Stereospecific Synthesis of New Trioxadecalin-Derived Liquid Crystals Bearing Halogen Substituents on the Phenyl Ring

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Reaction of pseudo-glucal **2** with various aryl Grignard reagents bearing halogen substituents, in the presence of a catalytic amount of $NiCl_2$(dppe) gives the corresponding β-*C*-aryl glycosides **4**. Deacetylation and hydrogenation of **4** leads to the β-*C*-aryl glycosides **5**, which can be used as chiral compounds in the synthesis of chiral liquid crystals. The reaction of compound **5** with aliphatic aldehydes leads to compounds **6**; similarly, reaction with *p*-alkoxy-substituted phenylboronic acids gives the bora analogues **7**. All the mesogenic properties depend strongly on small changes in the molecular structure. It is possible to obtain a wide array of different chiral effects such as helix inversion, blue phase, TGA phase, cholesteric phase, and smectic A phase, to name but a few, by changing a small part of the molecule while maintaining the basic mesogenic core.

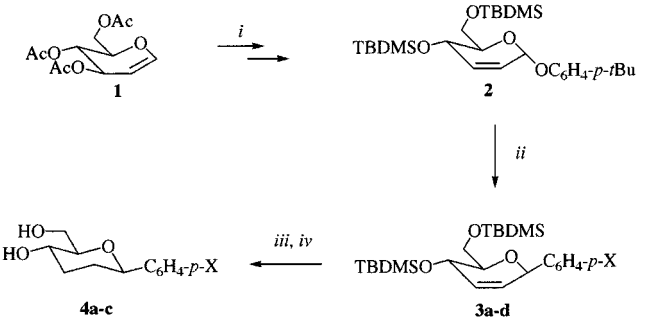
Introduction

During the last decade, chirality has become one of the most important and complex topics in liquid crystal research.[1] This is mainly due to the fact that molecular asymmetry imparts form chirality to the liquid crystalline phases and leads to possible new technical applications for chiral liquid crystals. Today, 16 000 among the 80 000 mesogenic known compounds are chiral.[2] Most of these compounds have a chiral center in the flexible wing, which induces the chirality by a steric hindrance and disturbs the mesogenic order.

While aiming to separate chiral effects from mesogenic effects by the isosteric replacement of $-CH_2-$ groups by $-O-$ groups in conformationally rigid units, one of us prepared previously liquid crystals bearing a chiral trioxadecalin core. These compounds exhibited interesting chiral effects such as cholesteric helix inversion, double inversion of the helical twist sense, and re-entrant TGB_A phases.[3] However, in all the substrates studied, the alkoxy-chain was directly bound to the phenyl ring situated on the pyranosyl moiety. It will be interesting to examine the influence of the nature of the functionalized group located on this aromatic ring on the mesogenic properties. While the previous methodology allowed the introduction of the alkoxy group only, the intention of this work was to develop a synthetic route to chiral liquid crystals with a chiral oxadecalin or oxabora-decalin system as the molecular core, bearing various substituents on the phenyl ring, and the study of their mesogenic properties. We were particularly interested in the synthesis of a homologous series of trioxadecalin derivatives bearing terminal halogen and trifluoromethyl group in the *para* positions on this ring, and *p*-alkoxy substituents on the phenyl ring directly bound to the dioxolane moiety. It should be noted that chiral liquid crystals from carbohydrates having fluorinated chains were recently prepared; these compounds are of special interest because the intramolecular contacts can cause unusual packings.[4]

Results and Discussion

The synthesis was based on the methodology published before by us, allowing the stereospecific introduction of various substituted aryl groups at the anomeric center of unsaturated carbohydrates.[5] The building block **4** for the synthesis of the new liquid crystals bearing a chiral trioxadecalin system was prepared according to Scheme 1.



a R = Cl ; **b** R = F ; **c** R = CF_3 ; **d** R = OCF_3

Scheme 1. Reagents and conditions: *i*: ref. [5]; *ii*: *p*-X−C_6H_4MgBr, cat. $NiCl_2$(dppe); *iii*: $Bu_4N^+F^-\cdot 3H_2O$; *iv*: H_2, cat. $[Rh(COD)_2]PF_6$ + dppb

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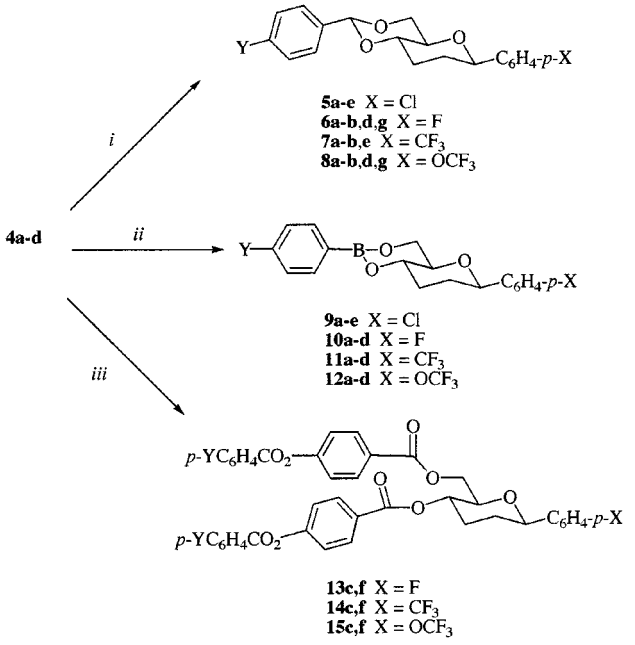
p-tert-Butylphenyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**2**) was synthesized from commercially available tri-*O*-acetyl-D-glucal (**1**). The reaction of the corresponding Grignard reagent prepared from 1-bromo-4-chlorobenzene, 1-bromo-4-fluorobenzene, 1-bromo-4-trifluoromethylbenzene, and 1-bromo-4-(trifluoromethyloxy)benzene, with the unsaturated carbohydrate **2** in the presence of catalytic $NiCl_2$(dppe) [dppe = 1,2-bis(diphenylphosphanyl)ethane] in tetrahydrofuran at −50 °C gave the β-*C*-aryl glycosides **3a**−**d** regio- and stereospecifically in 60%, 40%, 48%, and 52% yield, respectively. It is noteworthy that all attempts to prepare the corresponding β-*C*-*p*-bromophenyl glycoside failed, regardless of the conditions used. The desilylation of compounds **3a**−**d** was mediated by tetrabutylammonium fluoride to give the saturated diols. These were hydrogenated at atmospheric pressure in the presence of $[Rh(COD)_2]PF_6$ (COD: 1,5-cyclooctadiene) + dppb [dppb = 1,4-bis(diphenylphosphanyl)butane] prepared in situ, or $[Rh(COD)(dppb)]PF_6$ as the catalyst to give the corresponding saturated diols **4a**−**d**. The expected β configuration of compounds **4a**−**d** was confirmed by the ^1H NMR spectra. We observed both a large diaxial coupling constant between 1-H and 2-H_{ax} ($^3J_{1,2ax}$ = 10.7, 10.7, 10.1, and 10.5 Hz for **4a**, **4b**, **4c**, and **4d**, respectively), and a small coupling constant $^3J_{1,2eq}$ between 1-H and 2-H_{eq} (2.1 and 2.3 Hz for **4b** and **4d**, respectively; undetermined for **4a** and **4b**).

The conversion of diols **4a**−**d** into compounds **5**−**8** was carried out with the corresponding dimethyl acetals of 4-alkoxybenzaldehyde or 4-ethynylbenzaldehyde in an acid-catalyzed transacetalization reaction (Scheme 2). The methanol that formed during these reactions was distilled off to shift the equilibrium of the reaction. The boronic acid derivatives **9**−**12** were easily obtained by reaction of diols **4a**−**d** with the appropriate arylboronic acid, the water that formed being removed by azeotropic coevaporation with toluene. Finally, esterification of these diols **4a**−**d** with the corresponding alkoxyacids in the presence of dicyclohexyldiimide gave the diesters **13**−**15**. All the products were recrystallized from ethanol, and these compounds gave satisfactory analyses.



a Y = OCH_3 ; **b** Y = OC_4H_9 ; **c** Y = OC_6H_{13} ; **d** Y = OC_8H_{17} ; **e** Y = $OC_{10}H_{21}$; **f** Y = $OC_{14}H_{29}$; **g** Y = C≡CH

Scheme 2. Reagents and conditions: *i*: *p*-Y−C_6H_4−$CH(OMe)_2$, DMF, cat. TsOH; *ii*: *p*-Y−C_6H_4−$B(OH)_2$, toluene, Δ; *iii*: *p*-Y−C_6H_4−CO_2−C_6H_4−*p*-CO_2H, DCC

The mesomorphic properties of compounds **5**−**8** are summarized in Table 1. All the chloro derivatives **5a**−**5e** show a cholesteric phase (N*) that is monotropic for the methoxy compound **5a** and enantiotropic for all others. The long chain compounds **5c**−**5e** have an additional smectic A phase (S_A), and **5e** also has a TGB_A phase.[6] This homologous series of chiral compounds exhibit a new type of helical inversion, which is an inversion by chain length variation. The cholesteric phase of compound **5a** has a different sign

Table 1. Mesomorphism of compounds **5**−**8**

Compound	Y	X	Transition temperatures [°C][a]				
5a	OCH_3	Cl	C 190.3			N* 182.4	dec.
5b	OC_4H_9	Cl	C 155.6			(N*) 171.1	I[b]
5c	OC_6H_{13}	Cl	C 142.0	S_A 115.4		N* 163.3	I[c]
5d	OC_8H_{17}	Cl	C 128.6	S_A 132.9		N* 158.8	I
5e	$OC_{10}H_{21}$	Cl	C 122.1	S_A 134.3	TGB_A 134.5	N* 141.2	I
6a	OCH_3	F	C 181.2			N* 153.0	I
6b	OC_4H_9	F	C 146.5			N* 155.0	I
6d	OC_8H_{17}	F	C_2 105.0	C_1 116.4		N* 102.0	I
6g	C≡CH	F	C_2 169.0	C_1 188.0		N* 190.0	I[d]
7a	OCH_3	CF_3	C 201.8				I
7b	OC_4H_9	CF_3	C 184.7				I
7d	OC_8H_{17}	CF_3	C 156.7				I
8a	OCH_3	OCF_3	C 179.0			N* 145.6	I
8b	OC_4H_9	OCF_3	C 172.0	S_A 152.3			I
8d	OC_8H_{17}	OCF_3	C 156.7				I
8g	C≡CH	OCF_3	C_2 157.0	C_1 158.5		N* 171.0	I[e]

[a] C: crystalline phase; S_A: smectic A phase; N*: cholesteric phase; TGB_A: twist grain boundary phase; I: isotropic phase. − [b] No visible helical ordering. − [c] Helical inversion in contact with nonchiral nematics. − [d] Inversion temperature of helix at 144 °C. − [e] Tm_1 (melting point of a metastable crystalline modification) at 157.0 °C and Tm_2 at 151.0 °C.

to that of compound **5c**, the contact preparation between both compounds having a nematic line in between. Compound **5b**, with intermediate chain length, has a cholesteric phase with an infinitesimally long pitch: the texture is like the nonchiral nematic phase. It should also be noted that the pitch length decreases from compound **5b** to **5e**, that is, with increasing lateral chain length. The last compound **5e** has a TGB_A phase, which can only be observed for highly twisted cholesteric phases. The thermal stability of these compounds is low. The clearing temperatures decrease by about 5 °C after annealing for 10 min at 180 °C. The cholesteric phase of compound **5c** also shows a temperature-dependent helical inversion after this treatment. We noticed that the properties of the phase are very sensitive to impurities. The chirality effects in these compounds seem to be very sensitive to a small change in the left part of the substrate. The helical pitch is caused by the asymmetry of the molecular surface relative to the main axis of the molecule. This pitch is perpendicular to the main axis defined by order parameters of the rigid cone and the flexible wing for the cholesteric phase. As is shown in Figure 1, the main axis will shift if the chain length increases. This can explain the large difference in macroscopic behaviour, even if the main axis is rotated only about 0.1°, because the tilt angle between two individual molecules is much smaller than 0.1° for a helical pitch of 5 μm.

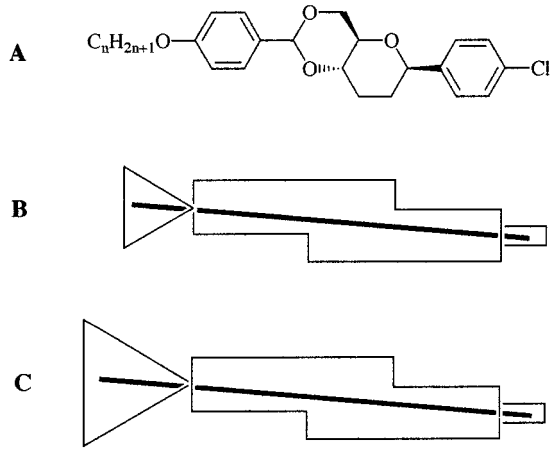


Figure 1. Shift of the main axis of trioxadecalin compounds upon temperature change

The fluoro compounds **6a−6d** only have cholesteric phases. The clearing temperatures are significantly lower than those of the corresponding chloro compounds **5**. The melting temperatures are only slightly lower; therefore the mesomorphic range is shorter for compounds **6a−6d** than for compounds **5a−5d**. Smectic phases are not observed here, neither are helical inversions in the cholesteric phase for these compounds. It should be noted that compound **6g**, which is conformationally more rigid than compounds **6a−6d**, shows a helical inversion of the cholesteric pitch at 144 °C.

Trifluoromethyl groups are commonly used to give nematic crystals with high Δε values for display applications. This high dipole moment may have some influences on the properties of cholesteric phases. However, the trifluoromethyl compounds **7a−7d** have very high melting temperatures, and therefore liquid crystalline behavior is not found for these compounds.

The presence of a trifluoromethyloxy group in compounds **8** instead of a trifluoromethyl group gives a quite different behaviour. Whereas compounds **7a−d** are nonmesogenic, compounds **8a** and **8b**, with a lower chain length, exhibit a monotropic cholesteric mesophase, and an enantiotropic S_A mesophase, respectively. Compound **8d**, however, has no mesogenic properties. In the case of compound **8g**, the presence of an alkyne moiety affords only a cholesteric phase.

The mesomorphic properties of the boratrioxadecalin compounds **9−12** are compiled in Table 2. It was expected that the replacement of the carbon atom in the trioxadecalin system bearing the second aromatic ring by a boron atom would cause a change of the molecular shape and hence of the mesogenic properties. We observed that the effect of the boron atom is very pronounced. As a general statement, these compounds have lower melting temperatures and higher clearing temperatures than the corresponding trioxadecalin compounds. We also noticed that the helical pitch of these compounds is shorter, and that blue phases and TGB_A phases were observed in many cases. Helical inversions cannot be observed for the bora compounds **9**, either in the pure form or in contact preparation with nematic compounds. However, the twisting power is enlarged for longer alkyl chains. This is displayed in the occurrence of a twisted mesophase.

The chloro compounds **9a** has no blue phase, whereas the longer chain compounds **9b−9e** have a blue phase and a TGB_A phase. Whereas compounds **7a−7d** are nonmesogenic, the bora analogues **11b−11d** have smectic A phases with high clearing temperatures, and **11a** has a blue phase. The same trends are observed for the fluoro compounds. All the fluoro compounds show a cholesteric phase and also a smectic A phase for **10b−10d**; moreover, compound **10c** shows a blue phase (BP),[7] and compound **10d** both a blue phase and a TGB_A phase.

All the compounds **12a−d**, obtained by the substitution of the trifluoromethyl group by a trifluoromethyloxy group, show a smectic A phase; compound **12a** also shows a blue phase.

Finally, compounds **13−15** (Table 3) are a new class of Y-shaped mesogenic compounds with a central chiral core. The long-chain compounds **13f**, **14f**, and **15f** show a smectic A phase, but they induce a blue phase for **15f** and two blue phases (BP_I and BP_{II}) for **13f** and **14f** in contact preparation with the nematic compound N4 (4-butyl-4′-methoxyazoxybenzene, K 16 N 76 I). The short-chain compounds **13c**, **14c**, and **15c**, have no smectic phase, but do have cholesteric and blue phases.

Conclusion

Condensation of various aryl Grignard reagents with *p*-*tert*-butylphenyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dide-

Table 2. Mesomorphism of compounds **9−12**

Compound	Y	X	Transition temperatures [°C][a]					
9a	OCH_3	Cl		C 170.6			N* 196.0	I
9b	OC_4H_9	Cl		C 157.0	S_A 156.7	TGB_A 156.9	N* 195.0	BP
9c	OC_6H_{13}	Cl		C 128.4	S_A 169.5	TGB_A 170.4	N* 187.0	BP
9d	OC_8H_{17}	Cl		C 117.9	S_A 174.0	TGB_A 174.2	N* 180.7	BP
9e	$OC_{10}H_{21}$	Cl		C 113.9	S_A 173.3			I
10a	OCH_3	F		C 156.0			N* 174.6	I
10b	OC_4H_9	F		C 132.7	S_A 138.5		N* 181.5	I
10c	OC_6H_{13}	F		C 101.7	S_A 147.4		N* 167.3	BP
10d	OC_8H_{17}	F		C 97.3	S_A 150.8	TGB_A 151.0	N* 162.1	BP
11a	OCH_3	CF_3	C_2 164.3	C_1 178.3			N* 161.0	BP
11b	OC_4H_9	CF_3		C 167.5	S_A 193.1			I
11c	OC_6H_{13}	CF_3		C 134.8	S_A 176.6			I
11d	OC_8H_{17}	CF_3		C 125.0	S_A 172.1			I
12a	OCH_3	OCF_3	C_2 142.5	C_1 164.7	S_A 135.0		N* 187.7	BP
12b	OC_4H_9	OCF_3	C_2 109.0	C_1 134.4	S_A 199.7			I
12c	OC_6H_{13}	OCF_3		C 103.8	S_A 193.1			I
12d	OC_8H_{17}	OCF_3		C 100.8	S_A 183.4			I

[a] C: crystalline phase; S_A: smectic A phase; N*: cholesteric phase; TGB_A: twist grain boundary phase; BP: blue phase; I: isotropic phase.

Table 3. Mesomorphism of compounds **13−15**

Compound	Y	X	Transition temperatures [°C][a]				
13c	OC_6H_{13}	F	C 154.5		N* 173.1	BP	2 × BP[b]
13f	$OC_{14}H_{29}$	F	C 128.1	S_A 183.6		I	2 × BP[b]
14c	OC_6H_{13}	CF_3	C 135.0		N* 196.0	I	2 × BP[b]
14f	$OC_{14}H_{29}$	CF_3	C 115.0	S_A 197.0		I	2 × BP[b]
15c	OC_6H_{13}	OCF_3	C 127.6		N* 203.2	I	BP[b]
15f	$OC_{14}H_{29}$	OCF_3	C 102.0	S_A 197.5		I	BP[b]

[a] C: crystalline phase; S_A: smectic A phase; N*: cholesteric phase; BP: blue phase; I: isotropic phase. − [b] Blue phase in contact with N4.

oxy-α-D-*erythro*-hex-2-enopyranoside in the presence of a nickel catalyst leads to the formation of the corresponding β-*C*-aryl-Δ^2-glycopyranosides, which are the key products for the synthesis of chiral trioxa- and trioxaboradecalins bearing various substituents in the *para* positions of the phenyl rings. These compounds show short pitch cholesterics, blue phases, TGB_A phases, and sign inversion of cholesterics depending on the substitution pattern. Work is in progress for the introduction of other heteroatoms and functionalities in the *para* position on the phenyl ring, in order to study their influences on the mesogenic properties of these compounds.

Experimental Section

General Remarks: All reactions were monitored by TLC (TLC plates GF_{254} Merck); detection was effected by Uv absorbance and spraying with a solution of ethanol-sulfuric acid (9:1), followed by heating. − Reactions involving organometallic catalysis were carried out in Schlenk tubes under an inert atmosphere. Tetrahydrofuran was distilled from sodium/benzophenone. − Column chromatography was performed on silica gel 60 (230−240 mesh, Merck). − Optical rotations were recorded using a Perkin−Elmer 241 polarimeter. − The NMR spectra (^1H: 200 or 400 MHz, ^{13}C: 50 or 100.6 MHz) were recorded on a Bruker AMX-200 or AMX-400 spectrometer with $SiMe_4$ as internal standard. − An Olympus BH optical polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to identify thermal transitions and characterize anisotropic textures. For further verification of the textures, a contact preparation with N4 (4-butyl-4′-methoxyazoxybenzene, K 16 N 76 I) was carried out. − Analysis by DSC was carried out on a Perkin−Elmer DSC7 instrument using heating and cooling rates of 5 K min^{-1}. − The following compounds were prepared according to literature procedures: *p*-*tert*-butylphenyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**2**),[5] *p*-alkoxybenzaldehyde dimethyl acetals,[8] phenylboronic acids,[9] [$NiCl_2$(dppe)],[10] and [$Rh(COD)_2$]PF_6.[11]

Standard Procedure for Nickel-Catalyzed Coupling Reaction: To a solution of the unsaturated carbohydrate **2** (223 mg, 0.44 mmol) and $NiCl_2$(dppe) (23 mg, 0.044 mmol) in 2 mL of THF was slowly added, at −30 °C, a solution of a Grignard reagent prepared from magnesium (64 mg, 2.6 mmol) and the appropriate bromide (2.18 mmol) in 5 mL of THF. The reaction was followed by TLC. After 24 h, diethyl ether (50 mL) was added, and the ethereal solution was washed with water (2 × 10 mL), and dried. After evaporation of the solvent under reduce pressure, the residue was purified by column chromatography using the indicated solvents as the eluent to give the corresponding C-glycoside **3**.

1-[5,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl]-4-chlorobenzene (3a): 124 mg, yield 60%; R_f = 0.5 (eluent: petroleum ether/dichloromethane, 10:3); $[\alpha]_D^{20}$ = +190.0 (c = 1, CH_2Cl_2). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.03 (s, 6 H, $SiCH_3$), 0.13 (s, 3 H, $SiCH_3$), 0.14 (s, 3 H, $SiCH_3$), 0.90 (s, 9 H, CH_3), 0.93 (s, 9 H, CH_3), 3.49 (ddd, J = 8.4, 4.4, 2.2 Hz, 1 H, H-5), 3.83 (dd, J = 11.4, 4.4 Hz, 1 H, H-6), 3.92 (dd, J = 11.4, 2.2 Hz, 1 H, H-6), 4.37 (dddd, J = 8.4, 3.0, 1.5, 1.5 Hz, 1 H, H-4), 5.13 (bs, 1 H, H-1), 5.71 (ddd, J = 10.2, 1.5, 1.5 Hz, 1 H, H-2), 5.80 (d,

J = 10.2, 1.5, 1.5 Hz, 1 H, H-3), 7.24−7.34 (m, 4 H, H_{arom}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −5.0 ($SiCH_3$), −4.9 ($SiCH_3$), −4.7 ($SiCH_3$), −4.2 ($SiCH_3$), 18.1 (CMe_3), 18.6 (CMe_3), 25.9 (CMe_3), 26.1 (CMe_3), 62.9 (C-6), 63.4 (C-4), 76.6 (C-5), 80.7 (C-1), 128.5, 128.6, 130.1, 130.4, 133.5, 140.0 (C-2, C-3, and C_{arom}). − $C_{24}H_{41}ClO_3Si_2$ (469.22): calcd. C 61.44, H 8.81; found C 61.55, H 8.92.

1-[5,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl]-4-fluorobenzene (3b): 79.6 mg, yield 40%; R_f = 0.2 (eluent: petroleum ether/dichloromethane, 5:1); $[\alpha]_D^{20}$ = +143.4 (c = 1.4, CH_2Cl_2). − ^1H NMR (200 MHz, $CDCl_3$): δ = −0.07 (s, 3 H, $SiCH_3$), −0.06 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.06 (s, 3 H, $SiCH_3$), 0.80 (s, 9 H, CH_3), 0.84 (s, 9 H, CH_3), 3.40 (ddd, J = 8.4, 4.3, 2.1 Hz, 1 H, H-5), 3.80 (dd, J = 11.5, 4.3 Hz, 1 H, H-6), 3.90 (dd, J = 11.5, 2.1 Hz, 1 H, H-6), 4.27 (dm, J = 8.4 Hz, 1 H, H-4), 5.04 (bs, 1 H, H-1), 5.71 (d, J = 10.2 Hz, 1 H, H-2), 5.78 (d, J = 10.2 Hz, 1 H, H-3), 7.25 (d, J = 8.7 Hz, 2 H, H_{arom}), 7.31 (d, J = 8.7 Hz, 2 H, H_{arom}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −5.0 ($SiCH_3$), −4.9 ($SiCH_3$), −4.7 ($SiCH_3$), −4.2 ($SiCH_3$), 18.1 (CMe_3), 18.6 (CMe_3), 25.9 (CMe_3), 26.1 (CMe_3), 62.9 (C-6), 63.5 (C-4), 76.5 (C-5), 80.7 (C-1), 115.2 (d, $^2J_{C-F}$ = 21.4 Hz), 128.8 (d, $^3J_{C-F}$ = 8.1 Hz), 130.2, 130.4, 137.2 (d, $^4J_{C-F}$ = 3.1 Hz), 160.0 (C-2, C-3 and C_{arom}). − $C_{24}H_{41}FO_3Si_2$ (452.75): calcd. C 63.39, H 9.05; found C 63.17, H 9.03.

1-[5,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl]-4-(trifluoromethyl)benzene (3c): 106 mg, yield 48%; R_f = 0.55 (eluent: petroleum ether/dichloromethane, 4:1); $[\alpha]_D^{20}$ = +145.0 (c = 0.5, $CHCl_3$). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.01 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$), 0.08 (s, 3 H, $SiCH_3$), 0.14 (s, 3 H, $SiCH_3$), 0.83 (s, 9 H, CH_3), 0.86 (s, 9 H, CH_3), 3.50 (ddd, J = 8.4, 4.1, 2.2 Hz, 1 H, H-5), 3.85 (dd, J = 11.4, 4.1 Hz, 1 H, H-6), 3.95 (dd, J = 11.4, 2.2 Hz, 1 H, H-6), 4.38 (dm, J = 8.4 Hz, 1 H, H-4), 5.21 (bs, 1 H, H-1), 5.71 (d, J = 10.2 Hz, 1 H, H-2), 5.80 (d, J = 10.2 Hz, 1 H, H-3), 7.46 (d, J = 8.2 Hz, 2 H, H_{arom}), 7.59 (d, J = 8.2 Hz, 2 H, H_{arom}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −5.1 ($SiCH_3$), −5.0 ($SiCH_3$), −4.7 ($SiCH_3$), −4.2 ($SiCH_3$), 18.1 (CMe_3), 18.5 (CMe_3), 25.9 (CMe_3), 26.0 (CMe_3), 62.8 (C-6), 63.3 (C-4), 76.6 (C-5), 80.6 (C-1), 128.5 (d, $^1J_{C-F}$ = 270.6 Hz, CF_3), 125.3 (d, $^3J_{C-F}$ = 3.8 Hz), 127.1, 129.7, 130.2, 130.6 and 145.3 (C-2, C-3 and C_{arom}). − MS (CI/NH_3): m/z = 520 [M + NH_4^+], 503 [M + H^+].

1-[5,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl]-4-(trifluoromethyloxy)benzene (3d): 118 mg, yield 52%; R_f = 0.6 (eluent: petroleum ether/dichloromethane, 4:1); $[\alpha]_D^{20}$ = +133.7 (c = 1.4, $CHCl_3$). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.04 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.14 (s, 3 H, $SiCH_3$), 0.15 (s, 3 H, $SiCH_3$), 0.90 (s, 9 H, CH_3), 0.93 (s, 9 H, CH_3), 3.47 (ddd, J = 8.2, 4.5, 1.8 Hz, 1 H, H-5), 3.84 (dd, J = 11.4, 4.5 Hz, 1 H, H-6), 3.92 (dd, J = 11.4, 1.8 Hz, 1 H, H-6), 4.37 (dm, J = 8.4 Hz, 1 H, H-4), 5.17 (bs, 1 H, H-1), 5.73 (d, J = 10.3 Hz, 1 H, H-2), 5.80 (d, J = 10.3 Hz, 1 H, H-3), 7.18 (d, J = 8.4 Hz, 2 H, H_{arom}), 7.47 (d, J = 8.4 Hz, 2 H, H_{arom}). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.2 ($SiCH_3$), −5.1 ($SiCH_3$), −4.8 ($SiCH_3$), −4.3 ($SiCH_3$), 18.0 (CMe_3), 18.4 (CMe_3), 25.8 (CMe_3), 25.9 (CMe_3), 62.7 (C-6), 63.3 (C-4), 76.4 (C-5), 80.6 (C-1), 120.5 (q, $^1J_{C-F}$ = 256.9 Hz, CF_3), 120.8, 128.8, 129.9, 130.3, 140.0 and 148.6 (C-2, C-3 and C_{arom}). − ^{19}F NMR (50 MHz, $CDCl_3$): δ = −58.4 (s). − MS (CI/NH_3): m/z = 536 [M + NH_4^+].

Standard Procedure for Preparation of Saturated *C*-Aryl Glycosides 4: The unsaturated *C*-aryl glycoside **3** (0.43 mmol) was stirred in THF (5 mL) at room temperature in the presence of tetrabutylammonium fluoride trihydrate (139 mg, 0.44 mmol). After 2 h, the solvent was evaporated and the crude residue treated with CH_2Cl_2 (25 mL) and H_2O (5 mL). Evaporation of the organic solvent gave quantitatively the crude diol. This crude diol was dissolved in ethanol (5 mL), and treated by molecular hydrogen at atmospheric pressure and room temperature in the presence of [Rh(COD)(dppb)]ClO_4 [dppb: 1,4-bis(diphenylphosphanyl)butane] (0.02 mmol). After 24 h, filtration of the solution and evaporation of the solvent gave a residue that was purified by column chromatography to afford the saturated *C*-aryl glycoside **4**.

4-Chloro-1-(2,3-dideoxy-β-D-*erythro*-hexopyranosyl)benzene (4a): 73 mg, yield 70%; R_f = 0.4 (eluent: petroleum ether/ethyl acetate, 1:3); $[\alpha]_D^{20}$ = +62.0 (c = 1.0, CH_2Cl_2). − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.59−1.76 (m, 2 H, H-2_{ax}, H-3_{ax}), 1.94 (m, 1 H, H-2_{eq}), 2.19−2.23 (m, 3 H, H-3_{eq}, OH), 3.41 (ddd, J = 9.2, 5.1, 4.6 Hz, 1 H, H-5), 3.69 (dm, J = 9.2 Hz, 1 H, H-4), 3.85 (dd, J = 11.7, 5.1 Hz, 1 H, H-6), 3.92 (dd, J = 11.7, 4.6 Hz, 1 H, H-6), 4.40 (bs, J = 10.7 Hz, 1 H, H-1), 7.23−7.64 (m, 4 H, H_{arom}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.5 and 32.9 (C-2 and C-3), 63.1 (C-6), 66.7 (C-4), 78.7 (C-5), 81.9 (C-1), 127.3, 128.5, 133.3 and 140.4 (C_{arom}). − $C_{12}H_{15}ClO_3$ (242.70): calcd. C 59.39, H 6.23; found C 59.19, H 6.15.

1-(2,3-Dideoxy-β-D-*erythro*-hexopyranosyl)-4-fluorobenzene (4b): 41 mg, yield 42%; R_f = 0.34 (eluent: petroleum ether/ethyl acetate, 1:4); $[\alpha]_D^{20}$ = +71.6 (c = 0.9, $CHCl_3$). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.57−1.78 (m, 2 H, H-2_{ax}, H-3_{ax}), 1.96 (m, 1 H, H-2_{eq}), 2.15−2.37 (m, 3 H, H-3_{eq}, OH), 3.41 (ddd, J = 9.2, 5.1, 4.4 Hz, 1 H, H-5), 3.70 (bd, J = 9.2 Hz, 1 H, H-4), 3.84 (dd, J = 11.4, 5.1 Hz, 1 H, H-6), 3.92 (dd, J = 11.4, 4.4 Hz, 1 H, H-6), 4.41 (dd, J = 10.7, 2.1 Hz, 1 H, H-1), 7.03 (d, J = 8.4 Hz, 2 H, H_{arom}), 7.29 (d, J = 8.4 Hz, 2 H, H_{arom}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.7 and 33.0 (C-2 and C-3), 63.4 (C-6), 67.2 (C-4), 78.8 (C-5), 81.9 (C-1), 115.2 (d, $^2J_{C-F}$ = 21.3 Hz), 129.2 (d, $^3J_{C-F}$ = 8.3 Hz), 137.7 (d, $^4J_{C-F}$ = 2.6 Hz) and 162.2 (d, $^1J_{C-F}$ = 245.6 Hz) (C_{arom}). − $C_{12}H_{15}FO_3$ (226.25): calcd. C 63.70, H 6.68; found C 63.60, H 6.75.

1-(2,3-Dideoxy-β-D-*erythro*-hexopyranosyl)-4-(trifluoromethyl)benzene (4c): 63 mg, yield 53%; R_f = 0.46 (eluent: petroleum ether/ethyl acetate, 1:4); $[\alpha]_D^{20}$ = +55.5 (c = 1.0, $CHCl_3$). − ^1H NMR (200 MHz, CD_3OH): δ = 1.60−1.79 (m, 2 H, H-2_{ax}, H-3_{ax}), 1.92−2.09 (m, 3 H, H-2_{eq}, OH), 2.27 (m, 1 H, H-3_{eq}), 3.44 (ddd, J = 9.2, 4.7, 4.6 Hz, 1 H, H-5), 3.75 (m, 1 H, H-4), 3.88 (dd, J = 11.5, 4.7 Hz, 1 H, H-6), 3.96 (dd, J = 11.5, 4.6 Hz, 1 H, H-6), 4.49 (bd, J = 10.1 Hz, 1 H, H-1), 7.46 (d, J = 8.3 Hz, 2H, H_{arom}), 7.61 (d, J = 8.3 Hz, 2 H, H_{arom}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 35.5 and 36.2 (C-2 and C-3), 65.2 (C-6), 68.7 (C-4), 81.3 (C-5), 86.1 (C-1), 127.0 (q, $^1J_{C-F}$ = 271.1 Hz, CF_3), 127.6 (q, $^3J_{C-F}$ = 3.9 Hz), 129.1, 132.0 (q, $^2J_{C-F}$ = 32.1 Hz) and 150.0 (C_{arom}). − $C_{13}H_{15}F_3O_3$ (276.26): calcd. C 56.52, H 5.47; found C 56.49, H 5.55.

1-(2,3-Dideoxy-β-D-*erythro*-hexopyranosyl)-4-(trifluoromethyloxy)benzene (4d): 37.7 mg, yield 30%; R_f = 0.36 (eluent: petroleum ether/ethyl acetate, 1:4); $[\alpha]_D^{20}$ = +48.5 (c = 1.2, $CHCl_3$). − ^1H NMR (200 MHz, CD_3OH): δ = 1.57−1.72 (m, 2 H, H-2_{ax}, H-3_{ax}), 1.99 (m, 1 H, H-2_{eq}), 2.12−2.31 (m, 3 H, H-3_{eq}, OH), 3.42 (ddd, J = 9.2, 4.8, 4.4 Hz, 1 H, H-5), 3.69 (dm, J = 9.2 Hz, 1 H, H-4), 3.84 (dd, J = 11.45, 4.8 Hz, 1 H, H-6), 3.94 (dd, J = 11.4, 4.4 Hz, 1 H, H-6), 4.44 (dd, J = 10.5, 2.3 Hz, 1 H, H-1), 7.22 (d, J = 8.5 Hz, 2H, H_{arom}), 7.36 (d, J = 8.5 Hz, 2 H, H_{arom}). − ^{13}C NMR (50 MHz, CD_3OD): δ = 35.5 and 36.1 (C-2 and C-3), 65.3 (C-6), 68.8 (C-4), 81.3 (C-5), 86.1 (C-1), 123.6 (q, $^1J_{C-F}$ = 255.5 Hz, CF_3), 123.1, 130.3, 144.7 and 151.2 (C_{arom}). − ^{19}F NMR (50 MHz,

$CDCl_3$): δ = −58.4 (s). − $C_{13}H_{15}F_3O_4$ (292.26): calcd. C 53.43, H 5.17; found C 53.32, H 5.00.

Standard Procedure for Preparation of Compounds 5−8: A flask containing of the diol **4** (0.16 mmol), 4-alkyloxybenzaldehyde dimethylacetal (0.20 mmol), and *p*-toluenesulfonic acid monohydrate (5.0 mg), dissolved in 5 mL of *N,N*-dimethylformamide, was connected to a rotary evaporator. The mixture was heated at reduced pressure (30 mbar) in a water-bath at 60 °C, until TLC revealed complete reaction. The solvent was removed in vacuo (10 hPA) at 75 °C. The solid residue was washed with a saturated solution of sodium hydrogen carbonate, filtered, washed with water and cold ethanol, and then recrystallized from ethanol to afford compounds **5−8**.

(1*S*,3*R*,6*R*,8*R*)-8-(4′-Chlorophenyl)-3-(4′′-methyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (5a): 28.8 mg, yield 50%; m.p. 190.3 °C; $[\alpha]_D^{20}$ = +43.0 (*c* = 0.1, CH_2Cl_2). − ^{1}H NMR (400 MHz, C_6D_6): δ = 1.33 (m, 1 H, H-9_{ax}), 1.47 (dddd, *J* = 13.7, 4.1, 3.1, 2.3 Hz, 1 H, H-9_{eq}), 1.61 (dddd, *J* = 12.2, 12.2, 11.5, 4.1 Hz, 1 H, H-10_{ax}), 1.92 (dddd, *J* = 11.7, 4.6, 4.1, 3.1 Hz, 1 H, H-10_{eq}), 3.26 (s, 3 H, CH_3), 3.30 (ddd, *J* = 11.5, 8.7, 4.1 Hz, 1 H, H-1), 3.42 (ddd, *J* = 10.2, 8.7, 5.1 Hz, 1 H, H-6), 3.65 (dd, *J* = 10.2, 10.2 Hz, 1 H, H-5_{ax}), 3.98 (dd, *J* = 11.4, 2.3 Hz, 1 H, H-8), 4.28 (dd, *J* = 10.2, 5.1 Hz, 1 H, H-5_{eq}), 5.50 (s, 1 H, H-3), 6.85 (d, *J* = 8.7 Hz, 2 H, H_{arom}), 6.95 (d, *J* = 8.1 Hz, 2 H, H_{arom}), 7.15 (d, *J* = 8.1 Hz, 2 H, H_{arom}), 7.65 (d, *J* = 8.7 Hz, 2 H, H_{arom}). − ^{13}C NMR (100 MHz, C_6D_6): δ = 29.4 and 33.5 (C-9 and C-10), 54.7 (CH_3), 69.5 (C-5), 74.3 (C-1), 78.1 (C-6), 78.6 (C-8), 102.0 (C-3), 113.7, 127.2, 127.9, 128.3, 128.5, 131.1 and 141.0 (C_{arom}). − $C_{20}H_{21}ClO_4$ (360.84): calcd. C 66.57, H 5.87; found C 66.08, H 5.85.

(1*S*,3*R*,6*R*,8*R*)-8-(4′-Fluorophenyl)-3-(4′′-methyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (6a): 35.8 mg, yield 65%; m.p. 181.2 °C; $[\alpha]_D^{20}$ = +45.7 (*c* = 0.6, $CHCl_3$). − ^{1}H NMR (400 MHz, C_6D_6): δ = 1.38 (m, 1 H, H-9_{ax}), 1.50 (m, 1 H, H-9_{eq}), 1.63 (dddd, *J* = 12.7, 12.2, 11.2, 4.1 Hz, 1 H, H-10_{ax}), 1.95 (dddd, *J* = 12.2, 5.1, 4.1, 3.1 Hz, 1 H, H-10_{eq}), 3.26 (s, 3 H, CH_3), 3.32 (m, 1 H, H-1), 3.44 (ddd, *J* = 10.2, 9.2, 4.6 Hz, 1 H, H-6), 3.67 (dd, *J* = 10.2, 10.2 Hz, 1 H, H-5_{ax}), 4.03 (dd, *J* = 10.7, 2.2 Hz, 1 H, H-8), 4.28 (dd, *J* = 10.2, 4.6 Hz, 1 H, H-5_{eq}), 5.50 (s, 1 H, H-3), 6.80- 6.87 (m, 4 H, H_{arom}), 7.01 (dd, *J* = 8.1, 5.6 Hz, 2 H, H′$_{arom}$), 7.64 (d, *J* = 8.6 Hz, 2 H, H′′$_{arom}$). − ^{13}C NMR (50 MHz, C_6D_6): δ = 29.6 and 33.8 (C-9 and C-10), 54.9 (CH_3), 69.8 (C-5), 74.6 (C-1), 78.4 (C-6), 79.0 (C-8), 102.2 (C-3), 113.9, 115.3 (d, $^2J_{C-F}$ = 21.4 Hz), 128.0 (d, $^3J_{C-F}$ = 8.1 Hz), 128.2, 131.4, 138.5 (d, $^4J_{C-F}$ = 3.0 Hz), 160.6 and 162.8 (d, $^1J_{C-F}$ = 245 Hz) (C_{arom}). − $C_{20}H_{21}FO_4$ (344.39): calcd. C 69.75, H 6.15; found C 69.19, H 6.15.

(1*S*,3*R*,6*R*,8*R*)-3-(4′′-Methyloxyphenyl)-8-[4′-(trifluoromethyl)phenyl]-2,4,7-trioxabicyclo[4.4.0]decane (7a): 27.7 mg, yield 44%; m.p. 201.8 °C; $[\alpha]_D^{20}$ = +36.7 (*c* = 0.4, $CHCl_3$). − ^{1}H NMR (400 MHz, C_6D_6): δ = 1.31 (m, 1 H, H-9_{ax}), 1.47 (dddd, *J* = 13.7, 3.6, 3.1, 2.1 Hz, 1 H, H-9_{eq}), 1.61 (dddd, *J* = 12.7, 12.2, 11.7, 3.6 Hz, 1 H, H-10_{ax}), 1.92 (dddd, *J* = 12.2, 4.1, 4.6, 3.1 Hz, 1 H, H-10_{eq}), 3.27 (s, 3 H, CH_3), 3.29 (m, 1 H, H-1), 3.41 (ddd, *J* = 10.2, 9.2, 4.6 Hz, 1 H, H-6), 3.65 (dd, *J* = 10.2, 10.2 Hz, 1 H, H-5_{ax}), 4.00 (dd, *J* = 11.2, 2.1 Hz, 1 H, H-8), 4.28 (dd, *J* = 10.2, 4.6 Hz, 1 H, H-5_{eq}), 5.50 (s, 1 H, H-3), 6.84 (d, *J* = 8.6 Hz, H_{arom}), 6.90 (d, *J* = 8.1 Hz, 2 H, H_{arom}), 7.01 (d, *J* = 8.1 Hz, 2 H, H_{arom}), 7.64 (d, *J* = 8.6 Hz, 2 H, H_{arom}). − ^{13}C NMR (50 MHz, C_6D_6): δ = 29.7 and 33.8 (C-9 and C-10), 55.0 (CH_3), 69.8 (C-5), 74.6 (C-1), 78.3 (C-6), 78.9 (C-8), 102.4 (C-3), 114.1, 125.6 (q, $^3J_{C-F}$ = 4.1 Hz), 126.5, 128.3, 131.4, 138.3, 146.7 and 160.9 (C_{arom}). − $C_{21}H_{20}F_3O_4$ (393.39): calcd. C 63.90, H 5.37; found C 63.67, H 5.42.

(1*S*,3*R*,6*R*,8*R*)-3-(4′′-Methyloxyphenyl)-8-[4′-(trifluoromethyloxy)phenyl]-2,4,7-trioxabicyclo[4.4.0]decane (8a): 34.8 mg, yield 53%; m.p. 179.0 °C; $[\alpha]_D^{20}$ = +29.9 (*c* = 1.3, $CHCl_3$). − ^{1}H NMR (400 MHz, C_6D_6): δ = 1.33 (dddd, *J* = 13.7, 13.2, 11.7, 4.1 Hz, 1 H, H-9_{ax}), 1.47 (dddd, *J* = 13.7, 4.1, 3.1, 2.5 Hz, 1 H, H-9_{eq}), 1.61 (dddd, *J* = 13.2, 12.2, 11.2, 4.1 Hz, 1 H, H-10_{ax}), 1.92 (dddd, *J* = 12.2, 4.6, 4.1, 3.1 Hz, 1 H, H-10_{eq}), 3.26 (s, 3 H, CH_3), 3.30 (m, 1 H, H-1), 3.42 (ddd, *J* = 10.2, 9.2, 4.6 Hz, 1 H, H-6), 3.65 (dd, *J* = 10.2, 10.2 Hz, 1 H, H-5_{ax}), 3.99 (dd, *J* = 11.2, 2.1 Hz, 1 H, H-8), 4.28 (dd, *J* = 10.2, 4.6 Hz, 1 H, H-5_{eq}), 5.50 (s, 1 H, H-3), 6.84 (d, *J* = 8.6 Hz, H_{arom}), 6.96 (d, *J* = 8.6 Hz, 2 H, H_{arom}), 6.99 (d, *J* = 8.6 Hz, 2 H, H_{arom}), 7.65 (d, *J* = 8.6 Hz, 2 H, H_{arom}). − ^{13}C NMR (50 MHz, C_6D_6): δ = 29.7 and 33.8 (C-9 and C-10), 55.0 (CH_3), 69.8 (C-5), 74.6 (C-1), 78.4 (C-6), 78.9 (C-8), 102.3 (C-3), 121.5 (q, $^3J_{C-F}$ = 246 Hz, CF_3), 114.1, 121.5, 127.7, 128.3, 131.5, 141.6, 148.9 and 160.8 (C_{arom}). − $C_{21}H_{21}F_3O_5$ (410.39): calcd. C 61.46, H 5.16; found C 61.78, H 5.21.

Standard Procedure for Preparation of Compounds 9−12: A solution of **4** (0.16 mmol) and 4-alkyloxyphenyl boronic acid (0.20 mmol) in 5 mL toluene was stirred at 45 °C under 60 mbar. The water produced in the reaction was co-evaporated three times with 5 mL of toluene. The remaining crystalline solid was recrystallized from ethanol to give compounds **9−12**.

(1*S*,6*R*,8*R*)-8-(4′-Chlorophenyl)-3-(4′′-methyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (9a): 28.7 mg, yield 50%; m.p. 170.6 °C; $[\alpha]_D^{20}$ = +42.0 (*c* = 0.1, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71−1.83 (m, 2 H, H-9_{ax}, H-9_{eq}), 2.05 (m, 1 H, H-10_{ax}), 2.38 (m, 1 H, H-10_{eq}), 3.62 (ddd, *J* = 10.2, 9.2, 5.1 Hz, 1 H, H-6), 3.82 (s, 3 H, CH_3), 3.88 (ddd, *J* = 10.9, 9.2, 4.3 Hz, 1 H, H-1), 3.96 (dd, *J* = 10.2, 10.2 Hz, 1 H, H-5), 4.25 (dd, *J* = 10.2, 5.1 Hz, 1 H, H-5), 4.51 (dd, *J* = 10.9, 2.3 Hz, 1 H, H-8), 6.88 (d, *J* = 8.7 Hz, 2 H, H_{arom}), 7.25−7.36 (m, 4 H, H_{arom}), 7.75 (d, *J* = 8.7 Hz, 2 H, H_{arom}). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.0 and 33.1 (C-9 and C-10), 55.1 (CH_3), 64.7 (C-5), 71.4 (C-1), 76.0 (C-6), 79.3 (C-8), 113.2, 127.3, 128.6, 133.5, 135.8, 140.0 and 161.9 (C_{arom}). − $C_{19}H_{20}BClO_4$ (358.63): calcd. C 63.63, H 5.62; found C 63.52, H 5.61.

(1*S*,6*R*,8*R*)-8-(4′-Fluorophenyl)-3-(4′′-methyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (10a): 37.2 mg, yield 68%; m.p. 156.0 °C; $[\alpha]_D^{20}$ = +21.3 (*c* = 1.1, $CHCl_3$). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72−1.86 (m, 2 H, H-9_{ax}, H-9_{eq}), 2.05 (dddd, *J* = 12.7, 11.7, 10.7, 4.1 Hz, 1 H, H-10_{ax}), 2.38 (dddd, *J* = 11.7, 4.6, 4.1, 3.1 Hz, 1 H, H-10_{eq}), 3.63 (ddd, *J* = 10.2, 9.2, 5.6 Hz, 1 H, H-6), 3.83 (s, 3 H, CH_3), 3.88 (ddd, *J* = 10.7, 9.2, 4.6 Hz, 1 H, H-1), 3.96 (dd, *J* = 10.2, 10.2 Hz, 1 H, H-5), 4.25 (dd, *J* = 10.2, 5.6 Hz, 1 H, H-5), 4.52 (dd, *J* = 10.7, 2.0 Hz, 1 H, H-8), 6.88 (d, *J* = 8.6 Hz, 2 H, H′′$_{arom}$), 7.03 (dd, J = 8.6, 8.6 Hz, 2 H, H′$_{arom}$), 7.33 (dd, J = 8.6, 5.1 Hz, 2 H, H′$_{arom}$), 7.75 (d, *J* = 8.6 Hz, 2 H, H′′$_{arom}$). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.0 and 33.1 (C-9 and C-10), 55.1 (CH_3), 64.8 (C-5), 71.4 (C-1), 76.0 (C-6), 79.4 (C-8), 115.2 (d, $^2J_{C-F}$ = 21.4 Hz), 127.6 (d, $^3J_{C-F}$ = 8.1 Hz), 135.7, 137.3 (d, $^4J_{C-F}$ = 3.6 Hz), 161.6 and 162.4 (d, $^1J_{C-F}$ = 246 Hz) (C_{arom}). − $C_{19}H_{20}BFO_4$ (342.18): calcd. C 66.69, H 5.89; found C 66.21, H 5.78.

(1*S*,6*R*,8*R*)-3-(4′′-methyloxyphenyl)-8-[4′-(trifluoromethylphenyl]-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (11a): 43.9 mg, yield 70%; m.p. 178.3 °C; $[\alpha]_D^{20}$ = +35.4 (*c* = 0.6, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75−1.83 (m, 2 H, H-9_{ax}, H-9_{eq}), 2.10 (dddd, *J* = 12.2, 11.7, 10.7, 4.1 Hz, 1 H, H-10_{ax}), 2.40 (dddd, *J* = 11.7, 4.5, 4.1, 3.1 Hz, 1 H, H-10_{eq}), 3.64 (ddd, *J* = 10.2, 9.1, 5.1 Hz, 1 H, H-6), 3.83 (s, 3 H, CH_3), 3.90 (ddd, *J* = 10.7, 9.1, 4.5 Hz, 1 H,

H-1), 3.99 (dd, J = 10.2, 10.2 Hz, 1 H, H-5), 4.27 (dd, J = 10.2, 5.1 Hz, 1 H, H-5), 4.61 (dd, J = 10.2, 2.0 Hz, 1 H, H-8), 6.88 (d, J = 8.6 Hz, 2 H, H_{arom}), 7.47 (d, J = 8.1 Hz, 2 H, H_{arom}), 7.61 (d, J = 8.1 Hz, 2 H, H_{arom}), 7.75 (d, J = 8.6 Hz, 2 H, H_{arom}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.0 and 33.2 (C-9 and C-10), 55.1 (CH_3), 64.7 (C-5), 71.3 (C-1), 76.0 (C-6), 79.2 (C-8), 113.2, 125.4 (q, $^3J_{C-F}$ = 3.6 Hz), 126.1, 130.0 (q, $^2J_{C-F}$ = 32.8 Hz), 135.8, 145.5 and 162.0 (C_{arom}). − $C_{20}H_{20}BF_3O_4$ (392.16): calcd. C 61.25, H 5.14; found C 61.34, H 5.17.

(1*S*,6*R*,8*R*)-3-(4′′-methyloxyphenyl)-8-[4′-(trifluoromethyloxy)phenyl]-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (12a): 54.2 mg, yield 83%; m.p. 164.7 °C; $[\alpha]_D^{20}$ = +27.5 (c = 1, $CHCl_3$). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72−1.85 (m, 2 H, H-9_{ax}, H-9_{eq}), 2.07 (dddd, J = 12.7, 12.2, 11.7, 2.6 Hz, 1 H, H-10_{ax}), 2.39 (dddd, J = 11.7, 4.6, 4.1, 3.1 Hz, 1 H, H-10_{eq}), 3.63 (ddd, J = 10.2, 9.2, 5.1 Hz, 1 H, H-6), 3.82 (s, 3 H, CH_3), 3.88 (ddd, J = 12.7, 9.2, 4.6 Hz, 1 H, H-1), 3.97 (dd, J = 10.2, 10.2 Hz, 1 H, H-5), 4.26 (dd, J = 10.2, 5.1 Hz, 1 H, H-5), 4.61 (dd, J = 10.7, 2.1 Hz, 1 H, H-8), 6.88 (d, J = 8.6 Hz, 2 H, H_{arom}), 7.19 (d, J = 8.6 Hz, 2 H, H_{arom}), 7.38 (d, J = 8.6 Hz, 2 H, H_{arom}), 7.75 (d, J = 8.6 Hz, 2 H, H_{arom}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.0 and 33.1 (C-9 and C-10), 55.1 (CH_3), 64.8 (C-5), 71.4 (C-1), 76.0 (C-6), 79.2 (C-8), 113.2, 120.5 (q, $^1J_{C-F}$ = 257 Hz, OCF_3), 121.0, 127.3, 135.8, 140.2, 148.7 and 162.0 (C_{arom}). − $C_{20}H_{20}BF_3O_5$ (408.18): calcd. C 58.85, H 4.94; found C 58.52, H 4.94.

Standard Procedure for Preparation of Esters 13−15: A solution of 4-(4-alkyloxybenzoyloxy)benzoic acid (1 mmol), *N,N′*-dicyclohexylcarbodiimide (1.1 mmol), the diol **4** (0.5 mmol), and 4-dimethylaminopyridine (0.05 mmol), in dichloromethane (5 mL) was allowed to stand at 25 °C until esterification was complete. After filtration of the *n,n′*-dicyclohexylurea and concentration of the filtrate, the residue was purified by column chromatography to give compounds **13−15**.

1-{4′,6′-di-*o*-[4′′-(4-hexyloxybenzoyloxy)benzoyl]-2′,3′-dideoxy-β-D-*erythro*-hexopyranosyl}-4-fluorobenzene (13c): 232 mg, yield 53%; m.p. 154.5 °C; $[\alpha]_D^{20}$ = +55.9 (c = 0.8, $CHCl_3$). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.1 Hz, 6 H, CH_3), 1.31−1.41 (m, 8 H, CH_2′′), 1.45−1.53 (m, 4 H, CH_2′′), 1.78−1.90 (m, 6 H, CH_2′′, H-2′$_{ax}$, H-2′$_{eq}$), 2.07 (m, 1 H, H-3′$_{ax}$), 2.51 (m, 1 H, H-3′$_{eq}$), 4.00−4.12 (t, m, 5 H, OCH_2, H-5′), 4.49 (dd, J = 12.2, 5.1 Hz, 1 H, H-6′), 4.54 (bd, J = 8.6 Hz, 1 H, H-1′), 4.67 (dd, J = 12.2, 3.0 Hz, 1 H, H-6′), 5.18 (m, 1 H, H-4′), 6.94 (d, J = 8.6 Hz, 4 H, H_{arom}), 7.04 (dd, J = 8.6, 8.6 Hz, 2 H, H_{arom}), 7.22 (d, J = 8.6 Hz, 2 H, H_{arom}), 7.27 (dd, J = 8.6, 6.6 Hz, 2 H, H_{arom}), 7.35 (d, J = 8.6 Hz, 2 H, H_{arom}), 8.04 (d, J = 8.6 Hz, 4 H, H_{arom}), 8.08 (d, J = 8.6 Hz, 4 H, H_{arom}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 25.7, 29.1, 29.8, 31.6 and 32.8 (CH_2′′, C-2′ and C-3′), 64.7 (C-6′), 68.4 (OCH_2′′), 69.4 (C-4′), 77.7 (C-5′), 78.9 (C-1′), 114.4, 115.2 (d, $^2J_{C-F}$ = 20.6 Hz), 121.1, 121.8, 122.0, 127.2, 127.3, 127.5 (d, $^3J_{C-F}$ = 8.6 Hz), 131.3, 131.4, 137.3 (d, $^4J_{C-F}$ = 3.6 Hz), 154.9, 155.1 and 162.2 (d, $^1J_{C-F}$ = 246 Hz) (C_{arom}), 163.7, 164.3, 164.9 and 165.7 (CO). − $C_{52}H_{55}FO_{11}$ (875.30): calcd. C 71.38, H 6.34; found C 71.56, H 6.36.

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[1] J. W. Goodby, *J. Mater. Chem.* **1991**, *1*, 307−318.
[2] V. Vill, *LiqCryst 3.3 − Database of Liquid Crystals*, LCI Publisher, Hamburg, **1999**.
[3] [3a] V. Vill, H.-W. Tunger, H. Stegemeyer, K. Diekmann, *Tetrahedron: Asymmetry* **1994**, *5*, 2443−2446. − [3b] V. Vill, H.-W. Tunger, *Liebigs Ann.* **1995**, 1055−1059. − [3c] V. Vill, H.-W. Tunger, *J. Chem. Soc., Chem. Commun.* **1995**, 1047−1048. − [3d] V. Vill, H.-W. Tunger, *Liq. Cryst.* **1996**, *20*, 449−452. − [3e] V. Vill, H.-W. Tunger, H. M. von Minden, *J. Mater. Chem.* **1996**, *6*, 739−745. − [3f] V. Vill, H.-W. Tunger, D. Peters, *Liq. Cryst.* **1996**, *20*, 547−552. − [3g] V. Vill, H. M. von Minden, D. W. Bruce, *J. Mater. Chem.* **1997**, *7*, 893−899.
[4] [4a] M. Hein, R. Miethchen, *Eur. J. Org. Chem*. **1999**, 2429−2432. − [4b] M. Hein, R. Miethchen, D. Schwäbisch, C. Schick, *Liq. Cryst*. **2000**, *27*, 163−168.
[5] C. Moineau, V. Bolitt, D. Sinou, *J. Org. Chem.* **1998**, *63*, 582−591.
[6] J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak, J. S. Patel, *Nature* **1989**, *337*, 449−452.
[7] D. Coates, G. W. Gray, *Phys. Lett. A* **1973**, *45*, 115−116.
[8] L. Claisen, *Justus Liebigs Ann. Chem*. **1919**, *418*, 69−97.
[9] [9a] J. R. Leebrick, H. E. Ramsden, *J. Org. Chem*. **1958**, *23*, 935−936. − [9b] R. L. Letsinger, S. B. Hamilton, *J. Am. Chem. Soc*. **1959**, *81*, 3009−3012.
[10] L. M. Venanzi, *J. Chem. Soc.* **1958**, 719−724.
[11] M. Green, T. A. Kuc, S. H. Taylor, *J. Chem. Soc., A* **1971**, 2334−2337.

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