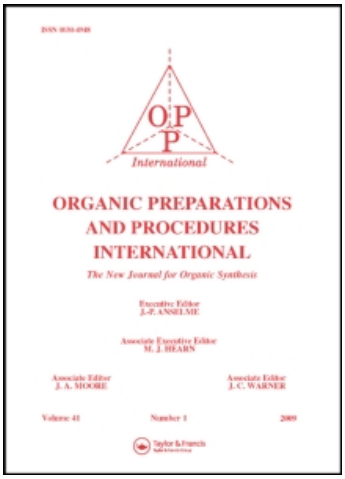

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Synthesis and Structure of Tetratosyl Bora Derivatives of Resorcinarenes From L-Proline and L-Prolinol

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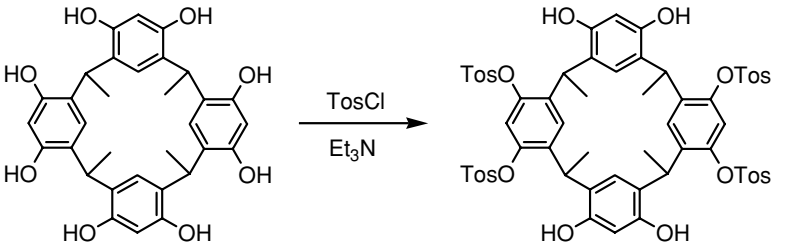
Organoboron compounds play an important role in asymmetric synthesis. In particular, the oxazaborolidines are highly useful as excellent chiral catalysts for the asymmetric reduction of prochiral ketones as well as for the other enantioselective reactions.[1–4] Formation of strong intramolecular coordinate bonds between the nitrogen and the boron atoms provides many possibilities for the synthesis of new hetero- or macrocyclic compounds.[5–9] In addition, some of these compounds have been recognized as biologically active substances.[10] Examples of the synthesis of chiral boron derivatives of resorcinarene have been reported.[11–14] Herein we describe the synthesis of new chiral di-boron derivatives of resorcinarenes from tetratosylresorcinarene, L-proline and L-prolinol.

The reaction of resorcinarene **1** with tosyl chloride in the presence of triethylamine gave the tetratosyl derivative of resorcinarene **2** in good yields (67%),[15] as shown in *Scheme 1*, that is consistent with the literature data.



1 **2**

Scheme 1

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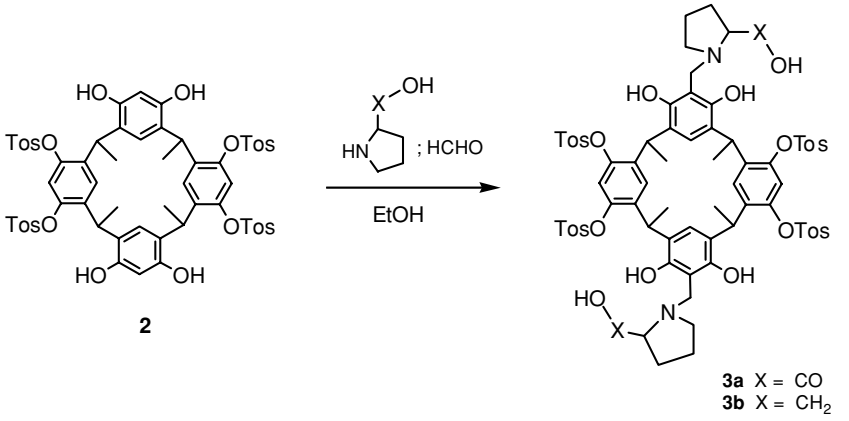
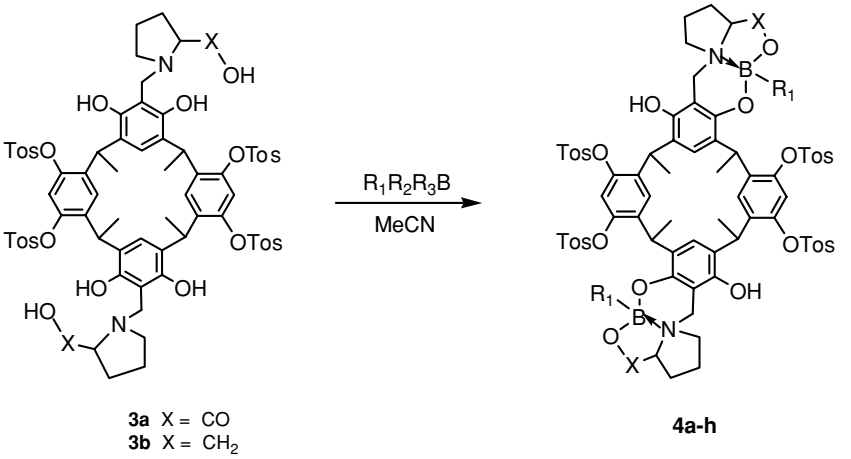
The resulting tetratosylresorcinarene **2** was converted into new disubstituted chiral products **3a** and **3b** using L-proline and L-prolinol according to *Scheme 2*.



Scheme 2

bis-L-Proline-tetratosylresorcinarene (**3a**) and *bis*-L-prolinol-tetratosylresorcinarene (**3b**) were synthesized by standard Mannich reaction using formaldehyde and correspondingly L-proline and L-prolinol. The reaction was carried out in ethanol under reflux for 4 hours. After cooling the reaction mixture to room temperature, spectrally pure L-proline derivatives of tetratosyloresorcinarene **3a** precipitated as a colorless solid, while the pure L-prolinol derivatives of tetratosylresorcinarenes **3b** were obtained by recrystallization from chloroform. The spectral data of these compounds are given in the Experimental Section. These L-proline and L-prolinol derivatives **3a** and **3b** having an electron lone pair at the nitrogen atom and the free hydroxy groups were then used for reaction with selected boron compounds such as boric acid, phenylboric acid, 3-chlorophenylboric acid, 3,5-dibromophenylboric acid as well as with trimethyl borate (*Scheme 3*). In all of these



Scheme 3

Table 1
Boron Derivatives of Tetratosylresorcinarenes **4a–h**

Product	X	R_1	R_2	R_3
out-(M,S,R,S_N,R_B) (**4a**)	C=O	OH	OH	OH
out-(M,S,R,S_N,S_B) (**4b**)	C=O	Ph	OH	OH
out-(M,S,R,S_N,S_B) (**4c**)	C=O	3-ClC_6H_5	OH	OH
out-(M,S,R,S_N,S_B) (**4d**)	C=O	3,5-$Br_2C_6H_4$	OH	OH
out-(M,S,R,S_N,R_B) (**4e**)	C=O	OMe	OMe	OMe
out-(M,S,R,S_N,R_B) (**4f**)	CH_2	Ph	OH	OH
out-(M,S,R,S_N,R_B) (**4g**)	CH_2	3-ClC_6H_5	OH	OH
out-(M,S,R,S_N,R_B) (**4h**)	CH_2	3,5-$Br_2C_6H_4$	OH	OH

reactions compounds **3a** and **3b**, by formation of a coordinate bond between the boron and the nitrogen atoms, afforded novel boron derivatives of the tetratosylresorcinarene **4a–h** containing bora-oxazine-oxazolidinone or bora-oxazine-oxazolidine rings (*Table 1*).
Reactions using *bis*-L-proline-tetratosylresorcinarene **3a** were carried out in acetonitrile heated at reflux while the reactions using *bis*-L-prolinol-tetratosylresorcinarene **3b** were performed in toluene with azeotropic removal of water from the reaction mixture.

The structures of all boron derivatives of the tetratosylresorcinarene **4a–h** were confirmed by ^1H and ^{13}C NMR spectroscopy and in addition, by two-dimensional $^1H,^1H$-COSY and $^1H,^1H$-NOESY experiments confirming their spatial structure. In all reactions, the boat conformer of *out*-(*M,S,R*)-bora-oxazine-oxazolidinone or *out*-(*M,S,R*)-bora-oxazine-oxazolidine derivatives of tetratosylresorcinarene were obtained (according to stereochemical nomenclature proposed for C_4 symmetric compounds reported in the literature[16,17]), with the bora-oxazine rings oriented outside of the resorcinarene cavity (*Isomerism "in-out"*).[18] Such arrangement of rings cause the phenyl groups attached to boron atoms to point to the inside of the resorcinarene cavity. There is the most important part of the $^1H,^1H$-NOESY spectrum (500 MHz) of bora-oxazine-oxazolidinone derivative **4d** with marked signals of coupling protons indicating the spatial structure of this compound in *Figure 1* . The comparison of the location of the signal of the methine proton H^1 of the L-proline moiety in the ^1H NMR spectrum ($CDCl_3$) of the *bis*-bora-L-proline-tetratosyl derivative **4d** and of L-proline derivative **3a** allowed us to rationalize that bora-oxazolidinone rings or the bora-oxazolidine rings in all of the boron derivatives are oriented outside of the resorcinarene cavity (isomer *out*). The methine signals of **4d** located at δ 3.92 is shifted downfield in comparison to the corresponding signal of **3a** (δ 3.67). The coupling in NOESY spectra of **4d** between the methine proton H^1 and the aminomethylene protons H^9 and between the aminomethylene protons H^8 and the L-proline proton H^7 lead to the conclusion that, in all the reactions, the isomers *out*-(*M,S,R*) of the bora-tetratosylresorcinarenes were obtained (*Figure 1*). These couplings are possible only when the bora-oxazine rings are closed in proposed direction and if the rings are oriented outside of the resorcinarene cavity.

In all of the reactions performed using L-proline-tetratosylresorcinarene **3a** as well as L-prolinol-tetratosylresorcinarene **3b**, two new stereogenic centers were generated at the boron atom and at the nitrogen atom as a result of forming bora-oxazine-oxazolidinone rings

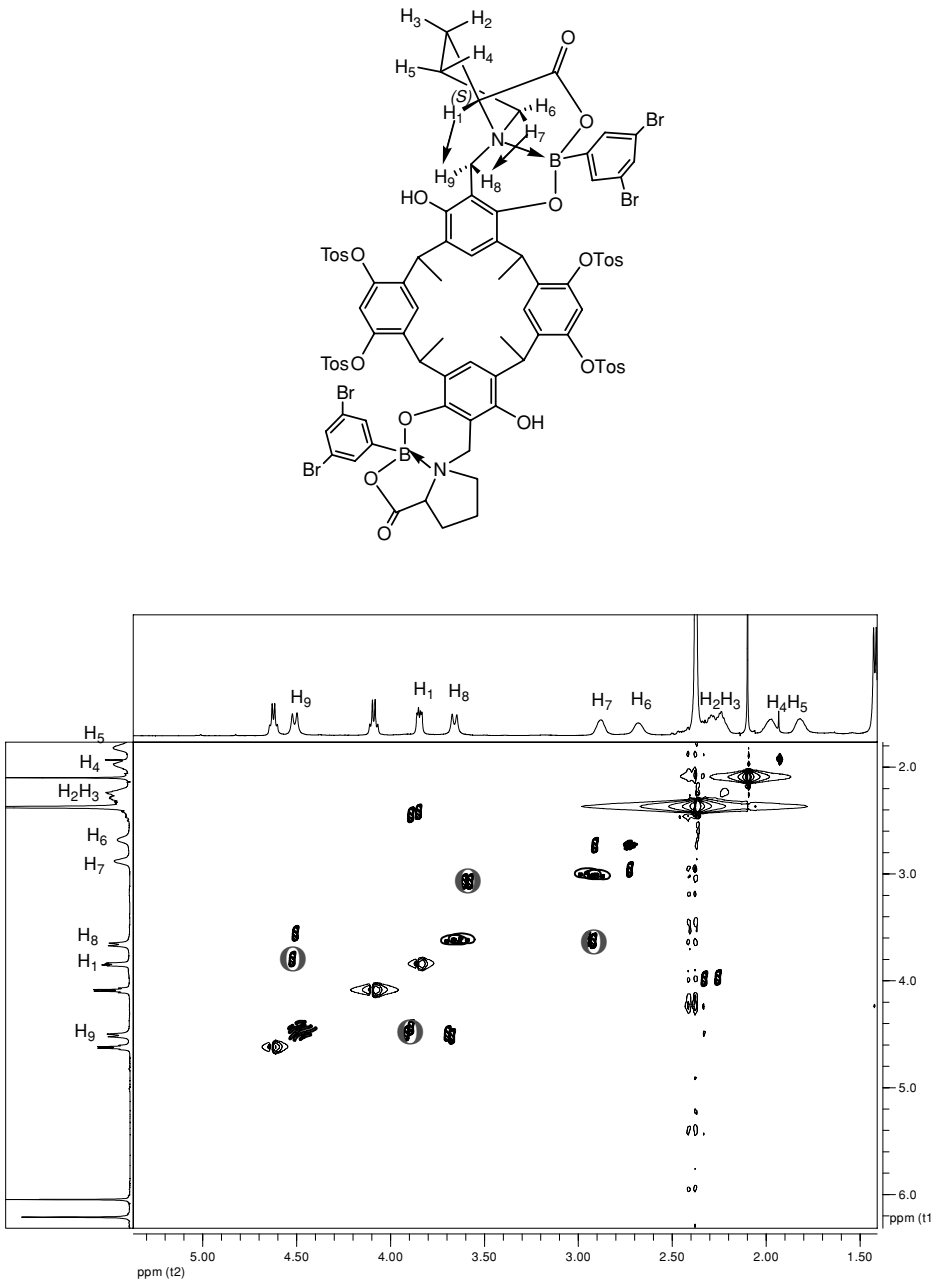


Figure 1. The most important portion of the ^{1}H,^{1}H-NOESY spectra (500 MHz) of bora–oxazine-oxazolidinone derivative **4d**.

or bora-oxazine-oxazolidine rings. In the case of the diastereoisomers **4b–e**, the nitrogen and boron atoms are of the *S*-configuration while in the case of **4a** and **4f–h** the nitrogen and boron atoms adopt *S*- and *R*-configurations respectively as shown in *Table 1*.

In conclusion this paper describes novel *bis*-L-proline and *bis*-L-prolinol derivatives of tetratosylresorcinarene synthesized *via* Mannich reaction from formaldehyde and

respectively L-proline and L-prolinol as well as the novel boron derivatives of tetratosylresorcinarene as results of reaction of these derivatives with boron compounds. The structures all of the received derivatives were confirmed by NMR-spectroscopy. In all of reactions, the conformer of *out*-bora-oxazine-oxazolidinone or *out*-bora-oxazine-oxazolidine derivatives of tetratosylresorcinarene was obtained with two new stereogenic centers at the boron and the nitrogen atoms. The phenyl groups linked to the boron atoms are oriented toward the resorcinarene cavity.

Experimental Section

All ^{1}H- and ^{13}C NMR, 2D NMR ((^{1}H,^{1}H-COSY and ^{1}H,^{1}H-NOESY) spectra were measured at 499.893 MHz, on a Bruker DRX 500 spectrometer. Mass spectra were recorded on an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik) and on a Bruker APEX III FT MS at the University in Bielefeld, with the electrospray (ES) technique. Melting points were determined with a Boëtius melting point instrument and are uncorrected. Optical rotation values were measured on an Optical Perkin–Elmer 341 Model polarimeter that was operated at λ 589 nm, which corresponds to the sodium D line at 25°C. Elemental analyses were performed by a Perkin–Elmer 2400 model instruments. All chromatographic manipulations used silica gel 60 (SiO_2, Merck, particle size 0.040–0.063 mm, 230–240 mesh) as the adsorbent. Reactions were monitored by thin layer chromatography (TLC) on plastic sheets coated with Merck Kieselgel 60 F254 silica gel. TLC plates were visualized by UV radiation at a wavelength of 254 nm. Reagents and solvents were obtained from Fluka and Merck and were used without purification.

Procedure for Tetratosylresorcinarene (2)

To a solution of resorcinarenes **1** (10 mmol, 5.45 g) in MeCN (100 ml), was added anhydrous Et_3N (40 mmol, 4.04 g) and the mixture was stirred at 25°C for 15 min. A solution of tosyl chloride (40 mmol, 7.68 g) in MeCN (50 ml) was added and the reaction mixture was stirred for 12 hours. The precipitated solid was collected and washed with MeCN (2 × 20 ml), water (20 ml), and then was dissolved in DMF (50 ml) and extracted with water-$CHCl_3$. The organic layer was dried with $MgSO_4$. After solvent removal the pure product was obtained as a colorless solid (7.73 g, 67%) mp. 311–312°C, *lit*.[15] mp. 310–313°C).

Procedure for bis-L-Proline- and bis-L-Prolinoltetratosyloresorincarene (3a and 3b)

To a warm solution of tetratosylresorcinarene **2** (4.3 mmol, 5.00 g), L-prolinol (8.7 mmol,0.90 ml) or L-proline (8.7 mmol, 1.00 g) in EtOH (120 ml), formaldehyde (8.7 mmol, 0.09 ml) was added and the mixture was refluxed gently. After 4 h, the reaction mixture was cooled to 25°C. In the case of reaction with L-proline, the precipitated white solid was collected and washed with EtOH to afford spectrally pure product. In the case of reaction using L-prolinol, the solvent was removed under vacuum and the residue was purified by crystallization from $CHCl_3$.

bis-L-Prolinetetratosylresorcinarene (3a), 70% yield, mp. 193–194°C, $[\alpha]_D^{25} = -5^\circ$ (CH_3OH, c 0.138).

^{1}H NMR (500 MHz) [$CDCl_3$, 25°C): δ 1.58 (d, J = 6.9Hz, 6H, -CH_3), 1.61 (d, J = 6.9Hz, 6H, -CH_3), 1.69 (m, 1H, H5), 1.86 (m, 1H, H4), 1.94 (m, 1H, H3), 2.26 (m, 1H, H2), 2.82 (s, 6H, Ar-CH_3), 2.88 (s, 6H, Ar-CH_3), 2.87 (q, J = 8.0Hz, 1H, H7), 3.16 (m, 1H, H6), 3.67 (dd, J = 8.0,4.0Hz, 1H, H1), 3.76 (s, 4H, -O*H*), 3.96 (d, J = 16.0Hz, 2H, H8), 4.03 (d, J = 12.0Hz, 2H, H9), 4.74 (k, J = 6.9Hz, 2H, -C*H*CH_3), 4.80 (q, J = 6.9Hz, 2H, -C*H*CH_3), 6.14 (s, 2H, Ar*H*), 7.88 (m, 3H, Ar*H*), 8.16 (d, J = 6.9Hz, 8H, Ar*H*), 8.19 (d, J = 6.9Hz, 8H, Ar*H*).

^{13}C NMR (500 MHz) DMSO-d_6, 25°C): δ 20.57, 20.87, 21.23, 22.68, 28.69, 30.20, 30.35, 49.64, 52.31, 65.94, 109.04, 113.18, 121.91, 122.23, 123.85, 127.97, 128.03, 130.33, 132.41, 138.14, 143.98, 144.03, 145.80, 151.46, 152.35, 175.35.

EI-MS (70 eV): m/z (%): 1415,6346.

IR [cm^{-1}]: (600, 724, 844, 920, 1008, 1136, 1184, 1192, 1320, 1556, 1600, 3000, 3480).

Anal. Calcd for $C_{72}H_{74}N_2O_{20}S_4$: C, 61.09; H, 5.27; N, 1.78; S, 9.06.

Found: C, 60.98; H, 5.29; N, 1.81; S, 9.08.

***bis*-L-Prolinoltetratosylresorcinarene (3b),** 65% yield, mp. 197–198 °C, $[\alpha]_D^{25} = +59°$ ($CHCl_3$, c 0.276).

^{1}H NMR (500 MHz) $CDCl_3$, 25°C): δ 1.31 (d, J = 6.9Hz, 6H, -CH_3), 1.38 (d, J = 6.9Hz, 6H, -CH_3), 1.90 (m, 4H, H5,H4,H3), 2.00 (m, 2H, H2), 2.38 (m, 2H, H6), 2.42 (s, 6H, Ar-CH_3), 2.44 (s, 6H, Ar-CH_3), 3.05 (m,2H, H7), 3.28 (m, 2H, H1), 3.78 (m, 4H, CH_2OH), 4.16 (d, J = 13.5Hz, 2H, H8), 4.33 (d, J = 13.5Hz, 2H, H9), 4.43 (m, 4H, -C*H*CH_3), 6.02 (s, 2H, Ar*H*), 6.57 (s, 2H, Ar*H*), 7.08 (s, 2H, Ar*H*), 7.38 (d, J = 8.0Hz, 4H, Ar*H*), 7.40 (d, J = 8.0Hz, 4H, Ar*H*), 7.85 (d, J = 8.0Hz, 4H, Ar*H*), 7.87 (d, J = 8.0Hz, 4H, Ar*H*).

^{13}C NMR (500 MHz) $CDCl_3$, 25°C): δ 19.78, 19.94, 21.81, 21.84, 22.77, 25.66, 25.96, 30.68, 32.60, 32.70, 45.75, 52.92, 60.64, 67.71, 76.75, 77.00, 77.26, 108.69, 115.59, 122.95, 126.67, 127.01, 128.46, 128.55, 130.35, 130.42, 131.91, 132.30, 138.86, 139.63, 145.11, 145.32, 146.06, 146.31, 152.76, 153.34.

EI-MS (70 eV): m/z (%): 1387,6682.

IR [cm^{-1}]: (840, 916, 1008, 1176, 1184, 1244, 1256, 1320, 1480, 1700, 2968, 3512).

Anal. Calcd for $C_{72}H_{78}N_2O_{18}S_4$: C, 62.32; H, 5.67; N, 2.09; S, 9.24.

Found: C, 62.27; H, 5.68; N, 2.13; S, 9.26.

General Procedure for the Synthesis of the Boron Derivatives from bis-L-Proline-tetratosylresorcinarene (4a–e)

A solution of *bis*-L-prolinetetratosylresorcinarene **3a** (0.7 mmol, 1.0 g) and corresponding derivative of boric acid in MeCN (50 ml) was heated under refluxed for 5h. After evaporation of the solvent, the residue was purified by crystallization from $CHCl_3$ or by column chromatography with acetone-hexane (2:3) as eluent.

Product of Reaction with B(OH)$_3$ (4a), 90% yield, was purified by crystallization from $CHCl_3$, mp. >340°C, $[\alpha]_D^{25} = -205°$ ($CHCl_3$, c 0.284).

^{1}H NMR (500 MHz) $CDCl_3$, 25°C): δ 1.19 (d, J = 6.9Hz, 6H, -CH_3), 1.46 (d, J = 6.9Hz, 6H, -CH_3), 2.03 (m, 4H, H4 i H5), 2.25 (m, 2H, H3), 2.27 (m, 2H, H2), 2.43 (s, 6H, Ar-CH_3), 2.51 (s, 6H, Ar-CH_3), 2.80 (m, 2H, H6), 3.60 (d, J = 16.0Hz, 2H, H8),

3.79 (dd, $J = 8.0$,4.0Hz 2H, H1), 4.16 (d, $J = 12.0$Hz, 2H, H9), 4.21 (m, 2H, H7), 4.35 (q, $J = 6.9$Hz, 2H, -C*H*CH_3), 4.56 (q, $J = 6.9$Hz, 2H, -C*H*CH_3), 6.29 (s, 2H, Ar*H*), 6.56 (s, 2H, Ar*H*), 7.10 (s, 2H, Ar*H*), 7.41 (d, $J = 6.9$Hz, 4H, Ar*H*), 7.50 (d, $J = 6.9$Hz, 4H, Ar*H*), 7.90 (d, $J = 6.9$Hz, 4H, Ar*H*), 8.06 (d, $J = 6.9$Hz, 4H, Ar*H*).

^{13}C NMR (500 MHz) $CDCl_3$, 25°C): δ 9.521, 20.943, 21.703, 21.856, 24.917, 29.102, 31.697, 32.459, 52.322, 59.077, 59.077, 69.109, 76.744, 76.999, 77.252, 108.269, 115.160, 119.233, 124.364, 125.927, 127.014, 128.357, 128.825, 130.128, 130.705, 130.897, 133.041, 138.171, 141.198, 144.417, 145.026, 145.714, 146.771, 150.223, 152.840, 171.906.

EI-MS (70 eV): m/z (%): 1467,2388.

IR [cm^{-1}]: (684, 792, 848, 972, 1020, 1092, 1128, 1176, 1368, 1488, 1600, 1740, 2968, 3432).

Anal. Calcd for $C_{72}H_{72}B_2N_2O_{22}S_4$: C, 58.94; H, 4.95; N, 1.91; S, 8.74; B, 1.47.

Found: C, 59.09; H, 5.05; N, 1.98; S, 8.77; B, 1.49.

Product of Reaction with PhB(OH)$_2$ (4b), 60% yield, was purified by crystallization from $CHCl_3$, mp. 218–219°C, $[\alpha]_D^{25} = -224^\circ$ ($CHCl_3$, c 0.208).

^{1}H NMR (500 MHz) $CDCl_3$, 25°C): δ 1.13 (d, $J = 6.5$Hz, 6H, -CH_3), 1.43 (d, $J = 6.5$Hz, 6H, -CH_3), 1.82 (m, 2H, H5), 1.85 (m, 2H, H4), 2.26 (m, 2H, H3), 2.33 (s, 6H, Ar-CH_3), 2.37 (s, 6H, Ar-CH_3), 2.43 (m, 2H, H2), 3.09 (m, 2H, H6), 3.58 (d, $J = 13.5$Hz, 2H, H8), 3.91 (dd, $J = 9.0$,3.5Hz, 2H, H1), 4.03 (m, 2H, H7), 4.13 (q, $J = 6.5$Hz, 2H, -C*H*CH_3), 4.26 (d, $J = 13.5$Hz, 2H, H9), 4.59 (q, $J = 6.5$Hz, 2H, -C*H*CH_3), 6.06 (s, 2H, Ar*H*), 6.27 (s, 2H, Ar*H*), 7.05 (s, 2H, Ar*H*), 7.32 (d, $J = 6.9$Hz, 4H, Ar*H*), 7.35 (d, $J = 8.0$Hz, 4H, Ar*H*), 7.38 (d, $J = 8.0$Hz, 4H, Ar*H*), 7.81 (d, $J = 8.0$Hz, 4H, Ar*H*).

^{13}C NMR (500 MHz) $CDCl_3$, 25°C): δ 18.955, 20.757, 21.717, 21.768, 23.527, 27.229, 32.055, 32.651, 49.735, 60.179, 66.251, 76.746, 77.000, 77.255, 105.795, 114.828, 117.946, 123.671, 126.223, 126.445, 127.699, 128.024, 128.140, 129.065, 129.963, 130.144, 130.429, 132.253, 133.715, 137.481, 140.514, 144.300, 145.115, 145.548, 146.371, 150.821, 153.010, 173.813.

EI-MS (70 eV): m/z (%): 1587,4360.

IR [cm^{-1}]: (744, 798, 840, 932, 1160, 1152, 1184, 1324, 1420, 1536, 1556, 1684, 2960, 3120).

Anal. Calcd for $C_{84}H_{80}B_2N_2O_{20}S_4$: C, 63.56; H, 5.08; N, 1.76; S, 8.08; B, 1.36.

Found: C, 63.58; H, 5.12; N, 1.78; S, 8.13; B, 1.39.

Product of Reaction with 3-ClPhB(OH)$_2$ (4c), 74% yield, was purified by column chromatography with acetone-hexane (2:3), mp. 213–214°C, $[\alpha]_D^{25} = -271^\circ$ ($CHCl_3$, c 0.164).

^{1}H NMR (500 MHz) $CDCl_3$, 25°C): δ 1.20 (d, $J = 6.9$Hz, 6H, -CH_3), 1.25 (m, 4H, H4 and H5), 1.50 (d, $J = 6.9$Hz, 6H, -CH_3), 1.89 (m, 4H, H2 and H3), 2.40 (s, 6H, Ar-CH_3), 2.44 (s, 6H, Ar-CH_3), 2.50 (m, 2H, H6), 3.65 (d, $J = 16.0$Hz, 2H, H8), 3.98 (dd, $J = 8.0$,4.0Hz, 2H, H1), 4.20 (q, $J = 6.9$Hz, 4H, -C*H*CH_3), 4.33 (d, $J = 12.0$Hz, 2H, H9), 4.52 (m, 2H, H7), 4.66 (q, $J = 6.9$Hz, 4H, -C*H*CH_3), 6.11 (s, 2H, Ar*H*), 6.34 (s, 2H, Ar*H*), 6.77 (s, 2H, Ar*H*), 7.41 (m, 10H, Ar*H*), 7.89 (d, $J = 6.9$Hz, 4H, Ar*H*).

^{13}C NMR (500 MHz) $CDCl_3$, 25°C): δ 18.991, 20.688, 21.717, 21.724, 21.806, 23.699, 27.266, 32.084, 32.644, 49.943, 60.347, 66.377, 76.750, 77.004, 77.258, 106.021, 115.027, 118.461, 123.909, 126.383, 126.459, 128.116, 128.182, 128.984, 129.590, 129.959,

130.136, 130.426, 130.477, 131.834, 133.693, 133.765, 137.463, 140.494, 144.296, 145.180, 145.472, 146.539, 150.820, 152.769, 173.372.

EI-MS (70 eV): m/z (%): 1656,3262.

IR [cm^{-1}]: (604, 784, 844, 932, 1080, 1192, 1288, 1324, 1420, 1540, 1568, 1688, 2968, 3472).

Anal. Calcd for $C_{84}H_{78}B_2Cl_2N_2O_{20}S_4$: C, 60.91; H, 4.75; N, 1.69; S, 7.74; B, 1.31; Cl, 4.28.

Found: C, 60.96; H, 4.77; N, 1.71; S, 7.76; B, 1.34; Cl, 4.29.

Product of Reaction with 3,5-Br$_2$PhB(OH)$_2$ (4d), 97% yield, was purified by column chromatography with acetone-hexane (2:3), mp. 235–236°C, $[\alpha]_D^{25} = -189^\circ$ ($CHCl_3$, c 0.230).

^{1}H NMR (500 MHz) $CDCl_3$, 25°C): δ 1.15 (d, $J = 6.9$Hz, 6H, -CH_3), 1.49 (d, $J = 6.9$Hz, 6H, -CH_3), 1.91 (m, 2H, H5), 2.05 (m, 2H, H4), 2.17 (s, 6H, Ar-CH_3), 2.30 (m, 4H, H2 and H3), 2.45 (s, 6H, Ar-CH_3), 2.74 (m, 2H, H6), 2.96 (m, 2H, H7), 3.76 (d, $J = 16.0$Hz, 2H, H8), 3.92 (dd, $J = 8.0$,4.0Hz, 2H, H1), 4.15 (q, $J = 6.9$Hz, 4H, -CHCH$_3$), 4.57 (d, $J = 12.0$Hz, 2H, H9), 4.69 (q, $J = 6.9$Hz, 4H, -CHCH$_3$), 6.11 (s, 2H, ArH), 6.28 (s, 2H, ArH), 6.76 (s, 2H, ArH), 7.05 (s, 2H, ArH), 7.13 (d, $J = 6.9$Hz, 4H, ArH), 7.37 (d, $J = 6.9$Hz, 4H, ArH), 7.44 (d, $J = 6.9$Hz, 4H, ArH), 7.61 (m, 2H, ArH), 7.67 (m, 2H, ArH), 7.91 (d, $J = 6.9$Hz, 4H, ArH).

^{13}C NMR (500 MHz) $CDCl_3$, 25°C): δ 18.750, 20.448, 21.721, 21.816, 24.140, 27.546, 30.913, 32.120, 32.575, 50.423, 60.723, 66.403, 76.744, 76.999, 77.252, 107.292, 115.527, 119.802, 123.001, 124.218, 126.544, 126.623, 128.116, 128.959, 129.794, 129.916, 130.540, 133.426, 133.591, 133.696, 137.467, 140.178, 144.353, 145.222, 146.676, 150.997, 152.531, 172.941.

EI-MS (70 eV): m/z (%): 1903,0204.

IR [cm^{-1}]: (600, 788, 932, 960, 1080, 1136, 1192, 1272, 1324, 1420, 1556, 1672, 2960, 3016).

Anal. Calcd for $C_{84}H_{76}B_2Br_4N_2O_{20}S_4$: C, 53.02; H, 4.03; N, 1.47; S, 6.74; B, 1.14; Br, 16.79.

Found: C, 53.00; H, 4.10; N, 1.43; S, 6.79; B, 1.18; Br, 16.82.

Product of Reaction with B(OCH$_3$)$_3$ (4e), 65% yield, was purified by column chromatography with acetone-hexane (2:3), mp. 189–190°C, $[\alpha]_D^{25} = -103^\circ$ ($CHCl_3$, c 0.362).

^{1}H NMR (500 MHz) $CDCl_3$, 25°C): δ 1.28 (d, $J = 6.9$Hz, 6H, -CH_3), 1.49 (d, $J = 6.9$Hz, 6H, -CH_3), 1.99 (m, 2H, H5), 2.10 (m, 2H, H4), 2.25 (m, 2H, H3), 2.25 (m, 2H, H2), 2.34 (s, 6H, Ar-CH_3), 2.48 (s, 6H, Ar-CH_3), 2.86 (m, 2H, H6), 3.21 (s, 6H, -OCH_3), 3.45 (d, $J = 14.9$Hz, 2H, H8), 3.75 (dd, $J = 8.0$,4.0Hz, 2H, H1), 4.02 (m, 2H, H7), 4.20 (d, $J = 14.9$Hz, 2H, H9), 4.24 (q, $J = 6.9$Hz, 4H, -CHCH$_3$), 4.51 (q, $J = 6.9$Hz, 4H, -CHCH$_3$), 6.20 (s, 2H, ArH), 6.57 (s, 2H, ArH), 6.76 (s, 2H, ArH), 7.07 (s, 2H, ArH), 7.43 (d, $J = 6.9$Hz, 4H, ArH), 7.51 (d, $J = 6.9$Hz, 4H, ArH), 7.84 (d, $J = 6.9$Hz, 4H, ArH), 8.01 (d, $J = 6.9$Hz, 4H, ArH).

^{13}C NMR (100 MHz) $CDCl_3$, 25°C): δ 20.316, 20.453, 20.791, 21.221, 23.661, 24.109, 24.337, 24.712, 25.791, 28.249, 28.825, 29.017, 29.144, 29.291, 29.437, 29.602, 29.821, 30.360, 30.452, 32.124, 33.322, 36.219, 40.734, 46.172, 50.066, 52.003, 52.670, 55.833, 58.364, 58.566, 67.367, 68.354, 79.185, 100.489, 109.017, 109.346, 113.888, 114.044, 124.710, 124.874, 125.148, 127.817, 127.890, 128.027, 128.585, 128.896, 130.239,

130.404, 132.241, 132.241, 132.314, 132.479, 132.762, 138.026, 138.282, 143.510, 143.793, 145.375, 145.695, 145.877, 149.954, 151.453, 151.855, 171.879, 172.127.

EI-MS (70 eV): m/z (%): 1497,3082.

IR [cm^{-1}]: (668, 760, 836, 992, 1072, 1192, 1224, 1324, 1372, 1484, 1600, 1748, 2968, 3080).

Anal. Calcd for $C_{74}H_{78}B_2N_2O_{22}S_4$: C, 59.36; H, 5.25; N, 1.87; S, 8.57; B, 1.44.

Found: C, 59.33; H, 5.23; N, 1.89; S, 8.55; B, 1.48.

General Procedure for the Synthesis of the Boron Derivatives from bis-L-Prolinol-tetratosylresorcinarene (4f–h)

A mixture of *bis*-L-prolinoltetratosyloresorcinarene **3b** (0.7 mmol, 0.97 g) and phenylboric acid (1.5 mmol) or its derivatives in toluene (50 ml) heated for 5h at 140°C with azeotropic socket. After evaporation of the solvent the residue was purified by column chromatography with acetone-hexane (2:3) as eluent.

Product of Reaction with PhB(OH)₂ (4f), 61% yield, mp. 295–296°C, $[\alpha]_D^{25} = +121^\circ$ ($CHCl_3$, c 0.234).

^{1}H NMR (500 MHz) $CDCl_3$, 25°C): δ 1.25 (d, $J = 6.9$Hz, 6H, -CH_3), 1.42 (d, $J = 6.9$Hz, 6H, -CH_3), 1.46 (m, 2H, H5), 1.51 (m, 2H, H4), 2.05 (m, 2H, H4), 2.16 (s, 6H, Ar-CH_3), 2.21 (s, 6H, Ar-CH_3), 2.44 (m, 2H, H2), 3.19 (m, 2H, H6), 3.35 (dd, $J = 9.0$,4.5Hz, 2H, H7), 3.41 (m, 2H, H1), 3.74 (d, $J = 15.5$Hz, 2H, H8), 4.05 (d, $J = 15.5$Hz, 2H, H9), 4.31 (dd, $J = 14.5$,7.0Hz, 2H, HA), 4.44 (dd, $J = 14.5$,7.0Hz, 2H, HB), 4.51 (q, $J = 7.0$Hz, 4H, -CHCH$_3$), 4.58 (q, $J = 7.0$Hz, 4H, -CHCH$_3$), 6.20 (s, 2H, ArH), 6.36 (s, 2H, ArH), 6.47 (d, $J = 7.0$Hz, 4H, ArH), 6.58 (d, $J = 7.0$Hz, 4H, ArH), 6.60 (s, 2H, ArH), 7.06 (s, 2H, ArH), 7.15 (s, 2H, ArH), 7.32 (d, $J = 7.0$Hz, 4H, ArH), 7.45 (m, 4H, ArH), 7.61 (d, $J = 7.0$Hz, 2H, ArH), 7.87 (d, $J = 7.0$Hz, 4H, ArH).

^{13}C NMR (500 MHz) $CDCl_3$, 25°C): δ 19.755, 20.857, 21.712, 21.759, 21.762, 22.878, 23.631, 26.889, 27.342, 30.921, 31.542, 32.055, 32.302, 32.653, 49.732, 60.279, 66.168, 76.744, 76.997, 77.256, 103.584, 107.792, 115.148, 117.926, 122.674, 126.893, 127.695, 128.124, 128.540, 128.673, 129.165, 129.183, 130.101, 130.229, 130.456, 130.621, 132.893, 133.915, 137.581, 144.728, 145.515, 145.858, 146.471, 150.182, 153.042.

EI-MS (70 eV): m/z (%): 1559,4696.

IR [cm^{-1}]: (744, 798, 840, 932, 1160, 1152, 1184, 1324, 1420, 1536, 1556, 1684, 2960, 3120).

Anal. Calcd for $C_{84}H_{84}B_2N_2O_{18}S_4$: C, 64.70; H, 5.43; N, 1.80; S, 8.22; B, 1.39.

Found: C, 64.68; H, 5.46; N, 1.83; S, 8.26; B, 1.35.

Product of Reaction with 3-ClPhB(OH)₂ (4g), 53% yield, mp. 267–268°C, $[\alpha]_D^{25} = +135^\circ$ ($CHCl_3$, c 0.276).

^{1}H NMR (500 MHz) $CDCl_3$, 25°C): δ 1.34 (d, $J = 6.9$Hz, 6H, -CH_3), 1.47 (d, $J = 6.9$Hz, 6H, -CH_3), 1.93 (m, 2H, H5), 2.01 (m, 2H, H4), 2.15 (s, 6H, Ar-CH_3), 2.19 (m, 2H, H3), 2.27 (s, 6H, Ar-CH_3), 2.37 (m, 2H, H2), 3.05 (m, 2H, H1), 3.32 (m, 4H, H6 and H7), 3.70 (d, $J = 15.5$Hz, 2H, H8), 4.06 (d, $J = 15.5$Hz, 2H, H9), 4.33 (dd, $J = 14.5$,6.8Hz, 2H, HA), 4.46 (dd, $J = 14.5$,6.8Hz, 2H, HB), 4.52 (q, $J = 6.9$Hz, 4H, -CHCH$_3$), 4.57 (q, $J = 6.9$Hz, 4H, -CHCH$_3$), 6.18 (s, 2H, ArH), 6.45 (s, 2H, ArH), 6.51 (d, $J = 7.0$Hz, 2H, ArH), 6.74 (s, 2H, ArH), 6.78 (d, $J = 7.0$Hz, 4H, ArH), 7.07 (s, 2H, ArH), 7.16 (s, 2H,

Ar*H*), 7.13 (s, 2H, Ar*H*), 7.06 (s, 2H, Ar*H*), 7.45 (m, 4H, Ar*H*), 7.64 (d, $J = 7.0$Hz, 2H, Ar*H*), 7.89 (d, $J = 7.0$Hz, 4H, Ar*H*).

^{13}C NMR (100 MHz) $CDCl_3$, 25°C): δ 19.197, 19.611, 20.151, 21.761, 21.799, 21.838, 21.869, 22.752, 25.623, 30.691, 30.918, 31.970, 32.266, 32.486, 32.861, 59.809, 67.809, 76.744, 76.999, 77.252, 103.631, 107.050, 115.034, 115.919, 120.045, 126.949, 128.161, 128.560, 128.681, 129.178, 130.069, 130.209, 130.412, 130.503, 130.674, 132.940, 133.919, 137.579, 144.737, 145.669, 145.805, 146.044, 146.534, 153.188.

EI-MS (70 eV): m/z (%): 1628,3598.

IR [cm^{-1}]: (664, 696, 844, 976, 1084, 1176, 1192, 1272, 1360, 1480, 1596, 2976, 3488).

Anal. Calcd for $C_{84}H_{82}B_2Cl_2N_2O_{18}S_4$: C, 61.96; H, 5.08; N, 1.72; S, 7.88; B, 1.33; Cl, 4.35.

Found: C, 62.03; H, 5.14; N, 1.71; S, 7.92; B, 1.35; Cl, 4.36.

Product of Reaction with 3,5-Br$_2$PhB(OH)$_2$ (4h), 78% yield, mp. 282–283°C, $[\alpha]_D^{25} = +106^\circ$ ($CHCl_3$, c 0.228).

^{1}H NMR (500 MHz) $CDCl_3$, 25°C): δ 1.27 (d, $J = 6.9$Hz, 6H, -CH_3), 1.50 (d, $J = 6.9$Hz, 6H, -CH_3), 1.95 (m, 2H, H5), 1.99 (m, 2H, H4), 2.16 (m, 2H, H3), 2.35 (s, 6H, Ar-CH_3), 2.47 (s, 6H, Ar-CH_3), 2.91 (m, 2H, H2), 3.01 (m, 2H, H6), 3.22 (m, 2H, H7), 3.28 (dd, $J = 9.0$,4.5Hz 2H, H1), 3.69 (d, $J = 15.5$Hz, 2H, H8), 4.08 (d, $J = 15.5$Hz, 2H, H9), 4.33 (dd, $J = 14.5$,7.0Hz, 2H, HA), 4.45 (dd, $J = 14.5$,7.0Hz, 2H, HB), 4.53 (q, $J = 7.0$Hz, 4H, -C*H*CH$_3$), 4.56 (q, $J = 7.0$Hz, 4H, -C*H*CH$_3$), 6.20 (s, 2H, Ar*H*), 6.36 (s, 2H, Ar*H*), 6.47 (d, $J = 7.0$Hz, 4H, Ar*H*), 6.58 (d, $J = 7.0$Hz, 4H, Ar*H*), 6.60 (s, 2H, Ar*H*), 7.06 (s, 2H, Ar*H*), 7.13 (s, 2H, Ar*H*), 7.06 (s, 2H, Ar*H*), 7.45 (m, 4H, Ar*H*), 7.64 (d, $J = 7.0$Hz, 2H, Ar*H*), 7.89 (d, $J = 7.0$Hz, 4H, Ar*H*).

^{13}C NMR (500 MHz) $CDCl_3$, 25°C): δ 19.298, 19.702, 20.299, 20.607, 21.663, 21.862, 22.983, 23.392, 25.273, 26.875, 29.665, 31.424, 31.985, 32.299, 32.540, 32.883, 34.627, 66.139, 68.031, 68.974, 76.747, 77.001, 77.255, 103.582, 103.950, 107.086, 115.247, 117.970, 122.735, 126.953, 127.671, 128.192, 128.336, 128.501, 128.611, 128.841, 129.563, 130.108, 130.270, 130.374, 130.471, 130.550, 130.619, 135.535, 135.756, 145.708, 146.588, 154.049.

EI-MS (70 eV): m/z (%): 1875,0540.

IR [cm^{-1}]: (552, 664, 840, 976, 1072, 1176, 1192, 1288, 1368, 1484, 1540, 1596, 2968, 3008).

Anal. Calcd for $C_{84}H_{80}B_2Br_4N_2O_{18}S_4$: C, 53.81; H, 4.30; N, 1.49; S, 6.84; B, 1.15; Br, 17.05.

Found: C, 53.79; H, 4.34; N, 1.53; S, 6.82; B, 1.18; Br, 17.08.

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