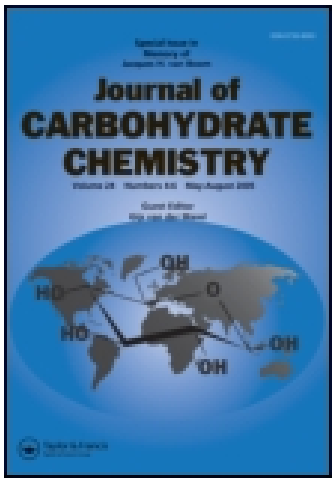

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lcar20

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Published online: 16 Aug 2006.

To cite this article: Bruno Bertini , Christophe Moineau , Denis Sinou & Volkmar Vill (2001) ENANTIOPURE TRIOXADECALIN DERIVED LIQUID CRYSTALS: INFLUENCE OF PHENYL SUBSTITUTION ON THE MESOGENIC PROPERTIES, Journal of Carbohydrate Chemistry, 20:3-4, 315-327, DOI: 10.1081/CAR-100104867

To link to this article: http://dx.doi.org/10.1081/CAR-100104867

J. CARBOHYDRATE CHEMISTRY, 20(3&4), 315–327 (2001)

ENANTIOPURE TRIOXADECALIN DERIVED LIQUID CRYSTALS: INFLUENCE OF PHENYL SUBSTITUTION ON THE MESOGENIC PROPERTIES

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ABSTRACT

Nickel(0)-catalyzed reaction of pseudo-glucal **1** with Grignard reagents derived from bromobenzene and 1-bromo-4-phenylbenzene gives the corresponding β-*C*-aryl glycosides **2**. Desilylation and hydrogenation of **2** leads to saturated β-*C*-aryl glycosides **4**, which can be used as chiral intermediates in the synthesis of chiral liquid crystals. The combination with *p*-alkoxy-substituted benzaldehyde leads to compounds **5**–**6**. Alternatively, reaction with *p*-alkoxy-substituted phenylboronic acids gives the bora analogues **7**–**9**. The mesogenic properties of these compounds are strongly influenced by the presence of an additional phenyl ring in the molecule.

INTRODUCTION

During the last decade, chirality has become one of the most important and complex topics in liquid crystal research.[1] Effectively, molecular asymmetry imparts chirality to liquid crystalline phases and this has led to a variety of technical applica-

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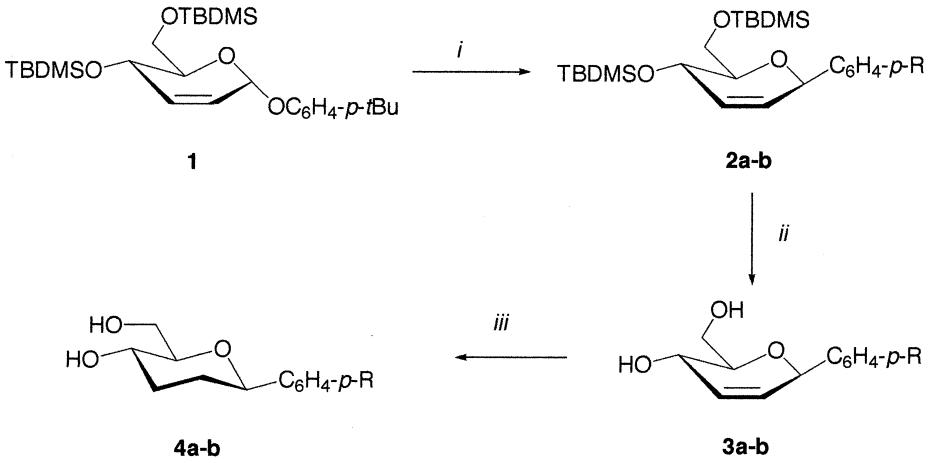
tions for chiral liquid crystals. Today, 16,000 among the 80,000 mesogenic known compounds are chiral,[2] with most of them having a chiral center in the flexible wing, which induces the chirality by steric hindrance and disturbs the mesogenic order.

Vill and coworkers[3] tried to separate chiral effects from mesogenic effects by the isosteric replacement of methylen units with oxygen atoms in conformationally rigid units. For this purpose they prepared new liquid crystals bearing a chiral trioxadecalin core, and found that these compounds exhibited interesting chiral effects such as cholesteric helix inversion, double inversion of the helical twist sense, and re-entrant TGB_A phases. However, all substrates studied had the alkoxy-chain directly bound to the phenyl ring situated on the pyranosyl moiety. We recently published the synthesis of a homologous series of trioxadecalin derivatives bearing terminal halogen and trifluoromethyl groups on the para position of the aromatic ring, and *p*-alkoxysubstituents on the para position of the phenyl ring directly bound to the dioxolane moiety, and examined the influence of these substituents on the mesogenic properties of these compounds.[4] In the continuation of this work, we present in this paper the influence of a biphenyl versus a phenyl group on the mesogenic properties of the related compounds.

RESULTS AND DISCUSSION

The building block **4** for the synthesis of the new liquid crystals bearing a chiral trioxadecalin system was prepared according to Scheme 1. *p-tert*-Butylphenyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1**) was synthesized following the procedure previously described starting from commercially available tri-*O*-acetyl-D-glucal.[5] Reaction of the Grignard reagent,



1 **2a-b** **3a-b** **4a-b**

a R = H ; **b** R = C_6H_5

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

Scheme 1.

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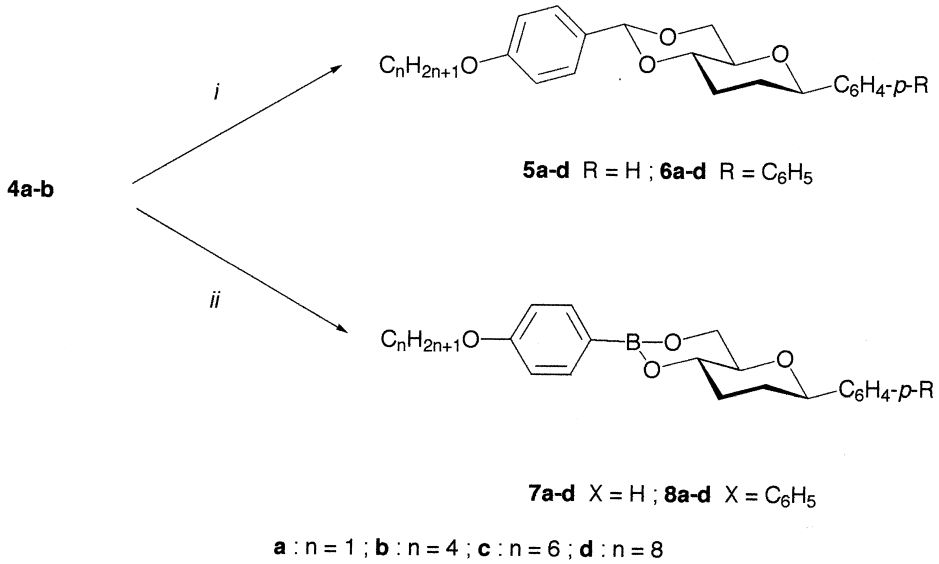
prepared from bromobenzene or 1-bromo-4-phenylbenzene, with the unsaturated carbohydrate **1** in the presence of a catalytic amount of $NiCl_2$(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane] in tetrahydrofuran at −40 °C gave regio- and stereospecifically the β-*C*-arylglycosides **2a** and **2b** in 83% [5] and 71% yields, respectively.

The desilylation of compounds **2a** and **2d** was mediated by hydrated tetrabutylammonium fluoride in tetrahydrofuran to give the unsaturated diols **3a** and **3b** in 75% and 90% yields, respectively. These unsaturated diols **3a** and **3b** were hydrogenated at atmospheric pressure in the presence of [Rh(COD)(dppb)]ClO_4 [COD: 1,5-cyclooctadiene; dppb : 1,4-bis(diphenylphosphino)butane] as the catalyst to give the corresponding saturated diols **4a** and **4b** in 95% and 90% yields, respectively.

The conversion of diols **4a** and **4b** to trioxadecalins **5a-d** and **6a-d** was carried out with the corresponding dimethyl acetals of 4-alkoxybenzaldehyde in an acid-catalyzed transacetalization reaction. The methanol formed was distilled off to shift the equilibrium of the reaction (Scheme 2). The boronic acid derivatives **7a-d and 8a-d** were readily obtained from diols **4a** and **4b** and the appropriate arylboronic acid; the water formed was removed by azeotropic coevaporation with toluene. All the products were recrystallized from ethanol and gave satisfactory elemental analysis.

The mesomorphic properties of compounds **5–8** are summarized in Table 1. The melting points of the trioxadecalins **5a-d** decrease with increasing chain



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

Scheme 2.

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Table 1. Mesomorphism of Compounds **6–9**[a]

Compound	R	n	Transition Temperatures [°C]					
5a	H	1	C_2 109.8	C_1 126.0			N* 130.3	I
5b	H	4	C_2 112.0	C_1 124.2			N* 128.3	I
5c	H	6		C 113.5			N* 113.6	I
5d	H	8	C_2 105.0	C_1 111.5			N* 111.6	I
6a	C_6H_5	1		C 175.2			N* 236.0	I
6b	C_6H_5	4		C 185.6			N* 222.0	I
6c	C_6H_5	6		C_1 174.8			N* 202.4	I
6d	C_6H_5	8		C_1 169.4	S_A 175.3	TGB_A 175.6	N* 201.2	BP
7a	H	1		C 147.8				I
7b	H	4		C 122.5	S_A 89.8		N* 98.2	BP_{UV}
7c	H	6		C 95.7	S_A 97.5		N* 103.7	BP
7d	H	8		C 99.7	S_A 103.6			I
8a	C_6H_5	1		C 184.5			N* 232.7	BP_{UV}
8b	C_6H_5	4		C 179.6			N* 229.6	BP_{UV}
8c	C_6H_5	6	C_2 150.0	C 156.5	S_A 190.5		N* 226.8	BP_{UV}
8d	C_6H_5	8		C 141.5	S_A 191.9	TGB_A 191.4	N* 207.0	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.

length, and they exhibit only a cholesteric phase (N*). Also the pitch length decreases in compound **5a** and **5d** with increasing lateral chain length. The presence of an additional phenyl ring in compounds **6a**-**d** results in significantly higher clearing temperatures than those of compounds **5a**-**d**. Also, a broader enantiotropic cholesteric phase is observed for **6a**-**d**, and compound **6d** showed an additional smectic A phase (S_A), a twist grain boundary phase (TGB_A) and a blue phase (BP), which is quite unusual in the trioxadecaline series.

The replacement of a tetrahedral carbon atom by a planar boron atom induces quite different mesogenic properties in the trioxaborabicyclo compounds. No mesogenic property is found for compound **7a**, which could be due to a lack of flexibility within the molecule. Compounds **7b**-**d** show a smectic A phase, that is monotropic for **8b**. A cholesteric phase is observed only for compounds **7b** and **7c**; this phase is observed to be monotropic for **8b**. A cubic blue phase is observed for compounds **7b** and **7c**, probably due to the high asymmetry of the mesophase.

Trioxaborabicyclo compounds **8a**-**d** display higher clearing temperatures and broader mesophases than the analogues **7a**-**d**; a temperature decrease with increasing chain length is observed. A monotropic cholesteric phase is observed for compounds **8a** and **8b**, whereas compounds **8c** and **8d** exhibit an additionnal smectic A phase. Compound **8d** shows a cubic TGB_A phase. Compounds **8a**–**8d** also show a blue phase.

CONCLUSIONS

Condensation of various aryl Grignard reagents derived from bromobenzene or 1-bromo-4-phenylbenzene with *p-tert*-butylphenyl 4,6-di-*O*-(*tert*-

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butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside in the presence of a nickel catalyst gives the corresponding β-*C*-aryl-Δ^2-glycopyranosides, which are the key intermediates for the synthesis of chiral trioxa- and trioxaboradecalin derivatives. These compounds show mesogenic properties that are strongly influenced by the presence of an additional phenyl ring in the molecule. Higher clearing temperatures are observed in this case, as well as broader enantiotropic cholesteric phases, smectic A phases, TGB_A phases and blue-phases.

EXPERIMENTAL

General Methods. 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 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, 300, or 400 MHz, ^{13}C: 50, 75, or 100 MHz) were recorded on a Bruker AMX-200, AMX-300, 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 procedure: *p-tert*-butylphenyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1**),[5] [4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl]benzene (**2a**),[5] *p*-alkoxybenzaldehyde dimethylacetals,[6] phenyl boronic acids,[7] $NiCl_2$(dppe).[8]

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 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 reduced pressure, the residue was purified by column chromatography using the indicated solvents as the eluent to give the corresponding *C*-glycoside **2**.

4-[4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl]biphenyl (2b) . Yield 71%; R_f 0.27 (petroleum ether/dichloromethane 4/1); $[\alpha]_D^{20}$ +126.8 (*c* 1.1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.01 (s, 3H, $SiCH_3$), 0.05 (s, 3H, $SiCH_3$), 0.14 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.91

(s, 9H, $SiCMe_3$), 0.94 (s, 9H, $SiCMe_3$),3.52 (ddd, J = 8.4, 4.5, 2.1 Hz, 1H, H-5), 3.85 (dd, J = 11.4, 4.5 Hz, 1H, H-6), 3.94 (dd, J = 11.4, 2.1 Hz, 1H, H-6), 4.39 (dd, J = 8.4, 2.9 Hz, 1H, H-4), 5.13 (d, J = 2.9 Hz, 1H, H-1), 5.44 (d, J = 10.2 Hz, 1H, H-2), 5.54 (d, J = 10.2 Hz, 1H, H-3), 7.33–7.48 (m, 5H, H_{arom}), 7.54–7.62 (m, 4H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ −5.1, −5.0, −4.2, 18.1, 18.5, 25.9, 26.0, 33.7, 63.0, 63.6, 77.1, 80.7, 127.1, 127.2, 127.3, 127.4, 128.8, 130.0, 130.5, 140.4, 140.6, 141.1.

Standard Procedure for Preparation of Unsaturated *C*-Arylglycosides 3. The unsaturated *C*-aryl glycoside **2** (0.43 mmol) was stirred in THF (5 mL) at room temperature in the presence of tetrabutylammonium chloride 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 **3** which was purified by flash-chromatography on silica.

(2,3-Dideoxy-β-D-*erythro*-hex-2-enopyranosyl)benzene (3a). Yield 75%; R_f 0.40 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ +192.1 (*c* 0.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.94 (s, 2H, OH), 3.59 (ddd, J = 8.7, 5.2, 4.1 Hz, 1H, H-5), 3.86 (dd, J = 11.6, 5.2 Hz, 1H, H-6), 3.96 (dd, J = 11.6, 4.1 Hz, 1H, H-6), 4.35 (ddd, J = 8.7, 1.6, 1.2 Hz, 1H, H-4), 5.18 (bs, 1H, H-1), 5.84 (d, J = 10.4 Hz, 1H, H-2), 5.92 (d, J = 10.4 Hz, 1H, H-3), 7.34 (bs, 5H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ 63.3, 64.3, 77.5, 79.5, 127.4, 128.4, 128.7, 129.0, 131.1.

Anal. Calcd for $C_{12}H_{14}O_3$ (206.24) : C, 69.89; H, 6.84%. Found: C, 69.81; H, 6.77%.

4-(2,3-Dideoxy-β-D-*erythro*-hex-2-enopyranosyl)biphenyl (3b). Yield 90%; R_f 0.37 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ +193.7 (*c* 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.80 (bs, 2H, OH), 3.61 (ddd, J = 8.7, 5.3, 4.1 Hz, 1H, H-5), 3.87 (dd, J = 11.6, 5.3 Hz, 1H, H-6), 3.97 (dd, J = 11.6, 4.1 Hz, 1H, H-6), 4.37 (ddd, J = 8.7, 3.0, 1.4 Hz, 1H, H-4), 5.22 (bs, 1H, H-1), 5.88 (d, J = 10.3 Hz, 1H, H-2), 5.95 (dd, J = 10.3, 1.4 Hz, 1H, H-3), 7.31–7.48 (m, 5H, H_{arom}), 7.55–7.60 (m, 4H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ 63.4, 64.5, 77.2, 79.5, 127.2, 127.5, 127.8,128.8, 129.1, 131.1, 139.3, 140.8, 141.4,161.9.

Anal. Calcd for $C_{18}H_{18}O_3$ (282.34): C, 76.57; H, 6.43%. Found: C, 75.81; H, 6.48%.

Standard Procedure for Preparation of Saturated *C*-Arylglycosides 4. The unsaturated diol **3** 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)] (0.02 mmol). After 24 h, filtration of the solution 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)benzene (4a). Yield 95%; R_f 0.38 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ +62.5 (*c* 1.5, $CHCl_3$); ^1H NMR

(200 MHz, $CDCl_3$) δ 1.63–1.75 (m, 4H, OH, H-3_{ax}, H-2_{ax}), 1.98 (m, 1H, H-2_{eq}), 2.18 (m, 1H, H-3_{eq}), 3.42 (ddd, J = 9.2, 5.0, 4.3 Hz, 1H, H-5), 3.71 (ddd, J = 10.2, 9.2, 4.9 Hz, 1H, H-4), 3.85 (dd, J = 11.6, 5.0 Hz, 1H, H-6), 3.95 (dd, J = 11.6, 4.3 Hz, 1H, H-6), 4.43 (dd, J = 10.6, 2.2 Hz, 1H, H-1), 7.28–7.35 (m, 5H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ 32.9, 33.0, 63.5, 67.3, 79.5, 81.9, 126.0, 127.7, 128.4.

Anal. Calcd for $C_{12}H_{16}O_3$(208.26) : C, 69.21; H, 7.74%. Found: C, 68.95; H, 7.80%.

4-(2,3-Dideoxy-β-D-*erythro*-hexanopyranosyl)biphenyl (4b). Yield 90%; R_f 0.34 (petroleum ether/ethyl acetate 1/4); $[\alpha]_D^{20}$ +76.8 (*c* 0.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.57–1.88 (m, 4H, OH, H-3_{ax}, H-2_{ax}), 2.02 (m, 1H, H-2_{eq}), 2.27 (m, 1H, H-3_{eq}), 3.45 (ddd, J = 9.2, 5.0, 4.5 Hz, 1H, H-5), 3.75 (ddd, J = 10.2, 9.2, 4.8 Hz, 1H, H-4), 3.87 (dd, J = 11.5, 5.0 Hz, 1H, H-6), 3.97 (dd, J = 11.5, 4.5 Hz, 1H, H-6), 4.47 (dd, J = 10.5, 2.2 Hz, 1H, H-1), 7.34–7.48 (m, 5H, H_{arom}), 7.55–7.60 (m, 4H, H_{arom}); ^{13}C (50 MHz, $CDCl_3$) δ 34.4, 34.8, 64.0, 67.6, 80.7, 84.8, 127.9, 128.0, 128.2, 128.5, 130.1, 141.8, 142.5, 143.3.

Anal. Calcd for $C_{18}H_{20}O_3$ (284.36): C, 76.03; H, 7.09%. Found: C, 75.75; H, 7.13%.

Standard Procedure for Preparation of Compounds 5–6. 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 complete reaction. The solvent was removed in vacuo (10 hPA) and 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 **5–6**.

***(1S,3R,6R,8R)*-8-Phenyl-3-(4′-methyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (5a).** Yield 28%; mp 126.0 °C; $[\alpha]_D^{20}$ +28.0 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.50–1.71 (m, 3H, 2 × H-9, H-10), 1.98 (m, 1H, H-10), 3.26 (s, 3H, OCH_3), 3.36 (m, 1H, H-1), 3.48 (ddd, J = 10.2, 9.6, 4.6 Hz, 1H, H-6), 3.69 (dd, J = 10.2, 10.2 Hz, 1H, H-5), 4.16 (bd, J = 10.7 Hz, 1H, H-8), 4.31 (dd, J = 10.2, 4.6 Hz, 1H, H-5), 5.50 (s, 1H, H-3), 6.83 (d, J = 8.1 Hz, 2H, H_{arom}), 7.10–7.29 (m, 5H, H_{arom}), 7.64 (d, J = 8.1 Hz, 2H, H_{arom}); ^{13}C (100 MHz, $CDCl_3$) δ 30.0, 34.2, 55.1, 70.1, 74.8, 78.7, 80.0, 102.4, 114.1, 126.4, 128.0, 128.5, 128.7, 128.8, 131.8, 138.2, 141.8, 160.8.

Anal. Calcd for $C_{20}H_{22}O_4$ (326.39): C, 73.60; H, 6.79%. Found: C, 73.35; H, 6.48%.

***(1S,3R,6R,8R)*-8-Phenyl-3-(4′-butyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (5b).** Yield 44%; mp 124.2 °C; $[\alpha]_D^{20}$ +25.7 (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7.6 Hz, 3H, CH_3), 1.32 (m, 2H, CH_2), 1.50–1.72 (m, 5H, CH_2, H-9, 2 × H-10), 1.95 (m, 1H, H-9), 3.36 (ddd, J = 10.7,

9.7, 4.6 Hz, 1H, H-1), 3.49 (ddd, J = 10.2, 9.7, 4.6 Hz, 1H, H-6), 3.58 (t, J = 6.6 Hz, 2H, OCH_2), 3.71 (dd, J = 10.2, 10.2 Hz, 1H, H-5), 4.16 (bd, J = 10.2 Hz, 1H, H-8), 4.34 (dd, J = 10.2, 4.6 Hz, 1H, H-5), 5.51 (s, 1H, H-3), 6.88 (d, J = 8.1 Hz, 2H, H_{arom}), 7.10–7.21 (m, 3H, H_{arom}), 7.28 (d, J = 8.1 Hz, 2H, H_{arom}), 7.69 (d, J = 8.1 Hz, 2H, H_{arom}); ^{13}C (100 MHz, $CDCl_3$) δ 14.3, 19.9, 30.0, 32.0, 34.2, 67.9, 70.1, 74.8, 78.7, 80.0, 102.4, 114.7, 126.5, 128.1, 128.5, 128.7, 128.8, 131.6, 138.2, 143.1, 160.5.

Anal. Calcd for $C_{23}H_{28}O_4$ (368.48): C, 74.97; H, 7.66%. Found: C, 75.04; H, 7.53%.

***(1S,3R,6R,8R)*-8-Phenyl-3-(4′-hexyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (5c).** Yield 56%; mp 113.5 °C; $[\alpha]_D^{20}$ +24.5 (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, J = 6.6 Hz, 3H, CH_3), 1.12–1.32 (m, 6H, CH_2), 1.48–1.69 (m, 5H, CH_2, H-9, 2 × H-10), 1.94 (m, 1H, H-9), 3.35 (m, 1H, H-1), 3.48 (ddd, J = 10.2, 9.2, 4.6 Hz, 1H, H-6), 3.59 (t, J = 6.1 Hz, 2H, OCH_2), 3.69 (dd, J = 10.2, 10.2 Hz, 1H, H-5), 4.15 (bd, J = 10.7 Hz, 1H, H-8), 4.32 (dd, J = 10.2, 4.6 Hz, 1H, H-5), 5.50 (s, 1H, H-3), 6.89 (d, J = 7.6 Hz, 2H, H_{arom}), 7.08–7.28 (m, 5H, H_{arom}), 7.64 (d, J = 7.6 Hz, 2H, H_{arom}); ^{13}C (100 MHz, $CDCl_3$) δ 14.6, 23.4, 26.4, 29.9, 32.3, 34.2, 68.3, 70.1, 74.8, 78.7, 80.0, 102.5, 114.7, 126.5, 128.0, 128.5, 128.8, 131.6, 138.2, 143.1, 160.5.

Anal. Calcd for $C_{25}H_{32}O_4$ (396.53): C, 75.73; H, 8.13%. Found: C, 75.51; H, 8.09%.

***(1S,3R,6R,8R)*-8-Phenyl-3-(4′-octyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (5d).** Yield 39%; mp 111.5 °C; $[\alpha]_D^{20}$ +23.4 (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 6.1 Hz, 3H, CH_3), 1.162–1.38 (m, 12H, CH_2), 1.48–1.71 (m, 5H, CH_2, H-9, 2 × H-10), 1.94 (m, 1H, H-9), 3.35 (m, 1H, H-1), 3.46 (ddd, J = 10.2, 9.2, 4.6 Hz, 1H, H-6), 3.61 (t, J = 6.1 Hz, 2H, OCH_2), 3.69 (dd, J = 10.2, 10.2 Hz, 1H, H-5), 4.14 (bd, J = 10.2 Hz, 1H, H-8), 4.31 (dd, J = 10.2, 4.6 Hz, 1H, H-5), 5.50 (s, 1H, H-3), 6.91 (d, J = 7.6 Hz, 2H, H_{arom}), 7.08–7.28 (m, 5H, H_{arom}), 7.66 (d, J = 7.6 Hz, 2H, H_{arom}); ^{13}C (100MHz, $CDCl_3$) δ 14.7, 23.4, 26.8, 30.0, 30.6, 34.2, 68.3, 70.1, 74.8, 78.7, 80.0, 102.5, 114.7, 126.5, 128.0, 128.5, 128.8, 131.6, 138.2, 143.1, 160.5.

Anal. Calcd for $C_{27}H_{36}O_4$ (424.58): C, 76.38; H, 8.55%. Found: C, 75.87; H, 8.60%.

***(1S,3R,6R,8R)*-8-Biphenyl-3-(4′-methyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (6a).** Yield 32%; mp 175.2 °C; $[\alpha]_D^{20}$ +34.2 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.50–1.71 (m, 3H, 2 × H-9, H-10), 1.98 (m, 1H, H-10), 3.26 (s, 3H, OCH_3), 3.36 (m, 1H, H-1), 3.48 (ddd, J = 10.2, 9.2, 4.6 Hz, 1H, H-6), 3.69 (dd, J = 10.2, 10.2 Hz, 1H, H-5), 4.16 (bd, J = 10.2 Hz, 1H, H-8), 4.31 (dd, J = 10.2, 4.6 Hz, 1H, H-5), 5.50 (s, 1H, H-3), 6.83 (d, J = 8.1 Hz, 2H, H_{arom}), 7.10–7.29 (m, 9H, H_{arom}), 7.64 (d, J = 8.1 Hz, 2H, H_{arom}); ^{13}C (100 MHz, $CDCl_3$) δ 30.0, 34.2, 55.1, 70.2, 74.9, 78.8, 79.8, 102.5, 114.2, 116.1, 127.0, 127.7, 127.9, 128.5, 128.7, 129.4, 131.8, 138.2, 141.8, 160.8.

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Anal. Calcd for $C_{26}H_{26}O_4$ (402.49): C, 77.59; H, 6.51%. Found: C, 77.23; H, 6.34%.

***(1S,3R,6R,8R)*-8-Biphenyl-3-(4′-butyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (6b).** Yield 46%; mp 186.6 °C; $[\alpha]_D^{20}$ +29.4 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 (t, *J* = 7.6 Hz, 3H, CH_3), 1.26 (m, 2H, CH_2), 1.45–1.72 (m, 5H, CH_2, H-9, 2 × H-10), 1.98 (m, 1H, H-9), 3.36 (ddd, *J* = 10.7, 9.7, 4.6 Hz, 1H, H-1), 3.45–3.59 (m, 3H, H-6, OCH_2), 3.71 (dd, *J* = 10.2, 10.2 Hz, 1H, H-5), 4.19 (bd, *J* = 9.2 Hz, 1H, H-8), 4.32 (dd, *J* = 10.2, 4.6 Hz, 1H, H-5), 5.51 (s, 1H, H-3), 6.88 (d, *J* = 7.6 Hz, 2H, H_{arom}), 7.08–7.21 (m, 3H, H_{arom}), 7.28 (m, 2H, H_{arom}), 7.42–7.49 (m, 4H, H_{arom}), 7.69 (d, *J* = 7.6 Hz, 2H, H_{arom}); ^{13}C (100 MHz, $CDCl_3$) δ 14.3, 19.9, 30.0, 32.0, 34.2, 67.9, 70.1, 74.8, 78.7, 80.0, 102.5, 114.7, 127.0, 127.7, 127.9, 128.5, 129.5, 131.6, 138.2, 143.1, 160.5.

Anal. Calcd for $C_{29}H_{32}O_4$ (444.57): C, 78.35; H, 7.26%. Found: C, 78.16; H, 7.12%.

***(1S,3R,6R,8R)*-8-Biphenyl-3-(4′-hexyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (6c).** Yield 60%; mp 174.8 °C; $[\alpha]_D^{20}$ +27.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J* = 6.6 Hz, 3H, CH_3), 1.19–1.32 (m, 6H, CH_2), 1.43–1.70 (m, 5H, CH_2, H-9, 2 × H-10), 1.98 (m, 1H, H-9), 3.37 (m, 1H, H-1), 3.48 (ddd, *J* = 10.2, 9.2, 4.6 Hz, 1H, H-6), 3.60 (t, *J* = 6.1 Hz, 2H, OCH_2), 3.70 (dd, *J* = 10.2, 10.2 Hz, 1H, H-5), 4.20 (bd, *J* = 9.7 Hz, 1H, H-8), 4.32 (dd, *J* = 10.2, 4.6 Hz, 1H, H-5), 5.50 (s, 1H, H-3), 6.89 (d, *J* = 8.1 Hz, 2H, H_{arom}), 7.11–7.20 (m, 3H, H_{arom}), 7.28 (d, *J* = 7.1 Hz, 2H, H_{arom}), 7.43–7.50 (m, 4H, H_{arom}), 7.66 (d, *J* = 7.6 Hz, 2H, H_{arom}); ^{13}C (100MHz, $CDCl_3$) δ 14.6, 23.3, 26.4, 29.9, 30.0, 32.3, 34.2, 68.3, 70.1, 74.9, 78.8, 79.8, 102.5, 114.7, 126.9, 127.7, 127.8, 128.5, 128.7, 129.5, 131.6, 141.2, 142.1, 160.5.

Anal. Calcd for $C_{31}H_{36}O_4$ (472.63): C, 78.78; H, 7.68%. Found: C, 78.18; H, 7.53%.

***(1S,3R,6R,8R)*-8-Biphenyl-3-(4′-octyloxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane (6d).** Yield 82%; mp 169.4 °C; $[\alpha]_D^{20}$ +27.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.6 Hz, 3H, CH_3), 1.14–1.74 (m, 12H, CH_2), 1.52–1.74 (m, 5H, CH_2, H-9, 2 × H-10), 1.98 (m, 1H, H-9), 3.38 (m, 1H, H-1), 3.51 (ddd, *J* = 10.2, 9.2, 4.6 Hz, 1H, H-6), 3.60 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.71 (dd, *J* = 10.2, 10.2 Hz, 1H, H-5), 4.21 (bd, *J* = 10.7 Hz, 1H, H-8), 4.34 (dd, *J* = 10.2, 4.6 Hz, 1H, H-5), 5.52 (s, 1H, H-3), 6.91 (d, *J* = 8.6 Hz, 2H, H_{arom}), 7.19–7.23 (m, 4H, H_{arom}), 7.30 (d, *J* = 7.6 Hz, 2H, H_{arom}), 7.44–7.50 (m, 3H, H_{arom}), 7.69 (d, *J* = 8.6 Hz, 2H, H_{arom}); ^{13}C (100 MHz, $CDCl_3$) δ 14.7, 23.5, 26.8, 30.0, 30.1, 32.6, 34.2, 68.3, 70.2, 74.9, 78.8, 79.8, 102.5, 114.7, 127.0, 127.7, 128.5, 128.7, 129.5, 131.6, 141.3, 142.1, 160.5.

Anal. Calcd for $C_{33}H_{40}O_4$ (500.68): C, 79.16; H, 8.05%. Found: C, 79.24; H, 8.04%.

Standard Procedure for Preparation of Compounds 7–8. 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 **7–8**.

***(1S,6R,8R)*-8-Phenyl-3-(4′-methyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (7a).** Yield 80%; mp 147.8 °C; $[\alpha]_D^{20}$ +38.9 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72–1.92 (m, 2H, H-9), 2.08 (m, 1H, H-10), 2.39 (dddd, *J* = 11.4, 4.4, 3.7, 3.3 Hz, 1H, H-10), 3.64 (ddd, *J* = 10.3, 9.2, 5.2 Hz, 1H, H-6), 3.82 (s, 3H, OCH_3), 3.89 (ddd, *J* = 10.7, 9.2, 4.4 Hz, 1H, H-1), 3.97 (dd, *J* = 10.3, 10.3 Hz, 1H, H-5), 4.27 (dd, *J* = 10.3, 5.2 Hz, 1H, H-5), 4.55 (dd, *J* = 11.0, 2.2 Hz, 1H, H-8), 6.89 (d, *J* = 8.8 Hz, 2H, H_{arom}), 7.32 (m, 1H, H_{arom}), 7.36 (m, 4H, H_{arom}), 7.76 (d, *J* = 8.8 Hz, 2H, H_{arom}); ^{13}C (75 MHz, $CDCl_3$) δ 31.2, 33.1, 55.1, 64.9, 71.6, 76.1, 80.1, 113.3, 126.0, 127.9, 128.5, 135.9, 141.6, 162.0.

Anal. Calcd for $C_{19}H_{21}O_4B$ (324.19): C, 70.12; H, 6.82%. Found: C, 70.10; H, 6.42%.

***(1S,6R,8R)*-8-Phenyl-3-(4′-butyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (7b).** Yield 63%; mp 122.5 °C; $[\alpha]_D^{20}$ +23.7 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.5 Hz, 3H, CH_3), 1.23 (m, 2H, CH_2), 1.68–1.92 (m, 4H, H-9, CH_2), 2.08 (m, 1H, H-10), 2.37 (m, 1H, H-10), 3.67 (ddd, *J* = 10.3, 9.9, 5.1 Hz, 1H, H-6), 3.85–4.05 (m, 4H, H-1, H-5, OCH_2), 4.26 (dd, *J* = 10.3, 5.1 Hz, 1H, H-5), 4.55 (bd, *J* = 9.9 Hz, 1H, H-8), 6.88 (d, *J* = 7.7 Hz, 2H, H_{arom}), 7.30 (m, 5H, H_{arom}), 7.74 (d, *J* = 7.7 Hz, 2H, H_{arom}); ^{13}C (75 MHz, $CDCl_3$) δ 13.9, 19.3, 31.1, 31.3, 33.1, 64.8, 67.5, 71.5, 76.0, 80.1, 113.8, 125.9, 127.8, 127.9, 128.4, 135.7, 141.5, 161.5.

Anal. Calcd for $C_{22}H_{27}O_4B$ (366.27): C, 72.09; H, 7.73%. Found: C, 72.92; H, 7.37%.

***(1S,6R,8R)*-8-Phenyl-3-(4′-hexyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (7c).** Yield 70%; mp 95.7 °C; $[\alpha]_D^{20}$ +24.5 (*c* 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.6 Hz, 3H, CH_3), 1.30–1.39 (m, 4H, CH_2), 1.46 (m, 2H, CH_2), 1.72–1.92 (m, 4H, H-9, CH_2), 2.07 (m, 1H, H-10), 2.37 (m, 1H, H-10), 3.64 (ddd, *J* = 9.9, 9.6, 5.5 Hz, 1H, H-6), 3.84–4.02 (m, 4H, H-1, H-5, OCH_2), 4.26 (dd, *J* = 10.3, 5.5 Hz, 1H, H-5), 4.54 (dd, *J* = 11.0, 2.2 Hz, 1H, H-8), 6.88 (d, *J* = 8.5 Hz, 2H, H_{arom}), 7.30 (m, 1H, H_{arom}), 7.38 (m, 4H, H_{arom}), 7.74 (d, *J* = 8.5 Hz, 2H, H_{arom}); ^{13}C (75 MHz, $CDCl_3$) δ 14.1, 22.7, 25.8, 29.3, 31.2, 31.7, 33.0, 64.9, 67.8, 71.6, 76.1, 80.1, 113.8, 125.9, 127.8, 127.9, 128.4, 135.7, 141.5, 161.5.

Anal. Calcd for $C_{24}H_{31}O_4B$ (394.32): C, 73.05; H, 7.92%. Found: C, 72.55; H, 7.92%.

***(1S,6R,8R)*-8-Phenyl-3-(4′-octyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (7d).** Yield 68%; mp 99.7 °C; $[\alpha]_D^{20}$ +17.0 (*c* 0.4, $CHCl_3$);

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H, CH_3), 1.23–1.36 (m, 8H, CH_2), 1.46 (m, 2H, CH_2), 1.72–1.92 (m, 4H, H-9, CH_2), 2.08 (m, 1H, H-10), 2.39 (m, 1H, H-10), 3.63 (ddd, J = 10.3, 9.6, 5.1 Hz, 1H, H-6), 3.84–4.02 (m, 4H, H-1, H-5, OCH_2), 4.26 (dd, J = 10.3, 5.1 Hz, 1H, H-5), 4.53 (bd, J = 11.0 Hz, 1H, H-8), 6.88 (d, J = 8.5 Hz, 2H, H_{arom}), 7.30 (m, 1H, H_{arom}), 7.34 (m, 4H, H_{arom}), 7.74 (d, J = 8.5 Hz, 2H, H_{arom}); ^{13}C (75 MHz, $CDCl_3$) δ 14.1, 22.7, 26.1, 29.2, 29.3, 29.4, 31.1, 31.8, 33.1, 64.8, 67.8, 71.5, 76.0, 80.1, 113.8, 125.9, 127.8, 128.5, 135.8, 141.5, 161.5.

Anal. Calcd for $C_{26}H_{35}O_4B$ (422.38): C, 73.89; H, 8.35%. Found: C, 73.59; H, 8.35%.

***(1S,6R,8R)*-8-Biphenyl-3-(4′-methyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (8a).** Yield 80%; mp 184.5 °C; $[\alpha]_D^{20}$ +30.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72–1.92 (m, 2H, H-9), 2.08 (m, 1H, H-10), 2.41 (m, 1H, H-10), 3.66 (ddd, J = 10.3, 9.2, 5.2 Hz, 1H, H-6), 3.83 (s, 3H, OCH_3), 3.91 (ddd, J = 10.7, 9.2, 4.4 Hz, 1H, H-1), 4.00 (dd, J = 10.3, 10.3 Hz, 1H, H-5), 4.28 (dd, J = 10.3, 5.2 Hz, 1H, H-5), 4.60 (dd, J = 11.0, 2.2 Hz, 1H, H-8), 6.90 (d, J = 8.5 Hz, 2H, H_{arom}), 7.35 (m, 1H, H_{arom}), 7.43 (m, 4H, H_{arom}), 7.59 (m, 4H, H_{arom}), 7.77 (d, J = 8.5 Hz, 2H, H_{arom}); ^{13}C (75 MHz, $CDCl_3$) δ 31.2, 33.0, 55.1, 64.9, 71.6, 76.1, 79.9, 113.3, 126.5, 127.2, 127.3, 127.4, 128.9, 135.9, 140.6, 140.9, 141.0, 162.0.

Anal. Calcd for $C_{25}H_{25}O_4B$ (400.29): C, 74.97; H, 6.30%. Found: C, 74.58; H, 6.36%.

***(1S,6R,8R)*-8-Biphenyl-3-(4′-butyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (8b).** Yield 69%; mp 179.6 °C; $[\alpha]_D^{20}$ +28.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3H, CH_3), 1.44–1.54 (m, 4H, CH_2), 1.73–1.95 (m, 4H, H-9, CH_2), 2.12 (m, 1H, H-10), 2.42 (m, 1H, H-10), 3.67 (ddd, J = 10.3, 9.9, 5.1 Hz, 1H, H-6), 3.88–4.04 (m, 4H, H-1, H-5, OCH_2), 4.27 (dd, J = 10.3, 5.1 Hz, 1H, H-5), 4.59 (bd, J = 10.3 Hz, 1H, H-8), 6.88 (d, J = 8.5 Hz, 2H, H_{arom}), 7.35 (m, 1H, H_{arom}), 7.44 (m, 4H, H_{arom}), 7.58 (d, J = 8.1 Hz, 4H, H_{arom}), 7.75 (d, J = 8.5 Hz, 2H, H_{arom}); ^{13}C (75 MHz, $CDCl_3$) δ 13.9, 19.3, 31.1, 31,3, 33.0, 64.8, 67.5, 71.5, 76.1, 79.8, 112.0, 113.8, 126.4, 127.1, 127.2, 127.3, 128.8, 135.8, 140.9, 141.5, 161.5.

Anal. Calcd for $C_{28}H_{31}O_4B$ (442.37): C, 76.02; H, 7.06%. Found: C, 75.39; H, 7.29%.

***(1S,6R,8R)*-8-Biphenyl-3-(4′-hexyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (8c).** Yield 70%; mp 156.5 °C; $[\alpha]_D^{20}$ +26.2 (*c* 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 6.8 Hz, 3H, CH_3), 1.29–1.40 (m, 4H, CH_2), 1.46 (m, 2H, CH_2), 1.73–1.97 (m, 4H, H-9, CH_2), 2.13 (m, 1H, H-10), 2.42 (m, 1H, H-10), 3.66 (ddd, J = 10.3, 9.9, 5.1 Hz, 1H, H-6), 3.88–4.04 (m, 4H, H-1, H-5, OCH_2), 4.28 (dd, J = 10.3, 5.1 Hz, 1H, H-5), 4.60 (dd, J = 11.0, 1.8 Hz, 1H, H-8), 6.88 (d, J = 8.8 Hz, 2H, H_{arom}), 7.35 (m, 1H, H_{arom}), 7.44 (m, 4H, H_{arom}), 7.58 (d, J = 8.4 Hz, 4H, H_{arom}), 7.75 (d, J = 8.8 Hz, 2H, H_{arom}); ^{13}C (75 MHz,

$CDCl_3$) δ 14.1, 22.7, 25.8, 29.3, 31.2, 31.7, 33.0, 64.9, 67.8, 71.6, 76.1, 79.9, 113.8, 126.5, 127.2, 127.4, 128.8, 135.8, 140.5, 140.9, 141.0, 161.6.

Anal. Calcd for $C_{30}H_{35}O_4B$ (470.42): C, 76.55; H, 7.50%. Found: C, 76.24; H, 7.48%.

***(1S,6R,8R)*-8-Biphenyl-3-(4′-octyloxyphenyl)-2,4,7-trioxa-3-borabicyclo[4.4.0]decane (8d).** Yield 80%; mp 141.5 °C; $[\alpha]_D^{20}$ +22.4 (*c* 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H, CH_3), 1.25–1.40 (m, 8H, CH_2), 1.46 (m, 2H, CH_2), 1.74–1.96 (m, 4H, H-9, CH_2), 2.13 (m, 1H, H-10), 2.42 (m, 1H, H-10), 3.66 (ddd, J = 10.3, 9.6, 5.1 Hz, 1H, H-6), 3.88–4.04 (m, 4H, H-1, H-5, OCH_2), 4.28 (dd, J = 10.3, 5.1 Hz, 1H, H-5), 4.58 (bd, J = 11.0 Hz, 1H, H-8), 6.87 (d, J = 8.5 Hz, 2H, H_{arom}), 7.34 (m, 1H, H_{arom}), 7.44 (m, 4H, H_{arom}), 7.58 (d, J = 8.1 Hz, 4H, H_{arom}), 7.74 (d, J = 8.5 Hz, 4H, H_{arom}); ^{13}C (75 MHz, $CDCl_3$) δ 14.1, 22.7, 26.1, 29.2, 29.3, 29.4, 31.1, 31.8, 33.0, 64.8, 67.8, 71.5, 76.0, 79.8, 113.8, 126.4, 127.1, 127.2, 127.3, 128.8, 135.8, 140.5, 140.8, 140;9, 161.5.

Anal. Calcd for $C_{32}H_{39}O_4B$ (498.48): C, 77.06; H, 7.89%. Found: C, 77.16; H, 7.85%.

ACKNOWLEDGMENTS

C. M. and B. B. thank the French Ministery of Education for a fellowship. Financial support by DAAD/Procope Programme is gratefully acknowledged.

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Received November 20, 2000
Accepted February 6, 2001

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