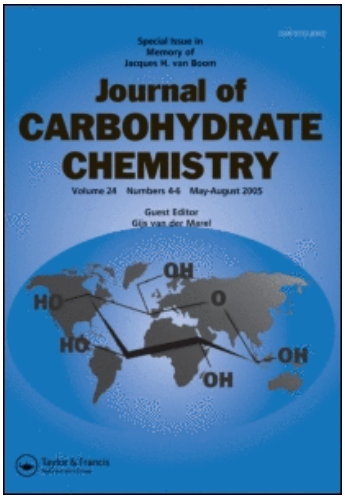



## Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

# Enantiopure Trioxadecalin Derived Liquid Crystals: Influence of the Nature of the Phenyl Substituent on the Mesogenic Properties

Bruno Bertini[a]; Monique Perrin[b]; Denis Sinou[a]; Alain Thozet[b]; Volkmar Vill[c]
[a] Laboratoire de Synthèse Asymétrique, associé au CNRS, CPE Lyon, Université Claude Bernard Lyon 1, Villeurbanne cédex, France [b] Laboratoire de Cristallographie, associé au CNRS, Université Claude Bernard Lyon 1, Villeurbanne cédex, France [c] Institute of Organic Chemistry, University of Hamburg, Hamburg, Germany

Online publication date: 12 November 2003

**To cite this Article** Bertini, Bruno , Perrin, Monique , Sinou, Denis , Thozet, Alain and Vill, Volkmar(2003) 'Enantiopure Trioxadecalin Derived Liquid Crystals: Influence of the Nature of the Phenyl Substituent on the Mesogenic Properties ', Journal of Carbohydrate Chemistry, 22: 7, 685 — 703
**To link to this Article: DOI:** 10.1081/CAR-120026468
**URL:** http://dx.doi.org/10.1081/CAR-120026468

JOURNAL OF CARBOHYDRATE CHEMISTRY
Vol. 22, Nos. 7 & 8, pp. 685–703, 2003

# Enantiopure Trioxadecalin Derived Liquid Crystals: Influence of the Nature of the Phenyl Substituent on the Mesogenic Properties†

**Bruno Bertini,[1] Monique Perrin,[2] Denis Sinou,[1,*] Alain Thozet,[2] and Volkmar Vill[3]**

[1]Laboratoire de Synthèse Asymétrique and [2]Laboratoire de Cristallographie, associé au CNRS, Université Claude Bernard Lyon 1, Villeurbanne cédex, France
[3]Institute of Organic Chemistry, University of Hamburg, Hamburg, Germany



## ABSTRACT

Reaction of pseudo-glucal **1** with Grignard reagents derived from 1-bromo-4-(trimethylsilyloxy)benzene, 1-bromo-4-methoxybenzene, 1-bromo-4-methoxymethoxybenzene, 1-bromo-4-dimethylaminobenzene, in the presence of a catalytic amount of $NiCl_2$(dppe), gives the corresponding unsaturated β-*C*-aryl glycosides **2**. Desilylation and hydrogenation of **2** leads to β-*C*-aryl glycosides **4**, which can be used as chiral precursor compounds in the synthesis of chiral liquid crystals. Combination of **4** with arylaldehydes leads to compounds **5–7**, whereas reaction with *p*-alkoxysubstituted phenylboronic acids gives the trioxaboradecalins **8–11**. The

†This paper is dedicated to Professor Gérard Descotes on the occasion of his 70th birthday.

*Correspondence: Denis Sinou, Laboratoire de Synthèse Asymétrique, associé au CNRS, CPE Lyon, Université Claude Bernard Lyon 1, 43, boulevard du 11 novembre 1918, 69622 Villeurbanne cédex, France; Fax: 33 4 78 89 89 14; E-mail: sinou@univ-lyon1.fr.



DOI: 10.1081/CAR-120026468
0732-8303 (Print); 1532-2327 (Online)




MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

mesogenic properties of these compounds are strongly influenced by the nature of the substituent on the phenyl ring in the molecule.

*Key Words:* *C*-Glycosides; Trioxadecalins; Trioxaboradecalins; Liquid crystals; Chirality.

## INTRODUCTION

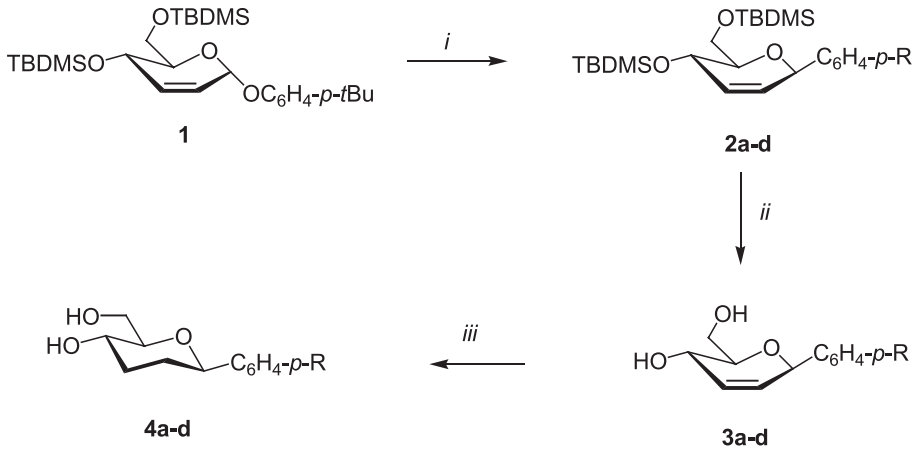
Chirality has become one of the most important and complex topics in liquid crystal research during the last decade.[1] Effectively, molecular asymmetry imparts form chirality to the liquid crystalline phases; in addition possible new technical applications for chiral liquid crystals can be found. Today, 16,000 of the 80,000 mesogenic known compounds are chiral,[2] most of them having a stereogenic center in the flexible wing, which induces chirality by steric hindrance and disturbs the mesogenic order.

Previously, V. Vill and coworkers prepared new liquid crystals bearing a chiral trioxadecalin core.[3–9] These compounds exhibited interesting chiral effects such as cholesteric helix inversion, double inversion of the helical twist sense, and re-entrant TGBA phases. All the studied substrates had the alkoxy chain directly bound to the *para* position of the phenyl ring linked to the pyranosyl moiety. We recently published the synthesis of a homologous series of trioxadecalin derivatives bearing a terminal halogen or trifluoromethyl group on the *para* position on this aromatic ring, and alkoxy substituents on the *para* position of the phenyl ring directly linked to the dioxolane moiety, and examined the influence of these substituents on the mesogenic properties of these compounds.[10] In the continuation of this work, we present in this paper the synthesis and the mesogenic properties of analogs bearing a hydroxy, a methoxy, a methoxymethoxy, or a dimethylamino group on the *para* position of the phenyl ring.

## RESULTS AND DISCUSSION

The preparation of the building blocks **4,** used as starting materials in the synthesis of the new liquid crystals bearing a chiral trioxadecalin system, is described in Scheme 1.

The reaction of the Grignard reagents prepared from 1-bromo-4-(trimethylsilyloxy)benzene, 1-bromo-4-methoxybenzene, 1-bromo-4-methoxymethoxybenzene, or 1-bromo-4-dimethylaminobenzene, with *p-tert*-butylphenyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1**)[11] in the presence of a catalytic amount of $NiCl_2$(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane] in tetrahydrofuran at −40°C gave regio- and stereospecifically the corresponding β-*C*-arylglycosides **2a**, **2b**, **2c**, and **2d**, in 48%, 51%, 80%, and 80% yield, respectively. It is to be noted that cleavage of the trimethysilyl group observed in the preparation of **2a** occurred readily during the aqueous treatment as well as upon purification by column chromatography. Desilylation of compounds **2a–d** was mediated by hydrated tetrabutylammonium fluoride in tetrahydrofuran to give the unsaturated diols **3a**, **3b**, **3c**, and **3d**, in 80%, 80%, 90%, and 80% yield, respectively. Hydrogenation of diols **3a–d** at atmospheric pressure in ethanol in the presence of the catalyst [Rh(COD)(dppb)]$ClO_4$ [COD: 1,5-cyclooctadiene; dppb:1,4-bis(diphenylphosphino)butane] gave the corresponding



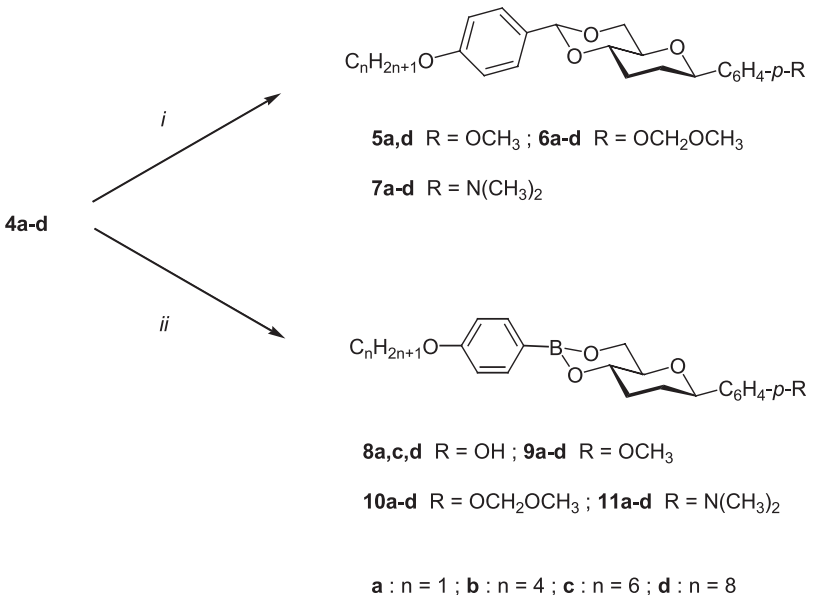

**a** R = OH ; **b** R = $OCH_3$ ; **c** R = $OCH_2OCH_3$ ; **d** R = $N(CH_3)_2$

***Scheme 1.*** Synthesis of building blocks **4**. Reagents and conditions: *i:* $BrMgC_6H_4$-*p*-R, $NiCl_2$(dppe), THF; *ii:* $Bu_4NF$, THF, 25°C; *iii:* $H_2$, [Rh(COD)(dppb)]$ClO_4$, EtOH.

saturated diols **4a**, **4b**, **4c**, and **4d**, in 65%, 60%, 60%, and 83% yield after column chromatography, respectively. $^1$H NMR data confirmed the β configuration of compounds **4a–d** as expected from previous work in this field.[11] Indeed for these compounds, a large diaxial coupling constant was observed between H-1 and H-2ax ($^3J_{1,2ax}$ = 10.2, 8.2, 10.4, and 11.0 Hz for **4a**, **4b**, **4c**, and **4d**, respectively), together with a small coupling constant $^3J_{1,2eq}$ between H-1 and H-2eq ($^3J_{1,2eq}$ = 2.1, 2.3, 2.2, and 2.2 Hz for **4a**, **4b**, **4c**, and **4d**, respectively). The conversion of diols **4a–d** to trioxadecalins **5–7** was carried out with the corresponding dimethyl acetals of 4-alkoxybenzaldehyde based on an acid-catalyzed transacetalization reaction, the methanol formed being distilled off to shift the equilibrium of the reaction (Scheme 2). On the other hand, the boronic acid derivatives **8–11** were easily obtained from diols **4a–d** and the appropriate arylboronic acid, the water formed being removed by azeotropic co-evaporation with toluene (Scheme 2). All the products were recrystallized from ethanol.

The mesomorphic properties of compounds **5–7** are summarized in Table 1. For trioxadecalins **5a** and **5d**, we observed only an enantiotropic cholesteric phase, in agreement with Vill and coworker's previous results on similar compounds.[7] The trioxadecalins **6a–d**, containing a methoxymethoxy substituent, had a similar behaviour, although it was not possible to determine the exact transition temperature for compounds **6b–d**. However, there is little influence of the chain length of the alkoxy substituent on the transition temperature of the crystalline phase. It is to be noticed that the analogous compound having a trifluoromethoxy group in the *para* position and previously described exhibited a quite different behaviour;[10] a monotropic cholesteric mesophase and an enantiotropic $S_A$ mesophase were observed for n = 1 and 4, but no mesogenic property when n = 8.

For trioxadecalins **7a–d**, having a dimethylamino substituent, the melting point decreased with increasing chain length. We observed a cholesteric phase, that is monotropic for **7b** and enantiotropic for all other compounds in the series. By




***Scheme 2.*** Synthesis of compounds **5**–**11**. Reagents and conditions: *i*: *p*-$C_nH_{2n+1}O$-$C_6H_4$-$CH(OMe)_2$, DMF, *p*-TsOH; *ii:* *p*-$C_nH_{2n+1}O$-$C_6H_4$-$B(OH)_2$, toluene, 45°C.

comparison of these compounds **7a–d** with the analogous chloro derivatives,[10] we observed that the cholesteric phase appeared at a lower temperature when the *para* substituent was a dimethylamino group.

The mesomorphic properties of the boratrioxadecalin compounds **8–11** are also compiled in Table 1. As previously noted in similar structures, the replacement of the carbon atom in the trioxadecalin system by a boron atom was expected to result in a change of the mesogenic properties of the target compounds.

Indeed, compound **8a** showed no mesogenic property. However, compound **8c** showed an $S_A$ phase, a $TGB_A$ phase, and a cholesteric phase, whereas compound **8d** exhibited only a smectic A phase. In this case, the increasing chain length obviously stabilized the lamellar $S_A$ phase.

For compounds **9a–d** bearing a methoxy substituent, the melting point decreased with increasing chain length. These compounds exhibited a high clearing temperature and a broad enantiotropic cholesteric phase, ranging from 10°C (for **5)** to from 60 to 90°C (for **9**). This difference is probably due to the substitution of the tetrahedral carbon atom by the planar boron atom, leading to a different binding angle of the left alkoxyphenyl unit in the two compounds. We also observed a blue phase with the pitch in the UV for compounds **9a–b**. This different behaviour between **8a–d** and **9a–d** could be due to the formation of an intermolecular hydrogen bond in the case of **8a–d**, due to the presence of the *p*-hydroxyl function. Compounds **9a–d**, as compared with the analogues bearing a trifluoromethoxy substituent in the *para* position[10] clearly show only an enantiotropic cholesteric phase, while the corresponding trifluoromethoxy analogues display a smectic A phase.

***Table 1.*** Mesomorphism of compounds **5**–**11**.[a]

| Compound | R | n | Transition temperatures [°C] | | | | | |
|---|---|---|---|---|---|---|---|---|
| **5a** | $OCH_3$ | 1 | C 195.0 | | | | N* 206.0 | I |
| **5d** | $OCH_3$ | 4 | C 135.7 | | | | N* 154.0 | I |
| **6a** | $OCH_2OCH_3$ | 1 | C 127.6 | | | | N* 140.3 | I |
| **6b** | $OCH_2OCH_3$ | 4 | C 142.0 | | | | ''N*'' | I |
| **6c** | $OCH_2OCH_3$ | 6 | C 133.5 | | | | ''N*'' | I |
| **6d** | $OCH_2OCH_3$ | 8 | C 142.7 | | | | ''N*'' | I |
| **7a** | $NMe_2$ | 1 | C 184.8 | | | | N* 179.0 | I |
| **7b** | $NMe_2$ | 4 | $C_1$ 129.0 | $C_2$ 155.9 | | | N* 160.9 | I |
| **7c** | $NMe_2$ | 6 | C 158.9 | | | | N* 145.0 | I |
| **7d** | $NMe_2$ | 8 | C 144.7 | | | | N* 133.9 | I |
| **8a** | OH | 1 | C 180.3 | | | | | I |
| **8c** | OH | 6 | C 80.9 | | $S_A$ 119.3 | $TGB_A$ 120.4 | N* 136.5 | BP |
| **8d** | OH | 8 | C 107.0 | | $S_A$ 144.2 | | | I |
| **9a** | $OCH_3$ | 1 | C 158.0 | | | | N* 211.1 | BP |
| **9b** | $OCH_3$ | 4 | C 116.3 | | | | N* 194.7 | $BP_{UV}$ |
| **9c** | $OCH_3$ | 6 | C 92.5 | | | | N* 180.7 | I |
| **9d** | $OCH_3$ | 8 | C 90.1 | | | | N* 151.5 | I |
| **10a** | $OCH_2OCH_3$ | 1 | $C_1$ 137.2 | $C_2$ 105.7 $C_3$ 89 | | | N* 164.3 | $BP_{UV}$ |
| **10b** | $OCH_2OCH_3$ | 4 | C 97.7 | | $S_A$ 86.9 | $TGB_A$ 88.0 | N* 167.2 | $BP_{UV}$ |
| **10c** | $OCH_2OCH_3$ | 6 | C 96.4 | | $S_A$ 104.4 | $TGB_A$ 107.0 | N* 135.0 | $BP_{UV}$ |
| **10d** | $OCH_2OCH_3$ | 8 | C 71.4 | | $S_A$ 115.4 | $TGB_A$ 116.0 | N* 128.7 | $BP_{UV}$ |
| **11a** | $NMe_2$ | 1 | C 188.2 | | | | N* 155.5 | $BP_{UV}$ |
| **11b** | $NMe_2$ | 4 | C 147.2 | | | | N* 176.1 | $BP_{UV}$ |
| **11c** | $NMe_2$ | 6 | C 141.6 | | | | N* 159.2 | $BP_{UV}$ |
| **11d** | $NMe_2$ | 8 | C 110.7 | | | | N* 149.1 | $BP_{UV}$ |

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

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Although both series shared the methoxymethoxy substituent, compounds **10a–d** exhibited a behaviour quite different from that of compounds **6a–d**. In the latter series, the melting point decreased with increasing chain length. For compound **10a**, we observed two crystal-crystal transitions, and a unique enantiotropic cholesteric phase. Conversely, compounds **10b–d** showed a $S_A$ phase, a $TGB_A$ phase and a cholesteric phase. In addition, all compounds exhibited a blue phase with the pitch in the UV.

Compounds **11** have very high clearing temperatures, which resemble those of compounds **7**, and exhibited a cholesteric phase that is monotropic for **11a** and enantiotropic for **11b–d**. All compounds showed also a blue phase. We noticed that the substitution of a methoxy group (compounds **9a–d**) by a dimethylamino group (compounds **11a–d**) gave higher transition temperatures for the crystalline phase and the cholesteric phase.

In order to obtain some more information on the quite different behaviour of these chiral trioxa- and trioxaboradecalins and eventually to have some information on the influence of a substitution of a carbon by a boron atom, the structures of compounds **6a** and **10** were determined by single-crystal X-ray diffraction analysis (Figure 1).[a] However, the structures of these compounds, in the solid state, seemed very similar and gave no further information concerning the differences of the mesogenic properties of these componds.

## CONCLUSION

Condensation of various aryl Grignard reagents with *p-tert*-butylphenyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside in the presence of a nickel catalyst leads to the formation of the corresponding β-*C*-aryl-$\Delta^2$-glycopyranosides, which are the key products for the synthesis of chiral trioxa- and trioxaboradecalins bearing various substituents such as a hydroxy, a methoxy, a methoxymethoxy, or a dimethylamino group on the *para* position of the phenyl ring. These compounds show short pitch cholesterics, blue phases, TGBA phases and sign inversion of cholesterics depending on the substitution pattern.

---

[a]X-ray data for **6a**: $C_{22}H_{26}O_6$, M = 386.43, monoclinic, a = 9.592(2), b = 8.611(2), c = 12.537(3) Å, β = 108.95(2)°, V = 979.3(3) $Å^3$, space group $P2_1$, Z = 2, $D_c$ = 1.310 Mg $m^{-3}$, μ (Mo kα) = 0.095 $mm^{-1}$, crystal size 0.25 × 0.20 × 0.15 mm. Data were measured at 293 K. R = 0.061, $R_w$ = 0.140 for 2353 independantly observed reflections with [I > 2σ(I)]. X-ray data for **10a**: $C_{21}H_{23}BO_6$, M = 382.2, monoclinic, a = 9.595(2), b = 8.555(2),c = 12.509(2) Å, b = 108.54(2)°, V = 973.5(3) $Å^3$, space group $P2_1$, Z = 2, $D_c$ = 1.304 Mg $m^{-3}$, μ (Mo kα) = 0.094 $mm^{-1}$, crystal size 0.35 × 0.30 × 0.15 mm. Data were measured at 173 K. R = 0.055, $R_w$ = 0.142 for 2353 independantly observed reflections with [I > 2σ(I)]. For all structures, intensities were measured by a Nonius Kappa CCD diffractometer using Mo kα radiation (l = 0.71073). The structure was solved by direct methods and refinements with full matrix least-squares were calculated using SHELX97. Crystallographic data (excluding structure factors) for the structures of compounds **6a** and **10a** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 187368 and 187367 respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) - 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].





Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

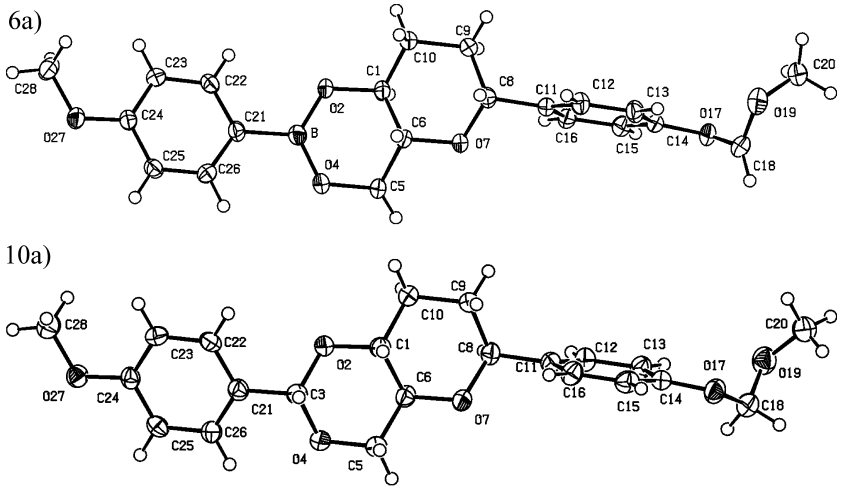



***Figure 1.*** X-ray structures of compound **6a** (upper structure) and compound **10a** (lower structure).

## EXPERIMENTAL

**General methods.** All reactions were monitored by TLC (TLC plates $GF_{254}$ Merck); detection was effected by UV absorbance and spraying with a 9:1 solution of ethanol-sulfuric acid, followed by heating. Reactions involving organometallic catalysis were carried out in a Schlenk tube 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 ($^1$H, 200 or 400 MHz; $^{13}$C, 50 or 100 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 Kmin$^{-1}$. 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 (**1**),[11] *p*-alkoxybenzaldehyde dimethyl acetals,[12] phenylboronic acids,[13,14] $NiCl_2$(dppe),[15] *(1S,3R,6R,8R)*-3,8-bis(4′-methoxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (**5a**).[7]

**Standard procedure for nickel-catalyzed coupling reaction.** To a solution of the unsaturated carbohydrate **1** (223 mg, 0.44 mmol) and $NiCl_2$(dppe) (23 mg, 0.044 mmol) in 2 mL of THF was slowly added at −40°C a solution of a Grignard reagent prepared from magnesium (64 mg, 2.6 mmol) and the appropriate aryl 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 ether solution was washed with water (2 × 10 mL), and dried. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography using the indicated solvents as the eluent to give the corresponding *C*-glycoside **2**.

**[4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl]-4-hydroxybenzene (2a):** yield 48%; oil; $R_f$ 0.36 (petroleum ether/dichloromethane 1/15); $[\alpha]_D^{20}$ + 233.8 (*c* 0.6, $CH_3OH$); $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 6H, $SiCH_3$), 0.14 (s, 6H, $SiCH_3$), 0.91 (s, 9H, $SiCMe_3$), 0.93 (s, 9H, $SiCMe_3$), 3.56 (ddd, 1H, $J_{5,4}$ = 8.4, $J_{5,6a}$ = 5.9, $J_{5,6b}$ = 1.9 Hz, H-5), 3.82 (dd, 1H, $J_{6a,6b}$ = 11.3, $J_{6a,5}$ = 5.9 Hz, H-6a), 3.94 (dd, 1H, $J_{6b,6a}$ = 11.3, $J_{6b,5}$ = 1.9 Hz, H-6b), 4.30 (dd, 1H, $J_{4,5}$ = 8.4, $J_{4,1}$ = 2.8 Hz, H-4), 5.05 (d, 1H, $J_{1,4}$ = 2.8 Hz, H-1), 5.72 (d, 1H, $J_{2,3}$ = 10.3 Hz, H-2), 5.78 (d, 1H, $J_{3,2}$ = 10.3 Hz, H-3), 7.69 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.06 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ −5.2, −5.0, −4.7, −4.2, 18.1, 18.5, 25.8, 26.0, 63.5, 64.0, 77.0, 80.8, 115.3,128.7, 129.6, 130.9, 132.9, 155.5.

Anal. Calcd for $C_{24}H_{42}O_4Si_2$ (450.77): C, 63.95; H, 9.39. Found: C, 63.94; H, 9.39.

**[4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl]-4-methoxybenzene (2b):** yield 51%; oil; $[\alpha]_D^{20}$ + 136.6 (*c* 1.1, $CH_3OH$); $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.01 (s, 3H, $SiCH_3$), 0.02 (s, 3H, $SiCH_3$), 0.13 (s, 3H, $SiCH_3$), 0.14 (s, 3H, $SiCH_3$), 0.89 (s, 9H, $SiCMe_3$), 0.93 (s, 9H, $SiCMe_3$), 3.50 (ddd, 1H, $J_{5,4}$ = 8.4, $J_{5,6a}$ = 6.3, $J_{5,6b}$ = 1.7 Hz, H-5), 3.77–3.92 (m, 5H, H-6a, H-6b, $OCH_3$), 4.36 (dd, 1H, $J_{4,5}$ = 8.4, $J_{4,1}$ = 2.6 Hz, H-4), 5.10 (d, 1H, $J_{1,4}$ = 2.6 Hz, H-1), 5.73 (d, 1H, $J_{2,3}$ = 11.0 Hz, H-2), 5.78 (d, 1H, $J_{3,2}$ = 11.0 Hz, H-3), 6.86 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.26 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ −5.1, −5.0, −4.7, −4.2, 18.9, 18.5, 25.9, 26.0, 55.3, 63.0, 63.6, 76.8, 80.7, 113.7, 128.4, 129.8, 130.8, 133.6, 159.2.

Anal. Calcd for $C_{25}H_{44}O_4Si_2$ (464.80): C, 64.60; H, 9.54. Found: C, 63.93; H, 9.47.

**[4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl]-4-methoxymethoxybenzene (2c):** yield 80%; oil; $R_f$ 0.40 (petroleum ether/ethyl acetate 10/1); $[\alpha]_D^{20}$ + 160 (*c* 1.0, $CH_3OH$); $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.05 (s, 6H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.16 (s, 3H, $SiCH_3$), 0.91 (s, 9H, $SiCMe_3$), 0.95 (s, 9H, $SiCMe_3$), 3.49 (s, 3H, $OCH_3$), 3;52 (m, 1H, H-5), 3.83 (dd, 1H, $J_{6a,6b}$ = 11.3, $J_{6a,5}$ = 4.7 Hz, 1H, H-6a), 3.95 (dd, 1H, $J_{6b,6a}$ = 11.3, $J_{6b,5}$ = 1.7 Hz, H-6b), 4.38 (dd, 1H, $J_{4,5}$ = 8.4, $J_{4,1}$ = 2.6 Hz, H-4), 5.12 (d, 1H, $J_{1,4}$ = 2.6 Hz, H-1), 5.18 (s, 2H, $OCH_2O$), 5.72 (d, 1H, $J_{2,3}$ = 10.9 Hz, H-2), 5.82 (d, 1H, $J_{3,2}$ = 10.9 Hz, H-3), 7.01 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.27 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ −4.5, −4.4, −4.1, −3.6, 18.7, 19.1, 26.8, 26.6, 56.6, 63.6, 64.3, 78.3, 81.4, 95.2, 116.7, 128.9, 130.4, 131.3, 135.5, 157.5.

Anal. Calcd for $C_{26}H_{46}O_5Si_2$ (494.82): C, 63.11; H, 9.37. Found: C, 63.53; H, 9.56.

**[4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl]-4-dimethylaminobenzene (2d):** yield 80%; oil; $R_f$ 0.21 (petroleum ether/dichloromethane 1/1); $[\alpha]_D^{20}$ + 179.8 (*c* 1.2, $CH_2Cl_2$); $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.02 (s, 6H, $SiCH_3$), 0.12 (s, 3H, $SiCH_3$), 0.13 (s, 3H, $SiCH_3$), 0.88 (s, 9H, $SiCMe_3$),

0.92 (s, 9H, $SiCMe_3$), 3.48 (ddd, 1H, $J_{5,4}$ = 8.8, $J_{5,6a}$ = 4.8, $J_{5,6a}$ = 2.2 Hz, H-5), 3.80 (dd, 1H, $J_{6a,6b}$ = 11.8, $J_{6a,5}$ = 4.8 Hz, H-6a), 3.90 (dd, 1H, $J_{6b,6a}$ = 11.8, $J_{6b,5}$ = 2.2 Hz, H-6b), 4.33 (dd, 1H, $J_{4,5}$ = 8.8, $J_{4,1}$ = 2.6 Hz, H-4), 5.06 (d, 1H, $J_{1,4}$ = 2.6 Hz, H-1), 5.75 (bs, 2H, H-2, H-3), 6.70 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.19 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ −4.9, −4.8, −4.5, −4.0, 18.2, 18.7, 26.2, 26.3, 41.0, 63.5, 64.2, 77.3, 81.0, 113.1, 126.3, 129.7, 131.3, 142.7, 150.5.

Anal. Calcd for $C_{26}H_{47}NO_3Si_2$ (477.84); C, 65.35; H, 9.91. Found: C, 64.86; H, 9.71.

**Standard procedure for the preparation of unsaturated *C*-arylglycosides 3.** The unsaturated *C*-aryl glycoside **2** (0.43 mmol) was stirred in THF (5 mL) at rt 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 **4** which was purified by flash-chromatography on silica.

**(2,3-Dideoxy-β-D-*erythro*-hex-2-enopyranosyl)-4-hydroxybenzene (3a):** yield 80%; oil; $R_f$ 0.2 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ + 211.0 (*c* 0.9, $CH_3OH$); $^1H$ NMR (200 MHz, $CD_3OH$) δ 3.53 (ddd, 1H, $J_{5,4}$ = 8.8, $J_{5,6a}$ = 6.5, $J_{5,6b}$ = 2.2 Hz, H-5), 3.67 (dd, 1H, $J_{6a,6b}$ = 11.8, $J_{6a,5}$ = 6.5 Hz, H-6a), 3.89 (dd, 1H, $J_{6b,6a}$ = 11.8, $J_{6b,5}$ = 2.2 Hz, H-6b), 4.11 (dm, 1H, $J_{4,5}$ = 8.8 Hz, H-4), 5.06 (bs, 1H, H-1), 5.79 (dm, 1H, $J_{2,3}$ = 11.5 Hz, H-2), 5.86 (dm, 1H, $J_{3,2}$ = 11.5 Hz, H-3), 6.73 (d, 2H, $J_{H,H}$ = 6.6 Hz, $H_{arom}$), 7.06 (d, 2H, $J_{H,H}$ = 6.6 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ 61.5, 62.3, 76.0, 81.0, 114.8, 128.5, 130.1, 130.2, 131.5, 156.9. HRMS: Calcd for $C_{12}H_{15}O_4$ (CI) $[M + H]^+$ *m/z* 223.0970. Found: 223.0969.

**(2,3-Dideoxy-β-D-*erythro*-hex-2-enopyranosyl)-4-methoxybenzene (3b):** yield 80%; oil; $R_f$ 0.35 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ + 241.8 (*c* 0.6, $CH_3OH$); $^1H$ NMR (200 MHz, $CDCl_3$) δ 2.04 (bs, 2H, 2 × OH), 3.58 (ddd, 1H, $J_{5,4}$ = 9.2, $J_{5,6a}$ = 5.5, $J_{5,6b}$ = 4.1 Hz, H-5), 3.80 (s, 3H, $OCH_3$), 3.84 (dd, 1H, $J_{6a,6b}$ = 11.8, $J_{6a,5}$ = 5.5 Hz, H-6a), 3.94 (dd, 1H, $J_{6b,6a}$ = 11.8, $J_{6b,5}$ = 4.1 Hz, H-6b), 4.33 (dm, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 5.10 (bs, 1H, H-1), 5.83 (dm, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 5.93 (dm, $J_{3,2}$ = 9.9 Hz, H-3), 6.88 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 7.24 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CD_3OD$) δ 56.0, 63.8, 64.6, 78.6, 82.4, 115.0, 130.1, 130.7, 132.5, 134.7, 161.2.

Anal. Calcd for $C_{13}H_{16}O_4$ (236.27): C, 66.09; H, 6.83. Found: C, 65.92; H, 6.95.

**(2,3-Dideoxy-β-D-*erythro*-hex-2-enopyranosyl)-4-methoxymethoxybenzene (3c):** yield 90%; oil; $R_f$ 0.30 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ + 164.5 (*c* 1.2, $CHCl_3$); $^1H$ NMR (200 MHz, $CDCl_3$) δ 1.70–1.90 (m, 2H, 2 × OH), 3.46 (s, 3H, $OCH_3$), 3.57 (ddd, 1H, $J_{5,4}$ = 8.8, $J_{5,6a}$ = 5.3, $J_{5,6b}$ = 4.1 Hz, H-5), 3.83 (dd, 1H, $J_{6a,6b}$ = 11.6, $J_{6a,5}$ = 5.3 Hz, H-6a), 3.94 (dd, 1H, $J_{6b,6a}$ = 11.6, $J_{6b,5}$ = 4.1 Hz, H-6b), 4.32 (dm, 1H, $J_{4,5}$ = 8.8 Hz, H-4), 5.13 (bs, 1H, H-1), 5.17 (s, 2H, $OCH_2O$), 5.82 (dm, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 5.92 (dm, 1H, $J_{3,2}$ = 10.2 Hz, H-3), 7.02 (d, 2H, $J_{H,H}$ = 8.7 Hz, $H_{arom}$), 7.25 (d, 2H, $J_{H,H}$ = 8.7 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ 56.0, 63.3, 64.4, 77.0, 79.5, 94.5, 116.4, 128.8, 129.1, 131.2, 133.8, 157.3.

Anal. Calcd for $C_{14}H_{18}O_5$ (266.30): C, 63.15; H, 6.81. Found: C, 62.71; H, 6.82.

**(2,3-Dideoxy-β-D-*erythro*-hex-2-enopyranosyl)-4-dimethylaminobenzene (3d):** yield 80%; oil; $R_f$ 0.22 (petroleum ether/ethyl acetate 1/5); $[\alpha]_D^{20}$ + 219.0 (*c* 1.2, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.88 (s, 1H, OH), 2.13 (s, 1H, OH), 2.95 (s, 6H, $CH_3$), 3.56 (ddd, 1H, $J_{5,4}$ = 8.8, $J_{5,6a}$ = 5.5, $J_{5,6b}$ = 4.0 Hz, H-5), 3.82 (dd, 1H, $J_{6a,6b}$ = 11.4, $J_{6a,5}$ = 5.5 Hz, H-6a), 3.93 (dd, 1H, $J_{6b,6a}$ = 11.4, $J_{6b,5}$ = 4.0 Hz, H-6b), 4.32 (bd, 1H, $J_{4,5}$ = 8.8 Hz, H-4), 5.08 (bs, 1H, H-1), 5.84 (bd, 1H, $J_{2,3}$ = 10.3 Hz, H-2), 5.91 (bd, 1H, $J_{3,2}$ = 10.3 Hz, H-3), 6.71 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.19 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ 40.7, 63.1, 64.2, 77.2, 112.6, 128.8, 128.2, 128.6, 129.0, 131.3, 150.6.

Anal. Calcd for $C_{14}H_{19}NO_3$ (249.31): C, 67.45; H, 7.68. Found: C, 67.64; H, 7.67.

**Standard procedure for the preparation of saturated *C*-arylglycosides 4.** The unsaturated diol **3** was dissolved in ethanol (5 mL), and treated with molecular hydrogen at atmospheric pressure and room temperature in the presence of [Rh(COD)(dppb)]$ClO_4$ (0.02 mmol). After 24 h, filtration of the mixture and evaporation of the solvent gave a residue, which was purified by column chromatography to afford the saturated *C*-aryl glycoside **4**.

**(2,3-Dideoxy-β-D-*erythro*-hexanopyranosyl)-4-hydroxybenzene (4a):** yield 65%; oil; $R_f$ 0.20 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ + 56.9 (*c* 0.8, $CH_3OH$); $^1H$ NMR (200 MHz, $CD_3OD$) δ 1.72–1.92 (m, 2H, H-$2_{ax}$, H-$3_{ax}$), 2.07 (m, 1H, H-$2_{eq}$), 2.34 (m, 1H, H-$3_{eq}$), 3.49 (ddd, 1H, $J_{5,4}$ = 9.5, $J_{5,6a}$ = 5.8, $J_{5,6b}$ = 2.4 Hz, H-5), 3.66 (dm, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.86 (dd, 1H, $J_{6a,6b}$ = 11.7, $J_{6a,5}$ = 5.8 Hz, H-6a), 4.05 (dd, 1H, $J_{6b,6a}$ = 11.7, $J_{6b,5}$ = 2.4 Hz, H-6b), 4.54 (dd, 1H, $J_{1,2a}$ = 10.2, $J_{1,2eq}$ = 2.1 Hz, H-1), 6.90 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.38 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CD_3OD$) δ 34.3, 63.9, 67.6, 80.8, 84.7, 116.1, 128.8, 128.4, 134.9, 158.0. HRMS: Calcd for $C_{12}H_{17}O_4$ (CI) $[M + H]^+$ *m/z* 225.1126. Found: 225.1129.

**(2,3-Dideoxy-β-D-*erythro*-hexanopyranosyl)-4-methoxybenzene (4b):** yield 60%; oil; $R_f$ 0.32 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ + 55.9 (*c* 0.6, $CH_2Cl_2$); $^1H$ NMR (200 MHz, $CDCl_3$) δ 1.59–1.79 (m, 2H, H-$2_{ax}$, H-$3_{ax}$), 1.93 (m, 1H, H-$2_{eq}$), 2.18-2.33 (m, 3H, H-$3_{eq}$, OH), 3.39 (ddd, 1H, $J_{5,4}$ = 9.2, $J_{5,6a}$ = 4.8, $J_{5,6b}$ = 4.4 Hz, H-5), 3.68 (dm, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 3.79 (s, 3H, $OCH_3$), 3.83 (dd, 1H, $J_{6a,6b}$ = 11.8, $J_{6a,5}$ = 4.8 Hz, H-6a), 3.91 (dd, 1H, $J_{6b,6a}$ = 11.8, $J_{6b,5}$ = 4.4 Hz, H-6b), 4.36 (dd, 1H, $J_{1,2ax}$ = 8.2, $J_{1,2eq}$ = 2.3 Hz, H-1), 6.87 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.26 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ 32.9, 33.0, 55.4, 63.6, 67.4, 79.3, 82.0, 113.9, 127.5, 134.2, 159.3.

Anal. Calcd for $C_{13}H_{18}O_4$ (238.29): C, 65.35; H, 7.61. Found: C, 64.90; H, 7.62.

**(2,3-Dideoxy-β-D-*erythro*-hexanopyranosyl)-4-methoxymethoxybenzene (4c):** yield 60%; oil; $R_f$ 0.25 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ + 49.1 (*c* 1.1, $CH_2Cl_2$); $^1H$ NMR (200 MHz, $CDCl_3$) δ 1.58–1.76 (m, 2H, H-$2_{ax}$, H-$3_{ax}$), 1.96 (m, 1H, H-$2_{eq}$), 2.05–2.21 (m, 3H, H-$3_{eq}$, OH), 3.39 (ddd, 1H, $J_{5,4}$ = 9.2, $J_{5,6a}$ = 4.9, $J_{5,6b}$ = 4.3 Hz, H-5), 3.46 (s, 3H, $OCH_3$), 3.66 (ddd, 1H, $J_{4,3ax}$ = 10.2, $J_{4,5}$ = 9.2, $J_{4,3eq}$ = 4.8 Hz, H-4), 3.81 (dd, 1H, $J_{6a,6b}$ = 11.6, $J_{6a,5}$ = 4.9 Hz, H-6a), 3.89 (dd, 1H, $J_{6b,6a}$ = 11.6, $J_{6b,5}$ = 4.3 Hz, H-6b), 4.36 (dd, 1H, $J_{1,2ax}$ = 10.4, $J_{1,2eq}$ = 2.2 Hz, H-1), 5.16 (s, 2H,





Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

$OCH_2O$), 7.00 (d, 2H, $J_{H,H}$ = 8.7 Hz, $H_{arom}$), 7.26 (d, 2H, $J_{H,H}$ = 8.7 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ 32.8, 33.0, 56.0, 63.7, 67.6, 79.1, 81.8, 94.5, 116.2, 127.3, 135.3, 156.8.

Anal. Calcd for $C_{14}H_{20}O_5$ (268.31): C, 62.67; H, 7.51. Found: C, 61.92; H, 7.43.

**(2,3-Dideoxy-β-D-*erythro*-hexanopyranosyl)-4-dimethylaminobenzene (4d):** yield 83%; oil; $R_f$ 0.2 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ + 51.2 (*c* 0.7, $CH_2Cl_2$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.66 (m, 1H, H-2ax), 1.78 (m, 1H, H-3ax), 1.92 (m, 1H, H-2eq), 2.12–2.32 (m, 3H, H-3eq, OH), 2.93 (s, 6H, $NMe_2$), 3.40 (ddd, 1H, $J_{5,4}$ = 9.2, $J_{5,6a}$ = 5.2, $J_{5,6b}$ = 4.1 Hz, H-5), 3.46, 3.68 (ddd, 1H, $J_{4,3ax}$ = 10.3, $J_{4,5}$ = 9.2, $J_{4,3eq}$ = 4.4 Hz, H-4), 3.81 (dd, 1H, $J_{6a,6b}$ = 11.6, $J_{6a,5}$ = 5.2 Hz, H-6a), 3.90 (dd, 1H, $J_{6b,6a}$ = 11.6, $J_{6b,5}$ = 4.4 Hz, H-6b), 4.34 (dd, 1H, $J_{1,2ax}$ = 11.0, $J_{1,2eq}$ = 2.2 Hz, H-1), 6.72 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.22 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ 34.3, 34.4, 41.5, 64.0, 67.8, 81.1, 84.9, 114.2, 128.5, 132.4, 152.1.

Anal. Calcd for $C_{14}H_{21}NO_3$ (251.33): C, 66.91; H, 8.42. Found: C, 66.58; H, 8.60.

**Standard procedure for the preparation of compounds 5–7.** A flask containing 0.16 mmol of the diol **4**, 0.22 mmol of 4-alkyloxybenzaldehyde dimethyl acetal, and 5.0 mg of *p*-toluenesulfonic acid monohydrate, dissolved in 5 mL of *N,N*-dimethylformamide, was connected to a rotatory evaporator. The mixture was heated at reduced pressure (30 mbar) in a water-bath at 60°C, until TLC revealed that the reaction was complete. 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 **5–7**.

***(1S,3R,6R,8R)*-8-(4-Methoxyphenyl)-3-(4-octyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (5d):** yield 39%; mp 135.7°C; $[\alpha]_D^{20}$ + 22.3 (*c* 0.5, $CHCl_3$); $^1H$ NMR (400 MHz, $C_6D_6$) δ 0.88 (t, 3H, $J_{H,H}$ = 6.6 Hz, $CH_3$), 1.12–1.33 (m, 12H, $CH_2$), 1.52–1.72 (m, 5H, $CH_2$, 2 × H-9, H-10), 1.98 (m, 1H, H-10), 3.28 (s, 3H, $OCH_3$), 3.37 (ddd, 1H, $J_{1,6}$ = 10.2, $J_{1,10ax}$ = 9.7, $J_{1,10eq}$ = 4.1 Hz, H-1), 3.49 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.7, $J_{6,5b}$ = 4.6 Hz, H-6), 3.60 (t, 2H, $J_{H,H}$ = 6.1 Hz, $OCH_2$), 3.69 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 4.14 (bd, 1H, $J_{8,9ax}$ = 9.7 Hz, H-8), 4.31 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 4.6 Hz, H-5b), 5.50 (s, 1H, H-3), 6.82 (d, 2H, $J_{H,H}$ = 8.6 Hz, 2 $H_{arom}$), 6.89 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.19 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.66 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $C_6D_6$) δ 14.3, 23.4, 26.8, 30.0, 30.1, 32.6, 34.2, 55.2, 68.3, 70.2, 74.9, 78.8, 79.4, 102.5, 114.3, 127.8, 128.5, 128.7, 131.7, 135.2, 160.0, 160.5.

Anal. Calcd for $C_{28}H_{38}O_5$ (454.61): C, 73.98; H, 8.43. Found: C, 73.91; H, 8.45.

***(1S,3R,6R,8R)*-8-(4-Methoxymethoxyphenyl)-3-(4-methoxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (6a):** yield 60%; mp 127.6°C; $[\alpha]_D^{20}$ + 27.4 (*c* 0.2, $CHCl_3$); $^1H$ NMR (400 MHz, $C_6D_6$) δ 1.48–1.72 (m, 3H, 2 × H-9, H-10), 1.96 (m, 1H, H-10), 3.12 (s, 3H, $OCH_3$), 3.38 (m, 1H, H-1), 3.50 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.6, $J_{6,5b}$ = 4.6 Hz, H-6), 3.69 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 4.14 (bd, 1H, $J_{8,9ax}$ = 10.7 Hz, H-8), 4.31 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 4.6 Hz, H-5b), 4.85 (s, 2H, $OCH_2O$), 5.51 (s, 1H, H-3), 6.88 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 7.06–7.30 (m, 4H,





MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

$H_{arom}$), 7.64 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $C_6D_6$) δ 29.9, 34.1, 55.8, 67.9, 70.2, 74.9, 78.8, 79.8, 94.4, 102.5, 114.3, 114.7, 127.8, 128.5, 128.7, 131.6, 136.0, 160.0, 160.5.

Anal. Calcd for $C_{22}H_{26}O_6$ (386.45): C, 68.38; H, 6.78. Found: C, 68.01; H, 6.77.

***(1S,3R,6R,8R)*-3-(4-Butyloxyphenyl)-8-(4-methoxymethoxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (6b):** yield 45%; mp 142.0°C; $[\alpha]_D^{20}$ + 23.4 (*c* 0.3, $CHCl_3$); $^1H$ NMR (400 MHz, $C_6D_6$) δ 0.81 (t, 3H, $J_{H,H}$ = 7.1 Hz, $CH_3$), 1.28 (m, 2H, $CH_2$), 1.45–1.71 (m, 5H, $CH_2$, 2 × H-9, H-10), 1.96 (m, 1H, H-10), 3.12 (s, 3H, $OCH_3$), 3.38 (m, 1H, H-1), 3.50 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.6, $J_{6,5b}$ = 4.6 Hz, H-6), 3.55 (t, 2H, $J_{H,H}$ = 6.1 Hz, $OCH_2$), 3.69 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 4.14 (bd, 1H, $J_{8,9ax}$ = 10.7 Hz, H-8), 4.31 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 4.6 Hz, H-5b), 4.85 (s, 2H, $OCH_2O$), 5.50 (s, 1H, H-3), 6.89 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 7.08–7.28 (m, 4H, $H_{arom}$), 7.65 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $C_6D_6$) δ 14.3, 19.9, 25.3, 30.1, 32.0, 34.2, 55.8, 67.9, 70.2, 74.9, 78.8, 79.8, 94.4, 102.5, 114.3, 114.7, 127.8, 128.5, 128.7, 131.6, 136.0, 160.0, 160.5.

Anal. Calcd for $C_{25}H_{32}O_6$ (428.53): C, 70.07; H, 7.53. Found: C, 69.85; H, 7.49.

***(1S,3R,6R,8R)*-3-(4-Hexyloxyphenyl)-8-(methoxymethoxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (6c):** yield 50%; mp 133.5°C; $[\alpha]_D^{20}$ + 22.8 (*c* 0.3, $CHCl_3$); $^1H$ NMR (400 MHz, $C_6D_6$) δ 0.82 (t, 3H, $J_{H,H}$ = 6.1 Hz, $CH_3$), 1.10-1.31 (m, 6H, $CH_2$), 1.48–1.68 (m, 5H, $CH_2$, 2 × H-9, H-10), 1.93 (m, 1H, H-10), 3.09 (s, 3H, $OCH_3$), 3.34 (ddd, 1H, $J_{1,6}$ = 10.2, $J_{1,10ax}$ = 9.7, $J_{1,10eq}$ = 4.1 Hz, H-1), 3.44 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.7, $J_{6,5b}$ = 4.6 Hz, H-6), 3.55 (t, 2H, $J_{H,H}$ = 6.1 Hz, $OCH_2$), 3.64 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 4.11 (bd, 1H, $J_{8,9ax}$ = 9.2 Hz, H-8), 4.28 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 4.6 Hz, H-5b), 4.84 (s, 2H, $OCH_2O$), 5.50 (s, 1H, H-3), 6.92 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 7.05–7.21 (m, 4H, $H_{arom}$), 7.64 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $C_6D_6$) δ 14.6, 23.3, 26.4, 29.9, 30.0, 32.3, 34.2, 55.9, 68.3, 70.1, 74.9, 78.8, 79.7, 94.9, 102.5, 114.7, 116.7, 127.8, 128.5, 128.7, 131.6, 136.4, 157.7, 160.5.

Anal. Calcd for $C_{27}H_{36}O_6$ (456.58): C, 71.03; H, 7.95. Found: C, 70.75; H, 7.77.

***(1S,3R,6R,8R)*-8-(4-Methoxymethoxyphenyl)-3-(4-octyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (6d):** yield 61%; mp 124.7°C; $[\alpha]_D^{20}$ + 19.5 (*c* 0.2, $CHCl_3$); $^1H$ NMR (400 MHz, $C_6D_6$) δ 0.90 (t, 3H, $J_{H,H}$ = 6.6 Hz, $CH_3$), 1.12-1.36 (m, 12H, $CH_2$), 1.46–1.72 (m, 5H, $CH_2$, 2 × H-9, H-10), 1.96 (m, 1H, H-10), 3.11 (s, 3H, $OCH_3$), 3.36 (m, 1H, H-1), 3.44 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 4.6 Hz, H-6), 3.55 (t, 2H, $J_{H,H}$ = 6.1 Hz, $OCH_2$), 3.64 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 4.14 (bd, 1H, $J_{8,9ax}$ = 9.7 Hz, H-8), 4.31 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 4.6 Hz, H-5b), 5.50 (s, 1H, H-3), 6.91 (d, 2H, $J_{H,H}$ = 7.1 Hz, $H_{arom}$), 7.05–7.18 (m, 4H, $H_{arom}$), 7.66 (d, 2H, $J_{H,H}$ = 7.1 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $C_6D_6$) δ 14.3, 23.4, 26.8, 30.0, 30.1, 32.6, 34.2, 55.8, 68.3, 70.2, 74.9, 78.8, 79.8, 94.9, 102.5, 114.7, 116.7, 127.8, 128.5, 128.7, 131.6, 136.0, 160.0, 160.5.

Anal. Calcd for $C_{29}H_{40}O_6$ (484.64): C, 71.87; H, 8.32. Found: C, 71.36; H, 8.28.

***(1S,3R,6R,8R)*-8-(4-Dimethylaminophenyl)-3-(4-methoxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (7a):** yield 46%; mp 184.8°C; $[\alpha]_D^{20}$ + 27.8 (*c* 0.3, $CHCl_3$); $^1H$

NMR (400 MHz, $C_6D_6$) δ 1.69–1.80 (m, 3H, 2 × H-9, H-10), 2.03 (m, 1H, H-10), 2.52 (s, 6H, $NMe_2$), 3.26 (s, 3H, $OCH_3$), 3.45 (m, 1H, H-1), 3.57 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 4.6 Hz, H-6), 3.74 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 4.27 (bd, 1H, $J_{8,9ax}$ = 10.7 Hz, H-8), 4.35 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 4.6 Hz, H-5b), 5.51 (s, 1H, H-3), 6.68 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 6.82 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.30 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.65 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $C_6D_6$) δ 30.2, 34.1, 40.7, 55.1, 70.3, 75.0, 79.0, 80.3, 102.4, 114.1, 127.6, 128.5, 128.7, 131.1, 131.9, 150.9, 160.8.

Anal. Calcd for $C_{22}H_{27}NO_4$ (369.46): C, 71.52; H, 7.37. Found: C, 71.15; H, 7.11.

***(1S,3R,6R,8R)*-3-(4-Butyloxyphenyl)-8-(4-dimethylaminophenyl)-2,4,7-trioxabicyclo[4.4.0]decane (7b):** yield 53%; mp 155.9°C; $[\alpha]_D^{20}$ + 26.0 (*c* 0.4, $CHCl_3$); $^1H$ NMR (400 MHz, $C_6D_6$) δ 0.78 (t, 3H, $J_{H,H}$ = 7.1 Hz, $CH_3$), 1.28 (m, 2H, $CH_2$), 1.50 (m, 2H, $CH_2$), 1.66–1.71 (m, 3H, 2 × H-9, H-10), 1.99 (m, 1H, H-10), 2.49 (s, 6H, $NMe_2$), 3.41 (m, 1H, H-1), 3.50–3.59 (m, 3H, H-6, $OCH_2$), 3.72 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 4.24 (bd, 1H, $J_{8,9ax}$ = 10.7 Hz, H-8), 4.31 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 4.6 Hz, H-5b), 5.50 (s, 1H, H-3), 6.63 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 6.88 (d, 2H, $J_{H,H}$ = 7.6 Hz, $H_{arom}$), 7.28 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 7.64 (d, 2H, $J_{H,H}$ = 7.6 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $C_6D_6$) δ 14.3, 19.9, 30.2, 32.0, 34.1, 40.2, 67.9, 70.3, 75.0, 79.0, 80.3, 102.5, 113.7, 114.7, 127.8, 128.5, 128.7, 131.6, 136.0, 150.4, 160.5.

Anal. Calcd for $C_{25}H_{33}NO_4$ (411.55): C, 72.96; H, 8.08. Found: C, 72.56; H, 8.07.

***(1S,3R,6R,8R)*-8-(4-Dimethylaminophenyl)-3-(4-hexyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (7c):** yield 49%; mp 158.9°C; $[\alpha]_D^{20}$ + 25.5 (*c* 0.2, $CHCl_3$); $^1H$ NMR (400 MHz, $C_6D_6$) δ 0.84 (t, 3H, $J_{H,H}$ = 7.1 Hz, $CH_3$), 1.12–1.36 (m, 6H, $CH_2$), 1.51–1.59 (m, 2H, H-9, H-10), 1.66–1.77 (m, 3H, H-9, $CH_2$), 2.00 (m, 1H, H-10), 2.51 (s, 6H, $NMe_2$), 3.45 (m, 1H, H-1), 3.52–3.62 (m, 3H, H-6, $OCH_2$), 3.72 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 4.26 (bd, 1H, $J_{8,9ax}$ = 9.7 Hz, H-8), 4.38 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 4.6 Hz, H-5b), 5.50 (s, 1H, H-3), 6.64 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 6.90 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 7.30 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 7.66 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $C_6D_6$) δ 14.6, 23.3, 26.4, 29.9, 30.2, 32.3, 34.1, 40.7, 68.3, 70.3, 75.0, 79.0, 80.3, 102.4, 113.1, 114.7, 127.6, 128.5, 128.7, 131.1, 131.8, 150.9, 160.4.

Anal. Calcd for $C_{27}H_{37}NO_4$ (439.60): C, 73.77; H, 8.48. Found: C, 73.56; H, 8.56.

***(1S,3R,6R,8R)*-8-(4-Dimethylaminophenyl)-3-(4-octyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (7d):** yield 64%; mp 144.7°C; $[\alpha]_D^{20}$ + 23.1 (*c* 0.3, $CHCl_3$); 1H NMR (400 MHz, $C_6D_6$) δ 0.96 (t, 3H, $J_{H,H}$ = 6.6 Hz, $CH_3$), 1.21–1.41 (m, 12H, $CH_2$), 1.58–1.68 (m, 2H, H-9, H-10), 1.72–1.82 (m, 3H, H-9, $CH_2$), 2.08 (m, 1H, H-10), 2.58 (s, 6H, $NMe_2$), 3.50 (m, 1H, H-1), 3.58–3.70 (m, 3H, H-6, $OCH_2$), 3.79 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 4.32 (bd, 1H, $J_{8,9ax}$ = 8.1 Hz, H-8), 4.38 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 4.6 Hz, H-5b), 5.57 (s, 1H, H-3), 6.70 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 6.97 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 7.36 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $C_6D_6$) δ 14.7, 23.5, 26.7, 30.0, 30.1, 30.2, 32.6, 34.2, 40.7, 68.3, 70.3, 75.0, 79.0, 80.3, 102.5, 113.1, 114.7, 127.6, 128.6, 128.7, 131.1, 131.8, 150.9, 160.4.

Anal. Calcd for $C_{29}H_{41}NO_4$ (467.65): C, 74.48; H, 8.84. Found: C, 73.98; H, 8.72.





MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

**Standard procedure for the preparation of compounds 8–11.** A solution of 0.14 mmol of compound **4** and 0.17 mmol of 4-alkyloxyphenyl boronic acid 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 **8–11**.

***(1S,6R,8R)*-8-(4-Hydroxyphenyl)-3-(4-methoxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (8a):** yield 50%; mp 180.3°C; $[\alpha]_D^{20}$ + 29.7 (*c* 0.1, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 1.68–1.92 (m, 2H, H-9), 2.04 (m, 1H, H-10), 2.37 (m, 1H, H-10), 3.58–3.88 (m, 6H, H-1, H-6, $OCH_3$, OH), 3.94 (dd, 1H, $J_{5a,5b}$ = 10.3, $J_{5a,6}$ = 10.3 Hz, H-5a), 4.24 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.48 (bd, 1H, $J_{8,9ax}$ = 8.8 Hz, H-8), 6.79 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 6.87 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.23 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 31.2, 32.9, 55.1, 64.9, 71.6, 76.1, 79.8, 113.2, 113.9, 127.4, 127.3, 135.8, 155.6, 161.9.

Anal. Calcd for $C_{19}H_{21}BO_4$ (324.19): C, 70.39; H, 6.53. Found: C, 70.24; H, 6.34.

***(1S,6R,8R)*-3-(4-Hexyloxyphenyl)-8-(4-hydroxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (8c):** yield 62%; mp 80.9°C; $[\alpha]_D^{20}$ + 24.5 (*c* 0.1, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J_{H,H}$ = 6.1 Hz, $CH_3$), 1.30–1.37 (m, 4H, $CH_2$), 1.45 (m, 2H, $CH_2$), 1.72–1.92 (m, 4H, H-9, $CH_2$), 2.04 (m, 1H, H-10), 2.38 (m, 1H, H-10), 3.63 (ddd, 1H, $J_{6,5a}$ = 10.3, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 5.1 Hz, H-6), 3.81 (s, 3H, $OCH_3$), 3.84–4.01 (m, 4H, H-1, H-5a, $OCH_2$), 4.25 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.49 (dd, 1H, $J_{8,9ax}$ = 9.9, 1.4 Hz, H-8), 6.87 (d, 2H, $J_{H,H}$ = 8.4 Hz, $H_{arom}$), 6.89 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.28 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.4 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 14.1, 26.1, 29.3, 31.1, 31.8, 32.9, 55.3, 64.9, 67.8, 71.5, 76.0, 79.8, 113.8, 127.3, 127.9, 133.6, 135.7, 155.6, 161.5.

Anal. Calcd for $C_{24}H_{31}BO_4$ (394.32): C, 73.10; H, 7.92. Found: C, 72.74; H, 7.92.

***(1S,6R,8R)*-8-(4-Hydroxyphenyl)-3-(4-octyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (8d):** yield 30%; $[\alpha]_D^{20}$ + 22.3 (*c* 0.7, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J_{H,H}$ = 6.8 Hz, $CH_3$), 1.23–1.28 (m, 8H, $CH_2$), 1.45 (m, 2H, $CH_2$), 1.71–1.88 (m, 4H, H-9, $CH_2$), 2.03 (m, 1H, H-10), 2.37 (m, 1H, H-10), 3.61 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 5.1 Hz, H-6), 3.87 (ddd, 1H, $J_{1,10ax}$ = 10.7, $J_{1,6}$ = 9.2, $J_{1,10eq}$ = 4.6 Hz, H-1), 3.94 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 3.97 (t, 2H, $J_{H,H}$ = 6.6 Hz, $OCH_2$), 4.24 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.47 (dd, 1H, $J_{8,9ax}$ = 10.7, $J_{8,9eq}$ = 2.0 Hz, H-8), 6.79 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 6.87 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.23 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ 14.5, 23.1, 26.5, 29.6, 29.7, 29.8, 31.5, 32.2, 32.3, 65.3, 68.2, 72.0, 76.5, 80.2, 114.2, 115.7, 127.9, 134.2, 136.2, 155.6, 161.9.

Anal. Calcd for $C_{26}H_{35}BO_4$ (422.38): C, 73.94; H, 8.35. Found: C, 73.59; H, 8.35.

***(1S,6R,8R)*-8-(4-Methoxyphenyl)-3-(4-methoxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (9a):** yield 60%; mp 158.0°C; $[\alpha]_D^{20}$ + 29.0 (*c* 1.0, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.68–1.92 (m, 2H, H-9), 2.07 (m, 1H, H-10), 2.37 (m, 1H, H-10), 3.58–3.88 (m, 8H, H-1, H-6, $OCH_3$), 3.94 (dd, 1H, $J_{5a,5b}$ = 10.3, $J_{5a,6}$ = 10.3





Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Hz, H-5a), 4.24 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.48 (bd, 1H, $J_{8,9a}$ = 8.8 Hz, H-8), 6.89 (d, 4H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.29 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.75 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 31.2, 32.9, 55.1, 55.4, 64.9, 71.6, 76.1, 79.8, 113.2, 113.9, 127.3, 127.4, 135.8, 159.3, 161.9.

Anal. Calcd for $C_{20}H_{23}BO_5$ (354.21): C, 67.82; H, 6.54. Found: C, 67.53; H, 6.49.

***(1S,6R,8R)*-3-(4-Butyloxyphenyl)-8-(4-methoxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (9b):** yield 74%; mp 116.3°C; $[\alpha]_D^{20}$ + 24.5 (*c* 0.9, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.96 (t, 3H, $J_{H,H}$ = 7.6 Hz, $CH_3$), 1.49 (m, 2H, $CH_2$), 1.70–1.90 (m, 4H, H-9, $CH_2$), 2.03 (m, 1H, H-10), 2.38 (m, 1H, H-10), 3.61 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 5.1 Hz, H-6), 3.81 (s, 3H, $OCH_3$), 3.84–4.02 (m, 4H, H-1, H-5a, $OCH_2$), 4.23 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.48 (dd, 1H, $J_{8,9ax}$ = 11.2, $J_{8,9eq}$ = 2.0 Hz, H-8), 6.87 (m, 4H, $H_{arom}$), 7.28 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $CDCl_3$) δ 13.9, 19.2, 31.1, 31.3, 32.8, 55.3, 64.9, 67.4, 71.5, 76.0, 79.8, 113.7, 113.8, 127.3, 133.6, 135.7, 159.2, 161.5.

Anal. Calcd for $C_{23}H_{29}BO_5$ (396.29): C, 69.71; H, 7.38. Found: C, 69.42; H, 7.46.

***(1S,6R,8R)*-3-(4-Hexyloxyphenyl)-8-(4-methoxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (9c):** yield 60%; mp 92.9°C; $[\alpha]_D^{20}$ + 23.5 (*c* 0.1, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J_{H,H}$ = 6.1 Hz, 3H, $CH_3$), 1.30–1.37 (m, 4H, $CH_2$), 1.45 (m, 2H, $CH_2$), 1.72–1.92 (m, 4H, H-9, $CH_2$), 2.04 (m, 1H, H-10), 2.38 (m, 1H, H-10), 3.62 (ddd, 1H, $J_{6,5a}$ = 10.3, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 5.1 Hz, H-6), 3.80 (s, 3H, $OCH_3$), 3.83–4.02 (m, 4H, H-1, H-5a, $OCH_2$), 4.24 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.51 (bd, 1H, $J_{8,9ax}$ = 11.0 Hz, H-8), 6.87 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 6.88 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.27 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 14.1, 22.7, 26.1, 29.3, 31.1, 31.8, 32.9, 55.3, 64.9, 67.8, 71.5, 76.0, 79.8, 113.7, 113.8, 127.3, 133.6, 135.7, 159.3, 161.5.

Anal. Calcd for $C_{25}H_{33}BO_5$ (424.24): C, 70.76; H, 7.84. Found: C, 70.26; H, 7.75.

***(1S,6R,8R)*-8-(4-Methoxyphenyl)-3-(4-octyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (9d):** yield 63%; mp 90.1°C; $[\alpha]_D^{20}$ + 21.0 (*c* 0.1, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H, $J_{H,H}$ = 7.0 Hz, $CH_3$), 1.25–1.39 (m, 8H, $CH_2$), 1.45 (m, 2H, $CH_2$), 1.72–1.92 (m, 4H, H-9, H-10, $CH_2$), 2.04 (m, 1H, H-9), 2.38 (m, 1H, H-10), 3.61 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 5.1 Hz, H-6), 3.87 (ddd, 1H, $J_{1,10ax}$ = 10.7, $J_{1,6}$ = 9.2, $J_{1,10eq}$ = 4.6 Hz, H-1), 3.94 (dd, 1H, $J_{5a,5b}$ = 10.2, $J_{5a,6}$ = 10.2 Hz, H-5a), 3.97 (t, 2H, $J_{H,H}$ = 6.6 Hz, $OCH_2$), 4.24 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.47 (dd, 1H, $J_{8,9ax}$ = 10.7, $J_{8,9eq}$ = 2.0 Hz, H-8), 6.79 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 6.87 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.23 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$); $^{13}C$ (50 MHz, $CDCl_3$) δ 14.5, 23.1, 26.5, 29.6, 29.7, 29.8, 31.5, 32.2, 32.3, 65.3, 68.2, 72.0, 76.5, 80.2, 114.2, 115.7, 127.9, 134.2, 136.2, 155.6, 161.9.

Anal. Calcd for $C_{27}H_{37}BO_5$ (452.40): C, 71.68; H, 8.24. Found: C, 70.99; H, 8.16.

***(1S,6R,8R)*-8-(4-Methoxymethoxyphenyl)-3-(4-methoxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (10a):** yield 57%; mp 137.2°C; $[\alpha]_D^{20}$ + 30.0 (*c* 0.5, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.68–1.92 (m, 2H, H-9), 2.04 (m, 1H, H-10),





MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

2.38 (m, 1H, H-10), 3.46 (s, 3H, $OCH_3$), 3.72 (ddd, 1H, $J_{6,5a}$ = 10.3, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 5.1 Hz, H-6), 3.82 (s, 3H, $OCH_3$), 3.87 (m, 1H, H-1), 3.95 (dd, 1H, $J_{5a,5b}$ = 10.3, $J_{5a,6}$ = 10.3 Hz, H-5a), 4.24 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.48 (dd, 1H, $J_{8,9a}$ = 10.7, $J_{8,9eq}$ = 1.9 Hz, H-8), 5.17 (s, 2H, $OCH_2O$), 6.89 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.04 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.28 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.75 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 31.2, 32.9, 55.1, 56.0, 64.9, 71.6, 76.1, 79.8, 94.5, 113.3, 116.3, 127.3, 135.0, 135.8, 156.9, 162.0.

Anal. Calcd for $C_{21}H_{25}BO_6$ (384.24): C, 65.64; H, 6.56. Found: C, 65.43; H, 6.49.

***(1S,6R,8R)*-3-(4-Butyloxyphenyl)-8-(4-methoxymethoxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (10b):** yield 64%; mp 97.7°C; $[\alpha]_D^{20}$ + 19.6 (*c* 0.4, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.97 (t, 3H, $J_{H,H}$ = 7.4 Hz, $CH_3$), 1.47 (m, 2H, $CH_2$), 1.70–1.90 (m, 4H, H-9, $CH_2$), 2.03 (m, 1H, H-10), 2.38 (m, 1H, H-10), 3.46 (s, 3H, $OCH_3$), 3.61 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 5.1 Hz, H-6), 3.84–4.00 (m, 4H, H-1, H-5a, $OCH_2$), 4.23 (dd, 1H, $J_{5a,5b}$ = 10.7, $J_{5a,6}$ = 5.1 Hz, H-5b), 4.48 (dd, 1H, $J_{8,9ax}$ = 11.2, $J_{8,9eq}$ = 2.0 Hz, H-8), 5.16 (s, 2H, $OCH_2O$), 6.86 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.02 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.27 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$), 7.73 (d, 2H, $J_{H,H}$ = 8.6 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 13.9, 19.3, 31.1, 31.3, 32.9, 55.4, 64.8, 67.4, 71.5, 76.0, 79.7, 94.4, 113.7, 116.2, 127.3, 134.9, 135.7, 156.9, 161.5.

Anal. Calcd for $C_{24}H_{31}BO_6$ (426.32): C, 67.62; H, 7.33. Found: C, 67.26; H, 7.23.

***(1S,6R,8R)*-3-(4-Hexyloxyphenyl)-8-(4-methoxymethoxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (10c):** yield 66%; mp 96.4°C; $[\alpha]_D^{20}$ + 22.2 (*c* 0.5, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J_{H,H}$ = 6.6 Hz, $CH_3$), 1.27–1.37 (m, 4H, $CH_2$), 1.45 (m, 2H, $CH_2$), 1.72–1.92 (m, 4H, H-9, $CH_2$), 2.04 (m, 1H, H-10), 2.38 (m, 1H, H-10), 3.47 (s, 3H, $OCH_3$), 3.63 (ddd, 1H, $J_{6,5a}$ = 10.3, $J_{6,1}$ = 9.9, $J_{6,5b}$ = 5.5 Hz, H-6), 3.84–4.02 (m, 4H, H-1, H-5a, $OCH_2$), 4.24 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.5 Hz, H-5b), 4.50 (dd, 1H, $J_{8,9ax}$ = 9.9, $J_{8,9eq}$ = 1.8 Hz, H-8), 5.17 (s, 2H, $OCH_2O$), 6.86 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.02 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.29 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 13.9, 25.6, 25.7, 29.2, 31.6, 32.0, 33.1, 55.9, 64.8, 67.4, 71.5, 76.0, 79.7, 94.4, 113.7, 116.2, 127.3, 134.9, 135.7, 156.9, 161.5.

Anal. Calcd for $C_{26}H_{35}BO_6$ (454.38): C, 68.73; H, 7.76. Found: C, 68.36; H, 7.77.

***(1S,6R,8R)*-8-(4-Methoxymethoxyphenyl)-3-(4-octyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (10d):** yield 62%; mp 71.7°C; $[\alpha]_D^{20}$ + 20.2 (*c* 0.4, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 7.0 Hz, $CH_3$), 1.25–1.38 (m, 8H, $CH_2$), 1.44 (m, 2H, $CH_2$), 1.72–1.92 (m, 4H, H-9, $CH_2$), 2.04 (m, 1H, H-10), 2.38 (m, 1H, H-10), 3.47 (s, 3H, $OCH_3$), 3.63 (ddd, 1H, $J_{6,5a}$ = 10.3, $J_{6,1}$ = 9.6, $J_{6,5b}$ = 5.1 Hz, H-6), 3.84–4.02 (m, 4H, H-1, H-5a, $OCH_2$), 4.24 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.48 (bd, 1H, $J_{8,9ax}$ = 10.1 Hz, H-8), 5.17 (s, 2H, $OCH_2O$), 6.87 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.02 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.28 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.73 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 14.5, 23.0, 26.4, 29.6, 29.7, 29.8, 31.3, 32.2, 33.5, 55.9, 64.8, 67.4, 71.5, 76.0, 79.7, 94.4, 113.7, 116.2, 127.3, 134.9, 135.7, 156.9, 161.9.

Anal. Calcd for $C_{28}H_{39}BO_6$ (482.43): C, 69.71; H, 8.15. Found: C, 69.54; H, 8.25.





Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

***(1S,6R,8R)*-8-(4-Dimethylaminophenyl)-3-(4-methoxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (11a):** yield 57%; mp 188.2°C; $[\alpha]_D^{20}$ + 25.1 (*c* 0.5, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.68–1.92 (m, 2H, H-9), 2.00 (m, 1H, H-10), 2.38 (m, 1H, H-10), 2.93 (s, 6H, $NMe_2$), 3.62 (ddd, 1H, $J_{6,5a}$ = 10.3, $J_{6,1}$ = 9.6, $J_{6,5b}$ = 5.1 Hz, H-6), 3.82 (s, 3H, $OCH_3$), 3.89 (m, 1H, H-1), 3.96 (dd, 1H, $J_{5a,5b}$ = 10.3, $J_{5a,6}$ = 10.3 Hz, H-5a), 4.24 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.45 (dd, 1H, $J_{8,9ax}$ = 10.7, $J_{8,9eq}$ = 2.2 Hz, H-8), 6.72 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 6.89 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.24 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.76 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 31.2, 32.9, 55.1, 55.4, 58.5, 64.9, 71.6, 76.1, 79.8, 113.3, 113.7, 127.3, 135.7, 135.8, 159.3, 161.5.

Anal. Calcd for $C_{21}H_{26}BNO_4$ (367.25): C, 68.68; H, 7.14. Found: C, 68.26; H, 7.01.

***(1S,6R,8R)*-3-(4-Butyloxyphenyl)-8-(4-dimethylaminophenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (11b):** yield 63%; mp 147.2°C; $[\alpha]_D^{20}$ + 22.3 (*c* 0.3, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.98 (t, 3H, $J_{H,H}$ = 7.6 Hz, $CH_3$), 1.50 (m, 2H, $CH_2$), 1.69–1.80 (m, 3H, H-9, $CH_2$), 1.88 (m, 1H, H-9), 2.01 (m, 1H, H-10), 2.36 (m, 1H, H-10), 2.94 (s, 6H, $NMe_2$), 3.61 (ddd, 1H, $J_{6,5a}$ = 10.2, $J_{6,1}$ = 9.2, $J_{6,5b}$ = 5.1 Hz, H-6), 3.82–4.02 (m, 4H, H-1, H-5a, $OCH_2$), 4.23 (dd, 1H, $J_{5b,5a}$ = 10.2, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.45 (dd, 1H, $J_{8,9ax}$ = 11.2, $J_{8,9eq}$ = 2.0 Hz, H-8), 6.74 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$), 6.88 (d, 2H, $J_{H,H}$ = 8.7 Hz, $H_{arom}$), 7.23 (d, 2H, $J_{H,H}$ = 8.7 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.1 Hz, $H_{arom}$); $^{13}C$ (100 MHz, $CDCl_3$) δ 13.9, 19.2, 31.1, 31.3, 35.5, 40.8, 64.9, 67.4, 71.6, 76.0, 80.1, 113.7, 113.8, 127.3, 133.6, 135.7, 159.2, 161.5.

Anal. Calcd for $C_{24}H_{32}BNO_4$ (409.34): C, 70.42; H, 7.88. Found: C, 69.99; H, 7.63.

***(1S,6R,8R)*-8-(4-Dimethylaminophenyl)-3-(4-hexyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (11c):** yield 62%; mp 141.5°C; $[\alpha]_D^{20}$ + 24.2 (*c* 0.4, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J_{H,H}$ = 7.4 Hz, $CH_3$), 1.29–1.37 (m, 4H, $CH_2$), 1.46 (m, 2H, $CH_2$), 1.70–1.92 (m, 4H, H-9, $CH_2$), 2.02 (m, 1H, H-10), 2.37 (m, 1H, H-10), 2.93 (s, 6H, $NMe_2$), 3.62 (ddd, 1H, $J_{6,5a}$ = 10.3, $J_{6,1}$ = 9.6, $J_{6,5b}$ = 5.1 Hz, H-6), 3.82–4.02 (m, 4H, H-1, H-5a, $OCH_2$), 4.23 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.45 (dd, 1H, $J_{8,9ax}$ = 11.0, $J_{8,9eq}$ = 1.8 Hz, H-8), 6.72 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 6.88 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.23 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.5 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 14.1, 22.6, 25.8, 29.2, 31.6, 32.0, 33.1, 64.9, 67.8, 71.6, 76.0, 80.0, 113.7, 127.2, 128.5, 135.7, 159.3, 161.5.

Anal. Calcd for $C_{26}H_{36}BNO_4$ (437.39): C, 71.40; H, 8.30. Found: C, 71.14; H, 8.48.

***(1S,6R,8R)*-8-(4-Dimethylaminophenyl)-3-(4-octyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (11d):** yield 58%; mp 110.7°C; $[\alpha]_D^{20}$ + 22.3 (*c* 0.3, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H, $J_{H,H}$ = 7.0 Hz, $CH_3$), 1.20–1.38 (m, 8H, $CH_2$), 1.45 (m, 2H, $CH_2$), 1.72–1.92 (m, 4H, H-9, $CH_2$), 2.01 (m, 1H, H-10), 2.38 (m, 1H, H-10), 2.94 (s, 6H, $NMe_2$), 3.61 (ddd, 1H, $J_{6,5a}$ = 10.3, $J_{6,1}$ = 9.9, $J_{6,5b}$ = 5.1 Hz, H-6), 3.82–4.02 (m, 4H, H-1, H-5a, $OCH_2$), 4.23 (dd, 1H, $J_{5b,5a}$ = 10.3, $J_{5b,6}$ = 5.1 Hz, H-5b), 4.45 (dd, 1H, $J_{8,9ax}$ = 11.0, $J_{8,9eq}$ = 2.9 Hz, H-8), 6.71 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 6.88 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$), 7.23 (d, 2H, $J_{H,H}$ = 8.8 Hz,

$H_{arom}$), 7.74 (d, 2H, $J_{H,H}$ = 8.8 Hz, $H_{arom}$); $^{13}C$ (75 MHz, $CDCl_3$) δ 14.1, 22.7, 26.0, 29.3, 29.4, 31.2, 31.8, 32.5, 64.9, 67.8, 71.6, 76.0, 80.0, 113.7, 127.2, 128.5, 135.7, 159.3, 161.5.

Anal. Calcd for $C_{28}H_{40}BNO_4$ (465.44): C, 72.26; H, 8.66. Found: C, 71.68; H, 8.37.

## ACKNOWLEDGMENTS

B. B. thanks the French Ministry of Education for a fellowship. Financial support by DAAD/Procope Programme is gratefully acknowledged.

## REFERENCES

1. Goodby, J.W. Chirality in liquid crystals. J. Mater. Chem. **1991**, *1* (3), 307–318.
2. Vill, V. *LiqCryst 3.3—Database of Liquid Crystals*; LCI Publisher: Hamburg, 1999.
3. Vill, V.; Tunger, H.-W.; Stegemeyer, H.; Diekmann, K. Sign inversion of the helical pitch in carbohydrate-based liquid crystals. Tetrahedron: Asymmetry **1994**, *5* (12), 2443–2446.
4. Vill, V.; Tunger, H.-W. Liquid crystals derived from carbohydrates: synthesis and properties of oxadecalin compounds. Liebigs Ann. **1995**, (6), 1055–1059.
5. Vill, V.; Tunger, H.-W. Carbohydrate-based liquid crystals: new compounds showing reentrant TGBA and cholesteric phases and dopant-induced TGBA, SA and SC* phases. J. Chem. Soc., Chem. Commun. **1995**, (10), 1047–1048.
6. Vill, V.; Tunger, H.-W.; Hensen, K.; Stegemeyer, H.; Diekmann, K. Cholesteric helix inversion: novel nitro compounds showing unusual changes of the cholesteric helical pitch. Liq. Cryst. **1996**, *20* (4), 449–452.
7. Vill, V.; Tunger, H.-W.; von Minden, H.M. Structural variation of liquid crystalline trioxadecalins. J. Mater. Chem. **1996**, *6* (5), 739–745.
8. Vill, V.; Tunger, H.-W.; Peters, D. Re-entrant and induced mesophases: mixed systems showing re-entrant TGBA and re-entrant cholesteric phases. Liq. Cryst. **1996**, *20* (5), 547–552.
9. Vill, V.; von Minden, H.M.; Bruce, D.W. Cholesteric helix inversion: investigations on the influence of the terminal group on the inversion of the helical pitch in trioxadecalins. J. Mater. Chem. **1997**, *7* (6), 893–899.
10. Bertini, B.; Moineau, C.; Sinou, D.; Gesekus, G.; Vill, V. Stereospecific synthesis of new trioxadecalin-derived liquid crystals bearing halogen substituents on the phenyl ring. Eur. J. Org. Chem. **2001**, (2), 375–381.
11. Moineau, C.; Bolitt, V.; Sinou, D. Synthesis of α- and β-*C*-aryl $\Delta^2$-glycopyranosides from p-tert-butylphenyl $\Delta^2$-glycopyranosides via Grignard reagents. J. Org. Chem. **1998**, *63* (3), 582–591.
12. Claisen, L.; Eisleb, O.; Kremers, F. Rearrangement of phenyl allyl ethers into the isomeric allyl phenols. Liebigs Ann. **1919**, *418*, 69–120.





Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

13. Leebrick, J.R.; Ramsden, H.E. Synthesis and reactions of *p*-vinylphenylmagnesium chloride. J. Org. Chem. **1958**, *23*, 935–936.
14. Letsinger, R.L.; Hamilton, S.B. Organoboron compounds. X. Popcorn polymers and highly cross-linked vinyl polymers containing boron. J. Am. Chem. Soc. **1959**, *81*, 3009–3012.
15. Venanzi, L.M. Tetrahedral nickel(II) complexes and the factors determining their formation. I. Bistriphenylphosphine nickel-(II) compounds. J. Chem. Soc. **1958**, 719–724.

Received February 7, 2003
Accepted August 8, 2003





MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016