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ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 1254–1263

Regioselective acylation of aminoresorcinarenes

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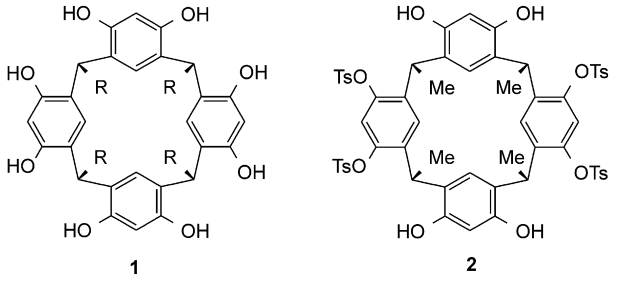
Received 4 July 2006; revised 7 November 2006; accepted 16 November 2006
Available online 15 December 2006

Abstract—The acid catalyzed hydrolytic cleavage of the oxazine rings in the readily available tetraoxazine derivatives of resorcinarenes results in tetraaminoresorcinarenes. A similar process applied to C_2-symmetrical bisoxazine resorcinarene tetratosylates affords C_{2v}-symmetrical resorcinarenediamines. The mild acylation of these resorcinareneamines with BOC-anhydride or *para*-nitrophenyl ester proceeds selectively at the nitrogen atoms without affecting the hydroxyl groups. Most of the resulting resorcinareneamides are thus obtained in preparative yields and can be easily purified by simple crystallizations. In the crystalline state the compounds obtained are found to bind chloride anions through hydrogen bonds and electrostatic interactions and to display a chiral arrangement of hydrogen bonded functional groups at the wide rim of the macrocycle.

1. Introduction

Preorganization of multiple functional groups on a molecular platform is an efficient methodology for the design of functional supramolecular systems, nanoscale species, and crystal structures.[1] Calixarenes[2] and resorcinarenes[3] **1** (Scheme 1) are very popular molecular scaffolds widely useful as building blocks for the synthesis of cation, anion and bifunctional receptors,[4] container molecules,[5] and self-assembling systems.[6]



R = CH_3 **1a** R = C_5H_{11} **1d**
R = C_2H_5 **1b** R = $C_{11}H_{23}$ **1e**
R = C_5H_{11} **1c**

Scheme 1.

Methods for the complete and selective functionalization of calixarenes at the wide and narrow rim of the macrocycle have been developed in order to preorganize multiple binding and/or catalytic subunits in close spatial proximity. Especially efficient is the use of calixarenes bearing several amino groups,[7] which can be readily transformed into various hydrogen bonding and metal coordinating fragments. This methodology has furnished efficient and selective cation,[8] anion,[9] and polytopic receptors[10] as well as highly stable self-assembling capsules[11] and functional nanostructures.[12]

Different types of aminoresorcinarenes have also been synthesized. For example, resorcinarene-based cavitands bearing amino or aminomethyl groups at the wide rim of the macrocycle were obtained in preparative yields. These compounds were used in the rational design of cation[13] and anion[14] receptors, nanoscale container molecules,[15] and molecular capsules.[16] A sequence of protection/deprotection procedures afforded cavitands bearing four propyleneamino groups at the narrow rim of the macrocycle. These receptors were shown to bind various guests in polar protic media.[17]

Several research groups have demonstrated the regioselective aminomethylation of octaols **1** with primary amines and formaldehyde to afford C_4-symmetrical tetraoxazine derivatives,[18] which can be transformed into resorcinarenes bearing four amino and eight hydroxy groups at the wide rim of the macrocycle. Similar transformations of C_{2v}-symmetrical resorcinarene tetratosylates[19] resulted in compounds bearing two oxazine rings and, after subsequent

Keywords: Resorcinarenes; Selective functionalization; Hydrogen bonds.
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0040–4020/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.tet.2006.11.044

hydrolysis, two amino groups.[20] The reaction of two resorcinarene tetraoxazines with acetic anhydride resulted in the N-acylation and cleavage of the oxazine rings and afforded in 17–18% yield the parent resorcinarenes bearing four acetamido and eight hydroxyl groups at the wide rim of the macrocycle.[21]

The present investigation seeks to evaluate the reactivity of tetra- and diamino-resorcinarenes with mild acylating agents in order to provide a versatile means for the selective modification of the amino groups in the presence of several hydroxyls. Herein we report preparative methods for the regioselective BOC-protection and N-acylation of such resorcinarene amines as well as the structural characterization and supramolecular properties of the compounds thus obtained.

2. Results and discussion

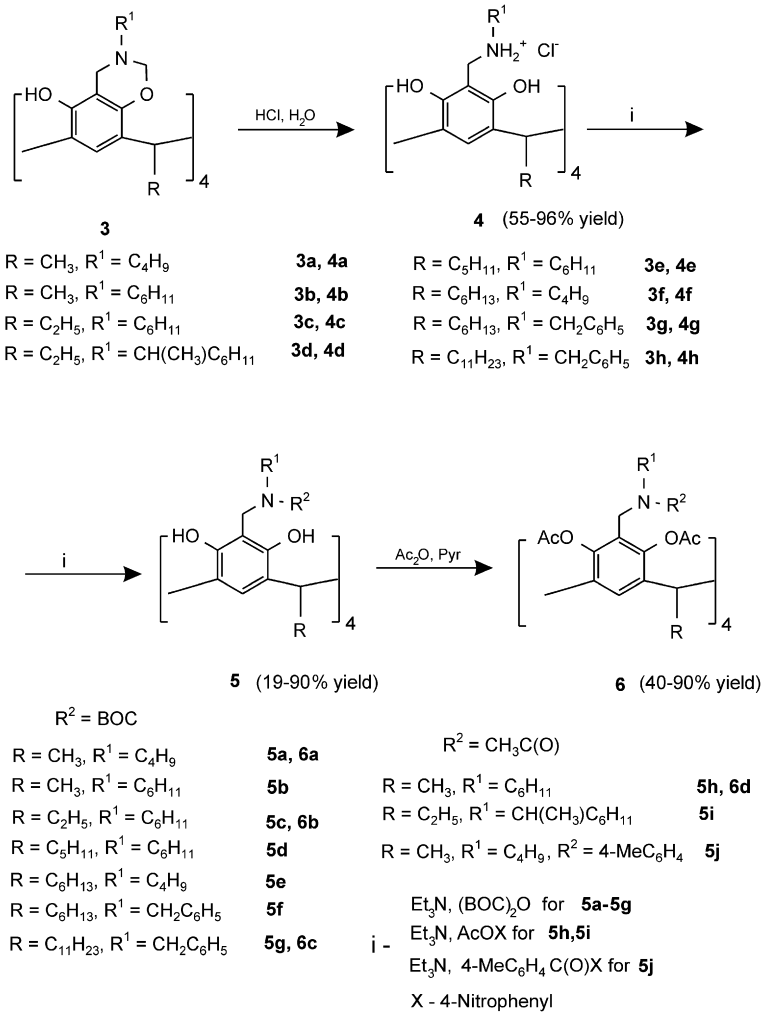
The regioselective Mannich type condensation of resorcinarenes **1** with primary amine and CH_2O affords C_4-symmetrical tetraoxazines **3a–h** (Scheme 2) in 34–99% yields. Compounds **3** precipitate from the reaction mixtures and can be obtained in high purity by simple crystallizations.

The acid catalyzed cleavage of the oxazine rings (HCl, *n*-BuOH, H_2O) readily transforms tetraoxazines **3** into tetraammonium salts **4** (55–96% yield).

The reaction of compounds **4** with BOC-anhydride in the presence of Et_3N as a base (CH_2Cl_2, 20 °C) leads to the regioselective acylation of the more nucleophilic nitrogen atoms whereas the OH groups remain intact. In this way, BOC-protected resorcinarenes **5a–g** are obtained in 50–90% yields.

The mild acylation of tetraammonium salts **4** with *para*-nitrophenyl esters (Et_3N, CH_2Cl_2) provides the corresponding tetraamides in 19–72% yield, including the chiral compound **5i** bearing four (*R*)-α-cyclohexylethyl fragments at the wide rim of the macrocycle. The acylation of compounds **4** with four moles of the relatively more reactive acetic anhydride (Et_3N, CH_2Cl_2, 20 °C) leads to inseparable complex mixtures of unidentified products.

The complete acylation of compounds **5** with acetic anhydride in pyridine at ambient temperature afforded octaacetates **6a–d** in 40–90% yields. In contrast the alkylation of resorcinarenes **5** with ethylbromoacetate (K_2CO_3, MeCN, reflux) resulted in complex mixtures, likely the result of the side reactions of the aminomethyl resorcinol fragments.



Scheme 2.

The ^{1}H NMR spectra of compounds **3** contain one set of signals for the protons of the resorcinol rings and the methine protons of the bridges. The methylene protons of the oxazine rings emerge as two pairs of AB doublets whose separation displays a marked dependence on the nature of the R substituent at the nitrogen atom. This pattern is consistent with the crown conformation produced by the C_4-symmetrical arrangement of the oxazine rings atop the crown conformation of the resorcinarene framework.

The ^{1}H NMR spectra of tetraammonium salts **4** in $CDCl_3$ contain one set of signals for the protons of the resorcinol rings and the methine protons of the bridges, which is in keeping with the C_{4v}-symmetrical crown conformation. The ^{1}H–^{14}N SGQC-NMR experiment indicates that the signals positioned at 7.7 and 9.3 ppm correspond to the NH- and OH- protons, respectively. Previously, we have reported[22] that in the crystalline state and in $CDCl_3$ the crown conformation of **4** is stabilized by hydrogen bonds between the neighboring OH groups and a cyclic hydrogen bonded array formed by the four ammonium fragments and chloride anions.

Compounds **4a** and **b** bearing short aliphatic residues at the nitrogen atoms and on the carbon atoms of the methine bridges are readily soluble in water at neutral pH. Their ^{1}H NMR spectra in D_2O contain one set of signals for the protons of the resorcinol rings and methine protons of the bridges, however, no signals emerge for the NH and OH groups, apparently, due to the fast H–D exchange.

The ^{1}H NMR spectra of tetraamides **5** measured in $CDCl_3$ at 295 K are sharp and contain one set of signals for the protons of the resorcinol rings and the methine protons of the bridges, which are typical for the crown conformation (Fig. 1a). Two broadened singlets for the OH protons are centered at 8.6 and 11.1 ppm indicating that the amide groups of compounds **5** are arranged in a C_4-symmetrical manner forming hydrogen bonds with the neighboring OH groups. It should be noted that such an arrangement has been previously observed in the crystal structure of a resorcinarene tetraacetamide of type **5**.[21]

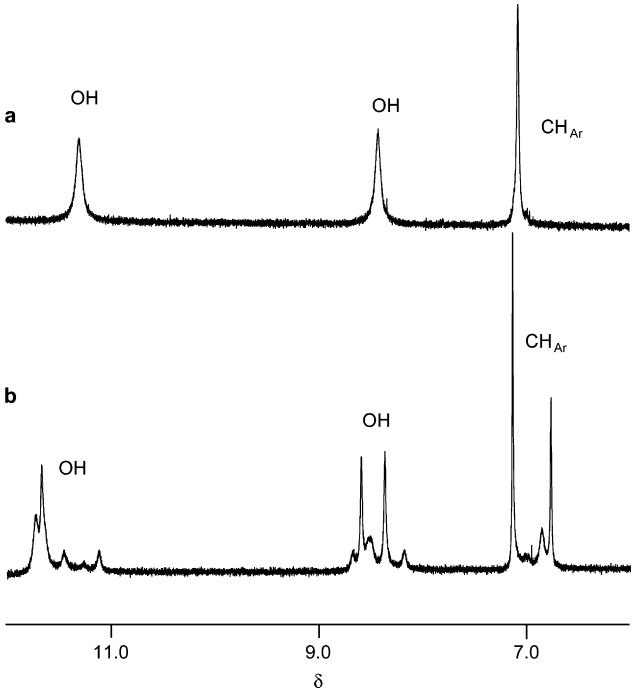


Figure 1. A section of the ^{1}H NMR spectrum of tetraamide **5d** (500 MHz, CD_2Cl_2) at 295 K (a) and at 223 K (b).

Decreasing the temperature to 223 K results in a complicated splitting of all the signals (Fig. 1b) likely produced by different combinations in the arrangements of the hydrogen bonded amide groups at the wide rim of the macrocycle.

The ^{1}H NMR spectra of octaesters **6** in DMSO-d_6 at 295 K contain broad and featureless signals, an apparent result of the fast pseudorotation of the *boat* conformations with two quasiparallel and quasicoplanar resorcinol rings.[23] This interconversion becomes fast at 378 K and the sharp spectrum observed corresponds to a time averaged C_{4v}-symmetrical structure.

C_2-Symmetrical bisoxazine derivatives **7** are obtained in 30–88% yields via the regio- and stereoselective Mannich type condensation of C_{2v}-symmetrical resorcinarene tetratosylate **2** (Scheme 1) with primary amines and formaldehyde. Subsequent cleavage of the heterocyclic rings (HCl, *n*-BuOH, H_2O) readily gives hydrochlorides **8** (58–74% yield), which are readily purified by simple re-crystallizations.

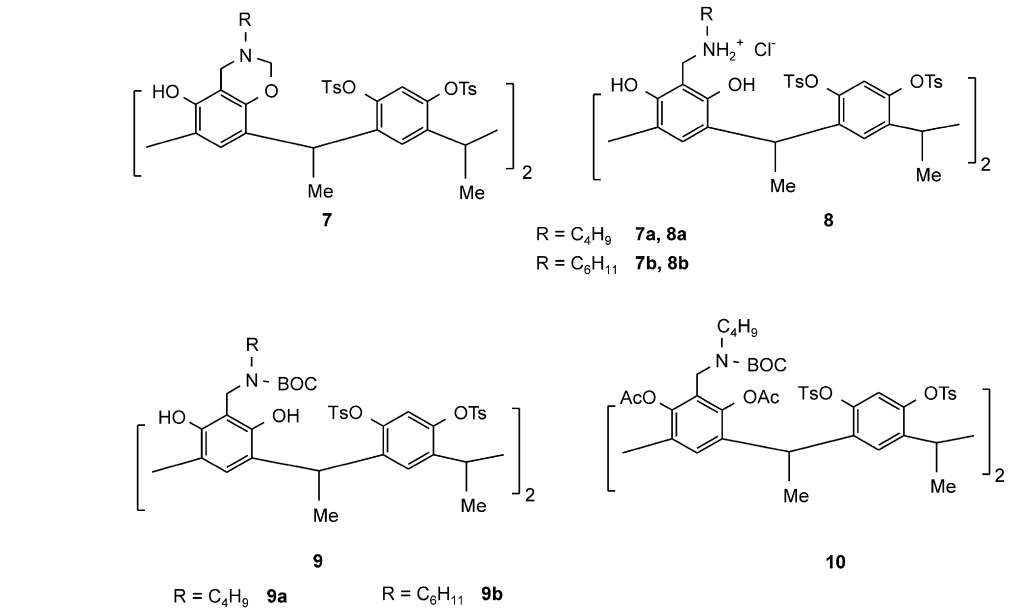
The amino groups of compounds **8** are regioselectively acylated with BOC-anhydride (Et_3N, CH_2Cl_2, rt) to give diamides **9** in 52–61% yield. Complete O-acylation of diamide **9a** with acetic anhydride (pyridine, at room temperature) affords octaester **10** in 80% yield (Scheme 3).

The slow crystallization of compound **8a** from $CHCl_3$ afforded diffraction quality crystals. In the crystalline state the molecule of **8a** adopts a *boat* conformation (Fig. 2a) in which the aminomethylated resorcinol rings are nearly parallel (dihedral angle 2.5°) whereas the ditosylated ones are quasicoplanar (dihedral angle 139.9°). It should be noted that an analogous conformation is adopted in the crystalline state by resorcinarene tetrasulfonates **2** and their bisoxazine derivatives **7**.[19c,d,20]

Two chloride anions are positioned above the tosylated resorcinol rings and form hydrogen bonds to four OH groups and one ammonium fragment.[24] The other ammonium group is hydrogen bonded to the OH and the SO_2 fragments of a neighboring molecule of **8a**. This results in the formation of hydrogen bonded molecular chains. Since all the OH groups are hydrogen bonded to the chloride anions, they do not form intramolecular hydrogen bonds with the sulfonyl fragments.

Slow crystallization of diamide **9a** from CH_2Cl_2/hexane gave crystals suitable for single crystal X-ray analysis. In the crystalline state the molecule of **9a** adopts a *boat* conformation (Fig. 3) in which the ditosylated resorcinol rings are quasicoplanar and the aminomethylated ones are quasiparallel.

The BOC fragments are arranged in a C_2-symmetrical manner forming intramolecular hydrogen bonds to the closest OH groups, resulting in two eight-membered hydrogen bonded rings. The other two hydroxyls are hydrogen bonded to the sulfonyl groups of the neighboring tosyl fragments.



Scheme 3.

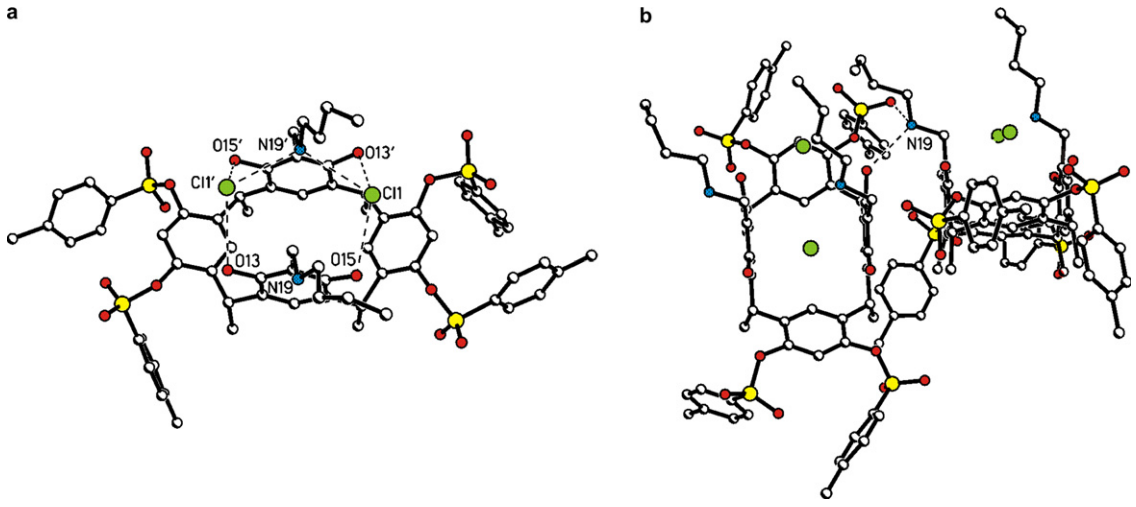


Figure 2. (a) Molecular structure of **8a**; (b) intermolecular hydrogen bonding contact between neighboring molecules of **8a**. Hydrogen bonds are shown in dotted lines, hydrogen atoms are omitted for clarity.

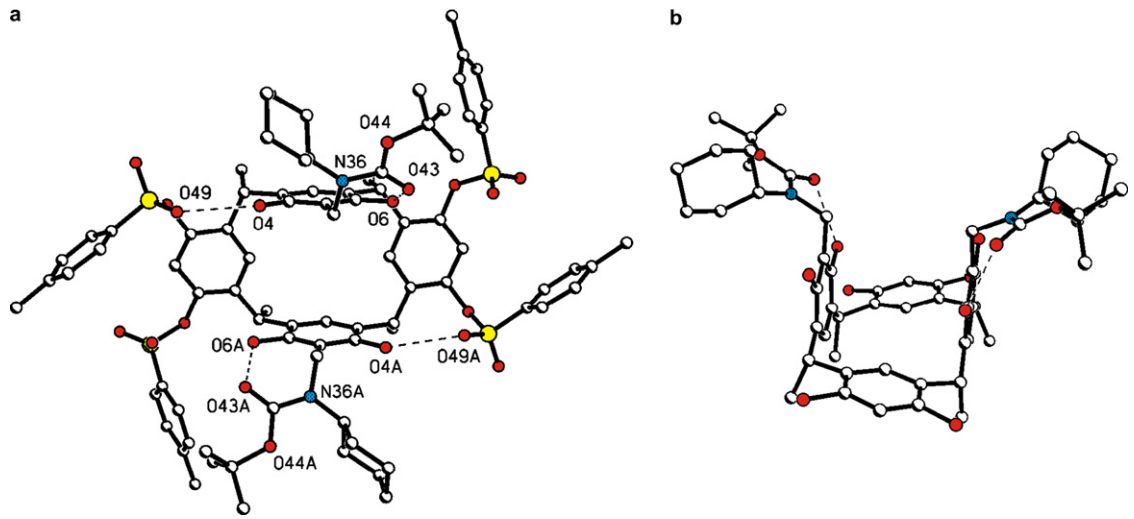


Figure 3. Molecular structure of **9a**. Hydrogen bonds are shown in dotted lines. Hydrogen atoms are omitted for clarity.

Apparently, the conformation of compound **9a** is chiral, the crystal containing both enantiomers in a centrosymmetrical disposition (*C*2/*c*).

The ^{1}H NMR spectra of bisammonium salts **8a** and **b** measured in $CDCl_3$ at 295 K correspond to the C_{2v}-symmetrical structure, since they display three singlets for the protons of the resorcinol rings, a quartet for the methine protons of the bridges and a singlet for the protons of the OH groups.

The ^{1}H NMR spectrum of diamide **9a** ($CDCl_3$, 295 K) contains one set of signals for the methine and methylene protons of the bridges and the protons of the tosyl fragments whereas the OH groups emerge as a broadened singlet at 7.5 ppm. This pattern corresponds to a C_{2v}-symmetrical structure, which is likely the time averaged combination of two C_2-symmetrical conformations similar to those found in the crystalline state.

The ^{1}H NMR spectrum of compound **9a** measured at 295 K in $CDCl_3$ and DMSO-d_6 contains broad signals, most probably due to the hindered interconversion of two *boat* conformers. The sharp spectrum measured in DMSO-d_6 at 378 K corresponds to the time averaged C_{2v}-symmetrical structure.

3. Conclusions

Readily available resorcinarene tetra- and diamines can be selectively acylated by BOC-anhydride or *para*-nitrophenol esters to give resorcinarene derivatives bearing OH and amido groups at the wide rim of the macrocycle. This simple and accessible preparative methodology allows the construction of novel resorcinarenes with widely variable solubility and extremely diverse structural and functional properties. On the other hand, unique arrangement of positively charged and hydrogen bonding groups at the wide rim of the resorcinarene diammonium salts may be utilized for design of novel macrocyclic anion receptors.

4. Experimental section

4.1. Reagents and methods

The NMR spectra were recorded on Bruker Avance DRX 500 (500 MHz) and Bruker DPX 250 (250 MHz) spectrometers using the residual solvent signals as an internal reference. Melting points were determined with a MEL TEMP2 capillary melting point apparatus and are uncorrected. ESI Mass-spectra were recorded on a Micromass LCT ESI-TOF instrument equipped with a Z geometry electrospray ion source. MALDI-TOF Mass-spectra were recorded on a Micromass MicrobeLynx MALDI-TOF. Known procedures have been used for the preparation of compounds **1**,[25] **2**,[19] **3h**,[18c] **7**, and **8**.[20] The purity of all new compounds was determined to be >95% by ^{1}H NMR spectroscopy.

4.1.1. Synthesis of tetraoxazines 3. To a solution of resorcinarene in ethanol, formaldehyde (37%) and amine were added. The mixture was stirred at room temperature for 8 h. The precipitate was filtered off, washed with ethanol, and dried in vacuo. Amounts of reagents and solvents are indicated below for each specific compound.

4.1.1.1. Compound 3a. Resorcinarene **1a** (3.0 g, 5.5 mmol), *n*-butylamine (4.4 ml, 44 mmol), formaline (10 ml, 0.12 mol), and ethanol (50 ml). Yield 5.0 g (97%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=7.2 Hz, 12H), 1.22–1.36 (m, 16H), 1.73 (d, J=7.2 Hz, 12H), 2.53–2.66 (m, 8H), 3.81 (q, J=7.3 Hz, 8H), 4.48 (q, J=7.1 Hz, 4H), 4.91 (s, 8H), 7.84 (s, 8H). ^{13}C NMR ($CDCl_3$) δ 14.14, 19.95, 20.51, 27.20, 30.32, 46.57, 51.49, 83.31, 108.82, 120.95, 124.73, 125.35, 147.85, 149.62. MS (ESI-TOF) 955.53 [M+Na, 100%]$^+$.

4.1.1.2. Compound 3b. Resorcinarene **1a** (3.0 g, 5.5 mmol), cyclohexylamine (5.1 ml, 44 mmol), formaline (10 ml, 0.12 mol), ethanol (50 ml). Yield 5.64 g (99%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 1.06–1.35 (m, 20H), 1.48–1.60 (m, 32H), 2.57 (m, 4H), 3.88 (q, J=7.0 Hz, 8H), 4.43 (q, J=7.25 Hz, 4H), 4.97 (q, J=9.7 Hz, 8H), 7.81 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 20.04, 25.36, 25.62, 26.07, 27.15, 31.40, 32.05, 43.80, 58.09, 80.89, 109.82, 120.82, 124.90, 125.22, 148.76, 149.20. MS (ESI-TOF) 1037.68 [M+H, 100%]$^+$. Anal. Calcd for $C_{64}H_{84}O_8N_4 \cdot 1.5H_2O$: C, 72.38; H, 8.19; N, 5.27. Found: C, 72.32; H, 8.14; N, 5.20.

4.1.1.3. Compound 3c. Resorcinarene **1b** (3.0 g, 5.0 mmol), *n*-butylamine (4.0 ml, 40 mmol), formaldehyde (37%, 10 ml, 0.12 mol), ethanol (50 ml). Yield 4.32 g (87%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J=7.2 Hz, 12H), 1.16–1.27 (m, 8H), 1.30–1.41 (m, 8H), 2.11–2.24 (m, 8H), 2.19–2.28 (m, 8H), 3.70 (q, J=16.4 Hz, 8H), 4.09 (t, J=7.8 Hz, 4H), 4.86–4.97 (m, 8H), 7.10 (s, 4H), 7.76 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 12.86, 14.15, 20.54, 26.86, 30.35, 35.057, 46.63, 51.50, 83.26, 108.82, 121.19, 123.61, 124.33, 148.36, 149.99. MS (ESI-TOF) 989.67 [M+H, 100%]$^+$. Anal. Calcd for $C_{60}H_{84}O_8N_4 \cdot 0.5H_2O$: C, 72.14; H, 8.51; N, 5.61. Found: C, 72.40; H, 8.42; N, 5.77.

4.1.1.4. Compound 3d. Resorcinarene **1b** (3.0 g, 5.0 mmol), cyclohexylamine (4.6 ml, 40 mmol), formaldehyde (37%, 10 ml, 0.12 mol), ethanol (50 ml). Yield 4.4 g (77%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=7.1 Hz, 12H), 1.10–1.42 (m, 24H), 1.54–1.99 (m, 16H), 2.08–2.19 (m, 8H), 2.50–2.62 (m, 4H), 3.69–3.84 (m, 8H), 4.05 (q, J=7.7 Hz, 4H), 5.05 (q, J=7.1 Hz, 8H), 7.09 (s, 4H), 7.84 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 12.85, 25.40, 25.67, 26.10, 26.93, 31.34, 32.12, 34.99, 43.87, 58.22, 80.84, 109.84, 121.05, 123.71, 124.22, 149.27, 149.55. MS (ESI-TOF) 1115.84 [M+Na, 100%]$^+$. Anal. Calcd for $C_{68}H_{92}O_8N_4 \cdot 0.5H_2O$: C, 74.05; H, 8.44; N, 5.08. Found: C, 74.24; H, 8.60; N, 5.16.

4.1.1.5. Compound 3e. Resorcinarene **1c** (3.0 g, 4.0 mmol), cyclohexylamine (3.6 ml, 31 mmol), formaldehyde (37%, 10 ml, 0.12 mol), and ethanol (50 ml). Yield 3.96 g (80%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J=6.7 Hz, 12H), 1.17–2.56 (m, 56H), 3.79–3.94 (m, 8H), 4.16 (t, J=7.8 Hz, 4H), 4.90–5.18 (m, 8H), 7.09 (s, 4H), 7.71 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 14.35, 22.92, 25.42, 25.69, 26.10, 27.99, 31.38, 32.13, 32.85, 33.88, 43.86, 58.29, 82.55, 109.81, 121.15, 123.80, 124.45, 149.17, 149.42. MS (ESI-TOF) 1261.99 [M+H, 100%]$^+$. Anal. Calcd for $C_{80}H_{116}O_8N_4 \cdot 0.5H_2O$: C, 75.59; H, 9.21; N, 4.40. Found: C, 75.46; H, 9.49; N, 4.30.

4.1.1.6. Compound 3f. Resorcinarene **1d** (2.0 g, 2.4 mmol), *n*-butylamine (2.2 ml, 19.2 mmol), formaldehyde (37%, 5 ml, 60 mmol), and ethanol (50 ml). Yield 2.07 g (71%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.81–0.94 (m, 24H), 1.15–1.47 (m, 48H), 2.09–2.21 (m, 8H), 2.51–2.63 (m, 8H), 3.64–3.77 (m, 8H), 3.99 (t, J=7.9 Hz, 4H), 4.89 (q, J=7.2 Hz, 8H), 7.09 (s, 4H), 7.71 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 14.14, 14.26, 20.54, 22.90, 28.28, 29.56, 30.34, 32.12, 32.91, 33.85, 51.48, 108.78, 121.31, 123.69, 124.53, 148.25, 149.88. MS (ESI-TOF) 1216.04 [M+H, 100%]$^+$. Anal. Calcd for $C_{76}H_{116}O_8N_4$: C, 75.21; H, 9.63; N, 4.62. Found: C, 75.36; H, 9.64; N, 4.62.

4.1.1.7. Compound 3g. Resorcinarene **1d** (2.0 g, 2.4 mmol), benzylamine (2.1 ml, 19.2 mmol), formaldehyde (37%, 5 ml, 60 mmol), and ethanol (50 ml). Yield 1.95 g (75%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.80–0.92 (m, 24H), 1.12–1.44 (m, 32H), 2.15–2.24 (m, 8H), 3.68 (q, J=5.4 Hz, 8H), 3.80–3.92 (m, 8H), 4.23 (t, J=7.7 Hz, 4H), 4.75–4.88 (m, 8H), 7.20–7.38 (m, 24H), 7.71 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 14.28, 22.93, 28.29, 29.57, 32.14, 32.95, 56.03, 108.72, 123.85, 124.65, 127.56, 128.61, 129.22, 138.11, 148.29, 149.99. MS (ESI-TOF) 1350.92 [M+H, 100%]$^+$. Anal. Calcd for $C_{88}H_{108}O_8N_4$: C, 78.30; H, 8.06; N, 4.15. Found: C, 77.08; H, 8.02; N, 4.05.

4.1.2. General procedure for the synthesis of compounds 4. To a solution of oxazine **3** in butanol, concd HCl and H_2O were added. The mixture was heated to reflux for 4 h. After the removal of water and formaldehyde by azeotropic distillation, the remaining butanol was evaporated, ethanol and toluene were added and solvents were evaporated in vacuo. The crude product was treated with acetonitrile, filtered off, washed with acetonitrile, and dried in vacuo. The amounts of reagents and solvents are indicated below for each specific compound.

4.1.2.1. Compound 4a. Tetraoxazine **3a** (3.0 g, 2.9 mmol), *n*-BuOH (50 ml), concd HCl (20 ml), and H_2O (10 ml). Yield 3.11 g (55%). Mp >300 °C. ^{1}H NMR (D_2O) δ 0.82 (t, J=7.4 Hz, 12H), 1.26–1.40 (m, 16H), 1.58–1.76 (m, 20H), 3.01 (t, J=7.8 Hz, 8H), 4.31 (s, 8H), 4.55 (q, J=7.0 Hz, 4H), 6.99 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 13.68, 19.17, 20.10, 27.73, 28.82, 43.53, 49.34, 108.99, 124.72, 127.54, 150.17. MS (MALDI-TOF) 883.38 [(M−4Cl)+H, 100%]$^+$. Anal. Calcd for $C_{52}H_{76}O_8N_4Cl_4\cdot 2.5H_2O$: C, 58.26; H, 7.56; N, 5.23. Found: C, 58.44; H, 7.97, N, 5.20.

4.1.2.2. Compound 4b. Tetraoxazine **3b** (4.0 g, 3.7 mmol), *n*-BuOH (50 ml), concd HCl (20 ml), and H_2O (10 ml). Yield 4.16 g (96%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 1.15–1.32 (m, 20H), 1.35–1.68 (m, 32H), 2.22–2.29 (m, 4H), 3.15 (s, 4H), 4.12–4.23 (m, 8H), 4.54 (q, J=7.0 Hz, 4H), 7.33 (s, 4H), 7.51 (s, 4H), 9.49 (s, 8H). ^{13}C NMR ($CDCl_3$) δ 13.48, 18.83, 19.11, 24.90, 28.71, 28.83, 34.76, 40.56, 59.47, 62.48, 108.77, 124.57, 127.33, 150.11. MS (ESI-TOF) 885.53 [(M−4Cl)+H, 100%]$^+$. Anal. Calcd for $C_{60}H_{84}O_8N_4Cl_4\cdot H_2O$: C, 62.70; H, 7.49; N, 4.84. Found: C, 62.50; H, 7.21; N, 4.81.

4.1.2.3. Compound 4c. Tetraoxazine **3c** (3.0 g, 3.0 mmol), *n*-BuOH (50 ml), concd HCl (20 ml), and H_2O (10 ml). Yield 2.58 g (78%). Mp >300 °C. ^{1}H NMR (D_2O) δ 0.81–0.97 (m, 24H), 1.29–1.40 (m, 16H), 2.10–2.21 (m, 8H), 3.00–3.12 (m, 8H), 4.12–4.25 (m, 12H), 7.19 (s, 4H), 7.71 (s, 4H), 9.35 (s, 8H). ^{13}C NMR ($CDCl_3$) δ 12.67, 13.68, 20.10, 26.14, 27.74, 36.65, 43.49, 49.30, 109.17, 124.92, 126.52, 150.65. MS (MALDI-TOF) 941.60 [(M−4Cl)+H, 100%]$^+$. Anal. Calcd for $C_{56}H_{88}O_8N_4Cl_4\cdot 2H_2O$: C, 59.89; H, 8.19; N, 4.99. Found: C, 59.81; H, 8.29; N, 5.13.

4.1.2.4. Compound 4d. Tetraoxazine **3d** (4.0 g, 3.7 mmol), *n*-BuOH (50 ml), concd HCl (20 ml), and H_2O (10 ml). Yield 4.16 g (96%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J=7.1 Hz, 12H), 1.11–1.42 (m, 40H), 2.12–2.21 (m, 8H), 3.08–3.22 (m, 4H), 4.12–4.25 (m, 12H), 7.19 (s, 4H), 7.48 (s, 4H), 9.46 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 12.74, 18.89, 24.93, 25.99, 28.81, 36.58, 40.68, 59.49, 108.92, 124.86, 126.29, 150.56. MS (ESI-TOF) 1045.72 [(M−4Cl)+H, 100%]$^+$. Anal. Calcd for $C_{64}H_{94}O_8N_4Cl_4$: C, 64.74; H, 8.08; N, 4.72. Found: C, 64.41; H, 8.39; N, 4.43.

4.1.2.5. Compound 4e. Tetraoxazine **3e** (1.45 g, 1.2 mmol), *n*-BuOH (40 ml), concd HCl (10 ml), and H_2O (5 ml). Yield 1.35 g (86%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=7.2 Hz, 12H), 1.11 (m, 8H), 1.41 (d, J=6.8 Hz, 12H), 1.66–2.26 (m, 40H), 3.28–3.37 (m, 4H), 4.07–4.19 (m, 12H), 6.84 (2H), 7.21 (s, 4H), 7.96 (s, 2H), 9.32 (s, 4H), 9.83 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 12.47, 12.71, 25.86, 26.16, 26.35, 26.47, 30.36, 36.56, 39.34, 41.91, 61.38, 108.90, 124.74, 125.99, 126.77, 150.10, 151.36. MS (ESI-TOF) 1157.87 [(M−4Cl)+H, 100%]$^+$. Anal. Calcd for $C_{72}H_{88}O_8N_4Cl_4$: C, 67.63; H, 6.88; N, 4.38. Found: C, 68.07; H, 6.51; N, 5.01.

4.1.2.6. Compound 4f. Tetraoxazine **3f** (3.5 g, 2.8 mmol), *n*-BuOH (50 ml), concd HCl (10 ml), and H_2O (5 ml). Yield 2.82 g (77%). ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J=6.8 Hz, 12H), 1.26–1.84 (m, 64H), 2.10–2.21 (m, 8H), 3.14 (s, 4H), 4.12–4.23 (m, 8H), 4.27 (t, J=7.7 Hz, 4H), 7.19 (s, 4H), 7.52 (s, 8H), 9.42 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 13.59, 14.28, 18.88, 22.86, 24.91, 24.99, 27.92, 28.84, 32.11, 33.00, 34.53, 34.82, 40.58, 59.42, 62.56, 108.86, 124.90, 126.44, 150.46. MS (ESI-TOF) 1213.97 [(M−4Cl)+H, 100%]$^+$. Anal. Calcd for $C_{76}H_{116}O_8N_4Cl_4\cdot 2H_2O$: C, 65.63; H, 8.62; N, 4.02. Found: C, 65.86; H, 9.21; N, 3.95.

4.1.2.7. Compound 4g. Tetraoxazine **3g** (1.5 g, 1.2 mmol), *n*-BuOH (30 ml), concd HCl (5 ml), and H_2O (5 ml). Yield 1.03 g (64%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.81–0.92 (m, 24H), 1.15–1.32 (m, 32H), 1.80–1.92 (m, 8H), 2.10–2.23 (m, 8H), 3.05–3.16 (m, 8H), 4.15–4.24 (m, 8H), 4.28 (t, J=7.7 Hz, 4H), 7.14 (s, 4H), 7.68 (m, 4H), 9.34 (s, 8H). ^{13}C NMR ($CDCl_3$) δ 13.69, 14.24, 20.11, 22.86, 27.75, 28.24, 29.57, 32.08, 32.90, 49.45, 109.05, 124.89, 126.59, 150.47. MS (ESI-TOF) 1166.24 [(M−4Cl)+H, 100%]$^+$. Anal. Calcd for $C_{72}H_{116}O_8N_4Cl_4\cdot 2H_2O$: C, 64.40; H, 8.93; N, 4.17. Found: C, 64.78; H, 9.20; N, 4.15.

4.1.2.8. Compound 4h. Tetraoxazine **3h** (1.5 g, 0.92 mmol), *n*-BuOH (30 ml), concd HCl (5 ml), and H_2O (5 ml). Yield 1.35 g (85%). Mp >300 °C. ^{1}H NMR

($CDCl_3$) δ 0.84 (t, J=6.8 Hz, 12H), 1.10–1.52 (m, 72H), 2.11 (s, 8H), 4.08 (s, 8H), 4.21 (m, 12H), 7.14 (s, 4H), 7.25–7.50 (m, 20H), 8.00 (s, 4H), 9.27 (s, 8H). ^{13}C NMR ($CDCl_3$) δ 14.32, 22.91, 28.25, 29.61, 29.91, 32.16, 32.95, 34.52, 42.63, 108.81, 121.01, 126.59, 129.34, 129.61, 129.91, 130.82, 150.44. MS (ESI-TOF) 1586.14 [(M−4Cl)+H, 100%]$^+$. Anal. Calcd for $C_{104}H_{148}O_8N_4Cl_4\cdot H_2O$: C, 71.17; H, 8.62, N, 3.25. Found: C, 71.16; H, 8.96; N, 3.21.

4.1.3. General procedure for selective BOC-protection of tetraamines 4. To a solution of compound **4** in dry THF, Et_3N and BOC-anhydride were added. The reaction mixture was stirred under nitrogen at room temperature overnight, the volatiles removed at reduced pressure. The solid residue was dissolved in CH_2Cl_2 and precipitated with MeCN. The precipitate was filtered off, washed with MeCN, and dried in vacuo. The amounts of reagents and solvent are indicated below for each specific compound.

4.1.3.1. Compound 5a. Compound **4a** (1.5 g, 1.5 mmol), BOC-anhydride (1.9 g, 7.3 mmol), Et_3N (1.0 ml, 7.2 mmol), and CH_2Cl_2 (25 ml). Yield 1.27 g (68%). Mp 199–200 °C. ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J=7.2 Hz, 12H), 1.12–1.45 (m, 34H), 1.74 (d, J=7.2 Hz, 12H), 3.33 (s, 8H), 4.28 (s, 8H), 4.67 (q, J=7.3 Hz, 4H), 7.35 (s, 4H), 8.64 (s, 4H), 11.13 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 13.91, 19.95, 28.43, 30.20, 40.63, 47.14, 80.95, 110.00, 112.55, 125.37, 151.33, 158.78. MS (ESI-TOF) 1307.80 [M+Na, 100%]$^+$. Anal. Calcd for $C_{72}H_{108}O_{16}N_4\cdot H_2O$: C, 66.66; H, 8.48; N, 4.31. Found: C, 66.76; H, 8.06; N, 4.70.

4.1.3.2. Compound 5b. Compound **4b** (0.5 g, 0.51 mmol) in 45 ml of CH_2Cl_2, BOC-anhydride (0.66 g, 3.0 mmol), and Et_3N (1.0 ml, 7.2 mmol). Yield 0.35 g (50%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 1.22–1.99 (m, 92H), 3.63 (s, 4H), 4.27–4.38 (m, 8H), 4.64 (q, J=7.3 Hz, 4H), 7.30 (s, 4H), 8.36 (s, 4H), 11.30 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 20.13, 25.67, 26.511, 26.58, 28.45, 28.53, 30.35, 30.63, 60.49, 81.14, 108.47, 122.43, 124.78, 158.81. MS (ESI-TOF) 1411.77 [M+Na, 100%]$^+$. Anal. Calcd for $C_{80}H_{116}O_{16}N_4\cdot 2H_2O$: C, 67.36; H, 8.42; N, 3.93. Found: C, 67.47; H, 8.14; N, 4.34.

4.1.3.3. Compound 5c. Compound **4c** (2.0 g, 1.7 mmol), BOC-anhydride (2.2 g, 10.8 mmol), Et_3N (1.2 ml, 8.4 mmol) in 25 ml CH_2Cl_2 . Yield 1.92 g (81%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J=7.0 Hz, 12H), 1.10–1.32 (m, 58H), 2.11–2.22 (m, 8H), 3.16 (s, 4H), 4.20–4.32 (m, 12H), 7.12 (s, 4H), 8.54 (s, 4H), 11.06 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 12.86, 26.03, 26.89, 27.32, 28.88, 30.79, 36.63, 42.75, 60.54, 81.43, 113.11, 123.40, 124.43, 150.65, 152.01, 159.17. MS (ESI-TOF) 1440.79 [M+Na, 100%]$^+$. Anal. Calcd for $C_{82}H_{120}O_{16}N_4$: C, 69.46; H, 8.53; N, 3.95. Found: C, 69.59; H, 8.55; N, 3.92.

4.1.3.4. Compound 5d. Compound **4e** (1.5 g, 1.1 mmol), BOC-anhydride (1.45 g, 6.6 mmol), Et_3N (0.8 ml, 5.5 mmol) in 30 ml CH_2Cl_2. Mp >300 °C. Yield 1.60 g (90%). ^{1}H NMR ($CDCl_3$) δ 0.84 (t, J=6.4 Hz, 12H), 1.15–1.43 (m, 100H), 2.11–2.23 (m, 8H), 3.61 (s, 4H), 4.30–4.42 (m, 12H), 7.12 (s, 4H), 8.54 (s, 4H), 11.06 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 9.05, 14.29, 22.93, 25.86, 26.71, 27.85, 28.70, 30.66, 32.09, 34.17, 34.28, 46.05, 60.32, 81.25, 112.87, 122.98, 124.43, 158.99. MS (ESI-TOF) 1614.37 [M+H, 100%]$^+$.

4.1.3.5. Compound 5e. Compound **4f** (0.8 g, 0.6 mmol), BOC-anhydride (0.8 g, 3.6 mmol), Et_3N (0.4 ml, 3.1 mmol) in 20 ml CH_2Cl_2. Yield 0.52 g (55%). Mp 165–166 °C. ^{1}H NMR ($CDCl_3$) δ 0.80–0.93 (m, 24H), 1.16–1.37 (m, 76H), 2.12–2.21 (m, 8H), 3.30–3.39 (m, 4H), 4.23–4.31 (m, 12H), 7.18 (s, 4H), 8.55 (s, 4H), 10.97 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 14.15, 14.23, 20.17, 22.92, 28.26, 28.64, 29.60, 30.47, 32.14, 34.12, 34.37, 47.43, 81.07, 112.60, 123.39, 124.56, 124.95, 150.45, 151.82, 158.95. MS (ESI-TOF) 1565.74 [M+H, 100%]$^+$. Anal. Calcd for $C_{92}H_{148}O_{16}N_4$: C, 70.54; H, 9.44; N, 3.57. Found: C, 70.42; H, 9.61; N, 3.57.

4.1.3.6. Compound 5f. Compound **4g** (0.8 g, 0.6 mmol), BOC-anhydride (0.8 g, 3.6 mmol), Et_3N (0.4 ml, 3.1 mmol) in 20 ml CH_2Cl_2. Crude product was purified by flash column chromatography (EtOAc/THF 1:2). Yield 0.53 g (55%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J=6.8 Hz, 12H), 1.20–1.42 (m, 68H), 2.20–2.31 (m, 8H), 4.25–4.62 (m, 20H), 7.20–7.34 (m, 24H), 8.67 (s, 4H), 11.01 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 14.18, 15.38, 22.83, 27.43, 28.22, 28.39, 29.53, 32.07, 34.36, 65.92, 81.77, 85.19, 112.32, 127.11, 127.77, 128.45, 138.59, 146.90. MS (ESI-TOF) 1724.75 [M+Na, 100%]$^+$.

4.1.3.7. Compound 5g. Compound **4h** (0.8 g, 0.4 mmol), BOC-anhydride (0.61 g, 2.8 mmol), Et_3N (0.32 ml, 2.3 mmol) in 25 ml CH_2Cl_2. Yield 0.49 g (53%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=6.8 Hz, 12H), 1.22–1.78 (m, 108H), 2.27 (br s, 8H), 4.30–4.44 (m, 20H), 7.24–7.36 (m, 24H), 8.72 (s, 4H), 11.06 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 14.33, 15.49, 22.92, 28.40, 28.51, 29.64, 29.96, 29.99, 30.05, 32.19, 34.13, 34.48, 51.06, 66.05, 76.72, 81.85, 112.38, 123.46, 124.83, 125.09, 127.18, 127.89, 128.54, 138.70, 150.53, 151.90, 158.99. MS (ESI-TOF) 2005.12 [M+Na, 100%]$^+$. Anal. Calcd for $C_{124}H_{180}O_{16}N_4$: C, 75.16; H, 9.08; N, 2.82. Found: C, 75.31; H, 9.21; N, 2.98.

4.1.3.8. Compound 5h. To a solution of compound **4b** (0.3 g, 0.3 mmol) in 10 ml of CH_2Cl_2, Et_3N (0.23 ml, 1.6 mmol) and a solution of *para*-nitrophenylacetate (0.38 g, 2.1 mmol) in 5 ml of CH_2Cl_2 were added. The mixture was stirred overnight. The solution was evaporated, the solid residue was dissolved in 5 ml of CH_2Cl_2 and extracted with 1 M K_2CO_3 until the yellow color of the aqueous layer disappeared. The organic layer was separated and evaporated in vacuo. The product was triturated with methanol, the precipitate formed was filtered off and washed with methanol. Yield 220 mg (72%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 1.26–1.33 (m, 12H), 2.19 (br s, 40H), 3.56–3.67 (m, 4H), 4.40–4.52 (m, 8H), 4.61 (q, J=7.2 Hz, 4H), 7.22 (s, 4H), 8.85 (s, 8H). MS (ESI-TOF) 1179.76 [M+Na, 100%]$^+$. Anal. Calcd for $C_{68}H_{92}O_{12}N_4\cdot 2H_2O$: C, 68.42; H, 8.04; N, 4.69. Found: C, 67.92; H, 7.91; N, 4.60.

4.1.3.9. Compound 5i. Compound **5i** was obtained as **5h** from compound **4d** (0.5 g, 0.4 mmol) and *para*-nitrophenylacetate (0.56 g, 3.1 mmol). Yield 0.35 g (69%). Mp >300 °C. ^{1}H NMR (toluene-d_8) δ 0.88–1.37 (m, 48H), 3.19 (s, 4H), 4.53–4.61 (m, 12H), 7.42 (s, 4H), 9.27 (s, 4H), 12.31 (s, 4H). MS (ESI-TOF) 1346.94 [M+Na, 100%]$^+$. Anal. Calcd

for $C_{80}H_{116}O_{12}N_4 \cdot 4H_2O$: C, 68.76; H, 8.30; N, 4.01. Found C, 69.08; H, 8.52; N, 4.08.

4.1.3.10. Compound 5j. Compound **5j** was prepared as **5h** from **4a** (0.4 g, 0.39 mmol) and *para*-nitrophenyl-4-methylbenzoate (0.8 g, 3.1 mmol). Yield 100 mg (18.5%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.82–0.93 (m, 12H), 1.14–1.35 (m, 16H), 1.78 (d, J=7.2 Hz, 12H), 2.37 (s, 12H), 3.26–3.37 (m, 8H), 4.58–4.68 (m, 12H), 7.12–7.23 (m, 16H), 7.44 (s, 4H), 8.82 (s, 4H), 11.73 (s, 4H). MS (ESI-TOF) 1401.8 [(M+2Na)−H, 100%]$^+$. Anal. Calcd for $C_{84}H_{100}O_{12}N_4$: C, 74.35; H, 7.37; N, 4.13. Found: C, 74.33; H, 7.81; N, 4.21.

4.1.3.11. Compound 6a. To a solution of compound **5a** (1.0 g, 0.8 mmol) in pyridine (25 ml) acetic acid anhydride (12.6 ml, 0.13 mol) was added in one portion and the reaction mixture was stirred overnight under nitrogen at room temperature. The solution was evaporated to dryness in vacuo, the residue was dissolved in toluene and the solvent was evaporated. The crude product was triturated with ether, filtered off, and washed with ether. Yield 1.04 g (82%). Mp 244–245 °C. ^{1}H NMR (DMSO-d_6) δ 0.82 (t, J=7.6 Hz, 12H), 1.16–1.54 (m, 64H), 2.26 (s, 24H), 2.71 (s, 8H), 4.02–4.16 (m, 12H), 7.18 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 14.10, 14.28, 19.96, 20.07, 20.87, 28.64, 28.71, 29.55, 29.74, 29.89, 30.13, 32.48, 39.25, 44.35, 76.71, 79.37, 79.73, 123.06, 125.13, 134.01, 146.13, 148.10, 155.59, 155.74, 169.03. MS (ESI-TOF) 1644.29 [M+Na, 100%]$^+$. Anal. Calcd for $C_{88}H_{124}O_{24}N_4$: C, 65.17; H, 7.71; N, 3.45. Found C, 65.43; H, 7.98; N, 3.54.

4.1.3.12. Compound 6b. Compound **6b** was obtained as **6a** form compound **5c** (2.0 g, 1.3 mmol). Yield 2.15 g (90.5%). Mp 190–192 °C. ^{1}H NMR (DMSO-d_6) δ 0.80 (t, J=7.3 Hz, 12H), 1.43–1.72 (m, 76H), 1.86–1.95 (m, 8H), 2.21 (s, 24H), 2.91 (s, 4H), 3.84 (t, J=7.4 Hz, 4H), 4.25 (s, 8H), 7.21 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 11.43, 19.59, 24.45, 25.00, 27.35, 28.81, 37.69, 39.65, 56.07, 78.26, 123.64, 124.19, 154.75, 167.08. MS (ESI-TOF) 1804.51 [M+Na, 100%]$^+$.

4.1.3.13. Compound 6c. Compound **6c** was obtained as **6a** from compound **5g** (0.3 g, 0.15 mmol). Yield 2.30 g (65.5%). Mp 119–120 °C. ^{1}H NMR (DMSO-d_6) δ 0.84 (t, J=7.1 Hz, 12H), 1.23–1.61 (m, 108H), 1.91 (br s, 8H), 2.01 (s, 24H), 3.85–4.00 (m, 16H), 4.17 (s, 4H), 6.94 (s, 4H), 7.26–7.42 (m, 20H). ^{13}C NMR ($CDCl_3$) δ 14.43, 20.51, 20.64, 23.02, 28.30, 28.63, 29.73, 30.07, 30.20, 32.26, 80.23, 80.44, 123.19, 126.97, 128.66, 138.42, 156.96, 182.44. MS (ESI-TOF) 2340.36 [M+Na, 100%]$^+$. Anal. Calcd for $C_{140}H_{196}O_{24}N_4$: C, 72.43; H, 8.48; N, 2.43. Found C, 71.52; H, 8.51; N, 2.50.

4.1.3.14. Compound 6d. To a solution of compound **5h** (0.5 g, 0.4 mmol) in CH_2Cl_2 (30 ml), Et_3N (0.3 ml, 2.1 mmol) and acetic acid anhydride (15 ml, 0.13 mol) were added. The mixture was stirred for five days at room temperature. The solution was evaporated in vacuo, the crude product was triturated with CH_2Cl_2 and hexane, filtered off, and washed with hexane. Yield 0.26 g (40%). Mp 214–215 °C. ^{1}H NMR (DMSO-d_6) δ 0.80 (t, J=7.3 Hz, 12H), 1.07–1.19 (m, 16H), 1.22–1.34 (m, 16H), 1.91 (s, 24H), 2.80 (s, 4H), 2.93 (s, 12H), 3.84 (t, J=7.3 Hz, 4H), 4.31 (s, 8H), 7.22 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 11.67, 12.76, 18.66, 19.66, 20.26, 26.59, 28.98, 38.43, 44.61, 122.32, 125.76, 132.79, 146.26, 167.69, 168.59. MS (ESI-TOF) 1549.59 [M+H, 100%]$^+$. Anal. Calcd for $C_{88}H_{116}O_{20}N_4 \cdot 3H_2O$: C, 65.89; H, 7.60; N, 3.49. Found C, 65.27; H, 7.55; N, 3.22.

Compounds **8** were obtained as compound **4a** from corresponding bisoxazines **7**. The amounts of reagents and solvent are indicated below for each specific compound.

4.1.3.15. Compound 8a. Bisoxazine **7a** (0.5 g, 0.4 mmol), *n*-BuOH (30 ml), concd HCl (5 ml), and H_2O (5 ml). Yield 300 mg (58%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=7.4 Hz, 6H), 1.25–1.85 (m, 20H), 2.47 (s, 12H), 2.82–2.97 (m, 8H), 3.81–3.92 (m, 8H), 4.51 (q, J=6.9 Hz, 4H), 6.39 (s, 4H), 6.43 (s, 4H), 6.59 (s, 4H), 7.37 (d, J=8.1 Hz, 8H), 7.80 (d, J=8.3 Hz, 8H), 8.67 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 13.67, 20.29, 21.27, 21.97, 27.28, 31.88, 42.43, 48.11, 77.70, 111.34, 115.87, 124.33, 126.69, 127.26, 128.89, 130.35, 132.40, 139.47, 145.03, 146.01, 152.54. MS (ESI-TOF) 1332.48 [(M–2Cl)+H, 100%]$^+$. Anal. Calcd. for $C_{70}H_{78}O_{16}N_2S_4Cl_2 \cdot 0.5H_2O$: C, 59.57; H, 5.60; N, 1.98; S, 9.07. Found: C, 59.50; H, 5.70; N, 2.04; S, 9.03.

4.1.3.16. Compound 8b. Bisoxazine **7b** (1.0 g, 0.68 mmol), *n*-BuOH (30 ml), concd HCl (5 ml), and H_2O (5 ml). Yield 730 mg (73.8%). Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 1.25–1.67 (m, 32H), 1.99 (d, J=7.0 Hz, 12H), 3.07–3.15 (m, 2H), 3.55–3.64 (m, 4H), 4.52 (q, J=7.0 Hz, 4H), 6.41 (s, 2H), 6.45 (s, 2H), 7.37 (d, J=8.1 Hz, 8H), 7.84 (d, J=6.4 Hz, 8H), 8.36 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 12.93, 21.99, 25.17, 28.45, 28.75, 38.82, 58.12, 112.23, 115.37, 122.26, 127.08, 128.89, 130.35, 132.66, 138.13, 145.28, 145.93, 153.19. MS (ESI-TOF) 1386.02 [(M−2Cl)+H, 100%]$^+$.

Compounds **9** were obtained as compound **5a** from corresponding salts **8**. The amounts of reagents and solvent are indicated below for each specific compound.

4.1.3.17. Compound 9a. Compound **8a** (0.25 g, 0.19 mmol), BOC-anhydride (0.25 g, 1.1 mmol), Et_3N (0.13 ml, 0.1 mmol), in 20 ml CH_2Cl_2. Yield 0.15 g, oil (52%). ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J=7.3, 6H), 1.26–1.68 (m, 38H), 2.48 (s, 12H), 3.20–3.29 (m, 4H), 4.14 (s, 4H), 4.40 (q, J=7.0 Hz, 4H), 6.23 (s, 4H), 6.71 (s, 4H), 6.99 (s, 4H), 7.38 (d, J=8.2 Hz, 8H), 7.87 (d, J=8.2 Hz, 8H). MS (ESI-TOF) 1533.52 [M+Na, 100%]$^+$. Anal. Calcd for $C_{80}H_{94}O_{20}N_2S_4$: C, 62.75; H, 6.13; N, 1.83; S, 8.37. Found: C, 63.01; H, 6.21; N, 1.68; S, 8.07.

4.1.3.18. Compound 9b. Compound **8b** (0.25 g, 0.17 mmol), BOC-anhydride (0.225 g, 1.0 mmol), Et_3N (0.12 ml, 0.85 mmol) in 20 ml CH_2Cl_2. The mixture was treated as for **5a**. Yield 0.16 g, oil (61%). Mp 184–185 °C. ^{1}H NMR ($CDCl_3$) δ 1.09–1.62 (m, 50H), 2.42 (s, 12H), 3.49–3.58 (m, 2H), 4.00–4.12 (m, 4H), 4.33 (q, J=7.0 Hz, 4H), 5.78 (s, 2H), 6.16 (s, 2H), 6.74 (s, 2H), 6.90 (s, 2H), 7.33 (d, J=8.1 Hz, 8H), 7.50 (s, 4H), 7.81 (d, J=8.2 Hz, 8H). MS (ESI-TOF) 1605.33 [M+Na, 100%]$^+$. Anal. Calcd for $C_{80}H_{96}O_{20}N_2S_4$: C, 62.67; H, 6.26; N, 1.82; S, 8.36. Found: C, 63.01; H, 6.21; N, 1.68; S, 8.07.

4.1.3.19. Compound 10. Compound **10** was obtained as **6a** from compound **9a** (0.07 g, 0.05 mmol): pyridine (10 ml), acetic acid anhydride (1 ml, 9.0 mmol). Yield 0.06 g (80%). Mp 166–167 °C. ^{1}H NMR (DMSO-d_6) δ 0.63 (t, J=7.3 Hz, 6H), 0.86–0.97 (m, 4H), 1.05–1.11 (m, 4H), 1.29 (s, 18H), 1.35 (d, J=7.1 Hz, 12H), 1.91 (s, 12H), 1.99 (s, 12H), 2.91 (s, 4H), 4.20 (q, J=6.7 Hz, 4H), 6.75 (s, 4H), 7.02 (s, 4H), 7.54 (d, J=8.0 Hz, 8H), 7.63 (s, 4H), 7.82 (d, J=8.5 Hz, 8H). MS (ESI-TOF) 1722.36 [M+Na, 100%]$^+$.

4.2. X-ray data collection and crystal structure determinations

X-ray data were collected at 173.0 K on a Nonius Kappa CCD diffractometer using graphite-monochromatized Mo Kα radiation. Structures were solved by SHELXS-97 and refined on F^2 by full-matrix least-squares techniques (SHELXL-97).[26] Hydrogen atoms were calculated to their idealized positions and refined as riding atoms (temperature factor 1.2 or 1.5 times C temperature factor). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-606116 and 606117. Copies of the data can be obtained, free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 123 336033 or e-mail: deposit@ccdc.cam.ac.uk) (Table 1).

Table 1. Crystallographic data for resorcinarenes **8a** and **9a**

	8a	**9a**
Formula	$C_{71}H_{81}O_{16}N_2S_4Cl_5$	$C_{84}H_{98}O_{20}N_2S_4$
Formula weight	1523.87	1583.88
Crystal system	Monoclinic	Monoclinic
Space group	*Pc* (no. 7)	*C*2/*c* (no. 15)
a (Å)	13.9354(2)	26.3240(6)
b (Å)	16.1270(3)	10.8202(2)
c (Å)	17.3280(3)	28.5847(4)
β (°)	110.696(1)	90.219(1)
V (Å^3)	3642.9(1)	8141.7(3)
Z	2	4
μ (mm^{-1})	0.381	0.189
Refl collected/unique/R_{int}	35829/13017/0.062	18564/6857/0.112
Final *R*/*Rw* values ($I>2\sigma I$)	0.066/0.161	0.079/0.171
S	1.046	1.024

Acknowledgements

This research was financially supported by Finnish Academy (project 63018) K.R. and A.S. and National Technology Agency of Finland (TEKES, project 40476/01) M.L. We thank Mr. Rejo Kauppinen for his assistance in variable temperature NMR measurements and Dr. Adel Rafai Far for correcting the manuscript.

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