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# Synthesis and Functionalization of Heteroatom-Bridged Bicyclocalixaromatics, Large Molecular Triangular Prisms with Electron-Rich and -Deficient Aromatic Interiors

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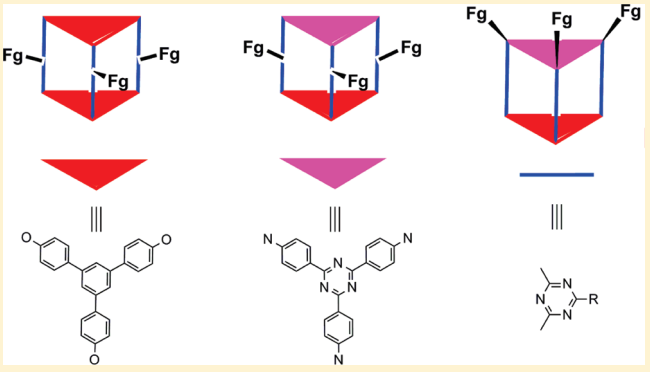
Supporting Information

**ABSTRACT:** The synthesis and functionalization of oxygen and nitrogen atom bridged bicyclocalixaromatics of triangular prism structures are reported. By means of a fragment coupling approach, molecular triangular prisms of electron-rich and electron-deficient aromatic interiors were prepared using 1,3,5-tri(*p*-hydroxyphenyl)benzene and 2,4,6-tri(*p*-aminophenyl)triazine as base units and chlorotriazines as pillars. Aromatic nucleophilic substitution reaction of chlorotriazine moieties with functionalized amines led to triangular prisms with functionalizations on the peripheral edge positions, while functionalized triangular prisms on the vertex nitrogen positions were obtained using 2,4,6-tri[(*p*-allylamino)phenyl]-triazine derivative as a starting material. Symmetrical and distorted molecular triangular prisms in the solid state were revealed by X-ray crystallography. As evidenced by NMR spectroscopic data, however, all cage molecules synthesized most probably adopted highly symmetric triangular prism structures in solution phase. The functionalized shape-persistent triangular prism structures might find applications in molecular recognition and in the construction of higher and more sophisticated molecular architectures in supramolecular chemistry.




## INTRODUCTION

High-level molecular architectures such as molecular cages have attracted continued attention because of their appealing topological structures and fascinating applications in chemistry, biology, and material science. Various shaped cage molecules including sphere, cylinder, cone, and prism, for example, have been synthesized through either the formation of chemical bonds[1] or the molecular assembly based on noncovalent interactions,[2,3] and they have been used as hosts to recognize guest species[4] and as confined microreactors to catalyze or facilitate the reactions.[5] In comparison with molecular cages constructed by intermolecular hydrogen bonds[2] and metal−ligand coordination bonds,[3] cage molecules synthesized from covalent chemical bonds possess high stability.[1] They are useful building blocks in the construction of higher level molecular assemblies such as porous materials.[6]

Heteroatom-bridged calixaromatics, also known as heteracalixaromatics,[7] are a new generation macrocyclic host molecules in supramolecular chemistry. In contrast to the methylene linkage in conventional calixarenes,[8] the bridging heteroatoms in heteracalixaromatics such as nitrogen can form $sp^2$ and $sp^3$ electronic configurations and different conjugation systems with their adjacent arene and heteroaromatic rings, yielding various bond lengths and bond angles. As the consequence, heteracalixaromatic macrocycles adopt varied conformational structures with self-tuned cavity sizes in response to the guest species.[9] In addition, through the inductive and conjugative effects, different heteroatoms and the substituents on the linking heteroatoms are able to regulate the electronic density of the linking aromatic rings, leading to the generation of cavities of fine-tuned electronic features.[10] The unique structural properties of heterocalixaromatics such as azacalixpyridines and oxacalix[2]arene[2]triazines, have found wide applications in supramolecular chemistry.[7a] They include molecular recognition of metal ions,[11] the formation of anion−$\pi$ complexes,[10] and selective binding with neutral molecules ranging from hydrogen bond donors[12] and acceptors[13] to fullerenes $C_{60}$ and $C_{70}$.[9b,14]

Heteracalixaromatics also provide a versatile platform for the construction of sophisticated molecular structures because the parent macrocyclic heteracalixaromatics are conveniently functionalized both on the aromatic rings and the bridging nitrogen atoms.[7a] For example, a few heteracalixazacrowns[15]

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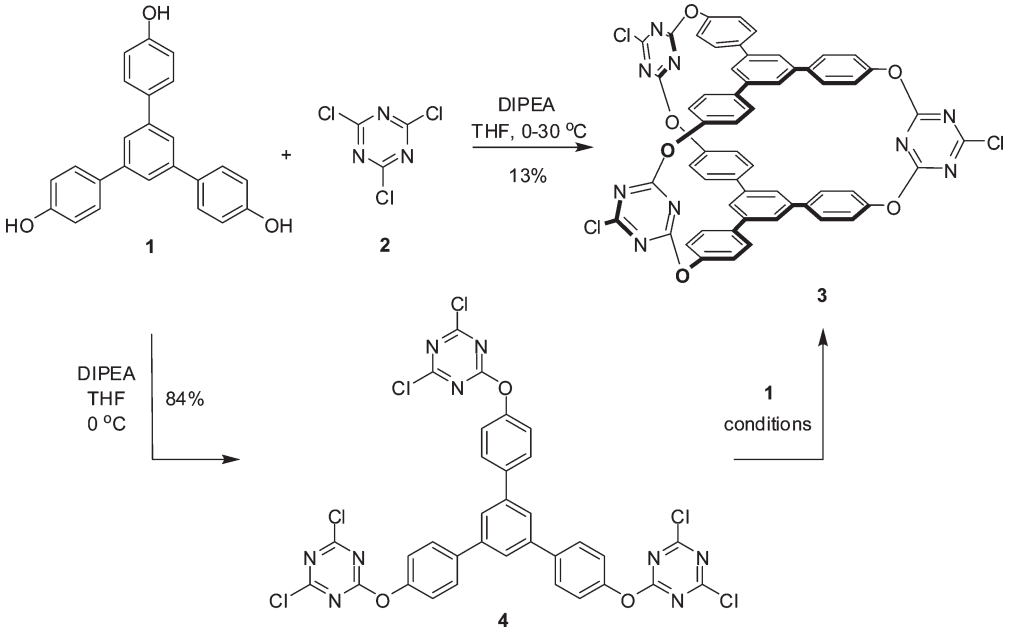
**Scheme 1. Synthesis of Parent Molecular Prism 3**




and bis-heteracalixaromatics[16] of a large and tunable cavity have been prepared efficiently from the aromatic nucleophilic substitution reactions of parent oxacalix[2]arene[2]triazine and -[2]pyrimidine derivatives with the appropriate diamines. Recently, we[10] and other groups[17] have reported the synthesis of oxygen-bridged bicyclcocalixaromatics starting from phloroglucinol and cyanuric chloride or 2,6-dihalopyridine derivatives.[10,17] The molecules, however, have a very small cavity and therefore have very limited applications.[10] Our interest in molecular cages[10,15,16] has led us to undertake the current study. We report herein the construction of large molecular triangular prisms based on nitrogen and oxygen atom bridged bicyclocalixaromatics employing 1,3,5-tri(*p*-hydroxyphenyl)benzene and 2,4,6-tri(*p*-aminophenyl)triazine as equilateral triangular bases or "top" and "bottom" and cyanuric chlorides as three pillars. The use of cyanuric chlorides has allowed us to functionalize the resulting triangular prisms on the edge positions around the periphery. Taking advantage of the nitrogen linkages in the prisms, we have also introduced the functional groups on the vertex positions.

## RESULTS AND DISCUSSION

We initiated our study with a one-pot synthesis of oxygen-bridged bicyclocalixaromatics **3** that contains an electron-rich 1,3,5-tri(*p*-oxaphenyl)benzene segment as both the top and the bottom (Scheme 1). After examining the conditions using different bases such as $K_2CO_3$, $Cs_2CO_3$, $Et_3N$, and diisopropylethylamine (DIPEA) in different solvents including acetone, acetonitrile, THF, 1,4-dioxane, and nitromethane, the reaction of 1,3,5-tri(*p*-hydroxyphenyl)benzene (TPHPB, **1**) with cyanuric chloride **2** gave the desired molecular cage product **3** in very low chemical yields (<13%) (Table S1, Supporting Information). In many cases, the starting materials were not fully consumed, and only oligomeric or polymeric substances were observed. A stepwise synthesis was then investigated (Scheme 1). In the presence of DIPEA as an acid scavenger, TPHPB (**1**) reacted with an excess amount of cyanuric chloride **2** at 0 °C in THF to afford intermediate **4** in 84% yield. The reaction of **4** with another 1 equiv of TPHPB (**1**) proceeded slowly at room temperature. The formation of molecular prism **3** was found to be dramatically dependent upon the conditions employed. As summarized in Table 1, when DIPEA was used as a base, the reaction in nitromethane, acetonitrile, acetone, and 1,4-dioxane at room temperature produced either none or a low yield of product **3** (entries 1−4, Table 1). The use of THF as the reaction media gave product **3** in 21% yield (entry 5, Table 1). The reaction was facilitated in refluxing THF, and the chemical yield of **3** was improved to 31% (entry 6, Table 1). Other bases such as $Et_3N$, $K_2CO_3$, or $Cs_2CO_3$ instead of DIPEA in refluxing THF, however, had a detrimental effect, forming product **3** in a diminished yield (entries 7−9, Table 1). It is interesting to note that the combination of $K_2CO_3$ as a base with acetone as solvent was beneficial for the

**Table 1. Reaction between Tri(*p*-hydroxyphenyl)benzene 2 and Intermediate 4[a]**

| entry | base[b] | solvent | time[c] (h) | temp (°C) | 3[d] (%) |
|---|---|---|---|---|---|
| 1 | DIPEA | $CH_3NO_2$ | 2 + 96 | rt | 0 |
| 2 | DIPEA | $CH_3CN$ | 2 + 72 | rt | 6 |
| 3 | DIPEA | acetone | 2 + 72 | rt | 15 |
| 4 | DIPEA | 1,4-dioxane | 2 + 120 | rt | 2 |
| 5 | DIPEA | THF | 2 + 72 | rt | 21 |
| 6 | DIPEA | THF | 2 + 40 | reflux | 31 |
| 7 | $Et_3N$ | THF | 2 + 72 | reflux | trace |
| 8 | $K_2CO_3$ | THF | 2 + 34 | reflux | 18 |
| 9 | $Cs_2CO_3$ | THF | 2 + 32 | reflux | 15 |
| 10 | $K_2CO_3$ | acetone | 2 + 39 | rt | 36 |
| 11[e] | DIPEA | THF | 5 + 40 | reflux | 35 |
| 12[e] | $K_2CO_3$ | acetone | 5 + 40 | rt | 38 |

[a] **1** (0.25 mmol) and **4** (0.25 mmol) were mixed and reacted in solution (1 L). [b] 3.6 equiv of base was used. [c] Mixing time plus further reaction time. [d] Isolated yield. [e] 2.5 mmol of the starting material was used.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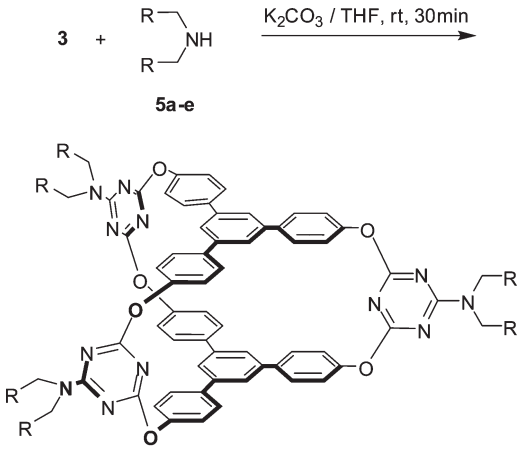
reaction even at ambient temperature, and the target product **3** was obtained in 36% yield (entry 10, Table 1). A further slight improvement of the isolated yield of product **3** was obtained when the reaction was performed on an increased scale (entries 11 and 12, Table 1).

Compound **3** adopts a triangular prism conformation (vide infra) with three chloro substituents being perpendicular to three edges (triazine rings) around the peripheral positions. Taking advantage of the reactivity of the chloro substituent on the triazine ring, we then studied the conversion of parent molecular cage **3** into functionalized triangular prisms. In the presence of $K_2CO_3$ in THF, dialkylamines **5a**−**c** bearing functional groups underwent rapid aromatic nucleophilic substitution reaction with chlorotriazines of **3** at room temperature to afford amino-substituted bicyclooxacalixaromatics **6a**−**c** in yields of 70−79%. Upon treatment of **3** with di(2-hydroxyethyl)amine **5d**, an ambident nitrogen and oxygen nucleophilic reagent, the reaction occurred exclusively on nitrogen rather than oxygen to produce polyhydroxylated prism **6d** in 61% yield. Following the same strategy of chemical manipulation, the molecular prism **3** was functionalized with three pairs of chelating di(2-pyridylmethyl)amino groups (Scheme 2).

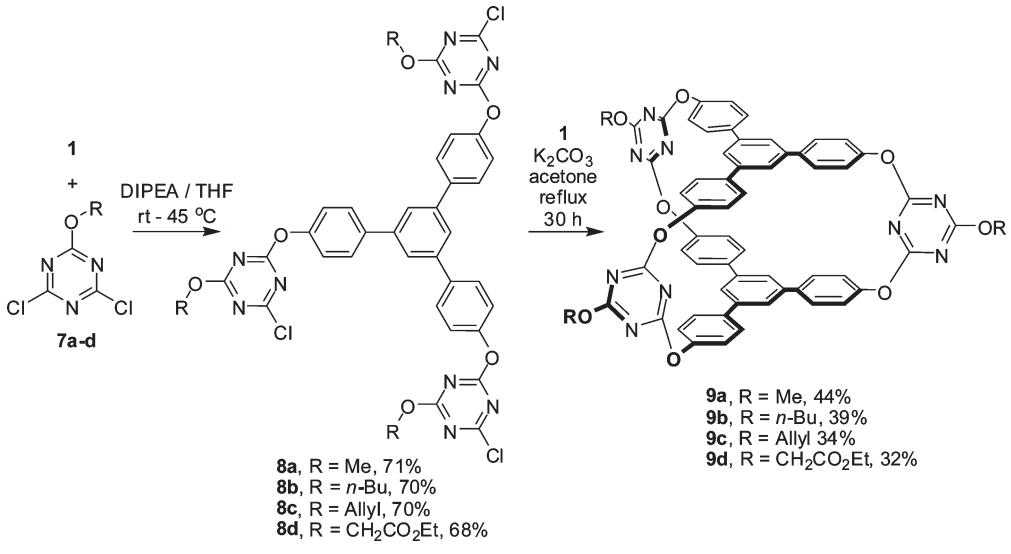
To prepare functionalized molecular prisms with more electron-deficient triazine rings,[10] aromatic nucleophilic reaction of **3** with alcohols was tested. Surprisingly, when we tried functionalizations of **3** using oxygen nucleophiles, the cage molecule underwent decomposition. For example, the treatment of **3** with an excess amount of methanol in the presence of $K_2CO_3$ in refluxing THF gave rise to TPHPB (**1**) and 2,4,6-trimethoxytriazine. No cage molecule was observed at all. Since all amino-substituted cage molecules **6a**−**e** did not decompose under the identical conditions, the formation of TPHPB (**1**) and 2,4,6-trimethoxytriazine is most probably due to the exhaustive cleavage of all oxygen−triazine bonds in the bridging positions of the initially formed methoxylated product by methanol under basic conditions. To circumvent this problem, the functionalized molecules **9a**−**d** were synthesized alternatively applying a similar stepwise route as that for the synthesis of **3**. Using prefunctionalized dichlorotriazines **7a**−**d**, intermediates **8a**−**d** were obtained readily from their reactions with TPHPB (**1**). The reaction between **1** and **8a**−**d** then took place efficiently in refluxing acetone with the aid of $K_2CO_3$ to furnish the *O*-substituted molecular prisms **9a**−**d** in 32−44% (Scheme 3).

Encouraged by the successful construction and functionalization of large molecular triangular prisms of electron-rich 1,3,5-triphenylbenzene interiors, we then focused on the synthesis of analogous triangular prism **13** which contains an electron-rich 1,3,5-triphenylbenzene base (bottom) and an electron-deficient 2,4,6-triphenyltriazine base (top). The cage molecule **13** has aromatic interiors of different electronic nature. Two approaches were designed to synthesize the target molecule **13**. In route A, 1,3,5-tri(4-butyloxy-6-chloro-1,3,5-triazin-2-yloxyphenyl)benzene derivative **8b** was used to react with 2,4,6-tri(*p*-aminophenyl)triazine **10**,[18] while route B involved the reaction between a triazine derivative **12** with TPHPB **1** (Scheme 4). For the reaction between **8b** and **10** (route A), a number of bases, solvents, and temperatures were screened (Table S2, Supporting Information), and a maximum yield of 14% was obtained when the reaction was carried out in refluxing acetone with $K_2CO_3$ as a base. Since the

**Scheme 2. Synthesis of *N*-Substituted Functionalized Molecular Prisms 6**




**Scheme 3. Synthesis of *O*-Substituted Functionalized Molecular Prisms 9**





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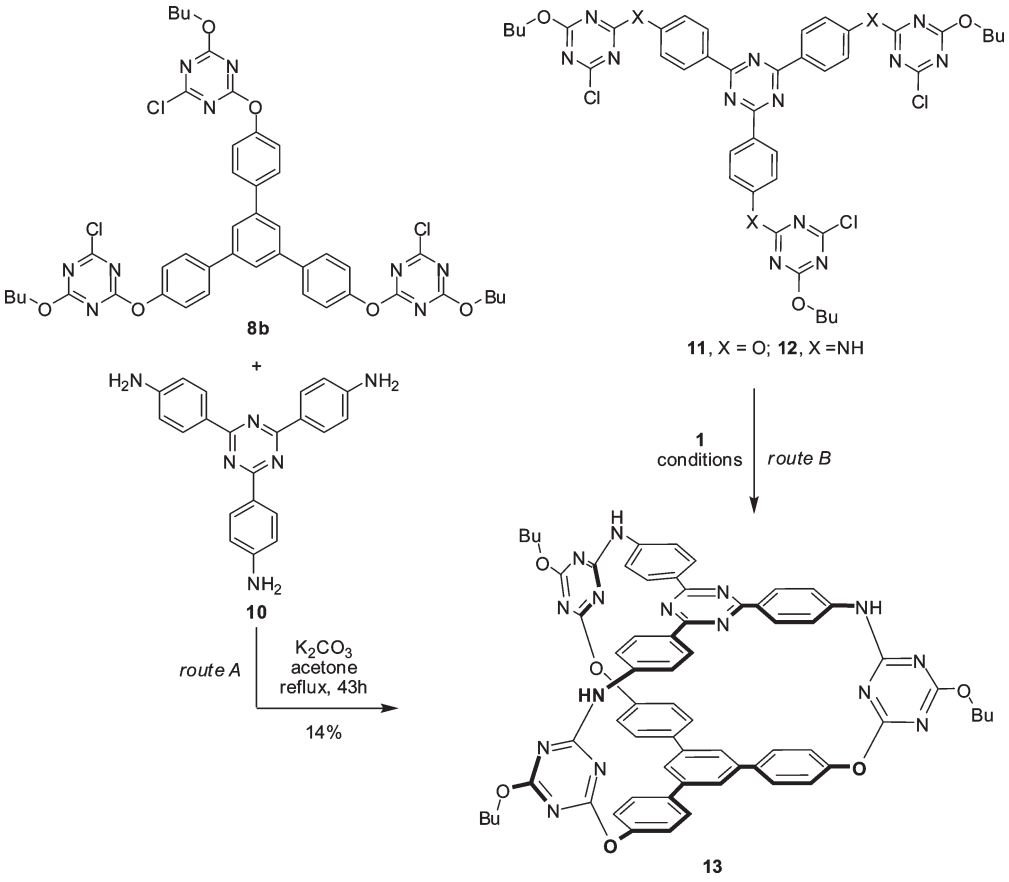
**Scheme 4. Synthesis of Molecular Cage 13**




preparation of 2,4,6-tri(4-butyloxy-6-chloro-1,3,5-triazin-2-yloxy-phenyl)triazine intermediate **11** was not high yielding (Supporting Information), nitrogen-linked intermediate **12**, which was derived from the reaction of 2,4,6-tri(*p*-aminophenyl)triazine **10** with 1-butyloxy-3,5-dichlorotriazine (Supporting Information), was applied to react with TPHPB **1** (Table 2). As indicated by the results in Table 2, the synthesis of **13** from the reaction of **1** and **12** was highly solvent and base dependent. For example, the reaction in refluxing THF with the use of $K_2CO_3$ and $Cs_2CO_3$ gave the cage molecule **13** in 16% and 5%, respectively (entries 1 and 2, Table 2). Organic bases including DIPEA, triethylamine, and 2,4,6-collidine gave virtually no desired product (entries 3−5, Table 2). When $K_2CO_3$ was used as a base, the reaction in chloroform did not yield any **13** (entry 6, Table 2), whereas in acetone and in 1,4-dioxane, cage molecule **13** was produced in 33% and 36% yield, respectively (entries 7 and 8, Table 2). Further increase of the polarity of the solvent led to the dramatically decrease of the chemical yield of **13** (entry 9, Table 2).

The method for the construction of nitrogen and oxygen bridged bicyclocalixaromatics was general, and it was extended easily to the synthesis of triangular prisms of both electron-rich and electron-deficient interiors with functional groups on the peripheral edges. Scheme 5 illustrates for instance the synthesis of the parent chloro-substituted *N*- and *O*-linked bicyclocalixaromatics **15** and its functionalization with di(2-hydroxyethyl)amine **5d** and di(2-pyridylmethyl)amine **5e**. To increase the solubility of products in organic solvents, 2,4,6-tri(*n*-butylaminophenyl)triazine (Supporting Information) was used as the starting material to

**Table 2. Synthesis of Cage Molecule 13 from the Reaction between 1 and 12**

| entry | base[a] | solvent | time (h) | temp (°C) | **13**[b] (%) |
|---|---|---|---|---|---|
| 1 | $K_2CO_3$ | THF | 28 | reflux | 16 |
| 2 | $Cs_2CO_3$ | THF | 34 | reflux | 5 |
| 3 | DIPEA | THF | 32 | reflux | trace |
| 4 | $Et_3N$ | THF | 60 | reflux | trace |
| 5 | 2,4,6-collidine | THF | 32 | reflux | 0 |
| 6 | $K_2CO_3$ | chloroform | 36 | reflux | 0 |
| 7 | $K_2CO_3$ | acetone | 20 | reflux | 33 |
| 8 | $K_2CO_3$ | 1,4-dioxane | 23 | reflux | 36 |
| 9 | $K_2CO_3$ | $CH_3CN$ | 18 | reflux | 4 |

[a] 3.6 equiv of base was used. [b] Isolated yield.

prepare segment **14** (Supporting Information). The reaction of intermediate **14** with TPHPB **1** in warm 1,4-dioxane gave 41% yield of **15** that bears three reactive chlorotriazine moieties. Nucleophilic aromatic substitution reaction of **15** with amines under very mild conditions furnished the functionalized molecular triangular prisms **16a** and **16b** (Scheme 5).

It is important to address that the introduction of nitrogen atoms as the linking units in bicyclocalixaromatics also allowed us to functionalize the triangular prisms at the vertexes. As a demonstration, the construction of *N*-methyl- and *N*-allyl-substituted molecular cages **18** was implemented. Thus, under the optimized conditions for the synthesis of **13**, the reaction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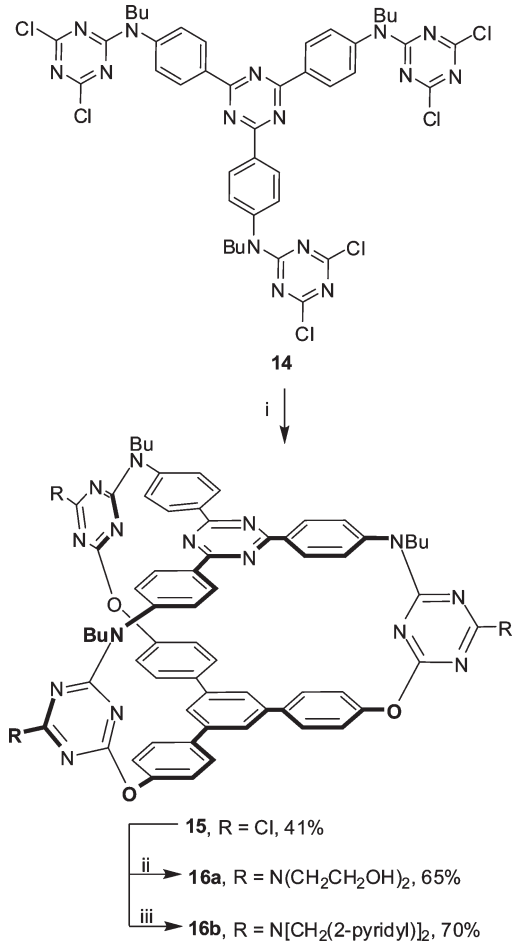
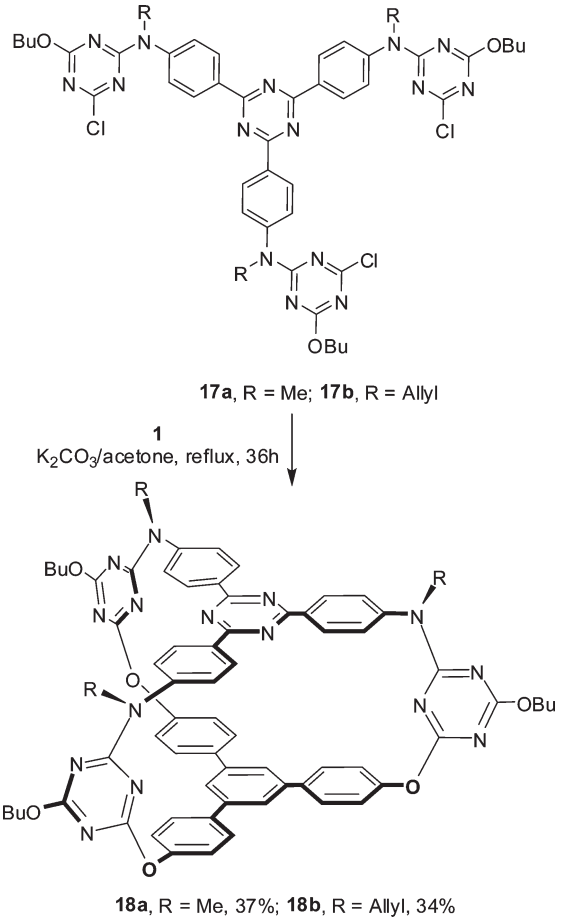
**Scheme 5. Synthesis of Peripherally Functionalized N- and O-Bridged Triangular Prisms 16**[a]




[a] Key: (i) **1**, $K_2CO_3$, 1,4-dioxane, 50 °C; (ii) di(2-hydroxyethyl)amine **5d**, $K_2CO_3$, THF, 45 °C; (iii) di(2-pyridylmethyl)amine **5e**, $K_2CO_3$, THF, 45 °C.

**Scheme 6. Synthesis of N-Functionalized Molecular Prisms 18**




of TPAPT derivatives **17a** and **17b**, which were obtained readily by means of *N*-alkylation of **12** with corresponding methyl iodide and allyl bromide under basic conditions (see the Supporting Information), with TPHPB (**1**) afforded the desired products **18a** and **18b** in 37% and 34% yield, respectively (Scheme 6). Being different from compounds **16**, molecular triangular prism **18b** has three functional groups on the vertex positions. It is worth noting that triangular prisms functionalized with allyl, ester, and pyridyl groups on the specific positions such as on peripheral edges and on vertexes would provide valuable handles for further molecular fabrications.

We also attempted the synthesis of triangular prisms having both electron-deficient 2,4,6-triphenyltriazine bases. Unfortunately, the reaction of TPAPB (**10**) and its *N*,*N*′,*N*″-trimethyl analogue with either **14** or **17a** did not form any cage molecules under various reaction conditions examined (see the Supporting Information).

The structures of all products synthesized were established on the basis of spectroscopic data and microanalysis. The three-dimensional structure of the large triangular prism of nitrogen and oxygen-bridged bicyclocalixaromatics was further proved unambiguously by the X-ray single-crystal structure of **3**, **6b**, **9b**, and **18b**. As shown in Figure 1, the chloro-substituted bicycloxacalixaromatics cage molecule **3** adopts a distorted triangular prism structure. Two tri(*p*-oxaphenyl)benzene bases, both slightly deviated from an equilateral triangle, are not eclipsed. Two central benzene rings from top and bottom are nearly face-to-face paralleled with a mean distance of 4.05 Å. Three triazine rings, which act as three pillars, extend outward yielding three similar and large V-shaped clefts. The distances between the upper rim carbons of triazines are in the range of 16.28−16.80 Å (Figure 1). While the peripherally butyloxy-substituted compound **9b** shows a twisted triangular prism structure similar to that of **3** in the solid state (see the Supporting Information), its diethylamino-substituted analogue **6b** (Figure 2), however, gives an almost symmetric triangular prism with a $D_{3h}$ symmetry. The mean edge length of two equilateral triangles is 12.28 Å, and the mean distance between two oxygen atoms of each edge of the prism is 4.59 Å, yielding an approximate volume of 300 Å$^3$.

The cage molecule **18b** composed of an electron-rich 1,3,5-tri(*p*-oxaphenyl)benzene bottom, and an electron-deficient 2,4,6-tri(*p*-azaphenyl)triazine top also exists as a distorted triangular prism (Figure 3). Noticeably, both top and bottom are an equilateral triangle in geometry, and they are face-to-face paralleled with a distance of 4.03 Å. In addition, all four aromatic rings and three nitrogen atoms in the 2,4,6-tri(*p*-azaphenyl)triazine segment form a planar top, while the four benzene rings of the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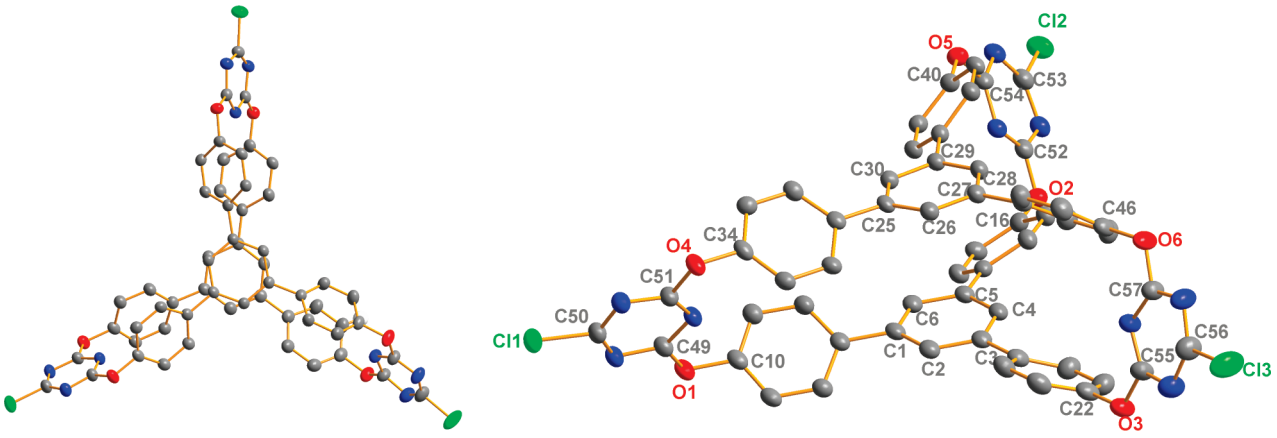


**Figure 1.** X-ray crystal structure of **3**: (a) top view; (b) side view. All hydrogen atoms and solvent molecules were omitted for clarity. Selected bond lengths (Å): O(1)−C(49), 1.35; O(1)−C(10), 1.45; O(2)−C(52), 1.34; O(2)−C(16), 1.43; O(3)−C(55), 1.35; O(3)−C(22), 1.43; O(4)−C(51), 1.35; O(4)−C(34), 1.43; O(5)−C(54), 1.34; O(5)−C(40), 1.42; O(6)−C(57), 1.37; O(6)−C(47), 1.44. Selected interatomic distances (Å): O(1)−O(2), 12.36; O(2)−O(3), 12.33; O(3)−O(1), 12.37; O(4)−O(5), 12.44; O(5)−O(6), 12.38; O(6)−O(4), 12.05; C(53)−C(56), 16.80; C(53)−C(50), 16.70; C(50)−C(56), 16.28.

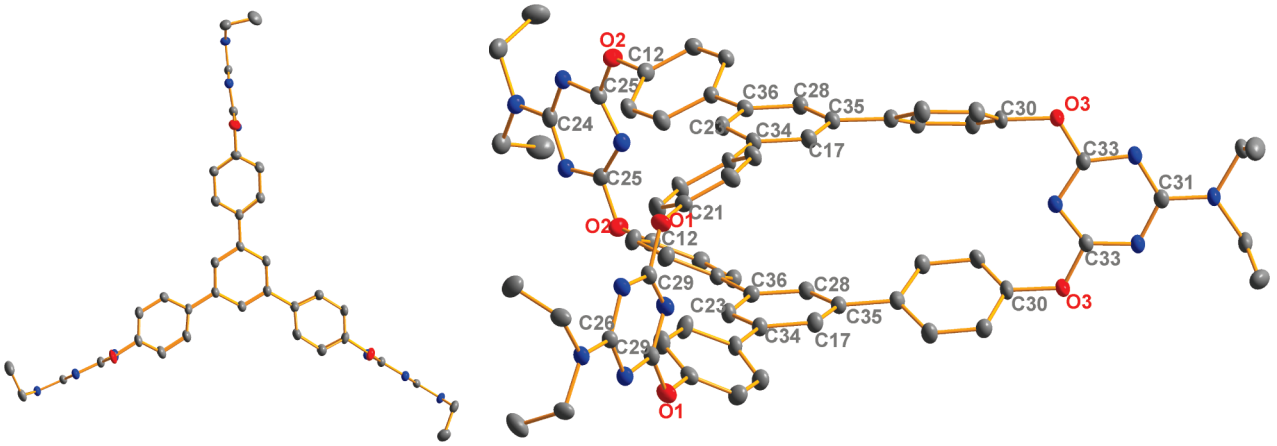


**Figure 2.** X-ray crystal structure of **6b**: (a) top view; (b) side view. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å): O(1)−C(29), 1.36; O(1)−C(21), 1.41; O(2)−C(25), 1.35; O(2)−C(12), 1.42; O(3)−C(33), 1.35; O(3)−C(30), 1.42. Selected interatomic distances (Å): O(1)−O(2), 12.24; O(1)−O(3), 12.14; O(2)−O(3), 12.47; C(26)−C(31), 16.68; C(24)−C(31), 17.11; C(24)−C(26), 16.41.

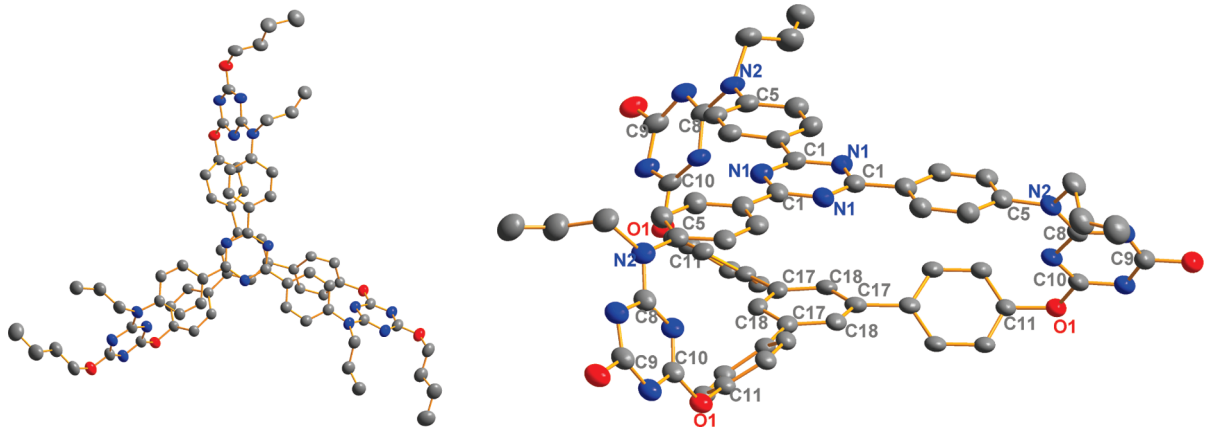


**Figure 3.** X-ray crystal structure of **18b**: (a) top view; (b) side view. All hydrogen atoms and butyl groups on oxygen atoms (side view) were omitted for clarity. Selected bond lengths (Å): O(1)−C(10), 1.33; O(1)−C(11), 1.42; N(2)−C(8), 1.38; N(2)−C(5), 1.41. Selected interatomic distances (Å): O(1)−O(1A), 12.19; N(2)−N(2A), 12.04; C(9)−C(9A), 16.43.

1,3,5-(triphenyl)benzene bottom, which are not coplanar, are not located at the plane defined by three oxygen atoms. Moreover, three allyl groups attach on the vertex positions of the triangular prism. It is also interesting to note that, in all prism molecules synthesized, all


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nitrogen and oxygen atoms on the vertexes form stronger conjugation systems with the pillar triazine rings than with the benzene rings of the base. This has been evidenced by the observation of different bond lengths. In all cases, for example, the bond length between vertex heteroatom and the carbon of triazine is shorter than that between vertex heteroatom and the carbon of the benzene (see the captions of Figures 1−3).

It was interesting to address that all cage compounds exhibit a single set of proton and carbon signals in their $^{1}H$ and $^{13}C$ NMR spectra, respectively (see the Supporting Information). The outcomes indicated that, in contrast to the structural distortions of triangular prisms observed in some cases in single crystals, all cage molecules obtained remain most likely their highly symmetric triangular prism structures in solution, although the possibility of fast equilibriums among different distorted isomers on the NMR time scale is hardly ruled out at this stage.

## CONCLUSION

In summary, we have synthesized large molecular triangular prisms of electron-rich and electron-deficient aromatic interiors using 1,3,5-tri(*p*-hydroxyphenyl)benzene and 2,4,6-tri(*p*-aminophenyl)triazine as top and bottom base units and triazine rings as pillars. Aromatic nucleophilic substitution reactions on chlorotriazines with functionalized amines led to triangular prisms with functionalizations on peripheral edge positions. When 2,4,6-tri-[(*p*-allylamino)phenyl]triazine derivative was used as a top segment, triangular prisms functionalized on the vertex nitrogen positions were obtained. The relatively convenient synthesis, site-specific functionalizations and the shape persistent triangular prism structures would render the resulting cage molecules useful in molecular recognition and in the construction of higher and more sophisticated molecular architectures in supramolecular chemistry.

## EXPERIMENTAL SECTION

**One-Pot Synthesis of 3.** To an ice-bath cooled solution of cyanuric chloride **2** (0.17 g, 0.9 mmol) in THF (60 mL) was added dropwise a mixture of 2,4,6-tri(*p*-hydroxyphenyl)benzene **1** (0.21 g, 0.6 mmol) and diisopropylethylamine (0.28 g, 0.38 mL, 2.16 mmol) in THF (40 mL) during 3 h. After addition, the temperature was gradually increased to 30 °C, and stirring was continued for another 3 days. The reaction mixture was then filtered, and solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100−200) with a mixture of petroleum ether and acetone as the mobile phase (3:1) to give pure **3** (0.041 g, 13%) as a white solid.

**Synthesis of Prism Molecule 3 from Reaction between 1 and 4.** *Synthesis of* ***4***. To an ice-bath cooled solution of cyanuric chloride **2** (16.59 g, 90 mmol) in THF (150 mL) was added dropwise a mixture of 2,4,6-tri(*p*-hydroxyphenyl)benzene **1** (7.09 g, 20 mmol) and diisopropylethylamine (10.08 g, 13.59 mL, 78 mmol) in THF (100 mL) during 2 h. The reaction mixture was stirred for another 4 h. After removal of diisopropylethylamine hydrochloride salt through filtration, the filtrate was concentrated and chromatographed on a silica gel column (100−200) with a mixture of petroleum ether and dichloromethane (4:1) as the mobile phase to give pure **4** (13.41 g, 84%) as a white solid: mp 243−244 °C; $^{1}H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.81 (s, 3H), 7.78 (d, $J$ = 8.7 Hz, 6H), 7.32 (d, $J$ = 8.7 Hz, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 173.2, 171.1, 150.8, 141.4, 139.6, 128.8, 125.4, 121.5; IR (KBr) $\nu$ 1511, 1425, 1298, 1198, 1012, 871 $cm^{-1}$; MS (EI) $m/z$ 795 (48), 797 (100), 799 (80), 801 (36), 803 (9). Anal. Calcd for $C_{33}H_{15}Cl_6N_9O_3$: C, 49.65; H, 1.89; N, 15.79. Found: C, 49.74; H, 2.17; N, 15.77.

*Synthesis of Prism Molecule* ***3***. To a stirred suspension of $K_2CO_3$ (finely ground) (1.24 g, 9 mmol) in acetone (500 mL) at room temperature were added dropwise solutions of 2,4,6-tri(*p*-hydroxyphenyl)benzene **1** (0.89 g, 2.5 mmol) in acetone (250 mL) and intermediate **4** (see the Supporting Information) (2 g, 2.5 mmol) in acetone (250 mL) at the same time and the same rate. After addition of the two reactants, which took about 5 h, the resulting mixture was stirred at room temperature for another 40 h. The mixture was then filtered, and solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100−200) with a mixture of petroleum ether and acetone (1:3) as the mobile phase to give pure **3** (1 g, 38%): mp >300 °C; $^{1}H$ NMR (300 MHz, DMSO) $\delta$ 7.86 (d, $J$ = 8.6 Hz, 12H), 7.68 (s, 6H), 7.31 (d, $J$ = 8.6 Hz, 12H); $^{13}C$ NMR (75 MHz, DMSO) $\delta$ 172.5, 171.7, 150.7, 139.6, 137.2, 127.6, 122.9, 121.5; IR (KBr) $\nu$ 1553, 1443, 1366, 1192, 950, 820 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1042.4 [M + $H^+$] (76), 1044.4 (100), 1046.4 (32). Anal. Calcd for $C_{57}H_{30}Cl_3N_9O_6$: C, 65.62; H, 2.90; N, 12.08. Found: C, 65.20; H, 3.22; N, 11.89.

**General Procedure for the Functionalization of 3 through Its Aromatic Nucleophilic Substitution Reaction with Amines 5a−e.** To a solution of **3** (0.21 g, 0.2 mmol) in THF (20 mL) at room temperature were added $K_2CO_3$ (finely ground) (0.1 g, 0.72 mmol) and amines **5a−e** (1.2 mmol) with constant stirring. Stirring was continued for a further 30 min. The mixture was then filtered, and solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100−200) with a mixture of solvents (see the Supporting Information) as the mobile phase to give pure products **6a−e**.

**6a** (0.169 g, 79%) as a white solid: mp >300 °C; $^{1}H$ NMR (300 MHz, DMSO) $\delta$ 7.72 (d, $J$ = 8.6 Hz, 12H), 7.61 (s, 3H), 7.18 (d, $J$ = 8.6 Hz, 12H), 3.21 (s, 18H); $^{13}C$ NMR (75 MHz, DMSO) $\delta$ 171.0, 167.9, 151.2, 139.8, 136.4, 127.1, 122.6, 122.0, 36.3; IR (KBr) $\nu$ 1599, 1514, 1375, 1205, 1069, 818 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1069.4 [M + $H^+$] (100), 1070.4 (62), 1071.4 (18), 1091.3 [M + $Na^+$]. Anal. Calcd for $C_{63}H_{48}N_{12}O_6$: C, 70.77; H, 4.53; N, 15.72. Found: C, 70.59; H, 4.62; N, 15.68.

**6b** (0.175 g, 76%) as a white solid: mp >300 °C; $^{1}H$ NMR (300 MHz, DMSO) $\delta$ 7.71 (d, $J$ = 8.5 Hz, 12H), 7.62 (s, 6H), 7.19 (d, $J$ = 8.3 Hz, 12H), 3.67−3.65 (m, 12H), 1.22 (t, $J$ = 6.9 Hz, 18H); $^{13}C$ NMR (75 MHz, DMSO) $\delta$ 171.1, 166.9, 151.2, 139.8, 136.3, 127.1, 122.6, 122.0, 41.4, 12.9; IR (KBr) $\nu$ 1598, 1515, 1381, 1218, 1080, 819 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1153.7 [M + $H^+$] (100), 1154.7 (73), 1155.7 (27) 1175.6 [M + $Na^+$]. Anal. Calcd for $C_{69}H_{60}N_{12}O_6$: C, 71.86; H, 5.24; N, 14.57. Found: C, 71.82; H, 5.38; N, 14.17.

**6c** (0.173 g, 70%) as a white solid: mp 269−270 °C; $^{1}H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.44 (s, 6H), 7.33 (d, $J$ = 8.4 Hz, 12H), 6.92 (d, $J$ = 8.4 Hz, 12H), 3.62 (t, $J$ = 7.8 Hz, 12H), 1.81 − 1.69 (m, 12H), 1.00 (t, $J$ = 7.3 Hz, 18H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 172.0, 168.1, 152.0, 141.1, 137.9, 126.9, 123.7, 122.8, 49.4, 20.9, 11.3; IR (KBr) $\nu$ 1601, 1515, 1381, 1213, 1080, 819 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1237.7 [M + $H^+$] (100), 1238.7 (98), 1239.7 (40). Anal. Calcd for $C_{75}H_{72}N_{12}O_6$: C, 72.80; H, 5.86; N, 13.58. Found: C, 72.76; H, 6.02; N, 13.19.

**6d** (0.153 g, 61%) as a white solid: mp 215−216 °C; $^{1}H$ NMR (300 MHz, DMSO) $\delta$ 7.72 (d, $J$ = 8.5 Hz, 12H), 7.62 (s, 6H), 7.19 (d, $J$ = 8.5 Hz, 12H), 4.87 (t, $J$ = 5.1 Hz, 6H), 3.76- 3.68 (m, 24H); $^{13}C$ NMR (75 MHz, DMSO) $\delta$ 171.0, 167.8, 151.2, 139.8, 136.4, 127.1, 122.6 122.0, 58.4, 50.6; IR (KBr) $\nu$ 3370, 1598, 1529, 1387, 1207, 1052, 818 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1249.5 [M + $H^+$] (100), 1250.5 (85), 1251.5 (31) 1271.5 [M + $Na^+$]. Anal. Calcd for $C_{69}H_{60}N_{12}O_{12}\cdot 3H_2O$: C, 63.59; H, 5.10; N, 12.90. Found: C, 63.56; H, 5.00; N, 12.69.

**6e** (0.196 g, 64%) as a white solid: mp 262−263 °C; $^{1}H$ NMR (300 MHz, $CDCl_3$) $\delta$ 8.59 (d, $J$ = 4.8 Hz, 6H), 7.72−7.66 (m, 6H), 7.45 (s, 6H), 7.38 (d, $J$ = 7.8 Hz, 6H), 7.34 (d, $J$ = 8.5 Hz, 12H), 7.23−7.19 (m, 6H), 6.92 (d, $J$ = 8.5 Hz, 12H), 5.18 (s, 12H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 172.4, 169.9, 156.9, 151.9, 149.6, 141.1, 138.0, 136.7, 127.0, 123.7, 122.7, 122.4, 122.2, 51.9; IR (KBr) $\nu$ 1592, 1533, 1385, 1208, 955,

819 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1531.5 [M + $H^+$] (85), 1532.5 (100), 1533.5 (31) 1553.5 [M + $Na^+$]. Anal. Calcd for $C_{93}H_{66}N_{18}O_6 \cdot 2H_2O$: C, 71.25; H, 4.50; N, 16.08. Found: C, 71.18; H, 4.36; N, 15.85.

**General Procedure for the Synthesis 8.** To a solution **7a**−**d** (see the Supporting Information) (9 mmol) in THF (30 mL) was added dropwise a mixture of 2,4,6-tri(*p*-hydroxyphenyl)benzene **1** (0.709 g, 2 mmol) and diisopropylethylamine (1 g, 1.36 mL, 7.8 mmol) in THF (20 mL) during 1 h at room temperature. The reaction mixture was stirred for another 6 h at 45 °C. After removal of diisopropylethylamine hydrochloride salt through filtration, the filtrate was concentrated and chromatographed on a silica gel column (100−200) with a mixture of solvents (see Table S8, Supporting Information) as the mobile phase to give pure **8a**−**d**.

**8a** (1.11 g, 71%) as a white solid: mp 209−210 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (s, 3H), 7.75 (d, $J$ = 8.7 Hz, 6H), 7.31 (d, $J$ = 8.6 Hz, 6H), 4.06 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 173.3, 172.8, 172.1, 151.1, 141.4, 139.1, 128.5, 125.2, 121.7, 56.2; IR (KBr) $\nu$ 1559, 1501, 1418, 1361, 1204, 1015, 815 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 784.2 [M + $H^+$] (84), 786.2 (100), 788.2 (20). Anal. Calcd for $C_{36}H_{24}Cl_3N_9O_6 \cdot H_2O$: C, 53.85; H, 3.26; N, 15.70. Found: C, 54.15; H, 3.21; N, 15.97.

**8b** (1.28 g, 70%) as a white solid: mp 134−135 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (s, 3H), 7.75 (d, $J$ = 8.6 Hz, 6H), 7.31 (d, $J$ = 8.6 Hz, 6H), 4.42 (t, $J$ = 6.6 Hz, 6H), 1.81 − 1.71 (m, 6H), 1.51 − 1.39 (m, 6H), 0.95 (t, $J$ = 7.4 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 173.2, 172.4, 172.1, 151.1, 141.5, 139.1, 128.5, 125.2, 121.7, 69.5, 30.3, 18.8, 13.6; IR (KBr) $\nu$ 2961, 1540, 1504, 1399, 1343, 1197, 992 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 910.3 [M + $H^+$] (76), 912.3 (100), 914.3 (25). Anal. Calcd for $C_{45}H_{42}Cl_3N_9O_6$: C, 59.31; H, 4.65; N, 13.83. Found: C, 59.03; H, 4.65; N, 13.48.

**8c** (1.21 g, 70%) as a white solid: mp 183−184 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.79 (s, 3H), 7.75 (d, $J$ = 8.6 Hz, 6H), 7.31 (d, $J$ = 8.6 Hz, 6H), 6.06−5.93 (m, 3H), 5.43−5.30 (m, 6H), 4.91 (d, $J$ = 5.8 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 166.3, 165.2, 165.1, 144.1, 134.5, 132.1, 123.6, 121.6, 118.3, 114.7, 113.0, 62.9; IR (KBr) $\nu$ 1558, 1505, 1482, 1384, 1200, 1002, 808 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 862.2 [M + $H^+$] (76), 864.2 (100), 866.2 (28) 884.2 [M + $Na^+$]. Anal. Calcd for $C_{42}H_{30}Cl_3N_9O_6$: C, 58.45; H, 3.50; N, 14.61. Found: C, 58.18; H, 3.61; N, 14.19.

**8d** (1.36 g, 68%) as a white solid: mp 92−93 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (s, 3H), 7.74 (d, $J$ = 8.6 Hz, 6H), 7.30 (d, $J$ = 8.6 Hz, 6H), 4.92 (s, 6H), 4.24 (q, $J$ = 7.1 Hz, 6H), 1.27 (t, $J$ = 7.1 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 173.3, 172.1, 172.0, 166.6, 151.0, 141.4, 139.1, 128.5, 125.2, 121.6, 64.3, 61.7, 14.0; IR (KBr) $\nu$ 2983, 1755, 1554, 1378, 1209, 1110, 812 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1000.5 [M + $H^+$] 1022.5 [M + $Na^+$] (74), 1024.5 (100), 1026.5 (20). Anal. Calcd for $C_{45}H_{36}Cl_3N_9O_{12}$: C, 53.98; H, 3.62; N, 12.59. Found: C, 53.96; H, 3.75; N,12.62.

**General Procedure for the Synthesis of Functionalized Prism Molecules 9.** To a stirred suspension of $K_2CO_3$ (finely ground) (0.62 g, 4.5 mmol) in acetone (250 mL) under reflux were added dropwise solutions of 2,4,6-tri(*p*-hydroxyphenyl)benzene **1** (0.45 g, 1.25 mmol) in acetone (125 mL) and intermediate **8a**−**d** (1.25 mmol) in acetone (125 mL) at the same time and the same rate. After addition of two reactants, which took about 2.5 h, the resulting mixture was refluxed for another 30 h. The mixture was then filtered and solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100−200) with a mixture of solvents (see Table S8, Supporting Information) as the mobile phase to give pure product **9a**−**d**.

**9a** (0.57 g, 44%) as a white solid: mp >300 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46 (s, 6H), 7.37 (d, $J$ = 8.6 Hz, 12H), 6.94 (d, $J$ = 8.5 Hz, 12H), 4.17 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 175.1, 173.5, 151.7, 141.0, 138.3, 127.2, 123.8, 122.4, 55.9; IR (KBr) $\nu$ 1580, 1507, 1367, 1211, 1110, 822 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1030.5 [M + $H^+$] (100), 1031.5 (54), 1032.5 (13) 1052.4 [M + $Na^+$]. Anal. Calcd for $C_{60}H_{30}N_9O_9 \cdot H_2O$: C, 68.76, H, 3.94; N, 12.03. Found: C, 68.81; H, 3.91; N, 11.78.

**9b** (0.56 g, 39%) as a white solid: mp 296−297 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46 (s, 6H), 7.36 (d, $J$ = 8.6 Hz, 12H), 6.93 (d, $J$ = 8.6 Hz, 12H), 4.54 (t, $J$ = 6.6 Hz, 6H), 1.91 − 1.81 (m, 6H), 1.60 − 1.48 (m, 6H), 1.02 (t, $J$ = 7.4 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 174.6, 173.4, 151.7, 141.0, 138.3, 127.2, 123.8, 122.4, 69.0, 30.6, 19.0, 13.7; IR (KBr) $\nu$ 2962, 1576, 1508, 1373, 1208, 1108, 818 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1156.5 [M + $H^+$] (100), 1157.5 (71), 1158.5 (11) 1178.6 [M + $Na^+$]. Anal. Calcd for $C_{69}H_{57}N_9O_9 \cdot H_2O$: C, 70.58; H, 5.06; N, 10.74. Found: C, 70.26; H, 4.96;N, 10.64.

**9c** (0.47 g, 34%) as a white solid: mp >300 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46 (s, 6H), 7.37 (d, $J$ = 8.6 Hz, 12H), 6.94 (d, $J$ = 8.6 Hz, 12H), 6.20−6.07 (m, 3H), 5.55−5.35 (m, 6H), 5.06 (d, $J$ = 5.6 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 174.4, 173.5, 151.7, 141.0, 138.3, 131.4, 127.2, 123.8, 122.4, 119.0, 69.3; IR (KBr) $\nu$ 1580, 1507, 1386, 1208, 1102, 822 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1108.6 [M + $H^+$] (100), 1109.6 (70), 1110.6 (26) 1130.6 [M + $Na^+$]. Anal. Calcd for $C_{66}H_{45}N_9O_9 \cdot 2H_2O$: C, 69.28; H, 4.32; N, 11.02. Found: C, 69.18; H, 4.26; N, 11.00.

**9d** (0.50 g, 32%) as a white solid: mp 299−300 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46 (s, 6H), 7.37 (d, $J$ = 8.6 Hz, 12H), 6.92 (d, $J$ = 8.6 Hz, 12H), 5.07 (s, 6H), 4.33 (q, $J$ = 7.1 Hz, 6H), 1.35 (t, $J$ = 7.1 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 174.3, 173.5, 167.4, 151.7, 141.0, 138.4, 127.2, 123.9, 122.4, 64.1, 61.7, 14.1; IR (KBr) $\nu$ 1752, 1572, 1509, 1380, 1203, 1126, 822 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1246.3 [M + $H^+$] (100), 1247.3 (73), 1248.3 (17) 1268.3 [M + $Na^+$]. Anal. Calcd for $C_{69}H_{51}N_9O_{15} \cdot 2H_2O$: C, 64.63; H, 4.32; N, 9.83. Found: C, 64.61; H, 4.07; N, 9.73.

**Synthesis of 12.** To a solution of **7b** (15 g, 67.5 mmol) in THF (150 mL) was added dropwise a mixture of 2,4,6-tri(*p*-aminophenyl)-triazine **10**[18] (5.32 g, 15 mmol) and diisopropylethylamine (7.56 g, 9.67 mL, 58.5 mmol) in THF (100 mL) during 2 h at 50 °C. The reaction mixture was stirred for another 5 h. After removal of diisopropylethylamine hydrochloride salt through filtration, the filtrate was concentrated and chromatographed on a silica gel column (100−200) with a mixture of petroleum ether and THF (2:1) as the mobile phase to give pure **12** (8.34 g, 61%) as a white solid: mp 198−199 °C; $^1$H NMR (300 MHz, THF) $\delta$ 10.82 (s, 1H), 9.94 (br, s, 2H), 8.78 (d, $J$ = 8.4 Hz, 6H), 7.97 (d, $J$ = 8.4 Hz, 6H), 4.47 (t, 6H), 1.91 − 1.76 (m, 6H), 1.65−1.39 (m, 6H), 1.01 (t, $J$ = 7.3 Hz, 9H); $^{13}$C NMR (75 MHz, THF) $\delta$ 172.2, 171.5, 171.2, 166.4, 143.4, 132.1, 130.4, 120.3, 69.2, 31.7, 20.1, 14.2 IR (KBr) $\nu$ 3399, 2960, 1559, 1506, 1362, 811, $cm^{-1}$; MS [MALDI-TOF] $m/z$ 910.6 [M + $H^+$] (68), 912.6 (100), 914.6 (34). Anal. Calcd for $C_{42}H_{42}Cl_3N_{15}O_3 \cdot H_2O$: C, 54.29; H, 4.77; N, 22.61. Found: C, 54.61; H, 4.76; N, 22.50.

**Synthesis of 13.** 2,4,6-Tri(*p*-hydroxyphenyl)benzene **1** (0.35 g, 1 mmol), intermediate **12** (0.91 g, 1 mmol) and $K_2CO_3$ (finely ground) (0.49 g, 3.6 mmol) were added in flask containing 400 mL of 1,4-dioxane and reaction mixture was refluxed for 23 h. The mixture was then filtered, and solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100−200) with chloroform and methanol (100: 1) as the mobile phase to give pure **13** (0.42 g, 36%) as a white solid: mp >300 °C; $^1$H NMR (300 MHz, DMSO) $\delta$ 10.23 (s, 3H), 8.03 (d, $J$ = 8.4 Hz, 6H), 7.83 (d, $J$ = 8.5 Hz, 6H), 7.74 (s, 3H), 7.32 (d, $J$ = 8.4 Hz, 6H), 7.26 (d, $J$ = 8.5 Hz, 6H), 4.39 (t, $J$ = 6.5 Hz, 6H), 1.86 − 1.62 (m, 6H), 1.58 − 1.34 (m, 6H), 0.97 (t, $J$ = 7.3 Hz, 9H); $^{13}$C NMR (75 MHz, DMSO) $\delta$ 172.5, 171.8, 171.7, 166.6, 151.5, 141.2, 140.0, 136.5, 132.3, 128.6, 127.5, 124.9, 122.8, 122.5, 66.9, 30.3, 18.6, 13.7; IR (KBr) $\nu$ 3393, 2958, 1573, 1508, 1362, 1203, 814 $cm^{-1}$; MS [MALDI-TOF] $m/z$ 1156.6 [M + $H^+$] (100), 1157.6 (71), 1158.6 (12) 1178.5 [M + $Na^+$]. Anal. Calcd for $C_{66}H_{57}N_{15}O_6 \cdot 2H_2O$: C, 66.49; H, 5.16; N, 17.62. Found: C, 66.46; H, 4.96; N, 17.67.

**Synthesis of 15.** To a stirred suspension of $K_2CO_3$ (finely ground) (1 g, 7.2 mmol) in 1,4-dioxane (300 mL) at 50 °C were added dropwise solutions of 2,4,6-tri(*p*-hydroxyphenyl)benzene **1** (0.71 g, 2 mmol)

in 1,4-dioxane (250 mL) and intermediate **14** (see the Supporting Information) (1.93 g, 2 mmol) in 1,4-dioxane (250 mL) at the same time and the same rate. After addition of the two reactants, which took about 3 h, the resulting mixture was stirred further for another 23 h. The mixture was then filtered, and solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100−200) with chloroform and methanol (100: 0.1) as the mobile phase to give pure **15** (0.99 g, 41%) as a white solid: mp >300 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.53 (d, $J$ = 8.4 Hz, 6H), 7.46 (s, 3H), 7.38 (d, $J$ = 8.5 Hz, 6H), 7.11 (d, $J$ = 8.4 Hz, 6H), 6.92 (d, $J$ = 8.5 Hz, 6H), 3.98 (t, $J$ = 7.4 Hz, 6H), 1.72 − 1.53 (m, 6H), 1.47 − 1.30 (m, 6H), 0.93 (t, $J$ = 7.3 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.0, 170.6, 170.5, 166.2, 151.5, 145.4, 140.6, 137.4, 134.9, 129.7, 128.0, 127.0, 123.3, 122.3, 49.1, 29.9, 19.8, 13.7; IR (KBr) $\nu$ 2929, 1566, 1508, 1383, 1196, 804 cm$^{-1}$; MS [MALDI-TOF] $m/z$ 1210.5 [M + H$^+$] (65), 1212.5 (100), 1214.5 (34). Anal. Calcd for $C_{66}H_{55}Cl_3N_{15}O_3$ [M + H]$^+$ 1210.3672, found 1210.3690 [M + H]$^+$.

**General Procedure for the Functionalization of 15 through Its Aromatic Nucleophilic Substitution.** To a solution of **15** (0.24 g, 0.2 mmol) in THF (20 mL) at 45 °C were added $K_2CO_3$ (finely ground) (0.1 g, 0.72 mmol) and amine **5d** or **5e** (1.2 mmol) with constant stirring. Stirring was continued for a further 10 h. The mixture was then filtered, and solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100−200) with a mixture of solvents (see the Supporting Information) as the mobile phase to give pure product **16a** or **16b**.

**16a** (0.18 g, 65%) as a white solid: mp 278−279 °C; $^1$H NMR (300 MHz, DMSO) $\delta$ 8.40 (d, $J$ = 8.3 Hz, 6H), 7.59 − 7.47 (m, 9H), 7.29 (d, $J$ = 8.3 Hz, 6H), 7.01 (d, $J$ = 8.3 Hz, 6H), 4.97 − 4.66 (br, m, 6H), 3.92 (t, $J$ = 6 Hz, 6H), 3.84 − 3.59 (m, 24H), 1.71 − 1.42 (m, 6H), 1.45 − 1.13 (m, 6H), 0.88 (t, $J$ = 7.2 Hz, 9H); $^{13}$C NMR (75 MHz, DMSO) $\delta$ 170.3, 169.9, 166.5, 165.3, 151.6, 146.6, 140.1, 135.8, 132.8, 128.8, 128.2, 126.8, 122.4, 58.9, 58.8, 51.0, 50.5, 48.1, 29.7, 19.4, 13.6; IR (KBr) $\nu$ 3398, 2930, 1576, 1507, 1362, 1204, 808 cm$^{-1}$; MS [MALDI-TOF] $m/z$ 1417.5 [M + H$^+$] (100), 1418.5 (87), 1419.5 (26) 1439.5 [M + Na$^+$]. Anal. Calcd for $C_{78}H_{84}N_{18}O_9 \cdot 4H_2O$: C, 62.89; H, 6.22; N, 16.92. Found: C, 63.17; H, 5.99; N, 16.65.

**16b** (0.24 g, 70%) as a white solid: mp 226−227 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.58 (d, $J$ = 3.7 Hz, 6H), 8.45 (d, $J$ = 8.4 Hz, 6H), 7.69 (q, $J$ = 7.3 Hz, 6H), 7.50 − 7.39 (m, 6H), 7.38 − 7.28 (m, 9H), 7.20 (dd, $J$ = 11.6, 4.9 Hz, 6H), 7.09 (d, $J$ = 8.4 Hz, 6H), 6.95 (d, $J$ = 8.5 Hz, 6H), 5.15 (d, $J$ = 35.6 Hz, 12H), 3.77 (t, $J$ = 7.1 Hz, 6H), 1.51 − 1.31 (m, 6H), 1.20 − 1.03 (m, 6H), 0.71 (t, $J$ = 7.3 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.9, 170.7, 168.0, 166.2, 158.2, 157.7, 152.0, 149.3, 146.9, 140.8, 136.9, 136.7, 136.7, 134.1, 129.1, 128.3, 126.7, 123.2, 122.7, 122.2, 121.9, 120.9, 52.3, 52.1, 48.8, 30.1, 19.90, 13.7; IR (KBr) $\nu$ 2929, 1573, 1508, 1477, 1364, 1205, 825 cm$^{-1}$; MS [MALDI-TOF] $m/z$ 1699.8 [M + H$^+$] (79), 1700.8 (100), 1701.8 (34). Anal. Calcd for $C_{102}H_{90}N_{24}O_3 \cdot 4H_2O$: C, 69.14; H, 5.57; N, 18.97. Found: C, 69.18; H, 5.26; N, 18.86.

**General Procedure for the Synthesis of 17.** To a mixture of **12** (1.82 g, 2 mmol) and $K_2CO_3$ (finely ground) (1.66 g, 12 mmol) in acetone (100 mL) at 80 °C was added methyl iodide or allyl bromide (18 mmol) dropwise with constant stirring. The reaction mixture was stirred for another 8 hand then filtered, and solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100−200) with a mixture of petroleum ether and chloroform (see Table S8, Supporting Information) as the mobile phase to give pure **17**.

**17a** (1.75 g, 92%) as white solid: mp 187−188 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.82 (d, $J$ = 8.6 Hz, 6H), 7.52 (d, $J$ = 8.6 Hz, 6H), 4.29 (br, s, 6H), 3.63 (s, 9H), 1.72 (br, m, 6H), 1.44−1.42 (br, m, 6H), 0.93 (t, $J$ = 7.1 Hz, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.8, 170.8, 170.4, 166.2, 146.7, 134.2, 129.7, 126.2, 68.1, 38.3, 30.4, 18.8, 13.5; IR (KBr) $\nu$ 2958, 1509, 1360, 1067, 810 cm$^{-1}$; MS [MALDI-TOF] $m/z$ 952.4 [M + H$^+$] (68), 954.4 (100), 956.4 (42) 974.4 [M + Na$^+$]. Anal. Calcd for $C_{45}H_{48}Cl_3N_{15}O_3$: C, 56.69; H, 5.08; N, 22.04. Found: C, 56.66; H, 5.18; N, 21.68.

**17b** (1.77 g, 86%) as a light yellow solid: mp 102−103 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.80 (d, $J$ = 8.6 Hz, 6H), 7.49 (d, $J$ = 8.6 Hz, 6H), 6.07−5.94 (m, 3H), 5.34 − 5.13 (m, 6H), 4.67 (d, $J$ = 5.5 Hz, 6H), 4.26 (br, m, 6H), 1.70 (br, m, 6H), 1.41 (br, m, 6H), 0.92 (br, m, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.0, 170.9, 170.6, 166.2, 145.7, 134.5, 132.2, 129.8, 127.1, 118.3, 68.2, 53.4, 30.5, 18.9, 13.6. IR (KBr) $\nu$ 2959, 1562, 1508, 1346, 1224, 808 cm$^{-1}$; MS [MALDI-TOF] $m/z$ 1030.6 [M + H$^+$] (67), 1032.6 (100), 1034.6 (34) 1052.6 [M + Na$^+$]; calcd for $C_{51}H_{55}Cl_3N_{15}O_3$ [M + H]$^+$ 1030.3672, found 1030.3688 [M + H]$^+$.

**Synthesis of 18.** Products **18a** and **18b** were prepared following the same procedure for the preparation of **13**. Compound **18a** (0.44 g, 37%) as a white solid: mp >300 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.48 (d, $J$ = 8.5 Hz, 6H), 7.46 (s, 3H), 7.38 (d, $J$ = 8.6 Hz, 6H), 7.15 (d, $J$ = 8.5 Hz, 6H), 6.96 (d, $J$ = 8.5 Hz, 6H), 4.50 (t, $J$ = 6.7 Hz, 6H), 3.52 (s, 9H), 1.95 − 1.76 (m, 6H), 1.62 − 1.47 (m, 6H), 1.02 (t, $J$ = 7.3 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 173.1, 171. 6, 170.7, 167.3, 151.8, 147.5, 140.7, 137.1, 134.3, 129.4, 127.2, 126.8, 123.2, 122.5, 67.9. 36.8, 30.8, 19.1, 13.8; IR (KBr) $\nu$ 2958, 1574, 1508, 1373, 1206, 820 cm$^{-1}$; MS [MALDI-TOF] $m/z$ 1198.9 [M + H$^+$] (100), 1199.9 (74), 1200.9 (13) 1220.9 [M + Na$^+$]. Anal. Calcd for $C_{69}H_{63}N_{15}O_6 \cdot H_2O$: C, 68.13; H, 5.39; N, 17.27. Found: C, 68.28; H, 5.41; N, 17.13.

**18b** (0.43 g, 34%) as a white solid: mp 285−286 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.48 (d, $J$ = 8.5 Hz, 6H), 7.44 (s, 3H), 7.36 (d, $J$ = 8.6 Hz, 6H), 7.12 (d, $J$ = 8.5 Hz, 6H), 6.94 (d, $J$ = 8.5 Hz, 6H), 6.03−5.90 (m, 3H), 5.20 − 5.12 (m, 6H), 4.57 (d, $J$ = 5.8 Hz, 6H), 4.48 (t, $J$ = 6.7 Hz, 6H), 1.94 − 1.77 (m, 6H), 1.62 − 1.47 (m, 6H), 1.01 (t, $J$ = 7.3 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 173.1, 171.8, 170.6, 167.2, 151.8, 146.2, 140.7, 137.2, 134.5, 132.8, 129.3, 128.3, 126.9, 123.3, 122.5, 118.2, 67.9, 51.8, 30.8, 19.1, 13.8. IR (KBr) $\nu$ 2958, 1572, 1508, 1360, 1202, 819 cm$^{-1}$; MS [MALDI-TOF] $m/z$ 1276.6 [M + H$^+$] (100), 1277.6 (79), 1278.6 (12) 1298.6 [M + Na$^+$]; calcd for $C_{75}H_{71}N_{15}O_6$ [M + 2H]$^+$ 638.7850, found 638.7844 [M + 2H]$^+$.

## ■ ASSOCIATED CONTENT

**Supporting Information.** Experimental procedures and compound characterization data; copies of $^1$H and $^{13}$C NMR spectra of products; X-ray structures of **3**, **6b**, **9b**, and **18b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org

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