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Polyols as Templates for the Synthesis of Macrocycles from Boronic Acid Building Blocks[‡]

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By using a norbornane tetraol **2** as a template, a bis(alkenyloxy)-substituted boronic acid **5** was bound twice, and the resulting bis(boronic acid ester) **6** was cyclized by ring-closing metathesis. The product bimacrocycle **7**, or its hydrogenated analogue **8**, are starting materials for subsequent reactions which give different *endo*-functionalized macrocycles as diboronic acids or diphenols. The bis(boronic acid) **12** proved to be a receptor for polyols.

Introduction

The synthesis of cyclic compounds usually is more difficult than that of acyclic analogues. Only five- and six-membered rings are an exception, because no large enthalpic and entropic penalties have to be paid upon cyclization.[1] While strain is the main obstacle for the formation of small (three- or four-membered) or medium-sized (seven- to twelve-membered) cycles, large rings (macrocycles) are usually unstrained. But entropy hinders their formation because only a few conformations of the non-macrocyclic precursor possess the proper orientation of the reactive groups for an intramolecular ring-closing reaction.[2]

Therefore a number of "tricks" have been developed to overcome this entropic problem. When analyzing ring-closing reactions, kinetically controlled and thermodynamically controlled reactions have to be discussed.

In kinetically controlled ring closures, the *intra*molecular macrocyclization competes with *inter*molecular oligo- or polymerizations, i.e. a unimolecular reaction competes with a bimolecular one. This is the reason why the high-dilution principle enables the synthetic chemist to obtain macrocycles in good yields under kinetic control. In a kinetically controlled, irreversible reaction, a macrocycle once formed remains a macrocycle.

High dilution may also help to obtain better yields of macrocycles in thermodynamically controlled reactions in which several products, macrocyclic or not, are in equilibrium with one another. In terms of entropy, it is more favorable to generate many macrocycles instead of one long polymer. But if a certain oligomer is distinctly more stable than the desired macrocycle, the equilibrium of a thermodynamically controlled reaction will favor this compound. In short, a thermodynamically controlled macrocyclization will preferentially form the most stable compound. The relative stabilities of all products, macrocyclic or acyclic, polymeric or not, determine the product distribution.

If the desired compound is not the most stable compound (in terms of free enthalpy), conditions must be modified to make the compound the most stable entity in the mixture. A very successful approach has been the use of templates. It exploits the fact that macrocycles do contain a hole. If a template is chosen which fits snugly into this hole, the resulting complex gains stability, and this may shift the equilibrium to the compound which is best complementary to the template. Numerous such syntheses are known.[3,4] Many of these have used the concept of dynamic combinatorial chemistry.[5–9] Besides metal ions as templates, organic templates have been used, too. For thermodynamic control, the ring-closing reaction has to be reversible and in recent publications, the transition-metal-catalyzed ring-closing metathesis[10,11] has been used increasingly. The interaction between the template and the ring-formation building blocks may be manifold: from covalent bonds[12,13] to complexation of ammonium ions[14] or complexation of transition metal ions.[15–17]

In this work, we have investigated a polyol as template and boronic acids as building blocks for the macrocycle. Boronic acids[18] have been chosen due to their broad potential to be converted into other functionalities. They may form esters with alcohols enabling the resulting macrocycles to act as sensors[19,20] or carriers,[21] but they may also be converted into a number of other functional groups (e.g. oxygenation to a phenol, Suzuki coupling with other moieties) or they may even be replaced by a hydrogen atom.

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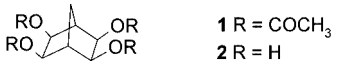
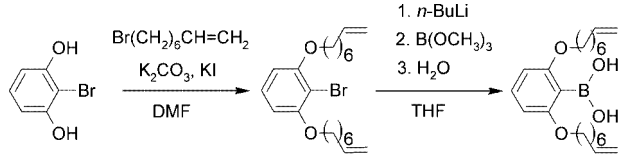
Results

As a first template, we have chosen a rigid tetraol **2**[22] which can be synthesized from 2,5-norbornadiene. In analogy to the tetrahydroxylation of 1,4-cyclohexadiene by osmium tetroxide,[23] **2** could be obtained in good yield. For better isolation, the tetraol **2** was first acetylated, purified as the tetraester **1** and then hydrolyzed to give pure tetraol **2** in 79% overall yield.

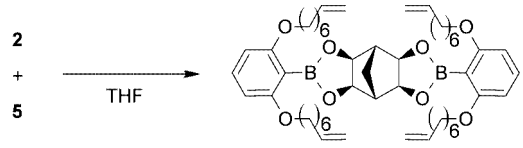


As building block for the macrocycle, the boronic acid **5** was synthesized in analogy to well-established syntheses of related boronic acids.[24] Starting from 2-bromoresorcinol (**3**),[25] the phenol groups were alkenylated, first giving the bromide **4** in 94% yield. Lithiation, reaction with trimethyl borate and hydrolysis yielded the desired boronic acid **5** in 77% yield.



3 **4** **5**

Next, 2 equiv. of the boronic acid **5** were mixed with the template **2**, and the bis(boronic ester) **6** was obtained after concentration. Without further purification, pure **6** was obtained, as determined by spectroscopy and by elemental analysis. The exact stoichiometry of the starting compounds is essential because any attempt to purify the diester led to decomposition of **6**.



6

This diester **6** was then treated with the Grubbs' catalyst (benzylidene)dichlorobis(tricyclohexylphosphane)ruthenium. As envisaged, the macrocycle formed around the template **2**, and the resulting bimacrocyclic diene **7** could be isolated in 47% yield. Besides the desired bimacrocycle, also the intermediate monomacrocycle, in which only two of the four terminal alkene groups have reacted to give one 1,2-disubstituted alkene, was formed. By adding Grubbs' catalyst to this by-product, also the monomacrocycle could be further cyclized to give additional **7**. When using other, shorter alkenyloxy-substituted phenylboronic acids,[24] the diester was also formed but metatheses gave no isolable bimacrocyclic material.

By using the same experimental conditions, the boronic acid **5** was mixed with the Grubbs' catalyst in the absence of the template and stirred. After 2 d, NMR analysis showed that two thirds of the vinyl groups were still intact. By mass spectrometry, no macrocycle **9** could be detected. These results clearly show the importance of the template. It brings together the two reaction components and stabilizes the reaction product.

Another experiment also shows the strong stability of the macrocycle when bound to the template. To prove the reversibility of the metathesis reaction, the product of the ring-closing metathesis, the bimacrocycle **7**, was mixed with Grubb's catalyst and 3-hexene. Although 3-hexene was added in a more than 10-fold excess, the bimacrocycle was only partially cleaved, as detected by MALDI mass spectrometry. Signals which correspond to the addition of 1 equiv. of hexene to the bimacrocycle **7** could be found, which proves the reversibility, and the signals of the unchanged starting material **7** prove the considerable stabilization by the template.

With the bimacrocyclic diene **7**, the task of selective macrocyclization is fulfilled. **7** can now be used as starting material for further modifications. To avoid side reactions and to simplify spectra, the alkene units have been reduced to alkanes. Thus, **8** was formed from **7** in 99% yield by using palladium on charcoal and hydrogen at ambient temperature and pressure.

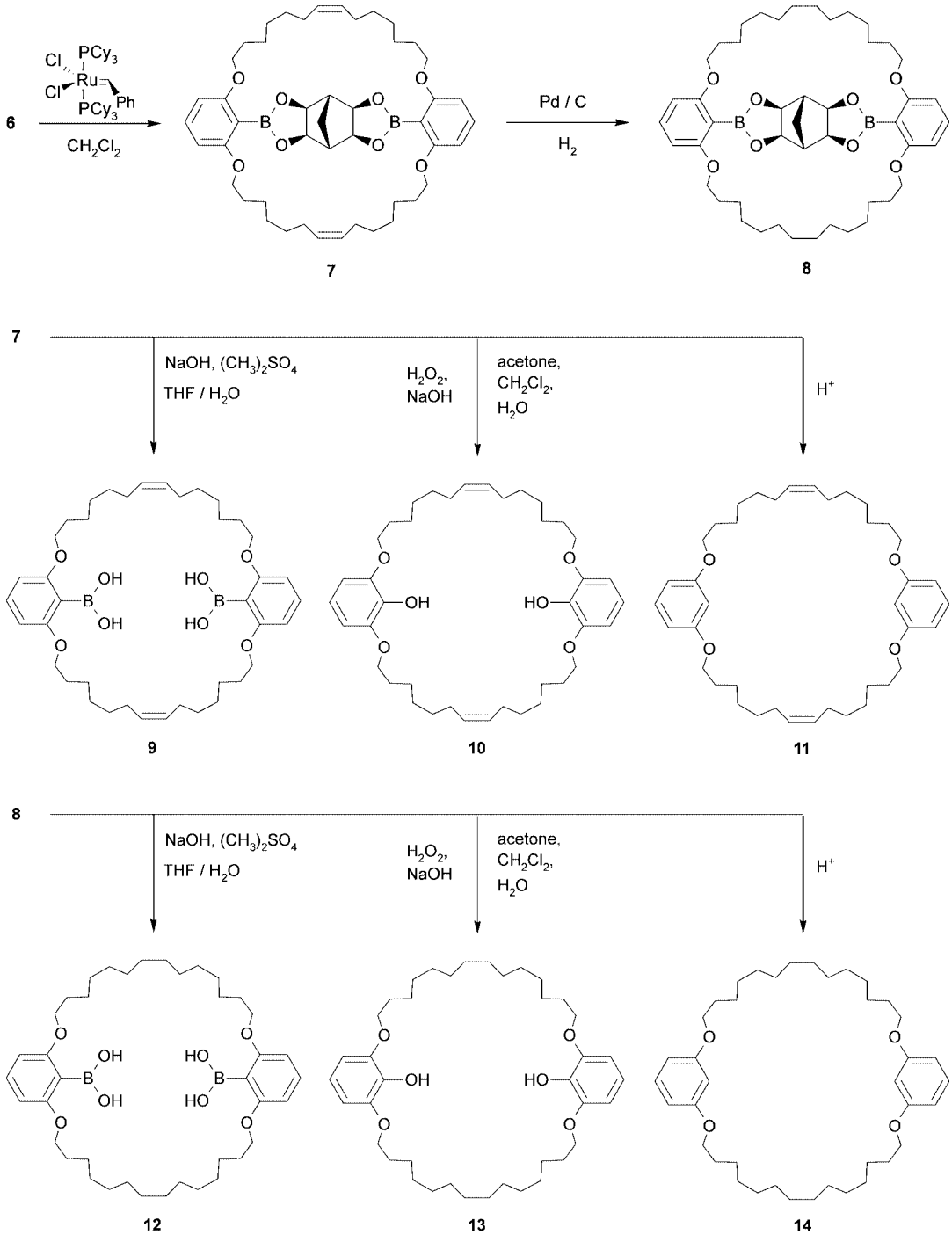
As stated above, formation of boronic esters was chosen for the connection of the building blocks to the template in order to allow easy modifications of the product which obviously must include the removal of the template.

Three reactions of the bimacrocyclic bis(boronic esters) **7** and **8** have been investigated. Obviously, the template can be removed by hydrolysis of the boronic esters. However, this reaction was more difficult than anticipated. The macrocyclic bis(boronic acids) **9** and **12** seem to be perfect ligands for the templates and therefore the free acids **9** and **12** could not be isolated when the esters were simply hydrolyzed using various conditions. However, the addition of dimethyl sulfate, which presumably scavenged the tetraol **2** by alkylation, allowed the generation of the free boronic acids **9** and **12** in 48 and 55% yield, respectively.

The macrocyclic bis(boronic acids) **9** and **12** are preorganized to complex a polyol. As expected from the difficulties to cleave the boronic acid esters, they are very good receptors for the tetraol **2**. This template is not soluble in chloroform but addition of the receptor **12** to chloroform dissolves the solid tetraol **2**. This reaction can easily be monitored by NMR spectroscopy. The signals of the macrocyclic diester **8** reappear slowly, and also the signal for the side product water can be recorded. Remarkably, only two sets of signals are observed during the reaction: those of the "empty" receptor **12** (decreasing with time), and those of the bis(boronic acid ester) **8** (increasing with time). Mono(boronic acid esters) would lead to an unsymmetric product which could not be found.

Next, the bis(esters) **7** and **8** were treated with hydrogen peroxide under alkaline conditions. The diphenols **10** and **13** were formed and could be isolated in 72 and 54% yield, respectively.

The third reaction involved the cleavage of the aryl–boron bond in the bimacrocycles **7** and **8**. The reduced products **11** and **14** were often found when the bimacrocycles **7** and **8** where exposed to an acidic medium (for instance



when trying to hydrolyze the boronates). Purposeful, the cleavage can be carried out when using trifluoroacetic acid in dichloromethane.

Outlook

By combination of polyols with alkenyl-substituted phenylboronic acids, boronates are formed which can be subjected to a macrocyclization by ring-closing metathesis. Because *both* reactions – the formation of the boronic acid esters, *and* the ring-closing metathesis – are reversible (and metathesis reactions are not inhibited by boronic acids or esters),[26] mixing of several analogues of the two classes of starting material will provide a dynamic combinatorial library.

Experimental Section

General Remarks: The following chemicals were obtained commercially and were used without further purification: (benzylidene)-dichlorobis(tricyclohexylphosphane)ruthenium (Aldrich), 8-bromo-1-octene (Aldrich), *n*-butyllithium solution (Acros), *N*-

methylmorpholine *N*-oxide monohydrate (Lancaster), 2,5-norbornadiene (Lancaster), osmium tetroxide solution (Fluka). 2-Bromo-1,3-dihydroxybenzene[25] was prepared according to literature procedures. Dry solvents were obtained with suitable desiccants. Column chromatography was carried out on silica gel (Macherey–Nagel). ^{1}H and ^{13}C NMR spectra were recorded with Bruker ARX 300 (300 MHz or 75 MHz), DRX 500 (500 MHz or 125 MHz), or Avance 600 (600 MHz or 150 MHz) spectrometers using tetramethylsilane as internal standard. IR spectra were measured with a Perkin–Elmer 1600 Series spectrometer. Mass spectra were recorded with Finnigan MAT 8200 or 8230 spectrometers, or with a MALDI-TOF mass spectrometer Biflex III (Bruker-Daltonics, using 4-hydroxy-α-cyanocinnamic acid as matrix). Elemental analyses were carried out with an EA3000CHNS instrument (HEKAtech).

***all-exo*-2,3,5,6-Tetraacetoxybicyclo[2.2.1]heptane (1):** 2,5-Norbornadiene (2.10 g, 22.8 mmol), dissolved in acetone (26 mL) and water (2.6 mL), was treated with *N*-methylmorpholine *N*-oxide monohydrate (7.98 g, 59.0 mmol). A combination of osmium tetroxide solution (2.4 mL, 2.5% in *tert*-butyl alcohol, 0.18 mmol), *tert*-butyl hydroperoxide solution (46 μL, 70% in water, 0.36 mmol) and *tert*-butyl alcohol (10 mL) was added and the reaction mixture was stirred at ambient temp. under nitrogen for 2.5 h. The solvents were removed in vacuo, and the residue was treated with acetic anhydride (11 mL) and pyridine (22 mL) for 18 h. After addition of ethyl acetate (40 mL), dichloromethane (100 mL) and sodium sulfite solution (1 M, 40 mL), the organic layer was separated and washed with saturated sodium hydrogencarbonate solution (40 mL) and brine (40 mL). The aqueous solution was extracted with dichloromethane (40 mL). The combined organic layers were dried with magnesium sulfate and concentrated in vacuo. Purification by chromatography on silica gel (0.04–0.063 mm) with dichloromethane/ethyl acetate (1:1, R_f = 0.72) and following recrystallization from ethyl acetate/cyclohexane gave pure and white **1** containing 0.5 equiv. of ethyl acetate. Yield: 6.66 g (89%). M.p. 135–136 °C. IR (KBr): $\tilde{\nu}$ = 1740 (s, C=O), 1231 (s, C–O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93 (m, ^4J = 0.7 Hz, ^3J = 1.4 Hz, 2 H, CH_2), 2.04 (s, 12 H, CH_3), 2.40 (t, ^3J = 1.4 Hz, 2 H, C*H*), 4.82 (t, ^4J = 0.7 Hz, 4 H, OC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.48 (q, *C*H$_3$), 29.45 (t, *C*H$_2$), 46.10 (d, *C*H), 71.90 (d, O*C*H), 169.61 (s, *C*=O) ppm. EI-MS (70 eV): *m*/*z* (%) = 328 (< 1) [M]$^+$, 285 (21) [M – $COCH_3$]$^+$, 225 (53), 95 (100). CI-MS (isobutane): *m*/*z* (%) = 329 (18) [M + H]$^+$, 269 (100) [M – $OOCCH_3$]$^+$. $C_{15}H_{20}O_8$ (328.32): calcd. C 54.87, H 6.14. $C_{15}H_{20}O_8 \cdot 0.5C_4H_8O_2$ (372.37): calcd. C 54.83, H 6.50; found C 54.95, H 6.55.

***all-exo*-Bicyclo[2.2.1]heptane-2,3,5,6-tetraol (2):** Tetraacetoxynorbornane **1** (522 mg, 1.59 mmol) was dissolved in dry methanol (25 mL) and treated with a freshly prepared solution of sodium (215 mg, 9.35 mmol), dissolved in dry methanol (5.5 mL). The reaction mixture was stirred at room temp. for 2 h and Amberlite IR-120 (H$^+$ form) was added until the solution reached pH = 4. The filtrate was concentrated and dried in vacuo which resulted in a pure white solid. Yield: 228 mg (89%). M.p. 191–194 °C. IR (KBr): $\tilde{\nu}$ = 3400–3200 (s, OH), 2965, 2948, 2923 (3 s, CH, CH_2), 1052 (C–OH). ^{1}H NMR (500 MHz, MeOD): δ = 1.70 (m_c, ^4J = 0.7 Hz, ^3J = 1.4 Hz, 2 H, CH_2), 2.06 (t, ^3J = 1.4 Hz, 2 H, C*H*), 3.61 (t, ^4J = 0.7 Hz, 4 H, OC*H*) ppm. ^{13}C NMR (125 MHz, MeOD): δ = 26.65 (t, *C*H$_2$), 51.78 (d, *C*H), 71.61 (d, O*C*H) ppm. CI-MS (isobutane), *m*/*z* (%) = 161 (67) [M + H]$^+$, 125 (100), 107 (37). $C_7H_{12}O_4$ (160.17): calcd. C 52.49, H 7.55; found C 52.32, H 7.68.

2-Bromo-1,3-bis(oct-7-enyloxy)benzene (4): 2-Bromo-1,3-dihydroxybenzene[25] (**3**, 1.48 g, 7.83 mmol) was dissolved in dry DMF (25 mL) and potassium carbonate (6.50 g, 47.1 mmol) and potassium iodide (524 mg, 3.16 mmol) were added. After treatment with 8-bromo-1-octene (3.90 g, 20.4 mmol), the reaction mixture was stirred under argon at 60 °C for 16 h. The solvent was removed in vacuo and the residue was distributed between sodium hydroxide solution (30 mL, 2 M) and diethyl ether (30 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with sodium hydroxide solution (3 × 30 mL, 2 M), with brine (30 mL) and then dried with magnesium sulfate. Removal of the solvent and purification by chromatography on silica gel (0.04–0.063 mm) with cyclohexane/ethyl acetate (9:1, R_f = 0.74) gave a colorless oil. Yield: 3.00 g (94%). IR (KBr): $\tilde{\nu}$ = 3075 (m, CH arom.), 2928, 2855 (2 s, aliph. C–H), 1639 (m, C=C), 1590 (s, arom.), 1459 (s), 1254 (s, C–O), 1096 (s), 1036 (m, CBr arom.) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34–1.45 [m, 8 H, O$(CH_2)_3$(C$H_2)_2$], 1.51 [m_c, 4 H, O$(CH_2)_2$CH_2], 1.82 (m_c, 4 H, OCH_2CH_2), 2.06 (m_c, 4 H, CH_2CH=), 3.99 (t, J = 6.5 Hz, 4 H, OCH_2), 4.93 (ddt, J_d = 10.2 Hz, J_d = 2.2 Hz, J_t = 1.2 Hz, 2 H, =CHH_{cis}), 4.99 (ddt, J_d = 17.1 Hz, J_d = 2.2 Hz, J_t = 1.6 Hz, 2 H, =CHH_{trans}), 5.81 (ddt, J_d = 17.1 Hz, J_d = 10.2 Hz, J_t = 6.7 Hz, 2 H, C*H*=), 6.51 (d, J = 8.3 Hz, 2 H, 4,6-*H*), 7.14 (t, J = 8.3 Hz, 1 H, 5-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.81 [t, O$(CH)_2$CH_2], 28.75, 28.77, 29.06 [t, OCH_2CH_2, O$(CH_2)_3$(C$H_2)_2$], 33.66 (t, *C*H$_2$CH=), 69.22 (t, OCH_2), 102.15 (s, 2-*C*), 105.65 (d, 4,6-*C*), 114.23 (t, =CH_2), 127.89 (d, 5-*C*), 138.98 (d, *C*H=), 156.76 (s, 1,3-*C*) ppm. EI-MS (70 eV): *m*/*z* (%) = 411, 409 (2, 2) [M + H]$^+$, 410, 408 (7, 8) [M]$^+$, 329 (18) [M – Br]$^+$, 298 (1) [M – C_8H_{14}]$^+$, 190, 188 (97, 100) [M – $C_{16}H_{28}$]$^+$, 110 (24) [resorcinol]$^+$, 69 (82). CI-MS (isobutane): *m*/*z* (%) = 411, 409 (24, 24) [M + H]$^+$, 329 (15) [M – Br]$^+$, 301, 299 (4, 3) [M – C_8H_{13}]$^+$, 190, 188 (4, 4) [M – $C_{16}H_{28}$]$^+$, 111 (100) [resorcinol + H]$^+$, 69 (19). HRMS ($C_{22}H_{33}BrO_2$): calcd. 408.16638; found 408.16636; ($C_{21}{}^{13}CH_{33}O_2Br$) calcd. 409.16974, found 409.16972; ($C_{22}H_{33}O_2{}^{81}Br$) calcd. 410.16434, found 410.16430; ($C_{21}{}^{13}CH_{33}O_2{}^{81}Br$) calcd. 411.16769, found 411.16808. $C_{22}H_{33}BrO_2$ (409.40): calcd. C 64.54, H 8.12; found C 64.37, H 8.16.

2,6-Bis(oct-7-enyloxy)phenylboronic Acid (5): 2-Bromo-1,3-bis(oct-7-enyloxy)benzene (**4**, 2.55 g, 6.23 mmol) was dissolved in dry THF (30 mL), cooled to –78 °C, and treated with *n*-butyllithium solution (2.70 mL, 6.75 mmol, 2.5 M in *n*-hexane). The reaction mixture was stirred under nitrogen at –78 °C for 1 h, then trimethyl borate (2.10 mL, 18.8 mmol) was added, and the solution was warmed slowly to ambient temperature. After addition of water (20 mL), the layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with brine (20 mL) and dried with magnesium sulfate. Removal of the solvent and purification by chromatography on a silica gel column (0.04–0.063 mm) with cyclohexane/ethyl acetate (6:1, R_f = 0.46) as eluent gave a colorless, crystalline solid. Yield: 1.79 g (77%). M.p. 29 °C. IR (KBr): $\tilde{\nu}$ = 3518 (s, O–H), 3076 (m, CH arom.), 2932, 2856 (2 s, aliph. C–H), 1640 (m, C=C), 1596 (s, arom.), 1461 (s), 1321 (s), 1229 (s, C–O), 1101 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34–1.51 [m, 12 H, O$(CH_2)_2$(C$H_2)_3$], 1.85 (m_c, 4 H, OCH_2CH_2), 2.05 (m_c, 4 H, CH_2CH=), 4.06 (t, J = 6.6 Hz, 4 H, OCH_2), 4.94 (ddt, J_d = 10.2 Hz, J_d = 2.2 Hz, J_t = 1.2 Hz, 2 H, =CHH_{cis}), 5.00 (ddt, J_d = 17.1 Hz, J_d = 2.2 Hz, J_t = 1.6 Hz, 2 H, =CHH_{trans}), 5.80 (ddt, J_d = 17.1 Hz, J_d = 10.2 Hz, J_t = 6.7 Hz, 2 H, C*H*=), 6.59 (d, J = 8.4 Hz, 2 H, 3,5-*H*), 7.34 (t, J = 8.4 Hz, 1 H, 4-*H*), 7.36 (s, 2 H, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.77 [t, O$(CH_2)_2$CH_2], 28.60, 28.65, 29.05 [t, OCH_2CH_2, O$(CH_2)_3$(C$H_2)_2$], 33.54 (t, *C*H$_2$CH=), 68.99 (t, OCH_2), 105.04 (d, 3,5-*C*), 114.32 (t, =CH_2), 132.77 (d, 4-*C*), 138.73 (d, *C*H=), 164.93

(s, 2,6-*C*) ppm. Because of relaxation effects with the ^{11}B isotope, the 1-C signal is of low intensity and missing in the spectrum. EI-MS (70 eV): *m/z* (%) = 375 (3) $[M + H]^+$, 374 (12) $[M]^+$, 330 (19) $[M – BO_2H]^+$, 264 (9) $[M – C_8H_{14}]^+$, 220 (7) $[M – C_8H_{15}BO_2]^+$, 154 (78) $[M – C_{16}H_{28}]^+$, 110 (100) [resorcinol]$^+$, 69 (79). CI-MS (isobutane): *m/z* (%) = 375 (40) $[M + H]^+$, 331 (56) $[M – BO_2]^+$, 265 (25) $[M – C_8H_{13}]^+$, 221 (3) $[M – C_8H_{14}BO_2]^+$, 155 (24) $[M – C_{16}H_{27}]^+$, 111 (100) [resorcinol + H]$^+$, 69 (22). $C_{22}H_{35}BO_4$ (374.32): calcd. C 70.59, H 9.42; found C 70.63, H 9.47.

***all-exo*-4,10-Bis[2,6-bis(oct-7-enyloxy)phenyl]-3,5,9,11-tetraoxa-4,10-diboratetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane (6):** *all-exo*-Bicyclo[2.2.1]heptanetetraol (**2**, 42.1 mg, 0.263 mmol) and 2,6-bis(oct-7-enyloxy)phenylboronic acid (**5**, 197 mg, 0.526 mmol) were dissolved in dry THF (20 mL) and stirred under nitrogen at ambient temp. for 20 h. The solution was concentrated and dried in vacuo to give **6** as a colorless oil. IR (KBr): $\tilde{\nu}$ = 3075 (CH arom.), 2930, 2856 (2 s, CH aliph), 1640 (m, C=C). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.50 [m, 24 H, $O(CH_2)_2(CH_2)_3$], 1.75 (m_c, 8 H, OCH_2CH_2), 2.04 (m_c, 8 H, CH_2CH=), 2.12 (m_c, 2 H, $CHCH_2CH$), 2.66 (m_c, 2 H, OCHC*H*), 3.94 (t, *J* = 6.6 Hz, 8 H, OCH_2), 4.45 (m_c, 4 H, OC*H*), 4.91 (ddt, J_d = 10.2 Hz, J_d = 2.2 Hz, J_t = 1.1 Hz, 4 H, $=CH_{cis}$), 4.98 (ddt, J_d = 17.1 Hz, J_d = 2.1 Hz, J_t = 1.6 Hz, 4 H, $=CH_{trans}$), 5.79 (ddt, J_d = 17.1 Hz, J_d = 10.2 Hz, J_t = 6.7 Hz, 4 H, C*H*=), 6.46 (d, *J* = 8.3 Hz, 4 H, 3,5-*H*), 7.23 (t, *J* = 8.3 Hz, 2 H, 4-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.82 (t, $CHCH_2CH$), 25.73 [t, $O(CH_2)_2CH_2$], 28.78, 28.89, 29.14 [t, OCH_2CH_2, $O(CH_2)_3(CH_2)_2$], 33.70 (t, CH_2CH=), 47.05 (d, OCH*C*H), 68.14 (t, OCH_2), 79.83 (d, O*C*H), 104.17 (d, 3,5-*C*), 114.28 (t, $=CH_2$), 131.71 (d, 4-*C*), 138.97 (d, *C*H=), 163.05 (s, 2,6-*C*) ppm. Because of relaxation effects with the ^{11}B isotope, the 1-C signal is of low intensity and missing in the spectrum. EI-MS (70 eV): *m/z* (%) = 836 (40) $[M]^+$, 726 (12) $[M – C_8H_{14}]^+$, 616 (7) $[M – C_{16}H_{28}]^+$, 506 (10) $[M – C_{24}H_{42}]^+$, 396 (56) $[M – C_{32}H_{56}]^+$, 330 (5) $[C_{22}H_{34}O_2]^+$, 69 (100). CI-MS (isobutane): *m/z* (%) = 837 (8) $[M + H]^+$, 331 (63) $[C_{22}H_{35}O_2]^+$, 69 (100). $C_{51}H_{74}B_2O_8$ (836.75): calcd. C 73.21, H 8.91. $C_{51}H_{74}B_2O_8 \cdot 0.5H_2O$ (845.76): calcd. C 72.43, H 8.94, found C 72.51, H 9.10.

1,18(1,3,2)-Dibenzena-35(4,10)-{*all-exo*-3,5,9,11-tetraoxa-4,10-diboratetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecana}bicyclo[16.16.1]pentatriacontaphane-9,26-diene (7): The bis(boronic acid ester) **6** (615 mg, 0.735 mmol) was dissolved in dry dichloromethane (100 mL) and allowed to react with (benzylidene)dichlorobis(tricyclohexylphosphane)ruthenium (44.0 mg, 0.0535 mmol). The solution was stirred at ambient temp. for 60 h, quenched with ethyl vinyl ether (20 mL), and filtered through a small pad of silica gel. The solvents were removed in vacuo and the crude product was purified by fractional crystallization from dichloromethane/ethanol to give a white solid. Yield: 0.271 g (47%). M.p. 209 °C. IR (KBr): $\tilde{\nu}$ = 2931, 2853 (2 s, CH, CH_2), 1599, 1452 (2 s, arom.) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$):[27] δ = 1.22–1.44 [m, 24 H, $O(CH_2)_2(CH_2)_3$], 1.66 (m_c, 8 H, OCH_2CH_2), 1.95 (m_c, 8 H, CH_2CH=), 1.98 (s, 2 H, $CHCH_2CH$), 2.61 (t, *J* = 1.4 Hz, 2 H, OCHC*H*), 3.86 (t, *J* = 6.4 Hz, 8 H, OCH_2), 4.32 (s, 4 H, OC*H*), 5.32 (m_c, 4 H, =C*H*), 6.40 (d, *J* = 8.3 Hz, 4 H, 4,6-*H*), 7.16 (t, *J* = 8.2 Hz, 2 H, 5-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$):[27] δ = 23.67 (t, $CHCH_2CH$), 25.57 [t, $O(CH_2)_2CH_2$], 28.21, 29.42, 29.45 [t, OCH_2CH_2, $O(CH_2)_3(CH_2)_2$], 31.89 (t, CH_2CH=), 46.67 (d, OCH*C*H), 68.62 (t, OCH_2), 80.01 (d, O*C*H), 104.70 (d, 4,6-*C*), 130.60 (d, =*C*H), 131.79 (d, 5-*C*), 163.15 (s, 1,3-*C*) ppm. Because of relaxation effects with the ^{11}B isotope, the 2-C signal is of a low intensity and has not been found. EI-MS (70 eV): *m/z* (%) = 780 (100) $[M]^+$, 588 (6) $[M – C_{14}H_{24}]^+$, 396 (54) $[M – C_{28}H_{48}]^+$. MALDI-MS: *m/z* = 781 [M + H]$^+$, 803 [M + Na]$^+$. $C_{47}H_{66}B_2O_8$ (780.64): calcd. C 72.31, H 8.52; found C 72.59, H 8.86.

1,18(1,3,2)-Dibenzena-35(4,10)-{*all-exo*-3,5,9,11-tetraoxa-4,10-diboratetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecana}bicyclo[16.16.1]pentatriacontaphane (8): The product of the ring-closing metathesis **7** (151 mg, 0.193 mmol) was dissolved in ethyl acetate (25 mL), palladium on activated charcoal (24.4 mg, 10% Pd) was added and hydrogen was bubbled through the mixture at ambient temp. for 2 h. The solution was stirred under hydrogen for additional 24 h. The catalyst was removed by filtration and the solution was concentrated and dried in vacuo to give a white solid. Yield: 150 mg (99%). M.p. 175 °C. IR (KBr): $\tilde{\nu}$ = 2926, 2852 (2 s, CH, CH_2), 1599, 1453 (2 s, arom.) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.20–1.38 [m, 32 H, $O(CH_2)_3(CH_2)_4$], 1.49 [m_c, 8 H, $O(CH_2)_2CH_2$], 1.73 (m_c, 8 H, OCH_2CH_2), 2.04 (t, *J* = 1.3 Hz, 2 H, $CHCH_2CH$), 2.69 (t, *J* = 1.4 Hz, 2 H, OCHC*H*), 3.95 (t, *J* = 6.0 Hz, 8 H, OCH_2), 4.41 (s, 4 H, OC*H*), 6.46 (d, *J* = 8.3 Hz, 4 H, 4,6-*H*), 7.16 (t, *J* = 8.2 Hz, 2 H, 5-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.71 (t, $CHCH_2CH$), 25.87 [t, $O(CH_2)_2CH_2$], 28.39, 28.51, 28.70, 29.02, 29.20 [t, OCH_2CH_2, $O(CH_2)_3(CH_2)_4$], 46.74 (d, OCH*C*H), 68.28 (t, OCH_2), 79.99 (d, O*C*H), 104.38 (d, 4,6-*C*), 131.83 (d, 5-*C*), 163.36 (s, 1,3-*C*) ppm. Because of relaxation effects with the ^{11}B isotope, the 2-C signal is of low intensity and is missing in the spectrum. EI-MS (70 eV): *m/z* (%) = 784 (100) $[M]^+$, 590 (2) $[M – C_{14}H_{26}]^+$, 396 (24) $[M – C_{28}H_{52}]^+$. MALDI-MS: *m/z* = 785 $[M + H]^+$, 807 $[M + Na]^+$. $C_{47}H_{70}B_2O_8$ (784.68): calcd. C 71.94, H 8.99; found C 71.91, H 9.38.

1,18(1,3)-Bis[2-(dihydroxyboro)benzena]cyclo[16.16]tetratriacontaphane-9,26-diene (9): The product of the ring-closing metathesis **7** (46.7 mg, 0.0589 mmol) was dissolved in a mixture of THF (7 mL) and water (0.7 mL). Sodium hydroxide (35.8 mg, 0.895 mmol) was added and the reaction mixture was stirred at ambient temp. for 0.5 h, treated with dimethyl sulfate (0.20 mL, 2.1 mmol) and was stirred at ambient temp. for additional 2.5 h. The mixture was acidified with sulfuric acid (0.08 mL, 2 N) and the THF was removed in vacuo. To the remaining aqueous layer, containing a white solid, water (7 mL) was added and the mixture extracted with dichloromethane (3 × 7 mL). The combined organic layers were dried with magnesium sulfate and the solvents evaporated in vacuo. Recrystallization from dichloromethane/ethyl acetate gave a colorless solid. Yield: 20.0 mg (48%). M.p. 134 –136 °C. IR (KBr): $\tilde{\nu}$ = 3532, 3459 (2 s, OH), 2921, 2852 (2 s, CH, CH_2), 1598, 1574, 1480, 1461 (4 s, arom.) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 1.3–1.4 [m, 16 H, $O(CH_2)_3(CH_2)_2$], 1.45 [m_c, 8 H, $O(CH_2)_2CH_2$], 1.82 (m_c, 8 H, OCH_2CH_2), 1.97 (m_c, 8 H, CH_2CH=), 4.04 (t, *J* = 6.3 Hz, 8 H, OCH_2), 5.35 (m_c, 4 H, C*H*=), 6.57 (d, *J* = 8.4 Hz, 4 H, 4,6-*H*), 7.33 (t, *J* = 8.4 Hz, 2 H, 5-*H*), 7.36 (s, 4 H, O*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.79 [t, $O(CH_2)_2CH_2$], 28.46, 29.01, 29.11 [t, OCH_2CH_2, $O(CH_2)_3(CH_2)_2$], 32.28 (t, CH_2CH=), 68.88 (t, OCH_2), 104.93 (d, 4,6-*C*), 130.35 (d, =*C*H), 132.82 (d, 5-*C*), 164.96 (s, 1,3-*C*) ppm. Because of relaxation effects with the ^{11}B isotope, the 2-C signal is of low intensity and is missing in the spectrum. EI-MS (70 eV): *m/z* (%) = 604 (28) $[M – 2\ BO_2H]^+$, 110 (100) [resorcinol]$^+$. $C_{40}H_{62}B_2O_8$ (692.54): calcd. C 69.37, H 9.02; found C 69.66, H 9.11.

1,18(1,3)-Bis(2-hydroxybenzena)cyclo[16.16]tetratriacontaphan-9,26-diene (10): The product of the ring-closing metathesis **7** (20.2 mg, 25.9 μmol) was dissolved in dichloromethane (4 mL) and acetone (12 mL), and treated with sodium hydroxide solution (1 mL, 2 N) and hydrogen peroxide solution (2 mL, 30%). Under generation of oxygen, the reaction mixture was stirred at ambient temp. for 4 h. The mixture was acidified with hydrochloric acid

(1 mL, 2 N) and the organic solvents were removed in vacuo. Water (4 mL) and dichloromethane (4 mL) were added to the remaining aqueous layer, and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 5 mL) and the combined organic layers were dried with magnesium sulfate and the solvents evaporated in vacuo. The crude product was purified by recrystallization from ethyl acetate/cyclohexane to give colorless needles of **10**·2H_2O. Yield: 11.9 mg (72%). M.p. 95–97 °C. IR (KBr): $\tilde{\nu}$ = 3511 (br., OH), 2924, 2852 (2 s, CH, CH_2), 1618, 1472 (2 s, arom.), 1100 (s, C–O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$):[28] δ = 1.30–1.40 [m, 16 H, $O(CH_2)_3(CH_2)_2$], 1.42–1.49 [m, 8 H, $O(CH_2)_2CH_2$], 1.79 (m_c, 8 H, OCH_2CH_2), 1.97 (m_c, 8 H, CH_2CH=), 4.02 (t, *J* = 6.4 Hz, 8 H, OCH_2), 5.37 (m_c, 4 H, C*H*=), 5.51 (s, 2 H, OH, exchanges with D_2O), 6.54 (d, *J* = 8.3 Hz, 4 H, 4,6-*H*), 6.73 [AB_2 (dd), *J* = 7.7 Hz, *J* = 8.9 Hz, 2 H, 5-*H*] ppm. ^{13}C NMR (125 MHz, $CDCl_3$):[28] δ = 25.87 [t, $O(CH_2)_2CH_2$], 28.67, 29.23, 29.29 [t, OCH_2CH_2, $O(CH_2)_3(CH_2)_2$], 32.34 (t, CH_2CH=), 69.28 (t, OCH_2), 106.19 (d, 4,6-*C*), 118.81 (d, 5-*C*), 130.35 (d, =*C*H), 135.63 (s, 2-*C*), 146.70 (s, 1,3-*C*) ppm. EI-MS (70 eV): *m*/*z* (%) = 636 (100) $[M]^+$, 318 (7) $[M]^{2+}$, 126 (50) [pyrogallol]$^+$. CI-MS (isobutane): *m*/*z* (%) = 637 (24) $[M + H]^+$, 139 (94), 69 (100). $C_{40}H_{60}O_6$ (636.90): calcd. C 75.43, H 9.50. $C_{40}H_{60}O_6$·2H_2O (672.97): calcd. C 71.39, H 9.59; found C 71.58, H 9.53.

1,18(1,3)-Bis[2-(dihydroxyboro)benzena]cyclo[16.16]tetratriacontaphane (12): The hydrogenated bimacrocycle **8** (73.7 mg, 0.0939 mmol) was dissolved in a mixture of THF (11 mL) and water (1 mL). Sodium hydroxide (49.7 mg, 1.24 mmol) was added and the reaction mixture was stirred at ambient temp. for 0.5 h, treated with dimethyl sulfate (0.330 mL, 3.48 mmol) and was stirred at ambient temp. for additional 4 h. The mixture was acidified with sulfuric acid (0.10 mL, 2 N) and the THF was removed in vacuo. To the remaining aqueous layer, containing a white solid, water (8 mL) was added and the mixture extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried with magnesium sulfate and the solvents evaporated in vacuo. Recrystallisation from dichloromethane/ethyl acetate gave a white solid. Yield: 35.9 mg (55%). M.p. 115–118 °C. IR (KBr): $\tilde{\nu}$ = 3524 (s, OH), 2926, 2851, (2 s, CH, CH_2), 1596, 1464 (2 s, arom.), 1104 (s, C–O) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 1.24–1.37 [m, 32 H, $O(CH_2)_3(CH_2)_4$], 1.47 [m_c, 8 H, $O(CH_2)_2CH_2$], 1.83 (m_c, 8 H, OCH_2CH_2), 4.07 (t, *J* = 6.3 Hz, 8 H, OCH_2), 6.59 (d, *J* = 8.4 Hz, 4 H, 4,6-*H*), 7.33 (t, *J* = 8.4 Hz, 2 H, 5-*H*), 7.36 (s, 4 H, O*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.00 [t, $O(CH_2)_2CH_2$], 29.08, 29.14, 29.18, 29.26 [t, OCH_2CH_2, $O(CH_2)_3(CH_2)_4$], 69.03 (t, OCH_2), 105.06 (d, 4,6-*C*), 132.75 (d, 5-*C*), 165.05 (s, 1,3-*C*) ppm. Because of relaxation effects with the ^{11}B isotope, the 2-C signal is of low intensity and is missing in the spectrum. EI-MS (70 eV): *m*/*z* (%) = 608 (89) $[M - 2\ BO_2H]^+$, 110 (100) [resorcinol]$^+$. MALDI-MS: *m*/*z* = 719 $[M + Na]^+$, 735 $[M + K]^+$. $C_{40}H_{66}B_2O_8$ (696.57): calcd. C 68.97, H 9.55; found C 69.10, H 9.61.

1,18(1,3)-Bis(2-hydroxybenzena)cyclo[16.16]tetratriacontaphane (13): The hydrogenated bimacrocycle **8** (52.2 mg, 66.5 μmol) was dissolved in dichloromethane (8 mL) and acetone (24 mL), and treated with sodium hydroxide solution (2 mL, 2 N) and hydrogen peroxide solution (4 mL, 30%). Under generation of oxygen, the reaction mixture was stirred at ambient temp. for 4 h. The mixture was acidified with hydrochloric acid (2 mL, 2 N) and the organic solvents were removed in vacuo. Water (4 mL) and dichloromethane (4 mL) were added to the remaining aqueous layer, and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 5 mL) and the combined organic layers were dried with magnesium sulfate and the solvents evaporated in vacuo. The crude product was purified by recrystallization from ethyl acetate/cyclohexane which gave colorless needles of **13**·H_2O. Yield: 22.9 mg (54%). M.p. 103 °C. IR (KBr): $\tilde{\nu}$ = 3489 (m, OH), 2922, 2850 (2 s, CH, CH_2), 1618, 1511, 1464 (3 s, arom.), 1100 (s, C–O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.2–1.4 [m, 32 H, $O(CH_2)_3(CH_2)_4$], 1.47 [m_c, 8 H, $O(CH_2)_2CH_2$], 1.80 (m_c, 8 H, OCH_2CH_2), 4.04 (t, *J* = 6.3 Hz, 8 H, OCH_2), 5.52 (s, 2 H, O*H*), 6.55 (d, *J* = 8.3 Hz, 4 H, 4,6-*H*), 6.74 [AB_2 (dd), *J* = 8.4 Hz, *J* = 8.2 Hz, 2 H, 5-*H*] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.08 [t, $O(CH_2)_2CH_2$], 29.28, 29.33, 29.35, 29.40 [t, OCH_2CH_2, $O(CH_2)_3(CH_2)_4$], 69.36 (t, OCH_2), 106.25 (d, 4,6-*C*), 118.83 (d, 5-*C*), 135.69 (s, 2-*C*), 146.71 (s, 1,3-*C*) ppm. EI-MS (70 eV): *m*/*z* (%) = 640 (100) $[M]^+$, 126 (68) [pyrogallol]$^+$. $C_{40}H_{64}O_6$ (640.93): calcd. C 74.96, H 10.06. $C_{40}H_{64}O_6$·H_2O (658.98): calcd. C 72.91, H 10.10; found C 73.06, H 10.17.

1,18(1,3)-Bis(benzena)cyclo[16.16]tetratriacontaphane (14): 14 was unintentionally obtained when the hydrogenated bimacrocycle **8** (240 mg, 0.306 mmol) was subjected to hydrolysis analogously to the synthesis of **12**, but using pH = 2 for workup (H_2SO_4). Yield: 133 mg (71%). M.p. 110–113 °C. IR (KBr): $\tilde{\nu}$ = 2915, 2848, (2 s, CH, CH_2), 1596, 1494, 1476 (3 s, arom.) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.24–1.38 [m, 32 H, $O(CH_2)_3(CH_2)_4$], 1.45 [m_c, 8 H, $O(CH_2)_2CH_2$], 1.76 (m_c, 8 H, OCH_2CH_2), 3.94 (t, *J* = 6.5 Hz, 8 H, OCH_2), 6.46–6.49 (m, 6 H, 2,4,6-*H*), 7.14 (m_c, 2 H, 5-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.98 [t, $O(CH_2)_2CH_2$], 29.14, 29.17, 29.26 29.35, 29.42 [t, OCH_2CH_2, $O(CH_2)_3(CH_2)_4$], 67.91 (t, OCH_2), 101.52 (d, 2-*C*), 106.65 (d, 4,6-*C*), 129.75 (d, 5-*C*), 160.37 (s, 1,3-*C*) ppm. EI-MS (70 eV): *m*/*z* (%) = 608 (100) $[M]^+$, 110 (44) [resorcinol]$^+$. $C_{40}H_{64}O_4$ (608.93): calcd. C 78.90, H 10.59; found C 79.11, H 11.01.

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[27] The NMR spectra of the analytically pure sample showed traces of additional compounds which probably can be assigned to incompletely cyclized material.
[28] As with **7**, traces of impurities could be found in the NMR spectra, see ref.[27]

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