties and H–C(6) in the ^{1}H-NMR spectra of **6** and **7** confirmed the *exo* relative configuration of the acetate groups in these adducts.

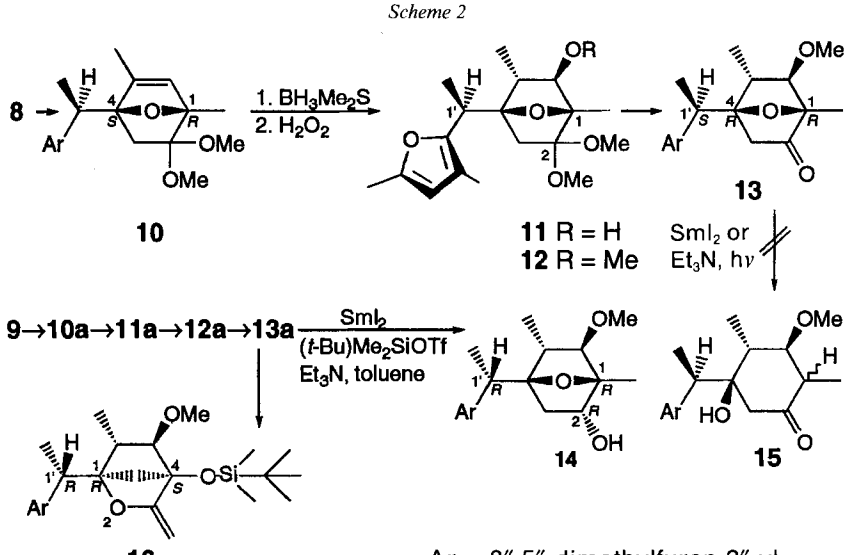


8 **9**

Exploratory Chemistry of 7-Oxanorbornenone 8. – Protection of the ketone moiety of **8** as a dimethyl acetal ($HC(OMe)_3$, K-10 montmorillonite) gave **10** (87%) the hydroboration of which ($BH_3 \cdot Me_2S$, Et_2O) followed by oxidative workup (30% H_2O_2, 2N NaOH) [7] provided the *exo*-alcohol **11** (79%; *Scheme 2*). No trace of *endo*-alcohol or of a regioisomeric alcohol could be detected (400-MHz ^{1}H-NMR) in the crude reaction mixture. The *exo* relative configuration of the OH group of **11** was given by its ^{1}H-NMR spectrum which showed also a typical W coupling constant ^4J of 1.9 Hz between H_{exo}–C(3) and H_{exo}–C(5) [8]. Alcohol **11** was converted into its methyl ether (NaH, MeI) **12** (95%). Acidic hydrolysis (acetone/H_2O, *Nafion NR50*) of **12** afforded ketone **13** (88%). Attempts to open the 7-oxanorbornanone ether bridge under basic conditions (E_{1cb}-type of β-C–O cleavage [9]) were not met with success. Applying the photo-induced reductive method of *Cossy* [10] to ketone **13a** derived from **9** (*via* dimethyl acetal **10a**, alcohol **11a**, and methyl ether **12a**; see *Exper. Part*) led to a complex mixture from which the *endo*-alcohol **14** was isolated in 5% yield only. Using SmI_2 (THF, HMPA) [11] led to the same product of reduction in a somewhat better yield (47%). No trace of the expected β-hydroxycyclohexanone **15** could be seen in the crude reaction mixture (*Scheme 2*).

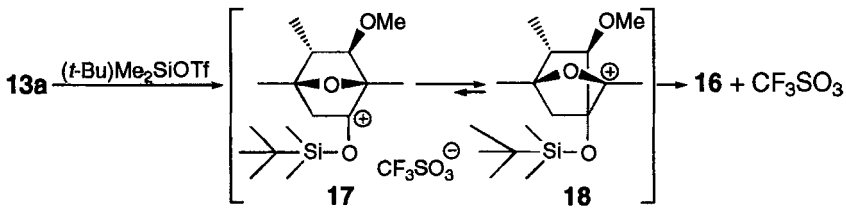
Under acidic conditions [12], the 7-oxanorbornanone **13a** refused to undergo oxa ring opening or was polymerized. We finally discovered that treatment of **13a** with (*t*-Bu)$Me_2SiOSO_2CF_3$ (CH_2Cl_2, 20°, 3 days) induces a skeletal rearrangement and silylation

Scheme 2



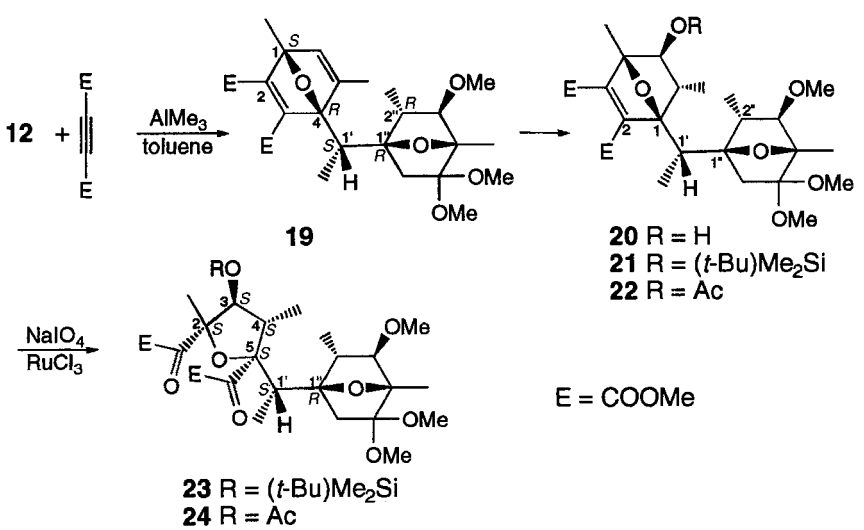
leading to the 3-methylidene-2-oxabicyclo[2.2.1]heptane derivative **16** in 50% yield. The structure of **16** was deduced from its spectral data (see *Exper. Part*) and with the help of double-irradiation experiments in its ^{1}H-NMR spectrum. Its formation can be interpreted (*Scheme 3*) in terms of the formation of the oxycarbenium intermediate **17** which undergoes a pinacol rearrangement into **18** that, after proton loss, generates **16**.

Scheme 3



The 2,4-dimethylfuran unit of **8** and **10–12** refused to add to dienophiles such as 1-cyanovinyl acetate or methyl bromopropynoate (prolonged heating or the use of *Lewis* acid led to polymerization only). We finally found that dimethyl acetylenedicarboxylate adds very slowly to **12** at 20° giving a mixture of the two possible *Diels-Alder* adducts in low yield together with polymers and products of decomposition. In the presence of 1 equiv. of Me_3Al and a three-fold excess of dimethyl acetylenedicarboxylate, **12** gave a major adduct **19** (0–20°, 14 h, toluene; *Scheme 4*). The crude reaction mixture was not purified because of the instability of the adducts obtained and was submitted directly to hydroboration with an excess of $BH_3 \cdot Me_2S$ in Et_2O. After oxidative workup using $NaBO_3 \cdot 4H_2O$, hydroxy diester **20** was isolated as the main compound (34% yield, two steps). Protection of alcohol **20** through silylation and acetylation provided **21** (85%) and

Scheme 4



22 (80%), respectively. The relative configuration of the 7-oxanorbornadiene moiety of **19** was not established unambiguously. However, it was consistent with the spectral data collected for **20–22** and with the facial selectivity expected for the *Diels-Alder* additions of **13** for which the face of the 3,5-dimethylfuran-2-yl moiety (see *Fig.*) *anti* with respect to C(3) of the 7-oxanorbornane unit is preferred. More work is definitely required to put this hypothesis on firmer ground.

Ozonolysis [13] of **21** and **22** failed to furnish the expected diketones **23** and **24**. Treatment of **21** and **23** with $NaIO_4/RuCl_3$ in a 2:2:3 mixture of $CCl_4/MeCN/H_2O$ [14] provided the desired products of C=C bond cleavage **23** (75%) and **24** (78%), respectively (*Scheme 4*). We are now exploring various routes to transform these compounds into long-chain polypropionate fragments.

Conclusion. – The 2,2′-ethylidenebis[3,5-dimethylfuran] (**1**) gives *Diels-Alder* mono-adducts much faster than the corresponding bis-adducts. With nonsymmetrical dienophiles such as 1-cyanovinyl acetate and methyl bromopropynoate, the cycloadditions are highly regioselective probably because of the '*para*'-orienting effect of the 5-methyl substituent. Face selectivity for the *Diels-Alder* additions of **1** is good only for the acetylenic dienophile (BrC≡C–COOMe). The *Diels-Alder* mono-adducts of **1** can be converted into polyfunctional 7-oxabicyclo[2.2.1]heptane derivatives, their 1-(3,5-dimethylfuran-2-yl)ethyl appendage adding only to very strong dienophiles such as methyl acetylenedicarboxylate.

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Experimental Part

General. See [1].

*(1*RS,*1′*RS,*2*SR,*4*SR*)-2*-exo-*Cyano-4-[1′-(3,5-dimethylfuran-2-yl)ethyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]-hept-5-en-2*-endo-*yl Acetate* (**4**). To the mixture of 2,2′-ethylidenebis[3,5-dimethylfuran] (0.46 g, 2.1 mmol) and 1-cyanovinyl acetate (0.23 g, 2.05 mmol), 2M Me_3Al in toluene (1.02 ml, 2.05 mmol) was added at −20°. The mixture was stirred at 0° for 4 days. Sat. aq. $NaHCO_3$ soln. was then added. After filtration and extraction with $CHCl_3$, the combined org. phase was dried ($MgSO_4$) and evaporated. The residue was crystallized from hexane: 0.21 g (31%) of **4**. M.p. 108–109°. UV (MeCN): 213 (6550). IR (CH_2Cl_2): 3500–3400, 2980, 2940, 2880, 2240, 1750, 1640, 1570, 1440, 1390, 1370, 1250, 1235, 1220, 1200, 1170, 1150, 1135, 1120, 1080, 1010, 1000, 980, 950, 940. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.75 (*d*, ^4J = 0.5, H–C(4″)); 5.70 (*q*, ^4J = 1.6, H–C(6)); 33.1 (*q*, ^3J = 7, H–C(1′)); 2.76 (*d*, ^2J = 13.5, H_{endo}–C(3)); 2.21 (*d*, ^4J = 0.5, Me–C(5″)); 2.05 (*s*, Ac); 1.92 (*s*, Me–C(3″)); 1.76 (*s*, Me–C(1)); 1.69 (*d*, ^4J = 1.6, Me–C(5)); 1.63 (*d*, ^2J = 13.5, H_{endo}–C(3)); 1.31 (*d*, ^3J = 7, Me(2′)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 169.2 (*s*, CO); 151.8 (*s*, C(5″)); 149.9 (*s*, C(2″)); 147.6 (*s*, C(5)); 129.4 (*d*, C(6)); 118.3 (*s*, CN); 116.1 (*s*, C(3″)); 108.8 (*d*, C(4″)); 92.7 (*s*, C(1)); 86.94 (*s*, C(4)); 79.00 (*s*, C(2)); 45.4 (*t*, C(3)); 31.9 (*d*, C(1′)); 20.7, 15.2, 14.9, 13.5, 12.1, 10.0 (6*q*, 6 Me). EI-MS: (70 eV): 329 (3, M^+), 218 (14), 204 (70), 203 (80), 159 (2), 123 (100), 109 (6), 91 (3), 77 (5), 65 (4), 55 (5). Anal. calc. for $C_{19}H_{23}NO_4$ (329.40): C 69.28, H 7.04, N 4.25; found: C 69.26, H 6.99, N 4.29.

*(1*RS,*1′*SR,*2*SR,*4*SR*)-2*-exo-*Cyano-4-[1′-(3,5-dimethylfuran-2-yl)ethyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]-hept-5-en-2*-endo-*yl Acetate* (**5**). *Lobar* column chromatography (AcOEt/light petroleum ether 1:6, 6.5 ml/min) of the mother liquor obtained above gave 10 g (15%) of **5**. Colorless liquid. UV (MeCN): 217 (1600). IR (CH_2Cl_2): 3050, 2980, 2940, 2880, 2240, 1755, 1630, 1580, 1430, 1390, 1370, 1235, 1210, 1200, 1170, 1090, 1075, 1050, 1000, 900, 810. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.74 (*s*, H–C(4″)); 5.71 (*q*, ^4J = 1.6, H–C(6)); 3.27 (*q*, ^3J = 7.2, H–C(1′)); 2.76 (*d*, ^2J = 13.4, H_{exo}–C(3)); 2.20 (*s*, Me–C(5″)); 2.03 (*s*, Ac); 1.96 (*s*, Me–C(3″)); 1.86 (*d*, ^4J = 1.6, Me–C(5));

1.74 (*s*, Me–C(1)); 1.63 (*d*, ^2J = 13.4, H_{endo}–C(3)); 1.36 (*d*, ^3J = 7.2, Me(2′)); structure confirmed by 2D ^{1}H-NOESY. ^{13}C-NMR (62.9 MHz, $CDCl_3$): 169.1 (*s*, CO); 151.2 (*s*, C(5″)); 149.5 (*s*, C(2″)); 147.5 (*s*, C(5)); 130.1 (*d*, C(6)); 118.2 (*s*, CN); 116.1 (*s*, C(3″)); 108.9 (*d*, C(4″)); 93.4 (*s*, C(1)); 87.0 (*s*, C(4)); 79.1 (*s*, C(2)); 47.5 (*t*, C(3)); 33.8 (*d*, C(1′)); 20.6 (*q*, *Me*CO); 15.2, 14.6, 13.4, 13.2, 10.4 (5*q*, 5 Me).

*(1*RS,*1′*RS,*4*SR*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-one* (**8**). A 30% MeONa soln. in MeOH (0.09 ml) was added into a soln. of **4** (0.08 g, 0.24 mmol) in MeOH (1 ml). The mixture was stirred at 25° for 2 h and then 30% aq. formaldehyde (0.09 ml) was added. After stirring for 15 min, the mixture was poured into H_2O/CH_2Cl_2 1:1. The aq. phase was extracted with CH_2Cl_2 (3 × 10 ml) and the combined org. phase washed with brine (10 ml, twice), dried ($MgSO_4$), and evaporated 0.058 g (92%) of **8**. Slightly yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.75 (br. *s*, H–C(4″)); 5.70 (*d*, ^4J = 1.6, H–C(6)); 3.37 (*q*, ^3J = 7.2, H–C(1′)); 2.21 (*s*, Me–C(5″)); 2.09 (*d*, ^2J = 15.8, H_{exo}–C(3)); 1.94 (*s*, Me–C(3″)); 1.90 (*d*, ^2J = 15.8, H_{endo}–C(3)); 1.72 (*d*, ^4J = 1.6, Me–C(5)); 1.47 (*s*, Me–C(1)); 1.37 (*d*, ^3J = 7.2, Me(2′)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 209.9 (*s*, C(2)); 154.3 (*s*, C(2″)); 149.8 (*s*, C(5″)); 147.8 (*s*, C(5)); 127.9 (*d*, C(6)); 115.9 (*s*, C(3″)); 108.7 (*d*, C(4″)); 91.0 (*s*, C(1)); 87.7 (*s*, C(4)); 36.3 (*t*, C(3)); 32.5 (*d*, C(1′)); 14.2, 13.5, 13.3, 12.2, 10.0 (5*q*, 5 Me).

*(1*RS,*1′*SR,*4*SR*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-one* (**9**). As described for **8** from **5**: 90% of **9**. Colorless oil. UV (MeCN): 216 (8800), 309 (1000). IR (CH_2Cl_2): 3050, 2990, 2920, 2880, 1750, 1640, 1570, 1440, 1410, 1380, 1150, 1100, 1060, 950, 880, 660. ^{1}H-NMR ($CDCl_3$, 250 MHz): 5.77 (br. *s*, H–C(4″)); 5.68 (*q*, ^4J = 1.6, H–C(6)); 3.36 (*d*, ^3J = 7.2, H–C(1′)); 2.21 (*s*, Me–C(5″)); 2.17 (*d*, ^2J = 15.8, H_{exo}–C(3)); 1.96 (*s*, Me–C(3″)); 1.86 (*d*, ^2J = 15.8, H_{endo}–C(3)); 1.87 (*d*, ^4J = 1.6, Me–C(5)); 1.46 (*s*, Me–C(1)); 1.44 (*d*, ^3J = 7.2, Me(2′)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 209.7 (*s*, CO); 154.2 (*s*, C(2″)); 149.6 (*s*, C(5″)); 147.8 (*s*, C(5)); 128.4 (*d*, C(6)); 117.1 (*s*, C(3″)); 109.0 (*d*, C(4″)); 91.7 (*s*, C(1)); 87.4 (*s*, C(4)); 38.1 (*t*, C(3)); 35.0 (*d*, C(1′)); 14.5, 14.0, 13.5, 12.3, 10.5 (5*q*, 5 Me). EI-MS (70 eV): 260 (29), 230 (2), 218 (37), 203 (100), 174 (2), 123 (82), 109 (21), 95 (88), 76 (12).

*(1*RS,*1′*RS,*4*SR*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-one Dimethyl Acetal* (**10**). To **8** (0.15 g, 0.577 mmol) in hexane (2.1 ml) and trimethyl orthoformate (7 ml), montmorillonite K-10 clay (4.2 g) was added, and the resulting suspension was stirred at 25° for 8 h. Then AcOEt was added, the clay was filtered off and washed with AcOEt (250 ml), the filtrate washed with sat. aq. $NaHCO_3$ soln. (25 ml, twice), dried ($MgSO_4$), and evaporated, and the colorless oil crystallized from light petroleum ether: 0.153 g (87%) of **10**. White crystals. M.p. 87–88°. IR (KBr): 2990, 2940, 2900, 2820, 1640, 1580, 1460, 1450, 1370, 1250, 1210, 1110, 1080, 1050, 1020, 980, 880, 860, 820. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.78 (br. *q*, ^4J = 1.6, H–C(6)); 5.73 (br. *s*, H–C(4″)); 3.33 (*q*, ^3J = 7.2, H–C(1′)); 3.30, 3.18 (2*s*, 2 MeO); 2.20 (br. *s*, Me–C(5″)); 2.18 (*d*, ^2J = 11.8, H_{exo}–C(3)); 1.92 (*s*, Me–C(3″)); 1.60 (*d*, ^4J = 1.6, Me–C(5)); 1.52 (*s*, Me–C(1)); 1.39 (*d*, ^2J = 11.8, H_{endo}–C(3)); 1.30 (*d*, ^3J = 7.2, Me(2′)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 149.4, 149.1, 148.8 (3*s*, C(2″), C(5″), C(5)); 131.4 (*d*, C(6)); 115.3 (*s*, C(3″)); 111.0 (*s*, C(2)); 108.5 (*d*, C(4″)); 90.8, 87.2 (2*s*, C(1), C(4)); 50.6, 50.3 (2*q*, C(8), C(9)); 38.6 (*t*, C(3)); 32.7 (*d*, C(1′)); 15.2, 14.7, 13.3, 12.5, 10.0 (5*q*, 5 Me). EI-MS (70 eV): 306 (2, M^+), 275 (12), 233 (7), 218 (38), 203 (100), 161 (3), 123 (29), 109 (16), 91 (6). Anal. calc. for $C_{18}H_{26}O_4$ (306.406): C 70.56, H 8.55; found: C 70.48, H 8.51.

*(1*RS,*1′*SR,*4*SR*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-one Dimethyl Acetal* (**10a**). As described for **10**, with **9** (154 mg, 0.59 mmol): 80% of **10a**. Colorless oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.85 (*q*, ^3J = 1.5, H–C(6)); 5.75 (br. *s*, H–C(4″)); 3.47 (*q*, ^3J = 7.0, H–C(1′)); 3.29, 3.08 (2*s*, 2 MeO); 2.29 (*d*, ^2J = 16.0, H_{exo}–C(3)); 2.11 (br. *s*, Me–C(5″)); 2.00 (*s*, Me–C(3″)); 1.97 (*d*, ^4J = 1.5, Me–C(5)); 1.78 (*s*, Me–C(1)); 1.64 (*d*, ^3J = 7.0, Me(2′)); 1.59 (*d*, ^2J = 16.0, H_{endo}–C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 149.0, 148.6, 148.5 (3*s*, C(5), C(2″), C(5″)); 132.2 (*s*, C(6)); 115.7 (*s*, C(3″)); 111.3 (*s*, C(2)); 108.9 (*d*, C(4″)); 92.2 (*s*, C(1)); 87.4 (*s*, C(4)); 50.6, 50.4 (2*q*, C(8), C(9)); 42.1 (*t*, C(3)); 35.2 (*d*, C(1′)); 15.3, 14.3, 14.0, 13.4, 10.5 (5*q*, 5 Me).

*(1*RS,*1′*SR,*4*RS,*5*RS,*6*RS*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-6-*exo*-hydroxy-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* (**11**). To a soln. of **10** (0.707 g, 2.31 mmol) in 10 ml of anh. Et_2O at −40°, 10M BH_3 in Me_2S (0.23 ml, 1.3 equiv.) was added dropwise under stirring. Then the cooling bath was removed and the mixture stirred at 25° for 3 h. More BH_3 in Me_2S (0.05 ml) was added and the mixture stirred for 2 more h. Aq. 3N NaOH (0.7 ml) and 30% H_2O_2 soln. (0.8 ml) were added, and the resulting mixture was heated under reflux for 3 h. The aq. layer was extracted with Et_2O (3 × 5 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. Chromatography (silica gel (35 g), AcOEt/light petroleum ether 1:6, R_f 0.07) gave a colorless oil that was crystallized from AcOEt/light petroleum ether: 0.59 g (79%) of **11**. Colorless crystals. M.p. 124–125°. UV (MeCN): 219 (8900). IR (CH_2Cl_2): 3600, 3040, 2980, 2960, 2880, 1450, 1370, 1120, 1100, 1050, 1030, 880. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.71 (br. *s*, H–C(4″)); 3.62 (*dd*, ^3J = 10, ^3J = 2.4, H–C(6)); 3.29, 3.19 (2*s*, 2 MeO); 3.13 (*q*, ^3J = 7.2, H–C(1′)); 2.19 (*d*, ^4J = 0.9, Me–C(5″)); 2.14 (*dd*, ^4J = 1.9, ^2J = 13.0, H_{exo}–C(3)); 1.91 (*s*, Me–C(3″));

1.79 (*d*, ^2J = 13.0, H_{endo}–C(3)); 1.69 (*ddq*, ^3J = 7.1, 2.4, ^4J = 1.9, H–C(5)); 1.51 (*d*, ^3J = 10.0, OH–C(6)); 1.40 (*s*, Me–C(1)); 1.30 (*d*, ^3J = 7.2, Me(2′)); 0.68 (*d*, ^3J = 7.1, Me–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 149.2, 148.6 (2*s*, C(2″), C(5″)); 115.3 (*s*, C(3″)); 108.5 (*d*, C(4″)); 108.1 (*s*, C(2)); 89.1, 88.4 (2*s*, C(1), C(4)); 81.1 (*d*, C(6)); 54.6 (*d*, C(5)); 50.1, 48.6 (2*q*, C(8), C(9)); 36.5 (*t*, C(3)); 36.1 (*d*, C(1′)); 14.7, 13.3, 13.3, 12.7, 9.8 (5*q*, 5 Me). EI-MS (70 eV): 324 (17, M^+), 275 (11), 251 (100), 203 (20), 169 (39), 155 (21), 123 (44), 109 (29), 85 (42). Anal. calc. for $C_{18}H_{28}O_5$ (324.41): C 66.64, H 8.70; found: C 65.70, H 8.64.

*(1*RS,*1′*RS,*4*RS,*5*RS,*6*RS*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-6*-exo-*hydroxy-1,5*-endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* (**11a**). As described for **11**, with **10a** (145 mg, 0.44 mmol): 0.104 g (68%) of **11a**. Colorless oil. UV (MeCN): 220 (7000). IR (CH_2Cl_2): 3600, 3060, 3000, 2940, 2840, 1570, 1450, 1380, 1340, 1280, 1120, 1050, 1030, 880. ^{1}H-NMR (250 MHz, C_6D_6): 5.66 (br. *s*, H–C(4″)); 3.82 (br. *d*, ^3J = 7.0, OH–C(6)); 3.21 (*q*, ^3J = 7.2, H–C(1′)); 3.06, 2.96 (2*s*, 2 MeO); 2.12 (*dq*, ^3J = 7.1, 7.0, H–C(5)); 2.05 (*d*, ^4J = 0.8, Me–C(5″)); 1.91, (*s*, H–C(3)); 1.86 (*s*, Me–C(3″)); 1.77 (br. *d*, ^3J = 7.0, H–C(6)); 1.62 (*s*, Me–C(1)); 1.52 (*d*, ^3J = 7.2, Me(2′)); 1.08 (*d*, ^3J = 7.1, Me–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 149.1, 148.0 (2*s*, C(2″), C(5″)); 115.1 (*s*, C(3″)); 108.8 (*d*, C(4″)); 108.0 (*s*, C(2)); 89.4, 89.3 (2*s*, C(1), C(4)); 81.0 (*d*, C(6)); 50.1 (2*q*, C(8), C(9)); 48.5 (*d*, C(5)); 41.6 (*t*, C(3)); 35.5 (*d*, C(1′)); 13.3, 12.8, 12.8, 10.3 (5*q*, 5 Me). EI-MS (70 eV): 324 (16, M^+), 306 (3), 292 (16), 251 (74), 217 (32), 202 (22), 169 (55), 139 (25), 123 (84), 109 (100), 95 (25), 80 (44).

*(1*RS,*1′*SR,*4*RS,*5*RS,*6*RS*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-6*-exo-*methoxy-1,5*-endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* (**12**). To a soln. of **11** (0.59 g, 1.81 mmol) in anh. Et_2O (10 ml), NaH (80% in white oil; 0.33 g, 6 equiv.) was introduced and the suspension stirred at 25° for 30 min. MeI (0.7 ml, 11 mmol, 1.54 g) was added. After stirring under N_2 at 25° for 2 days, MeI (1 ml) was added. After further stirring (24 h), purification by FC (silica gel (15 g), AcOEt/light petroleum ether 1:12, R_f 0.19) gave a colorless oil that was crystallized from AcOEt/light petroleum ether: 0.581 g (95%) of **12**. Colorless crystals. M.p. 127–128°. UV (MeCN): 219 (9100). IR (KBr): 3100, 2990, 2940, 2820, 1640, 1570, 1450, 1380, 1290, 1260, 1240, 1160, 1130, 1100, 1050, 940, 900, 880, 820, 790. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.70 (br. *s*, H–C(4″)); 3.33, 3.24, 3.20 (3*s*, 3 MeO); 3.16 (*q*, ^3J = 7.1, H–C(1′)); 2.18 (*dd*, ^4J = 2.5, ^2J = 13.0, H_{exo}–C(3)); 2.17 (*d*, ^4J = 0.9, Me–C(5″)); 1.91 (*s*, Me–C(3″)); 1.78 (*ddq*, ^4J = 2.5, ^3J(5,6) = 2.5, ^3J = 7.2, H–C(5)); 1.75 (*d*, ^2J = 13.0, H_{endo}–C(3)); 1.41 (*s*, Me–C(1)); 1.28 (*d*, ^3J = 7.1, Me(2′)); 0.62 (*d*, ^3J = 7.2, Me–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 149.2, 149.0 (2*s*, C(2″), C(5″)); 115.1 (*s*, C(3″)); 108.5 (*d*, C(4″)); 108.3 (*s*, C(2)); 89.8 (*d*, C(6)); 89.0, 88.7 (2*s*, C(1), C(4)); 56.9 (*q*, C(11)); 50.8 (*d*, C(5)); 50.1, 48.7 (2*q*, C(8), C(9)); 36.4 (*t*, C(3)); 36.1 (*d*, C(1′)); 14.9, 14.4, 13.4, 12.8, 9.8 (5*q*, 5 Me). CI-MS (NH_3): 356 (14, $[M + 18]^+$), 338 (15, M^+), 307 (100), 275 (52), 251 (96), 219 (10), 183 (17), 169 (42), 155 (13), 123 (70), 109 (17). Anal. calc. for $C_{19}H_{30}O_5$ (338.448): C 67.43, H 8.93; found: C 67.37, H 8.87.

*(1*RS,*1′*RS,*4*RS,*5*RS,*6*RS*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-6*-exo-*methoxy-1,5*-endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* (**12a**). As described for **12**, with **11a** (290 mg, 0.9 mmol): 0.180 g (60%) of **12a**. Colorless oil. UV (MeCN): 219 (8900). IR (CH_2Cl_2): 3100, 2990, 2940, 2840, 1580, 1450, 1380, 1340, 1250, 1110, 1080, 1050, 1030, 980, 880. ^{1}H-NMR (250 MHz, C_6D_6): 5.67 (br. *q*, H–C(4″)); 3.46 (*d*, ^3J = 2.6, H–C(6)); 3.30 (*q*, ^3J = 7.1, H–C(1′)); 3.22, 3.10, 2.99 (3*s*, 3 MeO); 2.42 (*dq*, ^3J = 7.0, 2.6, H–C(5)); 2.06 (*d*, ^4J = 0.6, Me–C(5″)); 1.97 (*s*, H_{exo}–C(3), H_{endo}–C(3)); 1.89 (*s*, Me–C(3″)); 1.75 (*s*, Me–C(1)); 1.61 (*d*, ^3J = 7.1, Me–C(1′)); 1.09 (*d*, ^3J = 7.0, Me–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 148.8, 148.1 (2*s*, C(2″), C(5″)); 115.3 (*s*, C(3″)); 108.7 (*d*, C(4″)); 108.0 (*s*, C(2)); 89.7 (*d*, C(6)); 89.1, 89.0 (2*s*, C(1), C(4)); 56.8 (*q*, C(11)); 49.9, 48.3 (2*q*, C(8), C(9)); 43.7 (*d*, C(5)); 42.0 (*t*, C(3)); 36.0 (*d*, C(1′)); 14.5, 13.2, 13.0, 12.6, 10.2 (5*q*, 5 Me). EI-MS (70 eV): 332 (0.4, M^+), 292 (3), 251 (44), 231 (292), 183 (34), 169 (59), 123 (100), 109 (20), 83 (44).

*(1*RS,*1′*SR,*4*RS,*5*RS,*6*RS*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-6*-exo-*methoxy-1,5*-endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one* (**13**). To a soln. of **12** (0.555 g, 1.64 mmol) in acetone (30 ml), H_2O (20 ml) and *Nafion NR50* (H^+ form, 0.8 g) were added. The mixture was heated under reflux for 3 h. After filtration and flash chromatography, a colorless oil was obtained that crystallized from light petroleum ether: 0.42 g (88%) of **13**. Colorless crystals. M.p. 88–89°. UV (MeCN): 218 (9000). IR (CH_2Cl_2): 3040, 2980, 2840, 2790, 1760, 1450, 1380, 1330, 1220, 1100, 1080, 990, 940. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.70 (br. *s*, H–C(4″)); 3.31 (*s*, MeO); 3.25 (*q*, ^3J = 7.1, H–C(1′)); 2.89 (*d*, ^3J = 2.8, H–C(6)); 2.48 (*dd*, ^3J = 18.0, ^4J = 2.1, H_{exo}–C(3)); 2.27 (*d*, ^2J = 18.0, H_{endo}–C(3)); 2.15 (*d*, ^4J = 0.7, Me–C(5″)); 1.97 (*ddq*, ^3J = 7.2, 2.8, ^4J = 2.1, H–C(5)); 1.90 (*s*, Me–C(3″)); 1.33 (*s*, Me–C(1)); 1.32 (*d*, ^3J = 7.1, Me(2′)); 0.56 (*d*, ^3J = 7.2, Me–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 214.0 (*s*, C(2)); 149.5, 147.9 (2*s*, C(2″), C(5″)); 115.6 (*s*, C(3″)); 108.6 (*d*, C(4″)); 89.9 (*d*, C(6)); 89.9, 88.3 (2*s*, C(1), C(4)); 57.6 (*q*, C(9)); 50.3 (*d*, C(5)); 39.5 (*t*, C(3)); 35.8 (*d*, C(1′)); 15.0, 14.6, 13.3, 10.2, 9.8 (5*q*, 5 Me). EI-MS (70 eV): 292 (23, M^+), 277 (2), 251 (5), 205 (6), 177 (25), 139 (100), 123 (64), 109 (43), 91 (13), 81 (4). Anal. calc. for $C_{17}H_{24}O_4$ (292.278): C 69.84, H 8.27; found: C 69.87, H 8.31.

*(1*RS,*1′*RS,*4*RS,*5*RS,*6*RS*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-6*-exo-*methoxy-1,5*-endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one* (**13a**). As described for **13**, with **12a** (180 mg, 0.54 mmol): 128 mg (81%) of **13a**.

Colorless crystals. M.p. 88–89°. UV (MeCN): 218 (11000). IR (CH_2Cl_2): 3040, 2980, 2840, 2780, 2720, 1760, 1580, 1450, 1380, 1330, 1230, 1100, 1080, 1030, 990, 970, 940. ^{1}H-NMR (250 MHz, C_6D_6): 5.63 (br. *s*, H–C(4″)); 3.23 (*q*, ^3J = 7.2, H–C(1′)); 2.99 (*s*, MeO); 2.82 (*d*, ^3J = 2.8, H–C(6)); 2.33 (*ddq*, ^3J = 7.1, 2.8, ^4J = 1.2, H–C(5)); 2.22 (*d*, ^2J = 17.0, H_{endo}–C(3)); 2.12 (*dd*, ^2J = 17.0, ^4J = 1.2, H_{exo}–C(3)); 2.01 (br. *s*, Me–C(5″)); 1.79 (*s*, Me–C(3″)); 1.57 (*s*, Me–C(1)); 1.48 (*d*, ^3J = 7.2, Me(2′)); 0.68 (*d*, ^3J = 7.1, Me–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 213.9 (*s*, C(2)); 149.4, 147.6 (2*s*, C(2″), C(5″)); 116.1 (*s*, C(3″)); 109.0 (*d*, C(4″)); 90.0 (*d*, C(6)); 88.9 (s, C(1), C(4)); 57.6 (*q*, C(9)); 44.7 (*d*, C(5)); 43.6 (*t*, C(3)); 35.8 (*d*, C(1′)); 15.6, 13.4, 12.8, 12.5, 10.3 (5*q*, 5 Me). EI-MS (70 eV): 292 (39, M^+), 249 (6), 205 (8), 177 (30), 139 (100), 123 (84), 109 (32), 95 (10), 77 (8). Anal. calc. for $C_{17}H_{24}O_4$ (292.378): C 69.84, H 8.22; found: C 69.91, H 8.12.

*(1*RS,*1′*RS,*2*RS,*4*RS,*5*RS,*6*RS*)-4-[1′-(3,5-Dimethylfuran-2-yl)ethyl]-6-*exo*-methoxy-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol* (**14**). To the soln. of **13a** (0.02 g, 0.071 mmol) in THF/HMPA 9:1 (0.4 ml), 3.1 ml of 0.0458M SmI_2 in THF was added dropwise (→ violet after addition of the first drop; color disappeared with time). After all SmI_2 was added, the color stayed violet-blue, and a white precipitate appeared. After 20 h stirring at 25°, the soln. turned colorless. HMPA (0.04 ml) and SmI_2 soln. (1 ml) were added. After stirring at 25° for 2 h the solvent was evaporated and the residue purified by FC (silica gel (1 g), AcOEt/light petroleum ether 1:6, R_f 0.05); 10 mg (47%) of **14**. Colorless oil. IR (CH_2Cl_2): 3600, 3040, 2980, 2920, 2820, 1600, 1450, 1380, 1230, 1100, 1080, 970, 950, 880. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.73 (br. *s*, H–C(4″)); 4.01 (*dd*, ^3J = 3.2, 10.0, H_{exo}–C(2)); 3.52 (*d*, ^3J = 3.1, H–C(6)); 3.37 (*s*, MeO); 3.14 (*q*, ^3J = 7.2, H–C(1′)); 2.20 (*d*, ^4J = 0.8, Me–C(5″)); 2.16 (*ddq*, ^3J = 7.1, 3.1, ^4J = 2.0, H–C(5)); 1.91 (*s*, Me–C(3″)); 1.90 (*ddd*, ^2J = 18.0, ^3J = 10.0, ^4J = 2.0, H_{exo}–C(3)); 1.66 (br. *s*, OH–C(2)); 1.57 (*dd*, ^2J = 18.0, ^3J = 3.2, H_{endo}–C(3)); 1.38 (*s*, Me–C(1)); 1.35 (*d*, ^3J = 7.1, Me(2′)); 0.95 (*d*, ^3J = 7.1, Me–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 149.1, 148.5 (2*s*, C(2″), C(5″)); 115.4 (*s*, C(3″)); 108.8 (*d*, C(4″)); 90.6, 86.2 (2*s*, C(1), C(4)); 88.0 (*d*, C(6)); 75.1 (*d*, C(2)); 56.9 (*q*, MeO); 45.3 (*d*, C(5)); 38.6 (*t*, C(3)); 33.7 (*d*, C(1′)); 14.6, 14.31, 13.4, 13.1, 10.0 (5*q*, 5 Me). EI-MS: (70 eV): 294 (34, M^+), 221 (3), 171 (3), 139 (79), 123 (100), 109 (18), 69 (7). Anal. calc. for $C_{17}H_{26}O_4$ (294.39): C 69.36, H 8.90; found: C 69.34, H 8.97.

*(1*RS,*1′*RS,*4*SR,*5*RS,*6*RS*)-4-[(*tert*-Butyl)dimethylsilyloxy]-1′-(3,5-dimethylfuran-2-yl)ethyl]-5-methoxy-6-methyl-3-methylidene-2-oxabicyclo[2.2.1]heptane* (**16**). To a soln. of **13a** (104 mg, 3.6 mmol) in anh. toluene (3 ml), Et_3N (5 equiv., 0.32 ml) and (*t*-Bu)$Me_2SiOSO_2CF_3$ (5 equiv., 0.4 ml) were added. After 3 days at 25°, only traces of starting material were visible by TLC (R_f 0.47) and a new product appeared (R_f 0.66, AcOEt/light petroleum ether 1:6). This product was decomposed on silica gel, on storage. It was partially decomposed by *Florisil*. After solvent evaporation, the crude oil was analyzed. IR (CH_2Cl_2): 2950, 2920, 2890, 2870, 1680, 1630, 1460, 1370, 1230, 1190, 1150, 1120, 1070, 1040, 1000, 960, 880, 870, 830. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.71 (*d*, ^3J = 0.9, H–C(4″)); 4.29, 4.02 (2 br. *s*, CH_2=C(3)); 3.46 (*s*, MeO); 3.19 (*d*, ^3J = 3.6, H–C(5)); 3.07 (*q*, ^3J = 7.3, H–C(1′)); 2.19 (*d*, ^4J = 0.9, Me–C(5″)); 1.96 (*dd*, ^2J = 12.1, ^4J = 1.9, H–C(7)); 1.95 (*s*, Me–C(3″)); 1.86 (*d*, ^2J = 12.1, H–C(7)); 1.74 (*m*, H–C(6)); 1.32 (*d*, ^3J = 7.3, Me(2′)); 1.03 (*d*, ^3J = 7.4, Me–C(6)); 0.93 (*s*, *t*-BuSi); 0.16, 0.15 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 161.6 (*s*, C(3)); 149.1, 148.0 (2*s*, C(2″), C(5″)); 115.7 (*s*, C(3″)); 109.1 (*d*, C(4″)); 91.1 (*d*, C(5)); 88.8, 85.1 (2*s*, C(1), C(4)); 77.6 (*t*, CH_2=C(3)); 58.6 (*q*, MeO); 45.3 (*d*, C(6)); 42.3 (*t*, C(7)); 33.3 (*d*, C(1′)); 25.6 (*q*, *t*-BuMe); 18.0 (*s*, *t*-Bu); 17.9, 13.9, 13.4, 10.5 (4*q*, 4 Me); −4.7, −5.0 (2*q*, MeSi). EI-MS (70 eV): 406 (24, M^+), 375 (27), 334 (11), 291 (65), 211 (12), 123 (100), 73 (54).

*(1*RS,*1′*RS,*1″*SR,*2″*SR,*3″*SR,*4*SR,*4″*SR*)-Dimethyl 1,5-Dimethyl-4-[1-(3-*exo*-5,5-trimethoxy-2-*endo*,4-dimethyl-7-oxabicyclo[2.2.1]hept-1-yl)ethyl]-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate* (**19**). A 2M soln. of Me_3Al in toluene (0.15 ml, 1 equiv.) was added to a mixture of **12** (103 mg, 0.3 mmol) and dimethyl acetylenedicarboxylate (0.11 ml, 0.89 mmol) cooled to 0°. The mixture was stirred at 0° for 15 h. MeOH (10 ml) was added to the orange-brown mixture (destruction of Me_3Al), and the mixture was filtered on silica gel. After solvent evaporation, the residue was purified by column chromatography (silica gel, AcOEt/light petroleum ether 1:6, R_f 0.11): 24 mg (18%) of **19**, unidentified products, and **12** (15%). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.30 (*q*, ^4J = 1.9, H–C(6)); 3.78, 3.77 (2*s*, 2 MeOOC); 3.32 (*s*, MeO); 3.30 (*d*, ^3J = 3.1, H–C(3″)); 3.21, 3.19 (2*s*, 2 MeO); 2.91 (*q*, ^3J = 7.2, H–C(1′)); 2.40 (*ddq*, ^3J = 7.3, 3.1, ^4J = 1.9, H–C(2″)); 2.13 (*dd*, ^2J = 12.8, ^4J = 1.9, H_{exo}–C(6″)); 2.02 (*d*, ^4J = 1.9, Me–C(5)); 1.86 (*d*, ^2J = 12.8, H_{endo}–C(6″)); 1.75, 1.37 (2*s*, Me–C(4″), Me–C(1)); 1.17 (*d*, ^3J = 7.2, Me(2′)); 1.10 (*d*, ^3J = 7.3, Me–C(2″)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 165.2, 164.9 (2*s*, 2 COO); 158.4 (*s*, C(5)); 156.9, 156.6 (2*s*, C(2), C(3)); 138.9 (*d*, C(6)); 107.6 (*s*, C(5″)); 100.4, 91.3, 88.0, 88.9 (4*s*, C(1), C(4), C(1″), C(4″)); 88.8 (*d*, C(3″)); 56.7, 52.1, 52.0, 50.0, 48.5 (5*q*, 5 MeO); 47.0 (*d*, C(2″)); 40.5 (*t*, C(6″)); 33.7 (*d*, C(1′)); 15.5, 15.2, 14.4, 14.2, 12.7 (5*q*, 5 Me). EI-MS (70 eV): 480 (0.15, M^+), 437 (16), 417 (40), 373 (14), 310 (8), 251 (13), 123 (30), 75 (100).

*(1*RS,*1′*SR,*2″*RS,*3″*RS,*4*SR,*4″*RS,*5*SR,*6*SR*)-Dimethyl 5-*exo*-Hydroxy-4,6-*endo*-dimethyl-1-[1-(3-*exo*-5,5-trimethoxy-2-*endo*,4-dimethyl-7-oxabicyclo[2.2.1]hept-1-yl)ethyl]-7-oxabicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate* (**20**). To the mixture of **12** (1.10 g, 3.25 mmol) and dimethyl acetylenedicarboxylate (1.2 ml, 1.38 g, 8.75 mmol),

2M Me_3Al (1.63 ml) was added at 0°. The soln. was stirred at 25° overnight. The resulting orange-brown soln. was cooled to −20°, and MeOH (50 ml) was added. The mixture was filtered on *Florisil* (10 g), and after solvent evaporation, the resulting oil was dried 1 h at 10^{-2} Torr. The flask was filled with Ar, and anh. Et_2O (10 ml) was added. At −40°, 10M $BH_3 \cdot Me_2S$ (0.98 ml) was added and the soln. stirred at 25° for 5 h. H_2O (5 ml), then $NaBO_3 \cdot 4\,H_2O$ (4.3 g) were added, and the mixture was stirred at 25° overnight. The aq. layer was extracted with Et_2O (10 ml, 4 times and the combined org. phase dried ($MgSO_4$) and evaporated. Column chromatography (silica gel (100 g), AcOEt/light petroleum ether 1:2, R_f 0.14) and crystallization from light petroleum ether gave 0.51 g (34%, two steps) of **20**. Colorless crystals. M.p. 78–79°. The chromatography yielded also 82 mg of **12**. **20**: UV (MeCN): 227 (4300). IR (KBr): 3500–3400, 2950, 2940, 2820, 1720, 1710, 1630, 1450, 1430, 1380, 1320, 1250, 1190, 1150, 1130, 1100, 1030, 1040, 900, 750. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.79, 3.72 (2*s*, 2 MeOOC); 3.56 (*d*, ^3J = 2.4, H–C(5)); 3.36 (*s*, MeO); 3.25 (*d*, ^3J = 2.9, H–C(3″)); 3.23, 3.19 (2*s*, 2 MeO); 2.88 (*q*, ^3J = 7.4, H–C(1′)); 2.82 (*dq*, ^3J = 7.0, 2.4, H–C(6)); 2.72 (*ddq*, ^3J = 7.1, 2.9, ^4J = 1.9, H–C(2″)); 2.07 (*d*, ^2J = 12.4, H_{endo}–C(6″)); 1.76 (*dd*, ^2J = 12.4, ^4J = 1.9, H_{exo}–C(6″)); 1.54 (*s*, Me–C(4)); 1.36 (*s*, Me–C(4″)); 1.18 (*d*, ^3J = 7.1, Me–C(2″)); 1.05 (*d*, ^3J = 7.0, Me–C(6)); 1.02 (*d*, ^3J = 7.4, Me(2′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 164.9, 163.4 (2*s*, 2 COO); 147.6, 145.2 (2*s*, C(2), C(3)); 107.3 (*s*, C(5″)); 95.4, 89.5, 89.1, 88.6 (4*s*, C(1), C(4), C(1″), C(4″)); 90.1 (*d*, C(3″)); 81.3 (*d*, C(5)); 56.9, 52.2, 52.1, 50.1, 48.5 (5*q*, 5 MeO); 48.0, 44.7 (2*d*, C(2″), C(6)); 43.8 (*t*, C(6″)); 16.1, 15.12, 14.0, 12.8, 12.6 (5*q*, 5 Me). EI-MS (70 eV): 498 (16, M^+), 435 (47), 411 (75), 288 (60), 183 (57), 105 (80), 75 (100).

*(1*RS,*1′*SR,*2″*RS,*3″*RS,*4*SR,*4″*RS,*5*SR,*6*SR*)-Dimethyl 5*-exo-*[(*tert*-Butyl)dimethylsilyloxy]-4,6*-endo-*dimethyl-1-[1-(3*-exo,*5,5-trimethoxy-2*-endo,*4-dimethyl-7-oxabicyclo[2.2.1]hept-1-yl)ethyl]-7-oxabicyclo-[2.2.1]hept-2-ene-2,3-dicarboxylate* (**21**). A mixture of **20** (100 mg, 0.2 mmol), anh. DMF (2.5 ml), 1*H*-imidazole (165 mg, 2.4 mmol), and (*t*-Bu)Me_2SiCl (310 mg, 2.1 mmol) was heated to 60° for 14 h. The mixture was filtered on silica gel and chromatographed (AcOEt/light petroleum ether 1:6, R_f 0.18): 104 mg (85%) of **21**. Colorless oil. UV (MeCN): 380 (690). IR (CH_2Cl_2): 2980, 2940, 2850, 1730, 1630, 1370, 1190, 1150, 1100, 1050, 850. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.80, 3.74 (2*s*, 2 MeO); 3.58 (*d*, ^3J = 2.6, H–C(5)); 3.29 (*s*, MeO); 3.27 (*d*, ^3J = 3.0, H–C(3″)); 3.23, 3.19 (2*s*, 2 MeO); 2.84 (*q*, ^3J = 7.4, H–C(1′)); 2.73 (*m*, H–C(2″), H–C(6)); 2.04 (*d*, ^2J = 12.6, H_{endo}–C(6″)); 1.77 (*dd*, ^2J = 12.6, ^4J = 1.8, H_{exo}–C(6″)); 1.45 (*s*, Me–C(4)); 1.32 (*s*, Me–C(4″)); 1.17 (*d*, ^3J = 7.1, Me–C(2″)); 1.02 (br. *d*, *J* = 7.4, Me–C(6), Me–C(2′)); 0.92 (*s*, *t*-BuSi); 0.08, 0.06 (2*s*, Me_2Si). ^{13}C-NMR (100.61 MHz, $CDCl_3$): 165.2, 163.6 (2*s*, 2 COO); 148.0, 145.2 (2*s*, C(2), C(3)); 107.2 (*s*, C(5″)); 95.3, 90.0, 89.1, 88.4 (4*s*, C(1), C(4), C(1″), C(4″)); 89.4 (*d*, C(3″)); 82.3 (*d*, C(5)); 56.6, 52.0 (3*q*, 3 MeO); 50.1, 48.4 (2*q*, 2 MeO); 45.4, 44.3 (2*d*, C(2″), C(6)); 43.9 (*t*, C(6″)); 36.0 (*d*, C(1′)); 25.8 (*q*, *t*-Bu); 19.2 (*s*); 16.2, 15.1, 14.0, 12.9, 12.7 (5*q*, 5 Me); −4.72, −5.11 (2*s*, Me_2Si). EI-MS (70 eV): 613 (1, M^+), 549 (26), 440 (30), 353 (50), 215 (30), 172 (56), 115 (99), 73 (100).

*(1*RS,*1′*SR,*2″*RS,*3″*RS,*4*SR,*4″*RS,*5*SR,*6*SR*)-Dimethyl 5*-exo-*Acetoxy-4,6*-endo-*dimethyl-1-[1-(3*-exo,*5,5-trimethoxy-2*-endo,*4-dimethyl-7-oxabicyclo[2.2.1]hept-1-yl)ethyl]-7-oxabicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate* (**22**). A mixture of **20** (0.43 g, 0.79 mmol), pyridine (1.8 ml), Ac_2O (1.5 ml), and 4-(dimethylamino)pyridine (3 mg) was stirred at 25° for 24 h. After cooling to 0°, sat. aq. $NaHCO_3$ soln. (10 ml) was added and the mixture extracted with $CHCl_3$ (10 ml, 3 times) and Et_2O (10 ml, 3 times). The combined org. extracts were dried ($MgSO_4$) and evaporated. The yellowish residue was recrystallized from Et_2O/light petroleum ether: 0.37 g (80%) of **22**. Colorless crystals. M.p. 162–163°. UV (MeCN): 225 (5700), 297 (400). IR (KBr): 2990, 2960, 2840, 1740, 1720, 1715, 1690, 1460, 1430, 1380, 1320, 1250, 1230, 1190, 1150, 1130, 1100, 1090, 1030, 900. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.64 (*d*, ^3J = 2.4, H–C(5)); 3.81, 3.74 (2*s*, 2 MeOOC); 3.33 (*s*, MeO); 3.26 (*d*, ^3J = 2.5, H–C(3″)); 3.24, 3.19 (2*s*, 2 MeO); 2.93 (*dq*, ^3J = 7.1, 2.4, H–C(6)); 2.89 (*q*, ^3J = 7.5, H–C(1′)); 2.71 (*ddq*, ^3J = 7.1, 2.5, ^4J = 1.8, H–C(2″)); 2.11 (*s*, Ac); 2.07 (*d*, ^2J = 12.5, H_{endo}–C(6″)); 1.78 (*dd*, ^2J = 12.5, ^4J = 1.8, H_{exo}–C(6″)); 1.50 (*s*, Me–C(4)); 1.34 (*s*, Me–C(4″)); 1.18 (*d*, ^3J = 7.1, Me–C(2″)); 1.09 (*d*, ^3J = 7.1, Me–C(6)); 1.03 (*d*, ^3J = 7.5, Me(2′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.8, 164.3, 163.4 (3*s*, 3 COO); 147.4, 145.8 (2*s*, C(2), C(3)); 107.3 (*s*, C(5″)); 95.6, 89.4, 88.5, 88.1 (4*s*, C(1), C(4), C(1″), C(4″)); 89.8 (*d*, C(3″)); 82.5 (*d*, C(5)); 56.2, 52.3, 50.2, 48.5 (5*q*, 5 Me); 44.9 (*d*, C(2″)); 43.8 (*d* and *t*, C(6), C(6″)); 35.8 (*d*, C(1′)); 21.0 (*q*, *Me*–C=O); 16.2, 15.1, 14.2, 13.1, 12.8 (5*q*, 5 Me). CI-MS (NH_3): 558 (100, $[M + 18]^+$), 540 (26, M^+), 509 (65), 477 (76), 453 (66), 353 (27), 288 (12), 183 (16), 105 (31), 75 (57). Anal. calc. for $C_{27}H_{40}O_{11}$ (540.257): C 59.97, H 7.46; found: C 59.96, H 7.60.

*(1′*RS,*1″*SR,*2*RS,*2″*SR,*3*RS,*3″*SR,*4*RS,*4″*SR,*5*RS*)-Dimethyl {3-[(*tert*-Butyl)dimethylsilyloxy]-2,3,4,5-tetrahydro-2,4-dimethyl-5-[1′-(3*-exo,*5,5-trimethoxy-2*-endo,*4-dimethyl-7-oxabicyclo[2.2.1]hept-1-yl)ethyl]furan-2,5-diyl}bis[glyoxylate]* (= *Dimethyl 3-[(*tert*-Butyl)dimethylsilyloxy]-2,3,4,5-tetrahydro-2,4-dimethyl-α,α′-dioxo-5-[1-(3*-exo,*5,5-trimethoxy-2*-endo,*4-dimethyl-7-oxabicyclo[2.2.1]hept-1-yl)ethyl]furan-2,5-diacetate* **23**). As described for **24**, with **21**. Purification by column chromatography (silica gel, light petroleum ether/AcOEt 1:6, R_f 0.16): 75% of **23**. Colorless oil. IR (CH_2Cl_2): 2950, 2940, 1730, 1720, 1390, 1220, 1170, 1070, 1030, 920, 840.

^{1}H-NMR (250 MHz, $CDCl_3$): 4.34 (*d*, $^3J(3,4) = 8.2$, H–C(3)); 3.86, 3.79 (2*s*, Ac); 3.35 (*s*, MeO); 3.28 (*d*, $^3J(3'',2'') = 2.5$, H–C(3'')); 3.21, 3.18 (2*s*, 2 MeO); 2.80 (*m*, H–C(4)); 2.50 (*q*, $^3J(1',2') = 7.3$, H–C(1')); 2.25 (*m*, H–C(2'')); 1.97 (*dd*, $^2J = 13.1$, $^4J = 1.8$, H_{exo}–C(6'')); 1.78 (*d*, $^2J = 13.1$, H_{endo}–C(6'')); 1.56 (*s*, Me–C(2)); 1.33 (*s*, Me–C(4'')); 1.25 (*d*, $^3J = 7.3$, Me(2')); 1.14 (*d*, $^3J = 7.1$, Me–C(4)); 1.07 (*d*, $^3J = 7.0$, Me–C(2'')); 0.91 (*s*, *t*-Bu); 0.14, 0.13 (2*s*, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 196.7, 195.5 (2*s*, 2 COO); 163.5, 163.4 (2*s*, 2 *C*OCOO); 107.5 (*s*, C(5'')); 92.3, 89.1, 88.8, 88.2 (4*s*, C(2), C(5), C(1''), C(4'')); 88.9 (*d*, C(3'')); 79.9 (*d*, C(3)); 56.9, 52.6, 52.3, 49.9, 48.5 (5*q*, 5 MeO); 48.3, 47.2, 45.9 (3*d*, C(2''), C(4), C(1')); 41.2 (*t*, C(6'')); 25.7 (br. *q*, *Me*$_3$CSi); 21.2, 15.1, 13.7, 12.6, 12.3 (5*q*, 5 Me); 18.0 (*s*, Me_3CSi); 0.6, 0.5 (2*q*, Me_2Si).

*(1'RS,1''SR,2RS,2''SR,3RS,3''SR,4RS,4''SR,5RS)-Dimethyl {3-Acetoxy-2,3,4,5-tetrahydro-2,4-dimethyl-5-[1-(3-*exo*,5,5-trimethoxy-2-*endo*,4-dimethyl-7-oxabicyclo[2.2.1]hept-1-yl)ethyl]furan-2,5-diyl}bis[glyoxylate]* (= *Dimethyl 3-Acetoxy-2,3,4,5-tetrahydro-2,4-dimethyl-α,α'-dioxo-5-[1-(3-*exo*,5,5-trimethoxy-2-*endo*,4-dimethyl-7-oxabicyclo[2.2.1]hept-1-yl)ethyl]furan-2,5-diacetate;* **24**). $NaIO_4$ (422 mg, 1.9 mmol) and $RuCl_3 \cdot n H_2O$ (2.2 mg) were added to a stirred mixture of **22** (269 mg, 0.48 mmol), CCl_4 (2 ml), MeCN (2 ml), and H_2O (3 ml). After stirring at 25° for 2.5 h, the aq. layer was extracted with $CHCl_2$ (3 × 5 ml) and Et_2O (2 × 5 ml), the combined org. extract dried ($MgSO_4$), filtered through a pad of silica gel/*Celite* 10:1, and evaporated and the residue recrystallized from Et_2O/light petroleum ether: 220 mg (78%) of **24**. Colorless crystals. M.p. 139–140°. UV (MeCN): 219 (4500). IR (KBr): 2990, 2970, 2820, 1740, 1730, 1460, 1450, 1430, 1370, 1305, 1270, 1230, 1120, 1090, 1050, 1030, 990, 880. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.62 (*d*, $^3J = 8.7$, H–C(3)); 3.85, 3.81 (2*s*, 2 MeOOC); 3.35 (*s*, MeO); 3.28 (*d*, $^3J = 2.4$, H–C(3'')); 3.21, 3.17 (2*s*, 2 MeO); 3.02 (*m*, H–C(4)); 2.91 (*q*, $^3J = 7.4$, H–C(1')); 2.29 (*ddq*, $^3J = 7.0, 2.4$, $^4J = 1.5$, H–C(5)); 2.13 (*s*, Ac); 1.96 (*dd*, $^2J = 13.1$, $^4J = 1.5$, H_{exo}–C(6'')); 1.82 (*d*, $^2J = 13.1$, H_{endo}–C(6'')); 1.63 (*s*, Me–C(2)); 1.33 (*s*, Me–C(4'')); 1.20 (*d*, $^3J = 7.4$, H–C(2')); 1.18 (*d*, $^3J = 7.1$, Me–C(4)); 1.07 (*d*, $^3J = 7.0$, Me–C(2'')). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 196.0, 193.8 (2*s*, 2 COO); 169.2, 163.3, 162.6 (3*s*, 3 CO); 107.4 (*s*, C(5'')); 92.7, 89.2, 87.8, 86.9 (4*s*, C(2), C(5), C(1''), C(4'')); 89.2 (*d*, C(3'')); 78.2 (*d*, C(3)); 57.0, 52.7, 49.9, 48.4 (5*q*, 5 MeO); 47.1, 45.7, 45.3 (3*d*, C(2''), C(4), C(1')); 41.2 (*t*, C(6'')); 21.4, 20.9, 15.3, 13.1, 12.5, 12.3 (6*q*, 6 Me). CI-MS (NH_3): 590 (100, $[M + 18]^+$), 572 (29, M^+), 509 (22), 485 (8), 425 (25), 243 (26), 183 (11), 123 (18), 75 (50). Anal. calc. for $C_{27}H_{40}O_{13}$ (572.247): C 56.62, H 7.04; found: C 56.74, H 6.98.

Determination of the Structure of $C_{19}H_{23}NO_4$ (**4**). Crystal data and details of intensity measurements and structure refinement are given in *Table 1*. Cell dimensions and reflections were measured on a *SYNTEX-P2$_1$* diffractometer. The data were corrected for variation of the experimental conditions and for *Lorentz*-polarization effects. For the determination of the structure as well as for the computation and the drawings, the SHELX system [15] was used. The H-atoms were restrained to adopt an ideal geometry, but their displacement parameters were refined.

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