Carbohydrate Research 345 (2010) 498–502

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Boronic acid mono- and diesters of the aldopentoses

Moritz M. Reichvilser, Christoph Heinzl, Peter Klüfers *

Ludwig-Maximilians-Universität, Department Chemie und Biochemie, Butenandtstraße 5–13, 81377 München, Germany

ARTICLE INFO

Article history:
Received 5 October 2009
Received in revised form 16 November 2009
Accepted 18 November 2009
Available online 4 December 2009

Keywords:
Boronic acid esters
X-ray diffraction
DFT calculations
Covalent organic frameworks (COFs)

ABSTRACT

The four aldopentoses ribose, arabinose, xylose, and lyxose were evaluated to test their suitability as linear linkers for the formation of intrinsically chiral covalent organic boronic ester networks. Based on X-ray crystal structures of the reaction products with phenylboronic acid, arabinose and xylose formed boronic acid diesters. Lyxose and ribose formed monoesters under the conditions employed. NMR shielding constants were calculated by DFT methods. The results are highly correlated with the experimentally observed NMR shift values.

1. Introduction

Boronic acids are widely used as reagents in organic synthesis, catalysts, protecting groups, enzyme inhibitors, affinity purification agents, receptors for saccharide sensing, neutron capturing agents for cancer therapy, bioconjugates, and protein labels.[1] The first boronic acid esters of monosaccharides were described about five decades ago.[2,3] Esters of aryl boronic acids with aromatic diols are a common base for covalent organic frameworks (COFs). Boronic esters show high thermal stability and, due to their synthesis by molecular self-assembly under equilibrium conditions, the products inherit a dynamic self-repair capability.[4–7] Introducing chirality into a framework opens up new fields of application such as heterogeneous asymmetric catalysis[8] or enantioselective separation.[9] As carbohydrates essentially are polyols, replacing the commonly used aromatic compounds with members of this most abundant natural chiral pool seems to be the obvious way to go for the synthesis of intrinsically chiral boronic ester COFs. In terms of the well-defined networks, a drawback of this strategy could be the introduction of conformational flexibility and structural isomerism. However, this could also be an opportunity for structural diversity and self-repair. The reversible formation of linear sugar-containing polymers in solution by condensation with diboronic acids has already been described.[10,11] Previous studies lack structural investigations in the solid state and of higher dimensional systems. The only boronic acid esters of carbohydrates for which X-ray structure determinations have been reported are the diesters of D-glucofuranose[12,13] and D-fructopyranose.[14]

The main objective of our study is to identify carbohydrates that are potentially suitable linear linkers—in both a geometrical and a chemical sense—for linear and higher dimensional boronic acid nodes. A prerequisite is the existence and adoption of appropriate conformations that allow the formation of boronic diesters. As the framework-forming reactions are carried out under equilibrium conditions, the existence of a thermodynamically highly favored product is desirable to obtain uniform networks. Aldopentoses with their four hydroxyl groups are the smallest suitable members from the monosaccharide pool. Boronic acid esters of this substance class have been prepared and characterized by NMR spectroscopy.[15–17] However, the described compounds were obtained from reactions in dry aprotic media (e.g., pyridine, acetone, and benzene) and the results are not necessarily transferable to aqueous solutions. The focus of this work, however, is the investigation of the metrical properties of the attempted COF building blocks by means of X-ray crystal-structure analysis. The experimental studies have been complemented by density functional calculations of NMR shielding constants to prove the applicability of inexpensive quantum chemical methods to the prediction of ^{13}C chemical shifts for the compound class under investigation.

2. Results and discussion

The four aldopentoses D-ribose, D-arabinose, D-xylose, and D-lyxose were treated with two equivalents of phenylboronic acid in 1:1 mixtures of water and methanol to allow the formation of pentose diesters with all four hydroxyl groups esterified. Before adding the boronic acid, the pure aqueous carbohydrate solution was stirred for some time to obtain the typical isomeric distribution between the anomeric furanose and pyranose forms. In

* Corresponding author. Fax: +49 89 2180 77407.
E-mail address: peter.kluefers@cup.lmu.de (P. Klüfers).

0008-6215/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2009.11.022

addition, the reactions were carried out with racemic mixtures, which frequently have a higher crystallization tendency.

2.1. Ribose

In the reaction of D-ribose with phenylboronic acid (1:2) a colorless solid was obtained. The NMR spectra of the substance redissolved in DMSO-d_6 showed a single major product PhB(β-D-Rib*p*2,4H$_{-2}$) (**1**), which was proved by ^{1}H and 2D NMR spectroscopy to contain two free hydroxyl groups, thus being a boronic acid monoester (Scheme 1). According to chemical shift values, the minor product was a pyranose as well. Based on the mass spectrum of the obtained solid, this minor product is assumed to be the diester (PhB)$_2$(α-D-Rib*p*H$_{-4}$). The 2D NMR experiments in conjunction with the results on analogous boric acid esters (DiolH$_{-2}$)B(OH) of 1,3-diols led to the assignment of the bonding sites, O2 and O4. The unusual low chemical shift of C3 is in agreement with quantum chemical calculations. Due to its conformation, the product has no possibility to react with a second equivalent of PhB(OH)$_2$.

2.2. Arabinose

The reaction of D-arabinose with two equivalents of phenylboronic acid gave, as the sole product, the diester (PhB)$_2$(β-D-Ara*p*H$_{-4}$) (**2**) as colorless crystals. In agreement with the formula (Scheme 1), the ^{13}C NMR spectrum showed signals of two phenyl groups and, in the aliphatic region, the characteristic signal set of a pyranose ring. The molecular structure of **2** was determined by single-crystal X-ray diffraction (Fig. 1). The pyranose ring adopts a slightly twisted boat conformation and bears two phenylboranediyl substituents bonded to O1/2 and O3/4. Each of the ester groups, including the phenyl ring and the sugar diol moiety, is planar (0.06 Å RMS deviation from the least-squares planes), the interplanar angle being 78.36(5)°.

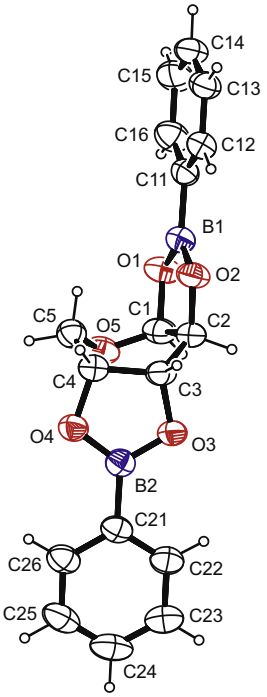


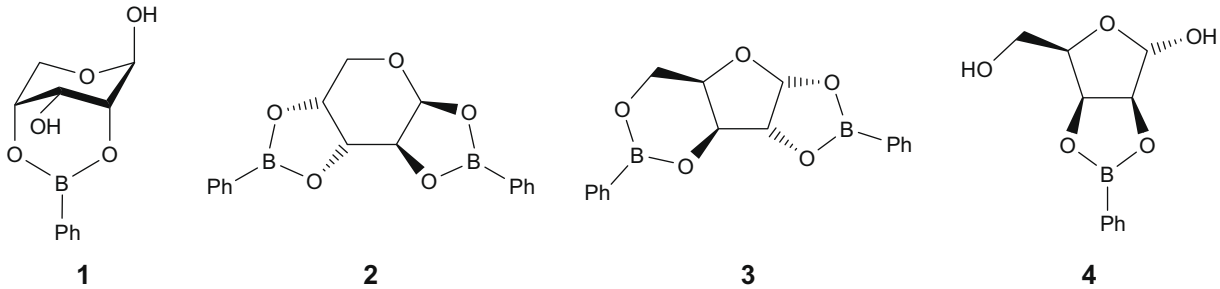
Figure 1. Structure of (PhB)$_2$(β-D-Ara*p*H$_{-4}$) in crystals of **2** (50% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances (Å) and angles (°) (with standard deviations of the last digit in parentheses): O1–B1 1.377(3), O2–B1 1.364(3), O3–B2 1.369(3), O4–B2 1.365(3), O2–B1–O1 113.04(19), O4–B2–O3 113.32(19), O1–C1–C2–O2 16.4(2), O3–C3–C4–O4 11.0(2). Puckering parameters[24] of the pyranose ring O5–C1–C2–C3–C4–C5: Q = 0.643(2) Å, θ = 100.16(18)°, φ = 145.6(2)°.

2.3. Xylose

The sole product of the reaction with D-xylose was the diester (PhB)$_2$(α-D-Xyl*f*H$_{-4}$) (**3**) in the α-furanose form (Scheme 1). The NMR signals of the carbohydrate ring were unambiguously assigned by routine 2D NMR experiments and are highly correlated with the values obtained by quantum chemical calculations. The two boronic acid ester groups present in **3** are derived from a 1,2-diol (O1/2) and a 1,3-diol (O3/5), respectively. A structural analysis (Fig. 2) was performed on a crystal obtained from racemic xylose under the same reaction conditions. The furanose ring adopts an envelope conformation on C4 which is, in addition, the only extraplanar atom of the dioxaborane ring. Each of the ester groups, including the phenyl ring and the participating carbon atoms of the carbohydrate, is planar (0.04 Å RMS deviation from the least-squares planes), the interplanar angle being 52.53(3)°.

2.4. Lyxose

The reaction of D-lyxose with the boronic acid gave a colorless solid. The ^{13}C NMR spectrum showed a signal set of the main product PhB(α-D-Lyx*f*2,3H$_{-2}$) (**4**) accompanied by weaker signals of byproducts, which also contained diesters according to mass spectra. Crystals suitable for X-ray diffraction were obtained and investigated. Figure 3 shows the molecular structure of **4**. In agreement with the spectroscopic data, the carbohydrate exists in the α-furanose form, adopting an envelope conformation. NMR spectra of redissolved crystals proved that the obtained structure of the monoester **4** corresponds to the main product of the reaction, which is geometrically unable to react with a second equivalent of boronic acid.



Scheme 1. Products of the reactions between phenylboronic acid and D-ribose (**1**), D-arabinose (**2**), D-xylose (**3**), and D-lyxose (**4**).

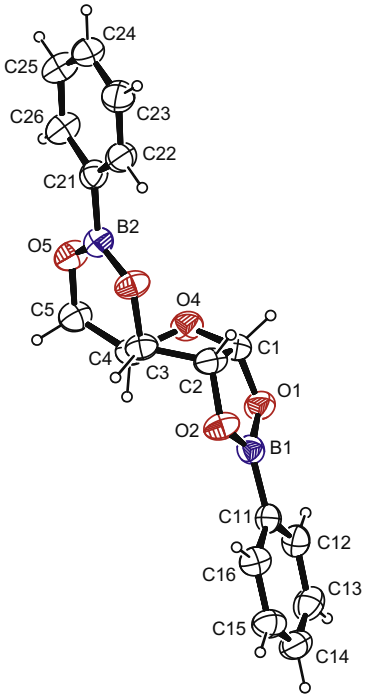


Figure 2. Structure of $(PhB)_2(\alpha$-D-Xyl*f*H$_{-4})$ in crystals of *rac*-**3** (50% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances (Å) and angles (°) (with standard deviations of the last digit in parentheses): O1–B1 1.3673(17), O2–B1 1.3756(17), O3–B2 1.3672(16), O5–B2 1.3525(17), O1–B1–O2 112.96(11), O5–B2–O3 123.08(12), O1–C1–C2–O2 −0.15(13). Puckering parameters[24] of the furanose ring O4–C1–C2–C3–C4: $Q_2 = 0.3752(15)$ Å, $\varphi_2 = 325.0(2)°$, envelope on C4.

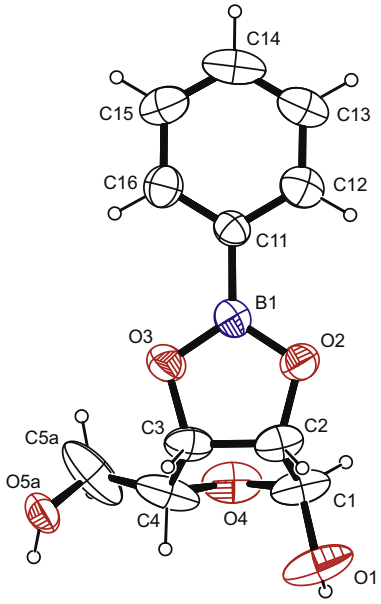


Figure 3. Structure of PhB(α-D-Lyx*f*2,3H$_{-2}$) in crystals of **4** (50% probability ellipsoids, hydrogen atoms with arbitrary radii, one orientation of the disordered hydroxymethyl group omitted for clarity). Interatomic distances (Å) and angles (°) (with standard deviations of the last digit in parentheses): O2–B1 1.373(6), O3–B1 1.368(6), O3–B1–O2 112.7(4), O2–C2–C3–O3 4.0(5). Puckering parameters[24] of the furanose ring O4–C1–C2–C3–C4: $Q_2 = 0.387(6)$ Å, $\varphi_2 = 355.4(8)°$, envelope on O4.

2.5. Product formation and hydrolytic properties

The hydrolytic behavior of the described compounds was examined for the monoester **1** and diester **2** as model compounds. After adding excess water to the NMR solutions in DMSO, the ^{13}C NMR spectra exclusively showed signals of the starting materials, thus indicating the complete hydrolysis of both types of esters, which is in agreement with previous studies.[1] The same seems to hold true for the water–methanol mixtures at the beginning of the ester syntheses: the products can only be present to a small extent in the solution equilibrium. During the evaporation of the more volatile and less polar methanol, the polarity of the residual liquid increases and the precipitation of the sparsely polar esters is the driving force of the reaction, leading to a quantitative conversion of the carbohydrate. The obtained product range should depend on the available isomers of the saccharide and the polarity of the esters to be formed. The synthesis of **3** documents that the employed reaction conditions are, in fact, equilibrium conditions: in the sole product $(PhB)_2(\alpha$-D-Xyl*f*H$_{-4})$ the carbohydrate exists in the α-furanose form, which in an aqueous solution of the free aldose is adopted by less than 1%[18] of the molecules. Therefore, it can be assumed that the isomerization of the aldose is very fast on the time scale of boronic ester formation and that, due to the formation of uniform diesters, the employed synthetic method is a valuable starting point for the synthesis of covalent frameworks from carbohydrates and boronic acids.

3. NMR calculations

Motivated by unusual shift values in the case of the ribose ester (**1**), the structures of **1–4** were optimized at the B3LYP/6-31+G(2d,p) level of theory with very tight convergence criteria and an ultra-fine integration grid using GAUSSIAN 03.[19] Solvation in DMSO was accounted for by applying the polarizable continuum model (PCM). Frequency analyses were performed to ensure that the obtained structures represent minima on the potential energy hypersurfaces. NMR shielding constants were derived from the optimized structures with the gauge-independent atomic orbital (GIAO) method at the PBE1PBE/6-311++G(2d,p) level of theory. The solvation model was applied here again.

Figure 4 shows a plot of the experimentally observed chemical shift values δ_{obs} against the quantum chemically calculated shielding

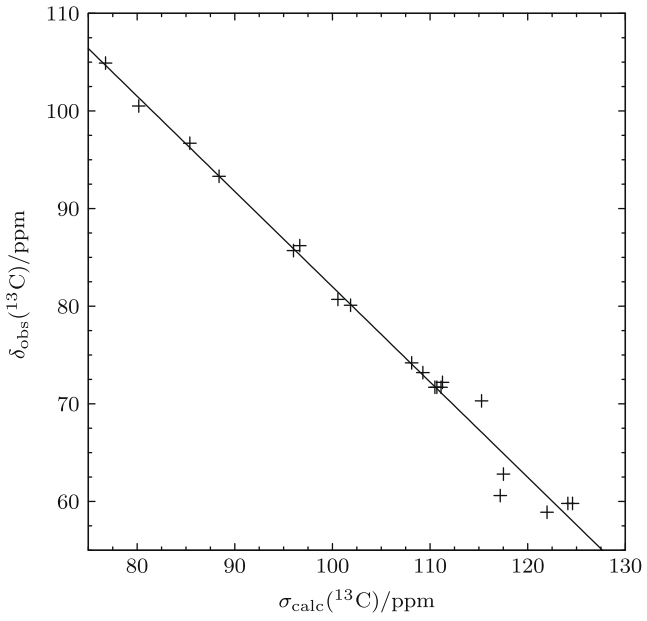


Figure 4. Linear correlation between calculated [PBE1PBE/6-311++G(2d,p)] ^{13}C NMR shielding constants σ_{calc} and experimentally observed chemical shifts δ_{obs} for compounds **1–4**.

constants σ_{calc} for compounds **1**–**4**. The obvious linear correlation is best described by the equation

$$\delta_{obs}/\text{ppm} = -(0.98 \pm 0.03) \cdot \sigma_{calc}/\text{ppm} + (180 \pm 3).$$

As the chemical shifts in furanoses and pyranoses are sensitive to conformational changes, the high correlation is strong evidence for the similarity of solution and solid-state structures. The comparatively inexpensive combination of the well-established DFT methods and basis sets[20] proved to be a reliable instrument for the prediction of NMR shifts, and will be helpful in further studies involving more complex carbohydrates and derivatives thereof.

4. Conclusions

The interplay between the aldopentose anomeric and furanose/pyranose equilibria and the increasing solvent polarity during the syntheses leads to the formation of single products in the case of the diesters of arabinose (**2**) and xylose (**3**), which are the least polar possible products. In the case of ribose and lyxose the main products are monoesters, which could be ascribed to ring strain in the conceivable diesters or a kinetic hindrance in their formation. The latter one could explain the observation of product mixtures in these cases.

The molecular structure of (PhB)$_2$(β-D-Ara*p*H$_{-4}$) (**2**) is quite similar to the diester (PhB)$_2$(β-D-Fru*p*2,3,4,5H$_{-4}$) of fructopyranose,[14] which features an additional dangling hydroxymethyl functionality on arabinose C1. With the four structurally characterized diesters of arabinose, xylose, glucose,[12,13] and fructose[14] a variety of possible linkers for boronic-ester-based COFs are available. The formation of larger building blocks and networks with di-, tri-, and tetraboronic acids is the subject of further studies.

5. Experimental

5.1. General methods

Materials: Reagent grade chemicals were purchased from ABCR, Acros, Fluka, and Glycon and were used as supplied.

NMR spectra were recorded at room temperature on Jeol Eclipse 270 (^{1}H: 270 MHz, ^{13}C: 67.9 MHz, ^{11}B: 86.7 MHz) and Jeol Eclipse 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz) NMR spectrometers. The signals of the deuterated solvent (^{13}C) and the residual protons therein (^{1}H) were used as an internal secondary reference for the chemical shift. ^{11}B NMR shift values were referenced externally to $BF_3{\cdot}Et_2O$. NMR signals were assigned by means of routine ^{1}H–^{1}H COSY45, DEPT135, ^{1}H–^{13}C HMQC, and ^{1}H–^{13}C HMBC experiments. ^{13}C NMR signals of the aromatic *ipso* carbon atoms were not detectable with routine experiments, presumably due to the magnetic interaction with the boron nuclei leading to fast relaxation.

High-resolution mass spectra were recorded on a Jeol JMS-700 spectrometer in DEI$^+$ mode. Elemental analyses were performed with an Elementar vario MICRO analyzer.

5.2. Crystal structure determination and refinement

Crystals suitable for X-ray crystallography were selected with the aid of a polarization microscope, mounted on the tip of a glass fiber, and investigated at 200(2) Kelvin on a Bruker-Nonius KappaCCD diffractometer equipped with a rotating Mo-anode and MONTEL graded multilayered X-ray optics (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97[21]) and refined by full-matrix, least-squares calculations on F^2 (SHELXL-97[21]). Hydrogen atoms were included in idealized positions, riding on their parent atoms. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Table 1 contains the crystallographic details.

Due to the absence of significant anomalous scattering, the absolute structure factor (Flack parameter) is omitted from the table. Friedel opposites have been merged and the absolute structures of **2** and **4** were assigned to match the known stereochemistry of the starting materials. The refined structures were analyzed with PLATON[22] and visualized with ORTEP-3.[23]

Crystallographic data are listed in Table 1. CCDC 748203–748205 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5.3. General procedure for boronic ester synthesis

A solution of phenylboronic acid (10.0 mmol, 1.22 g) in methanol (10 mL) was added to a stirred solution of the pentose (5.00 mmol, 0.751 g) in water (10 mL) at room temperature. After 2 h, the reaction mixture was evaporated to dryness under reduced pressure. Colorless precipitates were formed during the evaporation of the lower boiling methanol. Compounds **2** and **3** were obtained in a quantitative yield. In the case of **1** and **4**, the obtained solids contained residual boronic acid. Crystals were obtained upon slow evaporation of solutions from acetone.

5.4. PhB(β-D-Rib*p*2,4H$_{-2}$) (1)

^{11}B NMR (DMSO-d_6, 86.7 MHz, 25 °C): δ 29.5 (br). ^{1}H NMR (DMSO-d_6, 400 MHz, 22 °C): δ 7.80–7.76 (m, 2H), 7.46–7.29

Table 1
Crystallographic data for compounds **2**–**4**

	2	*rac*-**3**	**4**
CCDC number	748203	748204	748205
Empirical formula	$C_{17}H_{16}B_2O_5$	$C_{17}H_{16}B_2O_5$	$C_{11}H_{13}BO_5$
M/(g mol^{-1})	321.92	321.92	236.02
Color	colorless	colorless	colorless
Size (mm^3)	0.15 × 0.11 × 0.04	0.26 × 0.06 × 0.04	0.06 × 0.04 × 0.01
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$
a (Å)	9.3280(3)	16.8525(4)	4.5593(3)
b (Å)	10.1307(3)	5.05010(10)	6.3236(7)
c (Å)	17.0563(5)	21.4143(4)	37.906(4)
β (°)	90	121.1100(10)	90
V (Å^3)	1611.81(8)	1560.38(6)	1092.88(18)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.327	1.370	1.434
μ (mm^{-1})	0.095	0.098	0.111
Reflections measured	12,762	12,183	3486
θ (°)	3.20–27.48	3.63–27.49	3.60–25.04
Index ranges	$-12 \leqslant h \leqslant 12$ $-12 \leqslant k \leqslant 13$ $-22 \leqslant l \leqslant 22$	$-21 \leqslant h \leqslant 21$ $-6 \leqslant k \leqslant 6$ $-26 \leqslant l \leqslant 27$	$-3 \leqslant h \leqslant 4$ $-6 \leqslant k \leqslant 6$ $-41 \leqslant l \leqslant 31$
Independent reflections	2107	3576	993
Reflections observed [$I > 2\sigma(I)$]	1578	2842	708
R_{int}	0.0519	0.0304	0.0459
Mean $\sigma(I)/I$	0.0291	0.0329	0.0539
Reflections in refinement	2107	3576	993
Parameters	218	217	167
Restraints	0	0	0
Weighting scheme	0.0647, 0.0000	0.0527, 0.2612	0.0569, 0.4398
R_{all} (R_{obs})	0.0591 (0.0370)	0.0526 (0.0411)	0.0881 (0.0534)
wR_{all} (wR_{obs})	0.1019 (0.0921)	0.1135 (0.1054)	0.1286 (0.1129)
S	1.061	1.043	1.088
Residual densities (e/Å^3)	−0.198, 0.201	−0.240, 0.152	−0.215, 0.237

(m, 3H), 6.83 (d, 1H, $J_{1',1}$ 4.3 Hz, OH-1), 5.38 (d, 1H, $J_{3',3}$ 3.3 Hz, OH-3), 5.09–5.05 (m, 1H, H-1), 4.10–4.04 (m, 2H, H-3, H-4), 3.95–3.89 (m, 2H, H-2, H-5a), 3.61 (dd, 1H, $J_{5b,5a}$ 12.0, $J_{5b,4}$ 2.5 Hz, H-5b). ^{13}C NMR (DMSO-d_6, 101 MHz, 23 °C): δ 134.1, 130.0, 127.3, 93.3 (C-1), 71.7 (C-2), 70.3 (C-4), 62.8 (C-5), 60.6 (C-3). DEI-HRMS Calcd for $C_{11}H_{14}BO_5$ $[M+H]^+$: 237.0934. Found 237.0945. Anal. Calcd for $C_{11}H_{13}BO_5$: C, 55.98, H, 5.55. Found: C, 55.90; H, 5.19.

5.5. (PhB)$_2$(β-D-Arap*H*$_{-4}$) (2)

^{11}B NMR (DMSO-d_6, 86.7 MHz, 25 °C): δ 27.6 (br). ^{1}H NMR (DMSO-d_6, 270 MHz, 25 °C): δ 7.80–7.29 (m, 10H), 5.96 (d, 1H, $J_{1,2}$ 6.0 Hz, H-1), 5.10 (dd, 1H, $J_{3,4}$ 8.6, $J_{3,2}$ 2.4 Hz, H-3), 4.86 (dd, 1H, $J_{2,1}$ 6.0, $J_{2,3}$ 2.4 Hz, H-2), 4.79 (dd, 1H, $J_{4,3}$ 8.6, $J_{4,5a}$ 1.5 Hz, H-4), 3.77–3.57 (m, 2H, H-5a, H-5b). ^{13}C NMR (DMSO-d_6, 101 MHz, 24 °C): δ 134.6, 134.1, 131.9, 130.0, 128.1, 127.3, 96.7 (C-1), 72.2 (C-2), 71.72 (C-3/4), 71.66 (C-3/4), 59.8 (C-5). DEI-HRMS Calcd for $C_{17}H_{16}B_2O_5$ $[M]^+$: 322.1184. Found 322.1183. Anal. Calcd for $C_{17}H_{16}B_2O_5$: C, 63.42; H, 5.01. Found: C, 63.71; H, 5.01.

5.6. (PhB)$_2$(α-D-Xyl*f*H$_{-4}$) (3)

^{11}B NMR (DMSO-d_6, 86.7 MHz, 25 °C): δ 27.8 (br). ^{1}H NMR (DMSO-d_6, 400 MHz, 22 °C): δ 7.76–7.32 (m, 10H), 6.29 (d, 1H, $J_{1,2}$ 4.1 Hz, H-1), 5.03 (d, 1H, $J_{2,1}$ 4.1 Hz, H-2), 4.72 (d, 1H, J 2.8 Hz, H-3), 4.47–4.44 (m, 1H, H-4), 4.36–4.25 (m, 2H, H-5a, H-5b). ^{13}C NMR (DMSO-d_6, 101 MHz, 24 °C): δ 134.6, 133.5, 131.9, 131.0, 128.0, 127.6, 104.9 (C-1), 85.7 (C-2), 74.2 (C-3), 73.2 (C-4), 59.8 (C-5). DEI-HRMS Calcd for $C_{17}H_{16}B_2O_5$ $[M]^+$: 322.1184. Found 322.1189. Anal. Calcd for $C_{17}H_{16}B_2O_5$: C, 63.42; H, 5.01. Found: C, 63.24; H, 4.84.

5.7. PhB(α-D-Lyx*f*2,3H$_{-2}$) (4)

^{11}B NMR (DMSO-d_6, 86.7 MHz, 25 °C): δ 28.8 (br). ^{1}H NMR (DMSO-d_6, 400 MHz, 22 °C): δ 7.71–7.67 (m, 2H), 7.55–7.51 (m, 1H), 7.43–7.39 (m, 2H), 6.59 (d, 1H, $J_{1',1}$ 4.3 Hz, OH-1), 5.25 (d, 1H, $J_{1,1'}$ 4.3 Hz, H-1), 5.09 (dd, 1H, $J_{3,2}$ 6.1, $J_{3,4}$ 4.0 Hz, H-3), 4.82–4.80 (m, 2H, O5-H, H-2), 4.18–4.14 (m, 1H, H-4), 3.78–3.72 (m, 1H, H-5a), 3.56–3.50 (m, 1H, H-5b). ^{13}C NMR (DMSO-d_6, 101 MHz, 23 °C): δ 134.5, 131.8, 128.0, 100.5 (C^1), 86.2 (C^2), 80.7 (C^3), 80.1 (C^4), 58.9 (C^5). DEI-HRMS Calcd for $C_{11}H_{14}BO_5$ $[M+H]^+$: 237.0934. Found 237.0933. Anal. Calcd for $C_{11}H_{13}BO_5$: C, 55.98; H, 5.55. Found: C, 56.06; H, 5.29.

Acknowledgments

This work was supported within the functional asymmetric networks (FAN) project by the investment fund of LMUexcellent. M.M.R. thanks the Fonds der Chemischen Industrie for a Ph.D fellowship.

References

1. Hall, D. G.. In *Boronic Acids*; Hall, D. G., Ed., 1st ed.; Wiley-VCH: Weinheim, 2005; pp 1–99.
2. Kuivila, H. G.; Keough, A. H.; Soboczenski, E. J. *J. Org. Chem.* **1954**, *19*, 780–783.
3. Sugihara, J. M.; Bowman, C. M. *J. Am. Chem. Soc.* **1958**, *80*, 2443–2446.
4. Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166–1170.
5. El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Côté, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2007**, *316*, 268–272.
6. Fujita, N.; Shinkai, S.; James, T. D. *Chem. Asian J.* **2008**, *3*, 1076–1091.
7. Severin, K. *Dalton Trans.* **2009**, 5254–5264.
8. Ngo, H. L.; Lin, W. *Top. Catal.* **2005**, *34*, 85–92.
9. Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986.
10. Mikami, M.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1995**, 153–154.
11. Nakazawa, I.; Suda, S.; Masuda, M.; Asai, M.; Shimizu, T. *Chem. Commun.* **2000**, 881–882.
12. Draffin, S. P.; Duggan, P. J.; Fallon, G. D.; Tyndall, E. M. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *61*, o1733–o1735.
13. Chandran, S. K.; Nangia, A. *CrystEngComm* **2006**, *8*, 581–585.
14. Draffin, S. P.; Duggan, P. J.; Fallon, G. D. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2004**, *60*, o1520–o1522.
15. Wood, P. I.; Siddiqui, I. R. *Carbohydr. Res.* **1974**, *32*, 97–104.
16. Stacey, B. E.; Tierny, B. *Carbohydr. Res.* **1976**, *49*, 129–140.
17. Dahlhoff, W. V.; Schroth, G.; Gabor, B.; Köster, W. *Z. Naturforsch., B: J. Chem. Sci.* **1990**, *45*, 547–551.
18. Drew, K. N.; Zajicek, J.; Bondo, G.; Bose, B.; Serianni, A. S. *Carbohydr. Res.* **1998**, *307*, 199–209.
19. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. GAUSSIAN 03, Revision D.01., Gaussian, Inc.: Wallingford CT, 2004.
20. Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, 2001.
21. Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.
22. Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
23. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
24. Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.