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Novel starshaped initiators for the controlled radical polymerization based on resorcin[4]- and pyrogallol[4]arenes

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Abstract—Multifunctional macrocyclic initiators for the atom transfer radical polymerization (ATRP) based on different resorcin[4]- and pyrogallol[4]arenes have been synthesized. The initiators with 8, 12 and 16 tertiary α-bromoesters on the core were received by complete esterification of all phenolic groups with 2-bromo-isobutyryl bromide. The calixarene derivatives with aliphatic chains on the bridging methine carbon were obtained as their *rccc* (all *cis*) isomers, while the corresponding calixarenes with aromatic substituents gave mixtures of their *rccc* and *rctt* (*cis*, *cis*, *trans*, *trans*) isomers.

The HCl catalyzed condensation of resorcinol and pyrogallol with aliphatic and aromatic aldehydes gives cyclic, tetrameric products as a mixture of their diastereomers.[1,2] By using suitable reaction conditions and reaction times, very often only one isomer is obtained. Recently the formation of higher condensation products with ring sizes of $n = 4$–7 were reported for the Lewis acid catalyzed synthesis of resorcinarenes.[3]

The synthesis and use of different secondary and tertiary α-bromoester substituted calix[*n*]arenes as initiators for the atom transfer radical polymerization[4] (ATRP) has been reported, using calix[*n*]arenes ($n = 4$, 6, 8) derived from phenol and formaldehyde.[5–8] In connection with our search for new well defined starpolymers, we were interested in suitable highly functionalized starting materials. Herein we would like to report our results for the usage of different calixresorcin[4]- and calixpyrogallol[4]arenes to synthesize novel starshaped initiators for the controlled radical polymerization by ATRP, bearing a precise number of initiating sites.

The starting materials, the unsubstituted resorcin[4]- and pyrogallol[4]arenes were synthesized by HCl catalyzed cyclocondensation according to well known procedures.[1,2,9–11] The envisaged tertiary octa-, dodeca- or hexadeca α-bromoesters, of the resorcin[4]- and pyrogallol[4]arenes respectively, were prepared by slow addition of an excess of 2-bromo-isobutyryl bromide to the macrocyclic core in the presence of pyridine as a base.

The synthesized initiators for the ATRP are shown in Figure 1.[†]

RC5Br$_8$: ^{1}H NMR (500.1 MHz, $CDCl_3$, rt): δ (ppm) = 7.37 (s, 2H, H3*), 7.01 (s, 2H, H5), 6.80 (s, 2H, H5*), 6.15 (s, 2H, H3), 4.33 (dd, 4H, H1), 2.08 (s,

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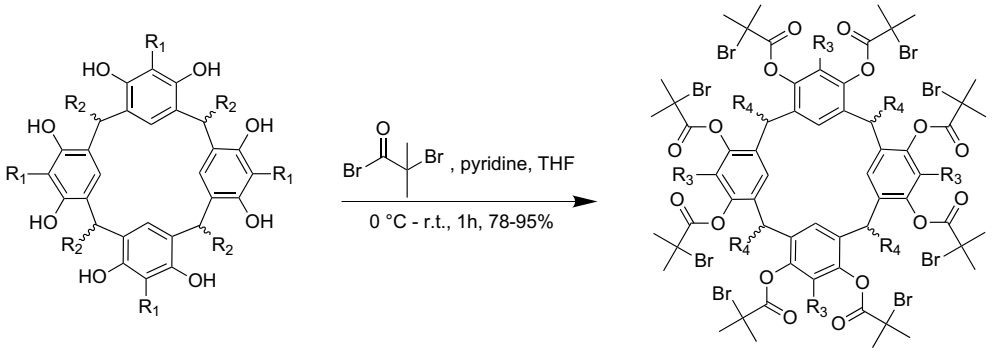
[†] General procedure for the synthesis of the acylated resorcin[4]- and pyrogallol[4]arenes: 1.00 g of resorcin[4]- or pyrogallol[4]arene were weighted into a 100 mL three-necked round bottom flask in an argon counterstream. Dry THF (50 mL) was added, followed by 4 equiv of pyridine per phenolic hydroxyl group. After complete dissolution of the solid, the mixture was cooled to 0 °C. Under stirring subsequently 4 equiv of 2-bromo-isobutyryl bromide per phenolic hydroxyl group were slowly added under stirring by syringe. Stirring was continued for 1 h and the reactions were controlled by MALDI-TOF-MS. The reactions were stopped when only peaks of the fully substituted initiators could be observed. The solvent and educts were removed under high vacuum by Kugel–Rohr distillation and the residues were dissolved in chloroform. After washing the organic phase with sat. K_2CO_3 solution and NaCl solution, the separated organic phase was dried over $MgSO_4$ and concentrated to 10 mL. The desired initiators were precipitated twice from an excess of methanol and further purified by flash-chromatography with chloroform.



Resorcinarenes		yield	isomer
RC5Br$_8$	: R_1 = H, R_2 = C_5H_{11}	82.4 %	*rccc*
RC11Br$_8$	: R_1 = H, R_2 = $C_{11}H_{23}$	86.2 %	*rccc*
RPhBr$_{12}$	: R_1 = H, R_2 = *p*-$C_6H_4OCOC(CH_3)_2Br$	94.6 %	*rccc* + *rctt*

Pyrogallolarenes		yield	isomer
PC5Br$_{12}$	: R_3 = $OCOC(CH_3)_2Br$, R_4 = C_5H_{11}	91.3 %	*rccc*
PC11Br$_{12}$	: R_3 = $OCOC(CH_3)_2Br$, R_4 = $C_{11}H_{23}$	88.1 %	*rccc*
PPhBr$_{16}$	: R_3 = $OCOC(CH_3)_2Br$, R_4 = *p*-$C_6H_4OCOC(CH_3)_2Br$	78.7 %	*rccc* + *rctt*; 48.2 % *rccc*

Figure 1. Synthesis of tertiary α-bromoesters of resorcin[4]- and pyrogallol[4]arenes.

12H, H4b2), 2.07 (s, 12H, H4b1), 1.91 (s, 12H, H4b1*), 1.88 (m, 8H, H6), 1.84 (s, 12H, H4b2*), 1.30 (broad m, 8H, H7), 1.23 (broad m, 16H, H8/9), 0.82 (t, 12H, ^3J(H,H) = 6.8 Hz, H10). ^{13}C NMR (125.7 MHz, $CDCl_3$, rt): δ (ppm) = 169.75 (s, C4a), 168.99 (s, C4a*), 148.68 (s, C4i*), 145.87 (s, C4i), 134.97 (s, C2i), 129.59 (s, C2i*), 127.75 (s, C3*), 126.67 (s, C3), 115.92 (s, C5*), 115.26 (s, C5), 55.73 (s, C4d*), 55.05 (s, C4d), 38.22 (s, C1), 34.81 (s, C6), 32.36 (s, C8), 30.82 (s, C4b1/4b2), 30.55 (s, C4b1*), 30.45 (s, C4b2*), 28.26 (s, C7), 22.61 (s, C9), 14.19 (s, C10). MALDI-TOF-MS (Dithranol): calcd for $C_{80}H_{104}Br_8O_{16}$: *m/z* = 1960.071 $[M]^+$; found: *m/z* = 1983.370 $[M+Na]^+$, 1999.330 $[M+K]^+$. EA: calcd for $C_{80}H_{104}Br_8O_{16}$: C 49.00%, H 5.35%; found: C 48.99%, H 5.37%.

RC11Br$_8$: ^{1}H NMR (500.1 MHz, $CDCl_3$, rt): δ (ppm) = 7.37 (s, 2H, H3*), 7.02 (s, 2H, H5), 6.80 (s, 2H, H5*), 6.15 (s, 2H, H3), 4.32 (dd, 4H, H1), 2.08 (s, 12H, H4b2), 2.07 (s, 12H, H4b1), 1.91 (s, 12H, H4b1*), 1.88 (m, 8H, H6), 1.84 (s, 12H, H4b2*), 1.32 (broad m, 8H, H7), 1.21 (broad m, 8H, H15), 1.19 (broad m, 56H, H8-14), 0.85 (t, 12H, ^3J(H,H) = 6.9 Hz, H16). ^{13}C NMR (125.7 MHz, $CDCl_3$, rt): δ (ppm) = 169.74 (s, C4a), 168.99 (s, C4a*), 148.67 (s, C4i*), 145.86 (s, C4i), 134.97 (s, C2i), 129.55 (s, C2i*), 127.80 (s, C3*), 126.66 (s, C3), 115.90 (s, C5*), 115.24 (s, C5), 55.69 (s, C4d*), 55.01 (s, C4d), 38.23 (s, C1), 34.81 (s, C6), 31.90 (s, C14), 30.80 (s, C4b1/4b2), 30.53 (s, C4b1*), 30.43 (s, C4b2*), 30.20 (s, C8), 29.84–29.35 (s, C9–13), 28.54 (s, C7), 22.66 (s, C15), 14.09 (s, C16). MALDI-TOF-MS (Dithranol): calcd for $C_{104}H_{152}Br_8O_{16}$: *m/z* = 2297.450 $[M]^+$; found: *m/z* = 2320.247 $[M+Na]^+$, 2336.266 $[M+K]^+$. EA: calcd for $C_{104}H_{152}Br_8O_{16}$: C 54.37%, H 6.67%; found: C 45.34%, H 6.71%.

RPhBr$_{12}$: ^{1}H NMR (500.1 MHz, $CDCl_3$, rt): δ (ppm) = 7.09 (s, 2H, H5_ct), 7.03 (s, 2H, H5*_cc), 6.96 (s, 8H, H5_cc and H8a_ct), 6.91 (s, 2H, H5*_ct), 6.90 (broad s, 8H, 7_ct), 6.81 (d, 8H, H7_cc), 6.70-6.48 (broad s, 8H, H8_cc), 6.40 (broad s, 4H, H8b_ct), 6.38 (s, 2H, H3_ct), 6.32 (s, 2H, H3_cc), 6.12 (s, 2H, H3*_cc), 6.07 (s, 2H, H3*_ct), 2.07 (d, 24H, H9b_ct), 2.05 (d, 24H, H9b_cc), 1.97 (s, 12H, H4b1*_ct), 1.94 (s, 12H, H4b1*_cc), 1.89 (s, 12H, H4b2*_ct), 1.84 (s, 12H, H4b2*_cc), 1.70 (s, 12H, H4b1_cc), 1.67 (s, 12H, H4b1_ct), 1.65 (s, 12H, H4b2_ct), 1.64 (s, 12H, H4b2_cc). ^{13}C NMR (125.7 MHz, $CDCl_3$, rt): δ (ppm) = 169.95 (s, C9a_cc), 169.92 (s, C9a_ct), 169.28 (s, C4a*_ct), 169.24 (s, C4a*_cc), 168.74 (s, C4a_ct), 168.70 (s, C4a_cc), 149.64 (s, C9i_cc), 149.45 (s, C9i_ct), 147.53 (s, C4i*_cc), 147.29 (s, C4i*_ct and C4i_ct), 147.03 (s, C4i_cc), 138.70 (s, C6i_ct), 136.33 (s, C6i_cc), 134.40 (s, C3*_ct), 132.68 (s, C2i*_cc), 132.34 (s, C3*_cc), 131.77 (s, C2i_cc), 131.72 (s, C2i*_ct), 130.80 (s, C2i_ct), 130.73 (s, C3_cc), 129.97 (s, C3_ct), 121.22 (s, C7_ct), 120.83 (s, C7_cc), 116.58 (s, C5_cc), 116.28 (s, C5_ct), 115.79 (s, C5*_cc and C5*_ct), 55.82 (s, C4d*_ct), 55.66 (s, C9d_ct), 55.53 (s, C9d_cc), 55.14 (s, C4d*_cc), 55.07 (s, C4d_cc), 55.02 (s, C4d_ct), 43.36 (s, C1_cc and C1_ct), 30.87–30.68 (s, C9b_cc and C9b_ct), 30.52 (s, C4b1_cc), 30.42 (s, C4b2*_ct), 30.31 (s, C4b1*_ct and C4b1_ct and C4b1*_cc and C4b2*_cc and C4b2_cc and C4b2_ct). MALDI-TOF-MS (Dithranol): calcd for $C_{100}H_{100}Br_{12}O_{24}$: *m/z* = 2644.672 $[M]^+$; found: *m/z* = 2667.204 $[M+Na]^+$, 2683.181 $[M+K]^+$. EA: calcd for $C_{100}H_{100}Br_{12}O_{24}$: C 45.41%, H 3.8%; found: C 45.48%, H 3.82%.

PC5Br$_{12}$: ^{1}H NMR (500.1 MHz, TCl, rt): δ (ppm) = 7.23 (s, 2H, H3*), 6.15 (s, 2H, H3), 4.26 (d, 4H, H1), 2.05 (s, 12H, H4b2), 2.03 (s, 12H, H4b1), 1.97 (s, 12H, H5b), 1.95 (s, 12H, H5b*), 1.91 (s, 12H, H4b1*), 1.80 (s, 12H, H4b2*), 1.77–1.55 (broad m, 8H, H6), 1.17 (broad m, 8H, H7), 1.11 (broad m, H8/9), 0.74 (t, 12H, ^3J(H,H) = 6.6 Hz, H10). ^{13}C NMR (125.7 MHz, TCl, rt): δ (ppm) = 168.80 (s, C4a), 167.28 (s, C4a*), 167.30 (s, C5a/5a*), 142.03 (s, C4i*), 138.99 (s, C4i), 137.13

(s, C5i*), 136.15 (s, C2i), 136.02 (s, C5i), 130.97 (s, C2i*), 125.67 (s, C3*), 124.10 (s, C3), 56.20 (s, C5d*), 56.06 (s, C4d*), 55.88 (s, C5d), 55.13 (s, C4d), 39.27 (s, C1), 35.27 (s, C6), 32.50 (s, C8), 31.77 (s, C5b*), 31.64 (s, C4b2), 31.60 (s, C4b1), 31.54 (s, C4b1*), 31.43 (s, C4b2*), 31.14 (s, C5b), 28.27 (s, C7), 22.91 (s, C9), 14.61 (s, C10). MALDI-TOF-MS (Dithranol): calcd for $C_{96}H_{124}Br_{12}O_{24}$: m/z = 2620.859 $[M]^+$; found: m/z = 2644.143 $[M+Na]^+$, 2660.139 $[M+K]^+$. EA: calcd for $C_{96}H_{124}Br_{12}O_{24}$: C 43.99%, H 4.77%; found: C 43.85%, H 4.70%.

PC11Br$_{12}$: ^{1}H NMR (500.1 MHz, TCl, rt): δ (ppm) = 7.23 (s, 2H, H3*), 6.14 (s, 2H, H3), 4.25 (d, 4H, H1), 2.05 (s, 12H, H4b2), 2.03 (s, 12H, H4b1), 1.97 (s, 12H, H5b), 1.94 (s, 12H, H5b*), 1.91 (s, 12H, H4b1*), 1.79 (s, 12H, H4b2*), 1.78–1.55 (broad m, 8H, H6), 1.17 (broad m, 8H, H15), 1.13 (broad m, 64H, H7–14), 0.78 (t, 12H, ^3J(H,H) = 6.9 Hz, H16). ^{13}C NMR (125.7 MHz, TCl, rt) : δ (ppm) = 168.80 (s, C4a), 168.30 (s, C4a*), 167.27 (s, C5a/5a*), 142.01 (s, C4i*), 138.95 (s, C4i), 137.11 (s, C5i*), 136.17 (s, C2i), 135.99 (s, C5i), 130.95 (s, C2i*), 125.60 (s, C3*), 124.05 (s, C3), 56.20 (s, C5d*), 56.07 (s, C4d*), 55.90 (s, C5d), 55.10 (s, C4d), 39.27 (s, C1), 35.26 (s, C6), 32.21 (s, C14), 31.77 (s, C5b*), 31.62 (s, C4b2), 31.58 (s, C4b1), 31.54 (s, C4b1*), 31.42 (s, C4b2*), 31.11 (s, C5b), 30.44 (s, C8), 30.26–29.65 (s, C9–13), 28.59 (s, C7), 23.02 (s, C15), 14.55 (s, C16). MALDI-TOF-MS (Dithranol): calcd for $C_{120}H_{172}Br_{12}O_{24}$: m/z = 2957.235 $[M]^+$; found: m/z = 2980.452 $[M+Na]^+$, 2997.480 $[M+K]^+$. EA: calcd for $C_{120}H_{172}Br_{12}O_{24}$: C 48.73%, H 5.86%; found: C 48.85%, H 5.94%.

PPhBr$_{16}$: ^{1}H NMR (500.1 MHz, TCl, rt) *rccc*-isomer: δ (ppm) = 6.87 (broad d, 4H, H7a), 6.75 (broad d, 4H, H8a), 6.70 (broad d, 4H, H8b), 6.31 (broad s, 4H, H7b), 6.20 (s, 2H, H3), 6.04 (s, 2H, H3*), 5.68 (broad s, 4H, H1), 2.01 (s, 12H, H4b1*), 1.98 (s, 12H, H9b1 or H9b2), 1.97 (s, 12H, H9b2 or H9b1), 1.95 (s, 12H, H5b*), 1.94 (s, 6H, H5b1), 1.91 (s, 6H, H5b2), 1.89 (s, 12H, H4b2*), 1.54 (s, 12H, H4b1), 1.43 (s, 12H, H4b2). ^{13}C NMR (125.7 MHz, TCl, rt) *rccc*-isomer: δ (ppm) = 170.33 (s, C9a), 168.90 (s, C4a*), 168.02 (s, C5a*), 167.34 (s, C4a), 166.27 (s, C5a), 149.99 (s, C9i), 140.93 (s, C4i*), 140.45 (s, C4i), 137.37 (s, C2i), 136.52 (s, C2i*), 135.22 (broad s, C6i), 134.72 (s, C5i* or C5i), 133.51 (s, C5i or C5i*), 131.16 (s, C7a), 130.38 (s, C7b and C3*), 127.80 (s, C3), 121.71 (s, C8b), 120.98 (s, C8a), 56.12 (s, C9d), 55.87 (s, C4d*), 55.72 (s, C5d), 55.41 (s, C4d), 44.33 (s, C1), 31.80 (s, C5b1), 31.40 (s, C4b1*), 31.25 (s, C9b1 or C9b2), 31.17 (s, C4b1 and C5b2), 31.14 (s, C4b2), 30.99 (s, C4b2* and C9b2 or C9b1). MALDI-TOF-MS (Dithranol): calcd for $C_{116}H_{120}Br_{16}O_{32}$: m/z = 3304.457 $[M]^+$; found: m/z = 3327.652 $[M+Na]^+$, 3343.564 $[M+K]^+$. EA: calcd for $C_{116}H_{120}Br_{16}O_{32}$: C 42.16%, H 3.66%; found: C 42.18%, H 3.67%.[‡]

[‡]Just now Tenhu and co-workers reported the synthesis of a similar initiator.[12]

Fast esterification was observed by following the course of the reaction with MALDI-TOF-MS. After a period of 1 h only peaks for the fully substituted products could be observed using either 4-nitroaniline (4-NA) or 1,8,9-trihydroxyanthracene (Dithranol) as matrix. Both matrices were found to be suitable for the matrix assisted laser desorption/ionization process. A better ionization could be observed by using 4-NA for the complete substituted products, while with Dithranol the ionization of the partially substituted products was favoured. Due to that, Dithranol was used to estimate the completion of the reaction. Solid reaction products were only received by removing the excess of 2-bromoisobutyryl bromide under high vacuum and precipitation with methanol.

In high resolution MALDI-TOF-MS experiments the expected $[M+Na]^+$ and $[M+K]^+$ were observed. The presence of eight bromine atoms attached to the macrocyclic core of the initiator **RC5Br$_8$** could be clearly evidenced by comparing the measured and the calculated isotopic distribution pattern (Fig. 2). Good agreement for the observed and calculated isotopic distribution patterns could be also found for **RPhBr$_{12}$** and **PPhBr$_{16}$** bearing 12, or 16 bromines, respectively.

The structure and conformation of the α-bromoesters of all six calixarenes has been determined by means of 2D NMR (COSY, HSQC, HMBC and ROESY) and temperature dependent NMR measurements due to a lack of good crystallographic data. Since the conformation of the initiator determines the general structure of the polymer derived from it, conformational information is important.

All α-bromoesters bearing aliphatic chains as residue on the bridging methine carbon are fixed in the C_{2v} boat conformation at room temperature. A conformational change from one boat conformation to the other is slow compared to the NMR timescale and could only be observed for the resorcin[4]arenes at temperatures above 100 °C in solution with 1,1,2,2-tetrachloroethane-d_2 (TCl). Temperature dependent NMR experiments of the substituted pyrogallol[4]arenes did not show coalescence for the proton signals, which indicates an even bigger constrain caused by the larger number of bulky substituents. The pyrogallol[4]arenes were found to be fixed in one of their boat conformations and do not undergo any conformational change. The free activation enthalpy for the conformational change of the resorcin[4]arene **RC5Br$_8$** from $boat_1$ to $boat_2$ (ΔG_c = 19.9 ± 4 kcal/mol) could be calculated from the determined coalescence temperatures T_c for the protons H4b/H4b* and H5/H5* (T_c = 406.2 K) using the coalescence point approximation.[13,14]

The ROESY measurements for the resorcin[4]arene initiator **RC5Br$_8$** show a negative crosspeak for the in-plane H5 protons and the out-of-plane H5* protons, which terms out to be the indicator of a conformational change between $boat_1$ and $boat_2$ which can only take place for the *rccc* isomer. But coevally an unusual positive crosspeak for H3/H3* was observed (Fig. 3).

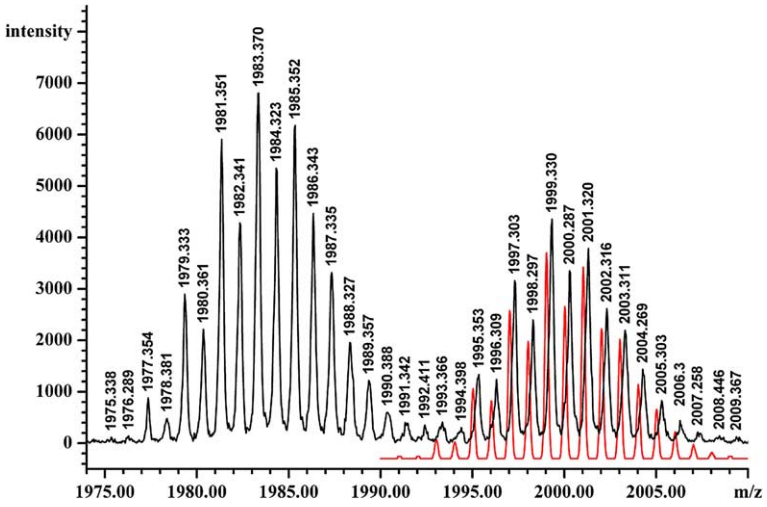


Figure 2. Overlayed calculated and measured MALDI-TOF mass spectra of initiator **RC5Br$_8$** showing the $[M+Na]^+$ and $[M+K]^+$ peaks. The red spectrum was calculated for $C_{80}H_{104}Br_8O_{16}K$.

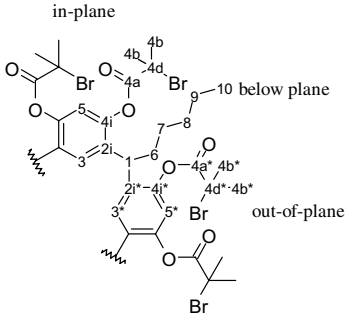


Figure 3. Numbered sketch of **RC5Br$_8$**.

The assignment of the in-plane protons H3 and the out-of-plane protons H3* was achieved by comparing the volume integrals for the crosspeak of H6/3 and H6/3* (see Fig. 4). The proximity of the out-of-plane standing proton H3* to the proton H6 of the axial chain R_4 is responsible for a higher volume integral, while the distance between the in-plane proton H3 and H6 is slightly bigger. Additionally a change of sign for H3/3* was observed for all resorcin[4]- and pyrogallol[4]arenes bearing aliphatic chains on the bridging carbon by changing the deuterated solvent. In chloroform-d_1 the H3/3* crosspeak is always positive whereas the value becomes negative in 1,1,2,2-tetrachloroethane-d_2 (TCl).

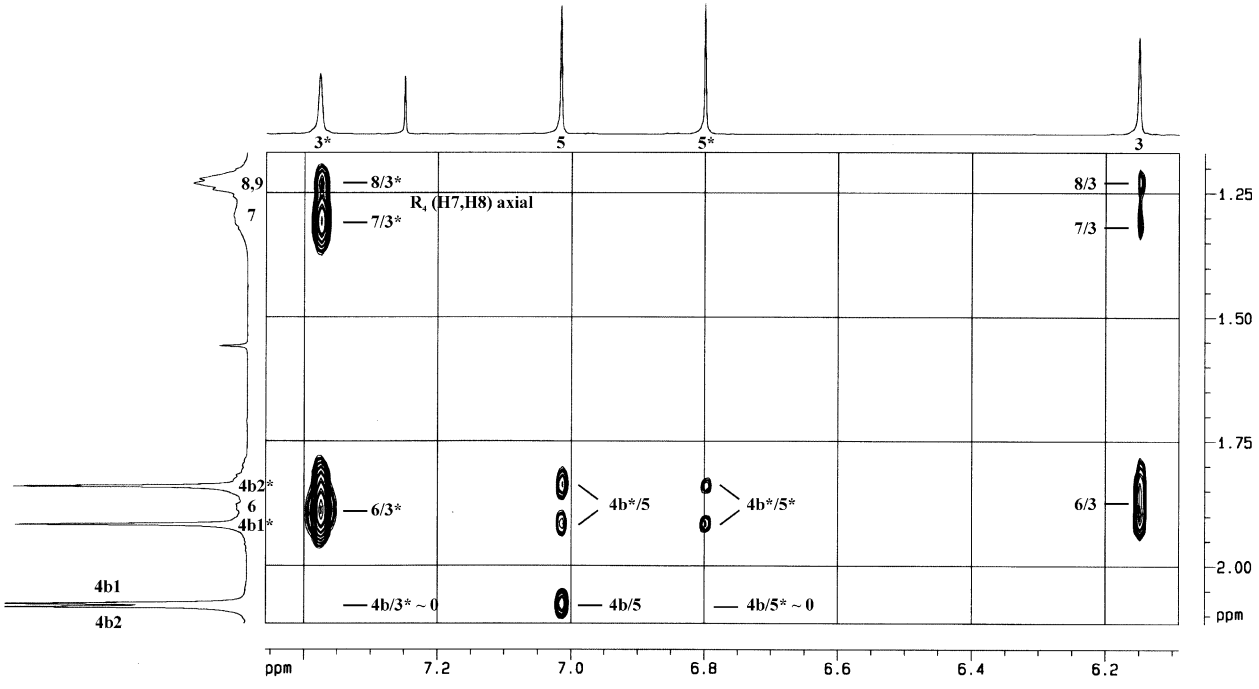


Figure 4. Selected part of the ROESY-NMR spectrum of **RC5Br$_8$**.

These experimental data show that the conformational reorientation from $boat_1$ to $boat_2$ is faster in TCl than in chloroform. The resorcin[4]arene **RPhBr$_{12}$** and the pyrogallol[4]arene **PPhBr$_{16}$** always show a positive crosspeak for H3/3*. The sequence of the appearance of the H3 and H3* signals is vice versa compared with the calixarenes bearing aliphatic chains. Additionally, the proton signals of the aromatic side groups on the bridging carbon always show negative crosspeaks due to a hindered rotation of the more sterically demanding aromatic substituents for both isomers (*rccc* and *rctt*) in the case of **RPhBr$_{12}$** and the *rccc* isomer for **RPhBr$_{16}$**. The proton signals for the terminal CH_3 groups of the tertiary bromide, substituted to the in-plane lying phenolic subunits, are also shifted to high field due to an increased sterical constrain.

The application of the synthesized initiators for the controlled radical polymerization of styrene and different functionalized (meth)acrylates is in progress.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.10.158.

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