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# Synthesis and Topological Determination of Hexakis-Substituted 1,4-Ditritylbenzene and Nonakis-Substituted 1,3,5-Tritritylbenzene Derivatives: Building Blocks for Higher Supramolecular Assemblies

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**Keywords:** Supramolecular chemistry / Microporous materials / Nanostructures / Substitution reactions

Based on trityl moieties, novel organic building blocks have been prepared and structurally investigated. Substituted hexaphenyl-*p*-xylene (1,4-ditritylbenzene) as well as extended analogues thereof were prepared. Furthermore, a new family based on a 1,3,5-tritritylbenzene motif, connecting three trityl groups through a formal mesitylene unit, was developed. Both families were further converted through six- and nine-fold substitution reactions, respectively, to yield potent molecular building blocks for supramolecular assemblies.

## Introduction

Porous materials play a pivotal role in modern material chemistry.[1,2] Over the last decade, hybrid materials with new properties have been developed with the advent of metal organic frameworks (MOFs),[3,4] with hundreds of new structures exhibiting original properties, in particular gas-storage abilities.[5,6] In addition, purely organic, mostly amorphous materials consisting of supramolecular assemblies such as covalent organic frameworks (COFs),[7] porous organic polymers (POPs),[8,9] hyper-cross-linked polymers (HCPs),[10] and polymeric porous networks (PPNs),[11,12] have emerged. The advantages of these wholly organic structures are their low densities and their water-stability. In addition, late-stage functionalization is easily possible with these materials.[13]

The structures of all these networks are inherently linked to the shape and connectivity of the building blocks or tectons used.[14] Mostly rigid organic building blocks bearing various shapes (linear, triangular and tetrahedral), are being used, resulting in different 1-, 2-, and 3-D networks. The latter share a broad variety of functional groups, but differ in the connection pattern (metal coordination, hydrogen-bonding or covalent bonds). Networks made up entirely of covalent bonds, may be generated through various reactions such as click chemistry,[9a,15–17] cross-coupling,[11,15,18] or condensation reactions.[7]

To create 3-D networks, the "knots" should be non-planar ($sp^3$ type). Therefore, a lot of organic networks are composed of tetrahedral building blocks. In particular, symmetrically substituted tetraphenylmethanes (TPMs; **1-X**, Figure 1)[9,18,19] and related systems (silanes,[20] adamantanes[3,21,22]) serve as building blocks of choice. In some cases, this led to the generation of crystalline structures with defined pore-size distribution,[23] although crystallinity is not a prerequisite to obtain highly porous materials with a sharp pore-size distribution.[24] The availability of varying functional groups on these building blocks is of high interest for screening processes. The combination of building block shape, functional group, and connection partner as well as solvents, reaction conditions, and other parameters influence the structural properties and consequently the applications of the networks, for example, gas absorption capacity and selectivity for different gases.

In light of these developments, new building block architectures are highly desirable. In particular, structures bearing octahedral shape would generate unique frameworks. Some fullerene-based molecules are known to have this form.[25] Only a few ditritylbenzenes have been reported so far.[26–31] We were among the first to use them as sixfold connecting tectons.[32–34] To the best of our knowledge only two other purely organic structures bearing six anchor points have been reported so far;[35] one is a flexible hexaaniline[35a] and the second is based on rigid hexasubstituted centrohexaindanes.[35b,35c]

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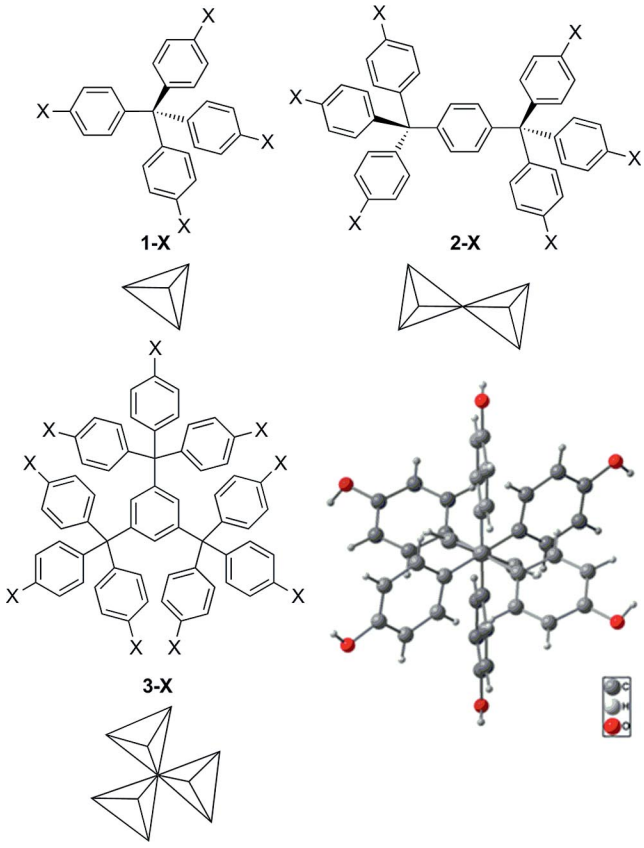



Figure 1. Tectons **1**–**3**-X based on a trityl substructure; X-ray structure of a HPX derivative **2**-OH.[32]

As a part of an ongoing nanostructure project, we are interested in easily accessible organic core structures[22,36] and, among others, in the generation of three-dimensional networks built up from organic DNA hybrid building blocks connected by Watson–Crick base pairing.[37,38] In this context, tetrakis(4-hydroxyphenyl)methane (**1**-OH) was used as a tetrahedral three-dimensional scaffold, the hydroxyl groups of which can be used to attach the DNA strands which act as sticky sites. Based on the first encouraging results obtained with this system,[37] expanded structures having a rigid three-dimensional motif and bearing additional hydroxyl groups, became of interest.[32] Thus, hexaphenyl-*p*-xylene (HPX) cores (**2**-X), namely 1,4-bis-[tris(4′-hydroxyphenyl)methyl]benzene (**2**-OH), first synthesized by Hatano and Kato in 2008,[26] came into focus. This molecule can be regarded as two TPM units linked through a shared phenyl ring (Figure 1).

Using an optimized synthetic procedure, we were able to obtain the pure material on a gram scale. We compared the ability to generate DNA-based networks of tectons **2**-OH and tetrakis(4-hydroxyphenyl)methane (**1**-OH).[32] The material generated by the expanded HPX building block showed different and promising properties compared with the TPM core. An X-ray analysis of tecton **2**-OH revealed a pseudo-octahedral structure in the solid state.[32] Indeed, three phenyl rings of the trityl moieties are oriented in a staggered manner when the molecule is observed along the phenylene axis.

To the best of our knowledge, the only other reported molecule of this type, in addition to the hexaalcohol **2**-OH,[26,32] is the unsubstituted 1,4-ditritylbenzene (**2**-H). Its synthesis was first described in 1957 by Benkeser and Schröder in small scale and in poor yield (9%) by reacting triphenylmethyl radicals with benzene.[29] Later, they devised a modular and high-yielding synthesis starting from dilithiobenzene and benzophenone.[30] Compound **2**-H was used as a reference molecule for their investigations of the Wieland reaction, involving trityl radicals. No further investigations, regarding derivatization reactions or structure modifications were reported. Interestingly, although three earlier patents exist, there is a general lack of original communications in this area.[31]

Tritritylarene cores **3**-X (nonaphenylmesitylenes; NPMs) can be seen as three TPM units linked through a shared phenyl ring (Figure 1). Each of these tectons offer nine anchor points for network generation and/or late-stage functionalization. To the best of our knowledge, such molecules have not yet been reported.

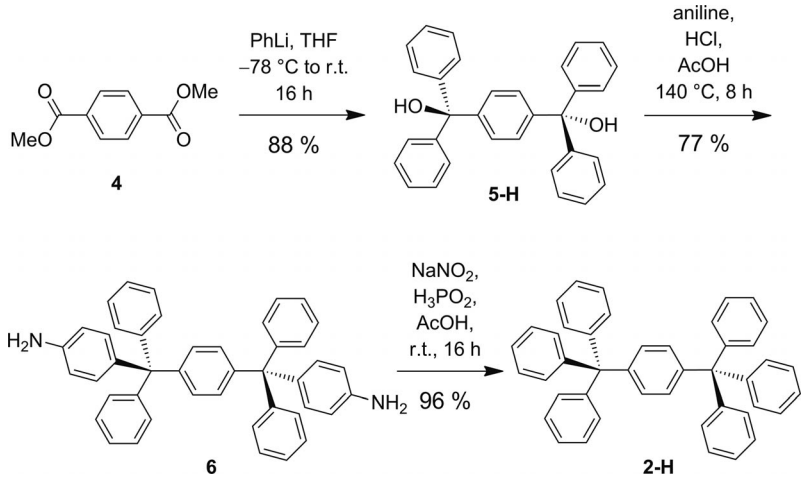
Herein, we report some new organic tectons exhibiting pseudo-octahedral structure (**2**-X; Figure 1) and novel expanded analogues thereof. In addition, we report synthetic access to the unprecedented 1,3,5-tritylbenzene (**3**-H) and its ninefold functionalization.

## Results and Discussion

We optimized the published synthesis of 1,4-ditritylbenzene (**2**-H) by performing the first step by reacting inexpensive and commercially available dimethyl terephthalate (**4**) with phenyllithium in 88% yield (Scheme 1). In the original publication, *p*-bis(diphenylhydroxymethyl)benzene (**5**-H) was obtained in only 25% yield.[30] The second step, the addition of **5**-H[39] to aniline in a Friedel–Crafts alkylation type reaction and subsequent removal of the amine group through diazotization and addition of a hydride donor, was carried out as described by Benkeser and Schröder (Scheme 1).[29,30]

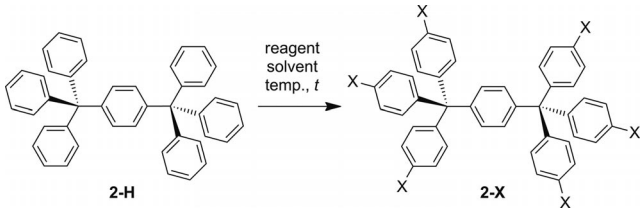
Thus, 1,4-ditritylbenzene (**2**-H) was readily available on a multigram scale in a good overall yield of 65%. With this HPX core in hand, we started investigating direct sixfold *para*-substitutions, in analogy to reactions performed on the TPM core.[16a,37] We explored five reactions, which delivered interesting key compounds for further derivatization reactions. The reaction conditions for these sixfold substitution reactions have to be chosen very carefully. On the one hand, the reaction has to go to completion to obtain the sixfold substituted derivative and to avoid less substituted species, which are very difficult to separate by classical purification methods. On the other hand, applying very harsh conditions can lead to the formation of byproducts such as *meta*- and poly-substituted derivatives. The results obtained under the optimized reaction conditions for these sixfold *para*-substitution reactions are summarized in Table 1.




Scheme 1. Optimized synthesis of unsubstituted 1,4-ditritylbenzene (**2**-H) in 65% overall yield.

Table 1. Sixfold substitutions starting from 1,4-ditritylbenzene (**2**-H).




| Entry | HPX | Reaction conditions | Yield [%] |
|---|---|---|---|
| 1 | **2**-Br | $Br_2$, room temp., 1 h | 92 |
| 2 | **2**-I | $I_2$, PIFA,[a] $CCl_4$, 60 °C, 6 d | 55 |
| 3 | **2**-$SO_3H$ | $ClSO_3H$, $CH_2Cl_2$, 35 °C, 90 min. | 46 |
| 4 | **2**-$NO_2$ | $HNO_3$, glacial acetic acid, 70 °C, 18 h | 21 |
| 5 | **2**-Ac[b] | AcCl, $AlCl_3$, $CS_2$, 75 °C, 18 h | 40 |

[a] Phenyliodine bis(trifluoroacetate). [b] Ac = $COCH_3$.

Hexabromide **2**-Br was obtained in pure form and excellent yield (92%) after simple recrystallization (Table 1, entry 1), as was hexaiodide **2**-I, albeit in only moderate 55% yield, mostly due to poor solubility in common organic solvents (Table 1, entry 2). This poor solubility was also observed for the hexasulfonic acid derivative **2**-$SO_3H$, which was obtained in pure form and 46% yield after simple washing of the crude reaction mixture (Table 1, entry 3).[40] The synthesis of the hexanitro derivative **2**-$NO_2$[41] is a good example showing the importance of the reaction conditions (Table 1, entry 4). When a mixture of $HNO_3$ (1 mL) in glacial acetic acid (15 mL) was used, the hexanitro compound was obtained in 21% yield after column chromatography. Performing the reaction in a different ratio of nitric and acetic acid led to byproducts that could not be separated from the desired HPX derivative **2**-$NO_2$ by standard purification methods. For the hexaacetyl derivative **2**-Ac, which could be obtained in 40% yield, *meta*-substituted phenyl rings were always formed irrespective of the reaction conditions used (Table 1, entry 5). This observation is in accordance with our investigations on the TPM cores. Ac-TPM was the only compound in the TPM series for which traces of *meta*-substituted byproducts could be detected.[42]

Single crystals of hexabromide **2**-Br and hexaiodide **2**-I were obtained and X-ray diffraction molecular structures of these HPXs were measured (Figure 2).[43] Both molecules showed the expected 3-D structure in the solid state, which

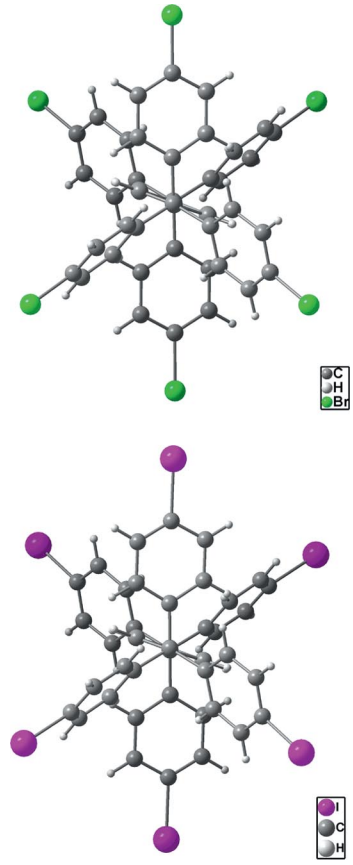



Figure 2. Molecular structure of hexabromide **2**-Br and hexaiodide **2**-I shown along the phenylene axis.

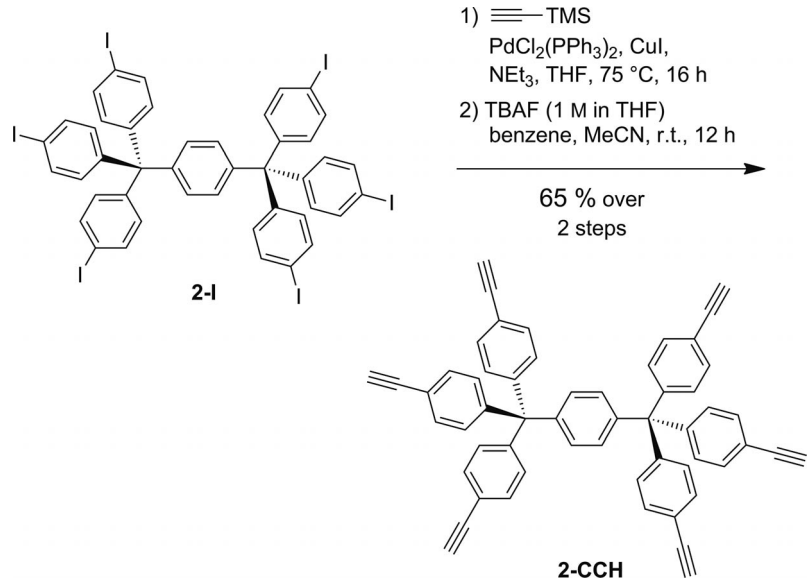
we previously reported for hexaalcohol **2**-OH. The three phenyl rings of the two trityl moieties are arranged in a staggered manner, leading to a pseudo-octahedral shape.

With these HPXs in hand, we investigated further derivatization reactions. Transformation of **2**-$NO_2$ into the corresponding hexamine was unsuccessful, and no conversion was observed when hexanitro derivative **2**-$NO_2$ was treated with hydrogen gas at atmospheric pressure and 12 bar, respectively, in the presence of palladium on charcoal (Pd/C), even under elevated temperatures (results not shown). **2**-Br and **2**-I served as starting materials for additional sixfold reactions. First, the well-established Sonogashira reaction was performed; in this palladium-catalyzed cross-coupling reaction, hexaiodide **2**-I was treated with trimethylsilylacetylene and the sixfold cross-coupling product was directly deprotected with tetrabutylammonium fluoride, yielding hexaalkyne **2**-CCH in 65% yield over two steps (Scheme 2).

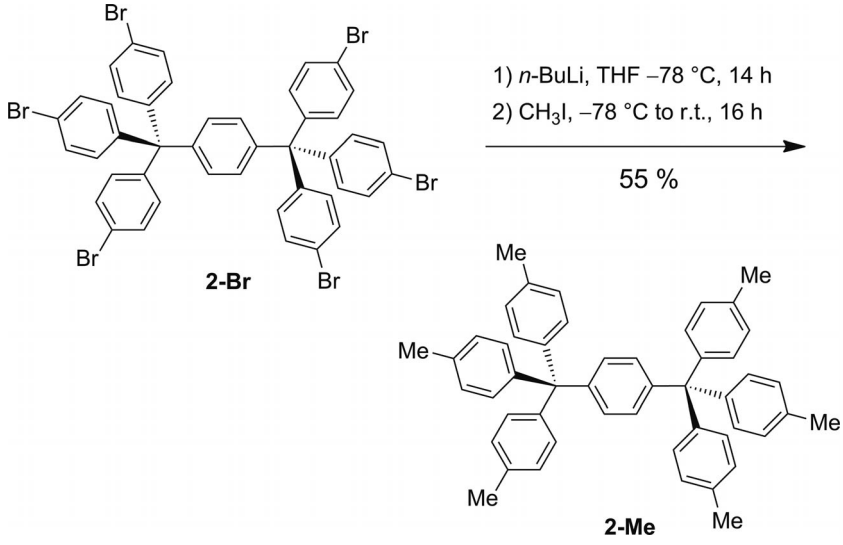
Hexaalkyne derivative **2**-CCH is expected to be a very important compound for modular syntheses such as cross-coupling reactions, click,[44] or thiol-yne[45] reactions.

Furthermore, we could successfully perform a sixfold lithiation[46] of hexabromide **2**-Br using *n*-butyllithium. The hexalithiated intermediate was treated with methyl iodide as electrophile, yielding 1,4-bis[tris(4′-methylphenyl)methyl]benzene (**2**-Me) in moderate yield after purification by column chromatography (Scheme 3). The sixfold lithiation and subsequent reaction with an electrophile using readily available hexabromide **2**-Br should give access to a broad variety of products.

After these encouraging results with hexabromide **2**-Br, we investigated the scope of the bromination reaction using

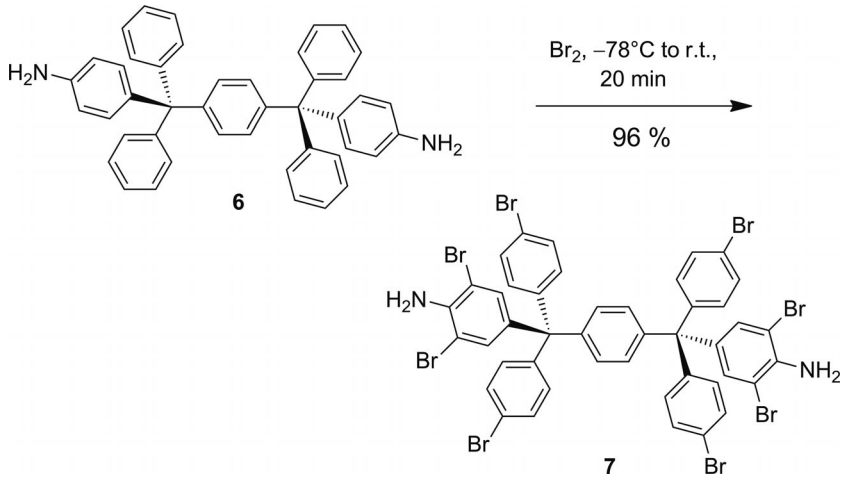



Scheme 2. Synthesis of 1,4-bis[tris(4′-ethynylphenyl)methyl]benzene (**2**-CCH) through sixfold Sonogashira cross-coupling reaction.




Scheme 3. Sixfold lithiation of hexabromide **2**-Br and reaction with methyl iodide as electrophile.

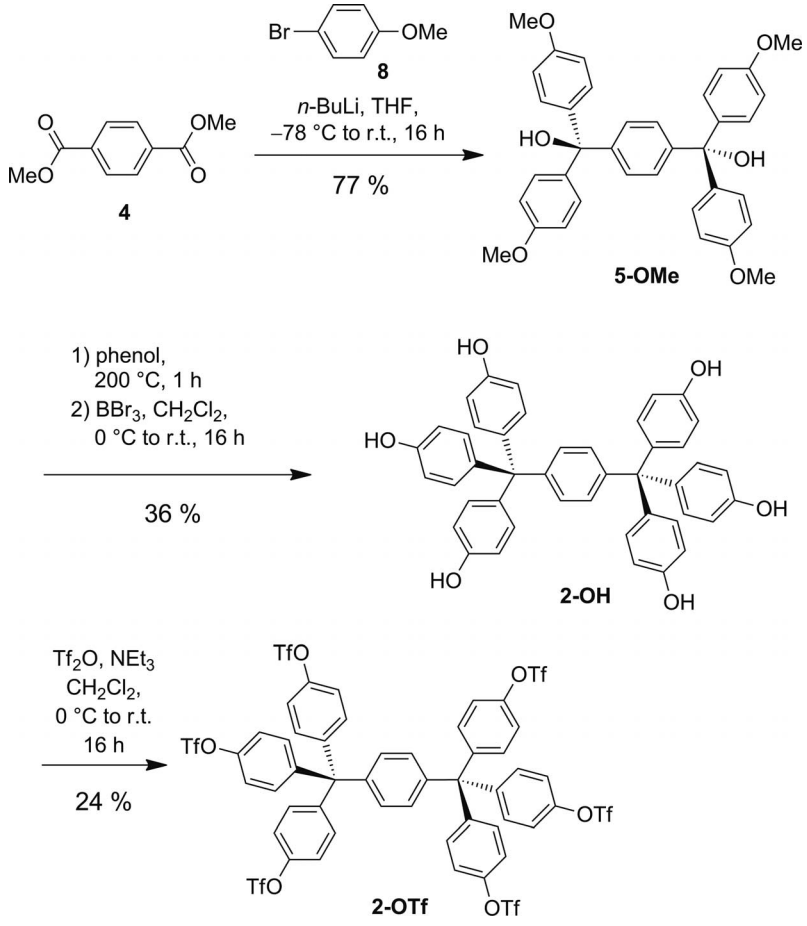
  




Scheme 4. Selective bromination of dianiline compound **6**.

dianiline compound **6**. The latter was selectively brominated in elementary bromine at room temperature within 20 min (Scheme 4). Pure compound **7** was obtained in 96% yield after simply washing the residue.

In addition to these reactions, hexaalcohol **2**-OH, prepared according the procedure depicted in Scheme 5 and published earlier,[32] could be converted into its triflate-protected form. Reaction with triflic anhydride led to the fully protected species **2**-OTf in 24% yield, showing that all hydroxyl groups are reactive in principle but giving low yields even for this simple reaction (Scheme 5). The low yield might be attributed to the solubility of hexaalcohol **2**-OH, which is generally very low both in organic solvents and in aqueous media. Although obtained in only poor yield, **2**-OTf is nevertheless a very interesting compound for further derivatization reactions. The molecular structure of **5**-OMe,




Scheme 5. Synthesis of 1,4-bis[tris(4′-hydroxyphenyl)methyl]benzene (**2**-OH) and subsequent sixfold triflate formation.

an intermediate in the synthesis of hexaalcohol and -triflate, was determined and shows once more the pseudo-octahedral shape of this class of compounds (Figure 3).

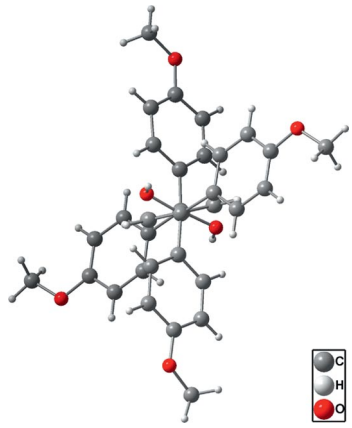



Figure 3. Molecular structure of compound **5**-OMe, which is a precursor of hexaalcohol **2**-OH.

We next turned to an expanded series of the HPX core, which was synthesized using phenylacetylene spacers. The so-called HPXXL system was designed to have additional spacers formally enlarging every C–aryl bond by a phenylacetylene unit when compared to the HPX skeleton. This enlargement is thought to reduce the steric hindrance at the trityl moieties, leaving more space for the attachment of larger sticky sites. Two main advantages are expected to arise from this enlargement. Firstly, generally higher surface area and larger pore-size are anticipated. Secondly, the acetylene moieties are often used to prepare inherently conducting or semiconducting materials and these units should allow further functionalization with, for example, organometallic complexes.[47] This could, in turn, lead to the generation of new microporous heterogeneous catalysts. Retrosynthetically, the HPXXL core **A** is built from a carbinol derivative **B**, which, in turn, is derived from the trityl derivative **C** (**11**-H; Scheme 6).

In principle, two synthetic approaches were envisaged to generate the HPXXL core **9**-OR. One route starts from the central unit, elongating both trityl moieties in parallel. The second option is to build up the tetraphenylmethane building block **B** and connect two of them through a symmetrical 1,4-substituted bifunctional phenylene (Scheme 6). To avoid sixfold reactions, we chose to use the second pathway to lengthen the two trityl moieties. As shown before, most sixfold reactions on 1,4-ditritylbenzene derivatives (**2**-X) are challenging and sometimes low yielding. We feared that these difficulties would become worse with an increasing sized scaffold, mainly because its solubility decreases with increasing size.

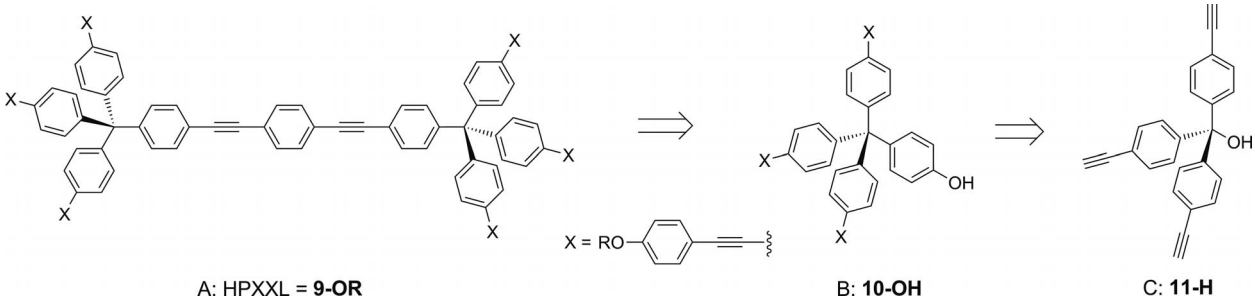
Building block **C** (**11**-H) is readily available in a few steps from substituted benzophenones **12**-X (see the Supporting Information for details). Subsequent Sonogashira coupling provided carbinol **16** in good overall yield (Scheme 7).

Alkyne **17**-CCH (X = CCH), which was required for dimerization, was accessible from **16** through a sequence of Friedel–Crafts alkylation, triflate formation, cross-coupling with trimethylsilylethyne, and desilylation (Scheme 8).

Reaction of alkyne **17**-CCH with 1,4-diiodobenzene under palladium catalysis (Sonogashira conditions) provided the HPXXL core **9**-OMe in 37% (69% based on recovered starting material; Scheme 9, left). This core exhibits a three-dimensional calculated latitude of 3.6 nm.

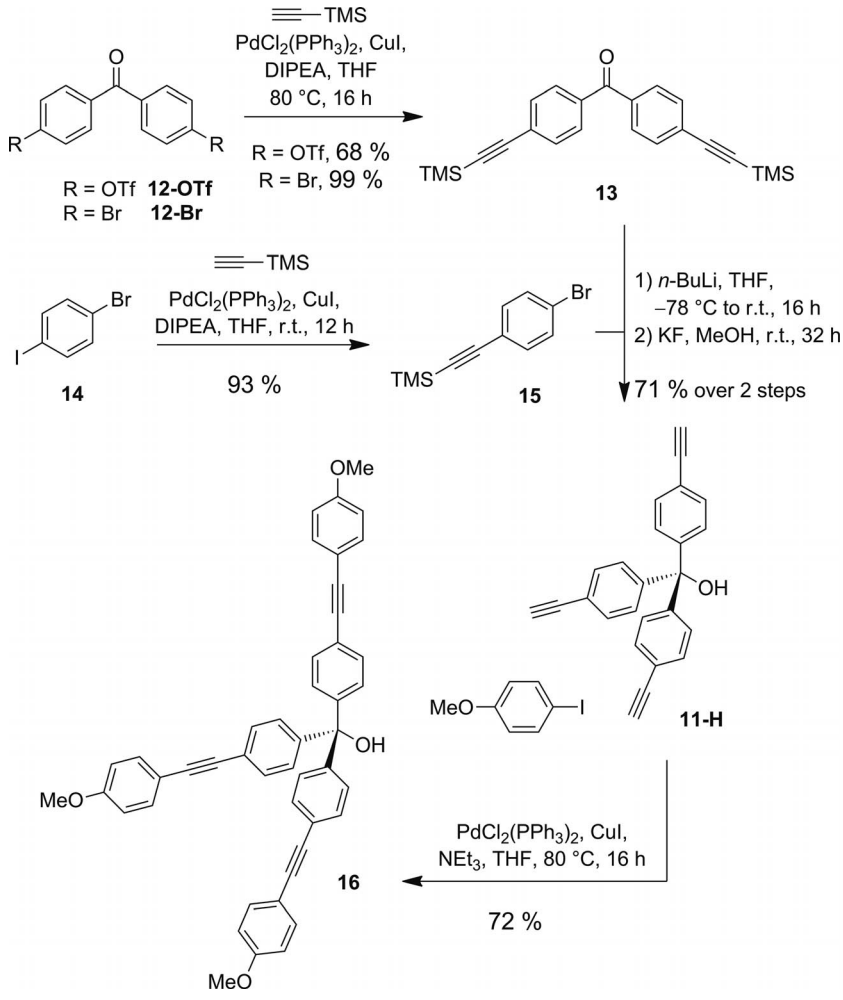
Because it was necessary to convert the triflate protected phenol **17**-OH (X = OH) into alkyne **17**-CCH and connect two of these building blocks through cross-coupling with 1,4-diiodobenzene, we also investigated a shorter route. An easier alternative would be the cross-coupling reaction of triflate intermediate **17**-OTf (X = OTf) with 1,4-diethynylbenzene, leading to HPXXL **9**-OMe with less synthetic effort (Scheme 9, right). Unfortunately, the use of 1,4-diethynylbenzene turned out to be inappropriate for this reaction. The triflate-protected starting material **17**-OTf could indeed be completely recovered after the reaction, whereas 1,4-ethynylbenzene had almost totally disappeared. Similar problems regarding the reactivity of 1,4-ethynylbenzene were observed for the generation of HCPs through click chemistry.[16a,42] In addition, reaction of the test building block **18** with 1,4-ethynylbenzene delivered product **19** in only poor yield (13%; Scheme 10). Neither longer reaction times nor the use of more equivalents of **18** resulted in better yields.

We then tried to generate the hexaalcohol from the expanded core **9**-OMe. The desired deprotection of the methoxy groups failed using boron tribromide. The cleavage was thus explored on the test compound (4-methoxyphenyl)-phenylacetylene. We observed that the deprotection is kinetically favored at low temperatures (–20 to 0 °C) and using

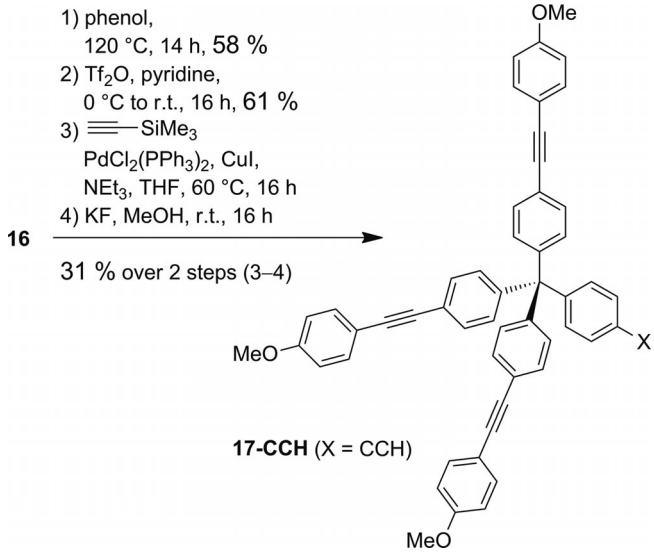



Scheme 6. Retrosynthetic synthesis of the expanded HPXXL system **9**-OR.




Scheme 7. Synthesis of carbinol derivative **16**.



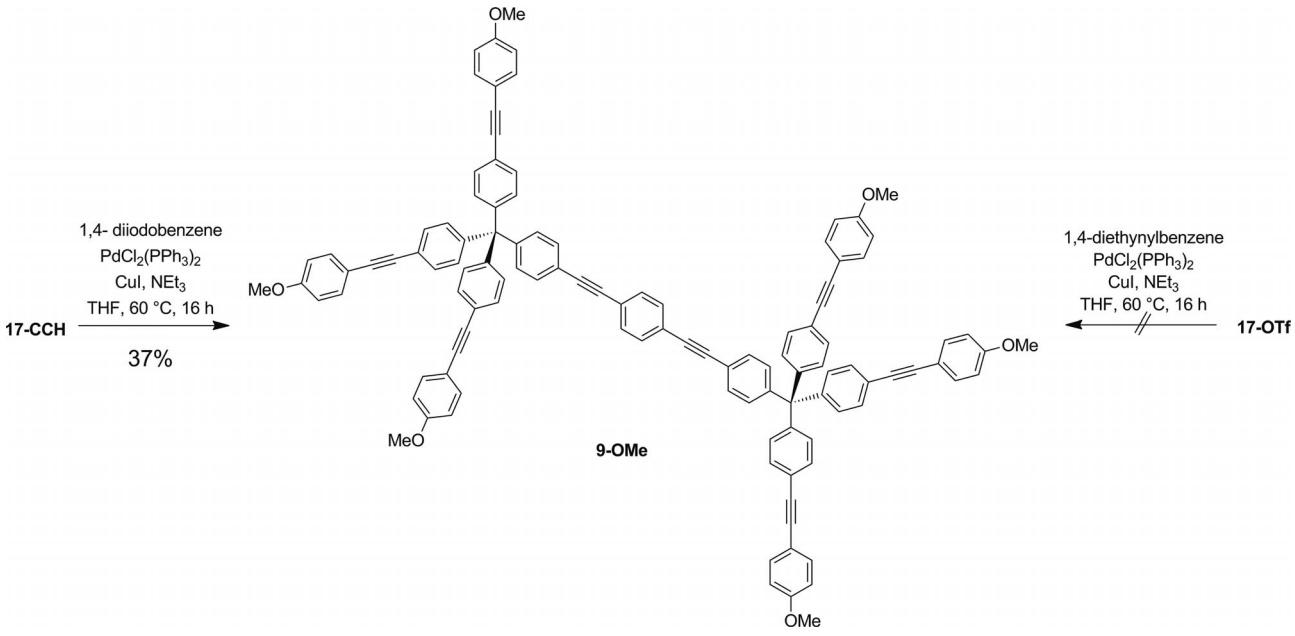

Scheme 8. Synthesis of alkyne **17**-CCH (X = CCH).

stoichiometric amounts of boron tribromide. These conditions allowed addition to the triple bond to be suppressed when applied to the test system but, unfortunately, failed when used to deprotect **9**-OMe (results not shown). We are currently exploring other possibilities to effectively generate the HPXXL hexaalcohol starting from **9**-OMe.

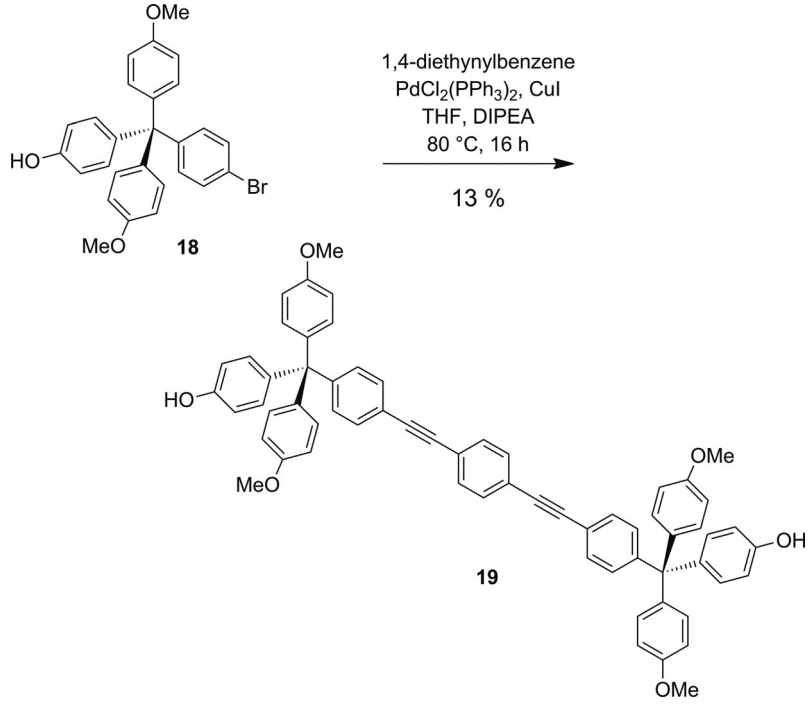
After preparing the HPX and expanded HPXXL cores, we wanted to explore the scope of our methodology and investigated 1,3,5-tritritylarene and nonaphenyl mesitylene cores, namely tritritylbenzene derivatives (**3**-X; Figure 1).[48,49] In these types of molecules, the central phenyl ring is crowded by three sterically demanding trityl moieties. Some related compounds such as hexaaryltruxene or analogues in which the central arene moiety is part of three fluorene units,[50] have shown interesting properties in material chemistry.[51,52]

In a first step, we investigated the synthesis of unsubstituted NPM **3**-H. In analogy to the synthesis of HPX **2**-H, we used commercially available trimethyl benzene-1,3,5-tricarboxylate (**20**) as starting material (Scheme 11). The sixfold addition of phenyllithium to the three ester moieties delivered the intermediate triol **21**-H in a remarkable 91% yield. It was found that when treating triol **21**-H with aniline in a Friedel–Crafts type reaction at elevated temperature in glacial acetic acid, addition of HCl was essential to obtain high yields. Triamine **22**-$NH_2$ was obtained in




Scheme 9. Synthesis of the HPXXL **9**-$OCH_3$.



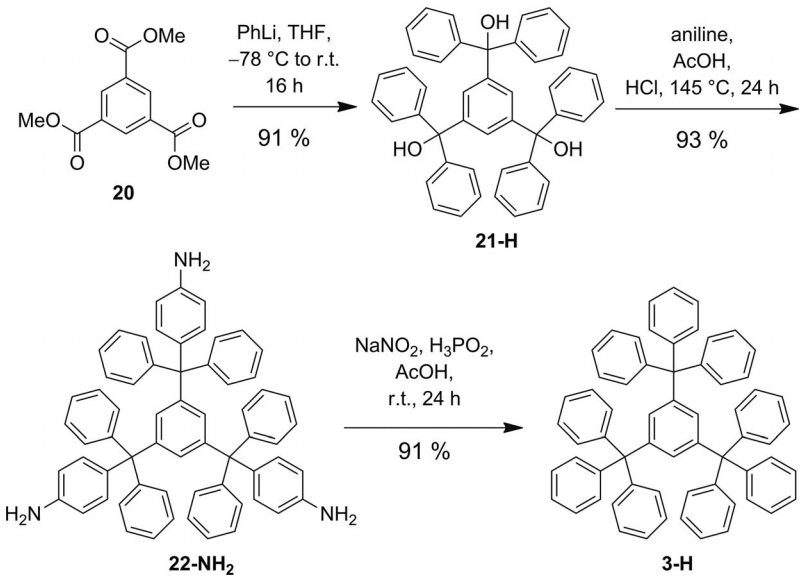

Scheme 10. Synthesis of semi-expanded 1,4-ditritylbenzene derivative **19**.

pure form without column chromatography by a simple washing procedure. Desamination of **22**-$NH_2$ through diazotization delivered the desired 1,3,5-tritritylbenzene **3**-H, which could again be isolated in excellent yield and in pure form by simple filtration followed by washing. NPM **3**-H, obtained in 77% overall yield by a three step procedure in gram scale, is similar to the related compounds TPM **1**-H and HPX **2**-H, and is a high-melting hydrocarbon (melting point with decomposition above 280 °C).

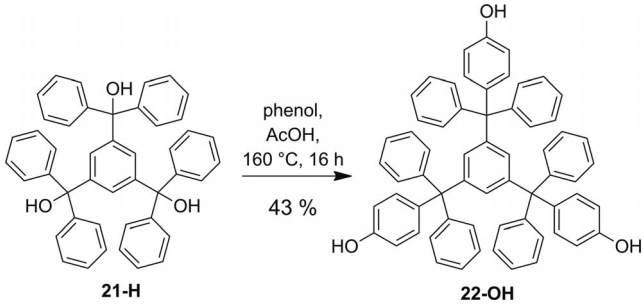
In analogy to the Friedel–Crafts reaction of **21**-H with aniline, **21**-H was treated with phenol to give triol **22**-OH, in moderate yields (Scheme 12). Product **22**-OH was accompanied by the formation of side products and required purification by column chromatography over silica gel.

The molecular structure of **21**-H is shown in Figure 4. As expected for trityl-based cores, the phenyl rings lie above and below the plane of the central benzene ring, the hydroxyl groups, however, are in-plane.




Scheme 11. Synthesis of unsubstituted 1,3,5-tritritylbenzene (**3**-H).




Scheme 12. Synthesis of trihydroxy-1,3,5-tritritylbenzene (**22**-OH).

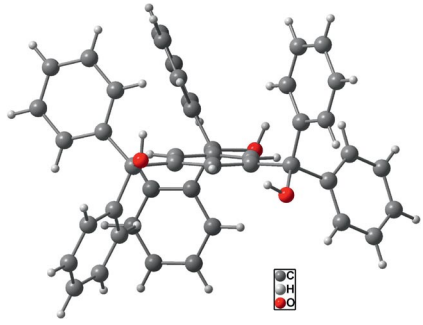
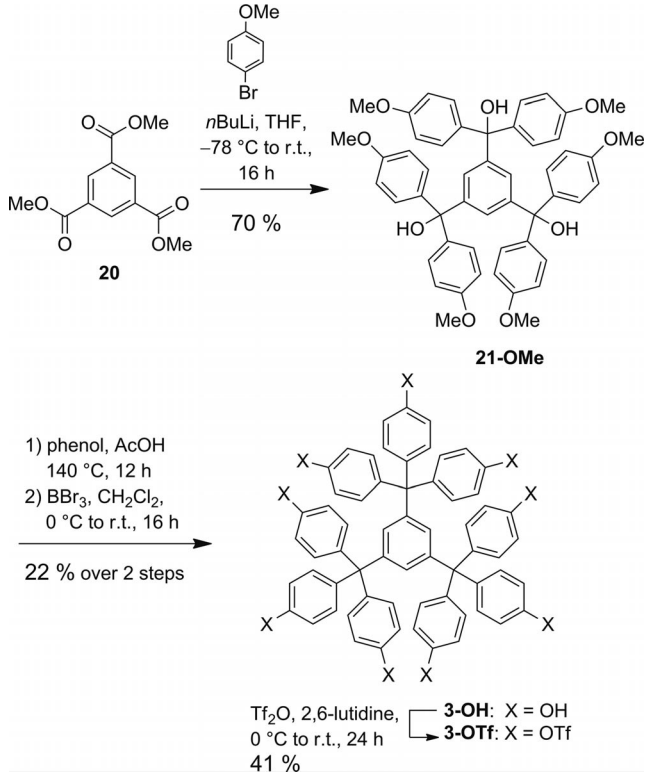


Figure 4. Molecular structure of **21**-H.

Likewise, the nonamethoxy derivative **21**-OMe was prepared from triester **20** and 4-lithioanisole, generated from bromoanisole, in 70% yield (Scheme 13). The yield was comparable (63%) when the reaction was carried out with the corresponding Grignard reagent (results not shown). As for **21**-H, the subsequent Friedel–Crafts product was formed along with side products. To minimize their formation, the progress of the reaction was monitored by TLC and stopped as soon as **21**-OMe had been completely consumed. The crude mixture was demethylated at low temperature to furnish nonaphenol **3**-OH in moderate yield over two steps. Finally, nonatriflate **3**-OTf was obtained in good yield by treatment with triflic anhydride.




Scheme 13. Synthesis of functionalized tritritylbenzene derivatives.

Single crystals of **3**-OTf could be obtained by recrystallization of the purified compound from tetrahydrofuran (THF). The molecular structure of **3**-OTf is shown in Figure 5.

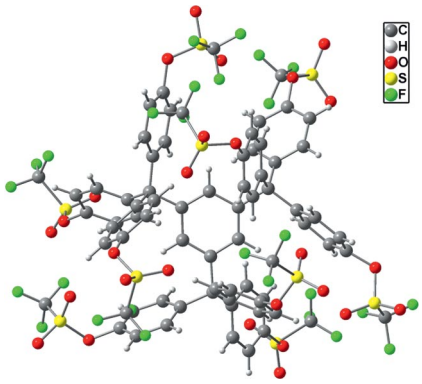
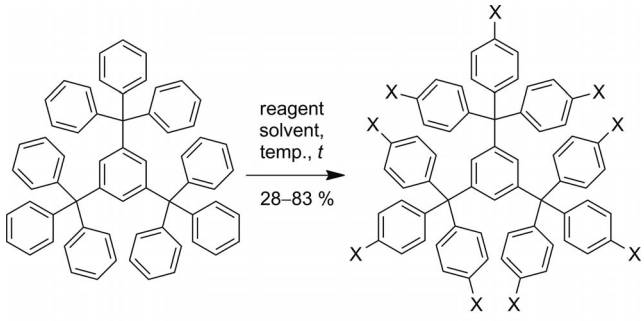



Figure 5. Molecular structure of **3**-OTf.

We then investigated the ninefold substitution reaction of the NPM core **3**-H. The temperature, stoichiometry, dilution, and reaction times were optimized to minimize side product formation, which mainly consisted of *meta*-substituted products (Table 2). The functionalization of parent hydrocarbon **3**-H to nonabromide **3**-Br (Table 2, entry 1) or nonaiodide **3**-I (Table 2, entry 2) proceeded smoothly. As observed for the HPX core before (Table 1), bromination gave better yields than iodination. The nonanitro compound **3**-$NO_2$ (Table 2, entry 3) and the nonasulfonic acid **3**-$SO_3H$ (Table 2, entry 4) were synthesized in good and moderate yields, respectively. These ninefold reactions prove that the NPM core can indeed be functionalized and thus should find application in material chemistry.

Table 2. Synthesis of functionalized tritritylbenzene derivatives.




**3-H** **3-X**

| Entry | NPM | Reaction conditions | Yield [%] |
|---|---|---|---|
| 1 | **3**-Br | $Br_2$, room temp., 1 h | 83 |
| 2 | **3**-I | $I_2$, PIFA, $CCl_4$, 80 °C, 24 h | 28 |
| 3 | **3**-$NO_2$ | $HNO_3$, –5 °C – room temp., 12 h | 60 |
| 4 | **3**-$SO_3H$ | $ClSO_3H$, $CH_2Cl_2$, room temp. – 35 °C, 12 h | 38 |

## Conclusions

We have synthesized new trityl-substituted arenes and explored their potential for further functionalization in order to act as molecular building blocks in supramolecular assemblies.

An optimized synthesis of HPX **2**-H was presented and further functionalized through sixfold substitution reactions to generate a series of interesting core structures. Hexaalcohol **2**-OH, as well as hexahalides **2**-Br and **2**-I, were transformed into hexatriflate **2**-OTf, the hexalithio derivative, and engaged in a Sonogashira cross-coupling reaction, respectively. This led to new interesting structures and showed the broad applicability of most of the precursor cores. In the HPX series, we have furthermore presented the synthesis of an expanded core named HPXXL. Finally, we have adapted our synthetic approach to the synthesis of completely novel NPM cores **3**-X, bearing nine functionalization or connection sites. We have shown that functionalization is possible with these cores in moderate to good yields.

Because the majority of the presented structures are easily accessible in a few steps in gram scale, these rigid cores should readily find application in material chemistry. We are currently investigating the potential of some of these compounds to act as tectons in purely organic networks.

## Experimental Section

**General Remarks:** $^1$H NMR spectra were recorded with a Bruker AM 400 (400 MHz) or a Bruker Avance DRX (500 MHz) spectrometer as solutions in $CDCl_3$ or [$D_6$]DMSO. Chemical shifts are expressed in parts per million (ppm, $\delta$) downfield from tetramethylsilane (TMS; $\delta$ = 0 ppm) and are referenced to $CHCl_3$ ($\delta$ = 7.26 ppm) or DMSO ($\delta$ = 2.50 ppm) as internal standard. All coupling constants are absolute values and $J$ values are expressed in Hertz [Hz]. The description of signals include: s singlet, br. s broad singlet, d doublet, m multiplet, dd doublet of doublets, AA′BB′ spin system of hydrogen atoms on a *para*-substituted phenyl ring. The spectra were analyzed according to first order. $^{13}$C NMR spectra were recorded with a Bruker AM 400 (100 MHz) or a Bruker Avance DRX (125 MHz) spectrometer as solutions in $CDCl_3$ or [$D_6$]DMSO. Chemical shifts are expressed in parts per million (ppm, $\delta$) downfield from tetramethylsilane (TMS; $\delta$ = 0 ppm) and are referenced to $CHCl_3$ ($\delta$ = 77.4 ppm) or DMSO ($\delta$ = 39.5 ppm) as internal standard. The signal structure was analyzed by DEPT and is described as follows: + denotes a primary or tertiary C-atom (positive signal), – a secondary C-atom (negative signal), and q a quaternary C-atom (no signal). Mass spectra (FAB and EI-MS) were recorded with a Finnigan MAT 95 spectrometer under fast atom bombardment (FAB) conditions with nitrobenzyl alcohol as matrix and reference. The molecular fragments are quoted as the relation between mass and charge ($m/z$), the intensities as a percentage relative to the intensity of the base signal (100%). The quasi-molecular ion is abbreviated [M + H$^+$] for FAB-MS. IR spectra were recorded with a FTIR Bruker IFS 88 spectrometer. IR spectra were recorded using the attenuated total reflection technique (ATR) or the DRIFT technique (diffused reflectance infrared Fourier transform-spectroscopy) for solids. IR spectra of oils were determined as KBr plates. The absorption band positions are given in wave numbers $\tilde{\nu}$ in cm$^{-1}$. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel coated aluminum plates (silica gel 60, $F_{254}$), detected under UV-light at 254 nm. Solvent mixtures are given as volume/volume. Melting points (m.p.) were determined with a Julabo ED-5 fully automated melting point apparatus and are uncorrected. All values are given as single points

measured by the apparatus according to the starting point of decomposition.

Solvents, reagents and chemicals were purchased from Acros, ABCR, Alfa Aesar, Fluka, Merck, Riedel-de Haën, or Sigma-Aldrich. Ethyl acetate, cyclohexane and dichloromethane were distilled from calcium hydride prior to use. Anhydrous toluene and THF were distilled from sodium using benzophenone as indicator in the case of THF. All other solvents, reagents, and chemicals were used as purchased. All reactions involving moisture-sensitive reactants were executed under an argon atmosphere, using oven-dried and/or flame-dried glassware.

**Crystal Structure Studies:** Single-crystal X-ray diffraction studies were carried out with a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Direct Methods (SHELXS-97[53]) were used for structure solution, and full-matrix least-squares refinement on $F^2$ (SHELXL-98[53]). H atoms were localized by difference Fourier synthesis and refined using a riding model [H(O) free]. Semi-empirical absorption corrections were applied for **2**-Br-thf, **2**-Br-dmf, **2**-I, and **3**-OTf. For **21**-H an extinction correction was applied.

In **2**-Br-thf, **2**-Br-dmf, and **2**-I there was either a slight disorder of the halogen atoms between the *p*- and the *m*-position in the range 98:2 or a 2nd substitution in the *m*-position (approx. 2%), which could not be refined reasonably. In **3**-OTf, two of the nine 4-trifluoromethylsulfonylphenyl substituents were disordered.

**2-Br-thf:** Yellow crystals; $C_{44}H_{28}Br_6+C_4H_8O$; $M$ = 1108.23; crystal size 0.30 × 0.30 × 0.10 mm; monoclinic; space group $C2/c$ (No. 15); $a$ = 13.903(1) Å, $b$ = 14.470(1) Å, $c$ = 21.365(2) Å, $\beta$ = 107.19(1)°; $V$ = 4106.1(6) Å$^3$; $Z$ = 4; $\rho$(calcd.) = 1.793 Mg m$^{-3}$; $F$(000) = 2168; $\mu$ = 5.904 mm$^{-1}$; 21155 reflections ($2\theta_{max}$ = 50°), 3610 unique [$R_{int}$ = 0.052], 271 parameters, 66 restraints, $R_1$ [$I > 2\sigma(I)$] = 0.054, $wR_2$ (all data) = 0.143, GooF = 1.09, largest diff. peak and hole 1.877 and –0.862 e Å$^{-3}$. The porosity was 12.9%[54] and the packing index 61.7.[55]

**2-Br-dmf:** Colorless crystals; $C_{44}H_{28}Br_6+C_3H_7NO$; $M$ = 1109.22; crystal size 0.20 × 0.15 × 0.10 mm; monoclinic; space group $C2/c$ (No. 15); $a$ = 13.813(1) Å, $b$ = 14.511(1) Å, $c$ = 21.449(2) Å, $\beta$ = 106.12(1)°; $V$ = 4130.2(6) Å$^3$; $Z$ = 4; $\rho$(calcd.) = 1.784 Mg m$^{-3}$; $F$(000) = 2168; $\mu$ = 5.870 mm$^{-1}$; 23724 reflections ($2\theta_{max}$ = 50°), 3622 unique [$R_{int}$ = 0.034], 248 parameters, 10 restraints, $R_1$ [$I > 2\sigma(I)$] = 0.052, $wR_2$ (all data) = 0.149, GooF = 1.04, largest diff. peak and hole 2.393 and –0.530 e Å$^{-3}$. The porosity was 12.5%[54] and the packing index 61.4.[55]

**2-I:** Colorless crystals; $C_{44}H_{28}I_6+C_4H_8O$; $M$ = 1390.17; crystal size 0.25 × 0.20 × 0.15 mm; monoclinic; space group $C2/c$ (No. 15); $a$ = 14.276(1) Å, $b$ = 14.866(1) Å, $c$ = 21.729(2) Å, $\beta$ = 106.68(1)°; $V$ = 4417.4(6) Å$^3$; $Z$ = 4; $\rho$(calcd.) = 2.090 Mg m$^{-3}$; $F$(000) = 2600; $\mu$ = 4.255 mm$^{-1}$; 18371 reflections ($2\theta_{max}$ = 55°), 5067 unique [$R_{int}$ = 0.041], 246 parameters, 16 restraints, $R_1$ [$I > 2\sigma(I)$] = 0.066, $wR_2$ (all data) = 0.176, GooF = 1.07, largest diff. peak and hole 3.507 and –1.006 e Å$^{-3}$. The porosity was 13.1%[54] and the packing index 60.7.[55]

**2-OH:**[32] Pale-yellow crystals; $C_{44}H_{34}O_6+5 \times C_6H_6$; $M$ = 1049.25; crystal size 0.50 × 0.25 × 0.20 mm; triclinic; space group $P\bar{1}$ (No. 2); $a$ = 10.729(1) Å, $b$ = 11.136(1) Å, $c$ = 13.397(1) Å, $\alpha$ = 75.80(1)°, $\beta$ = 74.97(1)°, $\gamma$ = 78.62(1)°; $V$ = 1483.3(2) Å$^3$; $Z$ = 1; $\rho$(calcd.) = 1.175 Mg m$^{-3}$; $F$(000) = 556; $\mu$ = 0.073 mm$^{-1}$, 21803 reflections ($2\theta_{max}$ = 55°), 6735 unique [$R_{int}$ = 0.035], 370 parameters, 3 restraints, $R_1$ [$I > 2\sigma(I)$] = 0.051, $wR_2$ (all data) = 0.124, GooF = 1.02, largest diff. peak and hole 0.247 and –0.295 e Å$^{-3}$. The porosity was 53.1%[54] and the packing index 37.9.[54]

**3-OTf:** Yellow crystals; $C_{72}H_{39}F_{27}O_{27}S_9+C_6H_6$; $M$ = 2215.68; crystal size 0.40 × 0.25 × 0.20 mm; monoclinic; space group $C2/c$ (No. 15); $a$ = 28.845(3) Å, $b$ = 17.401(2) Å, $c$ = 35.200(4) Å, $\beta$ = 93.06(1)°; $V$ = 17704(3) Å$^3$; $Z$ = 8; $\rho$(calcd.) = 1.663 Mg m$^{-3}$; $F$(000) = 8928; $\mu$ = 0.361 mm$^{-1}$; 59036 reflections ($2\theta_{max}$ = 55°), 19963 unique [$R_{int}$ = 0.029], 1232 parameters, 411 restraints, $R_1$ [$I > 2\sigma(I)$] = 0.102, $wR_2$ (all data) = 0.287, GooF = 1.03, largest diff. peak and hole 2.175 and –1.785 e Å$^{-3}$. The porosity was 9.5%[54] and the packing index 62.5.[54]

**5-OMe:** Colorless crystals; $C_{36}H_{34}O_6+C_6H_{12}$; $M$ = 646.79; crystal size 0.50 × 0.45 × 0.40 mm; monoclinic; space group $P2_1/n$ (No. 14); $a$ = 19.461(1) Å, $b$ = 8.079(1) Å, $c$ = 22.152(1) Å, $\beta$ = 106.20(1)°; $V$ = 3344.6(5) Å$^3$; $Z$ = 4; $\rho$(calcd.) = 1.284 Mg m$^{-3}$; $F$(000) = 1384; $\mu$ = 0.085 mm$^{-1}$; 43834 reflections ($2\theta_{max}$ = 55°), 7647 unique [$R_{int}$ = 0.022], 443 parameters, 2 restraints, $R_1$ [$I > 2\sigma(I)$] = 0.040, $wR_2$ (all data) = 0.102, GooF = 1.06, largest diff. peak and hole 0.323 and –0.211 e Å$^{-3}$. The porosity was 18.1%[54] and the packing index 59.5.[54]

**21-H:** Pale-yellow crystals; $C_{45}H_{36}O_3$; $M$ = 624.74; crystal size 0.48 × 0.16 × 0.08 mm; monoclinic; space group $P2_1/c$ (No. 14); $a$ = 9.1147(9) Å, $b$ = 23.1895(15) Å, $c$ = 15.7992(13) Å, $\beta$ = 90.850(8)°; $V$ = 3339.0(5) Å$^3$; $Z$ = 4; $\rho$(calcd.) = 1.243 Mg m$^{-3}$; $F$(000) = 1320; $\mu$ = 0.076 mm$^{-1}$; 21346 reflections ($2\theta_{max}$ = 50°), 5879 unique [$R_{int}$ = 0.035], 443 parameters, 6 restraints, $R_1$ [$I > 2\sigma(I)$] = 0.040, $wR_2$ (all data) = 0.089, GooF = 1.05, largest diff. peak and hole 0.197 and –0.164 e Å$^{-3}$. The porosity was 0.9%[54] and the packing index 67.0.[55]

CCDC-855064 (for **2**-Br-thf), -855065 (for **2**-Br-dmf), -855066 (for **2**-I), -785245 (for **2**-OH), -855067 (for **3**-OTf), -855068 (for **5**-OMe), and -855069 (for **21**-H) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Syntheses of 1,4-Dirityltbenzene Derivatives**

**1,4-Dirityltbenzene (2-H):** Dianiline **6** was suspended in glacial acetic acid (600 mL) and hypophosphoric acid (70 mL, 50% aqueous solution). At 10 °C, $NaNO_2$ (2.34 g, 33.9 mmol, 3 equiv.) was added in small amounts under vigorous stirring. The reaction mixture was stirred overnight at room temperature, then water (100 mL) was added and the formed solid was filtered off, washed with water, methanol, and diethyl ether (75 mL each) and dried in vacuo. Without further purification, 1,4-dirityltbenzene (**2**-H; 4.70 g, 96% and 74% overall yield) was obtained as a beige powder; $R_f$ = 0.30 (cyclohexane/ethyl acetate, 25:1); m.p. 296 °C (dec.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.11 (s, 4 H, 2-H, 3-H), 7.21–7.31 (m, 30 H, 2′-H, 3′-H, 4′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 64.6 ($C_q$, $C$(Ar)$_4$], 125.9 (+, $C$-4′), 127.3 (+, $C$-3′), 130.3 (+, $C$-2, $C$-3), 131.2 (+, $C$-2′), 144.2 ($C_q$, $C$-1, $C$-4), 146.7 ($C_q$, $C$-1′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3056, 3030, 1956, 1815, 1701, 1596, 1491, 1443, 1405, 1370, 1319, 1186, 1083, 1035, 1002, 890, 824, 748, 702, 642, 632, 532 cm$^{-1}$. MS (70 eV, EI): $m/z$ (%) = 562 (76) [M$^+$], 485 (100) [M$^+$ – $C_6H_5$], 409 (24) [$C_{32}H_{25}^+$], 319 (33) [$C_{25}H_{19}^+$], 243 (59) [$C_{19}H_{15}^+$], 165 (60) [$C_{13}H_9^+$]. HRMS (EI): calcd. for $C_{44}H_{34}$ 562.2660; found 562.2659.

**1,4-Bis[tris(4′-bromophenyl)methyl]benzene (2-Br):** Compound **2**-H (3.00 g, 5.33 mmol, 1 equiv.) was added in small portions to pure bromine (without any solvent) (4.9 mL, 15.3 g, 96.0 mmol, 18 equiv.) under vigorous stirring. The reaction mixture was stirred for 1 h at room temperature and then cooled to –78 °C. Ethanol (50 mL) was added and the reaction mixture was warmed to room temperature. The solid was filtered off and washed with satd. aque-

ous $Na_2S_2O_3$ solution (100 mL) and water (250 mL). Drying in vacuo afforded **2**-Br (5.15 g, 92%) as a light-yellow solid; $R_f$ = 0.72 (cyclohexane/ethyl acetate, 10:1); m.p. 323 °C (dec.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.99 (AA′BB′, $J$ = 8.7 Hz, 12 H, 2′-*H*), 7.01 (s, 4 H, 2-H, 3-H), 7.38 (AA′BB′, $J$ = 8.7 Hz, 12 H, 3′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 63.6 [$C_q$, *C*(Ar)$_4$], 120.7 ($C_q$, *C*-4′), 130.2 (+, *C*-2, *C*-3), 130.9 (+, *C*-2′), 132.5 (+, *C*-3′), 143.6 ($C_q$, *C*-1, *C*-4), 144.6 ($C_q$, *C*-1′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3545, 3365, 3054, 2929, 2834, 2740, 2599, 2355, 1940, 1700, 1601, 1575, 1504, 1419, 1390, 1312, 1215, 1173, 1115, 1015, 918, 809, 717, 666, 628, 543, 445, 417 cm$^{-1}$.

**1,4-Bis[tris(4′-iodophenyl)methyl]benzene (2-I):** Compound **2**-H (3.00 g, 5.33 mmol, 1 equiv.), iodine (7.98 g, 31.4 mmol, 5.9 equiv.) and [bis(trifluoroacetoxy)iodo]benzene (18.1 g, 42.1 mmol, 7.9 equiv.) were suspended in carbon tetrachloride (60 mL) and stirred for 6 d at 60 °C under an argon atmosphere. The solvent was removed under reduced pressure and the residue was suspended in acetone (150 mL) and stirred for 2 h at room temperature. The solid was filtered off and washed with acetone (50 mL). Drying in vacuo afforded the product **2**-I (3.90 g, 55%) as a white powder; $R_f$ = 0.61 (cyclohexane/ethyl acetate, 25:1); m.p. 377 °C (dec.). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.85 (AA′BB′, $J$ = 8.5 Hz, 12 H, 2′-H), 6.99 (s, 4 H, 2-H, 3-H), 7.57 (AA′BB′, $J$ = 8.5 Hz, 12 H, 3′-H) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 63.3 [$C_q$, *C*(Ar)$_4$], 92.8 ($C_q$, *C*-4′), 129.5 (+, *C*-2, *C*-3), 132.4 (+, *C*-2′), 136.6 (+, *C*-3′), 144.80 ($C_q$, *C*-1, *C*-4), 145.1 ($C_q$, *C*-1′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3430, 3057, 2922, 2847, 1914, 1659, 1580, 1561, 1483, 1447, 1393, 1317, 1277, 1192, 1068, 1004, 920, 808, 781, 758, 702, 639, 533, 507, 420 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 1317 (1) [M$^+$], 1191 (1) [M$^+$ – I], 1114 (1) [M$^+$ – $C_6H_5I$], 154 (100).

**4′-[1,4-Phenylenebis(methanetetrayl)]hexabenzenesulfonic Acid (2-SO$_3$H):** To a suspension of **2**-H (1.50 g, 2.67 mmol, 1 equiv.) in anhydrous $CH_2Cl_2$ (100 mL), chlorosulfonic acid (3.2 mL, 5.59 g, 48.0 mmol, 18 equiv.) was added dropwise under vigorous stirring. The resulting reaction mixture was heated at 35 °C for 90 min. The supernatant yellow solution was carefully decanted and the volatiles of this solution were removed under reduced pressure. The residual solid was washed with water (250 mL) and dried in vacuo. Without further purification, the title compound **2**-SO$_3$H (1.28 g, 46%) was obtained as a yellow solid; m.p. 398 °C (dec.). $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 7.05–7.10 (m, 16 H, 2-H, 3-H, 2′-H), 7.52 (AA′BB′, 12 H, 3′-H), 11.15 (br. s, 6 H, SO$_3$H) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 63.7 [$C_q$, *C*(Ar)$_4$], 125.0 (+, *C*-2′), 129.9 (+, *C*-2, *C*-3, *C*-3′), 143.5 ($C_q$, *C*-1, *C*-4), 145.2 ($C_q$, *C*-4′), 146.5 ($C_q$, *C*-1′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3370, 1654, 1583, 1490, 1373, 1168, 1082, 1034, 1005, 818, 729, 700, 628, 549, 420 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 1043 (1) [M + H$^+$], 154 (100). HRMS (FAB): calcd. for $C_{44}H_{35}O_{18}S_6^+$ 1043.0148; found 1043.0142.

**1,4-Bis[tris(4′-nitrophenyl)methyl]benzene (2-NO$_2$):** To a suspension of **2**-H (0.20 g, 0.36 mmol, 1 equiv.) in glacial acetic acid (15 mL), nitric acid (99%, 1.0 mL) was added dropwise at 65 °C. The formed reaction mixture was stirred for 18 h. After cooling to room temperature, water was added (100 mL) and the formed precipitate was filtered off and washed with water (200 mL). Flash column chromatography afforded **2**-NO$_2$ (62.9 mg, 21%) as a yellow powder; $R_f$ = 0.70 ($CH_2Cl_2$); m.p. 279 °C (dec.). $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 7.24 (s, 4 H, 2-H, 3-H), 7.52 (AA′BB′, $J$ = 9.0 Hz, 12 H, 2′-H), 8.22 (AA′BB′, $J$ = 9.0 Hz, 12 H, 3′-H) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 64.6 [$C_q$, *C*(Ar)$_4$], 123.5 (+, *C*-3′), 131.4 (+, *C*-2, *C*-3, *C*-2′), 145.9 ($C_q$, *C*-1, *C*-4, *C*-4′), 151.6 ($C_q$, *C*-1′) ppm. IR (DRIFT): $\tilde{\nu}$ = 2857, 1591, 1512, 1433, 1187, 1109, 1066, 1013, 839, 820, 744, 705, 570, 458 cm$^{-1}$.

**1,4-Bis[tris(4′-acetylphenyl)methyl]benzene (2-Ac):** A mixture of **2**-H (0.25 g, 0.44 mmol, 1 equiv.), acetyl chloride (0.24 mL, 0.268 g, 3.42 mmol, 7.7 equiv.) and anhydrous aluminum trichloride (0.42 g, 0.45 mmol, 7.6 equiv.) in $CS_2$ (10 mL) was heated to reflux for 18 h. After cooling to room temperature, the solvent was decanted. Ice (10 g), concd. HCl (7 mL), and $CH_2Cl_2$ (30 mL) were added to the residue and the mixture was stirred until the precipitate had completely dissolved. The organic layer was separated, dried with $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 3:1 → 1:1) afforded the product **2**-Ac (143 mg, 40%) as a yellow solid; $R_f$ = 0.22 (cyclohexane/ethyl acetate, 1:1); m.p. 134 °C (dec.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.58 (s, 18 H, $CH_3$), 7.10 (s, 4 H, 2-H, 3-H), 7.29 (AA′BB′, $J$ = 8.5 Hz, 12 H, 3′-H), 7.87 (AA′BB′, $J$ = 8.5 Hz, 12 H, 2′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 26.6 (+, *C*H$_3$), 65.0 [$C_q$, *C*(Ar)$_4$], 127.9 (+, *C*-2′), 130.4 (+, *C*-2, *C*-3), 130.9 (+, *C*-3′), 135.3 ($C_q$, *C*-4′), 143.4 ($C_q$, *C*-1, *C*-4), 150.4 ($C_q$, *C*-1′), 197.6 ($C_q$, *C*O) ppm. IR (DRIFT): $\tilde{\nu}$ = 2926, 1682, 1600, 1500, 1407, 1356, 1266, 1190, 1069, 1015, 959, 820, 761, 716, 691, 665, 591, 564, 525, 420 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 815 (5) [M + H$^+$], 154 (100). HRMS (FAB): calcd. for $C_{56}H_{47}O_6$ 815.3373; found 815.3373.

**1,4-Bis[tris(4′-ethynylphenyl)methyl]benzene (2-CCH):** A mixture of **2**-I (100 mg, 81.0 μmol, 1 equiv.), [$PdCl_2(PPh_3)_2$] (12.8 mg, 18.2 μmol, 0.2 equiv.), CuI (6.90 mg, 3.62 μmol, 0.5 equiv.) and trimethylsilylacetylene (90 μL, 67.0 mg, 0.68 mmol, 9 equiv.) in anhydrous THF (3 mL) and anhydrous triethylamine (5 mL) was stirred for 16 h at 75 °C under an argon atmosphere. The solvents were removed under reduced pressure and the residue was taken up in 1 M HCl (25 mL) and $CH_2Cl_2$ (50 mL), the organic phase was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude trimethylsilyl-protected acetylene **2**-CCTMS was used in the next step without further purification. A solution of the crude trimethylsilyl-protected acetylene **2**-CCTMS in benzene (7 mL) and acetonitrile (7 mL) was treated with tetrabutylammonium fluoride (0.13 g, 0.49 mmol, 6 equiv., 1 M in THF) for 16 h at room temperature. The volatiles were removed under reduced pressure and the residue was taken up in 1 M HCl (20 mL) and $CH_2Cl_2$ (50 mL). The organic phase was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 8:1) afforded the title compound **2**-CCH (35.5 mg, 65%) as a yellow solid; $R_f$ = 0.27 (cyclohexane/ethyl acetate, 8:1); m.p. 138 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.06 (s, 6 H, C≡CH), 7.03 (s, 4 H, 2-H, 3-H), 7.11 (AA′BB′, $J$ = 8.4 Hz, 12 H, 2′-H), 7.38 (AA′BB′, $J$ = 8.4 Hz, 12 H, 3′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 64.4 [$C_q$, *C*(Ar)$_4$], 77.5 (+, C≡*C*H), 83.2 ($C_q$, *C*≡CH), 120.1 ($C_q$, *C*-4′), 130.3 (+, *C*-2, *C*-3), 130.8 (+, *C*-2′), 131.5 (+, *C*-3′), 143.5 ($C_q$, *C*-1, *C*-4), 146.4 ($C_q$, *C*-1′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3230, 3033, 2925, 2850, 2214, 2108, 1929, 1602, 1570, 1498, 1447, 1407, 1248, 1116, 1019, 825, 796, 764, 701, 651, 574, 554, 415, 450, 409 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 707 (18) [M + H$^+$], 706 (16) [M$^+$], 605 (17) [M$^+$ – $C_8H_5$], 391 (18) [$C_{31}H_{19}^+$], 315 (24) [$C_{25}H_{15}^+$], 154 (100). HRMS (FAB): calcd. for $C_{56}H_{35}$ 707.2739; found 707.2743.

**1,4-Bis[tris(4′-methylphenyl)methyl]benzene (2-Me):** A solution of **2**-Br (0.25 g, 0.24 mmol, 1 equiv.) in anhydrous THF (50 mL) was cooled to –78 °C under an argon atmosphere. At this temperature, *n*-butyllithium (1.2 mL, 0.19 g, 2.89 mmol, 12 equiv., 2.5 M in hexane) was added dropwise and the reaction mixture was stirred for 14 h. Methyl iodide (1.3 mL, 1.23 g, 8.69 mmol, 36 equiv.) was

added dropwise and the reaction mixture was stirred for 16 h and warmed to room temperature. The reaction mixture was diluted with $CH_2Cl_2$ (100 mL) and treated with satd. aqueous $NH_4Cl$ (50 mL). The organic phase was separated and the aqueous phase was extracted with $CH_2Cl_2$ (2 × 100 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 25:1) afforded **2**-Me (86.0 mg, 55%) as a white powder; $R_f$ = 0.51 (cyclohexane/ethyl acetate, 25:1); m.p. 266 °C (dec.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.32 (s, 18 H, $CH_3$), 7.03–7.09 (m, 28 H, 2-H, 3-H, 2′-H, 3′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.9 (+, *C*H$_3$), 63.5 [$C_q$, *C*(Ar)$_4$], 127.9 (+, *C*-2′), 130.1 (+, *C*-2, *C*-3), 131.0 (+, *C*-3′), 135.2 ($C_q$, *C*-4′), 144.1 ($C_q$, *C*-1′), 144.5 ($C_q$, *C*-1, *C*-4) ppm. IR (Drift): $\tilde{\nu}$ = 3020, 2920, 2855, 1506, 1447, 1376, 1191, 1119, 1021, 807, 783, 754, 703, 640, 595, 573, 527, 495, 421 cm$^{-1}$. MS (70 eV, EI): *m*/*z* (%) = 646 (9) [$M^+$], 555 (50) [$M^+ - C_7H_7$], 464 (13) [$C_{36}H_{32}^+$], 285 (100) [$C_{22}H_{21}^+$]. HRMS (EI): calcd. for $C_{50}H_{46}$ 646.3600; found 646.3601.

**1,4-Bis[bis(4′-bromophenyl)(4′′-amino-3′′,5′′-dibromophenyl)methyl]benzene (7):** Compound **6** (200 mg, 0.34 mmol, 1 equiv.) was added in small portions to bromine (0.2 mL, 0.65 g, 4.08 mmol, 12 equiv.) under vigorous stirring at room temperature. The reaction mixture was stirred for 20 min and then cooled to –78 °C. Ethanol (15 mL) was added slowly and the reaction mixture was warmed to room temperature. The solid was filtered off and washed with satd. aqueous $Na_2S_2O_3$ (100 mL) and water (100 mL). Without further purification, the product (410 mg, 99%) was obtained as a beige solid; m.p. 181 °C (dec.). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 4.55 (s, 4 H, $NH_2$), 6.97–7.00 (m, 12 H, 2′-H, 2′′-H, 6′′-H), 7.07 (s, 4 H, 2-H, 3-H), 7.40 (AA′BB′, *J* = 8.7 Hz, 8 H, 3′-H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 62.9 [$C_q$, *C*(Ar)$_4$], 108.1 ($C_q$, *C*-3′′, *C*-5′′), 120.8 ($C_q$, *C*-4′), 130.2 (+, *C*-2, *C*-3), 131.0 (+, *C*-2′), 132.4 (+, *C*-3′), 133.8 (+, *C*-2′′, *C*-6′′), 136.5 ($C_q$, *C*-1′′), 140.5 ($C_q$, *C*-1, *C*-4), 143.7 ($C_q$, *C*-4′′), 144.5 ($C_q$, *C*-1′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3476, 3376, 3085, 2591, 2130, 1928, 1612, 1570, 1536, 1473, 1394, 1302, 1265, 1243, 1147, 1078, 1009, 939, 868, 814, 733, 682, 628, 541, 523 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 1222 (1) [$M^+$], 154 (100).

**1,4-Bis[tris(4′-hydroxyphenyl)methyl]benzene (2-OH):** Phenol (4.12 g, 43.8 mmol, 8 equiv.) and **5**-OMe (3.08 g, 5.47 mmol, 1 equiv.) was heated at 200 °C for 1 h under vigorous stirring. The residue was diluted with $CH_2Cl_2$ (100 mL) and cooled to 0 °C. Boron tribromide (3.1 mL, 8.22 g, 32.8 mmol, 6 equiv.) was added dropwise and the reaction mixture was stirred for 16 h and warmed to room temperature. Methanol (50 mL) was added carefully at 0 °C and the volatiles were removed under reduced pressure. This procedure was repeated five times. Flash column chromatography (cyclohexane/ethyl acetate, 1:2) yielded the title compound **2**-OH (1.31 g, 36%) as a reddish solid; $R_f$ = 0.28 (cyclohexane/ethyl acetate, 1:2); m.p. 218 °C (dec.). $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 6.63 (d, *J* = 8.8 Hz, 12 H, 3′-H), 6.82 (d, *J* = 8.8 Hz, 12 H, 2′-H), 6.93 (s, 4 H, 2-H, 3-H), 9.28 (s, 6 H, OH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 61.7 [$C_q$, *C*(Ar)$_4$], 113.9 (+, *C*-3′), 129.2 (+, *C*-2, *C*-3), 131.3 (+, *C*-2′), 137.43 ($C_q$, *C*-1′), 144.7 ($C_q$, *C*-1, *C*-4), 154.9 ($C_q$, *C*-4′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3372, 1699, 1610, 1507, 1436, 1364, 1232, 1178, 1112, 1016, 827, 600, 578, 541, 449 cm$^{-1}$. MS (70 eV, EI): *m*/*z* (%) = 658 (18) [$M^+$], 565 (42) [$M^+ - C_6H_5O$], 472 (8) [$M^+ - C_{12}H_{10}O_2$], 367 (6) [$C_{25}H_{19}O_3^+$], 291 (75) [$C_{19}H_{15}O_3^+$], 133 (100). HRMS (EI): calcd. for $C_{44}H_{34}O_6$ 658.2368; found 658.2355.

**1,4-Bis[tris(4′-trifluoromethylsulfonylphenyl)methyl]benzene (2-OTf):** Compound **2**-OH (100 mg, 0.15 mmol, 1 equiv.) was suspended in anhydrous $CH_2Cl_2$ (15 mL) and cooled to 0 °C. Triethylamine (0.32 mL, 0.23 g, 2.28 mmol, 15 equiv.) and trifluoromethanesulfonic anhydride (0.40 mL, 0.64 g, 2.28 mmol, 15 equiv.) were added and the reaction mixture was stirred for 16 h and warmed to room temperature. The volatiles were removed under reduced pressure and the residue was taken up in 1 M HCl (25 mL) and $CH_2Cl_2$ (50 mL). The organic phase was separated and the aqueous phase was extracted with $CH_2Cl_2$ (2 × 35 mL). The combined organic layers were washed with brine (50 mL), dried with $MgSO_4$, and the solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 4:1) afforded the product **2**-OTf (51.5 mg, 24%) as a white solid; $R_f$ = 0.45 (cyclohexane/ethyl acetate, 4:1); m.p. 190 °C (dec.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.06 (s, 4 H, 2-H, 3-H), 7.21 (br. s, 24 H, 2′-H, 3′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 63.6 [$C_q$, *C*(Ar)$_4$], 118.7 ($C_q$, $J_{C-F}$ = 320.6 Hz, *C*F$_3$), 121.0 (+, *C*-3′), 130.4 (+, *C*-2, *C*-3), 132.4 (+, *C*-2′), 145.3 ($C_q$, *C*-1′), 148.0 ($C_q$, *C*-1, *C*-4), 157.6 ($C_q$, *C*-4′) ppm. IR (ATR): $\tilde{\nu}$ = 2927, 1611, 1497, 1422, 1348, 1249, 1203, 1134, 1098, 1016, 954, 883, 827, 778, 751, 718, 639, 606, 574, 525, 500, 417 cm$^{-1}$.

## Syntheses of the Expanded 1,4-Dititylbenzene Derivatives (HPXXL)

**Tris[4-(4′-methoxyphenylethynyl)phenyl]methanol (16):** A mixture of **11**-H (1.00 g, 3.00 mmol, 1 equiv.), [$PdCl_2(PPh_3)_2$] (147 mg, 0.21 mmol, 7 mol-%), CuI (80.0 mg, 0.42 mmol, 0.14 equiv.), and 4-iodoanisole (2.60 g, 11.3 mmol, 3.8 equiv.) was dissolved in anhydrous THF (7 mL) and triethylamine (14 mL). The reaction mixture was stirred for 16 h at 80 °C. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (cyclohexane/ethyl acetate, 4:1) to yield **16** (1.41 g, 72%) as a white solid; $R_f$ = 0.19 (cyclohexane/ethyl acetate, 3:1); m.p. 171 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.83 (s, 9 H, $OCH_3$), 6.88 (AA′BB′, *J* = 8.9 Hz, 6 H, 3′-H), 7.25 (AA′BB′, *J* = 8.5 Hz, 6 H, 2-H), 7.45–7.49 (m, 12 H, 3-H, 2′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 55.3 (+, O*C*H$_3$), 81.6 ($C_q$, *C*OH), 87.68 [$C_q$, C≡*C*-Ar(OMe)], 89.9 [$C_q$, *C*≡C-Ar(OMe)], 114.0 (+, *C*-3′), 115.2 ($C_q$, *C*-1′), 122.86 ($C_q$, *C*-4), 127.8 (+, *C*-2), 131.1 (+, *C*-3), 133.1 (+, *C*-2′), 145.8 ($C_q$, *C*-1), 159.7 ($C_q$, *C*-4′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3466, 3037, 3002, 2958, 2836, 2535, 2215, 2029, 1919, 1602, 1569, 1515, 1464, 1440, 1404, 1287, 1250, 1174, 1138, 1106, 1030, 909, 830, 740, 667, 643, 596, 536 cm$^{-1}$. MS (FAB; 3-NBA): *m*/*z* (%) = 650 (14) [$M^+$], 633 (23) [$M^+$ – OH], 443 (14) [$M^+ - C_{15}H_{11}O$], 235 (46) [$C_{16}H_{11}O_2^+$], 154 (100). HRMS (FAB): calcd. for $C_{46}H_{34}O_4$ 651.2535; found 651.2533.

**4′′-{Tris[4-(4′-methoxyphenylethynyl)phenyl]methyl}phenol (17-OH):** A mixture of **16** (0.13 g, 0.20 mmol, 1 equiv.) and phenol (0.28 g, 3.00 mmol, 15 equiv.) was heated at 120 °C for 14 h. The reaction solution was diluted with $CH_2Cl_2$ (20 mL) and washed with 1 M NaOH (2 × 10 mL) and water (15 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 4:1) afforded **17**-OH (69.5 mg, 58%) as a yellow oil; $R_f$ = 0.12 (cyclohexane/ethyl acetate, 4:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.82 (s, 9 H, $OCH_3$), 6.74 (AA′BB′, *J* = 8.8 Hz, 2 H, 3′′-H), 6.88 (AA′BB′, *J* = 8.9 Hz, 6 H, 3′-H), 7.04 (AA′BB′, *J* = 8.8 Hz, 2 H, 2′′-H), 7.17 (AA′BB′, *J* = 8.6 Hz, 6 H, 2-H), 7.41 (AA′BB′, *J* = 8.6 Hz, 6 H, 3-H), 7.47 (AA′BB′, *J* = 8.9 Hz, 6 H, 2′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 55.3 (+, O*C*H$_3$), 64.1 [$C_q$, *C*(Ar)$_4$], 87.8 [$C_q$, C≡*C*-Ar(OMe)], 89.6 [$C_q$, *C*≡C-Ar(OMe)], 114.0 (+, *C*-3′), 114.6 (+, *C*-3′′), 115.3 ($C_q$, *C*-1′), 121.3 ($C_q$, *C*-4), 130.7 (+, *C*-2), 130.9 (+, *C*-3), 132.2 (+, *C*-2′′), 133.1 (+, *C*-2′), 138.0 ($C_q$, *C*-1′′), 146.3 ($C_q$, *C*-1), 153.9 ($C_q$, *C*-4′′), 159.6 ($C_q$, *C*-4′) ppm. IR

(DRIFT): $\tilde{\nu}$ = 3358, 2925, 2537, 2214, 2031, 1890, 1686, 1604, 1513, 1464, 1287, 1249, 1175, 1138, 1107, 1029, 910, 829, 737, 666, 643, 591, 526 cm$^{-1}$. MS (70 eV, EI): *m/z* (%) = 726 (11) [M$^+$], 633 (7) [M$^+$ – $C_6H_5O$], 519 (23) [M$^+$ – $C_{15}H_{11}O$], 221 (28) [$C_{16}H_{13}O^+$], 207 (40) [$C_{15}H_{11}O^+$], 133 (100). HRMS (EI): calcd. for $C_{52}H_{38}O_4$ 726.2770; found 726.2767.

**4′′-{Tris[4-(4′-methoxyphenylethynyl)phenyl]methyl}phenyltrifluoromethanesulfonate (17-OTf):** Compound **17**-OH (455 mg, 0.63 mmol, 1 equiv.) was suspended in anhydrous pyridine (15 mL) and cooled to 0 °C. Trifluoromethanesulfonic anhydride (0.13 mL, 220 mg, 0.75 mmol, 1.2 equiv.) was added dropwise and the reaction mixture was stirred for 16 h and warmed to room temperature. The reaction was quenched with satd. aqueous $NH_4Cl$ (25 mL) and water (25 mL) and the aqueous reaction mixture was extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 7:2) afforded product **17**-OTf (330 mg, 61%) as a light-brown oil; $R_f$ = 0.08 (cyclohexane/ethyl acetate, 25:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.83 (s, 9 H, $OCH_3$), 6.88 (AA′BB′, *J* = 8.9 Hz, 6 H, 3′-H), 7.14 (AA′BB′, *J* = 8.7 Hz, 6 H, 2-H), 7.19 (AA′BB′, *J* = 9.0 Hz, 2 H, 2′′-H), 7.31 (AA′BB′, *J* = 9.0 Hz, 2 H, 3′′-H), 7.44 (AA′BB′, *J* = 8.7 Hz, 6 H, 3-H), 7.47 (AA′BB′, *J* = 8.9 Hz, 6 H, 2′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 55.3 (+, O*C*H$_3$), 64.5 [$C_q$, *C*(Ar)$_4$], 87.5 [$C_q$, C≡*C*-Ar(OMe)], 90.0 [$C_q$, *C*≡C-Ar(OMe)], 114.0 (+, *C*-3′), 115.2 ($C_q$, *C*-1′), 118.7 ($C_q$, $J_{C,F}$ = 318.7 Hz, *C*F$_3$), 120.5 ($C_q$, *C*-4), 121.9 (+, *C*-3′′), 130.74 (+, *C*-3), 131.0 (+, *C*-2), 132.7 (+, *C*-2′′), 133.1 (+, *C*-2′), 145.2 ($C_q$, *C*-1), 146.4 ($C_q$, *C*-1′′), 147.8 ($C_q$, *C*-4′′), 159.7 ($C_q$, *C*-4′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3037, 2999, 2933, 2839, 2537, 2214, 2032, 1889, 1660, 1604, 1569, 1514, 1465, 1424, 1287, 1249, 1215, 1174, 1140, 1078, 1030, 888, 828, 753, 666, 641, 608, 575, 521, 416 cm$^{-1}$. MS (70 eV, EI): *m/z* (%) = 859 (64) [M$^+$], 651 (100) [M$^+$ – $C_{15}H_{11}O$], 633 (28) [M$^+$ – $C_7H_4F_3O_3S$]. HRMS (EI): calcd. for $C_{53}H_{38}F_3O_6S$ 859.2341; found 859.2339.

**4′′-{Tris[4-(4′-methoxyphenylethynyl)phenyl]methyl}phenylacetylene (17-CCH):** A mixture of **17**-OTf (0.31 g, 0.36 mmol, 1 equiv.), [$PdCl_2(PPh_3)_2$] (12.6 mg, 17.9 μmol, 5 mol-%), CuI (6.9 mg, 36.2 μmol, 0.10 equiv.), and trimethylsilylacetylene (0.12 mL, 81.8 mg, 0.72 mmol, 2 equiv.) in anhydrous THF (2.5 mL) and triethylamine (5 mL) was stirred at 60 °C for 16 h under an argon atmosphere. The volatiles were removed under reduced pressure and the residue was taken up in $CH_2Cl_2$ (50 mL) and water (35 mL). The organic layer was separated, dried with $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 9:1) afforded the trimethylsilyl-protected acetylene compound **17**-CCTMS (95.0 mg, 31%), which was directly desilylated.

Compound **17**-CCTMS was dissolved in $CH_2Cl_2$ (25 mL) and methanol (50 mL) and treated with potassium fluoride (18.0 mg, 0.33 mmol, 3 equiv.) for 16 h at room temperature. The solvents were removed under reduced pressure and the residue was taken up in $CH_2Cl_2$ (25 mL) and water (25 mL). The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 25 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. Without further purification, the title compound **17**-CCH (78.0 mg, 99%) was obtained as a yellow solid; $R_f$ = 0.18 (cyclohexane/ethyl acetate, 10:1); m.p. 67 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.07 (s, 1 H, C≡C*H*), 3.83 (s, 9 H, $OCH_3$), 6.87 (AA′BB′, *J* = 8.9 Hz, 6 H, 3′-H), 7.16 (AA′BB′, *J* = 8.7 Hz, 8 H, 2-H, 2′′-H), 7.41 (AA′BB′, *J* = 8.7 Hz, 8 H, 3-H, 3′′-H), 7.46 (AA′BB′, *J* = 8.9 Hz, 6 H, 2′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 55.0 (+, O*C*H$_3$), 64.4 [$C_q$, *C*(Ar)$_4$], 79.9 ($C_q$, *C*≡CH), 83.8 (+, C≡*C*H), 87.3 [$C_q$, C≡*C*-Ar(OMe)], 89.5 [$C_q$, *C*≡C-Ar(OMe)], 113.7 (+, *C*-3′), 114.9 ($C_q$, *C*-1′), 119.8 ($C_q$, *C*-4, *C*-4′′), 131.0 (+, *C*-2, *C*-2′′), 132.8 (+, *C*-3, *C*-3′′, *C*-2′), 145.1 ($C_q$, *C*-1, *C*-1′′), 159.3 ($C_q$, *C*-4′) ppm. IR (DRIFT): $\tilde{\nu}$ = 2923, 2852, 2212, 1725, 1603, 1568, 1511, 1463, 1439, 1286, 1246, 1173, 1138, 1106, 1028, 886, 820, 742, 722, 692, 664, 639, 596, 517 cm$^{-1}$.

**1,4-Bis[1′-ethynyl-4′-tri(4′′′-methoxytolanyl)methyl]benzene (9-OMe):** A mixture of **17**-CCH (70.0 mg, 95.3 μmol, 2.5 equiv.), [$PdCl_2(PPh_3)_2$] (2.1 mg, 3.05 μmol, 8 mol-%), CuI (1.2 mg, 6.09 μmol, 0.16 equiv.), and 1,4-diiodobenzene (12.6 mg, 38.2 μmol, 1 equiv.) in anhydrous THF (0.75 mL) and triethylamine (2.5 mL) was heated to 60 °C for 16 h under an argon atmosphere. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography (cyclohexane/ethyl acetate, 2:1). The title compound **9**-OMe (21.8 mg, 37%) was obtained as a beige solid; $R_f$ = 0.21 (cyclohexane/ethyl acetate, 2:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.83 (s, 18 H, $OCH_3$), 6.87 (AA′BB′, *J* = 8.9 Hz, 12 H, 3′′′-H), 7.14–7.21 (m, 16 H, 2′-H, 2′′-H), 7.40–7.50 (m, 32 H, 2-H, 3-H, 2′′′-H, 3′-H, 3′′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 55.3 (+, O*C*H$_3$), 64.8 [$C_q$, *C*(Ar)$_4$], 87.6 [$C_q$, *C*≡C(C-1)], 87.7 [$C_q$, *C*≡C(C-4′)], 89.8 [$C_q$, C≡*C*(C-4′)], 89.8 [$C_q$, C≡*C*(C-1)], 114.0 (+, *C*-3′′′), 115.3 ($C_q$, *C*-1′′′), 121.6 ($C_q$, *C*-1, *C*-4, *C*-4′, *C*-4′′), 130.9 (+, *C*-2, *C*-3, *C*-2′, *C*-2′′), 133.1 (+, *C*-3′, *C*-3′′, *C*-2′′′), 145.6 ($C_q$, *C*-1′, *C*-1′′), 159.6 ($C_q$, *C*-4′′′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3035, 2999, 2927, 2853, 2538, 2214, 2031, 1920, 1727, 1605, 1568, 1514, 1464, 1441, 1412, 1287, 1249, 1174, 1139, 1107, 1073, 1030, 958, 828, 742, 724, 693, 667, 528 cm$^{-1}$.

### Synthesis of 1,3,5-Tritritylbenzene Derivatives

**1,3,5-Tris(diphenylhydroxymethyl)benzene (21-H):** Phenyllithium (55 mL, 9.33 g, 111 mmol, 7 equiv., 2 M in butyl ether) was diluted with anhydrous THF (200 mL) and cooled to –78 °C under an argon atmosphere. A solution of trimethyl 1,3,5-benzenetricarboxylate (**20**; 4.00 g, 15.9 mmol, 1 equiv.) in anhydrous THF (40 mL) was added dropwise and the reaction mixture was stirred at –78 °C for 4 h and then warmed to room temperature over a period of 19 h. The reaction mixture was concentrated under reduced pressure and the residue was taken up in $CH_2Cl_2$ (100 mL) and satd. aqueous $NH_4Cl$ (100 mL) and stirred for 30 min. The organic layer was separated, dried with $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 3:2) afforded **21**-H (9.00 g, 91%) as a light-yellow solid; $R_f$ = 0.35 (cyclohexane/ethyl acetate, 1:1); m.p. 191 °C. $^1$H NMR (400 MHz, [$D_6$]DMSO): $\delta$ = 6.26 (s, 3 H, OH), 7.05–7.11 (m, 15 H, 2-H, 4-H, 6-H, 2′-H), 7.15–7.22 (m, 18 H, 3′-H, 4′-H) ppm. $^{13}$C NMR (100 MHz, [$D_6$]DMSO): $\delta$ = 80.6 (Cq, *C*OH), 126.1 (+, *C*-2, *C*-4, *C*-6), 126.3 (+, *C*-4′), 127.2 (+, *C*-2′), 127.57 (+, *C*-3′), 145.5 ($C_q$, *C*-1, *C*-3, *C*-5), 147.8 (Cq, *C*-1′) ppm. IR (ATR): $\tilde{\nu}$ = 3561, 3440, 3023, 1596, 1489, 1445, 1374, 1307, 1160, 1032, 1001, 924, 883, 853, 766, 727, 697, 647, 630, 598, 582, 426 cm$^{-1}$. MS (FAB, 3-NBA): *m/z* (%) = 624 (5) [M$^+$], 607 (100) [M$^+$ – OH], 590 (3) [M$^+$ – 2 × OH], 547 [M$^+$ – $C_6H_5$], 441 (2) [M$^+$ – $C_{13}H_{11}O$], 425 (5) [M$^+$ – $C_{13}H_{11}O_2$], 183 (14) [$C_{13}H_{11}O^+$], 105 (65) [$C_7H_5O^+$].

**1,3,5-Tris[(4′′-aminophenyldiphenyl)methyl]benzene (22-NH$_2$):** To a solution of aniline (1.31 mL, 1.34 g, 14.4 mmol, 9 equiv.), concd. HCl (1.5 mL), and glacial acetic acid (6 mL), **21**-H (1.00 g, 1.60 mmol, 1 equiv.) was added. The reaction mixture was heated at 145 °C for 24 h. After cooling to room temperature, the formed solid was filtered off and washed with glacial acetic acid (70 mL), water (70 mL), and diethyl ether (50 mL) successively. Drying in vacuo afforded the title compound **22**-NH$_2$ (1.20 g, 93%) as a grey

solid; m.p. 237 °C (dec.). $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 6.78–6.90 (m, 21 H, 2-H, 4-H, 6-H, 2′-H, 3′′-H), 6.93 (AA′BB′, $J$ = 8.6 Hz, 6 H, 2′′-H), 7.08–7.21 (m, 18 H, 3′-H, 4′-H) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 64.0 [C$_q$, *C*(Ar)$_4$], 119.2 (+, *C*-3′′), 125.6 (+, *C*-4′), 127.6 (+, *C*-3′), 129.3 (+, *C*-2, *C*-4, *C*-6), 129.8 (+, *C*-2′), 130.5 (+, *C*-2′′), 135.0 (C$_q$, *C*-1′′), 141.6 (C$_q$, *C*-4′′), 144.8 (C$_q$, *C*-1, *C*-3, *C*-5), 146.0 (C$_q$, *C*-1′) ppm. IR (ATR): $\tilde{\nu}$ = 2813, 2577, 1590, 1505, 1493, 1444, 1323, 1213, 1186, 1160, 1084, 1034, 1021, 1004, 868, 821, 770, 759, 745, 723, 704, 658, 629, 577, 532, 514, 489, 420 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 850 (55) [M + H$^+$], 772 (30) [M$^+$ – C$_6$H$_5$], 757 (43) [M$^+$ – C$_6$H$_6$N], 258 (100) [C$_{19}$H$_{16}$N$^+$], 180 (47) [C$_{13}$H$_{10}$N$^+$]. HRMS (FAB): calcd. for C$_{63}$H$_{52}$N$_3$ 850.4161; found 850.4157.

**1,3,5-Tritritylbenzene (3-H):** Compound **22**-NH$_2$ (1.00 g, 1.20 mmol, 1 equiv.) was suspended in glacial acetic acid (100 mL) and hypophosphoric acid (10 mL, 50% aqueous solution). Under vigorous stirring, sodium nitrite (6.20 g, 90.0 mmol, 38 equiv.) was added in small portions. The reaction mixture was stirred for 24 h at room temperature. Water (50 mL) was added to complete the precipitation. The formed solid was filtered off and washed with glacial acetic acid (50 mL), water (150 mL) and diethyl ether (25 mL). Drying in vacuo gave **3**-H (0.88 g, 91%) as a beige solid; $R_f$ = 0.23 (cyclohexane/ethyl acetate, 25:1); m.p. 282 °C (dec.). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.93 (s, 3 H, 2-H, 4-H, 6-H), 6.94–7.00 (m, 18 H, 2′-H), 7.06–7.13 (m, 27 H, 3′-H, 4′-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 65.0 [C$_q$, *C*(Ar)$_4$], 125.4 (+, *C*-4′), 127.4 (+, *C*-3′), 130.7 (+, *C*-2′), 131.5 (+, *C*-2, *C*-4, *C*-6), 145.2 (C$_q$, *C*-1, *C*-3, *C*-5), 146.7 (C$_q$, *C*-1′) ppm. IR (ATR): $\tilde{\nu}$ = 3054, 2923, 1739, 1591, 1490, 1441, 1371, 1236, 1084, 1034, 913, 843, 763, 752, 697, 644, 629, 531, 507, 488 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 804 (6) [M$^+$], 727 (10) [M$^+$ – C$_6$H$_5$], 243 (25) [C$_{19}$H$_{15}^+$], 81 (100). HRMS (FAB): calcd. for C$_{63}$H$_{48}$ 804.3756; found 804.3759.

**1,3,5-Tris[(4′′-hydroxyphenyldiphenyl)methyl]benzene (22-OH):** A mixture of **21**-H (0.20 g, 0.32 mmol, 1 equiv.) and phenol (0.60 g, 6.40 mmol, 20 equiv.) in glacial acetic acid (1 mL) was heated at 160 °C for 16 h. After cooling to room temperature, the crude product was purified by flash column chromatography (cyclohexane/ethyl acetate, 2:1) to give the title compound **22**-OH (117 mg, 43%) as a yellowish solid; $R_f$ = 0.46 (cyclohexane/ethyl acetate, 1:1); m.p. 226 °C (dec.). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.54 (AA′BB′, $J$ = 8.8 Hz, 6 H, 3′′-H), 6.78 (AA′BB′, $J$ = 8.8 Hz, 6 H, 2′′-H), 6.83 (s, 3 H, 2-H, 4-H, 6-H), 6.93–7.08 (m, 12 H, 2′-H), 7.06–7.11 (m, 18 H, 3′-H, 4′-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 64.3 [C$_q$, *C*(Ar)$_4$], 114.2 (+, *C*-3′′), 125.4 (+, *C*-4′), 127.3 (+, *C*-3′), 130.6 (+, *C*-2′), 131.4 (+, *C*-2, *C*-4, *C*-6), 131.9 (+, *C*-2′′), 139.2 (C$_q$, *C*-1′′), 145.4 (C$_q$, *C*-1, *C*-3, *C*-5), 146.9 (C$_q$, *C*-1′), 153.0 (C$_q$, *C*-4′′) ppm. IR (ATR): $\tilde{\nu}$ = 3373, 3054, 2918, 2850, 1592, 1506, 1490, 1441, 1235, 1177, 1111, 1033, 1013, 907, 867, 830, 759, 732, 701, 631, 581, 530, 426 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 852 (10) [M$^+$], 775 (29) [M$^+$ – C$_6$H$_5$], 759 [M$^+$ – C$_6$H$_6$O], 698 (1), [M$^+$ – C$_{12}$H$_{10}$], 647 (21) [C$_{51}$H$_{35}^+$], 259 (100) [C$_{19}$H$_{15}$O$^+$]. HRMS (FAB): calcd. for C$_{63}$H$_{48}$O$_3$ 852.3603; found 852.3607.

**Benzene-1,3,5-tris[bis(4′-methoxyphenyl)methanol] (21-OMe):** A solution of 4-bromoanisole (4.00 mL, 5.93 g, 31.7 mmol, 8 equiv.) in anhydrous THF (100 mL) was cooled to –78 °C under an argon atmosphere and treated with *n*-butyllithium (12.7 mL, 2.03 g, 31.7 mmol, 8 equiv., 2.5 M in hexane) for 1 h. A solution of **20** (1.00 g, 3.96 mmol, 1 equiv.) in anhydrous THF (15 mL) was added dropwise, the reaction mixture was stirred at –78 °C for 3 h and then warmed to room temperature over a period of 16 h. The solvent was evaporated and the residue was taken up in $CH_2Cl_2$ (75 mL) and ice/satd. aqueous $NH_4Cl$ (100 mL). The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 75 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 3:2) afforded the title compound **21**-OMe (2.23 g, 70%) as a yellowish solid; $R_f$ = 0.32 (cyclohexane/ethyl acetate, 1:1); m.p. 93 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.69 (s, 3 H, OH), 3.77 (s, 18 H, OCH$_3$), 6.71 (AA′BB′, $J$ = 8.9 Hz, 12 H, 3′-H), 7.01 (AA′BB′, $J$ = 8.9 Hz, 12 H, 2′-H), 7.08 (s, 3 H, 2-H, 4-H, 6-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.2 (+, O*C*H$_3$), 81.5 (C$_q$, *C*OH), 113.0 (+, *C*-3′), 126.2 (+, *C*-2, *C*-4, *C*-6), 128.9 (+, *C*-2′), 139.2 (C$_q$, C-1′), 146.3 (C$_q$, *C*-1, *C*-3, *C*-5), 158.4 (C$_q$, *C*-4′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3485, 3036, 3000, 2836, 2548, 2295, 2039, 1896, 1765, 1608, 1582, 1509, 1462, 1441, 1414, 1299, 1251, 1176, 1116, 1034, 925, 873, 832, 786, 746, 719, 701, 638, 606, 581, 413 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 804 (11) [M$^+$], 787 (100) [*M*$^+$ – OH], 770 (5) [*M*$^+$ – 2 × OH], 697 (10) [M$^+$ – C$_7$H$_7$O], 679 (9) [M$^+$ – C$_7$H$_7$O$_2$], 651 (6) [M$^+$ – C$_7$H$_7$O$_3$], 544 (17) [C$_{36}$H$_{32}$O$_5^+$], 243 (13) [C$_{15}$H$_{15}$O$_3^+$], 107 (100) [C$_7$H$_7$O$^+$]. HRMS (FAB): calcd. for C$_{51}$H$_{49}$O$_8$ 804.3298; found 804.3295.

**1,3,5-Tris[tris(4′-hydroxyphenyl)methyl]benzene (3-OH):** A mixture of **21**-OMe (1.00 g, 1.24 mmol, 1 equiv.) and phenol (3.51 g, 12.4 mmol, 10 equiv.) in glacial acetic acid (5 mL) were heated at 140 °C for 12 h. The solvent was removed under reduced pressure and the residue was taken up in $CH_2Cl_2$ (20 mL) and cooled to 0 °C under an argon atmosphere. Boron tribromide (0.51 mL, 1.34 g, 5.34 mmol, 12 equiv.) was added dropwise and the reaction mixture was stirred for 16 h and warmed to room temperature. Methanol (30 mL) was added carefully at 0 °C and the volatiles were removed under reduced pressure. This procedure was repeated four times. Flash column chromatography (cyclohexane/ethyl acetate, 1:10) afforded the product **3**-OH (0.26 g, 22%) as a reddish solid; $R_f$ = 0.19 (cyclohexane/ethyl acetate, 1:10); m.p. 216 °C. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 6.50 (AA′BB′, $J$ = 8.8 Hz, 18 H, 3′-H), 6.62 (AA′BB′, $J$ = 8.8 Hz, 18 H, 2′-H), 6.83 (s, 3 H, 2-H, 4-H, 6-H), 9.16 (s, 9 H, OH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 62.3 [C$_q$, *C*(Ar)$_4$], 113.9 (+, *C*-3′), 130.11 (+, *C*-2, *C*-4, *C*-6), 130.9 (+, *C*-2′), 137.7 (C$_q$, *C*-1′), 145.0 (C$_q$, *C*-1, *C*-3, *C*-5), 154.5 (C$_q$, *C*-4′) ppm. IR (DRIFT): $\tilde{\nu}$ = 3874, 3349, 3031, 2799, 2707, 2490, 2073, 1900, 1774, 1699, 1609, 1595, 1507, 1437, 1360, 1234, 1177, 1112, 1043, 1015, 947, 903, 872, 831, 744, 722, 686, 628, 601, 577, 524, 494, 414, 405 cm$^{-1}$. MS (FAB, 3-NBA): *m*/*z* (%) = 948 (10) [M$^+$], 855 (12) [M$^+$ – C$_6$H$_5$O], 289 (8) [C$_{44}$H$_{33}$O$_6^+$], 154 (100). HRMS (FAB): calcd. for C$_{63}$H$_{48}$O$_9$ 948.3298; found 948.3295.

**1,3,5-Tris[tris(4′-trifluoromethylsulfonylphenyl)methyl]benzene (3-OTf):** A suspension of **3**-OH (100 mg, 0.11 mmol, 1 equiv.) in anhydrous $CH_2Cl_2$ (15 mL) was cooled to 0 °C. 2,6-Lutidine (0.28 mL, 0.25 g, 2.37 mmol, 23 equiv.) and trifluoromethanesulfonic anhydride (0.39 mL, 0.67 g, 2.37 mmol, 23 equiv.) were added and the reaction mixture was stirred for 24 h and warmed to room temperature over this period. The volatiles were removed under reduced pressure and the residue was taken up in $CH_2Cl_2$ (100 mL). The organic phase was washed with 2 M HCl (2 × 50 mL), water (50 mL), and brine (50 mL), dried with $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/ethyl acetate, 5:1) afforded the title compound **3**-OTf (96.0 mg, 41%) as a brownish solid; $R_f$ = 0.34 (cyclohexane/ethyl acetate, 5:1); m.p. 214 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.69 (s, 3 H, 2-H, 4-H, 6-H), 6.92 (AA′BB′, $J$ = 9.0 Hz, 18 H, 2′-H), 7.12 (AA′BB′, $J$ = 9.0 Hz, 18 H, 3′-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 64.0 [C$_q$, *C*(Ar)$_4$], 118.6 (C$_q$, $J_{C-F}$ = 320.5 Hz, *C*F$_3$), 121.3 (+, *C*-3′), 131.2 (+, *C*-2, *C*-4, *C*-6), 131.8 (+, *C*-2′), 144.7 (C$_q$, *C*-1′), 145.5 (C$_q$, *C*-1, *C*-3, *C*-5), 147.9 (C$_q$, *C*-4′) ppm. IR

(ATR): ṽ = 3561, 3440, 3023, 1596, 1489, 1445, 1374, 1307, 1160, 1032, 1001, 924, 883, 853, 766, 727, 697, 647, 630, 598, 582, 426 $cm^{-1}$. MS (FAB, 3-NBA): *m/z* (%) = 2139 (11) [M + $H^+$], 1912 (10) [M + $H^+$ – $C_7H_4F_3O_3S$], 1686 (8) [M + $H^+$ – $C_{14}H_8F_6O_6S_2$], 687 (31) [$C_{22}H_{12}F_9O_9S_3^+$], 95 (100) [$CH_3O_3S^+$].

**1,3,5-Tris[tris(4′-bromophenyl)methyl]benzene (3-Br):** Compound **3**-H (200 mg, 0.25 mmol, 1 equiv.) was added in small portions to bromine (0.45 mL, 1.34 g, 8.40 mmol, 27 equiv.) under vigorous stirring. The reaction mixture was stirred for 1 h at room temperature and then cooled to –78 °C. Ethanol (15 mL) was added and the reaction mixture was warmed to room temperature. The solid was filtered off and washed with satd. aqueous $Na_2S_2O_3$ (50 mL), water (125 mL), and ethanol (25 mL). Drying in vacuo yielded **3**-Br (315 mg, 83%) as a yellow solid; $R_f$ = 0.59 (cyclohexane/ethyl acetate, 25:1); m.p. 166 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.69 (s, 3 H, 2-H, 4-H, 6-H), 6.71 (AA′BB′, *J* = 8.7 Hz, 18 H, 2′-H), 7.28 (AA′BB′, *J* = 8.7 Hz, 18 H, 3′-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 64.0 [$C_q$, *C*(Ar)$_4$], 120.6 ($C_q$, *C*-4′), 131.0 (+, *C*-2′), 131.2 (+, *C*-2, *C*-4, *C*-6), 131.9 (+, *C*-3′), 144.2 ($C_q$, *C*-1′), 145.1 ($C_q$, *C*-1, *C*-3, *C*-5) ppm. IR (ATR): ṽ = 2923, 1774, 1585, 1482, 1435, 1395, 1188, 1076, 1007, 870, 811, 740, 674, 656, 627, 534, 502, 422 $cm^{-1}$. MS (FAB, 3-NBA): *m/z* (%) = 1511/1513/1515/1517/1519/1521 (3/4/5/4/3/2) [$M^+$], 1352/1354/1356/1358/1360/1362/1364 (1/4/8/13/9/5/1) [$M^+$ – $C_6H_4Br$], 1274/1276/1278/1280/1282/1284 (1/2/3/3/2/2) [$M^+$ – $C_6H_4Br_2$], 477/479/481 (14/47/12) [$C_{19}H_{12}Br_3^+$].

**1,3,5-Tris[tris(4′-iodophenyl)methyl]benzene (3-I):** A mixture of **3**-H (200 mg, 0.25 mmol, 1 equiv.), iodine (0.76 g, 3.00 mmol, 12 equiv.), and [bis(trifluoroacetoxy)iodo]benzene (1.08 g, 2.50 mmol, 10 equiv.) was suspended in carbon tetrachloride (15 mL) and heated to 80 °C for 24 h. The solvent was removed under reduced pressure. Flash column chromatography (cyclohexane→cyclohexane/ethyl acetate, 20:1) afforded the title compound **3**-I (69.7 µg, 28%) as a yellow solid; $R_f$ = 0.35 (cyclohexane/ethyl acetate, 20:1); m.p. 108 °C (dec.). $^1$H NMR (400 MHz, [$D_6$]-DMSO): $\delta$ = 6.56–6.64 (m, 21 H, 2-H, 4-H, 6-H, 2′-H), 7.57 (AA′BB′, *J* = 8.1 Hz, 8 H, 3′-H) ppm. $^{13}$C NMR (100 MHz, [$D_6$]-DMSO): $\delta$ = 63.7 [$C_q$, *C*(Ar)$_4$], 92.7 ($C_q$, *C*-4′), 129.5 (+, *C*-2, *C*-4, *C*-6), 131.9 (+, *C*-2′), 136.68 (+, *C*-3′), 139.2 ($C_q$, *C*-1′), 144.6 ($C_q$, *C*-1, *C*-3, *C*-5) ppm. IR (ATR): ṽ = 2919, 2846, 1911, 1702, 1656, 1579, 1479, 1437, 1391, 1314, 1191, 1066, 1002, 869, 808, 735, 701, 670, 665, 651, 627, 531, 498, 434 $cm^{-1}$. MS (FAB, 3-NBA): *m/z* (%) = 1937 (1) [$M^+$], 1734 [$M^+$ – $C_6H_4I$], 621 (2) [$C_{19}H_{12}I_3^+$], 154 (100).

**1,3,5-Tris[tris(4′-nitrophenyl)methyl]benzene (3-$NO_2$):** Compound **3**-H (1.00 g, 1.55 mmol, 1 equiv.) was added in small portions to nitric acid (96%, 7.5 mL) at –5 °C under vigorous stirring. The reaction mixture was stirred for 4 h and warmed to room temperature. Glacial acetic acid (15 mL) and acetic anhydride (2.5 mL) were added and the reaction mixture was stirred for an additional 16 h. The formed solid was filtered off, washed with water (100 mL), and dried in vacuo. Without further purification, the title compound **3**-$NO_2$ (1.13 g, 60%) was obtained as a bright-yellow solid; m.p. 258 °C (decomposition). $^1$H NMR (400 MHz, [$D_6$]-DMSO): $\delta$ = 6.95 (s, 3 H, 2-H, 4-H, 6-H), 7.52 (AA′BB′, *J* = 9.0 Hz, 18 H, 2′-H), 8.11 (AA′BB′, *J* = 9.0 Hz, 18 H, 3′-H) ppm. $^{13}$C NMR (100 MHz, [$D_6$]DMSO): $\delta$ = 65.5 [$C_q$, *C*(Ar)$_4$], 123.4 (+, *C*-3′), 130.0 (+, *C*-2, *C*-4, *C*-6), 130.8 (+, *C*-2′), 145.51 ($C_q$, *C*-1, *C*-3, *C*-5, *C*-4′), 151.6 ($C_q$, *C*-1′) ppm. IR (DRIFT): ṽ = 3078, 2919, 2847, 2304, 1907, 1706, 1654, 1591, 1518, 1481, 1437, 1391, 1347, 1191, 1112, 1066, 1001, 906, 841, 818, 734, 706, 655, 627, 530, 498, 434 $cm^{-1}$. MS (FAB, 3-NBA): *m/z* (%) = 1210 (1) [M + $H^+$], 1194 (2) [M + $H^+$ – O], 1088 (1) [M + $H^+$ – $C_6H_4NO_2$], 154 (100).

**4,4′,4″,4‴,4⁗,4⁗′,4⁗″,4⁗‴,4⁗⁗-[Benzene-1,3,5-triyltris(methanetetrayl)]nonabenzenesulfonic Acid (3-$SO_3H$):** To a suspension of **3**-H (50.0 mg, 62.1 µmol, 1 equiv.) in anhydrous $CH_2Cl_2$ (5 mL), chlorosulfonic acid (0.11 mL, 195 mg, 1.68 mmol, 27 equiv.) was added dropwise and the reaction mixture was heated at 35 °C for 12 h. The supernatant solution was decanted and the solvent was removed under reduced pressure. The oily residue was taken up in water (10 mL) and the formed solid was filtered off and washed with water (75 mL). Drying in vacuo gave the title compound **3**-$SO_3H$ (36.0 mg, 38%) as a yellowish solid. $^1$H NMR (400 MHz, [$D_6$]DMSO): $\delta$ = 6.99 (AA′BB′, *J* = 8.3 Hz, 18 H, 2′-H), 7.13 (s, 3 H, 2-H, 4-H, 6-H), 7.47 (AA′BB′, *J* = 8.3 Hz, 18 H, 3′-H) ppm. $^{13}$C NMR (100 MHz, [$D_6$]DMSO): $\delta$ = 64.7 [$C_q$, *C*(Ar)$_4$], 125.3 (+, *C*-2, *C*-4, *C*-6, *C*-3′), 129.3 (+, *C*-2′), 144.0 ($C_q$, *C*-4′), 144.9 ($C_q$, *C*-1, *C*-3, *C*-5), 147.0 ($C_q$, *C*-1′) ppm.

**Supporting Information** (see footnote on the first page of this article): Synthetic procedures of HPX and HPXXL precursors, copies of NMR spectra, crystallographic data.

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