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Molecular Tectonics. Porous Hydrogen-Bonded Networks Built from Derivatives of Pentaerythrityl Tetraphenyl Ether

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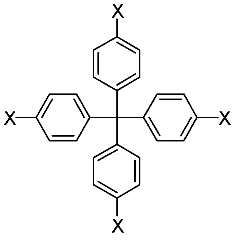
The symmetric four-armed geometry of pentaerythrityl tetraphenyl ether (**5**) makes it a valuable starting point for building complex molecular and supramolecular structures. In particular, it provides a core to which multiple sites of attractive intermolecular interaction can be attached, thereby creating compounds predisposed to form complex networks by association. To facilitate exploitation of the pentaerythrityl tetraphenyl ether core in such ways, we have prepared more than 20 new derivatives by efficient methods. Of special interest are compounds **3** and **4**, which incorporate four diaminotriazine groups attached to the meta and para positions of the pentaerythrityl tetraphenyl ether core. Crystallization of compounds **3** and **4** from DMSO/dioxane is directed by hydrogen bonding of the diaminotriazine groups according to well-established motifs, thereby producing three-dimensional networks. In forming these networks, each molecule of compound **3** forms a total of 12 hydrogen bonds with six others, whereas each molecule of compound **4** forms a total of 16 hydrogen bonds with four others. Both networks are highly porous and define significant interconnected channels for the inclusion of guests. In crystals of compounds **3** and **4**, the fraction of the volume accessible to guests is 66% and 57%, respectively. In both cases, the pentaerythrityl tetraphenyl ether cores adopt conformations that deviate substantially from tetrahedral geometry. It is noteworthy that the inherent flexibility of the core does not favor the formation of close-packed guest-free structures.

Introduction

Detailed structures of molecular crystals cannot yet be predicted reliably.[2] As a result, crystal engineers continue to rely heavily on qualitative guidelines. Among the most effective guidelines is the principle that certain sticky sites in molecules can form attractive intermolecular interactions according to well-established motifs, which have been called supramolecular synthons.[3] In favorable cases, the resulting association can lead to foreseeable three-dimensional structures. Purposefully built molecules with arrays of sticky sites have been called tectons from the Greek word for builder,[4] and the term molecular tectonics has been used to refer to the art and science of constructing ordered molecular materials from tectonic subunits.[5,6]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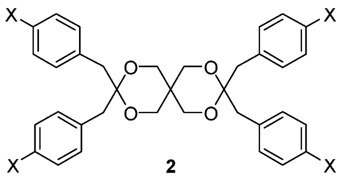
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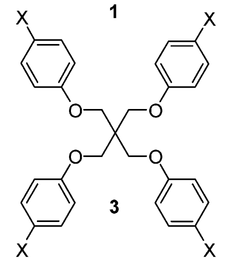
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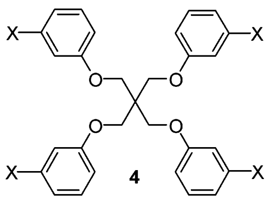
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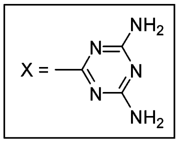

Tectons can be considered to consist of multiple peripheral sticky sites linked to a core that holds them in a suitable orientation. Previous research has emphasized sticky sites that use hydrogen bonding to direct association, joined to rigid cores that establish a well-defined geometry.[7−13] A representative example is tecton **1**,[8] in which four sticky diaminotriazine groups are grafted to the para positions of a nominally tetrahedral tetraphenylmethyl core. Crystallization of tecton **1** is directed by

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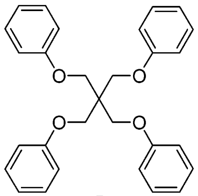
hydrogen bonding of the diaminotriazine groups to produce an open three-dimensional network. Approximately 42% of the volume is accessible for the inclusion of guests, which occupy prominent parallel channels that are nearly 12 Å across in the largest dimension. As illustrated by the behavior of compound **1**, tectons cannot usually form normal close-packed structures and simultaneously obey the strong directional interactions they are designed to form with adjacent molecules;[14] instead, open networks are favored, and significant voids are filled with guests.

Remarkably, even analogues that are more flexible are apparently unable to find periodic three-dimensional structures in which the dictates of close packing and hydrogen bonding are satisfied at the same time. For example, crystallization of tecton **2**, in which four diaminotriazine groups are attached flexibly to a core derived from pentaerythritol, yields an interpenetrated diamondoid network in which 60% of the volume is accessible to guests.[9] The guests occupy parallel helical channels with cross sections that measure approximately 11 × 12 Å^2.

The unexpectedly high porosity of the network constructed from tecton **2** encouraged us to examine the behavior of related tectons with even more flexible cores. High symmetry and structural simplicity made tectons **3** and **4** particularly attractive targets. In this paper, we show that they can be prepared conveniently from pentaerythritol and crystallized to produce highly porous hydrogen-bonded networks. In addition, we report effective syntheses of more than 20 new derivatives of pentaerythrityl tetraphenyl ether (**5**), which promise to be useful building blocks for the construction of molecular materials.



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Results and Discussion

Synthesis of Simple Derivatives of Pentaerythrityl Tetraphenyl Ether. The first synthesis of pentaerythrityl tetraphenyl ether (**5**) and various substituted derivatives was reported in 1936 by Backer and Dijken,[15] who made them by heating salts of phenols with pentaerythrityl tetrabromide. Surprisingly, the pentaerythrityl tetraphenyl ether core remained little used until recently, when promising applications in macromolecular chemistry,[16] medicinal chemistry,[17] the construction of dendrimers,[18] and other areas[19,20] have been uncovered. However, the potential of the pentaerythrityl tetraphenyl ether core in supramolecular chemistry is still underdeveloped, and no use of the core in crystal engineering has

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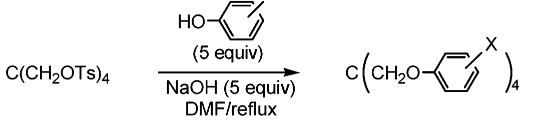
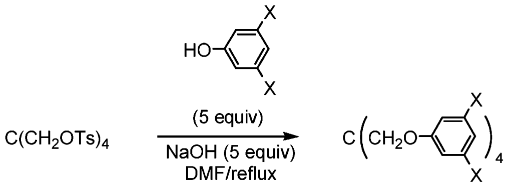
TABLE 1. One-Step Syntheses of Tetrasubstituted Pentaerythrityl Tetraphenyl Ethers from Pentaerythrityl Tetratosylate



entry	phenol	product	yield (%)
1	X = 4-F	**6**	50
2	X = 4-F[a]	**6**	78
3	X = 3-F	**7**	88
4	X = 4-NO$_2$[a]	**8**[25]	71
5	X = 3-NO$_2$	**9**	83
6	X = 4-Cl	**10**[15]	83
7	X = 3-Cl	**11**	81
8	X = 4-Br	**12**[15]	82
9	X = 3-Br	**13**	87
10	X = 2-Br	**14**	76
11	X = 4-I	**15**	80
12	X = 3-I	**16**	89
13	X = 4-CN	**17**[26]	90
14	X = 3-CN	**18**	92
15	X = 4-CHO	**19**[20]	70

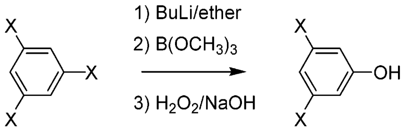
[a] Reaction performed in absolute ethanol at 170 °C

TABLE 2. One-Step Syntheses of Tetrakis(3,5-disubstituted) Pentaerythrityl Tetraphenyl Ethers from Pentaerythrityl Tetratosylate



entry	phenol	product	yield (%)
1	X = Br (**23**)	**20**	63
2	X = I (**24**)	**21**	80
3	X = OCH$_3$	**22**	70

SCHEME 1



X = Br, I

23 (X = Br) (76%)
24 (X = I) (69%)

been reported. The pioneering X-ray crystallographic studies of pentaerythrityl tetraphenyl ether (**5**) reported by Beintema and co-workers in 1935,[21] as well as our recent refinement,[22] are the only previous structural analyses of compounds of this type.[23]

To facilitate exploitation of the pentaerythrityl tetraphenyl ether core in crystal engineering and other areas of science, we created a library of selected derivatives by efficient methods. Many of the compounds were obtained as crystalline solids that needed no chromatographic purification. Our syntheses used the method originally reported by Backer and Dijken,[15] except that salts of phenols were heated not with pentaerythrityl tetrabromide but with pentaerythrityl tetratosylate,[24] which can be prepared simply and inexpensively on a large scale. Symmetrically tetrasubstituted pentaerythrityl tetraphenyl ethers **6**−**19** were made directly by this route and are listed in Table 1, along with the methods of synthesis and the yields obtained. Of these compounds, only **8**,[25] **10**,[15] **12**,[15] **17**,[26] and **19**[20] have been previously reported. It is noteworthy that this route provides in one step a wide variety of four-armed cores that can be used for further molecular construction; in contrast, similar derivatives of tetraphenylmethane, tetraphenylsilane, spirobifluorene,[10] and other cores that have already found wide use in chemistry typically require multistep syntheses.[27]

Most of the reactions summarized in Table 1 are straightforward and only several require commentary. Our preferred conditions (NaOH, DMF, reflux) failed to provide tetrakis[(4-nitrophenoxy)methyl)]methane (**8**)[25] in good yield, so the reaction was carried out by a less convenient method involving the use of absolute ethanol at 170 °C (Table 1, entry 4).[25] Improved yields of tetrakis[(4-fluorophenoxy)methyl]methane (**6**) were also obtained in this way (Table 1, entries 1 and 2). Halogenated pentaerythrityl tetraphenyl ethers **10**−**16** (Table 1, entries 6−12) represent valuable starting materials for making more elaborate molecules by standard C−C or C−heteroatom coupling reactions.

Similar reactions provided the tetrakis(3,5-disubstituted) derivatives **20**−**22** shown in Table 2. In the course of this work, we devised new syntheses of 3,5-dibromophenol (**23**)[28] and 3,5-diiodophenol (**24**)[29] by the routes summarized in Scheme 1. Derivatives of 4-hydroxybiphenyl could also be used to make pentaerythrityl tetrakis(biphenyl) ethers **25**−**28** (Table 3). Unidentified side reactions occurring in the reaction with 4-hydroxy-4′-iodobiphenyl under our standard conditions could be avoided by using K_2CO_3 in the presence of tetrabutylammonium bromide (Table 3, entry 2).

As summarized in Table 4, pentaerythrityl tetraphenyl ethers made directly in one step from pentaerythrityl

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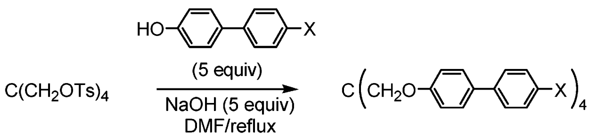
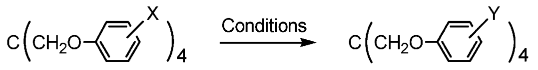
TABLE 3. One-Step Syntheses of Pentaerythrityl Tetrakis(biphenyl) Ethers from Pentaerythrityl Tetratosylate



entry	phenol	product	yield (%)
1	X = Br	**25**	82
2	X = I[a]	**26**	82
3	X = CN	**27**	89
4	X = NO_2	**28**	93

[a] Reaction performed with K_2CO_3 and tetrabutylammonium bromide

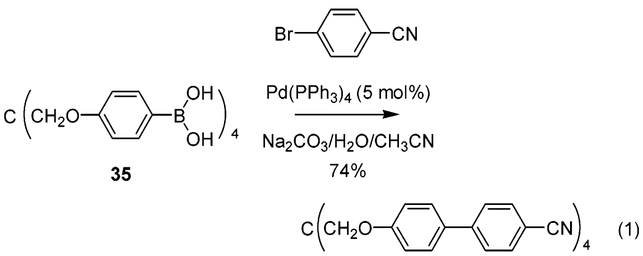
TABLE 4. Further Transformations of Pentaerythrityl Tetraphenyl Ethers



entry	starting compound (X)	conditions[a]	product (Y)	yield (%)
1	**8** (4-NO_2)[25]	a	**29** (4-NH_2)[25]	99
2	**9** (3-NO_2)	a	**30** (3-NH_2)	99
3	**29** (4-NH_2)[25]	b	**31** (4-NCO)	94
4	**29** (4-NH_2)[25]	c	**32** (4-NCS)	80
5	**19** (4-CHO)[18]	d	**33** (4-CH_2OH)	81
6	**33** (4-CH_2OH)	e	**34** (4-CH_2Cl)	81
7	**12** (4-Br)[16]	f	**35** (4-$B(OH)_2$)	98
8	**17** (4-CN)[26]	g	**36** (4-COOH)[31]	97
9	**18** (3-CN)	g	**37** (3-COOH)	96
10	**15** (4-I)	h	**38** (4-C≡CTMS)	92
11	**16** (3-I)	h	**39** (3-C≡CTMS)	96
12	**38** (4-C≡CTMS)	i	**40** (4-C≡CH)	95
13	**39** (3-C≡CTMS)	i	**41** (3-C≡CH)	94
14	**17** (4-CN)[26]	j	tecton **3** (4-DAT)[b]	95
15	**18** (3-CN)	j	tecton **4** (3-DAT)[b]	73

[a] (a) H_2/Pd/C; (b) triphosgene, $N(C_2H_5)_3$; (c) thiophosgene, $N(C_2H_5)_3$; (d) $NaBH_4$; (e) $SOCl_2$; (f) (1) BuLi, (2) $B(O\text{-}i\text{Pr})_3$, (3) HCl; (g) (1) KOH, (2) HCl; (h) $HC{\equiv}CSi(CH_3)_3$, $PdCl_2(PPh_3)_2$, CuI, $N(C_2H_5)_3$; (i) tetrabutylammonium fluoride; (j) dicyandiamide, KOH. [b] DAT = (4,6-diamino-1,3,5-triazin-2-yl).

tetratosylate (Table 1) can be subjected to further reactions to give an even broader range of nominally tetrahedral four-armed cores **29**−**41** for molecular construction. In particular, reduction of tetrakis[(4-nitrophenoxy)methyl)]methane (**8**)[25] and its 3-substituted isomer **9** provided the corresponding tetraamines **29**[25] and **30** (Table 4, entries 1 and 2). The 4-substituted tetraamine **29**[25] was then converted into tetraisocyanate **31** and tetraisothiocyanate **32** (Table 4, entries 3 and 4), which are attractive monomers for the synthesis of polyureas and polyurethanes. In addition, lithiation of tetrakis[(4-bromophenoxy)methyl)]methane (**12**),[15] followed by addition of $B(i\text{-PrO})_3$ and then HCl, gave a high yield of tetraboronic acid **35** (Table 4, entry 7). Previous research in molecular tectonics has established that such compounds can self-associate to form open hydrogen-bonded networks.[7,30] Moreover, tetraboronic acid **35** is a valuable intermediate for making more complex derivatives of pentaerythrityl tetraphenyl ether by Suzuki coupling, as confirmed by its reaction with 4-bromobenzonitrile to give a good yield of tetranitrile **25** (eq 1), also made by the route shown in Table 3.



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(1)

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Basic hydrolysis of tetrakis[(4-cyanophenoxy)methyl)]methane (**17**)[26] and its 3-substituted isomer **18** provided the corresponding tetraacids **36**[31] and **37** in high yields (Table 4, entries 8 and 9). Sonogashira coupling of tetrakis[(4-iodophenoxy)methyl)]methane (**15**) and its 3-substituted isomer **16** with (trimethylsilyl)acetylene gave the expected products **38** and **39**, respectively (Table 4, entries 10 and 11), which could be converted into tetraacetylenes **40** and **41** in excellent overall yield by treatment with tetrabutylammonium fluoride (Table 4, entries 12 and 13).

Synthesis of Tectons 3 and 4 with Pentaerythrityl Tetraphenyl Ether Cores. Although tectons can be created from the pentaerythrityl tetraphenyl ether core in many different ways, we elected to attach diaminotriazine groups as the sticky sites for the following reasons: (1) these groups are easily made by the reaction of nitriles with dicyandiamide;[32] (2) they self-associate according to established motifs to form robust networks held together by multiple hydrogen bonds;[8−10] and (3) the structures of other tectons with diaminotriazine groups are known,[8−10] including close relatives **1** and **2**, and informative comparisons can therefore be made. Tectons **3** and **4** were synthesized in 95% and 73% yields, respectively, by the reactions of tetrakis[(4-cyanophenoxy)methyl)]methane (**17**)[26] and its 3-substituted isomer **18** with dicyandiamide under standard conditions (Table 4, entries 14 and 15).[32] In both cases, colorless single crystals suitable for X-ray diffraction could be grown from DMSO/dioxane.

Porous Hydrogen-Bonded Network Constructed from Tecton 3. Tecton **3** crystallized in the orthorhombic space group $P2_12_12$ as an inclusion compound of approximate composition **3**·5DMSO·6dioxane.[33] Views of the structure are shown in Figures 1−4. Like more rigid analogues **1** and **2**, tecton **3** self-associates by hydrogen bonding of its diaminotriazine groups to form an open three-dimensional network with significant volume for the inclusion of guests. Each tecton forms a total of 14 hydrogen bonds with six neighboring tectons and two molecules of DMSO that form an integral part of the network.

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(30) For other boronic acids derived from pentaerythrityl phenyl ethers, see: Draffin, S. P.; Duggan, P. J.; Duggan, S. A. M. *Org. Lett.* **2001**, *3*, 917.

(31) Oike, H.; Imamura, H.; Imaizumi, H.; Tezuka, Y. *Macromolecules* **1999**, *32*, 4819.

(32) Simons, J. K.; Saxton, M. R. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 78.

(33) The composition was estimated by X-ray crystallography and by ^1H NMR spectroscopy of dissolved samples. The amount of any H_2O included could not be determined accurately.

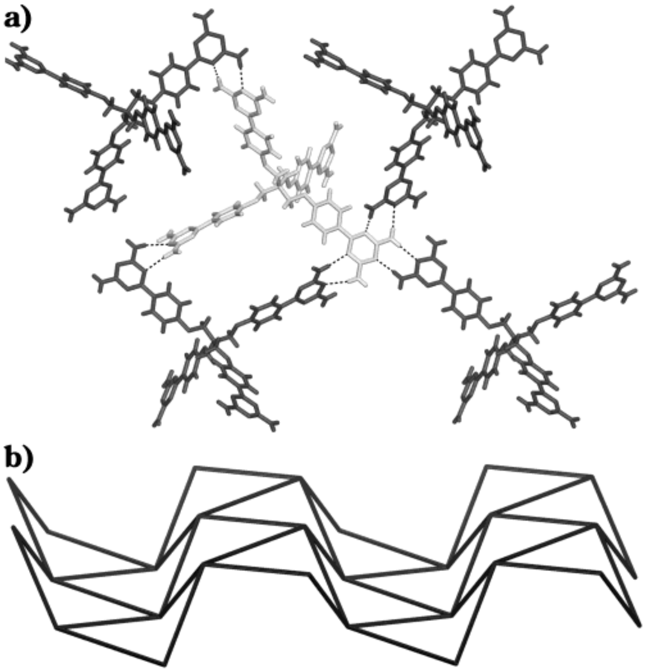


FIGURE 1. (a) Partial view of the structure of crystals of tecton **3** grown from DMSO/dioxane, showing a central tecton (light gray) surrounded by four hydrogen-bonded neighbors (dark gray). Hydrogen bonds appear as broken lines, and all guests are omitted for clarity. As shown in this view, three of the four diaminotriazine groups of the central tecton form a total of 10 hydrogen bonds according to standard motifs **42** and **43**. The fourth diaminotriazine and one of the other three form a total of four additional hydrogen bonds according to the motif shown in Figure 2a. (b) Representation of the corrugated 4-connected network defined by joining the central carbon atom of each tecton with the centers of the set of four neighbors shown in Figure 1a.

As shown in Figure 1a, three diaminotriazine groups of each tecton interact with five diaminotriazine groups provided by four neighboring tectons according to the normal motifs **42** and **43**.[8−10] A third alternative, motif **44**, is not observed, possibly because it would place both cores of adjacent tectons in close proximity to substituents on the triazine rings. Lines joining the central carbon atom of each tecton with the centers of the set of neighbors shown in Figure 1a define a corrugated 4-connected network that lies perpendicular to the *c* axis (Figure 1b).

Each tecton forms four more hydrogen bonds with two neighboring tectons and two molecules of DMSO according to the novel motif shown in Figure 2a. These additional interactions cause the corrugated 4-connected sheets to become stacked along *c* to form a three-dimensional 6-connected network (Figure 2b). The ultimate structure of tecton **3** can be considered to result from 2-fold interpenetration of this network along *c*, with the corrugated sheets of one network interleaved between those of the other.[34,35]

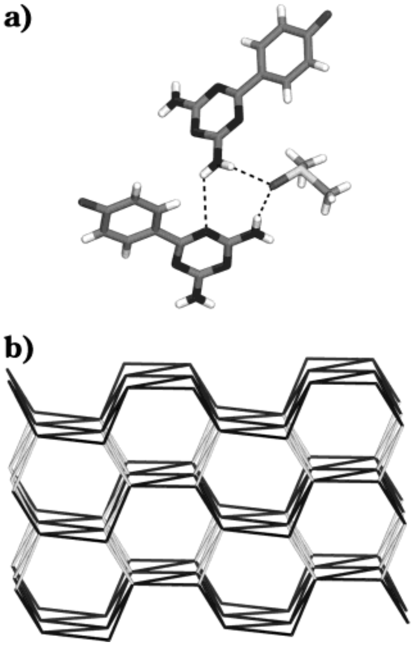
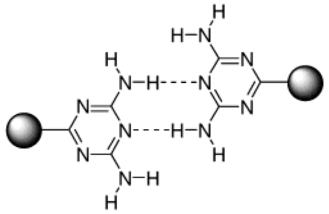


FIGURE 2. (a) Partial view of the structure of crystals of tecton **3** grown from DMSO/dioxane, showing how two of the diaminotriazine groups of each tecton (the group not engaged in hydrogen bonding according to the motif shown in Figure 1a, as well as one other group) each form two additional hydrogen bonds with a neighboring tecton and a molecule of DMSO. Hydrogen bonds appear as broken lines. For clarity, molecules not forming an integral part of the network are omitted, and only one of the four arms of each tecton is shown. (b) Representation of the three-dimensional 6-connected network that results when the corrugated 4-connected sheets defined in Figure 1a (dark gray) are joined by the additional interactions shown in Figure 2a (light gray).



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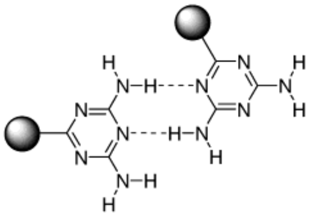

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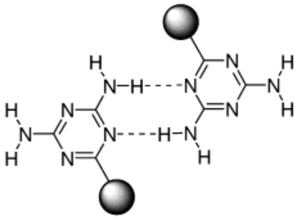

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In forming this structure, the four sticky arms of tecton **3** extend in directions that define a highly distorted

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(34) For discussions of interpenetration in networks, see: Batten, S. R. *CrystEngComm* **2001**, *18*, 1. Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

(35) An updated list of examples of interpenetration is available on the web site of Dr. Stuart R. Batten at Monash University (www.chem.monash.edu.au).

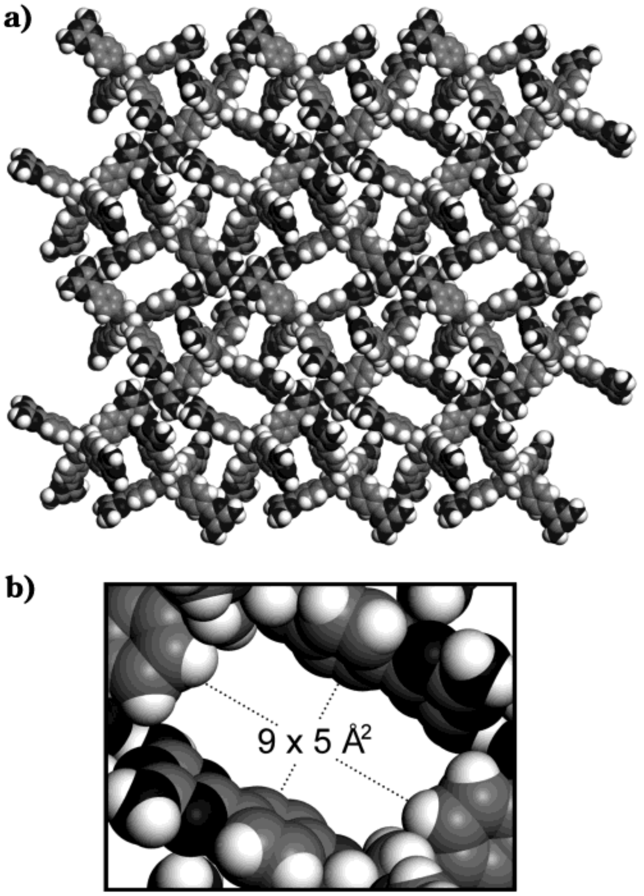

FIGURE 3. (a) View along the *c* axis of the network constructed from tecton **3** showing a 3 × 2 × 4 array of unit cells. Guests are omitted, and atoms are shown as spheres of van der Waals radii to reveal the cross sections of the channels. Atoms of hydrogen appear in light gray, atoms of carbon in dark gray, and atoms of nitrogen in black. (b) Enlarged view of the cross section of the larger channels along *c*.

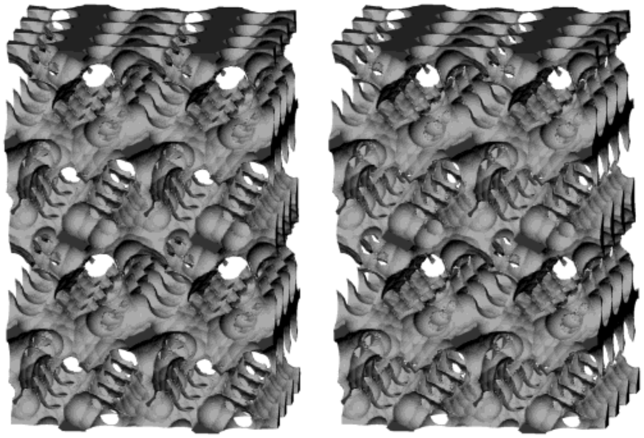

FIGURE 4. Stereoscopic representation of interconnected channels within the network constructed from tecton **3**. The image shows a 2 × 2 × 4 array of unit cells viewed along the *c* axis. The outsides of the channels appear in light gray, and dark gray is used to show where the channels are cut by the boundaries of the array. The surface of the channels is defined by the possible loci of the center of a sphere of diameter 4 Å as it rolls over the surface of the ordered network.[40]

tetrahedron. A measure of the distortion of the pentaerythrityl tetraphenyl ether core is provided by the six C−C−C angles formed by connecting the central carbon atom with the para positions of pairs of phenyl groups. In the structure of tecton **3**, these C−C−C angles range from 91.3° to 121.9°. Values similarly far from the tetrahedral ideal have also been observed in the crystal structure of pentaerythrityl tetraphenyl ether (**5**).[22]

Despite the complex connectivity, interpenetration, and structural deformation observed in crystals of tecton **3**, 66% of the volume remains accessible to guests.[36−38] It is noteworthy that a tecton with such a high degree of flexibility appears unable to crystallize as a guest-free structure that is both close-packed and fully hydrogen-bonded. Molecules of DMSO and dioxane that do not form an integral part of the network itself occupy interconnected channels. The most significant channels are aligned with the *c* axis and have cross sections measuring approximately 9 × 5 Å^2 at the narrowest points (Figure 3).[39] The connectivity of the channels is complex, as represented by the surface shown in Figure 4.[40]

In this structure, some of the molecules of DMSO and all of the molecules of dioxane are disordered, potentially mobile, and located in interconnected channels that in principle provide redundant paths of escape from the crystals. Moreover, the crystals are held together by robust networks of hydrogen bonds. As a result, guests can be exchanged in single crystals without loss of crystallinity. For example, single crystals of estimated composition **3**·5DMSO·6dioxane[33] and approximate dimensions 0.5 mm × 0.5 mm × 0.5 mm were suspended in tetrahydrofuran (THF) at 25 °C for 24 h. The recovered solid remained transparent and morphologically unchanged and continued to diffract and to exhibit uniform extinction between crossed polarizers. Single-crystal X-ray diffraction established that the space group remained unchanged, although the unit cell parameters varied in a modest but significant way; in particular, *V* decreased by 13% from 9660(2) Å^3 to 8435(45) Å^3. Analysis of the product by ^{1}H NMR spectroscopy in solution established that included dioxane had been replaced by THF but that only part of the included DMSO had been exchanged. These results suggest that exchange involves disordered molecules of DMSO and dioxane included as guests in crystals of tecton **3**; in contrast, there is little or no

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(36) The percentage of volume accessible to guests was estimated by the PLATON program.[37] PLATON calculates the accessible volume by allowing a spherical probe of variable radius to roll over the internal van der Waals surface of the crystal structure. PLATON uses a default value of 1.20 Å for the radius of the probe, which is an appropriate model for small guests such as water. The van der Waals radii used to define surfaces for these calculations are as follows: C: 1.70 Å, H: 1.20 Å, N: 1.55 Å, O: 1.52 Å, and S: 1.80 Å. If V is the volume of the unit cell and V_g is the guest-accessible volume as calculated by PLATON, then the porosity P in % is given by $100V_g/V$.

(37) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001. van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

(38) In our calculations of accessible volume, we have not included space occupied by those molecules of DMSO that form an integral part of the hydrogen-bonded network.

(39) The dimensions of a channel in a particular direction correspond to the cross section of an imaginary cylinder that could be passed through the hypothetical open network in the given direction in contact with the van der Waals surface. Such values are inherently conservative because they (1) measure the cross section at the most narrow constriction and (2) systematically underestimate the sizes of channels that are not uniform and linear.

(40) Representations of channels were generated by the Cavities option in the program ATOMS (*ATOMS*, Version 5.1; Shape Software: 521 Hidden Valley Road, Kingsport, TN 37663; www.shapesoftware.com).

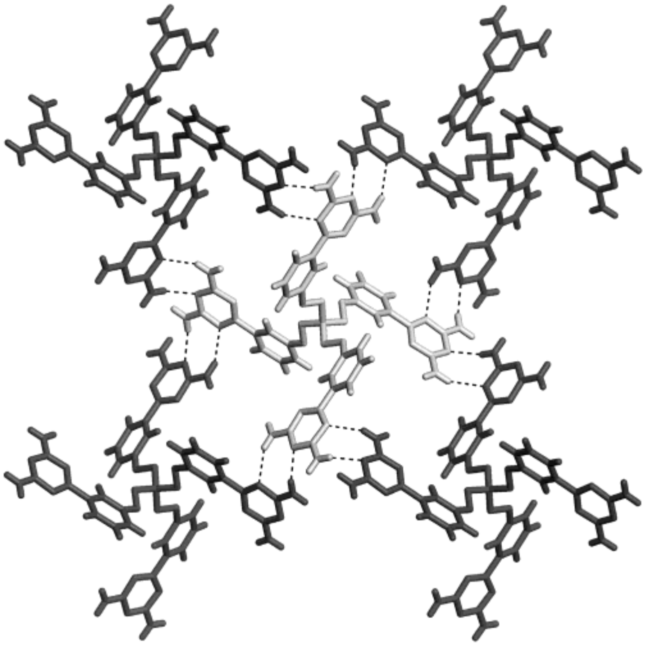

FIGURE 5. View of the structure of crystals of tecton **4** grown from DMSO/dioxane, showing a central tecton (light gray) surrounded by four hydrogen-bonded neighbors (dark gray). Hydrogen bonds appear as broken lines, and all guests are omitted for clarity.

exchange of molecules of DMSO that are ordered because they are an integral part of the hydrogen-bonded network or because they form extraneous hydrogen bonds with the network. The observed contraction of the unit cell is presumably a consequence of replacing a larger guest (dioxane) by a smaller guest (THF), and it allows the inner surface of the network to optimize its interactions with the new guest.

Porous Hydrogen-Bonded Network Constructed from Isomeric Tecton 4. Tecton **4** crystallized from DMSO/dioxane in the tetragonal space group I_1/a as an inclusion compound of well-defined composition **4**·8dioxane,[41] and its structure is shown in Figures 5−7. As expected, tecton **4** behaves like analogues **1**−**3** and self-associates by hydrogen bonding of its diaminotriazine groups to form an open three-dimensional network with significant volume for the inclusion of guests. In this case, each tecton forms a total of 16 hydrogen bonds with four neighboring tectons to create the simple and symmetric pattern shown in Figure 5, and a noninterpenetrated diamondoid network is formed.[42] The diaminotriazine groups of each tecton interact according to the normal motif **43**.[8−10] Like tecton **3** and pentaerythrityl tetraphenyl ether (**5**), tecton **4** has a conformation that deviates significantly from tetrahedral geometry, and the C−C−C angles defined by the central carbon atom and the para phenyl carbon atoms of the core have the values 74.6° and 129.2°.

Approximately 57% of the volume of crystals of tecton **4** remains available for including guests in interconnected channels.[36,37] Cross sections of channels along the *c* axis measure approximately 4 × 2 Å^2 (Figure 6),[39] and the connectivity of the channels is represented by the surface shown in Figure 7.[40] The included molecules of dioxane are all well-ordered, and both atoms of oxygen simultaneously accept hydrogen bonds from NH groups of diaminotriazines that are exposed on the walls of the channels. This arrangement makes the network and its guest highly complementary and explains two unusual observations:

(1) No DMSO is included in crystals of tecton **4** grown from DMSO/dioxane, whereas large amounts of DMSO are included in crystals of isomer **3** grown under similar conditions.

(2) Replacement of dioxane by THF or other polar solvents in single crystals of tecton **4** fails to give crystalline products.

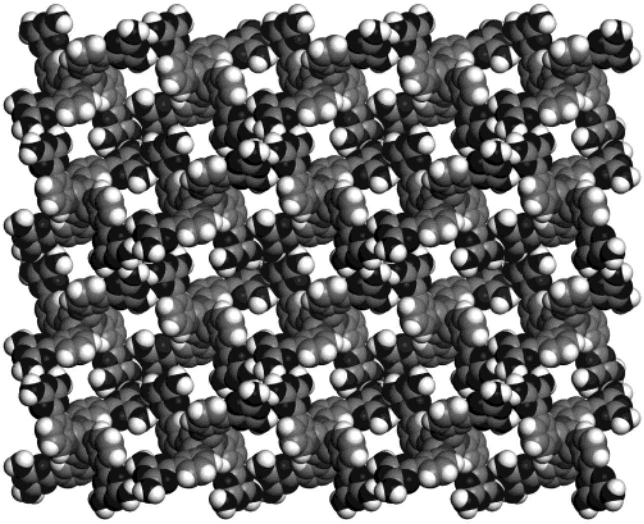

FIGURE 6. View along the *c* axis of the network constructed from tecton **4** showing a 2 × 2 × 2 array of unit cells. Guests are omitted, and atoms are shown as spheres of van der Waals radii to reveal the cross sections of the channels. Atoms of hydrogen appear in light gray, atoms of carbon in dark gray, and atoms of nitrogen in black.

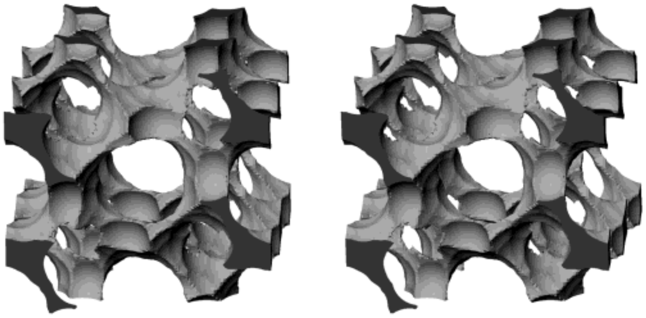

FIGURE 7. Stereoscopic representation of interconnected channels within the network constructed from tecton **4**. The image shows a 1 × 1 × 2 array of unit cells viewed along the *c* axis. The outsides of the channels appear in light gray, and dark gray is used to show where the channels are cut by the boundaries of the array. The surface of the channels is defined by the possible loci of the center of a sphere of diameter 4 Å as it rolls over the surface of the ordered tectonic network.[40]

Conclusions

Substituted derivatives of pentaerythrityl tetraphenyl ether (**5**) are easy to make and are promising four-armed

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[41] The composition was determined by X-ray crystallography and confirmed by ^{1}H NMR spectroscopy of dissolved samples.

[42] For a review of diamondoid hydrogen-bonded networks, see: Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283.

cores for building complex molecular and supramolecular structures. Diaminotriazine groups can be attached to produce tectons **3** and **4**, which crystallize to form networks held together by multiple hydrogen bonds. In these structures, the inherent flexibility of the pentaerythrityl tetraphenyl ether core allows tectons **3** and **4** to adopt conformations that deviate substantially from tetrahedral geometry. Surprisingly, this flexibility does not favor the formation of close-packed guest-free structures. Instead, the crystals include large amounts of guests, which occupy interconnected channels. These observations suggest that further exploration of the use of pentaerythrityl tetraphenyl ether (**5**) and related cores in crystal engineering will be highly productive.

Experimental Section

Tetrakis[(4-fluorophenoxy)methyl]methane (6). Synthesis 1. A stirred mixture of pentaerythrityl tetratosylate (4.00 g, 5.31 mmol),[24] 4-fluorophenol (2.98 g, 26.6 mmol), and NaOH (1.06 g, 26.5 mmol) in DMF (20 mL) was heated at reflux for 24 h. The solution was then cooled, water (100 mL) was added, and the mixture was extracted twice with diethyl ether. The organic layers were combined, washed with water and brine, and dried over Na_2SO_4. Removal of volatiles under reduced pressure left a residue that was purified by flash chromatography (silica, CH_2Cl_2 (30%)/hexane (70%), R_f 0.53) to give tetrakis[(4-fluorophenoxy)methyl]methane (**6**; 1.36 g, 2.65 mmol, 50%) as a colorless solid: mp 114−115 °C; IR (KBr) 3078, 2948, 2885, 1600, 1505, 1467, 1296, 1244, 1212, 1095, 1060, 1037, 825, 789, 761, 514 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, $^3J = 9.1$ Hz, $^3J_F = 8.2$ Hz, 8H), 6.92 (dd, $^3J = 9.1$ Hz, $^4J_F = 4.3$ Hz, 8H), 4.36 (s, 8H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.1; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6 (d, $^1J_F = 238.7$ Hz), 155.1 (d, $^4J_F = 1.4$ Hz), 116.0 (d, $^2J_F = 23.0$ Hz), 115.9 (d, $^3J_F = 7.1$ Hz), 67.4, 45.1; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{29}H_{24}O_4F_4$ *m/e* 512.161073, found 512.162644. Anal. Calcd for $C_{29}H_{24}F_4O_4$: C, 67.96; H, 4.72. Found: C, 67.63; H, 4.66.

Tetrakis[(4-fluorophenoxy)methyl]methane (6). Synthesis 2. A mixture of pentaerythrityl tetratosylate (2.00 g, 2.66 mmol),[24] 4-fluorophenol (1.49 g, 13.3 mmol), and NaOH (0.503 g, 12.6 mmol) in anhydrous ethanol (20 mL) was heated in a sealed tube at 170 °C for 24 h. A workup identical to the one described above in Synthesis 1 afforded tetrakis[(4-fluorophenoxy)methyl]methane (**6**; 1.06 g, 2.07 mmol, 78%).

Tetrakis[(3-fluorophenoxy)methyl]methane (7). By the method of Synthesis 1, pentaerythrityl tetratosylate (4.00 g, 5.31 mmol)[24] and 3-fluorophenol (2.98 g, 26.6 mmol) were converted into crude tetrakis[(3-fluorophenoxy)methyl]methane (**3**), which was purified as described in Synthesis 1 (R_f 0.56) to give the product as a colorless solid (2.40 g, 4.68 mmol, 88%): mp 68 °C; IR (KBr) 3068, 2939, 2889, 1618, 1592, 1491, 1466, 1277, 1266, 1161, 1134, 1045, 1036, 961, 843, 778, 756, 680, 516 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (dt, $^3J = 8.2$ Hz, $^4J_F = 6.9$ Hz, 4H), 6.73−6.63 (m, 12H), 4.32 (s, 8H); ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −111.8; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 (d, $^1J_F = 245.6$ Hz), 160.1 (d, $^3J_F = 10.9$ Hz), 130.5 (d, $^3J_F = 10.0$ Hz), 110.5 (d, $^4J_F = 2.9$ Hz), 108.3 (d, $^2J_F = 21.3$ Hz), 102.6 (d, $^2J = 24.9$ Hz), 66.7, 44.8; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{29}H_{24}O_4F_4$ *m/e* 512.161073, found 512.161401. Anal. Calcd for $C_{29}H_{24}F_4O_4$: C, 67.96; H, 4.72. Found: C, 67.53; H, 4.88.

Tetrakis[(4-nitrophenoxy)methyl]methane (8).[25] A mixture of pentaerythrityl tetratosylate (48.1 g, 63.9 mmol)[24] and sodium 4-nitrophenolate (51.4 g, 319 mmol) in anhydrous ethanol (500 mL) was heated in a sealed tube at 170 °C for 20 h. The mixture was cooled and filtered to separate a solid, which was washed first with water until the washings were no longer yellow and then with methanol. The solid was crystallized twice from DMSO to afford pure tetrakis[(4-nitrophenoxy)methyl]methane (**8**; 28.3 g, 45.6 mmol, 71%) as small light-brown crystals: mp 274−275 °C (lit.[25] mp 274 °C); IR (KBr) 3108, 3080, 2959, 1608, 1592, 1514, 1497, 1461, 1343, 1251, 1174, 1111, 1050, 1032, 852, 755, 690, 657 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 373 K) δ 8.18 (d, $^3J = 9.2$ Hz, 8H), 7.21 (d, $^3J = 9.2$ Hz, 8H), 4.52 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6, 373 K) δ 162.9, 141.2, 124.8, 114.8, 67.1, 44.4; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 621 (M + 1). Anal. Calcd for $C_{29}H_{24}N_4O_{12}$: C, 56.13; H, 3.90; N, 9.03. Found: C, 55.98; H, 3.81; N, 8.98.

General Procedure for Synthesizing Substituted Pentaerythrityl Tetraphenyl Ethers 9−22. A stirred mixture of pentaerythrityl tetratosylate (4.00 g, 5.31 mmol),[24] a substituted phenol (26.6 mmol), and NaOH (1.06 g, 26.5 mmol) in DMF (20 mL) was heated at reflux for 16 h. DMF was then removed by distillation under reduced pressure, and a 3:1 mixture of water/methanol (100 mL) was added to the residue. The resulting solid was separated by filtration, washed with water and methanol, dried under vacuum, and then crystallized to afford the desired substituted pentaerythrityl tetraphenyl ether.

Tetrakis[(3-nitrophenoxy)methyl]methane (9). The product was synthesized from 3-nitrophenol by the general procedure summarized above and crystallized from DMSO to give tetrakis[(3-nitrophenoxy)methyl]methane (**9**; 2.75 g, 4.43 mmol, 83%) as beige crystals: mp 192 °C; IR (KBr) 3098, 2937, 1616, 1582, 1521, 1460, 1351, 1246, 1026, 1013, 819, 736, 668 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.78 (s, 4H), 7.77 (d, $^3J = 8.3$ Hz, 4H), 7.53 (dd, $^3J = 8.5$ Hz, $^3J = 8.3$ Hz, 4H), 7.46 (d, $^3J = 8.5$ Hz, 4H), 4.49 (s, 8H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.9, 148.6, 130.7, 122.0, 115.9, 109.2, 66.6, 44.8; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 621 (M + 1). Anal. Calcd for $C_{29}H_{24}N_4O_{12}$: C, 56.13; H, 3.90; N, 9.03. Found: C, 55.95; H, 3.86; N, 9.04.

Tetrakis[(4-chlorophenoxy)methyl]methane (10).[15] The product was synthesized from 4-chlorophenol by the general procedure summarized above and crystallized from benzene/methanol to provide tetrakis[(4-chlorophenoxy)methyl]methane (**10**; 2.54 g, 4.39 mmol, 83%) as colorless crystals: mp 141−142 °C (lit.[15] mp 141−142 °C); IR (KBr) 3071, 2938, 2888, 1595, 1580, 1491, 1467, 1288, 1240, 1167, 1090, 1055, 1037, 824, 712, 672, 505 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, $^3J = 9.1$ Hz, 8H), 6.84 (d, $^3J = 9.1$ Hz, 8H), 4.29 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 129.6, 126.3, 116.1, 67.0, 45.0; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 576. Anal. Calcd for $C_{29}H_{24}Cl_4O_4$: C, 60.22; H, 4.18. Found: C, 60.07; H, 4.19.

Tetrakis[(3-chlorophenoxy)methyl]methane (11). The product was synthesized from 3-chlorophenol by the general procedure summarized above and crystallized from benzene/methanol to produce tetrakis[(3-chlorophenoxy)methyl]methane (**7**; 2.50 g, 4.32 mmol, 81%) as colorless crystals: mp 83 °C; IR (KBr) 3064, 2940, 2887, 1595, 1577, 1484, 1463, 1428, 1308, 1243, 1152, 1096, 1052, 1038, 888, 841, 773, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, $^3J = 8.3$ Hz, 4H), 6.95 (d, $^3J = 8.3$ Hz, 4H), 6.94 (s, 4H), 6.81 (d, $^3J = 8.3$ Hz, 4H), 4.31 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 135.1, 130.5, 121.6, 115.2, 113.3, 66.6, 44.8; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 576. Anal. Calcd for $C_{29}H_{24}Cl_4O_4$: C, 60.22; H, 4.18. Found: C, 59.89; H, 4.20.

Tetrakis[(4-bromophenoxy)methyl]methane (12).[15] The product was synthesized from 4-bromophenol by the general procedure summarized above and crystallized from benzene/hexane to afford tetrakis[(4-bromophenoxy)methyl]methane (**12**; 3.28 g, 4.34 mmol, 82%) as colorless crystals: mp 153−154 °C (lit.[15] mp 153−157 °C); IR (KBr) 3095, 2927, 2880, 1591, 1579, 1486, 1463, 1452, 1286, 1233, 1172, 1071, 1026, 1001, 826, 810, 677, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, $^3J = 8.9$ Hz, 8H), 6.81 (d, $^3J = 8.9$ Hz, 8H), 4.31 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 132.5, 116.6, 113.7, 66.8, 44.9; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 752. Anal. Calcd for $C_{29}H_{24}Br_4O_4$: C, 46.07; H, 3.20. Found: C, 46.16; H, 3.20.

Tetrakis[(3-bromophenoxy)methyl]methane (13). The product was synthesized from 3-bromophenol by the general procedure summarized above and crystallized from benzene/hexane to give tetrakis[(3-bromophenoxy)methyl]methane (**9**; 3.50 g, 4.63 mmol, 87%) as colorless crystals: mp 120−121 °C; IR (KBr) 3059, 2938, 2885, 1594, 1573, 1479, 1462, 1424, 1306, 1239, 1154, 1036, 866, 842, 774, 677 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.09 (m, 12H), 6.86 (d, $^3J = 8.0$ Hz, 4H), 4.30 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 130.8, 124.6, 123.1, 118.1, 113.8, 66.6, 44.9; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 752. Anal. Calcd for $C_{29}H_{24}Br_4O_4$: C, 46.07; H, 3.20. Found: C, 45.88; H, 3.10.

Tetrakis[(2-bromophenoxy)methyl]methane (14). The product was synthesized from 2-bromophenol by the general procedure summarized above and crystallized from benzene/hexane to provide tetrakis[(2-bromophenoxy)methyl]methane (**14**; 3.03 g, 4.01 mmol, 76%) as colorless crystals: mp 119 °C; IR (KBr) 3063, 2941, 2883, 1585, 1572, 1482, 1463, 1441, 1278, 1245, 1054, 1030, 747, 665 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, $^3J = 7.9$ Hz, $^4J = 1.5$ Hz, 4H), 7.28 (ddd, $^3J = 8.3$, $^3J = 7.6$ Hz, $^4J = 1.5$ Hz, 4H), 7.03 (dd, $^3J = 8.3$ Hz, $^4J = 1.3$ Hz, 4H), 6.85 (ddd, $^3J = 7.9$, $^3J = 7.6$ Hz, $^4J = 1.3$ Hz, 4H), 4.62 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 133.3, 128.8, 122.4, 113.6, 112.5, 67.6, 46.1; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 752. Anal. Calcd for $C_{29}H_{24}Br_4O_4$: C, 46.07; H, 3.20. Found: C, 46.49; H, 3.20.

Tetrakis[(4-iodophenoxy)methyl]methane (15). The product was synthesized from 4-iodophenol by the general procedure summarized above and crystallized from benzene/methanol to produce tetrakis[(4-iodophenoxy)methyl]methane (**15**; 4.03 g, 4.27 mmol, 80%) as colorless crystals: mp 163 °C; IR (KBr) 3063, 2936, 2884, 1584, 1484, 1465, 1282, 1238, 1173, 1049, 1001, 811, 683, 633, 504 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, $^3J = 8.6$ Hz, 8H), 6.68 (d, $^3J = 8.6$ Hz, 8H), 4.26 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 138.5, 117.2, 83.6, 66.7, 44.9; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 944. Anal. Calcd for $C_{29}H_{24}I_4O_4$: C, 36.89; H, 2.56. Found: C, 36.52; H, 2.43.

Tetrakis[(3-iodophenoxy)methyl]methane (16). The product was synthesized from 3-iodophenol by the general procedure summarized above and crystallized from benzene/methanol to afford tetrakis[(3-iodophenoxy)methyl]methane (**16**; 4.47 g, 4.73 mmol, 89%) as colorless crystals: mp 134−135 °C; IR (KBr) 3078, 3051, 2933, 2882, 1587, 1567, 1476, 1460, 1417, 1303, 1236, 1157, 1033, 989, 854, 843, 774, 677 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.28 (m, 8H), 7.00 (dd, $^3J = 8.1$, $^3J = 7.9$ Hz, 4H), 6.88 (dd, $^3J = 8.1$ Hz, $^4J = 1.8$ Hz, 4H), 4.27 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 131.0, 130.6, 124.0, 114.4, 94.6, 66.5, 44.9; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 944. Anal. Calcd for $C_{29}H_{24}I_4O_4$: C, 36.89; H, 2.56. Found: C, 37.03; H, 2.44.

Tetrakis[(4-cyanophenoxy)methyl]methane (17).[26] The product was synthesized from 4-cyanophenol by the general procedure summarized above and crystallized from 2-methoxyethanol to afford tetrakis[(4-cyanophenoxy)methyl]methane (**17**; 2.58 g, 4.77 mmol, 90%) as colorless crystals: mp 217−218 °C (lit.[26] mp 222−224 °C); IR (KBr) 3100, 3071, 2944, 2895, 2229, 1603, 1574, 1509, 1469, 1308, 1250, 1172, 1113, 1046, 1026, 839, 549 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, $^3J = 8.7$ Hz, 8H), 6.99 (d, $^3J = 8.7$ Hz, 8H), 4.41 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 134.3, 119.0, 115.4, 105.3, 66.5, 44.7; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 541 (M + 1). Anal. Calcd for $C_{33}H_{24}N_4O_4$: C, 73.32; H, 4.48; N, 10.36. Found: C, 73.05; H, 4.57, N, 10.32.

Tetrakis[(3-cyanophenoxy)methyl]methane (18). The product was synthesized from 3-cyanophenol by the general procedure summarized above and crystallized from benzene/hexane to give tetrakis[(3-cyanophenoxy)methyl]methane (**18**; 2.64 g, 4.88 mmol, 92%) as colorless crystals: mp 151−152 °C; IR (KBr) 3075, 3034, 2948, 2231, 1598, 1491, 1464, 1430, 1330, 1289, 1259, 1165, 1026, 939, 849, 787, 688 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, $^3J = 8.1$ Hz, $^3J = 7.8$ Hz, 4H), 7.29 (d, $^3J = 7.8$ Hz, 4H), 7.19 (s, 4H), 7.17 (d, $^3J = 8.1$ Hz, 8H), 4.38 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 130.7, 125.5, 120.0, 118.5, 117.7, 113.6, 66.5, 44.9; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 541 (M + 1). Anal. Calcd for $C_{33}H_{24}N_4O_4$: C, 73.32; H, 4.48; N, 10.36. Found: C, 73.01; H, 4.42, N, 10.35.

Tetrakis[(4-formylphenoxy)methyl]methane (19).[20] The product was synthesized from 4-hydroxybenzaldehyde under an inert atmosphere of N_2 by the general procedure summarized above and crystallized from benzene/hexane to afford tetrakis[(4-formylphenoxy)methyl]methane (**19**; 2.06 g, 3.73 mmol, 70%) as colorless crystals: mp 178−179 °C (lit.[20] mp 179−180 °C; IR (KBr) 3067, 2943, 2827, 2804, 2727, 1689, 1600, 1577, 1508, 1316, 1245, 1214, 1159, 1054, 1036, 870, 834, 683, 618 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 4H), 7.82 (d, $^3J = 8.7$ Hz, 8H), 7.06 (d, $^3J = 8.7$ Hz, 8H), 4.50 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 163.3, 132.0, 130.5, 114.6, 66.7, 44.8; MS (FAB, 3-nitrobenzyl alcohol) 553 (M + 1); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{33}H_{29}O_8$ *m*/*e* 553.18622, found 553.18736 (M + 1). Anal. Calcd for $C_{33}H_{28}O_8$: C, 71.73; H, 5.11. Found: C, 71.35; H, 5.07.

3,5-Dibromophenol (23).[28] A solution of 1,3,5-tribromobenzene (20.0 g, 63.5 mmol) in diethyl ether (300 mL) was stirred at −78 °C under N_2 and treated dropwise with butyllithium (25.4 mL, 2.50 M in hexane, 63.5 mmol). The resulting mixture was kept at −78 °C for 45 min, and then $B(OCH_3)_3$ (10.7 mL, 95.5 mmol) was added dropwise. The mixture was stirred at −78 °C for 20 min, and then the temperature was allowed to rise to 25 °C. After addition of aqueous HCl (1 N, 50 mL), the organic phase was separated, and volatiles were removed by evaporation under reduced pressure. The solid residue was dissolved in aqueous NaOH (1 N, 250 mL), the resulting solution was stirred and treated dropwise at 0 °C with aqueous H_2O_2 (50 mL, 30% w/w), and stirring was continued until no more gas was evolved (3 h). The mixture was then filtered, and the pH was reduced to 2 by addition of aqueous HCl (6 N). The acidified mixture was extracted twice with CH_2Cl_2, and the organic layers were combined and dried over Na_2SO_4. Removal of volatiles by evaporation under reduced pressure left a residue of 3,5-dibromophenol (**23**; 12.2 g, 48.4 mmol, 76%) as an off-white solid: mp 79 °C (lit.[28b] mp 80 °C; lit.[28c] mp 76−79 °C); IR (KBr) 3200 (b), 3063, 2941, 2884, 1585, 1573, 1481, 1462, 1441, 1279, 1244, 1053, 1029, 841, 747, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, $^4J = 1.6$ Hz, 1H), 6.96 (d, $^4J = 1.6$ Hz, 2H), 5.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 126.8, 123.3, 118.1; MS (MAB) calcd for $C_6H_4Br_2O$ *m*/*e* 249.86334, found 249.86337. Anal. Calcd for $C_6H_4Br_2O$: C, 28.61; H, 1.60. Found: C, 28.64; H, 1.44.

3,5-Diiodophenol (24).[29] A sample of 1,3,5-triiodobenzene (3.00 g, 6.58 mmol) was subjected to the same procedure used to synthesize 3,5-dibromophenol (**23**). Crystallization of the crude product from $CHCl_3$ provided 3,5-diiodophenol (**24**; 1.57 g, 4.54 mmol, 69%) as colorless crystals: mp 103−104 °C (lit.[29] mp 102−104 °C); IR (KBr) 3200 (b), 3070, 1576, 1558, 1410, 1212, 874, 841, 712, 665 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.19 (s, 2H), 4.75(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 138.1, 124.5, 94.8; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 346. Anal. Calcd for $C_6H_4I_2O$: C, 20.83; H, 1.17. Found: C, 20.90; H, 1.04.

Tetrakis[(3,5-dibromophenoxy)methyl]methane (20). The product was synthesized from pentaerythrityl tetratosylate (2.00 g, 2.66 mmol),[24] 3,5-dibromophenol (**23**; 3.35 g, 13.3 mmol), and NaOH (0.531 g, 13.3 mmol) by the general procedure summarized above. The crude product was crystallized from benzene/hexane to give tetrakis[(3,5-dibromophenoxy)methyl]methane (**20**; 1.80 g, 1.68 mmol, 63%) as colorless crystals: mp 196 °C; IR (KBr) 3086, 2936, 2886, 1583, 1561, 1435, 1418, 1251, 1228, 1053, 1038, 895, 828, 745, 662 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, $^4J = 1.3$ Hz, 4H), 7.02 (d, $^4J = 1.3$ Hz, 8H), 4.24 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 127.6, 123.5, 117.2, 66.5, 45.0; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 1072. Anal. Calcd for $C_{29}H_{20}Br_8O_4$: C, 32.50; H, 1.88. Found: C, 32.69; H, 1.79.

Tetrakis[(3,5-diiodophenoxy)methyl]methane (21). The product was synthesized from pentaerythrityl tetratosylate (392 mg, 0.521 mmol),[24] 3,5-diiodophenol (**24**; 900 mg, 2.60 mmol), and NaOH (104 mg, 2.60 mmol) by the general procedure summarized above. The crude product was crystallized from benzene/methanol to provide tetrakis[(3,5-diiodophenoxy)methyl]methane (**21**; 601 mg, 0.415 mmol, 80%) as beige crystals of a 2:1 solvate with benzene: mp 226 °C; IR (KBr) 3066, 2938, 2881, 1570, 1546, 1427, 1411, 1254, 1224, 1035, 876, 827, 708, 679, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, ^4J = 1.3 Hz, 4H), 7.37 (s, Ph-H), 7.22 (d, ^4J = 1.3 Hz, 8H), 4.18 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 138.7, 128.6 (Ph-H), 123.7, 94.9, 66.4, 45.1; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 1448. Anal. Calcd for $C_{29}H_{20}I_8O_4{\cdot}0.5\ C_6H_6$: C, 25.85; H, 1.56. Found: C, 25.93; H, 1.47.

Tetrakis[(3,5-dimethoxyphenoxy)methyl]methane (22). The product was synthesized from 3,5-dimethoxyphenol (4.10 g, 26.6 mmol) by the general procedure summarized above. The crude product was crystallized from benzene/methanol to afford tetrakis[(3,5-dimethoxyphenoxy)methyl]methane (**22**; 2.53 g, 3.72 mmol, 70%) as colorless crystals: mp 107 °C; IR (KBr) 3005, 2951, 2841, 1621, 1593, 1476, 1426, 1194, 1147, 1064, 818, 681 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (d, ^3J = 1.3 Hz, 8H), 6.11 (t, ^3J = 1.3 Hz, 4H), 4.31 (s, 8H), 3.78 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 160.9, 93.7, 93.6, 66.7, 55.5, 44.7; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 681 (M + 1). Anal. Calcd for $C_{37}H_{44}O_{12}$: C, 65.28; H, 6.52. Found: C, 65.19; H, 6.55.

Tetrakis[[(4′-bromo-1,1′-biphenyl-4-yl)oxy]methyl]methane (25). A mixture of pentaerythrityl tetratosylate (2.00 g, 2.66 mmol),[24] 4′-bromo-4-hydroxybiphenyl (3.31 g, 13.3 mmol), and NaOH (0.532 g, 13.3 mmol) in DMF (20 mL) was heated at reflux for 36 h. The mixture was allowed to cool, water (200 mL) was added, and the resulting precipitate was separated by filtration and washed with water and methanol. The crude solid was crystallized from benzene to give tetrakis[[(4′-bromo-1,1′-biphenyl-4-yl)oxy]methyl]methane (**25**; 2.32 g, 2.19 mmol, 82%) as colorless crystals: mp 190−191 °C; IR (KBr) 3035, 2949, 1605, 1516, 1481, 1466, 1238, 1174, 1038, 999, 811, 736, 504 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, ^3J = 8.5 Hz, 8H), 7.47 (d, ^3J = 8.8 Hz, 8H), 7.39 (d, ^3J = 8.5 Hz, 8H), 7.02 (d, ^3J = 8.8 Hz, 8H), 4.45 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 139.8, 133.2, 132.0, 128.5, 128.2, 121.1, 115.3, 66.8, 45.1; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 1056. Anal. Calcd for $C_{53}H_{40}Br_4O_4$: C, 60.03; H, 3.80. Found: C, 60.22; H, 3.71.

Tetrakis[[(4′-iodo-1,1′-biphenyl-4-yl)oxy]methyl]methane (26). A mixture of pentaerythrityl tetratosylate (0.578 g, 0.768 mmol),[24] 4-hydroxy-4′-iodobiphenyl (1.00 g, 3.38 mmol), K_2CO_3 (0.467 g, 3.38 mmol), and tetrabutylammonium bromide (0.272 g, 0.841 mmol) in DMF (12 mL) was heated at reflux for 36 h. The mixture was allowed to cool, water (200 mL) was added, and the resulting precipitate was separated by filtration and washed with water and methanol. The crude solid was crystallized from benzene to produce tetrakis[[(4′-iodo-1,1′-biphenyl-4-yl)oxy]methyl]methane (**26**; 0.789 g, 0.632 mmol, 82%) as colorless crystals: mp 221 °C; IR (KBr) 3034, 2933, 2879, 1605, 1515, 1479, 1466, 1239, 1174, 997, 807 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, ^3J = 8.5 Hz, 8H), 7.47 (d, ^3J = 8.8 Hz, 8H), 7.26 (d, ^3J = 8.5 Hz, 8H), 7.02 (d, ^3J = 8.8 Hz, 8H), 4.44 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 140.4, 138.0, 133.2, 128.8, 128.2, 115.3, 92.5, 66.8, 45.1; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 1248. Anal. Calcd for $C_{53}H_{40}I_4O_4$: C, 50.99; H, 3.23. Found: C, 51.23; H, 3.16.

Tetrakis[[(4′-cyano-1,1′-biphenyl-4-yl)oxy]methyl]methane (27). The crude product was prepared from pentaerythrityl tetratosylate (1.54 g, 2.05 mmol),[24] 4-cyano-4′-hydroxybiphenyl (2.00 g, 10.2 mmol), and NaOH (0.410 g, 10.2 mmol) by the method described above for compound **25**. Crystallization from 2-methoxyethanol gave tetrakis[[(4′-cyano-1,1′-biphenyl-4-yl)oxy]methyl]methane (**27**; 1.54 g, 1.82 mmol, 89%) as colorless crystals: mp 167−168 °C; IR (KBr) 3040, 2940, 2225, 1603, 1494, 1462, 1241, 1179, 1032, 1001, 820, 531 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, ^3J = 8.3 Hz, 8H), 7.63 (d, ^3J = 8.3 Hz, 8H), 7.54 (d, ^3J = 8.7 Hz, 8H), 7.08 (d, ^3J = 8.7 Hz, 8H), 4.49 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 145.2, 132.8, 132.4, 128.6, 127.3, 119.2, 115.5, 110.5, 66.7, 45.1; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 845 (M + 1). Anal. Calcd for $C_{57}H_{40}N_4O_4$: C, 81.02; H, 4.77; N, 6.63. Found: C, 81.02; H, 4.97; N, 6.27.

Tetrakis[[(4′-nitro-1,1′-biphenyl-4-yl)oxy]methyl]methane (28). The crude product was prepared from pentaerythrityl tetratosylate (1.40 g, 1.86 mmol),[24] 4-hydroxy-4′-nitrobiphenyl (2.00 g, 9.29 mmol), and NaOH (0.372 g, 9.30 mmol) by the method described above for compound **25**. Crystallization from DMF afforded tetrakis[[(4′-nitro-1,1′-biphenyl-4-yl)oxy]methyl]methane (**28**; 1.60 g, 1.73 mmol, 93%) as orange crystals: mp 233 °C; IR (KBr) 3072, 2940, 2885, 1595, 1518, 1340, 1243, 1176, 1109, 1041, 856, 825, 756 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (d, ^3J = 9.0 Hz, 8H), 7.86 (d, ^3J = 9.0 Hz, 8H), 7.72 (d, ^3J = 8.9 Hz, 8H), 7.16 (d, ^3J = 8.9 Hz, 8H), 4.44 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.4, 146.1, 146.0, 130.3, 128.6, 127.0, 124.0, 115.5, 66.1, 44.7. Anal. Calcd for $C_{53}H_{40}N_4O_{12}$: C, 68.83; H, 4.36; N, 6.06. Found: C, 68.74; H, 4.31; N, 6.13.

Tetrakis[(4-aminophenoxy)methyl]methane (29).[25] A suspension of tetrakis[(4-nitrophenoxy)methyl]methane (**8**; 15.4 g, 24.8 mmol) and 10% Pd/C (1.58 g) in THF (400 mL) was stirred for 70 h at 25 °C under an atmosphere of H_2 (180 psi) in a Parr reactor. The resulting mixture was filtered through Celite, and volatiles were removed from the filtrate by evaporation under reduced pressure. This yielded a residue of tetrakis[(4-aminophenoxy)methyl]methane (**29**; 12.3 g, 24.6 mmol, 99%) as a colorless solid, which was used without any further purification. Small beige crystals of analytical purity could be grown by slow evaporation of solutions in THF: mp 210−211 °C (lit.[25] mp 205−207 °C); IR (KBr) 3434, 3351, 3050, 2932, 2881, 1625, 1511, 1468, 1232, 1060, 1041, 832, 523 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.66 (d, ^3J = 8.4 Hz, 8H), 6.47 (d, ^3J = 8.4 Hz, 8H), 4.62 (s, 8H), 4.03 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.1, 142.7, 115.8, 114.9, 67.1, 44.6; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 500; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{29}H_{32}O_4N_4$ *m/e* 500.24237, found 500.24150. Anal. Calcd for $C_{29}H_{32}N_4O_4$: C, 69.58; H, 6.44; N, 11.19. Found: C, 69.33; H, 6.78; N, 10.91.

Tetrakis[(3-aminophenoxy)methyl]methane (30). A similar procedure converted tetrakis[(3-nitrophenoxy)methyl]methane (**9**; 2.40 g; 3.87 mmol) into tetrakis[(3-aminophenoxy)methyl]methane (**30**; 1.91 g, 3.82 mmol, 99%). Orange crystals of analytical purity were obtained by crystallization from toluene: mp 112 °C; IR (KBr) 3429, 3338, 3211, 3041, 2935, 2885, 1625, 1601, 1494, 1459, 1334, 1289, 1189, 1159, 1041, 835, 763, 686 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.87 (t, ^3J = 8.0 Hz, 4H), 6.20−6.08 (m, 12H), 5.04 (s, 8H), 4.10 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.6, 150.0, 129.6, 107.1, 102.1, 99.9, 65.7, 43.9; MS (FAB, thioglycerol) *m/e* 501 (M + 1); HRMS (FAB, thioglycerol) calcd for $C_{29}H_{33}O_4N_4$ *m/e* 501.25018, found 501.24900 (M + 1). Anal. Calcd for $C_{29}H_{32}N_4O_4$: C, 69.58; H, 6.44; N, 11.19. Found: C, 69.77; H, 6.65; N, 11.13.

Tetrakis[(4-isocyanatophenoxy)methyl]methane (31). A solution of triphosgene (1.82 g, 6.13 mmol) in dry THF (10 mL) was added dropwise under N_2 to a stirred solution of tetrakis[(4-aminophenoxy)methyl]methane (**29**; 2.05 g, 4.10 mmol) and triethylamine (4.57 mL, 32.8 mmol) in dry THF (70 mL) at −78 °C. The temperature of the resulting mixture was allowed to rise to 0 °C over 2 h, and solids were removed by filtration through Celite. Volatiles were removed from the filtrate by evaporation under reduced pressure to give tetrakis[(4-isocyanatophenoxy)methyl]methane (**31**; 2.34 g, 3.87 mmol, 94%) as a colorless solid, which was not subjected to further purification: mp 45 °C (softening); IR (KBr) 2945, 2887, 2279, 1524, 1457, 1240, 1172, 1054, 1034, 827, 558 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, ^3J = 8.8 Hz, 8H), 6.85 (d, ^3J = 8.8

Hz, 8H), 4.29 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 126.9, 126.1, 124.6, 116.0, 67.2, 44.9; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 604.

Tetrakis[(4-isothiocyanatophenoxy)methyl]methane (32). Thiophosgene (0.237 mL, 3.11 mmol) was added dropwise at −10 °C under N_2 to a stirred solution of tetrakis[(4-aminophenoxy)methyl]methane (**29**; 353 mg, 0.705 mmol) and triethylamine (0.79 mL, 5.7 mmol) in dry THF (12 mL). The temperature of the mixture was allowed to rise to 25 °C during 1 h, water was added, and the resulting solid was separated by filtration and washed with cold methanol. The crude product was crystallized from $CHCl_3$/hexane to provide tetrakis(4-isothiocyanatophenyl)methane (**32**; 379 mg, 0.567 mmol, 80%) as a colorless solid: mp 149−150 °C; IR (KBr) 3065, 2943, 2883, 2045(bs), 1602, 1580, 1503, 1465, 1301, 1244, 1167, 1055, 1036, 927, 831, 757, 637, 515 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, $^3J = 7.9$ Hz, 8H), 6.86 (d, $^3J = 7.9$ Hz, 8H), 4.31 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 134.5, 127.2, 124.6, 115.7, 66.8, 44.9; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 668. Anal. Calcd for $C_{33}H_{24}N_4O_4S_4\cdot H_2O$: C, 57.71; H, 3.82; N, 8.16; S, 18.67. Found: C, 57.74; H, 3.49; N. 8.22; S.18.57.

Tetrakis[[4-hydroxymethyl)phenoxy]methyl]methane (33). A solution of tetrakis[(4-formylphenoxy)methyl]methane (**19**; 3.11 g, 5.63 mmol) in methanol (100 mL) was stirred at −10 °C and treated with $NaBH_4$ (2.55 g, 67.4 mmol), added in small portions. The resulting mixture was stirred at 0 °C for 30 min and then at 25 °C for 7 h. The mixture was poured into cold water (600 mL), and the resulting precipitate was filtered, washed with water, and dried under vacuum. Crystallization from ethanol gave tetrakis[[(4-hydroxymethyl)phenoxy]methyl]methane (**33**; 2.57 g, 4.58 mmol, 81%) as a colorless solid: mp 136 °C; IR (KBr) 3260 (b), 2927, 2869, 1611, 1587, 1511, 1469, 1236, 1172, 1053, 1007, 825, 615 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.19 (d, $^3J = 8.5$ Hz, 8H), 6.92 (d, $^3J = 8.5$ Hz, 8H), 5.04 (t, $^3J = 5.5$ Hz, 4H), 4.38 (d, $^3J = 5.5$ Hz, 8H), 4.25 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.6, 135.0, 127.9, 114.3, 66.1, 62.5, 44.5; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 560. Anal. Calcd for $C_{33}H_{36}O_8$: C, 70.70; H, 6.47. Found: C, 70.73; H, 6.64.

Tetrakis[[(4-chloromethyl)phenoxy]methyl]methane (34). A stirred solution of tetrakis[[(4-hydroxymethyl)phenoxy]methyl]methane (**33**; 2.31 g, 4.12 mmol) in dioxane (60 mL) was treated dropwise with $SOCl_2$ (2.4 mL, 33 mmol) under N_2, and the mixture was then heated at reflux for 16 h. Volatiles were removed by evaporation under reduced pressure, and the residue was crystallized twice from benzene/hexane to give tetrakis[[(4-chloromethyl)phenoxy]methyl]methane (**34**; 2.11 g, 3.33 mmol, 81%) as off-white crystals: mp 170 °C; IR (KBr) 3044, 2935, 2882, 1610, 1512, 1472, 1305, 1239, 1172, 1063, 1046, 867, 834, 728, 656, 585 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, $^3J = 8.5$ Hz, 8H), 6.93 (d, $^3J = 8.5$ Hz, 8H), 4.58 (s. 8H), 4.38 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 130.4, 130.3, 115.0, 66.7, 46.4, 44.9; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 632. Anal. Calcd for $C_{33}H_{32}Cl_4O_4$: C, 62.48; H, 5.08. Found: C, 62.88; H, 5.08.

Tetraboronic Acid 35. A solution of tetrakis[(4-bromophenoxy)methyl]methane (**12**; 10.0 g, 13.2 mmol) in THF (300 mL) was stirred vigorously with a mechanical stirrer at −78 °C under dry N_2 and treated dropwise with a solution of butyllithium (26.5 mL, 2.50 M in hexane, 66.3 mmol). The resulting mixture was kept at −78 °C for 45 min, and then $B(O\text{-}i\text{Pr})_3$ (15.3 mL, 66.3 mmol) was added dropwise. The mixture was stirred at −78 °C for 20 min and warmed to 25 °C during 2 h. After addition of water (20 mL), the mixture was concentrated by partial evaporation of volatiles under reduced pressure. The concentrate was dissolved in aqueous NaOH (1 N, 200 mL), and the solution was washed with dichloromethane. Aqueous HCl (1 N) was then added until the pH was reduced to 2. The resulting precipitate was separated by filtration and dried to afford tetraboronic acid **35** (7.94 g, 12.9 mmol, 98%) as a colorless solid: mp >300 °C; IR (KBr) 3400−2800, 1602, 1409, 1351, 1235, 1183, 1015, 820, 648, 624, 526 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.79 (s, 8H), 7.70 (d, $^3J = 8.3$ Hz, 8H), 6.93 (d, $^3J = 8.3$ Hz, 8H), 4.30 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.4, 136.0, 126.1, 113.8, 65.8, 44.4; MS (FAB, 3-nitrobenzyl alcohol/ethylene glycol) *m*/*e* 720. Anal. Calcd for $C_{29}H_{32}B_4O_{12}\cdot 5\ H_2O$: C, 49.35; H, 6.00. Found: C, 48.94; H, 5.98.

Suzuki Coupling of Tetraboronic Acid 35 with 4-Bromobenzonitrile. Under N_2, deoxygenated water (15 mL) and acetonitrile (35 mL) were added to a deoxygenated mixture of tetraboronic acid **35** (1.34 g, 2.18 mmol), 4-bromobenzonitrile (1.98 g, 10.9 mmol), $Pd(PPh_3)_4$ (0.500 g, 0.433 mmol), and Na_2CO_3 (2.31 g, 21.8 mmol). The mixture was stirred at 80 °C for 72 h, water (200 mL) was added, and the resulting precipitate was separated by filtration. The crude solid was purified by flash chromatography (silica, $CH_3COOC_2H_5$ (35%)/hexane (65%), R_f 0.29) to give tetrakis[[(4′-cyano-1,1′-biphenyl-4-yl)oxy]methyl]methane (**27**; 1.36 g, 1.61 mmol, 74%) as a colorless solid.

Tetrakis[(4-carboxyphenoxy)methyl]methane (36).[31] A mixture of tetrakis[(4-cyanophenoxy)methyl]methane (**17**; 2.00 g, 3.70 mmol) and KOH (3.00 g, 53.5 mmol) in ethylene glycol (30 mL) was heated at reflux for 16 h. The solution was then cooled and acidified to pH 1 by the addition of aqueous HCl (1 N). The resulting precipitate was separated by filtration, washed with water, and dried under vacuum to provide tetrakis[(4-carboxyphenoxy)methyl]methane (**36**; 2.22 g, 3.60 mmol, 97%) as a colorless solid: mp >330 °C (lit.[31] mp >300 °C); IR (KBr) 3300−2500 (bs), 1683, 1604, 1428, 1302, 1245, 1173, 1043, 846, 769 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 12.62 (s, 4H), 7.86 (d, $^3J = 8.6$ Hz, 8H), 7.07 (d, $^3J = 8.6$ Hz, 8H), 4.40 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.9, 161.9, 131.3, 123.4, 114.4, 66.3, 44.2; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 613. Anal. Calcd for $C_{33}H_{28}O_{12}\cdot H_2O$: C, 62.46; H, 4.77. Found: C, 62.03; H, 4.61.

Tetrakis[(3-carboxyphenoxy)methyl]methane (37). A similar procedure converted tetrakis[(3-cyanophenoxy)methyl]methane (**18**; 493 mg, 0.912 mmol) into tetrakis[(3-carboxyphenoxy)methyl]methane (**37**; 538 mg, 0.873 mmol, 96%), which was obtained as a colorless solid: mp 302−303 °C; IR (KBr) 3300−2500 (bs), 1688, 1592, 1453, 1289, 1243, 1041, 756, 676 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 12.99 (s, 4H), 7.54−7.47 (m, 8H), 7.37 (dd, $^3J = 8.0$ Hz, $^3J = 7.9$ Hz, 4H), 7.24 (d, $^3J = 7.9$ Hz, 4H), 4.38 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1, 158.5, 132.2, 129.8, 122.0, 119.5, 114.9, 66.0, 44.4; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 613. Anal. Calcd for $C_{33}H_{28}O_{12}\cdot 1.5\ H_2O$: C, 61.59; H, 4.86. Found: C, 61.76; H, 4.48.

Tetrakis[[4-[(trimethylsilyl)ethynyl]phenoxy]methyl]methane (38). (Trimethylsilyl)acetylene (3.20 mL, 22.6 mmol) was added dropwise at 25 °C to a stirred mixture of tetrakis[(4-iodophenoxy)methyl]methane (**15**; 4.70 g, 4.98 mmol), CuI (0.0500 g, 0.263 mmol), and $PdCl_2(PPh_3)_2$ (0.340 g, 0.484 mmol) in deoxygenated triethylamine (60 mL). The black mixture was kept at 25 °C for 14 h, and volatiles were then removed by evaporation under reduced pressure. The solid residue was purified by flash chromatography (silica, CH_2Cl_2 (25%)/hexane (75%), R_f 0.24) to give tetrakis[[4-[(trimethylsilyl)ethynyl]phenoxy]methyl]methane (**38**; 3.77 g, 4.57 mmol, 92%) as a colorless solid: mp 143 °C; IR (KBr) 2956, 2149, 1603, 1506, 1247, 1232, 1030, 863, 843, 759, 542 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, $^3J = 8.8$ Hz, 8H), 6.82 (d, $^3J = 8.8$ Hz, 8H), 4.32 (s, 8H), 0.24 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 133.7, 116.1, 114.7, 105.2, 92.9. 66.8, 44.9, 0.3; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 825; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{49}H_{61}O_4Si_4$ *m*/*e* 825.36469, found 825.36470 (M + 1). Anal. Calcd for $C_{49}H_{60}O_4Si_4$: C, 71.31; H, 7.33. Found: C, 71.07; H, 7.71.

Tetrakis[[3-[(trimethylsilyl)ethynyl]phenoxy]methyl]methane (39). A similar procedure transformed tetrakis[(3-iodophenoxy)methyl]methane (**16**; 1.75 g, 1.85 mmol), CuI (0.0176 g, 0.0924 mmol), $PdCl_2(PPh_3)_2$ (0.130 g, 0.185 mmol), and (trimethylsilyl)acetylene (1.18 mL, 8.35 mmol) into tetrakis[[3-[(trimethylsilyl)ethynyl]phenoxy]methyl]methane (**39**;

1.46 g, 1.77 mmol, 96%), which was obtained after flash chromatography (R_f 0.36) as a colorless solid: T_g (TGA) 46.2 °C; IR (KBr) 3072, 2959, 2897, 2158, 1597, 1574, 1469, 1284, 1250, 1174, 1156, 1034, 956, 842, 784, 759, 684, 645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, $^3J = 8.2$ Hz, $^3J = 7.7$ Hz, 4H), 7.07 (d, $^3J = 7.7$ Hz, 4H), 7.03 (s, 4H), 6.88 (d, $^3J = 8.2$ Hz, 4H), 4.31 (s, 8H), 0.26 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 129.5, 125.1, 124.3, 117.5, 116.0, 105.0, 94.3, 66.4, 44.9, 0.2; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{49}H_{60}O_4Si_4$ *m/e* 824.35687, found 824.35930. Anal. Calcd for $C_{49}H_{60}O_4Si_4$: C, 71.31; H, 7.33. Found: C, 71.07; H, 7.84.

Tetrakis[(4-ethynylphenoxy)methyl]methane (40). At 25 °C, tetrabutylammonium fluoride (1.0 M in THF, 20 mL, 20 mmol) was added to a stirred solution of tetrakis[[(4-[(trimethylsilyl)ethynyl]phenoxy]methyl]methane (**38**; 3.30 g, 4.00 mmol) in THF (50 mL). After 3 h water was added, and the product was extracted with $CH_3COOC_2H_5$. The extracts were dried over $MgSO_4$ and filtered through silica gel. Volatiles were then removed by evaporation under reduced pressure, and the residue was crystallized from $CH_3COOC_2H_5$/hexane to provide tetrakis[(4-ethynylphenoxy)methyl]methane (**40**; 2.04 g, 3.80 mmol, 95%) as a colorless solid: mp 174 °C; IR (KBr) 3296, 2942, 2893, 2109, 1602, 1506, 1471, 1290, 1244, 1169, 1050, 1029, 833, 609, 535 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, $^3J = 8.8$ Hz, 8H), 6.86 (d, $^3J = 8.8$ Hz, 8H), 4.34 (s, 8H), 3.01 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 133.8, 115.0, 114.8, 83.6, 76.3, 66.7, 44.8; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 536, 537; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{37}H_{29}O_4$ *m/e* 537.20660, found 537.20450 (M + 1). Anal. Calcd for $C_{37}H_{28}O_4$: C, 82.81; H, 5.26. Found: C, 82.82; H, 5.44.

Tetrakis[(3-ethynylphenoxy)methyl]methane (41). A similar procedure using tetrakis[[3-[(trimethylsilyl)ethynyl]-phenoxy]methyl]methane (**39**; 845 mg, 1.02 mmol) and tetrabutylammonium fluoride (1.0 M, 5.0 mL, 5.0 mmol) provided tetrakis[(3-ethynylphenoxy)methyl]methane (**41**; 515 mg, 0.960 mmol, 94%) as colorless crystals: mp 118−119 °C; IR (KBr) 3299, 3070, 2946, 2886, 2111, 1594, 1583, 1490, 1462, 1425, 1320, 1283, 1260, 1155, 1041, 858, 789, 686 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, $^3J = 8.2$ Hz, $^3J = 7.8$ Hz, 4H), 7.10 (d, $^3J = 7.8$ Hz, 4H), 7.07 (s, 4H), 6.92 (d, $^3J = 8.2$ Hz, 4H), 4.33 (s, 8H), 3.06 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 129.5, 125.1, 123.2, 117.8, 115.9, 83.4, 76.6, 66.4, 44.7; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 536, 537; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{37}H_{28}O_4$ *m/e* 536.198760, found 536.197948. Anal. Calcd for $C_{37}H_{28}O_4$: C, 82.81; H, 5.26. Found: C, 82.76; H, 5.31.

Tecton 3. A mixture of tetrakis[(4-cyanophenoxy)methyl]-methane (**17**; 2.58 g, 4.77 mmol), dicyandiamide (3.21 g, 38.2 mmol), and powdered KOH (1.07 g, 19.1 mmol) in 2-methoxyethanol (90 mL) was heated at reflux for 16 h. The resulting mixture was cooled to 25 °C, and water (100 mL) was added. The resulting precipitate was separated by filtration and washed thoroughly with hot water. The crude solid was crystallized from DMF and triturated with CH_3OH to give tecton **3** (3.98 g, 4.54 mmol, 95%) as a colorless solid: mp 210−212 °C; IR (KBr) 3500−2900 (bs), 1607, 1539, 1442, 1397, 1243, 1162, 1049, 815 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.20 (d, $^3J = 8.7$ Hz, 8H), 7.09 (d, $^3J = 8.7$ Hz, 8H), 6.67 (bs, 16H), 4.43 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.7, 167.4, 160.9, 129.9, 129.4, 114.1, 66.4, 44.1; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 877 (M + 1); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{41}H_{41}N_{20}O_4$ *m/e* 877.361965, found 877.362190 (M + 1).

Tecton 4. A similar procedure converted tetrakis[(3-cyanophenoxy)methyl]methane (**18**; 600 mg, 1.11 mmol) into tecton **4** (710 mg, 0.810 mmol, 73%), which was obtained as a colorless solid: mp 188−189 °C; IR (KBr) 3500−2900, 1609, 1540, 1446, 1422, 1389, 1236, 1143, 1023, 824, 795, 737, 683, 616 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87−7.81 (m, 8H), 7.34 (t, $^3J = 8.1$ Hz, 4H), 7.16 (d, $^3J = 8.1$ Hz, 4H), 6.76 (bs, 16H), 4.43 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.8, 167.4, 158.3, 138.7, 129.2, 120.6, 117.4, 113.2, 66.4, 44.3; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 877 (M + 1); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{41}H_{41}N_{20}O_4$ *m/e* 877.361965, found 877.361672 (M + 1).

Crystallization of Tectons 3 and 4. Single crystals suitable for X-ray diffraction were obtained by allowing dioxane to diffuse slowly into solutions of tectons **3** and **4** in DMSO during 1 week at 25 °C. Tecton **3** crystallized as aggregates of colorless needles, whereas tecton **4** gave colorless blocks.

X-ray Crystallographic Studies. Data were collected using a Bruker SMART 2000 diffractometer with Cu Kα radiation at 223 K. The structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.[43] All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in ideal positions and refined as riding atoms.

Structure of Tecton 3. Crystals of compound **3** belong to the orthorhombic space group $P2_12_12$ with $a = 25.711(2)$ Å, $b = 37.260(3)$ Å, $c = 10.0841(9)$ Å, $V = 9660.5(15)$ Å^3, $D_{\mathrm{calcd}} = 1.227$ g/cm^3, and $Z = 4$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.1242$, $R_w = 0.3075$, and $GoF = 1.244$ for 12458 reflections with $I > 2\sigma(I)$.

Structure of Tecton 4. Crystals of compound **4** belong to the tetragonal space group I_1/a with $a = b = 27.734(1)$ Å, $c = 10.4865(4)$ Å, $V = 8065.8(5)$ Å^3, $D_{\mathrm{calcd}} = 1.303$ g/cm^3, and $Z = 4$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0447$, $R_w = 0.1318$, and $GoF = 1.047$ for 3737 reflections with $I > 2\sigma(I)$.

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Supporting Information Available: ORTEP drawings and tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds **3** and **4**; ^{1}H and ^{13}C NMR spectra for compounds **3**, **4**, and **31**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structures* and *SHELXL-97, Program for the Refinement of Crystal Structures*; Universität Göttingen: Germany, 1997.