Asymmetric Syntheses of New Polyhydroxylated Quinolizidines[1]): Cross-Aldol Reactions of 7-Oxabicyclo[2.2.1]heptan-2-one and 3a,4a,7a,7b-Tetrahydro[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazole-3-carbaldehyde Derivatives[2])

by **Christophe Schaller**[3]) and **Pierre Vogel***

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Dedicated to Professor *Pierre Sinaÿ* on the occasion of his 62nd birthday

The cross-aldolization of (−)-(1*S*,4*R*,5*R*,6*R*)-6-*endo*-chloro-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one ((−)-**25**) and of (+)-(3a*R*,4a*R*,7a*R*,7b*S*)- ((+)-**26**) and (−)-(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazole-3-carbaldehyde ((−)-**26**) was studied for the lithium enolate of (−)-**25** and for its trimethylsilyl ether (−)-**31** under *Mukaiyama*'s conditions (*Scheme 2*). Protocols were found for highly diastereoselective condensation giving the four possible aldols (+)-**27** ('*anti*'), (+)-**28** ('*syn*'), **29** ('*anti*'), and (−)-**30** ('*syn*') resulting from the exclusive *exo*-face reaction of the bicyclic lithium enolate of (−)-**25** and bicyclic silyl ether (−)-**31**. Steric factors can explain the selectivities observed. Aldols (+)-**27**, (+)-**28**, **29**, and (−)-**30** were converted stereoselectively to (+)-1,4-anhydro-3-{(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]-furo[2,3-*d*]isoxazol-3-yl]methyl}-3-deoxy-2,6-di-*O*-(methoxymethyl)-α-D-galactopyranose ((+)-**62**), its epimer at the exocyclic position (+)-**70**, (−)-1,4-anhydro-3-{(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]-dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-3-deoxy-2,6-di-*O*-(methoxymethyl)-α-D-galactopyranose ((−)-**77**), and its epimer at the exocyclic position (+)-**84**, respectively (*Schemes 3* and *5*). Compounds (+)-**62**, (−)-**77**, and (+)-**84** were transformed to (1*R*,2*R*,3*S*,7*R*,8*S*,9*S*,9a*S*)-1,3,4,6,7,8,9,9a-octahydro-8-[(1*R*,2*R*)-1,2,3-trihydroxypropyl]-2*H*-quinolizine-1,2,3,7,9-pentol (**21**), its (1*S*,2*S*,3*R*,7*R*,8*S*,9*S*,9a*R*) stereoisomer (−)-**22**, and to its (1*S*,2*S*,3*R*,7*R*,8*S*,9*R*,9a*R*) stereoisomer (+)-**23**, respectively (*Schemes 6* and *7*). The polyhydroxylated quinolizidines (−)-**22** and (+)-**23** adopt '*trans*-azadecalin' structures with chair/chair conformations in which H−C(9a) occupies an axial position *anti*-periplanar to the amine lone electron pair. Quinolizidines **21**, (−)-**22**, and (+)-**23** were tested for their inhibitory activities toward 25 commercially available glycohydrolases. Compound **21** is a weak inhibitor of β-galactosidase from jack bean, of amyloglucosidase from *Aspergillus niger*, and of β-glucosidase from *Caldocellum saccharolyticum*. Stereoisomers (−)-**22** and (+)-**23** are weak but more selective inhibitors of β-galactosidase from jack bean.

Introduction. – Polyhydroxylated indolizidine (=octahydroindolizine) alkaloids [2] such as swainsonine (**1**) [3], castanospermine (**2**) [4], and lentiginosine **3** [5] have attracted considerable interest due to their high activity as glycosidase inhibitors, and, probably as a consequence of this, they show a wide range of biological activities [6]. This has stirred a lot of activity toward the synthesis of analogues and the study of structure-activity relationships [2][7–9]. We have shown that indolizidinepentol **4** [10] that possesses the structure of **1** with two further OH substituents at C(5) and C(6) is,

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[1]) IUPAC name for quinolizidine: 1,3,4,6,7,8,9,9a-octahydro-2*H*-quinolizine.

[2]) For a preliminary report, see [1].

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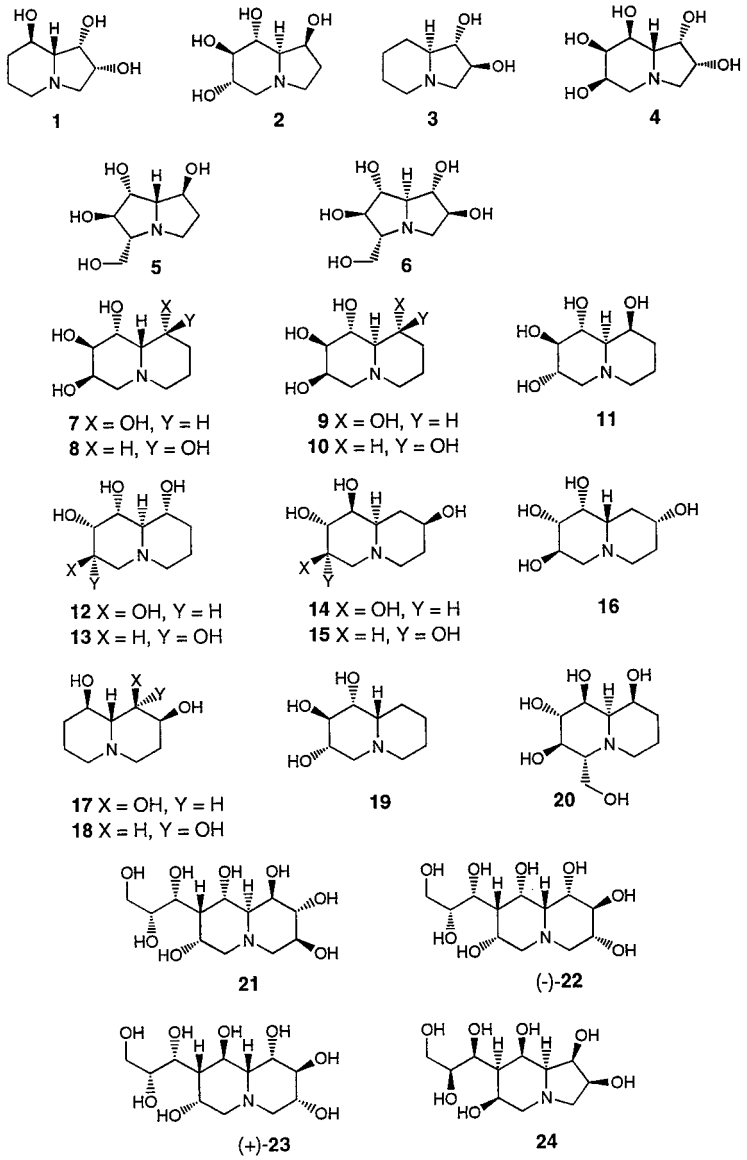
like swainsonine, a potent inhibitor of α-mannosidase, but, unlike the natural alkaloid **1**, it does not inhibit acidic β-galactosidases [11]. Ring-contracted analogues of polyhydroxylated indolizine alkaloids such as alexine (**5**) [12] and casuarine (**6**) [13] and stereoisomers [14] have also shown interesting glycohydrolase-inhibiting activities. Ring-expanded analogues of polyhydroxyindolizidines, the polyhydroxyquinolizidines, emerge as a new class of potential glycosidase inhibitors. The first derivatives **7** and **8** have been obtained by *Ganem* and co-workers [15]; **7** was also prepared by *Rassu et al.* [16] and by *Pearson* and *Hembre* [17]. The latter authors have also described the syntheses of **8**–**10** and shown [17b] **7** to be a weak inhibitor of α-L-fucosidase from bovine epididymis ($IC_{50} = 0.36$ mM). *Stütz* and co-workers realized the synthesis of the castanospermine analogue **11** [18] which inhibits β-glucosidase from *Aspergillus wentii* ($K_i = 25$ μM) and β-glucosidase from almonds ($K_i = 250$ μM). *Carretero et al.* [19] have prepared **12** and **13**; *Herczegh et al.* [20] described the syntheses of isomers **14**–**16**. The quinolizidinetriols **17** and **18** have been prepared by *Carretero et al.* [19], and **19** by *Pandit et al.* [21]. Very interesting is the analogue **20** of α-homonojirimycin prepared by *Liu* and co-workers [22] which is a potent inhibitor of α-glucosidase I from pig kidney ($IC_{50} = 0.15$ μM). In a preliminary communication [1], we presented the synthesis of (1*R*,2*R*,3*S*,7*R*,8*S*,9*S*,9a*S*)-1,3,4,6,7,8,9,9a-octahydro-8-[(1*R*,2*R*)-1,2,3-trihydroxypropyl]-2*H*-quinolizine-1,2,3,7,9-pentol (**21**), the first example of a new kind of polyhydroxyquinolizidines bearing a polyhydroxylated side chain. We report here the full details of our synthetic approach and its application to the preparation of stereoisomers (−)-**22** and (+)-**23**. Our method is similar to that which we had used to prepare analogue **24**, the first example of a 7-(1,2,3-trihydroxypropyl)octahydroindolizine-1,2,6,8-tetrol [23].

***retro*-Synthesis.** – A possible *retro*-synthetic analysis is to consider the quinolizidines to arise from a double reductive cyclization of 5-amino-5-deoxy-dialdose intermediates of type **A** (*Scheme 1*). The latter could be generated by reduction of the furoisoxazoline derivatives of type **B** and acetal hydrolysis. Cross-aldolization of enantiomerically pure 7-oxabicyclo[2.2.1]heptan-2-one (−)-**25** with aldehydes (+)-**26** and (−)-**26** that have been obtained enantiomerically pure [24] should enable us to generate a number of required aldols of type **D**. Analogous 7-oxabicyclo[2.2.1]heptanone derivatives have been converted to anhydrogalacturonic esters of type **C** that can be reduced to the corresponding 1,4-anhydro-galactopyranose derivatives **B** [23][25][26]. Both types of starting materials, (−)-**25** (PhSeCl adduct [27] to a 'naked sugar of the first generation' [28]) and (+)-**26** or (−)-**26**, are derived from inexpensive furan [24][29].

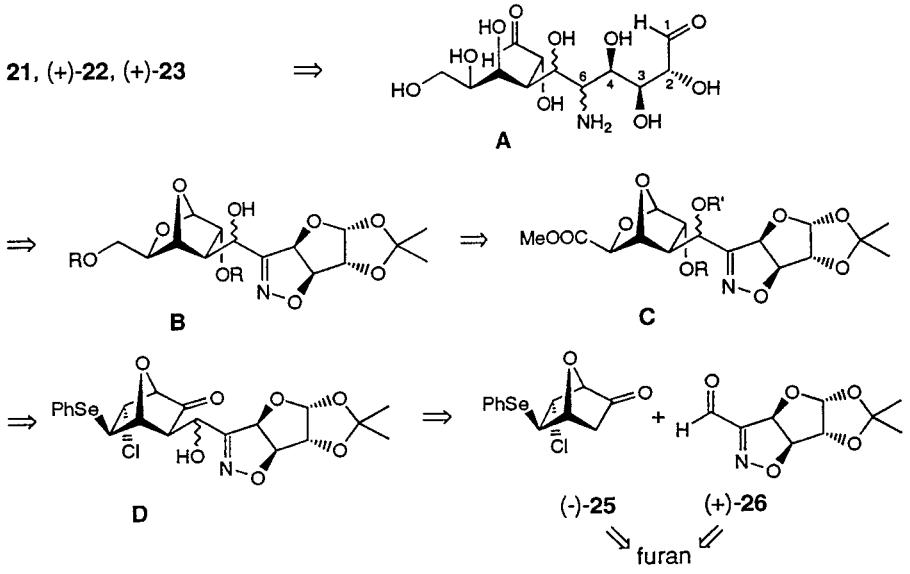
Cross-Aldol Condensations. – The reaction of the lithium enolate derived from the racemic ketone (±)-**25** with racemic aldehyde (±)-**26** led to mixtures of four aldols that could not be separated. Addition of aldehyde (+)-**26** to the lithium enolate of (−)-**25** generated by treatment with LiHMDS (=$(Me_3Si)_2NLi$) under various conditions gave mixture of '*anti*'- and '*syn*'-aldols (+)-**27** and (+)-**28** (*Scheme 2*, *Table 1*). The best yields were obtained with THF as solvent (90%) for an '*anti*'/'*syn*'-diastereoisomer ratio of 84:16. In the presence of an additive [30] such as DMF, DMPU, HMPT, HMPA, or TMEDA (see *Table 1*), the diastereoselectivity was better, but, sometimes,



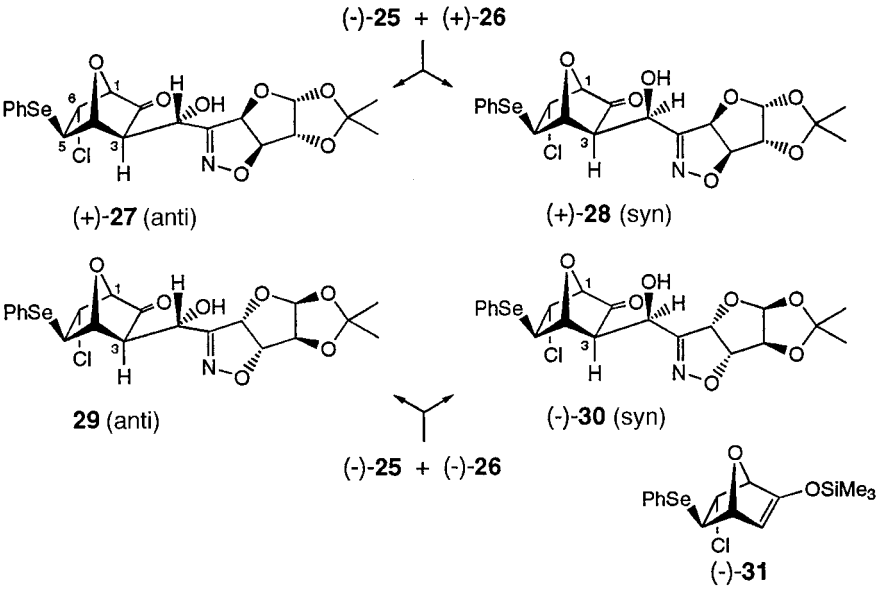
at the cost of lower yield. The best compromise was found when 10% of HMPT was used as additive (92% yield; '*anti*'/'*syn*'-aldol ratio 88 : 12). With the potassium enolate of (−)-**25** generated by treatment with $(Me_3Si)_2NK$, the yield of the cross-aldolization never exceeded 30%. Attempts using phosphazene bases such as P_4-*t*-Bu or P_4-*t*-Oct [31] were not met with success.

The reaction of the lithium enolate of (−)-**25** (generated by treatment with LiHMDS in THF) with aldehyde (−)-**26** (− 78°, 4 h) provided a 52 : 48 mixture of '*anti*'-

Scheme 1



Scheme 2



and '*syn*'-aldol **29** and (−)-**30** in 90% yield (*Scheme 2*). The same low diastereoselectivity was observed with glyme ($(MeOCH_2)_2$) as the solvent instead of THF (yield 73%). In the presence of 10% of HMPT or of 10% of TMEDA (in THF, −78°), 52:48 and 58:42 mixtures **29**/(−)-**30**, respectively, were obtained in 74% yield.

Table 1. *Yields and Diastereoselectivities of the Cross-Aldolizations of Aldehyde (+)-***26** *and Ketone (−)-***25**

Base[a])	Solvent	Temp. [°]	Additive[b])	(+)-**27**/(+)-**28**	Yield [%]
LiHMDS	Et_2O	−78	–	62:38	12
LiHMDS	THF	−78	–	84:16	90
LiHMDS	THF	−100	–	85:15	70
LiHMDS	glyme[c])	−78	–	87:13	84
KHMDS	THF	−78	–	82:18	30
LiHMDS	THF	−78	DMF (10%)	86:14	25
LiHMDS	TMF	−78	DMPU (15%)	93:7	35
LiHMDS	THF	−78	HMPT (10%)	88:12	92
LiHMDS	THF	−78	HMPA (10%)	90:10	75
LiHMDS	THF	−78	TMEDA (10%)	89:11	67

[a]) HMDS = Hexamethyldisilazane. [b]) DMPU = 1,3-Dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one; HMPA = $(Me_2N)_3PO$; HMPT = $(Me_2N)_3P$; TMEDA = $Me_2NCH_2CH_2NMe_2$. [c]) $MeOCH_2CH_2OMe$.

Under *Mukaiyama*'s conditions [32], the trimethylsilyl enol ether (−)-**31** derived from (−)-**25** (*Scheme 2*) reacted with both aldehydes (+)-**26** and (−)-**26** to give predominantly the corresponding '*syn*'-aldols (+)-**28** and (−)-**30**, respectively (*Tables 2* and *3*). The best '*syn*'/'*anti*' diastereoselectivity was observed when a precooled (−78°) solution of $TiCl_4$ in CH_2Cl_2 was added at −78° to the mixture of the enoxysilane (−)-**31** and aldehyde (+)-**26**. When $SnCl_4$ was used instead of $TiCl_4$ as promoter, lower yields and diastereoselectivities were found (*Table 2*). With $BF_3 \cdot Et_2O$, the results were even less satisfactory.

Table 2. *Yields and Diastereoselectivities of the* Mukaiyama *Cross-Aldolizations of (+)-***26** *and (−)-***31** *in* CH_2Cl_2 *at* −78°

Lewis acid	(+)-**27**/(+)-**28**	Yield [%]	*Method*
$BF_3 \cdot Et_2O$	43:57	21	[a])
$TiCl_4$ (0.3 equiv.)	24:76	24	[a])
$TiCl_4$ (1.0 equiv.)	8:92	15	[a])
$TiCl_4$ (1.0 equiv.)	13:87	53	[b])
$TiCl_4$ (1.0 equiv.)	10:90	55	[b])
$TiCl_4$ (1.0 equiv.)	5:95	65	[c])
$SnCl_4$ (1.0 equiv.)	35:65	37	[b])

[a]) Addition of (−)-**31** to a mixture of aldehyde (+)-**26** and promoter in CH_2Cl_2. [b]) Addition of the promoter in CH_2Cl_2 to a mixture (+)-**26**/(−)-**31**. [c]) Addition of the promoter in CH_2Cl_2 precooled to −78° to a mixture (+)-**26**/(−)-**31**

Table 3. *Yields and Diastereoselectivities of the* Mukaiyama *Cross-Aldolizations of (−)-***26** *and (−)-***31** *in* CH_2Cl_2 *at* −78°

Lewis acid	**29**/(−)-**30**	Yield [%]	*Method*
$TiCl_4$ (1.0 equiv.)	5:95	66	[c])
$TiCl_4$ (1.0 equiv.)	8:92	43	[a])
$SnCl_4$ (1.0 equiv.)	12:88	19	[b])

[a]) [b]) [c]) See *Table 2*.

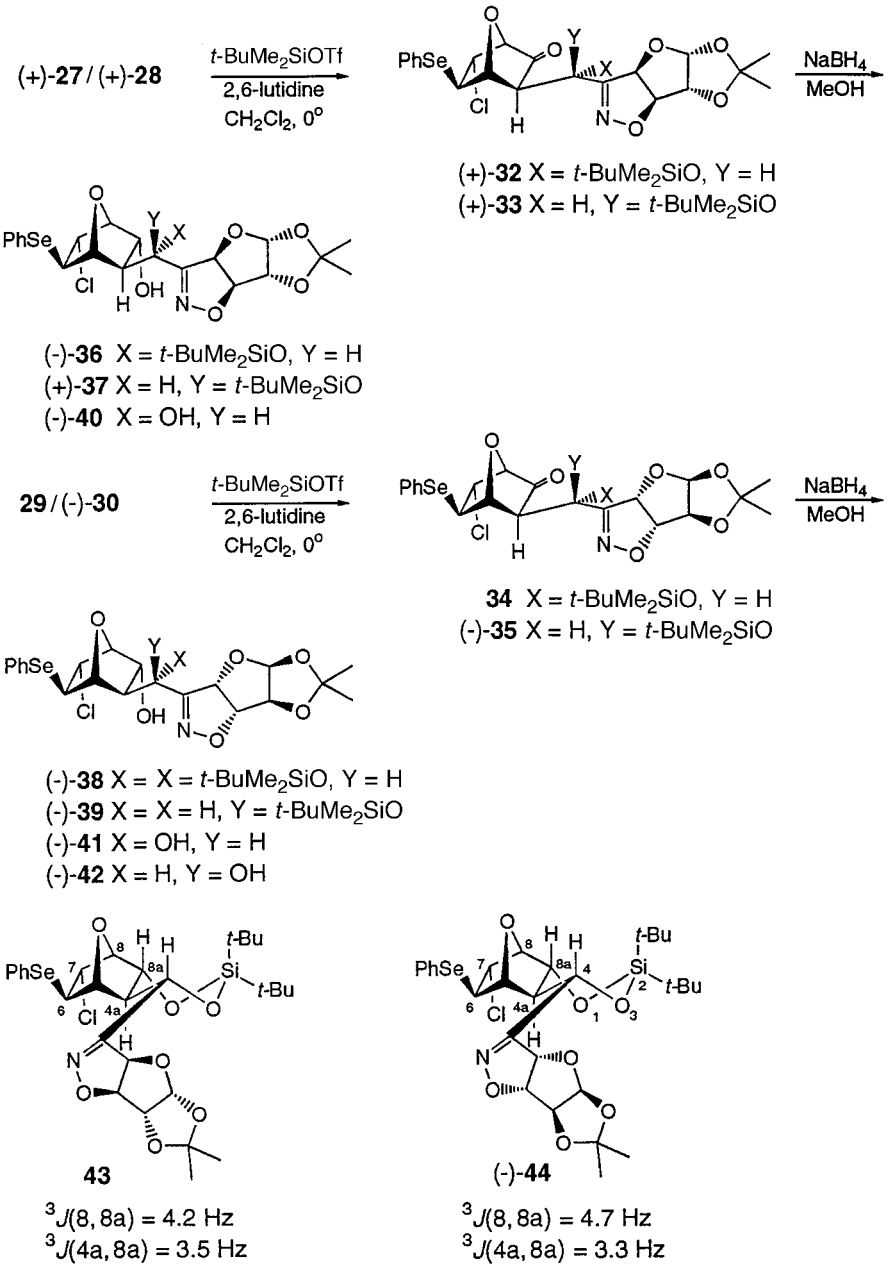
To determine the relative configurations of the four diastereoisomeric aldols (+)-**27**, (+)-**28**, **29**, and (−)-**30**, the mixtures (+)-**27**/(+)-**28** on one hand and **29**/(−)-**30** on the other hand were converted to the corresponding mixtures of (*tert*-butyl)dimethylsilyl ethers, *i.e.*, (+)-**32**/(+)-**33** and **34**/(−)-**35**, respectively (*Scheme 3*). Treatment of these mixtures with $NaBH_4$ in MeOH afforded the corresponding alcohol mixtures (−)-**36**/(+)-**37** and (−)-**38**/(−)-**39**. Separation by column chromatography (silica gel) gave the pure products (−)-**36**, (+)-**37**, (−)-**38**, and (−)-**39**. Deprotection of the silyl group in (−)-**36**, (−)-**38**, and (−)-**39** with Bu_4NF in THF provided the corresponding diols (−)-**40**, (−)-**41**, and (−)-**42**. These diols were unreactive under acidic conditions and refused to form cyclic acetonides in the presence of excess $Me_2C(OMe)_2$. However, reaction of diols (±)-**40** (obtained by aldol condensation of racemic ketone (±)-**25** and racemic aldehyde (±)-**26**) and (−)-**41** (derived from (−)-**25** and (−)-**26**) with $(t\text{-Bu})_2Si(OTf)_2$ in the presence of 2,6-lutidine (2,6-dimethylpyridine) in CH_2Cl_2 afforded the corresponding silanaphthalene derivatives (±)-**43** (40% yield) and (−)-**44** (45% yield), respectively (*Scheme 3*).

The *exo* relative configuration of aldols **27**–**30** (and of their silyl ethers) was inferred from the absence of coupling between vicinal protons H_{endo}–C(3) and H–C(4) [33] in the ^{1}H-NMR spectra of these compounds. The coupling constants of 4.7, 4.9, 4.7, and 4.2 Hz observed for ^3J(1,2*exo*) and of 4.6, 3.8, 4.7, and 4.8 Hz observed for ^3J(2*exo*, 3*endo*) in the ^{1}H-NMR spectra of (−)-**36**, (+)-**37**, (−)-**38**, and (−)-**39**, respectively, confirmed the *endo* relative configuration of OH–C(2) [23][25][28]. Typical *trans*-diaxial coupling constants ^3J(4,4a*endo*) = 10.8 and 11.4 Hz were observed in the ^{1}H-NMR spectra of the perhydro-1,3-dioxa-2-silanaphthalene derivatives (±)-**43** and (−)-**44**, respectively, thus confirming the '*anti*' relative configuration of aldols **27** and **29**. The 2D-NOESY ^{1}H-NMR spectrum of (−)-**44** showed cross-peaks for proton pairs H–C(4) (δ 4.53) and H–C(8a) (δ 4.66).

In general, only the 3-*exo*-aldols were observed in the cross-aldolizations. However, in large-scale preparations, the condensation of (+)-**26** with the lithium enolate of (−)-**25** produced 5–10% of a minor aldol **45** when the lithium aldolate was neutralized *via* cannulation into a 1N HCl solution stirred at 0°. This by-product was not seen when the workup consisted of the addition of AcOH/MeOH to the solution of the lithium aldolate stirred at −78°. This suggested that **45** arises from the acid-induced epimerization at C(3) of aldol (+)-**27**. The structure of **45** was confirmed by the following transformations (*Scheme 4*). Protection of the aldol **45** as (*tert*-butyl)dimethylsilyl ether gave (−)-**46** (70% yield). Reduction of ketone (−)-**46** with $NaBH_4$ in MeOH at 5° produced the *endo*-alcohol (+)-**47** (75% yield). Treatment of (+)-**47** with 1.2 equiv. of Bu_4NF in THF at 25° liberated the diol and induced elimination of HCl with formation of (+)-**48** in 70% yield. Treatment of the latter with $Me_2C(OMe)_2$ in acetone in the presence of *p*-toluenesulfonic acid (TsOH) furnished acetonide (+)-**49** in 89% yield. Reduction of aldol **45** with $NaBH_4$ in MeOH gave diol **50** (90% yield) that was protected as acetonide (−)-**51** (89% yield) on treatment with $Me_2C(OMe)_2$/acetone/TsOH (25°, 5 h). The 3-*endo* relative configuration of (−)-**46**, (+)-**47**, (+)-**48**, and **50**, the 2-*endo* relative configuration of (+)-**48** and **50**, and the relative configurations of (+)-**49** and (−)-**51** were established by spectroscopy, thus confirming the '*syn*' relative configuration of aldol **45** (3-epimer of (+)-**27**).

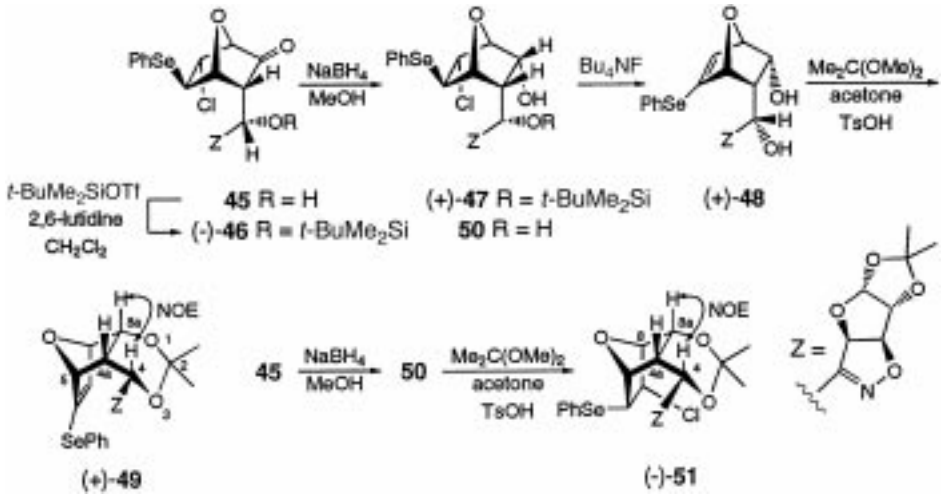
The ^{1}H-NMR spectra of (−)-**46**, (+)-**47**, (+)-**48**, and **50** showed ^3J(4,3*exo*) = 6.6, 5.5, 4.5, and 5.6 Hz, respectively, in accordance with the *endo* relative configuration at C(3) [33]. Coupling constants ^3J(1,2*exo*) =

Scheme 3



4.7 and 4.8 Hz were found for (+)-**48** and **50**, confirming the *endo* relative configuration of OH–C(2). Vicinal coupling constants $^3J(4,4a) = 6.4$ and 6.5 Hz, $^3J(4a,8a) = 8.0$ and 8.5 Hz, $^3J(4a,5) = 4.1$ and 4.7 Hz, and $^3J(8,8a) =$ 4.5 and 4.8 Hz were observed in the ^{1}H-NMR spectra of acetonides (+)-**49** and (–)-**51**, respectively. The 2D-NOESY spectrum of (+)-**49** exhibited NOEs between proton pairs H–C(4) (δ 5.25)/H–C(4a) (δ 2.47) and

Scheme 4



H–C(4)/H–C(8a) (δ 4.70). Similarly, the 2D-NOESY spectrum of (–)-**51** showed cross-peaks for H–C(4) (δ 5.19) with H–C(4a) (δ 2.24) and with H–C(8a) (δ 4.72), in accordance with the '*syn*' relative configuration of aldol **45**.

The good '*anti*' diastereoselectivity observed for the aldol reaction of (–)-**25** and (+)-**26** *via* the lithium enolate can be explained by the *Zimmerman-Traxler* model [34] (*Fig. 1*). For steric reasons, the transition state of that condensation adopts structure **52** (lithium chelated, chair-like conformation). To minimize 1,3-diaxial steric interactions, the isoxazolyl group occupies an equatorial position and the addition follows the *like* mode between the *Si* face of the aldehyde (adopting a *s-trans*-conformation) and the *Si* face of the lithium enolate as shown in *Fig. 1,a* with **52**. The lack of diastereoselectivity of the aldol reaction of the lithium enolate of (–)-**25** with (–)-**26** can be interpreted in terms of the two possible transition structures **53a** and **53c** (*Fig. 1,b*). In **53a**, which leads to '*anti*'-aldol **29**, the *s-trans*-conformer of aldehyde (–)-**26** approaches the *exo*-face of the bicyclic enolate with its concave face, thus introducing more severe steric repulsions than in the transition structure **52**, which implies the approach of the *s-trans*-conformer of aldehyde (+)-**26** with its convex face. The steric repulsions operating in **53a** make other transition states able to compete and lead to '*syn*'-aldol (–)-**30** concurrently with the formation of the '*anti*'-aldol **29**. Transition structure **53b**, in which the *s-cis* conformer of (–)-**26** would approach the enolate with its convex face, also suffers from repulsive steric interactions between the bridgehead H–C(4) of the bicyclic enolate and the tetrahydrofuran ring of the aldehyde. Transition structure **53c** in which the *s-trans*-conformer of (–)-**26** approaches the *exo*-face of the enolate by its convex face, and in which the imino moiety instead of the carbaldehyde function is coordinated to the lithium, can explain the formation of the '*syn*'-aldol (–)-**30**.

The *syn* diastereoselectivity observed for the *Mukaiyama* cross-aldol condensation of enoxysilane (–)-**31** with aldehydes (+)-**26** and (–)-**26** can be interpreted in terms of 'open transition structures' (*Noyori*'s model [32b] **54** and **55**, respectively, as shown in

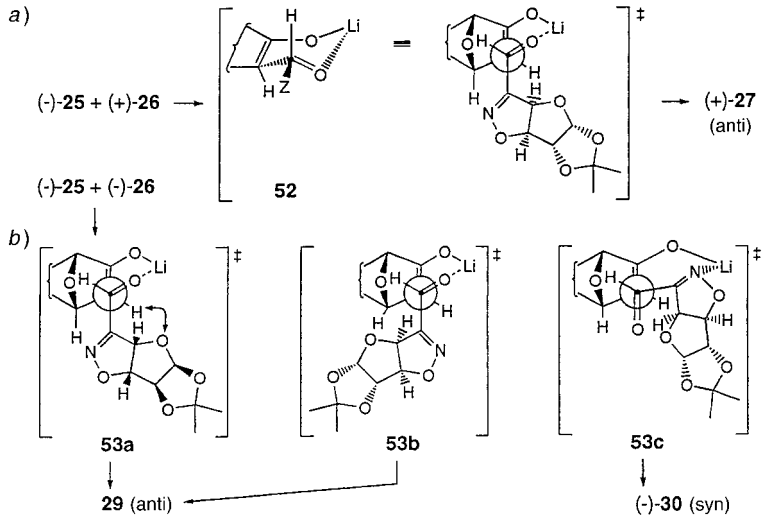


Fig. 1. *Possible transition states for the cross-aldolizations* a) *of (−)-***25** *and* (+)-**26**, *and* b) *of (−)-***25** *and (−)-***26** via *the lithium enolate of (−)-***25**

Fig. 2). These transition structures are similar to **53c** (*Fig. 1,b*). The *Lewis* acid promoter, $TiCl_4$, coordinates the aldehyde moiety and, possibly, the ether function of the tetrahydrofuran ring of (+)-**26** and (−)-**26**. The 1:1 complexes $TiCl_4$/aldehyde thus obtained approach the *exo*-face of the bicyclic enoxysilane (−)-**31** without severe steric interactions arising from the 7-oxabicyclo[2.2.1]heptene system as shown in *Fig. 2*. High *exo*-'*syn*' diastereoselectivity had been observed for the $TiCl_4$-promoted additions of 2,3-*O*-isopropylidene-D-glyceraldehyde to (1*R*)- and (1*S*)-7-oxabicyclo[2.2.1]heptan-2-one-derived silyl enol ethers [35]. In these latter cases, $TiCl_4$ also coordinates simultaneously to the carbaldehyde and an ethereal moiety of 2,3-*O*-isopropylidene-D-glyceraldehyde; the 1:1 *Lewis* complexes thus obtained approach the *exo* face of the enoxysilane in 'open transition states' in which steric repulsions are minimized.

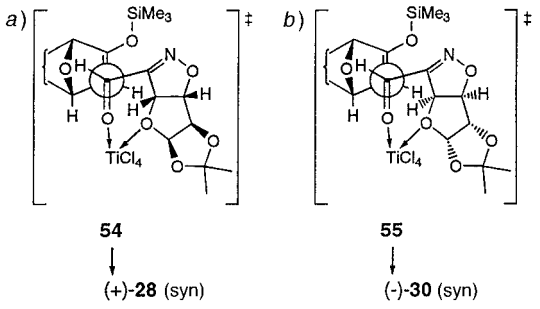


Fig. 2. *Possible transition states* (*Noyori*'s model) *for the* Mukaiyama *cross-aldol condensations of* a) *(−)-***31** *and (+)-***26** (**54**), *and* b) *(−)-***31** *and (−)-***26** (**55**)

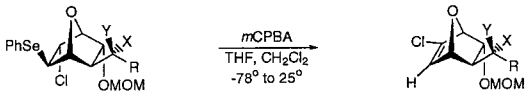
Conversion of the 7-Oxabicyclo[2.2.1]heptan-2-ols into 1,4-Anhydro-galactopyranose Derivatives. – Following protocols developed earlier in our laboratory [23][25], we converted the four 7-oxabicyclo[2.2.1]heptan-2-ol derivatives (−)-**36**, (+)-**37**, (−)-**38**, and (−)-**39** to the corresponding 1,4-anhydro-3-{[(*tert*-butyl)dimethylsilyloxy]-[3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-3-deoxy-2,6-di-*O*-(methoxymethyl)-α-D-galactopyranoses (+)-**62,** (+)-**70**, (−)-**77**, and (+)-**84**, respectively (*Scheme 5*).

Alcohol (−)-**36** was protected as the methoxymethyl ether (+)-**56** (86% yield) on treatment with $MeOCH_2Cl$ and Et_2NH in CH_2Cl_2 (0°, 1 h; then 25°, 15 h). Oxidative elimination of the phenylseleno group of (+)-**56** with *m*-chloroperbenzoic acid (*m*CPBA) in THF/CH_2Cl_2 (−78°, 2 h; then 25°, 4 h) [27] provided the corresponding chloroalkene (+)-**57** in 95% yield. Double hydroxylation of (+)-**57** with Me_3NO in the presence of a catalytical amount of OsO_4 in THF/H_2O 5:1 saturated with $NaHCO_3$ (25°, 2 h) was, as expected for steric reasons, highly *exo*-face selective, leading to the corresponding α-hydroxyketone of type **E**, which that was not isolated but directly esterified with 4-bromobenzenesulfonyl chloride and Et_3N in CH_2Cl_2 (0°, 1 h; then 25°, 12 h) giving brosylate (+)-**58** (88% yield based on (+)-**57**). *Baeyer-Villiger* oxidation of ketone (+)-**58** with *m*CPBA and $NaHCO_3$ (25°, 15 h) was highly regioselective [36], to give the uronolactone (+)-**59** as single product (92% yield). Treatment of (+)-**59** with MeOH under basic conditions led to mixtures of D-galacturonic and L-altruronic esters (+)-**60** and (+)-**61**, respectively. The best yield (90%) and selectivity in favor of (+)-**60** (5:1) was observed when (+)-**59** was methanolyzed with 25% MeOH in anhydrous DMF containing 2 equiv. of anhydrous K_2CO_3 at 0° for 30 min, then at 25° for 90 min. Prolonged exposure of pure methyl galacturonate (+)-**60** to the above basic conditions (25°, 4 days) did not lead to its epimerization to (+)-**61**, suggesting that the altruronic derivative (+)-**61** arises from epimerization of the starting uronolactone (+)-**59** or of the intermediate product of type **F** arising from the MeOH addition to (+)-**59**. Esters (+)-**60** and (+)-**61** were readily separated by column chromatography (silica gel). They arise most probably from the S_Ni displacement of intermediate of type **F** and of its 5-epimer, respectively. Reduction of esters (+)-**60** and (+)-**61** with $LiAlH_4$ (THF, 0°) afforded the corresponding primary alcohols, which were not isolated but directly protected as methoxymethyl ethers (+)-**62** (82%) and (+)-**63** (82%), respectively. The structures proposed for (+)-**60** to (+)-**63** were confirmed by their spectral data.

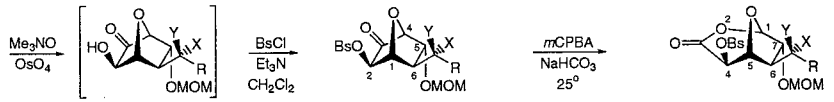
The *exo* relative configuration at C(3) of the 2,7-dioxabicyclo[2.2.1]heptane moieties in (+)-**60** and (+)-**62** was inferred from the absence of coupling constant between vicinal proton pairs H−C(3) and H−C(4), whereas for (+)-**61** and (+)-**63**, $^3J(3,4) = 4.0$ and 3.6 Hz, respectively, were observed in their ^{1}H-NMR spectra. The 2D-NOESY experiment with (+)-**60** established a cross-peak for proton pairs H−C(3) (δ 4.29) and H−C(5) (δ 2.13). The 2D-NOESY experiment with (+)-**63** revealed cross-peaks for proton pairs H−C(5) (δ 2.28) and CH_2−C(3) (δ 3.98 and 3.73).

The same reaction sequence that converted (−)-**36** to (+)-**62** and (+)-**63** was applied to (+)-**37**, (−)-**38**, and (−)-**39** and provided the 1,4-anhydro-α-D-galactopyranose derivatives (+)-**70**, (−)-**77** and (+)-**84**, respectively, with the same ease and with similar yields and diastereoselectivities (see (+)-**64** to (+)-**69**, (−)-**71** to (−)-**76**, and (−)-**78** to (+)-**83**, respectively). The structures of these compounds were established by their spectral data, especially by their 1D-^{1}H-NMR spectra and 2D-NOESY experiments (see the *Exper. Part* for details).

Scheme 5

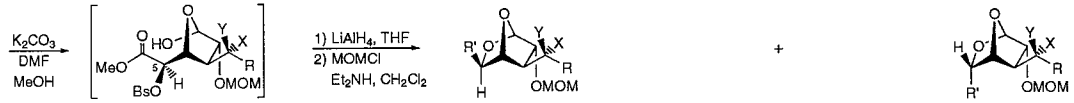


(–)-**36** → (+)-**56** X = *t*-BuMe$_2$SiO, Y = H, R = Z (+)-**57** X = *t*-BuMe$_2$SiO, Y = H, R = Z
(–)-**37** → (+)-**64** X = H, Y = *t*-BuMe$_2$SiO, R = Z (+)-**65** X = H, Y = *t*-BuMe$_2$SiO, R = Z
(+)-**38** → (–)-**71** X = *t*-BuMe$_2$SiO, Y = H, R = Z' (–)-**72** X = *t*-BuMe$_2$SiO, Y = H, R = Z'
(–)-**39** → (–)-**78** X = H, Y = *t*-BuMe$_2$SiO, R = Z' (–)-**79** X = H, Y = *t*-BuMe$_2$SiO, R = Z'



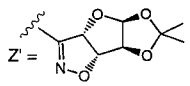
E

(+)-**58** X = *t*-BuMe$_2$SiO, Y = H, R = Z (+)-**59** X = *t*-BuMe$_2$SiO, Y = H, R = Z
(+)-**66** X = H, Y = *t*-BuMe$_2$SiO, R = Z (+)-**67** X = H, Y = *t*-BuMe$_2$SiO, R = Z
(–)-**73** X = *t*-BuMe$_2$SiO, Y = H, R = Z' (–)-**74** X = *t*-BuMe$_2$SiO, Y = H, R = Z'
(–)-**80** X = H, Y = *t*-BuMe$_2$SiO, R = Z' (+)-**81** X = H, Y = *t*-BuMe$_2$SiO, R = Z'



F

(+)-**60** X = *t*-BuMe$_2$SiO, Y = H, R = Z, R' = COOMe (+)-**61** X = *t*-BuMe$_2$SiO, Y = H, R = Z, R' = COOMe
(+)-**62** X = *t*-BuMe$_2$SiO, Y = H, R = Z, R' = CH$_2$OMOM (+)-**63** X = *t*-BuMe$_2$SiO, Y = H, R = Z, R' = CH$_2$OMOM
(+)-**68** X = H, Y = *t*-BuMe$_2$SiO, R = Z, R' = COOMe (+)-**69** X = H, Y = *t*-BuMe$_2$SiO, R = Z, R' = COOMe
(+)-**70** X = H, Y = *t*-BuMe$_2$SiO, R = Z, R' = CH$_2$OMOM (–)-**76** X = *t*-BuMe$_2$SiO, Y = H, R = Z', R' = COOMe
(–)-**75** X = *t*-BuMe$_2$SiO, Y = H, R = Z', R' = COOMe (+)-**83** X = H, Y = *t*-BuMe$_2$SiO, R = Z', R' = COOMe
(–)-**77** X = *t*-BuMe$_2$SiO, Y = H, R = Z', R' = CH$_2$OMOM
(–)-**82** X = H, Y = *t*-BuMe$_2$SiO, R = Z', R' = COOMe
(+)-**84** X = H, Y = *t*-BuMe$_2$SiO, R = Z', R' = CH$_2$OMOM

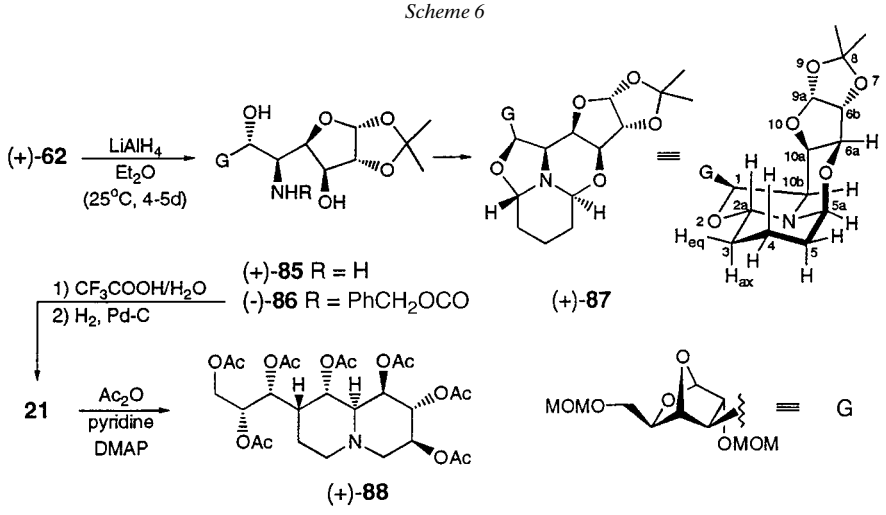


Z: see *Scheme 4*;
MOM = MeOCH$_2$;
Bs = 4-BrC$_6$H$_4$SO$_2$

The methyl anhydrogalactopyranuronate (+)-**60** was obtained in 30% overall yield in 9 steps from ketone (−)-**25** and aldehyde (+)-**26** (*Scheme 2*); its 1′-epimer (+)-**68** was obtained in 25% yield (9 steps) from enoxysilane (−)-**31** and (+)-**26** (*Scheme 2*). Similarly, (−)-**75** was obtained in 20% overall yield (9 steps) from (−)-**25** and (−)-**26**; its 1′-epimer (−)-**82** was obtained in 25% overall yield (9 steps) from (−)-**31** and (−)-**26**. In these latter procedures, mixtures of diastereoisomeric aldols, (+)-**27**/(+)-**28** on one hand and **29**/(−)-**30** on the other hand, could be used (see *Scheme 3*), and the separation of diastereoisomeric products was carried out at the level of the brosylate pairs (+)-**58**/(+)-**66** on one hand and (−)-**73**/(−)-**80** on the other hand.

Synthesis of Octahydro-8-(1,2,3-trihydroxypropyl)-2*H*-quinolizine-1,2,3,7,9-pentols. – The reduction of dihydroisoxazoles has been extensively studied by *Jäger* and co-workers [29][37]. When we tried to reduce dihydroisoxazole (+)-**60**, (−)-**75**, and (−)-**82** with $LiAlH_4$ simultaneously with the reduction of their methyl uronate moieties, complex mixtures of products were obtained that could not be purified. This forced us to reduce the esters first (faster reactions than the dihydroisoxazole reductions) and to protect the derived alcohols as the corresponding methoxymethyl ethers (+)-**62**, (−)-**77**, and (+)-**84**, respectively[4]). Their reduction with $LiAlH_4$ in Et_2O (25°, 5 days) generated the corresponding aminodiols, the reduction of the dihydroisoxazole moieties being accompanied by the cleavage of the silyl ether groups. In the case of (+)-**62**, aminodiol (+)-**85** was obtained as a single diastereoisomer that was protected as benzyl carbamate (−)-**86** (88% based on (+)-**62**) and purified as such. The *anti* relative configuration of the 1-amino-2-hydroxy moiety of (+)-**85** was expected [29][37] and confirmed by conversion into (+)-**87**, the product of condensation with glutaraldehyde in MeOH (25°) [38]. This reaction generated two further stereogenic centers, but because of the conformational anomeric effect [39] and of steric factors, (+)-**87** was the major product isolated in 65% yield (*Scheme 6*). The crude reaction mixture showed (^{1}H-NMR) the presence of less than 8% of another diastereoisomer that was not isolated.

Scheme 6



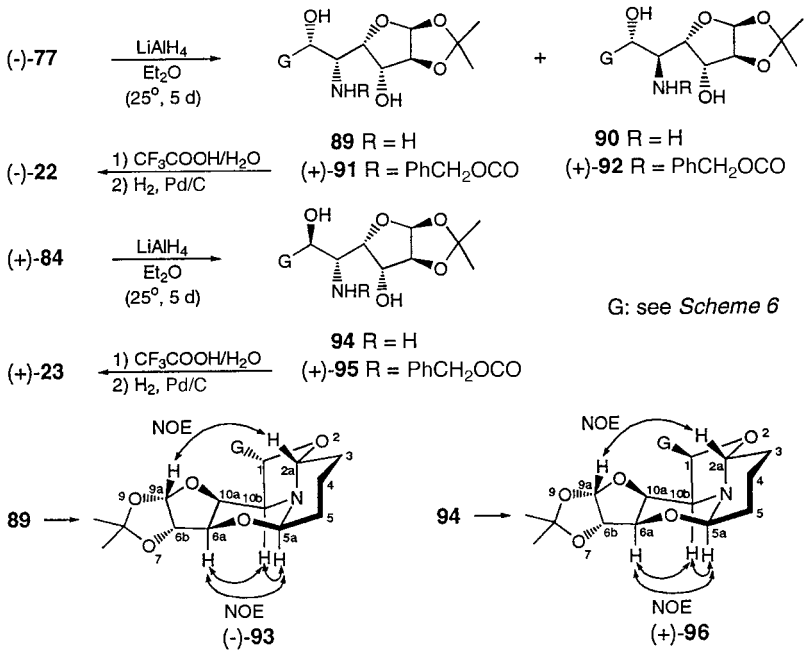
[4]) Diastereoisomer (+)-**70** was not transformed further for reasons of financial shortfall.

The ^{1}H-NMR spectrum of (+)-**87** exhibited coupling constants $^3J(2a,3ax) = 9.7$ and $^3J(2a,3eq) = 2.5$ Hz typical for an axial aminoacetal proton at C(2a), whereas $^3J(5a,5) = 2.9$ and 2.4 Hz are typical for an equatorial aminoacetal proton at C(5a). This is in agreement with the expected '*cis*-decalin' structure of N–C(2a)–C(3)–C(4)–C(5)–C(5a)–O(6)–C(6a)–C(10)–C(10b) due to the N–C–O anomeric effect [40]. Furthermore, the relatively small vicinal coupling constants $^3J(10b,10a) = 3.3$ and $^3J(6a,10a) = 1.8$ Hz are consistent with axial/equatorial relationships. The dihedral angle between H–C(1) and H–C(10b) must be close to 30° as given by $^3J(1,10b) = 6.5$ Hz [41] and shown by a molecular model of (+)-**87**. The 2D-NOESY experiment with (+)-**87** revealed correlation peaks between proton pairs H–C(10b) (δ 3.73)/H–C(5a) (δ 4.69), H–C(10b)/H–C(6a) (δ 4.17), and H–C(6a)/H–C(5a), confirming the *ido*-configuration of the 5-amino-5-deoxy-1,2-*O*-isopropylidenehexofuranose moiety of (+)-**85**. The observation of a strong NOE between protons H–C(2a) (δ 4.84) and H_{ax}–C(4) (δ 1.72) confirmed the axial position of H–C(2a) in the piperidine ring that adopts a chair conformation as shown (*Scheme 6*).

Acidic hydrolysis of benzyl carbamate (–)-**86** in CF_3COOH/H_2O 4:1 at room temperature (10 h) removed all acetal functions, generating a dialdose (mixture of furanoses, pyranoses, anomers) that was not isolated but directly submitted to the hydrogenolysis of the benzyl carbamate (H_2, Pd/C, H_2O), which liberated an amino-deoxy-dialdose intermediate of type **A** (see *Scheme 1*) that was cyclized reductively into quinolizidine **21**, which could not be purified. It was fully characterized as its octaacetate (+)-**88** (40% yield, based on (–)-**86**) obtained on treatment with Ac_2O/pyridine and 4-(dimethylamino)pyridine (DMAP) as catalyst.

The $LiAlH_4$ reduction of (–)-**77** (Et_2O, 25°, 5 d) led to a 6:1 mixture of diastereoisomeric aminodiols **89** and **90** that were protected and separated on preparative scale as benzyl carbamate (+)-**91** (74% yield base on (–)-**73**) and (+)-**92** (minor), respectively (*Scheme 7*). A pure analytical sample of the major amino diol **89**

Scheme 7



could be obtained by column chromatography (silica gel). It was condensed with glutaraldehyde (MeOH, 25°, 12 h) to give a major product (−)-**93** isolated in 65% yield. The structure of (−)-**93** was established by its spectra including its ^{1}H-NMR (*Table 4*) and 2D-NOESY data. Acidic hydrolysis, followed by catalytic hydrogenolysis of (+)-**91** provided quinolizidine (−)-**22** (60% yield after purification by column chromatography (silica gel)). The reduction of (+)-**84** by $LiAlH_4$ afforded a single aminodiol **94** that was protected as benzyl carbamate (+)-**95** (*Scheme 7*). Reaction of **94** with glutaraldehyde gave (+)-**96** (70% yield), the structure of which was established by its ^{1}H-NMR (*Table 4*) and its 2D-NOESY data. Acidic hydrolysis of (+)-**95** followed by catalytic hydrogenolysis liberated quinolizidine (+)-**23** (50% yield, after ion exchange (*Dowex*)).

Table 4. *^{1}H-NMR Data* ($CDCl_3$) *for the 1,2a,3,5,5a,6a,6b,9a,10a,10b-Decahydro-8,8-dimethyl-4*H*-2,6,7,9,10-pentaoxa-10c-azapentaleno[2,1-*d*]acenaphthylenes* (+)-**87**, (−)-**93**, *and* (+)-**96**[a])

	(+)-**87**	(−)-**93**	(+)-**96**
	δ [ppm] (^3J(H,H) [Hz]	δ [ppm] (^3J(H,H) [Hz]	δ [ppm] (^3J(H,H) [Hz]
H−C(1) (^3J(1,5′), ^3J(1,10b))	4.21 (11.6, 6.5)	4.47 (6.9, 2.3)	4.19 (11.2, 6.0)
H−C(2a) (^3J(2a,3ax), ^3J(2a,3eq))	4.84 (9.7, 2.5)	4.67 (10.3, 2.5)	4.89 (10.4, 2.5)
H−C(5a) (^3J(5a,5))	4.69 (2.9, 2.4)	4.65 [c])	4.68 (2.7, [b]))
H−C(6a) (^3J(6a,10a))	4.17 [b])	4.15 (2.0)	4.15 (1.6)
H−C(6b) (^3J(6b,9a))	4.48 (3.6)	4.55 (3.8)	4.46 (3.7)
H−C(9a)	5.82	5.92	5.92
H−C(10a) (^3J(10a,10b), ^3J(10a,6a))	3.98 (3.3, 1.8)	3.96 ([b]))	4.08 ([b]))
H−C(10b) (^3J(10b,1), ^3J(10b,10a))	3.73 (6.5, 3.3)	3.65 (2.3, 3.8)	3.61 (6.0, 3.3)

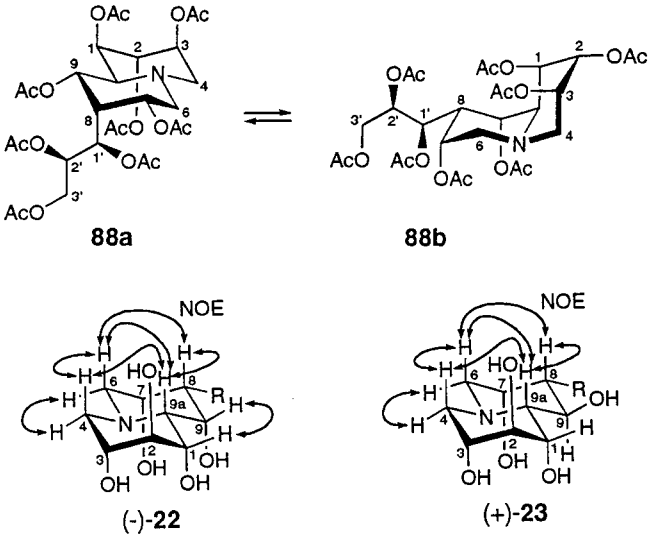
[a]) For further data, see *Exper. Part.* [b]) Not determined due to signal overlap or/and second-order effects.

Conformational Analysis of the Polyhydroxylated Quinolizidines. – The ^{1}H-NMR spectrum of crude **21** was difficult to analyze. We thus examined the 400-MHz-^{1}H-NMR spectrum of its polyacetate (+)-**88** ($CDCl_3$, 50°). Coupling constants between vicinal proton pairs and the 2D-NOESY data were consistent with two rapidly equilibrating '*trans*-decalin' and '*cis*-decalin' conformers **88a** and **88b** arising from the inversion of the tertiary amine (*Scheme 8*).

NOEs were observed between proton pairs H−C(9a) (δ 2.95)/H_{ax}−C(4) (δ 2.85), H−C(9a)/H_{ax}−C(6) (δ2.65), H−C(9) (δ 5.07)/H−C(7)(δ 5.25), H−C(9a)/H−C(1′) (δ 5.51), and H_{eq}−C(4) (δ 3.01)/H_{eq}−C(6) (δ 3.35) as expected for conformer **88a**. Since NOEs were also observed between proton pairs H−C(9) (δ 5.07)/H−C(2′) (δ 5.33), H−C(9)/H−C(1) (δ 4.98), H−C(9)/H−C(1′), H_{ax}−C(6)/H−C(8) (δ 2.65), and H−C(7) (δ 5.25 ppm)/H−C(1′), conformer **88b** is also present at equilibrium with **88a**.

The ^{1}H-NMR spectrum of polyhydroxylated quinolizidine (−)-**22** showed that this compound existed predominantly as a *trans*-azadecalin with expected chair-chair conformation in which the angular proton H−C(9a) resides in an axial position *anti*-periplanar to the lone electron pair of the N-atom. The ^{1}H-NMR spectrum of (+)-**23** was consistent with a similar '*trans*-azadecalin' structure in the chair-chair conformation. This is not surprising as (+)-**23** is the 9-epimer of (−)-**22**, which possesses an equatorial instead of an axial 9-OH group.

Scheme 8



The coupling constants $^3J(1,2) = 3.2$, $^3J(2,3) = 2.8$, and $^3J(3,4) = 2.0$ Hz (*Table 5*) of (−)-**22** confirmed the axial position for the OH groups at C(1), C(2), and C(3). The 2D-NOESY data revealed cross-peaks for proton pairs H−C(9a) (δ 2.28)/H−C(8) (δ 1.80), H−C(9a)/H_{ax}−C(6) (δ 2.31), H−C(9a)/H_{ax}−C(4) (δ 2.66), H−C(8)/H_{ax}−C(6), H_{ax}−C(6)/H_{ax}−C(4), H_{eq}−C(6) (δ 3.19)/H_{eq}−C(4) (δ 2.95) and H−C(1) (δ 4.0)/H−C(9) (δ 4.24).

Coupling constants $^3J(1,2) = 2.9$, $^3J(2,3) = 2.9$, and $^3J(3,4) = 1.7$ Hz (*Table 5*) of (+)-**23** confirmed the axial position of the OH groups at C(1), C(2), and C(3). The signal of H−C(9) was a *dd* with relatively large coupling constants $^3J(8,9) = 11.1$ and $^3J(9,9a) = 9.6$ Hz, a consequence of the *trans*-diaxial relationship of H−C(8)/H−C(9) and H−C(9)/H−C(9a). The coupling constants $^3J(7,8) = 3.2$ and $^3J(6,7) = 3.0$ and 1.4 Hz are in agreement with the axial/equatorial and equatorial/equatorial relationships between these vicinal protons. The 2D-NOESY experiment established correlation peaks between proton pairs H−C(9a) (δ 2.12)/H−C(8) (δ

Table 5. *^{1}H-NMR* (400 MHz) *Data for the Quinolizidinepentols* (−)-**22** *and* (+)-**23**

	(−)-**22** (in CD_3OD)	(+)-**23** (in D_2O)
	δ [ppm] (J(H,H) [Hz])	δ [ppm] (J(H,H) [Hz])
H−C(1) (^3J(1,2), ^3J(1,9a))	4.01 (3.2, 1.8)	3.98 (2.9, 1.6)
H−C(2) (^3J(2,3))	3.84 (2.8)	3.92 (2.9)
H−C(3) (^3J(3,4))	3.75 (2.0, 2.2)	3.79 (1.7, 2.1)
H_{eq}−C(4) (^2J(4ax,4eq))	2.95 (12.3)	2.76 (13.0)
H_{ax}−C(4)	2.66	2.48
H_{eq}−C(6) (^2J(6ax,6eq))	3.19 (12.2)	2.79 (12.7)
H_{ax}−C(6) (^3J(6ax,7))	2.31 (2.9, 1.8)	2.26 (3.0, 1.4)
H−C(7) (^3J(7,8))	4.24 (2.5)	4.29 (3.2)
H−C(8) (^3J(8,9), ^3J(8,1′))	1.80 (2.5, 10.2)	1.62 (11.1, 3.2)
H−C(9) (^3J(9,9a))	4.24 ([a]))	4.13 (9.6)
H−C(9a)	2.28	2.12
H−C(1′) (^3J(1′,2′))	4.14 (1.2)	3.98 (5.3)
H−C(2′) (^3J(2′,3′))	3.93 (6.3)	3.83 (6.9, 4.3)
H−C(3′)	3.75	3.63 & 3.53

[a]) Not determined due to signal overlap or/and second-order effects.

1.62), H–C(9a)/H_{ax}–C(6) (δ 2.26), H–C(9a)/H_{ax}–C(4) (δ 2.48), H–C(8)/H_{ax}–C(6), H_{ax}–C(6)/H_{ax}–C(4), and H_{eq}–C(6) (δ 2.79)/H_{eq}–C(4) (δ 2.76), in agreement with the structure and conformation shown.

Glycosidase Inhibition Assays. – The three polyhydroxylated quinolizidines **21**, (–)-**22**, and (+)-**23** have been tested for their inhibitory activities toward the following enzymes under optimal pH and standard conditions [42]: α-L-fucosidase from bovine epididymis and from human placenta, α-galactosidase from coffee beans, from *Aspergillus niger*, and from *Escherichia coli*, β-galactosidase from *E. coli*, from bovine liver, from *Aspergillus niger*, from *Aspergillus orizae*, and from jack beans, α-glucosidase (maltase) from yeast and from rice, α-glucosidase (isomaltase) from baker's yeast, amyloglucosidase from *Aspergillus niger* and from *Rhizopus* mold, β-glucosidase from almonds and from *Caldocellum saccharolyticum*, α-mannosidase from jack beans and from almonds, β-mannosidase from *Helix pomatia*, β-xylosidase from *Aspergillus niger,* α-*N*-acetylgalactosaminidase from chicken liver, and β-*N*-acetylglucosaminidase from jack beans, from bovine epididymis A, and from bovine epididymis B. At 1 mM concentration (solution buffered just before use) of **21**, β-galactosidase from jack bean, amyloglucosidase from *Aspergillus niger*, and β-glucosidase from *Caldocellum saccharolyticum* were inhibited by 30, 31, and 33%, respectively. Quinolizidines (–)-**22** and (+)-**23** were more selective inhibitors and inhibited only β-galactosidase from jack bean by 40% and 34%, respectively.

Conclusion. – Highly diastereoselective conditions were found for the cross-aldolizations of (–)-(1*S*,4*R*,5*R*,6*R*)-6-*endo*-chloro-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one ((–)-**25**) and the newly obtained, enantiomerically pure (+)-(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]-isoxazole-3-carbaldehyde ((+)-**26**) and its enantiomer (–)-**26**. The *exo*,'*anti*'-aldols (+)-**27** and **29**, and the *exo*,'*syn*'-aldol (–)-**30** were converted in 13 steps to (1*R*,2*R*,3*S*,7*R*,8*S*,9*S*,9a*S*)-8-(1,2,3-trihydroxypropyl)-2*H*-quinolizidine-1,2,3,7,9-pentol (**21**) and its diastereoisomers (–)-**22** (1*S*,2*S*,3*R*,7*R*,8*S*,9*S*,9a*R*) and (+)-**23** (1*S*,2*S*,3*R*,7*R*,8*S*,9*R*,9a*R*) in 11, 9, and 9% overall yield, respectively, starting from furoisoxazole-3-carbaldehydes (+)-**26** and (–)-**26**. These new polyhydroxylated quinolizidines are weak, but selective glycosidase inhibitors.

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Experimental Part

General. See [23]. CC = Column chromatography.

Enzymatic Assays. See [42b].

*(+)-(1*S*,3*S*,4*R*,5*R*,6*R*)-6-endo-Chloro-3-*exo*-{(*S*)-hydroxy[(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**27**). Under Ar, 1.6M BuLi in hexane (3.66 ml, 5.8 mmol) was added slowly to anh. THF (10 ml) and $Me_3SiNHSiMe_3$ (1.3 ml, 6.2 mmol) in a flame-dried flask at $-10°$, keeping the temp. at $-5°$. After stirring at $-5°$ for 15 min, the soln. was cooled to $-78°$ and (–)-(1*S*,4*R*,5*R*,6*R*)-6-*endo*-chloro-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one ((–)-**25**) [27] (1.42 g, 4.7 mmol) in anh. THF (15 ml) was added within 1 h. After stirring at $-78°$ for 15 min, a soln. of (+)-(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo-[2,3-*d*]isoxazole-3-carbaldehyde ((+)-**26**) [24] (1.0 g, 4.7 mmol) in anh. THF (10 ml) was added

within 1 h. After stirring at −78° for 3 h, AcOH (0.48 ml, 8.4 mmol) in MeOH (1.2 ml) was added slowly, and the cooling bath was removed. Once at 20°, the mixture was poured into a vigorously stirred mixture of sat. aq. $NaHCO_3$ soln. (50 ml) and CH_2Cl_2 (100 ml). The aq. phase was extracted with CH_2Cl_2 (50 ml, twice), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 4:1): 2.18 g (90%) of (+)-**27**. M.p. 111–112°. $[\alpha]_{589}^{25}=+50$, $[\alpha]_{577}^{25}=+52$, $[\alpha]_{546}^{25}=+61$, $[\alpha]_{435}^{25}=+115$, $[\alpha]_{405}^{25}=+150$ ($c=1.0$, $CHCl_3$). UV (MeCN): 273 (1500), 207 (9300). IR (KBr): 3460, 2990, 1770, 1385, 1230, 1105, 1020, 900. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61–7.65 (*m*, 2 arom. H); 7.35–7.32 (*m*, 3 arom. H); 5.77 (*d*, ^3J(4a″,7a″) = 3.6, H−C(4a″)); 5.68 (*d*, ^3J(3a″,7b″) = 6.4, H−C(3a″)); 4.96 (*d*, ^3J(7b″,3a″) = 6.4, H−C(7b″)); 4.84 (*dd*, ^3J(1′,3) = 8.3, ^3J(1′,OH−C(1′)) = 2.6, H−C(1′)); 4.78–4.76 (*m*, H−C(7a″), H−C(4)); 4.54 (*d*, ^3J(1,6) = 5.6, H−C(1)); 4.29 (*ddd*, ^3J(6,1) = 5.6, ^3J(6,5) = 2.8, ^4J(6,4) = 1.0, H−C(6)); 3.65 (*d*, ^3J(5,6) = 2.8, H−C(5)); 3.35 (*d*, ^3J(HO−C(1′),1′) = 2.6, OH−C(1′)); 2.78 (*d*, ^3J(3,1′) = 8.3, H−C(3)); 1.50 (*s*, Me); 1.37 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 204.9 (*s*, C(2)); 158.2 (*s*, C(3″)); 134.1 (*s*, arom. C); 133.8 (*d*, *J* = 161, 2 arom. C); 129.5 (*d*, *J* = 159, 2 arom. C); 128.2 (*d*, *J* = 161, arom. C); 113.9 (*s*, C(6″)); 106.1 (*d*, *J* = 184, C(4a″)); 87.1 (*d*, *J* = 163, C(7b″)); 86.5 (*d*, *J* = 154, C(3a″)); 84.9 (*d*, *J* = 168, C(7a″ or 4)); 84.6 (*d*, *J* = 162, C(7a″ or 4)); 83.0 (*d*, *J* = 166, C(1)); 66.0 (*d*, *J* = 149, C(1′)); 57.0 (*d*, *J* = 167, C(6)); 54.7 (*d*, *J* = 138, C(3)); 50.4 (*d*, *J* = 154, C(5)); 27.8 (*q*, *J* = 127, Me); 26.9 (*q*, *J* = 127, Me). CI-MS (NH_3): 533 (24, $[M+NH_4]^+$), 515 (53, M^+), 470 (4), 324 (40), 267 (12), 231 (48), 203 (17), 78 (100). Anal. calc. for $C_{21}H_{22}ClNO_7Se$ (514.82): C 48.99, H 4.31, N 2.72; found: C 49.00, H 4.41, N 2.65.

*(+)-(1*S*,3*S*,4*R*,5*R*,6*R*)-6*-endo-*Chloro-3*-exo-*{(*R*)-hydroxy[(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3*-d*]isoxazol-3-yl]methyl}-5*-exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**28**). A precooled (−78°) 0.5M $TiCl_4$ soln. in CH_2Cl_2 (2.24 ml, 1.12 mmol) was added dropwise to a soln. of (−)-(1*S*,4*R*,5*R*,6*R*)-6-*endo*-chloro-5-*exo*-(phenylseleno)-2-(trimethylsilyloxy)-7-oxabicyclo[2.2.1]hept-2-ene ((−)-**31**) [43] (540 mg, 1.12 mmol) and (+)-**26** (240 mg, 1.12 mmol) in CH_2Cl_2 (20 ml) at −78°. After 1 h, the mixture was poured into 1N HCl (40 ml), the aq. phase extracted with CH_2Cl_2 (30 ml, 3 times), the combined org. extract evaporated, and the residue purified by FC (light petroleum ether/AcOEt 4:1): 371 mg (65%). Colorless foam. $[\alpha]_{589}^{25}=+27$, $[\alpha]_{577}^{25}=+29$, $[\alpha]_{546}^{25}=+32$, $[\alpha]_{435}^{25}=+58$, $[\alpha]_{405}^{25}=+73$ ($c=1.3$, $CHCl_3$). UV (MeCN): 274 (2200), 216 (11000). IR (film): 3475, 2990, 2940, 1770, 1480, 1430, 1385, 1225, 1160, 1085, 1025, 900, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62–7.59 (*m*, 2 arom. H); 7.37–7.33 (*m*, 3 arom. H); 5.87 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4″)); 5.78 (*d*, ^3J(3a″,7b″) = 7.0, H−C(3a″)); 5.04 (*s*, H−C(4)); 5.01 (*d*, ^3J(7b″,3a″) = 7.0, H−C(7b″)); 4.88 (*d*, ^3J(1′,3) = 7.5, H−C(1′)); 4.78 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.50 (*dm*, ^3J(1,6) = 5.7, H−C(1)); 4.31 (*ddd*, ^3J(6,1) = 5.7, ^3J(6,5) = 3.0, ^4J(6,4) = 1.2, H−C(6)); 3.60 (*d*, ^3J(5,6) = 3.0, H−C(5)); 2.90 (br. *s*, OH−C(1′)); 2.85 (*d*, ^3J(3,1′) = 7.5, H−C(3)); 1.51 (*s*, Me); 1.38 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 202.3 (*s*, C(2)); 157.8 (*s*, C(3″)); 134.2 (*d*, *J* = 162, 2 arom. C); 133.9 (*s*, arom. C); 129.5 (*d*, *J* = 164, 2 arom. C); 128.3 (*d*, *J* = 161, arom. C); 114.1 (*s*, C(6″)); 106.0 (*d*, *J* = 185, C(4a″)); 86.5 (*d*, *J* = 163, C(7b″)); 86.4 (*d*, *J* = 163, C(3a″)); 84.9 (*d*, *J* = 158, C(7a″)); 84.3 (*d*, *J* = 171, C(4)); 82.8 (*d*, *J* = 172, C(1)); 65.0 (*d*, *J* = 150, C(1′)); 57.4 (*d*, *J* = 163, C(6)); 56.0 (*d*, *J* = 136, C(3)); 50.6 (*d*, *J* = 153, C(5)); 27.8 (*q*, *J* = 127, Me); 26.9 (*q*, *J* = 127, Me). CI-MS (NH_3): 516 (3, $[M+1]^+$), 515 (5, M^+), 514 (2), 441 (3), 338 (33), 312 (8), 191 (20), 157 (13), 71 (100). Anal. calc. for $C_{21}H_{22}ClNO_7Se$ (514.82): C 48.99, H 4.31, N 2.72; found: C 48.95, H 4.40, N 2.28.

*(1*S*,3*S*,4*R*,5*R*,6*R*)-6*-endo-*Chloro-3*-exo-*{(*S*)-hydroxy[(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3*-d*]isoxazol-3-yl]methyl}-5*-exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* (**29**). As described for (+)-**27**, with (−)-**25** and (−)-**26** [24]: **29**/(−)-**30** 1:1 (90%). This product was directly transformed into **34.**

*(−)-(1*S*,3*S*,4*R*,5*R*,6*R*)-6*-endo-*Chloro-3*-exo-*{(*R*)-hydroxy[(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3*-d*]isoxazol-3-yl]methyl}-5*-exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* ((−)-**30**). As described for (+)-**28**, with (−)-**31** and (−)-**26**: (−)-**30** (65%). Colorless foam. $[\alpha]_{589}^{25}=-28$, $[\alpha]_{577}^{25}=-30$, $[\alpha]_{546}^{25}=-34$, $[\alpha]_{435}^{25}=-50$, $[\alpha]_{405}^{25}=-54$ ($c=0.5$, $CHCl_3$). UV (MeCN): 272 (3000), 216 (13000). IR (film): 3465, 3060, 2990, 2450, 1770, 1480, 1440, 1380, 1225, 1080, 1020, 900, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63–7.60 (*m*, 2 arom. H); 7.37–7.33 (*m*, 3 arom. H); 5.68 (*d*, ^3J(3a″,7b″) = 6.5, H−C(3a″)); 5.63 (*d*, ^3J(4a″,7a″) = 3.6, H−C(4a″)); 5.04 (*d*, ^3J(7b″,3a″) = 6.5, H−C(7b″)); 4.97 (*d*, ^3J(1′,3) = 5.6, H−C(1′)); 4.96 (*s*, H−C(4)); 4.78 (*d*, ^3J(7a″,4a″) = 3.6, H−C(7a″)); 4.53 (*dm*, ^3J(1,6) = 5.8, H−C(1)); 4.31 (*ddd*, ^3J(6,1) = 5.8, ^3J(6,5) = 2.9, ^3J(6,4) = 1.1, H−C(6)); 3.62 (*d*, ^3J(5,6) = 2.9, H−C(5)); 2.77 (*d*, ^3J(3,1′) = 5.6, H−C(3)); 2.73 (br. *s*, OH−C(1′)); 1.50 (*s*, Me); 1.37 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 202.6 (*s*, C(2)); 158.1 (*s*, C(3″)); 134.3 (*d*, *J* = 161, 2 arom. C); 129.6 (*d*, *J* = 164, 2 arom. C); 128.4 (*d*, *J* = 161, arom. C); 128.3 (*s*, arom. C); 113.9 (*s*, C(6″)); 106.2 (*d*, *J* = 184, C(4a″)); 87.6 (*d*, *J* = 164, C(7b″)); 86.5 (*d*, *J* = 163, C(3a″)); 84.6 (*d*, *J* = 162, C(7a″)); 84.1 (*d*, *J* = 168, C(4)); 82.5 (*d*, *J* = 174, C(1)); 65.2 (*d*, *J* = 150, C(1′)); 57.3 (*d*, *J* = 166, C(6)); 55.1 (*d*, *J* = 135, C(3)); 50.8 (*d*, *J* = 154, C(5)); 27.7 (*q*, *J* = 127, Me); 26.8 (*q*, *J* = 127, Me). CI-MS (NH_3): 516 (61,

$[M+1]^+$), 515 (26, M^+), 514 (36), 470 (6), 355 (60), 338 (100), 324 (83), 278 (9), 191 (18), 157 (9), 109 (18), 81 (39). Anal. calc. for $C_{21}H_{22}ClNO_7Se$ (514.82): C 48.99, H 4.31, N 2.72; found: C 48.96, H 4.26, N 2.80.

*(+)-(1*S*,3*S*,4*R*,5*R*,6*R*)-3*-exo-*{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo-*chloro-5-*exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**32**). At 0°, 2,6-dimethylpyridine (2,6-lutidine; 1.4 ml, 12.8 mmol) and (*t*-Bu)$Me_2SiOSO_2CF_3$ (2.2 ml, 9.8 mmol) were added slowly to a soln. of (+)-**27** (2.20 g, 4.3 mmol) in dry CH_2Cl_2 (60 ml) at 0°. The mixture was stirred at 0° for 1 h and at 25° for 5 h. After addition of CH_2Cl_2 (100 ml), the mixture was washed with sat aq. $NaHCO_3$ soln. (50 ml, twice), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 10:1): 2.48 g (92%) of (+)-**32**. Colorless foam. $[\alpha]_{589}^{25} = +28$, $[\alpha]_{577}^{25} = +29$, $[\alpha]_{546}^{25} = +33$, $[\alpha]_{435}^{25} = +61$, $[\alpha]_{405}^{25} = +79$ ($c = 1.1$, $CHCl_3$). UV (MeCN): 272 (1400), 222 (5600). IR (film): 2930, 2850, 1775, 1250, 1230, 1100, 1025, 1000, 840, 780, 760. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62–7.59 (*m*, 2 arom. H); 7.38–7.28 (*m*, 3 arom. H); 5.79 (*d*, ^3J(4a″,7a″) = 3.5, H–C(4a″)); 5.51 (*d*, ^3J(3a″,7b″) = 6.0, H–C(3a″)); 4.98 (*d*, ^3J(1′,3) = 6.0, H–C(1′)); 4.86 (*d*, ^3J(7b″,3a″) = 6.0, H–C(7b″)); 4.81 (*s*, H–C(4)); 4.78 (*d*, ^3J(7a″,4a″) = 3.5, H–C(7a″)); 4.40 (*d*, ^3J(1,6) = 5.6, H–C(1)); 4.21 (*ddd*, ^3J(6,1) = 5.6, ^3J(6,5) = 3.2, ^4J(6,4) = 1.1, H–C(6)); 3.49 (*d*, ^3J(5,6) = 3.2, H–C(5)); 2.60 (*d*, ^3J(3,1′) = 6.0, H–C(3)); 1.51 (*s*, Me); 1.37 (*s*, Me); 0.87 (*s*, *t*-BuSi); 0.08 (*s*, MeSi); 0.05 (*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 201.6 (*s*, C(2)); 159.1 (*s*, C(3″)); 134.3 (*d*, *J* = 161, 2 arom. C); 129.6 (*d*, *J* = 159, 2 arom. C); 128.5 (*d*, *J* = 161, arom. C); 128.4 (*s*, arom. C); 113.4 (*s*, C(6″)); 106.2 (*d*, *J* = 184, C(4a″)); 87.5 (*d*, *J* = 163, C(7b″)); 86.8 (*d*, *J* = 164, C(3a″)); 84.2 (*d*, *J* = 162, C(4)); 84.1 (*d*, *J* = 161, C(7a″)); 82.8 (*d*, *J* = 172, C(1)); 66.5 (*d*, *J* = 147, C(1′)); 58.4 (*d*, *J* = 134, C(3)); 57.0 (*d*, *J* = 162, C(6)); 51.0 (*d*, *J* = 153, C(5)); 27.7 (*q*, *J* = 129, Me); 26.9 (*q*, *J* = 127, Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me_3*C*Si); −4.9 (*q*, *J* = 119, MeSi); −5.1 (*q*, *J* = 119, MeSi). CI-MS (NH_3): 630 (1, $[M+1]^+$), 572 (10), 531 (1), 470 (2), 312 (4), 242 (32), 157 (17), 129 (30), 75 (100). Anal. calc. for $C_{27}H_{36}NClO_7SeSi$ (629.08): C 5.55, H 5.77, N 2.23; found: C 51.68, H 5.72, N 2.23.

*(+)-(1*S*,3*S*,4*R*,5*R*,6*R*)-3*-exo-*{(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo-*chloro-5-*exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**33**). As described for (+)-**32**, with (+)-**28**, (+)-**33** (95%). Colorless foam. $[\alpha]_{589}^{25} = +22$, $[\alpha]_{577}^{25} = +22$, $[\alpha]_{546}^{25} = +26$, $[\alpha]_{435}^{25} = +44$, $[\alpha]_{405}^{25} = +54$ ($c = 1.2$, $CHCl_3$). UV (MeCN): 274 (3000), 215 (14200), 200 (18000). IR (film): 2980, 2955, 2930, 2860, 1775, 1255, 1085, 1040, 845, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63–7.60 (*m*, 2 arom. H); 7.35–7.31 (*m*, 3 arom. H); 6.01 (*d*, ^3J(4a″,7a″) = 3.5, H–C(4a″)); 5.76 (*d*, ^3J(3a″,7b″) = 7.4, H–C(3a″)); 4.97 (*d*, ^3J(7b″,3a″) = 7.4, H–C(7b″)); 4.83 (*s*, H–C(4)); 4.79 (*d*, ^3J(7a″,4a″) = 3.5, H–C(7a″)); 4.77 (*d*, ^3J(1′,3) = 9.4, H–C(1′)); 4.43 (*d*, ^3J(1,6) = 5.6, H–C(1)); 4.22 (*ddm*, ^3J(6,1) = 5.6, ^3J(6,5) = 3.3, H–C(6)); 3.55 (*d*, ^3J(5,6) = 3.3, H–C(5)); 2.90 (*d*, ^3J(3,1′) = 9.4, H–C(3)); 1.53 (*s*, Me); 1.39 (*s*, Me); 0.82 (*s*, *t*-BuSi); 0.05 (*s*, MeSi); −0.02 (*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 202.0 (*s*, C(2)); 156.4 (*s*, C(3″)); 134.4 (*d*, *J* = 162, 2 arom. C); 129.6 (*d*, *J* = 165, 2 arom. C); 128.4 (*d*, *J* = 161, arom. C); 128.3 (*s*, arom. C); 114.1 (*s*, C(6″)); 105.9 (*d*, *J* = 186, C(4a″)); 85.9 (*d*, *J* = 163, C(3a″)); 85.6 (*d*, *J* = 163, C(7b″)); 85.2 (*d*, *J* = 165, C(7a″)); 84.5 (*d*, *J* = 145, C(4)); 83.1 (*d*, *J* = 167, C(1)); 65.3 (*d*, *J* = 148, C(1′)); 57.2 (*d*, *J* = 164, C(6)); 56.8 (*d*, *J* = 140, C(3)); 50.7 (*d*, *J* = 153, C(5)); 27.9 (*q*, *J* = 127, Me); 26.8 (*q*, *J* = 125, Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 17.9 (*s*, Me_3*C*Si); −4.8 (*q*, *J* = 119, MeSi); −5.4 (*q*, *J* = 119, MeSi). CI-MS (NH_3): 630 (2, $[M+1]^+$), 572 (6), 414 (2), 312 (5), 242 (6), 83 (100).

*(1*S*,3*S*,4*R*,5*R*,6*R*)-3*-exo-*{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo-*chloro-5-*exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* (**34**). As described for (+)-**32**, from mixture of **29**/(−)-**30** 1:1: **34**/(−)-**35** 1:1. This product was converted directly to (−)-**38**.

*(−)-(1*S*,3*S*,4*R*,5*R*,6*R*)-3*-exo-*{(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo-*chloro-5-*exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* ((−)-**35**). As described for (+)-**32**, with pure (−)-**30**: (−)-**35** (93%). Colorless foam. $[\alpha]_{589}^{25} = -25$, $[\alpha]_{577}^{25} = -25$, $[\alpha]_{546}^{25} = -29$, $[\alpha]_{435}^{25} = -48$, $[\alpha]_{405}^{25} = -54$ ($c = 0.5$, $CHCl_3$). UV (MeCN): 272 (2600), 202 (13800). IR (film): 2990, 2955, 2930, 2860, 1770, 1470, 1375, 1255, 1230, 1090, 1025, 840, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61–7.59 (*m*, 2 arom. H); 7.35–7.32 (*m*, 3 arom. H); 5.74 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.65 (*d*, ^3J(3a″,7b″) = 6.4, H–C(3a″)); 5.05 (*d*, ^3J(7b″,3a″) = 6.4, H–C(7b″)); 4.87 (*d*, ^3J(1′,3) = 6.9, H–C(1′)); 4.83 (br. *s*, H–C(4)); 4.80 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.45 (*d*, ^3J(1,6) = 5.6, H–C(1)); 4.25 (*ddd*, ^3J(6,1) = 5.6, ^3J(6,5) = 2.9, ^4J(6,4) = 1.1, H–C(6)); 3.60 (*d*, ^3J(5,6) = 2.9, H–C(5)); 2.77 (*d*, ^3J(3,1′) = 6.9, H–C(3)); 1.50 (*s*, Me); 1.37 (*s*, Me); 0.84 (*s*, *t*-BuSi); 0.07 (*s*, MeSi); 0.04 (*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 202.9 (*s*, C(2)); 158.1 (*s*, C(3″)); 134.0 (*d*, *J* = 162, 2 arom. C); 129.6 (*d*, *J* = 165, 2 arom. C); 128.4 (*s*, arom. C); 128.3 (*d*, *J* = 161, arom. C); 113.6 (*s*, C(6″)); 106.2 (*d*, *J* = 184, C(4a″)); 87.7 (*d*, *J* = 163, C(7b″)); 86.4 (*d*, *J* = 163, C(3a″)); 84.5 (*d*, *J* = 161, C(7a″)); 84.3 (*d*, *J* = 161, C(4)); 82.6 (*d*, *J* = 170, C(1)); 65.5 (*d*, *J* = 147, C(1′)); 57.2

(*d*, *J* = 167, C(6)); 56.3 (*d*, *J* = 135, C(3)); 51.0 (*d*, *J* = 154, C(5)); 27.7 (*q*, *J* = 129, Me); 26.9 (*q*, *J* = 127, Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.7 (*q*, *J* = 119, MeSi); −5.2 (*q*, *J* = 119, MeSi). CI-MS (NH_3): 630 (21, $[M+1]^+$), 629 (5, M^+), 628 (11), 572 (6), 438 (9), 355 (48), 338 (100), 310 (14), 191 (42), 83 (83).

*(−)-(1*S*,2*R*,3*S*,4*R*,5*R*,6*R*)-3-*exo*-{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]-isoxazol-3-yl]methyl}-6-*endo*-chloro-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol* ((−)-**36**). $NaBH_4$ (150 mg, 3.95 mmol) was added portionwise to a soln. of (+)-**32** (2.48 g, 3.95 mmol) in MeOH (40 ml) cooled to 5°. After addition of H_2O (25 ml), the mixture was extracted with CH_2Cl_2 (4 × 40 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by FC (light petroleum ether/AcOEt 9 : 1): 2.27 g (91%) of (−)-**36**. Colorless foam. $[\alpha]_{589}^{25} = -10$, $[\alpha]_{577}^{25} = -10$, $[\alpha]_{546}^{25} = -11$, $[\alpha]_{435}^{25} = -23$, $[\alpha]_{405}^{25} = -31$ (*c* = 0.4, $CHCl_3$). UV (MeCN): 271 (2100), 216 (9700). IR (KBr): 3530, 2990, 2935, 2890, 1475, 1375, 1255, 1215, 1110, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60–7.57 (*m*, 2 arom. H); 7.35–7.30 (*m*, 3 arom. H); 5.75 (*d*, ^3J(4a″,7a″) = 3.4, H−C(4a″)); 5.40 (*d*, ^3J(3a″,7b″) = 6.2, H−C(3a″)); 4.77 (*d*, ^3J(7b″,3a″) = 6.2, H−C(7b″)); 4.76 (*d*, ^3J(7a″,4a″) = 3.4, H−C(7a″)); 4.64 (*d*, ^3J(1′,3) = 7.2, H−C(1′)); 4.47 (*dd*, ^3J(1,6) = 4.6, ^3J(1,2) = 4.7, H−C(1)); 4.42–4.35 (*m*, H−C(2)); 4.32 (*s*, H−C(4)); 4.25 (*ddd*, ^3J(6,5) = 4.3, ^3J(6,1) = 4.6, ^4J(6,4) = 1.1, H−C(6)); 3.54 (*d*, ^3J(5,6) = 4.3, H−C(5)); 2.70 (*d*, ^3J(OH−C(2),2) = 8.3, OH−C(2)); 2.14 (*dd*, ^3J(3,1′) = 7.2, ^3J(3,2) = 4.6, H−C(3)); 1.50 (*s*, Me); 1.37 (*s*, Me); 0.88 (*s*, *t*-BuSi); 0.09 (*s*, MeSi); 0.08 (*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 159.1 (*s*, C(3″)); 134.3 (*d*, *J* = 162, 2 arom. C); 129.4 (*d*, *J* = 158, 2 arom. C); 128.2 (*d*, *J* = 161, arom. C); 128.1 (*s*, arom. C); 113.5 (*s*, C(6″)); 106.1 (*d*, *J* = 184, C(4a″)); 87.3 (*d*, *J* = 162, C(7b″)); 86.5 (*d*, *J* = 163, C(3a″)); 86.2 (*d*, *J* = 163, C(4)); 84.3 (*d*, *J* = 161, C(7a″)); 78.4 (*d*, *J* = 166, C(1)); 77.0 (*d*, *J* = 162, C(2)); 68.3 (*d*, *J* = 145, C(1′)); 61.7 (*d*, *J* = 160, C(6)); 56.9 (*d*, *J* = 135, C(3)); 52.8 (*d*, *J* = 152, C(5)); 27.7 (*q*, *J* = 115, Me); 26.8 (*q*, *J* = 115, Me); 25.6 (*q*, *J* = 120, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.5 (*q*, *J* = 118, MeSi); −5.0 (*q*, *J* = 118, MeSi). CI-MS (NH_3): 574 (2), 342 (2), 314 (9), 242 (19), 158 (29), 129 (40), 78 (100). Anal. calc. for $C_{27}H_{38}ClNO_7SeSi$ (631.08): C 51.39, H 6.07, N 2.22; found: C 50.77, H 5.85, N 2.14.

*(+)-(1*S*,2*R*,3*S*,4*R*,5*R*,6*R*)-3-*exo*-{(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo*-chloro-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol* ((+)-**37**). As described for (−)-**36**, with (+)-**33**: 90% of (+)-**37**. Colorless foam. $[\alpha]_{589}^{25} = +40$, $[\alpha]_{577}^{25} = +39$, $[\alpha]_{546}^{25} = +46$, $[\alpha]_{435}^{25} = +77$, $[\alpha]_{405}^{25} = +90$ (*c* = 0.7, $CHCl_3$). UV (MeCN): 275 (2200), 215 (10000), 206 (10400). IR (film): 3510, 2955, 2930, 2860, 1470, 1375, 1255, 1220, 1105, 1065, 1000, 835, 760. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61–7.58 (*m*, 2 arom. H); 7.33–7.29 (*m*, 3 arom. H); 5.95 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.69 (*d*, ^3J(3a″,7b″) = 6.5, H−C(3a″)); 4.94 (*d*, ^3J(7b″,3a″) = 6.5, H−C(7b″)); 4.81 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.52 (*s*, H−C(4)); 4.47 (*dd*, ^3J(1,2) = 4.9, ^3J(1,6) = 4.9, H−C(1)); 4.39 (*d*, ^3J(1′,3) = 10.6, H−C(1′)); 4.23 (*ddd*, ^3J(6,5) = 5.0, ^3J(6,1) = 4.9, ^4J(6,4) = 1.4, H−C(6)); 4.03 (br. *s*, H−C(2)); 3.57 (*d*, ^3J(5,6) = 5.0, H−C(5)); 2.88 (br. *s*, OH−C(2)); 2.27 (*dd*, ^3J(3,1′) = 10.6, ^3J(3,2) = 3.8, H−C(3)); 1.53 (*s*, Me); 1.37 (*s*, Me); 0.81 (*s*, *t*-BuSi); 0.03 (*s*, MeSi); −0.03 (*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 157.5 (*s*, C(3″)); 134.3 (*d*, *J* = 162, 2 arom. C); 129.4 (*d*, *J* = 165, 2 arom. C); 128.6 (*s*, arom. C); 128.1 (*d*, *J* = 161, arom. C); 114.1 (*s*, C(6″)); 105.9 (*d*, *J* = 186, C(4a″)); 86.8 (*d*, *J* = 165, C(4)); 86.5 (*d*, *J* = 163, C(7b″)); 85.6 (*d*, *J* = 160, C(3a″)); 84.1 (*d*, *J* = 153, C(7a″)); 78.7 (*d*, *J* = 162, C(1)); 76.1 (*d*, *J* = 161, C(2)); 69.1 (*d*, *J* = 146, C(1′)); 61.7 (*d*, *J* = 160, C(6)); 57.0 (*d*, *J* = 137, C(3)); 51.6 (*d*, *J* = 152, C(5)); 27.8 (*q*, *J* = 127, Me); 26.7 (*q*, *J* = 125, Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 17.8 (*s*, Me$_3$*C*Si); −4.7 (*q*, *J* = 119, MeSi); −5.3 (*q*, *J* = 119, MeSi). CI-MS (NH_3): 649 (100, $[M+NH_4]^+$), 632 (72, $[M+1]^+$), 574 (20), 457 (55), 440 (57), 389 (29), 355 (60), 314 (70), 192 (54), 129 (34), 90 (68). Anal. calc. for $C_{27}H_{38}ClNO_7SeSi$ (631.08): C 51.39, H 6.07, N 2.22; found: C 51.41, H 5.58, N 2.33.

*(−)-(1*S*,2*R*,3*S*,4*R*,5*R*,6*R*)-3-*exo*-{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo*-chloro-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol* ((−)-**38**). As described for (−)-**36**, with **34**/(−)-**35** 1 : 1. FC (light petroleum ether/AcOEt 9 : 1) gave a first fraction containing (−)-**38** (41%). Colorless foam. $[\alpha]_{589}^{25} = -58$, $[\alpha]_{577}^{25} = -61$, $[\alpha]_{546}^{25} = -72$, $[\alpha]_{435}^{25} = -130$, $[\alpha]_{405}^{25} = -160$ (*c* = 0.5, $CHCl_3$). UV (MeCN): 272 (2500), 215 (13000), 199 (16600). IR (film): 3580, 2990, 2950, 2930, 2860, 1385, 1255, 1220, 1105, 1025, 840, 780, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.68–7.63 (*m*, 2 arom. H); 7.36–7.30 (*m*, 3 arom. H); 5.56 (*d*, ^3J(3a″,7b″) = 6.1, H−C(3a″)); 5.02 (*d*, ^3J(4a″,7a″) = 3.7, H−C(4a″)); 4.85 (*d*, ^3J(7b″,3a″) = 6.1, H−C(7b″)); 4.67 (*d*, ^3J(7a″,4a″) = 3.7, H−C(7a″)); 4.48–4.46 (*m*, H−C(1)); 4.47 (*d*, ^3J(1′,3) = 10.6, H−C(1′)); 4.31–4.20 (*m*, H−C(6), H−C(2)); 4.18 (*s*, H−C(4)); 3.54 (*d*, ^3J(5,6) = 4.2, H−C(5)); 2.57 (*d*, ^3J(OH−C(2),2) = 8.8, OH−C(2)); 2.27 (*dd*, ^3J(3,1′) = 10.6, ^3J(3,2) = 4.6, H−C(3)); 1.49 (*s*, Me); 1.33 (*s*, Me); 0.88 (*s*, *t*-BuSi); 0.12 (*s*, MeSi); −0.01 (*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.6 (*s*, C(3″)); 135.6 (*d*, *J* = 163, 2 arom. C); 129.3 (*d*, *J* = 166, 2 arom. C); 128.3 (*d*, *J* = 161, arom. C); 128.1 (*s*, arom. C); 113.3 (*s*, C(6″)); 106.0 (*d*, *J* = 184, C(4a″)); 87.7 (*d*, *J* = 162, C(7b″)); 86.3 (*d*, *J* = 163, C(4)); 85.7 (*d*, *J* = 154, C(3a″)); 84.2 (*d*, *J* = 161, C(7a″)); 79.6 (*d*, *J* = 151, C(2)); 78.6 (*d*, *J* = 159, C(1)); 69.9 (*d*, *J* = 142, C(1′)); 62.4 (*d*, *J* = 162, C(6)); 55.9 (*d*, *J* = 137, C(3)); 52.6 (*d*, *J* = 153, C(5));

27.5 (*q*, J = 127, Me); 26.7 (*q*, J = 127, Me); 25.5 (*q*, J = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.5 (*q*, J = 118, MeSi); −5.3 (*q*, J = 118, MeSi). CI-MS (NH_3): 574 (5), 314 (22), 279 (3), 242 (38), 184 (19), 157 (38), 129 (54), 75 (100). Anal. calc. for $C_{27}H_{38}ClNO_7SeSi$ (631.08): C 51.39, H 6.07, N 2.22; found: C 51.44, H 6.15, N 2.29.

*(−)-(1*S*,2*R*,3*S*,4*R*,5*R*,6*R*)-3*-exo-*{(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6*-endo-*chloro-5*-exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2*-endo-*ol* ((−)-**39**). As described for (−)-**36**, with pure (−)-**35**: (−)-**39** (90%). Colorless foam. $[\alpha]_{589}^{25} = -43$, $[\alpha]_{577}^{25} = -46$, $[\alpha]_{546}^{25} = -53$, $[\alpha]_{435}^{25} = -99$, $[\alpha]_{405}^{25} = -123$ (c = 0.5, $CHCl_3$). UV (MeCN): 271 (2200), 218 (8200). IR (KBr): 3475, 2990, 2955, 2930, 2895, 2860, 1480, 1380, 1250, 1210, 1160, 1105, 1025, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61–7.59 (*m*, 2 arom. H); 7.33–7.28 (*m*, 3 arom. H); 5.83 (*d*, ^3J(4a″, 7a″) = 3.6, H−C(4a″)); 5.64 (*d*, ^3J(3a″,7b″) = 6.3, H−C(3a″)); 4.93 (*d*, ^3J(7b″,3a″) = 6.3, H−C(7b″)); 4.81 (*d*, ^3J(7a″,4a″) = 3.6, H−C(7a″)); 4.55 (*s*, H−C(4)); 4.45–4.40 (*m*, H−C(6), H−C(1′)); 4.31 (*dd*, ^3J(6,5) = 4.2, ^3J(6,1) = 3.5, H−C(6)); 3.88–3.86 (*m*, H−C(2)); 3.58 (*d*, ^3J(5,6) = 4.2, H−C(5)); 2.82 (*d*, ^3J(OH−C(2),2) = 8.6, OH−C(2)); 2.18 (*dd*, ^3J(3,1′) = 9.8, ^3J(3,2) = 4.8, H−C(3)); 1.50 (*s*, Me); 1.36 (*s*, Me); 0.84 (*s*, *t*-BuSi); 0.05 (*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.0 (*s*, C(3″)); 135.3 (*s*, arom. C); 134.4 (*d*, J = 162, 2 arom. C); 129.4 (*d*, J = 159, 2 arom. C); 128.2 (*d*, J = 161, arom. C); 113.5 (*s*, C(6″)); 106.2 (*d*, J = 184, C(4a″)); 87.6 (*d*, J = 163, C(7b″)); 86.4 (*d*, J = 165, C(3a″)); 86.2 (*d*, J = 164, C(4)); 84.2 (*d*, J = 168, C(7a″)); 78.1 (*d*, J = 157, C(1)); 77.0 (*d*, J = 157, C(2)); 69.0 (*d*, J = 146, C(1′)); 62.3 (*d*, J = 163, C(6)); 56.4 (*d*, J = 135, C(3)); 52.7 (*d*, J = 152, C(5)); 27.7 (*q*, J = 127, Me); 26.8 (*q*, J = 127, Me); 25.7 (*q*, J = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.5 (*q*, J = 119, MeSi); −5.0 (*q*, J = 119, MeSi). CI-MS (NH_3): 574 (7), 342 (3), 314 (11), 242 (27), 158 (30), 129 (45), 78 (100). Anal. calc. for $C_{27}H_{38}ClNO_7SeSi$ (631.08): C 51.39, H 6.07, N 2.22; found: C 51.39, H 6.13, N 2.27.

*(−)-(1*S*,2*R*,3*R*,4*R*,5*R*,6*R*)-6*-endo-*Chloro-3*-exo-*{(*S*)-hydroxy[(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-5*-exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2*-endo-*ol* ((−)-**40**). To a soln. of (−)-**36** (90 mg, 0.142 mmol) in THF (1.5 ml), 1M TBAF in THF (0.17 ml, 0.17 mmol) was added. The mixture was stirred at 25° for 2 h, then AcOEt (10 ml) was added. The mixture was washed with brine (3 ml, 3 times), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 1:2.5): 58 mg (80%) of (−)-**40**. Colorless solid. M.p. 162–163°. $[\alpha]_{589}^{25} = -10$, $[\alpha]_{577}^{25} = -18$, $[\alpha]_{546}^{25} = -14$, $[\alpha]_{435}^{25} = -23$, $[\alpha]_{405}^{25} = -31$ (c = 0.1, $CHCl_3$). UV (MeCN): 270 (2100), 241 (3500), 209 (8200). IR (KBr): 3510, 3360, 3055, 2995, 2960, 1580, 1480, 1380, 1210, 1070, 1025, 1005. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62–7.58 (*m*, 2 arom. H); 7.36–7.30 (*m*, 3 arom. H); 5.77 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.65 (*d*, ^3J(3a″,7b″) = 6.6, H−C(3a″)); 4.93 (*d*, ^3J(7b″,3a″) = 6.6,H−C(7″)); 4.78 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.61 (*dd*, ^3J(1′,3) = 7.5, ^3J(1′,OH−C(1′)) = 7.5, H−C(1′)); 4.53–4.48 (*m*, H−C(2), H−C(1)); 4.43 (*s*, H−C(4)); 4.32 (*ddd*, ^3J(6,5) = 4.3, ^3J(6,5) = 4.2, J = 1.7, H−C(6)); 3.60 (*d*, ^3J(5,6) = 4.3, H−C(5)); 2.88 (*d*, ^3J(OH−C(2),2) = 7.9, OH−C(2)); 2.51 (*d*, ^3J(OH−C(1′),1′) = 5.7, OH−C(1′)); 2.28 (*dd*, ^3J(3,1′) = 7.5, ^3J(3,2) = 4.2, H−C(3)); 1.52 (*s*, Me); 1.38 (*s*, Me). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 160.6 (*s*, C(3″)); 133.5 (*d*, J = 162, 2 arom. C); 130.7 (*s*, arom. C); 130.2 (*d*, J = 160, 2 arom. C); 128.1 (*d*, J = 161, arom. C); 113.9 (*s*, C(6″)); 106.9 (*d*, J = 184, C(4a″)); 88.0 (*d*, J = 163, C(4)); 87.7 (*d*, J = 161, C(7b″)); 87.5 (*d*, J = 163, C(3a″)); 85.7 (*d*, J = 161, C(7a″)); 80.1 (*d*, J = 170, C(1)); 77.8 (*d*, J = 161, C(2)); 68.2 (*d*, J = 165, C(1′)); 62.0 (*d*, J = 158, C(6)); 56.5 (*d*, J = 138, C(3)); 52.6 (*d*, J = 153, C(5)); 28.0 (*q*, J = 129, Me); 27.1 (*q*, J = 130, Me). CI-MS (NH_3): 517 (4, M^+), 360 (3), 286 (5), 228 (23), 170 (25), 110 (23), 78 (100). Anal. calc. for $C_{21}H_{24}ClNO_7Se$ (516.80): C 48.80, H 4.68, N 2.71; found: C 48.84, H 4.76, N 2.75.

*(−)-(1*S*,2*R*,3*R*,4*R*,5*R*,6*R*)-6*-endo-*Chloro-3*-exo-*{(*S*)-hydroxy[(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-5*-exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2*-endo-*ol* ((−)-**41**). As described for (−)-**40**, with (−)-**38**: (−)-**41** (75%). Colorless foam. $[\alpha]_{589}^{25} = -50$, $[\alpha]_{577}^{25} = -53$, $[\alpha]_{546}^{25} = -60$, $[\alpha]_{435}^{25} = -108$, $[\alpha]_{405}^{25} = -134$ (c = 1.0, $CHCl_3$). UV (MeCN): 273 (3900), 244 (4400), 198 (14000). IR (film): 3515, 3390, 2990, 1580, 1380, 1210, 1065, 1005, 810. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.66–7.64 (*m*, 2 arom. H); 7.34–7.31 (*m*, 3 arom. H); 5.68 (*d*, ^3J(3a″,7b″) = 6.3, H−C(3a″)); 5.15 (*d*, ^3J(4a″,7a″) = 3.6, H−C(4a″)); 4.92 (*d*, ^3J(7b″,3a″) = 6.3, H−C(7b″)); 4.67 (*d*, ^3J(7a″,4a″) = 3.6, H−C(7a″)); 4.53 (*d*, ^3J(1′,3) = 10.1, H−C(1′)); 4.49 (*dd*, ^3J(2,3) = 4.7, ^3J(2,1) = 4.7, H−C(2)); 4.39 (*ddd*, ^3J(6,5) = 4.2, ^3J(6,1) = 3.8, J = 1.2, H−C(6)); 4.30–4.27 (*m*, H−C(1)); 4.25 (*s*, H−C(4)); 3.57 (*d*, ^3J(5,6) = 4.2, H−C(5)); 3.32 (br. *s*, OH); 2.72 (br. *s*, OH); 2.24 (*dd*, ^3J(3,1′) = 10.1, ^3J(3,2) = 4.7, H−C(3)); 1.47 (*s*, Me); 1.34 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.5 (*s*, C(3″)); 135.3 (*d*, J = 162, 2 arom. C); 129.4 (*d*, J = 165, 2 arom. C); 128.3 (*d*, J = 161, arom. C); 128.2 (*s*, arom. C); 113.5 (*s*, C(6″)); 106.0 (*d*, J = 185, C(4a″)); 87.6 (*d*, J = 162, C(4)); 86.5 (*d*, J = 155, C(7b″)); 86.0 (*d*, J = 162, C(3a″)); 84.4 (*d*, J = 162, C(7a″)); 78.7 (*d*, J = 151, C(1)); 78.4 (*d*, J = 164, C(2)); 68.8 (*d*, J = 147, C(1′)); 62.1 (*d*, J = 160, C(6)); 54.8 (*d*, J = 136, C(3)); 52.5 (*d*, J = 153, C(5)); 27.6 (*q*, J = 125, Me); 26.8 (*q*, J = 125, Me). CI-MS (NH_3): 519 (4, $[M+2]^+$), 518 (2, $[M+1]^+$), 517 (8, M^+), 360 (4), 314 (25), 259 (13), 228 (72),

192 (17), 157 (48), 111 (37), 78 (100). Anal. calc. for $C_{21}H_{24}ClNO_7Se$ (516.80): C 48.80, H 4.68, N 2.71; found: C 48.85, H 4.88, N 2.62.

*(−)-(1*S*,2*R*,3*R*,4*R*,5*R*,6*R*)-6-*endo*-Chloro-3-*exo*-[(*R*)-hydroxy[(3*aS*,4*aS*,7*aS*,7*bR*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-d]isoxazol-3-yl]methyl]-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol* ((−)-**42**). As described for (−)-**40**, with (−)-**39**: (−)-**42** (85%). Colorless foam. $[\alpha]_{589}^{25} = -64$, $[\alpha]_{577}^{25} = -68$, $[\alpha]_{546}^{25} = -77$, $[\alpha]_{435}^{25} = -135$, $[\alpha]_{405}^{25} = -165$ ($c = 1.0$, $CHCl_3$). UV (MeCN): 270 (3100), 242 (4900), 200 (15000). IR (KBr): 3440, 2985, 1480, 1375, 1220, 1160, 1080, 1020. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63–7.57 (*m*, 2 arom. H); 7.35–7.30 (*m*, 3 arom. H); 5.75 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.70 (*d*, ^3J(3a″,7b″) = 6.4, H−C(3a″)); 4.97 (*d*, ^3J(7b″,3a″) = 6.4, H−C(7b″)); 4.80 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.69 (*s*, H−C(4)); 4.51 (*d*, ^3J(1′,3) = 8.6, H−C(1′)); 4.46 (*dd*, ^3J(6,1) = 4.5, ^3J(6,5) = 4.2, H−C(6)); 4.37–4.34 (*m*, H−C(1)); 4.13–4.08 (*m*, H−C(2)); 3.60 (*d*, ^3J(5,6) = 4.2, H−C(5)); 2.87 (br. *s*, OH); 2.47 (br. *s*, OH); 2.20 (*dd*, ^3J(3,1′) = 8.6, ^3J(3,2) = 4.8, H−C(3)); 1.50 (*s*, Me); 1.37 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.4 (*s*, C(3″)); 134.3 (*d*, *J* = 162, 2 arom. C); 133.4 (*s*, arom. C); 129.4 (*d*, *J* = 162, 2 arom. C); 128.1 (*d*, *J* = 161, arom. C); 113.9 (*s*, C(6″)); 106.2 (*d*, *J* = 184, C(4a″)); 87.1 (*d*, *J* = 163, C(7b″)); 86.6 (*d*, *J* = 163, C(3a″)); 86.1 (*d*, *J* = 166, C(4)); 84.5 (*d*, *J* = 168, C(7a″)); 78.2 (*d*, *J* = 165, C(1 or 2)); 77.0 (*d*, *J* = 162, C(1 or 2)); 67.7 (*d*, *J* = 155, C(1′)); 62.3 (*d*, *J* = 162, C(6)); 55.6 (*d*, *J* = 135, C(3)); 52.3 (*d*, *J* = 152, C(5)); 27.7 (*q*, *J* = 125, Me); 26.8 (*q*, *J* = 127, Me). CI-MS (NH_3): 518 (3, $[M+1]^+$), 517 (7, M^+), 464 (2), 360 (4), 314 (9), 228 (85), 158 (43), 78 (100). Anal. calc. for $C_{21}H_{24}ClNO_7Se$ (516.80): C 48.80, H 4.68, N 2.71; found: C 48.91, H 4.56, N 2.63.

*(±)-(4*RS,*4a*SR,*5*SR,*6*SR,*7*SR,*8*RS,*8a*SR)-2,2-Di(*tert*-butyl)-7-chloro-4-[(3*aSR*,4*aSR*,7*aSR*,7*bRS*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-d]isoxazol-3-yl]-4a,5,6,7,8,8a-hexahydro-6-(phenylseleno)-5,8-epoxy-4*H*-1,3,2-benzodioxasiline* ((±)-**43**). Under Ar, 2,6-dimethylpyridine (0.011 ml, 0.09 mmol) and $(t\text{-Bu})_2Si(OSO_2CF_3)_2$ (0.012 ml, 0.036 mmol) were added to a soln. of (±)-**40** (15.3 mg, 0.029 mmol; obtained as (−)-**40** starting from (±)-**25** and (±)-**26**) in anh. CH_2Cl_2 (1.5 ml) at 0°. After stirring at 20° for 2 h and at 40° for 4 h, the mixture was poured into brine (2 ml) and extracted with CH_2Cl_2 (8 ml, 3 times). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by FC (light petroleum ether/AcOEt 3:1): 13 mg (40%) of (±)-**43**. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.59–7.57 (*m*, 2 arom. H); 7.34–7.31 (*m*, 3 arom. H); 5.70 (*d*, ^3J(4a′,7a′) = 3.5, H−C(4a′)); 5.51 (*d*, ^3J(3a′,7b′) = 6.4, H−C(3a′)); 4.83 (*d*, ^3J(7b′,3a′) = 6.4, H−C(7b′)); 4.78 (*dd*, ^3J(8a,8) = 4.2, ^3J(8a,4a) = 3.8, H−C(8a)); 4.76 (*d*, ^3J(7a′,4a′) = 3.5, H−C(7a′)); 4.49–4.47 (*m*, H−C(4), H−C(8)); 4.30 (*s*, H−C(5)); 4.15 (*dd*, ^3J(7,6) = 5.3, ^3J(7,8) = 3.5, H−C(7)); 3.51 (*d*, ^3J(6,7) = 5.3, H−C(6)); 2.23 (*dd*, ^3J(4a,4) = 10.8, ^3J(4a,8a) = 3.3, H−C(4a)); 1.49 (*s*, Me); 1.37 (*s*, Me); 1.05 (*s*, 2 *t*-Bu). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.6 (*s*, C(3′)); 134.0 (*d*, *J* = 160, 2 arom. C); 133.9 (*s*, arom. C); 129.2 (*d*, *J* = 162, 2 arom. C); 127.8 (*d*, *J* = 159, arom. C); 113.9 (*s*, C(6′)); 106.1 (*d*, *J* = 184, C(4a′)); 87.1 (*d*, *J* = 165, C(5)); 86.8 (*d*, *J* = 163, C(7b′)); 86.5 (*d*, *J* = 163, C(3a′)); 84.6 (*d*, *J* = 162, C(7a′)); 79.4 (*d*, *J* = 162, C(8)); 77.1 (*d*, *J* = 165, C(8a)); 68.6 (*d*, *J* = 147, C(4)); 60.4 (*d*, *J* = 161, C(7)); 56.5 (*d*, *J* = 136, C(4a)); 51.5 (*d*, *J* = 152, C(6)); 27.7 (*q*, *J* = 125, Me); 27.3 (*q*, *J* = 125, Me_3CSi); 27.1 (*q*, *J* = 125, Me_3CSi); 26.8 (*q*, *J* = 127, Me); 24.3 (*s*, Me_3CSi); 20.8 (*s*, Me_3CSi). CI-MS (NH_3): 658 (1, $[M+1]^+$), 618 (11), 358 (6), 269 (14), 225 (10), 157 (20), 77 (100).

*(−)-(4*S*,4a*R*,5*R*,6*R*,7*R*,8*S*,8a*R*)-2,2-Di(*tert*-butyl)-7-chloro-4-[(3*aS*,4*aS*,7*aS*,7*bR*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-d]isoxazol-3-yl]-4a,5,6,7,8,8a-hexahydro-6-(phenylseleno)-5,8-epoxy-4*H*-1,3,2-benzodioxasiline* ((−)-**44**). As described for (±)-**43**, with (−)-**41**: (−)-**44** (45%). Colorless oil. $[\alpha]_{589}^{25} = -31$, $[\alpha]_{577}^{25} = -35$, $[\alpha]_{546}^{25} = -39$, $[\alpha]_{435}^{25} = -70$, $[\alpha]_{405}^{25} = -87$ ($c = 0.6$, $CHCl_3$). UV (MeCN): 272 (2300), 216 (11600), 199 (15500). IR (film): 2965, 2935, 2860, 1470, 1385, 1230, 1135, 1090, 1025, 830, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.67–7.65 (*m*, 2 arom. H); 7.34–7.31 (*m*, 3 arom. H); 5.60 (*d*, ^3J(3a′,7b′) = 6.3, H−C(3a′)); 5.10 (*d*, ^3J(4a′,7a′) = 3.7, H−C(4a′)); 4.90 (*d*, ^3J(7b′,3a′) = 6.3, H−C(7b′)); 4.67 (*d*, ^3J(7a′,4a′) = 3.7, H−C(7a′)); 4.66 (*m*, H−C(8a)); 4.53 (*d*, ^3J(4,4a) = 11.4, H−C(4)); 4.44 (*dd*, ^3J(8,8a) = 4.7, ^3J(8,7) = 4.6, H−C(8)); 4.20–4.16 (*m*, H−C(7), H−C(5)); 3.50 (*d*, ^3J(6,7) = 5.0, H−C(6)); 2.29 (*dd*, ^3J(4a,4) = 11.4, ^3J(4a,8a) = 3.5, H−C(4a)); 1.48 (*s*, Me); 1.34 (*s*, Me); 1.04 (*s*, *t*-BuSi); 1.00 (*s*, *t*-BuSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.2 (*s*, C(3′)); 135.5 (*d*, *J* = 162, 2 arom. C); 129.3 (*d*, *J* = 161, 2 arom. C); 128.2 (*d*, *J* = 161, arom. C); 127.5 (*s*, arom. C); 113.4 (*s*, C(6′)); 106.0 (*d*, *J* = 185, C(4a′)); 87.9 (*d*, *J* = 163, C(7b′)); 87.2 (*d*, *J* = 163, C(5)); 85.7 (*d*, *J* = 157, C(3a′)); 84.4 (*d*, *J* = 161, C(7a′)); 79.5 (*d*, *J* = 148, C(8)); 78.2 (*d*, *J* = 150, C(8a)); 69.5 (*d*, *J* = 153, C(4)); 61.1 (*d*, *J* = 161, C(7)); 55.7 (*d*, *J* = 137, C(4a)); 51.8 (*d*, *J* = 148, C(6)); 27.5 (*q*, *J* = 127, Me); 27.2 (*q*, *J* = 126, Me); 27.0 (*q*, *J* = 126, Me_3CSi); 26.8 (*q*, *J* = 126, Me_3CSi); 20.8 (*s*, Me_3CSi); 19.9 (*s*, Me_3CSi). CI-MS (NH_3): 676 (11, $[M+NH_4]^+$), 658 (6, $[M+1]^+$), 657 (2, M^+), 618 (6), 484 (6), 398 (9), 338 (100), 191 (20), 126 (11).

*(1*S*,3*R*,4*R*,5*R*,6*R*)-6-*endo*-Chloro-3-*endo*-[(*S*)-hydroxy[(3*aR*,4*aR*,7*aR*,7*bS*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-d]isoxazol-3-yl]methyl]-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* (**45**). Depending on workup conditions after the aldol condensation of (+)-**26** *via* the lithium enolate of (−)-**25**,

45 was observed as a by-product accompanying (+)-**27**. **45**: 2nd fraction of the FC; not obtained as a pure substance. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60–7.56 (*m*, 2 arom. H); 7.36–7.28 (*m*, 3 arom. H); 5.74 (*d*, ^3J(4a″,7a″) = 3.5, H–C(4a″)); 5.61 (*d*, ^3J(3a″,7b″) = 6.5, H–C(3a″)); 5.11 (*d*, ^3J(4,3) = 5.9, H–C(4)); 4.99 (*d*, ^3J(1′,3) = 6.0, H–C(1′)); 4.91 (*d*, ^3J(7b″,3a″) = 6.5, H–C(7b″)); 4.76 (*d*, ^3J(7a″,4a″) = 3.5, H–C(7a)); 4.52 (*d*, ^3J(1,6) = 5.4, H–C(1)); 4.26–4.23 (*m*, H–C(5), H–C(6)); 3.50 (br. *s*, OH); 3.28 (*dd*, ^3J(3,1′) = 6.0, ^3J(3,4) = 5.9, H–C(3)); 1.49 (*s*, Me); 1.36 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 204.7 (*s*, C(2)); 158.3 (*s*, C(3″)); 134.0 (*d*, *J* = 162, 2 arom. C); 129.2 (*d*, *J* = 161, 2 arom. C); 128.6 (*s*, arom. C); 127.9 (*d*, *J* = 161, arom. C); 113.8 (*s*, C(6″)); 106.0 (*d*, *J* = 183, C(4a″)); 87.0 (*d*, *J* = 164, C(7b″)); 86.3 (*d*, *J* = 165, C(3a″)); 85.1 (*d*, *J* = 161, C(4)); 84.5 (*d*, *J* = 168, C(7a″)); 83.6 (*d*, *J* = 169, C(1)); 63.1 (*d*, *J* = 147, C(1′)); 57.8 (*d*, *J* = 166, C(6)); 56.7 (*d*, *J* = 133, C(3)); 46.0 (*d*, *J* = 160, C(5)); 27.6 (*q*, *J* = 126, Me); 26.7 (*q*, *J* = 127, Me).

*(−)-(1*S*,3*R*,4*R*,5*R*,6*R*)-3-*endo*-{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo*-*chloro*-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* ((−)-**46**). At 0°, 2,6-dimethylpyridine (0.46 ml, 4.2 mmol) and (*t*-Bu)$Me_2SiOSO_2CF_3$ (0.72 ml, 3.2 mmol) were added slowly to a soln. of crude **45** (720 mg, 1.4 mmol) in dry CH_2Cl_2 (17 ml). The mixture was stirred at 0° for 1 h and at 25° for 5 h. After addition of CH_2Cl_2 (40 ml), the mixture was washed with sat. aq. $NaHCO_3$ soln. (30 ml, twice), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 7:1): 614 mg (70%) of (−)-**46**. Colorless solid. M.p. 140–141°. $[\alpha]_{589}^{25} = -14$, $[\alpha]_{577}^{25} = -13$, $[\alpha]_{546}^{25} = -16$, $[\alpha]_{435}^{25} = -29$, $[\alpha]_{405}^{25} = -36$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 273 (2500), 200 (13000). IR (KBr): 2960, 2930, 1770, 1255, 1080, 1025, 890, 840, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63–7.60 (*m*, 2 arom. H); 7.34–7.27 (*m*, 3 arom. H); 5.75 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.51 (*d*, ^3J(3a″,7b″) = 6.3, H–C(3a″)); 5.01–4.99 (*m*, H–C(7b″), H–C(4)); 4.91 (*d*, ^3J(1′,3) = 7.5, H–C(1′)); 4.79 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.50 (*d*, ^3J(1,6) = 5.8, H–C(1)); 4.39 (*dd*, ^3J(6,1) = 5.8, ^3J(6,5) = 3.3, H–C(6)); 4.06 (*d*, ^3J(5,6) = 3.3, H–C(5)); 3.27 (*dd*, ^3J(3,1′) = 7.5, ^3J(3,4) = 6.6, H–C(3)); 1.48 (*s*, Me); 1.35 (*s*, Me); 0.85 (*s*, *t*-BuSi); 0.04 (*s*, MeSi); 0.03 (*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 203.0 (*s*, C(2)); 157.9 (*s*, C(3″)); 134.5 (*d*, *J* = 162, 2 arom. C); 129.5 (*d*, *J* = 161, 2 arom. C); 128.3 (*d*, *J* = 161, arom. C); 128.1 (*s*, arom. C); 113.6 (*s*, C(6″)); 106.3 (*d*, *J* = 184, C(4a″)); 87.7 (*d*, *J* = 163, C(7b″)); 86.6 (*d*, *J* = 163, C(3a″)); 85.2 (*d*, *J* = 164, C(4)); 84.2 (*d*, *J* = 161, C(7a″)); 84.0 (*d*, *J* = 170, C(1)); 65.1 (*d*, *J* = 145, C(1′)); 58.9 (*d*, *J* = 167, C(6)); 57.7 (*d*, *J* = 132, C(3)); 46.2 (*d*, *J* = 153, C(5)); 27.7 (*q*, *J* = 128, Me); 26.8 (*q*, *J* = 127, Me); 25.8 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me_3*C*Si); −4.7 (*q*, *J* = 118, 2 MeSi). CI-MS (NH_3): 630 (0.4, $[M+1]^+$), 572 (10), 530 (4), 470 (1), 380 (4), 312 (3), 242 (5), 129 (10), 75 (100). Anal. calc. for $C_{27}H_{36}ClNO_7SeSi$ (629.08): C 51.55, H 5.77, N 2.23; found: C 51.63, H 5.65, N 2.24.

*(−)-(1*S*,2*R*,3*S*,4*R*,5*R*,6*R*)-3-*endo*-{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo*-*chloro*-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol* ((+)-**47**). $NaBH_4$ (36.0 mg, 0.95 mmol) was added portionwise to a soln. of (−)-**46** (600 mg, 0.95 mmol) in MeOH (10 ml) and CH_2Cl_2 (3 ml) cooled to 5°. After addition of H_2O (5 ml), the mixture was extracted with CH_2Cl_2 (4 × 15 ml), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 7:2): 450 mg (75%) of (+)-**47**. Colorless oil. $[\alpha]_{589}^{25} = +5$, $[\alpha]_{577}^{25} = +3$, $[\alpha]_{546}^{25} = +3$, $[\alpha]_{435}^{25} = +3$; $[\alpha]_{405}^{25} = +2$ (*c* = 0.8, $CHCl_3$). UV (MeCN): 272 (2000), 219 (8100). IR (film): 3580, 2950, 2930, 2860, 1375, 1255, 1155, 1085, 1025, 840, 780, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.69–7.66 (*m*, 2 arom. H); 7.37–7.28 (*m*, 3 arom. H); 5.81 (*d*, ^3J(4a″,7a″) = 3.5, H–C(4a″)); 5.61 (*d*, ^3J(3a″,7b″) = 6.7, H–C(3a″)); 4.97 (*d*, ^3J(7b″,3a″) = 6.7, H–C(7b″)); 4.90 (*d*, ^3J(1′,3) = 10.6, H–C(1′)); 4.77 (*d*, ^3J(7a″,4a″) = 3.5, H–C(7a″)); 4.73 (*d*, ^3J(4,3) = 5.5, H–C(4)); 4.51–4.45 (*m*, H–C(6), H–C(2), H–C(1)); 3.89 (*d*, ^3J(5,6) = 4.5, H–C(5)); 3.03 (*ddd*, ^3J(3,1′) = 10.6, ^3J(3,2) = 5.5, ^3J(3,4) = 5.5, H–C(3)); 2.80 (*d*, ^3J(OH–C(2),2) = 7.6, OH–C(2)); 1.52 (*s*, Me); 1.37 (*s*, Me); 0.89 (*s*, *t*-BuSi); 0.10 (*s*, MeSi); 0.08 (*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$). 158.5 (*s*, C(3″)); 135.4 (*d*, *J* = 162, 2 arom. C); 129.2 (*d*, *J* = 161, 2 arom. C); 128.4 (*d*, *J* = 161, arom. C); 127.4 (*s*, arom. C); 113.9 (*s*, C(6″)); 106.0 (*d*, *J* = 184, C(4a″)); 87.8 (*d*, *J* = 166, C(4)); 87.2 (*d*, *J* = 162, C(3a″)); 86.4 (*d*, *J* = 163, C(7b″)); 84.7 (*d*, *J* = 161, C(7a″)); 78.9 (*d*, *J* = 162, C(1)); 72.9 (*d*, *J* = 152, C(2)); 65.4 (*d*, *J* = 146, C(1′)); 64.3 (*d*, *J* = 163, C(6)); 48.7 (*d*, *J* = 137, C(3)); 45.7 (*d*, *J* = 150, C(5)); 27.8 (*q*, *J* = 129, Me); 26.8 (*q*, *J* = 127, Me); 25.8 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me_3*C*Si); −3.7 (*q*, *J* = 119, MeSi); −4.4 (*q*, *J* = 119, MeSi). CI-MS (NH_3): 632 (1, $[M+1]^+$), 530 (1), 416 (1), 382 (6), 314 (12), 259 (14), 129 (37), 75 (100). Anal. calc. for $C_{27}H_{38}ClNO_7SeSi$ (631.08): C 51.39, H 6.07, N 2.22; found: C 51.45, H 6.03, N 2.22.

*(+)-(1*R*,2*R*,3*S*,4*R*)-3-*endo*-{(*S*)-Hydroxy[(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-5-(phenylseleno)-7-oxabicyclo[2.2.1]hept-5-en-1-*endo*-ol* ((+)-**48**). At 25°, 1M Bu_4NF in THF (0.63 ml, 0.62 mmol) was added to a soln. of (+)-**47** (332 mg, 0.52 mmol) in THF (8 ml), and the mixture was stirred for 2 h. After the addition of AcOEt (30 ml), the mixture was washed with brine (10 ml, 3 times), the org. phase dried ($MgSO_4$) and evaporated and the residue purified by FC (light petroleum ether/AcOEt 3:2): 150 mg (70%) of (+)-**48**. Colorless solid. M.p. 61–62°. $[\alpha]_{589}^{25} = +103$, $[\alpha]_{577}^{25} =$

+105, $[\alpha]_{546}^{25}$ = +119, $[\alpha]_{435}^{25}$ = +194, $[\alpha]_{405}^{25}$ = +226 (*c* = 1.1, $CHCl_3$). UV (MeCN): 253 (8800), 205 (22300). IR (KBr): 3430, 2990, 2930, 1375, 1215, 1100, 1020, 900, 780, 740, 690. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.59–7.55 (*m*, 2 arom. H); 7.35–7.28 (*m*, 3 arom. H); 6.54 (*d*, ^3J(6,1) = 1.9, H–C(6)); 5.80 (*d*, ^3J(3a″,7b″) = 6.5, H–C(3a″)); 5.79 (*d*, ^3J(4a″,7a″) = 3.5, H–C(4a″)); 5.01 (*ddd*, ^3J(1,2) = 4.7, ^3J(1,6) = 1.9, ^5J(1,4) = 0.9, H–C(1)); 4.96 (*d*, ^3J(7b″,3a″) = 6.5, H–C(7b″)); 4.85 (*d*, ^3J(4,3) = 4.5, H–C(4)); 4.78 (*d*, ^3J(7a″,4a″) = 3.5, H–C(7a″)); 4.57–4.52 (*m*, H–C(2), H–C(1′)); 2.92 (br. *s*, OH); 2.74 (*ddd*, ^3J(3,1′) = 10.6, ^3J(3,2) = 7.8, ^3J(3,4) = 4.5, H–C(3)); 2.59 (br. *s*, OH); 1.52, 1.38 (2*s*, 2 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 161.4 (*s*, C(3″)); 136.1 (*s*, C(5)); 135.5 (*d*, *J* = 155, C(6)); 133.1 (*d*, *J* = 162, 2 arom. C); 129.6 (*d*, *J* = 164, 2 arom. C); 128.1 (*d*, *J* = 161, arom. C); 127.4 (*s*, arom. C); 113.8 (*s*, C(6″)); 105.9 (*d*, *J* = 184, C(4a″)); 87.0 (*d*, *J* = 165, C(3a″)); 86.3 (*d*, *J* = 163, C(7b″)); 84.7 (*d*, *J* = 161, C(7a″)); 83.9 (*d*, *J* = 162, C(4)); 82.3 (*d*, *J* = 165, C(1)); 71.1 (*d*, *J* = 156, C(2)); 65.2 (*d*, *J* = 147, C(1′)); 48.5 (*d*, *J* = 138, C(3)); 27.7, 26.8 (2*q*, *J* = 127, 2 Me). CI-MS (NH_3): 482 (2, $[M+2]^+$), 480 (1, M^+), 224 (100), 195 (12), 144 (22), 115 (97), 78 (78). Anal. calc. for $C_{21}H_{23}NO_7Se$ (480.37): C 52.51, H 4.83, N 2.92; found: C 52.42, H 4.72, N 2.87.

*(+)-(4*S*,4a*S*,5*R*,8*R*,8a*R*)-4a,5,8,8a-Tetrahydro-2,2-dimethyl-6-(phenylseleno)-4-[(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]-5,8-epoxy-4*H*-1,3-benzodioxine* ((+)-**49**). A mixture of (+)-**48** (54 mg, 0.11 mmol), $(MeO)_2CMe_2$ (2 ml), and TsOH (15 mg) in acetone (2 ml) was stirred at 25° for 5 h. After the addition of AcOEt (20 ml), the mixture was washed with sat. aq. $NaHCO_3$ soln. (7 ml) and brine (7 ml), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 4:1): 51 mg (88%) of (+)-**49**. Colorless oil. $[\alpha]_{589}^{25}$ = +50, $[\alpha]_{577}^{25}$ = +61, $[\alpha]_{546}^{25}$ = +65, $[\alpha]_{435}^{25}$ = +108, $[\alpha]_{405}^{25}$ = +126 (*c* = 0.1, $CHCl_3$). UV (MeCN): 254 (7000), 205 (15500). IR (film): 2990, 1480, 1380, 1260, 1200, 1165, 1025, 890, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55–7.53 (*m*, 2 arom. H); 7.33–7.28 (*m*, 3 arom. H); 6.23 (*d*, ^3J(7,8) = 1.9, H–C(7)); 5.85 (*d*, ^3J(3a′,7b′) = 6.4, H–C(3a′)); 5.84 (*d*, ^3J(4a′,7a′) = 3.5, H–C(4a′)); 5.25 (*d*, ^3J(4,4a) = 6.4, H–C(4)); 5.22 (*dd*, ^3J(5,4a) = 4.1, ^5J(5,8) = 0.8, H–C(5)); 5.08 (*ddd*, ^3J(8,8a) = 4.5, ^3J(8,7) = 1.9, ^5J(8,5) = 0.8, H–C(8)); 5.03 (*d*, ^3J(7b′,3a′) = 6.4, H–C(7b′)); 4.83 (*d*, ^3J(7a′,4a′) = 3.5, H–C(7a′)); 4.70 (*dd*, ^3J(8a,4a) = 8.0, ^3J(8a,8) = 4.5, H–C(8a)); 2.47 (*ddd*, ^3J(4a,8a) = 8.0, ^3J(4a,4) = 6.4, ^3J(4a,5) = 4.1, H–C(4a)); 1.56, 1.50, 1.39, 1.29 (4*s*, 4 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.2 (*s*, C(3′)); 137.2 (*d*, *J* = 181, C(7)); 135.5 (*s*, C(6)); 133.5 (*d*, *J* = 161, 2 arom. C); 129.3 (*d*, *J* = 163, 2 arom. C); 128.1 (*s*, arom. C); 127.9 (*d*, *J* = 161, arom. C); 113.7 (*s*, C(6′)); 106.2 (*d*, *J* = 185, C(4a′)); 97.9 (*s*, C(2)); 87.6 (*d*, *J* = 167, C(3a′)); 86.2 (*d*, *J* = 163, C(7b′)); 84.8 (*d*, *J* = 161, C(7a′)); 82.4 (*d*, *J* = 166, C(5), C(8)); 69.5 (*d*, *J* = 159, C(8a)); 63.2 (*d*, *J* = 143, C(4)); 35.8 (*d*, *J* = 137, C(4a)); 29.0, 27.8, 26.8, 21.5 (4*q*, *J* = 127, 4 Me). CI-MS (NH_3): 522 (1, $[M+1]^+$), 306 (2), 244 (100), 195 (9), 144 (10), 115 (60), 85 (44), 83 (43). Anal. calc. for $C_{24}H_{27}NO_7Se$ (520.44): C 55.39, H 5.23, N 2.69; found: C 55.21, H 5.39, N 2.52.

*(1*S*,2*R*,3*S*,4*R*,5*R*,6*R*)-6-*endo*-Chloro-3-*endo*-[(*S*)-hydroxy[(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol* (**50**). $NaBH_4$ (10 mg, 0.95 mmol) was added portionwise to a soln. of **45** (134 mg, 0.26 mmol) in MeOH (8 ml) cooled to 5°. After the addition of H_2O (2 ml), the mixture was extracted with AcOEt (10 ml, 4 times), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 2:1): 65 mg (50%) of **50**. Colorless oil. IR (film): 3450, 2990, 2940, 1480, 1380, 1265, 1225, 115, 995. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.65–7.63 (*m*, 2 arom. H); 7.33–7.29 (*m*, 3 arom. H); 5.71 (*d*, ^3J(4a″,7a″) = 3.5, H–C(4a″)); 5.63 (*d*, ^3J(3a″,7b″) = 6.6, H–C(3a″)); 4.92 (*d*, ^3J(1′,3) = 7.5, H–C(1′)); 4.88 (*d*, ^3J(7b″,3a″) = 6.6, H–C(7b″)); 4.76 (*d*, ^3J(4,3) = 5.6, H–C(4)); 4.74 (*d*, ^3J(7a″,4a″) = 3.5, H–C(7a″)); 4.60 (*dd*, ^3J(2,3) = 10.1, ^3J(2,1) = 4.8, H–C(2)); 4.49 (*dd*, ^3J(1,6) = 4.9, ^3J(1,2) = 4.8, H–C(1)); 4.24 (*dd*, ^3J(6,1) = 4.9, ^3J(6,5) = 4.9, H–C(6)); 4.17 (*d*, ^3J(5,6) = 4.9, H–C(5)); 3.00 (br. *s*, 2 OH); 2.84 (*ddd*, ^3J(3,2) = 10.1, ^3J(3,1′) = 8.3, ^3J(3,4) = 5.6, H–C(3)); 1.59 (br. *s*, 2 OH); 1.50, 1.36 (2*s*, 2 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 159.9 (*s*, C(3″)); 134.6 (*d*, *J* = 163, 2 arom. C); 129.2 (*d*, *J* = 161, 2 arom. C); 128.8 (*s*, arom. C); 128.0 (*d*, *J* = 161, arom. C); 114.0 (*s*, C(6″)); 106.0 (*d*, *J* = 187, C(4a″)); 87.7 (*d*, *J* = 162, C(4)); 86.8 (*d*, *J* = 164, C(3a″)); 86.5 (*d*, *J* = 163, C(7b″)); 84.7 (*d*, *J* = 168, C(7a″)); 79.1 (*d*, *J* = 158, C(1)); 73.3 (*d*, *J* = 159, C(2)); 64.4 (*d*, *J* = 143, C(1′)); 62.0 (*d*, *J* = 157, C(6)); 47.3 (*d*, *J* = 136, C(3)); 46.7 (*d*, *J* = 153, C(5)); 27.8, 26.8 (2*q*, *J* = 127, 2 Me).

*(−)-(4*S*,4a*S*,5*R*,6*R*,7*R*,8*S*,8a*R*)-7-Chloro-2,2-dimethyl-6-(phenylseleno)-4-[(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]-4a,5,6,7,8,8a-hexahydro-5,8-epoxy-4*H*-1,3-benzodioxine* ((−)-**51**). A mixture of **50** (50 mg, 0.1 mmol), $(MeO)_2CMe_2$ (2 ml), and TsOH (15 mg) in acetone (2 ml) was stirred at 25° for 5 h. After the addition of AcOEt (20 ml), the mixture was washed with sat. aq. $NaHCO_3$ soln. (7 ml) and brine (7 ml), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 4:1): 48 mg (89%) of (−)-**51**. Colorless oil. $[\alpha]_{589}^{25}$ = −9, $[\alpha]_{577}^{25}$ = −10, $[\alpha]_{546}^{25}$ = −13, $[\alpha]_{435}^{25}$ = −31, $[\alpha]_{405}^{25}$ = −44 (*c* = 1.0, $CHCl_3$). UV (MeCN): 272 (2300), 200 (12500). IR (film): 2990,

2940, 1385, 1265, 1205, 1150, 1090, 1005, 870, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.66–7.64 (*m*, 2 arom. H); 7.35–7.28 (*m*, 3 arom. H); 5.78 (*d*, ^3J(4a′,7a′) = 3.6, H–C(4a′)); 5.40 (*d*, ^3J(3a′,7b′) = 6.5, H–C(3a′)); 5.19 (*d*, ^3J(4,4a) = 6.5, H–C(4)); 5.11 (*d*, ^3J(5,4a) = 4.7, H–C(5)); 4.75 (*d*, ^3J(7a′,4a′) = 3.6, H–C(7a′)); 4.72 (*dd*, ^3J(8a,4a) = 8.50, ^3J(8a,8) = 4.8, H–C(8a)); 4.56 (*ddd*, ^3J(8,8a) = 4.8, ^3J(8,7) = 4.1, ^5J(8,5) = 0.8, H–C(8)); 4.50 (*d*, ^3J(7b′,3a′) = 6.5, H–C(7b′)); 4.07 (*dd*, ^3J(7,6) = 7.5, ^3J(7,8) = 4.1, H–C(7)); 3.73 (*d*, ^3J(6,7) = 7.5, H–C(6)); 2.24 (*ddd*, ^3J(4a,8a) = 8.5, ^3J(4a,4) = 6.5, ^3J(4a,5) = 4.7, H–C(4a)); 1.52, 1.51, 1.50, 1.37 (4*s*, 4 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 157.9 (*s*, C(3′)); 135.5 (*d*, *J* = 162, 2 arom. C); 129.0 (*d*, *J* = 160, 2 arom. C); 128.3 (*s*, arom. C); 128.0 (*d*, *J* = 161, arom. C); 113.7 (*s*, C(6′)); 106.1 (*d*, *J* = 184, C(4a′)); 98.6 (*s*, C(2)); 87.6 (*d*, *J* = 163, C(5)); 86.5 (*d*, *J* = 162, C(3a′)); 86.3 (*d*, *J* = 163, C(7b′)); 84.7 (*d*, *J* = 161, C(7a′)); 80.5 (*d*, *J* = 164, C(8)); 69.7 (*d*, *J* = 157, C(8a)); 63.3 (*d*, *J* = 144, C(4)); 62.8 (*d*, *J* = 159, C(7)); 45.8 (*d*, *J* = 150, C(6)); 38.6 (*d*, *J* = 135, C(4a)); 28.5, 27.7, 26.8, 19.8 (4*q*, *J* = 127, 4-CH_3). CI-MS (NH_3): 557 (1, M^+), 197 (1), 83 (100). Anal. calc. for $C_{24}H_{28}ClNO_7Se$ (556.90): C 51.76, H 5.07, N 2.52; found: C 51.83, H 5.16, N 2.49.

*(+)-(1*S*,2*R*,3*R*,4*R*,5*R*,6*R*)-3-*exo*-{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo*-*chloro*-2-*endo*-(methoxymethyl)-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptane* ((+)-**56**). Under Ar, $MeOCH_2Cl$ (3.61 ml, 47.4 mmol) was added at 0° to a mixture of (−)-**36** (1.50 g, 2.37 mmol) and $EtN(i\text{-}Pr)_2$ (8.0 ml, 47.4 mmol) in dry CH_2Cl_2 (20 ml). The mixture was stirred at 0° for 1 h, then at 25° for 20 h. After the addition of CH_2Cl_2 (50 ml), the mixture was washed successively with 1N aq. HCl (15 ml), sat. aq. $NaHCO_3$ soln. (15 ml), and brine (15 ml), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 8:1): 1.38 g (86%) of (+)-**56**. Colorless oil. $[\alpha]_{589}^{25} = +9$, $[\alpha]_{577}^{25} = +8$, $[\alpha]_{546}^{25} = +8$, $[\alpha]_{435}^{25} = +9$, $[\alpha]_{405}^{25} = +7$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 270 (1400). IR (film): 2950, 2890, 2860, 1470, 1385, 1255, 1225, 1100, 1050, 1025, 840, 760. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62–7.57 (*m*, 2 arom. H); 7.35–7.28 (*m*, 3 arom. H); 5.79 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.39 (*d*, ^3J(3a″,7b″) = 6.0, H–C(3a″)); 4.77 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.75 (*d*, ^3J(7b″,3a″) = 6.0, H–C(7b″)); 4.71 (*d*, ^3J(1′,3) = 6.7, H–C(1′)); 4.66 (*AB*, J_{AB} = 6.6, 1 H, OCH_2O); 4.62 (*AB*, J_{AB} = 6.6, 1 H, OCH_2O); 4.56 (*s*, H–C(4)); 4.47 (*dd*, ^3J(1,2) = 4.5, ^3J(1,6) = 4.5, H–C(1)); 4.18 (*dd*, ^3J(2,1) = 4.5, ^3J(2,3) = 4.1, H–C(2)); 4.12 (*dd*, ^3J(6,5) = 5.2, ^3J(6,1) = 4.5, H–C(6)); 3.45 (*d*, ^3J(5,6) = 5.2, H–C(5)); 3.40 (*s*, MeO); 2.25 (*dd*, ^3J(3,1′) = 6.7, ^3J(3,2) = 4.1, H–C(3)); 1.51, 1.36 (2*s*, 2 Me); 0.86 (*s*, *t*-BuSi); 0.05 (*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 159.7 (*s*, C(3″)); 134.2 (*d*, *J* = 161, 2 arom. C); 129.4 (*d*, *J* = 159, 2 arom. C); 128.8 (*s*, arom. C); 128.1 (*d*, *J* = 161, arom. C); 113.3 (*s*, C(6″)); 106.2 (*d*, *J* = 184, C(4a″)); 96.9 (*t*, *J* = 163, OCH_2O); 87.6 (*d*, *J* = 162, C(7b″)); 86.8 (*d*, *J* = 164, C(3a″)); 85.6 (*d*, *J* = 164, C(4)); 84.1 (*d*, *J* = 162, C(7a″)); 79.8 (*d*, *J* = 149, C(2)); 78.7 (*d*, *J* = 163, C(1)); 68.1 (*d*, *J* = 146, C(1′)); 60.8 (*d*, *J* = 157, C(6)); 56.4 (*d*, *J* = 136, C(3)); 56.1 (*q*, *J* = 142, MeO); 52.3 (*d*, *J* = 152, C(5)); 27.6, 26.8 (2*q*, *J* = 127, 2 Me); 25.7 (*q*, *J* = 125, *Me*$_3$CSi); 18.1 (*s*, Me_3CSi); −4.8, −5.2 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 675 (9, M^+), 618 (4), 520 (8), 484 (15), 368 (10), 242 (3), 78 (100). Anal. calc. for $C_{29}H_{42}ClNO_8SeSi$ (675.15): C 51.59, H 6.27, N 2.07; found: C 51.45, H 6.38, N 1.95.

*(+)-(1*S*,2*R*,3*S*,4*R*)-3-*exo*-{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-chloro-2-*endo*-(methoxymethoxy)-7-oxabicyclo[2.2.1]hept-5-ene (=(+)-(1*S*,4*R*,5*S*,6*R*)-5-*exo*-{(*S*)-[(*tert*-Butyl)dimethylsilyloxy]-[(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-2-chloro-6-*endo*-(methoxymethoxy)-7-oxabicyclo[2.2.1]hept-2-ene,* (+)-**57**). A dried ($MgSO_4$) soln. of *m*-chloroperbenzoic acid (*Fluka*; 70%; 360 mg, 1.46 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise to a stirred soln. of (+)-**56** (820 mg, 1.22 mmol) in dry THF (40 ml), at −78°. The mixture was stirred at −78° for 2 h, then at 25° for 14 h. The yellow soln. was washed with sat. aq. $NaHCO_3$ soln. (15 ml, twice), then with brine (15 ml). The org. phase was dried ($MgSO_4$) and evaporated and the residue purified by FC (light petroleum ether/AcOEt 9:1): 598 mg (95%) of (+)-**57**. Colorless oil. $[\alpha]_{589}^{25} = +129$, $[\alpha]_{577}^{25} = +134$, $[\alpha]_{546}^{25} = +154$, $[\alpha]_{435}^{25} = +272$, $[\alpha]_{405}^{25} = +334$ (*c* = 1.1, $CHCl_3$). UV (MeCN): 209 (7000). IR (film): 2950, 2930, 2860, 1595, 1385, 1250, 1150, 1100, 1030, 840, 760. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.37 (*d*, ^3J(5,4) = 2.2, H–C(5)); 5.87 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.44 (*d*, ^3J(3a″,7b″) = 5.8, H–C(3a″)); 4.97 (*d*, ^3J(4,5) = 2.2, H–C(4)); 4.92 (*d*, ^3J(1′,3) = 6.5, H–C(1′)); 4.84 (*d*, ^3J(7b″,3a″) = 5.8, H–C(7b″)); 4.82 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.70–4.68 (*m*, H–C(1)); 4.69 (*AB*, J_{AB} = 6.7, 1 H, OCH_2O); 4.66 (*AB*, J_{AB} = 6.7, 1 H, OCH_2O); 4.17 (*dd*, ^3J(2,1) = 4.4, ^3J(2,3) = 2.4, H–C(2)); 3.39 (*s*, MeO); 2.02 (*dd*, ^3J(3,1′) = 6.5, ^3J(3,2) = 2.4, H–C(3)); 1.49, 1.36 (2*s*, 2 Me); 0.92 (*s*, *t*-BuSi); 0.11, 0.10 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.0 (*s*, C(3″)); 138.4 (*s*, C(6)); 130.1 (*d*, *J* = 180, C(5)); 113.2 (*s*, C(6″)); 106.3 (*d*, *J* = 183, C(4a″)); 96.9 (*t*, *J* = 163, OCH_2O); 87.8 (*d*, *J* = 163, C(7b″)); 87.1 (*d*, *J* = 164, C(3a″)); 84.0 (*d*, *J* = 162, C(7a″)); 82.3 (*d*, *J* = 169, C(1)); 81.2 (*d*, *J* = 166, C(4)); 76.3 (*d*, *J* = 165, C(2)); 68.2 (*d*, *J* = 145, C(1′)); 56.0 (*q*, *J* = 142, MeO); 53.2 (*d*, *J* = 139, C(3)); 27.7, 26.8 (2*q*, *J* = 127, 2 Me); 25.8 (*q*, *J* = 125, *Me*$_3$CSi); 18.2 (*s*, Me_3CSi); −4.8, −5.1 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 519 (1, $[M+1]^+$), 518 (3, M^+), 460

(2), 386 (10), 358 (62), 328 (5), 284 (12), 242 (45), 184 (24), 129 (100), 73 (65). Anal. calc. for $C_{23}H_{36}ClNO_8Si$ (518.07): C 53.32, H 7.00, N 2.70; found: C 53.19, H 7.01, N 2.63.

*(+)-(1*R*,2*R*,4*S*,5*R*,6*R*)-6-*exo-*{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-5-*endo-*(methoxymethoxy)-3-oxo-7-oxabicyclo[2.2.1]hept-2-*exo-*yl 4-Bromobenzenesulfonate* ((+)-**58**). $NaHCO_3$ (175 mg, 2.08 mmol), 0.1M OSO_4 in CCl_4 (0.1 ml) and $Me_3NO \cdot 2\,H_2O$ (234 mg, 2.08 mmol) were added successively to a stirred soln. of (+)-**57** (540 mg, 1.04 mmol) in THF/H_2O 5:1 (20 ml) at 25°. After stirring at 25° for 2 h, the yellow soln. was poured into CH_2Cl_2 (100 ml) and 1N aq. HCl (50 ml). The org. layer was washed with 10% aq. $NaHSO_3$ soln. (50 ml), the aq. phase extracted with CH_2Cl_2 (2 × 50 ml), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue dissolved in dry CH_2Cl_2 (5 ml) to which 4-bromobenzenesulfonyl chloride (405 mg, 1.56 mmol) and Et_3N (0.2 ml, 1.25 mmol) were added at 0°. The mixture was stirred at 0° for 1 h, then at 25° for 2 h and poured into CH_2Cl_2 (50 ml) and 1N aq. HCl (15 ml). The aq. layer was extracted with CH_2Cl_2 (10 ml, 3 times), the combined org. phase washed with 5% aq. Na_2CO_3 soln. (30 ml) and brine (20 ml), dried ($MgSO_4$), and evaporated, and the residue purified by FC (silica gel (10 g), light petroleum ether/AcOEt 6:1): 672 mg (88%) of (+)-**58**. Colorless solid. M.p. 55–56. $[\alpha]_{589}^{25} = +13$, $[\alpha]_{577}^{25} = +14$, $[\alpha]_{546}^{25} = +16$, $[\alpha]_{435}^{25} = +41$, $[\alpha]_{405}^{25} = +62$ ($c = 1.0$, $CHCl_3$). UV (MeCN): 235 (15300). IR (KBr): 2950, 1790, 1575, 1470, 1375, 1220, 1190, 1110, 1045, 995, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.81 (*d*, $^3J = 8.8$, 2 arom. H); 7.72 (*d*, $^3J = 8.8$, 2 arom. H); 5.86 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.51 (*d*, ^3J(3a″,7b″) = 6.1, H–C(3a″)); 4.92 (*d*, ^3J(7b″,3a″) = 6.1, H–C(7b″)); 4.83 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.78 (*s*, H–C(2)); 4.77 (*d*, ^3J(1′,6) = 7.4, H–C(1′)); 4.64 (*AB*, $J_{AB} = 6.9$, 1 H, OCH_2O); 4.52 (*AB*, $J_{AB} = 6.8$, 1 H, OCH_2O); 4.47 (*s*, H–C(1)); 4.40 (*dd*, $^3J(4,5) = 5.5$, $^5J(4,1) = 1.2$, H–C(4)); 4.17 (*ddd*, $^3J(5,4) = 5.5$, $^3J(5,6) = 2.7$, $^4J(5,1) = 1.2$, H–C(5)); 3.32 (*s*, MeO); 2.33 (*dd*, $^3J(6,1') = 7.4$, $^3J(6,5) = 2.7$, H–C(6)); 1.53, 1.38 (2*s*, 2 Me); 0.92 (*s*, *t*-BuSi); 0.13, 0.12 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.4 (*s*, C(3)); 159.1 (*s*, C(3′)); 134.8 (*s*, arom. C); 132.7 (*d*, $J = 171$, 2 arom. C); 129.6 (*s*, arom. C); 129.5 (*d*, $J = 176$, 2 arom. C); 113.6 (*s*, C(6′)); 106.2 (*d*, $J = 184$, C(4a″)); 97.1 (*t*, $J = 163$, OCH_2O); 87.7 (*d*, $J = 163$, C(7b″)); 86.7 (*d*, $J = 164$, C(3a″)); 84.1 (*d*, $J = 162$, C(7a″)); 81.6 (*d*, $J = 164$, C(2)); 80.7 (*d*, $J = 164$, C(4)); 77.0 (*d*, $J = 157$, C(1)); 76.0 (*d*, $J = 164$, C(5)); 67.2 (*d*, $J = 146$, C(1′)); 56.4 (*q*, $J = 143$, MeO); 52.9 (*d*, $J = 135$, C(6)); 27.7, 26.8 (2*q*, $J = 126$, 2 Me); 25.6 (*q*, $J = 120$, Me_3CSi); 18.0 (*s*, Me_3CSi); −4.7, −5.0 (2*q*, $J = 119$, MeSi). CI-MS (NH_3): 736 (11, $[M+1]^+$), 735 (6, M^+), 500 (7), 454 (7), 329 (8), 295 (10), 242 (72), 184 (21), 129 (66), 73 (100). Anal. calc. for $C_{29}H_{40}BrNO_{12}SSi$ (734.67): C 47.41, H 5.49, N 1.91; found: C 47.34, H 5.44, N 1.95.

*(+)-(1*R*,4*R*,5*R*,6*S*,7*R*)-4-*exo-*{[4-(Bromophenyl)sulfonyl]oxy}-6-*exo-*{(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-7-*endo-*(methoxymethoxy)-2,8-dioxabicyclo[3.2.1]octan-3-one* (= *5-O-[(4-Bromophenyl)sulfonyl]-3-{(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-3-deoxy-2-*O*-(methoxymethyl)-β-*L*-altrofuranurono-6,1-lactone*) ((+)-**59**). *m*-Chloroperbenzoic acid (85%; 174 mg, 0.85 mmol) and then $NaHCO_3$ (130 mg, 1.55 mmol) were added to a stirred soln. of (+)-**58** (565 mg, 0.77 mmol) in dry CH_2Cl_2 (20 ml) at 0°. The mixture was stirred at 0° for 5 h, then at 25° for 15 h. It was then poured into CH_2Cl_2 (50 ml) and sat. aq. $NaHSO_3$ soln. (20 ml). The aq. layer was extracted with CH_2Cl_2 (2 × 10 ml), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (20 ml) and brine (20 ml), dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 5:1): 532 mg of (+)-**59**. Colorless solid. M.p. 67–68°. $[\alpha]_{589}^{25} = +18$, $[\alpha]_{577}^{25} = +19$, $[\alpha]_{546}^{25} = +22$, $[\alpha]_{435}^{25} = +40$, $[\alpha]_{405}^{25} = +50$ ($c = 1.0$, $CHCl_3$). UV (MeCN): 235 (16100), 202 (15000). IR (KBr): 2930, 1770, 1575, 1390, 1375, 1205, 1190, 1105, 1060, 1010, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.83 (*d*, $^3J = 8.8$, 2 arom. H); 7.73 (*d*, $^3J = 8.8$, 2 arom. H); 5.82 (*d*, $^3J(1,7) = 3.5$, H–C(1)); 5.79 (*d*, ^3J(4a″,7a″) = 3.5, H–C(4a″)); 5.56 (*d*, ^3J(3a″,7b″) = 6.7, H–C(3a″)); 4.95 (*d*, ^3J(7b″,3a″) = 6.7, H–C(7b″)); 4.78 (*d*, ^3J(1′,6) = 5.7, H–C(1′)); 4.74 (*d*, ^3J(7a″,4a″) = 3.5, H–C(7a″)); 4.73 (*s*, H–C(4)); 4.64 (*AB*, $J_{AB} = 7.0$, 1 H, OCH_2O); 4.55 (br. *s*, H–C(5)); 4.50 (*AB*, $J_{AB} = 7.0$, 1 H, OCH_2O); 4.19 (*dd*, $^3J(7,6) = 4.5$, $^3J(7,1) = 3.5$, H–C(7)); 3.32 (*s*, MeO); 2.36 (*ddd*, $^3J(6,1') = 5.7$, $^3J(6,7) = 4.5$, $^4J = 1.9$, H–C(6)); 1.44, 1.32 (2*s*, 2 Me); 0.84 (*s*, *t*-BuSi); 0.06, 0.05 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.0 (*s*, C(3)); 158.0 (*s*, C(3′)); 134.3 (*s*, arom. C); 132.6 (*d*, $J = 171$, 2 arom. C); 129.9 (*d*, $J = 170$, 2 arom. C); 129.8 (*s*, arom. C); 113.9 (*s*, C(6′)); 106.0 (*d*, $J = 185$, C(4a″)); 102.1 (*d*, $J = 185$, C(1)); 97.5 (*t*, $J = 165$, OCH_2O); 87.0 (*d*, $J = 162$, C(7b″)); 86.9 (*d*, $J = 162$, C(3a″)); 84.7 (*d*, $J = 162$, C(4)); 80.2 (*d*, $J = 163$, C(5)); 80.1 (*d*, $J = 159$, C(7)); 76.5 (*d*, $J = 162$, C(7a″)); 67.5 (*d*, $J = 145$, C(1′)); 56.7 (*q*, $J = 143$, MeO); 48.2 (*d*, $J = 133$, C(6)); 27.8, 26.9 (2*q*, $J = 124$, 2 Me); 25.6 (*q*, $J = 125$, *t*-BuSi); 18.0 (*s*, Me_3CSi); −4.4, −4.8 (2*q*, $J = 118$, 2 MeSi). CI-MS (NH_3): 752 (8, $[M+1]^+$), 751 (10, M^+), 694 (5), 516 (18), 458 (5), 295 (8), 242 (100), 129 (60), 75 (94). Anal. calc. for $C_{29}H_{40}BrNO_{13}SSi$ (750.67): C 46.40, H 5.37, N 1.87; found: C 46.38, H 5.35, N 1.93.

*(+)-Methyl (1*R*,3*S*,4*R*,5*S*,6*R*)-5-*exo-*{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo-*(methoxymethoxy)-2,7-dioxa-*

bicyclo[2.2.1]heptan-3-exo-*carboxylate* (=*(+)-Methyl 1,5-Anhydro-3-[(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-3-deoxy-2-*O*-(methoxymethyl)-α-D-galactofuranuronate*; (+)-**60**) *and (+)-Methyl (1*R*,3*R*,4*R*,5*S*,6*R*)-5*-exo-*[(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo-*(methoxymethoxy)-2,7-dioxabicyclo[2.2.1]heptan-3-*endo-*carboxylate* (=*(+)-Methyl 1,5-Anhydro-3-[(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-3-deoxy-2-*O*-(methoxymethyl)-α-L-altrofuranuronate*, (+)-**61**). A soln. of (+)-**59** (0.5 g, 0.66 mmol) in anh. DMF (5.6 ml) was added to a soln. of anh. K_2CO_3 (184 mg, 1.33 mmol) in anh. DMF (3.4 ml) stirred at 0°. After stirring at 0° for 5 min, MeOH (2.25 ml) was added and the mixture stirred at 0° for 30 min, then at 25° for 90 min. After the addition of AcOEt (50 ml), the mixture was washed with brine (3 × 15 ml), the aq. phase extracted with AcOEt (2 × 10 ml), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 4:1): 270 mg (75%) of (+)-**60** and 54 mg (15%) of (+)-**61**.

Data of (+)-**60**: Colorless oil. $[\alpha]_{589}^{25} = +64$, $[\alpha]_{577}^{25} = +67$, $[\alpha]_{546}^{25} = +75$, $[\alpha]_{435}^{25} = +129$, $[\alpha]_{405}^{25} = +157$ ($c = 0.4$, $CHCl_3$). UV (MeCN): 200 (5800). IR (film): 2950, 2850, 1760, 1735, 1470, 1375, 1250, 1220, 1155, 1095, 995, 900, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.87 (*d*, ^3J(4a″,7a″) = 3.6, H−C(4a″)); 5.70 (*d*, ^3J(1,6) = 2.3, H−C(1)); 5.55 (*d*, ^3J(3a″,7b″) = 6.0, H−C(3a″)); 4.97 (*s*, H−C(4)); 4.90 (*d*, ^3J(7b″,3a″) = 6.0, H−C(7b″)); 4.82 (*d*, ^3J(7a″,4a″) = 3.6, H−C(7a″)); 4.76 (*d*, ^3J(1′,5) = 6.6, H−C(1′)); 4.71 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.64 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.29 (*s*, H−C(3)); 3.81 (*dd*, ^3J(6,5) = 3.0, ^3J(6,1) = 2.3, H−C(6)); 3.80 (*s*, COOMe); 3.43 (*s*, MeO); 2.13 (*dd*, ^3J(5,1′) = 6.6, ^3J(5,6) = 3.0, H−C(5)); 1.52, 1.37 (2*s*, 2 Me); 0.92 (*s*, *t*-BuSi); 0.12, 0.11 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.6 (*s*, *C*OOMe); 159.0 (*s*, C(3″)); 113.1 (*s*, C(6″)); 106.0 (*d*, *J* = 184, C(4a″)); 101.4 (*d*, *J* = 183, C(1)); 97.0 (*t*, *J* = 164, OCH_2O); 87.5 (*d*, *J* = 163, C(7b″)); 86.6 (*d*, *J* = 164, C(3a″)); 83.9 (*d*, *J* = 161, C(7a″)); 80.8 (*d*, *J* = 162, C(4)); 80.7 (*d*, *J* = 158, C(6)); 76.8 (*d*, *J* = 155, C(3)); 67.4 (*d*, *J* = 145, C(1′)); 55.9 (*q*, *J* = 142, MeO); 52.5 (*q*, *J* = 142, COO*Me*); 52.4 (*d*, *J* = 148, C(5)); 27.5, 26.6 (2*q*, *J* = 127, 2 Me); 25.5 (*q*, *J* = 120, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.9, −5.3 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 547 (44, $[M+1]^+$), 546 (100, M^+), 488 (18), 430 (11), 373 (11), 284 (9), 242 (17), 170 (13), 129 (33). Anal. calc. for $C_{24}H_{39}NO_{11}Si$ (545.65): C 52.83, H 7.20, N 2.57; found: C 52.89, H 7.15, N 2.49.

Data of (+)-**61**: Colorless oil. $[\alpha]_{589}^{25} = +75$, $[\alpha]_{577}^{25} = +76$, $[\alpha]_{546}^{25} = +87$, $[\alpha]_{435}^{25} = +150$, $[\alpha]_{405}^{25} = +182$ ($c = 0.3$, $CHCl_3$). UV (MeCN): 209 (4300). IR (film): 2950, 2895, 2850, 1765, 1730, 1470, 1375, 1220, 1150, 1055, 900, 870. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.84 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.59 (*d*, ^3J(1,6) = 2.0, H−C(1)); 5.50 (*d*, ^3J(3a″,7b″) = 5.9, H−C(3a″)); 4.90 (*d*, ^3J(3,4) = 4.0, H−C(3)); 4.85 (*d*, ^3J(7b″,3a″) = 5.9, H−C(7b″)); 4.80 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.70 (*d*, ^3J(1′,5) = 7.2, H−C(1′)); 4.69 (*AB*, J_{AB} = 6.9, 1 H, OCH_2O); 4.64 (*AB*, J_{AB} = 6.9, 1 H, OCH_2O); 4.46 (*d*, ^3J(4,3) = 4.0, H−C(4)); 3.77 (*s*, COOMe); 3.75 (*dd*, ^3J(6,5) = 2.9, ^3J(6,1) = 2.0, H−C(6)); 3.42 (*s*, MeO); 2.03 (*dd*, ^3J(5,1′) = 7.2, ^3J(5,6) = 2.9, H−C(5)); 1.48; 1.34 (2*s*, 2 Me); 0.88 (*s*, *t*-BuSi); 0.06, 0.05 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 168.5 (*s*, *C*OOMe); 159.3 (*s*, C(3″)); 113.2 (*s*, C(6″)); 106.3 (*d*, *J* = 184, C(4a″)); 102.6 (*d*, *J* = 183, C(1)); 97.0 (*t*, *J* = 163, OCH_2O); 87.9 (*d*, *J* = 162, C(7b″)); 86.5 (*d*, *J* = 164, C(3a″)); 83.9 (*d*, *J* = 161, C(7a″)); 81.3 (*d*, *J* = 161, C(6)); 79.3 (*d*, *J* = 163, C(4)); 77.6 (*d*, *J* = 157, C(3)); 67.6 (*d*, *J* = 146, C(1′)); 55.9 (*q*, *J* = 142, MeO); 52.2 (*q*, *J* = 148, COO*Me*); 48.7 (*d*, *J* = 136, C(5)); 27.6 (*q*, *J* = 127, Me); 26.8 (*q*, *J* = 125, Me); 25.6 (*q*, *J* = 120, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.8, −5.3 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 546 (2, $[M+1]^+$), 530 (11), 488 (55), 373 (17), 284 (7), 242 (19), 184 (10), 129 (22), 73 (100). Anal. calc. for $C_{24}H_{39}NO_{11}Si$ (545.65): C 52.83, H 7.20, N 2.57; found: C 52.84, H 7.20, N 2.51.

*(+)-1,4-Anhydro-3-[(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*R*,4aR,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-D-galactopyranose* ((+)-**62**). At 0° 1M $LiAlH_4$ in Et_2O (0.46 ml, 0.46 mmol) was added dropwise to a stirred soln. of (+)-**60** (250 mg, 0.46 mmol) in anh. THF (10 ml). After stirring at 0° for 10 min, a few drops of MeOH were added, and the mixture was poured into 1N aq. HCl (3 ml) and extracted with AcOEt (3 × 5 ml). The combined org. extract was washed with sat. aq. $NaHCO_3$ soln. (8 ml), dried ($MgSO_4$); and evaporated and the residue dissolved in anh. CH_2Cl_2 (5 ml) and cooled to 0°. (i-Pr)$_2$NEt (1.55 ml, 9.2 mmol) and $MeOCH_2Cl$ (0.7 ml, 9.2 mmol) were added successively, and the mixture was stirred at 0° for 1 h, then at 25° for 15 h. The soln. was poured into 1N aq. HCl (10 ml) and extracted with CH_2Cl_2 (15 ml, 3 times), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (light petroleum ether/AcOEt 4:1): 212 g (82%) of (4)-**62**. Colorless oil. $[\alpha]_{589}^{25} = +54$, $[\alpha]_{577}^{25} = +57$, $[\alpha]_{546}^{25} = +64$, $[\alpha]_{435}^{25} = +110$, $[\alpha]_{405}^{25} = +134$ ($c = 0.7$, $CHCl_3$). UV (MeCN): 210 (3600). IR (film): 2930, 2890, 2860, 1475, 1375, 1220, 1150, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.86 (*d*, ^3J(4a″,7a″) = 3.6, H−C(4a″)); 5.55 (*d*, ^3J(3a″,7b″) = 6.0, H−C(3a″)); 5.47 (*d*, ^3J(1,2) = 2.4, H−C(1)); 4.89 (*d*, ^3J(7b″,3a″) = 6.0, H−C(7b″)); 4.82 (*d*, ^3J(7a″,4a″) = 3.6, H−C(7a″)); 4.72 (*d*, ^3J(1′,3) = 7.0, H−C(1′)); 4.71 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.64–4.60 (*m*, 4 H, OCH_2O; H−C(4)); 3.93 (*dd*, ^3J(5,6*B*) = 8.0, ^3J(5,6*A*) = 5.2, H−C(5)); 3.81

(*dd*, $^3J(2,3)=2.8$, $^3J(2,1)=2.4$, H–C(2)); 3.46 (*dd*, $^2J(6A,6B)=10.3$, $^3J(6,5A)=5.2$, H_A–C(6)); 3.41–3.39 (*m*, H_B–C(6)); 3.40 (*s*, MeO); 3.35 (*s*, MeO); 2.05 (*dd*, $^3J(3,1')=7.0$, $^3J(3,2)=2.8$, H–C(3)); 1.51, 1.36 (2*s*, 2 Me); 0.91 (*s*, *t*-BuSi); 0.11, 0.09 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 159.5 (*s*, C(3″)); 113.3 (*s*, C(6″)); 106.2 (*d*, $J=183$, C(4a″)); 100.5 (*d*, $J=182$, C(1)); 97.0 (*t*, $J=163$, OCH_2O); 96.8 (*t*, $J=163$, OCH_2O); 87.6 (*d*, $J=162$, C(7b″)); 86.9 (*d*, $J=164$, C(3a″)); 84.1 (*d*, $J=161$, C(7a″)); 81.1 (*d*, $J=156$, C(2)); 78.8 (*d*, $J=163$, C(4)); 78.0 (*d*, *J*(C,H) = 162, C(5)); 68.0 (*t*, $J=144$, C(6)); 67.8 (*d*, $J=145$, C(1′)); 55.9, 55.3 (2*q*, $J=142$, 2 MeO); 52.8 (*d*, $J=136$, C(3)); 27.7 (*q*, $J=127$, Me); 26.8 (*q*, $J=125$, Me); 25.7 (*q*, $J=125$, *Me*$_3$CSi); 18.3 (*s*, Me$_3$*C*Si); −4.8, −5.1 (2*q*, $J=119$, 2 MeSi). CI-MS (NH_3): 563 (3, $[M+1]^+$), 562 (6, M^+), 530 (32), 504 (65), 373 (87), 328 (9), 284 (48), 242 (23), 184 (15), 129 (34), 73 (100). Anal. calc. for $C_{25}H_{43}NO_{11}Si$ (561.70): C 53.46, H 7.72, N 2.49; found: C 53.59, H 7.74, N 2.48.

*(+)-1,4-Anhydro-3-{(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-altropyranose* ((+)-**63**). As described for (+)-**62**, with (+)-**61**: **(+)-63** (82%). Colorless foam. $[\alpha]_{589}^{25}=+63$, $[\alpha]_{577}^{25}=+65$, $[\alpha]_{546}^{25}=+74$, $[\alpha]_{435}^{25}=+127$, $[\alpha]_{405}^{25}=+156$ ($c=0.4$, $CHCl_3$). UV (MeCN): 210 (4600). IR (film): 2935, 2890, 2860, 1470, 1385, 1375, 1250, 1155, 1090, 1040, 840, 780, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.87 (*d*, $^3J(4a'',7a'')=3.7$, H–C(4a″)); 5.57 (*d*, $^3J(3a'',7b'')=6.0$, H–C(3a″)); 5.50 (*d*, $^3J(1,2)=2.4$, H–C(1)); 4.86 (*d*, $^3J(7b'',3a'')=6.0$, H–C(7b″)); 4.82 (*d*, $^3J(7a'',4a'')=3.7$, H–C(7a″)); 4.70 (*AB*, $J_{AB}=6.8$, 1 H, OCH_2O); 4.68 (*d*, $^3J(1',3)=8.1$, H–C(1′)); 4.63–4.60 (*m*, 4 H, H–C(4), OCH_2O); 4.10 (*ddd*, $^3J(5,6A)=10.4$, $^3J(5,6B)=7.4$, $^3J(5,4)=3.6$, H–C(5)); 3.98 (*dd*, $^3J(6A,5)=10.4$, $^2J(6A,6B)=6.6$, H_A–C(6)); 3.76–3.70 (*m*, H–C(2), H_B–C(6)); 3.39, 3.36 (2*s*, 2 MeO); 2.28 (*dd*, $^3J(3,1')=8.1$, $^3J(3,2)=2.6$, H–C(3)); 1.50, 1.37 (2*s*, 2 Me); 0.91 (*s*, *t*-BuSi); 0.11, 0.09 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 159.6 (*s*, C(3″)); 113.2 (*s*, C(6″)); 106.3 (*d*, $J=183$, C(4a″)); 101.5 (*d*, $J=182$, C(1)); 96.9 (*t*, $J=163$, OCH_2O); 96.8 (*t*, $J=162$, OCH_2O); 87.9 (*d*, $J=162$, C(7b″)); 86.6 (*d*, $J=164$, C(3a″)); 84.0 (*d*, $J=161$, C(7a″)); 81.6 (*d*, $J=151$, C(2)); 80.1 (*d*, $J=161$, C(4)); 76.3 (*d*, $J=155$, C(5)); 68.0 (*d*, $J=145$, C(1′)); 66.1 (*t*, $J=143$, C(6)); 55.9, 55.4 (2*q*, $J=142$, 2 MeO); 47.2 (*d*, $J=136$, C(3)); 27.7 (*q*, $J=125$, Me); 26.8 (*q*, $J=124$, Me); 25.7 (*q*, $J=119$, *Me*$_3$CSi); 18.1 (*s*, Me$_3$CSi); −4.7, −5.1 (2*q*, $J=119$, 2 MeSi). CI-MS (NH_3): 563 (4, $[M+1]^+$), 562 (6, M^+), 530 (11), 504 (36), 428 (10), 373 (37), 284 (26), 242 (18), 149 (48), 75 (100). Anal. calc. for $C_{25}H_{43}NO_{11}Si$ (561.70): C 53.46, H 7.72, N 2.49; found: C 53.47, H 7.80, N 2.54.

*(+)-(1*S*,2*R*,3*R*,4*R*,5*R*,6*R*)-3-*exo*-{(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo*-(methoxymethyl)-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptane* ((+)-**64**). As described for (+)-**56**, with (+)-**37**: (+)-**64** (90%). Colorless oil. $[\alpha]_{589}^{25}=+50$, $[\alpha]_{577}^{25}=+51$, $[\alpha]_{546}^{25}=+58$, $[\alpha]_{435}^{25}=+94$, $[\alpha]_{405}^{25}=+110$ ($c=1.0$, $CHCl_3$). UV (MeCN): 270 (2500), 196 (14800). IR (film): 2990, 2960, 2860, 1470, 1375, 1225, 1155, 1055, 835, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61–7.58 (*m*, 2 arom. H); 7.31–7.29 (*m*, 3 arom. H); 5.89 (*d*, $^3J(4a'',7a'')=3.5$, H–C(4a″)); 5.74 (*d*, $^3J(3a'',7b'')=7.1$, H–C(3a″)); 4.91 (*d*, $^3J(7b'',3a'')=7.1$, H–C(7b″)); 4.69 (*d*, $^3J(7a'',4a'')=3.5$, H–C(7a″)); 4.58 (*AB*, $J_{AB}=6.5$, 1 H, OCH_2O); 4.55–4.53 (*m*, H–C(4), H–C(1)); 4.50 (*AB*, $J_{AB}=6.5$, 1 H, OCH_2O); 4.41 (*d*, $^3J(1',3)=10.0$, H–C(1′)); 4.17 (*ddd*, $^3J(6,5)=5.0$, $^3J(6,1)=4.8$, $^4J(6,2)=1.2$, H–C(6)); 4.00 (*dd*, $^3J(2,1)=3.3$, $^3J(2,3)=4.3$, H–C(2)); 3.53 (*d*, $^3J(5,6)=5.0$, H–C(5)); 3.36 (*s*, MeO); 2.51 (*dd*, $^3J(3,1')=10.0$, $^3J(3,2)=4.3$, H–C(3)); 1.52, 1.38 (2*s*, 2 Me); 0.83 (*s*, *t*-Bu); 0.04, −0.03 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 157.9 (*s*, C(3″)); 134.4 (*d*, $J=162$, 2 arom. C); 129.3 (*d*, $J=161$, 2 arom. C); 128.6 (*s*, arom. C); 128.0 (*d*, $J=161$, arom. C); 113.8 (*s*, C(6″)); 105.8 (*d*, $J=185$, C(4a″)); 96.8 (*t*, $J=163$, OCH_2O); 86.5 (*d*, $J=163$, C(3a″)); 85.8 (*d*, $J=162$, C(7b″)); 85.7 (*d*, $J=162$, C(4)); 84.9 (*d*, $J=161$, C(7a″)); 80.2 (*d*, $J=146$, C(2)); 78.9 (*d*, $J=163$, C(1)); 69.3 (*d*, $J=146$, C(1′)); 61.2 (*d*, $J=161$, C(6)); 56.5 (*q*, $J=142$, MeO); 54.4 (*d*, $J=139$, C(3)); 52.0 (*d*, $J=152$, C(5)); 27.8 (*q*, $J=127$, Me); 26.8 (*q*, $J=128$, Me); 25.6 (*q*, $J=125$, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.8, −5.3 (2*q*, $J=119$, 2 MeSi). CI-MS (NH_3): 676 (2, $[M+1]^+$), 675 (1, M^+), 662 (9), 617 (28), 530 (15), 328 (18), 242 (17), 129 (31), 73 (100). Anal. calc. for $C_{29}H_{42}ClNO_8SeSi$ (675.15): C 51.59, H 6.27, N 2.07; found: C 51.62, H 6.22, N 2.05.

*(+)-(1*S*,2*R*,3*S*,4*R*)-3-*exo*-{(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-chloro-2-*endo*-(methoxymethoxy)-7-oxabicyclo[2.2.1]hept-5-ene* ((+)-**65**; for systematic numbering, see (+)-**57**). As described for (+)-**57**, with (+)-**64**: (+)-**65** (90%). Colorless foam. $[\alpha]_{589}^{25}=+63$, $[\alpha]_{577}^{25}=+66$, $[\alpha]_{546}^{25}=+76$, $[\alpha]_{435}^{25}=+128$, $[\alpha]_{405}^{25}=+153$ ($c=0.9$, $CHCl_3$). UV (MeCN): 208 (7300). IR (film): 2950, 2935, 1595, 1470, 1370, 1050, 880, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.35 (*d*, $^3J(5,4)=2.2$, H–C(5)); 5.80 (*d*, $^3J(4a'',7a'')=3.5$, H–C(4a″)); 5.71 (*d*, $^3J(3a'',7b'')=6.8$, H–C(3a″)); 4.90 (*d*, $^3J(7b'',3a'')=6.8$, H–C(7b″)); 4.89 (*dd*, $^3J(4,5)=2.2$, $^5J(4,1)=1.0$, H–C(4)); 4.74 (*d*, $^3J(1,2)=4.2$, H–C(1)); 4.70 (*d*, $^3J(7a'',4a'')=3.5$, H–C(7a″)); 4.54 (*AB*, $J_{AB}=6.5$, 1 H, OCH_2O); 4.52 (*d*, $^3J(1',3)=10.4$, H–C(1′)); 4.51 (*AB*, $J_{AB}=6.5$, 1 H, OCH_2O); 4.04 (*dd*, $^3J(2,1)=4.2$, $^3J(2,3)=2.5$, H–C(2)); 3.35 (*s*, MeO); 2.23 (*dd*, $^3J(3,1')=10.4$, $^3J(3,2)=2.5$, H–C(3)); 1.49, 1.34 (2*s*, 2 Me); 0.90 (*s*, *t*-BuSi); 0.09, 0.00 (2*s*, 2 MeSi).

^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.9 (*s*, C(3″)); 137.7 (*s*, C(6)); 130.3 (*d*, *J* = 180, C(5)); 113.8 (*s*, C(6″)); 105.8 (*d*, *J* = 184, C(4a″)); 96.5 (*t*, *J* = 163, OCH_2O); 86.4 (*d*, *J* = 164, C(3a″)); 85.9 (*d*, *J* = 163, C(7b″)); 84.5 (*d*, *J* = 161, C(7a″)); 82.6 (*d*, *J* = 168, C(1)); 81.0 (*d*, *J* = 167, C(4)); 77.1 (*d*, *J* = 150, C(2)); 69.4 (*d*, *J* = 146, C(1′)); 56.1 (*q*, *J* = 142, MeO); 51.9 (*d*, *J* = 141, C(3)); 27.8 (*q*, *J* = 125, Me); 26.8 (*q*, *J* = 126, Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.8, −5.4 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 519 (2, $[M+1]^+$), 518 (2, M^+), 460 (4), 386 (11), 358 (66), 242 (21), 185 (30), 129 (39), 83 (100). Anal. calc. for $C_{23}H_{36}ClNO_8Si$ (518.07): C 53.32, H 7.00, N 2.70; found: C 53.35, H 7.13, N 2.70.

*(+)-(1*R*,2*R*,4*S*,5*R*,6*R*)-6-*exo*-[(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-5*-endo-*(methoxymethoxy)-3*-oxo-7*-oxabicyclo[2.2.1]hept-2*-exo-*yl 4-Bromobenzenesulfonate* ((+)-**66**). As described for (+)-**58**, with (+)-**65**: (+)-**66** (88%). Colorless foam. $[\alpha]_{589}^{25} = +4$, $[\alpha]_{577}^{25} = +4$, $[\alpha]_{546}^{25} = +4$, $[\alpha]_{435}^{25} = +11$, $[\alpha]_{405}^{25} = +18$ (*c* = 1.2, $CHCl_3$). UV (MeCN): 234 (19600). IR (film): 2960, 2860, 1790, 1575, 1475, 1375, 1190, 1095, 1045, 840, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.85 (*d*, ^3J = 8.8, 2 arom. H); 7.74 (*d*, ^3J = 8.8, 2 arom. H); 5.75 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.73 (*d*, ^3J(3a″,7b″) = 6.6, H−C(3a″)); 4.95 (*d*, ^3J(7b″,3a″) = 6.6, H−C(7b″)); 4.91 (*s*, H−C(2)); 4.76 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.53 (*d*, ^3J(1′,6) = 10.4, H−C(1′)); 4.48 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.45 (*m*, H−C(4), H−C(1)); 4.44 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 3.90 (*ddd*, ^3J(5,4) = 5.3, ^3J(5,6) = 2.8, ^3J(5,1) = 1.1, H−C(5)); 3.28 (*s*, MeO); 2.53 (*dd*, ^3J(6,1′) = 10.4, ^3J(6,5) = 2.8, H−C(6)); 1.55, 1.38 (2*s*, 2 Me); 0.93 (*s*, *t*-BuSi); 0.15, 0.04 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.0 (*s*, C(3)); 158.0 (*s*, C(3″)); 134.7 (*s*, arom. C); 132.7 (*d*, *J* = 171, 2 arom. C); 129.6 (*d*, *J* = 170, 2 arom. C); 129.5 (*s*, arom. C); 114.0 (*s*, C(6″)); 105.9 (*d*, *J* = 184, C(4a″)); 96.9 (*t*, *J* = 164, OCH_2O); 86.5 (*d*, *J* = 163, C(7b″)); 86.0 (*d*, *J* = 169, C(3a″)); 84.3 (*d*, *J* = 158, C(7a″)); 81.3 (*d*, *J* = 155, C(2)); 81.1 (*d*, *J* = 165, C(1)); 77.0 (*d*, *J* = 162, C(4)); 76.5 (*d*, *J* = 162, C(5)); 67.7 (*d*, *J* = 147, C(1′)); 56.4 (*q*, *J* = 143, MeO); 51.5 (*d*, *J* = 138, C(6)); 27.8 (*q*, *J* = 129, Me); 26.7 (*q*, *J* = 130, Me); 25.5 (*q*, *J* = 120, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.8, −5.4 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 753 (57, $[M+NH_4]^+$), 548 (100), 517 (31), 401 (5), 280 (4), 233 (10). Anal. calc. for $C_{29}H_{40}BrNO_{12}SSi$ (734.67): C 47.41, H 5.49, N 1.91; found: C 47.45, H 5.58, N 2.03.

*(+)-(1*R*,4*R*,5*R*,6*S*,7*R*)-4-*exo*-[[4-(Bromophenyl)sulfonyl]oxy]-6-*exo*-[(*R*)-[(*tert*-butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-7*-endo-*(methoxymethoxy)-2,8-dioxabicyclo[3.2.1]octan-3-one* ((+)-**67**). As described for (+)-**59**, with (+)-**66**: (+)-**67** (92%). Colorless solid. M.p. 66–67°. $[\alpha]_{589}^{25} = +53$, $[\alpha]_{577}^{25} = +55$, $[\alpha]_{546}^{25} = +63$, $[\alpha]_{435}^{25} = +107$, $[\alpha]_{405}^{25} = +128$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 234 (17300), 202 (15800). IR (KBr): 2930, 1770, 1575, 1470, 1370, 1190, 1060. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.86 (*d*, ^3J = 8.8, 2 arom. H); 7.71 (*d*, ^3J = 8.8, 2 arom. H); 5.85 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.82 (*d*, ^3J(1,7) = 3.4, H−C(1)); 5.71 (*d*, ^3J(3a″,7b″) = 6.7, H−C(3a″)); 4.98 (*d*, ^3J(7b″,3a″) = 6.7, H−C(7b″)); 4.88 (*dd*, ^3J(5,4) = 0.9, ^3J(5,6) = 1.9, H−C(5)); 4.83 (*d*, ^3J(4,5) = 0.9, H−C(4)); 4.77 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.68 (*d*, ^3J(1′,6) = 7.5, H−C(1′)); 4.59 (*AB*, J_{AB} = 7.0, 1 H, OCH_2O); 4.56 (*AB*, J_{AB} = 7.0, 1 H, OCH_2O); 3.90 (*dd*, ^3J(7,6) = 4.9, ^3J(7,1) = 3.6, H−C(7)); 3.36 (*s*, MeO); 2.41 (*ddd*, ^3J(6,1′) = 7.5, ^3J(6,7) = 5.0, ^3J(6,5) = 1.9, H−C(6)); 1.54, 1.39 (2*s*, 2 Me); 0.93 (*s*, *t*-BuSi); 0.16, 0.04 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.1 (*s*, C(3)); 158.1 (*s*, C(3″)); 134.7 (*s*, arom. C); 132.5 (*d*, *J* = 171, 2 arom. C); 129.8 (*d*, *J* = 170, 2 arom. C); 129.6 (*s*, arom. C); 114.1 (*s*, C(6″)); 106.1 (*d*, *J* = 185, C(4a″)); 101.4 (*d*, *J* = 192, C(1)); 97.3 (*t*, *J* = 164, OCH_2O); 86.8 (*d*, *J* = 163, C(7b″)); 85.8 (*d*, *J* = 164, C(3a″)); 84.4 (*d*, *J* = 168, C(7a″)); 81.2 (*d*, *J* = 145, C(7)); 79.0 (*d*, *J* = 152, C(5)); 76.5 (*d*, *J* = 159, C(4)); 67.9 (*d*, *J* = 146, C(1′)); 56.6 (*q*, *J* = 142, MeO); 47.8 (*d*, *J* = 136, C(6)); 27.8, 26.8 (2*q*, *J* = 126, 2 Me); 25.5 (*q*, *J* = 130, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.7, −5.3 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 769 (46, $[M+NH_4]^+$), 689 (12), 548 (100), 417 (5), 296 (3), 219 (5), 180 (31). Anal. calc. for $C_{29}H_{40}BrNO_{13}SSi$ (750.67): C 46.40, H 5.37, N 1.87; found: C 46.32, H 5.43, N 1.78.

*(+)-Methyl (1*R*,3*S*,4*R*,5*S*,6*R*)-5-*exo*-[(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-6-endo-(methoxymethoxy)-2,7-dioxabicyclo[2.2.1]heptan-3*-exo-*carboxylate* ((+)-**68**) *and (+)-Methyl (1*R*,3*R*,4*R*,5*S*,6*R*)-5-*exo*-[(*R*)-[(*tert*-Butyldimethylsilyloxy][(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-6-*endo-*(methoxymethoxy)-2,7-dioxabicyclo[2.2.1]heptane-3*-endo-*carboxylate* ((+)-**69**). As described for (+)-**60** and (+)-**61**, with (+)-**67**: (+)-**68**/(+)-**69** 4.5 : 1 (80%).

*Data of (+)-***68**: Colorless foam. $[\alpha]_{589}^{25} = +63$, $[\alpha]_{577}^{25} = +66$, $[\alpha]_{546}^{25} = +74$, $[\alpha]_{435}^{25} = +125$, $[\alpha]_{405}^{25} = +151$ (*c* = 0.3, $CHCl_3$). UV (MeCN): 210 (3400). IR (film): 2960, 2860, 1765, 1735, 1260, 1160, 1055, 880, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.79 (*d*, ^3J(4a″,7a″) = 3.4, H−C(4a″)); 5.77–5.75 (*m*, H−C(1), H−C(3a″)); 4.97 (*s*, H−C(4)); 4.94 (*d*, ^3J(7b″,3a″) = 6.9, H−C(7b″)); 4.70 (*d*, ^3J(7a″,4a″) = 3.4, H−C(7a″)); 4.58 (*AB*, J_{AB} = 6.7, 1 H, OCH_2O); 4.55 (*AB*, J_{AB} = 6.7, 1 H, OCH_2O); 4.43 (*d*, ^3J(1′,5) = 10.4, H−C(1′)); 4.35 (*s*, H−C(3)); 3.79 (*s*, COOMe); 3.60 (*dd*, ^3J(6,5) = 3.0, ^3J(6,1) = 2.4, H−C(6)); 3.38 (*s*, MeO); 2.40 (*dd*, ^3J(5,1′) = 10.4, ^3J(5,6) = 3.0, H−C(5)); 1.53, 1.38 (2*s*, 2 Me); 0.93 (*s*, *t*-BuSi); 0.13, 0.03 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.0

(*s*, *C*OOMe); 157.8 (*s*, C(3″)); 114.1 (*s*, C(6″)); 105.6 (*d*, *J* = 188, C(4a″)); 102.0 (*d*, *J* = 192, C(1)); 96.8 (*t*, *J* = 163, OCH_2O); 86.3 (*d*, *J* = 162, C(3a″)); 85.5 (*d*, *J* = 163, C(7b″)); 84.7 (*d*, *J* = 161, C(7a″)); 81.3 (*d*, *J* = 148, C(6)); 80.7 (*d*, *J* = 168, C(4)); 77.2 (*d*, *J* = 165, C(3)); 68.5 (*d*, *J* = 147, C(1′)); 56.0 (*q*, *J* = 142, MeO); 52.5 (*q*, *J* = 148, COOMe); 51.5 (*d*, *J* = 140, C(5)); 27.9 (*q*, *J* = 127, Me); 26.8 (*q*, *J* = 126, Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.7, −5.3 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 547 (41, $M+1]^+$), 546 (88, M^+), 545 (34), 514 (25), 488 (31), 373 (80), 328 (12), 284 (25), 242 (8), 73 (100). Anal. calc. for $C_{24}H_{39}NO_{11}Si$ (545.65): C 52.38, H 7.20, N 2.57; found: C 51.77, H 7.20, N 2.51.

Data of (+)- **69**: Colorless oil. $[\alpha]_{589}^{25} = +89$, $[\alpha]_{577}^{25} = +91$, $[\alpha]_{546}^{25} = +104$, $[\alpha]_{435}^{25} = +177$, $[\alpha]_{405}^{25} = +213$ (*c* = 0.4, $CHCl_3$). UV (MeCN): 209 (4600). IR (film): 3060, 2960, 2860, 1765, 1735, 1265, 1225, 1100, 1055, 880, 840, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.79 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.70 (*d*, ^3J(3a″,7b″) = 7.1, H−C(3a″)); 5.66 (*d*, ^3J(1,6) = 2.2, H−C(1)); 4.95 (*d*, ^3J(4,3) = 4.1, H−C(4)); 4.92 (*d*, ^3J(7b″,3a″) = 7.1, H−C(7b″)); 4.68 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.61 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.58 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.52 (*d*, ^3J(3,4) = 4.1, H−C(3)); 4.50 (*d*, ^3J(1′,5) = 9.3, H−C(1′)); 3.81 (*s*, COOMe); 3.63 (*dd*, ^3J(6,5) = 3.3, ^3J(6,1) = 2.2, H−C(6)); 3.44 (*s*, MeO); 2.24 (*dd*, ^3J(5,1′) = 9.3, ^3J(5,6) = 3.3, H−C(5)); 1.51, 1.38 (2*s*, 2 Me); 0.94 (*s*, *t*-BuSi); 0.14, 0.03 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 168.5 (*s*, *C*OOMe); 158.0 (*s*, C(3″)); 113.8 (*s*, C(6″)); 105.6 (*d*, *J* = 185, C(4a″)); 102.8 (*d*, *J* = 183, C(1)); 96.6 (*t*, *J* = 163, OCH_2O); 86.4 (*d*, *J* = 163, C(3a″)); 85.8 (*d*, *J* = 163, C(7b″)); 85.0 (*d*, *J* = 154, C(7a″)); 81.7 (*d*, *J* = 152, C(6)); 79.4 (*d*, *J* = 152, C(3 or 4)); 77.7 (*d*, *J* = 154, C(4 or 3)); 68.6 (*d*, *J* = 147, C(1′)); 55.8 (*q*, *J* = 143, MeO); 52.2 (*q*, *J* = 148, COO*Me*); 47.8 (*d*, *J* = 139, C(5)); 27.8, 26.9 (2*q*, *J* = 127, 2 Me); 25.5 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.8, −5.4 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 564 (74, $[M+NH_4]^+$), 563 (14), 546 (11, M^+), 514 (3), 488 (9), 373 (7), 284 (2), 108 (100), 79 (75). Anal. calc. for $C_{24}H_{39}NO_{11}Si$ (545.65): C 52.38, H 7.20, N 2.57; found: C 52.65, H 7.15, N 2.53.

*(+)-1,4-Anhydro-3-[(*R*)-[(*tert*-butyl)dimethylsilyloxy]-[(3a*R*,4a*R*,7a*R*,7b*S*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* ((+)-**70**). As described for (+)-**62**, with (+)-**68**, (+)-**70** (75%). Colorless oil. $[\alpha]_{589}^{25} = +73$, $[\alpha]_{577}^{25} = +75$, $[\alpha]_{546}^{25} = +86$, $[\alpha]_{435}^{25} = +147$, $[\alpha]_{405}^{25} = +175$ (*c* = 0.4, $CHCl_3$). UV (MeCN): 211 (4100). IR (film): 2960, 2935, 2890, 1475, 1375, 1225, 1155, 1055, 940, 880, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.81 (*d*, ^3J(4a″,7a″) = 3.4, H−C(4a″)); 5.76 (*d*, ^3J(3a″,7b″) = 7.0, H−C(3a″)); 5.54 (*d*, ^3J(1,2) = 2.3, H−C(1)); 4.93 (*d*, ^3J(7b″,3a″) = 7.0, H−C(7b″)); 4.70 (*d*, ^3J(7a″,4a″) = 3.4, H−C(7a″)); 4.63 (*s*, H−C(4)); 4.62 (*s*, OCH_2O); 4.57 (*AB*, J_{AB} = 6.6, 1 H, OCH_2O); 4.55 (*AB*, J_{AB} = 6.6, 1 H, OCH_2O); 4.45 (*d*, ^3J(1′,3) = 10.4, H−C(1′)); 3.99 (*dd*, ^3J(5,6*A*) = 7.8, ^3J(5,6*B*) = 5.6, H−C(5)); 3.61 (*dd*, ^3J(2,3) = 2.8, ^3J(2,1) = 2.3, H−C(2)); 3.46 (*dd*, ^2J(6*B*,6*A*) = 10.0, ^3J(6*B*,5) = 5.6, H_B−C(6)); 3.42 (*dd*, ^2J(6*A*,6*B*) = 10.0, ^3J(6*A*,5) = 7.8, H_A−C(6)); 3.37, 3.36 (2*s*, 2 MeO); 2.33 (*dd*, ^3J(3,1′) = 10.4, ^3J(3,2) = 2.8, H−C(3)); 1.53, 1.38 (2*s*, 2 Me); 0.92 (*s*, *t*-BuSi); 0.13, 0.04 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.0 (*s*, C(3″)); 114.0 (*s*, C(6″)); 105.6 (*d*, *J* = 184, C(4a″)); 100.9 (*d*, *J* = 181, C(1)); 96.6 (*t*, *J* = 167, OCH_2O); 96.5 (*t*, *J* = 160, OCH_2O); 86.4 (*d*, *J* = 163, C(3a″)); 85.6 (*d*, *J* = 163, C(7b″)); 84.7 (*d*, *J* = 167, C(7a″)); 81.4 (*d*, *J* = 151, C(2)); 78.5 (*d*, *J* = 166, C(4)); 77.6 (*d*, *J* = 156, C(5)); 68.7 (*d*, *J* = 146, C(1′)); 67.7 (*t*, *J* = 135, C(6)); 55.8, 55.2 (2*q*, *J* = 142, 2 MeO); 51.5 (*d*, *J* = 139, C(3)); 27.9, 26.8 (2*q*, *J* = 127, 2 Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.8, −5.3 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 563 (22, $[M+1]^+$), 562 (41, M^+), 530 (15), 504 (21), 428 (12), 373 (71), 328 (14), 284 (61), 242 (9), 129 (33), 73 (100). Anal. calc. for $C_{25}H_{43}NO_{11}Si$ (561.70): C 53.46, H 7.72, N 2.49; found: C 53.52, H 7.60, N 2.41.

*(−)-(1*S*,2*R*,3*R*,4*R*,5*R*,6*R*)-3-*exo-*[(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-6-*endo*-chloro-2-*endo*-(methoxymethyl)-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptane* ((−)-**71**). As described for (+)-**56**, with (−)-**38**: (−)-**71** (97%). Colorless oil. $[\alpha]_{589}^{25} = -62$, $[\alpha]_{577}^{25} = -65$, $[\alpha]_{546}^{25} = -75$, $[\alpha]_{435}^{25} = -134$, $[\alpha]_{405}^{25} = -165$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 272 (2100), 215 (11200). IR (film): 2955, 2930, 2860, 1470, 1385, 1375, 1255, 1220, 1155, 1105, 1050, 1015, 840, 780, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.68–7.64 (*m*, 2 arom. H); 7.34–7.30 (*m*, 3 arom. H); 5.55 (*d*, ^3J(3a″,7b″) = 6.1, H−C(3a″)); 5.09 (*d*, ^3J(4a″,7a″) = 3.6, H−C(4a″)); 4.83 (*d*, ^3J(7b″,3a″) = 6.1, H−C(7b″)); 4.71 (*AB*, J_{AB} = 6.6, 1 H, OCH_2O); 4.67 (*d*, ^3J(7a″,4a″) = 3.6, H−C(7a″)); 4.60 (*AB*, J_{AB} = 6.6, 1 H, OCH_2O); 4.50 (*dd*, ^3J(1,6) = 4.6, ^3J(1,2) = 4.6, H−C(1)); 4.46 (*d*, ^3J(1′,3) = 10.6, H−C(1′)); 4.23 (*s*, H−C(4)); 4.17–4.14 (*m*, H−C(2), H−C(6)); 3.47 (*d*, ^3J(5,6) = 5.2, H−C(5)); 3.41 (*s*, MeO); 2.41 (*dd*, ^3J(3,1′) = 10.6, ^3J(3,2) = 3.7, H−C(3)); 1.48, 1.33 (2*s*, 2 Me); 0.87 (*s*, *t*-BuSi); 0.09, 0.01 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.8 (*s*, C(3″)); 135.6 (*d*, *J* = 163, 2 arom. C); 129.2 (*d*, *J* = 166, 2 arom. C); 128.2 (*d*, *J* = 161, arom. C); 128.2 (*s*, arom. C); 113.3 (*s*, C(6″)); 106.0 (*d*, *J* = 185, C(4a″)); 96.6 (*t*, *J* = 163, OCH_2O); 87.5 (*d*, *J* = 163, C(7b″)); 86.6 (*d*, *J* = 163, C(4)); 85.8 (*d*, *J* = 164, C(3a″)); 84.2 (*d*, *J* = 161, C(7a″)); 81.4 (*d*, *J* = 148, C(2)); 79.3 (*d*, *J* = 161, C(1)); 69.3 (*d*, *J* = 151, C(1′)); 61.4 (*d*, *J* = 159, C(6)); 56.3 (*q*, *J* = 142, MeO); 54.8 (*d*, *J* = 138, C(3)); 51.7 (*d*, *J* = 153, C(5)); 27.5, 26.7 (2*q*, *J* = 127, 2 Me); 25.7 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.6, −4.7 (2*q*, *J* = 120, 2 MeSi). CI-MS (NH_3): 676 (6, $[M+1]^+$), 675 (3, M^+), 644 (5), 618 (10), 531 (12), 582 (3), 358 (7), 328 (14),

242 (30), 129 (41), 73 (100). Anal. calc. for $C_{29}H_{42}ClNO_8SeSi$ (675.15): C 51.59, H 6.27, N 2.07; found: C 51.49, H 6.38, N 1.98.

*(−)-(1*S*,2*R*,3*S*,4*R*)-3*-exo-*{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-chloro-2-*endo-*(methoxymethoxy)-7-oxabicyclo[2.2.1]hept-5-ene* ((−)-**72**; for systematic numbering, see (+)-**57**). As described for (+)-**57**, with (−)-**71**, (−)-**72** (86%). Colorless foam. $[\alpha]_{589}^{25} = -76$, $[\alpha]_{577}^{25} = -83$, $[\alpha]_{546}^{25} = -94$, $[\alpha]_{435}^{25} = -159$, $[\alpha]_{405}^{25} = -191$ ($c = 0.7$, $CHCl_3$). UV (MeCN): 208 (7100). IR (film): 3020, 2990, 2950, 2860, 1590, 1470, 1370, 1250, 1150, 1115, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.33 (*d*, $^3J(5,4) = 2.2$, H−C(5)); 5.85 (*d*, $^3J(4a'',7a'') = 3.6$, H−C(4a'')); 5.60 (*d*, $^3J(3a'',7b'') = 5.9$, H−C(3a'')); 4.90 (*d*, $^3J(7b'',3a'') = 5.9$, H−C(7b'')); 4.86 (*d*, $^3J(7a'',4a'') = 3.6$, H−C(7a'')); 4.77 (*AB*, $J_{AB} = 6.6$, 1 H, OCH_2O); 4.75 (*d*, $^3J(1,2) = 4.4$, H−C(1)); 4.58 (*AB*, $J_{AB} = 6.6$, 1 H, OCH_2O); 4.53 (*d*, $^3J(1',3) = 10.8$, H−C(1')); 4.52–4.51 (*m*, H−C(4)); 4.23 (*dd*, $^3J(2,1) = 4.4$, $^3J(2,3) = 2.2$, H−C(2)); 3.41 (*s*, MeO); 2.13 (*dd*, $^3J(3,1') = 10.8$, $^3J(3,2) = 2.2$, H−C(3)); 1.51, 1.37 (2*s*, 2 Me); 0.90 (*s*, *t*-BuSi); 0.14, 0.04 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 159.1 (*s*, C(3'')); 138.0 (*s*, C(6)); 129.9 (*d*, $J = 181$, C(5)); 113.6 (*s*, C(6'')); 106.3 (*d*, $J = 184$, C(4a'')); 96.1 (*t*, $J = 163$, OCH_2O); 87.5 (*d*, $J = 161$, C(7b'')); 85.9 (*d*, $J = 164$, C(3a'')); 84.1 (*d*, $J = 162$, C(7a'')); 82.8 (*d*, $J = 168$, C(1)); 82.2 (*d*, $J = 166$, C(4)); 77.5 (*d*, $J = 157$, C(2)); 69.5 (*d*, $J = 145$, C(1')); 55.9 (*q*, $J = 136$, MeO); 51.9 (*d*, $J = 140$, C(3)); 27.7, 26.8 (2*q*, $J = 127$, 2 Me); 25.7 (*q*, $J = 125$, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.6, −4.8 (2*q*, $J = 120$, 2 MeSi). CI-MS (NH_3): 518 (1, M^+), 460 (1), 386 (4), 358 (100), 328 (3), 284 (19), 242 (32), 184 (13), 129 (81), 73 (57). Anal. calc. for $C_{23}H_{36}ClNO_8Si$ (518.07): C 53.32, H 7.00, N 2.70; found: C 53.22, H 7.06, N 2.57.

*(−)-(1*R*,2*R*,4*S*,5*R*,6*R*)-6-*exo-*{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-5-*endo-*(methoxymethoxy)-3-oxo-7-oxabicyclo[2.2.1]hept-2-*exo-*yl 4-Bromobenzenesulfonate* ((−)-**73**). As described for (+)-**58**, with (−)-**72**: (−)-**73** (85%). Colorless solid. M.p. 57–58°. $[\alpha]_{589}^{25} = -97$, $[\alpha]_{577}^{25} = -103$, $[\alpha]_{546}^{25} = -117$, $[\alpha]_{435}^{25} = -198$, $[\alpha]_{405}^{25} = -235$ ($c = 0.8$, $CHCl_3$). UV (MeCN): 234 (12700), 199 (22000). IR (KBr): 2955, 2895, 2850, 1790, 1575, 1470, 1380, 1225, 1190, 1115, 995. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.82 (*d*, $^3J = 8.8$, 2 arom. H); 7.71 (*d*, $^3J = 8.8$, 2 arom. H); 6.13 (*d*, $^3J(4a'',7a'') = 3.6$, H−C(4a'')); 5.63 (*d*, $^3J(3a'',7b'') = 6.0$, H−C(3a'')); 4.96 (*d*, $^3J(7b'',3a'') = 6.0$, H−C(7b'')); 4.93 (*d*, $^3J(7a'',4a'') = 3.6$, H−C(7a'')); 4.70 (*AB*, $J_{AB} = 6.8$, 1 H, OCH_2O); 4.56 (*d*, $^3J(1',6) = 11.2$, H−C(1')); 4.52 (br. *s*, H−C(1)); 4.48 (*AB*, $J_{AB} = 6.8$, 1 H, OCH_2O); 4.45 (*m*, H−C(4), H−C(2)); 4.09 (*ddd*, $^3J(5,4) = 5.6$, $^3J(5,6) = 2.4$ $^4J(5,1) = 1.2$, H−C(5)); 3.31 (*s*, MeO); 2.44 (*dd*, $^3J(6,1') = 11.2$, $^3J(6,5) = 2.4$, H−C(6)); 1.55, 1.40 (2*s*, 2 Me); 0.88 (*s*, *t*-BuSi); 0.13, 0.03 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.9 (*s*, C(3)); 158.4 (*s*, C(3'')); 134.5 (*s*, arom. C); 132.6 (*d*, $J = 171$, 2 arom. C); 129.6 (*d*, $J = 170$, 2 arom. C); 129.6 (*s*, arom. C); 113.5 (*s*, C(6'')); 106.7 (*d*, $J = 187$, C(4a'')); 96.2 (*t*, $J = 164$, OCH_2O); 88.2 (*d*, $J = 162$, C(7'')); 85.4 (*d*, $J = 164$, C(3a'')); 84.0 (*d*, $J = 162$, C(7a'')); 82.1 (*d*, $J = 166$, C(1)); 81.0 (*d*, $J = 165$, C(2)); 76.7 (*d*, $J = 155$, C(5)); 76.4 (*d*, $J = 167$, C(4)); 68.1 (*d*, $J = 152$, C(1')); 56.2 (*q*, $J = 143$, MeO); 52.0 (*d*, $J = 138$, C(6)); 27.7 (*q*, $J = 127$, Me); 26.8 (*q*, $J = 127$, Me); 25.6 (*q*, $J = 125$, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.6, −5.0 (2*q*, $J = 120$, 2 MeSi). CI-MS (NH_3): 735 (2, M^+), 678 (8), 620 (1), 531 (3), 454 (8), 328 (11), 242 (27), 184 (20), 129 (48), 75 (100). Anal. calc. for $C_{29}H_{40}BrNO_{12}SSi$ (734.67): C 47.41, H 5.49, N 1.91; found: C 47.37, H 5.61, N 1.99.

*(−)-(1*R*,4*R*,5*R*,6*S*,7*R*)-4-*exo-*{[4-(Bromophenyl)sulfonyl]oxy}-6-*exo-*{(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-7-*endo-*(methoxymethoxy)-2,8-dioxabicyclo[3.2.1]octan-3-one* ((−)-**74**). As described for (+)-**59**, with (−)-**73**;(−)-**74** (93%). Colorless solid. M.p. 68–70°. $[\alpha]_{589}^{25} = -44$, $[\alpha]_{577}^{25} = -46$, $[\alpha]_{546}^{25} = -52$, $[\alpha]_{435}^{25} = -90$, $[\alpha]_{405}^{25} = -109$ ($c = 0.7$, $CHCl_3$). UV (MeCN): 235 (12300). IR (KBr): 2955, 2935, 2860, 1770, 1575, 1470, 1375, 1190, 1110, 1060, 1015, 840, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.80 (*d*, $^3J = 8.8$, 2 arom. H); 7.69 (*d*, $^3J = 8.8$, 2 arom. H); 6.22 (*d*, $^3J(4a'',7a'') = 3.6$, H−C(4a'')); 5.86 (*d*, $^3J(1,7) = 3.7$, H−C(1)); 5.57 (*d*, $^3J(3a'',7b'') = 5.7$, H−C(3a'')); 5.03 (*s*, H−C(4)); 4.95 (*d*, $^3J(7b'',3a'') = 5.7$, H−C(7b'')); 4.95 (*d*, $^3J(7a'',4a'') = 3.6$, H−C(7a'')); 4.72 (*AB*, $J_{AB} = 7.1$, 1 H, OCH_2O); 4.58 (*AB*, $J_{AB} = 7.1$, 1 H, OCH_2O); 4.56 (*d*, $^3J(1',6) = 10.7$, H−C(1')); 4.39 (br. *s*, H−C(5)); 4.02 (*dd*, $^3J(7,6) = 3.8$, $^3J(7,1) = 3.7$, H−C(7)); 3.39 (*s*, MeO); 2.45 (*ddd*, $^3J(6,1') = 10.7$, $^3J(6,7) = 3.8$, $^4J = 1.6$, H−C(6)); 1.55, 1.40 (2*s*, 2 Me); 0.89 (*s*, *t*-BuSi); 0.13, 0.03 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.2 (*s*, C(3)); 158.5 (*s*, C(3'')); 134.9 (*s*, arom. C); 132.4 (*d*, $J = 171$, 2 arom. C); 129.7 (*d*, $J = 170$, 2 arom. C); 129.6 (*s*, arom. C); 113.5 (*s*, C(6'')); 106.9 (*d*, $J = 187$, C(4a'')); 101.9 (*d*, $J = 191$, C(1)); 97.2 (*t*, $J = 164$, OCH_2O); 89.0 (*d*, $J = 162$, C(7b'')); 85.1 (*d*, $J = 164$, C(3a'')); 83.7 (*d*, $J = 168$, C(7a'')); 82.0 (*d*, $J = 162$, C(7)); 79.8 (*d*, $J = 162$, C(5)); 75.6 (*d*, $J = 155$, C(4)); 68.8 (*d*, $J = 146$, C(1')); 56.7 (*q*, $J = 143$, MeO); 48.0 (*d*, $J = 136$, C(6)); 27.6, 26.8 (2*q*, $J = 127$, 2 Me); 25.5 (*q*, $J = 125$, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.5, −5.1 (2*q*, $J = 122$, 2 MeSi). CI-MS (NH_3): 752 (5, $[M+1]^+$), 751 (3, M^+), 694 (3), 516 (6), 463 (2), 373 (2), 242 (21), 129 (20), 83 (100). Anal. calc. for $C_{29}H_{40}BrNO_{13}SSi$ (750.67): C 46.40, H 5.37; found: C 46.35, H 5.48.

*(−)-Methyl (1*R*,3*S*,4*R*,5*S*,6*R*)-5-*exo*-{(*S*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo*-(methoxymethoxy)-2,7-dioxabicyclo[2.2.1]heptan-3-*exo*-carboxylate* ((−)-**75**) *and (−)-Methyl (1*R*,3*R*,4*R*,5*S*,6*R*)-5-*exo*-{(*S*)-[(*tert*-Butyl)dimethylsilyloxy]-[(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo*-(methoxymethoxy)-2,7-dioxabicyclo[2.2.1]heptan-3-*endo*-carboxylate* ((−)-**76**). As described for (+)-**60**/(+)-**61**, with (−)-**74**: (−)-**75**/(−)-**76** 7:1 (65%).

*Data of (−)-***75**: Colorless foam. $[\alpha]_{589}^{25} = -62$, $[\alpha]_{577}^{25} = -63$, $[\alpha]_{546}^{25} = -70$, $[\alpha]_{435}^{25} = -128$, $[\alpha]_{405}^{25} = -155$ ($c = 0.4$, $CHCl_3$). UV (MeCN): 207 (4600). IR (film): 2955, 2935, 2860, 1765, 1735, 1470, 1375, 1225, 1155, 1095, 995, 840, 780, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.91 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.77 (*d*, ^3J(1,6) = 2.2, H−C(1)); 5.65 (*d*, ^3J(3a″,7b″) = 6.1, H−C(3a″)); 4.95 (*d*, ^3J(7b″,3a″) = 6.1, H−C(7b″)); 4.88 (*d*, ^3J(7a″,4a″) = 3.5,H−C(7a″)); 4.76 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.64 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.53 (*s*, H−C(4)); 4.49 (*d*, ^3J(1′,5) = 11.0, H−C(1′)); 4.35 (*s*, H−C(3)); 3.78 (*dd*, ^3J(6,5) = 2.9, ^3J(6,1) = 2.2, H−C(6)); 3.77 (*s*, COOMe); 3.44 (*s*, MeO); 2.30 (*dd*, ^3J(5,1′) = 11.0, ^3J(5,6) = 2.9, H−C(5)); 1.53, 1.39 (2*s*, 2 Me); 0.89 (*s*, *t*-BuSi); 0.12, 0.02 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.0 (*s*, *C*OOMe); 158.4 (*s*, C(3″)); 113.8 (*s*, C(6″)); 106.3 (*d*, *J* = 185, C(4a″)); 102.0 (*d*, *J* = 184, C(1)); 96.5 (*t*, *J* = 164, OCH_2O); 87.4 (*d*, *J* = 160, C(7b″)); 85.6 (*d*, *J* = 164, C(3a″)); 84.3 (*d*, *J* = 162, C(7a″)); 82.5 (*d*, *J* = 160, C(6)); 81.6 (*d*, *J* = 167, C(4)); 76.6 (*d*, *J* = 151, C(3)); 68.5 (*d*, *J* = 147, C(1′)); 56.0 (*q*, *J* = 138, MeO); 52.5 (*q*, *J* = 139, COO*Me*); 51.6 (*d*, *J* = 148, C(5)); 27.7, 26.8 (2*q*, *J* = 127, 2 Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.6, −5.0 (2*q*, *J* = 120, MeSi). CI-MS (NH_3): 546 (5, M^+), 515 (8), 488 (26), 373 (49), 328 (9), 284 (30), 242 (13), 184 (10), 73 (100). Anal. calc. for $C_{24}H_{39}NO_{11}Si$ (545.65): C 52.38, H 7.20, N 2.57; found: C 52.71, H 7.06, N 2.69.

*Data of (−)-***76**: Colorless foam. $[\alpha]_{589}^{25} = -71$, $[\alpha]_{577}^{25} = -74$, $[\alpha]_{546}^{25} = -84$, $[\alpha]_{435}^{25} = -145$, $[\alpha]_{405}^{25} = -177$ ($c = 1.2$, $CHCl_3$). UV (MeCN): 200 (6100). IR (film): 2960, 2935, 2895, 2860, 1765, 1735, 1375, 1220, 1155, 1095, 1060, 1000, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.84 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.69 (*d*, ^3J(1,6) = 2.4, H−C(1)); 5.58 (*d*, ^3J(3a″,7b″) = 6.2, H−C(3a″)); 4.90 (*d*, ^3J(7b″,3a″) = 6.2, H−C(7b″)); 4.81 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.78 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.69 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.63 (*d*, ^3J(3,4) = 3.9, H−C(3)); 4.48 (*d*, ^3J(1′,5) = 10.6, H−C(1′)); 4.46 (*d*, ^3J(3,4) = 3.9, H−C(4)); 3.82 (*m*, Me, H−C(6)); 3.48 (*s*, MeO); 2.29 (*dd*, ^3J(5,1′) = 10.6, ^3J(5,6) = 2.7, H−C(5)); 1.49, 1.37 (2*s*, 2 Me); 0.89 (*s*, *t*-BuSi); 0.11, 0.01 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 168.7 (*s*, *C*OOMe); 158.8 (*s*, C(3″)); 113.7 (*s*, C(6″)); 106.3 (*d*, *J* = 183, C(4a″)); 102.9 (*d*, *J* = 183, C(1)); 96.2 (*t*, *J* = 160, OCH_2O); 87.1 (*d*, *J* = 160, C(7b″)); 85.6 (*d*, *J* = 155, C(3a″)); 84.0 (*d*, *J* = 161, C(7a″)); 82.2 (*d*, *J* = 149, C(6)); 80.1 (*d*, *J* = 169, C(3)); 77.4 (*d*, *J* = 154, C(4)); 69.0 (*d*, *J* = 145, C(1′)); 55.8 (*q*, *J* = 144, MeO); 52.7 (*q*, *J* = 148, COO*Me*); 47.2 (*d*, *J* = 140, C(5)); 27.7, 26.9 (2*q*, *J* = 128, 2 Me); 25.6 (*q*, *J* = 124, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.7, −5.1 (2*q*, *J* = 120, 2 MeSi). CI-MS (NH_3): 546 (1, M^+), 530 (7), 488 (29), 456 (2), 373 (10), 284 (9), 184 (5), 129 (16), 73 (100). Anal. calc. for $C_{24}H_{39}NO_{11}Si$ (545.65): C 52.38, H 7.20, N 2.57; found: C 52.76, H 7.20, N 2.60.

*(−)-1,4-Anhydro-3-{(*S*)-[(*tert*-butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* (−)−**77**). As described for (+)-**62**, with (−)-**75**: (−)-**77** (80%). Colorless foam. $[\alpha]_{589}^{25} = -63$, $[\alpha]_{577}^{25} = -66$, $[\alpha]_{546}^{25} = -75$, $[\alpha]_{435}^{25} = -129$, $[\alpha]_{405}^{25} = -157$ ($c = 1.1$, $CHCl_3$). UV (MeCN): 209 (4700). IR (film): 2935, 2890, 1470, 1385, 1225, 1155, 1095, 1035, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.80 (*d*, ^3J(4a″,7a″) = 3.5, H−C(4a″)); 5.63 (*d*, ^3J(3a″,7b″) = 6.2, H−C(3a″)); 5.51 (*d*, ^3J(1,2) = 2.4, H−C(1)); 4.91 (*d*, ^3J(7b″,3a″) = 6.2, H−C(7b″)); 4.80 (*d*, ^3J(7a″,4a″) = 3.5, H−C(7a″)); 4.76 (*AB*, J_{AB} = 6.7, 1 H, OCH_2O); 4.60 (*AB*, J_{AB} = 6.7, 1 H, OCH_2O); 4.57 (*s*, 2 H, OCH_2O); 4.47 (*d*, ^3J(1′,3) = 11.0, H−C(1′)); 4.19 (*s*, H−C(4)); 3.94 (*dd*, ^3J(5,6*A*) = 8.7, ^3J(5,6*B*) = 4.9, H−C(5)); 3.79 (*dd*, ^3J(2,3) = 2.6, ^3J(2,1) = 2.4, H−C(2)); 3.42 (*dd*, ^2J(6*B*,6*A*) = 9.9, ^3J(6*B*,5) = 4.9, H$_B$−C(6)); 3.38, 3.32 (2*s*, 2 MeO); 3.29 (*dd*, ^2J(6*A*,6*B*) = 9.9, ^3J(6*A*,5) = 8.7, H$_A$−C(6)); 2.21 (*dd*, ^3J(3,1′) = 11.0, ^3J(3,2) = 2.6, H−C(3)); 1.49, 1.34 (2*s*, 2 Me); 0.86 (*s*, *t*-BuSi); 0.10, 0.0 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.5 (*s*, C(3″)); 113.7 (*s*, C(6″)); 106.2 (*d*, *J* = 185, C(4a″)); 100.7 (*d*, *J* = 180, C(1)); 96.4 (*t*, *J* = 166, OCH_2O); 96.0 (*t*, *J* = 164, OCH_2O); 87.1 (*d*, *J* = 162, C(7b″)); 85.7 (*d*, *J* = 164, C(3a″)); 84.3 (*d*, *J* = 161, C(7a″)); 82.1 (*d*, *J* = 151, C(2)); 79.5 (*d*, *J* = 161, C(4)); 77.2 (*d*, *J* = 151, C(5)); 68.7 (*d*, *J* = 147, C(1′)); 67.1 (*t*, *J* = 144, CH_2O); 55.7, 55.3 (2*q*, *J* = 142, 2 MeO); 51.5 (*d*, *J* = 138, C(3)); 27.7 (*q*, *J* = 127, Me); 26.8 (*q*, *J* = 125, Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.6, −5.0 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 563 (51, $[M+1]^+$), 562 (54, M^+), 504 (21), 446 (24), 373 (62), 317 (23), 284 (85), 242 (41), 129 (91), 100 (72), 75 (100). Anal. calc. for $C_{25}H_{43}NO_{11}Si$ (561.70): C 53.46, H 7.72, N 2.49; found: C 53.55, H 7.71, N 2.44.

*(−)-(1*S*,2*R*,3*R*,4*R*,5*R*,6*R*)-3-*exo*-{(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-*endo*-chloro-2-*endo*-(methoxymethyl)-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptane* ((−)-**78**). As described for (+)-**56**, with (−)-**39**; (−)-**78** (94%). Colorless oil. $[\alpha]_{589}^{25} = -16$, $[\alpha]_{577}^{25} = -19$, $[\alpha]_{546}^{25} = -20$, $[\alpha]_{435}^{25} = -41$, $[\alpha]_{405}^{25} = -54$ ($c = 1.0$, $CHCl_3$). UV (MeCN):

272 (2600), 199 (14400). IR (film): 2990, 2950, 2930, 2860, 1470, 1385, 1375, 1255, 1225, 1160, 1090, 1050, 895, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62–7.59 (*m*, 2 arom. H); 7.33–7.28 (*m*, 3 arom. H); 5.82 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.59 (*d*, ^3J(3a″,7b″) = 6.2, H–C(3a″)); 4.85 (*d*, ^3J(7b″,3a″) = 6.2, H–C(7b″)); 4.80 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.57 (*s*, H–C(4)); 4.56 (*AB*, J_{AB} = 6.7, 1 H, OCH_2O); 4.51 (*dd*, ^3J(1,6) = 4.6, ^3J(1,2) = 4.6, H–C(1)); 4.48 (*AB*, J_{AB} = 6.7, 1 H, OCH_2O); 4.46 (*d*, ^3J(1′,3) = 9.8, H–C(1′)); 4.21 (*ddd*, ^3J(6,5) = 4.7, ^3J(6,1) = 4.6, ^4J(6,4) = 1.1, H–C(6)); 3.77 (*ddd*, ^3J(2,3) = 4.8, ^3J(2,1) = 4.6, ^4J(2,4) = 1.1, H–C(6)); 3.51 (*d*, ^3J(5,6) = 4.7, H–C(5)); 3.36 (*s*, MeO); 2.26 (*dd*, ^3J(3,1′) = 9.8, ^3J(3,2) = 4.8, H–C(3)); 1.50, 1.36 (2*s*, 2 Me); 0.85 (*s*, *t*-BuSi); 0.05 (*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.0 (*s*, C(3″)); 134.4 (*d*, *J* = 162, 2 arom. C); 129.3 (*d*, *J* = 160, 2 arom. C); 128.6 (*s*, arom. C); 128.1 (*d*, *J* = 161, arom. C); 113.4 (*s*, C(6″)); 106.3 (*d*, *J* = 184, C(4a″)); 97.2 (*t*, *J* = 164, OCH_2O); 87.7 (*d*, *J* = 162, C(7b″)); 86.2 (*d*, *J* = 165, C(3a″)); 85.8 (*d*, *J* = 166, C(4)); 84.1 (*d*, *J* = 167, C(7a″)); 80.9 (*d*, *J* = 152, C(2)); 78.6 (*d*, *J* = 170, C(1)); 69.0 (*d*, *J* = 145, C(1′)); 61.1 (*d*, *J* = 159, C(6)); 56.4 (*q*, *J* = 142, MeO); 54.4 (*d*, *J* = 160, C(3)); 52.7 (*d*, *J* = 152, C(5)); 27.7, 26.9 (2*q*, *J* = 127, 2 Me); 25.7 (*q*, *J* = 125, *Me*$_3$CSi); 18.1 (*s*, Me$_3$*C*Si); –4.6, –5.2 (2*q*, *J* = 120, 2 MeSi). CI-MS (NH_3): 676 (3, $[M+1]^+$), 675 (1, M^+), 644 (6), 618 (9), 484 (2), 426 (5), 358 (7), 284 (5), 242 (43), 120 (60), 73 (100). Anal. calc. for $C_{29}H_{42}ClNO_8SeSi$ (675.15): C 51.59, H 6.27, N 2.07; found: C 50.56, H 6.27, N 2.02.

*(–)-(1*S*,2*R*,3*S*,4*R*)-3-*exo*-{(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-6-chloro-2-*endo*-(methoxymethoxy)-7-oxabicyclo[2.2.1]hept-5-ene* ((–)-**79**). As described for (+)-**57**, with (–)-**78**: (–)-**79** (92%). Colorless oil. $[\alpha]_{589}^{25} = -11$, $[\alpha]_{577}^{25} = -15$, $[\alpha]_{546}^{25} = -16$, $[\alpha]_{435}^{25} = -30$, $[\alpha]_{405}^{25} = -39$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 207 (8000). IR (film): 2955, 2930, 2860, 1595, 1475, 1375, 1250, 1230, 1160, 1085, 1055, 1025, 895, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.39 (*d*, ^3J(5,4) = 2.2, H–C(5)); 5.88 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.56 (*d*, ^3J(3a″,7b″) = 6.1, H–C(3a″)); 4.96 (*dd*, ^3J(4,5) = 2.2, ^5J(4,1) = 1.0, H–C(4)); 4.87 (*d*, ^3J(7b″,3a″) = 6.1, H–C(7b″)); 4.82 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.73 (*d*, ^3J(1,2) = 4.2, H–C(1)); 4.57 (*d*, ^3J(1′,3) = 10.4, H–C(1′)); 4.55 (*AB*, J_{AB} = 6.6, 1 H, OCH_2O); 4.50 (*AB*, J_{AB} = 6.6, 1 H, OCH_2O); 3.86 (*dd*, ^3J(2,1) = 4.2, ^3J(2,3) = 2.5, H–C(2)); 3.34 (*s*, MeO); 2.00 (*dd*, ^3J(3,1′) = 10.4, ^3J(3,2) = 2.5, H–C(3)); 1.50, 1.37 (2*s*, 2 Me); 0.93 (*s*, *t*-Bu); 0.11, 0.09 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.8 (*s*, C(3″)); 138.0 (*s*, C(6)); 130.2 (*d*, *J* = 180, C(5)); 113.3 (*s*, C(6″)); 106.3 (*d*, *J* = 183, C(4a″)); 96.9 (*t*, *J* = 163, OCH_2O); 87.8 (*d*, *J* = 162, C(7b″)); 86.4 (*d*, *J* = 163, C(3a″)); 84.1 (*d*, *J* = 161, C(7a″)); 82.4 (*d*, *J* = 169, C(1)); 81.3 (*d*, *J* = 167, C(4)); 77.9 (*d*, *J* = 155, C(2)); 69.0 (*d*, *J* = 145, C(1′)); 56.0 (*q*, *J* = 142, MeO); 51.9 (*d*, *J* = 139, C(3)); 27.7, 26.9 (2*q*, *J* = 125, 2 Me); 25.7 (*q*, *J* = 120, *Me*$_3$CSi); 18.2 (*s*, Me$_3$*C*Si); –4.6, –5.3 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 518 (1, M^+), 486 (5), 358 (51), 328 (9), 284 (15), 242 (43), 184 (26), 129 (100), 73 (64). Anal. calc. for $C_{23}H_{36}ClNO_8Si$ (518.07): C 53.32, H 7.00, N 2.70; found: C 52.78, H 6.95, N 2.76.

*(–)-(1*R*,2*R*,4*S*,5*R*,6*R*)-6-*exo*-{(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-5-*endo*-(methoxymethoxy)-3-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl 4-Bromobenzenesulfonate* ((–)-**80**). As described for (+)-**58**, with (–)-**79**: (–)-**80** (70%). Colorless solid. M.p. 65–66°. $[\alpha]_{589}^{25} = -44$, $[\alpha]_{577}^{25} = -46$, $[\alpha]_{546}^{25} = -53$, $[\alpha]_{435}^{25} = -90$, $[\alpha]_{405}^{25} = -107$ (*c* = 1.2, $CHCl_3$). UV (MeCN): 235 (15600), 199 (25000). IR (KBr): 2955, 2935, 2860, 1790, 1580, 1475, 1190, 1095, 1045, 995, 840, 780, 735. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.79, 7.69 (2*d*, ^3J = 8.8, 4 arom. H); 5.86 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.50 (*d*, ^3J(3a″,7b″) = 6.2, H–C(3a″)); 4.88 (*s*, H–C(3)); 4.87 (*d*, ^3J(7b″,3a″) = 6.2, H–C(7b″)); 4.80 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.56 (*d*, ^3J(1′,6) = 9.5, H–C(1′)); 4.46 (*m*, 3 H, OCH_2O, H–C(1)); 4.39 (*dd*, ^3J(4,5) = 5.3, ^5J(4,1) = 0.9, H–C(4)); 3.77 (*ddd*, ^3J(5,4) = 5.3, ^3J(5,6) = 3.0, ^4J(5,1) = 0.9, H–C(5)); 3.25 (*s*, MeO); 2.27 (*dd*, ^3J(6,1′) = 9.5, ^3J(6,5) = 2.9, H–C(6)); 1.48, 1.34 (2*s*, 2 Me); 0.90 (*s*, *t*-BuSi); 0.10, 0.07 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.8 (*s*, C(3)); 157.9 (*s*, C(3″)); 134.8 (*s*, arom. C); 132.5 (*d*, *J* = 171, 2 arom. C); 129.4 (*s*, arom. C); 129.3 (*d*, *J* = 170, 2 arom. C); 113.4 (*s*, C(6″)); 106.2 (*d*, *J* = 184, C(4a″)); 97.1 (*t*, *J* = 165, OCH_2O); 87.8 (*d*, *J* = 163, C(7b″)); 86.1 (*d*, *J* = 163, C(3a″)); 84.0 (*d*, *J* = 161, C(7a″)); 81.3 (*d*, *J* = 168, C(2)); 80.4 (*d*, *J* = 166, C(4)); 76.9 (*d*, *J* = 157, C(1)); 76.8 (*d*, *J* = 157, C(5)); 67.2 (*d*, *J* = 148, C(1′)); 56.2 (*q*, *J* = 143, MeO); 51.5 (*d*, *J* = 136, C(6)); 27.6 (*q*, *J* = 125, Me); 26.7 (*q*, *J* = 127, Me); 25.5 (*q*, *J* = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); –4.7, –5.3 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 753 (100, $[M+NH_4]^+$), 735 (13, M^+), 637 (20), 560 (9), 500 (17), 441 (11), 368 (15), 285 (13), 194 (13), 128 (16). Anal. calc. for $C_{29}H_{40}BrNO_{12}SSi$ (734.67): C 47.41, H 5.49, N 1.91; found: C 47.39, H 5.38, N 1.98.

*(+)-(1*R*,4*R*,5*R*,6*S*,7*R*)-4-*exo*-{[(4-Bromophenyl)sulfonyl]oxy}-6-*exo*-{(*R*)-[(*tert*-butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl}-7-*endo*-(methoxymethoxy)-2,8-dioxabicyclo[3.2.1]octan-3-one* ((+)-**81**). As described for (+)-**59**, with (–)-**80**: (+)-**81** (98%). Colorless solid. M.p. 65–66°. $[\alpha]_{589}^{25} = +0.5$, $[\alpha]_{577}^{25} = -0.4$, $[\alpha]_{546}^{25} = -0.2$, $[\alpha]_{435}^{25} = +0.3$, $[\alpha]_{405}^{25} = -0.8$ (*c* = 1.0, $CHCl_3$). UV (MeCN): 234 (17000). IR (KBr): 2960, 2935, 2860, 1770, 1575, 1375, 1190, 1060, 840, 780, 750. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.79, 7.67 (2*d*, ^3J = 8.7, 4 arom. H); 5.92 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.78 (*d*, ^3J(1,7) = 3.3, H–C(1)); 5.48 (*d*, ^3J(3a″,7b″) = 6.2, H–C(3a″)); 4.96 (*d*, ^3J(7b″,3a″) = 6.2, H–C(7b″)); 4.88

(*s*, H–C(4)); 4.83 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.78 (*d*, ^3J(1′,6) = 4.4, H–C(1′)); 4.71 (*d*, ^3J(5,6) = 1.7, H–C(5)); 4.59 (*s*, OCH_2O); 3.89 (*dd*, ^3J(7,6) = 6.0, ^3J(7,1) = 3.3, H–C(7)); 3.35 (*s*, MeO); 2.28–2.25 (*m*, H–C(6)); 1.48, 1.35 (2*s*, 2 Me); 0.88 (*s*, *t*-BuSi); 0.12 (*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.1 (*s*, C(3)); 158.8 (*s*, C(3″)); 134.7 (*s*, arom. C); 132.4 (*d*, *J* = 171, 2 arom. C); 129.7 (*d*, *J* = 170, 2 arom. C); 129.5 (*s*, arom. C); 113.6 (*s*, C(6″)); 106.3 (*d*, *J* = 185, C(4a″)); 101.3 (*d*, *J* = 188, C(1)); 97.2 (*t*, *J* = 164, OCH_2O); 88.0 (*d*, *J* = 163, C(7b″)); 85.9 (*d*, *J* = 163, C(3a″)); 84.1 (*d*, *J* = 162, C(7a″)); 80.6 (*d*, *J* = 161, C(7)); 78.3 (*d*, *J* = 149, C(5)); 77.2 (*d*, *J* = 157, C(4)); 66.8 (*d*, *J* = 145, C(1′)); 56.3 (*q*, *J* = 143, MeO); 46.3 (*d*, *J* = 132, C(6)); 27.6 (*q*, *J* = 127, Me); 26.8 (*q*, *J* = 129, Me); 25.5 (*q*, *J* = 130, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.4, −5.2, (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 769 (100, $[M+NH_4]^+$),720 (12), 653 (20), 600 (16), 532 (22), 458 (30), 409 (11), 355 (17), 285 (14), 203 (28). Anal. calc. for $C_{29}H_{40}BrNO_{13}SSi$ (750.67): C 46.40, H 5.37; found: C 46.37, H 5.24.

*(−)-Methyl (1*R*,3*S*,4*R*,5*S*,6*R*)-5-*exo*-[(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-6-*endo*-(methoxymethoxy)-2,7-dioxabicyclo[2.2.1]heptane-3-*exo*-carboxylate* ((−)-**82**) *and (+)-Methyl (1*R*,3*R*,4*R*,5*S*,6*R*)-5-*exo*-[(*R*)-[(*tert*-Butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-6-*endo*-(methoxymethoxy)-2,7-dioxabicyclo[2.2.1]heptane-3-*endo*-carboxylate* ((+)-**83**). As described for (+)-**60**/(+)-**61**, with (+)-**81**: (−)-**82** (60%) and (+)-**83** (15%).

*Data of (−)-***82**: Colorless oil. $[\alpha]_{589}^{25} = -8$, $[\alpha]_{577}^{25} = -11$, $[\alpha]_{546}^{25} = -8$, $[\alpha]_{435}^{25} = -17$, $[\alpha]_{405}^{25} = -24$ (*c* = 0.3, $CHCl_3$). UV (MeCN): 210 (5600). IR (film): 2955, 2860, 1765, 1735, 1470, 1375, 1225, 1160, 1055, 840, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.87 (*d*, ^3J(4a″,7a″) = 3.6, H–C(4a″)); 5.72 (*d*, ^3J(1,6) = 2.2, H–C(1)); 5.55 (*d*, ^3J(3a″,7b″) = 6.1, H–C(3a″)); 5.01 (*s*, H–C(4)); 4.87 (*d*, ^3J(7b″,3a″) = 6.1, H–C(7b″)); 4.82 (*d*, ^3J(7a″,4a″) = 3.6, H–C(7a″)); 4.56 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.53 (*AB*, J_{AB} = 6.8, 1 H, OCH_2O); 4.49 (*d*, ^3J(1′,5) = 10.1, H–C(1′)); 4.33 (*s*, H–C(3)); 3.78 (*s*, COOMe); 3.44 (*dd*, ^3J(6,5) = 3.0, ^3J(6,1) = 2.2, H–C(6)); 3.37 (*s*, MeO); 2.11 (*dd*, ^3J(5,1′) = 10.1, ^3J(5,6) = 3.0, H–C(5)); 1.51, 1.37 (2*s*, 2 Me); 0.93 (*s*, *t*-BuSi); 0.13, 0.09 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.7 (*s*, *C*OOMe); 159 (*s*, C(3″)); 113.5 (*s*, C(6″)); 106.2 (*d*, *J* = 184, C(4a″)); 101.5 (*d*, *J* = 191, C(1)); 97.0 (*t*, *J* = 164, OCH_2O); 87.8 (*d*, *J* = 163, C(7b″)); 86.1 (*d*, *J* = 167, C(3a″)); 84.0 (*d*, *J* = 162, C(7a″)); 81.7 (*d*, *J* = 162, C(6)); 80.9 (*d*, *J* = 167, C(4)); 76.9 (*d*, *J* = 158, C(3)); 68.1 (*d*, *J* = 146, C(1′)); 55.9 (*q*, *J* = 143, MeO); 52.6 (*q*, *J* = 148, COO*Me*); 51.5 (*d*, *J* = 137, C(5)); 27.7 (*q*, *J* = 127, Me); 26.9 (*q*, *J* = 126, Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 18.2 (*s*, Me$_3$*C*Si); −4.6, −5.3 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 563 (100, $[M+NH_3]^+$), 547 (28, $[M+1]^+$), 546 (82, M^+), 488 (5), 447 (4), 380 (2). Anal. calc. for $C_{24}H_{39}NO_{11}Si$ (545.65): C 52.38, H 7.20, N 2.57; found: C 52.64, H 7.32, N 2.55.

*Data of (+)-***83**: Colorless foam. $[\alpha]_{589}^{25} = +7$, $[\alpha]_{577}^{25} = +6$, $[\alpha]_{546}^{25} = +8$, $[\alpha]_{435}^{25} = +11$, $[\alpha]_{405}^{25} = +11$ (*c* = 0.9, $CHCl_3$). UV (MeCN): 208 (5500). IR (film): 2955, 2940, 2860, 1765, 1735, 1470, 1375, 1250, 1220, 1160, 1090, 1055, 875, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.83 (*d*, ^3J(4a″,7a″) = 3.7, H–C(4a″)); 5.61 (*d*, ^3J(1,6) = 2.3, H–C(1)); 5.48 (*d*, ^3J(3a″,7b″) = 6.1, H–C(3a″)); 4.91 (*d*, ^3J(3,4) = 4.0, H–C(3)); 4.84 (*d*, ^3J(7b″,3a″) = 6.1, H–C(7b″)); 4.79 (*d*, ^3J(7a″,4a″) = 3.7, H–C(7a″)); 4.57 (*AB*, J_{AB} = 7.0, 1 H, OCH_2O); 4.54 (*AB*, J_{AB} = 7.0, 1 H, OCH_2O); 4.51 (*d*, ^3J(4,3) = 4.0, H–C(4)); 4.47 (*d*, ^3J(1′,5) = 9.7, H–C(1′)); 3.80 (*s*, COOMe); 3.42 (*dd*, ^3J(6,5) = 3.2, ^3J(6,1) = 2.3, H–C(6)); 3.40 (*s*, MeO); 1.95 (*dd*, ^3J(5,1′) = 9.7, ^3J(5,6) = 3.2, H–C(5)); 1.50, 1.35 (2*s*, 2 Me); 0.91 (*s*, *t*-BuSi); 0.12, 0.05 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 168.5 (*s*, *C*OOMe); 158.1 (*s*, C(3″)); 113.3 (*s*, C86″)); 106.3 (*d*, *J* = 183, C(4a″)); 102.5 (*d*, ^3J = (184, C(1)); 97.0 (*t*, *J* = 164, OCH_2O); 88.0 (*d*, *J* = (163, C(7b″)); 86.3 (*d*, *J* = (164, C(3a″)); 84.1 (*d*, *J* = (167, C(7a″)); 82.2 (*d*, *J* = (152, C(6)); 79.7 (*d*, *J* = (168, C(3 or 4)); 77.6 (*d*, *J* = (158, C(4 or 3)); 68.2 (*d*, *J* = (146, C(1′)); 55.8 (*q*, *J* = 143, MeO); 52.3 (*q*, *J* = 148, COOMe); 47.7 (*d*, *J* = 137, C(5)); 27.7, 26.8 (2*q*, *J* = 127, 2 Me); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.6, −5.3 (2*q*, *J* = 119, 2 MeSi). CI-MS (NH_3): 546 (2, M^+), 530 (9), 488 (30), 373 (7), 284 (5), 242 (18), 184 (8), 129 (22), 85 (100). Anal. calc. for $C_{24}H_{39}NO_{11}Si$ (545.65): C 52.83, H 7.20, N 2.57; found: C 52.67, H 7.11, N 2.43.

*(+)-1,4-Anhydro-3-[(*R*)-[(*tert*-butyl)dimethylsilyloxy][(3a*S*,4a*S*,7a*S*,7b*R*)-3a,4a,7a,7b-tetrahydro-6,6-dimethyl[1,3]dioxolo[4,5]furo[2,3-*d*]isoxazol-3-yl]methyl]-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* ((+)-**84**). As described for (+)-**62**, with (−)-**82**: (+)-**84** (70%). Colorless solid. M.p. 94–95°. $[\alpha]_{589}^{25} = +0.1$, $[\alpha]_{577}^{25} = +2$, $[\alpha]_{546}^{25} = +1$, $[\alpha]_{435}^{25} = -2$, $[\alpha]_{405}^{25} = -6$ (*c* = 0.9, $CHCl_3$). UV (MeCN): 210 (6600). IR (KBr): 2960, 2890, 1475, 1375, 1260, 1165, 1105, 1070, 1030, 880, 845. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.87 (*d*, ^3J(4a″,7a″) = 3.5, H–C(4a″)); 5.56 (*d*, ^3J(3a″,7b″) = 6.1, H–C(3a″)); 5.51 (*d*, ^3J(1,2) = 2.3, H–C(1)); 4.87 (*d*, ^3J(7b″,3a″) = 6.1, H–C(7b″)); 4.82 (*d*, ^3J(7a″,4a″) = 3.5, H–C(7a″)); 4.68 (*s*, H–C(4)); 4.62 (*s*, OCH_2O); 4.55 (*AB*, J_{AB} = 6.9, 1 H, OCH_2O); 4.53 (*AB*, J_{AB} = 6.9, 1 H, OCH_2O); 4.49 (*d*, ^3J(1′,3) = 10.3, H–C(1′)); 3.99 (*dd*, ^3J(5,6*A*) = 7.9, ^3J(5,6*B*) = 5.5, H–C(5)); 3.47–3.40 (*m*, CH_2(6), H–C(2)); 3.35 (*s*, 2 MeO); 2.04 (*dd*, ^3J(3,1′) = 10.3, ^3J(3,2) = 2.9, H–C(3)); 1.51, 1.37 (2*s*, 2 Me); 0.92 (*s*, *t*-BuSi); 0.13, 0.10 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.2 (*s*, C(3″)); 113.4 (*s*, C(6″)); 106.3 (*d*, *J* = 184, C(4a″)); 100.5 (*d*, *J* = 181, C(1)); 97.0 (*t*, *J* = 164, OCH_2O); 96.6 (*t*, *J* = 163, OCH_2O); 87.8 (*d*, *J* = 161, C(7b″)); 86.3 (*d*, *J* = 155, C(3a″)); 84.1 (*d*, *J* = 161, C(7a″)); 82.9

(d, J = 163, C(2)); 78.7 (d, J = 166, C(4)); 77.9 (d, J = 151, C(5)); 68.3 (d, J = 146, C(1′)); 67.7 (t, J = 144, CH_2O); 55.7, 55.2 (2q, J = 142, 2 MeO); 51.6 (d, J = 136, C(3)); 27.7 (q, J = 128, Me); 26.9 (q, J = 126, Me); 25.6 (q, J = 125, Me_3CSi); 18.2 (s, Me_3CSi); −4.6, −5.3 (2q, J = 119, 2 MeSi). CI-MS (NH_3): 562 (100, M^+), 530 (5), 446 (13), 421 (3), 373 (5), 284 (4), 129 (8). Anal. calc. for $C_{25}H_{43}NO_{11}Si$ (561.70): C 53.46, H 7.72, N 2.49; found: C 53.55, H 7.65, N 2.37.

*1,4-Anhydro-3-[(6*S*)-5-[[(benzyloxy)carbonyl]amino]-5-deoxy-1,2-*O*-isopropylidene-β-*L*-idofuranos-6-*C*-yl]-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* ((−)-**86**). $LiAlH_4$ (120 mg, 3.18 mmol) was added portionwise to a soln. of (+)-**62** (198 mg, 0.35 mmol) in dry Et_2O (10 ml) at 25°. The mixture was stirred at 25° for 5 d. After hydrolysis with H_2O (0.1 ml), 20% aq. NaOH soln. (0.08 ml), and H_2O (0.3 ml), the soln. was filtered and the solvent evaporated. A small fraction of the residue was purified by CC (silica gel CH_2Cl_2/MeOH 20:1) to give the aminodiol (+)-**85** as colorless oil. The remainder of the residue was dissolved in 50% aq. EtOH (10 ml) and $NaHCO_3$ (53 mg, 0.63 mmol) was added. Then benzyl carbonochloridate (60 µl, 0.42 mmol) was added, and the mixture was stirred at 25° for 90 min. After the addition of AcOEt (20 ml), the mixture was washed twice with sat. aq. $NaHCO_3$ soln. (7 ml), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (AcOEt/light petroleum ether): 180 mg (88%) of (−)-**86**. Colorless solid.

*Data of the Intermediate 3-[(6*S*)-5-Amino-5-deoxy-1,2-*O*-isopropylidene-β-*L*-idofuranos-6-*C*-yl]-1,4-anhydro-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* ((+)-**85**)): $[\alpha]_{589}^{25} = +37$, $[\alpha]_{577}^{25} = +39$, $[\alpha]_{546}^{25} = +43$, $[\alpha]_{435}^{25} = +71$, $[\alpha]_{405}^{25} = +84$ (c = 1.1, $CHCl_3$). UV (MeCN): 195 (1600). IR (film): 3390, 3310, 2990, 2935, 2825, 1375, 1255, 1220, 1155, 1035, 870, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.92 (d, ^3J(1′,2′) = 3.7, H−C(1′)); 5.53 (d, ^3J(1,2) = 2.3, H−C(1)); 4.70 (s, 2 H, OCH_2O); 4.59 (s, 2 H, OCH_2O); 4.46 (d, ^3J(2′,1′) = 3.7, H−C(2′)); 4.43 (s, H−C(4)); 4.31–4.28 (m, H−C(4′), H−C(3′)); 4.00 (dd, ^3J(2,3) = 3.0, ^3J(2,1) = 2.3, H−C(2)); 3.93 (dd, ^3J(5,6A) = 7.9, ^3J(5,6B) = 5.2, H−C(5)); 3.69 (dd, ^3J(5′,6′) = 6.6, ^3J(6′,3) = 6.4, H−C(6′)); 3.44 (dd, ^2J(6B,6A) = 10.2, ^3J(6B,5) = 5.2, H_B−C(6)); 3.41 (s, MeO); 3.36 (dd, ^2J(6A,6B) = 10.2, ^3J(6A,5) = 7.9, H_A−C(6)); 3.32 (s, MeO); 3.20 (dd, ^3J(5′,6′) = 6.6, ^3J(5′,4′) = 1.9, H−C(5′)); 1.96 (dd, ^3J(3,6′) = 6.4, ^3J(3,2) = 3.0, H−C(3)); 1.44, 1.29 (2s, 2 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 111.5 (s, Me_2C); 105.0 (d, J = 183, C(1′)); 100.0 (d, J = 181, C(1)); 97.2, 96.7 (2t, J = 163, 2 OCH_2O); 85.3 (d, J = 161, C(2′)); 81.4 (d, J = 148, C(2)); 80.5 (d, J = 159, C(4)); 78.6 (d, J = 152, C(5)); 77.6 (d, J = 154, C(3′ or 4′)); 76.1 (d, J = 152, C(4′ or 3′)); 74.4 (d, J = 145, C(6′)); 67.7 (t, J = 144, C(6)); 55.9, 55.3 (2q, J = 142, 2 MeO); 52.9 (d, J = 133, C(5′)); 48.4 (d, J = 132, C(3)); 26.8, 26.1 (2q, J = 126, 2 Me). CI-MS (NH_3): 454 (25, $[M+2]^+$), 453 (67, $[M+1]^+$), 452 (100, M^+), 406 (22), 338 (59), 310 (9), 188 (47), 130 (11), 72 (32). Anal. calc. for $C_{19}H_{33}NO_{11}$ (451.47): C 50.55, H 7.37, N 3.10; found: C 50.45, H 7.26, N 3.03.

*Data of (−)-***86**: M.p. 49–50°. $[\alpha]_{589}^{25} = -2$, $[\alpha]_{577}^{25} = -2$, $[\alpha]_{546}^{25} = -2$, $[\alpha]_{435}^{25} = -5$, $[\alpha]_{405}^{25} = -7$ (c = 0.5, $CHCl_3$). UV (MeCN): 267 (500), 261 (600), 256 (600), 251 (600), 206 (8300). IR (film): 3420, 3055, 2990, 1710, 1515, 1455, 1265, 1220, 1110, 1075, 1040, 740, 700. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.34–7.30 (m, 5 arom. H); 5.89 (d, ^3J(1′,2′) = 3.7, H−C(1′)); 5.53 (d, ^3J(1,2) = 2.5, H−C(1)); 5.42 (d, ^3J(NH,5′) = 9.0, NH); 5.12 (AB, J_{AB} = 12,4, 1 H, CH_2); 5.08 (AB, J_{AB} = 12.4, 1 H, CH_2); 4.72, 4.66 (2 AB, J_{AB} = 6.9, OCH_2O); 4.60, 4.58 (2 AB, J_{AB} = 6.4, OCH_2O); 4.54 (s, H−C(4)); 4.50 (d, ^3J(2′,1′) = 3.7, H−C(2′)); 4.38 (dd, ^3J(4′,5′) = 5.0, ^3J(4′,3′) = 2.7, H−C(4′)); 4.24 (d, ^3J(3′,4′) = 2.7, H−C(3′)); 4.12 (m, H−C(5′)); 3.98 (dd, ^3J(2,3) = 2.8, ^3J(2,1) = 2.5, H−C(2)); 3.91 (dd, ^3J(5,6A) = 7.7, ^3J(5,6B) = 5.3, H−C(5)); 3.80 (dd, ^3J(6′,3) = 8.1, ^3J(6′,5′) = 5.8, H−C(6′)); 3.55 (br. s, OH−C(6′), OH−C(3′)); 3.45 (dd, ^2J(6B,6A) = 10.3, ^3J(6B,5) = 5.3, H_B−C(6)); 3.41 (s, MeO); 3.38–3.34 (m, H_A−C(6)); 3.34 (s, MeO); 2.01 (dd, ^3J(3,6′) = 8.1, ^3J(3,2) = 2.8, H−C(3)); 1.47, 1.30 (2s, 2 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 157.0 (s, CO); 136.1 (s, arom. C); 128.5 (d, J = 160, 2 arom. C); 128.2 (d, J = 160, 2 arom. C); 127.9 (d, J = 160, 2 arom. C); 111.7 (s, Me_2C); 104.2 (d, J = 183, C(1′)); 100.1 (d, J = 181, C(1)); 97.3 (t, J = 164, OCH_2O); 96.7 (t, J = 163, OCH_2O); 85.2 (d, J = 162, C(2′)); 82.2 (d, J = 148, C(2)); 80.9 (d, J = 162, C(4)); 78.7 (d, J = 144, C(4′)); 78.3 (d, J = 153, C(5)); 75.6 (d, J = 147, C(3′)); 73.3 (d, J = 146, C(6′)); 67.7 (t, J = 144, C(6)); 67.2 (t, J = 147, CH_2); 55.9, 55.3 (2q, J = 142, 2 MeO); 52.9 (d, J = 137, C(5′)); 49.6 (d, J = 134, C(3)); 26.8, 26.1 (2q, J = 128, 2 Me). CI-MS (NH_3): 587 (11, $[M+1]^+$), 586 (23, M^+), 554 (16), 452 (7), 379 (3), 321 (2), 280 (11), 188 (4), 91 (100). Anal. calc. for $C_{27}H_{39}NO_{13}$ (585.60): C 55.38, H 6.71, N 2.39; found: C 55.27, H 6.76, N 2.30.

*(+)-(1*S*,2a*S*,5a*S*,6a*S*,6b*R*,9a*R*,10a*R*,10b*S*)-1,2a,3,5,5a,6a,6b,9a,10a,10b-Decahydro-1-[(1*R*,3*R*,4*R*,5*S*,6*R*)-6-*endo*-(methoxymethoxy)-3-*exo*-[(methoxymethoxy)methyl]-2,7-dioxabicyclo[2.2.1]hept-5-yl]-8,8-dimethyl-4*H*-2,6,7,9,10-pentaoxa-10c-azapentaleno[2,1-*d*]acenaphthylene* ((+)-**87**). A mixture of (+)-**85** (66.6 mg, 0.148 mmol), MeOH (0.6 ml), and glutaraldehyde (0.026 ml, 0.148 mmol) was stirred at 25° for 12 h. The solvent was evaporated and the residue purified by FC (CH_2Cl_2/AcOEt 1:1): 50.4 mg (65%) of (+)-**87**. Colorless solid. M.p. 54–55°. $[\alpha]_{589}^{25} = +17$, $[\alpha]_{577}^{25} = +19$, $[\alpha]_{546}^{25} = +16$, $[\alpha]_{435}^{25} = +20$, $[\alpha]_{405}^{25} = +23$ (c = 0.4, $CHCl_3$). UV (MeCN): 197 (3300). IR (KBr): 2990, 2935, 2890, 1460, 1375, 1215, 1155, 1060, 1040, 960, 860, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.82 (d, ^3J(9a,6b) = 3.6, H−C(9a)); 5.53 (d, ^3J(1′,6′) = 2.4, H−C(1′)); 4.87 (AB, J_{AB} = 6.6,

1 H, OCH_2O); 4.84 (*dd*, $^3J(2a,3A) = 9.7$, $^3J(2a,3B) = 2.5$, H–C(2a)); 4.69 (*dd*, $^3J(5a,5A) = 2.9$, $^3J(5a,5B) = 2.4$, H–C(5a)); 4.67 (*AB*, $J_{AB} = 6.6$, 1 H, OCH_2O); 4.55 (*s*, 2 H, OCH_2O); 4.48 (*d*, $^3J(6b,9a) = 3.6$, H–C(6b)); 4.28 (*s*, H–C(4″)); 4.21 (*dd*, $^3J(1,5') = 11.6$, $^3J(1,10b) = 6.5$, H–C(1)); 4.17 (br. *s*, H–C(6a)); 4.03 (*dd*, $^3J(6',5') = 2.6$, $^3J(6',1') = 2.4$, H–C(6′)); 4.01 (*dd*, $^3J(3',8'A) = 8.8$, $^3J(3',8'B) = 4.8$, H–C(3′)); 3.98 (*dd*, $^3J(10a,10b) = 3.3$, $^3J(10a,6a) = 1.8$, H–C(10a)); 3.73 (*dd*, $^3J(10b,1) = 6.5$, $^3J(10b,10a) = 3.3$, H–C(10b)); 3.46 (*dd*, $^2J(8'B,8'A) = 9.7$, $^3J(8'B,3') = 4.8$, H_B–C(8′)); 3.41, 3.31 (2*s*, 2 MeO); 3.32–3.29 (*m*, H_A–C(8′)); 2.78 (*dd*, $^3J(5',1) = 11.6$, $^3J(5',6') = 2.6$, H–C(5′)); 1.96–1.92 (*m*, H–C(3)); 1.75–1.70 (*m*, 2 H–C(4)); 1.69–1.55 (*m*, 2 H–C(5)); 1.44, 1.31 (2*s*, 2 Me); 1.29–1.23 (*m*, 1 H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 111.9 (*s*, C(8)); 105.1 (*d*, $J = 184$, C(9a)); 100.4 (*d*, $J = 180$, C(1′)); 96.3, 96.2 (2*t*, $J = 164$, 2 OCH_2O); 86.6 (*d*, $J = 152$, C(2a)); 84.3 (*d*, $J = 155$, C(5a)); 82.8 (*d*, $J = 160$, C(6′)); 82.5 (*d*, $J = 160$, C(6b)); 80.3 (*d*, $J = 152$, C(6a)); 80.0 (*d*, $J = 153$, C(4′)); 79.2 (*d*, $J = 147$, C(1)); 77.7 (*d*, $J = 151$, C(3′)); 71.7 (*d*, $J = 147$, C(10a)); 67.1 (*t*, $J = 144$, OCH_2); 57.0 (*d*, $J = 139$, C(10b)); 55.7, 55.1 (2*q*, $J = 141$, 2 MeO); 47.4 (*d*, $J = 140$, C(5′)); 30.2 (*t*, $J = 130$, C(3)); 28.7 (*t*, $J = 130$, C(5)); 26.5, 26.3 (2*q*, $J = 127$, 2 Me); 18.7 (*t*, $J = 123$, C(4)). CI-MS (NH_3): 517 (43, $[M+1]^+$), 516 (93, M^+), 470 (38), 410 (11), 354 (8), 282 (100), 253 (20), 183 (9), 81 (23). Anal. calc. for $C_{24}H_{37}NO_{11}$ (515.55): C 55.91, H 7.23, N 2.72; found: C 55.99, H 7.27, N 2.75.

*(1*R*,2*R*,3*S*,7*R*,8*S*,9*S*,9a*S*)-1,3,4,6,7,8,9,9a-Octahydro-8-[(1*R*,2*R*)-1,2,3-trihydroxypropyl]-2*H*-quinolizine-1,2,3,7,9-pentol* (**21**) *and (−)-(1*R*,2*R*,3*S*,7*R*,8*S*,9*S*,9a*S*)-1,3,4,6,7,8,9,9a-Octahydro-8-[(1*R*,2*R*)-1,2,3-triacetoxypropyl]-2*H*-quinolizine-1,2,3,7,9-pentayl Pentacetate* ((+)-**88**). A soln. of (−)-**86** (60 mg, 0.12 mmol) in CF_3COOH/H_2O 2 : 1 (10 ml) was stirred at 25° for 15 h. The solvents were evaporated, and the residue was dissolved in H_2O (15 ml). Then 10% Pd/C (10 mg) was added, and the soln. was degassed, pressurized with H_2 (1 atm), and shaken at 25° for 15 h. After filtration through *Celite*, the solvent was evaporated giving **21** as a colorless oil. The residue was poured into Ac_2O (0.5 ml), pyridine (1 ml), and DMAP (5 mg), and the mixture was stirred at 25° for 15 h. After evaporation, the crude product was purified by CC (silica gel, AcOEt/light petroleum ether 3 : 1): 31 mg (40%) of **88**.

*Data of (+)-***88**: Yellow oil. $[\alpha]_{589}^{25} = +40$, $[\alpha]_{577}^{25} = +41$, $[\alpha]_{546}^{25} = +48$, $[\alpha]_{435}^{25} = +76$, $[\alpha]_{405}^{25} = +89$ ($c = 0.3$, $CHCl_3$). UV (MeCN): 199 (8500). IR (film): 2920, 2850, 1750, 1435, 1375, 1230, 1045, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.51 (*dd*, $^3J(1',8) = 7.8$, $^3J(1',2') = 4.1$, H–C(1′)); 5.33 (*ddd*, $^3J(2',3'B) = 6.8$, $^3J(2',3'A) = 4.1$, $^3J(2',1') = 4.1$, H–C(2′)); 5.25 (*ddd*, $^3J(7,6) = 9.7$, $^3J(7,6) = 4.9$, $^3J(7,8) = 4.9$, H–C(7)); 5.07 (*dd*, $^3J(9,8) = 4.8$, $^3J(9,9a) = 4.8$, H–C(9)); 5.03 (br. *s*, H–C(2)); 4.98 (br. *s*, H–C(1)); 4.76 (br. *s*, H–C(3)); 4.28 (*dd*, $^2J(3'A, 3'B) = 11.9$, $^3J(3'A,2') = 4.1$ H_A–C(3′)); 3.93 (*dd*, $^2J(3'B,3'A) = 11.9$, $^3J(3'B,2') = 6.8$, H_B–C(3′)); 3.37–3.33 (*m*, H_{eq}–C(6)); 3.01 (*dm*, $^2J(4eq,4ax) = 13.5$, H_{eq}–C(4)); 2.95 (*m*, H–C(9a)); 2.85 (*dm*, $^2J(4eq,4ax) = 13.5$, H_{ax}–C(4)); 2.67–2.60 (*m*, H_{ax}–C(6), H–C(8)); 2.15, 2.11, 2.10, 2.09, 2.07, 2.03 (6*s*, 8 AcO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.5, 170.3, 170.0, 169.8, 169.5, 169.2, 168.2 (7*s*, 8 AcO); 70.0 (*d*, $J = 140$, C(2′)); 68.2 (*d*, $J = 149$, C(9), C(1′)); 67.8 (*d*, $J = 148$, C(1), C(3)); 66.8 (*d*, $J = 150$, C(7)); 66.3 (*d*, $J = 147$, C(2)); 62.6 (*t*, $J = 149$, C(3′)); 57.1 (*d*, $J = 132$, C(9a)); 54.0 (*t*, $J = 137$, C(6)); 52.7 (*t*, $J = 134$, C(4)); 37.8 (*d*, $J = 130$, C(8)); 21.2, 21.0, 20.9, 20.8, 20.5 (5*q*, $J = 129$, 8 AcO). CI-MS (NH_3): 647 (7, $[M+1]^+$), 646 (5, M^+), 526 (8), 466 (3), 406 (3), 308 (2), 194 (3), 106 (48), 83 (100). Anal. calc. for $C_{28}H_{39}NO_{16}$ (645.61): C 52.09, H 6.09, N 2.17; found: C 52.09, H 6.42, N 2.30.

*1,4-Anhydro-3-[(6*S*)-5-[[(benzyloxy)carbonyl]amino]-5-deoxy-1,2-*O*-isopropylidene-β-*D*-idofuranos-6-*C*-yl]-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* ((+)-**91**) *and 1,4-Anhydro-3-[(6*S*)-5-[[(benzyloxy)carbonyl]amino]-5-deoxy-1,2-*O*-isopropylidene-α-*L*-glucofuranos-6-*C*-yl]-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* ((+)-**92**). As described for (−)-**86**, with (−)-**77**: (+)-**91**/(+)-**92** 6 : 1 (74%) which were separated by CC (silica gel, AcOEt/light petroleum ether).

*Data of the Major Intermediate 3-[(6*S*)-5-Amino-5-deoxy-1,2-*O*-isopropylidene-β-*D*-idofuranos-6-*C*-yl]-1,4-anhydro-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* (**89**): ^{1}H-NMR (400 MHz, $CDCl_3$): 5.95 (*d*, $^3J(1',2') = 3.6$, H–C(1′)); 5.54 (*d*, $^3J(1,2) = 2.4$, H–C(1)); 4.75, 4.65 (2 *AB*, $J_{AB} = 6.8$, 2 H, OCH_2O); 4.61 (*s*, 2 H, OCH_2O); 4.45 (*d*, $^3J(2',1') = 3.6$, H–C(2′)); 4.43 (*s*, H–C(4)); 4.32 (*d*, $^3J(3',4') = 2.7$, H–C(3′)); 4.15 (*dd*, $^3J(4',3') = 2.7$, $^3J(4',5') = 2.4$, H–C(4′)); 4.04 (*dd*, $^3J(2,3) = 2.7$, $^3J(2,1) = 2.4$, H–C(2)); 3.94 (*dd*, $^3J(5,6A) = 8.3$, $^3J(5,6B) = 5.0$, H–C(5)); 3.76 (*dd*, $^3J(6',3) = 8.5$, $^3J(6',5') = 2.2$, H–C(6′)); 3.47 (*dd*, $^2J(6B,6A) = 10.1$, $^3J(6B,5) = 5.0$, H_B–C(6)); 3.40 (*s*, MeO); 3.39–3.35 (*m*, H_A–C(6)); 3.35 (*s*, MeO); 3.27 (*dd*, $^3J(5',6') = 2.2$, $^3J(5',4') = 2.4$, H–C(5′)); 1.80 (*dd*, $^3J(3,6') = 8.5$, $^3J(3,2) = 2.70$, H–C(3)); 1.46 (*s*, Me); 1.31 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 111.8 (*s*, Me_2C); 105.2 (*d*, $J = 184$, C(1′)); 100.2 (*d*, $J = 181$, C(1)); 96.7 (*t*, $J = 162$, OCH_2O); 96.4 (*t*, $J = 164$, OCH_2O); 85.1 (*d*, $J = 164$, C(2′)); 81.2 (*d*, $J = 146$, C(2)); 80.0 (*d*, $J = 146$, C(4′)); 79.7 (*d*, $J = 159$, C(4)); 78.1 (*d*, $J = 157$, C(5)); 77.4 (*d*, $J = 157$, C(3′)); 74.2 (*d*, $J = 143$, C(6′)); 67.6 (*t*, $J = 144$, C(6)); 55.8, 55.4 (2*q*, $J = 142$, 2 MeO); 52.3 (*d*, $J = 132$, C(5′)); 49.1 (*d*, $J = 132$, C(3)); 26.8, 26.1 (2*q*, $J = 126$, 2 Me). CI-MS (NH_3): 453 (22, $[M+1]^+$), 452 (75, M^+), 436 (18), 406 (20), 344 (12), 284 (21), 229 (16), 209 (8), 188 (39), 130 (33), 85 (100).

Data of (+)-**91**: Colorless solid. M.p. 58–59°. $[\alpha]_{589}^{25}=+55$, $[\alpha]_{577}^{25}=+57$, $[\alpha]_{546}^{25}=+66$, $[\alpha]_{435}^{25}=+110$, $[\alpha]_{405}^{25}=+130$ ($c=1.0$, $CHCl_3$). UV (MeCN): 262 (1400), 257 (1300), 250 (1400), 205 (9800). IR (film): 3435, 2940, 1705, 1535, 1455, 1260, 1215, 1150, 1075, 1030. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.32 (*m*, 5 arom. H); 5.93 (*d*, $^3J(1',2')=3.7$, H–C(1′)); 5.53 (*d*, $^3J(1,2)=2.4$, H–C(1)); 5.29 (*d*, ^3J(NH,5′) = 9.3, NH); 5.18, 5.02 (2 *AB*, $J_{AB}=12.2$, CH_2); 4.77, 4.69 (2 *AB*, $J_{AB}=7.0$, 2 H, OCH_2O); 4.65 (*s*, 2 H, OCH_2O); 4.54 (*s*, H–C(4)); 4.51 (*d*, $^3J(2',1')=3.7$, H–C(2′)); 4.32 (*dd*, $^3J(4',5')=7.0$, $^3J(4',3')=2.3$, H–C(4′)); 4.27–4.23 (*m*, H–C(3′), H–C(5′)); 4.01 (*d*, ^3J(OH–C(6′),6′) = 5.8, OH–C(6′)); 3.92 (*dd*, $^3J(2,1)=2.4$, $^3J(2,3)=2.1$, H–C(2)); 3.8 (*t*, $^3J(5,6)=6.3$, H–C(5)); 3.75 (*dd*, $^3J(6',3)=10.9$, ^3J(6′,OH–C(6′) = 5.8, H–C(6′)); 3.47 (*d*, $^3J(6,5)=6.3$, 2 H–C(6)); 3.38 (*s*, MeO); 3.31 (br. *s*, OH–C(3′)); 3.27 (*s*, MeO); 1.71 (*dd*, $^3J(3,6')=10.9$, $^3J(3,2)=2.1$, H–C(3)); 1.49, 1.31 (2*s*, 2 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 157.0 (*s*, CO); 136.2 (*s*, arom. C); 128.5 (*d*, $J=$ 160, 2 arom. C); 128.3 (*d*, $J=160$, 2 arom. C); 128.2 (*d*, $J=159$, arom. C); 111.6 (*s*, Me_2C); 104.5 (*d*, $J=183$, C(1′)); 100.0 (*d*, $J=180$, C(1)); 97.0 (*t*, $J=165$, OCH_2O); 96.5 (*t*, $J=164$, OCH_2O); 85.5 (*d*, $J=161$, C(2′)); 83.0 (*d*, $J=153$, C(2)); 80.2 (*d*, $J=165$, C(4)); 80.0 (*d*, $J=166$, C(4′)); 78.4 (*d*, $J=152$, C(5)); 74.2 (*d*, $J=154$, C(3′)); 71.0 (*d*, $J=145$, C(6′)); 67.9 (*t*, $J=144$, C(6)); 67.1 (*t*, $J=148$, CH_2); 55.5, 55.2 (2*q*, $J=142$, 2 MeO); 52.5 (*d*, $J=$ 139, C(5′)); 50.3 (*d*, $J=135$, C(3)); 26.6, 26,1 (2*q*, $J=127$, 2 Me). CI-MS (NH_3): 587 (4, $[M+1]^+$), 586 (7, M^+), 554 (2), 478 (5), 338 (100), 310 (14), 191 (75), 83 (87). Anal. calc. for $C_{27}H_{39}NO_{13}$ (585.60): C 55.38, H 6.71, N 2.39; found: C 55.45, H 6.86, N 2.36.

Data of (+)-**92**: Colorless solid. M.p. 51–52°. $[\alpha]_{589}^{25}=+24$, $[\alpha]_{577}^{25}=+25$, $[\alpha]_{546}^{25}=+29$, $[\alpha]_{435}^{25}=+47$, $[\alpha]_{405}^{25}=+56$ ($c=1.1$, $CHCl_3$). UV (MeCN): 204 (7100). IR (film): 3405, 2990, 2940, 2895, 1695, 1515, 1375, 1300, 1220, 1150, 1075, 1040, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.32 (*m*, 5 arom. H); 5.89 (*d*, $^3J(1',2')=3.7$, H–C(1′)); 5.77 (*d*, ^3J(NH,5′) = 8.8, NH); 5.51 (*d*, $^3J(1,2)=2.6$, H–C(1)); 5.15, 5.11 (2 *AB*, $J_{AB}=12.2$, CH_2); 4.87, 4.74 (2 *AB*, $J_{AB}=7.2$, OCH_2O); 4.73 (*d*, ^3J(OH–C(3′),3′) = 2.2, OH–C(3′)); 4.63, 4.60 (2 *AB*, $J_{AB}=6.5$, OCH_2O); 4.53 (*s*, H–C(4)); 4.48 (*d*, $^3J(2',1')=3.7$, H–C(2′)); 4.21 (*dd*, $^3J(4',5')=10.3$, $^3J(4',3')=1.8$, H–C(4′)); 4.15 (*d*, ^3J(OH–C(6′),6′) = 6.8, OH–C(6′)); 4.09 (*dd*, ^3J(3′, OH–C(3′)) = 2.2, $^3J(3',4')=1.8$, H–C(3′)); 4.03–3.96 (*m*, H–C(5′), H–C(5)); 3.81 (*dd*, $^3J(2,1)=2.6$, $^3J(2,3)=2.5$, H–C(2)); 3.73 (*ddd*, $^3J(6',3)=11.1$, ^3J(6′,OH–C(6′)) = 6.8, $^3J(6',5')=2.3$, H–C(6′)); 3.47 (*s*, MeO); 3.45–3.39 (*m*, 2 H–C(6)); 3.36 (*s*, MeO); 2.41 (*dd*, $^3J(3,6')=11.1$, $^3J(3,2)=2.5$, H–C(3)); 1.45, 1.30 (2*s*, 2 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 157.6 (*s*, CO); 135.7 (*s*, arom. C); 128.6 (*d*, $J=161$, 2 arom. C); 128.4 (*d*, $J=161$, arom. C); 128.1 (*d*, $J=158$, 2 arom. C); 111.4 (*s*, Me_2C); 105.5 (*d*, $J=183$, C(1′)); 99.7 (*d*, $J=181$, C(1)); 98.0 (*t*, $J=165$, OCH_2O); 96.7 (*t*, $J=163$, OCH_2O); 84.9 (*d*, $J=153$, C(2)); 83.4 (*d*, $J=161$, C(2′)); 80.3 (*d*, $J=155$, C(4)); 79.0 (*d*, $J=132$, C(4′)); 78.4 (*d*, $J=154$, C(5)); 75.0 (*d*, $J=153$, C(3′)); 74.6 (*d*, $J=146$, C(6′)); 67.9 (*t*, $J=144$, C(6)); 67.6 (*t*, $J=$ 148, CH_2); 56.1 (*q*, $J=144$, MeO); 55.3 (*d*, $J=142$, MeO); 51.2 (*d*, $J=136$, C(5′)); 50.1 (*d*, $J=138$, C(3)); 26.7, 26.1 (2*q*, $J=129$, 2 Me). CI-MS (NH_3): 587 (1, $[M+1]^+$), 586 (2, M^+), 402 (3), 338 (60), 191 (13), 91 (100). Anal. calc. for $C_{27}H_{39}NO_{13}$ (585.60): C 55.38, H 6.71, N 2.39; found: C 55.33, H 6.88, N 2.36.

*(−)-(1*S*,2a*R*,5a*R*,6a*R*,6b*S*,9a*S*,10a*S*,10b*R*)-1,2a,3,5,5a,6a,6b,9a,10a,10b-Decahydro-1-{(1*R*,3*R*,4*R*,5*S*,6*R*)-6-*endo*-(methoxymethoxy)-3-*exo*-[(methoxymethoxy)methyl]-2,7-dioxabicyclo[2.2.1]hept-5-yl}-8,8-dimethyl-4*H*-2,6,7,9,10-pentaoxa-10c-azapentaleno[2,1-*d*]acenaphthylene* ((−)-**93**). As described for (+)-**87**, with **89**: (−)-**93** (50%). Colorless oil. $[\alpha]_{589}^{25}=-8$, $[\alpha]_{577}^{25}=-6$, $[\alpha]_{546}^{25}=-9$, $[\alpha]_{435}^{25}=-10$, $[\alpha]_{405}^{25}=-10$ ($c=0.5$, $CHCl_3$). UV (MeCN): 197 (4200). IR (film): 2935, 1375, 1215, 1155, 1115, 1060, 860. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.92 (*d*, ^3J(9a,6b) = 3.8, H–C(9a)); 5.51 (*d*, $^3J(1',6')=2.3$, H–C(1′)); 4.77 (*AB*, $J_{AB}=6.6$, 1 H, OCH_2O); 4.67 (*dd*, ^3J(2a,3*A*) = 10.3, ^3J(2a,3*B*) = 2.5, H–C(2a)); 4.66–4.65 (*m*, H–C(5a)); 4.64 (*AB*, $J_{AB}=6.6$, 1 H, OCH_2O); 4.62 (*s*, OCH_2O); 4.55 (*d*, ^3J(6b,9a) = 3.8, H–C(6b)); 4.53 (*s*, H–C(4′)); 4.47 (*dd*, $^3J(1,5')=6.9$, ^3J(1,10b) = 2.3, H–C(1)); 4.15 (*d*, ^3J(6a,10a) = 2.0, H–C(6a)); 3.98–3.94 (*m*, H–C(3′), H–C(10a)); 3.89 (*dd*, $^3J(6',5')=3.1$, $^3J(6',1')=2.3$, H–C(6′)); 3.65 (*dd*, ^3J(10b,10a) = 3.8, ^3J(10b,1) = 2.3, H–C(10b)); 3.45 (*dd*, $^2J(8'A,8'B)=10.1$, $^3J(8'A,3')=5.4$, H_A–C(8′)); 3.40 (*s*, MeO); 3.38 (*m*, H_B–C(8′)); 3.35 (*s*, MeO); 1.98–1.94 (*m*, 1 H–C(3)); 1.94 (*dd*, $^3J(5',1)=$ 6.9, $^3J(5',6')=3.1$, H–C(5′)); 1.74–1.53 (*m*, 2 H–C(4), 2 H–C(5)); 1.49, 1.32 (2*s*, 2 Me); 1.28–1.23 (*m*, 1 H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 111.5 (*s*, C(8)); 104.3 (*d*, $J=183$, C(9a)); 100.2 (*d*, $J=181$, C(1′)); 96.6 (*t*, $J=167$, OCH_2O); 96.2 (*t*, $J=164$, OCH_2O); 87.1 (*d*, $J=155$, C(2a)); 83.9 (*d*, $J=157$, C(6b)); 83.8 (*d*, $J=157$, C(5a)); 81.0 (*d*, $J=147$, C(6′)); 79.8 (*d*, $J=153$, C(4′)); 79.7 (*d*, $J=153$, C(6a)); 78.5 (*d*, $J=149$, C(3′ or 10a)); 76.5 (*d*, $J=147$, C(1)); 72.5 (*d*, $J=143$, C(10a or 3′)); 67.8 (*t*, $J=144$, OCH_2); 57.5 (*d*, $J=145$, C(10b)); 55.6 (*q*, $J=136$, MeO); 55.3 (*q*, $J=142$, MeO); 51.4 (*d*, $J=135$, C(5′)); 30.0 (*t*, $J=131$, C(3)); 28.9 (*t*, $J=131$, C(5)); 26.5, 26.0 (2*q*, $J=126$, 2 Me); 18.4 (*t*, $J=128$, C(4)). CI-MS (NH_3): 517 (43, $[M+1]^+$), 516 (93, M^+), 470 (38), 410 (11), 354 (8), 282 (100), 253 (20), 183 (9), 81 (23). Anal. calc. for $C_{24}H_{37}NO_{11}$ (515.55): C 55.91, H 7.23; found: C 55.82, H 7.05.

*(−)-(1*S*,2*S*,3*R*,7*R*,8*S*,9*S*,9a*R*)-1,3,4,6,7,8,9,9a-Octahydro-8-[(1*R*,2*R*)-1,2,3-trihydroxypropyl]-2*H*-quinolizine-1,2,3,7,9-pentol* ((−)-**22**). As described for **21** (see (+)-**88**), with (+)-**91**. The crude (−)-**22** was purified by CC (silica gel, CH_2Cl_2/MeOH/NH_4Cl 10 : 10 : 1): 22.3 mg (60%) of (−)-**22**. Colorless solid. M.p. 185–187°. $[\alpha]_{589}^{25}=$

-9, $[\alpha]_{577}^{25}=-10$, $[\alpha]_{546}^{25}=-10$, $[\alpha]_{435}^{25}=-16$, $[\alpha]_{405}^{25}=-35$ ($c=0.5$, MeOH). UV (MeCN): 203 (1700). IR (KBr): 3385, 2935, 1640, 1430, 1130, 1070. ^{1}H-NMR (400 MHz, CD_3OD): 4.25–4.23 (m, H–C(7), H–C(9)); 4.14 (dd, $^3J(1',8)=10.2$, $^3J(1',2')=1.2$, H–C(1')); 4.01 (ddd, $^3J(1,2)=3.2$, $^3J(1,9a)=1.8$, $^4J(1,3)=1.8$, H–C(1)); 3.93 (dt, $^3J(2',3')=6.3$, $^3J(2',1')=1.2$, H–C(2')); 3.84 (dd, $^3J(2,1)=3.2$, $^3J(2,3)=2.8$, H–C(2)); 3.77–3.72 (m, 2 H, H–C(3), H–C(3')); 3.19 (dd, ^2J(6eq,6ax) = 12.2, ^3J(6eq,7) = 2.9, H_{eq}–C(6)); 2.95 (dd, ^2J(4eq,4ax) = 12.3, ^3J(4eq,3) = 2.0, H_{eq}–C(4)); 2.66 (dd, ^2J(4ax,4eq) = 12.3, ^3J(4ax,3) = 2.2, H_{ax}–C(4)); 2.31 (dd, ^2J(ax,6eq) = 12.2, ^3J(6ax,7) = 1.8, H_{ax}–C(6)); 2.29–2.28 (m, H–C(9a)); 1.80 (ddd, $^3J(8,1')=10.2$, $^3J(8,9)=2.5$, $^3J(8,7)=2.5$, H–C(8)). ^{13}C-NMR (100.6 MHz, CD_3OD): 76.4 (d, $J=148$, C(1)); 73.6 (d, $J=147$, C(7 or 9)); 71.7 (d, $J=138$, C(2')); 71.1 (d, $J=146$, C(3)); 69.3 (d, $J=148$, C(2)); 68.4 (d, $J=141$, C(1')); 67.3 (d, $J=147$, C(9 or 7)); 65.4 (t, $J=140$, C(3')); 63.8 (t, $J=139$, C(6)); 62.0 (d, $J=132$, C(9a)); 57.9 (t, $J=131$, C(4)); 46.7 (d, $J=129$, C(8)). CI-MS (NH_3): 310 (10, $[M+1]^+$), 279 (7), 221 (11), 180 (25), 133 (139, 78 (34). Anal. calc. for $C_{12}H_{23}NO_8$ (309.32): C 46.60, H 7.49; found: C 46.18, H 7.75.

*(+)-1,4-Anhydro-3-[(6*R*)-5-[[(benzyloxy)carbonyl]amino]-5-deoxy-1,2-*O*-isopropylidene-β-*D*-idofuranos-6-*C*-yl]-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* ((+)-**95**). As described for (−)-**86**, with (+)-**84**: (+)-**95** (75%).

*Data of the Intermediate 3-[(6*R*)-5-Amino-5-deoxy-1,2-*O*-isopropylidene-β-*D*-idofuranos-6-*C*-yl]-1,4-anhydro-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*D*-galactopyranose* (**94**): UV (MeCN): 199 (1800). IR (film): 3360, 2985, 2940, 1380, 1215, 1155, 1105, 1070, 1040. ^{1}H-NMR (400 MHz, CD_3OD): 5.98 (d, $^3J(1',2')=3.7$, H–C(1')); 5.56 (d, $^3J(1,2)=2.2$, H–C(1)); 4.78 (s, H–C(4)); 4.71, 4.68 (2 AB, $J_{AB}=6.9$, 2 H, OCH_2O); 4.67, 4.65 (2 AB, $J_{AB}=6.9$, 2 H, OCH_2O); 4.48 (d, $^3J(2',1')=3.7$, H–C(2')); 4.42 (dd, $^3J(4',3')=2.8$, $^3J(4',5')=2.7$, H–C(4')); 4.22 (d, $^3J(3',4')=2.8$, H–C(3')); 3.99 (dd, $^3J(5,6A)=6.4$, $^3J(5,6B)=6.6$, H–C(5)); 3.76 (dd, $^3J(2,3)=3.3$, $^3J(2,1)=2.2$, H–C(2)); 3.55 (dd, $^3J(6',3)=8.4$, $^3J(6',5')=5.5$, H–C(6')); 3.45 (m, 2 H–C(6)); 3.44, 3.39 (2s, 2 MeO); 3.28 (dd, $^3J(5',6')=5.5$, $^3J(5',4')=2.7$, H–C(5')); 1.91 (dd, $^3J(3,6')=8.4$, $^3J(3,2)=3.3$, H–C(3)); 1.50, 1.34 (2s, 2 Me). ^{13}C-NMR (100.6 MHz, CD_3OD): 112.7 (s, Me_2C); 106.3 (d, $J=183$, C(1')); 101.7 (d, $J=182$, C(1)); 98.1, 97.8 (2t, $J=164$, 2 OCH_2O); 86.6 (d, $J=157$, C(2')); 84.5 (d, $J=152$, C(2)); 80.5 (d, $J=167$, C(4)); 79.9 (d, $J=153$, C(5)); 78.7 (d, $J=153$, C(3')); 78.1 (d, $J=146$, C(4')); 69.4 (t, $J=144$, C(6)); 56.3, 55.6 (2q, $J=142$, 2 MeO); 53.8 (d, $J=134$, C(5')); 51.4 (d, $J=132$, C(3)); 27.1, 26.5 (2q, $J=126$, 2 Me). CI-MS (NH_3): 453 (3, $[M+2]^+$), 452 (11, $[M+1]^+$), 406 (26), 344 88), 292 (8), 260 (4), 188 (71), 130 (60), 100 (100), 85 (55).

*Data of (+)-***95**: Colorless solid. M.p. 50–51°. $[\alpha]_{589}^{25}=+47$, $[\alpha]_{577}^{25}=+48$, $[\alpha]_{546}^{25}=+56$, $[\alpha]_{435}^{25}=+94$, $[\alpha]_{405}^{25}=+112$ ($c=1.1$, $CHCl_3$). UV (MeCN): 260 (1400), 205 (7800). IR (KBr): 3440, 2940, 1700, 1535, 1375, 1220, 1155, 1075, 1045, 700. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.30 (m, 5 arom. H); 5.90 (d, $^3J(1',2')=3.7$, H–C(1')); 5.52 (d, ^3J(NH,5') = 8.5, NH); 5.51 (d, $^3J(1,2)=2.1$, H–C(1)); 5.13, 5.06 (2 AB, $J_{AB}=12.3$, CH_2); 4.81 (s, H–C(4)); 4.64, 4.62 (2s, 2 OCH_2O); 4.49 (d, $^3J(2',1')=3.7$, H–C(2')); 4.43 (dd, $^3J(4',5')=4.5$, $^3J(4',3')=2.8$, H–C(4')); 4.26 (dd, ^3J(3',OH–C(3')) = 3.8, $^3J(3',4')=2.8$, H–C(3')); 4.05 (ddd, ^3J(5',NH) = 8.5, $^3J(5',6')=5.4$, $^3J(5',4')=4.5$, H–C(5')); 3.89 (dd, $^3J(5,6A)=6.6$, $^3J(5,6B)=6.1$, H–C(5)); 3.74–3.68 (m, H–C(6'), H–C(2)); 3.46–3.44 (m, H–C(6)); 3.38, 3.36 (2s, 2 MeO); 3.15 (d, ^3J(OH–C(3'),3') = 3.8, OH–C(3')); 3.09 (d, ^3J(OH–C(6'),6') = 6.7, OH–C(6')); 1.84 (dd, $^3J(3,6')=7.3$, $^3J(3,2)=3.2$, H–C(3)); 1.49, 1.31 (2s, 2 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 157.1 (s, CO); 136.0 (s, arom. C); 128.5 (d, $J=160$, 2 arom. C); 128.2 (d, $J=161$, arom. C); 128.0 (d, $J=158$, 2 arom. C); 111.8 (s, Me_2C); 104.2 (d, $J=184$, C(1')); 100.1 (d, $J=182$, C(1)); 97.0 (t, $J=164$, OCH_2O); 96.5 (t, $J=160$, OCH_2O); 85.1 (d, $J=161$, C(2')); 82.5 (d, $J=147$, C(2)); 79.1 (d, $J=167$, C(4)); 78.6 (d, $J=154$, C(5)); 77.9 (d, $J=167$, C(4')); 75.9 (d, $J=156$, C(3')); 73.9 (d, $J=147$, C(6')); 67.8 (t, $J=144$, C(6)); 67.1 (t, $J=148$, CH_2); 55.9, 55.2 (2q, $J=142$, 2 MeO); 51.9 (d, $J=137$, C(5')); 49.4 (d, $J=134$, C(3)); 26.7, 26.1 (2q, $J=127$, 2 Me). CI-MS (NH_3): 587 (2, $[M+1]^+$), 586 (4, M^+), 554 (2), 441 (3), 338 (94), 310 (6), 191 (44), 91 (100). Anal. calc. for $C_{27}H_{39}NO_{13}$ (585.60): C 55.38, H 6.71, N 2.39; found: C 55.45, H 6.85, N 2.37.

*(+)-(1*R*,2a*R*,5a*R*,6a*R*,6b*S*,9a*S*,10a*S*,10b*R*)-1,2a,3,5,5a,6a,6b,9a,10a,10b-Decahydro-1-[(1*R*,3*R*,4*R*,5*S*,6*R*)-6-*endo*-(methoxymethoxy)-3-*exo*-[(methoxymethoxy)methyl]-2,7-dioxabicyclo[2.2.1]hept-5-yl]-8,8-dimethyl-4*H*-2,6,7,9,10-pentaoxa-10c-azapentaleno[2,1-*d*]acenaphthylene* ((+)-**96**). As described for (+)-**87**, with **94**: (+)-**96** (70%). Colorless oil. $[\alpha]_{589}^{25}=+13$, $[\alpha]_{577}^{25}=+12$, $[\alpha]_{546}^{25}=+15$, $[\alpha]_{435}^{25}=+24$, $[\alpha]_{405}^{25}=+28$ ($c=0.9$, $CHCl_3$). UV (MeCN): 198 (1800). IR (film): 2930, 2880, 1375, 1215, 1155, 1120, 1060, 985, 860, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.92 (d, ^3J(9a,6b) = 3.7, H–C(9a)); 5.54 (d, $^3J(1',6')=2.2$, H–C(1')); 4.89 (dd, ^3J(2a,3) = 10.4, ^3J(2a,3) = 2.5, H–C(2a)); 4.84 (s, H–C(4')); 4.68 (d, ^3J(5a,5) = 2.7, H–C(5a)); 4.61 (s, 2 OCH_2O); 4.46 (d, ^3J(6b,9a) = 3.7, H–C(6b)); 4.19 (dd, $^3J(1,5')=11.2$, $^3J(1,10b)=6.0$, H–C(1)); 4.15 (d, ^3J(6a,10a) = 1.6, H–C(6a)); 4.11–4.06 (m, H–C(3'), H–C(10a)); 3.61 (dd, ^3J(10b,1) = 6.0, ^3J(10b,10a) = 3.3, H–C(10b)); 3.45–3.40 (m, H–C(6'), H–C(8')); 3.40, 3.35 (2s, 2 MeO); 2.73 (dd, $^3J(5',1)=11.2$, $^3J(5',6')=2.9$, H–C(5')); 1.95–1.92 (m, 1 H–C(3)); 1.74–1.67 (m, CH_2(5), 1 H–C(4)); 1.68–1.57 (m, 1 H–C(3)); 1.46, 1.31 (2s, 2 Me); 1.30–1.25 (m, 1 H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 111.8 (s, C(8)); 105.1 (d, $J=183$, C(9a)); 100.5

(d, J = 181, C(1′)); 96.9, 96.4 ($2t$, J = 163, 2 OCH_2O); 87.1 (d, J = 157, C(2a)); 84.2 (d, J = 155, C(5a)); 82.8 (d, J = 157, C(6′)); 82.7 (d, J = 157, C(6b)); 80.2 (d, J = 152, C(6a)); 80.0 (d, J = 151, C(4′)); 79.3 (d, J = 149, C(1)); 78.1 (d, J = 153, C(3′ or 10a)); 72.0 (d, J = 149, C(10a or 3′)); 67.9 (t, J = 143, OCH_2); 56.7 (d, J = 138, C(10b)); 56.0, 55.1 ($2q$, J = 142, 2 MeO); 46.9 (d, J = 140, C(5′)); 30.3 (t, J = 129, C(3)); 28.7 (t, J = 132, C(5)); 26.4, 26.3 ($2q$, J = 127, 2 Me); 18.8 (t, J = 126, C(4)). CI-MS (NH_3): 517 (5, $[M+1]^+$), 516 (13, M^+), 338 (14), 279 (4), 191 (20), 83 (100). Anal. calc. for $C_{24}H_{37}NO_{11}$ (515.55): C 55.91, H 7.23; found: C 55.98, H 7.33.

*(−)-(1*S*,2*S*,3*R*,7*R*,8*S*,9*R*,9a*R*)-1,3,4,6,7,8,9,9a-Octahydro-8-[(1*R*,2*R*)-1,2,3-trihydroxypropyl]-2*H*-quinolizine-1,2,3,7,9-pentol* ((+)-**23**). As described for **21** (see (+)-**88**), with (+)-**95**. The crude (+)-**23** was purified by CC (*Dowex* (OH^- form), H_2O): 18.6 mg (50%) of (+)-**23**. Colorless oil. $[\alpha]_{589}^{25} = +2$, $[\alpha]_{577}^{25} = +1$, $[\alpha]_{546}^{25} = -2$, $[\alpha]_{435}^{25} = -2$, $[\alpha]_{405}^{25} = -3$ (c = 0.2, H_2O). UV (MeCN): 201 (2000). IR (film): 3385, 2935, 1640, 1430, 1130, 1055. ^{1}H-NMR (400 MHz, D_2O): 4.29 (m, H−C(7)); 4.13 (dd, ^3J(9,8) = 11.1 ^3J(9,9a) = 9.6, H−C(9)); 4.00–3.96 (m, H−C(1), H−C(1′)); 3.92 (dd, ^3J(2,1) = 2.9, ^3J(2,3) = 2.9, H−C(2)); 3.83 (ddd, ^3J(2′,3′*B*) = 6.9, ^3J(2′,1′) = 5.3, ^3J(2′,3′) = 4.3, H−C(2′)); 3.79 (m, H−C(3)); 3.63 (dd, ^2J(3′*A*,3′*B*) = 11.8, ^3J(3′*A*,2′) = 4.3, H_A−C(3′)); 3.53 (dd, ^2J(3′*B*,3′*A*) = 11.8, ^3J(3′*B*,2′) = 6.9, H_B−C(3′)); 2.79 (dd, ^2J(6eq,6ax) = 12.7, ^3J(6eq,7) = 3.0, H_{eq}−C(6)); 2.76 (dd, ^2J(4eq,4ax) = 13.0, ^3J(4eq,3) = 1.7, H_{eq}−C(4)); 2.48 (dd, ^2J(4ax,4eq) = 13.0, ^3J(4ax,3) = 2.1, H_{ax}−C(4)); 2.26 (dd, ^2J(6ax,6eq) = 12.7, ^3J(6ax,7) = 1.4, H_{ax}−C(6)); 2.12 (dd, ^3J(9a,9) = 9.6, ^3J(9a,1) = 1.6, H−C(9a)); 1.62 (ddd, ^3J(8,9) = 11.1, ^3J(8,7) = 3.2, ^3J(8,1′) = 3.2, H−C(8)). ^{13}C-NMR (100.6 MHz, D_2O): 75.9 (d, J = 142, C(2′)); 72.3 (d, J = 143, C(1 or 1′)); 71.0 (d, J = 144, C(3)); 70.5 (d, J = 151, C(2)); 69.9 (d, J = 143, C(1′ or 1)); 69.0 (d, J = 139, C(7)); 67.2 (d, J = 139, C(9a)); 65.3 (t, J = 142, C(3′)); 64.8 (d, J = 148, C(9)); 62.7 (t, J = 145, C(6)); 57.6 (t, J = 145, C(4)); 49.2 (d, J = 127, C(8)). CI-MS (NH_3): 311 (73, $[M+2]^+$), 310 (47, $[M+1]^+$), 292 (22), 278 (12), 187 (73), 147 (39), 130 (68), 110 (100), 96 (94). Anal. calc. for $C_{12}H_{23}NO_8$ (309.32): C 46.60, H 7.49; found: C 46.33, H 7.79.

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